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SYNTHESIS OF CYSTEINE ANALOGUES IN ENANTIOPURE FORM

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Synthesis of Cysteine Analogues in Enantiopure Form

Memoria que, para optar al grado de Doctor en Química, presenta

Jaime Gracia Vitoria

Departamento de Química Orgánica
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Instituto de Síntesis Química y Catálisis Homogénea

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CARLOS CATIVIELA MARÍN, Catedrático del Departamento de Química Orgánica de la Universidad de Zaragoza y miembro del Instituto de Síntesis Química y Catálisis Homogénea,

IÑAKI OSANTE GARCIA, Doctor en Ciencias Químicas y miembro colaborador del grupo de Investigación "Aminoácidos y Péptidos" del Instituto de Síntesis Química y Catálisis Homogénea (ISQCH, centro mixto CSIC – Universidad de Zaragoza),

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que la Memoria "Synthesis of Cysteine Analogues in Enantiopure Form" ha sido realizada en el Departamento de Química Orgánica de la Facultad de Ciencias de la Universidad de Zaragoza bajo nuestra inmediata dirección y reúne las condiciones necesarias para su presentación.

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"And in the end, the love you take
is equal to the love you make"

The beatles, *Abbey road*, 1969

Abbreviations

$[\alpha]_D$	Specific rotation
Å	Angstrom
Alloc	Allyloxycarbonyl
Ac	Acetyl
anh.	Anhydrous
Aq.	Aqueous
Ar	Aryl
B.O.	Bond orders
Bn	Benzyl
brs	Broad singlet
^{t}Bu	*tert*-Butyl
Boc	*tert*-Butoxycarbonyl
^{o}C	Celsius degrees
Cat.	Catalytic
Cbz (Z)	Benzyloxycarbonyl
Cbz-OSu	Benzyloxycarbonylsuccinimide
cm	Centimetres
Config.	Configuration
Conv.	Conversion
CPME	Cyclopentyl methyl ether
δ	Chemical shift
d	Doublet
DABCO	1,4-Diazabicyclo[2.2.2]octane
DAST	(Diethylamino)sulfurtrifluoride
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCC	*N*,*N′*-Dicyclohexylcarbodiimide
dd	Doublet of doublets
ddd	Doublet of doublet of doublets
ddt	Doublet of doublet of triplets
d.e.	Diastereomeric excess
DEAD	Diethyl azodicarboxylate
DFT	Density functional theory
DIAD	Diisopropyl azodicarboxylate
DIPEA	*N*,*N*-Diisopropylethylamine
DIPP	Diisopropyl phosphoryl
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N′*-Dimethylformamide
DMOB	2,4-Dimethoxybenzyl
DMPU	1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)pyrimidinone
DNP	2,4-Dinitrophenyl
Dpm	Diphenylmethyl
DPPA	Diphenylphosphorazide
dq	Doublet of quartets
dqd	Doublet of quartet of doublets
d.r.	Diastereomeric ratio
dtd	Doublet of triplet of doublets

DTBM	3,5-Di-*tert*-butyl-4-methoxy
η	Chemical hardness
e.e.	Enantiomeric excess
ent.	Enantiomer
eq.	Equivalents
Et	Ethyl
EtOAc	Ethyl acetate
Fmoc	9-Fluorenylmethoxycarbonyl
FOXAP	Ferrocenyl oxazolinylphosphine
g	gram
G	Free energy
GEDT	Global electron density transfer
GSH	Reduced Glutathione
GSSG	Oxidized Glutathione
h	hour
HATU	1-[Bis(dimethylamino)methylene]-1*H*-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate
HBTU	*N,N,N′,N′*-Tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate
Het	Heteroaryl
HMPA	Hexamethylphosphoramide
HOAt	1-Hydroxy-7-azabenzotriazole
HRMS	High resolution mass spectrometry
Hz	Hertz
^{i}Pr	Isopropyl
IR	Infrared
IRC	Instrinsic reaction coordinate
J	Coupling constant
L384A	Methylaspartate ammonia lyase
LA	Lewis acid
LDA	Lithium diisopropylamide
LDEA	Lithium diethylamide
LG	Leaving group
LiHMDS	Lithium bis(trimethylsilyl)amide
μ	Electronic chemical potential
M.p.	Melting point
***m*-CPBA**	*m*-Chloroperbenzoic acid
m	Multiplet
M	Molar
MAO	Methylaluminoxane
MABR	Methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide)
Me	Methyl
mg	Miligram
MHz	Megahertz
mmol	Milimol
MS	Molecular sieves
Ms	Methanesulfonyl (mesyl)
MW	Microwave
ν	Wave number

N	Normal
N	Global nucleophilicity
NBS	*N*-Bromosuccinimide
NCI	Non-covalent interaction
NMO	Morpholine *N*-oxide
NMR	Nuclear magnetic resonance
n.O.e	Nuclear Overhauser effect
NOESY	Nuclear Overhauser effect spectroscopy
Np	Naphthyl
n.r.	No reaction
Ns	Nitrobenzenesulfonyl (nosyl)
NVOC	6-Nitroveratryloxycarbonyl
ω	Global electrophilicity
***p*-TSA**	*p*-Toluensulfonic acid
P_2-Et	1-Ethyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene)
Pg	Protecting group
Ph	Phenyl
Piv	*tert*-Butylcarbonyl (pivaloyl)
***P*k**	Parr functions
PLE	Pig liver esterase
PMB	*p*-Methoxybenzyl
PMP	*p*-Methoxyphenyl
PR	Product
PS	Proton sponge
py	Pyridine
q	Quartet
quin	Quintuplet
rac.	Racemic
r.r.	Regioisomeric ratio
s	Singlet
s.m.	Starting material
t	Triplet
TBAB	Tetra-n-butylammonium bromide
TBAF	Tetra-n-butylammonium fluoride
TBDMS	*tert*-Butyldimethylsilyl
TCP	Trichlorophenol
tdd	Triplet of doublets of doublets
TEA	Triethylamine
Temp. (T)	Temperature
Tf	Trifluoromethanesulfonyl (triflate)
TFA	Trifluoroacetic acid
TFAA	Trifluoroacetic anhydride
THF	Tetrahydrofuran
Thr	Threonine
TLC	Thin layer chromatography
TMAH	Tetramethylammonium hydroxide
TMEDA	*N,N,N′,N′*-Tetramethylethylendiamine
Tmob	Trimethoxybenzyl

TMS	Trimethylsilyl
TMSE	Trimethylsilylethyl
Trt	Trityl
TS	Transition state
Ts	*p*-Toluensulfonyl (tosyl)
UV	Ultraviolet
v/v	Volume/volume
w/w	Weight/weight

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Chapter I

Methodologies for the synthesis of cysteine derivatives

I. Methodologies for the synthesis of cysteine derivatives

1. INTRODUCTION

Cysteine is one of the 20 proteinogenic amino acids of great importance in life. Its world market per year is approximately of 4000 tons.[1] *L*-cysteine has shown many applications in different fields such as pharmaceutical, food and cosmetic industries, as chemical reagent and chiral building block. It is produced by acid or alkaline hydrolysis of poultry feathers, human hair or other protein-rich materials containing cysteine. However, these methods result in low yield and give rise to unpleasant odors, high energy cost and problems of waste treatment.[2] So, it is of public interest to develop a more economical, efficient and environmentally friendly way to produce *L*-cysteine. For this reason, enzymes and whole-cell biocatalyst, as a result of their complex chiral constitution, are predominantly suited for the manufacture of optically pure stereoisomers. The production of optically active intermediates is an area of growing interest in fine chemical industry and here bio-catalysis developed from a niche technology to a widely used manufacturing method. A production method for the manufacture of *L*-cysteine by fermentation with *E. Coli* strains[3] to replace the *L*-cysteine produced by extraction from human hair has been developed by Wacker Chemie.[4] Other successful microbial process used for industrial production of *L*-cysteine[5] involved the asymmetric conversion of *D*,*L*-2-aminothiazoline-4-carboxylic acid, the intermediate compound in the chemical synthesis of *D*,*L*-cysteine,[6] by enzymes from bacteria, *Pseudomonas thiazolinophilium and Pseudomonas desmolytica.*

On the other hand, *L*-cysteine plays a crucial role in protein folding, assembly, and stability through disulfide bonds.[7] Furthermore, *L*-cysteine containing proteins, such as Thioredoxine and peptides such as glutathione, are involved in protecting cells under oxidative stress in vivo.[8]

Cysteines play critical roles in biological processes and many cysteine derivatives have been used as intermediates in many fields from chemistry to biology. They have been used as intermediates in the synthesis of heterocycles and myriads of compounds such as thiazolidines frequently used as antioxidants,[9] many of which are of biological interest.[10] They have been incorporated in peptides such as lanthionines,[11] gluthatione[12] and many other compounds of practical and biomedical importance. Moreover, they have been used as ligands of metals in coordination chemistry,[13] as scaffolds in materials chemistry and nanoscience,[14] as catalyst in organic synthesis[15] or as an activator of side-chine N-S Acyl transfer and tail-to-side-chain cyclization in peptides.[16]

On the other hand, over the last few decades, it has been demonstrated that the modification of the core structure of a determined amino acid plays a fundamental role and hence the interest to prepare new amino acids related to the proteinogenic ones with the purpose to design and control the structure of the new compounds and improving the macroscopical properties of the compounds that containing them. In summary, the purpose of this chapter is to collect the synthesis of the modified cysteines reported in the literature, and classified according to the different structures gathered in *Figure 1*. This chapter is focused to the synthesis (stereoselective if possible) of such compounds and is organized following the same structure. Therefore, the different strategies reported in the literature regarding each family of compounds will be discussed.

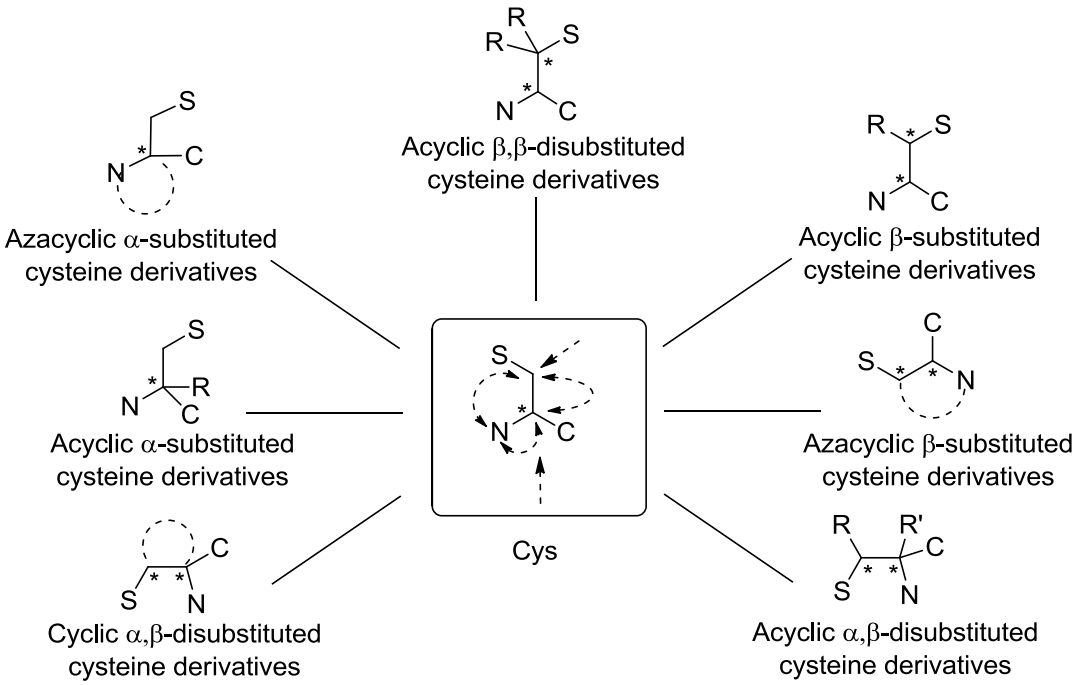


Figure 1. General structures of modified cysteines

2. SYNTHESIS OF ACYCLIC α-SUBSTITUTED CYSTEINE DERIVATIVES

These compounds belong to the family of so called quaternary amino acids (*Figure 2*) and have been reported to be of considerable interest. Their incorporation into peptides represents an effective and versatile strategy to restrict the conformational freedom, to stabilize defined secondary structures and to enhance the stability towards chemical and enzymatic hydrolysis. In this context, several reviews have been reported and many others have been published concerning the stereoselective synthesis.[17]

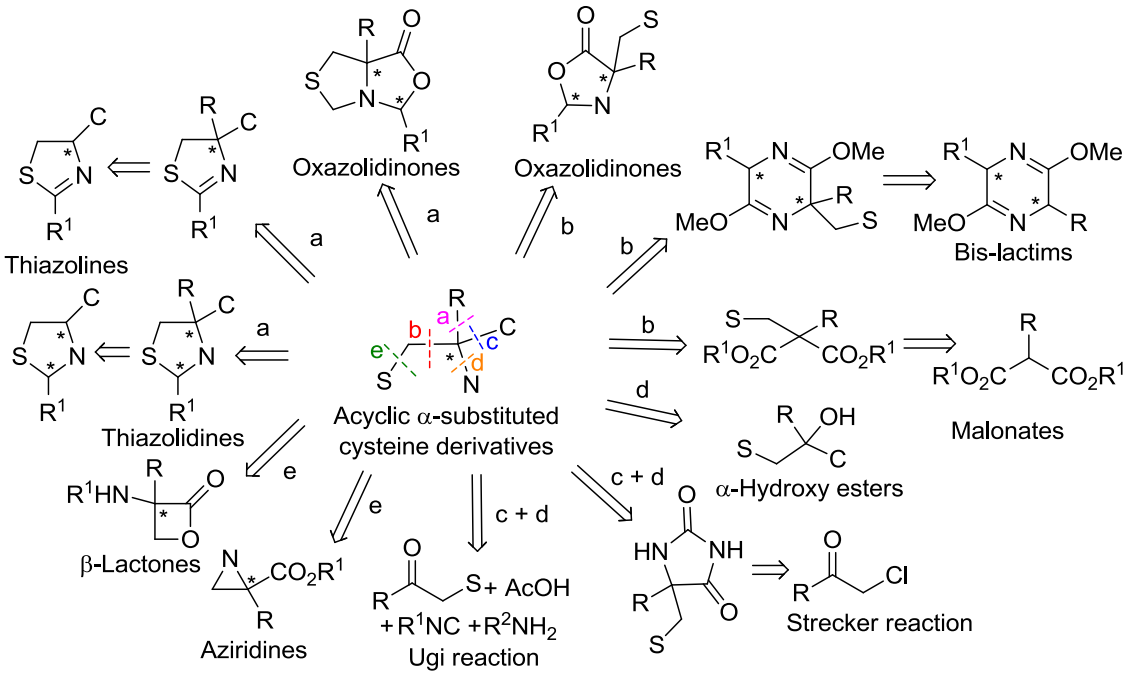


Figure 2. *The most relevant strategies to get α-alkyl cysteine derivatives are shown*

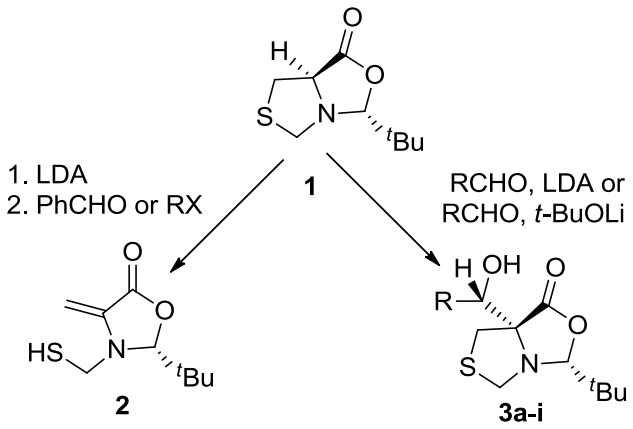
2.1. Alkylation of cyclic chiral amino acid equivalent enolates. Disconnection a)

It involves the use of cysteine equivalents (mostly cyclic) in basic medium, in which the enolate intermediate reacts with different electrophiles, incorporating in this step the substituent on Cα of the amino acid. The use of the cysteine itself as starting material is not recommended because of the position of the sulfur atom related to the anion formed in the alkylation reaction which can be easily eliminated. For this reason, the sulfur atom should be properly protected, for instance taking part of a cycle or the cited anion should be stabilized using low temperatures, and so on to increase the stability of the starting material and the stereoselectivity of the alkylation process. In this context, the literature discloses the use of thiazolidines, thiazolines and/or oxazolidinones as cyclic cysteine equivalents applying the strategy of the self-regeneration of stereocenters (*SRS*) or the use of thiazolines using chiral auxiliaries, chiral phase transfer catalyst and/or resolution procedures are also relevant.

2.1.1. Diastereoselective Cα-R bond formation *via* alkylation of cyclic chiral cysteine enolates equivalents

It is worth noting that the *SRS* principle consists of a chiral molecule, which generates a temporary stereogenic center, which in turn is used to introduce diastereoselectively a new substituent at original stereogenic center without

racemization and then the temporary center is removed.[18] Taking into account these facts, the bicyclic oxazolidinone **1**, as cyclic cysteine intermediate, reacted with base at -78 °C even after short reaction times but the formed enolate did not react with very reactive electrophiles and only the β-elimination product **2** was isolated along with other decomposition products (*Scheme 1*, *Table 1*).



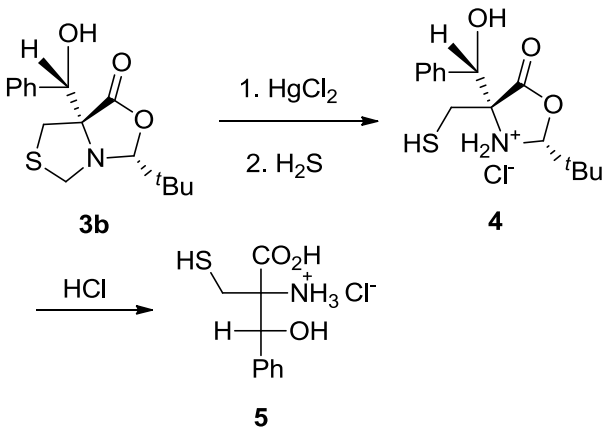
Scheme 1

Table 1. The results of using different aldehydes are shown

Entry	Aldehyde	d.r. (%)
3a	cinnamaldehyde	89
3b	benzaldehyde	92
3c	4-bromobenzaldehyde	82
3d	anisaldehyde	96
3e	piperonal	96
3f	furfural	88
3g	thiophene-2-carbaldehyde	94
3h	1-methylpyrrol-2-carbaldehyde	90
31	pyridin-3-carbaldehyde	65

This undesired process can be avoided by the addition of the bicyclic oxazolidinone **1**, easily synthesized from *L*-cysteine, formaldehyde and pivalaldehyde to a solution of non-enolizable aldehyde used as electrophile and LDA or *tert*-butyllithium at -78 °C as bases. Four possible bicylic oxazolidinones diastereoisomers can be obtained, but only one oxazolidinone **3a-i** is usually created with high diastereoselectivity in enantiopure form.[19]

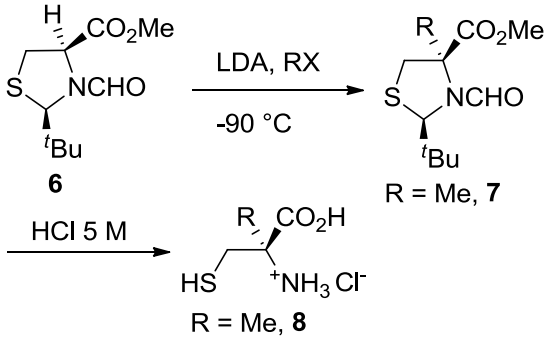
The benzaldehyde derivative **3b** has been used to exemplify the synthesis of (2*R*,3*R*)-α-hydroxymethylphenylcysteine **5** in enantiopure form by cleavage of the thiazolidine ring, followed by acidic hydrolysis of cyclic *N*,*O*-acetal (*Scheme 2*).



3b **4** **5**

Scheme 2

Pattenden *et al*.[20] have synthesized (*R*)- or (*S*)-alkylcysteine by a slight modification of the Seebach´s procedure. Starting from thiazolidine **6** and alkylhalides as electrophiles at -90 ºC thus avoided the abovementioned β-elimination process. Therefore, treatment of the *N*-formyl thiazolidine adduct **6**, easily available from *L*-cysteine methyl ester hydrochloride and pivalaldehyde, with LDA as base at low temperature (-90 ºC) in the presence of DMPU as co-solvent followed by reaction of the generated lithium enolate with a wide range of electrophiles (typically iodomethane) afforded the corresponding C4 methylated thiazolidine **7** with the methyl and *tert*-butyl groups located in a *trans* relative disposition. Hydrolysis of the heterocycle in the presence of HCl 5 M led to (*R*)-2-methylcysteine **8** in excellent yield and enantiomeric purity. The procedure can be extended to other good electrophiles allowing the synthesis of 2-alkyl substituted cysteines prepared by this modification of Seebach´s "self-regeneration of chirality" principle (*Scheme 3*).



6

R = Me, **7**

R = Me, **8**

Scheme 3

It is worth noting that an important review of the self-regeneration of stereocenters (*SRS*) procedure has been reported and a careful reading is

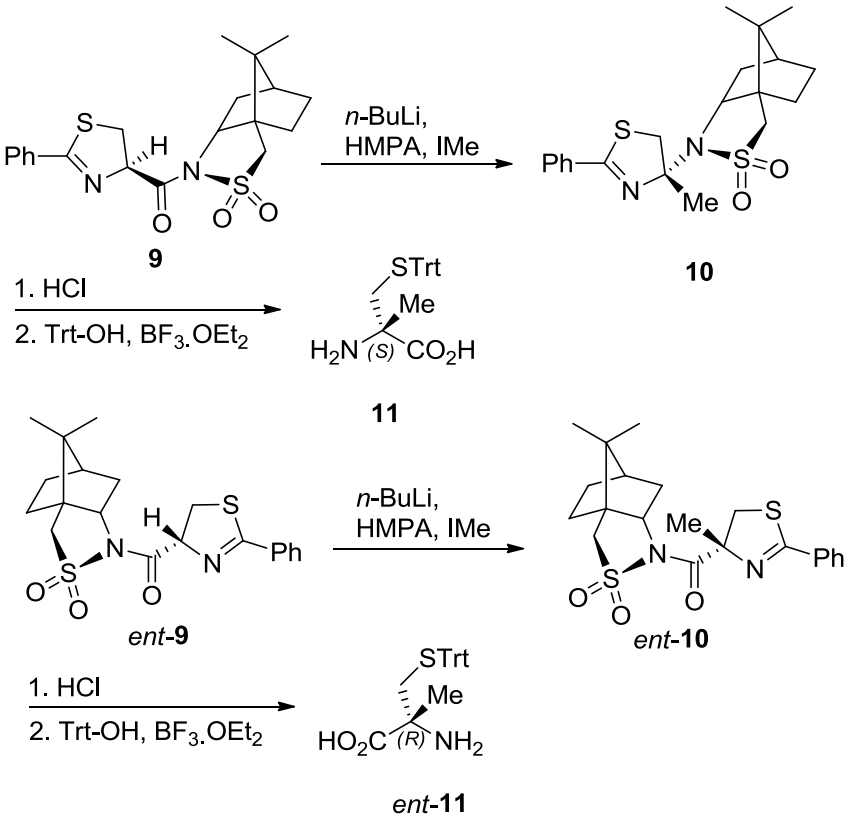
recommended. In this excellent revision the protocol is carefully explained and applications and limitations of the procedure are described.[18]

Such methodology for the synthesis of 2-methylcysteine has been used for synthetizing the thiazoline-based siderophore (*S*)-desferrithiocin previously isolated form *Streptomyces antibioticus*[21] and also for the synthesis of a fragment of Largazole analogues,[22] and Halipeptin A, a potent anti-inflamatory cyclodepsipeptide form a marine sponge.[23]

The use of thiazolidines derived from cysteine and a review focused on their use as building blocks in organic synthesis has been reported.[24] Many examples of this type of compounds has been reported with different modifications at the 2-position of the heterocyclic ring due to the use of these compounds as antioxidants in agricultural chemistry.[25]

On the other hand, the use of thiazolines[26] as chiral cyclic equivalents of cysteines has also been reported and these compounds have been frequently used as intermediates in the synthesis of 2-alkyl cysteines. In order to obtain enantioenriched or enantiopure compounds several strategies have been reported. The use of some chiral compounds is compulsory and in fact, several approaches are reflected in the literature.

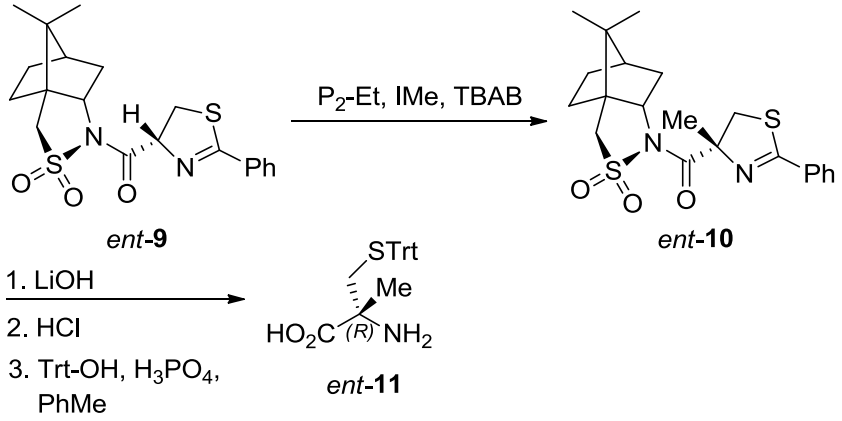
In some approaches, thiazolines were used as synthetic equivalents of α-alkylcysteines incorporating some chiral auxiliary in the carboxylic moiety as an exocyclic chiral appendage. The chiral auxiliaries employed were the (1*R*)-(+) or (1*S*)-(-)-camphorsultam, thus the diastereoselective alkylation of the enolate intermediate with iodomethane afforded both C4 methyl substituted thiazolines **10** and *ent*-**10**, respectively (*Scheme 4*).



Scheme 4

The subsequent hydrolysis of the camphorsultam chiral auxiliary and the cleavage of the thiazoline ring in acidic medium have allowed the access to enantiopure (*S*)-2-methylcysteine derivative **11** and (*R*)-2-methylcysteine derivative *ent*-**11**.[27]

It is important to note that the critical removal of the enolizable α proton of the thiazolines **9** and *ent*-**9** in a typical procedure was carried out using *n*-BuLi as base in the presence of HMPA, but the yields obtained were modest and the use of HMPA on scale is not desirable.[28] However, phosphazene bases provide an attractive alternative as extremely strong, non-ionic, non-charged nitrogen bases which generate highly reactive naked enolates, and also exhibit very low nucleophilicity and hence are inert towards the electrophilic component of the reaction (*Scheme 5*). So, the reaction of the thiazoline *ent*-**9** with P_2-Et in one hour in the presence of the phase transfer catalyst TBAB and IMe afforded the thiazoline *ent*-**10**, C4 methyl substituted, as a single diastereoisomer in high yield. Finally, the hydrolysis of the camphorsultam chiral auxiliary and the cleavage of the thiazoline ring in acidic medium afforded the enantiopure (*R*)-2-methylcysteine derivative *ent*-**11**.[29]

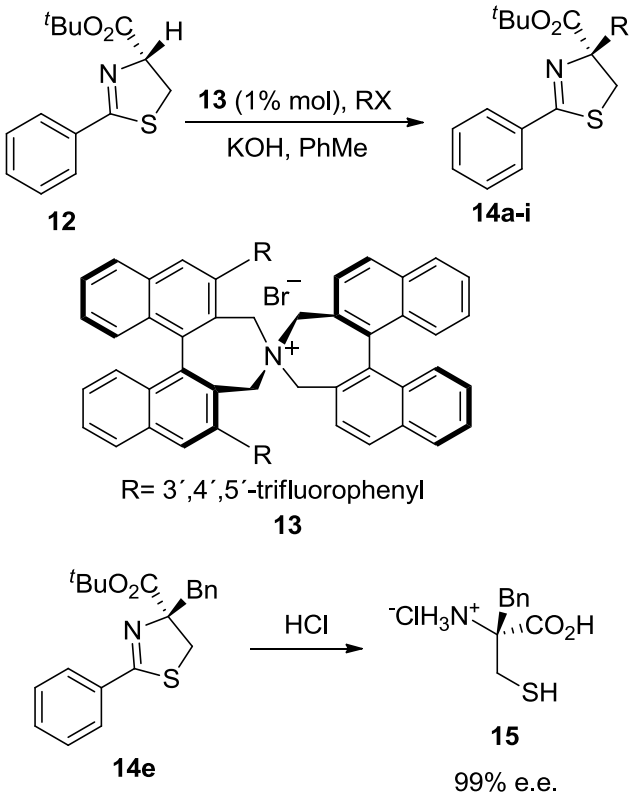


Scheme 5

2.1.2. Enantioselective Cα-R bond formation *via* alkylation of cyclic chiral cysteine enolates equivalents

Among the different approaches for the asymmetric synthesis of chiral compounds, we have highlighted those mediated by a chiral catalyst. The huge synthetic utility is due to the possibility of obtaining large quantities of enantioenriched or enantiomerically pure compounds using a relatively small amount of chiral catalyst. Several different synthetic routes have been developed for the asymmetric synthesis of α-amino acids using this approach to favour the formation of one of the two possible enantiomers,[30] but most of these methodologies cannot be applied to the creation of a quaternary stereocentre. Nevertheless, in recent years some progress has been made in this field and new catalyst that allow the enantioselective synthesis of α,α-dialkylamino acids have been developed. Suitable chiral catalyst to perform the enantioselective synthesis of optically active amino acids under phase-transfer conditions have been described[31] and this methodology has been extended to the asymmetric synthesis of α,α-dialkylamino acids.

In this context, an efficient enantioselective synthesis of (*R*)-alkylthiazolines **14a-i** (67→99% e.e.) (*Table 2*) starting from 2-phenylthiazoline-4-carboxylic acid *tert*-butyl ester **12** as cyclic cysteine equivalent using the chiral phase-transfer catalyst **13** containing an ammonium salt moiety has been reported. Thiazoline **14e** afforded after hydrolysis the (*R*)-2-benzylcysteine **15** in high yield and enantiomeric purity (*Scheme 6*).[32]

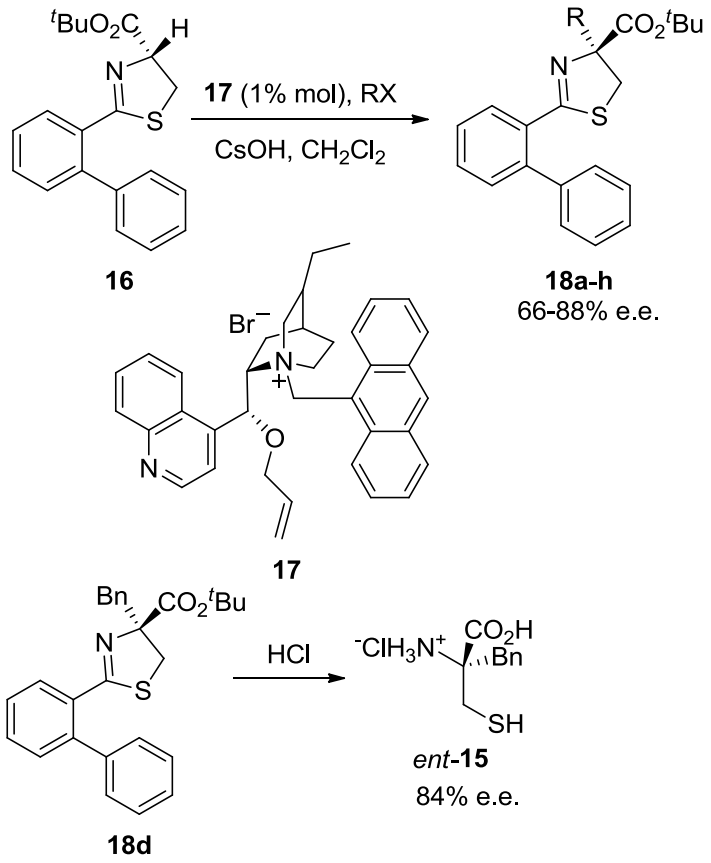


Scheme 6

Table 2. Enantioselective Phase-Transfer catalytic alkylation with **13**

Entry	RX	e.e. (%) (Cofig.)
14a	hexyl iodide	67 (*R*)
14b	allyl bromide	96 (*R*)
14c	2-methylallyl bromide	99 (*R*)
14d	propargyl bromide	97 (*R*)
14e	benzyl bromide	>99 (*R*)
14f	4-cyanobenzyl bromide	98 (*R*)
14g	4-fluorobenzyl bromide	84 (*R*)
14h	4-methylbenzyl bromide	96 (*R*)
14i	2-naphthylmethyl bromide	99 (*R*)

2-*o*-biphenylthiazoline-4-carboxylic acid *tert*-butyl ester **16** gave the corresponding alkylated products (*S*)-4-alkylthiazolines **18a-h** (66→88% e.e.) (*Table 3*) using the chiral phase-transfer catalyst **17**. Thiazoline **18d** afforded after hydrolysis the (*S*)-2-benzylcysteine *ent*-**15** in high yield and enantiomeric purity (*Scheme 7*).



Scheme 7

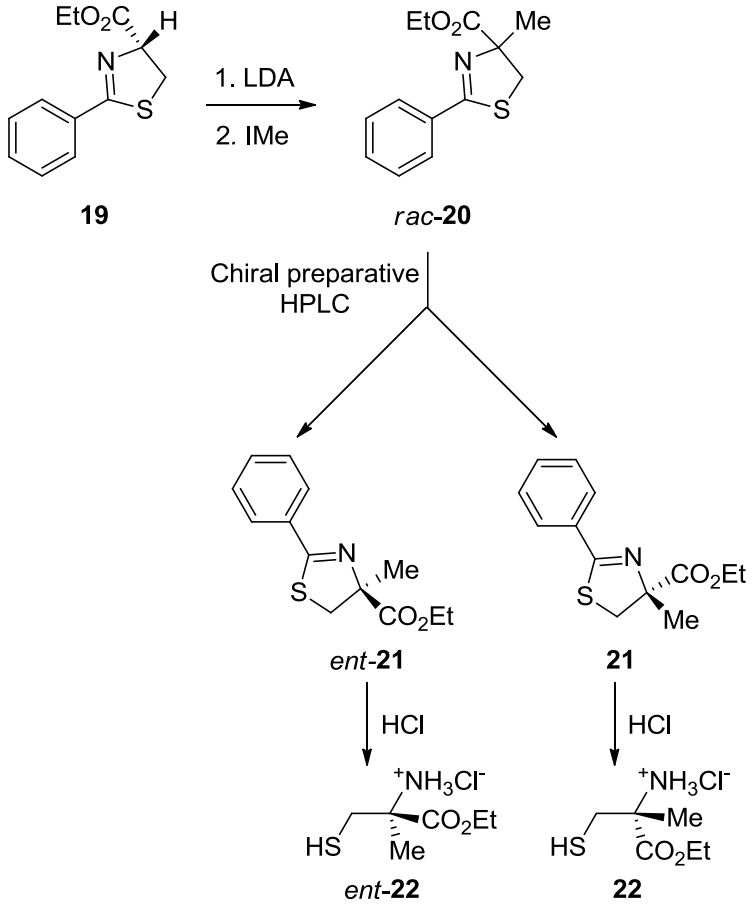
Table 3. Enantioselective Phase-Transfer catalytic alkylation with **17**

Entry	RX	e.e. (%) (Config.)
18a	Allyl bromide	88 (*S*)
18b	2-methylallyl bromide	87 (*S*)
18c	propargyl bromide	68 (*S*)
18d	benzyl bromide	84 (*S*)
18e	4-cyanobenzyl bromide	66 (*S*)
18f	4-fluorobenzyl bromide	85 (*S*)
18g	4-methylbenzyl bromide	75 (*S*)
18h	2-naphthylmethyl bromide	76 (*S*)

2.1.3. Resolution procedures

In addition to the procedures reported for the asymmetric synthesis of chiral non-racemic α,α-dialkylamino acids using either chiral auxiliaries or asymmetric catalysts, resolution procedures also enable the isolation of their enantiomerically pure forms from racemic mixtures afforded by non-asymmetric approaches. The main types of resolution procedures are enzymatic resolution of racemic amino acids, chemical resolution of diastereoisomers obtained from racemic amino acids and the use of preparative chromatography employing chiral stationary phases.[33]

The resolution of the racemic mixture of the C4 methyl thiazoline *rac*-**20** obtained by methylation of 4-ethoxycarbonyl-2-phenylthiazoline **19** was achieved by using preparative high pressure liquid chromatography with the chiral stationary phase cellulose triacetate. The enantiopure compounds **21** and *ent*-**21** were hydrolyzed to obtain the (*R*)-2-methylcysteine derivative **22** and (*S*)-2-methylcysteine derivative *ent*-**22** and applied to the synthesis of thiangazole (*Scheme 8*).[34]



Scheme 8

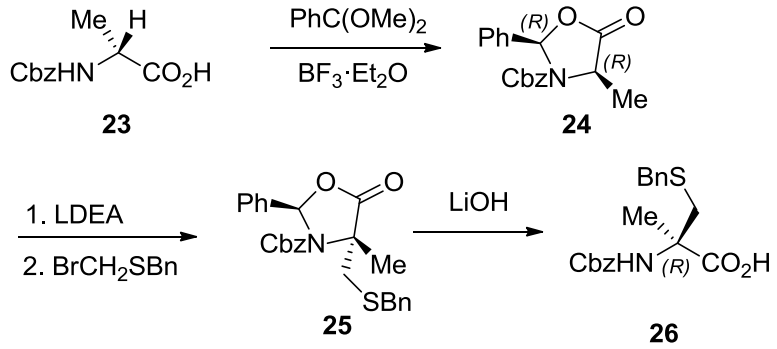
It is important to notice that both cyclic intermediates (thiazolidines and thiazolines) are easily available starting form enantiopure cysteine and the appropriate aldehydes or nitriles to set the substituents at 2-position of the heterocycle. Nevertheless some different alternatives have been reported.[35]

2.2. Incorporation of the lateral chain *via* electrophilic and nucleophilic addition of thiomethyl reagents. Disconnection b)

The most typical procedure requires the use of a chiral equivalent of a quaternary amino acid (typically alanine that is the starting point to the synthesis of

2-methylcysteine) and its reaction with an electrophile containing a halomethyl group bearing the thioether functionality. Alternatively, methylene dibromide can be used as alkylating agent to subsequently incorporate the thiol group in a nucleophilic substitution reaction on the bromomethyl derivative.

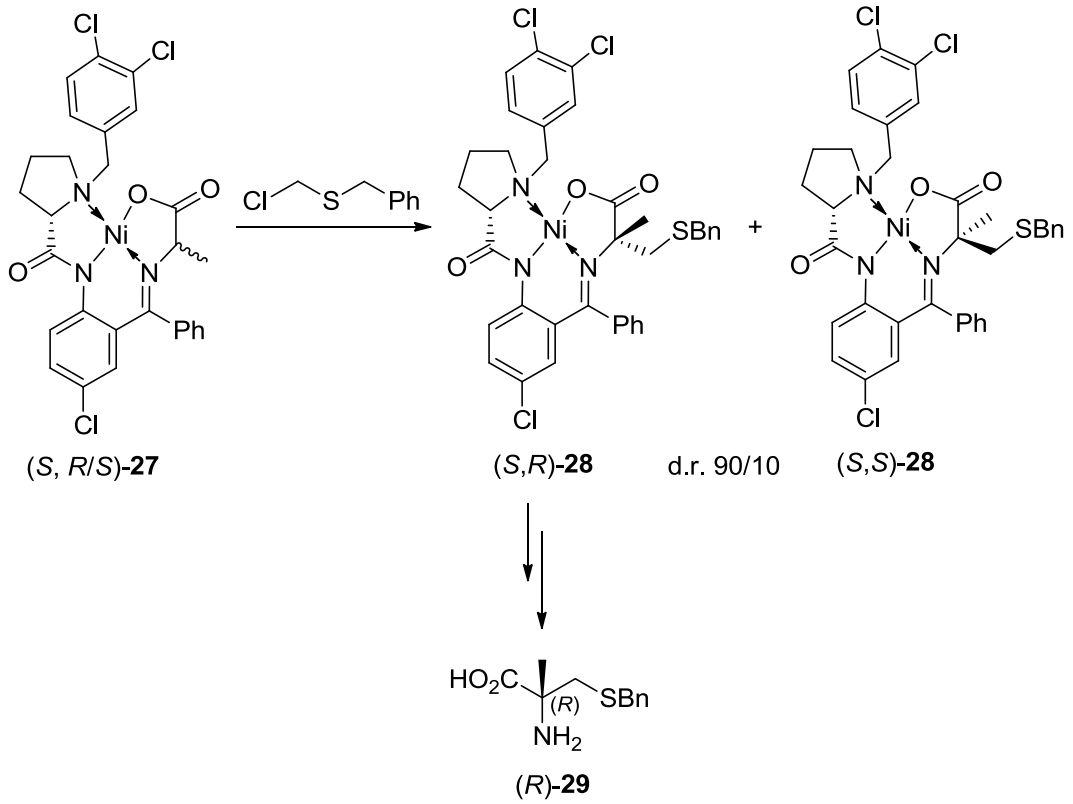
Among the chiral alanines equivalents to obtain (*R*) or (*S*)-methylcysteines, chiral oxazolidinones are suitable reagents to apply the methodology of self-regeneration of stereocentres (*SRS*) previously mentioned. Thus, the oxazolidinone **24** was synthesized by condensation of *D*-alanine **23** with benzaldehyde dimethylacetal in the presence of $BF_3{\cdot}OEt_2$, a modified method of Karady *et al*.[36] Under these conditions, the major isomer obtained was the (2*R*,4*R*)-oxazolidinone **24**, which crystallized easily as reported before. The alkylation of **24** with bromomethyl benzylsulfide proceeds using lithium diethylamide (LDEA) as a base with a reasonable yield and diastereoselectivity. By contrast, the alkylated product **25** was obtained in poor yield when the bases employed were lithium diisopropylamide (LDA) or lithium bis(trimethylsilyl)amide (LiHMDS) with or without dimethylpropyleneurea (DMPU) as the co-solvent. The same phenomenon had already been reported by Seebach *et al*.[37] Finally, the saponification of **25** with LiOH proceeded smoothly to afford (*R*)-2-methylcysteine derivative **26**.[38] Its enantiomer *ent*-**26** was obtained following the same synthetic route but starting from *L*-alanine (*Scheme 9*). The synthesis of 2-methylcysteines intermediates has been used to get thiangazole and mirabazole C.



Scheme 9

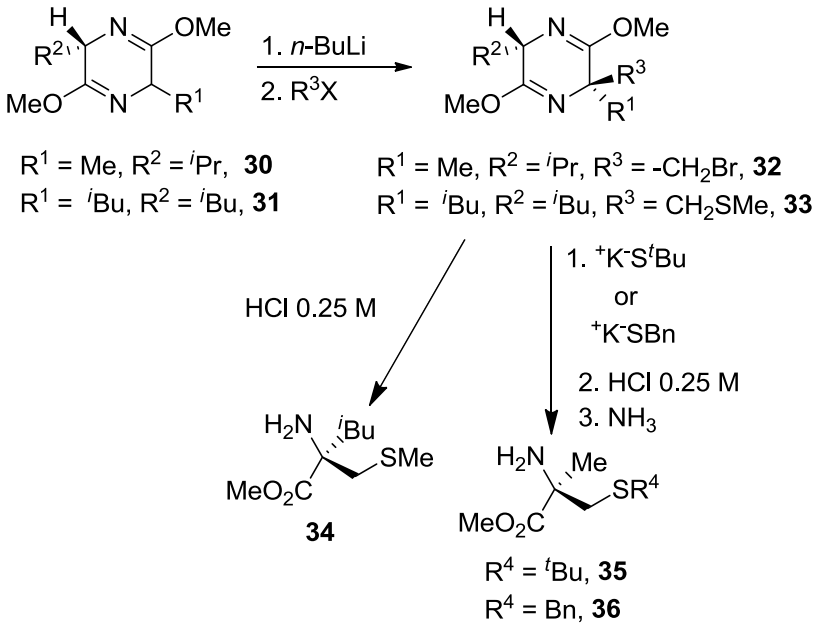
Very recently, the alkylation of chiral alanine Schiff base Ni(II) complexes has emerged as a suitable methodology for the asymmetric synthesis of (2*R*)-α-methylcysteine **29**.[39] In this sense, in a first step of the methodology the formation of the complex was performed. Thus, the synthesis of alanine-derived complex (*S*, *R*/*S*)-**27** was carried out by the *in situ* formation of the corresponding Schiff base between the ligand and racemic alanine, followed by the complexation with Ni^{II} ions

in presence of base. Then, benzyl chloromethyl sulfide was added in presence of base, triggering the alkylation of the alanine as a mixture of isomers (*S*,*R*)-**28** and (*S*,*S*)-**28** in favour of the complex of the isomer (*S*,*R*)-**28**. Final dissasembly of the majority complex resulted in the isolation of (2*R*)-α-methylcysteine **29** with good yield (*Scheme 10*).



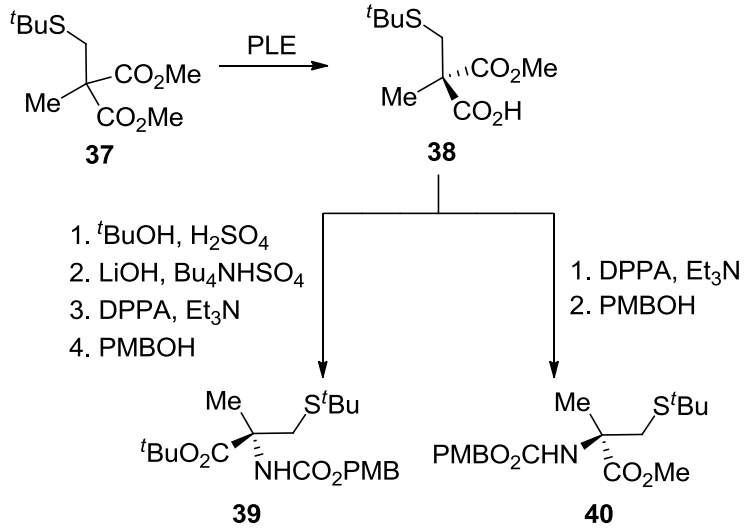
Scheme 10

Other approaches to obtain (*R*)-2-alkylcysteines through a diastereoselective alkylation of cyclic chiral amino acids equivalent enolates used chiral bis-lactim ethers as intermediates.[40] In this context, the bis-lactim ethers **30** and **31** obtained from *L*-Val-*L*-Ala or cyclo(*L*-Leu-*L*-Leu) reacted with dibromomethane[41] and methylchloromethyl sulfide,[42] respectively, in basic medium of *n*-BuLi affording diastereoselectively the alkylated products **32** and **33**. The alkyl group in both cases is located *trans* to the group at C6 in the bis-lactim ether. The hydrolysis of **33** in acidic medium led to the corresponding (*R*)-2-alkylcysteine derivative **34**. In contrast, the alkylated product **32** was treated with potassium *tert*-butylmercaptide or potassium benzylmercaptide obtaining the corresponding *S*-alkyl compounds which upon hydrolysis afforded the thiol protected (*R*)-2-methylcysteines methyl esters **35** and **36** (*Scheme 11*).



Scheme 11

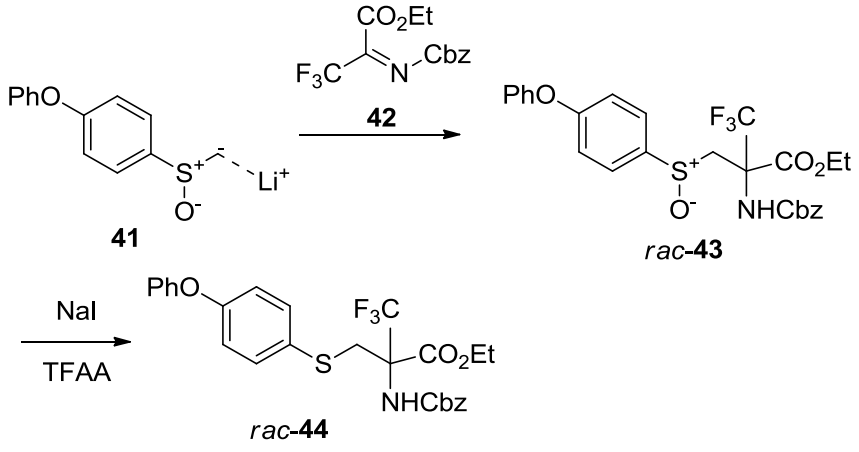
The desymmetrisation of compounds which have a symmetry plane by stereoselective differentiation between two enantiotopic groups has become a useful and elegant approach for the synthesis of enantiomerically pure compounds. Most desymmetrisation approaches for the asymmetric synthesis of α,α-dialkylamino acids are based upon enzymatic processes, since enzymes are capable of differentiating enantiotopic groups with high levels of enantioselectivity.[42] In this context, other "hidden" alanine equivalent has been used. The synthesis of (*R*)- and (*S*)-2-methylcysteines derivatives was carried out from an intermediate synthesized through a sequence of monomethylation of dimethylmalonate followed by the electrophilic alkylation with *tert*-butylchloromethyl sulfide obtaining an achiral diester **37** which was desymmetrized by selective enzymatic hydrolysis using the pig liver esterase (PLE) affording the acid **38**. Acid **38** was then treated with diphenylphosphoryl azide and triethylamine resulting in the rapid formation of the acyl azide that under reflux promoted a Curtius rearrangement to give the corresponding isocyanate, which when treated with *p*-methoxybenzyl alcohol afforded the (*R*)-2-methylcysteine derivative **40**. The conversion of acid **38** into protected (*S*)-2-methylcysteine derivative **39** involves swapping the ester and acid functionalities, followed by a Curtius rearrangement (*Scheme 12*).[44]



Scheme 12

This protocol starting from the enantioenriched (*R*)-2-methylcysteine has been used in the synthesis of a glutathione analogue.[45]

Another case involves the nucleophilic Mannich addition of sulfoxide-stabilized lithiated carbanion **41** to an *N*-Cbz imine **42** derived from trifluoromethylpyruvate affording a nearly equimolecular mixture of sulfoxide diastereoisomers *rac*-**43**, which were deoxygenated to the racemic cysteine *rac*-**44** bearing a trifluromethyl group at the C2 carbon according to the Drabowicz *et al*. protocol.[46] Only this case has been reported but it seems a potent alternative to the synthesis of the desired quaternary cysteines (*Scheme 13*).[47]

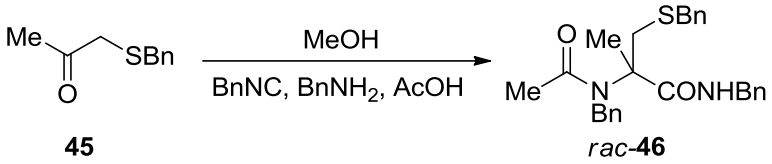


Scheme 13

2.3. Cα-N and Cα-CO bond formation by Ugi or Bucherer-Bergs reaction. Disconnections c) and d)

The third approach involves the disconnections **c** and **d** to introduce simultaneously the amine and carboxylic groups.

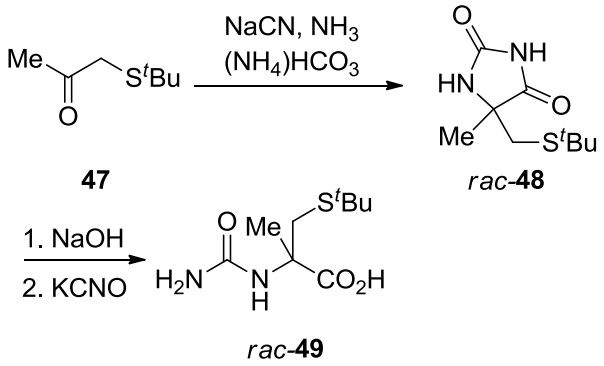
Thus, UGI four-component reaction has been used to prepare the racemic mixture of the 2-methylcysteine derivative *rac*-**46** starting from the methyl ketone **45** bearing a thiol group properly protected as a carbonyl building block, benzylamine, benzylisocianate and acetic acid. Also, this methodology has been explored for the synthesis of glutathione and homoglutathione analogues (*Scheme 14*).[48]



45 *rac*-**46**

Scheme 14

Another approach involved the formation of a hydantoine *rac*-**48** prepared *via* the Bucherer-Bergs reaction, using as the carbonyl source the methylketone **47** containing a thiol group properly protected. The hydantoine *rac*-**48** was hydrolized to give the *N*-carbamoyl-2-methylcysteine derivative *rac*-**49** in a one pot fashion (*Scheme 15*).[49]

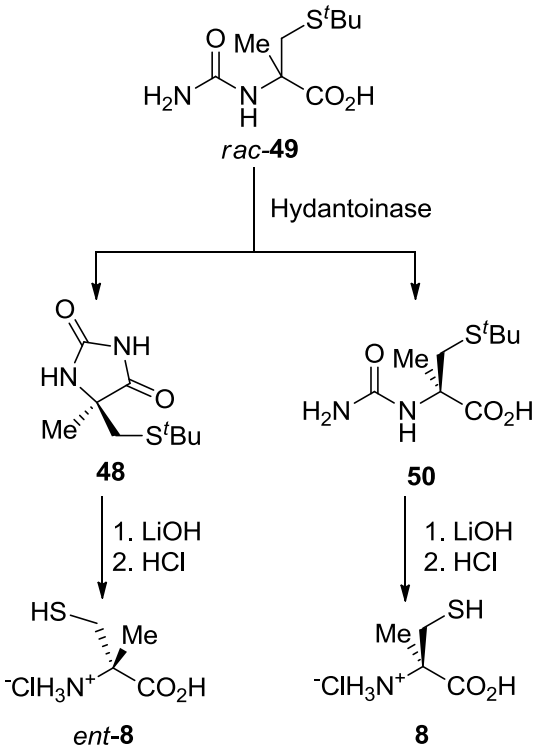


47 *rac*-**48**

rac-**49**

Scheme 15

The *N*-carbamoyl-2-methylcysteine derivative *rac*-**49** could be enzymatically resolved to give the (*R*)-*N*-carbamoyl-2-methylcysteine derivative **50** while the hydantoine **48** gave after hydrolysis the corresponding enantiopure (*R*)- and (*S*)-2-methylcysteines **8** and *ent*-**8**, respectively (*Scheme 16*).[49]



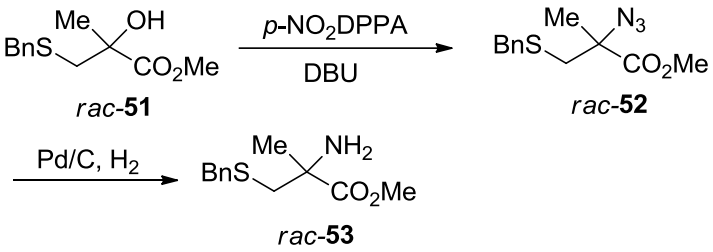
Scheme 16

Other papers related to the formation of hydantoines containing a latent cysteine derivative employing the Strecker or its variant Bucherer-Bergs as the main step have been reported.[50]

2.4. Cα-N bond formation by S_N2 reaction with nucleophilic nitrogen compounds. Disconnection d)

This involves the use of an equivalent or precursor of a quaternary amino acid that is able to react with nucleophilic nitrogen compounds under S_N2 fashion.

Shioiri *et al*.[51] recently reported the azidation reaction of the α-hydroxy ester *rac*-**51** with *p*-NO_2DPPA in the presence of DBU, to afford the desired azide *rac*-**52** in good yield. The reaction proceeded *via* a S_N2 mechanism with inversion of the configuration without a loss of enantiomeric purity when chiral α-hydroxy esters were used. Azide *rac*-**52** was easily converted into the amine by catalytic hydrogenation to obtain the racemic 2-methylcysteine *rac*-**53** derivative in good yield (*Scheme 17*).

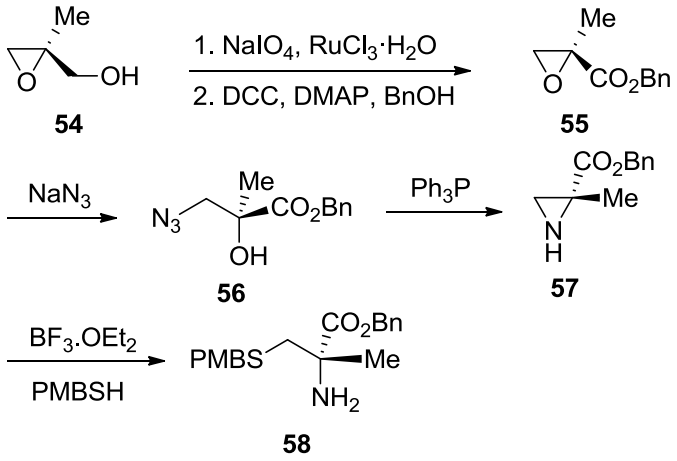


Scheme 17

2.5. Aziridines as building blocks. Disconnection e)

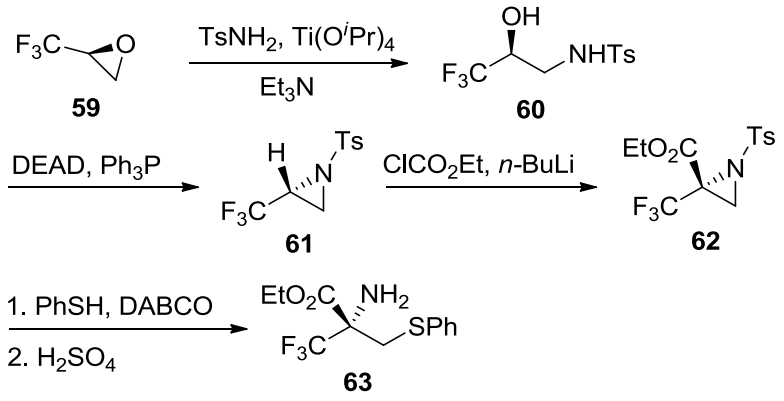
This involves the use of an equivalent or precursor of a quaternary amino acid with an electrophilic carbon located at α position of the carboxylic group able to react with nucleophilic sulfur compounds. It has been reported in recent years that chiral aziridines can be used as building blocks for the synthesis of α,α-dialkylamino acids.[52]

Goodman *et al*.[53] obtained (*S*)-2-methylcysteine derivative **58** in a multistep sequence from enantioenriched (*R*)-2-methylglycidol **54**. Then, **54** was oxidized with ruthenium (VIII) oxide and esterified providing the compound **55**. The regioselective ring opening of **55** with sodium azide afforded **56**, which was treated with triphenylphosphine to give the enantiomerically pure 2-methyl-2-aziridine carboxylic acid benzyl ester **57** in excellent yield. Finally, the (*S*)-2-methylcysteine derivative **58** was obtained by regioselective ring opening with toluenethiol at C3 of the aziridine **57** catalyzed by Lewis acid (*Scheme 18*). The (*R*)-2-methylcysteine derivative *ent*-**58** was obtained also based on *scheme 18* but using diethyl *L*-tartrate in Sharpless asymmetric epoxidation.



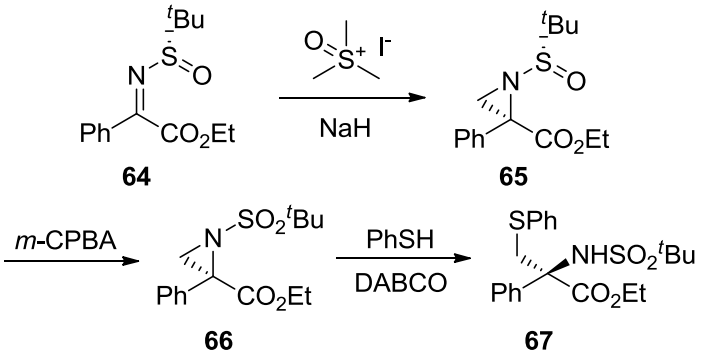
Scheme 18

The preparation of optically pure (*S*)-2-trifluoromethylcysteine derivative **63** started from (*S*)-*N*-tosyl-2-trifluoromethyl-2-ethyloxycarbonyl aziridine **62**. The first step of this synthesis was the obtention of chiral aziridine **61** as synthetic equivalent of chiral 2-trifluoromethyl amino acids. Thus, the treatment of the enantiomerically pure 2,3-epoxy-1,1,1-trifluoropropane **59** with $TsNH_2$ in the presence of the Lewis acid catalyst $Ti(O^iPr)_4$ and Et_3N afforded the amino alcohol **60** in high yield, which was then converted into the aziridine **61** by an intramolecular Mitsunobu reaction. The enantioselective desprotonation/alkylation of the aziridine **61** using *n*-BuLi as base and ethyl chloroformate as the electrophile afforded the ethyl (*S*)-2-trifluoromethylaziridine-2-carboxylate **62**. Aziridine **62** has two reaction sites for nucleophiles: the aziridine ring and the ester moiety. Therefore, there would be two competitive reactions with a nucleophile. In the case of using PhSH as nucleophile in the presence of DABCO, the nucleophilic addition was regioselective with the nucleophile attacking the aziridine ring to give the ring opening product (*S*)-2-trifluoromethylcysteine derivative **63** in good yield. The regioselectivity could be due to the high hindrance of the nucleophilic attack on the carbonyl carbon which is shielded by the bulky and negatively charged trifluoromethyl group (*Scheme 19*).[54]



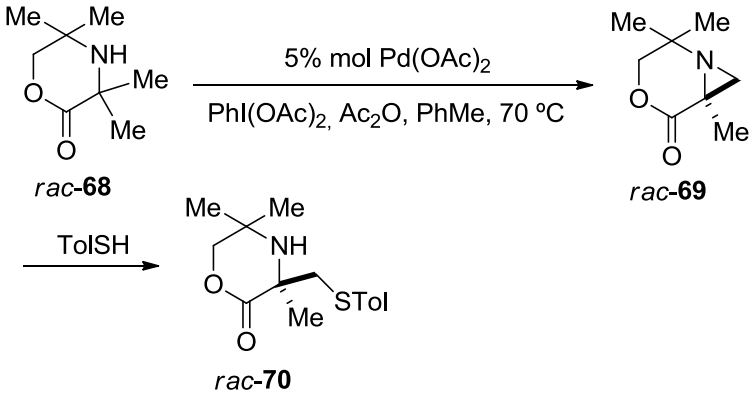
Scheme 19

Recently, it has been reported that the diastereoselective synthesis of ethyl 2-quaternary aziridine-2-carboxylate **65** can be carried out *via* Aza-Corey-Chaykovsky aziridination of *N*-*tert*-butanesulfinyl ketimino ester **64** as the key step of the synthesis. Oxidation of **65** with *m*-CPBA afforded **66**, which upon regioselective nucleophilic ring opening led to the (*R*)-2-phenylcysteine analog **67** incorporating a phenyl group at C2 position in four steps from commercially available ethyl benzoylformate. This compares favorably to other literature methods for the preparation of similar compounds (*Scheme 20*).[55]



Scheme 20

Another new and elegant method to obtain aziridines-2-carboxylates as possible intermediates of 2-alkylcysteines derivatives represents the directed C-H activation of simple methyl groups adjacent to secondary amines catalyzed by palladium.[56] So, the aliphatic secondary amine *rac*-**68** was treated with $Pd(OAc)_2$ and a four membered-ring intermediate resulted from the C-H activation of the methyl group (*Scheme 21*). Next, the reactivity of the strained cyclopalladium complex was evaluated under mild oxidant conditions using hypervalent iodine $PhI(OAc)_2$ to obtain the aziridine *rac*-**69** *via* C-N bond forming reductive elimination from a high oxidation state Pd(IV) intermediate. Finally, the regioselective nucleophilic ring opening of the aziridine *rac*-**69** led to the 2-methylcysteine analogue *rac*-**70**.



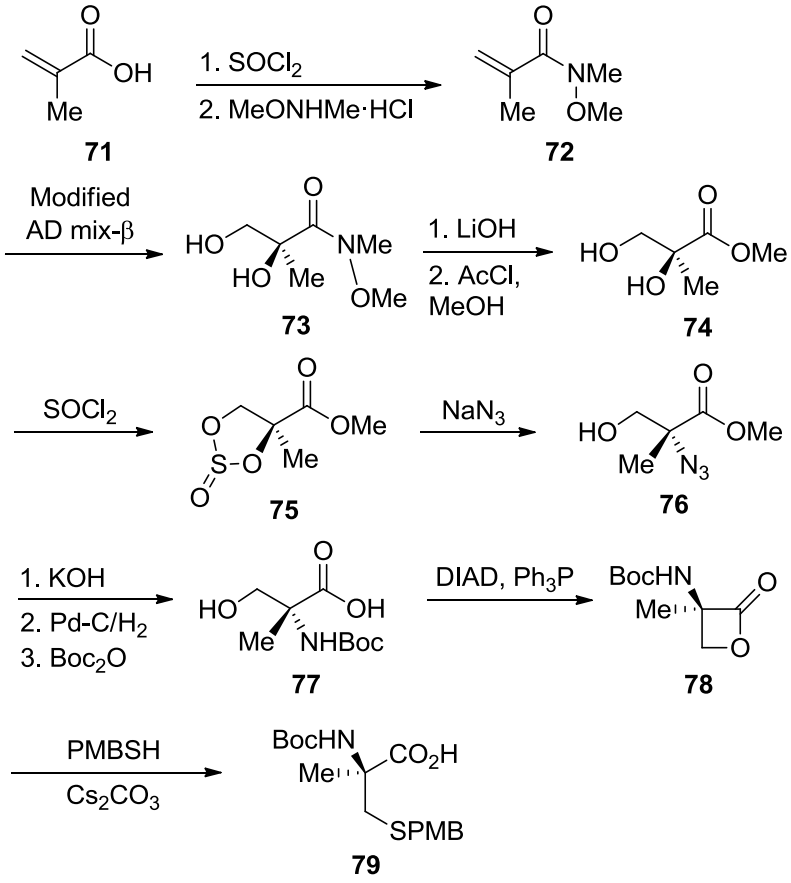
Scheme 21

2.6. β-lactones as building blocks. Disconnection e)

The ring opening of β-lactones is widely used for the asymmetric synthesis of β-disubstituted carboxylates and amino acids. This reaction strategy allows a variety of different substituted organocuprates to be employed in the ring opening of structurally diverse 4-substituted 2-oxetanones, resulting in enantiomerically enriched β-disubstituted carboxylic acids.[57] Vederas *et al*. opened serine lactones

with various nucleophiles, including amines, thiols, halogens and a variety of organometallic reagents.[58] Goodman *et al*. have applied this chemistry to the synthesis of lanthionine derivatives *via* regioselective ring opening of serine-β-lactones with a variety of cysteines.[59]

The enantioselective synthesis of (*S*)-*N*-Boc-2-methylcysteine **79** and lanthionine building blocks has been reported.[60] The synthesis started with the preparation of (*R*)-*N*-Boc-2-methylserine **77** (*Scheme 22*).



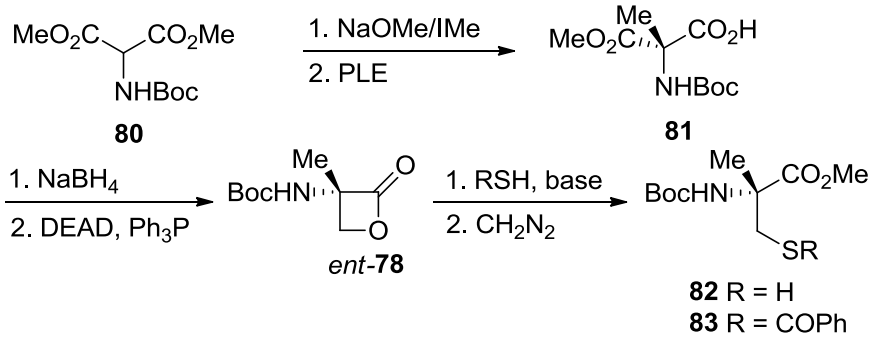
Scheme 22

The methacrylic acid **71** was transformed into the Weinreb amide **72**. This compound was submitted to Sharpless asymmetric dihydroxylation with a modified AD mix-β[61] to provide diol **73**. Diol **73** was saponified with lithium hydroxide and esterified with acidic methanol to give **74**. This compound under refluxing conditions was converted into cyclic sulfite **75** in the presence of thionyl chloride. The cyclic sulfite **75** was selectively opened with sodium azide at the tertiary carbon to afford the azido alcohol **76**. The azido alcohol **76** was saponified with potassium hydroxide and the azide was reduced with palladium on carbon. The amine group was protected with Boc_2O to give (*R*)-*N*-Boc-2-methylserine **77**. Finally, (*R*)-*N*-Boc-2-methylserine-β-lactone **78** was formed from (*R*)-*N*-Boc-2-

methylserine **77** through a Mitsunobu reaction using DIAD and Ph_3P. (*R*)-*N*-Boc-2-methylserine-β-lactone **78** was regioselectively opened with 4-methoxy-α-toluenethiol at the β-methylene carbon resulting in *O*-alkyl fission in the presence of Cs_2CO_3 to obtain the corresponding (*S*)-*N*-Boc-2-methylcysteine derivative **79**.

(*R*)-*N*-Boc-2-methylserine-β-lactone **78** was opened with Cbz- and Fmoc-protected cysteines and penicillamine derivatives resulting in the orthogonally protected lanthionine building blocks.

Chiral β-lactone *ent*-**78** as the key intermediate for the synthesis of (*R*)-2-methylcysteines derivatives **82** and **83** by nucleophilic ring opening with H_2S[62] and thiobenzoic acid,[63] respectively (*Scheme 23*).



Scheme 23

The synthetic route to the β-lactone *ent*-**78** consisted of alkylating the dimethyl *N*-Boc-aminomalonate **80** with NaOMe/IMe, and then was submitted to enzymatic desymmetrization to obtain compound **81**. Compound **81** was reduced and under Mitsunobu conditions the β-lactone *ent*-**78** was obtained, which was then reacted with H_2S in Et_3N or thiobenzoic acid in the presence of K_2CO_3 to obtain the corresponding (*R*)-2-methylcysteines **81** and **83**, respectively.

3. SYNTHESIS OF ACYCLIC β-SUBSTITUTED CYSTEINE DERIVATIVES

The general disconnection approaches to the synthesis of this family of cysteines are shown in the *Figure 3*.

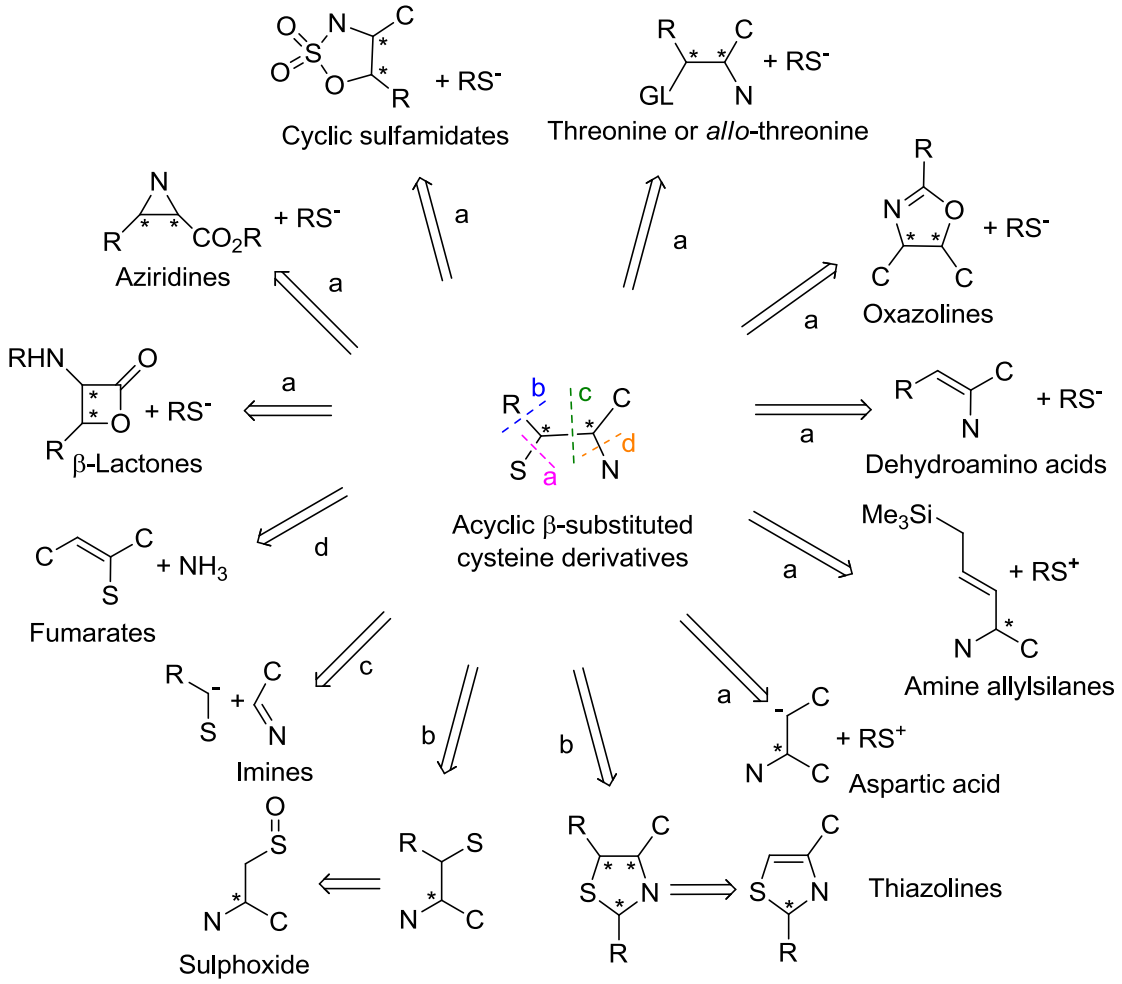


Figure 3. Routes to obtain β-substituted cysteines

Perhaps the most general and representative approach is the disconnection **a** that involves the use of an equivalent of sulfur nucleophile (typically thioacetates, thiocianates, alkyl/aryl thiols and so on) that reacts with an electrophilic carbon. The classification used in this introduction involves the type of synthetic equivalent containing this electrophilic carbon. Inside this reaction, perhaps the most obvious family of compounds are the corresponding serines, in which the hydroxy group can be transformed into a good leaving group, which in this case will be β-substituted and in particular the easily available threonines or *allo*-threonines that will allow the synthesis of enantiopure (or enantioenriched) β-methylcysteines. A selection of the most important ones is included. In some cases, the enantiopure compounds have been used as intermediates in the synthesis of other compounds of biological interest.

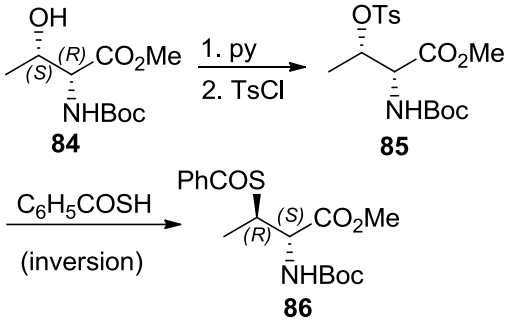
On the other hand, the disconnection **b** takes place using the cysteine or an analogue and the substituent group at the β-position is incorporated, basically through a Pummerer reaction or a Michael-addition. The disconnection **c** involves the creation of a bond between the α carbon and the β carbon, in a typical procedure between stabilized carbanions in the α position of a sulfur atom and an electrophile carbon, usually imines. Finally, the disconnection **d** involves the C-N bond formation through a conjugate addition between fumarates and ammonia.

3.1. Cβ-S bond formation using nucleophilic and electrophilic sulfur compounds. Disconnection a)

The first approach involves the disconnection **a** thus implying the formation of Cβ-S bond as the key step to the synthesis of β-alkylcysteines. Mainly, the starting materials employed are: threonine, *allo*-threonine, oxazolines and cyclic sulfamidates that *via* S_N2 reaction were allowed to install the sulfur atom at the β-position of the amino acid. The dehydroamino acids have also been used as starting materials, which after conjugate addition have given β-alkylcysteines derivatives. The diastereo- and regioselective ring opening of aziridines and β-lactones has been used to install the sulfur atom at β-position. Other intermediates such as amine allylsilanes and aspartic acid have scarcely been employed.

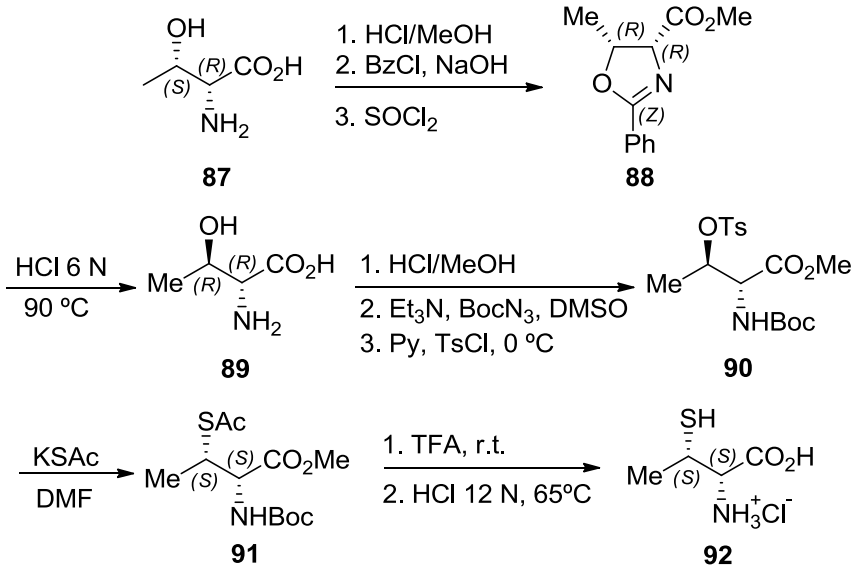
We found in the literature different alkyl substitutions at the β-position of the cysteine unit. Concerning to this assumption, the literature revealed a wide range of synthetic approaches to β-alkylcysteines derivatives. One of them, the most available, starts from commercial threonine and/or *allo*-threonine which installs the methyl group at the β-position.

So, Shiba *et al*.[64] reported on the synthesis of (2*S*,3*R*)-methylcysteine derivative **86** using protected *D*-threonine derivative **84** as starting material which after displacement of the *p*-toluenesulfonyloxy group placed at the β-carbon of the compound **85**, by S_N2 substitution with inversion of configuration with thiobenzoic acid gave the desired product (*Scheme 24*).



Scheme 24

In another example described by Gross *et al*.[65] the synthesis of (2*S*,3*S*)-3-methylcysteine derivative **89** was carried out starting from *D*-threonine **87**. The synthetic route involved the formation of the (4*R*,5*R*)-2-phenyl-5-methyloxazoline-4-carboxylic acid methyl ester **88** which upon ring opening in acidic conditions afforded *allo*-*D*-threonine **89**. A convenient protection of **89** and displacement of the *p*-toluenesulfonyloxy group at the β-carbon of the compound **90**, with inversion of configuration with potassium thiolacetate, afforded the (2*S,3S*)-3-methylcysteine derivative **91** in enantiopure form. The acidic hydrolysis of **91** allowed to obtain the (2*S,3S*)-3-methylcysteine **92** (*Scheme 25*). It is important to note that the synthetic methodology implied two inversions of configuration at the β-carbon of the *D*-threonine amino acid starting material.



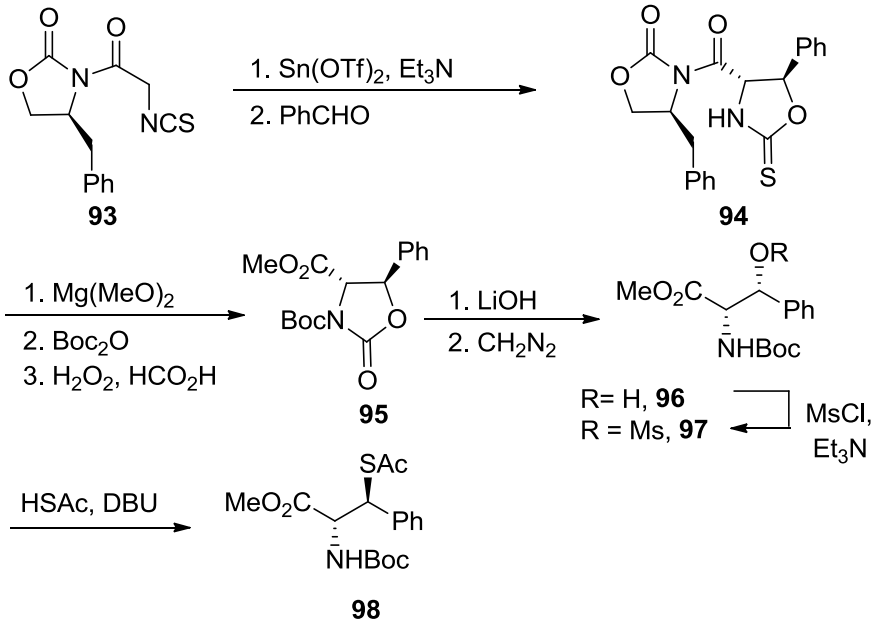
Scheme 25

In this context, we found other examples in which the key step to obtain β-methylcysteines derivatives is a S_N2 reaction from threonine and *allo*-threonine derivatives.[66] The same methodology was followed for the synthesis of β-

isopropylcysteines derivatives starting from commercially available (2*S*,3*S*) or (2*S*,3*R*)-3-hydroxyleucine.[67]

Moreover, the literature reveals a restricted range but not least of synthetic approaches to β-substituted cysteines derivatives bearing a phenyl group at the β-position which crucial step is also a S_N2 reaction.

In this sense, two diastereoselective routes to both (2*R*,3*S*)-3-phenylcysteine derivative **98** (*Scheme 26*) and (2*R*,3*R*)-3-phenylcysteine derivative **104** (*Scheme 27*) derivatives[68] from the corresponding *N*-Boc protected *threo*- and *erythro*-3-phenylserines **96** and **102** based directly on Evans methodology have been reported.[69]

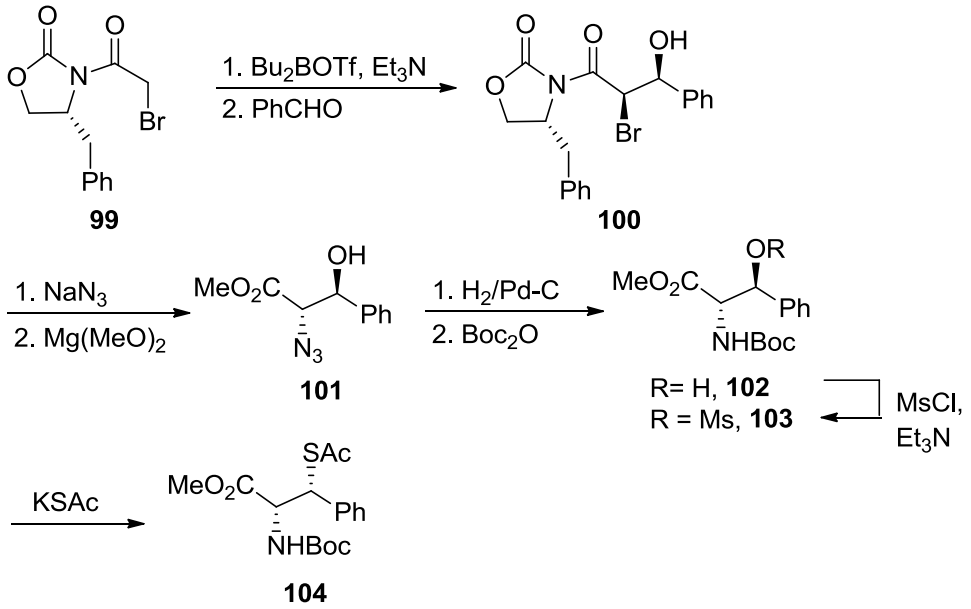


Scheme 26

The first approach implies the asymmetric aldol addition reaction of *N*-(isothiocyanoacetyl)oxazolidinone **93** with benzaldehyde to afford the compound **94** diastereoselectively. Straightforward manipulations of **94** led to its transformation into *N*-Boc protected *threo*-3-phenylserine **96**. Then, the S_N2 displacement of the corresponding benzylic mesylate **97** with thiolacetic acid in the presence of DBU rendered the (2*R*,3*S*)-3-phenylcysteine derivative **98** in high yield (*Scheme 26*).

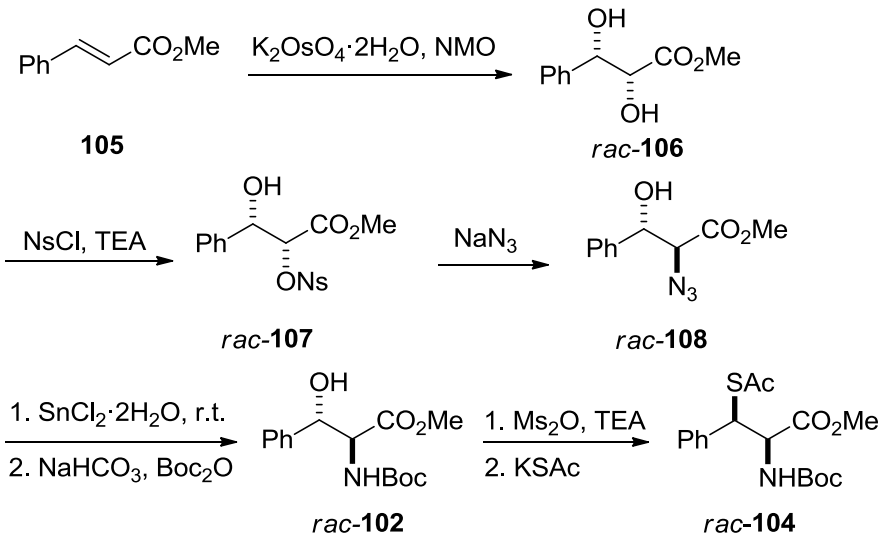
The other synthetic approach proceeded *via* an asymmetric aldol addition reaction of *N*-(bromoacetyl)oxazolidinone **99** with benzaldehyde in high diastereoselectivity to afford compound **100**. Standard transformations yielded the azide **101**, which was converted in two consecutive steps into *N*-Boc protected *erythro*-3-phenylserine **102**. S_N2 displacement of the obtained mesylate **103** was

carried out with the potassium salt of thiolacetic acid to afford (2*R*,3*R*)-3-phenylcysteine derivative **104** with good yield (*Scheme 27*).



Scheme 27

Another example to synthesize *threo*-3-phenylcysteine derivative *rac*-**104** in racemic form diastereoselectively involved the dihydroxylation of the commercially available methyl cinnamate **105** to obtain the *threo*-diol *rac*-**106**. The selective nosylation reaction of the α-hydroxy group that can be attributed because of the difference in pK_a value between the α- and β-hydroxyl groups gave compound *rac*-**107**. The treatment of the compound *rac*-**107** with NaN_3 afforded the azide alcohol *rac*-**108**. The susbsequent reduction and protection of *rac*-**108** led to *N*-Boc protected 3-phenylserine derivative *erythro*-*rac*-**102**. Finally, the S_N2 displacement of the mesyl sulfonate with potassium thioacetate gave the *threo*-3-phenylcysteine derivative *rac*-**104** (*Scheme 28*).[70]

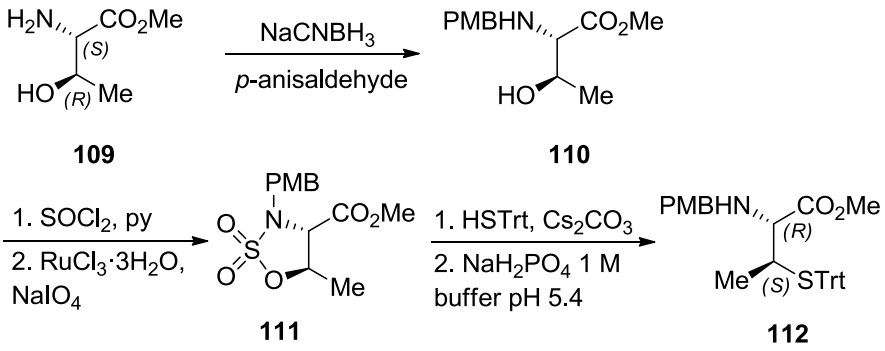


Scheme 28

In this context, Crich *et al*.[71] reported the synthesis of protected (2*R*,3*R*)-3-phenylcysteine starting from (2*S*,3*S*)-3-hydroxy-3-phenylserine under S_N2 displacement of the corresponding mesyl sulfonate as described previously.

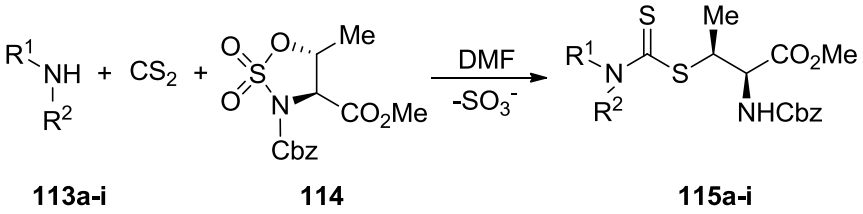
Sulfamidates are useful synthetic building blocks that can be opened stereo- and regioselectively by a variety of nucleophiles.[72] Therefore, suitably protected cysteines or nucleophilic thiol compounds could attack a cyclic sulfamidate derived from threonine to give orthogonally protected β-methyllanthionines or β-methylcysteines, respectively.

In this context, Vederas *et al*.[73] investigated the use of cyclic sulfamidates to prepare the orthogonally protected analogue of (2*R*,3*S*)-3-methylcysteine **112**. The synthetic methodology started from the commercially available *L*-threonine methyl ester **109** and the introduction of the PMB protecting group to obtain the compound **110** was carried out using a reductive amination procedure. The conversion of the compound **110** into the cyclic sulfamidate **111** was achieved *via* slight modification of the procedure detailed by Cohen *et al*.[74] Finally, the ring opening of the cyclic sulfamidate with trityl thiol in basic medium and acidic hydrolysis of the sulfamic acid intermediate gave the (2*R*,3*S*)-3-methylcysteine derivative **112** (*Scheme 29*).



Scheme 29

We found another example in the bibliography, which describes the usefulness of the regio- and stereoselective ring opening of sulfamidates to give β-methylcysteine derivatives **115a-i** after the reaction with dithiocarbamate anions. Hence, the dithiocarbamate anions generated *in situ* by the reaction with a wide range of amines **113a-i** and carbon disulfide reacted with the cyclic sulfamidate **114** to afford the β-methylcysteine derivatives **115a-i** in good to high yields. The reaction was presumed to proceed *via* S_N2 mechanism to give the product with inversion of configuration at the center of the sulfamidate (*Scheme 30*, *Table 4*).[75]



Scheme 30

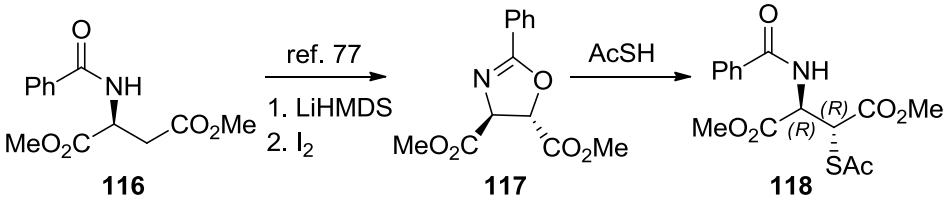
Table 4. Ring-opening of the cyclic sulfamidate **114** with dithiocarbamates anions

Entry	Amine	Yield (%)
115a	Piperidine	93
115b	Pyrrolidine	95
115c	Diisopropylamine	69
115d	Benzylamine	88
115e	(*S*)-1-phenylethanamine	92
115f	Proline methyl ester	87
115g	4-hydroxyproline methyl ester	85
115h	Proline	88
115i	N-Bn-Threo-OMe	91

An interesting application of cyclic sulfamidates obtained from unprotected *allo*-*L*-threonine has been reported. The reaction with 1-thio sugars in aqueous bicarbonate buffer afforded the corresponding *S*-linked β-methylcysteine derivatives with good diastereoselectivity after hydrolysis of the *N*-sulfates.[74]

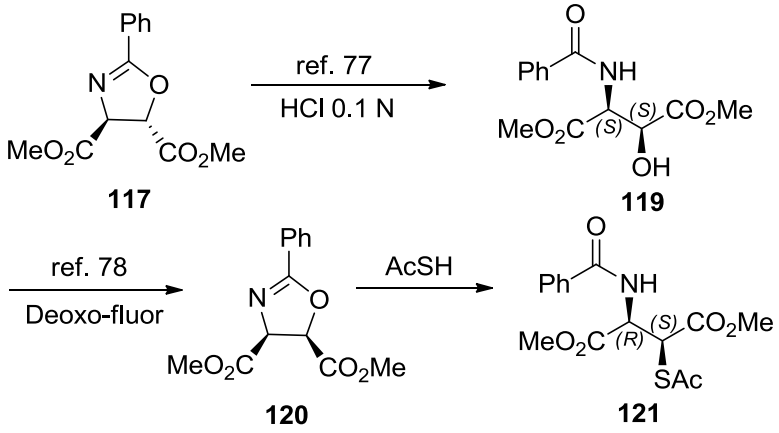
The ring opening of oxazolines derived from *L*-serine for the synthesis of the four diastereoisomers of 3-mercaptoaspartic acid derivatives has also been reported.[76]

The key intermediate, *trans*-(4*S*,5*S*)-oxazoline-4,5-dicarboxylic acid methyl ester **117** was synthesized from *L*-aspartic acid derivative **116** following the procedure described by Cardillo *et al*.[77] and subsequent treatment with LiHMDS and quenching the reaction with I_2. The nucleophilic ring-opening reaction of **117** with thiolacetic acid afforded the desired *erythro*-(2*R*,3*R*)-3-mercaptoaspartic acid methyl ester derivative **118** diastereoselectively with inversion of configuration at the C5 position of the parent oxazoline **117** (*Scheme 31*).



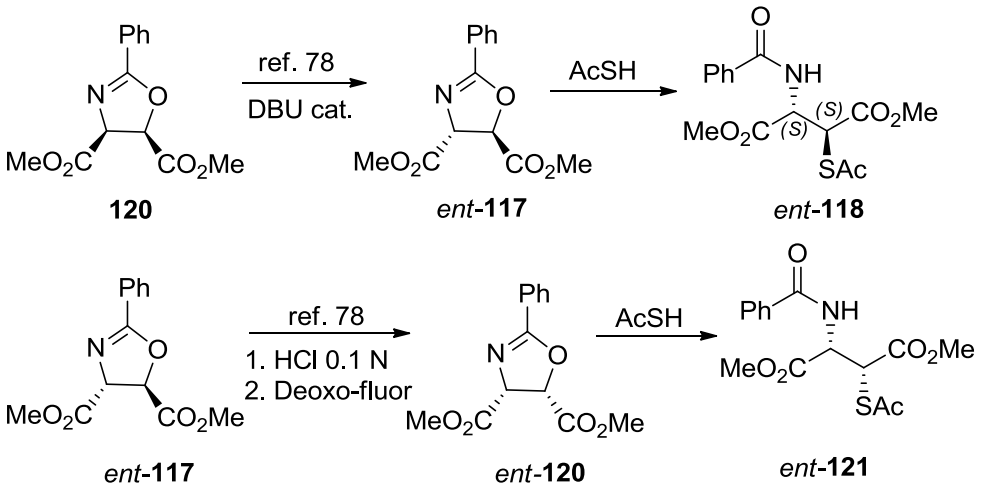
Scheme 31

Following the procedure reported by Campiani *et al*.[78], *trans*-(4*S*,5*S*)-oxazoline **117** was hydrolyzed to afford *threo*-(2*S*,3*S*)-3-hydroxyaspartic acid methyl ester derivative **119**, which was transformed into *cis*-(4*S*,5*R*)-oxazoline **120** by the treatment of deoxo-fluor with inversion of the configuration at the C5 carbon. The *cis*-(4*S*,5*R*)-oxazoline **120** was then reacted with neat thiolacetic acid to obtain *threo*-(2*R*,3*S*)-3-mercaptoaspartic acid methyl ester derivative **121** diastereoselectively with inversion of configuration at the C5 position of the parent oxazoline **120** (*Scheme 32*).



Scheme 32

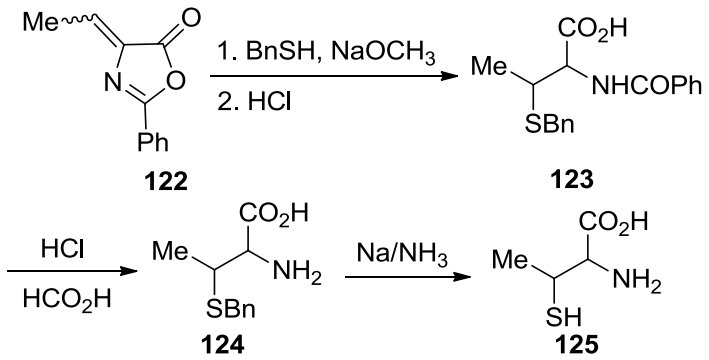
The diastereoisomer with (2*S*,3*S*) configuration *ent*-**118** was obtained after base-induced epimerization of **120** at C4 carbon due to the formation of the thermodynamically more stable *trans*-(4*R*,5*R*)-oxazoline isomer *ent*-**117** following the ring-opening with thiolacetic acid. The other diastereoisomer *ent*-**121** was obtained *via* a double epimerization of **120**, first at C4 carbon to obtain the *trans*-(4*R*,5*R*)-oxazoline isomer *ent*-**117** and after at C5 carbon on the oxazoline ring to afford the *cis*-(4*R*,5*S*)-oxazoline isomer *ent*-**120**. Finally, the ring-opening with thiolacetic acid gave *ent*-**121** (*Scheme 33*).



Scheme 33

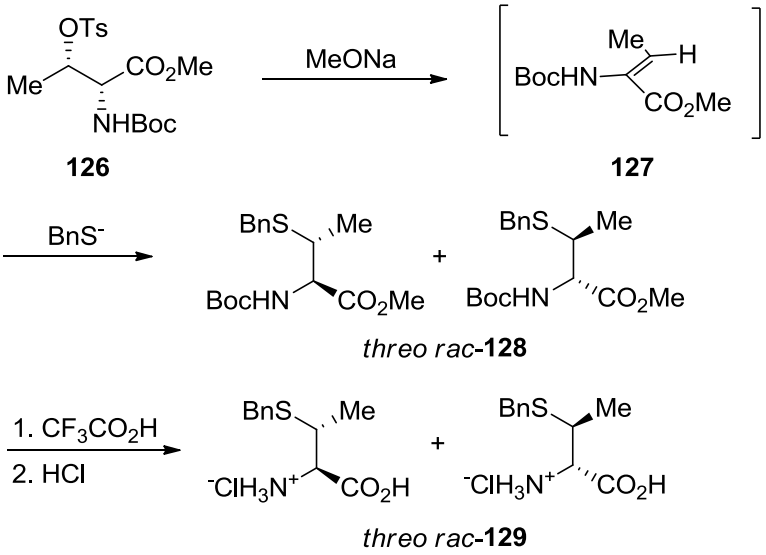
The conjugate addition of nucleophilic compounds to dehydroamino acids is an interesting tool for organic chemists to obtain β-mono or β,β-disubstituted amino acids. In the particular case of the conjugate addition of sulfur nucleophiles and β-mono or β,β-disubstituted dehydroamino acids and derivatives, an appropriate approach to obtain β-alkyl or β,β-dialkyl substituted cysteine derivatives has been reported.[79]

In this context, Carter *et al*.[80] have reported the synthesis of 3-methylcysteine **125** as diastereomeric mixture with the key reaction being a conjugate addition of benzylthiol to the oxazolone **122** (*Scheme 34*).



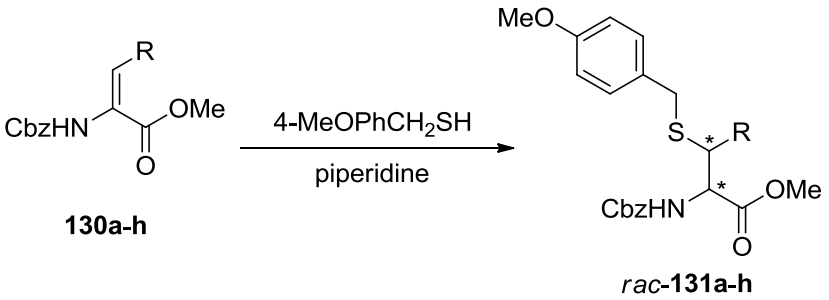
Scheme 34

Nagasawa *et al*.[81] have applied this methodology to obtain *threo*-3-methylcysteine derivative *rac*-**129** as racemic mixture from *N*-Boc-*O*-tosyl-*D*-threonine methyl ester **126**. The conjugate addition conditions employing MeONa and benzylthiol led to the plane *Z*-acrylate **127** intermediate losing the chirality of the starting material before the conjugate addition, obtaining the racemic mixture *threo*-3-methylcysteine derivative *rac*-**128** diastereoselectively, which after hydrolysis afforded the free amino acid in hydrochloride form *rac*-**129** (*Scheme 35*).



Scheme 35

Inguimbert *et al*.[82] reported the synthesis of racemic β-substituted cysteines derivatives *rac*-**131a-h** bearing a wide range of alkyl susbstituents at the β-position through a Michael addition of (4-methoxyphenyl)methanethiol to β-substituted *E*-dehydroamino acids **130a-h** (*Scheme 36*).

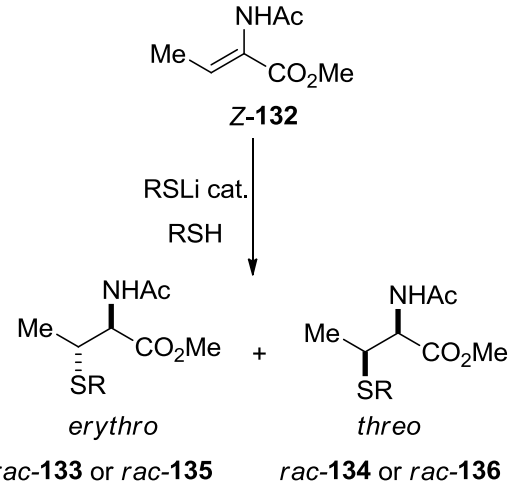


130a-h *rac*-**131a-h**

R = Me, **a**; R = Ph, **b**; R = *i*-Bu, **c**;
R = Bn, **d**; R = $PhCH_2CH_2$, **e**; R = 4-MeO-$PhCH_2CH_2$, **f**;
R = 2-MeO-$PhCH_2CH_2$, **g**; R = 4-Br-$PhCH_2CH_2$, **h**.

Scheme 36

The nature of the geometry, *Z* or *E*, of the dehydroamino esters in the stereoselectivity of the sulfa-Michael addition of thiols has been studied.[83] The reaction of *Z*-acrylate **132** with an excess of phenyl or benzylthiol and a catalytic amount of their lithium salt, in the conditions studied, gave the *threo*-3-methylcysteine derivatives *rac*-**134** or *rac*-**136** isomer as the major adduct, respectively (*Scheme 37*).



Z-**132**

erythro *threo*

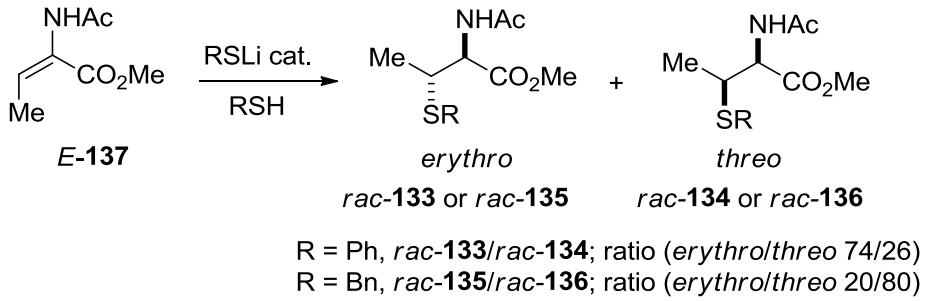
rac-**133** or *rac*-**135** *rac*-**134** or *rac*-**136**

R = Ph, *rac*-**133**/*rac*-**134**; ratio (*erythro*/*threo* 11/89)
R = Bn, *rac*-**135**/*rac*-**136**; ratio (*erythro*/*threo* 10/90)

Scheme 37

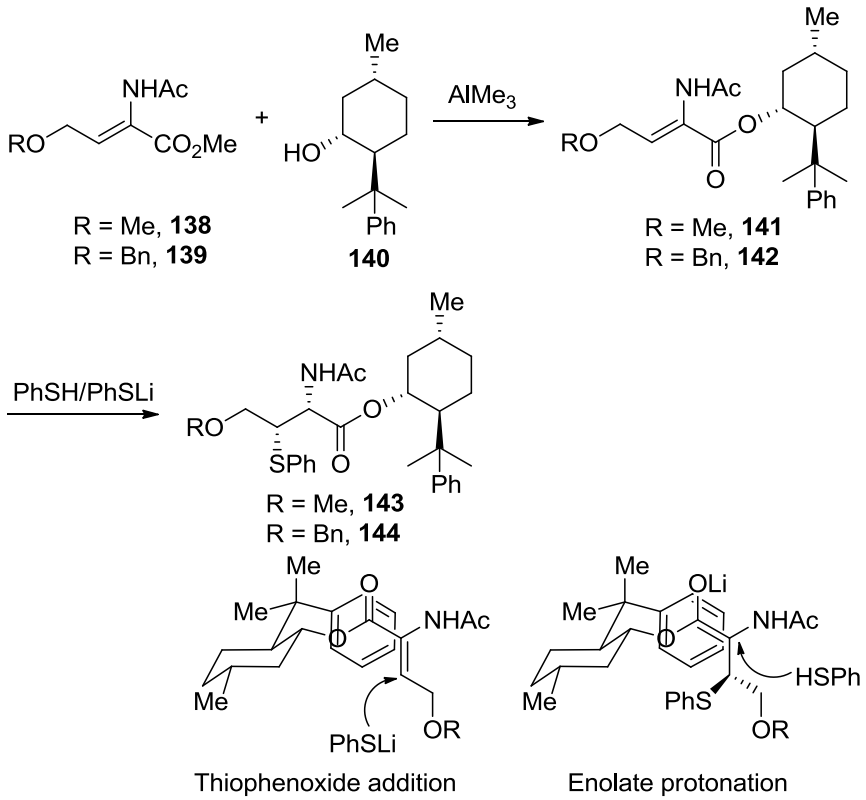
The reaction of the *E*-acrylate **137** with phenylthiol in the presence of catalytic amount of its lithium salt at room temperature gave a 50/50 mixture of the two adducts *erythro-rac*-**133** and *threo-rac*-**134**, due to the fact the *E*-dehydroamino acid ester **138** was readily isomerized to the more stable *Z*-**132** isomer in the presence of thiophenol at temperatures above 0 ºC. The addition of phenylthiol at -40 ºC afforded as the major isomer the *erythro-rac*-**133** (ratio

erythro/*threo* 74/26) and the addition of benzylthiol at -50 °C gave as the major isomer the *threo*-*rac*-**136** (ratio *erythro*/*threo* 20/80) (*Scheme 38*).



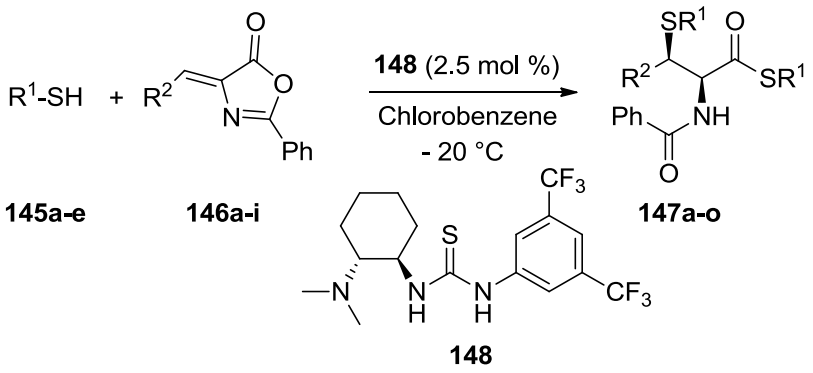
Scheme 38

The asymmetric synthesis of β-substituted cysteine derivatives **143** and **144** has been accomplished from the *Z*-acrylates **141** and **142** bearing at the carboxylic moiety a (-)-8-phenylmenthol group **140** as chiral auxiliary (*Scheme 39*).[84] Starting from the chiral acrylate **141**, the conjugate addition of thiophenol in the presence of its lithium salt in toluene at -78 °C gave the (2*R*,3*S*)-adduct **143** with high diastereoselectivity (d.r. 92/8). Similarly, the chiral acrylate **142** underwent diastereoselective addition of thiophenol in toluene to give as the major product (2*R*,3*S*)-adduct **144** (d.r. 86/14). The mechanism for the diastereoselective addition of thiophenol proposes would imply *s*-trans conformation of the *Z*-acrylate. Therefore, the lithium thiophenoxide would attack from a convex β-face to form the enolate, which was then protonated from the α-face due to the stereoelectronic effect of the newly introduced sulfur group.



Scheme 39

It has been demonstrated that the organocatalytic sulfa-Michael/ring opening process of *Z*-oxazolones **146a-i** by nucleophilic sulfur compounds **145a-e** is a valuable method to obtain β-arylsubstituted cysteine derivatives **147a-o** with high stereocontrol in the presence of chiral bifunctional thiourea-tertiary amine catalyst (Takemoto´s thiourea **148**). The results are shown in the *table 5*. All the reactions proceeded smoothly and provided the desired products in high yields (90-98%) with good diastereoselectivities (d.r. 92/8-98/2) and enantioselectivities (e.e. 75-89%) (*Table 5*). Subsequently, thiols **145b** and **145c** bearing electron-rich (*p*-Me, *p*-^{i}Pr) and electron-deficient **145d** and **145e** (*p*-Cl, *p*-Br) substituents on the aromatic ring gave the corresponding β-arylsubstituted cysteine derivative **147i-o** in excellent yields (93-98%) and with good diastereoselectivities (d.r. 92/8-98/2) and enantioselectivities (e.e. 82-85%) (*Table 5*, entries i-o) (*Scheme 40*, *Table 5*).[85]



Scheme 40

Table 5. sulfa-Michael/ring opening of *Z*-oxazolones **146a-i** by nucleophilic sulfur compounds **145a-e** in the presence of Takemoto´s thiourea **148**

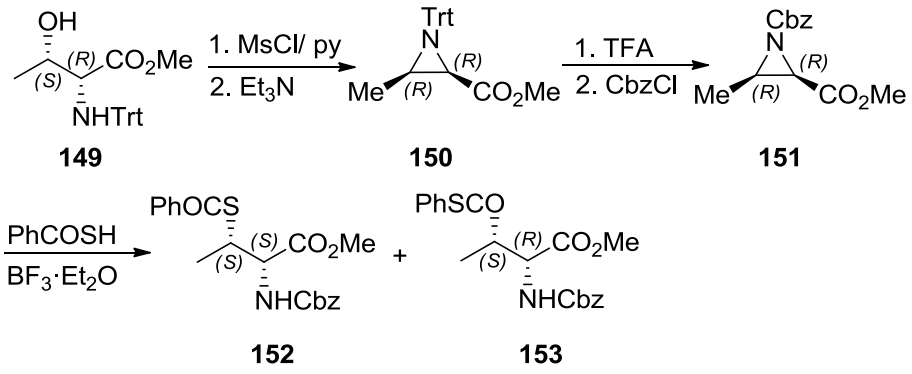
Entry	R1/R2	Yield (%)	d.r.	e.e. (%)
a	Ph (**145a**)/Ph (**146a**)	96	95/5	87
b	Ph (**145a**)/2-MeOC$_6$H$_4$ (**146b**)	92	97/3	85
c	Ph (**145a**)/3-MeOC$_6$H$_4$ (**146c**)	96	97/3	89
d	Ph (**145a**)/3-MeC$_6$H$_4$ (**146d**)	90	96/4	75
e	Ph (**145a**)/3-NO$_2$C$_6$H$_4$ (**146e**)	93	95/5	88
f	Ph (**145a**)/4-FC$_6$H$_4$ (**146f**)	98	96/4	88
g	Ph (**145a**)/2,4-Cl$_2$C$_6$H$_3$ (**146g**)	97	98/2	87
h	Ph (**145a**)/2-naphthyl (**146h**)	98	96/4	85
i	4-MeC$_6$H$_4$ (**145b**)/Ph (**146a**)	93	94/6	85
j	4-MeC$_6$H$_4$ (**145b**)/3-BrC$_6$H$_4$ (**146i**)	98	92/8	83
k	4-MeC$_6$H$_4$ (**145b**)/3-NO$_2$C$_6$H$_4$ (**146e**)	94	92/8	85
l	4-MeC$_6$H$_4$ (**145b**)/2,4-Cl$_2$C$_6$H$_3$ (**146g**)	95	96/4	84
m	4-^{i}PrC$_6$H$_4$ (**145c**)/3-BrC$_6$H$_4$ (**146i**)	96	92/8	84
n	4-ClC$_6$H$_4$ (**145d**)/3-MeOC$_6$H$_4$ (**146c**)	98	94/6	82
o	4-BrC$_6$H$_4$ (**145e**)/3-MeOC$_6$H$_4$ (**146c**)	93	95/5	83

Another organocatalytic sulfa-Michael addition between thiols and α,β-unsaturated *N*-acylated oxazolidin-2-ones produced β-alkyl or arylsubstituted cysteines in very good diastereoselectivity and high enantioselectivity employing as catalyst *Cinchona alkaloids* sulfonamide derivatives with a hydrogen bond donating group at its C6' position has been reported.[86]

A simple, efficient and green chemical ultrasound assisted sulfa-Michael addition reaction was reported between arylthiols and *Z*-oxazolones using the chiral heterogeneous catalyst Zn[(L)-Pro]$_2$ to obtain the β-arylsubstituted cysteine derivatives in good to excellent yields and high diastereoselectivity.[87]

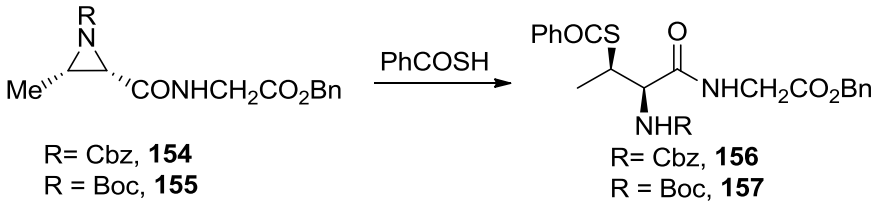
Another way to obtain β-substituted cysteines is the ring opening of aziridines with nucleophilic sulfur compounds, with retention of configuration on the β-carbon atom due to a double inversion mechanism. Wakamiya *et. al*.[88] reported the synthesis of the (2*R*,3*R*)-*N*-benzyloxycarbonyl-3-methyl-2-aziridinecarboxylic acid

methyl ester **151** from *N*-trityl-*D*-threonine methyl ester **149** after trityl group removal of (2*R*,3*R*)-*N*-trityl-3-methyl-2-aziridinecarboxylic acid methyl ester **150** and cyclization *via* S_N2 reaction with inversion of configuration at the C3 carbon. The ring opening of the aziridine **151** with thiobenzoic acid gave the desirable (2*S*,3*S*)-*S*-benzoyl-3-methylcysteine derivative **152** along with (2*R*,3*S*)-*O*-thiobenzoyl-3-methylserine derivative **153** (*Scheme 41*).



Scheme 41

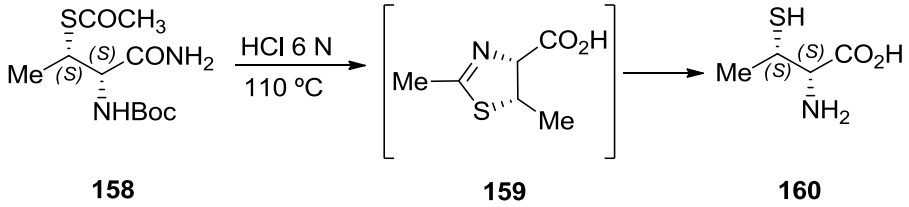
In the same report, the synthesis of these compounds was described without contamination with *O*-thiobenzoyl derivatives as it happens aforementioned. The reaction of the peptides containing *N*-acyl-3-methyl-2-aziridinecarboxylic acid **154** and **155** with thiobenzoic acid gave exclusively (2*R*,3*R*)-*S*-benzoyl-3-methylcysteinyl peptides **156** and **157** (*Scheme 42*).



Scheme 42

In order to obtain better results in the synthesis of enantiomerically pure 3-methylcysteine derivative **160**, Wakamiya *et al*.[89] continued their work to avoid the problem of formation of the *O*-thiobenzoyl derivative as by-product due to an equilibrium between thiobenzoic *S*-acid (PhCOSH) and *O*-acid (PhCSOH). The Boc group was adopted as *N*-protecting rather than benzyloxycarbonyl (Cbz) group to prevent the attack of the benzyl cation formed during the acid hydrolysis to free thiol group. They found that the most appropriate substrate was the (2*S*,3*S*)-*S*-acetyl-*N*-Boc-3-methylcysteinamide **158** which hydrolysis readily took place *via* a

labile thiazoline **159** to produce an enantiomerically pure (2*S*,3*S*)-3-methylcysteine **160** (*Scheme 43*).

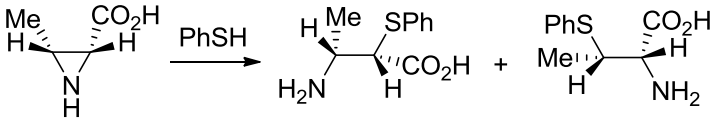


158 **159** **160**

Scheme 43

The ring opening of aziridines with a wide range of nucleophilic sulfur compounds to obtain optically active *S*-alkyl-β-methylcysteine derivatives has been explored by Nakajima *et al*.[90]

Hata *et al*.[91] carried out a study of the ring-opening of (2*R*,3*R*)-3-methyl-2-aziridinecarboxylic acid **161** using thiophenol as nuchleophile in aqueous solution at different pH values and different mixtures of protic and aprotic solvents. When the reaction was carried out in an aqueous phosphate buffer 0.2 M in a range of pH values from 6.0 to 10.0, the major product obtained in all cases was the 3-amino-2-phenylthiobutanoic acid **162**, while the ratio **162**/**163** was almost independent of the acidity of the reaction medium. However, the product ratio was largely dependent on the solvent used and 3-methylcysteine derivative **163** increased in going from protic to aprotic solvent (*Scheme 44*, *Table 6*). An extension of this methodology was reported for the synthesis of chiral *N*-phtalimido-β-phenylcysteine.[92]



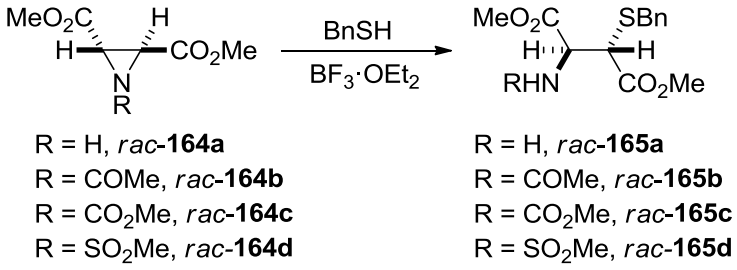
161 **162** **163**

Scheme 44

Table 6. Reaction conditions to the aziridine **161** ring-opening with thiophenol

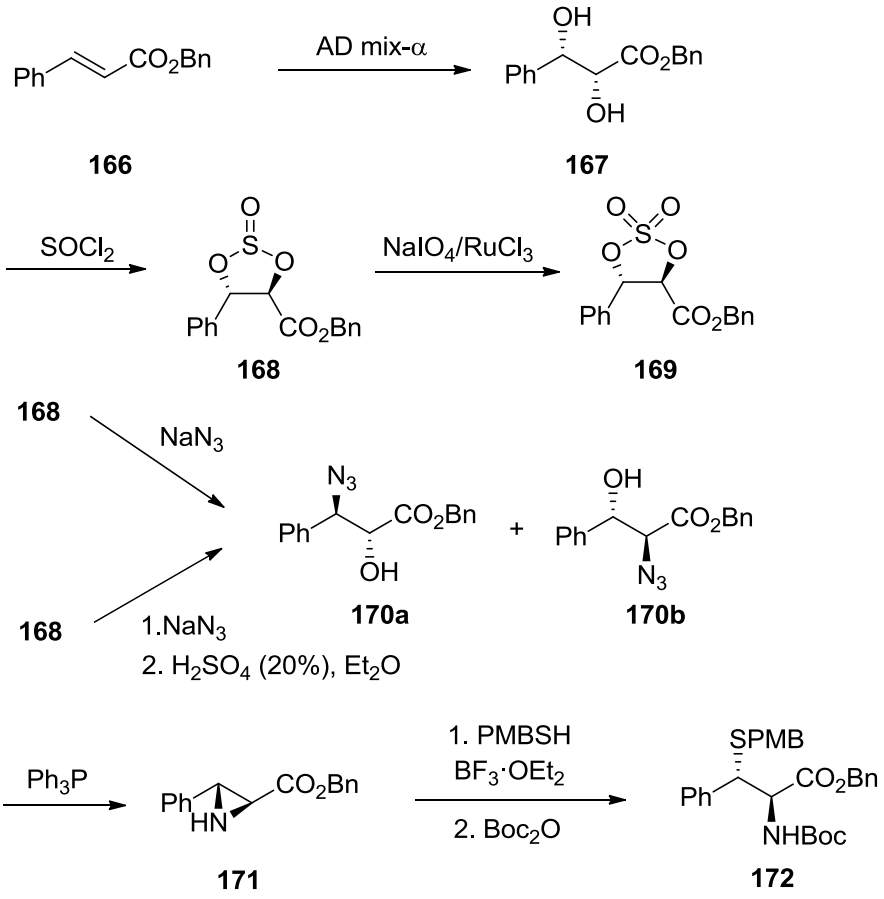
Phosphate buffer (pH)	Product ratio (159/160)	Solvent (v/v)	Product ratio (159/160)
6.0	2.1	Phosphate buffer (pH 8.0)	2.3
8.0	2.3	H_2O	2.35
9.0	2.2	EtOH/H_2O	1.65
10.0	2.1	DMF/H_2O	1.05

More recently, Antolini *et al*.[93] developed the diastereoselective synthesis of *erythro*-3-benzylthioaspartates derivatives *rac*-**165a-d** from racemic *trans*-aziridines *rac*-**164a-d** properly protected by ring opening with benzylthiol in the presence of boron trifluoride diethyl etherate. As expected, activated aziridines *rac*-**164b-d** displayed a higher reactivity than unactivated compound *rac*-**164a**, giving the ring-opening products *rac*-**165b-d** in higher chemical yields and in shorter reaction times (*Scheme 45*).



Scheme 45

Hruby *et al*.[94] have developed an asymmetric synthesis of (2*R*,3*S*)-*N*-Boc-3-phenylcysteine derivative **172** through an aziridine ring-opening (*Scheme 46*).

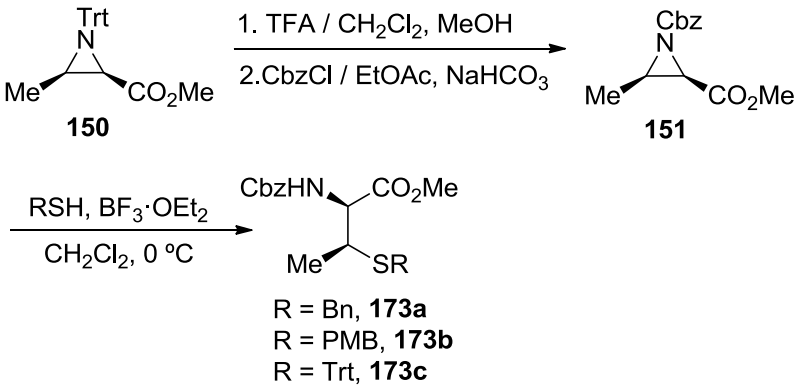


Scheme 46

The key reaction was the Sharpless asymmetric dihydroxylation of the cinnamate **166** in the presence of AD mix-α to yield the (2*R*,3*S*)-diol **167** with excellent enantiomeric purity and yield (e.e. >95 %). The (2*R*,3*S*)-diol **167** was converted into cyclic sulfite **168** as a mixture of diastereoisomers in a ratio 50/50 using $SOCl_2$, and then was oxidized to the cyclic sulfate **169** with RuO_4. Ring-opening of cyclic sulfate **169** in a S_N2 fashion with sodium azide provided the azido alcohols regioisomers **170a** and **170b** in a 86/14 ratio. Due to the instability of the cyclic sulfate **169** the ring opening was conducted from the cyclic sulfite **168** with sodium azide at higher temperature to give the regioisomers **170a** and **170b** in a 83/17 ratio in high yield. The mixtures of azides **170a** and **170b** under Staudinger conditions afforded the aziridine **171** in high yield with inversion of the configuration at the carbon bearing the leaving group. Therefore, from the cyclic sulfate **169** to aziridine **171**, the stereochemical configurations at both atoms were inverted. Finally, aziridine **171** was treated with PMBSH in the presence of $BF_3{\cdot}OEt_2$ followed by amino group protection to give the (2*R*,3*S*)-*N*-Boc-3-phenylcysteine derivative **172**. The S_N2 reaction was stereospecific at the benzylic C3 position. The regiochemistry of the ring opening was also specific.

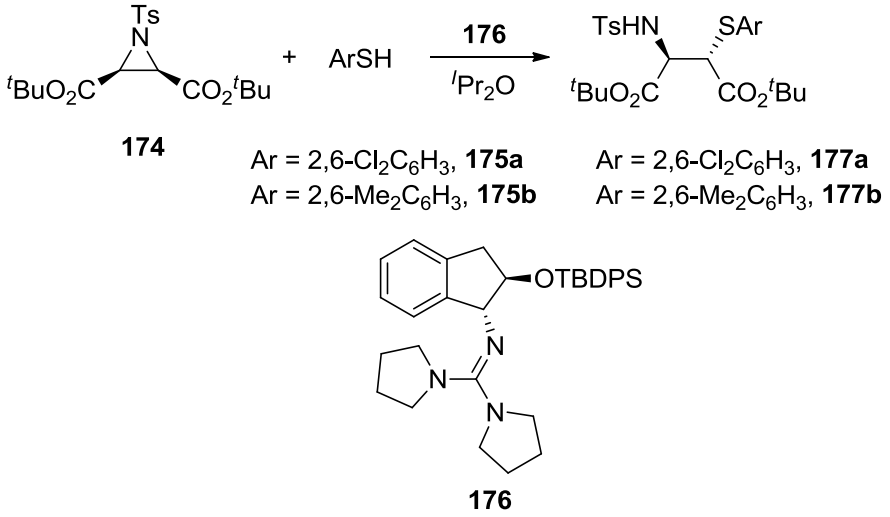
An extension of this work has been reported by Hruby *et al*.[95] to obtain *erythro*- and *threo*-3-substituted cysteines with a phenyl, propyl and *iso*-propyl groups at the β-position starting from the corresponding β-substituted cinnamates and applying the Sharpless asymmetric dihydroxylation with AD mix-α as the key step of this synthetic methodology.

VanNieuwenhze *et al*.[96] reported a regio- and stereoselective synthesis of protected 3-methylcysteines derivatives **173a-c** using the (2*R*,3*R*)-*N*-benzyloxycarbonyl-3-methyl-2-aziridinecarboxylic acid methyl ester **151**, bearing an electron withdrawing group at the nitrogen atom, obtained from (2*R*,3*R*)-*N*-trityl-3-methyl-2-aziridinecarboxylic acid methyl ester **150**. The ring opening reactions mediated by $BF_3{\cdot}OEt_2$ with various thiol nucleophiles as BnSH, PMBSH and TrtSH proceeded smoothly as a single diastereoisomer and regioisomer (*Scheme 47*).



Scheme 47

One efficient approach to enantioenriched *erythro*-3-arylthioaspartates **177a** and **177b** as cysteine derivatives used the organocatalytic desymmetrization ring-opening of *meso*-aziridine **174** with thiols **175a** and **175b**, in the presence of a chiral guanidine amino-indanol derivative **176** (*Scheme 48*).[97]

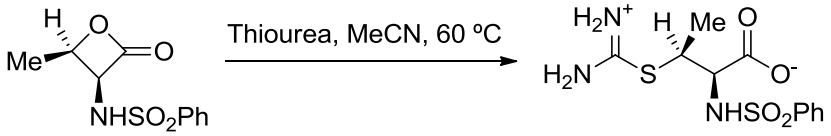


Scheme 48

Other reported articles about the ring opening of aziridines to obtain β-alkylcysteine derivatives have also been published.[98]

Apart from the abovementioned strategies, we found other types of suitable intermediates as the β-lactones, which after ring opening with appropriate sulfur nucleophiles produced the corresponding β-substituted cysteine derivatives.

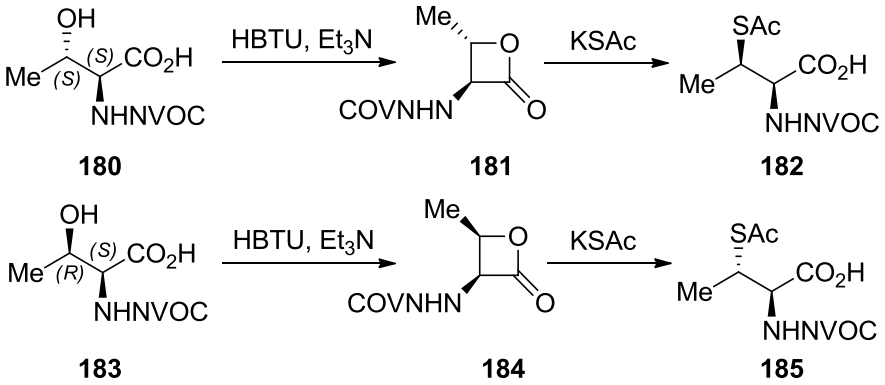
In this context, Vederas *et al*.[99] have studied the synthesis and reactivity of the β-lactone **178** obtained from *L*-threonine. The ring-opening of the β-lactone **178** with thiourea proceeded regio- and diastereoselectively to obtain the enantiomerically pure 3-methylcysteine derivative **179** (*Scheme 49*).



178 **179**

Scheme 49

Recently, Hecht *et al*.[100] have developed the synthesis of the diastereomeric 3-methylcysteines derivatives **182** and **185** in enantiopure form by the ring-opening methodology of the β-lactones **181** and **184,** obtained from *allo*-*L*-threonine **180** or *L*-threonine **183** derivatives, with the sulfur nucleophile (KSAc), respectively (*Scheme 50*).

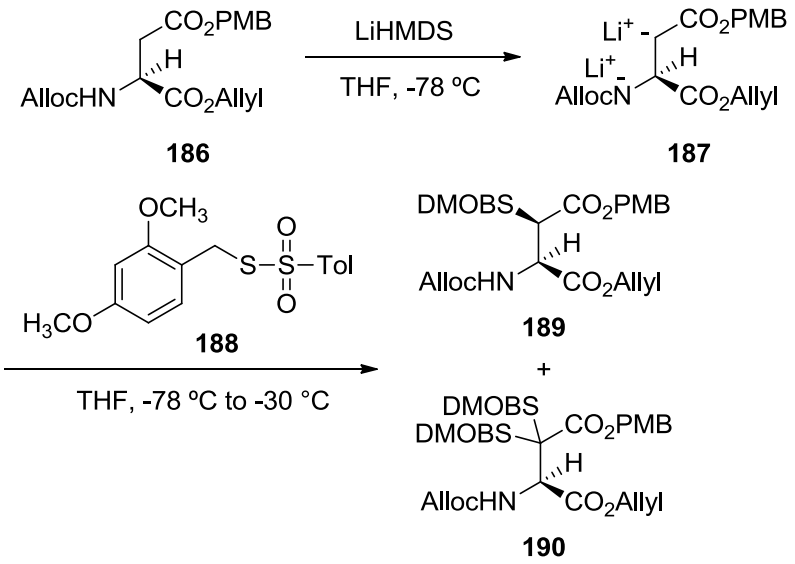


180 **181** **182**

183 **184** **185**

Scheme 50

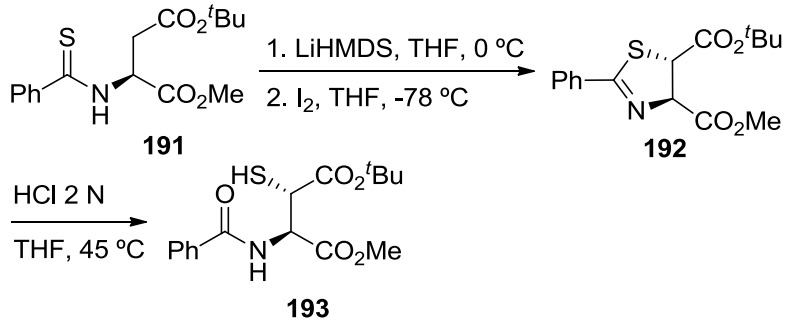
Another synthetic methodology to generate the Cβ-S bond has been accomplished using electrophilic sulfur reagents. Shibata *et al*.[101] designed a synthetic route *via* a β-aspartyl enolate sulfenylation to obtain protected (2*R*,3*R*)-3-mercapto aspartic ester derivative **189**. Hence, *L*-aspartic acid orthogonally protected **186** was treated at -78 ºC with lithium bis(trimethylsilyl)amide (LiHMDS) to form the dianion **187** which upon reaction with the bulky sulfenylation agent **188**, on the least hindered face without change in the spatial orientation of the C3 substituents led to the protected (2*R*,3*R*)-3-mercapto aspartic ester derivative **189** diastereoselectively with good yield along with a minor amount of the dialkylation product **190** (*Scheme 51*).



Scheme 51

This methodology has been applied to the synthesis of other orthogonally protected (2*R*,3*R*)-3-mercapto aspartic ester derivatives employing other sulfenylation agents such as PMB-S-S-DNP,[102] Me-S-S-DNP[103] and Tmob-S-SO_2-*p*-tol.[104]

In this sense, another elegant and stereoselective synthesis of β-thioaspartic derivative **193** has been accomplished from the thiobenzamidoaspartic ester derivative **191** (*Scheme 52*).

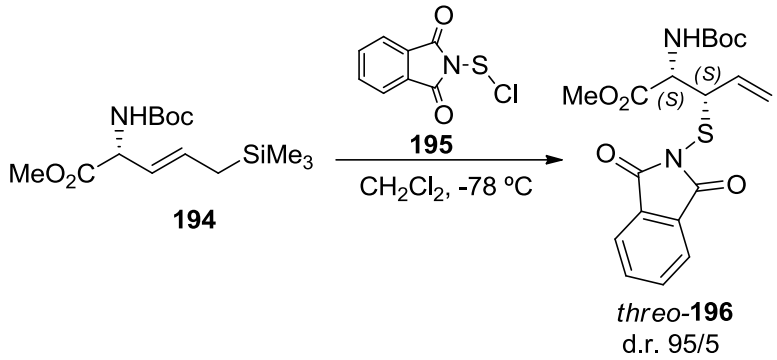


Scheme 52

The lithium dianion formed at 0 ºC using LiHMDS was quenched with I_2 and after acidic work-up gave the *trans*-thiazoline **192**. No *cis* isomer was detected. Finally, selective hydrolysis of thiazoline heterocyclic ring **192** using 2.0 N HCl afforded the β-thioaspartic ester derivative **193**.[105]

Reginato *et al*.[106] have reported the synthesis of enantiomerically enriched (2*S*,3*S*)-vinylcysteine derivative *threo*-**196** *via* reaction of sulfodesilylation of the

chiral *E*-allylsilane **194** using phthalimidosulfenyl chloride **195** as sulfenylation reagent (*Scheme 53*).



Scheme 53

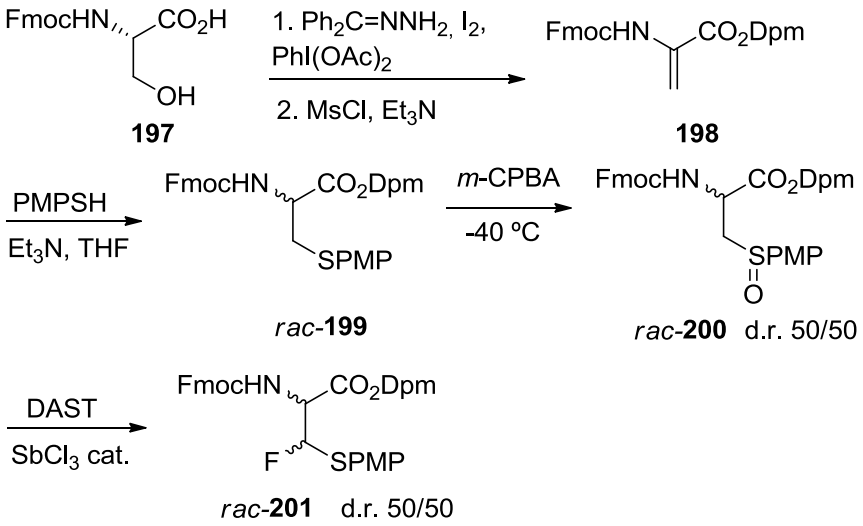
The reaction took place smoothly and diastereoselectively to give the adduct *threo*-(2*S*,3*S*)-**196** in a 95/5 ratio due to the presence of the amino group, since its ability at forming an intramolecular hydrogen bond may control the attack of the electrophile, assisting the formation of the *threo* diastereoisomer, where the amino and the sulfur groups are on the same side. It is important to note that the reaction took place regioselectively attacking the electrophilic sulfur atom at Cγ (C3), and the resulting intermediate underwent rapid loss of the silyl group, allowing the formation of the product with a net transposition of the double bond.

Recently, the radical addition of various xanthates to protected vinyl glycine has been reported to obtain a diastereomeric mixture of β-alkyl cysteines ideally equipped for native chemical ligation.[107]

3.2. Pummerer or Michael reactions to incorporate the substitution at Cβ carbon. Disconnection b)

The second approach involves the disconnection **b** to the synthesis of β-substituted cysteine derivatives incorporating in the last step the substituent at the β-position through a Pummerer reaction or a Michael addition.

A new type of β-substituted cysteines, the β-fluoro cysteine *rac*-**201** has been prepared by fluoro-Pummerer rearrangement of sulfoxides with diethylaminosulfurtrifluoride (DAST) (*Scheme 54*).[108]

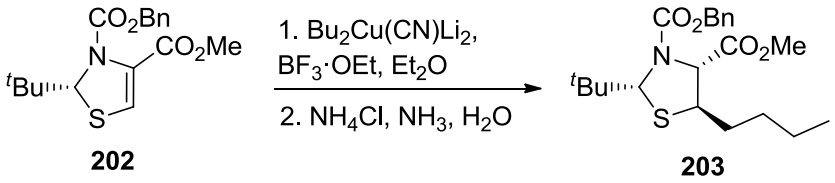


Scheme 54

The methodology involves the transformation of the Fmoc-serine **197** into the diphenylmethyl ester which was activated with methylsulfonyl chloride and treated with base to produce the dehydroalanine **198**. Thio-Michael addition of 4-methoxybenzenethiol to **198** provided the cysteine derivative *rac*-**199**. The oxidation of the sulfur atom of *rac*-**199** with *m*-CPBA into the corresponding sulfoxide *rac*-**200** afforded a 50/50 mixture of diastereoisomers. The fluoro-Pummerer rearrangement of the diastereomeric mixture of sulfoxides *rac*-**200** with the system DAST/$SbCl_3$ (cat.) produced the β-fluoro cysteine *rac*-**201** as a 50/50 mixture of diastereoisomers in good yield.

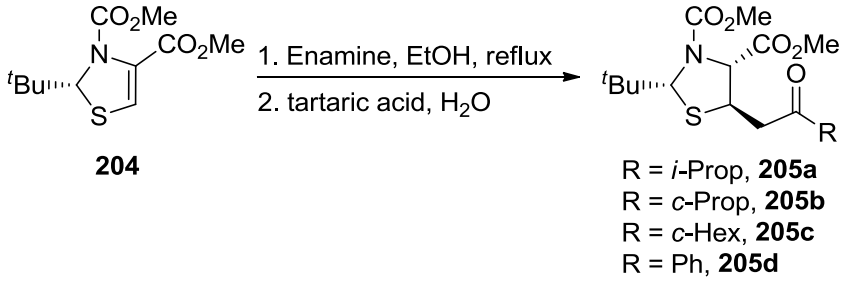
Recently, an efficient and convenient method has been developed for the synthesis of β-fluorocysteine derivatives in one step without control of the diastereoselectivity, using *N*-iodosuccinimide (NIS) and diethylaminosulfurtrifluoride (DAST) as the fluorine source.[109] In early works on the synthesis of β-fluorocysteine derivatives, XeF_2 was used as fluorination reagent and cysteine derivatives as substrates.[110]

In the second case, the study of a conjugate addition of nucleophiles over a cyclic derivative of dehydrocysteine was reported by Jeanguenat *et al*.,[111] who described the synthesis of β-modified cysteines through Michael addition of dibutyl cyanocuprate using $BF_3{\cdot}OEt_2$ activation to the chiral thiazoline **202** affording the latent β-butylcysteine derivative **203** in poor yield but excellent diastereoselectivity in enantiopure form (*Scheme 55*).



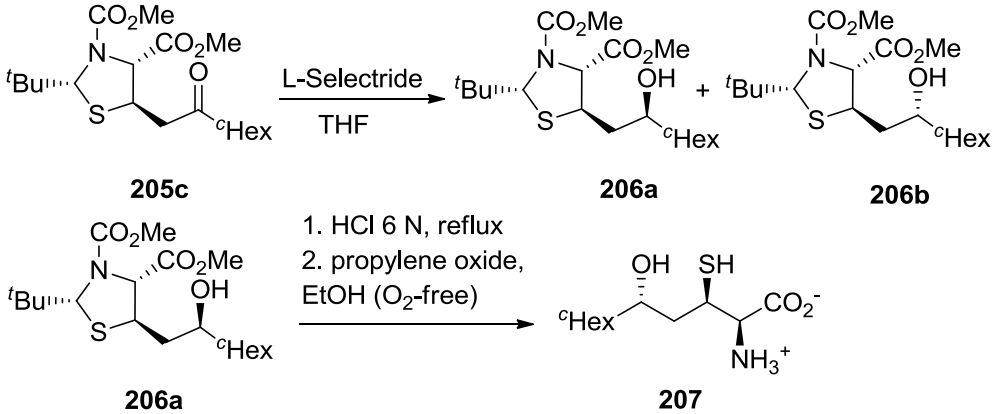
Scheme 55

During the course of the study of the reactivity of the chiral thiazoline **204**, it was thought that the Michael addition of enamines would lead to the desired β-alkylthiazolidine derivatives **205a-d**. Therefore, the enamines formed by 3-methylbutan-2-one, cyclopropyl and cyclohexyl methyl ketone and acetophenone by condensation with pyrrolidine reacted with the thiazoline **204** in refluxing ethanol to obtain β-alkylthiazolidine derivatives **205a-d** with good yields and diastereoselectivities in enantiopure form (*Scheme 56*).



Scheme 56

The cyclohexyl derivative **205c** was used in the synthesis of (2*R*,3*R*,5*R*)-β-hydroxyalkylcysteine **207** in enantiopure form (*Scheme 57*). The reduction of the ketone group to a secondary hydroxyl group afforded the diastereomeric mixture of **206a**/**206b** in a ratio 79/21. The two epimers **206a**/**206b** were readily isolated and the major one **206a** was submitted to cleavage the thiazolidine ring to afford the (2*R*,3*R*,5*R*)-β-hydroxyalkylcysteine **207** in enantiopure form.



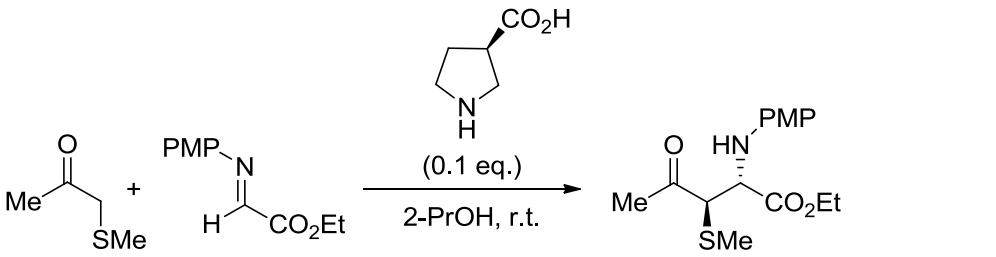
Scheme 57

3.3. Addition of nucleophilic thiomethyl reagents to imines derived of glycine. Disconnection c)

The third approach, the disconnection **c**, involves the use of stabilized carbanions placed in the α-position of a sulfur atom to be added to a glycine equivalent with an electrophile carbon (usually imines).

Mannich and *anti*-Mannich-type reactions are of great importance in organic chemistry due to their applications in the synthesis of amino acids, amino alcohols, amino carbonyls, and their derivatives containing two adjacent stereocenters. Therefore, there is a huge interest for direct catalysts reactions that afford *syn*- or *anti*-Mannich products with high diastereo- and enantioselectivities.[112] For this reason, Mannich and *anti*-Mannich reactions have been developed with unmodified carbonyl compounds with high enantioselectivities using proline and related amine-based organocatalysts.[113]

In this context, Tanaka *et al.*[114] have described the importance role of the 3-pyrrolidinecarboxylic acid and derivatives as organocatalysts in enantioselective *anti*-Mannich type reactions. In particular, the reaction of the ketone **208** bearing the sulfur atom protected and the imine **209** in the presence of 3-pyrrolidinecarboxylic acid led to the β-substituted cysteine derivative **210** in a ratio ≈50/50 (*erythro*/*threo*) with an enantiomeric excess for the *erythro*-isomer of 48% determined by chiral-phase HPLC (*Scheme 58*).



208 **209**

d.r. = 50/50; e.e. (*erythro*-**210**) 48%

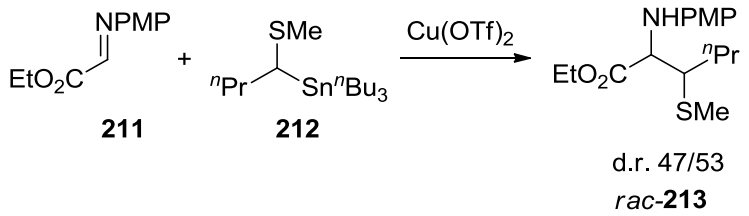
210

Scheme 58

The reaction of α-imino esters or analogues with organometallic compounds for the synthesis of amino acids is a promising reaction, if the carbon-carbon bond formation takes place regioselectively at the imino carbon.[115]

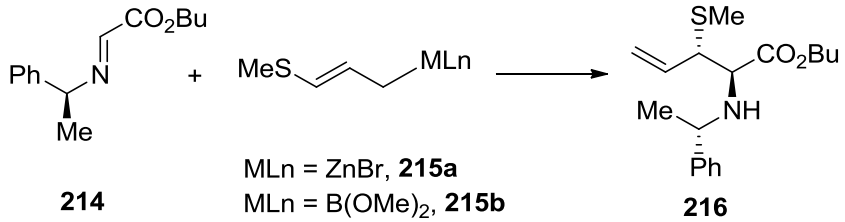
Kagoshima *et al*.[116] have reported the addition reaction of α-sulfurated alkylstannanes as nucleophile reagents to imines to produce vicinal amino sulfides. Hence, the Lewis acid mediated reaction of the α-sulfurated alkylstannane **212** with

the α-imino ester **211** afforded the β-substituted cysteine derivative *rac*-**213** in moderate yield and poor diastereoselectivity (*Scheme 59*).



Scheme 59

The last example of this type of disconnection that we were able to find was described by Yamamoto *et al*.[117] The reaction of the chiral α-imino ester **214** with allylic-organo zinc **215a** or allylic-organo boron **215b** compounds led regioselectively to the *threo*-3-vinylcysteine derivative **216** as major diastereoisomer (*Scheme 60*).

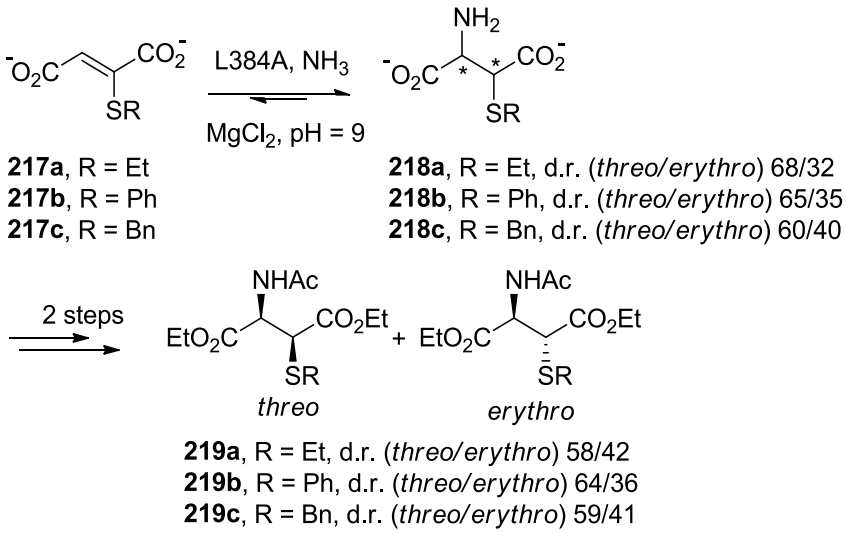


Scheme 60

The conveniently protected final 3-alkylcysteine compounds were used in the synthesis of lantibiotic Epilancin 15X analogues and fragments of Mersacidin or the lantibiotic Lacticin 3147.[118]

3.4. C-N bond formation by Michael-addition reaction. Disconnection d)

The fourth disconnection, **d**, involves the C-N bond formation as the key step of the synthesis of β-substituted cysteines derivatives **219a-c**. We found the engineering strategy to modify at carefully chosen sites of the methylaspartate ammonia lyase (L384A) for the asymmetric synthesis of unnatural amino acids such as β-substituted cysteines derivatives **219a-c** from fumarates **217a-c** and ammonia through a regioselective and diastereoselective Michael-addition (*Scheme 61*).[119]



217a, R = Et
217b, R = Ph
217c, R = Bn

218a, R = Et, d.r. (*threo/erythro*) 68/32
218b, R = Ph, d.r. (*threo/erythro*) 65/35
218c, R = Bn, d.r. (*threo/erythro*) 60/40

219a, R = Et, d.r. (*threo/erythro*) 58/42
219b, R = Ph, d.r. (*threo/erythro*) 64/36
219c, R = Bn, d.r. (*threo/erythro*) 59/41

Scheme 61

4. SYNTHESIS OF β,β-DISUBSTITUTED CYSTEINES DERIVATIVES

In the *figure 4* are shown the only two synthetic approaches to β,β-disubstituted cysteines. The disconnection **a** involves the insertion of an electrophilic or nucleophilic sulfur compound in the last step of the synthesis using a β,β-disubstituted dehydroamino acid as an acceptor. The disconnection **b** involves the insertion of the sulfur and nitrogen atom onto a 2-chloro-2-cycloalkylacetate compound using a one-pot sequence involving a Michael addition and an intramolecular substitution to obtain the thiazoline ring as the key intermediate (*Figure 4*)

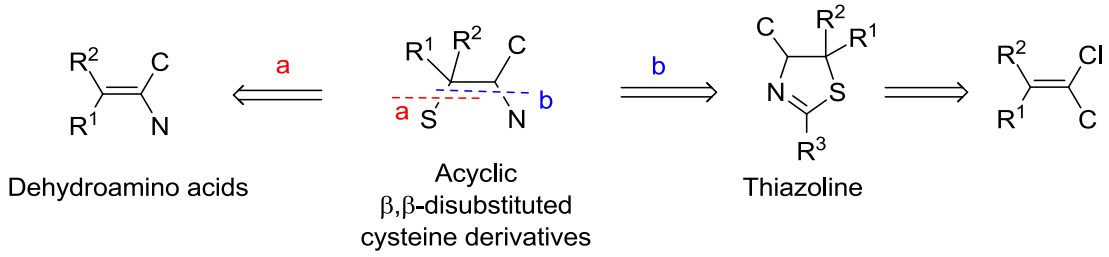


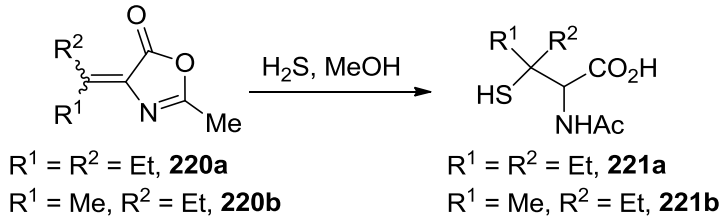
Figure 4. Synthetic routes to β,β-disubstituted cysteines

There is an important family of compounds with two substituents in the β position,[120] especially in the case of having similar groups avoiding in this way the presence of a new stereogenic centre being reminiscent of penicillamine (with two methyl groups) easily available from commercially sources. In fact, *D*-penicillamine has been used as starting material for the synthesis of numerous thiazolidines.[121]

The most typical synthesis for these compounds is the nucleophilic addition of sulfur nucleophiles over dehydroamino acid β,β-disubstituted derivatives. These

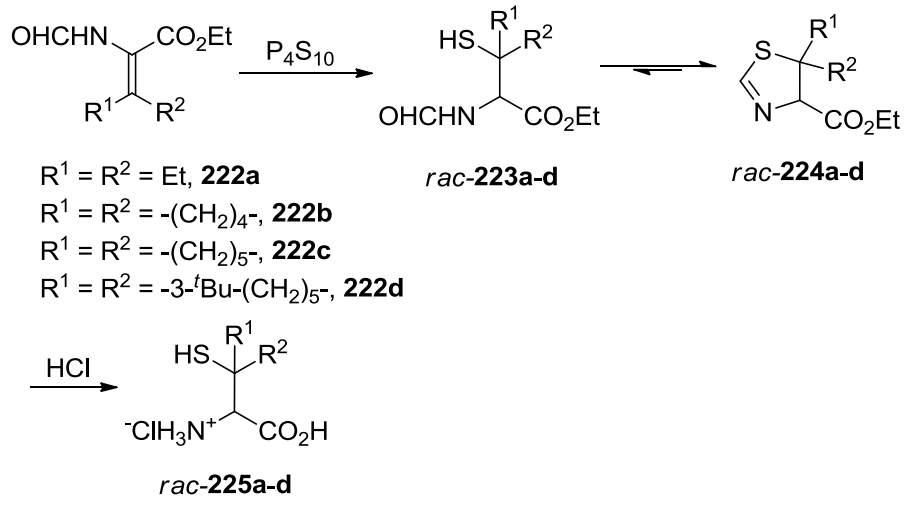
compounds must be especially activated taking into account the steric problems to produce the attack at the β position of the unsaturated system.

In this context, the synthesis of 3,3-diethylcysteine derivative **221a** and 3-ethyl-3-methylcysteine derivative **221b** was accomplished through the synthesis of the oxazolones **220a** and **220b**, respectively. The subsequent Michael addition of the sulfur nucleophilic atom using H_2S and opening of the heterocycle led to the diastereomeric mixture of the corresponding 3,3-dialkylcysteines derivatives **221a** and **221b** (*Scheme 62*).[122]



Scheme 62

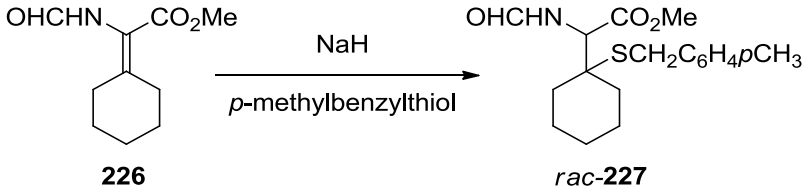
A general and relatively simple synthesis of nonproteinogenic β,β-disubstituted cysteines starting from *N*-formyl protected dehydroamino acid esters **222a-d** has been reported. The reaction with P_4S_{10} afforded a mixture of β-sulfhydryl amino acid ethyl ester *rac*-**223a-d** and 2-thiazoline-4-carboxylic acid ethyl esters *rac*-**224a-d**, which under acidic conditions led to the desired 3,3-dialkyl cysteines derivatives *rac*-**225a-d** (*Scheme 63*).[123]



Scheme 63

This procedure can be extended to the synthesis of *S*-protected 3,3-dialkylcysteine derivative *rac*-**227**, directly by Michael addition of *p*-

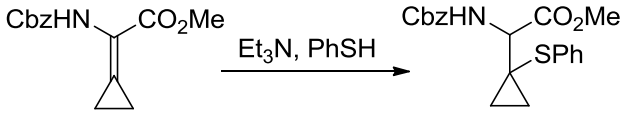
methylbenzylthiol to the dehydroamino acid derivative **226** using a catalytic amount of sodium hydride (*Scheme 64*).[124]



226 *rac*-**227**

Scheme 64

Recently, the synthesis of a cyclopropyl containing dehydroamino acid **228** has been described as a suitable substrate for Michael addition reactions with various nucleophiles. Among them, the reaction of **228** with thiophenol proceeded in almost a quantitative yield when the reaction was carried out in the presence of a catalytic amount of Et_3N to afford the 3,3-dialkylcysteine derivative *rac*-**229** bearing a cyclopropyl group at β-position (*Scheme 65*).[125]

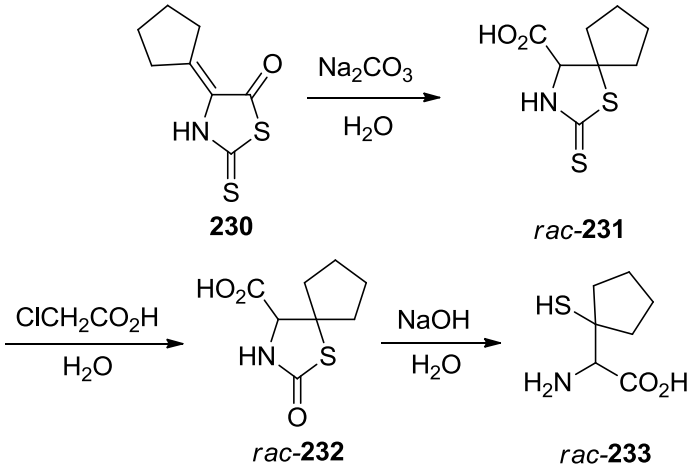


228 *rac*-**229**

Scheme 65

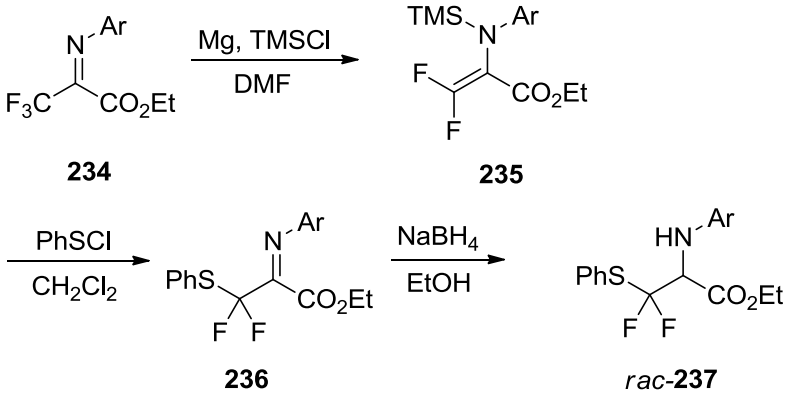
Some of these compounds have been used as intermediates in the synthesis of TACE inhibitors.[120]

Another interesting approach to β,β-dialkyl cysteines involves the treatment of **230** with sodium carbonate in water to afford the product *rac*-**231** *via* an intramolecular conjugate addition. The reaction of *rac*-**231** with chloroacetic acid led to the 2-oxo-5,5-tetramethylenethiazolidine-4-carboxylic acid *rac*-**232** which upon ring-opening in basic medium gave the 3,3-tetramethylenecysteine derivative *rac*-**233** (*Scheme 66*).[81]



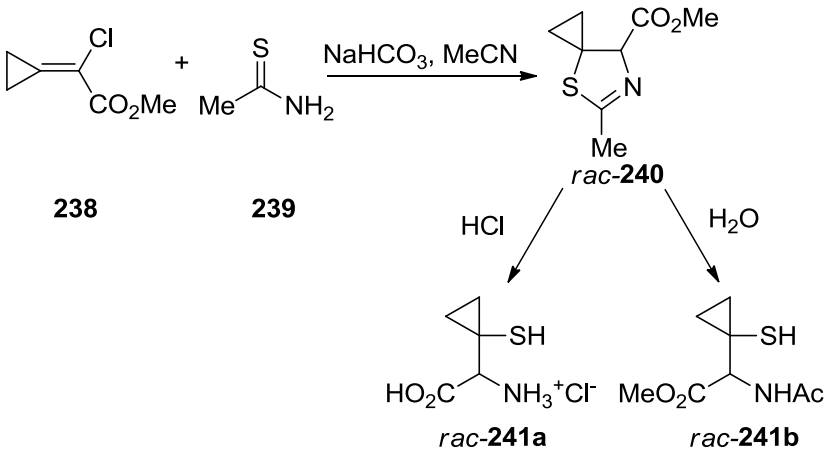
Scheme 66

In the case of β,β-disubstituted cysteines 3,3-difluorocysteine derivatives can be synthesized *via* Mg(0)-promoted selective defluorination of the trifluoromethylimine **234** as a key step, affording the compound **235**. The electrophilic addition of benzenesulfenyl chloride and the reduction of the resulting imine **236** with $NaBH_4$ provided 3,3-difluorocysteine derivative *rac*-**237** (*Scheme 67*).[126]



Scheme 67

Another alternative to obtain β,β-disubstituted cysteines involves the ring-opening of the thiazoline-4-carboxylate derivative *rac*-**240** incorporating a cyclopropyl group.[127] The thiazoline-4-carboxylate *rac*-**240** was used as a precursor for the cyclopropane analogue of penicillamine *rac*-**241a** and *rac*-**241b** and was synthesized from 2-chloro-2-cyclopropylideneacetate **238** and thioacetamide **239** by a one-pot reaction sequence: Michael addition and an intramolecular substitution. The ring-opening was carried out in acidic medium or refluxing in water, to obtain the 3,3-dialkylcysteine derivatives *rac*-**241a** and *rac*-**241b**, respectively (*Scheme 68*).[128]



Scheme 68

The formation of thiazolidines containing a latent β,β-dialkyl cysteine derivative employing the methodology of 1,3-dipolar cycloaddition reaction between azomethine ylides generated from aziridines and thioketones, as the main step, also has also been reported.[129]

5. SYNTHESIS OF ACYCLIC α,β-DISUBSTITUTED CYSTEINE DERIVATIVES

The strategy typically used (disconnection **a**) is the opening of aziridines because of being intermediates extremely versatile in organic synthesis. Due to ring strain, the reaction of aziridines leads to highly regio- and stereoselective ring-opening with a wide range of nucleophiles carbon-carbon or carbon-heteroatom bond formation. The disconnection **b**, hardly employed, involves the creation of a bond between the α carbon and the β carbon, in a typical procedure between stabilized carbanions in the α position of a sulfur atom (usually a sulfynil group) and an electrophile carbon, usually imines. (*Figure 5*).

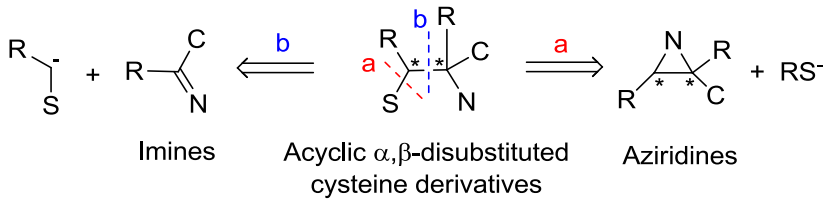
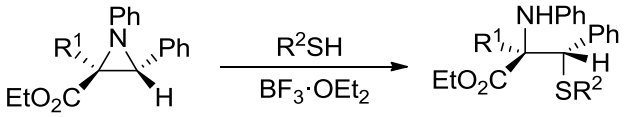


Figure 5. Synthetic routes to acyclic α,β-disubstituted cysteines derivatives

In this context, the regio- and stereoselective ring-opening of the aziridinyl esters **242a** and **242b** with soft nucleophiles as benzyl or phenylthiols in the presence of $BF_3{\cdot}OEt_2$ as Lewis acid has been reported. Under these conditions, both

aziridinyl esters **242a** and **242b** gave good yields of the corresponding 2,3-dialkylcysteine derivatives **243a-c** (*Scheme 68*).[130]

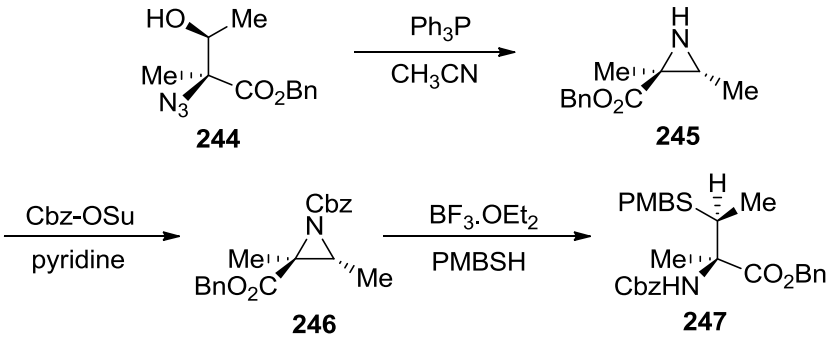


R^1 = Me, **242a**
R^1 = $(CH_2)_9CH_3$, **242b**

R^1 = Me, R^2 = Ph, **243a**
R^1 = $(CH_2)_9CH_3$, R^2 = Ph, **243b**
R^1 = $(CH_2)_9CH_3$, R^2 = Bn, **243c**

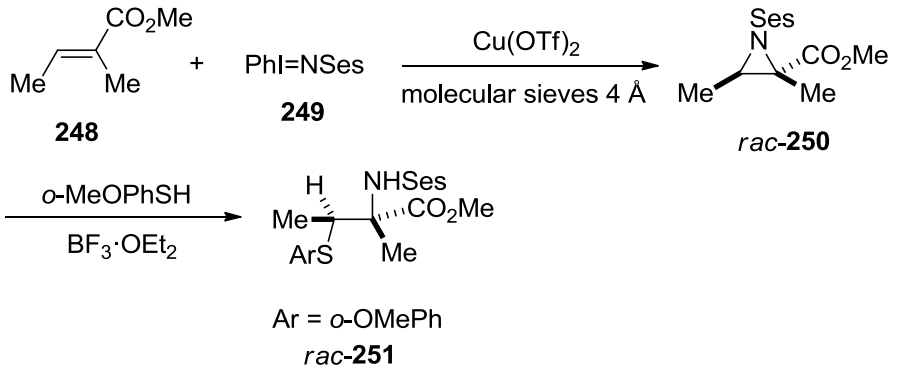
Scheme 69

Another approach involves the synthesis of (2*R*,3*S*)-2,3-dimethylcysteine derivative **247**, based on the Staundinger reaction of the azido alcohol **244**, which was converted into the (2*S*,3*R*)-2,3-dimethylaziridine-2-carboxylic acid benzyl ester **245** with no loss of enantiomeric purity. The activated (2*S*,3*R*)-*N*-benzyloxycarbonyl-aziridine-2-carboxylic acid benzyl ester **246** reacted with 4-methoxybenzylthiol to give the desired protected (2*R*,3*S*)-2,3-dimethylcysteine derivative **247** in the presence of $BF_3{\cdot}Et_2O$ (*Scheme 70*).[131]



Scheme 70

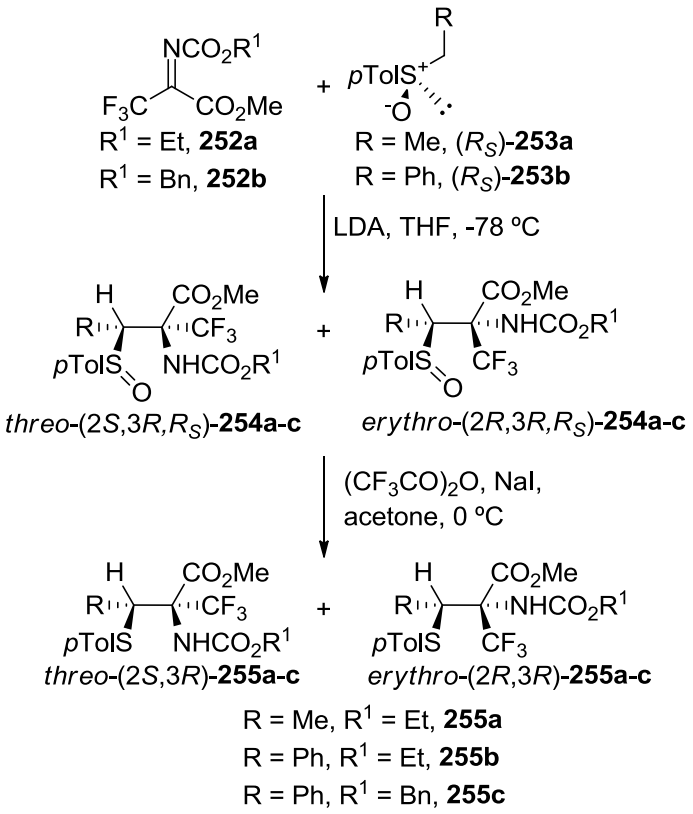
Besides, 2,3-dimethylcysteine derivative *rac*-**251** also can be obtained through the ring-opening of the aziridine-2-carboxylic acid methyl ester *rac*-**250** with *o*-MeOPhSH in the presence of $BF_3{\cdot}Et_2O$ (*Scheme 71*).



Scheme 71

It is important to note that the stereospecific synthesis of the *trans*-aziridine heterocyclic precursor *rac*-**250** was carried out using the poor olefin **248** and the iodinane **249** catalyzed by $Cu(OTf)_2$.[132]

Finally, it has been accomplished the synthesis of α,β-dialkyl cysteines *via* the reaction of the lithium enolates of ethyl and benzyl *p*-tolylsulfoxides **253a** and **253b**, which allowed to introduce the Cβ substitution of the amino acid and the ethoxycarbonyl-, **252a**, and benzyloxycarbonylimino **253b** derivatives of methyl trifluoropyruvate achieving the introduction of the trifluoromethyl substituent at Cα of the amino acid (*Scheme 72*).[133] In each case, the addition reaction of lithium intermediates of the sulfoxides (R_S)-**253a** and (R_S)-**253b** to imine derivatives **252a** and **252b** proceeded regioselectively at the imine carbon in good overall yields. These reactions were not highly diastereoselective, obtaining two major diastereoisomers *threo*-(2*S*,3*R*,R_S)-**254a-c** and *erythro*-(2*R*,3*R*,R_S)-**254a-c**, which could be isolated chromatographically and/or fractional crystallization in moderate yield. The optical purity was determined to be > 98% d.e. for all isomers by HPLC analysis. Configuration assignments of the obtained β-amino sulfoxides were determined by X-ray crystallography analysis as well as ^{19}F NMR and chemical correlation. The reduction of the sulfinyl group to the corresponding α,β-dialkyl cysteines *threo*-(2*S*,3*R*)-**255a-c** and *erythro*-(2*R*,3*R*)-**255a-c** was carried out employing trifluroacetic anhydride and NaI in acetone at 0 °C starting from each pure diastereoisomer in good yield.



Scheme 72

6. SYNTHESIS OF CYCLIC α,β-DISUBSTITUTED CYSTEINE DERIVATIVES

A classification based on the ring size has been used taking into account the papers found in the bibliographical revision. The strategies and disconnections to access to the cyclic α,β-dialkyl cysteine derivatives are summarized in the *Figure 6*. The disconnection **a** involves a β-sulfanyl dehydroamino acid as the key intermediate which after cycloaddition reactions led to the cycloalkyl unit being placed between α- and β- position of the cysteine derivative. The disconnection **b** requires a cyclic α,β-dialkylserine derivative that after S_N2 reaction lead to cyclic α,β-dialkylcysteine derivatives. The disconnection **a** + **b** implicates a dehydroamino acid, which after a cycloaddition with a vinylthioether lead a cycloalkyl unit being inserted between α- and β- positions and the sulfanyl group at the β-position of the cysteine derivative in a unique step (*Figure 6*).

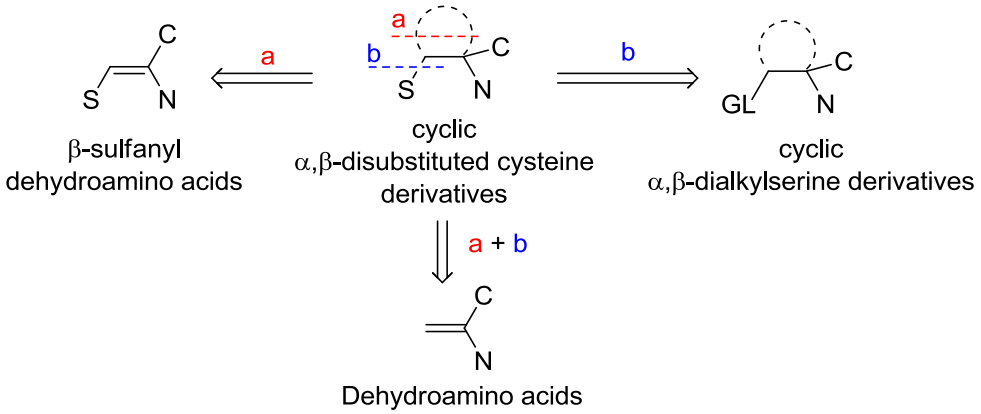
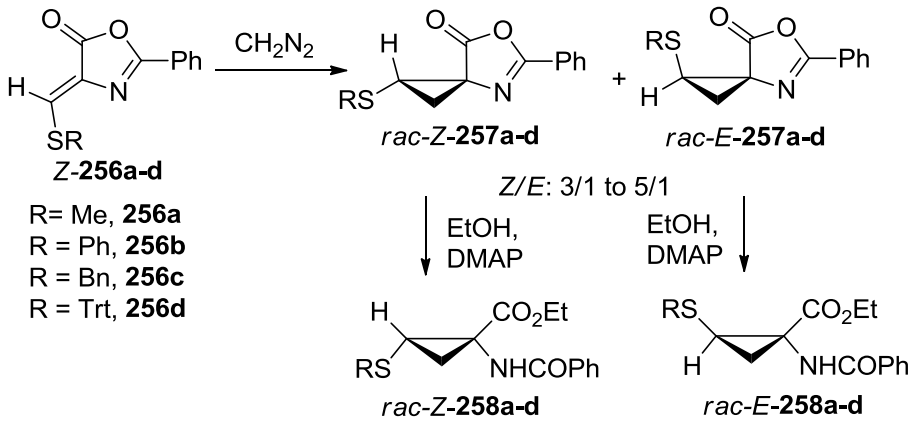


Figure 6. Synthetic routes to cyclic α,β-disubstituted cysteines derivatives

6.1. Cyclopropane derivatives

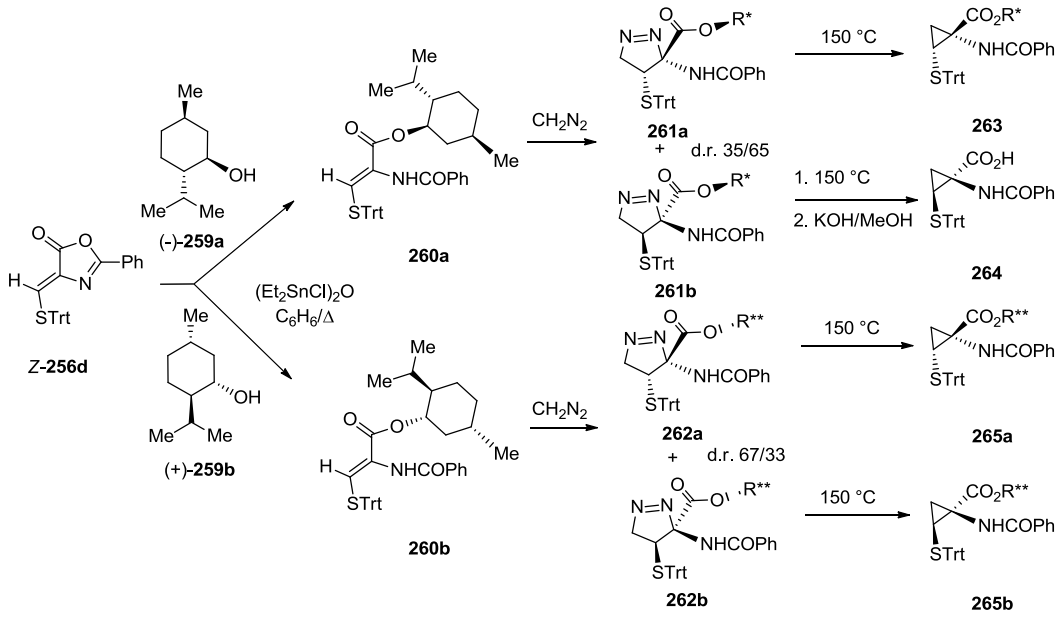
A summary of the strategies show that the cyclopropanation of dehydroamino acids β-substituted with a sulfanyl group is the only one described. Gelmi *et al*.[134] reported the reaction of the *Z*-oxazolones **256a-d** with diazomethane obtaining the two isomeric spirooxazolones *rac-Z*-**257a-d** and *rac-E*-**257a-d**, in a variable ratio, but the *Z*-isomer was always the major one (*Z*/*E*: 3/1 to 5/1) which had the same geometry at the double bond as the starting material *Z*-oxazolones **256a-d**. The subsequent heterocyclic ring-opening with ethanol in the presence of DMAP gave the 1-amino-2-mercaptocyclopropanecarboxylic acids derivatives *rac-Z*-**258a-d** and *rac-E*-**258a-d** orthogonally protected in good yield (*Scheme 73*).



Scheme 73

In addition, the asymmetric synthesis of 1-benzoylamino-2-tritylsulfanylcyclopropylcarboxylic acid **264** and the corresponding esters **263**, **265a** and **265b** has been carried out starting from the chiral *Z*-acrylates **260a** and **260b** that incorporate the chiral auxiliary menthol (-)-**259a** and (+)-**259b** at the carboxylic group, respectively. In this context, the reaction of these chiral *Z*-

acrylates **260a** and **260b** with diazomethane afforded the Δ^1-pyrazolines **261a-b** and **262a-b** as a diastereomeric mixture in a 35/65 and 67/33 ratio in enantiopure form, respectively. The diastereomeric mixtures of Δ^1-pyrazolines **261a-b** and **262a-b** were separated by means of column chromatography. During this process partial isomerization of the Δ^1-pyrazolines **261a-b** and **262a-b** to the corresponding Δ^2-pyrazolines was observed, respectively. The overall yield in both cases was good. Finally, the Δ^1-pyazolines were melted at 150 ºC obtaining the cylopropane derivatives **263**, **265a** and **265b**. The Δ^1-pyazoline **261b** was melted at 150 ºC and after saponification with KOH in MeOH led to the enantiopure 1-benzoylamino-2-tritylsulfanylcyclopropylcarboxylic acid **264** (*Scheme 74*).[135]

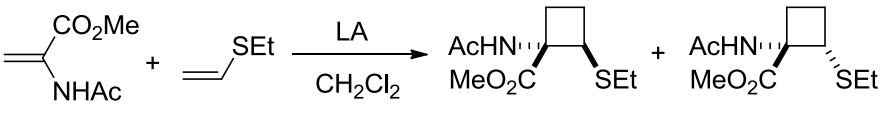


Scheme 74

6.2. Cyclobutane derivatives

Cyclobutane α-amino acids have received minor attention in comparison with other cycloalkane derivatives because few synthetic methods have been reported for their synthesis.[136] However, as molecular building blocks have gained importance in the past decade.[137]

Particularly, Avenoza *et al*.[138] have described the synthesis of cyclobutane amino acids as 2,3-disubstituted cysteine analogues *trans-rac*-**268a** and *cis-rac*-**268b** (*Scheme 75*).



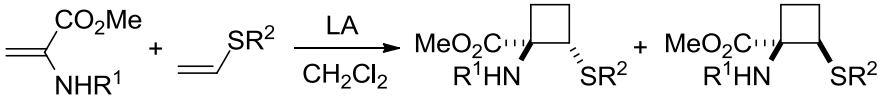
266 **267** *rac*-**268a** *trans* *rac*-**268b** *cis*

		d.r. (*trans*/*cis*) *rac*-**268a**/*rac*-**268b**	Yield (%)
LA	MABR	65/35	56
	MAO	7/93	61

Scheme 75

The methodology employed was a selective Michael-aldol reaction between the acrylate **266** and the monosubstituted donor alkene **267** using sterically hindered aluminium aryloxides as Lewis acids (MABR and MAO). It is important to note that the stereoselectivity inversion was promoted by MAO respect to MABR.

With the aim of achieving better stereoselectivity and yield of the Michael-aldol reaction to 2,3-disubstituted cysteine analogues *trans-rac*-**271a-c** and *cis-rac*-**271a-c** bearing a cyclobutyl group, has been also reported.[139] The effect of the trifluoroacetamide group in the acrylate **269** and the phenyl group attached to the sulfur atom in the vinyl thioether **270** has been studied. The results are gathered in the *Table 7*. Moderate to high selectivity were obtained in the case of the acrylate **266**, but poor yields of cycloadducts *trans-rac*-**271a** and *cis-rac*-**271a** were obtained. The yield of the cyclobutane derivatives could be increased by performing the reaction with the acrylate bearing the trifluoroacetamide group **269** and the vinylethyl thioether **267**, but in all cases, a diastereomeric mixture of cycloadducts *trans-rac*-**271b** and *cis-rac*-**271b** was obtained. Under these conditions, but changing the vinyl thioether to **270** the *trans-rac*-**271c** steroisomer was exclusively obtained with moderate yield. The use of MABR also afforded the *trans-rac*-**271c** steroisomer but with low yield (*Scheme 76* and *Table 7*).



R^1 = COMe, **266** R^2 = Et, **267**
R^1 = $COCF_3$, **269** R^2= Ph, **270**

rac-**271a-c** *trans* *rac*-**271a-c** *cis*

R^1 = COMe, R^2 = Ph, *rac*-**271a**
R^1 = $COCF_3$, R^2 = Et, *rac*-**271b**
R^1 = $COCF_3$, R^2 = Ph, *rac*-**271c**

Scheme 76

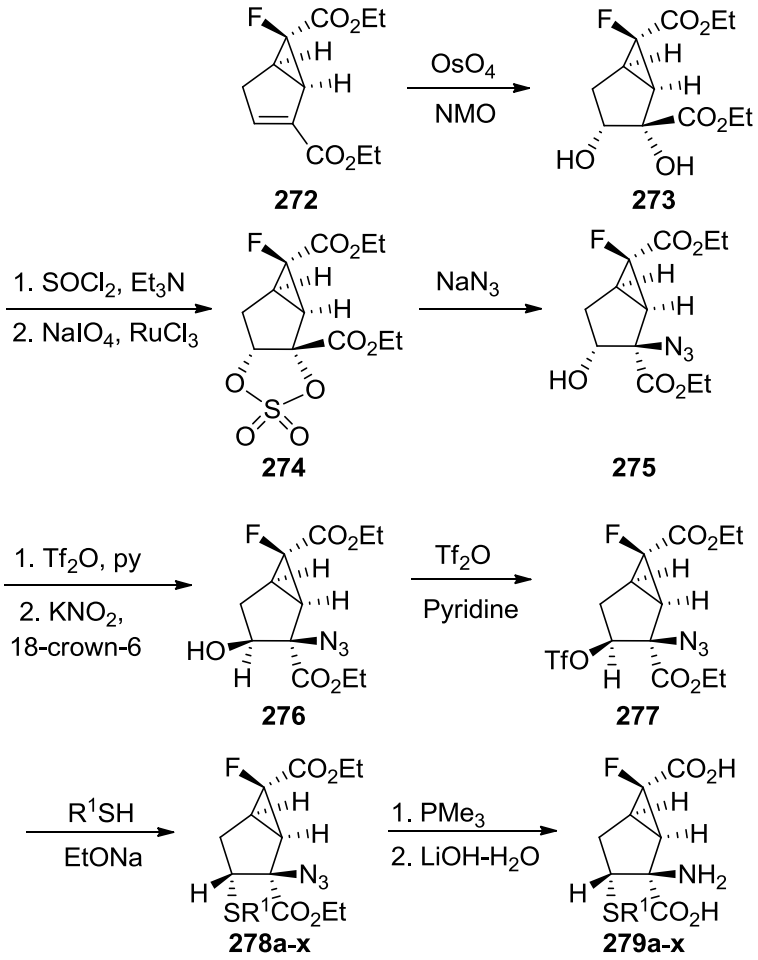
Table 7. Cyclobutyl cysteine analogues *trans-rac*-**271a-c** and *cis-rac*-**271a-c** synthesis

R1	R2	L.A.	d.r. (trans/cis)	Yield (%)
COMe	Ph	MABR	60/40	26
COMe	Ph	MAO	8/92	23
$COCF_3$	Et	MABR	87/13	69
$COCF_3$	Et	MAO	24/76	60
$COCF_3$	Ph	MABR	0/100	18
$COCF_3$	Ph	MAO	0/100	54

6.3. Cyclopentane derivatives

There is only one example described in the literature for the particular chiral synthesis of α,β-disubstituted cysteine analogues bearing a cyclopentyl ring.[140]

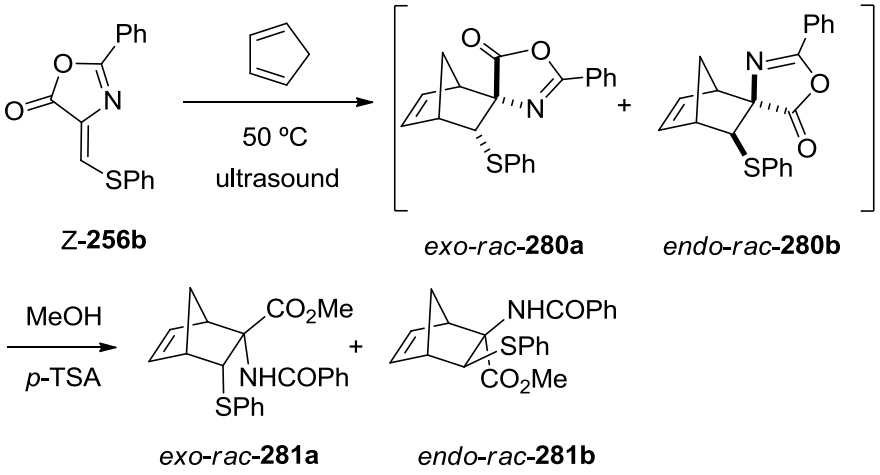
The synthetic approach implies the oxidation of the α,β-unsaturated carbonyl compound **272** with OsO_4 and *N*-methylmorpholine (NMO) to obtain the diol **273**. The single diastereoisomer observed is due to the reaction of the OsO_4 at the opposite face of the fused cyclopropane ring. Diol **273** was converted to the cyclic sulfate **274** in the presence of $SOCl_2$ and subsequent oxidation. Nucleophilic displacement by NaN_3 at the α-carbon of the cyclic sulfate **274** proceeded with good regioselectivity and the hydrolysis provided the compound **275**. The intermediate **276** in which the configuration of the hydroxyl group at the C3 position was inverted, was obtained from the compound **275** by treatment with trifluoromethanesulfonyl anhydride and pyridine, and then with KNO_2 in the presence of 18-crown-6 followed by post-treatment of the resulting nitrous ester with water. Moreover, the hydroxyl group of **276** was converted into the trifluoromethanesulfonyloxy group as a good leaving group affording **277** that under nucleophilic substitution reaction with various sodium salts derived from benzyl and alkylthiols proceeded to give the corresponding thioethers **278a-x**. A Staundinger reaction was then performed by trimethylphosphine in the presence of small amount of water in THF to obtain, after saponification, the compounds **279a-x** as α,β-disubstituted cysteine analogues bearing a cyclopentyl ring (*Scheme 77*).



Scheme 77

6.4. Bicyclic derivatives

As a consequence of our interest in this field, the literature revealed the Diels-Alder cycloaddition between β-sulfanyl substituted *Z*-oxazolone **256b** and cyclopentadiene described by Gelmi *et al*.[141] to obtain norbornene cysteine derivatives *exo-rac*-**281a** and *endo-rac*-**281b** (*Scheme 78*).[141c]



Scheme 78

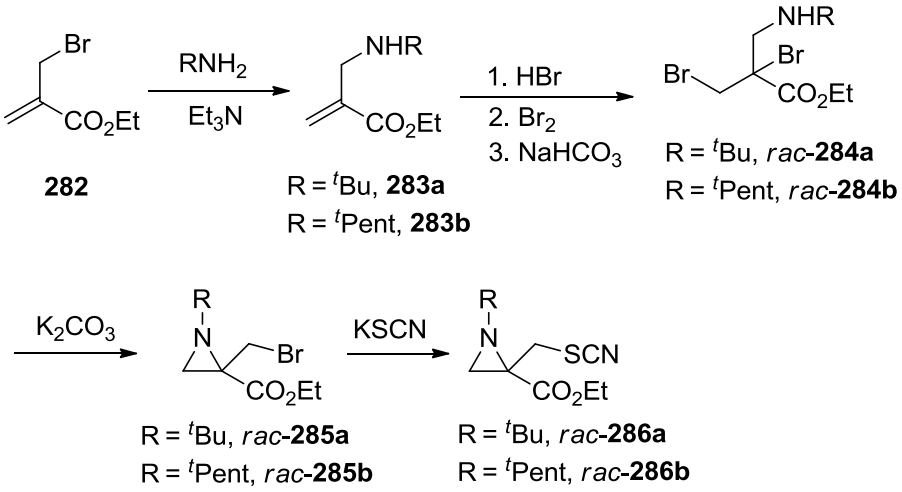
The reaction conditions were optimized, in terms of yield and selectivity. So, operating in neat conditions with ultrasound at 50 °C in the presence of an excess of diene and after oxazolone ring opening in acidic conditions afforded the norbornene cysteine derivatives *exo-rac*-**281a** and *endo-rac*-**281b** as a mixture of cycloadducts *exo*/*endo* 40/60 in good yield.

7. SYNTHESIS OF AZACYCLIC α-SUBSTITUTED CYSTEINE DERIVATIVES

7.1. Aziridine derivatives

Although the aziridine-2-carboxylic acids derivatives are of great importance in biology because their properties and in organic chemistry as building blocks in the preparation of proteinogenic and nonproteinogenic amino acids, the synthesis of azacyclic α-alkyl cysteine derivatives bearing an aziridine moiety has been scarcely explored. Only one example in the literature has been found. The synthetic methodology started from the reaction of 2-bromomethylacrylate **282** with primary amines in the presence of Et_3N leading to ethyl [(2-alkylamino)methyl]acrylates **283a** and **283b** in excellent yields. Subsequently, the amino group of ethyl [(2-alkylamino)methyl]acrylates **283a** and **283b** was protected by treatment with aqueous hydrobromic acid as the corresponding hydrobromide salt. The bromination followed by neutralization afforded the dibromopropanoates *rac*-**284a** and *rac*-**284b** in excellent yields. With the dibromo amino esters *rac*-**284a** and *rac*-**284b** in hand their ring closure was accomplished under basic conditions to obtain the aziridines *rac*-**285a** and *rac*-**285b**. Finally, ethyl 2-(thiocyanomethyl)aziridine-2-carboxylates *rac*-**286a** and *rac*-**286b** as azacyclic α-alkyl cysteine derivatives

were synthetized in moderate yield through a S_N2 reaction using KSCN (*Scheme 79*).[142]



Scheme 79

8. SYNTHESIS OF AZACYCLIC β-SUBSTITUTED CYSTEINE DERIVATIVES

The strategies and disconnections to access to the azacyclic β-alkylcysteine derivatives are summarized in the *Figure 7*. The disconnection **a** involves an azacyclic dehydroamino acid derivative as the key intermediates that after Michael addition or nucleophilic substitution with sulfur nucleophilic compounds lead to insert the sulfanyl group at the β-position, respectively. The disconnection **a** + **b** requires an imine as the key intermediate and a α-sulfanyl acid halide as ketene precursor that after an anionic nucleophilic catalyst lead to the azacyclic β-alkyl cysteine derivatives (*Figure 7*)

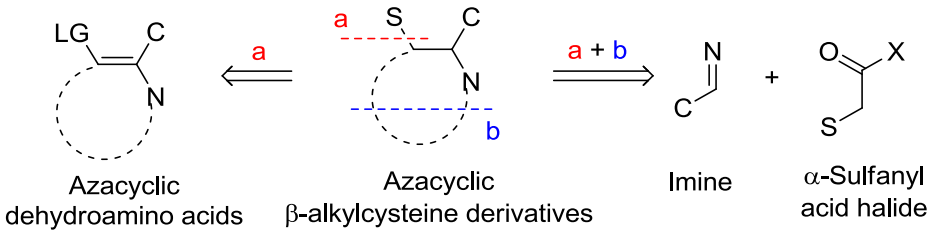
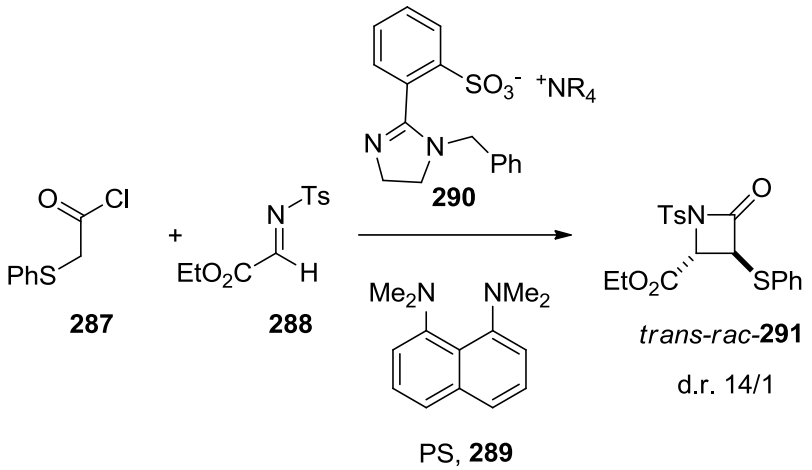


Figure 7. Azacyclic β-alkyl cysteines synthetic methodologies

8.1. Azetidine derivatives

One type of azacyclic β-alkyl cysteine derivatives described in the literature are β-lactams obtained *via* the ketene-imine cycloaddition reaction using α-(phenylthio)alkanoyl halides.[143] In this way, Weatherwax *et al*.[144] synthesized the azacyclic β-alkyl cysteine derivative *trans-rac*-**291** employing an anionic,

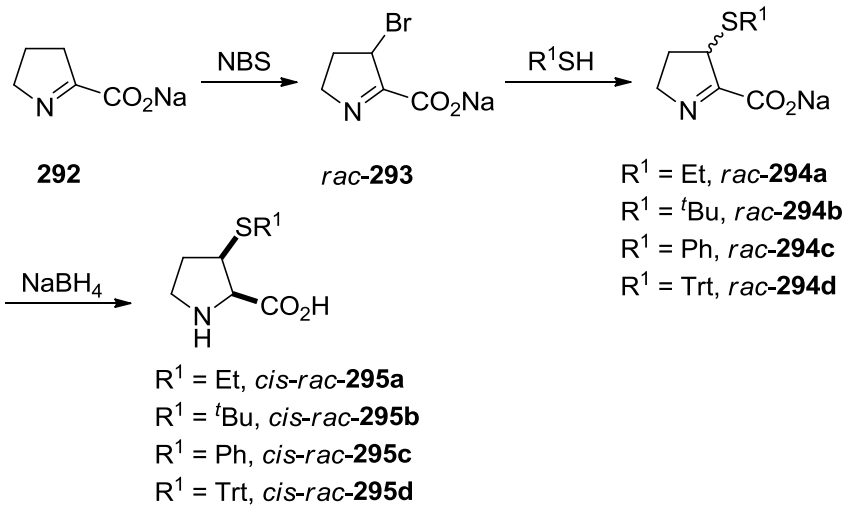
nucleophilic catalyst **290** based on a 2-aryl-2-imidazoline scaffold. The reaction between the acid chloride **287** bearing the phenylsulfanyl group (as ketene precursor), imino ester **288** in the presence of the proton sponge (PS) **289** and the catalyst **290** in a Staundinger type reaction allowed the β-lactam *trans-rac*-**291** to be obtained as cysteine derivative with good diastereoselectivity but in moderate yield (*Scheme 80*).



Scheme 80

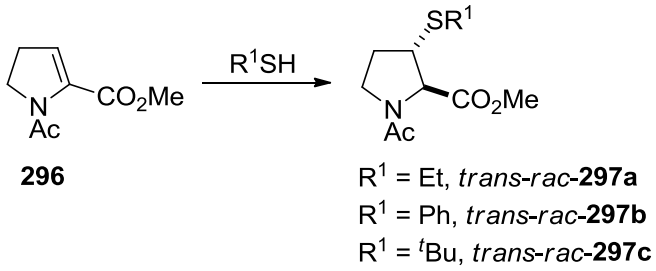
8.2. Pyrrolidine derivatives

The racemic azacyclic β-alkyl cysteine derivatives containing a cyclopentane ring both *cis* as *trans* has been reported by Häusler.[145] Sodium 3,4-dihydro-2*H*-pyrrole-5-carboxylate **292** was reacted with *N*-bromosuccinimide to obtain the intermediate *rac*-**293**. The halogen exchange with thiols afforded the thio compounds *rac*-**294a-d**. Finally, the reduction of the imine group with sodium borohydride led to *cis*-azacyclic β-alkyl cysteine derivatives *cis-rac*-**293a-d** (*Scheme 81*).



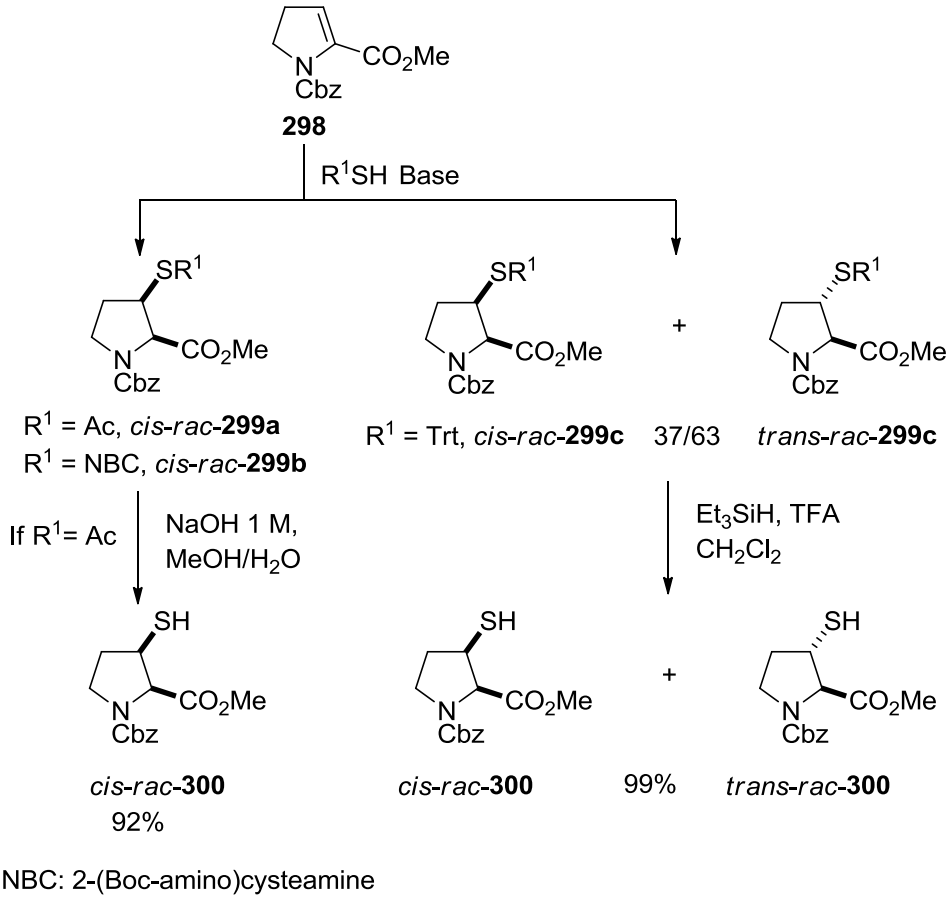
Scheme 81

The *trans*-azacyclic β-alkyl cysteine *trans-rac*-**297a-c** derivatives were obtained *via* thio-Michael addition of thioles to the cyclic dehydroamino acid derivative **296** (*Scheme 82*).



Scheme 82

In this year, our research group has reported the synthesis of *cis*-azacyclic β-alkyl cysteine *cis-rac*-**299a-b** and the mixture of *cis*- and *trans*-rac-**299c** by the addition of thiols to the dehydroproline **298** in presence of base. Final deprotection of sulfur atom led to the corresponding protected azacyclic β-alkyl cysteines *cis-rac*-**300** and *trans-rac*-**300**, respectively (*Scheme 83*).[146]



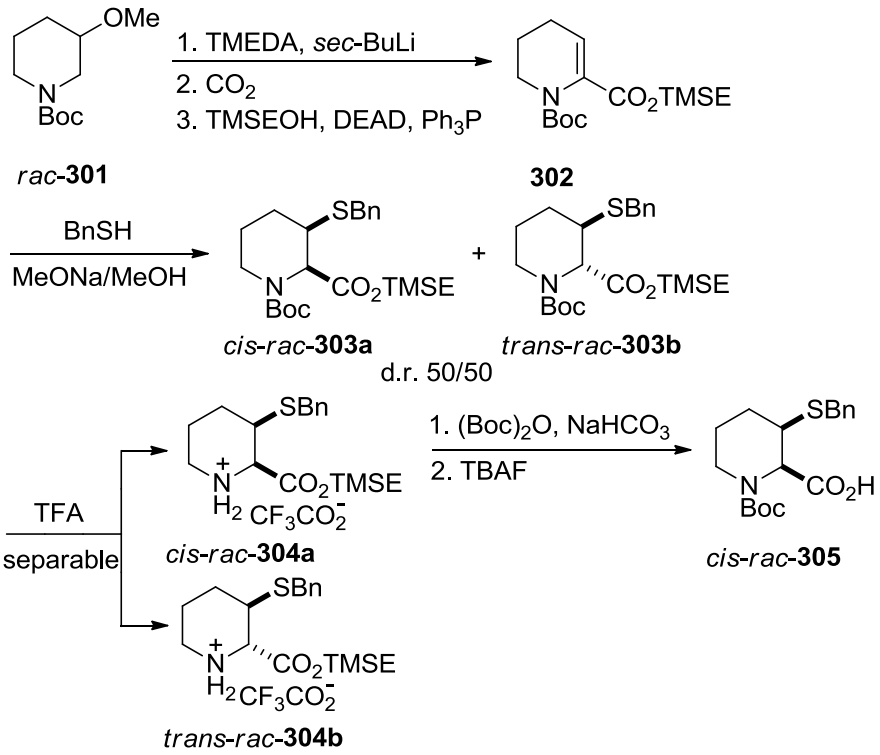
Scheme 83

Furthermore, other azacyclic β-alkyl cysteine pyrrolidine analogues have been used as intermediates incorporating the sulfanyl group after a conjugate addition reaction[147] or other kind of synthetic approaches[148] to obtain compounds of biological interest.

8.3. Piperidine derivatives

The synthesis of the racemic azacyclic β-alkyl cysteine derivatives containing a cyclohexane ring *cis-rac*-**305** has been reported by Hanessian *et al*.[145] The synthesis consisted on the lithiation reaction of the racemic *N*-Boc-3-methoxypiperidine *rac*-**301** employing *sec*-BuLi as base in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to obtain the corresponding α-lithiated heterocycle, which after quenching with CO_2 and esterification to the trimethylsilylethyl ester gave the dehydroamino acid **302**. The conjugate addition of benzyl mercaptan to the dehydroamino acid **302** gave a 50/50 diastereomeric mixture of the compounds *cis-rac*-**303a** and *trans-rac*-**303b**. Cleavage of the Boc group allowed for the chromatographic separation of the *cis-rac*-**304a** and *trans-rac*-**304b** isomers. The amine group of *cis-rac*-**304a** was re-protected with Boc_2O,

and the (trimethylsilyl)ethyl ester (TMSE) was cleaved affording the free acid *cis-rac*-**305** (*Scheme 84*). By similarity of the procedure depicted in *Scheme 83*, Gutiérrez *et al*.[146] also carried out the synthesis of azacyclic β-alkyl cysteine derivatives containing a cyclohexane as mixture of *cis* and *trans* isomers.



Scheme 84

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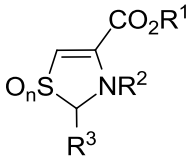
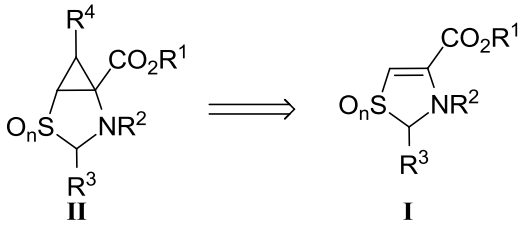
OBJECTIVES

1. To develop a versatile, coherent and efficient synthetic methodology to obtain enantiopure thiazolines **I** with different oxidation level on the sulfur atom (sulfanyl, sulfinyl and sulfonyl groups) in few steps and in multigram scale, as dehydrocysteine equivalents.



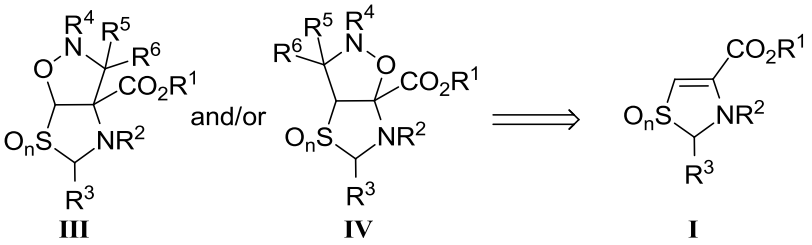
I

2. The evaluation of the 1,3-dipolar cycloaddition between thiazolines **I** as dipolarophiles and diazoalkanes as dipoles focusing on the regio-, diastereo- and enantioselectivities of the reactions to obtain thiazolidines **II**. Computational studies will be carried out to assess the experimental results.



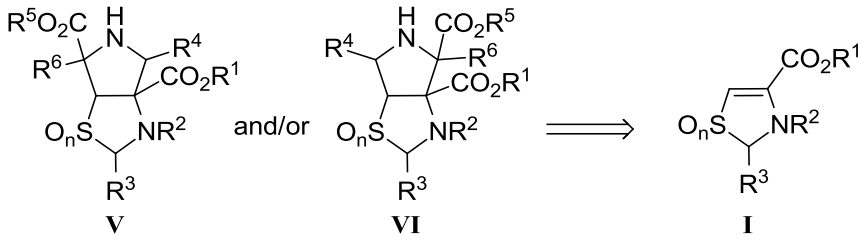
II **I**

3. For increasing the scope of the reactivity between thiazolines **I** and dipoles as well as to prepare compounds as isoxazolidines **III** and **IV** with a potential application in the biological field, the reactivity, regio-, diastereo- and enantioselectivity in the 1,3-dipolar cycloaddition reaction between thiazolines **I** and several nitrones will be tested. Computational studies will be carried out to assess the experimental results.



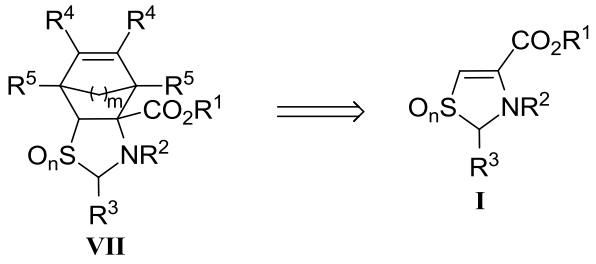
III **IV** **I**

4. The development of a methodology for the diastereoselective and enantioselective synthesis of sulfur substituted bis-amino acids, cysteine- or homocysteine-proline chimeras **V** and **VI** by means of 1,3-dipolar cycloaddition reaction between thiazolines **I** and some α-imino esters, derived from natural amino acids.



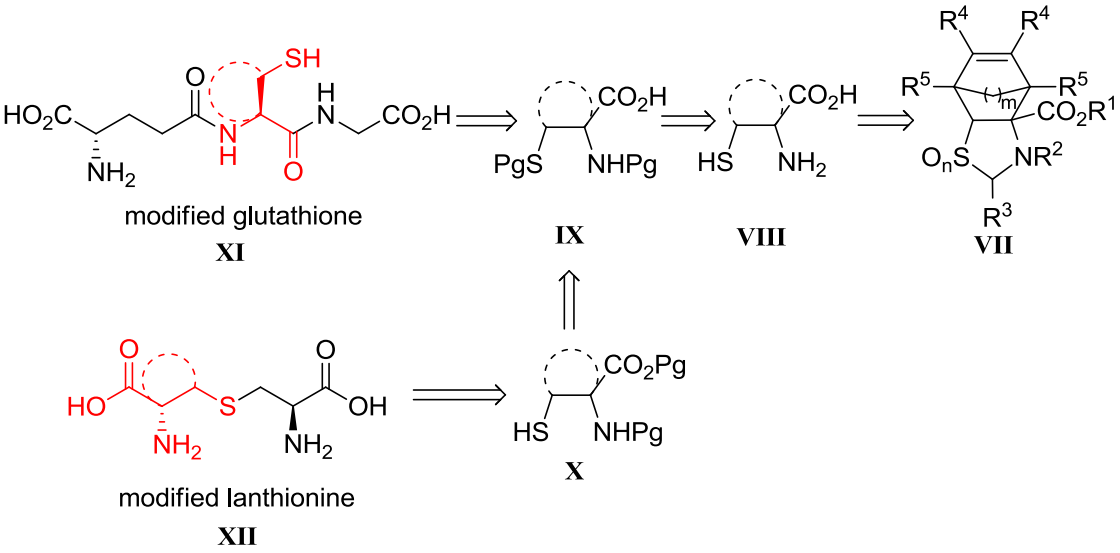
V **VI** **I**

5. The Diels-Alder reaction between thiazolines **I** and cyclic and acyclic dienes (cyclopentadiene, 1,3-cyclohexadiene, 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,4-dipehyl-1,3-butadiene and 2-trimethylsiloxy-1,3-butadiene) will be assessed focusing on the reactivity and stereoselectivity of different pairs diene/thiazoline to prepare thiazolidines **VII**. Computational studies will be carried out to evaluate the experimental results.



VII **I**

6. The synthesis of modified glutathione **XI** and lanthionine **XII** upon a proper designed methodology; thiazolidine **VII** ring opening and deprotection of the functional groups to prepare the modified cysteine free amino acids **VIII** and orthogonally protection of the amine and sulfur atom would lead to suitable intermediate **IX**. The coupling reactions between the intermediate **IX** and the appropriate amino acids and the nucleophilic attack of the thiol **X** over a suitable alanine equivalent will afford the corresponding modified glutathiones **XI** and lanthionines **XII**, respectively.



Chapter II

Synthesis of homochiral thiazolines as dehydrocysteine equivalents

II. Synthesis of homochiral thiazolines as dehydrocysteine equivalents

1. INTRODUCTION

Dehydroamino acids have attracted great attention since several years ago, due to their biological properties and importance as intermediates in Organic Chemistry as key tools to prepare important organic molecules. Dehydroamino acids are present in some dehydropeptides with interesting biological activities such as cephalosporines, a group of β-lactam antibiotics,[1] tentoxin a cyclic tetrapeptide with herbicidal activity[2] or azinomycin A which is known to be an antitumor agent[3] (*Figure 1*). The synthesis and reactivity of dehydroamino acids have been reviewed several times.[4–8]

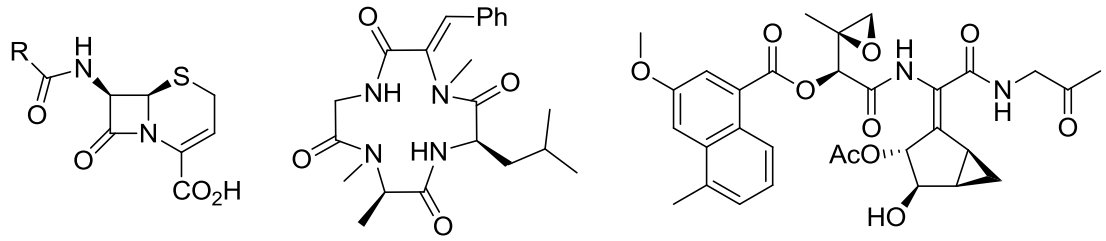


***Figure* 1**. Naturally occurring dehydropeptides

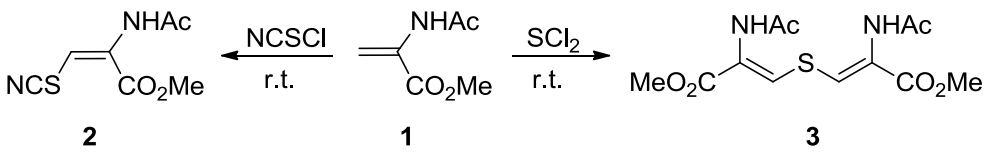
1.1. Synthesis of dehydrocysteines

Being the stereoselective synthesis of modified cysteines the main aim of this dissertation, a bibliographic review has been carried out in order to find the most suitable chiral dehydrocysteine derivative as a scaffold to achieve our goal.

Dehydrocysteine derivatives reported in the bibliography can be classified as acyclic or cyclic.

1.1.1. Acyclic dehydrocysteine derivatives

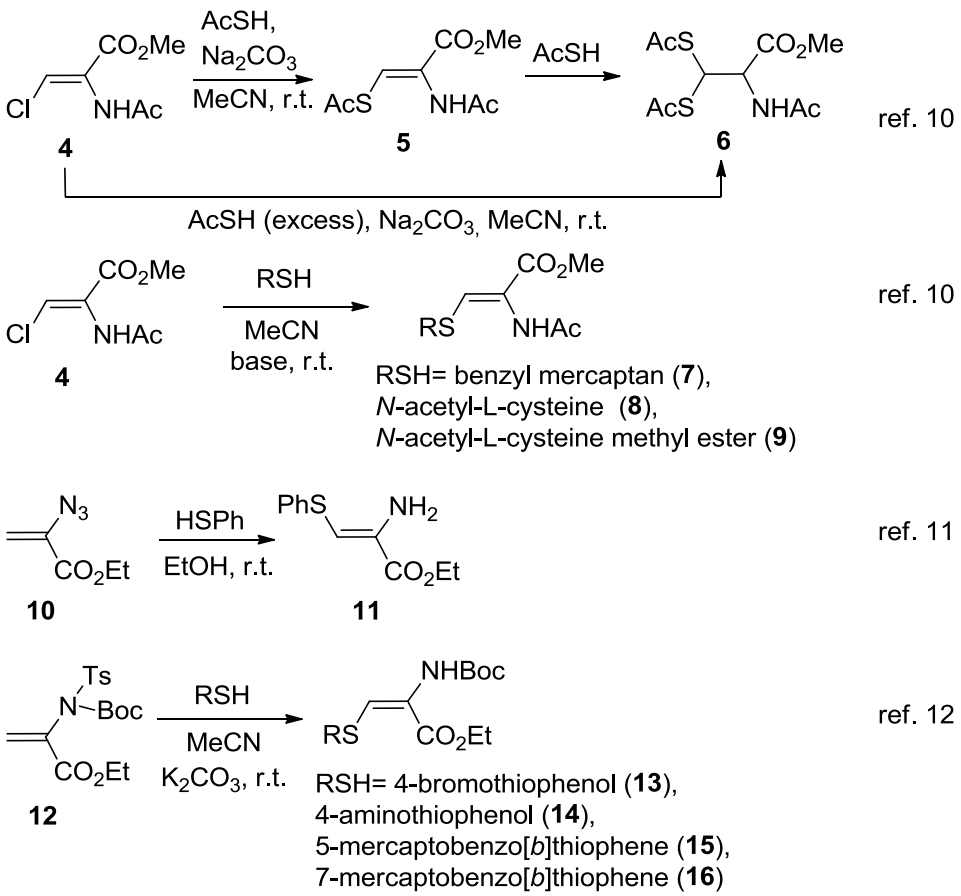
In 1972, Love *et al.*[9] reported the synthesis of acyclic dehydrocysteines **2** and **3** through the addition of thiocyanogen chloride or sulfur dichloride to methyl 2-acetamidoacrylate **1**, respectively (*Scheme 1*).



2 **1** **3**

***Scheme* 1**

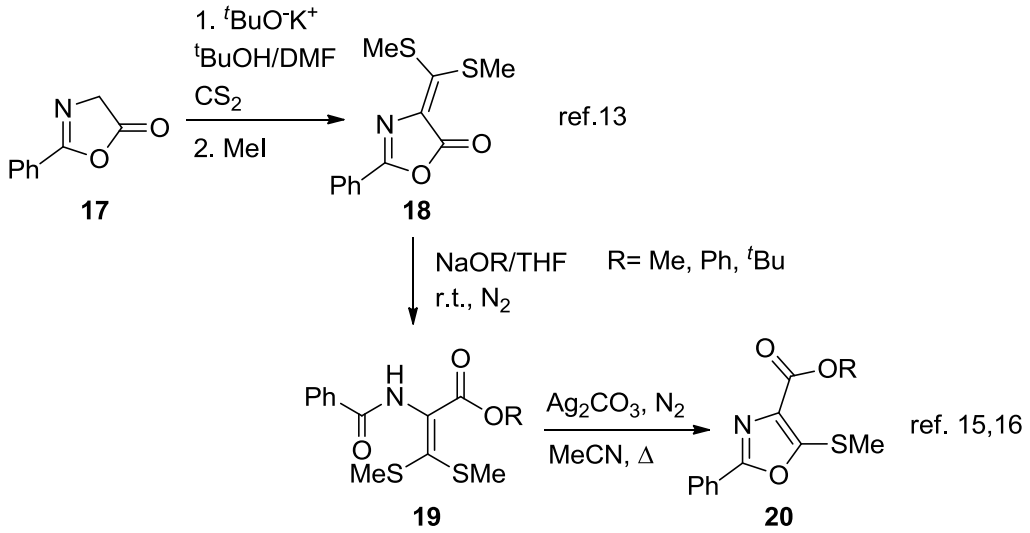
On the other hand, the treatment of *Z*-*N*-acetyl-β-chlorodehydroalanine methyl ester **4** with equimolar equivalents of thioacetic acid furnished **5** whereas the addition of more equivalents of thioacetic acid over **5** or an addition of thioacetic acid in excess provided **6**. Furthermore, the addition of benzyl mercaptan, *N*-acetyl-L-cysteine or *N*-acetyl-L-cysteine methyl ester to **4** in presence of base, allowed to obtain the corresponding *Z*-protected dehydrocysteines **7**-**9** through an addition/elimination reaction (*Scheme 2*).[10] The addition of thiophenol to 2-azidopropenoate **10** resulted in evolution of nitrogen gas to give *Z*-2-amino-3-phenylthiopropenoate **11** (*Scheme 2*).[11] Moreover, the addition of 4-bromothiophenol, 4-aminothiophenol or 5- and 7-mercaptobenzo[*b*]thiophenes to *N*-Boc-*N*-Tosyl protected dehydroalanine methyl ester **12** yielded the *E*-isomers of the corresponding dehydrocysteines **13**-**16** upon spontaneous elimination of the tosyl group (*Scheme 2*).[12]



Scheme 2

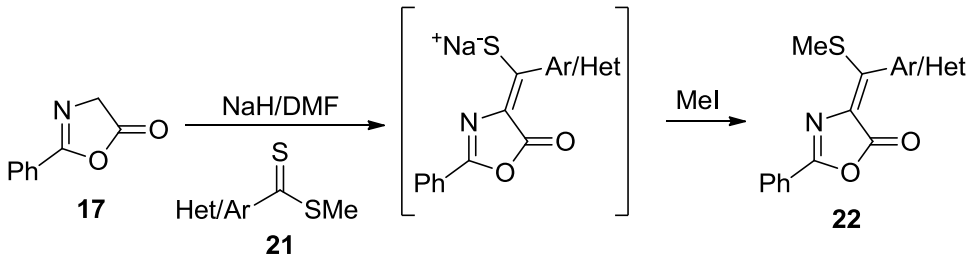
In 1965 Brown *et al*.[13] described the synthesis of 4-bis(methylthio)methylene-2-phenyl-2-oxazolin-5-one **18**, by condensation of 2-phenyl-5-oxazolone **17** with carbon disulfide followed by methylation with MeI. Later, Mukerjee *et al*.[14] developed a one-pot methodology for the synthesis of **18** starting from hippuric

acid. Besides, ring opening of **18** with sodium methoxide, ethoxide, *tert*-butoxide or phenoxide furnished the acyclic adducts **19**, respectively. A subsequent intramolecular cyclization gave 2-phenyl-4-carboalkoxy/phenoxy-5-(methylthio)oxazoles **20** (*Scheme 3*).[15,16]



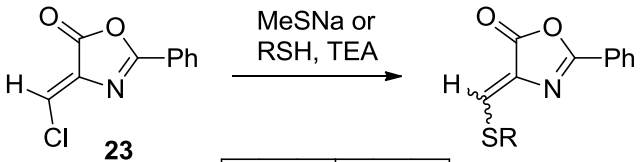
***Scheme* 3**

2-phenyl-5-oxazolone **17** has also been employed as starting material for the synthesis of 4-[methylthio(aryl/heteroaryl)methylene]-2-phenyloxazol-5-ones **22,** through an addition reaction of the appropriate (hetero)aryl dithioester **21**, followed by the methylation of the thiolate salt with MeI (*Scheme 4*).[17,18]



***Scheme* 4**

Gelmi *et al*.[19] prepared 4-(Alkyl- or phenyl-sulfanylmethylene)-2-phenyl-5(4*H*)-oxazolones **24a-d** by the substitution reaction of *Z*-4-chloromethylene-2-phenyl-5(4*H*)-oxazolone **23** with sodium thiomethoxide or the corresponding mercaptans in the presence of triethylamine, giving *Z* isomers as the major one in every case (*Scheme 5*).

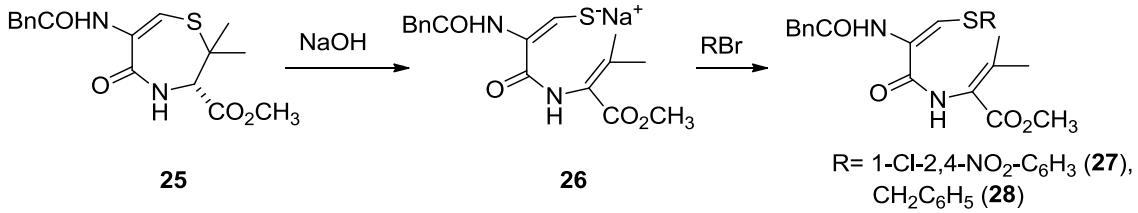


23 **24a-d**

	R	*Z*/*E*
24a	Me	90/10
24b	Ph	70/30
24c	CH_2Ph	85/15
24d	Ph_3C	Z

Scheme 5

Another approach to obtain acyclic dehydrocysteine derivatives is the proposed by Leonard *et al*.[20] Their methodology implied the ring opening of **25** with NaOH and a subsequent alkylation of **26** with 1-chloro-2,4-dinitrobenzene or benzyl bromide to afford *S*-substituted derivatives **27** and **28** (*Scheme 6*).

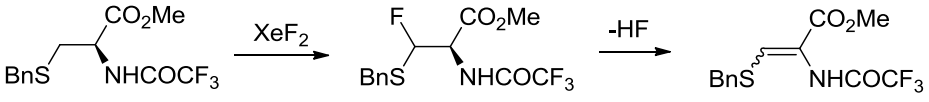


25 **26**

R= 1-Cl-2,4-NO_2-C_6H_3 (**27**),
$CH_2C_6H_5$ (**28**)

Scheme 6

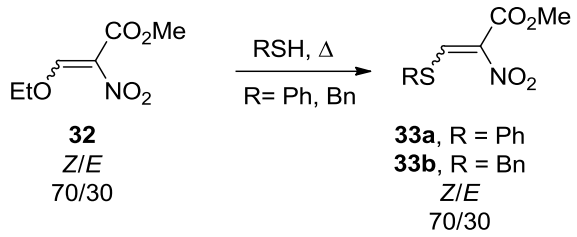
Huang *et al*.[21] described the decomposition of **30** resulted from the addition of XeF_2 to *S*-benzyl-*N*-trifluoroacetyl-L-cysteine methyl ester **29** that gave a mixture of *Z*- and *E*-*N*- trifluoroacetyl-3-benzylthio-2-aminopropenoate **31** (*Scheme 7*).



29 **30** **31**

Scheme 7

Finally, Gelmi *et al*.[22] reported the preparation of a mixture *Z*/*E* α-nitro-β-(phenylthio or benzylthio)acrylates **33a** and **33b**, as acyclic dehydrocysteine derivatives, from a mixture of *Z*/*E* α-nitroacrylates **32** with no modification in the *Z*/*E* ratio of the starting material. These electron poor alkenes were employed for the synthesis of modified cysteines (*Scheme 8*).



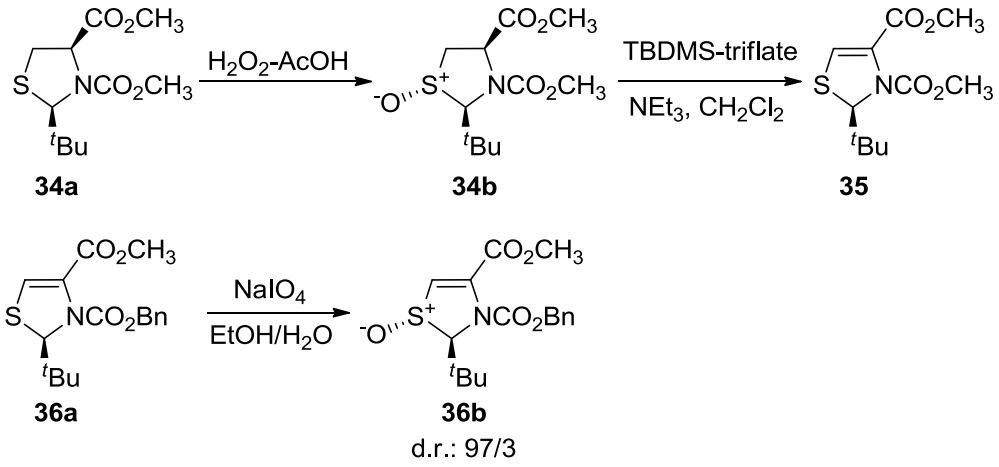
32
Z/*E*
70/30

33a, R = Ph
33b, R = Bn
Z/*E*
70/30

Scheme 8

1.1.2. Synthesis of cyclic dehydrocysteine derivatives

Another kind of dehydrocysteine derivatives are the thiazolines. In this sense, Seebach *et al.*[23] reported the synthesis of enantiomerically pure thiazolines **35** and **36a,b**. Thiazoline **35** was obtained in moderate yield through a Pummerer reaction from **34b** employing TBDMS-triflate. Alternately, oxidation of thiazoline **36a** with $NaIO_4$ resulted in a diastereomeric mixture of thiazolines in a ratio 97/3, favored to the (1*R*,2*R*) isomer **36b** (*Scheme 9*).

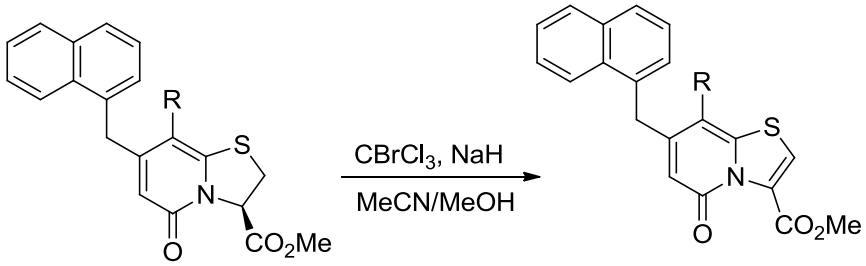


34a **34b** **35**

36a **36b**
d.r.: 97/3

Scheme 9

More recently, Chorell *et al*.[24] developed the formation of thiazoline **38** from thiazolidine **37** using $CBrCl_3$ in presence of NaH as base (*Scheme 10*), following the procedure previously described by Williams *et al*.[25] for the synthesis of thiazols from thiazolidines.

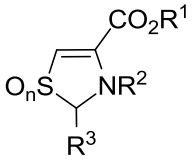


37 R= Cyclopropyl, 4-CF_3-Ph **38**

Scheme 10

2. OBJECTIVES

On the basis of these previous works, it was decided to develop a versatile, coherent and efficient synthetic methodology to obtain enantiopure thiazolines **I** with different oxidation level on the sulfur atom (sulfanyl, sulfinyl and sulfonyl groups) in few steps and in multigram scale.



I

3. RESULTS AND DISCUSSION

Target thiazolines **39a-c** (*Figure 2*) fulfills all our requirements, the methodology to perform the synthesis of these will be disclosed here below.

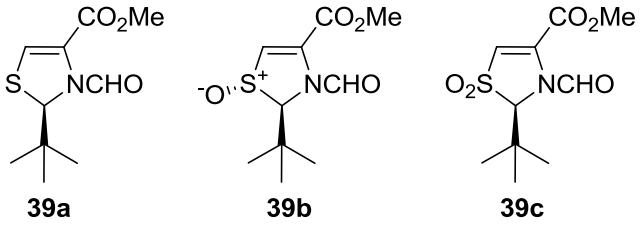
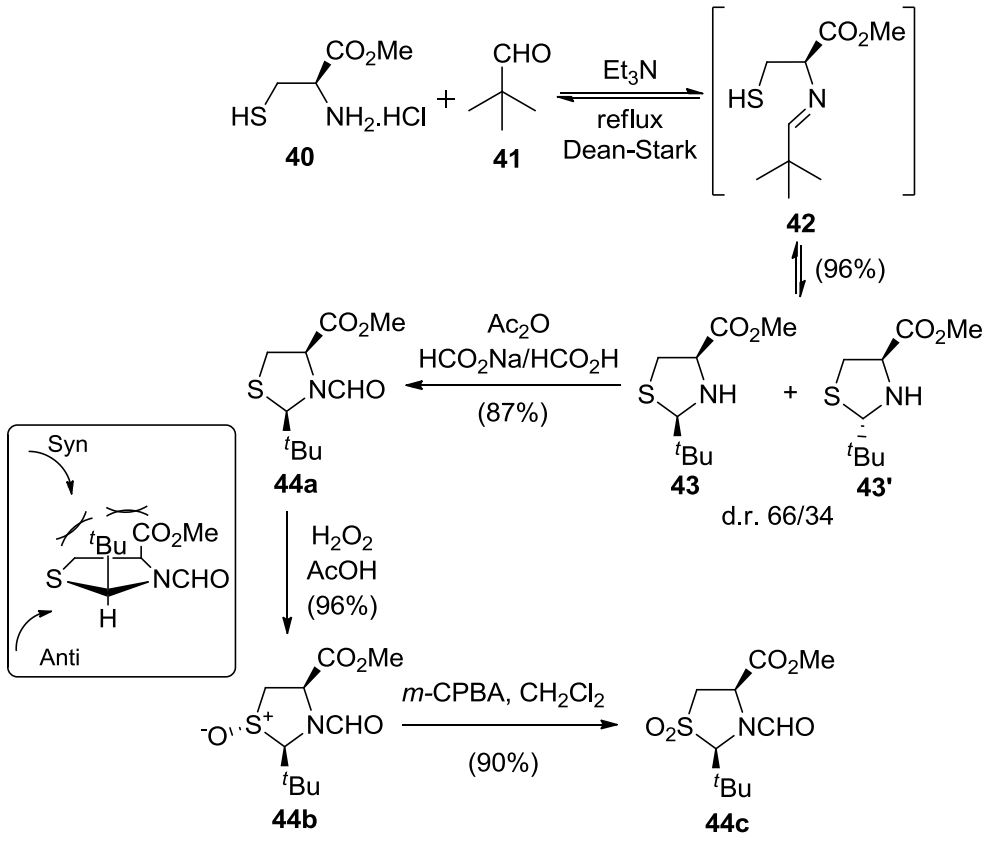


Figure 2. Target thiazolines

With the challenge of the synthesis of the target starting materials with sulfinyl **39b** and sulfonyl **39c** moieties, *a priori*, with an increased double bond electrophilicity and enhanced reactivity towards different organic reactions with respect to the parent thiazoline **39a**, we designed a novel, efficient and versatile synthetic methodology in comparison with the previous described by Seebach *et al*.[23] Their preparation started with the synthesis of thiazolidines **43** and **43'**. In this sense, the reaction of the *L*-cysteine methyl ester hydrochloride **40** with trimethylacetaldehyde **41** in the presence of triethylamine as a base, with continuous removing of water using a Dean-Stark equipment, afforded a 66/34 mixture of two diastereoisomers **43** and **43´**, owing to the equilibrium with the parent imine **42** (*Scheme 11*). Starting from the mixture of **43** and **43´**, the nitrogen protection was performed with the formyl group due to its low steric hindrance and chemical robustness. The reaction was carried out with sodium formate in the presence of acetic anhydride and formic acid obtaining (2*R*,4*R*)-thiazolidine **44a** as a single enantiomerically pure diastereoisomer in good yield.[26,27] Then, oxidation of the sulfanyl functionality in **44a** with H_2O_2/AcOH provided diastereoselectively the corresponding sulfinyl derivative **44b** in excellent yield. Only one product was obtained, the absolute configuration on the sulfur atom was established as *R* in comparison with equivalent thiazolines described in the literature.[28] This fact is in agreement with the oxidation through the *anti*-face respect to *tert*-butyl and methyl ester group. Further oxidation of **44b** with *m*-CPBA gave the sulfonyl thiazolidine **44c** in high yield (*Scheme 11*).

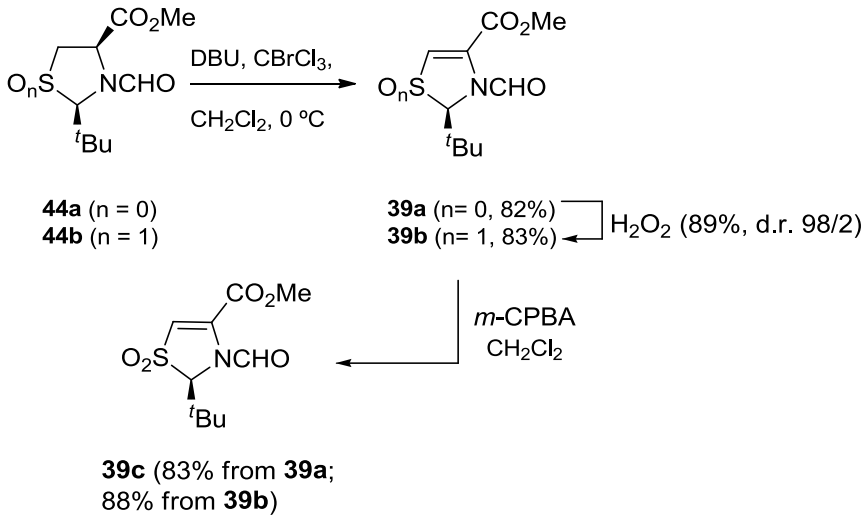


Scheme 11. Synthetic sequence towards thiazolidines **44a-c**

Structural assignments for the compound **44a-c** have been made on the basis of IR, ^{1}H NMR and ^{13}C NMR spectral data as well as NOESY and COSY. Comparison of the specific optical rotation of **44a** with the value given in the literature[26,27] corroborated the absolute configuration (2*R*,4*R*) showing a *syn* relationship between the *tert*-butyl group at C2 and the methyl ester group at C4 in the NOESY experiments.

With the compounds **44a-c** in hand, we examined the formation of the thiazoline ring according to the previously reported procedures.[25,29–32] In this sense, the reaction of the thiazolidines **44a** and **44b** with DBU and $CBrCl_3$ proceeded smoothly to furnish thiazolines **39a**[33] and **39b** in good yields. On the other hand, thiazolidine **44c** gave a complex mixture of products under the same reaction conditions perhaps because of the similar acidity of H4 and H5. Therefore, the preparation of thiazoline **39c** was carried out through direct oxidation of **44a** or **44b** with *m*-CPBA. ^{1}H NMR did not show the corresponding epoxides in the reaction crude as by-products of the reaction. Alternatively, oxidation of **39a** with H_2O_2/AcOH afforded **39b** in good yield but as diastereomeric mixture (d.r. 98/2) in favour of *R* isomer. Hence, the sequence of reactions leading to homoquiral

thiazolines **39a-c**, preserved the configurational integrity of the stereogenic centers (*Scheme 12*).



Scheme 12. Synthesis of thiazolines **39a-c**

From a spectroscopic point of view, ^{1}H NMR experiments revealed the effect of the sulfinyl and sulfonyl groups on H5 in thiazolidines **44a-c**. Due to this fact, the signal of the H5 proton *cis* to the oxygen bonded to the sulfur atom in **44b** and **44c** was shifted to lower fields as is shown in *Figure 3*.

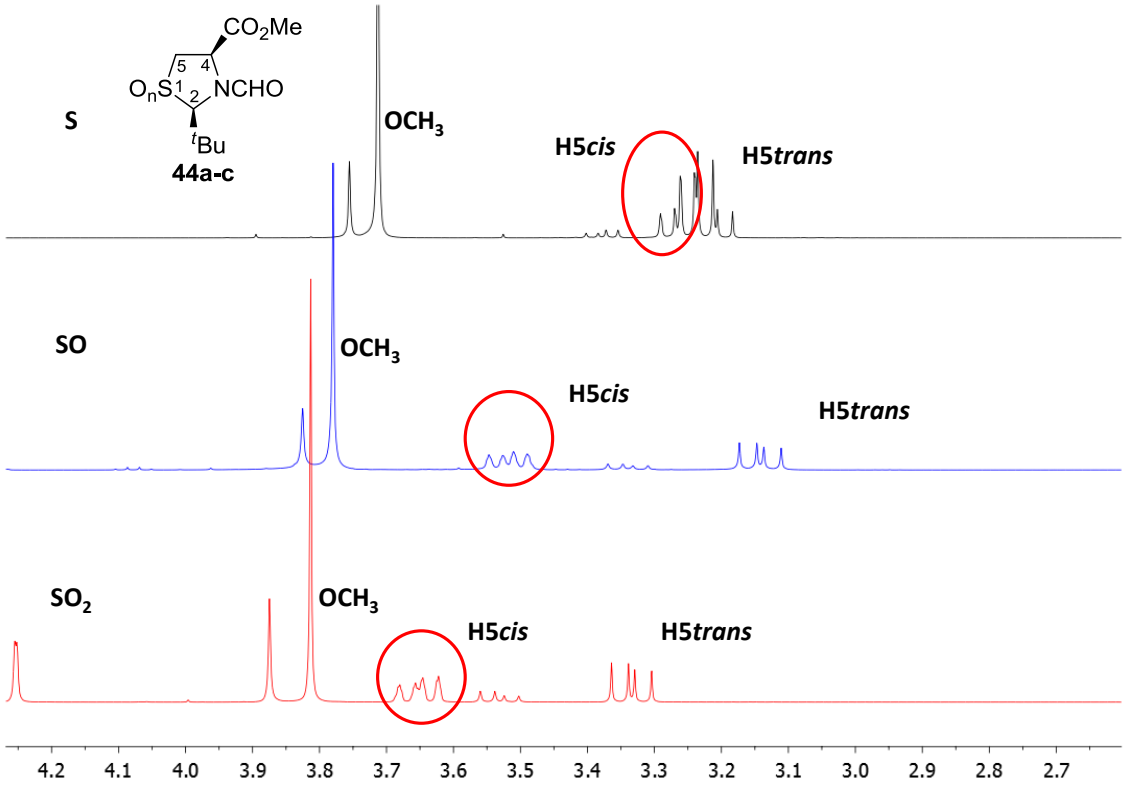


Figure 3. Chemical shift comparison for the proton H5 *cis* in thiazolines **44a-c**

On the other hand, the vinyl proton at C5 of thiazolines **39a-c** appears almost at the same chemical shift (≈7 ppm). Nevertheless, the proton H2 of **39b** and **39c** appears at the same chemical shift but in the case of **39a** is shifted to lower fields (*Figure 4*).

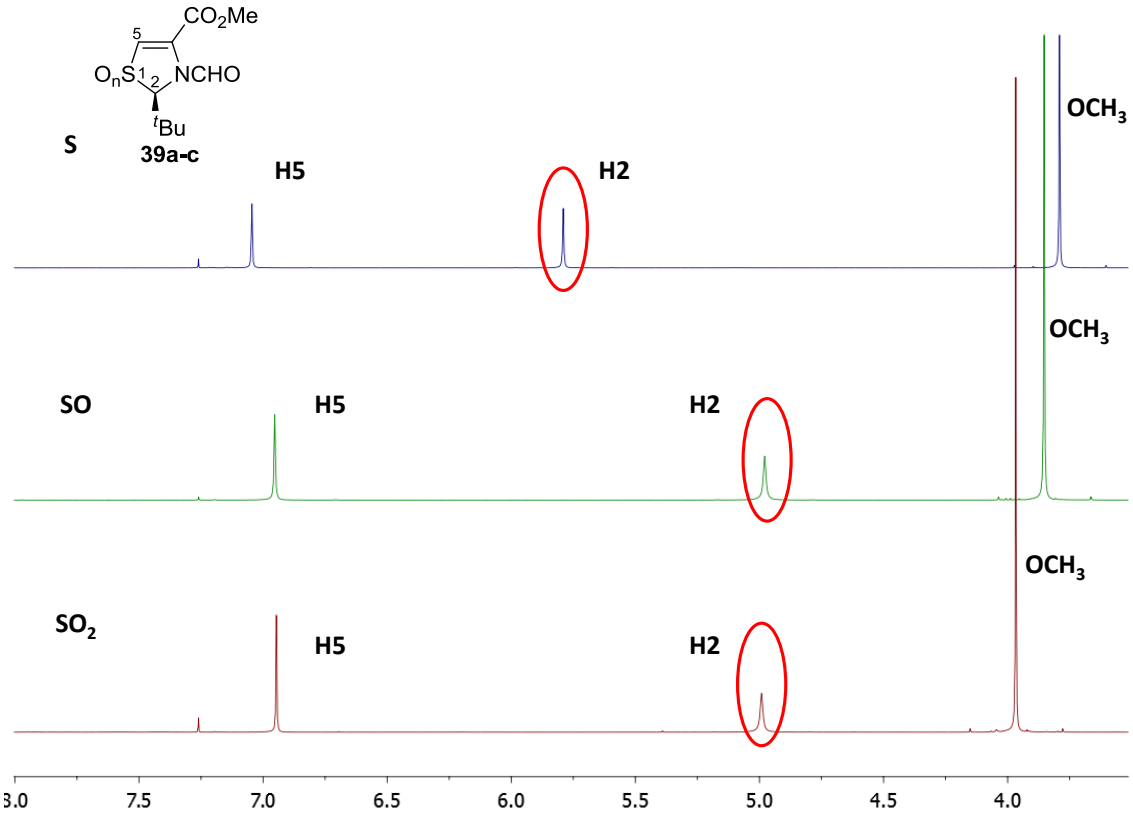


Figure 4. Chemical shift comparison for the protons H2 and H5 in thiazolines **39a**-**c**

4. CONCLUSIONS

We have developed a synthetic methodology that allowed to obtain the proposed thiazolines **39a**-**c** enantiomerically pure, in few steps, with good yields and in multigram scale. Our methodology has demonstrated to improve the previously reported results on the synthesis of this kind of compounds.

These versatile substrates would be, *a priori*, suitable to carry out several organic transformations as cycloadditions, due to their stereoelectronic features.

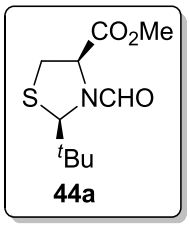
5. EXPERIMENTAL SECTION

5.1. General

All reagents were used as received from commercial suppliers without further purification. Thin-layer chromatography (TLC) was performed on Macherey-Nagel Polygram®SIL G/UV254 precoated silica gel polyester plates. The products were visualized by exposure to UV light, iodine vapour, submersion in ninhydrin stain, in ethanolic solution of phosphomolybdic acid or in an aqueous solution of sodium permanganate. Column chromatography was performed using 60 M (0.04-0.063 mm) silica gel from Macherey-Nagel. Melting points were determined on a Gallenkamp apparatus. IR spectra were registered on a Nicolet Avatar 360 FTIR spectrophotometer; vmax is given for the main absorption bands. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, AV-400 instrument at room temperature, unless otherwise indicated, and using the residual solvent signal as the internal standard; chemical shifts (δ) are expressed in parts per million and coupling constant (*J*) in hertz. Optical rotations were measured at room temperature using a JASCO P-1020 polarimeter. High-resolution mass spectra were obtained on a Bruker Microtof-Q spectrometer.

5.2. Synthesis of thiazolidines

Synthesis of (2*R*,4*R*)-Methyl 2-*tert*-butyl-3-formyl-1,3-thiazolidin-4-carboxylate 44a



44a

Acetic anhydride (42.5 mL, 0.45 mol) was added under stirring to a solution of (2*RS*, 4*R*)-Methyl 2-*tert*-butyl-1,3-thiazolidin-4-carboxilate **43** and **43´** (30.1 g, 0.15 mol) and sodium formate (12.2 g, 0.18 mol) in formic acid (350 mL) at 0-5 ºC for 1 hour. The reaction mixture was warmed to room temperature. After 24 h stirring, solvent was removed under reduced pressure and the obtained oil was treated with a saturated solution of $NaHCO_3$ (70 mL) at 0 ºC and diethyl ether (100 mL) was added. The aqueous phase was extracted with diethyl ether (3 x 30 mL) and the combined organic layers were dried over anhydrous magnesium sulfate, filtered off and the solvent was removed under reduced pressure. Crystallization in hexane/diethyl ether (90/10) afforded **44a** (29.8 g, 0.13 mol, 87% yield) as a crystalline white solid.

M.p.: 76-78 ºC

$[\alpha]_D^{22}$:-131º (*c* 1.0; $CHCl_3$), $[\alpha]_D^{lit}$:-130º (*c* 1.1, $CHCl_3$)[26,27]

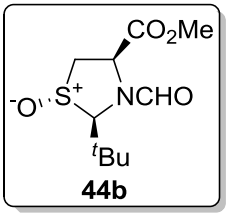
IR (KBr) ν 1749, 1667, 1364, 1201, 1177 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) [rotamers mixture ratio (1/0.15)] δ 8.30 (s, 1H, C*H*O, rot. maj.), 8.23 (s, 1H, C*H*O, rot. min.), 5.21 (s, 1H, H_2, rot. min.), 4.83 (t, *J* = 8.5 Hz, 1H, H_4, rot. maj.), 4.76 (dd, *J* = 8.6, 7.3 Hz, 1H, H_4, rot. min.), 4.71 (s, 1H, H_2, rot. maj.), 3.76 (s, 3H, OCH_3, rot. min.), 3.71 (s, 3H, OCH_3, rot. maj.), 3.38 (dd, *J* = 11.9, 7.2 Hz, 1H, H_{5cis}, rot. min.), 3.29-3.24 (m, 2H, H_5, both rot.), 3.21 (dd, *J* = 11.7, 9.1 Hz, 1H, H_{5trans}, rot. maj.), 0.98 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.91 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6 (*C*O_2Me, rot. min.), 170.0 (*C*O_2Me, rot. maj.), 163.9 (*C*HO, rot. min.), 162.6 (*C*HO, rot. maj.), 75.1 (C_2, rot. maj.), 71.4 (C_2, rot. min.), 63.7 (C_4, rot. min.), 61.4 (C_4, rot. maj.), 53.0 (O*C*H_3, rot. min.), 52.6 (O*C*H_3, rot. maj.), 38.9 (*C*(CH_3)$_3$, rot. min.), 38.5 (*C*(CH_3)$_3$, rot. maj.), 32.8 (C_5, rot. maj.), 32.0 (C_5, rot. min.), 26.7 (C(*C*H_3)$_3$, rot. min.), 26.3 (C(*C*H_3)$_3$, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{10}H_{18}NO_3S$ 232.1002; found 232.0983

Synthesis of (1*R*,2*R*,4*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-1,3-thiazolidin-4-carboxylate 44b



44b

Hydrogen peroxide (2.70 mL, 26.2 mmol) was added slowly over a solution of **44a** (6.0 g, 26.0 mmol) in acetic acid (60 mL) under stirring. The reaction mixture was monitored by TLC analysis (EtOAc/hexane 50/50) and was stirring at room temperature for 24 h. The solvent was removed under reduced pressure and the reaction crude obtained was crystallized in diethyl ether to give **44b** (6.2 g, 25.1 mmol, 96%) as a white solid.

M.p.: 154-156 °C

$[\alpha]_D^{23}$: -99° (*c* 1.1; $CHCl_3$)

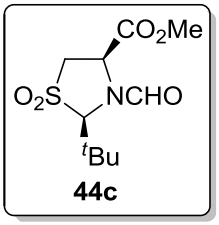
IR (KBr) v 1754, 1674, 1385, 1312, 1197, 1048, 1031 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.25)] δ 8.52 (s, 1H, C*H*O, rot. min.), 8.30 (s, 1H, C*H*O, rot. maj.), 5.37-5.26 (m, 2H, H_4, both rot.), 5.14 (d, *J* = 1.5 Hz, 1H, H_2, rot. min.), 4.56 (d, *J* = 1.4 Hz, 1H, H_2, rot. maj.), 3.83 (s, 3H, OCH_3, rot. min.), 3.78 (s, 3H, OCH_3, rot. maj.), 3.56-3.47 (m, 2H, H_5, both rot.), 3.34 (dd, *J* = 15.0, 8.9 Hz, 1H, H_{5cis}, rot. min.), 3.14 (dd, *J* = 14.6, 10.4 Hz, 1H, H_{5trans}, rot. maj.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.), 1.00 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.4 (*C*O_2Me, rot. min.), 170.0 (*C*O_2Me, rot. maj.), 165.1 (*C*HO, rot. min.), 163.7 (*C*HO, rot. maj.), 95.0 (C_2, rot. maj.), 92.2 (C_2, rot. min.), 61.0 (C_4, rot. min.), 59.2 (C_4, rot. maj.), 53.6 (O*C*H_3, rot. min.), 53.1 (O*C*H_3, rot. maj.), 52.0 (C_5, rot. maj.), 51.9 (C_5, rot. min.), 35.4 (*C*(CH_3)$_3$, rot. min.), 35.1 (*C*(CH_3)$_3$, rot. maj.), 27.7 (C(*C*H_3)$_3$, rot. min.), 27.3 (C(*C*H_3)$_3$, rot. maj.)

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{10}H_{17}NO_4SNa$ 270.0770; found 270.0756

Synthesis of (2*R*,4*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-1,3-thiazolidin-4-carboxylate 44c



44c

Over a solution of **44b** (489 mg, 2.12 mmol) in anhydrous dichloromethane (20 mL) under stirring and inert atmosphere at room temperature *m*-CPBA (70%, w/w) (1.15 g, 4.65 mmol) was added. After 8 h, an aqueous solution of $NaHCO_3$ 5% (30 mL) was added and the layers were separated. The aqueous phase was extracted with dichloromethane (3 x 30 mL). The combined organic layers were dried over magnesium sulfate anhydrous, filtered off and the solvent was removed under reduced pressure. The white solid obtained was purified by column chromatography (EtOAc/hexane 30/70) to give **44c** (500 mg, 1.92 mmol, 90%) as a white solid.

M.p.: 175-177 ºC

$[\alpha]_D^{23}$: -129º (*c* 1.0; $CHCl_3$)

IR (KBr) v 1758, 1688, 1359, 1249, 1199, 1121 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.34)] δ 8.38 (s, 1H, C*H*O, rot. min.), 8.31 (s, 1H, C*H*O, rot. maj.), 5.04 (t, *J* = 9.7, 1H, H_4, rot. maj.), 4.90 (t, *J* = 9.3, 1H, H_4, rot. min.), 4.86 (d, *J* = 1.4, 1H, H_2, rot. min.), 4.25 (d, *J* = 1.1, 1H, H_2, rot. maj.), 3.87 (s, 3H, OCH_3, rot. min.), 3.81 (s, 3H, OCH_3, rot. maj.), 3.69-3.61 (m, 2H, H_{5cis}, both rot.), 3.53 (dd, *J*= 14.2, 8.7, 1H, H_{5trans}, rot. min.), 3.33 (dd, *J* = 13.9, 10.1, 1H, H_{5trans}, rot. maj.), 1.21 (s, 9H, C(CH_3)$_3$, rot. maj.), 1.13 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 169.0 (*C*O_2Me, rot. min.), 168.3 (*C*O_2Me, rot. maj.), 164.7 (*C*HO, rot. min.), 163.8 (*C*HO, rot. maj.), 81.2 (C_2, rot. maj.), 77.6 (C_2, rot. min.), 54.0 (O*C*H_3, rot. min.), 53.9 (C_4, rot. min.), 53.5 (O*C*H_3, rot. maj.), 52.2 (C_4, rot. maj.), 48.9 (C_5, rot. maj.), 48.1 (C_5, rot. min.), 36.0 (*C*(CH_3)$_3$, rot. min.), 35.7 (*C*(CH_3)$_3$, rot. maj.), 26.5 (C(*C*H_3)$_3$, rot. min.), 26.1 (C(*C*H_3)$_3$, rot. maj.)

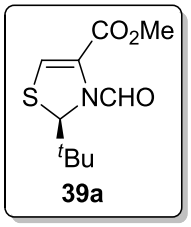
HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{10}H_{17}NO_5SNa$ 286.0720; found 286.0729

5.3. Synthesis of thiazolines

General procedure for the synthesis of 39a and 39b

Over a solution of **44a** or **44b** (1 eq.) in dichloromethane at 0 ºC DBU (1.8 eq.) and $CBrCl_3$ (1.3 eq.) were added. The reaction mixture was stirring at this temperature for 24 h. The reaction was monitored by TLC (EtOAc/hexane 50/50) until completion. Once the reaction finished an aqueous saturated solution of $NaHCO_3$ (same volume as dichloromethane) was added at 0 ºC and the reaction mixture was warmed to room temperature. The two layers were separated and the aqueous phase was extracted with dichloromethane (3 times). The combined organic layers were dried over magnesium sulfate anhydrous, filtered off and the solvent was removed under reduced pressure.

Synthesis of (2*R*)-Methyl 2-*tert*-butyl-3-formyl-2,3-dihydro-1,3-thiazol-4-carboxylate 39a[33]



39a

Following the general procedure, **44a** (4.70 g, 20.3 mmol) was dissolved in dichloromethane (40 mL) at 0 ºC and treated with DBU (5.47 mL, 36.6 mmol) and $CBrCl_3$ (2.60 mL, 26.4 mmol). The oily reaction crude was purified by column chromatography (EtOAc/hexane 10/90 to 30/70) to give **39a** (3.80 g, 16.6 mmol, 82%) as colorless oil.

$[\alpha]_D^{24}$: +175º (*c* 0.6; $CHCl_3$)

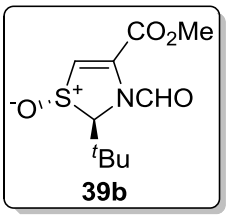
IR (neat) v 1717, 1653, 1578, 1439, 1288, 1243 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.81 (s, 1H, C*H*O), 7.05 (s, 1H, H_5), 5.79 (s, 1H, H_2), 3.79 (s, 3H, OCH_3), 0.92 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 164.0 (*C*HO), 159.3 (*C*O_2Me), 128.7 (C_5), 127.6 (C_4), 74.4 (C_2), 52.5 (O*C*H_3), 39.3 (*C*(CH_3)$_3$), 24.6 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{10}H_{15}NO_3SNa$ 252.0625; found 252.0647

Synthesis of (1*R*,2*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3-dihydro-1,3-thiazol-4-carboxylate 39b



39b

Following the general procedure, **44b** (12.5 g, 50.6 mmol) was dissolved in dichloromethane (150 mL) at 0 °C and treated with DBU (13.6 mL, 91.1 mmol) and $CBrCl_3$ (6.49 mL, 65.8 mmol). The obtained red oil was purified by column chromatography (EtOAc/hexane 50/50) to give **39b** (10.3 g, 42.0 mmol, 83%) as a brown solid.

M.p.: 75-77 °C

$[\alpha]_D^{22}$: -79° (*c* 1.1; $CHCl_3$)

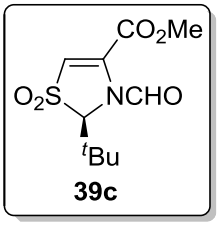
IR (KBr) ν 1737, 1698, 1591, 1368, 1245, 1200, 1050 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.97 (s, 1H, C*H*O), 6.95 (s, 1H, H_5), 4.98 (s, 1H, H_2), 3.85 (s, 3H, OCH_3), 0.92 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 162.0 (*C*HO), 159.8 (*C*O_2Me), 141.6 (C_4), 120.5 (C_5), 88.8 (C_2), 53.6 (O*C*H_3), 36.5 (*C*(CH_3)$_3$), 26.4 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{10}H_{15}NO_4SNa$ 268.0614; found 268.0601

Synthesis of (2*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3-dihydro-1,3-thiazol-4-carboxylate 39c



39c

Over a solution of **39a** or **39b** (1 eq.) in anhydrous dichloromethane under stirring and inert atmosphere at room temperature was added *m*-CPBA (70%, w/w) (2.2 eq. from **39a** or 1.2 eq. from **39b**), and the reaction mixture was stirring until completion. Then, an aqueous solution of $NaHCO_3$ 5% was added and the layers were separated. The aqueous phase was extracted with dichloromethane (3 times). The synthesis of **39c** was carried out from **39a** (0.17 g, 0.73 mmol) in anhydrous dichloromethane (5 mL) for 48 h. The white solid obtained after the treatment was purified by column chromatography (EtOAc/hexane 40/60) to give **39c** (0.16 g, 0.63 mmol, 83%) as a white solid. Synthesis of **39c** was also carried out from **39b** (2.16 g, 8.82 mmol) in anhydrous dichloromethane (15 mL) for 24 h. The white solid obtained after the treatment was purified by column chromatography (EtOAc/hexane 40/60) to give **39c** (2.06 g, 7.89 mmol, 88%) as a white solid.

M.p.: 127-129 ºC

$[\alpha]_D^{22}$: -77º (*c* 1.0, $CHCl_3$)

IR (KBr) v 1740, 1706, 1616, 1439, 1361, 1316, 1283, 1232, 1175 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.79 (s, 1H, C*H*O), 6.95 (s, 1H, H_5), 4.99 (s, 1H, H_2), 3.97 (s, 3H, OCH_3), 1.14 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 160.4 (*C*HO), 159.4 (*C*O_2Me), 139.7 (C_4), 122.1 (C_5), 81.5 (C_2), 54.3 (O*C*H_3), 38.0 (*C*$(CH_3)_3$), 26.0 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{10}H_{15}NO_5SNa$ 284.0563; found 284.0571

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Chapter III

Synthesis of cysteine analogues containing a ciclopropane ring between α and β positions

III. Synthesis of cysteine analogues containing a ciclopropane ring between α and β positions

1. INTRODUCTION

The simplest cyclopropane amino acid, 1-aminocyclopropanecarboxylic acid (ACC) was firstly synthetized in 1922[1] and since then the development of efficient synthetic routes to access to cyclopropane amino acids have been a challenge for organic chemists. The importance of ACC lies in its properties in herbicidal activity and its engagement in plant growth.[2,3] But, also ACC derivatives such as coronamic acid **45**, norcoronamic acid **46**, 2,3 methanovaline **47** or 2,3-methanoproline **48** among others, have been applied in biochemical studies for the understanding of the senescence of flowers (*Figure 5*). Cyclopropane amino acids,[4–6] are well known to induce important changes in the backbone torsion angles, thus stabilizing the secondary structure of peptides and highlights the effect of side-residues orientation on peptide secondary structure.

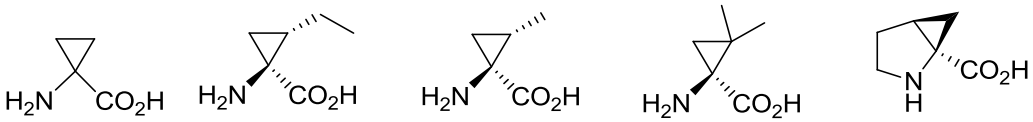
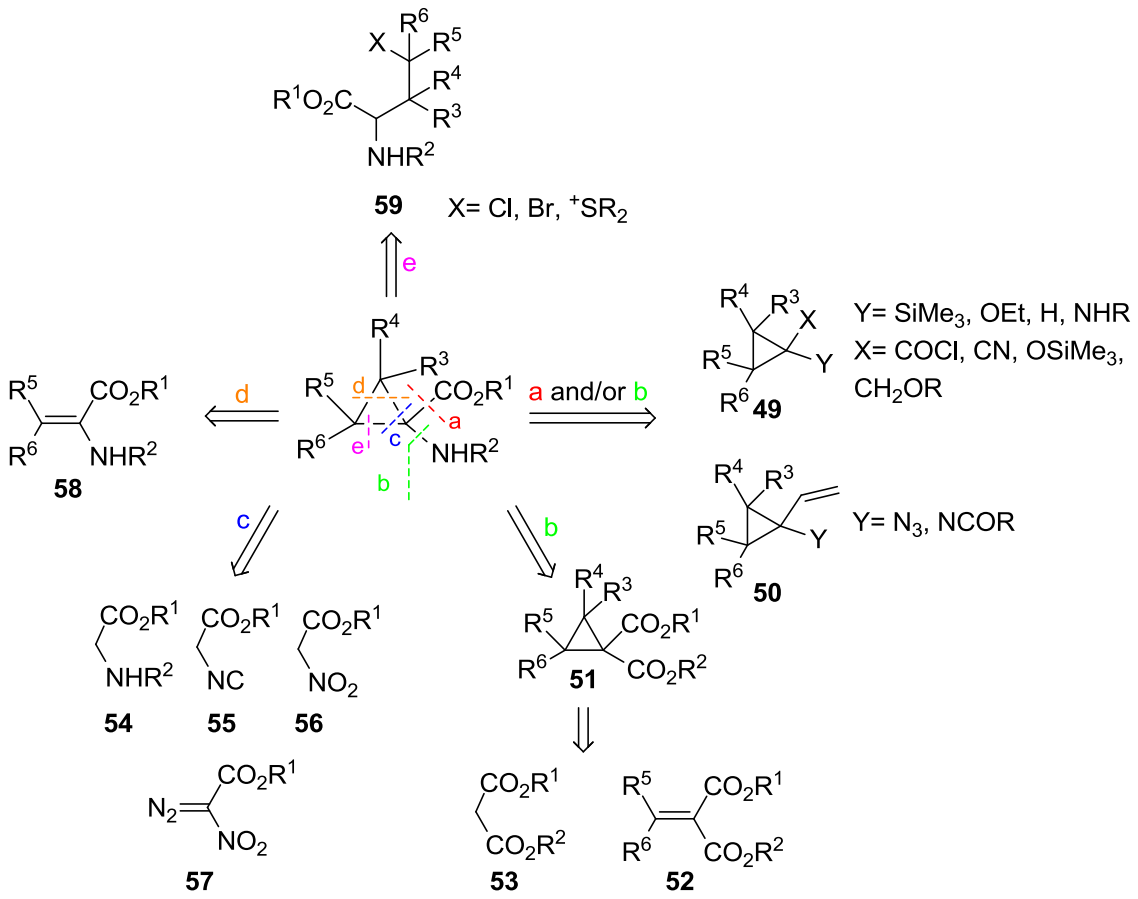


Figure 5. ACC and some ACC derivatives

Strategies to obtain ACC and ACC derivatives could be gathered in different groups based on the bond formed in the last step of the synthetic methodology (*Scheme 13*).[7]



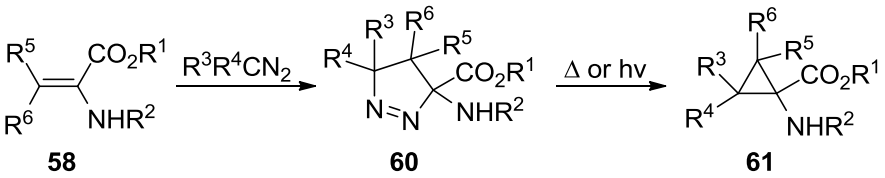
Scheme 13. Retrosynthetic analysis of the most commonly routes to access ACC

On this basis, disconnections **a** and **b** involve the bond formation between Cα and amine and/or carboxylic functions using as starting materials substituted cyclopropanes **49** or **50** as synthetic equivalents of cyclopropanone.[8] Another methodology regarding the disconnection **b** involves the transformation of a carboxylic moiety into amine function of cyclopropanes **51** through a Curtius or Hofmann rearrangement. The cyclopropane derivative **51** could be obtained either from the addition of dielectrophiles to malonates **53**[9] or by a 1,3-dipolar cycloaddition from methylenemalonates **52**.[10] Disconnection **c** entails the formation of two bonds through a cyclodialkylation by the addition of 1,2-dihaloalkanes to glycine equivalents **54**[8e,11] or isocyanoacetates **55**,[12] or by a metal-mediated cyclopropanation of alkenes with α-nitrodiazoacetates **57**[13] or methyl nitroacetates **56**, within the formation of a iodonium intermediate.[13e,14] On the other hand, disconnection **d** implies cycloaddition reactions with diazoalkanes or addition of ylides to dehydroamino acids **58**.[10a,15] Finally, the disconnection **e** implies the bond forming between Cα and Cβ through an intramolecular ciclyzation with a good leaving group at Cβ **59**.[16]

Due to the fact that our starting materials, thiazolines **39a**-**c**, are dehydroalanine synthetic equivalents, only the routes involving the use of dehydroamino acids as starting materials will be disclosed hereunder.

After a bibliographic revision for the synthesis of ACC derivatives, dehydroalanine amino acids have demonstrated to be an important template for the preparation of this cyclic amino acids.[7,17]

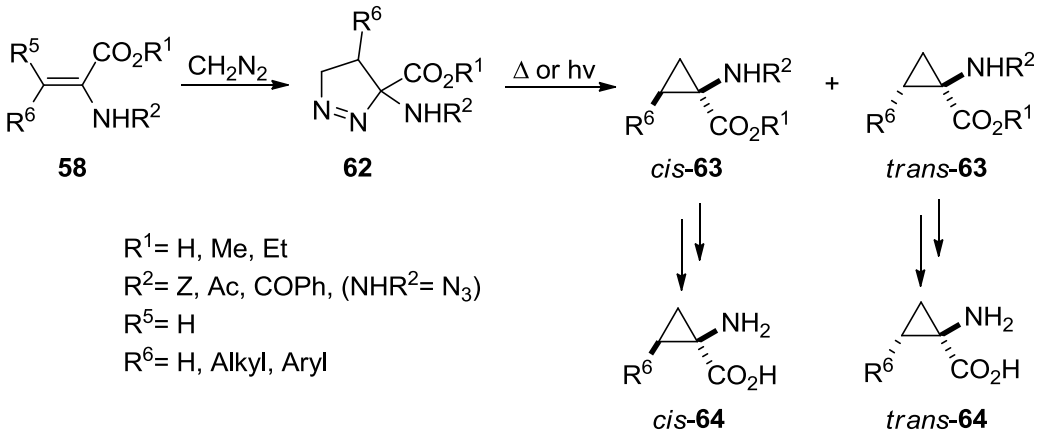
The most common strategy to obtain cyclopropane amino acids from dehydroalanine is the 1,3-dipolar cycloaddition between diazoalkanes and substituted 2-aminoacrylates **58**. In a first step of the synthesis a Δ^1-pyrazoline intermediate **60** is formed, which spontaneously or inductively evolves to give the cyclopropane amino acid **61** (*Scheme 14*).



R^1= Alkyl. 4-$O_2NC_6H_4$, } -N=C(Ph)-
R^2= Boc, Z, Ac, COPh, }
R^3= Ph, Alkyl, CO_2Me, CO_2Et
R^4= H, Me, Ph
R^5= H,
R^6= H, Aryl, SR, OR, Cl, } -$(CH_2)_n$-

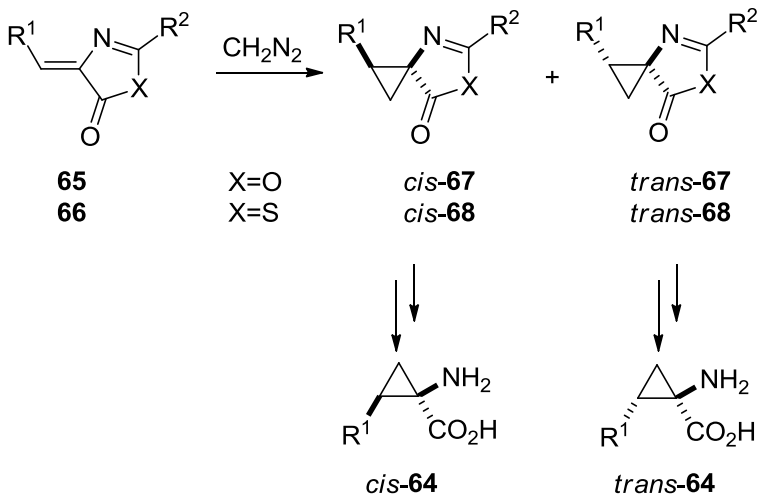
Scheme 14

In this sense, the addition of diazomethane to 2-aminoacrylic acid derivatives substituted at Cβ **58**, led to the formation of corresponding Δ^1-pyrazolines **62** intermediates, which could be isolated, in most cases. Thermal or photochemical induced extrusion of nitrogen led to the formation of the protected amino acid derivatives *cis*- and *trans*-**63**. The protecting group removal afforded the free amino acids *cis*- and *trans*-**64**[18] (*Scheme 15*).



Scheme 15

Oxazolone **65** or thiazolone **66**, have also been employed to carry out the 1,3-dipolar cycoladdition with diazoalkanes. The addition of diazomethane to the exocyclic double bond of these heterocycles provided in one step the diastereomeric spirocyclopropanated compounds **67** and **68**. The spirocycles obtained were transformed into the corresponding free amino acids *cis*- and *trans*-**64** (*Scheme 16*). The first reported addition reaction of diazomethane to oxazolone derivatives was in 1937,[19] and allowed to obtain 2-substituted oxazolinones *cis*- and *trans*-**67**. Since then, several 2-aryl- (*Table 1*, entries 2-14),[20]-heteroaryl- (entry 1),[18k,21]-methyl- (entries 15-16),[20c),20e)] halo-[22], acyloxy- (entries 17-18)[22a] and thio- (entries 19-22)[23] substituted spirocyclopropanated oxazolones *cis*- and *trans*-**67** have been prepared, and from them the corresponding 1-aminocyclopropanecarboxylic acids derivatives *cis*- and *trans*-**64**. It is important to note that both isomers *cis*- and *trans*-**64** are obtained from one diastereoisomer *Z*-**65** (*Table 1*) due to the stereochemical information is often lost during the cyclopropanation formation, particularly during the nitrogen extrusion. By similarity, alkylidenethiazolones *Z*-**66** led exclusively to spirocyclopropanated thiazolinones *cis*-**68**. Thus, reactions proceeded without loss of stereochemical information[24] (*Table 2*).



Scheme 16

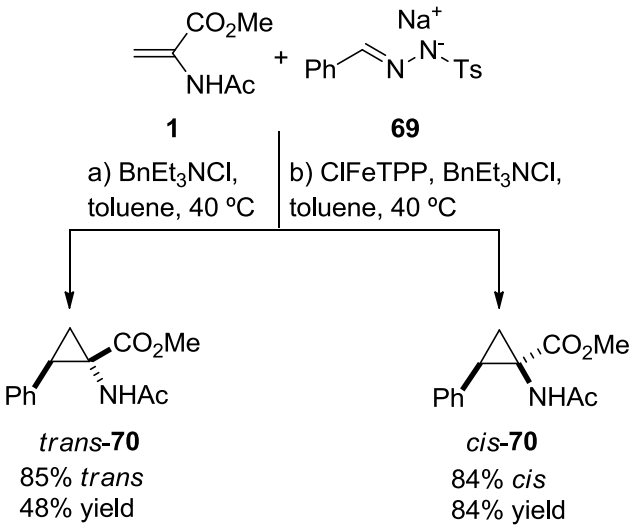
Table 1. Selected examples of the reactivity and selectivity for *Z*-oxazolones **65**

Entry	R^1	R^2	Yield (%)	*cis*/*trans* ratio	ref
1	3-(1-acetylindolyl)	Ph	46	*cis*	21a
2	Ph	Ph	70	79/21	20f
3	Ph	Ph	42	21/79	20d
4	Ph	Ph	70	21/79	20d
5	Ph	Ph	36	22/78	20d
6	4-MeC_6H_4	Ph	60	*cis*	20c
7	4-$MeOC_6H_4$	Ph	53	*cis*	20j
8	4-$MeOC_6H_4$	Ph	55	*cis*	20c
9	4-ClC_6H_4	Ph	50	*cis*	20c
10	4-$AcOC_6H_4$	Ph	38	*cis*	20j
11	4-AcO-3,5-$I_2C_6H_2$	Ph	50	*cis*	20j
12	4-MeO-3,5-$I_2C_6H_2$	Ph	55	*cis*	20j
13	4-(4-AcOPhO)-3,5-$I_2C_6H_2$	Ph	29	*cis*	20j
14	4-(4-AcOPhO)-3,5-$I_2C_6H_2$	Ph	32	*cis*	20j
15	Me	Ph	60	22/78	20f
16	Me	Ph	75	92/8	20c
17	OAc	Ph	76	55/45	22a
18	OPiv	Ph	73	41/59	22a
19	SMe	Ph	70	25/75	23
20	SPh	Ph	73	25/75	23
21	SBn	Ph	54	25/75	23
22	$SCPh_3$	Ph	67	25/75	23

Table 2. Selected examples of the reactivity and selectivity for *Z*-thiazolones **66**

Entry	R^1	R^2	Yield (%)	*cis*/*trans* ratio	ref
1	Ph	SBn	45	*cis*	[24b]
2	4-MeC_6H_4	SBn	45	*cis*	[24b]
3	3-$MeOC_6H_4$	SBn	45	*cis*	[24b]
4	4-$MeOC_6H_4$	SBn	45	*cis*	[24b]
5	3-ClC_6H_4	SBn	30	*cis*	[24b]
6	4-ClC_6H_4	SBn	35	*cis*	[24b]

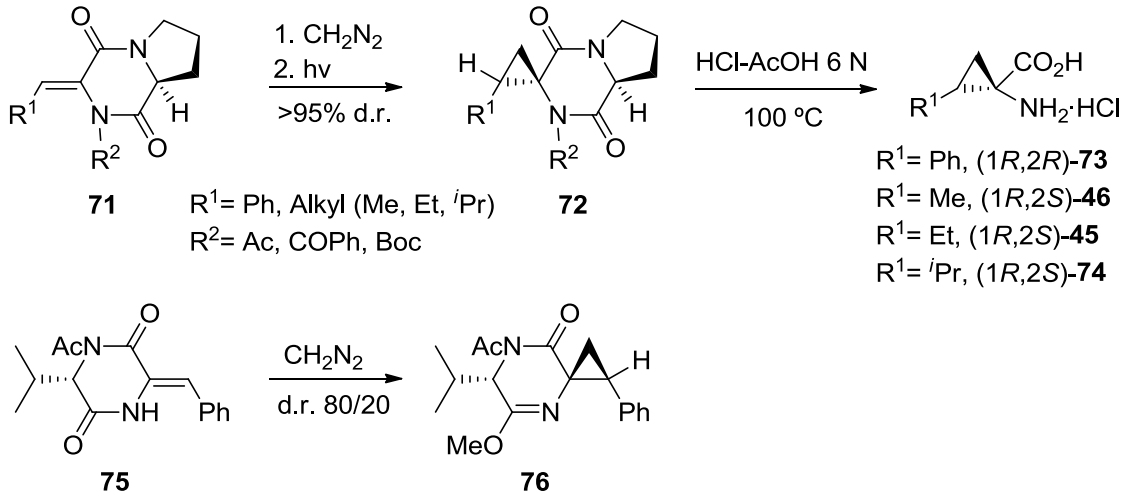
Besides diazomethane, other diazoalkanes have been employed for the synthesis of cyclopropane amino acids derivatives. Thus, the use of diazoethane,[20k,25,26] 1-diazopropane,[25] 2-diazopropane,[26] diazoisobutane,[25,26] phenyldiazomethane,[25,27] diphenyldiazomethane,[18k,28] ethyl diazoacetate[29] and 2,2,2-trifluorodiazoethane[30] in the 1,3-dipolar cycloaddition reaction with 2-aminoacrylic acid derivatives has also been reported. Moreover, tosylhydrazone salts have been employed as precursors of aryl, heteroaryl and vinyl diazocompounds, generated *in situ*, for the preparation of substituted cyclopropane amino acids.[15c,29a,31] With this regard, Adams *et al*.[29a] carried out the diastereoselective synthesis of both *cis* and *trans* isomers of aryl substituted cyclopropane amino acids by changing the reaction conditions. Thus, the reaction of **1** and **69** in the presence of the phase transfer catalyst benzyltriethylammonium chloride gave the cyclopropane amino acid in good yield with a diastereomeric ratio strongly in favour of the *trans*-**70** isomer. On the other side, the addition of *meso*-tetraphenylporphyrin iron (III) chloride (ClFeTPP) to the reaction switched the diastereoselectivity in favour of the *cis*-**70** isomer and also improved the reaction yield (*Scheme 17*).



Scheme 17

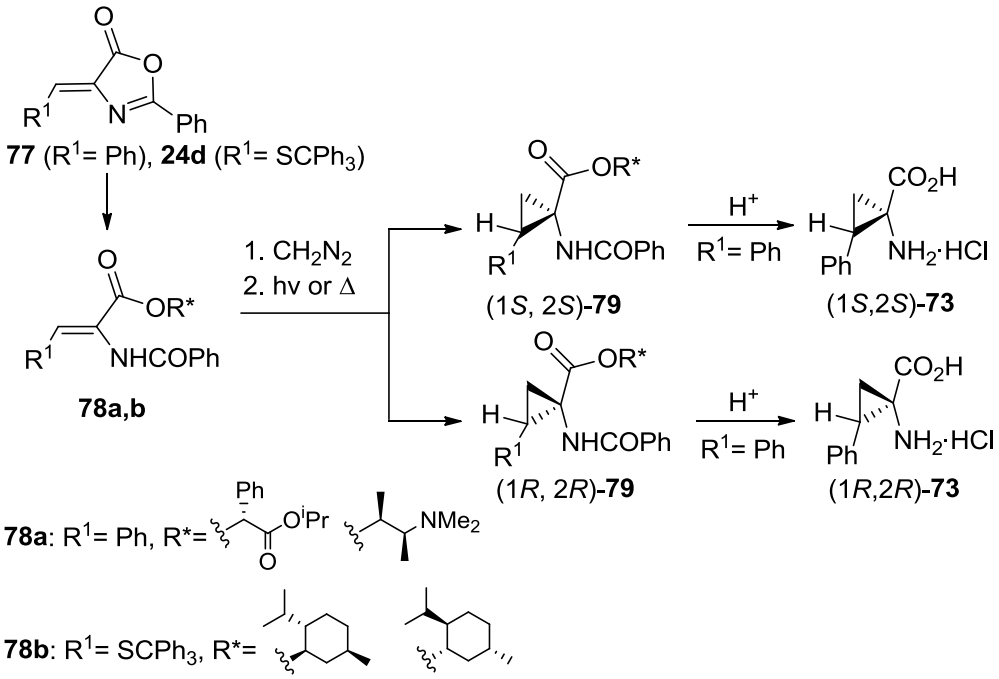
Diastereoselective cyclopropanations of dehydroalanines with diazoalkanes for the synthesis of chiral 1-aminocyclopropanecarboxylic acid derivatives have also been reported. In general, the induction of diastereoselectivity has been achieved through the use of chiral dipolarophiles.

In this context, diketopiperazines **71**, obtained from the corresponding alkyl or 5(4*H*)-benzylideneoxazolones and *L*-proline, have shown to be a very valuable synthetic tool for the asymmetric synthesis of cyclopropane amino acids. Thus, chiral diketopiperazines **71**[32] were subjected to react with diazomethane, obtaining the corresponding Δ^1-pyrazolines that after a photolysis reaction led to the spirocyclopropanated derivatives **72** as single diastereoisomers. These latter were hydrolyzed to afford the corresponding enantiopure cyclopropane amino acids (1*R*,2*R*)-**73** and (1*R*,2*S*)-**45**, (1*R*,2*S*)-**46** and (1*R*,2*S*)-**74**. Similarly, diketopiperazine **75**[33] reacted with diazomethane, obtaining the corresponding cyclopropane derivative **76** although in moderate yield and diastereoselectivity (*Scheme 18*).



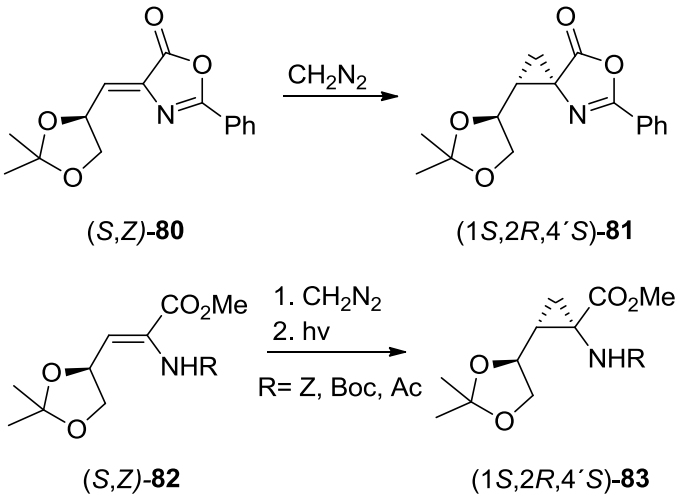
Scheme 18

The ring opening of oxazolone **77**, by the treatment with (*R*)-isopropyl mandelate,[32a] and (-)-*N*-methylephedrine,[32c] and oxazolone **24d**, with (+)- or (-)-menthol,[34] afforded the corresponding β-substituted 2-aminoacrylates **78a,b** which after addition of diazomethane and a subsequent nitrogen extrusion of the intermediate Δ^1-pyrazolines, led to the cyclopropane derivatives **79**. Finally, the chiral auxiliary in the cyclopropane derivatives **79**, substituted with a phenyl group at the β-position, was removed by an acidic hydrolysis to give 2-phenyl-1-aminocyclopropanecarboxylic acids (1*S*,2*S*)- and (1*R*,2*R*)-**73** (*Scheme 19*).



Scheme 19

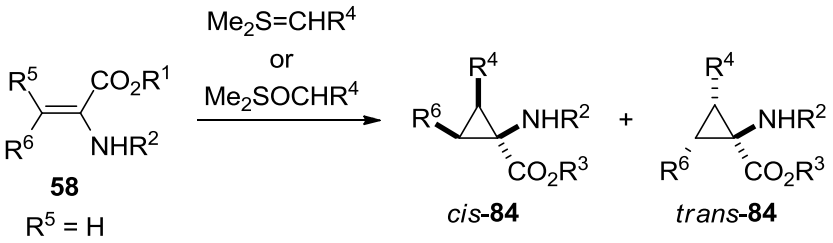
Another approach to chiral 2-substituted 2,3-methanoamino acids started employing the chiral *Z*-oxazolone **80**[35] and the chiral *Z* α-(acylamino)acrylate **82**,[36] both derived from 1,2-*O*-isopropylidene-*D*-glyceraldehyde. Under optimized conditions, the cyclopropanation of *Z*-oxazolone **80** gave (1*S*,2*R*,4´*S*)-**81** as major isomer. On the other hand, cyclopropanation of *Z*-acrylate **82** proceeded completely selective to the cyclopropane adduct (1*S*,2*R*,4´*S*)-**83** (*Scheme 20*). The transformation of the chiral 1,3-dioxolane group allowed to obtain several ACC derivatives.[35a,37]



Scheme 20

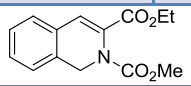
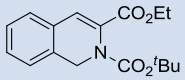
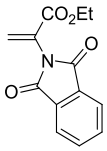
The addition of ylides to dehydroamino acids is also another valuable organic reaction to prepare substituted cyclopropane amino acids. The most commonly ylides employed are sulfonium and oxosulfonium ylides but the use of iodonium and phosphonium ylides have also been reported.

The addition of sulfonium[15e,38] or sulfoxonium[15j,39] ylides to dehydroamino acids such as **58** provided 1-aminocyclopropanecarboxylic acid derivatives *cis*- and *trans*-**84** in moderate to high yields with moderate to high diastereomeric ratios (*Scheme 21, Table 3*).



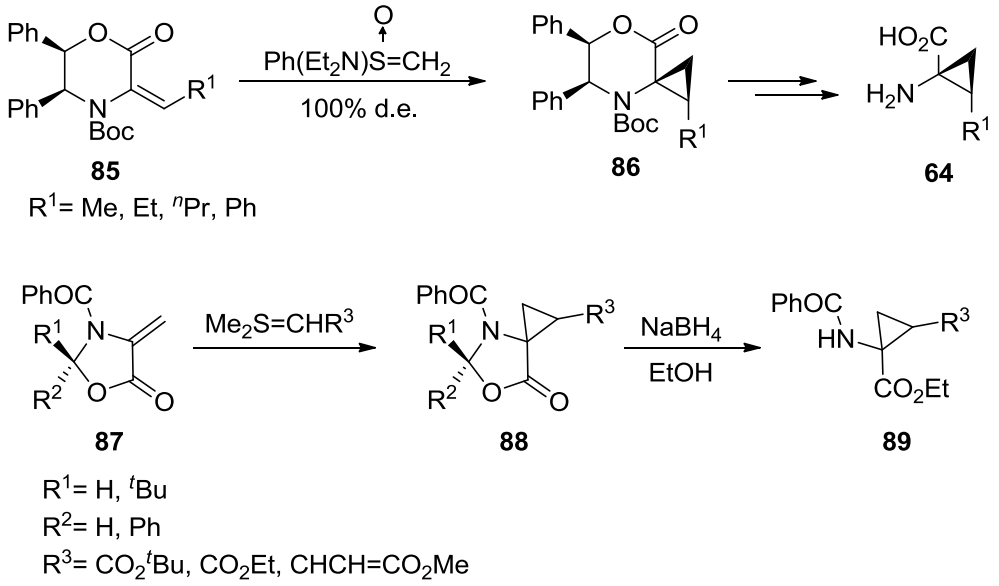
Scheme 21

Table 3. Selected examples for Michael addition of sulfonium or sulfoxonium ylides to *Z*-dehydroalanine equivalents **58**

Entry	R^6	R^1	R^2	ylide		Yield(%)/ *cis*:*trans* ratio	ref
				Me_2SCHR^4	Me_2SOCHR^4		
1	3-(1-acetylindolyl)	=C(Ph)-		COPh	-	49/*cis*	[38b]
2	Ph	=C(Ph)-		COPh	-	85/7:93	[38b]
3	4-AcOPh	=C(Ph)-		COPh	-	58/38:63	[38b]
4	PhCH=CH	=C(Ph)-		COPh	-	49/*cis*	[38b]
5	2-furyl	=C(Ph)-		COPh	-	57/8:92	[38b]
6	4-MeC_6H_4	Et	N≡C	-	H	52/50:50	[39b]
7				-	H	80/*cis*	[39a]
8				-	H	81/*cis*	[39a]
9				N^iPr_2	-	98/99:1	[15e]
10				CO_2Et	-	92/99:1	[15e]
11				COPh	-	96/97:3	[15e]
12				Ph	-	95/90:10	[15e]
13				*o*-CH_3Ph	-	95/99:1	[15e]
14				*p*-CH_3OPh	-	67/90:10	[15e]
15				*p*-NO_2Ph	-	71/99:1	[15e]

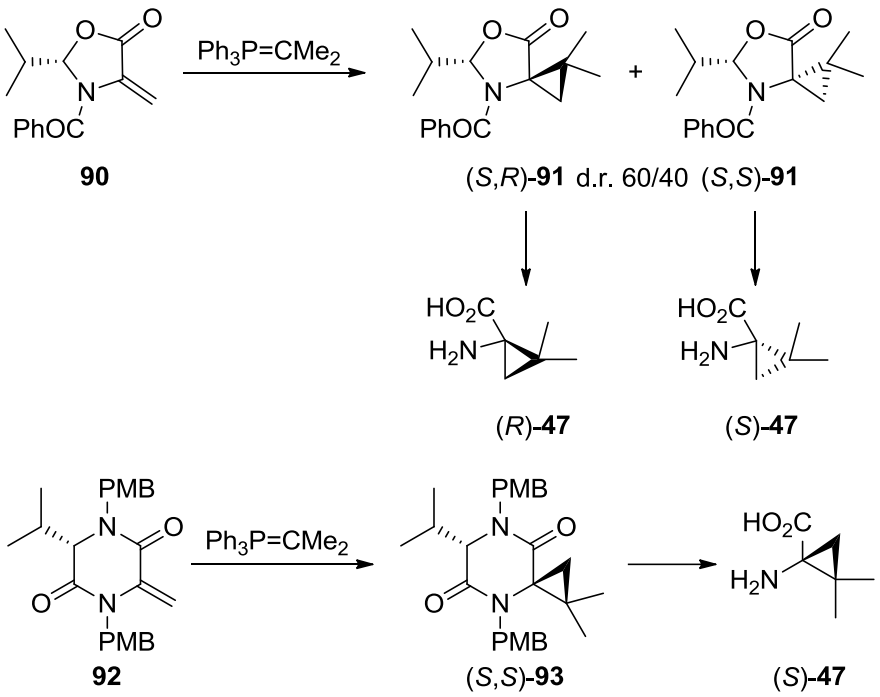
On the other hand, sulfoxonium ylides[40] have been more employed than sulfonium ylides[41] for the asymmetric synthesis of cyclopropane amino acids. Thus,

the cyclopropanation of **85** with dimethylsulfoxonium methylide resulted in the formation of the two corresponding diastereoisomers. Instead, the use of [(diethylamino)phenyl]oxosulfonium ylide allowed to obtain diastereoselectively the protected amino acids **86** in high yields which was easily converted to the corresponding free amino acids **64**.[40j,40l] Meanwhile, chiral methyleneoxazolidinones **87** were allowed to react with (dimethylsulfanylidene)acetates or butenoates giving diastereomeric mixtures of the corresponding spirocyclopropanes **88**, that were subjected to oxazolidinone ring opening to afford the protected cyclopropane amino acid derivatives **89** (*Scheme 22*).[41]



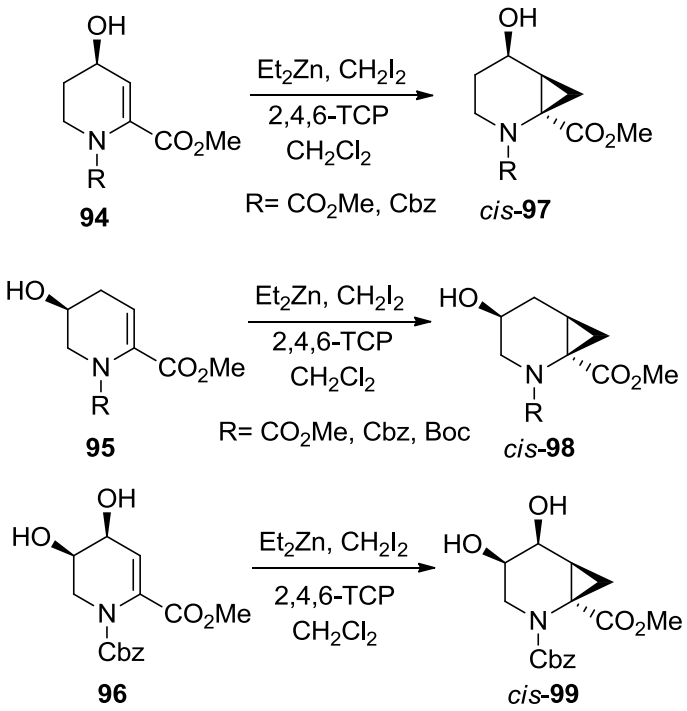
Scheme 22

Besides, the use of isopropylidenetriphenylphosphorane as ylide has been applied for the asymmetric cyclopropanation of the chiral α,β-dehydroamino acid derivatives **90**[42] and **92**.[43] While cyclopropanation reaction of **90** led to a mixture of diastereoisomers (*S*,*R*)- and (*S*,*S*)-**91** in a ratio 60/40, the cyclopropanation reaction of **92** led exclusively to (*S*,*S*)-**93**. Subsequent transformations of the obtained spirocyclopropanes (*S*,*S*)-**91** and (*S*,*S*)-**93** led to the corresponding methanovalines (*R*) and (*S*)-**47** (*Scheme 23*).



Scheme 23

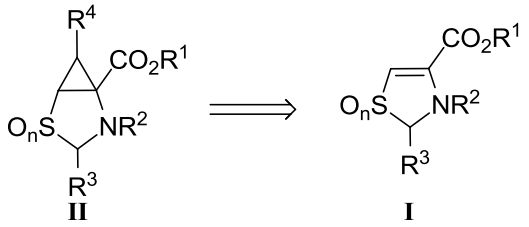
In spite of Simmons-Smith cyclopropanation[44] is a widely used method to form cyclopropanes from alkenes,[45] the use of α,β-dehydroamino acids in this kind of cycloaddition has been scarcely developed. Within this context, Occhiato *et al*.[46] described the synthesis of bicyclic cyclopropane amino acid derivatives **97-99** by the addition of CH_2I_2 under modified Simmons-Smith conditions (Charette´s carbenoid) to 4-hydroxy, 5-hydroxy or 4,5-dihydroxy-tetrahydropyridine derivatives **94-96**, respectively (*Scheme 24*).


OH
Et2Zn, CH2I2
2,4,6-TCP
CH2Cl2
CO2Me
N
R
R= CO2Me, Cbz
94
cis-97
HO
R= CO2Me, Cbz, Boc
95
cis-98
Cbz
96
cis-99
2,4,6-TCP= 2,4,6-trichlorophenol

Scheme 24

2. OBJECTIVES

Taking into account the abovementioned antecedents, the objectives proposed for this chapter are the study and evaluation of the 1,3-dipolar cycloaddition between homochiral thiazolines **I** as dipolarophiles and diazoalkanes as dipoles to obtain the bicylic thiazolidines **II**



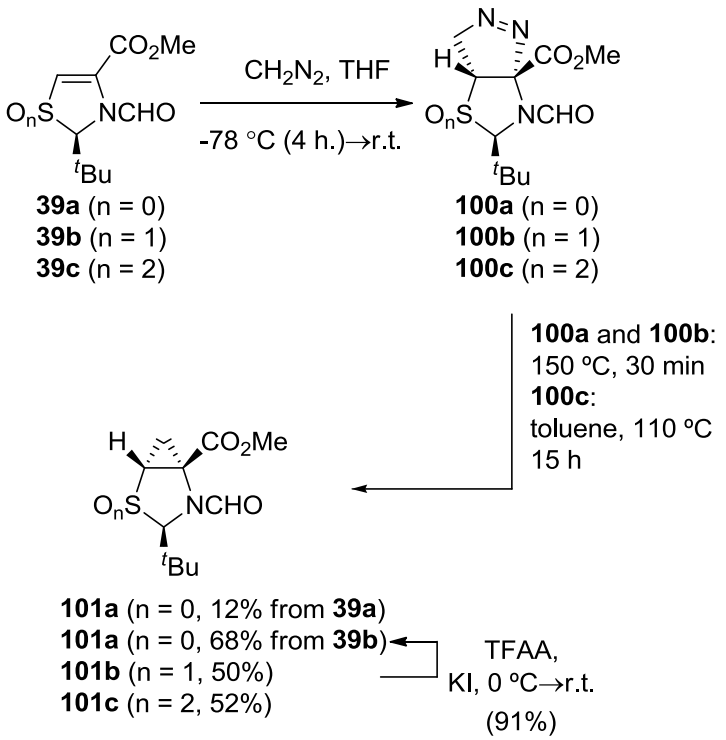
The differences of reactivity and regio- and diastereoselectivity of the different pairs of dipole/thiazoline will be discussed.

Moreover, computational studies will be discussed to deepen in the understanding of the reactivity and stereochemical course of these reactions.

3. RESULTS AND DISCUSSION

3.1. Synthesis of cyclopropane thiazolidines

Firstly, it was studied the reactivity, regio- and diastereoselectivity of the 1,3-dipolar cycloaddition reaction between thiazolines **39a-c** and diazomethane. Thus, an ethereal solution of diazomethane was added over a solution of the thiazoline **39a** in THF at -78 ºC and each day for 7 days was reloaded with additional freshly prepared diazomethane (5 eq.). The reaction mixture was stirred for 7 days at room temperature, monitored by TLC, affording Δ^1-pyrazoline **100a** with low yield. Further thermal nitrogen elimination at 150 ºC gave the bicyclic thiazolidine **101a** in 12% overall yield. Then, we carried out the 1,3-dipolar cycloaddition with thiazolines **39b** and **39c**, with an increased electrophilic character of the double bond respect to the thiazoline **39a**, due to the additional electron withdrawing effect of the sulfinyl and sulfonyl groups, respectively. The reaction of **39b** and **39c** with diazomethane at -78 ºC in THF afforded Δ^1-pyrazolines **100b** and **100c** with complete diastereoselectivity, a single cycloaddition product could be observed by ^{1}H NMR. Next, nitrogen extrusion of the obtained Δ^1-pyrazolines was mandatory to achieve the cyclopropane derivatives. For this purpose, thermal nitrogen elimination at 150 ºC starting from Δ^1-pyrazoline **100b** and from **100c** at 110 ºC afforded bicyclic thiazolidines **101b** and **101c**, respectively, in good yields.[34,47] In order to access to the target thiazolidine **101a**, we carried out the reduction of the sulfinyl group in **101b**. Between the different methods reported in the literature, the Baldwin *et al*.[48] protocol was selected because of the similarity of their azabicyclic compounds with ours. Thus, trifluoroacetic anhydride and KI were added sequentially to a solution of **101b** in acetone at 0 ºC. After 5 h at room temperature the bicyclic thiazolidine **101a** was obtained in 91% yield. The synthesis of **101a** (66% overall yield) could be carried out from **39b**, in three consecutive steps without intermediate **101b** purification (*Scheme 25*).



***Scheme 25*.** Synthesis of bicycles **101a-c**

Structural assignments for the compounds **101a**-**c** have been made on the basis of NOESY experiments. It was observed n.O.e between the protons of the *tert*-butyl group and both H_5 and the methyl group of methyl ester functionality. Thus, the (1*R*,3*R*,5*R*) configuration was assigned for **101a** and **101c** and (1*R*,3*R*,4*R*,5*R*) configuration for **101b**, respectively (*Figure 6)*. It is worth to note the presence of two sets of signals corresponding to both rotamers in almost all the ^{1}H NMR experiments of these bicyclic compounds, this fact is due to the pseudo-rotation of the formamide bond.

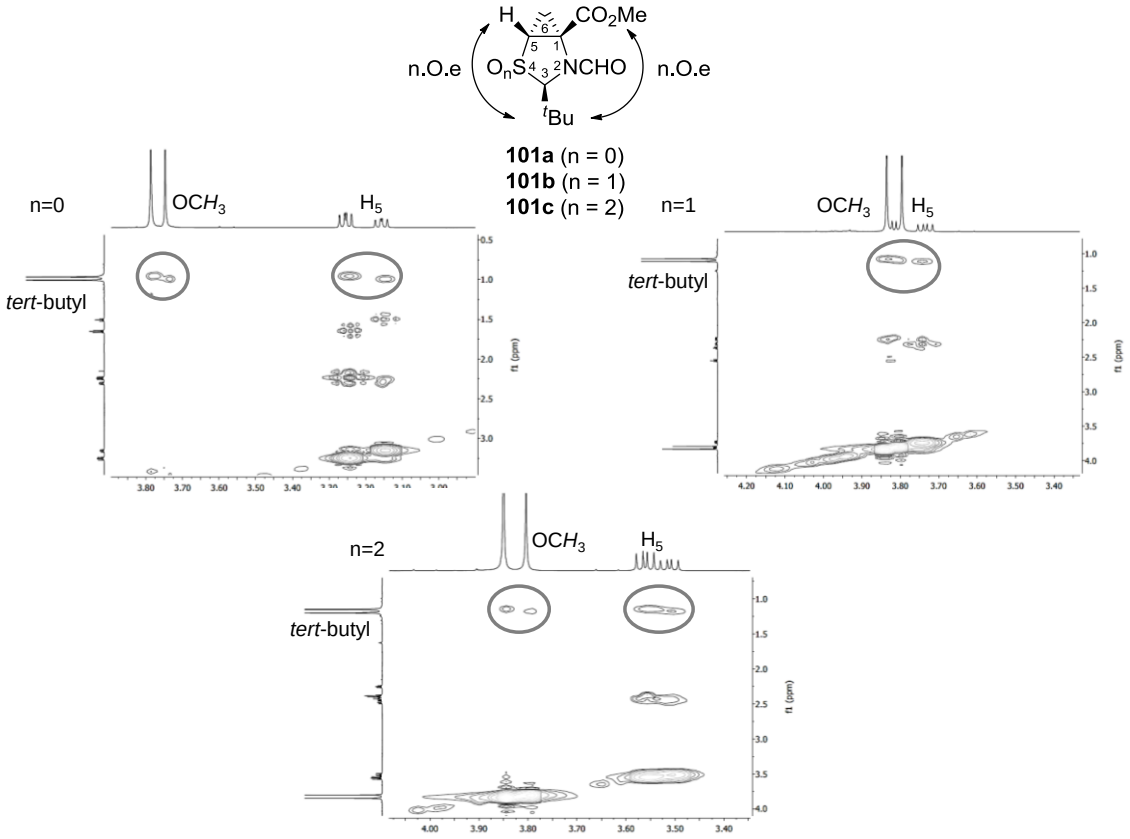


Figure 6. NOESY experiments of the bicyclic thiazolidines **101a-c**

An exhaustively analysis of the ^{1}H NMR of the thiazolidines **101a-c** reveled some features that are worth to note. The multiplicity found for the proton signal at C6, *cis* with respect to the proton at C5 in thiazolidines **101b** and **101c**, is a doublet of doublet of doublets with coupling constants of 9.0, 6.5 and 1.0 Hz. The smallest one is the coupling constant with the proton at C3. In addition, the proton signals at C3 appear as a doublet with a coupling constant of 0.7 Hz. Therefore, ^{1}H NMR experiments of homonuclear decoupling were performed radiating the proton signal at C3, and it was found that there was 5 bonds long range coupling in a zig-zag arrangement with the proton at C6. After an exhaustive review of the literature examples of these uncommon couplings were found[49] (*Figure 7*).

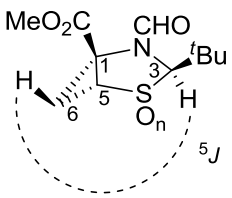


Figure 7

Besides, a comparison of the ^{1}H NMR spectra of **101a-c** revealed that the chemical shift of the H6 orientated *trans* to H5 is directly affected by the oxygen

bonded to the sulfur atom. In this sense, the chemical shift of proton H6 in thiazolidines **101b,c**, having sulfinyl or sulfonyl moieties, appeared in a range between 2.5 and 2.2 ppm, respectively, whereas for thiazolidine **101a**, bearing a sulfanyl moiety, the chemical shift was around 1.5 ppm (*Figure 8*). This behavior could be explained by the deshielding effect of the oxygen over the proton that is oriented in its same face.

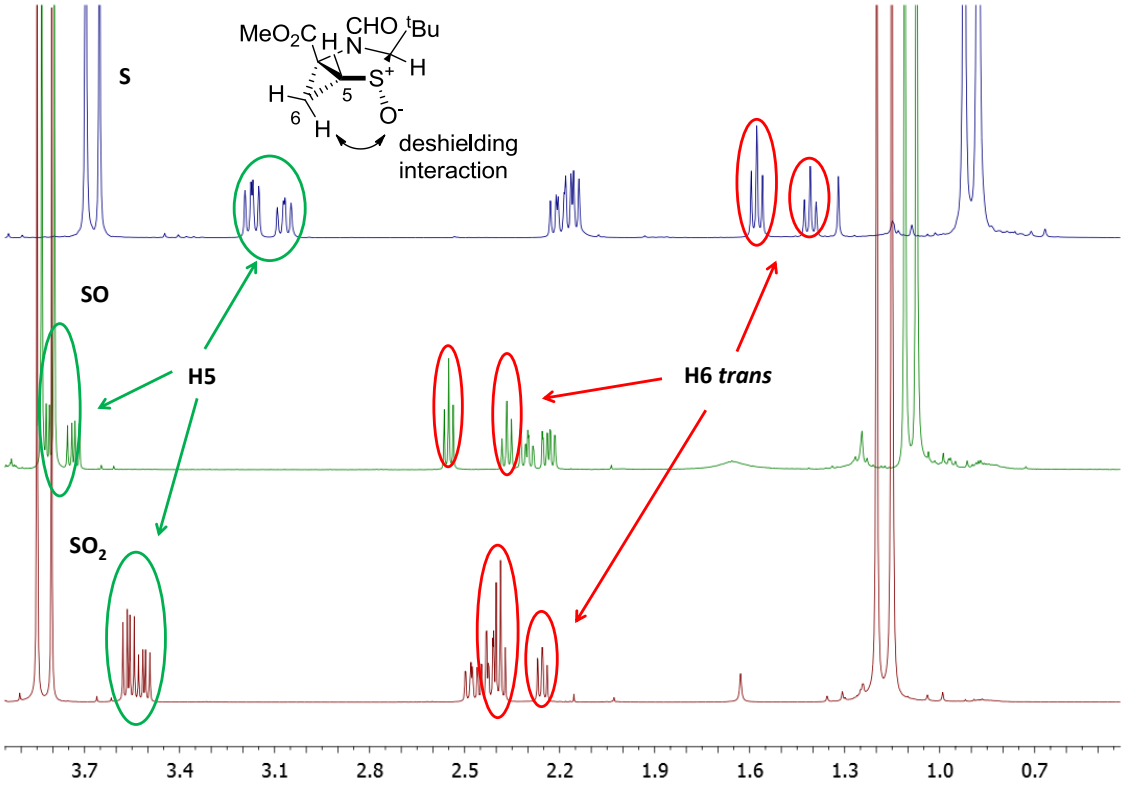
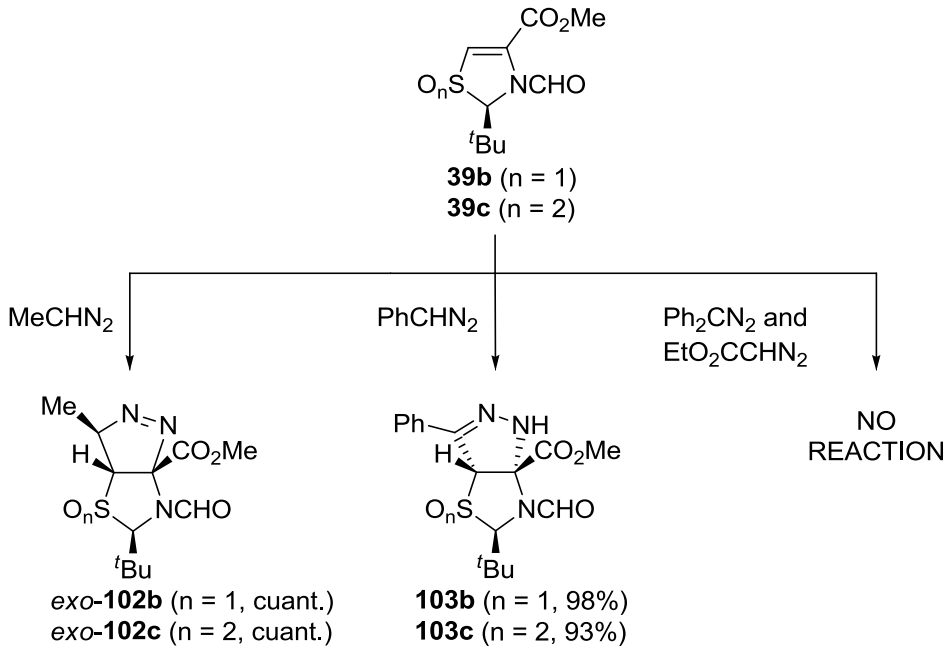


Figure 8. Proton spectra comparison for bicyclic thiazolidines **101a-c**

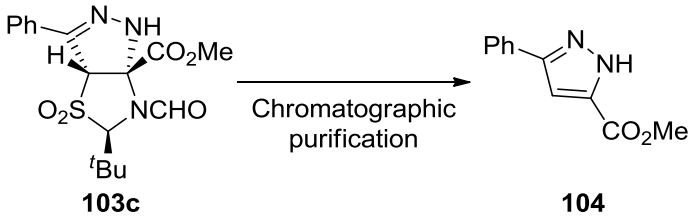
3.2. Synthesis of substituted cyclopropane thiazolidines

In addition of diazomethane, other diazoalkanes such as, diazoethane, phenyldiazomethane, diphenyldiazomethane and ethyl diazoacetate were employed as dipoles (*Scheme 26*). The reaction of thiazolines **39b** and **39c** with diazoethane afforded Δ^1-pyrazolines *exo*-**102b** and *exo*-**102c**, respectively, as single reaction products, while the reaction with phenyldiazomethane yielded isomeric Δ^2-pyrazolines **103b** and **103c**. On the other hand, no reaction was observed in any case with diphenyldiazomethane and ethyl diazoacetate.



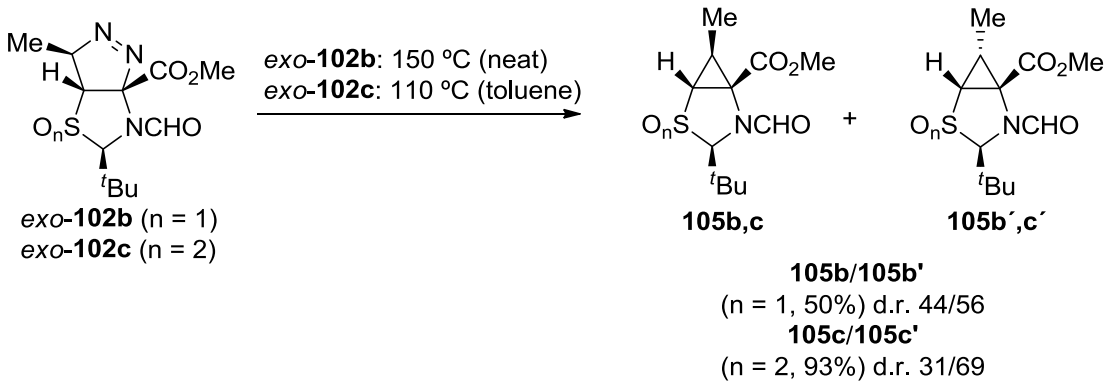
Scheme 26. 1,3-dipolar cycloaddition of thiazolines **39b** and **39c** with some diazoalkanes

Δ^2-Pyrazoline **103b** could be purified chromatographically, but Δ^2-pyrazoline **103c** was partially degraded to the pyrazole **104** during the chromatographic purification (*Scheme 27*) confirming the regioselectivity of the addition of phenyldiazomethane to the thiazoline **39c**. To prevent the formation of the by-product pyrazole **104**, the Δ^2-pyrazoline **103c** was precipitated directly from the reaction mixture.



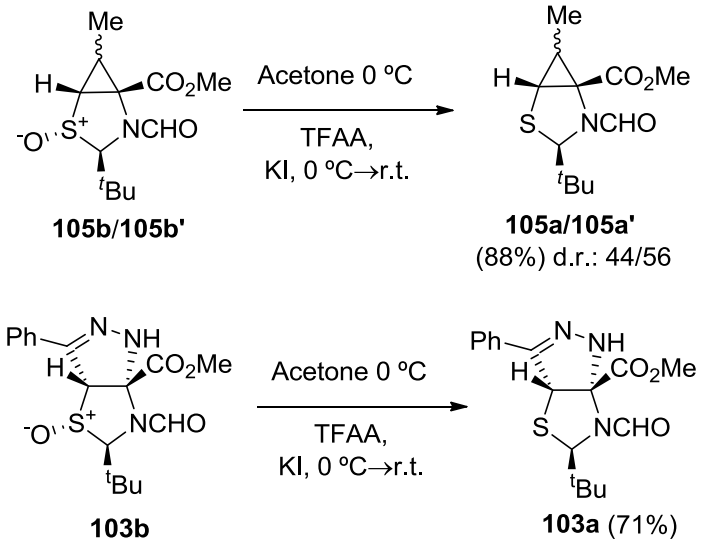
Scheme 27. Degradation of Δ^2-Pyrazoline **103c**

Thermal nitrogen elimination from Δ^1-pyrazolines *exo*-**102b** and *exo*-**102c** furnished bicyclic thiazolidines **105b**/**105b'** and **105c**/**105c'** as diastereomeric mixtures in 50% (d.r. 44/56) and 93% (d.r. 31/69) overall yields, respectively. The diastereomeric mixtures obtained are due to the radical mechanism of nitrogen extrusion.[50] Diastereomeric bicyclic thiazolidines **105c**/**105c´**were separated by column chromatography but the mixture **105b**/**105b´** could not be separated (*Scheme 28*).



Scheme 28. Thermal nitrogen extrusion of Δ^1-pirazolines *exo*-**102b** and *exo*-**102c**

For this reason, the inseparable epimeric mixture of thiazolidines **105b** and **105b'** was subjected to reduction with trifluoroacetic anhydride and KI. The resulting mixture **105a** and **105a'** was obtained in 88% yield and both diastereoisomers could be properly separated. The synthesis of **105a** and **105a'** mixture could be carried out in 60% yield in three consecutive steps, without intermediates purification, starting from **39b**. The same procedure was carried out to reduce the sulfinyl group of **103b**, affording the unstable Δ^2-pyrazoline **103a** in good yield (*Scheme 29*).



Scheme 29. Reduction of epimeric mixture **105b**/**105b´**and **103b**

Structural assignments for the compounds **105a**, **105a'**, **105c** and **105c'** have been made on the basis of NOESY experiments. It was observed n.O.e between the protons of the *tert*-butyl group, H5 and methyl group of the methyl ester, in both series. In addition, compounds **105a** and **105c** showed n.O.e between H5 and Me-C6. The compounds **105a'** and **105c'** showed n.O.e between H5 and H6 and Me-C6 and H3. Thus, the absolute configuration for **105a'** and

105c' was determined as (1*R*,3*R*,5*R*,6*R*) and (1*R*,3*R*,5*R*,6*S*) for **105a** and **105c** (*Figure 9*).

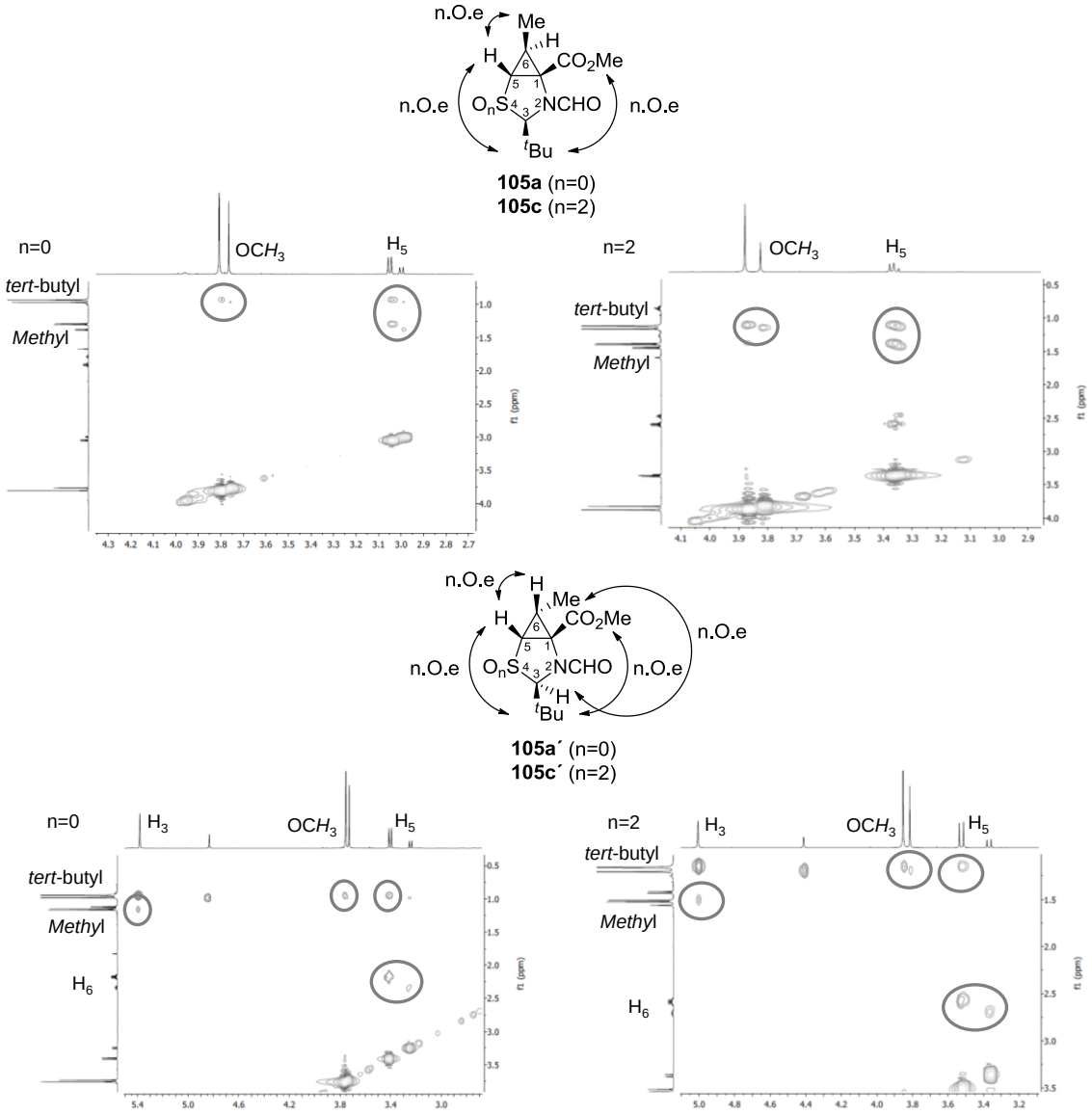


Figure 9. NOESY experiments and results for the bicyclic thiazolidines **105a,c** and **105a´,c´**

4. COMPUTATIONAL STUDIES

To gain deeper insight into the stereoselective 1,3-dipolar cycloaddition reaction involving diazoalkanes and thiazolines **39a-c**, full DFT calculations at M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31G+(d,p) level of theory were carried out (for details on computational methods see appendix).

Consistently with the experimental work no changes were made in the reagents to be calculated. We used for calculations thiazolines **39a-c** and diazoalkanes **D1-D6** (*Figure 10*).

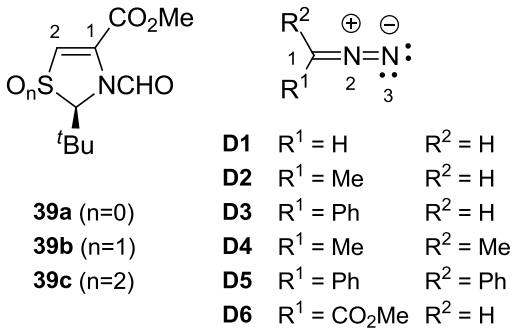


Figure 10. Reagents used in the computational study

The polar nature of the reactions has been evaluated through the analysis of the reactivity indices defined within the conceptual DFT.[51] The static global properties of the reagents, namely electronic chemical potential (μ), chemical hardness (η), global electrophilicity (ω), and global nucleophilicity (*N*), computed at M06-2X/6-311+G(d,p) are shown in *Table 4*.

Table 4. M06-2X/6-311+G(d,p) electronic chemical potential (μ), chemical hardness (η), global electrophilicity (ω), and global nucleophilicity (*N*), in eV of thiazolines **39a-c** and diazoalkanes **D1-D6**

	μ	η	ω	*N*	Δω 39a	Δω 39b	Δω 39c
39a	-4.11	6.58	1.28	3.77			
39b	-5.06	7.07	1.81	2.57			
39c	-5.27	7.23	1.92	2.27			
D1	-3.86	7.45	1.00	3.57	0.2784	0.8077	0.9187
D2	-3.61	7.05	0.92	4.03	0.3577	0.8870	0.9980
D3	-3.64	6.50	1.02	4.27	0.2603	0.7895	0.9006
D4	-3.29	6.86	0.79	4.45	0.4935	1.0227	1.1338
D5	-3.54	6.09	1.03	4.58	0.2489	0.7781	0.8892
D6	-4.47	7.55	1.32	2.92	-0.0432	0.4861	0.5971

The electronic chemical potentials (μ) of diazoalkanes are higher than that of thiazolines **39a-c** indicating that along polar reactions the global electron density

transfer (GEDT)[52] will flux from diazoalkanes towards the thiazolines. The only exception is the couple **D6/39a** which presents the opposite situation so, in that case it is expected the GEDT will move from the thiazoline **39a** to the diazoalkane **D6** although in a very low extent.

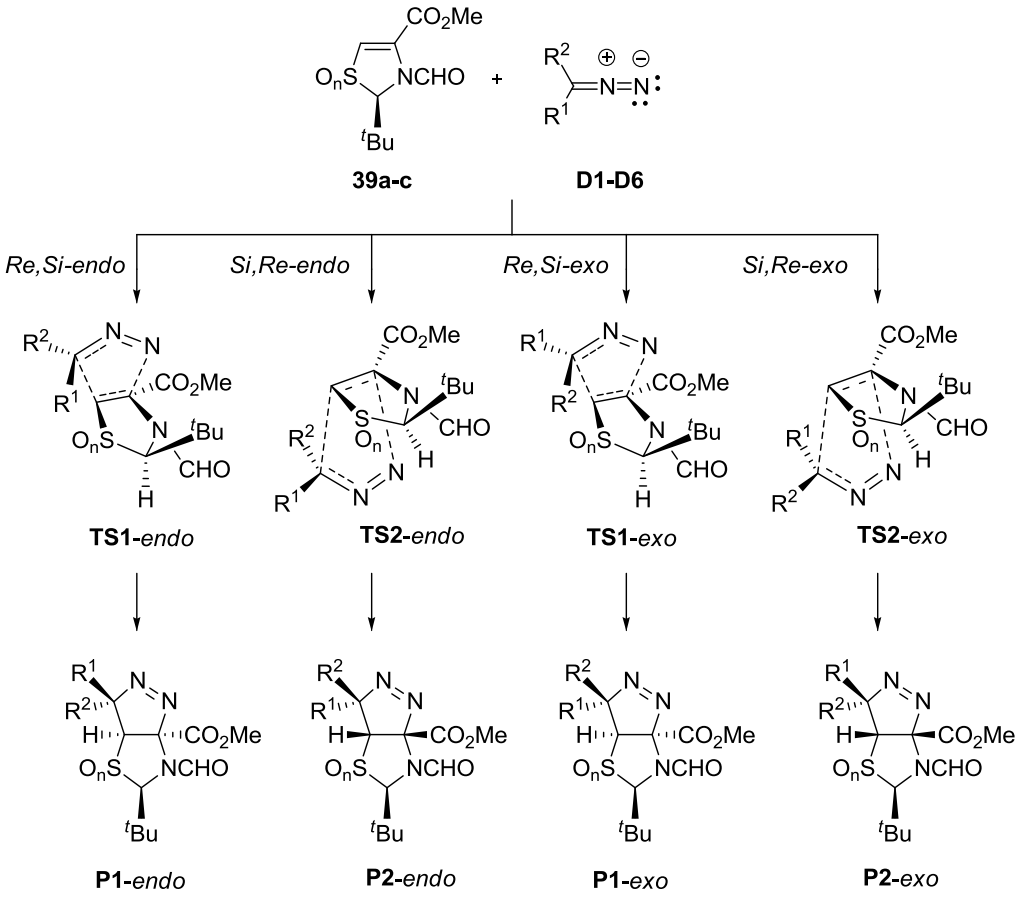
The electrophilicity ω of thiazoline **39a** is 1.28 eV being classified as a moderate electrophile. The values for **39b** and **39c** are 1.81 and 1.92 eV, respectively corresponding to strong electrophiles. Diazoalkanes **D1-D6** present lowers ω values but still in the range of moderate electrophiles. However, **D1-D5** have increased nucleophilicity indices *N* in the range 3.57-4.58 eV. The values of Δω indicate normal demand reactions in all cases except for the reaction of **39a** with **D6** which is predicted to be a slow (low absolute value of Δω) inverse demand cycloaddition reaction. According to these indices it is predicted faster reactions with thiazolines **39b** and **39c** and slower reactions with **39a**. As expected for polar reactions an increase of the electrophilic character of thiazolines should be accompanied by an increase of the polar character of the reaction that can be confirmed by the global GEDT at the transition structure (see below). Consequently, it is also predicted a decrease in the activation energy for the more polar reactions showing a higher GEDT although according to the above indices the reactions moves from non-polar to moderate polar. Considering that diazoalkanes have similar electrophilicity (moderate electrophiles), it is expected that differences in reactivity come from the thiazoline partner. In particular, higher activation energies are predicted for reactions with thiazoline **39a** -a moderate electrophile- than with **39b** and **39c** both strong electrophiles. These preliminary theoretical results on reactivity are in good agreement with the above described experimental findings.

The regioselectivity of the reaction can be predicted by considering that in a polar cycloaddition reaction between non-symmetrical compounds, the most favorable interaction is that between the most nucleophilic center of the nucleophile and the most electrophilic center of the electrophile.[53] Parr functions[54] derived from the changes of spin electron density reached via the GEDT process from the nucleophile to the electrophile have demonstrated to be excellent tools for studying the local reactivity.[55] Consequently, we calculated nucleophilic P_k^- Parr functions for diazoalkanes (the nucleophiles) and electrophilic P_k^+ Parr functions for thiazolines (the electrophiles).[56] The values are given in *Table 5*.

Table 5. M06-2X/6-311+G(d,p) Parr functions of thiazolines **39a-c** and diazoalkanes **D1-D6**

	P_k^+		P_k^-	
	C1	C2	C1	N3
39a	0.079	0.439	-	-
39b	0.237	0.255	-	-
39c	0.214	0.258	-	-
D1	-	-	0.782	0.537
D2	-	-	0.664	0.557
D3	-	-	0.428	0.402
D4	-	-	0.577	0.586
D5	-	-	0.477	0.374
D6	-	-	0.787	0.438

Analysis of the nucleophilic P_k^- Parr functions of diazoalkanes indicates that C1 is more nucleophilically activated than N3, except for **D4** which showed similar values for the two reactive centers. The electrophilic P_k^+ Parr functions of thiazolines indicate that C2 is the most electrophilic center of these molecules. Consequently, the most favorable electrophile-nucleophile interaction along the polar cycloaddition reactions of diazoalkanes **D1, D2, D3**, **D5** and **D6** with thiazolines **39a-c** will take place between the most nucleophilic C1 of diazoalkane and the most C2 electrophilic center of thiazolines. On the other hand, only two diastereoisomers are predictable for disubstituted diazoalkanes **D4** and **D5**. Next, we considered the formation of cycloadducts predicted by the DFT analysis based on reactivity indices. Four reaction channels were studied for the cycloaddition between thiazolines **39a-c** and diazoalkanes **D1**-**D6**: approaches by *Re,Si* and *Si,Re* faces of the thiazoline have been considered and in the case of non-symmetrical ($R^1 \neq R^2$) diazoalkanes **D2**, **D3** and **D6** *endo* and *exo* approaches completed the study. Consequently, four transition structures for diazoalkanes **D2**, **D3** and **D6** and two transition structures for diazoalkanes **D1**, **D4** and **D5**, leading to the corresponding cycloadducts have been located (a total of 54 transition structures have been optimized and characterized). The nomenclature for defining stationary points is given in *Scheme 30*.



Scheme 30. Calculated channels for the reaction between **39a-c** and **D1-D6** (*Endo* approach is defined with respect to R^1)

The corresponding transition structures and products will be named with letters and numbers corresponding to thiazolines and diazoalkanes, respectively. Thus, **TS1a2**-*endo* corresponds to the *Re,Si-endo* approach of the reaction between **39a** with **D2**; **TS2c3**-*exo* corresponds to the *Si,Re-exo* approach of the reaction between **39c** with **D3** and so on. For symmetrical diazoalkanes *endo/exo* descriptors will be omitted.

The polar nature of the studied reactions was confirmed by computing the GEDT at the transition structures. The natural atomic charges at the transition structures (obtained through a natural population analysis) were shared between the diazoalkane and the thiazoline frameworks. The values of the GEDT that fluxes from the diazoalkane framework to the thiazoline are represented in *Figure 11* (for numerical values see appendix). The observed trend in *Figure 11* is the opposite to that observed in *Figure 12* confirming the existing correlation between GEDT and activation energy.[57] *Figure 12* illustrates correlation between GEDT and activation energy for **TS1** and **TS2**. The observed dispersions from the linear correlation are due to dissimilar electronic structures of both thiazolines and diazoalkanes and

steric effects. Indeed, **TS1** and **TS2** are given separately due to the divergent steric effects. These results further confirm the higher polarity and thus lower energy barrier, for the cycloadditions of thiazoline **39c**.

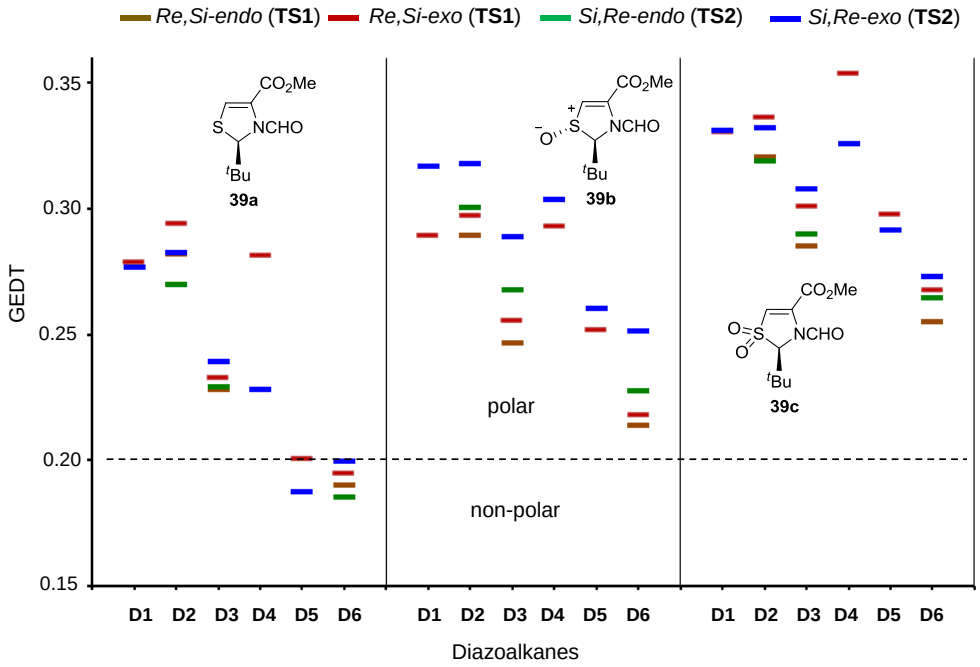


Figure 11. Global electronic density transfer (GEDT) calculated at M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p) level of theory for the reactions between **39a-c** and **D1-D6**

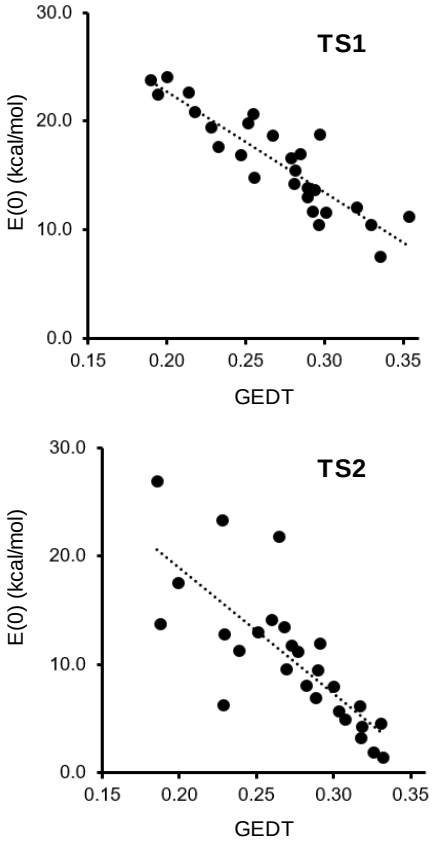


Figure 12. Plot for the activation energies versus the GEDT for **TS1** and **TS2** corresponding to the reactions between **39a-c** and **D1-D6**

In all cases the reactions showed to be concerted asynchronous in agreement with other cycloadditions of diazoalkanes with electron-deficient alkenes.[58] *Figure 13* collects the energy barriers for all the reactions studied including all the 54 approaches. The *Figure 13* is divided in three sections corresponding to thiazolines **39a-c**. Within each section, transition energy corresponding to the reaction with **D1-D6** is represented. The different energies to each dipole-dipolarophile approach are given in vertical according to the colour code. As expected, approaches by the less-hindered *Si,Re* face were always preferred. In the case of diazoalkanes **D2**, **D3** and **D6** the *Si,Re-exo* approach resulted the less energetic. By comparing thiazolines **39a-c** it is possible to appreciate a downward trend from **39a** to **39c**. The lowest barriers for each diazoalkane correspond to the reactions with **39c** in excellent agreement with experimental results that showed **39c** as the most reactive thiazoline. In fact, the highest barriers correspond to thiazoline **39a** in agreement with the fair reactivity found experimentally. Focusing on **39a**, calculations predict the lowest barrier with **D4** (20.3 kcal/mol), in agreement with the highest Δω value found for the couple **39a**/**D4** (see above).

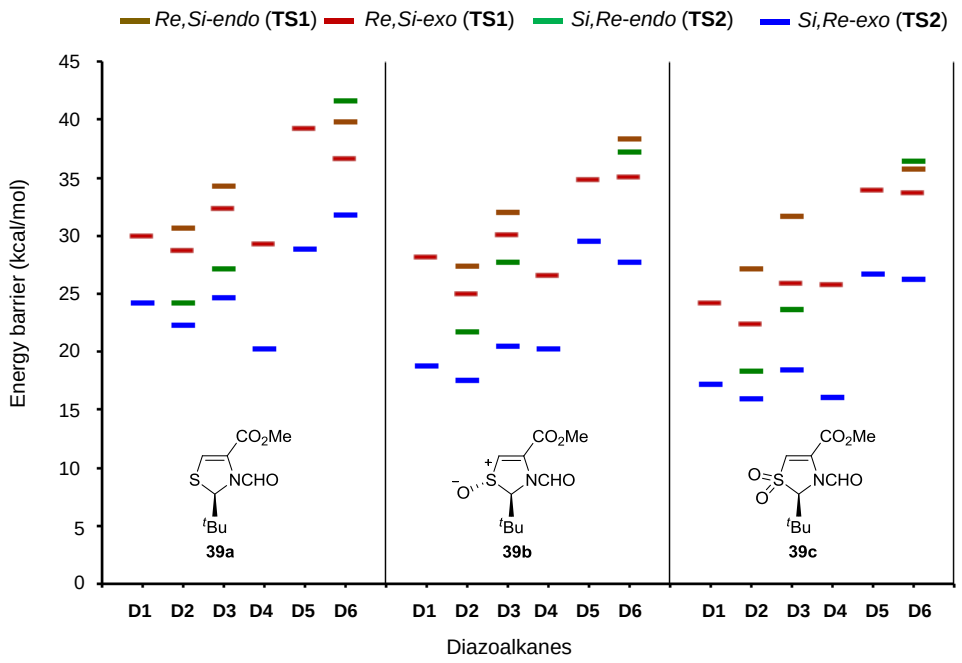


Figure 13. Energy barriers (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p) for the reactions between **39a-c** and **D1-D6**

Very similar relative reactivity against diazoalkanes is predicted for **39b** and **39c**. The reaction of **D2** with dipolarophiles **39b**,**c** has the same barrier as for **D2** and **D4** with **39a** (16.0 *vs.* 16.1 kcal/mol). This result suggests that the presence of an additional methyl is not enough to interfere sterically and, in consequence, the same reactivity is predicted (for **39c**). However, moving from Me to Ph changes dramatically the steric effects. Whereas **D3** has barriers of 20.5 and 18.4 kcal/mol for **39b** and **39c**, respectively, the energy barriers for diphenyldiazomethane **D5** are *ca.* 9 kcal/mol higher (**39b**: 29.5 kcal/mol; **39c**: 26.7 kcal/mol).

The geometries of the transition structures are given in the appendix. In all cases, expected distances for asynchronous concerted reactions are observed. In agreement with the polar character of the reactions, the more asynchronous processes correspond to cycloadditions with **39c**. As an example, the most stable transition structures for the reaction between **39c** and diazoalkanes **D1-D4** are illustrated in *Figure 14*.

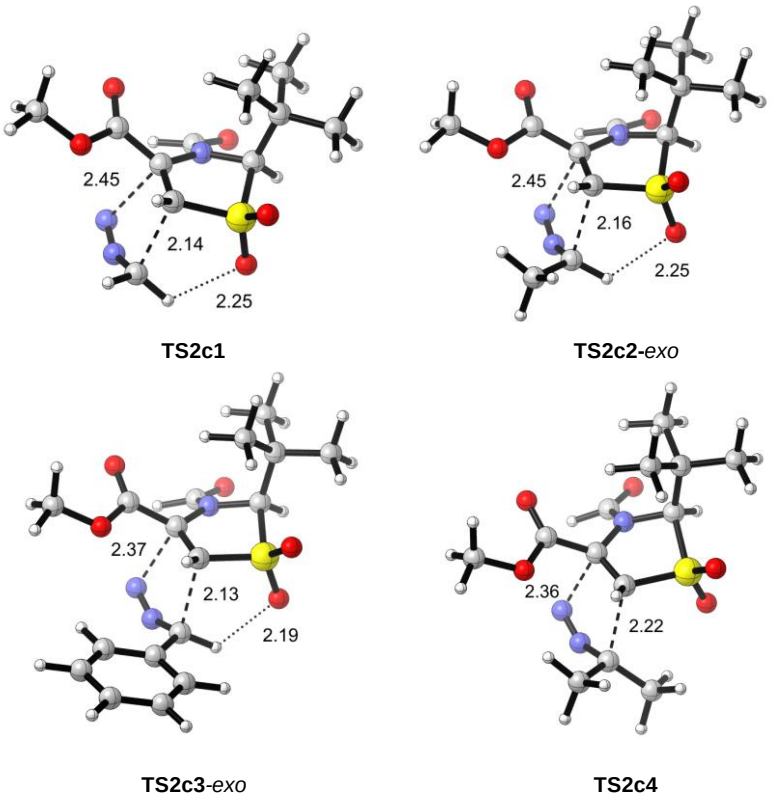


Figure 14. Most stable transition structures (M06-2X/6-31+G(d,p)) for the reaction of **39c** with **D1**, **D2**, **D3** and **D4**

In the case of non-symmetrical diazoalkanes like **D2** unfavorable steric interactions between the SO_n moiety and the incoming non-hydrogen substituent might be expected for the *endo* approach. However, as mentioned above, the same barrier is found for **D2** and **D4** despite the latter has an additional methyl group which could give unfavorable steric interactions. This result suggests a balance between the unfavourable steric interaction and the positive donor effect of the alkyl group. In the case of **D2** only one isomer is obtained. A close inspection of transition structures **TS2c1**, **TS2c2**, and **TS2c3** revealed a short distance between the hydrogen atom of the incoming diazoalkane and the oxygen atom of the sulfone/sulfoxide group revealing a favorable O···H interaction responsible of the observed high diastereoselectivity in the case of diazoalkanes **D2** and **D3** (*Figure 14*). For **D4** the interaction cannot be present and the similar reactivity with respect to **D3** is due to the additional methyl group that renders more nucleophilic the diazoalkane (as predicted by the reactivity indices).

The presence of the abovementioned interaction is confirmed through a NCI analysis. As an example, *Figure 15* illustrates such analysis for **TS2c1**. Similar results are observed for **TS2b1**; in **TS2a1** O···H interaction is impossible. Indeed, the lack of interaction in **TS2a1** contributes to the lower reactivity observed for **a**

series. The NCI analysis also reveals the asynchronicity of the forming bonds, showing that, in the transition structure, the C-C bond is more advanced than the C-N bond.

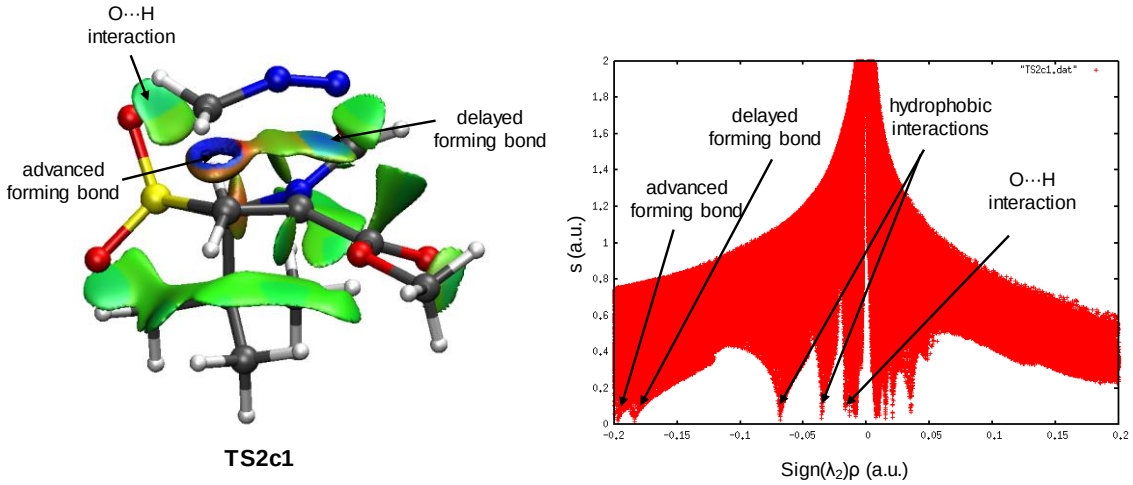
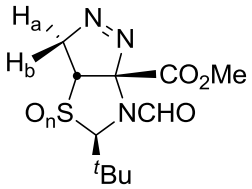
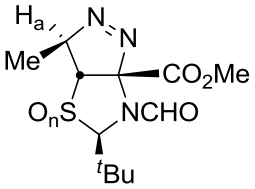


Figure 15. NCI Analysis for **TS2c1**. Left: Non-covalent interactions are shown as colored surfaces (blue: strong attractive; green: light attractive; red: repulsive). Right: NCI s(ρ) decaying curves representation with detail of interactions

The O···H interaction observed in the transition structures is also present in the final products as demonstrated by the observed NMR chemical shifts of the methylene protons which showed differences of *ca*. 1 ppm in the case of **P2b1** and **P2c1** derived from **D1**. Products derived from **D2** showed the only proton in the area of the more deshielded one of those derived from **D1** thus confirming also the stereochemical course of the reaction (*Figure 16*).



	δ H_a	δ H_b
n = 2	5.6 (dd)	4.8 (dd)
n = 1	5.4 (dd)	4.9 (dd)
n = 0	4.5 (m)	4.5 (m)



	δ H_a
n = 2	5.8 (dq)
n = 1	5.6 (dq)

Figure 16. Selected chemical shifts for **P2b1** and **P2c1** confirming the O··H interaction predicted by calculations (chemical shifts given in ppm)

5. CONCLUSIONS

1,3-dipolar cycloaddition reaction of several diazoalkanes such as diazomethane, diazoethane and diphenyldiazomethane and thiazolines **39b** and **39c** have been successfully studied.

Thiazoline **39a** has shown to be almost unreactive in cycloaddition reaction with diazomethane. However, the stereoelectronic properties of thiazolines **39b** and **39c** have made them excellent candidates for carrying out cycloaddition reactions with diazoalkanes as a key step in the synthesis of constrained cyclopropane cysteine analogues. The difference of this reactivity is explained by the enhanced electron-withdrawing effect of sulfinyl and sulfonyl groups against sulfanyl group.

Diazomethane, diazoethane and phenyldiazomethane reacted smoothly with thiazolines **39b** and **39c** but no reaction was observed for diphenyldiazomethane and ethyl diazoacetate. In the case of the reaction with phenyldiazomethane Δ^2-pyrazolines were obtained instead the expected Δ^1-pyrazolines. Constrained bicyclic analogues of cysteine were prepared from Δ^1-pyrazolines through sequential nitrogen extrusion and reduction of the sulfinyl moiety.

The computational study of the cycloaddition reaction is in excellent agreement with experimental observations. The lowest barriers for each diazoalkane correspond to the reactions with **39c** that showed it as the most reactive thiazoline. Very similar relative reactivity against diazoalkanes is predicted for **39b** and **39c**. In both cases the most reactive diazoalkane is **D2** although in the case of **39c**, the same barrier (16.0 *vs.* 16.1 kcal/mol) was found for **D4**. This result suggests that the presence of an additional methyl is not enough to interfere sterically and, in consequence, the same reactivity is predicted (for **39c**). However, moving from Me to Ph changes dramatically the steric effects. Whereas **D3** has barriers of 20.5 and 18.4 kcal/mol for **39b** and **39c**, respectively, the energy barriers for diphenyldiazomethane **D5** are *ca.* 9 kcal/mol higher (**39b**: 29.5 kcal/mol; **39c**: 26.7 kcal/mol). In fact, experimentally, while **D3** reacted smoothly with both **39b** and **39c** the reaction did not work with **D5**. Computational studies also predict correctly the experimentally observed lack of reactivity for **D6** for which barriers of 27.7 and 26.3 kcal/mol, in the best *Si,Re-exo* were calculated for **39b** and **39c**, respectively.

6. EXPERIMENTAL SECTION

6.1. General

All reagents were used as received from commercial suppliers without further purification. Thin-layer chromatography (TLC) was performed on Macherey-Nagel Polygram®SIL G/UV254 precoated silica gel polyester plates. The products were visualized by exposure to UV light, iodine vapour, submersion in ninhydrin stain, in ethanolic solution of phosphomolybdic acid or in an aqueous solution of sodium permanganate. Column chromatography was performed using 60 M (0.04-0.063 mm) silica gel from Macherey-Nagel. Melting points were determined on a Gallenkamp apparatus. IR spectra were registered on a Nicolet Avatar 360 FTIR spectrophotometer; vmax is given for the main absorption bands. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, AV-400 instrument at room temperature, unless otherwise indicated, and using the residual solvent signal as the internal standard; chemical shifts (δ) are expressed in parts per million and coupling constant (*J*) in hertz. Optical rotations were measured at room temperature using a JASCO P-1020 polarimeter. High-resolution mass spectra were obtained on a Bruker Microtof-Q spectrometer.

6.2. General procedure for synthesis of diazocompounds

The diazocompounds employed are very hazardous, so it is of extremely importance to be caution handling them.

Diazomethane generation: *N*-methyl-*N´*-nitro-*N*-nitrosoguanidine (50% w/w in water) (5 eq.) was added slowly over a mixture of potassium hydroxide aqueous solution 40% (4 mL) and diethyl ether (10 mL) at 0 ºC and the stirring was kept for 15 minutes. Then, the phases were separated and the aqueous phase was rejected.

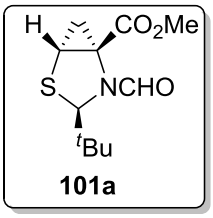
Diazoethane generation: Following the procedure described by Snell *et al.*[59] *N*-ethyl-*N*-nitrosourea (5 eq.) was added slowly over a mixture of potassium hydroxide aqueous solution 40% (5 mL) and diethyl ether (20 mL) at 0 ºC and the stirring was kept for 1 hour. Then, the phases were separated and the aqueous phase was rejected.

Phenyldiazomethane generation: Following the procedure described by Jimenez A. I.[60] benzaldehyde tosylhydrazone (1.30 g, 4.75 mmol) was dissolved in toluene (20 mL) and an aqueous solution of sodium hydroxide (15% w/w) (21 mL) and benzyltriethylammonium chloride (270 mg, 1.19 mmol) was added. The reaction mixture was stirred vigorously and heated at 80 ^{o}C for 2 hours. Once the reaction reached room temperature, the phases were separated and the aqueous phase was rejected.

6.3. General procedure for the 1,3-dipolar cycloaddition and thermal nitrogen extrusion

A solution of thiazoline **39a-c** (1 eq.) in the appropriate solvent, (tetrahydrofurane, dicholomethane or toluene) was cooled, if necessary, and the organic phase of the diazocompound (5 eq.) generation was added. The reaction mixture was allowed to react until all the starting material was consumed. Then, silicagel was added in order to destroy the excess of diazocompound and was filtered off over celite, washed with EtOAc and the solvent was removed under reduced pressure. The crude reaction without purification was subjected to thermal nitrogen extrusion and the consistent formation of the cyclopropane ring. The new crude reaction was purified by chromatographic column. (Thermal extrusion did not carry out in the case of using phenyldiazomethane because of the formation of the corresponding Δ^2-pyrazolines).

Synthesis of (1*R*,3*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4-thia-2-azabicyclo[3.1.0]hexan-1-carboxylate 101a



101a

Following the experimental procedure described above, thiazoline **39a** (136 mg, 0.59 mmol) was dissolved in THF (10 mL), cooled at -78 ºC and treated with diazomethane (2.97 mmol) for 4 hours at this temperature and for 7 days at room temperature. Each day freshly prepared diazomethane (2.97 mmol) was added to obtain the Δ^1-pyrazoline **100a**. The elimination of N_2 was carried out warming the oily reaction crude at 150 ºC for 1 hour. The new crude reaction was purified by column chromatography (EtOAc/hexane 30/70) to afford **101a** (17 mg, 0.07 mmol, 12% in two steps) as yellowish oil.

$[\alpha]_D^{23}$: -22º (*c* 1.1, $CHCl_3$)

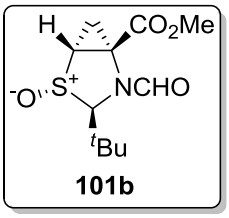
IR (nujol) ν 1738, 1690, 1363, 1334, 1310, 1251, 1196, 1170 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz) [rotamers mixture ratio (1/0.63)] δ 8.23 (s, 1H, C*H*O, rot. maj.), 8.15 (s, 1H, C*H*O, rot. min.), 5.34 (s, 1H, H_3, rot. maj.), 4.84 (s, 1H, H_3, rot. min.), 3.70 (s, 3H, OCH_3, rot. maj.), 3.65 (s, 3H, OCH_3, rot. min.), 3.17 (dd, *J* = 7.5, 5.6 Hz, 1H, H_5, rot. maj.), 3.07 (dd, *J* = 7.3, 5.8 Hz, 1H, H_5, rot. min.), 2.21 (dd, *J* = 7.5, 5.6 Hz, 1H, H_{6cis}, rot. min.), 2.16 (dd, *J* = 7.5, 5.1 Hz, 1H, H_{6cis}, rot. maj.), 1.58 (t, *J* = 5.3 Hz, 1H, H_{6trans}, rot. maj.), 1.41 (t, *J* = 5.6, 1H, H_{6trans}, rot. min.), 0.92 (s, 9H, C(CH_3)$_3$, rot. min.), 0.88 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.4 (*C*O_2Me, rot. maj.), 169.4 (*C*O_2Me, rot. min.), 164.0 (*C*HO, rot. maj.), 161.8 (*C*HO, rot. min.), 85.8 (C_3, rot. min.), 81.9 (C_3, rot. maj.), 52.9 (O*C*H_3, rot. maj.), 52.6 (O*C*H_3, rot. min.), 51.6 (C_1, rot. maj.), 49.9 (C_1, rot. min.), 39.1 (C_6, rot. maj.), 38.1 (*C*(CH_3)$_3$, rot. maj.), 37.7 (*C*(CH_3)$_3$, rot. min.), 36.7 (C_6, rot. min.), 32.7 (C_5, rot. min.), 32.2 (C_5, rot. maj.), 25.6 (C(*C*H_3)$_3$, rot. maj.), 25.2 (C(*C*H_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{11}H_{17}NO_3S$ 266.0821; found 266.0831

Synthesis of (1*R*,3*R*,4*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4-oxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 101b



101b

Following the experimental procedure described above, thiazoline **39b** (400 mg, 1.63 mmol) was dissolved in THF (10 mL), cooled at -78 °C and treated with diazomethane (8.15 mmol) for 4 hours at this temperature and for 1 hour at room temperature to obtain the Δ^1-pyrazoline **100b**. The elimination of N_2 was carried out warming the oily reaction crude at 150 °C for 1 hour. The new crude reaction was purified by column chromatography (EtOAc/hexane 80/20) to afford **101b** (210 mg, 0.81 mmol, 50% in two steps) as an off white solid.

M.p.: 166-168 °C

$[\alpha]_D^{23}$: -107° (*c* 1.0, $CHCl_3$)

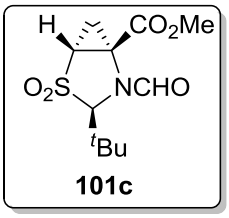
IR (KBr) v 1737, 1676, 1385, 1345, 1224, 1169, 1145, 1046, 1038 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.84)] δ 8.55 (s, 1H, C*H*O, rot. maj.), 8.18 (s, 1H, C*H*O, rot. min.), 4.97 (brs, 1H, H_3, rot. maj.), 4.30 (d, *J* = 0.7 Hz, 1H, H_3, rot. min.), 3.83 (s, 3H, OCH_3, rot. maj.), 3.82*overlapped (dd, *J* = 8.2, 4.9 Hz, 1H, H_5, rot. maj.), 3.79 (s, 3H, OCH_3, rot. min.), 3.73 (dd, *J* = 9.5, 5.6 Hz, 1H, H_5, rot. min.), 2.55 (t, *J* = 5.7 Hz, 1H, H_{6trans}, rot. maj.), 2.36 (t, *J* = 6.0 Hz, 1H, H_{6trans}, rot. min.), 2.30 (ddd, *J* = 9.5, 6.4, 1.0 Hz, 1H, H_{6cis}, rot. min.), 2.23 (ddd, *J* = 9.7, 5.8, 1.0 Hz, 1H, H_{6cis}, rot. maj.), 1.11 (s, 9H, C(CH_3)$_3$, rot. min.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR δ 168.8 (*C*O_2Me, rot. maj.), 167.9 (*C*O_2Me, rot. min.), 164.8 (*C*HO, rot. maj.), 162.6 (*C*HO, rot. min.), 104.6 (C_3, rot. min.), 101.7 (C_3, rot. maj.), 54.5 (C_1, rot. maj.), 53.7 (O*C*H_3, rot. maj.), 53.5 (C_1, rot. min.), 53.4 (O*C*H_3, rot. min.), 49.0 (C_5, rot. min.), 48.6 (C_5, rot. maj.), 35.7 (*C*(CH3)$_3$, rot. maj.), 35.3 *C*(CH3)$_3$, rot. min.), 27.0 (C(*C*H_3)$_3$), rot. maj.), 26.7 (C(*C*H_3)$_3$, rot. min.), 25.9 (C_6, rot. maj.), 24.0 (C_6, rot. min.)

HRMS (ESI-TOF) m/z: $[M + Na]^+$ calculated for $C_{11}H_{16}NO_4SNa$ 282.0770; found 282.0799

Synthesis of (1*R*,3*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 101c



101c

Following the experimental procedure described above, thiazoline **39c** (400 mg, 1.53 mmol) was dissolved in THF (10 mL), cooled at -78 °C and treated with diazomethane (7.65 mmol) for 4 hours at this temperature and for 1 hour at room temperature to obtain the Δ^1-pyrazoline **100c**. The elimination of N_2 was carried out dissolving the obtained crude in toluene (10 mL) and warming at 110 °C for 15 hours. After this time the solvent was removed under reduced pressure and the new crude reaction was purified by column chromatography (EtOAc/hexane 40/60) to afford **101c** (220 mg, 0.80 mmol, 52% in two steps) as a white solid.

M.p.: 125-127 °C

$[\alpha]_D^{23}$: -115° (*c* 1.0, $CHCl_3$)

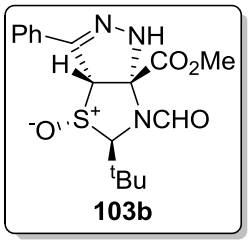
IR (KBr) v 1736, 1698, 1445, 1344, 1318, 1248, 1202, 1169, 1047 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.65)] δ 8.41 (s, 1H, C*H*O, rot. maj.), 8.15 (s, 1H, C*H*O, rot. min.), 4.91 (brs, 1H, H_3, rot. maj.), 4.30 (d, *J* = 0.8 Hz, 1H, H_3, rot. min.), 3.85 (s, 3H, OCH_3, rot. maj.), 3.80 (s, 3H, OCH_3, rot. min.), 3.56 (dd, *J* = 8.8, 5.5 Hz, 1H, H_5, rot. maj.), 3.51 (dd, *J* = 8.8, 5.5 Hz, 1H, H_5, rot. min.), 2.48 (ddd, *J* = 8.8, 6.6, 1.0 Hz, 1H, H_{6cis}, rot. min.), 2.43 (ddd, *J* = 8.8, 6.1, 1.0 Hz, 1H, H_{6cis}, rot. maj.), 2.39 (t, *J* = 5.8 Hz, 1H, H_{6trans}, rot. maj.), 2.28-2.23 (m, 1H, H_{6trans}, rot. min.), 1.20 (s, 9H, C(CH_3)$_3$, rot. min.), 1.15 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.1 (*C*O_2Me, rot. maj.), 167.2 (*C*O_2Me, rot. min.), 164.2 (*C*HO, rot. maj.), 162.9 (*C*HO, rot. min.), 91.1 (C_3, rot. min.), 87.2 (C_3, rot. maj.), 54.0 (O*C*H_3, rot. maj.), 53.6 (O*C*H_3, rot. min.), 47.4 (C_1, rot. maj.), 46.4 (C_1, rot. min.), 45.8 (C_5, rot. min.), 44.4 (C_5, rot. maj.), 36.5 (*C*$(CH_3)_3$, rot. maj.), 36.0 (*C*$(CH_3)_3$, rot. min.), 32.0 (C_6, rot. maj.), 30.1 (C_6, rot. min.), 25.8 (C(*C*H_3)$_3$, rot. maj.), 25.5 (C(*C*H_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{11}H_{16}NO_5SNa$ 298.0720; found 298.0717

Synthesis of (3a*S*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4-oxido-3-phenyl-3a,5,6,6a-tetrahydro-1*H*-pyrazolo[3,4-*d*]thiazole-6a-carboxylate 103b



103b

Following the experimental procedure described above, thiazoline **39b** (400 mg, 1.63 mmol) was dissolved in toluene (15 mL) and treated with phenyldiazomethane (4.75 mmol) for 6 hours at room temperature. The obtained brown oil was purified by column chromatography (EtOAc/hexane 50/50) to afford the Δ^2-pyrazoline **103b** (585 mg, 1.61 mmol, 98%) that was washed with chloroform, obtaining a white solid.

M.p.: 103-105 °C

$[\alpha]_D^{24}$: -173° (*c* 1.1, $CHCl_3$)

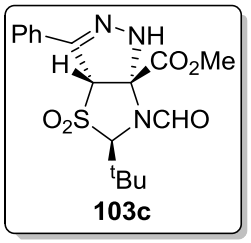
IR (KBr) ν 3286, 1747, 1679, 1462, 1349, 1249, 1060 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.27)] δ 8.75 (s, 1H, C*H*O, rot. min.), 8.26 (s, 1H, C*H*O, rot. maj.), 7.79-7.75 (m, 2H, H_{Ph}, rot. min.), 7.73-7.69 (m, 2H, H_{Ph}, rot. maj.), 7.56 (brs, 1H, N*H*, rot. maj.), 7.44-7.37 (m, 6H, H_{Ph}, both rot.), 7.13 (brs, 1H, N*H*, rot. min.), 5.63 (s, 1H, H_{3a}, rot. min.), 5.44 (s, 1H, H_5, rot. min.), 5.02 (s, 1H, H_{3a}, rot. maj.), 4.80 (s, 1H, H_5, rot. maj.), 3.93 (s, 3H, OCH_3, rot. min.), 3.85 (s, 3H, OCH_3, rot. maj.), 1.25 (s, 9H, C(CH_3)$_3$, rot. maj.), 1.09 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.6 (*C*O_2Me, rot. maj.), 168.1 (*C*O_2Me, rot. min.), 163.8 (*C*HO, rot. min.), 163.3 (*C*HO, rot. maj.), 145.6 (C_3, rot. min.), 141.8 (C_3, rot. maj.), 130.4 (C_{qPh}, rot. maj.), 130.0 (C_{Ph}, rot. min.), 129.1 (C_{Ph}, rot. min. and C_{Ph}, rot. maj.), 126.2 (C_{Ph}, rot. min.), 125.7 (C_{Ph}, rot. maj.), 95.9 (C_5, rot. maj.), 95.0 (C_5, rot. min.), 94.4 (C_{6a}, rot. maj.), 92.8 (C_{6a}, rot. min.), 77.2 (C_{3a}, rot. min.), 74.5 (C_{3a}, rot. maj.), 54.6 (O*C*H_3, rot. min.), 54.3 (O*C*H_3, rot. maj.), 36.1 (*C*(CH_3)$_3$, rot. min.), 35.9 (*C*(CH_3)$_3$, rot. maj.), 27.7 (C(*C*H_3)$_3$, rot. min.), 27.3 (C(*C*H_3)$_3$, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{17}H_{22}N_3O_4S$ 364.1326; found 364.1340

Synthesis of (3a*S*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4,4-dioxido-3-phenyl-3a,5,6,6a-tetrahydro-1*H*-pyrazolo[3,4-*d*]thiazole-6a-carboxylate 103c



103c

Following the experimental procedure described above, thiazoline **39c** (400 mg, 1.53 mmol) was dissolved in toluene (15 mL) and treated with phenyldiazomethane (4.75 mmol) for 4 hours at room temperature. The crude reaction subjected to chromatographic purification afforded the pyrazole **104**.[61] ^{1}H NMR of **104** is included in appendix and it is in accordance with the reported values. However, the obtained pale yellow oily crude reaction was purified by precipitation in Et_2O/Hexane affording the Δ^2-pyrazoline **103c** (538 mg, 1.42 mmol, 93%) as a white solid.

M.p.: 125-127 ºC

$[\alpha]_D^{21}$: -291º (*c* 0.7, $CHCl_3$)

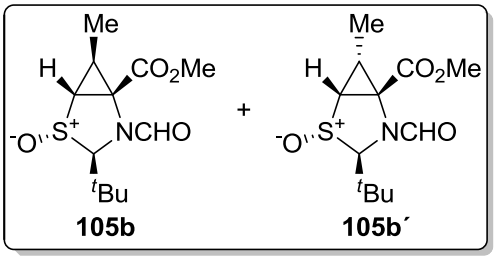
IR (KBr) v 3325, 1748, 1679, 1331, 1246, 1182, 1157, 1011 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.71)] δ 8.66 (s, 1H, C*H*O, rot. min.), 8.32 (s, 1H, C*H*O, rot. maj.), 7.84-7.80 (m, 2H, H_{Ph}, rot. min.), 7.79-7.74 (m, 2H, H_{Ph}, rot. maj.), 7.63 (brs, 1H, N*H*, rot. maj.), 7.48-7.38 (m, 6H, H_{Ph}, both rot.), 7.17 (brs, 1H, N*H*, rot. min.), 5.48 (s, 1H, H_{6a}, rot. min.), 5.20 (s, 1H, H_5, rot. min.), 4.92 (s, 1H, H_{6a}, rot. maj.), 4.54 (s, 1H, H_5, rot. maj.), 3.91 (s, 3H, OCH_3, rot. min.), 3.84 (s, 3H, OCH_3, rot. maj.), 1.33 (s, 9H, C(CH_3)$_3$, rot. maj.), 1.17 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 167.2 (*C*O_2Me, both rot.), 163.1 (*C*HO, rot. maj.), 163.0 (*C*HO, rot. min.), 145.2 (C_3, rot. min.), 141.0 (C_3, rot. maj.), 130.8 (C_{Ph}, rot. min.), 130.2 (C_{Ph}, rot. min.), 130.1 (C_{qPh}, rot. maj.), 129.5 (C_{qPh}, rot. min.), 129.2 (C_{Ph}, rot. maj.), 129.1 (C_{Ph}, rot. maj.), 126.9 (C_{Ph}, rot. min.), 126.4 (C_{Ph}, rot. maj.), 89.4 (C_{6a}, rot. maj.), 88.7 (C_{6a}, rot. min.), 82.6 (C_5, rot. maj.), 80.8 (C_5, rot. min.), 73.3 (C_{3a}, rot. min.), 72.6 (C_{3a}, rot. maj.), 54.8 (O*C*H_3, rot. min.), 54.5 (O*C*H_3, rot. maj.), 36.8 (*C*(CH_3)$_3$, rot. min.), 36.6 (*C*(CH_3)$_3$, rot. maj.), 26.5 (C(*C*H_3)$_3$, rot. min.), 26.0 (C(*C*H_3)$_3$, rot. maj.)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{17}H_{21}N_3O_5SNa$ 402.1094; found 402.1088

Synthesis of (1*R*,3*R*,4*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-oxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105b and **(1*R*,3*R*,4*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-oxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105b´**

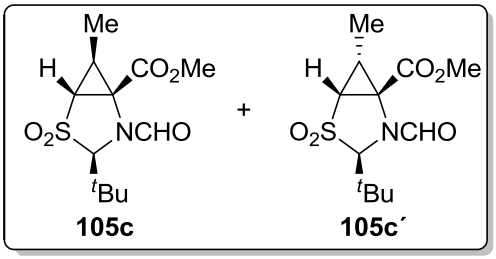


Following the experimental procedure described above, thiazoline **39b** (400 mg, 1.63 mmol) was dissolved in methylene chloride (10 mL), cooled at 0 ºC and treated with diazoethane (8.15 mmol) for 1 hour at this temperature and then was allowed to reach room temperature to obtain the Δ^1-pyrazoline *exo*-**102b**. The elimination of N_2 was carried out warming the obtained Δ^1-pyrazoline *exo*-**102b** at 150 ºC for 1 hour. The new crude reaction was purified by column chromatography (EtOAc/hexane 50/50) to afford **105b** and **105b´** (470 mg, 0.82 mmol, 50% in two steps) as a mixture of diastereoisomers in a ratio 44/56 (**105b**/**105b´**). Diastereoisomers could not be separated after column chromatography for a complete characterization of each one, but the ^{1}H NMR signals of each diastereoisomer could be elucidated from the mixture.

- 105b: ^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.59)] δ 8.58 (s, 1H, C*H*O, rot. maj.), 8.16 (s, 1H, C*H*O, rot. min.), 4.91 (s, 1H, H_3, rot. maj.), 4.25 (s, 1H, H_3, rot. min.), 3.83 (s, 3H, OCH_3, rot. maj.), 3.78 (s, 3H, OCH_3, rot. min.), 3.62 (d, *J* = 5.7, 1H, H_5, rot. maj.), 3.57 (d, *J* = 6.4, 1H, H_5, rot. min.), 2.83-2.72 (m, 1H, H_6, rot. min.), 2.69-2.54 (m, 1H, H_6, rot. maj.), 1.48 (d, *J* = 6.5, 3H, CH_3, rot. min.), 1.41 (d, *J* = 6.5, 3H, CH_3, rot. maj.), 1.04 (s, 9H, C(CH_3)$_3$, rot. min.), 1.01 (s, 9H, C(CH_3)$_3$, rot. maj.)

- 105b´: ^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.53)] δ 8.45 (s, 1H, C*H*O, rot. maj.), 8.35 (s, 1H, C*H*O, rot. min.), 5.14 (s, 1H, H_3, rot. maj.), 4.57 (s, 1H, H_3, rot. min.), 3.79 (s, 3H, OCH_3, rot. maj.), 3.76 (s, 3H, OCH_3, rot. min.), 3.54 (d, *J* = 9.9, 1H, H_5, rot. maj.), 3.37 (d, *J* = 9.8, 1H, H_5, rot. min.), 2.83-2.72 (m, 1H, H_6, rot. min.), 2.69-2.54 (m, 1H, H_6, rot. maj.), 1.65 (d, *J* = 6.7, 3H, CH_3, rot. maj.), 1.59 (d, *J* = 6.8, 3H, CH_3, rot. min.), 1.10 (s, 9H, C(CH_3)$_3$, rot. min.), 1.06 (s, 9H, C(CH_3)$_3$, rot. maj.)

Synthesis of (1*R*,3*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105c and **(1*R*,3*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105c´**



Following the experimental procedure described above, thiazoline **39c** (400 mg, 1.53 mmol) was dissolved in THF (10 mL), cooled at -78 ºC and treated with diazoethane (7.65 mmol) for 1 hour at this temperature and then was allowed to reach room temperature to obtain the Δ^1-pyrazoline *exo*-**102c**. The elimination of N_2 was carried out dissolving the obtained Δ^1-pyrazoline *exo*-**102c** in toluene and warming at 110 ºC for 2 hours. The new crude reaction was purified by column chromatography (EtOAc/hexane 40/60) to afford **105c** and **105c´** (413 mg, 1.43 mmol, 93% in two steps) as a mixture of diastereoisomers in a ratio 31/69 (**105c**/**105c´**). Analytical samples of both compounds, as white solids, could be obtained by column chromatography for its characterization.

(1*R*,3*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105c

M.p.: 100-102 ºC

$[\alpha]_D^{24}$: -125º (*c* 1.0, $CHCl_3$)

IR (KBr) v 1746, 1702, 1347, 1235, 1136, 1102 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.45)] δ 8.46 (s, 1H, C*H*O, rot. maj.), 8.12 (s, 1H, C*H*O, rot. min.), 4.84 (s, 1H, H_3, rot. maj.), 4.21 (s, 1H, H_3, rot. min.), 3.88 (s, 3H, OCH_3, rot. maj.), 3.83 (s, 3H, OCH_3, rot. min.), 3.37 (d, *J* = 5.6, 1H, H_5, rot. maj.), 3.35*overlapped (d, *J* = 5.7, 1H, H_5, rot. min.), 2.63-2.56 (m, 1H, H_6, rot. maj.), 2.47 (quin, *J* = 6.2, 1H, H_6, rot. min.), 1.45 (d, *J* = 6.5, 3H, CH_3, rot. min.), 1.39 (d, *J* = 6.5, 3H, CH_3, rot. maj.), 1.16 (s, 9H, C(CH_3)$_3$, rot. min.), 1.12 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 166.7 (*C*O_2Me, rot. maj.), 166.5 (*C*O_2Me, rot. min.), 164.5 (*C*HO, rot. maj.), 163.1 (*C*HO, rot. min.), 90.1 (C_3, rot. min.), 85.8 (C_3, rot. maj.), 53.7 (O*C*H_3, rot. maj.), 53.4 (O*C*H_3, rot. min.), 51.8 (C_1, rot. maj.), 50.9 (C_5, rot. min.), 50.6 (C_1, rot. min.), 49.0 (C_5, rot. maj.), 41.3 (C_6, rot. maj.),

40.1 (C_6, rot. min.), 36.4 ($C(CH_3)_3$, rot. maj.), 35.8 ($C(CH_3)_3$, rot. min.), 26.0 ($C(CH_3)_3$, rot. maj.), 25.7 ($C(CH_3)_3$, rot. min.), 12.0 (CH_3, rot. min.), 11.9 (CH_3, rot. maj.)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{12}H_{19}NO_5SNa$ 312.0876; found 312.0869

(1*R*,3*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105c´

M.p.: 100-102 °C

$[\alpha]_D^{24}$: -95° (*c* 1.0, $CHCl_3$)

IR (KBr) ν 1741, 1700, 1324, 1252, 1171, 1128 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.38)] δ 8.27 (s, 1H, C*H*O, rot. min.), 8.26 (s, 1H, C*H*O, rot. maj.), 5.00 (s, 1H, H_3, rot. maj.), 4.41 (d, *J* = 0.7, 1H, H_3, rot. min.), 3.85 (s, 3H, OCH_3, rot. maj.), 3.81 (s, 3H, OCH_3, rot. min.), 3.52 (d, *J* = 9.4, H_5, 1H, rot. maj.), 3.37 (d, *J* = 9.4, 1H, H_5, rot. min.), 2.70 (dqd, *J* = 9.3, 6.7, 0.8, 1H, H_6, rot. min.), 2.58 (dqd, *J* = 9.4, 6.7, 0.9, 1H, H_6, rot. maj.), 1.52 (d, *J* = 6.7, 3H, CH_3, rot. maj.), 1.42 (d, *J* = 6.7, 3H, CH_3, rot. min.), 1.21 (s, 9H, $C(CH_3)_3$, rot. min.), 1.16 (s, 9H, $C(CH_3)_3$, rot. maj.)

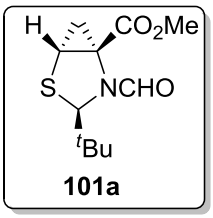
^{13}C NMR ($CDCl_3$, 100MHz) δ 169.1 (CO_2Me, rot. maj.), 168.1 (CO_2Me, rot. min.), 164.7 (*C*HO, rot. maj.), 162.2 (*C*HO, rot. min.), 92.0 (C_3, rot. min.), 88.3 (C_3, rot. maj.), 53.9 (O*C*H_3, rot. maj.), 53.5 (O*C*H_3, rot. min.), 51.5 (C_1, both rot.), 47.7 (C_5, rot. maj.), 47.6 (C_5, rot. min.), 38.0 (C_6, rot. maj.), 37.5 ($C(CH_3)_3$, rot. maj.), 36.7 ($C(CH_3)_3$, rot. min.), 36.4 (C_6, rot. maj.), 25.9 ($C(CH_3)_3$, rot. maj.), 25.5 ($C(CH_3)_3$, rot. min.), 9.4 (CH_3, rot. min.), 8.9 (CH_3, rot. maj.)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{12}H_{19}NO_5SNa$ 312.0876; found 312.0852

6.4. General procedure for deoxigenation of sulfoxides

Over a stirred solution of a bicyclic thiazolidine sulfoxide (1 eq.) in acetone at 0 ºC, trifluoroacetic anhydride (2 eq.) and potassium iodide (4 eq.) were added. The reaction mixture was stirred at room temperature and monitored by TLC (EtOAc/hexane) until completion. The mixture was treated with an aqueous solution of $Na_2S_2O_3$ (5%) and diluted with dichloromethane at room temperature and was stirred for 30 minutes. The phases were separated and the aqueous phase was extracted with dichloromethane and the combined organic layers were dried over magnesium sulfate anhydrous, filtered off and the solvent was evaporated under reduced pressure. The obtained residue was purified by column chromatography.

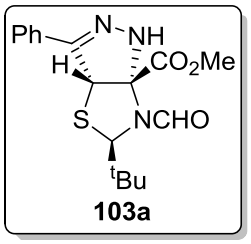
Synthesis of (1*R*,3*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4-thia-2-azabicyclo[3.1.0]hexan-1-carboxylate 101a



101a

The crude of the reaction of the nitrogen extrusion of the intermediate Δ^1-pyrazoline **100b** was dissolved in acetone (6 mL) at 0 ºC and following the general experimental procedure for the deoxigenation of sulfoxides, the reaction was completed in 90 min. The brown oil obtained was purified by column chromatography (EtOAc/hexane 20/80) to afford **101a** (270 mg, 1.11 mmol, 68% in 3 steps) as a yellow oil.

Synthesis of (3a*S*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-3-phenyl-3a,5,6,6a-tetrahydro-1*H*-pyrazolo[3,4-*d*]thiazole-6a-carboxylate 103a



103a

Following the experimental procedure described above for the deoxigenation of sulfoxides the Δ^2-pyrazoline **103b** (156 mg, 0.43 mmol) was dissolved in acetone (5 mL) at 0 °C, the reaction was completed in 4 hours. The brown oil obtained was purified by column chromatography (EtOAc/hexane 10/90) to afford **103a** (113 mg, 0.33 mmol, 77%) as a colourless oil.

$[\alpha]_D^{24}$: -7° (*c* 0.9, $CHCl_3$)

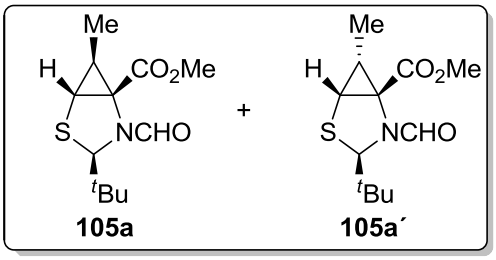
IR (neat) ν 3281, 1745, 1668, 1351, 1305, 1252, 1232, 1198, 1012 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.14)] δ 8.54 (s, 1H, C*H*O, rot. min.), 8.34 (s, 1H, C*H*O, rot. maj.), 7.69-7.66 (m, 2H, H_{Ph}, rot. min.), 7.65-7.61 (m, 2H, H_{Ph}, rot. maj.), 7.48 (brs, 1H, N*H*, rot. maj.), 7.43-7.34 (m, 6H, H_{Ph}, both rot.), 6.89 (brs, 1H, N*H*, rot. min.), 5.61 (s, 1H, H_5, rot. min.), 5.58 (s, 1H, H_{3a}, rot. min.), 5.01 (s, 1H, H_5, rot. maj.), 4.90 (s, 1H, H_{3a}, rot. maj.), 3.90 (s, 3H, O*C*H_3, rot. min.), 3.81 (s, 3H, O*C*H_3, rot. maj.), 1.15 (s, 9H, C(*C*H_3)$_3$, rot. maj.), 1.01 (s, 9H, C(*C*H_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 169.1 (*C*O_2Me, rot. maj.), 168.7 (*C*O_2Me, rot. min.), 162.8 (*C*HO, rot. maj.), 162.6 (*C*HO, rot. min.), 151.5 (C_3, rot. min.), 147.8 (C_3, rot. maj.), 130.4 (C_{qPh}, rot. maj.), 130.2 (C_{Ph}, rot. min.), 129.7 (C_{Ph}, rot. maj.), 129.0 (C_{Ph}, rot. min.), 128.9 (C_{Ph}, rot. maj.), 126.6 (C_{Ph}, rot. min.), 126.0 (C_{Ph}, rot. maj.), 95.3 (C_{6a}, rot. maj.), 93.7 (C_{6a}, rot. min.), 77.1 (C_5, rot. maj.), 75.4 (C_5, rot. min.), 59.0 (C_{3a}, rot. min.), 56.8 (C_{3a}, rot. maj.), 54.3 (O*C*H_3, rot. min.), 54.0 (O*C*H_3, rot. maj.), 39.7 (*C*(CH$_3$)$_3$, rot. min.), 39.2 (*C*(CH$_3$)$_3$, rot. maj.), 26.7 (C(*C*H$_3$)$_3$, rot. min.), 26.3 (C(*C*H$_3$)$_3$, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{17}H_{21}N_3O_3SNa$ 370.1196; found 370.1190

Synthesis of (1*R*,3*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105a and **(1*R*,3*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105a´**



The crude of the reaction of the nitrogen extrusion of the intermediate Δ^1-pyrazoline *exo***-102b** was dissolved in acetone (6 mL) at 0 ºC and following the general experimental procedure for the deoxigenation of sulfoxides, the reaction was completed in 4 hours. The brown oil obtained was purified by column chromatography (EtOAc/hexane 10/90) to afford a mixture of diastereoisomers **105a**/**105a´** in a ratio 44/56 (250 mg, 0.97 mmol, 60% in 3 steps). Both isomers could be separated for a proper characterization, **105a** as a yellow oil and **105a´** as colourless oil.

(1*R*,3*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105a

$[\alpha]_D^{24}$: -57º (*c* 1.2, $CHCl_3$)

IR (neat) v 1731, 1691, 1364, 1331, 1305, 1232, 1195 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.41)] δ 8.36 (s, 1H, C*H*O, rot. maj.), 8.22 (s, 1H, C*H*O, rot. min.), 5.41 (s, 1H, H_3, rot. maj.), 4.85 (s, 1H, H_3, rot. min.), 3.81 (s, 3H, OCH_3, rot. maj.), 3.76 (s, 3H, OCH_3, rot. min.), 3.05 (d, *J* = 5.8, 1H, H_5, rot. maj.), 3.00 (d, *J* = 6.1, 1H, H_5, rot. min.), 1.95-1.88 (m, 1H, H_6, rot. maj.), 1.79 (q, *J* = 6.4, 1H, H_6, rot. min.), 1.38 (d, *J* = 6.5, 3H, CH_3, rot. min.), 1.30 (d, *J* = 6.4, 3H, CH_3, rot. maj.), 0.97 (s, 9H, C(CH_3)$_3$, rot. min.), 0.93 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 169.1 (*C*O_2Me, rot. maj.), 168.9 (*C*O_2Me, rot. min.), 164.5 (*C*HO, rot. maj.), 162.3 (*C*HO, rot. min.), 85.8 (C_3, rot. min.), 81.1 (C_3, rot. maj.), 56.2 (C_1, rot. maj.), 54.0 (C_1, rot. min.), 53.1 (O*C*H_3, rot. maj.), 52.8 (O*C*H_3, rot. min.), 49.2 (C_6, rot. maj.), 47.8 (C_6, rot. min.), 38.9 (C_5, rot. min.), 38.1 (*C*$(CH_3)_3$, rot. maj.), 37.8 (*C*$(CH_3)_3$, rot. min.), 37.4 (C_5, rot. maj.), 26.1 (C(*C*H_3)$_3$, rot. maj.), 25.7 (C(*C*H_3)$_3$, rot. min.), 12.6 (*C*H_3, both rot.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{12}H_{19}NO_3SNa$ 280.0978; found 280.0973

(1*R*,3*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate 105a´

$[\alpha]_D^{24}$: +24° (*c* 0.5, $CHCl_3$)

IR (neat) ν 1732, 1692, 1438, 1395, 1364, 1309, 1250, 1171 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.39)] δ 8.28 (s, 1H, C*H*O, rot. min.), 8.05 (s, 1H, C*H*O, rot. maj.), 5.38 (s, 1H, H_3, rot. maj.), 4.83 (s, 1H, H_3, rot. min.), 3.76 (s, 3H, OCH_3, rot. maj.), 3.73 (s, 3H, OCH_3, rot. min.), 3.40 (d, *J* = 7.9, 1H, H_5, rot. maj.), 3.24 (d, *J* = 7.8, 1H, H_5, rot. min.), 2.37-2.30 (m, 1H, H_6, rot. min.), 2.22-2.13 (m, 1H, H_6, rot. maj.), 1.16 (d, *J* = 6.2, 3H, CH_3, rot. maj.), 1.12 (d, *J* = 6.2, 3H, CH_3, rot. min.), 0.98 (s, 9H, C(CH_3)$_3$, rot. min.), 0.95 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.3 (*C*O_2Me, rot. maj.), 170.2 (*C*O_2Me, rot. min.), 164.2 (*C*HO, rot. maj.), 161.6 (*C*HO, rot. min.), 87.0 (C_3, rot. min.), 83.1 (C_3, rot. maj.), 54.5 (C_1, rot. maj.), 54.2 (C_1, rot. min.), 53.1 (O*C*H_3, rot. maj.), 52.8 (O*C*H_3, rot. min.), 38.7 (*C*(CH_3)$_3$, rot. maj.), 38.2 (*C*(CH_3)$_3$, rot. min.), 38.1 (C_5, rot. maj.), 37.9 (C_5, rot. min.), 36.9 (C_6, rot. maj.), 34.4 (C_6, rot. min.), 25.8 (C(*C*H_3)$_3$, rot. maj.), 25.4 (C(*C*H_3)$_3$, rot. min.), 8.9 (*C*H_3, rot. min.), 8.6 (*C*H_3, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{12}H_{19}NO_3SNa$ 280.0978; found 280.0979

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[56] We excluded from these calculations the reaction between **39a** and **D6** predicted to be of inverse demand, i.e diazoalkane and thiazoline acting as electrophile and nucleophile, respectively.

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Chapter IV

Synthesis of cysteine analogues bearing an isoxazolidine ring between α and β positions

IV. Synthesis of cysteine analogues bearing an isoxazolidine ring between α and β positions

1. INTRODUCTION

Isoxazolidines have been of great interest since several years ago. On the one side, they are considered versatile synthetic intermediates in organic chemistry due to the labile nature of the N-O bond under mild conditions. Thus, the reductive ring opening allows to obtain 1,3 amino alcohols and diverse heterocycles such as α-amino lactones, α-hydroxy lactams or β-lactams, among others.[1] Moreover, isoxazolidines have been studied for years due to their applications in medicine such as antiviral[2], antifungal/antimicrobial[3] agents or for their anti-inflammatory,[4] cytotoxic and antitumor/ anticancer[2a,5] activities among others[1,3a,3b] (*Figure 17*).

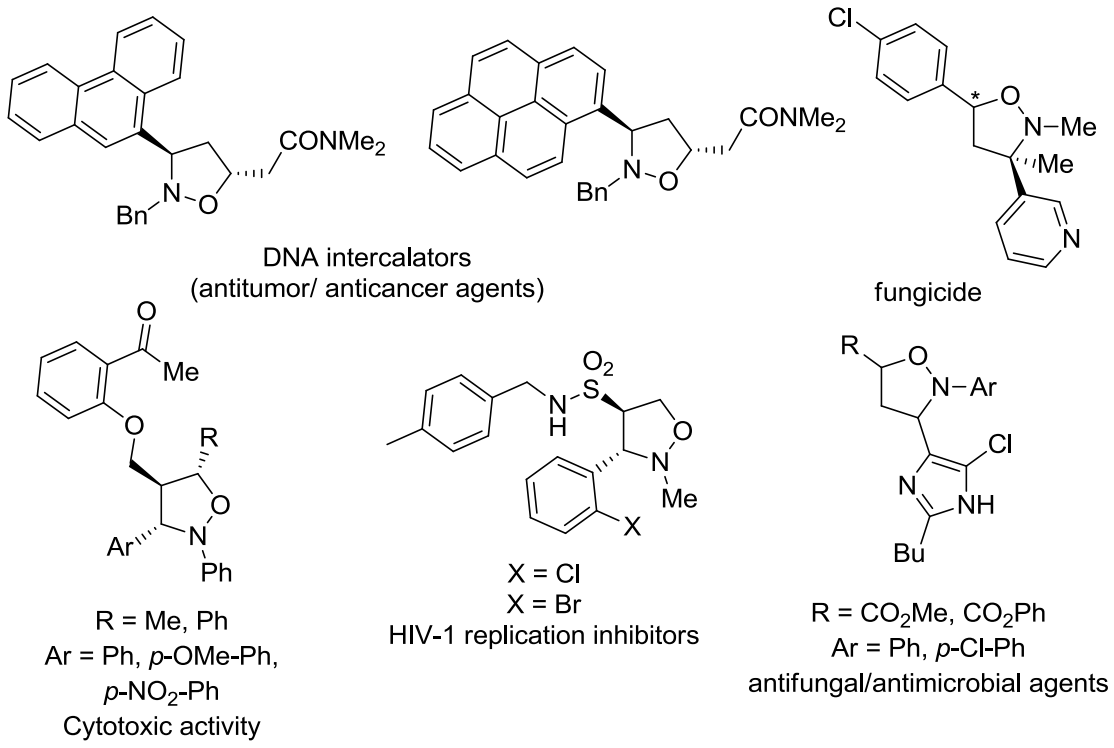
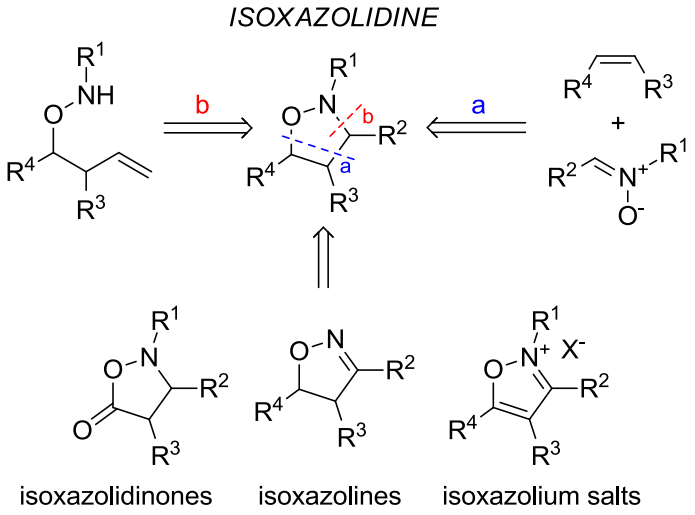


Figure 17. Some examples of isoxazolidines with medicinal applications

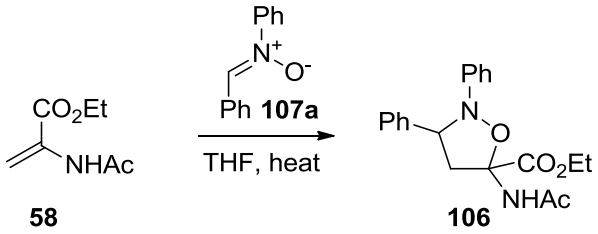
Because of the great importance of isoxazolidine ring, several synthetic procedures have been developed in order to obtain them. The most important are; 1,3-dipolar cycloaddition reaction between an alkene and a nitrone (disconnection ***a***, *Scheme 31*), firstly described by Morita *et al.*[6] in 1967. Since then a vast number of related papers have been published.[7] This method allows the formation of up to three stereogenic carbons in just one reaction step, using as starting materials nitrones and alkenes with different substituents in the carbons. Within this context, it has been considered as a valuable strategy to develop the diastereo- and enantioselective synthesis of highly substituted isoxazolidines by either metal or organocatalysis.[1,7b,8] Another approach to prepare such compounds is by the cyclization of unsaturated hydroxylamines, either by electrophilic cyclizations,[9]

Palladium-mediated cyclizations,[8a,10] radical cyclizations[11] or Michael additions[12] (disconnection ***b***, *Scheme 31*). The selective reduction of isoxazolidinones,[13] isoxazolines[14] and isoxazolium salts[15] also allows to obtain the target isoxazolidines (*Scheme 31*).



Scheme 31. Main synthetic routes to obtain the isoxazolidine ring

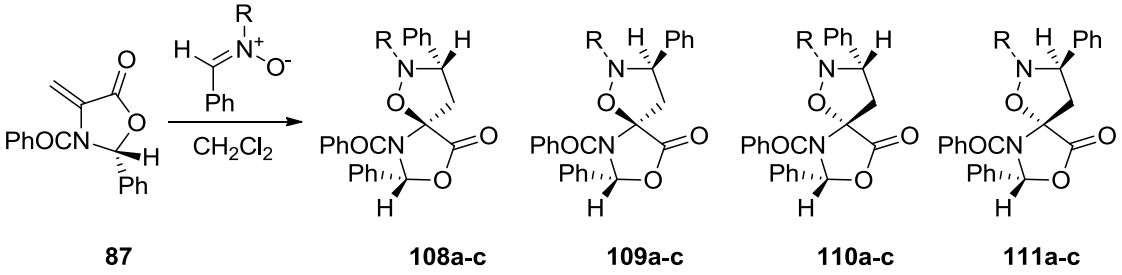
However, the synthesis of α-amino acids incorporating an isoxazolidine scaffold has been scarcely described. To the best of our knowledge few examples involving the 1,3-dipolar cycloaddition between nitrones and dehydroamino acids as dipolarophiles have been reported. In this sense, Horikawa *et al.*[16] described the 1,3-dipolar cycloaddition of ethyl *N*-acetyl-α,β-dehydroalaninate **58** with *C*,*N*-diphenylnitrone **107a** under thermic activation, affording regioselectively the mixture of 5,5-disubstituted isoxazolidines **106** in a ratio 71/29, although the relative configuration of no one diastereoisomer was reported (*Scheme 32*).



Scheme 32

Later, Pyne *et al.*[17] described the 1,3-dipolar cycloaddition between the chiral oxazolidinone **87** and some acyclic nitrones **107a-c** and cyclic nitrones **107d-e**. The results and conditions for the reaction are shown in *table 6* and *table 7*.

Table 6. Results and conditions for 1,3-dipolar cycloaddition between the oxazolidinone **87** and nitrones **107a-c**



87 **108a-c** **109a-c** **110a-c** **111a-c**

R= Ph (**107a**), ^{t}Bu (**107b**), Me (**107c**)

Entry	Dipole	Time (d)	Temp. (°C)	Yield %[a]	Products ratio[b]
					108a/109a
1	**107a**	7	r.t.	94	70/30
2		3	60	99	62/38
					108b/111b
3	**107b**	10	r.t.	36	88/12
4		22	r.t.	52	88/12
5		31	r.t.	69	89/11
6		3	60	4	72/28
7		10	60	49	55/45
8		22	60	66	33/67
					108c/109c/110c/111c
9	**107c**	15	r.t.	50	28/44/22/6
10		8	60	53	11/30/39/20

[a]Isolated yield. [b]Determined on the reaction mixture by ^{1}H NMR.

As it is gathered in the table above all reactions proceeded with complete regioselectivity to give 5,5 disubstituted cycloadducts, which are in fact formed by the addition of the oxygen to the quaternary carbon of the double bond, independently of the nitrone employed. When the reaction of the oxazolidinone **87** and nitrone **107a** was carried out at room temperature and a long reaction time (7 days) a mixture of products **108a** and **109a** was obtained in favour of the isomer resulted from an *endo* approach (*Table 6*, entry 1). This reaction was also carried out at 60 °C, without an appreciable change in the diastereomeric ratio (entry 2). Therefore, the increase in reaction temperature showed no influence on the diastereomeric ratio and yield (entry 1 *vs*. entry 2). In order to determinate if there was interconversion of **108a** into **109a** a solution of diastereomerically pure **108a** was heated at 60 °C for 3 days but neither interconversion of **108a** into **109a** nor formation of nitrone **107a** and oxazolidinone **87** were detected.

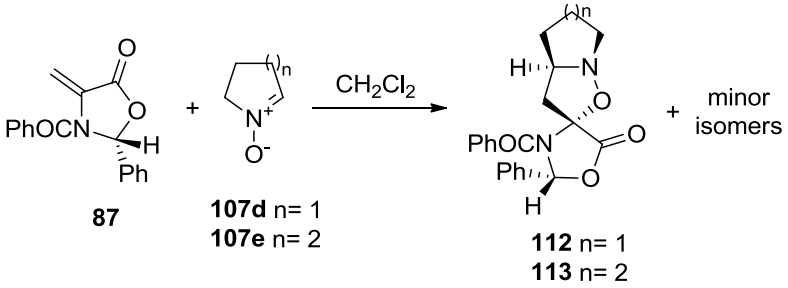
In contrast, they found out that cycloaddition reactions of **87** and nitrones **107b** and **107c** were reversible at 60 °C. Moreover, oxazolidinone **87** and nitrones **107b,c** were always detected in the reaction crude mixtures. In this sense, the

reaction between **87** and **107b** at room temperature afforded a mixture of diastereoisomers **108b** and **111b** in a ratio 88/12 (*Table 6*, entries 3 and 4). The diastereomeric ratio remained unchanged for 31 days (*Table 6*, entries 3-5). However, the diastereomeric ratio switched with the reaction time and the temperature (entries 6-8). Thus, the diastereoisomer **108b** is favored kinetically and **111b** is thermodynamically more stable.

Cycloaddition of oxazolidinone **87** and nitrone **107c** at room temperature gave four diastereoisomers **108**-**111c** (*Table 6,* entry 9). Instead, the reaction carried out at 60 ºC gave also a mixture of the same four diastereoisomers although the major cycloadducts were the spirocyclic isoxazolidines **109c** and **110c** (entry 10). Therefore, the pair **87**/**107b** showed the same behavior than the pair **87**/**107c**.

On the other hand, the cycloadditions between the oxazolidinone **87** and cyclic nitrone **107d** were highly diastereoselective at room temperature and at 40 ºC although cycloadduct **112** was obtained in low yields in both cases (*Table 7*, entries 1 and 2). The reaction of the oxazolidinone **87** and nitrone **107e** gave three diastereomeric cycloadducts being **113** the major one (entries 3 and 4). However, the stereochemistry of the two minor cycloadducts could not be determined.

Table 7. Results and conditions for the 1,3-dipolar cycloaddition between oxazolidinone **87** and cyclic nitrones **107d** and **107e**



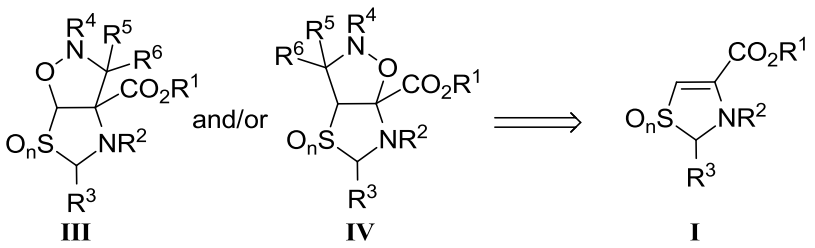
Entry	Dipole	Time (d)	Temp. (ºC)	Yield %[a]	Products ratio[b]
					112/ minor isomer
1	**107d**	2	r.t.	27	>98/<2
2		2	40	33	92/8
					113/ minor isomers
3	**107e**	1.5	r.t.	25	85/15
4		1.5	40	30	70/15/15

[a]Isolated yield. [b]Determined on the reaction mixture by ^{1}HNMR.

2. OBJECTIVES

Due to the few articles published on 1,3-dipolar cycloaddition between nitrones and α,β-dehydroamino acids, we envisioned a good opportunity to extend the knowledge in this field.

Thus, our main objective is to disclose the reactivity, regio-, diastereo- and enantioselectivity in the 1,3-dipolar cycloaddition reaction between our homochiral thiazolines **I** and several nitrones. The obtained bicyclic isoxazolidine rings **III** and/or **IV** could have applications in biological and medicinal fields.



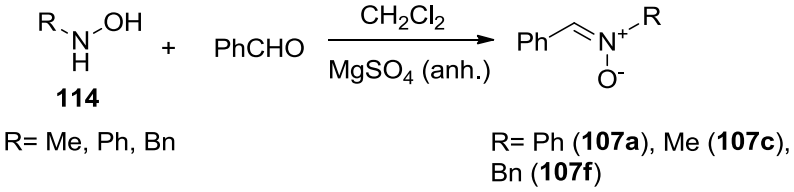
III **IV** **I**

3. RESULTS AND DISCUSSION

As it has been mentioned, the reactivity, regio- and diastereoselectivity between thiazolines **39a**-**c** and nitrones will be depicted hereunder.

3.1. 1,3-Dipolar cycloaddition reaction between thiazolines 39a-c and acyclic nitrones with different *N*-substitution

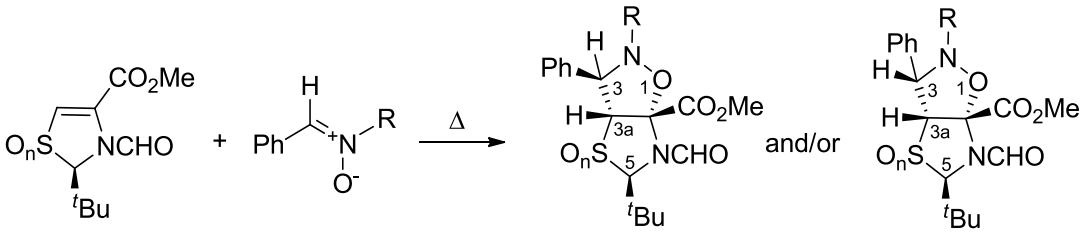
Firstly, we explored if the substitution on nitrogen atom of the nitrone exerts some influence in the reactivity, regio- or diastereoselectivity in 1,3-dipolar cycloaddition reaction between the cited thiazolines **39a**-**c** and various nitrones. In this sense, nitrones **107a**, **107c** and **107f** were obtained by condensation of the corresponding *N*-alkyl- or arylhydroxylamine **114** and benzaldehyde, as it is described in the bibliography[18] obtaining the target nitrones **107a, 107c** and **107f** in good yields (*Scheme 33*).



Scheme 33. Synthetic procedure to obtain nitrones **107a**, **107c** and **107f**

1,3-dipolar cycloaddition reactions between thiazolines **39a**-**c** and nitrones **107a, 107c** and **107f** were performed under thermic activation[3a,19] in a sealed tube using toluene as solvent (*Table 8*).

Table 8. Results and conditions for the 1,3-dipolar cycloaddition reactions between thiazolines **39a**-**c** and nitrones **107a**, **107c** and **107f**



39a n= 0
39b n= 1
39c n= 2

107a R= Ph
107c R= Me
107f R= Bn

115-117a-c

115-117a´-c´

Entry[a]	n	R	T. (°C)	Time (h)	Yield (%)[b] (Recovered s.m.)	*exo*/*endo* ratio[c] (115-117a-c/115-117a´-c´)
1	0	Me	80	24	-	-
2	0	Me	120	96	traces	-
3	0	Me	100	96	29 (36)	39/61 (**115a/115a´**)
4	0	Me	100	72	39 (29)	41/59 (**115a/115a´**)
5	1	Me	100	5	73	100/0 (**115b/115b´**)
6	2	Me	60	3	86	100/0 (**115c/115c´**)
7	0	Ph	100	96	-	-
8	0	Ph	100	48	3 (64)	58/42 (**116a/116a´**)
9	0	Ph	100	13	49 (34)	85/15 (**116a/116a´**)
10	1	Ph	100	5	85	100/0 (**116b/116b´**)
11	2	Ph	60	3	90	100/0 (**116c/116c´**)
12	0	Bn	100	96	50 (47)	52/48 (**117a/117a´**)
13	0	Bn	100	48	24 (40)	73/27 (**117a/117a´**)
14	1	Bn	100	3	95	100/0 (**117b/117b´**)
15	2	Bn	60	3	91	100/0 (**117c/117c´**)

[a]All reactions were carried out with 3 eq. of nitrone. [b]Isolated yield. [c]Determined by ^{1}H NMR.

Within this context, a solution of thiazoline **39a** and nitrone **107c** (3 eq.) in toluene was allowed to stir at 80 °C for 1 day, but no product formation could be observed by TLC and ^{1}H NMR of the reaction mixture, recovering the starting thiazoline **39a** unaltered (*Table 8*, entry 1). Then, the reaction temperature was increased up to 120 °C and was allowed to stir for 4 days, but only traces of the desired product could be detected by ^{1}H NMR (entry 2). Taking into account these results, it was decided to carry out another reaction, heating a mixture of thiazoline **39a** and nitrone **107c** in toluene at 100 °C for 4 days, affording a mixture of **115a** and **115a´** cycloadducts in a ratio *exo*/*endo* 39/61 in low yield and an incomplete conversion (entry 3). The reaction yield was slightly improved when the reaction time was shortened to 3 days without changing the diastereomeric ratio (entry 4).

It was next attempted the reactivity of thiazolines **39b** and **39c** with nitrone **107c**. These thiazolines showed to be much more reactive and selective. Within this context, a solution of thiazoline **39b** and nitrone **107c** was heated at 100 °C for 5 hours affording exclusively **115b** with good yield (*Table 3*, entry 5). Starting from

thiazoline **39c** the reaction mixture was heated at 60 ºC for 3 hours to obtain a single product **115c** with very good yield (entry 6). These results showed that the electronic features of both sulfinyl and sulfonyl groups in thiazolines **39b,c**, respectively, are determinant in the reactivity and diastereoselectivity of this kind of 1,3-dipolar cycloaddition.

After this first reactivity screening between thiazolines **39a**-**c** and nitrone **107c** in the 1,3-dipolar cycloaddition, *N*,*C*-diphenylnitrone **107a** and *N*-benzyl-*C*-phenylnitrone **107f** were tested. Thus, a solution of thiazoline **39a** and nitrone **107a** in toluene was heated at 100 ºC for 4 days, but it was no possible to identify any cycloadduct from ^{1}H NMR of the reaction mixture, recovering unreacted thiazoline **39a** (*Table 8,* entry 7). As it is well-known that *N*-aryl nitrones are more reactive than *N*-alkyl nitrones.[20] Thus, the reaction was repeated in the same conditions heating for 48 hours (entry 8), but only traces of the target compound were observed in ^{1}H NMR. In view of these results, the reaction time was considerably reduced to 13 hours, obtaining a mixture of **116a** and **116a´** cycloadducts in a ratio *exo*/*endo* 85/15 in moderate yield (entry 9).

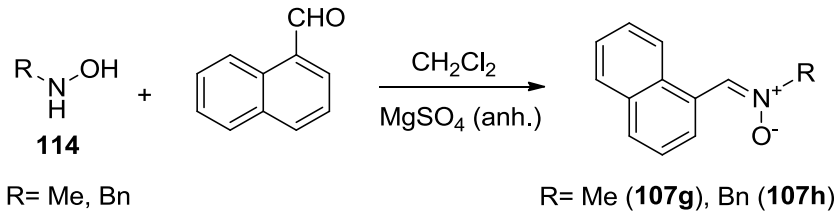
Furthermore, the reaction of **39b** with **107a** at 100 ºC for 5 hours proceeded with very good yield to obtain exclusively the cycloadduct **116b** (entry 10) and a solution of thiazoline **39c** and nitrone **107a** in toluene heated at 60 ºC for 3 hours afforded **116c** in excellent yield (entry 11).

Finally, thiazoline **39a** and nitrone **107f** were heated at 100 ºC for 4 and 2 days. In this case, longer reaction times showed a better yield, 50% *vs*. 24% (*Table 8*, entries 12 and 13) although the diastereomeric ratios obtained **117a**/**117a´** were 52/48 and 73/27, respectively. This difference in the selectivity could be due to cycloreversion processes.

On the other hand, the 1,3 dipolar cycloaddition reactions regarding the use of thiazolines **39b** or **39c** as starting materials and the nitrone **107f** afforded cycloadducts **117b** and **117c**, respectively in excellent yields and selectivities in few hours (*Table 8*, entries 14 and 15).

In order to increase the knowledge of the reactivity and diastereoselectivity of the reaction, it was decided to change the phenyl substituent on the iminium carbon for another aryl substituent. In this sense, *Z*-*N*-(1-naphthylmethylene)methanamine oxide **107g** and *Z*-*N*-(1-naphthylmethylene)benzenamine oxide **107h**[21] were prepared following the same

procedure applied for the synthesis of the other nitrones in this chapter (*Scheme 34*).

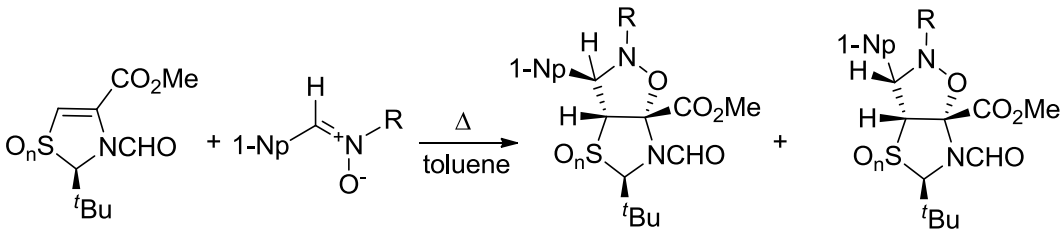


R= Me, Bn

R= Me (**107g**), Bn (**107h**)

Scheme 34. Synthetic procedure to obtain nitrones **107g,h**

***Table* 9**. Results and conditions for the 1,3-Dipolar cycloaddition reaction between thiazolines **39a**-**c** and nitrones **107g** and **107h**



39a n= 0
39b n= 1
39c n= 2

107g R= Me
107h R= Bn

exo
118a-c
119b,c

endo
118a´-c´
119b´,c´

Entry[a]	n	R	T. (°C)	Time (h)	Yield (%)[b] (Recovered s.m.)	*exo*/*endo* ratio[c] (118-119a-c/118-119a´-c´)
1	0	Me	100	24	32 (45)	60/40 (**118a/118a´**)
2	0	Me	100	48	30 (60)	34/66 (**118a/118a´**)
3	0	Me	100	72	32 (33)	19/81 (**118a/118a´**)
4	1	Me	100	3	98	100/0 (**118b/118b´**)
5	2	Me	60	3	98	100/0 (**118c/118c´**)
6	1	Bn	100	5	94	100/0 (**119b/119b´**)
7	2	Bn	60	5	86	100/0 (**119c/119c´**)

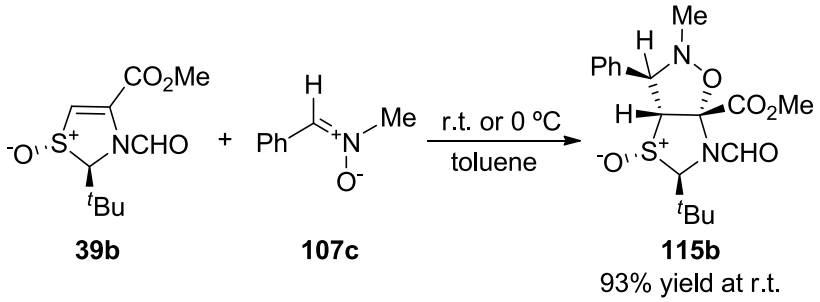
[a]All reactions were carried out with 3 eq. of nitrone. [b]Isolated yield. [c]Determined by ^{1}H NMR

In this sense, three solutions of thiazoline **39a** and nitrone **107g** in toluene were heated at 100 °C for 1, 2 or 3 days, respectively. While mixture of cycloadducts **118a**/**118a´** were obtained in similar yields, the diastereoisomeric ratio **118a**/**118a´** switched from 60/40 for 1 day to 34/66 for 2 days and 19/81 for 3 days (*Table 9*, entries 1-3). These results suggested the possibility of cycloreversion processes; the *exo* isomer **118a** seemed to turn into the *endo* isomer **118a´** increasing the reaction time. Hence, a pure sample of *endo* isomer **118a´** was heated at 100 °C. The presence of the starting material **39a** along with nitrone **107g** in the ^{1}H NMR of the reaction mixture, confirmed the suspected cycloreversion.

On the other hand, reactions regarding the use of sulfinyl thiazoline **39b** and sulfonyl thiazoline **39c** with nitrone **107g** were carried out at 100 ºC and 60 ºC, respectively, affording in few hours the cycloadducts **118b,c** with excellent yields and total diastereoselectivities (*Table 9*, entries 4 and 5).

This sequence of 1,3-dipolar reactions with thiazolines and nitrones had confirmed the difference on the reactivity and diastereoselectivity of thiazoline **39a** in comparison with thiazolines **39b** and **39c**. Thus, it was decided to carry out the cycloaddition reaction between the more reactive thiazolines **39b** and **39c** and *Z*-*N*-(1-Naphthylmethylene)benzenamine oxide **107h**. Thus, both solutions of thiazolines **39b,c** and nitrone **107h** in toluene were heated at 100 ºC and 60 ºC for 5 hours affording the bicyclic cycloadducts **119b,c** in excellent yields (*Table 9*, entries 6 and 7).

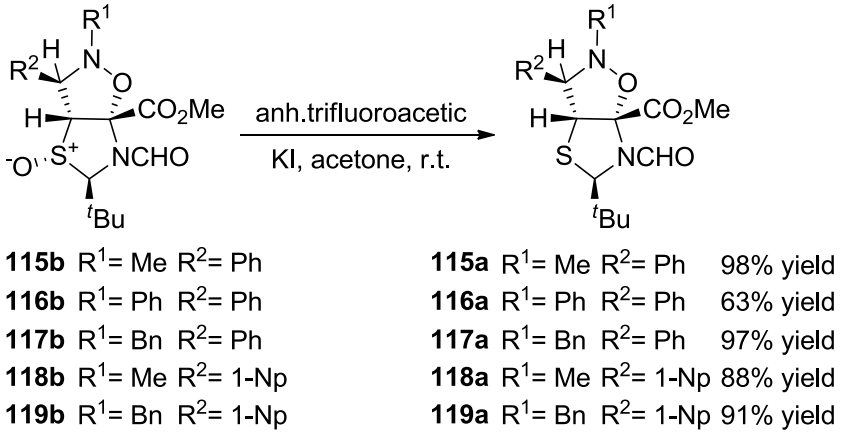
In order to know if kinetic conditions the selectivity of the reaction changed, a set of 1,3-dipolar cycloadditions between thiazoline **39b** and *N*-methyl-*C*-phenyl nitrone **107c** (3 eq. and 1 eq.) were carried out in toluene for 8 days at 0 ºC and at room temperature (3 eq. of **107c**). The reactions carried out at 0 ºC proceeded very slowly, thus giving the starting thiazoline **39b** as major product detected in the crude reaction by ^{1}H NMR analysis, along with a few amount of the *exo* compound **115b**, even after 8 days stirring. However, the reaction carried out at room temperature afforded **115b** in excellent yield. Therefore, it was concluded that product **115b** was the more favored under thermodynamic control (100 ºC) and kinetic conditions (0-25 ºC) (*Scheme 35*).



Scheme 35. Kinetic conditions for the 1,3-dipolar cycloaddition between **39b** and **107c**

Finally, the sulfinyl group of the compounds **115**-**119b** was reduced to sufanyl moiety following the experimental procedure described by Baldwin *et al.*[22] So, bicyclic compounds **115**-**119b** were dissolved in acetone at 0 ºC and then trifluoroacetic anhydride (2 eq.) and KI (4 eq.) were added. Then, the reaction mixture was allowed to proceed at room temperature to obtain the sulfanyl derivatives **115-119a** (*Scheme 36*) with very good yields. Therefore, bicycles **115-**

118a were obtained either from reduction of sulfinyl group of bicyclic isoxazolidines **115**-**118b** and by 1,3-dipolar cycloaddition of thiazoline **39a** and the corresponding nitrones.



Scheme 36. Reduction of the sulfinyl group of **115-119b**

Structural elucidation of the obtained cycloadducts was made on the basis of ^{1}H NMR. The presence of two doublets corresponding to H3 and H3a, corroborated both the regioselectivity observed and the formation of two diastereoisomers when thiazoline **39a** was employed as starting material (*Figure 18*).

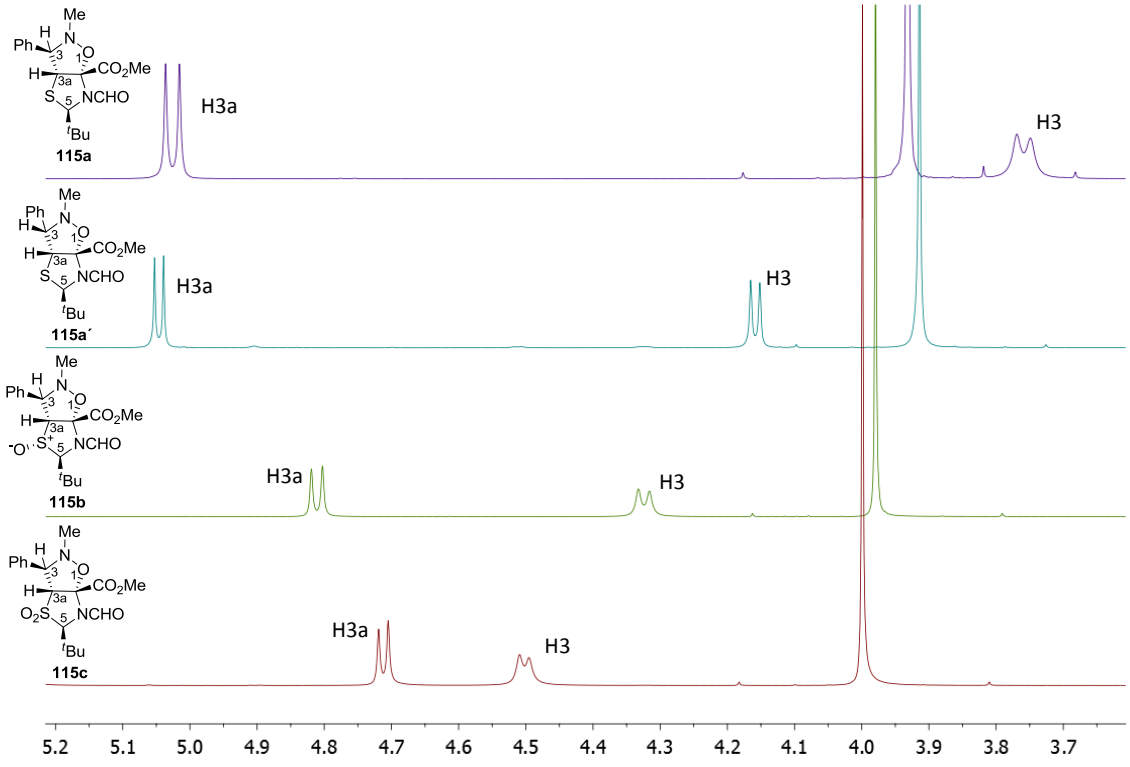


Figure 18. ^{1}H NMR of **115a-c** and **115a´**

NOESY experiments of each compound were made to determinate the configuration of the stereogenic carbons, especially C3. However, the analysis of the NOESY correlations was difficult due to the cross peaks between vicinal H3 and H3a protons, which made the elucidation less reliable. The cross peaks between H3 and H3a were present in every NOESY experiment of each bicyclic isoxazolidine, although the intensity of these cross peaks for *exo* isomers was weak and for *endo* isomers was intense. Instead, the cross peaks between H3a and the phenyl substituent in isoxazolidines **115a-c** (*exo*) were intense while the signal of that cross peak for **115a´** (*endo*) was weak (*Figure 19*). This fact and the presence of other cross peaks between non vicinal protons, as the cross peak between H5 and the phenyl group located at C3 that was observed in NOESY experiment of **117a´** (*endo*), allowed us to make a preliminary assignation of the steriogenic carbons. Thus, the pre-assigned absolute configuration for the *exo* thiazolidine-isoxazolidine rings bearing a sulfanyl or sulfonyl groups was (3*R*,3a*R*,5*R*,6a*S*) and for the *exo* having a sulfinyl moiety (3*R*,3a*R*,4*R*,5*R*,6a*S*). On the contrary, for the *endo* bicyclic isoxazolidines with a sulfanyl or sulfonyl was (3*S*,3a*R*,5*R*,6a*S*) and for the *endo* bearing a sulfinyl group (3*S*,3a*R*,4*R*,5*R*,6a*S*).

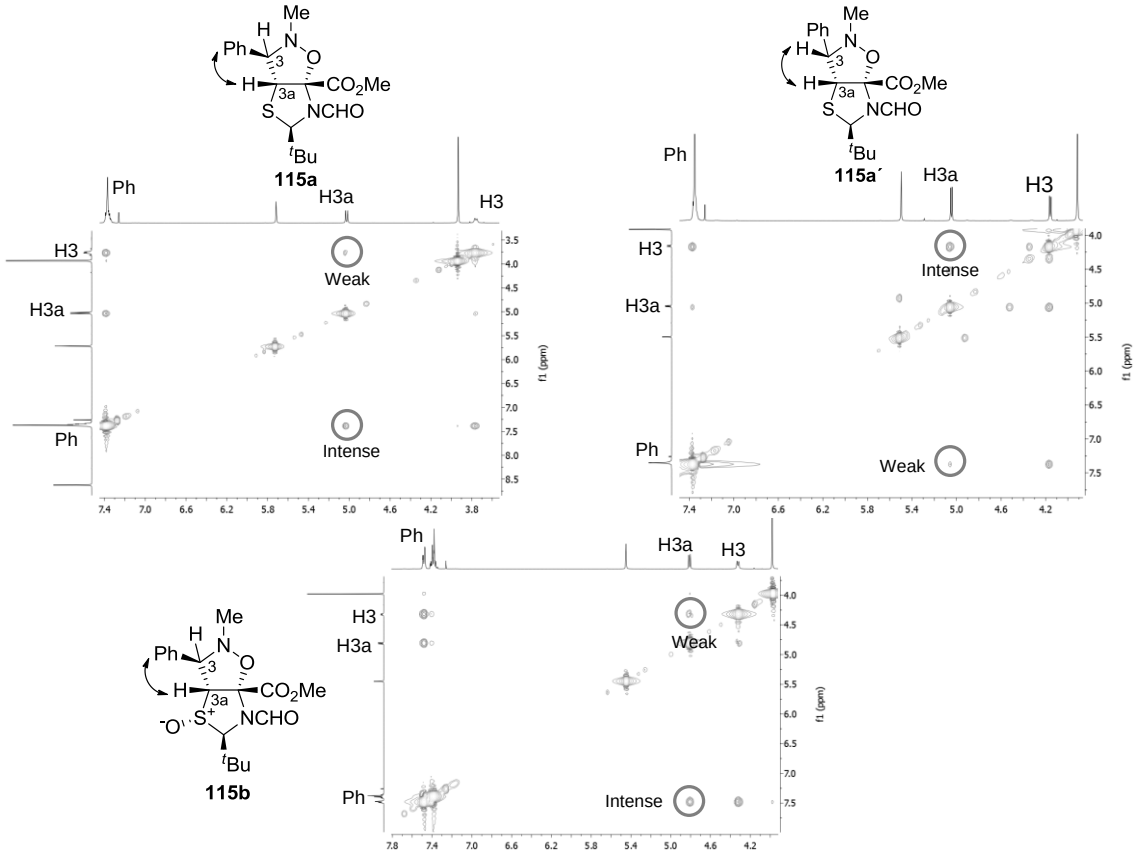


Figure 19. NOESY experiments of **115a,b** and **115a´**

However, we thought to perform an exhaustive analysis of the coupling constants and chemical shifts in ^{1}H NMR of every product obtained that would allow us to support the stereochemical evidences retrieved from NOESY experiments.

In the bibliography is well documented and accepted that in isoxazolidine rings the *J trans* values (0-6 Hz) are smaller than *J cis* values (≥6 Hz).[5l,23] In *table 10* are depicted all the coupling constants for the obtained cycloadducts.

Table 10. Representative coupling constants (*J* in Hz) and chemical shifts values (δ in ppm) for bicyclic isoxazolidines **115-118a-c** and **115-118a´**

Entry[a]	Product	N-R[1]	C-R[2]	H3	H3a	H5	*J* H3-H3a
1	**115a**	Me	Ph	3.76	5.03	5.72	6.2*
2	**115a´**	Me	Ph	4.16	5.05	5.50	5.4
3	**115b**	Me	Ph	4.32	4.81	5.45	6.6
4	**115c**	Me	Ph	4.50	4.71	5.25	5.7
5	**116a**	Ph	Ph	4.63	5.09	5.67	4.1*
6	**116a´**	Ph	Ph	5.02	5.25	5.56	5.7
7	**116b**	Ph	Ph	5.02	4.90	5.52	5.9
8	**116c**	Ph	Ph	5.21	4.81	5.30	4.9
9	**117a**	Bn	Ph	4.05	5.06	5.72	5.4*
10	**117a´**	Bn	Ph	4.39	5.07	5.53	5.6
11	**117b**	Bn	Ph	4.66	4.86	5.45	6.3
12	**117c**	Bn	Ph	4.77	4.82	5.26	5.4
13	**118a**	Me	1-Np	4.66	5.05	5.78	5.9*
14	**118a´**	Me	1-Np	4.88	5.35	5.49	5.3
15	**118b**	Me	1-Np	5.19	4.75	5.54	6.4
16	**118c**	Me	1-Np	5.37	4.70	5.32	5.6

[a]^{1}H NMR recorded in $CDCl_3$ as solvent.*Obtained from the reduction of sulfinyl group.

The *J*-values of almost every compound are in a range between 5 and 7 Hz, which could be in agreement for both *cis* and *trans* disposition between H3 and H3a. However, for the bicyclic isoxazolidine **116a** the $J_{H3\text{-}H3a}$ value is 4.1 Hz (*Table 10*, entry 5) which is smaller enough to conclude that H3 and H3a are in *trans* disposition. Although the $J_{H3\text{-}H3a}$ value for **116a´** is 5.7 Hz (entry 6) corresponds unequivocally to a *cis* arrangement between H3 and H3a.

On this basis, as the cycloadduct **116a** is also obtained by reduction of sulfinyl moiety, and during that reaction the stereogenic carbons remained unaltered, it is possible to affirm that of 5.9 Hz for isoxazolidine **116b** (*Table 10*, entry 7) corresponds to a *trans* disposition of H3 and H3a. Therefore, the coupling constant $J_{H3\text{-}H3a}$ of 4.9 Hz for the bicyclic isoxazolidine **116c** bearing a sulfonyl group (entry 8), corresponds to a *trans* spatial arrangement between H3 and H3a.

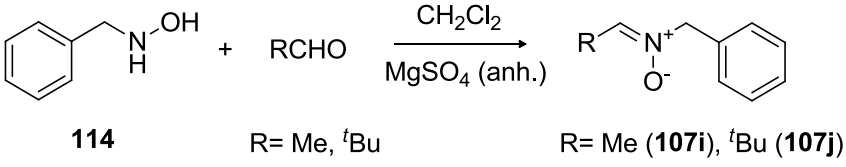
Moreover, some systematic patterns were observed in the chemical shifts of H3, H3a and H5. Within this context, if we pay attention to H5 chemical shifts, it is

possible to realize that the higher value of each group (*Table 10*, entries 1-4, 5-8, 9-12 and 13-16) belongs to the bicyclic isoxazolidines obtained from the reduction of the sulfinyl moiety **115-118a**, which have a value around 5.7 ppm (entries 1, 5, 9 and 13). It was also noted that the chemical shift of H3 in bicyclic isoxazolidines **115-118a** was always the smallest of its group (entries 1, 5, 9 and 13). This effect is in agreement with the proposed spatial assignment of the cycloadducts, since oxygen of sulfinyl and sulfonyl groups should exerts a deshielding effect in the chemical shift of H3 which is *cis* to the oxygen on the sulfur in compounds **115-118b,c** (entries 3 and 4, 7 and 8, 11 and 12, 15 and 16). In this sense, the difference between the chemical shifts of H3 protons corresponding to *exo* isomers **115-118b** and its reduced analogues **115-118a** are in a range from 0.4 to 0.6 ppm (entries 1 and 3, 5 and 7, 9 and 11 and 13 and 15), while differences of the chemical shift of the same proton for *exo* isomers **115-118b** and *endo* isomers **115-118a´** are in a range from 0 to 0.31 ppm (entries 2 and 3, 6 and 7, 10 and 11 and 14 and 15). Henceforth, it was certainty concluded that every sulfinyl and sulfonyl bicyclic cycloadducts **115-118b,c**, obtained by cycloaddition of the corresponding thiazolines **39b,c** are *exo*-isomers, as well as the sulfanyl bicyclic products **115-118a** obtained from the sulfinyl reduction of the isoxazolidines **115-118b**.

Therefore, we have found a rare case in which the *J cis* value is not always higher than *J trans* value in bicyclic isoxazolidine rings (*Table 10*, entries 1 and 2, 5 and 6, 9 and 10, 13 and 14).

3.2. 1,3-Dipolar cycloaddition reaction between thiazolines 39b,c and nitrones with different *C*-alkyl substitution

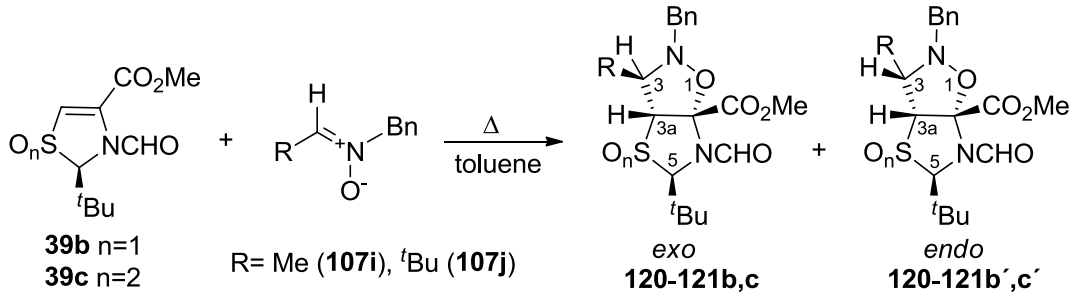
Furthermore, in order to increase the scope of the reaction, *N*-benzyl-*C*-alkyl nitrones were synthetized starting from *N*-benzyl hydroxylamine and pivalaldehyde or acetaldehyde, accordingly to the procedure previously cited in this chapter, of Dondoni *et al*,[18a] affording *Z*- *N*-benzyl-*C*-alkyl nitrones **107i** and **107j** with very good yields, respectively. The *Z* stereochemistry is well documented for the reported nitrones **107i**[24] and **107j**[24] (*Scheme 37*).



Scheme 37. Synthetic procedure for the synthesis of nitrones **107i,j**

Then, it was carried out the 1,3-dipolar cycloaddition between thiazolines **39b-c** and nitrones **107i,j**, under the same conditions performed in this chapter, by heating a solution of the corresponding thiazoline and nitrone in toluene in a sealed tube (*Table 11*).

Table 11. Results and conditions for the 1,3-dipolar cycloaddition between thiazolines **39b,c** and nitrones **107i,j**

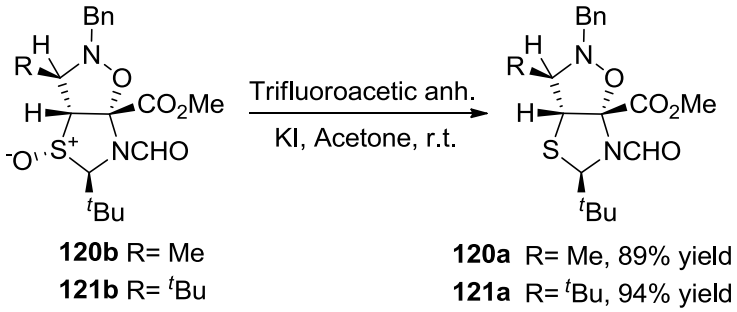


Entry[a]	n	R	T (ºC)	Time (h)	Yield (%)[b]	*exo*/*endo* ratio[c] (120-121b,c/120-121b´,c´)
1	1	Me	100	7	58	100/0 (**120b/120b´**)
2	1	Me	80	7	90	100/0 (**120b/120b´**)
3	2	Me	60	8	96	84/16 (**120c/120c´**)
4	2	Me	80	5	76	84/16 (**120c/120c´**)
5	1	^{t}Bu	100	5	91	100/0 (**121b/121b´**)
6	2	^{t}Bu	60	7	65	100/0 (**121c/121c´**)
7	2	^{t}Bu	80	7	74	100/0 (**121c/121c´**)

[a]All reactions were carried out with 3 eq. of nitrone. [b]Isolated yield. [c]Determined by ^{1}H NMR

In this way, thiazoline **39b** and nitrone **107i** were dissolved in toluene and heated at 100 ºC for 7 hours, affording the corresponding bicyclic isoxazolidine **120b** in moderate yield (*Table 11*, entry 1). This result was not in accordance with the results obtained previously for the 1,3-dipolar cycloaddition between thiazoline **39b** and other nitrones. So, it was thought that this nitrone was labile and could decompose at 100 ºC. Therefore, the reaction carried out at 80 ºC afforded **120b** in 90% yield (entry 2). Otherwise, thiazoline **39c** and *C*-methyl *N*-benzyl nitrone **107i** were dissolved in toluene and heating at 60 ºC and 80 ºC for 8 and 5 hours affording diastereomeric mixtures of bicyclic isoxazolidines **120c** and **120c´** in a ratio 84/16 in both cases (*Table 11*, entries 3 and 4). The best yield was obtained operating at 60 ºC (entry 3). Finally, it was carried out the 1,3-dipolar cycloaddition between thiazolines **39b,c** and *C-tert*-butyl *N*-benzyl nitrone **107j**. Hence, the reaction between thiazoline **39b** and nitrone **107j** afforded the corresponding bicyclic isoxazolidine **121b** in 91% yield (*Table 11*, entry 5) but the reaction starting from thiazoline **39c** led to the bicyclic isoxazolidine **121c** in 65% yield (entry 6). Due to this result, it was decided to carry out the cycloaddition between **39c** and nitrone **107j** at 80 ºC increasing the yield up to 74% under these new conditions (entry 7).

In addition, sulfinyl thiazolidines **120b** and **121b** were reduced to the corresponding sulfanyl bicyclic isoxazolidines **120a** and **121a**, following the experimental conditions described before, in very good yields (*Scheme 38*).



120b R= Me
121b R= ^{t}Bu

120a R= Me, 89% yield
121a R= ^{t}Bu, 94% yield

Scheme 38. Reduction of the sulfinyl group of **120b** and **121b**

The structural elucidation was made on the basis of ^{1}H NMR experiments. In this sense, the regiochemistry remained unaltered compared with the previous bicyclic isoxazolidines synthetized in this chapter. Values of coupling constants for bicyclic isoxazolidines **120a-c** and **121a-c** are in a range between 2-4 Hz (*Table 12*, entries 1-2 and 5-7). These low values are completely in agreement with a *trans* disposition between vicinal protons H3 and H3a.[23c] Thus, the cycloaddition reaction took place through an *exo* approach by the opposite face of the bulky *tert*-butyl group. Within this context, the identification of both isomers obtained in the 1,3-dipolar cycloaddition between thiazoline **39c** and nitrone **107i** was also made on the base of $J_{H3\text{-}H3a}$ values. Hence, the coupling constant value between H3 and H3a for the isolated cycloadduct **120c** is 3.0 Hz (entry 3) and for the isolated cycloadduct **120c´** is 5.6 Hz (entry 4) which are reasonable values for *trans* and *cis* arrangement, respectively.

Table 12. Coupling constants and chemical shifts values for **120-121a-c** and **121c´**

Entry[a]	Product	R[2]	H3	H3a	H5	J H3-H3a
1	**120a**	Me	3.31	4.65	5.67	2.2
2	**120b**	Me	3.84	4.49	5.41	4.0
3	**120c**	Me	4.05	4.35	5.21	3.0
4	**120c´**	Me	3.47	4.29	5.13	5.6
5	**121a**	^{t}Bu	3.27	5.06	5.84	2.2
6	**121b**	^{t}Bu	3.71	5.03	5.39	3.1
7	**121c**	^{t}Bu	3.90	4.71	5.39	2.9

3.3. Mechanistic consideration of the 1,3-dipolar cycloadditions between thiazolines 39a-c and nitrones

To rationalize the observed reactivity and selectivities of the cycloadditions, the reactions were studied at B3LYP-D3BJ/Def2SVP level of theory to calculate geometries of stationery points and then single point calculations at B3LYP-D3BJ/Def2TZVP level of theory were performed (see appendix, *Tables A19-A30*). The cycloaddition between thiazolines (**39a-c**) and four nitrones (**107a**, **107c**, **107f**, **107i**) have been studied (*Figure 20*). In the case of sulfoxide derivatives both relative orientations (Sa for *trans*, Sb for *cis)* between the oxygen and *tert*-butyl groups have been considered; the most stable Sa was considered for calculating energy barriers.

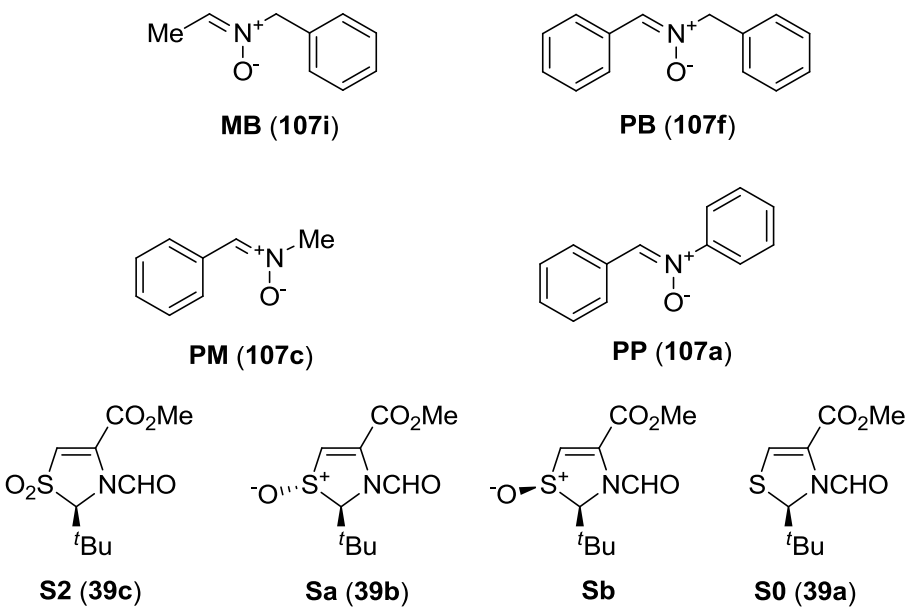
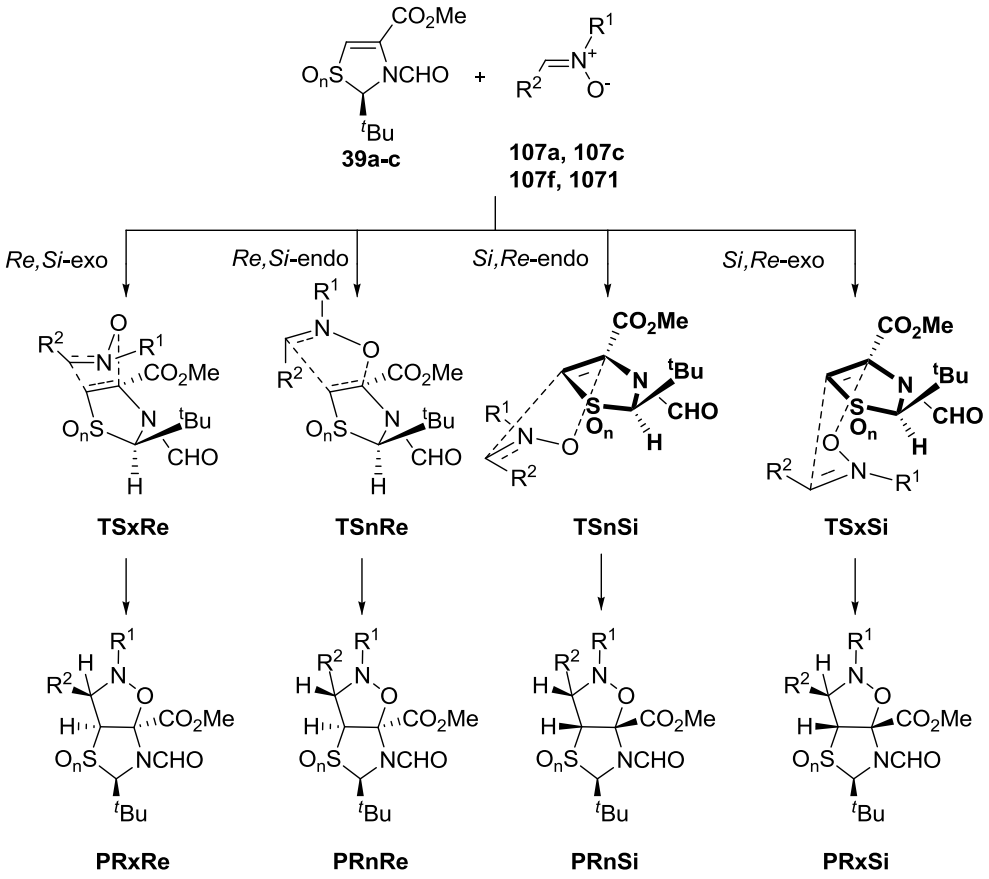


***Figure 20*.** Thiazolines and nitrones employed for the calculations

The nomenclature used for transition states (TS) and products (PR) includes two previous abbreviations and two later abbreviations. The first abbreviation refers to the thiazoline employed (S2 for **39c**, Sa for **39b**, Sb for the diastereoisomer (at the sulfur atom) of **39b**, and S0 for **39a**). The second abbreviation is referred to the nitrone employed (MB for **107i**, PB for **107f**, PM for **107c** and PP for **107a**). The later abbreviations indicate the *exo* and *endo* (x/n) approaches by *Re* and *Si* faces (*Re/Si* refers to carbon bearing the ester group, i.e: C4 of the thiazoline ring. Actually, *Re* corresponds to 4*Re*,5*Si* and *Si* corresponds to 4*Si,*5*Re*). For instance, S2-MB-TSnRe corresponds to the transition state of the reaction between S2 and MB, by the *Re* face of S2 following an *endo* approach. In *Scheme 39* are represented the four possible approaches between thiazolines **39a-c** and nitrones.



***Scheme 39*.** Approaches for the cycloaddition between **39a-c** and **107a**, **107c**, **107f**, **107i**

The analysis of the optimized transition structures and the corresponding IRCs revealed concerted processes in all cases, as expected. *Figure 21* collects the energy barriers for all the reactions studied. The *Figure 21* is divided into four sections corresponding to nitrones studied **107i** (MB), **107f** (PB), **107c** (PM) and **107a** (PP). Within each section the energy of transition structures corresponding to the reaction with S2, Sa, Sb and S0 are represented. The different energy barriers for each reaction are given in vertical according to the colour code.

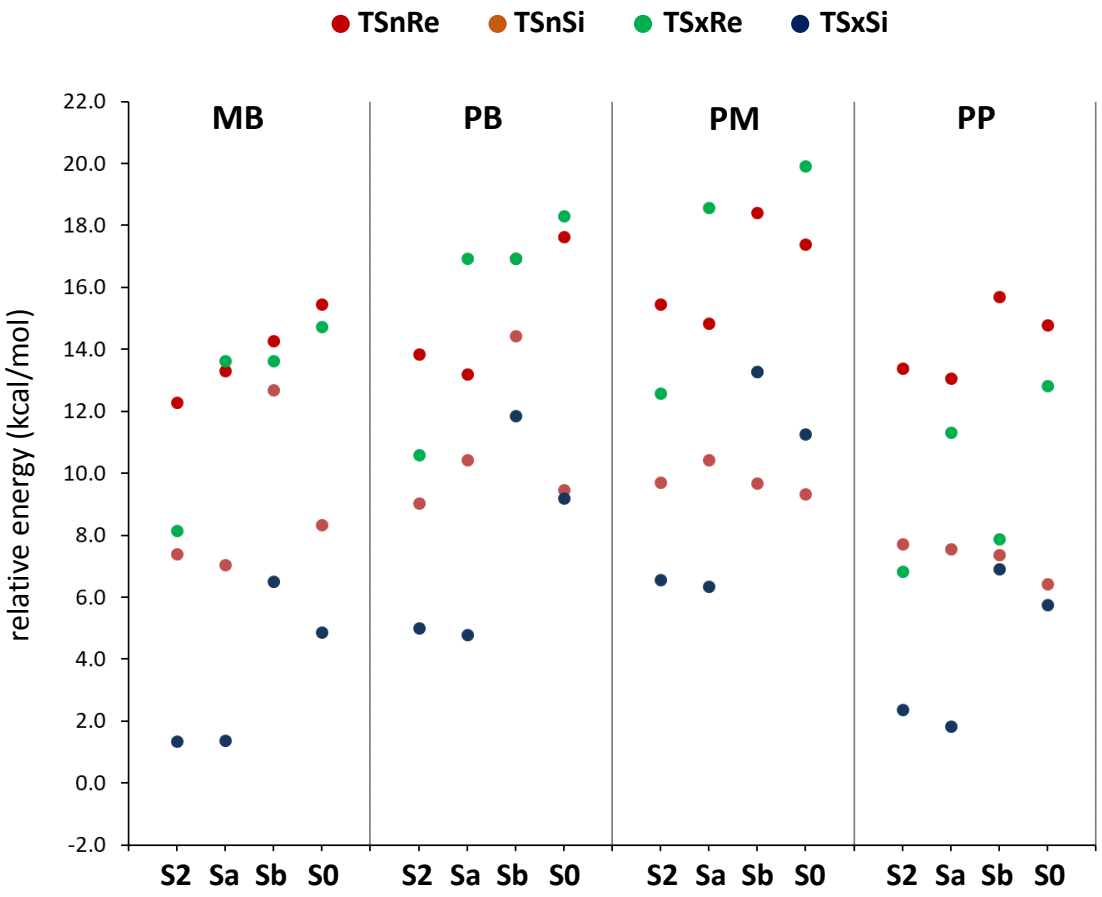


Figure 21. Energy barriers for the 1,3-dipolar cycloaddition reactions between S2, Sa, Sb and S0 and nitrones MB, PB, PM and PP

As expected, approaches by the less-hindered *Si,Re* face were always preferred. In all cases the *exo* approach resulted the less energetic, except for S0 and PM. By comparing thiazolines, there is a downward trend from S0 to S2. The obtention of the cycloadducts **115-117b,c** (Si-*exo*) for S2 and Sa and mixtures of compounds **115-117a**/**115-117a´**for S0 is in agreement with the observed differences in energy barriers of the reactions (TS; see *Figure 21*) thus reflecting a process under kinetic control.

However, when cycloadducts are heated by a prolonged time, a cycloreversion takes place, the starting material being observed in the reaction mixture, pointing to the possibility of a thermodynamic control of the reaction. Under thermodynamic control (*Figure 22*) only Sa when reacted with the four nitrones studied, are predicted to give the same cycloadduct (Si-*exo* approach) **115-117b** and **120b**, for instance; Sa-MB-TSxSi and Sa-MB-PRxSi have the lower energy of its section in both cases, and a different distribution of products (including mixtures) should be observed for the rest of reactions.

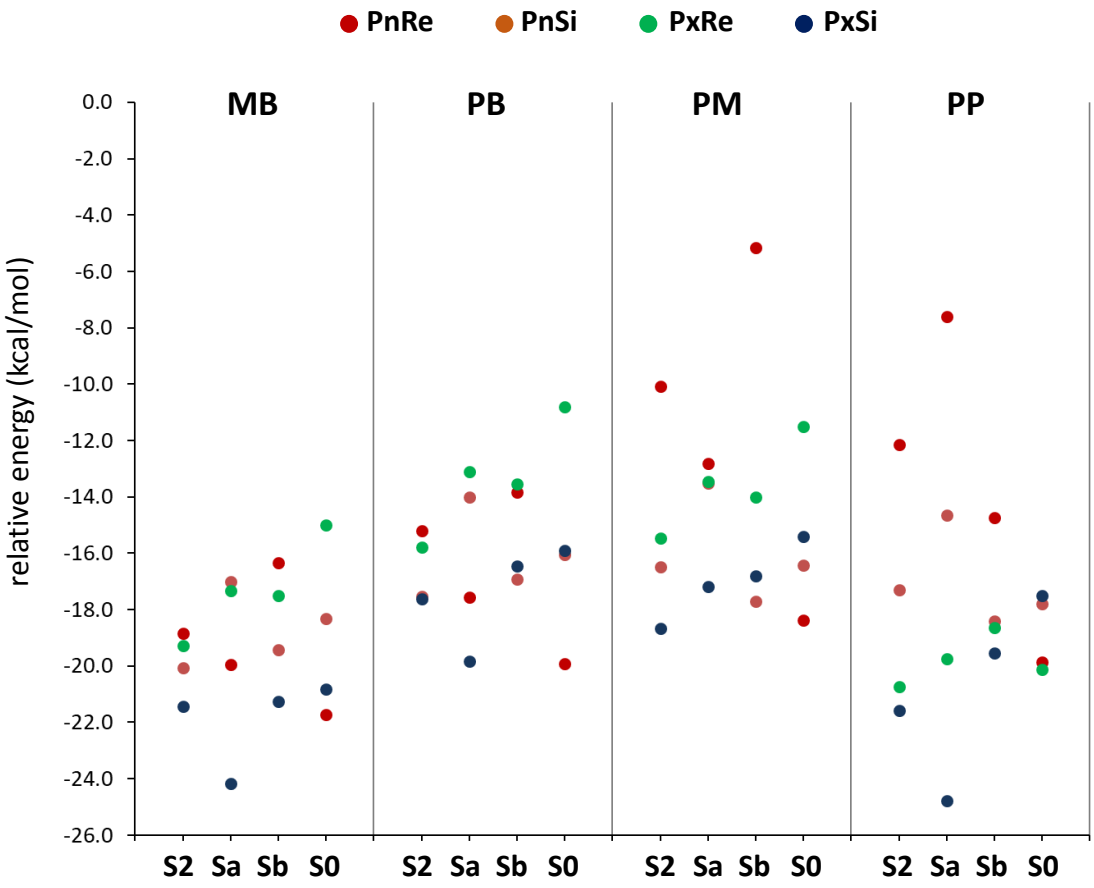


Figure 22. Relative energies for the products of the 1,3-dipolar cycloaddition reactions between S2, Sa, Sb and S0 and nitrones MB, PB, PM and PP

The explanation for the observed kinetic control, despite the abovementioned experimental observation, arises from the fact that under cycloreversion conditions (long reaction time at the same temperature or higher temperature used for the reaction) only starting materials and decomposition products from nitrone (aldehyde and hydroxylamine) were observed when a pure sample of **117c** was submitted at such conditions. Thus, once cycloreverted, the reaction cannot proceed again to form the reaction cycloadducts (*Figure 23*). This rationale is supported by the observation that prolonged reaction times lead to a lowering of the chemical yield as it was depicted in *Table* 8 (entries 2-4, 8 and 9).

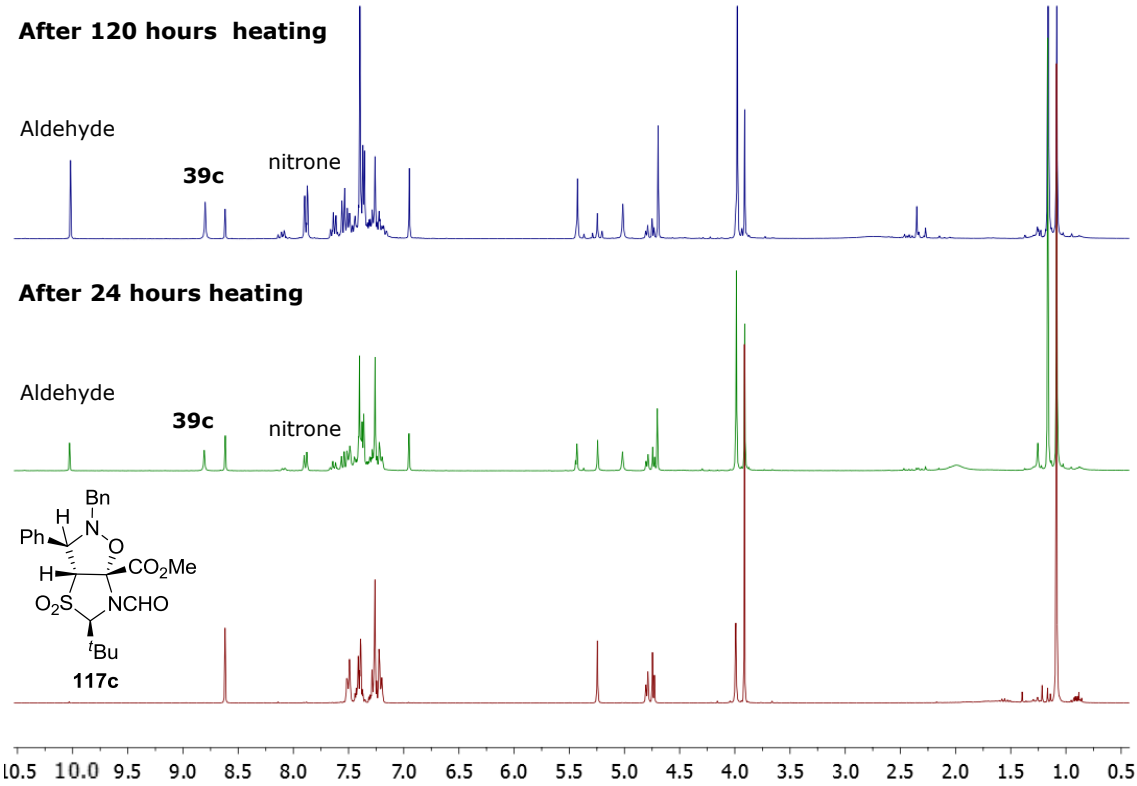


Figure 23. Cycloreversion observed for **117c** when heating

The geometries of the transition structures are given in appendixes. In all cases, expected distances for asynchronous concerted reactions are observed. As an example, the most stable transition structures for the reaction between thiazolines **39a-c** and nitrones **107a**, **107c**, **107f** and **107i** are illustrated in *Figure 24*.

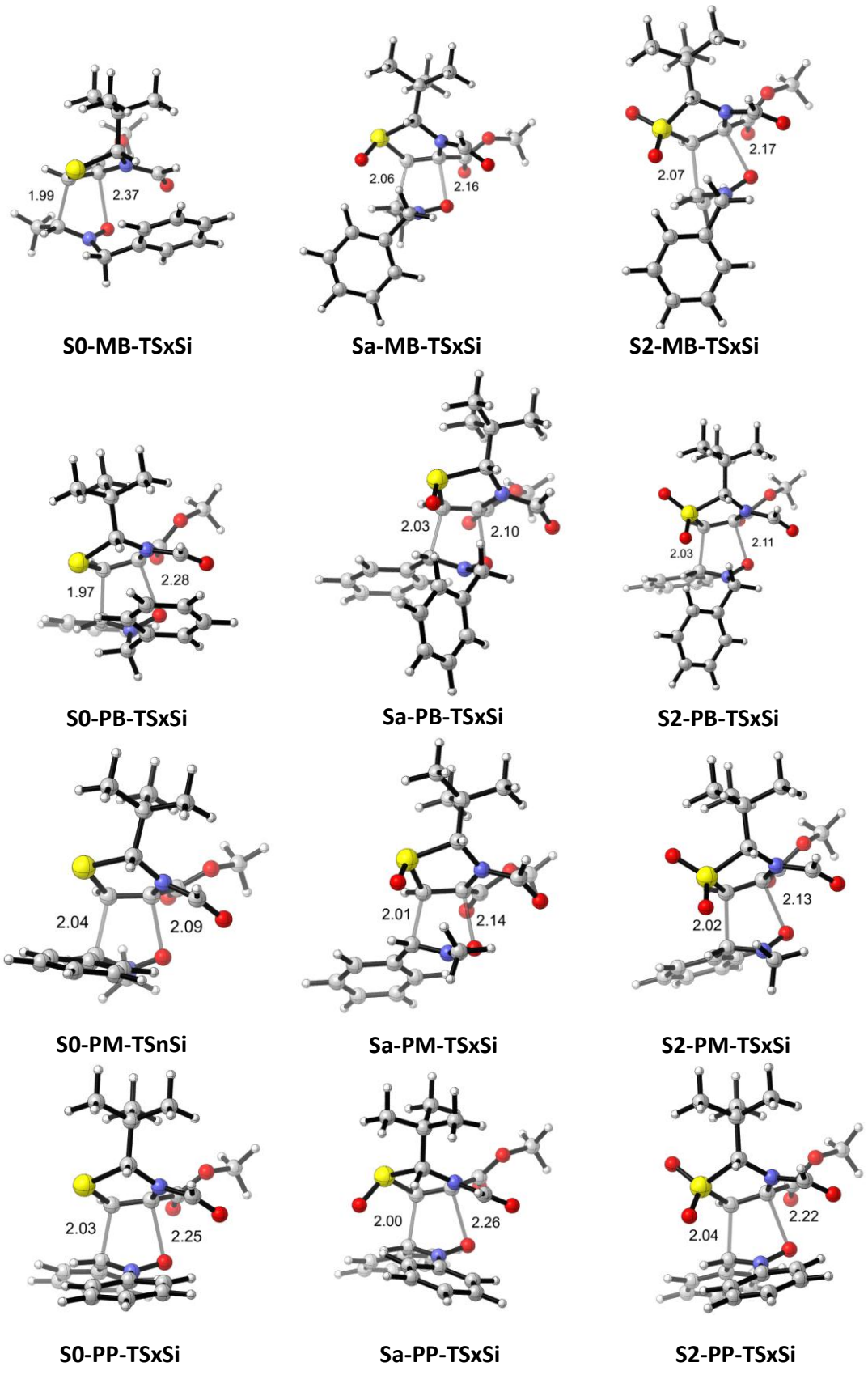
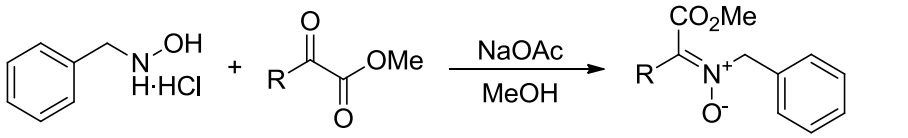


Figure 24. Most stable transition structures (B3LYP-D3BJ/Def2SVP) for the reaction of thiazolines **39a-c** and nitrones **107a**, **107c**, **107f** and **107i**

3.4. 1,3-Dipolar cycloaddtions between thiazolines 39b,c and nitrones 122a,b derived from ketones

Encouraged by the previously results, it was decided to extend the methodology developed for the 1,3-dipolar cycloaddition between thiazolines **39b,c** and nitrones **122a,b** prepared from methyl pyruvate and methyl 2-oxobutanoate, respectively, following the procedure reported by Nguyen *et al*.[25] Therefore, *N*-benzylhydroxylamine hydrochloride **114**·HCl and NaOAc were suspended in methanol at room temperature, and methyl pyruvate or methyl 2-oxobutanoate were added, leading to the corresponding nitrones **122a,b** as the *E* isomer exclusively (*Scheme 40*).

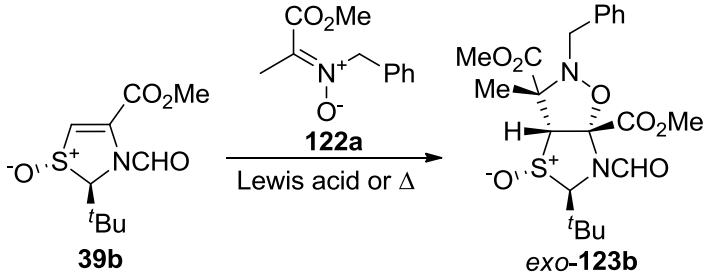


114·HCl R = Me, Et R = Me (**122a**), Et (**122b**)

Scheme 40. Synthetic procedure for the synthesis of nitrones **122a,b**

Then, 1,3-dipolar cycloaddition reactions were carried out between thiazoline **39b** and nitrone **122a** (*Table 13*).

Table 13. Reaction conditions and results for the cycloaddition between **39b** and nitrone **122a**



Entry	Temp. (°C)	Time (d)	solvent	Catalyst	Yield (%)[a]
1	80	3	Toluene	No	22%
2	100	2	Toluene	No	23%
3	80	6	Toluene	No	33%
4	r.t.	3	CH_2Cl_2	$Cu(OTf)_2$ 0.2 eq	0
5	r.t.	3	Toluene	$Cu(OTf)_2$ 0.2 eq	0
6	80	1	Toluene	$Cu(OTf)_2$ 1 eq	0
7	r.t.	2	Toluene	$TiCl_4$ 0.2 eq	0
8	80	2	Toluene	$Ti(O^iPr)_4$ 0.2 eq	<33%[b]
9	80	3	Toluene	$Ti(O^iPr)_4$ 0.2 eq	33%
10	80	3	Acetonitrile	$Ti(O^iPr)_4$ 0.2 eq	<33%[b]
11	100	3	Toluene	$Ti(O^iPr)_4$ 0.2 eq	<33%[b]
12	80	14	Toluene	$Ti(O^iPr)_4$ 0.2 eq	51%

[a]Isolated yield. [b]Estimated in comparision with ^{1}H NMR of the reaction crude of entry 9.

Within this context, thiazoline **39b** and nitrone **122a** were heated at 80 ºC and 100 ºC affording exclusively one isomer **123b**, (*Table* 13, entries 1-3).

In view of these results, it was decided to investigate if the addition of a Lewis acid could improve the reaction between thiazoline **39b** and nitrone **122a**.[7b] To this end, copper (II) trifluoromethanesulfonate, titanium tetrachloride and titanium tetraisopropoxide were tested as Lewis acid catalysts for the 1,3-cycloaddition reaction between thiazoline **39b** and nitrone **122a**. The reaction in the presence of $Cu(OTf)_2$ and $TiCl_4$ did not progress (*Table 13*, entries 4-7). However, a solution of thiazoline **39b**, nitrone **122a** and $Ti(O^iPr)_4$ heated at 80 ºC for 3 days afforded **123b** in 33% yield (entry 9), thus decreasing the reaction time with respect to the reaction carried out without Lewis acid (entry 3). Finally, the reaction time was increased to 14 days in presence of $Ti(O^iPr)_4$, obtaining a yield of 51% (entry 12). Hence, the use of $Ti(O^iPr)_4$ improved the results obtained under thermic activation (entry 3 *vs*. entry 12)

Stereochemical outcome of the reaction was determined on the basis of NOESY experiments of the bicyclic isoxazolidine **123b**, in which could be observed n.O.e correlation between H3a and the methyl group placed at C3, so the reaction took place through an *exo* approach by the less hindered face of the thiazoline **39b** (*Figure 25*).

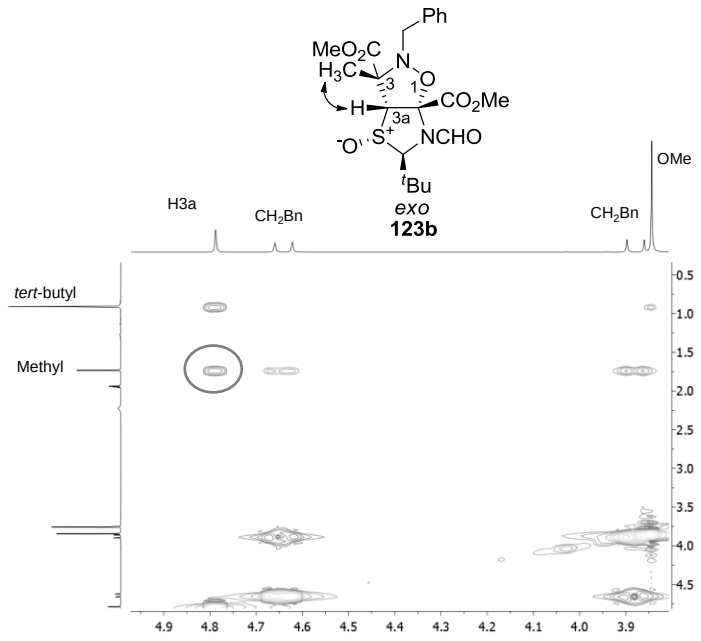
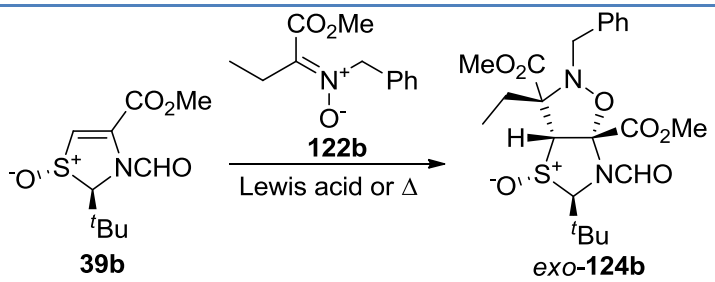


Figure 25. NOESY experiment of **123b**

On the other hand, it was also carried out the 1,3-dipolar cycloaddition reaction between **39b** and nitrone **122b** (*Table 14*).

Table 14. Results and conditions for the 1,3-dipolar cycloaddition between **39b** and nitrone **122b**



Entry	Temp. (°C)	Time (d)	solvent	Catalyst	Yield (%)[a]
1	100	3	Toluene 0.5mL	No	0%
2	80	3	Toluene 0.5mL	No	n.d.
3	100	8	Toluene 3mL	$Ti(O^iPr)_4$ 0.2 eq	0%
4	80	8	Toluene 3mL	$Ti(O^iPr)_4$ 0.2 eq	5%
5	80	4	Toluene 3mL	$Ti(O^iPr)_4$ 0.2 eq	72%

[a]Isolated yield.

The 1,3-dipolar cycloaddition between thiazoline **39b** and nitrone **122b** did not progress under thermic conditions (*Table 14*, entries 1 and 2), thus the reaction was performed using $Ti(O^iPr)_4$ as Lewis acid catalyst (entries 3-5). The best result was obtained when the reaction was stirring for 4 days at 80° C (entry 5) affording the diastereoisomer **124b** exclusively. Furthermore, we could deduce that the products formed underwent some transformation in the reaction mixture after 8 days stirring (entries 3 and 4). This fact could be corroborated by comparing the ^1H NMR of a sample taken the second reaction day and the ^1H NMR of the crude reaction after 8 days. The stereochemical assignment of **124b** was confirmed by n.O.e correlation between H3a and both CH_3 and CH_2 of the ethyl group at C3 position of bicyclic compound **124b** (*Figure 26*).

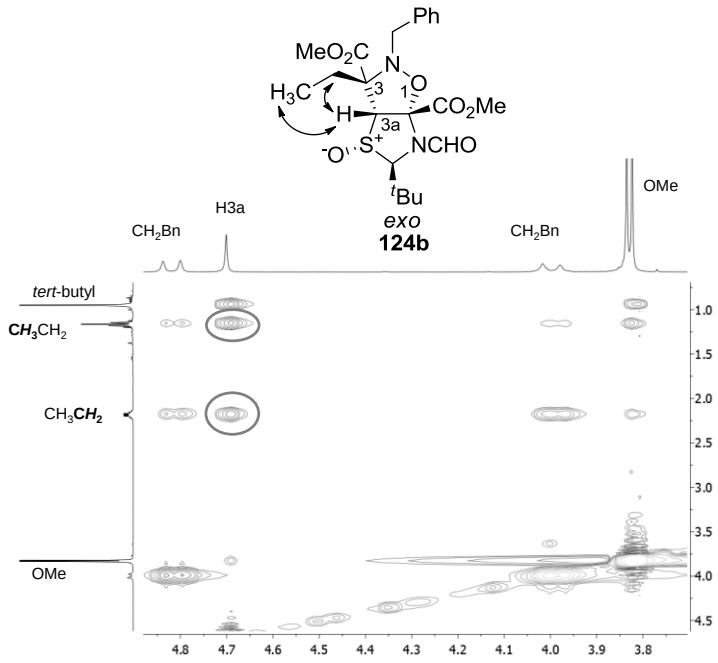
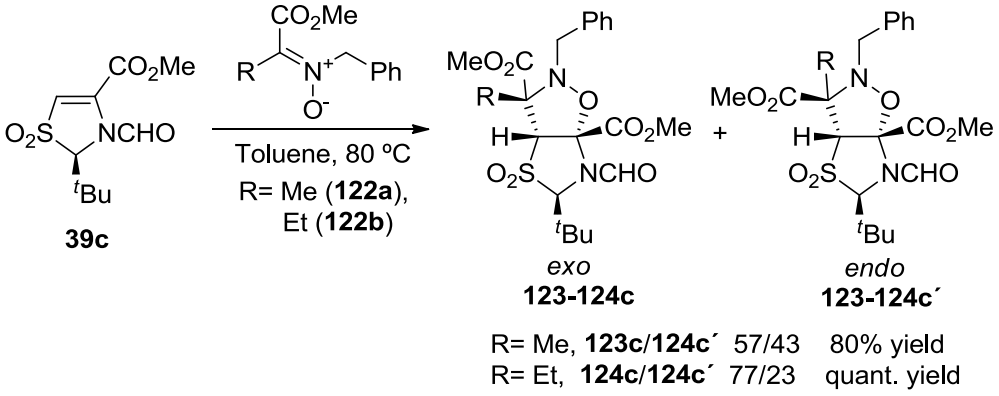


Figure 26. NOESY experiment of **124b**

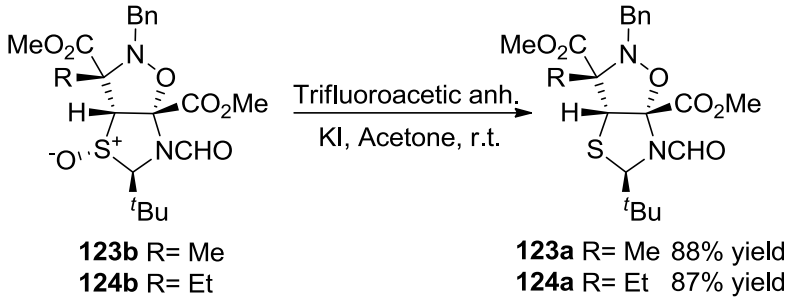
Therefore, the addition of Lewis acid catalyst demonstrated to be crucial for the improvement of the reaction yield between thiazoline **39b** and nitrone **122a** but especially between thiazoline **39b** and nitrone **122b**.

On the other hand, thiazoline **39c** showed good reactivity under thermic conditions by heating two solutions with nitrones **122a** and **122b** in toluene at 80 ºC, affording the corresponding bicyclic isoxazolidines with good yields as mixtures of *exo* and *endo* diastereoisomers **123c**/**123c´** in a ratio 57/43 and **124c**/**124c´** in a ratio 77/23, respectively (*Scheme 41*). Only analytical samples of **123c** and **123c´** could be isolated allowing its proper identification.



Scheme 41. Results and conditions for the 1,3-dipolar cycloaddition between thiazoline **39c** and nitrones **122a** and **122b**

Finally, the sulfinyl group of the bicyclic isoxazolidines **123b** and **124b** was reduced to sulfanyl moiety, following the conditions previously described in this chapter, thus obtaining the corresponding bicyclic isoxazolidines **123a** and **124a** with high yields (*Scheme 42*).



Scheme 42. Reduction of the sulfinyl group of **123b** and **124b**

4. CONLUSIONS

Thiazolines **39b,c** have demonstrated to be highly reactivite scaffolds in the 1,3-dipolar cycloaddition reaction with *Z*-*C*-alkyl- and aryl- substituted acyclic nitrones **107a**, **107c**, **107g-j**, yielding exclusively the *exo* diastereoisomers enantiomerically pure. However, thiazoline **39a** reacted smoothly with these nitrones to obtain mixtures of *exo* and *endo* diastereoisomers in moderate yields and conversions. The DFT calculations have been very useful to rationalize and enlighten the results obtained experimentally.

On the other hand, the thiazoline **39c** showed high reactivity towards *E*-α-substituted ester nitrones **122a,b** giving mixtures of diastereoisomers. However, thiazoline **39b** showed a very low reactivity, but the use of $Ti(O^iPr)_4$ allowed to improve the outcome of that reactions, obtaining exclusively one diastereoisomer in moderate to good yields.

Reduction of sulfinyl moiety of bicyclic isoxazolidines **115-121b**, **123b** and **124b** allowed to obtain the corresponding sulfanyl compounds **115-121a**, **123a** and **124a** in good yields and without losing enantiomeric purity.

Moreover, ^{1}H NMR spectroscopy of the coupling constants values for a *cis* disposition of vicinal protons H3 and H3a are not always higher than the values for a *trans* disposition for the obtained bicyclic isoxazolidines **115-118a**/**115-118a´** and do not fulfill the accepted standard for coupling constant values in isoxazolidine rings.

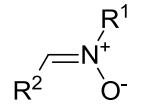
5. EXPERIMENTAL SECTION

5.1. General

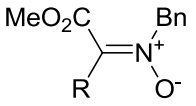
All reagents were used as received from commercial suppliers without further purification. Thin-layer chromatography (TLC) was performed on Macherey-Nagel Polygram®SIL G/UV254 precoated silica gel polyester plates. The products were visualized by exposure to UV light, iodine vapour, submersion in ninhydrin stain, in ethanolic solution of phosphomolybdic acid or in an aqueous solution of sodium permanganate. Column chromatography was performed using 60 M (0.04-0.063 mm) silica gel from Macherey-Nagel. Melting points were determined on a Gallenkamp apparatus. IR spectra were registered on a Nicolet Avatar 360 FTIR spectrophotometer; vmax is given for the main absorption bands. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, AV-400 instrument at room temperature, unless otherwise indicated, and using the residual solvent signal as the internal standard; chemical shifts (δ) are expressed in parts per million and coupling constant (*J*) in hertz. Optical rotations were measured at room temperature using a JASCO P-1020 polarimeter. High-resolution mass spectra were obtained on a Bruker Microtof-Q spectrometer.

5.2. Synthesis of nitrones

Z-*N*-aryl or alkyl-substituted nitrones **107a**, **107c**, **107f-j** were synthetized following the procedure developed by Dondoni *et al*.[18a] Nitrones **122a,b** with *E* configuration were obtained following the procedure described by Nguyen *et al*.[25]



R^1= Me, Ph, Bn
R^2= Me, Ph, 1-Np, ^{t}Bu
107a, **107c**, **107f-j**

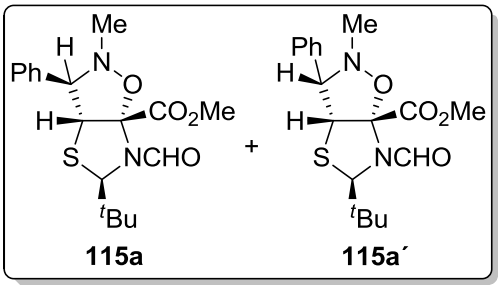


R= Me (**122a**),
R= Et (**122b**)

5.3. 1,3-Dipolar cycloaddition between thiazolines 39a-c and nitrones 107a, 107c, 107f-j and 122a,b

In a sealed tube, the corresponding thiazoline **39a-c** (1 eq.) and nitrone **107a**, **107c**, **107f-j** (3 eq.) were dissolved in toluene (0.1 mL for each 0.01 g of thiazoline) and heated until completion. The reaction was monitored by TLC. Once the reaction finished the solvent was removed under vacuum and the reaction crude was purified.

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115a and **(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115a´**



Following the general procedure, thiazoline **39a** (54.4 mg, 0.24 mmol) and nitrone **107c** (96.3 mg, 0.71 mmol) were dissolved in toluene (0.5 mL) and heated at 100 ºC for 72 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 10/90) to afford **115a** and **115a´** as mixture of diastereoisomers in a ratio 40/60, which could be separated. Major diastereoisomer **115a´** (17.7 mg, 0.05 mmol, 20 % yield) as a yellow oil and the minor **115a** (15.8 mg, 0.04 mmol, 19% yield) as a colourless oil. Unreacted starting material was also recovered (15.8 mg, 0.07 mmol, 29%).

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115a

$[\alpha]_D^{21}$: -42º (*c* 0.7; $CHCl_3$)

IR (neat) ν 1746, 1685, 1455, 1435, 1364, 1348, 1285, 1252, 1231, 1183, 1090, 1020 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.62 (s, 1H, C*H*O), 7.40-7.33 (m, 5H, H_{Ph}), 5.72 (s, 1H, H_2), 5.03 (d, *J* = 6.2, 1H, H_{3a}), 3.92 (s, 3H, OCH_3), 3.76 (d, *J* = 6.2, 1H, H_3), 2.65 (s, 3H, NCH_3), 0.87 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.2 (*C*O_2Me), 162.2 (*C*HO), 135.7 (C_{qPh}), 129.1 (C_{Ph}), 129.0 (C_{Ph}), 128.3 (C_{Ph}), 99.7 (C_{6a}), 83.0 (C_3), 75.9 (C_5), 64.5 (C_{3a}), 53.8 (O*C*H_3), 43.2 (N*C*H_3), 39.5 (*C*(CH$_3$)$_3$), 26.4 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{18}H_{24}N_2O_4SNa$ 387.1349; found 387.1362

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115a´

$[\alpha]_D^{21}$: +103º (*c* 1.1; $CHCl_3$)

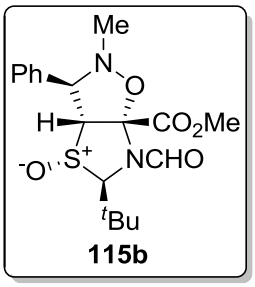
IR (neat) ν 1750, 1679, 1454, 1435, 1362, 1349, 1299, 125, 1213, 1177, 1146, 1020 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.65 (s, 1H, C*H*O), 7.37-7.33 (m, 5H, H_{Ph}), 5.50 (s, 1H, H_2), 5.05 (d, *J* = 5.4, 1H, H_{3a}), 4.16 (d, *J* = 5.4, 1H, H_3), 3.91 (s, 3H, OCH_3), 2.69 (s, 3H, NCH_3), 0.83 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 167.0 (*C*O_2Me), 162.1 (*C*HO), 132.8 (C_{qPh}), 128.9 (C_{Ph}), 128.8 (C_{Ph}), 128.5 (C_{Ph}), 99.9 (C_{6a}), 76.4 (C_3), 72.3 (C_5), 65.1 (C_{3a}), 54.1 (O*C*H_3), 43.1 (N*C*H_3), 39.7 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{18}H_{24}N_2O_4SNa$ 387.1349; found 387.1354

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-4-oxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115b



115b

Following the general procedure, thiazoline **39b** (45.8 mg, 0.19 mmol) and nitrone **107c** (101 mg, 0.75 mmol) were dissolved in toluene (0.5 mL) and heated at 100 ºC for 5 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 30/70) to afford **115b** (53.3 mg, 0.14 mmol, 73% yield) as a colourless oil.

$[\alpha]_D^{24}$: +14º (*c* 0.5; $CHCl_3$)

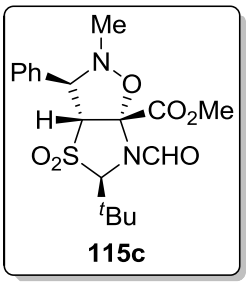
IR (neat) v: 1745, 1693, 1478, 1456, 1437, 1401, 1370, 1344, 1286, 1253, 1181, 1064 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.80 (s, 1H, C*H*O), 7.50-7.46 (m, 2H, H_{Ph}), 7.42-7.36 (m, 3H, H_{Ph}), 5.45 (s, 1H, H_5), 4.81 (d, *J* = 6.6, 1H, H_{3a}), 4.32 (d, *J* = 6.6, 1H, H_3), 3.98 (s, 3H, OCH_3), 2.70 (s, 3H, NCH_3), 0.98 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.3 (CO_2Me), 162.8 (*C*HO), 135.3 (C_{qPh}), 129.2 (C_{Ph}), 128.9 (C_{Ph}), 100.0 (C_{6a}), 96.2 (C_5), 76.4 (C_{3a}), 69.5 (C_3), 54.1 (OCH_3), 42.7 (NCH_3), 36.3 (*C*(CH_3)$_3$), 27.3 (C(CH_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{18}H_{24}N_2O_5SNa$ 403.1286; found 403.1298

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-4,4-dioxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115c



115c

Following the general procedure thiazoline **39c** (50.2 mg, 0.19 mmol) and nitrone **107c** (104 mg, 0.77 mmol) were dissolved in toluene (0.5 mL) and heated at 60 ºC for 3 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 20/80) to afford **115c** (65.7 mg, 0.16 mmol, 86% yield) as a white solid.

M.p.: 134-136 ºC

$[\alpha]_D^{24}$: -111º (*c* 1.0; $CHCl_3$)

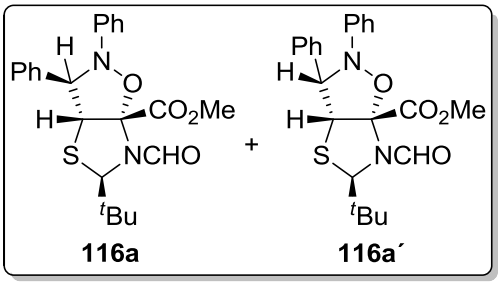
IR (KBr) ν 1746, 1702, 1605, 1438, 1338, 1320, 1288, 1250, 1223, 1189, 1121, 1024 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.75 (s, 1H, C*H*O), 7.46-7.36 (m, 5H, H_{Ph}), 5.25 (s, 1H, H_5), 4.71 (d, *J* = 5.7, 1H, H_{3a}), 4.50 (d, *J* = 5.5, 1H, H_3), 4.00 (s, 3H, OCH_3), 2.72 (s, 3H, NCH_3), 1.09 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 167.3 (*C*O_2Me), 162.1 (*C*HO), 134.8 (C_{qPh}), 129.5 (C_{Ph}), 129.3 (C_{Ph}), 128.5 (C_{Ph}), 94.3 (C_{6a}), 82.6 (C_5), 74.8 (C_{3a}), 70.7 (C_3), 54.3 (O*C*H_3), 42.9 (N*C*H_3), 37.0 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{18}H_{25}N_2O_6S$ 397.1428; found 397.1424

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 116a and **(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 116a´**



116a **116a´**

Following the general procedure, thiazoline **39a** (53.7 mg, 0.23 mmol) and nitrone **107a** (139 mg, 0.70 mmol) were dissolved in toluene (0.5 mL) and heated at 100 ºC for 13 hours. The reaction crude was purified by column chromatography (Et_2O/hexane 20/80) to afford a mixture of cycloadducts *exo*/*endo* 85/15. Major diastereoisomer **116a** (43.1 mg, 0.10 mmol, 43 % yield) as a yellow oil. Also unreacted starting material **39a** (17.1 mg, 0.07 mmol, 32%) was recovered. The minor diastereoisomer, cycloadduct **116a´**, and the starting material could not be completely separated. However, ^{1}H NMR and ^{1}H NOESY were acquired for its correct stereochemical identification albeit it was not characterized.

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 116a

$[\alpha]_D^{21}$: -6º (*c* 0.9; $CHCl_3$)

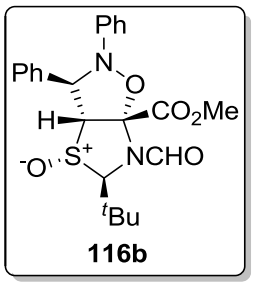
IR (neat) ν 1747, 1686, 1597, 1490, 1364, 1346, 1286, 1252, 1234, 1187, 1100, 1031 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.80 (s, 1H, C*H*O), 7.41-7.31 (m, 5H, $H_{Ph\text{-}C3}$), 7.21-7.15 (m, 2H, $H_{Ph\text{-}N2}$), 7.03-6.97 (m, 1H, $H_{Ph\text{-}N2}$), 6.93-6.88 (m, 2H, $H_{Ph\text{-}N2}$), 5.67 (s, 1H, H_2), 5.09 (d, *J* = 4.1, 1H, H_{3a}), 4.63 (d, *J* = 4.1, 1H, H_3), 3.89 (s, 3H, OCH_3), 0.91 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 167.6 (CO_2Me), 162.0 (*C*HO), 147.5 (C_{qPh}), 137.1 (C_{qPh}), 129.0 (C_{Ph}), 128.8 (C_{Ph}), 128.7 (C_{Ph}), 127.8 (C_{Ph}), 124.3 (C_{Ph}), 117.8 (C_{Ph}), 100.2 (C_{6a}), 78.4 (C_3), 75.4 (C_5), 65.2 (C_{3a}), 53.9 (OCH_3), 39.6 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{23}H_{26}N_2O_4SNa$ 449.1505; found 449.1518

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4-oxido-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 116b



116b

Following the general procedure, thiazoline **39b** (41.3 mg, 0.17 mmol) and nitrone **107a** (133 mg, 0.67 mmol) were dissolved in toluene (0.4 mL) and heated at 100 ºC for 5 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 30/70) to afford **116b** (63.6 mg, 0.14 mmol, 85% yield) as a brown solid.

M.p.: 156-158 ºC

$[\alpha]_D^{23}$: +25º (*c* 1.0; $CHCl_3$)

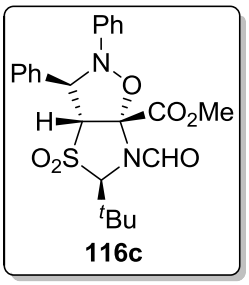
IR (KBr) v 1745, 1689, 1490, 1355, 1299, 1258, 1235, 1060 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.94 (s, 1H, C*H*O), 7.50-7.44 (m, 2H, $H_{Ph\text{-}C3}$), 7.41-7.35 (m, 3H, $H_{Ph\text{-}C3}$), 7.21-7.15 (m, 2H, $H_{Ph\text{-}N2}$), 7.11-7.05 (m, 1H, $H_{Ph\text{-}N2}$), 7.04-6.99 (m, 2H, $H_{Ph\text{-}N2}$), 5.52 (s, 1H, H_5), 5.02 (d, *J* = 5.9, 1H, H_3), 4.90 (d, *J* = 5.9, 1H, H_{3a}), 4.02 (s, 3H, OCH_3), 1.03 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.2 (*C*O_2Me), 162.8 (*C*HO), 146.8 (C_{qPh}), 136.1 (C_{qPh}), 129.3 (C_{Ph}), 129.1 (C_{Ph}), 128.80 (C_{Ph}), 128.75 (C_{Ph}), 126.1 (C_{Ph}), 120.5 (C_{Ph}), 99.8 (C_{6a}), 96.2 (C_5), 76.8 (C_{3a}), 67.8 (C_3), 54.3 (O*C*H_3), 36.4 (*C*(CH_3)$_3$), 27.4 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{23}H_{26}N_2O_5SNa$ 465.1455; found 465.1458

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4,4-dioxido-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 116c



116c

Following the general procedure, thiazoline **39c** (74.8 g, 0.29 mmol) and nitrone **107a** (170 mg, 0.86 mmol) were dissolved in toluene (0.7 mL) and heated at 60 ºC for 3 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 20/80) to afford **116c** (63.6 mg, 0.26 mmol, 90% yield) as a colourless oil that precipitates in Et_2O as white solid.

M.p.: 178-180 ºC

$[\alpha]_D^{22}$: -117º (*c* 1.0; $CHCl_3$)

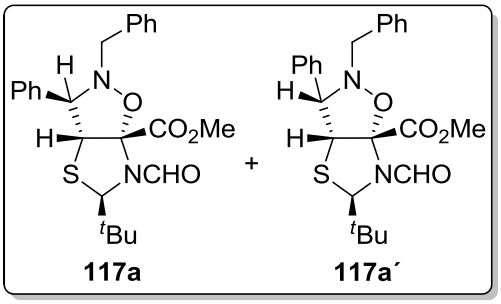
IR (KBr) v 1742, 1693, 1497, 1455, 1370, 1344, 1286, 1253, 1062 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.88 (s, 1H, C*H*O), 7.46-7.34 (m, 5H, H_{Ph}), 7.24-7.18 (m, 2H, H_{Ph}), 7.13-7.08 (m, 1H, H_{Ph}), 7.03-6.99 (m, 2H, H_{Ph}), 5.30 (s, 1H, H_5), 5.21 (d, *J* = 4.9, 1H, H_3), 4.81 (d, *J* = 4.9, 1H, H_{3a}), 4.02 (s, 3H, OCH_3), 1.13 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 167.0 (*C*O_2Me), 162.1 (*C*HO), 146.2 (C_{qPh}), 135.6 (C_{qPh}), 129.4 (C_{Ph}), 129.3 (C_{Ph}), 129.0 (C_{Ph}), 128.3 (C_{Ph}), 126.3 (C_{Ph}), 120.0 (C_{Ph}), 94.0 (C_{6a}), 82.3 (C_5), 75.0 (C_{3a}), 68.5 (C_3), 54.5 (O*C*H_3), 37.1 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{23}H_{26}N_2O_6SNa$ 481.1404; found 481.1417

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117a and **(3*S*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117a´**



Following the general procedure, thiazoline **39a** (95.7 mg, 0.42 mmol) and nitrone **107f** (0.26 g, 1.25 mmol) were dissolved in toluene (1 mL) and heated at 100 ºC for 96 hours. The reaction crude was purified by column chromatography (Et_2O/hexane 20/80) to afford a mixture of diastereoisomers *exo*/*endo* 52/48. Major diastereoisomer **117a** (50.0 mg, 0.11 mmol, 27 % yield) as a white solid and the minor diastereoisomer **117a´** (42.8 mg, 0.10 mmol, 23% yield) as a colourless oil. The unreacted starting material **39a** (44.6 mg, 0.20 mmol, 47%) was recovered.

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117a

M.p.: 110-112 ºC

$[\alpha]_D^{24}$: -66º (*c* 1.0; $CHCl_3$)

IR (neat) ν 1745, 1682, 1495, 1454, 1366, 1346, 1298, 1252, 1232, 1191, 1033 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.43 (s, 1H, C*H*O), 7.49-7.45 (m, 2H, H_{Ar}), 7.43-7.34 (m, 3H, H_{Ar}), 7.32-7.23 (m, 5H, H_{Ar}), 5.68 (s, 1H, H_5), 5.02 (d, *J* = 5.0, 1H, H_{3a}), 4.17 (d, *J* = 4.9, 1H, H_3), 3.98 (s, 2H, CH_2Ph), 3.83 (s, 3H, OCH_3), 0.85 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 168.8 (*C*O_2Me), 162.4 (*C*HO), 137.8 (C_{qBn}), 137.4 (C_{qPh}), 129.9 (C_{Ar}), 129.7 (C_{Ar}), 129.3 (C_{Ar}), 129.14 (C_{Ar}), 129.08 (C_{Ar}), 128.3 (C_{Ar}), 101.3 (C_{6a}), 80.0 (C_3), 76.0 (C_5), 65.2 (C_{3a}), 60.0 (*C*H_2Ph), 54.3 (O*C*H_3), 40.0 (*C*(CH_3)$_3$), 26.6 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{24}H_{28}N_2O_4SNa$ 463.1662; found 463.1653

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117a´

$[\alpha]_D^{24}$: 108º (*c* 1.2; $CHCl_3$)

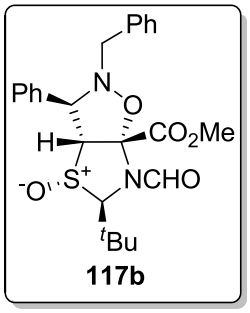
IR (neat) v 1749, 1681, 1496, 1454, 1362, 1298, 1210, 1180, 1034 cm^{-1}

RMN ^{1}H ($CDCl_3$, 400MHz) δ 8.43 (s, 1H, C*H*O), 7.46-7.42 (m, 2H, H_{Ar}), 7.40-7.27 (m, 8H, H_{Ar}), 5.53 (s, 1H, H_5), 5.07 (d, *J* = 5.6, 1H, H_{3a}), 4.39 (d, *J* = 5.6, 1H, H_3), 4.18 (d, *J* = 15.2, 1H, C*H*$_2$Ph), 3.85 (s, 3H, OC*H*$_3$), 3.78 (d, *J* = 15.3, 1H, C*H*$_2$Ph), 0.83 (s, 9H, C(C*H*$_3$)$_3$)

RMN ^{13}C ($CDCl_3$, 100MHz) δ 166.9 (*C*O_2Me), 162.0 (*C*HO), 136.3 (C_{qBn}), 132.9 (C_{qPh}), 129.0 (C_{Ar}), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 128.3 (C_{Ar}), 127.5 (C_{Ar}), 100.0 (C_{6a}), 73.6 (C_3), 72.2 (C_5), 64.4 (C_{3a}), 59.1 (*C*H_2Ph), 54.0 (O*C*H_3), 39.5 (*C*$(CH_3)_3$), 26.4 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{24}H_{29}N_2O_4S$ 441.1843; found 441.1837

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-4-oxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117b



117b

Following the general procedure, thiazoline **39b** (56.5 g, 0.23 mmol) and nitrone **107f** (146 mg, 0.69 mmol) were dissolved in toluene (0.5 mL) and heated at 100 ºC for 3 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 40/60) to afford **117b** (100 mg, 0.22 mmol, 95% yield) as a white solid.

M.p.: 143-145 ºC

$[\alpha]_D^{22}$: -44º (*c* 1.0; $CHCl_3$)

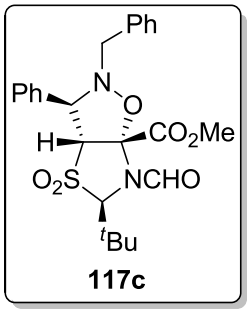
IR (KBr) v 1742, 1693, 1497, 1455, 1370, 1286, 1220, 1196, 1062 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.60 (s, 1H, C*H*O), 7.55 (dd, *J* = 8.1, 1.3, 2H, H_{Ar}), 7.47-7.37 (m, 3H, H_{Ar}), 7.31-7.21 (m, 5H, H_{Ar}), 5.31 (s, 1H, H_5), 4.90 (d, *J* = 6.1, 1H, H_{3a}), 4.59 (d, *J* = 6.1, 1H, H_3), 3.96 (s, 2H, CH_2Ph), 3.89 (s, 3H, OCH_3), 0.96 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 168.9 (*C*O_2Me), 163.5 (*C*HO), 137.9 (C_{qBn}), 136.8 (C_{qPh}), 130.02 (C_{Ar}), 129.97 (C_{Ar}), 129.7 (C_{Ar}), 129.1 (C_{Ar}), 129.0 (C_{Ar}), 128.2 (C_{Ar}), 101.2 (C_{6a}), 97.0 (C_5), 76.7 (C_{3a}), 68.1 (C_3), 59.5 (*C*H_2Ph), 54.6 (O*C*H_3), 36.8 (*C*(CH_3)$_3$), 27.3 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{24}H_{28}N_2O_5SNa$ 479.1611; found 479.1622

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-4,4-dioxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117c



117c

Following the general procedure, thiazoline **39c** (53.0 mg, 0.20 mmol) and nitrone **107f** (129 g, 0.61 mmol) were dissolved in toluene (0.5 mL) and heated at 60 ºC for 3 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 20/80) to afford **117c** (87.5 g, 0.18 mmol, 91% yield) as a white solid.

M.p.: 134-136 ºC

$[\alpha]_D^{24}$: -139º (*c* 0.8; $CHCl_3$)

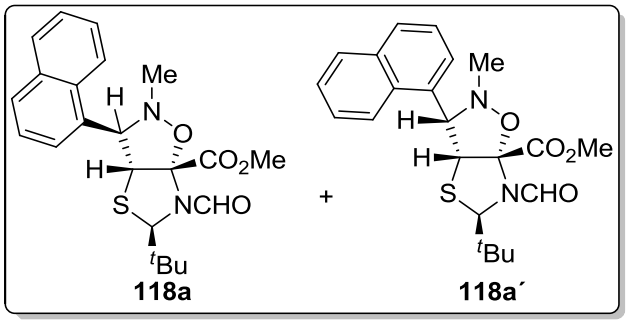
IR (KBr) v 1753, 1685, 1335, 1290, 1253, 1221, 1189 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.57 (s, 1H, C*H*O), 7.57-7.53 (m, 2H, H_{Ar}), 7.48-7.40 (m, 3H, H_{Ar}), 7.33-7.23 (m, 2H, H_{Ar}), 5.24 (s, 1H, H_5), 4.80 (d, *J* = 5.3, 1H, H_3), 4.77 (d, *J* = 5.2, 1H, H_{3a}), 4.01 (d, *J* = 15.4, 1H, CH_2Ph), 3.97 (d, *J* = 15.2, 1H, CH_2Ph), 3.92 (s, 3H, OCH_3), 1.06 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 168.0 (*C*O_2Me), 162.8 (*C*HO), 137.3 (C_{qBn}), 136.0 (C_{qPh}), 130.4 (C_{Ar}), 130.2 (C_{Ar}), 129.5 (C_{Ar}), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 128.4 (C_{Ar}), 95.3 (C_{6a}), 83.0 (C_5), 75.2 (C_{3a}), 69.0 (C_3), 59.5 (*C*H_2Ph), 54.9 (O*C*H_3), 37.5 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{24}H_{28}N_2O_6SNa$ 495.1560; found 495.1562

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118a and **(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118a´**



Following the general procedure, thiazoline **39a** (107 mg, 0.47 mmol) and nitrone **107g** (0.26 g, 1.40 mmol) were dissolved in toluene (1 mL) and heated at 100 ºC for 24 hours. The reaction crude was purified by column chromatography (Et_2O/hexane 30/70) to afford a mixture of *exo*/*endo* diastereoisomers in a ratio 60/40. Major diastereoisomer **118a** (36.8 mg, 0.09 mmol, 19 % yield) as a colourless oil and the minor diastereoisomer **118a´** (26.1 mg, 0.06 mmol, 13% yield) as a white solid. The unreacted starting material **39a** (48.6 mg, 0.21 mmol, 45%) was recovered.

(3*R*,3a*R*,5*R*,6a*S*)-methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118a

$[\alpha]_D^{21}$: -150º (*c* 1.2; $CHCl_3$)

IR (neat) ν 1746, 1685, 1435, 1364, 1349, 1288, 1230, 1183, 1031 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.70 (s, 1H, C*H*O), 8.10 (d, *J* = 8.4, 1H, H_{Ar}), 7.90 (dd, *J* = 8.4, 0.9, 1H, H_{Ar}), 7.84 (d, *J* = 8.2, 1H, H_{Ar}), 7.75 (m, 1H, H_{Ar}), 7.60 (ddd, *J* = 8.5, 6.9, 1.5, 1H, H_{Ar}), 7.56-7.48 (m, 2H, H_{Ar}), 5.78 (s, 1H, H_2), 5.05 (d, *J* = 5.9, 1H, H_{3a}), 4.66 (d, *J* = 5.9, 1H, H_3), 3.92 (s, 3H, OCH_3), 2.79 (s, 3H, NCH_3), 0.86 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.2 (*C*O_2Me), 162.2 (*C*HO), 133.9 (C_{qAr}), 132.1 (C_{qAr}), 131.5 (C_{qAr}), 129.2 (C_{Ar}), 129.0 (C_{Ar}), 126.8 (C_{Ar}), 126.0 (C_{Ar}), 125.8 (C_{Ar}), 125.0 (C_{Ar}), 122.9 (C_{Ar}), 100.3 (C_{6a}), 77.9 (C_3), 76.1 (C_5), 64.5 (C_{3a}), 53.8 (O*C*H_3), 44.0 (N*C*H_3), 39.5 (*C*(CH_3)$_3$), 26.3 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{22}H_{26}N_2O_4SNa$ 437.1505; found 437.1523.

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118a´

M.p.: 160-162 ºC

$[\alpha]_D^{24}$: 193º (*c* 1.0; $CHCl_3$)

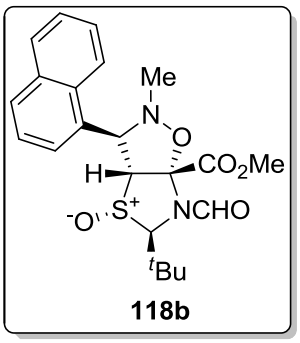
IR (neat) v 1743, 1682, 1434, 1347, 1299, 1250, 1207, 1177, 1090 cm^{-1}

RMN ^{1}H ($CDCl_3$, 400MHz) δ 8.71 (s, 1H, C*H*O), 8.00 (d, *J* = 8.4, 1H, H_{Ar}), 7.91 (d, *J* = 7.6, 1H, H_{Ar}), 7.85 (d, *J* = 8.2, 1H, H_{Ar}), 7.64-7.59 (m, 2H, H_{Ar}), 7.56-7.47 (m, 2H, H_{Ar}), 5.49 (s, 1H, H_2), 5.35 (d, *J* = 5.3, 1H, H_{3a}), 4.88 (d, *J* = 5.3, 1H, H_3), 3.99 (s, 3H, OCH_3), 2.80 (s, 3H, NCH_3), 0.81 (s, 9H, C(CH_3)$_3$)

RMN ^{13}C ($CDCl_3$, 100MHz) δ 167.2 (*C*O_2Me), 162.1 (*C*HO), 133.7 (C_{qAr}), 131.3 (C_{qAr}), 129.4 (C_{Ar}), 129.1 (C_{Ar}), 128.2 (C_{qAr}), 127.0 (C_{Ar}), 126.5 (C_{Ar}), 126.0 (C_{Ar}), 125.2 (C_{Ar}), 121.9 (C_{Ar}), 100.0 (C_{6a}), 72.44 (C_3), 72.40 (C_5), 63.9 (C_{3a}), 54.2 (O*C*H_3), 43.3 (N*C*H_3), 39.7 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{22}H_{27}N_2O_4S$ 415.1686; found 415.1672

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118b



118b

Following the general procedure, thiazoline **39b** (0.12 g, 0.48 mmol) and nitrone **107g** (0.26 g, 1.42 mmol) were dissolved in toluene (1 mL) and heated at 100 ºC for 3 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 30/70) to afford **118b** (0.20 g, 0.47 mmol, 98% yield) as an orange solid.

M.p.: 61-63 ºC

$[\alpha]_D^{21}$: -85º (*c* 1.0; $CHCl_3$)

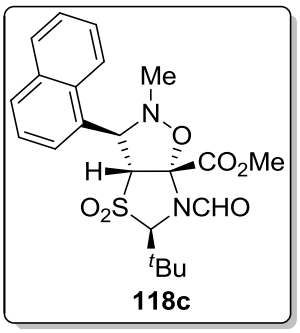
IR (neat) v 1745, 1691, 1435, 1400, 1369, 1342, 1283, 1219, 1059 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.88 (s, 1H, C*H*O), 8.20 (d, *J* = 8.5, 1H, H_{Ar}), 7.92 (dd, *J* = 8.5, 1.0, 1H, H_{Ar}), 7.88 (d, *J* = 7.6, 2H, H_{Ar}), 7.62 (ddd, *J* = 8.5, 6.9, 1.5, 1H, H_{Ar}), 7.57-7.52 (m, 2H, H_{Ar}), 5.54 (s, 1H, H_5), 5.19 (d, *J* = 6.4, 1H, H_3), 4.75 (d, *J* = 6.4, 1H, H_{3a}), 3.99 (s, 3H, OCH_3), 2.80 (s, 3H, NCH_3), 0.97 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.4 (*C*O_2Me), 163.0 (*C*HO), 133.9 (C_{qAr}), 132.0 (C_{qAr}), 131.8 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 127.4 (C_{Ar}), 126.3 (C_{Ar}), 126.0 (C_{Ar}), 125.8 (C_{Ar}), 122.8 (C_{Ar}), 100.5 (C_{6a}), 96.2 (C_5), 76.6 (C_{3a}), 64.9 (C_3), 54.1 (O*C*H_3), 43.3 (N*C*H_3), 36.3 (*C*(CH_3)$_3$), 27.3 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{22}H_{26}N_2O_5SNa$ 453.1455; found 453.1476

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118c



118c

Following the general procedure, thiazoline **39c** (0.11 g, 0.42 mmol) and nitrone **107g** (0.23 g, 1.27 mmol) were dissolved in toluene (1 mL) and heated at 60 ºC for 3 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 20/80) to afford **118c** (0.18 g, 0.41 mmol, 98% yield) as a white solid.

M.p.: 142-144 ºC

$[\alpha]_D^{24}$: -265º (*c* 1.0; $CHCl_3$)

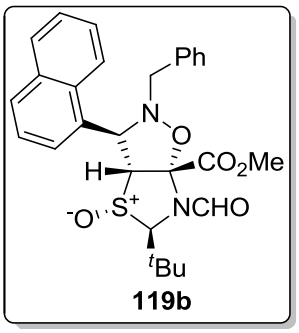
IR (neat) ν 1745, 1702, 1439, 1456, 1368, 1316, 1280, 1217, 1027 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.83 (s, 1H, C*H*O), 8.22 (d, *J* = 8.4, 1H, H_{Ar}), 7.93-7.87 (m, 2H, H_{Ar}), 7.81 (dd, *J* = 7.3, 0.9, 1H, H_{Ar}), 7.64 (ddd, *J* = 8.5, 6.9, 1.4, 1H, H_{Ar}), 7.58-7.49 (m, 2H, H_{Ar}), 5.37 (d, *J* = 5.6, 1H, H_3), 5.32 (s, 1H, H_5), 4.70 (d, *J* = 5.6, 1H, H_{3a}), 4.01 (s, 3H, OCH_3), 2.81 (s, 3H, NCH_3), 1.07 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 167.4 (*C*O_2Me), 162.3 (*C*HO), 134.0 (C_{qAr}), 131.4 (C_{qAr}), 130.8 (C_{qAr}), 129.7 (C_{Ar}), 129.2 (C_{Ar}), 127.3 (C_{Ar}), 126.4 (C_{Ar}), 125.7 (C_{Ar}), 125.6 (C_{Ar}), 122.5 (C_{Ar}), 94.8 (C_{6a}), 82.6 (C_5), 75.0 (C_{3a}), 66.0 (C_3), 54.3 (O*C*H_3), 43.5 (N*C*H_3), 37.1 (*C*(CH_3)$_3$), 26.4 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{22}H_{27}N_2O_6S$ 447.1584; found 447.1562

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-(1-naphthyl)-4-oxidohexahydrothiazolo[5,4-d]isoxazole-6a-carboxylate 119b



119b

Following the general procedure, thiazoline **39b** (53.3 mg, 0.22 mmol) and nitrone **107h** (170 mg, 0.65 mmol) were dissolved in toluene (0.5 mL) and heated at 100 ºC for 5 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 30/70) to afford **119b** (104 mg, 0.21 mmol, 94% yield) as a white solid.

M.p.: 145-146 ºC

$[\alpha]_D^{23}$: -72º (*c* 1.0; $CHCl_3$)

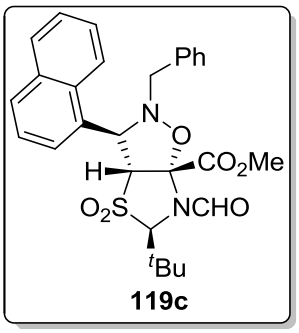
IR (KBr) v 1742, 1687, 1342, 1292, 1255, 1220, 1062 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.67 (s, 1H, C*H*O), 8.14 (d, *J* = 8.5, 1H, H_{Np}), 8.02-7.97 (m, 2H, H_{Np}), 7.94 (d, *J* = 8.2, 1H, H_{Np}), 7.66 (ddd, *J* = 8.5, 6.9, 1.4, 1H, H_{Np}), 7.62-7.56 (m, 1H, H_{Np}), 7.35-7.21 (m, 5H, H_{Bn}), 5.42 (d, *J* = 5.9, 1H, H_3), 5.40 (s, 1H, H_5), 4.85 (d, *J* = 5.9, 1H, H_{3a}), 4.07 (s, 2H, CH_2Ph), 3.89 (s, 3H, OCH_3), 0.93 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 168.9 (*C*O_2Me), 163.5 (C*H*O), 137.9 (C_{qPh}), 134.9 (C_{qNp}), 133.3 (C_{qNp}), 132.4 (C_{qNp}), 130.1 (C_{Ar}), 129.9 (C_{Ar}), 129.2 (C_{Ar}), 129.1 (C_{Ar}), 128.3 (C_{Ar}), 128.0 (C_{Ar}), 127.1 (C_{Ar}), 126.9 (C_{Ar}), 126.8 (C_{Ar}), 123.4 (C_{Ar}), 101.8 (C_{6a}), 96.9 (C_5), 76.8 (C_{3a}), 63.6 (C_3), 60.1 (*C*H_2Ph), 54.6 (O*C*H_3), 36.9 (*C*(CH_3)$_3$), 27.3 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{28}H_{30}N_2O_5SNa$ 529.1768; found 529.1779

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-(1-naphthyl)-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 119c



119c

Following the general procedure, thiazoline **39c** (53.1 mg, 0.20 mmol) and nitrone **107h** (160 mg, 0.61 mmol) were dissolved in toluene (0.5 mL) and heated at 60 ºC for 5 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 20/80) to afford **119c** (91.5 mg, 0.17 mmol, 86%yield) as a white solid.

M.p.: 138-140 ºC

$[\alpha]_D^{24}$: -199º (*c* 1.0; $CHCl_3$)

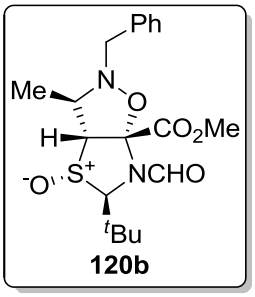
IR (KBr) v 1748, 1694, 1334, 1294, 1192, 1153, 1087, 1019 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.64 (s, 1H, C*H*O), 8,20 (d, *J* = 8.5, 1H, H_{Np}), 8.01-7.94 (m, 3H, H_{Np}), 7.66 (ddd, *J* = 8.5, 6.9, 1.5, 1H, H_{Np}), 7.62-7.57 (m, 2H, H_{Np}), 7.31-7.23 (m, 5H, H_{Bn}), 5.63 (d, *J* = 5.3, 1H, H_3), 5.30 (s, 1H, H_5), 4.75 (d, *J* = 5.3, 1H, H_{3a}), 4.08 (s, 2H, CH_2Ph), 3.92 (s, 3H, OCH_3), 1.02 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 168.0 (*C*O_2Me), 162.9 (*C*HO), 137.3 (C_{qPh}), 134.9 (C_{qNp}), 132.0 (C_{qNp}), 131.9 (C_{qNp}), 130.4 (C_{Ar}), 130.1 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (C_{Ar}), 127.9 (C_{Ar}), 127.2 (C_{Ar}), 126.92 (C_{Ar}), 126.85 (C_{Ar}), 123.2 (C_{Ar}), 95.8 (C_{6a}), 83.1 (C_5), 75.3 (C_{3a}), 64.2 (C_3), 60.2 (*C*H_2Ph), 54.9 (O*C*H_3), 37.6 (*C*(CH_3)$_3$), 26.4 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{28}H_{30}N_2O_6SNa$ 545.1717; found 545.1696

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 120b



120b

Following the general procedure, thiazoline **39b** (40.3 mg, 0.16 mmol) and nitrone **107i** (73.6 mg, 0.49 mmol) were dissolved in toluene (0.4 mL) and heated at 80 ºC for 7 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 50/50) to afford **120b** (58.0 mg, 0.14 mmol, 90% yield) as a white solid.

M.p.: 104-106 ºC

$[\alpha]_D^{21}$: -37º (*c* 0.8; $CHCl_3$)

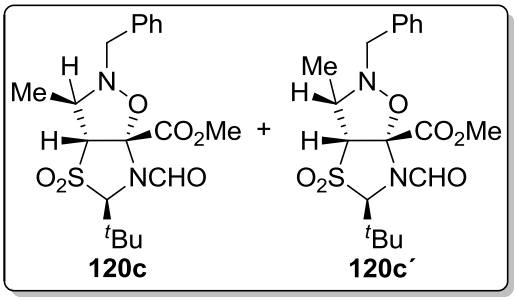
IR (KBr) v 1749, 1682, 1373, 1350, 1315, 1279, 1229, 1175, 1056 cm^{-1}

^{1}H NMR (DMSO-*d*6, 400MHz, 80 ºC) δ 8.49 (s, 1H, C*H*O), 7.33-7.28 (m, 4H, H_{Ph}), 7.27-7.23 (m, 1H, H_{Ph}), 5.15 (s, 1H, H_2), 4.66 (d, *J* = 3.5, 1H, H_{3a}), 4.18 (d, *J* = 14.6, 1H, CH_2Ph), 4.06 (d, *J* = 14.6, 1H, CH_2Ph), 3.85 (s, 3H, OCH_3), 3.78 (qd, *J* = 6.6, 3.5, 1H, H_3), 1.37 (d, *J* = 6.6, 1H, C_3-CH_3), 0.97 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (DMSO-*d*6, 100MHz, 80 ºC) δ 166.7 (*C*O_2Me), 161.7 (*C*HO), 136.7 (C_{qPh}), 127.7 (C_{Ph}), 127.6 (C_{Ph}), 126.6 (C_{Ph}), 100.6 (C_{6a}), 93.8 (C_5), 74.9 (C_{3a}), 58.1 (C_3), 57.5 (*C*H_2Ph), 53.4 (O*C*H_3), 35.3 (*C*(CH_3)$_3$), 26.3 (C(*C*H_3)$_3$), 15.3 (C_3-*C*H_3)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{19}H_{27}N_2O_5S$ 395.1635; found 395.1642

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 120c and **(3*S*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 120c´**



Following the general procedure, thiazoline **39c** (53.1 mg, 0.20 mmol) and nitrone **107i** (91.0 mg, 0.61 mmol) were dissolved in toluene (0.5 mL) and heated at 60 ºC for 8 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 30/70) affording a mixture of diastereoisomers *exo* and *endo* 84/16. Major diastereoisomer **120c** (67.8 mg, 0.16 mmol, 81 % yield) as a white solid and minor diastereoisomer **120c´** (12.5 mg, 0.03 mmol, 15% yield) also as a white solid.

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 120c

M.p.: 90-92 ºC

$[\alpha]_D^{24}$: -50º (*c* 1.5; $CHCl_3$)

IR (KBr) v 1752, 1701, 1495, 1442, 1370, 1333, 1203, 1151, 1087 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz, 50 ºC) δ 8.55 (s, 1H, C*H*O), 7.33-7.25 (m, 5H, H_{Ph}), 5.21 (s, 1H, H_5), 4.32 (d, *J* = 3.0, 1H, H_{3a}), 4.13 (d, *J* = 14.1, 1H, CH_2Ph), 4.07 (d, *J* = 14.2, 1H, CH_2Ph), 4.07-4.02 (m, 1H, H_3), 3.88 (s, 3H, OCH_3), 1.34 (d, *J* = 6.6, 3H, C_3-CH_3), 1.10 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz, 50 ºC) δ 166.5 (*C*O_2Me), 162.1 (*C*HO), 136.0 (C_{qPh}), 128.6 (C_{Ph}), 128.5 (C_{Ph}), 127.9 (C_{Ph}), 95.4 (C_{6a}), 82.2 (C_5), 74.6 (C_{3a}), 59.9 (C_3), 58.5 (*C*H_2Ph), 54.1 (O*C*H_3), 37.1 (*C*(CH_3)$_3$), 26.6 (C(*C*H_3)$_3$), 15.7 (C_3-*C*H_3)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{19}H_{26}N_2O_6SNa$ 433.1404; found 433.1415

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 120c´

M.p.: 44-46 ºC

$[\alpha]_D^{24}$: 67º (*c* 0.8; $CHCl_3$)

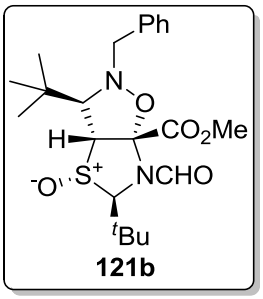
IR (KBr) v 1755, 1692, 1455, 1370, 1331, 1297, 1209, 1152, 1043 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.56 (s, 1H, C*H*O), 7.33-7.27 (m, 5H, H_{Ph}), 5.13 (s, 1H, H_5), 4.33 (d, *J* = 14.9, 1H, CH_2Ph), 4.29 (d, *J* = 5.6, 1H, H_{3a}), 3.82 (d, *J* = 14.9, 1H, CH_2Ph)* overlapped, 3.82 (s, 3H, OCH_3), 3.51-3.43 (m, 1H, H_3), 1.68 (d, *J* = 6.8, 3H, C_3-CH_3), 1.06 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 165.9 (*C*O_2Me), 162.1 (*C*HO), 135.1 (C_{qPh}), 128.7 (C_{Ph}), 128.5 (C_{Ph}), 127.8 (C_{Ph}), 93.8 (C_{6a}), 81.6 (C_5), 72.2 (C_{3a}), 64.7 (C_3), 59.1 (*C*H_2Ph), 54.3 (O*C*H_3), 36.7 (*C*(CH_3)$_3$), 26.5 (C(*C*H_3)$_3$), 10.3 (C_3-*C*H_3)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{19}H_{26}N_2O_6SNa$ 433.1404; found 433.1393

Synthesis of (3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-3,5-di-*tert*-butyl-6-formyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 121b



121b

Following the general procedure, thiazoline **39b** (52.1 mg, 0.21 mmol) and nitrone **107j** (131 mg, 0.64 mmol) were dissolved in toluene (0.5 mL) and heated at 100 ºC for 5 hours. The reaction crude was purified by column chromatography (EtOAc/hexane 20/80) to afford **121b** (84.5 mg, 0.19 mmol, 91% yield) as a white solid.

M.p.: 137-139 ºC

$[\alpha]_D^{24}$: +2º (*c* 0.9; $CHCl_3$)

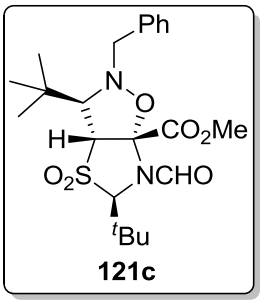
IR (KBr) v 1749, 1679, 1368, 1343, 1315, 1294, 1220, 1173, 1061 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.58 (s, 1H, C*H*O), 7.41-7.37 (m, 2H, H_{Ph}), 7.35-7.25 (m, 3H, H_{Ph}), 5.22 (s, 1H, H_5), 5.07 (d, *J* = 3.1, 1H, H_{3a}), 4.25 (d, *J* = 12.9, 1H, CH_2Ph), 4.20 (d, *J* = 12.9, 1H, CH_2Ph), 3.82 (s, 3H, OCH_3), 3.63 (d, *J* = 3.1, 1H, H_3), 1.01 (s, 9H, C_5-C(CH_3)$_3$), 0.88 (s, 9H, C_3-C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 167.1 (*C*O_2Me), 163.6 (*C*HO), 138.1 (C_{qPh}), 130.6 (C_{Ph}), 129.2 (C_{Ph}), 128.5 (C_{Ph}), 107.0 (C_{6a}), 95.4 (C_5), 74.1 (C_{3a}), 72.4 (C_3), 63.5 (*C*H_2Ph), 54.7 (O*C*H_3), 37.3 (C_5-*C*(CH_3)$_3$), 35.1 (C_3-*C*(CH_3)$_3$), 27.3 (C(*C*H_3)$_3$), 27.0 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{22}H_{32}N_2O_5SNa$ 459.1924; found 459.1929

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-3,5-di-*tert*-butyl-6-formyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 121c



121c

Following the general procedure, thiazoline **39c** (76.7 mg, 0.29 mmol) and nitrone **107j** (121 mg, 0.59 mmol) were dissolved in toluene (0.8 mL) and heated at 80 ºC for 7 hours. The reaction crude was purified by column chromatography (CH_2Cl_2/Hexane 90/10) to afford **121c** (97.8 mg, 0.21 mmol, 74% yield) as a white solid.

M.p.: 127-129 ºC

$[\alpha]_D^{23}$: -57º (*c* 0.9; $CHCl_3$)

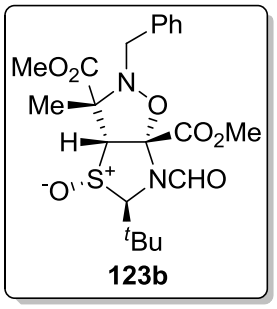
IR (KBr) v 1748, 1691, 1371, 1342, 1290, 1246, 1182, 1167, 1086 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.56 (s, 1H, C*H*O), 7.39-7.28 (m, 5H, H_{Ph}), 5.31 (s, 1H, H_5), 4.69 (d, *J* = 2.4, 1H, H_{3a}), 4.27 (s, 2H, CH_2Ph), 3.84 (s, 3H, OCH_3), 3.82 (d, *J* = 2.8, 1H, H_3), 1.11 (s, 9H, C_5-C(CH_3)$_3$), 0.93 (s, 9H, C_3-C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 166.7 (*C*O_2Me), 162.9 (*C*HO), 138.0 (C_{qPh}), 129.8 (C_{Ph}), 129.3 (C_{Ph}), 128.5 (C_{Ph}), 99.5 (C_{6a}), 82.9 (C_5), 74.7 (C_3), 73.1 (C_{3a}), 64.3 (*C*H_2Ph), 54.9 (O*C*H_3), 38.0 (C_5-*C*(CH_3)$_3$), 34.4 (C_3-*C*(CH_3)$_3$), 27.0 (C_3-C(*C*H_3)$_3$), 26.7 (C_5-C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{22}H_{32}N_2O_6SNa$ 475.1873; found 475.1890

Synthesis of (3*S*,3a*R*,4*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 123b



123b

In a sealed tube, thiazoline **39b** (53.3 mg, 0.22 mmol) and $Ti(O^iPr)_4$ (43.5 mg, 0.01 mmol) were dissolved in toluene (3 mL) in presence of molecular sieves, 4 Å (0.1 g). Then, the nitrone **122a** (90.2 mg, 0.43 mmol) was added to the reaction mixture and was allowed to stir at 80 ºC during 14 days. After this time, the crude reaction was filtered off over celite washing with EtOAc. The obtained oil was purified by column chromatography (EtOAc/hexane 30/70) to give **123b** (50.6 mg, 0.11 mmol, 51% yield) as a colourless oil that precipitates in Et_2O.

M.p.: 151-153 ºC

$[\alpha]_D^{24}$: +174º (*c* 0.6; $CHCl_3$)

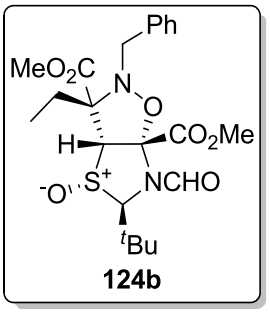
IR (KBr) v 1745, 1681, 1372, 1352, 1296, 1245, 1141, 1064 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.29 (s, 1H, C*H*O), 7.34-7.25 (m, 5H, H_{Ph}), 5.05 (s, 1H, H_5), 4.79 (s, 1H, H_{3a}), 4.64 (d, *J* = 15.0, 1H, CH_2Ph), 3.88 (d, *J* = 15.1, 1H, CH_2Ph), 3.84 (s, 3H, C_{6a}-OCH_3), 3.76 (s, 3H, C_3-OCH_3), 1.73 (s, 3H, CH_3), 0.91 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 171.0 (C_3-*C*O_2Me), 167.2 (C_{6a}-*C*O_2Me), 162.7 (*C*HO), 138.8 (C_{qPh}), 129.2 (C_{Ph}), 128.9 (C_{Ph}), 128.1 (C_{Ph}), 99.9 (C_{6a}), 91.9 (C_5), 78.4 (C_{3a}), 72.8 (C_3), 56.3 (*C*H_2Ph), 55.1 (C_{6a}-O*C*H_3), 53.1 (C_3-O*C*H_3), 36.5 (*C*(CH_3)$_3$), 27.2 (C(*C*H_3)$_3$), 18.3 (*C*H_3)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{21}H_{29}N_2O_7S$ 453.1690; found 453.1675

Synthesis of (3*S*,3a*R*,4*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 124b



124b

In a sealed tube, thiazoline **39b** (55.4 mg, 0.23 mmol) and $Ti(O^iPr)_4$ (45.2 mg, 0.01 mmol) were dissolved in toluene (3 mL) in presence of molecular sieves, 4 Å (0.1 g). Then, the nitrone **122b** (0.1 g, 0.45 mmol) was added to the reaction mixture and was allowed to stir at 80 °C during 4 days. After this time, the crude reaction was filtered off over celite washing with EtOAc. The obtained oil was purified by column chromatography (EtOAc/hexane 20/80) to give **124b** (75.8 mg, 0.16 mmol, 72% yield) as a colourless oil.

$[\alpha]_D^{24}$: +129° (*c* 0.5; $CHCl_3$)

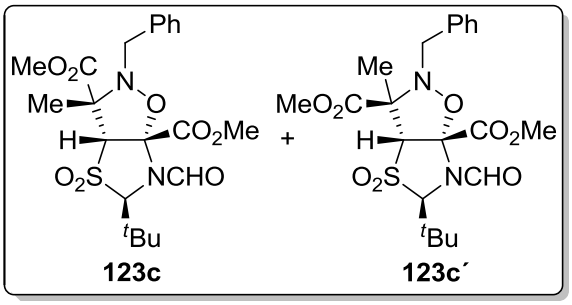
IR (neat) v 1748, 1731, 1685, 1455, 1348, 1301, 1239, 1134, 1067 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.33 (s, 1H, C*H*O), 7.38-7.33 (m, 2H, H_{Ph}), 7.32-7.28 (m, 2H, H_{Ph}), 7.24-7.20 (m, 1H, H_{Ph}), 5.27 (s, 1H, H_5), 4.82 (d, *J* = 15.0, 1H, CH_2Ph), 4.70 (s, 1H, H_{3a}), 4.00 (d, *J* = 15.3, 1H, CH_2Ph), 3.84 (s, 3H, C_3-OCH_3), 3.82 (s, 3H, C_{6a}-OCH_3), 2.18 (m, 2H, CH_2CH$_3$), 1.16 (t, *J* = 7.5, 3H, CH$_2$CH_3), 0.95 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.8 (C_3-*C*O$_2$Me), 166.4 (C_{6a}-*C*O$_2$Me), 162.4 (*C*HO), 137.5 (C_{qPh}), 128.4 (C_{Ph}), 127.8 (C_{Ph}), 127.2 (C_{Ph}), 99.4 (C_{6a}), 91.2 (C_5), 75.8 (C_3), 75.3 (C_{3a}), 55.3 (*C*H$_2$Ph), 54.3 (O*C*H$_3$), 52.6 (O*C*H$_3$), 36.0 (*C*(CH$_3$)$_3$), 27.2 (C(*C*H$_3$)$_3$), 24.4 (*C*H$_2$CH$_3$), 9.4 (CH$_2$*C*H$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{22}H_{31}N_2O_7S$ 467.1846; found 467.1845

Synthesis of (3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 123c and **(3*R*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 123c´**



In a sealed tube, thiazoline **39c** (86.0 mg, 0.33 mmol) and nitrone **122a** (0.14 g, 0.66 mmol) were dissolved in toluene (0.9 mL) and the reaction was allowed to stir at 80 ºC for 26 hours. Once the reaction finished, the solvent was evaporated off and the obtained oil was purified by column chromatography (EtOAc/hexane 10/90) to give a mixture of diastereoisomers **123c**/**123c´** (0.12 g, 0.26 mmol, 80% yield) in a ratio 57/43, determined by ^{1}H NMR, as a colourless oil. Analytical samples of both *exo* and *endo* isomers could be isolated for a properly assignation of the ^{1}H and ^{13}C NMR data.

123c. **^{1}H NMR** (CD_3CN, 400MHz) δ 8.19 (s, 1H, C*H*O), 7.35-7.28 (m, 5H, H_{Ph}), 5.06 (s, 1H, H_5), 4.67 (s, 1H, H_{3a}), 4.64 (d, *J* = 14.8, 1H, CH_2Ph), 3.88 (d, *J* = 14.8, 1H, CH_2Ph), 3.88*overlapped (s, 3H, C_{6a}-OCH_3), 3.78 (s, 3H, C_{6a}-OCH_3), 1.70 (s, 3H, CH_3), 1.01 (s, 9H, C(CH_3)$_3$)

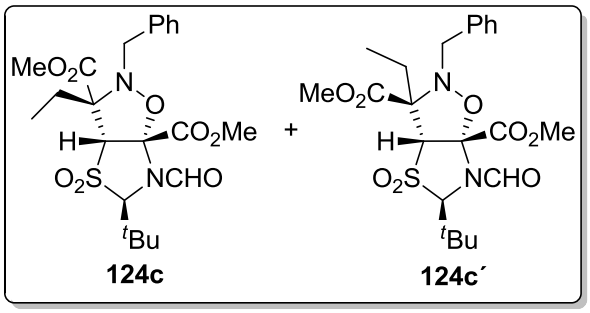
^{13}C NMR (CD_3CN, 100MHz) δ 169.8 (C_{6a}-*C*O_2Me), 166.3 (C_{6a}-*C*O_2Me), 161.9 (*C*HO), 138.3 (C_{qPh}), 129.3 (C_{Ph}), 129.1 (C_{Ph}), 128.4 (C_{Ph}), 95.5 (C_{6a}), 81.6 (C_5), 76.1 (C_{3a}), 73.6 (C_3), 56.4 (*C*H_2Ph), 55.4 (O*C*H_3), 53.2 (O*C*H_3), 37.5 (*C*(CH_3)$_3$), 26.6 (C(*C*H_3)$_3$), 17.6 (*C*H_3)

123c´. **^{1}H NMR** (CD_3CN, 400MHz) δ 8.27 (s, 1H, C*H*O), 7.37-7.27 (m, 5H, H_{Ar}), 5.08 (s, 1H, H_5), 4.81 (s, 1H, H_{3a}), 4.71 (d, *J* = 16.2, 1H, CH_2Ph), 4.33 (d, *J* = 16.0, 1H, CH_2Ph), 3.81 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 1.93 (s, 3H, CH_3), 1.04 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 170.8 (C_3-*C*O_2Me), 166.3 (C_{6a}-*C*O_2Me), 162.2 (*C*HO), 138.9 (C_{qAr}), 129.3 (C_{Ar}), 128.7 (C_{Ar}), 128.3 (C_{Ar}), 94.9 (C_{6a}), 82.4 (C_5), 74.4 (C_{3a} ó C_3), 74.2 (C_3 ó C_{3a}), 55.2 (*C*H_2Ph), 53.9 (O*C*H_3), 53.4 (O*C*H_3), 37.2 (*C*(CH_3)$_3$), 26.6 (C(*C*H_3)$_3$), 15.2 (*C*H_3)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{21}H_{28}N_2O_8SNa$ 491.1459; found 491.1472

Synthesis of (3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 124c and **(3*R*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 124c´**



In a sealed tube, thiazoline **39c** (50.5 mg, 0.19 mmol) and nitrone **122b** (0.13 g, 0.58 mmol) were dissolved in toluene (0.5 mL) and the reaction mixture was stirring for 21 hours at 80 ◦C. Then, the solvent was evaporated and the crude was purified by column chromatography (EtOAc/hexane 10/90) to give an inseparable mixture of diastereoisomers **124c**/**124c´** (91.6 mg, 0.19 mmol, 100% yield) in a ratio 77/23, determined by ^{1}H NMR, as a colourless oil.

124c. **^{1}H NMR** (CD_2Cl_2, 400MHz) δ 8.16 (s, 1H, C*H*O), 7.34-7.26 (m, 5H, H_{Ph}), 5.11 (s, 1H, H_2), 4.82 (d, *J* = 14.6, 1H, CH_2Ph), 4.57 (s, 1H, H_{3a}), 3.93 (d, *J* = 14.7, 1H, CH_2Ph), 3.86 (s, 3H, C_{6a}-OCH_3), 3.83 (s, 3H, C_3-OCH_3), 2.17-2.11 (m, 2H, CH_2CH$_3$), 1.15 (t, *J* = 7.5, 3H, CH$_2$CH_3), 1.03 (s, 9H, C(CH_3)$_3$)

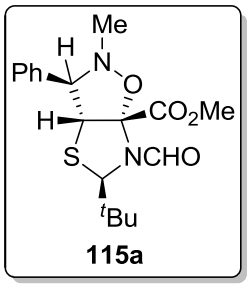
124c´. **^{1}H NMR** (CD_2Cl_2, 400MHz) δ 8.18 (s, 1H, C*H*O), 7.34-7.26 (m, 5H, H_{Ph}), 5.11 (s, 1H, H_2), 5.00 (s, 1H, H_{3a}), 4.49 (d, *J* = 15.8, 1H, CH_2Ph), 4.33 (d, *J* = 15.9, 1H, CH_2Ph), 3.83 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 2.18 (qd, *J* = 15.2, 7.6, 1H, CH_2CH$_3$), 2.09-2.04 (m, 1H, CH_2CH$_3$) 1.18 (t, *J* = 7.6, 3H, CH$_2$CH_3), 1.06 (s, 9H, C(CH_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{22}H_{30}N_2O_8SNa$ 505.1615; found 505.1613

5.4. General procedure for deoxigenation of sulfoxides

Over a stirred solution of a bicyclic thiazolidine sulfoxide (1 eq.) in acetone at 0 ºC, trifluoroacetic anhydride (2 eq.) and potassium iodide (4 eq.) were added. The reaction mixture was stirred at room temperature and monitored by TLC (EtOAc/hexane) until completion. The mixture was treated with an aqueous solution of $Na_2S_2O_3$ (5%) and diluted with dichloromethane at room temperature and was stirred for 30 minutes. The phases were separated and the aqueous phase was extracted with dichloromethane. Then, the combined organic layers were dried over magnesium sulfate anhydrous, filtered off and the solvent was evaporated under reduced pressure. The obtained residue was purified by column chromatography.

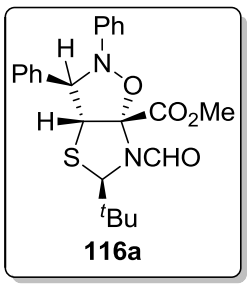
Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 115a



115a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **115b** (124 mg, 0.33 mmol) was dissolved in acetone (5 ml) at 0 ºC. The reaction was completed in 4 hours. Then, the obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **115a** (118 mg, 0.32 mmol, 98% yield) as a white solid.

Synthesis (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 116a

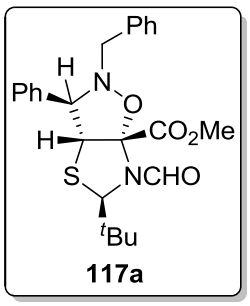


116a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **116b** (37.3 mg, 0.08 mmol) was dissolved in acetone (3 ml) at 0 ºC. The reaction was completed in 4 hours. Then, the obtained residue was

purified by column chromatography (EtOAc/hexane 20/80) to give **116a** (22.8 mg, 0.05 mmol, 63% yield) as a yellowish oil.

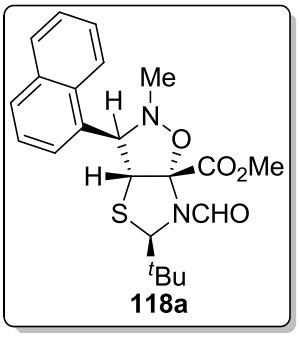
Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 117a



117a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **117b** (0.89 g, 1.94 mmol) was dissolved in acetone (15 ml) at 0 °C. The reaction was completed in 3 hours. Then, the obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **117a** (0.83 g, 1.88 mmol, 97% yield) as a white solid.

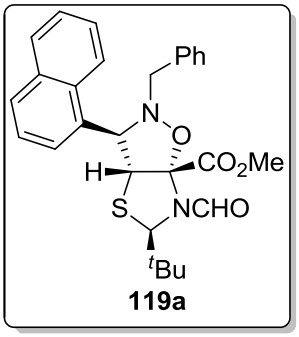
Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 118a



118a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **118b** (0.14 g, 0.34 mmol) was dissolved in acetone (5 ml) at 0 °C. The reaction was completed in 3 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 10/90) to give **118a** (0.12 g, 0.30 mmol, 88% yield) as a colourless oil.

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 119a



119a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **119b** (0.57 g, 1.12 mmol) was dissolved in acetone (15 ml) at 0 °C. The reaction was completed in 6 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **119a** (0.50 g, 1.02, 91% yield) as a white solid.

M.p.: 151-153 °C

$[\alpha]_D^{24}$: -117° (*c* 1.1; $CHCl_3$)

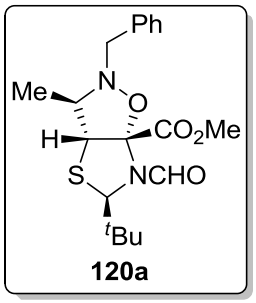
IR (KBr) v 1742, 1682, 1361, 1349, 1311, 1295, 1253, 1180, 1024 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.61 (s, 1H, C*H*O), 8.05 (d, *J* = 8.4, 1H, H_{Np}), 7.94-7.90 (m, 1H, H_{Np}), 7.86 (t, *J* = 7.4, 2H, H_{Np}), 7.62 (ddd, *J* = 8.4, 6.9, 1.4, 1H, H_{Np}), 7.58-7.49 (m, 2H, H_{Np}), 7.30-7.25 (m, 5H, H_{Ph}), 5.80 (s, 1H, H_5), 5.07 (d, *J* = 5.1, 1H, H_{3a}), 4.94 (d, *J* = 5.1, 1H, H_3), 4.20 (d, *J* = 14.6, 1H, CH_2Ph), 4.14 (d, *J* = 14.6, 1H, CH_2Ph), 3.82 (s, 3H, OCH_3), 0.87 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 168.0 (*C*O_2Me), 162.3 (*C*HO), 136.5 (C_{qPh}), 134.0 (C_{qNp}), 132.6 (C_{qNp}), 131.3 (C_{qNp}), 129.3 (C_{Ar}), 129.0 (C_{Ar}), 128.5 (C_{Ar}), 128.3 (C_{Ar}), 127.5 (C_{Ar}), 126.9 (C_{Ar}), 126.0 (C_{Ar}), 125.9 (C_{Ar}), 125.0 (C_{Ar}), 122.8 (C_{Ar}), 101.1 (C_{6a}), 76.0 (C_5), 74.8 (C_3), 64.5 (C_{3a}), 60.2 (*C*H_2Ph), 53.6 (O*C*H_3), 39.6 (*C*(CH_3)$_3$), 26.4(C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{28}H_{30}N_2O_4SNa$ 513.1818; found 513.1818

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 120a



120a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **120b** (0.14 g, 0.36 mmol) was dissolved in acetone (5 ml) at 0 °C. The reaction was completed in 6 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **120a** (0.12 g, 0.32, 89% yield) as a colourless oil.

$[\alpha]_D^{23}$: +28° (*c* 0.9; $CHCl_3$)

IR (neat) v 1749, 1682, 1454, 1364, 1350, 1297, 1211, 1178, 1059 cm^{-1}

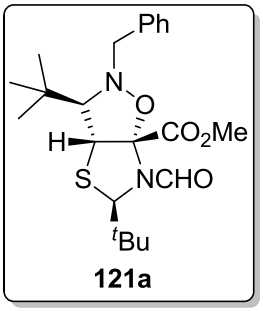
^{1}H NMR ($CDCl_3$, 400MHz, 50 °C) δ 8.47 (s, 1H, C*H*O), 7.32-7.22 (m, 5H, H_{Ph}), 5.67 (s, 1H, H_5), 4.65 (d, *J* = 2.2, 1H, H_{3a}), 4.23 (d, *J* = 13.9, 1H, CH_2Ph), 4.11 (d, *J* = 13.9, 1H, CH_2Ph), 3.81 (s, 3H, OCH_3), 3.31 (qd, *J* = 6.6, 2.6, 1H, H_3), 1.24 (d, *J* = 6.6, 3H, CH_3), 0.88 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz, 50 °C) δ 167.2 (*C*O_2Me), 162.1 (*C*HO), 136.6 (C_{qPh}), 128.6 (C_{Ph}), 128.4 (C_{Ph}), 127.6 (C_{Ph}), 101.8 (C_{6a}), 74.1 (C_5), 68.8 (C_3), 63.3 (C_{3a}), 58.9 (*C*H_2Ph)*, 53.5 (O*C*H_3), 39.3 (*C*(CH_3)$_3$), 26.4 (C(*C*H_3)$_3$), 15.9 (*C*H_3)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{19}H_{26}N_2O_4SNa$ 401.1505; found 401.1509

*Although *C*H_2Ph (58.9 ppm) cannot be clearly appreciated, the cross peaks in HSQC experiment allowed us to identify it properly.

Synthesis of (3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-3,5-di-tert-butyl-6-formylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate 121a



121a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **121b** (0.32 g, 0.74 mmol) was dissolved in acetone (10 ml) at 0 °C. The reaction was completed in 6 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 10/90) to give **121a** (0.29 g, 0.70 mmol, 94% yield) as a white solid.

M.p.: 97-99 °C

$[\alpha]_D^{24}$: +31° (*c* 1.1; $CHCl_3$)

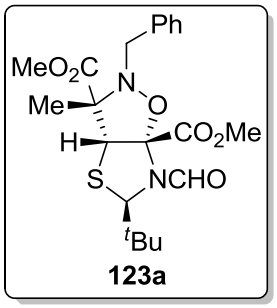
IR (KBr) v 1749, 1677, 1365, 1348, 1297, 1249, 1234, 1102 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.44 (s, 1H, C*H*O), 7.38-7.26 (m, 5H, H_{Ph}), 5.76 (s, 1H, H_5), 5.03 (d, *J* = 2.2, 1H, H_{3a}), 4.46 (d, *J* = 13.5, 1H, CH_2Ph), 4.37 (d, *J* = 13.5, 1H, CH_2Ph), 3.78 (s, 3H, OCH_3), 3.28 (d, *J* = 2.2, 1H, H_3), 0.88 (s, 9H, C_5-C(CH_3)$_3$), 0.86 (s, 9H, C_3-C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 167.4 (CO_2Me), 162.7 (*C*HO), 138.5 (C_{qPh}), 130.1 (C_{Ph}), 129.2 (C_{Ph}), 128.4 (C_{Ph}), 106.3 (C_{6a}), 85.7 (C_3), 74.9 (C_5), 65.0 (CH_2Ph), 58.8 (C_{3a}), 54.3 (OCH_3), 39.9 (C_5-*C*(CH_3)$_3$), 35.0 (C_3-*C*(CH_3)$_3$), 27.0 (C_3-C(*C*H_3)$_3$), 26.7 (C_5-C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{22}H_{32}N_2O_4SNa$ 443.1975; found 443.1990

Synthesis of (3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methylhexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 123a



123a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **123b** (0.11 g, 0.26 mmol) was dissolved in acetone (5 ml) at 0 °C. The reaction was completed in 2 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 10/90) to give **123a** (0.1 g, 0.23 mmol, 88% yield) as a white solid.

M.p.: 115-117 °C

$[\alpha]_D^{26}$: +172° (*c* 1.1; $CHCl_3$)

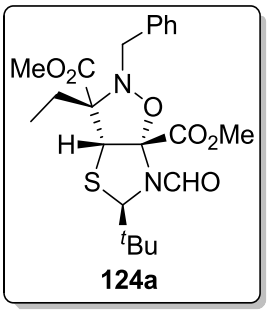
IR (neat) v 1752, 1748, 1684, 1365, 1309, 1282, 1247, 1180, 1109 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.07 (s, 1H, C*H*O), 7.38-7.24 (m, 5H, H_{Ph}), 5.53 (s, 1H, H_5), 4.90 (s, 1H, H_{3a}), 4.38 (d, *J* = 14.5, 1H, CH_2Ph), 3.81 (s, 3H, C_{6a}-OCH_3), 3.80 (s, 3H, C_3-OCH_3), 3.80*overlapped (d, *J* = 13.8, 1H, CH_2Ph), 1.63 (s, 3H, CH_3), 0.82 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.0 (C_3-*C*O_2Me), 166.2 (C_{6a}-*C*O_2Me), 161.7 (*C*HO), 137.0 (C_{qPh}), 128.4 (C_{Ph}), 128.2 (C_{Ph}), 127.6 (C_{Ph}), 99.7 (C_{6a}), 76.1 (C_5), 71.7 (C_{3a}), 65.7 (C_3), 55.2 (*C*H_2Ph), 54.1 (C_{6a}-O*C*H_3), 52.5 (C_3-O*C*H_3), 39.2 (*C*(CH_3)$_3$), 26.3 (C(*C*H_3)$_3$), 16.7 (*C*H_3)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{21}H_{29}N_2O_6S$ 437.1741; found 437.1734

Synthesis of (3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formylhexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate 124a



124a

Following the general procedure for the reduction of sulfoxides to thioethers, bicyclic isoxazolidine **124b** (42.4 mg, 0.09 mmol) was dissolved in acetone (3 ml) at 0 °C. The reaction was completed in 2.5 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 10/90) to give **124a** (35.6 mg, 0.08 mmol, 87% yield) as a colourless oil.

$[\alpha]_D^{26}$: +141° (*c* 0.5; $CHCl_3$)

IR (neat) v 1748, 1683, 1363, 1350, 1299, 1243, 1207, 1179, 1134 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.05 (s, 1H, C*H*O), 7.36-7.23 (m, 5H, H_{Ph}), 5.50 (s, 1H, H_5), 5.03 (s, 1H, H_{3a}), 4.58 (d, *J* = 14.4, 1H, CH_2Ph), 3.93 (d, *J* = 14.4, 1H, CH_2Ph), 3.81 (s, 3H, C_3-OCH_3), 3.80 (s, 3H, C_{6a}-OCH_3), 2.19 (dq, *J* = 14.4, 7.4, 1H, C$H_2$$CH_3$), 2.04 (dq, *J* = 15.2, 7.7, 1H, C$H_2$$CH_3$), 1.13 (t, *J* = 7.5, 3H, CH_2CH_3), 0.83 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 169.0 (C_3-*C*O_2Me), 166.4 (C_{6a}-*C*O_2Me), 161.8 (*C*HO), 137.5 (C_{qPh}), 128.4 (C_{Ph}), 128.1 (C_{Ph}), 127.5 (C_{Ph}), 99.7 (C_{6a}), 79.8 (C_3), 71.7 (C_5), 63.7 (C_{3a}), 55.4 (*C*H_2Ph), 54.0 (O*C*H_3), 52.2 (O*C*H_3), 39.2 (*C*(CH_3)$_3$), 26.3 (C(*C*H_3)$_3$), 24.0 (*C*$H_2$$CH_3$), 10.2 ($CH_2$*C*$H_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{22}H_{30}N_2O_6SNa$ 473.1717; found 473.1697

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Chapter V

Synthesis of bis-amino acids: pyrrolidine-thiazolidine fused bicyclic scaffolds as precursors of cysteine-proline chimeras

V. Synthesis of bis-amino acids: pyrrolidine-thiazolidine fused bicyclic scaffolds as precursors of cysteine-proline chimeras

1. INTRODUCTION

Proline is the unique amino acid in which the amino function is bonded to the side chain forming thus a pyrrolidine ring. This special feature confers it singular properties, such as the high propensity to induce β-turns in the secondary structure of peptides and proteins[1] which are very important in molecular recognition processes. Within this context, prolines are crucial in nucleating the secondary structures and therefore in the biological behavior of peptides.[2] Hence, the incorporation of proline into peptides often improves the stability and selectivity of the modified peptides.[3] Besides, proline is also considered as a privilege scaffold for the synthesis and developments of new catalysts, both for their application in organocatalysis and as ligands or auxiliaries for asymmetric synthesis.[4]

The preparation of new proline analogues has been widely reported. In this sense, there are a vast number of papers and patents focused in the synthesis of quaternary prolines (especially α-methylathed)[5] which are usually prepared from proline by a deprotonation/alkylation strategy.[5b] The synthesis of β, γ and δ substituted prolines has been described by many diverse strategies.[4d,6] It is worth highlighting the important role of some proline analogues as 4-hydroxyproline, 3- or 4-ketoprolines and pyroglutamic acid as suitable starting materials for the synthesis of such substituted prolines.[7] Moreover, the synthesis and applications of bicyclic fused prolines derivatives have also been broadly developed.[8]

However, other strategies involve the creation of the pyrrolidine ring. In this context, the synthetic approaches to achieve this ring could be classified by means of the last bond created to access the pyrrolidine ring (*Figure 27*).

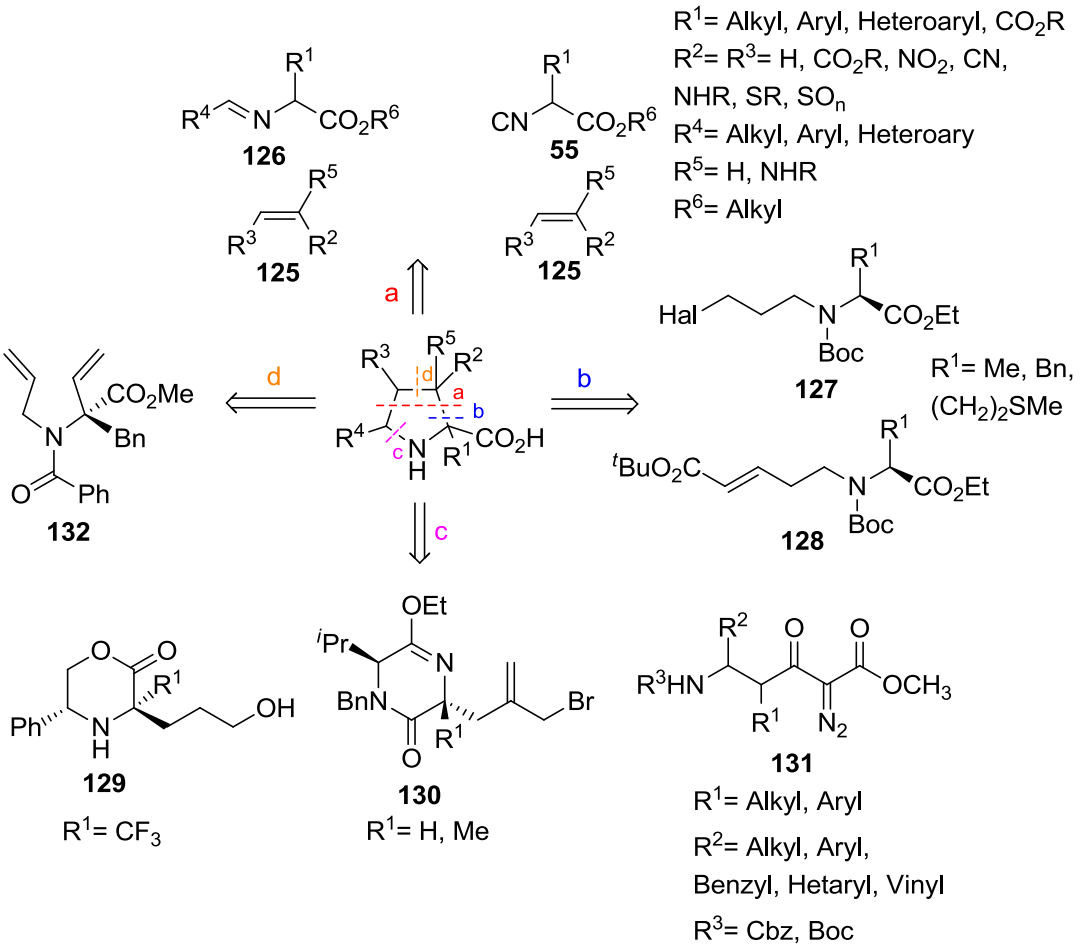


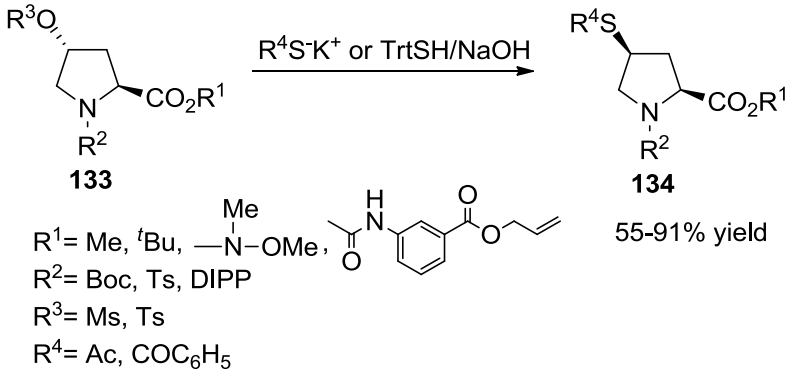
Figure 27. Retrosynthetic analysis of most commonly routes to access the pyrrolidine ring

The disconnection ***a***, which is one of the most extended methodology to access the pyrrolidine ring, diastereo- and enantioselectively by the use of different chiral ligands, chiral auxiliarires or organocatalyst,[9] implies the 1,3-dipolar cycloaddition between alkenes **125** (which could be a dehydroamino acid, R^2= CO_2R and R^5= NHR) and azomethine ylides, usually generated from α-imino esters **126** in the presence of a metal salt[5,10] or by the [3+2] cycloaddition between an alkene **125** and an isocyano ester derivative **55**.[11] Besides, the cyclization between α and β carbons of the pyrrolidine ring (disconnection ***b***) has also been reported as an appropriate strategy to prepare substituted prolines from *N*-Boc-*N*-ω-bromoalkyl-α-amino acid derivatives **127**[12] or by the intramolecular conjugate addition of an enolate generated from **128**.[13] This strategy is also useful for the preparation of prolines with vicinal substituted stereogenic carbons. Another suitable route is the bond formation between the nitrogen and the δ carbon of the proline (disconnection ***c***) by an intramolecular cyclization of chiral scaffolds **129**[14] and **130**[15] or from δ-amino-α-diazo β-ketoesters **131**,[6a,16] among others.[17] Finally, ring closing metathesis has demonstrated to be also a powerful tool for the synthesis of

prolines, starting from molecules with two double bond adequately located as **132** (disconnection ***d***).[18]

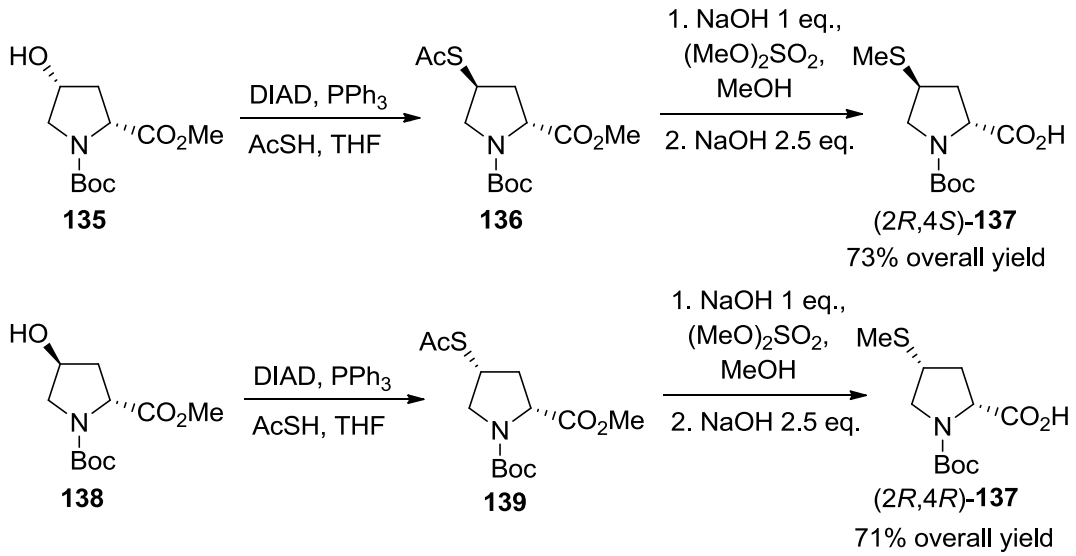
Among all the possible substitutions on prolines, those analogues that bear side-chains belonging to other amino acids, so called chimeras,[19] have been of singular interest for the advancement of new peptide-based therapeutics[20] and the elucidation of biologically active conformations involved in molecular recognition processess.[21] At this family of compounds belongs the cysteine-prolines chimeras, which are indeed the 3-mercaptoproline derivatives. In addition, 4-mercaptoprolines could be considered as homocysteine-proline hybrids.

Within this context, the synthesis of 3-mercaptoprolines derivatives, has already been depicted in this dissertation, Chapter I 8.2 (azacyclic β-substituted cysteine derivatives), which has been mostly carried out *via* a thio-Michael addition of thiols to dehydroproline derivatives. The synthesis of 4-mercaptoprolines has also attracted much attention since several years ago. Thus, the preparation of protected (4*S*)-mercaptoprolines **134** has been generally achieved *via* a S_N2 reaction by the nucleophilic attack of a thiolate over 4-mesyl or tosyl-proline derivative **133**,[22] prepared from (4*R*)-hydroxyproline (*Scheme 43*).



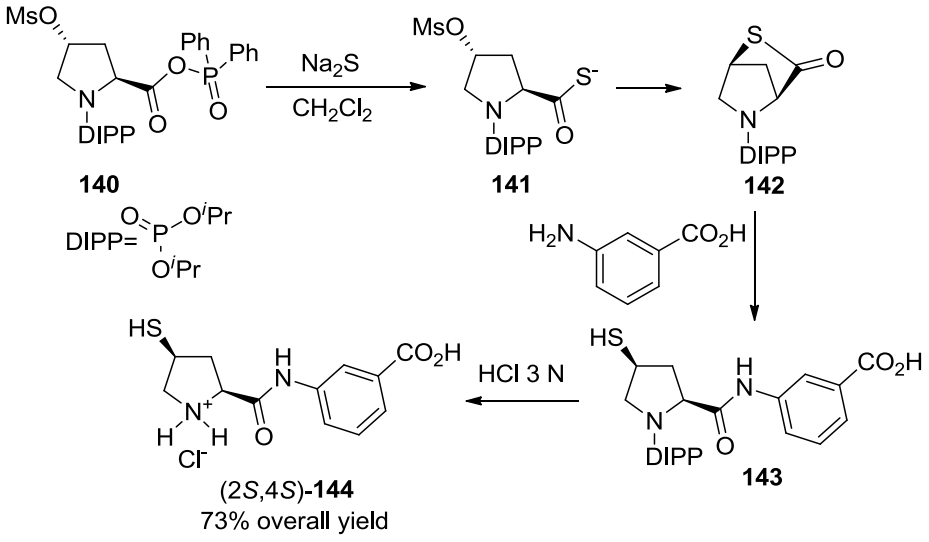
Scheme 43

Mitsunobu reaction has been reported as a good approach to obtain (2*R*,4*S*)-*N*-Boc-4-(methylthio)proline **137** and its diastereoisomer (2*R*,4*R*)-**137**. In this sense, 4-hydroxyprolines **135** or **138** reacted with thiolacetic acid under Mitsunobu conditions affording *S*-acetyl intermediates **136** and **139**, that were transformed into the corresponding (2*R*,4*S*)-*N*-Boc-4-(methylthio)proline **137** and its diastereoisomer (2*R*,4*R*)-**137**, respectively (*Scheme 44*).[21b]



Scheme 44

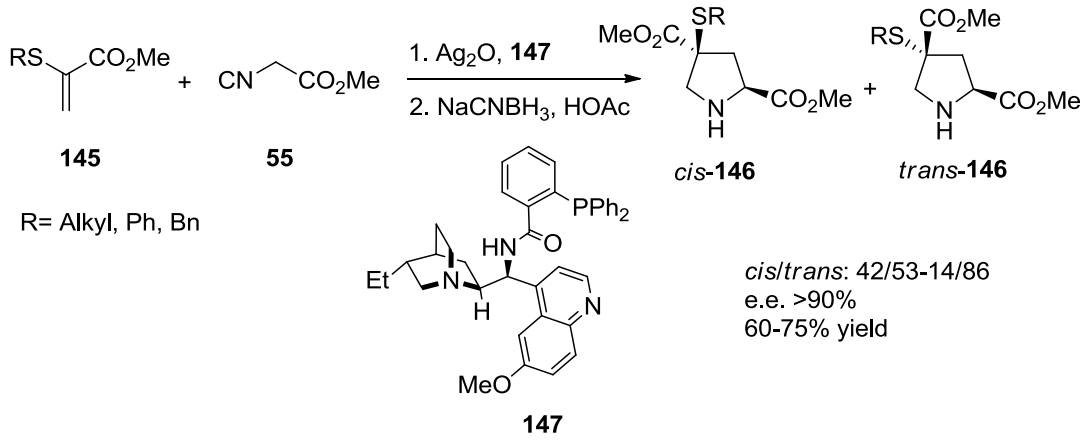
Brands *et al.*[23] reported the synthesis of the 4-mercaptoproline derivative **144**, a precursor of the antibiotic Ertapenem, through a one-pot methodology that involved the formation of the key thiolactone intermediate **142** whose ring opening and acid hydrolysis led to the target (2*S*,4*S*)-mercaptoproline derivative **144** (*Scheme 45*).



Scheme 45

Recently, the 1,3-dipolar cycloaddition has emerged as a suitable methodology for the enantioselective synthesis of 4-mercaptoprolines. In this sense, Wang *et al.*[24] described the 1,3-dipolar cycloaddition reaction between methyl isocyanoacetate **55** and α-thiacrylates **145** affording the mixture of *cis*- and

trans-4-mercaptoprolines **146** in excellent yields and enantioselectivities for both diastereoisomers in presence of the chiral ligand **147** (*Scheme 46*).



Scheme 46

On the other hand, proline-cysteine hybrids could also take part of bis-amino acids as 4-aminopyrrolidine-2,4-dicarboxylate derivatives which are valuable products for its applications in different fields. It has been demonstrated that some compounds of this family have activity as agonists for metabotropic glutamate receptors, which are involved in the pathologies of neurodegenerative diseases,[25] in particular (2*R*,4*R*)-4-aminopyrrolidine-2,4-dicarboxylic acid **148**.[26] Moreover, the bis-amino acid **148** has been employed as monomer for the synthesis of bis-peptides with a well-defined length and structure as **149** (*Figure 28*). The applications of such scaffolds are still under development which are envisioned to find it usefulness in molecular recognition, nanoscience or multifunctional catalysis.[27] The reported strategies for the enantioselective synthesis of the bis-amino acids 4-amino-4-carboxylate proline derivatives have been designed starting from enantiopure materials such as commercially available 4-hydroxyproline, that after protection of the functional groups and oxidation of the hydroxyl group to carbonyl group, could be subjected firstly, to a Bucherer-Bergs reaction and then to several organic transformations which lead finally to the target compounds.[25c,28]

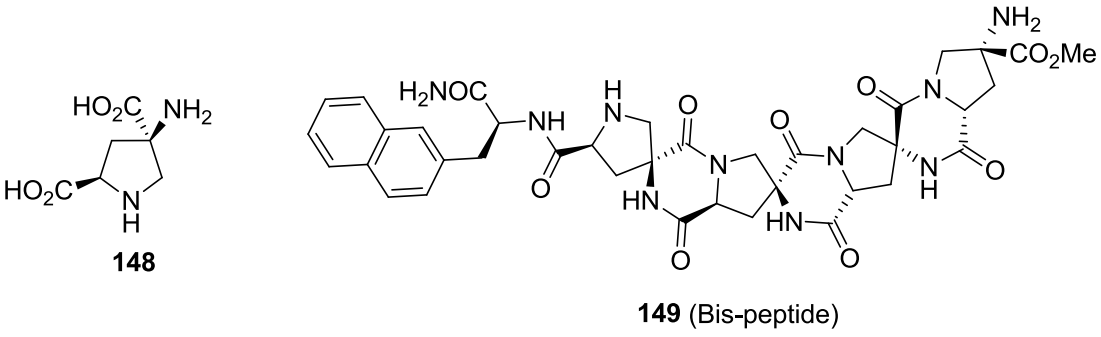
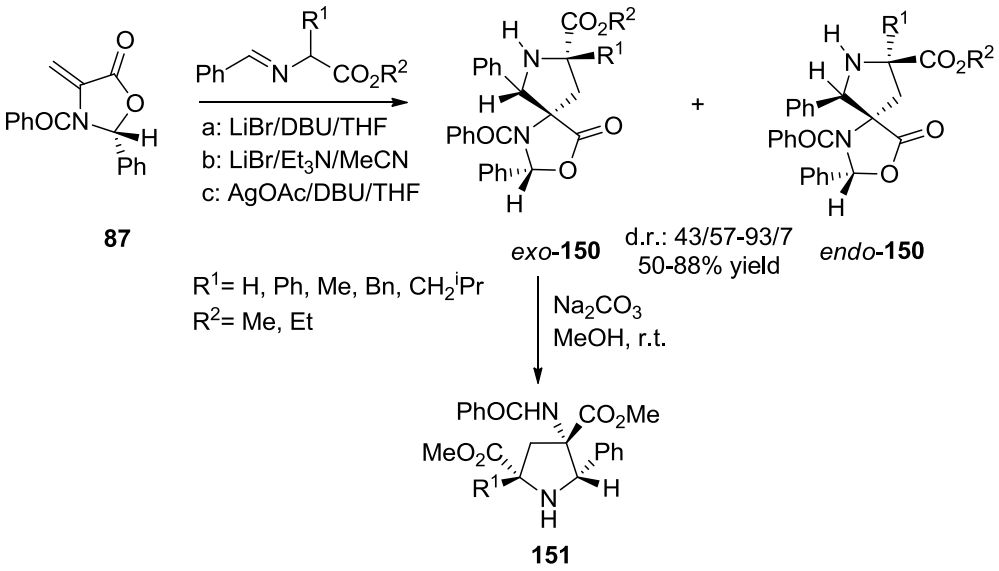


Figure 28

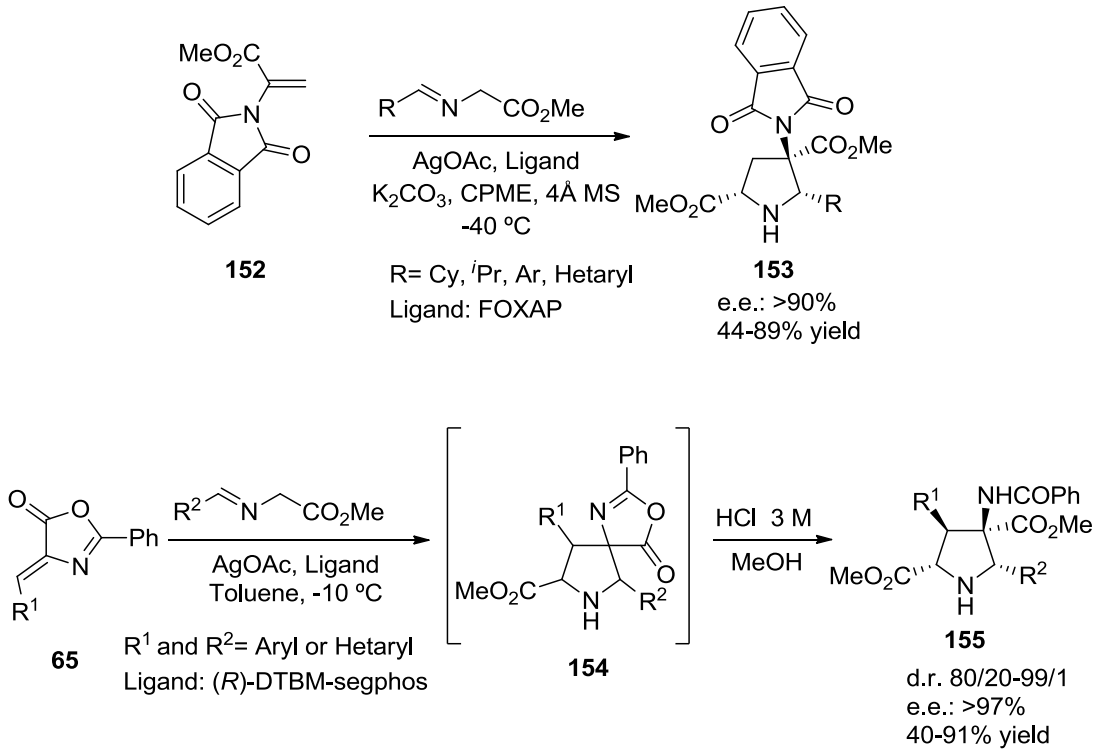
Although, the preparation of such compounds by means of 1,3-dipolar reaction between conveniently substituted dehydroalanines and α-imino esters has been scarcely explored in the bibliography, it is indeed, *a priori*, a versatile methodology due to the wide range of substituents on both the alkene and the α-imino ester.

Within this context, Pyne *et al.*[29] reported the first preparation of highly substituted prolines bearing two amine and carboxylic functions. In particular, the 1,3-dipolar cycloaddition between the chiral oxazolidinone **87** and some azomethine ylides, generated *in situ* from α-imino esters in the presence of a metal salt and base, gave the corresponding spirooxazolidinones as a mixture of *exo* and *endo* isomers **150** in favour of the *exo* isomer with complete regioselectivity and high enantiopurity. Further transformation of the *exo* cycloadduct **150** with sodium bicarbonate led to the protected highly substituted prolines **151** (*Scheme 47*).



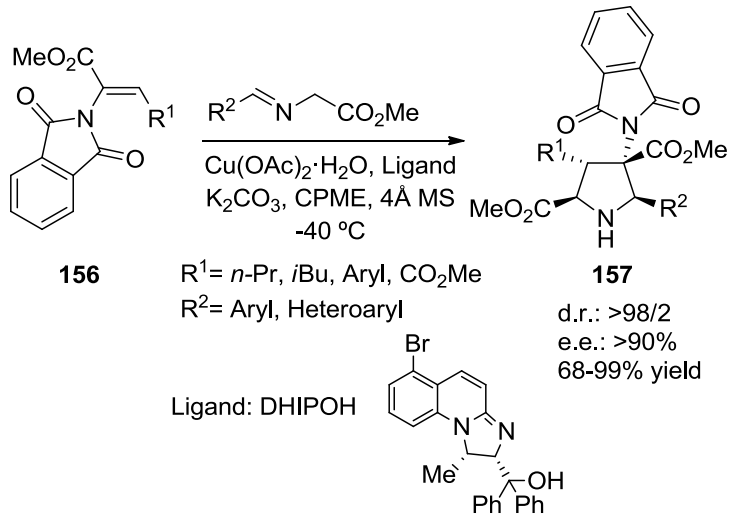
Scheme 47

In this sense, Wang *et al.*[30] and González-Esguevillas *et al.*[31] developed the 1,3-dipolar cycloaddition between α-phthalimidoacrylates **152** and oxazolones **65** with azomethine ylides, using chiral metal complex catalysts to obtain the corresponding protected bis-amino acids **153** and **155**, respectively. In both cases, the cycloadducts **153** and **155** could be obtained with excellent diastereo- and enantioselectivities, and proceeded with complete regioselectivity in favour of the 2,4-addition (*Scheme 48*).



Scheme 48

Finally, Wang *et al*.[32] developed another catalytic system to perform the 1,3-dipolar cycloaddition between the trisubstituted α-phthalimidoacrylates **156** and azomethine ylides. In this case, they employed the chiral ligand DHIPOH and the metal salt $Cu(OAc)_2 \cdot H_2O$ in presence of K_2CO_3 as base. Thus, the corresponding prolines **157** were obtained in good to excellent yields and excellent diastereo- and enantioselectivities (*Scheme 49*).

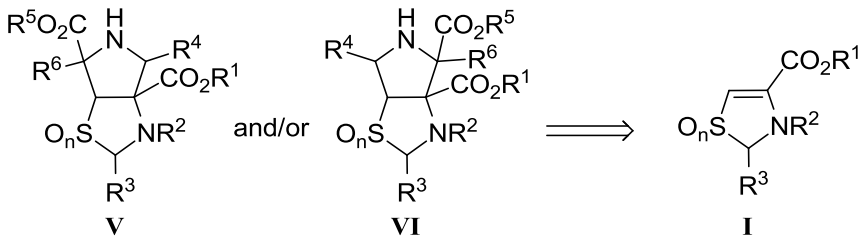


Scheme 49

2. OBJECTIVES

Taking into account these antecedents and our characteristic dehydroamino acid templates, the development of a methodology for the diastereoselective and enantioselective synthesis of sulfur substituted bis-amino acids, cysteine- or homocysteine-proline chimeras, is a great challenge. To the best of our knowledge it would be the first time to describe a synthetic methodology for preparation of bis-amino acids based on pyrrolidine scaffold bearing a sulfur substitution in position 3 or 4 of the pyrrolidine ring.

Within this purpose, the 1,3-dipolar cycloaddition reaction between thiazolines **I** and some α-imino esters, derived from natural amino acids, will be studied in order to determinate the regio-, diastereo- and enantioselectivity of the cycloadducts obtained **V** and/or **VI**.



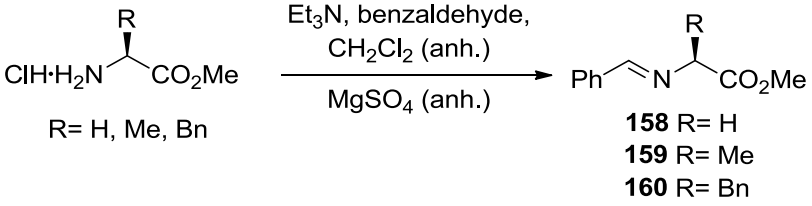
V **VI** **I**

3. RESULTS AND DISCUSSION

In order to obtain highly substituted prolines, in particular proline-cysteine hybrids, it was decided to perform the 1,3-dipolar cycloaddition between thiazolines **39a-c** and some azomethine ylides.

3.1. 1,3-Dipolar cycloaddition between thiazolines 39a-c and *N*-benzylidene substituted α-imino esters 158-160

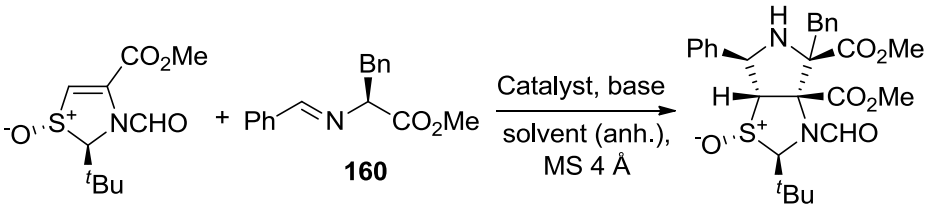
To this end, thiazolines **39a-c** were subjected firstly to react with α-imino esters **158-160**, prepared from the condensation of benzaldehyde and glycine methyl ester, *L*-alanine methyl ester and *L*-phenylalanine methyl ester in presence of triethylamine and $MgSO_4$ (anh.) as it is reported in the bibliography[33] (*Scheme 50*).



Scheme 50. Synthesis of α-imino esters **158-160**

Thiazoline **39b** and α-imino ester **160** were chosen as model substrates for a first screening of the 1,3-dipolar cycloaddition reaction conditions. In this sense, it was decided to perform the reaction in similar conditions of the previously reported examples for the addition of azomethine ylides to other dehydroamino acids.[29-32] Thus, a combination between different solvents (CH_3CN, THF, CH_2Cl_2 and EtOAc), bases (DBU, DBN, Cs_2CO_3, ^tBuOK and K_2CO_3) and Lewis acids catalysts (AgOAc, $Cu(OAc)_2$ and LiBr) were employed at room temperature to find out the more suitable conditions.

Table 15. Reaction conditions and results for the 1,3-dipolar cycloaddition between thiazoline **39b** and α-imino ester **160**



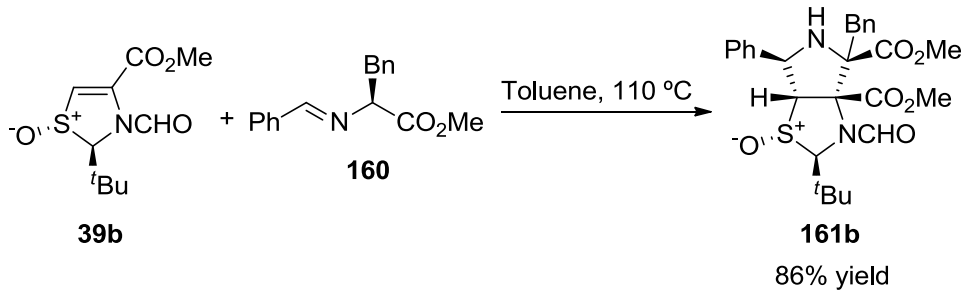
39b **160** **161b**

Entry[a]	Solvent	Base	Catalyst	Time (h)	Yield (%)[b]
1	CH_2Cl_2	DBU 1 eq.	AgOAc 1 eq.	48	31
2	CH_3CN	DBU 1 eq.	AgOAc 1 eq.	32	67
3	THF	DBU 1 eq.	AgOAc 1 eq.	30	62
4	THF	DBU 0.2 eq.	AgOAc 0.2 eq.	17	55
5	THF	DBU 1 eq.	AgOAc 1 eq.	15	78[c]
6	THF	DBN 1 eq.	AgOAc 1 eq.	24	79
7	THF	Cs_2CO_3 1 eq.	AgOAc 1 eq.	120	-
8	THF	^{t}BuOK 1 eq.	AgOAc 1 eq.	48	-
9	THF	K_2CO_3 1 eq.	AgOAc 1 eq.	48	-
10	EtOAc	K_2CO_3 1 eq.	AgOAc 1 eq.	96	-
11	THF	DBU 1 eq.	$Cu(OAc)_2$ 1 eq.	48	42
12	EtOAc	DBU 1 eq.	$Cu(OAc)_2$ 1 eq.	24	52
13	EtOAc	DBU 0.5 eq.	$Cu(OAc)_2$ 0.5 eq.	40	65
14	EtOAc	DBU 0.2 eq.	$Cu(OAc)_2$ 0.2 eq.	16	61
15	EtOAc	DBU 0.2 eq.	LiBr 0.2 eq.	24	30

[a]Reactions carried out at r.t. in presence of 1 eq. of α-imino ester. [b]Isolated yield. [c]1.3 eq. of α-imino ester.

The screening began by testing the influence of the solvent in the 1,3-dipolar cycloaddition, in presence of DBU (1 eq.) as base and AgOAc (1 eq.) as Lewis acid catalyst. Poor yield was obtained when methylene chloride was employed as solvent (*Table 15*, entry 1). Instead, the use of acetonitrile and tetrahydrofurane afforded exclusively the bicyclic thiazolidine **161b** in good yields in both cases (entries 2 and 3). The use of Lewis acid catalyst and base in sub-stoichiometric amount did not improve the previous results (entry 4). However, the use of 1.3 eq of α-imino ester **160** achieved better results (entry 5). Next, the change of base was assessed. Within this context, the reaction carried out in the presence of DBN (entry 6) gave good yield but reactions using Cs_2CO_3 (entry 7), ^{t}BuOK (entry 8) and K_2CO_3 (entries 9 and 10) did not progress. Besides, the use of other catalyst was also examined. The results using $Cu(OAc)_2$ as catalyst were different depending on the reaction solvent. In this sense, the use of EtOAc as solvent in comparison with THF showed to be better when $Cu(OAc)_2$ was employed as catalyst (entry 11 *vs.* entry 12). The reduction of the catalyst amount from 1 eq. to 0.5 and 0.2 eq. led to an enhancement of the reaction yield (entries 12 *vs*. 13 and entry 12 *vs*. entry 14). However, the use of an inorganic catalyst such as LiBr did not show the same efficiency as the other catalysts (entry 15).

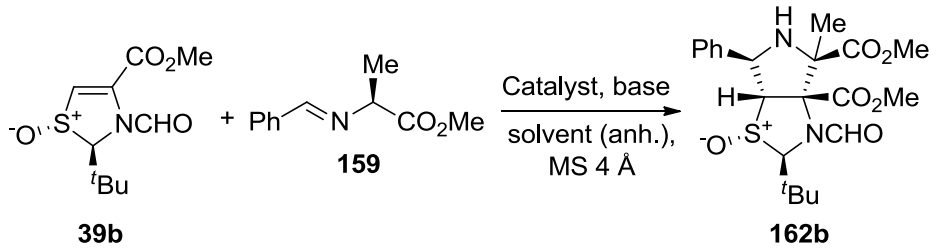
On the other hand, the thermic activation for the reaction between alkenes and azomethine ylides[34] is a methodology scarcely employed in the last years.[35] However, the 1,3-dipolar cycloaddition between thiazoline **39b** and α-imino ester **160** in toluene at 110 ºC for 24 hours gave the bicyclic pyrrolidine-thiazolidine **161b** in high yield as a single diastereoisomer in enantiopure form (*Scheme 51*).



Scheme 51. Thermic activation conditions for the 1,3-dipolar cycloaddition between **39b** and **160**

Then, it was carried out the 1,3-dipolar cycloaddition between thiazoline **39b** and α-imino ester **159** under the optimized conditions for the synthesis of the bicyclic pyrrolidine-thiazolidine compound **161b** (*Table 16*).

Table 16. Reaction conditions and results for the 1,3-dipolar cycloaddition between thiazoline **39b** and α-imino ester **159**



Entry[a]	Solvent	Base	Catalyst	Time (h)	Yield (%)[b]
1	Toluene	-	-	24	83[c]
2	THF	DBN 1 eq.	AgOAc 1 eq.	48	62
3	THF	DBU 0.2 eq.	AgOAc 0.2 eq.	30	80[d]
4	EtOAc	DBU 0.2 eq.	$Cu(OAc)_2$ 0.2 eq.	24	66
5	EtOAc	DBU 1 eq.	$Cu(OAc)_2$ 1 eq.	24	73

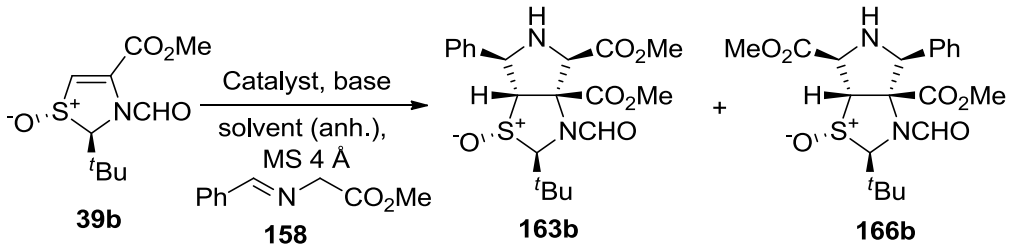
[a]Room temperature. [b]Isolated yield. [c]110 ºC without MS 4Å. [d]1.3 eq. of iminoester.

As it is shown in *table 16*, the best result was obtained for the reaction performed under thermic activation, rendering exclusively the bicyclic pyrrolidine-thiazolidine **162b** in high yield as a single diastereoisomer (*Table 16*, entry 1). Similarly, the reaction carried out using AgOAc as catalyst in stoichiometric (entry 2) and sub-stoichiometric amount and a slightly excess of α-imino ester (entry 3), afforded the bicyclic proline-thiazolidine **162b** in high yield as a single diastereoisomer. The use of $Cu(OAc)_2$ as catalyst in sub-stoichiometric and

stoichiometric amount gave also good yields, respectively (entry 4 and entry 5). However, the yield was worse in comparison with the use of AgOAc as catalyst or the thermic activation conditions (entries 4 and 5 *vs*. entries 1 and 3).

On the other hand, the reaction between thiazoline **39b** and *N*-benzylidene glycine methyl ester **158** was also performed under thermic activation and using Lewis acid catalysts conditions (*Table 17*).

Table 17. Reaction conditions and results for the 1,3-dipolar cycloaddition between thiazoline **39b** and α-imino ester **158**



39b **158** **163b** **166b**

Entry[a]	Solvent	Base	Catalyst	Time (h)	Yield (%)[b]	163b/166b ratio[c]
1	toluene	-	-	24	-	-
2	CH_3CN	DBU 1 eq.	AgOAc 1 eq.	15	27	100/0 (**163b**/**166b**)
3	toluene	DBU 1 eq.	AgOAc 1 eq.	19	29	100/0 (**163b**/**166b**)
4	THF	DBU 1 eq.	AgOAc 1 eq.	24	47	100/0 (**163b**/**166b**)
5	EtOAc	DBU 1 eq.	AgOAc 1 eq.	24	35	100/0 (**163b**/**166b**)
6	THF	DBU 0.2 eq.	AgOAc 0.2 eq.	48	19	0/100 (**163b**/**166b**)
7	EtOAc	DBU 1 eq.	$Cu(OAc)_2$ 1 eq.	24	11	44/56 (**163b**/**166b**)
8	EtOAc	DBU 0.5 eq.	$Cu(OAc)_2$ 0.5 eq	24	33	69/31 (**163b**/**166b**)
9	EtOAc	DBU 0.2 eq.	$Cu(OAc)_2$ 0.2 eq	24	57	69/31 (**163b**/**166b**)

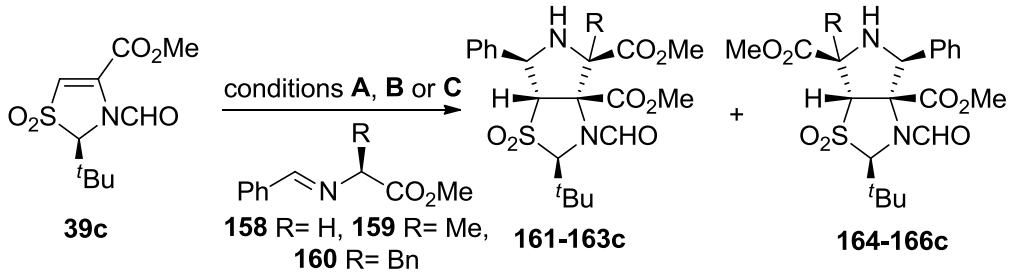
[a]All the reactions were carried out at r.t. unless entry 1 that was carried out at 110 °C [b]Isolated yield. [c]Determined by ^{1}H NMR.

The 1,3-dipolar cycloaddition reaction between thiazoline **39b** and α-imino ester **158** under thermic activation (110 °C) resulted unsuccessfully (*Table 17*, entry 1). Then, the cycloaddition was carried out using the metal salts AgOAc and $Cu(OAc)_2$ as it is shown in *Table 17*. The reactions carried out in presence of AgOAc as Lewis acid gave a single regioisomer **163b** (entries 2-5), or **166b** (entry 6). The reaction performed with $Cu(OAc)_2$ as Lewis acid afforded two regioisomers **163b** and **166b** in different ratios using stoichiometric or sub-stoichiometric amounts (entries 7-9). The best result was obtained employing $Cu(OAc)_2$ and DBU in sub-stoichiometric amount (0.2 eq.), to give as major adduct **163b** in moderate yield (entry 9). Minor by-products were detected in every reaction crude by ^{1}H NMR although were not isolated.

Next, it was tested the reactivity of sulfonyl thiazoline **39c** and α-imino esters **158-160**. Both thermic and Lewis acid catalyst conditions were attempted. In this

sense, three different conditions were established, one of them regarding the thermic activation conditions; method **A**: toluene, 80 ºC, and two corresponding with Lewis acid catalyst conditions; method **B**: AgOAc (1eq.), DBU (1 eq.), EtOAc, room temperature, MS 4Å, and method **C**: AgOAc (1 eq.), DBN (1 eq.), EtOAc, room temperature, MS 4Å. The results obtained are gathered in *table 18*.

Table 18. Reaction conditions and results for the 1,3-dipolar cycloaddition between thiazoline **39c** and α-imino esters **158-160**



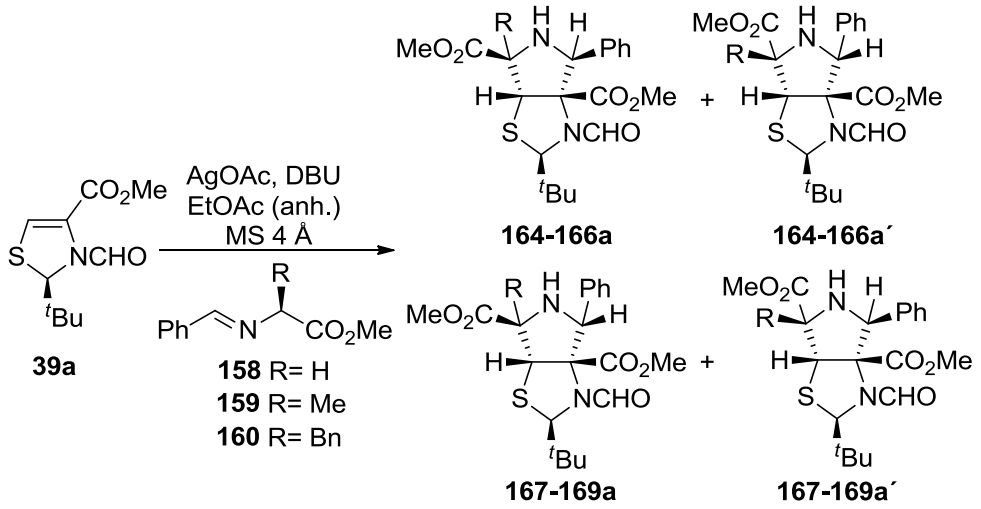
Entry	R	Conditions	Time	Yield (%)[a]	Products ratio[b]
1	Bn	**A**	20	95	100/0 (**161c/164c**)
2	Bn	**B**	24	24	100/0 (**161c/164c**)
3	Bn	**C**	24	30	100/0 (**161c/164c**)
4	Bn	**C**	48	66	100/0 (**161c/164c**)
5	Me	**A**	15	91	100/0 (**162c/165c**)
6	Me	**B**	36	33	70/30 (**162c/165c**)
7	H	**A**	48	70	67/33 (**163c/166c**)
8	H	**B**	16	65	76/24 (**163c/166c**)

[a]Isolated yield. [b]Determined by ^{1}H NMR.

Thermic activation (method **A**) was the most effective methodology for the reaction between thiazoline **39c** and α-imino esters **160** (*Table 18*, entry 1) and **159** (entry 5) giving the cycloadducts **161c** and **162c** in excellent yields as single diastereoisomers in enantiopure form, respectively. Indeed, methods **B** and **C**, involving the use of Lewis acids catalysts, gave in general poor to moderate yields (entry 1 *vs.* entries 2-4; entry 5 *vs.* entry 6) and mixture of regioisomers **162c**/**165c** in a ratio 70/30 (entry 5 *vs.* entry 6). However, the reaction between the thiazolidine **39c** and α-imino ester **158** gave similar yields and selectivities for methods **A** and **B**, affording in both cases a mixture of regioisomers **163c**/**166c** in a ratio 67/33 (entry 7) and 76/24 (entry 8) in good yields.

Finally, it was carried out the cycloaddition between thiazoline **39a** and α-imino esters **158-160** in presence of AgOAc, DBU and anhydrous ethyl acetate as solvent as it is depicted in *table 19*.

Table 19. Reaction conditions and results of the 1,3-dipolar cycloaddition reactions between thiazoline **39a** and α-imino esters **158-160**



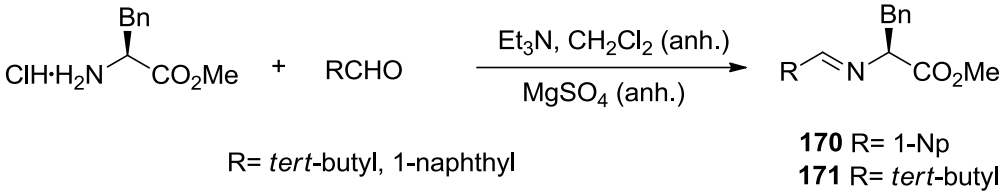
Entry[a]	R	DBU eq.	AgOAc eq.	Time (h)	Yield (%)[b]	Products ratio[c]
1	Bn	1	1	72	65	68/32 (**164a´/167a´**)
2	Bn	0.5	0.5	72	68	65/35 (**164a´/167a´**)
3	Me	1	1	72	70	41/24/34 (**165a/165a´/168a´**)
4	Me	0.5	0.5	72	75	37/24/39 (**165a/165a´/168a´**)
5	Me	0.2	0.2	72	81	41/47/11 (**165a/165a´/168a´**)
6	H	0.5	0.5	72	53	31/46/23 (**166a/166a´/169a**)
7	H	0.2	0.2	80	72	48/31/21 (**166a/166a´/169a**)

[a]Reactions carried out at r.t. and 1 eq. of α-imino ester. [b]Isolated yields. [C]Isolated.

1,3-Dipolar cycloaddition between thiazoline **39a** and α-imino ester **160** proceeded in good yields to afford mixtures of diastereoisomers **164a´/167a´** in ratios 68/32 and 65/35 (*Table 19*, entries 1 and 2), respectively. However, the cycloadditions between thiazoline **39a** and α-imino ester **159** in different conditions, basically changing the amount of reagents, DBU and Lewis acid, afforded mixtures of 3 isomers **165a**/**165a´**/**168a´** in good to high yields in different ratios (entries 3-5). Finally, the 1,3-cycloaddition of thiazoline **39a** and α-imino ester **158** provided also mixtures of three isomers. Reaction carried out with both DBU and Lewis acid (0.5 eq.) afforded a mixture of isomers **166a**/**166a´**/**169a** in a ratio 31/46/23 with an overall yield of 53% (entry 6), while the reaction carried out with both DBU and Lewis acid (0.2 eq.) provided a mixture of isomers **166a**/**166a´**/**169a** in a ratio 48/31/21 and a better overall yield of 72% (entry 6 *vs.* entry 7). The products ratio was affected by the decreased of base and Lewis acid employed. In this sense, the mixture of cycloadducts was enriched in favour of isomer **166a**, decreasing the isomer **166a´** (entries 6 *vs.* 7).

3.2. 1,3-Dipolar cycloaddition between thiazolines 39b and 39c and *N*-(1-naphthyl) or -(2,2-dimethylpropylidene)phenylalanine methyl ester 170 and 171

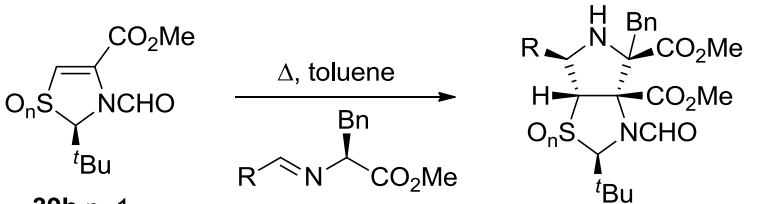
To expand the scope of the 1,3-dipolar cycloaddition, it was carried out the reaction between the thiazolines **39b** and **39c** and α-imino esters with other type of substitution at the iminium carbon and *L*-phenylalanine methyl ester as amino acid. The substituents chosen were the 1-naphthyl and the *tert*-butyl groups. Therefore, the corresponding α-imino esters **170** and **171** were obtained following the methodology performed for the synthesis of *N*-benzylidene substituted α-imino esters previously depicted in this chapter (*Scheme 52*).



Scheme 52. Synthesis of α-imino esters **170** and **171**

In view of the different results obtained in the 1,3-dipolar cycloaddition between thiazolines **39a-c** and α-imino esters using Lewis acids as catalysts, it was decided to carried out the 1,3-dipolar cycloadditions between thiazolines **39b** and **39c** and α-imino esters **170** and **171** under thermic activation (*Table 20*).

Table 20. Reaction conditions and results for the 1,3-dipolar cycloaddition between thiazolines **39b,c** and α-imino esters **170** and **171**



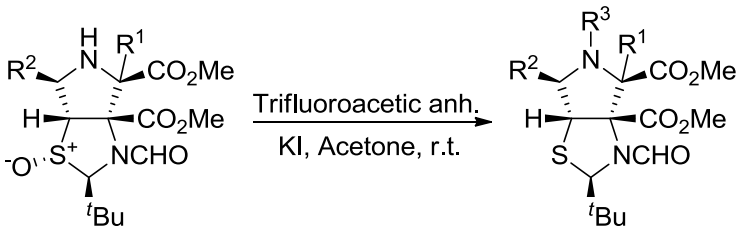
Entry	n	R	Temp. (°C)	Time (h)	Yield (%)[a]
1	1	1-Np	110	60	94
2	2	1-Np	80	60	94
3	1	*tert*-butyl	110	33	61
4	2	*tert*-butyl	80	36	86

[a]Isolated yield.

1,3-Dipolar cycloadditions reactions between thiazolines **39b,c** and *N*-(1-naphthylmethylene)-phenylalanine methyl ester **170**, proceeded at 110 ºC and 80 ºC, to afford the bicyclic compounds **172b** and **172c** in excellent yields and selectivities as enantiopure products (*Table 20*, entries 1 and 2). The 1,3-cycloaddition reaction under thermic conditions between thiazolines **39b,c** and *N*-(2,2-dimethylpropylidene)-phenylalanine methyl ester **171** provided the enantiomerically pure pyrrolidine-thiazolidine bicyclic rings **173b** and **173c** in moderate to high yield (entries 3 and 4) as single diastereoisomers, respectively.

3.3. Reduction of the sulfinyl moiety of bicyclic thiazolidines 161b, 162b, 172b and 173b

In addition, the sulfinyl group of bicyclic thiazolidines **161b**, **162b**, **172b** and **173b** was reduced onto its corresponding sulfanyl group, following the experimental procedure described by Baldwin *et al*.[36] already employed in this dissertation. Thus, over solutions of **161b**, **162b**, **172b** and **173b** in acetone at 0 ºC, trifluoroacetic anhydride and KI were added. The resulting reaction mixtures were stirred until completion at room temperature, obtaining the corresponding reduced bicyclic thiazolidines **161a**, **172a** and **173a** in excellent yields. However, the reaction of **162b** in such conditions gave as result not only the reduction of the sulfinyl group but also the trifluoroacetyl protection of the amine group, thus affording the thiazolidine **174a** in good yield (*Scheme 53*).



	R^1	R^2
161b	Bn	Ph
162b	Me	Ph
172b	Bn	1-Np
173b	Bn	^{t}Bu

	R^1	R^2	R^3	yield (%)
161a	Bn	Ph	H	95
172a	Bn	1-Np	H	94
173a	Bn	^{t}Bu	H	97
174a	Me	Ph	$COCF_3$	81

Scheme 53. Reduction of the sulfinyl group of **161b**, **162b**, **172b** and **173b**

3.4. Interpretation of the stereochemical outcome of the cycloadditions between thiazolines 39a-c and α-imino esters 158-160

The regiochemistry of every major cycloadducts formed in the reactions between sulfinyl and sulfonyl thiazolines **39b,c** and α-imino esters **159** and **160** was proposed by the analysis of COSY and HMBC experiments and suggests that sulfonyl and sulfinyl moieties exerts the control of the regiochemistry of the cycloadditions resulting therefore in favour of the 2,3-addition. However, 1,3-dipolar cycloadditions between thiazolines **39b,c** and *N*-(phenylmethylene)glycine methyl ester **158** provided mixtures of regioisomers **163b,c** and **166b,c** favored to the regioisomers **163b,c**, corresponding to the 2,3-addition due to the electron withdrawing feature of the sulfinyl and sulfonyl moieties. In this context, the HMBC experiment of **163c**, showed a cross peak between the H6a and the quaternary carbon of the phenyl substituent placed at C6. On the contrary, such cross peak was not detected in the HMBC experiment of regioisomer **166c** corresponding to a 2,4-addition (*Figure 29*).

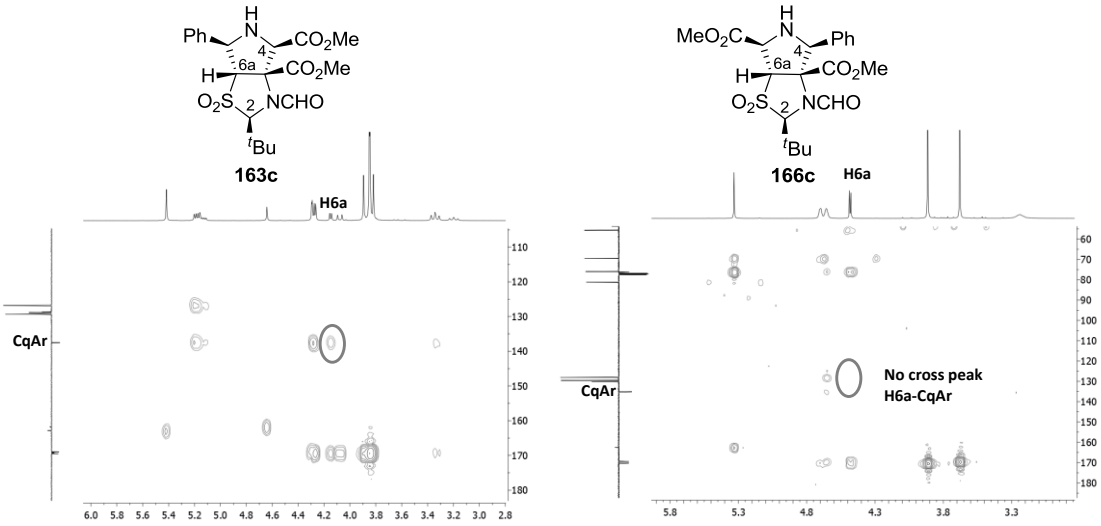


Figure 29. HMBC experiments for **163c** and **166c**

This behavior has already been reported in the bibliography for the cycloaddition between the unsymmetrically 1,2-diactivated *Z*-sulfonyl acrylate and azomethine ylides in which the regiochemistry control is dominated by the sulfonyl group.[37] On the contrary, the reaction carried out between thiazoline **39a** as dipolarophile and α-imino esters **158-160** provided the regioisomers controlled by the ester function, as expected, thus obtaining exclusively the products derived from a 2,4-addition.

The structural elucidation of the stereogenic carbons of every bicyclic pyrrolidine-thiazolidine compounds was made on the basis of NOESY experiments. In this sense, an intense cross peak between H6a and the *tert*-butyl group, located at C2, was observed for each product. Besides, cross peak between methyl group of CO_2Me at C3a and *tert*-butyl group was also detected for almost all bicyclic compounds. Therefore, it was confirmed that the addition of the azomethine ylides took place by the less hindered face of the chiral thiazolines **39a-c**, which is indeed the opposite of the bulky *tert*-butyl group. In addition, the different cross peaks detected from every single product allowed us to assign properly the configuration of all the stereogenic carbons of each bicyclic pyrrolidine-thiazolidine ring. For instance, NOESY experiments of both **162b** and **162c** not only showed the previously cited cross peaks between H6a and the *tert*-butyl group but also between H2 and H6 and H2 and the methyl substituent placed at C4 (*Figure 30*). On the contrary, NOESY experiment of the regiosiomer **165a´** showed the particular n.O.e between the methyl group at C6 and both H6a and H4 (*Figure 30*).

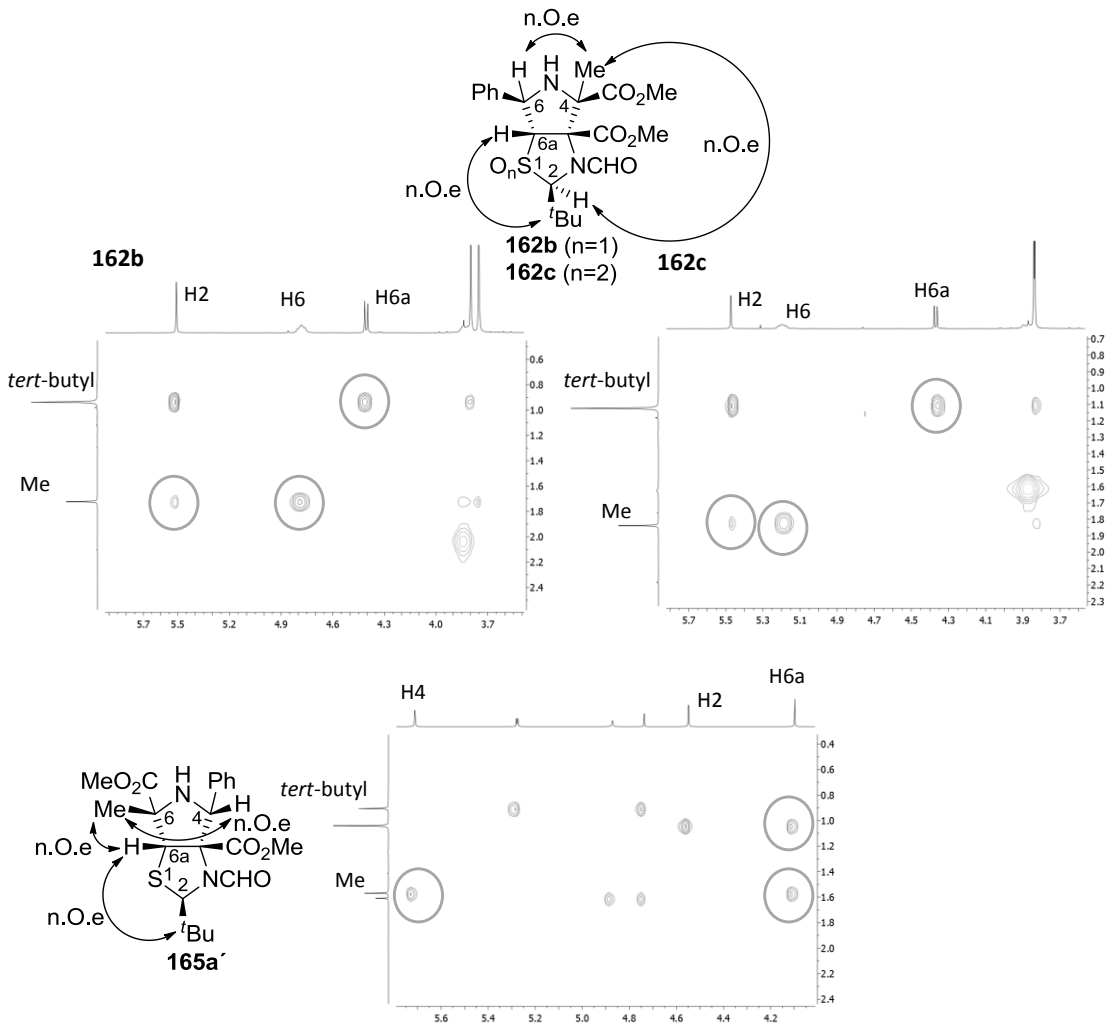
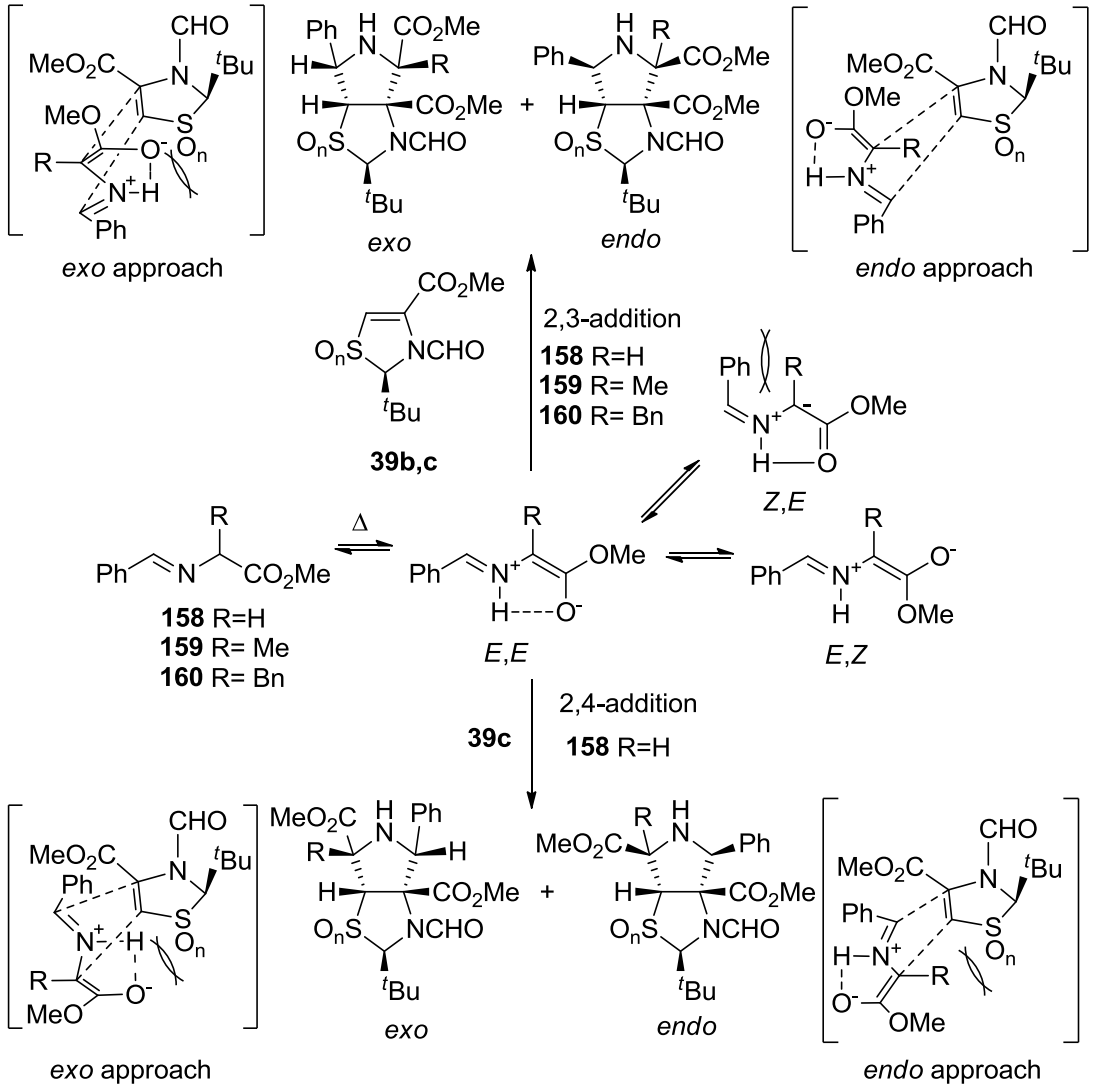


Figure 30. NOESY experiments of compounds **162b,c** and **165a´**

As well, the analysis of the approaches between thiazolines **39a-c** and α-imino esters **158-160** helped us to rationalize the stereochemical outcome of the cycloaddition reactions, taking into account some important facts regarding to the behavior of α-imino esters in the reaction conditions. Within this context, it is already known that α-imino esters undergo 1,2 prototropy when heating, triggered the formation of the azomethine ylide of configuration *E*,*E* which is also able to form the *E*,*Z* isomer through a stereomutation process by the rotation of the bond between the quaternary and the carbonyl carbons.[34a,38] On the contrary, the rotation between the nitrogen atom and the iminium carbon to give the *Z*,*E* isomer is not usually observed due to the steric hindrance of the resulting structure (*Scheme 54*). Within this context, reactions carried out under thermic activation starting from **39b,c** and α-imino esters **159** and **160** lead exclusively to the formation of the cycloadducts **161-162b** and **161-162c** *via* the 2,3-addition through an *endo* approach. Therefore, only the *E*,*E* isomer of the azomethine ylides derived from α-imino esters **159** (R= Me) and **160** (R= Bn) were reactive enough under the thermic conditions performed to lead the products with such regio- and diastereoselectivities observed (*Scheme 54*). The 1,3-dipolar cycloaddition reaction between thiazoline **39c** and α-imino ester **158** derived from the condensation of glycine and benzaldehyde, rendered two regioisomers corresponding to a 2,3- and 2,4 additions, **163c** and **166c**, favored to the 2,3 addition but it was found a complete selectivity in favour of the *endo* approach. The possible explanation of this results could be the lack of lateral chain in the α carbon of the α-imino ester **158** allowing both the 2,4-addition and 2,3-addition because of the minimum steric hindrance caused by the hydrogen in comparison with the methyl or benzyl groups.



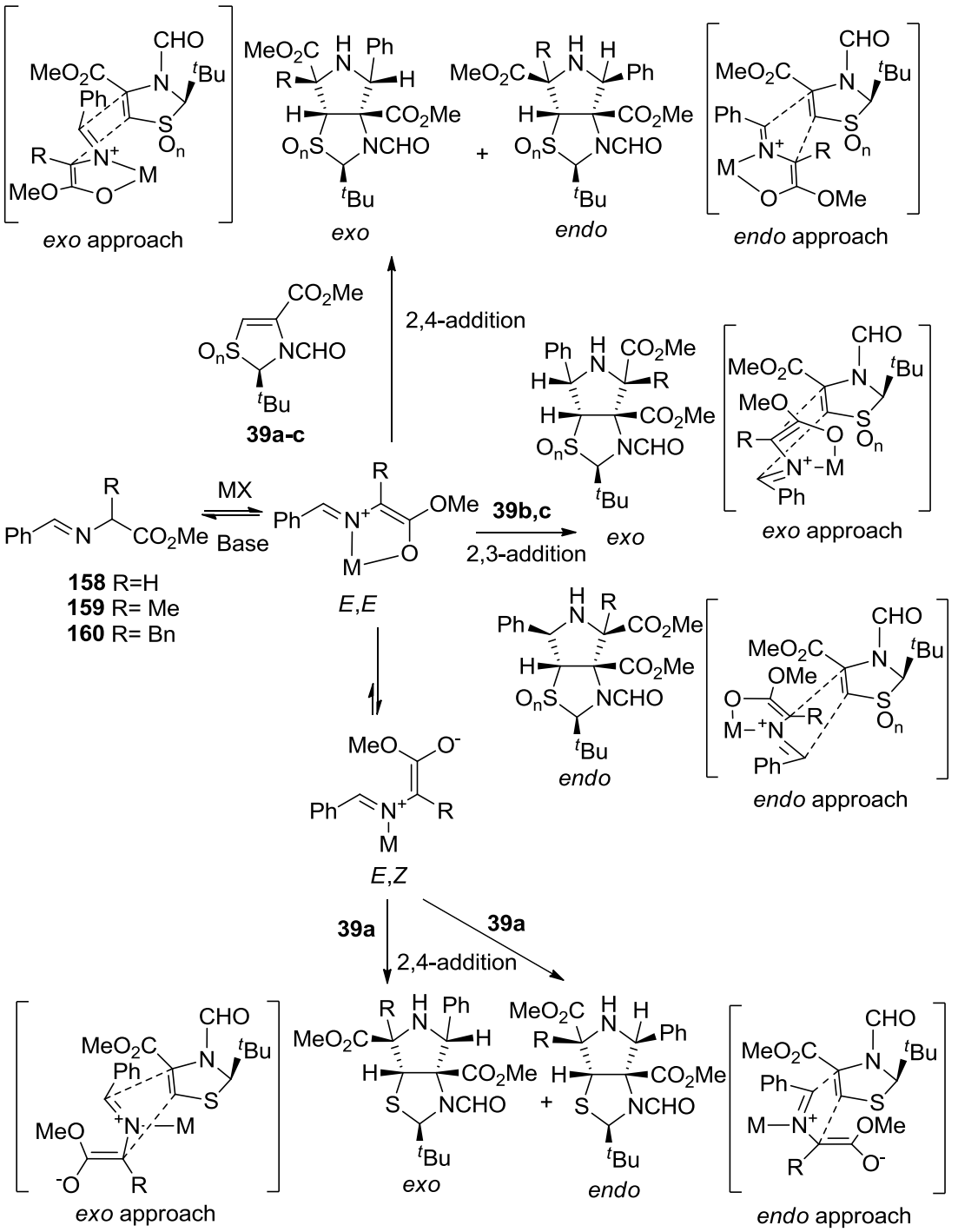
Scheme 54. Mechanistic model proposed for the observed selectivity under thermic activation

On the other hand, in reactions carried out under Lewis acid conditions the coordination of α-imino ester both by the imine and the ester moieties to the metal center, promote the deprotonation of the α-hydrogen by the base, thus forming mostly the azomethine ylide of configuration *E*,*E* and in less ratio the *E*,*Z* isomer.[39] Within this context, reactions between thiazolines **39b,c** and α-imino ester **158** performed under Lewis acid catalyst gave mixture of regioisomers **163b**/**166b** and **163c**/**166c** through an *endo* approach by the less hindered face of the thiazoline ring, corresponding to a 2,3- and 2,4-additions (*Scheme 55*). Such additions could be favored not only for the lack of steric hindrance of the hydrogen but also for a possible interaction between the carbonyl group of the ester moiety of the thiazoline ring and the metal center of the ylide.

However, reactions between thiazoline **39a** and α-imino esters **158-160** in presence of a metal salt, progressed with less diastereoselectivity than starting from its analogues **39b,c** but with complete regioselectivity, leading exclusively to the products derived from a 2,4-addition as it has been previously described. In this sense, the 1,3-dipolar cycloaddition employing the α-imino ester **160** (R= Bn), gave a mixture of cycloadducts **164a´**/**167a´**, in favour of the isomer corresponding to the addition of the *E*,*E* azomethine ylide through an *exo* approach **164a´** which formation could be favored by an interaction between the metal center and the sulfur atom. The minor cycloadduct **167a´**corresponds to the addition of the *E*,*Z* azomethine ylide by an *endo* approach (*Scheme 55*).

On the other hand, the reaction between the thiazoline **39a** with the azomethine ylide derived from α-imino ester **159** (R= Me), gave mixtures of 3 products **165a**/**165a´**/**168a´**. The first one **165a** corresponds to an *endo* approach of the *E*,*E*-azomethine ylide. An *exo* approach of the thiazoline **39a** and the *E*,*E*-azomethine ylide led to **165a´** isomer in which an interaction between the sulfur atom and the metal center could favored its formation. The last one, the isomer **168a´** is obtained through an *endo* approach of the minor *E,Z* isomer of the azomethine ylide and thiazoline **39a**. In this way, the interaction of the carbonyl group of the methyl ester of the thiazoline **39a** and the metal center of the azomethine ylide could stabilize the reaction intermediate (*Scheme 55*).

Finally, the reaction between thiazoline **39a** and α-imino ester **158** gave a mixture of three bicyclic thiazolidines **166a**/**166a´**/**169a**. The major isomer obtained **166a**, derived from an *endo* approach of the *E*,*E* ylide and thiazoline **39a**. The cycloadduct **166a´**was obtained through and *exo* approach of the *E*,*E* ylide and thiazoline **39a** in high ratio probably due to a sulfur-metal stabilizing interaction. The minor isomer **169a** was obtained from the addition of the minor *E*,*Z* isomer of the ylide through an *exo* approach, perhaps due to a sulfur-metal stabilizing interaction. (*Scheme 55*).



Scheme 55. Mechanistic model proposed for the observed selectivity under Lewis acid catalyst conditions

4. CONCLUSIONS

The 1,3 dipolar cycloaddition reactions between thiazolines **39b,c** and α-imino esters **159**, **160**, **170** and **171** under thermic activation took place exclusively through an *endo* approach and a regiochemistry governed by the sulfinyl or sulfonyl moieties in high yields obtaining the corresponding products in enantiopure form. The same reactions carried out under Lewis acid catalyst conditions gave worse yields, in general. However, reaction of thiazolines **39b,c** and α-imino ester **158** under Lewis acid catalyst and thermic conditions, gave mixtures of regioisomers corresponding to a 2,3- and 2,4-additions.

On the other hand, the regiochemistry of the 1,3-dipolar cycloaddition between thiazoline **39a** and α-imino esters **158-160** under Lewis acid conditions was controlled by the ester function of the thiazoline **39a**, thus giving mixtures of enantiopure diastereoisomers by a 2,4-addition. The diastereomeric mixtures obtained were dependent on the substitution in the Cα of the α-imino ester and the amount of both base and Lewis acid employed. These mixtures of products were rationalized by a study of the theoretical approaches of each α-imino ester to the thiazoline **39a**.

In addition, the reduction of the sulfinyl groups of bicyclic pyrrolidine-thiazolidine rings were carried out with satisfactory results.

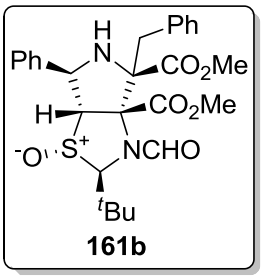
5. EXPERIMENTAL SECTION

5.1. General

All reagents were used as received from commercial suppliers without further purification. Thin-layer chromatography (TLC) was performed on Macherey-Nagel Polygram®SIL G/UV254 precoated silica gel polyester plates. The products were visualized by exposure to UV light, iodine vapour, submersion in ninhydrin stain, in ethanolic solution of phosphomolybdic acid or in an aqueous solution of sodium permanganate. Column chromatography was performed using 60 M (0.04-0.063 mm) silica gel from Macherey-Nagel. Melting points were determined on a Gallenkamp apparatus. IR spectra were registered on a Nicolet Avatar 360 FTIR spectrophotometer; vmax is given for the main absorption bands. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, AV-400 instrument at room temperature, unless otherwise indicated, and using the residual solvent signal as the internal standard; chemical shifts (δ) are expressed in parts per million and coupling constant (*J*) in hertz. Optical rotations were measured at room temperature using a JASCO P-1020 polarimeter. High-resolution mass spectra were obtained on a Bruker Microtof-Q spectrometer.

5.2 Synthesis of protected bis-amino acids from 1,3-dipolar cycloaddition between thiazolines 39a-c and α-imino esters 158-160, 170 and 171

Synthesis of (1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 161b



161b

A solution of thiazoline **39b** (0.21 g, 0.85 mmol) and α-imino ester **160** (0.23 g, 0.85 mmol) in anhydrous toluene (2 mL) was heated at 110 °C for 24 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 40/60) to give **161b** (0.37 g, 0.73 mmol, 86% yield) as a white solid.

M.p.: 169-171 °C

$[\alpha]_D^{24}$: -0.2° (*c* 1.0, $CHCl_3$)

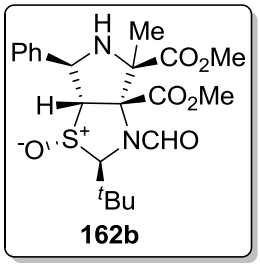
IR (KBr) ν 3347, 1737, 1723, 1672, 1439, 1343, 1297, 1177, 1055 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 9.16 (s, 1H, C*H*O), 7.57-7.53 (m, 2H, H_{Ar}), 7.48-7.43 (m, 2H, H_{Ar}), 7.48-7.36 (m, 1H, H_{Ar}), 7.27-7.16 (m, 5H, H_{Ar}), 5.51 (s, 1H, H_2), 4.94 (d, *J* = 6.3, 1H, H_6), 4.55 (d, *J* = 7.0, 1H, H_{6a}), 3.82 (s, 1H, C_{3a}-OC*H*$_3$), 3.76 (s, 1H, C_4-OC*H*$_3$), 3.73 (d, *J* = 14.7, 1H, C*H*$_2$Ph), 3.50 (brs, 1H, N*H*), 3.13 (d, *J* = 13.9, 1H, C*H*$_2$Ph), 0.99 (s, 9H, C(C*H*$_3$)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 172.4 (*C*O_2Me), 172.1 (*C*O_2Me), 165.8 (*C*HO), 139.3 (C_{qPh}), 136.7 (C_{qBn}), 131.3 (C_{Ar}), 130.2 (C_{Ar}), 129.6 (C_{Ar}), 129.1 (C_{Ar}), 128.2 (C_{Ar}), 127.8 (C_{Ar}), 97.7 (C_2), 89.6 (C_{3a}), 80.1 (C_4), 77.3 (C_{6a}), 57.0 (C_6), 55.0 (C_{3a}-O*C*H$_3$), 54.1 (C_4-O*C*H$_3$), 37.5 (*C*(CH$_3$)$_3$), 37.3 (*C*H$_2$Ph), 27.9 (C(*C*H$_3$)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{27}H_{32}N_2O_6SNa$ 535.1873; found 535.1869

Synthesis of (1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-methyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 162b



162b

A solution of thiazoline **39b** (0.21 g, 0.86 mmol) and α-imino ester **159** (0.16 g, 0.86 mmol) in anhydrous toluene (2 mL) was heated at 110 ºC for 24 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 40/60) to give **162b** (0.31 g, 0.71 mmol, 83% yield) as a white solid.

M.p.: 131-133 ºC

$[\alpha]_D^{22}$: -17º (*c* 1.1, $CHCl_3$)

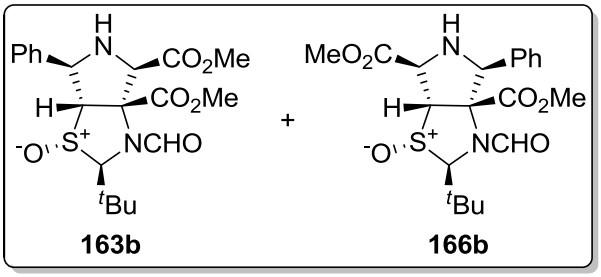
IR (KBr) ν 3305, 1737, 1673, 1430, 1347, 1298, 1275, 1158, 1062 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.03)] δ 8.80 (s, 1H, C*H*O, rot. maj.), 8.14 (s, 1H, C*H*O, rot. min.), 7.53-7.51 (m, 4H, H_{Ph}, both rot.), 7.40-7.37 (m, 3H, H_{Ph}, both rot.), 7.34-7.30 (m, 3H, H_{Ph}, both rot.), 5.51 (s, 1H, H_2, rot. maj.), 4.86 (s, 1H, H_2, rot. min.), 4.78 (t, *J*= 7.7, 2H, H_6, both rot.), 4.41 (d, *J* = 7.1, 1H, H_{6a}, rot. maj.), 4.33 (d, *J* = 7.0, 1H, H_{6a}, rot. min.), 3.84 (brs, 1H, *N*H, rot. maj.), 3.80 (s, 3H, C_{3a}-OCH_3, rot. maj.), 3.75 (s, 3H, C_4-OCH_3, rot. maj.), 3.74 (s, 6H, OCH_3, rot. min.), 1.72 (s, 6H, C_4-CH_3, both rot.), 0.98 (s, 9H, C(CH_3)$_3$, rot. min.), 0.94 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.2 (C_4-*C*O_2Me), 171.7 (C_{3a}-*C*O_2Me), 164.6 (*C*HO), 138.0 (C_{qPh}), 129.2 (C_{Ph}, rot. maj.), 129.1 (C_{Ph}, rot. min.), 128.6 (C_{Ph}, rot. maj.), 128.5 (C_{Ph}, rot. min.), 127.2 (C_{Ph}, rot. maj.), 127.1 (C_{Ph}, rot. min.), 101.0 (C_2, rot. min.), 96.6 (C_2, rot. maj.), 88.5 (C_{3a}, rot. min.), 88.1 (C_{3a}, rot. maj.), 76.8 (C_{6a}, rot. maj.), 76.5 (C_{6a}, rot. min.), 75.9 (C_4, rot. maj.), 73.9 (C_4, rot. min.), 57.5 (C_6, rot. min.), 56.6 (C_6, rot. maj.), 54.0 (C_{3a}-O*C*H_3, rot. maj.), 53.5 (C_4-O*C*H_3, rot. maj.), 52.9 (O*C*H_3, rot. min.), 36.7 (*C*(CH_3)$_3$, rot. maj.), 35.8 (*C*(CH_3)$_3$, rot. min.), 27.5 (C(*C*H_3)$_3$, rot. maj.), 26.8 (C(*C*H_3)$_3$, rot. min.), 20.4 (C_4-*C*H_3, rot. maj.), 18.8 (C_4-*C*H_3, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{21}H_{28}N_2O_6SNa$ 459.1560; found 459.1569

Synthesis of (1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 163b and **(1*R*,2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1-oxido-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166b**



163b + 166b

Method A: Over a solution of **39b** (0.22 g, 0.90 mmol) and α-imino ester **158** (0.18g, 0.90 mmol) in dry THF (15 mL) at room temperature, DBU (0.14 mL, 0.90 mmol) and AgOAc (0.15 g, 0.90 mmol) were sequentially added. The reaction crude was allowed to stir at room temperature for 24 hours. Then, the reaction mixture was filtered over celite and the solvent was evaporated. The obtained oil was purified by column chromatography (EtOAc/hexane 30/70) to give **163b** (0.18 g, 0.43 mmol, 47% yield) as a white solid.

Method B: Over a solution of **39b** (0.22 g, 0.90 mmol), α-imino ester **158** (0.16 g, 0.90 mmol) and $Cu(OAc)_2$ (0.03 g, 0.18 mmol) in anhydrous EtOAc (5 mL), DBU (0.03 mL, 0.18 mmol) was added. The reaction mixture was allowed to stir at room temperature for 24 hours. Then, the solvent was evaporated off and the crude reaction was purified by column chromatography (EtOAc/hexane 40/60) to give **163b** (0.15 g, 0.35 mmol, 39% yield) and **166b** (0.07 g, 0.17 mmol, 18% yield) both as white solids.

(1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 163b

M.p.: 126-128 °C

$[\alpha]_D^{27}$: -7° (*c* 1.0, $CHCl_3$)

IR (neat) ν 3307, 1757, 1736, 1669, 1436, 1376, 1307, 1200, 1053 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.48)] δ 8.82 (s, 1H, *C*HO, rot. maj.), 8.22 (s, 1H, *C*HO, rot. min.), 7.58-7.55 (m, 4H, H_{Ph}, both rot.), 7.44-7.33 (m, 6H, H_{Ph}, both rot.), 5.60 (s, 1H, H_2, rot. maj.), 4.98 (d, *J* = 6.7, 1H, H_6, rot. maj.), 4.91 (d, *J* = 6.8, 1H, H_6, rot. min.), 4.85 (s, 1H, H_2, rot. min.), 4.41 (d, *J* = 6.8, 1H, H_{6a}, rot. maj.), 4.27 (d, *J* = 6.8, 1H, H_{6a}, rot. min.), 4.23 (brs, 1H, H_4, rot. maj.), 4.05 (s, 1H, H_4, rot. min.), 3.91 (s, 3H, C_{3a}-OC*H*$_3$, rot. min.), 3.85

(s, 3H, C_{3a}-OCH_3, rot. maj.), 3.80 (s, 3H, C_4-OCH_3, rot. maj.), 3.77 (s, 3H, C_4-OCH_3, rot. min.), 3.32 (brs, 2H, *N*H, both rot.), 1.03 (s, 9H, C(CH_3)$_3$, rot. min.), 0.98 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.5 (C_{3a}-*C*O_2Me, rot. min.), 170.4 (C_{3a}-*C*O_2Me, rot. maj.), 169.5 (C_4-*C*O_2Me, rot. min.), 169.1 (C_4-*C*O_2Me, rot. maj.), 163.5 (*C*HO, rot. maj.), 161.9 (*C*HO, rot. min.), 137.9 (C_{qPh}, rot. maj.), 129.3 (C_{Ph}, rot. maj.), 129.2 (C_{Ph}, rot. min.), 128.8 (C_{Ph}, rot. maj.), 128.7 (C_{Ph}, rot. min.), 127.3 (C_{Ph}, rot. maj.), 100.7 (C_2, rot. min.), 96.5 (C_2, rot. maj.), 84.2 (C_{3a}, rot. maj.), 83.0 (C_{3a}, rot. min.), 77.4 (C_{6a}, rot. min.), 76.6 (C_{6a}, rot. maj.), 74.1 (C_4, rot. maj.), 73.0 (C_4, rot. min.), 59.0 (C_6, rot. min.), 58.8 (C_6, rot. maj.), 54.1 (C_{3a}-O*C*H$_3$, rot. maj.), 53.7 (C_{3a}-O*C*H$_3$, rot. min.), 53.4 (C_4-O*C*H$_3$, rot. maj.), 52.5 (C_4-O*C*H$_3$, rot. min.), 36.1 (*C*(CH$_3$)$_3$, rot. maj.), 35.4 (*C*(CH$_3$)$_3$, rot. min.), 27.6 (C(*C*H$_3$)$_3$, rot. maj.), 27.1 (C(*C*H$_3$)$_3$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calculated for $C_{20}H_{27}N_2O_6S$ 423.1584; found 423.1599

(1*R*,2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1-oxido-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166b

M.p.: 131-133 °C

$[\alpha]_D^{22}$: +38° (*c* 1.0, $CHCl_3$)

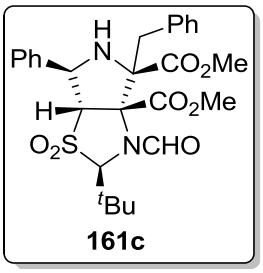
IR (KBr) ν 3355, 2957-2879, 1758, 1733, 1673, 1439, 1365, 1054 cm^{-1}

^{1}H NMR ($(CD_3)_2CO$, 400MHz) δ 8.39 (s, 1H, C*H*O), 7.49-7.43 (m, 3H, H_{Ph}), 7.41-7.38 (m, 2H, H_{Ph}), 5.44 (s, 1H, H_2), 4.72 (d, *J* = 5.5, 1H, H_{6a}), 4.57 (d, *J* = 5.5, 1H, H_6), 4.53 (s, 1H, H_4), 3.85 (s, 3H, C_6-OCH_3), 3.72 (s, 3H, C_{3a}-OCH_3), 3.54 (brs, 1H, *N*H), 0.99 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($(CD_3)_2CO$, 100MHz) δ 171.8 (C_6-*C*O_2Me), 170.8 (C_{3a}-*C*O_2Me), 163.2 (*C*HO), 137.2 (C_{qPh}), 130.2 (C_{Ph}), 129.9 (C_{Ph}), 129.1 (C_{Ph}), 95.2 (C_2), 83.2 (C_{3a}), 78.2 (C_4), 73.3 (C_{6a}), 56.1 (C_6), 53.8 (C_{3a}-O*C*H$_3$), 53.1 (C_6-O*C*H$_3$), 36.7 (*C*(CH$_3$)$_3$), 27.9 (C(*C*H$_3$)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calculated for $C_{20}H_{27}N_2O_6S$ 423.1584; found 423.1603

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 161c



161c

A solution of thiazoline **39c** (0.14 g, 0.52 mmol) and α-imino ester **160** (0.14 g, 0.52 mmol) in anhydrous toluene (2 mL) was heated at 80 ºC for 20 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **161c** (0.26 g, 0.49 mmol, 95% yield) as a white solid.

M.p.: 184-186 ºC

$[\alpha]_D^{22}$: -65º (*c* 1.0, $CHCl_3$)

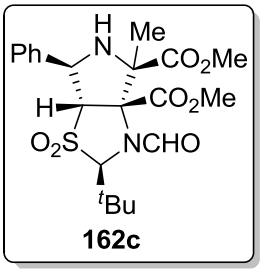
IR (KBr) ν 3313, 1737, 1691, 1450, 1431, 1349, 1305, 1265, 1006 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 9.16 (s, 1H, C*H*O), 7.58-7.53 (m, 2H, H_{Ph}), 7.50-7.44 (m, 2H, H_{Ph}), 7.43-7.38 (m, 1H, H_{Ph}), 7.30-7.20 (m, 5H, H_{ArBn}), 5.52 (s, 1H, H_2), 5.28 (dd, *J* = 11.7, 6.4, 1H, H_6), 4.44 (d, *J* = 6.4, 1H, H_{6a}), 3.82 (s, 3H, C_{3a}-OCH_3), 3.75 (s, 3H, C_4-OCH_3), 3.66 (d, *J* = 14.0, 1H, CH_2Ph), 3.55 (d, *J* = 11.5, 1H, N*H*), 3.27 (dd, *J* = 14.0, 1.3, 1H, CH_2Ph), 1.10 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 171.30 (*C*O_2Me), 171.26 (*C*O_2Me), 165.5 (*C*HO), 138.8 (C_{qPh}), 136.1 (C_{qBn}), 131.3 (C_{Ar}), 130.2 (C_{Ar}), 129.8 (C_{Ar}), 129.2 (C_{Ar}), 128.1 (C_{Ar}), 128.0 (C_{Ar}), 85.1 (C_2), 83.2 (C_{3a}), 81.2 (C_4), 74.4 (C_{6a}), 58.4 (C_6), 55.3 (C_{3a}-O*C*H_3), 54.4 (C_4-O*C*H_3), 38.4 (*C*(CH_3)$_3$), 36.5 (*C*H_2Ph), 27.1 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{27}H_{32}N_2O_7SNa$ 551.1822; found 551.1848

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-methyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 162c



162c

A solution of thiazoline **39c** (0.15 g, 0.58 mmol) and α-imino ester **159** (0.11 g, 0.58 mmol) in anhydrous toluene (2 mL) was heated at 80 °C for 15 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **162c** (0.24 g, 0.53 mmol, 91% yield) as a white solid.

M.p.: 184-186 °C

$[\alpha]_D^{22}$: -67° (*c* 1.0, $CHCl_3$)

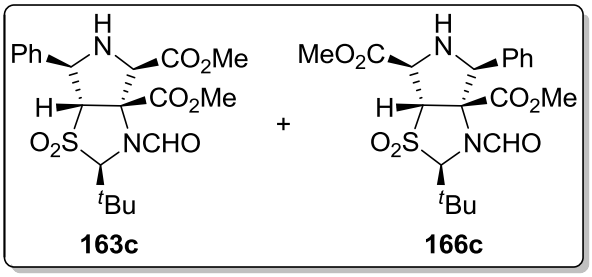
IR (KBr) ν 3309, 1742, 1680, 1432, 1330, 1312, 1298, 1278, 1112 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.03)] δ 8.80 (s, 1H, C*H*O, rot. maj.), 8.21 (s, 1H, C*H*O, rot. min.), 7.53-7.50 (m, 4H, H_{Ph}, both rot.), 7.45-7.41 (m, 3H, H_{Ph}, both rot.), 7.39-7.34 (m, 3H, H_{Ph}, both rot.), 5.45 (s, 1H, H_2, rot. maj.), 5.18 (dd, *J*= 10.3, 6.7, 1H, H_6, both rot.), 4.74 (s, 1H, H_2, rot. min.), 4.35 (d, *J* = 6.5, 2H, H_{6a}, rot. maj.), 4.31 (d, *J* = 6.5, 1H, H_{6a}, rot. min.), 3.88 (brs, 1H, *N*H, rot. maj.), 4.85 (s, 6H, OCH_3, rot. min.), 3.82 (s, 3H, OCH_3, rot. maj.), 3.82 (s, 3H, OCH_3, rot. maj.)*overlapped, 1.82 (s, 3H, C_4-CH_3, rot. maj.), 1.74 (s, 3H, C_4-CH_3, rot. min.), 1.16 (s, 9H, C(CH_3)$_3$, rot. min.), 1.10 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.5 (C_4-*C*O_2Me), 170.9(C_{3a}-*C*O_2Me), 164.4 (*C*HO), 137.6 (C_{qPh}), 129.4 (C_{Ar}), 128.8 (C_{Ar}), 126.8 (C_{Ar}), 84.5 (C_2), 82.1 (C_{3a}), 76.8 (C_4), 73.8 (C_{6a}), 58.3 (C_6), 54.4 (O*C*H_3), 53.9 (O*C*H_3), 37.7 (*C*(CH_3)$_3$), 26.9 (C(*C*H_3)$_3$), 20.1 (C_4-*C*H_3)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{21}H_{28}N_2O_7SNa$ 475.1509; found 475.1504

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 163c and **(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1,1-dioxido-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166c**



163c + **166c**

A solution of thiazoline **39c** (0.16 g, 0.61 mmol) and α-imino ester **158** (0.11 g, 0.61 mmol) in anhydrous toluene (2 mL) was heated at 80 ºC for 48 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **163c** and **166c** as a mixture of regioisomers in a ratio 67/33 (0.19 g, 0.43 mmol, 70% yield as mixture of regioisomers), respectively. Pure samples of both regioisomers could be obtained as white solids for its proper characterization.

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 163c

M.p.: 204-206 ºC

$[\alpha]_D^{22}$: -95º (*c* 1.0, $CHCl_3$)

IR (KBr) ν 3311, 1759, 1739, 1678, 1438, 1372, 1314, 1211, 1029 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.43)] δ 8.70 (s, 1H, *C*HO, rot. maj.), 8.23 (s, 1H, *C*HO, rot. min.), 7.55-7.48 (m, 4H, H_{Ph}, both rot.), 7.46-7.33 (m, 6H, H_{Ph}, both rot.), 5.42 (s, 1H, H_2, rot. maj.), 5.18 (dd, *J* = 11.6, 5.9, 1H, H_6, rot. maj.), 5.13 (dd, *J* = 12.5, 6.6, 1H, H_6, rot. min.), 4.64 (s, 1H, H_2, rot. min.), 4.28 (d, *J* = 12.8, 1H, H_4, rot. maj.), 4.28* overlapped (d, *J* = 6.0, 1H, H_{6a}, rot. maj.), 4.15 (d, *J* = 5.9, 1H, H_{6a}, rot. min.), 4.08 (d, *J* = 13.7, 1H, H_4, rot. min.), 3.89 (s, 3H, C_{3a}-OCH_3, rot. min.), 3.85 (s, 3H, OCH_3, rot. maj.), 3.85 (s, 3H, OCH_3, rot. maj.), 3.82 (s, 3H, C_4-OCH_3, rot. min.), 3.34 (t, *J* = 12.3, 1H, *N*H, rot. maj.), 3.20 (t, *J* = 12.7, 1H, *N*H, rot. min.), 1.17 (s, 9H, C(CH_3)$_3$, rot. min.), 1.11 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 169.5 (*C*O_2Me, rot. maj.), 169.3 (*C*O_2Me, rot. min.), 169.2 (*C*O_2Me, rot. min.), 169.0 (*C*O_2Me, rot. maj.), 162.8 (*C*HO, rot. maj.), 161.7 (*C*HO, rot. min.), 137.5 (C_{qPh}, rot. maj.), 137.5 (C_{qPh}, rot. min.), 129.4 (C_{Ar}, rot. maj.), 129.3 (C_{Ar}, rot. min.), 128.8 (C_{Ar}, rot. maj.), 128.7 (C_{Ar}, rot. min.),

126.84 (C_{Ar}, rot. maj.), 126.81 (C_{Ar}, rot. min.), 87.8 (C_2, rot. min.), 83.3 (C_2, rot. maj.), 78.7 (C_{3a}, rot. maj.), 77.1 (C_{3a}, rot. min.), 74.0 (C_{6a}, rot. min.), 72.8 (C_4 or C_{6a}, rot. maj.), 72.6 (C_4 or C_{6a}, rot. maj.), 71.4 (C_4, rot. min.), 60.1 (C_6, rot. min.), 59.9 (C_6, rot. maj.), 54.4 (O*C*H_3, rot. maj.), 53.9 (C_{3a}-O*C*H_3, rot. min.), 53.7 (O*C*H_3, rot. maj.), 52.7 (C_4-O*C*H_3, rot. min.), 36.7 (*C*$(CH_3)_3$, rot. maj.), 36.1 (*C*$(CH_3)_3$, rot. min.), 26.7 (C(*C*$H_3)_3$, rot. maj.), 26.2 (C(*C*$H_3)_3$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{20}H_{26}N_2O_7SNa$ 461.1353; found 461.1372

(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1,1-dioxido-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166c

M.p.: 75-77 ºC

$[\alpha]_D^{22}$: -14º (*c* 0.8, $CHCl_3$)

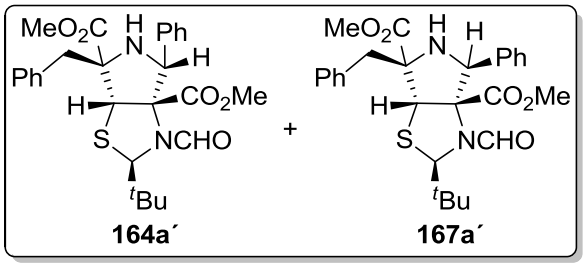
IR (KBr) ν 3350, 1747, 1688, 1459, 1437, 1344, 1247, 1185, 1114 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.32 (s, 1H, C*H*O), 7.41-7.37 (m, 3H, H_{Ph}), 7.32-7.28 (m, 2H, H_{Ph}), 5.33 (s, 1H, H_2), 4.70 (d, *J* = 2.3, 1H, H_6), 4.66 (brs, 1H, H_4), 4.48 (d, *J* = 4.2, 1H, H_{6a}), 3.92 (s, 3H, C_6-OC*H*$_3$), 3.68 (s, 3H, C_{3a}-OC*H*$_3$), 3.24 (brs, 1H, *N*H), 1.10 (s, 9H, C(C*H*$_3)_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.2 (C_6-*C*O_2Me), 169.4 (C_{3a}-*C*O_2Me), 162.5 (*C*HO), 135.1 (C_{qPh}), 130.1 (C_{Ar}), 129.5 (C_{Ar}), 128.1 (C_{Ar}), 81.2 (C_2), 76.3 (C_{3a}), 76.0 (C_4), 69.6 (C_{6a}), 55.7 (C_6), 53.7 (O*C*H_3), 53.6 (O*C*H_3), 37.0 (*C*$(CH_3)_3$), 26.8 (C(*C*$H_3)_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{20}H_{26}N_2O_7SNa$ 461.1353; found 461.1361

Synthesis of (2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 6-benzyl-2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 164a´ and **(2*R*,3a*R*,4*S*,6*S*,6a*R*)-Dimethyl 6-benzyl-2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 167a´**



Over a solution of thiazoline **39a** (0.20 g, 0.87 mmol), α-imino ester **160** (0.23 g, 0.87 mmol) and AgOAc (0.15 g, 0.87 mmol) in dry EtOAc (5 mL), DBU (0.13 mL, 0.87 mmol) was added and the reaction mixture was allowed to stir at room temperature for 72 hours. Then, the reaction mixture was filtered through celite and the solvent was evaporated off. The crude reaction was purified by column chromatography (EtOAc/hexane 10/90) to give **164a´** (0.19 g, 0.38 mmol, 44% yield) as a white solid and **167a´** (105 mg, 0.21 mmol, 24% yield) as colourless oil.

(2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 6-benzyl-2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 164a´

M.p.: 73-75 ºC

$[\alpha]_D^{22}$: +111º (*c* 0.9, $CHCl_3$)

IR (KBr) ν 3415, 1738, 1672, 1455, 1434, 1363, 1347, 1308, 1031 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.45)] δ 7.60-7.56 (m, 2H, H_{Ar}, rot. maj.), 7.52 (s, 1H, C*H*O, rot. maj.), 7.47-7.38 (m, 4H, H_{Ph}, both rot.), 7.32-7.16 (m, 15H, H_{Ph}, both rot. + C*H*O, rot. min.), 5.86 (s, 1H, H_4, rot. maj.), 5.32 (d, *J* = 0.7, 1H, H_2, rot. min.), 5.05 (brs, 1H, H_4, rot. min.), 4.89 (s, 1H, H_{6a}, rot. min.), 4.60 (s, 1H, H_2, rot. maj.), 4.20 (s, 1H, H_{6a}, rot. maj.), 3.93 (s, 3H, C_{3a}-OCH_3, rot. min.), 3.85 (s, 3H, C_{3a}-OCH_3, rot. maj.), 3.67 (s, 3H, C_6-OCH_3, rot. maj.), 3.65 (s, 3H, C_6-OCH_3, rot. min.), 3.38 (d, *J* = 13.6, 1H, CH_2Ph, rot. min.), 3.35 (d, *J* = 13.2, 1H, CH_2Ph, rot. maj.), 3.25 (brs, 1H, N*H*, rot. min.), 3.14 (d, *J* = 13.8, 1H, CH_2Ph, rot. min.), 3.01 (d, *J* = 13.3, 1H, CH_2Ph, rot. maj.), 2.93 (brs, 1H, N*H*, rot. maj.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.94 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.6 (C_{3a}-*C*O_2Me, rot. min.), 172.0 (C_{3a}-*C*O_2Me, rot. maj.), 171.7 (C_6-*C*O_2Me, rot. maj.), 171.1 (C_6-*C*O_2Me, rot. min.), 161.5 (*C*HO, rot. min.), 159.6 (*C*HO, rot. maj.), 138.9 (C_{qPh}, rot. maj.), 136.0 (C_{qBn}, rot. maj.),

135.6 (C_{qBn}, rot. min.), 130.0 (C_{Ar}), 129.9 (C_{Ar}), 129.82 (C_{Ar}), 129.80 (C_{Ar}), 129.6 (C_{Ar}), 128.4 (C_{Ar}), 128.2 (C_{Ar}), 128.0 (C_{Ar}), 127.22 (C_{Ar}), 127.16 (C_{Ar}), 83.3 (C_{3a}, rot. min.), 83.0 (C_{3a}, rot. maj.), 76.3 (C_2, rot. maj.), 74.3 (C_6, rot. min.), 74.0 (C_6, rot. maj.), 73.2 (C_2, rot. min.), 71.0 (C_4, rot. min.), 67.4 (C_4, rot. maj.), 64.8 (C_{6a}, rot. min.), 61.4 (C_{6a}, rot. maj.), 53.9 (C_{3a}-O*C*H$_3$, rot. min.), 53.4 (C_{3a}-O*C*H$_3$, rot. maj.), 52.34 (C_6-O*C*H$_3$, rot. min.), 52.26 (C_6-O*C*H$_3$, rot. min.), 42.3 (*C*H$_2$Ph, rot. maj.), 41.0 (*C*H$_2$Ph, rot. min.) 40.8 (*C*(CH$_3$)$_3$, rot. min.), 38. 8 (*C*(CH$_3$)$_3$, rot. maj.), 27.4 (C(*C*H$_3$)$_3$, rot. min.), 27.1 (C(*C*H$_3$)$_3$, rot. maj.)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{27}H_{32}N_2O_5SNa$ 519.1924; found 519.1905

(2*R*,3a*R*,4*S*,6*S*,6a*R*)-Dimethyl 6-benzyl-2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 167a´

$[\alpha]_D^{22}$: -22° (*c* 0.5, $CHCl_3$)

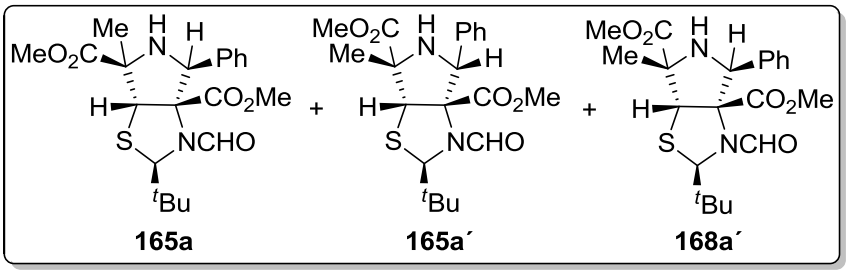
IR (neat) v 3349, 2953-2871, 1740, 1674, 1434, 1362, 1308, 1079 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.09 (s, 1H, C*H*O), 7.38-7.34 (m, 3H, H_{Ph}), 7.32-7.29 (m, 2H, H_{Ph}), 7.20-7.16 (m, 5H, H_{Bn}) 5.58 (s, 1H, H_2), 5.23 (s, 1H, H_{6a}), 4.80 (s, 1H, H_4), 3.71 (s, 3H, C_6-OC*H*$_3$), 3.55 (s, 3H, C_{3a}-OC*H*$_3$), 3.33 (d, *J* = 12.5, 1H, C*H*$_2$Ph), 3.05 (d, *J* = 12.5, 1H, C*H*$_2$Ph), 0.96 (s, 9H, C(C*H*$_3$)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 173.9 (C_6-*C*O$_2$Me), 170.7 (C_{3a}-*C*O$_2$Me), 162.5 (*C*HO), 136.8 (C_{qAr}), 136.6 (C_{qAr}), 130.1 (C_{Ar}), 129.5 (C_{Ar}), 129.3 (C_{Ar}), 128.3 (C_{Ar}), 128.1 (C_{Ar}), 127.2 (C_{Ar}), 83.3 (C_{3a}), 75.5 (C_4), 73.6 (C_2), 71.7 (C_6), 64.9 (C_{6a}), 53.0 (C_{3a}-O*C*H$_3$), 52.8 (C_6-O*C*H$_3$), 44.0 (*C*H$_2$Ph), 40.4 (*C*(CH$_3$)$_3$), 27.2 (C(*C*H$_3$)$_3$)

HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calculated for $C_{27}H_{33}N_2O_5S$ 497.2105; found 497.2097

Synthesis of (2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 165a, (2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 165a´ and (2*R*,3a*R*,4*S*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 168a´



Over a solution of thiazoline **39a** (0.26 g, 1.15 mmol), α-imino ester **159** (0.23, 1.15 mmol) and AgOAc (38.5 mg, 0.23 mmol) in anhydrous EtOAc (5 mL) DBU (0.04 mL, 0.23 mmol) was added. The reaction mixture was allowed to stir at room temperature for 72 hours. Then, the reaction crude was filtered over celite and the resulting solution was evaporated to dryness. The crude obtained was purified by column chromatography (EtOAc/hexane 20/80) to give three fractions; **165a** (0.16 g, 0.39 mmol, 34% yield) as a white solid, **165a´** (0.19 g, 0.44 mmol, 38% yield) as a white solid and **168a´** (45.1 mg, 0.10 mmol, 9% yield) as a white solid.

(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 165a

M.p.: 160-162 ºC

$[\alpha]_D^{22}$: +17º (*c* 0.9, $CHCl_3$)

IR (KBr) v 3318, 1737, 1680, 1431, 1363, 1257, 1224, 1143, 1095 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.02 (s, 1H, C*H*O), 7.38-7.34 (m, 3H, H_{Ph}), 7.30-7.27 (m, 2H, H_{Ph}), 5.57 (s, 1H, H_2), 5.11 (s, 1H, H_{6a}), 4.68 (s, 1H, H_4), 3.91 (s, 3H, C_6-OCH_3), 3.68 (brs, 1H, *N*H), 3.60 (s, 3H, C_{3a}-OCH_3), 1.59 (s, 3H, C_6-CH_3), 0.93 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 175.9 (C_6-*C*O_2Me), 170.8 (C_{3a}-*C*O_2Me), 162.4 (*C*HO), 135.9 (C_{qPh}), 129.6 (C_{Ar}), 129.3 (C_{Ar}), 128.2 (C_{Ar}), 83.7 (C_{3a}), 74.8 (C_4), 74.1 (C_2), 66.8 (C_6), 64.1 (C_{6a}), 53.4 (C_6-O*C*H_3), 53.1 (C_{3a}-O*C*H_3), 40.4 (*C*(CH_3)$_3$), 27.1 (C(*C*H_3)$_3$), 25.7 (C_6-*C*H_3)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{21}H_{28}N_2O_5SNa$ 443.1611; found 443.1609

(2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 165a´

M.p.: 46-48 °C

$[\alpha]_D^{22}$: +33° (*c* 1.0, $CHCl_3$)

IR (KBr) ν 3438, 1736, 1672, 1455, 1434, 1364, 1349, 1291, 1144 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.50)] δ 7.53-7.49 (m, 2H, H_{Ar}, rot. maj.), 7.44 (s, 1H, C*H*O, rot. maj.), 7.40-7.36 (m, 5H, H_{Ph}, rot. min.), 7.31-7.26 (m, 2H, H_{Ph}, rot. maj.), 7.25-7.21 (m, 1H, H_{Ph}, rot. maj.), 7.15 (d, *J* = 0.7, 1H, C*H*O, rot. min.), 5.71 (s, 1H, H_4, rot. maj.), 5.27 (d, *J* = 0.6, 1H, H_2, rot. min.), 4.87 (s, 1H, H_4, rot. min.), 4.74 (s, 1H, H_{6a}, rot. min.), 4.55 (s, 1H, H_2, rot. maj.), 4.10 (s, 1H, H_{6a}, rot. maj.), 3.87 (s, 3H, C_{3a}-OCH_3, rot. min.), 3.80 (s, 3H, C_6-OCH_3, rot. min.), 3.79 (s, 3H, C_{3a}-OCH_3, rot. maj.), 3.78 (s, 3H, C_6-OCH_3, rot. maj.), 1.61 (s, 3H, C_6-CH_3, rot. min.), 1.57 (s, 3H, C_6-CH_3, rot. maj.), 1.04 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.91 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 173.0 (C_6-*C*O_2Me, rot. maj.), 172.5 (*C*O_2Me, rot. min.), 172.4 (*C*O_2Me, rot. min.), 171.9 (C_{3a}-*C*O_2Me, rot. maj.), 161.4 (*C*HO, rot. min.), 159.6 (*C*HO, rot. maj.), 138.6 (C_{qPh}, rot. maj.), 135.2 (C_{qPh}, rot. min.), 129.7 (C_{Ar}), 129.6 (C_{Ar}), 128.2 (C_{Ar}), 128.1 (C_{Ar}), 83.7 (C_{3a}, rot. maj.), 83.6 (C_{3a}, rot. min.), 76.2 (C_2, rot. maj.), 73.3 (C_2, rot. min.), 70.9 (C_4, rot. min.), 67.8 (C_6, rot. min.), 68.6 (C_6, rot. maj.), 67.8 (C_4, rot. maj.), 64.9 (C_{6a}, rot. min.), 62.2 (C_{6a}, rot. maj.), 53.8 (O*C*H_3, rot. min.), 53.3 (O*C*H_3, rot. maj.), 52.8 (O*C*H_3, rot. min.), 52.7 (O*C*H_3, rot. min.), 40.7 (*C*(CH_3)$_3$, rot. min.), 39.3 (*C*(CH_3)$_3$, rot. maj.), 27.3 (C(*C*H_3)$_3$, rot. min.), 26.9 (C(*C*H_3)$_3$, rot. maj.), 24.3 (C_6-*C*H_3, rot. maj.), 23.3 (C_6-*C*H_3, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{21}H_{28}N_2O_5SNa$ 443.1611; found 443.1616

(2*R*,3a*R*,4*S*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 168a´

M.p.: 58-60 °C

$[\alpha]_D^{22}$: +62° (*c* 0.9, $CHCl_3$)

IR (KBr) ν 3438, 1738, 1678, 1434, 1366, 1314, 1242, 1184 cm^{-1}

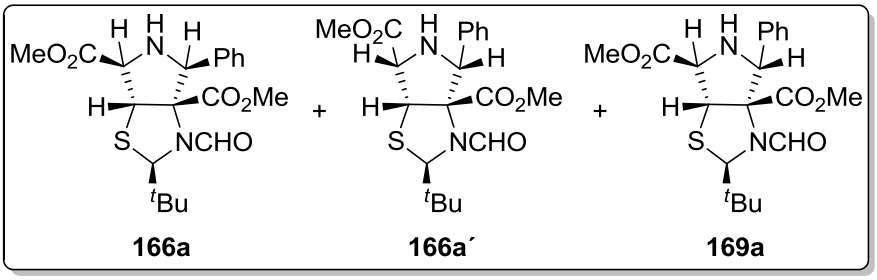
^{1}H NMR ($CDCl_3$, 400MHz) δ 8.13 (s, 1H, C*H*O), 7.34 (s, 5H, H_{Ph}), 5.51 (s, 1H, H_2), 4.72 (s, 1H, H_4), 4.65 (s, 1H, H_{6a}), 3.79 (s, 3H, C_6-OCH_3), 3.60 (s, 3H, C_{3a}-OCH_3), 2.92 (brs, 1H, *N*H), 1.74 (s, 9H, C_6-CH_3), 0.88 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 174.5 (C_6-*C*O_2Me), 170.8 (C_{3a}-*C*O_2Me), 162.0 (*C*HO), 136.5 (C_{qPh}), 129.5 (C_{Ph}), 128.9 (C_{Ph}), 128.7 (C_{Ph}), 82.7 (C_{3a}), 74.3 (C_2 or

C_4), 74.2 (C_2 or C_4), 68.4 (C_6), 64.2 (C_{6a}), 53.1 (C_{3a}-O*C*H$_3$), 52.3 (C_6-O*C*H$_3$), 40.1 (*C*(CH$_3$)$_3$), 26.9 (C(*C*H$_3$)$_3$), 26.3 (C_6-*C*H$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{21}H_{29}N_2O_5S$ 421.1792; found 421.1801

Synthesis of (2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166a, (2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166a´ and (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 169a



Over a solution of thiazoline **39a** (0.17g, 0.74 mmol), α-imino ester **158** (0.13 g, 0.74 mmol) and AgOAc (24.8 mg, 0.15 mmol) in anhydrous EtOAc (5mL), DBU (0.02 mL, 0.15 mmol) was added. The reaction mixture was allowed to stir for 80 hours at room temperature. Then, the reaction mixture was filtered over celite and the residue was concentrated under vacuum and then purified by column chromatography (EtOAc/hexane 30/70) to give three fractions; **166a** (0.10 g, 0.25 mmol, 34% yield) as a white solid, **166a´** (64.7 mg, 0.16 mmol, 21% yield) as a white solid and **169a** (44.0 mg, 0.11 mmol, 14% yield) as a colourless oil.

(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166a

M.p.: 130-132 ºC

$[\alpha]_D^{22}$: +15º (*c* 0.9, $CHCl_3$)

IR (KBr) v 3355, 1737, 1722, 1682, 1434, 1312, 1244, 1223, 1160 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.07 (s, 1H, C*H*O), 7.38-7.35 (m, 3H, H_{Ph}), 7.30-7.27 (m, 2H, H_{Ph}), 5.63 (s, 1H, H_2), 4.71 (d, *J* = 4.0, 1H, H_{6a}), 4.57 (s, 1H, H_4), 4.04 (d, *J* = 4.0, 1H, H_6), 3.87 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 0.91 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.2 (*C*O_2Me), 170.9 (*C*O_2Me), 162.1 (*C*HO), 135.2 (C_{qPh}), 129.7 (C_{Ph}), 129.3 (C_{Ph}), 128.2 (C_{Ph}), 82.7 (C_{3a}), 76.2 (C_4), 74.8 (C_2), 65.7 (C_6), 59.8 (C_{6a}), 53.2 (O*C*H_3), 53.1 (O*C*H_3), 40.2 (*C*(CH_3)$_3$), 26.9 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{20}H_{26}N_2O_5SNa$ 429.1455; found 429.1466

(2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 166a´

M.p.: 165-167 ºC

$[\alpha]_D^{22}$: +15º (*c* 1.0, $CHCl_3$)

IR (KBr) v 3316, 1750, 1728, 1683, 1433, 1354, 1316, 1259, 1173 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/1)] δ 7.55-7.53 (m, 2H, H_{Ph}), 7.48 (s, 1H, *C*HO), 7.40-7.23 (s, 8H, H_{Ph}), 7.10 (d, *J* = 0.7, 1H, C*H*O), 5.39 (s, 1H, H_4), 5.26 (s, 1H, H_2), 4.69 (d, *J* = 4.6, 1H, H_{6a}), 4.60-4.59 (m, 2H, H_4 + H_2), 4.45 (d, *J* = 4.5, 1H, H_6), 4.25-4.21 (m, 2H, H_{6a} + H_6), 3.90 (s, 3H, C_{3a}-OCH_3), 3.82 (s, 3H, C_{3a}-OCH_3), 3.80 (s, 3H, C_6-OCH_3), 3.79 (s, 3H, C_6-OCH_3), 1.04 (s, 9H, C(CH_3)$_3$), 0.93 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.8 (C_{3a}-*C*O_2Me), 171.2 (C_{3a}-*C*O_2Me), 169.7 (C_6-*C*O_2Me), 169.3 (C_6-*C*O_2Me), 161.8 (*C*HO), 159.3 (*C*HO), 138.6 (C_{qPh}), 135.3 (C_{qPh}), 129.8 (C_{Ph}), 129.6 (C_{Ph}), 128.3 (C_{Ph}), 128.2 (C_{Ph}), 83.6 (C_{3a}), 83.3 (C_{3a}), 76.8 (C_2 or C_4), 74.4 (C_2 or C_4), 73.2 (C_2), 69.8 (C_4), 62.6 (C_6), 61.1 (C_{6a} or C_6), 61.0 (C_{6a} or C_6), 58.1 (C_{6a} or C_6), 53.8 (O*C*H_3), 53.3 (O*C*H_3), 52.75 (O*C*H_3), 52.70 (O*C*H_3), 41.1 (*C*(CH_3)$_3$), 39.5 (*C*(CH_3)$_3$), 27.4 (C(*C*H_3)$_3$), 26.8 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{20}H_{26}N_2O_5SNa$ 429.1455; found 429.1463

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate 169a

$[\alpha]_D^{22}$: +5º (*c* 1.1, $CHCl_3$)

IR (neat) v 3347, 1735, 1669, 1434, 1362, 1303, 1218, 1178, 1021 cm^{-1}

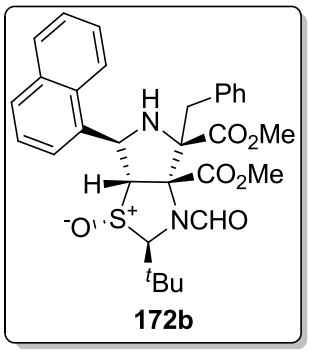
^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.77)] δ 7.59 (s, 1H, *C*HO, rot. min.), 7.56-7.53 (s, 2H, H_{Ph}, rot. min.), 7.40-7.35 (m, 6H, H_{Ph}, both rot.), 7.30-7.22 (m, 2H, H_{Ph}, rot. maj.), 7.14 (d, *J* = 0.6, 1H, C*H*O, rot. maj.), 5.50 (s, 1H, H_4, rot. min.), 5.37 (s, 1H, H_2, rot. maj.), 4.88 (d, *J* = 0.6, 1H, H_{6a}, rot. maj.), 4.86 (s, 1H, H_4, rot. maj.), 4.57 (s, 1H, H_2, rot. min.), 4.46 (d, *J* = 1.1, 1H, H_{6a}, rot. min.), 3.99-3.98 (m, 2H, H_6, both rot.), 3.84 (s, 3H, C_6-OCH_3, rot. maj.), 3.82 (s, 3H, C_{3a}-OCH_3, rot. maj.), 3.80 (s, 3H, C_6-OCH_3, rot. min.), 3.75 (s, 3H, C_{3a}-OCH_3, rot. min.), 1.05 (s, 9H, C(CH_3)$_3$, rot. min.), 0.92 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.6 (C_{3a}-*C*O_2Me, rot. maj.), 171.9 (C_6-*C*O_2Me, rot. maj.), 171.6 (C_6-*C*O_2Me, rot. min.), 171.0 (C_{3a}-*C*O_2Me, rot. min.), 161.9 (*C*HO, rot. min.), 159.8 (*C*HO, rot. maj.), 139.6 (C_{qPh}, rot. min.), 136.5 (C_{qPh}, rot. maj.), 130.10 (C_{Ar}, rot. maj.), 130.06 (C_{Ar}, rot. min.), 129.6 (C_{Ar}, rot. min.), 129.4 (C_{Ar}, rot. maj.), 127.9 (C_{Ar}, rot. min.), 127.8 (C_{Ar}, rot. maj.), 82.1 (C_{3a}, rot. min.), 81.3

(C_{3a}, rot. maj.), 77.1 (C_2, rot. min.), 73.4 (C_2, rot. maj.), 73.2 (C_4, rot. maj.), 68.6 (C_4, rot. min.), 64.4 (C_6, rot. maj.), 63.6 (C_6, rot. min.), 59.9 (C_{6a}, rot. maj.), 56.9 (C_{6a}, rot. min.), 53.8 (O*C*H_3, rot. maj.), 53.3 (O*C*H_3, rot. min.), 52.9 (O*C*H_3, rot. min.), 52.7 (O*C*H_3, rot. maj.), 41.0 (*C*(CH_3)$_3$, rot. maj.), 39.3 (*C*(CH_3)$_3$, rot. min.), 27.4 (C(*C*H_3)$_3$, rot. maj.), 26.9 (C(*C*H_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{20}H_{27}N_2O_5S$ 407.1635; found 407.1643

Synthesis of (1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-(1-naphthyl)-1-oxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 172b



172b

A solution of thiazoline **39b** (0.18 g, 0.75 mmol) and α-imino ester **170** (0.24 g, 0.75 mmol) in anhydrous toluene (2 mL) was heated at 110 ºC for 60 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **172b** (0.40 g, 0.71 mmol, 94% yield) as an orange solid.

M.p.: 94-96 ºC

$[\alpha]_D^{22}$: +29º (*c* 1.0, $CHCl_3$)

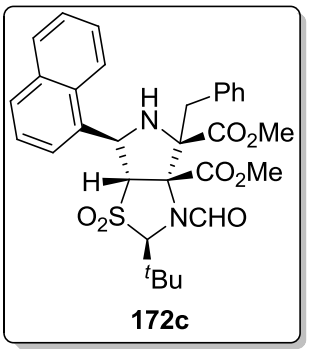
IR (KBr) ν 3349, 1742, 1680, 1435, 1345, 1299, 1272, 1181, 1056 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.33 (s, 1H, C*H*O), 8.28 (d, *J* = 8.5, 1H, H_{Np}), 8.08 (d, *J* = 7.2, 1H, H_{Np}), 7.90 (m, 1H, H_{Np}), 7.86 (d, *J* = 8.2, 1H, H_{Np}), 7.61 (ddd, *J* = 8.5, 6.9, 1.4, 1H, H_{Np}), 7.55 (m, 2H, H_{Np}), 7.26-7.18 (m, 5H, H_{Ph}), 5.82 (m, *J* = 7.7, 1H, H_6), 5.72 (s, 1H, H_2), 4.54 (d, *J* = 6.7, 1H, H_{6a}), 4.04 (d, *J* = 14.1, 1H, CH_2Ph), 3.87 (s, 1H, C_{3a}-OCH_3), 3.76 (s, 1H, C_4-OCH_3), 3.38 (d, 1H, *J* = 9.2, *N*H), 3.32 (d, *J* = 14.1, 1H, CH_2Ph), 1.01 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.1 (C_4-*C*O_2Me), 171.3 (C_{3a}-*C*O_2Me), 165.5 (*C*HO), 135.3 (C_{qPh}), 134.9 (C_{qNp}), 133.9 (C_{qNp}), 131.7 (C_{qNp}), 130.4 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 127.2 (C_{Ar}), 126.2 (C_{Np}), 125.7 (C_{Np}), 124.2 (C_{Np}), 123.1 (C_{Np}), 96.1 (C_2), 87.9 (C_{3a}), 79.1 (C_4), 76.1 (C_{6a}), 54.1 (C_{3a}-O*C*H$_3$), 53.3 (C_4-O*C*H$_3$), 50.9 (C_6), 37.4 (*C*H$_2$Ph), 37.0 (*C*(CH$_3$)$_3$), 27.8 (C(*C*H$_3$)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{31}H_{34}N_2O_6SNa$ 585.2030; found 585.2038

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-(1-naphthyl)-1,1-dioxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 172c



172c

A solution of thiazoline **39c** (0.13 g, 0.51 mmol) and α-imino ester **170** (0.16 g, 0.51 mmol) in anhydrous toluene (2 mL) was heated at 80 ºC for 60 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **172c** (0.28 g, 0.48 mmol, 94% yield) as a white solid.

M.p.: 177-179 ºC

$[\alpha]_D^{22}$: -35º (*c* 1.0, $CHCl_3$)

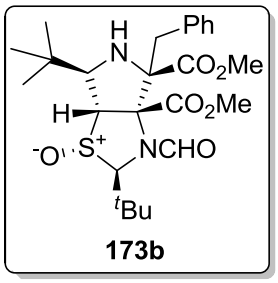
IR (KBr) ν 3361, 1743, 1689, 1445, 1342, 1329, 1301, 1276, 1111 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.25 (s, 1H, C*H*O), 8.22-8.17 (m, 1H, H_{Np}), 7.92 (d, *J* = 7.3, 1H, H_{Np}), 7.89-7.85 (m, 2H, H_{Np}), 7.58-7.49 (m, 3H, H_{Np}), 7.31-7.22 (m, 5H, H_{Ph}), 6.06 (dd, *J* = 9.0, 6.5, 1H, H_6), 5.58 (s, 1H, H_2), 4.62 (d, *J* = 6.2, 1H, H_{6a}), 3.92 (d, *J* = 14.3, 1H, C*H*$_2$Ph), 3.87 (s, 1H, C_{3a}-OC*H*$_3$), 3.75 (s, 1H, C_4-OC*H*$_3$), 3.45 (d, *J* = 14.2, 1H, C*H*$_2$Ph), 3.42 (d, *J* = 8.2, 1H, *N*H)*overlapped, 1.14 (s, 9H, C(C*H*$_3$)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.0 (C_4-*C*O_2Me), 170.6 (C_{3a}-*C*O_2Me), 165.1 (*C*HO), 135.0 (C_{qPh}), 134.0 (C_{qNp}), 133.7 (C_{qNp}), 131.6 (C_{qNp}), 130.3 (C_{Ar}), 129.6 (C_{Ar}), 128.9 (C_{Ar}), 128.7 (C_{Ar}), 127.5 (C_{Ar}), 127.0 (C_{Ar}), 126.3 (C_{Np}), 125.5 (C_{Np}), 123.8 (C_{Np}), 123.4 (C_{Np}), 84.1 (C_2), 81.8 (C_{3a}), 80.1 (C_4), 72.6 (C_{6a}), 54.4 (C_{3a}-O*C*H$_3$), 53.6 (C_4-O*C*H$_3$), 52.8 (C_6), 37.9 (*C*(CH$_3$)$_3$), 36.6 (*C*H$_2$Ph), 27.0 (C(*C*H$_3$)$_3$)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{31}H_{34}N_2O_7SNa$ 601.1979; found 601.1975

Synthesis of (1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2,6-di-*tert*-butyl-3-formyl-1-oxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 173b



173b

A solution of thiazoline **39b** (0.16 g, 0.64 mmol) and α-imino ester **171** (0.16 g, 0.64 mmol) in anhydrous toluene (2 mL) was heated at 110 ºC for 33 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **173b** (0.19 g, 0.39 mmol, 61% yield) as a white solid.

M.p.: 196-198 ºC

$[\alpha]_D^{22}$: -49º (*c* 1.0, $CHCl_3$)

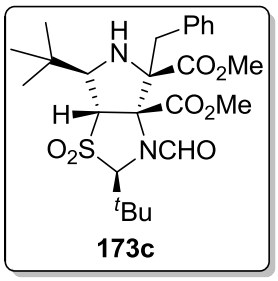
IR (KBr) v 3338, 1741, 1733, 1671, 1305, 1276, 1230, 1180, 1054 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.16 (s, 1H, C*H*O), 7.24-7.13 (m, 5H, H_{Ph}), 5.58 (s, 1H, H_2), 4.12 (d, *J* = 7.4, 1H, H_{6a}), 3.80 (d, *J* = 7.3, 1H, H_6), 3.75 (s, 1H, C_{3a}-OC*H*$_3$), 3.69 (s, 1H, C_4-OC*H*$_3$), 3.63 (d, *J* = 14.1, 1H, C*H*$_2$Ph), 3.14 (brs, 1H, *N*H), 3.06 (d, *J* = 14.1, 1H, C*H*$_2$Ph), 1.10 (s, 9H, C_6-C(C*H*$_3$)$_3$), 1.04 (s, 9H, C_2-C(C*H*$_3$)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.7 (C_4-*C*O$_2$Me), 171.3 (C_{3a}-*C*O$_2$Me), 165.4 (*C*HO), 135.6 (C_{qPh}), 130.6 (C_{Ar}), 128.1 (C_{Ar}), 127.0 (C_{Ar}), 95.8 (C_2), 88.7 (C_{3a}), 79.0 (C_4), 71.1 (C_{6a}), 61.3 (C_6), 53.8 (C_{3a}-O*C*H$_3$), 53.2 (C_4-O*C*H$_3$), 36.9 (C_2-*C*(CH$_3$)$_3$), 36.3 (*C*H$_2$Ph), 32.6 (C_6-*C*(CH$_3$)$_3$), 27.8 (C_2-C(*C*H$_3$)$_3$), 26.7 (C_6-C(*C*H$_3$)$_3$)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{25}H_{36}N_2O_6SNa$ 515.2186; found 515.2204

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2,6-di-*tert*-butyl-3-formyl-1,1-dioxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 173c



173c

A solution of thiazoline **39c** (0.18 g, 0.70 mmol) and α-imino ester **171** (0.17 g, 0.70 mmol) in anhydrous toluene (2 mL) was heated at 80 ºC for 36 hours. Then, the solvent was evaporated off and the obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **173c** (0.30 g, 0.60 mmol, 86% yield) as a white solid.

M.p.: 184-186 ºC

$[\alpha]_D^{22}$: -86º (*c* 1.0, $CHCl_3$)

IR (KBr) v 3338, 1743, 1685, 1316, 1245, 1226, 1215, 1156, 1008 cm^{-1}

^{1}H NMR ($(CD_3)_2CO$, 400MHz) δ 9.09 (s, 1H, C*H*O), 7.28-7.18 (m, 5H, H_{Ph}), 5.45 (s, 1H, H_2), 4.19 (d, *J* = 6.8, 1H, H_{6a}), 4.04-3.99 (m, 1H, H_6), 3.85 (s, 1H, C_{3a}-OCH_3), 3.78 (s, 1H, C_4-OCH_3), 3.59 (d, *J* = 13.9, 1H, CH_2Ph), 3.25-3.16 (m, 2H, *N*H + CH_2Ph), 1.14 (s, 9H, C_2-C(CH_3)$_3$), 1.09 (s, 9H, C_6-C(CH_3)$_3$)

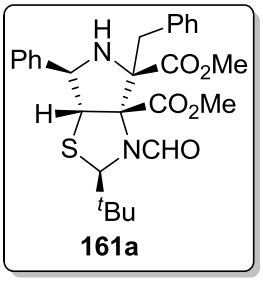
^{13}C NMR ($(CD_3)_2CO$, 100MHz) δ 171.23 (*C*O_2Me), 171.22 (*C*O_2Me), 165.1 (*C*HO), 136.3 (C_{qPh}), 131.3 (C_{Ar}), 128.8 (C_{Ar}), 127.8 (C_{Ar}), 85.0 (C_2), 84.0 (C_{3a}), 80.4 (C_4), 69.5 (C_{6a}), 65.0 (C_6), 54.6 (C_{3a}-O*C*H_3), 53.9 (C_4-O*C*H_3), 38.3 (C_2-*C*$(CH_3)_3$), 36.1 (*C*H_2Ph), 32.8 (C_6-*C*$(CH_3)_3$), 27.22 (C(*C*H_3)$_3$), 27.16 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{25}H_{36}N_2O_7SNa$ 531.2135; found 531.2136

5.3. General procedure for deoxigenation of sulfoxides

Over a stirred solution of a bicyclic thiazolidine sulfoxide (1 eq.) in acetone at 0 ºC, trifluoroacetic anhydride (2 eq.) and potassium iodide (4 eq.) were added. The reaction mixture was stirred at room temperature and was monitored by TLC (EtOAc/hexane) until completion. The mixture was treated with an aqueous solution of $Na_2S_2O_3$ (5%) and dichloromethane at room temperature and was stirred for 30 minutes the phases were separated and the aqueous phase was extracted with dichloromethane, the combined organic layers were dried over magnesium sulfate anhydrous, filtered off and the solvent was evaporated under reduced pressure. The obtained residue was purified by column chromatography.

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 161a



161a

Following the general procedure described above, bicyclic thiazolidine **161b** (0.92 g, 1.79 mmol) was dissolved in acetone (10 mL). The reaction was allowed to stir at room temperature for 3 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **161a** (0.84 g, 1.70 mmol, 95% yield) as a white solid.

M.p.: 127-129 ºC

$[\alpha]_D^{22}$: -53º (*c* 1.1, $CHCl_3$)

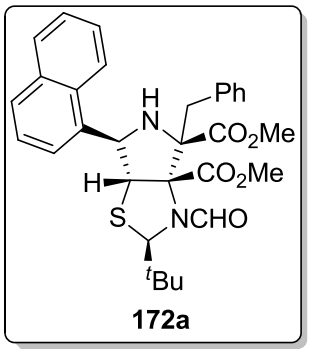
IR (KBr) v 3344, 1741, 1681, 1666, 1439, 1349, 1305, 1276, 1177 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 9.03 (s, 1H, C*H*O), 7.54-7.51 (m, 2H, H_{Ph}), 7.45-7.41 (m, 2H, H_{Ph}), 7.39-7.34 (m, 2H, H_{Ph}), 7.27-7.20 (m, 5H, H_{ArBn}), 5.85 (s, 1H, H_2), 4.67 (d, *J* = 5.8, 1H, H_6), 4.61 (d, *J* = 5.8, 1H, H_{6a}), 3.76 (s, 3H, C_{3a}-OCH_3), 3.63 (s, 3H, C_4-OCH_3), 3.61 (d, *J* = 13.9, 1H, CH_2Ph), 3.19 (dd, *J* = 14.0, 1.3, 1H, CH_2Ph), 2.66 (brs, 1H, N*H*), 0.91 (s, 9H, C(CH_3)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 172.5 (*C*O_2Me), 171.9 (*C*O_2Me), 164.6 (*C*HO), 140.6 (C_{qPh}), 136.6 (C_{qBn}), 131.4 (C_{Ar}), 130.0 (C_{Ar}), 129.3 (C_{Ar}), 129.1 (C_{Ar}), 128.0 (C_{Ar}), 127.7 (C_{Ar}), 88.0 (C_{3a}), 80.8 (C_4), 77.5 (C_2), 68.5 (C_6), 64.8 (C_{6a}), 54.6 (O*C*H_3), 53.9 (O*C*H_3), 41.1 (*C*(CH_3)$_3$), 37.2 (*C*H_2Ph), 27.3 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{27}H_{32}N_2O_5SNa$ 519.1924; found 519.1910

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-(1-naphthyl)hexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 172a



172a

Following the general procedure described above, bicyclic thiazolidine **172b** (0.18 g, 0.33 mmol) was dissolved in acetone (5 mL). The reaction was allowed to stir at room temperature for 6 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **172a** (0.17 g, 0.31 mmol, 94% yield) as a white solid.

M.p.: 158-160 °C

$[\alpha]_D^{22}$: -31° (*c* 1.0, $CHCl_3$)

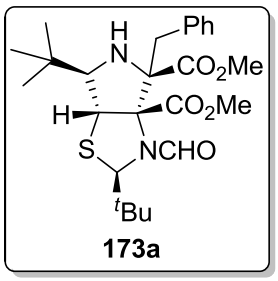
IR (KBr) v 3345, 1744, 1678, 1437, 1350, 1301, 1269, 1242, 1028 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.12 (d, *J* = 0.6, 1H, C*H*O), 8.09-8.05 (m, 1H, H_{Np}), 7.98 (d, *J* = 7.2, 1H, H_{Np}), 7.90-7.87 (m, 1H, H_{Np}), 7.83 (d, *J* = 8.2, 1H, H_{Np}), 7.57-7.50 (m, 3H, H_{Np}), 7.30-7.20 (m, 5H, H_{Ph}), 5.90 (m, 1H, H_2), 5.40 (dd, *J* = 8.0, 5.5, 1H, H_6), 4.77 (d, *J* = 5.4, 1H, H_{6a}), 3.84 (d, 1H, *J* = 14.1, CH_2Ph), 3.79 (s, 1H, C_{3a}-OCH_3), 3.71 (s, 1H, C_4-OCH_3), 3.41 (brs, 1H, *N*H), 3.40 (d, 1H, *J* = 14.1, CH_2Ph), 0.94 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.64 (*C*O_2Me), 171.59 (*C*O_2Me), 164.7 (*C*HO), 135.5 (C_{qAr}), 135.4 (C_{qAr}), 133.9 (C_{qNp}), 131.7 (C_{qNp}), 130.2 (C_{Ar}), 129.0 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 127.3 (C_{Ar}), 126.7 (C_{Np}), 126.0 (C_{Np}), 125.7 (C_{Np}), 123.6 (C_{Np}), 123.2 (C_{Np}), 86.4 (C_{3a}), 79.7 (C_4), 76.6 (C_2), 62.6 (C_{6a}), 62.3 (C_6), 53.8 (C_{3a}-O*C*H_3), 53.2 (C_4-O*C*H_3), 40.7 (*C*(CH_3)$_3$), 37.7 (*C*H_2Ph), 27.2 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{31}H_{34}N_2O_5SNa$ 569.2081; found 569.2063

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2,6-di-*tert*-butyl-3-formylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 173a



173a

Following the general procedure described above, bicyclic thiazolidine **173b** (0.17 g, 0.35 mmol) was dissolved in acetone (5 mL). The reaction was allowed to stir at room temperature for 6 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **173a** (0.16 g, 0.34 mmol, 97% yield) as a white solid.

M.p.: 81-83 °C

$[\alpha]_D^{22}$: -66° (*c* 1.1, $CHCl_3$)

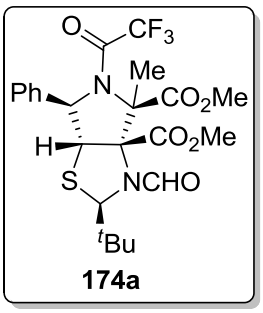
IR (KBr) v 3331, 1746, 1732, 1671, 1478, 1433, 1368, 1209, 1000 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 9.03 (s, 1H, C*H*O), 7.25-7.19 (m, 3H, H_{Ph}), 7.17-7.13 (m, 2H, H_{Ph}), 5.80 (s, 1H, H_2), 4.29 (d, *J* = 6.2, 1H, H_{6a}), 3.72 (s, 1H, C_{3a}-OC*H*$_3$), 3.63 (s, 1H, C_4-OC*H*$_3$), 3.48 (d, *J* = 14.0, 1H, C*H*$_2$Ph), 3.36 (dd, *J* = 12.0, 6.2, 1H, H_6), 3.27 (d, *J* = 12.0, 1H, *N*H), 3.13 (d, *J* = 14.0, 1H, C*H*$_2$Ph), 1.05 (s, 9H, C_6-C(C*H*$_3$)$_3$), 0.95 (s, 9H, C_2-C(C*H*$_3$)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.7 (C_{3a}-*C*O$_2$Me), 171.2 (C_4-*C*O$_2$Me), 164.4 (*C*HO), 135.6 (C_{qPh}), 130.5 (C_{Ar}), 128.1 (C_{Ar}), 127.1 (C_{Ar}), 87.3 (C_{3a}), 79.7 (C_4), 76.6 (C_2), 74.1 (C_6), 58.2 (C_{6a}), 53.4 (C_{3a}-O*C*H$_3$), 53.0 (C_4-O*C*H$_3$), 40.5 (C_2-*C*(CH$_3$)$_3$), 36.1 (*C*H$_2$Ph), 32.4 (C_6-*C*(CH$_3$)$_3$), 27.11 (C(*C*H$_3$)$_3$), 27.07 (C(*C*H$_3$)$_3$).

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{25}H_{36}N_2O_5SNa$ 499.2237; found 499.2247

Synthesis of (2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-5-(2,2,2-trifluoroacetyl)-3-formyl-4-methyl-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate 174a



174a

Following the general procedure described above, bicyclic thiazolidine **162b** (0.21 g, 0.48 mmol) was dissolved in acetone (5 mL). The reaction was allowed to stir at room temperature for 4 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **174a** (0.20 g, 0.39 mmol, 81% yield) as a white solid.

M.p.: 48-50 °C

$[\alpha]_D^{26}$: -62° (*c* 1.1, $CHCl_3$)

IR (KBr) v 1748, 1741, 1732, 1682, 1435, 1416, 1261, 1197, 1008 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.61 (s, 1H, C*H*O), 7.47-7.45 (m, 2H, H_{Ph}), 7.38-7.34 (m, 2H, H_{Ph}), 7.30-7.27 (m, 1H, H_{Ph}), 5.48 (s, 1H, H_2), 5.40 (brs, 1H, H_6), 4.79 (d, *J* = 1.4, 1H, H_{6a}), 3.81 (s, 1H, C_4-OCH_3), 3.44 (s, 1H, C_{3a}-OCH_3), 1.96 (s, 1H, C_4-CH_3), 0.87 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 169.5 (C_4-*C*O_2Me), 168.5 (C_{3a}-*C*O_2Me), 164.2 (*C*HO), 157.3 (q, *J* = 38.6, *C*OCF_3), 140.2 (C_{qPh}), 128.3 (C_{Ph}), 128.2 (C_{Ph}), 125.9 (C_{Ph}), 115.4 (q, *J* = 288.1, CO*C*F_3), 80.5 (C_{3a} + C_4), 74.2 (C_2), 66.9 (q, *J* = 3.3, C_6), 61.3 (C_{6a}), 53.7 (O*C*H_3), 53.6 (O*C*H_3), 40.6 (*C*(CH_3)$_3$), 27.2 (C(*C*H_3)$_3$), 20.4 (C_4-*C*H_3).

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{23}H_{27}F_3N_2O_6SNa$ 539.1434; found 539.1456

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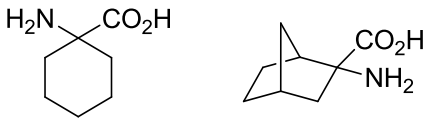
Chapter VI

Synthesis of modified cysteine bearing cyclohexane rings between α and β positions and preparation of modified glutathiones and lanthionines

VI. Synthesis of modified cysteine bearing cyclohexane rings between α and β positions and preparation of modified glutathiones and lanthionines

1. INTRODUCTION

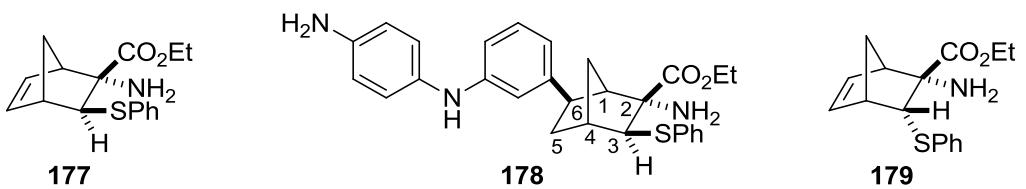
1-Aminocyclohexanecarboxylic acid **175** and peptides containing it have shown to be of interest in biological medicinal field[1] and organic chemistry.[2] In particular, 2-aminonorbornane-2-carboxylic acid **176** has attracted special attention for their bulkiness and conformational restriction, which confers more resistance to metabolic enzymes in peptides including such amino acid. Within this context, several potentially useful effects of this amino acid in biological systems have been reported.[3] For instance, it has been demonstrated its effect in insulin secretion as a selective activator of glutamate dehydrogenase (GDH)[4] and it also plays an important role in the cell-membrane transport system as an *L*-amino acid carrier inhibitor[4c,5] (*Figure 31*). In the last years, the use of unnatural constrained norbornene α,α-disubstituted amino acids has emerged as a powerful tool to improve the material properties of peptides containing it.[6]



175 **176**

Figure 31. Chemical structure of 1-aminocyclohexanecarboxylic acid **175** and 2-aminonorbornane-2-carboxylic acid **176**

Recently, it has been demonstrated that α,β-cycloaliphatic amino acids with sulfanyl substituent in β position, as 2-amino-3-(phenylsulfanyl)norbornene-2-carboxylate **177** could be used for the design of new and effective Rac1 inhibitors acting as modulators of the protein-protein interaction between Rac1-Tiam1.[7] Thus, (1*R**,2*R**,3*S**,4*R**,6*R**)-ethyl 2-amino-6-(3-((4-aminophenyl)amino)phenyl)-3-(phenylsulfanyl)norbornane-2-carboxylate **178** (*Figure 32*) showed to be the most effective after pharmacological analyses. Moreover, 3-sulfanyl norbornene amino acid **179**, epimer of **177**, has revealed as an effective inducer of 3_{10}-helix secondary structures when incorporated into peptides.[8]



177 **178** **179**

Figure 32. Chemical structure of **177**, **178** and **179**

Taking into account the importance of these amino acids, the reported synthetic routes to obtain these cyclic and bicyclic amino acids could be classify according to the bonds created in the last step of their synthesis (*Figure 33*).

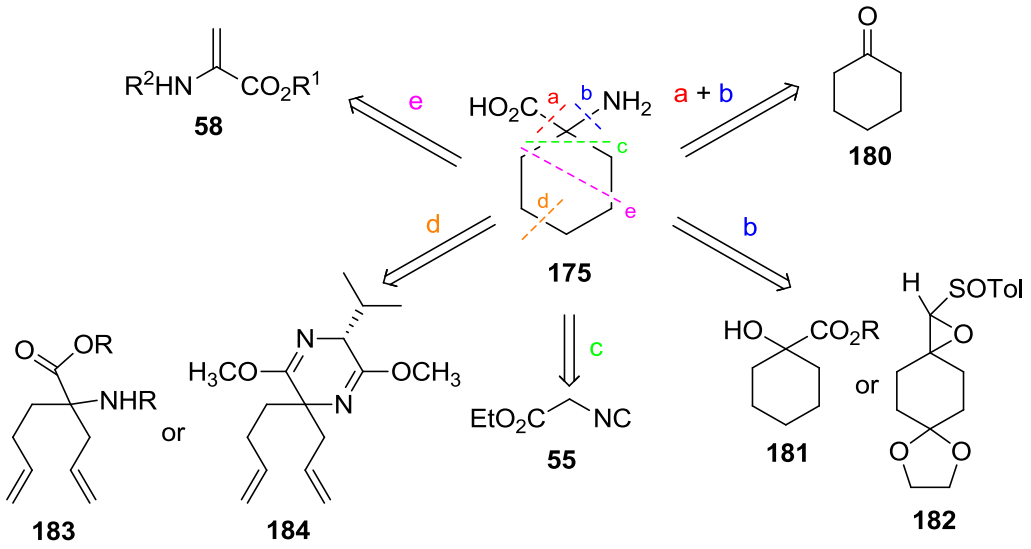
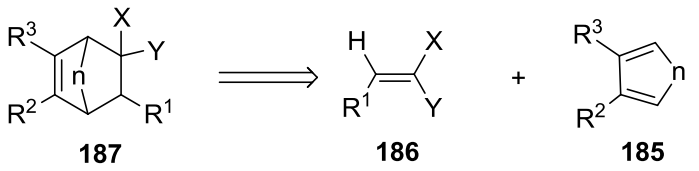


Figure 33. Disconnections to obtain 1-aminocyclohexanecarboxlic acid **175** derivatives

In this sense, disconnection ***a*** + ***b*** is one of the most popular and efficient routes to obtain 1-aminocyclohexanecarboxylic acid derivatives. This synthesis starts from cyclohexanones **180**, and involves a Bucherer-Bergs reaction that was firstly reported in 1934[9] and optimized later.[10] Disconnection ***b*** implies the bond formation between the Cα and the amine moiety, commonly by a nucleophilic substitution of the hydroxyl group of 1-hydroxycyclohexanecarboxylate **181** by the azidating agent bis(*p*-nitrophenyl)phosphorazidate (*p*-NO_2-DPPA)[11], and subsequent reduction of the azide into amine function, or by the ring opening of the sulfinyloxirane **182** by a primary amine.[12] Disconnection ***c***, starts from glycine equivalents such as ethyl isocyanoacetate **55** which leads to a six membered ring by the addition of 1,5-dibromopentane.[13] Disconnection ***d*** requires the use of Grubbs catalyst to carry out a ring closing metathesis of **183**[14] and **184**[15] that allows to obtain the corresponding six membered ring amino acid. Finally, disconnection ***e*** implies a Diels-Alder[16] reaction, between dehydroalanine derivatives **58** and dienes.

In a general point of view, Diels-Alder cycloaddition reaction between reactive dienes **185** and dehydroamino acids equivalents **186**, has demonstrated to be a valuable methodology to prepare 1-aminocyclohexanecarboxylic acid derivatives[17] **187** (*Figure 34*). On the basis of the disconnection ***e*** (*Figure 33*) a bibliographic revision has revealed that the synthesis of α,β-cyclohexene amino acids **187**, cyclic and bicyclic, can be achieved in racemic and asymmetric fashion and can be

collected in two different groups depending on the substitution or not in the β position (R^1) derived from β-substituted dehydroamino acid derivatives.



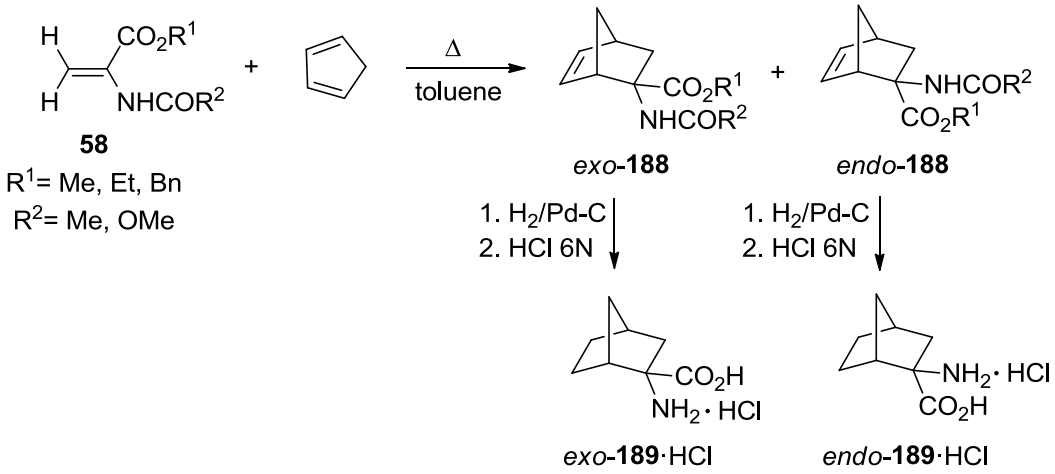
n= 0,1, 2
R^1= H, Me, Ph, Cl, SR, OR
R^2= H, Me
R^3= H, Me, OTMS

X= CONHR´, CO_2R´, CN
Y= NHCOR´, NO_2, N=C=O, N=C(R´R´´)

Figure 34. Synthesis of cyclohexene amino acids through Diels-Alder reaction

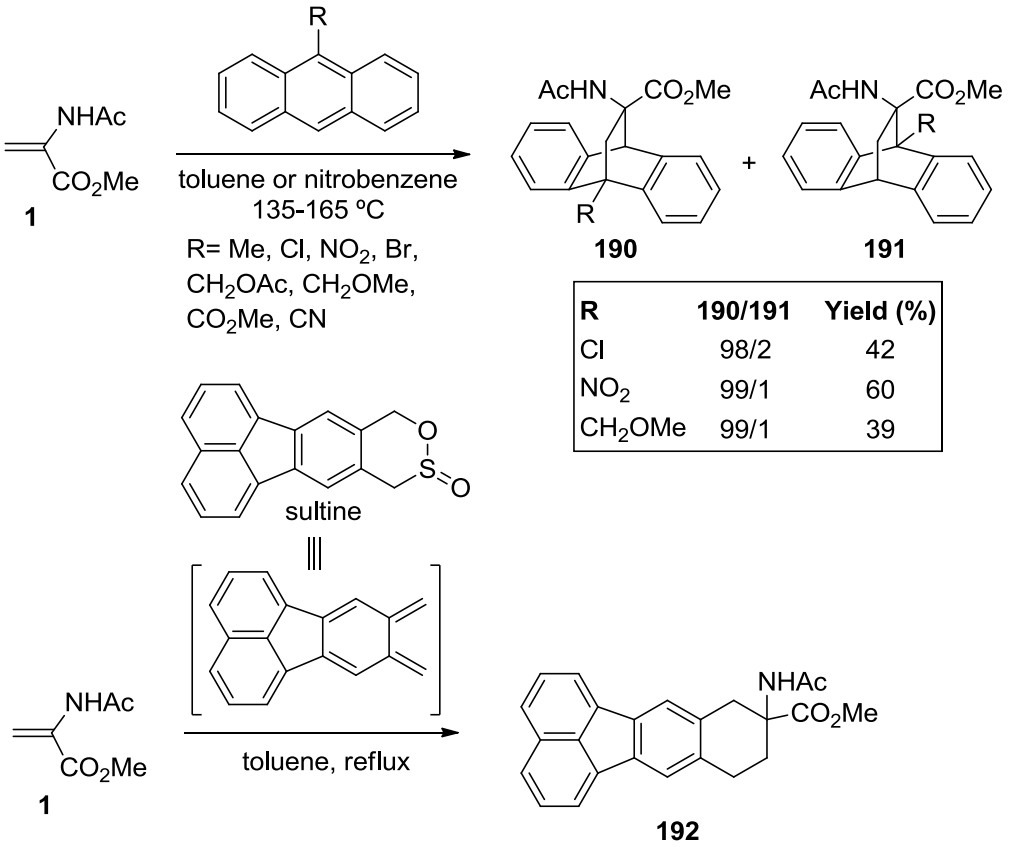
1.1. Synthesis of cyclohexane amino acids without β-substitution

Horikawa *et al*.[18] reported in 1980 the first Diels-Alder cycloaddition between *N*-acylaminoacrylates **58** and cyclopentadiene (*Scheme 56*). These reactions led to mixtures of *exo* and *endo* isomers, preferentially to the *D*,*L*-*exo* pair **188** but the reaction led exclusively to the *D*,*L*-*exo* pair **188** when R^1= R^2= Me. The obtained mixture of *exo* and *endo* cycloadducts **188** was separated by means of column chromatography and then transformed into the corresponding amino acids *exo*-**189**·HCl and *endo*-**189**·HCl, respectively.



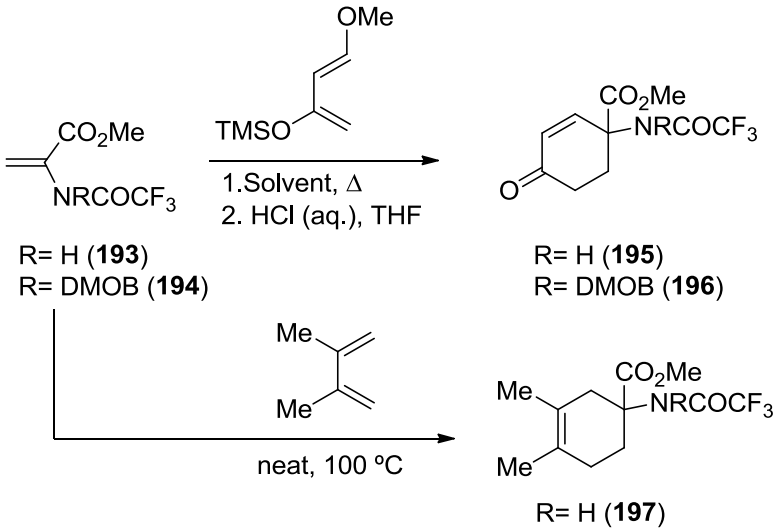
Scheme 56

Besides, methyl 2-acetamidoacrylate **1** has been a valuable template for the synthesis of conformationally constrained α,β-cycloaliphatic amino acids **190**, **191** and **192** by Diels-Alder reaction with dienes such as anthracenes[19] and fluoranthene-fused sultine[20] in racemic form, respectively (*Scheme 57*).



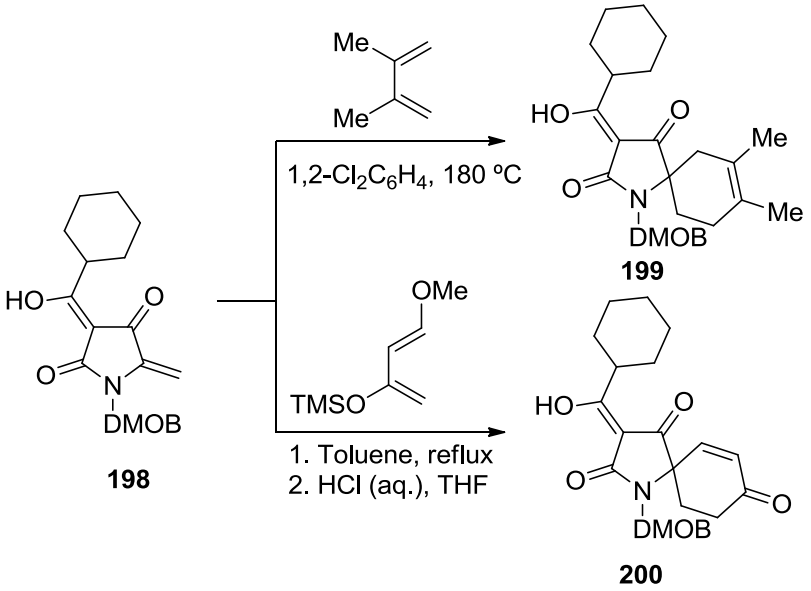
Scheme 57

More recently, Butt *et al*.[21] have reported the cycloaddition reaction between 2-trifluoroacetamidoacrylic acid methyl ester **193** and its DMOB-protected derivative **194** as dienophiles and the Danishefsky´s diene. Besides, it has been carried out the Diels-Alder reaction between **193** and 2,3-dimethyl-1,3-butadiene. It was observed a better yield employing dienophile **193** under thermic activation (*Scheme 58*).



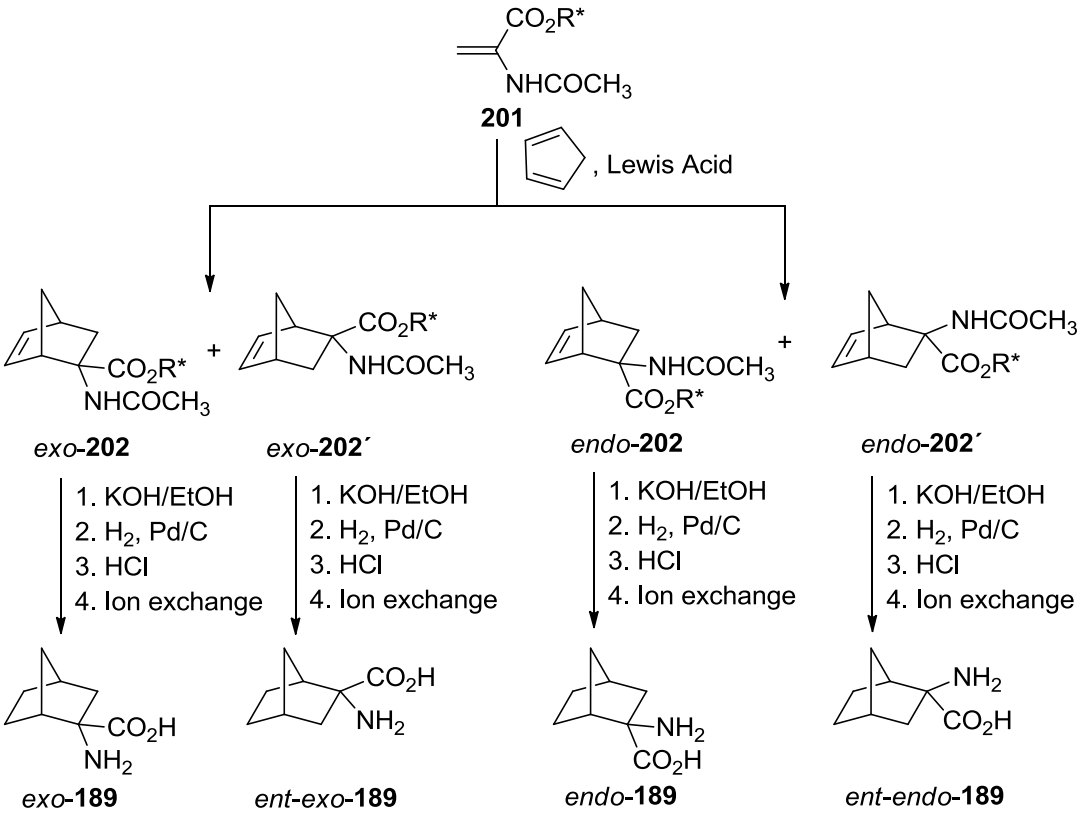
Scheme 58

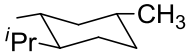
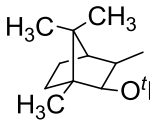
Butt *et al*.[21] also reported the reactivity of 3-(cyclohexylhydroxymethylene)-1-(2,4-dimethoxybenzyl)-5-methylenepyrrolidine-2,4-dione **198** with 2,3-dimethyl-1,3-butadiene and the Danishefsky´s diene. Once optimized the reaction conditions, the corresponding cycloadducts **199** and **200** were obtained in moderate yield under thermic activation (*Scheme 59*).



Scheme 59

Cativiela *et al*.[22] developed the asymmetric synthesis of 2-aminonorbornane-2-carboxylic acids *exo*- and *endo*-**189** and its enantiomers starting from the chiral *N*-acetyl-α,β-dehydroalaninates **201** and cyclopentadiene in presence of Lewis acid catalysts. The yield of the Diels-Alder reaction and both *exo*/*endo* diastereoselectivities and *exo* and *endo* enantioselectivities depend on the nature of the Lewis acid and the chiral auxiliary employed. In this sense, titanium tetrachloride was found to be the most appropriate Lewis acid catalyst. Whereas acrylate derived from (-)-menthol **201** gave preferentially the cycloadducts derived from an *exo* approach (entries 1-7), the acrylate of (-)-*cis*-3-isobornyl neopentyl ether **201** favored the formation of the *endo* stereoisomers (entries 8-11). This latter acrylate **201** showed better diastereoselectivities than the one derived from the (-)-menthol (entries 1-7 *vs.* 8-11) (*Scheme 60*). In addition, it was also performed the Diels-Alder reaction between (-)-menthyl α,β-dehydroalaninate **201** and cyclopentadiene employing heterogeneous catalyst, obtaining the best results when SiO_2 was employed as support for different Lewis acids such as $TiCl_4$ or $AlEt_2Cl$.[23]

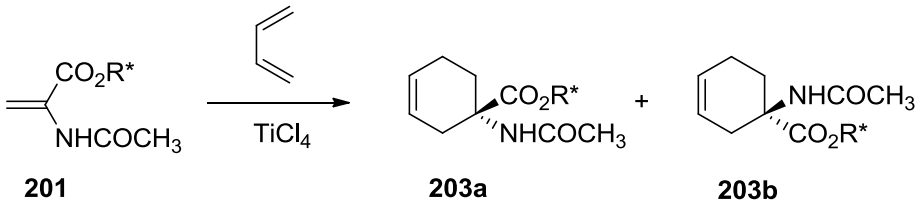


Entry	R*	LA/eq.	T	yield (%)	*exo*/*endo*	*exo* **202**/**202´**	*endo* **202**/**202´**
1		$TiCl_4$/1.1	25 ºC	100	69/31	95/5	23/77
2		$TiCl_4$/0.75	25 ºC	100	81/19	97/3	14/86
3		$TiCl_4$/1.1	0 ºC	100	79/21	92/8	14/86
4		$TiCl_4$/0.75	0 ºC	99	81/19	90/10	11/89
5		$TiCl_4$/1.1	-20 ºC	98	78/22	92/8	14/86
6		$TiCl_4$/0.75	-20 ºC	100	81/19	91/9	13/87
7		$AlCl_3$/1.1	25 ºC	74	74/26	90/10	19/81
8		$TiCl_4$/0.75	25 ºC	95	45/55	>99/1	>1/99
9		$TiCl_4$/1.1	0 ºC	94	38/62	>99/1	>1/99
10		$TiCl_4$/0.5	0 ºC	100	38/62	>99/1	>1/99
11		$AlCl_3$/1.1	25 ºC	34	56/44	>99/1	>1/99

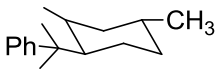
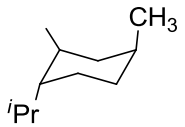
Scheme 60

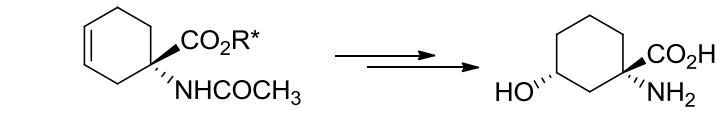
Moreover, the Diels-Alder reaction between 2-acetamidoacrylates and 1,3-butadiene was carried out in order to obtain homoserine analogues in both racemic[24] and asymmetric[25] fashion. The authors described the Diels-Alder reaction between chiral dehydroalaninates **201** bearing, (-)-menthol, (+)-menthol or (-)-8-phenylmenthol, as chiral auxiliaries and 1,3-butadiene in presence of $TiCl_4$ as Lewis acid. Facial diastereoselectivity depended on the nature of the chiral auxiliary, obtaining the best results when (-)-8-phenylmenthol was used as chiral auxiliary since the isomer **203a** was obtained exclusively (*Scheme* 6, entries 1 and 2). However, the use of (-)-menthol as chiral auxiliary gave mixtures of

diastereoisomers **203a** and **203b** in favour of the diastereoisomer **203a** (entries 3 and 4). On the contrary, the use of (+)-menthol as chiral auxiliary switched the diastereoselection to give **203b** as major cycloadduct (entries 5-8). The major cycloadduct **203a**, bearing the chiral auxiliary (-)-8-phenylmenthol was subjected to further reactions to obtain the target constrained chiral homoserine **204** (*Scheme 61*).



201 **203a** **203b**

Entry	R*	LA/eq.	T	t (d)	conv. (%)	**203a/203b**
1		$TiCl_4$/1.0	0 ºC	9	28	>99/1
2		$TiCl_4$/1.0	25 ºC	6	91	>99/1
3		$TiCl_4$/1.0	0 ºC	9	71	71/29
4		$TiCl_4$/1.0	25 ºC	5	80	70/30
5		$TiCl_4$/1.0	0 ºC	9	73	30/70
6		$TiCl_4$/1.0	-25 ºC	10	45	28/72
7		$TiCl_4$/2.0	-25 ºC	7	53	31/69
8		$TiCl_4$/1.0	25 ºC	4	82	29/71



R*= (-)-8-phenylmenthol

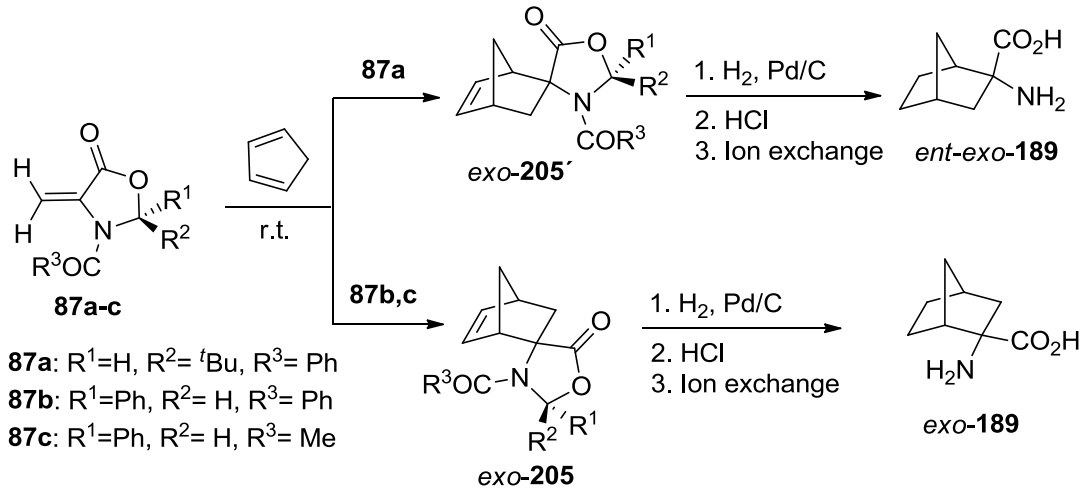
203a **204**

(homoserine derivative)

Scheme 61

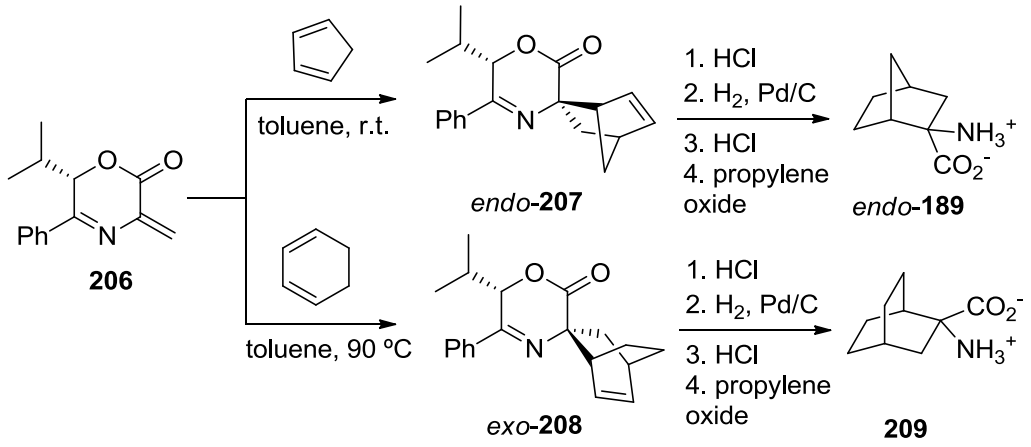
Pyne *et al*.[26] carried out the Diels-Alder reaction in an asymmetric fashion employing (2*S*)- and (2*R*)-3-acyl-2-alkyl-4-methylen-1,3-oxazolidin-5-ones **87a-c** and cyclopentadiene or 1,3-cyclohexadiene. It is important to note that the cycloaddition reaction carried out between (2*R*)-3-benzoyl-2-*tert*-butyl-4-methylen-1,3-oxazolidin-5-one **87a** and cyclopentadiene, afforded almost exclusively one diastereoisomer *exo*-**205´**, the corresponding from the addition of cyclopentadiene through the opposite face of the bulky *tert*-butyl group. Besides, the cycloaddition reaction starting from (2*S*)-aryl derivatives **87b,c** as dienophiles and cyclopentadiene as diene, afforded as the major cycloadduct the corresponding *exo*-**205**. Finally, subsequent transformation of the cycloadducts *exo*-**205** and *exo*-

205´ allowed to obtain the free amino acids *exo*-**189** and its enantiomer, respectively (*Scheme 62*).



Scheme 62

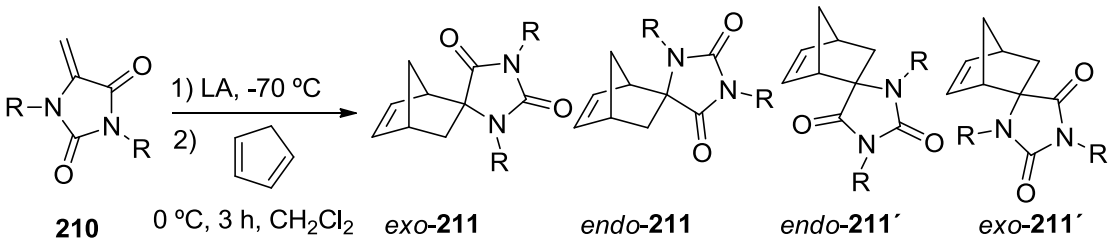
Nájera *et al*.[27] reported the use of (6*S*)-6-isopropyl-3-methylene-5-phenyl-3,6-dihydro-2*H*-1,4-oxazin-2-one **206** as chiral dienophile in Diels-Alder reactions with cyclopentadiene and 1,3-cyclohexadiene for the synthesis of enantiomerically pure bicyclic amino acids *endo*-**189** and **209**, respectively. The cycloaddition reaction between the chiral oxazinone **206** and cyclopentadiene proceeded with high *endo*-selectivity affording in good yield the cycloadduct *endo*-**207**, but the reaction between the same dienophile **206** and 1,3-cyclohexadiene took place through an *exo* approach and also in good yield obtaining exclusively the cycloadduct *exo*-**208** (*Scheme 63*).



Scheme 63

Yamada *et al*.[28] described the asymmetric Diels-Alder reaction between chiral 5-methylene hydantoine **210**, bearing *S*-(1)-phenylethyl groups at N1 and N3 as

dienophile, and cyclopentadiene, isoprene and 2,3-dimethyl-1,3-butadiene as dienes in the presence of Lewis acids as catalysts. The reaction between hydantoine **210** and cyclopentadiene in presence of Me_2AlCl and Et_2AlCl gave mixtures of cycloadducts *exo*-**211**/ *exo*-**211´** and *endo*-**211**/*endo*-**211´** in excellent yields, high *exo* selectivities and also high enantioselectivities for each stereoisomer obtained (*Scheme 64*).

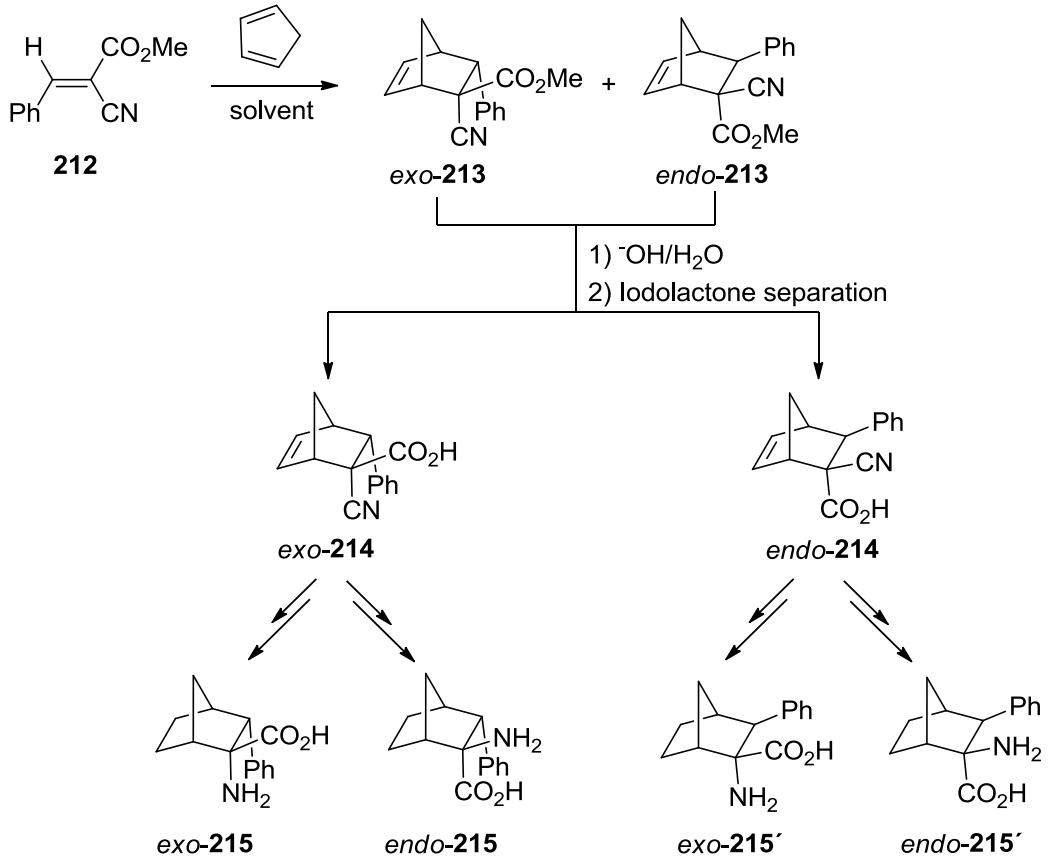


LA	*exo*-211	*exo*-211´	*endo*-211	*endo*-211´
Me_2AlCl	51	32	8	3
Et_2AlCl	58	39	3	traces
e.e. >99% for every stereoisomer				

Scheme 64

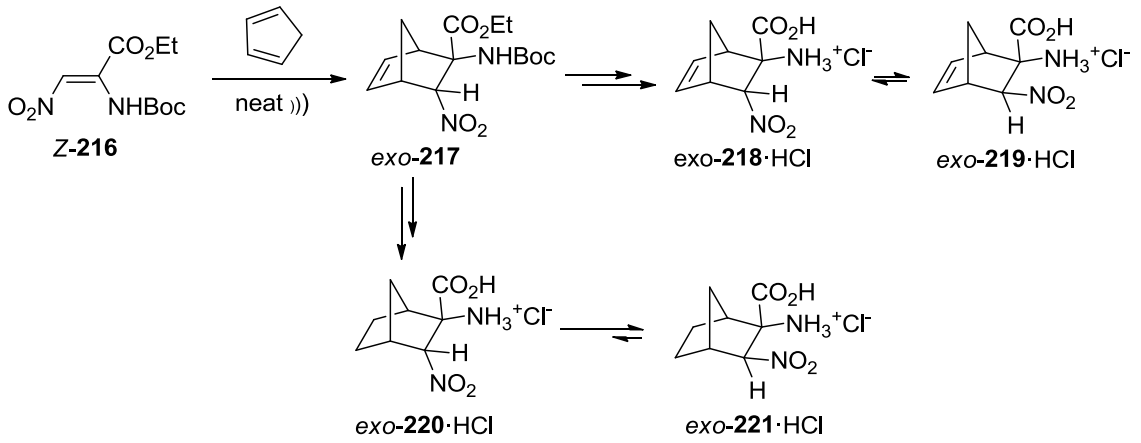
1.2. Synthesis of cyclohexane amino acids with substitution in β-position

Cativiela *et al*.[29] described the Diels-Alder reaction between *E*-methyl α-cyanocinnamate **212** and cyclopentadiene for the synthesis of conformationally constrained phenylalanine analogues. In this sense, the Diels-Alder reaction between the dienophile **212** and cyclopentadiene afforded a mixture of cycloadducts *exo*-**213** and *endo*-**213** in a ratio 38/62 in racemic form. Both cycloadducts were converted into the carboxylic acids *exo*-**214** and *endo*-**214** which were easily separated by means of the iodolactone transformation. Once separated *exo*-**214** and *endo*-**214** were transformed and separated after a well-designed methodology into 4 *D*,*L*-pairs of 2-amino-3-phenylnorbornane-2-carboxylic acids *exo*/*endo* **215** and *exo*/*endo* **215´** (*Scheme 65*).



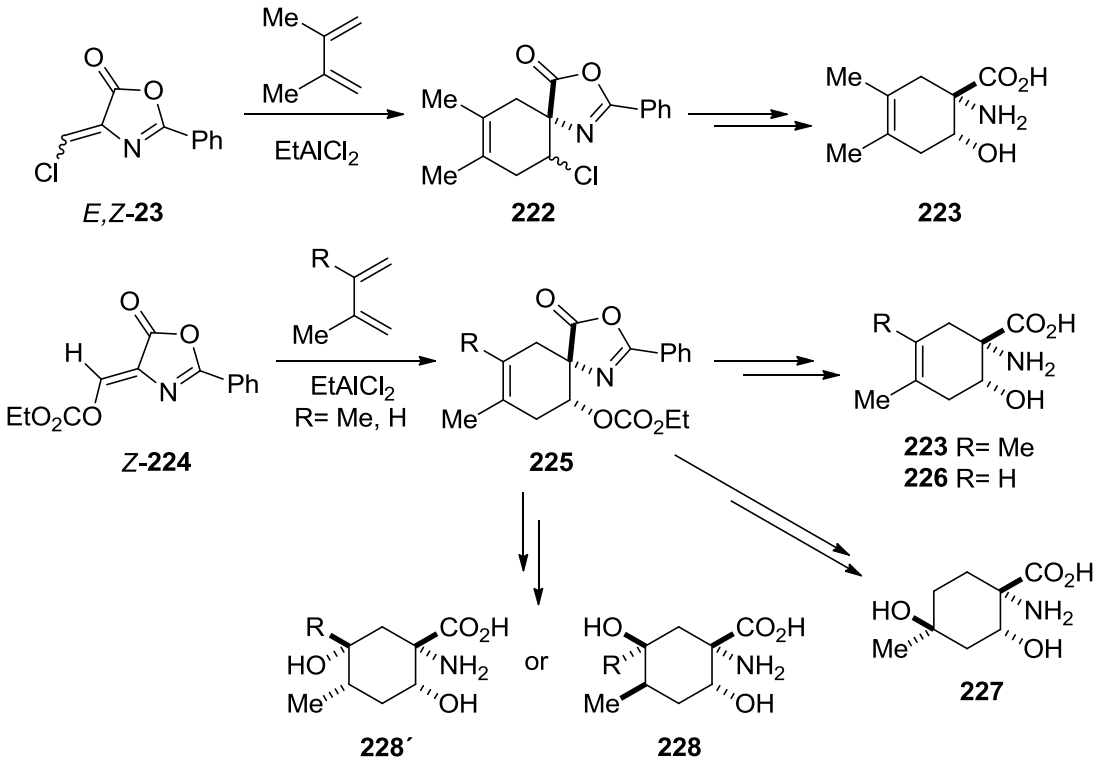
Scheme 65

Gelmi *et al*.[30] reported on the use of ethyl *Z*-2-*N*-Boc-3-nitroacrylate **216** as dienophile in the Diels-Alder reaction for the synthesis of 2-amino-3-nitronorbornene- and 2-amino-3-nitronorbornane-2-carboxylic acids *exo*-**218**, *exo*-**219** and *exo*-**221**. Within this context, the cycloaddition reaction of **216** with cyclopentadiene afforded exclusively the cycloadduct *exo*-**217**, which was transformed into the corresponding norbornene or norbornane hydrochloride amino acids *exo*-**218** and *exo*-**220**, respectively. The epimerization process at the Cβ carbon bonded to the nitro moiety was observed. Thus, *exo*-**218**·HCl partially epimerized into *exo*-**219**·HCl, and *exo*-**220**·HCl was completely transformed into *exo*-**221**·HCl (*Scheme 66*).



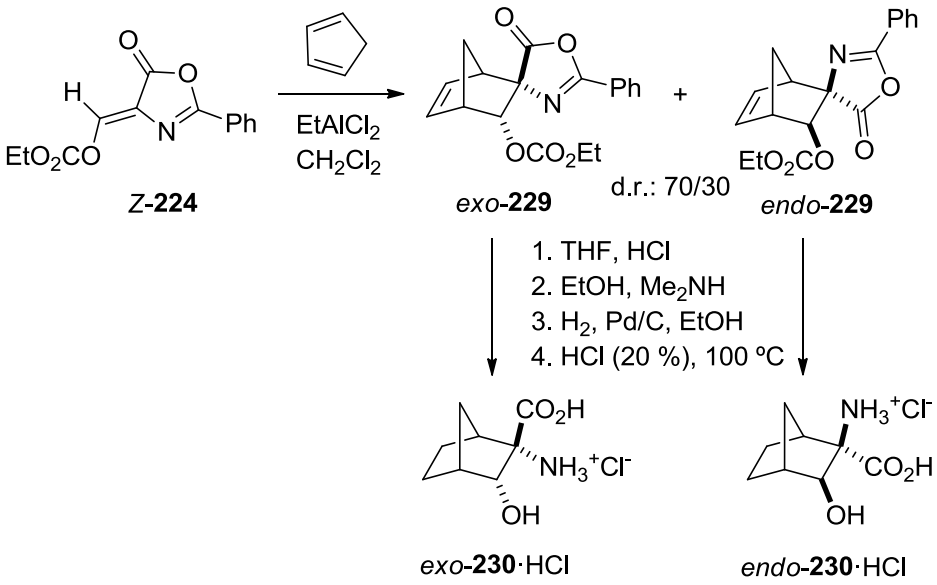
Scheme 66

Gelmi´s research group also carried out the racemic synthesis of 1-amino-2-hydroxycyclohexenecarboxylic acids **223** and **226**, 1-amino-2,4-dihydroxycyclohexanecarboxylic acid **227** and 1-amino-2,5-dihydroxycyclohexanecarboxylic acids **228** and **228´** with high diastereo- and regioselectivities as constrained serine analogues from the mixture of *E*- and *Z*-4-chloromethylene-5(4*H*)-oxazolone **23**[31] or *Z*-ethyl 2-phenyl-4-methylenecarbonate-5(4*H*)-oxazolone **224**,[32] and the acyclic dienes, 2,3-dimethyl-1,3-butadiene and/or 2-methyl-1,3-butadiene (*Scheme 67*).



Scheme 67

They also described the racemic synthesis of 2-amino-3-hydroxynorbornane-2-carboxylic acids *exo*-**230** and *endo*-**230**.[33] Thus, the Diels-Alder reaction between *Z*-ethyl 2-phenyl-4-methylenecarbonate-5(4*H*)-oxazolone **224** and cyclopentadiene gave the corresponding cycloadducts *exo*-**229** and *endo*-**229** in a ratio 70/30 in good yield. The corresponding constrained serines *exo*-**230**·HCl and *endo*-**230**·HCl were obtained after hydrogenation reaction of the cycloadducts and hydrolysis of the protecting groups, (*Scheme 68*). The study of the asymmetric synthesis of these amino acids using bis-oxazolines as chiral ligands did not lead to any satisfactory results.[34]

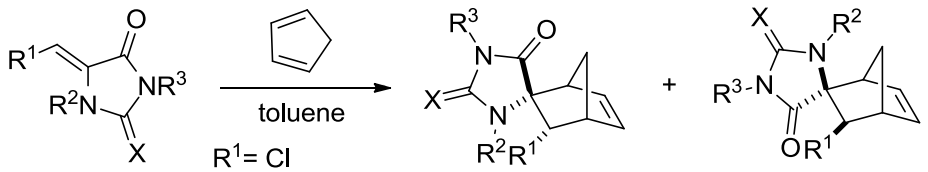


Z-**224** *exo*-**229** *endo*-**229**

exo-**230**·HCl *endo*-**230**·HCl

Scheme 68

Cernak *et al*.[35] reported an extensive study of the cycloaddition between *Z*-5-chloromethylene or methylene hydantoines and thiohydantoines **231** and cyclopentadiene to obtain key intermediates for the synthesis of Palau´s amine. The results showed that the reactions proceeded faster starting from thiohydantoines **231** (X = S). The diastereoselectivity of the reaction using both hydantoines and thiohydantoines was highly favored to the *exo*-**232** isomer (*Scheme 69*).

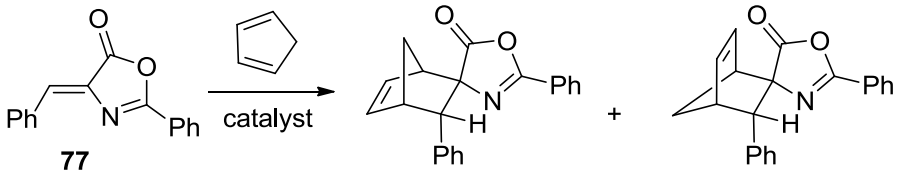


Z-**231** *exo*-**232** *endo*-**232**

X	R^1	R^2	R^3	T (ºC)	conv. (%)	*exo*/*endo*
O	Cl	Boc	Boc	90	53	76/24
O	Cl	Bn	Bn	150	-	-
O	Cl	H	Boc	90	57	89/11
S	Cl	Cbz	Bn	40	40	80/20
S	Cl	Bn	Bn	40	76	87/13

Scheme 69

On the other hand, Cativiela *et al*.[36] firstly described the use of *Z* and *E*-2-phenyl-4-benzylidene-5(4*H*)-oxazolone **77** as dienophile in the Diels-Alder reaction with various dienes. The reaction between the *Z*-oxazolone **77** and cyclopentadiene in presence of $TiCl_4$ or $AlCl_3$ as Lewis acids catalysts gave mixture of racemic cycloadducts *exo*-**233** and *endo*-**233** in favour of the *endo*-**233** diastereoisomer (*Scheme 70*).

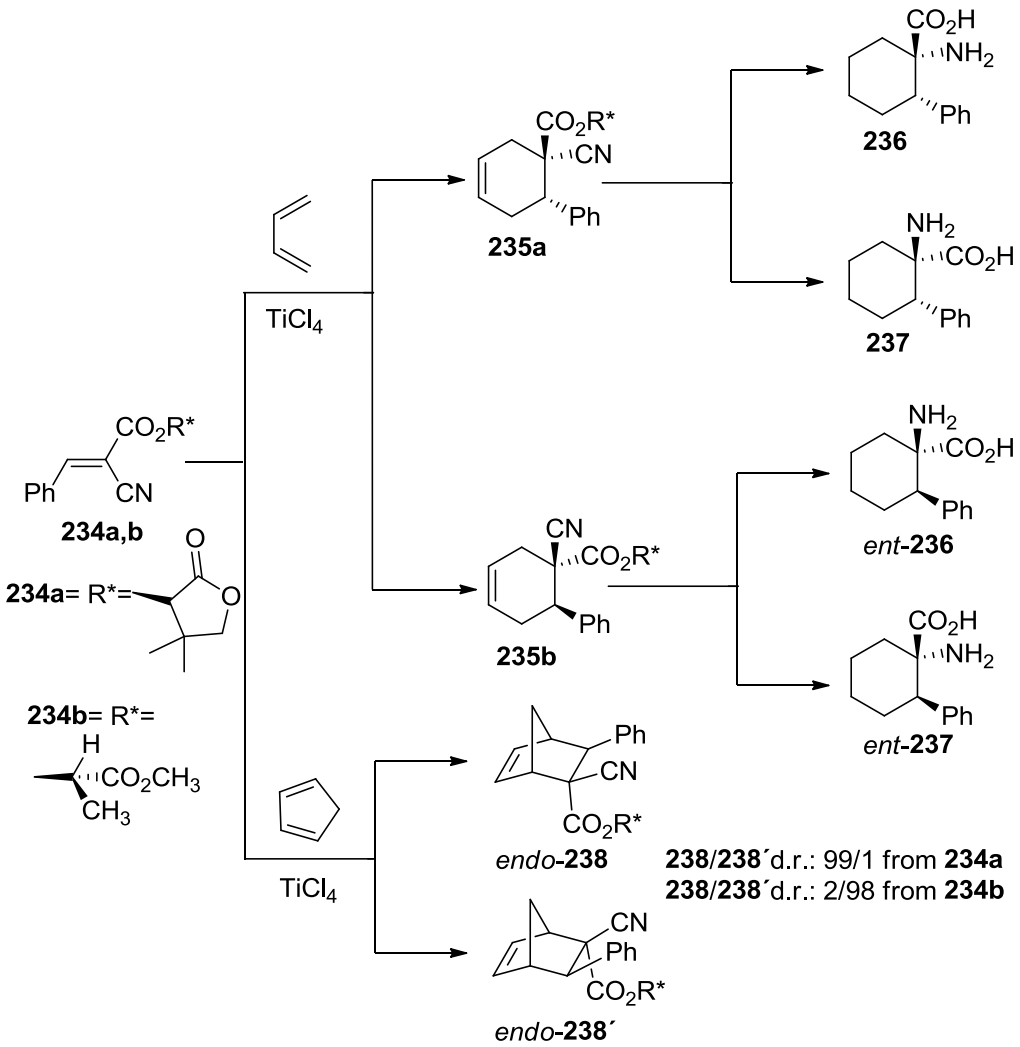


77 *exo*-**233** *endo*-**233**

Scheme 70

On the other hand, Cativiela *et al*.[37] reported on the enantiomerically pure synthesis of the four 1-amino-2-phenylcyclohexanecarboxylic acids **236**, *ent*-**236**, **237** and *ent*-**237** *via* a synthetic sequence which started from *E*-2-cyanocinnamates **234a,b**, bearing the chiral auxiliaries (*S*)-ethyl lactate or (*R*)-pantolactone, respectively. The Diels-Alder reaction between the *E*-2-cyanocinnamates **234a,b** and 1,3-butadiene in the presence of $TiCl_4$ as Lewis acid catalyst afforded the corresponding major cycloadducts **235a** and **235b**, respectively. These cycloadducts were transformed, after complementary degradation sequences, into enantiopure 1-amino-2-phenylcyclohexanecarboxylic acids **236**, *ent*-**236**, **237** and *ent*-**237** (*Scheme 71*). Besides, cycloadducts **235a** and **235b** were also transformed into enantiomerically pure constrained α-amino-γ-

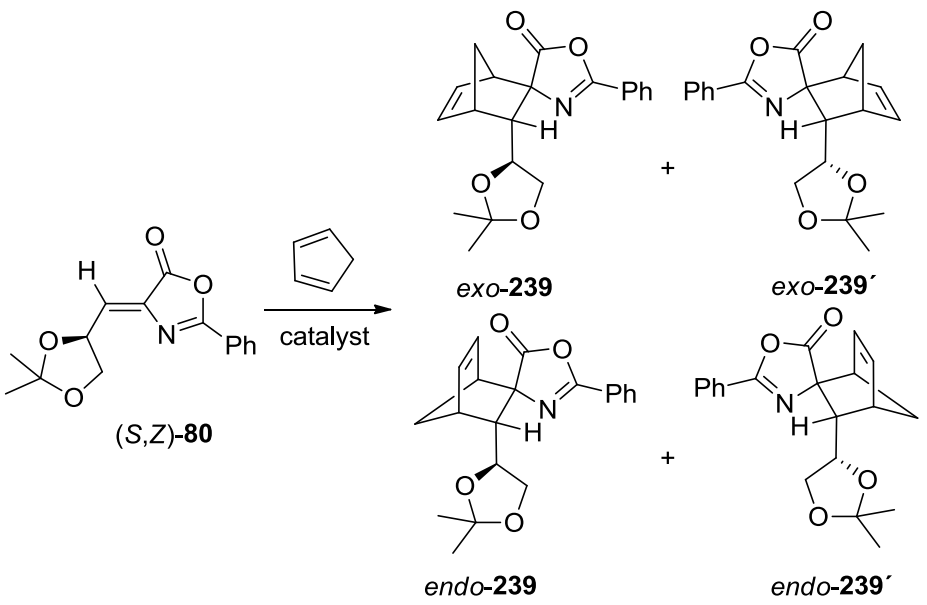
hydroxy acids.[38] Moreover, the dienophiles **234a,b** reacted with 2,3-dimethyl-1,3-butadiene within the same Lewis acid giving as well preferentially one diastereoisomer in function of the chiral auxiliary employed.[39] The study of the behavior of these chiral dienophiles **234a,b** in the Diels-Alder reaction was completed by the addition of cyclopentadiene using homogeneous[40] and heterogeneous catalysts.[40] Among the Lewis acids employed under homogeneous conditions, $TiCl_4$ gave the best results both on the reaction yield and diastereoselectivities, obtaining preferentially the *endo* cycloadducts both from **234a** and **234b** with excellent diastereoselective ratios. However, starting from the chiral cyanocinnamate derived from the (*R*)-pantolactone **234a** was obtained preferentially the diastereoisomer *endo*-**238** and in case of starting from **234b** the major diastereoisomer obtained was *endo*-**238´** (*Scheme 71*).



Scheme 71

Later, it was described the asymmetric version of the Diels-Alder reaction between the homochiral oxazolone *Z*-2-phenyl-4-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-

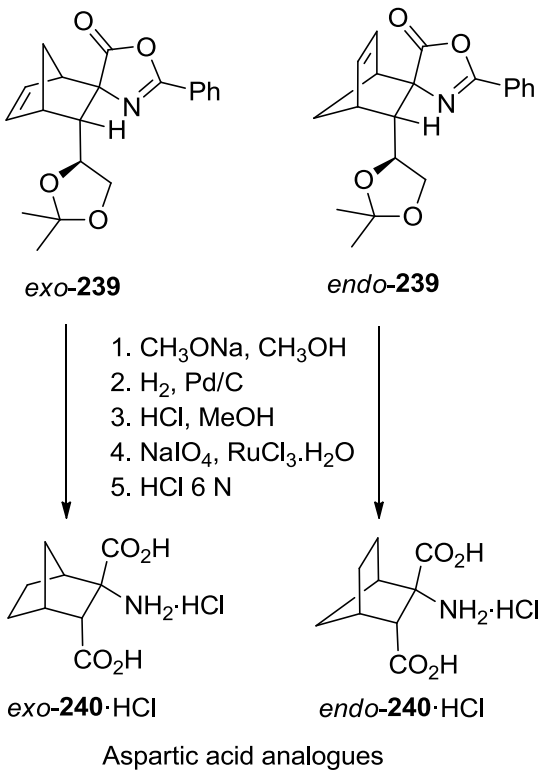
ylmethylene]-5(4*H*)-oxazolone **80** and cyclopentadiene and other dienes.[41] The effects of the Lewis acids in the *endo*/*exo* diastereoselectivity and the doble bond facial selectivity were studied.[42] They concluded that the use of different Lewis acid catalysts had not significant influence on *exo*/*endo* ratio or double bond facial selectivity of the obtained cycloadducts *exo*-**239**, *exo*-**239´**, *endo*-**239** and *endo*-**239´** (*Scheme 72*). Cycloadducts derived from *E*-oxazolone **80** were observed in the Diels-Alder reactions carried out in the presence of some Lewis acid such as $EtAlCl_2$, $AlCl_3$ and $TiCl_4$ due to a *Z*/*E* isomerization.[43]



Catalyst	*exo*/*endo*	d.r. *exo*	d.r. *endo*
none	64/36	90/10	96/4
$LiClO_4$	56/44	80/20	78/22
$EtAlCl_2$	72/28	95/5	97/3
$AlCl_3$	73/27	93/7	97/3
$TiCl_4$	75/25	93/7	98/2
BF_3	77/23	94/6	94/6
ZnI_2	60/40	77/23	66/34

Scheme 72

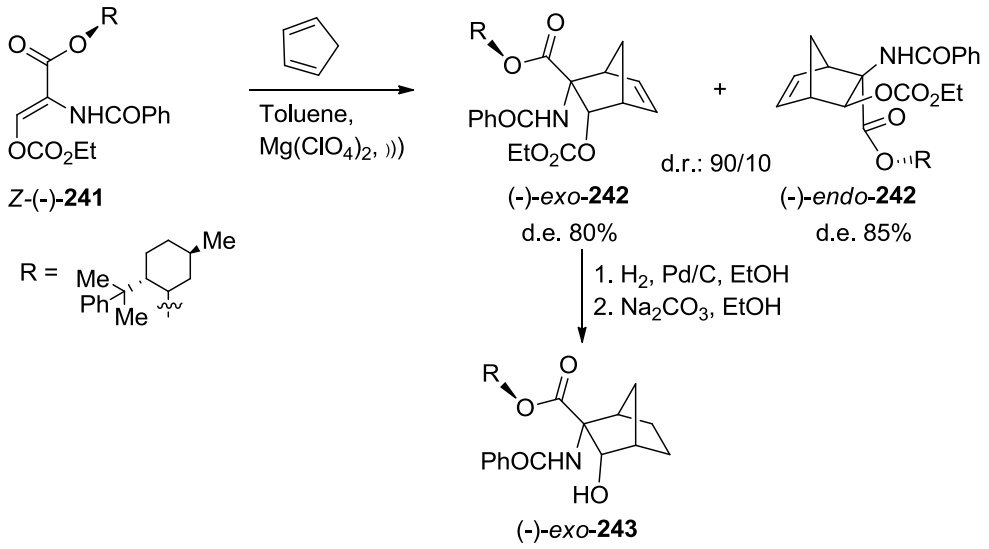
Besides, a synthetic route was designed in order to obtain constrained (*S*)-Aspartic acid analogues *exo*-**240**·HCl and *endo*-**240**·HCl from the major cycloadducts obtained *exo*-**239** and *endo*-**239**, respectively (*Scheme 73*).[44]



Scheme 73

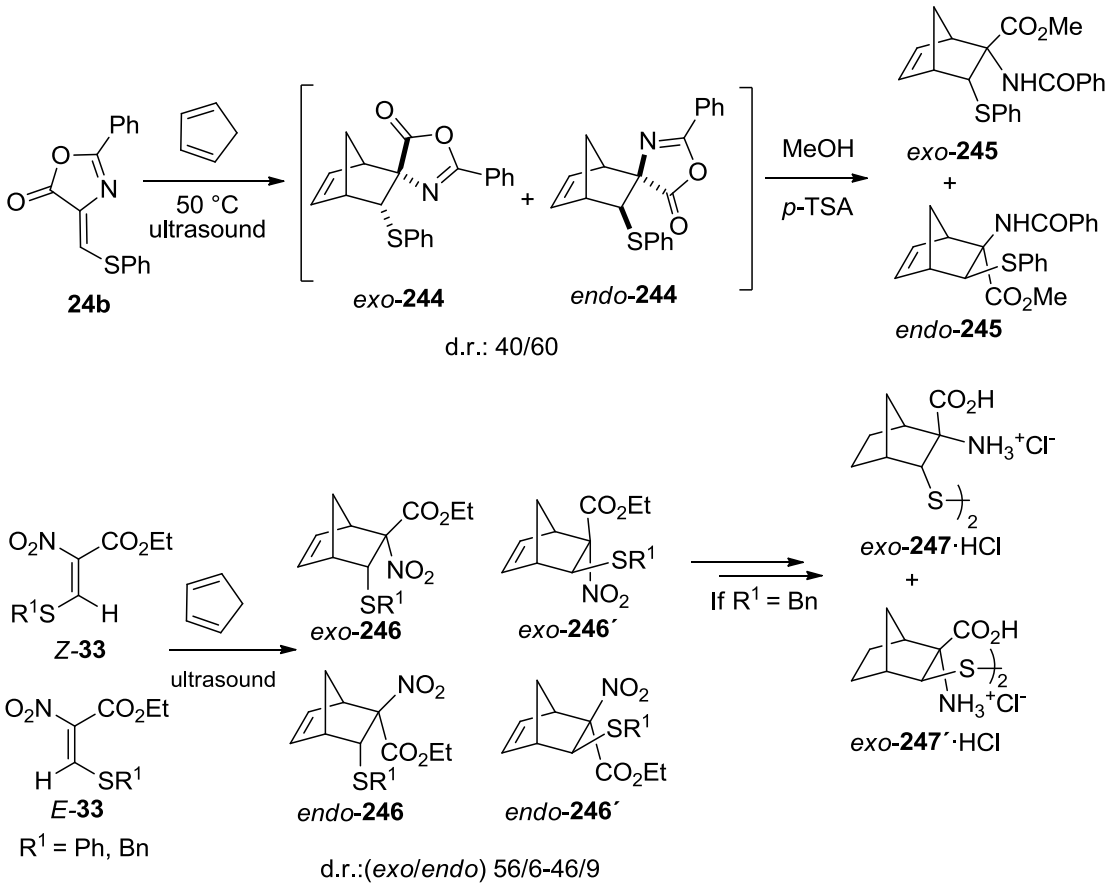
The use of heterogeneous catalysts was also applied for the Diels-Alder reaction between the *E*-2-phenyl-4-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-ylmethylene]-5(4*H*)-oxazolone **80** and cyclic and acyclic dienes, concluding that some heterogeneous catalysts (SiO_2-Al, SiO_2-Ti and SiO_2-Zn) improved the selectivity of the Diels-Alder reaction, by reducing the percentage of *E*/*Z* isomerization, especially using $ZnCl_2$ supported on SiO_2.[45]

Gelmi *et al*.[46] reported the enantioselective Diels-Alder reaction between the chiral acrylate *Z*-(-)-Phenylmenthyl 2-benzoylamino-3-ethoxycarbonyloxyacrylate **241** and cyclopentadiene to prepare the cycloadducts (-)-*exo*-**242** and (-)-*endo*-**242** in a ratio 90/10 in high yields. The (-)-*exo*-**242** adduct was further elaborated to obtain the constrained serine analogue (-)-*exo*-**243** (*Scheme 74*).



Scheme 74

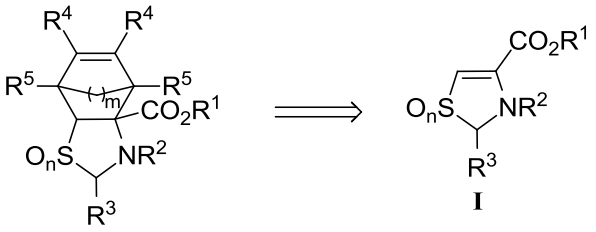
Recently, as it has been depicted in Chapter I 6.4 (Synthesis of cyclic α,β-dialkyl cysteine derivatives) Gelmi *et al*.[47] carried out the racemic synthesis of modified cysteines, incorporating a norbornene scaffold through the Diels-Alder reaction between *Z*-β-sulfanyl-methylene-5(4*H*)-oxazolone **24b** and a mixture of *Z* and *E*-β-sulfanyl-α-nitroacrylates **33** and cyclopentadiene. The reaction between *Z*-oxazolone **24b** and cyclopentadiene gave the racemic mixture of diastereoisomers *exo*-**244** and *endo*-**244** in a ratio 40/60 when the reaction was carried out at 50 ºC and under ultrasounds activation. The oxazolone ring opening of such cycloadducts gave the mixture of *exo*-**245** and *endo*-**245.** On the contrary, the reaction between the *Z*/*E* mixture of β-sulfanyl-α-nitroacrylates **33** gave mixtures of 4 diastereoisomers *exo*/*endo* **246** and *exo*/*endo* **246´** in favour of the *exo*-adducts. Thus, major cycloadducts *exo*-**246** and *exo*-**246´** could be fully deprotected to give the corresponding modified cystines as *exo*-**247**·HCl and *exo*-**247´**·HCl (*Scheme 75*).


Ph
O
N
O
SPh
24b
50 °C
ultrasound
exo-244
endo-244
MeOH
p-TSA
CO2Me
NHCOPh
SPh
exo-245
endo-245
d.r.: 40/60
O2N
CO2Et
R1S
H
Z-33
ultrasound
CO2Et
NO2
SR1
exo-246
exo-246´
If R1 = Bn
CO2H
NH3+Cl-
S
2
exo-247·HCl
exo-247´·HCl
E-33
endo-246
endo-246´
R1 = Ph, Bn
d.r.:(exo/endo) 56/6-46/9

Scheme 75

2. OBJECTIVES

In this chapter, Diels-Alder reaction between homochiral thiazolines **I** and cyclic (cyclopentadiene and 1,3-cyclohexadiene) and acyclic (1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,4-dipehyl-1,3-butadiene and 2-trimethylsiloxy-1,3-butadiene) dienes will be carried out. The study will be focused on the reactivity and stereoselectivity of different pairs diene/thiazoline for the obtention of the cycloadducts **VII**. Conditions of the hydrogenation of the obtained Diels-Alder cycloadducts and the reduction of the sulfinyl moiety will be also studied. Final cleavage of protecting groups, both the amino and carboxylic functions, and thiazolidine ring opening will be carried out in order to obtain cysteine derivatives as free amino acids.



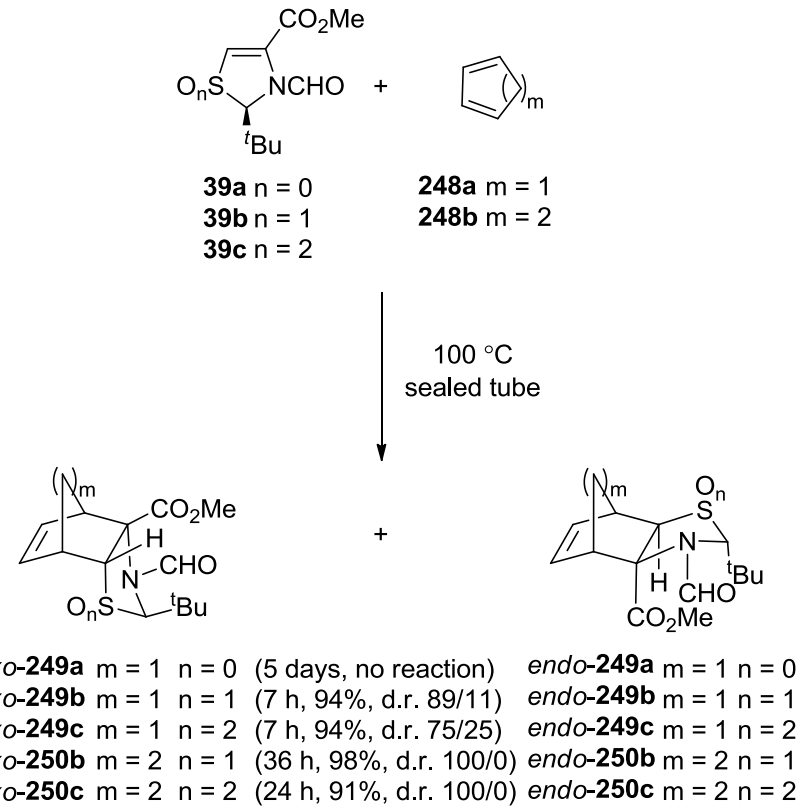
VII **I**

3. RESULTS AND DISCUSSION

3.1. Diels-Alder cycloaddition between homochiral thiazolines 39a-c and cyclic dienes

Next, our challenge was the synthesis of chiral β-sulfanyl α,β-cycloaliphatic thiazolidines by Diels-Alder cycloaddition reaction. Initially, thiazolines **39a-c** were essayed in the reaction with cyclopentadiene **248a** (*Scheme 76*). Thus, thiazoline **39a**, bearing the β-sulfanyl group, was employed as dienophile, but after 5 days stirring at 100 ºC in presence of cyclopentadiene **248a**, the thiazoline **39a** remained unaltered as it could be observed by ^{1}H NMR. Therefore, it was proved that thiazoline **39a** was not a good dienophile, probably owing to the donor character of sulfur atom. The next attempts were carried out employing the thiazolines **39b** and **39c** within sulfinyl and sulfonyl groups, with electron withdrawing features and probably more reactive towards dienes, respectively. Both reactions were completed after 7 hours affording the mixtures of cycloadducts *exo*/*endo* **249b** (d.r. 89/11) and *exo*/*endo* **249c** (d.r. 75/25), respectively, after analysis of reaction crude by ^{1}H NMR, with excellent yield in both series (*Scheme 76*).

Encouraged by these results, we also decided to carry out the Diels-Alder cycloaddition with thiazolines **39b** and **39c** and 1,3-cyclohexadiene **248b** in a sealed tube at 100 ºC. Reactions took place in 36 hours and 24 hours, affording exclusively the *exo* adducts **250b** and **250c** in excellent yields, respectively (*Scheme 76*).



exo-**249a**	m = 1	n = 0	(5 days, no reaction)	*endo*-**249a**	m = 1 n = 0
exo-**249b**	m = 1	n = 1	(7 h, 94%, d.r. 89/11)	*endo*-**249b**	m = 1 n = 1
exo-**249c**	m = 1	n = 2	(7 h, 94%, d.r. 75/25)	*endo*-**249c**	m = 1 n = 2
exo-**250b**	m = 2	n = 1	(36 h, 98%, d.r. 100/0)	*endo*-**250b**	m = 2 n = 1
exo-**250c**	m = 2	n = 2	(24 h, 91%, d.r. 100/0)	*endo*-**250c**	m = 2 n = 2

***Scheme 76*.** Diels-Alder reaction between thiazolines **39a-c** and cyclic dienes **248a,b**

Structural assignments for the compounds *exo*-**249b,c**, *exo*-**250b,c** and *endo*-**249b,c** have been made on the basis of NOESY experiments, since it was observed n.O.e between the protons of the *tert*-butyl group and H7a and between proton H7a and one proton on the bridge (C8) for *exo*-**249b,c** and *exo*-**250b,c**. On the other hand, compounds *endo*-**249b,c** showed n.O.e between H7a and H6 and also between *tert*-butyl group and H7a (*Figure 35*).

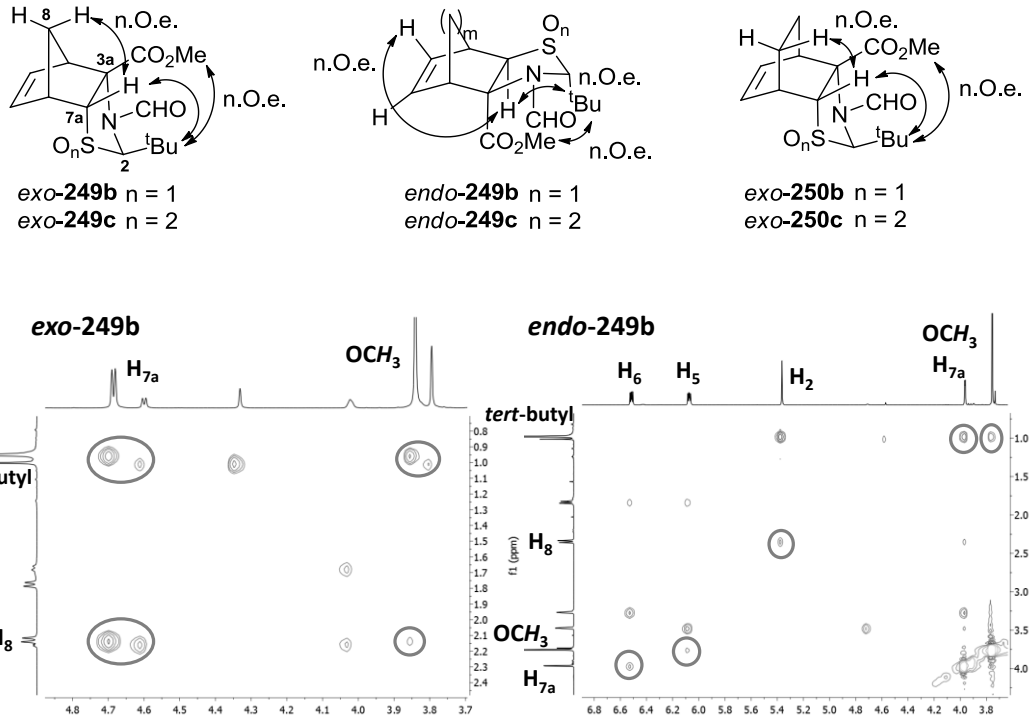


Figure 35. NOESY correlations for bicyclic thiazolidines *exo*-**249b,c**, *exo*-**250b,c** and *endo*-**249b,c**

In order to check the reversibility of the reaction, pure adduct *exo*-**249b** was dissolved in toluene and heated at 100 ºC in a sealed tube for 7 hours in presence of cyclopentadiene and no changes were observed confirming that the reaction is not reversible.

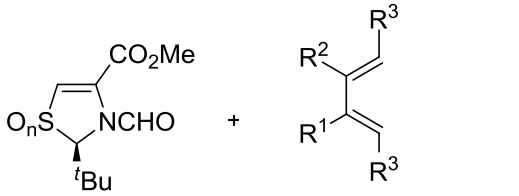
3.2. Diels-Alder cycloaddition between homochiral thiazolines 39b,c and acyclic dienes

Encouraged by the previous results, it was carried out the Diels-Alder reaction employing acyclic dienes such as 1,3-butadiene **251a**, 2,3-dimethyl-1,3-butadiene **251b**, *trans*, *trans*-1,4-diphenyl-1,3-butadiene **251c** and the unsymmetrical diene 2-trimethylsiloxy-1,3-butadiene **251d** and homochiral thiazolines **39b** and **39c**. The Diels-Alder cycloaddition carried out between thiazolines **39b,c** and 1,3-butadiene **251a** and 2,3-dimethyl-1,3-butadiene **251b**, afforded exclusively a single diastereoisomer **252b**, **252c**, **253b** and **253c** enantiomerically pure in excellent yield in each case. Thiazoline **39c** was more reactive against dienes **251a,b** than thiazoline **39b**, probably due to the more electron-withdrawing feature of the sulfonyl functionality respect to the sulfinyl group (*Scheme 77*).

As well, it was assessed the behavior of the hindered *trans*, *trans*-1,4-diphenyl-1,3-butadiene **251c**, whereas the reaction with thiazoline **39b** did not lead to the bicyclic thiazolidine *exo*-**254b** after stirring at 120 ºC for 21 days, the

reaction with thiazoline **39c** afforded the bicyclic thiazolidine *exo*-**254c** in moderate yield as a single diastereoisomer after 21 days at 120 ºC (*Scheme 77*).

Finally, the Diels-Alder reaction was carried out using the unsymmetrical diene 2-trimethylsiloxy-1,3-butadiene **251d**. Thus, Diels-Alder reactions with the thiazolines **39b** and **39c** were completed after 4 and 1 days, respectively. The reaction crudes were treated, without purification, with HCl 1 N in THF for 1 day, obtaining the mixture of regioisomers **255b**/**256b** in a ratio 66/34 from thiazoline **39b** in excellent yield and exclusively the bicyclic thiazolidine **255c** in good yield from thiazoline **39c** (*Scheme 77*).

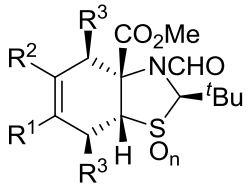


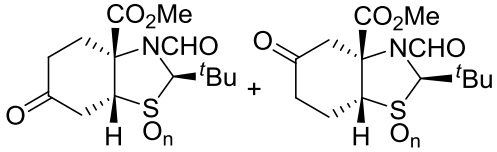
39a n = 0
39b n = 1
39c n = 2

	R^1	R^2	R^3
251a	H	H	H
251b	Me	Me	H
251c	H	H	Ph
251d	H	TMSO	H

251a-c
sealed tube

251d
sealed tube,
then 1 N HCl, THF





255b n = 1 (3 d, 95%, r.r. 66/34) **256b** n = 1
255c n = 2 (1 d, 68%, r.r. 100/0) **256c** n = 2

	R^1	R^2	R^3	n	T(ºC)	t(d)	yield (%)
252b	H	H	H	1	100	10	94
252c	H	H	H	2	100	5	98
253b	Me	Me	H	1	100	3	95
253c	Me	Me	H	2	100	0.5	98
exo-**254b**	H	H	Ph	1	120	21	n.r.
exo-**254c**	H	H	Ph	2	120	21	45

Scheme 77. Diels-Alder reaction using acyclic dienes **251a-d**

Structural assignments of compounds **252b,c**, **253b,c**, *exo*-**254c**, **255b,c** and **256b** have also been made on the basis of NOESY experiments. Within this context, it was observed n.O.e between the protons of the *tert*-butyl group and H6 of the single adduct obtained in every case (*Figure 36*). Besides, the cycloadduct

254c showed n.O.e between the methyl ester group and both phenyl groups; H2 and H8; H6 and the phenyl group located at the carbon C5 and no n.O.e between *tert*-butyl group and H2 (*Figure 37*).

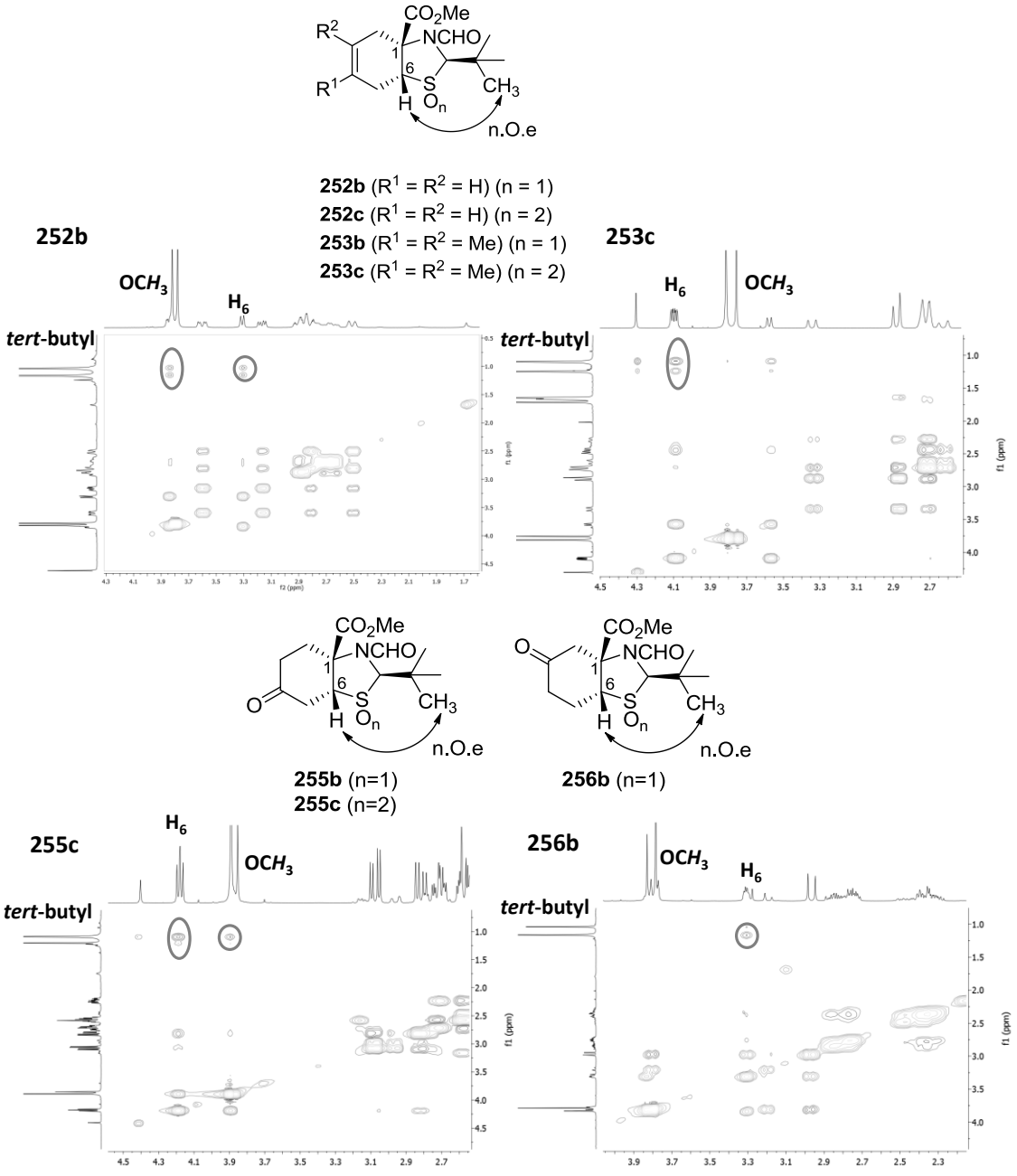


Figure 36. NOESY correlation for bicyclic thiazolidines **252b,c**, **253b,c**, **255b,c** and **256b**

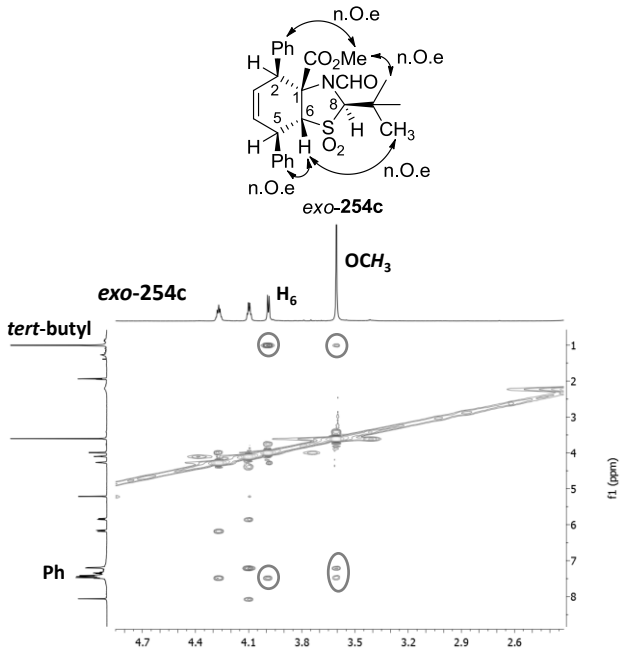
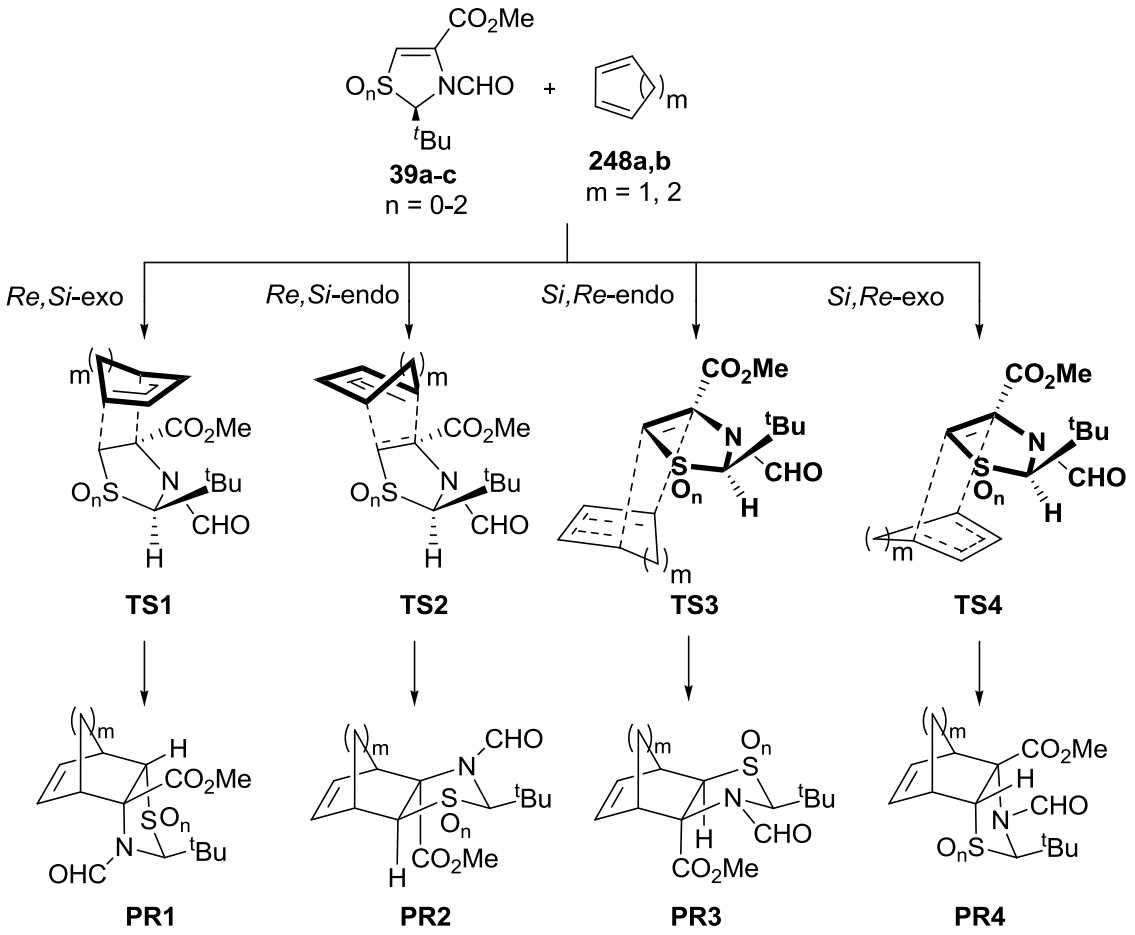


***Figure 37*.** NOESY correlation for bicyclic thiazolidine *exo*-**254c**

3.3. Mechanistic considerations

To rationalize the observed reactivity and selectivities of the cycloadditions, the reactions were studied at B3LYP-D3BJ/Def2SVP level of theory to calculate geometries of stationery points and then single point calculations at B3LYP-D3BJ/Def2TZVP level of theory were performed (for details see appendix). We studied as a model the reaction between thiazolines **39a-c** and dienes **248a**, **248b**, **251c** and **251d**. Admittedly, dienes **251a,b** should be similar to cyclic ones whereas **251c,d** have different electronic and steric features. Both diastereofaces *Re,Si* and *Si,Re* and *exo/endo* chanels (referred to the ester moiety) were considered. The approaches considered are illustrated for dienes **248a,b** in *Scheme 78*. The same approaches were studied for **251c** and **251d** (see appendix). For unsymmetrical diene **251d** the formation of two regioisomers was also taken into account. A total of 60 transition structures were calculated.



Scheme 78. Approaches for the cycloaddition between **39a-c** and **248a,b**

The nomenclature used for transition states (**TS**) and products (**PR**: **1** for *Re,Si-exo*, **2** for *Re,Si-endo*, **3** for *Si,Re-endo* and **4** for *Si,Re-exo*) includes two previous letters indicating diene (**a** for **248a**, **b** for **248b**, **c** for **251c** and **d** for **251d**) and thiazolines (**a** for **39a**, **b** for **39b** and **c** for **39c**), respectively. For **da**, **db** and **dc** series the prefix 13 and 14 before **TS** or **PR**, indicate the regioselectivity. The analysis of the optimized transition structures and the corresponding IRCs revealed concerted processes in all cases. *Figure 38* collects the energy barriers for all the reactions studied. The figure is divided into four sections corresponding to dienes **248a,b** and **251c,d**. Within each section transition structures corresponding to the reaction with **39a-c** are represented. The different energy barriers for each reaction are given in vertical according to the colour code. For diene **251d**, 8 transition states, 13TSs and 14TSs leading to regioisomeric **13-PRs** and **14-PRs**, have been calculated, actually, corresponding to the 1,4- and 1,3-approach leading to the isolated compounds **255** and **256**, respectively.

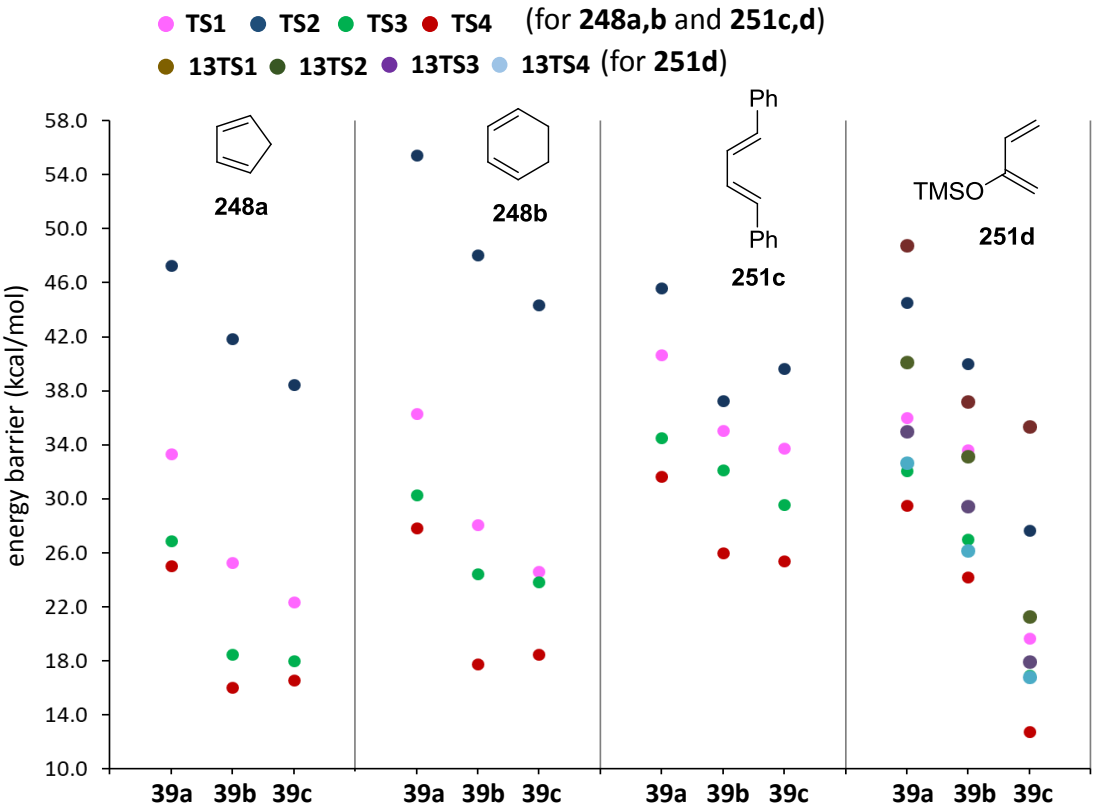


Figure 38. Energy barriers for the Diels-Alder reactions between **39a-c** and dienes **248a,b** and **251c,d**

As expected, approaches by the less-hindered *Si,Re* face were always preferred. In all cases the *exo* approach resulted the less energetic. By comparing thiazolines there is a downward trend from **39a** to **39c**. In fact, the highest barriers correspond to **39a** in agreement with the observed lack of reactivity. Similar barriers are observed for all the dienes except for **251c** which exhibited the highest barriers, due to steric reasons, in agreement with experimental observations. For diene **251d** the 1,4-approach was showed to be the preferred one, also in good agreement with experimental findings. In all cases **TS4** corresponding to a *Si,Re-exo* approach was found the most favorable. The diastereoselectivity was also well-rationalized by molecular modeling calculation. For diene **248a** close barriers between **TS3** and **TS4** predict the obtention of mixtures of **PR3** and **PR4**, the latter being predominant. For dienes **248b**, **251c** and **251d** the larger differences between **TS3** and **TS4** predict the obtention of a single diastereomer. These predictions are in full agreement with that observed experimentally. The geometries of the transition structures are given in appendix. In all cases, expected distances for asynchronous concerted reactions are observed. As an example, the most stable transition structures for the reaction between **39c** and dienes **248a,b** and **251c,d** are illustrated in *Figure 39*.

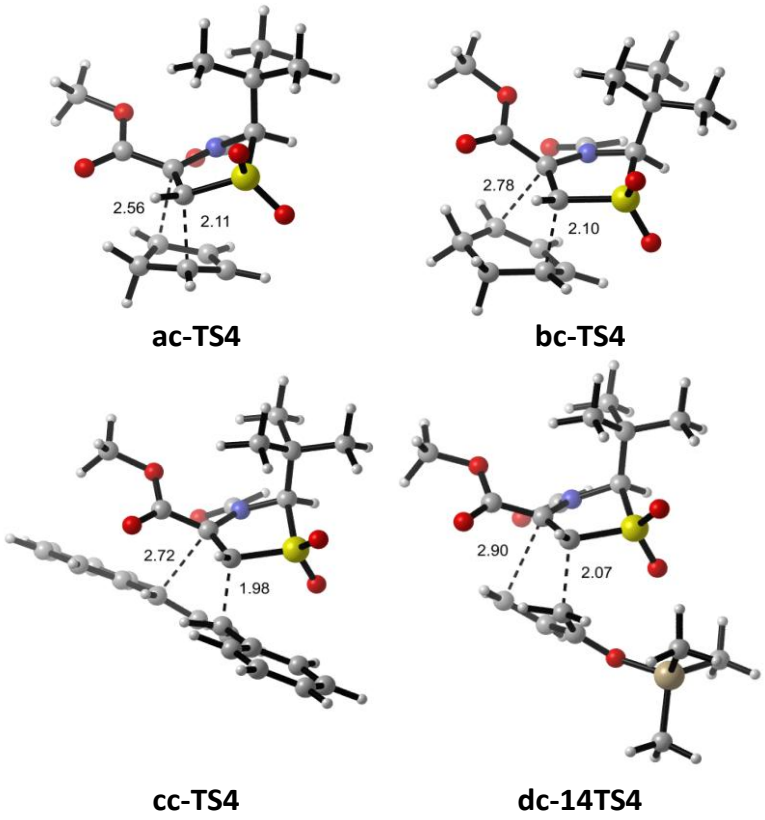


Figure 39. Most stable transition structures (B3LYP-D3BJ/Def2SVP) for the reaction of **39c** **248a,b** and **251c,d**

Essentially, similar geometries are observed for the studied dienes, the main differences being in forming bond distances. A calculation of bond orders according to Pauling's equation[48] using the correction applied to transition structures[49] gave an idea of the asynchronicity of the reactions. The obtained values are listed in *Table 21*. The less asynchronous reactions were those with cyclic dienes **248a** (through **ac-TS4**) and **248b** (through **bc-TS4**). The most asynchronous reaction was that with diene **251c** (through **cc-TS4**) due to the diverse steric interactions with the two different sides of the dienophile. The asynchronicity of the reaction with diene **251d** (through **dc-TS4**) was due to the electronic effects exerted by the siloxy substituent of the diene.

Table 21. Bond orders for the preferred transition structures

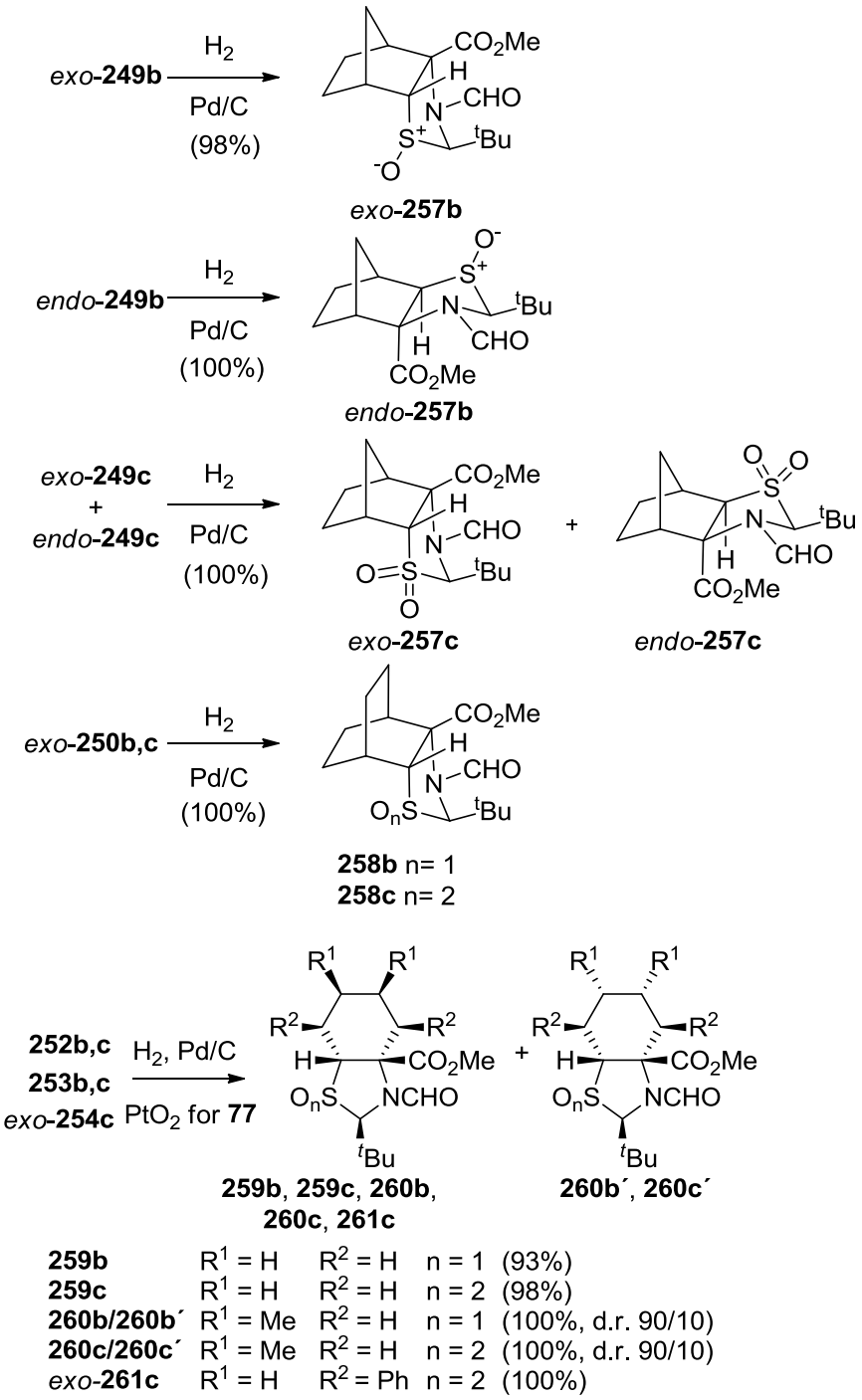
	C1-C3[a]	B.O. (C1-C3)[b]	C2-C4[a]	B.O. (C2-C4)[b]	Δ(B.O.)
ac-TS4	2.56	0.18	2.11	0.39	0.20
bc-TS4	2.78	0.13	2.10	0.39	0.27
cc-TS4	2.72	0.14	1.98	0.48	0.34
dc-TS4	2.90	0.10	2.07	0.41	0.31

[a]Given in angstrom. [b]Calculated according Pauling's equation.[48] A standard value of 1.54 Å was considered for $C(sp^3)$-$C(sp^3)$ distance. A value of c = 0.6 was considered according to corrections for transition structures.[49]

3.4. Synthesis of modified cysteines from the Diels-Alder cycloadducts

Next, it was conducted the hydrogenation of the double bond of the bicyclic or tricyclic thiazolidines obtained after Diels-Alder reaction. The reactions were carried out, in general, over Pd/C (10%) at 1 atmosphere of hydrogen affording the hydrogenated thiazolidines *exo*-**257b,c**, *exo*-**258b,c**, *endo*-**257b,c´ 259b,c**, **260b,c** and *exo*-**261c**, in excellent yield in every case (*Scheme 79*). The hydrogenation reaction of the bicylic thiazolidines **253b** and **253c** employing Pd/C (10%) at 1 atmosphere of hydrogen did not afford the corresponding hydrogenated thiazolidines **260b**/**260b'** or **260c**/**260c'**. However, the hydrogenation reaction over PtO_2 in acetic acid converted the stabilized tetrasubstituted alkene to the hydrogenated bicyclic thiazolidines **260b**/**260b'** and **260c**/**260c'** in excellent yield as a mixture of diastereoisomers in a ratio 90/10 in both cases in favour of the diastereomers **260b** and **260c** in which the methyl groups are located towards the *tert*-butyl group, respectively (*Scheme 79*). Minor adducts **260b,c** could not be isolated. Thus, the addition of hydrogen to the double bond occurs *anti* to the *tert*-butyl group.

NOESY experiments of the hydrogenated bicyclic thiazolidines **260b** and **260c** confirmed the disposition of both methyl groups located at the cyclohexane ring. In this sense, it was observed n.O.e between the *tert*-butyl group and H6 and the methyl ester group and also between the methyl ester group and the methyl group at C3 (*Figure 40*).



259b	R^1 = H	R^2 = H	n = 1	(93%)
259c	R^1 = H	R^2 = H	n = 2	(98%)
260b/260b´	R^1 = Me	R^2 = H	n = 1	(100%, d.r. 90/10)
260c/260c´	R^1 = Me	R^2 = H	n = 2	(100%, d.r. 90/10)
exo-**261c**	R^1 = H	R^2 = Ph	n = 2	(100%)

***Scheme 79*.** Double bond hydrogenation of the bicyclic and tricylic thiazolidines

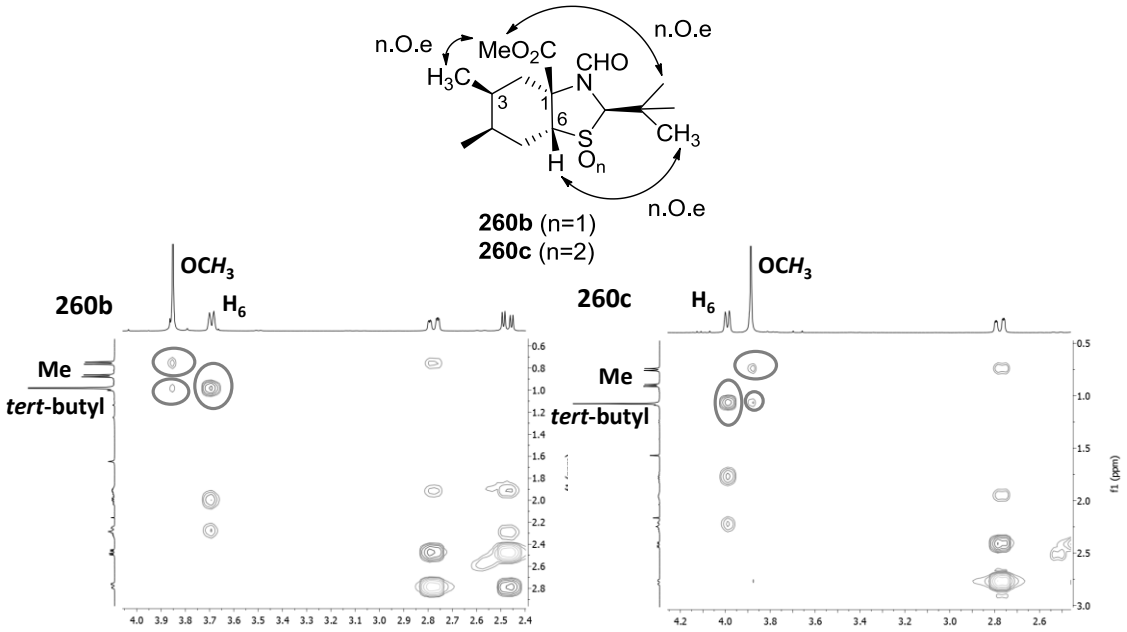
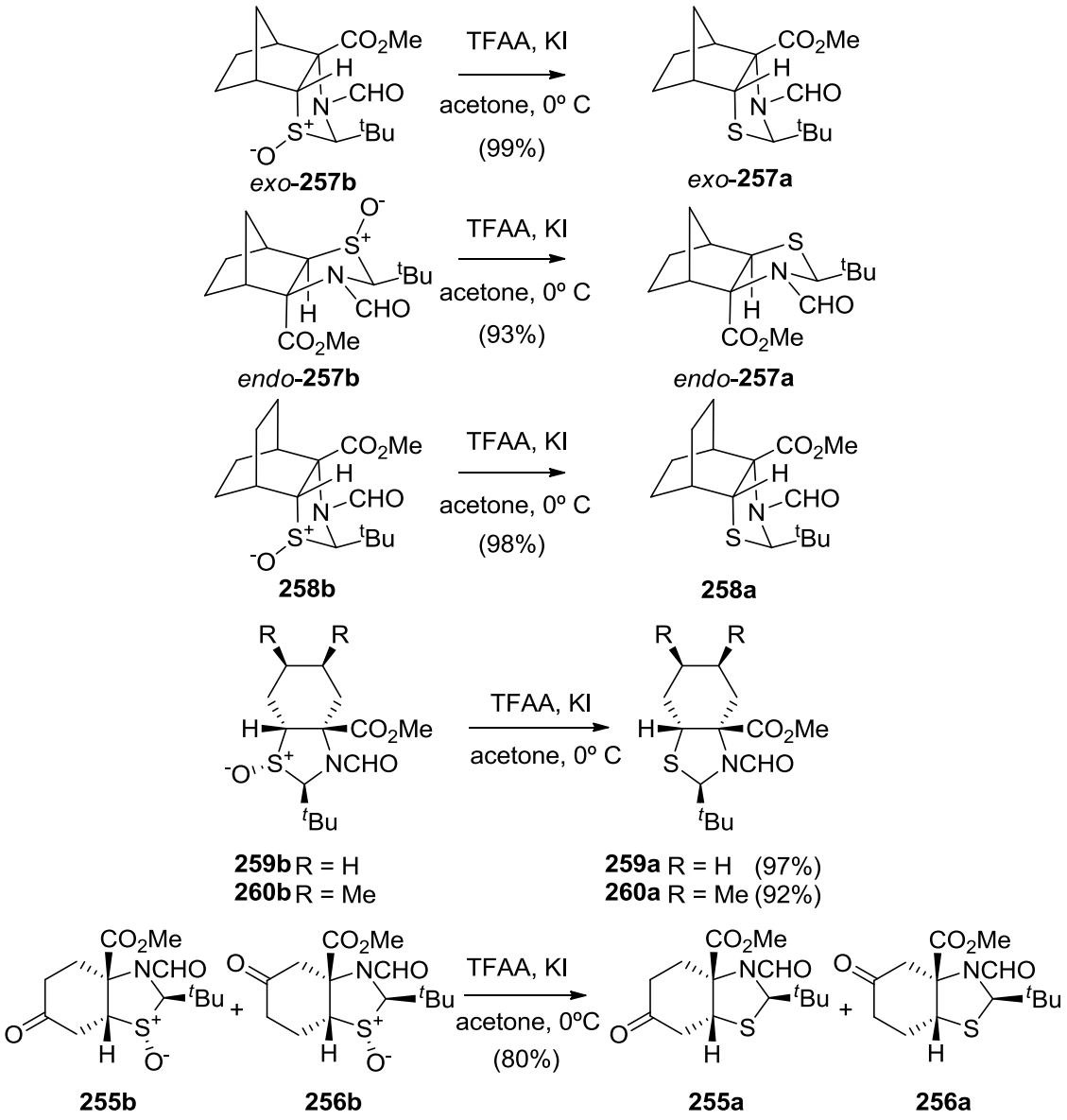


Figure 40. NOESY experiments of **260b** and **260c**

Then, it was proceeded to carry out the sulfinyl group reduction of the thiazolidines **255b**, **256b**, *exo*-**257b**, *endo*-**257b** and **258-260b**. Within this context, the reductions were carried out under the conditions reported by Baldwin *et al.*[50] Thus, over the solution of the abovementioned thiazolidines in acetone at 0 ºC, trifluoroacetic anhydride and KI were sequentially added. The resulting reaction mixture was allowed to proceed at room temperature in a range from 2 to 5 hours to afford the corresponding thiazolidines **255a**, **256a**, *exo*-**257a**, *endo*-**257a** and **258-260a** in good yields (*Scheme 80*).

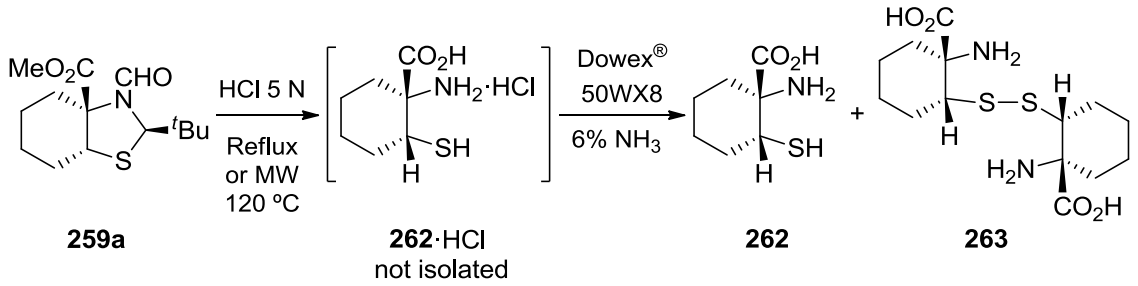


Scheme 80. Sulfinyl group reduction of thiazolidines **255b**, **256b**, *exo*-**257b**, *endo*-**257b** and **258-260b**

NOESY experiments of reduction products showed similar stereochemistry as starting material, thus confirming that the reaction conditions employed did not modify the configuration of the stereogenic carbons of the starting material.

Finally, hydrolysis of sulfanyl thiazolidines was made to obtain the fully deprotected amino acids. Within this context, it was tested the conditions of the hydrolysis reactions with the bicyclic thiazolidine **259a** in HCl 5 N under microwave radiation for 3 hours at 120 ºC[51] and at reflux for 20 hours, affording the amino acid hydrochloride **262** in both cases. ^{1}H NMR of the crude reactions showed minor by-products in the reaction performed under microwave conditions. In both cases, the purification using ion exchange resin Dowex® 50WX8 revealed the presence, along

with the free amino acid **262**, of the oxidized derivative **263**, upon analysis by ^{13}C NMR (*Scheme 81*). It could be observed that in a stored sample of the free amino acid **262**, dissolved in D_2O, for 2 weeks the intensity of the signals belonging to the free amino acid **262** decreased in favour of the corresponding signals of the dimer **263**. In particular, it was observed that signal of the carbon bonded to the sulfur atom in the free amino acid **262**, 40.6 ppm, decreased in favour of the corresponding signal of its oxidized derivative **263**, 51.5 ppm (*Figure 36*). We observed that the basic medium necessary to elute the amino acid **262** favored the formation of the dimer **263**.



***Scheme 81*.** Hydrolysis reaction of the bicyclic thiazolidine **259a**

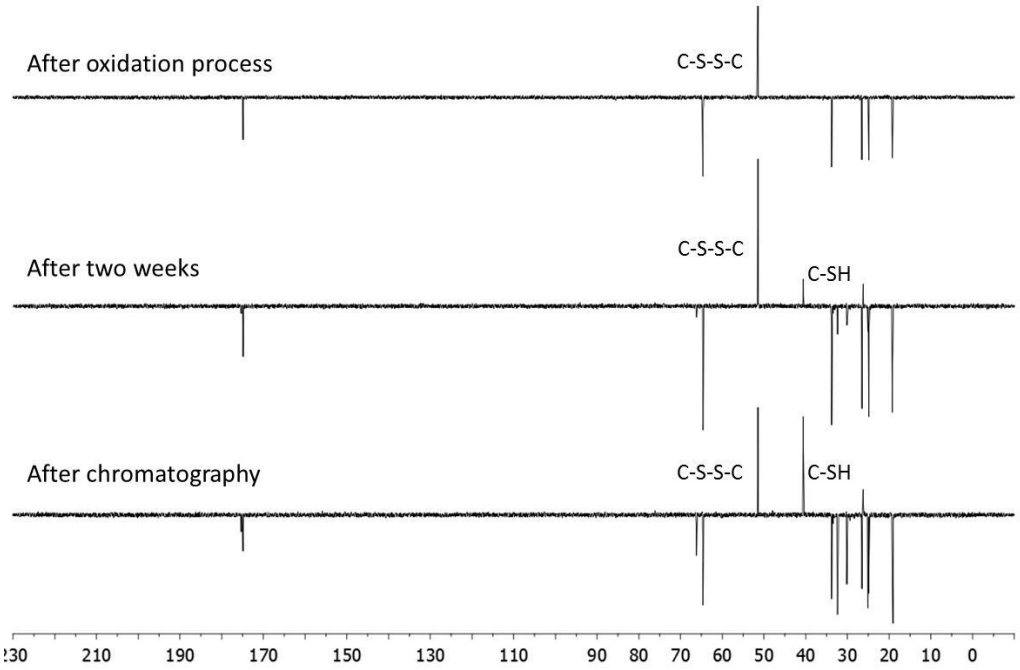
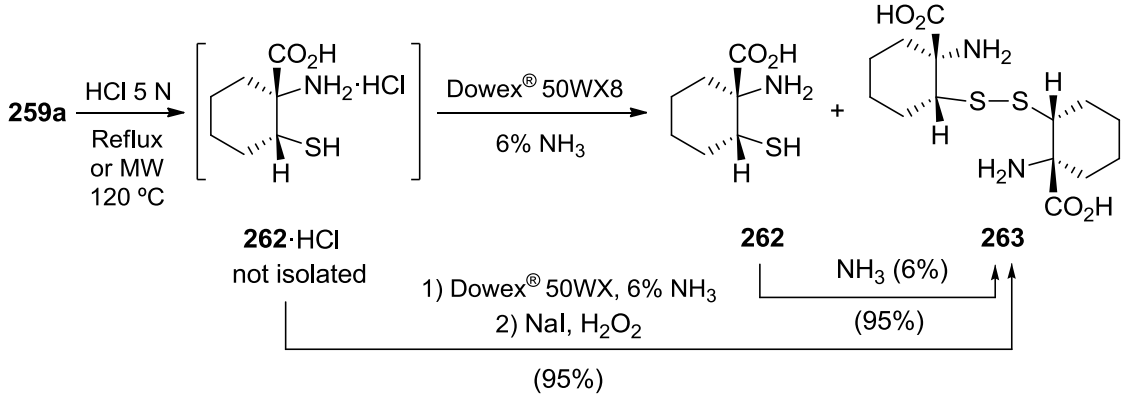


Figure 36. ^{13}C NMR signals of the free amino acid **262** and its oxidized derivative **263**

Considering these results, it was thought to protect the thiol group of the free amino acid **262** as the dimer form **263**. In addition, the mixture of **262** and **263** obtained after exchange chromatography, was treated with H_2O_2 in the presence of

NaI in catalytic amount for 40 minutes at room temperature,[52] affording the dimer **263** in excellent yield after chromatographic purification with the resin Dowex® 50WX8 in two reaction steps (*Scheme 82, table 22*).



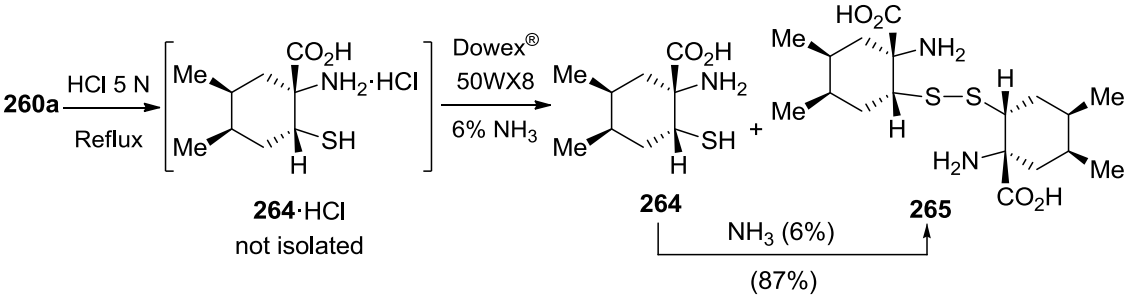
Scheme 82. Different approaches for the synthesis of cystine **263**

Table 22. Reagents and conditions for the hydrolysis and oxidation reaction to obtain the amino acid dimer **263**

	Hydrolysis			Oxidation	
entry	**HCl**	**Temp. (°C)**	**time (h)**	**reagents**	**Yield (%)[b]**
1	5 N	120[a]	3	NaI/H_2O	95
2	5 N	Reflux	20	NaI/H_2O	72
3	5 N	Reflux	24	NH_3	95

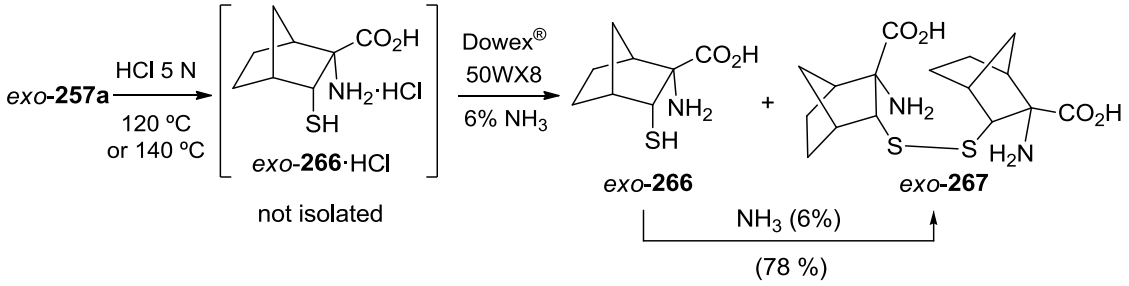
[a]Reaction carried out under microwave conditions. [b]Isolated yield considering two steps.

In view of the mentioned results, we decided to carry out the reaction sequence; hydrolysis, ion exchange purification and oxidation starting from the bicyclic thiazolidine **260a** using HCl 5 N at reflux for the hydrolysis and aqueous NH_3 (6% v/v) for the oxidation, obtaining the dimer **265** in good yield, taking into account two consecutive reactions steps (*Scheme 83*). Same behavior was observed in ^{13}C NMR for the chemical shift of the signals of the carbon bounded to the sulfur atom for the pair of compounds **264**/**265**. In this particular case the signal for the carbon bonded to the sulfur atom in the amino acid **264** appears at 35.8 ppm and switch to 46.8 ppm in the dimer **265**.



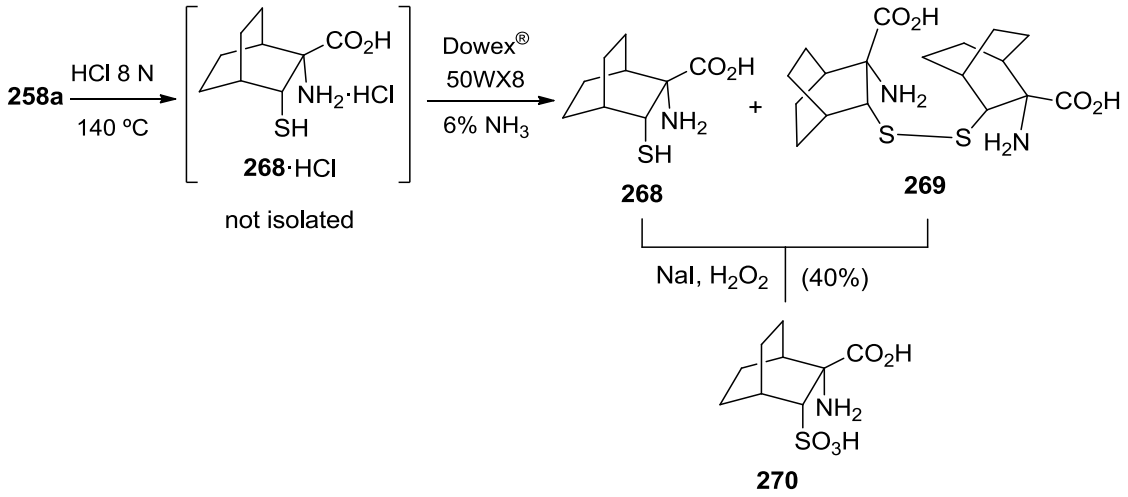
Scheme 83. Synthesis of the cycloaliphatic amino acid **265**

Continuing our research work, we performed the hydrolysis of the tricylic thiazolidine *exo*-**257a** under two different conditions using HCl 5 N at 120 ºC and 140 ºC, obtaining the amino acid *exo*-**266** along with the dimer *exo*-**267** in both cases. The chromatographic purification of the reaction carried at 120 ºC with the resin Dowex® 50WX8 using as eluent aqueous NH_3 (6% v/v) afforded the dimer *exo*-**267** exclusively in good yield, 74%. The chromatographic purification of the reaction carried at 140 ºC gave also a mixture of the amino acid *exo*-**266** and the dimer *exo*-**267**. The mixture was submitted to oxidation with aqueous NH_3 (6% v/v) rendering the dimer *exo*-**267** in good yield, 78% (*Scheme 84*).



Scheme 84. Synthesis of the cycloaliphatic amino acid *exo*-**267**

Finally, the tricyclic thiazolidine **258a** was subjected to hydrolysis reaction using HCl 5 N at 120 ºC and 140 ºC. However, the starting material was recovered in both cases. In view of these results, we attempted to increase the concentration of hydrogen chloride. Thus, the hydrolysis reactions carried out with HCl 6 N at 120 ºC and using microwave radiation gave the same unsatisfactory result. However, the hydrolysis reaction carried out with HCl 8 N at 140 ºC was completed in few hours (*Scheme 85*). The chromatography purification with the resin Dowex® 50WX8 using as eluent aqueous NH_3 (6% v/v) afforded a mixture of the free amino acid **268** and the dimer **269**. Thus, the mixture of **268** and **269** was subjected to air oxidation in presence of aqueous aqueous NH_3 (6% v/v), but the ratio remained almost unaltered. For the purpose of getting the complete conversion of the cysteine **268** to its oxidized dimer **269**, the oxidation reaction was carried out using NaI and H_2O_2. Surprisingly, overoxidation of the sulfur atom took place and the corresponding sulfonic acid **270** was obtained (*Scheme 85*).

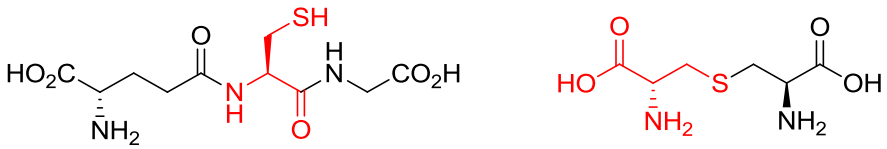


***Scheme 85*.** Synthesis of the cycloaliphatic amino acid **270**

3.5. Synthesis of modified glutathione and lanthionine starting from modified cystine 263

Having achieved our main goal, the synthesis of modified cysteines as free amino acid, we decided to develop a synthetic methodology to prepare bioactive organic molecules and peptides.

Glutathione is a small tripeptide γ-Glu-Cys-Gly (*Figure 41*), naturally synthetized by living organisms. Reduced glutathione (GSH) plays a crucial role for life as it is considered as a potent natural antioxidant,[53] being the most abundant non-protein thiol in eukaryotic cells[54] and is involved in several physiological processes.[55] Within this context, GSH protects sulfhydryl groups of peptides, DNA, proteins and other biomolecules, against electrophiles from xenobiotic sources or those generated by endogenous oxidation processes.[56] Due to this property, glutathione slows down the aging process and protects against cell damage,[57] the GSSG/GSH ratio being an important marker of oxidative stress.[58] In addition, many diseases, caused by viruses, have been observed to induce a decrease in glutathione levels in the body, making it more vulnerable.[59] Lanthionines are bis-amino acids which structure consists in two alanines bonded by a thioether bridge (*Figure 41*). Lanthionines are key constituents of some lantibiotics,[60] such as nisin, subtilisin or cinnamycine,[61] a family of peptides with bactericidal activity, mainly against a wide range of Gram-positive bacterias[62] as they inhibit the cell wall synthesis or are added to lipid II, resulting in the formation of pores in the cell membrane.[63] Lantibiotics can also act as food preservatives, immunostimulants and antitumor agents.[64]



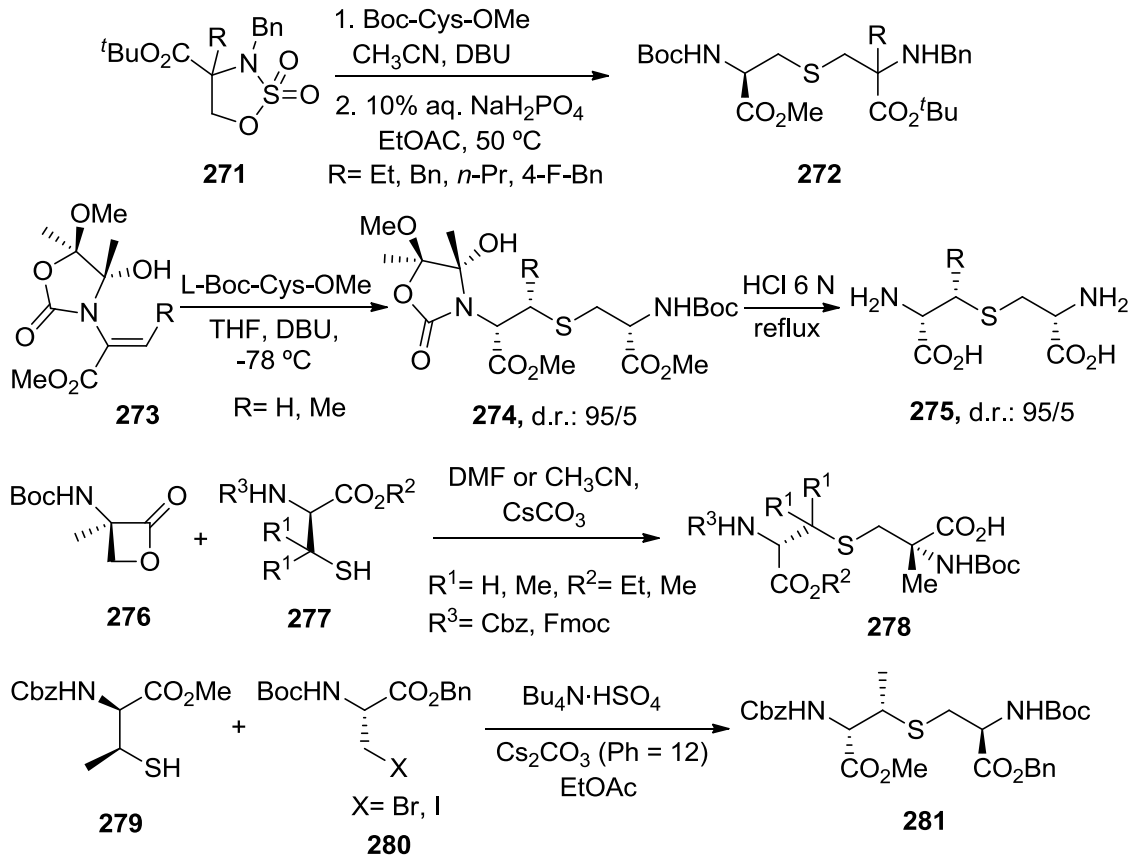
Glutathione Lanthionine

Figure 41. Glutathione and lanthionine structures

On the other hand, both glutathione and lanthionine have been targets of structural modification due to its molecular simplicity. However, the synthesis of glutathiones and lanthiones incorporating conformationally restricted cysteines has been scarcely explored.

Within this context, several synthetic methodologies have been developed on the synthesis of modified glutathiones,[65] based on the classical pathway for the peptide synthesis, by either the substitution of the terminal amino acids with others. For instance, the replacement of the glycine with a cysteine residue[66] or the glutamic acid with a proline.[67] Moreover, it is worth to highlight the replacement of natural *L*-cysteine with thiazolidine analogues,[68] dithiolane cycle[69] or α- and β-substituted cysteines.[70]

Among all the strategies described in the bibliography for the preparation of lanthionines,[71] only few examples concerning the synthesis of α-alkyllanthionines and β-alkyllanthionines have been reported. The methodologies developed for the synthesis of α-alkyllanthionines were based on the nuclephilic attack of the thiol group of protected *L*-cysteine over cyclic sulfamidates **271**[72] or β-substituted dehydrobutyrine **273**,[73] thus obtaining the corresponding modified lanthionines **272** and **274**, respectively. Similarly, the nuchleophilic attack of the thiol group of β,β-dialkyl cysteines over serine β-lactones **276**[74] or β-bromo or iodoalanine **280**[74a,75] yielded the modified lanthionines **278** and **281**, respectively (*Scheme 86*).

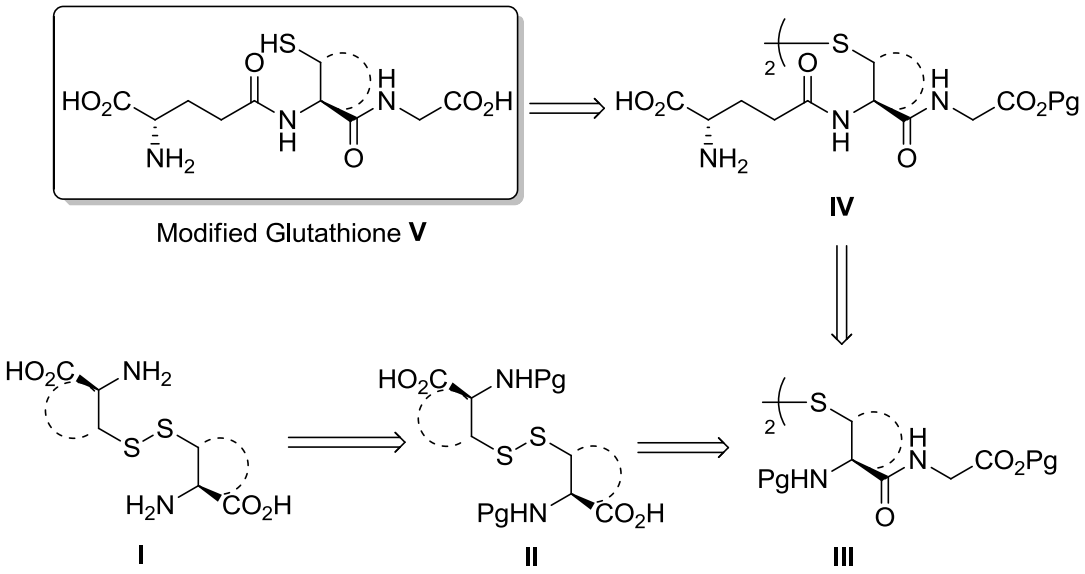


Scheme 86

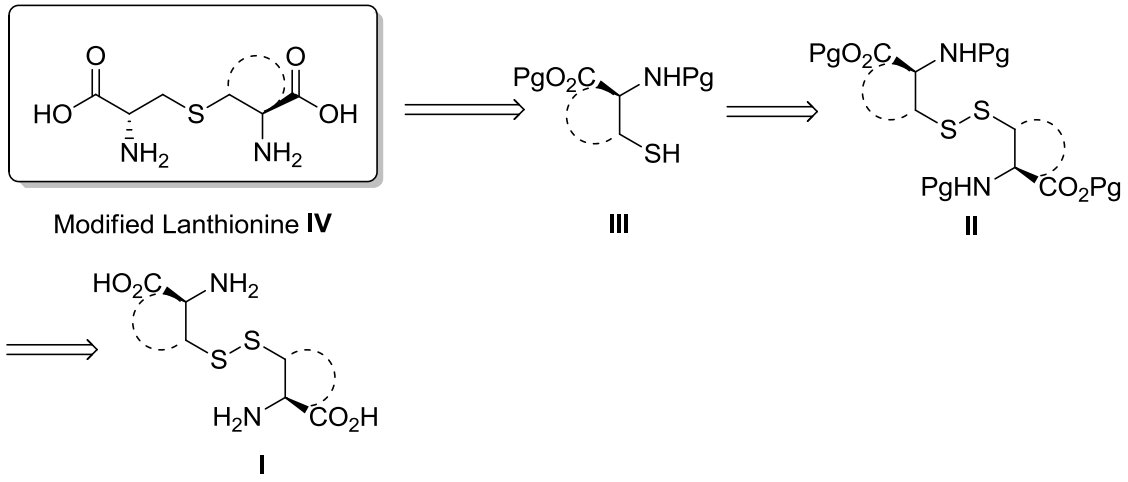
Taking into account our modified cysteines, we though retro-synthetic routes to obtain the corresponding modified glutathiones and lanthionines, respectively.

In this sense, the glutathione synthesis could begin by protecting the amine function of the cystine **I**. The next step could be the coupling reaction between the acid of the modified cystine **II** and the amine group of the amino acid glycine adequately protected, affording the dipeptide **III**. Subsequently, the deprotection of the amine function of the dipeptide **III** following by a coupling reaction with the amino acid glutamic acid conveniently protected could lead to the glutathione analogue as an oxidized form **IV**. Finally, the disulfide bridge cleavage and hydrolysis of the protecting groups could afford the desire modified glutathione **V** (*Scheme 87*).

On the other hand, the synthesis of modified lanthionines could begin by protecting the amine function of the cystine **I** and then the protection of the carboxylic function to obtain the cystine **II** orthogonally protected. The dimer **II** could be reduced to the corresponding thiol **III** which by the S_N2 reaction with an alanine equivalent could afford a modified lanthionine **IV** (*Scheme 88*).



Scheme 87. Retrosynthetic analysis to prepare modified glutathione



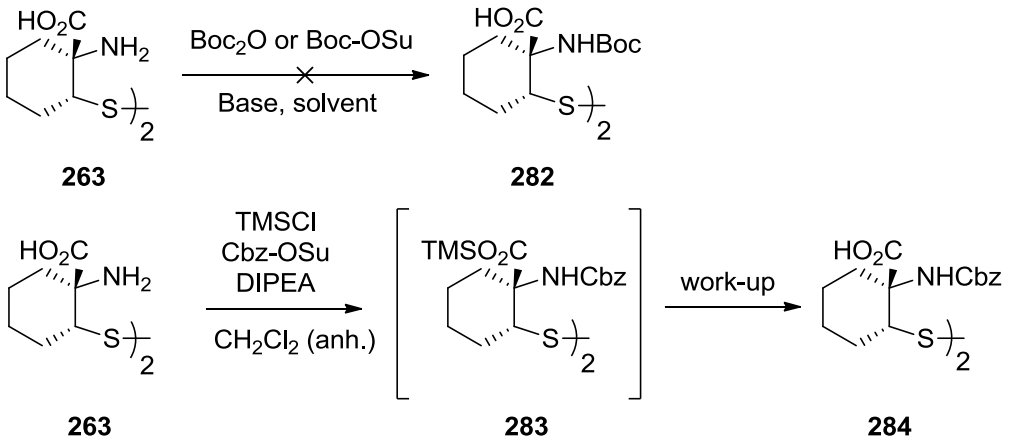
Scheme 88. Retrosynthetic analysis to prepare modified lanthionine

3.5.1. Synthesis of modified glutathione

Based on the retro-synthetic route proposed to obtain the modified glutathione, the first step of the synthesis consisted in the protection of the amine function. In this sense, it was firstly thought to protect the amine moiety as *tert*-butoxy carbonyl group, following the classical methodology, employing *tert*-butoxy carbonyl anhydride (Boc_2O) or Boc-OSu in presence of base (TMAH, NEt_3, $NaHCO_3$) and different solvents (DMF, MeCN, MeCN/H_2O, Dioxane). Unfortunately, all our efforts were unsuccessful (*Scheme 89*).

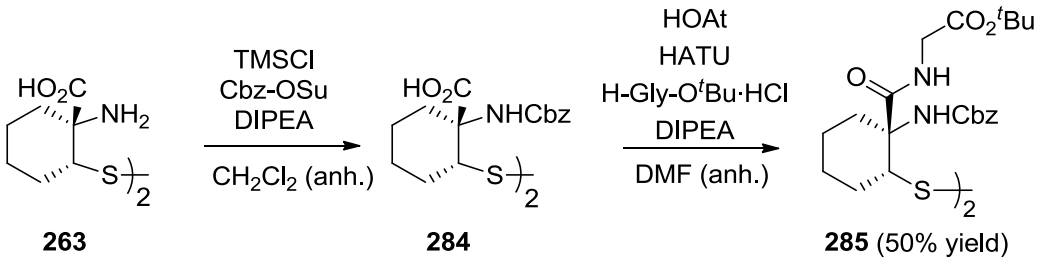
To overcome this problem it was decided to change the protecting group to a less bulky one. Thus, we attempted the Cbz protection employing benzyl chloroformate Cbz-Cl in presence of Na_2CO_3 as it is described in the bibliography.[76]

However, the reaction did not lead to the desire protected amino acid. Then, it was used Cbz-OSu as protecting reagent also in presence of base NEt_3,[77] but the results were unsatisfactory once again. Finally, it was decided to try the amine protection with the protocol which protect temporarily the carboxylic acid moiety as trimethylsiloxy group by the addition of TMSCl.[78] Thus, over a solution of the amino acid **263** in anhydrous methylenechloride, TMSCl (6 eq.) and DIPEA (8 eq.) were added at 0 ºC. After 30 minutes Cbz-OSu (2.2 eq.) was added and the work-up afforded the protected amino acid **284** (*Scheme 89*).



Scheme 89. Protection of the amine function of cystine **263**

The *N*-Cbz protected amino acid **284** was employed in the next reaction without purification. Thus, the coupling reaction between amino acid **284** and H-Gly-O^{t}Bu·HCl was carried out in DMF in presence of the coupling reagents HATU and HOAt and DIPEA as base, leading to the formation of the dipeptide **285** after 3 days in good yield after two reaction steps (*Scheme 90*).



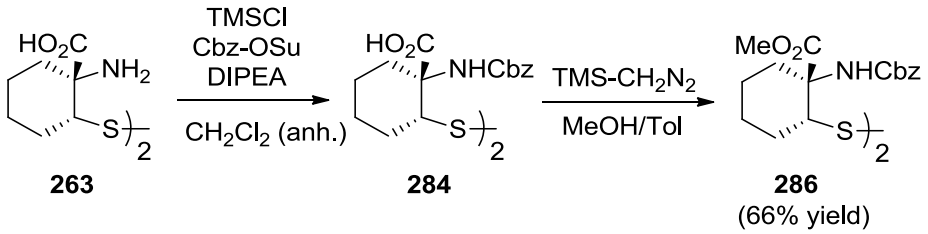
Scheme 90. Synthesis of dipeptide **285**

Next, it was proposed the Cbz cleavage of the dipeptide **285** under hydrogenation conditions using Pd/C or Pt_2O. However, the reactions did not take place due to the sulfur atoms inactivated the catalytic system. Thus, we considered the use of Et_3SiH in presence of $Pd(OAc)_2$[79] but the same problem of inactivation was found. Finally, we also tried a reported procedure for switching the Cbz group

for a trifluoroacetyl group[80] albeit the reaction did not proceeded as we expected. In view of these results, it was decided to focus our efforts on the synthesis of other bioactive compounds.

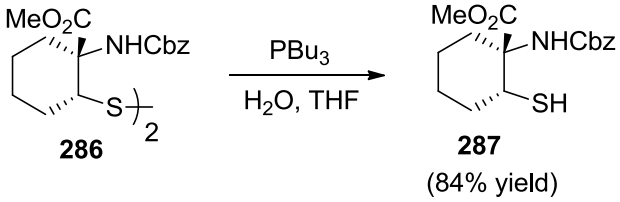
3.5.2. Synthesis of modified lanthionines

The preparation of the modified lanthionine started protecting the amine group of the cystine **263** following the previously optimized conditions. Then, it was carried out the protection of the carboxylic group as methyl ester, employing trimethylsilyldiazomethane (TMS-CH_2N_2) as alkylating reagent, affording the protected amino acid **286** in good yield after two reaction steps (*Scheme 91*).



Scheme 91. Protection of the amine and carboxylic acid functions of cystine **263**

In order to prepare our target modified lanthionines the reduction of the disulfide bond was mandatory. To this end, amino acid dimer **286** was reduced to the corresponding thiol **287** by the treatment with *n*-tributylphosphine in presence of water.[81] The optimization of the reaction conditions was necessary due to the formation of a by-product, the protected 1-aminocyclohexanecarboxylic acid **175**, by a desulfurization process triggered by the phosphine reagent. Formation of this by-product was observed to be favored by the absence of water in the reaction. Finally, it was possible to obtain the thiol **287** in good yield, 84% (*Scheme 92*).



Scheme 92. Disulfide bond reduction of the dimer **286**

Due to the easy oxidation of the thiol **287** to its corresponding disulfide bridge **286**, even detected after column chromatography purification of thiol **287**, it had to be employed quickly in the last reaction step. The formation of the thiol group was easily confirmed by ^{1}H NMR experiment before using it in the next reaction. The multiplicity of the signal corresponding to the CH bonded directly to the sulfur

atom, change from a *dd* to a *dt*, indicating the presence of a new vicinal proton, corresponding to the thiol group (*Figure 42*).

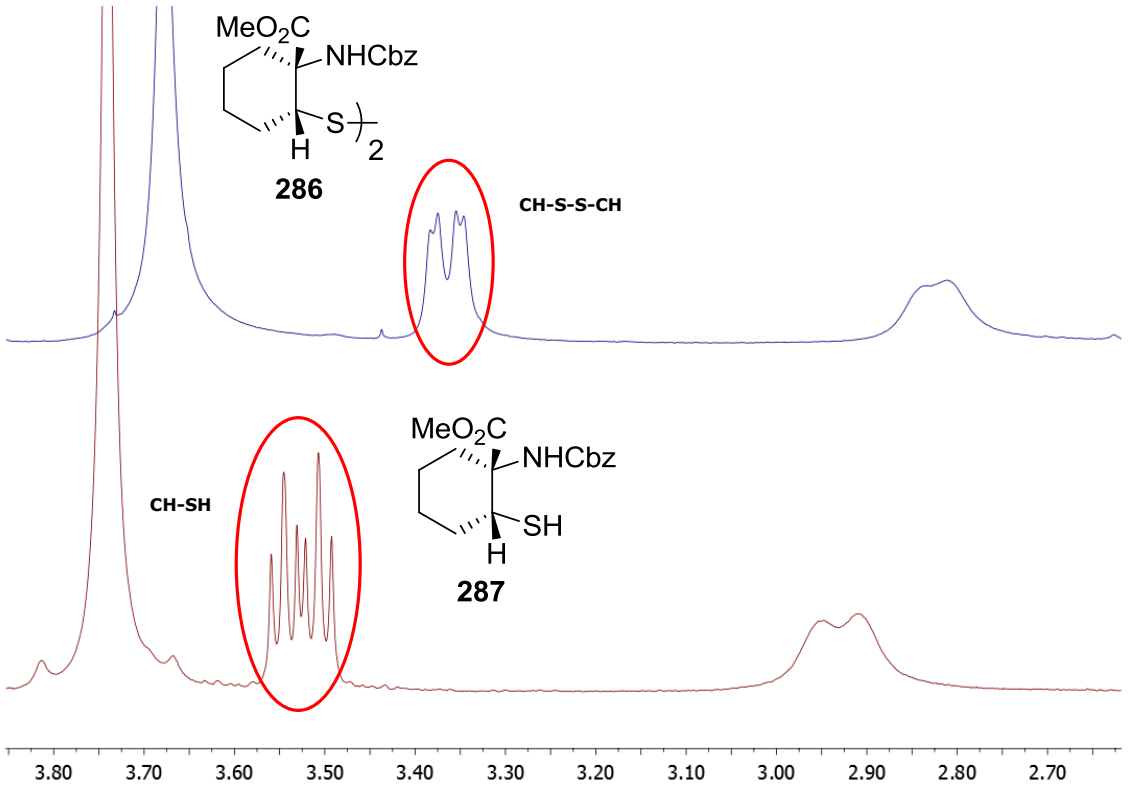
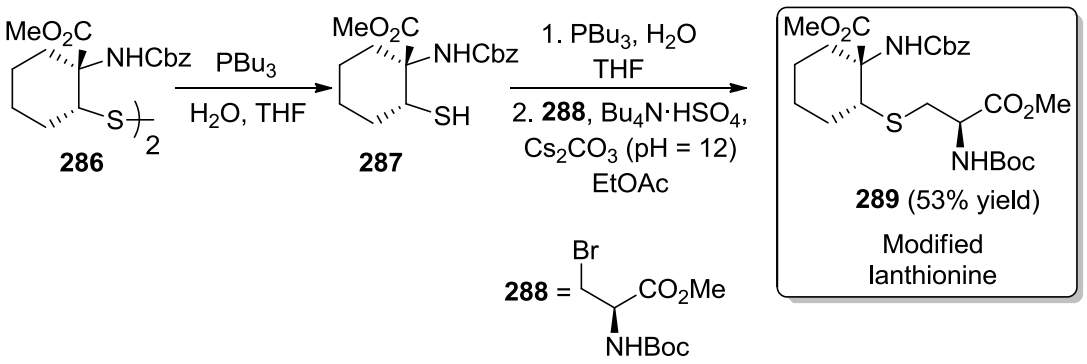


Figure 42. ^{1}H NMR comparison of **286** and **287**

Thus, freshly purified thiol **287** was subjected to react with β-bromoalanine **288**, prepared from *L*-Serine according to the method reported in the bibliography,[82] in presence of an aqueous solution of Cs_2CO_3 (pH≈12) and the phase transfer reagent tetrabutylammonium bisulfate ($BuN_4{\cdot}HSO_4$),[74a] affording the corresponding modified lanthionine **289** in good yield after two reaction steps from **286** (*Scheme 93*).



Scheme 93. Reaction sequence to prepare the modified lanthionine **289**

4. CONCLUSIONS

The Diels-Alder reaction between thiazoline **39a** and cyclopentadiene showed to be unsuccessful. However, **39b** and **39c** showed good reactivity and excellent selectivity with both cyclic and acyclic dienes. Both the reactivity and stereoselectivity observed experimentally were correctly predicted by DFT calculations.

Enantiomerically pure thiazoline **39b** has shown to be a suitable precursor of modified constrained cysteines after further hydrogenation of the cycloadducts, reduction of the sulfoxide moiety and hydrolysis of the resulting bicyclic thiazolidines.

The free modified constrained cysteines were not stable to air and they were purified as the corresponding cystines. The methodology designed improves substantially previous results obtained for similar derivatives and provides enantiomerically pure cystines starting from **39b**.

Finally, it was possible to obtain the conformationally restricted lanthionine **289** in enantiopure form and also a dipeptide **285**, precursor for the synthesis of modified glutathiones.

5. EXPERIMENTAL SECTION

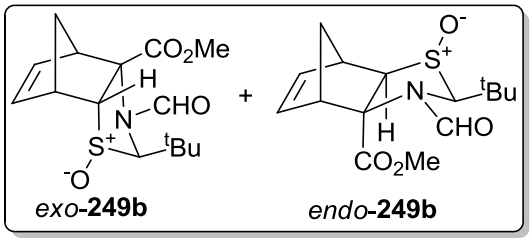
5.1. General

All reagents were used as received from commercial suppliers without further purification. Thin-layer chromatography (TLC) was performed on Macherey-Nagel Polygram®SIL G/UV254 precoated silica gel polyester plates. The products were visualized by exposure to UV light, iodine vapour, submersion in ninhydrin stain, in ethanolic solution of phosphomolybdic acid or on an aqueous solution of sodium permanganate. Column chromatography was performed using 60 M (0.04-0.063 mm) silica gel from Macherey-Nagel. Melting points were determined on a Gallenkamp apparatus. IR spectra were registered on a Nicolet Avatar 360 FTIR spectrophotometer; vmax is given for the main absorption bands. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300, AV-400 instrument at room temperature, unless otherwise indicated, and using the residual solvent signal as the internal standard; chemical shifts (δ) are expressed in parts per million and coupling constant (*J*) in hertz. Optical rotations were measured at room temperature using a JASCO P-1020 polarimeter. High-resolution mass spectra were obtained on a Bruker Microtof-Q spectrometer. All Dienes employed in this chapter were commercially available and has been used without further purification or drying.

5.2. General procedure for the Diels-Alder cycloadittions between thiazolines 39a-c and dienes

In a sealed tube, the diene (6 eq.) was added to thiazoline **39b** or **39c** (1 eq.). The reaction mixture was allowed to stir at 100 ^{o}C and was monitored by TLC (EtOAc/hexane) until the starting material was consumed.

Synthesis of (1*R*,2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *exo*-249b and **(1*R*,2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-249b**



Following the experimental described above, thiazoline **39b** (0.52 g, 2.10 mmol) and cyclopentadiene **248a** (1.03 mL, 12.3 mmol) were heated at 100 °C. The reaction mixture was allowed to stir for 7 hours. Then, the crude reaction was purified by column chromatography (EtOAc/hexane 40/60) to give the mixture of cycloadducts *exo*-**249b** and *endo*-**249b** (0.61 g, 1.97 mmol, 94% yield) as a mixture of adducts in a ratio *exo*/*endo* 89/11. Pure samples of both adducts could be isolated in order to characterized them, *exo*-**249b** as a white solid and *endo*-**249b** as a beige solid.

(1*R*,2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *exo*-249b

M.p.: 78-80 °C

$[\alpha]_D^{23}$: +31° (*c* 1.00; $CHCl_3$)

IR (KBr) ν 1732, 1673, 1477, 1400, 1354, 1316, 1251, 1243, 1178 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.25)] δ 8.44 (s, 1H, C*H*O, rot. maj.), 8.10 (s, 1H, C*H*O, rot. min.), 6.77 (dd, *J* = 5.5, 3.0, 1H, H_6, rot. maj.), 6.64 (dd, *J* = 5.4, 3.0, 1H, H_6, rot. min.), 6.02 (dd, *J* = 5.2, 3.0, 1H, H_5, rot. min.), 5.99 (dd, *J* = 5.6, 3.1, 1H, H_5, rot. maj.), 4.99 (s, 1H, H_2, rot. maj.), 4.69 (d, *J* = 3.8, 1H, H_{7a}, rot. maj.), 4.60 (d, *J* = 3.7, 1H, H_{7a}, rot. min.), 4.33 (s, 1H, H_2, rot. min.), 4.04-4.01 (m, 1H, H_4, rot. min.), 3.84 (s, 3H, OCH_3, rot. maj.), 3.80 (s, 3H, OCH_3, rot. min.), 3.53-3.49 (m, 1H, H_4, rot. maj.), 3.43-3.38 (m, 1H, H_7, rot. maj.), 3.38-3.35 (m, 1H, H_7, rot. min.), 2.15-2.11 (m, 2H, H_8, both rot.), 1.80-1.76 (m, 1H, H_8, rot. maj.), 1.70-1.67 (m, 1H, H_8, rot. min.), 1.01 (s, 9H, C(CH_3)$_3$, rot. min.), 0.95 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.5 (*C*O_2Me, rot. min.), 172.4 (*C*O_2Me, rot. maj.), 163.5 (*C*HO, rot. maj.), 161.6 (*C*HO, rot. min.), 141.3 (C_6, rot. maj.), 139.1

(C_6, rot. min.), 132.1 (C_5, rot. min.), 128.7 (C_5, rot. maj.), 101.4 (C_2, rot. min.), 98.3 (C_2, rot. maj.), 85.3 (C_{3a}, rot. maj.), 84.4 (C_{3a}, rot. min.), 72.0 (C_{7a}, rot. min.), 70.6 (C_{7a}, rot. maj.), 54.7 (C_4, rot. maj.), 54.3 (C_4, rot. min.), 53.8 (O*C*H_3, rot. maj.), 53.4 (O*C*H_3, rot. min.), 50.3 (C_8, rot. maj.), 49.2 (C_8, rot. min.), 45.5 (C_7, both rot.), 36.5 (*C*(CH_3)$_3$, rot. maj.), 35.8 (*C*(CH_3)$_3$, rot. min.), 27.3 (C(*C*H_3)$_3$, rot. maj.), 26.9 (C(*C*H_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{15}H_{21}NO_4SNa$ 334.1083; found 334.1098

(1*R*,2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-249b

M.p.: 152-154 °C

$[\alpha]_D^{23}$: -174° (*c* 0.8; $CHCl_3$)

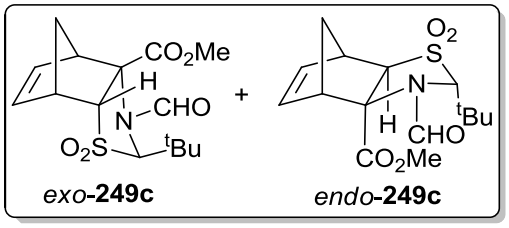
IR (KBr) ν 2994-2964, 1743, 1666, 1402, 1347, 1304, 1248, 1053 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.05)] δ 8.78 (s, 1H, C*H*O, rot. maj.), 8.24 (s, 1H, C*H*O, rot. min.), 6.51 (dd, *J* = 5.6, 3.2, 1H, H_6, rot. maj.), 6.43 (dd, *J* = 5.5, 3.1, 1H, H_6, rot. min.), 6.07 (dd, *J* = 5.6, 3.1, 2H, H_5, both rot.), 5.36 (s, H_2, 1H, rot. maj.), 4.71 (dd, *J* = 2.7, 1.5, 1H, H_4, rot. min.), 4.57 (s, 1H, H_2, rot. min.), 3.96 (dd, *J* = 1.4, 0.6, 1H, H_{7a}, rot. maj.), 3.90 (d, *J* = 1.9, 1H, H_{7a}, rot. min.), 3.76 (s, OC*H*$_3$, 3H, rot. maj.), 3.73 (s, 3H, OC*H*$_3$, rot. min.), 3.47 (dd, *J* = 3.1, 1.5, 1H, H_4, rot. maj.), 3.29-3.25 (m, 1H, H_7, rot. maj.), 3.25-3.23 (m, 1H, H_7, rot. min.), 2.37-2.32 (m, 1H, H_8, rot. maj.), 2.23-2.18 (m, 1H, H_8, rot. min.), 1.84 (ddd, *J* = 9.9, 3.4, 1.7, 1H, H_8, rot. maj.), 1.81-1.77 (m, 1H, H_8, rot. min.), 1.01 (s, 9H, C(C*H*$_3$)$_3$, rot. min.), 0.98 (s, 9H, C(C*H*$_3$)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.3 (*C*O_2Me, rot. maj.), 162.2 (*C*HO, rot. maj.), 141.0 (C_4, rot. maj.), 139.2 (C_6, rot. min.), 137.1 (C_5, rot. min.), 135.5 (C_5, rot. maj.), 102.6 (C_2, rot. min.), 98.2 (C_2, rot. maj.), 83.0 (C_{3a}, rot. maj.), 69.4 (C_{7a}, rot. min.), 67.7 (C_{7a}, rot. maj.), 53.4 (O*C*H_3, rot. maj.), 53.1 (O*C*H_3, rot. min.), 51.2 (C_4, rot. maj.), 47.8 (C_8, rot. min.), 47.1 (C_8, rot. maj.), 46.7 (C_4, rot. maj.), 44.0 (C_7, rot. maj.), 43.9 (C_7, rot. min.), 36.4 (*C*(CH_3)$_3$, rot. maj.), 35.8 (*C*(CH_3)$_3$, rot. min.), 27.5 (C(*C*H_3)$_3$, rot. maj.), 27.2 (C(*C*H_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{15}H_{21}NO_4SNa$ 334.1083; found 334.1096.

Synthesis of (2*R*,3a*R*,4*R*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *exo*-249c and **(2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-249c**



Following the experimental described above, thiazoline **39c** (0.45 g, 1.73 mmol) and cyclopentadiene **248a** (0.85 mL, 10.4 mmol) were allowed to stir at 100 °C for 7 hours. The crude reaction was purified by column chromatography (EtOAc/hexane 20/80) to give the mixture of cycloadducts *exo*-**249c** and *endo*-**249c** (0.53 g, 1.63 mmol, 94% yield) as a mixture of adducts in a ratio 75/25. Analytical samples of both cycloadducts could be separated to identify as *exo* or *endo* isomers.

Exo-**249c**. **^{1}H NMR** ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.26)] δ 8.38 (s, 1H, C*H*O, rot. maj.), 8.16 (s, 1H, C*H*O, rot. min.), 6.73 (dd, *J* = 5.6, 3.0, 1H, H_6, rot. maj.), 6.57 (dd, *J* = 5.8, 2.8, 1H, H_6, rot. min.), 6.10 (dd, *J* = 5.6, 2.8, 1H, H_5, rot. maj.), 6.08 (dd, *J* = 5.5, 3.1, 1H, H_5, rot. min.), 4.95 (s, 1H, H_2, rot. maj.), 4.47 (d, *J* = 3.9, 1H, H_{7a}, rot. maj.), 4.27 (d, *J* = 3.8, 1H, H_{7a}, rot. min.), 4.21 (s, 1H, H_2, rot. min.), 4.07-4.04 (m, 1H, H_4 or H_7, rot. min.), 3.89 (s, 3H, OCH_3, rot. maj.), 3.83 (s, 3H, OCH_3, rot. min.), 3.56-3.50 (m, 2H, H_4 + H_7, rot. maj.), 3.49-3.45 (m, 1H, H_4 or H_7, rot. min.), 2.05-1.99 (m, 2H, H_8, both rot.), 1.87-1.83 (m, 1H, H_8, rot. maj.), 1.77-1.72 (m, 1H, H_8, rot. min.), 1.16 (s, 9H, C(CH_3)$_3$, rot. min.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.8 (*C*O_2Me, rot. maj.), 162.9 (*C*HO, rot. maj.), 140.8 (C_6, rot. maj.), 129.5 (C_5, rot. maj.), 85.7 (C_2, rot. maj.), 77.4 (C_{3a}, rot. maj.), 68.0 (C_{7a}, rot. maj.), 54.0 (C_4, rot. maj.), 53.7 (O*C*H_3, rot. maj.), 50.0 (C_8, rot. maj.), 44.7 (C_7, rot. maj.), 37.6 (*C*(CH_3)$_3$, rot. maj.), 26.9 (C(*C*H_3)$_3$, rot. maj.)

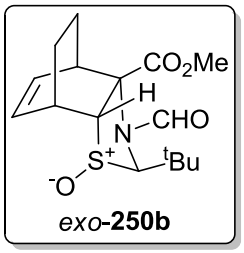
Endo-**249c**. **^{1}H NMR** ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.06)] δ 8.78 (s, 1H, C*H*O, rot. maj.), 8.21 (s, 1H, C*H*O, rot. min.), 6.46 (dd, *J* = 5.6, 3.2, 1H, H_4, rot. maj.), 6.38 (dd, *J* = 5.5, 3.1, 1H, H_6, rot. min.), 6.05 (dd, *J* = 5.6, 3.3, 2H, H_5, both rot.), 5.32 (s, H_2, 1H, rot. maj.), 4.81-4.78 (m, 1H, H_4, rot. min.),

4.48 (s, 1H, H_2, rot. min.), 3.79 (s, 3H, OCH_3, rot. maj.), 3.79* overlapped (m, 1H, H_{7a}, rot. maj.), 3.77 (s, OCH_3, 3H, rot. min.), 3.77* overlapped (m, 1H, H_6, rot. min.), 3.67 (dd, *J* = 3.1, 1.5, 1H, H_4, rot. maj.), 3.53-3.50 (m, 1H, H_7, rot. maj.), 3.49-3.47 (m, 1H, H_7, rot. min.), 2.31 (d, *J* = 10.2, 1H, H_8, rot. maj.), 2.22-2.17 (m, 1H, H_8, rot. min.), 1.88 (ddd, *J* = 10.2, 3.1, 1.5, 1H, H_8, rot. maj.), 1.85-1.81 (m, 1H, H_8, rot. min.), 1.13 (s, 9H, C(CH_3)$_3$, rot. min.), 1.09 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.7 (*C*O_2Me), 161.9 (*C*HO), 140.2 (C_4), 135.3 (C_5), 85.4 (C_2), 77.4 (C_{3a}), 67.1 (C_{7a}), 53.6 (O*C*H_3), 51.8 (C_4), 46.1 (C_8), 44.7 (C_7), 37.5 (*C*(CH_3)$_3$), 27.0 (C(*C*H_3)$_3$

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{15}H_{21}NO_5SNa$ 350.1033; found 350.1037

Synthesis of (1*R*,2*R*,3a*R*,4*R*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate *exo*-250b



exo-**250b**

Following the experimental described above, thiazoline **39b** (0.59 g, 2.42 mmol) and 1,3-cyclohexadiene **248b** (1.37 mL, 14.5 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 36 hours. Then, the crude reaction was purified by column chromatography (EtOAc/hexane 50/50) to give the cycloadduct *exo*-**250b** (0.77 g, 2.37 mmol, 98% yield) as a white solid.

M.p.: 194-196 ºC

$[\alpha]_D^{23}$: +32º (*c* 1.0; $CHCl_3$)

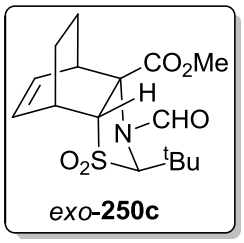
IR (neat) v 1730, 1660, 1351, 1306, 1269, 1229, 1199, 1031 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.06)] δ 8.75 (s, 1H, C*H*O, rot. maj.), 8.18 (s, 1H, C*H*O, rot. min.), 6.48-6.41 (m, 1H, H_6, rot. maj.), 6.39-6.34 (m, 1H, H_6, rot. min.), 6.14-6.10 (m, 1H, H_5, rot. min.), 6.09-6.03 (s, 1H, H_5, rot. maj.), 4.94 (s, 1H, H_2, rot. maj.), 4.53-4.49 (m, 1H, H_4, rot. min.), 4.26 (d, *J* = 2.6, 1H, H_{7a}, rot. maj.), 4.23 (d, *J* = 2.3, 1H, H_{7a}, rot. min.), 4.14 (s, 1H, H_2, rot. min.), 3.82 (s, 3H, OCH_3, rot. maj.), 3.80 (s, 3H, OCH_3, rot. min.), 3.47-3.41 (m, 1H, H_4, rot. maj.), 3.18-3.13 (m, 1H, H_7, rot. maj.), 3.12-3.08 (m, 1H, H_7, rot. min.), 1.83-1.70 (m, 3H, H_9, both rot.), 1.55-1.44 (m, 2H, H_8, rot. maj. + H_9, rot. maj.), 1.37-1.24 (m, 3H, H_8, both rot.), 0.98 (s, 9H, C(CH_3)$_3$, rot. min.), 0.94 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.1 (*C*O_2Me, rot. maj.), 162.8 (*C*HO, rot. maj.), 135.6 (C_6, rot. maj.), 133.7 (C_6, rot. min.), 128.9 (C_5, rot. min.), 125.5 (C_5, rot. maj.), 97.3 (C_2, rot. min.), 92.7 (C_2, rot. maj.), 79.5 (C_{3a}, rot. maj.), 68.7 (C_{7a}, rot. min.), 67.5 (C_{7a}, rot. maj.), 53.7 (O*C*H_3, rot. maj.), 53.4 (O*C*H_3, rot. min.), 38.4 (C_4, rot. maj.), 36.0 (*C*(CH_3)$_3$, rot. maj.), 35.6 (*C*(CH_3)$_3$, rot. min.), 35.3 (C_4, rot. maj.), 30.5 (C_7, rot. min.), 30.3 (C_7, rot. maj.), 27.6 (C(*C*H_3)$_3$, rot. maj.), 27.3 (C(*C*H_3)$_3$, rot. min.), 23.6 (C_9, rot. min.), 23.1 (C_9, rot. maj.), 21.0 (C_8, rot. maj.), 20.2 (C_8, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{16}H_{23}NO_4SNa$ 348.1240; found 348.1233

Synthesis of (2*R*,3a*R*,4*R*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3,3a,4,7,7a-hexahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate *exo*-250c



exo-**250c**

Following the experimental described above, thiazoline **39c** (0.38 g, 1.47 mmol) and 1,3-cyclohexadiene **248b** (0.87 mL, 8.83 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 24 hours. Then, the reaction crude was purified by column chromatography (EtOAc/hexane 30/70) to give the cycoadduct *exo*-**250c** (0.45 g, 1.34 mmol, 91% yield) as a white solid.

M.p.: 185-187 ºC

$[\alpha]_D^{23}$: -24º (*c* 1.0; $CHCl_3$)

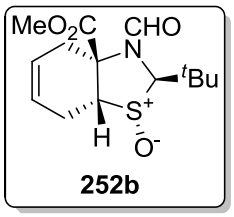
IR (KBr) v 1742, 1677, 1482, 1437, 1403, 1348, 1316, 1200, 1069 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.04)] δ 8.71 (s, 1H, C*H*O, rot. maj.), 8.13 (s, 1H, C*H*O, rot. min.) 6.48 (t, *J* = 7.3, 1H, H_6, rot. maj.), 6.37 (t, *J* = 7.0, 1H, H_6, rot. min.), 6.12 (t, *J* = 7.3, 2H, H_5, both rot.), 4.84 (s, H_2, 1H, rot. maj.), 4.50-4.45 (m, 1H, H_4, rot. min.), 4.10 (d, *J* = 2.5, 1H, H_{7a}, rot. maj.), 4.00 (s, 1H, H_2, rot. min.) 3.87 (s, 3H, OCH_3, rot. maj.), 3.84 (s, 3H, OCH_3, rot. min.), 3.49-3.44 (m, 1H, H_4, rot. maj.), 3.32-3.26 (m, 2H, H_7, both rot.), 1.70-1.57 (m, 1H, H_9), 1.53-1.40 (m, 2H, H_8, rot. maj. + H_9, rot. maj.), 1.39-1.30 (m, 1H, H_8), 1.09 (s, 9H, C(CH_3)$_3$, rot. min.), 1.05 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.5 (*C*O_2Me), 162.2 (*C*HO), 134.0 (C_6), 125.2 (C_5), 78.3 (C_2), 72.1 (C_{3a}), 64.6 (C_{7a}), 53.9 (O*C*H_3), 37.2 (C_4), 36.9 (*C*(CH_3)$_3$), 29.5 (C_7), 27.0 (C(*C*H_3)$_3$), 22.2 (C_9), 21.0 (C_8)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{16}H_{23}NO_5SNa$ 364.1189; found 364.1195

Synthesis of (1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate 252b



252b

Following the experimental described above, thiazoline **39b** (1.5 g, 6.1 mmol), and a solution of 1,3-butadiene **251a** (20% w/w) in toluene (9.9 g, 36.7 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 5 days. Then, 1,3-butadiene **251a** (20% w/w) in toluene (4.5 g, 18.3 mmol) were added and allow to stir for 5 more days. Finally, the solvent was evaporated off and the brown solid obtained was purified by column chromatography (EtOAc/hexane 50/50) to give the cycloadduct **252b** (1.72 g, 5.7 mmol, 94% yield) as a beige solid.

M.p.: 98-101 ºC

$[\alpha]_D^{23}$: +7º (*c* 1.0; $CHCl_3$)

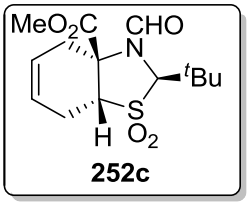
IR (KBr) v 1740, 1661, 1344, 1304, 1260, 1238, 1220, 1163, 1066 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/1)] δ 8.82 (s, 1H, C*H*O, rot. 1), 8.28 (s, 1H, C*H*O, rot. 2), 5.92-5.83 (m, 2H, H_3 or H_4, both rot.), 5.78-5.40 (m, 1H, H_3 or H_4), 5.69-5.61 (m, 1H, H_3 or H_4), 5.27 (s, 1H, H_8, rot. 1), 4.62 (s, 1H, H_8, rot. 2), 3.87-3.83 (m, 1H, H_6, rot. 1), 3.82 (s, 3H, OCH_3, rot. 1), 3.78 (s, 3H, OCH_3, rot. 2), 3.60 (dd, *J* = 17.6, 5.6 Hz, 1H, CH_2), 3.31 (d, *J* = 9.1 Hz, H_6, 1H, rot. 2), 3.17 (dd, *J* = 14.9, 6.8 Hz, 1H, CH_2), 2.96-2.59 (m, 5H, CH_2, both rot.), 2.56-2.46 (m, 1H, CH_2), 1.17 (s, 9H, C(CH_3)$_3$, rot. 1), 1.04 (s, 9H, C(CH_3)$_3$, rot. 2)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.25 (*C*O_2Me, rot. 1), 171.21 (*C*O_2Me, rot. 2), 164.5 (*C*HO, rot. 1), 163.0 (*C*HO, rot. 2), 126.4 (C_3 or C_4), 125.9 (C_3 or C_4), 122.9 (C_3 or C_4), 120.2 (C_3 or C_4), 92.5 (C_8, rot. 1), 90.2 (C_8, rot. 2), 70.2 (C_1, rot. 1), 69.2 (C_1, rot. 2), 57.4 (C_6, rot. 1), 57.2 (C_6, rot. 2), 53.9 (O*C*H_3, rot. 1), 53.4 (O*C*H_3, rot. 2), 36.4 (*C*(CH_3)$_3$, rot. 1), 36.2 (*C*H_2), 35.9 (*C*(CH_3)$_3$, rot. 2), 31.6 (*C*H_2), 28.3 (C(*C*H_3)$_3$, rot. 1), 27.9 (C(*C*H_3)$_3$, rot. 2), 21.6 (*C*H_2), 21.4 (*C*H_2)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{14}H_{21}NO_4SNa$ 322.1083; found 322.1081

Synthesis of (1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate 252c



252c

Following the procedure described previously, thiazoline **39c** (0.12 g, 0.44 mmol), and a solution of 1,3-butadiene **251a** (20% w/w) in toluene (0.8 g, 2.8 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 5 days. Then, the solvent was evaporated off and the brown solid obtained was purified by column chromatography (EtOAc/hexane 40/60) to give the cycloadduct **252c** (0.136g, 0.43 mmol, yield 98%) as a white solid.

M.p.: 139-141 ºC

$[\alpha]_D^{23}$: +87º (*c* 1.0; $CHCl_3$)

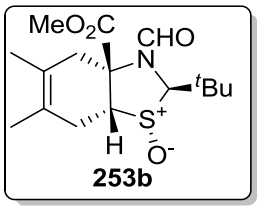
IR (KBr) v 1743, 1679, 1670, 1464, 1325, 1256, 1240, 1131 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.64)] δ 8.78 (s, 1H, C*H*O, rot. maj.), 8.29 (s, 1H, C*H*O, rot. min.), 5.93-5.86 (m, 1H, H_4, rot. maj.), 5.85-5.78 (m, 1H, H_3, rot. min.), 5.75-5.61 (m, 2H, H_3, rot. maj + H_4, rot. min.), 5.00 (s, 1H, H_8, rot. maj.), 4.34 (s, 1H, H_8, rot. min.), 4.06 (dd, *J* = 9.2, 3.0 Hz, 1H, H_6, rot. maj.), 3.85 (s, 3H, OCH_3, rot. maj.), 3.79 (s, 3H, OCH_3, rot. min.), 3.62-3.53 (m, 2H, H_6, rot. min. + H_2, rot. min.), 3.13 (dd, *J* = 15.4, 7.1, 1H, H_2, rot. maj.), 2.86-2.60 (m, 4H, H_2, rot. maj. + H_5, both rot.), 2.56-2.43 (m, 1H, H_5, rot. min.), 2.37-2.26 (m, 1H, H_2, rot. min.), 1.27 (s, 9H, C(CH_3)$_3$, rot. min.), 1.13 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.7 (*C*O_2Me, rot. maj.), 170.4 (*C*O_2Me, rot. min.), 164.0 (*C*HO, rot. maj.), 162.6 (*C*HO, rot. min.), 125.3 (C_4, rot. min.), 125.1 (C_4, rot. maj.), 122.0 (C_3, rot. maj.), 119.5 (C_3, rot. min.), 79.6 (C_8, rot. min.), 76.6 (C_8, rot. maj.), 63.3 (C_1, rot. maj.), 61.6 (C_1, rot. min.), 56.5 (C_6, rot. min.), 54.7 (C_6, rot. maj.), 54.1 (O*C*H_3, rot. maj.), 53.6 (O*C*H_3, rot. min.), 37.0 (*C*(CH_3)$_3$, rot. maj.), 36.7 (*C*(CH_3)$_3$, rot. min.), 34.1 (C_2, rot. maj.), 30.1 (C_2, rot. min.), 27.1 (C(*C*H_3)$_3$, rot. maj.), 26.5 (C(*C*H_3)$_3$, rot. min.), 18.2 (C_5, rot. maj.), 17.7 (C_5, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{14}H_{21}NO_5SNa$ 338.1033; found 338.1037

Synthesis of (1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7-oxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate 253b



253b

Following the experimental described above, thiazoline **39b** (1.5 g, 6.1 mmol), and 2,3-dimethyl-1,3-butadiene **251b** (4.15 mL, 36.6 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 3 days. Then, the crude reaction was purified by column chromatography (EtOAc/hexane 40/60) to give the cycloadduct **253b** (1.91g, 5.8 mmol, 95% yield) as a white solid.

M.p.: 132-134 ºC

$[\alpha]_D^{23}$: +19º (*c* 1.1; $CHCl_3$)

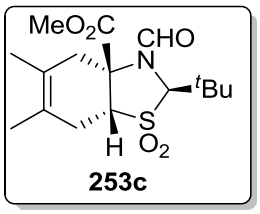
IR (KBr) v 1743, 1672, 1436, 1426, 1370, 1358, 1307, 1161, 1072 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.54)] δ 8.81 (s, 1H, C*H*O, rot. maj.), 8.26 (s, 1H, C*H*O, rot. min.), 5.27 (s, 1H, H_8, rot. maj.), 4.59 (s, 1H, H_8, rot. min.), 3.92 (ddd, 1H, *J* = 9.7, 5.3, 1.2, H_6, rot. maj.), 3.78 (s, 3H, OCH_3, rot. maj.), 3.74 (s, 3H, OCH_3, rot. min.), 3.40-3.30 (m, 2H, H_6, rot. min. + H_2, rot. min.), 2.92 (d, *J* = 14.1, 1H, H_2, rot. maj.), 2.86-2.78 (m, 2H, H_2, rot. maj. + H_5, rot. maj.), 2.71 (d, *J* = 19.5, 1H, H_5, rot. min.), 2.56-2.42 (m, 3H, H_2, rot. min. + H_5, both rot.), 1.70 (s, 3H, C$H_{3(4)}$, rot. maj.), 1.67 (s, 3H, C$H_{3(3)}$, rot. min.), 1.66 (s, 3H, C$H_{3(4)}$, rot. min.), 1.64 (s, 3H, C$H_{3(3)}$, rot. maj.), 1.15 (s, 9H, C(CH_3)$_3$, rot. min.), 1.01 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.5 (*C*O_2Me, rot. min.), 171.2 (*C*O_2Me, rot. maj.), 164.3 (*C*HO, rot. maj.), 163.1 (*C*HO, rot. min.), 126.0 (C_3 or C_4, rot. maj.), 125.8 (C_3 or C_4, rot. min.), 122.3 (C_3 or C_4, rot. maj.), 119.2 (C_3 or C_4, rot. min.), 92.5 (C_8, rot. min.), 90.7 (C_8, rot. maj.), 71.8 (C_1, rot. maj.), 70.5 (C_1, rot. min.), 58.6 (C_6, rot. maj.), 58.2 (C_6, rot. min.), 53.7 (O*C*H_3, rot. maj.), 53.3 (O*C*H_3, rot. min.), 42.4 (C_2, rot. maj.), 37.0 (C_2, rot. min.), 36.3 (*C*(CH_3)$_3$, rot. maj.), 35.9 (*C*(CH_3)$_3$, rot. min.), 28.2 (C(*C*H_3)$_3$, rot. maj.), 27.9 (C(*C*H_3)$_3$, rot. min.), 27.2 (C_5, rot. min.), 26.9 (C_5, rot. maj.), 19.4 (*C*$H_{3(3)}$, rot. min.), 19.3 (*C*$H_{3(3)}$, rot. maj.), 18.9 (*C*$H_{3(4)}$, rot. maj.), 18.6 (*C*$H_{3(4)}$, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{16}H_{25}NO_4SNa$ 350.1397; found 350.13837

Synthesis of (1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate 253c



253c

Following the experimental described above, thiazoline **39c** (0.33 g, 1.25 mmol), and 2,3-dimethyl-1,3-butadiene **251b** (0.85 mL, 7.50 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 12 hours. Then, the crude reaction was purified by column chromatography (EtOAc/hexane 30/70) to give the cycloadduct **253c** (0.42 g, 1.22 mmol, 98% yield) as a white solid.

M.p.: 136-138 ºC

$[\alpha]_D^{23}$: -87º (*c* 1.00; $CHCl_3$)

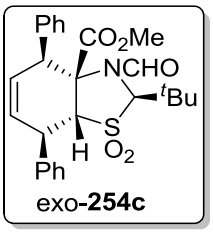
IR (KBr) v 1739, 1672, 1461, 1377, 1350, 1330, 1288, 1183, 1105 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.38)] δ 8.80 (s, 1H, C*H*O, rot. maj.), 8.29 (s, 1H, C*H*O, rot. min.), 5.02 (s, 1H, H_8, rot. maj.), 4.31 (s, 1H, H_8, rot. min.), 4.11 (ddd, 1H, *J* = 9.5, 4.7, 1.5, H_6, rot. maj.), 3.83 (s, 3H, OCH_3, rot. maj.), 3.78 (s, 3H, OCH_3, rot. min.), 3.59 (d, 1H, *J* = 8.8, H_6, rot. min.), 3.36 (d, 1H, *J* = 17.1, H_2, rot. min.), 2.90 (d, 1H, *J* = 14.9, H_2, rot. maj.), 2.79-2.70 (m, 2H, H_2, rot. maj.+ H_5, rot. maj.), 2.65 (d, 1H, *J* = 19.5, H_5, rot. min.), 2.47 (dd, 1H, *J* = 17.5, 10.3, H_5, rot. maj.), 2.42-2.35 (m, 1H, H_5, rot. min.), 2.31 (d, 1H, *J* = 17.2, H_2, rot. min.), 1.73 (s, 3H, C$H_{3(4)}$, rot. maj.), 1.70-1.65 (m, 9H, C$H_{3(4)}$ rot. min. + C$H_{3(4)}$ both rot.), 1.27 (s, 9H, C(CH_3)$_3$, rot. min.), 1.12 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 170.7 (*C*O_2Me, rot. maj.), 170.6 (*C*O_2Me, rot. min.), 163.7 (*C*HO, rot. maj.), 162.7 (*C*HO, rot. min.), 125.5 (C_3 or C_4, rot. maj.), 124.7 (C_3 or C_4, rot. min.), 121.9 (C_3 or C_4, rot. maj.), 118.7 (C_3 or C_4, rot. min.), 79.6 (C_8, rot. min.), 77.0 (C_8, rot. maj.), 65.1 (C_1, rot. maj.), 62.7 (C_8, rot. min.), 57.5 (C_6, rot. min.), 56.0 (C_6, rot. maj.), 54.0 (O*C*H_3, rot. maj.), 53.5 (O*C*H_3, rot. min.), 40.2 (C_2, rot. maj.), 36.8 (*C*(CH_3)$_3$, rot. maj.), 36.6 (*C*(CH_3)$_3$, rot. min.), 35.5 (C_2, rot. min.), 27.0 (C(*C*H_3)$_3$, rot. maj.), 26.4 (C(*C*H_3)$_3$, rot. min.), 24.1 (C_5, rot. maj.), 23.5 (C_5, rot. min.), 19.4 (*C*$H_{3(3)}$, rot. maj.), 19.2 (*C*$H_{3(3)}$, rot. min.), 18.7 (*C*$H_{3(4)}$, rot. maj.), 18.3 (*C*$H_{3(4)}$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{16}H_{25}NO_5SNa$ 366.1346; found 366.1350

Synthesis of (1*R*,2*S*,5*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-2,5-diphenyl-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate exo-254c



Following the experimental described above, thiazoline **39c** (0.20 g, 0.75 mmol) and 1,4-diphenyl-1,3-butadiene **251c** (0.46 g, 2.24 mmol), were dissolved in toluene (1 mL). The reaction mixture was allowed to stir at 120 ºC for 21 days. Then, the crude reaction obtained was purified by column chromatography (EtOAc/hexane 30/70) to give the cycloadduct *exo*-**254c** (0.16 g, 0.34 mmol, 45% yield) as an orange oil.

$[\alpha]_D^{21}$: -63º (*c* 0.4; $CHCl_3$)

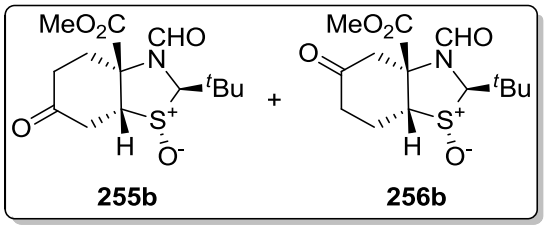
IR (neat) ν 1742, 1682, 1494, 1485, 1454, 1370, 1243, 1179, 1083 cm^{-1}

^{1}H NMR (CD_3CN, 400MHz) δ 8.06 (s, 1H, C*H*O), 7.50-7.38 (m, 7H, H_{Ar}), 7.37-7.32 (m, 1H, H_{Ar}), 7.21-7.17 (m, 2H, H_{Ar}), 6.17 (dt, *J* = 10.0, 2.9, 1H, H_4), 5.84 (dt, *J* = 10.0, 2.9, 1H, H_3), 5.21 (s, 1H, H_8), 4.29-4.25 (m, 1H, H_5), 4.10 (dd, *J* = 5.7, 2.8, 1H, H_2), 3.99 (d, *J* = 3.6, 1H, H_6), 3.60 (s, 1H, O*C*H_3), 1.01 (s, 9H, C(C*H*$_3$)$_3$)

^{13}C NMR (CD_3CN, 100MHz) δ 170.6 (*C*O_2Me), 165.1 (*C*HO), 143.6 (C_{qPh}), 141.4 (C_{qPh}), 131.2 (C_{Ar}), 130.6 (C_3), 130.1 (C_{Ar}), 129.8 (C_{Ar}), 129.5 (C_{Ar}), 129.2 (C_{Ar}), 128.9 (C_4), 128.4 (C_{Ar}), 75.9 (C_8), 68.3 (C_1), 65.5 (C_6), 53.9 (O*C*H_3), 51.1 (C_2), 38.2 (*C*(CH_3)$_3$), 36.6 (C_5), 27.5 (C(*C*H_3)$_3$)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{26}H_{29}NO_5S$ 468.1839; found 468.1856

Synthesis of (1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 255b and **(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-3-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 256b**



Following the procedure described previously, thiazoline **39b** (0.97 g, 3.95 mmol), and 2-trimethylsiloxy-1,3-butadiene **251d** (4.18 mL, 23.7 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 3 days. Then, the reaction crude was dissolved in THF (30 mL) and HCl 1 N (10 mL) was added. This mixture was allowed to stir at room temperature for 1 day. After this time, the solvent was evaporated off and methylene chloride (30 mL) was added. The phases were separated and the aqueous phase was extracted three times with 10 mL of methylene chloride. Finally, the combined organic phases were dried under anhydrous $MgSO_4$, filtered off and evaporated under reduced pressure. The obtained residue was purified by column chromatography (EtOAc/hexane 50/50) to give the cycloadducts **255b** and **256b** as a mixture of regioisomers (1.18 g, 3.75 mmol, yield 95%, in two reaction steps) in a ratio 66/34. Both regioisomers could be separated for their correct characterization, **255b** as a white solid and **256b** as a pale brown solid.

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 255b

M.p.: 125-127 ºC

$[\alpha]_D^{23}$: -51º (*c* 1.0; $CHCl_3$)

IR (KBr) v 1743, 1726, 1670, 1371, 1342, 1325, 1245, 1071, 1045 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.28)] δ 8.81 (s, 1H, C*H*O, rot. maj.), 8.29 (s, 1H, C*H*O, rot. min.), 5.41 (s, 1H, H_8, rot. maj.), 4.67 (s, 1H, H_8, rot. min.), 4.18 (t, *J* = 7.3, 1H, H_6, rot. maj.), 3.87 (s, 3H, OCH_3, rot. maj.), 3.85 (s, 3H, OCH_3, rot. min.), 3.76 (ddd, 1H, *J* = 7.6, 3.2, 1.0, H_6, rot. min.), 3.18-3.13* overlapped (m, 1H, H_2, rot. min.), 3.14 (dd, *J* = 16.2, 7.2, 1H, H_5, rot. maj.), 3.01 (ddd, *J* = 16.8, 3.1, 1.2, 1H, H_5, rot. min.), 2.88-2.78 (m, 3H, H_5, both rot. + H_2, rot. min.), 2.82 (dd, *J* = 16.1, 7.6, 1H, H_5, rot. maj.), 2.75-2.53 (m, 4H, H_2, rot. maj. + H_3, both rot.), 2.48 (dtd, *J* = 16.6, 5.2, 1.0, 1H, H_3, rot.

min.), 2.26-2.13 (m, 1H, H_3, rot. maj.), 1.12 (s, 9H, C(CH_3)$_3$, rot. min.), 1.01 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 205.4 (C_4, rot. maj.), 205.3 (C_4, rot. min.), 172.0 (CO_2Me, rot. maj.), 171.2 (CO_2Me, rot. min.), 163.1 (CHO, rot. maj.), 162.8 (CHO, rot. min.), 93.4 (C_8, rot. min.), 89.8 (C_8, rot. maj.), 70.3 (C_1, rot. min.), 70.2 (C_1, rot. maj.), 61.9 (C_6, rot. min.), 60.9 (C_6, rot. maj.), 54.2 (OCH_3, rot. maj.), 53.6 (OCH_3, rot. min.), 36.3 (C_3, rot. min.), 36.2 ($C(CH_3)_3$, rot. maj.), 35.9 ($C(CH_3)_3$, rot. min.), 35.8 (C_5, rot. min.), 35.6 (C_5, rot. maj.), 33.7 (C_3, rot. maj.), 32.2 (C_2, rot. maj.), 28.9 (C_2, rot. min.), 28.0 (C(CH_3)$_3$, rot. maj.), 27.7 (C(CH_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{14}H_{21}NO_5SNa$ 338.1033; found 338.1049

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-3-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 256b

M.p.: 208-210 °C

$[\alpha]_D^{23}$: +76° (*c* 1.0; $CHCl_3$)

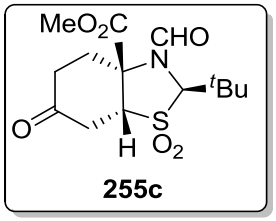
IR (KBr) ν 1731, 1712, 1678, 1350, 1309, 1078, 1038 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.36)] δ 8.61 (s, 1H, CHO, rot. min.), 8.25 (s, 1H, CHO, rot. maj.), 5.38 (s, 1H, H_8, rot. min.), 4.73 (s, 1H, H_8, rot. maj.), 3.87-3.82*overlapped (m, 2H, H_2, rot. maj. + H_6, rot. min.), 3.85 (s, 3H, OCH_3, rot. min.), 3.81 (s, 3H, OCH_3, rot. maj.), 3.36-3.28 (m, 2H, H_6, rot. maj. + H_2, rot. min.), 3.22 (d, 1H, *J* = 14.5, H_2, rot. min.), 2.99 (d, 1H, *J* = 15.3, H_2, rot. maj.), 2.93-2.72 (m, 4H, H_4, both rot. + H_5, both rot.), 2.55-2.48 (m, 1H, H_4, rot. min.), 2.47-2.28 (m, 3H, H_4, rot. maj. + H_5, both rot.), 1.19 (s, 9H, C(CH_3)$_3$, rot. maj.), 1.06 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 204.6 (C_3, rot. maj.), 204.0 (C_3, rot. min.), 171.3 (CO_2Me, rot. min.), 170.7 (CO_2Me, rot. maj.), 163.0 (CHO, rot. min.), 162.1 (CHO, rot. maj.), 94.1 (C_8, rot. maj.), 91.4 (C_8, rot. min.), 73.1 (C_1, rot. maj.), 71.6 (C_1, rot. min.), 58.9 (C_6, rot. min.), 57.7 (C_6, rot. maj.), 54.3 (OCH_3, rot. min.), 53.7 (OCH_3, rot, maj.), 50.8 (C_2, rot. min.), 45.8 (C_2, rot. maj.), 36.5 ($C(CH_3)_3$, rot. min.), 35.98 (C_4, rot. maj.), 35.97 ($C(CH_3)_3$, rot. maj.), 35.4 (C_4, rot. min.), 28.2 (C(CH_3)$_3$, rot. min.), 27.8 (C(CH_3)$_3$, rot. maj.), 20.0 (C_5, rot. maj.), 19.3 (C_5, rot. min.)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{14}H_{21}NO_5SNa$ 338.1033; found 338.1055

Synthesis of (1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 255c



255c

Following the procedure described previously, thiazoline **39c** (0.55 g, 2.05 mmol), and 2-trimethylsiloxy-1,3-butadiene **251d** (2.17 mL, 12.3 mmol) were heated at 100 ºC. The reaction mixture was allowed to stir for 1 day. Then, the reaction crude was dissolved in THF (20 mL) and HCl 1 N (10 mL) was added. This mixture was allowed to stir at room temperature for 1 day. After this time, the solvent was evaporated off and methylene chloride (30 mL) was added. The phases were separated and the aqueous phase was extracted three times with 10 mL of methylene chloride. Finally, the combined organic phases were dried under anhydrous $MgSO_4$, filtered off and evaporated under reduced pressure. The obtained residue was purified by column chromatography (EtOAc/hexane 50/50) to give the cycloadduct **255c** (0.46 g, 1.39 mmol, yield 68%, in two reaction steps) as a pale brown solid.

M.p.: 164-166 ºC

$[\alpha]_D^{22}$: -143º (*c* 1.0; $CHCl_3$)

IR (KBr) ν 1742, 1681, 1328, 1312, 1291, 1281, 1245, 1215, 1198, 1176, 1145, 1119 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.19)] δ 8.75 (s, 1H, C*H*O, rot. maj.), 8.29 (s, 1H, C*H*O, rot. min.), 5.16 (s, 1H, H_8, rot. maj.), 4.40 (s, 1H, H_8, rot. min.), 4.18 (t, *J* = 7.1, H_6, 1H, rot. maj.), 3.89 (s, 3H, OCH_3, rot. maj.), 3.88-3.86 (m, 1H, H_6, rot. min.), 3.85 (s, 1H, OCH_3, rot. min.), 3.18-3.12 (m, 1H, H_2, rot. min.), 3.08 (dd, *J* = 16.6, 6.3, 1H, H_5, rot. maj.), 2.96 (dd, *J* = 17.1, 1.6, 1H, H_5, rot. min.), 2.82 (dd, *J* = 16.6, 7.5, 1H, H_5, rot. maj.), 2.80-2.77* overlapped (m, 1H, H_5, rot. min.), 2.76-2.66 (m, 3H, H_3, rot. min. + H_2, both rot.), 2.62-2.51 (m, 2H, H_2, rot. maj. + H_3, rot. maj.), 2.48-2.41 (m, 1H, H_3, rot. min.), 2.29-2.17 (m, 1H, H_3, rot. maj.), 1.20 (s, 9H, C(CH_3)$_3$, rot. min.), 1.09 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 203.7 (C_4, rot. min.), 203.1 (C_4, rot. maj.), 171.4 (*C*O_2Me, rot. maj.), 170.4 (*C*O_2Me, rot. min.), 162.4 (*C*HO, rot. min.), 162.3 (*C*HO, rot. maj.), 80.7 (C_8, rot. min.), 76.4 (C_8, rot. maj.), 64.1 (C_1, rot. maj.), 63.0 (C_1, rot. min.), 60.4 (C_6, rot. min.), 57.5 (C_6, rot. maj.), 54.4 (O*C*H_3, rot.

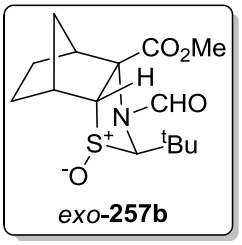
maj.), 53.8 (O*C*H_3, rot. min.), 36.8 (*C*(CH_3)$_3$, rot. maj.), 36.6 (*C*(CH_3)$_3$, rot. min.), 35.9 (C_3, rot. min.), 33.6 (C_3, rot. maj.), 32.4 (C_5, rot. maj.), 32.0 (C_5, rot. min.), 30.8 (C_2, rot. maj.), 27.8 (C_2, rot. min.), 26.9 (C(*C*H_3)$_3$, rot. maj.), 26.4 (C(*C*H_3)$_3$, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{14}H_{21}NO_6SNa$ 354.0982; found 354.0995

5.3. General procedure for hydrogenation of Diels-Alder adducts

Over a solution of the corresponding thiazolidine in ethyl acetate or acetic acid a catalytic amount of Pd/C (10%) or PtO_2 was added. Then, H_2 gas was bubbled and the reaction was left to stir until reaction completion, monitoring by TLC. Once the reaction had finished the reaction crude was filtered over celite and the residue evaporated under vacuum.

Synthesis of (1*R*,2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *exo*-257b



exo-**257b**

Following the experimental procedure described above, thiazolidine *exo*-**249b** (116 mg, 0.38 mmol) was dissolved in EtOAc (5 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 7 hours. The product *exo*-**257b** (114 mg, 0.37 mmol, 98% yield) was obtained pure as a white solid.

M.p.: 118-120 ºC

$[\alpha]_D^{23}$: -65º (*c* 1.1; $CHCl_3$)

IR (KBr) v 1733, 1670, 1477, 1449, 1400, 1356, 1315, 1220, 1054 cm^{-1}

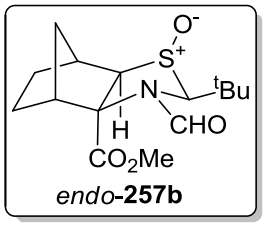
^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.16)] δ 8.43 (s, 1H, C*H*O, rot. min.), 8.38 (s, 1H, C*H*O, rot. maj.), 5.34 (s, 1H, H_2, rot. maj.), 4.55 (s, 1H, H_2, rot. min.), 4.09 (dd, *J* = 4.8, 1.1, 1H, H_{7a}, rot. maj.), 3.84 (dd, *J* = 4.5, 1.3, 1H, H_{7a}, rot. min.), 3.79 (s, 3H, OCH_3, rot. maj.), 3.72 (s, 3H, OCH_3, rot. min.), 3.42-3.38 (m, 1H, H_4, rot. min.), 3.19 (ddt, *J* = 12.2, 8.7, 3.1, 1H, H_6, rot. maj.), 3.06-3.00 (m, 1H, H_7, rot. maj.), 2.94-2.91 (m, 1H, H_7, rot. min.), 2.90 (d, *J* = 4.8, 1H, H_4, rot. maj.), 2.81-2.73 (m, 1H, H_6, rot. min.), 2.21-2.13 (m, 1H, H_8, rot. maj.), 2.16-2.10* overlapped (m, 1H, H_8, rot. min.), 1.87-1.77 (m, 1H, H_5, rot. maj.), 1.77-1.66 (m, 2H, H_5, rot. maj. + H_6, rot. min.), 1.64-1.58 (m, 3H, H_5, rot. min. + H_8, both rot.), 1.51-1.41 (m, 1H, H_6, rot. min.), 1.38-1.28 (m, 1H, H_6, rot. maj.), 1.13 (s, 9H, C(CH_3)$_3$, rot. min.), 0.95 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.7 (*C*O_2Me, rot. maj.), 172.4 (*C*O_2Me, rot. min.), 163.8 (*C*HO, rot. maj.), 161.4 (*C*HO, rot. min.), 99.6 (C_2, rot. maj.), 98.4 (C_2, rot. min.), 80.9 (C_{3a}, rot. maj.), 79.4 (C_{3a}, rot. min.), 63.2 (C_{7a}, rot. min.),

62.9 (C_{7a}, rot. maj.), 53.8 (O*C*H_3, rot. maj.), 53.1 (O*C*H_3, rot. min.), 48.2 (C_4, rot. maj.), 46.5 (C_4, rot. min.), 42.8 (C_8, rot. maj.), 41.15 (C_8, rot. min.), 41.07 (C_7, rot. maj.), 40.2 (C_7, rot. min.), 36.6 (*C*$(CH_3)_3$, rot. maj.), 35.7 (*C*$(CH_3)_3$, rot. min.), 27.7 (C(*C*$H_3)_3$, rot. min.), 27.5 (C(*C*$H_3)_3$, rot. maj.), 23.5 (C_5, rot. min.), 22.75 (C_6, rot. min.), 22.70 (C_6, rot. maj.), 22.3 (C_5, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{15}H_{23}NO_4SNa$ 336.1240; found 336.1245

Synthesis of (1*R*,2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-257b



endo-**257b**

Following the experimental procedure described above, thiazolidine *endo*-**249b** (73.8 mg, 0.24 mmol) was dissolved in EtOAc (5 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 7 hours. The product *endo*-**257b** (74.9 mg, 0.24 mmol, 100% yield) was obtained pure as a white solid.

M.p.: 161-163 ºC

$[\alpha]_D^{21}$: -80º (*c* 0.8; $CHCl_3$)

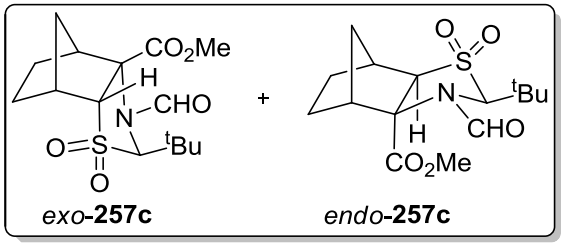
IR (KBr) v 1738, 1674, 1472, 1372, 1348, 1320, 1286, 1217, 1048 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.04)] δ 8.75 (s, 1H, C*H*O, rot. maj.), 8.26 (s, 1H, C*H*O, rot. min.), 5.14 (s, 1H, H_2, rot. maj.), 4.32 (s, 1H, H_2, rot. min.), 4.19 (d, *J* = 3.0, 1H, H_4, rot. min.), 3.81 (s, 3H, OCH_3, rot. maj.), 3.78 (s, 3H, OCH_3, rot. min.), 3.78 (d, *J* = 1.4, 1H, H_{7a}, rot. maj.), 3.76-3.75 (m, 1H, H_{7a}, rot. min.), 2.90 (m, *J* = 3.7, 1H, H_4, rot. maj.), 2.79 (d, *J* = 4.1, 1H, H_7, rot. maj.), 2.74 (d, *J* = 4.6, 1H, H_7, rot. min.), 2.17-2.10 (m, 1H, H_8, rot. maj.), 2.06-2.01 (m, 1H, H_8, rot. min.), 1.86-1.77 (m, 1H, H_6, rot. maj.), 1.67-1.57 (m, 2H, H_5, rot. maj. + H_6, rot. min.), 1.50-1.40 (m, 2H, H_6, rot. maj. + H_8, rot. maj.), 1.29-1.21 (m, 1H, H_5, rot. maj.), 0.99 (s, 9H, C(CH_3)$_3$, rot. min.), 0.96 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.5 (*C*O_2Me, rot. maj.), 162.2 (*C*HO, rot. maj.), 98.4 (C_2, rot. min.), 93.3 (C_2, rot. maj.), 82.1 (C_{3a}, rot. maj.), 69.9 (C_{7a}, rot. min.), 68.3 (C_{7a}, rot. maj.), 53.4 (O*C*H_3, rot. maj.), 53.1 (O*C*H_3, rot. min.), 45.5 (C_4, rot. maj.), 40.4 (C_4, rot. min.), 38.12 (C_7, rot. maj.), 38.07 (C_7, rot. min.), 37.9 (C_8, rot. min.), 37.1 (C_8, rot. maj.), 36.8 (*C*$(CH_3)_3$, rot. min.), 36.2 (*C*$(CH_3)_3$, rot. maj.), 27.7 (C(*C*H_3)$_3$, rot. maj.), 27.4 (C(*C*H_3)$_3$, rot. min.), 26.9 (C_6, rot. maj.), 26.7 (C_6, rot. min.), 24.5 (C_5, rot. maj.), 24.2 (C_5, rot. min.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{15}H_{23}NO_4SNa$ 336.1240; found 336.1234

Synthesis of (2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *exo*-257c and **(2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-257c**



Following the experimental procedure described above, the mixture of thiazolidines *exo*-**249c**/*endo*-**249c** (0.21 g, 0.63 mmol) was dissolved in EtOAc (5 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled into the solution and the reaction was left to stir at room temperature for 7 hours. Finally, the reaction was filtered over celite, washing with EtOAc and the solvent was removed under vacuum to obtain the mixture of pure products *exo*-**257c**/*endo*-**257c** (0.21 g, 0.63 mmol, 100% yield). The products could not be separated by column chromatography, but signals of both *exo* and *endo* adducts could be identified from the mixture by their relative integration.

Exo-**249c**. **^{1}H NMR** ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.33)] δ 8.54 (s, 1H, C*H*O, rot. min.), 8.30 (s, 1H, C*H*O, rot. maj.), 5.14 (s, 1H, H_2, rot. maj.), 4.29 (s, 1H, H_2, rot. min.), 4.21 (dd, *J* = 4.9, 0.9, 1H, H_{7a}, rot. maj.), 3.83 (s, 3H, OCH_3, rot. maj.), 3.74 (s, 3H, OCH_3, rot. min.), 3.57 (dd, *J* = 4.5, 1.3, 1H, H_{7a}, rot. min.) 3.43-3.39 (m, 1H, H_4, rot. min.), 3.00-2.91 (m, 2H, H_7, rot. maj. + CH_2, rot. maj.), 2.89 (d, *J* = 4.9, 1H, H_4, rot. maj.), 2.80-2.76 (1H, m, H_7, rot. min.), 2.15-2.06 (m, 1H, H_8, rot. maj.), 1.81-1.59 (m, 3H, H_8 + CH_2, rot. maj.), 1.42-1.35 (m, 1H, CH_2, rot. maj.), 1.32 (s, 9H, C(CH_3)$_3$, rot. min.), 1.05 (s, 9H, C(CH_3)$_3$, rot. maj.)

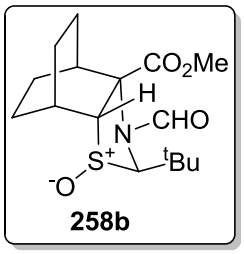
^{13}C NMR ($CDCl_3$, 100MHz) δ 171.9 (*C*O_2Me, rot. maj.), 170.6 (*C*O_2Me, rot. min.), 163.6 (*C*HO, rot. maj.), 161.2 (*C*HO, rot. min.), 85.6 (C_2, rot. maj.), 84.9 (C_2, rot. min.), 75.0 (C_{3a}, rot. maj.), 72.6 (C_{3a}, rot. min.), 67.0 (C_{7a}, rot. min.), 64.4 (C_{7a}, rot. maj.), 54.0 (O*C*H_3, rot. maj.), 53.2 (O*C*H_3, rot. min.), 47.0 (C_4, rot. maj.), 45.5 (C_4, rot. min.), 41.8 (C_8, rot. maj.), 39.9 (C_8, rot. min.), 39.7 (C_7, rot. maj.), 39.1 (C_7, rot. min.), 37.6 (*C*(CH_3)$_3$, rot. maj.), 35.9 (*C*(CH_3)$_3$, rot. min.), 27.5 (C(*C*H_3)$_3$, rot. min.), 26.9 (C(*C*H_3)$_3$, rot. maj.), 23.3 (C_5, rot. min.), 23.2 (C_6, rot. maj.), 22.8 (C_6, rot. min.), 22.0 (C_5, rot. maj.)

Endo-**249c**. **^{1}H NMR** ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.04)] δ 8.75 (s, 1H, C*H*O, rot. maj.), 8.19 (s, 1H, C*H*O, rot. min.), 4.95 (s, 1H, H_2, rot. maj.), 4.26 (d, *J* = 4.0, 1H, H_4, rot. min.), 4.12 (s, 1H, H_2, rot. min.), 3.83 (s, 3H, OCH_3, rot. maj.), 3.80 (s, 3H, OCH_3, rot. min.), 3.70 (d, *J* = 1.6, 1H, H_{7a}, rot. min.), 3.68 (d, *J* = 1.5, 1H, H_{7a}, rot. maj.), 3.09-3.06 (m, 1H, H_4, rot. maj.), 3.00-2.92 (m, 1H, H_7, rot. maj.), 2.14-2.07 (m, 1H, H_8, rot. maj.), 1.83-1.58 (m, 2H, CH_2, rot. maj.), 1.47-1.42 (m, 2H, H_8, rot. maj. + CH_2, rot. maj.), 1.26-1.17 (m, 1H, CH_2, rot. maj.), 1.09 (s, 9H, C(CH_3)$_3$, rot. min.), 1.06 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.0 (*C*O_2Me, rot. maj.), 161.9 (*C*HO, rot. maj.), 78.0 (C_2, rot. maj.), 75.9 (C_{3a}, rot. maj.), 67.7 (C_{7a}, rot. maj.), 53.5 (O*C*H_3, rot. maj.), 45.6 (C_4, rot. maj.), 38.8 (C_7, rot. maj.), 37.0 (*C*(CH_3)$_3$, rot. maj.), 35.6 (C_8, rot. maj.), 27.0 (C(*C*H_3)$_3$, rot. maj.), 26.0 (C_6, rot. maj.), 24.6 (C_5, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{15}H_{23}NO_5SNa$ 352.1189; found 352.1198

Synthesis of (1*R*,2*R*,3a*R*,4*S*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxidooctahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate 258b



258b

Following the experimental procedure described above, thiazolidine *exo*-**250b** (0.55 g, 1.69 mmol) was dissolved in EtOAc (15 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 7 hours. The product **258b** (0.55 g, 1.69 mmol, 100% yield) was obtained pure as a white solid.

M.p.: 165-167 ºC

$[\alpha]_D^{23}$: -99º (*c* 1.1; $CHCl_3$)

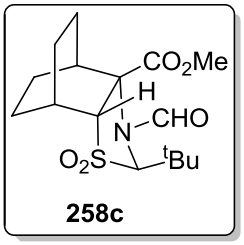
IR (neat) v 1731, 1664, 1480, 1453, 1424, 1399, 1347, 1307, 1107 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.03)] δ 8.64 (s, 1H, C*H*O, rot. maj.), 8.38 (s, 1H, C*H*O, rot. min.), 5.21 (s, 1H, H_2, rot. maj.), 4.41 (s, 1H, H_2, rot. min.), 3.89 (d, *J* = 2.3, 1H, H_{7a}, rot. maj.), 3.85 (d, *J* = 2.4, 1H, H_{7a}, rot. min.), 3.78 (s, 3H, O*C*H_3, rot. maj.), 3.76 (s, 3H, O*C*H_3, rot. min.), 2.54-2.41 (m, 3H, H_4 + H_7 + C*H*$_2$), 1.89-1.78 (m, 1H, C*H*$_2$), 1.74-1.63 (m, 3H, C*H*$_2$), 1.58-1.49 (m, 1H, C*H*$_2$), 1.41-1.30 (m, 1H, C*H*$_2$), 1.26-1.12 (m, 1H, C*H*$_2$), 0.99 (s, 9H, C(C*H*$_3$)$_3$, rot. min.), 0.94 (s, 9H, C(C*H*$_3$)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.9 (*C*O_2Me), 163.2 (*C*HO), 92.7 (C_2), 74.1 (C_{3a}), 62.3 (C_{7a}), 53.6 (O*C*H_3), 36.0 (*C*(CH_3)$_3$), 32.8 (C_4), 27.8 (C(*C*H_3)$_3$), 27.2 (*C*H_2), 26.6 (C_7), 21.1 (*C*H_2), 20.8 (*C*H_2), 20.1 (*C*H_2)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{16}H_{26}NO_4S$ 328.1577; found 328.1576

Synthesis of (2*R*,3a*R*,4*S*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxidooctahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate 258c



258c

Following the experimental procedure described above, thiazolidine *exo*-**250c** (0.43 g, 1.26 mmol) was dissolved in EtOAc (10 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 1 day. The obtained solid was purified by column chromatography (EtOAc/hexane 40/60) to give **258c** (0.43 g, 1.25 mmol, 100% yield) as a white solid.

M.p.: 198-200 ºC

$[\alpha]_D^{23}$: -144º (*c* 1.1; $CHCl_3$)

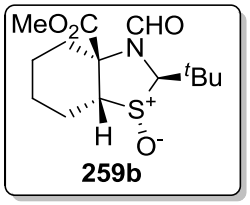
IR (KBr) v 1747, 1671, 1485, 1428, 1316, 1246, 1220, 1109 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.62 (s, 1H, C*H*O), 5.01 (s, 1H, H_2), 4.03 (d, *J* = 3.0, 1H, H_{7a}), 3.85 (s, 3H, OCH_3), 2.60-2.53 (m, 2H, H_4 + CH_2), 2.52-2.47 (m, 1H, H_7), 1.87-1.75 (m, 1H, CH_2), 1.74-1.65 (m, 2H, CH_2), 1.64-1.52 (m, 2H, CH_2), 1.41-1.22 (m, 2H, CH_2), 1.08 (s, 9H, C(CH_3)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.2 (*C*O_2Me), 162.8 (*C*HO), 77.5 (C_2), 68.1 (C_{3a}), 61.5 (C_{7a}), 53.8 (O*C*H_3), 36.8 (*C*(CH_3)$_3$), 31.8 (C_4), 27.1 (C(*C*H_3)$_3$), 25.7 (*C*H_2), 24.1 (C_7), 21.4 (*C*H_2), 20.4 (*C*H_2), 19.3 (*C*H_2)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{16}H_{25}NO_5SNa$ 366.1346; found 366.1348

Synthesis of (1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 259b



259b

Following the experimental procedure described above, thiazolidine **252b** (0.50 g, 1.69 mmol) was dissolved in EtOAc (5 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 1 day. The obtained solid was purified by column chromatography (EtOAc/hexane 50/50) to give **259b** (0.47 g, 1.57 mmol, 93% yield) as a white solid.

M.p.: 113-115 ºC

$[\alpha]_D^{23}$: +29º (*c* 1.0; $CHCl_3$)

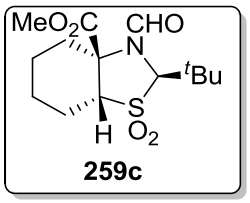
IR (KBr) v 1741, 1667, 1457, 1346, 1307, 1283, 1242, 1230, 1052 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.36)] δ 8.83 (s, 1H, C*H*O, rot. maj.), 8.22 (s, 1H, C*H*O, rot. min.), 5.19 (s, 1H, H_8, rot. maj.), 4.56 (s, 1H, H_8, rot. min.), 3.86 (s, 3H, OCH_3, rot. maj.), 3.79 (s, 3H, OCH_3, rot. min.), 3.49-3.45 (m, 1H, H_6, rot. maj.), 3.20-3.13 (m, 1H, H_2, rot. min.), 3.09-3.05 (m, 1H, H_6, rot. min.), 2.73-2.66 (m, 1H, H_2, rot. maj.), 2.59-2.49 (m, 2H, H_5, both rot.), 2.27 (dt, *J* = 13.4, 3.7, 1H, H_2, rot. maj.), 2.19-2.06 (m, 1H, H_5, rot. maj.), 2.00-1.87 (m, 3H, H_2, rot. min. + H_5, rot. min. + H_4, rot. min.), 1.86-1.68 (m, 4H, H_3, both rot. + H_4, rot. maj. + H_5, rot. min.), 1.66-1.51 (m, 2H, H_4, both rot.), 1.34-1.17 (m, 2H, H_3, both rot.), 1.12 (s, 9H, C(CH_3)$_3$, rot. min.), 0.99 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.6 (*C*O_2Me, rot. min.), 171.4 (*C*O_2Me, rot. maj.), 164.7 (*C*HO, rot. maj.), 162.6 (*C*HO, rot. min.), 93.9 (C_8, rot. min.), 90.8 (C_8, rot. maj.), 71.3 (C_1, rot. min.), 70.6 (C_1, rot. maj.), 58.8 (C_6, rot. min.), 57.9 (C_6, rot. maj.), 53.7 (O*C*H_3, rot. maj.), 53.0 (O*C*H_3, rot. min.), 37.1 (C_2, rot. maj.), 36.3 (*C*(CH_3)$_3$, rot. maj.), 35.9 (*C*(CH_3)$_3$, rot. min.), 30.9 (C_2, rot. min.), 28.3 (C(*C*H_3)$_3$, rot. maj.), 27.8 (C(*C*H_3)$_3$, rot. min.), 23.83 (C_5, rot. min.), 23.75 (C_5, rot. maj.), 21.7 (C_3, rot. min.), 21.0 (C_3, rot. maj.), 20.7 (C_4, rot. maj.), 20.5 (C_4, rot. min.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{14}H_{23}NO_4SNa$ 324.1240; found 324.1267

Synthesis of (1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 259c



259c

Following the experimental procedure described above, thiazolidine **252c** (0.38 g, 1.21 mmol) was dissolved in EtOAc (5 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 1 day. The obtained solid was purified by column chromatography (EtOAc/hexane 40/60) to give **259c** (0.37 g, 1.19 mmol, 98% yield) as a white solid.

M.p.: 114-116 ºC

$[\alpha]_D^{23}$: +124º (*c* 1.0; $CHCl_3$)

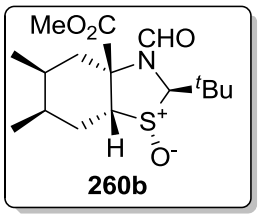
IR (KBr) v 1745, 1669, 1458, 1439, 1320, 1281, 1248, 1173, 1123 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.17)] δ 8.79 (s, 1H, C*H*O, rot. maj.), 8.24 (s, 1H, C*H*O, rot. min.), 4.95 (s, 1H, H_8, rot. maj.), 4.28 (s, 1H, H_8, rot. min.), 3.90 (s, 3H, OCH_3, rot. maj.), 3.82 (s, 3H, OCH_3, rot. min.), 3.76-3.71 (m, 1H, H_6, rot. maj.), 3.42-3.38 (m, 1H, H_6, rot. min.), 3.16-3.10 (m, 1H, H_2, rot. min.), 2.70-2.60 (m, 1H, H_2, rot. maj.), 2.53-2.44 (m, 2H, H_5, both rot.), 2.19 (dt, *J* = 13.5, 3.6, 1H, H_2, rot. maj.), 2.06-1.94 (m, 1H, H_5, rot. maj.), 1.89-1.61 (m, 9H, H_2, rot. min. + H_3, both rot. + H_4, both rot. + H_5, rot. min.), 1.35-1.24 (m, 1H, H_3, rot. maj.), 1.23 (s, 9H, C(CH_3)$_3$, rot. min.), 1.09 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.2 (*C*O_2Me, rot. maj.), 164.2 (*C*HO, rot. maj.), 80.6 (C_8, rot. min.), 76.7 (C_8, rot. maj.), 63.9 (C_1, rot. maj.), 63.7 (C_1, rot. min.), 58.3 (C_6, rot. min.), 55.5 (C_6, rot. maj.), 54.0 (O*C*H_3, rot. maj.), 53.2 (O*C*H_3, rot. min.), 36.9 (*C*(CH$_3$)$_3$, rot. maj.), 36.6 (*C*(CH$_3$)$_3$, rot. min.), 35.3 (C_2, rot. maj.), 28.8 (C_2, rot. min.), 27.0 (C(*C*H$_3$)$_3$, rot. maj.), 26.5 (C(*C*H$_3$)$_3$, rot. min.), 21.9 (C_3, rot. min.), 21.5 (C_3, rot. maj.), 20.5 (C_4, rot. maj.), 20.2 (C_4, rot. min.), 19.6 (C_5, rot. min.), 19.4 (C_5, rot. maj.)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{14}H_{23}NO_5SNa$ 340.1189; found 340.1165

Synthesis of (1*R*,3*S*,4R,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7-oxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 260b



260b

Following the experimental procedure described above, thiazolidine **253b** (0.30 g, 0.92 mmol) was dissolved in acetic acid (5 mL) and PtO_2 was added in catalytic amount. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 4 days. The obtained solid was purified by column chromatography (EtOAc/hexane 40/60) to give **260b** (0.27 g, 0.82 mmol, 89% yield) as a white solid.

M.p.: 134-136 ºC

$[\alpha]_D^{23}$: -29º (*c* 1.0; $CHCl_3$)

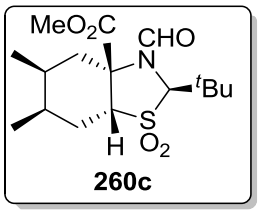
IR (KBr) v 1740, 1669, 1457, 1437, 1345, 1314, 1301, 1173, 1034 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.03)] δ 8.91 (s, 1H, C*H*O, rot. maj.), 8.84 (s, 1H, C*H*O, rot. min.), 5.20 (s, 1H, H_8, rot. min.), 5.17 (s, 1H, H_8, rot. maj.), 3.86 (s, 3H, OCH_3, rot. min.), 3.85 (s, 3H, OCH_3, rot. maj.), 3.71-3.67 (m, 1H, H_6, rot. maj.), 3.51-3.49 (m, 1H, H_6, rot. min.), 2.78 (ddd, *J* = 13.1, 3.4, 1.4, 1H, H_2, rot. maj.), 2.61-2.56 (m, 1H, H_2, rot. min.), 2.47 (dd, *J* = 13.1, 4.6, H_2, 1H, rot. maj.) 2.34-2.23 (m, 2H, H_4, rot. maj. + H_5, rot. maj.), 2.04-1.87 (m, 2H, H_3, rot. maj. + H_5, rot. maj.), 1.00 (s, 9H, C(CH_3)$_3$, rot. min.), 0.98 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.87 (d, 9H, *J* = 6.7, C_3-CH_3, rot. min. + C_4-CH_3, both rot.), 0.75 (d, 3H, *J* = 7.5, C_3-CH_3, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.1 (*C*O_2Me), 165.0 (*C*HO), 90.8 (C_8), 68.4 (C_1), 58.1 (C_6), 53.7 (OCH_3), 44.0 (C_2), 36.2 (*C*(CH_3)$_3$), 31.0 (C_3), 29.0 (C_4), 28.3 (C(*C*H_3)$_3$), 26.6 (C_5), 18.9 (C_4-*C*H_3), 11.2 (C_3-*C*H_3)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{16}H_{27}NO_4SNa$ 352.1553; found 352.1529

Synthesis of (1*R*,3*S*,4*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 260c



260c

Following the experimental procedure described above, thiazolidine **253c** (0.30 g, 0.87 mmol) was dissolved in acetic acid (5 mL) and PtO_2 was added in catalytic amount. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature for 3 days. The obtained solid was purified by column chromatography (EtOAc/hexane 40/60) to give the desire product **260c** (0.26 g, 0.76 mmol, 88% yield) as a white solid.

M.p.: 107-109 ºC

$[\alpha]_D^{23}$: -103º (*c* 1.0; $CHCl_3$)

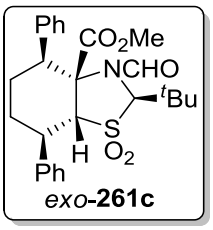
IR (KBr) v 1740, 1695, 1457, 1350, 1325, 1264, 1241, 1175, 1080 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.03)] δ 8.86 (s, 1H, C*H*O, rot. maj.), 8.79 (s, 1H, C*H*O, rot. min.), 4.94 (s, 1H, H_8, rot. min.), 4.92 (s, 1H, H_8, rot. maj.), 4.01-3.96 (m, 1H, H_6, rot. maj.), 3.88 (s, 6H, OCH_3, both rot.), 3.79-3.76 (m, 1H, H_6, rot. min.), 2.77 (ddd, *J* = 13.2, 3.0, 1.1, 1H, H_2, rot. maj.), 2.54-2.49 (m, 1H, H_2, rot. min.), 2.41 (dd, *J* = 13.3, 4.6, H_2, 1H, rot. maj.) 2.30-2.19 (m, 2H, H_4, rot. maj. + H_5, rot. maj.), 2.00-1.91 (m, 1H, H_3, rot. maj.), 2.82-1.72 (m, 2H, H_5, rot. maj.), 1.08 (s, 9H, C(CH_3)$_3$, rot. min.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.87 (d, 3H, *J* = 6.7, C_4-CH_3, rot. maj.), 0.75 (d, 3H, *J* = 7.5, C_3-CH_3, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.7 (*C*O_2Me), 164.3 (*C*HO), 76.6 (C_8), 62.1 (C_1), 56.2 (C_6), 54.0 (O*C*H_3), 42.1 (C_2), 36.7 (*C*(CH_3)$_3$), 31.8 (C_3), 28.9 (C_4), 27.0 (C(*C*H_3)$_3$), 22.0 (C_5), 18.9 (C_4-*C*H_3), 10.7 (C_3-*C*H_3)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{16}H_{27}NO_5SNa$ 368.1502; found 368.1481

Synthesis (1*R*,2*S*,5*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-2,5-diphenyl-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate *exo*-261c



exo-**261c**

Following the experimental procedure described above, thiazolidine *exo*-**254c** (146 mg, 0.31 mmol) was dissolved in EtOAc (5 mL) and Pd/C 10% was added. Then, H_2 gas was bubbled and the reaction was left to stir at room temperature overnight. The product *exo*-**261c** (145 mg, 0.31 mmol, 100% yield) was obtained pure as a white solid

M.p.: 87-89 ºC

$[\alpha]_D^{26}$: -123º (*c* 1.0; $CHCl_3$)

IR (KBr) v 1737, 1674, 1494, 1485, 1459, 1321, 1293, 1242, 1138 cm^{-1}

^{1}H NMR (CD_2Cl_2, 400MHz) δ 7.55 (s, 1H, C*H*O), 7.44-7.35 (m, 7H, H_{Ph}), 7.34-7.29 (m, 1H, H_{Ph}), 7.14 (dd, *J* = 7.6, 1.7, 2H, H_{Ph}), 5.08 (s, 1H, H_8), 4.22 (d, *J* = 8.7, 1H, H_6), 3.86 (s, 3H, OCH_3), 3.85-3.78 (m, 1H, H_5), 3.73-3.67 (m, 1H, H_2), 2.41-2.28 (m, 1H, H_4), 2.13-1.98 (m, 3H, H_3 + H_4), 0.99 (s, 9H, C(CH_3)$_3$)

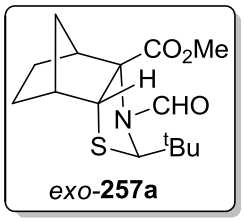
^{13}C NMR (CD_2Cl_2, 100MHz) δ 171.3 (*C*O_2Me), 164.3 (*C*HO), 142.7 (C_{qPh}), 140.9 (C_{qPh}), 129.7 (C_{Ph}), 129.4 (C_{Ph}), 129.0 (C_{Ph}), 128.0 (C_{Ph}), 127.9 (C_{Ph}), 75.0 (C_8), 69.6 (C_1), 66.2 (C_6), 53.8 (O*C*H_3), 48.4 (C_2), 37.7 (*C*(CH_3)$_3$), 35.5 (C_5), 28.9 (C_3), 27.5 (C(*C*H_3)$_3$), 27.3 (C_4)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{26}H_{31}NO_5SNa$ 492.1815; found 492.1806

5.4. General procedure for deoxigenation of sulfoxides

Over a stirred solution of a bicyclic thiazolidine sulfoxide (1 eq.) in acetone at 0 ºC, trifluoroacetic anhydride (2 eq.) and potassium iodide (4 eq.) were added. The reaction mixture was stirred at room temperature and was monitored by TLC (EtOAc/hexane) until completion. The mixture was treated with an aqueous solution of $Na_2S_2O_3$ (5%) and dichloromethane at room temperature and was stirred for 30 minutes. The phases were separated and the aqueous phase was extracted with dichloromethane, the combined organic layers were dried over magnesium sulfate anhydrous, filtered off and the solvent was evaporated under reduced pressure. The obtained residue was purified by column chromatography.

Synthesis of (2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyloctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *exo*-257a.



exo-**257a**

Following the general procedure described above, thiazolidine *exo*-**257b** (0.52 g, 1.65 mmol) was dissolved in acetone (15 mL). The reaction was allowed to stir at room temperature for 4 hours. The obtained residue was purified by column chromatography (EtOAc/ hexane 30/70) to give *exo*-**257a** (0.49 g, 1.63 mmol, 99% yield) as a colourless oil.

$[\alpha]_D^{23}$: +2º (*c* 1.2; $CHCl_3$)

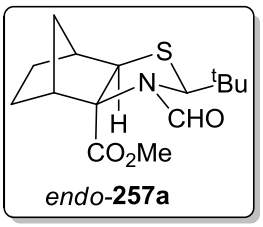
IR (neat) v 1737, 1679, 1477, 1395, 1365, 1311, 1246, 1178, 1063 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.09)] δ 8.37 (s, 1H, C*H*O, rot. min.), 8.10 (s, 1H, C*H*O, rot. maj.), 5.61 (s, 1H, H_2, rot. maj.), 5.00 (s, 1H, H_2, rot. min.), 4.55 (dd, *J* = 4.7, 1.1, 1H, H_{7a}, rot. maj.), 4.42 (dd, *J* = 4.5, 1.4, 1H, H_{7a}, rot. min.), 3.75 (s, 3H, O*C*H_3, rot. maj.), 3.70 (s, 3H, O*C*H_3, rot. min.), 3.21-3.17 (m, 1H, H_4, rot. min.), 2.64-2.58 (m, 1H, H_4, rot. maj.), 2.36-2.30 (m, 1H, H_7, rot. maj.), 2.28-2.23 (m, 1H, H_7, rot. min.), 2.20-2.06 (m, 4H, H_6, both rot. + H_8, both rot.), 1.62 (dt, *J* = 10.7, 1.6, 1H, H_8, rot. maj.), 1.57-1.54 (m, 2H, H_6, rot. min. + H_8, rot. min.), 1.51 (dt, *J* = 9.6, 4.3, 1H, H_5, rot. maj.), 1.42-1.28 (m, 4H, H_5, both rot. + H_6, both rot.), 0.89 (s, 9H, C(CH_3)$_3$, rot. min.), 0.83 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 173.2 (*C*O_2Me, rot. min.), 172.9 (*C*O_2Me, rot. maj.), 163.4 (*C*HO, rot. maj.), 161.0 (*C*HO, rot. min.), 82.0 (C_2, rot. min.), 80.5 (C_{3a}, rot. min.), 80.1 (C_{3a}, rot. maj.), 77.3 (C_2, rot. maj.), 56.9 (C_{7a}, rot. min.), 55.0 (C_{7a}, rot. maj.), 53.4 (O*C*H_3, rot. maj.), 52.9 (O*C*H_3, rot. min.), 47.7 (C_4, rot. maj.), 46.2 (C_4, rot. min.), 40.5 (C_7, rot. min.), 40.1 (C_7, rot. maj.), 39.6 (C_8, rot. maj.), 39.5 (*C*$(CH_3)_3$, rot. maj.), 39.0 (C_8, rot. min.), 38.7 (*C*$(CH_3)_3$, rot. min.), 26.7 (C(*C*$H_3)_3$, rot. min.), 26.4 (C(*C*$H_3)_3$, rot. maj.), 23.8 (C_6, rot. min.), 23.0 (C_6, rot. maj.), 22.7 (C_5, rot. min.), 22.0 (C_5, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{15}H_{23}NO_3SNa$ 320.1291; found 320.1285

Synthesis of (2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyloctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-257a



endo-**257a**

Following the general procedure described above, thiazolidine *endo*-**257b** (35.1 mg, 0.11 mmol) was dissolved in acetone (5 mL). The reaction was allowed to stir at room temperature for 4 hours. The obtained residue was purified by column chromatography (EtOAc/ hexane 10/90) to give the desire product *endo*-**257a** (31.1 mg, 0.10 mmol, 93% yield) as a transparent oil that turned into a white solid.

M.p.: 108-110 °C

$[\alpha]_D^{23}$: -34° (*c* 0.8; $CHCl_3$)

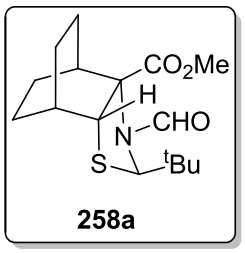
IR (KBr) v 2996-2873, 1742, 1667, 1479, 1358, 1326, 1226, 1043 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.04)] δ 8.58 (s, 1H, C*H*O, rot. maj.), 8.41 (s, 1H, C*H*O, rot. min.), 5.55 (s, 1H, H_2, rot. maj.), 4.75 (s, 1H, H_2, rot. min.), 4.16-4.13 (m, 1H, H_4, rot. min.), 4.09 (d, *J* = 2.0, 1H, H_{7a}, rot. maj.), 4.08 (d, *J* = 2.4, 1H, H_{7a}, rot. min.), 3.77 (s, 3H, OCH_3, rot. maj.), 3.75 (s, 3H, OCH_3, rot. min.), 2.78-2.74 (m, 1H, H_4, rot. maj.), 2.23-2.20 (m, 1H, H_7, rot. maj.), 2.19-2.17 (m, 1H, H_7, rot. min.), 2.14-2.08 (m, 1H, H_8, rot. maj.), 1.69 (tdd, *J* = 12.2, 4.6, 3.5, 1H, H_6, rot. maj.), 1.59-1.48 (m, 1H, H_5, rot. maj.), 1.42-1.34 (m, 1H, H_6, rot. maj.), 1.29 (ddd, *J* = 10.6, 3.5, 1.6, 1H, H_8, rot. maj.), 1.19-1.11 (m, 1H, H_5, rot. maj.), 0.89 (s, 9H, C(CH_3)$_3$, rot. min.), 0.86 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 171.8 (*C*O_2Me, rot. maj.), 161.5 (*C*HO, rot. maj.), 80.4 (C_{3a}, rot. maj.), 78.5 (C_2, rot. min.), 72.3 (C_2, rot. maj.), 59.1 (C_{7a}, rot. min.), 57.5 (C_{7a}, rot. maj.), 53.0 (O*C*H_3, rot. maj.), 47.8 (C_4, rot. maj.), 43.7 (C_7, rot. maj.), 39.3 (*C*(CH_3)$_3$, rot. maj.), 34.0 (C_8, rot. maj.), 27.0 (C(*C*H_3)$_3$, rot. maj.), 26.6 (C(*C*H_3)$_3$, rot. min.), 26.4 (C_6, rot. maj.), 23.9 (C_5, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{15}H_{23}NO_3SNa$ 320.1291; found 320.1296

Synthesis of (2*R*,3a*R*,4*S*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyloctahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate 258a



258a

Following the general procedure described above, thiazolidine **258b** (0.51 g, 1.57 mmol) was dissolved in acetone (10 mL). The reaction was allowed to stir at room temperature for 3 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give **258a** (0.48 g, 1.54 mmol, 98% yield) as a white solid.

M.p.: 96-98 °C

$[\alpha]_D^{23}$: -43° (*c* 1.0; $CHCl_3$)

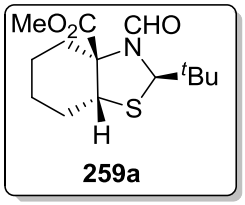
IR (KBr) v 1742, 1679, 1462, 1364, 1308, 1245 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.03)] δ 8.47 (s, 1H, C*H*O, rot. min.), 8.42 (s, 1H, C*H*O, rot. maj.), 5.47 (s, 1H, H_2, rot. maj.), 4.71 (s, 1H, H_2, rot. min.), 4.41 (dd, *J* = 3.5, 0.9, 1H, H_{7a}, rot. maj.), 4.37 (dd, *J* = 3.3, 1.2, 1H, H_{7a}, rot. min.), 3.76 (s, 3H, OCH_3, rot. maj.), 3.73 (s, 3H, OCH_3, rot. min.), 2.23-2.18 (m, 1H, H_4, rot. maj.), 2.09-1.99 (m, 1H, CH_2, rot. maj.), 1.81-1.76 (m, 1H, H_7, rot. maj.), 1.73-1.51 (m, 4H, CH_2, rot. maj.), 1.41-1.21 (m, 3H, CH_2, rot. maj.), 0.89 (s, 9H, C(CH_3)$_3$, rot. min.), 0.86 (s, 9H, C(CH_3)$_3$, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 173.1 (*C*O_2Me), 162.5 (*C*HO), 73.1 (C_{3a}), 70.6 (C_2), 53.2 (O*C*H_3), 51.6 (C_{7a}), 39.4 (*C*(CH$_3$)$_3$), 33.8 (C_4), 27.9 (C_7), 27.0 (C(*C*H_3)$_3$), 24.8 (*C*H_2), 20.9 (*C*H_2), 19.4 (*C*H_2), 18.8 (*C*H_2)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{16}H_{26}NO_3S$ 312.1628; found 312.1606

Synthesis of (1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 259a



259a

Following the general procedure described above, thiazolidine **259b** (0.84 g, 2.78 mmol) was dissolved in acetone (40 mL). The reaction was allowed to stir at room temperature for 3 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 20/80) to give **259a** (0.76 g, 2.70 mmol, 97% yield) as a white solid.

M.p.:103-105 °C

$[\alpha]_D^{23}$: -35° (*c* 1.0; $CHCl_3$)

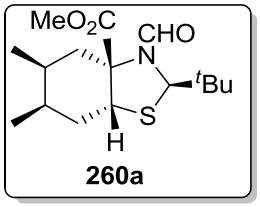
IR (KBr) v 1735, 1698, 1655, 1457, 1361, 1318, 1288, 1241 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.47)] δ 8.44 (s, 1H, C*H*O, rot. min.), 8.22 (s, 1H, C*H*O, rot. maj.), 5.21 (s, 1H, H_8, rot. min.), 4.63 (s, 1H, H_8, rot. maj.), 4.21 (t, *J* = 3.9, 1H, H_6, rot. min.), 3.97-3.93 (m, 1H, H_6, rot. maj.), 3.82 (s, 3H, OCH_3, rot. min.), 3.76 (s, 3H, OCH_3, rot. maj.), 2.86-2.78 (m, 1H, H_2, rot. maj.), 2.31-2.21 (m, 1H, H_2, rot. min.), 2.16-2.04 (m, 1H, H_2, rot. min.), 1.96-1.37 (m, 13H, H_2, rot. maj. + H_3, both rot. + H_4, both rot. + H_5, both rot.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.98 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.3 (*C*O_2Me, rot. min.), 172.2 (*C*O_2Me, rot. maj.), 163.7 (*C*HO, rot. min.), 162.0 (*C*HO, rot. maj.), 73.0 (C_8, rot. maj.), 70.8 (C_1, rot. min.), 70.40 (C_8, rot. maj.), 70.37 (C_1, rot. maj.), 53.2 (O*C*H_3, rot. min.), 52.6 (O*C*H_3, rot. maj.), 48.6 (C_6, rot. maj.), 47.7 (C_6, rot. min.), 40.1 (*C*(CH_3)$_3$, rot. min.), 39.5 (*C*(CH_3)$_3$, rot. maj.), 34.5 (C_2, rot. min.), 28.3 (C_2, rot. maj.), 27.5 (C(*C*H_3)$_3$, rot. min.), 27.0 (C(*C*H_3)$_3$, rot. maj.), 25.8 (*C*H_2, rot. min.), 24.6 (*C*H_2, rot. maj.), 23.5 (*C*H_2, rot. maj.), 22.9 (*C*H_2, rot. min.), 19.9 (*C*H_2, rot. min.), 19.5 (*C*H_2, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calculated for $C_{14}H_{23}NO_3SNa$ 308.1291; found 308.1282

Synthesis (1*R*,3*S*,4*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 260a.



260a

Following the general procedure described above, thiazolidine **260b** (0.30 g, 0.91 mmol) was dissolved in acetone (15 mL). The reaction was allowed to stir at room temperature for 3 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 10/90) to give **260a** (0.26 g, 0.84 mmol, 92% yield) as a colourless oil that turned into a white solid.

M.p.: 68-70 °C

$[\alpha]_D^{23}$: -43° (*c* 0.8; $CHCl_3$)

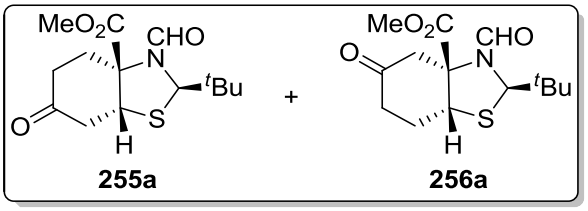
IR (KBr) ν 1739, 1679, 1459, 1364, 1309, 1259, 1224, 1114, 1031 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.09)] δ 8.49 (s, 1H, C*H*O, rot. maj.), 8.34 (s, 1H, C*H*O, rot. min.), 5.26 (s, 1H, H_8, rot. maj.), 4.73 (s, 1H, H_8, rot. min.), 4.14-4.08 (m, 1H, H_6 rot. maj.), 3.82 (dd, *J* = 7.7, 4.4, 1H, H_6, rot. min.), 3.73 (s, 3H, OCH_3, rot. maj.), 3.68 (s, 3H, OCH_3, rot. min.), 2.65 (dd, *J* = 14.3, 3.1, 1H, H_2, rot. min.), 2.16 (dd, *J* = 14.6, 4.0, 1H, H_2, rot. maj.), 2.12-2.02 (m, 2H, H_2, both rot.), 1.92-1.82 (m, 2H, H_4, both rot.), 1.80-1.69 (m, 4H, H_3, both rot. + H_5, both rot.), 1.60-1.56 (m, 1H, H_5, rot. min.), 1.52 (ddd, *J* = 14.6, 7.3, 4.0, 1H, H_5, rot. maj.), 0.97 (s, 9H, C(CH_3)$_3$, rot. min.), 0.88 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.81 (d, *J* = 7.0, 9H, C_4-CH_3, both rot. + C_3-CH_3, rot. min.), 0.73 (d, *J* = 7.1, 3H, C_3-CH_3, rot. maj.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.6 (*C*O_2Me, rot. min.), 172.5 (*C*O_2Me, rot. maj.), 164.2 (*C*HO, rot. maj.), 162.5 (*C*HO, rot. min.), 74.7 (C_8, rot. min.), 73.5 (C_1, rot. min.), 71.0 (C_1, rot. maj.), 70.5 (C_8, rot. maj.), 52.9 (O*C*H_3, rot. maj.), 52.4 (O*C*H_3, rot. min.), 46.2 (C_6, rot. min.), 44.7 (C_6, rot. maj.), 39.1 (*C*(CH_3)$_3$, rot. maj.), 38.4 (*C*(CH_3)$_3$, rot. min.), 38.1 (C_2, rot. maj.), 33.3 (C_5, rot. maj.), 30.5 (C_3, rot. maj.), 30.3 (C_3, rot. min.), 29.9 (C_4, rot. maj.), 29.8 (C_4, rot. min.), 27.5 (C(*C*H_3)$_3$, rot. maj.), 27.3 (C(*C*H_3)$_3$, rot. min.), 16.8 (*C*H_3, rot. min.), 15.0 (*C*H_3, rot. maj.), 14.9 (*C*H_3, rot. maj.), 14.6 (*C*H_3, rot. min.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{16}H_{27}NO_3SNa$ 336.1604; found 336.1605

Synthesis (1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 255a and **(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 256a**



Following the general procedure described above, a mixture of thiazolidines **255b** and **256b** (1.00 g, 3.20 mmol) was dissolved in acetone (10 mL). The reaction was allowed to stir at room temperature for 2 hours. The obtained residue was purified by column chromatography (EtOAc/hexane 60/40) to give **255a** and **256a** (0.76 g, 2.56 mmol, 80% yield as mixture of both regioisomers). Analytical samples of each regioisomer could be obtained in order to characterize them, both as white solids.

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 255a

M.p.: 113-115 °C

$[\alpha]_D^{22}$: +50° (*c* 1.0; $CHCl_3$)

IR (KBr) v 2977-2874, 1733, 1662, 1354, 1311, 1253, 1150 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.50)] δ 8.54 (s, 1H, C*H*O, rot. min.), 8.30 (s, 1H, C*H*O, rot. maj.), 5.43 (s, 1H, H_8, rot. min.), 4.68 (s, 1H, H_8, rot. maj.), 4.56-4.51 (m, 1H, H_6, rot. min.), 4.21-4.17 (m, 1H, H_6, rot. maj.), 3.86 (s, 3H, OCH_3, rot. min.), 3.83 (s, 3H, OCH_3, rot. maj.), 3.07-2.96 (m, 2H, H_2, rot. maj. + H_5, rot. min.), 2.88-2.77 (m, 2H, H_3, rot. maj. + H_5, rot. maj.), 2.58-2.38 (m, 7H, H_2, both rot. + H_3, both rot. + H_5, both rot.), 2.36-2.28 (m, 1H, H_3, rot. min.), 1.07 (s, 9H, C(CH_3)$_3$, rot. maj.), 0.94 (s, 9H, C(CH_3)$_3$, rot. min.)

^{13}C NMR ($CDCl_3$, 100MHz) δ 207.1 (C_4, rot. maj.), 206.5 (C_4, rot. min.), 172.9 (*C*O_2Me, rot. min.), 171.5 (*C*O_2Me, rot. maj.), 162.04 (*C*HO, rot. min.), 161.97 (*C*HO, rot. maj.), 73.6 (C_8, rot. maj.), 70.6 (C_8, rot. min.), 69.6 (C_1, rot. min.), 69.3 (C_1, rot. maj.), 53.8 (O*C*H_3, rot. min.), 53.2 (O*C*H_3, rot. maj.), 49.3 (C_6, rot. maj.), 48.2 (C_6, rot. min.), 40.5 (C_5, rot. min.), 40.3 (*C*(CH_3)$_3$, rot. min.), 39.6 (*C*(CH_3)$_3$, rot. maj.), 38.9 (C_5, rot. maj.), 36.3 (C_3, rot. maj.), 33.2 (C_3, rot. min.), 32.4 (C_2, rot. min.), 27.7 (C_2, rot. maj.), 27.2 (C(*C*H_3)$_3$, rot. min.), 26.9 (C(*C*H_3)$_3$, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{14}H_{21}NO_4SNa$ 322.1083; found 322.1080

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate 256a

M.p.: 120-122 °C

$[\alpha]_D^{23}$: +10° (*c* 1.1; $CHCl_3$)

IR (KBr) ν 1731, 1713, 1673, 1488, 1454, 1355, 1311, 1287, 1239 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) [rotamers mixture ratio (1/0.10)] δ 8.27 (s, 1H, C*H*O, rot. min.), 8.24 (s, 1H, C*H*O, rot. maj.), 5.30 (s, 1H, H_8, rot. min.), 4.75 (s, 1H, H_8, rot. maj.), 4.23 (t, *J* = 4.3, 1H, H_6, rot. min.), 3.98 (t, *J* = 3.4, 1H, H_6, rot. maj.) 3.83 (s, 3H, OCH_3, rot. min.), 3.77 (s, 3H, OCH_3, rot. maj.), 3.58 (ddd, *J* = 15.3, 1.5, 0.9, 1H, H_2, rot. maj.), 2.97 (d, *J* = 14.6, 1H, H_2, rot. min.), 2.92 (d, *J* = 14.8, 1H, H_2, rot. min.), 2.61 (d, *J* = 15.1, 1H, H_2, rot. maj.), 2.60-2.52 (m, 2H, H_4, both rot.), 2.35-2.29 (m, 2H, H_4, both rot.), 2.22-2.09 (m, 4H, H_5, both rot.), 1.11 (s, 9H, C(CH_3)$_3$, rot. maj.), 1.03 (s, 9H, C(CH_3)$_3$, rot. min.)

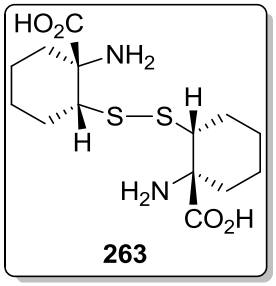
^{13}C NMR ($CDCl_3$, 100MHz) δ 204.9 (C_3, rot. maj.), 204.1 (C_3, rot. min.), 171.0 (*C*O_2Me, rot. maj.), 162.2 (*C*HO, rot. min.), 161.6 (*C*HO, rot. maj.), 74.1 (C_1, rot. maj.), 74.0 (C_1, rot. min.), 73.2 (C_8, rot. maj.), 71.0 (C_8, rot. min.), 53.8 (O*C*H_3, rot. min.), 53.3 (O*C*H_3, rot. maj.), 48.9 (C_2, rot. min.), 47.5 (C_6, rot, min.), 47.0 (C_6, rot. maj.), 43.9 (C_2, rot. maj.), 40.5 (*C*(CH_3)$_3$, rot. min.), 39.5 (*C*(CH_3)$_3$, rot. maj.), 34.9 (C_4, rot. maj.), 34.8 (C_4, rot. min.), 27.4 (C(*C*H_3)$_3$, rot. min.), 26.9 (C(*C*H_3)$_3$, rot. maj.), 24.0 (C_5, rot. min.), 22.3 (C_5, rot. maj.)

HRMS (ESI-TOF) *m*/*z*: [M + Na]$^+$ calculated for $C_{14}H_{21}NO_4SNa$ 322.1083; found 322.1081

5.5. General procedure for the hydrolysis of thiazolidines

A suspension of the corresponding thiazolidine in HCl 5 N was heated and left to stir until all the starting material was consumed. Then, the crude reaction was washed with Et_2O and the aqueous phase was concentrated under vacuum. The obtained residue was purified by ion exchange chromatography (Dowex® 50WX8 resin). The product was eluted with aqueous ammonia (6% v/v).

Synthesis of (1*R*,1'*R*,2R,2'*R*)-2,2'-Disulfanediylbis(aminocyclohexanecarboxylic acid) 263



263

Following the general procedure described above, thiazoline **259a** (0.80 g, 2.81 mmol), was suspended in HCl 5 N (20 mL). The reaction was allowed to stir under reflux for 24 hours. After purification by ionic exchange chromatography the obtained solid was dissolved in aqueous NH_3 (6% v/v) and stirred overnight. Then, the solution was evaporated off obtaining **263** (0.47 g, 1.33 mmol, 95% yield) as a white solid.

M.p.: 215-225 ºC (decomposes)

$[\alpha]_D^{23}$: +97º (c 0.9; H_2O)

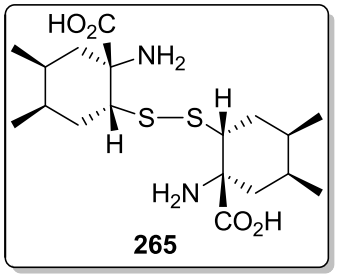
IR (KBr) v 3431, 3429, 2937, 2864, 1662, 1626, 1586, 1549, 1529, 1515, 1499, 1448, 1382, 1353, 1202 cm^{-1}

^{1}H NMR (D_2O, 400MHz) δ 3.48 (dd, *J* = 12.7, 4.5, 2H, $H_{2'}$), 2.23-2.13 (m, 2H, $H_{6'}$), 2.02 (dd, *J* = 9.1, 3.4, 4H, $H_{3'}$), 1.97-1.90 (m, 2H, $H_{4'}$), 1.82-1.73 (m, 2H, $H_{5'}$), 1.28-1.46 (m, 4H, $H_{5'}$+ $H_{6'}$), 1.42-1.28 (m, 2H, $H_{4'}$)

^{13}C NMR (D_2O, 100MHz) δ 174.9 (CO_2H), 64.6 ($C_{1'}$), 51.5 ($C_{2'}$), 33.8 ($C_{3'}$), 26.5 ($C_{6'}$), 24.9 ($C_{5'}$), 19.2 ($C_{4'}$)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{14}H_{25}N_2O_4S_2$ 349.1250; found 349.1260

Synthesis of (1*R*,1'*R*,3*S*,3'*S*,4*R*,4'*R*,6*R*,6'*R*)-6,6'-Disulfanediylbis(1-amino-3,4-dimethylcyclohexanecarboxylic acid) 265



265

Following the general procedure described above, thiazoline **260a** (85.1 mg, 0.27 mmol), was suspended in HCl 5 N (10 mL). The reaction was allowed to stir under reflux for 62 hours. After purification by ionic exchange chromatography the obtained solid was dissolved in aqueous NH_3 (6% v/v) and stirred for 19 hours. Then, the solution was evaporated off obtaining **265** (46.5 mg, 0.12 mmol, 87% yield) as a white solid.

M.p.: 300-308 ºC (decomposes)

$[\alpha]_D^{23}$: +48º (c 0.2; H_2O)

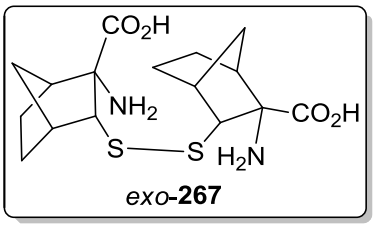
IR (KBr) v 3419-2875, 1657, 1524, 1403, 1260 cm^{-1}

^{1}H NMR (D_2O, 400MHz) δ 3.72 (dd, *J* = 13.7, 4.1, 2H, $H_{6'}$), 2.17-1.94 (m, 6H, C*H* + CH_2), 1.88-1.70 (m, 6H, C*H* + CH_2), 1.04 (d, *J* = 7.1, 6H, CH_3), 0.95 (d, *J* = 6.4, 6H, CH_3)

^{13}C NMR (D_2O, 100MHz) δ 174.9 (*C*O_2H), 65.0 ($C_{1'}$), 46.5 ($C_{6'}$), 35.7 (*C*H_2), 33.8 (CH_3), 32.6 (*C*H), 28.3 (*C*H), 18.0 (*C*H_3), 10.6 (*C*H_3)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_{18}H_{33}N_2O_4S_2$ 405.1876; found 405.1889

Synthesis of (1*R*,1'*R*,2*R*,2'*R*,3*R*,3'*R*,4*S*,4'*S*)-3,3'-Disulfanediylbis(2-aminobicyclo[2.2.1]heptane-2-carboxylic acid) *exo*-267



exo-**267**

Following the general procedure described above, thiazoline *exo*-**257a** (0.13 g, 0.45 mmol), was suspended in HCl 5 N (10 mL) in a sealed tube. The reaction was allowed to stir at 140 ºC for 14 hours. After purification by ionic exchange chromatography the obtained solid was dissolved in aqueous NH_3 (6% v/v) and stirring for 19 hours. Then, the solution was evaporated off obtaining *exo*-**267** (67.0 mg, 0.18 mmol, 78% yield) as a white solid.

M.p.: 220 ºC (decomposes)

$[\alpha]_D^{24}$: +357º (c 0.1; H_2O)

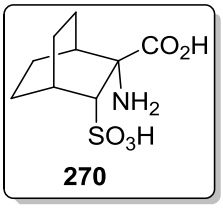
IR (KBr) v 3464-2879, 1575, 1506, 1364 cm^{-1}

^{1}H NMR (D_2O, 400MHz) δ 3.98 (dd, *J* = 3.6, 1.6, 2H, $H_{3'}$), 2.63-2.58 (m, 4H, C*H*), 2.15-2.10 (m, 2H, CH_2), 1.64-1.48 (m, 8H, CH_2), 1.44-1.37 (m, *2*H, CH_2)

^{13}C NMR (D_2O, 100MHz) δ 176.5 (*C*O_2H), 65.5 ($C_{2'}$), 58.7 ($C_{3'}$), 46.0 (*C*H), 42.2 (*C*H), 37.3 (*C*H_2), 23.1 (*C*H_2), 20.8 (*C*H_2)

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calculated for $C_{16}H_{25}N_2O_4S_2$ 373.1250; found 373.1243.

Synthesis of (1*S*,2*R*,3*R*,4*S*)-2-Amino-3-sulfobicyclo[2.2.2]octane-2-carboxylic acid 270



270

Following the general procedure described above, thiazoline **258a** (77.4 mg, 0.24 mmol), was suspended in HCl 8 N (10 mL) in a sealed tube. The reaction was allowed to stir at 140 ºC for 14 hours. After purification by ionic exchange chromatography the obtained solid was subjected to oxidation with NaI/H_2O_2. Thus, the mentioned obtained solid was dissolved in H_2O (5 mL) and H_2O_2 (35%) (34 µL, 0.39 mmol) and NaI (0.5 mg, 0.04 mmol) were added. Then, the reaction was stirring for 17 hours. Finally, the reaction was quenched with Na_2SO_3 (0.1 g). Purification by ionic exchange chromatography using water as eluent afforded the product **270** (24.4 mg, 0.10 mmol, 40% yield) as a purple solid.

M.p.: 180 ºC (decomposes)

$[\alpha]_D^{24}$: +70º (c 0.2; H_2O)

IR (KBr) v 3384-2876, 1736, 1523, 1408, 1115 cm^{-1}

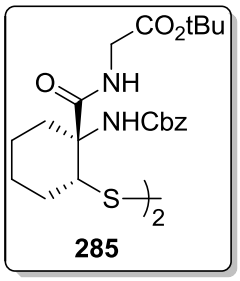
^{1}H NMR (D_2O, 400MHz) δ 3.97 (s, 1H, H_3), 2.31 (brs, 1H, C*H*), 2.17 (brs, 1H, C*H*), 2.14-2.07 (m, 2H, CH_2), 1.88-1.77 (m, 2H, CH_2), 1.75-1.58 (m, 5H, CH_2)

^{13}C NMR (D_2O, 100MHz) δ 172.5 (*C*O_2H), 61.9 (C_2), 58.3 (C_3), 32.9 (*C*H), 26.1 (*C*H), 25.1 (*C*H_2), 20.7 (*C*H_2), 19.1 (*C*H_2), 18.4 (*C*H_2)

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calculated for $C_9H_{16}NO_5S$ 250.0744; found 250.0730.

5.6. Experimental procedure for the synthesis of dipeptide 285 and lanthionine 289

Synthesis of Di-*tert*-butyl 2,2'-(((1*R*,1'*R*,2*R*,2'*R*)-2,2'-disulfanediylbis((((benzyloxy)carbonyl)amino)cyclohexanecarbonyl))bis(azanediyl))diacetate 285



285

Over a solution of **263** (78.2 mg, 0.22 mmol) in anhydrous dichloromethane (3 mL) at 0 °C, DIPEA (0.23 mL, 1.34 mmol) and TMSCl (0.11 mL, 0.90 mmol) were added. The mixture was allowed to stir for 30 minutes at 0 °C and Cbz-OSu (0.12 g, 0.49 mmol) was added. After one day, the reaction was reloaded with Cbz-OSu (0.12 g, 0.49 mmol). The reaction mixture was allowed to stir for 4 days. Then, the solvent was evaporated off and the crude was partitioned between an aqueous solution of $NaHCO_3$ (5% w/w, 5 mL) and Et_2O (5 mL). The organic phase was discarded and the aqueous phase was acidified with HCl 1 N until pH = 1. Then, the aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic layers were washed with water (5 mL), dried under anhydrous $MgSO_4$, filtered off and concentrated under vacuum. The obtained solid was subjected to react without further purification. Thus, over a solution of the obtained residue (0.14 g, 0.23 mmol), HATU (0.26 g, 0.69 mmol), HOAt (93.3 mg, 0.69 mmol) and H-Gly-O^{t}Bu·HCl (0.12 g, 0.69 mmol) in anhydrous DMF (1 mL), DIPEA (0.16 mL, 0.91 mmol) was added. The reaction mixture was allowed to react for 3 days and EtOAc (15 mL) was added. This organic solution was washed with Brine (4 x 10 mL) and the organic phase obtained was dried over anhydrous $MgSO_4$, filtered off and evaporated under vacuum. The obtained residue was purified by column chromatography (EtOAc/hexane 30/70) to give the dipeptide **285** (95.0 mg, 0.11 mmol, 50% yield in two reaction steps) as a white solid.

M.p.: 54-56 ºC

$[\alpha]_D^{23}$: +27º (*c* 0.9; $CHCl_3$)

IR (KBr) v 3336, 1728, 1661, 1504, 1454, 1367, 1239, 1219, 1152 cm^{-1}

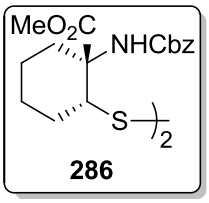
^{1}H NMR ($CDCl_3$, 400MHz) δ 7.40-7.31 (m, 10H, H_{Ph}), 7.18 (brs, 2H, N*H*), 5.59 (brs, 2H, N*H*), 5.14 (s, 4H, CH_2Ph), 3.95 (dd, *J* = 18.3, 5.1, 2H, CH_2-CO$_2$^{t}Bu),

3.84 (dd, *J* = 18.3, 4.5, 2H, C*H*$_2$-CO$_2$^{t}Bu), 3.55 (dd, *J* = 12.0, 3.4, 2H, H$_2$), 2.82 (d, *J* = 11.5, 2H, C*H*$_2$), 2.05-1.97 (m, 2H, C*H*$_2$), 1.79-1.70 (m, 4H, C*H*$_2$), 1.59-1.22 (m, 10H, C*H*$_2$), 1.45 (s, 18H, C(C*H*$_3$)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.4 (*C*O$_2$^{t}Bu), 168.6 (*C*ONH), 155.5 (*C*ONH), 136.3 (C_{qPh},), 128.7 (C_{Ph}), 128.33 (C_{Ph}), 128.26 (C_{Ph}), 82.2 (*C*(CH$_3$)$_3$), 67.2 (*C*H$_2$Ph), 63.9 (C_1), 53.6 (C_2), 42.8 (*C*H$_2$-CO$_2$^{t}Bu), 31.5 (*C*H$_2$), 28.2 (C(*C*H$_3$)$_3$), 27.1 (*C*H$_2$), 25.3 (*C*H$_2$), 20.4 (*C*H$_2$)

HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calculated for $C_{42}H_{58}N_4O_{10}S_2Na$ 865.3487; found 865.3465

Synthesis of (1*R*,1'*R*,2*R*,2'*R*)-Dimethyl 2,2'-disulfanediylbis((((benzyloxy)carbonyl)amino)cyclohexanecarboxylate) 286.



286

Over a solution of **263** (0.14 g, 0.40 mmol) in anhydrous dichloromethane (7 mL) at 0 ºC, DIPEA (0.41 mL, 2.40 mmol) and TMSCl (0.20 mL, 1.60 mmol) were added. The mixture was allowed to stir for 30 minutes at 0 ºC and Cbz-OSu (0.22 g, 0.87 mmol) was added. After one day, the reaction was reloaded with Cbz-OSu (0.22 g, 0.87 mmol). The reaction mixture was allowed to stir for 4 days. Then, the solvent was evaporated off and the crude was partitioned between an aqueous solution of $NaHCO_3$ (5% w/w, 5 mL) and Et_2O (5 mL). The organic phase was discarded and the aqueous phase was acidified with HCl 1 N until pH=1. Then, the aqueous phase was extracted with EtOAc (3 x 15 mL) and the combined organic layers were washed with water (5 mL), dried under anhydrous $MgSO_4$, filtered off and concentrated under vacuum. The obtained solid was subjected to react without further purification. Thus, over a solution of the obtained residue (0.22 g, 0.36 mmol) in toluene and methanol (2/1, 4.5 mL), trimethylsilyldiazomethane (1.07 mL, 2.14 mmol) was added. The reaction mixture was allowed to react for 2 hours. Then, SiO_2 was added in order to quench the excess of diazocompound, the crude reaction was filtered off and the solvent evaporated under vacuum. The obtained solid was purified by column chromatography (EtOAc/Hexane 20/80) to give **286** (0.17 g, 0.26 mmol, 66% yield in two reaction steps) as a colourless oil.

$[\alpha]_D^{23}$: +125º (*c* 0.8; $CHCl_3$)

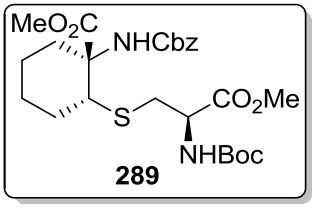
IR (neat) v 3362, 1714, 1497, 1450, 1280, 1225, 1055 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.36-7.29 (m, 10H, H_{Ph}), 5.34 (brs, 2H, N*H*), 5.13 (d, *J* = 12.2, 2H, CH_2Ph), 5.06 (d, *J* = 12.3, 2H, CH_2Ph), 3.68 (s, 6H, OCH_3), 3.36 (dd, *J* = 11.4, 3.4, 2H, H_2), 2.83 (d, *J* = 12.0, 2H, CH_2), 2.03-1.98 (m, 2H, CH_2), 1.85-1.79 (m, 2H, CH_2), 1.74-1.73 (m, 2H, CH_2), 1.59-1.39 (m, 8H, CH_2)

^{13}C NMR ($CDCl_3$, 100MHz) δ 172.9 (*C*O_2Me), 155.6 (*C*ONH), 136.5 (C_{qPh},), 128.6 (C_{Ph}), 128.22 (C_{Ph}), 128.18 (C_{Ph}), 66.8 (*C*H_2Ph), 62.9 (C_1), 55.1 (C_2), 52.8 (OCH_3), 32.1 (*C*H_2), 27.7 (*C*H_2), 25.4 (*C*H_2), 20.3 (*C*H_2)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{32}H_{40}N_2O_8S_2Na$ 667.2118; found 667.2131

Synthesis of (1*R*,2*R*)-Methyl 1-(((benzyloxy)carbonyl)amino)-2-(((*R*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)thio)cyclohexanecarboxylate 289



Over a solution of **286** (0.12 g, 0.18 mmol) in THF (4 mL) and water (0.2 mL), PBu_3 (52 µL, 0.20 mmol) was added and the reaction mixture was allowed to stir for 5 minutes at room temperature. The solvent was evaporated under vacuum and the reaction crude was purified by column chromatography in (EtOAc/Hexane 10/90). The obtained thiol **287** was quickly employed in the next reaction in order to prevent the formation of the disulfide bridge. Thus, over a solution of the thiol **287** (0.10 g, 0.32 mmol) and the bromide **288** (0.23 g, 0.65 mmol) in EtOAc (5 mL) a solution of Cs_2CO_3 (0.42 g, 1.32 mmol) in H_2O (2 mL, pH ≈ 12) was added and after that $Bu_4N{\cdot}HSO_4$ (0.44 g, 1.30 mmol) was added. The reaction mixture was allowed to stir at room temperature for 20 hours. Then, the phases were separated and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with saturated $NaHCO_3$ aqueous solution (5 mL) and Brine (5 mL). The final organic layer was dried under $MgSO_4$ anhydrous, filtered off and concentrated under vacuum. The obtained solid was purified by column chromatography (CH_2Cl_2/Et_2O 93/7) to afford **289** (0.10 g, 0.19 mmol, 53% yield in two reaction stpes) as a colourless oil.

$[\alpha]_D^{25}$: +39º (*c* 0.7; $CHCl_3$)

IR (neat) v 3358, 1710, 1497, 1452, 1280, 1222, 1160, 1054 cm^{-1}

^{1}H NMR ($CDCl_3$, 400MHz) δ 7.37-7.29 (m, 5H, H_{Ph}), 5.34 (d, *J* = 7.2, 1H, *N*HBoc), 5.18 (s, 1H, *N*HCbz), 5.12 (d, *J* = 12.2, 1H, C*H*$_2$Ph), 5.08 (d, *J* = 12.6, 2H, C*H*$_2$Ph), 4.50-4.49 (m, 1H, C*H*-CH_2S), 3.74 (s, 3H, OC*H*$_3$), 3.73 (s, 3H, OC*H*$_3$), 3.26 (dd, *J* = 11.2, 3.7, 1H, H_2), 2.93 (dd, *J* = 13.8, 4.5, 1H, C*H*$_2$), 2.87 (dd, *J* = 13.7, 4.9, 1H, C*H*$_2$S), 2.79 (d, *J* = 11.1, 1H, C*H*$_2$S), 1.93-1.80 (m, 2H, C*H*$_2$), 1.73-1.70 (m, 1H, C*H*$_2$), 1.61-1.51 (m, 2H, C*H*$_2$), 1.47-1.36 (m, 2H, C*H*$_2$), 1.44 (s, 9H, C(C*H*$_3$)$_3$)

^{13}C NMR ($CDCl_3$, 100MHz) δ 173.1 (*C*O_2Me), 171.1 (*C*O_2Me), 155.8 (*C*ONH), 155.1 (*C*ONH), 136.5 (C_{qPh},), 128.6 (C_{Ph}), 128.2 (C_{Ph}), 80.4 (*C*(CH_3)$_3$), 66.8 (*C*H_2Ph), 63.5 (C_1), 53.9 (*C*H-CH_2S), 52.8 (O*C*H_3), 52.7 (O*C*H_3), 53.9 (C_2), 34.0 (*C*H_2), 31.8 (*C*H_2), 29.6 (*C*H_2), 28.4 (C(*C*H_3)$_3$), 25.2 (*C*H_2), 20.3 (*C*H_2)

HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calculated for $C_{25}H_{36}N_2O_8SNa$ 547.2085; found 547.2091

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CONCLUSIONS

1. A general methodology for the synthesis of homochiral thiazolines in multigram scale, in which the sulfur atom possesses a different oxidation level, indeed as sulfanyl, sulfinyl or sulfonyl group, has been successfully developed starting from the readily available *L*-Cysteine.

2. The preparation of modified cyclic α,β-substituted cysteines with different nature and ring size has been achieved with good results. Such analogues have been obtained starting from the cited homochiral thiazolines by means of cycloaddition reactions such as 1,3-dipolar cycloadditions with diazoalkanes, nitrones and azomethine ylides as dipoles or Diels-Alder cycloaddition reactions with dienes. In this sense, the synthesis of enantiopure cysteine analogues incorporating a cyclopropane ring between the positions α and β has been accomplished by the 1,3-dipolar cycloaddition reaction employing diazolkanes and the subsequent nitrogen extrusion of the *exo*-Δ^1-pyrazoline intermediate. The incorporation of heterocyclic rings between the positions α and β of the cysteine backbone has also been achieved through 1,3-dipolar cycloadditions using nitrones and α-imino esters, to give the corresponding bicyclics isoxazolidine-thiazolidine *exo* cycloadducts and pyrrolidine-thiazolidine *endo* cycloadducts, respectively. Diels-Alder reaction between the homochiral sulfinyl and sulfonyl thiazolines and dienes under thermic activation gave the corresponding cycloadducts in good to excellent yields and excellent diastereoselectivities in favour of *exo* cycloadducts. The subsequent appropriate synthetic sequence of reductions and hydrolysis afforded the enantiomerically pure cysteines analogues incorporating cyclohexane and norbornane rings between α and β positions. The results depended on the thiazoline starting material. Therefore, the oxidation of the sulfur atom as sulfanyl, sulfinyl or sulfonyl moieties had a key role. In fact, the 1,3-dipolar cycloadditions starting from the sulfanyl thiazoline afforded worst chemical yield and diastereoselectivity in comparison with the obtained from the sulfinyl and sulfonyl thiazolines.

The high diastereoselectivity observed in these reactions could be explained in terms of the so-called self-regeneration of chirality and provides evidence of the synthetic usefulness of this kind of thiazolines in cycloaddition reactions. The enhancement of the reactivity and sometimes the *exo*/*endo* diastereoselectivity and regioselectivity of the reaction (nitrones and

azomethine ylides as dipoles) could be explained due to stereo-electronic effects of either sulfinyl or sulfonyl moieties.

The computational study for the 1,3-dipolar cycloaddition reactions between homochiral thiazolines and diazoalkanes and nitrones as well as the computational calculations for the Diels-Alder cycloaddition were in excellent agreement with experimental observations.

3. The reduction of the sulfinyl moiety of the cycloadducts to sulfanyl group allowed us to obtain the corresponding bicyclic or tricyclic cysteine precursors as thiazolidine moiety fused with rings of different size and nature (carbocyclic or heterocyclic).

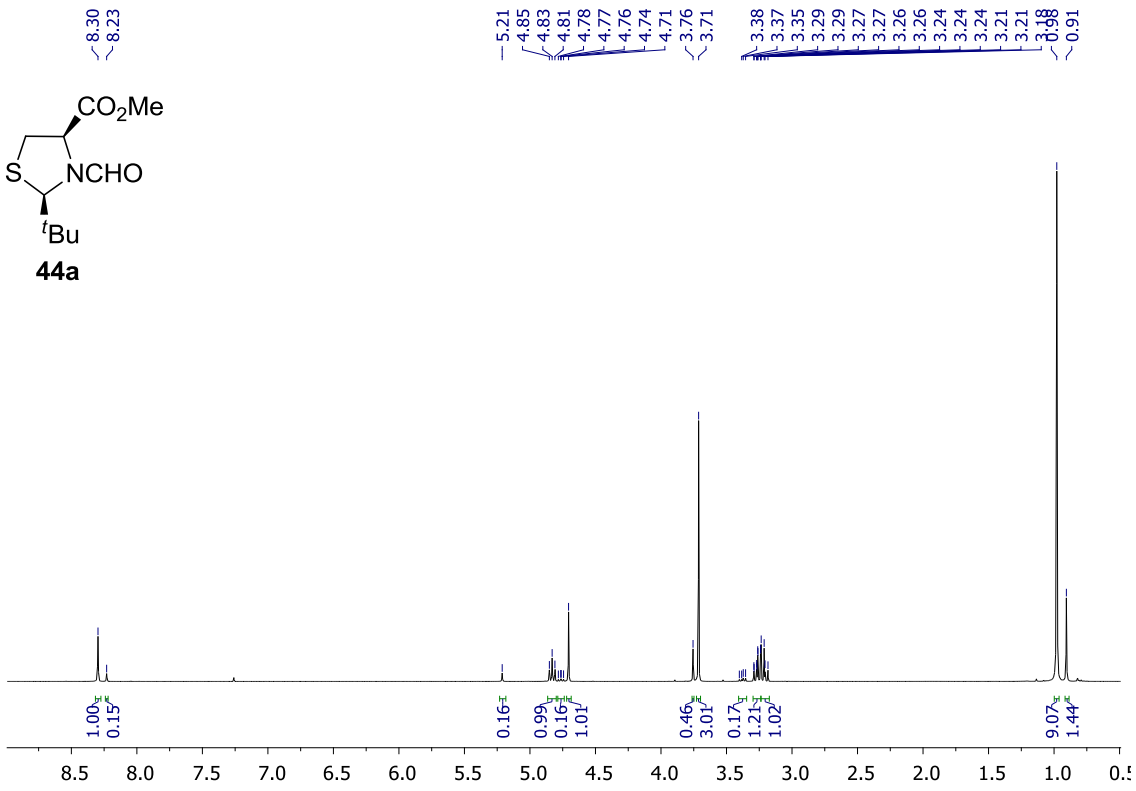
Finally, the thiazolidine ring cleavage and deprotection of the functional groups from the Diels-Alder cycloadduts was achieved with satisfactory results upon treatment with concentrated hydrogen chloride. In addition, the modified cysteine bearing a cyclohexane scaffold between α and β carbons was employed for the preparation of glutathione and lanthionine analogues. Within this context, a modified lanthionine was successfully obtained as single enantiomer.

Appendix

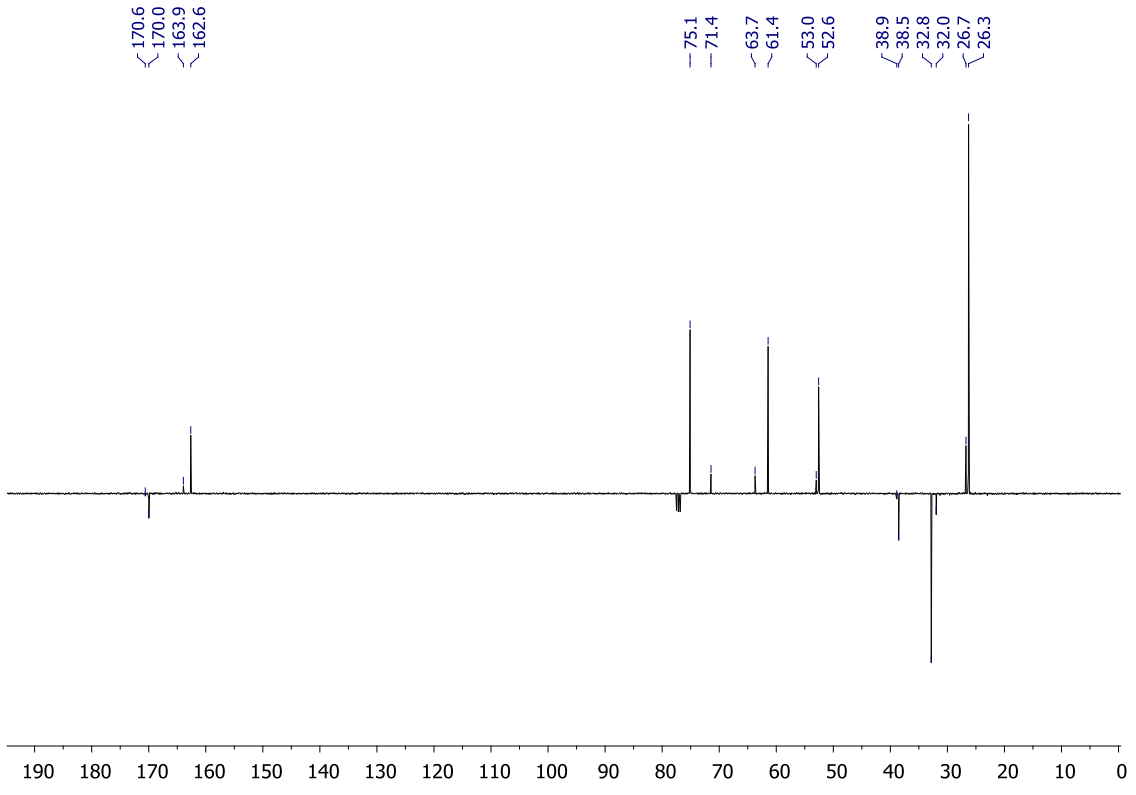
Table of contents

NMR spectra of Chapter II

(2*R*,4*R*)-Methyl 2-*tert*-butyl-3-formyl-1,3-thiazolidin-4-carboxylate (44a)

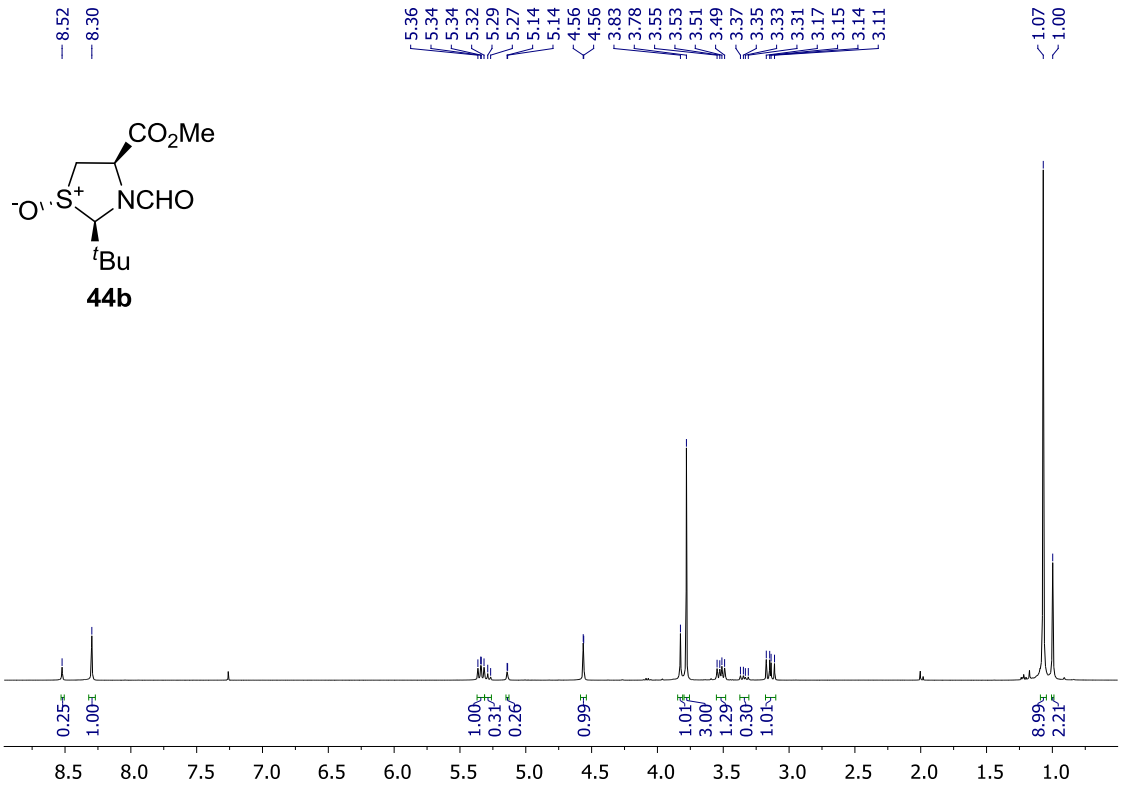


^{1}H-NMR ($CDCl_3$, 400 MHz)



^{13}C-NMR ($CDCl_3$, 100 MHz)

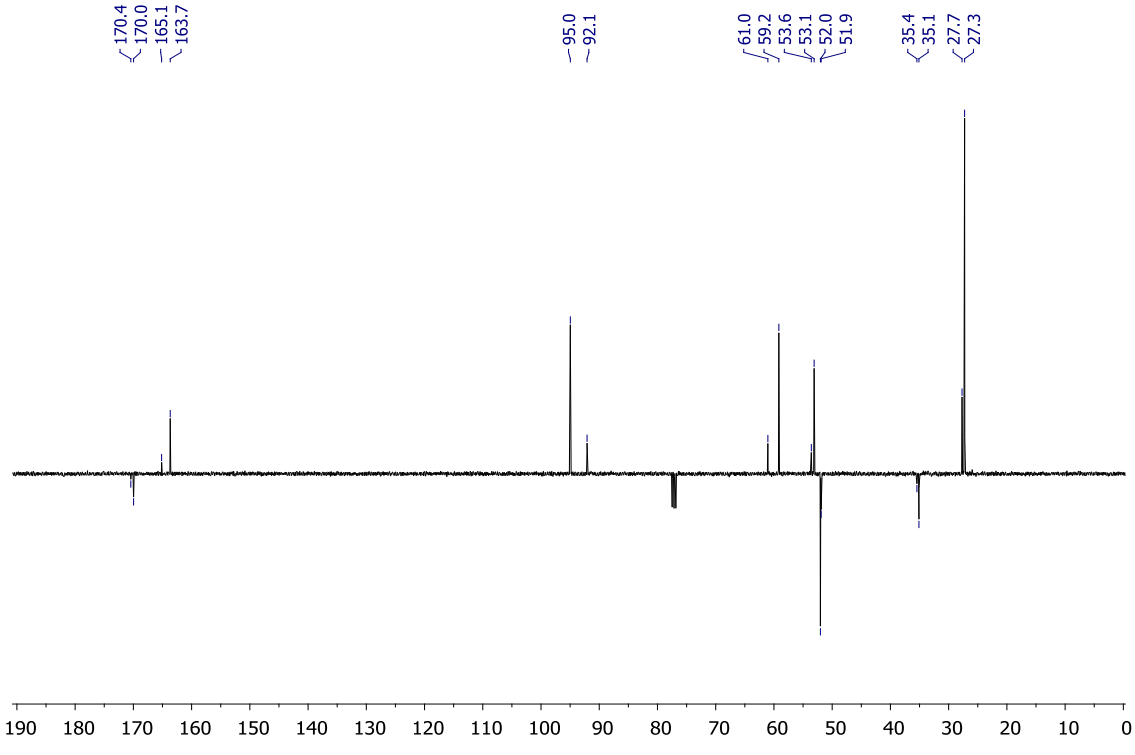
(1*R*,2*R*,4*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-1,3-thiazolidin-4-carboxylate (44b)



CO_2Me, ^-O, S^+, NCHO, ^{t}Bu

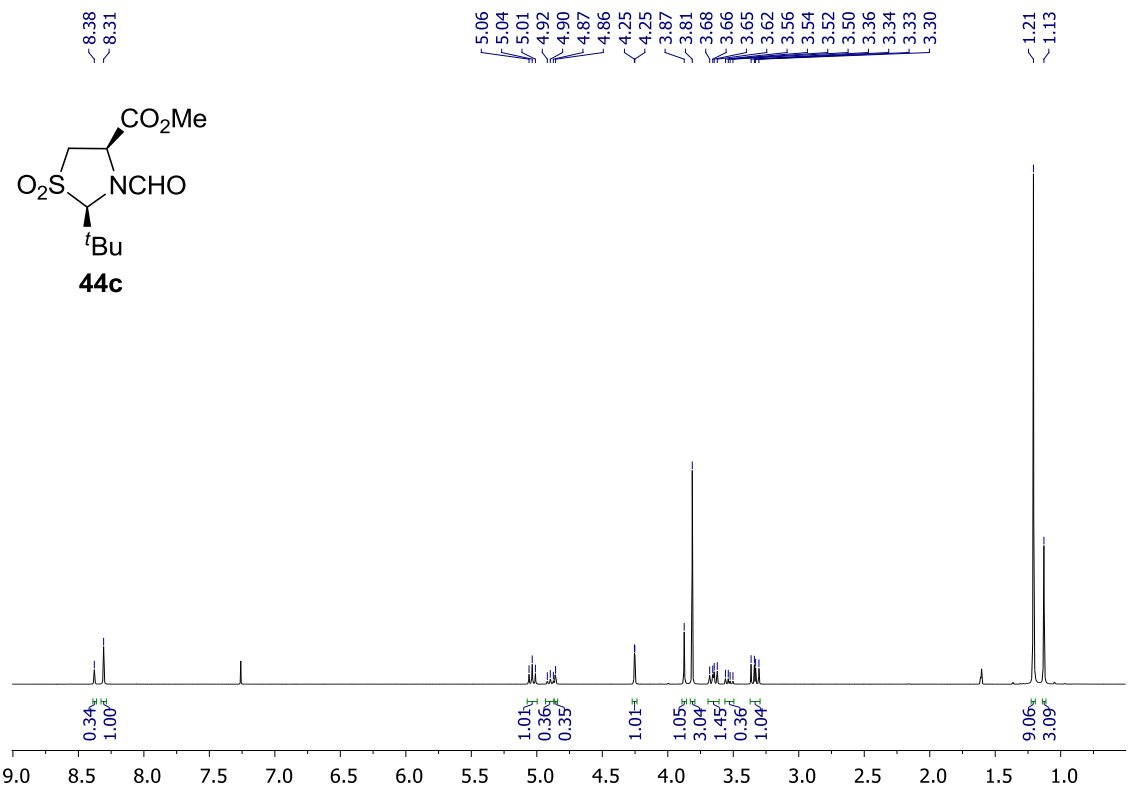
44b

^{1}H-NMR ($CDCl_3$, 400 MHz)

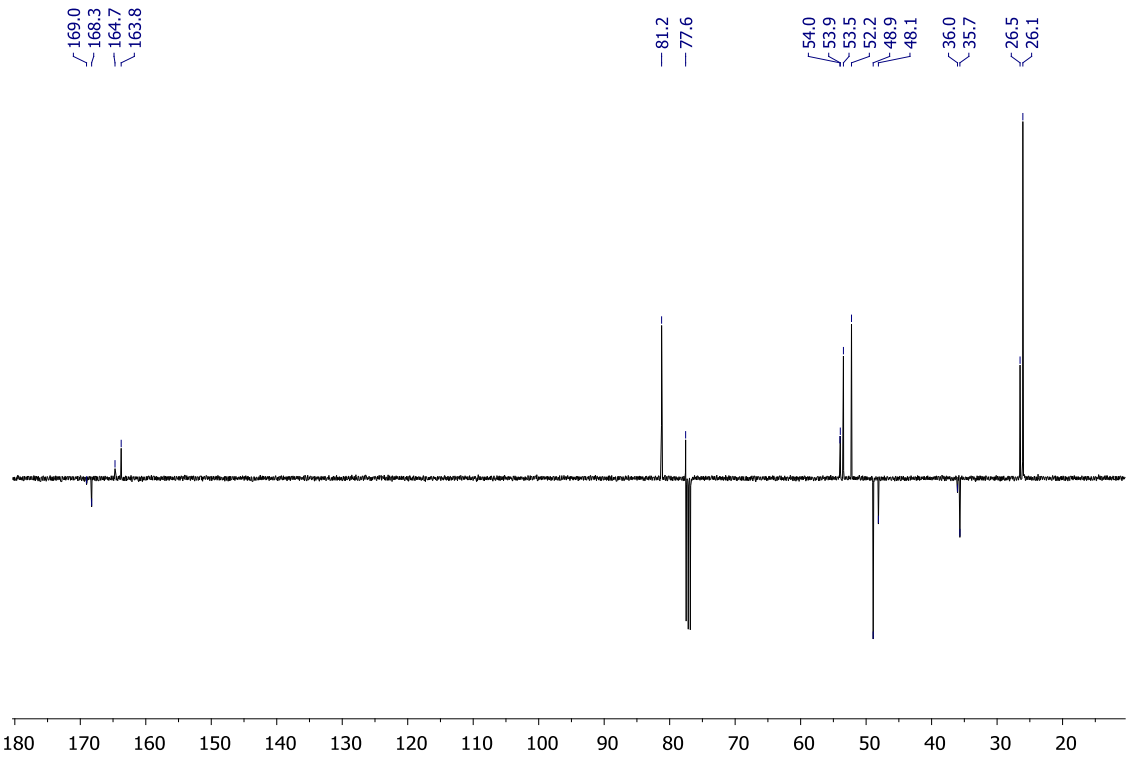


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,4*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-1,3-thiazolidin-4-carboxylate (44c)

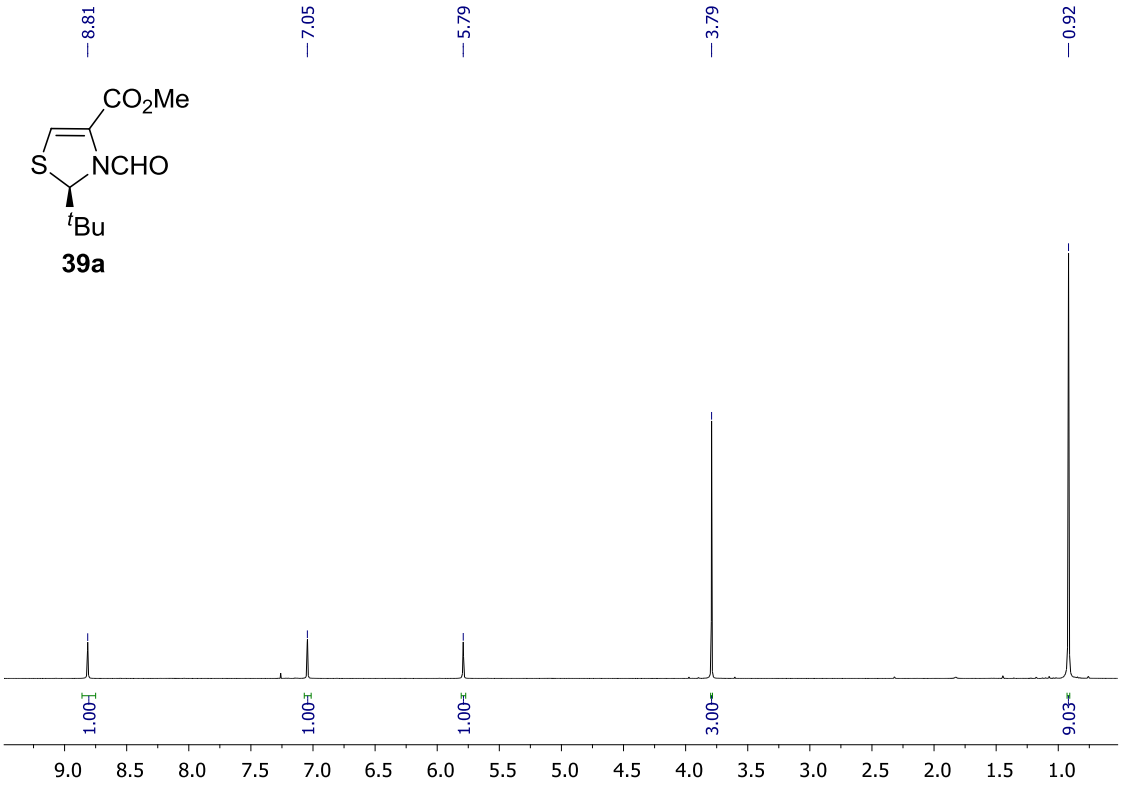


^{1}H-NMR ($CDCl_3$, 400 MHz)

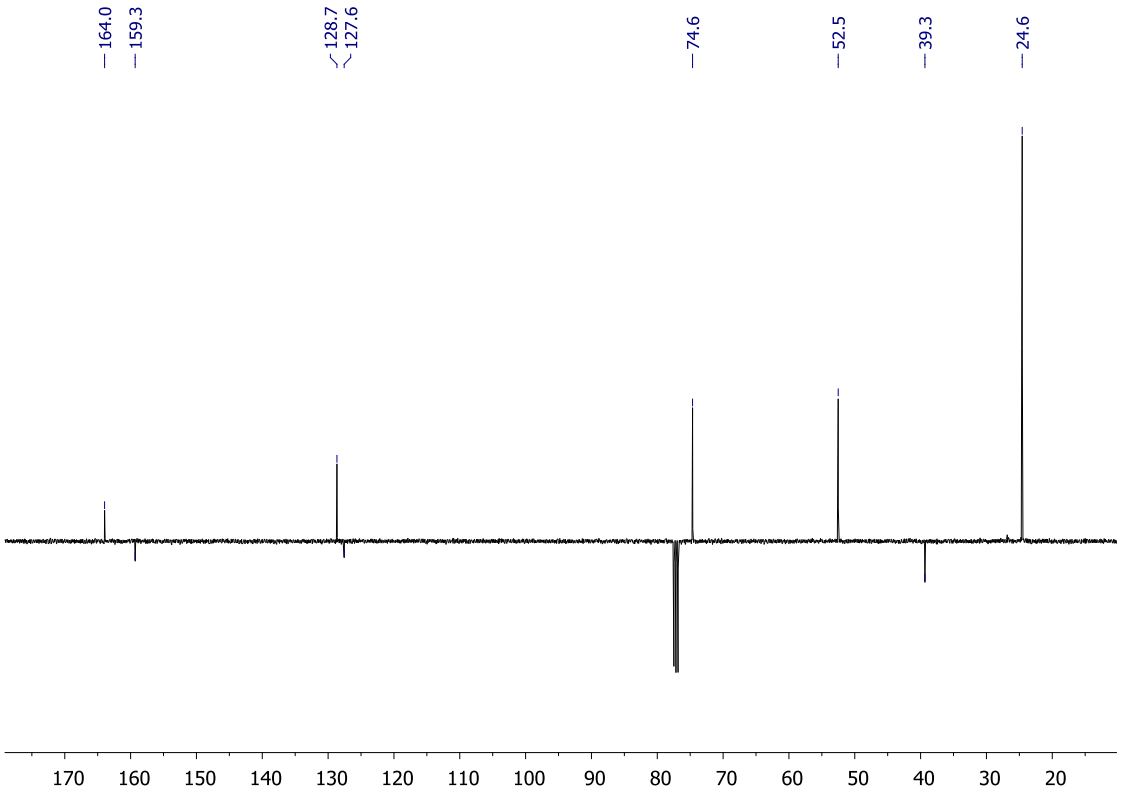


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*)-Methyl 2-*tert*-butyl-3-formyl-2,3-dihydro-1,3-thiazol-4-carboxylate (39a)

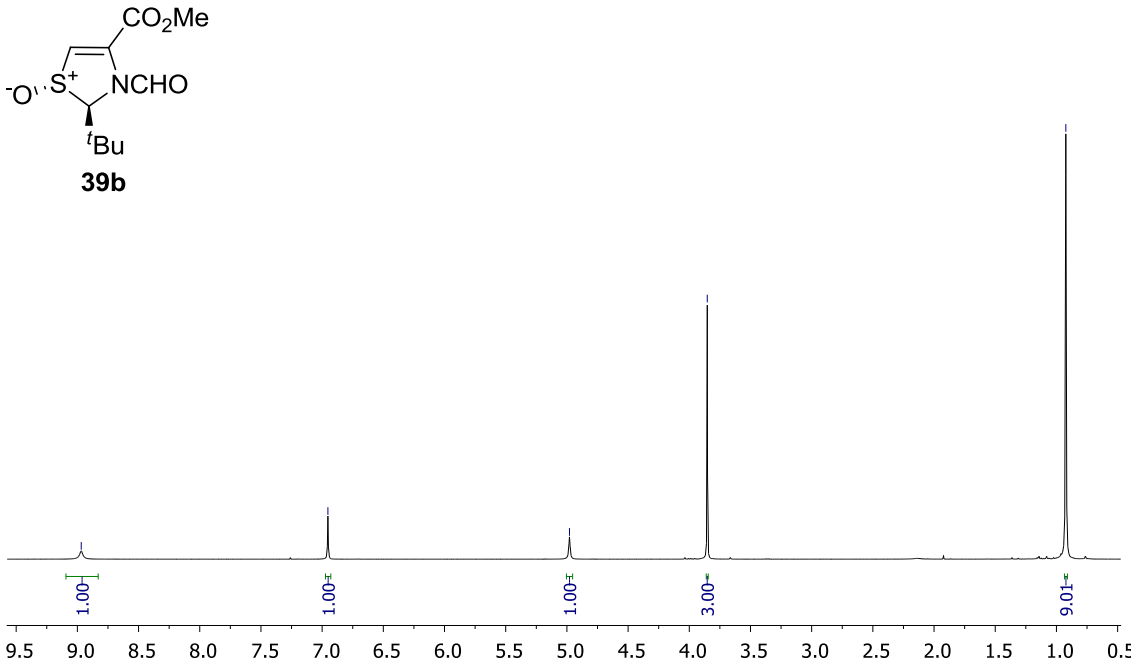


^{1}H-NMR ($CDCl_3$, 400 MHz)

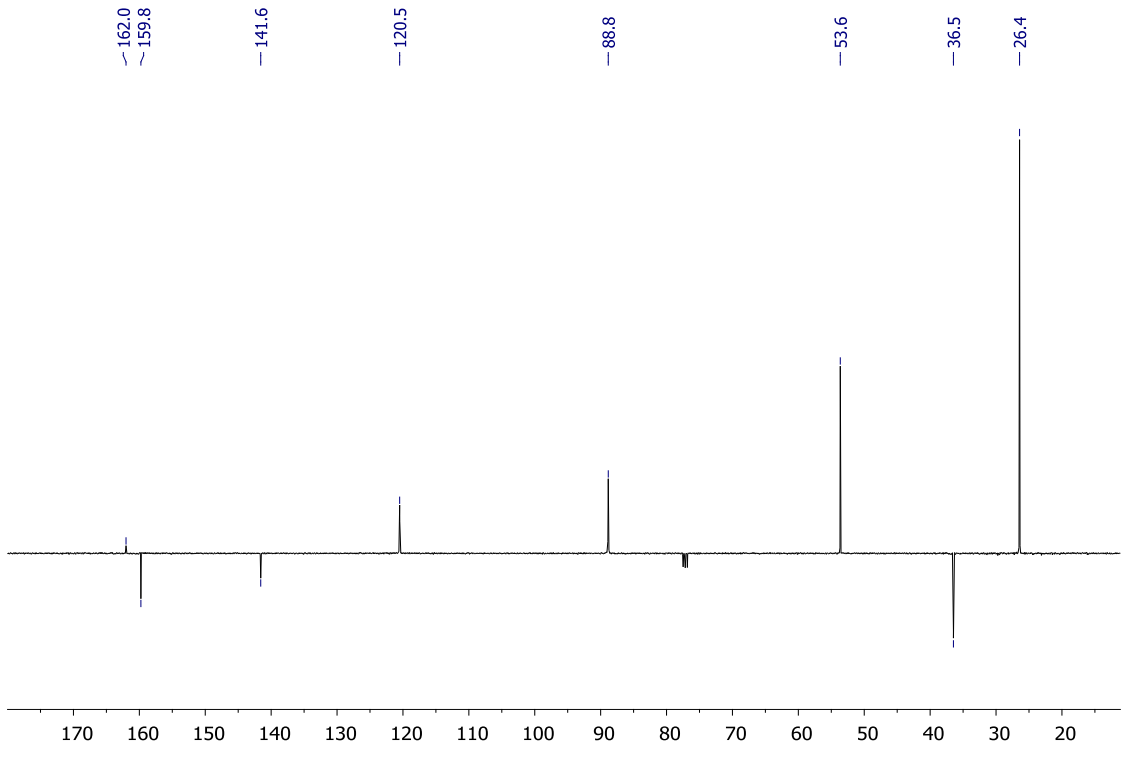


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3-dihydro-1,3-thiazol-4-carboxylate (39b)

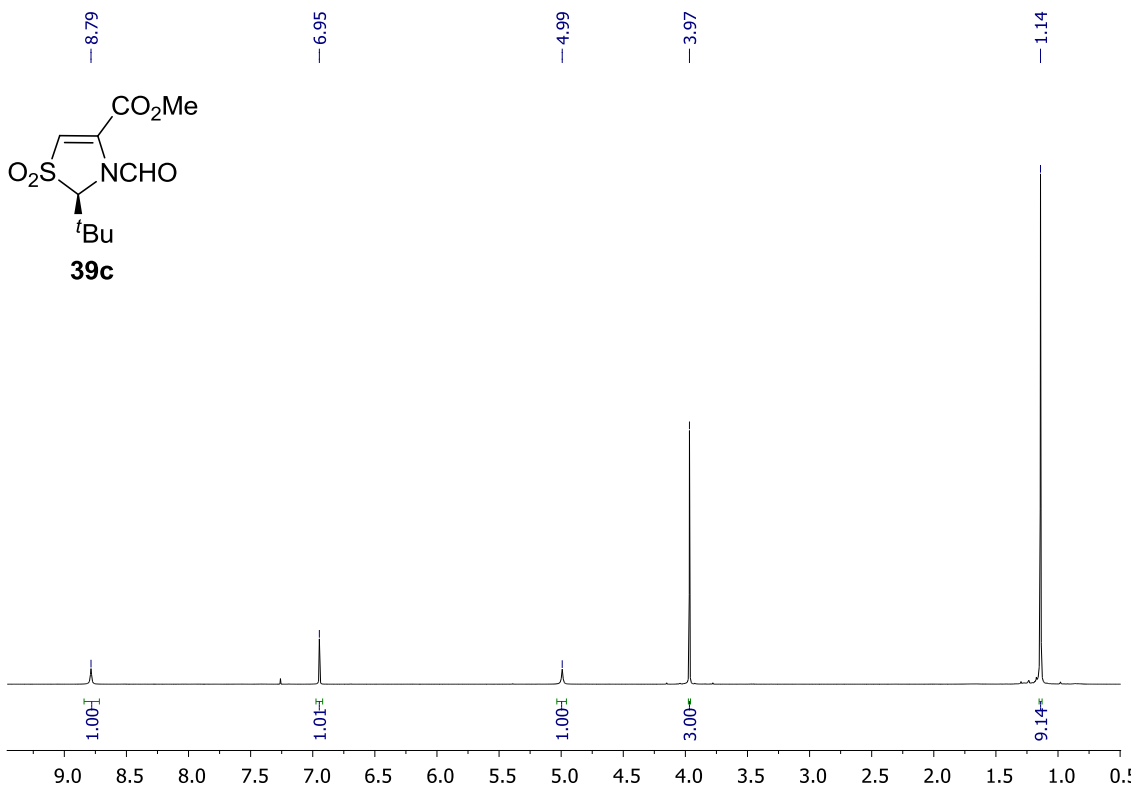


^{1}H-NMR ($CDCl_3$, 400 MHz)

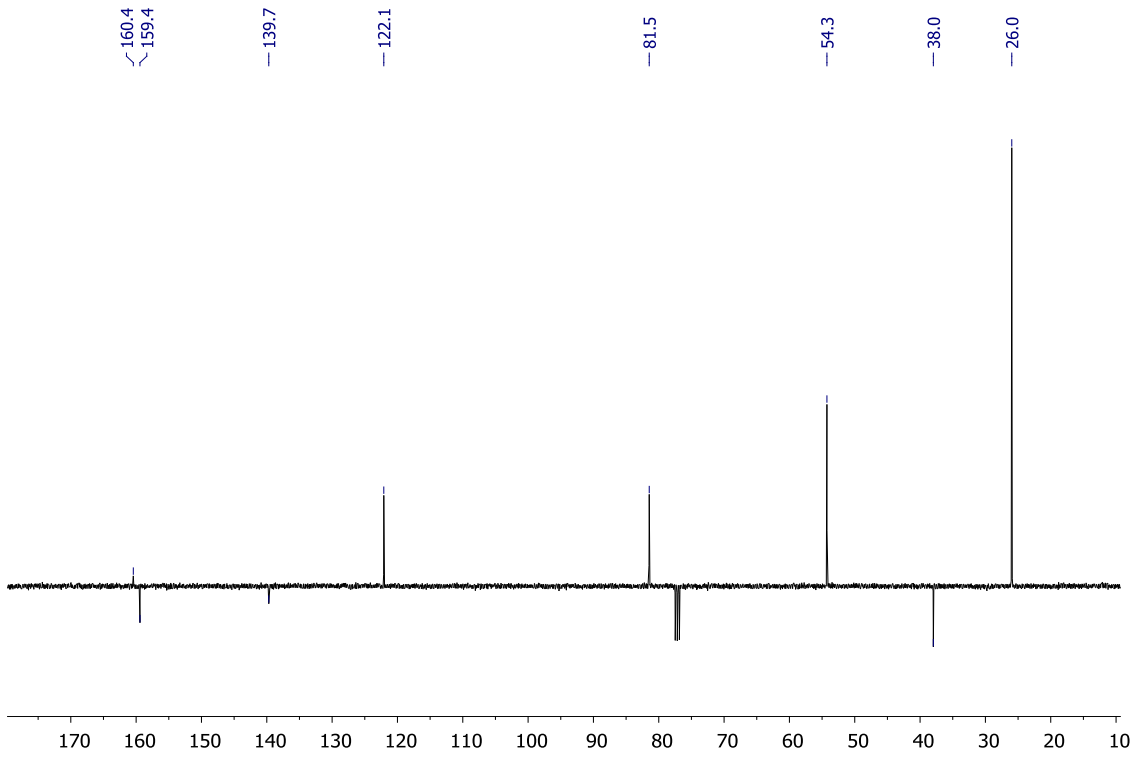


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3-dihydro-1,3-thiazol-4-carboxylate (39c)



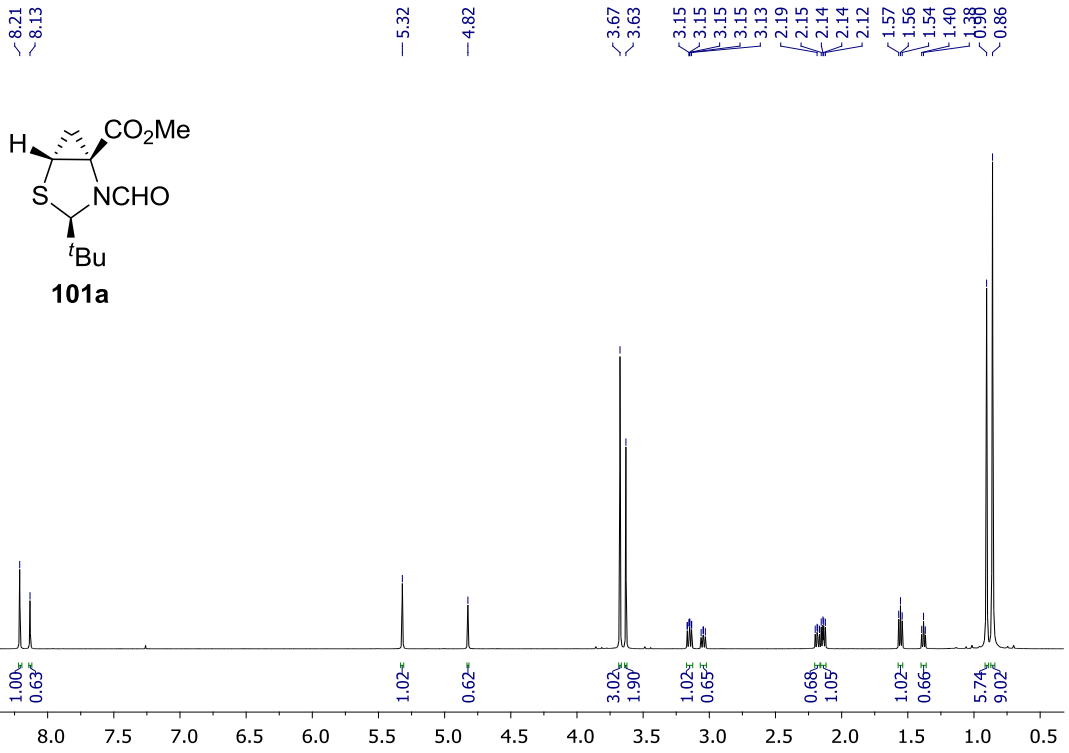
^{1}H-NMR ($CDCl_3$, 400 MHz)



^{13}C-NMR ($CDCl_3$, 100 MHz)

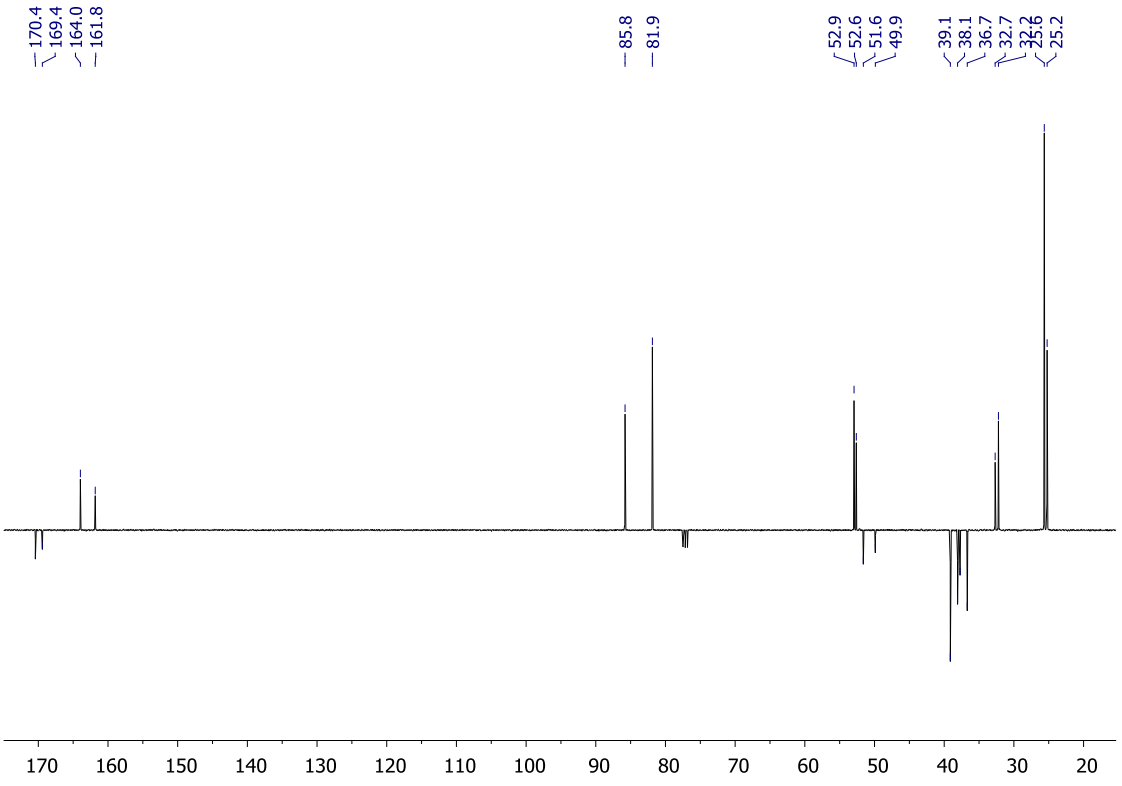
NMR spectra of Chapter III

(1*R*,3*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4-thia-2-azabicyclo[3.1.0]hexan-1-carboxylate (101a)



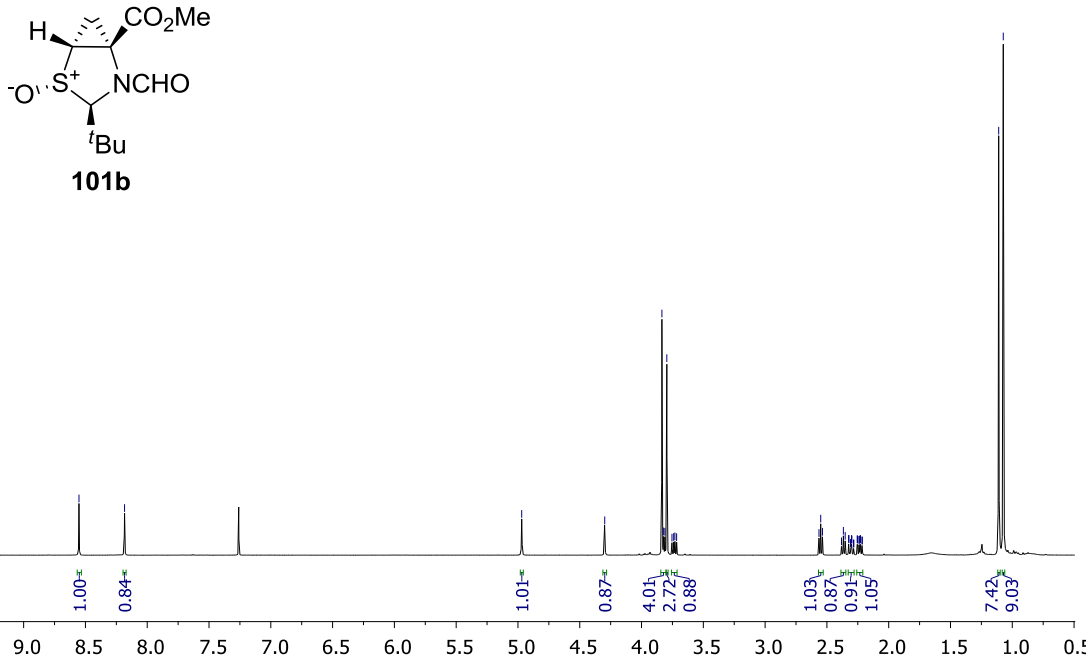
101a

^{1}H-NMR ($CDCl_3$, 400 MHz)



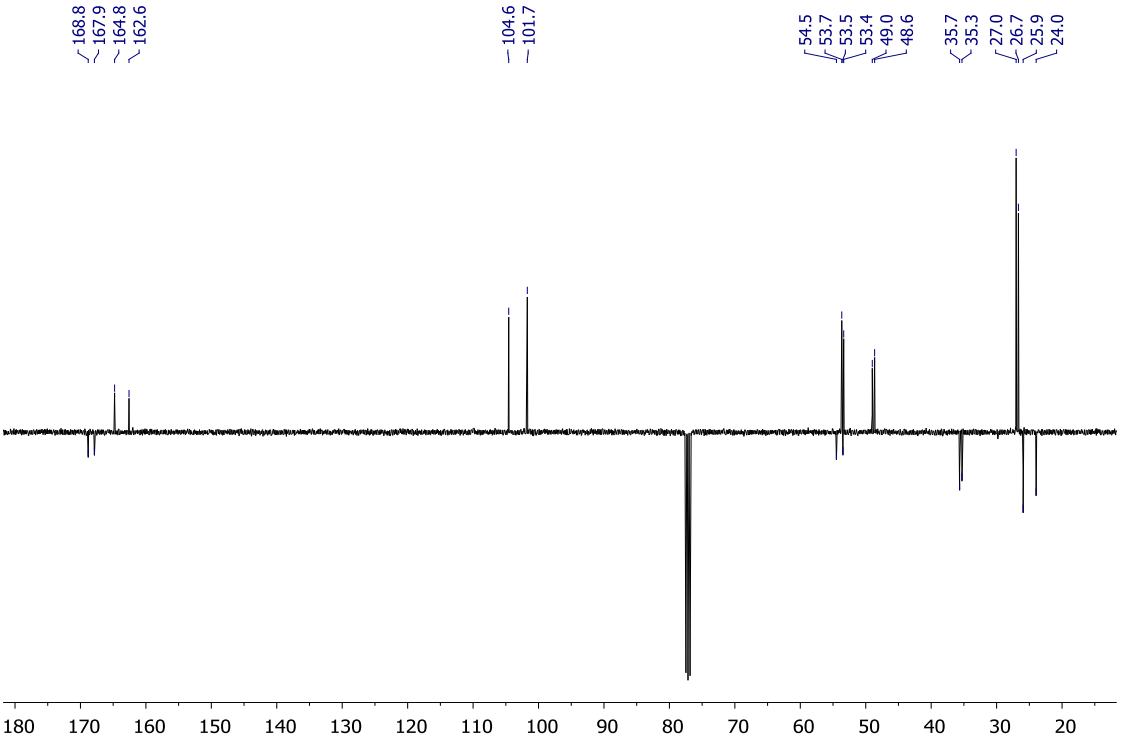
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*R*,4*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4-oxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate (101b)



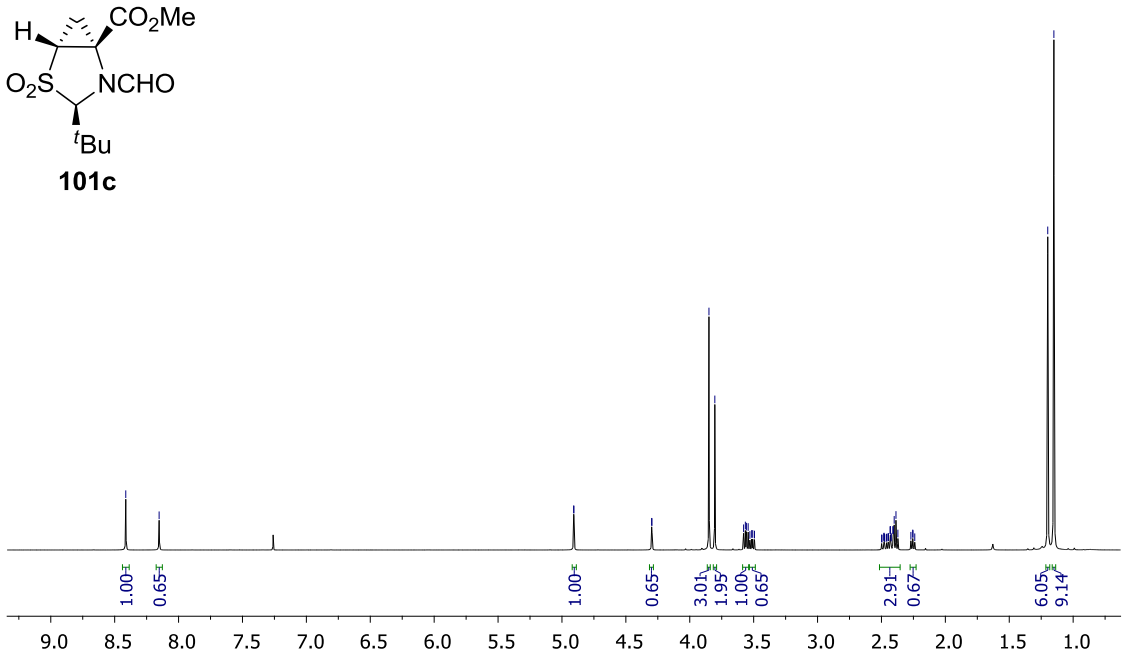
101b

^{1}H-NMR ($CDCl_3$, 400 MHz)



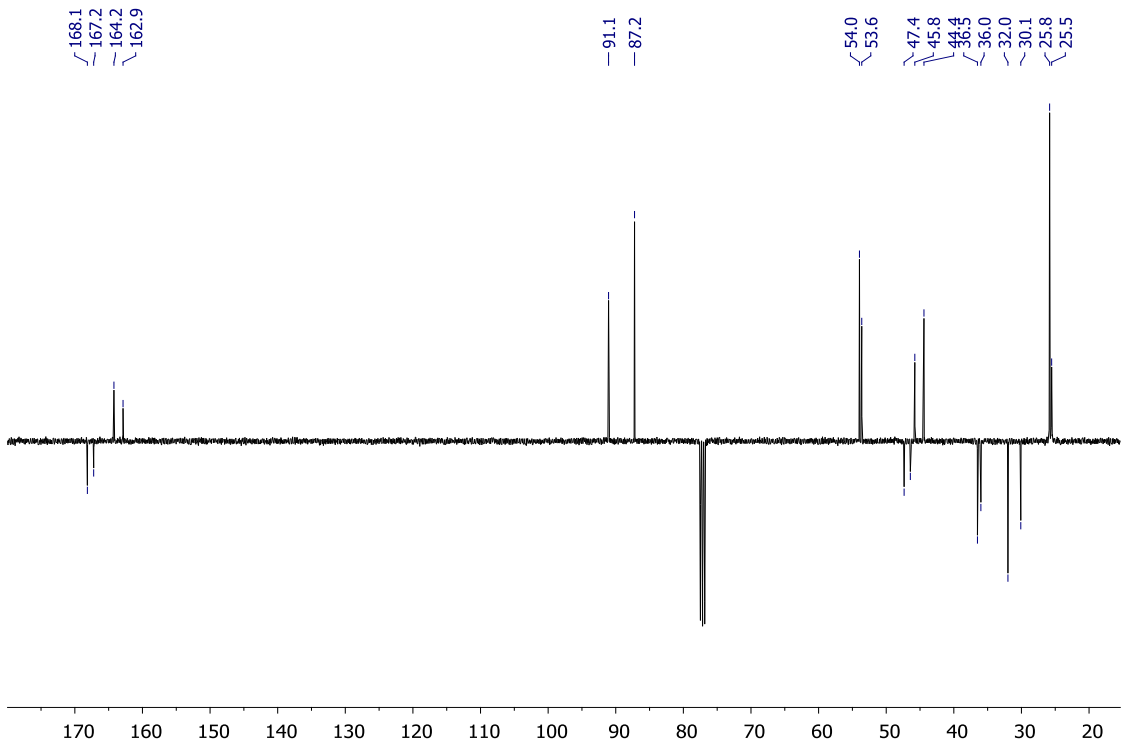
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*R*,5*R*)-Methyl 3-*tert*-butyl-2-formyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate (101c)



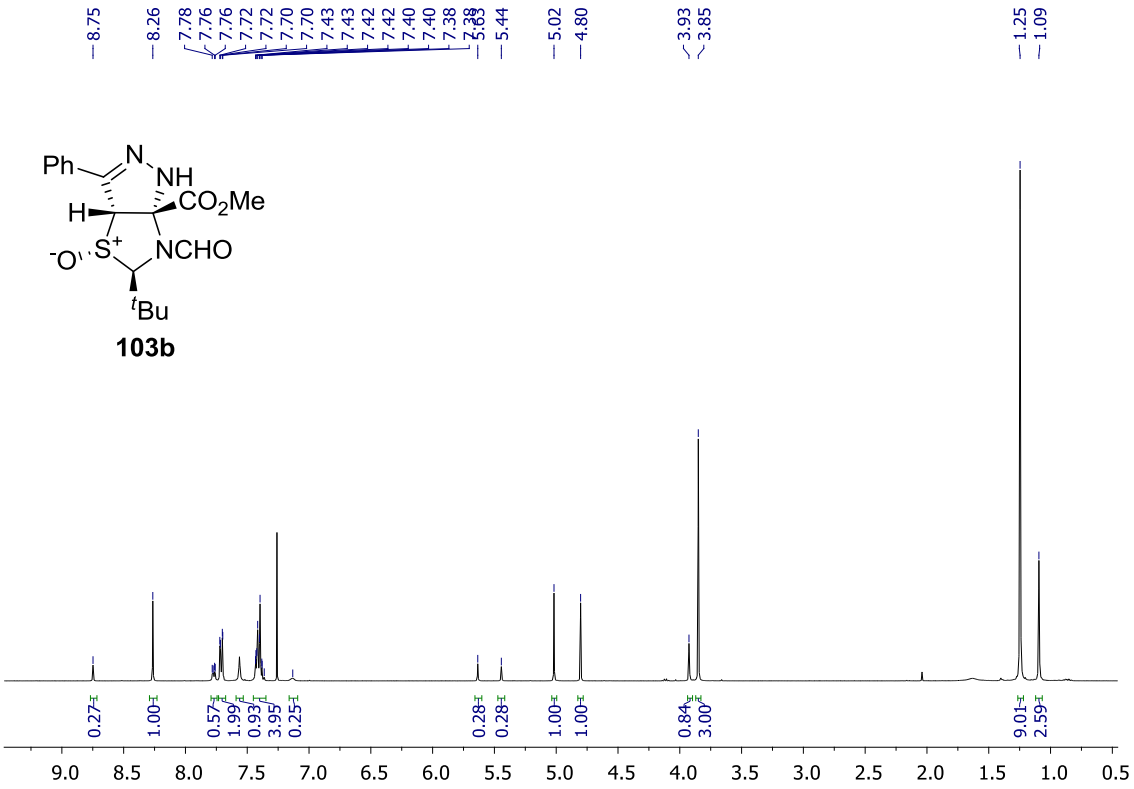
101c

^{1}H-NMR ($CDCl_3$, 400 MHz)

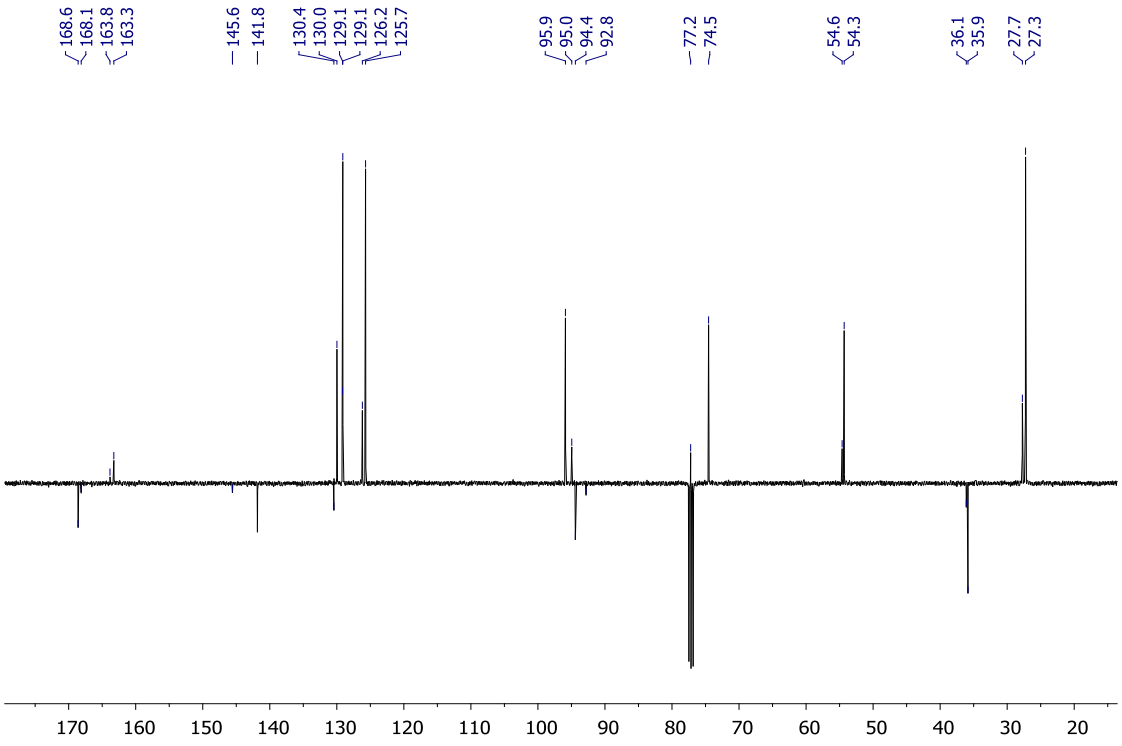


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3a*S*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4-oxido-3-phenyl-3a,5,6,6a-tetrahydro-1*H*-pyrazolo[3,4-*d*]thiazole-6a-carboxylate (103b)

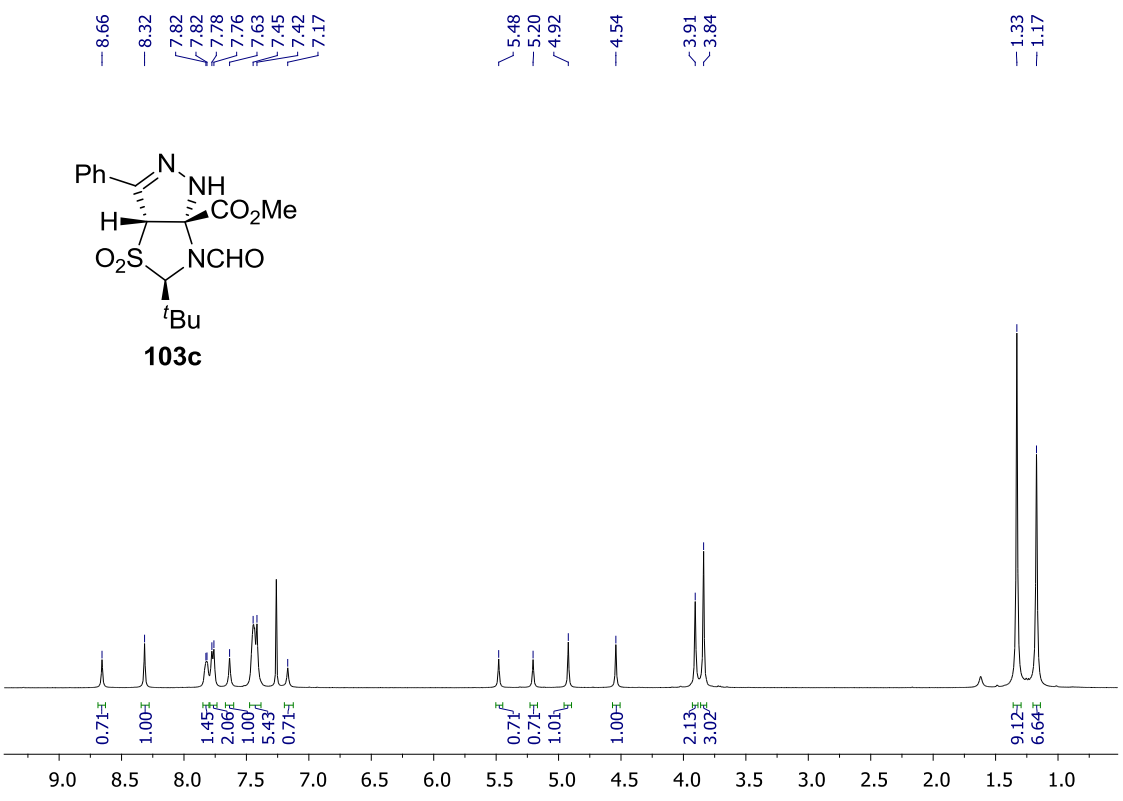


^{1}H-NMR ($CDCl_3$, 400 MHz)

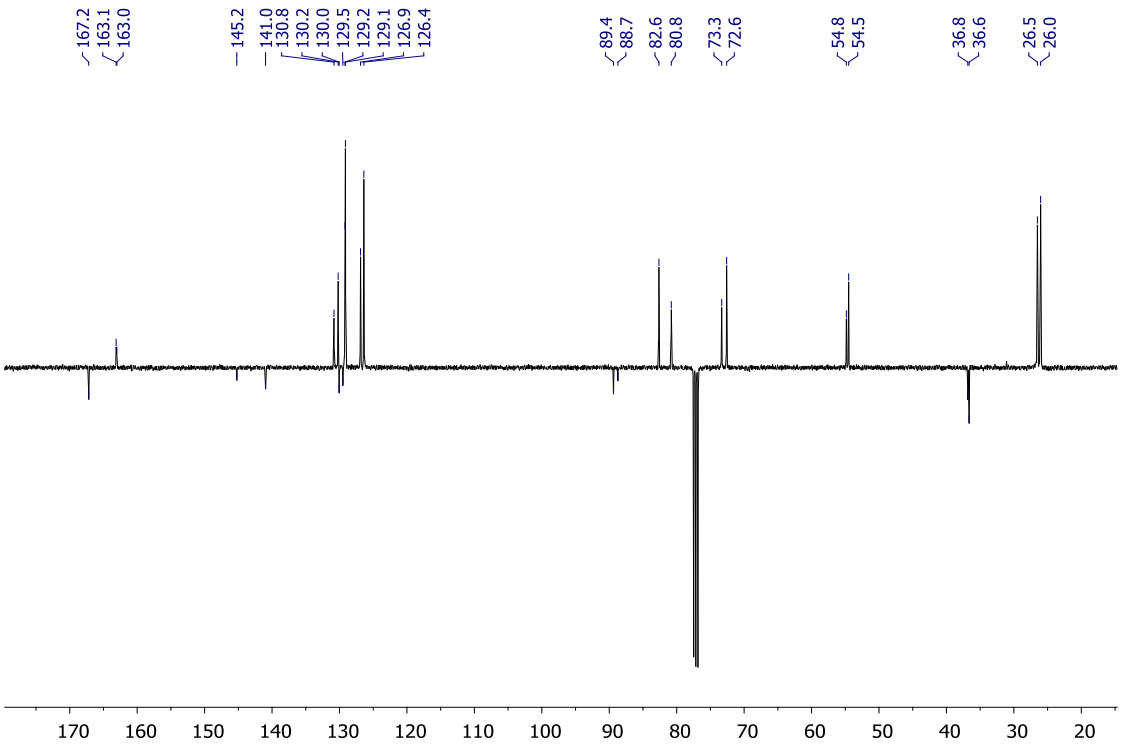


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3a*S*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4,4-dioxido-3-phenyl-3a,5,6,6a-tetrahydro-1*H*-pyrazolo[3,4-*d*]thiazole-6a-carboxylate (103c)

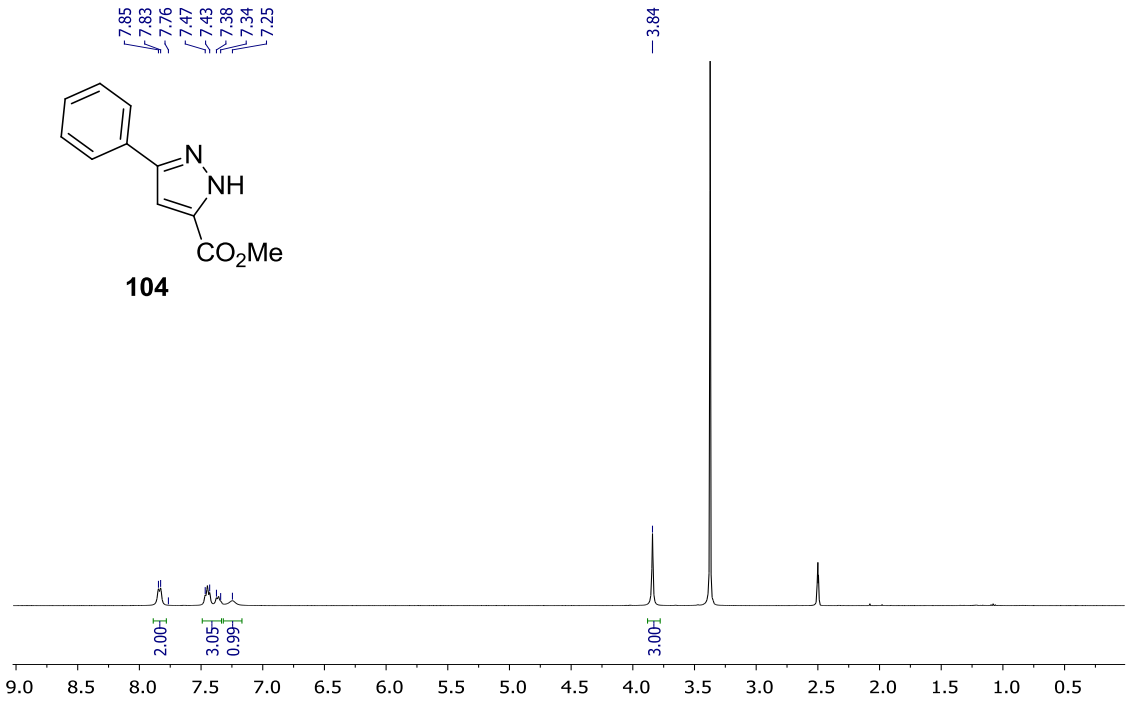


^{1}H-NMR ($CDCl_3$, 400 MHz)



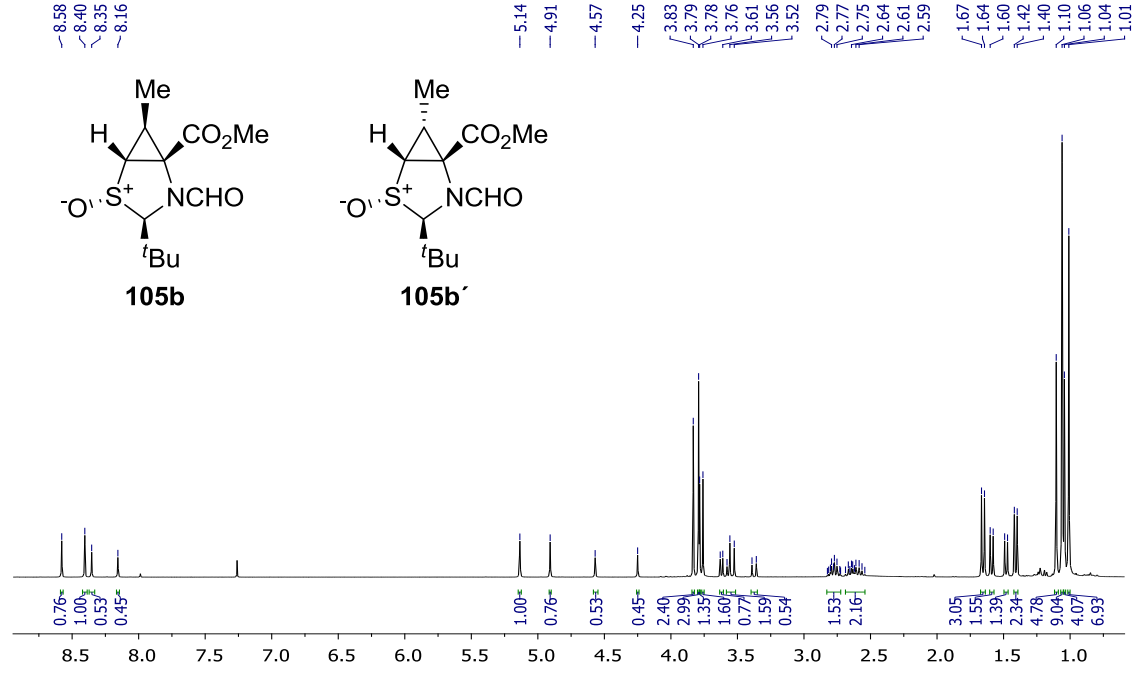
^{13}C-NMR ($CDCl_3$, 100 MHz)

Methyl 3-phenyl-1H-pyrazole-5-carboxylate (104)



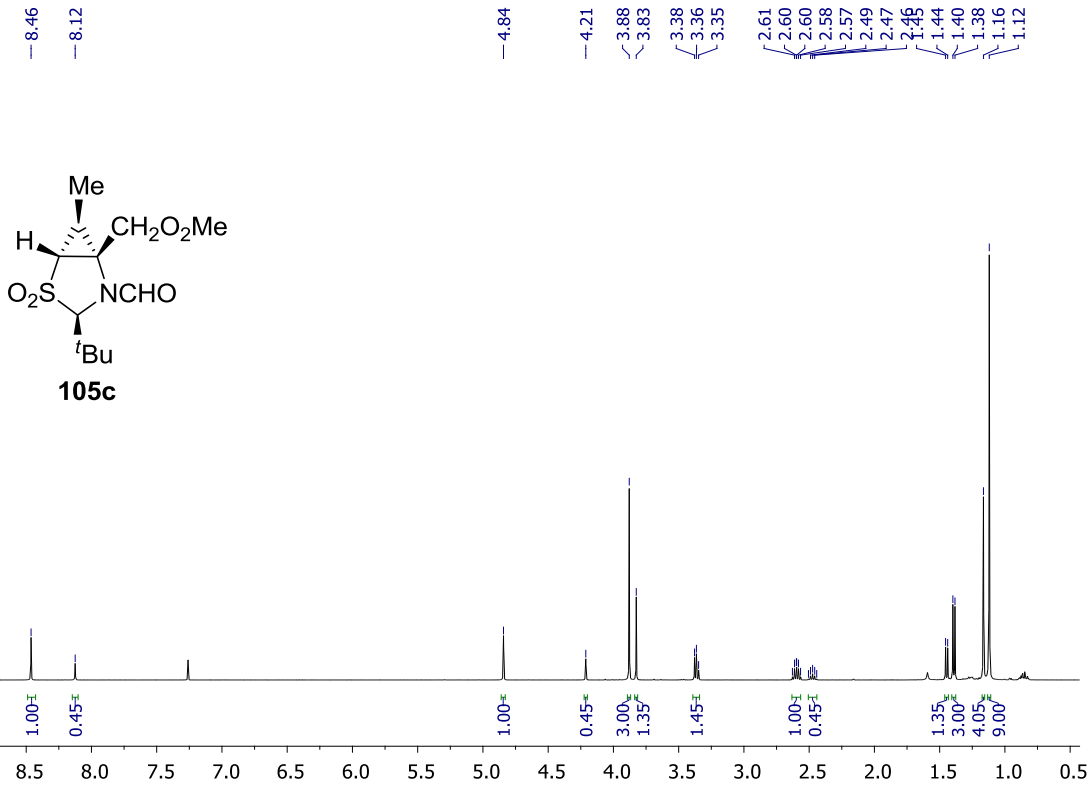
^{1}H-NMR (DMSO-*d6*, 400 MHz)

(1*R*,3*R*,4*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-oxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate and (1*R*,3*R*,4*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-oxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate and (105b and 105b´)

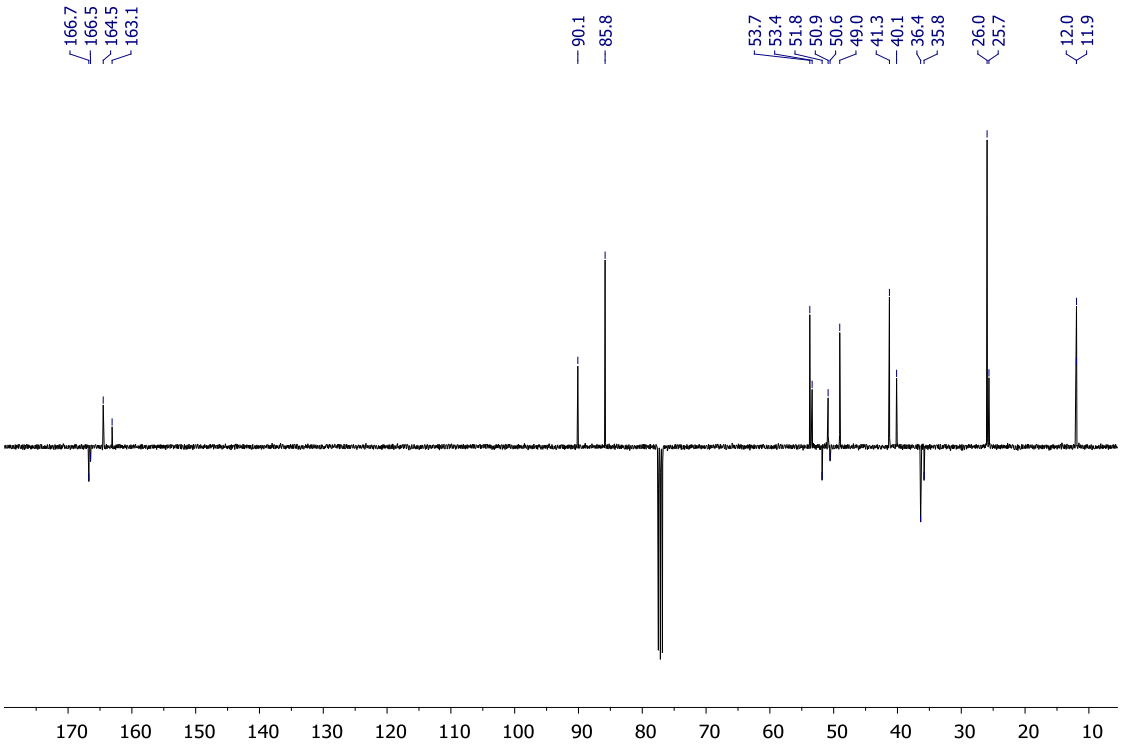


^{1}H-NMR ($CDCl_3$, 400 MHz)

(1*R*,3*R*,5*R*,6*S*)-Methyl-3 *tert*-butyl-2-formyl-6-methyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate (105c)

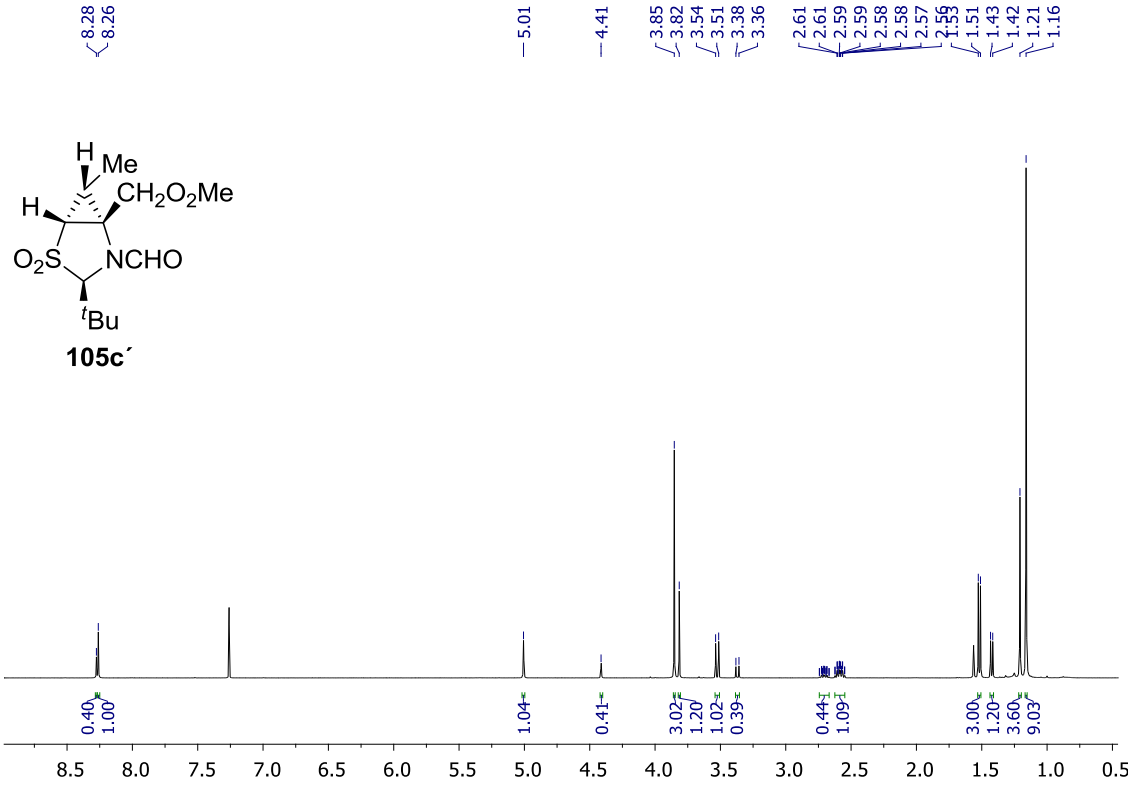


^{1}H-NMR ($CDCl_3$, 400 MHz)

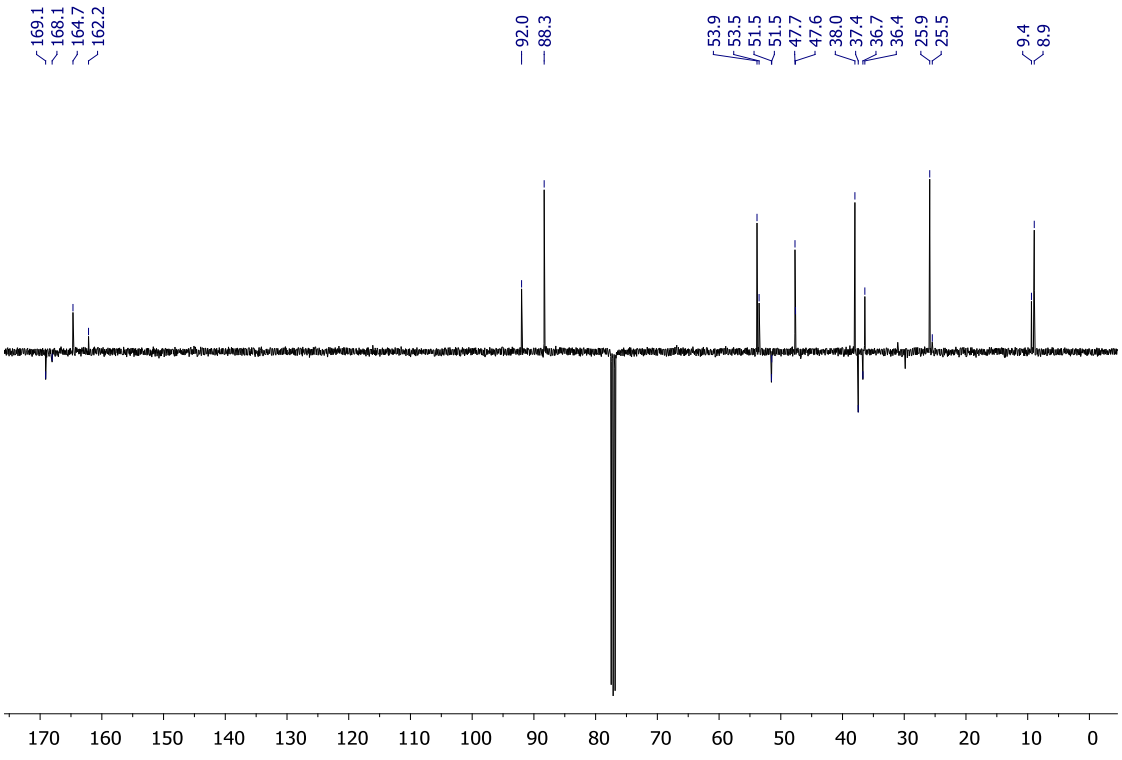


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*R*,5*R*,6*R*)-Methyl-3-*tert*-butyl-2-formyl-6-methyl-4,4-dioxido-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate (105c´)

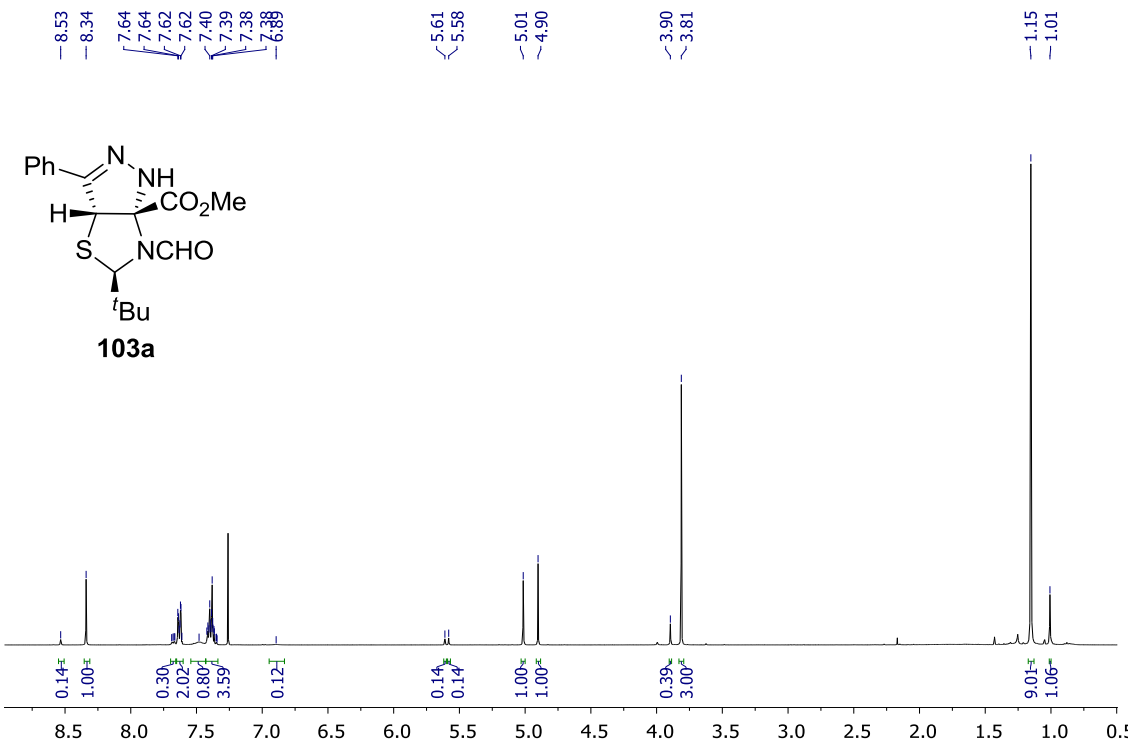


^{1}H-NMR ($CDCl_3$, 400 MHz)

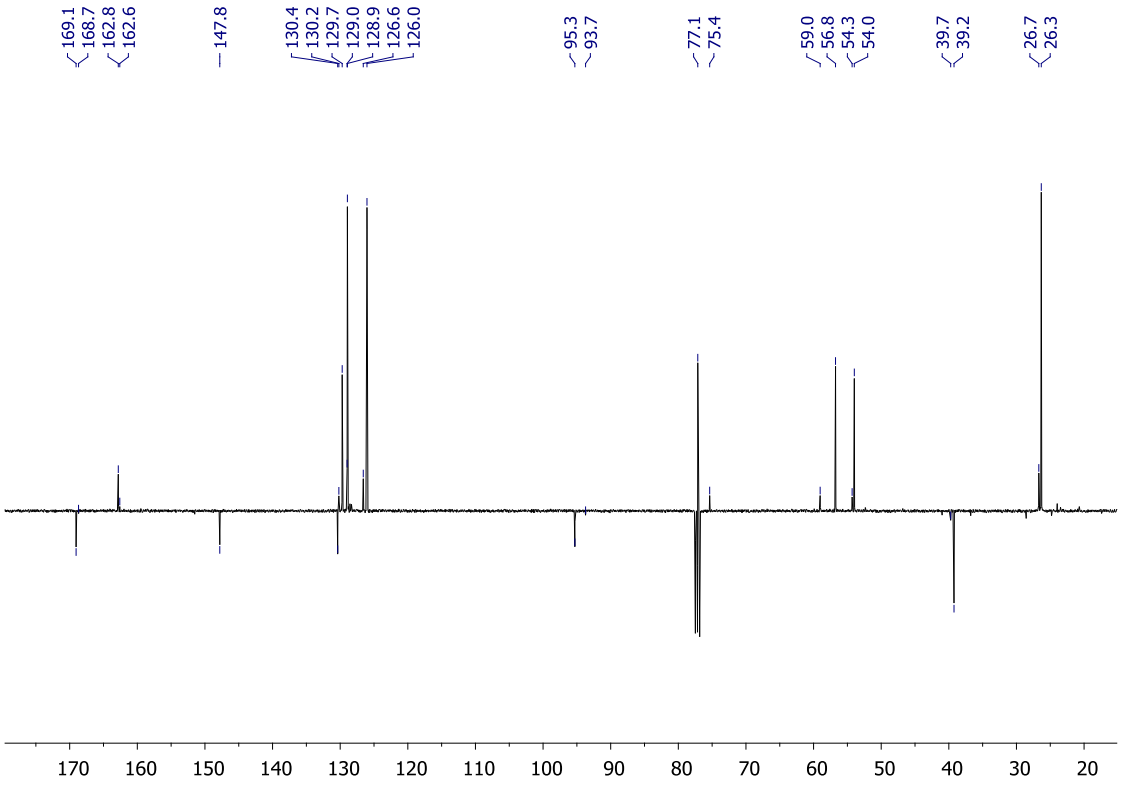


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3a*S*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-3-phenyl-3a,5,6,6a-tetrahydro-1*H*-pyrazolo[3,4-*d*]thiazole-6a-carboxylate (103a)

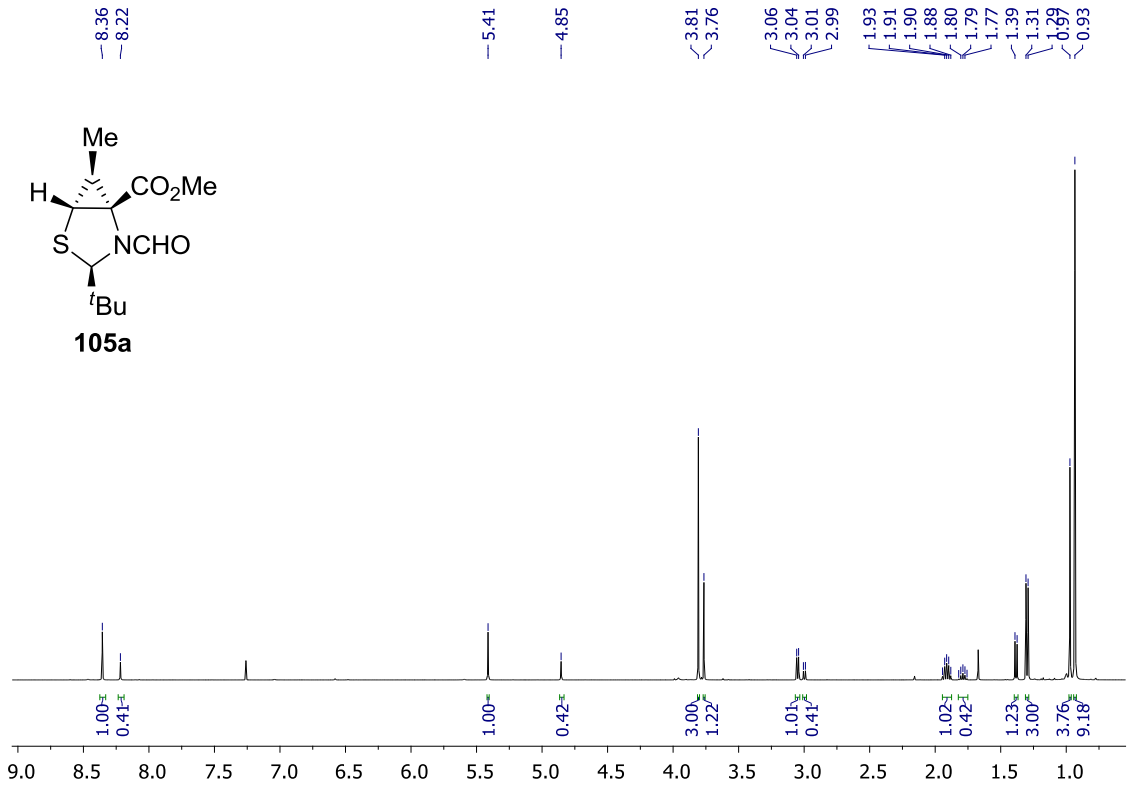


^{1}H-NMR ($CDCl_3$, 400 MHz)

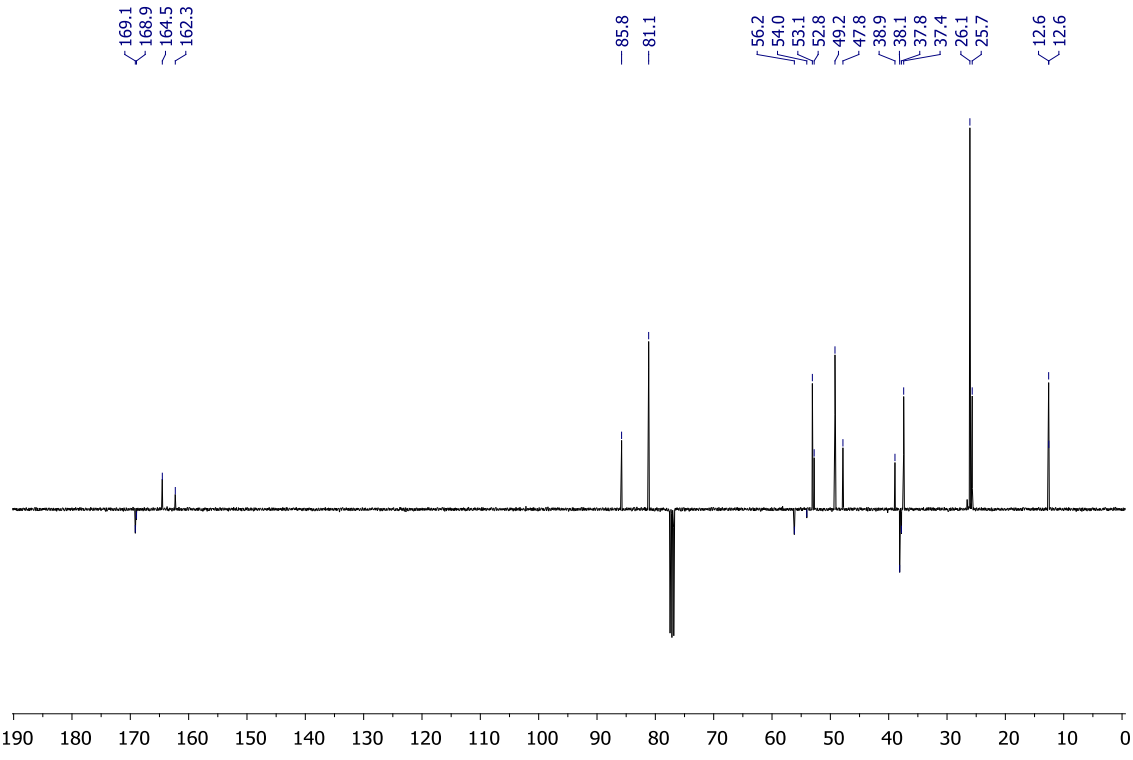


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*R*,5*R*,6*S*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate (105a)

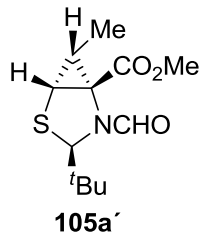


^{1}H-NMR ($CDCl_3$, 400 MHz)



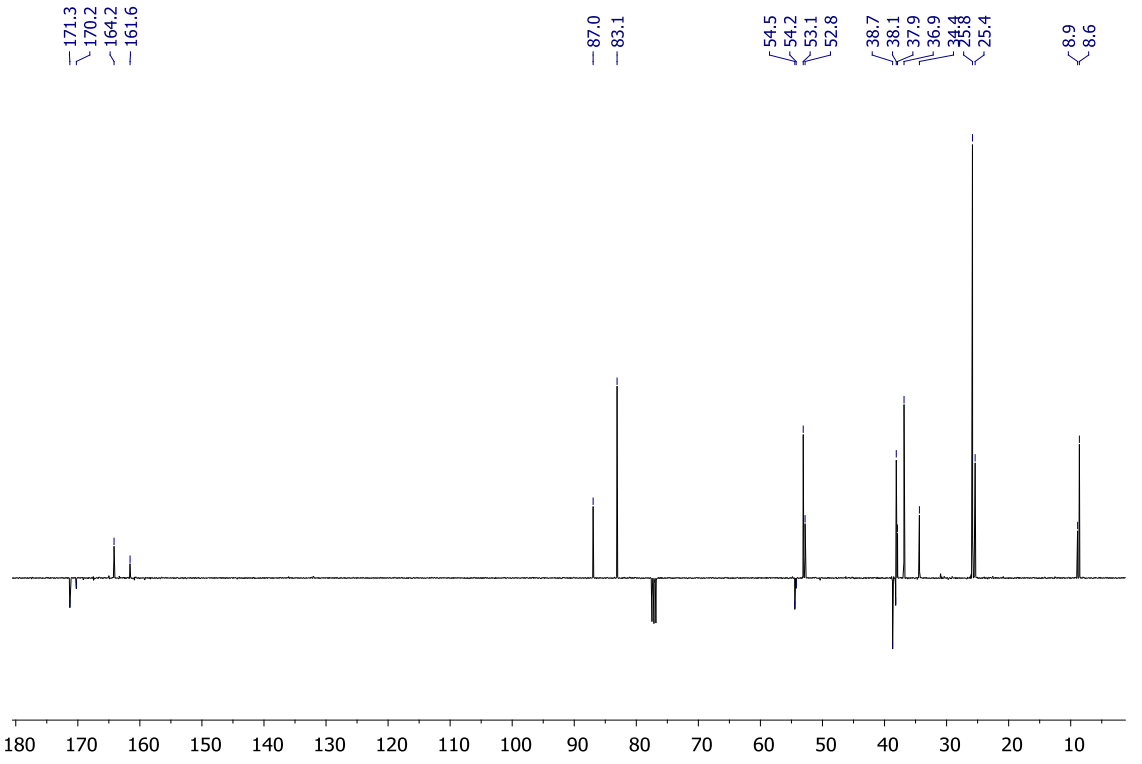
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*R*,5*R*,6*R*)-Methyl 3-*tert*-butyl-2-formyl-6-methyl-4-thia-2-azabicyclo[3.1.0]hexane-1-carboxylate (105a´)



105a´

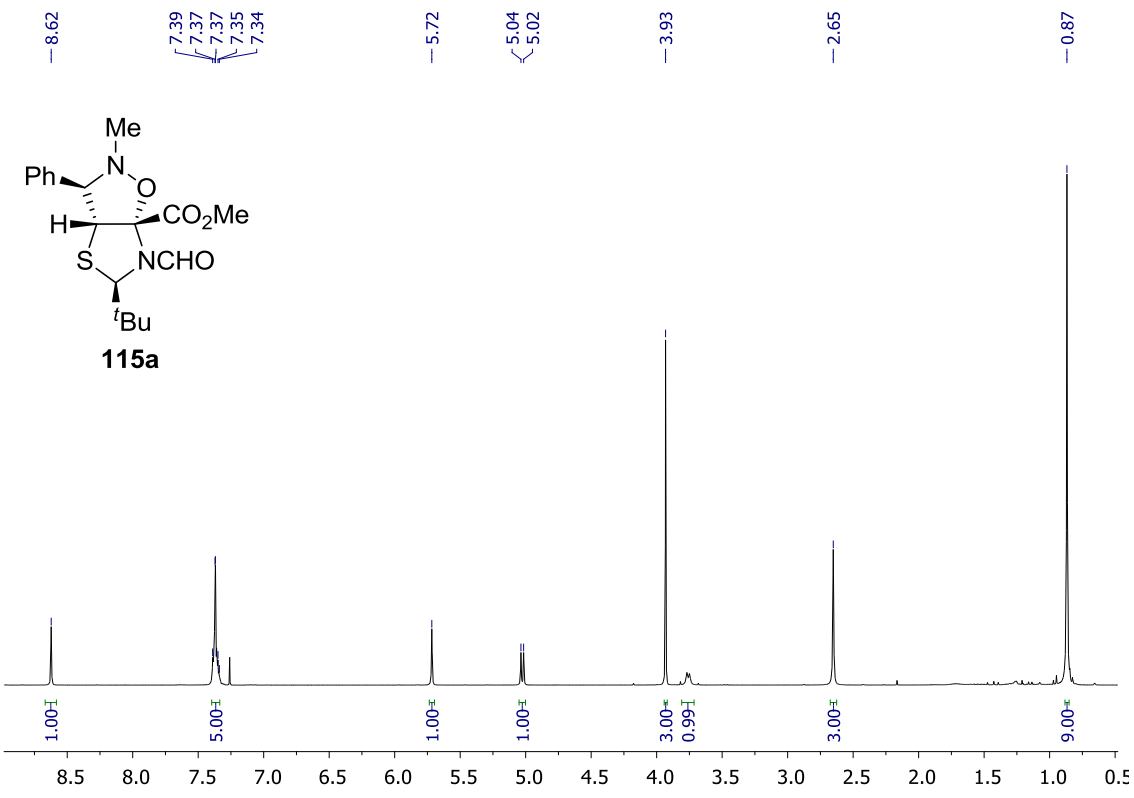
^{1}H-NMR ($CDCl_3$, 400 MHz)



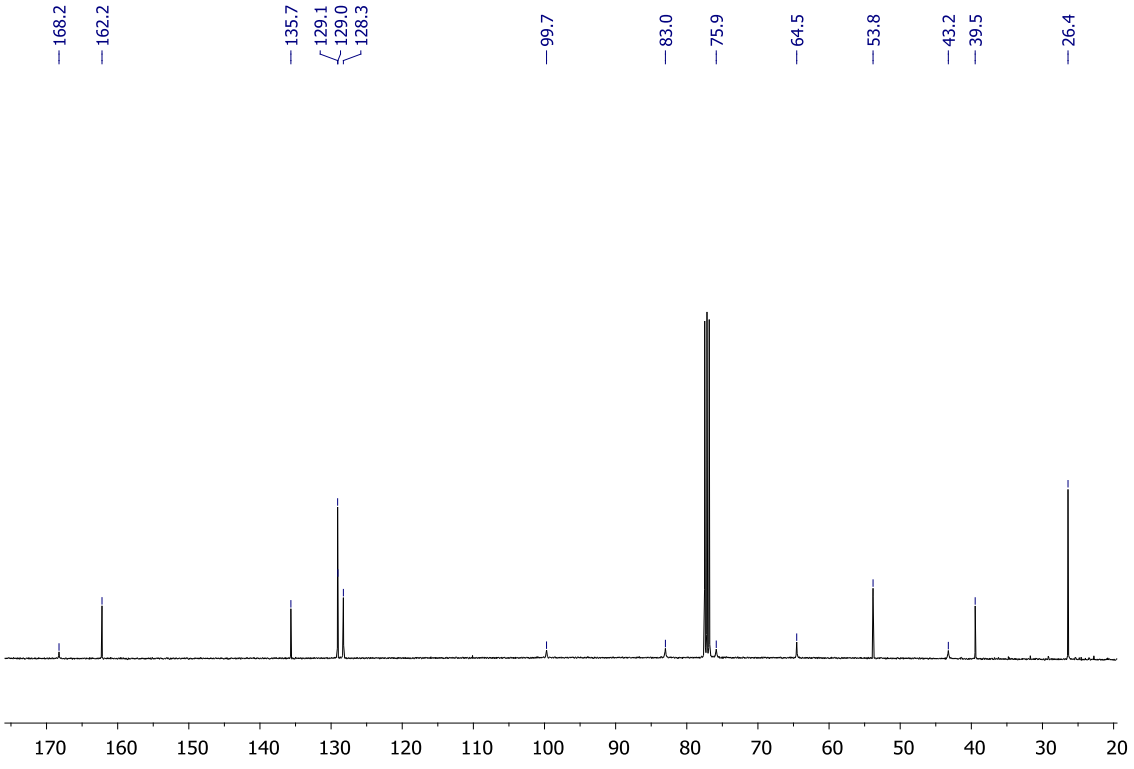
^{13}C-NMR ($CDCl_3$, 100 MHz)

NMR spectra of Chapter IV

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (115a)

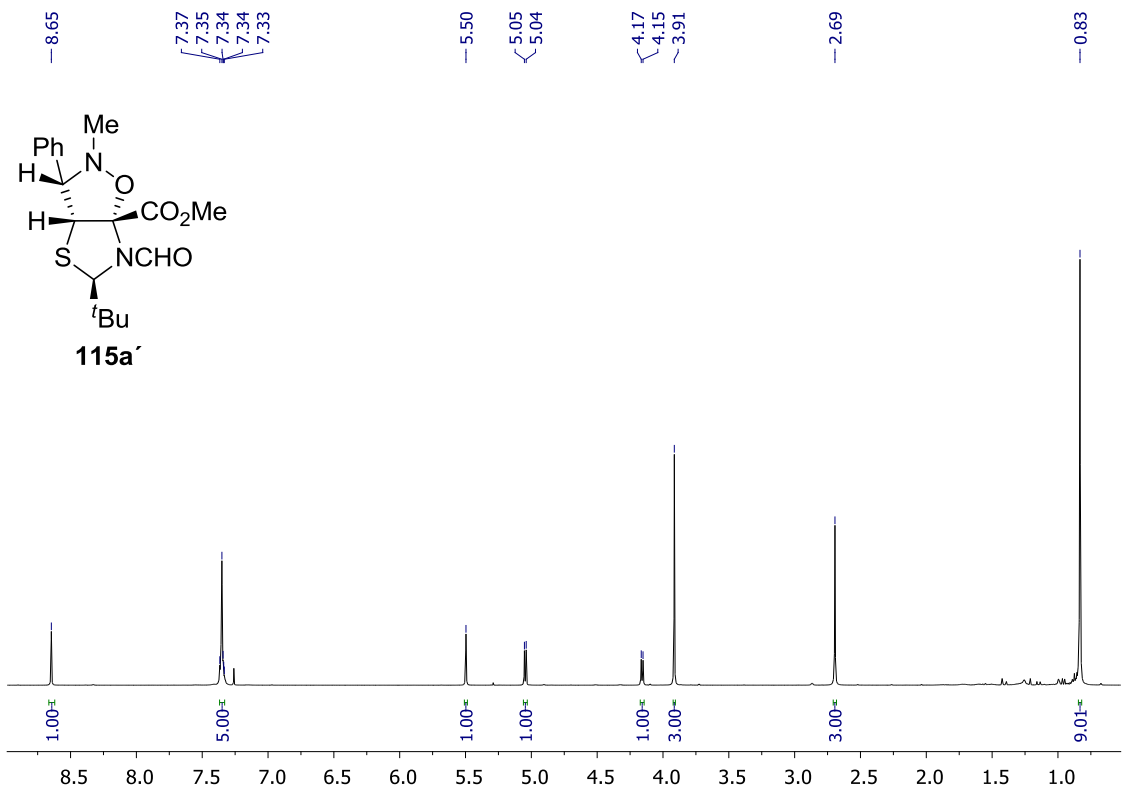


^{1}H-NMR ($CDCl_3$, 400 MHz)

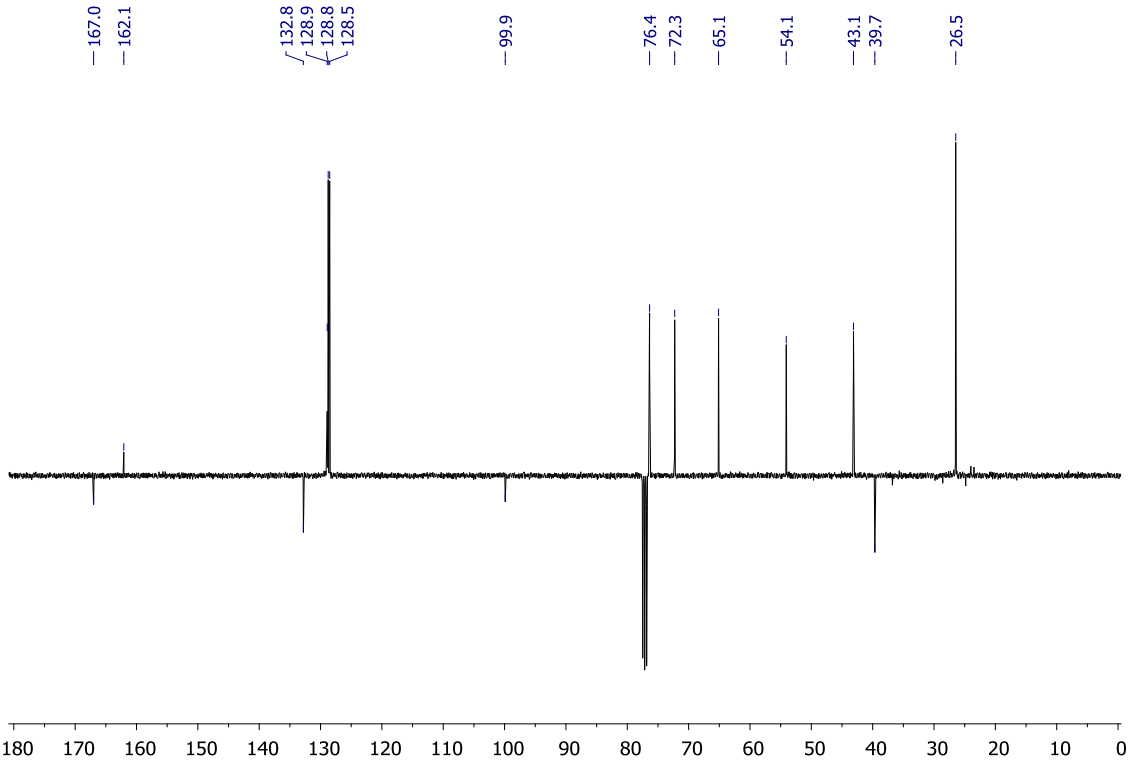


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (115a´)

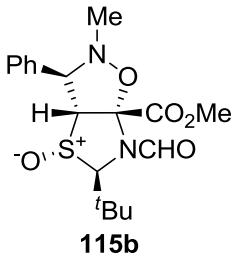


^{1}H-NMR ($CDCl_3$, 400 MHz)



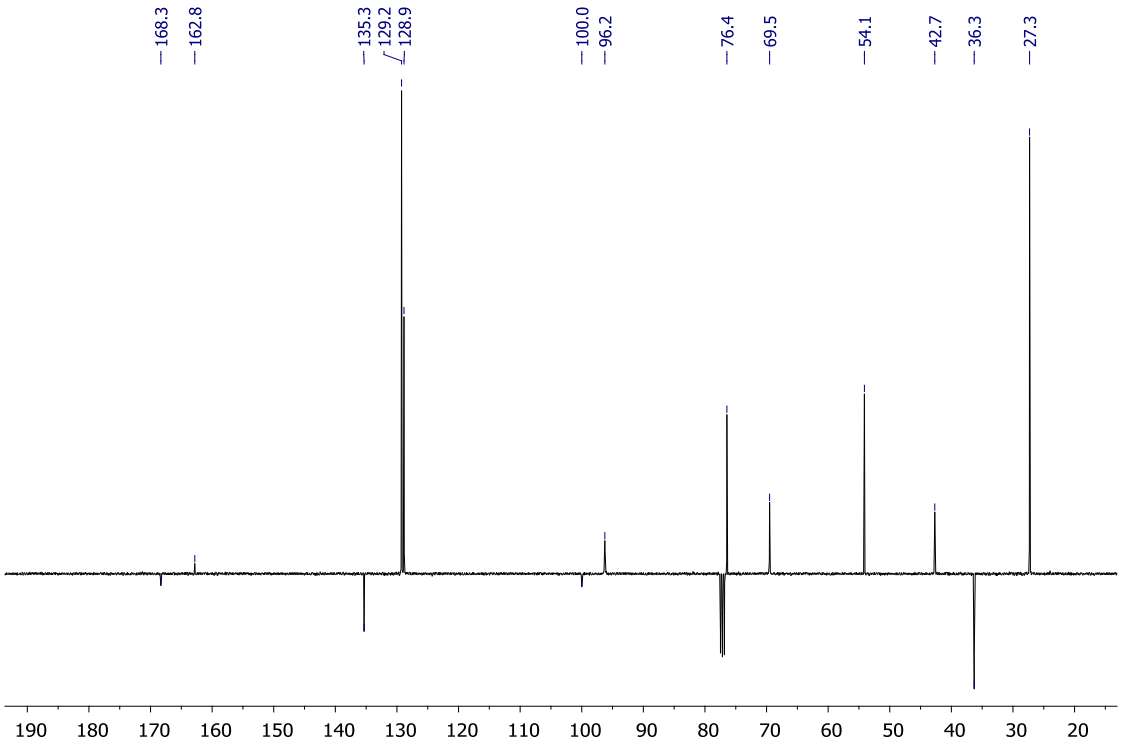
^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-4-oxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (115b)



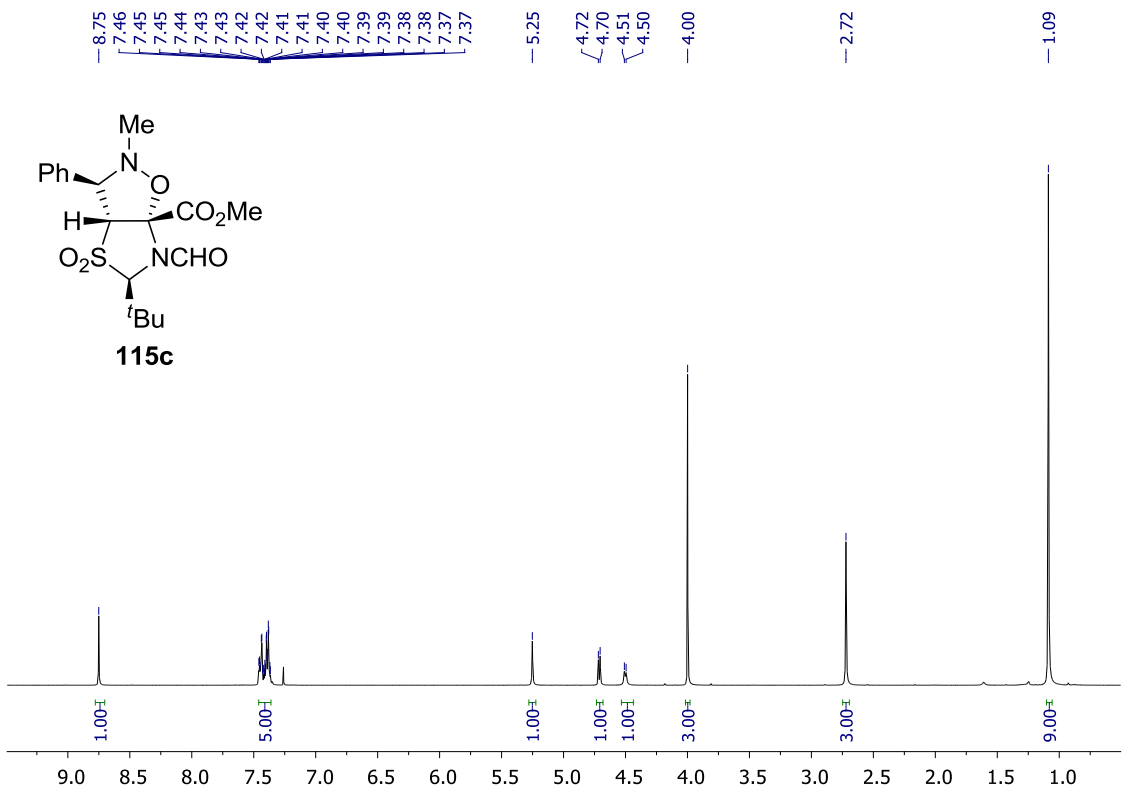
115b

^{1}H-NMR ($CDCl_3$, 400 MHz)

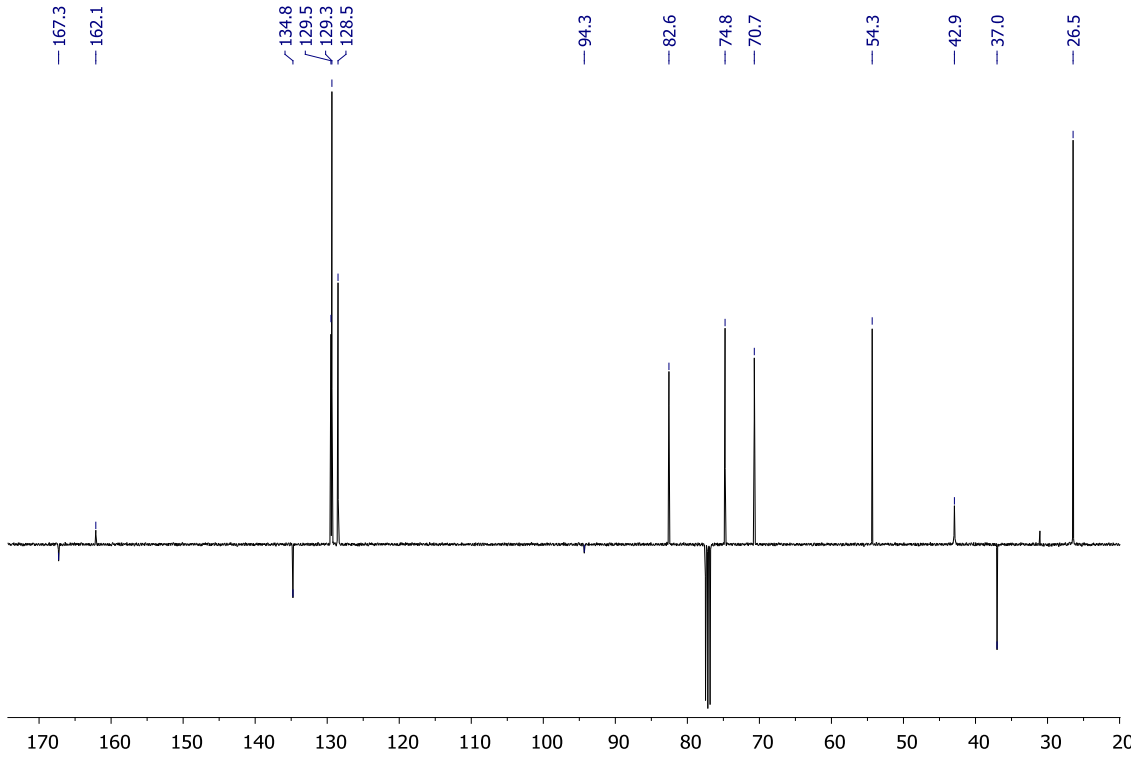


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-4,4-dioxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (115c)

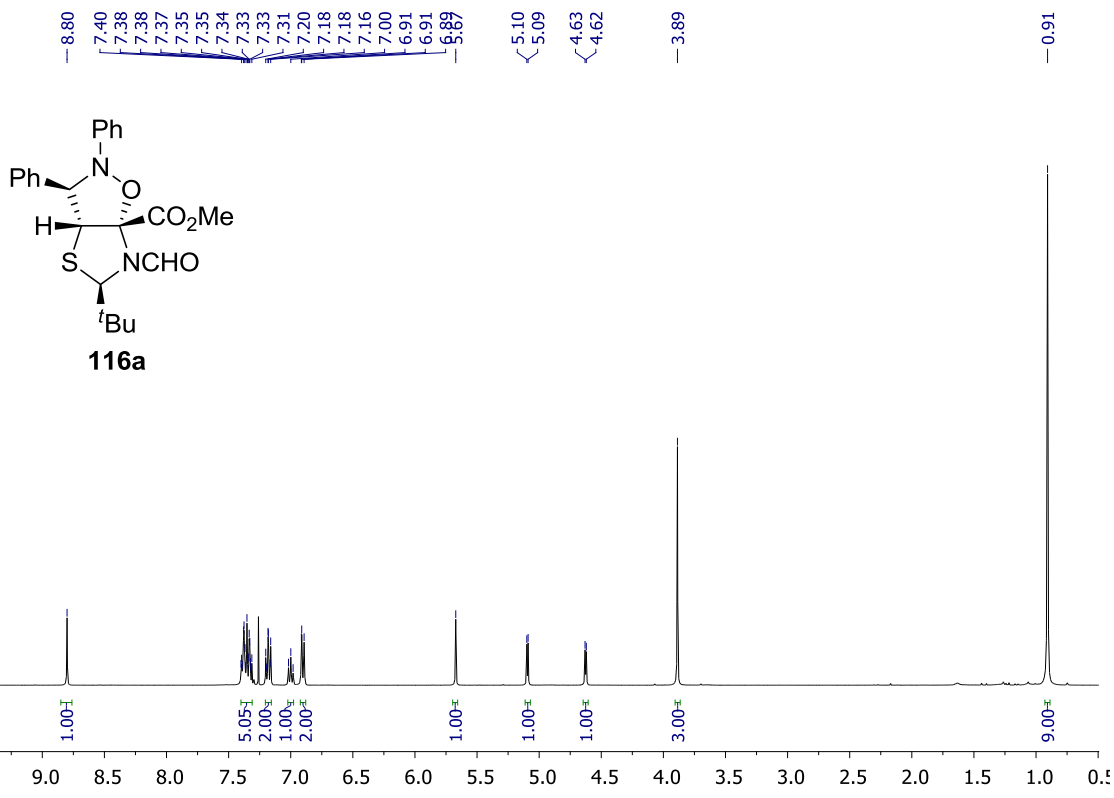


^{1}H-NMR ($CDCl_3$, 400 MHz)

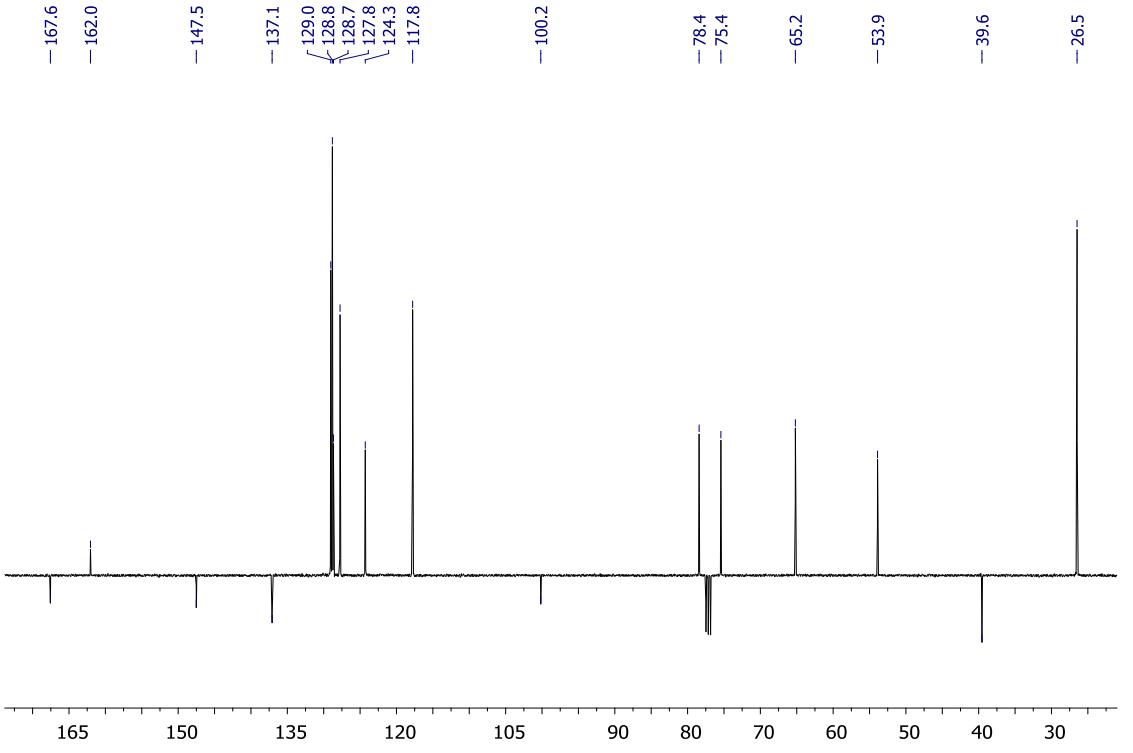


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (116a)

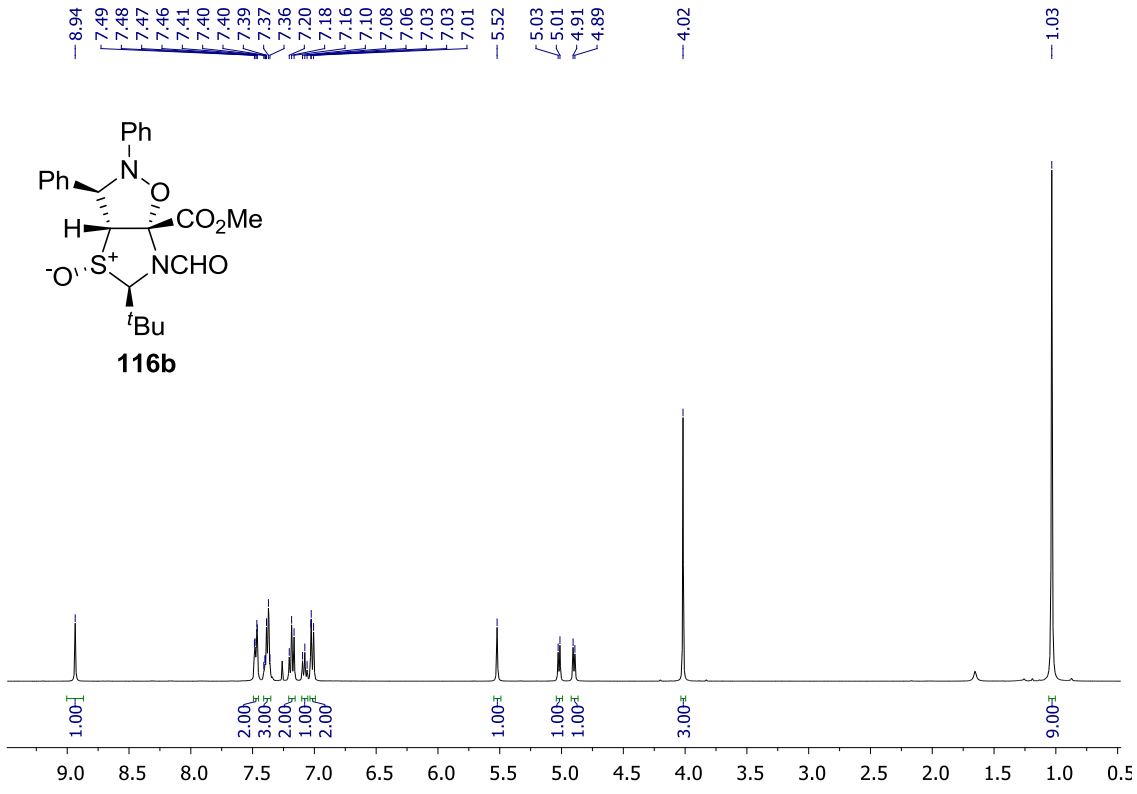


^{1}H-NMR ($CDCl_3$, 400 MHz)

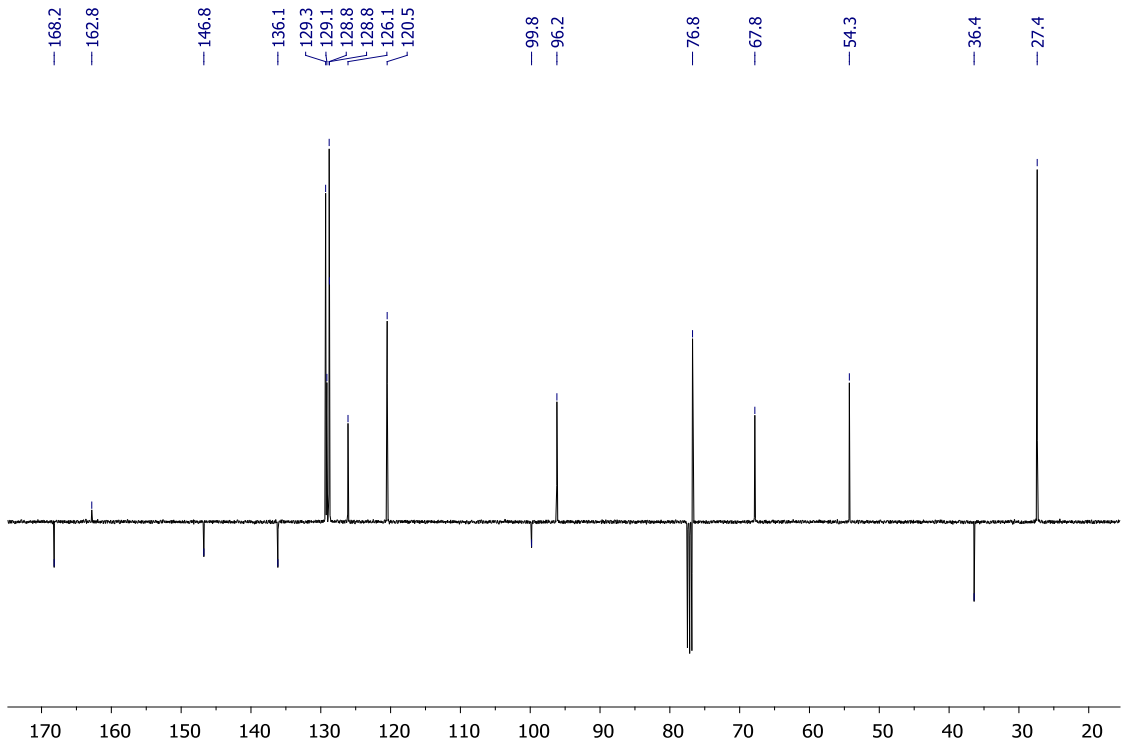


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4-oxido-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (116b)

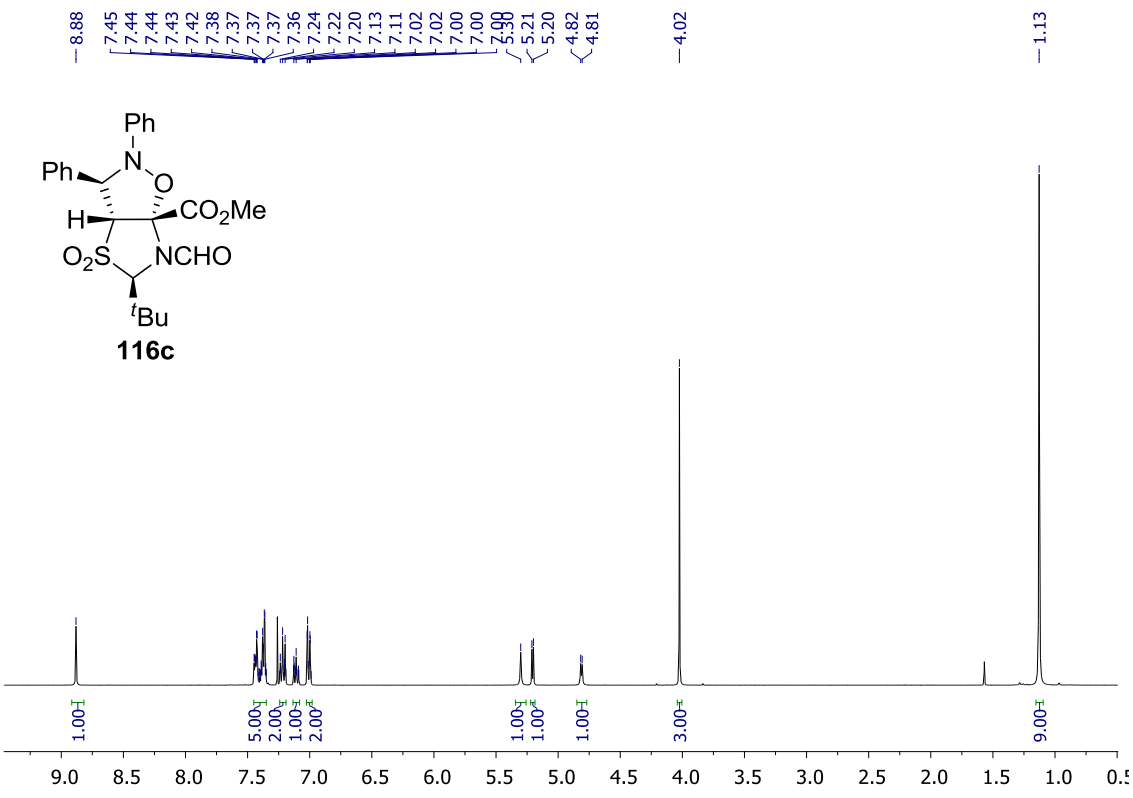


^{1}H-NMR ($CDCl_3$, 400 MHz)

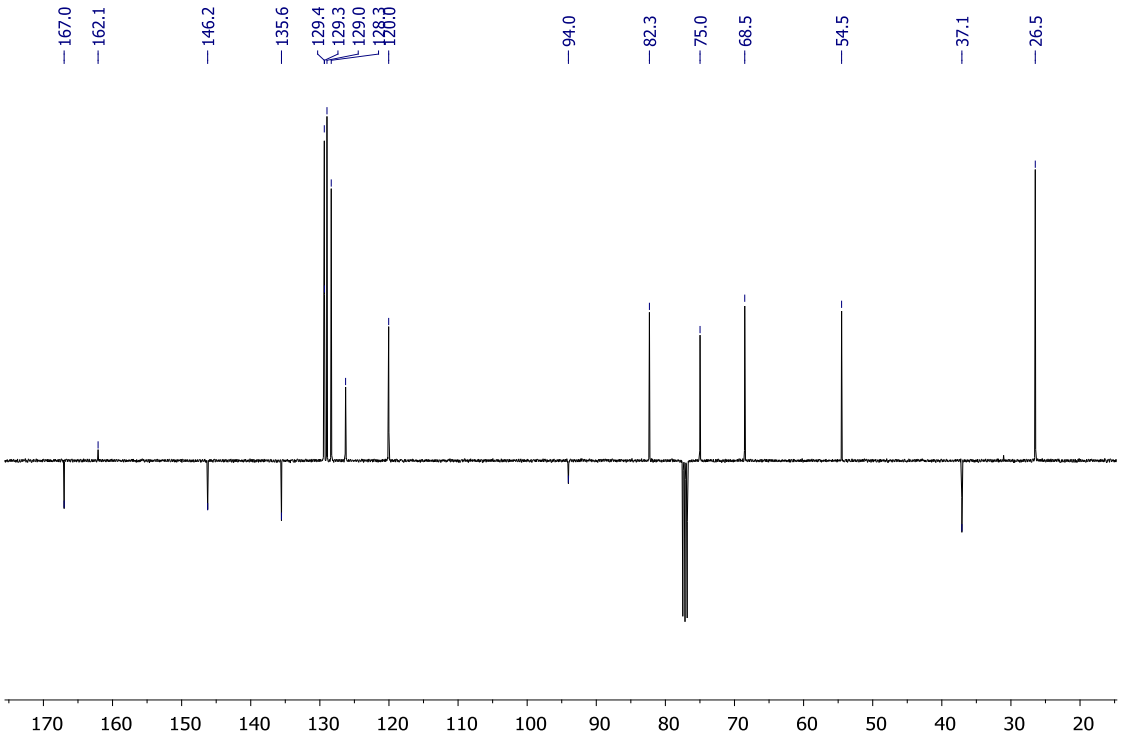


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-4,4-dioxido-2,3-diphenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (116c)

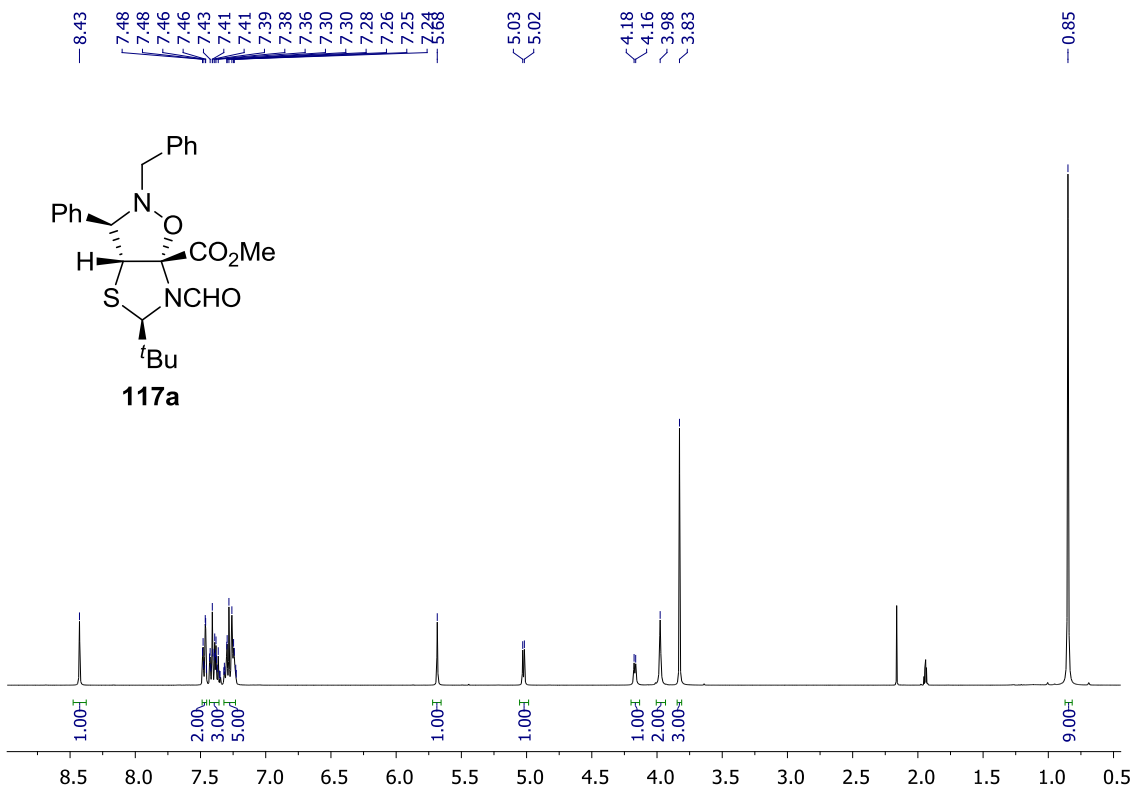


^{1}H-NMR ($CDCl_3$, 400 MHz)



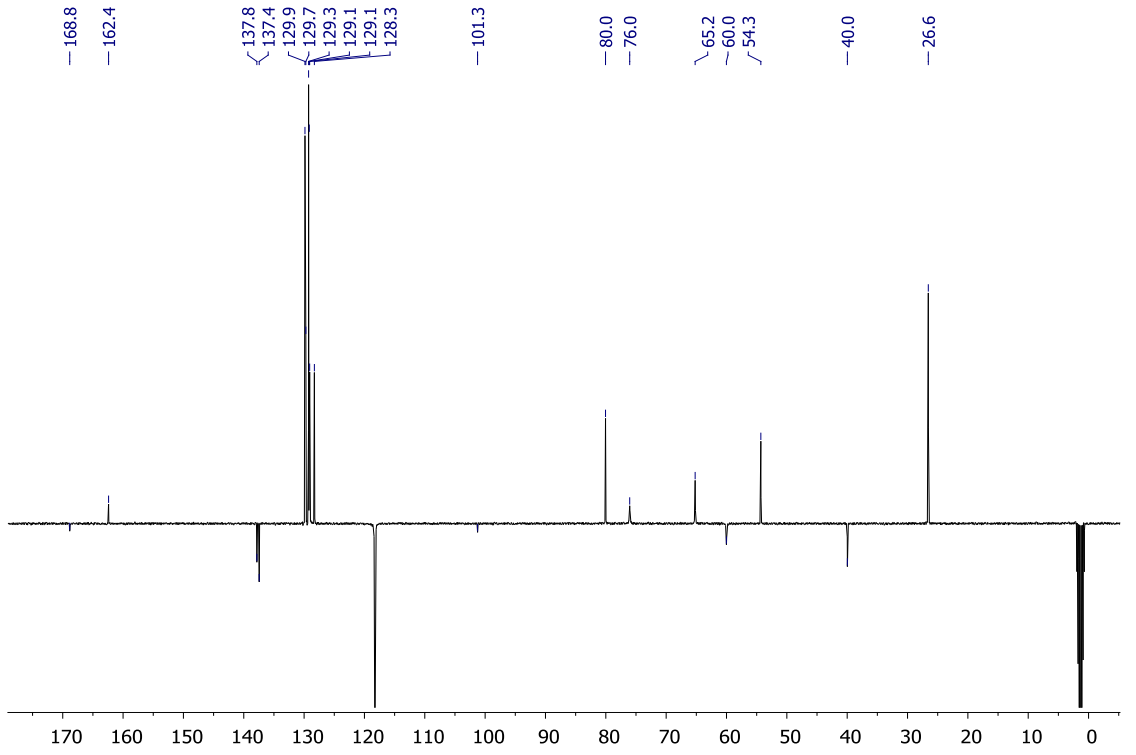
^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (117a)



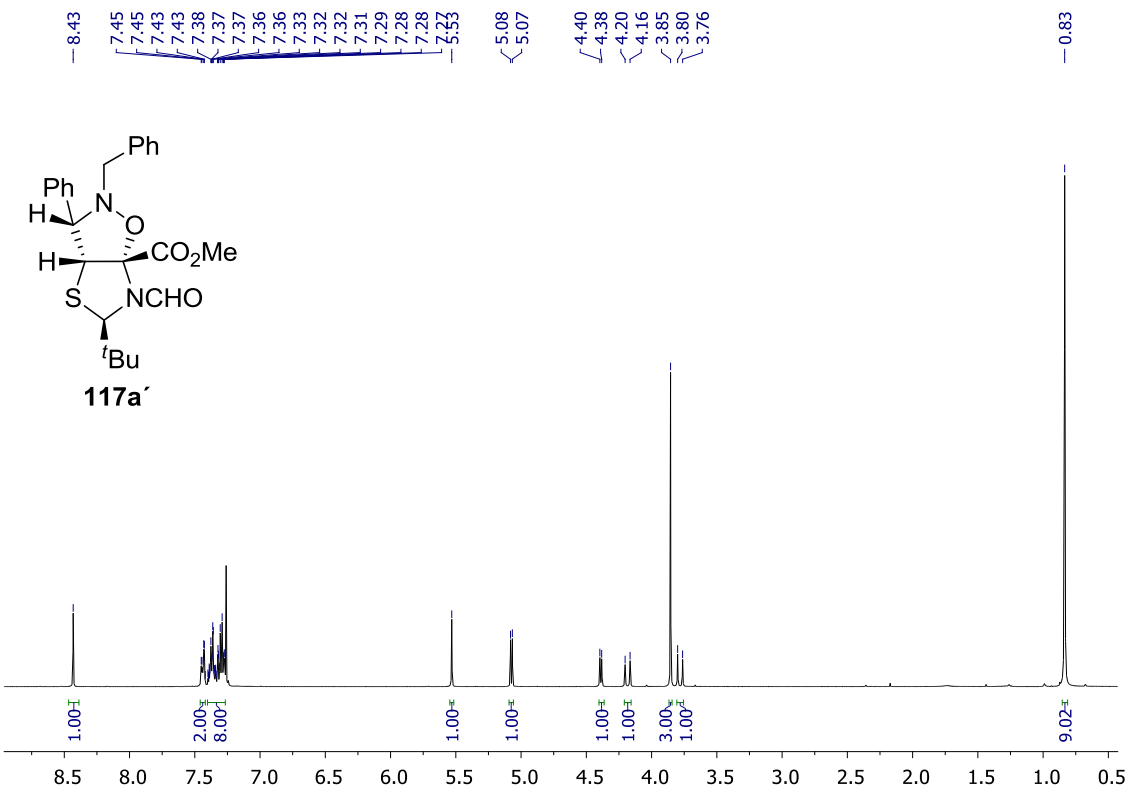
117a

^{1}H-NMR (CD_3CN, 400 MHz)

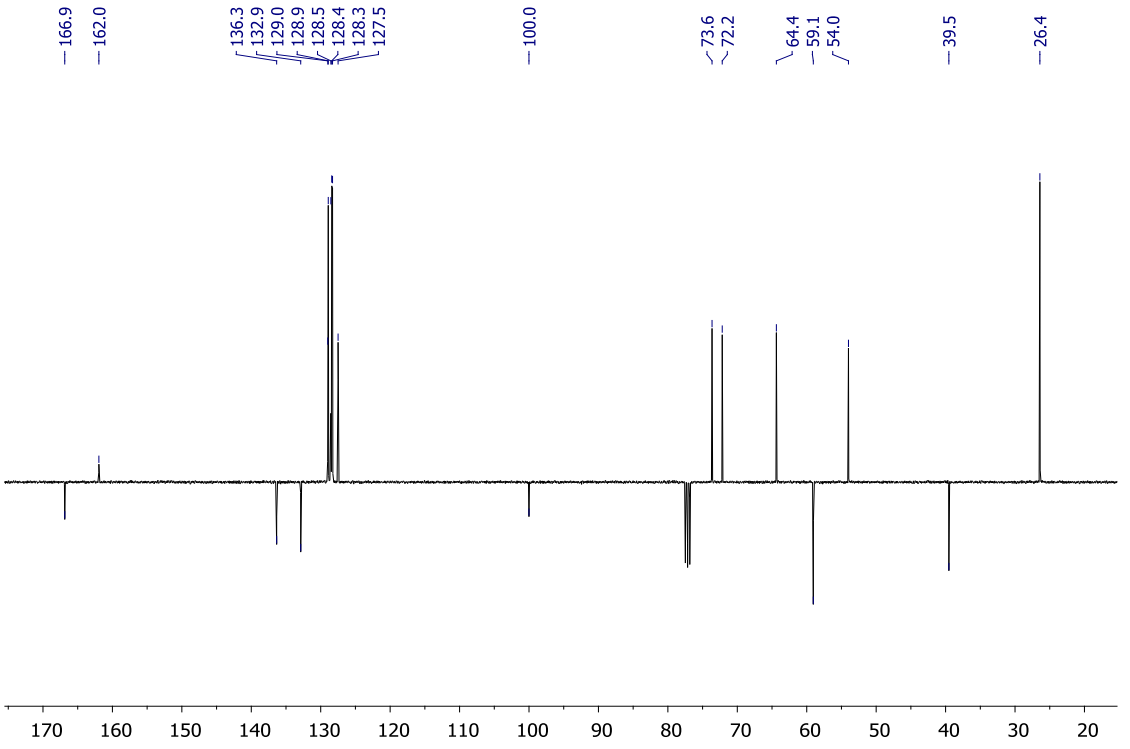


^{13}C-NMR (CD_3CN, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (117a´)

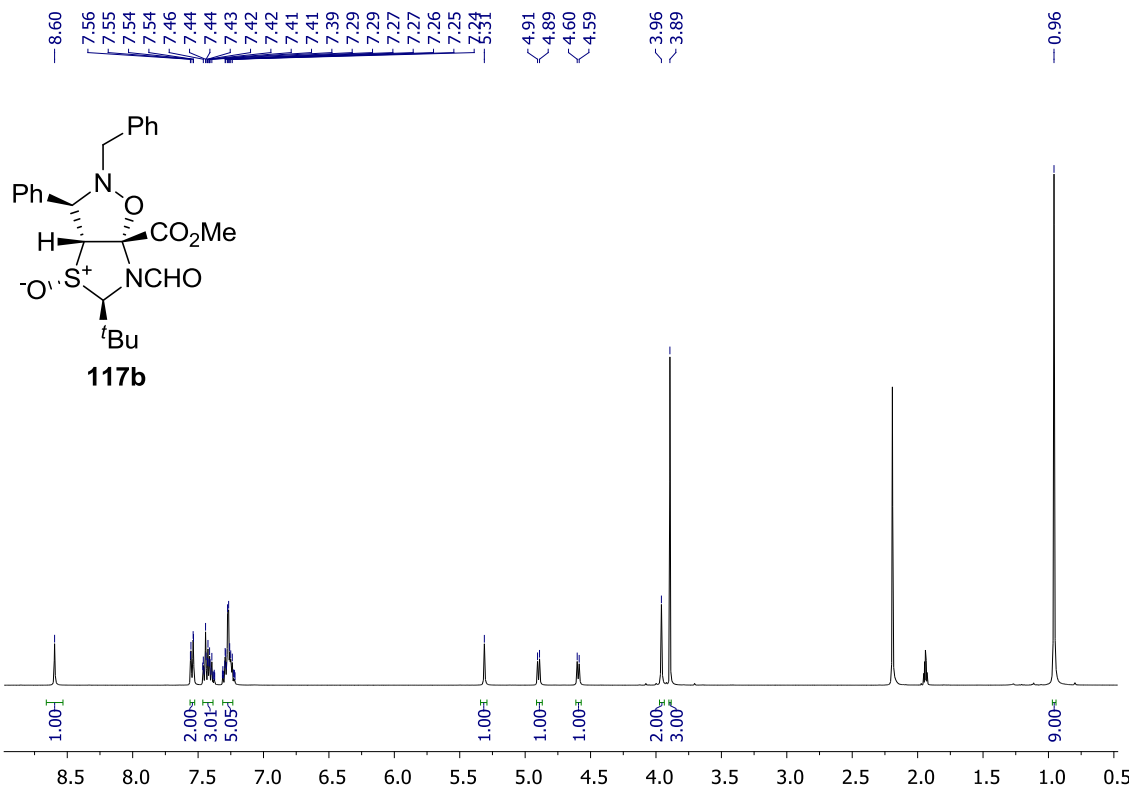


^{1}H-NMR ($CDCl_3$, 400 MHz)



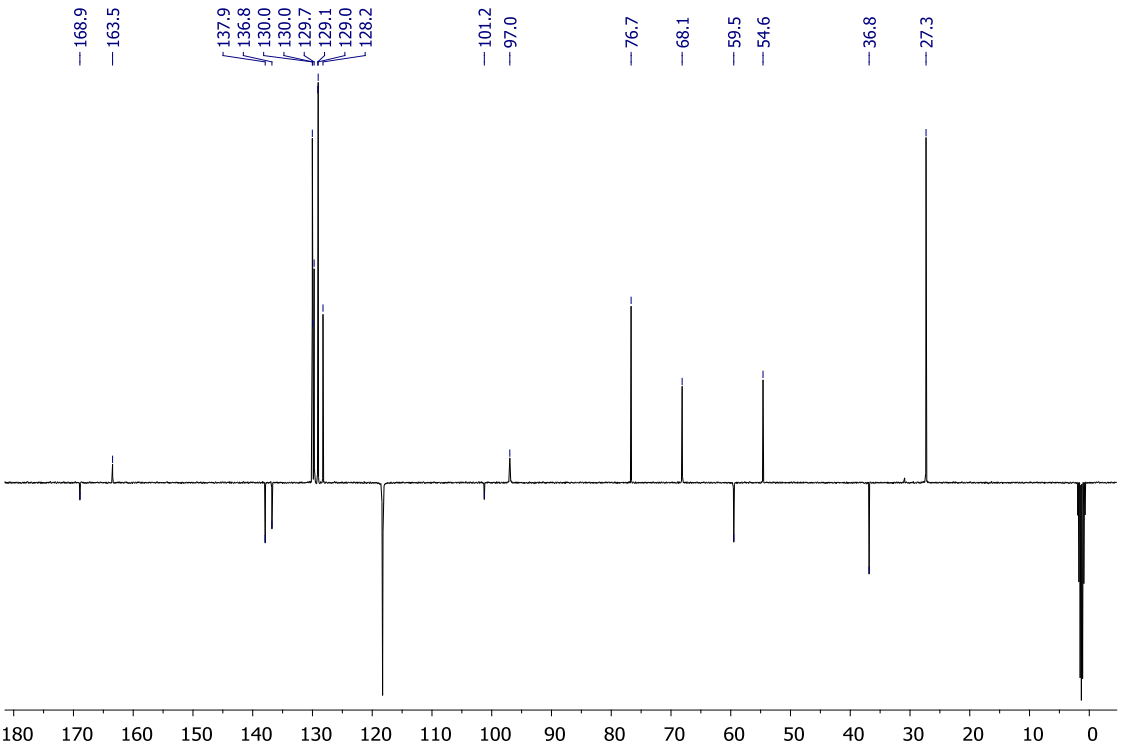
^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-4-oxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (117b)



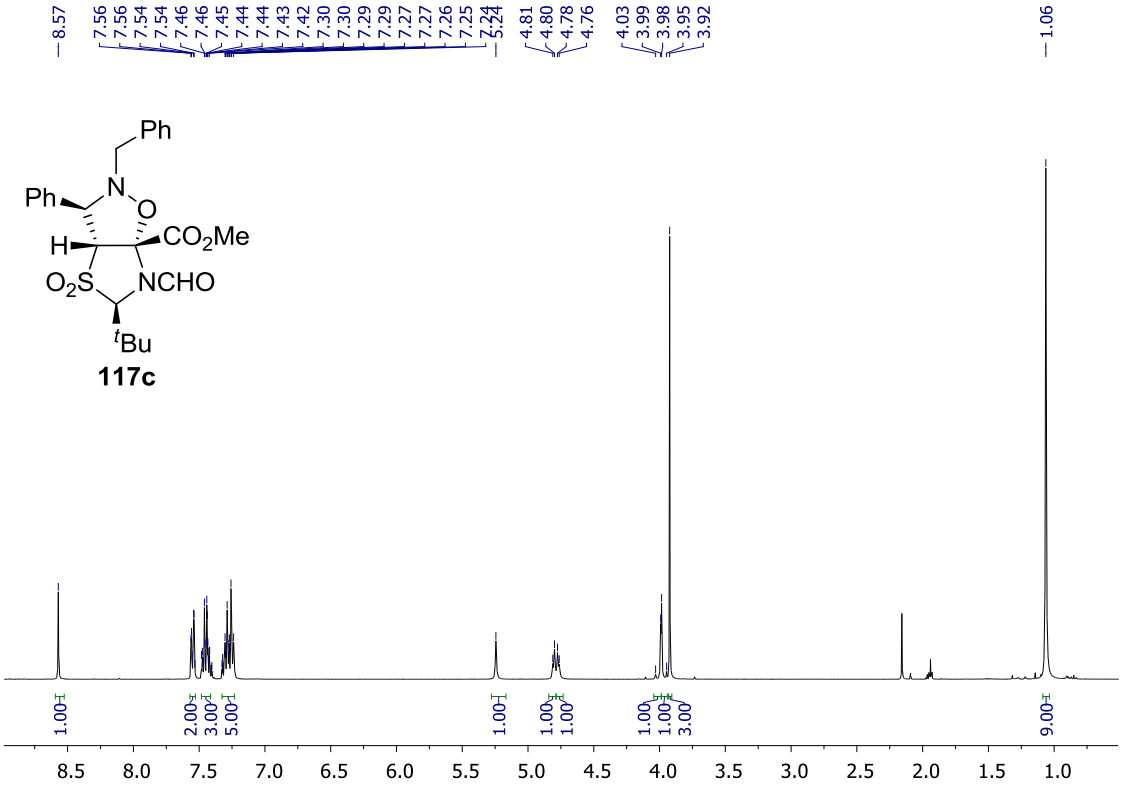
117b

^{1}H-NMR (CD_3CN, 400 MHz)

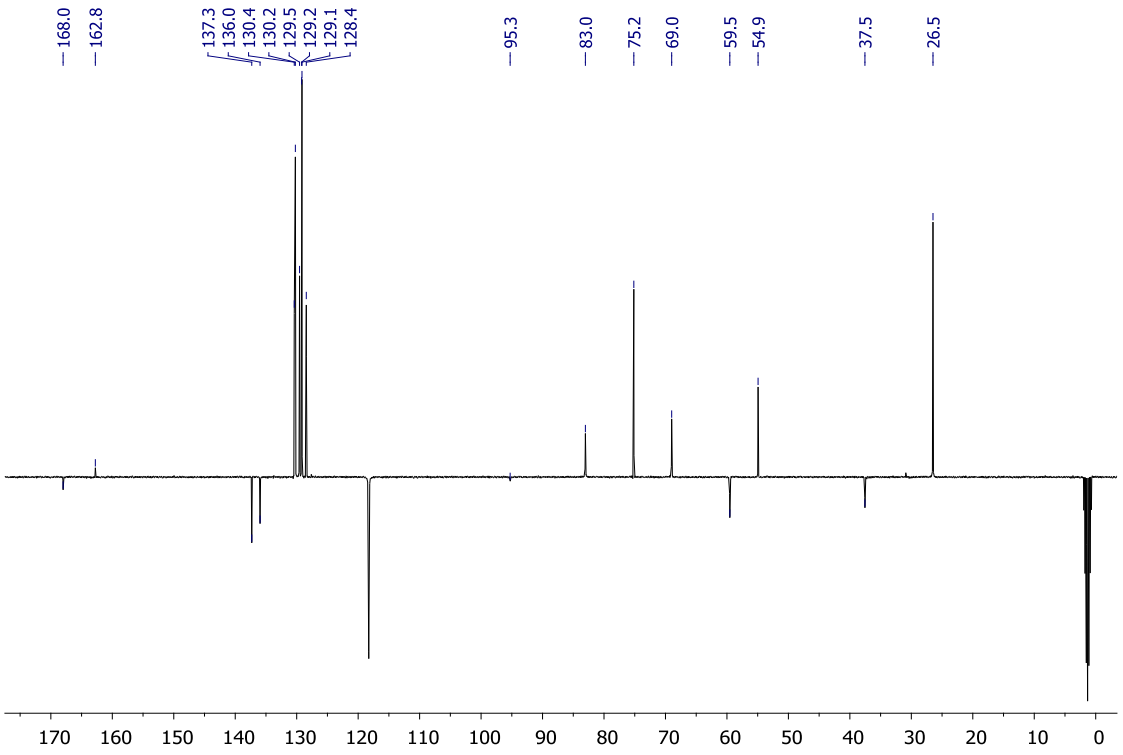


^{13}C-NMR (CD_3CN, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-4,4-dioxido-3-phenylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (117c)

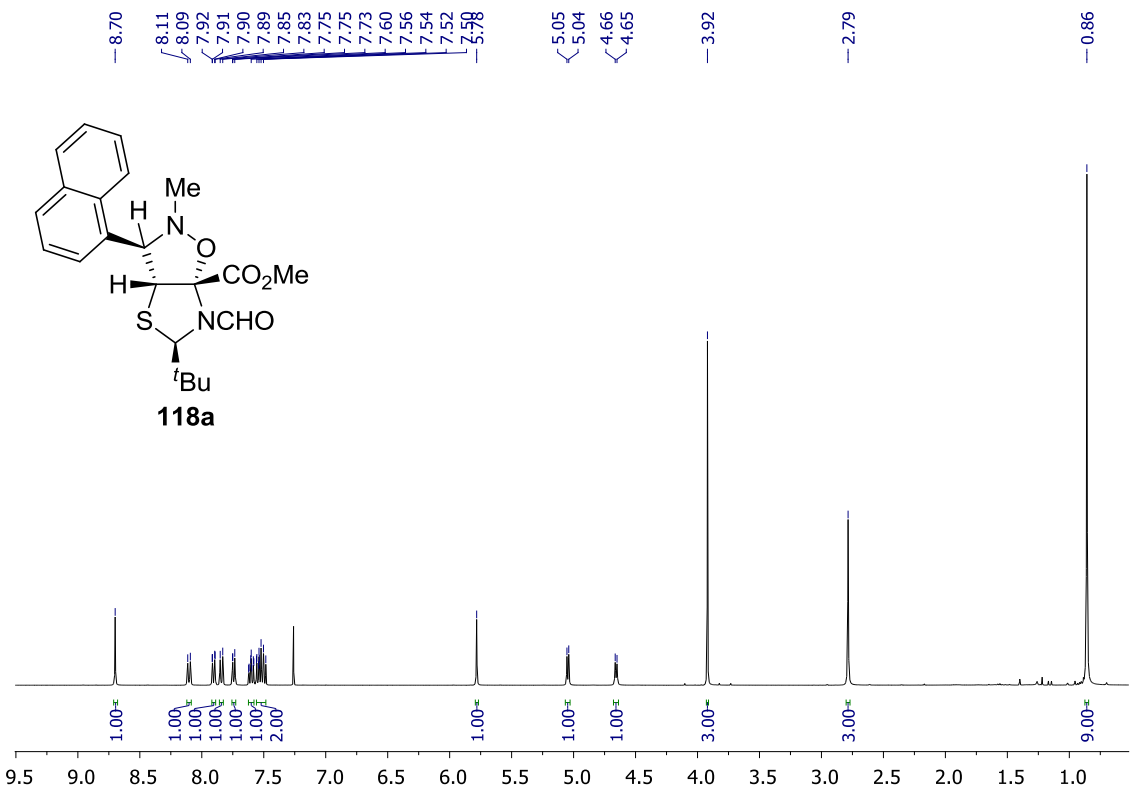


^{1}H-NMR (CD_3CN, 400 MHz)

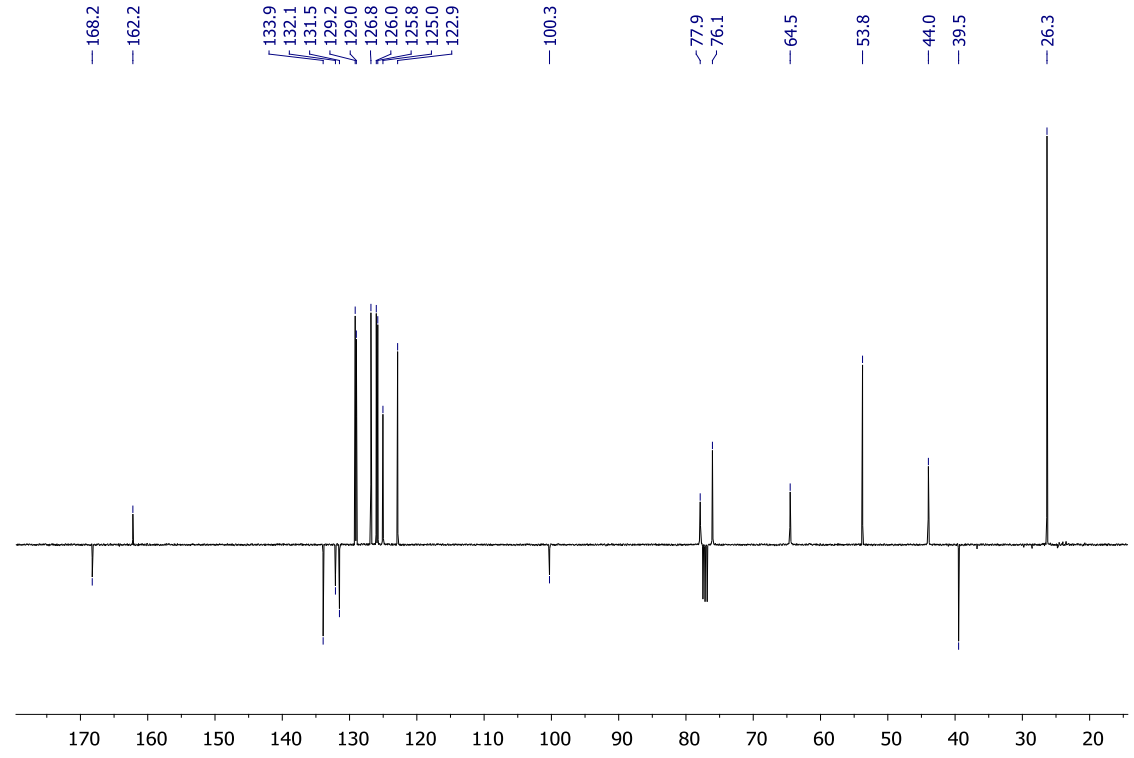


^{13}C-NMR (CD_3CN, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (118a)

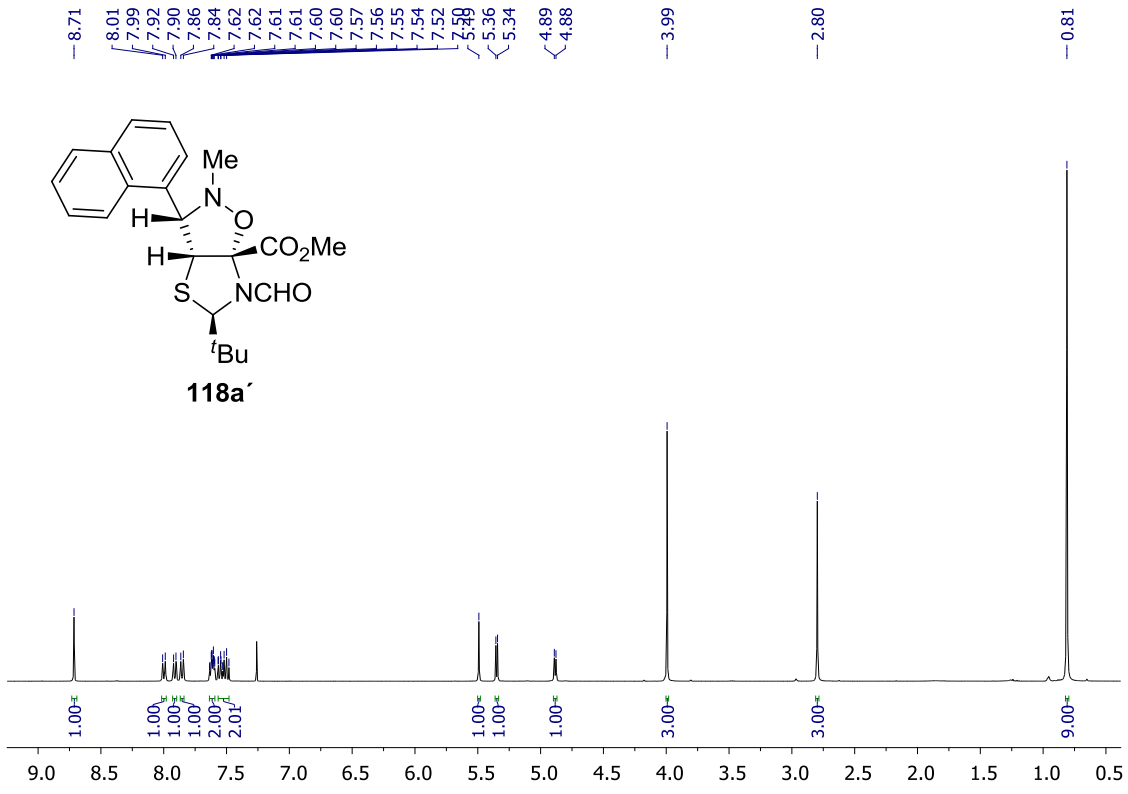


^{1}H-NMR ($CDCl_3$, 400 MHz)

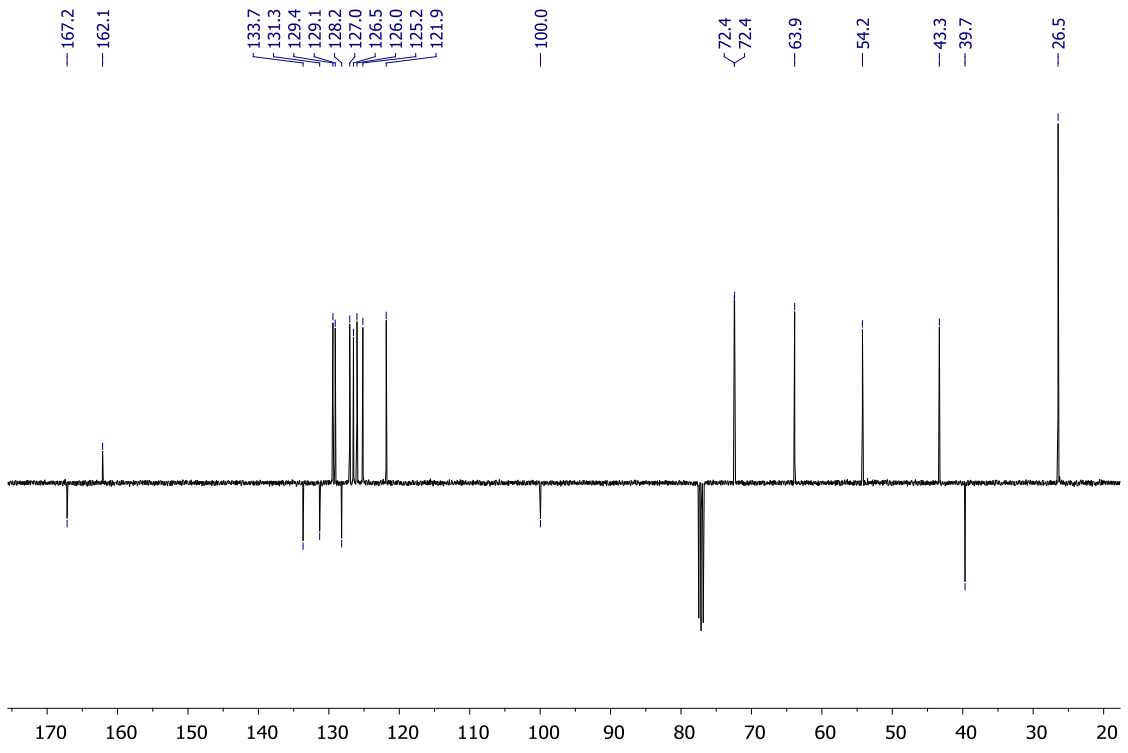


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (118a´)

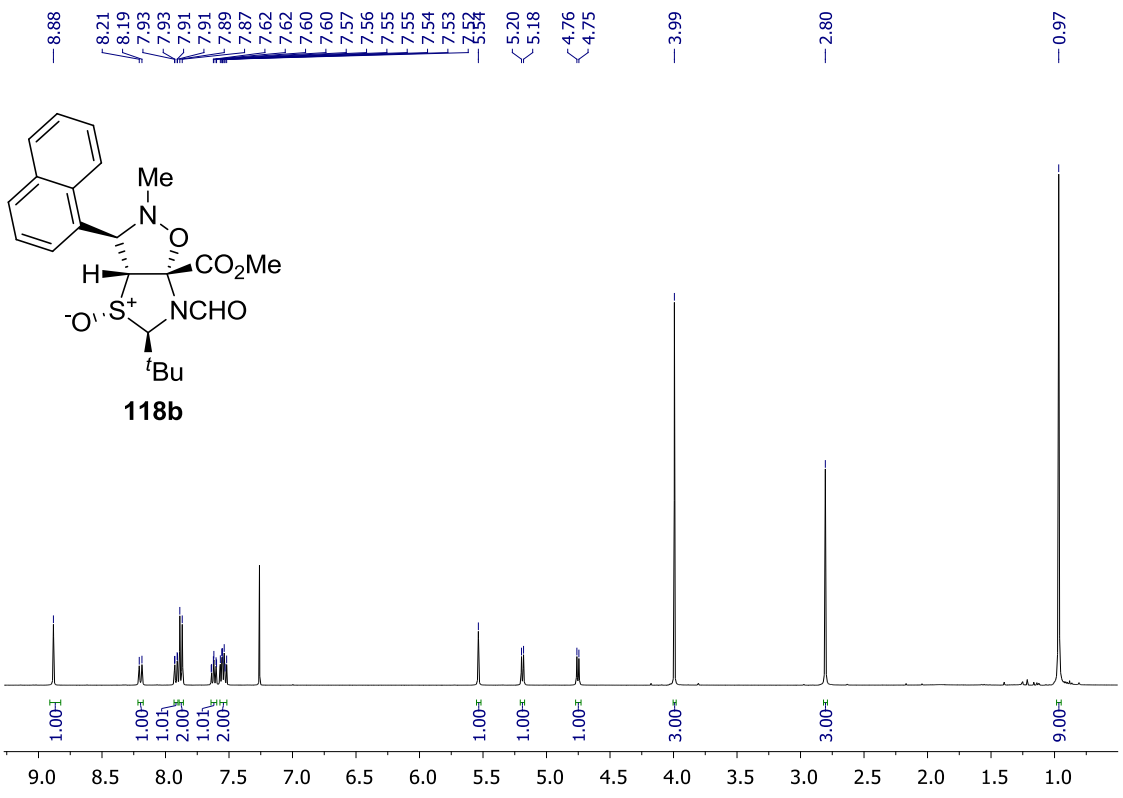


^{1}H-NMR ($CDCl_3$, 400 MHz)

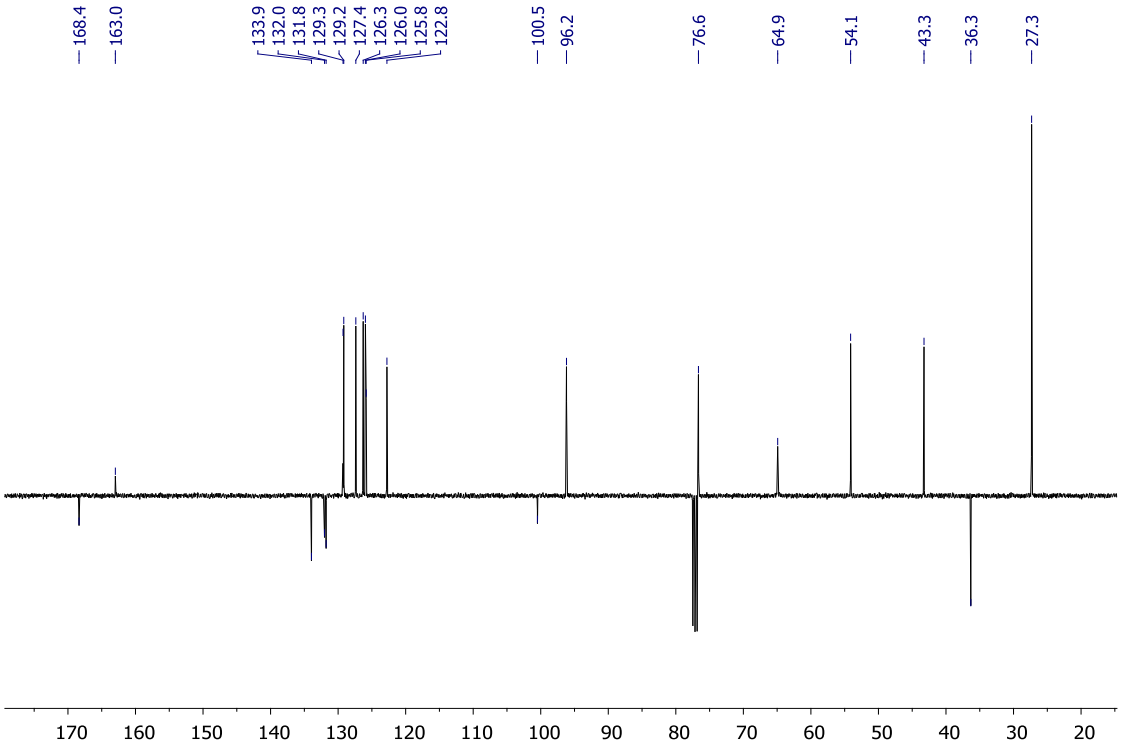


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (118b)

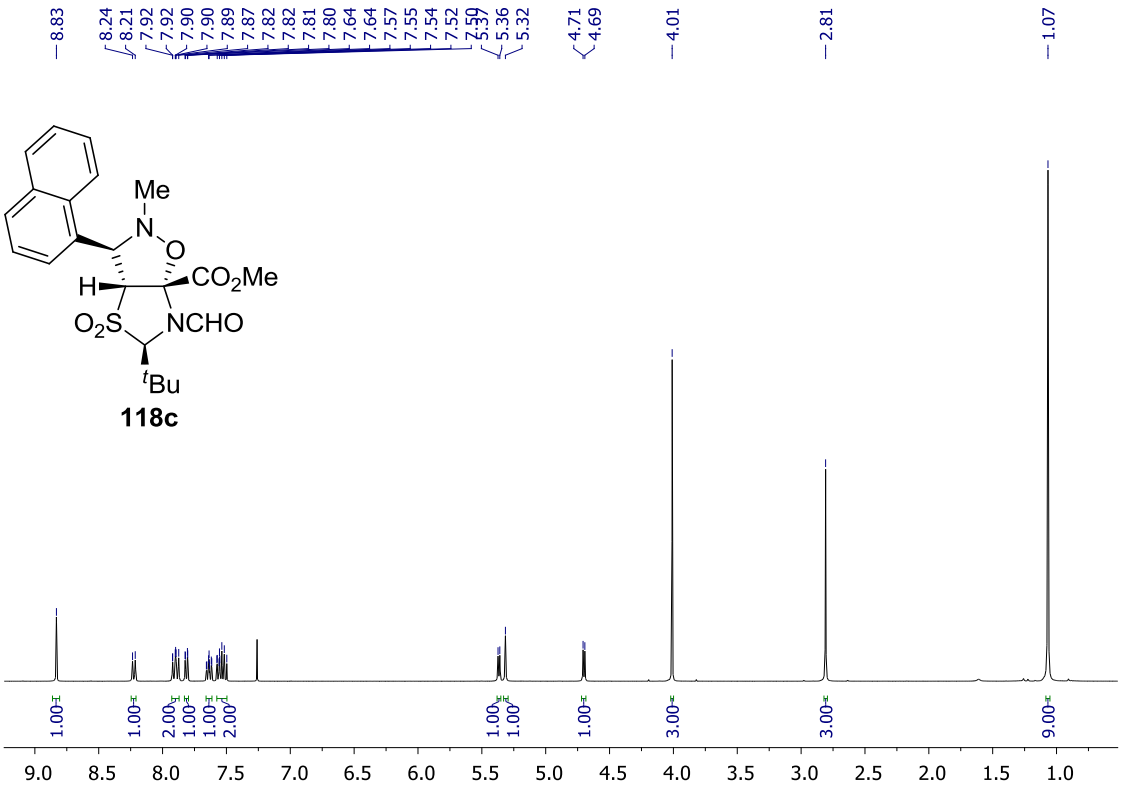


^{1}H-NMR ($CDCl_3$, 400 MHz)

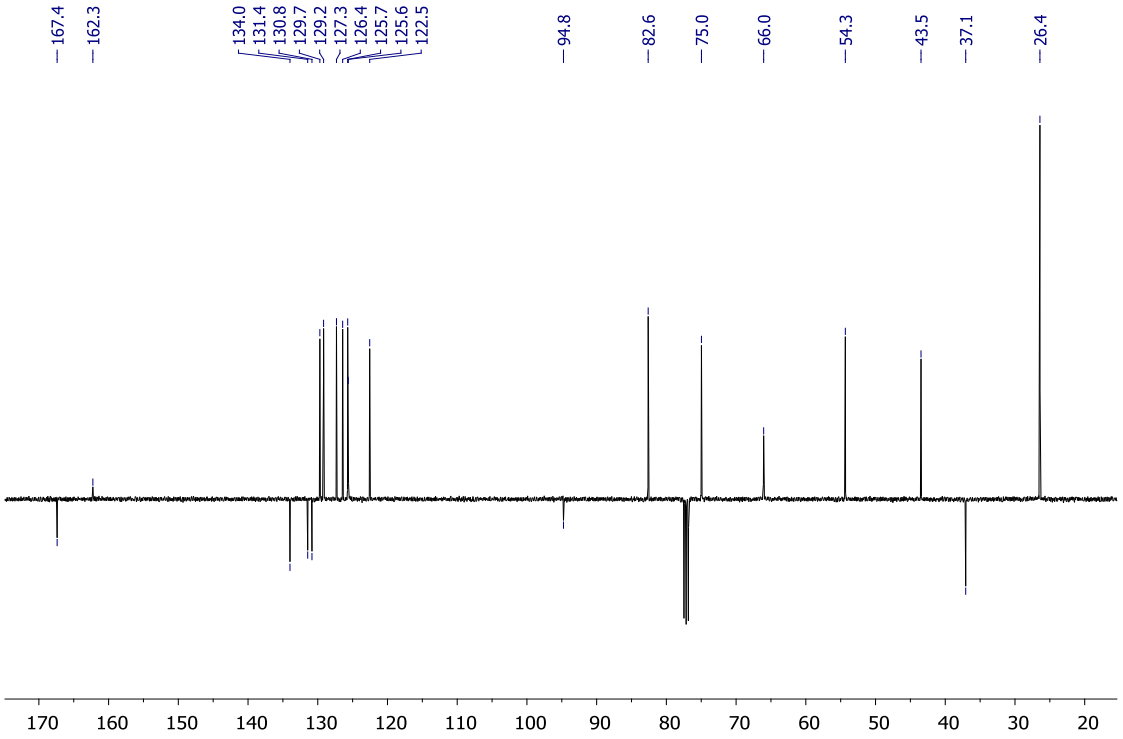


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 5-*tert*-butyl-6-formyl-2-methyl-3-(1-naphthyl)-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (118c)

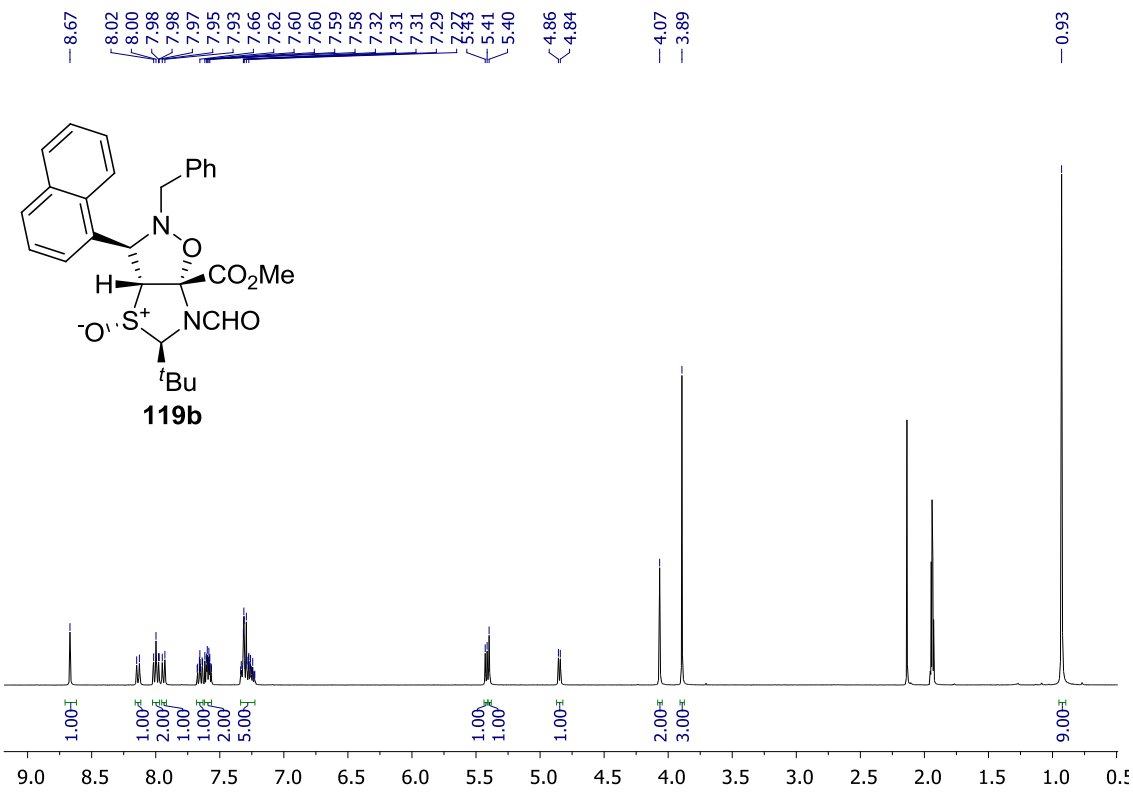


^{1}H-NMR ($CDCl_3$, 400 MHz)

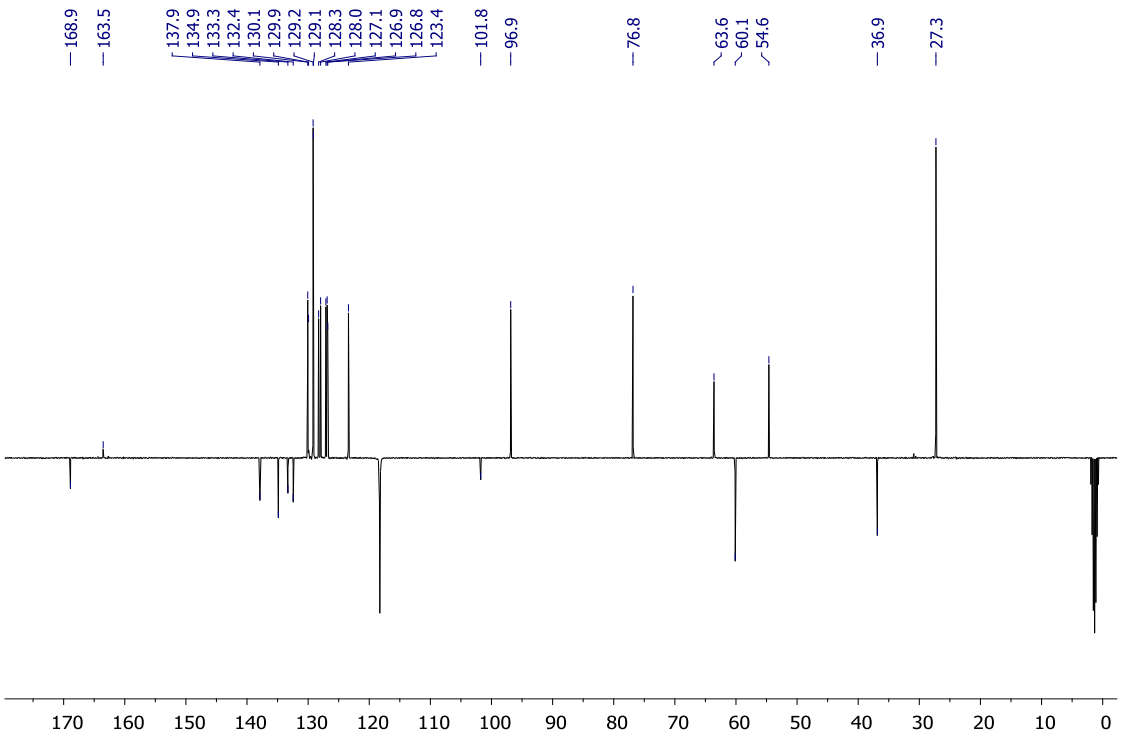


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-(1-naphthyl)-4-oxidohexahydrothiazolo[5,4-d]isoxazole-6a-carboxylate (119b)

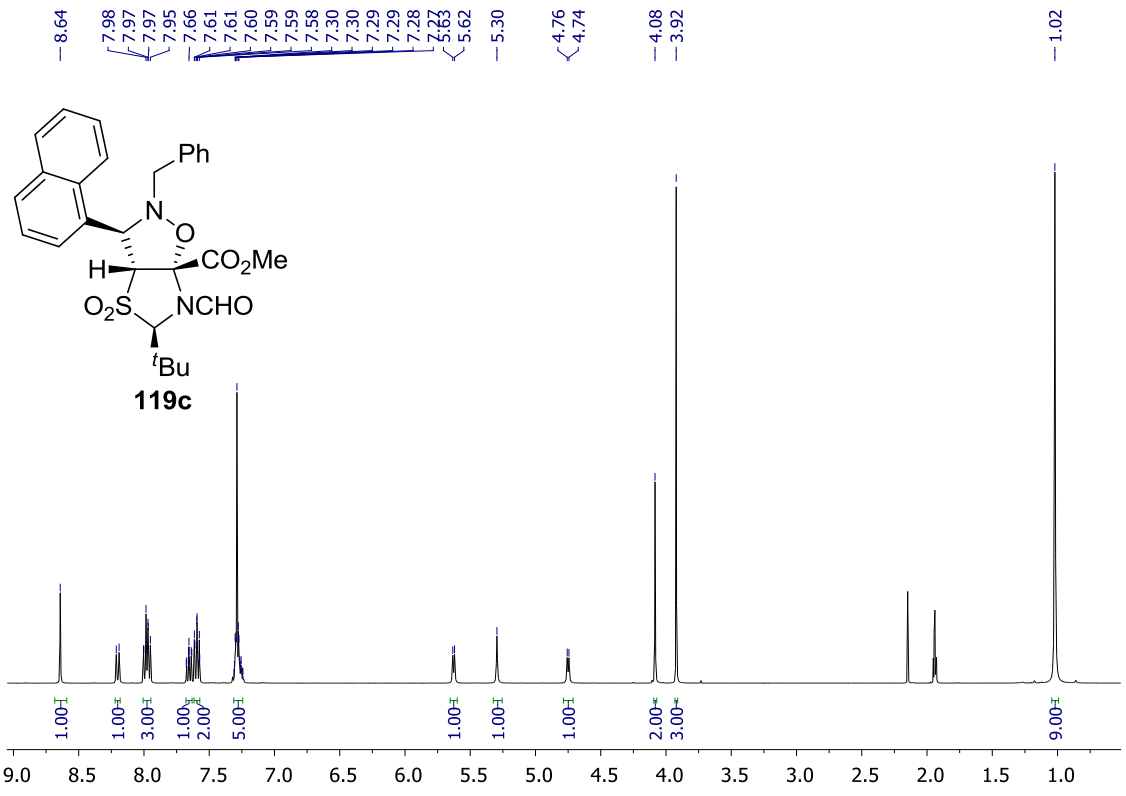


^{1}H-NMR (CD_3CN, 400 MHz)

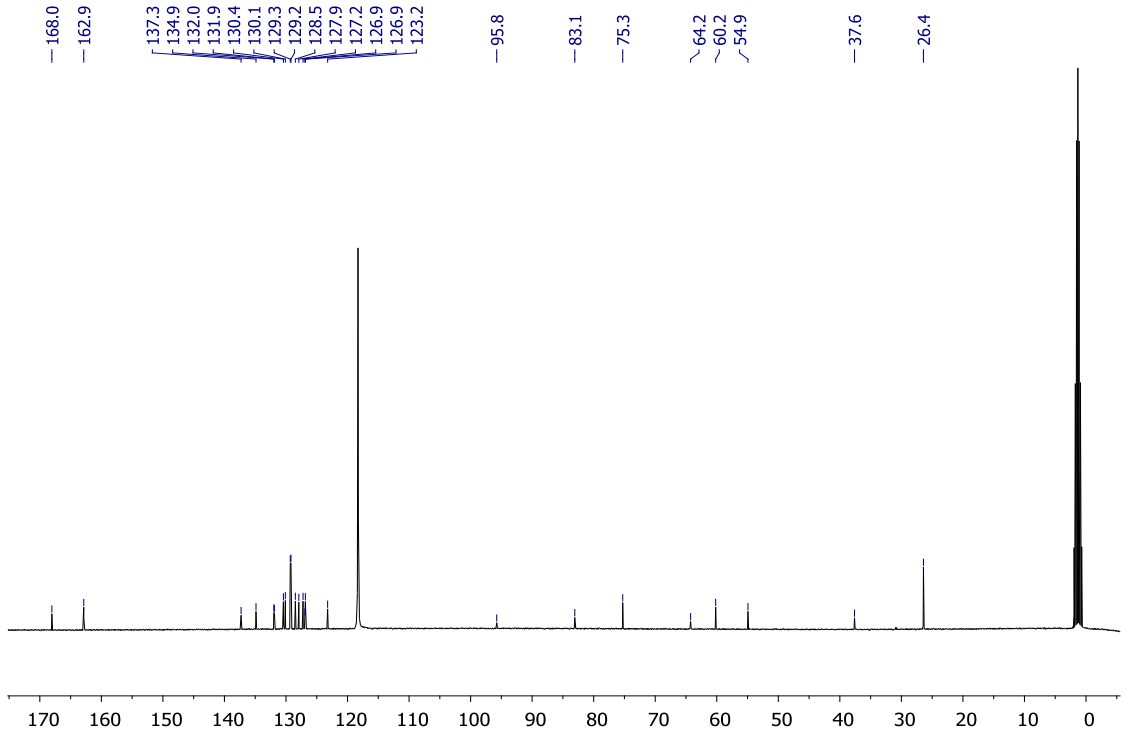


^{13}C-NMR (CD_3CN, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-(1-naphthyl)-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (119c)

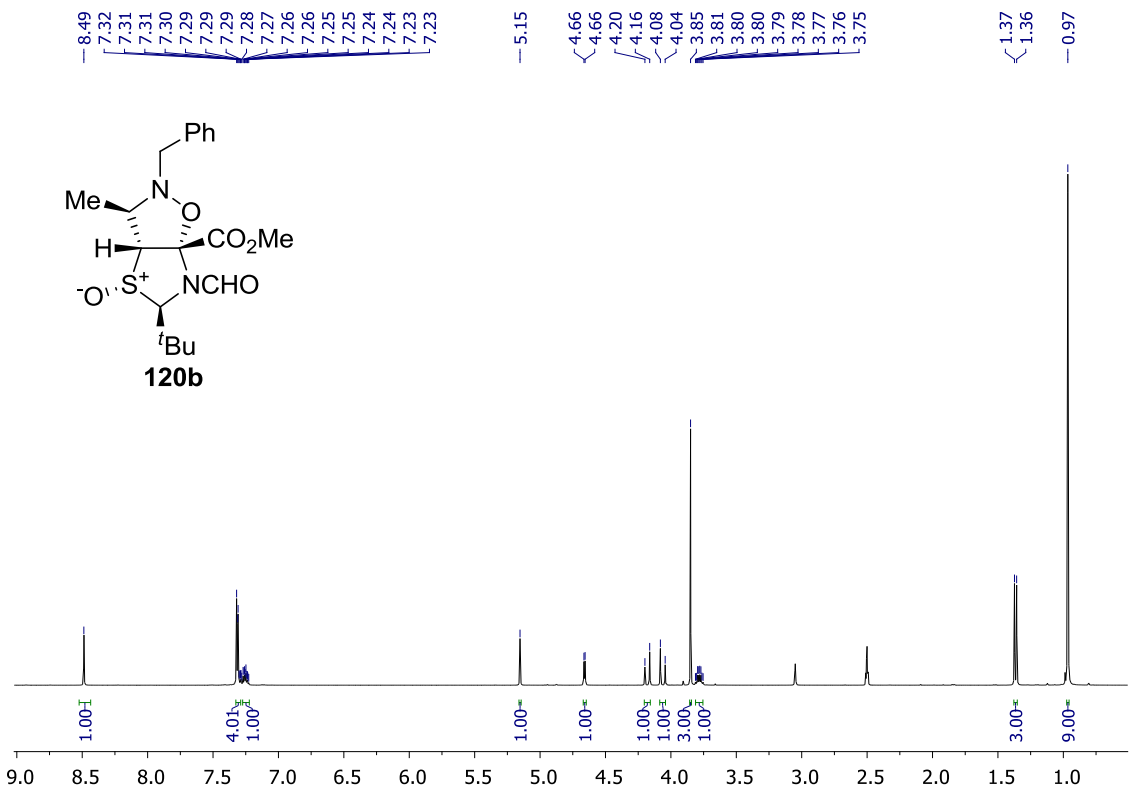


^{1}H-NMR (CD_3CN, 400 MHz)

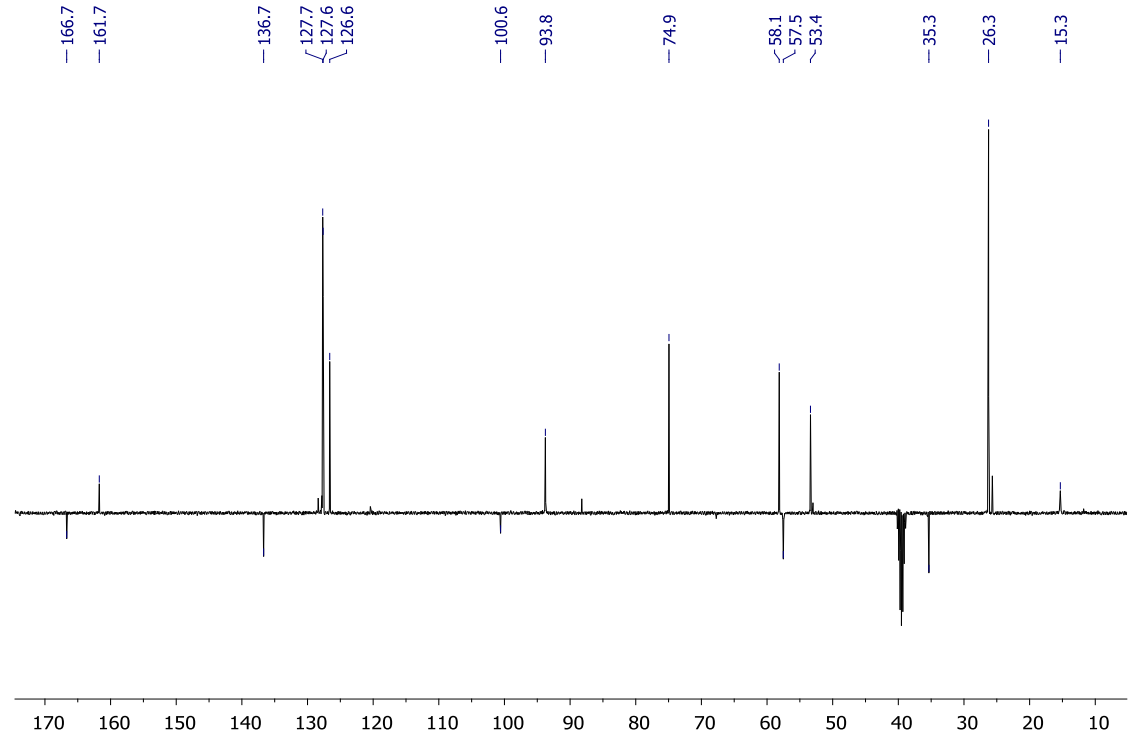


^{13}C-NMR (CD_3CN, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (120b)

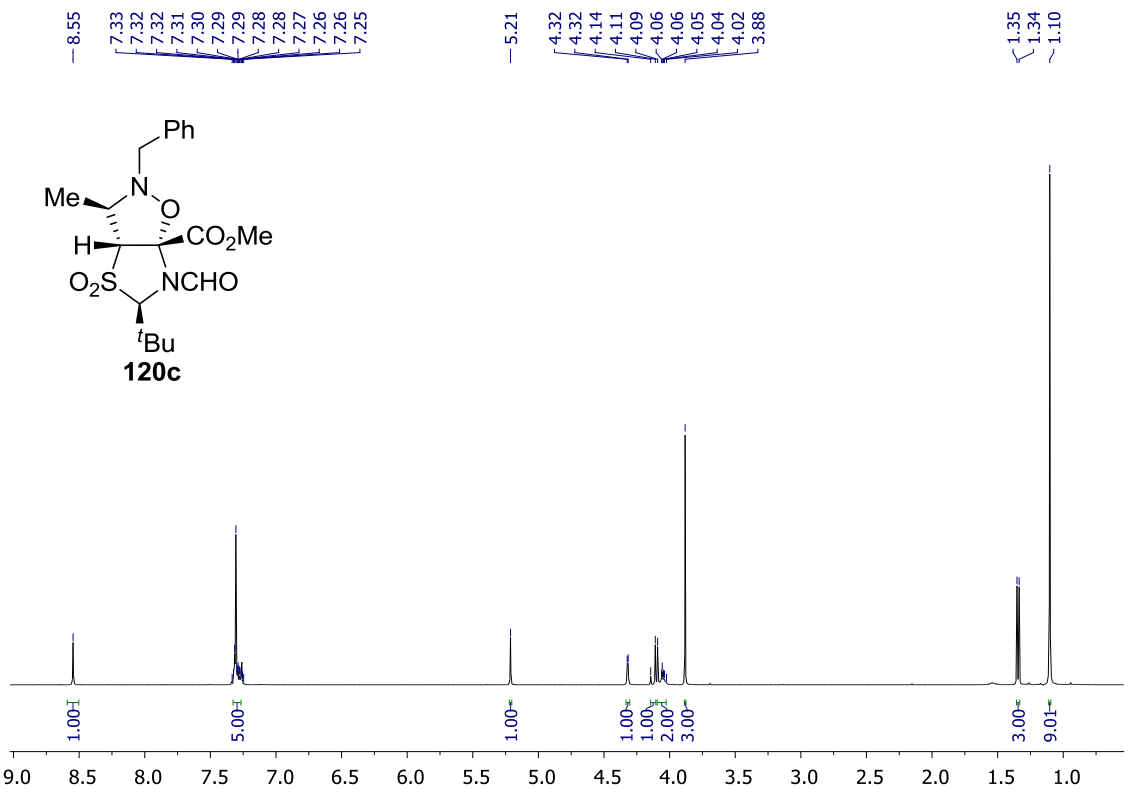


^{1}H-NMR (DMSO-*d*6, 400 MHz)

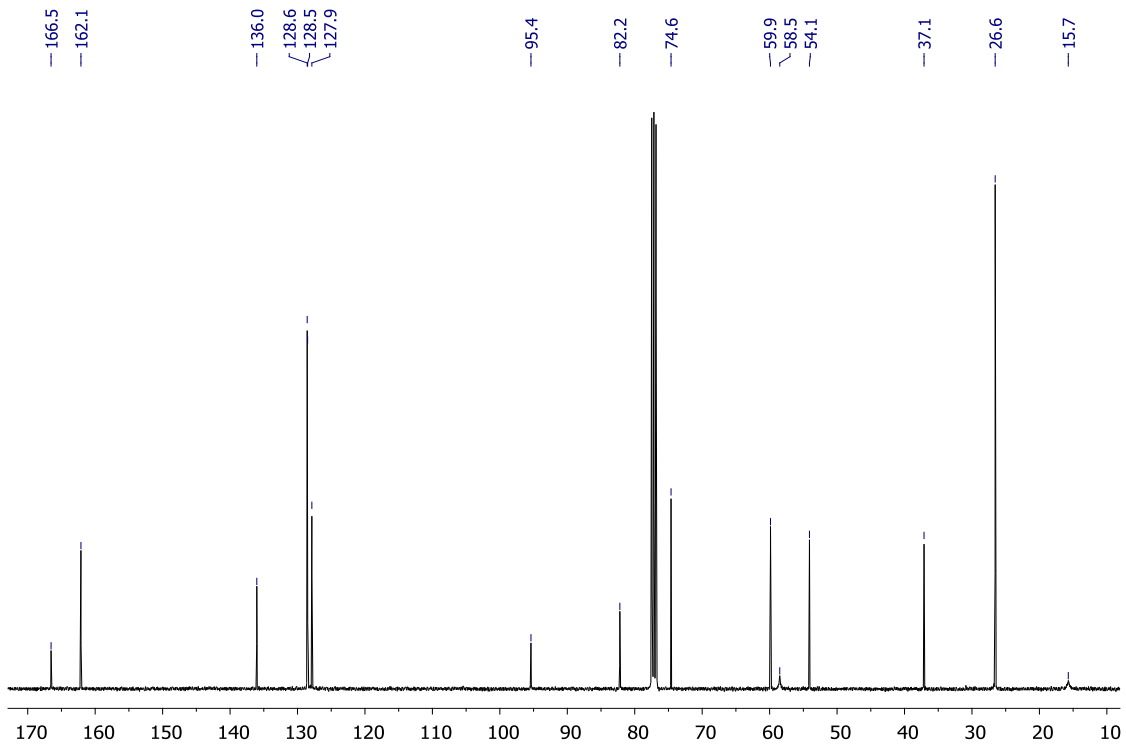


^{13}C-NMR (DMSO-*d*6, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (120c)

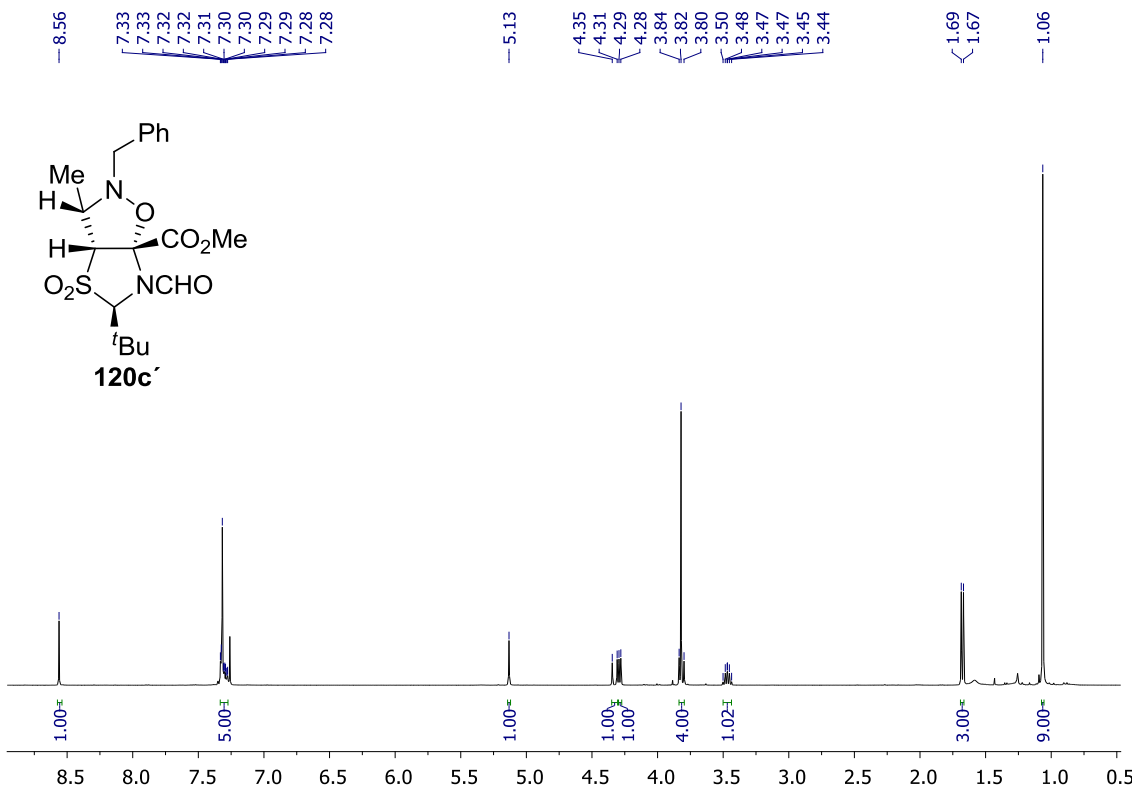


^{1}H-NMR ($CDCl_3$, 400 MHz)

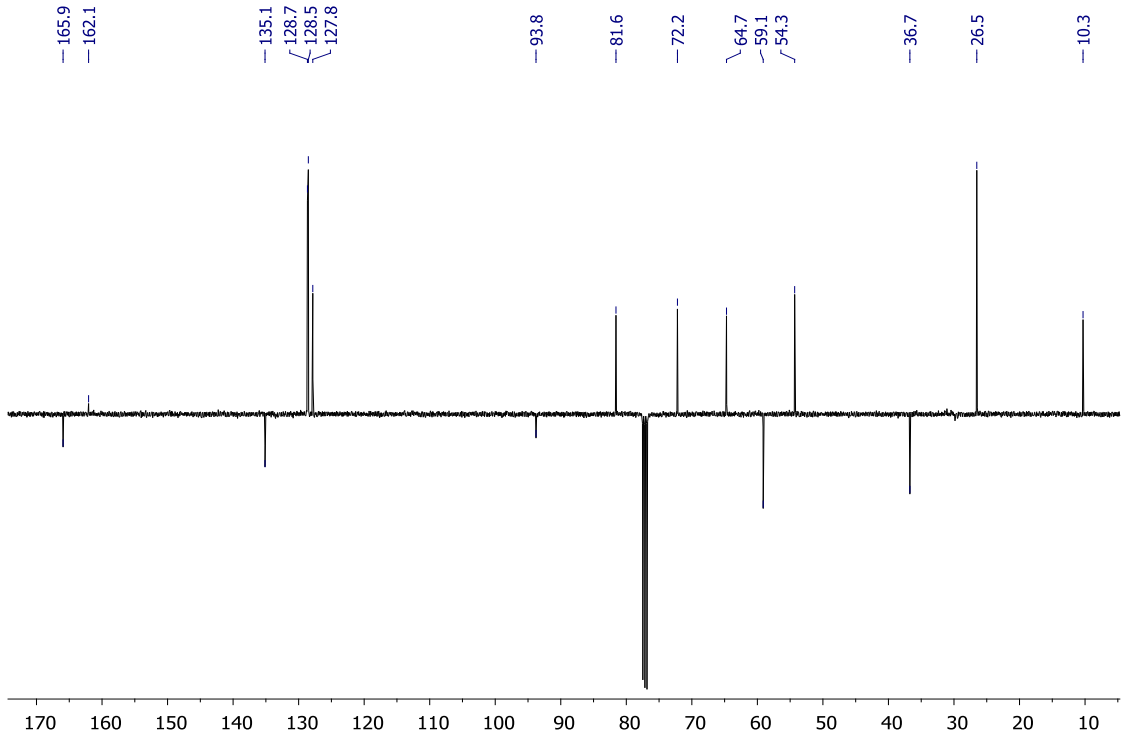


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (120c´)

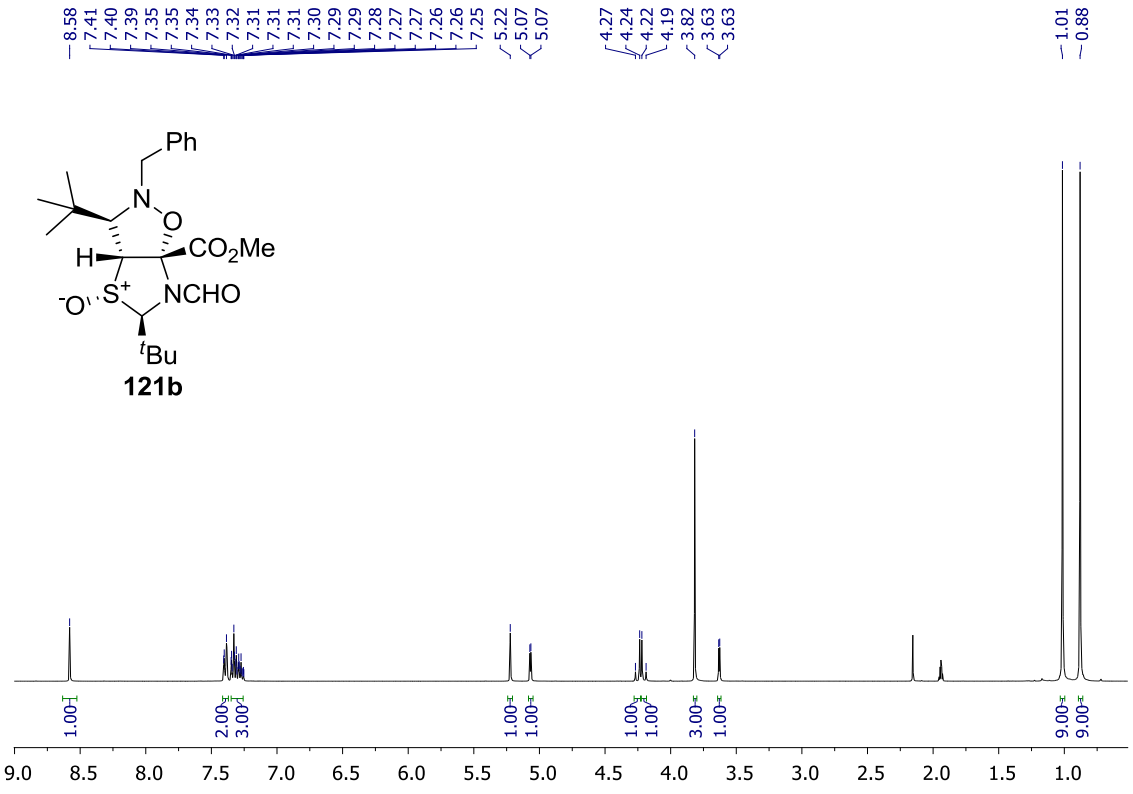


^{1}H-NMR ($CDCl_3$, 400 MHz)

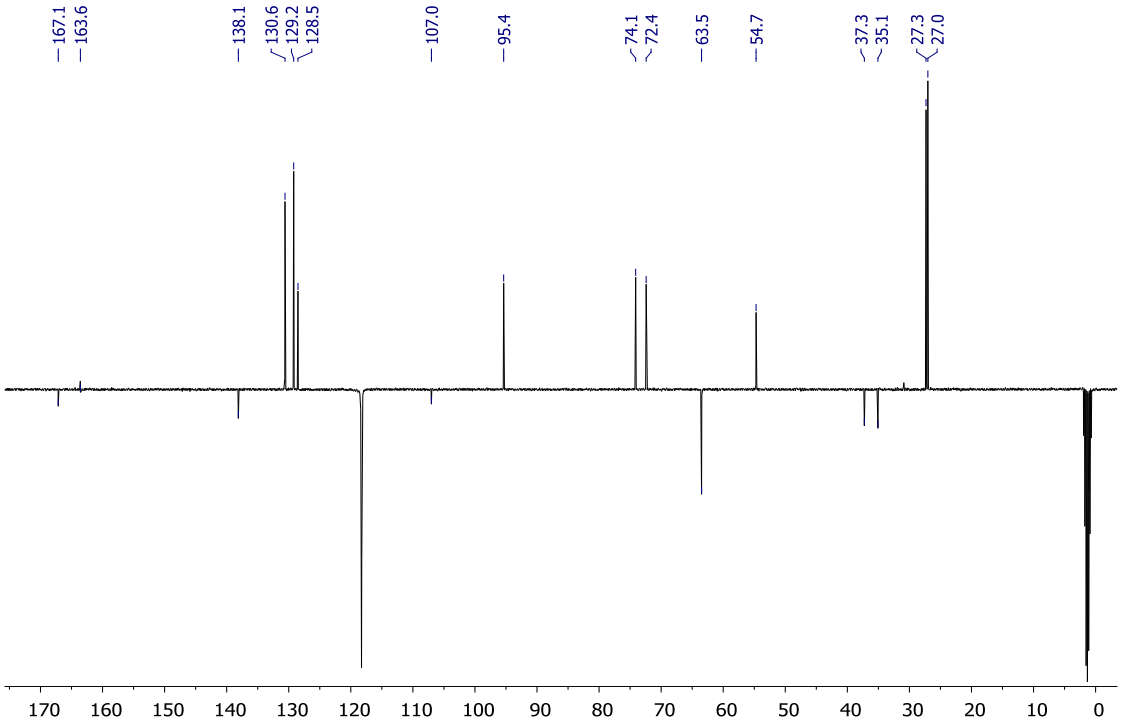


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,4*R*,5*R*,6a*S*)-Methyl 2-benzyl-3,5-di-*tert*-butyl-6-formyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (121b)

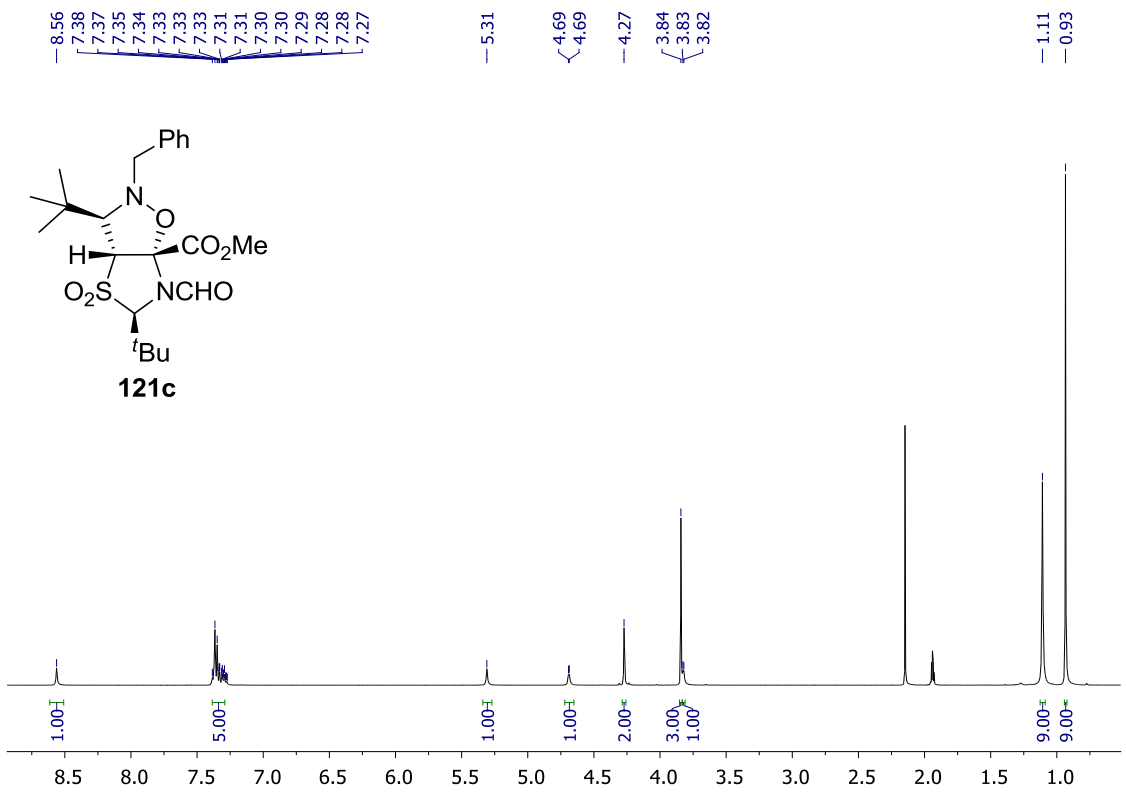


^{1}H-NMR (CD_3CN, 400 MHz)

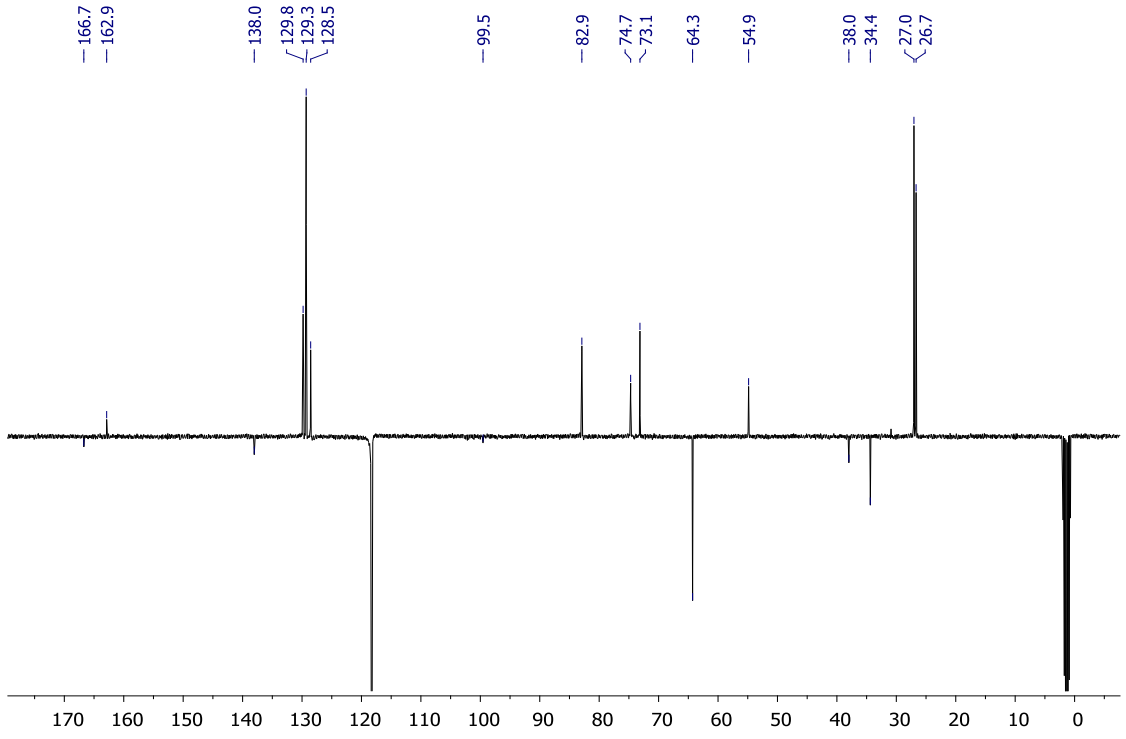


^{13}C-NMR (CD_3CN, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-3,5-di-*tert*-butyl-6-formyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (121c)

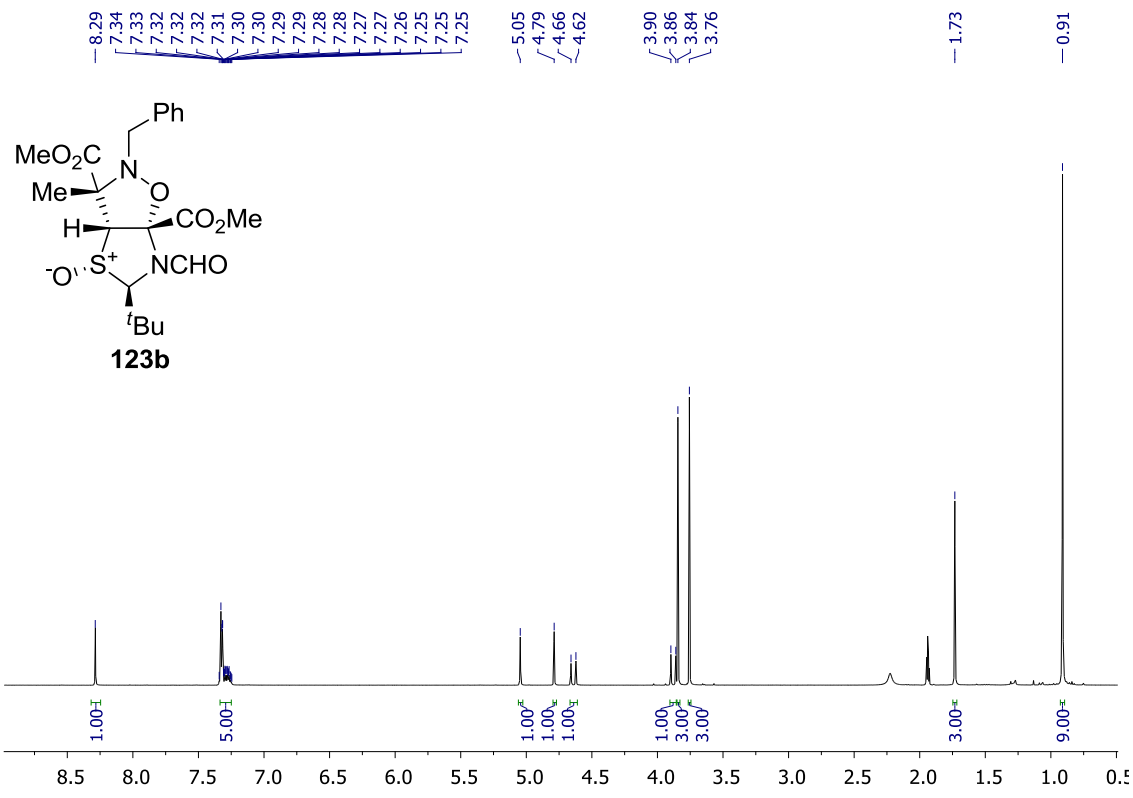


^{1}H-NMR (CD_3CN, 400 MHz)

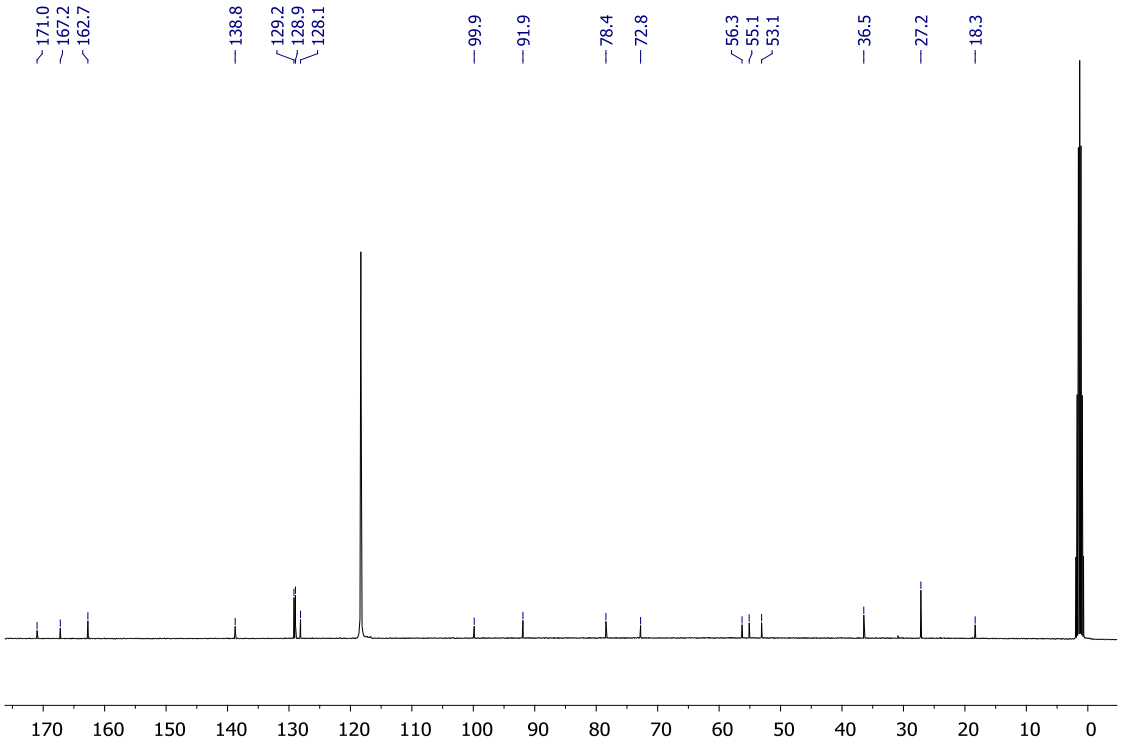


^{13}C-NMR (CD_3CN, 100 MHz)

(3*S*,3a*R*,4*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (123b)

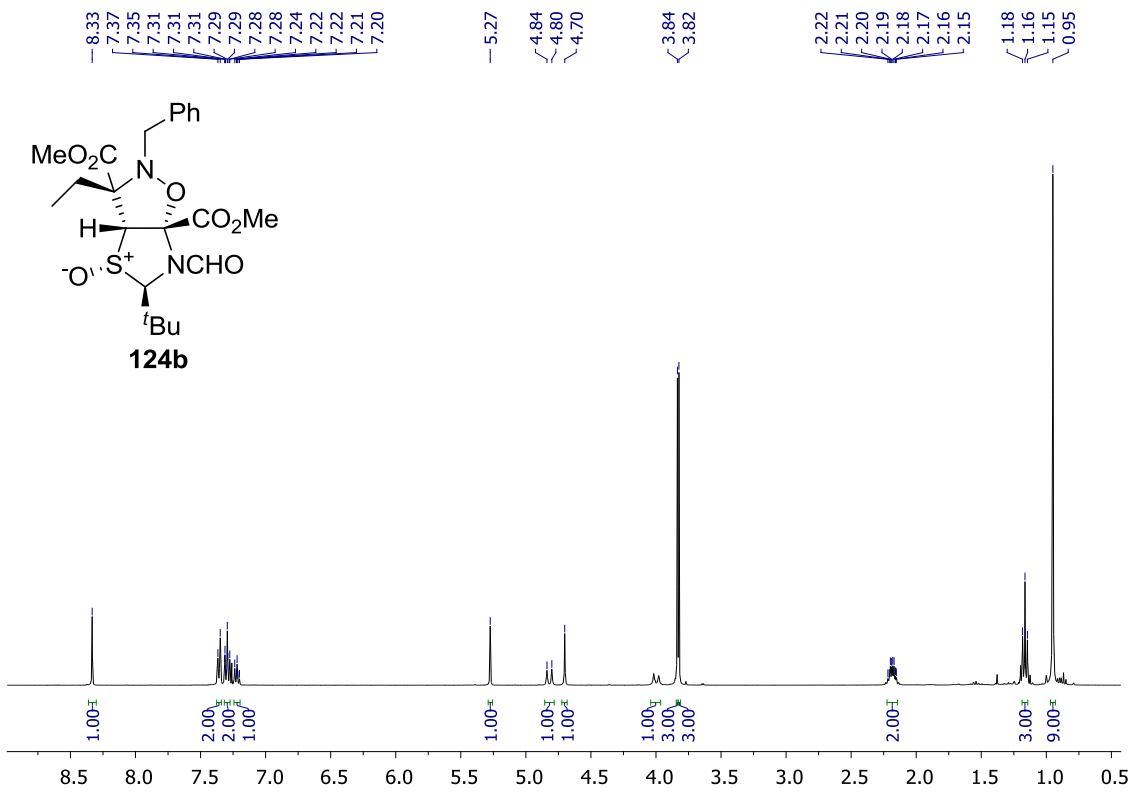


^{1}H-NMR (CD_3CN, 400 MHz)

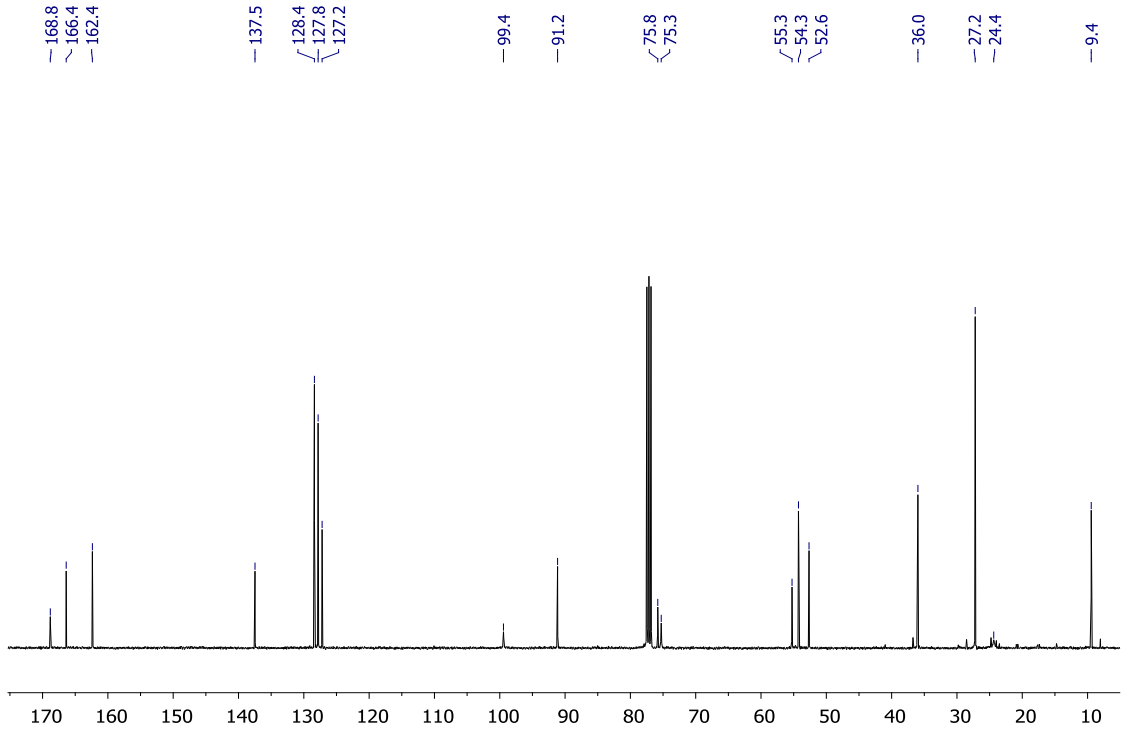


^{13}C-NMR (CD_3CN, 100 MHz)

(3*S*,3a*R*,4*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formyl-4-oxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (124b)

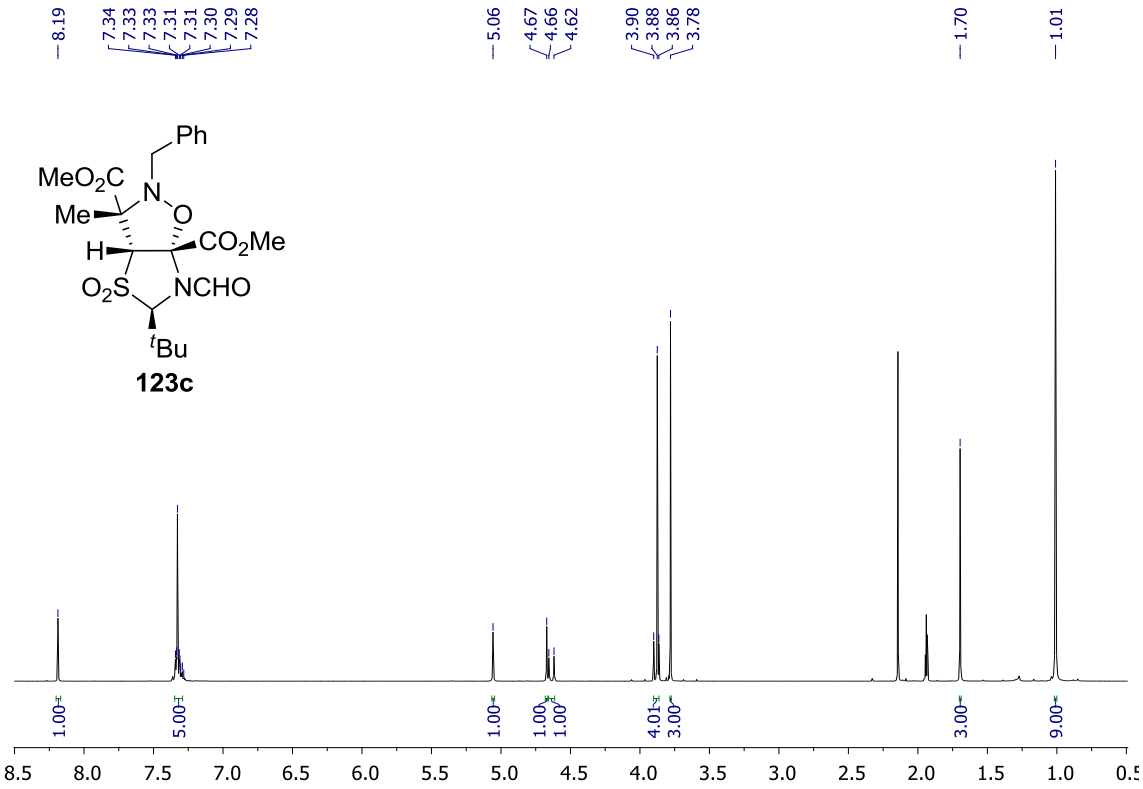


^{1}H-NMR ($CDCl_3$, 400 MHz)

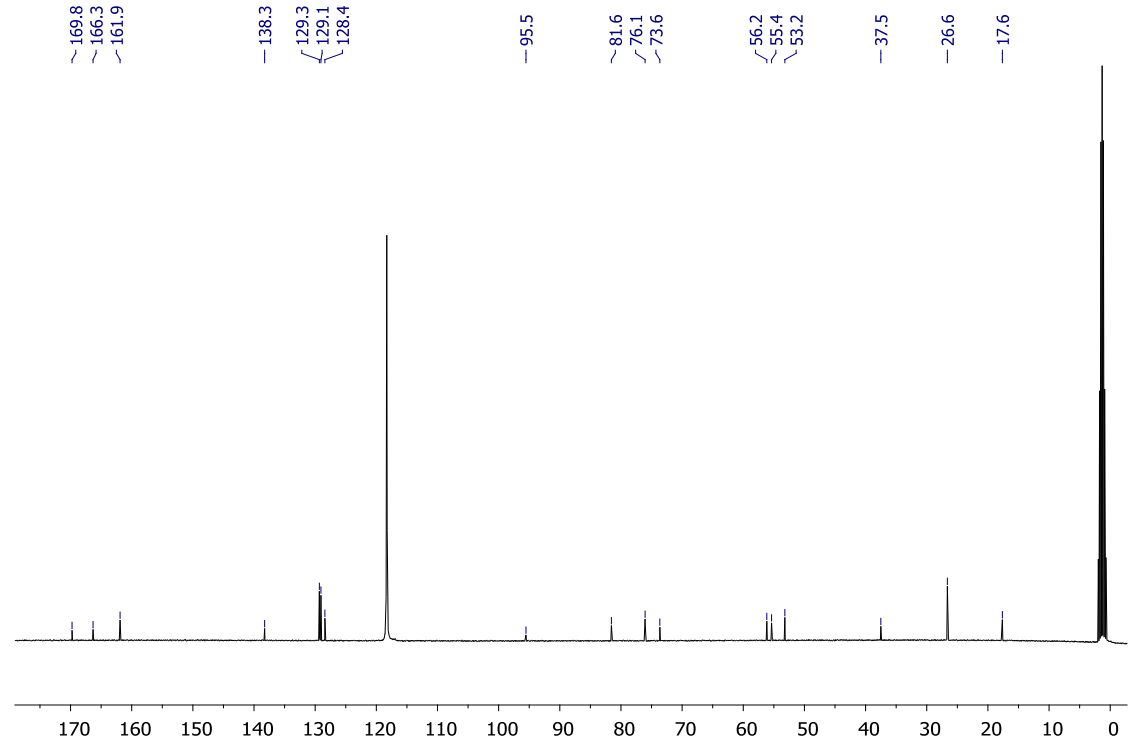


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (123c)

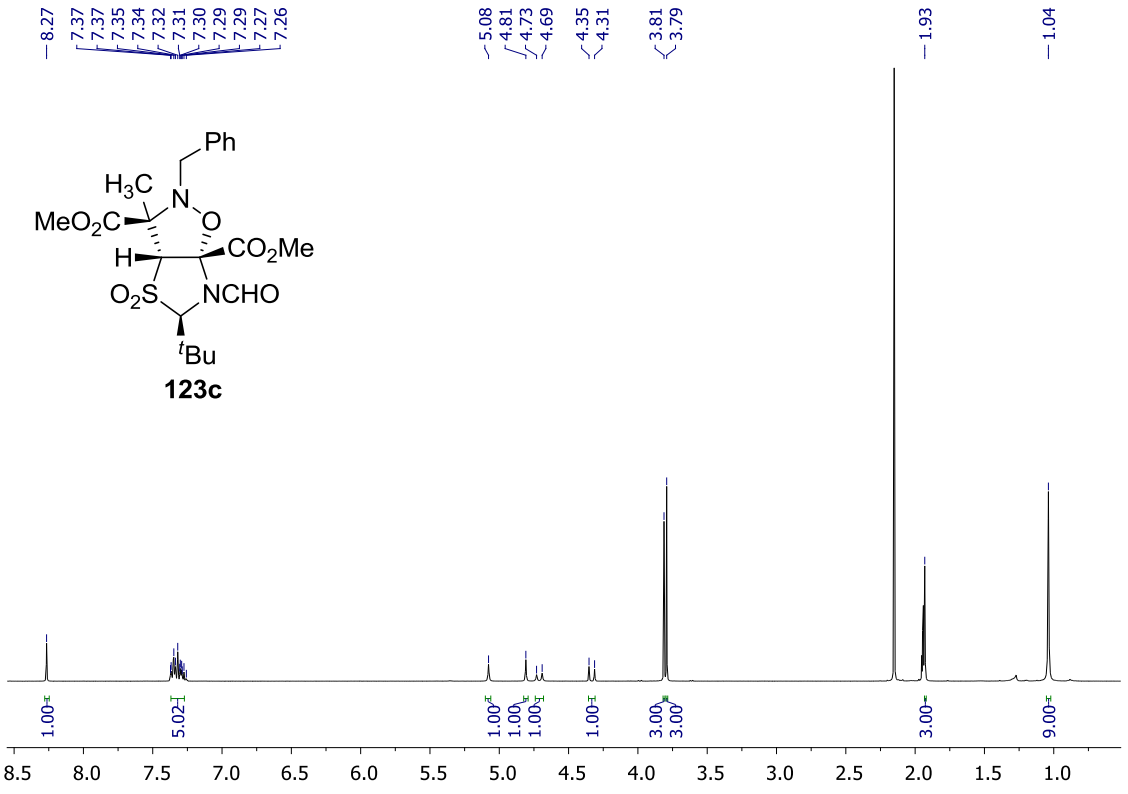


^{1}H-NMR (CD_3CN, 400 MHz)

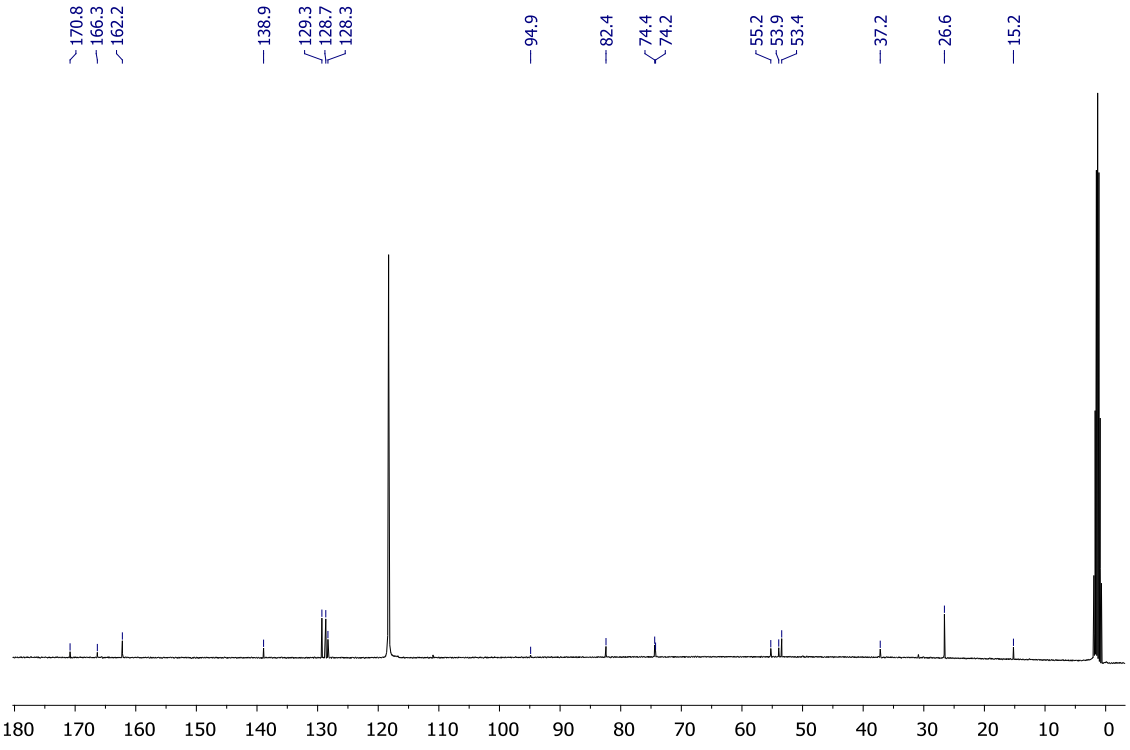


^{13}C-NMR (CD_3CN, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (123c)

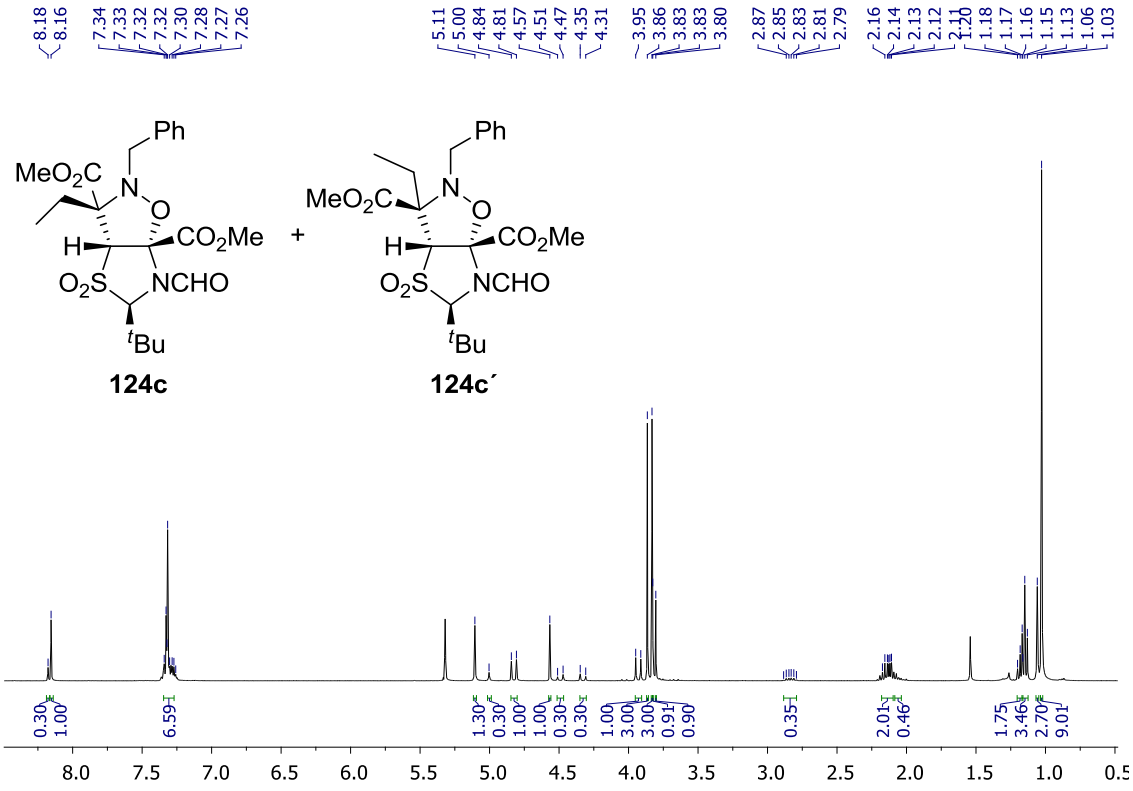


^{1}H-NMR (CD_3CN, 400 MHz)



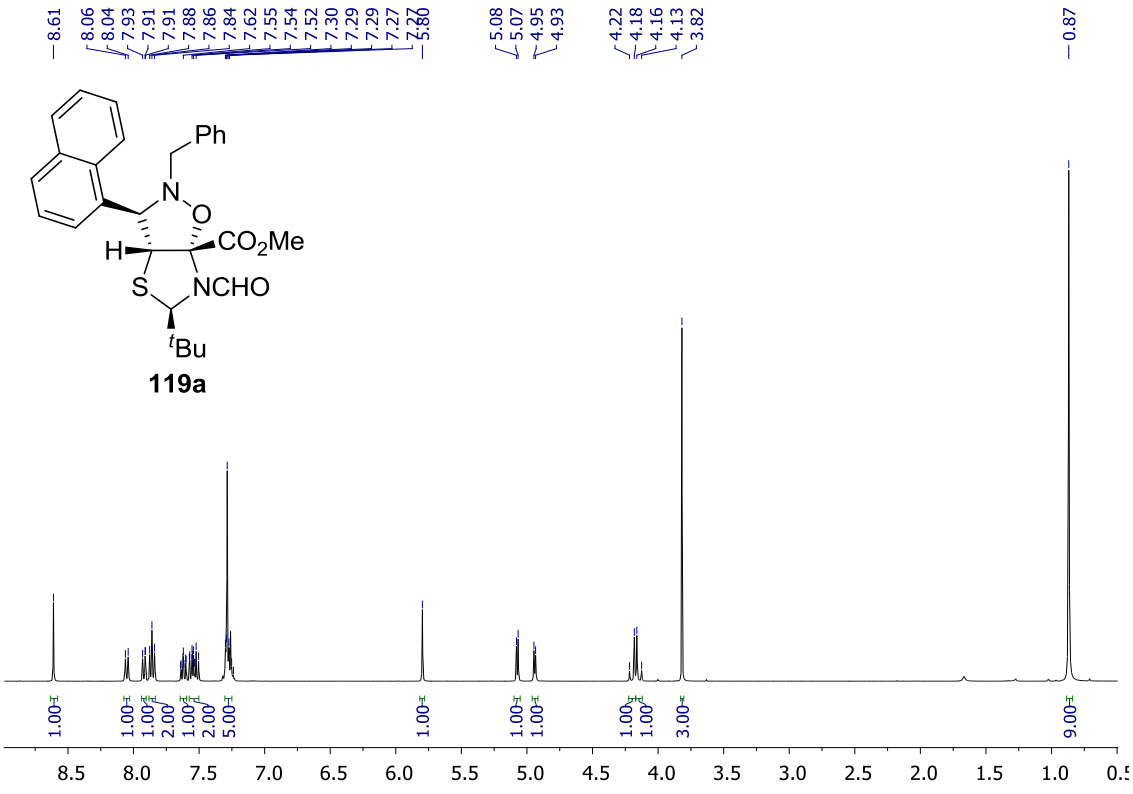
^{13}C-NMR (CD_3CN, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (124c) and **(3*R*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formyl-4,4-dioxidohexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (124c´)**

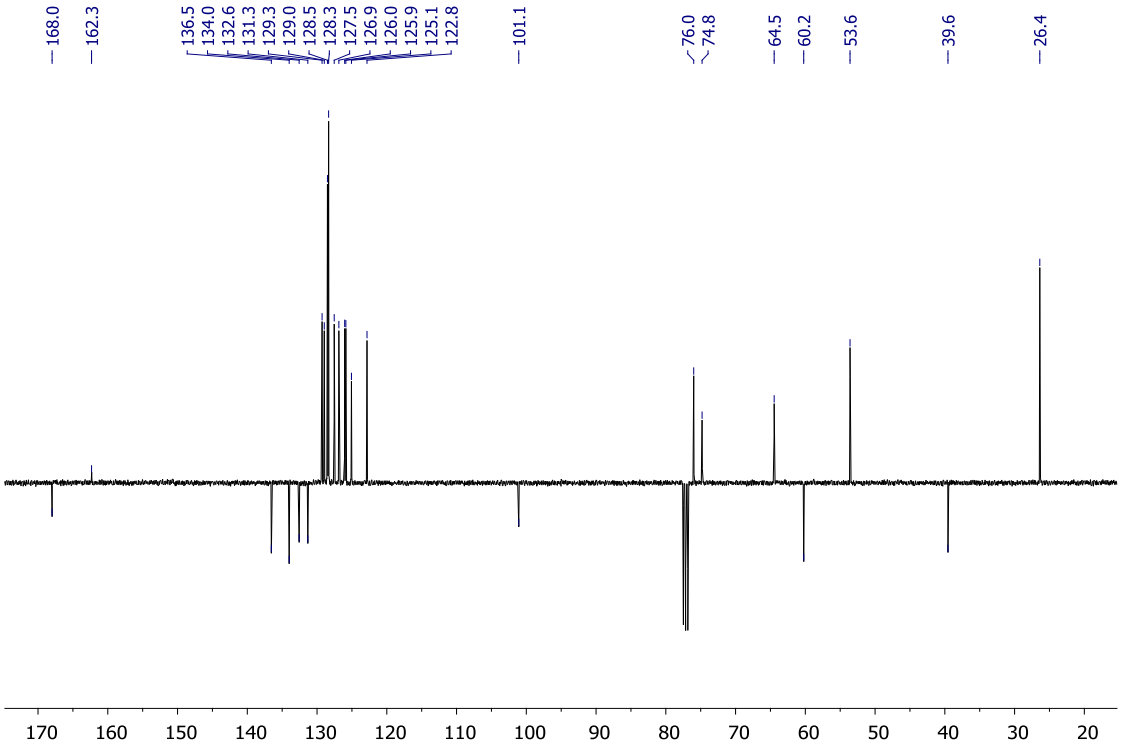


^{1}H-NMR (CD_2Cl_2, 400 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-(1-naphthyl)hexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (119a)

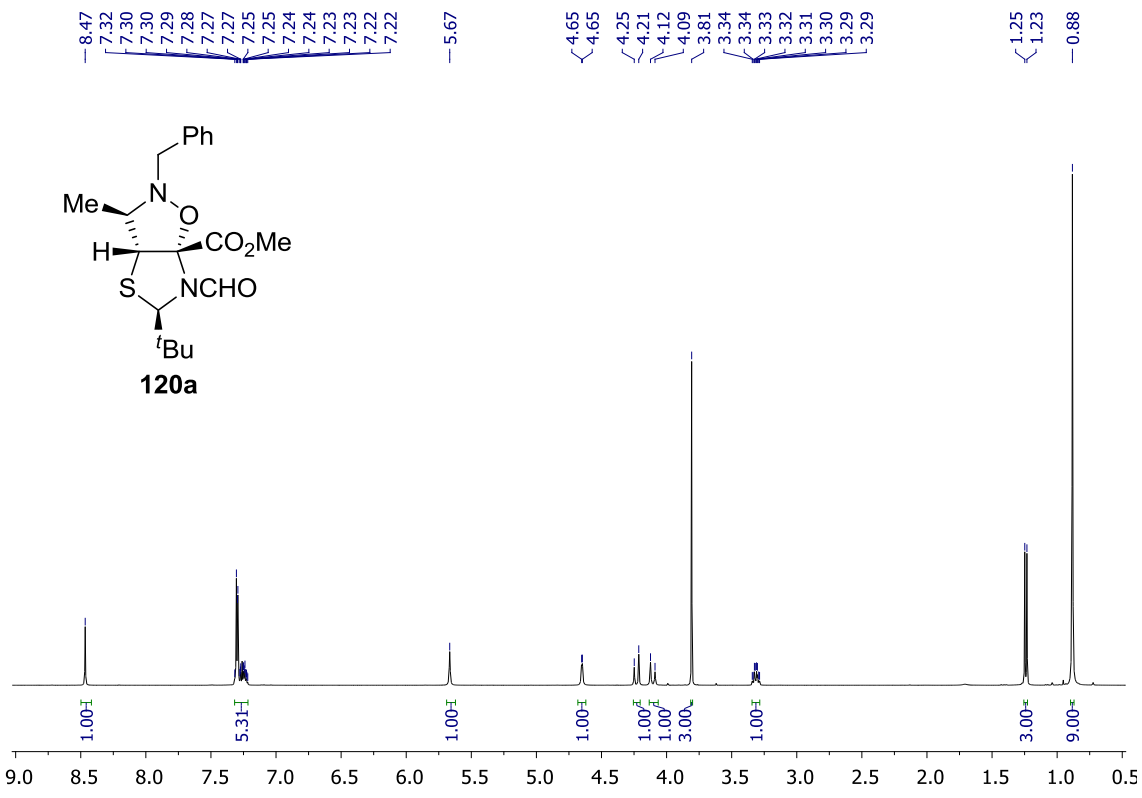


^{1}H-NMR ($CDCl_3$, 400 MHz)

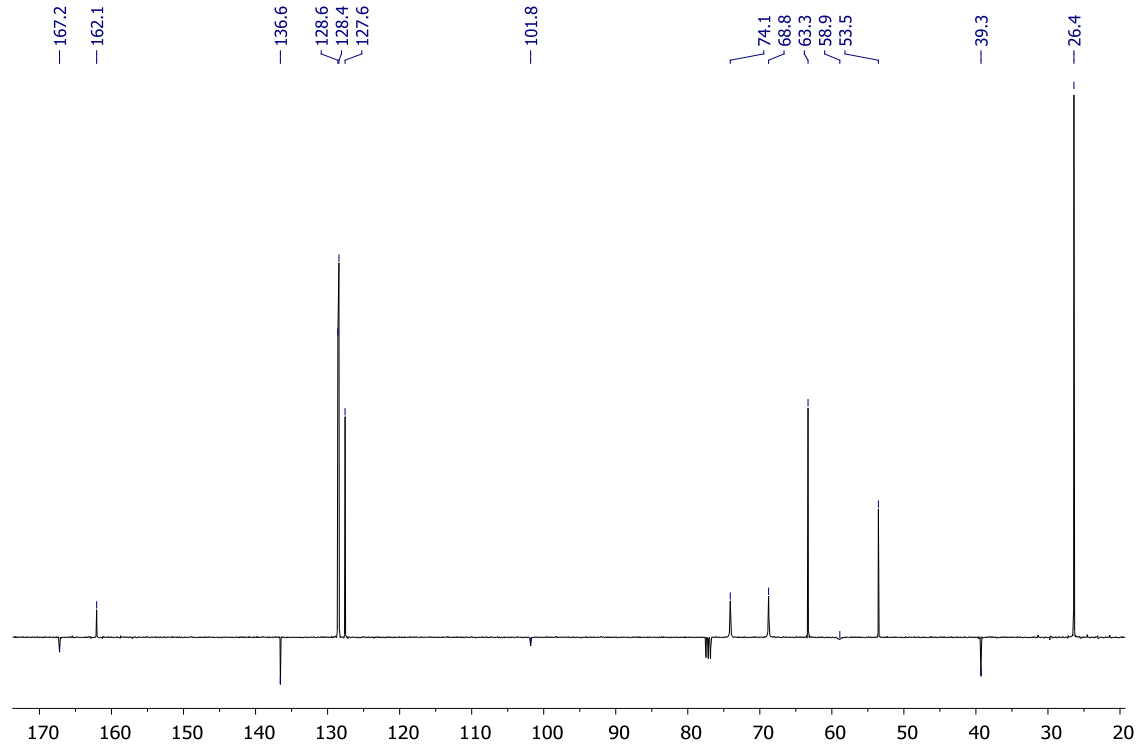


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methylhexahydrothiazolo[5,4-*d*]isoxazole-6a-carboxylate (120a)

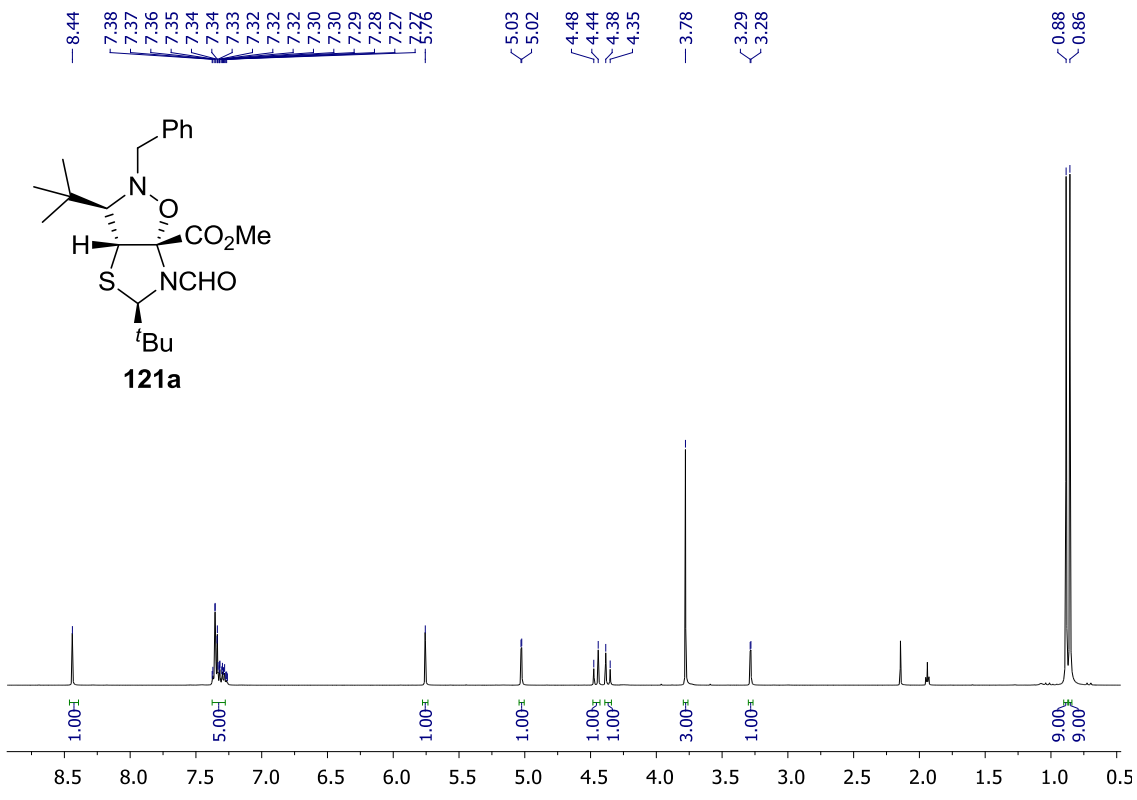


^{1}H-NMR ($CDCl_3$, 400 MHz)

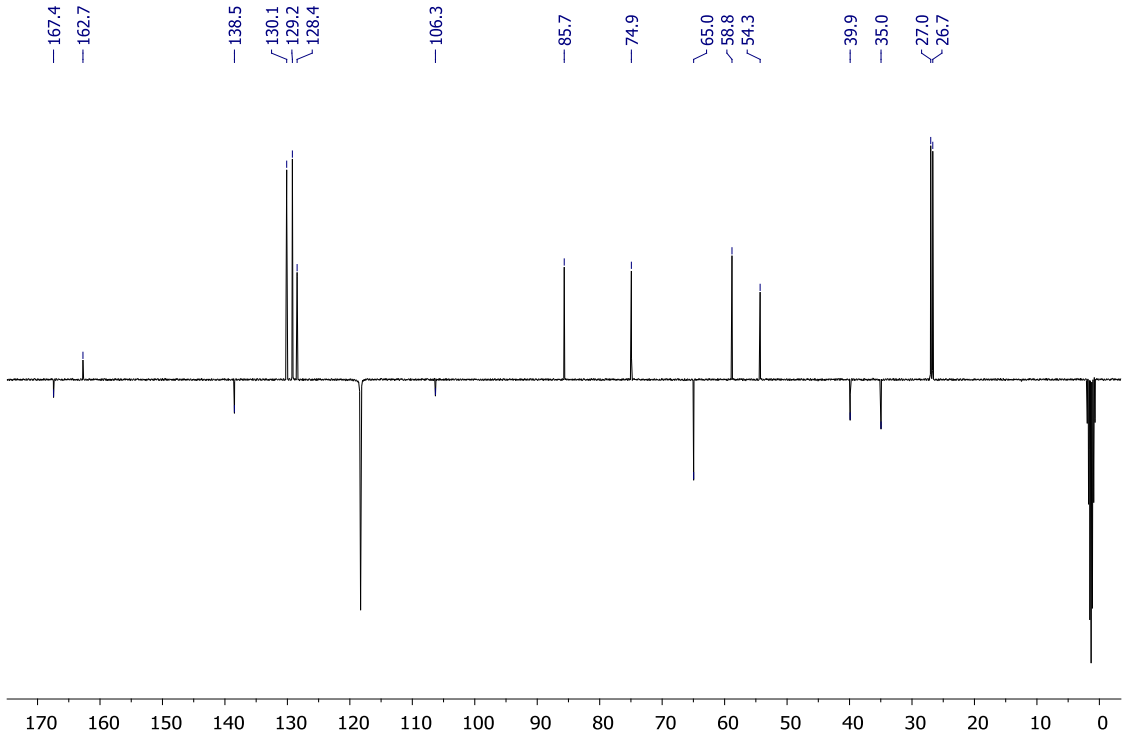


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*R*,3a*R*,5*R*,6a*S*)-Methyl 2-benzyl-3,5-di-tert-butyl-6-formylhexahydrothiazolo[5,4-d]isoxazole-6a-carboxylate (121a)

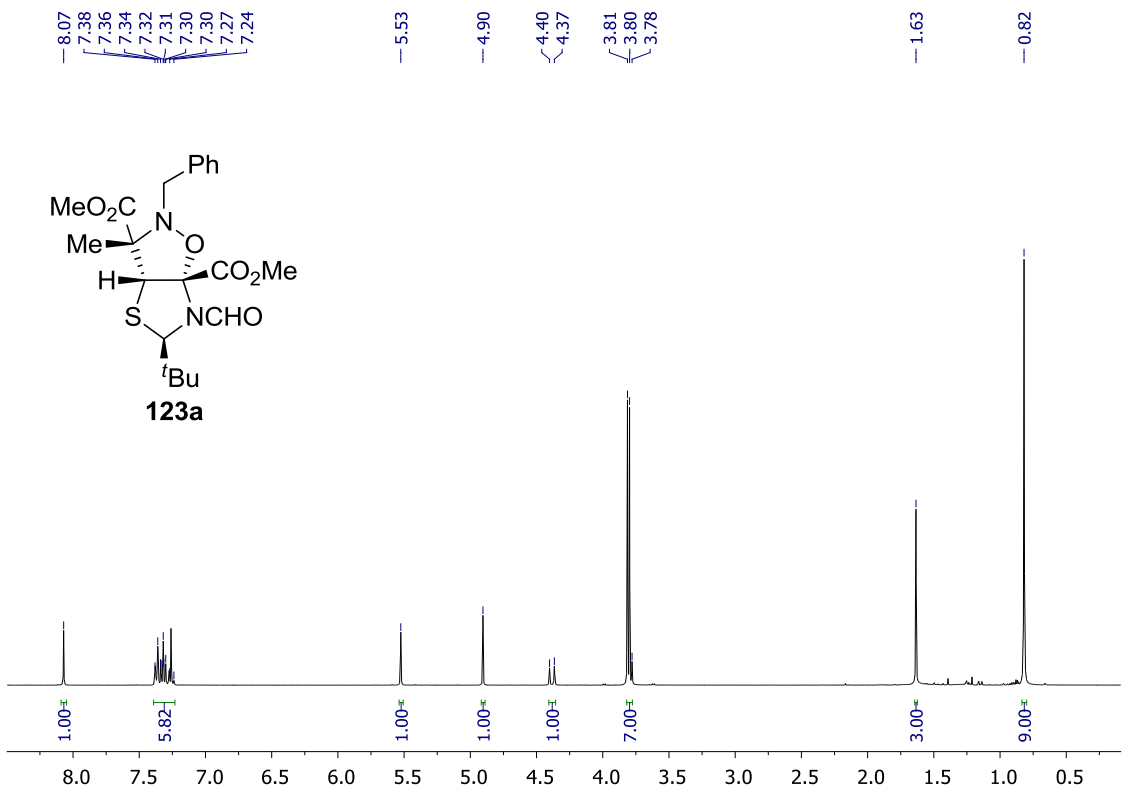


^{1}H-NMR (CD_3CN, 400 MHz)

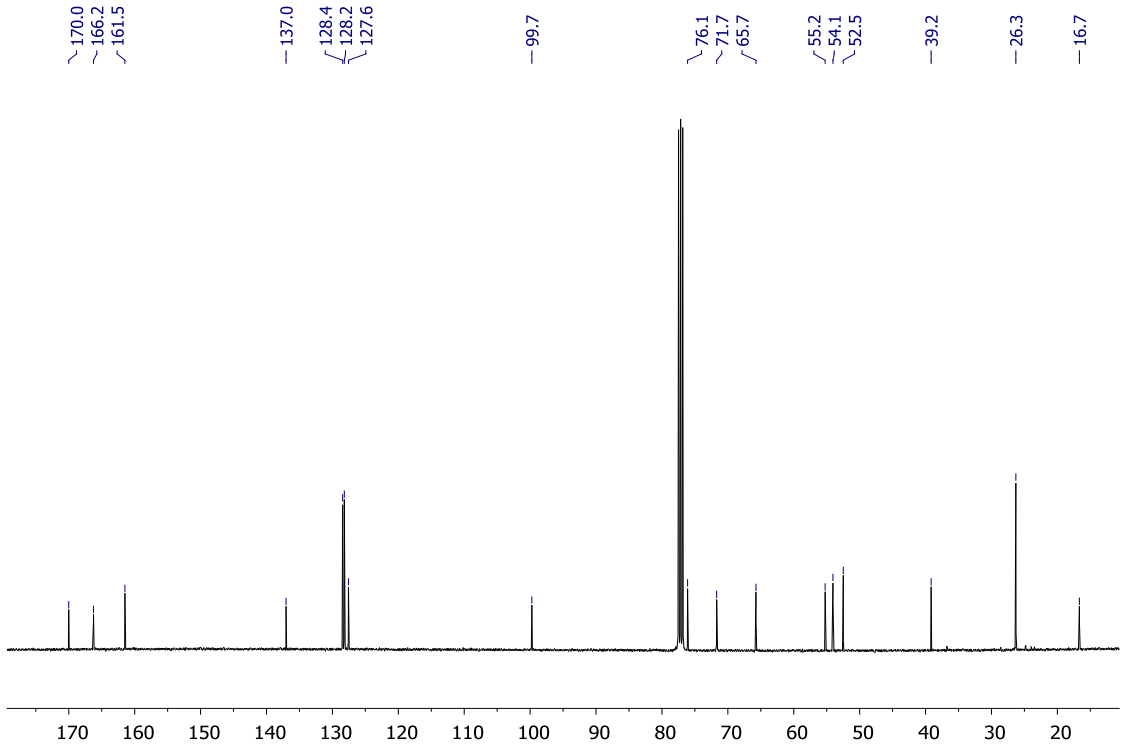


^{13}C-NMR (CD_3CN, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-6-formyl-3-methylhexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (123a)

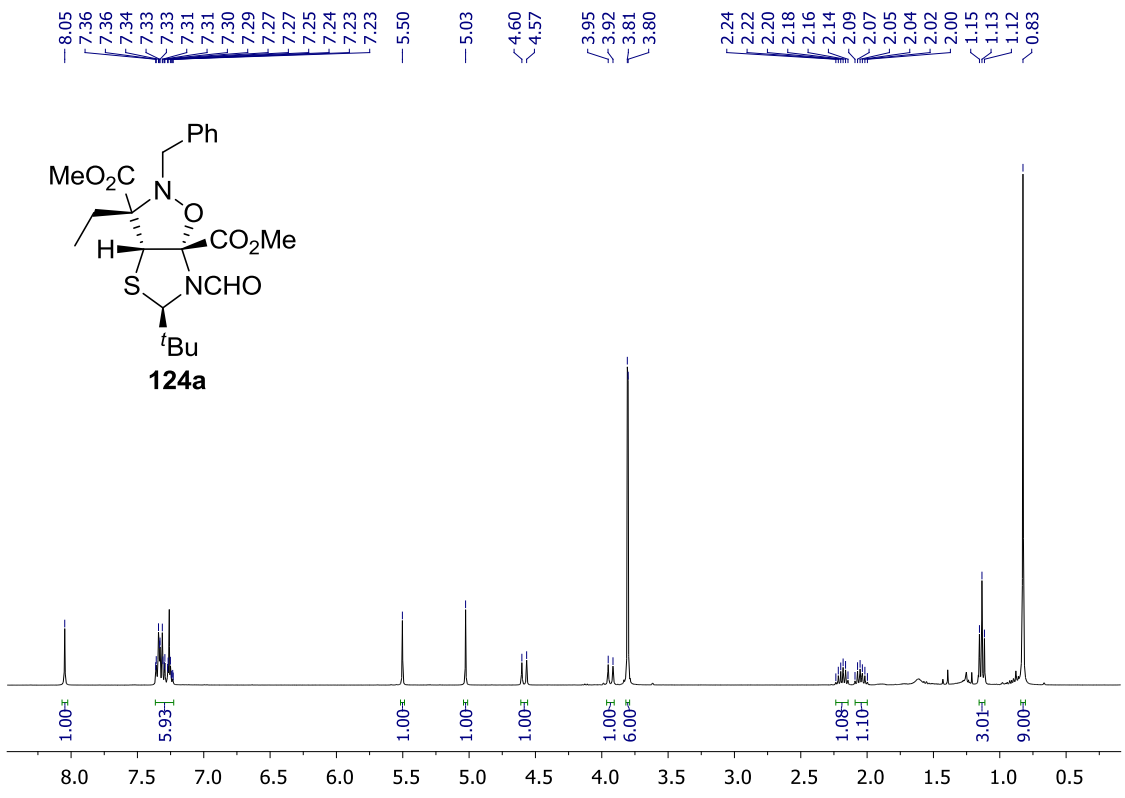


^{1}H-NMR ($CDCl_3$, 400 MHz)

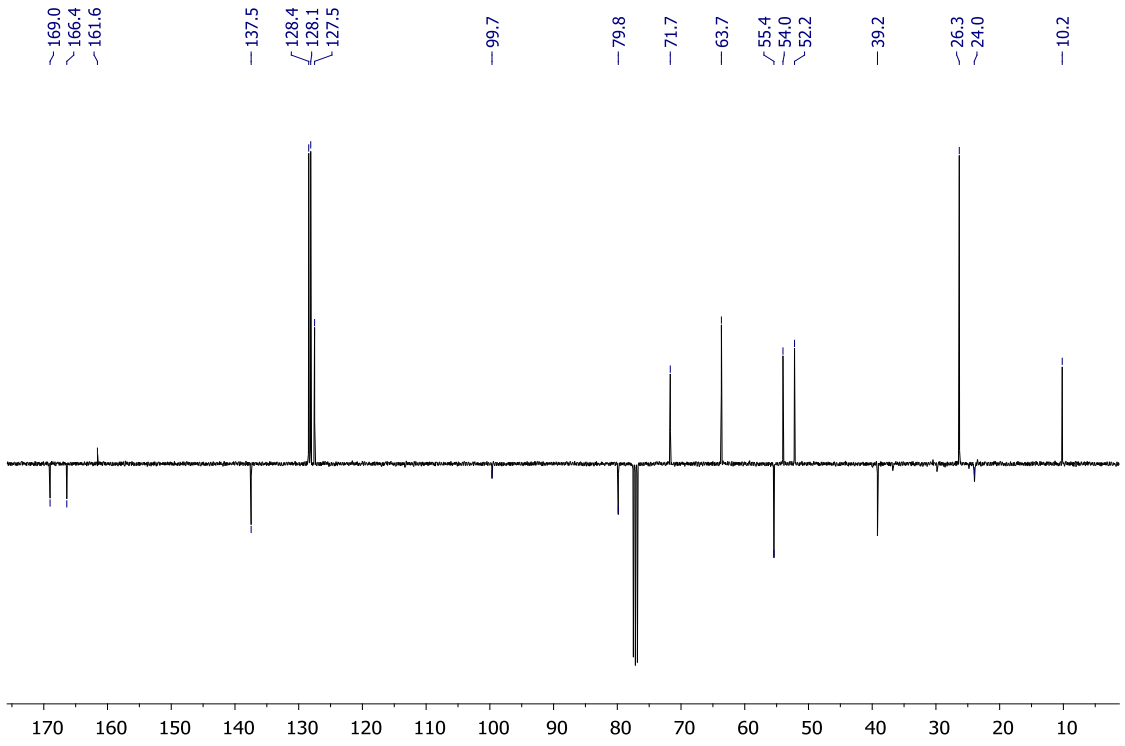


^{13}C-NMR ($CDCl_3$, 100 MHz)

(3*S*,3a*R*,5*R*,6a*S*)-Dimethyl 2-benzyl-5-*tert*-butyl-3-ethyl-6-formylhexahydrothiazolo[5,4-*d*]isoxazole-3,6a-dicarboxylate (124a)



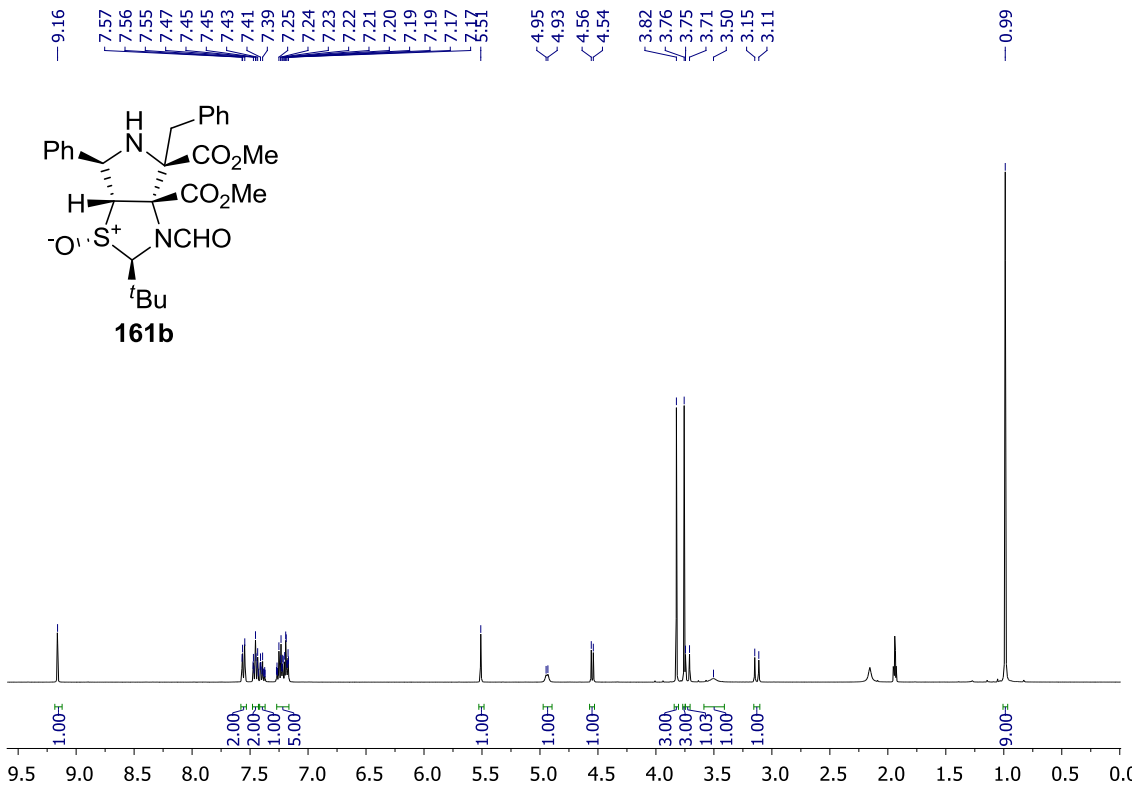
^{1}H-NMR ($CDCl_3$, 400 MHz)



^{13}C-NMR ($CDCl_3$, 100 MHz)

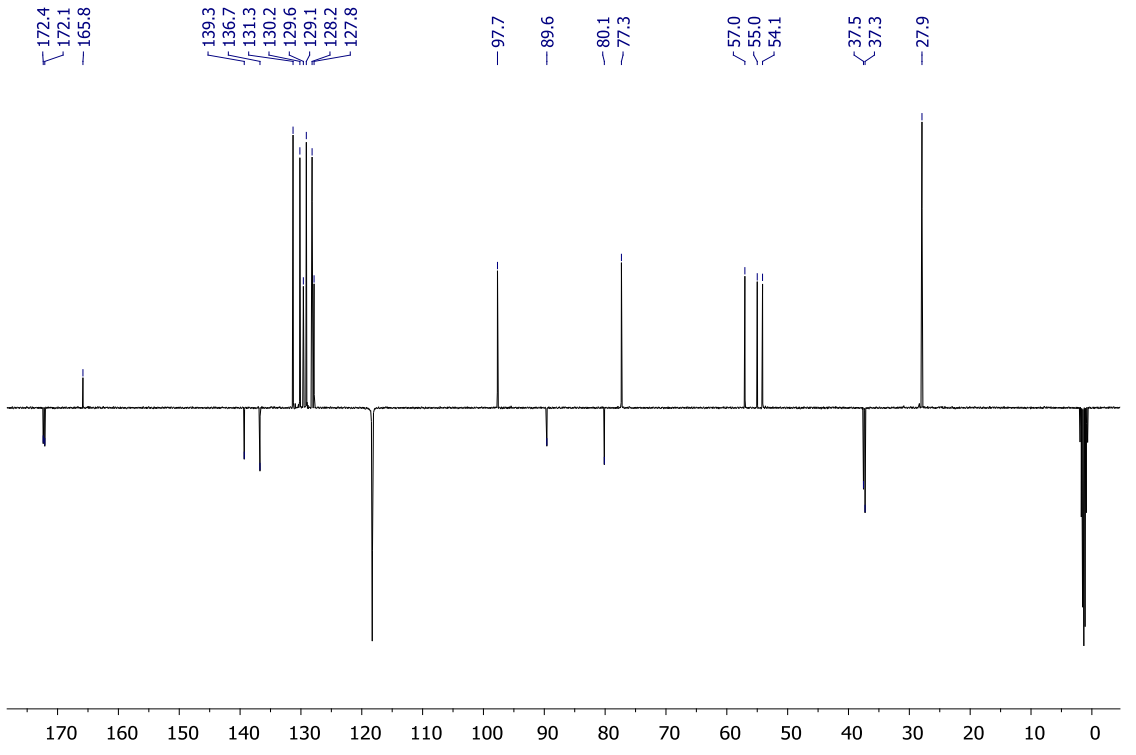
NMR spectra of Chapter V

(1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (161b)



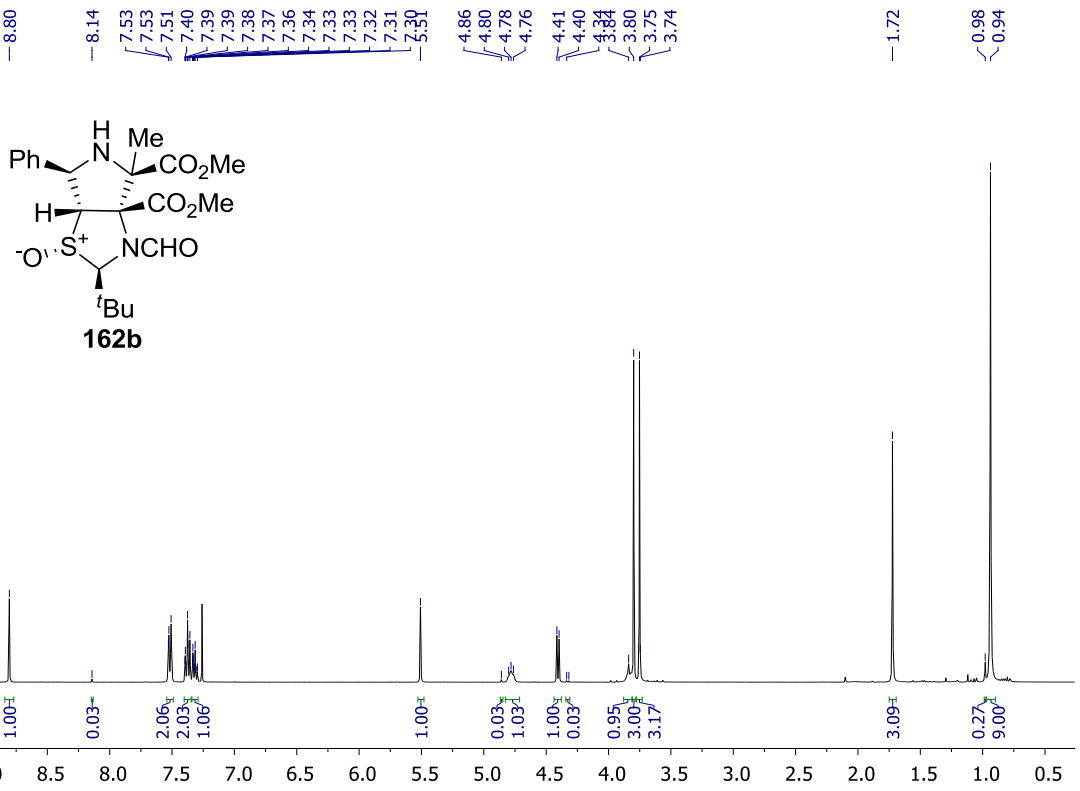
161b

^{1}H-NMR (CD_3CN, 400 MHz)

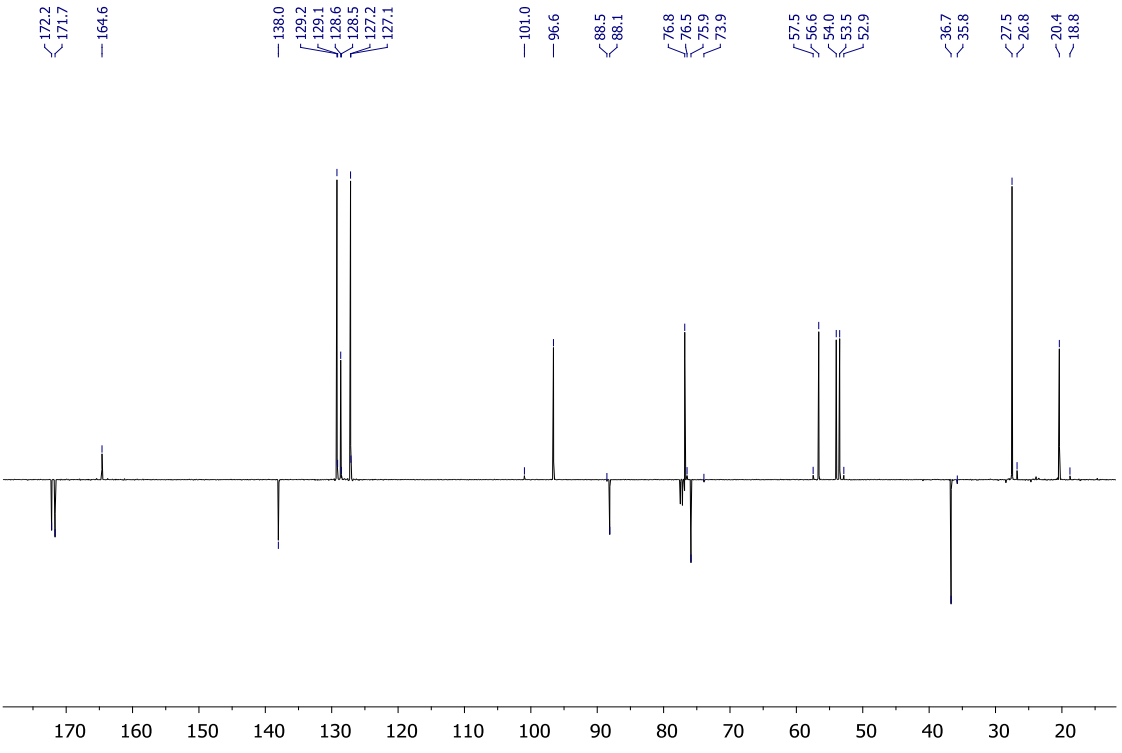


^{13}C-NMR (CD_3CN, 100 MHz)

(1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-methyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (162b)

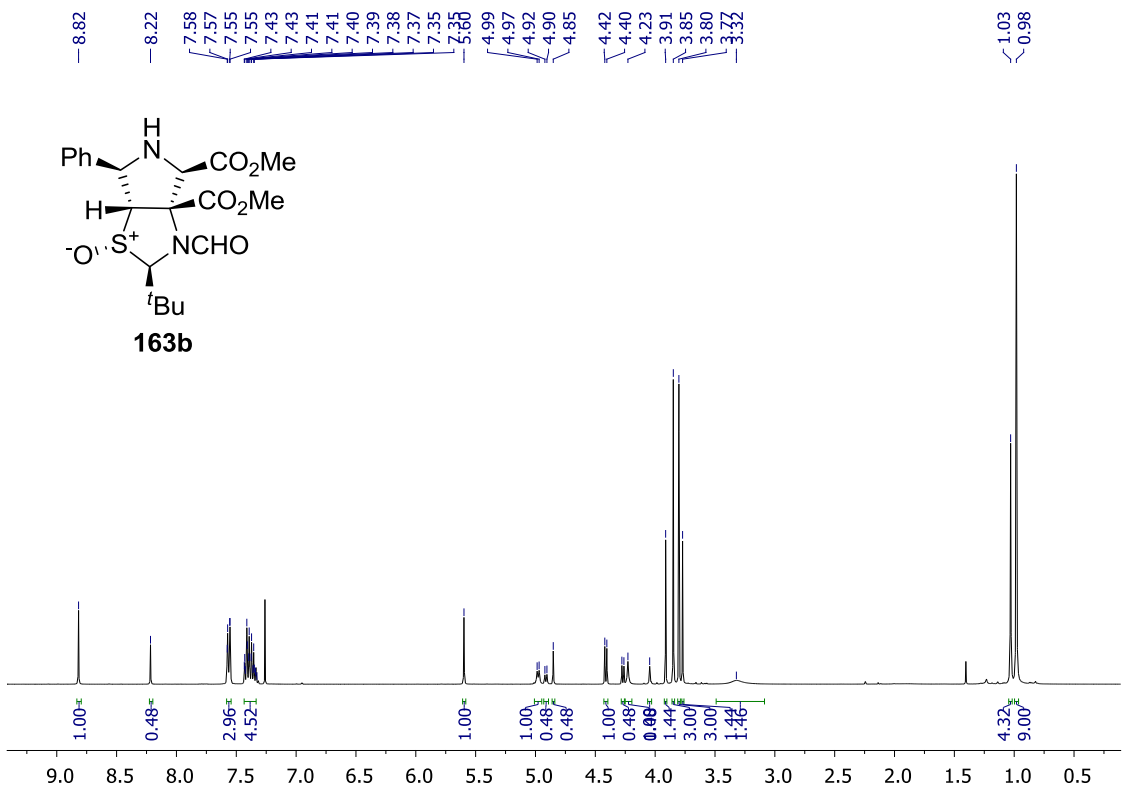


^{1}H-NMR ($CDCl_3$, 400 MHz)

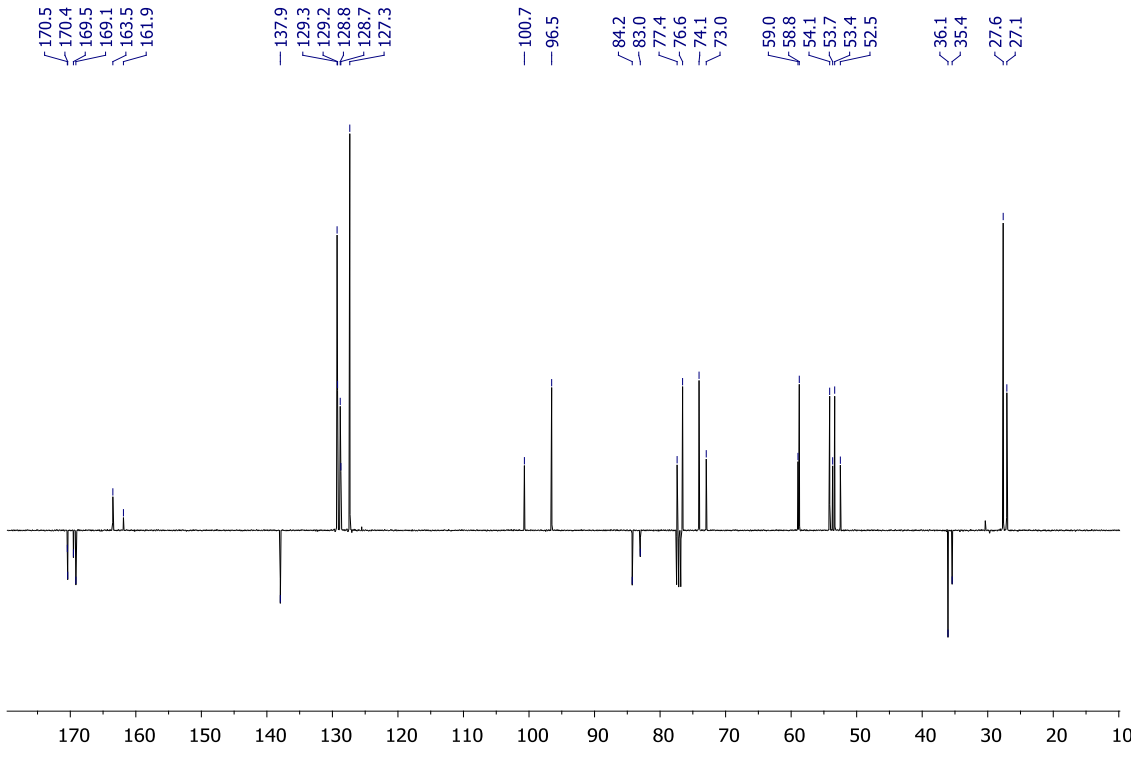


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1-oxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (163b)

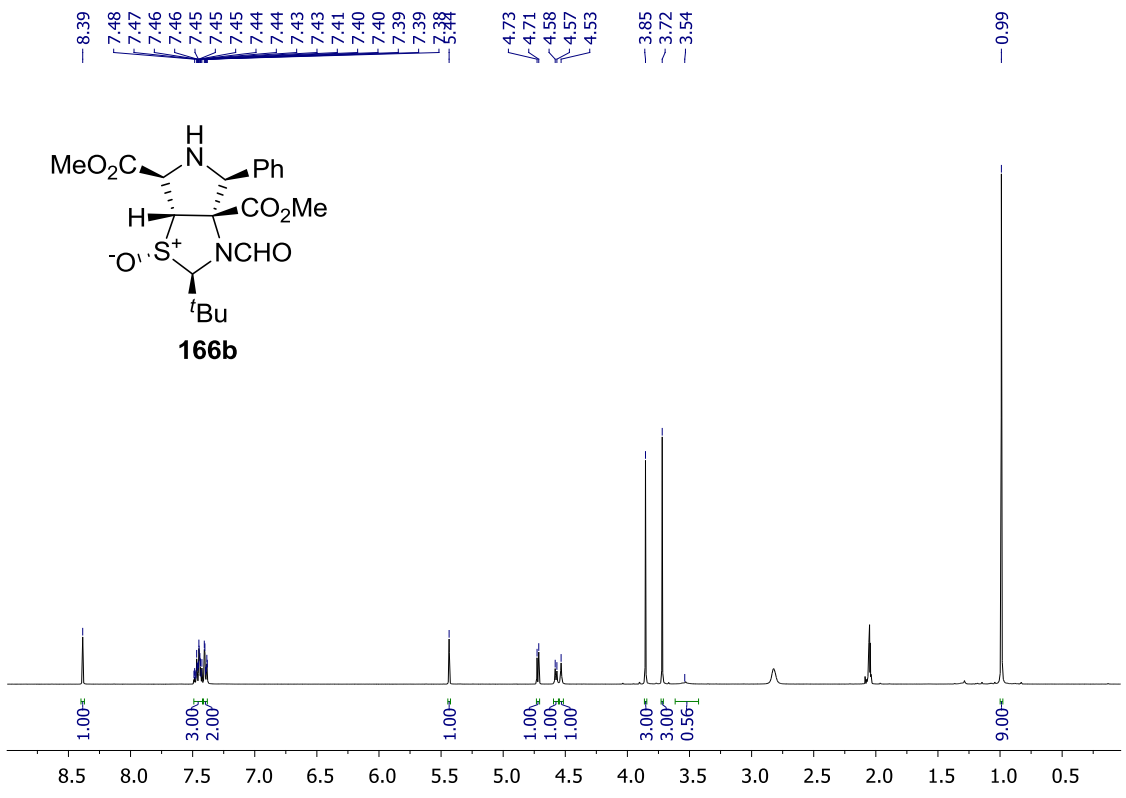


^{1}H-NMR ($CDCl_3$, 400 MHz)



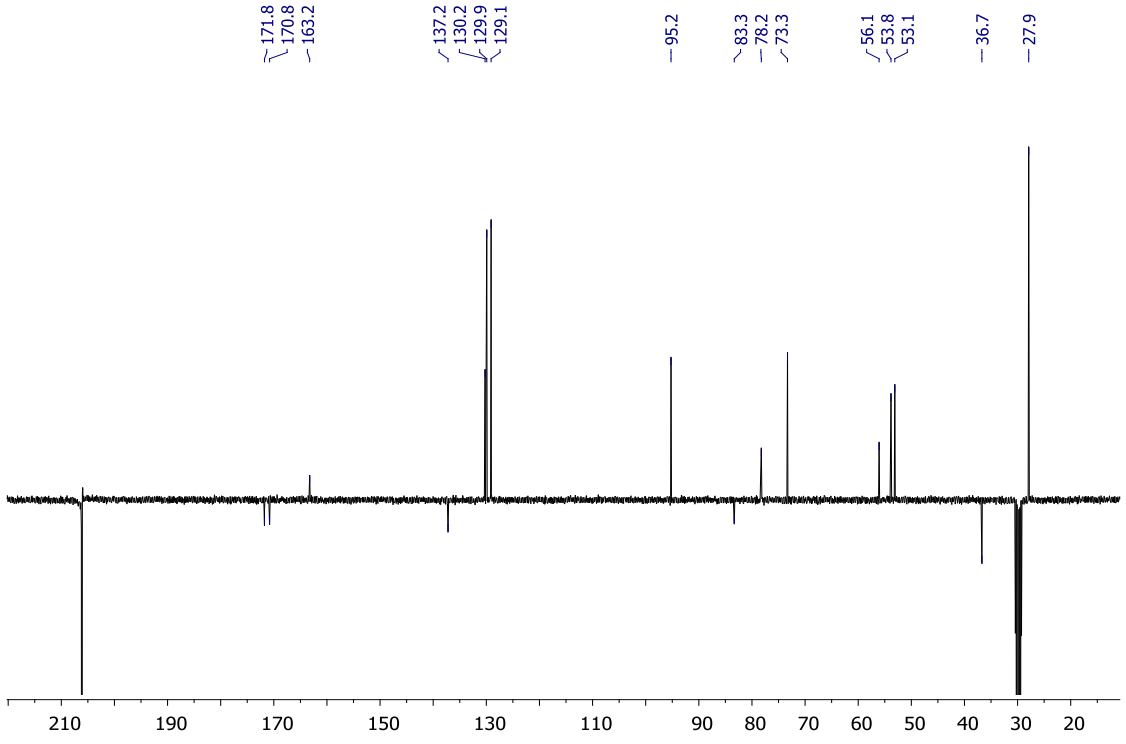
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1-oxido-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (166b)



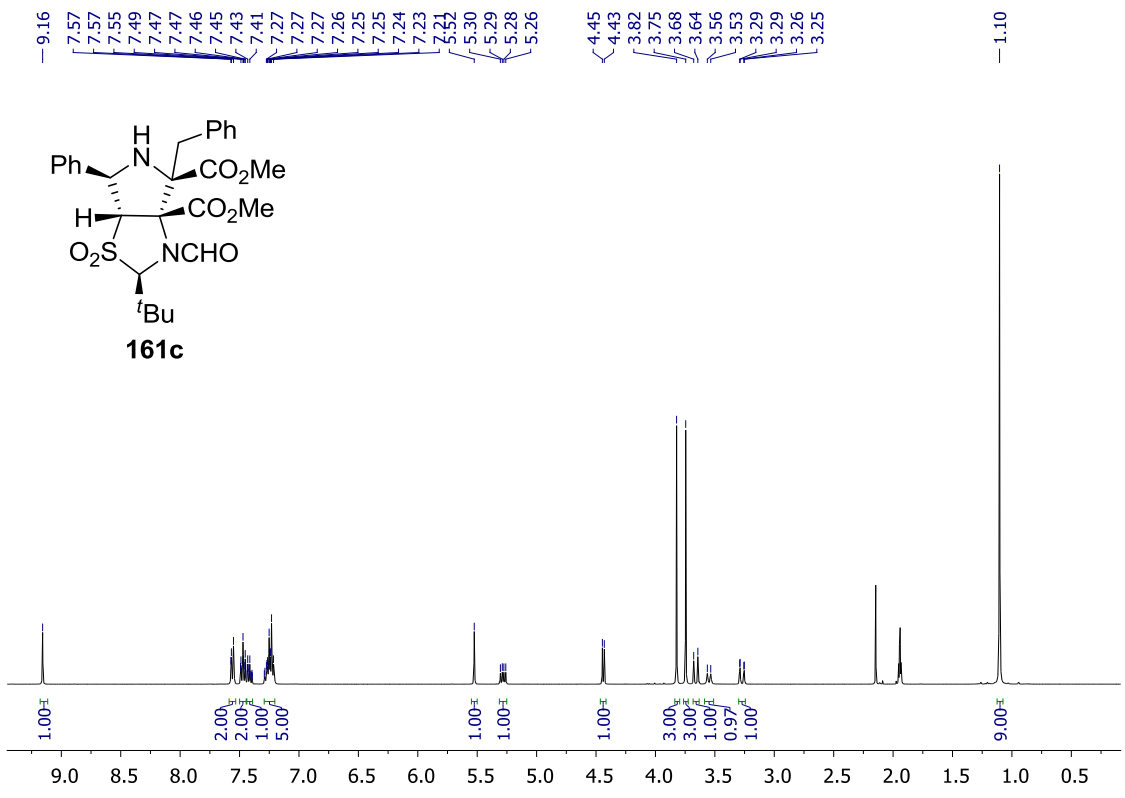
166b

^{1}H-NMR ((CD$_3$)$_2$CO, 400 MHz)



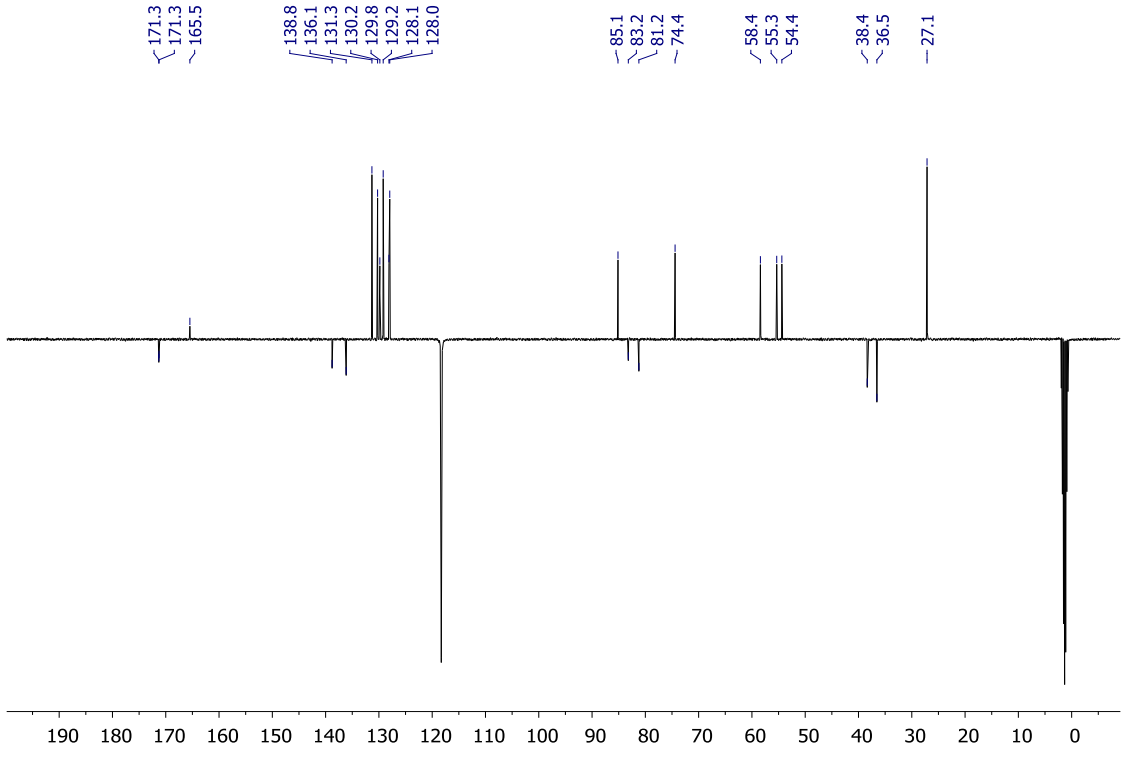
^{13}C-NMR ((CD$_3$)$_2$CO, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (161c)



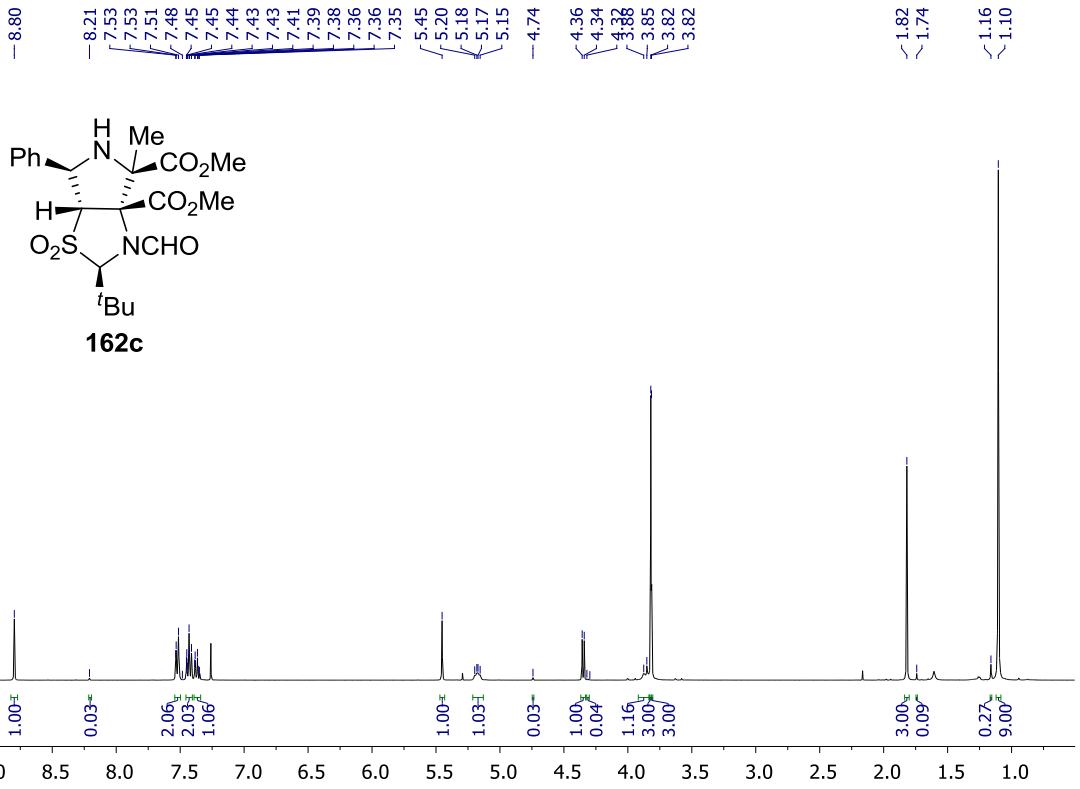
161c

^{1}H-NMR (CD_3CN, 400 MHz)



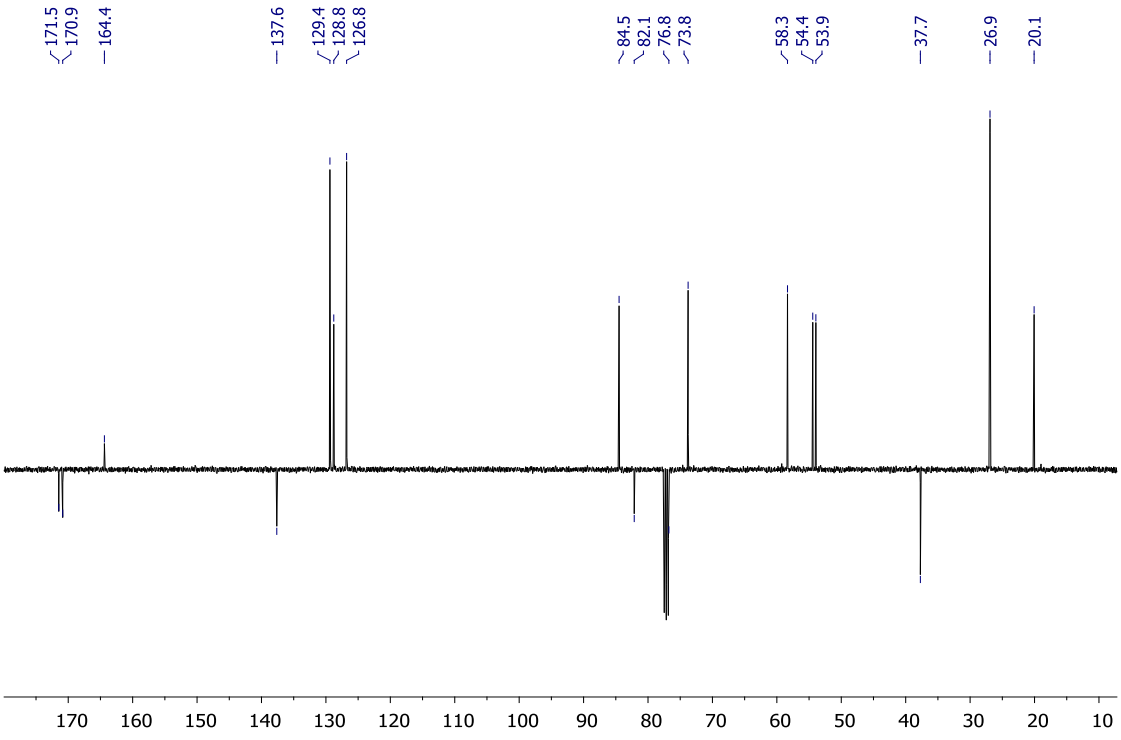
^{13}C-NMR (CD_3CN, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-methyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (162c)



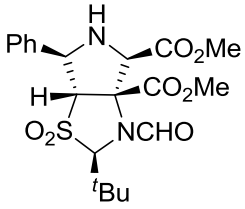
162c

^{1}H-NMR ($CDCl_3$, 400 MHz)



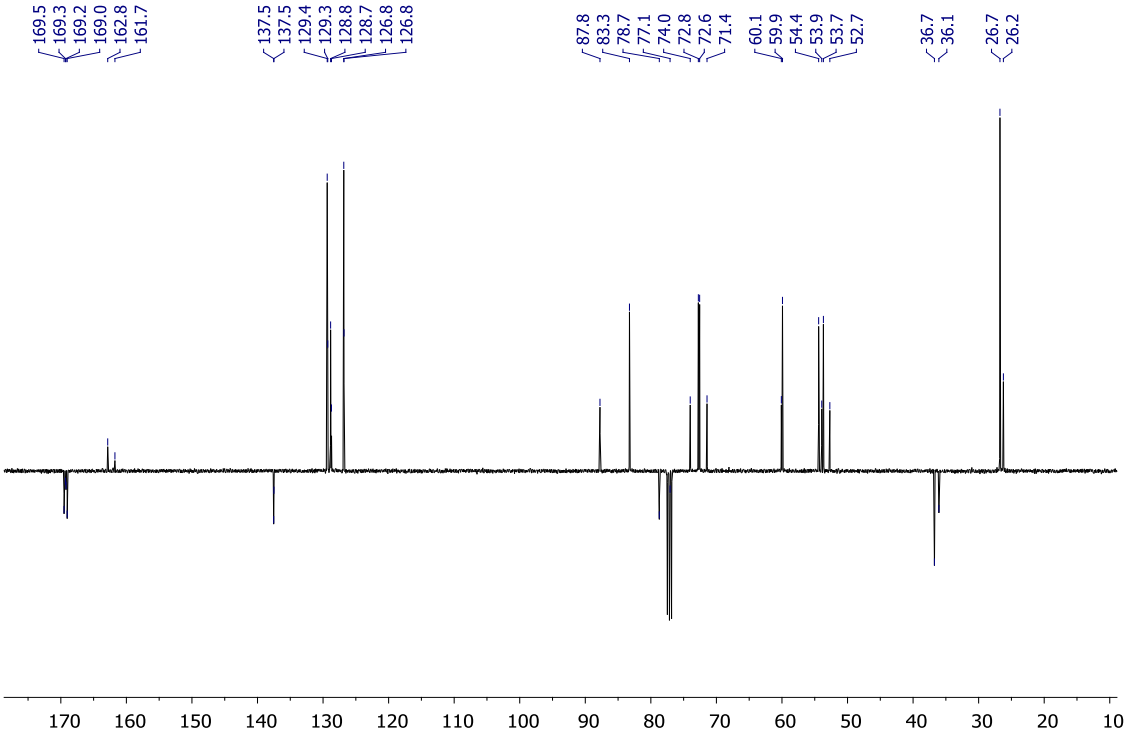
^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1,1-dioxido-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (163c)



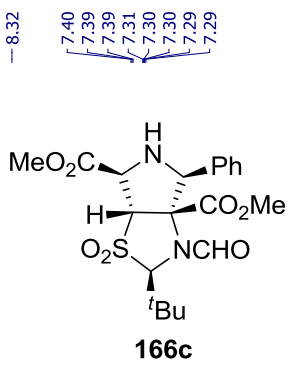
163c

^{1}H-NMR ($CDCl_3$, 400 MHz)



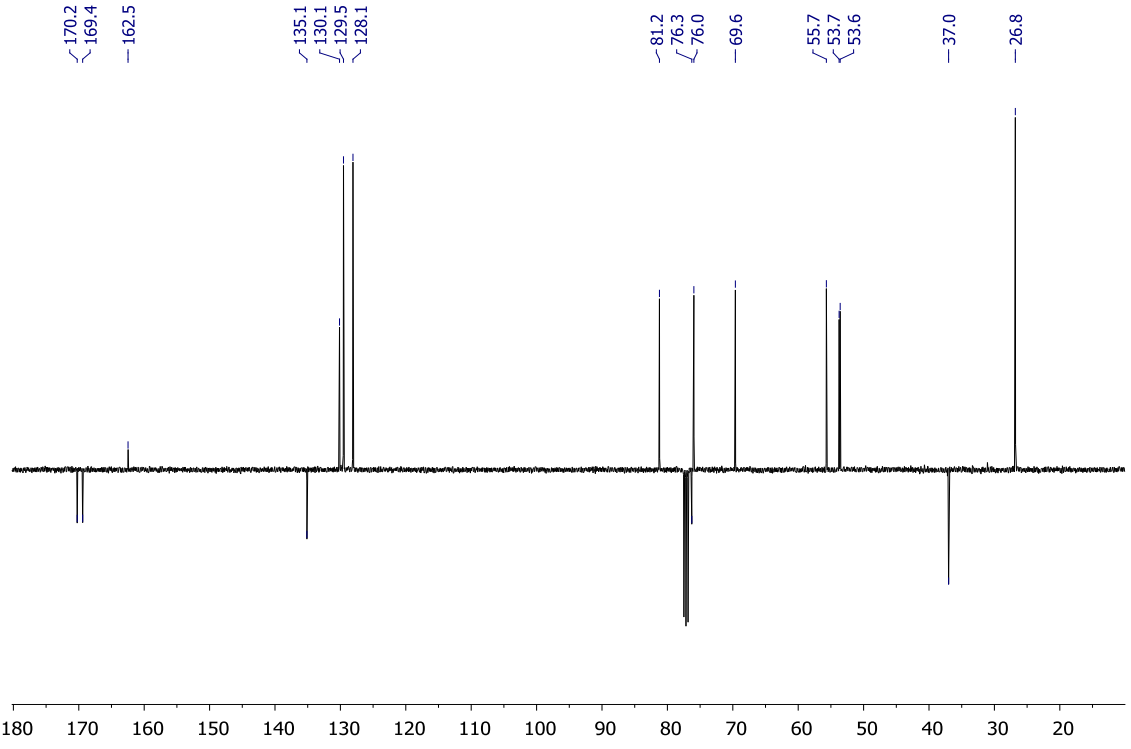
^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-1,1-dioxido-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (166c)



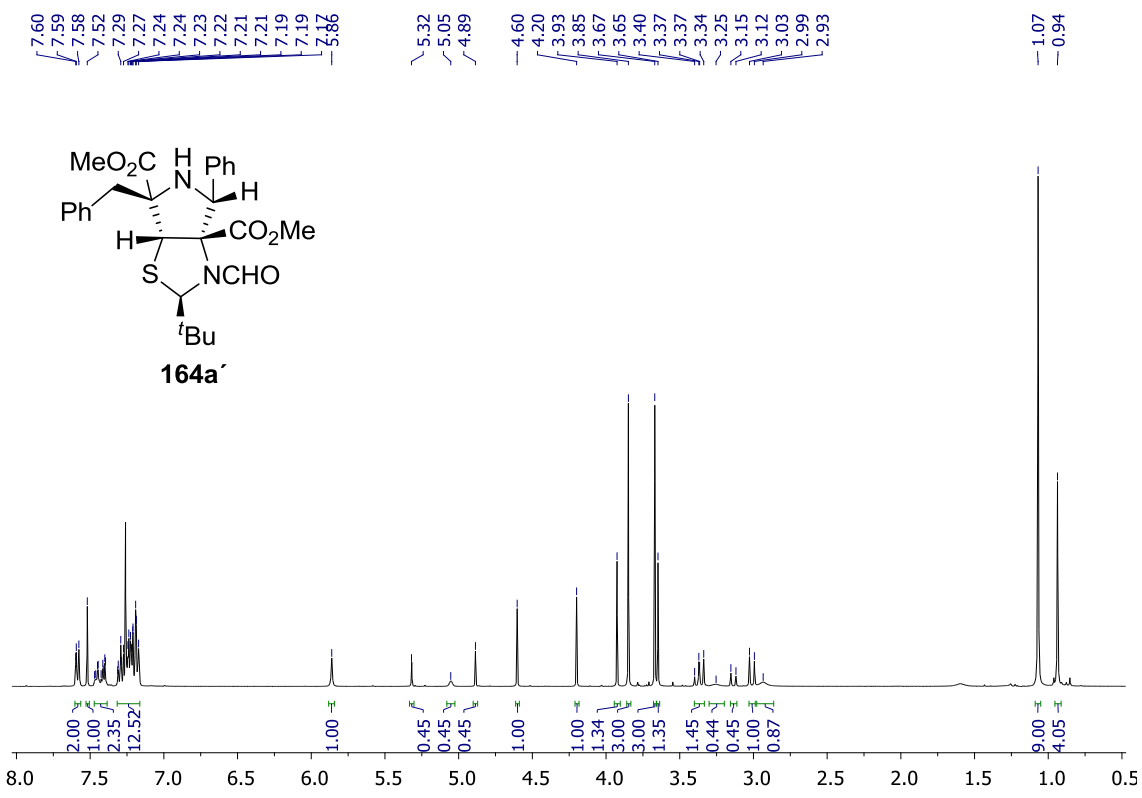
166c

^{1}H-NMR ($CDCl_3$, 400 MHz)



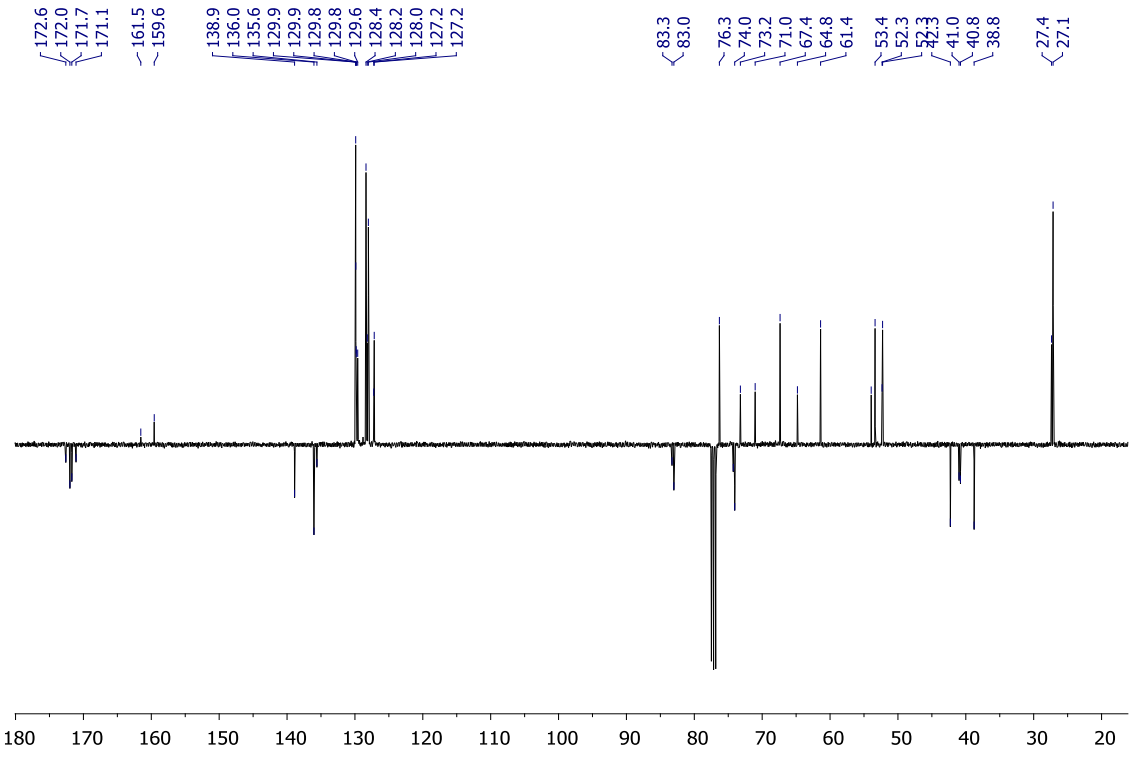
^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 6-benzyl-2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (164a´)



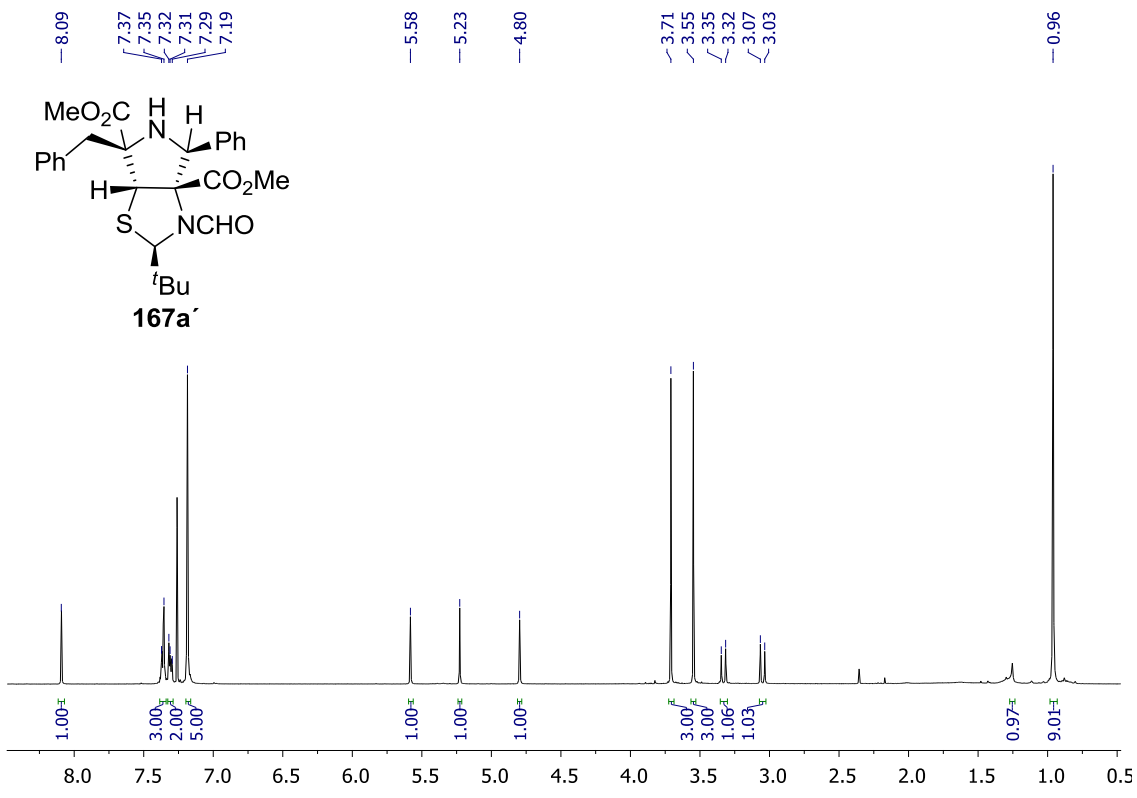
164a´

^{1}H-NMR ($CDCl_3$, 400 MHz)

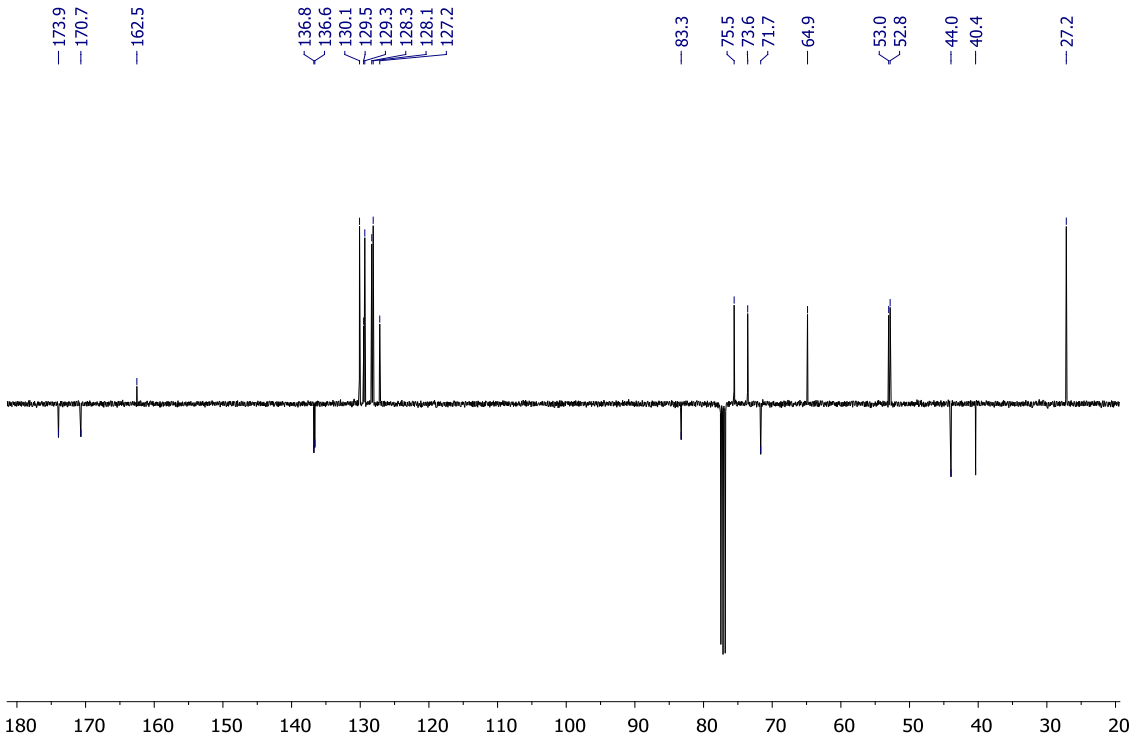


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,6*S*,6a*R*)-Dimethyl 6-benzyl-2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (167a´)

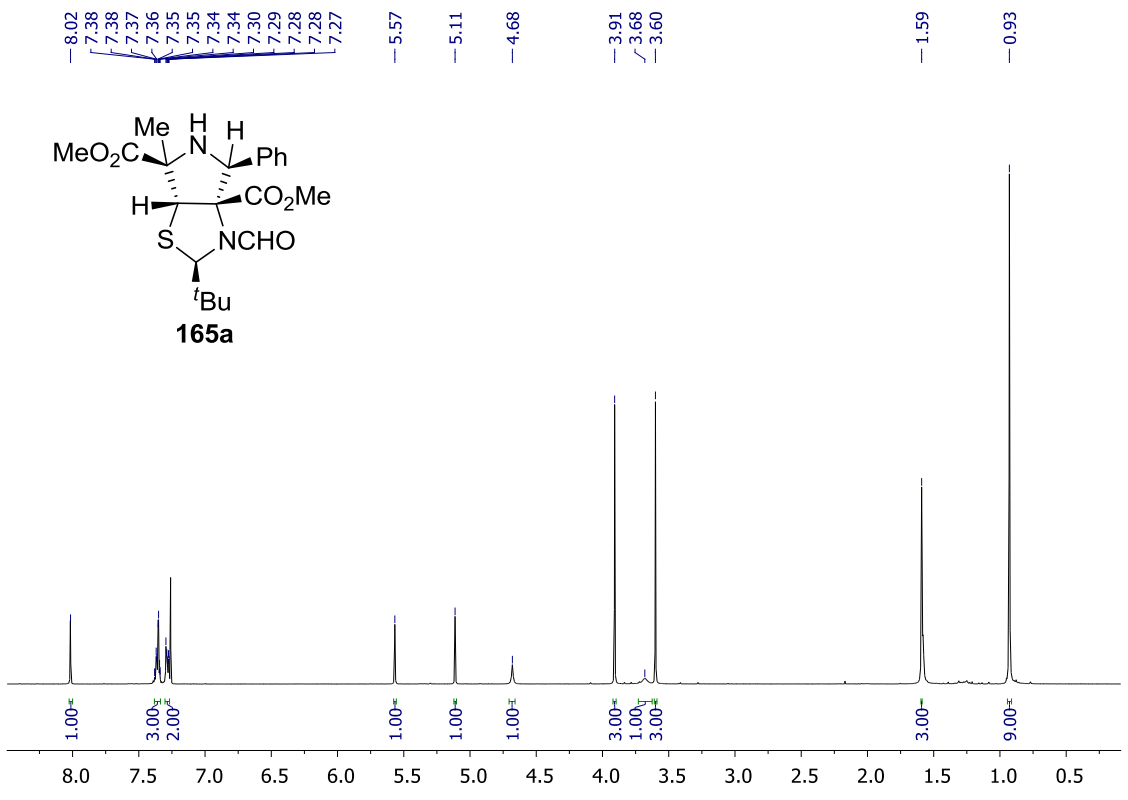


^{1}H-NMR ($CDCl_3$, 400 MHz)

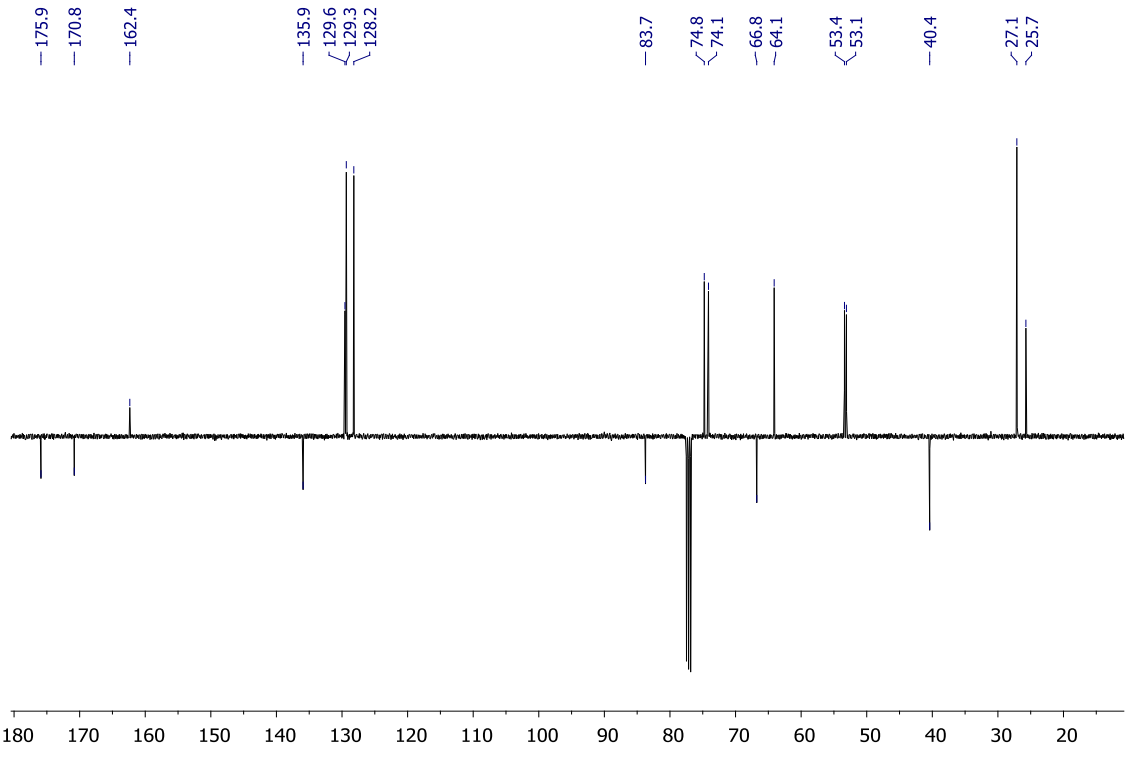


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (165a)

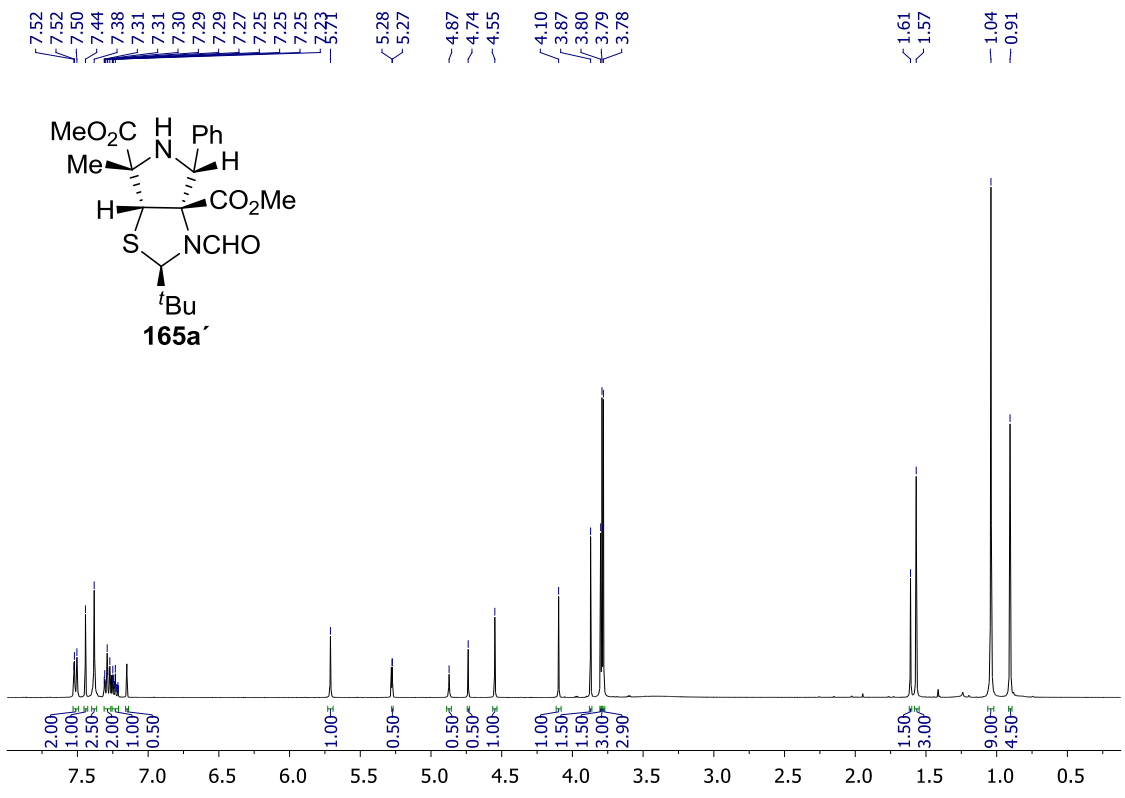


^{1}H-NMR ($CDCl_3$, 400 MHz)

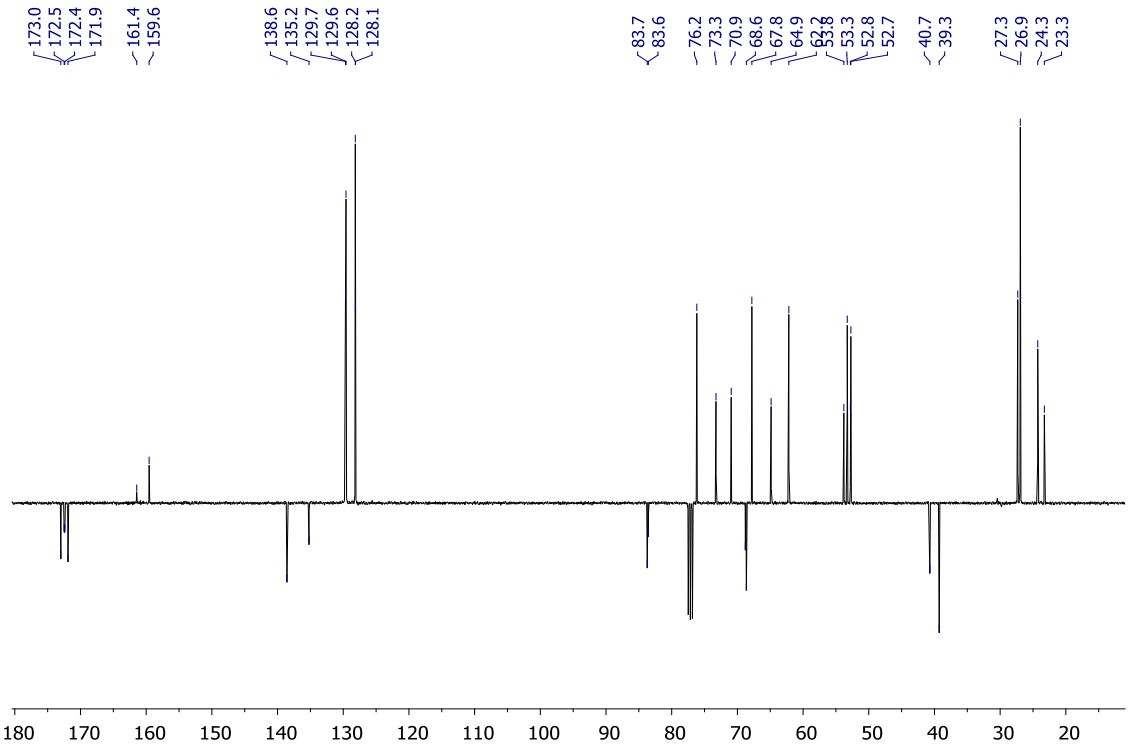


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (165a´)

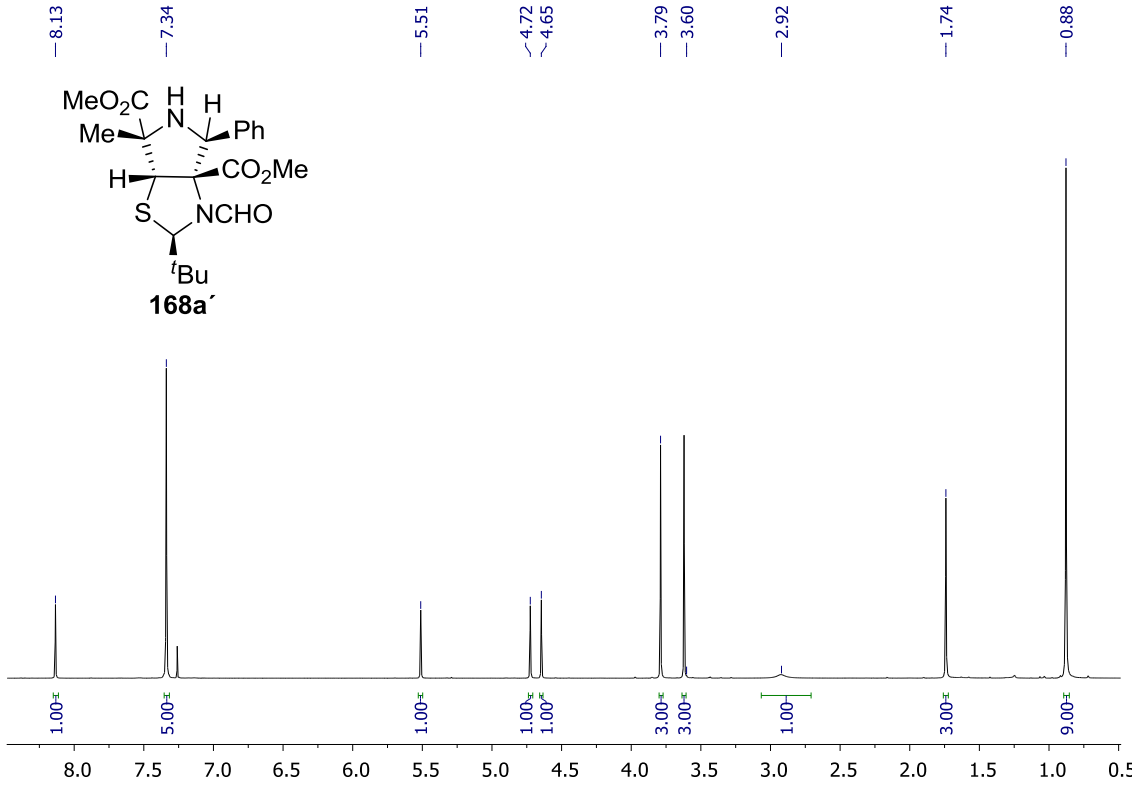


^{1}H-NMR ($CDCl_3$, 400 MHz)

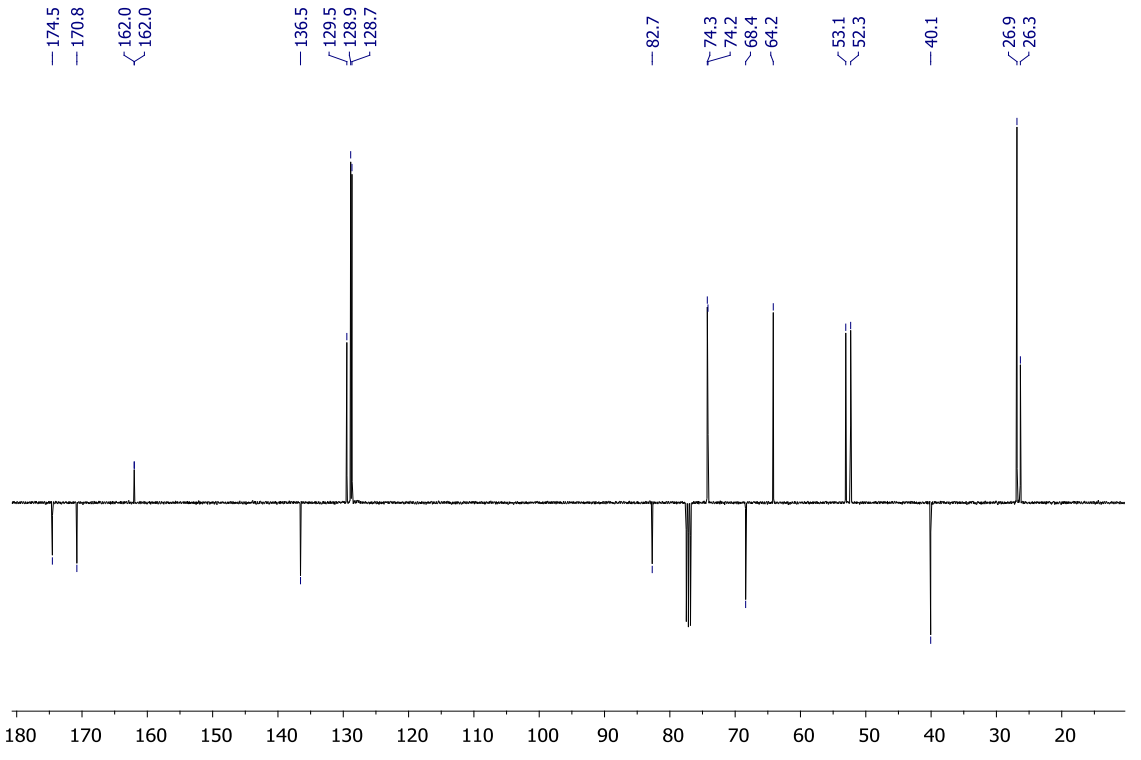


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-6-methyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (168a´)

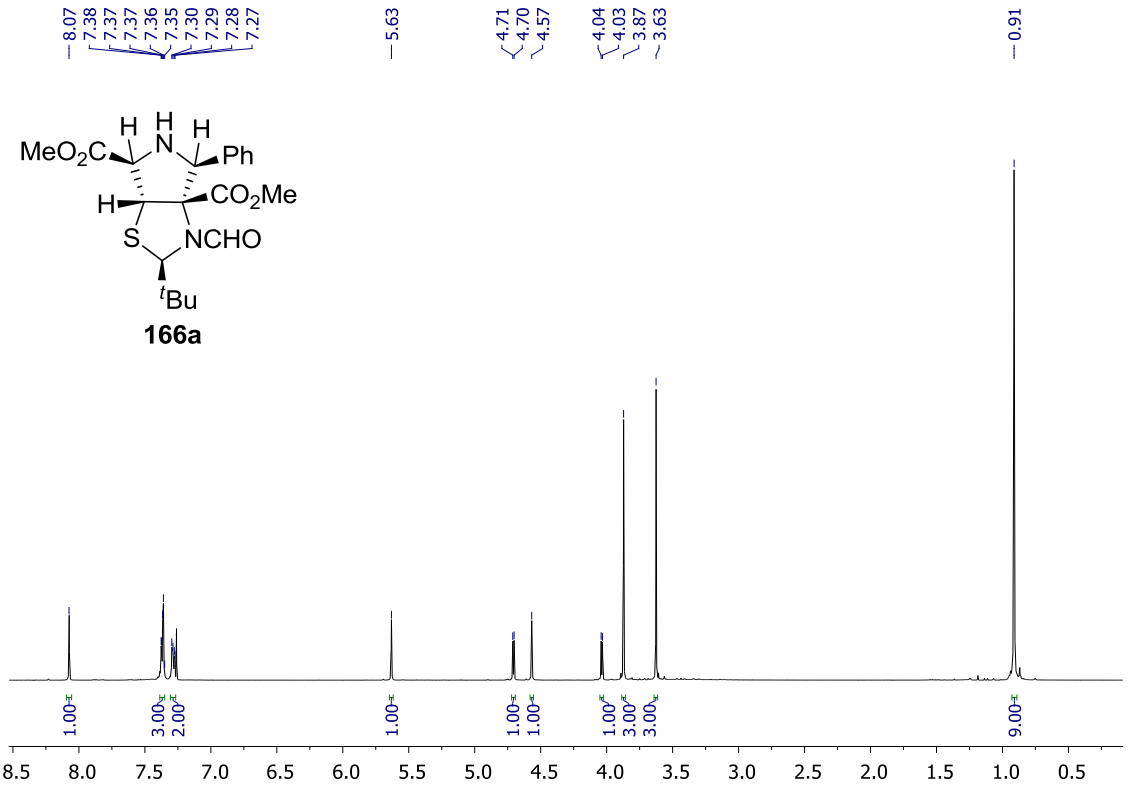


^{1}H-NMR ($CDCl_3$, 400 MHz)

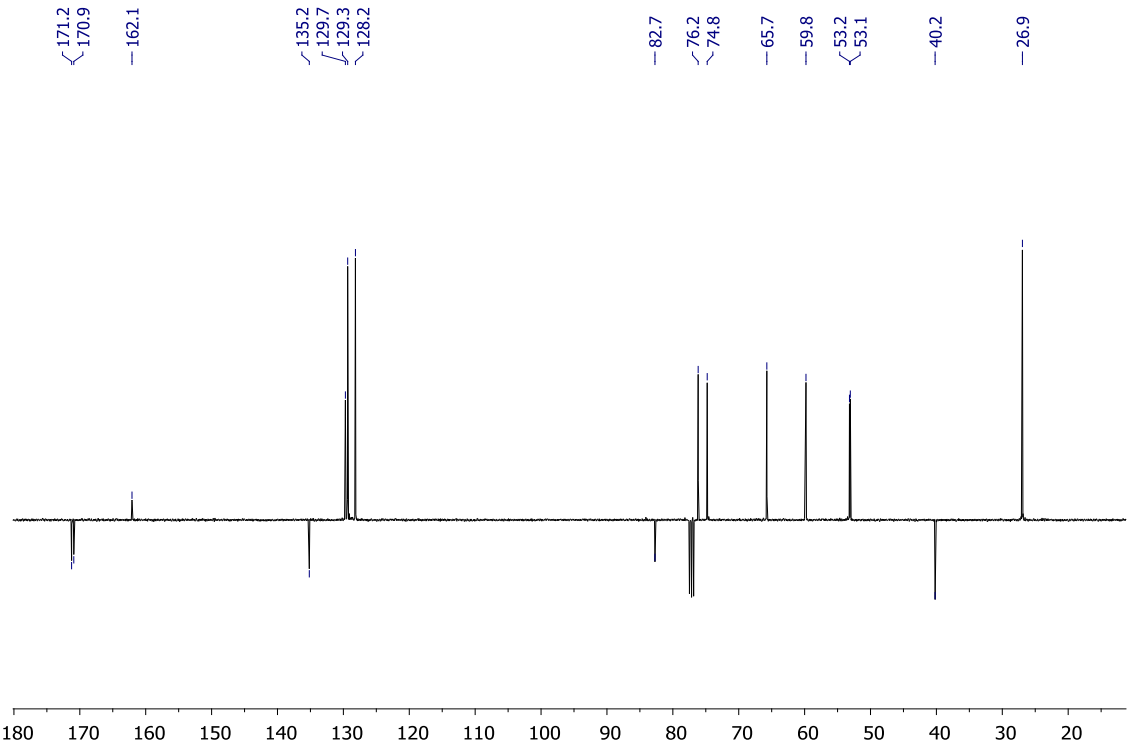


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (166a)

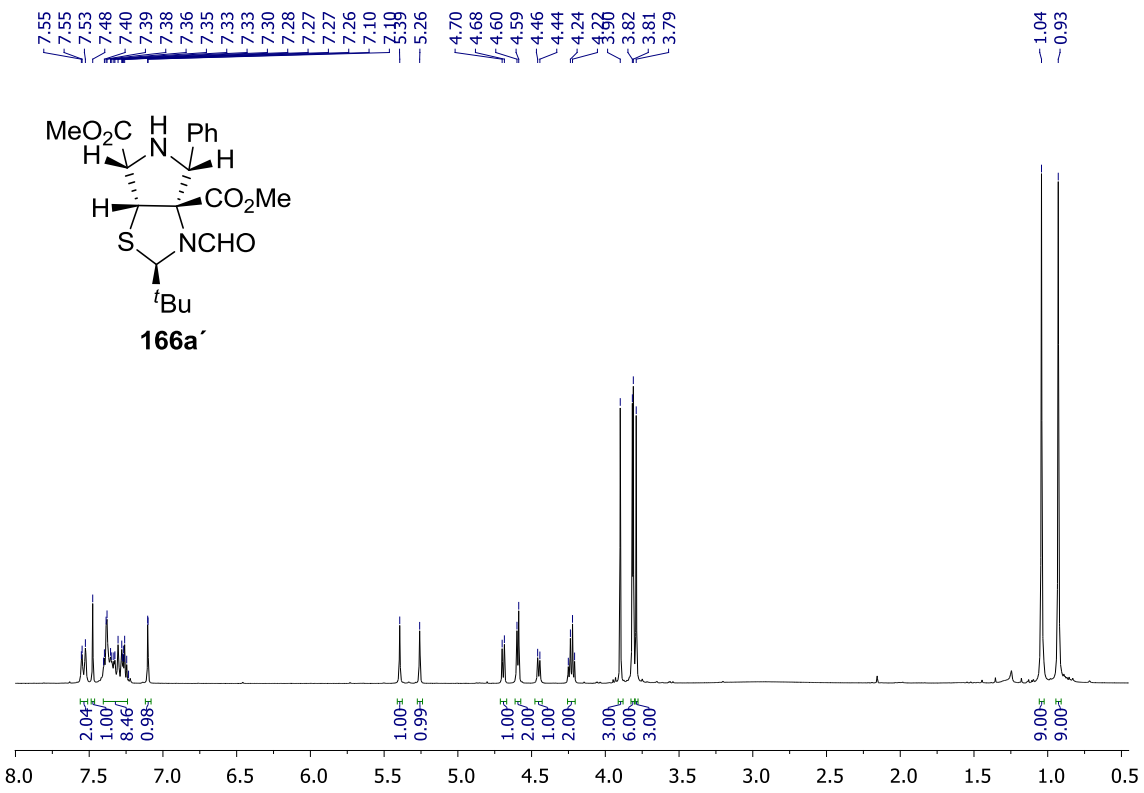


^{1}H-NMR ($CDCl_3$, 400 MHz)

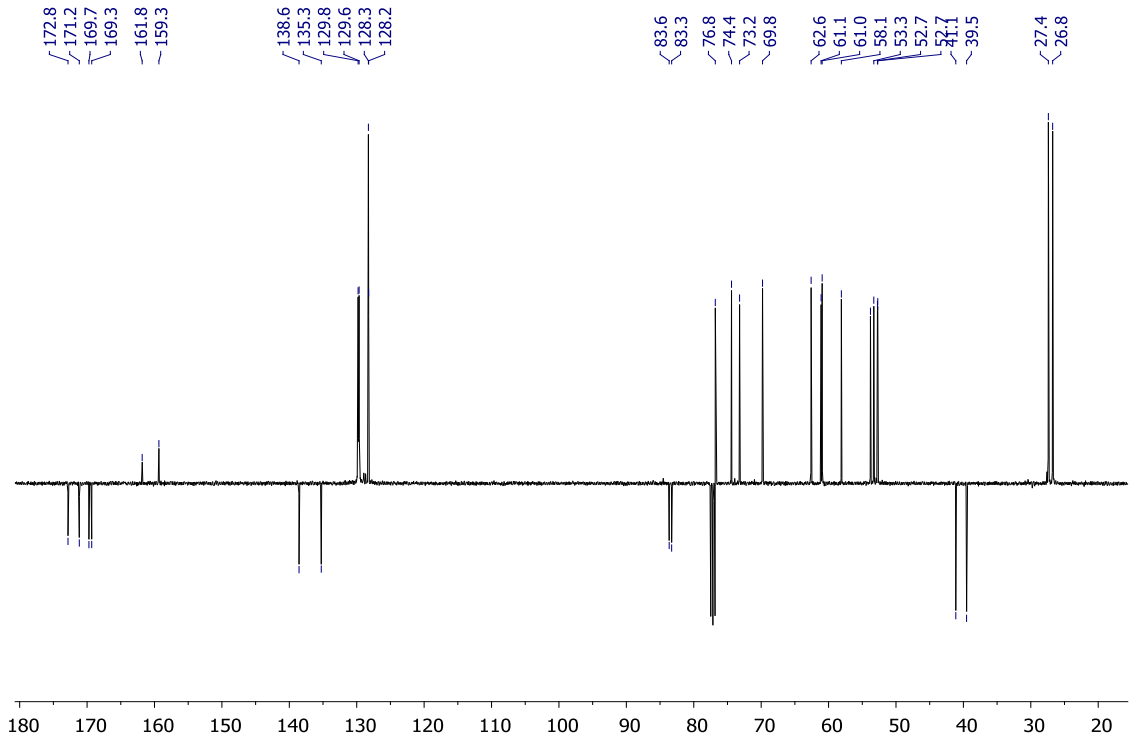


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*S*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (166a´)

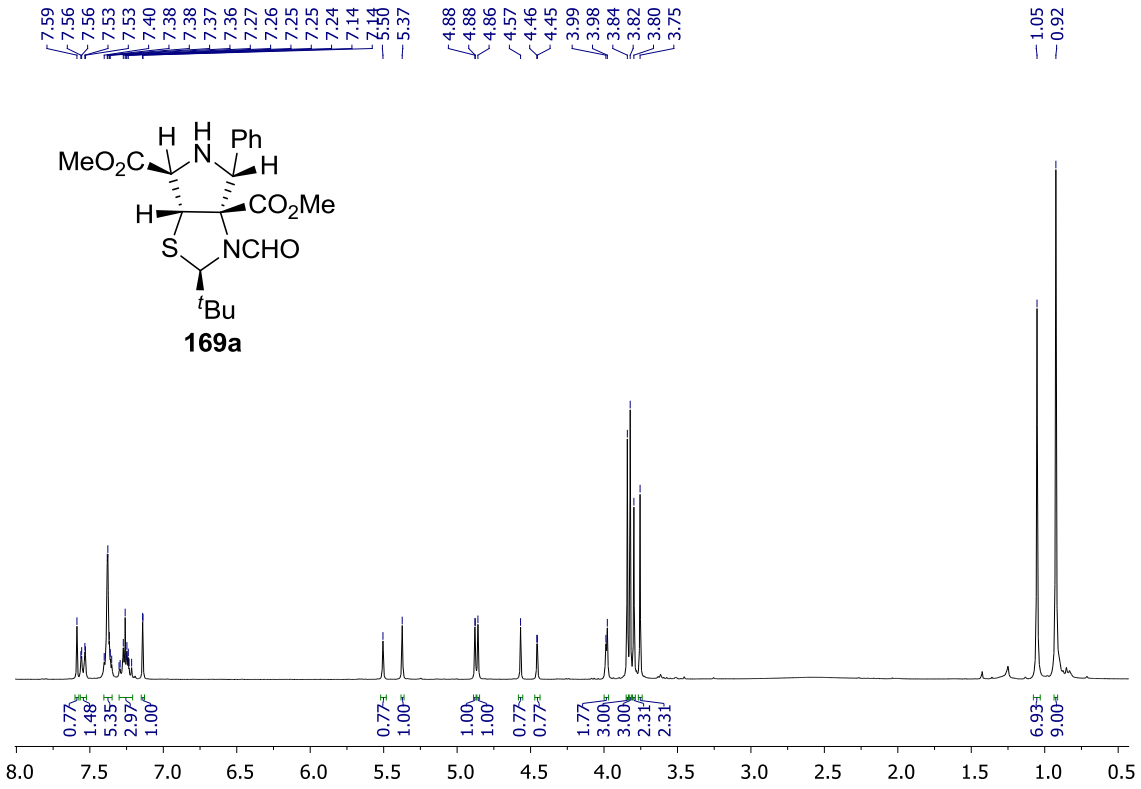


^{1}H-NMR ($CDCl_3$, 400 MHz)



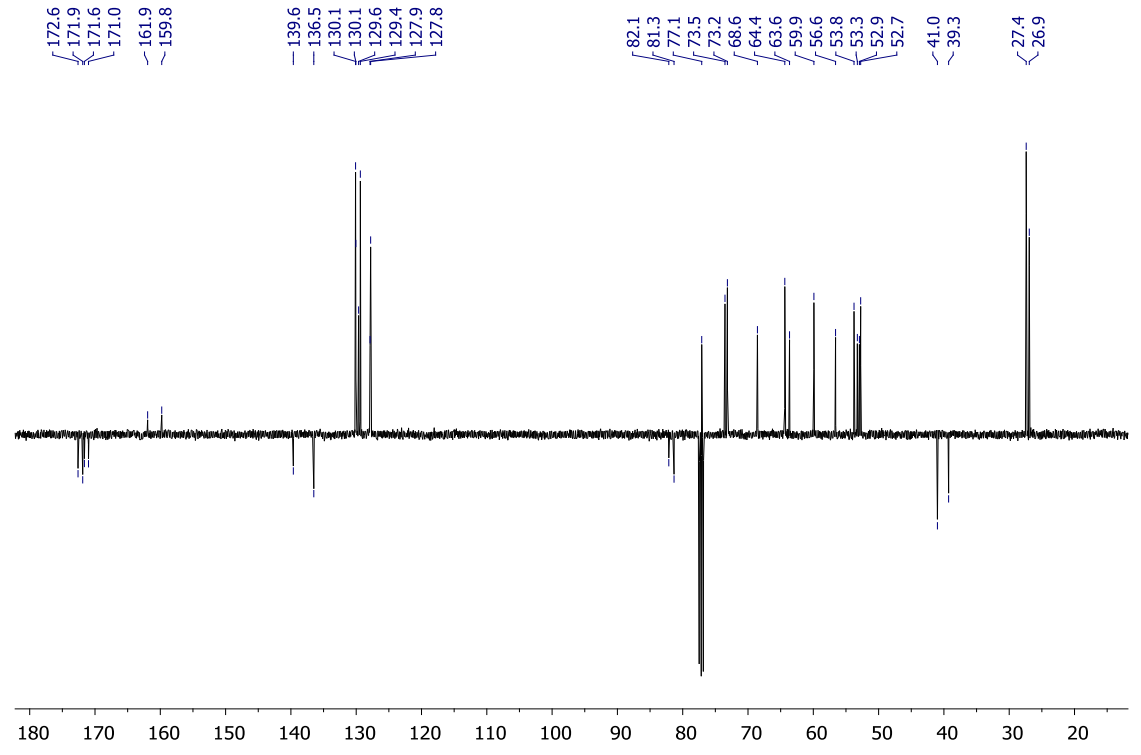
^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-3-formyl-4-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,6-dicarboxylate (169a)



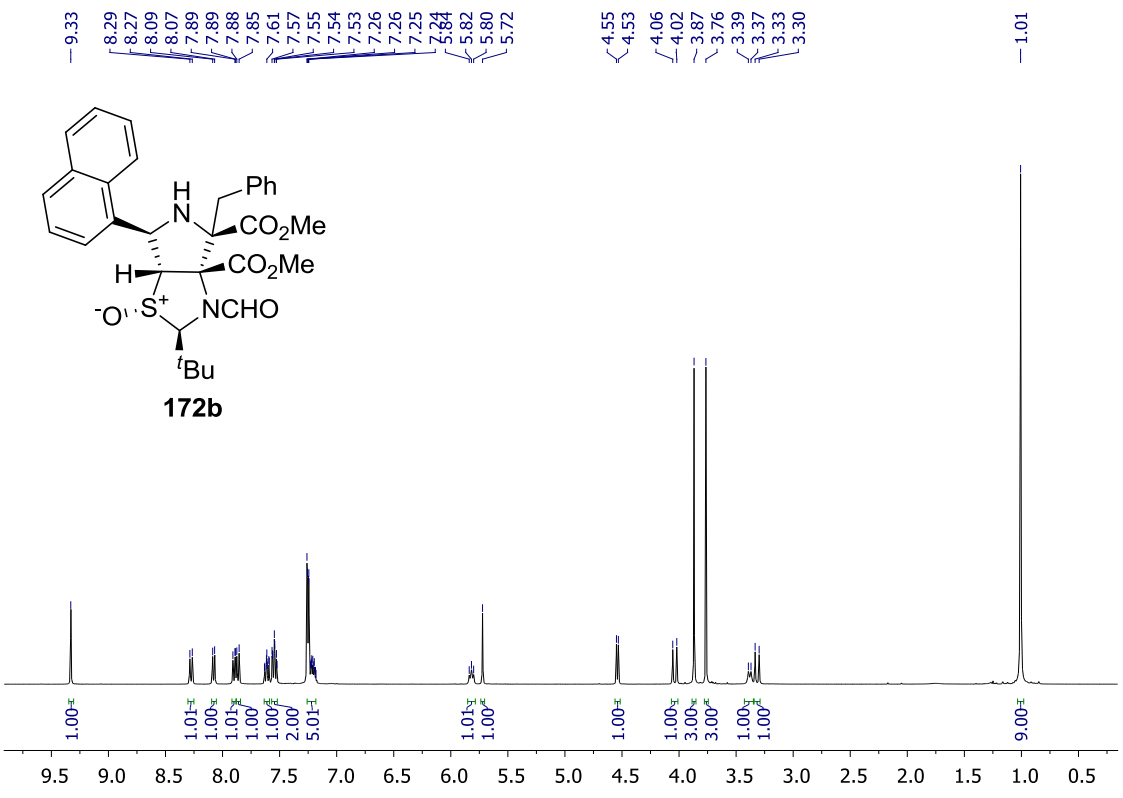
169a

^{1}H-NMR ($CDCl_3$, 400 MHz)

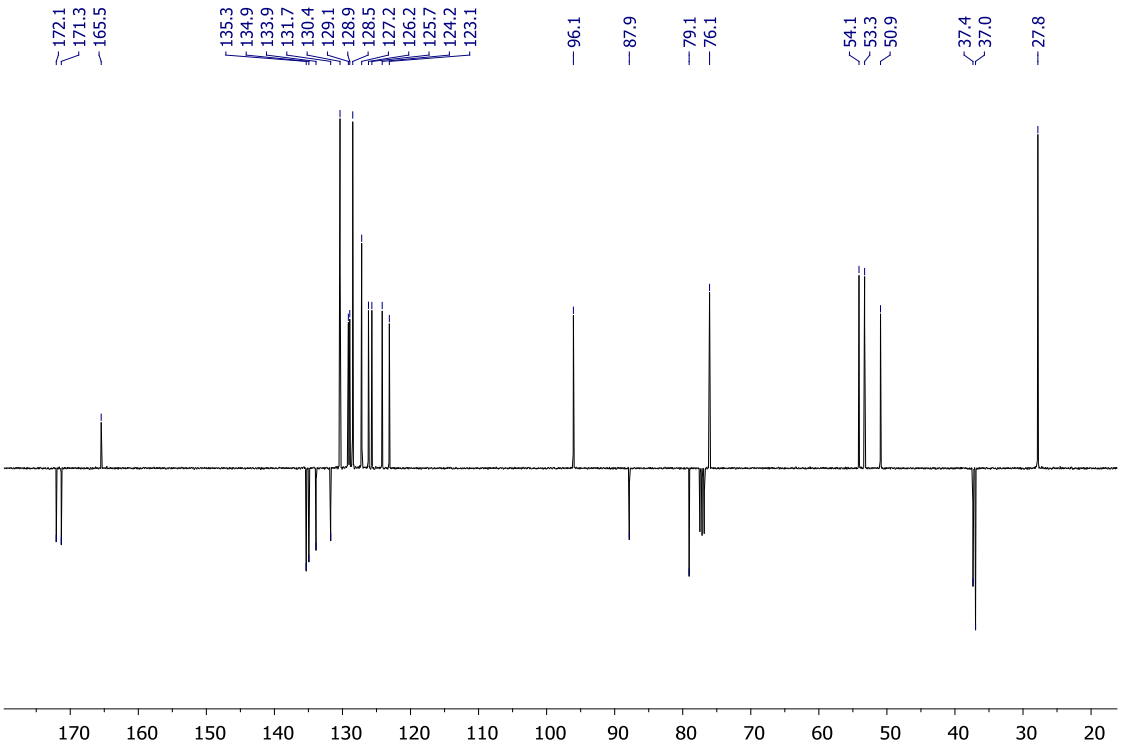


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-(1-naphthyl)-1-oxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (172b)

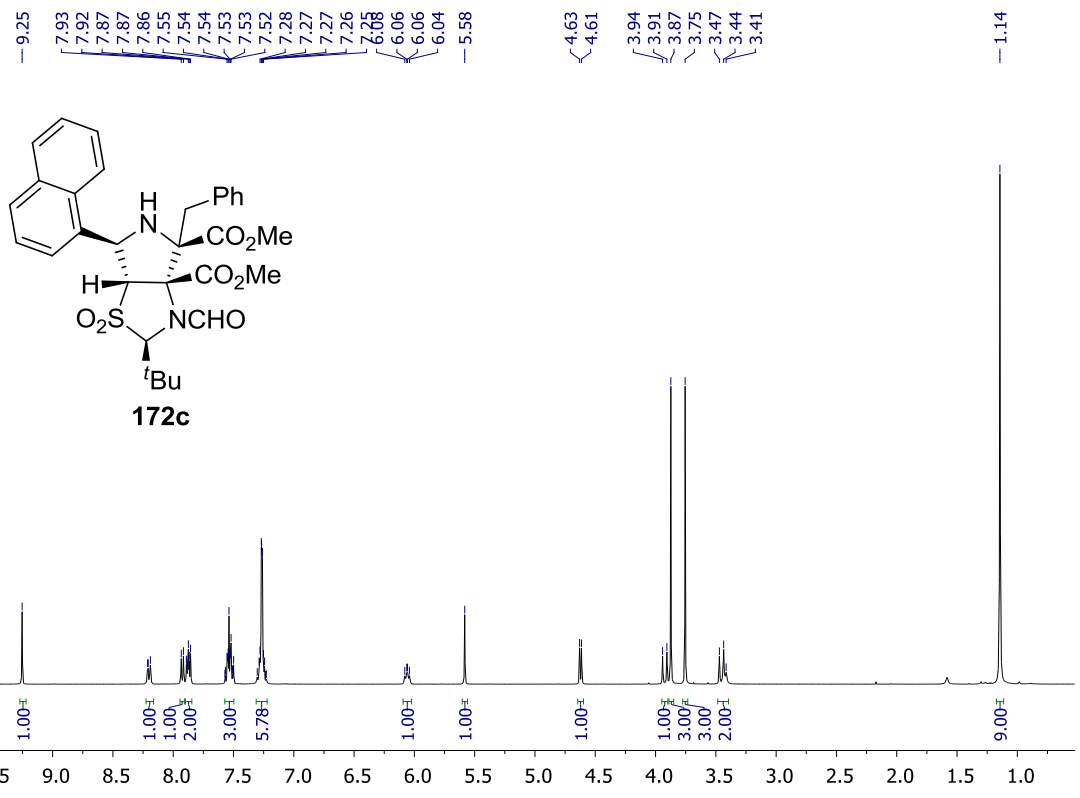


^{1}H-NMR ($CDCl_3$, 400 MHz)

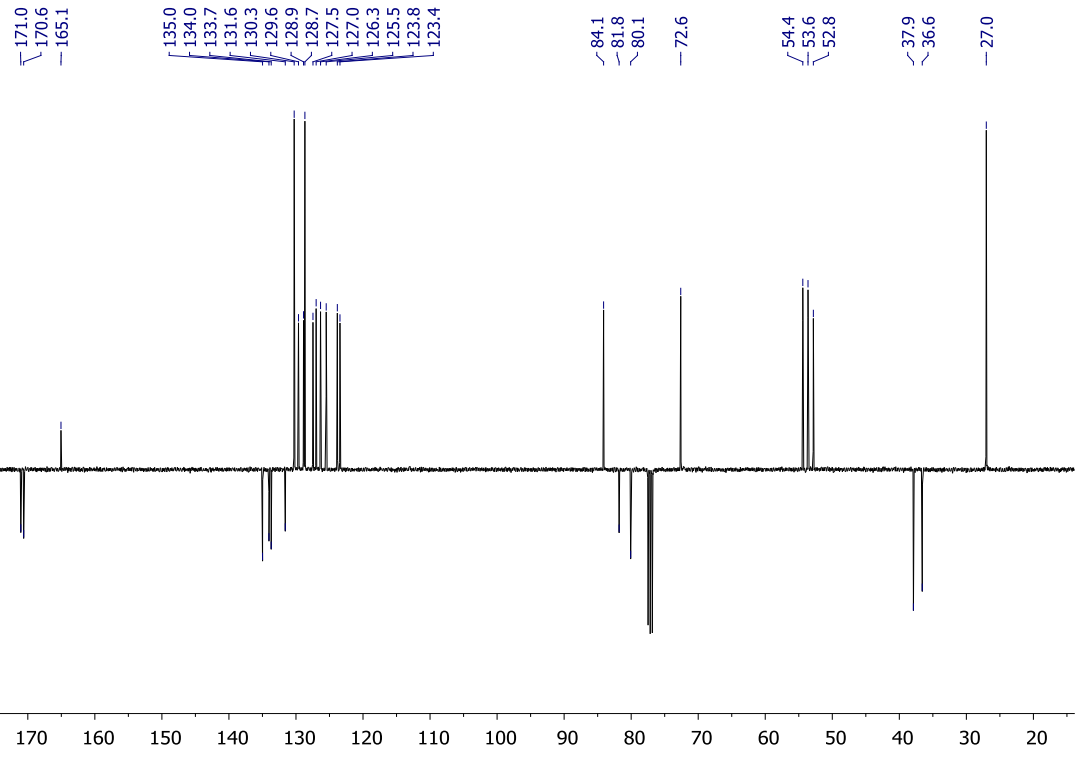


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-(1-naphthyl)-1,1-dioxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (172c)

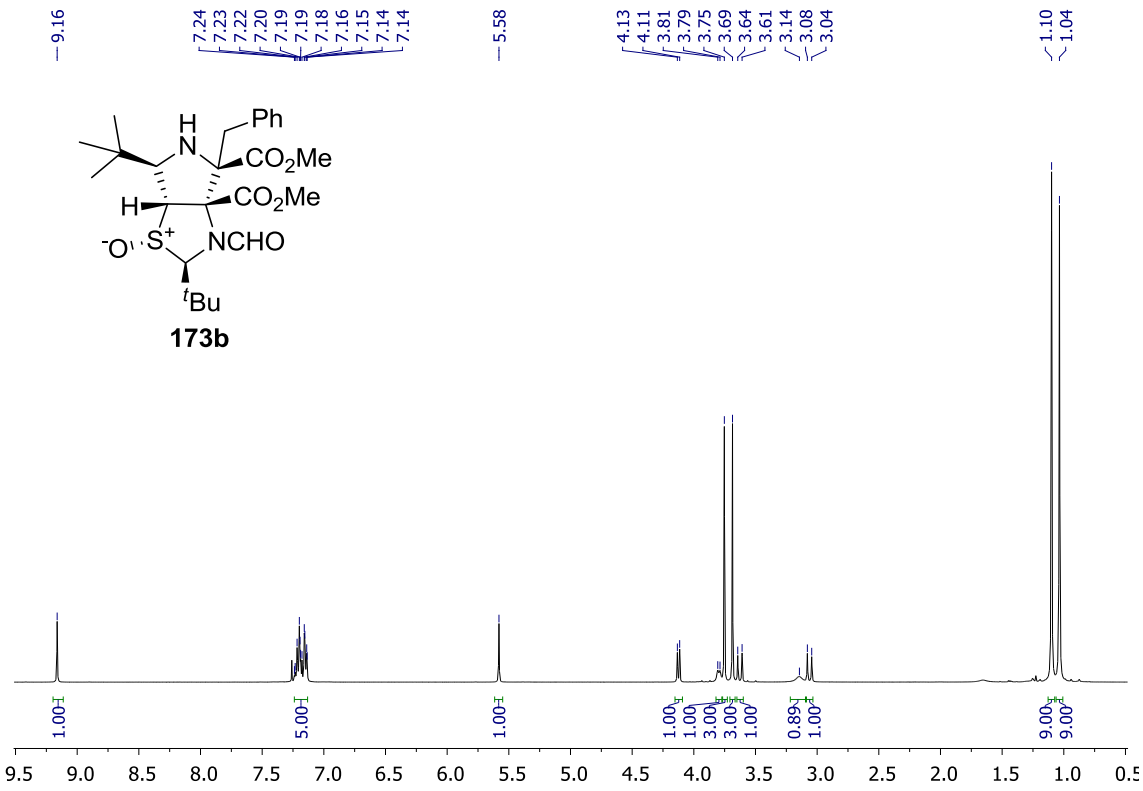


^{1}H-NMR ($CDCl_3$, 400 MHz)

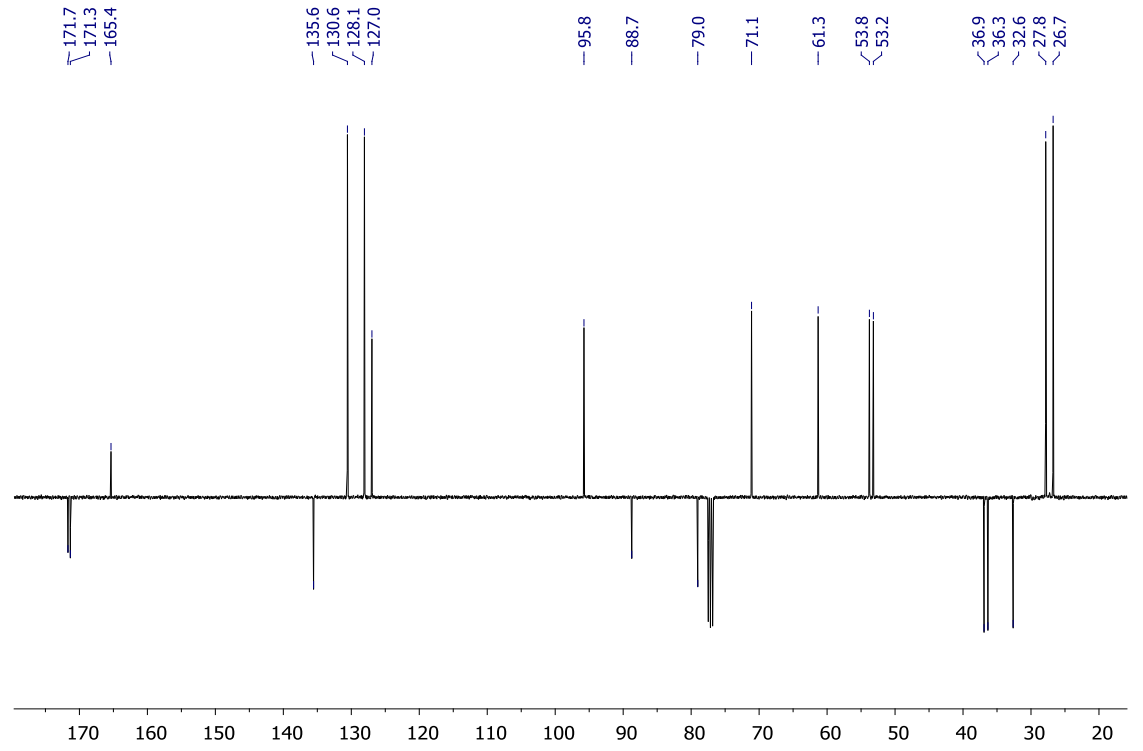


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2,6-di-*tert*-butyl-3-formyl-1-oxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (173b)

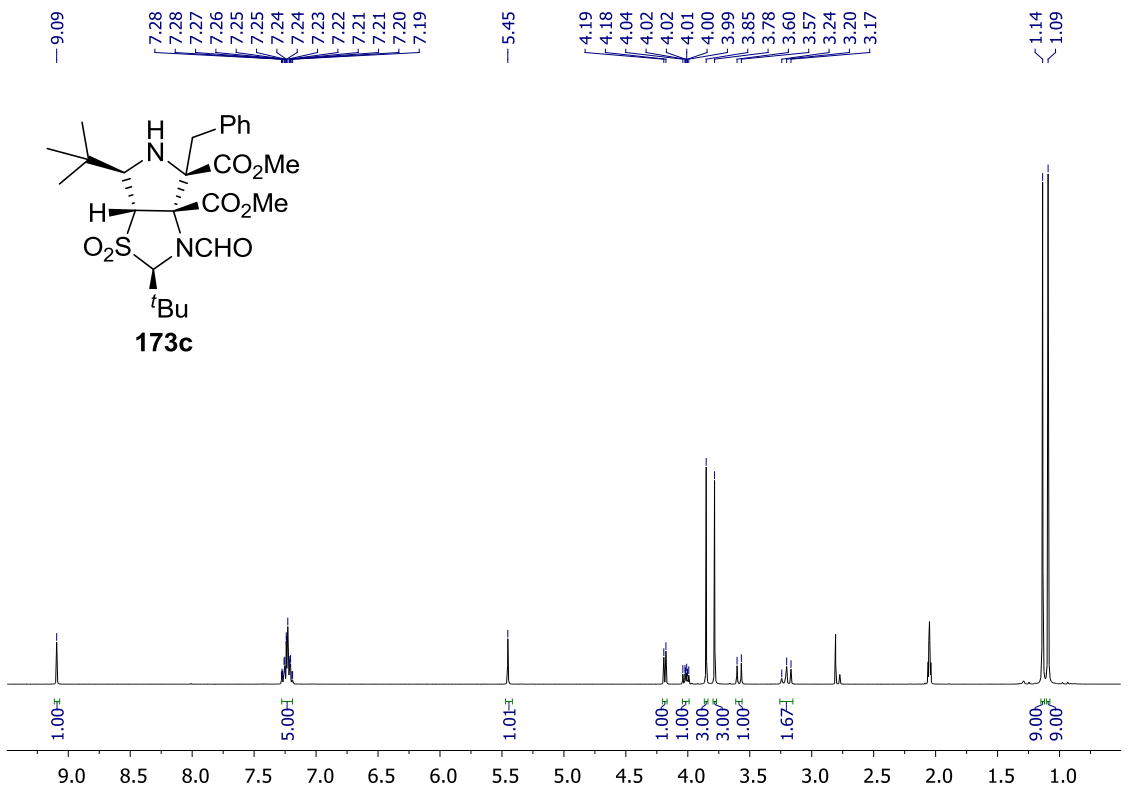


^{1}H-NMR ($CDCl_3$, 400 MHz)

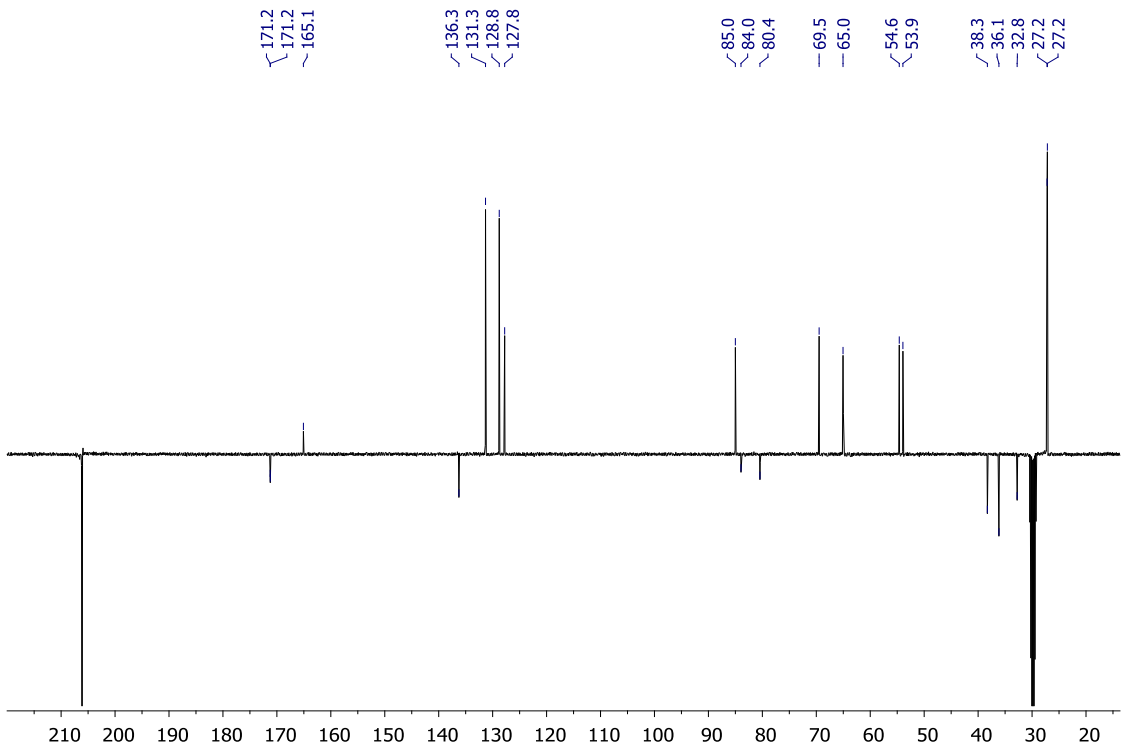


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2,6-di-*tert*-butyl-3-formyl-1,1-dioxidohexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (173c)

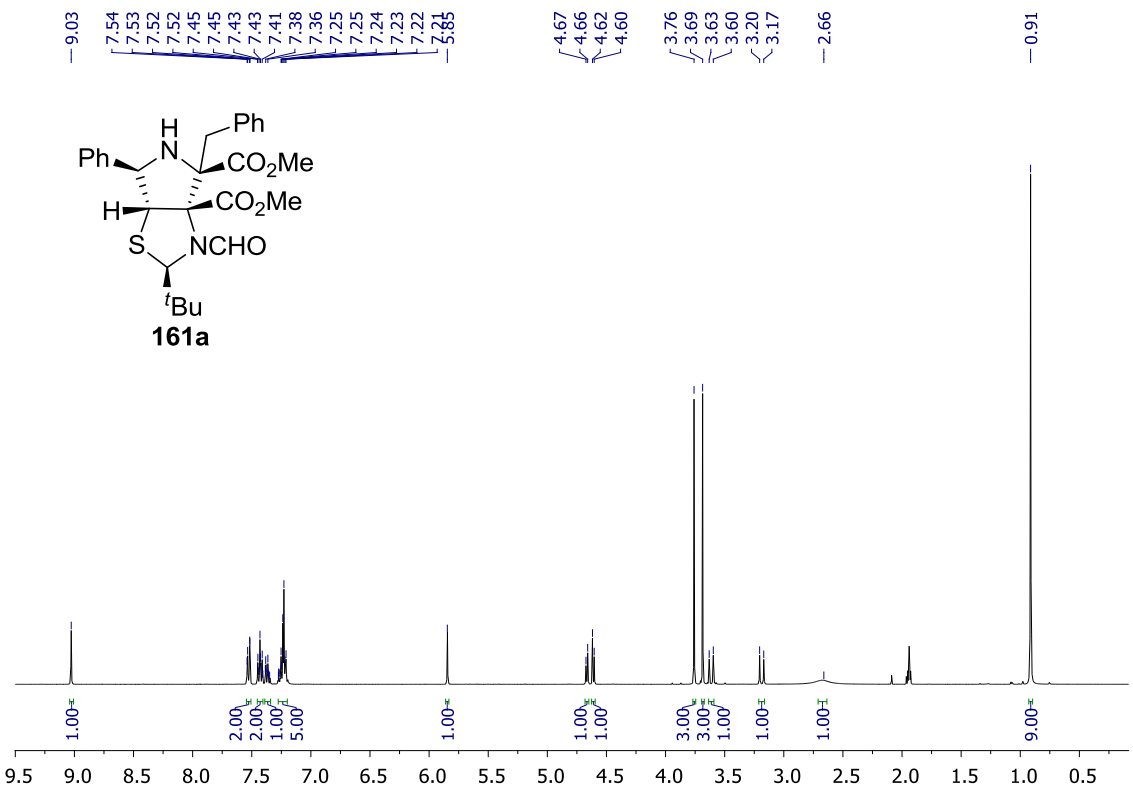


^{1}H-NMR ((CD$_3$)$_2$CO, 400 MHz)

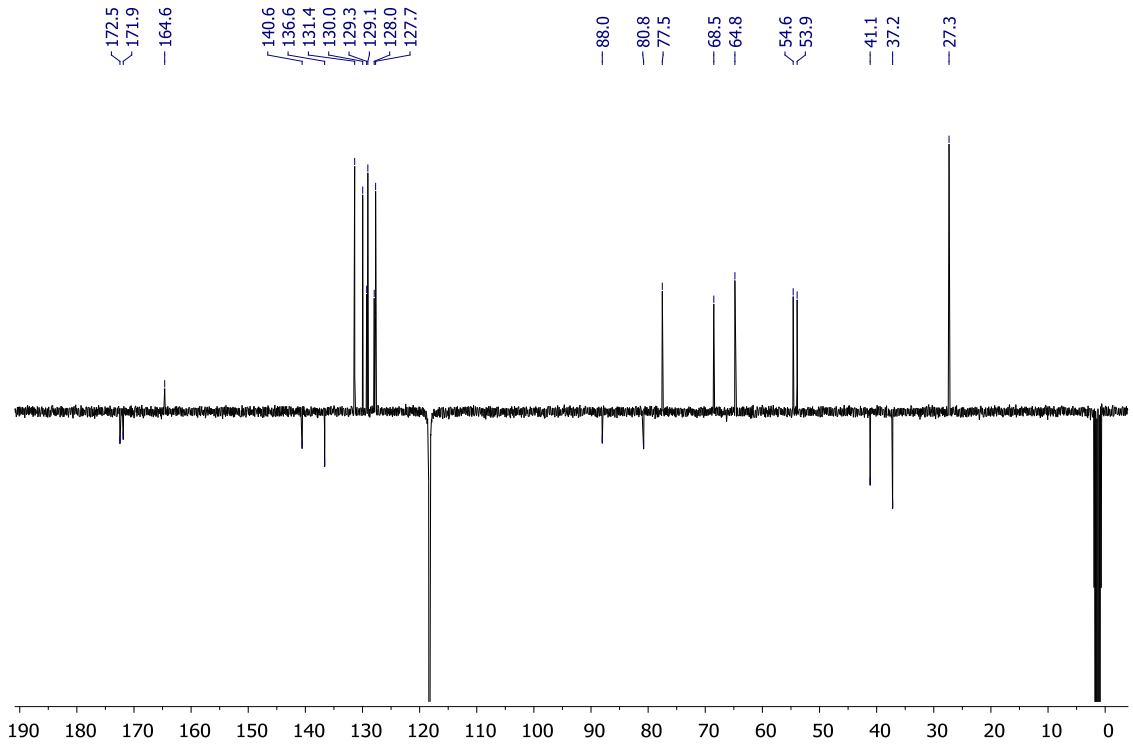


^{13}C-NMR ((CD$_3$)$_2$CO, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (161a)

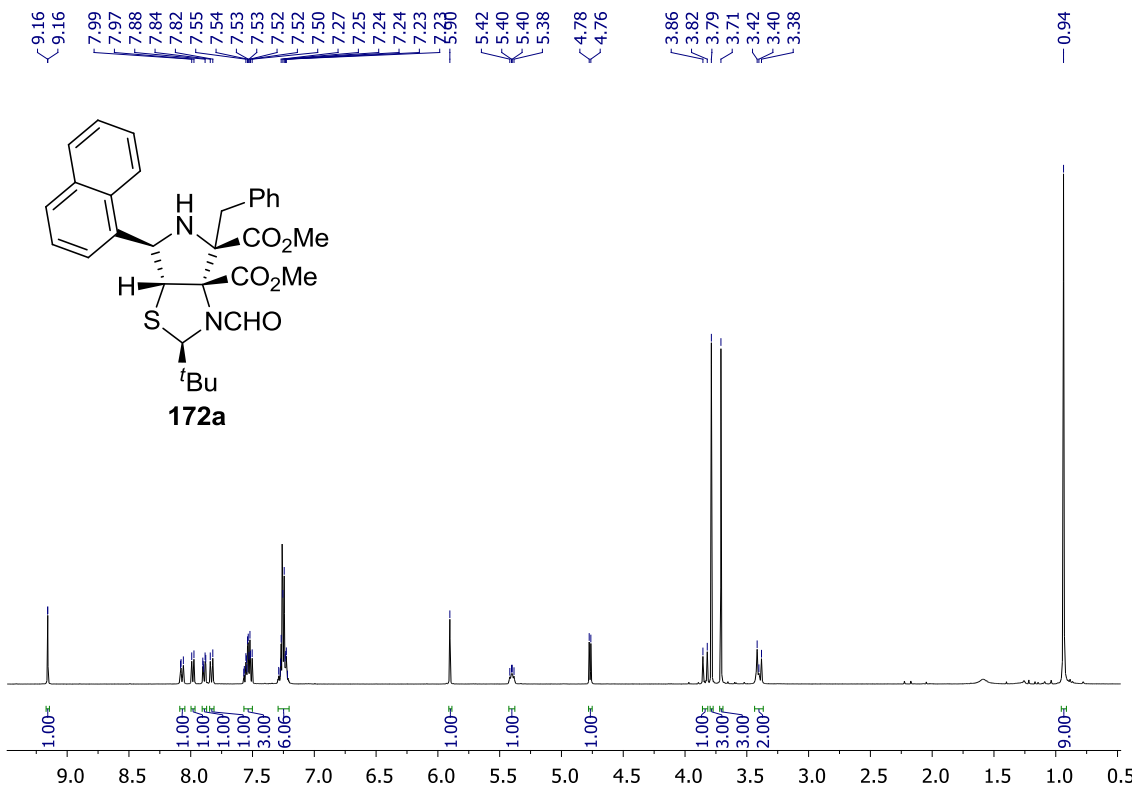


^{1}H-NMR (CD_3CN, 400 MHz)

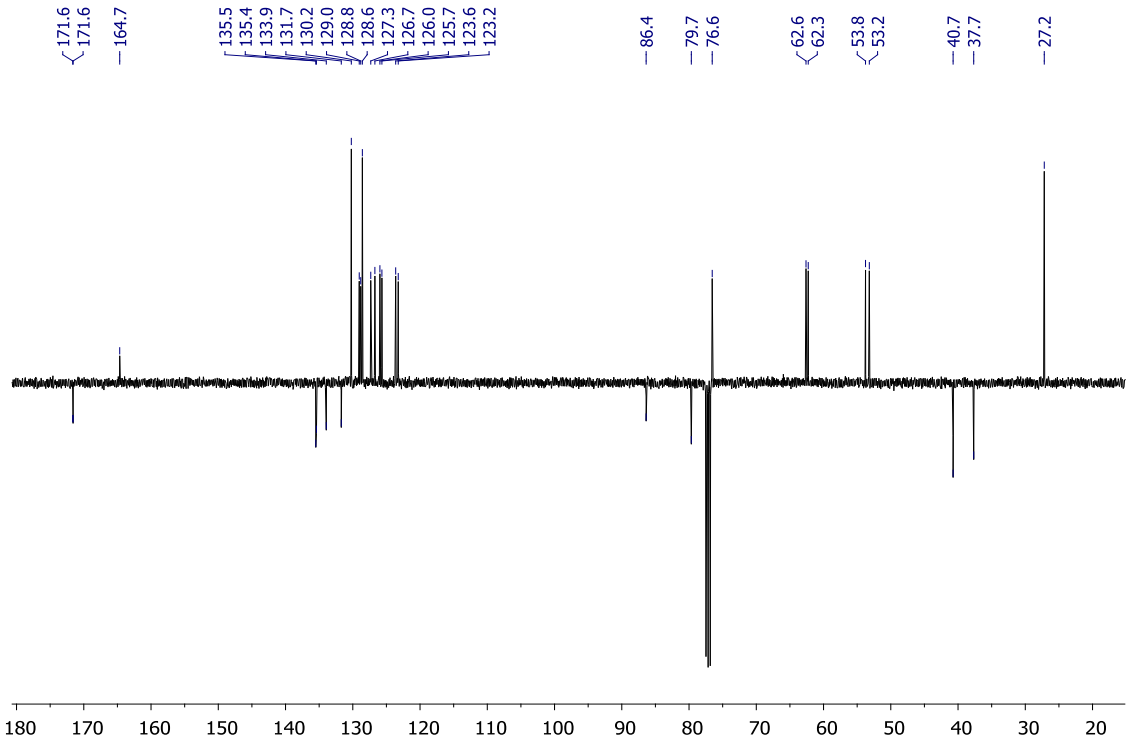


^{13}C-NMR (CD_3CN, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2-*tert*-butyl-3-formyl-6-(1-naphthyl)hexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (172a)

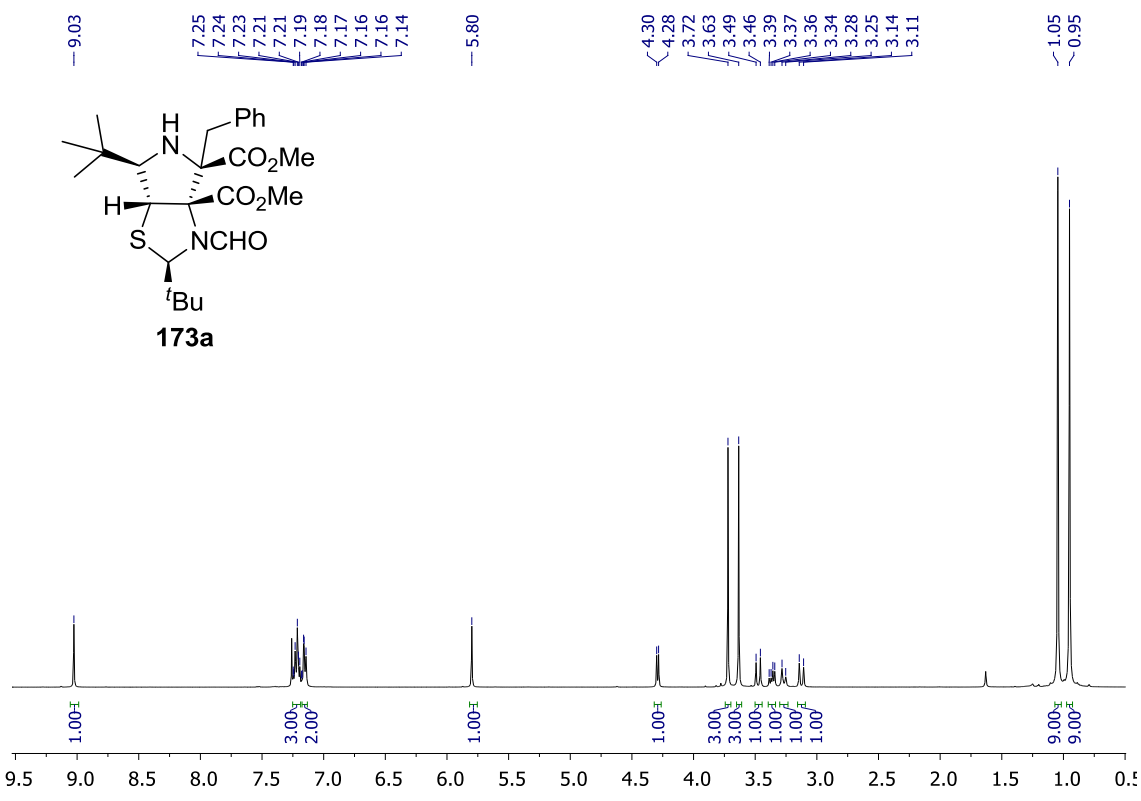


^{1}H-NMR ($CDCl_3$, 400 MHz)

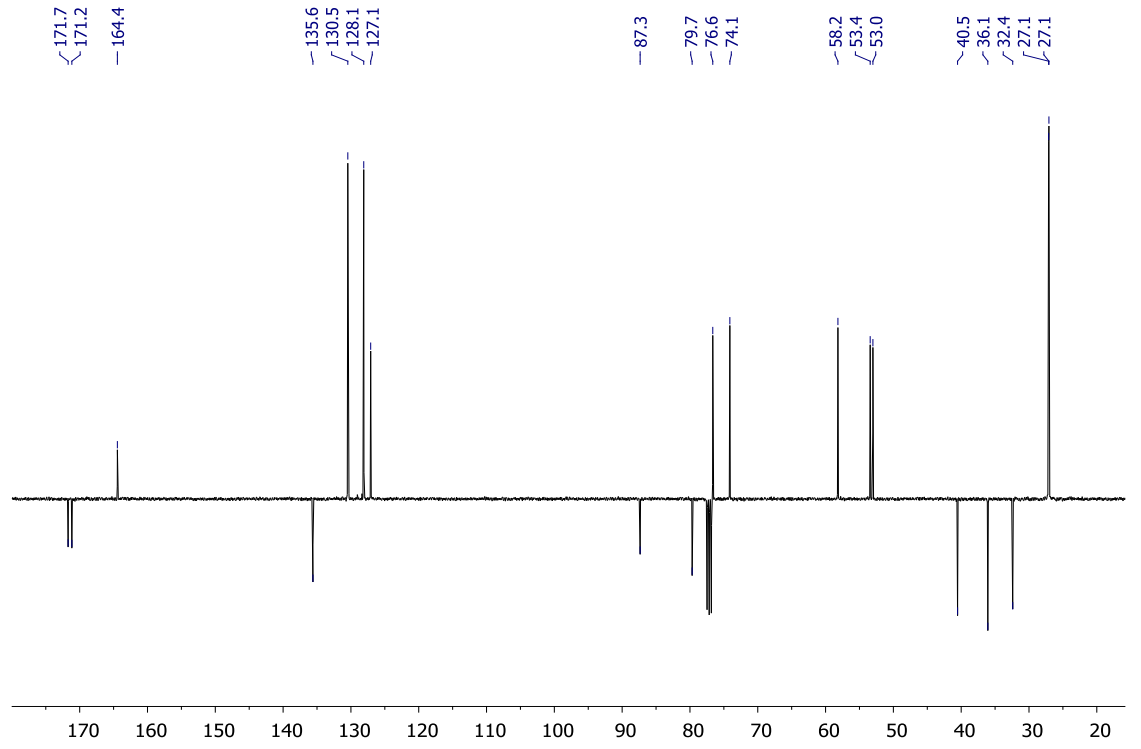


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 4-benzyl-2,6-di-*tert*-butyl-3-formylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (173a)

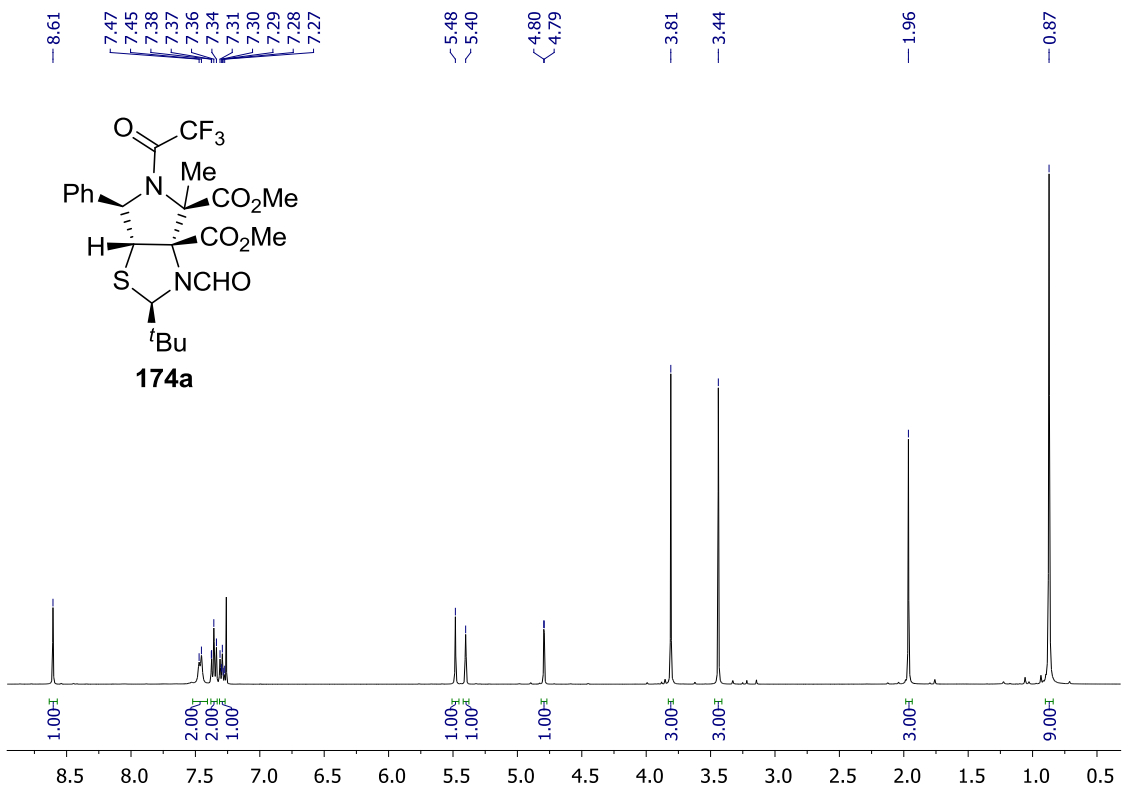


^{1}H-NMR ($CDCl_3$, 400 MHz)

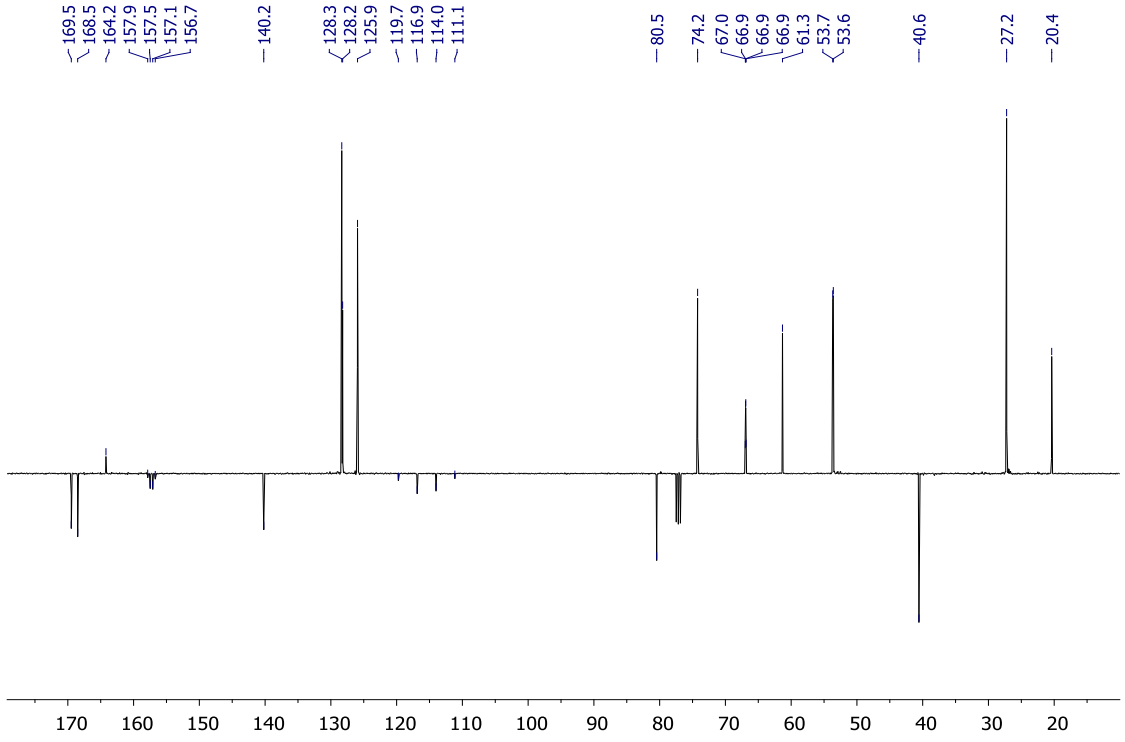


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,6*R*,6a*R*)-Dimethyl 2-*tert*-butyl-5-(2,2,2-trifluoroacetyl)-3-formyl-4-methyl-6-phenylhexahydro-2*H*-pyrrolo[3,4-*d*]thiazole-3a,4-dicarboxylate (174a)



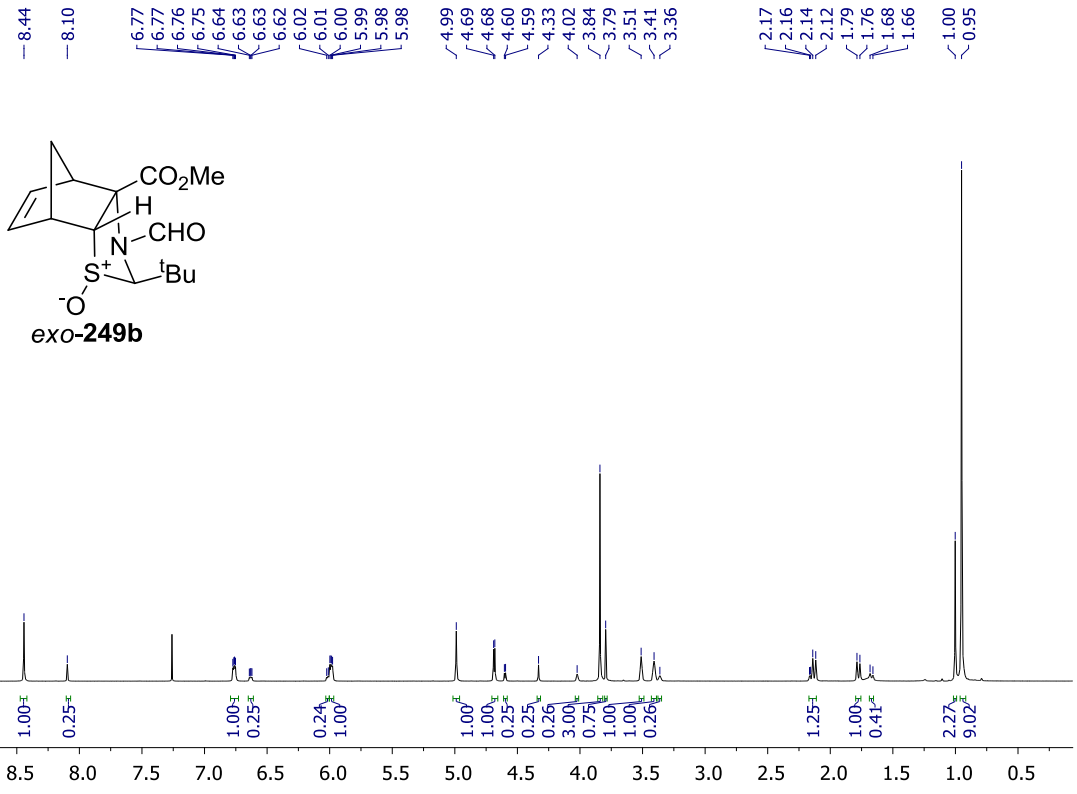
^{1}H-NMR ($CDCl_3$, 400 MHz)



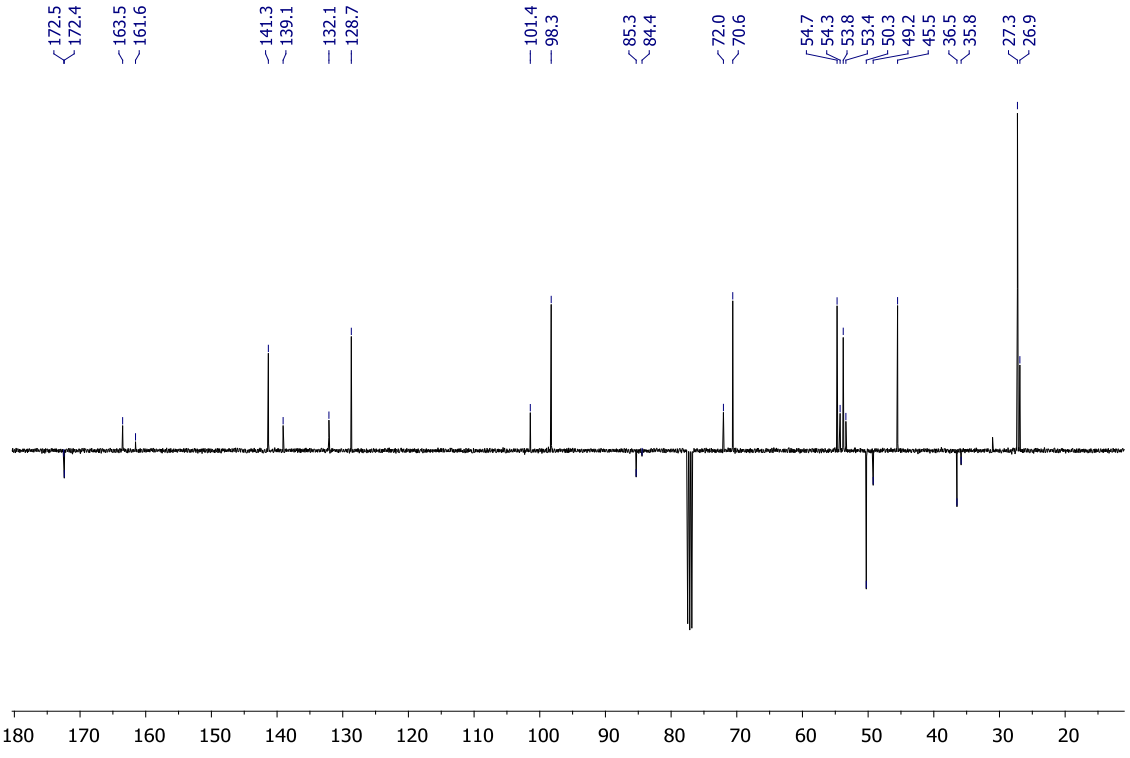
^{13}C-NMR ($CDCl_3$, 100 MHz)

NMR spectra of chapter VI

(1*R*,2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*exo*-249b)

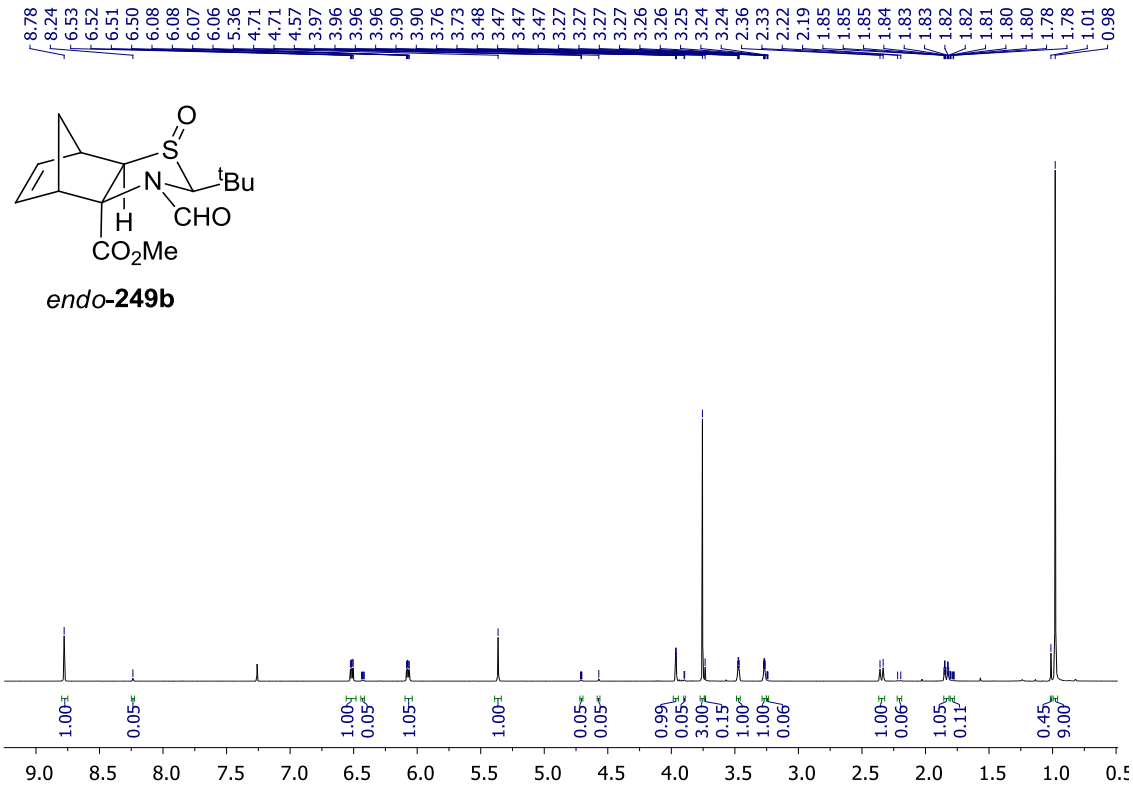


^{1}H-NMR ($CDCl_3$, 400 MHz)



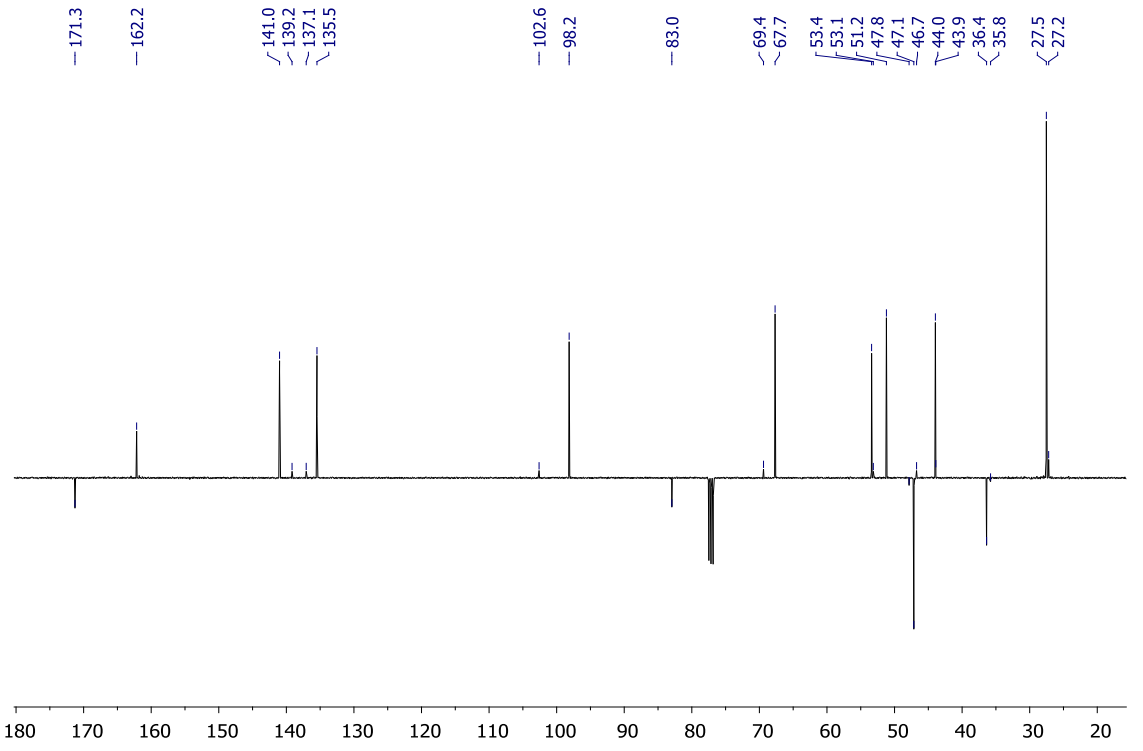
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*endo*-249b)



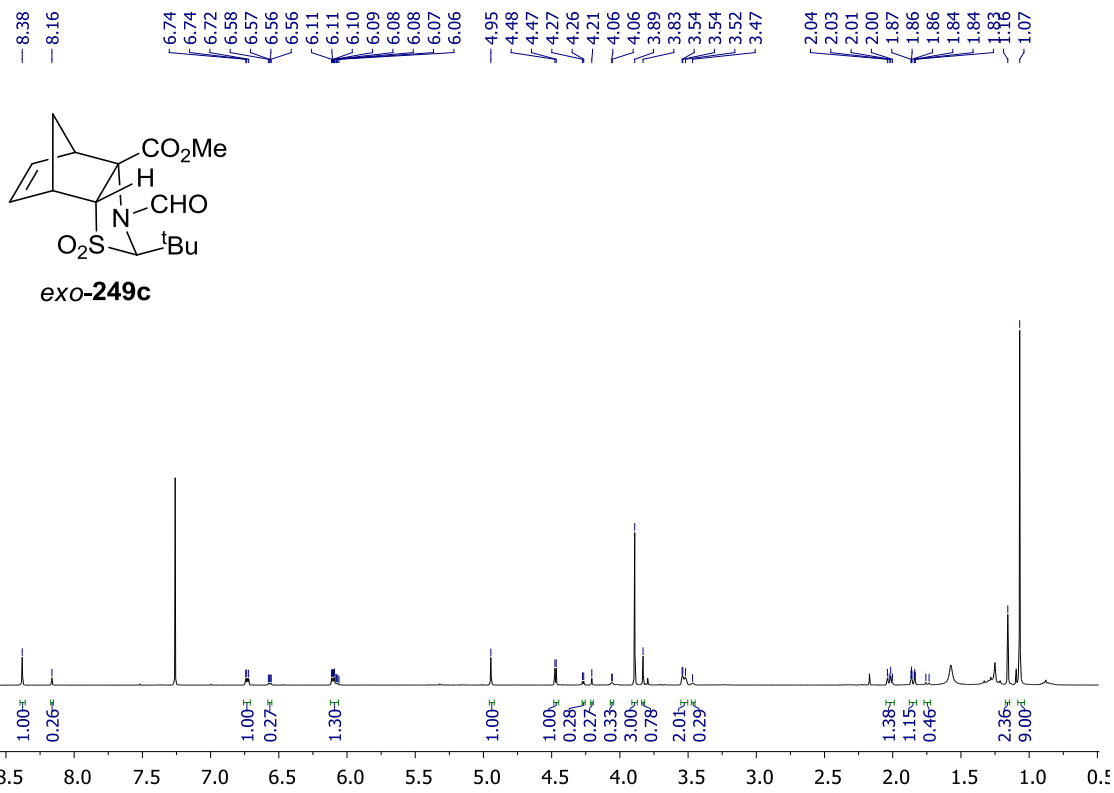
endo-**249b**

^{1}H-NMR ($CDCl_3$, 400 MHz)

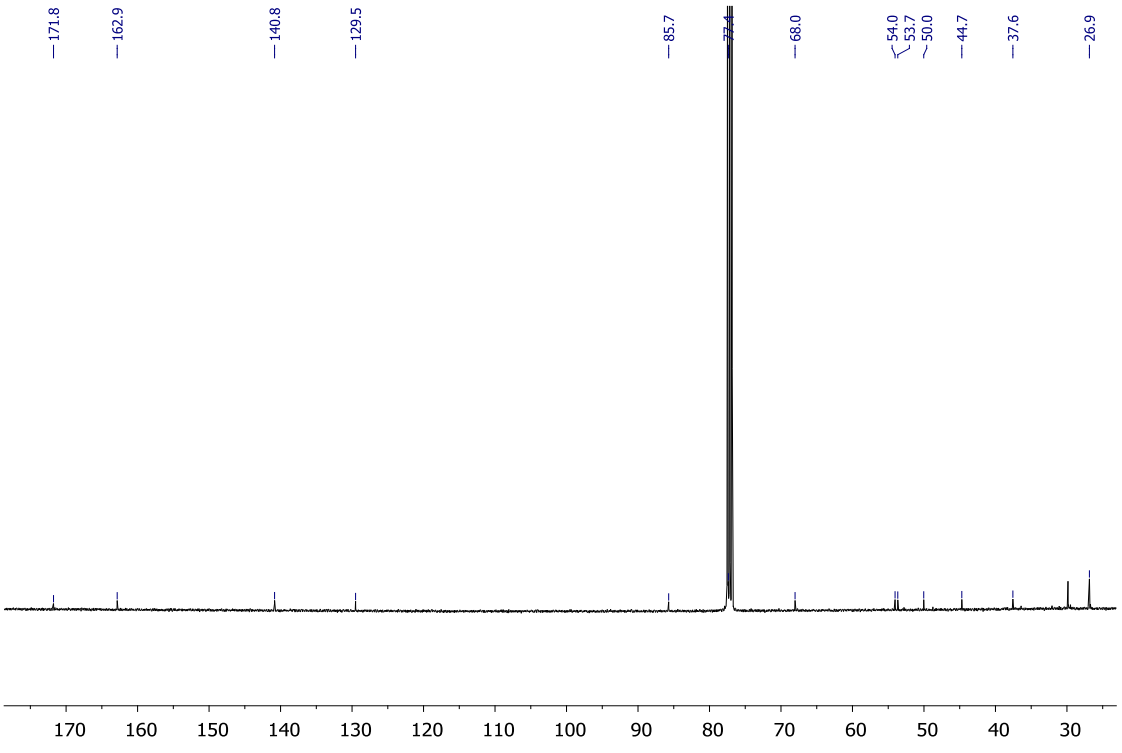


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*exo*-249c)

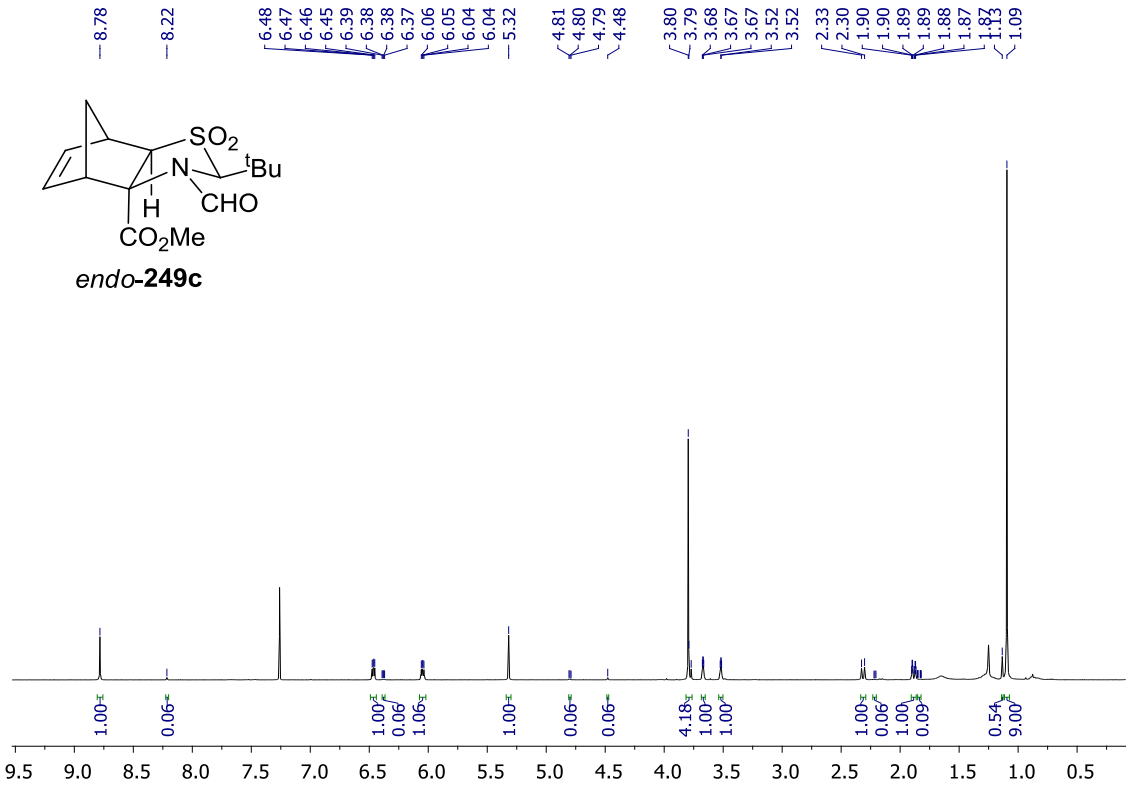


^{1}H-NMR ($CDCl_3$, 400 MHz)

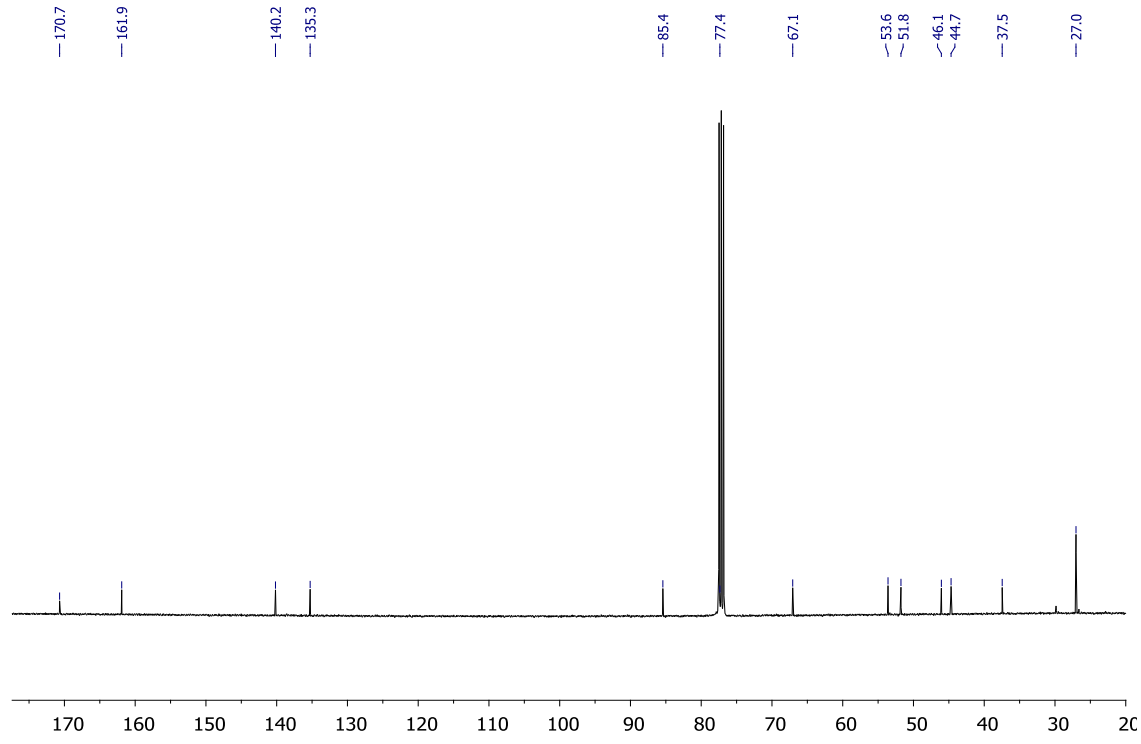


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3,3a,4,7,7a-hexahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate *endo*-249c

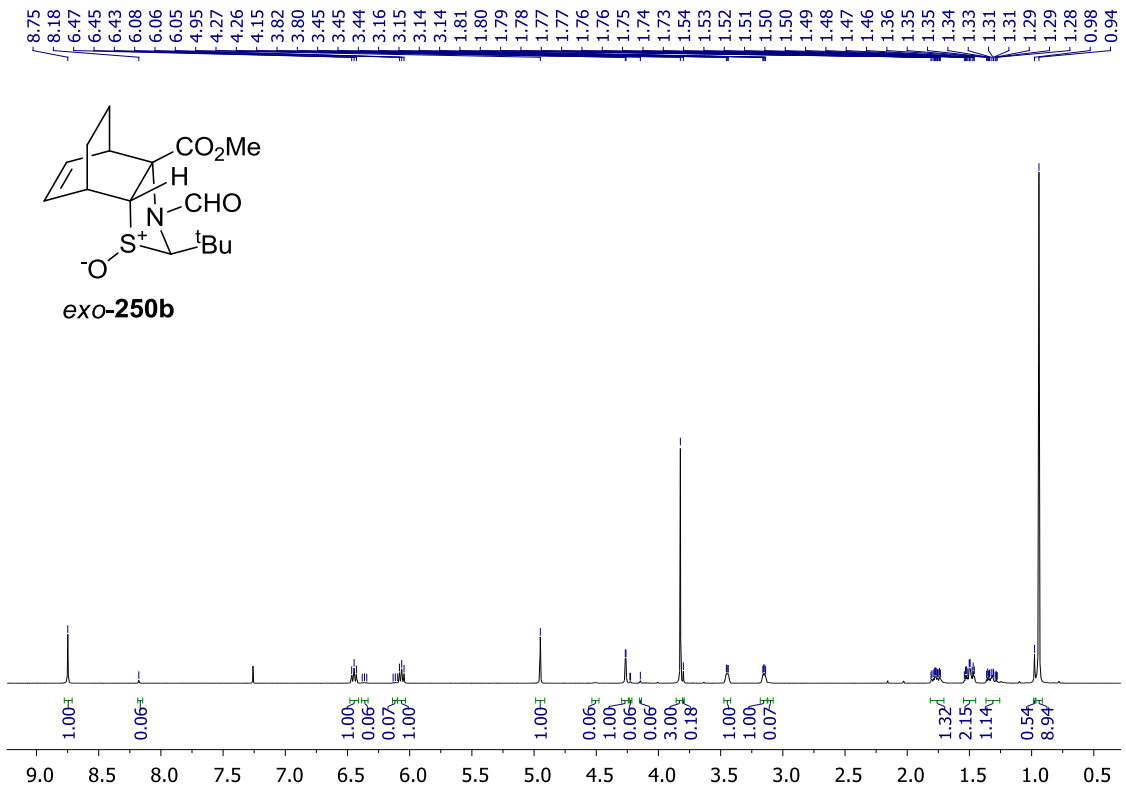


^{1}H-NMR ($CDCl_3$, 400 MHz)



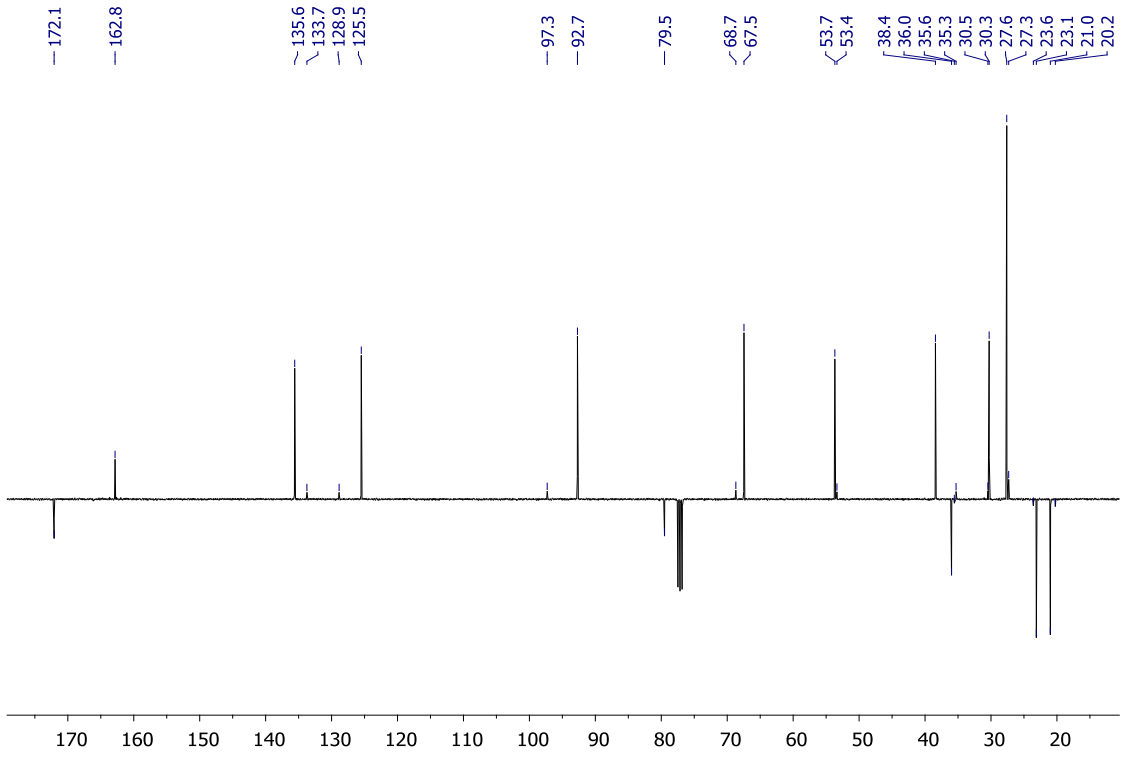
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*R*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxido-2,3,3a,4,7,7a-hexahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate (*exo*-250b)



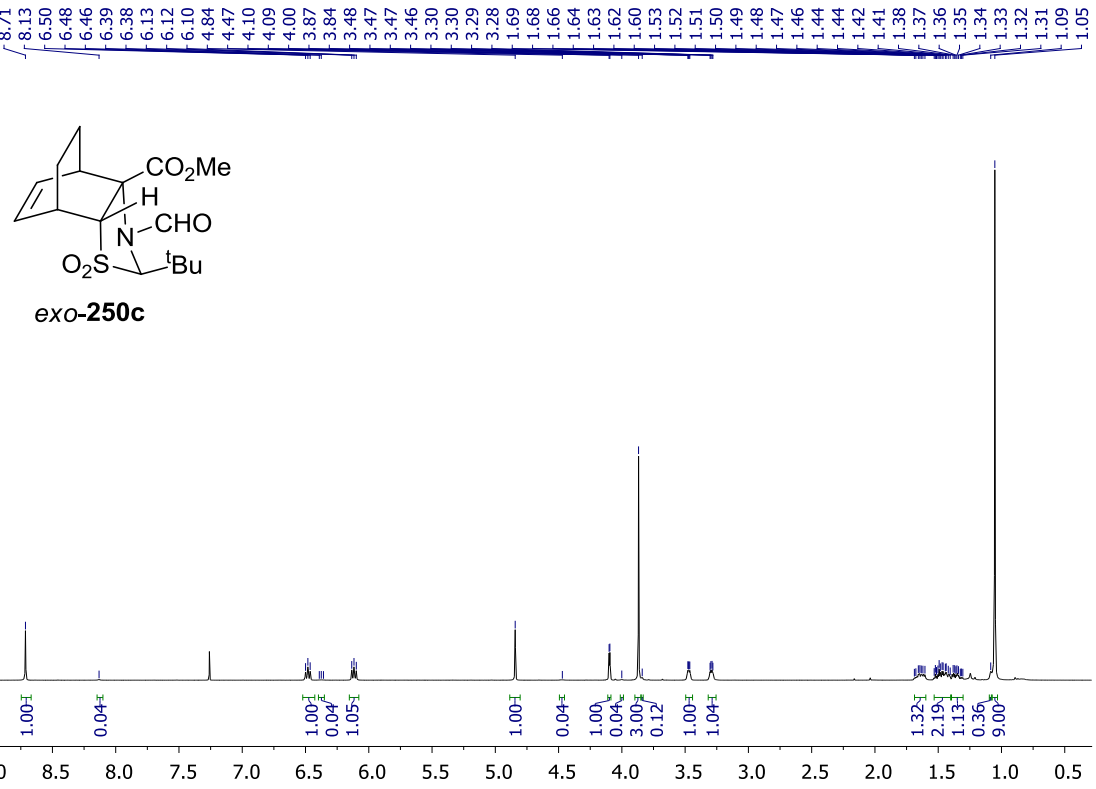
exo-**250b**

^{1}H-NMR ($CDCl_3$, 400 MHz)

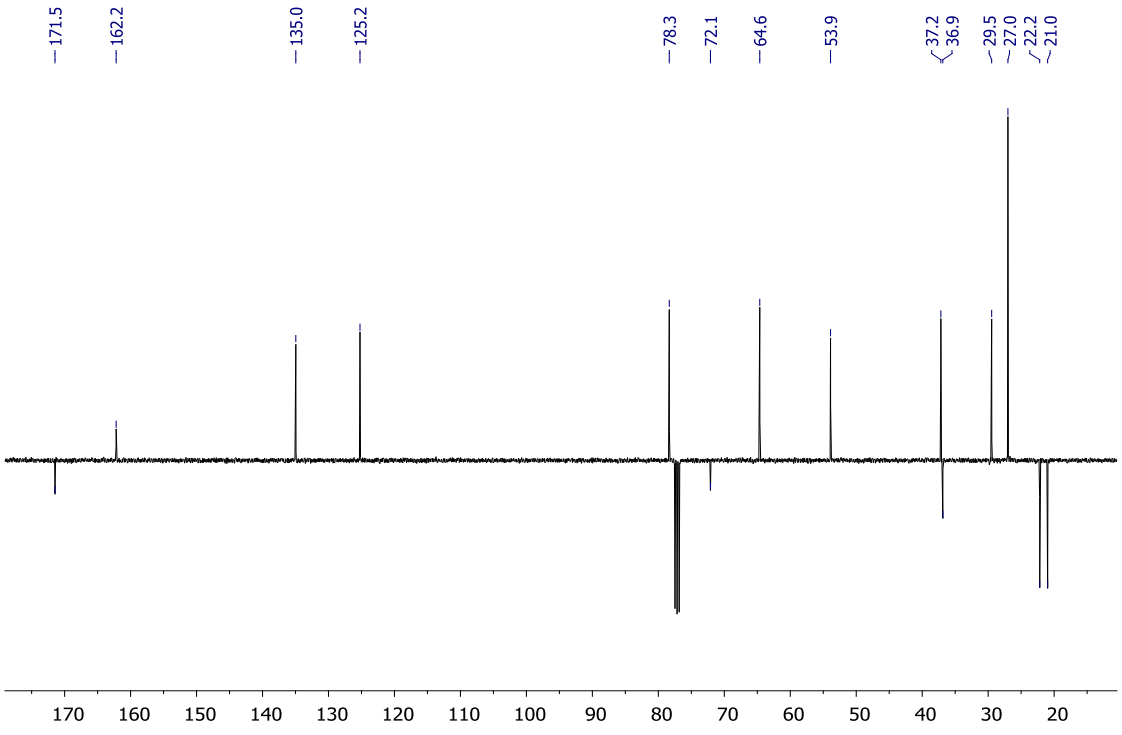


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxido-2,3,3a,4,7,7a-hexahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate (*exo*-250c)

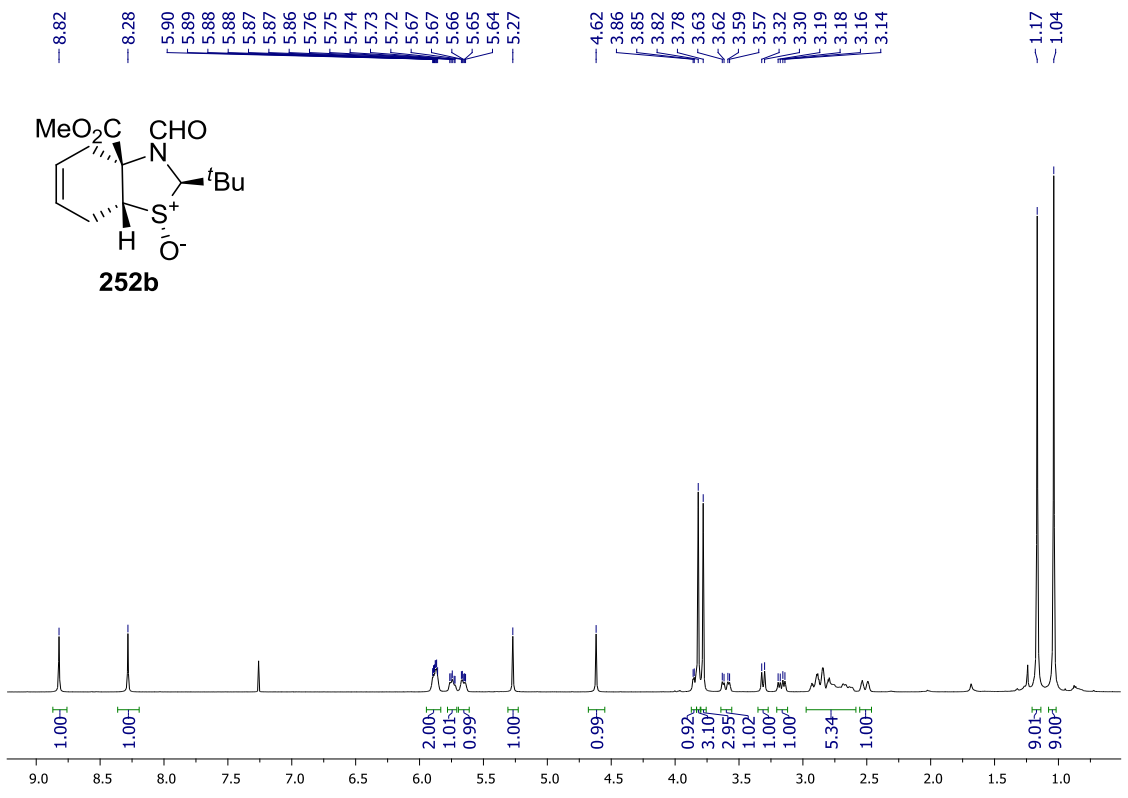


^{1}H-NMR ($CDCl_3$, 400 MHz)

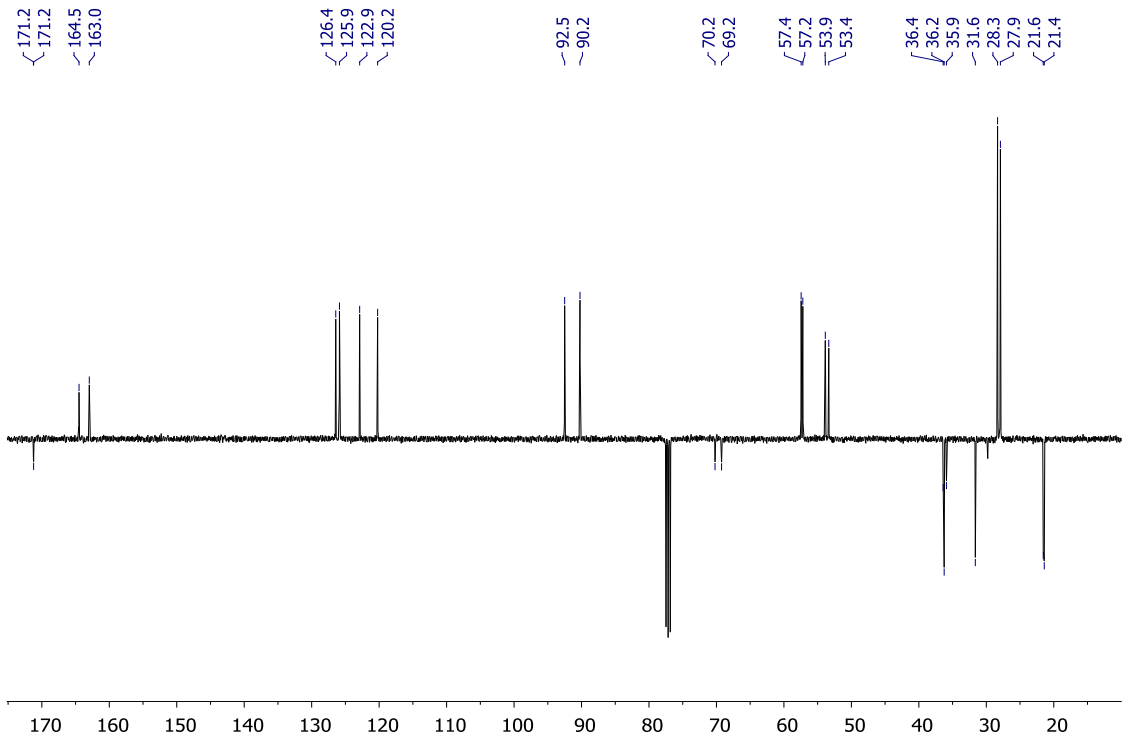


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate (252b)

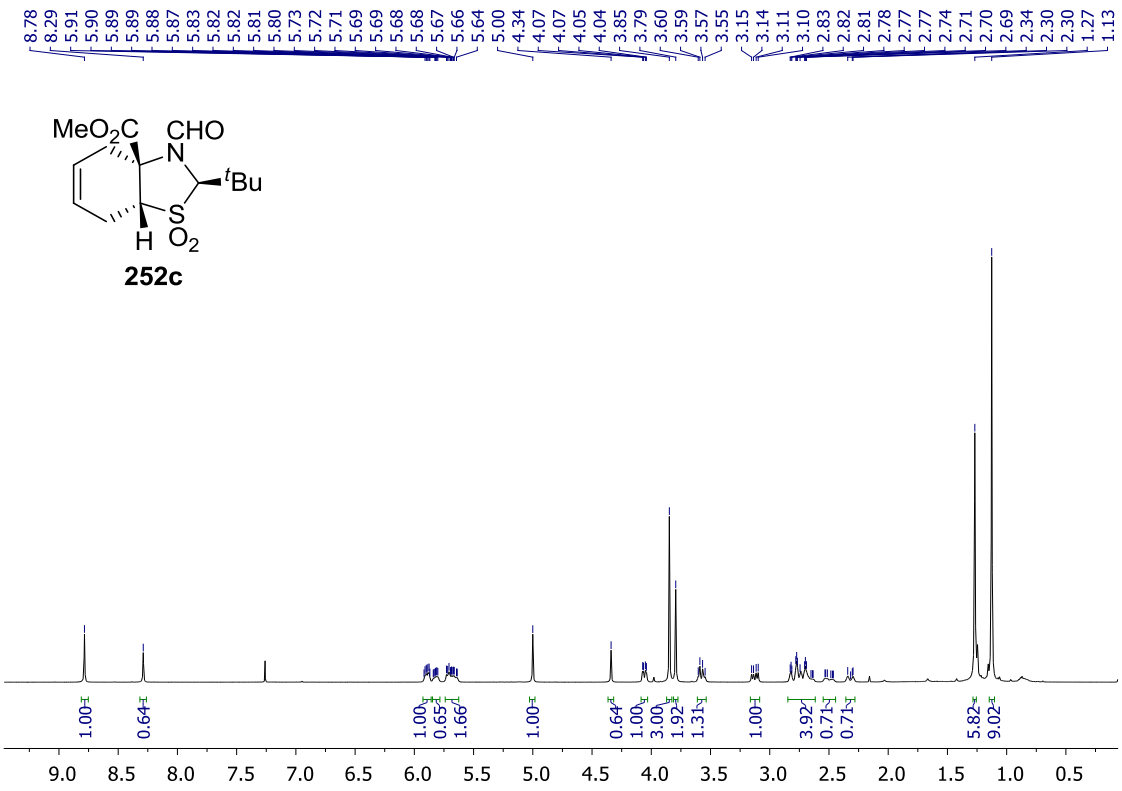


^{1}H-NMR ($CDCl_3$, 400 MHz)

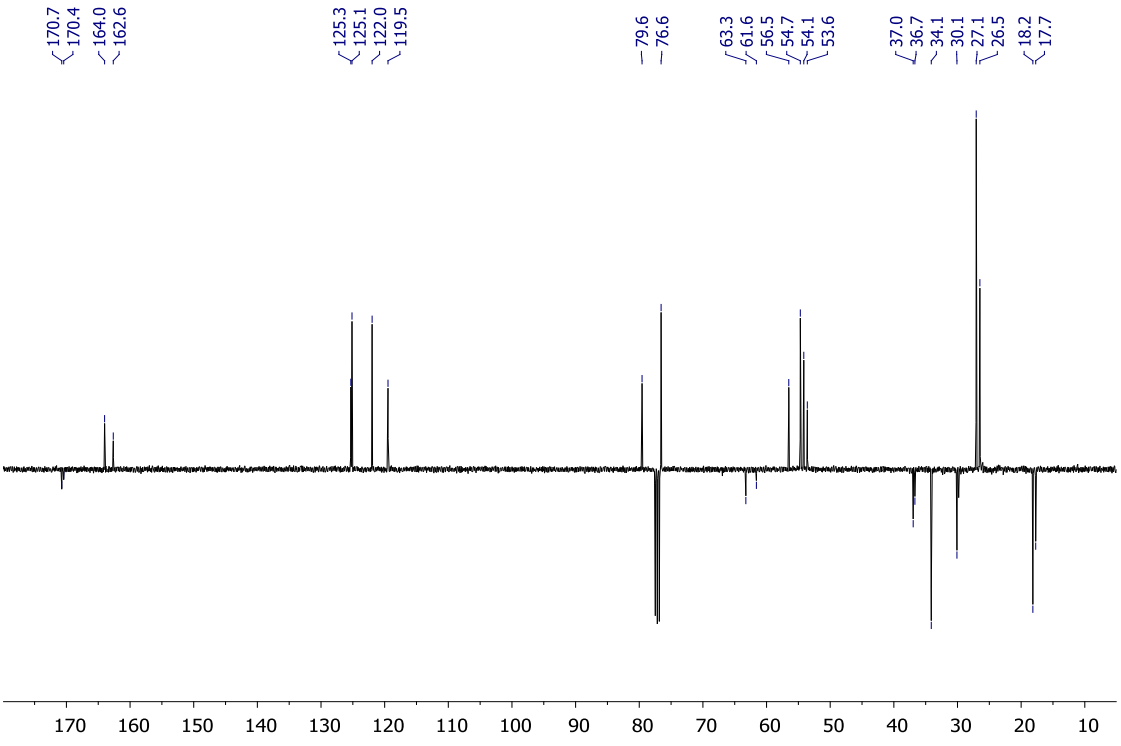


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate (252c)

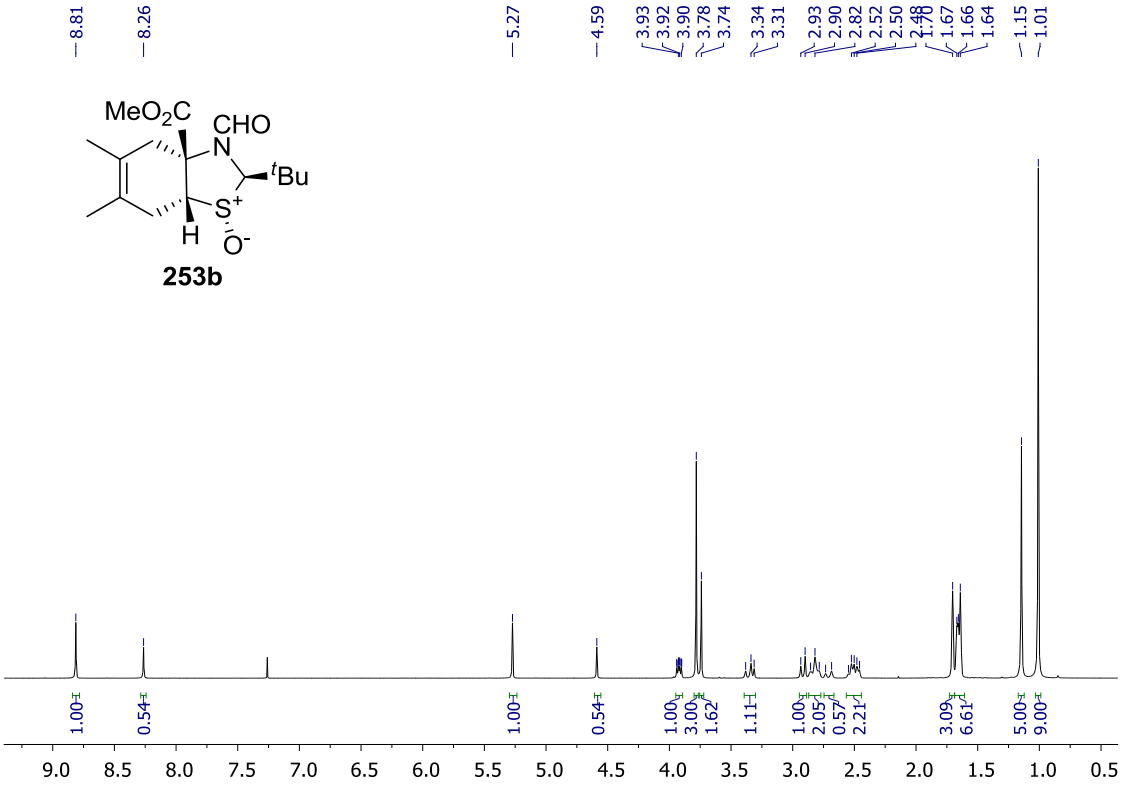


^{1}H-NMR ($CDCl_3$, 400 MHz)

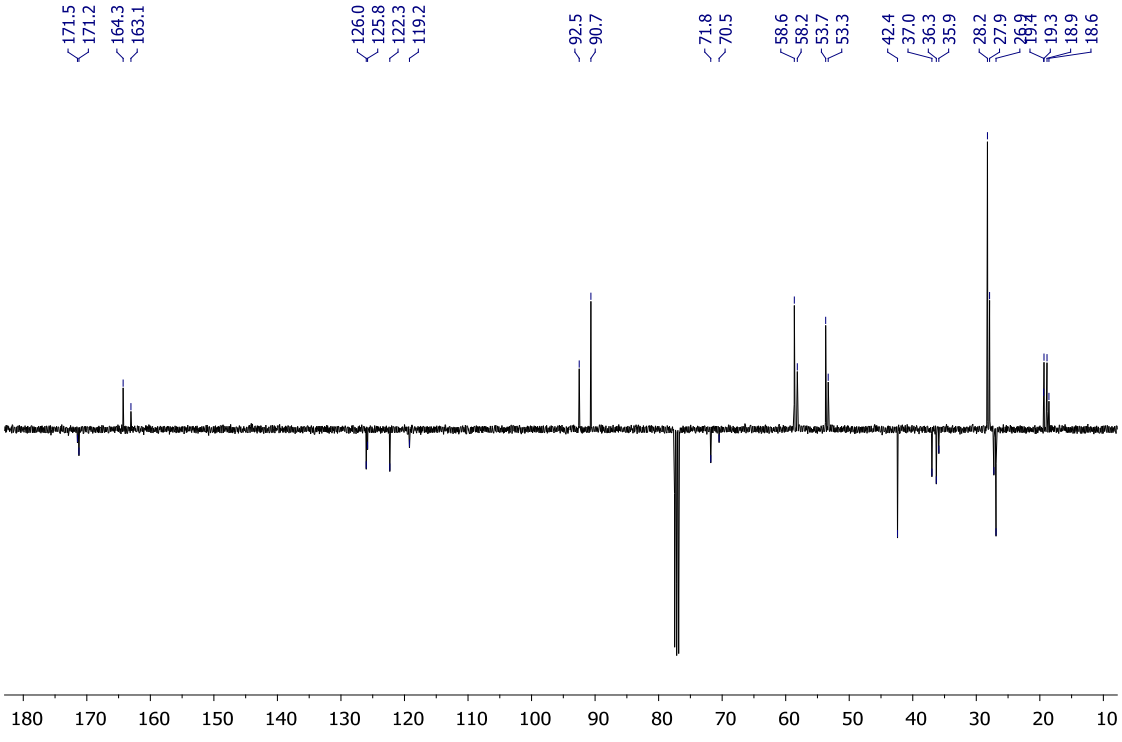


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7-oxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate (253b)

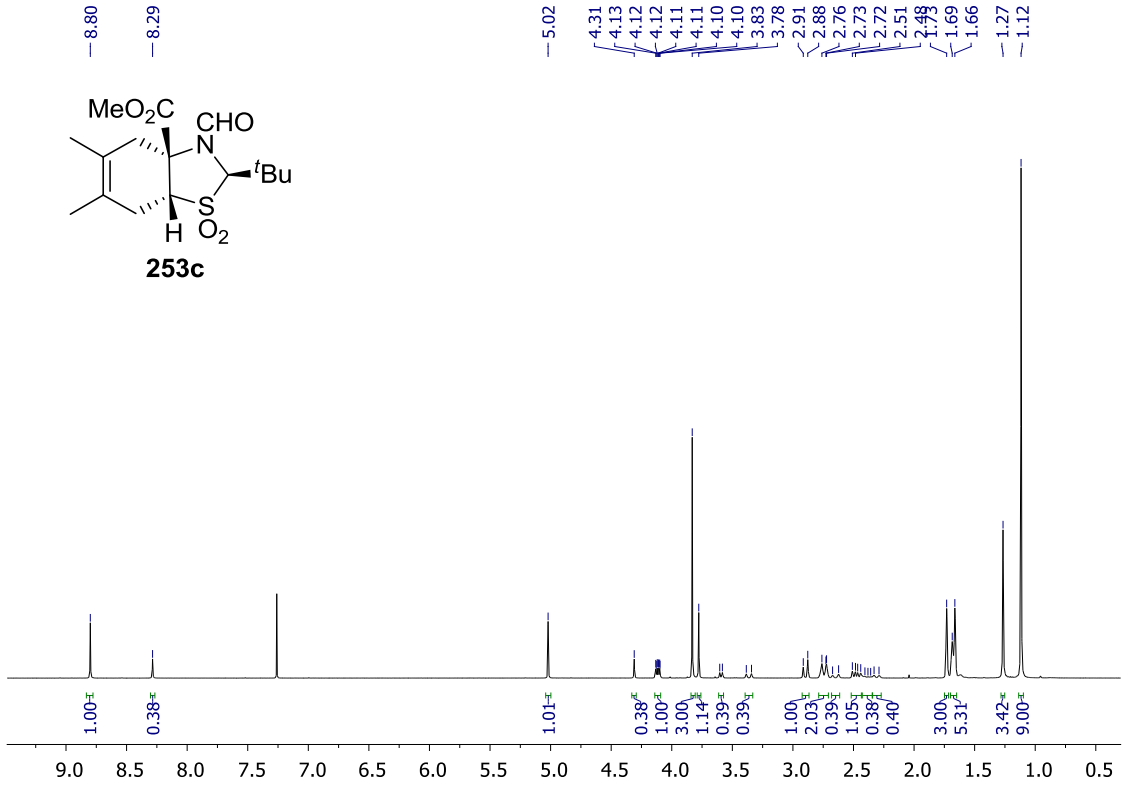


^{1}H-NMR ($CDCl_3$, 400 MHz)

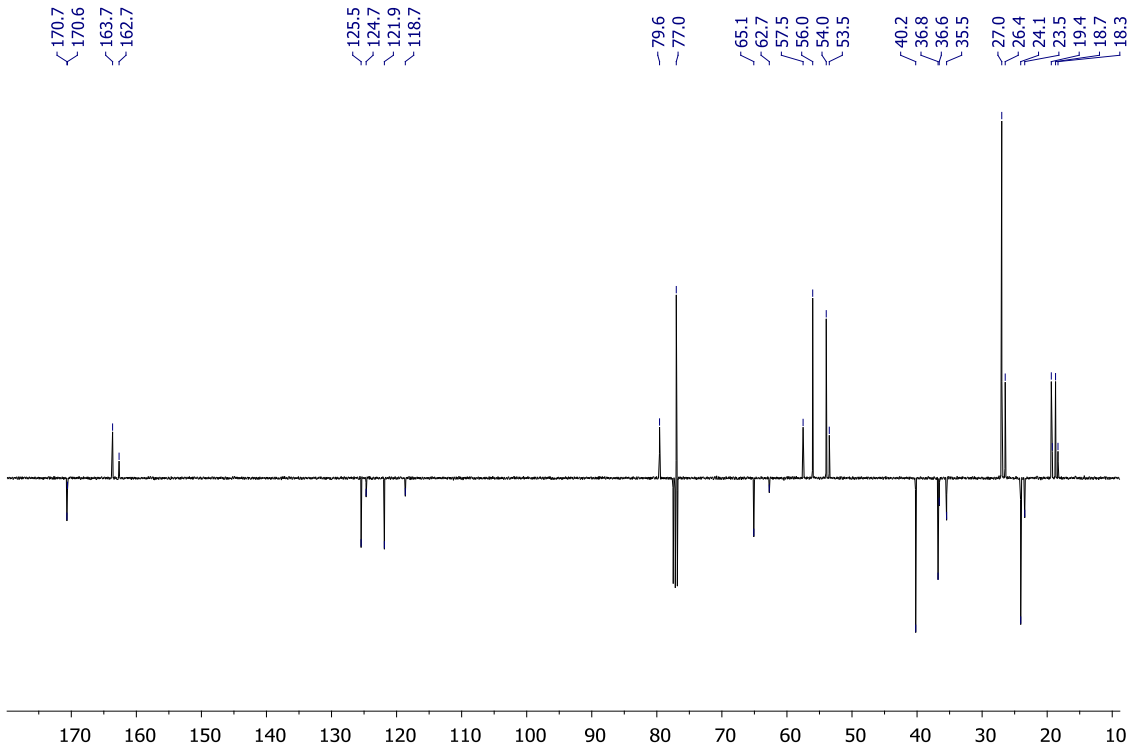


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate (253c)

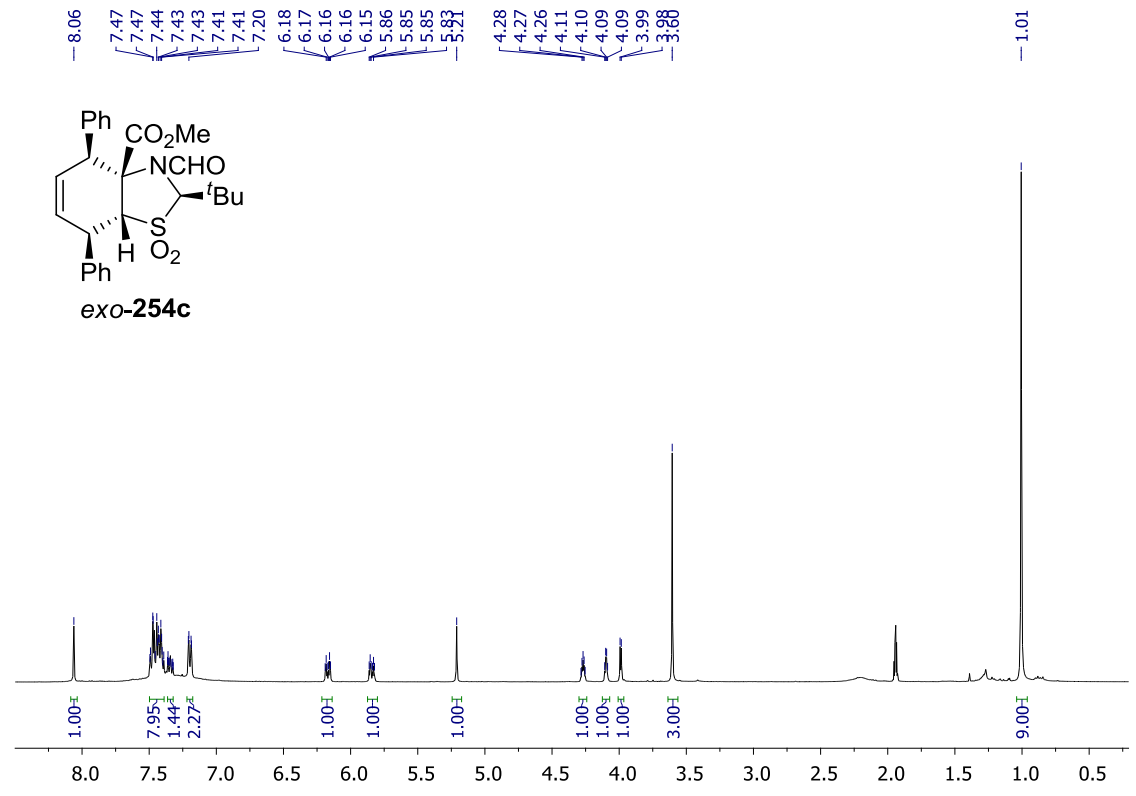


^{1}H-NMR ($CDCl_3$, 400 MHz)

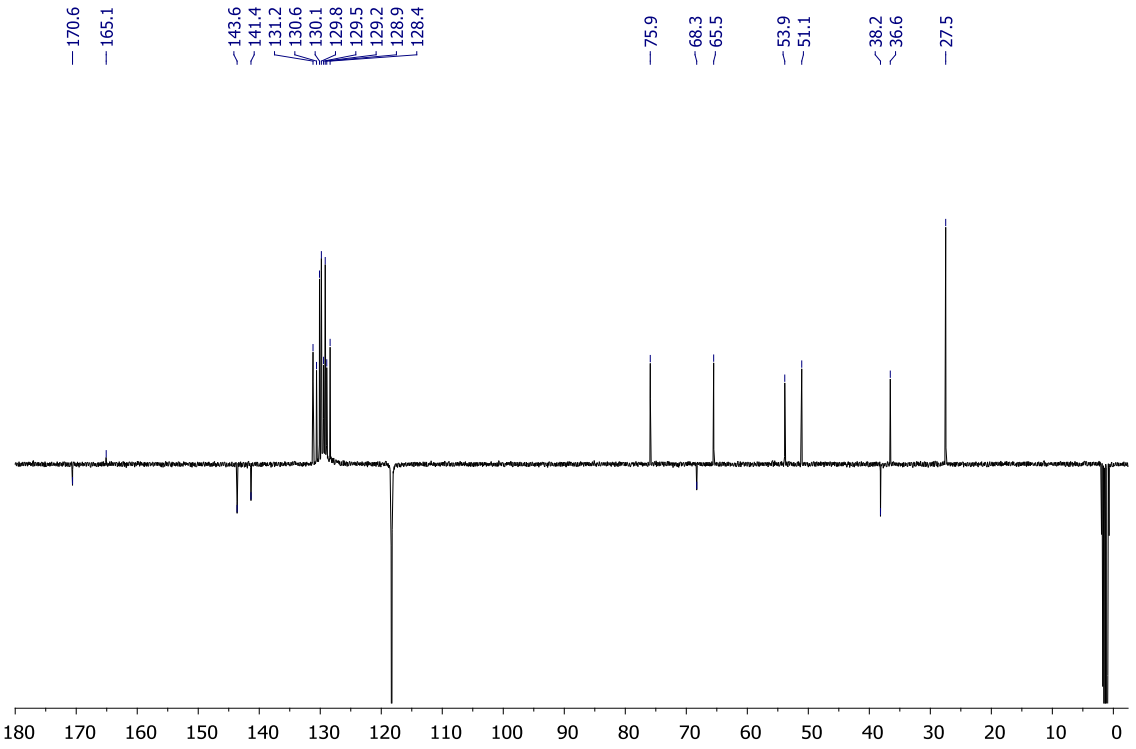


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*S*,5*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-2,5-diphenyl-7-thia-9-azabicyclo[4.3.0]non-3-ene-1-carboxylate (*exo*-254c)

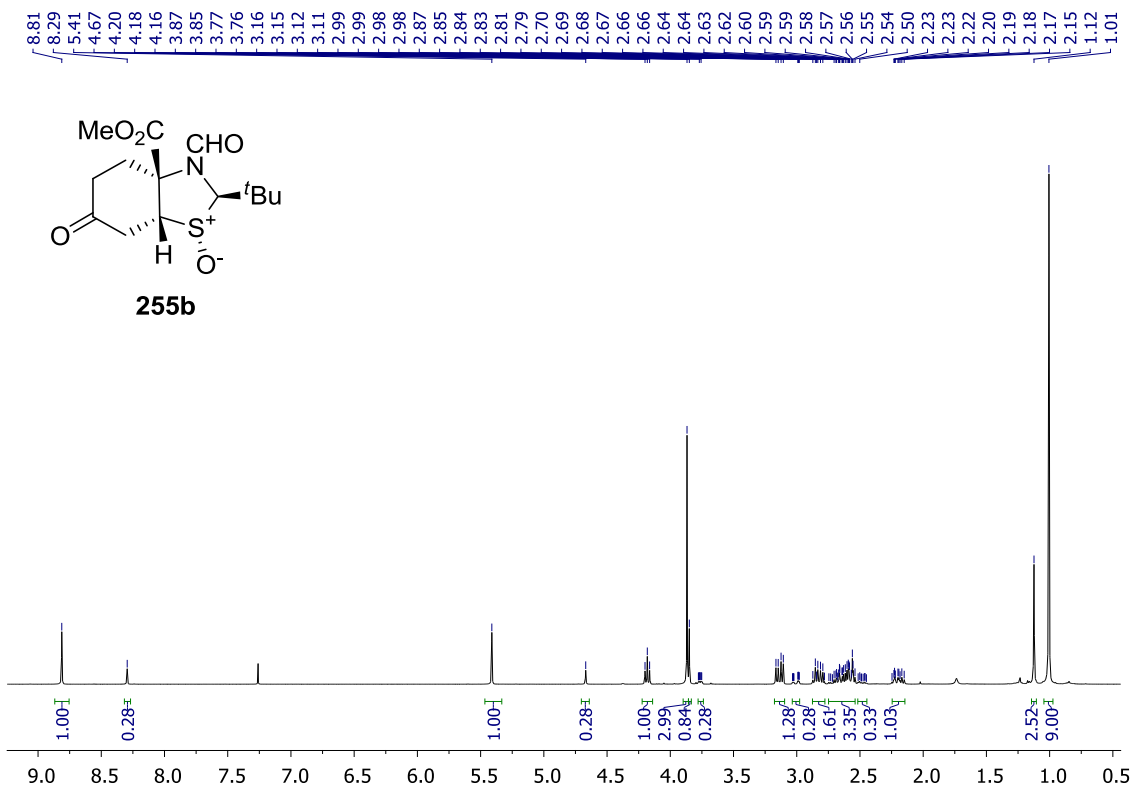


^{1}H-NMR (CD_3CN, 400 MHz)

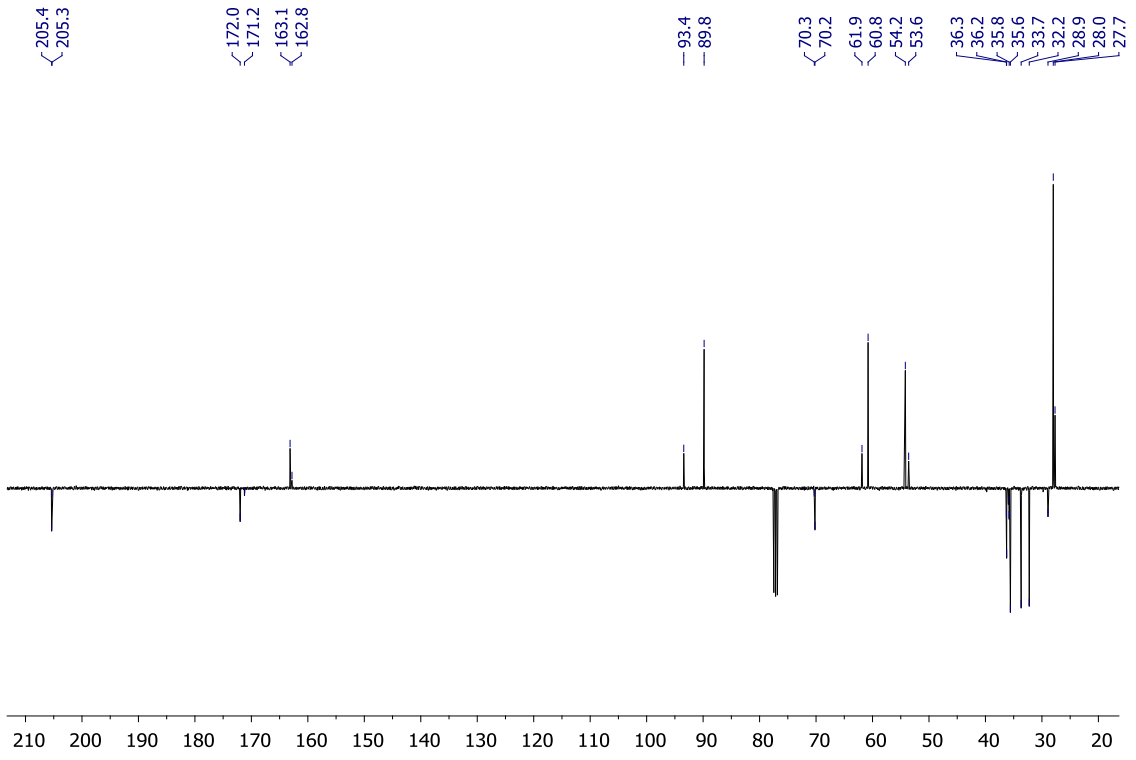


^{13}C-NMR (CD_3CN, 100 MHz)

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (255b)

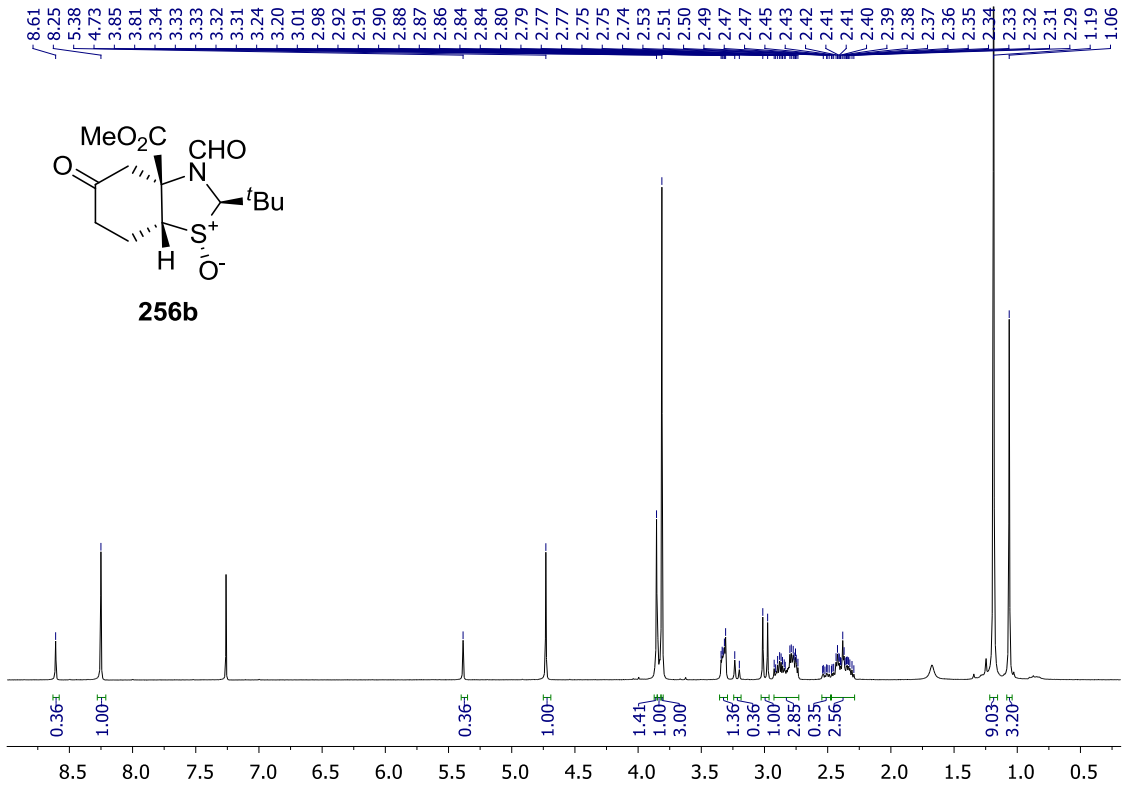


^{1}H-NMR ($CDCl_3$, 400 MHz)

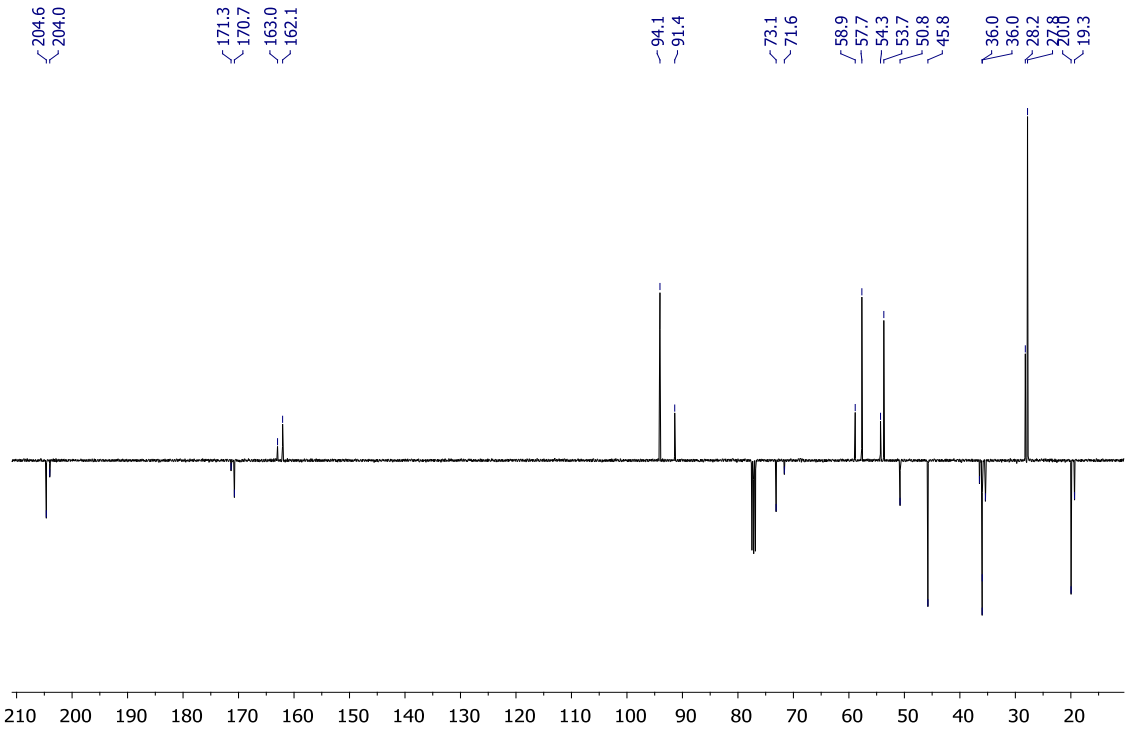


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-3-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (256b)

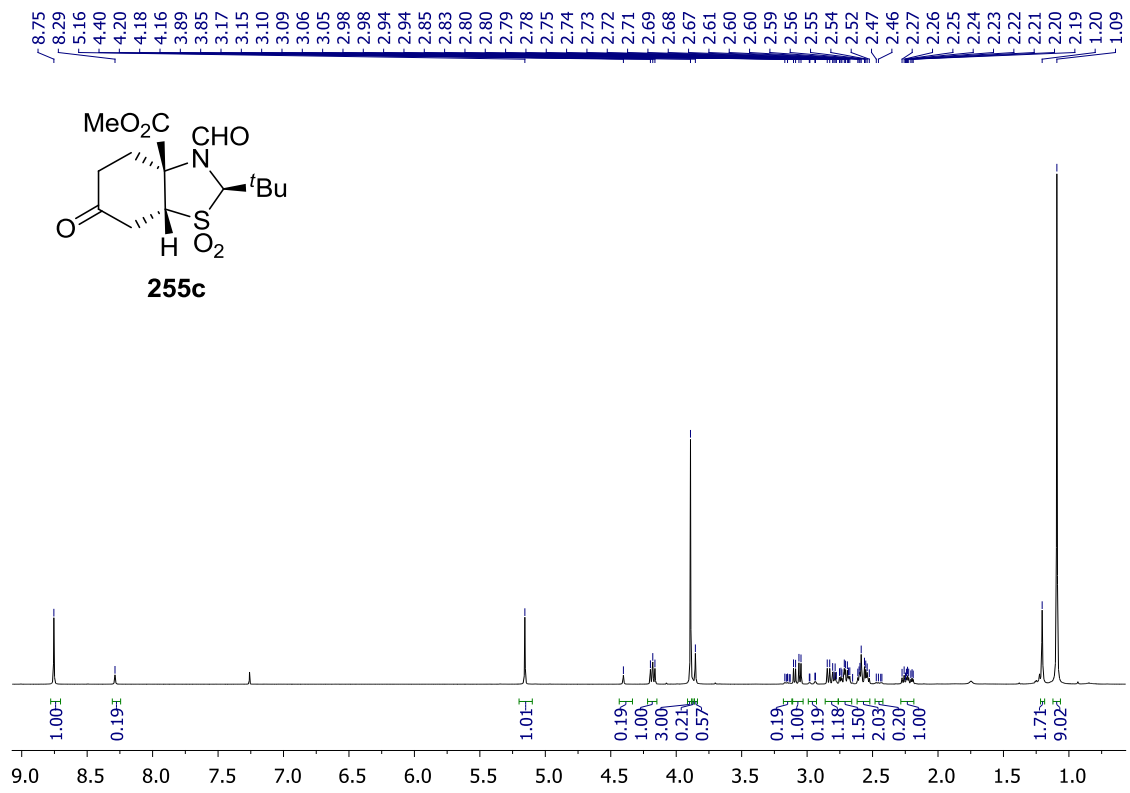


^{1}H-NMR ($CDCl_3$, 400 MHz)

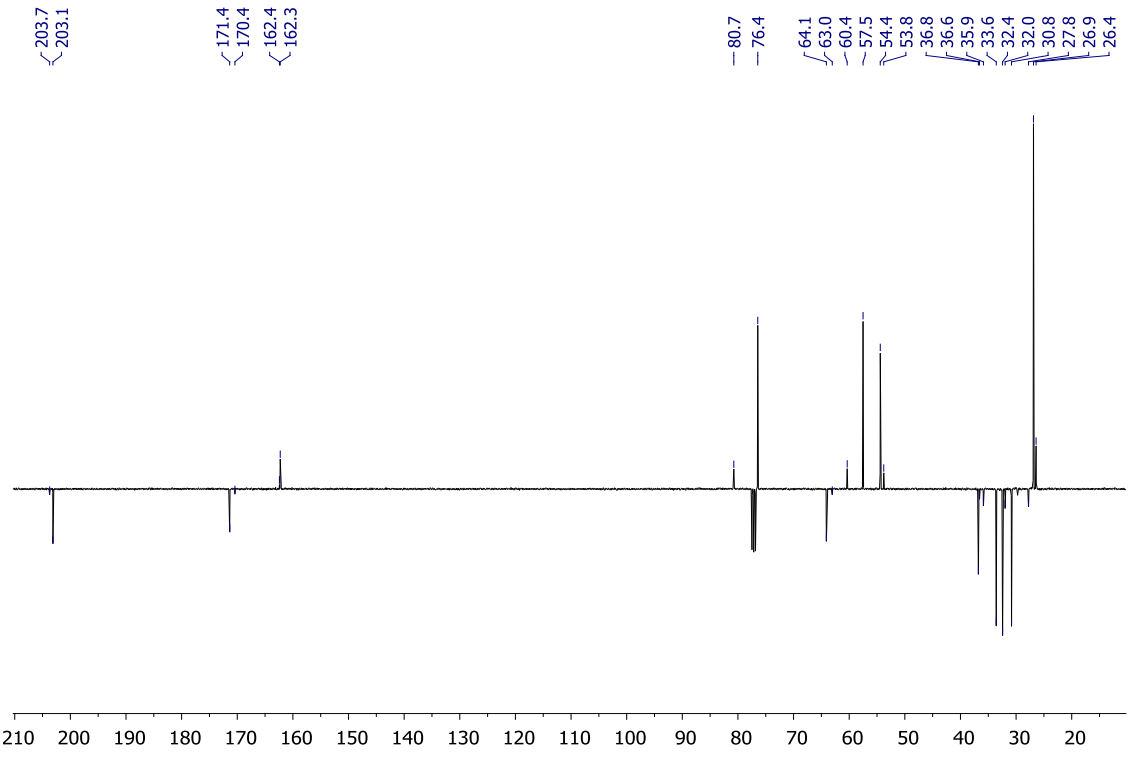


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (255c)

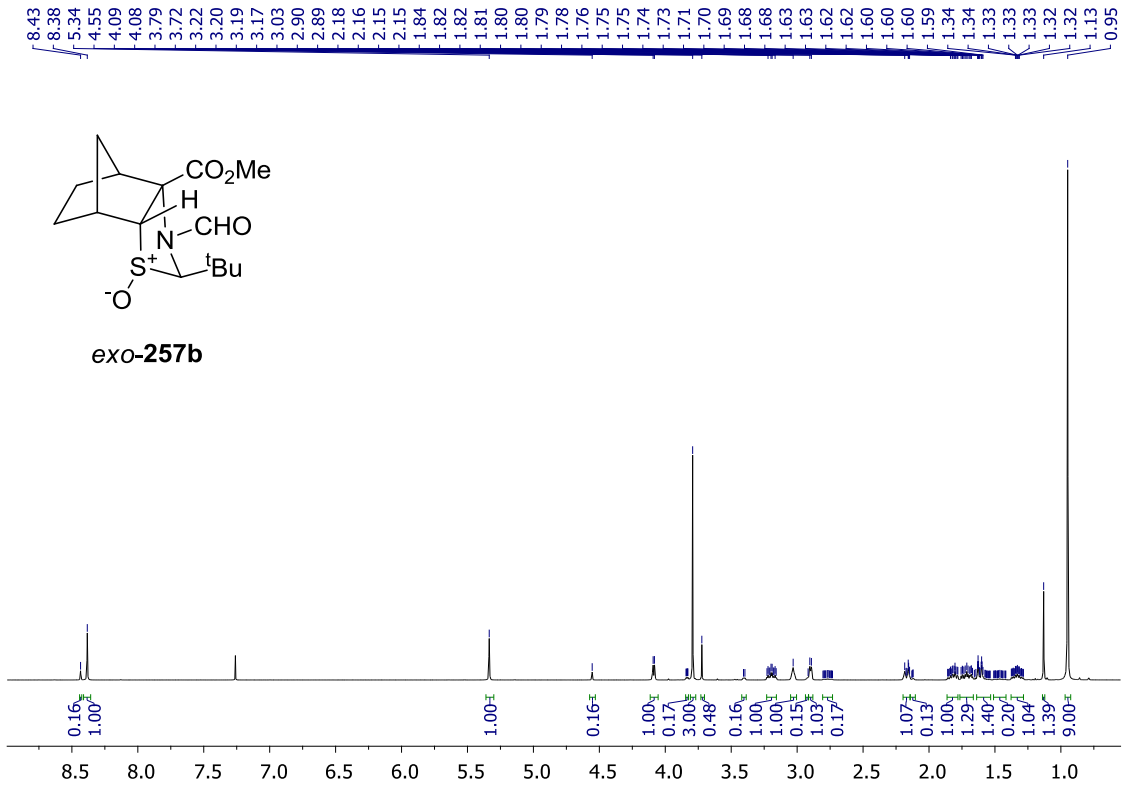


^{1}H-NMR ($CDCl_3$, 400 MHz)



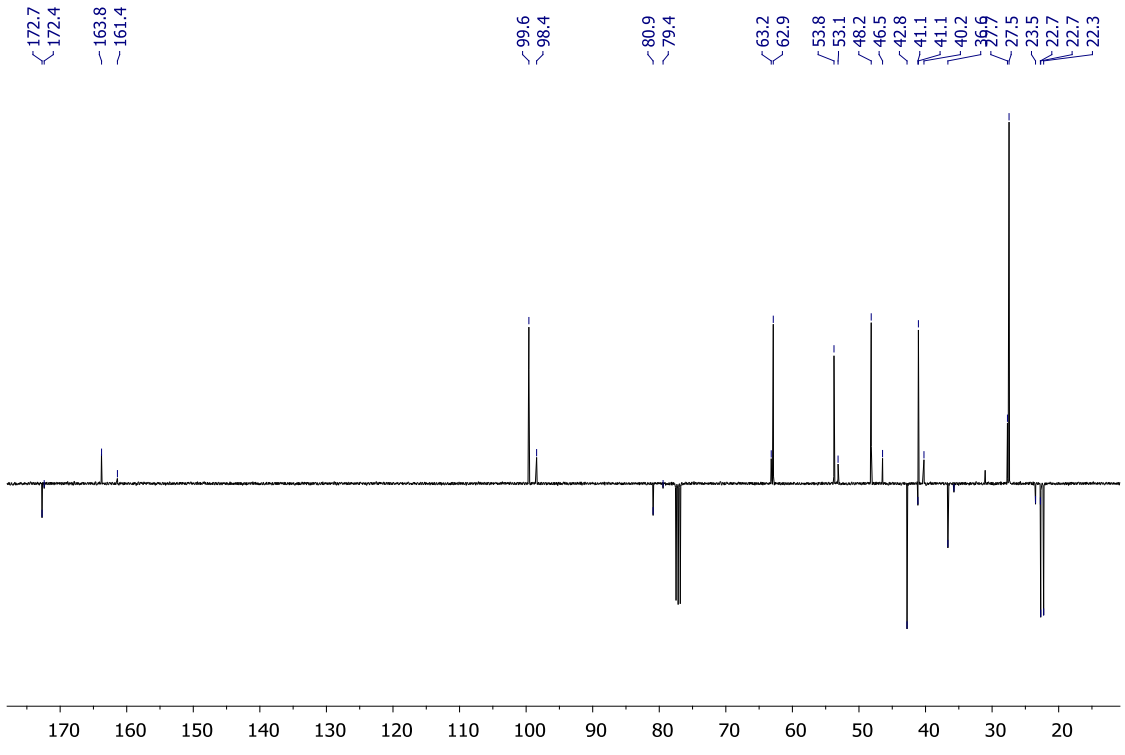
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*exo*-257b)



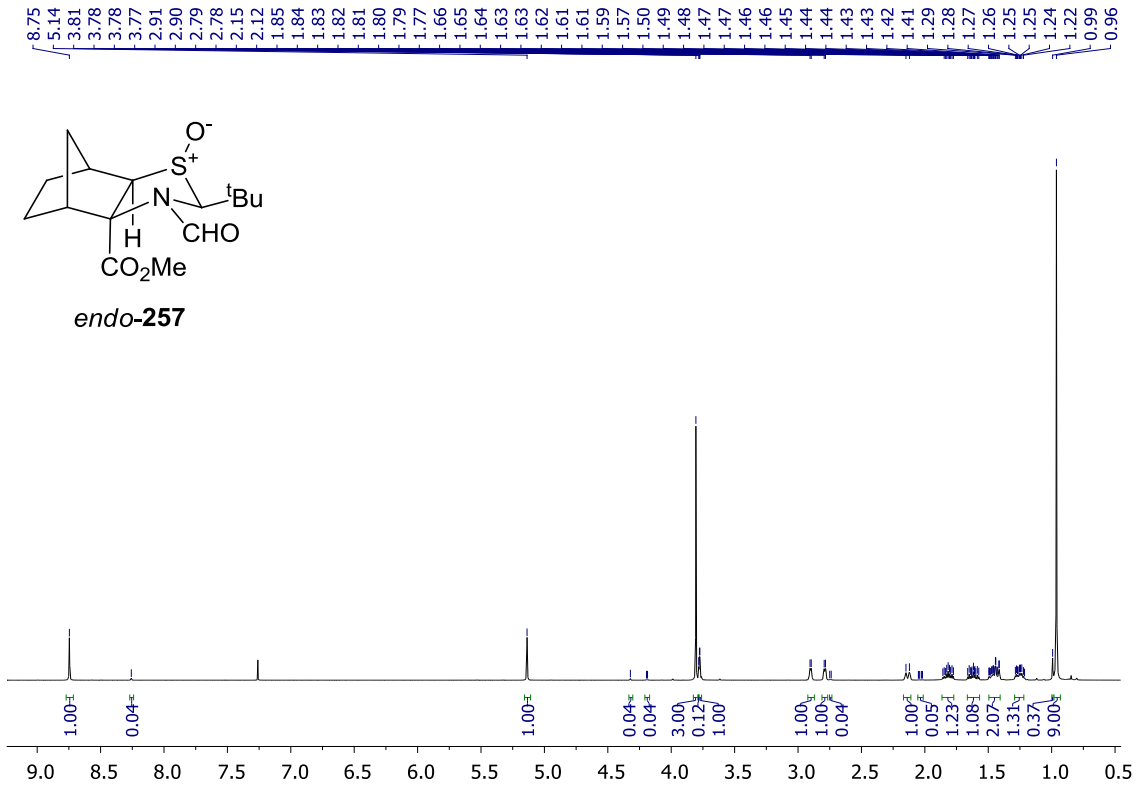
exo-**257b**

^{1}H-NMR ($CDCl_3$, 400 MHz)



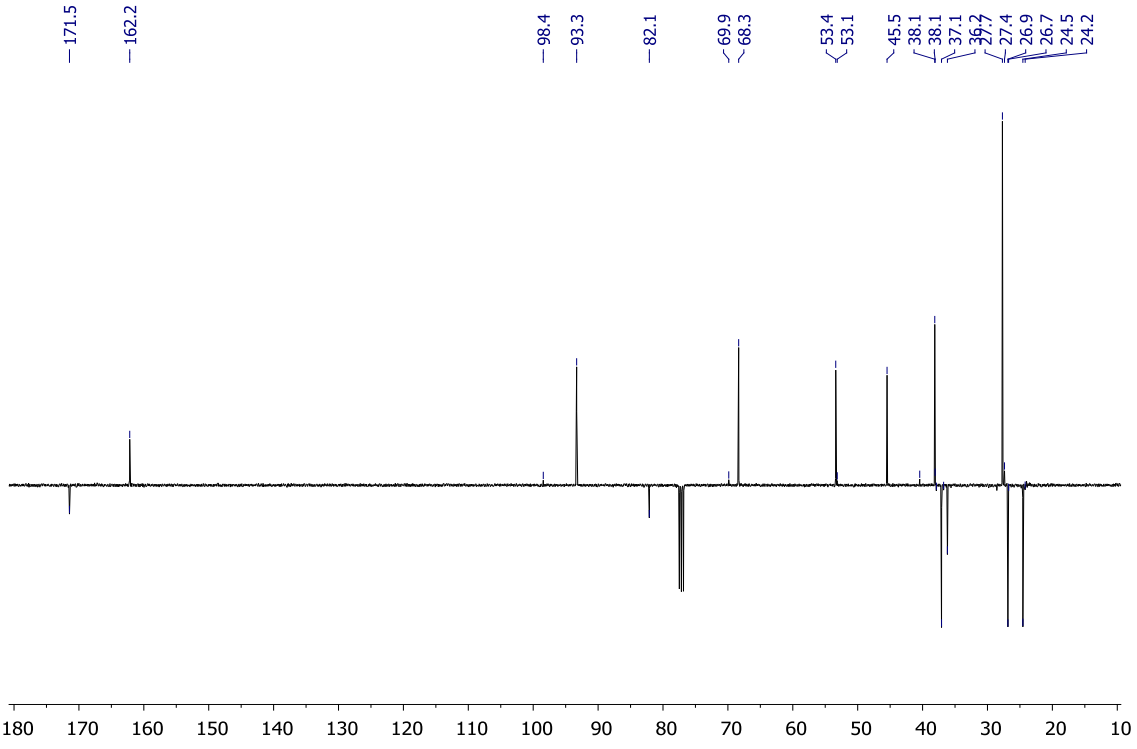
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*endo*-257b)



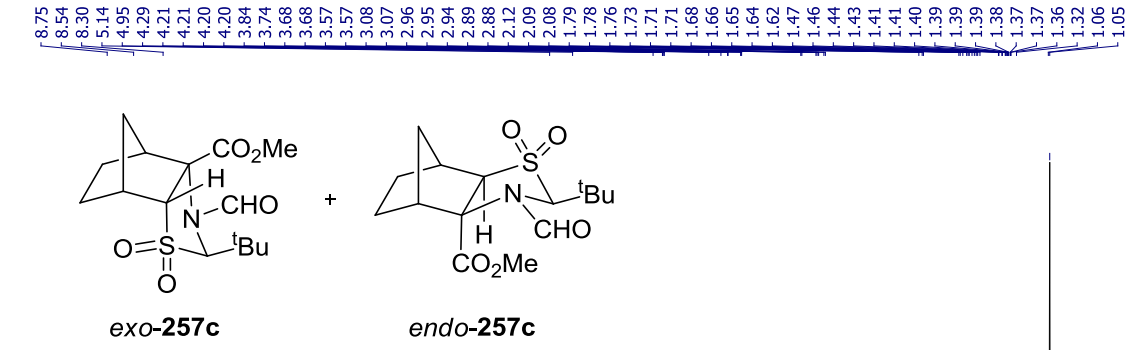
endo-**257**

^{1}H-NMR ($CDCl_3$, 400 MHz)



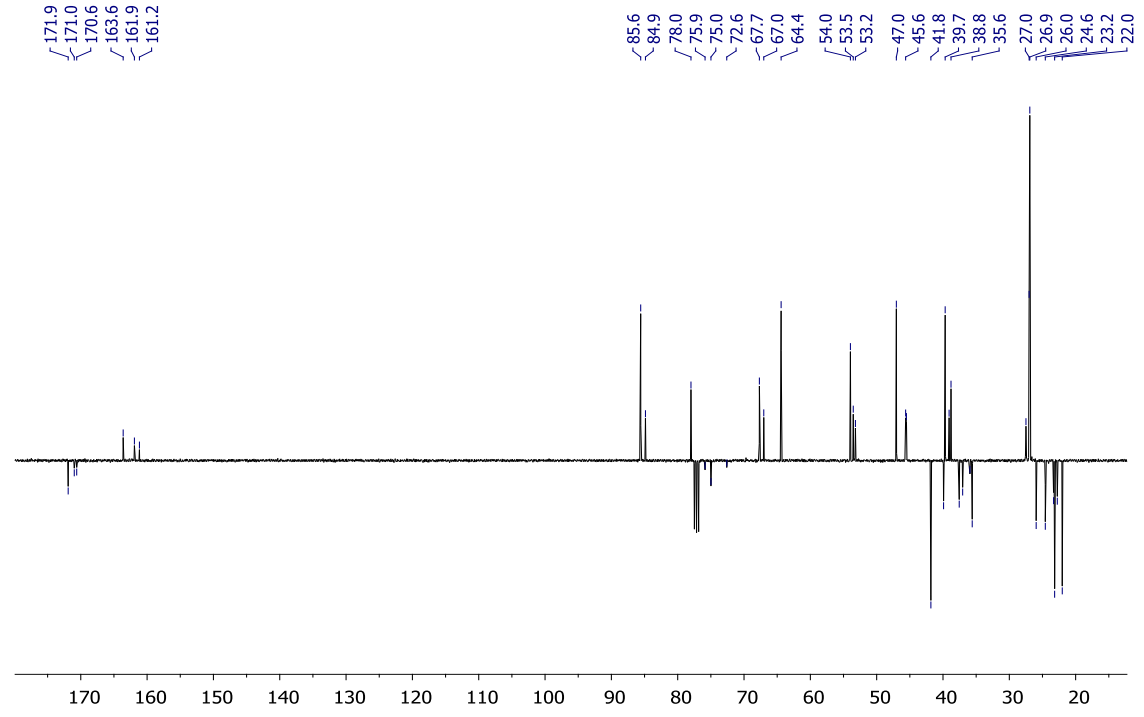
^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*exo*-257c) and **(2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxidooctahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*endo*-257c)**



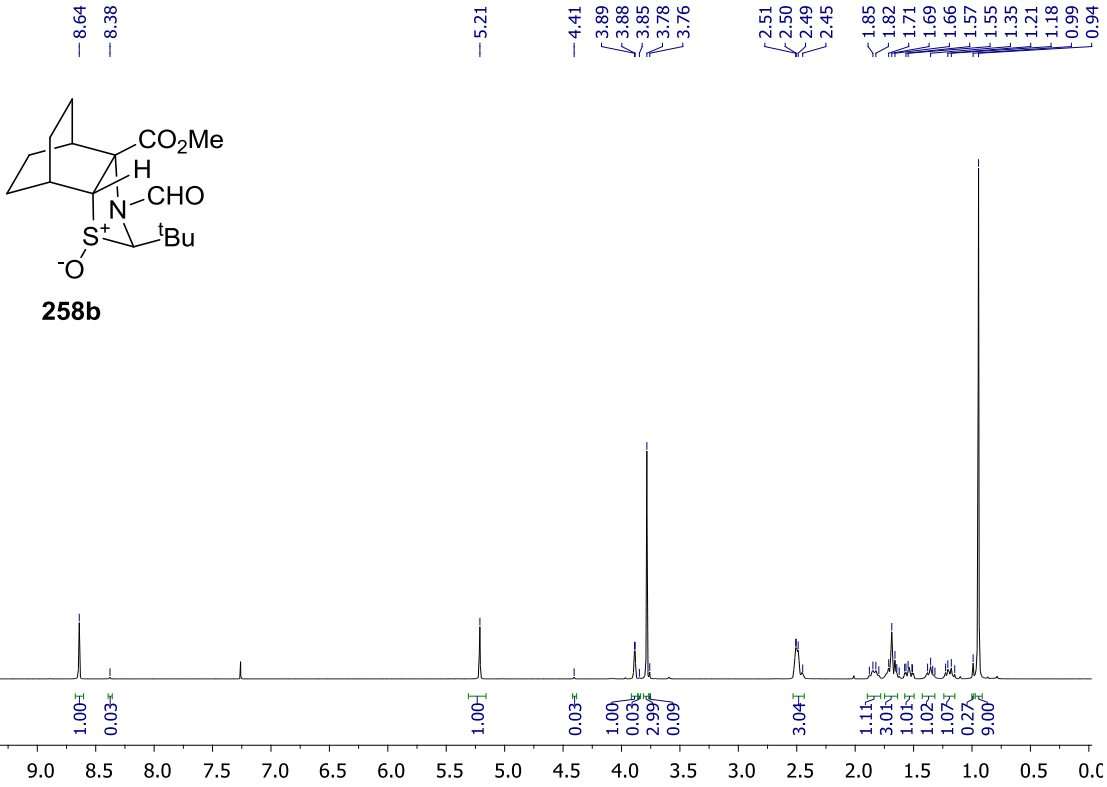
exo-**257c** *endo*-**257c**

^{1}H-NMR ($CDCl_3$, 400 MHz)



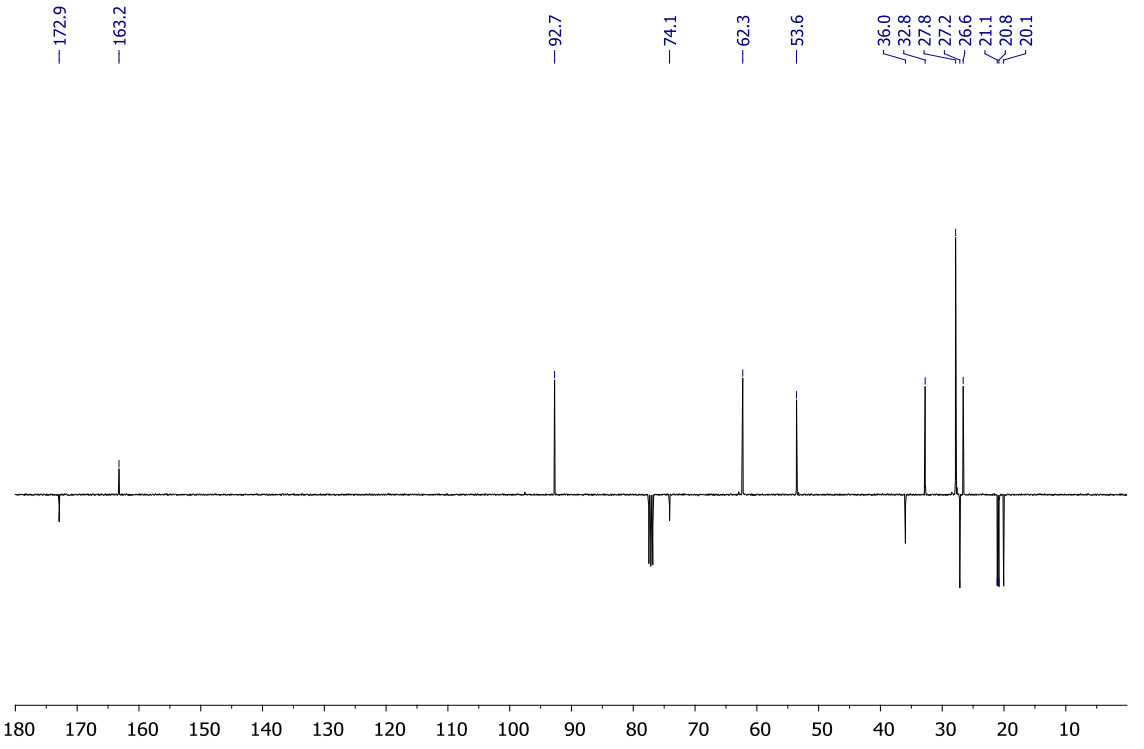
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*,3a*R*,4*S*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1-oxidooctahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate (258b)



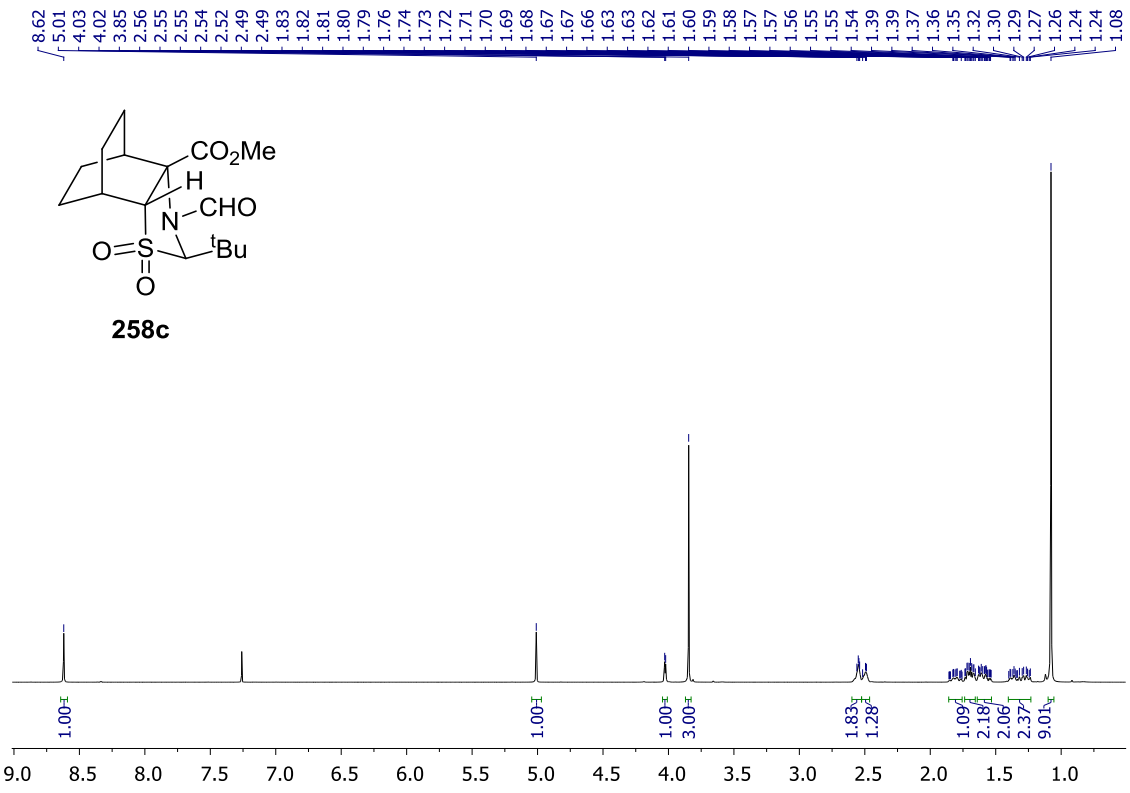
258b

^{1}H-NMR ($CDCl_3$, 400 MHz)

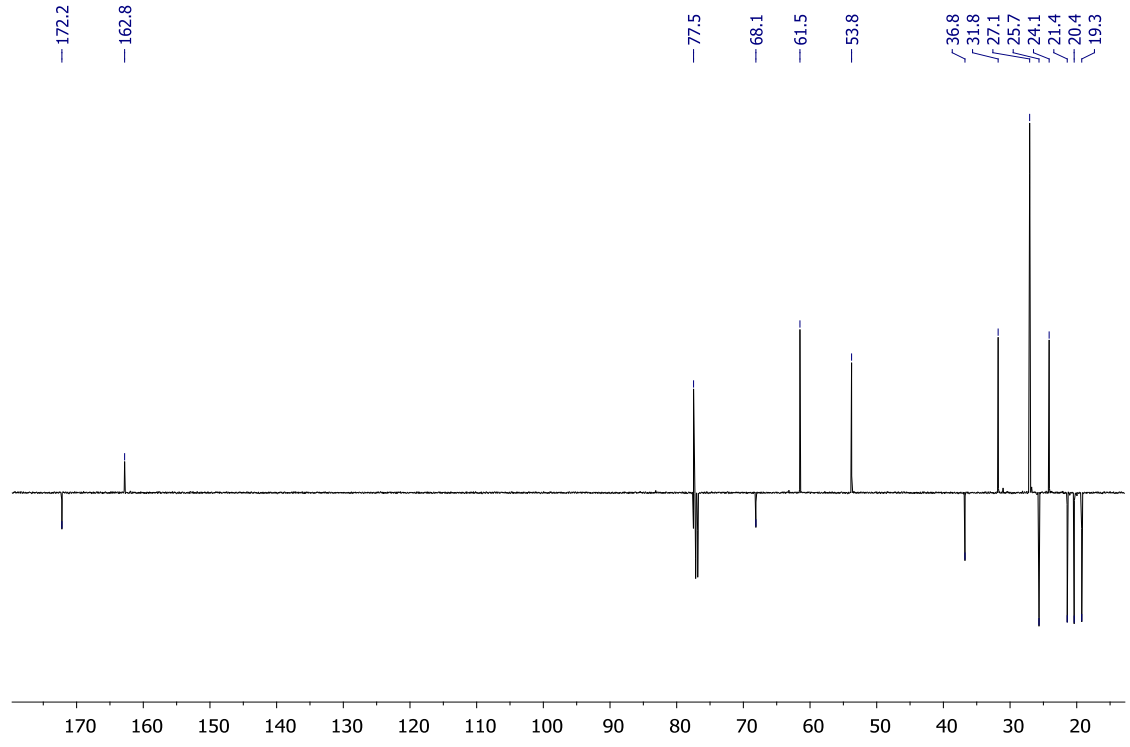


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-1,1-dioxidooctahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate (258c)

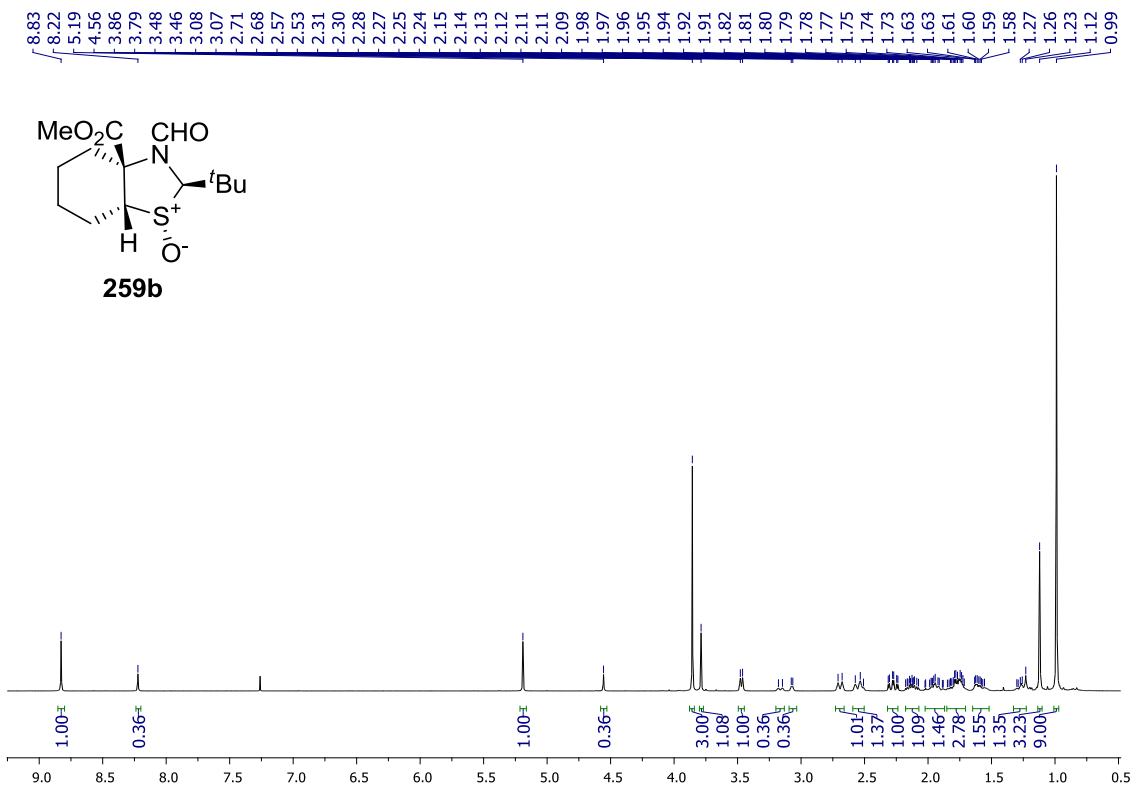


^{1}H-NMR ($CDCl_3$, 400 MHz)

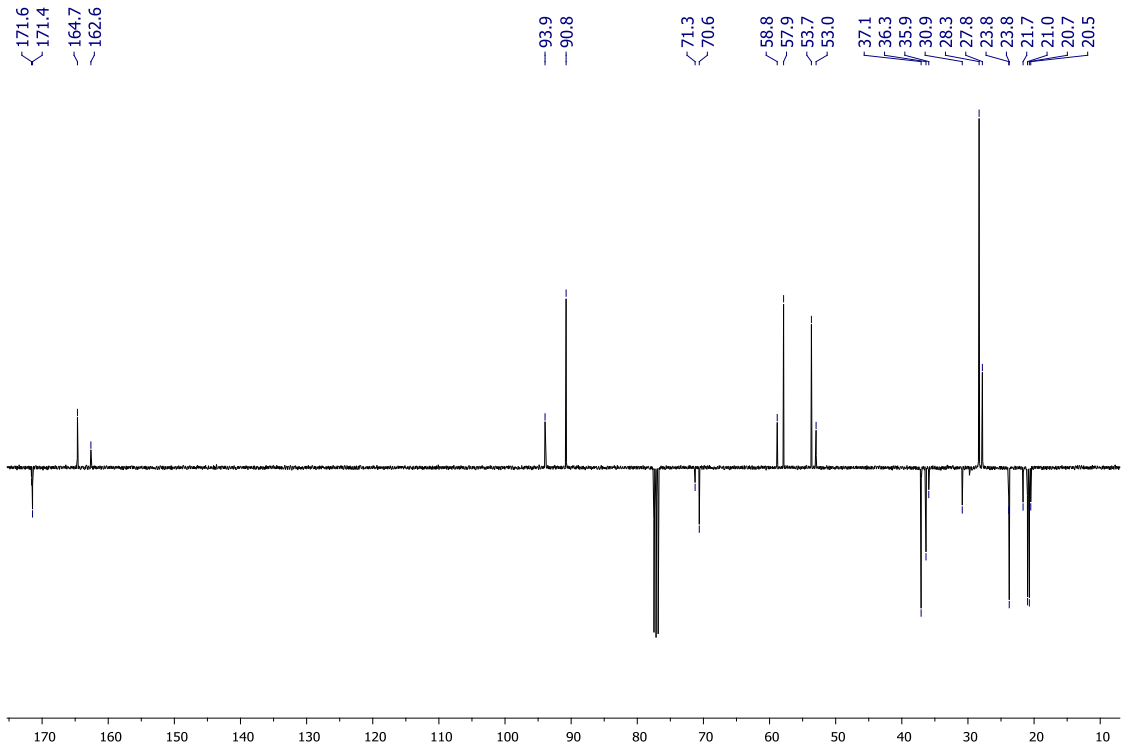


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-oxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (259b)

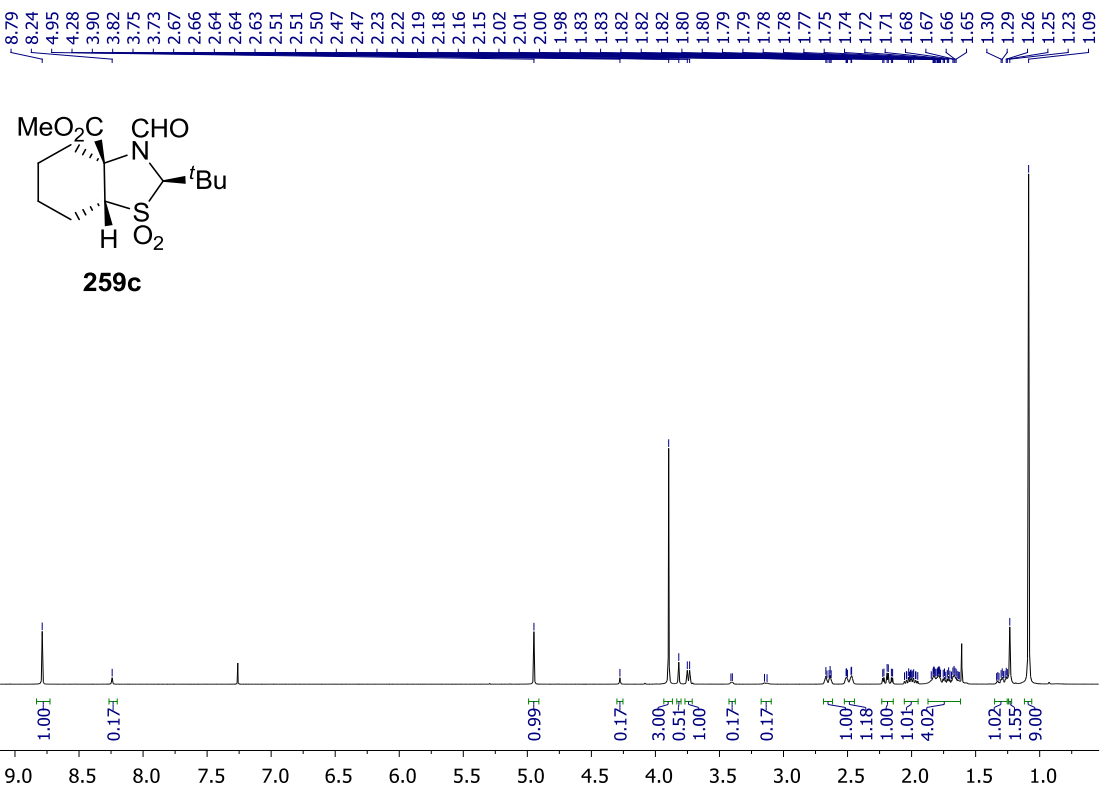


^{1}H-NMR ($CDCl_3$, 400 MHz)

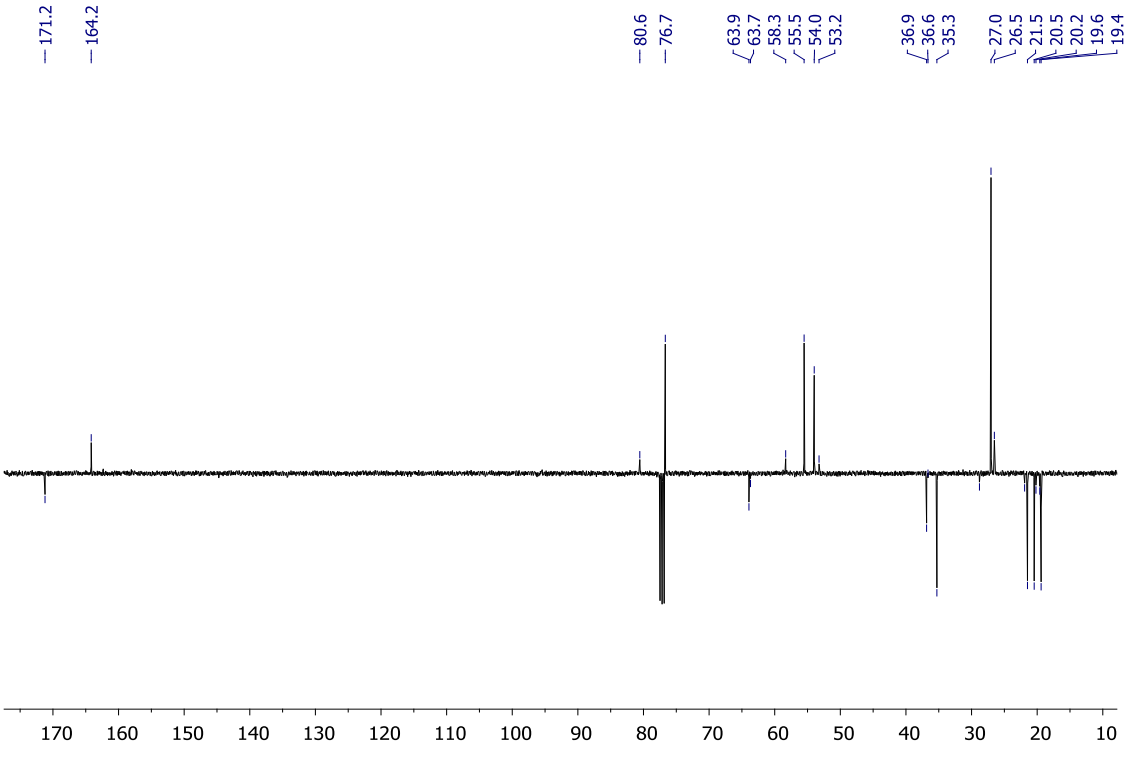


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (259c)

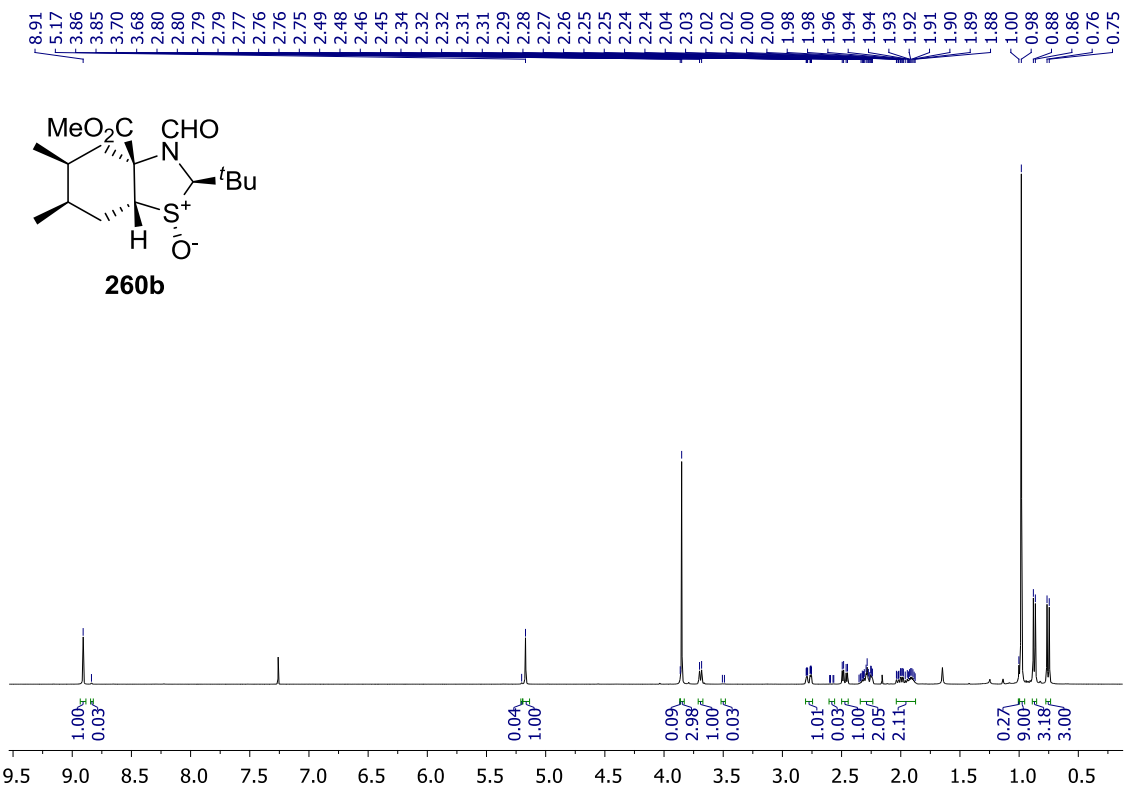


^{1}H-NMR ($CDCl_3$, 400 MHz)

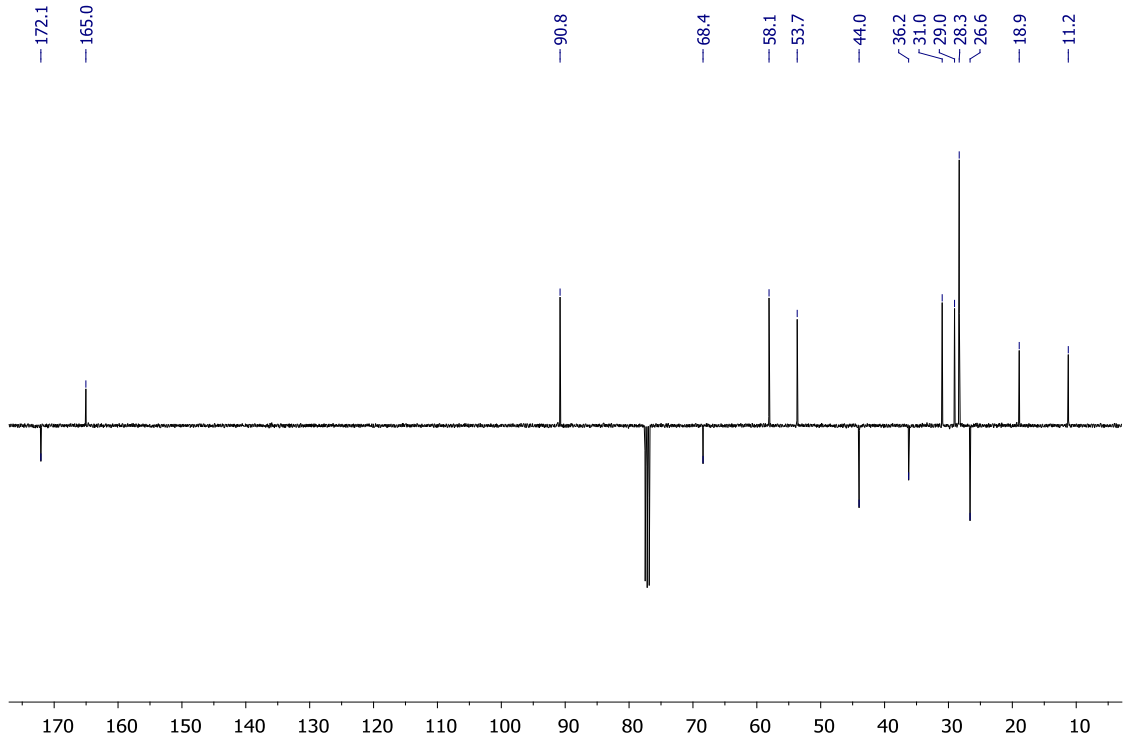


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*S*,4R,6*R*,7*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7-oxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (260b)

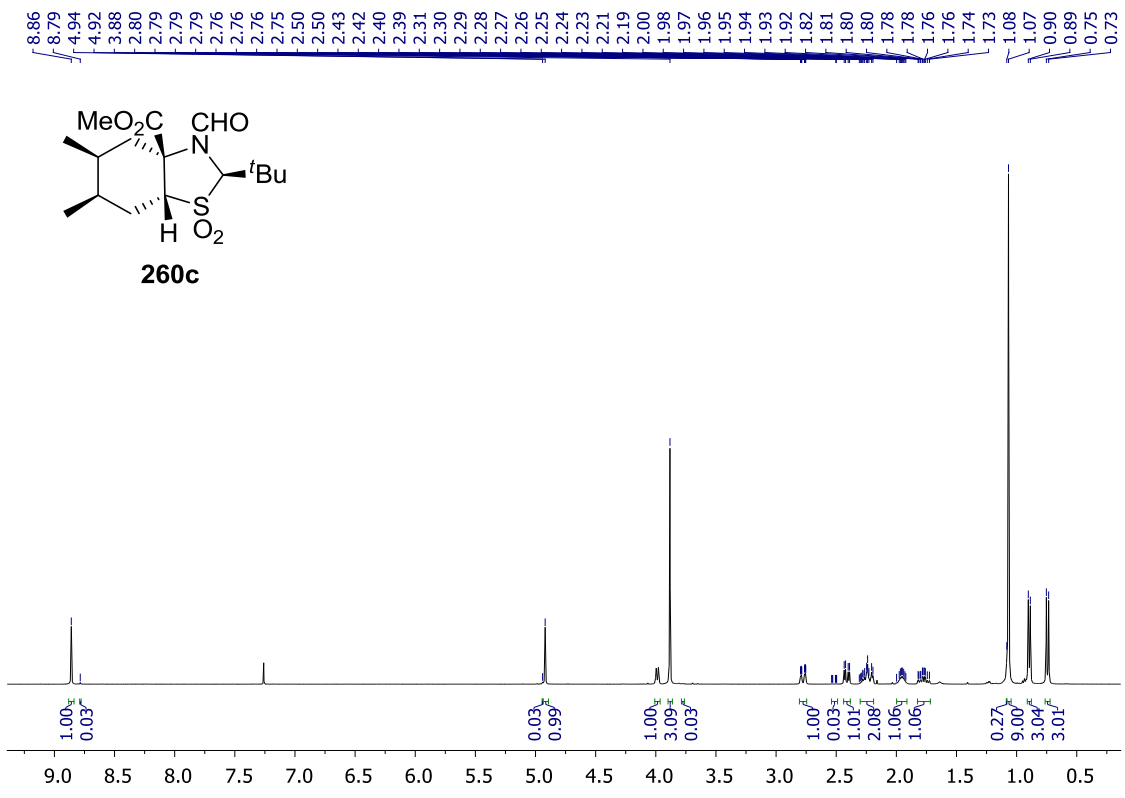


^{1}H-NMR ($CDCl_3$, 400 MHz)

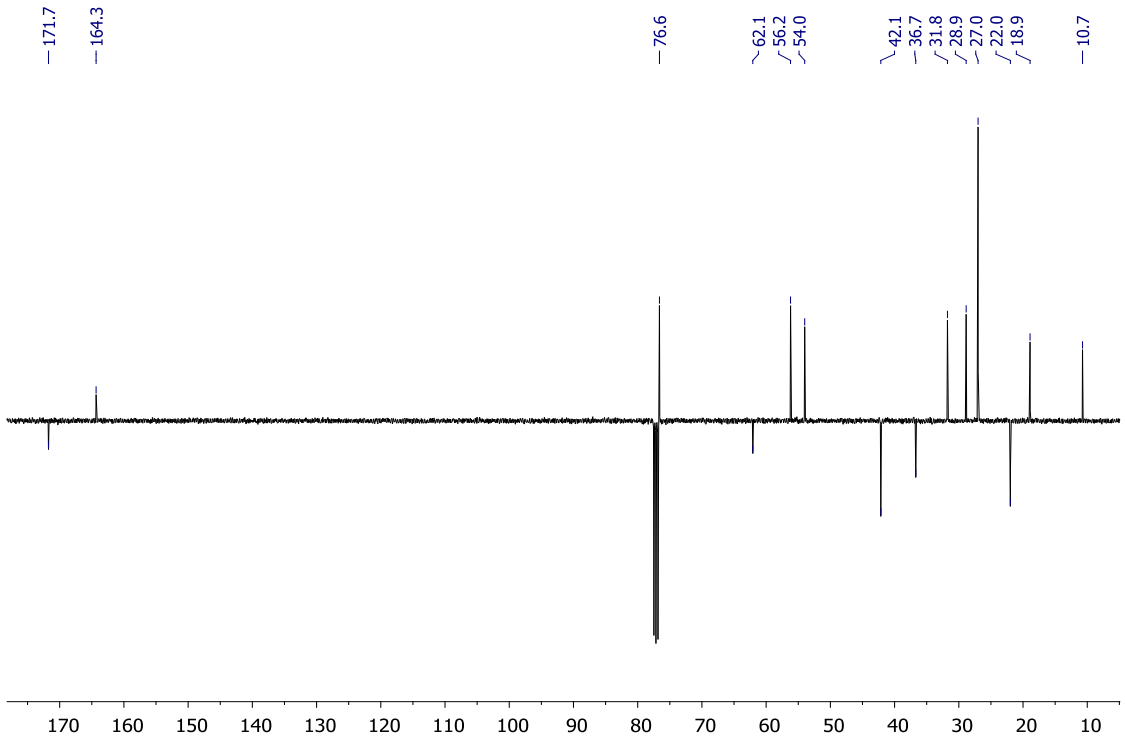


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*S*,4*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7,7-dioxido-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (260c)

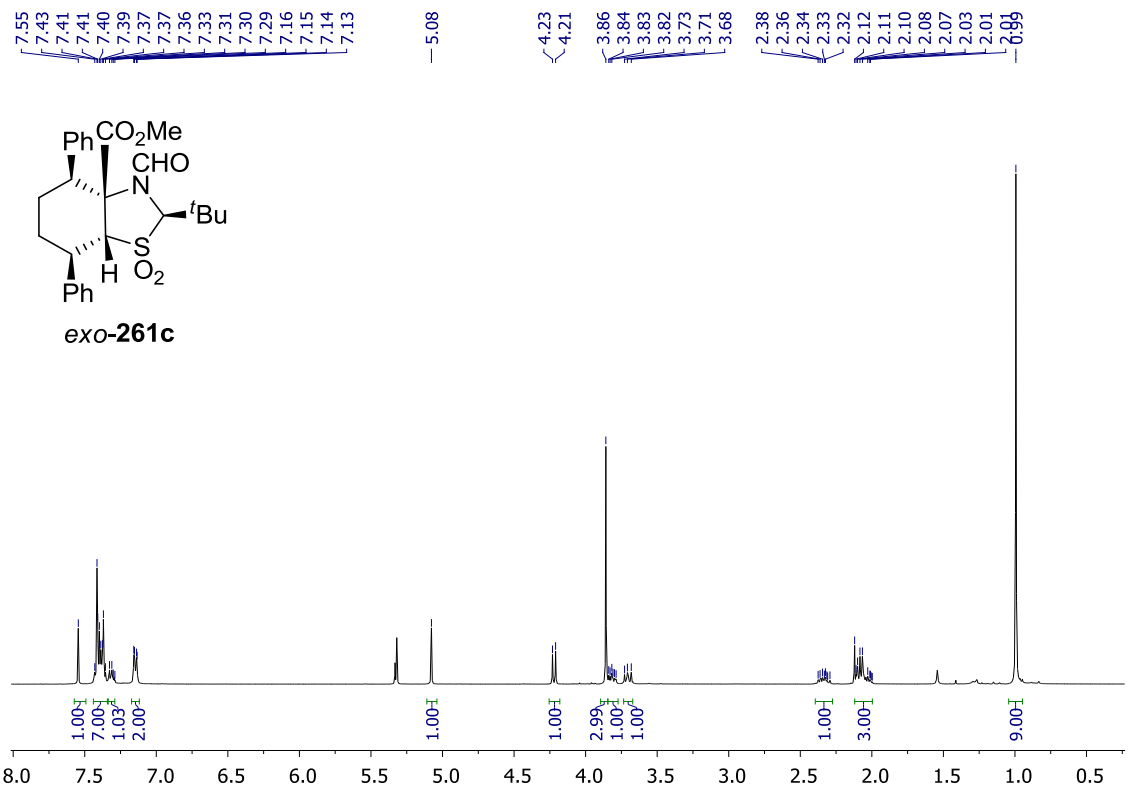


^{1}H-NMR ($CDCl_3$, 400 MHz)

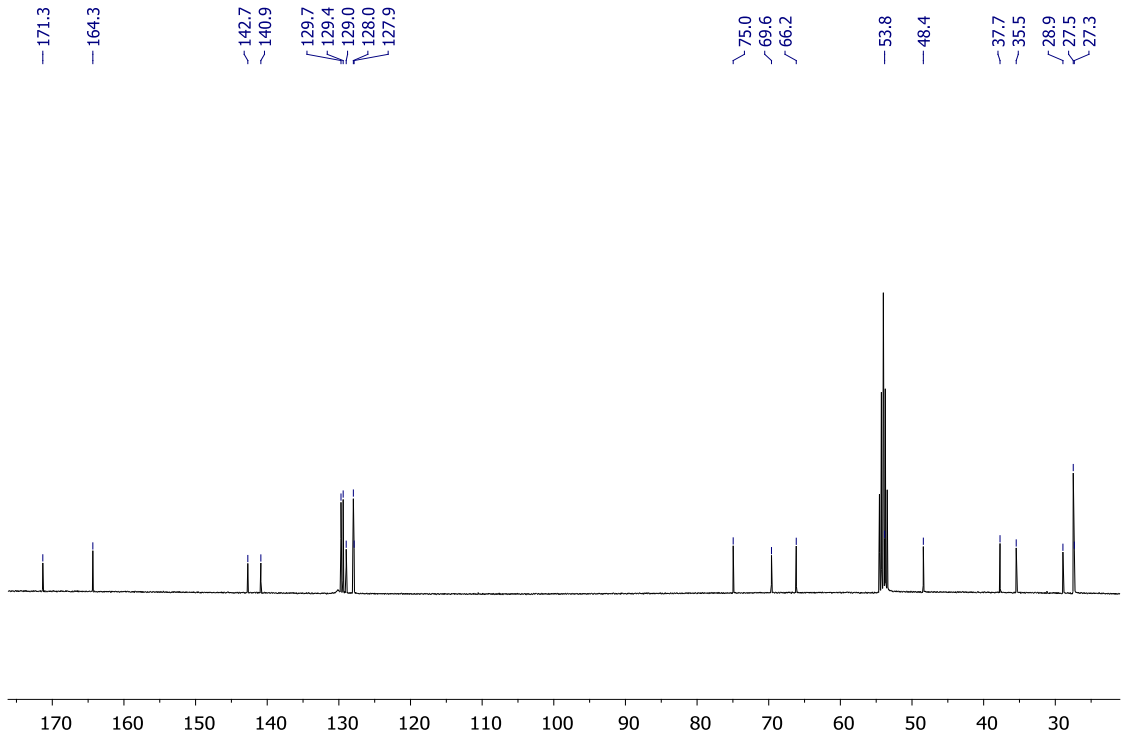


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*S*,5*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7,7-dioxido-2,5-diphenyl-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (*exo*-261c)

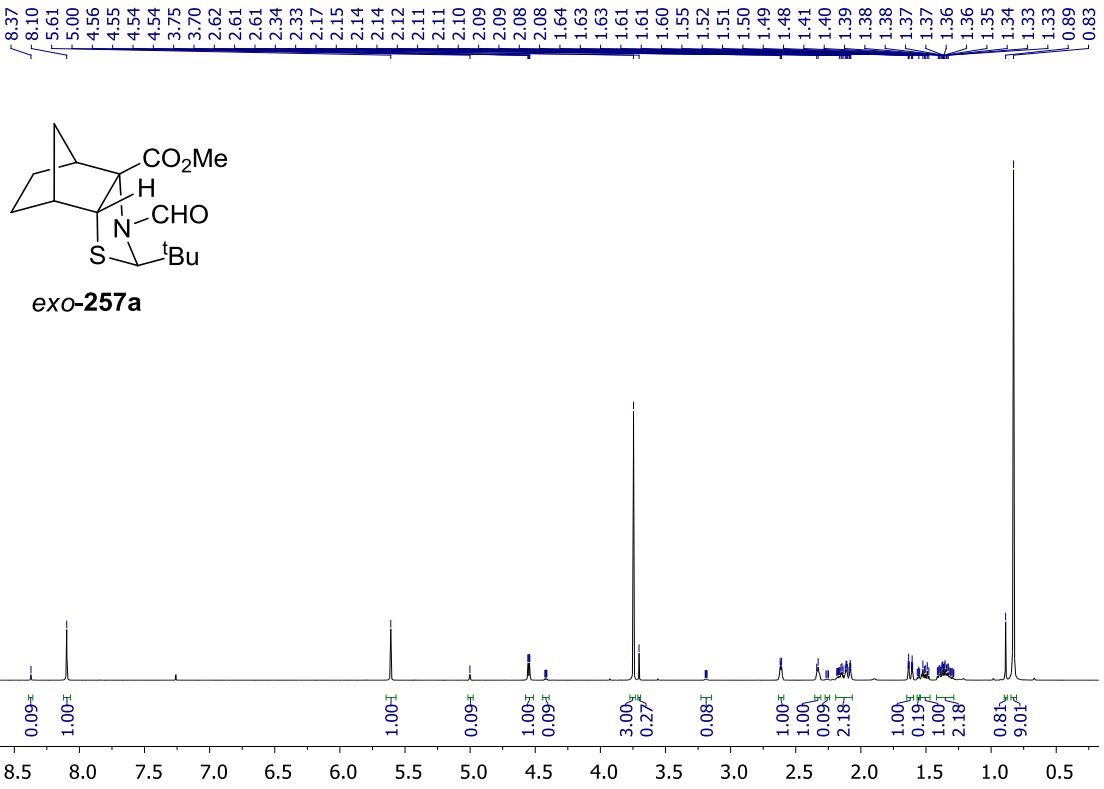


^{1}H-NMR (CD_2Cl_2, 400 MHz)



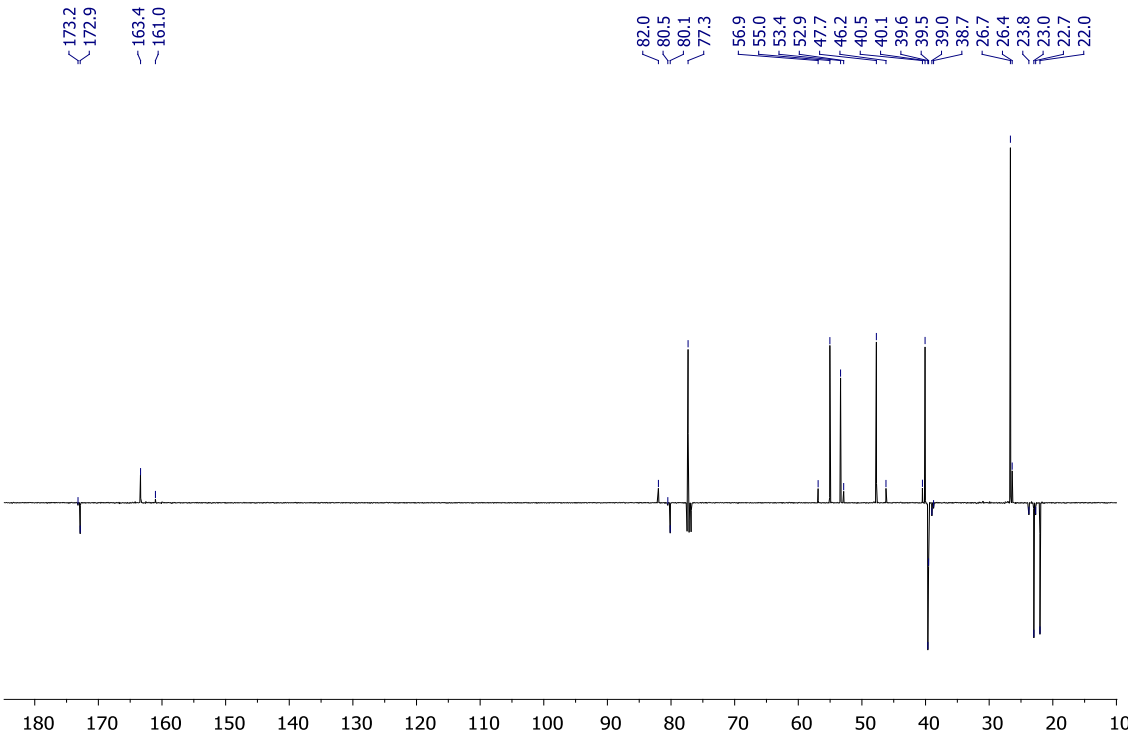
^{13}C-NMR (CD_2Cl_2, 100 MHz)

(2*R*,3a*R*,4*S*,7*R*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-octahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*exo*-257a)



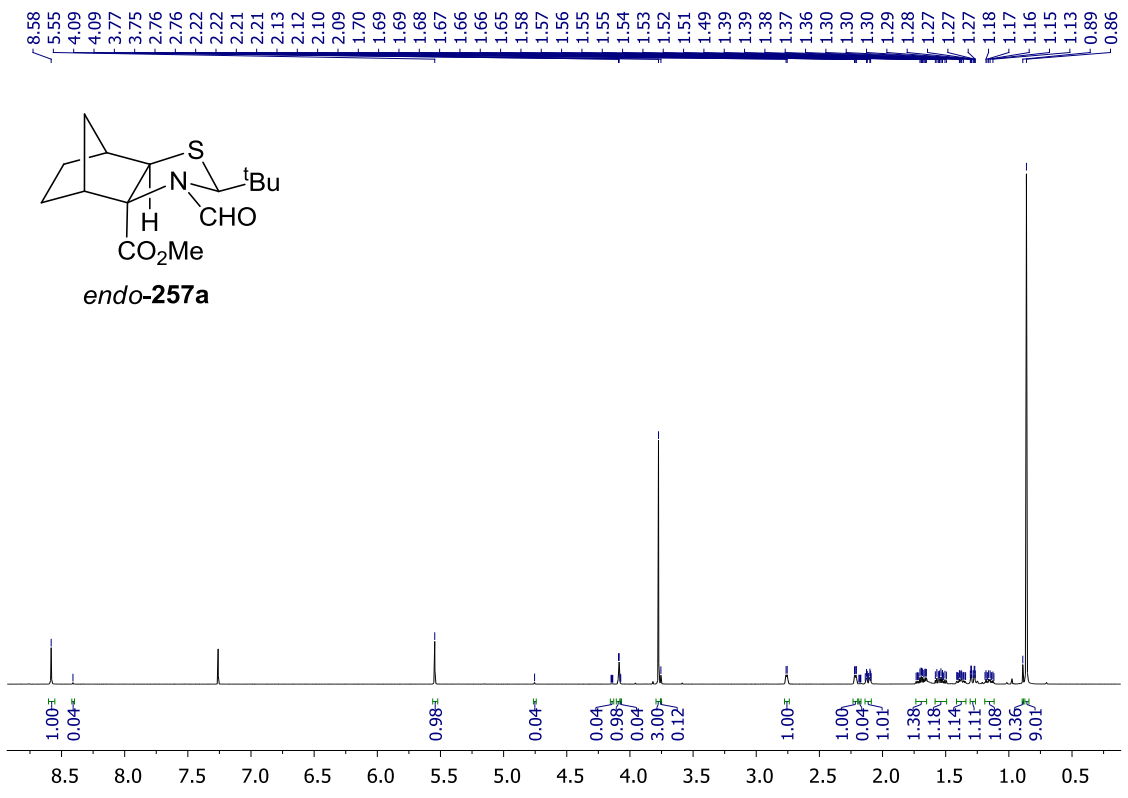
exo-**257a**

^{1}H-NMR ($CDCl_3$, 400 MHz)



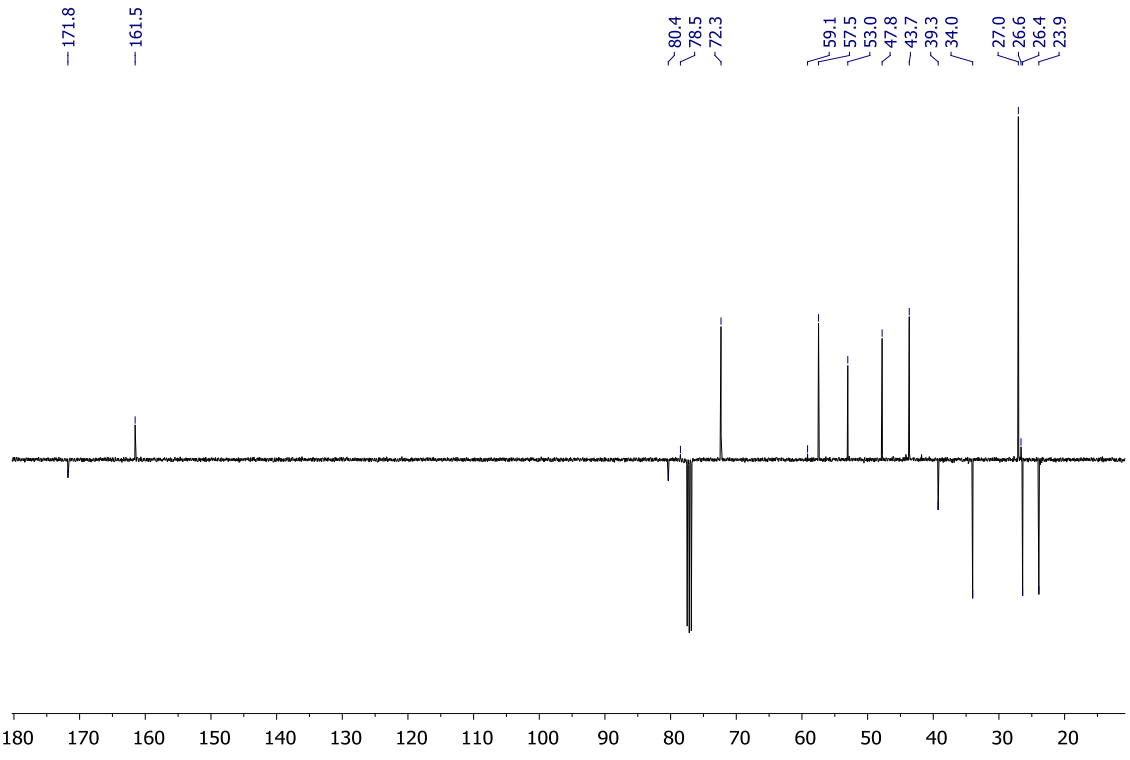
^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*R*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-octahydro-4,7-methanobenzo[*d*]thiazole-3a-carboxylate (*endo*-257a)



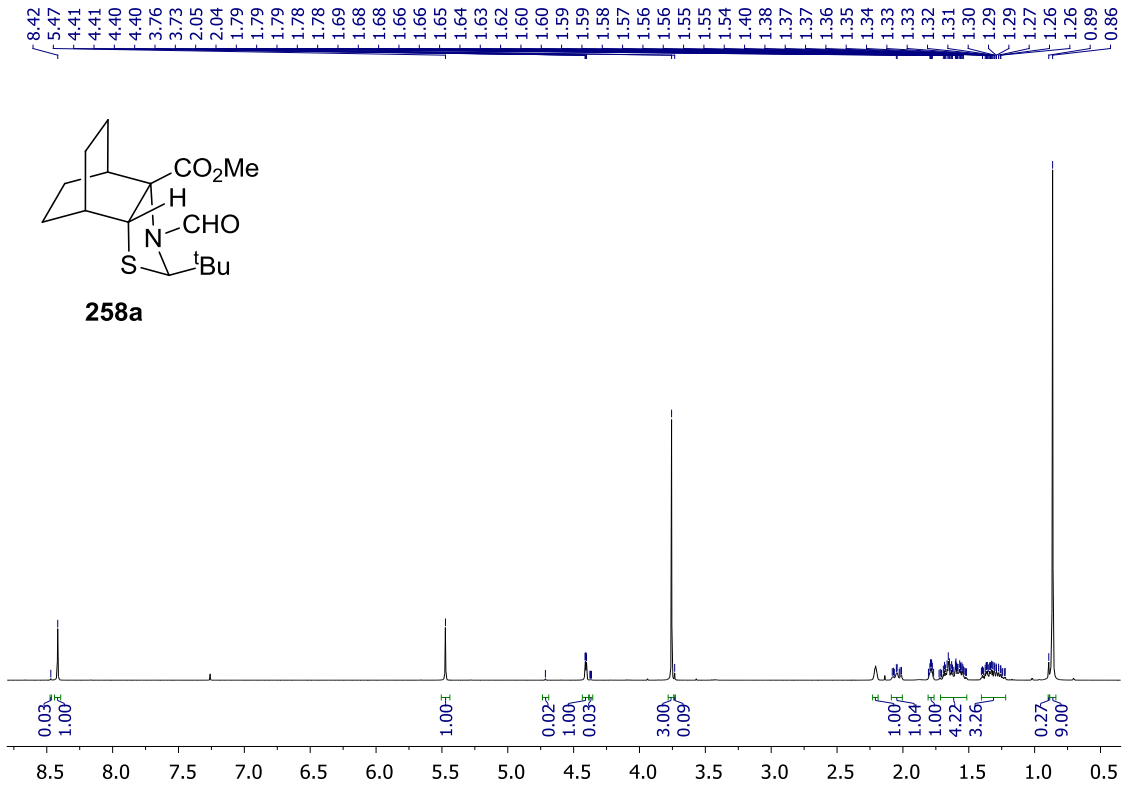
endo-**257a**

^{1}H-NMR ($CDCl_3$, 400 MHz)

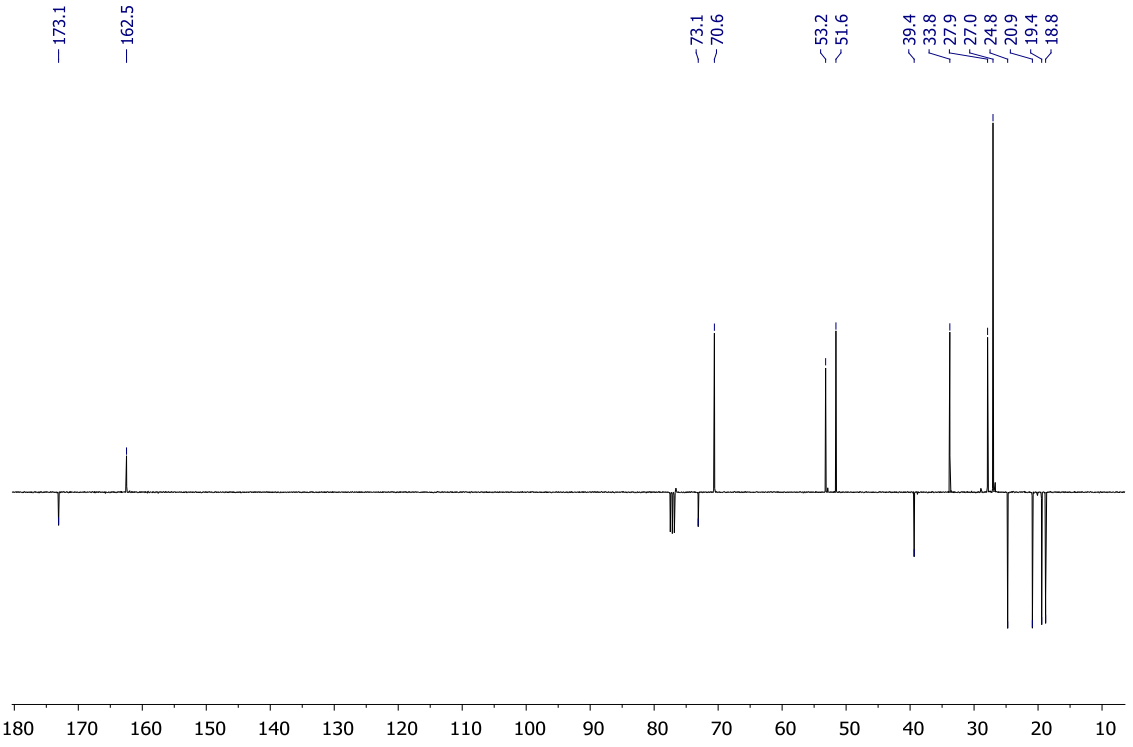


^{13}C-NMR ($CDCl_3$, 100 MHz)

(2*R*,3a*R*,4*S*,7*S*,7a*R*)-Methyl 2-*tert*-butyl-3-formyl-octahydro-4,7-ethanobenzo[*d*]thiazole-3a-carboxylate (258a)

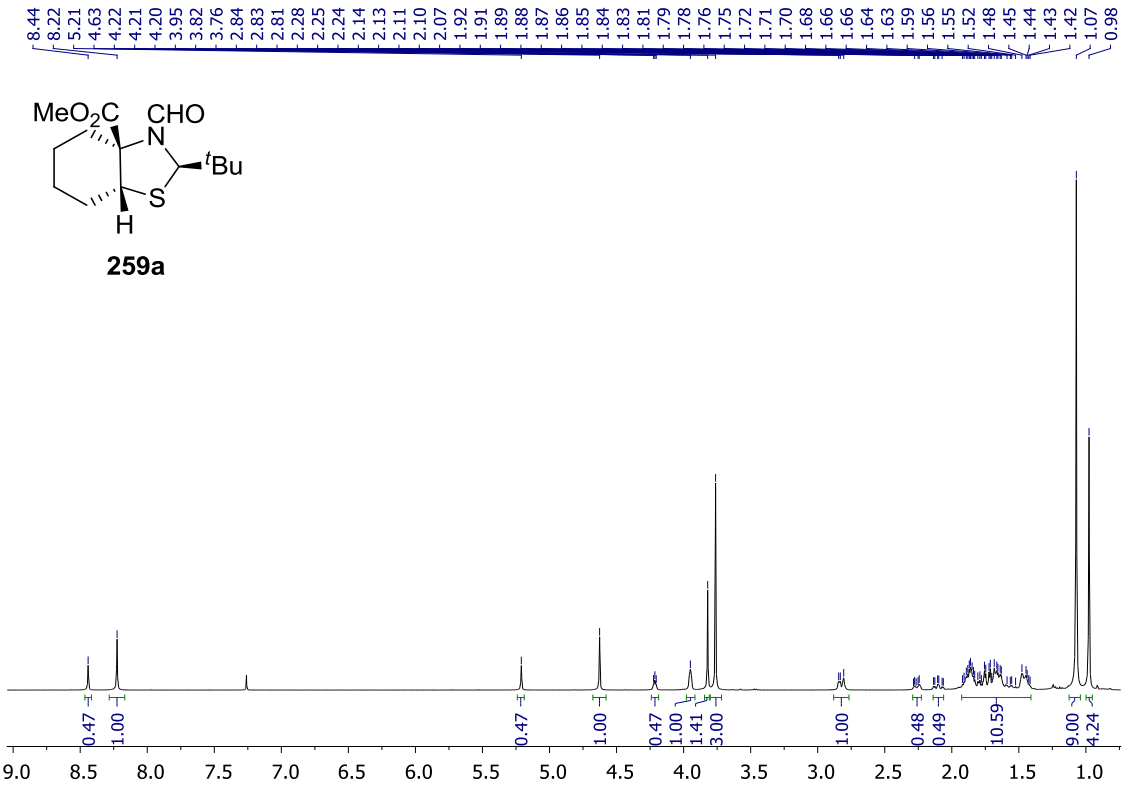


^{1}H-NMR ($CDCl_3$, 400 MHz)

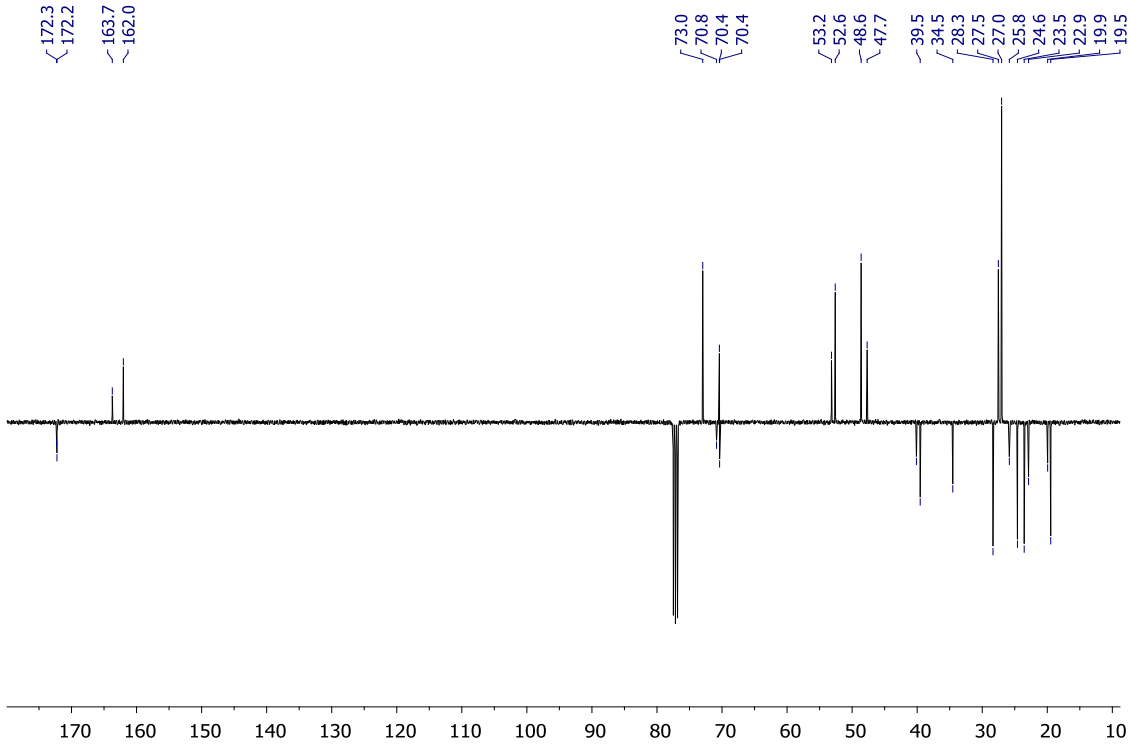


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (259a)

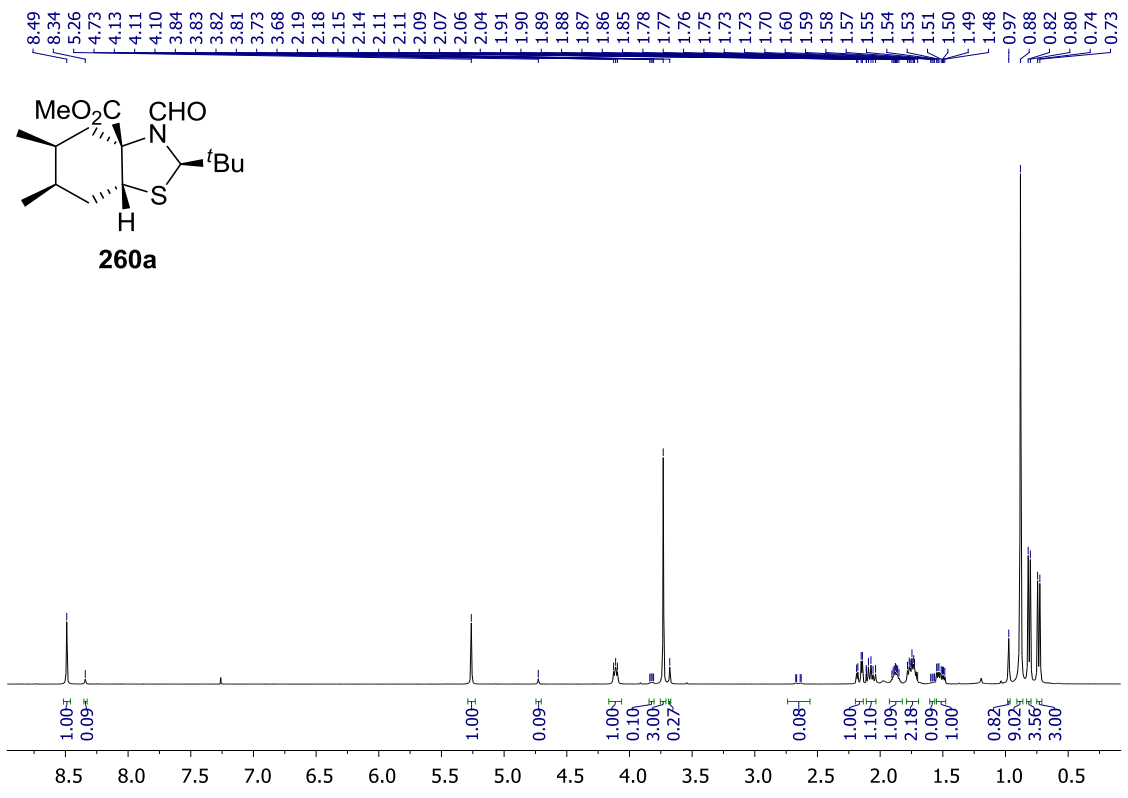


^{1}H-NMR ($CDCl_3$, 400 MHz)

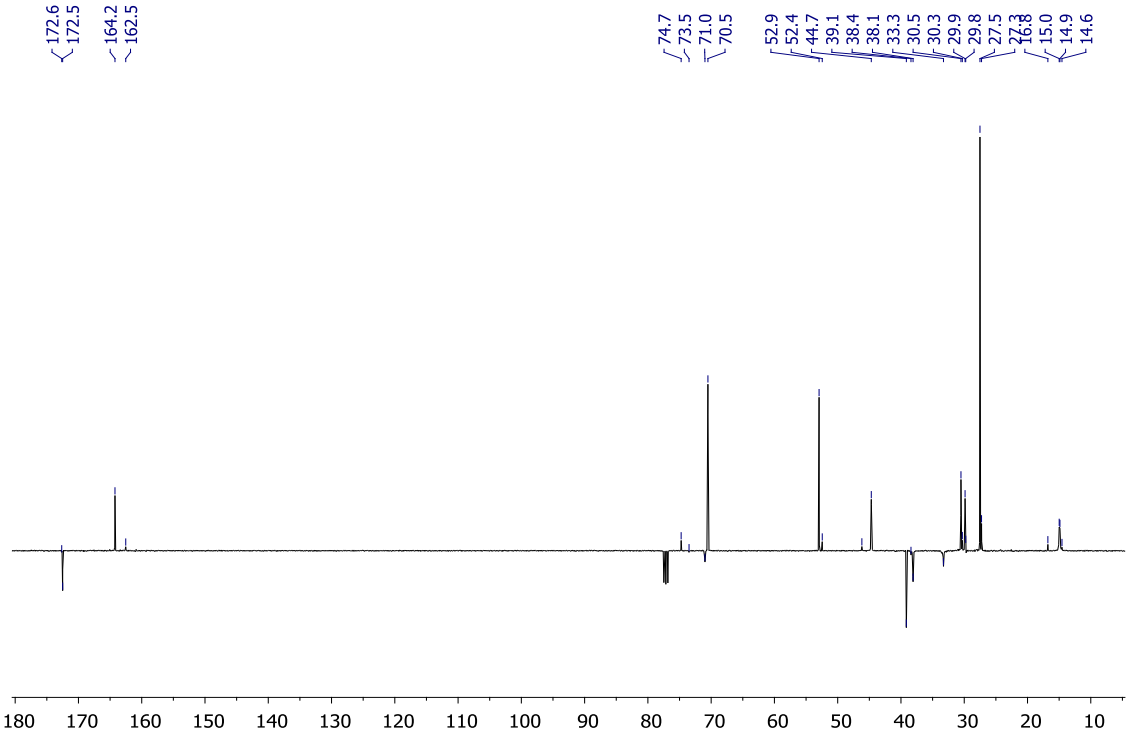


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,3*S*,4*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3,4-dimethyl-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (260a)

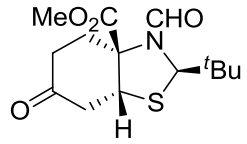


^{1}H-NMR ($CDCl_3$, 400 MHz)



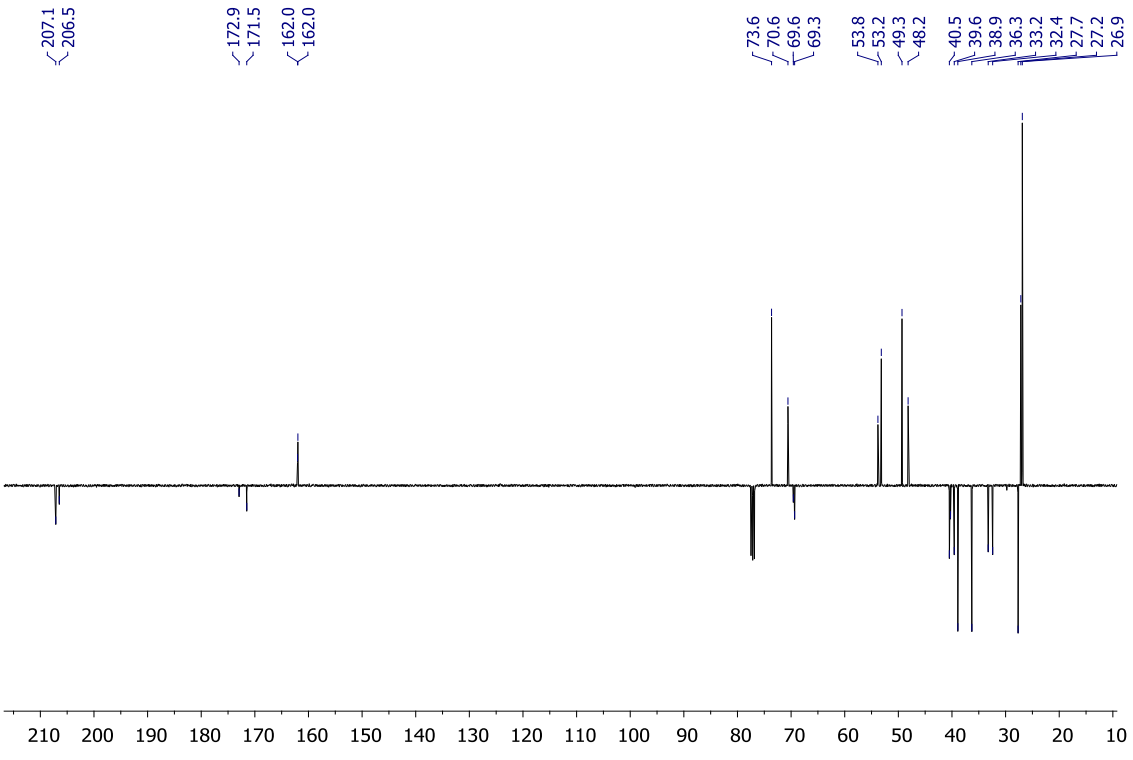
^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-4-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (255a)



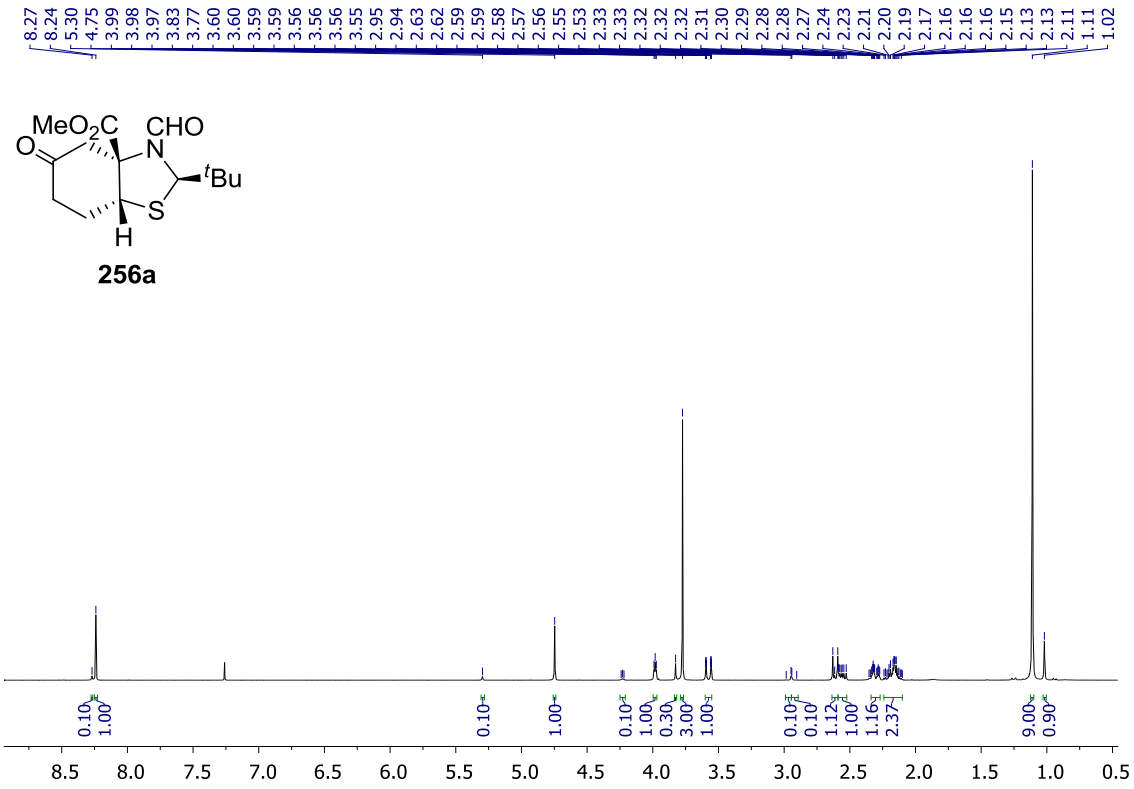
255a

^{1}H-NMR ($CDCl_3$, 400 MHz)

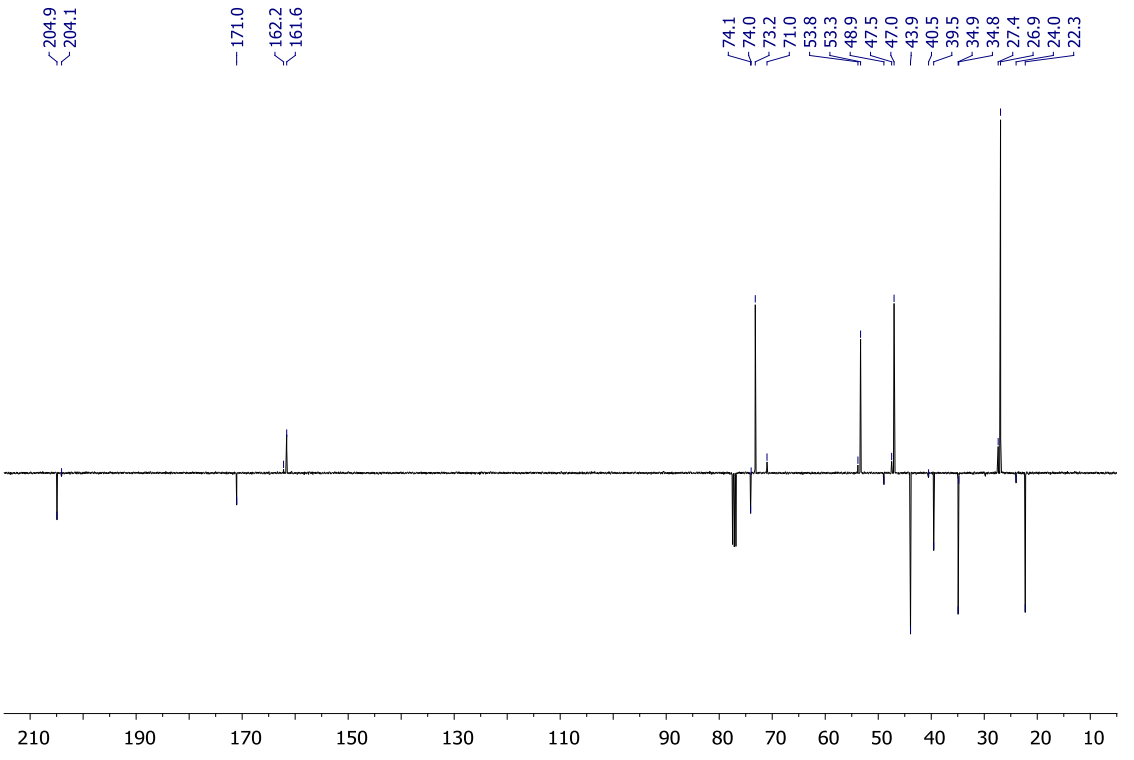


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,6*R*,8*R*)-Methyl 8-*tert*-butyl-9-formyl-3-oxo-7-thia-9-azabicyclo[4.3.0]nonane-1-carboxylate (256a)

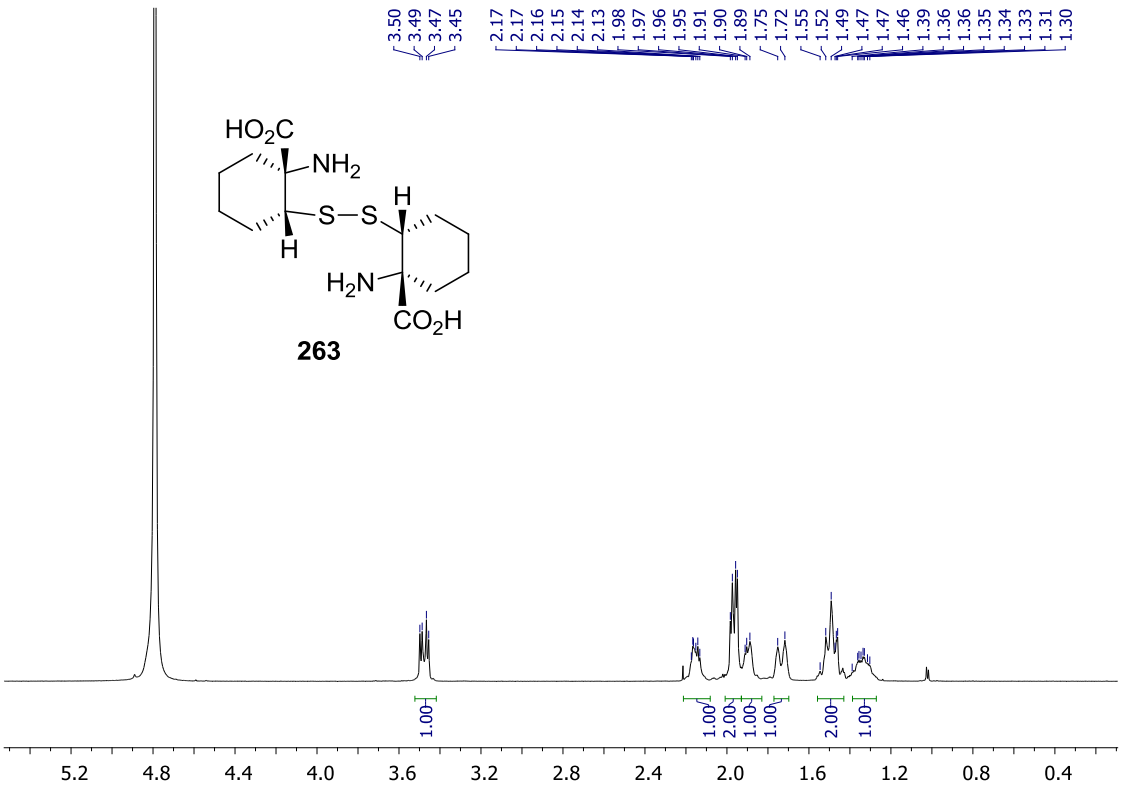


^{1}H-NMR ($CDCl_3$, 400 MHz)

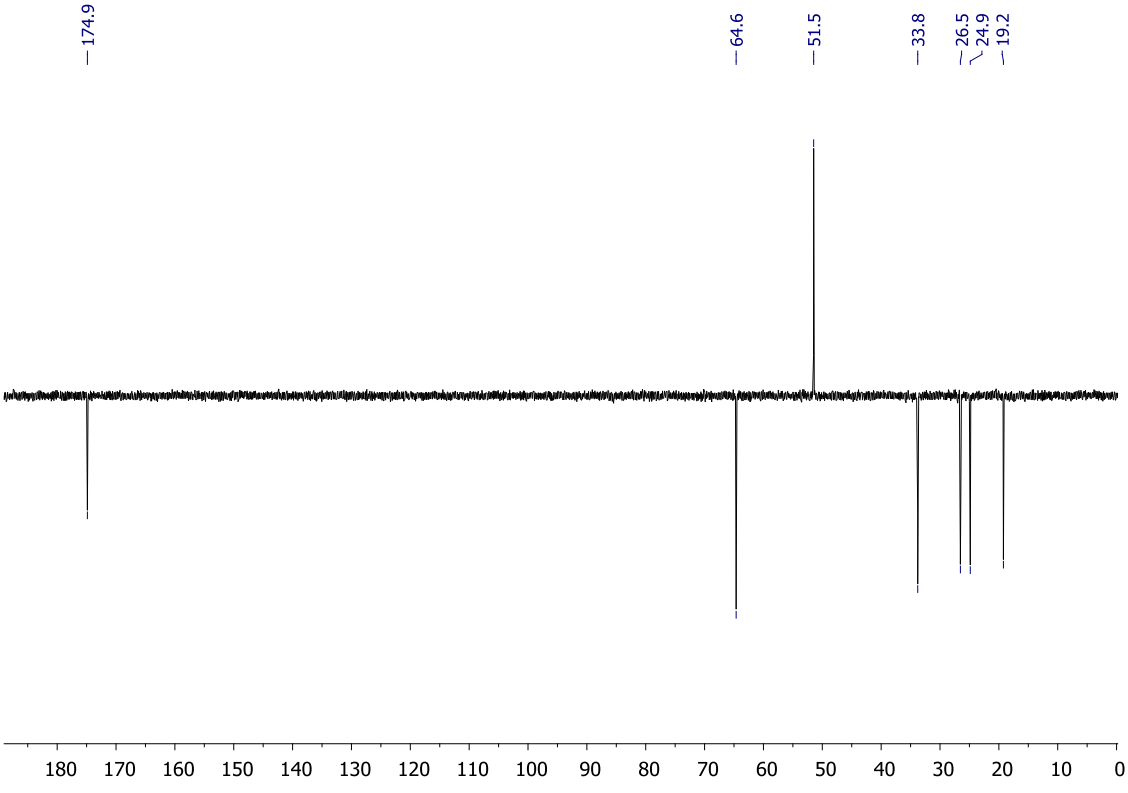


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,1'*R*,2R,2'*R*)-2,2'-Disulfanediylbis(aminocyclohexanecarboxylic acid) (263)

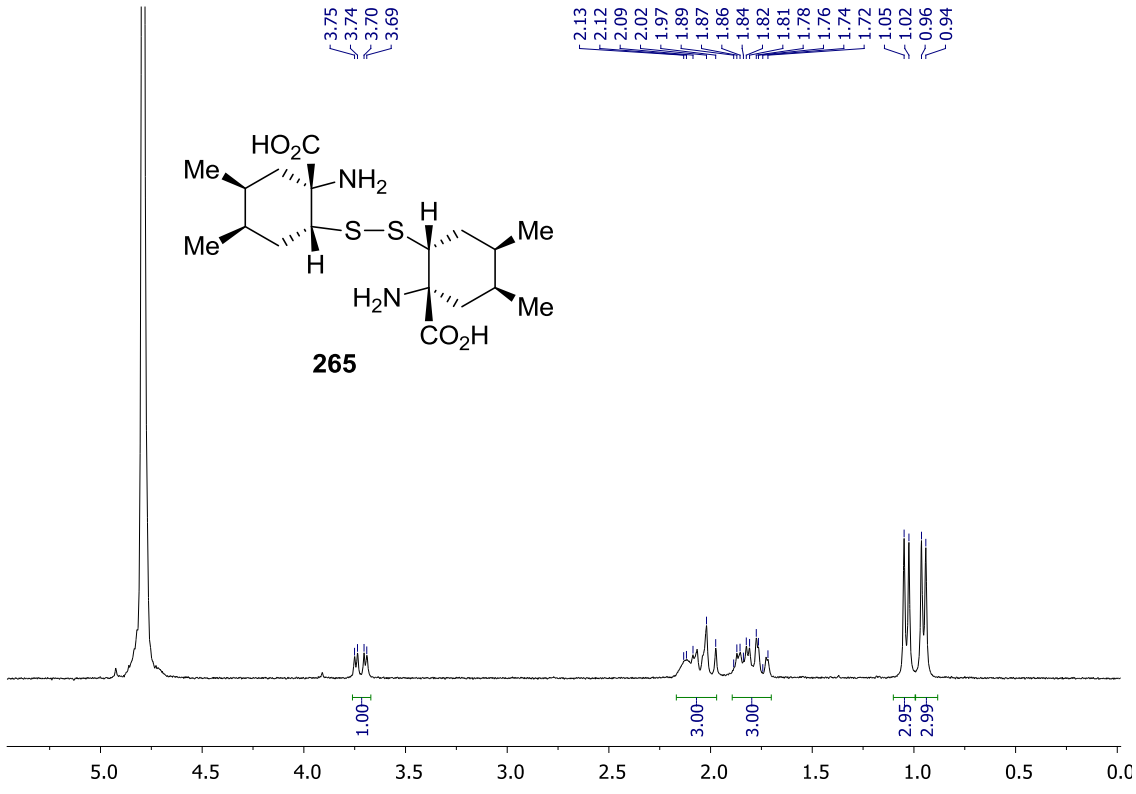


^{1}H-NMR (D_2O, 400 MHz)

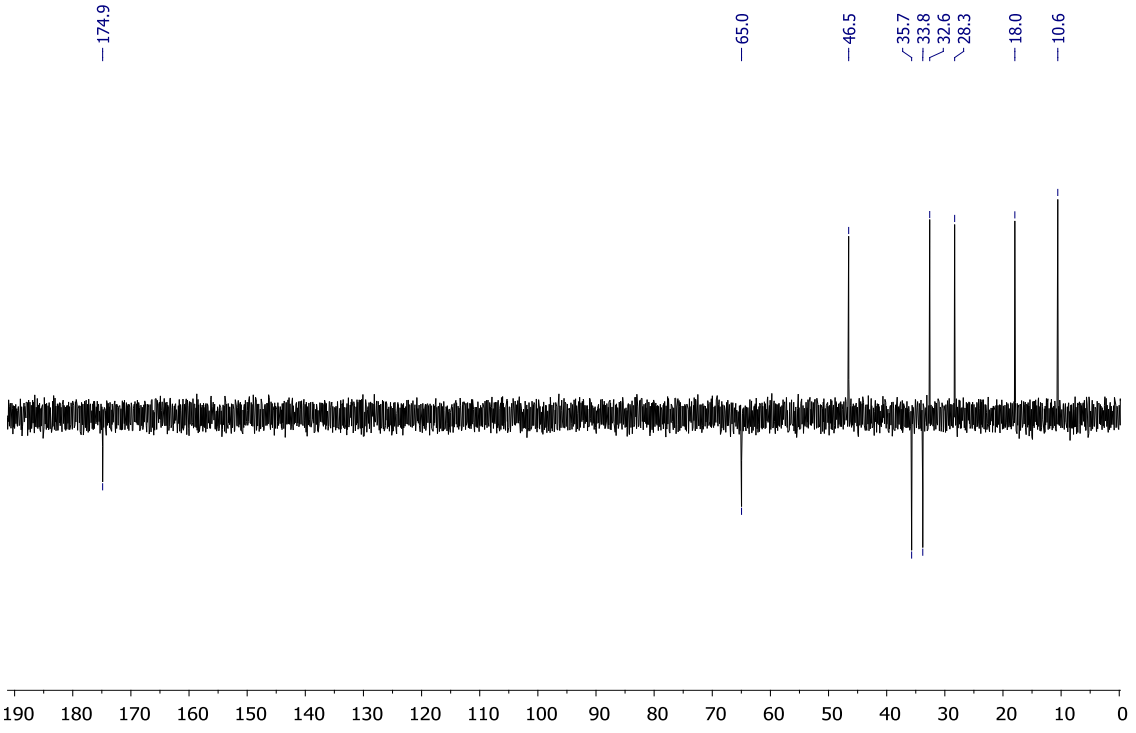


^{13}C-NMR (D_2O, 100 MHz)

(1*R*,1'*R*,3*S*,3'*S*,4*R*,4'*R*,6*R*,6'*R*)-6,6'-Disulfanediylbis(1-amino-3,4-dimethylcyclohexanecarboxylic acid) (265)

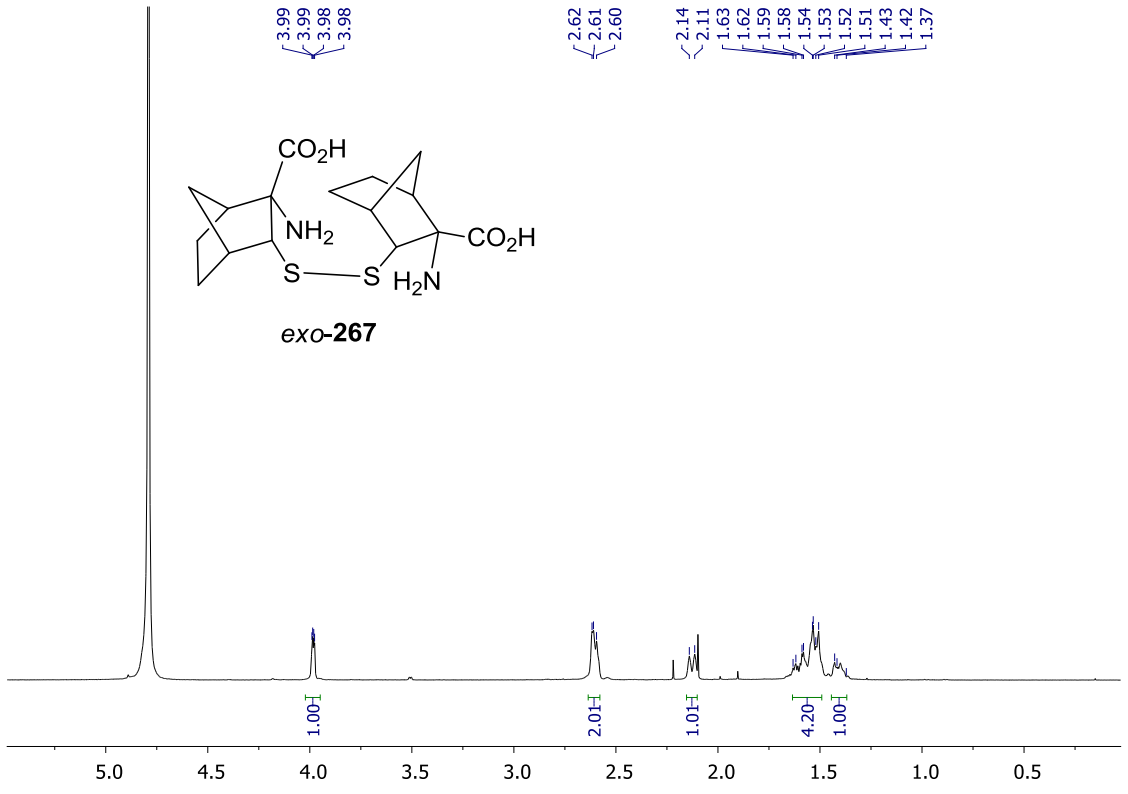


^{1}H-NMR (D_2O, 400 MHz)



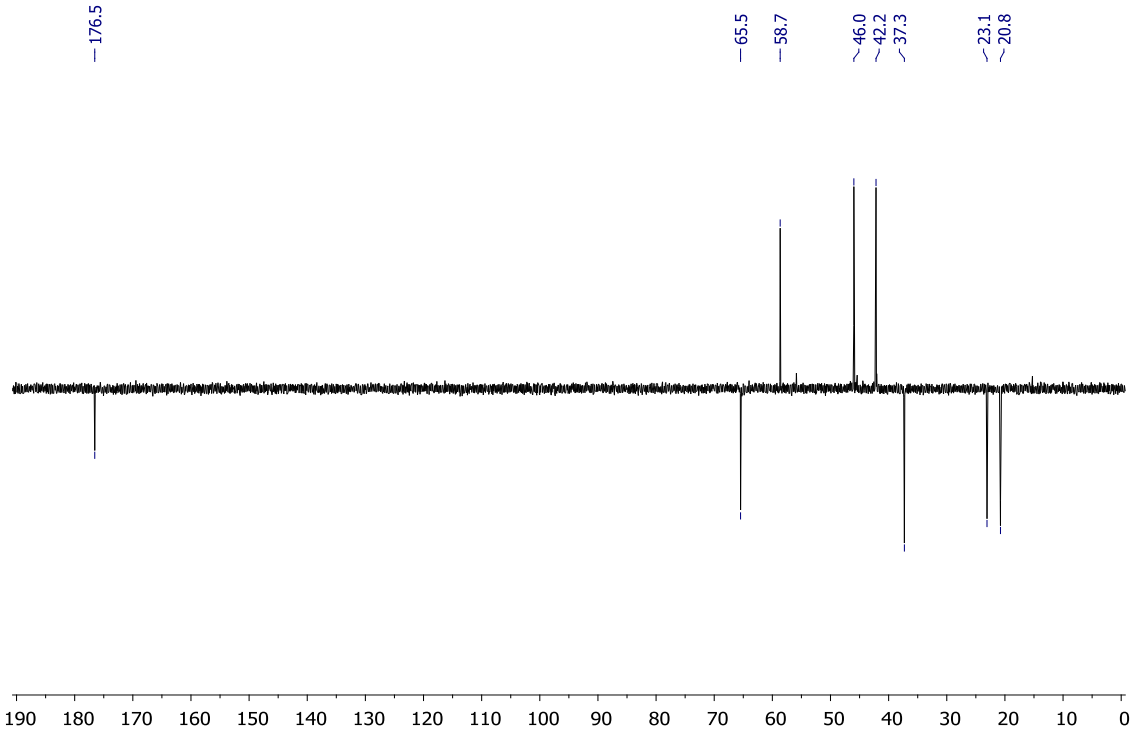
^{13}C-NMR (D_2O, 100 MHz)

(1*R*,1'*R*,2*R*,2'*R*,3*R*,3'*R*,4*S*,4'*S*)-3,3'-Disulfanediylbis(2-aminobicyclo[2.2.1]heptane-2-carboxylic acid) (*exo*-267)



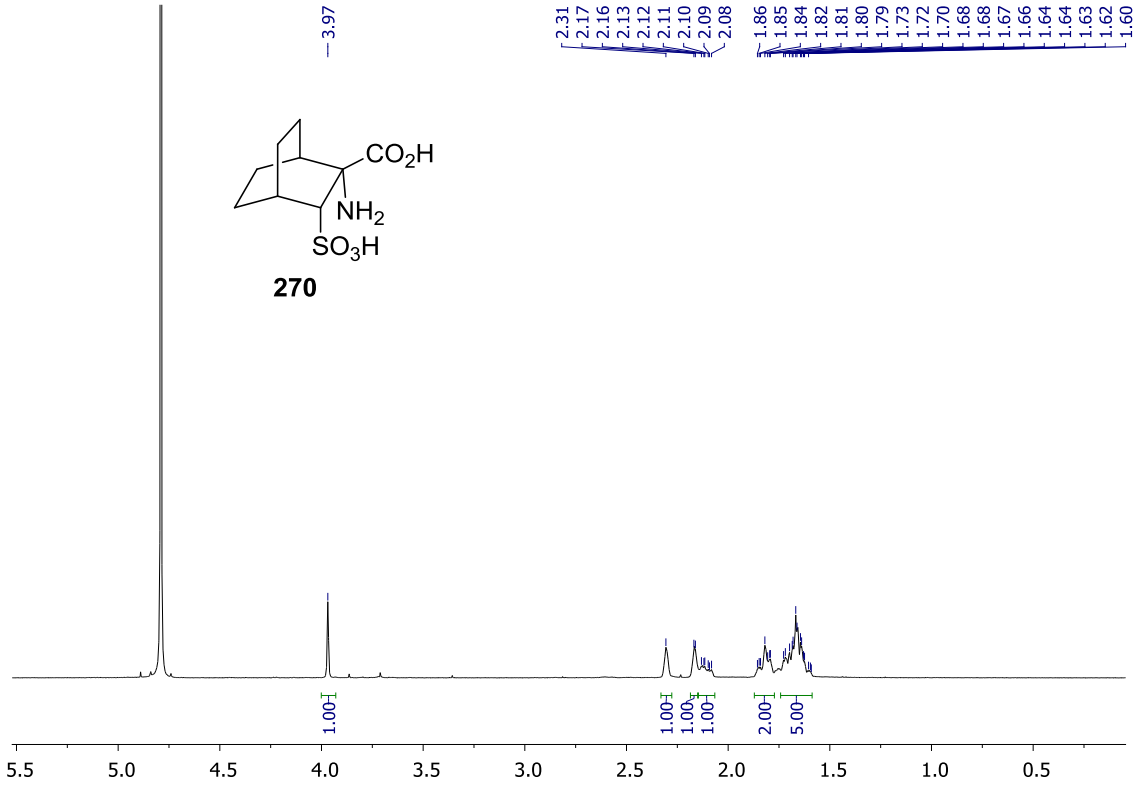
exo-267

^{1}H-NMR (D_2O, 400 MHz)

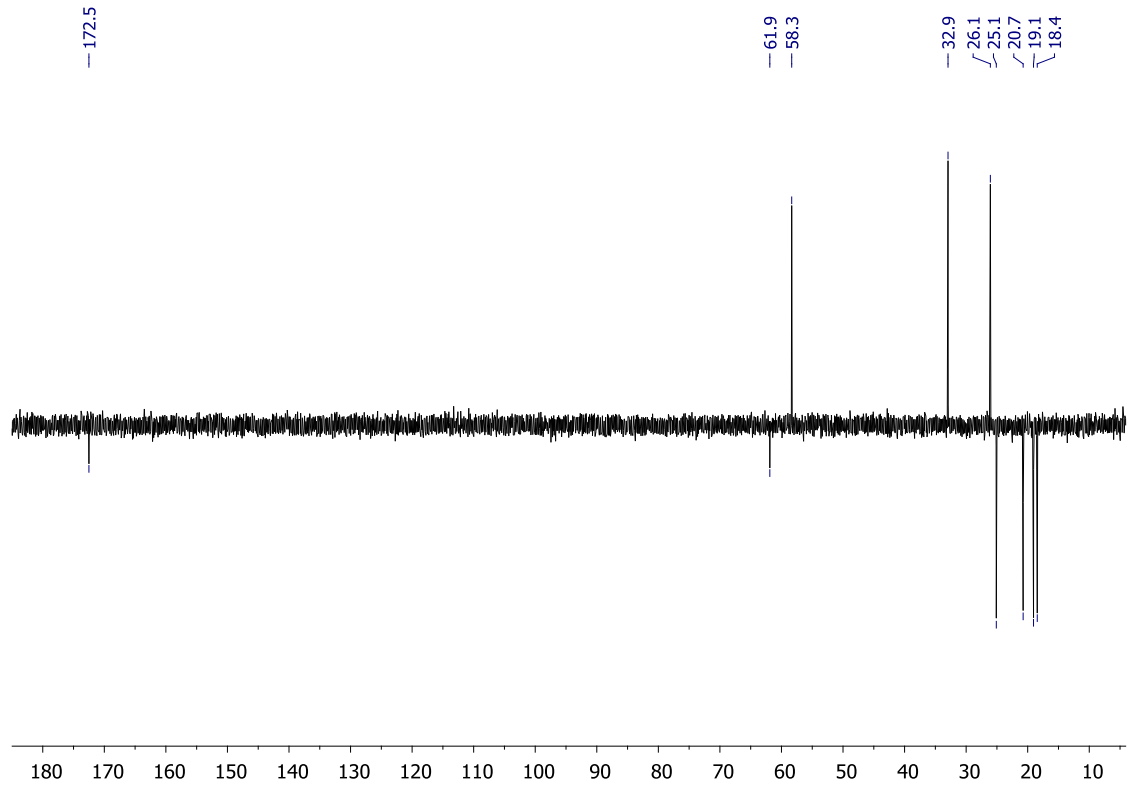


^{13}C-NMR (D_2O, 100 MHz)

(1*S*,2*R*,3*R*,4*S*)-2-Amino-3-sulfobicyclo[2.2.2]octane-2-carboxylic acid (270)

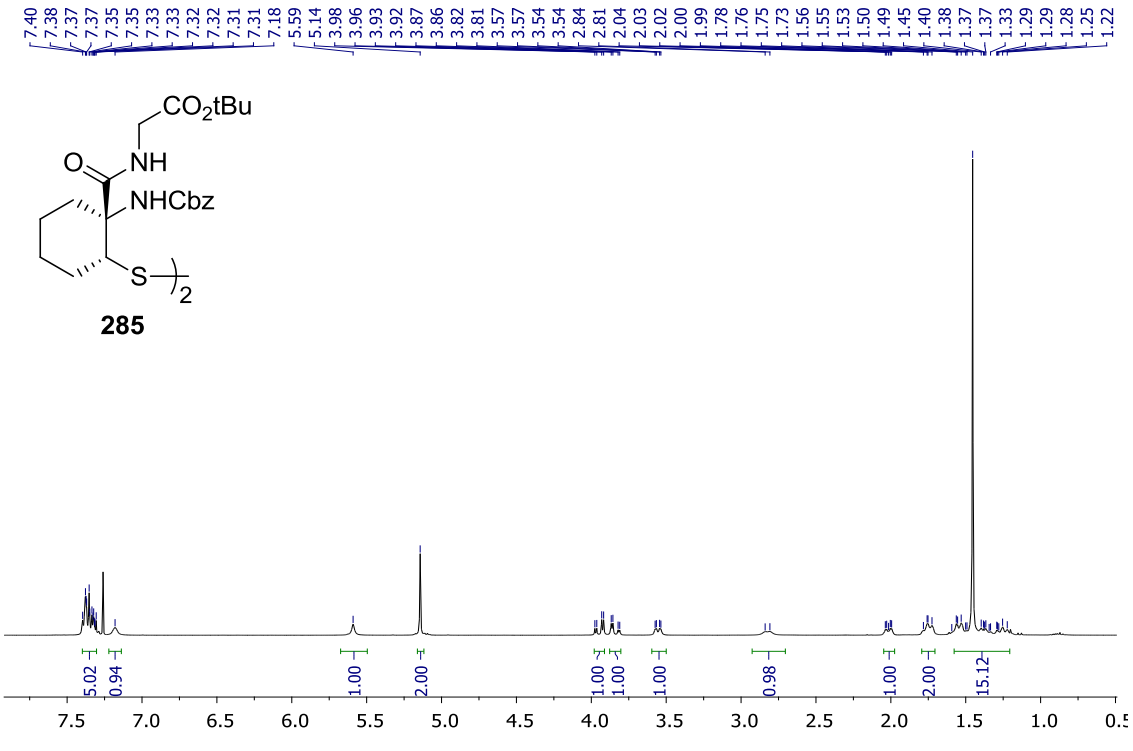


^{1}H-NMR (D_2O, 400 MHz)

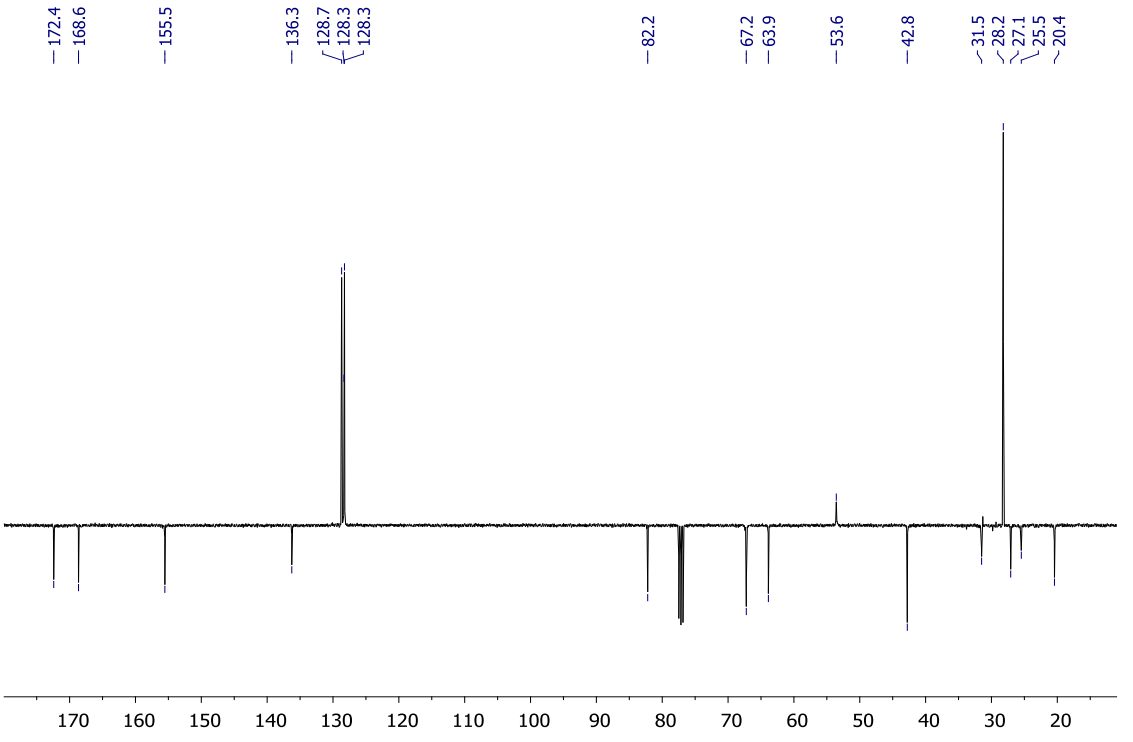


^{13}C-NMR (D_2O, 100 MHz)

Di-*tert*-butyl 2,2'-(((1*R*,1'*R*,2*R*,2'*R*)-2,2'-disulfanediylbis((((benzyloxy)carbonyl)amino)cyclohexanecarbonyl))bis(azanediyl))diacetate (285)

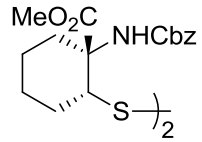


^{1}H-NMR ($CDCl_3$, 400 MHz)

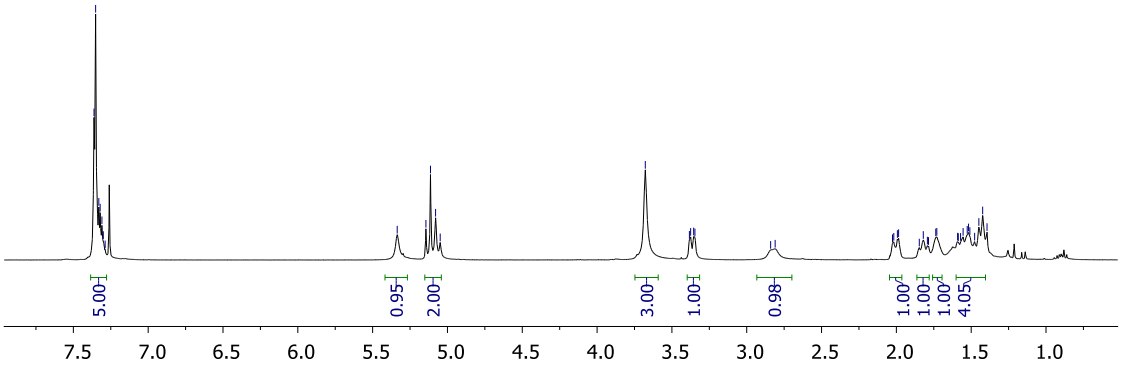


^{13}C-NMR ($CDCl_3$, 100 MHz)

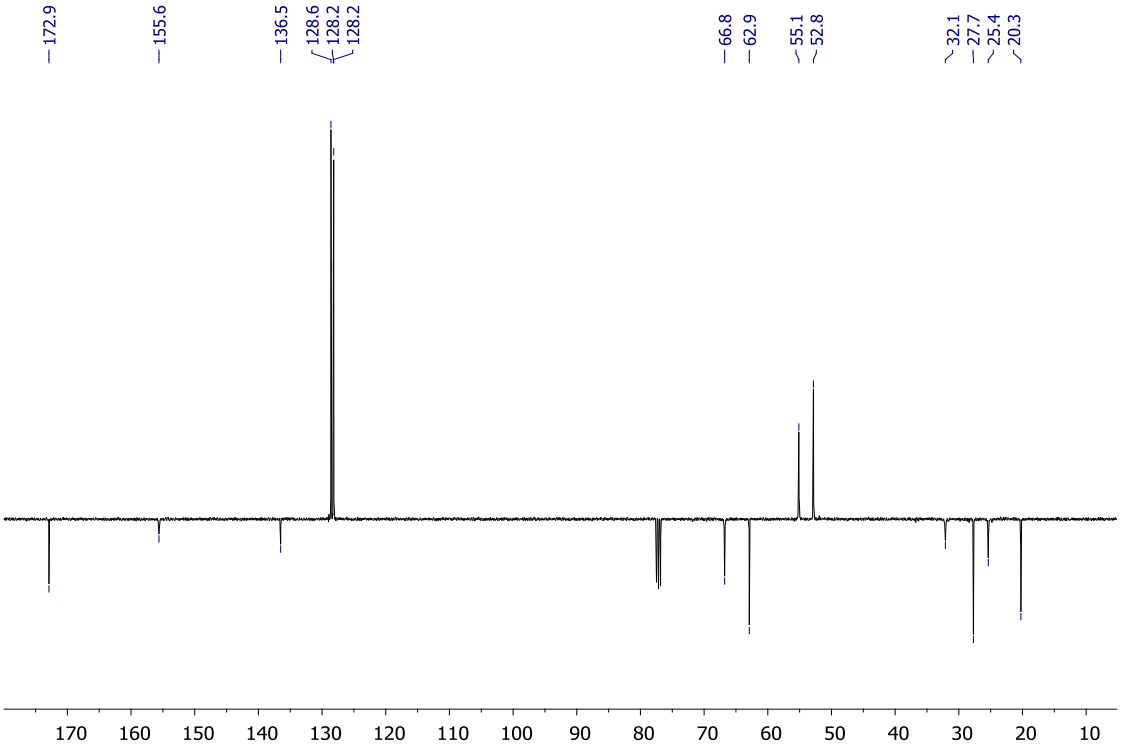
(1*R*,1'*R*,2*R*,2'*R*)-Dimethyl 2,2'-Disulfanediylbis((((benzyloxy)carbonyl)amino)cyclohexanecarboxylate) (286)



286

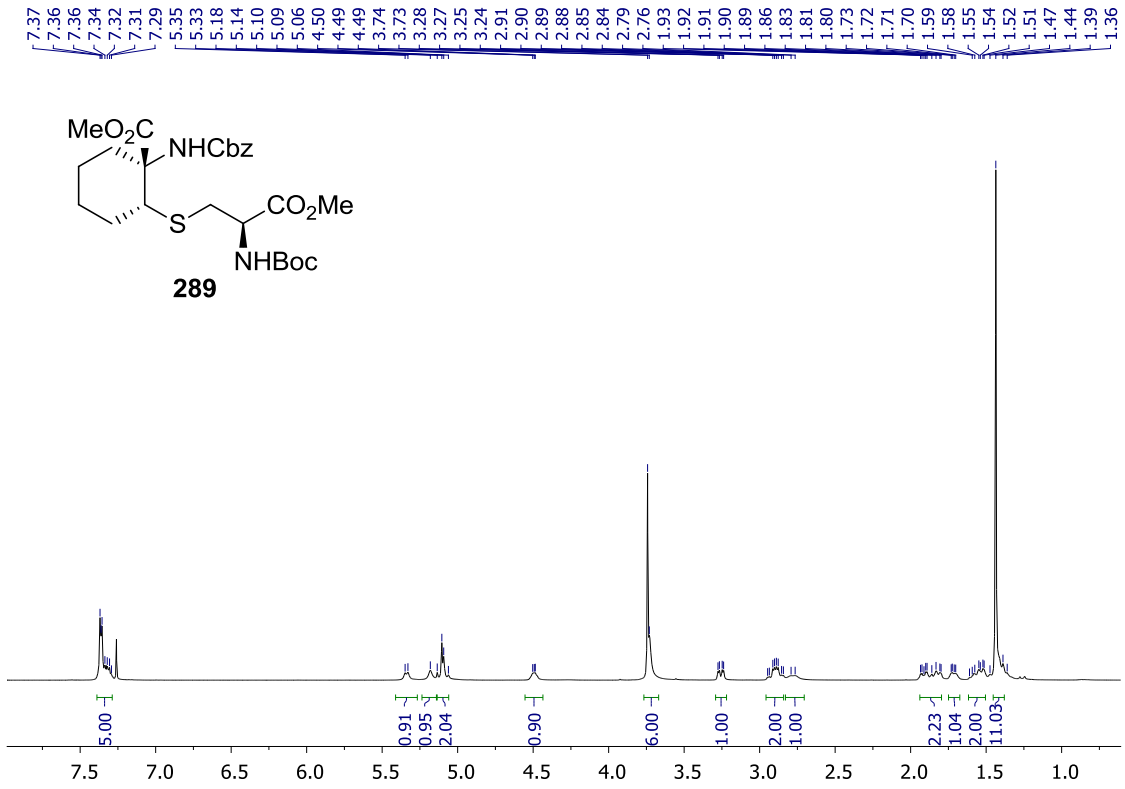


^{1}H-NMR ($CDCl_3$, 400 MHz)

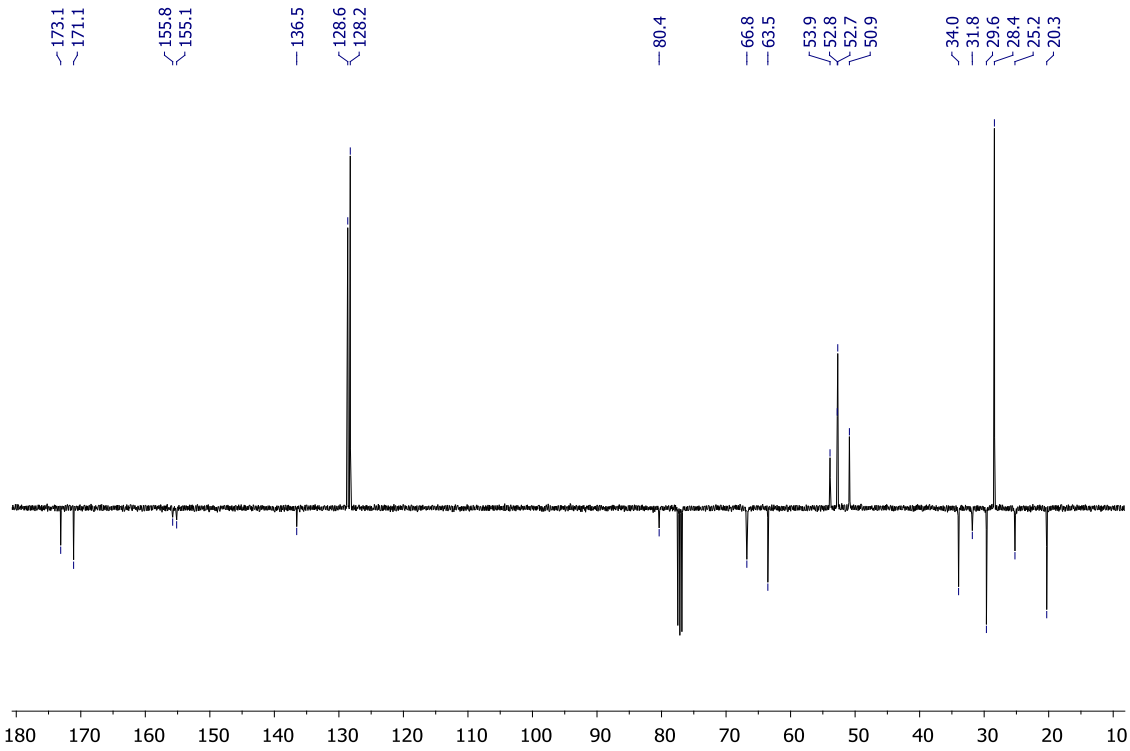


^{13}C-NMR ($CDCl_3$, 100 MHz)

(1*R*,2*R*)-Methyl 1-(((benzyloxy)carbonyl)amino)-2-(((*R*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)thio)cyclohexanecarboxylate 289



^{1}H-NMR ($CDCl_3$, 400 MHz)



^{13}C-NMR ($CDCl_3$, 100 MHz)

Computational methods of Chapter III

Computational Methods

All of the calculations were performed using the Gaussian09 program.[1] Computations were done using Truhlar's functional M06-2X[2] were carried out. Standard basis sets 6-31G+(d,p) and 6-311+G(d,p) were employed.[3] Analytical second derivatives of the energy were calculated to classify the nature of every stationary point, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. The thermal and entropic contributions to the free energies were also obtained from the vibrational frequency calculations, using the unscaled frequencies. All transition structures were characterized by one imaginary frequency and were confirmed to connect to reactants and products by intrinsic reaction coordinate (IRC) calculations.[4] The IRC paths were traced using the second order González-Schlegel integration method.[5] Solvent effects were considered using the polarizable continuum model (PCM).[6] Full optimizations were carried out at M06-2X/6-31+G(d,p) level of theory and then single point calculations were carried out at 3ζ M06-2X/6-311+G(d,p)/PCM=THF level. Reactivity indices and global electron density transfer (GEDT) were calculated as reported[7] at M06-2X/6-311+G(d,p) level of theory. NCI (non-covalent interactions) were computed using the methodology previously described.[8] Data were obtained with the NCIPLOT program.[9] A density cutoff of ρ=0.1 a.u. was applied and the pictures were created for an isosurface value of s=0.4 and colored in the

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT,: **2009**.

[2] Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157-167.

[3] (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261. (b) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209-214. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

[4] (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161-4163. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363-368.

[5] (a) González, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523-5527. (b) González, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853-5860.

[6] Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027-2094.

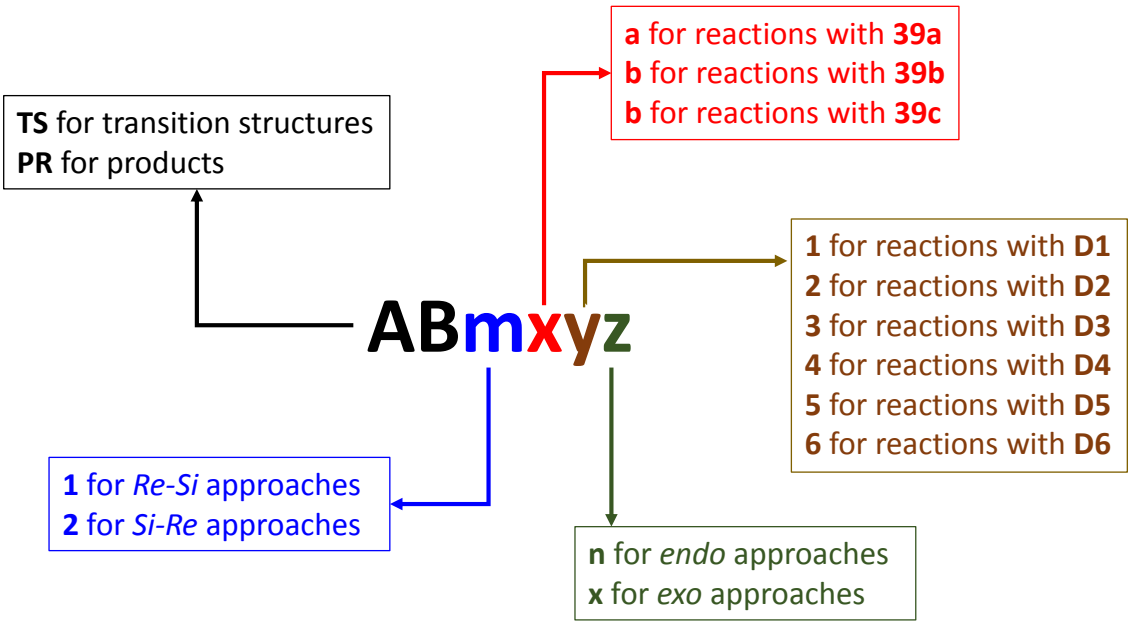
[7] (a) Pérez, P.; Domingo, L. R.; A. Aizman; Contreras, R. *Theor. Aspects Chem. React.* **2008**, *19*, 139-201. (b) Pérez, P.; Domingo, L. R.; José Aurell, M.; Contreras, R. *Tetrahedron* **2003**, *59*, 3117-3125.

[8] (a) Johnson, E. R.; Keinan, S.; Mori-Sanchez, P.; Contreras-Garcia, J.; Cohen, A. J.; Yang, W. *J. Am. Chem. Soc.* **2010**, *132*, 6498-6506. (b) Lane, J. R.; Contreras-Garcia, J.; Piquemal, J.-P.; Miller, B. J.; Kjaergaard, H. G. *J. Chem. Theory Comput.* **2013**, *9*, 3263-3266.

[9] Contreras-Garcia, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.* **2011**, *7*, 625-632.

[-0.02,0.02] a.u. sign(λ_2)ρ range using VMD software.[10] Structural representations were generated using CYLview.[11]

Nomenclature



Energy values

Table A1. Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **D1**.

	E_0	ΔE_0	G	ΔG_0	im. freq
39a	-1068.394775		-1068.437762		
D1	-148.683937		-148.707481		
Reagents	-1217.078712	0.0	-1217.145243	0.0	
TS1a1	-1217.052260	16.6	-1217.097596	29.9	-541.1
TS2a1	-1217.038724	25.1	-1217.085132	37.7	-539.6
PR1a1	-1217.126465	-30.0	-1217.170115	-15.6	
PR2a1	-1217.111898	-20.8	-1217.156586	-7.1	

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[11] Legault, C. Y. *Université de Sherbrooke* **2009**, http://www.cylview.org.

***Table A2*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **D2**

	E_0	ΔE_0	G	ΔG_0	im. freq
39a	-1068.394775		-1068.437762		
D2	-187.960846		-187.988353		
Reagents	-1256.355621	0.0	-1256.426115	0.0	
TS1a2n	-1256.331057	15.4	-1256.377385	30.6	-482.9
TS1a2x	-1256.333852	13.7	-1256.380380	28.7	-499.8
TS2a2n	-1256.340382	9.6	-1256.387535	24.2	-436.9
TS2a2x	-1256.342760	8.1	-1256.390545	22.3	-442.6
PR1a2n	-1256.391193	-22.3	-1256.437150	-6.9	
PR1a2x	-1256.390396	-21.8	-1256.436805	-6.7	
PR2a2n	-1256.406281	-31.8	-1256.451857	-16.2	
PR2a2x	-1256.408281	-32.2	-1256.452357	-18.3	

***Table A3*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **D3**

	E_0	ΔE_0	G	ΔG_0	im. freq
39a	-1068.394775		-1068.437762		
D3	-379.628417		-379.660239		
Reagents	-1448.023192	0.0	-1448.098001	0.0	
TS1a3n	-1447.992162	19.5	-1448.043389	34.3	-504.9
TS1a3x	-1447.995074	17.6	-1448.046564	32.3	-524.6
TS2a3n	-1448.002830	12.8	-1448.054725	27.2	-466.9
TS2a3x	-1448.005301	11.2	-1448.058659	24.7	-481.1
PR1a3n	-1448.049506	-16.5	-1448.100761	-1.7	
PR1a3x	-1448.047683	-15.4	-1448.099105	-0.7	
PR2a3n	-1448.064497	-25.9	-1448.115222	-10.8	
PR2a3x	-1448.062064	-24.4	-1448.112211	-8.9	

***Table A4*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **8a** and **D4**

	E_0	ΔE_0	G	ΔG_0	im. freq
39a	-1068.394775		-1068.437762		
D4	-227.239622		-227.268732		
Reagents	-1295.634397	0.0	-1295.706494	0.0	
TS1a4	-1295.619517	9.3	-1295.668618	23.8	-492.3
TS2a4	-1295.624493	6.2	-1295.674114	20.3	-408.8
PR1a4	-1295.669603	-22.1	-1295.717128	-6.7	
PR2a4	-1295.672656	-24.0	-1295.719144	-7.9	

***Table A5*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **8a** and **D5**

	E_0	ΔE_0	G	ΔG_0	im. freq
39a	-1068.394775		-1068.437762		
D5	-610.567782		-610.606226		
Reagents	-1678.962557	0.0	-1679.043988	0.0	
TS1a5	-1678.924227	24.1	-1678.981526	39.2	-444.7
TS2a5	-1678.940712	13.7	-1678.998021	28.8	-446.7
PR1a5	-1678.991466	-18.1	-1679.049060	-3.2	
PR2a5	-1678.995305	-20.5	-1679.051887	-5.0	

***Table A6*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **8a** and **D6**

	E_0	ΔE_0	G	ΔG_0	im. freq
39a	-1068.394775		-1068.437762		
D6	-376.512427		-376.543689		
Reagents	-1444.907202	0.0	-1444.981451	0.0	
TS1a6n	-1444.869300	23.8	-1444.918000	39.8	-566.3
TS1a6x	-1444.871450	22.4	-1444.923115	36.6	-559.9
TS2a6n	-1444.864316	26.9	-1444.915207	41.6	-516.7
TS2a6x	-1444.879340	17.5	-1444.930715	31.8	-532.7
PR1a6n	-1444.935293	-17.6	-1444.984921	-2.2	
PR1a6x	-1444.926654	-12.2	-1444.977064	2.8	
PR2a6n	-1444.941309	-21.4	-1444.991439	-6.3	
PR2a6x	-1444.942200	-22.0	-1444.990854	-5.9	

***Table A7*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **D1**

	E_0	ΔE_0	G	ΔG_0	im. freq
39b	-1143.557977		-1143.602092		
D1	-148.683937		-148.707481		
Reagents	-1292.241914	0.0	-1292.309573	0.0	
TS1b1	-1292.219821	13.9	-1292.264744	28.1	-478.2
TS2b1	-1292.209856	20.1	-1292.257211	32.9	-434.9
PR1b1	-1292.297793	-35.1	-1292.343669	-21.4	
PR2b1	-1292.283110	-25.9	-1292.329130	-12.3	

***Table A8*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **D2**

	E_0	ΔE_0	G	ΔG_0	im. freq
39b	-1143.557977		-1143.602092		
D2	-187.960846		-187.988353		
Reagents	-1331.518823	0.0	-1331.590445	0.0	
TS1b2n	-1331.498064	13.0	-1331.546757	27.4	-439.4
TS1b2x	-1331.502039	10.5	-1331.550746	24.9	-437.1
TS2b2n	-1331.506293	7.9	-1331.555892	21.7	-388.5
TS2b2x	-1331.513685	3.2	-1331.562573	17.5	-373.8
PR1b2n	-1331.560850	-26.4	-1331.608449	-11.3	
PR1b2x	-1331.562497	-27.4	-1331.610233	-12.4	
PR2b2n	-1331.574607	-35.0	-1331.621451	-19.5	
PR2b2x	-1331.576428	-36.1	-1331.623253	-20.6	

***Table A9*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **D3**

	E_0	ΔE_0	G	ΔG_0	im. freq
39b	-1143.557977		-1143.602092		
D3	-379.628417		-379.660239		
Reagents	-1523.186394	0.0	-1523.262331	0.0	
TS1b3n	-1523.159520	16.9	-1523.211289	32.0	-456.0
TS1b3x	-1523.162878	14.8	-1523.214524	30.0	-468.6
TS2b3n	-1523.164970	13.4	-1523.218186	27.7	-422.7
TS2b3x	-1523.175461	6.9	-1523.229665	20.5	-421.4
PR1b3n	-1523.217406	-19.5	-1523.270074	-4.9	
PR1b3x	-1523.217355	-19.4	-1523.270490	-5.1	
PR2b3n	-1523.231147	-28.1	-1523.282187	-12.5	
PR2b3x	-1523.233479	-29.5	-1523.284997	-14.2	

***Table A10*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **D4**

	E_0	ΔE_0	G	ΔG_0	im. freq
39b	-1143.557977		-1143.602092		
D4	-227.239622		-227.268732		
Reagents	-1370.797599	0.0	-1370.870824	0.0	
TS1b4	-1370.779003	11.7	-1370.828579	26.5	-424.8
TS2b4	-1370.788514	5.7	-1370.838539	20.3	-357.9
PR1b4	-1370.840191	-26.7	-1370.888569	-11.1	
PR2b4	-1370.807073	-5.9	-1370.852907	11.2	

***Table A11*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **D5**

	E_0	ΔE_0	G	ΔG_0	im. freq
39b	-1143.557977		-1143.602092		
D5	-610.567782		-610.606226		
Reagents	-1754.125759	0.0	-1754.208318	0.0	
TS1b5	-1754.094135	19.8	-1754.152910	34.8	-402.2
TS2b5	-1754.103299	14.1	-1754.161241	29.5	-414.7
PR1b5	-1754.151052	-15.9	-1754.208421	-0.1	
PR2b5	-1754.164014	-24.0	-1754.221576	-8.3	

***Table A12*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **D6**

	E_0	ΔE_0	G	ΔG_0	im. freq
39b	-1143.557977		-1143.602092		
D6	-376.512427		-376.543689		
Reagents	-1520.070404	0.0	-1520.145781	0.0	
TS1b6n	-1520.034341	22.6	-1520.084621	38.4	-546.9
TS1b6x	-1520.037133	20.9	-1520.089980	35.0	-523.9
TS2b6n	-1520.033312	23.3	-1520.086554	37.2	-481.5
TS2b6x	-1520.049769	12.9	-1520.101602	27.7	-496.8
PR1b6n	-1520.093937	-14.8	-1520.145681	0.1	
PR1b6x	-1520.094300	-15.0	-1520.146479	-0.4	
PR2b6n	-1520.113169	-26.8	-1520.164374	-11.7	
PR2b6x	-1520.112406	-26.4	-1520.162324	-10.4	

***Table A13*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **D1**

	E_0	ΔE_0	G	ΔG_0	im. freq
39c	-1218.751588		-1218.796030		
D1	-148.683937		-148.707481		
Reagents	-1367.435525	0.0	-1367.503511	0.0	
TS1c1	-1367.418864	10.5	-1367.465168	24.1	-475.8
TS2c1	-1367.428431	4.5	-1367.475879	17.3	-401.8
PR1c1	-1367.493325	-36.3	-1367.538823	-22.2	
PR2c1	-1367.480142	-28.0	-1367.526635	-14.5	

***Table A14*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **D2**

	E_0	ΔE_0	G	ΔG_0	im. freq
39c	-1218.751588		-1218.796030		
D2	-187.960846		-187.988353		
Reagents	-1406.712434	0.0	-1406.784383	0.0	
TS1c2n	-1406.693250	12.0	-1406.741274	27.1	-398.6
TS1c2x	-1406.700448	7.5	-1406.748864	22.3	-410.7
TS2c2n	-1406.705712	4.2	-1406.755149	18.3	-363.3
TS2c2x	-1406.710195	1.4	-1406.758884	16.0	-352.5
PR1c2n	-1406.756702	-27.8	-1406.804484	-12.6	
PR1c2x	-1406.759347	-29.4	-1406.807184	-14.3	
PR2c2n	-1406.771032	-36.8	-1406.818264	-21.3	
PR2c2x	-1406.773013	-38.0	-1406.820861	-22.9	

***Table A15*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **D3**

	E_0	ΔE_0	G	ΔG_0	im. freq
39c	-1218.751588		-1218.796030		
D3	-379.628417		-379.660239		
Reagents	-1598.380005	0.0	-1598.456269	0.0	
TS1c3n	-1598.352914	17.0	-1598.405799	31.7	-426.5
TS1c3x	-1598.361582	11.6	-1598.415114	25.8	-458.0
TS2c3n	-1598.364857	9.5	-1598.418694	23.6	-391.6
TS2c3x	-1598.372123	4.9	-1598.426947	18.4	-400.0
PR1c3n	-1598.413807	-21.2	-1598.466372	-6.3	
PR1c3x	-1598.415888	-22.5	-1598.469291	-8.2	
PR2c3n	-1598.426636	-29.3	-1598.479355	-14.5	
PR2c3x	-1598.428673	-30.5	-1598.480563	-15.2	

***Table A16*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **D4**

	E_0	ΔE_0	G	ΔG_0	im. freq
39c	-1218.751588		-1218.796030		
D4	-227.239622		-227.268732		
Reagents	-1445.991210	0.0	-1446.064762	0.0	
TS1c4	-1445.973351	11.2	-1446.023824	25.7	-340.5
TS2c4	-1445.988269	1.8	-1446.039118	16.1	-329.4
PR1c4	-1446.033495	-26.5	-1446.082478	-11.1	
PR2c4	-1445.956910	21.5	-1446.005684	37.1	

***Table A17*.** Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **D5**

	E_0	ΔE_0	G	ΔG_0	im. freq
39c	-1218.751588		-1218.796030		
D5	-610.567782		-610.606226		
Reagents	-1829.319370	0.0	-1829.402256	0.0	
TS1c5	-1829.289409	18.8	-1829.348168	33.9	-363.8
TS2c5	-1829.300374	11.9	-1829.359685	26.7	-383.3
PR1c5	-1829.347447	-17.6	-1829.404812	-1.6	
PR2c5	-1829.358357	-24.5	-1829.415755	-8.5	

Table A18. Calculated (M06-2X/6-311+G(d,p)/PCM=THF//M06-2X/6-31+G(d,p)) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **D6**

	E_0	ΔE_0	G	ΔG_0	im. freq
39c	-1218.751588		-1218.796030		
D6	-376.512427		-376.543689		
Reagents	-1595.264015	0.0	-1595.339719	0.0	
TS1c6n	-1595.231105	20.7	-1595.282716	35.8	-512.6
TS1c6x	-1595.234195	18.7	-1595.286210	33.6	-509.2
TS2c6n	-1595.229331	21.8	-1595.281691	36.4	-441.2
TS2c6x	-1595.245277	11.8	-1595.297823	26.3	-478.1
PR1c6n	-1595.293238	-18.3	-1595.344180	-2.8	
PR1c6x	-1595.292892	-18.1	-1595.343324	-2.3	
PR2c6n	-1595.306163	-26.4	-1595.356528	-10.5	
PR2c6x	-1595.306580	-26.7	-1595.357391	-11.1	

NCI Analysis

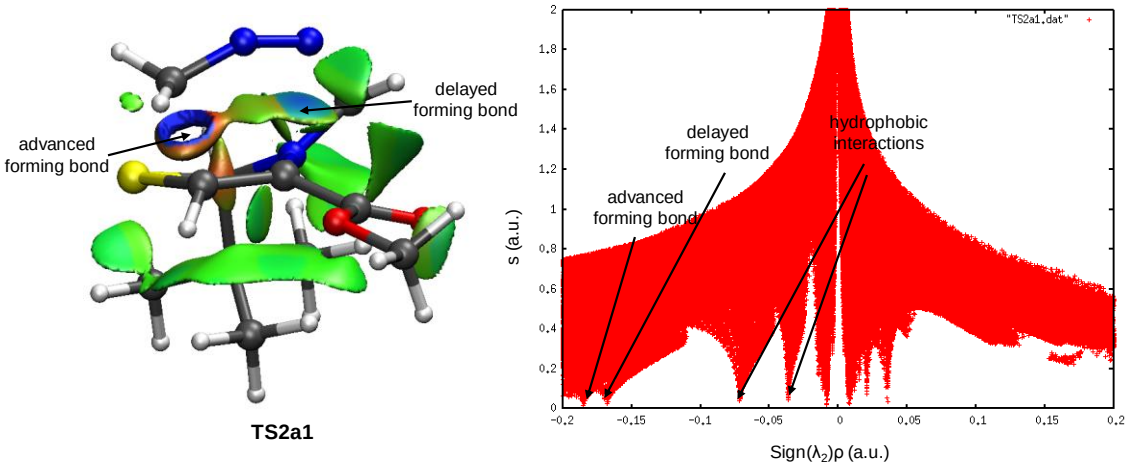

Figure A1. NCI Analysis for **TS2a1**. Left: Non-covalent interactions are shown as colored surfaces (blue: strong attractive; green: light attractive; red: repulsive). Right: NCI s(ρ) decaying curves representation with detail of interactions

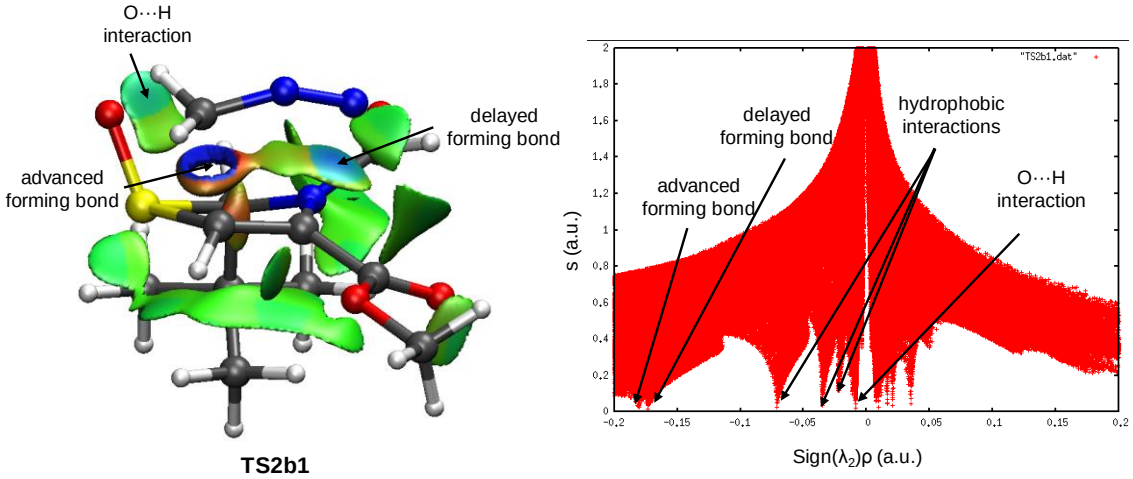

Figure A2. NCI Analysis for **TS2b1**. Left: Non-covalent interactions are shown as colored surfaces (blue: strong attractive; green: light attractive; red: repulsive). Right: NCI s(ρ) decaying curves representation with detail of interactions

Cartesian coordinates

C39a
0 1

C	1.6298817296	0.6048389921	-1.3291983178
C	-0.7472063449	0.5171337491	-1.0040322010
C	-0.5556287314	-0.7225048333	-1.4824453015
C	-1.9736569547	0.9981069629	-0.3372626074
O	-2.0852861188	2.0785116408	0.1982926924
O	-2.9566765338	0.0872375040	-0.3888695855
C	-4.1737359032	0.4729953779	0.2567748038
H	2.2184116299	1.1461181518	-2.0757734242
H	-1.3010407634	-1.5060200099	-1.4860794689
H	-4.5790237404	1.3734749276	-0.2091826870
H	-4.8517862101	-0.3682508427	0.1271335668
H	-3.9935506750	0.6666785249	1.3160460407
N	0.3918030150	1.3537496209	-1.1060569308
C	2.4800560247	0.4148499484	-0.0537740088
C	3.7281705561	-0.3973985094	-0.4160329286
H	3.4714796473	-1.4145259529	-0.7289199689
H	4.2920033125	0.0844434212	-1.2231445923
H	4.3876031797	-0.4714553293	0.4540971090
C	2.9049352564	1.8087075560	0.4313085495
H	2.0377917311	2.4127754244	0.7138630445
H	3.5496177548	1.7068678689	1.3104185070
H	3.4526017980	2.3527905580	-0.3440693383
C	1.6926608348	-0.2898928032	1.0544808308
H	2.3288202321	-0.4043026629	1.9380583942
H	0.8153560266	0.2959382977	1.3488679931
H	1.3647592490	-1.2874992219	0.7447151654
S	1.0575831408	-0.9983130376	-2.0816335894
C	0.3235030464	2.6791663123	-1.4891818020
O	1.2966197405	3.3225031156	-1.8219439832
H	-0.6917696593	3.0929684286	-1.4361053217

C39b
0 1

C	1.6317085362	0.4379471951	-1.2304105995
C	-0.7175109635	0.3998718739	-0.8810514088
C	-0.5425754155	-0.9039050567	-1.1269321832
C	-1.9812422856	0.9930866886	-0.3368903573
O	-2.0703795965	2.1149152875	0.1016065312
O	-2.9833885673	0.1167380667	-0.3765470743
C	-4.2286181956	0.5885733119	0.1550657501
H	2.1950240765	0.8403967585	-2.0792404555
H	-1.2941422614	-1.6736815667	-1.0264748736
H	-4.5707695204	1.4563347725	-0.4118023332
H	-4.9219855318	-0.2426486777	0.0490615276
H	-4.1072813605	0.8651065696	1.2039245279
N	0.4069794442	1.2140700591	-1.0651554405
C	2.5188757502	0.3918883995	0.0345528535
C	3.8001618731	-0.3834385339	-0.2991313920
H	3.5995726041	-1.4308742183	-0.5444432648
H	4.3269226833	0.0733777967	-1.1438909940
H	4.4727684354	-0.3668171258	0.5640065825
C	2.8915719723	1.8298221071	0.4200264925
H	2.0066320006	2.4076715082	0.7026764462
H	3.5717394658	1.8084971655	1.2779225224
H	3.3827436631	2.3507837586	-0.4065599393
C	1.7905599011	-0.2715350521	1.2102357934
H	2.4328173312	-0.2477029094	2.0963282689
H	0.8658182577	0.2618762823	1.4555088238
H	1.5456341542	-1.3197338028	1.0052344785

S	1.0898866090	-1.2699008995	-1.7656088406
O	0.9919268084	-1.3019241933	-3.2669247710
C	0.3448108121	2.5126961432	-1.5631453340
O	1.3238113244	3.1052434208	-1.9514309077
H	-0.6641748949	2.9414916608	-1.5485545295

C39c
0 1

C	1.6528668431	0.3341430546	-1.1779314718
C	-0.7343776119	0.3206921837	-0.8668783135
C	-0.5972467715	-0.9996343420	-1.0067053016
C	-1.9703839195	0.9897780980	-0.3445285024
O	-2.0198257704	2.1496121703	-0.0149327820
O	-2.9858289263	0.1337253244	-0.2727114452
C	-4.2058946037	0.6730538183	0.2565756300
H	2.2376019932	0.6671469110	-2.0410745664
H	-1.3241044687	-1.7736599502	-0.8082258747
H	-4.5573246676	1.4886797848	-0.3777611781
H	-4.9119960289	-0.1540168118	0.2533984252
H	-4.0414491737	1.0439491407	1.2695894003
N	0.4064972057	1.1009626074	-1.1327012268
C	2.4901851486	0.4330739328	0.1182084969
C	3.7962099065	-0.3522542631	-0.0692919933
H	3.6218544545	-1.4251284168	-0.1663727988
H	4.3397238799	0.0001577652	-0.9532390661
H	4.4387260263	-0.1866201835	0.8011811243
C	2.8344939622	1.9171451605	0.3239314365
H	1.9384944303	2.5191832269	0.5020091617
H	3.4833187134	2.0090517951	1.2008182201
H	3.3570031555	2.3333327499	-0.5419882256
C	1.7214458220	-0.0728450218	1.3453514206
H	2.3321347239	0.0922551411	2.2384300390
H	0.7866975928	0.4832202826	1.4811898831
H	1.5000843369	-1.1412973848	1.2800835097
S	1.0293177413	-1.3531875168	-1.6245752556
O	1.6412014513	-2.4222823225	-0.8429559902
O	0.9857522638	-1.4528161987	-3.0789523320
C	0.3445300230	2.3352305163	-1.7773251797
O	1.3226567032	2.8841430700	-2.2238036230
H	-0.6676804651	2.7549097084	-1.8198386207

D1
0 1

N	-2.0662732332	1.1013672774	1.7708889760
N	-1.9915639986	1.8591671914	0.9275702051
C	-1.9062435465	2.7223110594	-0.0330465682
H	-0.9390325420	2.8766905513	-0.4825309339
H	-2.8075007708	3.2352595817	-0.3262469916

D2
0 1

N	-1.8389320000	-0.3197930000	-0.0000150000
N	-0.7830860000	0.1137870000	0.0000430000
C	0.4183650000	0.5882270000	-0.0000720000
C	1.6035360000	-0.3357440000	0.0000060000
H	1.2731890000	-1.3769340000	0.0005880000
H	2.2280680000	-0.1816530000	-0.8856550000
H	2.2285200000	-0.1807290000	0.8851990000
H	0.4929460000	1.6664580000	0.0000650000

D3
0 1

N	-1.8053923077	-0.3078512800	0.0004322571
N	-0.7519837686	0.1200370985	0.0001435621

C	0.4683714727	0.5659492612	-0.0001733742
H	0.5782462137	1.6409705236	-0.0004619795
C	1.5956595248	-0.3589413747	-0.0000752287
C	2.8974681461	0.1645663685	-0.0005450092
C	1.4285936897	-1.7524106176	0.0004800569
C	3.9997671648	-0.6823927393	-0.0004756159
H	3.0399594191	1.2417880186	-0.0010006371
C	2.5368407991	-2.5931314771	0.0005572131
H	0.4296086078	-2.1808713551	0.0008583090
C	3.8277872989	-2.0665784250	0.0000815808
H	4.9994113490	-0.2585078232	-0.0008547930
H	2.3884201259	-3.6686766331	0.0009995649
H	4.6889189647	-2.7265366654	0.0001290136

D4
0 1

N	-2.1274660000	0.0001880000	-0.0002910000
N	-0.9816650000	0.0004120000	0.0004130000
C	0.3076120000	-0.0000190000	0.0001680000
C	1.0412910000	1.3111410000	-0.0000660000
H	1.6843470000	1.3967020000	0.8840440000
H	1.6829180000	1.3969510000	-0.8851850000
H	0.3478820000	2.1545680000	0.0005960000
C	1.0405180000	-1.3115410000	-0.0000720000
H	0.3465130000	-2.1544380000	-0.0001360000
H	1.6827780000	-1.3975580000	-0.8847780000
H	1.6829580000	-1.3979100000	0.8844190000

D5
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N	0.0035056482	2.1028416276	0.0061374394
C	0.0014680935	0.7966542094	0.0034935926
C	1.3188692992	0.1340324570	0.0307447239
C	1.4670150658	-1.1257851438	0.6302292418
C	2.4507452999	0.7582321815	-0.5128472120
C	2.7131257103	-1.7428352887	0.6731715512
H	0.6046170099	-1.6117818769	1.0760230464
C	3.6966427413	0.1419178856	-0.4553015919
H	2.3530372975	1.7297730034	-0.9905758667
C	3.8344547928	-1.1142053897	0.1328992681
H	2.8100714727	-2.7167930538	1.1431190618
H	4.5607396989	0.6420866830	-0.8815974090
H	4.8052884542	-1.5973352465	0.1727822887
C	-1.3179895356	0.1382567680	-0.0264551226
C	-1.4700347091	-1.1186759824	-0.6309973523
C	-2.4479415599	0.7637947535	0.5195975968
C	-2.7180618022	-1.7316591273	-0.6764642342
H	-0.6091351645	-1.6055694108	-1.0787046191
C	-3.6957519502	0.1516045329	0.4595308251
H	-2.3472326595	1.7331012232	1.0012255541
C	-3.8374526586	-1.1017096993	-0.1337158958
H	-2.8180192605	-2.7034158497	-1.1503210399
H	-4.5583059122	0.6527521686	0.8877975378
H	-4.8097869291	-1.5816437435	-0.1755772682

D6
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N	-1.7599024099	-0.4245252661	0.0000407869
N	-0.7329399817	0.0395201103	0.0000182161
C	0.4652089067	0.5663446925	-0.0000100642
H	0.5426107082	1.6414478348	-0.0000673402
C	1.6300943043	-0.3034246706	0.0000399213
O	2.7718196702	0.0983685752	0.0000098289

O	1.2902864810	-1.6093678335	0.0001239461
C	2.3936032800	-2.5180462755	0.0001789345
H	3.0077617386	-2.3661139605	0.8901521335
H	1.9524239079	-3.5129768616	0.0002979659
H	3.0076971446	-2.3663009048	-0.8898711088

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C	1.4989891184	-0.3895868653	0.3698099744
C	-0.9518647635	-0.2446822491	0.4397676799
C	-0.6155131489	0.8151932962	-0.6175217196
C	-1.8116239233	-1.3623707801	-0.1710702591
O	-1.5236763776	-2.5299005990	-0.1811188600
O	-2.9149706122	-0.8440166922	-0.7180678011
C	-3.8064496738	-1.7924381775	-1.3220831623
N	-1.7931365167	0.4865345765	1.4580477766
N	-2.1031641379	1.6136692372	1.0827232008
C	-1.6068571652	1.9303432525	-0.2736044638
H	1.6313644373	-1.0715466336	-0.4819309888
H	-0.7489125830	0.4395217676	-1.6334310805
H	-4.6426038313	-1.2088238804	-1.7007596896
H	-4.1415968425	-2.5140626679	-0.5751962213
H	-3.2976414136	-2.3181541286	-2.1321318668
H	-2.4799272242	1.9299775390	-0.9339436886
N	0.2465346504	-0.7494757937	1.0702351985
C	2.8319847854	-0.3453011171	1.1709219031
C	3.8273654050	0.5428021402	0.3949416980
H	4.8201124071	0.4267305395	0.8397545166
H	3.8962810314	0.2503222515	-0.6588331139
H	3.5670412296	1.6048137169	0.4476595536
C	2.6317947118	0.2486888060	2.5687221579
H	2.0942361803	-0.4379848824	3.2236887040
H	3.6108479048	0.4490934720	3.0163503169
H	2.0843928692	1.1960193880	2.5155403414
C	3.4662264289	-1.7454963290	1.2282020833
H	3.7233608154	-2.0848524454	0.2177839346
H	4.3960976826	-1.6892363753	1.8041918067
H	2.8138195943	-2.4778018306	1.6982417943
S	1.1089649616	1.2786124227	-0.3192289193
C	0.0519985549	-1.6949563247	2.0548337080
O	0.9041798823	-2.3416707139	2.6212064615
H	-1.0139522318	-1.7843402939	2.3139676464
H	-1.1733032853	2.9331472137	-0.2628709417

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C	1.4950609456	-0.3573898305	0.4034758453
C	-0.9523982188	-0.2433311058	0.4758686619
C	-0.6235922731	0.8556416282	-0.5420936775
C	-1.8005479739	-1.3501569455	-0.1713287458
O	-1.4919729314	-2.5111721781	-0.2280466917
O	-2.9189360873	-0.8334077998	-0.6879478428
C	-3.8000595653	-1.7755027016	-1.3170880136
N	-1.7994003054	0.4509068213	1.5173684735
N	-2.1449348977	1.5727808575	1.1584313452
C	-1.6783898821	1.9264815797	-0.2079318824
H	1.6274580436	-0.9935728320	-0.4829825925
H	-0.7195427145	0.5060800479	-1.5723220971
H	-4.6527520278	-1.1941520007	-1.6609699876
H	-4.1105959485	-2.5317476223	-0.5943858420
H	-3.2927159861	-2.2591374317	-2.1538368952
H	-2.5544174570	1.7665842989	-0.8489711468
N	0.2487607867	-0.7616770145	1.0892790689
C	2.8326277162	-0.3457385112	1.1976721260

C	3.8230663935	0.5730779850	0.4528006225
H	4.8172141993	0.4450894930	0.8912897138
H	3.8904413172	0.3192684780	-0.6110552382
H	3.5585175697	1.6313797925	0.5429956192
C	2.6412956605	0.1888721289	2.6208378167
H	2.0989593946	-0.5210941340	3.2466385702
H	3.6232797194	0.3608950592	3.0737750158
H	2.1028229584	1.1426857606	2.6107662662
C	3.4656633848	-1.7476938265	1.1938194358
H	3.7148420976	-2.0472372186	0.1688364018
H	4.3998908030	-1.7156285718	1.7647035332
H	2.8166028493	-2.4981479797	1.6396077621
S	1.0887653022	1.3404442895	-0.1952242831
C	0.0622743086	-1.7372783066	2.0442231293
O	0.9194461444	-2.3913147550	2.5950193186
H	-1.0034652217	-1.8461551703	2.2969792095
C	-1.2560957670	3.3854006462	-0.2675076286
H	-0.4547252684	3.5873047972	0.4467717801
H	-0.9055105361	3.6394766962	-1.2717066480
H	-2.1080014323	4.0236119263	-0.0245660025

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C	1.4320049650	-0.4145788032	0.3754282030
C	-1.0147143484	-0.2837455452	0.4627179106
C	-0.7091576463	0.8069616933	-0.5763952508
C	-1.7710286869	-1.4635245258	-0.1681876503
O	-1.3557194484	-2.5916868348	-0.2213166221
O	-2.9386450238	-1.0580099414	-0.6714518582
C	-3.7297164406	-2.0797310639	-1.2951051967
N	-1.9234367138	0.3808648773	1.4646497679
N	-2.2194629180	1.5272471884	1.1406527014
C	-1.6535110092	1.9509308433	-0.1619027200
H	1.5283169331	-1.1386912756	-0.4457526831
H	-0.9131406118	0.4672698426	-1.5944281975
H	-4.6427602818	-1.5851257388	-1.6196693588
H	-3.9498886919	-2.8695254264	-0.5749598272
H	-3.1903713343	-2.5028623634	-2.1446843471
N	0.1966600556	-0.7207766630	1.1268476804
C	2.7892174189	-0.3518040498	1.1352230269
C	3.7709568890	0.4913306242	0.2951759251
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H	3.8126900866	0.1489188005	-0.7449513280
H	3.5178965888	1.5561545387	0.3033375760
C	2.6332265780	0.3009858345	2.5120150670
H	2.0860231823	-0.3439117077	3.2008836849
H	3.6257119952	0.4874965541	2.9354174236
H	2.1144876200	1.2622584747	2.4313740715
C	3.4113579078	-1.7549977785	1.2340671910
H	3.6311615217	-2.1422643292	0.2320402810
H	4.3607179542	-1.6830022099	1.7756710929
H	2.7696409144	-2.4598890273	1.7576308250
S	1.0421093719	1.2251693746	-0.3765024438
C	0.0189282310	-1.6515887969	2.1294981062
O	0.8835740422	-2.2621400752	2.7162821232
H	-1.0458715788	-1.7603644359	2.3876453373
C	-2.7979850554	2.2296018132	-1.1315157679
H	-2.4001388399	2.6024868254	-2.0788179980
H	-3.3685248039	1.3168529577	-1.3186641785
H	-3.4665411706	2.9842483013	-0.7119234600
H	-1.1007872725	2.8760959099	0.0352180587

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C	-1.6282519666	-0.9437011002	-0.4843691483
C	-0.7960575347	1.2690518590	0.1791768067
C	0.3606015078	0.7461459566	-0.6796123729
C	-1.3798993044	2.5563177025	-0.4263134062
O	-2.5214729634	2.6981686257	-0.7762767283
O	-0.4273195932	3.4865652412	-0.5397651000
C	-0.8549186882	4.7412695750	-1.0903310748
N	-0.1523389940	1.6173844105	1.5003386004
N	1.0737706843	1.5929944096	1.4419203393
C	1.5909099317	1.2854851578	0.0820471713
H	-2.0457819024	-0.7200056700	-1.4761434173
H	0.3263359858	1.1259437582	-1.7030720418
H	0.0331152851	5.3690819600	-1.1129693360
H	-1.6255321157	5.1799802759	-0.4541936647
H	-1.2548153876	4.5912290849	-2.0947212747
H	1.8632789871	2.2618466808	-0.3385595894
N	-1.7987248272	0.2492089891	0.3768247293
C	-2.2056941221	-2.3086852336	-0.0070979587
C	-1.4581443303	-3.4352666171	-0.7509618793
H	-1.9765511164	-4.3806631720	-0.5652201590
H	-1.4463711467	-3.2676326762	-1.8337926831
H	-0.4268741152	-3.5532292352	-0.4038551666
C	-2.0122420987	-2.5037568916	1.4999534118
H	-2.6678367296	-1.8509529058	2.0777573118
H	-2.2484090276	-3.5405134126	1.7612273389
H	-0.9723600309	-2.3112741675	1.7863077746
C	-3.6824635101	-2.4370774122	-0.4176131029
H	-3.7713042054	-2.4404670859	-1.5105235683
H	-4.0695987695	-3.3942046698	-0.0519714049
H	-4.2980663882	-1.6387397254	-0.0099917818
S	0.2052642043	-1.0575128174	-0.6574405959
C	-2.8897212156	0.6175010576	1.1332491162
O	-3.8986206043	-0.0257970798	1.3174660700
H	-2.7299198180	1.5969286174	1.6100763249
C	2.8083949817	0.3971292766	0.1168153755
C	3.7303606397	0.4507929564	-0.9306960030
C	3.0026543846	-0.5144961977	1.1569233771
C	4.8310313707	-0.4027963856	-0.9461889692
H	3.5857363268	1.1632947467	-1.7398024318
C	4.1082158602	-1.3613881570	1.1463299467
H	2.2882767049	-0.5569252393	1.9738297039
C	5.0215426015	-1.3102599289	0.0944633632
H	5.5415941817	-0.3545635605	-1.7651599983
H	4.2546086397	-2.0640371291	1.9604115356
H	5.8814732286	-1.9725248712	0.0877885601

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C	-2.2310520303	-0.2296407593	-0.5572469711
C	-0.1750583683	0.8835211540	0.2257689173
C	0.3904266215	-0.4610818878	-0.2505773401
C	0.4166735321	2.0325751174	-0.6071952509
O	-0.2166168551	2.7549570172	-1.3317257432
O	1.7368076572	2.0678520804	-0.4452010103
C	2.4484536504	3.0341536131	-1.2287910552
N	0.3118522123	1.0225331533	1.6448541253
N	1.1007049556	0.1361527070	1.9609710183
C	1.3906123574	-0.8231410458	0.8701418818
H	-2.2287786896	0.0352732727	-1.6234563730
H	0.8833603597	-0.3823402049	-1.2210898878
H	3.5002776948	2.8679565404	-1.0031902426
H	2.1393220520	4.0420566804	-0.9462665995
H	2.2471269781	2.8737758371	-2.2895900681
N	-1.6210848751	0.8804258987	0.2069917806

C	-3.6621316049	-0.7121713974	-0.1689642094
C	-3.8305656974	-2.1699848392	-0.6457448084
H	-4.8842763036	-2.4492106925	-0.5535198566
H	-3.5453515045	-2.2881045324	-1.6972447916
H	-3.2508417992	-2.8754334468	-0.0423136016
C	-3.8731957354	-0.6623479433	1.3465781786
H	-3.9550294413	0.3644762914	1.7057772850
H	-4.8020019845	-1.1848950497	1.5981391066
H	-3.0508717035	-1.1612397318	1.8708875260
C	-4.7252510953	0.1044981249	-0.9228386960
H	-4.6359282449	-0.0654481697	-2.0023909421
H	-5.7186191906	-0.2395649243	-0.6153077496
H	-4.6518316806	1.1702609685	-0.7203905691
S	-1.0159580175	-1.5982645801	-0.3182346551
C	-2.2195717722	2.0561916396	0.6070244407
O	-3.3957682855	2.3322815034	0.5382154708
H	-1.4865036760	2.7444363375	1.0563062871
H	1.1737282273	-1.8165574084	1.2815449581
C	2.8517315837	-0.7774615165	0.4651732960
C	3.7288972654	0.1987198719	0.9396213459
C	3.3238391645	-1.7492729438	-0.4218580463
C	5.0601520855	0.2036336553	0.5247034352
H	3.3700099498	0.9542641981	1.6313120838
C	4.6510764756	-1.7393538233	-0.8418044682
H	2.6463224442	-2.5189265923	-0.7870419533
C	5.5239266859	-0.7604411855	-0.3677271235
H	5.7374632280	0.9626067641	0.9044390325
H	5.0053673912	-2.4985748186	-1.5319047706
H	6.5609979828	-0.7539859334	-0.6880963862

PR1a4
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C	1.3878978411	-0.3851515404	0.3659885902
C	-1.0500924597	-0.2635741430	0.4442234307
C	-0.7632037410	0.8698918654	-0.5538638324
C	-1.7187691943	-1.4708130107	-0.2349928383
O	-1.2381269748	-2.5733210898	-0.2839041633
O	-2.8897909635	-1.1287270367	-0.7751712713
C	-3.6003565801	-2.1893555316	-1.4296286310
N	-2.0226503420	0.3198268979	1.4348093037
N	-2.3503623004	1.4668503911	1.1491661937
C	-1.7434683539	1.9926907782	-0.1049363576
H	1.4677792349	-1.1299782784	-0.4384490507
H	-0.9937678362	0.5615670250	-1.5757478572
H	-4.5252813745	-1.7436656859	-1.7894963724
H	-3.8058564756	-2.9914787301	-0.7187688569
H	-3.0066409189	-2.5811785486	-2.2576273835
N	0.1595882479	-0.6614026586	1.1385220664
C	2.7538006958	-0.3174929257	1.1098037549
C	3.7352634433	0.5001892591	0.2439859447
H	4.7418668349	0.3906671967	0.6582718171
H	3.7592380172	0.1408565585	-0.7909789782
H	3.4972427623	1.5683604621	0.2390892747
C	2.6172656728	0.3628631427	2.4750371660
H	2.0759068069	-0.2660756835	3.1833322402
H	3.6156732053	0.5539500784	2.8824373743
H	2.1013779099	1.3247881326	2.3808608640
C	3.3659856755	-1.7235898310	1.2297212182
H	3.5755923213	-2.1299764334	0.2331967049
H	4.3194158621	-1.6497185311	1.7637454833
H	2.7223037411	-2.4134574930	1.7701311845
S	1.0069925551	1.2430726509	-0.4163916325
C	-0.0153373662	-1.5924415866	2.1431561890
O	0.8530928683	-2.1844348351	2.7435508954

H	-1.0805867280	-1.7180024470	2.3902415803
C	-1.1140774236	3.3425538970	0.2318919768
H	-0.3781259143	3.2517639809	1.0327463877
H	-0.6174832762	3.7567657170	-0.6511832848
H	-1.8997428233	4.0334297397	0.5471338383
C	-2.8820010868	2.1751054393	-1.1126304106
H	-3.3465453531	1.2163287698	-1.3539521788
H	-3.6421477184	2.8423034291	-0.6986493464
H	-2.4864467009	2.6219493988	-2.0298885731

PR1a5
0 1

C	2.7499140559	0.2309145727	-0.8438395396
C	0.7860318036	-1.0941924393	-0.1595907188
C	0.0547167315	0.0274796146	-0.9132842311
C	0.0871689465	-2.4298699823	-0.5042273390
O	0.0344226926	-2.8567613742	-1.6305329948
O	-0.4998537251	-2.9749239707	0.5493146349
C	-1.3722435790	-4.0790691198	0.2674275440
N	0.5434103063	-0.7714380322	1.2864011258
N	-0.3730658415	0.0314987992	1.4281765776
C	-1.0157048833	0.4353442712	0.1197254966
H	3.3490855451	0.0742197273	-1.7465056089
H	-0.3545908328	-0.3423844787	-1.8491978634
H	-1.7645537631	-4.3886495603	1.2334086271
H	-0.8154823162	-4.8865437615	-0.2112363996
H	-2.1771997903	-3.7398307867	-0.3895326434
N	2.1842077555	-1.0777149617	-0.4905588863
C	3.6665049017	0.8912879289	0.2192851588
C	4.1569642002	2.2221092020	-0.3696363788
H	4.8912094219	2.6737904842	0.3045982284
H	4.6405020747	2.0741327167	-1.3422141902
H	3.3357183209	2.9359700728	-0.4929750907
C	2.9566782129	1.1477408323	1.5499801642
H	2.6575151488	0.2108670845	2.0280033643
H	3.6424561706	1.6694771644	2.2258536009
H	2.0658989491	1.7713084340	1.4207887293
C	4.8800880002	-0.0149831973	0.4669008080
H	5.4194995860	-0.2314965774	-0.4594167224
H	5.5625682947	0.4833846304	1.1635138201
H	4.5831976807	-0.9688475454	0.9123536668
S	1.3060697645	1.3014297485	-1.2761198276
C	2.8730289796	-2.2183147209	-0.8460896943
O	3.9647127268	-2.2165864229	-1.3690745194
H	2.3447449716	-3.1483828933	-0.5897372990
C	-2.3045139562	-0.3954874108	0.0118313103
C	-3.0548080697	-0.6207889717	1.1742155633
C	-2.7821056628	-0.8983965068	-1.2015322143
C	-4.2405092089	-1.3462633408	1.1238873616
H	-2.7002206080	-0.2261574293	2.1210529433
C	-3.9781413318	-1.6172389504	-1.2517183325
H	-2.2400345141	-0.7410970393	-2.1281653364
C	-4.7081836301	-1.8492705526	-0.0906079449
H	-4.8046344397	-1.5122761577	2.0363943262
H	-4.3318531638	-1.9949658735	-2.2060619706
H	-5.6364989383	-2.4104006765	-0.1309907777
C	-1.3529546040	1.9178061104	0.1348722738
C	-1.1255228034	2.7135858695	1.2572727674
C	-1.8914060885	2.4957502940	-1.0186331123
C	-1.4291916499	4.0752953919	1.2200835494
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C	-2.1871325691	3.8542960111	-1.0557167286
H	-2.0803813690	1.8791633115	-1.8949362585
C	-1.9568206258	4.6494575240	0.0672681592

H	-1.2453177985	4.6875997905	2.0975627383
H	-2.5991553706	4.2915793159	-1.9597053689
H	-2.1882524958	5.7096159850	0.0410099732

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C	-0.3595068473	1.3421083554	-0.1097773004
C	0.7770232753	0.5071460969	-0.7502226392
C	-0.1310630529	2.8049193302	-0.5286127211
O	-0.7378360658	3.3873828407	-1.3881944955
O	0.9216603330	3.2985563048	0.1240372619
C	1.3056169390	4.6314276294	-0.2455637792
N	-0.1370685414	1.2204994667	1.3751730265
N	0.9048194719	0.6362966806	1.6578931584
C	1.6983205162	0.2791850992	0.4615130783
H	-2.3380964705	-0.5897076668	-1.8265373368
H	1.2972556319	1.0591547904	-1.5333152807
H	2.1506681549	4.8783020625	0.3930101727
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H	2.5361651518	0.9870112362	0.4354925443
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C	-2.2559070352	-1.6101446030	0.0684074695
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H	-2.7188869576	-3.7226390040	0.0061962166
H	-2.7312950669	-2.9574129913	-1.5890041298
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C	-1.4703661434	-1.6666117679	1.3790809445
H	-1.5687712889	-0.7351532048	1.9434949966
H	-1.8741364790	-2.4728592499	2.0003598757
H	-0.4069156945	-1.8744954384	1.2248947714
C	-3.7194056297	-1.2686151887	0.3846390747
H	-4.3271799728	-1.1940084949	-0.5212669408
H	-4.1348671622	-2.0539188803	1.0249939633
H	-3.8033125332	-0.3202761602	0.9225042201
S	0.0195284419	-0.9626391561	-1.5061087627
C	-2.7551893689	1.6236371900	-0.6444603404
O	-3.7754208789	1.2535755158	-1.1799829370
H	-2.6384930114	2.6251076272	-0.2125792377
C	2.2698013881	-1.1225811966	0.5619479814
O	2.0555011069	-1.9140409104	1.4396904586
O	3.0536793486	-1.3538018888	-0.5004849268
C	3.5722098240	-2.6864607550	-0.5945519134
H	4.1806903512	-2.7012878239	-1.4963907972
H	4.1736657062	-2.9193286977	0.2859920153
H	2.7472668683	-3.3982424138	-0.6705404856

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C	0.8845275935	1.9459465726	-0.3886020609
O	0.3243711548	2.7952004465	-1.0302311846
O	2.1990899263	1.8675293312	-0.1946059651
C	2.9902495261	2.8440443460	-0.8860984866
N	0.7488560027	0.5388664567	1.6364108787
N	1.5028080001	-0.4270961008	1.7096614184
C	1.6499910232	-1.1332998135	0.4014878756
H	-2.0749690440	0.3367977699	-1.5430914061
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H	4.0217195750	2.6280801923	-0.6166474967
H	2.7036542819	3.8472494946	-0.5667701297

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C	-3.7894103763	-1.8474596407	-0.6752785663
H	-4.8520097897	-2.0498155985	-0.5121775569
H	-3.6084642782	-1.8655641616	-1.7558734935
H	-3.2263477302	-2.6627490617	-0.2099787859
C	-3.5350006552	-0.5776669796	1.4627464799
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H	-5.4849686924	0.2085312360	-0.2768584205
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S	-0.9199343908	-1.5478369220	-0.5696156019
C	-1.7005220650	2.0489479360	0.8934755670
O	-2.8431551471	2.4450470711	0.9261249040
H	-0.8806334865	2.5983743711	1.3832971279
H	1.5062883964	-2.2010215767	0.6036780342
C	3.0690148986	-0.9677236359	-0.1392752103
O	3.3316593314	-0.7028919783	-1.2868374320
O	3.9722439856	-1.2013439614	0.8080957277
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H	5.9293001581	-1.3307520088	1.2781128380
H	5.5426638796	-1.8144362849	-0.4080331214
H	5.5494935027	-0.0902420835	0.0388444360

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C	-0.9985602322	-0.1919701159	0.4722757557
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C	-1.7585875469	-1.3626512245	-0.1706403975
O	-1.4043982826	-2.5117768385	-0.1364625922
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C	-3.6718497327	-1.9245329707	-1.4000077076
N	-1.9341005145	0.4877321893	1.4387984904
N	-2.2333957486	1.6210656923	1.0773747232
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N	0.1961775822	-0.6293862841	1.1639775082
C	2.8054899682	-0.3461248820	1.1621954894
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C	2.7307180079	0.2412486250	2.5779875861
H	2.1774021111	-0.4114546964	3.2534056411
H	3.7502377419	0.3412998812	2.9659224686
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C	3.3537538261	-1.7829710420	1.1676525034
H	3.5333949373	-2.1279867626	0.1421940352
H	4.3144940507	-1.7896280017	1.6932968649
H	2.6855073422	-2.4795992118	1.6697347711
S	1.0920921073	1.3755696616	-0.2724875580
C	-0.0030382584	-1.5478064774	2.1804270152
O	0.8459281073	-2.1770451914	2.7662507324
H	-1.0708538133	-1.6272060039	2.4343304196

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H	-1.1234248610	2.9766507504	-0.0487104717

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C	1.4422677750	-0.2849579785	0.4621955316
C	-0.9849872485	-0.1837023819	0.5320256941
C	-0.6575421570	0.9389882574	-0.4397461572
C	-1.7327389975	-1.3385596894	-0.1532000180
O	-1.3860666459	-2.4894994238	-0.1227607373
O	-2.8082925199	-0.8770035111	-0.7938180553
C	-3.5998230708	-1.8695984415	-1.4655723819
N	-1.9250888980	0.4544310419	1.5311465887
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H	1.4846545729	-0.8309578844	-0.4946215554
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H	-4.4381450869	-1.3295139635	-1.8996146656
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H	-3.0047476339	-2.3563744948	-2.2403130260
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N	0.2220375821	-0.6327379382	1.2009434481
C	2.8236691188	-0.3686993950	1.1558900020
C	3.8226729007	0.4663719835	0.3268988093
H	4.8307214635	0.2534902061	0.6942181896
H	3.7829947468	0.2215168806	-0.7389057517
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C	2.7867023399	0.1966595188	2.5805498025
H	2.2224308265	-0.4423300758	3.2595425252
H	3.8121087268	0.2732007175	2.9567043668
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C	3.3367661654	-1.8185165456	1.1253182131
H	3.4735172972	-2.1475205040	0.0888682181
H	4.3149408430	-1.8559130805	1.6164675471
H	2.6707260124	-2.5091617932	1.6384337835
S	1.0543326015	1.4748475226	-0.0524482705
C	0.0299919481	-1.5724363033	2.2024178503
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O	1.6818595488	1.7550095042	-1.3934391072
C	-1.3590385189	3.4391389376	-0.1443333075
H	-0.6548402641	3.6461937586	0.6653223287
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C	-0.7878598051	0.8615873205	-0.4620021349
C	-1.6861923469	-1.5017037879	-0.1808287251
O	-1.2325249472	-2.6155194727	-0.1434492338
O	-2.7905689309	-1.1478485118	-0.8411098798
C	-3.4749096827	-2.2151766232	-1.5141984068
N	-2.0856387391	0.2686194109	1.4790781420
N	-2.4211138980	1.4129906742	1.1924255145
C	-1.7680922691	1.9562731705	-0.0201284214
H	1.3917805899	-0.9377418157	-0.4409838655
H	-0.9218630077	0.5726316341	-1.5066500483
H	-4.3484183801	-1.7586120107	-1.9746060102
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H	-2.8226115762	-2.6590514033	-2.2685723132
N	0.1479591288	-0.6360956116	1.2313477212
C	2.7571508557	-0.3276327429	1.1263373314

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H	3.6510981924	0.1809295745	-0.8223585961
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C	2.7600632114	0.2967977686	2.5282490505
H	2.2310686928	-0.3292308888	3.2464743028
H	3.7992707253	0.3903759888	2.8619551497
H	2.3110290457	1.2932205082	2.5118799505
C	3.2960518987	-1.7682786922	1.1409395509
H	3.4141042164	-2.1431210190	0.1170656366
H	4.2849955249	-1.7692044765	1.6114922508
H	2.6520461767	-2.4448394571	1.6996505175
S	0.9655633050	1.3780967957	-0.2356293621
C	-0.0041176008	-1.5390487550	2.2704900854
O	0.8770839731	-2.0987863240	2.8792327411
H	-1.0669585228	-1.6770992911	2.5191147898
O	0.9577652244	2.3858106539	0.8858645008
C	-2.8332812256	2.3161111072	-1.0495845271
H	-3.3723791886	1.4207538387	-1.3705737607
H	-3.5453130870	3.0217788663	-0.6169686228
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C	-1.4115341456	2.4927091542	-0.3539606380
O	-2.5879187384	2.5901210128	-0.5813436412
O	-0.4980677761	3.4306513319	-0.6121475509
C	-1.0067469924	4.6478708483	-1.1808841463
N	-0.0954579785	1.6793992337	1.5657358702
N	1.1299288975	1.6699042446	1.4967708248
C	1.6453686664	1.2952451310	0.1574705914
H	-1.9090380948	-0.5492950993	-1.4579999504
H	0.3662756179	1.0429007924	-1.6321573820
H	-0.1397844020	5.2894325185	-1.3216797338
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N	-1.6899160523	0.1868156407	0.5202550576
C	-2.2610533986	-2.2685544389	-0.1722763755
C	-1.6296610187	-3.3158439704	-1.1141911278
H	-2.2281480036	-4.2296241247	-1.0557533447
H	-1.6105989447	-2.9783597933	-2.1548131115
H	-0.6042797082	-3.5751185726	-0.8322530396
C	-2.0341420410	-2.7216221608	1.2747021126
H	-2.5951377119	-2.1155225624	1.9857967577
H	-2.3650964521	-3.7603515811	1.3760614453
H	-0.9699918863	-2.6891573531	1.5359231275
C	-3.7553324725	-2.2067592036	-0.5322751633
H	-3.8748838165	-2.0205309622	-1.6057787895
H	-4.2119046507	-3.1774690418	-0.3115070226
H	-4.2901763426	-1.4423782354	0.0273149519
S	0.2626117272	-1.0861608433	-0.6340528974
C	-2.7164603831	0.5019177319	1.3982429944
O	-3.6843706971	-0.1718620486	1.6590394677
H	-2.5305563436	1.4695642902	1.8870819891
O	0.5632423784	-1.4524498720	-2.0655451504
C	2.8592229431	0.3935694195	0.2344441117
C	3.3601140512	-0.1676686730	-0.9450452885
C	3.4897111691	0.1192510115	1.4493858735
C	4.4749731316	-0.9999744980	-0.9071729903

H	2.8654042451	0.0199596204	-1.8948494114
C	4.6093422393	-0.7118636411	1.4812293996
H	3.1069786772	0.5553236136	2.3656603471
C	5.1038908890	-1.2732048983	0.3068471639
H	4.8464561090	-1.4389417126	-1.8274747359
H	5.0918343652	-0.9213034344	2.4307832855
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C	-2.1552159719	-0.2575915318	-0.3975641206
C	-0.1527828198	0.8840897483	0.3723029372
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O	1.6787294925	2.0175918722	-0.5590284911
C	2.3028906386	2.9820767560	-1.4176159618
N	0.4107501920	1.1501060338	1.7459531115
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C	1.4795092559	-0.7371316702	1.0605112972
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H	3.3727499596	2.8279214326	-1.2913479649
H	2.0121262163	3.9898776320	-1.1162386334
H	2.0027242549	2.8071491591	-2.4522157939
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C	-3.6340800848	-0.6857656082	-0.2380981671
C	-3.7909600667	-2.0884020847	-0.8627235981
H	-4.8591820675	-2.3137868620	-0.9290356823
H	-3.3620046942	-2.1444214097	-1.8678593144
H	-3.3243934381	-2.8746549275	-0.2608962695
C	-4.0555394108	-0.7621895614	1.2341290125
H	-4.1107736971	0.2235166040	1.6959741415
H	-5.0469999921	-1.2226564322	1.2948525846
H	-3.3671336333	-1.3908951190	1.8105981011
C	-4.5414033379	0.2558101451	-1.0482367994
H	-4.2982640735	0.1875936169	-2.1147351597
H	-5.5811714709	-0.0653025624	-0.9245116739
H	-4.4636409146	1.2920736051	-0.7262375495
S	-0.9956920163	-1.6585016831	0.0479706366
C	-2.2220765477	1.9752645221	0.8991602647
O	-3.4058237299	2.2134178673	0.9061694979
H	-1.4834004148	2.6703012512	1.3260273674
O	-0.8047239056	-2.5526573281	-1.1485326596
H	1.3105051415	-1.6928453741	1.5745739105
C	2.9025410824	-0.7205571944	0.5359281567
C	3.8238738885	0.2597763023	0.9021517694
C	3.2811724339	-1.7260617021	-0.3582466271
C	5.1143919905	0.2338585325	0.3732428280
H	3.5333214472	1.0432908189	1.5949383733
C	4.5679367634	-1.7469247771	-0.8880907088
H	2.5624378697	-2.4918234898	-0.6459969404
C	5.4886354675	-0.7652386198	-0.5224002206
H	5.8286865790	0.9976492465	0.6655781157
H	4.8515811247	-2.5314001075	-1.5823795136
H	6.4938011199	-0.7825047783	-0.9316220905

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C	1.3414694040	-0.2860535275	0.4485149097
C	-1.0679346949	-0.1947592616	0.5119539184
C	-0.7791912814	0.9637817887	-0.4375406944
C	-1.6370699223	-1.4396250701	-0.1905850987
O	-1.1664719253	-2.5426857325	-0.0914858321

O	-2.7135593030	-1.1294724986	-0.9119052327
C	-3.3369757749	-2.2278925450	-1.5957248209
N	-2.1279824535	0.3263759148	1.4497796679
N	-2.4993877530	1.4563499225	1.1477017619
C	-1.8359950087	2.0278298440	-0.0568859307
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H	-0.8317683129	0.6902568437	-1.4952553818
H	-4.1840939028	-1.7981590233	-2.1260453192
H	-3.6682108456	-2.9739254743	-0.8717366832
H	-2.6294403929	-2.6818645531	-2.2916103046
N	0.1393178278	-0.5250071388	1.2559083674
C	2.7484192782	-0.3494369257	1.0900997304
C	3.7341401132	0.3584360150	0.1360128250
H	4.7509426227	0.1517018109	0.4821129847
H	3.6391004729	0.0022664469	-0.8943334953
H	3.6048529225	1.4450051844	0.1225408702
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H	3.8386924004	0.4300188341	2.7746817289
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C	3.2126531163	-1.8124805588	1.1881793235
H	3.2777892396	-2.2546759023	0.1874553803
H	4.2163281382	-1.8341170479	1.6262276263
H	2.5566343988	-2.4200399729	1.8081024092
S	0.9856088883	1.4266160344	-0.2153764027
C	-0.0372118605	-1.3939713391	2.3250876308
O	0.8293938708	-1.9186086480	2.9825812610
H	-1.1052048691	-1.5285845990	2.5503709690
O	1.5353175675	1.5353546346	-1.6149553377
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H	-2.1210488092	4.0587371921	0.5903562630
C	-2.9048137672	2.1761318547	-1.1429688958
H	-3.3048856682	1.2018653065	-1.4320777458
H	-3.7217817713	2.8018574613	-0.7752811363
H	-2.4609543429	2.6556323062	-2.0203022868

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C	-0.5238512106	-1.1867677646	-0.4329905575
C	0.0439617676	-0.0554706534	0.4106485006
C	-0.0461680551	-2.5412141144	0.1251464559
O	-0.5926823484	-3.0809416392	1.0533421209
O	1.0480251439	-2.9677790478	-0.4876959851
C	1.7089355410	-4.0899272245	0.1148236718
N	0.0462251335	-0.9427370047	-1.7967784466
N	0.9733704456	-0.1386065516	-1.7712146316
C	1.3020273919	0.3520960910	-0.3851166182
H	-2.4914967573	-0.5838011059	1.5106363846
H	0.2206216631	-0.3332251449	1.4516067684
H	2.5284157865	-4.3379013704	-0.5562342564
H	1.0139701702	-4.9243377207	0.2195011699
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C	-3.9760869897	0.4026825138	0.2481273139
C	-4.1337684319	1.6930949595	1.0806033202
H	-5.1872283694	1.9866604963	1.0563543692
H	-3.8353360062	1.5509466660	2.1235346166
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H	-4.2679057192	-0.1447499212	-1.8518197235
H	-5.1376278032	1.3026200152	-1.3258310406

H	-3.3956943041	1.3890126446	-1.6104880680
C	-5.0345783455	-0.5809265534	0.7756589391
H	-4.9259375876	-0.7029870761	1.8593774462
H	-6.0291164979	-0.1626472310	0.5873804664
H	-4.9770216634	-1.5559063158	0.2967543652
S	-1.2884471506	1.2092498239	0.5157221116
C	-2.5844525666	-2.1056131952	-1.2034952973
O	-3.7679502012	-2.3213000295	-1.3115564880
H	-1.8322287036	-2.7192475122	-1.7303248762
O	-1.2271600989	1.7300746883	1.9290176149
C	2.5540700482	-0.4064180925	0.0807764723
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C	2.8033780245	-0.6218668370	1.4383104200
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H	3.3081125593	-0.6866400945	-1.9165115871
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H	2.1167847732	-0.2534764361	2.1950581443
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C	1.9391014236	2.4797226487	-1.6239450072
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H	1.3168108875	2.1080118235	1.7018672615
C	2.2307632981	4.5715197135	-0.4459747527
H	2.5081579717	4.3237403999	-2.5664259515
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H	2.4700957975	5.6302164382	-0.4548851780

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C	-0.0258470828	1.3022006529	0.2612760142
C	0.9408707242	0.3773869741	-0.4662915109
C	-0.1873799693	2.6440924584	-0.4719324577
O	-1.2399810653	3.1099550507	-0.8178163224
O	1.0073140164	3.2013812347	-0.6757489040
C	0.9882893515	4.4769127573	-1.3374464464
N	0.6353034113	1.5827476026	1.5905719367
N	1.7796047204	1.1426093215	1.6491773909
C	2.2097768939	0.4990933278	0.3921923712
H	-1.6650505102	-0.1300050765	-1.4625539232
H	1.1080783733	0.6187928222	-1.5182125632
H	2.0292635775	4.7824792076	-1.4125490401
H	0.4140918138	5.1905962949	-0.7446129851
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H	2.9282021435	1.1780730060	-0.0810730804
N	-1.2939708450	0.6347058558	0.4841413675
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H	-3.1756648562	-3.4865003296	-0.8357064364
H	-2.1348423670	-2.6072221165	-1.9745947099
H	-1.4416820233	-3.3665369865	-0.5368093426
C	-2.6211212022	-1.9110034984	1.3857619335
H	-2.9883529847	-1.0949025620	2.0077140919
H	-3.2784184776	-2.7739089866	1.5340861843
H	-1.6196441329	-2.1981558574	1.7270300967
C	-3.9874557682	-1.0444738578	-0.5830876997
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H	-4.7417800786	-1.7995151368	-0.3377830673

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C	-2.2105417258	1.3509847457	1.2426015906
O	-3.3681588747	1.0700486131	1.4370919799
H	-1.7371150231	2.2310900923	1.7022772739
O	0.3741117318	-1.8128449448	-1.8941288030
C	2.8996249197	-0.8306135247	0.6624345003
O	3.0399577819	-1.3469374763	1.7373557185
O	3.2782259213	-1.3552102149	-0.5062307672
C	3.8002334830	-2.6899957210	-0.4521141199
H	4.0044907035	-2.9626501210	-1.4847153914
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H	3.0542683937	-3.3581440871	-0.0172972698

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C	0.7851032535	1.9511044644	-0.4110516981
O	0.1129859367	2.7721194275	-0.9771624957
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C	2.7854079341	2.9032424836	-1.1790156195
N	0.8755745292	0.6926905509	1.7072268231
N	1.6574451925	-0.2472140774	1.8194055031
C	1.7322430344	-1.0788305747	0.5804075426
H	-1.8403899179	0.2324132436	-1.4419856526
H	0.9192835021	-0.4760570710	-1.3627358233
H	3.8388498477	2.6346530060	-1.1461772093
H	2.6176702924	3.8909905888	-0.7460568606
H	2.4097258499	2.8796937137	-2.2029183753
N	-1.2244863190	0.8129098429	0.5061148112
C	-3.4310805440	-0.4422583106	-0.1091636940
C	-3.7745042059	-1.7457279159	-0.8611066916
H	-4.8589191818	-1.8835068495	-0.8252789829
H	-3.4627056906	-1.7136242932	-1.9094103628
H	-3.3162101783	-2.6293080256	-0.4054919791
C	-3.6808796206	-0.6643432824	1.3869297344
H	-3.6067663005	0.2633019268	1.9550724310
H	-4.6892439498	-1.0683298531	1.5228960100
H	-2.9757809614	-1.3952703915	1.8001971783
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H	-5.3883241955	0.3844657157	-0.4736853523
H	-4.1492030857	1.6313644212	-0.2744886335
S	-0.8784209300	-1.6291506347	-0.3111729883
C	-1.6880531436	1.9402841212	1.1673693943
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O	-0.9026593844	-2.3077591006	-1.6519281558
H	1.6059328097	-2.1219563550	0.8954742901
C	3.1221958179	-0.9654688643	-0.0470966931
O	3.3269811930	-0.6978546243	-1.2037907143
O	4.0639086540	-1.2394254338	0.8501271164
C	5.4118255475	-1.1820017652	0.3652533127
H	6.0372538274	-1.4453881500	1.2151662963
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C	1.4723882525	-0.3450855058	0.4107461471
C	-0.9934568923	-0.1878827906	0.4578291826
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C	-1.7815732105	-1.3426406870	-0.1827783189
O	-1.4433846545	-2.4963202270	-0.1628643988
O	-2.8797340056	-0.8705828191	-0.7718304186
C	-3.7242077255	-1.8555590622	-1.3899194666
N	-1.8913716275	0.4736382022	1.4781006977
N	-2.1921607641	1.6195906108	1.1626867768
C	-1.6285894168	2.0442815993	-0.1335495540
H	1.5768043545	-0.9877934035	-0.4772940032
H	-0.8168937354	0.5998089674	-1.5991596215
H	-4.5685702015	-1.3025025793	-1.7945681577
H	-4.0530826678	-2.5792687133	-0.6424626912
H	-3.1767544662	-2.3705100866	-2.1811913085
H	-2.4641026217	2.1783201256	-0.8252636191
N	0.2218011573	-0.6495463485	1.1174513156
C	2.8284484696	-0.3155543064	1.1776307906
C	3.8198454990	0.5699305636	0.3916545297
H	4.8101510388	0.4396413459	0.8366482651
H	3.8833194271	0.2827258842	-0.6627681998
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C	2.6769287894	0.2488835618	2.5952724796
H	2.1050719334	-0.4217893055	3.2375778447
H	3.6754835486	0.3605759149	3.0301878147
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C	3.4325128623	-1.7307320467	1.1892214874
H	3.6545610216	-2.0573230505	0.1665528129
H	4.3791819955	-1.6993562542	1.7385124882
H	2.7818022331	-2.4592201391	1.6677389010
S	1.0572890439	1.2967952049	-0.3256641318
C	0.0219183992	-1.6150568890	2.0944000987
O	0.8747091135	-2.2722929135	2.6388260700
H	-1.0432082351	-1.6982682496	2.3552743284
O	1.1449309748	2.3586717562	0.6750526718
O	1.6954706806	1.4466630561	-1.6293332342
H	-1.1203123194	3.0009786309	0.0133700179

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C	-0.9671921690	-0.1701577389	0.5085117007
C	-0.6668896966	0.9390828575	-0.4934787494
C	-1.7689437808	-1.3092838137	-0.1463185377
O	-1.4368604165	-2.4645942843	-0.1470466572
O	-2.8670221227	-0.8259485584	-0.7287957783
C	-3.7080882870	-1.8012767927	-1.3663888296
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H	1.5807181672	-0.8877613504	-0.4859160240
H	-0.6800423185	0.6164645872	-1.5359602544
H	-4.5583602366	-1.2445769372	-1.7534116146
H	-4.0283001547	-2.5463295821	-0.6364842228
H	-3.1614072730	-2.2921992051	-2.1734167152
H	-2.6020673856	1.7739188831	-0.8221824932
N	0.2466509199	-0.6621226308	1.1446616891
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C	3.8453593500	0.5648642440	0.4383404644
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H	3.8785657979	0.3435916865	-0.6331585420
H	3.6156573532	1.6264761923	0.5659458047
C	2.7524075092	0.1378005313	2.6447849495
H	2.1963217266	-0.5621292345	3.2682233746
H	3.7661581034	0.2167253340	3.0510998420
H	2.2878424367	1.1251710012	2.6987522069
C	3.4299111849	-1.7740760045	1.1152170711

H	3.6198432767	-2.0521950357	0.0720304280
H	4.3895811691	-1.7912079740	1.6421633768
H	2.7737974305	-2.5116996641	1.5730363035
S	1.0579668161	1.3846673511	-0.1455301282
C	0.0485098072	-1.6432631498	2.1040261593
O	0.8970114130	-2.3245288013	2.6260731517
H	-1.0154775804	-1.7191626257	2.3730050104
O	1.1065847389	2.3247085931	0.9721686112
O	1.7211907063	1.6936401084	-1.4087997501
C	-1.3961734697	3.4689330832	-0.2767150995
H	-0.6688510818	3.7589696095	0.4802759817
H	-0.9816111985	3.6864875448	-1.2650599426
H	-2.3064075372	4.0570336483	-0.1456781892

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C	1.4049456321	-0.3653318612	0.4329491645
C	-1.0508056375	-0.2475880586	0.4901567417
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C	-1.7349625743	-1.4632049308	-0.1572177381
O	-1.3222487033	-2.5910604084	-0.0894167214
O	-2.8382469128	-1.0855865618	-0.8019195515
C	-3.5836392773	-2.1441788144	-1.4249400548
N	-2.0190887339	0.3535072356	1.4834759510
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H	-0.9476334792	0.5743724777	-1.5547737380
H	-4.4397531917	-1.6623672460	-1.8919000470
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H	4.7645364365	0.3831862695	0.6946564953
H	3.7742191331	0.1730151310	-0.7572164235
H	3.5279271762	1.5786489626	0.3009959355
C	2.6978524383	0.3158316430	2.5423778631
H	2.1449505827	-0.3143817168	3.2394606103
H	3.7146293438	0.4359975321	2.9305654455
H	2.2345081928	1.3044963664	2.4946530033
C	3.3715241131	-1.7425466007	1.2106827158
H	3.5432597986	-2.1266418641	0.1985223228
H	4.3418257314	-1.6962280973	1.7158121219
H	2.7342456775	-2.4349991975	1.7562693913
S	0.9747828579	1.2507713324	-0.3519208006
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O	0.8666468540	-2.1637204794	2.7827187822
H	-1.0654900966	-1.6574947643	2.4700257002
O	1.1165834224	2.3474014573	0.6046563111
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C	-2.8180169924	2.3601939671	-1.0507683498
H	-2.3775040200	2.7870010436	-1.9549533413
H	-3.3925255975	1.4693476680	-1.3178839680
H	-3.4916567051	3.0968894486	-0.6089643365
H	-1.1456588058	2.8973262943	0.2219408498

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C	-1.0501936927	-0.3722127289	0.2696493117
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H	2.7233837305	-1.3135489122	1.8124600413
H	4.1708730396	-0.3658869600	1.4591396132
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H	3.2604082673	-1.6674463472	-1.9371594406
H	4.4135695291	-1.8176281242	-0.6052656022
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S	0.7140839311	1.4433632893	-0.4702535413
C	0.3579934431	-2.1742976760	0.9813930057
O	1.3070396261	-2.9194178880	1.0042213999
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C	-1.4631828539	3.9020976686	1.8661392692
C	-1.1868029874	5.4340456408	-0.4494000770
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C	0.3349325330	2.1103596210	-0.6078650005
O	-0.4050171834	2.8378383213	-1.2164754968
O	1.6630345374	2.1711511058	-0.6166028300
C	2.2391367371	3.2076036124	-1.4259861981
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H	1.9393506566	3.0748329645	-2.4670158767
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H	-4.8315945410	-2.3508124482	-0.8487819803

H	-3.4365498916	-2.1021183983	-1.9093653240
H	-3.2264506967	-2.8467115333	-0.3105667433
C	-3.9539728151	-0.7655734288	1.2553516254
H	-4.0075286941	0.2217444256	1.7154765947
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H	-4.5728586934	1.2656989412	-0.6600705002
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O	-0.8019985504	-2.2505404272	-1.5908002910
H	1.1408994118	-1.6985217139	1.4328153495
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C	3.8100079628	0.1745092522	0.8095602900
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C	5.1255270900	0.0633164477	0.3598803203
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C	4.6120348632	-2.0678539952	-0.6453413753
H	2.5874327728	-2.7578864286	-0.3993680045
C	5.5280676396	-1.0528376222	-0.3699328296
H	5.8377605494	0.8513999257	0.5843794173
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C	-3.3373190690	-2.2071328424	-1.5646466387
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H	1.3467252413	-0.9834378391	-0.3959959968
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H	-4.1944329973	-1.7862317912	-2.0857602878
H	-3.6524260473	-2.9535347027	-0.8341553984
H	-2.6336953076	-2.6563929736	-2.2675362348
N	0.1439060466	-0.4886872299	1.2681033478
C	2.7726602169	-0.3531709296	1.1174292142
C	3.7582029680	0.3781750224	0.1801279854
H	4.7722032124	0.1783197758	0.5374549502
H	3.6857682518	0.0220660679	-0.8525692422
H	3.6135347392	1.4617428228	0.1831743131
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H	-3.7714125208	2.7717538587	-0.7635492737
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H	4.6955630497	2.4330215451	0.0799729846
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C	-3.0762410802	0.2723331314	-0.0202280789
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H	-4.8801456424	-0.8904073013	-0.0731759957
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C	-3.8184409997	1.3417946893	-0.8408184772
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H	-4.8384490889	1.4303773588	-0.4524638680
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S	-0.9175229184	-1.5396542461	-0.2612925427
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O	-1.2909104892	-2.4141898308	-1.3677750973
C	3.2714968210	-1.4917760735	-0.1040413568
C	4.3242671239	-1.2742460886	0.7920033381
C	3.5542466190	-1.5858666079	-1.4690591483
C	5.6291973951	-1.1383669833	0.3265758860
H	4.1190595325	-1.2054452453	1.8552476052
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C	5.9050802989	-1.2270712350	-1.0376701727
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H	6.9234373859	-1.1244324370	-1.3986019272
C	1.6077622972	-3.1576622523	0.7249457784
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C	1.2477390705	-5.8880431196	1.1884719267
H	1.6944459656	-5.4300209719	3.2437613531
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H	1.1004675610	-6.9476634532	1.3718031025

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C	1.1668504745	-0.2146164992	-0.5365112657
C	-1.1675427907	-0.4207474603	0.2556159374
C	-1.2603543799	0.9374000307	-0.4356731291
C	-2.1048849298	-1.4398349683	-0.4157884146
O	-1.7576621485	-2.5017076630	-0.8581786181
O	-3.3479036480	-0.9582329793	-0.4524958952
C	-4.3295456445	-1.8287321694	-1.0407297767
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C	2.6862616076	-0.2167657876	-0.1828010776
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H	4.4390251828	0.8893734326	-0.7431534807
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C	2.9262897063	-0.1428267889	1.3299535962
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S	0.4690251925	1.4964645017	-0.5558405318
C	0.3599335245	-2.1253195675	0.9638559481
O	1.3603029990	-2.7992188621	0.9858743740
H	-0.5593254582	-2.4177413713	1.4921521478
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O	0.7143939069	2.1138636102	-1.8523987061
C	-1.7563959050	3.1935859399	0.7630124856
O	-1.8208432394	3.7807639121	1.8044728123
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H	-0.5518455039	5.2718337531	-1.3820648031
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C	-0.9562802284	-0.3481445725	0.3194379103
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C	-1.8996050709	-1.3173301146	-0.4153394601
O	-1.5387996921	-2.3059297176	-0.9974503256
O	-3.1438653730	-0.8594279782	-0.3497714853
C	-4.1280002042	-1.5984624121	-1.0895761326
N	-1.4973163119	-0.1235748195	1.7056475601
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N	0.4046774192	-0.8585660785	0.4058605113
C	2.9001370595	-0.2770489943	-0.1691127226
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H	4.6791192259	0.7598212513	-0.7795506580
H	3.3473369020	0.9780777310	-1.9239699055
H	3.3664337744	1.8710453680	-0.3875140481
C	3.1697696568	-0.2069467788	1.3380710887
H	2.8226650822	-1.1050602790	1.8507609345
H	4.2507574588	-0.1279290064	1.4926638737
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C	3.5011413377	-1.5486859926	-0.7946778648
H	3.4031604603	-1.5187080758	-1.8859525508
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H	3.0422514075	-2.4591674638	-0.4159146698
S	0.7367755634	1.5134178460	-0.5125253538
C	0.5132495257	-2.1070904451	1.0012455119
O	1.4933932109	-2.8094029147	1.0272135614
H	-0.4256681961	-2.3886287098	1.5019963297
O	1.1112424247	2.2240928701	0.7099944686
O	0.9474080114	2.1218804380	-1.8201613278
H	-1.2113086009	2.7703278016	0.9865312423
C	-3.1381808478	2.3034024899	0.1634298656
O	-3.5344302910	2.1241655458	-0.9613483937
O	-3.8202592952	2.9155477655	1.1235375852
C	-5.1283148217	3.3738843390	0.7555478742
H	-5.5403480668	3.8262162188	1.6546291047
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C	1.5806166635	0.2315145928	0.1872562331
C	-0.9039291994	0.1893865296	0.3297937862
C	-0.7240380341	1.1408860858	-0.8532757966
C	-1.7154863280	-1.0753467962	0.0187667236
O	-1.4686161404	-2.1648311855	0.4627588015
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C	-3.6320467014	-1.8740374293	-1.0678402837
N	-1.7513449412	0.9805194720	1.3116882611
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C	-1.7372343371	2.2460164995	-0.5672758011
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H	-0.8251487733	0.6723855424	-1.8312742146
H	-4.4057686337	-1.4588384966	-1.7095382465
H	-4.0585540173	-2.2633380829	-0.1421306539
H	-3.0830360586	-2.6666441190	-1.5791380848
H	-1.3301794823	3.2573490739	-0.6442123124
H	-2.6271152112	2.1635812970	-1.1970492988
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C	2.1873649554	-0.8794529046	-0.7046717094
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H	2.8929040455	-2.8923172913	-0.4052024161
H	3.0160823135	-1.8846245411	1.0547323505
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C	1.2807311637	-1.2720002504	-1.8793052039
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H	0.3024239126	-1.6202368790	-1.5286123335

C	3.5485619227	-0.3972901670	-1.2256022778
H	4.2171712559	-0.1523043828	-0.3930582002
H	4.0182488252	-1.1999844711	-1.8027669354
H	3.4540400054	0.4781081648	-1.8724139922
S	0.9940277018	1.7367370600	-0.6893700956
O	0.9802175402	2.8433097424	0.2644726224
C	0.4712173807	-0.5481938142	2.2365971821
O	1.5265589808	-0.6913181676	2.8110223407
H	-0.5081667934	-0.7434288216	2.6937730448
O	1.5865787453	1.9117272983	-2.0118006924

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C	-1.2902059216	-1.5040308677	-0.1722038883
O	-0.7537362869	-2.5747546965	-0.0605521002
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C	-3.0948084753	-2.4760915328	-1.3072558426
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H	-4.0326630563	-2.1348891537	-1.7401112554
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H	-2.4602010017	-2.9395587582	-2.0647626841
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H	1.2606919996	0.3550241539	-2.4688835567
H	2.3595330233	-1.0111267874	-2.6946598459
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H	4.2669819999	0.4279466281	-1.8544001945
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C	0.8234105247	-1.0333902509	2.0800932055
O	1.8910747387	-1.0346956375	2.6556573666
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H	-2.0076903753	3.5532610018	-1.1983072623
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C	1.2290248130	1.3955897818	-0.1946617642
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C	3.0219283679	2.3253939883	-1.3809843840
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H	-1.0508321107	-3.4782324408	-1.1800920195
S	0.3729789894	-1.3038944713	-0.0003228771
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H	1.2720093216	-1.0906422681	2.3006573342
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C	3.7734911625	-1.7642875347	1.4063779180
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H	4.2619112822	-1.7356479753	2.3854514570
H	3.0926194564	-2.6215316297	1.3925136983
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C	2.4386198440	1.6290976823	-1.4671016072
O	3.6088634336	1.5118290666	-1.7641482225
H	1.8145529711	2.4766056595	-1.7843185727
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C	-2.8035966198	-0.6257112938	-0.4179252377
C	-3.7040457533	0.3865288582	-0.7509634598
C	-3.1598678355	-1.5670262590	0.5516645258
C	-4.9421710025	0.4579653259	-0.1133166653
H	-3.4362463350	1.1198780774	-1.5052341560
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H	-2.4652964268	-2.3650775457	0.8076272076
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C	0.8711865083	-0.9104899688	-0.4660117229
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H	-2.3522576630	-1.1172398045	0.9898924017
H	1.0107926633	-0.5942454058	-1.5012898026
H	3.2237218720	2.8314234904	-1.9741584887
H	2.5196012756	3.6750329113	-0.5534220595
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C	-2.5357930292	-0.0373131852	-0.8712658656
C	-3.3009711909	1.1472310927	-0.2653465380
H	-3.9718865969	1.5705363084	-1.0203058777
H	-3.8943248077	0.8393110908	0.6001227805
H	-2.6127317233	1.9338546900	0.0598587527
C	-1.6956413583	0.4593184898	-2.0525141573
H	-1.1488444679	-0.3594000459	-2.5315137805
H	-2.3551068234	0.9053440385	-2.8040537009
H	-0.9914487843	1.2398542575	-1.7457325033
C	-3.5335997364	-1.0908639790	-1.3658834905
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H	-3.0216699594	-1.9463176100	-1.8187876620
S	-0.5681055910	-2.0341611191	-0.3365153349
C	-1.1633699201	0.8162736206	2.1211335045
O	-2.2619850289	0.6727904015	2.6169673657
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C	2.2026831958	-2.9851545859	0.4230725899
H	2.0235256456	-3.5560610628	-0.4934671424
H	3.1833757900	-3.2610164522	0.8180698499
H	1.4397003504	-3.2513146620	1.1556430561
C	3.4057447317	-1.1379544569	-0.7542869699
H	3.3576721483	-1.7136639825	-1.6836705358
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C	-0.1667813838	4.2700640729	0.1356070001
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C	-1.3487702807	-0.0059770361	-0.3648946891
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H	0.0675910576	0.5339399221	1.2479780737
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C	3.4202256317	-0.5365059943	1.1020100167
C	4.6905823637	0.1308619515	0.5568525223
H	5.3849457081	0.3182567583	1.3827789803
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H	3.4414168917	0.6678306452	2.8936212427
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H	4.3060163844	-2.5291934126	1.1419091574
H	4.4771731347	-1.6206818752	2.6508543654
H	2.9128465557	-2.3382705700	2.2302149710
S	0.8690956504	-1.5985928520	0.3726283928
C	2.8989560590	0.4690043004	-2.1015704049
O	3.8928018199	-0.1527463636	-2.4139330552
H	2.4915394820	1.2976771050	-2.6990833328
C	-2.0210283261	-1.3774293765	-0.2931360950
C	-2.2999084725	-1.9326626104	0.9596375791
C	-2.3620719070	-2.0875891228	-1.4442639484
C	-2.8950398308	-3.1857382505	1.0611096213
H	-2.0448401544	-1.3877700773	1.8650997000
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C	-3.2317167644	-3.8949932090	-0.0916072909
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H	-3.2244079964	-3.8850004644	-2.2432070092
H	-3.6981649693	-4.8719286443	-0.0134864778
C	-2.3263410791	1.0437671396	0.1800748363
C	-3.2608142487	1.6266830801	-0.6811889261
C	-2.3481602649	1.3940543270	1.5322370881
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H	-3.2678240356	1.3502790500	-1.7303730870
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H	-1.6468548870	0.9505466815	2.2327978244
C	-4.1821024374	2.9192340263	1.1436222083
H	-4.8890836856	3.0095679747	-0.8886485247
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C	-0.5017049510	1.0525641513	0.3692191996
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C	-1.2501313112	2.1562562148	-0.3906732167
O	-2.4419392323	2.3124659562	-0.3745962265
O	-0.3845044784	2.9392547675	-1.0423710232
C	-0.9639591125	4.0620931145	-1.7246999693
N	0.2455500483	1.7590153466	1.4853490221
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C	1.8473084399	1.1388208362	0.0258133058
H	-1.3184544320	-1.9401151669	1.3974025109
H	0.4551690127	0.4817496516	-1.5299714896
H	-0.1299462876	4.5857099299	-2.1866644983
H	-1.4787842749	4.7040656540	-1.0079953186
H	-1.6729853984	3.7138873843	-2.4777784834
H	2.0755703691	1.9575039906	-0.6687039710
N	-1.3924996383	0.0711663537	0.9213859108
C	-2.1512314728	-1.8042798563	-0.5960088481
C	-3.5933234674	-1.6203699974	-0.1026182053
H	-4.2837986626	-2.0402072364	-0.8416191208
H	-3.7564087275	-2.1212518334	0.8556445201
H	-3.8360023008	-0.5609356515	0.0253750411
C	-1.9699833886	-1.0304198907	-1.9056660127
H	-0.9671803155	-1.1721281199	-2.3226601918
H	-2.6911946124	-1.3922217140	-2.6454847517
H	-2.1641920098	0.0388937099	-1.7635499290
C	-1.8842033662	-3.2948544152	-0.8338725364

H	-2.0182630863	-3.8705655838	0.0888541318
H	-2.5884849187	-3.6848396477	-1.5755019847
H	-0.8697415380	-3.4671028363	-1.2073106218
S	0.5923633895	-1.3843025317	0.0408302398
C	-2.1809514310	0.3672254308	2.0124004578
O	-2.8021917347	-0.4675981744	2.6340750123
H	-2.1912908002	1.4388523523	2.2569222106
C	3.1073310953	0.3065725009	0.1989358804
O	3.7990283587	0.2694983616	1.1784646538
O	3.3403663096	-0.3802829156	-0.9298163553
C	4.4680714242	-1.2633815403	-0.8830917662
H	4.5104177672	-1.7368645002	-1.8617206836
H	5.3799799306	-0.6977155020	-0.6830535817
H	4.3222243345	-2.0074178324	-0.0971405356

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C	-2.1398318403	-0.4993664708	0.3081733693
C	0.0554925229	0.6020886259	0.5552137267
C	0.4385356240	-0.6619960903	-0.2295746863
C	0.4922734911	1.9021408920	-0.1355774315
O	-0.2157066987	2.8544283632	-0.3285095570
O	1.7794948839	1.8193629872	-0.4762717676
C	2.3245448269	2.9653728861	-1.1442747034
N	0.8769020913	0.5123575493	1.8233478339
N	1.7370323055	-0.3612475875	1.7702446787
C	1.7267672937	-1.0923798736	0.4729892824
H	-2.8374872894	-0.8252525313	1.0869081659
H	0.6084052571	-0.4792025990	-1.2911567921
H	3.3479016525	2.6964703252	-1.3971222727
H	2.2994007583	3.8289155099	-0.4772677108
H	1.7467933267	3.1789147263	-2.0449142227
N	-1.3460406481	0.5914107082	0.8664949375
C	-2.9503613649	-0.1224978267	-0.9569228043
C	-3.8496681334	1.0760552621	-0.6232598625
H	-4.4903657601	1.2956823450	-1.4837046730
H	-4.4834039722	0.8745156154	0.2448534910
H	-3.2541993353	1.9686121772	-0.4072387527
C	-2.0441722332	0.2459321297	-2.1352069737
H	-1.4216046996	-0.5992573421	-2.4469734626
H	-2.6613486376	0.5368923905	-2.9913037945
H	-1.4069646199	1.1034041113	-1.8921863279
C	-3.8252577862	-1.3236540442	-1.3324372448
H	-4.4983992573	-1.5931921881	-0.5107147158
H	-4.4420039869	-1.0763162178	-2.2022081749
H	-3.2186607216	-2.1989009218	-1.5869370208
S	-0.9184843671	-1.8486561996	0.0546228643
C	-1.8447975313	1.3722434418	1.8853558416
O	-2.9694599703	1.2643012129	2.3247641086
H	-1.1164574228	2.1075440333	2.2576986172
H	1.7500737036	-2.1621157104	0.7124672818
C	2.9841352924	-0.8039849038	-0.3445194573
O	3.0032485378	-0.7873084990	-1.5501810439
O	4.0507722442	-0.6388963813	0.4321828139
C	5.2868915762	-0.4286336356	-0.2600459436
H	6.0412891433	-0.3263187956	0.5169215482
H	5.5051686262	-1.2802801706	-0.9071891866
H	5.2272861188	0.4775776965	-0.8661259782

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C	1.5484475254	0.2106360294	0.2531042288
C	-0.9127590656	0.0988305533	0.2424266975
C	-0.6509290358	1.0271831998	-0.9472384827

C	-1.6851079666	-1.1783976372	-0.1122672377
O	-1.4271177672	-2.2730892630	0.3143573251
O	-2.7017347727	-0.8948106920	-0.9303449041
C	-3.5554494334	-2.0014888056	-1.2586165177
N	-1.8348407522	0.8918554487	1.1454425104
N	-2.2068917045	1.9384050193	0.6256740771
C	-1.6699866399	2.1458072695	-0.7337552191
H	2.2349425533	0.6043382657	1.0114766867
H	-0.7423256503	0.5347126066	-1.9149069163
H	-4.3243634739	-1.5942093986	-1.9113106437
H	-3.9945709471	-2.4115899328	-0.3477294837
H	-2.9807624590	-2.7774908639	-1.7673057322
H	-1.2347453218	3.1487213945	-0.7628861587
H	-2.5121253177	2.0867257495	-1.4284740164
N	0.3232253602	-0.1852082225	0.9219194815
C	2.2591274933	-0.8871111973	-0.5739278982
C	2.4698957426	-2.1117429818	0.3261535806
H	3.0280809636	-2.8736482304	-0.2281565547
H	3.0289359328	-1.8504453183	1.2285191168
H	1.5127468606	-2.5440773027	0.6339861912
C	1.4447153284	-1.3087360103	-1.8038616134
H	1.3177022395	-0.4879102567	-2.5201529272
H	1.9700621743	-2.1139244290	-2.3266823982
H	0.4624859177	-1.6994850303	-1.5173890231
C	3.6226469286	-0.3427538970	-1.0201780110
H	4.2283005302	-0.0487764897	-0.1566450265
H	4.1695311933	-1.1186103129	-1.5648055379
H	3.5245929763	0.5237097139	-1.6827546532
S	1.0769812739	1.6841360781	-0.7652611998
O	0.9610220278	2.8527383343	0.1790301550
C	0.3446592657	-0.5954869782	2.2388902061
O	1.3665196139	-0.7241199294	2.8770320165
H	-0.6575185937	-0.7959524828	2.6425138823

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C	1.6216661973	0.3050723634	0.2739791251
C	-0.7696183973	-0.2417837085	0.4324495255
C	-0.7750700763	0.8548617902	-0.6335703995
C	-1.3625839396	-1.5787567636	-0.0310942489
O	-0.8813681723	-2.6552389548	0.2069895182
O	-2.4961611115	-1.3844951920	-0.7117852530
C	-3.1801390513	-2.5789606909	-1.1198032284
N	-1.7031401435	0.2968785712	1.5039325044
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C	-2.0607054358	1.6287372228	-0.3038915017
H	2.3104755580	0.6860493031	1.0371127028
H	-0.7689974651	0.4770995613	-1.6564534355
H	-4.0624421884	-2.2412588495	-1.6589949962
H	-3.4604446896	-3.1622992829	-0.2412064604
H	-2.5337860874	-3.1779437645	-1.7636551824
N	0.5593745648	-0.4095754167	0.9551213543
C	2.4183134927	-0.4899785885	-0.7862767665
C	2.9062090478	-1.7928298738	-0.1380949892
H	3.5356994843	-2.3365552755	-0.8503645978
H	3.4861476499	-1.5940382394	0.7668914356
H	2.0615232995	-2.4335514315	0.1347564911
C	1.5806798076	-0.8364401859	-2.0229510966
H	1.2683793229	0.0589027964	-2.5744314377
H	2.1804874745	-1.4441918120	-2.7075171196
H	0.6979226437	-1.4283310174	-1.7558119930
C	3.6262473462	0.3580649672	-1.2046875443
H	4.2601803777	0.5863954941	-0.3416654202
H	4.2327737574	-0.1920657622	-1.9307832247

H	3.3243779723	1.3029260401	-1.6693854131
S	0.7806946345	1.8282806263	-0.3666402339
C	0.7815787474	-0.9847980183	2.1884602627
O	1.8724627229	-1.0255542932	2.7144641434
H	-0.1292885579	-1.4058162145	2.6366143427
O	0.5468558627	2.6774463428	0.8575414337
C	-2.1130600362	3.1329804245	-0.5342679167
H	-1.4124715462	3.6570606317	0.1151637773
H	-1.8760272855	3.3568836991	-1.5789040150
H	-3.1257264443	3.4881202346	-0.3320900405
H	-2.8780677755	1.1526205825	-0.8612008525

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C	1.6470740254	0.3666019365	0.1561922975
C	-0.7337624251	-0.1531149108	0.4854208164
C	-0.8178152790	0.9485112035	-0.5765390766
C	-1.2892974006	-1.5199817662	0.0613094137
O	-0.7808040164	-2.5733797428	0.3436265629
O	-2.4292458761	-1.3824011119	-0.6195423754
C	-3.0845718527	-2.6089989472	-0.9754277360
N	-1.6482716383	0.3197739972	1.5965895047
N	-2.2432159812	1.3500752983	1.2987229901
C	-1.9303617452	1.8665793526	-0.0530297157
H	2.4003910225	0.7789035042	0.8368514896
H	-1.0142534587	0.5702033329	-1.5806794649
H	-3.9826524464	-2.3152446786	-1.5145679828
H	-3.3369006974	-3.1681153684	-0.0729369810
H	-2.4297602531	-3.2122703152	-1.6066866122
N	0.6201099920	-0.2597743471	0.9634448495
C	2.3393499676	-0.5257545156	-0.9032599813
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H	3.3511790988	-2.4317543797	-0.9449399696
H	3.4295317955	-1.6230989863	0.6382871243
H	1.9291312814	-2.4085775376	0.1171065003
C	1.4181043179	-0.8722753625	-2.0815788830
H	1.1039241116	0.0182207496	-2.6392036900
H	1.9575273843	-1.5176433223	-2.7818294210
H	0.5322089384	-1.4272265565	-1.7558765474
C	3.5671603194	0.2327729190	-1.4246589131
H	4.2615492945	0.4581342020	-0.6086754420
H	4.0986224388	-0.3815677679	-2.1582068732
H	3.2938303161	1.1742080833	-1.9137199759
S	0.8139089391	1.8452228059	-0.5825050799
C	0.9226983163	-0.7861672032	2.2012161064
O	2.0465670207	-0.8092815689	2.6542970162
H	0.0424803155	-1.1798451828	2.7282187463
O	0.7114819550	2.8758434762	0.5131238600
H	-1.5569179161	2.8843260993	0.1124123791
C	-3.2021400146	1.8890561382	-0.8947841095
H	-3.5802384826	0.8753051257	-1.0491494721
H	-3.9688574282	2.4804937747	-0.3899853808
H	-2.9964085655	2.3446159265	-1.8667759284

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C	-1.4951106883	-1.3236008734	0.5370339258
C	-0.8486950180	1.0449835135	0.4013555723
C	0.2464571342	0.3690892925	-0.4233829657
C	-1.6348664580	2.1213966155	-0.3589926524
O	-2.8338902895	2.2167321754	-0.3618163318
O	-0.8039834014	2.9454332784	-1.0042282401
C	-1.4329632780	4.0321074338	-1.7011984305
N	-0.0697064097	1.7522171864	1.5006544247

N	1.1349116888	1.7830144661	1.2668193712
C	1.4878911056	1.1937518160	-0.0493490446
H	-1.6154908774	-1.9650547337	1.4177503054
H	0.0607244441	0.3549516354	-1.4971088159
H	-0.6198036807	4.6132277331	-2.1303610865
H	-2.0145835349	4.6334566223	-1.0007584477
H	-2.0899327275	3.6429764506	-2.4810366217
H	1.5130138321	2.0598687733	-0.7243512975
N	-1.7234026247	0.0481007451	0.9563417329
C	-2.3917842254	-1.8514582397	-0.6052978473
C	-3.8554580154	-1.6203960927	-0.2045021028
H	-4.5110683880	-2.0501898457	-0.9691198564
H	-4.0817793124	-2.0852391993	0.7585521196
H	-4.0758034286	-0.5514431044	-0.1230198046
C	-2.1292336238	-1.1503801054	-1.9435559125
H	-1.1221870729	-1.3546922292	-2.3272338312
H	-2.8388923639	-1.5203627304	-2.6900839107
H	-2.2787840394	-0.0673191385	-1.8647316244
C	-2.1356018712	-3.3569103838	-0.7545114324
H	-2.3487468138	-3.8842924300	0.1811471489
H	-2.7898533495	-3.7695775061	-1.5287473956
H	-1.1009635639	-3.5722560320	-1.0422308930
S	0.3280856201	-1.3737885319	0.2015067124
C	-2.5177948458	0.3238314915	2.0490156009
O	-3.1606336387	-0.5197317871	2.6344043195
H	-2.5122527107	1.3878995549	2.3256985790
O	0.9517785342	-1.2838274029	1.5706992664
C	2.8394860226	0.5225151746	-0.1052116733
C	3.4355280440	0.3483707828	-1.3568430214
C	3.5034209015	0.0839660005	1.0414727736
C	4.6779118505	-0.2711958273	-1.4696986202
H	2.9275628905	0.7060257366	-2.2507574745
C	4.7527147981	-0.5217926336	0.9283188251
H	3.0291762764	0.1999518748	2.0094896422
C	5.3398929740	-0.7047211171	-0.3225781858
H	5.1306676814	-0.4042744721	-2.4472108158
H	5.2642430101	-0.8615021245	1.8231910803
H	6.3118814432	-1.1812988125	-0.4035320637

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C	2.3557819281	-0.5286051962	-0.2286021459
C	0.3180567824	0.8172607602	-0.5543114129
C	-0.2771039412	-0.5099475149	-0.0762532128
C	-0.0143331994	2.0203955279	0.3403418258
O	0.7691885308	2.8804817330	0.6480660058
O	-1.2978414179	1.9842398520	0.6934258721
C	-1.7681698872	3.0861929302	1.4810062485
N	-0.3775821134	1.0872379326	-1.8731565276
N	-1.2717578000	0.2794271725	-2.1020666208
C	-1.4424665973	-0.7489551086	-1.0515985417
H	3.1114291758	-0.8622237969	-0.9490064983
H	-0.5929820666	-0.5007607340	0.9670280454
H	-2.8300899925	2.9005921137	1.6306027919
H	-1.6023889828	4.0227202358	0.9457076638
H	-1.2385474896	3.1132417987	2.4352960527
N	1.7349138899	0.6712547607	-0.7573917155
C	2.9917925250	-0.4124435664	1.1781428288
C	3.9479576286	0.7872543598	1.1842028361
H	4.4498610644	0.8413659972	2.1560173874
H	4.7043368747	0.6976800731	0.4002483502
H	3.4040412738	1.7238764724	1.0271760958
C	1.9407677736	-0.2158123485	2.2787394952
H	1.2610520211	-1.0723664839	2.3632156806

H	2.4435703183	-0.1072070119	3.2446463664
H	1.3568824088	0.6964669291	2.1167294748
C	3.7848629481	-1.6981768664	1.4468708148
H	4.5589955237	-1.8453560907	0.6866024851
H	4.2791979329	-1.6307131349	2.4208631985
H	3.1417613824	-2.5846362167	1.4601655699
S	1.0277514031	-1.8166232172	-0.3012190236
C	2.4419855536	1.5224094720	-1.5803020545
O	3.6119113883	1.3617342251	-1.8519403978
H	1.8355121719	2.3575556005	-1.9579397568
O	0.9167869794	-2.2545333321	-1.7395801803
H	-1.3180588310	-1.7063039624	-1.5745143968
C	-2.8192398114	-0.6791857037	-0.4231113047
C	-3.6532706252	0.4264525313	-0.5917647947
C	-3.2522877580	-1.7499476036	0.3635702611
C	-4.9022258084	0.4622427596	0.0267341390
H	-3.3289255481	1.2565299751	-1.2115120036
C	-4.4960406818	-1.7099465797	0.9887532727
H	-2.6140148342	-2.6233089837	0.4836514065
C	-5.3246625769	-0.6010090062	0.8215684266
H	-5.5478849293	1.3229337563	-0.1192976329
H	-4.8214107118	-2.5477746077	1.5973308526
H	-6.2979958751	-0.5704879025	1.3009687733

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C	1.6881610211	0.4975752947	0.1692242958
C	-0.5858764127	-0.3376691957	0.5310659025
C	-0.8433203225	0.7867042680	-0.4803182803
C	-0.8724956657	-1.7830347214	0.0798848043
O	-0.2933276072	-2.7348871442	0.5346758869
O	-1.8417507438	-1.8591861696	-0.8336387240
C	-2.1924950459	-3.1893379190	-1.2457116037
N	-1.5643041809	-0.0592078605	1.6536484484
N	-2.3528340405	0.8364720331	1.3671033129
C	-2.1807631969	1.4110444998	0.0032327126
H	2.4179170369	0.9767780196	0.8310054704
H	-0.9207030763	0.4252258777	-1.5074290633
H	-2.9920848034	-3.0690294025	-1.9737686824
H	-2.5302558674	-3.7675859252	-0.3842958006
H	-1.3259922368	-3.6782252265	-1.6948099711
N	0.7735088356	-0.2486315378	1.0057758769
C	2.4366720419	-0.2781210216	-0.9405656070
C	3.0572344254	-1.5334887393	-0.3130747731
H	3.6676892053	-2.0490704052	-1.0620186207
H	3.6890091776	-1.2754574221	0.5412300815
H	2.2828422580	-2.2238486305	0.0367573991
C	1.5341164518	-0.6918285006	-2.1106622648
H	1.1110688625	0.1749084874	-2.6328162863
H	2.1277225465	-1.2513449077	-2.8406343953
H	0.7173405673	-1.3493311585	-1.7943334512
C	3.5511068873	0.6354028333	-1.4690980178
H	4.2433296489	0.9098162413	-0.6665489462
H	4.1234031526	0.1152281018	-2.2435244556
H	3.1523181593	1.5558792422	-1.9095262771
S	0.6475732204	1.9071857940	-0.4297287009
C	1.1737365154	-0.7394881674	2.2298973883
O	2.3091402999	-0.6355987172	2.6424283727
H	0.3615244696	-1.2286319751	2.7837604606
O	0.5354911372	2.8018414229	0.7768709685
C	-3.3657149655	0.9153688728	-0.8395511874
H	-4.2988926115	1.2032124790	-0.3491171623
H	-3.3289222600	1.3956136897	-1.8221627816
H	-3.3506250790	-0.1663021505	-0.9693845098

C	-2.2697321043	2.9371968732	0.1098996426
H	-1.6032531431	3.3367966528	0.8702419071
H	-2.0113728912	3.3896098935	-0.8535889438
H	-3.3026116659	3.2044213212	0.3458295750

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C	2.5813635551	-0.7780938195	-0.2150911612
C	0.7926072185	0.8630123050	-0.6933388232
C	0.0994671740	-0.1245522513	0.2371907306
C	0.7078302099	2.3117785297	-0.1686402914
O	1.2317805471	2.6576606834	0.8621946444
O	-0.0071767574	3.0948794899	-0.9616935402
C	-0.2268601839	4.4287505091	-0.4830286649
N	0.0060865924	0.7314878472	-1.9694597517
N	-1.0797427835	0.1916433166	-1.7831318053
C	-1.3265998386	-0.1458154054	-0.3285609011
H	3.1433035230	-1.3680799371	-0.9489213840
H	0.1763985781	0.1301986837	1.2917861526
H	-0.7885707227	4.9285273055	-1.2688818922
H	0.7287276646	4.9247725516	-0.3045066177
H	-0.8048525778	4.3894426269	0.4433809903
N	2.1667792870	0.4558916702	-0.8732710908
C	3.4251873737	-0.6398483257	1.0747268424
C	4.5816472439	0.3285705919	0.7941130440
H	5.2359499412	0.3721862454	1.6710426428
H	5.1693125707	0.0101914490	-0.0710733257
H	4.2051967828	1.3378244263	0.5993259464
C	2.6197767712	-0.1189973655	2.2711050921
H	1.8248082492	-0.8173075570	2.5635562111
H	3.2869506942	-0.0177537463	3.1332007832
H	2.1901952485	0.8662979301	2.0661748780
C	3.9919003802	-2.0274948789	1.4037847881
H	4.6094328166	-2.4062939777	0.5825665484
H	4.6205078458	-1.9672176338	2.2977179117
H	3.1989651508	-2.7565700240	1.6036874548
S	1.0062384999	-1.7300907983	-0.0026038910
C	2.8865056682	0.9443207880	-1.9421129859
O	3.9662616591	0.5141533042	-2.2816511795
H	2.3804335427	1.7812788178	-2.4501807960
O	0.6711017873	-2.2184440086	-1.3861434717
C	-2.0619974843	-1.4701639094	-0.1738288959
C	-2.4542707636	-1.8675837643	1.1074955387
C	-2.3415002051	-2.2904644238	-1.2663346949
C	-3.1149201508	-3.0780058387	1.2985176044
H	-2.2542370588	-1.2210053946	1.9597214515
C	-3.0153845376	-3.4952298312	-1.0738091725
H	-2.0074261902	-1.9978045881	-2.2550770405
C	-3.4008701222	-3.8931674782	0.2043646229
H	-3.4120198181	-3.3791726297	2.2981067200
H	-3.2261946352	-4.1311239392	-1.9278106874
H	-3.9187789789	-4.8361471571	0.3490416598
C	-2.2016027613	0.9975612331	0.2060348494
C	-3.3329175149	1.3525867240	-0.5412985206
C	-1.9370178590	1.6834316589	1.3927466610
C	-4.1664528217	2.3810374177	-0.1172228569
H	-3.5511718256	0.8166732898	-1.4603443799
C	-2.7815707951	2.7093023392	1.8230762607
H	-1.0742248419	1.4434235795	2.0060872160
C	-3.8936646151	3.0657767937	1.0683105181
H	-5.0354669787	2.6461600320	-0.7111067818
H	-2.5596946039	3.2261500145	2.7517520595
H	-4.5479811501	3.8649655294	1.4018717813

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C	-1.1428010636	-1.3007849570	0.4789637965
C	-0.4896256347	1.0707636208	0.3835252545
C	0.5998980669	0.4232156507	-0.4777765767
C	-1.2900106331	2.1588807502	-0.3458352859
O	-2.4851157585	2.2792953798	-0.2923957976
O	-0.4681621449	2.9633108083	-1.0257890627
C	-1.0999151747	4.0672296520	-1.6938907485
N	0.2738845543	1.7781777204	1.4853506497
N	1.4826252765	1.7972289049	1.2817864981
C	1.8551723100	1.1647136813	-0.0017819328
H	-1.2164859305	-1.9709872893	1.3434213262
H	0.4349851671	0.5193309110	-1.5502848512
H	-0.2966267133	4.6086266933	-2.1883913656
H	-1.6056484212	4.7002346302	-0.9630512754
H	-1.8257663617	3.6951816543	-2.4190800467
H	2.0656520356	1.9954220338	-0.6883199283
N	-1.3416116375	0.0589330510	0.9458182426
C	-2.1047044168	-1.7800545395	-0.6346884048
C	-3.5468695937	-1.5448327175	-0.1661629791
H	-4.2380143260	-1.9392891101	-0.9184849129
H	-3.7421421850	-2.0405811404	0.7883885619
H	-3.7501915217	-0.4768141647	-0.0405922161
C	-1.8846478478	-1.0281037436	-1.9533228470
H	-0.8901292796	-1.2133440435	-2.3770728558
H	-2.6176844029	-1.3672928735	-2.6918102436
H	-2.0326237266	0.0500795017	-1.8245624704
C	-1.8790845126	-3.2822941186	-0.8501022576
H	-2.0495768806	-3.8397673002	0.0769498818
H	-2.5818209109	-3.6578786486	-1.6003976320
H	-0.8659938544	-3.5019728693	-1.2032000114
S	0.6368448597	-1.3756695542	-0.0253615883
C	-2.1108824359	0.3094436801	2.0640527004
O	-2.7278088828	-0.5529684111	2.6494199499
H	-2.1087851538	1.3677325021	2.3602092234
O	1.4394079440	-1.4231385875	1.2519383972
C	3.1516344685	0.3755911862	0.1361023564
O	4.0011569508	0.5810114621	0.9542761984
O	3.2377667363	-0.5214993159	-0.8600155064
C	4.3522473807	-1.4186821340	-0.7598850034
H	4.2848773634	-2.0702909192	-1.6288430190
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H	4.2682308424	-1.9901866547	0.1672490623

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C	-2.1023725589	-0.4954006997	0.3090453743
C	0.0533972622	0.6692386742	0.5740552673
C	0.4729128722	-0.5746079024	-0.2160257344
C	0.4084571933	1.9852776665	-0.1342402495
O	-0.3505313754	2.9024870966	-0.3060095623
O	1.6843450114	1.9551499248	-0.5166680789
C	2.1665144207	3.1275443385	-1.1882873540
N	0.9116118007	0.6321612983	1.8184198198
N	1.7804866736	-0.2311033931	1.7675578387
C	1.7359201610	-1.0206251672	0.5065888753
H	-2.7774406595	-0.9023722449	1.0710725963
H	0.6498612795	-0.4010054309	-1.2781731091
H	3.2010066864	2.9099587635	-1.4447189114
H	2.0992177731	3.9887269174	-0.5214130198
H	1.5742126526	3.3113382026	-2.0861116439
N	-1.3396888297	0.5827447297	0.9139763502
C	-2.9063116219	-0.1328114458	-0.9631177036

C	-3.7851421664	1.0857552269	-0.6520413219
H	-4.4080095596	1.3109585170	-1.5240344821
H	-4.4337049041	0.8997803696	0.2080452391
H	-3.1720715918	1.9653302527	-0.4328166673
C	-1.9942429927	0.2020984734	-2.1503837641
H	-1.3889560210	-0.6566651441	-2.4648844284
H	-2.6088375903	0.4935065337	-3.0077150201
H	-1.3366963435	1.0480396506	-1.9232773099
C	-3.7994015694	-1.3284826220	-1.3186011886
H	-4.4738194852	-1.5733736677	-0.4914007914
H	-4.4134888944	-1.0842777435	-2.1908697436
H	-3.2149289525	-2.2217562937	-1.5631431679
S	-0.8648726815	-1.8389864879	0.0065915275
C	-1.8743857999	1.3278156420	1.9439663427
O	-3.0083359145	1.1890229854	2.3459766062
H	-1.1657367950	2.0607634528	2.3556496019
O	-0.5728858345	-2.4786541072	1.3407464429
H	1.6980662169	-2.0720779252	0.8216296856
C	2.9980137978	-0.8108644247	-0.3228674024
O	2.9994083695	-0.6966542426	-1.5243495798
O	4.0863227781	-0.8180299812	0.4384435665
C	5.3281251809	-0.6693484773	-0.2609411980
H	6.0984853144	-0.7018702822	0.5061659632
H	5.4547091308	-1.4837509740	-0.9765426730
H	5.3467935669	0.2848259411	-0.7913269921

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C	1.5520099230	0.2034885172	0.2310946255
C	-0.9128682401	0.1357784902	0.3336801407
C	-0.6872494299	1.0767859346	-0.8587658083
C	-1.7917806856	-1.0776197270	0.0048083273
O	-1.5664261134	-2.2048626373	0.3576504610
O	-2.8603128977	-0.6988473875	-0.7039687838
C	-3.7935209570	-1.7441727427	-1.0146560606
N	-1.7097436397	0.9745085167	1.3168934233
N	-2.1149370122	2.0184050379	0.8136881089
C	-1.7399982595	2.1581088619	-0.6098342676
H	2.2650567446	0.5159346064	1.0013395137
H	-0.8225230631	0.5747553974	-1.8171568169
H	-4.5951021261	-1.2649024695	-1.5723148583
H	-4.1713687165	-2.1892900195	-0.0927986984
H	-3.3041783082	-2.5124262935	-1.6160561946
H	-1.3919250558	3.1790878252	-0.7814856594
H	-2.6519235832	1.9912265554	-1.1924022033
N	0.3443172378	-0.2481227308	0.9153119385
C	2.2260830756	-0.8710162975	-0.6571746585
C	2.5435293062	-2.0947249173	0.2138808841
H	3.0959936681	-2.8290775149	-0.3816788500
H	3.1473357631	-1.8222603975	1.0840777000
H	1.6267514034	-2.5706602945	0.5753339613
C	1.3290694098	-1.3064081476	-1.8198402897
H	1.1240206164	-0.4757456473	-2.5034141248
H	1.8324947587	-2.0909996970	-2.3936235981
H	0.3850761328	-1.7276402566	-1.4556183541
C	3.5326899011	-0.2846010906	-1.2035873314
H	4.1939748213	0.0301094655	-0.3883311891
H	4.0629644465	-1.0412487349	-1.7902974912
H	3.3460176332	0.5776568493	-1.8516834256
S	1.0113325571	1.7131318741	-0.6685674205
C	0.4068525427	-0.7179712765	2.2086558761
O	1.4448291293	-0.8707594172	2.8167908653
H	-0.5820719825	-0.9451172349	2.6312052586

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C	1.5716832081	-0.1487626212	0.4222926924
C	-0.9121374340	-0.2134412822	0.4234615498
C	-0.6799328320	0.9886535009	-0.4881119684
C	-1.7083568324	-1.3623470804	-0.2104123276
O	-1.4750430415	-2.5274543766	-0.0277691318
O	-2.7095764355	-0.8871010660	-0.9545707696
C	-3.5732454163	-1.8804869043	-1.5308963297
N	-1.7970818678	0.3496977080	1.5293536015
N	-2.2310950522	1.4617115032	1.2486640819
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H	2.2744267595	0.0027367295	1.2499967664
H	-0.6650500235	0.7554870711	-1.5525574427
H	-4.3345302397	-1.3258838362	-2.0748690538
H	-4.0198916175	-2.4846344553	-0.7397270407
H	-3.0020960397	-2.5230871143	-2.2031917249
H	-2.6708417333	1.7090986925	-0.7414953742
N	0.3403200239	-0.6828347548	0.9772262140
C	2.2417324028	-0.9884391510	-0.6906126445
C	2.4410124932	-2.4049109676	-0.1294720964
H	2.9821857583	-3.0051378200	-0.8679662546
H	3.0166285751	-2.3889776645	0.7999697235
H	1.4815267598	-2.8918313122	0.0717747439
C	1.3969328521	-1.0796730588	-1.9678010032
H	1.2887163067	-0.1085541159	-2.4599203935
H	1.8946882917	-1.7523571307	-2.6729567774
H	0.4096304942	-1.5102458838	-1.7632967022
C	3.6116664485	-0.3730964068	-1.0089742308
H	4.2325529172	-0.3213444798	-0.1079199876
H	4.1316404948	-1.0065907576	-1.7344643142
H	3.5210105827	0.6301735145	-1.4318645895
S	1.0051692041	1.5378887096	-0.0390460752
C	0.3671403451	-1.4106440928	2.1526295048
O	1.3926709475	-1.7030572558	2.7246554345
H	-0.6337432872	-1.6969730237	2.5026248837
O	0.9342289506	2.3101362528	1.1991694811
O	1.6694234462	2.0862128490	-1.2181425286
C	-1.5697861434	3.4452983018	-0.1129751746
H	-0.8266970151	3.7351676649	0.6290349341
H	-1.2214000738	3.7517031020	-1.1032367009
H	-2.5080061119	3.9617378920	0.0992136392

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C	1.6192158317	0.0271198625	0.3335357945
C	-0.8515483258	-0.2364026225	0.4834194548
C	-0.7796652273	1.0385676803	-0.3570257144
C	-1.5376025741	-1.4409726948	-0.1775096855
O	-1.1952323887	-2.5816112629	-0.0104534640
O	-2.5832677207	-1.0532812497	-0.9084327320
C	-3.3502707653	-2.1154009344	-1.4983172470
N	-1.7531620088	0.1400282927	1.6477025406
N	-2.2333126065	1.2609900163	1.5188571580
C	-1.8323210490	1.9585526085	0.2754244520
H	2.3702728364	0.2150289261	1.1093565055
H	-0.9094578666	0.8815758120	-1.4281207413
H	-4.1666220924	-1.6277063627	-2.0268015655
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H	-2.7242938744	-2.6851494668	-2.1873940456
N	0.4682960651	-0.5885098842	0.9711441649
C	2.2587805707	-0.7527977666	-0.8410990441
C	2.5753800409	-2.1674726858	-0.3318150431
H	3.1014277014	-2.7155853841	-1.1201094420

H	3.2085904886	-2.1394917547	0.5589133941
H	1.6614275325	-2.7167727616	-0.0851539385
C	1.3409219543	-0.8655990717	-2.0666075670
H	1.1352903191	0.1074407595	-2.5209366224
H	1.8373445171	-1.4842893438	-2.8207013394
H	0.4000452511	-1.3692864145	-1.8187502706
C	3.5688455151	-0.0523506764	-1.2300996539
H	4.2491223101	0.0013421788	-0.3731078484
H	4.0675399932	-0.6308394515	-2.0141086797
H	3.3967961335	0.9580781577	-1.6084372531
S	0.9136626624	1.6706010529	-0.0839660273
C	0.6321851387	-1.3501281052	2.1134733325
O	1.7146314416	-1.5743264858	2.6065507238
H	-0.3168404761	-1.7272476113	2.5170911499
O	0.8924698644	2.4715391577	1.1379552966
O	1.4354579487	2.2380784542	-1.3234747825
H	-1.3922444576	2.9072262173	0.6015439336
C	-3.0645077417	2.2180902327	-0.5850862370
H	-3.5162078837	1.2771300905	-0.9064599994
H	-3.7983369139	2.7883606471	-0.0120599173
H	-2.7817586317	2.7991760363	-1.4660272226

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C	1.5560620158	0.1728236781	0.3590780284
C	-0.8657628078	-0.3778031601	0.4358270144
C	-0.8942239329	0.8228586607	-0.5060699482
C	-1.4519978180	-1.6686334789	-0.1533777123
O	-0.9900379461	-2.7642834892	0.0230554893
O	-2.5568951515	-1.4038092105	-0.8541358440
C	-3.2372930573	-2.5508185941	-1.3902377935
N	-1.7996896694	0.0359589104	1.5643431664
N	-2.4369377994	1.0469560860	1.2888802783
C	-2.1732350665	1.5588569586	-0.0763603640
H	2.2348576782	0.4740342506	1.1652967225
H	-0.8689554313	0.5677591211	-1.5651858398
H	-4.1129819877	-2.1578337439	-1.9015754718
H	-3.5252269370	-3.2214878295	-0.5792198304
H	-2.5818920173	-3.0777553538	-2.0856398506
H	-2.9995280355	1.1544817323	-0.6778404932
N	0.4695211320	-0.5879551338	0.9520367855
C	2.3511425653	-0.5414975212	-0.7598012802
C	2.8281115840	-1.8876338404	-0.1920536903
H	3.4640796797	-2.3792360284	-0.9352123434
H	3.4024209080	-1.7541402036	0.7286543353
H	1.9829728989	-2.5483355371	0.0258507638
C	1.5105826036	-0.8117105818	-2.0141450117
H	1.2025557060	0.1129433606	-2.5109565999
H	2.1113612923	-1.3853096778	-2.7266696712
H	0.6315326942	-1.4231903805	-1.7777253491
C	3.5731449980	0.3166451761	-1.1153853627
H	4.1976020680	0.4851419423	-0.2310521180
H	4.1825499724	-0.2112977258	-1.8556731598
H	3.2864152322	1.2841498762	-1.5335754734
S	0.6600147648	1.7084138454	-0.1150981475
C	0.6703248485	-1.2797887402	2.1321374182
O	1.7473443534	-1.3527440669	2.6792718656
H	-0.2433860603	-1.7570248788	2.5111031188
O	0.4546757156	2.4770687517	1.1073348082
O	1.1902770731	2.3368099659	-1.3206315443
C	-2.1870101589	3.0679875665	-0.1782224315
C	-1.8884014022	3.6560184039	-1.4089092248
C	-2.4986468372	3.8744988864	0.9163932657
C	-1.8923613078	5.0415425636	-1.5445972146

H	-1.6338448425	3.0346874573	-2.2646038906
C	-2.5082748299	5.2600809434	0.7753174536
H	-2.7169964322	3.4189135494	1.8758895412
C	-2.2049721880	5.8468602484	-0.4514199470
H	-1.6466812086	5.4893221349	-2.5021295626
H	-2.7446504777	5.8822297053	1.6326616339
H	-2.2059780710	6.9273652915	-0.5545039985

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C	1.6292146433	0.2099365011	0.3118504207
C	-0.8046814854	-0.2635443769	0.5388272386
C	-0.8609296966	0.9370049187	-0.4025729421
C	-1.4252865825	-1.5548468870	-0.0151744588
O	-0.9749935728	-2.6554231920	0.1649170186
O	-2.5465251139	-1.2715494852	-0.6721758492
C	-3.2832252033	-2.3932297847	-1.1798982313
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N	-2.3074396426	1.1819657322	1.4795941508
C	-2.0009062816	1.7972030875	0.1680522647
H	2.3670194624	0.5217570061	1.0600340462
H	-0.9818481578	0.6870289420	-1.4563783285
H	-4.1544781134	-1.9656452888	-1.6720134623
H	-3.5772499402	-3.0463741698	-0.3562722125
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N	0.5501711398	-0.4728385963	1.0068347038
C	2.3254763176	-0.5829730690	-0.8206978130
C	2.7935413698	-1.9189058457	-0.2225186145
H	3.3572492882	-2.4671044184	-0.9843311615
H	3.4376368024	-1.7648099370	0.6471731560
H	1.9446876082	-2.5380540305	0.0839965026
C	1.3989928913	-0.8752528717	-2.0086441237
H	1.0730810660	0.0386383896	-2.5130044974
H	1.9440848488	-1.4796581104	-2.7401095103
H	0.5293744928	-1.4661427248	-1.6997347323
C	3.5514238076	0.2140159815	-1.2889123740
H	4.2347626276	0.3999973154	-0.4531245689
H	4.0952842819	-0.3698170197	-2.0380712769
H	3.2732936905	1.1705069975	-1.7368670139
S	0.7607126124	1.7482791036	-0.1950090899
C	0.8030803017	-1.1398437299	2.1913981101
O	1.9083767335	-1.2259604285	2.6763221343
H	-0.0987831187	-1.5816290542	2.6361146906
O	0.6698815277	2.6157227777	0.9773956101
O	1.2076120295	2.2913041889	-1.4747031010
H	-1.6490220295	2.8101532201	0.4006616180
C	-3.2222283946	1.8838808262	-0.7241425157
C	-4.4167289887	1.2316848286	-0.4204580232
C	-3.1250899177	2.6353615728	-1.8982312847
C	-5.5040149798	1.3307264805	-1.2881374015
H	-4.4981119682	0.6499980685	0.4927510583
C	-4.2082739963	2.7261510613	-2.7671970023
H	-2.1957825531	3.1519076501	-2.1320647114
C	-5.4022423868	2.0728048335	-2.4627270711
H	-6.4344441833	0.8284276282	-1.0413363946
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H	-6.2509612742	2.1475618774	-3.1352076587

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C	-0.8294012050	0.8363738322	-0.3364284156
C	-1.1294934788	-1.7685394532	-0.1179628966

O	-0.6861803762	-2.8250284750	0.2486328429
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C	-2.5288987282	-2.8456507932	-1.6524512891
N	-1.6797308199	-0.1969264624	1.6564326380
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H	2.4365396261	0.4745991060	1.0669174203
H	-0.8851060523	0.6414855977	-1.4083143803
H	-3.2730966495	-2.5463368732	-2.3873755294
H	-2.9701499840	-3.4769859426	-0.8798220142
H	-1.7008460059	-3.3746637003	-2.1276852037
N	0.6471385374	-0.5510864676	1.0281986674
C	2.3906669766	-0.5580793407	-0.8475165464
C	2.8732412415	-1.9166314971	-0.3163834103
H	3.4470588509	-2.4208042908	-1.1007037906
H	3.5114022287	-1.7967410688	0.5633951226
H	2.0311341386	-2.5592303859	-0.0391516904
C	1.4828122119	-0.7918002340	-2.0629651800
H	1.1531395395	0.1470562141	-2.5168059950
H	2.0463633631	-1.3464153659	-2.8198447394
H	0.6109767417	-1.4062205817	-1.8120895667
C	3.6032453766	0.2849396844	-1.2679141888
H	4.2848969413	0.4312438769	-0.4231849314
H	4.1555991856	-0.2395475319	-2.0538884909
H	3.3040844955	1.2628824622	-1.6536849410
S	0.7696575404	1.7043525774	-0.0794931955
C	0.9328729768	-1.2296661739	2.1978842419
O	2.0493538818	-1.2935359511	2.6623888213
H	0.0490515514	-1.6952816675	2.6520038657
O	0.7353267731	2.4870686168	1.1526154725
O	1.1720989213	2.3318578313	-1.3360326887
C	-3.3072242861	1.2687270921	-0.7134472467
H	-4.2208334516	1.5892824486	-0.2072360599
H	-3.1892872026	1.8605776451	-1.6260627779
H	-3.3965082520	0.2155348290	-0.9789513997
C	-2.0304819671	3.0305982938	0.5011043329
H	-1.3800918646	3.2551693622	1.3432706055
H	-1.6539731112	3.5593627363	-0.3806271184
H	-3.0387573957	3.3922675534	0.7152523680

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C	-1.6637280449	-0.5466728437	0.3345061479
C	0.5392234084	0.5780831232	0.5215380992
C	0.9157367389	-0.5667037809	-0.4226599552
C	0.7432328490	2.0053453448	-0.0213925263
O	0.0401279797	2.9365292866	0.2734876095
O	1.8116253594	2.0587693424	-0.8043510980
C	2.1862851922	3.3531320887	-1.2965244894
N	1.5213419353	0.4265945079	1.6643617958
N	2.4120892847	-0.3749665020	1.4122703360
C	2.3395584905	-0.9717603725	0.0409996690
H	-2.2899901956	-1.0332635212	1.0910140318
H	0.8552543450	-0.2972321945	-1.4760649817
H	3.0842179197	3.1819950030	-1.8877337647
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N	-0.8126306318	0.4100873350	1.0141287008
C	-2.5519814664	0.0090235933	-0.8047700042
C	-3.3439954453	1.1922984927	-0.2271772251
H	-4.0373982370	1.5595166821	-0.9907544030
H	-3.9184224590	0.8977078795	0.6552710854
H	-2.6793167351	2.0145110234	0.0565832862
C	-1.7471625879	0.5013929390	-2.0148307970

H	-1.2190504237	-0.3140914913	-2.5178660508
H	-2.4357089388	0.9470808939	-2.7393624686
H	-1.0377204651	1.2879579955	-1.7319159322
C	-3.5308253055	-1.0910662808	-1.2381284172
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H	-4.2146132099	-0.6898978563	-1.9929229441
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S	-0.4112614294	-1.8084567557	-0.1249586583
C	-1.2226834084	0.9849014081	2.2025658255
O	-2.3086678879	0.7740365148	2.6942690480
H	-0.4672575591	1.6476602441	2.6443384028
O	-0.1089441405	-2.5581835816	1.0879877632
O	-0.7248841056	-2.4942032780	-1.3764326761
C	2.6375442079	-2.4695326576	0.1066716675
C	2.3379699529	-3.2800017419	-0.9903195219
C	3.2611252184	-3.0265002363	1.2232405485
C	2.6367459717	-4.6385164234	-0.9621133769
H	1.8448023905	-2.8664255172	-1.8658318543
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H	3.4959358523	-2.4040230373	2.0789322348
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C	4.5689199832	0.2329817531	-0.1893336241
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C	5.5836459475	0.8052071334	-0.9560001042
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H	2.5092334089	-0.7471175592	-2.7091476139
C	5.4917392469	0.8262341667	-2.3450840981
H	6.4504137641	1.2316164941	-0.4606504293
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H	6.2837617597	1.2681662610	-2.9411587532

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C	1.3921718137	0.3286280573	0.2799200061
C	-0.9768419039	-0.4097686270	0.3997981745
C	-1.1203693270	0.7543177743	-0.5830976207
C	-1.4493302751	-1.7645124204	-0.1473735417
O	-0.9002677007	-2.8110029132	0.0705459906
O	-2.5700492543	-1.6128877405	-0.8558621882
C	-3.1590429431	-2.8286311898	-1.3481880436
N	-1.9405744845	-0.0673515296	1.5232561173
N	-2.6622624083	0.8849758044	1.2498557116
C	-2.4191699226	1.4167193922	-0.1057180644
H	2.0465728361	0.7306770796	1.0622340379
H	-1.1367595027	0.4665486059	-1.6334878908
H	-4.0646532873	-2.5245619953	-1.8677344701
H	-3.3904050759	-3.4906189356	-0.5123502382
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H	-3.2537003950	1.0620151049	-0.7243364078
N	0.3694407456	-0.4762210778	0.9226441188
C	2.2380134151	-0.3918706701	-0.8000710731
C	2.8046237850	-1.6685501841	-0.1579898684
H	3.4727429446	-2.1554590980	-0.8754381106
H	3.3687340694	-1.4452643968	0.7514650291
H	2.0071081427	-2.3732338477	0.0980892435
C	1.4177030221	-0.7912385108	-2.0338356625
H	1.0415374760	0.0779951037	-2.5805187897
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H	0.5872688598	-1.4527376211	-1.7602395496

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H	4.0088247835	0.7868932802	-0.3334658736
H	4.0516431484	-0.0150974238	-1.9077387089
H	3.0593645005	1.4370385602	-1.6906484866
S	0.3908431894	1.7584244947	-0.3001821254
C	0.6330339263	-1.0930157364	2.1333118784
O	1.7139231386	-1.0428903151	2.6744315952
H	-0.2330615725	-1.6315098574	2.5399745311
O	0.1148832179	2.6177417798	0.8503313365
O	0.9044624737	2.3224558326	-1.5420580549
C	-2.4639998112	2.9418765039	-0.1189384077
O	-3.0252280964	3.6293918645	0.6851787119
O	-1.8180226287	3.3724165101	-1.2063191989
C	-1.5982786960	4.7883036490	-1.2764753200
H	-0.9963155249	4.9424451188	-2.1691600919
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H	-1.0581320262	5.1101317132	-0.3837569313

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C	1.6403414788	0.1984107545	0.3530507782
C	-0.8009202275	-0.2703915396	0.5011240377
C	-0.8187435190	0.9492786024	-0.4206770780
C	-1.4399396833	-1.5296895652	-0.1054604889
O	-0.9707625012	-2.6344042414	-0.0360977655
O	-2.5920078421	-1.2069665620	-0.6858529508
C	-3.3185841249	-2.2863764621	-1.2918850935
N	-1.7100648073	0.1225767215	1.6485559492
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C	-1.9681437945	1.7821377415	0.1258550407
H	2.3542272076	0.4757082260	1.1371364946
H	-0.9170112772	0.7313815027	-1.4848487807
H	-4.1804384122	-1.8234597765	-1.7673063012
H	-3.6263268771	-2.9996812523	-0.5253213443
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C	2.3722307020	-0.5442985121	-0.7918442277
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H	3.4035172032	-2.4225354765	-1.0090307913
H	3.4388991769	-1.7939113620	0.6543143369
H	1.9606234163	-2.5350034551	0.0146827048
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H	1.1820326525	0.1527908674	-2.5008480542
H	2.0394129657	-1.3692804279	-2.7525769831
H	0.5933199865	-1.3689947665	-1.7547620312
C	3.6123857522	0.2707346437	-1.1856380578
H	4.2685485096	0.4200542763	-0.3210224523
H	4.1802195338	-0.2815262951	-1.9408519613
H	3.3482047254	1.2455739494	-1.6017357089
S	0.7901933724	1.7571536256	-0.1185411215
C	0.7571452373	-1.2431597097	2.1383849958
O	1.8462618781	-1.3608159136	2.6513360336
H	-0.1597806502	-1.7014373635	2.5337835887
O	0.6360825900	2.5726215704	1.0848022928
O	1.2937322229	2.3546397527	-1.3495270836
H	-1.6863540867	2.8204902862	0.3405214779
C	-3.1793196694	1.8074998569	-0.8040616050
O	-3.1369906639	1.5123803685	-1.9719031969
O	-4.2601014846	2.2397042846	-0.1649653814
C	-5.4462488124	2.3473694643	-0.9631235520
H	-6.2105179897	2.7368029438	-0.2944990472
H	-5.2743443732	3.0268854692	-1.7996439069
H	-5.7288380412	1.3646818466	-1.3459376206

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C	-1.5130223643	0.3023605980	0.4352772059
C	0.8926301256	0.2521565206	0.2247498863
C	0.7134346417	-0.9893702672	0.8173085522
C	2.2389584488	0.8247431179	0.0594165175
O	2.5240156886	1.9541469930	-0.2765687783
O	3.1802266466	-0.1134953987	0.3222410421
C	4.5304297782	0.3370582945	0.1778875662
H	-2.0512352688	0.9061968717	1.1762666947
H	1.4620645616	-1.4053498424	1.4807944301
H	4.7228701678	1.1775971355	0.8471280491
H	5.1526490160	-0.5159281182	0.4427026750
H	4.7161991498	0.6488792067	-0.8522065550
N	1.5228307558	-0.6771622802	-2.0144709695
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C	1.0872633982	-2.5291999231	-0.5732160654
H	1.9544232367	-3.0515676318	-0.1773971677
H	0.1890047933	-3.1228416516	-0.7195770266
N	-0.2938730712	1.0216616249	0.0645750784
C	-0.3247035590	2.4093085116	0.1734236686
O	-1.3526692604	3.0178286329	0.3864164938
H	0.6491514285	2.8835709941	0.0250748084
C	-2.4779229523	-0.0528763537	-0.7195782357
C	-3.7273724995	-0.7101226482	-0.1163532160
H	-3.5052521727	-1.6710479990	0.3586823539
H	-4.1910322101	-0.0575051677	0.6309027860
H	-4.4636101416	-0.8919307117	-0.9054511746
C	-2.8998346562	1.2327177520	-1.4439784614
H	-2.0405901738	1.7342445955	-1.8983298365
H	-3.6065287708	0.9765448023	-2.2407665677
H	-3.3755236592	1.9398566272	-0.7608146003
C	-1.8305821096	-0.9933292378	-1.7377572878
H	-2.5463980817	-1.2279314590	-2.5318995748
H	-0.9622845970	-0.5198077720	-2.2040356487
H	-1.5332891963	-1.9434735819	-1.2788922418
S	-0.9769858618	-1.2006094700	1.4073870257
O	-0.9665360650	-0.8278771891	2.8670359024

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C	1.5173747929	0.5560836918	-0.3996914091
C	-0.8913476592	0.2784359386	-0.2239344361
C	-0.5856308596	-0.9902199480	-0.7213902052
C	-2.2649540834	0.7242904618	-0.0387371863
O	-2.6513615978	1.8408713023	0.2472390134
O	-3.1300657555	-0.3169439495	-0.2047483060
C	-4.5044705420	0.0153391805	-0.0018684804
H	2.0421257243	1.1364453666	-1.1656256899
H	-1.2769650269	-1.4919771395	-1.3881501014
H	-4.8069628167	0.8175083187	-0.6775606931
H	-5.0617538438	-0.8961153867	-0.2137264999
H	-4.6694843221	0.3380933621	1.0287911024
N	-1.3743972932	-0.5397964062	2.1370612602
N	-1.2849773474	-1.6130882764	1.7597432732
C	-1.0945673911	-2.4468353947	0.7122604912
N	0.2112042765	1.1885570541	-0.1996759728
C	0.0886489804	2.5110822417	-0.5945087014
O	1.0453645356	3.1985910612	-0.8962723567
H	-0.9429816756	2.8762263615	-0.5796008440
C	2.4330347923	0.5015989498	0.8457180410
C	3.7199054054	-0.2398870292	0.4638418109
H	3.5285935657	-1.2959949323	0.2472803938
H	4.1923548825	0.2141318432	-0.4150255453

H	4.4357625369	-0.1894482838	1.2903645293
C	2.7862368856	1.9410058861	1.2468228528
H	1.8932826324	2.5033652397	1.5332887518
H	3.4691714554	1.9193141694	2.1029969407
H	3.2668299394	2.4803920936	0.4258686190
C	1.7573531420	-0.1887092428	2.0265759819
H	2.4550209547	-0.2570276477	2.8676997628
H	0.8800289865	0.3756175001	2.3556225392
H	1.4476820581	-1.2052851704	1.7646703419
S	1.1308733203	-1.1043696214	-1.1402341049
C	-0.0340311947	-3.5108067653	0.8089557144
H	-0.3472057930	-4.3449856579	1.4430016058
H	0.1437669114	-3.8975124906	-0.1982691039
H	0.9099592085	-3.1075626285	1.1778165720
H	-2.0688115047	-2.7624751021	0.3373961584

TS1a2x
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C	1.4585121632	0.4746943376	-0.4266526954
C	-0.9576350179	0.2726343129	-0.2444840487
C	-0.6791330059	-1.0146417919	-0.7066870804
C	-2.3211731086	0.7608074220	-0.0958798743
O	-2.6816029530	1.8949994099	0.1534780794
O	-3.2158754276	-0.2549348286	-0.2668505170
C	-4.5811936990	0.1197667284	-0.0806467759
H	2.0082901045	1.0550020676	-1.1751564658
H	-1.4049921979	-1.5213527324	-1.3342800479
H	-4.8581361178	0.9158491487	-0.7743790837
H	-5.1632052027	-0.7799617884	-0.2780967278
H	-4.7436370749	0.4672477156	0.9424653580
N	-1.5770950416	-0.5077411147	2.1166829273
N	-1.4027024006	-1.5789709893	1.7658196239
C	-1.0470619315	-2.4217507735	0.7716532780
N	0.1725850969	1.1468975300	-0.2173978220
C	0.0993223270	2.4856139775	-0.5681066892
O	1.0811579553	3.1417416491	-0.8601183095
H	-0.9158868240	2.8919221044	-0.5291442120
C	2.3601260984	0.3585826786	0.8256910501
C	3.6446990728	-0.3768715671	0.4250023766
H	3.4448607140	-1.4141646561	0.1379209033
H	4.1401333106	0.1260862497	-0.4135611771
H	4.3438913377	-0.3890231055	1.2670104201
C	2.7233612508	1.7751826897	1.2947011291
H	1.8352654930	2.3300965339	1.6104350774
H	3.4065115146	1.7093087516	2.1483272605
H	3.2067821038	2.3491848465	0.4996913217
C	1.6645200789	-0.3762223236	1.9680907566
H	2.3404836474	-0.4563816607	2.8255682067
H	0.7739242409	0.1708463097	2.2904136816
H	1.3839055281	-1.3926866162	1.6705112211
S	1.0203214176	-1.1533122142	-1.2027958210
C	-2.1230866246	-3.3499456993	0.2636233123
H	-3.0293411633	-2.7846241790	0.0339140192
H	-1.7585982680	-3.8153247668	-0.6560185411
H	-2.3561728264	-4.1476983219	0.9737139236
H	-0.0636211003	-2.8524432341	0.9575482922

TS1a3n
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C	-1.0305765011	-1.6389322686	0.3994106639
C	-1.4593083034	0.7428292982	0.1593095316
C	-0.2455174402	0.8240204403	0.8529580451
C	-2.2792132976	1.9281214160	-0.0766060926
O	-3.4158032960	1.9731852297	-0.5021291799

O	-1.5745022131	3.0575587961	0.2131409388
C	-2.2797586929	4.2770253971	-0.0298678670
H	-1.5407636595	-2.3117071447	1.0967115819
H	-0.0920504377	1.6247684181	1.5664138771
H	-3.1966074889	4.3101673205	0.5616348935
H	-1.6007099303	5.0741158792	0.2691798274
H	-2.5354744758	4.3631272600	-1.0882095321
N	-0.5561928524	1.4472831222	-2.0069952882
N	0.4597649619	1.7127388805	-1.5510541884
C	1.1557736611	1.7858501579	-0.3844419061
N	-1.9836053365	-0.5804901638	0.0451944489
C	-3.3298133863	-0.8712396222	0.2065634548
O	-3.7338992220	-1.9918583704	0.4500705498
H	-3.9841415239	-0.0054656746	0.0697345128
C	-0.5153712935	-2.4947209794	-0.7818141502
C	0.5124124308	-3.4952032194	-0.2377928449
H	1.4200736281	-2.9917573419	0.1107646600
H	0.0958003519	-4.0789817353	0.5915090202
H	0.7987152104	-4.1961124675	-1.0282935283
C	-1.6979106037	-3.2693338564	-1.3797729590
H	-2.4568691003	-2.5923987912	-1.7815073769
H	-1.3369708048	-3.9029132924	-2.1972373453
H	-2.1829228626	-3.9026558855	-0.6314823448
C	0.1203580474	-1.6320024147	-1.8670628013
H	0.5449218541	-2.2694362838	-2.6502918635
H	-0.6241319274	-0.9767417563	-2.3292412908
H	0.9296678024	-1.0245394642	-1.4506413433
S	0.3159753846	-0.7770559152	1.3448462523
H	1.0649569017	2.7941352860	0.0212343017
C	2.4827360606	1.1485241697	-0.2913948166
C	3.1525778112	1.2320486425	0.9352895244
C	3.0634864633	0.4285560989	-1.3398794067
C	4.3700883812	0.5853609277	1.1180429005
H	2.7101706172	1.7960840835	1.7534050987
C	4.2832650479	-0.2163281534	-1.1533769780
H	2.5696732192	0.3848570580	-2.3069630090
C	4.9379059380	-0.1452159682	0.0749640018
H	4.8749984953	0.6523784800	2.0763476365
H	4.7263555553	-0.7700979503	-1.9750582289
H	5.8889618259	-0.6482996425	0.2156926200

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C	2.4398030272	-0.4215476074	-0.4338742357
C	0.4930064741	1.0319874682	-0.2759859895
C	-0.1589934277	-0.1456990425	-0.6546048764
C	-0.2150350664	2.3115732232	-0.2531729052
O	0.2609243711	3.4233239554	-0.1347143544
O	-1.5522162162	2.1049755374	-0.3620751130
C	-2.3527415307	3.2851495683	-0.3225093316
H	3.2042402965	-0.3869361750	-1.2169151234
H	-1.0597521781	-0.0928353345	-1.2564564966
H	-2.0790657410	3.9599595857	-1.1363118508
H	-3.3807018733	2.9419502615	-0.4380704757
H	-2.2198532455	3.8044492688	0.6298829678
N	-0.2901383768	1.0263327399	2.0335763766
N	-0.9316235370	0.0941043383	1.8599596462
C	-1.3074868082	-0.8316955347	0.9397779484
N	1.9182187635	0.9428601787	-0.2830750936
C	2.7412767817	1.9782743636	-0.7009395750
O	3.9022496773	1.8037893203	-1.0178992511
H	2.2513222075	2.9559973575	-0.6937066862
C	3.0988382671	-1.0342917285	0.8258230641
C	3.5784385599	-2.4473985871	0.4710657301

H	2.7401975659	-3.1158000372	0.2500215488
H	4.2476147709	-2.4302579122	-0.3968800726
H	4.1343974609	-2.8715351752	1.3130368702
C	4.3154247776	-0.1789895427	1.2092295373
H	4.0169452524	0.8371179600	1.4822488915
H	4.8151603977	-0.6310298980	2.0727170209
H	5.0307088947	-0.1040376010	0.3859867080
C	2.1443214557	-1.0882241314	2.0160519613
H	2.6391893775	-1.5688198090	2.8661369437
H	1.8554692383	-0.0801817713	2.3259642311
H	1.2471907393	-1.6722225300	1.7826556668
S	1.0118427688	-1.4036478306	-1.0955492282
H	-0.8340918431	-1.7951698717	1.1274748106
C	-2.7331772222	-0.8584358273	0.5501310230
C	-3.1776798443	-1.9204610328	-0.2448391640
C	-3.6214011381	0.1710064526	0.8812330675
C	-4.4901850084	-1.9479220945	-0.7098021883
H	-2.4913206562	-2.7243099341	-0.5008528830
C	-4.9340227112	0.1334263572	0.4248123264
H	-3.2831721745	0.9953970548	1.5032667634
C	-5.3723571957	-0.9227118950	-0.3751197560
H	-4.8246638412	-2.7749593570	-1.3277986100
H	-5.6200113858	0.9296914323	0.6970351905
H	-6.3974641039	-0.9481211630	-0.7300700340

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C	1.4989790542	0.5304746652	-0.3944156793
C	-0.9048727251	0.2255989924	-0.1935606533
C	-0.5936277370	-1.0438025918	-0.6979521461
C	-2.2724807047	0.6979969598	-0.0163078300
O	-2.6295989301	1.8143321190	0.3067375796
O	-3.1681049547	-0.3028726620	-0.2350216403
C	-4.5320023971	0.0601817078	-0.0155292284
H	2.0180217820	1.1140356023	-1.1619758791
H	-1.2901481189	-1.5380026950	-1.3676645620
H	-4.8270032888	0.8639433541	-0.6930108083
H	-5.1124895941	-0.8401345506	-0.2159345389
H	-4.6762883651	0.3917689708	1.0151135950
N	-1.3986228168	-0.6368182097	2.0999164188
N	-1.2787490899	-1.7167768765	1.7455379608
C	-1.0229612506	-2.5622665082	0.7080438349
N	0.1897960725	1.1501339837	-0.1904290088
C	0.0551996532	2.4639608678	-0.6137500191
O	1.0053500599	3.1482698503	-0.9426442388
H	-0.9755709533	2.8284782804	-0.5951671603
C	2.4117295166	0.4983378435	0.8552169182
C	3.6734215069	-0.3066110446	0.5245108582
H	3.4457310096	-1.3652902449	0.3637881938
H	4.1659817695	0.0809409854	-0.3751783538
H	4.3862630865	-0.2353250371	1.3520372124
C	2.8149218046	1.9442579850	1.1828551434
H	1.9434573167	2.5544347650	1.4350104444
H	3.4950459977	1.9446789092	2.0414457353
H	3.3168347149	2.4221166314	0.3364560464
C	1.7053757396	-0.0974744151	2.0691542085
H	2.3852585568	-0.1079627621	2.9275075900
H	0.8248490225	0.4939229230	2.3373982050
H	1.3912857421	-1.1271136496	1.8812709814
S	1.1207322834	-1.1251226939	-1.1462488014
C	-2.2624431222	-3.2708770232	0.1970278257
H	-3.1039658486	-2.5846958986	0.1056466177
H	-2.0306815115	-3.6749499972	-0.7932949674
H	-2.5326414359	-4.1125978296	0.8430868496

C	0.1755602444	-3.4668964656	0.8776813651
H	-0.0678393213	-4.3192447216	1.5209596784
H	0.4434894234	-3.8527780422	-0.1100206486
H	1.0466475387	-2.9478648168	1.2748120311

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C	-2.3666804994	-0.3732930314	-0.8523556570
C	-0.5314647745	-1.4851185231	0.1700139268
C	0.2089176765	-0.5861142501	-0.6017184837
C	-0.2021878999	-2.9174103369	0.2540095146
O	-0.9806419502	-3.8032053590	0.5311684186
O	1.1116733633	-3.1273369032	0.0255979576
C	1.5340594329	-4.4886205450	0.1236224133
H	-2.4818824257	-1.1325113068	-1.6391631451
H	1.0404747535	-0.9502399298	-1.1940683514
H	1.0104829193	-5.1029951791	-0.6119882679
H	2.6042840913	-4.4772447067	-0.0763591248
H	1.3295268509	-4.8770588873	1.1236591679
N	0.5411139655	-1.2236812809	2.1458852649
N	1.2602897112	-0.3952400073	1.8072361909
C	1.5591419554	0.4260958364	0.7467737190
N	-1.8885402440	-1.0699329821	0.3565594642
C	-3.6451239942	0.4895969018	-0.8415481496
C	-3.6611197049	1.2768657445	-2.1675737587
H	-2.8966556245	2.0602818044	-2.1932554697
H	-3.5114421411	0.6169428114	-3.0298487012
H	-4.6352873032	1.7616402888	-2.2814985281
C	-4.8884125899	-0.4165167923	-0.8505143507
H	-4.9460640156	-1.0465757887	0.0351566150
H	-5.7847252174	0.2120534812	-0.8869846704
H	-4.8906292449	-1.0491411974	-1.7458552172
C	-3.6774145956	1.4886669574	0.3185463079
H	-4.5680232397	2.1194299051	0.2230537639
H	-3.7243679548	0.9819805970	1.2840464709
H	-2.7985140713	2.1411465805	0.2873617738
S	-0.8649139761	0.6206689005	-1.3453471866
C	-2.5531421958	-1.4649465638	1.4913603145
O	-3.7136734382	-1.2469050514	1.7751125219
H	-1.8805844446	-2.0173278467	2.1636150616
C	1.0912490156	1.8277376226	0.9787412529
C	1.8896286536	2.9314782817	0.6643022921
C	-0.1842199715	2.0397377899	1.5206304077
C	1.4151167576	4.2244214119	0.8795982833
H	2.8867195103	2.7856356216	0.2628576027
C	-0.6460650932	3.3291529373	1.7527027932
H	-0.8244009149	1.1897561699	1.7495042919
C	0.1507318707	4.4271603077	1.4264714486
H	2.0443880888	5.0731311100	0.6312866093
H	-1.6340385879	3.4763041852	2.1779158709
H	-0.2135993137	5.4346203348	1.6006287255
C	2.8943553145	0.1651236640	0.1387906944
C	3.1383612813	0.6365634291	-1.1585098636
C	3.8840497217	-0.5765808351	0.7897935715
C	4.3524220188	0.3784972456	-1.7854151013
H	2.3680173277	1.2029168826	-1.6775622467
C	5.0966747404	-0.8401716302	0.1545479542
H	3.7113712104	-0.9400142414	1.7986823972
C	5.3372078633	-0.3620315123	-1.1305560754
H	4.5264649118	0.7513245470	-2.7897901804
H	5.8575694544	-1.4148407597	0.6731553580
H	6.2842939660	-0.5636239022	-1.6203678912

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C	1.4524847008	-0.7928015746	0.5722012968
C	-0.9018906803	-1.1785991102	0.1712246679
C	-1.0412787794	-0.0808461156	1.0178659604
C	-1.8413481174	-2.3117266273	0.2412360961
O	-1.5976339300	-3.4593461964	-0.0553289808
O	-3.0580801419	-1.8978193927	0.6632017664
C	-4.0374129355	-2.9342674840	0.7798381143
H	1.6705698043	-1.5183424372	1.3683088540
H	-1.7807790073	-0.0950697185	1.8082277503
H	-3.7067556642	-3.6880308776	1.4970421697
H	-4.9444235772	-2.4434897842	1.1282371936
H	-4.2021203723	-3.4100769842	-0.1888309784
N	-1.9261884205	-0.3588935399	-1.7021374625
N	-2.1810683370	0.6577307555	-1.2454081533
C	-2.1186682197	1.3735312378	-0.0975552181
H	-3.0793445819	1.4760902429	0.3987505775
N	0.4226539065	-1.3665746063	-0.3206315948
C	2.7983763883	-0.2966631284	-0.0277011829
C	3.4183223565	0.7151282016	0.9594784594
H	2.8846973447	1.6706127190	0.9666073965
H	3.4431166213	0.3208111577	1.9822650564
H	4.4504719967	0.9153046808	0.6573352542
C	3.8058751634	-1.4552787310	-0.1304346904
H	3.4384442939	-2.2719641162	-0.7473802256
H	4.7348227477	-1.0767783749	-0.5708342146
H	4.0462705144	-1.8361530250	0.8691596518
C	2.5851156597	0.3957337317	-1.3775093377
H	3.4961476309	0.9360867180	-1.6564961530
H	2.3627401208	-0.3251232406	-2.1661401157
H	1.7627343028	1.1180703810	-1.3152688849
S	0.5497044584	0.6226617174	1.3834009248
C	0.6049441377	-2.1725772510	-1.4208684596
O	1.6662978467	-2.5569253163	-1.8650761829
H	-0.3536046306	-2.4332482249	-1.8886563603
C	-1.2560297004	2.5821085121	-0.0925582853
O	-1.2713242814	3.3706522245	0.8215239862
O	-0.4285531677	2.6270054562	-1.1374220001
C	0.5652228475	3.6581723473	-1.0757841666
H	1.1535318747	3.5500601099	-1.9848619731
H	0.0877517176	4.6386378174	-1.0323372710
H	1.1865381096	3.5119798459	-0.1886162847

TS1a6x

0 1

C	2.2364853556	-0.0293380555	-0.3824536772
C	0.0061058237	0.9372979077	-0.2914015513
C	-0.3397410401	-0.3279494000	-0.7856625341
C	-0.9826939476	2.0125495980	-0.2257987479
O	-0.7917314958	3.1845530252	0.0266984147
O	-2.2251826142	1.5093173150	-0.4465849608
C	-3.2899145256	2.4408609831	-0.2545770213
H	3.0128087075	0.2252820868	-1.1115744157
H	-1.1715424764	-0.4398572837	-1.4723399693
H	-3.1690763528	3.3012729915	-0.9151821188
H	-4.2026504841	1.8970235085	-0.4937805688
H	-3.3075389358	2.7831437871	0.7830846208
N	-0.8354847636	0.6096014434	1.9651197979
N	-1.2800643571	-0.4097673934	1.7047270841
C	-1.4282727536	-1.2898578869	0.6765099089
N	1.4087231844	1.1707363925	-0.2023116062
C	1.9922772234	2.3920144974	-0.5069401916
O	3.1785866295	2.5084898121	-0.7431802624
H	1.2875922920	3.2288889853	-0.4896558671

C	2.9498225515	-0.5582819304	0.8858662048
C	3.7674354711	-1.7925089522	0.4836939419
H	3.1242744929	-2.6227206738	0.1742865832
H	4.4538143794	-1.5592921947	-0.3383907987
H	4.3681314502	-2.1316933971	1.3334295568
C	3.9057118458	0.5257781565	1.4032419691
H	3.3601278023	1.4221119294	1.7118282487
H	4.4498573579	0.1407474713	2.2722919580
H	4.6265651084	0.8249226754	0.6378055731
C	1.9675996155	-0.9217882515	1.9970835714
H	2.5085369969	-1.3622374624	2.8406412523
H	1.4496262353	-0.0310125628	2.3626202078
H	1.2326736018	-1.6589597783	1.6528044247
S	1.1099051966	-1.2686992503	-1.1777175901
H	-0.8709932383	-2.2142586964	0.8060713912
C	-2.8113998282	-1.4455022304	0.1457908095
O	-3.0306576514	-2.1126009069	-0.8370219591
O	-3.7318762671	-0.7519999274	0.8199136253
C	-5.0569827443	-0.8249630146	0.2800256563
H	-5.4177304133	-1.8548334921	0.3089434488
H	-5.6653151502	-0.1845659932	0.9158345477
H	-5.0620262822	-0.4725358325	-0.7538459564

TS1b1
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C	-1.5130223652	0.3023606003	0.4352772044
C	0.8926301247	0.2521565209	0.2247498867
C	0.7134346401	-0.9893702650	0.8173085564
C	2.2389584479	0.8247431168	0.0594165138
O	2.5240156877	1.9541469899	-0.2765687886
O	3.1802266456	-0.1134953987	0.3222410431
C	4.5304297773	0.3370582927	0.1778875632
H	-2.0512352714	0.9061968756	1.1762666908
H	1.4620645594	-1.4053498383	1.4807944362
H	4.7228701678	1.1775971387	0.8471280395
H	5.1526490149	-0.5159281183	0.4427026783
H	4.7161991487	0.6488791967	-0.8522065605
N	1.5228307555	-0.6771622922	-2.0144709674
N	1.3931358334	-1.7381175847	-1.6143663210
C	1.0872633957	-2.5291999270	-0.5732160535
H	1.9544232334	-3.0515676344	-0.1773971524
H	0.1890047906	-3.1228416558	-0.7195770129
N	-0.2938730715	1.0216616263	0.0645750774
C	-0.3247035582	2.4093085128	0.1734236693
O	-1.3526692596	3.0178286347	0.3864164924
H	0.6491514300	2.8835709947	0.0250748115
C	-2.4779229513	-0.0528763528	-0.7195782381
C	-3.7273724947	-0.7101226569	-0.1163532208
H	-3.5052521636	-1.6710480132	0.3586823361
H	-4.1910322034	-0.0575051869	0.6309027914
H	-4.4636101399	-0.8919307123	-0.9054511784
C	-2.8998346618	1.2327177540	-1.4439784579
H	-2.0405901815	1.7342446062	-1.8983298273
H	-3.6065287721	0.9765448042	-2.2407665680
H	-3.3755236717	1.9398566222	-0.7608145941
C	-1.8305821039	-0.9933292287	-1.7377572946
H	-2.5463980765	-1.2279314541	-2.5318995799
H	-0.9622845965	-0.5198077542	-2.2040356563
H	-1.5332891792	-1.9434735715	-1.2788922535
S	-0.9769858637	-1.2006094646	1.4073870297
O	-0.9665360670	-0.8278771774	2.8670359049

TS1b2n
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C	-1.5729350829	0.4315804414	0.4218563138
C	0.8313976591	0.5108954971	0.2606181761
C	0.7277216667	-0.7011327258	0.9288099959
C	2.1382910395	1.1444035954	0.0279483426
O	2.3518329738	2.2538031459	-0.4110614257
O	3.1369147788	0.2845035428	0.3484648742
C	4.4561949756	0.7908665082	0.1249051379
H	-2.1617785075	0.9985201426	1.1538138782
H	1.4602253727	-1.0180040480	1.6625732861
H	4.6186689394	1.6982392494	0.7095421992
H	5.1319368234	0.0003222985	0.4470376608
H	4.5992247126	1.0164478465	-0.9340821952
N	1.4697347951	-0.5283216658	-1.9260321416
N	1.5233402354	-1.5621301973	-1.4391852066
C	1.4375444569	-2.2912427337	-0.3090804677
N	-0.3913045733	1.2175267415	0.0750567582
C	-0.4887958396	2.5977882027	0.2234942340
O	-1.5483663867	3.1545561777	0.4217102664
H	0.4663613744	3.1198160087	0.1162169828
C	-2.4855130567	0.0334244806	-0.7593874838
C	-3.6542407151	-0.8000314086	-0.2157397509
H	-3.3292139301	-1.7768901146	0.1559728957
H	-4.1666014630	-0.2773046324	0.5993487425
H	-4.3836853878	-0.9726037711	-1.0131600744
C	-3.0473654639	1.3073669970	-1.4058919727
H	-2.2489465012	1.9306193564	-1.8170029823
H	-3.7190450153	1.0258797910	-2.2241962209
H	-3.6012290787	1.9122955025	-0.6833792806
C	-1.7196480360	-0.7560393621	-1.8206972881
H	-2.4023149415	-1.0737702475	-2.6154265157
H	-0.9352132528	-0.1416666961	-2.2712143797
H	-1.2621670414	-1.6580914253	-1.3999119597
S	-0.9722045059	-1.0436326712	1.4069913103
O	-1.0910283824	-0.7102976213	2.8732232678
C	0.5707197129	-3.5227530209	-0.2690273199
H	1.0632409525	-4.3765611354	-0.7430603994
H	0.3931923955	-3.7762512368	0.7796049807
H	-0.3970675171	-3.3622160601	-0.7450136055
H	2.4350378149	-2.3921527522	0.1200603673

TS1b2x
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C	1.4130672740	0.4800760209	-0.4036093598
C	-0.9875445526	0.2927062240	-0.2272342557
C	-0.7154299530	-0.9933757314	-0.6667330600
C	-2.3684210745	0.7921120341	-0.1353712005
O	-2.7276757016	1.9323347097	0.0667372033
O	-3.2499879222	-0.2263125088	-0.2955950664
C	-4.6253615060	0.1582804120	-0.2188826927
H	1.9328174041	1.0216412080	-1.2036646964
H	-1.4247838764	-1.5357197511	-1.2827421064
H	-4.8654745824	0.8676052100	-1.0131986783
H	-5.1944348637	-0.7619913797	-0.3427742999
H	-4.8366856939	0.6178759874	0.7487045165
N	-1.6054216635	-0.4403997532	2.0849011422
N	-1.3960307521	-1.5287960090	1.8048926923
C	-1.0141723928	-2.4174463692	0.8689718622
N	0.1416504330	1.1570751327	-0.1487574701
C	0.0825855641	2.5155116634	-0.4472126532
O	1.0730005188	3.1615902105	-0.7200595661
H	-0.9251483656	2.9352939028	-0.3852640947
C	2.3671742124	0.3411647905	0.8048436007
C	3.6568494460	-0.3396266517	0.3256704008
H	3.4879783944	-1.3738426248	0.0098071270

H	4.1011966595	0.2064853233	-0.5133128045
H	4.3877331397	-0.3549322550	1.1402417411
C	2.7149217320	1.7401007171	1.3319995910
H	1.8262743622	2.2563554979	1.7058526090
H	3.4283582916	1.6428860570	2.1575156596
H	3.1568430608	2.3632995410	0.5509982434
C	1.7356720765	-0.4647582874	1.9402557730
H	2.4390213646	-0.5463679345	2.7750143118
H	0.8341459380	0.0320028993	2.3092550714
H	1.4900122993	-1.4850361020	1.6235116107
S	0.9971065413	-1.1602481919	-1.1987273274
O	1.0084933700	-0.9646441136	-2.6929594165
C	-2.0753899520	-3.3586337029	0.3543080922
H	-2.9840180142	-2.8038830982	0.1088281245
H	-1.6953582648	-3.8288521251	-0.5565156962
H	-2.3090262728	-4.1502137332	1.0709768747
H	-0.0375932082	-2.8438031189	1.0937085276

TS1b3n
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C	-1.0839127935	-1.6147563649	0.4142040852
C	-1.5038220902	0.7470227712	0.1535223167
C	-0.2982091818	0.8365254133	0.8414663869
C	-2.3334344294	1.9451128698	-0.0678304347
O	-3.4697179535	1.9901188518	-0.4854289310
O	-1.6266903139	3.0626435864	0.2312077396
C	-2.3360774347	4.2889983250	0.0280876026
H	-1.5887562067	-2.2483241778	1.1537526782
H	-0.1225928545	1.6193502620	1.5706532546
H	-3.2365350203	4.3111315632	0.6443977268
H	-1.6476584276	5.0784850842	0.3244281324
H	-2.6175235197	4.3922561089	-1.0219468208
N	-0.5965849180	1.4699797527	-1.9891473981
N	0.4324948660	1.7130106927	-1.5457478650
C	1.1546039631	1.7642750862	-0.4019245320
N	-2.0167864852	-0.5695816497	-0.0071716041
C	-3.3731280956	-0.8740294704	0.0674930960
O	-3.7707674157	-1.9978482097	0.2936427010
H	-4.0289190721	-0.0194782877	-0.1187161837
C	-0.5116156817	-2.5020240893	-0.7139432812
C	0.3959938828	-3.5648843230	-0.0783708068
H	1.2892422839	-3.1287436913	0.3799740321
H	-0.1419927373	-4.1335919728	0.6879070913
H	0.7284856355	-4.2691859171	-0.8472634569
C	-1.6611569271	-3.2086672581	-1.4449488662
H	-2.3294171750	-2.4891347432	-1.9264600946
H	-1.2430378168	-3.8575062309	-2.2222424929
H	-2.2605673921	-3.8143107768	-0.7610104643
C	0.2791953054	-1.6669300003	-1.7199727163
H	0.7253506266	-2.3184875804	-2.4790173665
H	-0.3765580566	-0.9550806010	-2.2299138798
H	1.0956879636	-1.1241313047	-1.2309036681
S	0.2706628915	-0.7779633794	1.3982935761
O	-0.0874444184	-0.8655596297	2.8617726900
H	1.0692557166	2.7607786787	0.0326060619
C	2.4861944849	1.1288057755	-0.3353235587
C	3.1575356194	1.1705030960	0.8927852572
C	3.0771896060	0.4737873240	-1.4205903661
C	4.3903732947	0.5442052687	1.0396003888
H	2.7047185691	1.6814392453	1.7394434865
C	4.3134254774	-0.1487247509	-1.2691727397
H	2.5758444969	0.4620027922	-2.3849690737
C	4.9709905351	-0.1198098619	-0.0406329644
H	4.8966115541	0.5746162795	1.9988790891

H	4.7661524568	-0.6519758869	-2.1174937958
H	5.9343321880	-0.6059616691	0.0729559683

TS1b3x
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C	2.3671897355	-0.3705496695	-0.4339150118
C	0.4837098562	1.1370838345	-0.2545085942
C	-0.2051549707	-0.0175656451	-0.6046719261
C	-0.1855565362	2.4512886393	-0.2802823178
O	0.3297268362	3.5447744654	-0.1876275139
O	-1.5219964833	2.2872358583	-0.4012495102
C	-2.2803031158	3.4983665570	-0.4204950083
H	3.0774836425	-0.3494355862	-1.2696348141
H	-1.1225190838	0.0302445996	-1.1816110322
H	-1.9657773076	4.1305357281	-1.2529636109
H	-3.3175876313	3.1890187689	-0.5450714020
H	-2.1445604682	4.0443613939	0.5160126871
N	-0.3294701665	1.1956676286	2.0159328410
N	-0.9374722534	0.2306270393	1.8981001799
C	-1.2823718893	-0.7635482238	1.0460610309
N	1.8993989476	0.9994288759	-0.2065848083
C	2.7818204691	2.0254235449	-0.5360379928
O	3.9360826585	1.8105905019	-0.8428108617
H	2.3405594018	3.0229377182	-0.4685215040
C	3.0336639331	-1.0829822373	0.7667395791
C	3.5587814139	-2.4419501981	0.2816514955
H	2.7527188010	-3.1054963209	-0.0479507436
H	4.2614409644	-2.3178391889	-0.5489919402
H	4.0885033928	-2.9426227951	1.0981126401
C	4.2215110248	-0.2488159185	1.2662717930
H	3.8950015079	0.7252225770	1.6421223054
H	4.7106138912	-0.7840570332	2.0873568567
H	4.9508109433	-0.0725050710	0.4727232496
C	2.0602924926	-1.2865508114	1.9290636861
H	2.5814632796	-1.7518055487	2.7715002511
H	1.6622943060	-0.3286878517	2.2754131221
H	1.2372190068	-1.9547395641	1.6528331712
S	0.9173993832	-1.3259845884	-1.1245898577
O	0.9983456508	-1.2548060723	-2.6270956617
H	-0.7827543317	-1.6972160605	1.2991061019
C	-2.6971316471	-0.8733856605	0.6339450133
C	-3.1090689350	-2.0602157618	0.0195468164
C	-3.5962062016	0.1921990273	0.7536676517
C	-4.4060289893	-2.1807740362	-0.4722642060
H	-2.4097726777	-2.8869948794	-0.0783013651
C	-4.8946383901	0.0610412860	0.2741808806
H	-3.2774401661	1.1187258056	1.2235642999
C	-5.3024785496	-1.1223630534	-0.3431452350
H	-4.7153147944	-3.1035866180	-0.9520962957
H	-5.5926918060	0.8854977704	0.3809386764
H	-6.3155081439	-1.2182512262	-0.7198501158

TS1b4
0 1

C	1.4567320453	0.5394986036	-0.3821033598
C	-0.9283284999	0.2441990606	-0.1856716029
C	-0.6250499087	-1.0190494315	-0.6842384880
C	-2.3130159711	0.7186772966	-0.0290623859
O	-2.6720361687	1.8321050502	0.2887002699
O	-3.1935438607	-0.2827449380	-0.2622576722
C	-4.5677569522	0.0806732928	-0.1026939584
H	1.9541226022	1.0812808277	-1.1964061271
H	-1.2999503463	-1.5404369811	-1.3554037057
H	-4.8335898557	0.8739649875	-0.8036552875

H	-5.1369639677	-0.8236141654	-0.3144676942
H	-4.7517305134	0.4260522385	0.9167632583
N	-1.4111958516	-0.6021192794	2.0734688327
N	-1.2681844564	-1.6944498570	1.7587512863
C	-1.0015212974	-2.5650783339	0.7526125213
N	0.1614590075	1.1648957647	-0.1385789460
C	0.0348151041	2.4987593256	-0.5191912634
O	0.9913963967	3.1758869075	-0.8329715716
H	-0.9903060310	2.8754421410	-0.4783831100
C	2.4092839023	0.4897877164	0.8345049438
C	3.6637515423	-0.3098165261	0.4558734733
H	3.4544623350	-1.3770097122	0.3323121827
H	4.1034629135	0.0616361464	-0.4766969048
H	4.4155120747	-0.2058039203	1.2443899637
C	2.8289747182	1.9260605806	1.1814227609
H	1.9695892628	2.5368883227	1.4692313559
H	3.5302813375	1.8998616833	2.0225157295
H	3.3128720202	2.4174908596	0.3329294056
C	1.7341522987	-0.1264036247	2.0580975620
H	2.4348989903	-0.1510925322	2.8989622865
H	0.8591241705	0.4577604167	2.3578448531
H	1.4161492836	-1.1546213898	1.8658371581
S	1.1069276660	-1.1258539982	-1.1624987857
O	1.1614945438	-0.9495448206	-2.6603420946
C	-2.2357596847	-3.2742519268	0.2301185438
H	-3.0745830281	-2.5875184404	0.1221563166
H	-1.9918190643	-3.6891799175	-0.7525293718
H	-2.5146513862	-4.1077724610	0.8830682790
C	0.1917661787	-3.4763735234	0.9351705095
H	-0.0716554895	-4.3314169692	1.5672399001
H	0.4720846141	-3.8620654781	-0.0489783465
H	1.0606090557	-2.9752143354	1.3596424139

TS1b5
0 1

C	-2.3238155777	-0.3720773082	-0.8059840932
C	-0.5274164055	-1.5251949150	0.2196067581
C	0.2397973667	-0.6801868844	-0.5614044375
C	-0.2599736058	-2.9682558884	0.3657138839
O	-1.0789350170	-3.7961068748	0.6960614558
O	1.0315609949	-3.2522052059	0.1114353250
C	1.3823252880	-4.6329834514	0.2355121855
H	-2.3822040355	-1.1260158555	-1.6072258637
H	1.0369358058	-1.0513463482	-1.1970831010
H	0.7925311834	-5.2365481157	-0.4572527781
H	2.4413504861	-4.6883654058	-0.0098213812
H	1.2005398705	-4.9778724348	1.2556508592
N	0.6525638720	-1.2417982249	2.1990398452
N	1.3382200599	-0.4216543179	1.7878292390
C	1.5921749108	0.3969144249	0.7252351823
N	-1.8584432418	-1.0404658746	0.4217175327
C	-3.5943744163	0.4943319150	-0.8397226577
C	-3.6145948146	1.2132652273	-2.2051251010
H	-2.8462842401	1.9895421950	-2.2822112001
H	-3.4658533097	0.5170314578	-3.0363532531
H	-4.5879264709	1.6974998139	-2.3277305959
C	-4.8392876399	-0.4078797510	-0.7905499908
H	-4.8984820477	-0.9812428182	0.1330269205
H	-5.7340108811	0.2196037040	-0.8660163383
H	-4.8420988287	-1.0944347541	-1.6447306386
C	-3.6131646712	1.5554668777	0.2650718421
H	-4.5023257429	2.1833662684	0.1424855954
H	-3.6504069330	1.1073598709	1.2593939095
H	-2.7358956317	2.2078040612	0.1880861806

S	-0.7954067015	0.5831185275	-1.3666849089
O	-0.6553093538	0.3311205562	-2.8497012128
C	-2.5095267044	-1.3484330181	1.5936566408
O	-3.6486833507	-1.0618579429	1.8968238819
H	-1.8422574182	-1.8989873198	2.2736184086
C	1.0833510376	1.7888484160	0.9593388659
C	1.8275471490	2.9074001063	0.5776166874
C	-0.1684952028	1.9721065464	1.5632190329
C	1.3198333198	4.1896421754	0.7858154819
H	2.8051823395	2.7818267813	0.1250116032
C	-0.6630011195	3.2507945659	1.7838659969
H	-0.7702293920	1.1104220518	1.8485223222
C	0.0789595434	4.3658528519	1.3907207996
H	1.9057894566	5.0511182943	0.4820322016
H	-1.6348985833	3.3764318787	2.2509138272
H	-0.3113152026	5.3649469535	1.5556677665
C	2.9162216765	0.1740289830	0.0760284151
C	3.0881151822	0.5899786811	-1.2513091686
C	3.9666208309	-0.4693725358	0.7347661296
C	4.2970469297	0.3700866643	-1.9018975223
H	2.2690851555	1.0737275126	-1.7803564362
C	5.1731595093	-0.6961635475	0.0743309845
H	3.8454498046	-0.7852852437	1.7669069929
C	5.3438079397	-0.2745820471	-1.2412840655
H	4.4161340071	0.6941831161	-2.9306528957
H	5.9818590897	-1.1982185983	0.5957621744
H	6.2855247309	-0.4483637963	-1.7516022875

TS1b6n
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C	1.4122544332	-0.7069898483	0.5087321662
C	-0.9074875930	-1.1164419736	0.1392938519
C	-1.0598795786	-0.0382450382	0.9946523287
C	-1.7744876471	-2.3098931798	0.2200909597
O	-1.4754253546	-3.4205254948	-0.1520481500
O	-2.9718388292	-1.9949319609	0.7536579831
C	-3.8741339852	-3.0969409133	0.9038910121
H	1.4891226250	-1.3919534845	1.3678773485
H	-1.7216327916	-0.0641189841	1.8533562047
H	-3.4262003828	-3.8662367681	1.5354169760
H	-4.7655391350	-2.6838404864	1.3721037669
H	-4.1107288610	-3.5255126987	-0.0720569788
N	-2.1476478630	-0.3140700848	-1.6522093944
N	-2.3595854382	0.6908310289	-1.1552561840
C	-2.1839240598	1.4340481287	-0.0434419810
H	-3.0889465308	1.5690377778	0.5411586120
N	0.3980436242	-1.2188879608	-0.4290718014
C	2.8266386330	-0.3164676221	0.0302402494
C	3.4714367188	0.5481239597	1.1355418585
H	3.0395059917	1.5536768921	1.1890076816
H	3.3742136719	0.0902541881	2.1247621672
H	4.5356080330	0.6612053606	0.9090334437
C	3.7031660060	-1.5728736382	-0.1069953975
H	3.2933690363	-2.2872298582	-0.8176027170
H	4.6988993419	-1.2734267273	-0.4513955107
H	3.8210888869	-2.0567911410	0.8690526822
C	2.7869171557	0.4985832638	-1.2668713156
H	3.7820962724	0.9117773324	-1.4623899277
H	2.4954530481	-0.1114539166	-2.1223119152
H	2.0899677769	1.3404087390	-1.1748596301
S	0.5477107489	0.7560848435	1.3177644862
O	0.7988495201	0.6229583961	2.7959675247
C	0.5540166032	-1.9036304278	-1.6157833592
O	1.6004522536	-2.1944286497	-2.1528748697

H	-0.4210791102	-2.1582170670	-2.0538595938
C	-1.3183412516	2.6407053416	-0.1759654135
O	-1.3267291877	3.5314838466	0.6354777865
O	-0.5018554389	2.5554428724	-1.2283011970
C	0.4548245597	3.6198100981	-1.3383534539
H	1.0160471901	3.4136266547	-2.2472731892
H	-0.0604178996	4.5793872412	-1.4043866824
H	1.1093838074	3.6144309590	-0.4629974280

TS1b6x
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C	2.1905760588	-0.0016850436	-0.3721414989
C	-0.0145396068	0.9835709357	-0.2693787980
C	-0.3787391157	-0.2839952457	-0.7152063984
C	-0.9993758251	2.0830970582	-0.2754207717
O	-0.7916368650	3.2640275246	-0.1024649627
O	-2.2388537859	1.5795832767	-0.4674227798
C	-3.2954220701	2.5409634143	-0.4146592820
H	2.9271683336	0.2314269770	-1.1509140831
H	-1.2134780319	-0.4319625893	-1.3923583461
H	-3.1659798301	3.2898078492	-1.1981063564
H	-4.2125702095	1.9755330437	-0.5718692129
H	-3.3070431069	3.0344645858	0.5595534771
N	-0.8667258959	0.7246643231	1.9703564228
N	-1.2623420220	-0.3289797058	1.7710437458
C	-1.3807808426	-1.2823400451	0.8156817238
N	1.3838396285	1.1991946019	-0.1410866486
C	1.9955753246	2.4279795275	-0.3764520924
O	3.1842517756	2.5241680413	-0.5973999088
H	1.3100787628	3.2779599615	-0.3196525311
C	2.9294789768	-0.5870258768	0.8543935840
C	3.7775205778	-1.7744990951	0.3762072124
H	3.1639511616	-2.6060285743	0.0150966788
H	4.4557484757	-1.4738723638	-0.4293680841
H	4.3868326283	-2.1466885442	1.2056885754
C	3.8629628869	0.4774451419	1.4463366526
H	3.3016463131	1.3430791365	1.8094748026
H	4.4069761795	0.0427103691	2.2918394512
H	4.5823060888	0.8352701285	0.7062703191
C	1.9591350149	-1.0446865576	1.9448042435
H	2.5166571443	-1.4930440959	2.7729742502
H	1.3988465876	-0.1959083965	2.3450197552
H	1.2628221345	-1.8070293600	1.5751626623
S	1.0699903077	-1.2514172966	-1.1923283667
O	1.2117051072	-1.0750382453	-2.6800577511
H	-0.8010383510	-2.1816250089	1.0052284206
C	-2.7549681051	-1.5160274137	0.2836398841
O	-2.9512831481	-2.2952085411	-0.6162345407
O	-3.6851106027	-0.7509623070	0.8560868564
C	-4.9982042027	-0.8800943380	0.2945015861
H	-5.3554458420	-1.9050312691	0.4093306923
H	-5.6231962579	-0.1878618297	0.8549174137
H	-4.9768287519	-0.6226531537	-0.7665829963

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C	1.4465734188	0.4554489829	-0.3750969307
C	-0.9864009766	0.2682006651	-0.2681562349
C	-0.7553218483	-1.0154482439	-0.7356105248
C	-2.3542158292	0.7892392341	-0.1222396543
O	-2.6802798881	1.9210978560	0.1646627747
O	-3.2553372900	-0.1978036324	-0.3388067025
C	-4.6226960879	0.1989567620	-0.1926766988
H	1.9895904817	1.0149058791	-1.1455299610

H	-1.4609198640	-1.5207194496	-1.3845236198
H	-4.8570843545	1.0102676391	-0.8841263285
H	-5.2102877022	-0.6873586579	-0.4247910747
H	-4.8102456955	0.5334319575	0.8299781265
N	-1.6079785244	-0.5455518344	2.0735338188
N	-1.3960760250	-1.6074998040	1.7218237001
C	-1.0129799703	-2.4526970949	0.7571362890
H	-1.8169906598	-3.0961535537	0.4111053466
H	-0.0342737233	-2.9028713282	0.9047891703
N	0.1608424009	1.1210107739	-0.1632545966
C	0.1046510921	2.4720897883	-0.5085061370
O	1.0974287366	3.1124718031	-0.7789018519
H	-0.9058291597	2.8888689619	-0.4806675152
C	2.3589972383	0.3139132637	0.8674311734
C	3.6870804106	-0.3257575572	0.4364224719
H	3.5640187886	-1.3626550471	0.1190838029
H	4.1442762812	0.2419440701	-0.3818259216
H	4.3833728774	-0.3051802452	1.2807267450
C	2.6501174900	1.7303340953	1.3903872393
H	1.7382878523	2.2274707168	1.7339840427
H	3.3374798827	1.6543974358	2.2392756118
H	3.1061096555	2.3584864067	0.6214352635
C	1.7075684077	-0.4866086620	1.9963871068
H	2.3900330805	-0.5226188044	2.8513071738
H	0.7891598538	0.0043425690	2.3311716221
H	1.5000103942	-1.5182620570	1.6992472650
S	0.9573757798	-1.1160586611	-1.2304746203
O	1.5933488489	-2.3007127890	-0.6470113206
O	1.0345946272	-0.9063514386	-2.6730220510

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C	-1.5166598994	0.6152600752	0.3594964155
C	0.9170965092	0.5207220247	0.2423925081
C	0.7561688364	-0.7039448905	0.8772199444
C	2.2597725720	1.0955539657	0.0513026856
O	2.5355141242	2.2032347710	-0.3538438170
O	3.2058769807	0.1777720109	0.3629074260
C	4.5541721386	0.6189898192	0.1698918913
H	-2.0881608970	1.2324685478	1.0622174157
H	1.4678661678	-1.0642338620	1.6105180574
H	4.7575309855	1.4956494547	0.7873967797
H	5.1815076712	-0.2180177486	0.4710308768
H	4.7205781299	0.8721486581	-0.8792490548
N	1.5291712982	-0.4565860802	-1.9391738496
N	1.5286710008	-1.5118761362	-1.5005910466
C	1.3793241915	-2.3021250872	-0.4190913846
N	-0.2646028161	1.3119717972	0.0680414589
C	-0.2694617602	2.6930034663	0.2645039783
O	-1.2902285552	3.3128390109	0.4719344549
H	0.7192802397	3.1518946144	0.1841219164
C	-2.4135406301	0.2895694318	-0.8575518036
C	-3.7105558163	-0.3676492163	-0.3611936434
H	-3.5395673039	-1.3626280301	0.0530042418
H	-4.1928720407	0.2529477094	0.4025185557
H	-4.4075855839	-0.4583074484	-1.2002964439
C	-2.7743292020	1.6204265127	-1.5370137976
H	-1.8856263648	2.1300233425	-1.9203627377
H	-3.4382753530	1.4114075747	-2.3823634926
H	-3.2819761128	2.3004864579	-0.8484568870
C	-1.7094465638	-0.5991020720	-1.8834541301
H	-2.3964760092	-0.8149631452	-2.7079770401
H	-0.8382289432	-0.0868892271	-2.3016450763
H	-1.4032747733	-1.5525104293	-1.4452889724

S	-0.9478827601	-0.8163693885	1.3896592280
O	-1.5511639268	-2.0837441621	0.9766723196
O	-1.0177616233	-0.4263046136	2.7955652824
C	0.4961178517	-3.5202180624	-0.5039526131
H	1.0232899067	-4.3428537531	-0.9960558668
H	0.2345308580	-3.8256145814	0.5105374403
H	-0.4350164648	-3.3141051588	-1.0289212189
H	2.3597019379	-2.4536471520	0.0354819994

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C	1.4435243004	0.4525512287	-0.4075301896
C	-0.9861627058	0.2757340654	-0.2592664284
C	-0.7647090057	-1.0160707981	-0.7041334456
C	-2.3501685997	0.8013945758	-0.1051288960
O	-2.6729859578	1.9424188151	0.1466612324
O	-3.2581384623	-0.1917105918	-0.2737270630
C	-4.6214453211	0.2162680077	-0.1256449931
H	1.9803266901	0.9970015113	-1.1930628318
H	-1.4862320515	-1.5338421036	-1.3276208463
H	-4.8753015858	0.9678869738	-0.8753859672
H	-5.2146643265	-0.6852109545	-0.2706862012
H	-4.7849422179	0.6328853614	0.8702836257
N	-1.5900293402	-0.5105960694	2.0910958981
N	-1.3874595264	-1.5807398812	1.7529308394
C	-1.0192484163	-2.4569446212	0.8064402399
N	0.1641192202	1.1290499147	-0.1907602006
C	0.1077425338	2.4720768504	-0.5647398811
O	1.0990877511	3.1035951794	-0.8605979209
H	-0.9010677577	2.8924762716	-0.5338973042
C	2.3678609069	0.3280171900	0.8272687068
C	3.6897018989	-0.3265724460	0.3980646695
H	3.5617663562	-1.3716665624	0.1107698943
H	4.1374776549	0.2177320622	-0.4409779510
H	4.3960726259	-0.2837516266	1.2331225342
C	2.6710034215	1.7531545208	1.3195973124
H	1.7633950722	2.2648650144	1.6522703050
H	3.3581584232	1.6902148372	2.1697084237
H	3.1315782395	2.3605435783	0.5366503925
C	1.7230156545	-0.4481604872	1.9770430539
H	2.4067499876	-0.4592207610	2.8317746041
H	0.8001984461	0.0425481273	2.3003680247
H	1.5232809542	-1.4876394537	1.7035765753
S	0.9347316942	-1.1294039771	-1.2304068208
O	1.5778732581	-2.3078409303	-0.6414850771
O	0.9894153126	-0.9431667532	-2.6776984615
C	-2.0769832108	-3.4027779604	0.2976472879
H	-2.9977171218	-2.8590128413	0.0708190968
H	-1.6998853352	-3.8603833718	-0.6205198973
H	-2.2895277818	-4.2040229626	1.0099252775
H	-0.0135632077	-2.8441758319	0.9638847127

TS1c3n
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C	1.5284575665	-0.6002261638	0.3499853693
C	-0.9051783753	-0.4747702937	0.2154270088
C	-0.7264169749	0.7651831941	0.8224622459
C	-2.2594659098	-1.0459700081	0.0820973417
O	-2.5564069867	-2.1635182928	-0.2771123769
O	-3.1890236374	-0.1078881456	0.3799870106
C	-4.5459754548	-0.5438405103	0.2381445766
H	2.0845297925	-1.2166856016	1.0656123159
H	-1.4282049211	1.1345262126	1.5609082374
H	-4.7365968889	-1.3989804728	0.8887233655

H	-5.1580533099	0.3073795949	0.5307615745
H	-4.7432180259	-0.8280241210	-0.7975337702
N	-1.5031869428	0.3990659572	-1.9410817034
N	-1.5188673040	1.4871209220	-1.5820599706
C	-1.3732325106	2.3032362532	-0.5114162951
N	0.2660654185	-1.2825680114	0.0619812759
C	0.2562095975	-2.6643271504	0.2543523149
O	1.2697077093	-3.2930120758	0.4704711548
H	-0.7355455861	-3.1144557774	0.1648637206
C	2.4374258655	-0.3021326536	-0.8656297431
C	3.7465634795	0.3257302373	-0.3628881248
H	3.5935478503	1.3241220843	0.0502380331
H	4.2132091593	-0.3062773217	0.4013080735
H	4.4480160964	0.4030897550	-1.1998122706
C	2.7712337571	-1.6396927401	-1.5442909718
H	1.8733227161	-2.1302339469	-1.9311908902
H	3.4424086904	-1.4441961303	-2.3872048163
H	3.2627343851	-2.3307437203	-0.8550478468
C	1.7558799872	0.6094550859	-1.8855890003
H	2.4484074525	0.8144612401	-2.7090030079
H	0.8742871214	0.1175654298	-2.3079771941
H	1.4742182369	1.5663952129	-1.4390567074
S	0.9779232861	0.8609508465	1.3487099345
O	1.6177756724	2.1048988301	0.9316761076
O	1.0084233055	0.4840894719	2.7608388904
H	-2.3458816006	2.4411343931	-0.0366183337
C	-0.5219570820	3.5054042205	-0.6054624665
C	-0.4781567163	4.3494310983	0.5082240365
C	0.2442385382	3.8091747265	-1.7340994968
C	0.3512272791	5.4639233889	0.5086599276
H	-1.0750870094	4.1161313115	1.3867121630
C	1.0688794174	4.9300020636	-1.7315137808
H	0.1869010258	3.1786976323	-2.6176469289
C	1.1309687220	5.7547008987	-0.6097439673
H	0.3919328395	6.1033050966	1.3843080773
H	1.6606436955	5.1615530794	-2.6113903784
H	1.7780725930	6.6257258204	-0.6099148943

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C	1.5915209443	0.3600985809	-0.4001994216
C	-0.8315011126	0.6077100236	-0.2083480937
C	-0.8455699265	-0.6847322290	-0.7162332701
C	-2.0832778186	1.3683796774	-0.0524033474
O	-2.2008462322	2.5356400686	0.2536056282
O	-3.1436920940	0.5606666275	-0.2760096303
C	-4.4213429907	1.1766881725	-0.0995292664
H	2.2012821336	0.8409677696	-1.1737213908
H	-1.6509380460	-1.0380509783	-1.3524708799
H	-4.5266271470	2.0320509733	-0.7693994443
H	-5.1511915106	0.4055166712	-0.3426307191
H	-4.5376972114	1.5138689250	0.9332253685
N	-1.5155514924	-0.1039787998	2.0447119759
N	-1.5312043188	-1.2037233029	1.7306584941
C	-1.3196442097	-2.0947607873	0.7383514057
N	0.4525610002	1.2379556088	-0.1230230726
C	0.6340622777	2.5898080733	-0.4203571665
O	1.7180110794	3.0481766374	-0.7099675187
H	-0.2810875499	3.1822475514	-0.3382061247
C	2.5038744936	0.0148811901	0.8019252286
C	3.6902704148	-0.8173383192	0.2928903614
H	3.3813738425	-1.7986759711	-0.0724447799
H	4.2162140891	-0.2902542255	-0.5110419480
H	4.4016797316	-0.9646129514	1.1117336805

C	3.0449145983	1.3368594779	1.3705122600
H	2.2392776237	1.9625282436	1.7655437361
H	3.7316830577	1.1068110781	2.1915969885
H	3.5802531968	1.9141335526	0.6131490344
C	1.7660088244	-0.7197796141	1.9231827282
H	2.4556525944	-0.8865164363	2.7567410267
H	0.9384428830	-0.1126330066	2.3018193714
H	1.4028481716	-1.6983880813	1.5988263038
S	0.8003743031	-1.0678250565	-1.2808475135
O	1.2356003766	-2.3688454786	-0.7589240547
O	0.8719587871	-0.8250839461	-2.7186008692
H	-0.3754382281	-2.6265204153	0.8510273874
C	-2.4682063440	-2.8730415634	0.2318432070
C	-2.1912497023	-3.9385463819	-0.6314029627
C	-3.7945446009	-2.5248928898	0.5072449872
C	-3.2363921316	-4.6508627600	-1.2134461253
H	-1.1572835705	-4.1949102444	-0.8500935377
C	-4.8334699023	-3.2493043309	-0.0673223282
H	-4.0101836673	-1.6955219705	1.1760229397
C	-4.5579003259	-4.3106439551	-0.9307709694
H	-3.0162775892	-5.4735868918	-1.8857895118
H	-5.8621462043	-2.9862831915	0.1584926039
H	-5.3715930969	-4.8706960644	-1.3798581309

TS1c4
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C	1.3310024275	0.3162390244	-0.5592369368
C	-0.9929404863	0.1030250586	-0.0599449571
C	-0.8020636775	-1.2565044053	-0.2506441636
C	-2.1976920724	0.8092519195	-0.5275759772
O	-2.2845879862	2.0007536870	-0.7182703332
O	-3.2267498251	-0.0492609691	-0.7064718541
C	-4.4374962919	0.5540558747	-1.1741381958
H	1.1504653337	0.4829430701	-1.6317712111
H	-1.3866107250	-1.8130550524	-0.9755553570
H	-4.2744956670	1.0260063317	-2.1449723233
H	-5.1573557989	-0.2584581842	-1.2585221155
H	-4.7833674973	1.3062165589	-0.4624956007
N	-2.0726952372	-0.1609227587	2.1310808984
N	-1.9756317645	-1.2948410940	2.0576054444
C	-1.6067248931	-2.4021409564	1.3708289389
N	0.1945222679	0.8604805638	0.1943211303
C	2.7991847011	0.6812398098	-0.2434624236
C	3.6931362231	-0.3608706104	-0.9495870122
H	3.6577658180	-1.3379795761	-0.4600025360
H	3.4186455471	-0.4900463646	-2.0019108080
H	4.7270083904	-0.0059911412	-0.9105110459
C	3.1114058570	2.0463300001	-0.8813808586
H	2.4740597522	2.8378322659	-0.4898935931
H	4.1537094308	2.3031210010	-0.6646576355
H	3.0013107647	1.9944155774	-1.9707294244
C	3.1268377889	0.6817366677	1.2552693670
H	4.2063905611	0.8273234329	1.3692048226
H	2.6221730301	1.4951472326	1.7766434173
H	2.8653122143	-0.2728646202	1.7173216525
S	0.9727598087	-1.5017050486	-0.4009618037
O	1.2291738748	-2.1868098816	-1.6667684914
C	0.0951387297	2.0201000673	0.9361485147
O	0.9572603844	2.8549908202	1.0923568679
H	-0.8983729388	2.1000308275	1.3995453673
C	-0.6372362947	-3.3097141039	2.0953591222
H	-0.1254357388	-3.9325595820	1.3588888885
H	0.1239938325	-2.7490518577	2.6353416723
H	-1.1878840760	-3.9625729988	2.7820397005

O	1.5503900384	-2.0380722788	0.8319032374
C	-2.7764653612	-3.0937610237	0.6986473736
H	-2.3701476999	-3.7868458054	-0.0435557173
H	-3.3584444081	-3.6769178981	1.4192825697
H	-3.4244046062	-2.3737256200	0.1946658896

TS1c5
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C	-2.3494516307	-0.5078153261	-0.6167039536
C	-0.4561714844	-1.6302879394	0.3239859952
C	0.2930210605	-0.9068312929	-0.5911412429
C	-0.2801459508	-3.0788988991	0.5606861366
O	-1.1209934765	-3.8028236720	1.0431100674
O	0.9461502059	-3.4913724719	0.1946207735
C	1.2050313188	-4.8833094152	0.4032073757
H	-2.6226718048	-1.3547413575	-1.2626547384
H	1.0366312037	-1.3959955841	-1.2117642448
H	0.4969944797	-5.4883378167	-0.1661880350
H	2.2222797100	-5.0472148199	0.0527909095
H	1.1151428664	-5.1269348698	1.4637662776
N	1.0031488315	-1.3194864502	2.0877234010
N	1.6368115846	-0.5233800707	1.5631522847
C	1.7168713883	0.3043931315	0.4755651890
N	-1.7365454073	-1.0471579879	0.6071523581
C	-3.5241237697	0.4923201431	-0.5954210564
C	-3.6572299327	1.0734542997	-2.0197670632
H	-2.8397211140	1.7533649128	-2.2708034991
H	-3.6998054813	0.2824119279	-2.7764967212
H	-4.5918584055	1.6392952848	-2.0728165659
C	-4.8277695745	-0.2738025140	-0.3075909082
H	-4.8197197741	-0.7542964476	0.6690748736
H	-5.6616440749	0.4355057281	-0.3370126535
H	-5.0068135540	-1.0282542298	-1.0822590662
C	-3.3138201726	1.6386584494	0.3995944865
H	-4.1601573788	2.3296449044	0.3208907283
H	-3.2750224541	1.2718487305	1.4279055957
H	-2.4005966333	2.1925198434	0.1672069762
S	-0.8376871899	0.1269419449	-1.5204159974
O	-0.8707241749	-0.3878524686	-2.8900121436
C	-2.2649732503	-1.2181377464	1.8679088150
O	-3.3578677455	-0.8685937018	2.2549413914
H	-1.5364669730	-1.7149855531	2.5272882211
O	-0.5936951580	1.5546424269	-1.3219170040
C	1.2476706515	1.6873596603	0.8272781102
C	1.9369060915	2.8173234416	0.3832707554
C	0.1046037193	1.8469867301	1.6190236631
C	1.4711727984	4.0899144598	0.7069829370
H	2.8350419916	2.7094582102	-0.2146540260
C	-0.3512886340	3.1158383626	1.9475607114
H	-0.4515451544	0.9769690114	1.9614701165
C	0.3286420968	4.2437444977	1.4867213681
H	2.0097953531	4.9618081605	0.3501797959
H	-1.2468922400	3.2239374957	2.5513352804
H	-0.0317515884	5.2364944179	1.7368238595
C	2.9284612075	0.1142560743	-0.3722573907
C	2.8904989008	0.5819691669	-1.6933475941
C	4.0616729576	-0.5563231590	0.0914003156
C	3.9797278491	0.3794314887	-2.5328211538
H	2.0026583641	1.0972127513	-2.0565492614
C	5.1483698371	-0.7607630777	-0.7579097193
H	4.1001059682	-0.9090084878	1.1180870792
C	5.1116914480	-0.2930713209	-2.0684085596
H	3.9405801553	0.7414121556	-3.5550803841
H	6.0260107127	-1.2809546138	-0.3877936092

H	5.9595444305	-0.4508265179	-2.7271182567

TS1c6n
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C	1.4753517403	0.9260527147	-0.4997148377
C	-0.8903768263	1.0262317158	-0.1152252529
C	-0.9451748145	-0.0912769433	-0.9352582454
C	-1.9046663437	2.0994913722	-0.2133948332
O	-1.7390102123	3.2532856611	0.1041512157
O	-3.0674784252	1.6095405166	-0.6876915678
C	-4.1151668783	2.5775931942	-0.8309685146
H	1.4466008553	1.5783076806	-1.3852889884
H	-1.5677890730	-0.1337652590	-1.8204892861
H	-3.8116698217	3.3577821913	-1.5312308645
H	-4.9726354996	2.0276107077	-1.2136641817
H	-4.3421375403	3.0294780367	0.1363304717
N	-1.9985355257	0.1102430570	1.7190227594
N	-2.1802897985	-0.8913237041	1.2070679098
C	-2.0433911494	-1.5994652894	0.0669146963
H	-2.9578063084	-1.6074924545	-0.5216583376
N	0.4004609356	1.3322887133	0.4192199647
C	2.9453133281	0.7708333752	-0.0401228854
C	3.6813460028	-0.0668907398	-1.1082061253
H	3.3818713764	-1.1182637309	-1.0940143675
H	3.5228732698	0.3257258980	-2.1180309578
H	4.7530235904	-0.0238777846	-0.8941796487
C	3.6113814830	2.1584872993	-0.0287488436
H	3.1264949707	2.8438711810	0.6645133651
H	4.6561980479	2.0395018234	0.2769827398
H	3.6081999140	2.5932183424	-1.0350317406
C	3.0849110744	0.0774371185	1.3212222424
H	4.1487584863	-0.1050257250	1.5065823414
H	2.7073439898	0.7033102161	2.1302199774
H	2.5701100435	-0.8860741038	1.3289316999
S	0.7497313280	-0.6481356265	-1.1677775431
O	1.0484638796	-1.7672360239	-0.2733915607
O	1.0127576769	-0.7640082116	-2.5974062066
C	0.4709424365	2.0996687392	1.5665136807
O	1.4662415161	2.5975789405	2.0395846070
H	-0.5192166432	2.2034682909	2.0305347177
C	-1.3337630382	-2.9155324192	0.1331201031
O	-1.2934352518	-3.6432467291	-0.8259702373
O	-0.7876730853	-3.1415457427	1.3219421474
C	0.0939339266	-4.2734319836	1.3722426192
H	0.4683440547	-4.3029762580	2.3930622133
H	-0.4544526279	-5.1853987920	1.1301359491
H	0.9051549367	-4.1218952647	0.6579506053

TS1c6x
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C	1.6602750933	0.3594325102	-0.3737116866
C	-0.7749496575	0.5042396766	-0.2887839742
C	-0.7259019421	-0.7855061935	-0.8066616445
C	-2.0675926303	1.1929657727	-0.1399222575
O	-2.2569236572	2.3493634644	0.1673368839
O	-3.0736293765	0.3141902867	-0.3564327445
C	-4.3869151799	0.8366296945	-0.1373267722
H	2.2817418618	0.8488450571	-1.1323531764
H	-1.4564615037	-1.1597003490	-1.5179572198
H	-4.5750898864	1.6804984136	-0.8033448934
H	-5.0681136373	0.0157082114	-0.3549292089
H	-4.4924190487	1.1626239823	0.8997571561
N	-1.4005936927	-0.2308453387	1.9889262439
N	-1.4337529550	-1.3182259621	1.6503610494

C	-1.2889916572	-2.1591415541	0.6012931884
N	0.4741666239	1.1917493813	-0.1657563060
C	0.5989781919	2.5414852782	-0.5006161970
O	1.6693689483	3.0496614786	-0.7512712286
H	-0.3500574682	3.0849721964	-0.4848986828
C	2.5366043454	0.0778410949	0.8703833316
C	3.7651250931	-0.7353465832	0.4330629947
H	3.5027852395	-1.7452748093	0.1134944438
H	4.2930842075	-0.2318947722	-0.3846258950
H	4.4593309264	-0.8120298038	1.2757217739
C	3.0196877279	1.4337390261	1.4101366350
H	2.1828705768	2.0542659393	1.7432234451
H	3.6745543227	1.2554653653	2.2693601104
H	3.5743659326	1.9939676417	0.6535596284
C	1.7794858594	-0.6396665130	1.9897690456
H	2.4638756490	-0.8214491403	2.8245337189
H	0.9658743141	-0.0121328657	2.3647910839
H	1.3906028341	-1.6099797437	1.6663551196
S	0.9732998023	-1.1245486829	-1.2523103081
O	1.4141797666	-2.3849516148	-0.6498564762
O	1.1195972658	-0.9224630692	-2.6893143778
H	-0.4155670823	-2.8090595376	0.6423741927
C	-2.5527735466	-2.7557817329	0.0742853508
O	-2.5662977696	-3.3852321699	-0.9536796928
O	-3.6244663693	-2.4693544984	0.8160599809
C	-4.8661437060	-2.9584607980	0.2907910980
H	-4.8487281906	-4.0487927646	0.2455714074
H	-5.6312675357	-2.6117027967	0.9823073869
H	-5.0307078299	-2.5594293878	-0.7124268973

TS2a1
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C	1.5938897973	0.2055106765	0.3078005630
C	-0.7755240374	-0.1028653238	-0.0082201078
C	-0.6131652123	0.9723920178	-0.8732731661
C	-1.7627525387	-1.1631641703	-0.2036019634
O	-1.7229673099	-2.2664205023	0.2981661621
O	-2.7714920153	-0.7504009101	-1.0089695224
C	-3.7835694052	-1.7304745118	-1.2503533524
N	-2.3375039729	0.9800823042	1.5225274972
N	-2.3128082721	1.9263821443	0.8869274098
C	-1.8530203713	2.5481509490	-0.2103612702
H	2.1755288114	0.5975575397	1.1473732755
H	-1.0753174705	0.9577670089	-1.8535153493
H	-4.5105547607	-1.2487875775	-1.9022815293
H	-4.2485293205	-2.0349973239	-0.3104441712
H	-3.3538456376	-2.6088160976	-1.7362111275
H	-1.1805080607	3.3729921096	0.0102452890
H	-2.6288906173	2.7230687913	-0.9513544139
N	0.3442211637	-0.3264559347	0.8349983061
C	2.4454233150	-0.8319392444	-0.4596253216
C	2.8543759490	-1.9299472310	0.5333081014
H	3.5087871625	-2.6486789865	0.0287908593
H	3.3875786092	-1.5145334911	1.3938797820
H	1.9810453050	-2.4704160895	0.9094797550
C	1.6665857155	-1.4648144066	-1.6166035331
H	1.3347029944	-0.7107952368	-2.3384499554
H	2.3112987722	-2.1752695787	-2.1443784209
H	0.7947799380	-2.0157585489	-1.2480765354
C	3.7025164513	-0.1325867880	-0.9878876020
H	4.2603692606	0.3452044283	-0.1740658206
H	4.3639145371	-0.8657521111	-1.4601588043
H	3.4548655844	0.6286923128	-1.7344744822
S	1.0442367281	1.6396902809	-0.7328122049

C	0.2412840215	-0.7077029782	2.1505055187
O	1.1845798690	-0.7531118820	2.9149931900
H	-0.7855629828	-0.9828846386	2.4317789448

TS2a2n
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C	1.5452718337	-0.0236131134	0.4372965611
C	-0.8263177306	-0.1729184446	0.0254814276
C	-0.5913726102	1.0024092171	-0.6774076702
C	-1.8356593657	-1.1617008429	-0.3502039993
O	-1.8478987270	-2.3234419341	-0.0032909469
O	-2.8017467600	-0.6082057702	-1.1233955251
C	-3.8412281747	-1.5071865300	-1.5154773499
N	-2.4312341600	0.7058210001	1.5897340963
N	-2.3765318255	1.7447967988	1.1159456392
C	-1.8573534634	2.5345140514	0.1552071785
H	2.1140197369	0.2294841080	1.3369292473
H	-1.0274684768	1.1456899946	-1.6589244095
H	-4.5277670836	-0.9180729221	-2.1213901423
H	-4.3487574188	-1.9067079671	-0.6350251936
H	-3.4290534328	-2.3353377178	-2.0957534875
H	-2.5856917282	2.6892370023	-0.6404890005
N	0.2577494264	-0.5618761091	0.8558517650
C	2.3797312311	-0.9896314573	-0.4339052700
C	2.6964619658	-2.2323796486	0.4107791436
H	1.7841783516	-2.7734462106	0.6775968266
H	3.3368598482	-2.9080236037	-0.1660829936
H	3.2125895132	-1.9667084142	1.3383080523
C	1.6229520136	-1.4193652058	-1.6943683270
H	1.3598648726	-0.5587053732	-2.3185815177
H	2.2558704978	-2.0858688094	-2.2894885684
H	0.7103091346	-1.9679632481	-1.4377313423
C	3.6892666512	-0.2903373408	-0.8155511617
H	4.2374769181	0.0341805875	0.0766007622
H	4.3320592433	-0.9825169862	-1.3683704423
H	3.5104974956	0.5828164568	-1.4512727359
S	1.0907416625	1.5542041789	-0.4267350212
C	0.0969735868	-1.1037033352	2.1070739491
O	1.0117088798	-1.2844041283	2.8867945689
H	-0.9482014888	-1.3701148427	2.3210309966
C	-1.0598816236	3.7302383858	0.6065792522
H	-0.3562820609	3.4520908110	1.3935248476
H	-0.4805046200	4.0986644597	-0.2435190642
H	-1.7042437721	4.5407277532	0.9589447947

TS2a2x
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C	1.5022184130	0.0086937869	0.4552052695
C	-0.8582941097	-0.1826578611	0.0124424529
C	-0.6349331409	0.9914620074	-0.6923113486
C	-1.8752323015	-1.1673668677	-0.3451003723
O	-1.8919577644	-2.3280682234	0.0053759383
O	-2.8459187092	-0.6128630337	-1.1153011338
C	-3.8807391822	-1.5143917227	-1.5137720675
N	-2.4525658742	0.7620781770	1.6156078686
N	-2.3803402117	1.7744233409	1.0917936329
C	-1.8937950647	2.5149090274	0.0823071801
H	2.0590372242	0.2625458607	1.3621475070
H	-1.0576186935	1.1241190307	-1.6831296867
H	-4.5676300244	-0.9257133479	-2.1204002645
H	-4.3900563718	-1.9187097926	-0.6366097345
H	-3.4642485171	-2.3390531359	-2.0958711600
N	0.2203281142	-0.5554818134	0.8566741729
C	2.3586569756	-0.9372224280	-0.4167139773

C	2.7004287504	-2.1728995312	0.4292881522
H	1.7989881002	-2.7298677862	0.7002605267
H	3.3522278826	-2.8374079930	-0.1476719148
H	3.2130630484	-1.8958528113	1.3555551077
C	1.6137832387	-1.3833567986	-1.6784673592
H	1.3308952854	-0.5286603677	-2.3022434686
H	2.2637232188	-2.0332678391	-2.2736010135
H	0.7147160112	-1.9542110103	-1.4228217192
C	3.6533666947	-0.2106284922	-0.7971995446
H	4.1858147031	0.1416870417	0.0940359483
H	4.3177217964	-0.8950861193	-1.3341245013
H	3.4568223416	0.6479667136	-1.4470682080
S	1.0268119400	1.5892429353	-0.3937259694
C	0.0534907079	-1.1040854003	2.1043985000
O	0.9640964700	-1.2833947072	2.8891736652
H	-0.9911270235	-1.3796113006	2.3093161368
C	-2.8719209158	2.8875239316	-1.0040617828
H	-3.5762899797	3.6625794196	-0.6898545039
H	-2.3025072972	3.2737336430	-1.8533388726
H	-3.4227428461	2.0005760263	-1.3291343212
H	-1.1886126989	3.2659127813	0.4343822151

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C	-0.9437040543	-1.2368869377	0.0223941337
C	-0.8084672985	1.1646098512	-0.2396997216
C	0.1308145410	0.8117314101	-1.2105222603
C	-1.7585202849	2.2723229571	-0.3687019824
O	-2.7968587539	2.3742356397	0.2486994531
O	-1.3196198220	3.2057158510	-1.2437436769
C	-2.1756261666	4.3410201049	-1.3897741094
N	0.4931591453	2.6091588011	1.0236468085
N	1.4622041825	2.3890979542	0.4518788702
C	2.0044984013	1.6200915542	-0.5315349202
H	-0.5254523102	-1.9001780567	0.7862421175
H	0.1531621499	1.3473180009	-2.1528830303
H	-1.6921317095	4.9811139307	-2.1259618388
H	-2.2806316522	4.8615490086	-0.4355240333
H	-3.1627646120	4.0304947078	-1.7380246798
H	2.3498209552	2.2226450109	-1.3695718058
N	-1.1266134784	0.0795521581	0.6231363123
C	-2.2466412421	-1.8558549235	-0.5346927114
C	-3.2101604069	-2.0747046302	0.6403387908
H	-3.5094228838	-1.1232236190	1.0896381636
H	-4.1130011325	-2.5786223428	0.2791352057
H	-2.7557974441	-2.6892330116	1.4235244822
C	-2.9105859544	-0.9376836327	-1.5649235956
H	-2.2361718397	-0.7197167385	-2.3997891522
H	-3.8022930758	-1.4278320635	-1.9695277913
H	-3.2276311371	0.0038439607	-1.1036933884
C	-1.9046542282	-3.2086025976	-1.1690068068
H	-1.4040285954	-3.8673270258	-0.4496636500
H	-2.8224324834	-3.7075053205	-1.4958420813
H	-1.2567434930	-3.0909391233	-2.0436190890
S	0.3503283751	-0.9559414505	-1.2774018831
C	-1.2675766748	0.2187159207	1.9798831326
O	-1.3392864264	-0.7159448000	2.7545694339
H	-1.3164379007	1.2723563583	2.2939503366
C	2.8815886175	0.5224189376	-0.0826493337
C	3.8932082942	0.0628734291	-0.9292150927
C	2.6271852621	-0.1518276956	1.1185274039
C	4.6434713886	-1.0575515189	-0.5793407683
H	4.0883441683	0.5775725174	-1.8664354480
C	3.3878640204	-1.2591262409	1.4719533097

H	1.8252174679	0.1817660372	1.7738051179
C	4.3960405223	-1.7176000732	0.6222387175
H	5.4242649018	-1.4114639370	-1.2448624945
H	3.1844991972	-1.7729963984	2.4058398389
H	4.9831084701	-2.5882559636	0.8957967166

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C	-2.3806971947	-0.6675775699	0.3315921057
C	-0.4941427707	0.8212972911	0.1137674784
C	0.1710709522	-0.3656630028	-0.1794392890
C	-0.1527338146	2.1152566754	-0.4820956212
O	-0.8911307459	3.0737556655	-0.5551690176
O	1.1265383243	2.1262029915	-0.9205525469
C	1.5565222520	3.3551305220	-1.5070611482
N	0.7326667619	1.3875781390	2.0483948557
N	1.4093288869	0.4662949896	1.9732527904
C	1.7267858268	-0.6191481061	1.2294866084
H	-2.9396397246	-1.0128447208	1.2064108887
H	0.8677285107	-0.4167324179	-1.0100469606
H	2.5981360971	3.1971047658	-1.7854277241
H	1.4651654003	4.1714120402	-0.7870327126
H	0.9561257684	3.5882502146	-2.3889839600
N	-1.7917320183	0.6260114647	0.6548421034
C	-3.3224599884	-0.6401465759	-0.8945901435
C	-4.5002677482	0.2884099481	-0.5650909900
H	-4.1627550872	1.3181353273	-0.4160353684
H	-5.2115109491	0.2798286242	-1.3978242866
H	-5.0202790876	-0.0283849976	0.3439715948
C	-2.6123849854	-0.1220420769	-2.1489949247
H	-1.7490376363	-0.7428862245	-2.4109250440
H	-3.3082247211	-0.1406171591	-2.9942660874
H	-2.2811313606	0.9133458633	-2.0143502612
C	-3.8477695983	-2.0600481968	-1.1330103006
H	-4.3425871337	-2.4532399403	-0.2371962849
H	-4.5827104087	-2.0523034282	-1.9440267210
H	-3.0418919345	-2.7452201210	-1.4148874155
S	-0.9042279218	-1.7684034230	0.1131279756
C	-2.3326000937	1.4189786926	1.6374352824
O	-3.3730432928	1.1650836378	2.2114021226
H	-1.7301792448	2.3166949176	1.8377566454
H	1.4217493855	-1.5442752324	1.7165970681
C	3.0326181367	-0.6123901472	0.5389970008
C	3.5834283586	-1.8349401147	0.1408334265
C	3.6819048379	0.5803117373	0.1972670366
C	4.7707759430	-1.8660369076	-0.5863681942
H	3.0807307058	-2.7622155967	0.4040477185
C	4.8740318992	0.5429906450	-0.5171082595
H	3.2494711076	1.5339614000	0.4874629425
C	5.4213834006	-0.6781830817	-0.9129777777
H	5.1905632081	-2.8196725467	-0.8900968730
H	5.3785806847	1.4708675131	-0.7681185398
H	6.3507730124	-0.7022014776	-1.4725821923

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C	1.5452499059	-0.0125251210	0.4491139181
C	-0.8260238884	-0.1475696691	0.0390742131
C	-0.5857051612	1.0285578680	-0.6592289659
C	-1.8318656626	-1.1372714955	-0.3425346472
O	-1.8406655228	-2.3013841647	-0.0035705228
O	-2.8009610837	-0.5853910897	-1.1147093427
C	-3.8295982930	-1.4898885454	-1.5222788904
N	-2.4224908353	0.7334708602	1.5925477832

N	-2.3795898038	1.7736034513	1.1164175452
C	-1.8850199725	2.5733058397	0.1462501960
H	2.1223820887	0.2300732364	1.3462580095
H	-1.0193272776	1.1792572353	-1.6422247710
H	-4.5267208259	-0.8968146929	-2.1127816009
H	-4.3279515484	-1.9157237829	-0.6489544653
H	-3.4093902195	-2.2988827677	-2.1234011637
N	0.2557506519	-0.5423226100	0.8711070901
C	2.3645231594	-0.9820298555	-0.4340648208
C	2.6731380634	-2.2321541965	0.4024510049
H	1.7549489015	-2.7625789511	0.6708422198
H	3.3024564790	-2.9123520624	-0.1813075949
H	3.1963740894	-1.9772531638	1.3290772488
C	1.5962533692	-1.3984425363	-1.6923028250
H	1.3208232986	-0.5313879693	-2.3022011874
H	2.2274769566	-2.0522117242	-2.3032956816
H	0.6906748489	-1.9574530322	-1.4336112025
C	3.6771313412	-0.2921998047	-0.8213499354
H	4.2319376244	0.0290042036	0.0679903874
H	4.3120071002	-0.9893979184	-1.3772657738
H	3.4994420641	0.5820361826	-1.4558659342
S	1.0971304807	1.5736847915	-0.4007658649
C	0.0949998473	-1.0982872969	2.1151709127
O	1.0116417052	-1.2952743034	2.8893038313
H	-0.9514343602	-1.3597815211	2.3293510417
C	-2.8608376036	2.8433694558	-0.9772742654
H	-3.6079843477	3.5937094345	-0.6974196728
H	-2.2939589401	3.2370454725	-1.8261456462
H	-3.3603584040	1.9220072103	-1.2871249283
C	-1.0597774345	3.7351195056	0.6404539277
H	-0.4474635607	4.1008733729	-0.1883536010
H	-1.6981583136	4.5583684566	0.9800205110
H	-0.3878686864	3.4343311376	1.4462354137

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C	-2.3723403669	0.7851687226	0.2381603587
C	-0.9127799416	-0.9837200182	-0.5403362163
C	-0.0487662483	-0.4178974312	0.4027681680
C	-1.0476637292	-2.4292006452	-0.7650070882
O	-2.0156277888	-2.9673649793	-1.2574733831
O	0.0681979762	-3.0915607747	-0.3972653867
C	0.0461835981	-4.4994612056	-0.6398000935
N	0.4313454279	-0.9420203885	-2.3482221033
N	1.3154897232	-0.3867137755	-1.8668551857
C	1.6911918629	0.2404415250	-0.7010944068
H	-2.6439917491	1.7422322363	-0.2196699841
H	0.5487831573	-1.0630125536	1.0374277180
H	1.0036773049	-4.8727369746	-0.2805116311
H	-0.0709999339	-4.6970738082	-1.7076452835
H	-0.7784735587	-4.9661625665	-0.0974682432
N	-2.0224917880	-0.1421887765	-0.8324375503
C	-3.5375695115	0.2980603637	1.1311427649
C	-4.7949910190	0.1892253044	0.2566205043
H	-4.6755274772	-0.5771330414	-0.5146008359
H	-5.6488768523	-0.0898344810	0.8830077323
H	-5.0210036408	1.1363020819	-0.2429291371
C	-3.2387878112	-1.0702327335	1.7515103810
H	-2.3324617630	-1.0445346062	2.3656140311
H	-4.0734628473	-1.3688711213	2.3943610744
H	-3.1261495780	-1.8355220568	0.9760546085
C	-3.7719946798	1.3415057401	2.2290556595
H	-3.9659250039	2.3309018055	1.7983098786
H	-4.6439180384	1.0614428244	2.8285255712

H	-2.9119734624	1.4168729460	2.9023385029
S	-0.7831238758	1.0093666413	1.1695603038
C	-2.5218196316	0.0220773403	-2.0990001046
O	-3.3291348631	0.8791394199	-2.4036365079
H	-2.1156301352	-0.7115961204	-2.8113487680
C	1.6385661111	1.7286470119	-0.8268856981
C	2.6238680100	2.5508129223	-0.2745479344
C	0.5499595679	2.3193181014	-1.4852479688
C	2.5137935929	3.9378740204	-0.3673151063
H	3.4857171531	2.1132221497	0.2176186290
C	0.4507174051	3.7001056178	-1.5903351788
H	-0.2321233137	1.6961425980	-1.9140296627
C	1.4312719360	4.5158276874	-1.0240723030
H	3.2864893445	4.5650282242	0.0660348266
H	-0.3982730940	4.1384444124	-2.1049789114
H	1.3511757296	5.5956418832	-1.0986594946
C	2.8174374439	-0.4325717200	0.0043956148
C	3.0264296908	-0.1525044630	1.3624766845
C	3.6257885021	-1.3842084226	-0.6240051233
C	4.0287291950	-0.8072451816	2.0704144042
H	2.3936066242	0.5751908156	1.8662176722
C	4.6235334758	-2.0440435973	0.0913546012
H	3.4816693976	-1.6033305256	-1.6778600608
C	4.8309131879	-1.7573588204	1.4379108565
H	4.1779570944	-0.5793468783	3.1210766207
H	5.2439391001	-2.7786341719	-0.4123336455
H	5.6112250903	-2.2686655569	1.9921078301

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C	-2.1927742140	-0.3683580032	0.3538058803
C	-0.0318770781	0.6785379485	0.1182304862
C	0.3223913172	-0.5968890500	-0.3223209916
C	0.5936182652	1.9016063173	-0.3961095327
O	0.1261209688	3.0166951662	-0.3241963495
O	1.8052520263	1.6337963053	-0.9332042752
C	2.5187066207	2.7792866479	-1.4031901353
N	1.3248199322	0.7412057478	2.0290571618
N	1.8185191274	-0.2664421723	1.8132498623
C	1.8892775157	-1.2601457457	0.8949525788
H	-2.7739157899	-0.6432915030	1.2388123812
H	0.9078715331	-0.7356482973	-1.2255007446
H	3.4572085810	2.3993551878	-1.8037787564
H	2.7025780370	3.4734624221	-0.5804827378
H	1.9482086249	3.2898345231	-2.1816580577
N	-1.3161320967	0.7396302023	0.7164017794
C	-3.1590349871	-0.0495515716	-0.8097552281
C	-4.0911657341	1.0822657901	-0.3528033508
H	-3.5344410609	2.0044856841	-0.1638697044
H	-4.8271807307	1.2844729336	-1.1380355347
H	-4.6233737439	0.8179807542	0.5659593136
C	-2.4090132880	0.3953669623	-2.0688958960
H	-1.7225122470	-0.3798689997	-2.4257480219
H	-3.1289841338	0.5993388388	-2.8681329469
H	-1.8460524142	1.3172830403	-1.8863366676
C	-3.9932980351	-1.3008990828	-1.1059310165
H	-4.5180743412	-1.6471017793	-0.2077964007
H	-4.7479184711	-1.0714450727	-1.8646503220
H	-3.3735714516	-2.1197722824	-1.4844533780
S	-1.0116478766	-1.7494275618	-0.0128252708
C	-1.6221724966	1.5625208680	1.7752724846
O	-2.6673638390	1.5052105417	2.3906860226
H	-0.8254254115	2.2878073444	1.9923084874
H	1.5331225418	-2.2252984421	1.2417918330

C	3.0997387091	-1.2650499135	0.0310043015
O	3.2341193288	-2.0709160675	-0.8589173158
O	3.9409795399	-0.2631999735	0.2926521914
C	5.0431275952	-0.1472610055	-0.6142617983
H	5.6002721844	0.7274327076	-0.2849302837
H	5.6647412825	-1.0434611879	-0.5677690357
H	4.6734407103	-0.0175412218	-1.6337240116

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C	1.5472930722	0.2219422267	0.2568934594
C	-0.8091343527	-0.1156990956	-0.0496632908
C	-0.6860182965	0.9660862442	-0.9034380766
C	-1.7862168491	-1.2012401047	-0.2112565166
O	-1.7113290980	-2.2868835876	0.3215898604
O	-2.7986079277	-0.8375979691	-1.0258145383
C	-3.7983266895	-1.8413996322	-1.2248471023
N	-2.4019709111	0.9618422032	1.4801134499
N	-2.2697584594	1.9368898829	0.9059900345
C	-1.7184591998	2.6276255043	-0.0940089529
H	2.1104521817	0.7178118768	1.0551745625
H	-1.2048740681	0.9851540908	-1.8551960458
H	-4.5247672121	-1.4018912343	-1.9058950058
H	-4.2670595891	-2.1002291842	-0.2730669344
H	-3.3537329032	-2.7385932299	-1.6601054554
H	-0.9182701864	3.3009548645	0.2136787105
H	-2.4343386128	2.9625261534	-0.8385270146
N	0.3132073562	-0.3188695755	0.7941445831
C	2.4325279877	-0.8167481571	-0.4682982208
C	2.7946985739	-1.9213983461	0.5332484624
H	3.4698204408	-2.6367161897	0.0517865516
H	3.2876174272	-1.5122513437	1.4195814693
H	1.9027996018	-2.4616258381	0.8636836197
C	1.7002208023	-1.4460705243	-1.6604463202
H	1.4390313849	-0.7036081756	-2.4239839130
H	2.3497567316	-2.1892136209	-2.1340863250
H	0.7881517755	-1.9585163399	-1.3366275754
C	3.7169425477	-0.1224803711	-0.9389153649
H	4.2431199828	0.3419005998	-0.0977844807
H	4.3889084534	-0.8599661528	-1.3887160069
H	3.5223516187	0.6493016484	-1.6907110572
S	1.0317613136	1.5977659353	-0.8973415385
O	1.1005013625	2.8986362741	-0.1264304294
C	0.2174706780	-0.6784925830	2.1199348794
O	1.1650057870	-0.6954756596	2.8771337094
H	-0.8042317241	-0.9631735893	2.4096798134

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C	1.5865723913	-0.1006722658	0.4956545604
C	-0.7740908322	-0.1939646570	0.0903249759
C	-0.5197777938	0.9663208559	-0.6222125259
C	-1.8320391263	-1.1503203642	-0.2785936751
O	-1.8688658402	-2.3157148865	0.0451552840
O	-2.7913433038	-0.5484487479	-1.0156722033
C	-3.8735761579	-1.4009230367	-1.4033013478
N	-2.2649216387	0.7435000381	1.6639056170
N	-2.2696292388	1.7659126770	1.1511962590
C	-1.8766498847	2.5250117936	0.1152031949
H	2.1630022061	0.1609312688	1.3896582740
H	-0.9018187741	1.1174932813	-1.6248205423
H	-4.5459458379	-0.7761705004	-1.9885303618
H	-4.3801760116	-1.7914863069	-0.5184844560
H	-3.5025284871	-2.2352110187	-2.0017984804

H	-2.6211757096	2.4431321535	-0.6786327571
N	0.3012292113	-0.6454484650	0.8930476071
C	2.4131866711	-1.0187123389	-0.4300211082
C	2.6802220596	-2.3333175011	0.3161519759
H	1.7479860567	-2.8615663841	0.5360883301
H	3.3040068235	-2.9827488108	-0.3072405193
H	3.1951502627	-2.1553584588	1.2645089233
C	1.6698232651	-1.3273571003	-1.7358722249
H	1.4791487649	-0.4236333587	-2.3272907981
H	2.2783755674	-1.9994454771	-2.3493867148
H	0.7160410341	-1.8284679924	-1.5386901979
C	3.7511797819	-0.3326227835	-0.7346578087
H	4.2907807262	-0.0941164066	0.1883086333
H	4.3813817883	-1.0032684119	-1.3271486939
H	3.6210164565	0.5923989553	-1.3053861016
S	1.1768685191	1.5385779056	-0.2862495138
O	1.1451143641	2.5406492417	0.8450806441
C	0.1370934697	-1.2561525308	2.1162913991
O	1.0588314573	-1.5181349131	2.8598436320
H	-0.9129383262	-1.4969941109	2.3345162798
C	-1.3190058114	3.9005068031	0.3798203380
H	-0.6742240008	3.8998455408	1.2558505371
H	-0.7064654993	4.1980529794	-0.4744158016
H	-2.1301412624	4.6270271840	0.4903733075

TS2b2x
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C	1.4131738496	0.0328500418	0.3778924077
C	-0.9297725953	-0.2439019354	-0.0686438216
C	-0.7679614124	0.9374734783	-0.7653603410
C	-1.9175961553	-1.2807724642	-0.3958118765
O	-1.8809106033	-2.4246639613	0.0015647074
O	-2.8934454623	-0.8001305307	-1.1960136290
C	-3.9021028190	-1.7509556751	-1.5485745471
N	-2.5729859460	0.6485716554	1.5183850549
N	-2.4008487001	1.6943920182	1.0939538491
C	-1.8130791247	2.5195128309	0.2235155577
H	1.9318219169	0.4411644386	1.2526117488
H	-1.2724152822	1.0983672673	-1.7125894111
H	-4.6011692187	-1.2147862686	-2.1881844535
H	-4.4036191646	-2.1191836417	-0.6511853430
H	-3.4590588701	-2.5938214993	-2.0828386464
N	0.1564792691	-0.5676647571	0.7856694320
C	2.3403410871	-0.9201601135	-0.4096727832
C	2.7019292097	-2.1023182482	0.4999271644
H	1.8157347899	-2.6832909517	0.7698598112
H	3.3966197942	-2.7636028083	-0.0287840516
H	3.1748590176	-1.7634376620	1.4261076749
C	1.6478842174	-1.4537225925	-1.6702649452
H	1.3913943038	-0.6516759965	-2.3724873901
H	2.3203458945	-2.1434279782	-2.1902453964
H	0.7368657313	-2.0053556271	-1.4139783316
C	3.6234175816	-0.1668415422	-0.7837673027
H	4.1167733280	0.2386628705	0.1063097868
H	4.3223817879	-0.8542594672	-1.2702969738
H	3.4345959114	0.6583380098	-1.4778192307
S	0.9522110236	1.5251573624	-0.6530288175
O	1.0322851292	2.7517466221	0.2313468275
C	-0.0041063735	-1.0813780890	2.0534085786
O	0.9039062235	-1.1899632603	2.8505307351
H	-1.0376988641	-1.3973555763	2.2554067268
C	-2.6880535116	3.1734607748	-0.8139291113
H	-3.2617288391	4.0087216158	-0.4032339452
H	-2.0373921218	3.5689557280	-1.5979404695

H	-3.3745108647	2.4477621910	-1.2584635574
H	-0.9905949476	3.0815880814	0.6679246624

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C	-1.5760905165	-1.3665817931	0.4949974959
C	-1.0715634007	0.9337935802	0.0568942391
C	-0.0116995659	0.3711714160	-0.6363905684
C	-1.6841368645	2.2184485629	-0.3170958161
O	-2.7946738780	2.5884205103	-0.0109830797
O	-0.8180483550	2.9705476951	-1.0340398362
C	-1.3181184547	4.2544359215	-1.4218895645
N	0.2730536177	2.0132157964	1.6930597940
N	1.2508807784	1.8122213344	1.1350964611
C	1.8104463347	1.3609225218	-0.0072927612
H	-1.5468802639	-1.9605052406	1.4146694431
H	0.2318750625	0.6218942346	-1.6622142995
H	-0.5172760202	4.7235152382	-1.9906001228
H	-1.5621199105	4.8455232545	-0.5368951733
H	-2.2138578526	4.1427291820	-2.0357717942
H	1.7670765122	2.1610711601	-0.7484797058
N	-1.8187456649	0.0229809026	0.8429219315
C	-2.5830888579	-1.9755254947	-0.5014701852
C	-3.9812019944	-1.8737605603	0.1245955723
H	-4.2730138126	-0.8294827809	0.2695356941
H	-4.7120228585	-2.3476683995	-0.5390333613
H	-4.0157874078	-2.3681948863	1.0995813880
C	-2.5793464714	-1.2418899060	-1.8481328695
H	-1.6084505922	-1.3154551526	-2.3532443529
H	-3.3288498165	-1.6902650170	-2.5082863991
H	-2.8313281927	-0.1835341845	-1.7244514255
C	-2.2280649376	-3.4535483514	-0.7102096320
H	-2.2121654741	-3.9925068049	0.2431462165
H	-2.9793639988	-3.9265127530	-1.3503321672
H	-1.2532023495	-3.5787080071	-1.1924375417
S	0.1876688194	-1.3597541644	-0.0918005312
O	0.9994643276	-1.3227412483	1.1840635039
C	-2.4149702313	0.3504609092	2.0406140106
O	-2.9454095932	-0.4667971187	2.7633269925
H	-2.3793504170	1.4272291903	2.2569972078
C	3.0403558815	0.5496733125	-0.0100466988
C	3.7176912371	0.4131036019	-1.2265671958
C	3.5315971142	-0.0967257784	1.1301748742
C	4.8642192472	-0.3736749539	-1.3096617366
H	3.3470441622	0.9255236926	-2.1116307719
C	4.6857022692	-0.8631115687	1.0464703923
H	2.9921024567	-0.0179303092	2.0678554995
C	5.3527882516	-1.0100344457	-0.1718206009
H	5.3789797186	-0.4781378260	-2.2593805275
H	5.0597576500	-1.3617220560	1.9347232476
H	6.2508753119	-1.6167382159	-0.2298032449

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C	-2.1901971870	-0.6673910178	0.2353961201
C	-0.4723821619	1.0012980928	0.0216513805
C	0.3159955733	-0.0926323859	-0.2954184683
C	-0.2839094776	2.3566916564	-0.5158479225
O	-1.1223184638	3.2312178852	-0.4965572817
O	0.9545192100	2.5196932900	-1.0246090383
C	1.2187499751	3.8184856661	-1.5612843301
N	0.8264637336	1.6807083612	1.9174150201
N	1.4493543571	0.7225331777	1.8751257137
C	1.6893109049	-0.4460448375	1.2515610725

H	-2.5836410091	-1.1803607178	1.1202094935
H	1.0700172615	-0.0291868969	-1.0734356706
H	2.2415728326	3.7799764893	-1.9322824138
H	1.1163735847	4.5775342632	-0.7829800847
H	0.5228918577	4.0423466224	-2.3723530028
N	-1.7223552405	0.6568717325	0.6017999934
C	-3.2311357151	-0.6747668948	-0.9072686317
C	-4.4590632376	0.1235208205	-0.4494403677
H	-4.2089600451	1.1751663875	-0.2838681851
H	-5.2292409382	0.0733818470	-1.2263579163
H	-4.8707804959	-0.2743574849	0.4822940605
C	-2.6653994847	-0.0324186054	-2.1802315136
H	-1.7939821402	-0.5740204068	-2.5667120908
H	-3.4312116204	-0.0407139376	-2.9625184161
H	-2.3826512911	1.0103827288	-2.0015778161
C	-3.6494157117	-2.1253496602	-1.1808585364
H	-4.0351399453	-2.6012259347	-0.2726446089
H	-4.4448919601	-2.1419931773	-1.9323037480
H	-2.8221500516	-2.7324565105	-1.5625661902
S	-0.6609451777	-1.6312976054	-0.2510226161
O	-0.2412238249	-2.4843456720	0.9297327164
C	-2.2770755185	1.3349758190	1.6638550587
O	-3.2473846582	0.9397946822	2.2755689224
H	-1.7544765780	2.2773549898	1.8844688319
H	1.2196041291	-1.2904688377	1.7611081076
C	3.0033875852	-0.6621652234	0.6174365776
C	3.3784744792	-1.9786005037	0.3289227092
C	3.8207734905	0.4003220628	0.2142025493
C	4.5685507579	-2.2289988269	-0.3493747881
H	2.7285021074	-2.7956164247	0.6322880617
C	5.0145457397	0.1415656141	-0.4510445894
H	3.5231743920	1.4250808635	0.4231970659
C	5.3908615631	-1.1718592263	-0.7357192238
H	4.8556379245	-3.2519063626	-0.5708832717
H	5.6523193638	0.9668209040	-0.7513988228
H	6.3224381113	-1.3690048051	-1.2563299096

TS2b4
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C	1.5663994708	-0.0385153929	0.4508362413
C	-0.8022675904	-0.1164620279	0.0791087572
C	-0.5553365126	1.0459151576	-0.6375091609
C	-1.8083243656	-1.1254012569	-0.3042130539
O	-1.7928037420	-2.2857741343	0.0385788375
O	-2.7783590785	-0.5913463989	-1.0758927308
C	-3.8021782473	-1.5080907607	-1.4758787573
N	-2.3371587363	0.7472246717	1.5710070620
N	-2.3333285596	1.8015443627	1.1203196626
C	-1.8892052019	2.6319506551	0.1541032903
H	2.1621983915	0.2556836582	1.3216758388
H	-0.9717081131	1.1927854420	-1.6282290226
H	-4.5098274267	-0.9222651350	-2.0604053123
H	-4.2869441378	-1.9371648022	-0.5968929081
H	-3.3758570790	-2.3119034495	-2.0792518277
N	0.2795960606	-0.5411279431	0.8918307526
C	2.3624621179	-1.0144021679	-0.4441726734
C	2.5940420630	-2.3111511432	0.3432443318
H	1.6479966687	-2.8190936996	0.5524474375
H	3.2207328255	-2.9855707131	-0.2500553225
H	3.0890787539	-2.1165209075	1.2986908256
C	1.6068759768	-1.3463982438	-1.7375694581
H	1.4278251701	-0.4568182116	-2.3532504483
H	2.2008672576	-2.0459523643	-2.3346811613
H	0.6468853042	-1.8272643984	-1.5228294080

C	3.7168181598	-0.3745117418	-0.7750804125
H	4.2716671457	-0.1341261480	0.1383082945
H	4.3208108431	-1.0752350399	-1.3601458626
H	3.6072350101	0.5426228897	-1.3629702406
S	1.1772006046	1.5641962451	-0.4160966993
O	1.2744244463	2.6474307958	0.6315976220
C	0.1261556434	-1.1196675545	2.1302980382
O	1.0539028522	-1.3601396252	2.8745468341
H	-0.9225159565	-1.3525095555	2.3644563392
C	-2.8697727858	2.7853538920	-0.9905304095
H	-3.6750822980	3.4804541535	-0.7305098254
H	-2.3262427477	3.2088222757	-1.8400819070
H	-3.2925397464	1.8219171390	-1.2818357199
C	-1.2350019832	3.9061926230	0.6354167476
H	-0.5799468971	4.2836764851	-0.1518776876
H	-2.0072183952	4.6581044015	0.8384953822
H	-0.6160559352	3.7392364079	1.5144886643

TS2b5
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C	-2.1141743218	0.6570422166	0.3816807574
C	-0.8700794150	-1.2029711453	-0.5367795740
C	0.0880687382	-0.7847076915	0.3839729371
C	-1.1216240836	-2.6024412257	-0.9257422071
O	-2.1318723080	-2.9913896112	-1.4697048494
O	-0.0774558522	-3.3988762304	-0.6317436054
C	-0.2283942279	-4.7638127580	-1.0310286179
N	0.5733893578	-1.1273266919	-2.3306936929
N	1.4007192752	-0.5356108846	-1.7996133344
C	1.6847788851	0.1474691059	-0.6384517365
H	-2.0549912013	1.6997929065	0.0430665618
H	0.7090848250	-1.5337244590	0.8666632342
H	0.6853195591	-5.2636727045	-0.7146086036
H	-0.3500888706	-4.8278776752	-2.1143981298
H	-1.1000034495	-5.2071383595	-0.5454357917
N	-1.9173337954	-0.2551442975	-0.7355342963
C	-3.4192542368	0.4028070113	1.1728610022
C	-4.6245442330	0.6634677560	0.2600527160
H	-4.6658210661	-0.0532383468	-0.5641412425
H	-5.5441409936	0.5607119312	0.8462230877
H	-4.5919711845	1.6677687386	-0.1717036242
C	-3.4774028228	-1.0478298396	1.6690992996
H	-2.6679283455	-1.2770202011	2.3708469910
H	-4.4245198449	-1.2172399723	2.1912720782
H	-3.4275091261	-1.7489377113	0.8286791011
C	-3.4719676952	1.3817490899	2.3533052339
H	-3.3955650262	2.4187696734	2.0085729738
H	-4.4258846765	1.2690662515	2.8777086302
H	-2.6739230372	1.2064258771	3.0823969247
S	-0.6430297820	0.4083861509	1.5303500106
O	0.1500267515	1.6849808042	1.6475732769
C	-2.3651703685	0.0592315552	-1.9966429157
O	-3.0093005028	1.0552157439	-2.2586156864
H	-2.0715879190	-0.6912173468	-2.7467769616
C	1.5084909400	1.6295834770	-0.8394399475
C	2.4428885804	2.5471529742	-0.3560671768
C	0.3817471512	2.0991594406	-1.5210146392
C	2.2191183193	3.9134236138	-0.5052060044
H	3.3382050540	2.2025511584	0.1487292488
C	0.1585474555	3.4616194535	-1.6685973459
H	-0.3376641312	1.4032323321	-1.9389650389
C	1.0743797470	4.3760066047	-1.1488875454
H	2.9455516157	4.6177839236	-0.1124436855
H	-0.7320996781	3.8018527311	-2.1876953879

H	0.9008420783	5.4421167512	-1.2548835897
C	2.8653845954	-0.3689479437	0.1137010424
C	3.0195406857	0.0273959966	1.4501346767
C	3.7695138058	-1.2748912290	-0.4462751522
C	4.0716112882	-0.4770382676	2.2061863919
H	2.3085819931	0.7304618660	1.8809107048
C	4.8189246435	-1.7796473395	0.3209620181
H	3.6646823253	-1.5759674967	-1.4846778185
C	4.9745485047	-1.3823594224	1.6458210674
H	4.1843257340	-0.1627069522	3.2389585563
H	5.5190068843	-2.4793278389	-0.1244606355
H	5.7950394018	-1.7722364926	2.2396533143

TS2b6x
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C	-2.1308446552	-0.3698117040	0.3344889791
C	-0.0323026208	0.7695323794	0.0891869012
C	0.3934163215	-0.4731333472	-0.3628610596
C	0.5188612214	2.0439539507	-0.4010447249
O	-0.0249299672	3.1213886780	-0.3061586371
O	1.7356374921	1.8635961489	-0.9527130029
C	2.3656177125	3.0573086719	-1.4259770752
N	1.4043593659	0.8803653228	1.9749529277
N	1.8473690498	-0.1481329707	1.7618582689
C	1.8599040346	-1.1993462113	0.9180903329
H	-2.6551704076	-0.7514091190	1.2174402393
H	0.9970135900	-0.5764263392	-1.2588503687
H	3.3296923031	2.7432495966	-1.8223441891
H	2.4962542183	3.7647481636	-0.6046809765
H	1.7599282083	3.5214558485	-2.2068781953
N	-1.3033990742	0.7600628190	0.7148444456
C	-3.1315613108	-0.0729222670	-0.8056793967
C	-4.0524274373	1.0681092641	-0.3524185230
H	-3.4909011065	1.9956260562	-0.2077531973
H	-4.8108395058	1.2444548904	-1.1223628803
H	-4.5536333889	0.8275789433	0.5892211145
C	-2.4116602684	0.3491558838	-2.0931664312
H	-1.7524924571	-0.4383051518	-2.4781209307
H	-3.1533701460	0.5644821438	-2.8690586257
H	-1.8214087101	1.2582633521	-1.9357336733
C	-3.9729450729	-1.3310379758	-1.0567009531
H	-4.4805034079	-1.6529786423	-0.1410322307
H	-4.7400083874	-1.1160832355	-1.8071426966
H	-3.3707027802	-2.1661240428	-1.4287223402
S	-0.9335959682	-1.7201432401	-0.1337210913
O	-0.6396161921	-2.5134945519	1.1228426757
C	-1.6308354594	1.5446160304	1.7990900251
O	-2.6695769955	1.4306773391	2.4141562544
H	-0.8585788110	2.2915072703	2.0332761012
H	1.3753319158	-2.0950609481	1.3089854029
C	3.0707101556	-1.3502619880	0.0678167873
O	3.1382378445	-2.1928729328	-0.7937552891
O	4.0026861712	-0.4261886561	0.3129693445
C	5.1423231779	-0.4663834735	-0.5549269885
H	5.7919707606	0.3387240728	-0.2182301064
H	5.6438589713	-1.4320190889	-0.4700023824
H	4.8297816166	-0.3106359397	-1.5894428348

TS2c1
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C	1.5169399372	0.0284656023	0.4226610589
C	-0.8649561397	-0.1491906748	-0.0026285007
C	-0.6873793330	1.0070474682	-0.7346659222
C	-1.8500556158	-1.1922679104	-0.3295205100

O	-1.8149278109	-2.3308632542	0.0789641067
O	-2.8185640974	-0.7104781666	-1.1335646339
C	-3.8230442249	-1.6613876719	-1.5035153889
N	-2.4831466190	0.8176472953	1.5686060017
N	-2.3868107834	1.8225897474	1.0436402114
C	-1.8749140936	2.5879641845	0.0776724111
H	2.0864759088	0.3449324347	1.3026527428
H	-1.0547701367	1.1333811744	-1.7460353128
H	-4.5104817797	-1.1236003025	-2.1537450247
H	-4.3378487947	-2.0295952934	-0.6138103200
H	-3.3700232715	-2.5030760000	-2.0306064085
H	-1.1642893191	3.3306948148	0.4311332879
H	-2.6007613184	2.8671475494	-0.6805799008
N	0.2236531696	-0.4819806720	0.8542913604
C	2.3465585007	-0.9518911155	-0.4347118409
C	2.5969884821	-2.1973836629	0.4313335246
H	1.6625616880	-2.7133140101	0.6707455446
H	3.2360551580	-2.8897352173	-0.1262041629
H	3.0938264343	-1.9409071097	1.3713655500
C	1.6139059473	-1.3809578998	-1.7122542252
H	1.4185456944	-0.5366776006	-2.3796429808
H	2.2391843994	-2.0980951959	-2.2537772521
H	0.6711109364	-1.8847240858	-1.4726350179
C	3.6957522404	-0.3020292014	-0.7726158999
H	4.2127886444	0.0193596887	0.1387028551
H	4.3329634225	-1.0391539607	-1.2713510909
H	3.5831671245	0.5575643732	-1.4361444041
S	0.9865886507	1.5971403371	-0.4038310590
O	1.6490671146	1.8611683319	-1.6783886175
O	0.9685345135	2.6423944865	0.6237199865
C	0.0599973177	-0.9943247721	2.1236904964
O	0.9751512132	-1.1578666757	2.9005232142
H	-0.9861431598	-1.2511720351	2.3433741215

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C	1.6300191212	-0.0994131954	0.4856453446
C	-0.7601993644	-0.1773799437	0.0952914540
C	-0.5417260736	0.9911714946	-0.6062205168
C	-1.8084516376	-1.1503789533	-0.2555767330
O	-1.8250972824	-2.3120162625	0.0803500735
O	-2.7813388135	-0.5636511165	-0.9838511644
C	-3.8545059274	-1.4324107744	-1.3649935059
N	-2.2807869658	0.7842932612	1.7030029021
N	-2.3011236166	1.7812510493	1.1465289827
C	-1.9404654931	2.5280010597	0.0947893119
H	2.2223245389	0.1221786372	1.3794717633
H	-0.8575118237	1.1546350323	-1.6293324782
H	-4.5425089511	-0.8152775013	-1.9398131726
H	-4.3443599978	-1.8356610129	-0.4764660031
H	-3.4747624164	-2.2565253741	-1.9718453011
H	-2.6817291672	2.4126970271	-0.6970050791
N	0.3320858089	-0.6150148134	0.8969796099
C	2.4180988593	-1.0164039093	-0.4727828441
C	2.6256850612	-2.3518279386	0.2592983274
H	1.6730407674	-2.8557905115	0.4477844759
H	3.2408743137	-3.0068883942	-0.3661646681
H	3.1296393349	-2.2095204057	1.2196189762
C	1.6683504300	-1.2831779923	-1.7842751136
H	1.5147555583	-0.3673074905	-2.3629092302
H	2.2619523409	-1.9699273676	-2.3963164221
H	0.7017565161	-1.7634090108	-1.5965975880
C	3.7867134714	-0.3810656892	-0.7545117367
H	4.3257324014	-0.1881758069	0.1800220160

H	4.3902066897	-1.0755965806	-1.3475116010
H	3.6979185538	0.5554987415	-1.3091756560
S	1.1099783618	1.5465971141	-0.1701315338
O	1.8084201635	1.9715878387	-1.3815674380
O	1.0547532316	2.4479663591	0.9822302533
C	0.1747436364	-1.2066610521	2.1329699039
O	1.1012097114	-1.4618161035	2.8708804712
H	-0.8754250846	-1.4353378677	2.3629014459
C	-1.3690087015	3.9047112385	0.3136245448
H	-0.7468281190	3.9351783349	1.2057470271
H	-0.7359929263	4.1578599722	-0.5415199388
H	-2.1684031702	4.6487547580	0.3790747811

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C	1.5145704410	0.0208789350	0.4272361383
C	-0.8655268968	-0.1663654632	-0.0007024648
C	-0.6946554695	1.0019061804	-0.7107303862
C	-1.8567980003	-1.2004751473	-0.3343664921
O	-1.8198497789	-2.3473822891	0.0500287858
O	-2.8365952658	-0.7019038838	-1.1163853140
C	-3.8421718521	-1.6479226023	-1.4955507058
N	-2.4788431451	0.7680415674	1.5847372302
N	-2.3982343152	1.7838297149	1.0726749150
C	-1.9257108910	2.5812878627	0.1117559540
H	2.0776405978	0.3276623668	1.3147441751
H	-1.0745950354	1.1535945803	-1.7150459997
H	-4.5501694950	-1.0938865654	-2.1092775094
H	-4.3314951546	-2.0529042273	-0.6076460776
H	-3.3957492073	-2.4659474689	-2.0641069419
N	0.2270525496	-0.5143609936	0.8456346196
C	2.3572357864	-0.9351985057	-0.4447106043
C	2.6131209129	-2.1955109958	0.3976651634
H	1.6811054844	-2.7225990953	0.6220379745
H	3.2603717858	-2.8723793845	-0.1693743781
H	3.1024576770	-1.9540706125	1.3456288388
C	1.6352061271	-1.3434161245	-1.7351885572
H	1.4434129015	-0.4866389986	-2.3875092834
H	2.2672024264	-2.0484702506	-2.2848055452
H	0.6914738564	-1.8540533215	-1.5140598634
C	3.7022292031	-0.2669618193	-0.7626275041
H	4.2165754166	0.0308984527	0.1582222333
H	4.3448782294	-0.9843216063	-1.2828707666
H	3.5847978605	0.6112713662	-1.4006967659
S	0.9695909760	1.5985568475	-0.3729284261
O	1.6308566945	1.8926382203	-1.6419209961
O	0.9439333971	2.6263958486	0.6723510711
C	0.0675644903	-1.0407620918	2.1099732311
O	0.9852280711	-1.2044348344	2.8843270175
H	-0.9760639750	-1.3090480279	2.3277396841
C	-2.8870840789	2.9859569903	-0.9758612086
H	-3.5642433541	3.7814373620	-0.6530923871
H	-2.3028847847	3.3630030183	-1.8189890633
H	-3.4706925071	2.1245779110	-1.3101855499
H	-1.1948364880	3.2937744254	0.4902461091

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C	1.6127617547	0.1937884540	0.5234009882
C	-0.6525923870	-0.5127889240	0.0287614873
C	-0.7202458874	0.6862256440	-0.6570348093
C	-1.3736500550	-1.7265480022	-0.3960591704
O	-1.0879644225	-2.8579391234	-0.0796871668
O	-2.4333712834	-1.4063656050	-1.1680515731

C	-3.2017612774	-2.5249605895	-1.6266600604
N	-2.4065986416	-0.0316509314	1.5496736506
N	-2.7118854652	0.9301541966	1.0106118782
C	-2.5224976029	1.7362098340	-0.0513409777
H	2.0936670693	0.5364383986	1.4454279922
H	-1.0015205546	0.7763188092	-1.6993600763
H	-4.0055129328	-2.1034749384	-2.2273626144
H	-3.6022375654	-3.0799148483	-0.7762622114
H	-2.5767864044	-3.1887779280	-2.2269885478
H	-3.1420299714	1.3928704605	-0.8810339283
N	0.4856025761	-0.6605503296	0.8706914801
C	2.6499284925	-0.4520790905	-0.4190997129
C	3.1860310187	-1.7041161596	0.2937856004
H	2.3966756231	-2.4464696628	0.4448911142
H	3.9672775026	-2.1569251568	-0.3254905285
H	3.6121968419	-1.4591060929	1.2708937835
C	2.0447870184	-0.8717781461	-1.7648196616
H	1.6593973631	-0.0157323931	-2.3265828580
H	2.8238586598	-1.3461874701	-2.3702056646
H	1.2451319317	-1.6074931563	-1.6255630182
C	3.8064144600	0.5343864482	-0.6349515068
H	4.2412498110	0.8399588684	0.3233705582
H	4.5942391904	0.0426611922	-1.2146028803
H	3.4877460553	1.4273548490	-1.1768366372
S	0.6933781982	1.6619797268	-0.1185478515
O	1.3061170072	2.2991598117	-1.2813136856
O	0.3384179308	2.4603087938	1.0533577418
C	0.4491645337	-1.3152206060	2.0834842767
O	1.3815100158	-1.3369137827	2.8569446115
H	-0.5071470842	-1.8271519576	2.2607313515
C	-2.3890355960	3.1942113349	0.1149217464
C	-2.3737489995	3.9760980301	-1.0437487323
C	-2.2344694133	3.8023525001	1.3648734164
C	-2.1899174558	5.3531139782	-0.9558766038
H	-2.4912587528	3.5046037382	-2.0165918525
C	-2.0654911011	5.1777776755	1.4479298139
H	-2.2303103351	3.1974504036	2.2667327042
C	-2.0389155185	5.9567746785	0.2900085186
H	-2.1682068742	5.9521176899	-1.8603241750
H	-1.9441989668	5.6442135284	2.4200833696
H	-1.9013325460	7.0307870999	0.3605265410

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C	1.6404202468	0.2401767601	0.3666719067
C	-0.6648107909	-0.4696604794	0.0716897036
C	-0.8183707499	0.7489678410	-0.5632960904
C	-1.3870149964	-1.6948327403	-0.3123660298
O	-1.0392285118	-2.8207861094	-0.0376158782
O	-2.5093269442	-1.3985814953	-0.9950747241
C	-3.2788433494	-2.5282135336	-1.4170431416
N	-2.2805198940	-0.0734748799	1.7653178831
N	-2.5032603942	0.9806309667	1.3835604615
C	-2.2705572763	1.9297454941	0.4586906945
H	2.1805866545	0.6260602874	1.2375724449
H	-1.2989723215	0.8623935771	-1.5293905752
H	-4.1412755405	-2.1157411302	-1.9386656907
H	-3.5902853108	-3.1159749438	-0.5511413231
H	-2.6905463719	-3.1589184773	-2.0864295366
N	0.5394749116	-0.5970932742	0.8232189014
C	2.6142622292	-0.4506161988	-0.6138809199
C	3.2056931956	-1.6636468074	0.1218927048
H	2.4344597621	-2.4033885477	0.3552944057
H	3.9492350819	-2.1385183709	-0.5262921214

H	3.6903567830	-1.3717920104	1.0578855251
C	1.9135254550	-0.9427774784	-1.8869531168
H	1.4909180603	-0.1202287751	-2.4707837690
H	2.6462123026	-1.4592425000	-2.5154210613
H	1.1253384566	-1.6641792951	-1.6458815680
C	3.7489902911	0.5246864798	-0.9580079088
H	4.2485158242	0.8770541483	-0.0482765124
H	4.4963824796	0.0039855494	-1.5650710376
H	3.3923556104	1.3887787993	-1.5225198927
S	0.6987246729	1.6860422822	-0.3070406881
O	1.1815015847	2.1667648314	-1.5989219293
O	0.5300649334	2.6468831511	0.7888076643
C	0.6047887366	-1.2341539562	2.0437301916
O	1.5904460505	-1.2280115156	2.7484669262
H	-0.3273409023	-1.7585711804	2.2980277219
H	-1.6584813738	2.7410348717	0.8514748756
C	-3.3491847789	2.2498171535	-0.4965271191
C	-3.2647928780	3.4531712031	-1.2043144884
C	-4.3909780887	1.3552596378	-0.7676578545
C	-4.2185353251	3.7615091320	-2.1708707731
H	-2.4500956264	4.1424320118	-0.9978016773
C	-5.3478681321	1.6754048376	-1.7242807390
H	-4.4518617812	0.4135768425	-0.2285067358
C	-5.2637070108	2.8768727607	-2.4292614769
H	-4.1463703966	4.6958533297	-2.7179097807
H	-6.1620448571	0.9854373324	-1.9222114914
H	-6.0113260398	3.1211987286	-3.1768359898

TS2c4
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C	1.6162436514	-0.0451429854	0.4493829389
C	-0.7808279132	-0.0893148587	0.0894916433
C	-0.5651937024	1.0862661560	-0.6047001019
C	-1.7755848717	-1.1093500165	-0.2924104409
O	-1.7496573512	-2.2660694745	0.0597378542
O	-2.7432392028	-0.5861772558	-1.0720650329
C	-3.7546025371	-1.5136237494	-1.4817787979
N	-2.3640615174	0.7798464492	1.6091365857
N	-2.3690998880	1.8161858421	1.1234691214
C	-1.9465585361	2.6484748127	0.1546668053
H	2.2302130607	0.2012040576	1.3217430515
H	-0.9123842558	1.2513129243	-1.6185487855
H	-4.4494639575	-0.9392241556	-2.0920887350
H	-4.2583322875	-1.9309494722	-0.6079648535
H	-3.3100486409	-2.3240261589	-2.0624912439
N	0.3130790325	-0.5077788337	0.9018865181
C	2.3655726663	-1.0223563601	-0.4816436284
C	2.5710154103	-2.3247589315	0.3086252403
H	1.6169518520	-2.8119095334	0.5309957776
H	3.1727041573	-3.0121437424	-0.2949653245
H	3.0882951900	-2.1440697496	1.2552652000
C	1.5790253938	-1.3397484875	-1.7596025777
H	1.4195852066	-0.4501398243	-2.3755989235
H	2.1480686222	-2.0621544007	-2.3536077702
H	0.6139533697	-1.8002262666	-1.5222534405
C	3.7368758598	-0.4239822881	-0.8259465383
H	4.3009080558	-0.1922311021	0.0847246011
H	4.3155819002	-1.1578538794	-1.3959307496
H	3.6493083074	0.4840539028	-1.4265827319
S	1.1307467189	1.5859072109	-0.2739995562
O	1.7708866327	1.9017464691	-1.5499318219
O	1.2007712796	2.5584163300	0.8170537845
C	0.1590975678	-1.0734389941	2.1483239146
O	1.0866411259	-1.3216851883	2.8876823209

H	-0.8922535610	-1.2848300400	2.3895205740
C	-2.9136915516	2.7715666579	-1.0032974596
H	-3.7344732557	3.4546898929	-0.7610097598
H	-2.3659035990	3.1953039324	-1.8499333040
H	-3.3146244922	1.7977579867	-1.2905867364
C	-1.2894392201	3.9272740764	0.6165919951
H	-0.6024533422	4.2687970889	-0.1614538061
H	-2.0519632279	4.6999868002	0.7684024575
H	-0.7098329197	3.7827365986	1.5262526865

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C	-2.1254232927	-0.6683230310	-0.4094325530
C	-0.8446748918	1.1673729966	0.5703660155
C	0.0862834837	0.8638948351	-0.4134941424
C	-1.1585463166	2.5261968657	1.0507137538
O	-2.1530716033	2.8163344472	1.6767211228
O	-0.1862458042	3.3993481796	0.7357966262
C	-0.4018567969	4.7367846010	1.1962954515
N	0.7031143003	1.1121020413	2.2985855281
N	1.5418394328	0.6304278592	1.6839904364
C	1.8276916541	0.0294520473	0.4837456861
H	-2.0502212376	-1.7305368091	-0.1467440243
H	0.6033005548	1.6551104309	-0.9477284301
H	0.4615595046	5.3054327545	0.8561214569
H	-0.4731693511	4.7528185124	2.2858053961
H	-1.3225193258	5.1392117117	0.7693604886
N	-1.8280537499	0.1472059364	0.7643864305
C	-3.4944068197	-0.3686519662	-1.0652210083
C	-4.5878404051	-0.7878884522	-0.0690816464
H	-4.5735486895	-0.1688073861	0.8316187622
H	-5.5630683379	-0.6632793798	-0.5510923147
H	-4.4795394845	-1.8318732142	0.2389517669
C	-3.6682990336	1.1243445279	-1.3748621101
H	-2.9721415064	1.4707484677	-2.1406819911
H	-4.6875968689	1.2917888871	-1.7379984251
H	-3.5392843227	1.7233647092	-0.4661242650
C	-3.6345677969	-1.2264019529	-2.3317065354
H	-3.4932899587	-2.2888292020	-2.1010978195
H	-4.6450332133	-1.1067903123	-2.7349650567
H	-2.9246943920	-0.9359579970	-3.1091769917
S	-0.6552547965	-0.3475120393	-1.5128605538
O	-1.0045783816	0.3969958298	-2.7234107452
O	0.1096380797	-1.5822399722	-1.6739709290
C	-2.1464790179	-0.2970263855	2.0263094506
O	-2.7338107798	-1.3340053880	2.2553527205
H	-1.8036313454	0.3963232873	2.8103318887
C	1.7847259026	-1.4676368719	0.6089609405
C	2.7309162183	-2.2750413533	-0.0246354488
C	0.7608048693	-2.0683245334	1.3503635901
C	2.6247343440	-3.6622733685	0.0500322904
H	3.5454752790	-1.8294007929	-0.5844078188
C	0.6564521444	-3.4502370394	1.4240937962
H	0.0276056231	-1.4597204110	1.8703620567
C	1.5870462756	-4.2539204095	0.7639758982
H	3.3598583338	-4.2806811906	-0.4548033502
H	-0.1549677965	-3.8935415091	1.9925964919
H	1.5050844802	-5.3350081578	0.8129673205
C	2.9085358200	0.6871182518	-0.3062770184
C	2.9751501193	0.4217220054	-1.6812655026
C	3.8068725927	1.5894351858	0.2675012652
C	3.9348560401	1.0517460551	-2.4647864415
H	2.2717556359	-0.2784380631	-2.1285557904
C	4.7638966944	2.2210011613	-0.5259494455

H	3.7686697218	1.7887949231	1.3345961215
C	4.8323645640	1.9534098199	-1.8900716223
H	3.9765334926	0.8418814168	-3.5286589369
H	5.4600127002	2.9187295094	-0.0714746633
H	5.5798964554	2.4441389320	-2.5049371722

TS2c6
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C	1.6667331386	0.2154317433	0.4296117506
C	-0.6536222074	-0.3969452288	0.0540304626
C	-0.7413930143	0.8485075237	-0.5487317818
C	-1.4358323137	-1.5647306245	-0.3886754492
O	-1.1718972491	-2.7166991486	-0.1306646010
O	-2.5130707521	-1.1773551994	-1.0979972893
C	-3.3523707371	-2.2443633222	-1.5513443000
N	-2.2061971374	0.0614624862	1.7971784162
N	-2.4215790457	1.1086541352	1.4049561975
C	-2.1960157580	1.9959977675	0.4145242501
H	2.2057560953	0.5189268023	1.3332438816
H	-1.1378869834	1.0122100701	-1.5460958735
H	-4.1708232733	-1.7670821596	-2.0870637242
H	-3.7265368123	-2.8162277268	-0.6999809810
H	-2.7938720635	-2.9086585142	-2.2136409836
N	0.5321457730	-0.6119796625	0.8137120750
C	2.6310618240	-0.4364218327	-0.5861511104
C	3.1654494916	-1.7222826708	0.0656678781
H	2.3661026225	-2.4517459587	0.2273152645
H	3.9078933399	-2.1720115064	-0.6014543961
H	3.6388365000	-1.5180666723	1.0301441102
C	1.9362766566	-0.8037399838	-1.9036577726
H	1.5556452984	0.0771307759	-2.4285754023
H	2.6619415390	-1.2957503883	-2.5592016150
H	1.1178469432	-1.5122513566	-1.7335810592
C	3.8065342108	0.5181615950	-0.8396949759
H	4.3067978691	0.7767671313	0.1003962331
H	4.5413466163	0.0186296992	-1.4788610209
H	3.4914075847	1.4382924288	-1.3362647422
S	0.7822531166	1.7345857625	-0.1420945625
O	1.3330476641	2.3287727341	-1.3541690762
O	0.5554915028	2.5733271136	1.0389550936
C	0.5554543354	-1.3207057574	1.9975758658
O	1.5314145983	-1.3918906804	2.7111875520
H	-0.3985244313	-1.8239500211	2.2089830704
H	-1.6494555944	2.8850395662	0.7182088809
C	-3.2937889554	2.1508484928	-0.5825666152
O	-3.1620333952	2.8428454069	-1.5610603100
O	-4.3632149144	1.4049365702	-0.3021436620
C	-5.4004619319	1.4367868401	-1.2911454005
H	-6.1822019866	0.7812225736	-0.9133494553
H	-5.7714677174	2.4559733889	-1.4116039008
H	-5.0140015563	1.0772036176	-2.2469713617

Computational methods of Chapter IV

Computational Methods

All of the calculations were performed using the Gaussian09 program.[1] Molecular geometries were optimized with the B3LYP functional[12] including the D3BJ dispersion correction of Grimme.[13] The electronic configuration of the molecular systems was described with the standard split-valence basis set def2SVP,[14] which showed to be adequate for that functional.[15] Single point calculations using def2TZVP basis set, considering solvent effects were carried out over optimized geometries. Analytical second derivatives of the energy were calculated to classify the nature of every stationary point, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. All transition structures were characterized by one imaginary frequency and were confirmed to connect to reactants and products by intrinsic reaction coordinate (IRC) calculations. The IRC paths were traced using the Hratchian-Schlegel algorithm.[16] The thermal and entropic contributions to the free energies were also obtained from the vibrational frequency calculations, using the unscaled frequencies. All discussions are based on values of free energies (G). However the individual reactions involved on the study are bimolecular processes. In order to avoid errors due to entropic effects when comparing all stationery points in an only energy diagram, we used corrected free energy (G_{corr}) values following Morokuma's model[17] based on consideration of translational entropy. Structural representations were generated using CYLView.[11]

[12] (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

[13] (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104-154119. (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[14] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 227-236.

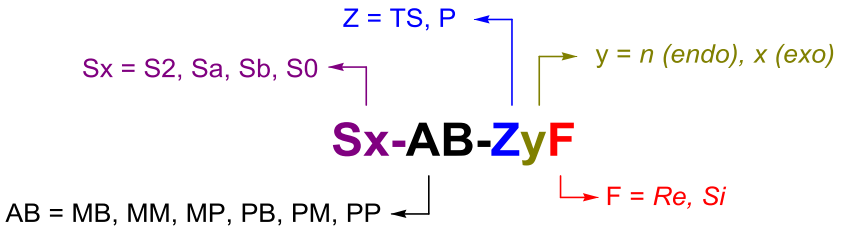
[15] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

[16] H. P. Hratchian, H. B. Schlegel, *J. Phys. Chem. A* **2002**, *106*, 165-169.

[17] R. Tanaka, M. Yamashita, L. W. Chung, K. Morokuma, K. Nozaki, *Organometallics* **2011**, *30*, 6742-6750.

Nomenclature

The nomenclature of the stationary points is explained in *figure A3*. For instance, **S2-MB-TSnRe** corresponds to the transition structure of the reaction between **S2** and **MB**, by the *Re* face of **S2** following an *endo* approach (*endo/exo* refers to the ester group)



Sx: dipolarophile; AB: dipole; Z: point; y: endo/exo approach of the dipolarophile; F: diastereoface of the dipolarophile

Figure A3

The cycloaddition between four nitrones (**MB**, **PB**, **PM** and **PP**) and dipolarophiles (**S2**, **Sa,b** and **S0**) have been studied (*Figure A4*). In the case of sulfoxide derivatives both relative orientations (**Sa** for *trans*, **Sb** for *cis)* between the oxygen and tert-butyl groups have been considered; the most stable **Sa** was considered for calculating energy barriers.

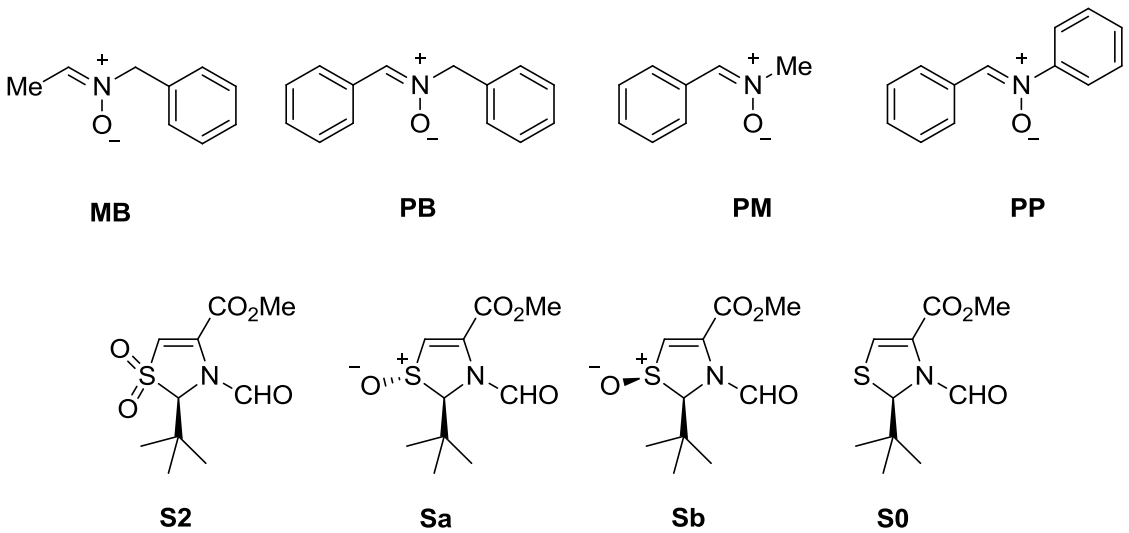


Figure A4

Endo and *exo* approaches by *Re* and *Si* faces were calculated (*Re/Si* refers to carbon bearing the ester group, i.e: C4 of the thiazolidine ring. Actually, *Re* corresponds to 4*Re*,5*Si* and *Si* corresponds to 4*Si*,5*Re*).

Energy values

Table A19. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **MB** and **S2**

	E(0)	ΔE(0)[a]	G	ΔG[a]	Im. Freq.
MB	-479.529894		-479.510862		
S2	-1219.295405		-1219.268320		
S2-MB-TSnRe	-1698.796559	18.0	-1698.759595	12.3	-261.1
S2-MB-TSnSi	-1698.804250	13.2	-1698.767401	7.4	-347.3
S2-MB-TSxRe	-1698.803897	13.4	-1698.766199	8.1	-356.7
S2-MB-TSxSi	-1698.814614	6.7	-1698.777027	1.4	-334.2
S2-MB-PnRe	-1698.846315	-13.2	-1698.809198	-18.8	
S2-MB-PnSi	-1698.847362	-13.8	-1698.811153	-20.1	
S2-MB-PxRe	-1698.846982	-13.6	-1698.809899	-19.3	
S2-MB-PxSi	-1698.849455	-15.2	-1698.813320	-21.4	

[a]Referred to the sum of reagents

Table A20. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PB** and **S2**

	E(0)	ΔE(0)[a]	G	ΔG[a]	Im. Freq.
PB	-671.304585		-671.283583		
S2	-1219.295405		-1219.268320		
S2-PB-TSnRe	-1890.569825	18.9	-1890.529828	13.9	-320.4
S2-PB-TSnSi	-1890.577304	14.2	-1890.537518	9.0	-327.1
S2-PB-TSxRe	-1890.576003	15.1	-1890.535001	10.6	-339.6
S2-PB-TSxSi	-1890.584841	9.5	-1890.543944	5.0	-445.2
S2-PB-PnRe	-1890.615760	-9.9	-1890.576147	-15.2	
S2-PB-PnSi	-1890.620328	-12.8	-1890.579831	-17.5	
S2-PB-PxRe	-1890.616685	-10.5	-1890.577073	-15.8	
S2-PB-PxSi	-1890.619676	-12.4	-1890.579984	-17.6	

[a]Referred to the sum of reagents

Table A21. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PM** and **S2**

	E(0)	ΔE(0)[a]	G	ΔG[a]	Im. Freq.
PM	-440.228608		-440.211243		
S2	-1219.295405		-1219.268320		
S2-PM-TSnRe	-1659.491292	20.5	-1659.454948	15.4	-311.9
S2-PM-TSnSi	-1659.500293	14.9	-1659.464078	9.7	-325.7
S2-PM-TSxRe	-1659.496186	17.5	-1659.459530	12.6	-346.5
S2-PM-TSxSi	-1659.505488	11.6	-1659.469109	6.6	-448.5
S2-PM-PnRe	-1659.531286	-4.6	-1659.495616	-10.1	
S2-PM-PnSi	-1659.540696	-10.5	-1659.505810	-16.5	
S2-PM-PxRe	-1659.540112	-10.1	-1659.504214	-15.5	
S2-PM-PxSi	-1659.545159	-13.3	-1659.509299	-18.7	

[a]Referred to the sum of reagents

Table A22. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PP** and **S2**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PP	-631.998037		-631.977483		
S2	-1219.295405		-1219.268320		
S2-PP-TSnRe	-1851.263164	19.0	-1851.224466	13.4	-424.6
S2-PP-TSnSi	-1851.272933	12.9	-1851.233511	7.7	-352.0
S2-PP-TSxRe	-1851.274413	11.9	-1851.234916	6.8	-365.5
S2-PP-TSxSi	-1851.281464	7.5	-1851.242020	2.4	-430.3
S2-PP-PnRe	-1851.304181	-6.7	-1851.265144	-12.1	
S2-PP-PnSi	-1851.311563	-11.4	-1851.273374	-17.3	
S2-PP-PxRe	-1851.317965	-15.4	-1851.278852	-20.7	
S2-PP-PxSi	-1851.318504	-15.7	-1851.280191	-21.6	

[a]Referred to the sum of reagents

Table A23. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **MB** and **Sa**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
MB	-479.529894		-479.510862		
Sa	-1144.039440		-1144.012943		
Sb-MB-TSnRe	-1623.537258	18.6	-1623.501045	14.3	-322.9
Sb-MB-TSnSi	-1623.540631	16.6	-1623.503602	12.7	-383.4
Sb-MB-TSxRe	-1623.539298	17.5	-1623.502077	13.6	-376.0
Sb-MB-TSxSi	-1623.550185	10.3	-1623.513455	6.5	-436.1
Sa-MB-TSnRe	-1623.539034	17.8	-1623.502599	13.3	-297.2
Sa-MB-TSnSi	-1623.549755	10.7	-1623.512589	7.0	-411.4
Sa-MB-TSxRe	-1623.539298	17.5	-1623.502077	13.6	-376.0
Sa-MB-TSxSi	-1623.558539	5.2	-1623.521613	1.4	-371.3
Sb-MB-PnRe	-1623.586070	-14.2	-1623.549834	-16.3	
Sb-MB-PnSi	-1623.590256	-17.0	-1623.554761	-19.4	
Sb-MB-PxRe	-1623.587924	-15.5	-1623.551676	-17.5	
Sb-MB-PxSi	-1623.593920	-19.1	-1623.557669	-21.2	
Sa-MB-PnRe	-1623.592269	-17.8	-1623.555605	-20.0	
Sa-MB-PnSi	-1623.586493	-14.6	-1623.550900	-17.0	
Sa-MB-PxRe	-1623.587914	-15.2	-1623.551423	-17.3	
Sa-MB-PxSi	-1623.598703	-22.1	-1623.562332	-24.2	

[a]Referred to the sum of reagents

Table A24. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PB** and **Sa**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PB	-671.304585		-671.283583		
Sa	-1144.039440		-1144.012943		
Sb-PB-TSnRe	-1815.308835	21.0	-1815.269553	16.9	-457.6
Sb-PB-TSnSi	-1815.312896	19.1	-1815.273528	14.4	-393.9
Sb-PB-TSxRe	-1815.310059	20.7	-1815.269518	16.9	-389.2
Sb-PB-TSxSi	-1815.317650	15.6	-1815.277611	11.9	-437.9
Sa-PB-TSnRe	-1815.315000	17.5	-1815.275493	13.2	-396.1
Sa-PB-TSnSi	-1815.319960	14.0	-1815.279916	10.4	-467.5
Sa-PB-TSxRe	-1815.310059	20.7	-1815.269518	16.9	-389.2
Sa-PB-TSxSi	-1815.329146	8.4	-1815.288905	4.8	-460.0
Sb-PB-PnRe	-1815.357361	-11.1	-1815.318574	-13.8	
Sb-PB-PnSi	-1815.363070	-14.9	-1815.323491	-16.9	
Sb-PB-PxRe	-1815.357790	-11.6	-1815.318115	-13.5	
Sb-PB-PxSi	-1815.361390	-13.8	-1815.322748	-16.5	
Sa-PB-PnRe	-1815.363462	-14.9	-1815.324506	-17.6	
Sa-PB-PnSi	-1815.358591	-12.0	-1815.318854	-14.0	
Sa-PB-PxRe	-1815.357413	-10.9	-1815.317415	-13.1	
Sa-PB-PxSi	-1815.367936	-17.7	-1815.328120	-19.8	

[a]Referred to the sum of reagents

Table A25. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PM** and **Sa**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PM	-440.228608		-440.211243		
Sa	-1144.039440		-1144.012943		
Sb-PM-TSnRe	-1584.230473	22.4	-1584.194854	18.4	-438.0
Sb-PM-TSnSi	-1584.244165	13.8	-1584.208760	9.7	-426.1
Sb-PM-TSxRe	-1584.238741	17.4	-1584.203032	13.3	-385.1
Sb-PM-TSxSi	-1584.238812	17.6	-1584.203034	13.3	-402.6
Sa-PM-TSnRe	-1584.236399	19.0	-1584.200543	14.8	-375.3
Sa-PM-TSnSi	-1584.243111	14.6	-1584.207547	10.4	-458.4
Sa-PM-TSxRe	-1584.230713	22.9	-1584.194571	18.6	-374.8
Sa-PM-TSxSi	-1584.249714	10.5	-1584.214069	6.3	-463.1
Sb-PM-PnRe	-1584.267172	-2.8	-1584.232414	-5.2	
Sb-PM-PnSi	-1584.286580	-14.7	-1584.252396	-17.7	
Sb-PM-PxRe	-1584.281605	-11.6	-1584.246530	-14.0	
Sb-PM-PxSi	-1584.286181	-14.5	-1584.250980	-16.8	
Sa-PM-PnRe	-1584.279780	-10.3	-1584.244615	-12.8	
Sa-PM-PnSi	-1584.280026	-10.5	-1584.245708	-13.5	
Sa-PM-PxRe	-1584.281008	-10.7	-1584.245624	-13.5	
Sa-PM-PxSi	-1584.286769	-15.0	-1584.251563	-17.2	

[a]Referred to the sum of reagents

Table A26. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PP** and **Sa**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PP	-631.998037		-631.977483		
Sa	-1144.039440		-1144.012943		
Sb-PP-TSnRe	-1776.004226	19.6	-1775.965391	15.7	-391.6
Sb-PP-TSnSi	-1776.017379	11.5	-1775.978701	7.4	-421.7
Sb-PP-TSxRe	-1776.016579	11.8	-1775.977861	7.9	-407.1
Sb-PP-TSxSi	-1776.017302	11.6	-1775.979424	6.9	-408.3
Sa-PP-TSnRe	-1776.008741	17.3	-1775.969622	13.1	-413.7
Sa-PP-TSnSi	-1776.017205	11.7	-1775.978399	7.5	-453.9
Sa-PP-TSxRe	-1776.011413	15.5	-1775.972377	11.3	-378.1
Sa-PP-TSxSi	-1776.026299	5.9	-1775.987490	1.8	-474.9
Sb-PP-PnRe	-1776.052513	-12.3	-1776.013927	-14.7	
Sb-PP-PnSi	-1776.057238	-15.6	-1776.019747	-18.4	
Sb-PP-PxRe	-1776.058390	-16.4	-1776.020130	-18.6	
Sb-PP-PxSi	-1776.059186	-16.7	-1776.021551	-19.5	
Sa-PP-PnRe	-1776.040684	-5.4	-1776.002560	-7.6	
Sa-PP-PnSi	-1776.051349	-11.7	-1776.013760	-14.6	
Sa-PP-PxRe	-1776.060470	-17.2	-1776.021900	-19.8	
Sa-PP-PxSi	-1776.074509	-20.2	-1776.029924	-24.8	

[a]Referred to the sum of reagents

Table A27. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **MB** and **S0**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
MB	-479.529894		-479.510862		
S0	-1068.817126		-1068.790630		
S0-MB-TSnRe	-1548.312190	23.0	-1548.276849	15.5	-341.8
S0-MB-TSnSi	-1548.324263	15.0	-1548.288203	8.3	-413.8
S0-MB-TSxRe	-1548.314049	21.4	-1548.277996	14.7	-452.4
S0-MB-TSxSi	-1548.329463	11.7	-1548.293753	4.9	-477.1
S0-MB-PnRe	-1548.371237	-16.8	-1548.336092	-21.7	
S0-MB-PnSi	-1548.365183	-12.9	-1548.330669	-18.3	
S0-MB-PxRe	-1548.360758	-10.1	-1548.325411	-15.0	
S0-MB-PxSi	-1548.369804	-15.8	-1548.334652	-20.8	

[a]Referred to the sum of reagents

Table A28. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PB** and **S0**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PB	-671.304585		-671.283583		
S0	-1068.817126		-1068.790630		
S0-PB-TSnRe	-1740.085213	24.1	-1740.046104	17.6	-456.1
S0-PB-TSnSi	-1740.097429	16.9	-1740.059118	9.5	-330.2
S0-PB-TSxRe	-1740.084456	24.9	-1740.045037	18.3	-463.3
S0-PB-TSxSi	-1740.098557	15.8	-1740.059571	9.2	-483.1
S0-PB-PnRe	-1740.143366	-14.4	-1740.105932	-19.9	
S0-PB-PnSi	-1740.137495	-10.5	-1740.099786	-16.0	
S0-PB-PxRe	-1740.130214	-5.9	-1740.091422	-10.8	
S0-PB-PxSi	-1740.138075	-10.9	-1740.099562	-15.9	

[a]Referred to the sum of reagents

Table A29. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PM** and **S0**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PM	-440.228608		-440.211243		
S0	-1068.817126		-1068.790630		
S0-PM-TSnRe	-1509.008794	24.5	-1508.974136	17.4	-403.4
S0-PM-TSnSi	-1509.021488	16.5	-1508.987014	9.3	-451.4
S0-PM-TSxRe	-1509.005149	27.1	-1508.970146	19.9	-449.3
S0-PM-TSxSi	-1509.018642	18.5	-1508.983926	11.3	-479.1
S0-PM-PnRe	-1509.065092	-13.1	-1509.031157	-18.4	
S0-PM-PnSi	-1509.061287	-10.5	-1509.028036	-16.4	
S0-PM-PxRe	-1509.053564	-5.5	-1509.020227	-11.5	
S0-PM-PxSi	-1509.060597	-10.2	-1509.026428	-15.4	

[a]Referred to the sum of reagents

Table A30. Absolute (hartree) and relative (kcal/mol) energies of the stationary points corresponding to the reaction between **PP** and **S0**

	E(0)	**ΔE(0)**[a]	**G**	**ΔG**[a]	**Im. Freq.**
PP	-631.998037		-631.977483		
S0	-1068.817126		-1068.790630		
S0-PP-TSnRe	-1700.781567	22.5	-1700.744553	14.8	-412.8
S0-PP-TSnSi	-1700.794690	14.2	-1700.757873	6.4	-424.1
S0-PP-TSxRe	-1700.785553	19.9	-1700.747657	12.8	-438.9
S0-PP-TSxSi	-1700.796750	12.8	-1700.758960	5.7	-472.6
S0-PP-PnRe	-1700.837084	-14.6	-1700.799783	-19.9	
S0-PP-PnSi	-1700.833031	-11.9	-1700.796458	-17.8	
S0-PP-PxRe	-1700.837396	-15.0	-1700.800159	-20.1	
S0-PP-PxSi	-1700.833590	-12.4	-1700.796026	-17.5	

[a]Referred to the sum of reagents

Optimized geometries

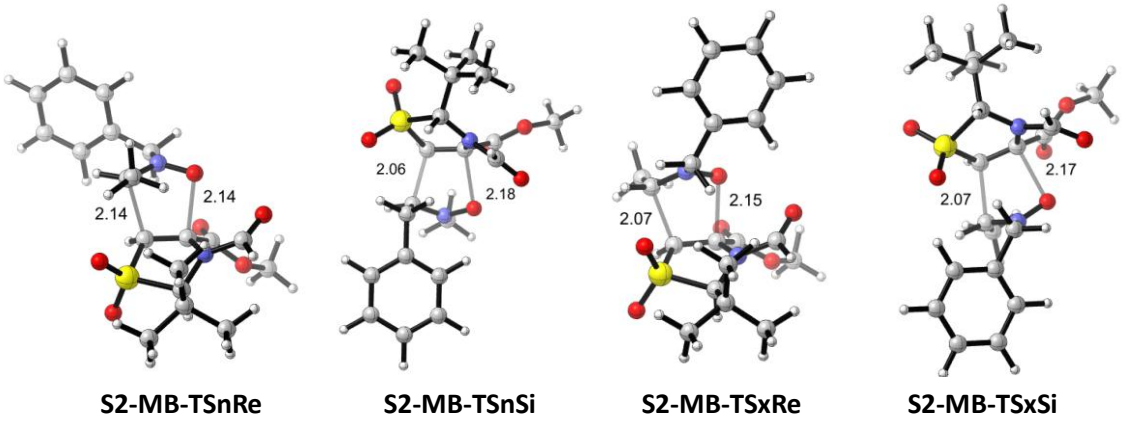


Figure A5. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **MB** and **S2**

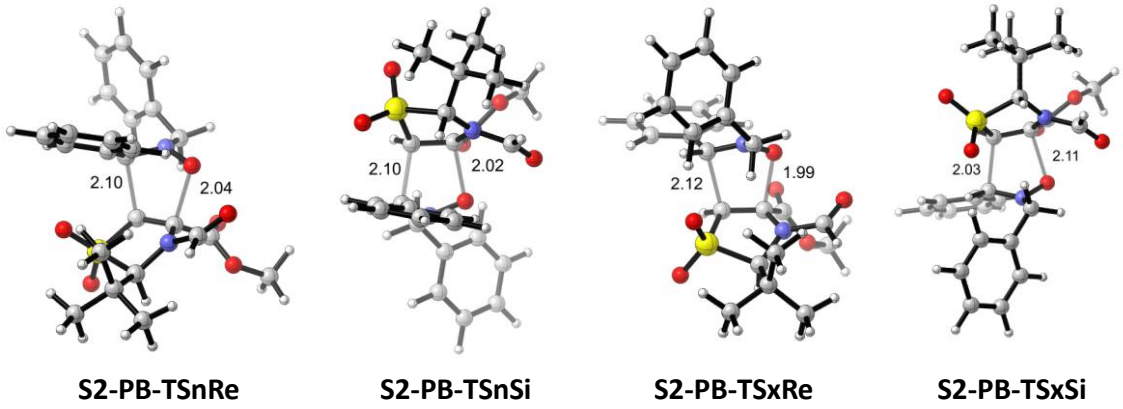


Figure A6. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PB** and **S2**

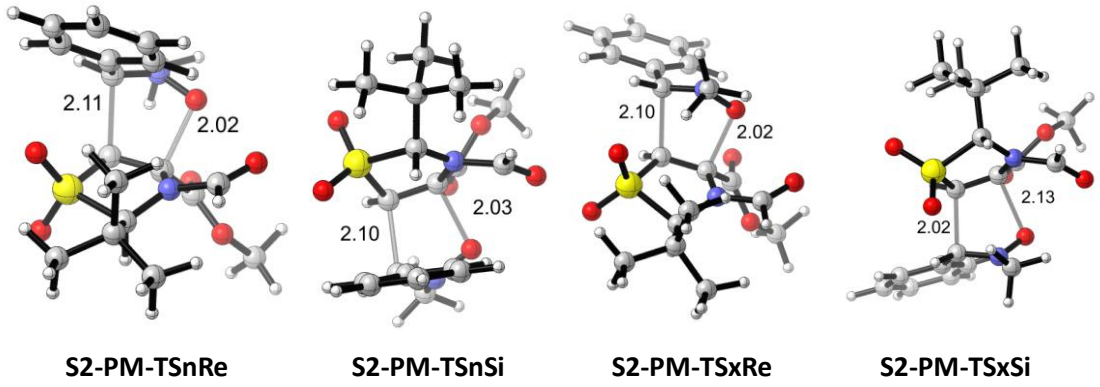


Figure A7. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PM** and **S2**

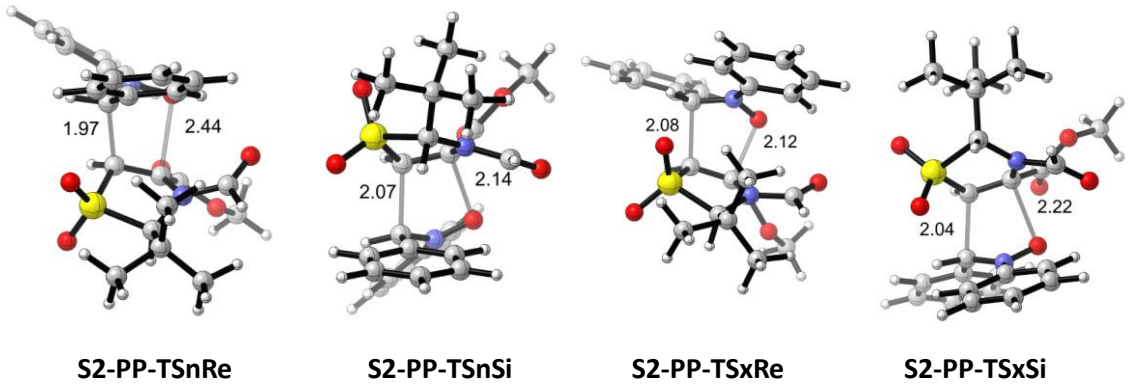


Figure A8. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PP** and **S2**

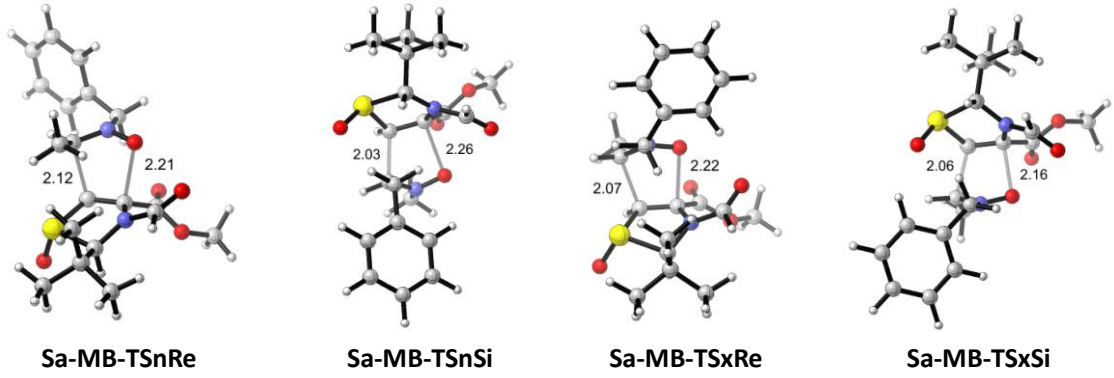


Figure A9. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **MB** and **Sa**

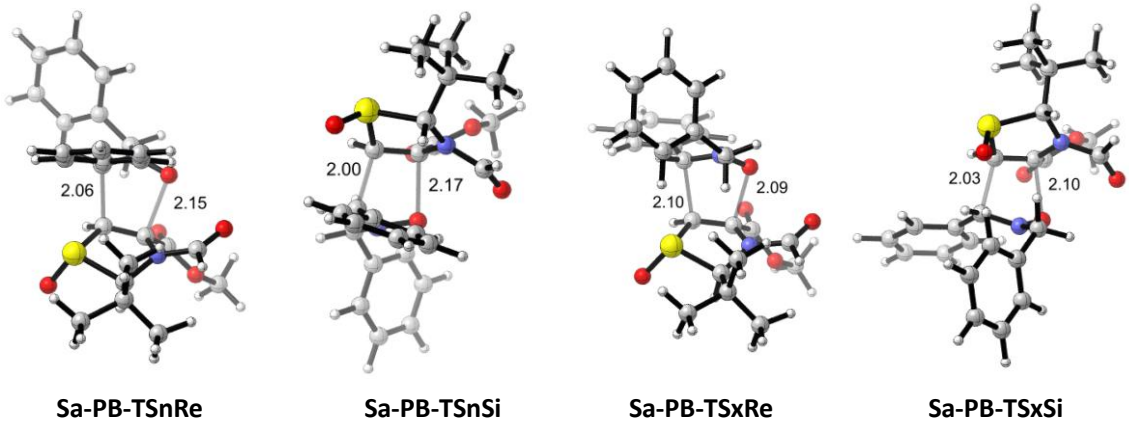


Figure A10. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PB** and **Sa**

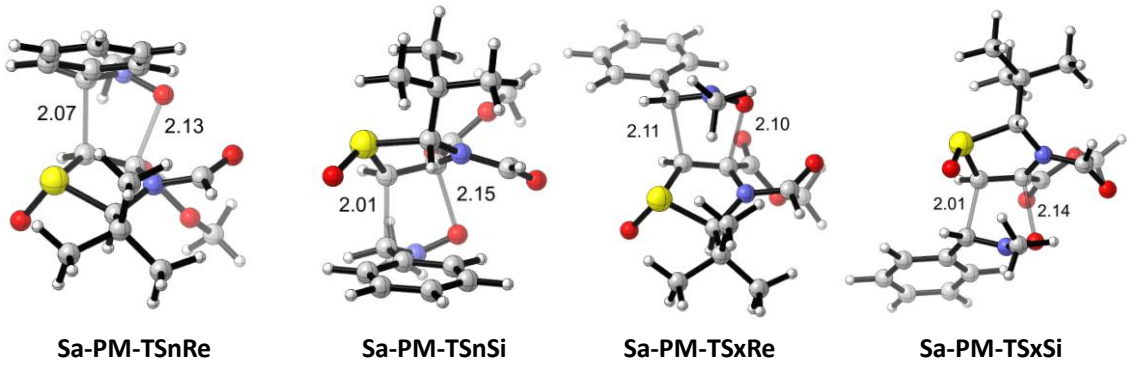


Figure A11. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PM** and **Sa**

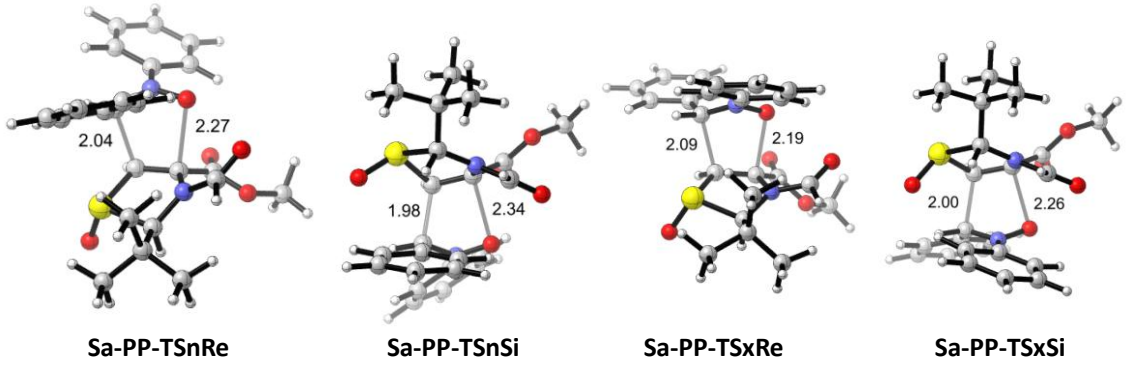


Figure A12. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PP** and **Sa**

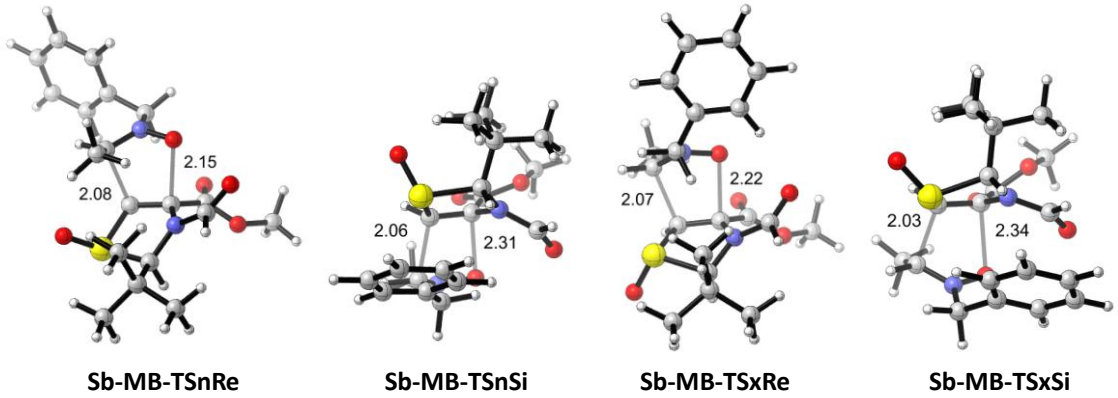


Figure A13. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **MB** and **Sb**

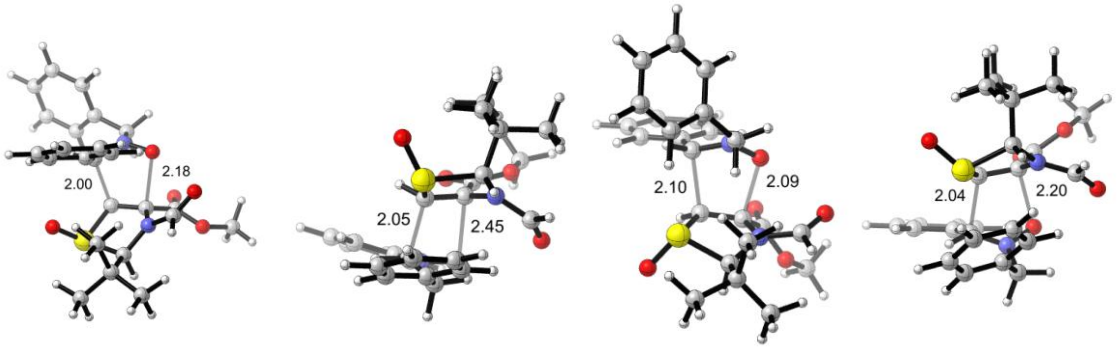


Figure A14. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PB** and **Sb**

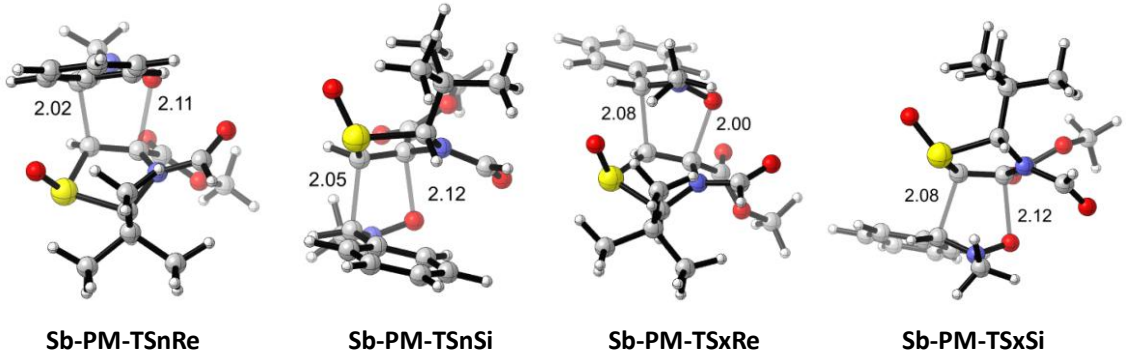


Figure A15. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PM** and **Sb**

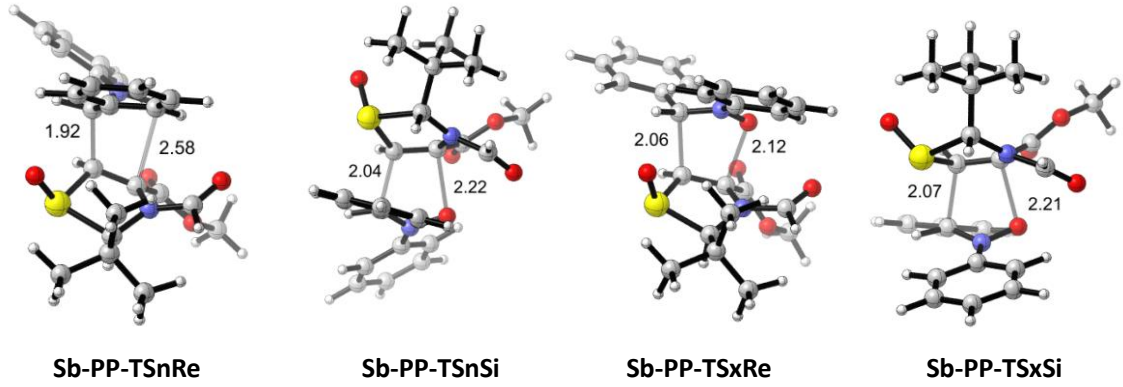


Figure A16. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PP** and **Sb**

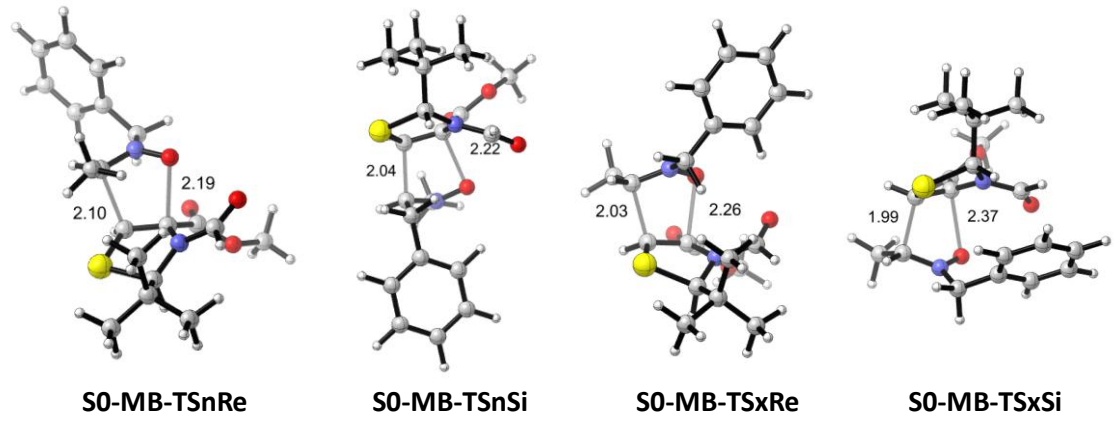


Figure A17. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **MB** and **S0**

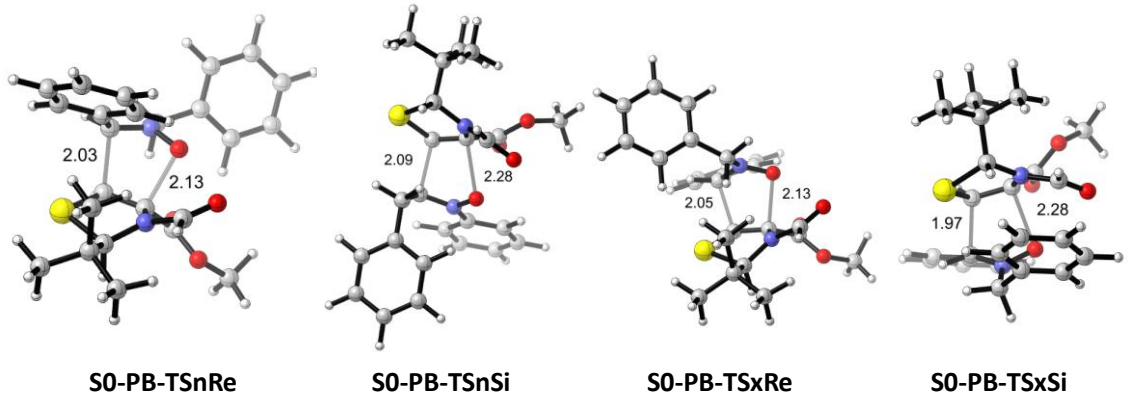


Figure A18. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PB** and **S0**

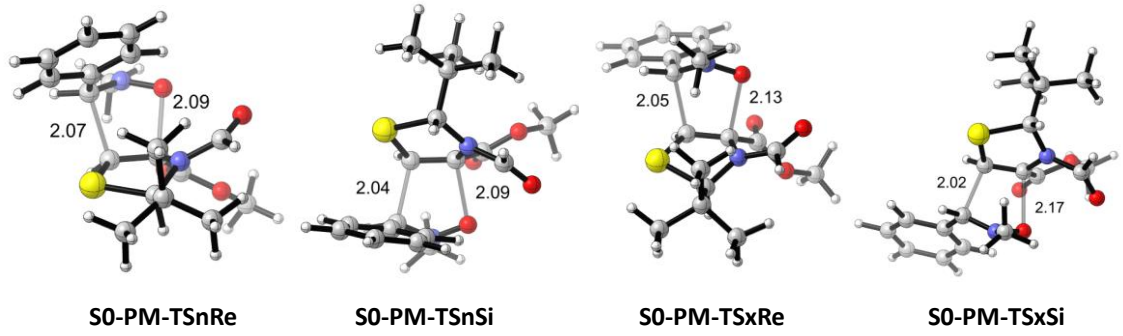


Figure A19. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PM** and **S0**

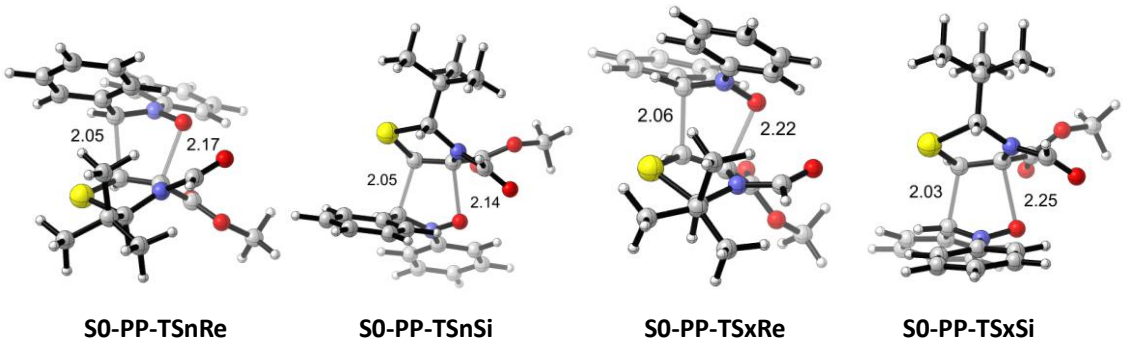


Figure A20. Optimized (B3LYP-D3BJ/def2SVP) geometries of the transition structures corresponding to the reaction between **PP** and **S0**

Cartesian coordinates

MB

0 1

N	0	-0.5018909653	0.0055035406	-0.1787804236
O	0	-0.6174559402	1.1468255159	-0.7128200619
C	0	-1.7790133025	-0.7042826495	0.1186947872
C	0	0.6458197725	-0.5403209303	0.1392295118
H	0	0.6198062909	-1.5264711733	0.6018869210
C	0	1.8962187296	0.2134810313	-0.1336684662
H	0	1.8854851185	1.1821619166	0.3970702370
H	0	1.9690522077	0.4643055564	-1.2066287568
H	0	2.7830249078	-0.3594394435	0.1690236980
H	0	-1.5640311999	-1.7677134745	0.2846976079
H	0	-2.3742079821	-0.5962810040	-0.7991134567
C	0	-2.4844667120	-0.1050501543	1.3099732969
C	0	-2.9148506944	1.2309228184	1.2864290739
C	0	-2.7067806589	-0.8751124565	2.4588032269
C	0	-3.5541603357	1.7803156528	2.3984669614
H	0	-2.7181428161	1.8316841541	0.3976237204
C	0	-3.3551607415	-0.3262413156	3.5687037365
H	0	-2.3719578422	-1.9159722982	2.4857959253
C	0	-3.7791019814	1.0040786837	3.5403715935
H	0	-3.8820437479	2.8224027834	2.3734484831
H	0	-3.5261291567	-0.9390816719	4.4570139450
H	0	-4.2849360104	1.4367219485	4.4069663393

PB

0 1

N	0	-2.1846314253	0.0477054286	-0.2214539811
O	0	-2.1883478760	1.2439297600	-0.6311411180
C	0	-3.5396876978	-0.5550427867	-0.0404581065
C	0	-1.1239608002	-0.6718935703	0.0900221618
H	0	-1.3372672594	-1.6845643468	0.4306028073
H	0	-3.4491297020	-1.6484663779	-0.0431053331
H	0	-4.0991998346	-0.2370785446	-0.9309942375
C	0	0.2579037222	-0.2409962591	0.0286361305
C	0	1.2475107299	-1.1791425903	0.4025663707
C	0	0.6701348083	1.0489295805	-0.3761898860
C	0	2.5978787142	-0.8456054678	0.3753576229
H	0	0.9426792309	-2.1806059904	0.7186494388
C	0	2.0269955041	1.3720914505	-0.3997936112
H	0	-0.0909738533	1.7704216847	-0.6631537045
C	0	2.9947890352	0.4349706934	-0.0273554317
H	0	3.3464039716	-1.5854369135	0.6690319450
H	0	2.3320232762	2.3732377402	-0.7144409300
H	0	4.0547626593	0.6991670183	-0.0498187781
C	0	-4.1932765027	-0.0717419023	1.2304525798
C	0	-4.4802181803	1.2904578286	1.4103453956
C	0	-4.5050481018	-0.9776786230	2.2523081852
C	0	-5.0676234684	1.7317032105	2.5965674082
H	0	-4.2159584058	1.9946248249	0.6201948958
C	0	-5.1014916897	-0.5357140624	3.4364928062
H	0	-4.2819634745	-2.0402316312	2.1205090991
C	0	-5.3825531967	0.8210629357	3.6108126549
H	0	-5.2838034355	2.7943948831	2.7303903972
H	0	-5.3435687347	-1.2530062828	4.2243313018
H	0	-5.8470483733	1.1699641301	4.5362521671

PM

0 1

N	0	-2.3138938503	-1.8873457425	0.5712016146
O	0	-1.5464773524	-2.5928210351	-0.1409402583
C	0	-3.6939888777	-1.7834544118	0.0531964747
C	0	-1.9944294867	-1.2629517832	1.6914220053
H	0	-2.8037433668	-0.7028744648	2.1581124519
H	0	-3.6334906591	-1.3555800235	-0.9566309246
H	0	-4.3257975606	-1.1637040766	0.7010958709
H	0	-4.0939040534	-2.8038177433	-0.0202834568
C	0	-0.6950999028	-1.2611664822	2.3327609019
C	0	-0.5649938026	-0.5245193918	3.5328721328
C	0	0.4380281468	-1.9444978104	1.8354578855
C	0	0.6475470728	-0.4697639768	4.2127371588
H	0	-1.4331893551	0.0091284020	3.9295485891
C	0	1.6487773098	-1.8823226800	2.5258654083
H	0	0.3378978425	-2.5111618190	0.9129162105
C	0	1.7632351288	-1.1502950638	3.7109269723
H	0	0.7258951519	0.1054807782	5.1384282617
H	0	2.5167896477	-2.4154646941	2.1299891240
H	0	2.7166070073	-1.1087438314	4.2430979774

PP

0 1

N	0	-2.1345720000	0.0196272413	0.1408051190
O	0	-2.1064860692	1.2589310388	0.4037810660
C	0	-1.0743993225	-0.7354546787	-0.1085112042
H	0	-1.2927319777	-1.7636345539	-0.3885879166
C	0	0.3081804905	-0.3133501191	-0.0661984638
C	0	1.2882341667	-1.2864751666	-0.3755527500
C	0	0.7375187865	0.9932634065	0.2639046980
C	0	2.6427073384	-0.9721147394	-0.3548364183
H	0	0.9710121213	-2.3006358290	-0.6335386727
C	0	2.0990238017	1.2958214290	0.2834214717
H	0	-0.0147093496	1.7425474946	0.4966533967
C	0	3.0556203453	0.3242237847	-0.0238710744
H	0	3.3823858521	-1.7389170922	-0.5971398357
H	0	2.4166937101	2.3091390886	0.5414248041
H	0	4.1192445845	0.5737191125	-0.0070949718
C	0	-3.4627430987	-0.5816574180	0.0895718658
C	0	-3.6950021095	-1.9017328930	0.4849550119
C	0	-4.5124297984	0.2364905530	-0.3347123335
C	0	-4.9927195953	-2.4147126449	0.4204521824
H	0	-2.8813053678	-2.5183583305	0.8682539838
C	0	-5.8026452082	-0.2879827813	-0.4008121583
H	0	-4.2896553594	1.2704772167	-0.5956333955
C	0	-6.0466520054	-1.6139025619	-0.0274052818
H	0	-5.1803503220	-3.4430847321	0.7372616565
H	0	-6.6247928603	0.3448276313	-0.7427035598
H	0	-7.0599245130	-2.0190993563	-0.0737475593

S0

0 1

C	0	-0.0096723681	-1.6536397245	0.4350980809
C	0	-0.8837826773	-0.7026210919	0.0529528793
C	0	-2.2828220464	-0.6266490427	0.5315040706
O	0	-2.9289701373	-1.5784030559	0.8996593948
O	0	-2.7119079916	0.6455246195	0.5782553820
C	0	-4.0790654946	0.8297269242	0.9367487574
H	0	-0.2578735900	-2.5007235848	1.0731084007
H	0	-4.7346351992	0.3499443873	0.1946289656

H	0	-4.2882097880	0.3964411435	1.9261406366
H	0	-4.2486033010	1.9130232330	0.9472107167
C	0	1.1387030813	0.3600686863	-0.6668453933
H	0	1.5832753815	0.5222935190	-1.6592877939
N	0	-0.3104508800	0.2827749519	-0.7934711216
C	0	-0.9639288829	0.6941955726	-1.9408052805
H	0	-0.3073044113	1.3267572245	-2.5832253332
O	0	-2.1064633882	0.4217420308	-2.2188958683
S	0	1.6301553595	-1.3691354059	-0.1171536611
C	0	1.6358241644	1.4769466086	0.2874240346
C	0	1.1998659975	2.8229666235	-0.3184869124
H	0	0.1038400447	2.9010786750	-0.3714918013
H	0	1.5660229327	3.6527489674	0.3053696228
H	0	1.6082843605	2.9622666491	-1.3330322143
C	0	3.1685794228	1.4182555335	0.3558794042
H	0	3.5531927349	2.2401358537	0.9787581062
H	0	3.5141005609	0.4708224579	0.7965290598
H	0	3.6198829849	1.5171431834	-0.6454027153
C	0	1.0318925366	1.3355969577	1.6913772030
H	0	1.3085418415	0.3752648970	2.1503436530
H	0	1.4060686301	2.1420402236	2.3410318053
H	0	-0.0651398777	1.4067029826	1.6612619216

S2

0 1

C	0	-0.2377606469	-0.7059737693	-1.3676462294
C	0	-0.3285642610	0.6035687337	-1.1034212602
C	0	-1.6108839342	1.2856043822	-0.7235227730
O	0	-2.6780965631	1.0233096988	-1.2110644030
O	0	-1.4042803662	2.1372624112	0.2858704456
C	0	-2.5316657261	2.9200948093	0.6864125898
H	0	-1.0372393216	-1.4435336534	-1.3764865701
H	0	-2.8366419709	3.5811280925	-0.1381820471
H	0	-3.3772849717	2.2733852925	0.9613018456
H	0	-2.2002784959	3.5116909765	1.5474501180
C	0	2.0803292406	0.4984127316	-1.0075178061
H	0	2.8320241306	0.8092847882	-1.7465131830
N	0	0.8840107849	1.3238366383	-1.1248914785
C	0	0.9232389358	2.6180458880	-1.6247838395
H	0	1.9622256483	3.0081308340	-1.6903772231
O	0	-0.0526821137	3.2473588195	-1.9499795218
S	0	1.4589992566	-1.1441023164	-1.6934486439
O	0	1.8399270093	-2.2990460703	-0.8708380646
O	0	1.7244672443	-1.1475044190	-3.1333983709
C	0	2.6937488636	0.4617735457	0.4127673695
C	0	3.0716548633	1.9059860340	0.7932213965
H	0	2.1845573791	2.5501445160	0.8844409148
H	0	3.5828011524	1.9049912724	1.7679421229
H	0	3.7597401181	2.3550923634	0.0585367281
C	0	3.9708898631	-0.3948073203	0.3722376023
H	0	4.4519321862	-0.3908874823	1.3621814909
H	0	3.7517825058	-1.4348259881	0.0996035882
H	0	4.6952759662	0.0131303809	-0.3520153383
C	0	1.6957121379	-0.0789495023	1.4498144944
H	0	1.4271560564	-1.1232043673	1.2443192931
H	0	2.1489646478	-0.0328877053	2.4518465360
H	0	0.7790863910	0.5300643952	1.4715571969

Sa

0 1

C	0	-0.0306513786	-1.6271639622	0.5708571165
C	0	-0.8800057901	-0.7160102458	0.0713794840

C	0	-2.3390771019	-0.6593856445	0.4169057763
O	0	-3.0458579180	-1.6260973778	0.5261584794
O	0	-2.7057555488	0.6015911281	0.6800416129
C	0	-4.0979306092	0.8099407197	0.9240062173
H	0	-0.3033066993	-2.4581323085	1.2189950306
H	0	-4.6743355904	0.5673405936	0.0189563645
H	0	-4.4488059449	0.1789472463	1.7534254322
H	0	-4.2081388075	1.8719514070	1.1722718377
C	0	1.1399748071	0.3266812032	-0.6324734721
H	0	1.6137047813	0.3672897826	-1.6241959104
N	0	-0.3054297446	0.2593768635	-0.7576074668
C	0	-0.9870629653	0.7614607610	-1.8561663736
H	0	-0.3361096734	1.4067858109	-2.4869407797
O	0	-2.1453590190	0.5320178354	-2.1038492128
S	0	1.6712782238	-1.3938735492	0.0090454166
O	0	1.9066085945	-2.2871579950	-1.1788283799
C	0	1.6485820950	1.4773018649	0.2682768296
C	0	1.1795708688	2.8137082024	-0.3342042001
H	0	0.0826510346	2.8971079305	-0.3260555000
H	0	1.5820034627	3.6519359635	0.2554485256
H	0	1.5319687234	2.9354056292	-1.3712499002
C	0	3.1852871134	1.4427903187	0.2830439919
H	0	3.5760771860	2.2814804974	0.8791339576
H	0	3.5696995466	0.5105724737	0.7228874677
H	0	3.5964091047	1.5333262626	-0.7353614113
C	0	1.0962129918	1.3522333235	1.6976931900
H	0	1.4343265644	0.4252828456	2.1856266922
H	0	1.4459086767	2.1990672306	2.3081300975
H	0	-0.0037959835	1.3634081890	1.7030390870

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O	0	2.6993596940	2.7310879336	-0.8466538816
C	0	3.2366610241	4.0528681476	-0.8914205392
O	0	1.0509509116	3.4249813512	0.5276990151
C	0	1.6708694165	2.5487742096	-0.0057037551
C	0	1.2671840966	1.0538757953	0.0329131328
C	0	0.6377996390	0.6808444241	-1.3307722938
O	0	0.2472363487	0.9053297695	0.9865074770
N	0	-0.9512254523	0.3690943694	0.3429237996
C	0	-2.0536121123	0.9158067000	1.1241469946
C	0	-0.8565793563	0.8337735187	-1.0417594843
H	0	3.6660062933	4.3103446740	0.0882052462
H	0	2.4561920782	4.7847987856	-1.1455932388
H	0	4.0193891020	4.0404960259	-1.6593397190
H	0	0.9639628633	1.3623776905	-2.1245634188
H	0	-1.0728317814	1.9235660921	-1.0909791206
C	0	-1.7826100514	0.0918625778	-1.9951624079
H	0	-1.5695277873	0.4005287307	-3.0306365393
H	0	-1.6304455319	-0.9925148719	-1.9084143589
H	0	-2.8356095799	0.3136605300	-1.7822907709
H	0	-1.7872921578	0.7455135193	2.1787914866
H	0	-2.1420695900	2.0115797829	0.9864905761
N	0	2.4016181115	0.1867165029	0.2740883875
C	0	2.3878575548	-1.1416232249	-0.3343302007
C	0	3.4823780731	0.6291820742	0.9941346333
H	0	3.3872244751	-1.3270708977	-0.7612470161
S	0	1.2220318178	-1.0037359306	-1.7646700233
C	0	2.0670781956	-2.3441391509	0.6061335731
H	0	4.3357348273	-0.0820234333	0.9555305251
O	0	3.5327163846	1.6815040129	1.5927942702
C	0	3.1487438531	-2.4386786614	1.6967880839
C	0	2.1234404307	-3.6204931105	-0.2511559446

C	0	0.6946617816	-2.2187848402	1.2733932647
H	0	3.1089214245	-1.5863771047	2.3910990526
H	0	2.9907612879	-3.3500589054	2.2938348413
H	0	4.1631739727	-2.4951947946	1.2684348441
H	0	1.9649757277	-4.5080125613	0.3802772001
H	0	1.3419244194	-3.6161663558	-1.0260424892
H	0	3.1016772715	-3.7322124254	-0.7480917811
H	0	-0.1038368011	-2.1230392673	0.5266873374
H	0	0.5010061463	-3.1087038931	1.8928963445
H	0	0.6484576668	-1.3278894635	1.9139166509
C	0	-3.3559541053	0.2199337074	0.8076492375
C	0	-4.5001976209	0.9550534756	0.4766713692
C	0	-3.4357657655	-1.1805879668	0.8443332201
C	0	-5.7053604304	0.3071168041	0.1867517071
H	0	-4.4449254639	2.0463235456	0.4390251204
C	0	-4.6353065928	-1.8292072240	0.5505482108
H	0	-2.5418156682	-1.7562616360	1.0920230092
C	0	-5.7747931205	-1.0871485426	0.2196991385
H	0	-6.5900324869	0.8945783040	-0.0707940183
H	0	-4.6838140873	-2.9206169497	0.5791136507
H	0	-6.7136813459	-1.5960628425	-0.0113633988

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O	0	2.5957768559	-2.3357690592	-0.8833261502
C	0	3.3238559030	-3.4755702768	-1.3348353137
O	0	0.9902069213	-3.6858444123	-0.0566878632
C	0	1.4803275360	-2.5994347427	-0.1876368761
C	0	0.8257386045	-1.2865211352	0.2693613456
C	0	0.0261405499	-0.6334930591	-0.9025744461
O	0	-0.1374491864	-1.6017460704	1.2311081588
N	0	-1.1311160623	-0.5412850788	1.1224406125
C	0	-2.2117959628	-0.9606496648	1.9908413435
C	0	-1.4036408397	-0.5535751567	-0.3173781710
H	0	3.6854417569	-4.0564020078	-0.4730775362
H	0	2.6915504063	-4.1246180200	-1.9588372195
H	0	4.1698017616	-3.0886630790	-1.9156320595
H	0	0.0392183072	-1.2594938078	-1.8030693070
H	0	-1.9141909610	-1.5019365025	-0.5868044638
C	0	-2.2333914531	0.6346207842	-0.8072341948
H	0	-2.1697872517	0.6378875488	-1.9087785024
H	0	-1.7502858569	1.5617764855	-0.4712607665
H	0	-2.6623450186	-1.9195982168	1.6686472859
H	0	-2.9839996583	-0.1823985939	1.9960675613
H	0	-1.8121686057	-1.0760781754	3.0075573653
N	0	1.8020805722	-0.3202162953	0.7619776090
C	0	1.5843313944	1.0770701996	0.3765447272
C	0	2.6991766816	-0.7923038401	1.6821645312
H	0	0.8034956688	1.5131779837	1.0207101684
S	0	0.8579678079	0.9233784336	-1.3213240217
C	0	2.8110923188	2.0379994817	0.3557919122
H	0	3.3388073855	-0.0135249601	2.1336185981
O	0	2.8023342217	-1.9652640372	1.9794881469
C	0	2.4127331856	3.2895243349	-0.4576103623
C	0	4.0331306041	1.3812881171	-0.3050393627
C	0	3.1393438996	2.5402997795	1.7775589481
H	0	1.4751681892	3.7308937636	-0.0841456616
H	0	3.2023671979	4.0514076456	-0.3736058593
H	0	2.2839838855	3.0635970173	-1.5263632026
H	0	4.8182078851	2.1347725017	-0.4729491461
H	0	4.4687301067	0.5822057830	0.3102273110
H	0	3.7580973036	0.9414517844	-1.2748456669
H	0	3.4983085134	1.7559845227	2.4560649964

H	0	3.9298081214	3.3048354115	1.7237611374
H	0	2.2550890574	3.0052682863	2.2416043923
C	0	-3.6862012691	0.6187456237	-0.3923116640
C	0	-4.5449642533	-0.4109112724	-0.8067041007
C	0	-4.2074998199	1.6329297495	0.4229983295
C	0	-5.8820042607	-0.4338921066	-0.4061642262
H	0	-4.1620203143	-1.2078458261	-1.4500327985
C	0	-5.5461157234	1.6160424902	0.8248649921
H	0	-3.5509661685	2.4427115028	0.7524768381
C	0	-6.3874240430	0.5793245977	0.4144035320
H	0	-6.5339226713	-1.2459382344	-0.7373618866
H	0	-5.9318467351	2.4151945495	1.4625926529
H	0	-7.4335004878	0.5617232530	0.7289993334

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O	0	-2.4495720550	2.0307166163	-1.2316731113
C	0	-3.2231933758	3.0869853882	-1.8037312175
O	0	-0.9874708712	3.5424516014	-0.4281873493
C	0	-1.3201836624	2.4046381681	-0.6084561475
C	0	-0.5893239105	1.1749551011	-0.0321092916
C	0	-1.0737055489	0.8994605370	1.4159467000
N	0	1.3092748683	1.0344453084	1.3084194399
O	0	0.7723193860	1.5247182997	0.0765373272
C	0	1.8248239206	-0.3302723514	1.1390230322
C	0	0.1978523381	1.2039549814	2.2477584312
H	0	-3.4986882620	3.8262540697	-1.0372993862
H	0	-2.6473548454	3.5929777092	-2.5923769828
H	0	-4.1187620895	2.6164295680	-2.2263881657
H	0	-1.9040231560	1.5610881746	1.6943397419
H	0	0.3114965460	0.4788696829	3.0667493129
C	0	0.1836859265	2.6318144208	2.7902097429
H	0	-0.6578341425	2.7778603982	3.4858121664
H	0	0.0887527512	3.3485932547	1.9616298809
H	0	1.1242956849	2.8370291311	3.3201317527
H	0	2.0401071893	-0.6908307983	2.1554610394
H	0	1.0626849747	-1.0043421552	0.7178394865
N	0	-0.8126689792	-0.0236054496	-0.8479898738
C	0	-1.7976459074	-0.9837814700	-0.3340953576
C	0	-0.4632936433	0.0979635179	-2.1713689834
H	0	-2.8098283287	-0.6280138907	-0.5931032600
S	0	-1.6306713262	-0.8355394611	1.5032455698
C	0	-1.6890431736	-2.4758922533	-0.7815423064
H	0	-0.6951598765	-0.7925791394	-2.7812678504
O	0	0.0680028911	1.0851191426	-2.6359511027
C	0	-2.2497636879	-2.6761202155	-2.2078362213
C	0	-2.5936652589	-3.3046862206	0.1565287662
C	0	-0.2493500083	-2.9987426082	-0.6926237072
H	0	-1.5620141643	-2.3534468828	-2.9999968263
H	0	-2.4400989445	-3.7467556456	-2.3777299061
H	0	-3.2040273335	-2.1425165251	-2.3428629479
H	0	-2.6158385248	-4.3515376834	-0.1814159013
H	0	-2.2274555986	-3.3003477260	1.1936267766
H	0	-3.6285091513	-2.9266882607	0.1553008898
H	0	-0.2128106120	-4.0506270526	-1.0152730878
H	0	0.4411811083	-2.4276372664	-1.3294810686
H	0	0.1246469835	-2.9481110140	0.3396823966
C	0	3.0900463906	-0.4063145448	0.3139137837
C	0	3.1413653342	0.0627987449	-1.0098510217
C	0	4.2350067275	-1.0046952639	0.8584335045
C	0	4.3128376174	-0.0673227613	-1.7589806739
H	0	2.2726515898	0.5528625280	-1.4483328117
C	0	5.4054261642	-1.1400685770	0.1067960796

H	0	4.2109483624	-1.3708943407	1.8889581143
C	0	5.4472799368	-0.6705537255	-1.2075595581
H	0	4.3372932109	0.3095023029	-2.7845873327
H	0	6.2866210645	-1.6088714910	0.5520907042
H	0	6.3607084711	-0.7710348730	-1.7991101888

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O	0	-3.0819056188	1.5336388970	0.5003582725
C	0	-4.1702486332	2.4272302898	0.2546133945
O	0	-1.8202405108	2.6820941096	-0.9550769123
C	0	-1.9477405021	1.7966866015	-0.1492733783
C	0	-0.7947822153	0.8364647767	0.2236835424
C	0	-0.1352281008	0.1969988427	-1.0342443270
N	0	1.4881965878	1.3361928175	0.2858871938
O	0	0.1967735204	1.6987037923	0.7701350569
C	0	2.1133061729	0.3751206475	1.2052679185
C	0	1.2453095151	0.8961049228	-1.0895676602
H	0	-4.4423311286	2.4192505428	-0.8111999421
H	0	-3.8930003476	3.4512870695	0.5427530151
H	0	-5.0023402745	2.0668809479	0.8701010869
H	0	-0.7274090329	0.3827645246	-1.9379749433
H	0	2.0292254500	0.1767620933	-1.3653126387
C	0	1.2656628377	2.0839375170	-2.0469744974
H	0	1.0805145929	1.7500070580	-3.0803287470
H	0	0.4905270028	2.8117302649	-1.7720649842
H	0	2.2496299211	2.5716706400	-2.0034687809
H	0	2.0873797339	0.8575641051	2.1945114325
H	0	1.5655050686	-0.5780776353	1.2781554310
N	0	-1.1843928625	-0.2363544269	1.1282282808
C	0	-1.2394140518	-1.5910259086	0.6010887528
C	0	-1.4108632513	0.0166540155	2.4658919150
H	0	-0.8756126773	-2.2746585165	1.3847246464
S	0	0.0196066539	-1.6113799839	-0.7436041686
C	0	-2.6380955919	-2.1164675376	0.1498258567
H	0	-1.5193999535	-0.9309094158	3.0455685770
O	0	-1.4757871108	1.1088946389	2.9722427554
C	0	-3.1543778407	-1.4120547147	-1.1126994028
C	0	-3.6443965302	-1.9126854329	1.2942899162
C	0	-2.4859014829	-3.6195136292	-0.1353982210
H	0	-2.4609677363	-1.5487049576	-1.9550834645
H	0	-4.1274181751	-1.8372340554	-1.4041056276
H	0	-3.3048435737	-0.3392901670	-0.9411847764
H	0	-4.6143668469	-2.3573568658	1.0224292671
H	0	-3.3079667016	-2.3997319067	2.2237604106
H	0	-3.8067460002	-0.8448620351	1.4985262924
H	0	-2.1479797910	-4.1662267241	0.7603615361
H	0	-3.4496241954	-4.0499485744	-0.4476821627
H	0	-1.7583484519	-3.7989633787	-0.9420684390
C	0	3.5361061749	0.1112525551	0.7791979508
C	0	3.9605317410	-1.1865658157	0.4686157793
C	0	4.4477459103	1.1717678945	0.6606331915
C	0	5.2776952506	-1.4276933259	0.0646470370
H	0	3.2469328210	-2.0117448113	0.5352347787
C	0	5.7609579226	0.9339443574	0.2538715861
H	0	4.1109354518	2.1869545526	0.8821125398
C	0	6.1805494855	-0.3678819293	-0.0430619890
H	0	5.5964087821	-2.4459152532	-0.1717455448
H	0	6.4631526376	1.7669731095	0.1679509632
H	0	7.2094679552	-0.5533385822	-0.3609177691

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O	0	1.6658031512	3.0012546800	-0.6124103159
C	0	1.4729035265	4.3866181446	-0.8742477629
O	0	-0.4445511272	2.6042268027	-1.2796128530
C	0	0.5937333228	2.2130915681	-0.7833940409
C	0	0.8520682862	0.8151935672	-0.3767241144
C	0	0.2849984407	-0.2445327617	-1.1212744573
O	0	-0.6546155608	0.9046854084	1.2135713616
N	0	-1.5757944609	0.2755394419	0.5972244090
C	0	-2.6707319392	1.0622957060	-0.0150671690
C	0	-1.2573141482	-0.9525266855	0.1141467616
H	0	0.7026435928	4.8004495234	-0.2061224201
H	0	1.1589717755	4.5518873617	-1.9160801728
H	0	2.4381434851	4.8708204953	-0.6822805000
H	0	-0.3104376163	0.0100047573	-2.0001133581
H	0	-2.0296437819	-1.3725518890	-0.5394622085
C	0	-0.5714536719	-1.9162410748	1.0381597645
H	0	-0.1320498184	-2.7526480300	0.4818699447
H	0	0.2191598593	-1.4133545599	1.6072495936
H	0	-1.3159541703	-2.3199487930	1.7460442488
H	0	-2.6886163910	1.9966380099	0.5613672065
H	0	-2.3893472677	1.3289029576	-1.0437893465
N	0	2.0623555310	0.4455812434	0.2716531075
C	0	2.8251632930	-0.5417823038	-0.5059311880
C	0	2.4678723741	1.0753701543	1.4351885181
H	0	3.3406069609	-0.0112891499	-1.3268061148
S	0	1.4886613933	-1.5543531733	-1.3475562443
C	0	3.8752015090	-1.4499171593	0.1893784285
H	0	3.4294214212	0.6834225649	1.8148681256
O	0	1.8620185932	1.9555636497	1.9961482709
C	0	5.1705375306	-0.6640459704	0.4887449043
C	0	4.2643490732	-2.5476918715	-0.8259079404
C	0	3.3223625346	-2.1216290029	1.4545112818
H	0	5.0579312748	0.0994525417	1.2684261510
H	0	5.9511363288	-1.3615185519	0.8297272667
H	0	5.5431480232	-0.1640040342	-0.4193050183
H	0	5.0993252414	-3.1425546300	-0.4261506338
H	0	3.4302696901	-3.2369777512	-1.0235048599
H	0	4.5886739716	-2.1131796370	-1.7849855579
H	0	2.4089265380	-2.6872217089	1.2235927959
H	0	4.0676929259	-2.8230403527	1.8606592330
H	0	3.0796247775	-1.3997463343	2.2463052935
C	0	-3.9858129362	0.3296967483	0.0415521707
C	0	-4.7066261416	0.0626138147	-1.1285879420
C	0	-4.5051860775	-0.1030165864	1.2720517361
C	0	-5.9275695810	-0.6176398444	-1.0747620343
H	0	-4.3069271346	0.3930068017	-2.0911160880
C	0	-5.7200415768	-0.7859510299	1.3284327029
H	0	-3.9449399875	0.0967628594	2.1893561272
C	0	-6.4357116373	-1.0443585730	0.1536254764
H	0	-6.4802092808	-0.8166785933	-1.9961045505
H	0	-6.1140115946	-1.1167910855	2.2924931991
H	0	-7.3879355241	-1.5782976642	0.1981478121

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O	0	3.2847572481	-0.2420091466	0.4616307933
C	0	4.5129334370	-0.9600927372	0.4104691092
O	0	2.6246980601	-1.2819475505	-1.4220224360
C	0	2.3819694823	-0.5463782171	-0.4853611051
C	0	1.1048502235	0.1617091580	-0.2859352479
C	0	0.2671309715	0.4764363279	-1.3865412633
O	0	0.1445379562	-1.7645683381	0.2484770059

N	0	-0.4713779978	-1.9316848847	-0.8574275012
C	0	0.0746814069	-2.8862294179	-1.8263129486
C	0	-1.2474804276	-0.8907784611	-1.2612857433
H	0	5.0376013484	-0.7757703325	-0.5391646593
H	0	5.1107779993	-0.6005708046	1.2565278285
H	0	4.3302916695	-2.0407534121	0.5066402133
H	0	0.6417186356	0.2508023334	-2.3873762842
H	0	-1.6620209506	-1.0236990582	-2.2674773854
C	0	-2.2026398242	-0.2994308901	-0.2403262501
H	0	-2.6612475681	0.5984853403	-0.6716474563
H	0	-1.6355029900	0.0154812912	0.6440072057
H	0	0.5392400208	-3.6947385958	-1.2502711133
H	0	0.8476942536	-2.4070522866	-2.4441769576
H	0	-0.7423337562	-3.2812979634	-2.4448370065
N	0	0.8851293219	1.0201502317	0.8175607879
C	0	0.4185028824	2.3552978560	0.4581153350
C	0	0.9064213926	0.6055878766	2.1406375487
H	0	-0.3438443375	2.6763832055	1.1845158111
S	0	-0.4352158924	2.1217287064	-1.1835610186
C	0	1.5297211447	3.4421884989	0.4025933646
H	0	0.5139835758	1.4073591741	2.8107616812
O	0	1.2882619480	-0.4617227974	2.5451893805
C	0	0.8724726046	4.7739534726	0.0087480944
C	0	2.6297185776	3.0726622743	-0.6016562940
C	0	2.1522566973	3.5784565908	1.8027392316
H	0	0.0788043258	5.0565867463	0.7202346859
H	0	1.6208315041	5.5811867169	0.0033384576
H	0	0.4296988823	4.7201551551	-0.9976646235
H	0	3.3758610641	3.8809814071	-0.6537235588
H	0	3.1491280012	2.1539914209	-0.2957375738
H	0	2.2145642524	2.9272609568	-1.6096742101
H	0	2.6733024926	2.6579087342	2.1042051697
H	0	2.8920242272	4.3939870158	1.8040703249
H	0	1.3931902324	3.8163734957	2.5658230962
C	0	-3.2647727746	-1.3028267814	0.1518743953
C	0	-4.5145778490	-1.3150232787	-0.4824034505
C	0	-2.9967982836	-2.2658408747	1.1389155755
C	0	-5.4811021074	-2.2650267785	-0.1401421624
H	0	-4.7355070000	-0.5671962400	-1.2496967337
C	0	-3.9618183420	-3.2144499953	1.4818663004
H	0	-2.0207427465	-2.2664305343	1.6291250560
C	0	-5.2065465911	-3.2180562694	0.8437129888
H	0	-6.4526141888	-2.2575034950	-0.6407235120
H	0	-3.7417949428	-3.9548463523	2.2550683919
H	0	-5.9615882696	-3.9596044929	1.1159016624

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O	0	-1.9030998065	2.5060756789	-1.5837402493
C	0	-2.0890637819	3.8013257107	-2.1440180196
O	0	-1.2590531599	3.4595195319	0.3499315478
C	0	-1.4125448094	2.4697660292	-0.3345626126
C	0	-1.1292623758	1.0939974210	0.1210747572
C	0	-1.2718256077	0.7477590226	1.4839890980
N	0	1.2847952050	0.6963053475	1.2237664783
O	0	1.0950922371	1.4641988708	0.2328163623
C	0	1.7847553341	-0.6676267317	0.9221165803
C	0	0.5560352997	0.9517460982	2.3432211660
H	0	-2.8060499522	4.3887563163	-1.5504461787
H	0	-1.1339654028	4.3466054512	-2.1780012110
H	0	-2.4707048414	3.6425968310	-3.1599548302
H	0	-1.7912594774	1.4522916746	2.1367426158
H	0	0.6457981425	0.1672564251	3.1030780412

C	0	0.4921107619	2.3703751678	2.8444327436
H	0	-0.2365909482	2.4447475426	3.6650571341
H	0	0.1955366032	3.0584011738	2.0435639830
H	0	1.4793251600	2.6671270818	3.2373008113
H	0	1.8441323999	-1.2190591409	1.8684994213
H	0	1.0244953525	-1.1504887046	0.2952651267
N	0	-1.2581057479	-0.0228219169	-0.7573821171
C	0	-2.1564192829	-1.0440904886	-0.1914732141
C	0	-0.6095984829	-0.0816556639	-1.9721145765
H	0	-3.1899353046	-0.6636510716	-0.2714640572
S	0	-1.7458031763	-0.9838659361	1.6313011992
C	0	-2.1537674425	-2.4972370927	-0.7333135126
H	0	-0.8719447851	-0.9853494978	-2.5504630453
O	0	0.1735194921	0.7424145723	-2.3871603991
C	0	-2.8431748538	-2.5681646294	-2.1131089993
C	0	-3.0277787091	-3.3317298370	0.2301490177
C	0	-0.7486619830	-3.1188265072	-0.7732153405
H	0	-2.2857791228	-2.0708317689	-2.9167112725
H	0	-2.9656838436	-3.6218159295	-2.4076800479
H	0	-3.8457359466	-2.1140661403	-2.0712253858
H	0	-3.1611748815	-4.3456936086	-0.1759707008
H	0	-2.5667745349	-3.4294556771	1.2240926429
H	0	-4.0258759835	-2.8840804620	0.3583210136
H	0	-0.8171538834	-4.1718372663	-1.0870124573
H	0	-0.0720511872	-2.6114776036	-1.4742797778
H	0	-0.2861117511	-3.0923062488	0.2237623296
C	0	3.1229233978	-0.6363538601	0.2283418791
C	0	3.2290119156	-0.1727732061	-1.0927777259
C	0	4.2756334520	-1.0612706824	0.9014718609
C	0	4.4757110925	-0.1397976514	-1.7206125004
H	0	2.3386184615	0.1773327083	-1.6180822737
C	0	5.5212586865	-1.0326431768	0.2686386251
H	0	4.1982479611	-1.4206337900	1.9317275239
C	0	5.6225627417	-0.5699230117	-1.0453725818
H	0	4.5508798579	0.2254598032	-2.7477263406
H	0	6.4123296325	-1.3701494609	0.8036041029
H	0	6.5948808789	-0.5446406956	-1.5437236344

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O	0	2.4710140653	-0.6964277037	1.8912470837
C	0	3.3529138874	-1.3638877879	2.7866490917
O	0	2.5838450211	-2.4586482919	0.4962421157
C	0	2.0893410438	-1.3949459611	0.8058310227
C	0	1.0659845174	-0.6820906483	0.0210757461
C	0	1.0428541085	-0.7379933126	-1.3899796945
N	0	-1.0136684562	-2.2084141263	-0.9269152291
O	0	-0.5714130717	-2.3811759230	0.2473136973
C	0	-2.3856305679	-1.6761949636	-1.1234143492
C	0	-0.1147414047	-2.2578813718	-1.9469901402
H	0	4.2906511460	-1.6432106302	2.2830211369
H	0	2.8794264912	-2.2757614776	3.1802616197
H	0	3.5501875437	-0.6584264805	3.6028497311
H	0	1.9466842831	-1.0731757322	-1.9044376643
H	0	-0.5510898192	-1.9686000546	-2.9099696593
C	0	0.8608207442	-3.4065534390	-1.9850962667
H	0	1.6046602933	-3.2407396295	-2.7785651258
H	0	1.3858127035	-3.5100287053	-1.0284158965
H	0	0.3201923721	-4.3403963533	-2.2155237358
H	0	-2.4437051391	-1.2909076850	-2.1482280623
H	0	-3.0570817355	-2.5495778582	-1.0549938942
N	0	0.3730480549	0.4245881764	0.5488932312
C	0	0.2495604794	1.5553709722	-0.3638099007

C	0	-0.2844896336	0.4128512537	1.7660701685
H	0	-0.7428400088	2.0090352717	-0.2318397647
S	0	0.2667515627	0.7621001050	-2.0411369177
C	0	1.3294934649	2.6582321046	-0.1828209942
H	0	-0.8662954732	1.3479933512	1.9180168170
O	0	-0.2581771144	-0.4903517206	2.5648780004
C	0	2.7476132680	2.1064022600	-0.3817807554
C	0	1.2086974264	3.2306131537	1.2404210030
C	0	1.0437755488	3.7714169559	-1.2021710517
H	0	2.8679225501	1.6735197539	-1.3856869258
H	0	3.4838037248	2.9182016117	-0.2712898510
H	0	2.9806536529	1.3357510440	0.3664055637
H	0	1.9084090954	4.0716051213	1.3653819772
H	0	0.1931211698	3.6082816593	1.4426914097
H	0	1.4572222730	2.4755475155	2.0004657220
H	0	0.0308949630	4.1866286268	-1.0682471898
H	0	1.7631913699	4.5957582396	-1.0803143889
H	0	1.1281845562	3.3978171547	-2.2339963169
C	0	-2.8302056649	-0.6333119543	-0.1316947086
C	0	-3.0779688048	-0.9812188634	1.2031549097
C	0	-3.0585470175	0.6859203998	-0.5475869351
C	0	-3.5409938602	-0.0239658753	2.1072057807
H	0	-2.8773622687	-1.9993677646	1.5373113694
C	0	-3.5263892452	1.6439209007	0.3552917357
H	0	-2.8602919577	0.9616549785	-1.5857800699
C	0	-3.7670135361	1.2893870817	1.6868083652
H	0	-3.7101664362	-0.3034362558	3.1490030221
H	0	-3.7067107877	2.6676607876	0.0179292017
H	0	-4.1319133775	2.0368770904	2.3954209664

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O	0	2.6821001519	2.7078705530	-0.8886775277
C	0	3.2307622759	4.0241050357	-0.9555220335
O	0	1.0575346413	3.4320345530	0.4982856804
C	0	1.6624567266	2.5444039283	-0.0336832585
C	0	1.2433404629	1.0546833936	0.0224074833
C	0	0.5859808768	0.6809095622	-1.3288799289
O	0	0.2358849279	0.9260486206	0.9952827708
N	0	-0.9695586230	0.3803418031	0.3765978288
C	0	-2.0736343812	0.9104555359	1.1742076687
C	0	-0.9033017519	0.8604061958	-1.0012048939
H	0	3.6760143197	4.2884639732	0.0151197546
H	0	2.4534228543	4.7602783336	-1.2069884857
H	0	4.0024999385	3.9959543400	-1.7340264995
H	0	0.8974572268	1.3550941107	-2.1339820000
H	0	-1.0893106888	1.9551848647	-1.0314915030
H	0	-1.7915020147	0.7462137510	2.2238443812
H	0	-2.1842752711	2.0023012522	1.0261609398
N	0	2.3705737258	0.1757334236	0.2477917665
C	0	2.3332673474	-1.1529703807	-0.3596572729
C	0	3.4670414915	0.6095537603	0.9493192158
H	0	3.3208011425	-1.3464762887	-0.8100657848
S	0	1.1314936696	-1.0124126350	-1.7601270794
C	0	2.0273772172	-2.3506493574	0.5923860513
H	0	4.3136789750	-0.1085750444	0.8967768244
O	0	3.5358174604	1.6622423453	1.5455365269
C	0	3.1487916920	-2.4674654512	1.6400967778
C	0	2.0250173738	-3.6278204109	-0.2656363951
C	0	0.6857163610	-2.1996991219	1.3149277199
H	0	3.1498219731	-1.6179243405	2.3388828131
H	0	2.9990565803	-3.3786154644	2.2395895029
H	0	4.1447599007	-2.5384341974	1.1724325493

H	0	1.8790741046	-4.5125652931	0.3727064961
H	0	1.2114277743	-3.6100892699	-1.0065551908
H	0	2.9789348696	-3.7561454099	-0.8040588324
H	0	-0.1425809634	-2.0936020583	0.6037667704
H	0	0.5027919446	-3.0837773047	1.9458450208
H	0	0.6796674788	-1.3053794973	1.9525592470
C	0	-3.3534798541	0.1760144112	0.8562668978
C	0	-4.3543152816	0.7669100483	0.0781413345
C	0	-3.5183008216	-1.1494739877	1.2820681675
C	0	-5.4923418487	0.0437314526	-0.2870176683
H	0	-4.2282992113	1.7955248965	-0.2681099525
C	0	-4.6548697592	-1.8741908405	0.9238124162
H	0	-2.7339863690	-1.6179515824	1.8820788176
C	0	-5.6429430108	-1.2799588932	0.1316730808
H	0	-6.2579084988	0.5129123760	-0.9091561989
H	0	-4.7704154827	-2.9080501865	1.2585906029
H	0	-6.5297296329	-1.8490576311	-0.1575581457
C	0	-1.8780802852	0.1895309858	-1.9387272297
C	0	-2.4763422931	0.9465445493	-2.9531759430
C	0	-2.1981961934	-1.1696032658	-1.8226728489
C	0	-3.3850171683	0.3611691880	-3.8377861242
H	0	-2.2401239759	2.0107158494	-3.0409165811
C	0	-3.1159858179	-1.7516360028	-2.6964766302
H	0	-1.7475038921	-1.7554211834	-1.0247541329
C	0	-3.7113563146	-0.9904802623	-3.7068836071
H	0	-3.8474213216	0.9653428376	-4.6219894785
H	0	-3.3751956103	-2.8064346935	-2.5811621618
H	0	-4.4330637575	-1.4492349560	-4.3870181381

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O	0	2.3214903584	-2.4781811532	-1.0097549754
C	0	2.8566407110	-3.7226761724	-1.4573269033
O	0	0.7097118217	-3.5661130420	0.1330367763
C	0	1.3071247786	-2.5613689446	-0.1400924272
C	0	0.8786401436	-1.1545768252	0.3126636416
C	0	0.0694495960	-0.4642536765	-0.8294998650
O	0	-0.0175645744	-1.3081321163	1.3778886622
N	0	-1.0869515311	-0.3305489908	1.1904454915
C	0	-1.3542606069	-0.4576172951	-0.2540461045
H	0	3.2945558936	-4.2671593766	-0.6074204043
H	0	2.0738606260	-4.3454368539	-1.9149489129
H	0	3.6322912430	-3.4763013977	-2.1922964119
H	0	0.1142514992	-1.0339177083	-1.7654168432
H	0	-1.7773968969	-1.4621876173	-0.4542699290
C	0	-2.2740007739	0.6168753692	-0.8280220982
H	0	-2.2374582310	0.5045178598	-1.9268586802
H	0	-1.8365768570	1.6003364774	-0.6085131892
N	0	2.0035251017	-0.3065698222	0.6734765335
C	0	1.7468881558	1.1243403769	0.4767519181
C	0	2.9954139596	-0.8769583157	1.4280581298
H	0	1.0245346574	1.4630521888	1.2369429508
S	0	0.8499317903	1.1517025104	-1.1456387175
C	0	2.9496046226	2.1095105179	0.4637714425
H	0	3.7673765586	-0.1660465479	1.7700949596
O	0	3.0495704393	-2.0620460472	1.6870544167
C	0	2.4426579499	3.4503880383	-0.1120713850
C	0	4.1021342373	1.5973911888	-0.4142250016
C	0	3.4221540848	2.4102089239	1.9019316265
H	0	1.5478343389	3.8051981715	0.4231148872
H	0	3.2258436014	4.2164992480	-0.0083455315
H	0	2.1945534889	3.3724372877	-1.1808922983
H	0	4.8585430022	2.3879474881	-0.5368783536

H	0	4.6076419653	0.7218281655	0.0155244205
H	0	3.7320660280	1.3137489891	-1.4103990530
H	0	3.8538791642	1.5446558793	2.4202871452
H	0	4.1970007519	3.1920110594	1.8781225505
H	0	2.5877454600	2.7840122479	2.5160000439
C	0	-3.7170652124	0.5811927111	-0.3724469481
C	0	-4.4509619769	-0.6124577641	-0.3196148824
C	0	-4.3522771705	1.7694676956	0.0119707428
C	0	-5.7702429144	-0.6211625927	0.1334754170
H	0	-3.9813815384	-1.5551752406	-0.6076953603
C	0	-5.6772440140	1.7685539653	0.4541480295
H	0	-3.7921019466	2.7080096885	-0.0204956223
C	0	-6.3892216196	0.5696065736	0.5246573119
H	0	-6.3160320792	-1.5658871137	0.1886506460
H	0	-6.1503267601	2.7066627178	0.7549391223
H	0	-7.4209682357	0.5611088992	0.8838981600
C	0	-2.1594983495	-0.7373119869	2.0485468368
C	0	-2.9417314459	0.2607189515	2.6338077869
C	0	-2.4576525619	-2.0900204020	2.2638012611
C	0	-4.0622751708	-0.0882053535	3.3885989576
H	0	-2.6747717110	1.3045990452	2.4682532981
C	0	-3.5649990353	-2.4307744660	3.0413738862
H	0	-1.8112163281	-2.8533776859	1.8289563084
C	0	-4.3767724825	-1.4341274935	3.5933095012
H	0	-4.6884584196	0.6949289260	3.8213131739
H	0	-3.7986736791	-3.4842050701	3.2144412759
H	0	-5.2497085467	-1.7073545696	4.1907993159

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O	0	-2.3744580784	2.1065135836	-1.2406208348
C	0	-3.1071500722	3.1785898707	-1.8369170107
O	0	-0.7629722372	3.5564368382	-0.6262537631
C	0	-1.1874233282	2.4397949365	-0.7029882568
C	0	-0.5222174481	1.1904661938	-0.0879298244
C	0	-1.0407612442	0.9546765122	1.3529527940
N	0	1.3507194598	1.0072634375	1.2890597866
O	0	0.8500082000	1.4832951565	0.0363162015
C	0	1.8481875488	-0.3678468411	1.1501729589
C	0	0.2339200402	1.1982852720	2.2110851978
H	0	-3.2922627874	3.9772565029	-1.1036476052
H	0	-2.5428087863	3.5988838240	-2.6822449438
H	0	-4.0531464701	2.7470494555	-2.1848727091
H	0	-1.8382389049	1.6590283665	1.6171780178
H	0	0.2975324742	0.4429830592	3.0067360998
H	0	2.0511912639	-0.7115780658	2.1746124239
H	0	1.0774829675	-1.0351952942	0.7333530928
N	0	-0.7855846487	-0.0092493442	-0.8933127736
C	0	-1.8051816656	-0.9342926367	-0.3806958717
C	0	-0.4440169204	0.0930983122	-2.2201879654
H	0	-2.8027256389	-0.5615809435	-0.6702483853
S	0	-1.6735697748	-0.7530335046	1.4545044352
C	0	-1.7193093642	-2.4391008395	-0.7922041228
H	0	-0.7246794518	-0.7862602102	-2.8255735705
O	0	0.1275548550	1.0538134091	-2.6925357970
C	0	-2.2384785714	-2.6615313455	-2.2311316907
C	0	-2.6722907820	-3.2232657409	0.1363138902
C	0	-0.2957069896	-2.9922972381	-0.6488004355
H	0	-1.5058455748	-2.4000174891	-3.0056755201
H	0	-2.4728452978	-3.7274110784	-2.3733830189
H	0	-3.1607547162	-2.0896679255	-2.4207797514
H	0	-2.7060753983	-4.2782157839	-0.1743047311
H	0	-2.3412162424	-3.1987330643	1.1849116461

H	0	-3.6980823136	-2.8239270956	0.0898010120
H	0	-0.2726516418	-4.0499319757	-0.9533887579
H	0	0.4255832625	-2.4463073056	-1.2737611017
H	0	0.0473066571	-2.9326658033	0.3936671817
C	0	3.1190496670	-0.4708965768	0.3375403917
C	0	3.1674317011	-0.0820970278	-1.0119817682
C	0	4.2746905726	-1.0052547159	0.9240538515
C	0	4.3464950739	-0.2277029420	-1.7460013886
H	0	2.2915025067	0.3618835517	-1.4837237861
C	0	5.4530421880	-1.1563091112	0.1880295919
H	0	4.2527558724	-1.3078011549	1.9749596572
C	0	5.4917185254	-0.7671839173	-1.1524193955
H	0	4.3687146822	0.0869070419	-2.7923717565
H	0	6.3426986692	-1.5745547094	0.6655523295
H	0	6.4112972228	-0.8805010539	-1.7319586920
C	0	0.2221655231	2.5798797482	2.8421237368
C	0	-0.4853037969	2.7714686072	4.0368210807
C	0	0.8653386286	3.6694966575	2.2435684284
C	0	-0.5503282761	4.0334793773	4.6311597892
H	0	-0.9860996824	1.9219933542	4.5119704734
C	0	0.7992454688	4.9316582077	2.8386550759
H	0	1.4027292122	3.5244501035	1.3074650056
C	0	0.0940265625	5.1188144112	4.0305941054
H	0	-1.0984102941	4.1677706886	5.5669930947
H	0	1.3014106749	5.7770101682	2.3622108081
H	0	0.0475356885	6.1081390874	4.4923229799

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O	0	-2.9669329034	1.5774097781	0.0913267354
C	0	-3.9713207109	2.5698992326	-0.1282572995
O	0	-1.3967662171	3.1810187186	0.0520600830
C	0	-1.7114351860	2.0356473343	0.2073655313
C	0	-0.7054209244	0.8929755190	0.5021556727
C	0	-0.0764662610	0.2829902726	-0.7747731917
N	0	1.6201031520	1.2564257934	0.5713399721
O	0	0.3629424517	1.5173361503	1.1993581070
C	0	2.3547349829	0.2553152485	1.3514010961
C	0	1.3148839295	0.9526862083	-0.8214542071
H	0	-3.7433894905	3.1628382031	-1.0258118302
H	0	-4.0272304374	3.2439739758	0.7388141819
H	0	-4.9149548974	2.0252966511	-0.2516584336
H	0	-0.6741889133	0.4772970629	-1.6728998400
H	0	2.0638184476	0.2398159604	-1.1950111004
H	0	2.4459894911	0.6803171772	2.3634699680
H	0	1.8169747184	-0.7033260642	1.4331237499
N	0	-1.3166312972	-0.1861932511	1.2618370022
C	0	-1.3069243246	-1.5402955481	0.7196469184
C	0	-1.8215516409	0.1061530057	2.5051459886
H	0	-1.0163319603	-2.2321303268	1.5269715361
S	0	0.0783396422	-1.5298534689	-0.4884898487
C	0	-2.6441043894	-2.0740679792	0.1100601380
H	0	-2.0870272916	-0.8054773283	3.0863566655
O	0	-1.9584659765	1.2291059791	2.9341242071
C	0	-2.9974925022	-1.3981938685	-1.2229056084
C	0	-3.7934785645	-1.8515253023	1.1061930164
C	0	-2.4558142775	-3.5829764165	-0.1190018290
H	0	-2.2293113670	-1.5981282253	-1.9838869152
H	0	-3.9536467868	-1.7965936862	-1.5969928472
H	0	-3.1077217797	-0.3141670146	-1.1003352861
H	0	-4.7133192347	-2.3169623010	0.7195654880
H	0	-3.5823912704	-2.3079524645	2.0866098542
H	0	-3.9964600403	-0.7809010215	1.2528248305

H	0	-2.2501968692	-4.1122333701	0.8261092564
H	0	-3.3656788605	-4.0198123301	-0.5580456378
H	0	-1.6214486260	-3.7785833194	-0.8106510421
C	0	3.7192198688	0.0339865929	0.7472787346
C	0	4.1400597478	-1.2520091946	0.3861821574
C	0	4.5747233224	1.1213553674	0.5102927920
C	0	5.4011022802	-1.4550672519	-0.1835145302
H	0	3.4685221328	-2.0992993117	0.5468212117
C	0	5.8303347393	0.9212470970	-0.0638176136
H	0	4.2380764030	2.1276529792	0.7681921716
C	0	6.2487101114	-0.3686134233	-0.4097155487
H	0	5.7181347185	-2.4644665676	-0.4570208965
H	0	6.4873278379	1.7755974441	-0.2444001977
H	0	7.2325526444	-0.5240779326	-0.8590674974
C	0	1.3348240926	2.1809261871	-1.7176287239
C	0	1.2492533509	2.0061101458	-3.1058777411
C	0	1.4340827915	3.4732832100	-1.1951948585
C	0	1.2609167469	3.1075809885	-3.9633264134
H	0	1.1821531112	0.9960023867	-3.5225043988
C	0	1.4446652717	4.5761771848	-2.0526890523
H	0	1.4867649401	3.6022192277	-0.1151270470
C	0	1.3583789419	4.3988795359	-3.4357403238
H	0	1.2002814175	2.9579470137	-5.0441296415
H	0	1.5145681305	5.5831062882	-1.6342225464
H	0	1.3679122235	5.2643488984	-4.1028291685

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O	0	-0.6442435492	3.1049345119	-0.2096408763
C	0	-0.1391839339	4.4287908795	-0.3509209718
O	0	0.9900344202	2.6565975650	1.2675270370
C	0	0.0577521186	2.2822112399	0.5807489348
C	0	-0.4697613111	0.8992933969	0.5557542656
C	0	-0.3908619192	0.0787773428	1.7170855570
O	0	1.2794515418	0.1853315206	-0.4207066971
N	0	1.8112160273	-0.4545036607	0.5519708393
C	0	2.9100963587	0.2054171510	1.3027304152
C	0	0.9782069089	-1.3280216444	1.1981893923
H	0	0.8469325769	4.4108904607	-0.8394931280
H	0	-0.0404997415	4.9204345390	0.6282217368
H	0	-0.8596260010	4.9638580317	-0.9812301439
H	0	0.1034570999	0.5046822188	2.5933015369
H	0	1.3858423836	-1.6815344444	2.1509368771
H	0	2.4736683310	1.0170374216	1.9033206619
H	0	3.3348521669	-0.5592059681	1.9674389509
N	0	-1.6097698293	0.5754773263	-0.2373332064
C	0	-2.7585269472	0.2224373948	0.6082169434
C	0	-1.5931401743	0.6945245647	-1.6131929121
H	0	-3.1449752678	1.1552557297	1.0564445296
S	0	-1.9706343602	-0.7041334273	2.0349309391
C	0	-3.9742431490	-0.5443783200	0.0289904192
H	0	-2.5553926784	0.4032998430	-2.0729695398
O	0	-0.6478608706	1.0631781225	-2.2679466908
C	0	-4.8387334834	0.3875455423	-0.8469503020
C	0	-4.8545762407	-0.9500288438	1.2325269224
C	0	-3.5657909295	-1.8157342247	-0.7261824652
H	0	-4.3481079101	0.7042000687	-1.7759334942
H	0	-5.7660296065	-0.1335649526	-1.1309469781
H	0	-5.1222435127	1.2957081884	-0.2915059632
H	0	-5.7987381541	-1.3831574187	0.8695118053
H	0	-4.3630585273	-1.7075877335	1.8608816118
H	0	-5.1016754491	-0.0825328446	1.8651703334
H	0	-2.9377124534	-2.4590406547	-0.0957094790

H	0	-4.4650724762	-2.3832725903	-1.0126692488
H	0	-3.0002320290	-1.6052717341	-1.6429260067
C	0	0.2504089901	-2.3759695439	0.4418088955
C	0	-0.2568996395	-3.4698484793	1.1642878193
C	0	0.0763509123	-2.3491869761	-0.9538943721
C	0	-0.9093425818	-4.5181800010	0.5159373668
H	0	-0.1321901777	-3.5008984461	2.2496311100
C	0	-0.5572917301	-3.4110492253	-1.6003891922
H	0	0.4422359564	-1.4957450648	-1.5217127235
C	0	-1.0562104719	-4.4956531692	-0.8736336145
H	0	-1.2969790675	-5.3582828393	1.0970233142
H	0	-0.6721454753	-3.3819221776	-2.6866526633
H	0	-1.5612291800	-5.3176290443	-1.3865678464
C	0	3.9589748325	0.7417475838	0.3654948152
C	0	3.9374968145	2.0858609474	-0.0286306127
C	0	4.9485880526	-0.1075191355	-0.1481977267
C	0	4.8973331776	2.5719184915	-0.9197320710
H	0	3.1562492428	2.7389165614	0.3636837301
C	0	5.9065311582	0.3772254551	-1.0402200053
H	0	4.9659031410	-1.1593621356	0.1512057283
C	0	5.8821734869	1.7205622854	-1.4274706234
H	0	4.8741504565	3.6218072641	-1.2221674263
H	0	6.6743995820	-0.2933492369	-1.4336692021
H	0	6.6316000913	2.1026162884	-2.1250953056

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O	0	2.2622114653	-2.2993896451	0.9579481396
C	0	2.3245485180	-3.6997180847	1.2056169117
O	0	0.7286345929	-2.6711075998	-0.6541684528
C	0	1.3670319409	-1.9051232488	0.0383715345
C	0	1.2974750493	-0.4413705373	-0.0998733088
C	0	0.8423192069	0.1208972491	-1.3103952243
O	0	-0.7099984801	-0.5153402577	0.9754170564
N	0	-1.4112202637	-0.4787222026	-0.0960485524
C	0	-1.1560379067	0.5746027475	-0.9181858755
H	0	1.3559992447	-4.0683440706	1.5759058112
H	0	2.5799206243	-4.2511966456	0.2881555068
H	0	3.0990956770	-3.8401522857	1.9690117017
H	0	0.6744876653	-0.5491152075	-2.1551876960
H	0	-1.6734921629	0.5374119152	-1.8786582050
C	0	-1.0875280798	1.9454859043	-0.2731815838
H	0	-0.7318991497	2.6674182443	-1.0178006807
H	0	-0.3559937374	1.9279210598	0.5436765182
N	0	2.0514246675	0.4592236061	0.6791063138
C	0	2.7432799343	1.4808256874	-0.1018368164
C	0	1.9980150723	0.5368788624	2.0649966181
H	0	2.6895528165	2.4417947017	0.4320074119
S	0	1.7241712642	1.6454836351	-1.6564952806
C	0	4.2365485364	1.1614050605	-0.3954915155
H	0	2.5249250037	1.4519724086	2.4261479353
O	0	1.4692488870	-0.2528417243	2.8022218946
C	0	4.8127953063	2.3034303558	-1.2463693881
C	0	4.3882193869	-0.1798213667	-1.1259035932
C	0	4.9946326714	1.0949748644	0.9417529106
H	0	4.7088964890	3.2758591295	-0.7368295646
H	0	5.8846230812	2.1357446889	-1.4326137092
H	0	4.3084226573	2.3703325394	-2.2223444267
H	0	5.4492074774	-0.3625908744	-1.3572709674
H	0	4.0318013863	-1.0115485338	-0.5016665410
H	0	3.8281508697	-0.1826623984	-2.0724120159
H	0	4.6440871380	0.2596726950	1.5656649601
H	0	6.0683440295	0.9395730960	0.7540292066

H	0	4.8889986692	2.0289911127	1.5175576254
C	0	-2.4518990812	2.3473892891	0.2447516656
C	0	-3.3054497898	3.1488172047	-0.5258531249
C	0	-2.9021283247	1.8816752023	1.4914182531
C	0	-4.5811010535	3.4848918522	-0.0640965803
H	0	-2.9642714009	3.5185146470	-1.4973040535
C	0	-4.1762014518	2.2165071969	1.9528158651
H	0	-2.2457406222	1.2467304559	2.0903014365
C	0	-5.0199256490	3.0185687574	1.1774544560
H	0	-5.2323905817	4.1150019950	-0.6749990515
H	0	-4.5127493672	1.8497279675	2.9256905454
H	0	-6.0160268801	3.2811936046	1.5418739113
C	0	-2.1728478193	-1.6352808507	-0.4608703026
C	0	-2.9446715950	-1.6792428414	-1.6288654216
C	0	-2.1861869646	-2.7156762238	0.4318624643
C	0	-3.6970747880	-2.8201636717	-1.9155966245
H	0	-2.9812603459	-0.8345921043	-2.3156055299
C	0	-2.9463237338	-3.8428781191	0.1377830525
H	0	-1.5852161469	-2.6464569908	1.3363698756
C	0	-3.7016032426	-3.9065389833	-1.0390255156
H	0	-4.2917944198	-2.8504065000	-2.8314188429
H	0	-2.9476475712	-4.6844205931	0.8344794269
H	0	-4.2958537192	-4.7942591752	-1.2660625634

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O	0	-2.7042328652	2.7629599919	-0.6102134878
C	0	-3.0544999440	4.1013542440	-0.9458905306
O	0	-0.5864932785	3.4300723836	-0.2440017162
C	0	-1.4045306299	2.5463033639	-0.3416571499
C	0	-1.1194268210	1.1044434674	-0.1142864625
C	0	-0.2914592516	0.7154970416	0.9693174662
N	0	1.0876268158	0.0402860219	-1.0969839374
O	0	0.3410719928	0.9178502292	-1.6550660385
C	0	0.8249630227	-1.3671265685	-1.4950425587
C	0	1.5479328604	0.3337383867	0.1534630230
H	0	-2.7980067672	4.7928519300	-0.1290554188
H	0	-2.5226646112	4.4200821048	-1.8549987175
H	0	-4.1369813151	4.0993642674	-1.1227712864
H	0	0.0280285011	1.4821675762	1.6769978489
H	0	1.9258546228	-0.5461709597	0.6807262204
H	0	0.6751683878	-1.3159577323	-2.5816830679
H	0	-0.1173902874	-1.6823721360	-1.0319848760
N	0	-2.1004919191	0.1223566974	-0.4419331791
C	0	-2.4972750910	-0.6609351788	0.7394710344
C	0	-2.6629709046	0.0743058222	-1.7032795584
H	0	-3.1319646880	-0.0162848284	1.3732385340
S	0	-0.8885330228	-0.8349539807	1.6735248974
C	0	-3.2323376510	-2.0173946080	0.5818145337
H	0	-3.4311189338	-0.7152305316	-1.7987653938
O	0	-2.3592968426	0.7967127984	-2.6219755926
C	0	-4.7072088942	-1.7913963629	0.1839460242
C	0	-3.2549578604	-2.6808461607	1.9767498507
C	0	-2.5319811420	-2.9696527687	-0.3991480282
H	0	-4.8370943390	-1.3839366197	-0.8263779442
H	0	-5.2481412340	-2.7495708095	0.2199984217
H	0	-5.1995472705	-1.1026494655	0.8883145166
H	0	-3.8764433527	-3.5884505695	1.9453783526
H	0	-2.2482623039	-2.9777438317	2.3063979618
H	0	-3.6788440150	-2.0060014110	2.7368911418
H	0	-3.0640159053	-3.9330414130	-0.4257909335
H	0	-2.5025043665	-2.5804143156	-1.4257783598
H	0	-1.4982716584	-3.1675172356	-0.0825998726

C	0	2.3149978937	1.5669567141	0.4454382090
C	0	3.0860587989	1.5798232646	1.6221253604
C	0	2.3194439778	2.7009746793	-0.3835068686
C	0	3.8475623828	2.6961883526	1.9660557258
H	0	3.0931154549	0.6979348774	2.2692029439
C	0	3.0962293522	3.8086296351	-0.0433134114
H	0	1.6984886859	2.7098316702	-1.2754238924
C	0	3.8567096953	3.8161002886	1.1294449861
H	0	4.4411640024	2.6884677079	2.8834050151
H	0	3.0926185470	4.6840327714	-0.6969854624
H	0	4.4531100340	4.6930682243	1.3927872504
C	0	1.9416940257	-2.3042611353	-1.1266376590
C	0	1.7978750181	-3.2001540695	-0.0583657351
C	0	3.1572449608	-2.2686079050	-1.8257597425
C	0	2.8453037949	-4.0540807041	0.2986813728
H	0	0.8630680605	-3.2100018424	0.5069174544
C	0	4.2058317536	-3.1169824315	-1.4682061934
H	0	3.2795857601	-1.5655911479	-2.6539152307
C	0	4.0510295159	-4.0136620048	-0.4055374813
H	0	2.7199572326	-4.7497277829	1.1318828650
H	0	5.1477676251	-3.0807930471	-2.0206577571
H	0	4.8715533901	-4.6791689540	-0.1268474661

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O	0	0.0860322427	-2.2426841409	-2.1234628490
C	0	0.6533140651	-2.8931210240	-3.2549651340
O	0	2.1252267478	-1.4633038542	-1.5722871259
C	0	0.9290701635	-1.4845756065	-1.3952854776
C	0	0.2240255517	-0.7485844175	-0.3244002031
C	0	0.8117410054	-0.5814798179	0.9548748756
N	0	0.9782371747	1.8258661786	0.1064283182
O	0	0.8447192577	1.3225465933	-1.0550659019
C	0	0.0521368652	2.8928544782	0.5540162931
C	0	1.7608505249	1.1404562290	0.9928345215
H	0	1.4732933081	-3.5630176070	-2.9552640233
H	0	1.0476565256	-2.1504953196	-3.9647668292
H	0	-0.1601998921	-3.4637978225	-3.7189515736
H	0	1.6596057432	-1.2192296657	1.2139203427
H	0	1.6325493919	1.4975630015	2.0198409434
H	0	0.1180248781	2.9441918970	1.6474003874
H	0	0.4623230618	3.8356560242	0.1526259277
N	0	-1.1795345384	-0.6478571828	-0.3124048720
C	0	-1.8050423365	-0.9217841299	0.9770324390
C	0	-1.9225952572	-0.1899735954	-1.3863099152
H	0	-2.6456191371	-0.2272208922	1.1159047417
S	0	-0.4973168819	-0.4467404727	2.2012442108
C	0	-2.3251200450	-2.3760595755	1.1531979509
H	0	-2.9948015393	-0.0772323451	-1.1164213754
O	0	-1.4793422220	0.0785123262	-2.4752858900
C	0	-1.1963707245	-3.4065226056	1.0140952810
C	0	-3.3906404499	-2.6506573471	0.0776015695
C	0	-2.9710077000	-2.4792925512	2.5433119182
H	0	-0.4076293917	-3.2352311315	1.7611718134
H	0	-1.5956543090	-4.4213709419	1.1682865247
H	0	-0.7486098683	-3.3697131134	0.0111412612
H	0	-3.8353382576	-3.6450079814	0.2386054254
H	0	-4.2066132061	-1.9105173606	0.1136138889
H	0	-2.9554584708	-2.6412948831	-0.9323731268
H	0	-3.7924497425	-1.7524994775	2.6583755768
H	0	-3.3894682595	-3.4858686675	2.6968057085
H	0	-2.2341638367	-2.2939250906	3.3396182388
C	0	-1.3800415077	2.7496677232	0.1094521171

C	0	-1.7325895651	2.9696214110	-1.2287304604
C	0	-2.3845880690	2.4501759432	1.0404702621
C	0	-3.0670947687	2.8878575199	-1.6297311181
H	0	-0.9520086087	3.1781990761	-1.9611063046
C	0	-3.7210536769	2.3716361712	0.6414923130
H	0	-2.1117225378	2.2712177398	2.0828882412
C	0	-4.0640331366	2.5898524201	-0.6970956432
H	0	-3.3257560525	3.0422281239	-2.6791625960
H	0	-4.4965398123	2.1446935545	1.3773681248
H	0	-5.1086909028	2.5290996953	-1.0117484467
C	0	3.1748328149	0.7976693326	0.6815039385
C	0	4.0052811881	0.4506020291	1.7613241708
C	0	3.7159290654	0.8218948060	-0.6127776360
C	0	5.3494828293	0.1382803493	1.5579704060
H	0	3.5932022272	0.4339610590	2.7748092978
C	0	5.0650090784	0.5267720593	-0.8094828259
H	0	3.0679610703	1.0520840138	-1.4549775566
C	0	5.8849746999	0.1790098595	0.2676540309
H	0	5.9809240557	-0.1284110392	2.4089046543
H	0	5.4752141694	0.5513178539	-1.8217829123
H	0	6.9376789982	-0.0627288090	0.1022620819

S0-PM-PnRe

0 1

O	0	1.2833522487	1.4604190314	1.9409967361
C	0	2.2673327688	2.0776839091	2.7709719163
O	0	2.8535286733	0.9880020533	0.3922450963
C	0	1.7064541497	1.0634932874	0.7321760458
C	0	0.5180474077	0.5269032669	-0.1039304450
C	0	0.0342636342	-0.7990839556	0.5308111480
O	0	0.9978415369	0.1962169020	-1.3841393530
N	0	0.8069364720	-1.2303747766	-1.6243179747
C	0	1.9128139914	-1.6337346685	-2.4659889639
C	0	0.8137660315	-1.8311362606	-0.2961225426
H	0	2.6069216014	3.0149998045	2.3058265803
H	0	3.1318284405	1.4131942708	2.9142341863
H	0	1.7754761381	2.2838457535	3.7291157842
H	0	0.2947174039	-0.8596942616	1.5928520656
H	0	1.8426284948	-1.8446523785	0.1238797525
H	0	1.8450734978	-1.1119837366	-3.4306456150
H	0	2.8927731216	-1.4115914926	-2.0015491577
H	0	1.8201214377	-2.7150412157	-2.6436416945
N	0	-0.5930044322	1.4525632509	-0.1365553103
C	0	-1.9405894507	0.8936335535	-0.2311054639
C	0	-0.3874715597	2.8035445608	-0.0139582411
H	0	-2.5794958218	1.4290481016	0.4904538672
S	0	-1.7893111810	-0.8479057071	0.3800188283
C	0	-2.6433604323	0.9907607748	-1.6204063690
H	0	-1.3380967175	3.3653989642	0.1122159687
O	0	0.6976433691	3.3429379142	-0.0163167098
C	0	-2.8414256941	2.4717625235	-1.9893387359
C	0	-4.0271573644	0.3329237881	-1.4791200835
C	0	-1.8442463809	0.3032004336	-2.7309962394
H	0	-1.8851302580	2.9791271998	-2.1844153203
H	0	-3.4394027991	2.5446034121	-2.9108145190
H	0	-3.3783033780	3.0253330278	-1.2012528354
H	0	-4.5917902307	0.4335605062	-2.4185786396
H	0	-3.9383893441	-0.7408267465	-1.2543897496
H	0	-4.6207268515	0.8050076838	-0.6783860156
H	0	-1.6632889776	-0.7531107652	-2.4961253339
H	0	-2.3982990174	0.3663629149	-3.6806947297
H	0	-0.8626538356	0.7774389569	-2.8634436868
C	0	0.2679332636	-3.2386042893	-0.2782982261

C	0	0.7346272080	-4.1441938270	0.6835761672
C	0	-0.7286399551	-3.6480605820	-1.1753233388
C	0	0.2072842459	-5.4349976659	0.7603760747
H	0	1.5207842496	-3.8347296787	1.3780017687
C	0	-1.2493648407	-4.9419019143	-1.1043287607
H	0	-1.0837018447	-2.9442711764	-1.9270701413
C	0	-0.7875548570	-5.8369117259	-0.1351634456
H	0	0.5791130915	-6.1304593733	1.5165631559
H	0	-2.0233215313	-5.2523265714	-1.8104241182
H	0	-1.1982518822	-6.8479787361	-0.0809573922

S0-PM-PnSi

0 1

O	0	-0.8975702188	-2.3536778455	-0.9814823999
C	0	-1.3649653307	-3.5902012229	-1.5165216022
O	0	-2.9946133688	-1.8383669003	-0.3334774204
C	0	-1.8175170288	-1.6103645270	-0.3509243327
C	0	-1.1698008209	-0.3302916818	0.2004447082
C	0	-1.0138967374	0.7388425146	-0.9279038555
O	0	-2.0641992251	0.2344224558	1.1182349633
N	0	-1.7861265345	1.6568187355	1.0753938613
C	0	-2.8253951011	2.2878542855	1.8582570398
C	0	-1.8430202084	1.9260579455	-0.3612333353
H	0	-1.7152722492	-4.2437486835	-0.7036239925
H	0	-2.1943322560	-3.4254731184	-2.2203976710
H	0	-0.5090807508	-4.0450266864	-2.0294691766
H	0	-1.4424994537	0.3971360021	-1.8774032482
H	0	-2.8813384536	1.7868075809	-0.7275023080
H	0	-3.8383139629	2.0444011146	1.4817015994
H	0	-2.6704133943	3.3749708175	1.8147991319
H	0	-2.7411814412	1.9558315378	2.9021115102
N	0	0.1400578847	-0.5796240302	0.7900804277
C	0	1.1986367017	0.3898585226	0.4941315992
C	0	0.1946714050	-1.5957864360	1.7065724181
H	0	1.1126403512	1.2483088552	1.1810824284
S	0	0.7554036802	0.9947462085	-1.1976862302
C	0	2.6774958157	-0.1087925308	0.5126454095
H	0	1.1589016239	-1.6741019578	2.2392585621
O	0	-0.7263461742	-2.3577960917	1.9199106381
C	0	3.5353909796	0.9412907506	-0.2279643643
C	0	2.8197972071	-1.4654238242	-0.1936301236
C	0	3.2256691595	-0.1656574164	1.9540625146
H	0	3.3736519600	1.9525335189	0.1780000633
H	0	4.6017848507	0.6960989049	-0.1113538674
H	0	3.3182002228	0.9660647853	-1.3057565978
H	0	3.8852312091	-1.7101867371	-0.3250156775
H	0	2.3587730124	-2.2858335069	0.3736995692
H	0	2.3419314468	-1.4366744843	-1.1837053117
H	0	2.7616076479	-0.9405630558	2.5774773483
H	0	4.3048570354	-0.3819027053	1.9277823635
H	0	3.0912136715	0.8017249771	2.4638032578
C	0	-1.3703465503	3.3074771577	-0.7279579940
C	0	-1.9333353627	3.9628331646	-1.8298100652
C	0	-0.3443895768	3.9403248326	-0.0113765068
C	0	-1.4747927820	5.2237116209	-2.2195828156
H	0	-2.7403481822	3.4802780671	-2.3879761158
C	0	0.1060219768	5.2053263206	-0.3916479669
H	0	0.0875725852	3.4351567950	0.8530250488
C	0	-0.4534196121	5.8486436022	-1.4998437504
H	0	-1.9220038446	5.7219046906	-3.0830544828
H	0	0.9020891453	5.6911103932	0.1779163188
H	0	-0.0969377513	6.8372510651	-1.7988662691

S0-PM-PxRe

0 1

O	0	-1.2577583188	2.2830552304	-0.8274647997
C	0	-1.9746234700	3.4192180197	-1.3127509273
O	0	-3.1614699189	1.4697998344	0.0617265873
C	0	-1.9783840861	1.4023877054	-0.1086890132
C	0	-1.0747658679	0.2331665423	0.3379952606
C	0	-0.9515838159	-0.8132869600	-0.7989657746
N	0	-1.6772258217	-1.8352946661	1.2367385612
O	0	-1.7351123061	-0.4142446745	1.4002178035
C	0	-0.5330507103	-2.3703717480	1.9611516160
C	0	-1.6942278621	-2.0438583530	-0.2080611439
H	0	-2.8254551365	3.1052362671	-1.9351703868
H	0	-2.3543441631	4.0154709161	-0.4700412477
H	0	-1.2594386005	4.0039548517	-1.9035098058
H	0	-1.4287306070	-0.4660606351	-1.7229572392
H	0	-1.1350038600	-2.9622709981	-0.4373629330
H	0	-0.5860353572	-3.4681260869	1.9057260783
H	0	-0.6304261184	-2.0757205786	3.0151303275
H	0	0.4450583480	-2.0374822373	1.5778203740
N	0	0.2673177501	0.7022287894	0.7019778710
C	0	1.3296205497	0.4706730508	-0.2859346918
C	0	0.2921456228	1.7156212510	1.6334231639
H	0	1.2789182287	1.2601095446	-1.0556556689
S	0	0.8234422744	-1.1076290278	-1.1033942608
C	0	2.8073744031	0.3853510671	0.2118431104
H	0	1.3069494352	2.0825849943	1.8694735102
O	0	-0.7016386536	2.1644382597	2.1617363243
C	0	3.3899749421	1.7898675726	0.4867030612
C	0	3.6488127524	-0.2123548324	-0.9371145983
C	0	2.9387495535	-0.5030890035	1.4549905769
H	0	3.0505749205	2.2289054648	1.4336543885
H	0	4.4869784902	1.7244632982	0.5481327862
H	0	3.1429490760	2.4921799646	-0.3252374494
H	0	4.7136328748	-0.2016845199	-0.6600778132
H	0	3.3738514954	-1.2555806180	-1.1512893141
H	0	3.5347503385	0.3707855508	-1.8647996187
H	0	3.9925477297	-0.5560413164	1.7693488885
H	0	2.3526211429	-0.1163086044	2.3007978724
H	0	2.5944638935	-1.5257801477	1.2445980205
C	0	-3.0988900611	-2.1687646432	-0.7720846237
C	0	-4.2043091279	-1.6058158170	-0.1231680457
C	0	-3.2837654628	-2.8315460427	-1.9930319254
C	0	-5.4754588562	-1.7092201247	-0.6931321698
H	0	-4.0589806590	-1.0750573478	0.8168106381
C	0	-4.5552206495	-2.9353422401	-2.5615620755
H	0	-2.4238866482	-3.2778162529	-2.5024659155
C	0	-5.6562446326	-2.3723683688	-1.9101017270
H	0	-6.3314482023	-1.2625747774	-0.1816180469
H	0	-4.6869585839	-3.4619032860	-3.5100499919
H	0	-6.6534000939	-2.4519656568	-2.3499993529

S0-PM-PxSi

0 1

O	0	1.1622086029	2.1723485333	-1.3117417168
C	0	1.8007023369	3.3159635154	-1.8760227692
O	0	2.9013024052	1.8814736916	0.0985604933
C	0	1.7939439039	1.6105427610	-0.2681299871
C	0	0.9452189974	0.4482537075	0.2851277853
C	0	0.9087189632	-0.7277840142	-0.7493649288
N	0	2.4643508280	-1.1015461737	0.9336259233
O	0	1.5399849164	-0.1065881018	1.4348040616

C	0	2.9467297554	-1.8283433450	2.0822136791
C	0	1.6362099645	-1.8652043680	0.0038730053
H	0	2.8220350071	3.0732886196	-2.2050379418
H	0	1.8499350537	4.1230136026	-1.1296841228
H	0	1.1842791012	3.6227176390	-2.7297112018
H	0	1.4387155723	-0.4659842346	-1.6716387770
H	0	0.8787583921	-2.4677422487	0.5465733700
H	0	3.6292678277	-2.6118188878	1.7237408508
H	0	3.5035009696	-1.1408101926	2.7333710187
H	0	2.1245092718	-2.2965415434	2.6618618270
N	0	-0.4137529974	0.8286099595	0.5970699175
C	0	-1.3536914128	-0.2884513271	0.4495219999
C	0	-0.6534208550	2.0800720665	1.1053222982
H	0	-1.1229694254	-1.0247546718	1.2382292077
S	0	-0.8251609443	-1.0584902385	-1.1578050214
C	0	-2.8822564023	-0.0291365229	0.4867834031
H	0	-1.7138351411	2.2660558153	1.3473874301
O	0	0.2034120243	2.9226728370	1.2670333910
C	0	-3.3212051513	1.0625580037	-0.5039029371
C	0	-3.3404966329	0.2897332746	1.9253604983
C	0	-3.5719776843	-1.3535170030	0.0903738715
H	0	-2.9207167509	0.8593011717	-1.5077469366
H	0	-4.4200432452	1.0849340733	-0.5681073306
H	0	-2.9905138727	2.0681060293	-0.2113839033
H	0	-4.4378165892	0.3747926869	1.9517532532
H	0	-3.0509515297	-0.5195541779	2.6140667309
H	0	-2.9322481770	1.2266573192	2.3252136585
H	0	-3.2146384066	-2.1932272485	0.7069043992
H	0	-4.6587453618	-1.2622804838	0.2374548471
H	0	-3.3977498759	-1.6088154887	-0.9651601500
C	0	2.4519904972	-2.7618111272	-0.8919369647
C	0	1.9494477724	-4.0059051749	-1.2910896695
C	0	3.6958392897	-2.3338020785	-1.3804235880
C	0	2.6773352879	-4.8149203083	-2.1678873742
H	0	0.9785348350	-4.3384217296	-0.9150978247
C	0	4.4255969082	-3.1459191179	-2.2501623413
H	0	4.0817871171	-1.3638317969	-1.0597772739
C	0	3.9179404821	-4.3873515657	-2.6476875017
H	0	2.2754266475	-5.7838029876	-2.4739739800
H	0	5.3966384616	-2.8083610827	-2.6207249186
H	0	4.4901282537	-5.0211713656	-3.3294474300

S0-PM-TSnRe

0 1

O	0	-3.3550418092	1.0443474537	0.3687236787
C	0	-4.7741456076	1.1138183985	0.4628285935
O	0	-3.5512285387	-0.8259126631	-0.8640081939
C	0	-2.8581903824	-0.0214951516	-0.2759962314
C	0	-1.3740725129	-0.0553568247	-0.2346661420
C	0	-0.6513501877	-0.5248463945	-1.3674589880
O	0	-1.3458228631	-1.7964808151	0.9205308664
N	0	-0.9891028439	-2.6513607799	0.0283992938
C	0	-2.0385192722	-3.4623304681	-0.5941290486
C	0	0.1266809429	-2.3152289772	-0.6856598635
H	0	-5.1676244724	0.2370485409	0.9986582693
H	0	-5.2336569558	1.1486186400	-0.5365921627
H	0	-4.9981393622	2.0306728635	1.0213465612
H	0	-1.2324792381	-0.8942664383	-2.2151559626
H	0	0.2586704984	-2.9211906645	-1.5882301822
H	0	-2.7636343381	-3.7079277444	0.1905801019
H	0	-2.5584553245	-2.8918760503	-1.3782671042
H	0	-1.5949484155	-4.3818625481	-0.9992836750
N	0	-0.6487778053	0.9502212072	0.4699034268

C	0	0.1141170141	1.8019616026	-0.4539176844
C	0	-0.7949011059	1.1231764122	1.8320151686
H	0	-0.6031390482	2.4683226848	-0.9659422854
S	0	0.6806465269	0.5988720698	-1.7726848606
C	0	1.2802237321	2.6883427654	0.0529050434
H	0	-0.1604477535	1.9393755347	2.2239910707
O	0	-1.5173469308	0.4664091912	2.5428244254
C	0	0.7403403970	3.9169336979	0.8161843100
C	0	1.9961625784	3.2372243219	-1.2017629134
C	0	2.2974546722	1.9027119068	0.8901688297
H	0	0.2634302493	3.6706871437	1.7731775863
H	0	1.5711853909	4.6051156864	1.0357327156
H	0	0.0045205985	4.4649755443	0.2063615417
H	0	2.7533548550	3.9766689675	-0.9005248999
H	0	2.5135922717	2.4413629945	-1.7577664895
H	0	1.2906061191	3.7351985194	-1.8859048783
H	0	2.6665865054	1.0293423848	0.3363764450
H	0	3.1565063178	2.5475206914	1.1334911858
H	0	1.8785105742	1.5359806965	1.8361879261
C	0	1.3950774100	-1.9719784599	-0.0042242614
C	0	2.5754560280	-1.9929143602	-0.7674296318
C	0	1.4822548384	-1.6587965765	1.3648246837
C	0	3.8129952757	-1.7231620332	-0.1838236023
H	0	2.5212560827	-2.2294804403	-1.8331855633
C	0	2.7249767589	-1.4130673716	1.9490392612
H	0	0.5718032538	-1.6121356816	1.9595893488
C	0	3.8932562053	-1.4382542924	1.1819100341
H	0	4.7177052276	-1.7431486390	-0.7960414061
H	0	2.7775725707	-1.1853489065	3.0164823088
H	0	4.8612968732	-1.2323516388	1.6448193537

S0-PM-TSnSi

0 1

O	0	3.1089776325	-0.0836721976	0.6737234467
C	0	4.4866584543	-0.4399051677	0.7347211244
O	0	2.8116606951	-1.5959757545	-0.9645438706
C	0	2.3544603365	-0.7857332805	-0.1845921034
C	0	0.9211409706	-0.4177251013	-0.1012433563
C	0	0.0931778929	-0.4955787401	-1.2610050570
O	0	0.4377057093	-2.2521425934	0.7700978708
N	0	-0.1390108419	-2.8332458932	-0.2253072773
C	0	0.6564070943	-3.7830702767	-1.0072577940
C	0	-1.1070958235	-2.0884060825	-0.8460226329
H	0	4.5977361823	-1.4942359302	1.0283774927
H	0	4.9736729558	-0.2936294063	-0.2411592074
H	0	4.9361600422	0.2140127414	1.4914352529
H	0	0.5655903533	-0.8310701921	-2.1870906496
H	0	-1.3937512611	-2.4925842209	-1.8228844991
H	0	1.2991213522	-3.2565378800	-1.7289241823
H	0	-0.0157317800	-4.4864638802	-1.5174226997
H	0	1.2986596631	-4.3228489175	-0.3015705140
N	0	0.4606055126	0.5700392930	0.8037679407
C	0	-0.3105444836	1.6580620165	0.2028749163
C	0	0.5174149002	0.4347310391	2.1812836806
H	0	-1.1950573525	1.8540347480	0.8282607470
S	0	-0.9156351220	0.9762419319	-1.4184625875
C	0	0.4764863110	2.9880301527	0.0181761640
H	0	-0.1071005286	1.2118163333	2.6802387203
O	0	1.1373490040	-0.3998072899	2.7894922886
C	0	-0.4656376971	4.0080921644	-0.6403160884
C	0	1.7278499148	2.7790814761	-0.8452269420
C	0	0.9015851193	3.5165642227	1.3987860347
H	0	-1.3726470602	4.1666803018	-0.0336836025

H	0	0.0404656342	4.9796514415	-0.7487104176
H	0	-0.7759936344	3.6786904648	-1.6437996711
H	0	2.2492960424	3.7381702088	-0.9903523319
H	0	2.4267061951	2.0834534884	-0.3597527004
H	0	1.4634641215	2.3801265866	-1.8354260767
H	0	1.6233651950	2.8452691493	1.8868049869
H	0	1.3879285814	4.4981183766	1.2871583660
H	0	0.0371574488	3.6476352717	2.0699847987
C	0	-2.2426369560	-1.5144832063	-0.0868047577
C	0	-3.3854767653	-1.1332815111	-0.8102760054
C	0	-2.2266014752	-1.3080118485	1.3050677513
C	0	-4.4829400906	-0.5573581524	-0.1711179912
H	0	-3.4109270569	-1.2865746731	-1.8921709981
C	0	-3.3295529593	-0.7378919173	1.9423684621
H	0	-1.3478494370	-1.6006293866	1.8759525854
C	0	-4.4575611405	-0.3532195586	1.2105925435
H	0	-5.3596052069	-0.2662726547	-0.7545252978
H	0	-3.3045521476	-0.5921914399	3.0252248048
H	0	-5.3142784946	0.0992467445	1.7158313334

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0 1

O	0	0.5789975728	2.9631528171	-0.8179649945
C	0	0.1340749935	4.2849699482	-1.1034508256
O	0	-1.5642248309	2.2828238367	-0.7259700967
C	0	-0.3859796290	2.0576496198	-0.5795924968
C	0	0.1772944747	0.7406349846	-0.1815369155
C	0	-0.3587297206	-0.4503163912	-0.7331623048
N	0	-0.9628900841	-0.6234807940	1.7717101024
O	0	-0.8225898788	0.6468377908	1.6975526367
C	0	0.0449671814	-1.3493417321	2.5525650295
C	0	-1.5841420343	-1.2318208270	0.7190471844
H	0	-0.5145514571	4.2993993135	-1.9924352477
H	0	-0.4305142231	4.6919642739	-0.2511062260
H	0	1.0380246270	4.8814446664	-1.2770637617
H	0	-1.1132355567	-0.3631744948	-1.5165730722
H	0	-1.4109256618	-2.3128632726	0.6960563530
H	0	-0.3583902588	-2.3189300215	2.8738719027
H	0	0.2792989516	-0.7296803489	3.4260428340
H	0	0.9520165418	-1.5073464818	1.9545242183
N	0	1.5608375985	0.6217292011	0.1449906067
C	0	2.2462934511	-0.3229027795	-0.7521955606
C	0	2.1388669566	1.4331177454	1.1024661402
H	0	2.3564990056	0.1678266469	-1.7356801592
S	0	0.9578910500	-1.6518278979	-1.0054843424
C	0	3.6286374742	-0.9163250288	-0.3763422536
H	0	3.2214571832	1.2441799037	1.2243557278
O	0	1.5479085350	2.2578849908	1.7572834535
C	0	4.7419049069	0.1391420116	-0.5523730569
C	0	3.9271202276	-2.0366158398	-1.3975786821
C	0	3.6522025990	-1.5234474772	1.0342696973
H	0	4.6944722210	0.9608775723	0.1729472092
H	0	5.7251472601	-0.3418106848	-0.4341752862
H	0	4.7046848529	0.5803103012	-1.5608251415
H	0	4.9515156868	-2.4100862630	-1.2488604715
H	0	3.2417477200	-2.8895711728	-1.2840906599
H	0	3.8475270000	-1.6689846002	-2.4327056322
H	0	4.6333903779	-1.9847272997	1.2254099616
H	0	3.4778765350	-0.7782014287	1.8223032105
H	0	2.8867795230	-2.3071643708	1.1303025063
C	0	-2.9359775697	-0.8385234770	0.2582307933
C	0	-3.6480716014	-1.7689256568	-0.5208012562
C	0	-3.5334217600	0.3973971152	0.5573458623

C	0	-4.9295531020	-1.4786882202	-0.9878280305
H	0	-3.1914943626	-2.7346614290	-0.7566006241
C	0	-4.8218660589	0.6758394273	0.1008441053
H	0	-2.9731355729	1.1345068252	1.1263969403
C	0	-5.5228606588	-0.2524195930	-0.6741802360
H	0	-5.4683558222	-2.2136452829	-1.5907026011
H	0	-5.2761454780	1.6398247708	0.3415281421
H	0	-6.5274251859	-0.0202078966	-1.0360616819

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0 1

O	0	-1.0679316492	2.5768912128	-0.8337243506
C	0	-0.8171901050	3.8186553601	-1.4839149290
O	0	1.0571431458	1.9553443205	-1.2454066976
C	0	-0.0146868099	1.7453197192	-0.7256045352
C	0	-0.3424966576	0.5364196402	0.0611483213
C	0	0.2516193888	-0.7145622569	-0.2474685670
N	0	1.3046105186	-0.1340661707	2.0294588943
O	0	1.0060851631	1.0587037440	1.6800966516
C	0	0.5628188646	-0.7083624153	3.1602036218
C	0	1.7893684046	-0.9537174324	1.0476552737
H	0	-0.4753912276	3.6593403279	-2.5177993924
H	0	-0.0451834287	4.3860789496	-0.9431570336
H	0	-1.7673052104	4.3660825172	-1.4725111842
H	0	0.8239223131	-0.7964090735	-1.1732356933
H	0	1.7557569228	-2.0104726389	1.3340802607
H	0	1.2277953643	-1.3496795622	3.7560178687
H	0	0.2098592779	0.1350244424	3.7640480655
H	0	-0.2898022484	-1.3040419488	2.8010863060
N	0	-1.5984725802	0.3957093831	0.7057607137
C	0	-2.2918106677	-0.8536572106	0.4088147970
C	0	-2.0861227199	1.2651380041	1.6660124300
H	0	-2.8226590824	-1.1911917518	1.3120687568
S	0	-0.9120695627	-2.0585480840	0.0973418193
C	0	-3.3212055348	-0.7727224646	-0.7540627787
H	0	-3.0242161095	0.8664944537	2.1210315107
O	0	-1.5864876455	2.3093955592	1.9979764357
C	0	-2.6590864767	-0.3624817251	-2.0765694516
C	0	-4.3921508762	0.2684955373	-0.3855517895
C	0	-3.9797176336	-2.1532718294	-0.8980895670
H	0	-1.8592351286	-1.0634595980	-2.3564837381
H	0	-3.4084254661	-0.3632758621	-2.8836416214
H	0	-2.2385802080	0.6502804908	-2.0113683742
H	0	-5.1731424422	0.2912286343	-1.1613123498
H	0	-4.8824133356	0.0290701317	0.5723219074
H	0	-3.9624466859	1.2784970935	-0.3155875233
H	0	-4.4710691249	-2.4640689889	0.0390173623
H	0	-4.7471636199	-2.1297044154	-1.6868321688
H	0	-3.2394902499	-2.9213796128	-1.1693528365
C	0	2.9829521818	-0.6017532964	0.2410240185
C	0	3.6567065909	-1.6545165833	-0.4044117705
C	0	3.4658092507	0.7087015515	0.0905514046
C	0	4.7905440368	-1.4099378729	-1.1786118222
H	0	3.2893476201	-2.6786389688	-0.2907086100
C	0	4.6097791470	0.9456512895	-0.6718164971
H	0	2.9285611483	1.5298858349	0.5576997537
C	0	5.2731831728	-0.1049080977	-1.3119879937
H	0	5.3020723743	-2.2400329339	-1.6717036391
H	0	4.9766878663	1.9690352167	-0.7795106680
H	0	6.1620427345	0.0925213806	-1.9160735910

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0 1

O	0	0.9103112368	1.7937473641	2.3037128370
C	0	1.7438165187	2.5601363844	3.1763026410
O	0	2.6864088219	1.2967221706	1.0021902820
C	0	1.5049857480	1.3184463518	1.2012873238
C	0	0.4636580449	0.6380441114	0.2808065152
C	0	-0.1366037654	-0.5875000508	0.9965254357
O	0	1.0971006215	0.1131454710	-0.8682700216
N	0	1.4598303438	-1.2431454021	-0.6337327556
C	0	0.8323240931	-1.7182418942	0.6027986970
H	0	2.0826045015	3.4681177890	2.6561286740
H	0	2.6203357025	1.9758046520	3.4911951617
H	0	1.1226725841	2.8232903609	4.0405962069
H	0	-0.1520138796	-0.4465064738	2.0818537860
H	0	1.6001658431	-1.7789912549	1.3981277108
N	0	-0.6054068125	1.5135348053	-0.1139766566
C	0	-1.8866303820	0.8853009372	-0.4459594883
C	0	-0.4623773602	2.8800054890	-0.0991121582
H	0	-2.6795320495	1.4894709750	0.0238890930
S	0	-1.8663363431	-0.7554998486	0.4126013404
C	0	-2.2536218269	0.7592762233	-1.9575677821
H	0	-1.4278863909	3.4030135962	-0.2704322180
O	0	0.5779504107	3.4678346343	0.0952060128
C	0	-2.2748811620	2.1592105736	-2.5945517314
C	0	-3.6730956219	0.1663405670	-2.0177939091
C	0	-1.2879793849	-0.1353062667	-2.7428272286
H	0	-1.2711687191	2.6084699947	-2.6310083772
H	0	-2.6364214261	2.0873701295	-3.6318089999
H	0	-2.9484127349	2.8470253982	-2.0571213812
H	0	-4.0127665107	0.1027016247	-3.0626730280
H	0	-3.7002985088	-0.8502470546	-1.5957924373
H	0	-4.3970030834	0.7884486840	-1.4655850063
H	0	-1.2317083639	-1.1386703804	-2.2989040999
H	0	-1.6419155889	-0.2348438919	-3.7809150704
H	0	-0.2738828624	0.2818734002	-2.7545879750
C	0	2.8272561566	-1.4946310986	-0.8495322774
C	0	3.6464462557	-0.5640262442	-1.5098093633
C	0	3.3682034965	-2.7298202736	-0.4466528252
C	0	4.9831134739	-0.8717583130	-1.7565127965
H	0	3.2316624663	0.3989254898	-1.7972658146
C	0	4.7092494521	-3.0199421862	-0.7044330459
H	0	2.7415991829	-3.4723454128	0.0474506132
C	0	5.5270087414	-2.0976962233	-1.3603585759
H	0	5.6112344752	-0.1335331834	-2.2615246696
H	0	5.1136813245	-3.9841662528	-0.3862520212
H	0	6.5755507846	-2.3294823759	-1.5589177027
C	0	0.1777841153	-3.0792595151	0.4730679075
C	0	-0.1487697212	-3.7910568930	1.6344374672
C	0	-0.1431950437	-3.6194739281	-0.7762079100
C	0	-0.8035311495	-5.0214495817	1.5496008965
H	0	0.1112502017	-3.3796490724	2.6142136302
C	0	-0.7919621788	-4.8532151129	-0.8618541048
H	0	0.1322759161	-3.0636501747	-1.6731825479
C	0	-1.1278577722	-5.5552898081	0.2989546543
H	0	-1.0558103807	-5.5674264037	2.4617426696
H	0	-1.0357026262	-5.2691212932	-1.8424144849
H	0	-1.6354912239	-6.5202996726	0.2299975687

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0 1

O	0	-0.6296744132	-2.4478599607	-0.4887098932
C	0	-0.9224576437	-3.7953656637	-0.8560317249
O	0	-2.8168252340	-2.0748958266	-0.1065828468

C	0	-1.6729926327	-1.7141224187	-0.0876017604
C	0	-1.2240746781	-0.2903924399	0.2845893923
C	0	-1.2674265440	0.6804076721	-0.9243900294
O	0	-2.1869328778	0.2086465799	1.1646974024
N	0	-2.0433801556	1.6336942542	1.0871562909
C	0	-2.0056214205	1.9375841540	-0.3402098092
H	0	-1.3139745525	-4.3476200293	0.0109968916
H	0	-1.6702347356	-3.8266880080	-1.6622595864
H	0	0.0255399972	-4.2321042455	-1.1916779929
H	0	-1.8590449521	0.2587367813	-1.7448669960
H	0	-3.0296487277	1.9474539885	-0.7617923356
N	0	0.1235896559	-0.2454079161	0.8430091742
C	0	1.1300433888	0.5942682454	0.1827099251
C	0	0.3057068779	-0.9632885213	1.9960830242
H	0	1.1834302527	1.5771522015	0.6793249354
S	0	0.4278675020	0.8721961200	-1.5071554636
C	0	2.5845243227	0.0345891065	0.0627830961
H	0	1.2781213734	-0.7812032538	2.4901979388
O	0	-0.5236989437	-1.7259313646	2.4475182614
C	0	3.3301221979	0.9030864258	-0.9740981130
C	0	2.5858242040	-1.4305124665	-0.3931867526
C	0	3.3564006278	0.1888720264	1.3906041870
H	0	3.2745703539	1.9731171279	-0.7173470518
H	0	4.3919160190	0.6160103200	-1.0029892450
H	0	2.9271815398	0.7733971087	-1.9892519506
H	0	3.6202042411	-1.7688059443	-0.5611788699
H	0	2.1291841332	-2.0941997527	0.3545143262
H	0	2.0196578498	-1.5491854715	-1.3277107291
H	0	3.0509693009	-0.5325882755	2.1592570221
H	0	4.4293607060	0.0200705133	1.2115955503
H	0	3.2434320480	1.2035628123	1.8050073938
C	0	-2.9677012386	2.2492317610	1.9518600449
C	0	-3.2780944834	1.6277362860	3.1763211892
C	0	-3.5483396370	3.4897080722	1.6391022457
C	0	-4.1448112219	2.2513707905	4.0703431959
H	0	-2.8402988499	0.6563415213	3.4031056520
C	0	-4.4066533660	4.1054738574	2.5540519708
H	0	-3.3250709076	3.9854280670	0.6958950990
C	0	-4.7118479088	3.4955132368	3.7712685483
H	0	-4.3813028506	1.7553656273	5.0149880979
H	0	-4.8461977924	5.0731196122	2.2995654590
H	0	-5.3883499032	3.9798787792	4.4786727702
C	0	-1.3263580850	3.2510284248	-0.6480570340
C	0	-1.5874252414	3.8867325447	-1.8677027493
C	0	-0.4048641760	3.8243279531	0.2364309594
C	0	-0.9249739435	5.0674507520	-2.2090809159
H	0	-2.3144743037	3.4511651828	-2.5587168349
C	0	0.2539589249	5.0081463960	-0.1008892629
H	0	-0.2257577134	3.3426921130	1.1985982909
C	0	0.0011134221	5.6303524679	-1.3265606112
H	0	-1.1355697158	5.5517230648	-3.1655539819
H	0	0.9656089850	5.4503624060	0.6005843141
H	0	0.5173718756	6.5565158350	-1.5898204589

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0 1

O	0	-1.1868820826	3.0429707482	-0.5195047623
C	0	-1.8449974593	4.2702326723	-0.8390000950
O	0	-3.1326459835	2.1898193100	0.2279297694
C	0	-1.9500926727	2.1021993879	0.0487182725
C	0	-1.1304708842	0.8230517268	0.3196932645
C	0	-1.2297174625	-0.1482431581	-0.8699122461
N	0	-1.5433694542	-1.2186098378	1.2352609004

O	0	-1.7765623267	0.1651013748	1.3748587991
C	0	-1.4152453497	-1.5408160470	-0.1875776804
H	0	-2.7014915841	4.0882666855	-1.5043977086
H	0	-2.2057352567	4.7561961604	0.0793701738
H	0	-1.0961391489	4.8977907443	-1.3360333155
H	0	-2.1196957001	0.0797500892	-1.4678996425
H	0	-0.5141476553	-2.1477375351	-0.3371822710
N	0	0.2896545535	1.0941395785	0.5534492911
C	0	1.2417403463	0.8375866103	-0.5348380429
C	0	0.5542347852	2.0700275725	1.4922825853
H	0	1.6085044228	1.8050073768	-0.9159835170
S	0	0.2210425165	0.1337035780	-1.9170701756
C	0	2.4937495181	-0.0307111200	-0.2038079749
H	0	1.5964089074	2.4462741472	1.4579589935
O	0	-0.2701795754	2.4918735886	2.2722751592
C	0	3.2972589029	0.5964633127	0.9491793651
C	0	3.3744264075	-0.0380282665	-1.4660829908
C	0	2.1306206376	-1.4646351781	0.1865345604
H	0	2.7539021919	0.5397701000	1.9035837596
H	0	4.2393321588	0.0421350212	1.0792445374
H	0	3.5592858772	1.6480324377	0.7485353429
H	0	4.2918188537	-0.6180460254	-1.2840261471
H	0	2.8515150137	-0.4984721303	-2.3184234838
H	0	3.6734142627	0.9827706743	-1.7561240096
H	0	3.0443008894	-2.0350720570	0.4128836834
H	0	1.4988170838	-1.4863308692	1.0818350346
H	0	1.6081004856	-1.9803895553	-0.6315207549
C	0	-0.6976669291	-1.7672091363	2.2031096092
C	0	-0.3691528441	-3.1340068628	2.1230529286
C	0	-0.2050155077	-0.9965312135	3.2714826531
C	0	0.4858203555	-3.7003593128	3.0680126402
H	0	-0.7892305208	-3.7492449061	1.3257697257
C	0	0.6443108468	-1.5844653640	4.2091817020
H	0	-0.4853372854	0.0529094631	3.3471655877
C	0	1.0066287057	-2.9319416739	4.1132177143
H	0	0.7404757796	-4.7601148875	2.9872875597
H	0	1.0297776659	-0.9727709526	5.0290055558
H	0	1.6742399309	-3.3809346248	4.8513981044
C	0	-2.6184941693	-2.2801277008	-0.7306106907
C	0	-2.4519357110	-3.3386207429	-1.6290219842
C	0	-3.9122992244	-1.8775702286	-0.3686190994
C	0	-3.5657780459	-3.9953864477	-2.1626249552
H	0	-1.4432970682	-3.6544638963	-1.9105637969
C	0	-5.0226922430	-2.5323328590	-0.9014273241
H	0	-4.0375384739	-1.0484103915	0.3319293642
C	0	-4.8524923593	-3.5931076081	-1.7991239310
H	0	-3.4261836730	-4.8254036059	-2.8594253530
H	0	-6.0280813485	-2.2157311774	-0.6136461784
H	0	-5.7241590097	-4.1066871880	-2.2117265462

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O	0	1.3701849964	1.9717689975	-1.2762043802
C	0	2.1455541242	3.0518661656	-1.7953289898
O	0	2.9544477706	1.5578977767	0.2791808453
C	0	1.8611262025	1.3796675050	-0.1782658592
C	0	0.8719580291	0.3082438552	0.3232670784
C	0	0.7731320392	-0.8681644866	-0.7033565499
N	0	2.2319827568	-1.3377087891	1.0414173524
O	0	1.3555625649	-0.2947060827	1.5023764256
C	0	1.4583992778	-2.0498964099	0.0356711216
H	0	3.1673379478	2.7214785105	-2.0332853692
H	0	2.1958595515	3.8633619931	-1.0541378865

H	0	1.6299461464	3.3926017388	-2.7011518613
H	0	1.3042193277	-0.6294217421	-1.6306096966
H	0	0.6778072092	-2.6861549392	0.4969441254
N	0	-0.4544766849	0.8120858985	0.5807885008
C	0	-1.4721436369	-0.2404499288	0.4655610114
C	0	-0.6066884101	2.0959383845	1.0418625984
H	0	-1.3035868821	-0.9554313199	1.2881285025
S	0	-0.9794504395	-1.1124395010	-1.1011492873
C	0	-2.9776440154	0.1300505732	0.4672525319
H	0	-1.6551044778	2.3730645307	1.2446314278
O	0	0.3102366278	2.8728281379	1.2018081193
C	0	-3.3240621781	1.2059089597	-0.5758441555
C	0	-3.4291580593	0.5437017372	1.8837032205
C	0	-3.7554332847	-1.1581795937	0.1171749374
H	0	-2.9287237479	0.9301691835	-1.5643178607
H	0	-4.4174634851	1.3053594130	-0.6567035521
H	0	-2.9243910614	2.1969466346	-0.3221156873
H	0	-4.5183003866	0.7038473697	1.8901950993
H	0	-3.2030967726	-0.2510107381	2.6118544906
H	0	-2.9630952904	1.4683753861	2.2474106598
H	0	-3.4684825679	-1.9927469058	0.7759397697
H	0	-4.8346789237	-0.9829223211	0.2412880967
H	0	-3.5856177883	-1.4720515885	-0.9232761262
C	0	2.8375704104	-1.9780821181	2.1343795478
C	0	3.3475276150	-1.1822355505	3.1774999973
C	0	2.9858689274	-3.3728709620	2.1884947787
C	0	3.9931433100	-1.7820792763	4.2543316661
H	0	3.2295182631	-0.1007965421	3.1137273975
C	0	3.6544514540	-3.9573644937	3.2686397045
H	0	2.6005578644	-4.0037644496	1.3890159091
C	0	4.1558590951	-3.1725178458	4.3071756684
H	0	4.3831797363	-1.1551369385	5.0600555760
H	0	3.7722617077	-5.0435234025	3.2957180040
H	0	4.6704463835	-3.6366582360	5.1513723624
C	0	2.3188943905	-2.8768580615	-0.8894619767
C	0	1.8116111591	-4.0567176442	-1.4459072527
C	0	3.6017354256	-2.4405227074	-1.2485519016
C	0	2.5776378949	-4.7973915949	-2.3501533718
H	0	0.8100104534	-4.3953959077	-1.1681696260
C	0	4.3682063524	-3.1847324553	-2.1467934183
H	0	3.9916410607	-1.5214180086	-0.8061464274
C	0	3.8588821001	-4.3639451775	-2.7004984921
H	0	2.1735736836	-5.7177192959	-2.7786266620
H	0	5.3713286684	-2.8439226317	-2.4142386930
H	0	4.4614763749	-4.9454339947	-3.4022978634

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O	0	-0.3702222442	3.3872785409	0.0550243992
C	0	-1.1946230869	4.5467946942	0.0912984019
O	0	-2.0496732212	2.2478850902	-0.9219557156
C	0	-0.9416268249	2.2742943037	-0.4299343868
C	0	-0.0394571045	1.1017760535	-0.3598570223
C	0	-0.1776162964	0.0615146345	-1.3133815011
O	0	-1.2507225801	0.2237828679	1.2130096913
N	0	-1.8365876314	-0.6818943975	0.5141753363
C	0	-0.9930848764	-1.4752084682	-0.2208752157
H	0	-2.0646600146	4.3821556065	0.7450549671
H	0	-1.5591419576	4.8030799188	-0.9150251370
H	0	-0.5695120948	5.3536804879	0.4924603777
H	0	-0.9731271106	0.1666508870	-2.0538285449
H	0	-1.4971956358	-2.0689753294	-0.9848724531
N	0	1.2923098462	1.2094835913	0.1258527602

C	0	2.2658345230	0.9166552435	-0.9377796310
C	0	1.5694029513	1.6106823306	1.4198286438
H	0	2.2915183471	1.7879983183	-1.6160058524
S	0	1.4256486333	-0.4358160262	-1.9286694984
C	0	3.7351195559	0.5544118532	-0.6038022173
H	0	2.6549813646	1.6435626277	1.6254853527
O	0	0.7433930924	1.8909794162	2.2542169749
C	0	4.5182245614	1.8083696819	-0.1589628780
C	0	4.3840453467	0.0830134834	-1.9247538505
C	0	3.8459680412	-0.5783434142	0.4245940608
H	0	4.1974733155	2.2116764722	0.8098011049
H	0	5.5867202282	1.5590703781	-0.0684530371
H	0	4.4248844149	2.6139203643	-0.9046291568
H	0	5.4640899622	-0.0630776293	-1.7733231421
H	0	3.9652336996	-0.8752708525	-2.2661364399
H	0	4.2526782703	0.8247319450	-2.7287495555
H	0	3.2760702789	-1.4583193090	0.0983000602
H	0	4.9007423938	-0.8727198739	0.5413453502
H	0	3.4690465267	-0.2942662980	1.4155335725
C	0	0.1365670403	-2.1751571521	0.4287194084
C	0	0.7080426921	-3.2618365485	-0.2578399426
C	0	0.6418879352	-1.8398418800	1.6989653707
C	0	1.7410841152	-4.0071908841	0.3089496470
H	0	0.3297367142	-3.5296358547	-1.2476384611
C	0	1.6590754335	-2.6036628587	2.2717156606
H	0	0.2298370874	-0.9819577063	2.2269019596
C	0	2.2168344169	-3.6844441987	1.5828512710
H	0	2.1701925552	-4.8469680849	-0.2426599148
H	0	2.0297330055	-2.3392515537	3.2650274334
H	0	3.0222681350	-4.2691695484	2.0335297045
C	0	-3.2355675038	-0.5611462937	0.2497313596
C	0	-3.9209411651	0.5458576003	0.7691327836
C	0	-3.9374353543	-1.5600144203	-0.4402491384
C	0	-5.2914549441	0.6651065180	0.5640662690
H	0	-3.3555456114	1.2992378475	1.3122902126
C	0	-5.3121795896	-1.4233370208	-0.6459096644
H	0	-3.4323677967	-2.4568393181	-0.7984543449
C	0	-5.9956440283	-0.3120976709	-0.1497935440
H	0	-5.8172058222	1.5361029056	0.9620186876
H	0	-5.8509330377	-2.2036500996	-1.1883808598
H	0	-7.0714169516	-0.2112769711	-0.3087107159

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O	0	-0.0625065481	-3.0199405037	-0.6335831487
C	0	0.6365163038	-4.2602321933	-0.6650573560
O	0	1.4990610263	-2.1953934758	0.7669887415
C	0	0.5096923906	-2.0408454032	0.0832604346
C	0	-0.2367117456	-0.7657146661	0.0018013369
C	0	-0.1458467613	0.1580147207	1.0784709252
O	0	1.2481373720	0.0735193995	-1.2824854206
N	0	1.8824285328	0.7889870975	-0.4177703415
C	0	1.0862228757	1.6174882735	0.3339259483
H	0	1.6368533822	-4.1274368431	-1.1037574557
H	0	0.7518960963	-4.6719671176	0.3489284467
H	0	0.0356910559	-4.9325088896	-1.2889727397
H	0	0.4475415846	-0.1436138665	1.9438457004
H	0	1.5810912237	2.0152729611	1.2213134463
N	0	-1.4347405206	-0.6231180985	-0.7300799266
C	0	-2.5503281718	-0.0541906809	0.0259037348
C	0	-1.5298527715	-0.7810557701	-2.1051886292
H	0	-3.0658131813	0.6887874919	-0.6015010602
S	0	-1.7510364394	0.8657267634	1.4323347748

C	0	-3.5884461662	-1.1018654034	0.5217767400
H	0	-2.5096503847	-0.4005213447	-2.4768992700
O	0	-0.6898924211	-1.2505575168	-2.8283382943
C	0	-4.6683160909	-0.3593836375	1.3241238896
C	0	-2.9198835862	-2.1774505837	1.3884870797
C	0	-4.2425716658	-1.7739430686	-0.6977720364
H	0	-5.1539318647	0.4217459884	0.7159421156
H	0	-5.4488373325	-1.0623175227	1.6534042755
H	0	-4.2452207079	0.1166203909	2.2218284956
H	0	-3.6764163863	-2.8877907095	1.7568524019
H	0	-2.1786879644	-2.7446769525	0.8074899244
H	0	-2.4185007701	-1.7299021845	2.2590049581
H	0	-3.5170561374	-2.3662961393	-1.2745491066
H	0	-5.0356633591	-2.4604387637	-0.3629906207
H	0	-4.7048731286	-1.0347566796	-1.3722312369
C	0	0.1637162166	2.5785419977	-0.3091649103
C	0	-0.2596377540	3.6799481658	0.4551901280
C	0	-0.3292873100	2.4397388982	-1.6203466875
C	0	-1.1484574053	4.6190300849	-0.0660455734
H	0	0.1124099193	3.7982864936	1.4762847947
C	0	-1.2124115457	3.3862896497	-2.1411221156
H	0	-0.0089245795	1.5908161495	-2.2206088930
C	0	-1.6320308862	4.4739090167	-1.3686408029
H	0	-1.4646254791	5.4660206205	0.5473383158
H	0	-1.5782071119	3.2697095931	-3.1643628358
H	0	-2.3302336165	5.2061326415	-1.7812111587
C	0	3.2062560279	0.4039901215	-0.0463194423
C	0	3.7840114053	-0.6973141718	-0.6946292198
C	0	3.9560467509	1.1427769137	0.8798710650
C	0	5.0868477999	-1.0737037329	-0.3859690887
H	0	3.1877240283	-1.2423123995	-1.4232630896
C	0	5.2607739297	0.7487649210	1.1857235835
H	0	3.5464070129	2.0347599639	1.3532196689
C	0	5.8323982618	-0.3602210354	0.5602826232
H	0	5.5262786301	-1.9386147087	-0.8883901515
H	0	5.8354403043	1.3266750025	1.9132358516
H	0	6.8544896628	-0.6615902574	0.7992882111

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O	0	0.2654808146	3.5469674128	-0.6252435210
C	0	0.9365797026	4.6725858003	-1.1815568192
O	0	2.2392594435	2.4790406687	-0.4485265164
C	0	1.0330490025	2.4755294208	-0.3642176315
C	0	0.2317418401	1.3175915718	0.1033243934
C	0	0.7187520219	0.4828762893	1.1330615428
N	0	0.7680272666	-1.0789156508	-0.9431983506
O	0	0.8980691406	0.0287457218	-1.5708170173
C	0	1.4830385175	-1.1916032008	0.2186441348
H	0	1.7271700630	5.0334011087	-0.5063556791
H	0	1.3938650951	4.4079269503	-2.1468360364
H	0	0.1711192274	5.4448297077	-1.3251417221
H	0	1.6319465867	0.7782305702	1.6515987501
H	0	1.1431822842	-2.0039392008	0.8622356190
N	0	-1.1842575192	1.3127559065	0.0111163225
C	0	-1.8339150090	1.0455935035	1.3098416591
C	0	-1.8325909267	1.6230597641	-1.1676559173
H	0	-1.8037142263	1.9767284979	1.9032816862
S	0	-0.6406014492	-0.1231632471	2.1385412581
C	0	-3.2880177830	0.5006047003	1.3621337376
H	0	-2.9299082951	1.6582335387	-1.0532475141
O	0	-1.2855094922	1.8228634472	-2.2274297730
C	0	-4.3092838652	1.6287366944	1.1004788449

C	0	-3.5372474732	0.0256250239	2.8116403155
C	0	-3.5025601202	-0.6847344116	0.4109447911
H	0	-4.2905097081	2.0194579462	0.0751508382
H	0	-5.3267466550	1.2491647768	1.2811480869
H	0	-4.1422341860	2.4756748764	1.7848688662
H	0	-4.5980073675	-0.2393463705	2.9352561472
H	0	-2.9424468068	-0.8663392287	3.0575345062
H	0	-3.2981551340	0.8135379828	3.5435783308
H	0	-4.4948088400	-1.1284647718	0.5865068591
H	0	-3.4531285134	-0.3987156470	-0.6471755292
H	0	-2.7447836003	-1.4633042128	0.5753259623
C	0	2.9447928014	-0.9718891231	0.2679566275
C	0	3.6419399855	-1.5646989456	1.3380758846
C	0	3.6630359905	-0.2151341922	-0.6743445456
C	0	5.0227860591	-1.4182623812	1.4620722497
H	0	3.0922116039	-2.1554957314	2.0765702822
C	0	5.0467185716	-0.0859222641	-0.5535431503
H	0	3.1253268744	0.2799123359	-1.4781217463
C	0	5.7318226331	-0.6788390293	0.5108702197
H	0	5.5466686142	-1.8879638611	2.2979939957
H	0	5.5934844901	0.5022982371	-1.2942205628
H	0	6.8143247460	-0.5613740518	0.6023404029
C	0	-0.3673032837	-1.8935034224	-1.2573965231
C	0	-1.1897565705	-1.4764879634	-2.3145159661
C	0	-0.6316239263	-3.1012605283	-0.5951420591
C	0	-2.2920173210	-2.2492443741	-2.6739456454
H	0	-0.9549466084	-0.5404048929	-2.8180051439
C	0	-1.7444463604	-3.8591395986	-0.9614939323
H	0	0.0186311629	-3.4621958789	0.2005059986
C	0	-2.5820570310	-3.4390790008	-1.9984062193
H	0	-2.9330983167	-1.9139125065	-3.4927151693
H	0	-1.9501148746	-4.7933707355	-0.4339441120
H	0	-3.4476322759	-4.0405050307	-2.2842225101

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O	0	0.7890079395	-2.6115792692	1.8882064340
C	0	0.4307736840	-3.6528195522	2.7910112952
O	0	-1.3594624968	-2.4696274092	1.2252772498
C	0	-0.2247049059	-2.0513263477	1.2027080461
C	0	0.2298251125	-0.9098598178	0.3810412934
C	0	-0.3652049523	-0.6231003818	-0.8697583236
N	0	-1.1504811165	1.3735392720	0.5767178896
O	0	-1.0035959558	0.5572068092	1.5524759170
C	0	-1.7243129152	0.8478213383	-0.5506410644
H	0	-0.0513943956	-4.4865700338	2.2587154235
H	0	-0.2649676878	-3.2749100441	3.5549503477
H	0	1.3647904651	-3.9841729078	3.2603829229
H	0	-1.0477274808	-1.3584658679	-1.2990774728
H	0	-1.6086837908	1.4788750398	-1.4321258739
N	0	1.5321044040	-0.3760617866	0.4976004191
C	0	2.2223798419	-0.1657637752	-0.7741563493
C	0	2.0879696395	0.0800142505	1.6788837602
H	0	2.7982727761	0.7698693004	-0.7159851134
S	0	0.8469296777	0.1125509625	-1.9863394703
C	0	3.1832800889	-1.3174604942	-1.1851847183
H	0	3.0623904945	0.5859472664	1.4920447352
O	0	1.5954058627	-0.0153653784	2.7752027308
C	0	2.4402699045	-2.6544682464	-1.3119317718
C	0	4.2799737416	-1.4530554408	-0.1145146699
C	0	3.8296894547	-0.9383233364	-2.5264299757
H	0	1.6296582716	-2.5901361079	-2.0523572601
H	0	3.1387611350	-3.4400963282	-1.6400911297

H	0	2.0155010450	-2.9642711745	-0.3467710032
H	0	5.0142596516	-2.2112735507	-0.4277897078
H	0	4.8237266600	-0.5060629798	0.0358591264
H	0	3.8642964612	-1.7749445315	0.8516728443
H	0	4.3735141135	0.0182448011	-2.4539175798
H	0	4.5503279387	-1.7114015434	-2.8341814603
H	0	3.0741248137	-0.8451417628	-3.3212413919
C	0	-3.0230919614	0.1377406399	-0.5125529683
C	0	-3.7395098588	0.0621718167	-1.7221698075
C	0	-3.5692986046	-0.4567067573	0.6378469245
C	0	-4.9750952334	-0.5804013688	-1.7843129547
H	0	-3.3238266982	0.5224217825	-2.6233402183
C	0	-4.8139287695	-1.0833795760	0.5733571962
H	0	-3.0035987628	-0.4355965850	1.5649743437
C	0	-5.5190667765	-1.1538598124	-0.6312961926
H	0	-5.5172252727	-0.6265575023	-2.7318008235
H	0	-5.2289201614	-1.5382630384	1.4757858706
H	0	-6.4876962759	-1.6577775605	-0.6733681513
C	0	-0.3491995056	2.5626294745	0.5755068929
C	0	-0.3276617598	3.4596360483	-0.5027446752
C	0	0.3897896098	2.8423943102	1.7352679078
C	0	0.4648764324	4.6055736781	-0.4312214518
H	0	-0.9161076762	3.2793884922	-1.4007802315
C	0	1.1748144298	3.9923111669	1.7920475788
H	0	0.3466567351	2.1375766901	2.5629910452
C	0	1.2231728612	4.8780665467	0.7106729374
H	0	0.4830902113	5.2937969100	-1.2794176006
H	0	1.7530754126	4.1978823032	2.6960014151
H	0	1.8379991448	5.7792943693	0.7608888645

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O	0	2.3232098000	2.6222493692	-1.4055610272
C	0	2.8301468439	3.7549136677	-2.1157052232
O	0	0.2522682171	3.5151203007	-1.4419960354
C	0	1.0191341993	2.6654564084	-1.0879353008
C	0	0.6149177497	1.3748692773	-0.3469423770
C	0	0.2303239247	0.2964409124	-1.3858315239
O	0	-0.5500308020	1.6365930835	0.3713917473
N	0	-1.4384560120	0.4994618665	0.1588058191
C	0	-2.7445678915	0.9234013650	0.6266405201
C	0	-1.2914182152	0.2635626643	-1.2782335644
H	0	2.7458223989	4.6579717838	-1.4937656046
H	0	2.2681989077	3.9120576026	-3.0479694963
H	0	3.8823642516	3.5352828176	-2.3311631282
H	0	0.6123811424	0.4861896723	-2.3952103309
H	0	-1.6573832321	1.1505588956	-1.8400324101
C	0	-1.9785568249	-0.9885023027	-1.8081717230
H	0	-1.6799686045	-1.1485556170	-2.8555834721
H	0	-1.7070180400	-1.8721562171	-1.2199222842
H	0	-3.0694268822	-0.8702642379	-1.7777976259
H	0	-2.5670347275	1.4258289660	1.5908824438
H	0	-3.2034867694	1.6755694224	-0.0473047047
N	0	1.7045063722	0.8673351112	0.5068535423
C	0	2.4301462056	-0.3035751692	0.0358544016
C	0	2.1760798875	1.7824173562	1.4243272393
H	0	3.1092761829	-0.0325087569	-0.7927994506
S	0	1.0988244863	-1.2373875806	-0.8667247450
C	0	3.2071264963	-1.1886623159	1.0530572195
H	0	2.9963801922	1.4048018450	2.0602985864
O	0	1.7268504048	2.9015437277	1.5277369916
O	0	0.2978821000	-2.0327348774	0.0760376845
O	0	1.6615768514	-1.8674263974	-2.0676437295

C	0	4.5947954619	-0.5662914706	1.3196004591
C	0	3.4644220953	-2.5694576046	0.4071353443
C	0	2.4242950923	-1.3812439638	2.3614604403
H	0	4.5549607718	0.4142309138	1.8119405528
H	0	5.1721797781	-1.2352575466	1.9758410024
H	0	5.1590228645	-0.4494851606	0.3808661932
H	0	4.1475182400	-3.1418125653	1.0519655020
H	0	2.5396491520	-3.1503979646	0.2980533789
H	0	3.9290997268	-2.4755695775	-0.5856012224
H	0	1.4228906461	-1.7818790075	2.1593084921
H	0	2.9632708772	-2.0930034139	3.0054495198
H	0	2.3108355778	-0.4464200171	2.9276820838
C	0	-3.6670970948	-0.2590235110	0.8270889241
C	0	-5.0319287141	-0.1480284608	0.5343441750
C	0	-3.1732693094	-1.4722155520	1.3298473512
C	0	-5.8958683137	-1.2261418938	0.7480217620
H	0	-5.4224889987	0.7905558345	0.1311190380
C	0	-4.0351146728	-2.5504857756	1.5368449348
H	0	-2.1037746592	-1.5683003153	1.5244888179
C	0	-5.3988552273	-2.4314706756	1.2494391815
H	0	-6.9586909996	-1.1251362124	0.5147811770
H	0	-3.6378189589	-3.4932343806	1.9211556885
H	0	-6.0708859384	-3.2778363120	1.4108287449

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O	0	-2.4312892741	2.2783872915	-1.4087533315
C	0	-2.9863258172	3.3115954535	-2.2222946226
O	0	-0.5657456867	3.5047392768	-1.0802936901
C	0	-1.2490595972	2.5478655293	-0.8471369322
C	0	-0.7892298962	1.3480179678	0.0013266188
C	0	-0.1977694647	0.2539714892	-0.9353607809
O	0	0.2793320316	1.7600350286	0.8039561996
N	0	1.1697152763	0.6057664948	0.8891603644
C	0	2.3720134030	1.1072725692	1.5228927599
C	0	1.2801838622	0.2410759452	-0.5263817789
H	0	-3.2074748176	4.1954735390	-1.6056671592
H	0	-2.2859430578	3.5997654575	-3.0199173425
H	0	-3.9090797059	2.9010909640	-2.6485653739
H	0	-0.3578433339	0.4592148107	-1.9998056690
H	0	1.7348528910	1.0871104006	-1.0825604293
C	0	2.0896983806	-1.0304756884	-0.7993158668
H	0	1.8103692786	-1.3888729055	-1.8036698992
H	0	1.7738138732	-1.8163002187	-0.1048611320
H	0	2.8559160755	1.9084200281	0.9329566163
H	0	3.0751346244	0.2747293229	1.6457831125
H	0	2.1028995982	1.4983338904	2.5133628686
N	0	-1.8821973550	0.7839145744	0.8042333598
C	0	-1.8615654044	-0.6550618633	1.0118587561
C	0	-2.6213287668	1.6978136326	1.5202671618
H	0	-1.0366682162	-0.9435479086	1.6857340478
S	0	-1.2176812087	-1.2418769036	-0.6305363956
C	0	-3.1698017324	-1.3837078540	1.4365934922
H	0	-3.3301240647	1.2453136727	2.2348661620
O	0	-2.5130588301	2.8962492557	1.3805901391
O	0	-2.2794487932	-1.2157277666	-1.6470066295
O	0	-0.4146605628	-2.4574596130	-0.4433154689
C	0	-3.0276293184	-2.8875020888	1.1084640452
C	0	-4.4052525670	-0.8343506253	0.7018441701
C	0	-3.3333994469	-1.2826183532	2.9681464547
H	0	-2.0959540667	-3.3091049947	1.5130609047
H	0	-3.8734247172	-3.4292936199	1.5569936152
H	0	-3.0447077786	-3.0745918045	0.0267968647

H	0	-5.2681421617	-1.4847944249	0.9115407397
H	0	-4.6784261372	0.1801946242	1.0220699143
H	0	-4.2351309506	-0.8170823537	-0.3822415425
H	0	-3.4440738308	-0.2538316508	3.3362938883
H	0	-4.2330414378	-1.8374758141	3.2756860597
H	0	-2.4696860429	-1.7312359271	3.4836328679
C	0	3.5885538213	-0.8365781408	-0.7354997065
C	0	4.2398793748	0.0958744203	-1.5571835764
C	0	4.3639764271	-1.6011330025	0.1474652496
C	0	5.6235470690	0.2695349655	-1.4882877179
H	0	3.6597145363	0.6956109824	-2.2638891257
C	0	5.7495727929	-1.4328507942	0.2190659446
H	0	3.8714636224	-2.3367453594	0.7891401176
C	0	6.3839045385	-0.4930449986	-0.5966431509
H	0	6.1111319992	1.0021124763	-2.1360440386
H	0	6.3346225764	-2.0380010782	0.9158748418
H	0	7.4665020189	-0.3572082706	-0.5414219765

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O	0	-2.0702491825	2.4547758237	-0.9602258497
C	0	-2.7093099751	3.6668442762	-1.3732931657
O	0	-0.4750302582	3.6461174163	0.0949957627
C	0	-0.9331440055	2.5987894097	-0.2640244605
C	0	-0.3685826226	1.2213665400	0.1388509692
C	0	-0.8734223510	0.8210530066	1.5423163402
N	0	1.4925380646	0.5948474246	1.3785110850
O	0	1.0228943697	1.3697589192	0.2724588141
C	0	1.8622563723	-0.7568394769	0.9409941176
C	0	0.4271772723	0.7267219053	2.3715243636
H	0	-2.9308746830	4.3024527726	-0.5037827446
H	0	-2.0557284732	4.2210286737	-2.0622275516
H	0	-3.6341277015	3.3668077962	-1.8792939446
H	0	-1.6087059140	1.5188154763	1.9578586077
H	0	0.4146168488	-0.1706160792	3.0055708067
C	0	0.6288702855	1.9919745120	3.2033642515
H	0	-0.1828935070	2.1114633435	3.9379409431
H	0	0.6496997354	2.8737580268	2.5461631981
H	0	1.5876984373	1.9334128384	3.7365307476
H	0	1.9689870230	-1.3491691500	1.8597750172
H	0	1.0603697563	-1.2323830903	0.3552490495
N	0	-0.7439719885	0.1637647065	-0.8286465477
C	0	-1.9108264760	-0.6432484686	-0.4895626953
C	0	-0.3048669800	0.3844148501	-2.1193432170
H	0	-2.8319987680	-0.0455199065	-0.6028982804
S	0	-1.7902925487	-0.7484060746	1.3638641822
C	0	-2.1246330710	-2.0280921337	-1.1661264173
H	0	-0.6019541759	-0.4026398327	-2.8345280795
O	0	0.3629901593	1.3420189905	-2.4385295395
O	0	-0.9288983084	-1.8636688499	1.7951866712
O	0	-3.1333003393	-0.5915481913	1.9330941028
C	0	-2.7668558326	-1.8324470064	-2.5574472398
C	0	-3.1489739830	-2.8240550038	-0.3246229480
C	0	-0.8182687922	-2.8297570534	-1.2684655471
H	0	-2.1043095331	-1.3576276470	-3.2923543187
H	0	-3.0473953772	-2.8148792814	-2.9663575236
H	0	-3.6835583204	-1.2261743191	-2.4858715930
H	0	-3.4156148244	-3.7439914904	-0.8653031869
H	0	-2.7425789431	-3.1161042618	0.6520203904
H	0	-4.0708478506	-2.2479708638	-0.1551380913
H	0	-1.0245971540	-3.8045570305	-1.7359310232
H	0	-0.0580233408	-2.3238677302	-1.8803027874
H	0	-0.3926088496	-3.0092793998	-0.2729529466

C	0	3.1615410822	-0.7938868390	0.1676106501
C	0	3.3222215173	-0.0910176966	-1.0381221600
C	0	4.2260053184	-1.5752515819	0.6374329988
C	0	4.5225363655	-0.1721883871	-1.7470657604
H	0	2.5151465864	0.5375839634	-1.4144393394
C	0	5.4254607008	-1.6611774394	-0.0748778689
H	0	4.1147445720	-2.1258541896	1.5759457709
C	0	5.5769756267	-0.9578863967	-1.2715815426
H	0	4.6335475507	0.3856163233	-2.6803100028
H	0	6.2432602337	-2.2760113963	0.3093164810
H	0	6.5136382819	-1.0196417070	-1.8311859379

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O	0	2.9555942228	2.0421011342	0.5745119312
C	0	3.9091491898	3.0256393665	0.9830022652
O	0	1.3139874542	3.5771019287	0.6829155883
C	0	1.7003271461	2.4724520308	0.4200841722
C	0	0.7651573335	1.3157110583	0.0086535521
C	0	0.1664406613	0.6376014204	1.2512636530
N	0	-1.5547941315	1.2975651533	-0.2425489574
O	0	-0.3368714991	1.9089002210	-0.6569465480
C	0	-1.9075926543	0.1887984715	-1.1350864680
C	0	-1.3384220432	0.9689446461	1.1650686750
H	0	3.5961513876	3.5021413107	1.9233477073
H	0	4.0080163356	3.7991379828	0.2075635512
H	0	4.8574112519	2.4920612023	1.1162492522
H	0	0.6313037281	0.9582662597	2.1895820541
H	0	-1.9443924100	0.0890945105	1.4229125445
C	0	-1.6897691188	2.1571506519	2.0568704593
H	0	-1.4934767351	1.9236092292	3.1149346524
H	0	-1.0961891722	3.0364851768	1.7670469614
H	0	-2.7550587164	2.3980575626	1.9379974296
H	0	-1.8197719068	0.5937742008	-2.1543139867
H	0	-1.2327961234	-0.6798154385	-1.0547394711
N	0	1.4508098987	0.3196387189	-0.8305781582
C	0	1.4447782654	-1.0980779579	-0.4963527298
C	0	1.9123748128	0.8100089837	-2.0360785360
H	0	0.7330322583	-1.6543041935	-1.1290394710
S	0	0.5792461992	-1.1412044524	1.1702193297
C	0	2.7980157394	-1.8725907650	-0.4879162612
H	0	2.1637729888	0.0215220871	-2.7710951227
O	0	2.0135914364	1.9909971262	-2.2752202306
O	0	1.4958955396	-1.3989961073	2.2901592054
O	0	-0.6223088774	-1.9752881662	1.0165636528
C	0	3.8712316889	-1.1501958171	0.3393691404
C	0	3.3200072301	-2.0479724948	-1.9300027375
C	0	2.5191672305	-3.2881437188	0.0626353361
H	0	3.5767365369	-1.0592921302	1.3911699398
H	0	4.8136406462	-1.7171238458	0.2881523250
H	0	4.0525561896	-0.1408788839	-0.0549900456
H	0	4.1330329554	-2.7896921475	-1.9235282472
H	0	2.5379272463	-2.4192386742	-2.6121848515
H	0	3.7408629963	-1.1222734800	-2.3445518983
H	0	1.7378217709	-3.7963121314	-0.5255583222
H	0	3.4356798536	-3.8923767439	-0.0084347621
H	0	2.2102607646	-3.2733994315	1.1146699480
C	0	-3.3235734928	-0.2566515598	-0.8582076688
C	0	-3.5939355208	-1.5567546960	-0.4138506754
C	0	-4.3852475284	0.6468603849	-1.0194288924
C	0	-4.9093547766	-1.9559118053	-0.1545274297
H	0	-2.7653908436	-2.2484314535	-0.2491786458
C	0	-5.6966473347	0.2498140003	-0.7579982554

H	0	-4.1703452671	1.6678511363	-1.3434020208
C	0	-5.9622438579	-1.0554078764	-0.3276286272
H	0	-5.1086419842	-2.9729809867	0.1916672235
H	0	-6.5170017836	0.9596321543	-0.8901338692
H	0	-6.9897301708	-1.3662931624	-0.1232146596

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O	0	-1.5528834151	2.4185152021	-0.5676171367
C	0	-2.5156133722	3.3917196115	-0.9680689535
O	0	-2.9553109123	0.7863886224	-1.2135208506
C	0	-1.9232237564	1.1385191313	-0.6855579677
C	0	-0.8690776261	0.2108291171	-0.1831369186
C	0	-0.5778596440	-0.9687599498	-0.8949330173
O	0	-2.1237985073	-0.6539229823	1.3124982161
N	0	-2.3148027218	-1.7930224909	0.7649579627
C	0	-3.5878665860	-1.9653603385	0.0188213923
C	0	-1.2074635556	-2.5031062911	0.4630039578
H	0	-3.4293893426	3.2953097357	-0.3634102545
H	0	-2.7786368707	3.2676193220	-2.0290383880
H	0	-2.0484706712	4.3689334714	-0.7981938111
H	0	-1.1488904244	-1.2175357129	-1.7910315019
H	0	-1.3936504388	-3.3916336994	-0.1459127452
C	0	-0.1286079609	-2.5996089943	1.5022899720
H	0	0.7725583986	-3.0506533872	1.0796120814
H	0	0.1142527479	-1.6192151266	1.9259761806
H	0	-0.5057568532	-3.2400945942	2.3186134966
H	0	-4.3473160926	-1.5157123348	0.6732879706
H	0	-3.5307484511	-1.3399254111	-0.8836542981
N	0	0.2670247559	0.7376256837	0.5085902152
C	0	1.5060014907	0.5883355844	-0.2593737984
C	0	0.0949788522	1.5061564679	1.6504742133
H	0	1.4884749346	1.2972205490	-1.1049252800
S	0	1.1882321593	-1.0151471173	-1.2065722177
C	0	2.8986424356	0.6569233737	0.4096809757
H	0	1.0548596125	1.8602569598	2.0691401878
O	0	-0.9707740795	1.7619395789	2.1516471501
O	0	1.8549249080	-2.1923591458	-0.6219590365
O	0	1.4091730401	-0.7282416939	-2.6306736448
C	0	3.2610285636	2.1256815192	0.7233591864
C	0	3.9348048921	0.1688794097	-0.6308433412
C	0	2.9860451882	-0.2174447139	1.6695804387
H	0	2.6496327215	2.5767819308	1.5152149066
H	0	4.3090311935	2.1750203352	1.0563236107
H	0	3.1659862618	2.7537109828	-0.1764209192
H	0	4.9474960018	0.3416861014	-0.2375253023
H	0	3.8324947915	-0.9023735692	-0.8427627348
H	0	3.8401747032	0.7195749300	-1.5793369496
H	0	2.7515444761	-1.2625520811	1.4315670740
H	0	4.0088985512	-0.1775379153	2.0746661392
H	0	2.3033574821	0.1197942678	2.4625725827
C	0	-3.8911004830	-3.4025943247	-0.2991787534
C	0	-3.8236126997	-3.8680668705	-1.6188946220
C	0	-4.2210105207	-4.3055318531	0.7235651455
C	0	-4.0806251143	-5.2100202314	-1.9148624878
H	0	-3.5684438655	-3.1704765186	-2.4210404673
C	0	-4.4744678701	-5.6460520926	0.4317317863
H	0	-4.2760738609	-3.9505669937	1.7562604557
C	0	-4.4044599107	-6.1013137308	-0.8895481560
H	0	-4.0267150039	-5.5589747171	-2.9486827050
H	0	-4.7312819588	-6.3393621911	1.2361681655
H	0	-4.6044634628	-7.1507217449	-1.1183188642

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O	0	0.7102876557	2.6077168670	-0.1329257108
C	0	1.2885470633	3.8492741088	-0.5303938197
O	0	2.1430043088	1.5219570521	-1.4842438340
C	0	1.2694480083	1.5056983103	-0.6430149276
C	0	0.6562493859	0.2640845431	-0.1071796972
C	0	0.6693867029	-0.9318446494	-0.8575900387
O	0	2.4771664447	-0.1569516250	1.0153569826
N	0	2.8911597341	-1.1383766014	0.3085546263
C	0	3.9525439407	-0.8804307136	-0.6671732503
C	0	1.9999508035	-2.1471311510	0.1408464007
H	0	2.3495275828	3.8857001540	-0.2428377243
H	0	1.2124760354	3.9842909247	-1.6195351070
H	0	0.7242771322	4.6281415205	-0.0044537061
H	0	1.0726096842	-0.9163860727	-1.8722872528
H	0	2.3248433313	-2.9181372246	-0.5658585465
C	0	1.2807384612	-2.6489867703	1.3827342207
H	0	0.5438615050	-3.3952107161	1.0722620083
H	0	0.7425681418	-1.8212896393	1.8575183862
H	0	3.5478913617	-0.3163784562	-1.5204088717
H	0	4.3916647463	-1.8335868477	-0.9877439005
H	0	4.7108575219	-0.2656580293	-0.1668564286
N	0	-0.3979858056	0.3088013233	0.8494768580
C	0	-1.6040913509	-0.4398792430	0.5015307169
C	0	-0.2268612346	0.8116042782	2.1347762515
H	0	-1.8852941687	-1.1243324718	1.3159716342
S	0	-0.9950607541	-1.6158739874	-0.8382343891
C	0	-2.8325884530	0.4136386909	0.0899651654
H	0	-1.0875446659	0.5385550403	2.7866538946
O	0	0.7173678476	1.4474432401	2.5225995610
O	0	-1.5678229741	-1.3235033595	-2.1616681341
O	0	-1.1027483176	-2.9914842510	-0.3343127908
C	0	-3.9704293324	-0.5410615653	-0.3166825808
C	0	-2.4882290286	1.3955835152	-1.0417047096
C	0	-3.2928587503	1.2254259714	1.3158316241
H	0	-4.2085899536	-1.2438235949	0.4987310828
H	0	-4.8804308912	0.0390403073	-0.5328707825
H	0	-3.7160206836	-1.1197176212	-1.2137950929
H	0	-3.3703277718	2.0137405919	-1.2697857928
H	0	-1.6748534155	2.0685539973	-0.7340480537
H	0	-2.1901528358	0.8698781832	-1.9564117345
H	0	-2.5527958426	1.9828151616	1.6124039990
H	0	-4.2226632653	1.7586259598	1.0650893621
H	0	-3.5028637283	0.5788887580	2.1833099465
C	0	2.2737281071	-3.2388610561	2.3613433065
C	0	2.5957127222	-4.6024174966	2.3160174053
C	0	2.9128940287	-2.4208169805	3.3069988182
C	0	3.5371692110	-5.1427291010	3.1961605915
H	0	2.0970631903	-5.2488283441	1.5880402161
C	0	3.8520540104	-2.9608238712	4.1878215865
H	0	2.6715152078	-1.3561561370	3.3405586038
C	0	4.1683673509	-4.3220635768	4.1344686981
H	0	3.7737238058	-6.2087586582	3.1524507290
H	0	4.3386349936	-2.3146800432	4.9226914560
H	0	4.9018720166	-4.7430161837	4.8264096847

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O	0	-1.9328993260	2.4010231849	-0.4950152182
C	0	-3.0432116676	3.2637678168	-0.7350664571
O	0	-3.1959895702	0.6276555450	-1.0679707843

C	0	-2.1634229952	1.0910223555	-0.6408355793
C	0	-0.9838486391	0.2626419492	-0.2729262809
C	0	-0.7025029406	-0.9033123412	-1.0133137488
N	0	-1.3774647736	-1.8285142624	1.2834943759
O	0	-2.0006779104	-0.7205251415	1.3470292004
C	0	-0.2826170920	-2.0314730688	2.2629599517
C	0	-1.4322247460	-2.4852761886	0.0996422186
H	0	-3.4083130689	3.1531001485	-1.7670079759
H	0	-3.8653472929	3.0290340875	-0.0430164139
H	0	-2.6794475675	4.2834452996	-0.5618982860
H	0	-1.2193865248	-1.0941861826	-1.9539810590
H	0	-0.7213934092	-3.3134413311	0.0257183902
C	0	-2.7672683783	-2.6479748849	-0.5764334405
H	0	-2.6284315824	-3.0189152281	-1.6020896383
H	0	-3.3157232199	-1.6986627691	-0.6075324896
H	0	-3.3619743965	-3.3944342910	-0.0228349791
H	0	0.2472572879	-2.9495567298	1.9876430309
H	0	0.4128662069	-1.1930001849	2.1420806752
N	0	0.1723335912	0.8574106865	0.3312784507
C	0	1.3965383166	0.6233868825	-0.4429790300
C	0	0.0710462016	1.6417686581	1.4670121004
H	0	1.3506070880	1.2135658304	-1.3744825935
S	0	1.0754940493	-1.0961313782	-1.1241809897
C	0	2.8049093614	0.7929642736	0.1790602216
H	0	1.0296975656	2.1179173037	1.7387766225
O	0	-0.9385375553	1.7995641379	2.1106399225
O	0	1.5554785551	-2.1385445246	-0.1937728620
O	0	1.4846624119	-1.1479027908	-2.5328701177
C	0	3.1596973667	2.2939922115	0.2544733448
C	0	3.8197109091	0.1475866603	-0.7938551819
C	0	2.9464369979	0.1170750435	1.5535929823
H	0	2.5270515825	2.8663324518	0.9457123131
H	0	4.1997577461	2.4045008179	0.5975224803
H	0	3.0825089572	2.7638611729	-0.7385828152
H	0	4.8394117210	0.3809875468	-0.4536553153
H	0	3.7177990214	-0.9448974177	-0.8273130652
H	0	3.7037397879	0.5330823288	-1.8177660603
H	0	3.9862226706	0.2187184739	1.9001351283
H	0	2.3036449260	0.5661536184	2.3233344582
H	0	2.7120347983	-0.9523205873	1.4837472233
C	0	-0.8164423873	-2.0927599143	3.6717639093
C	0	-1.2897641946	-0.9301064271	4.3001199324
C	0	-0.8595033399	-3.3120327727	4.3595084405
C	0	-1.7973781840	-0.9971262585	5.5988727683
H	0	-1.2725105813	0.0198810001	3.7622061941
C	0	-1.3634892618	-3.3759021099	5.6614277440
H	0	-0.4916505832	-4.2199612613	3.8731318710
C	0	-1.8346039761	-2.2168700387	6.2825964072
H	0	-2.1661297724	-0.0886932491	6.0812947121
H	0	-1.3882739300	-4.3320059082	6.1898550029
H	0	-2.2299098932	-2.2632071726	7.3003605491

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O	0	0.0182539995	2.8497857098	-0.4323968530
C	0	0.2495038162	4.1545255582	-0.9604259576
O	0	1.6747541492	2.0410396886	-1.7268657526
C	0	0.8452709673	1.8854522850	-0.8596999816
C	0	0.5999606863	0.5912761247	-0.1788170108
C	0	0.8375911696	-0.6267150640	-0.8464662860
N	0	2.7275591487	-0.5622713254	0.9097287475
O	0	2.5186939755	0.6905673429	0.8307071195
C	0	2.4626078778	-1.2077285536	2.2245654855

C	0	2.7190576072	-1.2591609107	-0.2526900702
H	0	0.1323879836	4.1592575677	-2.0543739219
H	0	1.2666742606	4.4915663697	-0.7127694779
H	0	-0.4938124490	4.8086565923	-0.4899659781
H	0	0.9818946425	-0.6473357891	-1.9269260154
H	0	2.7008750523	-2.3430180204	-0.1063629417
C	0	3.5135079477	-0.7345585892	-1.4188212426
H	0	3.2539587574	-1.2879586962	-2.3326696616
H	0	3.3287314114	0.3342868559	-1.5805905512
H	0	4.5867461010	-0.8956828374	-1.2201088750
H	0	2.6082480969	-0.3952897023	2.9468586389
H	0	1.4156404347	-1.5329401905	2.2448338744
N	0	-0.3511284445	0.4700573851	0.8788208900
C	0	-1.3542909387	-0.5707615924	0.6909093232
C	0	-0.2866701278	1.1777234365	2.0716175064
H	0	-1.5630819761	-1.0732959355	1.6459937787
S	0	-0.3608717622	-1.8373372252	-0.2663016450
C	0	-2.6841275608	-0.1195031644	0.0362980793
H	0	-1.0611394348	0.8158106082	2.7877482951
O	0	0.4925933523	2.0564683323	2.3288250917
O	0	-1.0638878044	-2.4128425421	-1.4218870232
O	0	0.2172288932	-2.7541159662	0.7359466458
C	0	-2.4798018295	0.4463726906	-1.3788642931
C	0	-3.2910318935	0.9842034165	0.9220852576
C	0	-3.6373418625	-1.3274037916	0.0106101170
H	0	-2.0515522090	-0.3012829780	-2.0585569244
H	0	-3.4534374608	0.7576573915	-1.7880123013
H	0	-1.8330332014	1.3344197619	-1.3575694534
H	0	-4.2768842266	1.2692390381	0.5237961709
H	0	-3.4379709852	0.6428591352	1.9594997077
H	0	-2.6615414927	1.8859212712	0.9337582068
H	0	-3.8144417544	-1.7114013548	1.0289308836
H	0	-4.6106445086	-1.0257783507	-0.4055621982
H	0	-3.2378436835	-2.1429648494	-0.6061068930
C	0	3.3837532666	-2.3708996527	2.4815255852
C	0	2.9234275527	-3.6887767613	2.3542876564
C	0	4.7257256139	-2.1435652710	2.8224944630
C	0	3.7921782293	-4.7624929236	2.5718035332
H	0	1.8841161260	-3.8631485651	2.0683559283
C	0	5.5932199372	-3.2153672079	3.0364388333
H	0	5.0896975862	-1.1170589959	2.9205889445
C	0	5.1265305126	-4.5285169153	2.9125465466
H	0	3.4236260822	-5.7862596783	2.4722092914
H	0	6.6357144578	-3.0275175974	3.3044760234
H	0	5.8046527607	-5.3682958944	3.0825823739

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O	0	2.2621479735	2.4880383836	-0.3909850771
C	0	2.6271192962	3.8669721667	-0.4947556858
O	0	0.3048251662	3.0648165452	0.5683505719
C	0	1.1079913711	2.2346249794	0.2394671135
C	0	0.8472125130	0.7138114531	0.3145687094
C	0	0.2892369810	0.2515387482	-1.0286301242
O	0	-0.1652285102	0.4277396419	1.2411009915
N	0	-1.4402144615	0.2292142787	0.5573264584
C	0	-2.3926672235	1.1482363803	1.1886787568
C	0	-1.2070462155	0.4989921975	-0.8667239523
H	0	2.7892219527	4.2863627109	0.5089772359
H	0	1.8367314744	4.4419070383	-0.9987483472
H	0	3.5564191579	3.8949906482	-1.0756945960
H	0	0.7311669893	0.7476719973	-1.9000276478

H	0	-1.3430682871	1.5786665916	-1.0823212993
H	0	-2.3302092607	0.9578051302	2.2692101767
H	0	-2.1011974793	2.1992203614	1.0103739509
N	0	2.0604854674	-0.0356837474	0.6288619318
C	0	2.4280903437	-1.1523774345	-0.2387188610
C	0	2.8230773533	0.4632674622	1.6573776377
H	0	3.0888811251	-0.8117990214	-1.0551460280
S	0	0.8357000672	-1.4925686282	-1.1585255127
C	0	3.0310492249	-2.4410542637	0.3992092760
H	0	3.7520621884	-0.1041350079	1.8441650683
O	0	2.5167409524	1.4493507887	2.2912375816
O	0	-0.0282407972	-2.3697367529	-0.3609666245
O	0	1.1438406020	-1.8029778356	-2.5569840830
C	0	4.5497395573	-2.2596256145	0.6112149188
C	0	2.8719854497	-3.6099782667	-0.6008660468
C	0	2.3324150737	-2.7896703198	1.7221012125
H	0	4.8053751866	-1.5097472347	1.3716137294
H	0	4.9837005583	-3.2135169281	0.9474890130
H	0	5.0506484662	-1.9775210340	-0.3285362131
H	0	3.4363562397	-4.4770372853	-0.2273506789
H	0	1.8245717147	-3.9152725221	-0.7147565761
H	0	3.2650411553	-3.3507582308	-1.5954884128
H	0	1.2460739036	-2.8612422562	1.5833466398
H	0	2.7055056623	-3.7586668596	2.0875763843
H	0	2.5286713193	-2.0439353426	2.5059085283
C	0	-3.7835322683	0.8634300566	0.6781436120
C	0	-4.3695386864	1.6727029536	-0.3014684087
C	0	-4.4748951198	-0.2728796454	1.1211011402
C	0	-5.6164562090	1.3479619612	-0.8421592674
H	0	-3.8361398820	2.5589445307	-0.6551522155
C	0	-5.7211641215	-0.5989084418	0.5875203726
H	0	-4.0157080190	-0.9146319338	1.8772312879
C	0	-6.2927217813	0.2087543577	-0.4014252602
H	0	-6.0570521831	1.9829523336	-1.6143448601
H	0	-6.2479094891	-1.4900208572	0.9375634164
H	0	-7.2651252048	-0.0506476962	-0.8268520158
C	0	-2.1028161960	-0.2736345743	-1.8155426680
C	0	-2.3259949782	0.2509181033	-3.0945838778
C	0	-2.6977093831	-1.4867219786	-1.4562162671
C	0	-3.1296396684	-0.4290002352	-4.0105118995
H	0	-1.8754582219	1.2081445300	-3.3736648942
C	0	-3.5106131525	-2.1608650837	-2.3686076883
H	0	-2.5154905808	-1.8866367413	-0.4613642984
C	0	-3.7277996489	-1.6381647187	-3.6460238344
H	0	-3.2967173384	-0.0096883308	-5.0054437617
H	0	-3.9796671722	-3.1032925285	-2.0765473357
H	0	-4.3653965567	-2.1701650587	-4.3562208162

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O	0	2.0363288581	-2.4545295956	-1.0953286570
C	0	2.4043334174	-3.7365682218	-1.6058971006
O	0	0.3720385658	-3.3814732903	0.1150127814
C	0	1.0668491475	-2.4474588983	-0.1758568607
C	0	0.8101711842	-1.0091557763	0.3136221480
C	0	0.0176516134	-0.2543115737	-0.7877616807
O	0	-0.0408133512	-1.0647672671	1.4275201966
N	0	-1.0741358460	-0.0392461381	1.2133567184
C	0	-1.3898285887	-0.2466038407	-0.2073338920
H	0	2.8303607539	-4.3499752259	-0.7981725072
H	0	1.5307337864	-4.2551759326	-2.0270415863
H	0	3.1556525387	-3.5514948850	-2.3824451247
H	0	0.1068822083	-0.7120141136	-1.7788694339

H	0	-1.7673177749	-1.2777892161	-0.3553825006
C	0	-2.4238856153	0.7306510758	-0.7783323821
H	0	-2.2635118964	0.7799046931	-1.8677610385
H	0	-2.2255857110	1.7365180098	-0.3918865779
N	0	2.0441783897	-0.2834353052	0.6216209492
C	0	1.9181960171	1.1660884134	0.5537567405
C	0	3.0013438779	-0.9801378831	1.3267803766
H	0	1.2328071215	1.5304930369	1.3377345110
S	0	0.8596768295	1.3703116825	-0.9670098154
C	0	3.1939468540	2.0530568549	0.5228181645
H	0	3.8493393311	-0.3612294885	1.6658214277
O	0	2.9357864885	-2.1696717639	1.5456545224
O	0	1.6699301125	1.2740830575	-2.1909610645
O	0	-0.0493805760	2.5075179254	-0.7758985465
C	0	2.8026551281	3.4517707267	-0.0066253187
C	0	4.2889079566	1.4693132034	-0.3865327222
C	0	3.7076705743	2.2568055646	1.9643167660
H	0	1.9448105699	3.8704630823	0.5397784149
H	0	3.6574159806	4.1320839786	0.1223248804
H	0	2.5491578135	3.4293757412	-1.0745270634
H	0	5.1050050937	2.2014034456	-0.4849124272
H	0	4.7280803955	0.5445578045	0.0119243325
H	0	3.8887682926	1.2561215531	-1.3859756196
H	0	4.0272620941	1.3295145687	2.4582365209
H	0	4.5757544799	2.9335147177	1.9486812182
H	0	2.9318754911	2.7204640500	2.5936019248
C	0	-3.8464346856	0.2998000750	-0.4952530450
C	0	-4.3547382301	-0.8870796504	-1.0449784430
C	0	-4.6786988149	1.0574017365	0.3369260723
C	0	-5.6513131041	-1.3147776487	-0.7564239170
H	0	-3.7262550190	-1.4889073556	-1.7081554065
C	0	-5.9762854325	0.6329792027	0.6323376459
H	0	-4.2979174137	1.9832457266	0.7724537898
C	0	-6.4660329055	-0.5568354795	0.0899207517
H	0	-6.0274992232	-2.2430455093	-1.1933306713
H	0	-6.6040021782	1.2326381464	1.2957205139
H	0	-7.4794236883	-0.8921688373	0.3229721104
C	0	-2.1312509973	-0.3019893916	2.1412539031
C	0	-2.6078334148	0.7710477595	2.8956853637
C	0	-2.7028051591	-1.5743308143	2.2705256546
C	0	-3.6914243997	0.5860757696	3.7575878339
H	0	-2.1284120114	1.7445883954	2.7800633351
C	0	-3.7802697764	-1.7541540270	3.1361406940
H	0	-2.2878032974	-2.4090971665	1.7032548970
C	0	-4.2812836355	-0.6742868409	3.8732348916
H	0	-4.0744685644	1.4272994926	4.3398977077
H	0	-4.2356280673	-2.7420278071	3.2362941682
H	0	-5.1303852277	-0.8207820258	4.5449262051

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0 1

O	0	-2.3402648314	1.9762605934	-1.3924298996
C	0	-3.0919926977	3.0032004291	-2.0474064948
O	0	-0.7942998103	3.4946641576	-0.7705216719
C	0	-1.1884926014	2.3660262668	-0.8227097940
C	0	-0.5116891560	1.1642809583	-0.1309198944
C	0	-1.0169214983	1.0022886489	1.3177361412
N	0	1.3671139303	0.9994664064	1.2297907408
O	0	0.8528645777	1.4728112858	-0.0181837349
C	0	1.9142433163	-0.3545894008	1.0748327809
C	0	0.2652103354	1.1738839373	2.1713689270
H	0	-3.3309947925	3.8141072432	-1.3442390583
H	0	-2.5133367782	3.4178012424	-2.8854002338

H	0	-4.0082947993	2.5249093932	-2.4121508643
H	0	-1.8169650708	1.6986764212	1.5887648202
H	0	0.3106719759	0.3769983223	2.9257416162
H	0	2.0705949054	-0.7306769461	2.0947666871
H	0	1.1906886712	-1.0332990036	0.5958936478
N	0	-0.7570161029	-0.0995685619	-0.8692047444
C	0	-1.8507703114	-0.9367120104	-0.3867453569
C	0	-0.3173942195	-0.0920934607	-2.1780120220
H	0	-2.8210315979	-0.4697838340	-0.6289695603
S	0	-1.7750201918	-0.6562160644	1.4480099726
C	0	-1.9059085327	-2.4440290621	-0.7710595612
H	0	-0.5172267916	-1.0307660735	-2.7239000893
O	0	0.2548628213	0.8490679449	-2.6800938999
O	0	-0.8158105129	-1.5680620708	2.0979900834
O	0	-3.1403142699	-0.5293253640	1.9681095978
C	0	-2.5241815234	-2.5994044736	-2.1782421310
C	0	-2.8698524923	-3.1569690025	0.2055502325
C	0	-0.5234249792	-3.1096058680	-0.6988078805
H	0	-1.8899267572	-2.2194654381	-2.9893912229
H	0	-2.6963672637	-3.6674042059	-2.3800964932
H	0	-3.4969987794	-2.0866943133	-2.2397504315
H	0	-3.0282404741	-4.1888329360	-0.1406341728
H	0	-2.4648129195	-3.2047587686	1.2243202247
H	0	-3.8489134432	-2.6568156009	0.2476219941
H	0	-0.6174113270	-4.1745814967	-0.9602034342
H	0	0.1988640315	-2.6606062066	-1.3952394160
H	0	-0.1100838497	-3.0396692368	0.3154606746
C	0	3.2290238572	-0.3757296119	0.3280944538
C	0	3.3242880326	0.0454774680	-1.0086407619
C	0	4.3816103963	-0.8531807287	0.9666593611
C	0	4.5470445517	-0.0113776842	-1.6805791815
H	0	2.4470091828	0.4407633234	-1.5206308573
C	0	5.6043272203	-0.9156539362	0.2926776477
H	0	4.3217141903	-1.1810891661	2.0083171219
C	0	5.6900626789	-0.4937235353	-1.0356019945
H	0	4.6056672974	0.3261391294	-2.7183688254
H	0	6.4912713867	-1.2912289395	0.8090225016
H	0	6.6443143713	-0.5382260837	-1.5663657121
C	0	0.2759683621	2.5267334953	2.8591345726
C	0	-0.3085638580	2.6477839498	4.1261771877
C	0	0.8145327738	3.6589874598	2.2354690018
C	0	-0.3544670831	3.8868951760	4.7696895561
H	0	-0.7279217872	1.7640927777	4.6166669475
C	0	0.7681830717	4.8964855395	2.8811593072
H	0	1.2571041478	3.5670424587	1.2439227504
C	0	0.1855538496	5.0150747846	4.1465434565
H	0	-0.8059442329	3.9688747969	5.7613176266
H	0	1.1894762326	5.7760655418	2.3886474549
H	0	0.1541219381	5.9855839334	4.6476332162

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0 1

O	0	-3.0788661812	1.8208563788	-0.3903773964
C	0	-4.1287284946	2.7527753012	-0.6579264654
O	0	-1.6621069682	3.5202616461	0.0418370462
C	0	-1.9136920539	2.3500955121	0.0014631036
C	0	-0.8810753160	1.2234968528	0.2272870891
C	0	-0.2889444328	0.7725118312	-1.1167868170
N	0	1.4480108215	1.3380139941	0.4052288340
O	0	0.2025019259	1.7809912213	0.9455055159
C	0	1.9356206727	0.1622880179	1.1315421842
C	0	1.2082407259	1.1404550493	-1.0236355952
H	0	-3.8174282813	3.4786113326	-1.4232201350

H	0	-4.3927739429	3.2954706878	0.2616034021
H	0	-4.9795015326	2.1589719098	-1.0116720344
H	0	-0.7900964067	1.2134864551	-1.9840664403
H	0	1.8164784926	0.2952152888	-1.3723162572
H	0	1.8894952721	0.4285969522	2.1978633160
H	0	1.3146092404	-0.7377070488	0.9800034012
N	0	-1.4962526589	0.0804860159	0.9236073437
C	0	-1.2754204656	-1.2787424555	0.4543881971
C	0	-2.1423920632	0.4014381436	2.0980374878
H	0	-0.3975613766	-1.7391745905	0.9376136727
S	0	-0.6375500609	-1.0120151708	-1.2891323452
C	0	-2.4509620646	-2.3035501342	0.5029662248
H	0	-2.4461854948	-0.4748140414	2.6969116977
O	0	-2.3521678782	1.5405301280	2.4491215459
O	0	-1.6961852354	-1.1249418846	-2.3026244212
O	0	0.6023438618	-1.7917449980	-1.4293725186
C	0	-3.7632443195	-1.6748142114	0.0132165772
C	0	-2.6253996421	-2.8588281754	1.9350292889
C	0	-2.0607249179	-3.5138850562	-0.3779482927
H	0	-3.6545556039	-1.2771554852	-1.0032639071
H	0	-4.5574496023	-2.4370910937	0.0107318893
H	0	-4.0882720470	-0.8524253217	0.6670612058
H	0	-3.2712055506	-3.7488517172	1.8956555949
H	0	-1.6617906719	-3.1671964618	2.3712529728
H	0	-3.1097070203	-2.1548791791	2.6239968982
H	0	-1.0818514038	-3.9237252223	-0.0829169215
H	0	-2.8099080589	-4.3083782336	-0.2480790470
H	0	-2.0242614984	-3.2599368320	-1.4435644763
C	0	3.3522050518	-0.1429095949	0.7094620394
C	0	3.6615221077	-1.3458008793	0.0626320032
C	0	4.3671459224	0.8013283441	0.9241529932
C	0	4.9731476135	-1.6133743974	-0.3427861253
H	0	2.8645237465	-2.0633482016	-0.1452818923
C	0	5.6745483089	0.5359458442	0.5173046848
H	0	4.1183830202	1.7521350468	1.4009558541
C	0	5.9814034120	-0.6749676755	-0.1140777631
H	0	5.2035662687	-2.5551678448	-0.8465514243
H	0	6.4590282171	1.2767502518	0.6899781597
H	0	7.0058708337	-0.8817367891	-0.4331212442
C	0	1.5341202007	2.3610514030	-1.8606069264
C	0	2.0288644646	2.1820368220	-3.1581318145
C	0	1.3195151156	3.6575565679	-1.3746594211
C	0	2.3077026845	3.2858139099	-3.9681661854
H	0	2.2058091988	1.1703753648	-3.5347151696
C	0	1.6000448104	4.7589277200	-2.1858623253
H	0	0.9201130720	3.7985852818	-0.3702062293
C	0	2.0933610246	4.5779062498	-3.4818450676
H	0	2.7002198055	3.1353841913	-4.9767173576
H	0	1.4285389266	5.7673116458	-1.8017434147
H	0	2.3127390663	5.4436901842	-4.1114088426

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0 1

O	0	3.3595044772	0.7811357105	-0.5221657704
C	0	4.7830153784	0.8213976929	-0.6123665221
O	0	3.5054642353	-1.0538588702	0.7685894423
C	0	2.8406009343	-0.2449755514	0.1604620528
C	0	1.3458832520	-0.2222408947	0.1445054403
C	0	0.6319238685	-0.5609065328	1.3213007297
O	0	1.1718592780	-1.9944819384	-0.8424917758
N	0	0.7203052570	-2.7536983425	0.0951513213
C	0	1.7163564200	-3.5828310740	0.8124814106
C	0	-0.3928450482	-2.2942859824	0.7310182739

H	0	5.1596723680	-0.0836032988	-1.1112586419
H	0	5.2350913832	0.8873669580	0.3883612499
H	0	5.0247472688	1.7116867309	-1.2046619255
H	0	1.1850797189	-0.9033514625	2.1979374540
H	0	-0.6028995880	-2.8106951047	1.6707437296
H	0	2.3774397327	-3.9608009860	0.0199229046
H	0	2.3281844374	-2.9262127513	1.4491595718
N	0	0.6683061864	0.7822574234	-0.6235951365
C	0	0.0495600607	1.8058064549	0.2239133364
C	0	0.8240383875	0.8464067563	-1.9965314904
H	0	0.8466790944	2.4227969609	0.6730188306
S	0	-0.4497784921	0.8056202709	1.7411442923
C	0	-1.0618246805	2.7465525797	-0.2974425029
H	0	0.2685547649	1.6901837840	-2.4444167649
O	0	1.4738159920	0.0698578175	-2.6529026057
O	0	-1.8719441263	0.4325432538	1.7656363813
O	0	0.1191845507	1.4845108062	2.9144384821
C	0	-0.4442455927	3.8491323125	-1.1856523222
C	0	-1.6641640466	3.4679248016	0.9323147829
C	0	-2.1732337421	1.9891308436	-1.0385049683
H	0	-0.0314814461	3.4795181044	-2.1331534546
H	0	-1.2216444321	4.5867077592	-1.4372791497
H	0	0.3598011139	4.3793380431	-0.6511498599
H	0	-2.3496382193	4.2550551706	0.5850303598
H	0	-2.2335180698	2.7823130182	1.5718223635
H	0	-0.8822322839	3.9431804907	1.5442918328
H	0	-2.5948732817	1.1953500800	-0.4097249765
H	0	-2.9809231346	2.6898844186	-1.3010066766
H	0	-1.8198982836	1.5277842092	-1.9703946463
C	0	-1.6035992527	-1.9205924381	-0.0364572643
C	0	-2.8346884436	-1.9729276732	0.6400251881
C	0	-1.5958468954	-1.6000250540	-1.4068337171
C	0	-4.0280637032	-1.7054130583	-0.0253245876
H	0	-2.8507764464	-2.2102012034	1.7052878663
C	0	-2.7962496896	-1.3500416154	-2.0725969832
H	0	-0.6512744076	-1.5582848738	-1.9443319645
C	0	-4.0132798372	-1.3919458491	-1.3875419780
H	0	-4.9729059869	-1.7409943172	0.5214470802
H	0	-2.7758322531	-1.1099635368	-3.1383401442
H	0	-4.9480657471	-1.1817094333	-1.9128384931
C	0	1.0751005782	-4.6949757379	1.5964753846
C	0	1.2073820635	-4.7506629371	2.9896348407
C	0	0.3159317090	-5.6798616954	0.9450727902
C	0	0.5988860476	-5.7746643445	3.7222039668
H	0	1.7938811977	-3.9848548217	3.5042011968
C	0	-0.2965877089	-6.6989581769	1.6741934914
H	0	0.2001413098	-5.6378146688	-0.1410676382
C	0	-0.1553155390	-6.7492258226	3.0656436383
H	0	0.7126677799	-5.8077398577	4.8082515545
H	0	-0.8861350201	-7.4592791785	1.1564717471
H	0	-0.6344952174	-7.5483190581	3.6361459728

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0 1

O	0	3.3338808821	0.4532325924	0.3861670504
C	0	4.7570165781	0.3866609554	0.4658077466
O	0	3.2992403591	-1.5570061175	-0.6156095385
C	0	2.7192894153	-0.6139519012	-0.1236833890
C	0	1.2294481424	-0.4566380664	-0.1098214356
C	0	0.4901716529	-0.7148314521	-1.2940453033
O	0	0.8509695125	-2.1776930478	0.8758728870
N	0	0.2611542231	-2.8882836851	-0.0311181896
C	0	1.1059717099	-3.8647733345	-0.7582868265

C	0	-0.7719574977	-2.2703977714	-0.6620095961
H	0	5.0600956983	-0.4196208523	1.1501715478
H	0	5.1945678074	0.1981633657	-0.5252271957
H	0	5.0840579321	1.3577874536	0.8548877143
H	0	1.0095450097	-1.1258598522	-2.1627115685
H	0	-1.0839766381	-2.7595463685	-1.5893827750
H	0	1.8855547825	-3.2993925021	-1.2916818749
H	0	0.4537643984	-4.3740037295	-1.4805388433
N	0	0.6451466055	0.5602134353	0.6936754433
C	0	-0.4105690840	1.3720525190	0.0772013909
C	0	0.8514281684	0.5401376218	2.0668278816
H	0	-1.4068487641	1.0512586521	0.4193460303
S	0	-0.3816567440	0.7820898994	-1.6992306680
C	0	-0.2898799997	2.9196071388	0.1923136332
H	0	0.1475184096	1.2052455577	2.6044462096
O	0	1.6822697376	-0.1310392992	2.6256777285
O	0	0.5410623824	1.5807243118	-2.5239924336
O	0	-1.7507611345	0.5912993011	-2.1896972404
C	0	-1.2835832275	3.5479315593	-0.8087076690
C	0	1.1441599710	3.3948593877	-0.0865548938
C	0	-0.7149591422	3.3791079315	1.6029402575
H	0	-2.3041009654	3.1630064550	-0.6552374555
H	0	-1.3068335606	4.6380375967	-0.6613905271
H	0	-0.9961751057	3.3568367605	-1.8502499004
H	0	1.1995911818	4.4877352760	0.0357771562
H	0	1.8564644044	2.9339517162	0.6132930374
H	0	1.4560009850	3.1379516499	-1.1058872656
H	0	0.0363347814	3.1455525155	2.3694554902
H	0	-0.8371926576	4.4730560374	1.6021987284
H	0	-1.6765950984	2.9338230707	1.9051385508
C	0	-1.8805647289	-1.6487014103	0.1038573779
C	0	-3.0631276764	-1.3376847680	-0.5888141768
C	0	-1.8187972913	-1.3930594264	1.4880649504
C	0	-4.1432073101	-0.7518373767	0.0695733414
H	0	-3.1249766406	-1.5299736972	-1.6600577114
C	0	-2.9068975640	-0.8175350114	2.1442904803
H	0	-0.9155411645	-1.6482027834	2.0377442242
C	0	-4.0668487096	-0.4813747676	1.4380791691
H	0	-5.0462056677	-0.5025919643	-0.4917221273
H	0	-2.8451871739	-0.6285858078	3.2187161040
H	0	-4.9110851062	-0.0188941180	1.9549545442
C	0	1.7287868952	-4.8525802435	0.1929044081
C	0	2.9752888644	-4.5818815798	0.7732147083
C	0	1.0505255108	-6.0289738730	0.5389618401
C	0	3.5340344825	-5.4811910267	1.6840837776
H	0	3.4954539334	-3.6610224948	0.5057726660
C	0	1.6097513822	-6.9283347311	1.4488188677
H	0	0.0751734360	-6.2423669151	0.0921808678
C	0	2.8542062211	-6.6542232604	2.0237451312
H	0	4.5063147181	-5.2638312806	2.1328247432
H	0	1.0744939214	-7.8446710196	1.7092062617
H	0	3.2943695567	-7.3565982152	2.7358758473

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0 1

O	0	0.6082523711	2.8515705496	-1.1753432357
C	0	0.2917720595	4.1393405405	-1.7024561328
O	0	-1.5746393176	2.4923274617	-0.7584967059
C	0	-0.4224545308	2.1536797525	-0.6735491571
C	0	0.0470420088	0.8553480629	-0.0802823245
C	0	-0.4840639472	-0.3610110649	-0.5731882864
N	0	-1.0915609847	-0.2626685735	1.9381911987
O	0	-0.9450492865	0.9832292433	1.6395674855

C	0	-0.0882396191	-0.8352802965	2.8719118784
C	0	-1.7146711260	-1.0399762479	1.0190980838
H	0	-0.4542219159	4.0598948773	-2.5069109660
H	0	-0.1104683224	4.7850643779	-0.9078787644
H	0	1.2321761879	4.5511744863	-2.0874864543
H	0	-1.2048106271	-0.3720961321	-1.3900629478
H	0	-1.5127339104	-2.1051827905	1.1537735017
H	0	0.1759049723	0.0076766913	3.5230749829
H	0	0.7968610410	-1.1332960896	2.2992159577
N	0	1.4273034682	0.7472964906	0.3019159159
C	0	2.1648220561	-0.2399696935	-0.4931742930
C	0	1.9838944074	1.7237517185	1.1114357374
H	0	2.2804071033	0.1443276181	-1.5218453731
S	0	0.8442783654	-1.5383693994	-0.7655944648
C	0	3.5275342647	-0.8070183039	-0.0246894140
H	0	3.0627638186	1.5675927305	1.2936407044
O	0	1.3659245290	2.6458386916	1.5844289978
O	0	0.8530536335	-2.5302816585	0.3326052443
O	0	0.9001627713	-2.0169532405	-2.1518405550
C	0	4.6417437966	0.2199840891	-0.3239314243
C	0	3.8338247834	-2.0554935369	-0.8840596590
C	0	3.5355622194	-1.2104900073	1.4582872334
H	0	4.5676291939	1.1401856817	0.2702943955
H	0	5.6210232035	-0.2316707901	-0.1034892250
H	0	4.6358011178	0.5047163715	-1.3877391693
H	0	4.8576001122	-2.3961141743	-0.6694867185
H	0	3.1485338255	-2.8835783790	-0.6617080815
H	0	3.7648760430	-1.8346238877	-1.9596902205
H	0	4.5243624552	-1.6182569272	1.7180891562
H	0	3.3426212209	-0.3637592496	2.1315248718
H	0	2.7854875351	-1.9868414504	1.6532501543
C	0	-3.0478982367	-0.7331232799	0.4606345880
C	0	-3.7562510276	-1.8010206929	-0.1207189730
C	0	-3.6374474705	0.5425914218	0.4940319172
C	0	-5.0284682612	-1.6040497795	-0.6558536006
H	0	-3.3035440316	-2.7959791337	-0.1452866396
C	0	-4.9163173159	0.7290840954	-0.0309452745
H	0	-3.0799635644	1.3795614726	0.9065807212
C	0	-5.6141132032	-0.3354737011	-0.6093861870
H	0	-5.5659664354	-2.4432666042	-1.1034341516
H	0	-5.3659516504	1.7242096902	0.0005485685
H	0	-6.6115065809	-0.1765798093	-1.0264193501
C	0	-0.6354722724	-2.0008050336	3.6519813492
C	0	-0.2604555921	-3.3130922619	3.3330123520
C	0	-1.5563812689	-1.7844634851	4.6879765045
C	0	-0.7913325142	-4.3916281761	4.0471546331
H	0	0.4339095896	-3.4830778562	2.5078269980
C	0	-2.0887018634	-2.8607583044	5.3983116998
H	0	-1.8582740890	-0.7629441127	4.9346369848
C	0	-1.7047330448	-4.1679849876	5.0798506108
H	0	-0.4917687443	-5.4108146151	3.7915028609
H	0	-2.8041849781	-2.6810856628	6.2043128108
H	0	-2.1200877913	-5.0111705352	5.6370856113

S2-PB-TSxSi

0 1

O	0	-1.2549291819	2.6672933296	-0.8088822911
C	0	-1.1560059699	3.9085856225	-1.5044541375
O	0	0.8883205745	2.2153161659	-1.3328194427
C	0	-0.1338534114	1.9317176079	-0.7551604386
C	0	-0.3068949125	0.7099225598	0.0731516162
C	0	0.4087009463	-0.4761394126	-0.2232764773
N	0	1.4031362596	0.2722984337	2.0168683189

O	0	1.0109408171	1.4014588511	1.5659170588
C	0	0.7496305925	-0.2208874619	3.2580536312
C	0	1.9379094746	-0.5966134276	1.1096639290
H	0	-0.8809017440	3.7448631206	-2.5570774064
H	0	-0.3942017929	4.5492111388	-1.0365572726
H	0	-2.1444548131	4.3770579665	-1.4321085817
H	0	0.9567291275	-0.5676602306	-1.1614002552
H	0	1.9585889137	-1.6239758100	1.4819034273
H	0	0.4380508804	0.6961146780	3.7731586389
H	0	-0.1378581851	-0.8032719075	2.9814000071
N	0	-1.5416557547	0.4507160921	0.7450058176
C	0	-2.1751151759	-0.8199994244	0.4143858473
C	0	-2.0799358831	1.2697320311	1.7277924958
H	0	-2.6297165038	-1.2604212030	1.3130862982
S	0	-0.6661775303	-1.8859030722	0.1167978876
C	0	-3.2163135578	-0.7873575231	-0.7326581074
H	0	-2.9805866023	0.7981182669	2.1858433847
O	0	-1.6470622224	2.3383151110	2.0696607023
O	0	-0.7476162776	-2.7360466212	-1.0790629672
O	0	-0.3490373876	-2.5182965529	1.4130890263
C	0	-2.6047622217	-0.3498526977	-2.0740541482
C	0	-4.3125920230	0.2206594635	-0.3417161611
C	0	-3.8373615684	-2.1907739046	-0.8485331849
H	0	-1.8112091468	-1.0327282852	-2.4027502835
H	0	-3.3903591256	-0.3479535597	-2.8454527064
H	0	-2.2058917153	0.6715176543	-2.0099161512
H	0	-5.1079003655	0.2064421325	-1.1026859533
H	0	-4.7750148458	-0.0309652606	0.6263700912
H	0	-3.9184652010	1.2459774434	-0.2885439330
H	0	-4.3094750320	-2.4929461328	0.1009653019
H	0	-4.6186408130	-2.1900959708	-1.6237732897
H	0	-3.0851827854	-2.9429274977	-1.1201172298
C	0	3.1042136099	-0.2450392174	0.2630974410
C	0	3.8737549952	-1.3112855757	-0.2348377237
C	0	3.4747047098	1.0726645849	-0.0519634449
C	0	4.9950923363	-1.0703245364	-1.0282979381
H	0	3.5919688634	-2.3388533958	0.0106302261
C	0	4.6062389784	1.3075659966	-0.8332360831
H	0	2.8634332874	1.8991777593	0.3011248710
C	0	5.3665452213	0.2434482261	-1.3273477107
H	0	5.5833883498	-1.9094255656	-1.4068752603
H	0	4.8872928951	2.3361611666	-1.0708057302
H	0	6.2451353089	0.4373554513	-1.9473219426
C	0	1.6865839994	-1.0560554142	4.0900195914
C	0	1.5398673832	-2.4485852627	4.1468105519
C	0	2.7405329625	-0.4483760813	4.7886358217
C	0	2.4295790213	-3.2209518265	4.8997406915
H	0	0.7335024991	-2.9222022279	3.5828171955
C	0	3.6302013041	-1.2194515191	5.5370783865
H	0	2.8633453057	0.6370087606	4.7401913677
C	0	3.4747066955	-2.6087921527	5.5952884987
H	0	2.3061689848	-4.3058632186	4.9393139910
H	0	4.4471115202	-0.7366859653	6.0787562706
H	0	4.1704824026	-3.2127431794	6.1827532674

S2-PM-PnRe

0 1

O	0	1.0007310610	2.3427840558	0.6157988656
C	0	1.5780737745	3.4711244440	1.2799954967
O	0	2.9628778621	1.2516028562	0.7483905268
C	0	1.8128062017	1.3058449581	0.4029544885
C	0	1.0790913748	0.1179831542	-0.2607803557
C	0	0.8082634597	-0.9987779085	0.7528625253

O	0	1.9250950912	-0.4669017107	-1.2316042281
N	0	2.2981935836	-1.8011318476	-0.8445806153
C	0	3.5873977935	-1.7660951318	-0.1688063072
C	0	1.1725056980	-2.2846833842	-0.0514526966
H	0	2.4061958874	3.8788586810	0.6830649727
H	0	1.9573631970	3.1769619975	2.2690921957
H	0	0.7738841738	4.2088623331	1.3794184339
H	0	1.4541808001	-0.9082018658	1.6334904098
H	0	1.5399141038	-3.0405398903	0.6561887836
H	0	4.3108071699	-1.2858676579	-0.8402801613
H	0	3.5908752715	-1.2127753916	0.7874503571
H	0	3.9018825254	-2.8072659547	-0.0037666178
N	0	-0.2140510205	0.5067299181	-0.8572914251
C	0	-1.3590608996	0.5453816768	0.0625288981
C	0	-0.1002124433	1.4138691150	-1.9032495898
H	0	-1.3378452230	1.4807851289	0.6437668171
S	0	-0.8451378593	-0.6623546527	1.4138958782
C	0	-2.8057782533	0.3214542383	-0.4563421465
H	0	-1.0734006806	1.7631835569	-2.2897224974
O	0	0.9570333719	1.7828221106	-2.3550659310
O	0	-1.6372149149	-1.8968765179	1.4825285119
O	0	-0.6641472765	0.1519015697	2.6233218498
C	0	-3.2830678655	1.5329174101	-1.2900870996
C	0	-3.7244305105	0.2637232570	0.7864813555
C	0	-2.9325713756	-0.9540655353	-1.2944300501
H	0	-2.8999004040	1.5208484259	-2.3192667915
H	0	-4.3803979593	1.5005770163	-1.3658566973
H	0	-3.0101597348	2.4920270667	-0.8213519656
H	0	-4.7713248236	0.1931028402	0.4563961445
H	0	-3.5158432580	-0.6051185570	1.4214046832
H	0	-3.6252999784	1.1764373793	1.3959902159
H	0	-2.6623222097	-1.8479368817	-0.7205369608
H	0	-3.9715665637	-1.0671380503	-1.6408111576
H	0	-2.2833176164	-0.9110024010	-2.1789593058
C	0	0.1082872294	-2.9234839369	-0.9275008068
C	0	-0.7297084864	-3.9112081767	-0.3954890202
C	0	0.0062071214	-2.6024140504	-2.2875312427
C	0	-1.6725955547	-4.5517868801	-1.2007632853
H	0	-0.6568377585	-4.1702377545	0.6619181696
C	0	-0.9311370123	-3.2497147771	-3.0951106744
H	0	0.6704974561	-1.8497435498	-2.7102777439
C	0	-1.7773253303	-4.2211372269	-2.5545420224
H	0	-2.3234911592	-5.3156409160	-0.7691979576
H	0	-0.9993236468	-2.9921126893	-4.1548343364
H	0	-2.5113245496	-4.7254995530	-3.1876558998

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0 1

O	0	-0.9027631752	-2.3476188688	-0.9852567699
C	0	-1.3869577116	-3.5560793751	-1.5698155873
O	0	-2.9972363796	-1.7720696293	-0.3783907204
C	0	-1.8129967365	-1.5838785078	-0.3787296443
C	0	-1.1468228412	-0.3124608273	0.1789540769
C	0	-1.0173176759	0.7643925350	-0.9372176729
O	0	-2.0147754799	0.2475717958	1.1204581902
N	0	-1.7359689090	1.6702208591	1.0861383673
C	0	-2.7742325367	2.2879679118	1.8849144250
C	0	-1.8103436216	1.9533716094	-0.3485616213
H	0	-1.7693623836	-4.2262774491	-0.7856079140
H	0	-2.1962505157	-3.3464044417	-2.2845237253
H	0	-0.5302878955	-4.0113123542	-2.0800174918
H	0	-1.4133794651	0.4334972451	-1.9034014845
H	0	-2.8505017145	1.7996632378	-0.7035005815

H	0	-3.7863136320	2.0380162307	1.5123859641
H	0	-2.6301457516	3.3761529580	1.8523371967
H	0	-2.6776670935	1.9435949229	2.9233466441
N	0	0.1776072306	-0.5844369719	0.7564352953
C	0	1.2584867300	0.3404752418	0.4576226066
C	0	0.2070238320	-1.5982290966	1.6863081361
H	0	1.1638725061	1.2689822242	1.0470783023
S	0	0.7801325946	0.9184896441	-1.2442045086
C	0	2.7297414323	-0.1689076455	0.5201332117
H	0	1.1669220522	-1.6911463835	2.2238956827
O	0	-0.7361402101	-2.3264520922	1.9035216659
O	0	1.0894033693	-0.1152962600	-2.2430991072
O	0	1.2208524109	2.2990769962	-1.4551806224
C	0	3.6214683078	0.7846976831	-0.3073618687
C	0	2.8712084709	-1.5926760783	-0.0457724166
C	0	3.2367487186	-0.0892708629	1.9756644096
H	0	3.4705553027	1.8367602183	-0.0246589450
H	0	4.6760487013	0.5281483585	-0.1280125027
H	0	3.4317952047	0.6919278148	-1.3846824960
H	0	3.9399557928	-1.8419535307	-0.1311823824
H	0	2.4098822287	-2.3556603487	0.5957579558
H	0	2.4136591491	-1.6606690249	-1.0409294162
H	0	2.6838986281	-0.7315441121	2.6743048438
H	0	4.2915844215	-0.4020376642	2.0115771940
H	0	3.1803261731	0.9437552685	2.3537165696
C	0	-1.3839394288	3.3559143915	-0.7115914709
C	0	-1.8498955775	3.9194293427	-1.9047750116
C	0	-0.5289695018	4.1020766278	0.1082459900
C	0	-1.4552542629	5.2033992529	-2.2847172220
H	0	-2.5272911450	3.3472493806	-2.5450121988
C	0	-0.1458862848	5.3909405696	-0.2624988545
H	0	-0.1580566804	3.6617820744	1.0346836964
C	0	-0.6020457869	5.9432288745	-1.4623221037
H	0	-1.8201318648	5.6291470099	-3.2222885902
H	0	0.5221125579	5.9643622440	0.3844982520
H	0	-0.2950823535	6.9500547819	-1.7549924454

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0 1

O	0	-1.1080188063	2.3847497034	-0.6777209771
C	0	-1.7299230511	3.5818003444	-1.1552092810
O	0	-3.1053114839	1.6272978244	0.0410093738
C	0	-1.9188501029	1.5078892774	-0.0632701175
C	0	-1.1159410655	0.2625495196	0.3680701302
C	0	-1.0542237123	-0.7764986698	-0.7720789595
N	0	-1.7787386873	-1.7775325105	1.2699208433
O	0	-1.8370645660	-0.3539393238	1.4010341034
C	0	-0.6766305159	-2.3035765277	2.0635610250
C	0	-1.7420956871	-2.0269200343	-0.1689635561
H	0	-2.5453688705	3.3413373913	-1.8526083224
H	0	-2.1404463749	4.1554042270	-0.3117029994
H	0	-0.9435199312	4.1530038414	-1.6619654866
H	0	-1.5152512386	-0.4371287292	-1.7052350655
H	0	-1.1189196106	-2.9117286408	-0.3590989052
H	0	-0.7313549757	-3.4010473837	2.0204743857
H	0	-0.8325591888	-1.9907393381	3.1049185945
H	0	0.3228510658	-1.9876931135	1.7261211345
N	0	0.2675927711	0.6137390445	0.7694910185
C	0	1.2941383100	0.4756116346	-0.2587780290
C	0	0.3407015079	1.5268586830	1.8076822890
H	0	1.1697935884	1.2588227870	-1.0265648600
S	0	0.7099938746	-1.0209906301	-1.1893654092
C	0	2.7956772151	0.4006135537	0.1409154387

H	0	1.3731809692	1.7682937493	2.1184153849
O	0	-0.6334029692	2.0034095099	2.3408125847
O	0	1.1831309248	-2.2692115764	-0.5623180121
O	0	0.9052208355	-0.7986754564	-2.6259757445
C	0	3.3398744552	1.8273066034	0.3743001731
C	0	3.5873830224	-0.1760338093	-1.0553951632
C	0	3.0229142019	-0.4856604255	1.3743825519
H	0	2.9170214210	2.3267949844	1.2553276211
H	0	4.4291783415	1.7785510279	0.5234771180
H	0	3.1507762655	2.4678891317	-0.5014042404
H	0	4.6633874478	-0.1000193729	-0.8402811097
H	0	3.3552780166	-1.2340925476	-1.2319483638
H	0	3.3842584393	0.3795880269	-1.9829686433
H	0	4.0989606956	-0.5237784697	1.6029091706
H	0	2.5075173870	-0.1039918636	2.2670607424
H	0	2.6740451924	-1.5094511079	1.1875038307
C	0	-3.1170870609	-2.2332443095	-0.7756785600
C	0	-4.2382739245	-1.5518455154	-0.2836508589
C	0	-3.2563234897	-3.0871792418	-1.8765429082
C	0	-5.4828034979	-1.7311875697	-0.8907814640
H	0	-4.1279672477	-0.8746794590	0.5634959587
C	0	-4.5028103442	-3.2645560943	-2.4828554258
H	0	-2.3829878679	-3.6223159283	-2.2611451491
C	0	-5.6197122274	-2.5858574295	-1.9892611011
H	0	-6.3527342695	-1.1959088453	-0.5028174930
H	0	-4.6014903437	-3.9387318204	-3.3370534707
H	0	-6.5966236676	-2.7238375112	-2.4589575365

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0 1

O	0	1.1958043328	1.9489119285	-1.4157862601
C	0	1.8781366669	3.0342533572	-2.0448250829
O	0	2.8862682890	1.7067892633	0.0636526531
C	0	1.7855728785	1.4425955655	-0.3236769162
C	0	0.8860390121	0.3331524817	0.2702876013
C	0	0.8400823110	-0.8720921494	-0.7075881938
N	0	2.4137474495	-1.1628675857	0.9851131241
O	0	1.4334371939	-0.2030635499	1.4483833063
C	0	2.8604019481	-1.8926584482	2.1468934169
C	0	1.6650833650	-1.9569234432	0.0033647934
H	0	2.8978971679	2.7393998055	-2.3326102797
H	0	1.9344683322	3.8890052365	-1.3545695871
H	0	1.2873465120	3.2947461300	-2.9308664769
H	0	1.1816214213	-0.6241379881	-1.7174137140
H	0	0.9679526771	-2.6565267983	0.5026435368
H	0	3.5779697347	-2.6529721706	1.8074131661
H	0	3.3717621275	-1.2018157612	2.8307323331
H	0	2.0258235979	-2.3914995606	2.6805869864
N	0	-0.4655593554	0.7913648635	0.5567976525
C	0	-1.4598643296	-0.2716420845	0.5781628046
C	0	-0.6296303415	2.0755969705	1.0349308371
H	0	-1.2574095720	-0.9600326278	1.4163141248
S	0	-0.9243658223	-1.3095229241	-0.8857101611
C	0	-2.9758050258	0.0638094802	0.5570724678
H	0	-1.6642784525	2.3054926100	1.3389925458
O	0	0.2657465945	2.8848575520	1.1098438769
O	0	-1.4051192421	-0.7378963018	-2.1503298926
O	0	-1.1440842424	-2.7319785210	-0.5772101545
C	0	-3.3316484804	1.1517557014	-0.4724633492
C	0	-3.4309535933	0.4589242849	1.9781392070
C	0	-3.7422884080	-1.2269591796	0.1876946975
H	0	-2.9228674312	0.9011217928	-1.4594882488
H	0	-4.4269327317	1.2214609014	-0.5560030499

H	0	-2.9660391619	2.1486249053	-0.1919238155
H	0	-4.5158857360	0.6447029711	1.9741324364
H	0	-3.2328373957	-0.3556049400	2.6924173148
H	0	-2.9463004808	1.3656603645	2.3643498406
H	0	-3.4431901030	-2.0766416821	0.8188848115
H	0	-4.8189498187	-1.0541214569	0.3316308151
H	0	-3.5855415988	-1.5104900830	-0.8615175573
C	0	2.5648155874	-2.7329588174	-0.9287125193
C	0	2.0913330836	-3.9134785417	-1.5157151878
C	0	3.8386096111	-2.2529893376	-1.2624360800
C	0	2.8889624457	-4.6136873761	-2.4237709976
H	0	1.0874384248	-4.2685104826	-1.2695734813
C	0	4.6362669504	-2.9604836996	-2.1649959068
H	0	4.1911986403	-1.3267574922	-0.8043146925
C	0	4.1643112527	-4.1409764321	-2.7468567043
H	0	2.5131061208	-5.5326921419	-2.8797531195
H	0	5.6315398443	-2.5862712398	-2.4170351643
H	0	4.7896227402	-4.6916056488	-3.4537604269

S2-PM-TSnRe

0 1

O	0	1.5732123276	2.4484629434	0.5339375624
C	0	2.5131291020	3.4262108332	0.9779541241
O	0	2.9555494902	0.8184285644	1.2325012575
C	0	1.9416151473	1.1704393140	0.6735259443
C	0	0.9080530017	0.2350488195	0.1285933916
C	0	0.5931176344	-0.9448215804	0.8481977317
O	0	2.1318048473	-0.5587512770	-1.2725213673
N	0	2.3311562140	-1.7408914753	-0.7949131110
C	0	3.5577276387	-1.9475408799	-0.0227901441
C	0	1.2025646494	-2.4443453415	-0.5060166801
H	0	3.4551036242	3.3317057530	0.4180186413
H	0	2.7253208495	3.3036418374	2.0503630438
H	0	2.0511415287	4.4014383579	0.7847152308
H	0	1.1666891480	-1.1900069036	1.7441746475
H	0	1.3803870752	-3.3169446935	0.1294460030
H	0	4.3790482928	-1.4901454287	-0.5878616220
H	0	3.4874988211	-1.4418340018	0.9521080147
H	0	3.7370078539	-3.0239567547	0.0951918240
N	0	-0.2390769566	0.7752962376	-0.5427121972
C	0	-1.4589030690	0.6634009476	0.2627400456
C	0	-0.0917095829	1.5232589946	-1.6970196661
H	0	-1.3909749207	1.3695508940	1.1080310741
S	0	-1.1653243387	-0.9496052727	1.1910458875
C	0	-2.8704295130	0.7785037114	-0.3589699006
H	0	-1.0569890210	1.8990076637	-2.0820270626
O	0	0.9601591076	1.7384546520	-2.2476888247
O	0	-1.8648576266	-2.1056119245	0.6104730463
O	0	-1.3457680012	-0.6657110574	2.6220662337
C	0	-3.1976172515	2.2592664487	-0.6528579748
C	0	-3.8829769565	0.3167466161	0.7167121046
C	0	-3.0305008828	-0.0886096603	-1.6158985714
H	0	-2.5908822152	2.6996240389	-1.4545663417
H	0	-4.2507455014	2.3407879523	-0.9625566403
H	0	-3.0652413588	2.8773886531	0.2492086182
H	0	-4.9026412212	0.5287109101	0.3625901759
H	0	-3.8107574270	-0.7600332479	0.9130210904
H	0	-3.7344669177	0.8524779508	1.6668418597
H	0	-2.7820929503	-1.1361144539	-1.4055035885
H	0	-4.0747681400	-0.0422313465	-1.9618349897
H	0	-2.3924157089	0.2485377702	-2.4437219637
C	0	0.1449188760	-2.6428607341	-1.5239079478
C	0	-0.7066766080	-3.7494748993	-1.3620709325

C	0	0.0014165195	-1.8387754269	-2.6702781026
C	0	-1.6811007163	-4.0469243942	-2.3109633049
H	0	-0.6140008262	-4.3720622614	-0.4702507069
C	0	-0.9648712728	-2.1520407805	-3.6265469950
H	0	0.6536703377	-0.9797350817	-2.8100482460
C	0	-1.8141155628	-3.2473999086	-3.4497728698
H	0	-2.3397507676	-4.9050431496	-2.1603292094
H	0	-1.0593135213	-1.5239711852	-4.5155838817
H	0	-2.5774539709	-3.4782360624	-4.1967012506

S2-PM-TSnSi

0 1

O	0	3.3315896186	0.1867138049	0.4321832164
C	0	4.7476186050	0.0222565425	0.4874784631
O	0	3.1648295784	-1.7092874157	-0.7634238004
C	0	2.6494719931	-0.7835242747	-0.1791557423
C	0	1.1728364901	-0.5338264686	-0.1450635901
C	0	0.4151872867	-0.7148725357	-1.3304042304
O	0	0.7119960768	-2.2795025797	0.7876064182
N	0	0.0961141218	-2.9273177550	-0.1498074235
C	0	0.8965763569	-3.8966118119	-0.8992073030
C	0	-0.9103821229	-2.2434329514	-0.7565462302
H	0	5.0031516091	-0.8941419451	1.0395653601
H	0	5.1717768042	-0.0432573642	-0.5253015746
H	0	5.1346716657	0.9037928857	1.0115300027
H	0	0.9119333571	-1.1139586604	-2.2174643497
H	0	-1.2394490292	-2.6832394707	-1.7026022733
H	0	1.6754954409	-3.3764956828	-1.4779051298
H	0	0.2414505926	-4.4914703048	-1.5486646965
H	0	1.3904897876	-4.5501296337	-0.1690524934
N	0	0.6440606375	0.4804099435	0.6997682223
C	0	-0.3545558383	1.3808286816	0.1122506890
C	0	0.8150433410	0.3882066396	2.0755949064
H	0	-1.3673005495	1.1300302746	0.4652195401
S	0	-0.4003119899	0.8283275639	-1.6764699899
C	0	-0.1096108974	2.9110027112	0.2561578021
H	0	0.1331829821	1.0687686631	2.6234442655
O	0	1.5903433751	-0.3511937787	2.6268795620
O	0	0.5340323974	1.5995411189	-2.5141561846
O	0	-1.7912055968	0.7161545587	-2.1284558413
C	0	-1.0861696030	3.6381629765	-0.6926851627
C	0	1.3476123442	3.2799806334	-0.0625500851
C	0	-0.4428897672	3.3655714820	1.6923871061
H	0	-2.1279832316	3.3332801376	-0.5051520532
H	0	-1.0158994813	4.7234385201	-0.5255441880
H	0	-0.8551368450	3.4461442008	-1.7480105742
H	0	1.4972818481	4.3589229911	0.0984151914
H	0	2.0432758271	2.7342232221	0.5916137605
H	0	1.6002432675	3.0408475986	-1.1022047124
H	0	0.3128041857	3.0461158246	2.4228791182
H	0	-0.4691411721	4.4656179654	1.7226980413
H	0	-1.4284457414	2.9972616036	2.0203723970
C	0	-1.9946596113	-1.6054178001	0.0292993608
C	0	-3.1712448162	-1.2466700821	-0.6505681277
C	0	-1.9190087942	-1.3769998150	1.4175972035
C	0	-4.2317477297	-0.6450126738	0.0245252446
H	0	-3.2432829288	-1.4151362962	-1.7253875179
C	0	-2.9876102103	-0.7842264357	2.0905854476
H	0	-1.0214311364	-1.6692895647	1.9576795194
C	0	-4.1415901540	-0.4036711501	1.3976003975
H	0	-5.1298911228	-0.3595087005	-0.5271939168
H	0	-2.9151203231	-0.6173763740	3.1680265189
H	0	-4.9702968982	0.0716169816	1.9278244366

S2-PM-TSxRe

0 1

O	0	-1.7542004941	2.5641679937	-0.4518978398
C	0	-2.7497089229	3.5651388635	-0.6588826777
O	0	-3.3314473242	0.9671918959	-0.6296258272
C	0	-2.1966058995	1.2988421726	-0.3971753925
C	0	-1.0798408975	0.3459812363	-0.0936497817
C	0	-0.8604349982	-0.7626179304	-0.9453119243
N	0	-1.3953951339	-1.7518920468	1.3785543402
O	0	-1.9885460001	-0.6115877044	1.4313369731
C	0	-0.2664574726	-1.9665032949	2.2938004891
C	0	-1.4709432669	-2.4196021591	0.1974469881
H	0	-3.2940871624	3.3867323608	-1.5979749220
H	0	-3.4688332048	3.5627046633	0.1735649371
H	0	-2.2165395472	4.5224386725	-0.6977084682
H	0	-1.4626319115	-0.9090383314	-1.8415410703
H	0	-0.6923095644	-3.1800834818	0.0889332438
H	0	-0.3300768109	-2.9752726878	2.7259464129
H	0	-0.3609826943	-1.2142096547	3.0844016171
H	0	0.6875520713	-1.8586057263	1.7616314114
N	0	0.1340367692	0.8627297989	0.4713170100
C	0	1.2870555296	0.7059304131	-0.4215629314
C	0	0.0809095631	1.6602059271	1.6033574262
H	0	1.1621560970	1.3803040961	-1.2868544972
S	0	0.8988619186	-0.9427226643	-1.2194224274
C	0	2.7417413983	0.8338468065	0.0932424241
H	0	1.0725948968	2.0464316589	1.9011775387
O	0	-0.9284993712	1.9054511491	2.2167023541
O	0	1.4568566647	-2.0558676042	-0.4202244554
O	0	1.1941921316	-0.8794658594	-2.6556817964
C	0	3.0995909255	2.3271782879	0.2593150397
C	0	3.6744510927	0.2747937367	-1.0061345244
C	0	2.9918014331	0.0576963416	1.3962140318
H	0	2.5390839208	2.8316861955	1.0571924251
H	0	4.1687256999	2.4193261124	0.5043751227
H	0	2.9217419892	2.8785149692	-0.6772896004
H	0	4.7190647494	0.4774339965	-0.7270123633
H	0	3.5618060899	-0.8104548504	-1.1265292695
H	0	3.4825423500	0.7481823686	-1.9806357179
H	0	4.0431303937	0.1839058811	1.6970093752
H	0	2.3673836568	0.4095230965	2.2291287801
H	0	2.8046129700	-1.0133591281	1.2497274490
C	0	-2.7493004348	-2.7438182654	-0.4724408115
C	0	-2.7336174635	-3.8012114203	-1.4006878495
C	0	-3.9557193853	-2.0644555541	-0.2286182008
C	0	-3.8974766697	-4.1798060392	-2.0687903717
H	0	-1.7979967790	-4.3326275136	-1.5954622252
C	0	-5.1188621282	-2.4578270567	-0.8906397905
H	0	-3.9655704183	-1.2200449796	0.4558572551
C	0	-5.0968042449	-3.5091858704	-1.8120227082
H	0	-3.8688838997	-5.0029487800	-2.7865252978
H	0	-6.0512536487	-1.9238415703	-0.6933567351
H	0	-6.0114679026	-3.8027933411	-2.3326753576

S2-PM-TSxSi

0 1

O	0	0.0814428622	2.8893428647	-0.0510959159
C	0	0.3568097710	4.2475783955	-0.3877886642
O	0	1.6474438920	2.2181908590	-1.5251854772
C	0	0.8413651913	1.9658518486	-0.6610534865
C	0	0.5539232479	0.5958668387	-0.1703215265

C	0	0.7128067897	-0.5331405644	-1.0087053519
N	0	2.5611069901	-0.8434261860	0.7367690971
O	0	2.4678988728	0.4278401909	0.7600707601
C	0	2.2622956651	-1.5783263957	1.9747289354
C	0	2.4412416402	-1.4403548951	-0.4877357054
H	0	0.1953511993	4.4237166199	-1.4617689815
H	0	1.3991152372	4.4987166124	-0.1423355318
H	0	-0.3323589147	4.8548174689	0.2106308365
H	0	0.8674577224	-0.4039212425	-2.0803083012
H	0	2.2201301505	-2.5085853659	-0.4072602605
H	0	3.1156513686	-2.2222198712	2.2347572428
H	0	2.1148313435	-0.8236047947	2.7551616780
H	0	1.3634316768	-2.1962779959	1.8411500881
N	0	-0.3931927581	0.3695423117	0.8747297709
C	0	-1.4792397622	-0.5435998470	0.5398226135
C	0	-0.2746393225	0.8723397872	2.1622663004
H	0	-1.7263479647	-1.1701963010	1.4083333332
S	0	-0.5907954973	-1.7209248298	-0.6107209109
C	0	-2.7697688240	0.1059522435	-0.0200095395
H	0	-1.0797567667	0.4687309773	2.8195947197
O	0	0.5783678899	1.6269991317	2.5499286999
O	0	-1.3350995209	-2.0542107790	-1.8332137530
O	0	-0.0864753601	-2.8211685412	0.2348350154
C	0	-2.5292267497	0.8566349313	-1.3404366584
C	0	-3.2816519466	1.1105198601	1.0285519664
C	0	-3.8165087507	-1.0065399763	-0.2083822488
H	0	-2.1564399570	0.1889208397	-2.1274547220
H	0	-3.4798977825	1.2904462875	-1.6872500292
H	0	-1.8228583794	1.6857522986	-1.1986502668
H	0	-4.2415115161	1.5309528045	0.6913861257
H	0	-3.4540826490	0.6314100214	2.0058404601
H	0	-2.5795233897	1.9460393830	1.1641588849
H	0	-4.0187357130	-1.5235598901	0.7442628581
H	0	-4.7645480788	-0.5710794917	-0.5590778203
H	0	-3.4863664962	-1.7493954109	-0.9462484966
C	0	3.3227506305	-1.0926831994	-1.6305313129
C	0	3.4974872686	-2.0747848145	-2.6216663433
C	0	3.9762523581	0.1431965595	-1.7687240924
C	0	4.3148052630	-1.8346865372	-3.7261075086
H	0	2.9901469314	-3.0382322988	-2.5210310771
C	0	4.8039805333	0.3714548621	-2.8682636614
H	0	3.8140127944	0.9200459962	-1.0260162095
C	0	4.9745488756	-0.6089062990	-3.8502528433
H	0	4.4408524650	-2.6083482961	-4.4870702055
H	0	5.3092203984	1.3351780331	-2.9651362955
H	0	5.6165230606	-0.4164451937	-4.7131894685

S2-PP-PnRe

0 1

O	0	0.8019853187	2.5427861936	0.5569661069
C	0	1.2710643781	3.7337321940	1.1977311621
O	0	2.8182354731	1.5907844579	0.8413727170
C	0	1.6863367956	1.5495553823	0.4438950856
C	0	1.0507107728	0.2828247338	-0.1783030181
C	0	0.7718546272	-0.7833352716	0.8824537615
O	0	1.9758939815	-0.3212095728	-1.0635076464
N	0	2.3060869361	-1.6316337759	-0.6141822864
C	0	1.1705869615	-2.1060947813	0.1637163312
H	0	2.1140546983	4.1595608993	0.6354751790
H	0	1.5977057828	3.5083954210	2.2229447059
H	0	0.4224840526	4.4269708134	1.2071315123
H	0	1.4051515458	-0.6414412198	1.7667586912
H	0	1.5322490576	-2.7992684603	0.9318910808

N	0	-0.2249116775	0.5689350959	-0.8641972019
C	0	-1.4101990693	0.6350194344	0.0051620808
C	0	-0.0908188391	1.4112876875	-1.9615532797
H	0	-1.4409138383	1.6112139059	0.5131228983
S	0	-0.9115026236	-0.4475860882	1.4642223098
C	0	-2.8277826444	0.3295926261	-0.5494434110
H	0	-1.0537454432	1.6913119269	-2.4228023088
O	0	0.9754386826	1.7947924764	-2.3790060407
O	0	-1.6669238707	-1.6995188482	1.5972354456
O	0	-0.7981415170	0.4605549069	2.6125726344
C	0	-3.3004623136	1.4616402816	-1.4902731785
C	0	-3.7917354836	0.3394715143	0.6598715384
C	0	-2.8928543386	-1.0075359793	-1.2922018761
H	0	-2.8735775270	1.3837439578	-2.4992566298
H	0	-4.3923576077	1.3921718659	-1.6077750668
H	0	-3.0723128231	2.4603702993	-1.0846617395
H	0	-4.8228730426	0.2129293470	0.2984374359
H	0	-3.5844212398	-0.4725102803	1.3666352942
H	0	-3.7407558298	1.2980569762	1.2010122859
H	0	-2.6275031481	-1.8487130389	-0.6417626942
H	0	-3.9143742922	-1.1714645492	-1.6687949822
H	0	-2.2098850054	-1.0149968634	-2.1518249575
C	0	3.6244672147	-1.7551197094	-0.1192287337
C	0	4.5670896661	-0.7268143597	-0.2661732223
C	0	4.0203746056	-2.9807962528	0.4476410605
C	0	5.8740470985	-0.9192057812	0.1819203284
H	0	4.2636548307	0.2162902934	-0.7113982669
C	0	5.3299684059	-3.1531350241	0.8966249737
H	0	3.3157797729	-3.8119774685	0.5097656748
C	0	6.2663043932	-2.1239858050	0.7712314753
H	0	6.5945087374	-0.1051436355	0.0708451038
H	0	5.6194963365	-4.1099406438	1.3379775967
H	0	7.2914176498	-2.2628017146	1.1208728131
C	0	0.1589490006	-2.8314215012	-0.7054848877
C	0	-0.6722504987	-3.8069557709	-0.1415265653
C	0	0.1111924611	-2.6081570710	-2.0875117320
C	0	-1.5572094681	-4.5316995978	-0.9410981260
H	0	-0.6390986960	-3.9902604103	0.9334751284
C	0	-0.7682970682	-3.3391953620	-2.8885621107
H	0	0.7736295636	-1.8666648266	-2.5334363297
C	0	-1.6090390458	-4.2981865772	-2.3181250499
H	0	-2.2036554718	-5.2859772645	-0.4867287985
H	0	-0.7947066450	-3.1581984950	-3.9657653741
H	0	-2.2971060930	-4.8693590506	-2.9459502371

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O	0	-0.5534379257	-2.5187766921	-0.1777986350
C	0	-0.7978681444	-3.8544719704	-0.6209732676
O	0	-2.6998746165	-1.9756416275	-0.5760243371
C	0	-1.5914254655	-1.6940606872	-0.2072877226
C	0	-1.2086549572	-0.2575342919	0.2069803446
C	0	-1.3139271493	0.7281162405	-0.9810889792
O	0	-2.2012700791	0.1868835498	1.0789406706
N	0	-2.0758611778	1.6147703131	1.0551081826
C	0	-1.9846155131	1.9877439187	-0.3569178656
H	0	-1.5401812182	-4.3417873210	0.0275491501
H	0	-1.1716370560	-3.8501731663	-1.6551262349
H	0	0.1656753133	-4.3731032636	-0.5614065779
H	0	-1.9137251366	0.3075656351	-1.7947867552
H	0	-2.9911279660	2.0599848224	-0.8110865746
N	0	0.1400801241	-0.1364729695	0.7818983956
C	0	1.1595970677	0.6176206962	0.0550092208

C	0	0.3259875715	-0.7132679168	2.0203745498
H	0	1.1983782533	1.6697904035	0.3824094752
S	0	0.3837101936	0.7673088943	-1.6257799295
C	0	2.6141824047	0.0517277578	-0.0094629236
H	0	1.3040868813	-0.4635978045	2.4751117424
O	0	-0.4951321981	-1.4079351762	2.5726790762
O	0	0.5076137338	-0.5062931672	-2.3551736394
O	0	0.7656996322	2.0239103388	-2.2692189419
C	0	3.3365394240	0.6673207981	-1.2294093109
C	0	2.6250249981	-1.4793139954	-0.1305158385
C	0	3.4001530652	0.5074164303	1.2382062100
H	0	3.2665860690	1.7650963029	-1.2356296962
H	0	4.4007741431	0.3921463484	-1.1881778306
H	0	2.9313801678	0.2936690914	-2.1786788605
H	0	3.6628138900	-1.8241805108	-0.2570378844
H	0	2.2165339411	-1.9728601706	0.7623376254
H	0	2.0347623219	-1.8050010689	-0.9959097835
H	0	3.0327631366	0.0658866773	2.1741297148
H	0	4.4533209152	0.2050992703	1.1336468200
H	0	3.3753836422	1.6036933285	1.3439941634
C	0	-3.0301181605	2.1947697445	1.9122466399
C	0	-3.3482147019	1.5416368679	3.1176026914
C	0	-3.6280679023	3.4290319408	1.6107983716
C	0	-4.2488622012	2.1270332823	4.0037469174
H	0	-2.8861065823	0.5795267848	3.3372189473
C	0	-4.5195523862	4.0067205676	2.5191204071
H	0	-3.3907874230	3.9518125374	0.6854982751
C	0	-4.8379694449	3.3636777598	3.7155881730
H	0	-4.4928199899	1.6084028198	4.9341243000
H	0	-4.9733399484	4.9706291620	2.2762226904
H	0	-5.5402958006	3.8183533660	4.4174280651
C	0	-1.2628225006	3.3047716645	-0.5542110153
C	0	-1.4809578901	4.0343369675	-1.7275798635
C	0	-0.3659676267	3.7941624849	0.4021328352
C	0	-0.7914202114	5.2243675385	-1.9578057680
H	0	-2.1851692601	3.6596404970	-2.4750870490
C	0	0.3213024769	4.9883270423	0.1744580419
H	0	-0.2294220015	3.2421316607	1.3331376770
C	0	0.1163630168	5.7022363214	-1.0085465323
H	0	-0.9610715637	5.7801978400	-2.8826663794
H	0	1.0153320993	5.3661205971	0.9290779722
H	0	0.6564066662	6.6348441656	-1.1875295001

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O	0	-1.1148294373	2.5448173444	-0.6560880785
C	0	-1.7349963286	3.7612184507	-1.0866317996
O	0	-3.1163720200	1.7422878438	0.0001503974
C	0	-1.9267520199	1.6376489501	-0.0972095749
C	0	-1.1241312593	0.3786460664	0.2816563547
C	0	-1.0795069794	-0.6357735016	-0.8808652204
N	0	-1.6332159008	-1.6659081804	1.1690521149
O	0	-1.8490861627	-0.2759134170	1.3002259066
C	0	-1.6636271662	-1.9323330476	-0.2649707736
H	0	-2.5411734289	3.5497115636	-1.8037634247
H	0	-2.1565156784	4.2946548660	-0.2225322569
H	0	-0.9440468560	4.3558401031	-1.5577096013
H	0	-1.6025200736	-0.3031782174	-1.7832390696
H	0	-0.9866936777	-2.7628596887	-0.4923152001
N	0	0.2552243118	0.6953064088	0.6967493995
C	0	1.3063590393	0.5641836779	-0.3067406050
C	0	0.3406374357	1.5556622479	1.7749720453
H	0	1.2601896393	1.4059123094	-1.0188109488

S	0	0.6755561469	-0.8208216833	-1.3745754762
C	0	2.7827375768	0.3559509402	0.1426237993
H	0	1.3751982636	1.7810925117	2.0856244237
O	0	-0.6290832313	2.0067030366	2.3407188265
O	0	1.1479445530	-2.1382529987	-0.9152790633
O	0	0.8327323181	-0.4266401825	-2.7783748859
C	0	3.4179253315	1.7169015955	0.5060242583
C	0	3.5843858011	-0.1770231859	-1.0684982823
C	0	2.8843467147	-0.6303042893	1.3149292377
H	0	3.0221988642	2.1636377406	1.4270563160
H	0	4.4984870154	1.5775600058	0.6605241766
H	0	3.2886865924	2.4458357119	-0.3097538923
H	0	4.6541346527	-0.1792137437	-0.8133792950
H	0	3.3015787470	-1.2033196558	-1.3319096469
H	0	3.4483137529	0.4592278462	-1.9563747176
H	0	3.9443633931	-0.8043937837	1.5552171816
H	0	2.3940688560	-0.2537543274	2.2227519533
H	0	2.4219124956	-1.5940842928	1.0669786931
C	0	-0.6200931770	-2.1617093970	2.0201974466
C	0	-0.0219097933	-3.4095504266	1.7821148962
C	0	-0.2711433736	-1.4442006141	3.1784224917
C	0	0.9417554091	-3.9017755914	2.6631365319
H	0	-0.2954120098	-4.0001575883	0.9085618227
C	0	0.6910418541	-1.9517010512	4.0498230084
H	0	-0.7586016765	-0.4926205260	3.3824729001
C	0	1.3133058139	-3.1781094567	3.7983187362
H	0	1.4066691525	-4.8676232181	2.4514175696
H	0	0.9543219294	-1.3761986704	4.9409904756
H	0	2.0686397435	-3.5694424094	4.4827775566
C	0	-3.0475324395	-2.2526855660	-0.7919641545
C	0	-3.2019843775	-3.3143169150	-1.6909601496
C	0	-4.1676756671	-1.4935612669	-0.4212072487
C	0	-4.4599085548	-3.6220361030	-2.2172067495
H	0	-2.3310385324	-3.9096313014	-1.9797798040
C	0	-5.4229350844	-1.8044906829	-0.9462999511
H	0	-4.0533714157	-0.6558748132	0.2679980725
C	0	-5.5735517655	-2.8668855964	-1.8440179838
H	0	-4.5686556268	-4.4559077954	-2.9147408407
H	0	-6.2910667791	-1.2098156113	-0.6522825957
H	0	-6.5590858202	-3.1056516242	-2.2509933421

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O	0	1.3819215457	1.7268160106	-1.4617332940
C	0	2.1879999264	2.7288956385	-2.0850774696
O	0	2.9634917209	1.3921811178	0.1175386506
C	0	1.8648568491	1.2142446670	-0.3237099737
C	0	0.8444966072	0.2095991762	0.2607069610
C	0	0.7072146029	-1.0064529605	-0.6880705487
N	0	2.2169438299	-1.3864174823	1.0477965012
O	0	1.3107044907	-0.3512819472	1.4636437818
C	0	1.5229118525	-2.1219052921	-0.0111921455
H	0	3.1921911115	2.3383984784	-2.3050297821
H	0	2.2789428984	3.5992667735	-1.4187041996
H	0	1.6697832480	3.0058101137	-3.0105040207
H	0	1.0033308940	-0.7836891500	-1.7174467066
H	0	0.8259721954	-2.8723019348	0.4045342126
N	0	-0.4630917332	0.7892912477	0.5160849760
C	0	-1.5257326320	-0.2030099079	0.6222200774
C	0	-0.5300166385	2.1071675514	0.9227657473
H	0	-1.3473659988	-0.8466558862	1.4997889716
S	0	-1.0861082036	-1.3656359476	-0.7775372268
C	0	-3.0165607533	0.2277344540	0.6057242389

H	0	-1.5458363581	2.4312746992	1.2030809919
O	0	0.4244432052	2.8484761184	0.9606263899
O	0	-1.5750360030	-0.8581054471	-2.0664798239
O	0	-1.3611235510	-2.7505115774	-0.3641605249
C	0	-3.3282090892	1.2655765349	-0.4876107166
C	0	-3.4125001504	0.7447933977	2.0052789653
C	0	-3.8685644631	-1.0347562468	0.3398354713
H	0	-2.9658767367	0.9220161526	-1.4647259964
H	0	-4.4183180250	1.4042776474	-0.5494535921
H	0	-2.8894332737	2.2519451974	-0.2849654545
H	0	-4.4845119630	0.9943211508	2.0106761096
H	0	-3.2441304624	-0.0293888987	2.7701103928
H	0	-2.8668210788	1.6454626660	2.3173373335
H	0	-3.6080045130	-1.8564304300	1.0231297462
H	0	-4.9292869175	-0.7861275811	0.4907365971
H	0	-3.7527940111	-1.3975682379	-0.6901612747
C	0	2.7598274014	-2.0422887725	2.1635306892
C	0	3.1184561773	-1.2836013255	3.2930424502
C	0	2.9995258486	-3.4261106443	2.1508754170
C	0	3.7045251070	-1.9092859299	4.3898632091
H	0	2.9344739047	-0.2099087517	3.2850282548
C	0	3.6040895405	-4.0341206067	3.2545929696
H	0	2.7364760824	-4.0286058456	1.2825840101
C	0	3.9551383054	-3.2867672848	4.3793537577
H	0	3.9761284485	-1.3108037408	5.2629846682
H	0	3.7922246981	-5.1102622500	3.2302386086
H	0	4.4208800855	-3.7703112466	5.2406804436
C	0	2.4733610210	-2.7961271346	-0.9751669750
C	0	2.0381126145	-3.9256229861	-1.6790755704
C	0	3.7489607428	-2.2719719332	-1.2175585057
C	0	2.8761151015	-4.5326062391	-2.6174776783
H	0	1.0355663056	-4.3207396745	-1.4936038988
C	0	4.5862556378	-2.8853029652	-2.1522502003
H	0	4.0757782440	-1.3901086664	-0.6628845702
C	0	4.1531688623	-4.0150831266	-2.8531221565
H	0	2.5314629233	-5.4136641529	-3.1639161856
H	0	5.5844230948	-2.4791604749	-2.3327906833
H	0	4.8112622407	-4.4929040034	-3.5827608391

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O	0	3.3576809815	0.8611451768	-1.1293011435
C	0	4.7442214454	0.8622147916	-1.4548552327
O	0	3.7293965851	-0.7886364972	0.3555192991
C	0	2.9615485249	-0.0595718083	-0.2372089001
C	0	1.5026302546	-0.0135258523	-0.0111426527
C	0	0.9230298981	-0.4869230061	1.1768674032
O	0	1.3753385840	-2.2962066078	-0.8513769288
N	0	0.9189265115	-2.7617967379	0.2316839877
C	0	-0.1516646326	-2.0880146809	0.7832649908
H	0	5.0366854464	-0.1021672479	-1.8969209392
H	0	5.3579059995	1.0374938529	-0.5585417161
H	0	4.8854997818	1.6701563208	-2.1826988410
H	0	1.5864340516	-0.8601096495	1.9612338284
H	0	-0.4086008104	-2.4313413765	1.7864477167
N	0	0.6871650036	0.9530775274	-0.6776003911
C	0	0.0806864068	1.9001279681	0.2614250038
C	0	0.6016704322	0.9878530253	-2.0566905284
H	0	0.8659565484	2.5725774116	0.6452888439
S	0	-0.1542826251	0.8235905674	1.8035755456
C	0	-1.1605360659	2.7457916471	-0.1019405459
H	0	0.0206585308	1.8513459504	-2.4269630358
O	0	1.0941410917	0.1660710924	-2.7923699633

O	0	-1.5311528631	0.3568689357	2.0315611525
O	0	0.5556346648	1.4960316405	2.8995403363
C	0	-0.7475811779	3.9070222761	-1.0329649600
C	0	-1.6671245107	3.3976271399	1.2070861543
C	0	-2.2846430141	1.9047294962	-0.7239544449
H	0	-0.4222740372	3.5833128241	-2.0301051734
H	0	-1.6084888750	4.5779166958	-1.1755781929
H	0	0.0678075793	4.4980726761	-0.5868228481
H	0	-2.4533604539	4.1274016403	0.9637287871
H	0	-2.0954106648	2.6581816488	1.8949936863
H	0	-0.8588583726	3.9314313355	1.7305680883
H	0	-2.5645458355	1.0716738252	-0.0672439808
H	0	-3.1732487651	2.5368097857	-0.8753859300
H	0	-2.0080111231	1.4843301917	-1.6996002293
C	0	-1.3380372911	-1.8007737247	-0.0661456546
C	0	-2.5979476445	-1.8265716763	0.5603852412
C	0	-1.2767237945	-1.5851434211	-1.4542973403
C	0	-3.7655131262	-1.6418671024	-0.1753647990
H	0	-2.6583576225	-1.9765776011	1.6390688862
C	0	-2.4522096632	-1.4097939072	-2.1878708307
H	0	-0.3139011226	-1.5566984925	-1.9565288593
C	0	-3.6972268017	-1.4320408805	-1.5565806200
H	0	-4.7327162457	-1.6607680040	0.3319403478
H	0	-2.3842291710	-1.2442978731	-3.2656972309
H	0	-4.6121502485	-1.2845151588	-2.1355094640
C	0	1.7125364557	-3.6622466026	1.0112676079
C	0	3.0900151431	-3.7374940290	0.7700966636
C	0	1.1030087507	-4.4936705525	1.9627492412
C	0	3.8583384974	-4.6339634128	1.5093207297
H	0	3.5332921106	-3.0653780927	0.0396128842
C	0	1.8873729256	-5.3828672938	2.6977501626
H	0	0.0219316876	-4.4749311246	2.1054487124
C	0	3.2654730300	-5.4545573354	2.4755676066
H	0	4.9355835158	-4.6833131270	1.3363084147
H	0	1.4140936073	-6.0332549378	3.4364671664
H	0	3.8765106427	-6.1527072093	3.0518638184

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O	0	3.3090841170	0.4510580614	0.7511408990
C	0	4.7205401734	0.3979682723	0.9451624673
O	0	3.4376880024	-1.3468672659	-0.5919371096
C	0	2.7814491134	-0.5191797657	-0.0029040906
C	0	1.2987215106	-0.3864007975	-0.1095307799
C	0	0.6386408553	-0.6196986886	-1.3360294064
O	0	0.8767321888	-2.3232646326	0.7051476030
N	0	0.3027356456	-2.8851632249	-0.3033218477
C	0	-0.6865345309	-2.1447709600	-0.8939099861
H	0	4.9999338382	-0.5316863373	1.4628890561
H	0	5.2486777721	0.4391066447	-0.0188708315
H	0	4.9746901371	1.2677269131	1.5621129656
H	0	1.2129247941	-1.0117312818	-2.1790407155
H	0	-0.9754924794	-2.4942669507	-1.8866635526
N	0	0.6105845109	0.5394986968	0.7170035812
C	0	-0.3885798419	1.3921786255	0.0605906758
C	0	0.6447947225	0.3987525457	2.1000354144
H	0	-1.4100220065	1.0749686069	0.3216632998
S	0	-0.2436521910	0.8780291997	-1.7371952581
C	0	-0.2495439403	2.9292644387	0.2540506168
H	0	-0.1295332312	1.0169537835	2.5961061476
O	0	1.3995440601	-0.3217549787	2.7021372163
O	0	0.7083810274	1.7246435185	-2.4741789907
O	0	-1.5767829672	0.6795080416	-2.3160086950

C	0	-1.1911204860	3.6192159837	-0.7554756628
C	0	1.2028163790	3.3937394254	0.0634468782
C	0	-0.7220313630	3.3227520715	1.6688647293
H	0	-2.2240779802	3.2492295577	-0.6566011869
H	0	-1.2002941013	4.7027368820	-0.5640936157
H	0	-0.8670204092	3.4653312344	-1.7926035479
H	0	1.2727675745	4.4734777410	0.2674855387
H	0	1.8765480867	2.8675238809	0.7554540667
H	0	1.5508548970	3.2057611808	-0.9589521242
H	0	-0.0092879250	3.0230600109	2.4493235578
H	0	-0.8130929948	4.4183515995	1.7243070329
H	0	-1.7077442838	2.8911372942	1.9068147693
C	0	-1.8089199704	-1.6053311346	-0.0871949491
C	0	-2.9818749672	-1.2281923357	-0.7658687186
C	0	-1.7767652839	-1.4967244391	1.3173982711
C	0	-4.0770173686	-0.7183784055	-0.0702044795
H	0	-3.0245056420	-1.3110153342	-1.8514545513
C	0	-2.8795138259	-0.9958015469	2.0092494768
H	0	-0.8839617679	-1.8059333142	1.8555418154
C	0	-4.0273569595	-0.5901927177	1.3203858020
H	0	-4.9720926721	-0.4183879544	-0.6193893545
H	0	-2.8375157311	-0.9195466560	3.0984119540
H	0	-4.8830490158	-0.1858102887	1.8663267454
C	0	0.9789107679	-3.9314610110	-1.0040060735
C	0	2.3316476352	-4.1758153019	-0.7393032139
C	0	0.2701973584	-4.7461923711	-1.9001343326
C	0	2.9775260580	-5.2167817252	-1.4036759818
H	0	2.8582406957	-3.5279259258	-0.0443220086
C	0	0.9329672687	-5.7794277808	-2.5633775092
H	0	-0.7992636547	-4.5995538229	-2.0570681095
C	0	2.2884298481	-6.0174790782	-2.3206436604
H	0	4.0368276149	-5.3973132681	-1.2077616903
H	0	0.3790834237	-6.4116335193	-3.2609307070
H	0	2.8038639541	-6.8294506855	-2.8381848695

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O	0	0.5422301066	3.0953504212	-0.8816794090
C	0	0.1203996381	4.4250569250	-1.1796283851
O	0	-1.6084635294	2.4696800433	-0.6508709095
C	0	-0.4300339627	2.2275743040	-0.5672344275
C	0	0.1279718014	0.8948472543	-0.1837240235
C	0	-0.4094223743	-0.2804686978	-0.7458358376
N	0	-0.9257204102	-0.4970673643	1.7796175922
O	0	-0.9244625127	0.7800018902	1.6539428357
C	0	-1.5173715660	-1.1889158296	0.7615491872
H	0	-0.5832707191	4.4320264385	-2.0251212232
H	0	-0.3735204247	4.8716617608	-0.3039212587
H	0	1.0295218290	4.9847568597	-1.4294284919
H	0	-1.1648413555	-0.2291372835	-1.5296174708
H	0	-1.2316682571	-2.2390574845	0.7198625723
N	0	1.5031014116	0.7757645596	0.1796986279
C	0	2.2528977128	-0.1684311890	-0.6583978173
C	0	2.0584119627	1.6429931799	1.1041075050
H	0	2.4190234621	0.2875086784	-1.6495186184
S	0	0.9290514958	-1.4234940931	-1.0926266058
C	0	3.5784173412	-0.8065969084	-0.1714745778
H	0	3.1460165542	1.5003978171	1.2245079108
O	0	1.4318489533	2.4627177171	1.7320750532
O	0	0.9171378724	-2.5569159766	-0.1459691117
O	0	0.9929730789	-1.6971591444	-2.5332814835
C	0	4.7385297011	0.1973402528	-0.3507916586
C	0	3.8913115871	-2.0008767814	-1.1043687826

C	0	3.4924586228	-1.3050645312	1.2792451771
H	0	4.6664426672	1.0831599632	0.2938157395
H	0	5.6886792038	-0.3022812693	-0.1076348187
H	0	4.8000083076	0.5442346287	-1.3944041955
H	0	4.9031169318	-2.3710587434	-0.8827851567
H	0	3.1888494099	-2.8305381155	-0.9569089860
H	0	3.8603054288	-1.7070537421	-2.1645212951
H	0	4.4193080299	-1.8409564286	1.5353388717
H	0	3.3748714152	-0.4893917548	2.0045610343
H	0	2.6494674206	-1.9945457753	1.4094307235
C	0	-2.8975308938	-0.9141007865	0.3083407475
C	0	-3.5646768899	-1.9641846398	-0.3507529189
C	0	-3.5656681526	0.3087045728	0.4969035171
C	0	-4.8738832885	-1.8049524569	-0.8024673386
H	0	-3.0498094949	-2.9166775641	-0.5037943210
C	0	-4.8806765535	0.4553602761	0.0552413899
H	0	-3.0407447031	1.1375925390	0.9640797594
C	0	-5.5382478933	-0.5923881764	-0.5962896157
H	0	-5.3775778644	-2.6303252033	-1.3108984787
H	0	-5.3913252369	1.4087833114	0.2089177816
H	0	-6.5645409626	-0.4627697050	-0.9481259859
C	0	0.0016019606	-1.0771211428	2.7091427456
C	0	0.7330340257	-0.2019289923	3.5242668158
C	0	0.1386762680	-2.4632802918	2.8581049523
C	0	1.6294943524	-0.7203015406	4.4568182201
H	0	0.5945412414	0.8700947991	3.3992993671
C	0	1.0467216655	-2.9660104124	3.7899444598
H	0	-0.4393788591	-3.1570906367	2.2513769183
C	0	1.7981058449	-2.1020033444	4.5908938267
H	0	2.2018603126	-0.0337724535	5.0850330650
H	0	1.1616602643	-4.0474712604	3.8901672428
H	0	2.5029667027	-2.5039726826	5.3218348138

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O	0	-1.2011401591	2.7205771345	-0.6885454981
C	0	-1.0308035589	4.0449211026	-1.1888939944
O	0	0.9714506772	2.2928120742	-1.1032753943
C	0	-0.0956444267	1.9608514411	-0.6442069565
C	0	-0.3523190162	0.6417900903	-0.0148045080
C	0	0.3422680393	-0.5126463931	-0.4258590660
N	0	1.2903071309	-0.1330659868	1.9468643731
O	0	1.0400234459	1.0837990100	1.6503228494
C	0	1.8068087265	-0.8972696180	0.9339855066
H	0	-0.6541426122	4.0269548466	-2.2223865341
H	0	-0.3171222056	4.6000793733	-0.5625019243
H	0	-2.0200480448	4.5154919174	-1.1465456113
H	0	0.9334663958	-0.5056055882	-1.3417812934
H	0	1.7338821035	-1.9680136150	1.1196180330
N	0	-1.5850387084	0.3507657338	0.6289777306
C	0	-2.2422807284	-0.8839789873	0.2106271684
C	0	-2.1124148440	1.1053204103	1.6652514364
H	0	-2.6421163821	-1.4152100737	1.0857803368
S	0	-0.7702619284	-1.9293321389	-0.2889449555
C	0	-3.3440249087	-0.7237538642	-0.8679443306
H	0	-3.0112427467	0.6154269902	2.1009522333
O	0	-1.6595208980	2.1428391970	2.0762584180
O	0	-0.9009576129	-2.5525063334	-1.6143623466
O	0	-0.4437956529	-2.7810234448	0.8669441850
C	0	-2.7999727147	-0.0988740062	-2.1634393284
C	0	-4.4377343740	0.2016047967	-0.3026013947
C	0	-3.9559511875	-2.1106023065	-1.1356489505
H	0	-2.0278766292	-0.7271014600	-2.6246728387

H	0	-3.6234558163	0.0132088488	-2.8856368818
H	0	-2.3894139935	0.9025557755	-1.9719698106
H	0	-5.2708536135	0.2560601005	-1.0199729781
H	0	-4.8437678948	-0.1754117388	0.6498881318
H	0	-4.0673472560	1.2256331501	-0.1482167533
H	0	-4.3714311228	-2.5431186806	-0.2104347112
H	0	-4.7795293339	-2.0197746394	-1.8601640678
H	0	-3.2141273286	-2.8076346600	-1.5459933426
C	0	3.0245645096	-0.4996692145	0.1899189516
C	0	3.7578189865	-1.5372478162	-0.4154429130
C	0	3.4775822858	0.8241967353	0.0582008604
C	0	4.9250978616	-1.2643184767	-1.1274454891
H	0	3.4096348496	-2.5694766714	-0.3200632609
C	0	4.6548847267	1.0881012914	-0.6420464072
H	0	2.8932999877	1.6336898199	0.4871493892
C	0	5.3798330814	0.0526739316	-1.2392520609
H	0	5.4830528031	-2.0817474952	-1.5899764493
H	0	4.9997146475	2.1204464648	-0.7355340242
H	0	6.2942971980	0.2718045890	-1.7956333998
C	0	0.6999696433	-0.6737986110	3.1386335159
C	0	0.8545256847	-2.0177674444	3.5052202059
C	0	0.0089974393	0.2137477353	3.9763432825
C	0	0.2784364033	-2.4751919745	4.6896081363
H	0	1.4056272247	-2.7158324970	2.8792239233
C	0	-0.5587465288	-0.2592215437	5.1581521520
H	0	-0.0820206460	1.2554544279	3.6772978426
C	0	-0.4328629688	-1.6040927473	5.5195308817
H	0	0.3912939695	-3.5262477078	4.9640539841
H	0	-1.1015077409	0.4351792476	5.8036701452
H	0	-0.8770566780	-1.9700259009	6.4477972721

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O	0	2.9449889312	2.1974529125	-0.4544511428
C	0	3.7344178430	3.3502996143	-0.7524828491
O	0	1.1332397918	3.5065579753	-0.1585924089
C	0	1.6667270225	2.4330617700	-0.1229064406
C	0	0.9332700515	1.1065680118	0.1523560199
C	0	0.3741825952	0.5451884687	-1.1656903326
O	0	-0.1831798774	1.3872739494	0.9471828314
N	0	-1.3251459931	0.7067712408	0.3420527344
C	0	-2.4939597594	1.3496464716	0.9240770372
C	0	-1.0984151605	0.9259227989	-1.0909269122
H	0	3.8125201958	3.9945798370	0.1355193943
H	0	3.2833941727	3.9292571177	-1.5717906216
H	0	4.7237677992	2.9774387331	-1.0426305070
H	0	0.9010657193	0.8669540079	-2.0736653602
H	0	-1.1777270594	2.0080727078	-1.3265574428
C	0	-2.0220543330	0.1263928823	-2.0002590105
H	0	-1.6486272067	0.1674718843	-3.0342865003
H	0	-2.0702219726	-0.9261894174	-1.6888641647
H	0	-3.0427309642	0.5289564654	-1.9791827528
H	0	-2.3016748221	1.3927534600	2.0076494218
H	0	-2.6004220158	2.3950000568	0.5730056893
N	0	1.8096283994	0.0952889518	0.7515694387
C	0	2.1804218528	-1.0187412605	-0.1089590580
C	0	2.4368616162	0.4888534664	1.9121481299
H	0	2.9080524094	-0.7058423375	-0.8811358487
S	0	0.6190732210	-1.2924841987	-1.1358746657
C	0	2.6516411410	-2.3477875610	0.5387092229
H	0	3.0948440856	-0.2792359624	2.3565988452
O	0	2.2779909687	1.5817921262	2.4095198646
O	0	1.0396508335	-1.6708071837	-2.5363548943

C	0	4.1301281173	-2.2495757432	0.9713855974
C	0	2.5891035099	-3.4607148575	-0.5320939423
C	0	1.7452815705	-2.7413049568	1.7155955906
H	0	4.3124810169	-1.5288048636	1.7786473736
H	0	4.4731865598	-3.2319433957	1.3311855534
H	0	4.7649370142	-1.9656715783	0.1174271415
H	0	3.0624424400	-4.3699715964	-0.1322519717
H	0	1.5579119498	-3.7183877078	-0.8121384788
H	0	3.1127297135	-3.1703812188	-1.4545505272
H	0	0.6897188741	-2.7607203743	1.4035554478
H	0	2.0123145260	-3.7473491761	2.0736588928
H	0	1.8277770604	-2.0524055740	2.5674097543
C	0	-3.7522810215	0.5571446630	0.6550104169
C	0	-4.9186161452	1.1949782841	0.2164393111
C	0	-3.7718157127	-0.8313289214	0.8551938272
C	0	-6.0872287884	0.4628665651	-0.0160832024
H	0	-4.9105898254	2.2755961778	0.0498518227
C	0	-4.9350679975	-1.5643502077	0.6185098833
H	0	-2.8565940524	-1.3303665016	1.1795354119
C	0	-6.0975680497	-0.9194317316	0.1820512464
H	0	-6.9896225893	0.9746704504	-0.3592182290
H	0	-4.9364101168	-2.6460960531	0.7740309196
H	0	-7.0077445391	-1.4943946714	-0.0044565559

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O	0	2.3252483457	-2.4886047309	-1.0124583969
C	0	2.9102924049	-3.7135093323	-1.4535166110
O	0	0.7783625969	-3.6354828896	0.1662257180
C	0	1.3214605507	-2.6097790963	-0.1291146453
C	0	0.8431722818	-1.2110631642	0.2935718534
C	0	0.0483680076	-0.5517045617	-0.8697677754
O	0	-0.0744705140	-1.3556642327	1.3369226539
N	0	-1.0322712408	-0.2659440981	1.1643552877
C	0	-2.1004915648	-0.5612304668	2.0968588597
C	0	-1.3547809284	-0.3971415327	-0.2604422864
H	0	3.3743425246	-4.2332918815	-0.6021174882
H	0	2.1516623713	-4.3715871639	-1.9021668493
H	0	3.6710832792	-3.4408148905	-2.1947067643
H	0	0.0299616095	-1.1769301269	-1.7698245180
H	0	-1.8454137364	-1.3803970549	-0.4242909906
C	0	-2.2658535784	0.7071146951	-0.8083625672
H	0	-2.1666319681	0.7003345784	-1.9053773479
H	0	-1.8842499468	1.6836164729	-0.4928319613
H	0	-2.5978150952	-1.5250402829	1.8764644103
H	0	-2.8410796053	0.2458072790	2.0476710814
H	0	-1.6751528138	-0.5965238545	3.1089727334
N	0	1.9549931234	-0.3283239675	0.6612828153
C	0	1.7188201067	1.0802224377	0.3821717891
C	0	2.9452197126	-0.8790453219	1.4384543264
H	0	0.8679367512	1.4567453134	0.9741973685
S	0	1.0105611608	0.9758349048	-1.3657957178
C	0	2.8976904921	2.0833312561	0.4554985214
H	0	3.7004194705	-0.1562473950	1.7901128643
O	0	3.0034615749	-2.0596241974	1.7100435600
O	0	0.0812764156	2.1454758278	-1.5916249824
C	0	2.4423461621	3.4139588291	-0.1856034949
C	0	4.1348073337	1.5785995943	-0.3073920744
C	0	3.2268406831	2.4064546068	1.9291168083
H	0	1.4902048789	3.7639275896	0.2393445968
H	0	3.2097393883	4.1800042053	0.0019379758
H	0	2.2992620096	3.3344089589	-1.2711449337
H	0	4.8873255701	2.3797975729	-0.3644480196

H	0	4.6150179842	0.7109767671	0.1643819033
H	0	3.8681541056	1.2930873821	-1.3364235956
H	0	3.5887000676	1.5472791715	2.5082915848
H	0	4.0095304797	3.1798375365	1.9687384547
H	0	2.3375745292	2.8031785252	2.4431179945
C	0	-3.7225126070	0.5503736093	-0.4339414548
C	0	-4.4466398800	-0.6007903608	-0.7799952405
C	0	-4.3884529972	1.5688123228	0.2626839405
C	0	-5.7906556929	-0.7372811759	-0.4271179810
H	0	-3.9545274643	-1.4041314517	-1.3352312912
C	0	-5.7342440188	1.4387659333	0.6166453160
H	0	-3.8396759743	2.4749987960	0.5329008696
C	0	-6.4394806318	0.2820503303	0.2762474867
H	0	-6.3354711121	-1.6428193578	-0.7052863855
H	0	-6.2326751278	2.2443792208	1.1613955164
H	0	-7.4909174737	0.1760628715	0.5535040831

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O	0	-2.4371953062	1.9628481368	-1.2590483627
C	0	-3.2576018514	2.9853412948	-1.8302400901
O	0	-1.0468974025	3.5316170814	-0.4361670812
C	0	-1.3370077668	2.3824868575	-0.6187817182
C	0	-0.5666976110	1.1833538807	-0.0304529736
C	0	-1.0269603049	0.8913552070	1.4117054859
N	0	1.3316062233	1.1167549629	1.3186523248
O	0	0.7874051369	1.5683374725	0.0730068839
C	0	1.8464251212	-0.2504862261	1.1884138414
C	0	0.2081088853	1.2846570206	2.2465376249
H	0	-3.5761166526	3.7015566105	-1.0588726101
H	0	-2.6999768511	3.5260671686	-2.6086411630
H	0	-4.1244869133	2.4738949294	-2.2644097382
H	0	-1.9518523463	1.4054792635	1.7045056945
H	0	0.3441753645	0.5988156436	3.0964668846
C	0	0.1291444469	2.7284783172	2.7363382888
H	0	-0.7268995231	2.8589138141	3.4163223363
H	0	0.0143880378	3.4127632413	1.8838206171
H	0	1.0533884339	2.9886960570	3.2710438837
H	0	2.0713958849	-0.5786124763	2.2135452621
H	0	1.0814537798	-0.9471352994	0.7964498398
N	0	-0.7497583436	-0.0362021571	-0.8333196623
C	0	-1.7287910778	-0.9820090064	-0.3159455676
C	0	-0.3432978610	0.0616470102	-2.1467169839
H	0	-2.7535547978	-0.5779015123	-0.4084686044
S	0	-1.5009196572	-0.8988596761	1.5581698565
C	0	-1.7061357788	-2.4511107525	-0.8168851348
H	0	-0.4957326372	-0.8596398530	-2.7358242546
O	0	0.1577661195	1.0609960405	-2.6138384705
O	0	-2.8836444100	-0.9290028545	2.1604633324
C	0	-2.3842102455	-2.5640493005	-2.2001690436
C	0	-2.5589643397	-3.3055563916	0.1485596008
C	0	-0.2774953720	-3.0154671516	-0.8460276163
H	0	-1.8286679321	-2.0793193408	-3.0127750414
H	0	-2.4881739504	-3.6259848442	-2.4708026425
H	0	-3.3937711032	-2.1251529956	-2.1733447803
H	0	-2.6699485996	-4.3171024110	-0.2695081609
H	0	-2.0951307689	-3.4074179515	1.1402325410
H	0	-3.5603478161	-2.8767818108	0.2984190122
H	0	-0.2985274562	-4.0701757120	-1.1597374799
H	0	0.3856580771	-2.4750031538	-1.5353585303
H	0	0.1791914603	-2.9761142575	0.1547571198
C	0	3.1013650355	-0.3722399775	0.3521774832
C	0	3.1791028843	0.1236372978	-0.9601058128

C	0	4.2082032796	-1.0515485467	0.8810458219
C	0	4.3405067198	-0.0601659493	-1.7139437972
H	0	2.3407102635	0.6722567747	-1.3869971594
C	0	5.3674545614	-1.2400223458	0.1240790373
H	0	4.1637278204	-1.4389778619	1.9030665214
C	0	5.4365179040	-0.7435906141	-1.1792182068
H	0	4.3866440512	0.3380418557	-2.7305963017
H	0	6.2190189413	-1.7707547661	0.5570423331
H	0	6.3417892436	-0.8851417426	-1.7747256393

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O	0	-2.9362380117	1.6282811636	0.7715137385
C	0	-4.0246472403	2.5432732237	0.6157452488
O	0	-2.0503445096	2.3400970279	-1.1667926064
C	0	-2.0036230669	1.6539514512	-0.1773195698
C	0	-0.8125856684	0.7229564639	0.1343989133
C	0	-0.2015178104	0.1096971999	-1.1474410264
N	0	1.4603402076	1.2293925304	0.1555825420
O	0	0.1670297610	1.6161521357	0.6253420341
C	0	2.0968232562	0.3177197445	1.1181819501
C	0	1.2239499589	0.7076746028	-1.1926979744
H	0	-4.5801297664	2.3262523130	-0.3089158108
H	0	-3.6505361473	3.5759198629	0.5699777780
H	0	-4.6645315457	2.4039709281	1.4942783246
H	0	-0.7863867921	0.3631612907	-2.0385841454
H	0	1.9632562468	-0.0834072751	-1.3845837100
C	0	1.3339483118	1.8210066525	-2.2307168645
H	0	1.1555088265	1.4287026254	-3.2445401826
H	0	0.5928694001	2.6069165885	-2.0254859379
H	0	2.3400281920	2.2610502191	-2.1922389537
H	0	1.9585886670	0.7919981506	2.1006854321
H	0	1.6341889036	-0.6805042894	1.1325786189
N	0	-1.1218679472	-0.3791930526	1.0445119607
C	0	-1.3350912431	-1.6784743031	0.4480055817
C	0	-1.1345324645	-0.2313358739	2.4216887271
H	0	-0.9226558714	-2.4521795505	1.1127695151
S	0	-0.1832007494	-1.7588888532	-1.0316768238
C	0	-2.7900889520	-2.0729751562	0.0661993683
H	0	-1.2142591095	-1.2266060805	2.9229352485
O	0	-1.0597988486	0.8056065833	3.0272796651
O	0	1.1670868626	-2.1936624041	-0.5027128137
C	0	-3.3137285204	-1.2888284074	-1.1492438365
C	0	-3.7066534368	-1.8117363789	1.2717226879
C	0	-2.7884989973	-3.5755550769	-0.2637957178
H	0	-2.6832379747	-1.4394426504	-2.0394550308
H	0	-4.3261162883	-1.6361595578	-1.4063847038
H	0	-3.3858254244	-0.2129193054	-0.9483721211
H	0	-4.7306538456	-2.1447045821	1.0411383132
H	0	-3.3693178547	-2.3655681373	2.1621067712
H	0	-3.7416746100	-0.7419162174	1.5208057121
H	0	-2.4492248573	-4.1720407612	0.5979733807
H	0	-3.8037126123	-3.9095991495	-0.5265652125
H	0	-2.1301082334	-3.8053566296	-1.1159957014
C	0	3.5648501095	0.1890427592	0.7878200756
C	0	4.1065139155	-1.0442887401	0.4038660949
C	0	4.3993901687	1.3163656782	0.8366874222
C	0	5.4667330298	-1.1537628973	0.0953032817
H	0	3.4467493194	-1.9108770321	0.3280980237
C	0	5.7550762012	1.2083069559	0.5258610423
H	0	3.9710205051	2.2826357740	1.1137649161
C	0	6.2935039162	-0.0301183423	0.1572547320
H	0	5.8790896174	-2.1214906459	-0.2013385578

H	0	6.3968745067	2.0918784666	0.5714356086
H	0	7.3558075162	-0.1153680414	-0.0851864078

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O	0	1.5820209326	3.0430694144	-0.7040993713
C	0	1.4465766833	4.4044767559	-1.1022163721
O	0	-0.5902990109	2.7093034663	-1.1703711106
C	0	0.4632800951	2.3088367230	-0.7217704768
C	0	0.6972877552	0.9293353161	-0.2217696263
C	0	0.0776358577	-0.1614619043	-0.8471389345
O	0	-0.7228813416	1.1317667414	1.4554100876
N	0	-1.6589705527	0.4237723445	0.9581285450
C	0	-2.7858285809	1.1585846601	0.3259328604
C	0	-1.3385124367	-0.8331039207	0.5820962867
H	0	0.7411808900	4.9282194593	-0.4400645138
H	0	1.0788222180	4.4759667906	-2.1367515336
H	0	2.4462644526	4.8470492462	-1.0176922734
H	0	-0.5619846564	-0.0136536569	-1.7194957460
H	0	-2.1285332902	-1.3497746324	0.0301253108
C	0	-0.5133830687	-1.6639013555	1.5246749485
H	0	-0.1264463602	-2.5597348848	1.0235262770
H	0	0.3185929392	-1.0828466109	1.9385567011
H	0	-1.1518426448	-1.9945979946	2.3619919180
H	0	-2.9732118367	1.9992722221	1.0079280604
H	0	-2.4140238567	1.5823538366	-0.6179357233
N	0	1.9225854941	0.5844877821	0.4137759693
C	0	2.6247050439	-0.4688995070	-0.3189277801
C	0	2.3904619529	1.3053132907	1.5003240924
H	0	3.0016032712	-0.0595833536	-1.2740600335
S	0	1.2431741287	-1.5585445562	-1.0779520606
C	0	3.7344803155	-1.3139876325	0.3432621243
H	0	3.3588217251	0.9239937966	1.8746182477
O	0	1.8237052380	2.2440870299	2.0027096666
O	0	1.5851091068	-1.6172471094	-2.5470389177
C	0	5.0368130785	-0.4932582025	0.4705572710
C	0	4.0539356456	-2.4904928560	-0.6083089524
C	0	3.2975485793	-1.8869436120	1.7001510597
H	0	4.9631148033	0.3518408479	1.1665973865
H	0	5.8474913910	-1.1445374129	0.8324654154
H	0	5.3385595047	-0.0948225164	-0.5105417197
H	0	4.9471379884	-3.0205038704	-0.2450645566
H	0	3.2322591786	-3.2203176910	-0.6539314818
H	0	4.2456697149	-2.1446057846	-1.6344806051
H	0	2.3846660825	-2.4908747264	1.5916068173
H	0	4.0863707077	-2.5423946198	2.1003768647
H	0	3.0995096001	-1.1095690588	2.4508006293
C	0	-4.0067069409	0.3040666006	0.1288946404
C	0	-4.4187466838	-0.0614193461	-1.1593399543
C	0	-4.7387082273	-0.1605597696	1.2329085640
C	0	-5.5407741422	-0.8748506722	-1.3446702685
H	0	-3.8540291587	0.2974418969	-2.0238790047
C	0	-5.8565186175	-0.9753990513	1.0513983924
H	0	-4.4243794668	0.1203654603	2.2417869930
C	0	-6.2601525324	-1.3346683793	-0.2394348204
H	0	-5.8524539338	-1.1495344003	-2.3551200517
H	0	-6.4191616943	-1.3293220196	1.9186180577
H	0	-7.1368093402	-1.9709755732	-0.3818522985

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O	0	-2.4503888855	2.5860581763	0.3908409358

C	0	-3.0058404849	3.8951716568	0.2991024996
O	0	-1.2771229275	2.9674479360	-1.4903311638
C	0	-1.5339258568	2.2663255241	-0.5334681604
C	0	-0.9426665410	0.9297570433	-0.2928342435
C	0	-0.4644181429	0.1400250917	-1.3587753502
O	0	1.0594008261	1.8803876066	0.1332163610
N	0	1.6339930852	1.4508927883	-0.9226767138
C	0	1.8039017682	2.3970696893	-2.0270496666
C	0	1.5518855126	0.1118518340	-1.1386091129
H	0	-2.2133245278	4.6531517132	0.3849480631
H	0	-3.5250648722	4.0349251994	-0.6608671387
H	0	-3.7096445359	3.9856418534	1.1349011944
H	0	-0.5674835603	0.5419359040	-2.3698547566
H	0	1.9644234933	-0.2156337904	-2.0984169546
C	0	1.8474798105	-0.7964805747	0.0415650658
H	0	1.5147287784	-1.8063488382	-0.2206517515
H	0	1.2783296544	-0.4487679152	0.9102740077
H	0	0.8171208194	2.6613178807	-2.4362640790
H	0	2.4527270195	1.9559550740	-2.7942387962
H	0	2.2696674555	3.3021283586	-1.6164129306
N	0	-1.2448373987	0.1737473624	0.8666572108
C	0	-1.5964275670	-1.2131980087	0.6050587551
C	0	-0.9524196946	0.6131528269	2.1520175531
H	0	-0.9578105656	-1.9097964860	1.1715467128
S	0	-1.1328550568	-1.5522317029	-1.2182351657
C	0	-3.0941522131	-1.5602692062	0.8097461360
H	0	-1.0286739596	-0.2231295487	2.8848989312
O	0	-0.6488243851	1.7356250545	2.4609562609
O	0	-0.0847319022	-2.6366832646	-1.2857613232
C	0	-3.2931860296	-3.0463933566	0.4669176014
C	0	-3.9758583682	-0.6698431216	-0.0811211657
C	0	-3.4869807560	-1.3347114767	2.2797182182
H	0	-2.6801720146	-3.6900847607	1.1179282279
H	0	-4.3478940658	-3.3281862247	0.6068393058
H	0	-3.0245630268	-3.2754744849	-0.5757564470
H	0	-5.0386984796	-0.9020043231	0.0876382987
H	0	-3.8170938653	0.3935335361	0.1503175164
H	0	-3.7652517397	-0.8308006951	-1.1494959764
H	0	-3.4355315395	-0.2722221722	2.5584384422
H	0	-4.5249144431	-1.6664438343	2.4385411396
H	0	-2.8442271889	-1.9089247088	2.9660898179
C	0	3.3277269073	-0.7764128649	0.3565272252
C	0	4.1772638110	-1.7733920997	-0.1426142840
C	0	3.8791872354	0.2615079733	1.1256024330
C	0	5.5497390761	-1.7389800984	0.1205757567
H	0	3.7552965486	-2.5872746342	-0.7388557372
C	0	5.2494715333	0.2959542034	1.3900360269
H	0	3.2216623493	1.0436403748	1.5122421776
C	0	6.0893763211	-0.7035556776	0.8876900599
H	0	6.1984825286	-2.5261760035	-0.2717272685
H	0	5.6646561434	1.1061403692	1.9948000685
H	0	7.1614719179	-0.6767421574	1.0975171827

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O	0	-1.7361985057	2.8461148688	-1.3206753753
C	0	-1.8829722504	4.2044607572	-1.7265834600
O	0	-0.9743431721	3.5408822395	0.6794000061
C	0	-1.2102253201	2.6489342327	-0.1047688639
C	0	-1.0051250847	1.2100436259	0.1934966475
C	0	-1.2028602676	0.7178079929	1.4926286815
N	0	1.3540654711	0.5180172285	1.2369552652
O	0	1.1974352136	1.4120214060	0.3481441739

C	0	1.7657619840	-0.8251461392	0.7592860359
C	0	0.6657500777	0.6764947569	2.3932921087
H	0	-2.5506257033	4.7484311115	-1.0416552343
H	0	-0.9050522302	4.7082182667	-1.7383052472
H	0	-2.3081430704	4.1762757230	-2.7369354948
H	0	-1.7144279481	1.3093842822	2.2539129021
H	0	0.7083015793	-0.1994228666	3.0505648839
C	0	0.6627492179	2.0259709993	3.0576745834
H	0	-0.0648837606	2.0361297787	3.8819219265
H	0	0.4063054663	2.8185371614	2.3443344431
H	0	1.6618159450	2.2242857487	3.4823317817
H	0	1.7693807033	-1.5021628783	1.6227842566
H	0	0.9926577682	-1.1637061692	0.0569778036
N	0	-1.1804832680	0.2145844821	-0.8175450462
C	0	-2.1432260126	-0.8072721579	-0.3951327017
C	0	-0.5352985158	0.2881530530	-2.0360197085
H	0	-3.1486008026	-0.3558302742	-0.3145162890
S	0	-1.7678172332	-1.0233853345	1.4636338480
C	0	-2.2485677456	-2.1670338342	-1.1201813139
H	0	-0.8467616738	-0.5125467485	-2.7299496490
O	0	0.2915079720	1.1182294297	-2.3359423684
O	0	-3.1034807794	-1.0805207581	2.1648691491
C	0	-2.9331962711	-2.0034500353	-2.4948212340
C	0	-3.1804841109	-3.0695906274	-0.2781180944
C	0	-0.8854792124	-2.8679913847	-1.2462046201
H	0	-2.3410470051	-1.4385445732	-3.2259090961
H	0	-3.1242802857	-2.9969094136	-2.9291977301
H	0	-3.9029721670	-1.4941207344	-2.3834843405
H	0	-3.3686172941	-4.0042336729	-0.8273876859
H	0	-2.7447472878	-3.3345275646	0.6954508201
H	0	-4.1457734546	-2.5821918398	-0.0780976052
H	0	-1.0178592018	-3.8617937622	-1.7003859723
H	0	-0.1666450072	-2.3167214556	-1.8678873801
H	0	-0.4344727011	-3.0159718837	-0.2532437943
C	0	3.1165831767	-0.7951481474	0.0900880646
C	0	3.2774039681	-0.1736744396	-1.1584561372
C	0	4.2257348720	-1.3770121133	0.7171647027
C	0	4.5359235867	-0.1414345022	-1.7619825741
H	0	2.4219569880	0.2990822770	-1.6443666981
C	0	5.4829650677	-1.3480536100	0.1079124096
H	0	4.1053405868	-1.8601574656	1.6910803733
C	0	5.6393292608	-0.7282412165	-1.1339995664
H	0	4.6547603634	0.3469162243	-2.7321396554
H	0	6.3400534838	-1.8086088750	0.6050606601
H	0	6.6210885908	-0.7025461685	-1.6132525909

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O	0	2.9477034646	2.2576037589	-0.2076822755
C	0	3.6804479122	3.4697509161	-0.0460421031
O	0	1.6702978502	2.8047660813	1.5653041731
C	0	1.9144041004	2.0762489811	0.6301868913
C	0	1.1412003241	0.8521983870	0.3120416657
C	0	0.5444734465	0.0919992627	1.3434431893
N	0	-1.4743470799	1.0987975148	0.1049986330
O	0	-0.6155302543	1.9833345661	-0.2221056840
C	0	-2.0422204225	0.2646241071	-0.9876136725
C	0	-1.4344978156	0.6593648876	1.3867344454
H	0	4.1248833869	3.5282451696	0.9588476887
H	0	3.0196676093	4.3371934602	-0.1900304973
H	0	4.4630943484	3.4569612907	-0.8137621794
H	0	0.7944392282	0.3241687803	2.3798321355
H	0	-2.0432708552	-0.2330402091	1.5553874800

C	0	-1.3712030237	1.6782271014	2.4939130044
H	0	-1.1586268688	1.1834937836	3.4527278026
H	0	-0.5997597217	2.4333045714	2.2990840653
H	0	-2.3532932873	2.1734506866	2.5809633717
H	0	-1.8857076139	0.8691942761	-1.8891773820
H	0	-1.4629034467	-0.6655023636	-1.0455158854
N	0	1.3959881095	0.0888967578	-0.8564999332
C	0	1.5596383345	-1.3330644497	-0.6106302674
C	0	1.3325205889	0.5857458097	-2.1493017930
H	0	1.0448189988	-1.9255358673	-1.3815484944
S	0	0.5580613345	-1.6931676121	0.9507428841
C	0	3.0269165180	-1.8149577888	-0.4658038033
H	0	1.4173853886	-0.2405579981	-2.8941533222
O	0	1.1952580513	1.7408975318	-2.4574881947
O	0	-0.8192993819	-2.1508485479	0.5017304500
C	0	3.7207435778	-1.1508913757	0.7350633489
C	0	3.7988592133	-1.4516612597	-1.7457008674
C	0	3.0166184078	-3.3430957459	-0.2968259407
H	0	3.2095831172	-1.3802683091	1.6828942882
H	0	4.7543905187	-1.5211945002	0.8180971750
H	0	3.7640734676	-0.0597502050	0.6138645349
H	0	4.8249867398	-1.8463005770	-1.6845296051
H	0	3.3273000638	-1.8855681757	-2.6419519869
H	0	3.8668735131	-0.3621929480	-1.8783668327
H	0	2.5313468769	-3.8364872441	-1.1544190697
H	0	4.0472457298	-3.7234721083	-0.2286879962
H	0	2.4858716137	-3.6510834031	0.6168259659
C	0	-3.4973695032	-0.0486960451	-0.7553418009
C	0	-3.8856993112	-1.3149964926	-0.2958566612
C	0	-4.4758413997	0.9343245274	-0.9662865873
C	0	-5.2350186467	-1.5940590051	-0.0583417586
H	0	-3.1162463495	-2.0687139142	-0.1138298233
C	0	-5.8221678970	0.6558658593	-0.7266901424
H	0	-4.1760281975	1.9243492209	-1.3209903128
C	0	-6.2044560077	-0.6112662352	-0.2729982659
H	0	-5.5291384177	-2.5844645159	0.2977008468
H	0	-6.5770783015	1.4273611263	-0.8971034729
H	0	-7.2588520310	-0.8307245193	-0.0877694285

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O	0	2.8718481888	2.2335463496	-0.4235439869
C	0	3.6087760797	3.4234836459	-0.7104339799
O	0	1.0196146734	3.4622557830	-0.0455529397
C	0	1.5953312238	2.4096592874	-0.0536810603
C	0	0.9158688819	1.0496546681	0.1985933317
C	0	0.3295225937	0.5246800203	-1.1215787104
O	0	-0.1769266996	1.2649301685	1.0454339656
N	0	-1.3457175874	0.6220176402	0.4489345713
C	0	-2.4826639862	1.3103551214	1.0631040702
C	0	-1.1524638317	0.8742166699	-0.9825168663
H	0	3.6880804482	4.0458114312	0.1929694483
H	0	3.1130116388	4.0066877841	-1.5003350258
H	0	4.6026254432	3.0966409936	-1.0381442410
H	0	0.8056224551	0.9083820964	-2.0330586767
H	0	-1.2493509243	1.9582411000	-1.1973906025
H	0	-2.2926546377	1.2883166280	2.1455501504
H	0	-2.5105999789	2.3718435833	0.7505314840
N	0	1.8421249863	0.0469042117	0.7283123819
C	0	2.2217314401	-1.0189846425	-0.1877310602
C	0	2.4955732132	0.4175186144	1.8820115477
H	0	2.9229993933	-0.6542473533	-0.9613675779
S	0	0.6506644124	-1.3007436248	-1.1987664773

C	0	2.7428705765	-2.3600113951	0.3948949232
H	0	3.1943282066	-0.3436080870	2.2731127384
O	0	2.3171766652	1.4841495888	2.4276525037
O	0	1.0756916557	-1.5883790051	-2.6166473356
C	0	4.2299503443	-2.2414939518	0.7914989724
C	0	2.6780030652	-3.4344930624	-0.7145005330
C	0	1.8790010998	-2.8189955749	1.5800040196
H	0	4.4176198401	-1.5450475970	1.6186589420
H	0	4.6055480064	-3.2271828379	1.1070442089
H	0	4.8342610385	-1.9126987064	-0.0684407246
H	0	3.1873923294	-4.3440900825	-0.3625244102
H	0	1.6459126794	-3.7110315240	-0.9726950214
H	0	3.1647104210	-3.0961815872	-1.6406485670
H	0	0.8155747314	-2.8496804204	1.2967011388
H	0	2.1773039876	-3.8319481347	1.8908590467
H	0	1.9711119513	-2.1617132258	2.4555689081
C	0	-3.7802819963	0.6103484982	0.7423311372
C	0	-4.6602847123	1.1255185962	-0.2157171956
C	0	-4.0875204206	-0.6102792703	1.3589939897
C	0	-5.8157654305	0.4258719987	-0.5704181019
H	0	-4.4238537166	2.0715789337	-0.7085146213
C	0	-5.2427453911	-1.3107741688	1.0113125880
H	0	-3.3998322028	-1.0195799448	2.1035533903
C	0	-6.1070029062	-0.7964522132	0.0393069784
H	0	-6.4847121902	0.8322193996	-1.3323739988
H	0	-5.4696858030	-2.2633513079	1.4964089335
H	0	-7.0078570405	-1.3478586278	-0.2404553221
C	0	-2.0897160888	0.1072528822	-1.8859969797
C	0	-2.5203917520	0.7016412124	-3.0776017481
C	0	-2.5330871651	-1.1832964782	-1.5670304463
C	0	-3.3853940039	0.0230382964	-3.9383151490
H	0	-2.1844983739	1.7116972059	-3.3275284358
C	0	-3.4065780745	-1.8566142869	-2.4202026502
H	0	-2.2201020515	-1.6376865553	-0.6287785571
C	0	-3.8344449943	-1.2576755198	-3.6082192196
H	0	-3.7156684032	0.4997379109	-4.8642010357
H	0	-3.7626370040	-2.8530315498	-2.1496262440
H	0	-4.5205439133	-1.7869336645	-4.2736562879

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0 1

O	0	1.9453175491	-2.5509729595	-1.0871917014
C	0	2.2966345220	-3.8763079255	-1.4877081940
O	0	0.4470862750	-3.3681112191	0.3896939671
C	0	1.0915354804	-2.4600029507	-0.0587969237
C	0	0.8829252233	-0.9834140381	0.3321873261
C	0	0.0907698062	-0.2753281590	-0.7896548527
O	0	0.0759023652	-0.9216398556	1.4744715889
N	0	-1.0913261622	-0.0743985919	1.1915192052
C	0	-1.3305500450	-0.3174284149	-0.2421439592
H	0	2.8344292893	-4.3785328380	-0.6699725439
H	0	1.3993774951	-4.4597842910	-1.7401138000
H	0	2.9475584555	-3.7697290292	-2.3636103620
H	0	0.1940825152	-0.7827085739	-1.7551717476
H	0	-1.6650807454	-1.3672896694	-0.3767621945
C	0	-2.3503311455	0.6155264712	-0.9015953540
H	0	-2.2742607640	0.4312942367	-1.9885658929
H	0	-2.0372439122	1.6519583218	-0.7402267691
N	0	2.1334226170	-0.2652554746	0.5488445770
C	0	1.9201648055	1.1739449895	0.5225400451
C	0	3.1779575260	-0.9441549394	1.1342084751
H	0	1.1899072444	1.4678883332	1.2968522250
S	0	0.8864902798	1.4170547533	-1.0440056246

C	0	3.1330217140	2.1353585274	0.5509648652
H	0	4.0536233134	-0.3113995609	1.3570401430
O	0	3.1655035096	-2.1342974346	1.3640566025
O	0	-0.0802966719	2.5392627851	-0.7472237366
C	0	2.6340643621	3.5575955077	0.2079165516
C	0	4.2020229659	1.7363239442	-0.4803867297
C	0	3.7146693023	2.2158680469	1.9791259308
H	0	1.7812231261	3.8523566373	0.8360527771
H	0	3.4547139381	4.2717491922	0.3731054463
H	0	2.3129553872	3.6518975082	-0.8385218529
H	0	4.9794262451	2.5138201562	-0.5309820474
H	0	4.7014890759	0.7867907110	-0.2449460334
H	0	3.7560720029	1.6403651685	-1.4823463850
H	0	4.1398543584	1.2728486337	2.3454691075
H	0	4.5183579379	2.9678774723	2.0053898674
H	0	2.9375644515	2.5301601583	2.6928221189
C	0	-3.7882532447	0.4276671745	-0.4673064006
C	0	-4.3796295287	-0.8382971190	-0.3528103970
C	0	-4.5660872415	1.5540913223	-0.1668096880
C	0	-5.6996735464	-0.9753427846	0.0777619682
H	0	-3.7988990809	-1.7360001490	-0.5757486333
C	0	-5.8922704947	1.4235800421	0.2513461280
H	0	-4.1160547164	2.5471184891	-0.2472312280
C	0	-6.4619156756	0.1556389117	0.3838047317
H	0	-6.1334903804	-1.9726889133	0.1813037575
H	0	-6.4781438095	2.3158955834	0.4857023031
H	0	-7.4941406249	0.0473406327	0.7251902465
C	0	-2.1383449653	-0.5223542336	2.0602023694
C	0	-3.0140305674	0.4413072893	2.5649513642
C	0	-2.3242219285	-1.8800298289	2.3561856821
C	0	-4.1167766583	0.0454779001	3.3230516480
H	0	-2.8315353100	1.4906504147	2.3321561360
C	0	-3.4144144186	-2.2633967364	3.1379632723
H	0	-1.6100815339	-2.6125515581	1.9771685148
C	0	-4.3188822655	-1.3066270915	3.6111527734
H	0	-4.8174548300	0.7972829207	3.6924455534
H	0	-3.5628108460	-3.3199215726	3.3746755974
H	0	-5.1781006660	-1.6153408031	4.2112929159

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0 1

O	0	-2.3611955881	2.0377644032	-1.1540917047
C	0	-3.1457879362	3.1001360380	-1.7021040193
O	0	-0.7882397525	3.5224832401	-0.5182280085
C	0	-1.1837699334	2.3975438761	-0.6164929525
C	0	-0.4740762485	1.1564749833	-0.0372002802
C	0	-0.9417095882	0.8677836404	1.4004666354
N	0	1.4216413389	1.0254227479	1.3146274832
O	0	0.8965746329	1.4739870525	0.0602422883
C	0	1.9279723052	-0.3459230392	1.1891973113
C	0	0.3072652110	1.2102339503	2.2402974715
H	0	-3.3529970275	3.8619173236	-0.9363948348
H	0	-2.6106885498	3.5741580625	-2.5377996802
H	0	-4.0778019503	2.6420717250	-2.0532506009
H	0	-1.8482063078	1.4074067146	1.7008653759
H	0	0.4164110737	0.4999649461	3.0738940149
H	0	2.1364455678	-0.6811397454	2.2152386954
H	0	1.1623191983	-1.0308723968	0.7785381747
N	0	-0.7255983075	-0.0468260770	-0.8497384522
C	0	-1.7395705425	-0.9541963937	-0.3271997749
C	0	-0.3371765347	0.0449983490	-2.1684379439
H	0	-2.7454549849	-0.5013535930	-0.3957395355
S	0	-1.4590774959	-0.9094883616	1.5381465145

C	0	-1.7921277145	-2.4160689062	-0.8471390461
H	0	-0.5484402717	-0.8596542120	-2.7651067576
O	0	0.2091333601	1.0217627931	-2.6326683914
O	0	-2.8181951705	-0.9048459577	2.1925332889
C	0	-2.4986021530	-2.4821412088	-2.2190452367
C	0	-2.6654250225	-3.2435207580	0.1236259028
C	0	-0.3903755505	-3.0422074926	-0.9070974438
H	0	-1.9368179294	-2.0128143037	-3.0364115484
H	0	-2.6543031451	-3.5351324804	-2.4995821435
H	0	-3.4871074926	-1.9995438488	-2.1689931180
H	0	-2.8295008555	-4.2435311124	-0.3045630911
H	0	-2.1902378244	-3.3787001932	1.1058139824
H	0	-3.6437560422	-2.7720916102	0.2962976333
H	0	-0.4635847432	-4.0942501689	-1.2218875236
H	0	0.2809742777	-2.5296114611	-1.6097057070
H	0	0.0882215846	-3.0246494533	0.0841574565
C	0	3.1950729047	-0.4572627170	0.3706611453
C	0	3.2536575106	-0.0397331648	-0.9696014970
C	0	4.3364252426	-1.0312551702	0.9475850190
C	0	4.4306923760	-0.1964924472	-1.7045427680
H	0	2.3886074649	0.4326340795	-1.4335347986
C	0	5.5122113611	-1.1930259181	0.2098934350
H	0	4.3061093820	-1.3564002086	1.9914878487
C	0	5.5619843094	-0.7752570412	-1.1214558314
H	0	4.4620553466	0.1402798463	-2.7436781609
H	0	6.3910356941	-1.6418934101	0.6793474282
H	0	6.4797122371	-0.8967623960	-1.7021217580
C	0	0.2242801650	2.6208075473	2.8001576757
C	0	-0.6931304156	2.8802284648	3.8279989875
C	0	1.0153502791	3.6602202698	2.3034179393
C	0	-0.8165471630	4.1649877488	4.3588499558
H	0	-1.3164460123	2.0689509514	4.2176586422
C	0	0.8891651915	4.9466366245	2.8345102585
H	0	1.7174447930	3.4552695639	1.4963190753
C	0	-0.0230456689	5.2032784575	3.8606779905
H	0	-1.5305763097	4.3553463466	5.1637289131
H	0	1.5064382813	5.7556225762	2.4368037840
H	0	-0.1178620870	6.2110579253	4.2721881918

Sa-PB-PxSi

0 1

O	0	-2.9009732810	1.6309622405	1.0988364290
C	0	-3.9946767828	2.5524146919	1.0745881227
O	0	-2.0874080595	2.5333822634	-0.7920316403
C	0	-2.0057998959	1.7530413964	0.1211937223
C	0	-0.8059284958	0.7980749359	0.3005072041
C	0	-0.2031002878	0.3514315579	-1.0511621280
N	0	1.4688079593	1.2954750585	0.3776993237
O	0	0.1751731297	1.6272612875	0.8892203567
C	0	2.1112543299	0.2883743449	1.2351566162
C	0	1.2454993685	0.9035273558	-1.0137326545
H	0	-4.5863609452	2.4229411336	0.1559787758
H	0	-3.6230048996	3.5862794476	1.1129510622
H	0	-4.5992335645	2.3271564494	1.9602751753
H	0	-0.7721603727	0.7377572617	-1.9030317962
H	0	1.9479303642	0.0927505173	-1.2544142250
H	0	1.9869977917	0.6586177556	2.2631905959
H	0	1.6405204333	-0.7030409381	1.1515718346
N	0	-1.1023451926	-0.4093198607	1.0710020392
C	0	-1.3387039182	-1.6188307478	0.3164305780
C	0	-1.0895062593	-0.4408111530	2.4560293296
H	0	-0.9283129525	-2.4748861131	0.8724623250
S	0	-0.2029702356	-1.5208207082	-1.1735596145

C	0	-2.8014291631	-1.9475762869	-0.0966213276
H	0	-1.1735158782	-1.4921704407	2.8245006802
O	0	-0.9901279428	0.5070516442	3.1901218025
O	0	1.1513445713	-2.0165492501	-0.7106030073
C	0	-3.3271913237	-1.0144938925	-1.2009149722
C	0	-3.7036153572	-1.8295659844	1.1417391364
C	0	-2.8187466344	-3.3975239187	-0.6107804430
H	0	-2.7018468355	-1.0537345845	-2.1065112281
H	0	-4.3421906559	-1.3231271502	-1.4943727263
H	0	-3.3940183376	0.0285046161	-0.8684932529
H	0	-4.7337613576	-2.1192483074	0.8820120780
H	0	-3.3652567284	-2.4947286972	1.9519696911
H	0	-3.7226975298	-0.7992480293	1.5235953169
H	0	-2.4769021734	-4.0997177504	0.1661483539
H	0	-3.8400477795	-3.6868603556	-0.9013554469
H	0	-2.1718301374	-3.5255079999	-1.4926469146
C	0	3.5726715224	0.1857396279	0.8696212505
C	0	4.1073642829	-1.0198748106	0.3984573345
C	0	4.4050710256	1.3109069341	0.9688859276
C	0	5.4608156807	-1.1067369374	0.0556289684
H	0	3.4478428318	-1.8819604792	0.2801264394
C	0	5.7536994893	1.2257254836	0.6233143752
H	0	3.9797256060	2.2583438937	1.3077691838
C	0	6.2864764954	0.0136366122	0.1692130621
H	0	5.8680574497	-2.0528684851	-0.3096569218
H	0	6.3938405689	2.1076901781	0.7058872880
H	0	7.3432177113	-0.0529787197	-0.1016016816
C	0	1.4392549759	2.0437096938	-1.9915705405
C	0	1.9020767510	1.7661696284	-3.2832375372
C	0	1.1325318213	3.3643202518	-1.6408819832
C	0	2.0543540992	2.7928851404	-4.2189863661
H	0	2.1570188049	0.7378817531	-3.5561641745
C	0	1.2870120158	4.3900797470	-2.5747211936
H	0	0.7741390036	3.5792766965	-0.6341376152
C	0	1.7457815812	4.1087016660	-3.8656234047
H	0	2.4242987250	2.5652115194	-5.2217105377
H	0	1.0460955683	5.4180341516	-2.2929515774
H	0	1.8670846595	4.9149855149	-4.5931245175

Sa-PB-TSnRe

0 1

O	0	-1.6138825119	3.4547714686	-0.5571525016
C	0	-1.5224829704	4.8669305869	-0.7262223813
O	0	0.4971027084	3.4290749943	0.2164726597
C	0	-0.5068675642	2.8398091189	-0.1248031249
C	0	-0.6824405565	1.3659708052	-0.0502054795
C	0	-0.0401369241	0.6232896800	0.9594994235
O	0	0.7614103493	1.0229598109	-1.6052992163
N	0	1.7082366985	0.5504332846	-0.8836821583
C	0	2.7945865915	1.4880402537	-0.5084068056
C	0	1.3732112343	-0.4803331481	-0.0605157008
H	0	-0.7374556935	5.1159887354	-1.4556131549
H	0	-1.2853353349	5.3609942092	0.2279282273
H	0	-2.5020006305	5.1930555070	-1.0956398334
H	0	0.5746608851	1.1308770297	1.7063741200
H	0	2.1381812648	-0.7048519573	0.6873429162
H	0	2.9638156068	2.0821474752	-1.4172660215
H	0	2.4063404279	2.1755063103	0.2578232722
N	0	-1.9036218566	0.7580490885	-0.4681385272
C	0	-2.5868023751	0.1429157765	0.6701231866
C	0	-2.3628661646	0.8607944821	-1.7677132502
H	0	-2.8996540442	0.9373592606	1.3719604487
S	0	-1.1817122354	-0.5834705088	1.7452337533

C	0	-3.7500190545	-0.8534729234	0.4899442975
H	0	-3.3262504250	0.3386664306	-1.9153752174
O	0	-1.7932668676	1.4388640984	-2.6614660138
O	0	-1.4614320211	-0.0682083329	3.1371299750
C	0	-5.0236937467	-0.1192859193	0.0182640462
C	0	-4.0735130828	-1.4381678080	1.8847785869
C	0	-3.3809959347	-2.0138299586	-0.4449411737
H	0	-4.9432772688	0.3052093202	-0.9905625726
H	0	-5.8705272408	-0.8229886294	0.0102213255
H	0	-5.2751374475	0.7011524046	0.7084199210
H	0	-4.9866128378	-2.0484248849	1.8167948567
H	0	-3.2688542825	-2.0865165489	2.2609133105
H	0	-4.2352904061	-0.6481794225	2.6325588705
H	0	-2.4687781525	-2.5191692184	-0.0976174401
H	0	-4.1946468738	-2.7556365666	-0.4580579515
H	0	-3.2044413696	-1.6956413995	-1.4804188415
C	0	0.6679537243	-1.6781188147	-0.5798285911
C	0	0.7078698019	-2.8458377253	0.2044030082
C	0	0.0162475474	-1.7221945165	-1.8267562750
C	0	0.1207653819	-4.0289610861	-0.2420444614
H	0	1.2131070299	-2.8250781855	1.1731413749
C	0	-0.5464105715	-2.9163415557	-2.2790460102
H	0	-0.0381591994	-0.8195938980	-2.4323376688
C	0	-0.5036953506	-4.0702834938	-1.4919932010
H	0	0.1606801582	-4.9235981349	0.3835096681
H	0	-1.0364597208	-2.9387308712	-3.2553292249
H	0	-0.9587903466	-4.9973842002	-1.8482589843
C	0	4.0386702324	0.7747880635	-0.0546629460
C	0	4.5168597656	0.9400775122	1.2514389118
C	0	4.7258041730	-0.0845184921	-0.9265647976
C	0	5.6641736963	0.2653969469	1.6805549352
H	0	3.9849483755	1.6052004667	1.9369040159
C	0	5.8673893544	-0.7626102611	-0.4994095974
H	0	4.3543106117	-0.2250860198	-1.9450279548
C	0	6.3401314317	-0.5881169805	0.8062673326
H	0	6.0279291137	0.4062100245	2.7010844680
H	0	6.3935178819	-1.4290724795	-1.1870249340
H	0	7.2352570161	-1.1182852042	1.1400011009

Sa-PB-TSnSi

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O	0	-0.0400760742	-3.0872857513	0.6855992987
C	0	-0.7762819079	-4.2994222989	0.8282599053
O	0	-1.4774013969	-2.4095257751	-0.9055458563
C	0	-0.5402344854	-2.1846187548	-0.1659392118
C	0	0.2311811543	-0.9166784394	-0.1530750214
C	0	0.4042756554	-0.1531358239	-1.3326913145
O	0	-1.4875796823	0.2042639517	0.5382821294
N	0	-1.6704683589	0.9292159853	-0.5016505767
C	0	-2.7351559625	0.5008449164	-1.4432601782
C	0	-0.5542320810	1.5653243045	-0.9751724432
H	0	-1.7735182555	-4.0907455828	1.2436515360
H	0	-0.8933326832	-4.8047748515	-0.1416202514
H	0	-0.2019499265	-4.9232848794	1.5231177209
H	0	-0.0944972594	-0.5148227749	-2.2358221049
H	0	-0.6938738692	2.0036672665	-1.9678114394
H	0	-2.4157591420	-0.4510160910	-1.8955411013
H	0	-2.8060447100	1.2755281314	-2.2185008721
N	0	1.2544405531	-0.6854796955	0.8008879471
C	0	2.4939233686	-0.1347290104	0.2612994684
C	0	0.9836827421	-0.6404057565	2.1619836936
H	0	2.6852053131	0.8828670688	0.6395507808
S	0	2.1812997233	0.1137257217	-1.6061104796

C	0	3.7471036330	-1.0355718032	0.4205789910
H	0	1.8141934770	-0.1598837795	2.7226748941
O	0	-0.0211419922	-1.0460314160	2.6887642617
O	0	2.5279103794	1.5202656345	-2.0134187462
C	0	4.9278575625	-0.3289285625	-0.2694060460
C	0	3.4923934909	-2.4168193716	-0.2054140250
C	0	4.0974051601	-1.2220881814	1.9071638895
H	0	5.1288606048	0.6496675021	0.1948420013
H	0	5.8372621218	-0.9426180705	-0.1811871763
H	0	4.7479174224	-0.1522607366	-1.3406090331
H	0	4.3615176230	-3.0727504141	-0.0431878125
H	0	2.6101958632	-2.8937912765	0.2472209323
H	0	3.3262912461	-2.3436742870	-1.2907902132
H	0	3.3442168007	-1.8223306685	2.4374044939
H	0	5.0572816504	-1.7551363811	1.9923313646
H	0	4.2044573171	-0.2554343919	2.4248330668
C	0	0.2626816884	2.4186629701	-0.0646045490
C	0	1.0523707259	3.4247163073	-0.6475201385
C	0	0.2401415338	2.3072834819	1.3380837617
C	0	1.8256046855	4.2739743838	0.1415473308
H	0	1.0791228267	3.5251774265	-1.7318120917
C	0	1.0157959925	3.1608807674	2.1248548956
H	0	-0.3951012952	1.5591558963	1.8045791409
C	0	1.8205443470	4.1380809174	1.5322562259
H	0	2.4400059605	5.0410992018	-0.3348725494
H	0	0.9846875611	3.0596773703	3.2124785684
H	0	2.4323682262	4.7982952562	2.1519273146
C	0	-4.0491514795	0.3257228117	-0.7304638018
C	0	-4.3927594880	-0.9186831460	-0.1852153240
C	0	-4.9211203651	1.4107569823	-0.5703806051
C	0	-5.5961846660	-1.0722710429	0.5065520967
H	0	-3.7054264043	-1.7576152308	-0.3059520598
C	0	-6.1243997897	1.2569121638	0.1209718231
H	0	-4.6544802066	2.3851831782	-0.9895400054
C	0	-6.4632924736	0.0130062289	0.6614397598
H	0	-5.8582118696	-2.0452979433	0.9291734361
H	0	-6.7989733966	2.1085098611	0.2379968052
H	0	-7.4046441886	-0.1100304991	1.2026874938

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O	0	-2.9412381790	2.5211321601	-0.7238641986
C	0	-3.4593316769	3.8025332067	-1.0717858687
O	0	-0.8911464385	3.4232387633	-0.5048120058
C	0	-1.6153667841	2.4593027390	-0.5234864317
C	0	-1.1730614177	1.0589328585	-0.2425451991
C	0	-0.3756352643	0.7864762175	0.8865060764
N	0	1.1377374555	0.1742926430	-1.1146924774
O	0	0.3187341270	0.9724527403	-1.6993734697
C	0	0.9932552730	-1.2586183143	-1.4789480900
C	0	1.5623210611	0.5296846612	0.1261536129
H	0	-3.2317614072	4.5429505485	-0.2904476840
H	0	-3.0216807877	4.1453240737	-2.0212482268
H	0	-4.5433517275	3.6752796672	-1.1779303425
H	0	-0.1497805415	1.5531388380	1.6286874073
H	0	2.0055973016	-0.3021286390	0.6803499633
H	0	0.8535504919	-1.2471379519	-2.5681036893
H	0	0.0664571463	-1.6376433844	-1.0296652766
N	0	-2.0340339054	-0.0286341496	-0.5880837536
C	0	-2.3995818749	-0.8239604223	0.5862210439
C	0	-2.5659841833	-0.1213218401	-1.8619069040
H	0	-3.0367463340	-0.2189933965	1.2571210679
S	0	-0.8122047683	-0.8224899353	1.6440758505

C	0	-3.0138763927	-2.2340474582	0.4437165936
H	0	-3.2524606281	-0.9801364288	-1.9781898698
O	0	-2.3125620727	0.6370824702	-2.7662768253
O	0	-1.2612464304	-0.5593276941	3.0606128934
C	0	-4.4933051396	-2.1337954660	0.0111964398
C	0	-3.0124132299	-2.8887468240	1.8443061694
C	0	-2.2146272635	-3.1338346143	-0.5120333580
H	0	-4.6342269822	-1.7371152356	-1.0022744820
H	0	-4.9526787410	-3.1340786563	0.0372660470
H	0	-5.0540646025	-1.4886028412	0.7050028301
H	0	-3.5660504834	-3.8386311202	1.7996870847
H	0	-1.9963067536	-3.1105524693	2.2010572493
H	0	-3.4860242036	-2.2421008318	2.5969050241
H	0	-2.6655746456	-4.1374302391	-0.5421435905
H	0	-2.1867335672	-2.7537119131	-1.5422805587
H	0	-1.1770856772	-3.2528213741	-0.1659860885
C	0	2.1810951289	1.8391452740	0.4238383937
C	0	2.9172611753	1.9420520026	1.6188578956
C	0	2.0855858457	2.9595350285	-0.4185442771
C	0	3.5464169965	3.1358285899	1.9682932468
H	0	2.9987233130	1.0725080854	2.2771756815
C	0	2.7316161036	4.1460725214	-0.0712727584
H	0	1.4886063035	2.8963538330	-1.3243336841
C	0	3.4570710059	4.2432519796	1.1195002101
H	0	4.1127813687	3.1996608042	2.9003461004
H	0	2.6513456039	5.0108258426	-0.7339582790
H	0	3.9495817338	5.1809595884	1.3880411855
C	0	2.1691835275	-2.0999504561	-1.0680491938
C	0	2.0745597497	-2.9735357876	0.0239268339
C	0	3.3894624244	-1.9933324876	-1.7515470086
C	0	3.1765672352	-3.7356244161	0.4218111666
H	0	1.1349623366	-3.0399832269	0.5775027240
C	0	4.4918743894	-2.7503808838	-1.3536623536
H	0	3.4726098681	-1.3077774935	-2.5989079468
C	0	4.3868407888	-3.6248937193	-0.2666143806
H	0	3.0893247531	-4.4137908296	1.2738260376
H	0	5.4372805022	-2.6601155236	-1.8936830669
H	0	5.2499840932	-4.2185571135	0.0434855101

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O	0	-3.0018720783	1.6381545347	1.6403329179
C	0	-3.5849190871	2.7799636503	2.2638671371
O	0	-1.3929098995	2.9515830696	0.7698849554
C	0	-1.8595770447	1.8545853012	0.9652395983
C	0	-1.2690516944	0.5910104279	0.4522768381
C	0	-0.5987512995	0.5519633701	-0.7985324511
N	0	1.2506535002	0.0690202218	0.9031730406
O	0	0.4569840909	0.7474081712	1.6432416116
C	0	1.4554277019	-1.3598662144	1.2572175925
C	0	1.3838210890	0.4840566185	-0.3899860139
H	0	-3.8378842367	3.5476567473	1.5173357013
H	0	-2.8860873155	3.2150980000	2.9933807522
H	0	-4.4886936384	2.4217924512	2.7707962141
H	0	-0.6189711527	1.4394868897	-1.4326302898
H	0	1.8039323702	-0.2934923935	-1.0322098518
H	0	1.2000684939	-1.4094803615	2.3227983034
H	0	0.7544160423	-1.9684584839	0.6716703756
N	0	-1.8221120693	-0.6674575024	0.8089891745
C	0	-2.1420760146	-1.5215909816	-0.3209714408
C	0	-1.9292768708	-1.1346562498	2.1092347619
H	0	-1.8611175746	-2.5646810342	-0.1128690745
S	0	-0.9409740825	-1.0180251288	-1.6866638952

C	0	-3.6127232885	-1.4594381916	-0.8107898204
H	0	-2.2581480208	-2.2005605247	2.1208027918
O	0	-1.6929821544	-0.5053921379	3.1077872737
O	0	0.2521509398	-1.9540025662	-1.5876124095
C	0	-3.9764232075	-0.0584835629	-1.3302630447
C	0	-4.5446260993	-1.8098531090	0.3614373523
C	0	-3.7869964741	-2.5014257759	-1.9279893465
H	0	-3.3352372210	0.2473156804	-2.1714738699
H	0	-5.0171942975	-0.0550285587	-1.6896885380
H	0	-3.8953054488	0.6931025948	-0.5335282110
H	0	-5.5880354007	-1.8351959818	0.0106643889
H	0	-4.3112044999	-2.7997972172	0.7850178417
H	0	-4.4789913044	-1.0604930597	1.1634764187
H	0	-3.5449646677	-3.5151549024	-1.5700963928
H	0	-4.8298005841	-2.5085379229	-2.2800659088
H	0	-3.1438015884	-2.2848799730	-2.7945976625
C	0	1.8219626550	1.8574668553	-0.7405318319
C	0	2.4444606078	2.0275793611	-1.9898880543
C	0	1.6567905799	2.9725462926	0.0980727214
C	0	2.8978129415	3.2826832962	-2.3960801712
H	0	2.5824626472	1.1615648919	-2.6430602625
C	0	2.1253424104	4.2224456894	-0.3076235150
H	0	1.1462012399	2.8530900836	1.0501483585
C	0	2.7413574183	4.3856618918	-1.5521047146
H	0	3.3817524653	3.3973886122	-3.3689546986
H	0	1.9936192638	5.0823917470	0.3532849030
H	0	3.0965881835	5.3706301507	-1.8646788094
C	0	2.8692934207	-1.8024358946	0.9842386118
C	0	3.1579786858	-2.6019824061	-0.1301351349
C	0	3.9158756573	-1.3863951811	1.8203483115
C	0	4.4750899774	-2.9874576576	-0.3977280858
H	0	2.3417328608	-2.9024751842	-0.7911255965
C	0	5.2303648054	-1.7692625987	1.5515360549
H	0	3.6949205537	-0.7549906249	2.6852654037
C	0	5.5121047839	-2.5730146240	0.4413716334
H	0	4.6911221942	-3.6122220103	-1.2678527609
H	0	6.0387973182	-1.4416613430	2.2096593469
H	0	6.5413934178	-2.8741732421	0.2314874699

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O	0	0.9766059621	2.3583482008	0.5159649701
C	0	1.5432117619	3.5212020180	1.1261882608
O	0	2.9325715484	1.2759463340	0.7534607521
C	0	1.7915195561	1.3109392483	0.3744221303
C	0	1.0824823815	0.1022052101	-0.2740328943
C	0	0.8001994336	-1.0035069786	0.7551036313
O	0	1.9556834864	-0.4772946096	-1.2299604989
N	0	2.3568331861	-1.7970797355	-0.8228240799
C	0	3.6428134287	-1.7186544150	-0.1430213697
C	0	1.2510416964	-2.2810800695	-0.0102389951
H	0	2.3745055005	3.9023311370	0.5158570713
H	0	1.9177869517	3.2820697336	2.1319546699
H	0	0.7353094708	4.2597697376	1.1806077604
H	0	1.3596830762	-0.8633029280	1.6872836204
H	0	1.6359892155	-3.0197459232	0.7072397188
H	0	4.3562979772	-1.2294655252	-0.8186254265
H	0	3.6228776924	-1.1500522843	0.8037130964
H	0	3.9845217450	-2.7483125655	0.0403874016
N	0	-0.1990739933	0.4461060708	-0.8934109933
C	0	-1.3207429575	0.4486373084	0.0390504093
C	0	-0.1316536698	1.2435482453	-2.0239442189
H	0	-1.2365412053	1.2981231406	0.7394294210

S	0	-0.9654074826	-0.9332950645	1.2935913486
C	0	-2.7737880454	0.3708068112	-0.4961478915
H	0	-1.1220712904	1.4540769930	-2.4687147256
O	0	0.8996653082	1.6538129431	-2.5002319043
O	0	-0.9895988936	-0.2295349290	2.6304307778
C	0	-3.2494822736	1.7570082841	-0.9837856641
C	0	-3.6942185710	-0.0080322226	0.6875043726
C	0	-2.9106496969	-0.6891769405	-1.5950668249
H	0	-2.7345169447	2.1120147040	-1.8852451795
H	0	-4.3229335199	1.7114254447	-1.2237951619
H	0	-3.1134279851	2.5147504737	-0.1962441866
H	0	-4.7454456698	0.1146865053	0.3875646045
H	0	-3.5600731522	-1.0568285333	0.9905872764
H	0	-3.5083292442	0.6235451129	1.5691936073
H	0	-2.5816356926	-1.6738618235	-1.2349183106
H	0	-3.9634716825	-0.7757546977	-1.9057028481
H	0	-2.3148732527	-0.4517880044	-2.4869661990
C	0	0.1655181079	-2.9340065494	-0.8518570170
C	0	-0.7597648392	-3.7948121165	-0.2451602839
C	0	0.0820228420	-2.7076465770	-2.2317376815
C	0	-1.7584092084	-4.4139452385	-1.0005107670
H	0	-0.6964985205	-3.9912886191	0.8281338279
C	0	-0.9125546230	-3.3314432736	-2.9878974984
H	0	0.8059310433	-2.0449852680	-2.7048316280
C	0	-1.8370447189	-4.1827945365	-2.3765455705
H	0	-2.4701709121	-5.0848009165	-0.5138156112
H	0	-0.9656546736	-3.1491622714	-4.0639043975
H	0	-2.6147428130	-4.6683176998	-2.9707779110

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O	0	-1.0741406608	-2.3928071908	-1.0531563089
C	0	-1.5473157120	-3.6471420856	-1.5433835457
O	0	-3.0815950359	-1.9914625257	-0.1018680815
C	0	-1.9306493236	-1.7111415245	-0.2768862534
C	0	-1.2575754651	-0.4159173638	0.2022362876
C	0	-1.1725410491	0.6185449888	-0.9504963732
O	0	-2.0830417168	0.1719541103	1.1615069528
N	0	-1.7466224937	1.5816059360	1.1128692937
C	0	-2.7429554683	2.2522877506	1.9199993018
C	0	-1.8142417560	1.8815844812	-0.3212987608
H	0	-1.7340773193	-4.3309604096	-0.7020539662
H	0	-2.4803544908	-3.5190793120	-2.1116193125
H	0	-0.7539550999	-4.0428142324	-2.1886325563
H	0	-1.7343208057	0.2982998934	-1.8348560680
H	0	-2.8725218423	1.8661846779	-0.6561847117
H	0	-3.7716378679	2.0489221812	1.5636346889
H	0	-2.5475343661	3.3322973735	1.8749200735
H	0	-2.6491316645	1.9138528343	2.9608064253
N	0	0.1051615363	-0.6463130424	0.7024993350
C	0	1.0859669527	0.3664040520	0.3385511136
C	0	0.2639534324	-1.7165562943	1.5478997693
H	0	0.8536929383	1.3256349242	0.8255316863
S	0	0.6147661967	0.6340277542	-1.4806199505
C	0	2.5969916682	0.0682756004	0.4973122797
H	0	1.2710474918	-1.8021336728	1.9897473537
O	0	-0.6210463432	-2.5097779013	1.7904811234
O	0	1.0206050259	2.0046880786	-1.9520574727
C	0	3.3798099314	1.1884082651	-0.2253479551
C	0	2.9923792088	-1.2818353333	-0.1251809967
C	0	3.0016131259	0.1493601529	1.9850905030
H	0	3.0473240208	2.1864386306	0.0971044927
H	0	4.4497314563	1.0857194766	0.0105330326

H	0	3.2629609127	1.1509075321	-1.3157957603
H	0	4.0887354871	-1.3789415039	-0.1337841410
H	0	2.5911598441	-2.1469480901	0.4196079533
H	0	2.6396898711	-1.3514652752	-1.1653668278
H	0	2.5352663608	-0.6148387126	2.6202229522
H	0	4.0921970155	0.0277154002	2.0756195521
H	0	2.7392606186	1.1341525872	2.4023005326
C	0	-1.2308105577	3.2341864984	-0.6650567686
C	0	-1.6205502046	3.8583600723	-1.8550727666
C	0	-0.3072228361	3.8746941346	0.1690692586
C	0	-1.0734490525	5.0868348631	-2.2245856636
H	0	-2.3515385180	3.3709875735	-2.5063079993
C	0	0.2321044352	5.1097242962	-0.1927530653
H	0	-0.0096983651	3.3972747624	1.1035812368
C	0	-0.1413683258	5.7153602844	-1.3946635675
H	0	-1.3770630509	5.5570098218	-3.1628857796
H	0	0.9538677463	5.5993282403	0.4655916867
H	0	0.2876263149	6.6783210220	-1.6815809323

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0 1

O	0	-1.2091304486	2.1711330958	-0.8199802658
C	0	-1.9091009244	3.2896816014	-1.3697404926
O	0	-3.1435914701	1.3668936841	0.0123710988
C	0	-1.9560815766	1.3006895422	-0.1190047992
C	0	-1.0696956673	0.1406656772	0.3815305075
C	0	-0.9117111231	-0.9413910357	-0.7017869102
N	0	-1.7346687759	-1.8995514007	1.3024924730
O	0	-1.7511329695	-0.4740643634	1.4515060651
C	0	-0.6029134679	-2.4508761265	2.0312919590
C	0	-1.7391173372	-2.1156289934	-0.1408951258
H	0	-2.7241749507	2.9512720264	-2.0260494251
H	0	-2.3355232480	3.9033636492	-0.5628370647
H	0	-1.1687956121	3.8643564380	-1.9386284715
H	0	-1.2101146754	-0.6240494457	-1.7086482513
H	0	-1.2395626445	-3.0733091717	-0.3547851101
H	0	-0.6794091975	-3.5477968644	1.9991580658
H	0	-0.6809475892	-2.1277022832	3.0780122492
H	0	0.3881164271	-2.1526917530	1.6411012254
N	0	0.2763285778	0.6046237517	0.7580761604
C	0	1.3122772119	0.3756107183	-0.2419148303
C	0	0.3000901404	1.5903918329	1.7253843611
H	0	1.1419680224	1.0042395066	-1.1350874289
S	0	0.8903388452	-1.3321606880	-0.9204651385
C	0	2.8049755768	0.4644398281	0.1712630066
H	0	1.3163733961	1.9172892859	2.0104690054
O	0	-0.6995042165	2.0445482910	2.2327847462
O	0	1.1476202976	-1.3056922596	-2.4067235907
C	0	3.2586746867	1.9385849817	0.2474242480
C	0	3.6561282349	-0.1904659477	-0.9404077136
C	0	3.0687207231	-0.2727069264	1.4928876236
H	0	2.7805511627	2.5130261798	1.0507422517
H	0	4.3448048389	1.9792343516	0.4225100561
H	0	3.0533475302	2.4550129513	-0.7031498120
H	0	4.7207222086	-0.0048101263	-0.7338263107
H	0	3.5136052368	-1.2793393813	-0.9931179583
H	0	3.4158270725	0.2175285687	-1.9328061278
H	0	4.1462528371	-0.2645862496	1.7171812332
H	0	2.5469702743	0.1800129988	2.3472190485
H	0	2.7502318061	-1.3244436158	1.4239519769
C	0	-3.1340837057	-2.1414959789	-0.7430784074
C	0	-4.2572194664	-1.7297327675	-0.0203396782
C	0	-3.2829510395	-2.5627375087	-2.0719001029

C	0	-5.5177620043	-1.7445783636	-0.6234367872
H	0	-4.1331466470	-1.3871055241	1.0060616485
C	0	-4.5427173522	-2.5788593223	-2.6723281424
H	0	-2.4042993877	-2.8809604099	-2.6421246127
C	0	-5.6653533079	-2.1685837853	-1.9461833903
H	0	-6.3902673527	-1.4149094454	-0.0544578138
H	0	-4.6487716244	-2.9145959664	-3.7067172027
H	0	-6.6532821550	-2.1783296464	-2.4129747851

Sa-PM-PxSi

0 1

O	0	1.3171613623	2.0004980966	-1.4405985890
C	0	2.0201161584	3.1097734742	-2.0007533390
O	0	2.8828512348	1.8012786455	0.1772761686
C	0	1.8218155949	1.5132067964	-0.2935717271
C	0	0.8929639788	0.4004222706	0.2399999144
C	0	0.8507686635	-0.7820453865	-0.7628340210
N	0	2.3468471472	-1.1618977971	0.9848725764
O	0	1.3935508850	-0.1628298459	1.4247197508
C	0	2.6958118226	-1.9338103292	2.1537783019
C	0	1.6060615214	-1.9061660431	-0.0442708489
H	0	3.0714865512	2.8498659885	-2.1920532531
H	0	1.9826393682	3.9621472350	-1.3062108308
H	0	1.5078874172	3.3573279743	-2.9382850093
H	0	1.2698588607	-0.5215709704	-1.7393010179
H	0	0.8586539285	-2.5887372316	0.4061816446
H	0	3.3924335309	-2.7227662176	1.8366162852
H	0	3.2032378483	-1.2817914286	2.8777646391
H	0	1.8113422773	-2.4007960158	2.6327744353
N	0	-0.4676527342	0.8506946202	0.4833788077
C	0	-1.4024412856	-0.2628300419	0.5198573870
C	0	-0.6948030904	2.1578176677	0.8546679183
H	0	-1.1070046269	-0.9692753167	1.3144587052
S	0	-0.9418080927	-1.2401180036	-1.0437162854
C	0	-2.9264704877	-0.0153939567	0.6094763436
H	0	-1.7546911394	2.3784206456	1.0649497345
O	0	0.1690543374	3.0021162446	0.9300466863
O	0	-1.1052867153	-2.7098319764	-0.7096753729
C	0	-3.4308857484	0.9359820630	-0.4901486550
C	0	-3.3029853951	0.4879479296	2.0196567467
C	0	-3.6348996039	-1.3773768780	0.4288764710
H	0	-3.1219320620	0.5802594656	-1.4848756353
H	0	-4.5308303669	0.9703011310	-0.4733808092
H	0	-3.0702216752	1.9672022469	-0.3778827361
H	0	-4.3983636546	0.5616584199	2.1015108636
H	0	-2.9570895014	-0.2218169157	2.7870181940
H	0	-2.8907644119	1.4740092504	2.2691968231
H	0	-3.2438981471	-2.1333617787	1.1254476835
H	0	-4.7102292771	-1.2484894041	0.6227054536
H	0	-3.5198339992	-1.7836089820	-0.5849481752
C	0	2.5102819284	-2.7029390187	-0.9554912140
C	0	1.9843040071	-3.8062220553	-1.6419100438
C	0	3.8411355766	-2.3213337762	-1.1720381159
C	0	2.7870237424	-4.5272394196	-2.5286602469
H	0	0.9370066876	-4.0769269742	-1.4856276221
C	0	4.6426584068	-3.0501928431	-2.0547347269
H	0	4.2346706570	-1.4529607274	-0.6402740143
C	0	4.1189845463	-4.1540349732	-2.7338787425
H	0	2.3707357611	-5.3860501556	-3.0609635618
H	0	5.6820422056	-2.7523904777	-2.2141497822
H	0	4.7475309973	-4.7220795252	-3.4240898285

Sa-PM-TSnRe

0 1

O	0	3.4113296155	0.7614250585	-0.5864512794
C	0	4.8319995901	0.7607902500	-0.7012756293
O	0	3.5347530249	-1.0468435855	0.7445399692
C	0	2.8771329657	-0.2362673916	0.1278246596
C	0	1.3902184389	-0.1831052391	0.1286796945
C	0	0.6693867258	-0.5547631451	1.2804425205
O	0	1.2203919679	-2.0261494927	-0.9295185833
N	0	0.8130364010	-2.7725603415	0.0310907226
C	0	1.8112302454	-3.6095281723	0.7034567344
C	0	-0.2701915253	-2.3153383547	0.7159583000
H	0	5.1774759397	-0.1665108630	-1.1819576910
H	0	5.3047927611	0.8409502703	0.2890407713
H	0	5.0874591666	1.6283074162	-1.3212956983
H	0	1.1997924232	-0.8679783504	2.1827149040
H	0	-0.4473252496	-2.8463851816	1.6564234510
H	0	2.4483067862	-4.0414114387	-0.0776731119
H	0	2.4392501593	-2.9917100221	1.3627060063
H	0	1.3051888904	-4.4076333170	1.2621656476
N	0	0.7009176720	0.8016759079	-0.6400647691
C	0	-0.0059815688	1.7363471192	0.2360713899
C	0	0.8246239283	0.8691732747	-2.0151408304
H	0	0.7357042335	2.3109451420	0.8204461756
S	0	-0.6569250397	0.6547021539	1.6716851816
C	0	-1.0841133222	2.7032072195	-0.2943990158
H	0	0.2312307040	1.6941574014	-2.4508889112
O	0	1.4887144338	0.1195240983	-2.6891237031
O	0	-0.2240082769	1.3788994409	2.9243627767
C	0	-0.4357342964	3.8394977277	-1.1143150509
C	0	-1.7453119114	3.3719088432	0.9333535283
C	0	-2.1748756998	1.9747393119	-1.0918901311
H	0	0.0312258570	3.5020123507	-2.0483471482
H	0	-1.2033135103	4.5820499639	-1.3823123796
H	0	0.3358546952	4.3533973857	-0.5200152114
H	0	-2.4238282749	4.1667704539	0.5889855580
H	0	-2.3406272856	2.6605029429	1.5239162575
H	0	-0.9997905402	3.8162109163	1.6087958136
H	0	-2.6221730153	1.1685574487	-0.4935027130
H	0	-2.9757374012	2.6811836441	-1.3602739969
H	0	-1.8031719086	1.5244720351	-2.0213348922
C	0	-1.5099723512	-1.9020812980	0.0130841986
C	0	-2.6900567569	-1.8075645757	0.7737069265
C	0	-1.5749637047	-1.6520201077	-1.3707129102
C	0	-3.9051538693	-1.4804631657	0.1733852474
H	0	-2.6537645449	-1.9986442361	1.8491892112
C	0	-2.7987986845	-1.3505254960	-1.9692244853
H	0	-0.6645114236	-1.7014646324	-1.9649121753
C	0	-3.9651647841	-1.2573456268	-1.2051712877
H	0	-4.8089625634	-1.4093228153	0.7827391223
H	0	-2.8359327308	-1.1732255521	-3.0466722078
H	0	-4.9166443857	-1.0074533756	-1.6802659560

Sa-PM-TSnSi

0 1

O	0	3.2171981003	0.3165799075	0.7497476950
C	0	4.6238650919	0.1569754233	0.9152033115
O	0	3.2081478000	-1.3928674196	-0.7115179815
C	0	2.6113062502	-0.5730691008	-0.0466592213
C	0	1.1371797031	-0.3791300269	-0.0817338661
C	0	0.4066218014	-0.6289137490	-1.2689092011
O	0	0.7713728220	-2.3018370204	0.7964349627
N	0	0.2162630680	-2.8762899870	-0.2109815757

C	0	1.0700924266	-3.7579148134	-1.0093965480
C	0	-0.7983178205	-2.1702321070	-0.7986698733
H	0	4.8483247036	-0.8311314089	1.3431996927
H	0	5.1451314574	0.2502865547	-0.0492856869
H	0	4.9405337002	0.9498644968	1.6029718376
H	0	0.9662056641	-1.0238452116	-2.1209323750
H	0	-1.1039870418	-2.5737893356	-1.7685194313
H	0	1.8649064481	-3.1701064947	-1.4946664218
H	0	0.4612213031	-4.2960432145	-1.7472878171
H	0	1.5397315776	-4.4726549067	-0.3214381919
N	0	0.4927055953	0.5564879081	0.7671921295
C	0	-0.4811796184	1.4234516753	0.1110503595
C	0	0.5163755861	0.4270190180	2.1491957386
H	0	-1.5032591914	1.2394421239	0.4808137058
S	0	-0.5394224967	0.8571699287	-1.7111473607
C	0	-0.1425726294	2.9377076352	0.1306238586
H	0	-0.2697578382	1.0522577343	2.6252266074
O	0	1.2673291457	-0.2778324144	2.7743024218
O	0	-1.9584219443	0.5748636980	-2.1254345785
C	0	-1.2349415096	3.6767271097	-0.6631050961
C	0	1.2443162892	3.1802896799	-0.4876581694
C	0	-0.1433328156	3.4773046627	1.5715210934
H	0	-2.2259299751	3.5261964553	-0.2060609590
H	0	-1.0248988955	4.7570758442	-0.6761261324
H	0	-1.3012007099	3.3376817962	-1.7079460592
H	0	1.5062943435	4.2476599713	-0.4239389053
H	0	2.0151343095	2.6029174199	0.0444201335
H	0	1.2685000066	2.8925027150	-1.5495340469
H	0	0.6880672938	3.0713381716	2.1654237410
H	0	-0.0251752051	4.5720359582	1.5517416141
H	0	-1.0887367534	3.2522646971	2.0905944977
C	0	-1.9408841820	-1.6753493675	0.0208190845
C	0	-3.1567404448	-1.4261281564	-0.6387515737
C	0	-1.8823697587	-1.4981481558	1.4157220002
C	0	-4.2742439548	-0.9816395857	0.0647674069
H	0	-3.2183783119	-1.5584635288	-1.7183694661
C	0	-3.0046603626	-1.0531285739	2.1169897053
H	0	-0.9591873050	-1.7215278216	1.9436257853
C	0	-4.2001619861	-0.7813982392	1.4457081588
H	0	-5.2049790114	-0.7838234885	-0.4714366117
H	0	-2.9402831716	-0.9220122883	3.1999700739
H	0	-5.0734145533	-0.4250961687	1.9976935345

Sa-PM-TSxRe

0 1

O	0	0.5238142015	2.9639753827	-0.9694225905
C	0	0.1001389590	4.2590459533	-1.3876113784
O	0	-1.6286787008	2.3421439163	-0.7545678685
C	0	-0.4522068362	2.1114712290	-0.6211517304
C	0	0.1056246840	0.8171010262	-0.1262345402
C	0	-0.3876206158	-0.4023479787	-0.6258113888
N	0	-1.0179249899	-0.4384964526	1.8903421258
O	0	-0.9091590682	0.8268418727	1.7070900064
C	0	0.0049103392	-1.0660621402	2.7334505240
C	0	-1.6235705330	-1.1535896173	0.9058086983
H	0	-0.5696547522	4.1905041945	-2.2577820852
H	0	-0.4333880694	4.7677440779	-0.5708697503
H	0	1.0122796386	4.8101927506	-1.6459510143
H	0	-1.1136266734	-0.4381125587	-1.4387969741
H	0	-1.4204940123	-2.2278947406	0.9730001819
H	0	-0.3811815880	-2.0008416005	3.1610196799
H	0	0.2409730863	-0.3533909839	3.5320129473
H	0	0.9154136036	-1.2737554523	2.1538815822

N	0	1.4816929230	0.7389141599	0.2524664572
C	0	2.2074418433	-0.2374745986	-0.5645287410
C	0	2.0185533870	1.6445054526	1.1505095024
H	0	2.2536117697	0.1200761665	-1.6095147576
S	0	0.9445963973	-1.6457039334	-0.8060308559
C	0	3.5982361520	-0.7635242385	-0.1479401674
H	0	3.1006753662	1.4906344170	1.3164916834
O	0	1.3900746134	2.5077482373	1.7133895441
O	0	1.0232024484	-2.0276148259	-2.2643294804
C	0	4.6799838175	0.3135434643	-0.3829389174
C	0	3.9497778516	-1.9433124869	-1.0836098552
C	0	3.6186428887	-1.2722642605	1.3019649652
H	0	4.5933935332	1.1845930520	0.2787540532
H	0	5.6762381063	-0.1245854060	-0.2162102978
H	0	4.6427248947	0.6761000992	-1.4218476149
H	0	4.9861773104	-2.2593936723	-0.8918416400
H	0	3.2987691666	-2.8145860145	-0.9240742555
H	0	3.8603111411	-1.6623146880	-2.1429136970
H	0	4.6097472646	-1.6884948509	1.5385827433
H	0	3.4058336425	-0.4851141099	2.0383598223
H	0	2.8818517712	-2.0788357597	1.4389482795
C	0	-2.9651351078	-0.8300353754	0.3752983831
C	0	-3.6405023671	-1.8454192025	-0.3273044591
C	0	-3.5903173670	0.4174901434	0.5423525449
C	0	-4.9141124834	-1.6253694683	-0.8495425977
H	0	-3.1603256881	-2.8188278566	-0.4622559742
C	0	-4.8713753775	0.6253766249	0.0311205995
H	0	-3.0578359936	1.2174538198	1.0496731125
C	0	-5.5357757589	-0.3863748279	-0.6679668302
H	0	-5.4240584032	-2.4237928479	-1.3935982300
H	0	-5.3481994615	1.5986839709	0.1676642014
H	0	-6.5343659539	-0.2091750622	-1.0745199462

Sa-PM-TSxSi

0 1

O	0	-1.2127910961	2.7578394211	-0.6435333091
C	0	-1.0613064051	4.0742966759	-1.1686282003
O	0	0.9405179314	2.3249912665	-1.1446444879
C	0	-0.1040981882	1.9963014382	-0.6332773639
C	0	-0.3320225382	0.6938186388	0.0379614341
C	0	0.3258090752	-0.4849546809	-0.3960741224
N	0	1.3064091472	-0.0806406887	1.9305024050
O	0	1.0304639981	1.1276335447	1.6239107065
C	0	0.6139757519	-0.6790043123	3.0815125835
C	0	1.7922851047	-0.8677546138	0.9244092274
H	0	-0.7301677379	4.0423557297	-2.2174551872
H	0	-0.3194492490	4.6365074834	-0.5824938981
H	0	-2.0464283062	4.5490892565	-1.0894016512
H	0	0.9121054441	-0.4489730881	-1.3154620913
H	0	1.7113068224	-1.9325823903	1.1592243323
H	0	1.3562469110	-1.0343322851	3.8123850017
H	0	0.0067315495	0.1148856792	3.5302851604
H	0	-0.0031683358	-1.5254100379	2.7437939357
N	0	-1.5518052782	0.4158499939	0.7080608536
C	0	-2.1883075390	-0.8229475141	0.2972041840
C	0	-2.0571477253	1.1574110279	1.7633460819
H	0	-2.6008243629	-1.3556004958	1.1667641966
S	0	-0.7813731355	-1.9482129407	-0.2625084084
C	0	-3.2730715318	-0.6829968757	-0.8028817699
H	0	-2.9562127616	0.6618772376	2.1996918836
O	0	-1.6011962392	2.1884792638	2.1862064677
O	0	-0.3933866992	-2.7948271793	0.9381221142
C	0	-2.6794485909	-0.1456603089	-2.1157169274

C	0	-4.3572676869	0.2925447534	-0.3147475910
C	0	-3.9013561044	-2.0676403317	-1.0318431094
H	0	-1.8897109335	-0.8040787139	-2.5095078485
H	0	-3.4687609919	-0.0815973666	-2.8807625243
H	0	-2.2628411130	0.8614002284	-1.9793212029
H	0	-5.1665586527	0.3499888440	-1.0591608965
H	0	-4.8028568165	-0.0373228710	0.6373956539
H	0	-3.9533555825	1.3064840238	-0.1807695604
H	0	-4.3431079220	-2.4643911837	-0.1035389344
H	0	-4.7020424185	-2.0004269824	-1.7840629445
H	0	-3.1626834515	-2.7982122048	-1.3953887482
C	0	3.0088104564	-0.5048936347	0.1539324164
C	0	3.7374683969	-1.5619844758	-0.4199473446
C	0	3.4592066820	0.8134047637	-0.0294851504
C	0	4.8960094184	-1.3133733938	-1.1562783440
H	0	3.3932472370	-2.5903883307	-0.2792697237
C	0	4.6265167119	1.0543391541	-0.7548014455
H	0	2.8798465460	1.6368885465	0.3800393366
C	0	5.3463662229	-0.0009170713	-1.3231140209
H	0	5.4513625768	-2.1464821675	-1.5937497139
H	0	4.9683971063	2.0832556974	-0.8893332301
H	0	6.2539443036	0.1991224706	-1.8978282251

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0 1

O	0	0.8252726804	2.4404630321	0.8318043373
C	0	1.3345528951	3.6432958162	1.4168046462
O	0	2.9276254867	1.7293268059	0.4693466200
C	0	1.7445108218	1.5810578810	0.3577064210
C	0	1.0466724412	0.3294202687	-0.2263652431
C	0	0.7405440413	-0.6982161969	0.8604887689
O	0	1.9321160159	-0.3252226317	-1.1178716145
N	0	2.2542819836	-1.6155117242	-0.6129795388
C	0	1.1133077736	-2.0531109357	0.1789748993
H	0	1.8788421143	4.2282760056	0.6614872972
H	0	2.0178509061	3.4098873961	2.2460075777
H	0	0.4620788635	4.1994072545	1.7789260893
H	0	1.4229196398	-0.5657888847	1.7107396830
H	0	1.4674359605	-2.7264268275	0.9677202400
N	0	-0.2206968753	0.6777853975	-0.8850680575
C	0	-1.4129223140	0.6832621090	-0.0200646931
C	0	-0.0669599515	1.6365549239	-1.8748663491
H	0	-1.4949279464	1.6733723572	0.4581556754
S	0	-0.9519943406	-0.3733890504	1.5223576670
C	0	-2.8092038867	0.3246168628	-0.5979207958
H	0	-1.0186448327	2.0008609698	-2.2993128079
O	0	1.0133867436	2.0434201076	-2.2383716755
O	0	-1.6931476786	-1.6872769510	1.5934602837
C	0	-3.2761847479	1.3908778511	-1.6129259618
C	0	-3.8095520626	0.3664157336	0.5800174444
C	0	-2.8294941306	-1.0464203430	-1.2781310572
H	0	-2.7690172533	1.2976015046	-2.5831965740
H	0	-4.3506755809	1.2495808008	-1.8057193635
H	0	-3.1380999632	2.4171140100	-1.2350746905
H	0	-4.8280980341	0.2059621652	0.1961985587
H	0	-3.6058099565	-0.4162197249	1.3212338585
H	0	-3.7950698971	1.3493772362	1.0804359654
H	0	-2.5587495386	-1.8450004381	-0.5793916259
H	0	-3.8388174298	-1.2497013243	-1.6691131662
H	0	-2.1281510623	-1.0733142373	-2.1215029742
C	0	3.5763841485	-1.7453982837	-0.1379586833
C	0	4.5435711165	-0.7565643234	-0.3770052454
C	0	3.9548219981	-2.9409322887	0.5024099666

C	0	5.8555338391	-0.9553669259	0.0530443410
H	0	4.2523167305	0.1634749446	-0.8754911822
C	0	5.2706931800	-3.1194916571	0.9301378663
H	0	3.2317613658	-3.7468866632	0.6378151732
C	0	6.2310968631	-2.1283494282	0.7135526496
H	0	6.5943418324	-0.1713848444	-0.1309747060
H	0	5.5456039659	-4.0527443062	1.4278838734
H	0	7.2608943217	-2.2727954094	1.0468968895
C	0	0.1127808722	-2.8104988420	-0.6771740174
C	0	-0.7045554693	-3.7874390689	-0.0955600694
C	0	0.0825220834	-2.6337403512	-2.0659601242
C	0	-1.5586804177	-4.5576790163	-0.8850387562
H	0	-0.6870563144	-3.9314804321	0.9851490343
C	0	-0.7677023325	-3.4093037788	-2.8573755833
H	0	0.7324029101	-1.8898341001	-2.5256901921
C	0	-1.5951076204	-4.3687665161	-2.2697833389
H	0	-2.1952933621	-5.3118091319	-0.4165531384
H	0	-0.7818689257	-3.2614088886	-3.9398930974
H	0	-2.2603500300	-4.9752392683	-2.8892318444

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0 1

O	0	-0.8411693668	-2.4533375244	-0.7394860163
C	0	-1.1748692988	-3.7839762348	-1.1369922417
O	0	-2.9252718991	-2.1603543486	0.0742990002
C	0	-1.8004463165	-1.7826621576	-0.0845516985
C	0	-1.2803224885	-0.3840570272	0.2857940087
C	0	-1.3262062249	0.5783339403	-0.9211657038
O	0	-2.1693824602	0.1625576926	1.2089923299
N	0	-1.9560674147	1.5827981286	1.1117237978
C	0	-1.9484406783	1.8761837012	-0.3239648561
H	0	-1.3620075721	-4.4051321910	-0.2486663400
H	0	-2.0746737064	-3.7884411271	-1.7694746146
H	0	-0.3095316015	-4.1626124597	-1.6935684348
H	0	-1.9629385397	0.1879054628	-1.7226454804
H	0	-2.9859697061	1.9254407995	-0.7087654678
N	0	0.1009834231	-0.4191453657	0.7838878346
C	0	1.0453267404	0.5109813338	0.1810581222
C	0	0.3325406846	-1.3190775363	1.7955541238
H	0	0.8935195920	1.5391656993	0.5426499426
S	0	0.4072036325	0.5618250154	-1.6053661284
C	0	2.5597369624	0.1784306159	0.2186980728
H	0	1.3404476560	-1.2571573206	2.2405755769
O	0	-0.5006684937	-2.1142777066	2.1757138830
O	0	0.7565011489	1.8744137087	-2.2509944493
C	0	3.2841427382	1.1052770055	-0.7844394540
C	0	2.8340107861	-1.2822062678	-0.1769541107
C	0	3.1436785191	0.5119228937	1.6083739769
H	0	3.0054869586	2.1594006037	-0.6391401457
H	0	4.3704980345	1.0073395508	-0.6393728687
H	0	3.0587489255	0.8558181316	-1.8296639115
H	0	3.9162007506	-1.4337017080	-0.3085711137
H	0	2.4902824507	-2.0070406358	0.5732959864
H	0	2.3380529376	-1.5286545194	-1.1279715053
H	0	2.7318960637	-0.0935233601	2.4262212448
H	0	4.2322476793	0.3471490084	1.5983489265
H	0	2.9679032388	1.5705141624	1.8558760015
C	0	-2.8454833788	2.2450821052	1.9841622178
C	0	-3.1181901344	1.6714537658	3.2399358951
C	0	-3.4278005985	3.4774810345	1.6460259438
C	0	-3.9500352281	2.3325239744	4.1400089277
H	0	-2.6821015223	0.7044069872	3.4873090242
C	0	-4.2495679503	4.1331439949	2.5670994765

H	0	-3.2327391943	3.9393926377	0.6800154397
C	0	-4.5173793888	3.5698897796	3.8149464333
H	0	-4.1581806858	1.8725195162	5.1091293492
H	0	-4.6899309169	5.0948828728	2.2928697708
H	0	-5.1655907984	4.0852968999	4.5268644029
C	0	-1.2561712093	3.1841638020	-0.6501534597
C	0	-1.5305371929	3.8071039100	-1.8721605838
C	0	-0.3520573508	3.7818457384	0.2340953842
C	0	-0.8831639534	4.9899249976	-2.2248646863
H	0	-2.2445998648	3.3510926839	-2.5631366044
C	0	0.2929897098	4.9699032577	-0.1149578151
H	0	-0.1728700283	3.3225886731	1.2071042021
C	0	0.0372473079	5.5719915907	-1.3487763239
H	0	-1.0948388324	5.4586818814	-3.1885878942
H	0	0.9945171638	5.4305619484	0.5847654627
H	0	0.5454708414	6.4992266154	-1.6235952000

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0 1

O	0	-1.2227631635	2.2821699826	-0.8819158367
C	0	-1.9241114620	3.3973201557	-1.4381090430
O	0	-3.1670803787	1.4306001344	-0.1213700676
C	0	-1.9748632931	1.3891774468	-0.2203168534
C	0	-1.0857309153	0.2374666415	0.2873348363
C	0	-0.9105963272	-0.8542662477	-0.7833225622
N	0	-1.6392146521	-1.7897269373	1.2324491001
O	0	-1.7898912687	-0.3850398582	1.3489087643
C	0	-1.6982074970	-2.0452432801	-0.2009539375
H	0	-2.7101568711	3.0548788009	-2.1268865377
H	0	-2.3883773647	3.9902350955	-0.6366683103
H	0	-1.1751807673	3.9934555098	-1.9723126219
H	0	-1.2076640521	-0.5588461837	-1.7970150417
H	0	-1.1736804554	-2.9824594641	-0.4256695373
N	0	0.2480712348	0.6989396588	0.6894890728
C	0	1.3240527757	0.4391292718	-0.2588498854
C	0	0.2605482742	1.6610355835	1.6755768692
H	0	1.2207797989	1.0751621204	-1.1572115671
S	0	0.8942943529	-1.2544878656	-0.9588860604
C	0	2.7957538943	0.4670279806	0.2350791083
H	0	1.2715552319	1.9999765854	1.9620837054
O	0	-0.7462231270	2.0847537273	2.1987671959
O	0	1.1879627499	-1.2175013992	-2.4383814926
C	0	3.3090131297	1.9190961864	0.3428516836
C	0	3.6761790137	-0.2201751777	-0.8340733135
C	0	2.9507145786	-0.2888952808	1.5631042618
H	0	2.8159078372	2.5121578839	1.1235153860
H	0	4.3846476537	1.9100312694	0.5770169049
H	0	3.1793032700	2.4484403520	-0.6141407262
H	0	4.7349959092	-0.0737654608	-0.5737782257
H	0	3.4979933215	-1.3036695240	-0.8906895255
H	0	3.5020736016	0.1939617113	-1.8378487659
H	0	4.0164194648	-0.3599194013	1.8294892875
H	0	2.4308944008	0.2002172554	2.3975215111
H	0	2.5507781786	-1.3110203192	1.4875198109
C	0	-0.5847571861	-2.2952756399	2.0297462560
C	0	-0.0378925010	-3.5676245277	1.7896110653
C	0	-0.1337499105	-1.5561536764	3.1381447422
C	0	0.9691416195	-4.0654216699	2.6183637294
H	0	-0.3971511170	-4.1810847090	0.9630087391
C	0	0.8679611573	-2.0700197907	3.9592809858
H	0	-0.5763711477	-0.5825362574	3.3410367068
C	0	1.4362620071	-3.3216441818	3.7042154539
H	0	1.3882164477	-5.0524043952	2.4081121615

H	0	1.2092674903	-1.4777886907	4.8120243422
H	0	2.2239263189	-3.7166943663	4.3488461036
C	0	-3.1102728091	-2.1299312522	-0.7501419665
C	0	-3.2849927521	-2.6020023730	-2.0585689027
C	0	-4.2246055265	-1.7289616335	-0.0074860999
C	0	-4.5606361640	-2.6781843143	-2.6192629133
H	0	-2.4142823124	-2.9139423342	-2.6440417531
C	0	-5.5014699966	-1.8074311929	-0.5697658397
H	0	-4.0862731863	-1.3428450772	1.0014781441
C	0	-5.6741064828	-2.2804037990	-1.8726120470
H	0	-4.6860823402	-3.0523151010	-3.6381082710
H	0	-6.3670232138	-1.4882002722	0.0153721314
H	0	-6.6746523819	-2.3382868990	-2.3078113947

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0 1

O	0	1.4592330305	1.8583921687	-1.4676461807
C	0	2.2452188337	2.9125169704	-2.0263742728
O	0	2.9623219539	1.5891343997	0.1994308419
C	0	1.8987161787	1.3627617200	-0.3004619149
C	0	0.8916445563	0.3190925510	0.2292907205
C	0	0.7840569492	-0.8727949247	-0.7514889403
N	0	2.2286740215	-1.3175203266	1.0186331134
O	0	1.3464997544	-0.2554713139	1.4290748937
C	0	1.5132870994	-2.0248221161	-0.0465178109
H	0	3.2835146742	2.5848260926	-2.1804788704
H	0	2.2386040212	3.7785440727	-1.3481249895
H	0	1.7763881829	3.1715121792	-2.9831439573
H	0	1.1875239705	-0.6375398828	-1.7404386712
H	0	0.7548770284	-2.7215530098	0.3594522484
N	0	-0.4397228198	0.8483977547	0.4623892946
C	0	-1.4272415587	-0.2184682056	0.5473507397
C	0	-0.5961286788	2.1762690498	0.7972365253
H	0	-1.1543972396	-0.9098037691	1.3627428488
S	0	-1.0327630215	-1.2659378386	-0.9888713247
C	0	-2.9358827973	0.1050582606	0.6447810738
H	0	-1.6423526964	2.4590249155	1.0011679272
O	0	0.3124676682	2.9740006515	0.8477180274
O	0	-1.2442226053	-2.7175392986	-0.6091619615
C	0	-3.4082303319	1.0400460067	-0.4825296775
C	0	-3.2696577487	0.6751917631	2.0401518670
C	0	-3.7081099105	-1.2283332450	0.5209339411
H	0	-3.1323924089	0.6335744020	-1.4675301105
H	0	-4.5046515944	1.1307965155	-0.4528819093
H	0	-2.9946540254	2.0551275506	-0.4128752283
H	0	-4.3593836277	0.8009240182	2.1327479635
H	0	-2.9445389887	-0.0208141090	2.8287967522
H	0	-2.8109212286	1.6504313374	2.2477310755
H	0	-3.3437685941	-1.9760372162	1.2405738821
H	0	-4.7740347039	-1.0435305556	0.7210577581
H	0	-3.6244183626	-1.6750896476	-0.4789839224
C	0	2.7143645184	-1.9984210693	2.1476189299
C	0	3.1038225749	-1.2512270018	3.2747802499
C	0	2.8685133889	-3.3940457585	2.1520848636
C	0	3.6358607737	-1.8993350301	4.3858589718
H	0	2.9846022450	-0.1684441331	3.2528469341
C	0	3.4208491111	-4.0261846368	3.2697956192
H	0	2.5773621207	-3.9882897318	1.2871515062
C	0	3.8023430414	-3.2897471477	4.3917860172
H	0	3.9317126511	-1.3094968731	5.2570381655
H	0	3.5425389566	-5.1121088392	3.2589161688
H	0	4.2265744209	-3.7916969934	5.2640482936
C	0	2.4299525680	-2.7786965547	-0.9831507793

C	0	1.8981576960	-3.8317701388	-1.7393311880
C	0	3.7691412058	-2.4071068008	-1.1518635551
C	0	2.7051111469	-4.5148915567	-2.6521043926
H	0	0.8455412908	-4.0985699788	-1.6120090643
C	0	4.5740490284	-3.0969662362	-2.0618369241
H	0	4.1706000568	-1.5822530049	-0.5602222624
C	0	4.0457691140	-4.1514282668	-2.8125222921
H	0	2.2858025462	-5.3360872145	-3.2385046549
H	0	5.6214003634	-2.8099372361	-2.1834026599
H	0	4.6784810108	-4.6900326076	-3.5221291188

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0 1

O	0	-0.2703593101	-3.4100748222	-0.5594469513
C	0	-1.0079007081	-4.6166035396	-0.7271838991
O	0	-2.0447063623	-2.4884551022	0.4760517514
C	0	-0.9265195038	-2.3934985508	0.0190267418
C	0	-0.0917039863	-1.1718881012	0.0979975749
C	0	-0.2804851011	-0.2316714261	1.1203900306
O	0	-1.4530374762	-0.1045267460	-1.3753783135
N	0	-1.9506951297	0.7298167470	-0.5455701152
C	0	-1.0481105947	1.4263189254	0.2116435140
H	0	-1.8735777605	-4.4504263207	-1.3861810016
H	0	-1.3716053008	-4.9925339601	0.2408477381
H	0	-0.3175648061	-5.3348906298	-1.1854596510
H	0	-1.0347019741	-0.4090178615	1.8907215164
H	0	-1.4969183439	1.9621326422	1.0498047924
N	0	1.2353284232	-1.1549706917	-0.4181627969
C	0	2.1947777153	-0.9337060998	0.6635122651
C	0	1.5074486245	-1.3820995186	-1.7543218459
H	0	2.1653292567	-1.8003207421	1.3483415497
S	0	1.3306425749	0.3129629971	1.8331439873
C	0	3.6651126974	-0.5554983035	0.3964771360
H	0	2.5914189960	-1.3669699783	-1.9715402859
O	0	0.6750866745	-1.5688886785	-2.6086659897
O	0	1.4337180694	-0.3185211162	3.2000805008
C	0	4.4403803321	-1.7694573521	-0.1591062448
C	0	4.3052730943	-0.2125284844	1.7618844532
C	0	3.7947092055	0.6704287814	-0.5180147444
H	0	4.1064362499	-2.0900171435	-1.1542753227
H	0	5.5092167373	-1.5170808619	-0.2381273453
H	0	4.3476838647	-2.6315850113	0.5196614121
H	0	5.3886917369	-0.0746330409	1.6279348214
H	0	3.9032074354	0.7188000741	2.1868143085
H	0	4.1428228477	-1.0091063939	2.5025062249
H	0	3.2258048872	1.5197471897	-0.1143406478
H	0	4.8508899345	0.9738358305	-0.5875430052
H	0	3.4334384715	0.4896132534	-1.5382432236
C	0	0.0799233198	2.1464650440	-0.4276973354
C	0	0.6761250140	3.1930427911	0.3019462261
C	0	0.5402919716	1.8838278274	-1.7321831944
C	0	1.6923479436	3.9672759778	-0.2558450270
H	0	0.3296461649	3.4073397299	1.3158966129
C	0	1.5410668280	2.6786377616	-2.2925438601
H	0	0.1042969483	1.0622142480	-2.2968875324
C	0	2.1238545011	3.7173650735	-1.5618693869
H	0	2.1410943304	4.7742922081	0.3277579260
H	0	1.8769112563	2.4713166643	-3.3113175393
H	0	2.9157345833	4.3260135662	-2.0045112925
C	0	-3.3323003028	0.6307899297	-0.1847221064
C	0	-4.0554575980	-0.5030176346	-0.5742891357
C	0	-3.9713463036	1.6850593684	0.4840308172
C	0	-5.4085710483	-0.5911313690	-0.2589446046

H	0	-3.5353478456	-1.3035824607	-1.0929769553
C	0	-5.3267242888	1.5793975735	0.8008080550
H	0	-3.4304207903	2.5994358074	0.7297414339
C	0	-6.0496618784	0.4418896692	0.4344695343
H	0	-5.9675025907	-1.4832156352	-0.5501164049
H	0	-5.8209957348	2.4016589382	1.3229283825
H	0	-7.1108209513	0.3633449571	0.6805654527

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O	0	-0.3021154628	-3.1949891196	-0.9953892880
C	0	0.2089928573	-4.4835594205	-1.3211762612
O	0	1.6385818733	-2.7037447383	0.0314120066
C	0	0.5465147212	-2.3628089017	-0.3707744467
C	0	-0.0551223655	-1.0283871194	-0.1541313320
C	0	0.3039321368	-0.2077188719	0.9314234975
O	0	1.6120093868	-0.0175167761	-1.4496396684
N	0	2.0520021470	0.7472574438	-0.5268285734
C	0	1.0995162103	1.4458760588	0.1806789531
H	0	1.0699432646	-4.3935561873	-2.0003542541
H	0	0.5297504227	-5.0201548019	-0.4156695915
H	0	-0.6093833740	-5.0188278848	-1.8171863136
H	0	1.1051364573	-0.5657119222	1.5841766637
H	0	1.4854267723	1.9302078941	1.0792425455
N	0	-1.3170922474	-0.6878015247	-0.6978244248
C	0	-2.2178693378	-0.0111460349	0.2302688590
C	0	-1.5502635057	-0.6740383807	-2.0665377500
H	0	-2.4568826219	1.0102856892	-0.1064607243
S	0	-1.2053743832	0.2403539466	1.8379094267
C	0	-3.5052377015	-0.7946726026	0.5956908448
H	0	-2.4954412952	-0.1428193533	-2.3088533297
O	0	-0.8255840016	-1.1502253330	-2.9034273644
O	0	-1.2363067011	1.6817633214	2.2711650454
C	0	-4.2817816104	0.0310621128	1.6368033028
C	0	-3.1448685472	-2.1821339440	1.1519388143
C	0	-4.3970932519	-0.9738237591	-0.6452633071
H	0	-4.5641644366	1.0152739400	1.2302904692
H	0	-5.2034335260	-0.4969637214	1.9251206144
H	0	-3.7003630854	0.2094373713	2.5541552644
H	0	-4.0607538213	-2.7560670329	1.3609032808
H	0	-2.5403945934	-2.7477892145	0.4272282396
H	0	-2.5761642214	-2.1061796549	2.0910089530
H	0	-3.9421547473	-1.6472295633	-1.3857301395
H	0	-5.3576978702	-1.4206248584	-0.3446870690
H	0	-4.6141906034	-0.0101736004	-1.1333239343
C	0	0.0931179575	2.2669125308	-0.5494013879
C	0	-0.4870113384	3.3512927009	0.1351183027
C	0	-0.2536015433	2.0599234092	-1.8980468386
C	0	-1.4123541098	4.1812652736	-0.4953782830
H	0	-0.2284667984	3.5264581901	1.1776705456
C	0	-1.1786925526	2.8963650328	-2.5251442512
H	0	0.2058014422	1.2437028685	-2.4483476687
C	0	-1.7725149314	3.9507926945	-1.8261337365
H	0	-1.8555314173	5.0115255939	0.0591947634
H	0	-1.4359972536	2.7153791432	-3.5715754003
H	0	-2.5039494137	4.5963944424	-2.3185090939
C	0	3.3542694969	0.5164105451	0.0155123720
C	0	3.9861463756	-0.7104160292	-0.2235538105
C	0	4.0071591643	1.5299072142	0.7331574538
C	0	5.2657990886	-0.9245867069	0.2848345070
H	0	3.4473865961	-1.4810298097	-0.7693530359
C	0	5.2860499557	1.2976657485	1.2401359481
H	0	3.5357888189	2.5044568682	0.8673825807

C	0	5.9189735805	0.0709909973	1.0198194517
H	0	5.7540862373	-1.8864701934	0.1129914888
H	0	5.7952717998	2.0877496258	1.7964688928
H	0	6.9214209076	-0.1067115965	1.4154251911

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O	0	0.2606912135	3.4831386125	-0.9947319578
C	0	0.9044603793	4.5932732792	-1.6147942929
O	0	2.2473990739	2.4376871282	-0.8264583873
C	0	1.0461989612	2.4354904921	-0.7053408613
C	0	0.2637992878	1.3002088680	-0.1405458876
C	0	0.7423441459	0.5815032624	0.9644574720
N	0	0.8044507262	-1.1783491547	-0.9564180024
O	0	0.9587434051	-0.1210115456	-1.6619506965
C	0	1.4939386106	-1.2173755775	0.2213992105
H	0	1.7074265908	4.9884156492	-0.9747884988
H	0	1.3385909444	4.2922539183	-2.5799197751
H	0	0.1263924977	5.3505098915	-1.7684742005
H	0	1.6285879701	0.9033158723	1.5121250380
H	0	1.1316928686	-1.9756545154	0.9171894944
N	0	-1.1515116818	1.2566876779	-0.2619846051
C	0	-1.8143627356	1.0996836412	1.0386325326
C	0	-1.7755530399	1.4766475277	-1.4751156547
H	0	-1.7077464004	2.0330195224	1.6208513432
S	0	-0.6209606952	0.0131630697	2.0474085762
C	0	-3.2701370033	0.5893816140	1.1382510938
H	0	-2.8757838970	1.5045596241	-1.3892250050
O	0	-1.2016370828	1.6081790536	-2.5309385454
O	0	-0.4797337234	0.7094855175	3.3787460117
C	0	-4.2692947219	1.7093267060	0.7750272937
C	0	-3.5399437362	0.2354121668	2.6198425582
C	0	-3.4944662606	-0.6685370476	0.2864241960
H	0	-4.2182674265	2.0311510755	-0.2731258394
H	0	-5.2963834895	1.3563531072	0.9559658493
H	0	-4.1028520460	2.5959382188	1.4065497791
H	0	-4.6114734413	0.0223534367	2.7498627612
H	0	-2.9845526205	-0.6580582555	2.9404397488
H	0	-3.2611041963	1.0564977887	3.2960485305
H	0	-4.4925718601	-1.0854319050	0.4908322443
H	0	-3.4316256063	-0.4777632565	-0.7922128443
H	0	-2.7514115840	-1.4435544071	0.5253829338
C	0	2.9518739585	-0.9904861609	0.3009074712
C	0	3.6167082992	-1.5231914034	1.4221595359
C	0	3.6957429157	-0.2869211146	-0.6628933116
C	0	4.9934709684	-1.3693623883	1.5757573288
H	0	3.0455372432	-2.0688987873	2.1785989247
C	0	5.0754916334	-0.1509414995	-0.5102987084
H	0	3.1816448753	0.1652155367	-1.5063696855
C	0	5.7291822464	-0.6839699619	0.6044946500
H	0	5.4929948276	-1.7896879043	2.4516859749
H	0	5.6435547227	0.3958275903	-1.2664063581
H	0	6.8086666415	-0.5606428030	0.7199651907
C	0	-0.3361650091	-2.0039704044	-1.2311413393
C	0	-1.1263971965	-1.6667890984	-2.3396143803
C	0	-0.6342689837	-3.1468714140	-0.4745890634
C	0	-2.2328188936	-2.4515318561	-2.6580475427
H	0	-0.8635881613	-0.7824909416	-2.9171566089
C	0	-1.7521815646	-3.9161894457	-0.8006762651
H	0	-0.0053956815	-3.4535801882	0.3602564232
C	0	-2.5585720521	-3.5735506669	-1.8891153777
H	0	-2.8485528210	-2.1794266521	-3.5185137919
H	0	-1.9849221452	-4.7989133672	-0.2008994774

H	0	-3.4276742501	-4.1840431260	-2.1428882021

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O	0	-1.2639243038	-2.4171478628	-2.1770423874
C	0	-1.1822935686	-3.3550566075	-3.2467509519
O	0	0.9284240874	-2.7243260570	-1.7482942998
C	0	-0.1083271286	-2.1339898269	-1.5517796759
C	0	-0.2755677564	-1.0603202611	-0.5470288927
C	0	0.4654834723	-1.0290951358	0.6514444907
N	0	1.2942593302	1.0522092012	-0.6247536125
O	0	1.1652386735	0.2909864342	-1.6418218366
C	0	1.7968395639	0.4609772861	0.5036215153
H	0	-0.7973674762	-4.3229229594	-2.8923081784
H	0	-0.5140873022	-2.9768060852	-4.0345824231
H	0	-2.2018947696	-3.4642201949	-3.6349981195
H	0	1.1177037025	-1.8733308831	0.8787081331
H	0	1.6742562619	1.0642783856	1.4023775917
N	0	-1.4121487175	-0.2267480203	-0.5022936711
C	0	-1.9495838220	0.0083905845	0.8293303559
C	0	-1.8784823241	0.5025810732	-1.5899925649
H	0	-2.0772439600	1.0850031038	1.0217167304
S	0	-0.5918369388	-0.5124085924	2.0535188968
C	0	-3.2539464885	-0.7681598709	1.1490433783
H	0	-2.6256443829	1.2620005875	-1.2703606882
O	0	-1.5121985411	0.3723486946	-2.7288054585
O	0	-0.0519528816	0.7230520690	2.7451016768
C	0	-3.0252500911	-2.2824644710	1.0109639116
C	0	-4.3664706288	-0.3439563326	0.1749992393
C	0	-3.6865714680	-0.4094504351	2.5806019919
H	0	-2.2624449682	-2.6444877969	1.7174730611
H	0	-3.9592617831	-2.8246504741	1.2246069544
H	0	-2.7070226788	-2.5408274058	-0.0095570433
H	0	-5.3109509706	-0.8323672145	0.4609352682
H	0	-4.5336963009	0.7447749254	0.1960242686
H	0	-4.1418955485	-0.6443357707	-0.8587587080
H	0	-3.8646793237	0.6731071690	2.6827920125
H	0	-4.6213641071	-0.9319435844	2.8345896338
H	0	-2.9321551303	-0.6980086695	3.3283792537
C	0	3.0727530850	-0.2984507173	0.4759816798
C	0	3.8358101042	-0.2810329518	1.6579690949
C	0	3.5401704119	-1.0315114680	-0.6293838967
C	0	5.0522133901	-0.9595791778	1.7313903149
H	0	3.4683674237	0.2744896921	2.5249330168
C	0	4.7643556382	-1.6970493760	-0.5519395877
H	0	2.9309260838	-1.0907036755	-1.5276733828
C	0	5.5236875619	-1.6663713457	0.6216443433
H	0	5.6342375137	-0.9322754175	2.6556560992
H	0	5.1203782219	-2.2604124322	-1.4177373337
H	0	6.4762870795	-2.1990946716	0.6743018115
C	0	0.5832053810	2.3016688130	-0.6345154540
C	0	0.1838396736	2.9564276025	0.5392770382
C	0	0.2945097298	2.8506059723	-1.8922308755
C	0	-0.5078874198	4.1652756380	0.4386005036
H	0	0.3384095069	2.5021541114	1.5179276945
C	0	-0.3907853094	4.0613754430	-1.9719031958
H	0	0.5931005108	2.3017384419	-2.7834718794
C	0	-0.7944509668	4.7261892647	-0.8096808525
H	0	-0.8327321106	4.6668474303	1.3532843147
H	0	-0.6142148515	4.4855689979	-2.9534010063
H	0	-1.3326763885	5.6743008243	-0.8762772996

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O	0	3.0105623661	2.0920693737	-0.4515389712
C	0	3.8853862459	3.1877768086	-0.7260733499
O	0	1.2819813542	3.5239309931	-0.2409599633
C	0	1.7368740330	2.4177789891	-0.1666231846
C	0	0.9141916559	1.1437764625	0.1111373119
C	0	0.3836919071	0.5727480788	-1.2264504766
O	0	-0.2134245080	1.5174470554	0.8404408631
N	0	-1.3444325898	0.8205142725	0.2415602688
C	0	-2.5357190609	1.4452125208	0.7785231852
C	0	-1.0866180945	0.9861136848	-1.1886809810
H	0	3.9692872357	3.8348106834	0.1593207699
H	0	3.5075111896	3.7872138538	-1.5674631066
H	0	4.8596734243	2.7486496427	-0.9714818059
H	0	0.9269474593	0.9405995902	-2.1075112804
H	0	-1.1194513257	2.0672139113	-1.4498481511
C	0	-2.0322483851	0.2203400184	-2.1057591027
H	0	-1.6885804996	0.3228087673	-3.1472394001
H	0	-2.0734627447	-0.8416324494	-1.8373162940
H	0	-3.0472053792	0.6345754003	-2.0438439067
H	0	-2.3357419652	1.5932223295	1.8518114265
H	0	-2.7141664690	2.4517879707	0.3456363716
N	0	1.7092614086	0.1077438618	0.7686774596
C	0	2.1175745195	-1.0006106397	-0.0834447670
C	0	2.3097108686	0.4939230757	1.9466380013
H	0	2.9009622668	-0.6616952566	-0.7904626394
S	0	0.6579658305	-1.2776887248	-1.2386174044
C	0	2.5870023287	-2.3313111884	0.5708292408
H	0	2.9079720035	-0.2978941671	2.4322104067
O	0	2.1880059460	1.6034825386	2.4172035560
O	0	-0.4398616591	-1.9876558970	-0.4798952454
C	0	4.0653633506	-2.2163314553	0.9992362569
C	0	2.5221956729	-3.4445502385	-0.4992199615
C	0	1.6869237998	-2.7317361638	1.7524859229
H	0	4.2449430625	-1.4502798214	1.7646792907
H	0	4.4013066845	-3.1785323204	1.4158206940
H	0	4.7077108238	-1.9822910366	0.1351230483
H	0	3.0066568424	-4.3523903312	-0.1099889627
H	0	1.4835456982	-3.7018880476	-0.7499612621
H	0	3.0498868373	-3.1538683704	-1.4221553679
H	0	0.6327729332	-2.7257767861	1.4459790972
H	0	1.9558290138	-3.7449751181	2.0896355971
H	0	1.7969500901	-2.0590848712	2.6140028427
C	0	-3.7497709823	0.5571931734	0.6059388937
C	0	-5.0161089572	1.1248133133	0.4167817221
C	0	-3.6276581088	-0.8395430362	0.6629456714
C	0	-6.1488645278	0.3145944154	0.2972755106
H	0	-5.1168246645	2.2124699677	0.3594596187
C	0	-4.7594734343	-1.6474775733	0.5370574955
H	0	-2.6344792501	-1.2801205360	0.7700212383
C	0	-6.0230918377	-1.0755657152	0.3571529691
H	0	-7.1307665421	0.7714065525	0.1502615275
H	0	-4.6519656615	-2.7344828035	0.5747164538
H	0	-6.9062262050	-1.7115277577	0.2577008725

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O	0	2.4004508100	-2.4630719029	-0.9590250846
C	0	2.9777724921	-3.6773191776	-1.4346247107
O	0	0.7678848979	-3.6180354993	0.0847290171
C	0	1.3473572582	-2.5939919109	-0.1472948347
C	0	0.8595786651	-1.2041033829	0.3014909680

C	0	0.0528005412	-0.5328383182	-0.8423905748
O	0	-0.0648189383	-1.3853249377	1.3418449996
N	0	-1.0856061650	-0.3584710811	1.1604193584
C	0	-2.1528848516	-0.7406463662	2.0633214459
C	0	-1.3681442934	-0.4818563517	-0.2732390454
H	0	3.3939154739	-4.2493666208	-0.5918053195
H	0	2.2251693529	-4.2947145596	-1.9469412728
H	0	3.7741869249	-3.3848391316	-2.1289631614
H	0	0.1280965942	-1.0617996038	-1.7998136686
H	0	-1.8350531395	-1.4675437615	-0.4781921658
C	0	-2.2548444052	0.6346426038	-0.8368018548
H	0	-2.1669678334	0.5924517334	-1.9359676232
H	0	-1.8459654965	1.6075291131	-0.5303009526
H	0	-2.5734589199	-1.7343938350	1.8174533111
H	0	-2.9469873650	0.0135972780	2.0096030294
H	0	-1.7491266559	-0.7638002817	3.0845200753
N	0	1.9520312634	-0.3194190710	0.6833304321
C	0	1.7040934024	1.0919337029	0.4240207046
C	0	2.9174232773	-0.8528180785	1.5035936988
H	0	0.9028977684	1.4615808520	1.0904029007
S	0	0.8222637164	1.1075879155	-1.2442699343
C	0	2.8921829542	2.0923319707	0.4402362771
H	0	3.6530758137	-0.1168936951	1.8720077002
O	0	2.9739185872	-2.0285249771	1.7951989468
O	0	1.8141862336	0.8223216844	-2.3488244688
C	0	2.4365896741	3.3812786793	-0.2812117492
C	0	4.1237248268	1.5337252304	-0.2966074413
C	0	3.2284055502	2.4917957339	1.8921652700
H	0	1.4792951147	3.7549302324	0.1170196343
H	0	3.1906084662	4.1686819023	-0.1331013326
H	0	2.3324309763	3.2199407511	-1.3637854949
H	0	4.8582576784	2.3407928678	-0.4440423603
H	0	4.6279322966	0.7341950956	0.2628291342
H	0	3.8294546133	1.1357480554	-1.2769456300
H	0	3.5536599759	1.6495847391	2.5172496779
H	0	4.0443748136	3.2312168686	1.8899191219
H	0	2.3570951852	2.9534512272	2.3836187253
C	0	-3.7136015035	0.5461569514	-0.4510961797
C	0	-4.4879603405	-0.5670470317	-0.8114065722
C	0	-4.3233855237	1.5757118347	0.2787161218
C	0	-5.8307677996	-0.6548773755	-0.4402292704
H	0	-4.0359403272	-1.3776391350	-1.3894175346
C	0	-5.6682027615	1.4934916371	0.6505162596
H	0	-3.7336082241	2.4510491270	0.5641806855
C	0	-6.4255085662	0.3749682150	0.2951950422
H	0	-6.4169348709	-1.5307952854	-0.7283845232
H	0	-6.1243910087	2.3059624036	1.2212038232
H	0	-7.4761552088	0.3064939659	0.5864993994

Sb-MB-PxRe

0 1

O	0	-2.3851520689	1.9162919870	-1.3451721113
C	0	-3.1517092663	2.9472379984	-1.9733497799
O	0	-0.9901355876	3.4693644148	-0.4999474356
C	0	-1.2934260021	2.3234532878	-0.6763741407
C	0	-0.5581391570	1.1209136104	-0.0501474360
C	0	-1.0417456373	0.8812481084	1.3989777074
N	0	1.3405005376	0.9718793888	1.2745806779
O	0	0.7935549993	1.4899469666	0.0588916282
C	0	1.9150148117	-0.3606223085	1.0540634135
C	0	0.2428195663	1.0932504516	2.2337714667
H	0	-3.4812269920	3.6915736246	-1.2337120941
H	0	-2.5468393604	3.4532104869	-2.7396653329

H	0	-4.0138308845	2.4502033261	-2.4333084410
H	0	-1.8515835341	1.5609031593	1.6925832336
H	0	0.3424531609	0.2962075149	2.9840274706
C	0	0.2562038057	2.4780494698	2.8789297295
H	0	-0.5808974465	2.5913357769	3.5862142076
H	0	0.1756907671	3.2536352536	2.1028581967
H	0	1.2012149411	2.6256937808	3.4197772671
H	0	2.0948559733	-0.7761215165	2.0543362184
H	0	1.1989294516	-1.0399385499	0.5664726602
N	0	-0.7688849860	-0.1177273577	-0.8132184459
C	0	-1.8273449512	-0.9806886936	-0.3027493104
C	0	-0.3403159445	-0.0823840550	-2.1236746163
H	0	-2.8103878119	-0.5075763232	-0.4937531654
S	0	-1.7314367363	-0.8370898161	1.5748051539
C	0	-1.8996352887	-2.4656495197	-0.7609251343
H	0	-0.5156387719	-1.0205359492	-2.6793717682
O	0	0.2033177379	0.8794636218	-2.6207496252
O	0	-0.6222702117	-1.7168582284	2.1167851694
C	0	-2.5641035319	-2.5661474482	-2.1513778160
C	0	-2.8241945917	-3.2252061871	0.2181609921
C	0	-0.5135806152	-3.1306666818	-0.7514316695
H	0	-1.9750296242	-2.1164826467	-2.9605464257
H	0	-2.7082307209	-3.6266429595	-2.4089530963
H	0	-3.5549484060	-2.0844025888	-2.1497656567
H	0	-3.0090375276	-4.2381182374	-0.1690359659
H	0	-2.3673221517	-3.3274118846	1.2121196375
H	0	-3.8009956587	-2.7256835938	0.3238391751
H	0	-0.6138848992	-4.1926297862	-1.0241833169
H	0	0.1813403830	-2.6691147925	-1.4668385483
H	0	-0.0675442955	-3.0661153751	0.2497185162
C	0	3.2177220755	-0.3216082129	0.2864495271
C	0	3.2906845578	0.1840453737	-1.0223806137
C	0	4.3827702554	-0.8347311298	0.8732396651
C	0	4.5025571789	0.1746054856	-1.7162045722
H	0	2.4028274055	0.6046554420	-1.4943445153
C	0	5.5947360503	-0.8494820453	0.1772425351
H	0	4.3404883000	-1.2299678581	1.8922417216
C	0	5.6578536497	-0.3431993797	-1.1225257273
H	0	4.5426581288	0.5771702327	-2.7315471798
H	0	6.4909974733	-1.2542902180	0.6541956374
H	0	6.6033984506	-0.3500674191	-1.6705996671

Sb-MB-PxSi

0 1

O	0	-3.0329354966	1.5745513690	0.6487564055
C	0	-4.1338695192	2.4566654407	0.4122969731
O	0	-1.9020506743	2.5321703866	-1.0365043669
C	0	-1.9699829429	1.7369170162	-0.1348437722
C	0	-0.7996164773	0.7974181467	0.2321092729
C	0	-0.1415852011	0.1563132839	-1.0072808949
N	0	1.4757521701	1.3318875258	0.2669680559
O	0	0.1827302059	1.6764904869	0.7668297187
C	0	2.1166651852	0.3742874965	1.1761256925
C	0	1.2208603476	0.8736611877	-1.1016248030
H	0	-4.5209669305	2.3210319591	-0.6084183851
H	0	-3.8171674657	3.5018906075	0.5367834773
H	0	-4.8961243186	2.1936908111	1.1542636050
H	0	-0.7389033750	0.2206253270	-1.9238929275
H	0	2.0144614147	0.1647263302	-1.3815804184
C	0	1.2078473502	2.0440464721	-2.0792186661
H	0	1.0158480352	1.6853696716	-3.1024084826
H	0	0.4222212091	2.7623726306	-1.8103928766
H	0	2.1838130798	2.5489832987	-2.0568309551

H	0	2.0649471700	0.8356276013	2.1741164055
H	0	1.5920428829	-0.5960197590	1.2368262457
N	0	-1.1571300189	-0.2885339375	1.1469539634
C	0	-1.3158283737	-1.6184678760	0.5932297555
C	0	-1.3313080135	-0.0622997732	2.5025849296
H	0	-1.0050433333	-2.3424102094	1.3624818785
S	0	0.0723691986	-1.6740124697	-0.6992377059
C	0	-2.7166916282	-2.0550293464	0.0839008995
H	0	-1.4620164298	-1.0242240906	3.0542466536
O	0	-1.3317496934	1.0131128081	3.0429028648
O	0	-0.3378419816	-2.3907794566	-1.9635362423
C	0	-3.1603180949	-1.3184571809	-1.1913095492
C	0	-3.7343451572	-1.7861611999	1.2067379171
C	0	-2.6527609274	-3.5699458902	-0.1891771002
H	0	-2.4662169025	-1.5095498482	-2.0191687583
H	0	-4.1563331175	-1.6802169625	-1.4904642247
H	0	-3.2522817664	-0.2375027537	-1.0259853276
H	0	-4.7243969066	-2.1583525654	0.9000301909
H	0	-3.4597765995	-2.3070116271	2.1382733934
H	0	-3.8242218418	-0.7119412067	1.4203327653
H	0	-2.3877589092	-4.1240877180	0.7267077080
H	0	-3.6367481931	-3.9324741900	-0.5239939919
H	0	-1.9153792626	-3.8014797921	-0.9689358349
C	0	3.5482548349	0.1449429394	0.7590742546
C	0	4.0133769032	-1.1451051169	0.4763565139
C	0	4.4272003190	1.2308904046	0.6254958156
C	0	5.3392043722	-1.3536803998	0.0831407867
H	0	3.3279278399	-1.9927945874	0.5576484710
C	0	5.7490698278	1.0249396259	0.2299315180
H	0	4.0584904590	2.2392265703	0.8257051408
C	0	6.2094994854	-0.2688430314	-0.0403505778
H	0	5.6893447894	-2.3659226866	-0.1327648201
H	0	6.4259813159	1.8771524391	0.1313477842
H	0	7.2449501564	-0.4286741614	-0.3504673751

Sb-MB-TSnRe

0 1

O	0	1.6104551279	3.0283062345	-0.6516048733
C	0	1.5118080758	4.3850646313	-1.0763559789
O	0	-0.5366080561	2.7074089278	-1.2324406058
C	0	0.4849044911	2.3056566121	-0.7160286990
C	0	0.6719984018	0.9355279491	-0.1659943032
C	0	0.0138978438	-0.1647638924	-0.7627811947
O	0	-0.7473428720	1.2603629555	1.4179224551
N	0	-1.6783581810	0.4991883149	0.9802984806
C	0	-2.7893957154	1.1648423031	0.2562047551
C	0	-1.3150434257	-0.7808182333	0.7149968189
H	0	0.7777882143	4.9260685629	-0.4609290279
H	0	1.2001024244	4.4450898224	-2.1299462028
H	0	2.5102816528	4.8186612056	-0.9444554246
H	0	-0.6820437427	0.0408462262	-1.5793732371
H	0	-2.0809061814	-1.3672240868	0.1998870152
C	0	-0.5047544711	-1.4975571960	1.7581390998
H	0	-0.0991665548	-2.4245369039	1.3437519343
H	0	0.3099513597	-0.8679664708	2.1301721671
H	0	-1.1734466334	-1.7300163640	2.6051812285
H	0	-3.0210156675	2.0482183801	0.8674900267
H	0	-2.3950437512	1.5329035212	-0.7023601544
N	0	1.8993054706	0.5669158091	0.4538837994
C	0	2.5970071643	-0.4453337857	-0.3290397285
C	0	2.3784011455	1.2554420001	1.5582017924
H	0	3.0060395997	0.0435066812	-1.2330872795
S	0	1.1958976189	-1.4815466636	-1.1881311396

C	0	3.7038899552	-1.3352041940	0.2810220804
H	0	3.3321240580	0.8389272195	1.9318108732
O	0	1.8307466273	2.1971749971	2.0745312484
O	0	0.8849688230	-2.7883851174	-0.4864894902
C	0	5.0017459034	-0.5229201102	0.4895637683
C	0	4.0428008350	-2.4301957267	-0.7580231015
C	0	3.2457504484	-2.0041526779	1.5864619565
H	0	4.9313326851	0.2340836958	1.2806694391
H	0	5.8160776151	-1.2085824774	0.7706025962
H	0	5.3002486463	-0.0121485252	-0.4398458421
H	0	4.9142341167	-3.0040566656	-0.4090823500
H	0	3.2112831208	-3.1326919148	-0.8986088493
H	0	4.3058870232	-1.9873511921	-1.7328206943
H	0	2.3457626751	-2.6061488420	1.4077111598
H	0	4.0405058161	-2.6675427582	1.9618023888
H	0	3.0241025359	-1.2723814328	2.3763283230
C	0	-3.9863414256	0.2734158739	0.0753136200
C	0	-4.3550362996	-0.1739310711	-1.1998915529
C	0	-4.7388179117	-0.1435267794	1.1844955236
C	0	-5.4549093704	-1.0205771081	-1.3680187423
H	0	-3.7742714200	0.1470477382	-2.0687485801
C	0	-5.8342192756	-0.9917132692	1.0205476850
H	0	-4.4570397932	0.1996137149	2.1835995825
C	0	-6.1949746679	-1.4323787247	-0.2576375483
H	0	-5.7325518399	-1.3596879590	-2.3687828824
H	0	-6.4122344292	-1.3091144763	1.8917339884
H	0	-7.0536857898	-2.0955017579	-0.3861983235

Sb-MB-TSnSi

0 1

O	0	3.1655620651	0.9248152392	0.4665378433
C	0	4.5791849178	1.0605506584	0.3552454726
O	0	3.2196678032	-0.6897924440	-1.0979867251
C	0	2.6037155133	-0.0335163251	-0.2829241183
C	0	1.1477699915	-0.1425062256	-0.0448908857
C	0	0.2822759869	-0.7279771773	-0.9827376852
O	0	1.6236115401	-2.1291221000	1.0235747126
N	0	1.0952262489	-2.8600606810	0.1232754119
C	0	1.9869407560	-3.5084169653	-0.8442388389
C	0	-0.1930969228	-2.5663727654	-0.1970060467
H	0	4.8671016392	1.3273815602	-0.6727387848
H	0	4.8632684668	1.8568267824	1.0534003174
H	0	5.0779538649	0.1184751666	0.6269877794
H	0	0.6678041823	-1.0249122122	-1.9613396549
H	0	-0.5874363537	-3.1482422973	-1.0362717001
C	0	-1.1161073687	-2.3609193311	0.9903425802
H	0	-0.5901402040	-1.7514299234	1.7336335720
H	0	-1.2302960051	-3.3613266481	1.4510966215
H	0	2.8163547787	-3.9491178929	-0.2772884104
H	0	2.3946135241	-2.7534554727	-1.5324943313
H	0	1.4384950636	-4.2910113944	-1.3843130428
N	0	0.4629111719	0.7289462355	0.8388837484
C	0	-0.6659310680	1.4308404761	0.2309450135
C	0	0.6806857565	0.7796658891	2.2057861374
H	0	-1.5214310371	1.4251059439	0.9208202337
S	0	-1.2402773586	0.2904531039	-1.2184923578
C	0	-0.3808225668	2.8900884916	-0.2060554015
H	0	-0.0832226882	1.4229106334	2.7031819507
O	0	1.5534738895	0.2092898731	2.8084803899
O	0	-1.0212678873	0.9619815168	-2.5568377366
C	0	-1.6598454321	3.4695849322	-0.8391982811
C	0	0.8103815293	2.9731613214	-1.1750310942
C	0	-0.0447557303	3.7111683405	1.0538341663

H	0	-2.5150497503	3.3869217630	-0.1469824870
H	0	-1.5140222937	4.5383990148	-1.0595764648
H	0	-1.9117871178	2.9567745335	-1.7757278633
H	0	0.9679057088	4.0219794903	-1.4727730600
H	0	1.7301265087	2.6241760328	-0.6847717826
H	0	0.6273951992	2.3772863683	-2.0771156050
H	0	0.8881898463	3.3716711323	1.5270936260
H	0	0.0942331149	4.7665377298	0.7717916971
H	0	-0.8539105309	3.6691456396	1.8014545290
C	0	-2.4835741763	-1.7933283903	0.7055167669
C	0	-2.9790950090	-0.7487249446	1.4966615895
C	0	-3.2859520597	-2.2820809455	-0.3362071801
C	0	-4.2222566929	-0.1705972720	1.2268688262
H	0	-2.3734889528	-0.3774473544	2.3275097556
C	0	-4.5262876332	-1.7072344122	-0.6115320332
H	0	-2.9316857712	-3.1097659496	-0.9560008202
C	0	-4.9937103016	-0.6395296886	0.1616239521
H	0	-4.5863294241	0.6516395945	1.8477036875
H	0	-5.1300250948	-2.0882963737	-1.4384770904
H	0	-5.9604696366	-0.1823112766	-0.0608128987

Sb-MB-TSxRe

0 1

O	0	-1.7361985047	2.8461148691	-1.3206753756
C	0	-1.8829722490	4.2044607575	-1.7265834603
O	0	-0.9743431716	3.5408822396	0.6794000060
C	0	-1.2102253195	2.6489342329	-0.1047688640
C	0	-1.0051250845	1.2100436260	0.1934966474
C	0	-1.2028602673	0.7178079931	1.4926286814
N	0	1.3540654714	0.5180172282	1.2369552649
O	0	1.1974352139	1.4120214058	0.3481441737
C	0	1.7657619840	-0.8251461395	0.7592860357
C	0	0.6657500780	0.6764947568	2.3932921085
H	0	-2.5506257021	4.7484311119	-1.0416552349
H	0	-0.9050522287	4.7082182668	-1.7383052470
H	0	-2.3081430686	4.1762757235	-2.7369354953
H	0	-1.7144279477	1.3093842826	2.2539129021
H	0	0.7083015795	-0.1994228668	3.0505648837
C	0	0.6627492185	2.0259709992	3.0576745833
H	0	-0.0648837601	2.0361297787	3.8819219263
H	0	0.4063054669	2.8185371614	2.3443344429
H	0	1.6618159456	2.2242857483	3.4823317815
H	0	1.7693807033	-1.5021628786	1.6227842564
H	0	0.9926577682	-1.1637061694	0.0569778034
N	0	-1.1804832681	0.2145844822	-0.8175450462
C	0	-2.1432260129	-0.8072721575	-0.3951327016
C	0	-0.5352985159	0.2881530527	-2.0360197085
H	0	-3.1486008028	-0.3558302736	-0.3145162887
S	0	-1.7678172334	-1.0233853342	1.4636338482
C	0	-2.2485677464	-2.1670338338	-1.1201813136
H	0	-0.8467616743	-0.5125467487	-2.7299496490
O	0	0.2915079722	1.1182294290	-2.3359423685
O	0	-3.1034807795	-1.0805207573	2.1648691494
C	0	-2.9331962719	-2.0034500349	-2.4948212337
C	0	-3.1804841118	-3.0695906267	-0.2781180939
C	0	-0.8854792134	-2.8679913848	-1.2462046199
H	0	-2.3410470058	-1.4385445731	-3.2259090959
H	0	-3.1242802870	-2.9969094132	-2.9291977296
H	0	-3.9029721677	-1.4941207336	-2.3834843401
H	0	-3.3686172952	-4.0042336723	-0.8273876854
H	0	-2.7447472888	-3.3345275638	0.6954508206
H	0	-4.1457734555	-2.5821918390	-0.0780976048
H	0	-1.0178592032	-3.8617937623	-1.7003859719

H	0	-0.1666450081	-2.3167214560	-1.8678873800
H	0	-0.4344727020	-3.0159718837	-0.2532437941
C	0	3.1165831768	-0.7951481478	0.0900880644
C	0	3.2774039682	-0.1736744403	-1.1584561376
C	0	4.2257348720	-1.3770121134	0.7171647027
C	0	4.5359235868	-0.1414345030	-1.7619825743
H	0	2.4219569881	0.2990822760	-1.6443666986
C	0	5.4829650678	-1.3480536103	0.1079124098
H	0	4.1053405869	-1.8601574655	1.6910803735
C	0	5.6393292609	-0.7282412171	-1.1339995664
H	0	4.6547603636	0.3469162232	-2.7321396558
H	0	6.3400534839	-1.8086088750	0.6050606604
H	0	6.6210885910	-0.7025461691	-1.6132525908

Sb-MB-TSxSi

0 1

O	0	1.6897024945	-0.2447865119	1.9781397861
C	0	2.1788057635	-0.6719591151	3.2462118419
O	0	2.0780731828	-2.3001841896	1.1503051860
C	0	1.6194777067	-1.1864664578	1.0232675751
C	0	0.9880463099	-0.6739454760	-0.2138171756
C	0	1.4551247132	-1.0302297468	-1.4860885556
N	0	-0.7372280280	-2.3919992715	-1.4918666798
O	0	-0.7198768495	-2.2691257764	-0.2301459071
C	0	-1.9404879710	-1.9614657557	-2.2481357488
C	0	0.4390904326	-2.6698636360	-2.1111022553
H	0	2.1647608105	0.2140874736	3.8919036046
H	0	3.2005277096	-1.0706187209	3.1592028981
H	0	1.5273644999	-1.4553908357	3.6610158858
H	0	2.4637384676	-1.4188154918	-1.6438027871
H	0	0.3720771459	-2.6119017089	-3.2038647057
C	0	1.3097603838	-3.7687876933	-1.5598474428
H	0	2.2852032929	-3.7650204707	-2.0676752866
H	0	1.4707560704	-3.6453437882	-0.4826013986
H	0	0.8290304277	-4.7431021836	-1.7539291600
H	0	-1.6634323974	-1.9240994614	-3.3089229443
H	0	-2.6737251795	-2.7756876157	-2.1228265008
N	0	0.2476810988	0.5282634845	-0.2084856350
C	0	0.5723146610	1.4554082395	-1.2838470170
C	0	-0.7611369022	0.8016864911	0.6983149900
H	0	-0.3477295684	1.9639529829	-1.6042016920
S	0	0.9920732119	0.2616676333	-2.7172313655
C	0	1.6618085286	2.5084062781	-0.9679383524
H	0	-1.2501619784	1.7744165723	0.4754667078
O	0	-1.0923338799	0.0812906308	1.6069227314
O	0	2.2510161798	0.6592634445	-3.4556162387
C	0	3.0251550628	1.8653746226	-0.6635748299
C	0	1.2071735655	3.3087770611	0.2671506258
C	0	1.7638549538	3.4612190141	-2.1731303784
H	0	3.3889915647	1.2862116479	-1.5216514556
H	0	3.7597889446	2.6563003522	-0.4441047604
H	0	2.9647077685	1.2161754447	0.2212730871
H	0	1.9283450744	4.1179856796	0.4616503268
H	0	0.2191061799	3.7726933888	0.1145465753
H	0	1.1634201557	2.6759703682	1.1656180709
H	0	0.7948681107	3.9508295399	-2.3688256258
H	0	2.4999197675	4.2527342931	-1.9634503539
H	0	2.0790136308	2.9253155301	-3.0774473501
C	0	-2.5600044510	-0.6616013229	-1.8052165958
C	0	-3.2590020299	-0.5879322409	-0.5924392899
C	0	-2.4917344518	0.4733100613	-2.6257257691
C	0	-3.8738380554	0.6035624591	-0.2052716672
H	0	-3.2937149727	-1.4605394443	0.0602694290

C	0	-3.1063396669	1.6667165368	-2.2386160875
H	0	-1.9525804441	0.4208630290	-3.5741627590
C	0	-3.7982625076	1.7331198984	-1.0250347804
H	0	-4.3990367952	0.6529465071	0.7506559024
H	0	-3.0510209469	2.5430666225	-2.8889888744
H	0	-4.2818626948	2.6645115379	-0.7208245582

Sb-PB-PnRe

0 1

O	0	2.3544903642	2.3770465071	-0.3510963690
C	0	2.7887929714	3.7290712404	-0.5123959076
O	0	0.3805072988	3.1021046401	0.4606327112
C	0	1.1527486662	2.2132924471	0.2225253643
C	0	0.8135146007	0.7144009202	0.3713681659
C	0	0.2677467390	0.1928482151	-0.9564330172
O	0	-0.2314062565	0.5496877473	1.2886872464
N	0	-1.4871967604	0.2998254289	0.5853682001
C	0	-2.4547250813	1.2417414767	1.1514353684
C	0	-1.2203145699	0.5074329188	-0.8418648765
H	0	2.9046399817	4.2056751522	0.4720823788
H	0	2.0609244989	4.3049948975	-1.1025704393
H	0	3.7546450721	3.6818030392	-1.0293012735
H	0	0.7393078880	0.6438569322	-1.8398840103
H	0	-1.3186513399	1.5822010377	-1.1018680065
H	0	-2.4040327701	1.1133171405	2.2418602883
H	0	-2.1709667596	2.2851744433	0.9188783425
N	0	1.9750835566	-0.0799274241	0.7303449624
C	0	2.3377180818	-1.1463400416	-0.2028445204
C	0	2.7226923769	0.3825751622	1.7852254972
H	0	2.9284292141	-0.7317449428	-1.0434749859
S	0	0.7124132745	-1.6153844519	-1.0426791699
C	0	3.0699496398	-2.4064768871	0.3464396326
H	0	3.6148212737	-0.2288566577	2.0107627902
O	0	2.4388428075	1.3821177188	2.4099145683
O	0	-0.1087165443	-2.3950757797	-0.0478723488
C	0	4.5854739041	-2.1362844950	0.4548815360
C	0	2.8986431709	-3.5523677017	-0.6766351259
C	0	2.4826930974	-2.8547603384	1.6959899897
H	0	4.8418392184	-1.3389650354	1.1651050797
H	0	5.0965403898	-3.0500528814	0.7955363482
H	0	5.0083091209	-1.8609013400	-0.5247773045
H	0	3.5471185272	-4.3944130379	-0.3923294780
H	0	1.8636130356	-3.9211279571	-0.6979963810
H	0	3.1862226034	-3.2383269478	-1.6932672249
H	0	1.3900881305	-2.9382628356	1.6266756824
H	0	2.9009834661	-3.8363284363	1.9682114259
H	0	2.7234662863	-2.1588869420	2.5115450223
C	0	-3.8372401964	0.9164380860	0.6422053906
C	0	-4.4412840513	1.6946161708	-0.3510799670
C	0	-4.5025358236	-0.2273458891	1.1058246873
C	0	-5.6822325196	1.3338629395	-0.8832688224
H	0	-3.9261293172	2.5843994602	-0.7224492073
C	0	-5.7419602694	-0.5896447632	0.5801127956
H	0	-4.0266857001	-0.8461154823	1.8705851597
C	0	-6.3331594961	0.1884815366	-0.4211363260
H	0	-6.1375233470	1.9454019009	-1.6659002960
H	0	-6.2481785397	-1.4863317155	0.9459882892
H	0	-7.3006269850	-0.0991656300	-0.8397554605
C	0	-2.1234776442	-0.2756990692	-1.7742733832
C	0	-2.3831720109	0.2467172335	-3.0476647779
C	0	-2.6845707975	-1.5044887519	-1.4075966506
C	0	-3.1878049512	-0.4491002386	-3.9516084822
H	0	-1.9639968304	1.2174913840	-3.3287752397

C	0	-3.4966820945	-2.1946769501	-2.3089946681
H	0	-2.4708470690	-1.9045170641	-0.4188042894
C	0	-3.7499221636	-1.6735114855	-3.5808532357
H	0	-3.3864860135	-0.0287214441	-4.9404312348
H	0	-3.9391008958	-3.1483467161	-2.0114950025
H	0	-4.3893110683	-2.2175075236	-4.2804048604

Sb-PB-PnSi

0 1

O	0	1.9719644172	-2.5656263413	-0.9958211196
C	0	2.3101597847	-3.8951077169	-1.3926572890
O	0	0.4191474442	-3.3524379596	0.4384791774
C	0	1.0914134621	-2.4569705400	0.0015074976
C	0	0.8903696282	-0.9765444988	0.3828342235
C	0	0.0989449319	-0.2733833467	-0.7355832435
O	0	0.0752255875	-0.9026984873	1.5272097166
N	0	-1.1220906291	-0.1096786019	1.2158437882
C	0	-1.3293581897	-0.3539949421	-0.2234448241
H	0	2.8208051219	-4.4087516014	-0.5646170232
H	0	1.4090844188	-4.4624289202	-1.6674717090
H	0	2.9822321215	-3.7953805520	-2.2529708397
H	0	0.2650922182	-0.7093646626	-1.7274732461
H	0	-1.6714942984	-1.3958111217	-0.3830131289
C	0	-2.3134298278	0.6139022231	-0.8829292935
H	0	-2.2330342536	0.4489390493	-1.9722771606
H	0	-1.9757626388	1.6431275878	-0.6979834772
N	0	2.1321412638	-0.2576239412	0.5943212470
C	0	1.9196411410	1.1848222601	0.5430827703
C	0	3.1646477774	-0.9179762586	1.2211159111
H	0	1.2435421657	1.4798077269	1.3668012566
S	0	0.7800241201	1.4483834068	-0.9497430225
C	0	3.1350678620	2.1464924166	0.5102948566
H	0	4.0323177126	-0.2749048972	1.4477666059
O	0	3.1484954403	-2.1017267619	1.4827198500
O	0	1.5824498637	1.3876626302	-2.2309419071
C	0	2.6244155692	3.5365328029	0.0664002455
C	0	4.2094387914	1.6797933838	-0.4889507429
C	0	3.7130001854	2.3183607544	1.9309378231
H	0	1.7638805630	3.8654102955	0.6712076602
H	0	3.4268780744	4.2779863360	0.1956987745
H	0	2.3362631346	3.5385449625	-0.9943226568
H	0	4.9596616532	2.4754693654	-0.6176686108
H	0	4.7432758848	0.7811648454	-0.1502296956
H	0	3.7504668494	1.4627303727	-1.4627241688
H	0	4.1071683112	1.3893049998	2.3634929890
H	0	4.5417923520	3.0427678761	1.9035262439
H	0	2.9478781730	2.7079375713	2.6210740801
C	0	-3.7597453713	0.4767003006	-0.4576961074
C	0	-4.3928144807	-0.7718568336	-0.3797208510
C	0	-4.4969728892	1.6198676500	-0.1229947481
C	0	-5.7158281929	-0.8757551360	0.0498513092
H	0	-3.8423968732	-1.6811237325	-0.6303188462
C	0	-5.8262307248	1.5224962157	0.2950062956
H	0	-4.0158808501	2.6004035930	-0.1757624975
C	0	-6.4381361479	0.2713380080	0.3912538207
H	0	-6.1834050994	-1.8601253280	0.1250350780
H	0	-6.3809894721	2.4269007550	0.5565734472
H	0	-7.4729100363	0.1884633475	0.7316723115
C	0	-2.1671681226	-0.6020069097	2.0662049313
C	0	-3.0561588378	0.3276450335	2.6086269759
C	0	-2.3342763658	-1.9731648914	2.3065078726
C	0	-4.1545101338	-0.1131061185	3.3487670484
H	0	-2.8894156838	1.3884265277	2.4206460161

C	0	-3.4208128441	-2.4030016165	3.0686457586
H	0	-1.6066820283	-2.6791354940	1.9024684113
C	0	-4.3388956202	-1.4784682034	3.5793424504
H	0	-4.8648563278	0.6135105422	3.7488154864
H	0	-3.5548903145	-3.4701241607	3.2620721027
H	0	-5.1944894107	-1.8233707443	4.1647709062

Sb-PB-PxRe

0 1

O	0	-2.3031330316	1.9547654934	-1.4894636673
C	0	-3.0210114556	2.9667054509	-2.2015554812
O	0	-0.7683430185	3.4825834771	-0.8702511679
C	0	-1.1609846275	2.3518543023	-0.9017247882
C	0	-0.4960625433	1.1641519864	-0.1741280955
C	0	-1.0312259265	1.0163838202	1.2679373506
N	0	1.3600893639	1.0188146846	1.2155274902
O	0	0.8623511299	1.4898962222	-0.0405171454
C	0	1.9206827106	-0.3304297270	1.0684886524
C	0	0.2394826801	1.1730944212	2.1424088116
H	0	-3.2750406280	3.8034864022	-1.5346291346
H	0	-2.4104768666	3.3485706766	-3.0325252721
H	0	-3.9295301667	2.4860594629	-2.5829110915
H	0	-1.8048620653	1.7519695143	1.5165436431
H	0	0.2740529496	0.3507889903	2.8702704104
H	0	2.0796388279	-0.6966914379	2.0912690323
H	0	1.2004259692	-1.0210759138	0.6017740313
N	0	-0.7284820244	-0.1065539271	-0.8800754888
C	0	-1.8377459335	-0.9029109353	-0.3672727742
C	0	-0.2721389517	-0.1463490926	-2.1809048848
H	0	-2.7936420996	-0.4056310726	-0.6216027094
S	0	-1.8062620711	-0.6639849193	1.4992265397
C	0	-1.9478107483	-2.4071571847	-0.7508967020
H	0	-0.4592776163	-1.1058465903	-2.6944462049
O	0	0.3063865549	0.7766906317	-2.7114668716
O	0	-0.7491504392	-1.5550979726	2.1229699216
C	0	-2.5684861393	-2.5578008939	-2.1571276070
C	0	-2.9322696656	-3.0825570738	0.2316040180
C	0	-0.5875588999	-3.1172793810	-0.6588825480
H	0	-1.9344416174	-2.1775818360	-2.9679149674
H	0	-2.7471458295	-3.6244268609	-2.3622501044
H	0	-3.5382908465	-2.0384625085	-2.2171709771
H	0	-3.1404035510	-4.1070973985	-0.1104638485
H	0	-2.5140456483	-3.1491003501	1.2453228690
H	0	-3.8933847371	-2.5448888866	0.2763850190
H	0	-0.7161119818	-4.1877016637	-0.8821874827
H	0	0.1469145457	-2.7161331654	-1.3712834815
H	0	-0.1733460902	-3.0169757923	0.3529288209
C	0	3.2374096532	-0.3448125968	0.3247523029
C	0	3.3380816869	0.0748967415	-1.0122094062
C	0	4.3893263024	-0.8190151950	0.9675839390
C	0	4.5637570065	0.0197168144	-1.6791108091
H	0	2.4622940688	0.4668917609	-1.5288664090
C	0	5.6150344325	-0.8797837365	0.2988890095
H	0	4.3258580863	-1.1459808071	2.0093436936
C	0	5.7055354225	-0.4592930977	-1.0295361059
H	0	4.6253330446	0.3560136382	-2.7172061773
H	0	6.5006289748	-1.2528766513	0.8195215756
H	0	6.6620433598	-0.5022951251	-1.5565008151
C	0	0.2540391782	2.5035617621	2.8695782893
C	0	-0.1623804788	2.5585295105	4.2050862417
C	0	0.6403676383	3.6843092204	2.2192816689
C	0	-0.1965475860	3.7770705988	4.8895100937
H	0	-0.4549233940	1.6377233161	4.7184358301

C	0	0.6066829682	4.8997806664	2.9048491192
H	0	0.9559397246	3.6464403722	1.1762505893
C	0	0.1885242071	4.9513771012	4.2389097888
H	0	-0.5162633922	3.8061188027	5.9340737509
H	0	0.9096155314	5.8154554372	2.3912955657
H	0	0.1667868236	5.9055845150	4.7710090602

Sb-PB-PxSi

0 1

O	0	-2.9935005286	1.5662454626	0.2931283306
C	0	-4.0080411076	2.5529596245	0.0887251968
O	0	-1.4182600138	3.1294555936	-0.0435674756
C	0	-1.7308816210	2.0066639206	0.2352787266
C	0	-0.7022672616	0.8817940992	0.5208477341
C	0	-0.0708614540	0.2725551038	-0.7406554565
N	0	1.6185154037	1.2800553980	0.5656844216
O	0	0.3610016347	1.5356860213	1.1995415753
C	0	2.3576250219	0.2856111058	1.3489823115
C	0	1.3060288242	0.9514796852	-0.8212029178
H	0	-3.8716240422	3.0540080323	-0.8803648958
H	0	-3.9649264024	3.3057405344	0.8890100632
H	0	-4.9632822103	2.0159150421	0.1179736485
H	0	-0.6720903330	0.3498405869	-1.6530863569
H	0	2.0572690006	0.2359480599	-1.1887761715
H	0	2.4386020704	0.7091806320	2.3622060881
H	0	1.8286070506	-0.6796836058	1.4390917043
N	0	-1.2698619029	-0.2236268919	1.2919725912
C	0	-1.3688951437	-1.5451800225	0.6955997509
C	0	-1.7262750470	0.0387635921	2.5663483956
H	0	-1.1351307482	-2.2852247015	1.4774917958
S	0	0.1451118929	-1.5641415133	-0.4374393824
C	0	-2.7017684311	-1.9834206163	0.0233261131
H	0	-2.0042430206	-0.8885309922	3.1174719762
O	0	-1.8107251921	1.1463415820	3.0395467648
O	0	-0.1020724192	-2.2620025879	-1.7526125930
C	0	-2.9924504865	-1.2607562783	-1.3037234783
C	0	-3.8528845921	-1.7123281317	1.0074844762
C	0	-2.5961295716	-3.5002262397	-0.2268534227
H	0	-2.2252948730	-1.4903088430	-2.0533669422
H	0	-3.9639895743	-1.6031911020	-1.6932959878
H	0	-3.0613038918	-0.1763650697	-1.1584912264
H	0	-4.7927164516	-2.0982463274	0.5827383217
H	0	-3.6956742871	-2.2197244317	1.9730174436
H	0	-3.9805955291	-0.6362622455	1.1908257249
H	0	-2.4542626313	-4.0493779016	0.7189743203
H	0	-3.5238627661	-3.8690421787	-0.6903507152
H	0	-1.7605559699	-3.7330448648	-0.9005561511
C	0	3.7241576741	0.0658312034	0.7489987657
C	0	4.1545028520	-1.2212631978	0.4038026989
C	0	4.5709096649	1.1573159674	0.5004632540
C	0	5.4167226506	-1.4212785532	-0.1639887358
H	0	3.4922174504	-2.0738136585	0.5754326887
C	0	5.8279812899	0.9596266401	-0.0710825501
H	0	4.2272309822	2.1640309475	0.7468429748
C	0	6.2556190689	-0.3309036668	-0.4026579725
H	0	5.7404791577	-2.4311980124	-0.4267431906
H	0	6.4785193383	1.8166609893	-0.2615100201
H	0	7.2400723435	-0.4839655922	-0.8512765339
C	0	1.3079659763	2.1554401779	-1.7478122051
C	0	1.1644256575	1.9406811733	-3.1254625625
C	0	1.4484808222	3.4584224716	-1.2646984288
C	0	1.1615480870	3.0179781284	-4.0128135884
H	0	1.0609589087	0.9200779897	-3.5077768516

C	0	1.4450573154	4.5366155254	-2.1532109647
H	0	1.5452776048	3.6156958791	-0.1911825566
C	0	1.3020872182	4.3215327543	-3.5260966346
H	0	1.0547476742	2.8397505387	-5.0855689657
H	0	1.5481727717	5.5536124886	-1.7672681424
H	0	1.2998977362	5.1676741257	-4.2175278310

Sb-PB-TSnRe

0 1

O	0	-1.6284114392	3.4695552031	-0.7105607652
C	0	-1.5410222177	4.8703696733	-0.9568715832
O	0	0.4821979549	3.4922024145	0.0653803807
C	0	-0.5167291319	2.8798850699	-0.2529064181
C	0	-0.6802390252	1.4108235579	-0.1163464632
C	0	0.0523736037	0.6933982753	0.8591865489
O	0	0.7785856668	1.0730491502	-1.7018118259
N	0	1.6943969921	0.5534754054	-0.9780107377
C	0	2.8059552164	1.4505067224	-0.5779998858
C	0	1.2911006617	-0.4817286185	-0.1748846431
H	0	-0.7584618105	5.0811607341	-1.7008367057
H	0	-1.3023749450	5.4173674159	-0.0323038503
H	0	-2.5221451489	5.1735056140	-1.3413743878
H	0	0.7705816556	1.2628522221	1.4542297230
H	0	2.0421286352	-0.7727337635	0.5627357906
H	0	3.0853886893	1.9670671194	-1.5073954564
H	0	2.4005607240	2.2138165722	0.1036168944
N	0	-1.9158142429	0.7758414470	-0.4349551343
C	0	-2.5403236056	0.2251865728	0.7614685372
C	0	-2.4387090323	0.8049987211	-1.7147615859
H	0	-2.9284897089	1.0685831301	1.3624767947
S	0	-1.0638263867	-0.2793773072	1.9220949783
C	0	-3.6315977368	-0.8670524584	0.6958567740
H	0	-3.4081262339	0.2791982632	-1.7853269091
O	0	-1.9086477639	1.3276760074	-2.6653291407
O	0	-0.7284831361	-1.7516634494	1.8878439107
C	0	-4.9704348007	-0.2697456959	0.2088702867
C	0	-3.8783965028	-1.3565071505	2.1428737054
C	0	-3.1968869716	-2.0584268067	-0.1712770072
H	0	-4.9578338779	0.0549922029	-0.8393044989
H	0	-5.7605815906	-1.0309260066	0.3014862048
H	0	-5.2643359465	0.5948738099	0.8254326782
H	0	-4.7470178769	-2.0316106818	2.1531625045
H	0	-3.0176298868	-1.9106669312	2.5386366698
H	0	-4.1044352194	-0.5147429946	2.8183697536
H	0	-2.2318362061	-2.4536250804	0.1711767446
H	0	-3.9481736757	-2.8605425413	-0.1002560538
H	0	-3.0958423026	-1.7920164543	-1.2313707639
C	0	0.5951721442	-1.6464947837	-0.7914849650
C	0	0.7708961834	-2.8980863146	-0.1750413216
C	0	-0.1297896517	-1.5824905381	-1.9946679866
C	0	0.2333382530	-4.0534534900	-0.7352132672
H	0	1.3204898363	-2.9586439639	0.7648493302
C	0	-0.6554655079	-2.7467077933	-2.5597072977
H	0	-0.2688678657	-0.6258526250	-2.4911554062
C	0	-0.4857064969	-3.9823422330	-1.9327471549
H	0	0.3747908504	-5.0136448011	-0.2339067262
H	0	-1.2116722125	-2.6785739943	-3.4978254591
H	0	-0.9097729964	-4.8877684254	-2.3739063419
C	0	3.9646333964	0.7074657545	0.0262245999
C	0	4.3198714742	0.9117706245	1.3656377322
C	0	4.6891566594	-0.2233440572	-0.7348948905
C	0	5.3817909822	0.2039179657	1.9369295769
H	0	3.7592451976	1.6341598645	1.9649350693

C	0	5.7453117477	-0.9349061454	-0.1658226540
H	0	4.4128844957	-0.3949086814	-1.7785343188
C	0	6.0946791186	-0.7220209574	1.1724593353
H	0	5.6499875869	0.3751892993	2.9820719703
H	0	6.3005051749	-1.6582524596	-0.7676536487
H	0	6.9226672538	-1.2788526088	1.6174477607

Sb-PB-TSnSi

0 1

O	0	1.1773269365	3.0476554997	0.6430719698
C	0	2.2409774016	3.9938762408	0.6287365176
O	0	2.4118857029	1.6692192876	-0.6465322386
C	0	1.4144525815	1.8899578455	0.0062734248
C	0	0.2837364715	0.9480875670	0.1199230297
C	0	0.1742318261	-0.1595872616	-0.7248421253
O	0	1.8399868313	-0.2046602434	1.6268111244
N	0	1.9961481710	-1.1353670093	0.7684052734
C	0	0.8537366151	-1.7582331667	0.3666181400
H	0	3.1357323626	3.5737689899	1.1123071174
H	0	2.5009428705	4.2768507993	-0.4024417566
H	0	1.8811790294	4.8653746196	1.1886222560
H	0	0.8390876092	-0.2482840562	-1.5880336796
H	0	0.9945527747	-2.5508208114	-0.3694427071
C	0	-0.1381919501	-2.0337534402	1.4794981993
H	0	-0.2206504823	-1.1383991085	2.1045495991
H	0	0.3420060567	-2.7990035614	2.1205389017
N	0	-0.9348933325	1.2686981063	0.7613096717
C	0	-2.1142606976	1.0092111915	-0.0611305431
C	0	-1.0545992603	1.5715978406	2.1081123090
H	0	-2.9068290993	0.5618723795	0.5545725163
S	0	-1.5816508986	-0.4289619478	-1.2414853058
C	0	-2.6795063673	2.2474067645	-0.7996241471
H	0	-2.1275691408	1.6693106306	2.3969315316
O	0	-0.1467784053	1.7002790143	2.8891222108
O	0	-1.6024726809	0.0207778021	-2.6859734297
C	0	-3.9010140799	1.8104706826	-1.6294984048
C	0	-1.6137768351	2.9193805018	-1.6814544233
C	0	-3.1467151984	3.2608759188	0.2631943574
H	0	-4.6531305121	1.3151296897	-0.9920586297
H	0	-4.3791304634	2.6937796463	-2.0804794492
H	0	-3.6135635661	1.1245514941	-2.4358334055
H	0	-2.0581452592	3.7851612332	-2.1975196040
H	0	-0.7817731841	3.2911980924	-1.0661166123
H	0	-1.2282885363	2.2232989757	-2.4360714829
H	0	-2.3069711559	3.6388704402	0.8645654288
H	0	-3.6093230127	4.1252942011	-0.2381899566
H	0	-3.8988362511	2.8272005381	0.9426722804
C	0	-1.5008760603	-2.5220614940	1.0579004973
C	0	-2.6479377481	-1.9246622947	1.5964021038
C	0	-1.6610559360	-3.5615529477	0.1295645107
C	0	-3.9237905333	-2.3190634355	1.1848800597
H	0	-2.5350773519	-1.1322205231	2.3405708059
C	0	-2.9317634060	-3.9569351197	-0.2872004575
H	0	-0.7825190702	-4.0596330983	-0.2888797397
C	0	-4.0687381885	-3.3272908397	0.2297648789
H	0	-4.8065267617	-1.8337807788	1.6084570524
H	0	-3.0376268840	-4.7564917285	-1.0241238136
H	0	-5.0637306587	-3.6301691479	-0.1040289903
C	0	3.2382169275	-1.2141827277	0.0540219479
C	0	3.3686355537	-1.9167397860	-1.1502724725
C	0	4.3446215613	-0.5705624493	0.6222910207
C	0	4.6117174351	-1.9669336654	-1.7839748333
H	0	2.5169270637	-2.4104311593	-1.6170549495

C	0	5.5789515350	-0.6339452884	-0.0163564643
H	0	4.2027420856	-0.0182653851	1.5495641805
C	0	5.7202289998	-1.3307357398	-1.2218683275
H	0	4.7077416404	-2.5051001355	-2.7295354711
H	0	6.4399760060	-0.1300708299	0.4285188259
H	0	6.6899129191	-1.3743938119	-1.7222623224

Sb-PB-TSxRe

0 1

O	0	-2.9412381794	2.5211321581	-0.7238642048
C	0	-3.4593316779	3.8025332039	-1.0717858765
O	0	-0.8911464399	3.4232387633	-0.5048120095
C	0	-1.6153667847	2.4593027383	-0.5234864356
C	0	-1.1730614174	1.0589328585	-0.2425452011
C	0	-0.3756352656	0.7864762196	0.8865060764
N	0	1.1377374561	0.1742926426	-1.1146924750
O	0	0.3187341278	0.9724527400	-1.6993734679
C	0	0.9932552728	-1.2586183148	-1.4789480875
C	0	1.5623210596	0.5296846611	0.1261536162
H	0	-3.2317614116	4.5429505460	-0.2904476911
H	0	-3.0216807862	4.1453240716	-2.0212482333
H	0	-4.5433517280	3.6752796630	-1.1779303536
H	0	-0.1497805430	1.5531388423	1.6286874050
H	0	2.0055972988	-0.3021286392	0.6803499675
H	0	0.8535504891	-1.2471379520	-2.5681036864
H	0	0.0664571474	-1.6376433849	-1.0296652715
N	0	-2.0340339041	-0.0286341507	-0.5880837549
C	0	-2.3995818755	-0.8239604211	0.5862210434
C	0	-2.5659841788	-0.1213218448	-1.8619069063
H	0	-3.0367463359	-0.2189933942	1.2571210652
S	0	-0.8122047719	-0.8224899303	1.6440758552
C	0	-3.0138763926	-2.2340474575	0.4437165948
H	0	-3.2524606211	-0.9801364355	-1.9781898721
O	0	-2.3125620680	0.6370824646	-2.7662768283
O	0	-1.2612464396	-0.5593276835	3.0606128953
C	0	-4.4933051376	-2.1337954671	0.0111964336
C	0	-3.0124132364	-2.8887468183	1.8443061730
C	0	-2.2146272591	-3.1338346167	-0.5120333501
H	0	-4.6342269747	-1.7371152487	-1.0022744938
H	0	-4.9526787410	-3.1340786563	0.0372660504
H	0	-5.0540646025	-1.4886028331	0.7050028136
H	0	-3.5660504885	-3.8386311153	1.7996870889
H	0	-1.9963067617	-3.1105524609	2.2010572593
H	0	-3.4860242149	-2.2421008239	2.5969050228
H	0	-2.6655746423	-4.1374302411	-0.5421435829
H	0	-2.1867335569	-2.7537119177	-1.5422805515
H	0	-1.1770856748	-3.2528213770	-0.1659860747
C	0	2.1810951281	1.8391452736	0.4238383972
C	0	2.9172611721	1.9420520028	1.6188579005
C	0	2.0855858471	2.9595350275	-0.4185442747
C	0	3.5464169930	3.1358285901	1.9682932520
H	0	2.9987233081	1.0725080860	2.2771756872
C	0	2.7316161047	4.1460725204	-0.0712727556
H	0	1.4886063068	2.8963538314	-1.3243336829
C	0	3.4570710046	4.2432519793	1.1195002144
H	0	4.1127813633	3.1996608049	2.9003461068
H	0	2.6513456068	5.0108258411	-0.7339582770
H	0	3.9495817323	5.1809595881	1.3880411901
C	0	2.1691835283	-2.0999504570	-1.0680491947
C	0	2.0745597542	-2.9735357852	0.0239268359
C	0	3.3894624227	-1.9933324905	-1.7515470142
C	0	3.1765672409	-3.7356244129	0.4218111668
H	0	1.1349623434	-3.0399832215	0.5775027305

C	0	4.4918743888	-2.7503808860	-1.3536623610
H	0	3.4726098635	-1.3077774987	-2.5989079545
C	0	4.3868407920	-3.6248937185	-0.2666143853
H	0	3.0893247618	-4.4137908238	1.2738260402
H	0	5.4372804998	-2.6601155275	-1.8936830780
H	0	5.2499840973	-4.2185571122	0.0434855039

Sb-PB-TSxSi

0 1

O	0	0.1489203944	3.3174138159	0.9305242377
C	0	0.8200987122	4.5339197497	1.2460474128
O	0	2.1111699950	2.4255035551	0.2785421673
C	0	0.9280936650	2.3109513341	0.4960021571
C	0	0.1531641281	1.0669088954	0.2769906839
C	0	0.5025172197	0.1440807878	-0.7257896940
N	0	1.1728623714	-1.1320405642	1.4416273392
O	0	1.2355076783	0.0547387267	1.9006914381
C	0	0.3438695348	-2.1195545090	2.1841668020
C	0	1.6054063383	-1.3271494976	0.1629284912
H	0	1.3312873717	4.9397737809	0.3601330710
H	0	1.5668501110	4.3665715988	2.0363056906
H	0	0.0458049712	5.2273622414	1.5950683532
H	0	1.2087156684	0.4056380554	-1.5156341458
H	0	1.2580298102	-2.2751750608	-0.2584055613
H	0	1.0144484815	-2.9441581994	2.4737068708
H	0	0.0472224672	-1.5763338827	3.0886479703
N	0	-1.2231575136	0.9964743823	0.6110224883
C	0	-2.0867928933	0.5786282567	-0.4880767186
C	0	-1.7386479716	1.2269874738	1.8729660062
H	0	-2.9277356582	0.0009235467	-0.0820937983
S	0	-0.9952720875	-0.7206287549	-1.3753121487
C	0	-2.6383104377	1.7056603803	-1.3935625531
H	0	-2.8460103979	1.0972755979	1.8781444230
O	0	-1.1039698672	1.5118856358	2.8575514445
O	0	-0.9965602991	-0.5317647176	-2.8765945058
C	0	-1.5295023064	2.4572769601	-2.1490486369
C	0	-3.3921760437	2.7075152618	-0.4990047638
C	0	-3.6305037331	1.0672396404	-2.3832774215
H	0	-0.9507702772	1.7747890377	-2.7836856351
H	0	-1.9863341655	3.2253856567	-2.7930480333
H	0	-0.8566031724	2.9737635833	-1.4509762488
H	0	-3.8573870291	3.4813661489	-1.1295000511
H	0	-4.1965419361	2.2199726978	0.0759343128
H	0	-2.7121909338	3.2107391284	0.2039017589
H	0	-4.4478175411	0.5571224774	-1.8458479594
H	0	-4.0833516395	1.8467505186	-3.0153383238
H	0	-3.1273070618	0.3406742718	-3.0339131640
C	0	-0.8569217818	-2.6556456703	1.4477418402
C	0	-2.1192479794	-2.0828069596	1.6506798665
C	0	-0.7374164757	-3.7257754741	0.5484093822
C	0	-3.2286712599	-2.5328197278	0.9325028947
H	0	-2.2286291642	-1.2856711044	2.3878799807
C	0	-1.8408224960	-4.1678018355	-0.1825880928
H	0	0.2293263677	-4.2193930447	0.4175198328
C	0	-3.0875179946	-3.5626385679	-0.0018740078
H	0	-4.2085011483	-2.0805541578	1.1047971593
H	0	-1.7293992032	-4.9900348168	-0.8928422423
H	0	-3.9518501031	-3.9069590278	-0.5740567847
C	0	2.9783633722	-0.9647421547	-0.2708701634
C	0	3.4610397639	-1.5671583375	-1.4465053380
C	0	3.8069787423	-0.0748900009	0.4307894860
C	0	4.7476030018	-1.2947620585	-1.9103446326
H	0	2.8188558035	-2.2571567467	-2.0015116120

C	0	5.0990351818	0.1807149251	-0.0288835011
H	0	3.4236839338	0.4251603866	1.3167692318
C	0	5.5735910635	-0.4203221968	-1.1982326511
H	0	5.1070634665	-1.7701919204	-2.8259675673
H	0	5.7358527010	0.8734713094	0.5261105030
H	0	6.5826712555	-0.2041028301	-1.5571383398

Sb-PM-PnRe

0 1

O	0	1.0529764212	2.2509145961	0.8357003018
C	0	1.6908299123	3.3777307400	1.4434722259
O	0	3.0654252354	1.3316725808	0.4207861985
C	0	1.8704447581	1.3214019004	0.3138919233
C	0	1.0586658306	0.1653168392	-0.3146012940
C	0	0.7732983384	-0.9230660136	0.7222840624
O	0	1.8467064047	-0.4615624021	-1.3087787047
N	0	2.2309351898	-1.7771419388	-0.8815525786
C	0	3.5379110541	-1.7326357907	-0.2442364917
C	0	1.1186682012	-2.2372397065	-0.0540279502
H	0	2.2664206847	3.9352999106	0.6904571267
H	0	2.3722818948	3.0522720250	2.2427843546
H	0	0.8865990801	4.0015434618	1.8506306471
H	0	1.4721897927	-0.8382469889	1.5639783199
H	0	1.5015789603	-2.9712041870	0.6686586517
H	0	4.2387615822	-1.2493745259	-0.9366423283
H	0	3.5714847263	-1.1791415909	0.7121421771
H	0	3.8618167648	-2.7717876957	-0.0838687949
N	0	-0.2215319807	0.6310382420	-0.8616540060
C	0	-1.3738258173	0.5919241896	0.0503788738
C	0	-0.0777806426	1.6658013061	-1.7724422528
H	0	-1.4122262132	1.5399056883	0.6142411940
S	0	-0.8847423750	-0.6083150220	1.4754048794
C	0	-2.7978324328	0.3095768200	-0.5030443181
H	0	-1.0331614886	2.1198252678	-2.0888233388
O	0	0.9963689799	2.0468750960	-2.1794567461
O	0	-1.6745938663	-1.8951940804	1.4744200721
C	0	-3.2751050336	1.4602026492	-1.4157713246
C	0	-3.7596341954	0.2768125928	0.7064802071
C	0	-2.8642839771	-1.0025522048	-1.2897182806
H	0	-2.7965678365	1.4382252186	-2.4045492067
H	0	-4.3568117221	1.3495104999	-1.5873392951
H	0	-3.1101778651	2.4507793197	-0.9611664919
H	0	-4.7929119082	0.1659882095	0.3449685225
H	0	-3.5492203277	-0.5646100787	1.3778900190
H	0	-3.7087535240	1.2175446989	1.2804446716
H	0	-2.5889284739	-1.8597998914	-0.6660590530
H	0	-3.8879056768	-1.1568336431	-1.6657354450
H	0	-2.1873171483	-0.9725351189	-2.1529024157
C	0	0.0582114486	-2.9198640440	-0.9023943469
C	0	-0.7555114284	-3.9093833347	-0.3370543280
C	0	-0.0459161268	-2.6540863905	-2.2735549640
C	0	-1.6762663615	-4.6047803377	-1.1211577438
H	0	-0.6827582975	-4.1230987673	0.7298683951
C	0	-0.9626391404	-3.3551267447	-3.0603533044
H	0	0.5972980591	-1.8977906477	-2.7213501249
C	0	-1.7849061194	-4.3275078520	-2.4869804968
H	0	-2.3091180404	-5.3686193033	-0.6633188595
H	0	-1.0340855131	-3.1372046158	-4.1287812814
H	0	-2.5030019468	-4.8743775951	-3.1030100670

Sb-PM-PnSi

0 1

O	0	-0.9865273926	-2.4015189865	-0.9826862681
C	0	-1.4708552462	-3.6207936169	-1.5406240640
O	0	-3.0597747792	-1.8719878396	-0.2720227765
C	0	-1.8806297936	-1.6583834227	-0.3292910926
C	0	-1.2104110864	-0.3780166212	0.2008499121
C	0	-1.1068995998	0.6960260276	-0.9166254035
O	0	-2.0707911935	0.1834090203	1.1563826993
N	0	-1.8007228260	1.6054107199	1.1158820945
C	0	-2.8344371076	2.2288069528	1.9137257087
C	0	-1.8697479527	1.8962372895	-0.3174282793
H	0	-1.7890613138	-4.3021821837	-0.7372996666
H	0	-2.3257964151	-3.4333334558	-2.2069325631
H	0	-0.6333459377	-4.0526117408	-2.1007552096
H	0	-1.5227163440	0.3652139671	-1.8751132242
H	0	-2.9172816319	1.8210714225	-0.6745285854
H	0	-3.8492827702	1.9769849983	1.5492124904
H	0	-2.6891620986	3.3173422142	1.8706264149
H	0	-2.7341207759	1.8959051449	2.9556709719
N	0	0.1277149091	-0.6184695146	0.7282184321
C	0	1.1322103321	0.3863884945	0.4124802445
C	0	0.2414936929	-1.6492439259	1.6293951411
H	0	0.9630101049	1.2990148781	1.0118592047
S	0	0.6741888456	0.9764520287	-1.3236047570
C	0	2.6376776145	0.0043813231	0.4857102018
H	0	1.2352298674	-1.7262476151	2.1049954178
O	0	-0.6633766177	-2.4148146479	1.8849905492
O	0	1.0204089486	-0.1051189195	-2.3215693188
C	0	3.4334918438	1.0553565084	-0.3217350764
C	0	2.9057377530	-1.3847599461	-0.1218760543
C	0	3.1381943315	0.0938098059	1.9424026872
H	0	3.1682461559	2.0835162853	-0.0264319120
H	0	4.5097116847	0.9200574367	-0.1374384631
H	0	3.2645251497	0.9433908431	-1.4023190569
H	0	3.9910882556	-1.5276154050	-0.2415698553
H	0	2.5379900747	-2.2031415482	0.5119263412
H	0	2.4232971546	-1.4670721310	-1.1049427193
H	0	2.6328306662	-0.6016250099	2.6258205193
H	0	4.2138207297	-0.1395366303	1.9763626009
H	0	3.0022424196	1.1114723920	2.3425247456
C	0	-1.3168367149	3.2569957165	-0.6760302775
C	0	-1.7209017640	3.8681903278	-1.8696837404
C	0	-0.3644508189	3.8976129677	0.1287807202
C	0	-1.1717491249	5.0899580755	-2.2636140457
H	0	-2.4705400754	3.3802053050	-2.4985949939
C	0	0.1785066466	5.1241690978	-0.2602794173
H	0	-0.0594199724	3.4297366816	1.0659360683
C	0	-0.2183473365	5.7210390272	-1.4597578532
H	0	-1.4930049401	5.5530507245	-3.1994624501
H	0	0.9170751960	5.6158879779	0.3774012345
H	0	0.2099594530	6.6784252864	-1.7652619758

Sb-PM-PxRe

0 1

O	0	-1.0856609225	2.4363534730	-0.6119846288
C	0	-1.6936299291	3.6571794768	-1.0422264879
O	0	-3.0937082708	1.6828675839	0.0743390585
C	0	-1.9075004122	1.5494668488	-0.0230584886
C	0	-1.1213101265	0.2880395867	0.3934459790
C	0	-1.0551373779	-0.7372450989	-0.7623896444
N	0	-1.8037043029	-1.7533454586	1.2693728352
O	0	-1.8662604756	-0.3301268794	1.4077274329
C	0	-0.7082229797	-2.2809532024	2.0727175278
C	0	-1.7382902651	-1.9970714994	-0.1710754594

H	0	-2.5119432455	3.4550990347	-1.7487055790
H	0	-2.0986936742	4.2022426868	-0.1773553284
H	0	-0.9006533521	4.2403029693	-1.5250838764
H	0	-1.5492926188	-0.3856030397	-1.6754727406
H	0	-1.0902725619	-2.8681356804	-0.3449719796
H	0	-0.7918640247	-3.3776996744	2.0658804640
H	0	-0.8510716918	-1.9290620227	3.1033844303
H	0	0.2944331267	-2.0068234438	1.7093940754
N	0	0.2563191376	0.6074273506	0.7964067442
C	0	1.2509509041	0.4535298681	-0.2589629438
C	0	0.3619758048	1.4964283488	1.8503872413
H	0	1.1001365744	1.2413711219	-1.0222126651
S	0	0.7209119042	-1.0707191680	-1.2257250642
C	0	2.7628707402	0.4101210659	0.1034897498
H	0	1.4027049314	1.7000234657	2.1616162836
O	0	-0.5943017368	1.9909438599	2.4016398275
O	0	1.1462775174	-2.3282436269	-0.4908640825
C	0	3.2974818293	1.8414503237	0.3285909512
C	0	3.5319122121	-0.1563338604	-1.1119270362
C	0	3.0320767160	-0.4866028792	1.3223184792
H	0	2.8695287428	2.3429213445	1.2056730157
H	0	4.3874927376	1.8032450126	0.4779284467
H	0	3.1019231294	2.4768186939	-0.5499454119
H	0	4.6132937738	-0.0559425663	-0.9366672389
H	0	3.3175751748	-1.2227358950	-1.2673399039
H	0	3.2917453489	0.3939626909	-2.0361817755
H	0	4.1157062310	-0.5327682972	1.5122456773
H	0	2.5504283867	-0.1098578920	2.2354513822
H	0	2.6642997197	-1.5040217603	1.1351716563
C	0	-3.0996730906	-2.2350557465	-0.7943028961
C	0	-4.2206858582	-1.4944699252	-0.3920011794
C	0	-3.2326454753	-3.1839227502	-1.8148356704
C	0	-5.4544560089	-1.7077317048	-1.0090249973
H	0	-4.1180995267	-0.7466260804	0.3952476895
C	0	-4.4691587239	-3.3954497538	-2.4322371587
H	0	-2.3621688281	-3.7696329803	-2.1248723968
C	0	-5.5835051328	-2.6563137604	-2.0294124028
H	0	-6.3231633956	-1.1266059373	-0.6901299940
H	0	-4.5619936806	-4.1441424636	-3.2228389074
H	0	-6.5525347840	-2.8205991487	-2.5070537500

Sb-PM-PxSi

0 1

O	0	1.2393225592	2.0692240600	-1.3750645324
C	0	1.9259725856	3.1757969657	-1.9576029477
O	0	2.9158991941	1.7681139666	0.1080023580
C	0	1.8151788451	1.5239466251	-0.2963401091
C	0	0.9061209460	0.4049074996	0.2561923319
C	0	0.8478930069	-0.7836053575	-0.7443456989
N	0	2.3831784157	-1.1523945133	0.9599921890
O	0	1.4472877205	-0.1584727683	1.4312882342
C	0	2.8236746428	-1.8944386850	2.1151652156
C	0	1.6015256152	-1.9110646206	-0.0177195076
H	0	2.9529704818	2.8964834609	-2.2355542457
H	0	1.9642998460	4.0095710965	-1.2406787109
H	0	1.3496607928	3.4603223218	-2.8458273829
H	0	1.2548354232	-0.5376795456	-1.7308853576
H	0	0.8637027787	-2.5706225431	0.4912721586
H	0	3.5139762046	-2.6767559924	1.7691973441
H	0	3.3628124744	-1.2176103650	2.7915938980
H	0	1.9810314156	-2.3656603651	2.6625433808
N	0	-0.4437463317	0.8383175095	0.5340521897
C	0	-1.3959270299	-0.2621935502	0.4892761691

C	0	-0.6500207792	2.1116585703	1.0167463598
H	0	-1.1421765034	-0.9893479523	1.2829291301
S	0	-0.9141804629	-1.2238106812	-1.0784286304
C	0	-2.9202535280	0.0117707816	0.5465172171
H	0	-1.7011878271	2.3208087711	1.2777358383
O	0	0.2268091125	2.9375820382	1.1389857020
O	0	-1.3449263758	-0.4374297614	-2.2917871148
C	0	-3.3663782185	1.1133138739	-0.4353462792
C	0	-3.3401231321	0.3365939732	1.9950778533
C	0	-3.6363581949	-1.2989173294	0.1492145440
H	0	-2.9327445587	0.9375679167	-1.4286688433
H	0	-4.4643264953	1.1007139559	-0.5178114136
H	0	-3.0808608039	2.1220407433	-0.1084741508
H	0	-4.4288153385	0.4963898228	2.0354818465
H	0	-3.0969910646	-0.4984856666	2.6713188494
H	0	-2.8612642583	1.2392313527	2.3978935010
H	0	-3.2588395032	-2.1618141833	0.7211817028
H	0	-4.7128689505	-1.2043409055	0.3552738937
H	0	-3.5220474694	-1.5095761881	-0.9242806715
C	0	2.4775911760	-2.7479109019	-0.9173094486
C	0	2.0697570029	-4.0248178184	-1.3180347780
C	0	3.6891738425	-2.2278987351	-1.3968411084
C	0	2.8594528851	-4.7772905273	-2.1921048905
H	0	1.1259077836	-4.4315484239	-0.9450679551
C	0	4.4799326619	-2.9826774030	-2.2642325574
H	0	4.0027556593	-1.2340443064	-1.0704142878
C	0	4.0663908258	-4.2576206152	-2.6657689491
H	0	2.5317612187	-5.7727983952	-2.5006588449
H	0	5.4250600043	-2.5741829359	-2.6299723336
H	0	4.6863506950	-4.8458155691	-3.3465108271

Sb-PM-TSnRe

0 1

O	0	3.4075996032	0.7279761000	-0.6851094133
C	0	4.8230178850	0.7049412309	-0.8526266383
O	0	3.5620557988	-1.0095298066	0.7343357945
C	0	2.8896213437	-0.2297473561	0.0939458522
C	0	1.4019275943	-0.1704766175	0.1329983406
C	0	0.7059326409	-0.5399298095	1.3120902493
O	0	1.2280740375	-2.0378990981	-0.8308221872
N	0	0.7535230737	-2.7285651219	0.1432506416
C	0	1.7010981352	-3.5508119094	0.8973328615
C	0	-0.3413120465	-2.1799733768	0.7561694220
H	0	5.1403223768	-0.2481400100	-1.3011308938
H	0	5.3342017580	0.8255459356	0.1143101471
H	0	5.0637569696	1.5388397679	-1.5226184872
H	0	1.3028403549	-0.9498096248	2.1307204387
H	0	-0.5925216371	-2.6614982269	1.7059394242
H	0	2.2886325216	-4.1237478136	0.1689050641
H	0	2.3903250935	-2.9104282039	1.4692896853
H	0	1.1509512487	-4.2358456915	1.5552402853
N	0	0.6950816762	0.8185416944	-0.6128282167
C	0	0.0701868825	1.7931648966	0.2738623708
C	0	0.7566559346	0.8637396619	-1.9936444032
H	0	0.8691076120	2.4307876177	0.6967367241
S	0	-0.3764871080	0.8059787646	1.8846407037
C	0	-1.0854220926	2.7085607056	-0.1907324842
H	0	0.1596854300	1.6931265337	-2.4144361325
O	0	1.3730085901	0.0874664449	-2.6827923556
O	0	-1.8209423643	0.3693263756	1.9562473432
C	0	-0.5573213778	3.8224745192	-1.1217427175
C	0	-1.6389043320	3.4227203751	1.0653952327
C	0	-2.2161024448	1.9079939348	-0.8543257230

H	0	-0.1992044304	3.4584077532	-2.0930378972
H	0	-1.3687918909	4.5383943920	-1.3248275421
H	0	0.2671314015	4.3770524404	-0.6454867016
H	0	-2.3673707963	4.1867148358	0.7555295091
H	0	-2.1509351073	2.7241597322	1.7395619273
H	0	-0.8368512565	3.9354501535	1.6219378288
H	0	-2.5638630666	1.1070437693	-0.1892653142
H	0	-3.0644378833	2.5761438077	-1.0706148597
H	0	-1.9052679292	1.4492017373	-1.8019432364
C	0	-1.5376906088	-1.8285892927	-0.0590758064
C	0	-2.7882948578	-1.8576100522	0.5826652331
C	0	-1.4943453803	-1.5737294145	-1.4416204771
C	0	-3.9633255184	-1.6323087395	-0.1287796223
H	0	-2.8349757077	-2.0385476330	1.6571360537
C	0	-2.6771120572	-1.3626721921	-2.1534100023
H	0	-0.5374399365	-1.5543010851	-1.9568898017
C	0	-3.9126415450	-1.3818194390	-1.5036786358
H	0	-4.9229216352	-1.6502013212	0.3927905027
H	0	-2.6248127400	-1.1724471538	-3.2281511527
H	0	-4.8335942116	-1.2038311906	-2.0643089336

Sb-PM-TSnSi

0 1

O	0	3.2073293522	0.3278973777	0.6895654649
C	0	4.6238878456	0.1983966582	0.7834895764
O	0	3.1604918753	-1.3732168423	-0.7797360819
C	0	2.5835412084	-0.5606727722	-0.0898043266
C	0	1.1045986599	-0.3851959254	-0.0677460431
C	0	0.3461402003	-0.6238337384	-1.2351469149
O	0	0.7866566843	-2.2620186518	0.8637165268
N	0	0.2655156472	-2.9114963995	-0.1204391799
C	0	1.1597145427	-3.7959352904	-0.8714198741
C	0	-0.7593233326	-2.2788035488	-0.7570245675
H	0	4.8914047261	-0.7907573838	1.1833734382
H	0	5.0934270954	0.3194047060	-0.2040732649
H	0	4.9556057265	0.9882765429	1.4674605278
H	0	0.8556862656	-0.9182683643	-2.1557052437
H	0	-1.0215661145	-2.7315971901	-1.7186417733
H	0	1.8694552234	-3.1981121634	-1.4637998733
H	0	0.5675469299	-4.4642338752	-1.5102435462
H	0	1.7266238731	-4.3835318501	-0.1388502537
N	0	0.4780773334	0.5274452486	0.8084606739
C	0	-0.5199038273	1.4120323636	0.2017995889
C	0	0.5608018072	0.4051571014	2.1891958651
H	0	-1.4915581306	1.2822256413	0.7055551872
S	0	-0.8494485723	0.7142823702	-1.5620019556
C	0	-0.1354758335	2.9167791860	0.1763086408
H	0	-0.2091629340	1.0287174354	2.6937910673
O	0	1.3384817703	-0.2920846967	2.7892708090
O	0	-0.2049837523	1.5680132259	-2.6311499109
C	0	-1.2308539437	3.6904050792	-0.5832311217
C	0	1.2468150208	3.1186095198	-0.4679254579
C	0	-0.0872518257	3.4578326844	1.6187012737
H	0	-2.2234557880	3.5108115665	-0.1363887082
H	0	-1.0311645192	4.7712111741	-0.5215951787
H	0	-1.2615463308	3.4118053831	-1.6440815793
H	0	1.5091260231	4.1882650414	-0.4516670596
H	0	2.0164253913	2.5696608086	0.0943483731
H	0	1.2494187554	2.7695734117	-1.5075021184
H	0	0.7381233990	3.0224680261	2.1998859040
H	0	0.0791642641	4.5458373668	1.5864553574
H	0	-1.0312444911	3.2796503089	2.1595097534
C	0	-1.9246095388	-1.7393594386	-0.0079766976

C	0	-3.0749852634	-1.4004284960	-0.7436078736
C	0	-1.9345946263	-1.5484819145	1.3865942976
C	0	-4.1966890095	-0.8617223612	-0.1134307275
H	0	-3.0880217559	-1.5568703452	-1.8247648702
C	0	-3.0627119625	-1.0177728035	2.0134395094
H	0	-1.0531135377	-1.8160403511	1.9651461689
C	0	-4.1919609706	-0.6610390916	1.2691723792
H	0	-5.0766804621	-0.5996792406	-0.7050220716
H	0	-3.0559028198	-0.8797103103	3.0973268279
H	0	-5.0675262781	-0.2365951833	1.7659220631

Sb-PM-TSxRe

0 1

O	0	0.6087551830	2.9975826518	-0.9454705690
C	0	0.2506105469	4.3180220342	-1.3475246879
O	0	-1.5706344859	2.4943231181	-0.6904105596
C	0	-0.4071101285	2.2006389758	-0.5756433182
C	0	0.0910641602	0.8760348364	-0.0826969925
C	0	-0.4179450558	-0.3214829751	-0.6569329338
N	0	-1.0029373967	-0.4074240472	1.8497980695
O	0	-0.9254120759	0.8618037758	1.6350550960
C	0	-0.0032478247	-1.0078280449	2.7424829863
C	0	-1.5779885307	-1.1460304205	0.8625959613
H	0	-0.4464479851	4.2935667883	-2.1983970154
H	0	-0.2285564084	4.8522664076	-0.5136960898
H	0	1.1860253805	4.8160981866	-1.6293622568
H	0	-1.1744335217	-0.2611905659	-1.4396366500
H	0	-1.3069310711	-2.2039324999	0.9161234201
H	0	-0.5110498123	-1.6039959200	3.5153482430
H	0	0.5374828024	-0.1790244374	3.2122531588
H	0	0.6732753063	-1.6529861064	2.1637243013
N	0	1.4591933970	0.7499187034	0.2991856059
C	0	2.1759942535	-0.1906176940	-0.5622802403
C	0	2.0164721608	1.6337680786	1.2077244155
H	0	2.2793695694	0.2709480115	-1.5630885453
S	0	0.8962800066	-1.5381009081	-0.9592059982
C	0	3.5533781807	-0.7713390583	-0.1563481990
H	0	3.0924162916	1.4486675711	1.3800014287
O	0	1.4052085587	2.5078129456	1.7730971818
O	0	0.8868016687	-2.5901102986	0.1439722629
C	0	4.6583569479	0.2855502804	-0.3735616349
C	0	3.8652792582	-1.9412231658	-1.1176664589
C	0	3.5682099160	-1.3083890542	1.2844740746
H	0	4.5726519723	1.1582332445	0.2865952573
H	0	5.6420617502	-0.1708696664	-0.1834278301
H	0	4.6531304210	0.6506916724	-1.4129073437
H	0	4.8972095122	-2.2844885061	-0.9510819404
H	0	3.1957299100	-2.7950210876	-0.9445977930
H	0	3.7824236093	-1.6317887716	-2.1721316391
H	0	4.5555285953	-1.7448614725	1.5017263791
H	0	3.3825340388	-0.5249399529	2.0320815658
H	0	2.8077162399	-2.0904355610	1.4043675726
C	0	-2.9413372042	-0.8807128484	0.3483561245
C	0	-3.6143421718	-1.9546251708	-0.2623769552
C	0	-3.5860648293	0.3651963424	0.4415742223
C	0	-4.9054806830	-1.7945806356	-0.7652342238
H	0	-3.1187679139	-2.9266593124	-0.3360444229
C	0	-4.8824196971	0.5147136424	-0.0518590366
H	0	-3.0562588488	1.2093544734	0.8759489645
C	0	-5.5456609283	-0.5567015077	-0.6579675658
H	0	-5.4147365312	-2.6394636966	-1.2350209214
H	0	-5.3741547118	1.4871593072	0.0268989728
H	0	-6.5576798214	-0.4265906619	-1.0490384433

Sb-PM-TSxSi

0 1

O	0	-1.1547934740	2.6704643910	-0.6564024448
C	0	-0.9810338107	3.9564190160	-1.2468758766
O	0	1.0001674496	2.1907838194	-1.0973133055
C	0	-0.0595072737	1.8958779660	-0.5992453504
C	0	-0.3239436765	0.6136710352	0.1072054275
C	0	0.2821087821	-0.5863938926	-0.3133634327
N	0	1.3509540611	-0.1366687400	1.9980782016
O	0	0.9992735889	1.0598285539	1.6995942850
C	0	0.6339197308	-0.7838326215	3.1049087056
C	0	1.8723218449	-0.8891516720	0.9889189828
H	0	-0.6436008986	3.8648004723	-2.2900842281
H	0	-0.2351602831	4.5374765011	-0.6848067720
H	0	-1.9601288579	4.4474011819	-1.1998605702
H	0	0.8245975192	-0.6597754822	-1.2571470285
H	0	1.8758250604	-1.9604815889	1.2197855060
H	0	1.3167383180	-1.4409715763	3.6612106688
H	0	0.2680579093	0.0195635075	3.7536532263
H	0	-0.2146313767	-1.3783406546	2.7326009844
N	0	-1.5656658583	0.3832492631	0.7628636844
C	0	-2.2609253236	-0.8295877064	0.3458784602
C	0	-2.0774791301	1.1856794440	1.7693623349
H	0	-2.7901805242	-1.2556957604	1.2119413663
S	0	-0.8081327437	-2.0327312694	0.0112388772
C	0	-3.2629814110	-0.6765185320	-0.8253125731
H	0	-3.0179495770	0.7512983281	2.1831467795
O	0	-1.5890106375	2.2085010777	2.1757781738
O	0	-0.9730550028	-2.7884213924	-1.2871264427
C	0	-2.5762407633	-0.2477508177	-2.1332283156
C	0	-4.2925045615	0.4001615077	-0.4336879286
C	0	-3.9873345182	-2.0229570538	-1.0084975011
H	0	-1.8238452928	-0.9821515706	-2.4462386971
H	0	-3.3332553579	-0.1677070051	-2.9292964066
H	0	-2.1075714264	0.7399921369	-2.0266135370
H	0	-5.0586714106	0.4731598444	-1.2212156081
H	0	-4.8081348581	0.1531631235	0.5087035636
H	0	-3.8229629321	1.3892562379	-0.3298699666
H	0	-4.5130904670	-2.3160888095	-0.0840367124
H	0	-4.7416457840	-1.9357044488	-1.8056082208
H	0	-3.2835086823	-2.8187253655	-1.2837516537
C	0	3.0271895932	-0.4548152326	0.1712416398
C	0	3.7149469044	-1.4493723221	-0.5482471660
C	0	3.4650713030	0.8771978737	0.0846784810
C	0	4.8196512250	-1.1252314338	-1.3343974525
H	0	3.3791821856	-2.4885608394	-0.4874742917
C	0	4.5811923867	1.1923343671	-0.6901917899
H	0	2.9149291136	1.6542166447	0.6087666749
C	0	5.2586120046	0.2001967186	-1.4045907064
H	0	5.3419276758	-1.9091548349	-1.8877139805
H	0	4.9140630423	2.2311159130	-0.7488529691
H	0	6.1246422150	0.4591886981	-2.0183750952

Sb-PP-PnRe

0 1

O	0	0.7712328156	2.5445135745	0.5190425208
C	0	1.2316779900	3.7609888627	1.1150256559
O	0	2.7901995629	1.6147625278	0.8505317740
C	0	1.6625410431	1.5536087945	0.4415653891
C	0	1.0488207180	0.2753332449	-0.1734794198
C	0	0.7481009870	-0.7822323542	0.8954991590

O	0	2.0021852891	-0.3181439285	-1.0405760185
N	0	2.3423411994	-1.6235066426	-0.5869847887
C	0	1.2280892805	-2.0936949394	0.2164039506
H	0	2.0615796796	4.1798651658	0.5281441734
H	0	1.5763936635	3.5760977595	2.1425418415
H	0	0.3741091355	4.4433257378	1.1125216933
H	0	1.2930972518	-0.5963972827	1.8289017981
H	0	1.6098053422	-2.7682344829	0.9928668918
N	0	-0.2064693294	0.5258970128	-0.8853191112
C	0	-1.3793301937	0.5502743137	-0.0148946583
C	0	-0.0960284448	1.2789072638	-2.0433857625
H	0	-1.3655998757	1.4537169929	0.6183281035
S	0	-1.0357004098	-0.7059721815	1.3703258290
C	0	-2.7968491986	0.3763137459	-0.6180124204
H	0	-1.0620264421	1.4335841980	-2.5590891655
O	0	0.9502674542	1.7073969977	-2.4686936445
O	0	-1.1226745729	0.1144783219	2.6350653944
C	0	-3.2955232528	1.7086792274	-1.2198611886
C	0	-3.7633624563	0.0359677184	0.5399945272
C	0	-2.8367664796	-0.7525417324	-1.6529972419
H	0	-2.7500278615	2.0200740280	-2.1196696795
H	0	-4.3537857965	1.6073136863	-1.5056332119
H	0	-3.2233582582	2.5225104926	-0.4813938937
H	0	-4.8016365945	0.0990935477	0.1822655137
H	0	-3.6067043173	-0.9861917826	0.9147205080
H	0	-3.6460987628	0.7279347327	1.3877255463
H	0	-2.5052907173	-1.7022319354	-1.2119203771
H	0	-3.8654851006	-0.8902017045	-2.0206552935
H	0	-2.1930756124	-0.5511181249	-2.5202421367
C	0	3.6683515663	-1.7390758464	-0.1120025490
C	0	4.5952804183	-0.6944987725	-0.2413673850
C	0	4.0861701628	-2.9729901694	0.4204929471
C	0	5.9092098754	-0.8808498964	0.1891854084
H	0	4.2736627809	0.2557828544	-0.6575663444
C	0	5.4019053808	-3.1391349018	0.8530828205
H	0	3.3913551322	-3.8135511311	0.4690721908
C	0	6.3234388910	-2.0946198053	0.7440084798
H	0	6.6176714921	-0.0544352009	0.0925626043
H	0	5.7085243547	-4.1024795550	1.2680359448
H	0	7.3537943698	-2.2282494747	1.0801182076
C	0	0.1894579295	-2.8315520337	-0.6124879300
C	0	-0.7398568892	-3.6689908173	0.0200346756
C	0	0.1664996429	-2.7169339601	-2.0078471446
C	0	-1.6831737120	-4.3764241019	-0.7287625057
H	0	-0.7214512303	-3.7789478777	1.1071583940
C	0	-0.7719433352	-3.4296874965	-2.7570122630
H	0	0.8955655699	-2.0725305793	-2.4990820750
C	0	-1.7004537116	-4.2585058524	-2.1214514137
H	0	-2.3988788760	-5.0289146490	-0.2233677681
H	0	-0.7776773077	-3.3355938149	-3.8454631888
H	0	-2.4338706000	-4.8149871341	-2.7096177030

Sb-PP-PnSi

0 1

O	0	-0.5873990816	-2.5386808765	-0.1875329015
C	0	-0.8266820534	-3.8616964487	-0.6659988487
O	0	-2.7449966345	-2.0063970709	-0.5358535577
C	0	-1.6308419594	-1.7202736849	-0.1862972249
C	0	-1.2456421126	-0.2870263143	0.2312981808
C	0	-1.3727527744	0.7017931084	-0.9470602412
O	0	-2.2298722016	0.1548732207	1.1214249363
N	0	-2.1086805153	1.5828605832	1.1011329415
C	0	-2.0084655549	1.9653469330	-0.3060515275

H	0	-1.5731070756	-4.3684051423	-0.0371762772
H	0	-1.1918395375	-3.8299909272	-1.7029072220
H	0	0.1373107140	-4.3805263174	-0.6142130463
H	0	-1.9999573944	0.2883509055	-1.7436772406
H	0	-3.0128428616	2.0950630736	-0.7524723876
N	0	0.1059285771	-0.1576064805	0.7664759561
C	0	1.0642315435	0.6457212534	0.0128907440
C	0	0.3412172514	-0.7378764452	1.9925929418
H	0	1.0790141203	1.6904152454	0.3688094261
S	0	0.2919888711	0.8282704984	-1.7029267932
C	0	2.5359838927	0.1397853486	-0.1048582623
H	0	1.3351969608	-0.4871556845	2.4114744553
O	0	-0.4547485098	-1.4402363094	2.5736731392
O	0	0.4190381494	-0.4892003545	-2.4416114787
C	0	3.1890415076	0.8266040809	-1.3261354046
C	0	2.5914377410	-1.3846654235	-0.2880727473
C	0	3.3526443720	0.5763217632	1.1296177774
H	0	3.0654772224	1.9214195456	-1.2906829497
H	0	4.2682270244	0.6129701572	-1.3317070176
H	0	2.7724590032	0.4516501299	-2.2715206976
H	0	3.6316886060	-1.6933714338	-0.4766385136
H	0	2.2395164709	-1.9213834554	0.6041641683
H	0	1.9649547035	-1.6892352300	-1.1361713480
H	0	3.0374114569	0.0837283080	2.0588735435
H	0	4.4120462502	0.3189420110	0.9759358356
H	0	3.2905555360	1.6658538502	1.2830865871
C	0	-3.0578881766	2.1645283240	1.9586277071
C	0	-3.4051621322	1.4996602820	3.1496264281
C	0	-3.6223304461	3.4186896164	1.6722962105
C	0	-4.3006367658	2.0931262200	4.0356331704
H	0	-2.9675564766	0.5237587602	3.3575173120
C	0	-4.5095725967	4.0032799371	2.5802188884
H	0	-3.3635369541	3.9501511100	0.7572841944
C	0	-4.8566170435	3.3484769036	3.7623748570
H	0	-4.5672723616	1.5655245318	4.9546974958
H	0	-4.9375770502	4.9816934066	2.3485734262
H	0	-5.5554831890	3.8083736776	4.4642272113
C	0	-1.2106129808	3.2404291582	-0.5113050543
C	0	-1.2611329833	3.8807311906	-1.7567642909
C	0	-0.3941291526	3.7695634828	0.4957169107
C	0	-0.4943883539	5.0210734099	-1.9999364243
H	0	-1.9031814392	3.4793314596	-2.5457550498
C	0	0.3702707557	4.9143885205	0.2541844488
H	0	-0.3730503856	3.2810568184	1.4706247600
C	0	0.3270450373	5.5397456849	-0.9942924087
H	0	-0.5392669123	5.5073560294	-2.9770676033
H	0	0.9988344558	5.3218556083	1.0495186484
H	0	0.9256413940	6.4340540812	-1.1820241331

Sb-PP-PxRe

0 1

O	0	-1.1161507264	2.6227136347	-0.5914927392
C	0	-1.7315056962	3.8606869380	-0.9600581836
O	0	-3.1178458762	1.8170402177	0.0577871897
C	0	-1.9292901687	1.7040691233	-0.0476908542
C	0	-1.1338016251	0.4317930070	0.2980032801
C	0	-1.1001026492	-0.5567607231	-0.8875361233
N	0	-1.6291358730	-1.6196560209	1.1570561261
O	0	-1.8674657122	-0.2357296303	1.3032998380
C	0	-1.6410166739	-1.8749722787	-0.2790741408
H	0	-2.5537630259	3.6883949942	-1.6697036780
H	0	-2.1318552005	4.3623601099	-0.0672399142
H	0	-0.9435797779	4.4683133420	-1.4200124468

H	0	-1.6895385702	-0.2169312781	-1.7462964729
H	0	-0.9229230863	-2.6732048477	-0.5045311283
N	0	0.2430452580	0.7159675364	0.7020585787
C	0	1.2639719967	0.5683590966	-0.3291555568
C	0	0.3625423612	1.5572816143	1.7902115752
H	0	1.2216039702	1.4363113401	-1.0151850613
S	0	0.6555063167	-0.7985666258	-1.4847206846
C	0	2.7459354981	0.3374724228	0.0931213605
H	0	1.4051441071	1.7523763072	2.0935733343
O	0	-0.5892498320	2.0241185786	2.3758984929
O	0	1.0852269829	-2.1648564283	-0.9878836686
C	0	3.4127788188	1.6711315532	0.4997146381
C	0	3.5275795068	-0.1650967594	-1.1439364531
C	0	2.8419051551	-0.6980212951	1.2236300100
H	0	3.0557606121	2.0762818864	1.4547609295
H	0	4.4958888354	1.5108680488	0.6116696022
H	0	3.2677199628	2.4429752258	-0.2733716808
H	0	4.6005984026	-0.1950431338	-0.9040894774
H	0	3.2237466796	-1.1778153959	-1.4377679052
H	0	3.3998365597	0.5125613507	-2.0045436408
H	0	3.9003846837	-0.8982594874	1.4517006352
H	0	2.3592947528	-0.3519869876	2.1475833911
H	0	2.3591904408	-1.6396502930	0.9320117487
C	0	-0.6269391637	-2.1160054212	2.0178938593
C	0	-0.0190699823	-3.3589486329	1.7769800795
C	0	-0.2968019297	-1.4070155865	3.1872025886
C	0	0.9341026649	-3.8543146621	2.6672773225
H	0	-0.2754669021	-3.9400296373	0.8924467334
C	0	0.6558445476	-1.9176839748	4.0672911341
H	0	-0.7898102133	-0.4584680761	3.3917172213
C	0	1.2868674585	-3.1393441707	3.8140318121
H	0	1.4072345175	-4.8156878988	2.4529500466
H	0	0.9045551898	-1.3483104449	4.9666456273
H	0	2.0346125068	-3.5333279170	4.5054077923
C	0	-3.0100668157	-2.2472593767	-0.8090537644
C	0	-3.1376686851	-3.3548270242	-1.6548130679
C	0	-4.1478468408	-1.4906326255	-0.4876891690
C	0	-4.3851672918	-3.7104625313	-2.1770131304
H	0	-2.2531937570	-3.9482805932	-1.9034226726
C	0	-5.3922266811	-1.8488529372	-1.0079358916
H	0	-4.0546919992	-0.6197156912	0.1635837959
C	0	-5.5153470602	-2.9574274739	-1.8531266475
H	0	-4.4728195396	-4.5801974811	-2.8326554919
H	0	-6.2738481878	-1.2564813220	-0.7514484799
H	0	-6.4924881532	-3.2336778637	-2.2567656582

Sb-PP-PxSi

0 1

O	0	1.4113988417	1.8389831352	-1.4111240849
C	0	2.2148699833	2.8673378794	-1.9906227429
O	0	2.9805303705	1.4535221253	0.1677251759
C	0	1.8838900395	1.2899540062	-0.2875443602
C	0	0.8596512591	0.2725255652	0.2598917591
C	0	0.7159746535	-0.9310349165	-0.7071395531
N	0	2.1934672456	-1.3658926692	1.0372966952
O	0	1.3230620214	-0.3080523241	1.4609365066
C	0	1.4661006663	-2.0821850551	-0.0050745998
H	0	3.2276279163	2.4962805831	-2.2055769705
H	0	2.2842332460	3.7185774586	-1.2972149947
H	0	1.7082648934	3.1661359216	-2.9157170898
H	0	1.0799832987	-0.7134710912	-1.7165272148
H	0	0.7328349097	-2.7931278602	0.4315947559
N	0	-0.4490380185	0.8249181181	0.5085036071

C	0	-1.4756180648	-0.2097538790	0.5411910893
C	0	-0.5575290023	2.1331438759	0.9279526140
H	0	-1.2576952265	-0.9006098225	1.3763613091
S	0	-1.0804950253	-1.2972366772	-0.9664725601
C	0	-2.9763236773	0.1714543710	0.5972135738
H	0	-1.5900599587	2.4343815342	1.1717812651
O	0	0.3801488258	2.8941202830	1.0133249909
O	0	-1.4920618791	-0.5677581996	-2.2213844745
C	0	-3.3607856329	1.2405213894	-0.4445400819
C	0	-3.3507857259	0.6107315937	2.0279928823
C	0	-3.7849074436	-1.1090926554	0.2887547933
H	0	-2.9593861820	0.9742288449	-1.4311756425
H	0	-4.4581307368	1.3020965394	-0.5107395447
H	0	-2.9987215936	2.2442342421	-0.1844491410
H	0	-4.4258033504	0.8448405513	2.0709386699
H	0	-3.1522800904	-0.1958610431	2.7515415677
H	0	-2.8077669230	1.5025292543	2.3689577986
H	0	-3.4592795222	-1.9585972739	0.9104300364
H	0	-4.8495852843	-0.9283688184	0.4984157053
H	0	-3.6996989240	-1.3926725598	-0.7705608781
C	0	2.7523198694	-2.0185118115	2.1464017125
C	0	3.1599489871	-1.2479011527	3.2514897747
C	0	2.9564044285	-3.4080991747	2.1556635328
C	0	3.7588203861	-1.8672335974	4.3446305179
H	0	3.0032008533	-0.1702163635	3.2251396725
C	0	3.5745154458	-4.0103808001	3.2553967746
H	0	2.6578250240	-4.0203019896	1.3061405105
C	0	3.9739156372	-3.2509794075	4.3554527354
H	0	4.0691999670	-1.2591240893	5.1979408789
H	0	3.7357233654	-5.0911886711	3.2472039330
H	0	4.4502704869	-3.7295637229	5.2137559250
C	0	2.3880953534	-2.8264033764	-0.9451604438
C	0	1.9707201592	-4.0264929679	-1.5308332619
C	0	3.6381990925	-2.2895080080	-1.2810163338
C	0	2.7939980658	-4.6887767077	-2.4455159425
H	0	0.9960166610	-4.4466127474	-1.2675732619
C	0	4.4615029842	-2.9553890773	-2.1903419573
H	0	3.9580845750	-1.3561043657	-0.8130365048
C	0	4.0420823371	-4.1547183861	-2.7754684925
H	0	2.4605668520	-5.6256616780	-2.8978557407
H	0	5.4387699518	-2.5367393231	-2.4421354247
H	0	4.6892624177	-4.6737818991	-3.4863258859

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O	0	-0.1372165888	-3.4398630064	-1.0043767384
C	0	-0.8509246330	-4.6103426361	-1.3858006126
O	0	-2.0095961161	-2.6409387610	-0.0451862229
C	0	-0.8534753404	-2.4858681928	-0.3863914034
C	0	-0.0443582984	-1.2885170634	-0.0974703007
C	0	-0.4212056679	-0.3607997663	0.8884060551
O	0	-1.7374415918	-0.0000795322	-1.5514920748
N	0	-2.0109244857	0.7679610756	-0.5884711874
C	0	-0.9429213031	1.3145720508	0.1012065512
H	0	-1.6615459485	-4.3573990537	-2.0859253515
H	0	-1.2905501149	-5.1081687959	-0.5081623604
H	0	-0.1209894375	-5.2668174047	-1.8747734589
H	0	-1.3275657433	-0.5965297811	1.4531298994
H	0	-1.2455526366	1.8786186674	0.9844836814
N	0	1.3362434038	-1.2158253790	-0.4294147221
C	0	2.1456606827	-1.0242340182	0.7656903442
C	0	1.7776123416	-1.3539060226	-1.7320793705
H	0	2.1606808964	-1.9769265459	1.3257561923

S	0	1.0013012234	-0.0223083782	1.9932823243
C	0	3.5839241417	-0.4648238766	0.7096115413
H	0	2.8791951300	-1.3549903994	-1.8128725020
O	0	1.0507539651	-1.4574714597	-2.6921837634
O	0	1.2916284893	1.4598385863	2.0645755395
C	0	4.5573911377	-1.5292409733	0.1564831562
C	0	4.0267920643	-0.1886111981	2.1660981812
C	0	3.6589947037	0.8395172513	-0.0975216656
H	0	4.4058736607	-1.7600055325	-0.9056978957
H	0	5.5904381374	-1.1634296053	0.2623653144
H	0	4.4760049444	-2.4717611819	0.7213129208
H	0	5.0931021002	0.0820874108	2.1754076057
H	0	3.4663723645	0.6423467105	2.6136024781
H	0	3.9065819712	-1.0838358149	2.7986592805
H	0	2.9587386737	1.5824697567	0.3042182631
H	0	4.6777206098	1.2533630734	-0.0382229587
H	0	3.4213814081	0.6932065912	-1.1592699153
C	0	0.1300070090	1.9900384898	-0.6820292821
C	0	0.6832147082	3.1649909955	-0.1388100091
C	0	0.5465369562	1.5734570581	-1.9573935011
C	0	1.6254423408	3.9041203240	-0.8488147573
H	0	0.3829399661	3.4871475584	0.8582090028
C	0	1.4921729156	2.3199876117	-2.6652792842
H	0	0.1336229908	0.6693369139	-2.3940846528
C	0	2.0370983986	3.4823191916	-2.1177966718
H	0	2.0441680040	4.8115076540	-0.4074429431
H	0	1.8060345627	1.9754254201	-3.6534781215
H	0	2.7809017477	4.0584606977	-2.6737734479
C	0	-3.3201233752	0.7380743803	-0.0136582090
C	0	-4.1240996951	-0.3897393802	-0.2254850610
C	0	-3.7996831700	1.8386054865	0.7121402409
C	0	-5.4085111974	-0.4147680397	0.3135843760
H	0	-3.7077480961	-1.2344773642	-0.7700272988
C	0	-5.0871378416	1.7959432425	1.2475380057
H	0	-3.1882886492	2.7343513048	0.8281664845
C	0	-5.8938845151	0.6710492996	1.0513813775
H	0	-6.0334935436	-1.2982014305	0.1654303929
H	0	-5.4656968624	2.6538005087	1.8075413789
H	0	-6.9020007978	0.6419842828	1.4707911559

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O	0	-0.1945405433	-3.2068946265	-0.7325693917
C	0	0.3485347750	-4.5137541972	-0.8959687731
O	0	1.6641619811	-2.5842806717	0.3726151609
C	0	0.5929376199	-2.3123191363	-0.1221476108
C	0	-0.0454356764	-0.9726567615	-0.0482627328
C	0	0.1959145024	-0.1145389803	1.0390776360
O	0	1.4811601126	-0.0525760449	-1.3698114890
N	0	2.0387279934	0.7264879287	-0.5122387930
C	0	1.1827833843	1.4819308144	0.2414217668
H	0	1.2522858371	-4.4772338263	-1.5225234969
H	0	0.6116157111	-4.9530431057	0.0777561629
H	0	-0.4304215341	-5.1067213657	-1.3894589952
H	0	0.8676784934	-0.4358523313	1.8385432763
H	0	1.6517062130	1.9407872165	1.1144728601
N	0	-1.2575199393	-0.6916206741	-0.7070117215
C	0	-2.2603481496	0.0179862286	0.0927044815
C	0	-1.3903268127	-0.7840858141	-2.0875408514
H	0	-2.5242265118	0.9717966138	-0.3919013040
S	0	-1.3594889396	0.5796474456	1.6988881699
C	0	-3.5499515421	-0.7919621992	0.3989004223
H	0	-2.3119854311	-0.2710705346	-2.4369325567

O	0	-0.6129434517	-1.3214779894	-2.8342604730
O	0	-1.7167201562	-0.3000529522	2.8744103896
C	0	-4.4338614176	0.0375719131	1.3509531767
C	0	-3.2062885962	-2.1644857600	1.0025750032
C	0	-4.3392001713	-1.0132192759	-0.9064598317
H	0	-4.6392226680	1.0365903991	0.9303338506
H	0	-5.4017382774	-0.4674935087	1.4918371077
H	0	-3.9675167759	0.1548090984	2.3373618040
H	0	-4.1336530864	-2.7293161886	1.1873856221
H	0	-2.5844542417	-2.7461597725	0.3062207943
H	0	-2.6653474887	-2.0521581608	1.9498062478
H	0	-3.8166615448	-1.6869843229	-1.6002520681
H	0	-5.3045711476	-1.4845767817	-0.6649460649
H	0	-4.5505160976	-0.0652339087	-1.4280327025
C	0	0.1350899693	2.3198715665	-0.3943250027
C	0	-0.4773072572	3.3115311784	0.3950774520
C	0	-0.2701031701	2.1788172142	-1.7351382957
C	0	-1.4880525746	4.1195466198	-0.1259720525
H	0	-0.1582686024	3.4489463256	1.4304441807
C	0	-1.2735012512	2.9971720830	-2.2543675427
H	0	0.2032201073	1.4203800132	-2.3549573107
C	0	-1.8967846470	3.9592154202	-1.4523790167
H	0	-1.9544816440	4.8784078536	0.5061649705
H	0	-1.5744341192	2.8762143783	-3.2977291450
H	0	-2.6904365030	4.5879024531	-1.8626797200
C	0	3.3801801114	0.4651916888	-0.0931290493
C	0	3.9736442440	-0.7593122386	-0.4223715071
C	0	4.1141735995	1.4516216494	0.5823251770
C	0	5.2908343491	-1.0027806595	-0.0405001803
H	0	3.3819802892	-1.5058273015	-0.9450043729
C	0	5.4304517882	1.1902319414	0.9657635562
H	0	3.6770149259	2.4312505412	0.7802850757
C	0	6.0231653710	-0.0371327089	0.6591010848
H	0	5.7475724551	-1.9645777558	-0.2842907671
H	0	5.9990818893	1.9600880387	1.4921957078
H	0	7.0545942471	-0.2379130684	0.9568486818

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O	0	0.1882170214	3.5060602765	-0.9966492734
C	0	0.7765461557	4.6305360485	-1.6461770891
O	0	2.1972514575	2.4902492159	-0.9505232391
C	0	1.0044115493	2.4648811534	-0.7705464132
C	0	0.2655879414	1.3049987910	-0.1880992517
C	0	0.7807316220	0.6276274154	0.9409178610
N	0	0.7903595337	-1.1460577234	-0.9426701407
O	0	0.9673087395	-0.0780696361	-1.6337146948
C	0	1.4565576344	-1.1914176157	0.2497661552
H	0	1.6204820407	5.0249440901	-1.0608093234
H	0	1.1416567101	4.3449368648	-2.6439724363
H	0	-0.0168694633	5.3823735074	-1.7339803538
H	0	1.7036138989	0.9854664762	1.3977892252
H	0	1.0470277366	-1.9172800511	0.9505319372
N	0	-1.1469430499	1.2310429317	-0.2805669508
C	0	-1.7856618001	1.1219931035	1.0322751148
C	0	-1.7902782825	1.4302109068	-1.4894424305
H	0	-1.7319053823	2.1122750019	1.5227870991
S	0	-0.5322619852	0.1724896915	2.1182056697
C	0	-3.2276524302	0.5750596887	1.1818039963
H	0	-2.8894823900	1.3950111652	-1.3999749733
O	0	-1.2252544739	1.6046267180	-2.5431386347
O	0	-0.7706289701	-1.3277618400	2.0580493145
C	0	-4.2589554340	1.6513007828	0.7764514388

C	0	-3.4665707217	0.2935116287	2.6842173100
C	0	-3.4301742496	-0.7273968742	0.3915020817
H	0	-4.2386885849	1.9110364341	-0.2896954345
H	0	-5.2722029982	1.2824468365	0.9984765357
H	0	-4.1070394880	2.5793531651	1.3506467006
H	0	-4.5269428960	0.0464645837	2.8418116932
H	0	-2.8672706938	-0.5557030860	3.0377493897
H	0	-3.2356626584	1.1767775582	3.3022630901
H	0	-4.4287049157	-1.1378972456	0.6079982409
H	0	-3.3622344975	-0.5820945353	-0.6946720522
H	0	-2.6767751815	-1.4709622503	0.6795226536
C	0	2.9228550163	-1.0091548311	0.3398666957
C	0	3.5659398195	-1.6096694190	1.4384982113
C	0	3.6915581334	-0.2862619441	-0.5897129056
C	0	4.9468135668	-1.5043659795	1.6025182969
H	0	2.9732388361	-2.1709203640	2.1661453653
C	0	5.0742664816	-0.1971644525	-0.4265602546
H	0	3.1951037367	0.2179950423	-1.4147938617
C	0	5.7071625744	-0.7992337894	0.6652692012
H	0	5.4302456802	-1.9791554213	2.4596420112
H	0	5.6619827776	0.3647250948	-1.1563009923
H	0	6.7895836907	-0.7146595451	0.7886471257
C	0	-0.3385504300	-1.9704906680	-1.2605923457
C	0	-1.0805162952	-1.6422857285	-2.4042179188
C	0	-0.6647621104	-3.1067975141	-0.5084765636
C	0	-2.1726190512	-2.4299096143	-2.7638999509
H	0	-0.7951802377	-0.7642003904	-2.9796959049
C	0	-1.7646792591	-3.8805371545	-0.8782157926
H	0	-0.0878499449	-3.3861433404	0.3701391799
C	0	-2.5261828284	-3.5478506110	-2.0017068413
H	0	-2.7515421270	-2.1650509010	-3.6518398041
H	0	-2.0245294660	-4.7553662709	-0.2780864850
H	0	-3.3831140573	-4.1620973760	-2.2867162823

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O	0	-1.1771095977	-2.3965727107	-2.0450221317
C	0	-1.0072021224	-3.4582868382	-2.9808669304
O	0	0.9949155305	-2.5650427533	-1.4740794962
C	0	-0.0712892345	-2.0038314617	-1.3923988206
C	0	-0.3359732048	-0.8383285512	-0.5101353271
C	0	0.2894058722	-0.7099716963	0.7395329031
N	0	1.3615773775	1.2216441939	-0.6134835126
O	0	1.0702509600	0.4692114807	-1.6100282349
C	0	1.8800161693	0.5838598342	0.4777052503
H	0	-0.6288014681	-4.3628462362	-2.4818801322
H	0	-0.2951481033	-3.1642672687	-3.7661125617
H	0	-1.9969470996	-3.6424789181	-3.4149383663
H	0	0.8293726371	-1.5359015885	1.2048823659
H	0	1.8745859534	1.1897040499	1.3849149713
N	0	-1.5491173313	-0.1130209252	-0.5872288797
C	0	-2.2214729331	0.1052247492	0.6910904986
C	0	-2.0550763468	0.4364506131	-1.7513396842
H	0	-2.6768692887	1.1068601271	0.6902070938
S	0	-0.7572606557	0.2411897846	1.9180706119
C	0	-3.2913704587	-0.9473182046	1.0738390871
H	0	-2.9708947227	1.0352586633	-1.5467846012
O	0	-1.5712093960	0.3246434072	-2.8501958721
O	0	-0.9560853775	-0.6213829255	3.1438504439
C	0	-2.6879670352	-2.3538720701	1.2279247630
C	0	-4.3506587836	-0.9881304664	-0.0440540737
C	0	-3.9649040063	-0.4915287916	2.3814787489
H	0	-1.9233621001	-2.3731564989	2.0143489344

H	0	-3.4851337313	-3.0626463582	1.5023745709
H	0	-2.2522340517	-2.6997045902	0.2799851493
H	0	-5.1582857275	-1.6771312429	0.2482878157
H	0	-4.8048986522	0.0009817909	-0.2177300448
H	0	-3.9284425004	-1.3538893515	-0.9915637627
H	0	-4.4244498864	0.5039512789	2.2601897779
H	0	-4.7661367347	-1.1960484136	2.6530025627
H	0	-3.2445930645	-0.4514741903	3.2081242608
C	0	3.0387689726	-0.3303195342	0.3940177973
C	0	3.7320411905	-0.5834392218	1.5932662493
C	0	3.4801763927	-0.9437820784	-0.7908965382
C	0	4.8454384298	-1.4213675456	1.6114126470
H	0	3.3939729139	-0.1127618784	2.5209613561
C	0	4.6059745336	-1.7668593517	-0.7689325320
H	0	2.9256728962	-0.7837028779	-1.7112297182
C	0	5.2887254727	-2.0140851097	0.4252669657
H	0	5.3712334751	-1.6066360272	2.5508778523
H	0	4.9418832286	-2.2355179250	-1.6967294852
H	0	6.1616875567	-2.6711082098	0.4335399447
C	0	0.7331906162	2.5118024336	-0.5464505434
C	0	0.8744929521	3.3629556901	0.5595777969
C	0	-0.0001280580	2.9304628302	-1.6664991081
C	0	0.2403000467	4.6058711728	0.5579628575
H	0	1.4718110106	3.0768261749	1.4239906372
C	0	-0.6240698908	4.1765733577	-1.6542407268
H	0	-0.0794528245	2.2592829714	-2.5190857069
C	0	-0.5152375589	5.0185428952	-0.5427588692
H	0	0.3467788048	5.2588318943	1.4271135228
H	0	-1.1995784163	4.4922143633	-2.5275863011
H	0	-1.0049996296	5.9945980549	-0.5385834752

Computational methods of chapter VI

Computational Methods

All of the calculations were performed using the Gaussian09 program.[1] Molecular geometries were optimized with the B3LYP functional[12] including the D3BJ dispersion correction of Grimme.[13] The electronic configuration of the molecular systems was described with the standard split-valence basis set def2SVP,[14] which showed to be adequate for that functional.[15] Single point calculations using def2TZVP basis set were carried out over optimized geometries Analytical second derivatives of the energy were calculated to classify the nature of every stationary point, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. All transition structures were characterized by one imaginary frequency and were confirmed to connect to reactants and products by intrinsic reaction coordinate (IRC) calculations. The IRC paths were traced using the Hratchian-Schlegel algorithm.[16] The thermal and entropic contributions to the free energies were also obtained from the vibrational frequency calculations, using the unscaled frequencies. All discussions are based on values of free energies (G). The individual reactions involved on the study are bimolecular processes. In order to avoid errors due to entropic effects when comparing all stationery points in an only energy diagram, we used corrected free energy (G_{corr}) values following Morokuma's model[17] based on consideration of translational entropy.

Structural representations were generated using CYLView.[11]

Energy Values

***Table A31*.** Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **248a**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39a	-1068.826028		-1068.869504		
248a	-194.099294		-194.125908		
aa-TS1	-1262.885869	24.8	-1262.933922	33.3	-392.8
aa-TS2	-1262.862891	39.2	-1262.911749	47.3	-530.4
aa-TS3	-1262.895073	19.0	-1262.942598	26.9	-458.8
aa-TS4	-1262.898288	17.0	-1262.945498	25.0	-405.3
aa-PR1	-1262.904731	12.9	-1262.951178	17.2	
aa-PR2	-1262.931173	-3.7	-1262.978533	2.4	
aa-PR3	-1262.935999	-6.7	-1262.982402	-1.2	
aa-PR4	-1262.940957	-9.8	-1262.987048	-4.0	

[a]Referred to the reagents (**39a** + **248a**)

***Table A32*.** Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **248a**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39b	-1144.043069		-1144.088318		
248a	-194.099294		-194.125908		
ab-TS1	-1338.113275	18.3	-1338.162559	25.3	-371.2
ab-TS2	-1338.087637	34.3	-1338.137751	41.8	-522.2
ab-TS3	-1338.121498	13.1	-1338.170467	18.5	-399.7
ab-TS4	-1338.126460	10.0	-1338.175230	16.0	-359.1
ab-PR1	-1338.128284	8.8	-1338.176906	10.6	
ab-PR2	-1338.157526	-9.5	-1338.206465	-5.9	
ab-PR3	-1338.163047	-13.0	-1338.210100	-9.8	
ab-PR4	-1338.165926	-14.8	-1338.213186	-11.0	

[a]Referred to the reagents (**39b** + **248a**)

***Table A33*.** Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **248a**.

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39c	-1219.298553		-1219.343999		
248a	-194.099294		-194.125908		
ac-TS1	-1413.372709	15.8	-1413.422171	22.4	-288.9
ac-TS2	-1413.347695	31.5	-1413.397402	38.5	-502.7
ac-TS3	-1413.378735	12.0	-1413.427910	18.0	-375.5
ac-TS4	-1413.381630	10.2	-1413.430650	16.6	-312.4
ac-PR1	-1413.418959	-13.2	-1413.467943	-10.5	
ac-PR2	-1413.417645	-12.4	-1413.466262	-9.1	
ac-PR3	-1413.421430	-14.8	-1413.469430	-11.3	
ac-PR4	-1413.424260	-16.6	-1413.471946	-12.6	

[a]Referred to the reagents (**39c** + **248a**)

***Table A34*.** Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **248b**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39a	-1068.826028		-1068.869504		
248b	-233.407009		-233.435255		
ba-TS1	-1302.188415	28.0	-1302.238355	36.3	-408.5
ba-TS2	-1302.159538	46.1	-1302.207257	55.5	-504.4
ba-TS3	-1302.197227	22.5	-1302.245747	30.3	-404.0
ba-TS4	-1302.201263	19.9	-1302.250202	27.9	-412.1
ba-PR1	-1302.252862	-12.4	-1302.300481	-6.9	
ba-PR2	-1302.252868	-12.4	-1302.300651	-6.8	
ba-PR3	-1302.255436	-14.1	-1302.303028	-9.1	
ba-PR4	-1302.260362	-17.1	-1302.307886	-11.6	

[a]Referred to the reagents (**39a** + **248b**)

***Table A35*.** Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **248b**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39b	-1144.043069		-1144.088318		
248b	-233.407009		-233.435255		
bb-TS1	-1377.415968	21.4	-1377.467159	28.1	-379.6
bb-TS2	-1377.384737	41.0	-1377.435564	48.1	-483.1
bb-TS3	-1377.419822	19.0	-1377.470512	24.4	-365.8
bb-TS4	-1377.430445	12.3	-1377.480637	17.8	-360.8
bb-PR1	-1377.478800	-18.0	-1377.528953	-15.2	
bb-PR2	-1377.478247	-17.7	-1377.528742	-15.2	
bb-PR3	-1377.478519	-17.8	-1377.526785	-15.1	
bb-PR4	-1377.486685	-23.0	-1377.535217	-19.7	

[a]Referred to the reagents (**39b** + **248b**)

***Table A36*.** Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **248b**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39c	-1219.298553		-1219.343999		
248b	-233.407009		-233.435255		
bc-TS1	-1452.676022	18.5	-1452.727028	24.6	-273.6
bc-TS2	-1452.644081	38.6	-1452.696238	44.4	-418.0
bc-TS3	-1452.677324	17.7	-1452.727458	23.8	-346.0
bc-TS4	-1452.685377	12.7	-1452.735928	18.5	-292.1
bc-PR1	-1452.737610	-20.1	-1452.787859	-17.6	
bc-PR2	-1452.736016	-19.1	-1452.785672	-16.3	
bc-PR3	-1452.737907	-20.3	-1452.787038	-17.4	
bc-PR4	-1452.745332	-25.0	-1452.794321	-21.5	

[a]Referred to the reagents (**39c** + **248b**)

Table A37. Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **251c**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39a	-1068.826028		-1068.869504		
251c	-618.147445		-618.188336		
ca-TS1	-1686.933071	25.4	-1686.993034	40.7	-520.6
ca-TS2	-1686.925137	30.3	-1686.985196	45.6	-557.4
ca-TS3	-1686.941596	20.0	-1687.002797	34.5	-496.7
ca-TS4	-1686.946695	16.8	-1687.007373	31.7	-509.4
ca-PR1	-1686.973012	0.3	-1687.030404	17.2	
ca-PR2	-1686.992147	-11.7	-1687.050734	4.5	
ca-PR3	-1686.992891	-12.2	-1687.052100	3.6	
ca-PR4	-1687.000716	-17.1	-1687.057450	0.2	

a: Referred to the reagents (**2a** + **8c**)

Table A38. Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **251c**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39b	-1144.043069		-1144.088318		
251c	-618.147445		-618.188336		
cb-TS1	-1762.159925	19.2	-1762.220825	35.0	-494.4
cc-TS2	-1762.155012	22.3	-1762.217225	37.3	-481.3
cb-TS3	-1762.163184	17.1	-1762.225397	32.2	-474.0
cb-TS4	-1762.172775	11.1	-1762.235265	26.0	-471.9
cb-PR1	-1762.200691	-6.4	-1762.259524	10.7	
cb-PR2	-1762.216509	-16.3	-1762.277351	-0.4	
cb-PR3	-1762.220656	-18.9	-1762.278327	-1.0	
cb-PR4	-1762.223427	-20.7	-1762.283286	-4.2	

[a]Referred to the reagents (**39b** + **251c**)

Table A39. Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **251c**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39c	-1219.298553		-1219.343999		
251c	-618.147445		-618.188336		
cc-TS1	-1837.417789	17.7	-1837.478597	33.7	-477.0
cc-TS2	-1837.407421	24.2	-1837.469179	39.6	-519.4
cc-TS3	-1837.421856	15.1	-1837.485213	29.6	-476.5
cc-TS4	-1837.429335	10.5	-1837.491902	25.4	-477.7
cc-PR1	-1837.458022	-7.5	-1837.518962	8.4	
cc-PR2	-1837.474573	-17.9	-1837.532610	-0.2	
cc-PR3	-1837.477650	-19.9	-1837.535867	-2.2	
cc-PR4	-1837.460808	-9.3	-1837.521467	6.8	

[a]Referred to the reagents (**39c** + **251c**)

Table A40. Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39a** and **251d**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39a	-1068.826028		-1068.869504		
251d	-639.950343		-639.990915		
da-13TS1	-1708.737284	24.5	-1708.796501	40.1	-427.7
da-13TS2	-1708.721917	34.2	-1708.782718	48.8	-533.2
da-13TS3	-1708.746614	18.7	-1708.804689	35.0	-444.6
da-13TS4	-1708.749481	16.9	-1708.808388	32.7	-420.4
da-14TS1	-1708.741224	22.1	-1708.803048	36.0	-496.5
da-14TS2	-1708.729020	29.7	-1708.789439	44.5	-483.6
da-14TS3	-1708.749323	17.0	-1708.809272	32.1	-507.1
da-14TS4	-1708.752560	14.9	-1708.813350	29.5	-489.8
da-13PR1	-1708.815784	-24.7	-1708.871687	-7.1	
da-13PR2	-1708.816299	-25.1	-1708.872973	-7.9	
da-13PR3	-1708.822152	-28.7	-1708.879357	-11.9	
da-13PR4	-1708.813083	-23.0	-1708.871103	-6.7	
da-14PR1	-1708.814743	-24.1	-1708.870758	-6.5	
da-14PR2	-1708.814967	-24.2	-1708.871400	-6.9	
da-14PR3	-1708.812545	-22.7	-1708.868838	-5.3	
da-14PR4	-1708.817103	-25.6	-1708.875690	-9.6	

[a]Referred to the reagents (**39a** + **251b**)

Table A41. Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39b** and **251d**

	E(0)	ΔE(0)[a]	G	ΔG[a]	im. freq.
39b	-1144.043069		-1144.088318		
251d	-639.950343		-639.990915		
db-13TS1	-1783.965009	17.8	-1784.026397	33.2	-382.4
db-13TS2	-1783.960527	20.6	-1784.019923	37.2	-412.1
db-13TS3	-1783.972944	12.8	-1784.032341	29.4	-404.4
db-13TS4	-1783.977860	9.8	-1784.037547	26.2	-329.8
db-14TS1	-1783.965409	17.6	-1784.025643	33.6	-492.3
db-14TS2	-1783.952965	25.4	-1784.015481	40.0	-486.3
db-14TS3	-1783.975007	11.5	-1784.036230	27.0	-425.7
db-14TS4	-1783.980914	7.8	-1784.040699	24.2	-362.0
db-13PR1	-1784.043199	-31.2	-1784.103149	-15.0	
db-13PR2	-1784.043715	-31.6	-1784.102641	-14.7	
db-13PR3	-1784.049068	-34.9	-1784.107834	-17.9	
db-13PR4	-1784.043549	-31.5	-1784.101659	-14.1	
db-14PR1	-1784.041773	-30.3	-1784.103547	-15.3	
db-14PR2	-1784.041431	-30.1	-1784.102572	-14.6	
db-14PR3	-1784.048045	-34.3	-1784.105947	-16.8	
db-14PR4	-1784.044635	-32.1	-1784.103792	-15.4	

[a]Referred to the reagents (**39b** + **251d**)

Table A42. Calculated (b3lyp-d3bj/def2tzvp//b3lyp-d3bj/def2svp) absolute (hartrees) and relative (kcal/mol) energies for the reaction between **39c** and **251d**

	E(0)	**ΔE(0)[a]**	**G**	**ΔG[a]**	**im. freq.**
39c	-1219.298553		-1219.343999		
251d	-639.950343		-639.990915		
dc-13TS1	-1859.224785	15.1	-1859.287047	21.3	-331.7
dc-13TS2	-1859.207370	26.1	-1859.266891	35.3	-450.4
dc-13TS3	-1859.231337	11.0	-1859.290942	18.0	-391.5
dc-13TS4	-1859.233461	9.7	-1859.293852	16.8	-316.0
dc-14TS1	-1859.227907	13.2	-1859.288397	19.7	-307.1
dc-14TS2	-1859.215480	21.0	-1859.277884	27.6	-465.2
dc-14TS3	-1859.234579	9.0	-1859.294157	16.9	-415.3
dc-14TS4	-1859.236943	7.5	-1859.297889	12.8	-283.1
dc-13PR1	-1859.299697	-31.9	-1859.358778	-28.0	
dc-13PR2	-1859.302231	-33.5	-1859.362292	-29.3	
dc-13PR3	-1859.306217	-36.0	-1859.363746	-30.8	
dc-13PR4	-1859.302026	-33.3	-1859.361553	-30.2	
dc-14PR1	-1859.297197	-30.3	-1859.357443	-27.3	
dc-14PR2	-1859.302492	-33.6	-1859.358092	-27.4	
dc-14PR3	-1859.305888	-35.8	-1859.363987	-30.4	
dc-14PR4	-1859.298829	-31.3	-1859.358653	-28.0	

[a]Referred to the reagents (**39c** + **251d**)

Cartesian Coordinates

C39a

0 1

C	0	1.6289887230	0.6053927244	-1.3305301939
C	0	-0.7531193935	0.5266093710	-1.0079932672
C	0	-0.5613864510	-0.7263756049	-1.4790365185
C	0	-1.9772452785	1.0164789918	-0.3492188273
O	0	-2.1064657502	2.1149565202	0.1453981888
O	0	-2.9515469791	0.0873741128	-0.3597705835
C	0	-4.1777662490	0.4630825061	0.2651497101
H	0	2.2278545725	1.1353138569	-2.0831813116
H	0	-1.3161033359	-1.5100579161	-1.4754681585
H	0	-4.6066034941	1.3528495299	-0.2197834993
H	0	-4.8512910727	-0.3950292362	0.1538535157
H	0	-4.0200051465	0.6902547673	1.3302687313
N	0	0.3903783185	1.3574575217	-1.1315766203
C	0	2.4825836910	0.4165927685	-0.0495851386
C	0	3.7352081317	-0.3912300191	-0.4223981730
H	0	3.4759082945	-1.4011243641	-0.7761906556
H	0	4.3137202771	0.1140145612	-1.2129252328
H	0	4.3905873701	-0.5011476355	0.4550355084
C	0	2.9058875263	1.8097567204	0.4505210322
H	0	2.0353917326	2.4019269888	0.7673108437
H	0	3.5758186340	1.7025190952	1.3180230447
H	0	3.4296598345	2.3799571511	-0.3299716760
C	0	1.6976012642	-0.3004844232	1.0572286859
H	0	2.3324201998	-0.4184942334	1.9490823191
H	0	0.8106404216	0.2794825255	1.3529463171
H	0	1.3719279753	-1.3017782759	0.7389392698
S	0	1.0536069034	-1.0196309170	-2.0708656280
C	0	0.3412772993	2.6889868513	-1.5090701006
O	0	1.3159613839	3.3192808268	-1.8558757050
H	0	-0.6795931325	3.1127584146	-1.4399652371

C39b

0 1

C	0	1.6364264423	0.4394991289	-1.2312865624
C	0	-0.7178413414	0.4103838643	-0.8870480664
C	0	-0.5433163094	-0.9066309087	-1.1068077842
C	0	-1.9817220316	1.0152415197	-0.3607237213
O	0	-2.0889749107	2.1558716412	0.0230003562
O	0	-2.9765788912	0.1230687817	-0.3484322289
C	0	-4.2280813416	0.5819626685	0.1698704951
H	0	2.2101478680	0.8208191419	-2.0866024544
H	0	-1.3074424658	-1.6718824009	-0.9953679707
H	0	-4.5985419091	1.4352086848	-0.4169224061
H	0	-4.9169405887	-0.2668095247	0.0917468130
H	0	-4.1201947442	0.8967499472	1.2183879874
N	0	0.4105745926	1.2158012308	-1.0961998298
C	0	2.5203909410	0.3960765336	0.0400876018
C	0	3.8099466829	-0.3677690627	-0.3044899414
H	0	3.6067430532	-1.4080769195	-0.6008109904
H	0	4.3512201117	0.1230120205	-1.1287434534
H	0	4.4779144845	-0.3929839361	0.5700248679
C	0	2.8819666759	1.8340669477	0.4514149438
H	0	1.9902585100	2.3961298344	0.7652764624
H	0	3.5813943125	1.8088288905	1.3018761109
H	0	3.3501606837	2.3854144925	-0.3756718432
C	0	1.7946372937	-0.2911133785	1.2086921233

H	0	2.4385327257	-0.2861109006	2.1017384938
H	0	0.8635588543	0.2358438163	1.4659735994
H	0	1.5463487736	-1.3395323215	0.9814097157
S	0	1.0894811576	-1.2977038023	-1.7711132810
O	0	0.9626580044	-1.3220089068	-3.2721739558
C	0	0.3668887261	2.5187380853	-1.5932895639
O	0	1.3468797829	3.0996917500	-1.9928225865
H	0	-0.6485980332	2.9564398722	-1.5690370312

C39c

0 1

C	0	1.6524958558	0.3329285736	-1.1712905935
C	0	-0.7408497671	0.3297894132	-0.8731965816
C	0	-0.6052564525	-1.0000133136	-1.0034538008
C	0	-1.9743292844	1.0079006611	-0.3626966161
O	0	-2.0337688643	2.1761940768	-0.0643867869
O	0	-2.9893161886	0.1473815857	-0.2621618095
C	0	-4.2145793487	0.6731350363	0.2592643875
H	0	2.2439763184	0.6431643252	-2.0423062774
H	0	-1.3439782154	-1.7702307779	-0.7989598211
H	0	-4.5807185332	1.4937470165	-0.3746251908
H	0	-4.9250442149	-0.1610649233	0.2590549225
H	0	-4.0659765535	1.0545671635	1.2801268622
N	0	0.4065712761	1.0988814706	-1.1524675820
C	0	2.4955323350	0.4424369416	0.1238338345
C	0	3.8071454717	-0.3332929552	-0.0915992025
H	0	3.6250325462	-1.4015039722	-0.2655269230
H	0	4.3641975418	0.0745987640	-0.9505948170
H	0	4.4465780211	-0.2329864309	0.7986968510
C	0	2.8270717985	1.9295801401	0.3516205349
H	0	1.9231449737	2.5162480967	0.5714625838
H	0	3.5036910534	2.0185836692	1.2155687443
H	0	3.3153064379	2.3778981653	-0.5247295801
C	0	1.7383032258	-0.0891844462	1.3518487299
H	0	2.3553028425	0.0571017596	2.2515914977
H	0	0.7984150639	0.4634139523	1.5064804304
H	0	1.5137266328	-1.1599144085	1.2624761034
S	0	1.0294255609	-1.3814584043	-1.6059959776
O	0	1.6233487963	-2.4534929226	-0.7971743203
O	0	0.9986700886	-1.4954692112	-3.0663622305
C	0	0.3634178556	2.3352983325	-1.8002913353
O	0	1.3426483016	2.8710050725	-2.2568429023
H	0	-0.6555006049	2.7644615795	-1.8383901339

C248a

0 1

H	0	2.0874504758	-0.8953176987	2.5971226159
C	0	2.3087529599	-1.1572927660	1.5608343244
H	0	2.7063924616	-0.5332583722	-1.4487680971
C	0	3.0587176832	-0.4356465489	0.6968386561
C	0	1.8256486461	-2.3708019758	0.8868099015
H	0	4.1480914725	-1.4011965713	-0.9205322325
C	0	3.1102492883	-1.1523099125	-0.6245952267
H	0	3.5566188141	0.5134933944	0.8982925081
H	0	1.1979446827	-3.1308970704	1.3555626668
C	0	2.2822711169	-2.3853525373	-0.3868005259
H	0	2.0967183888	-3.1526279412	-1.1392786006

C248b

0 1

H	0	1.6612754489	-0.8732997826	2.6779474965
C	0	2.0543826452	-0.8861264894	1.6574926749
C	0	3.0006454305	-0.0079833983	1.2758429245
C	0	1.5088351165	-1.8581141177	0.7035768049
H	0	3.3814463975	0.7413197233	1.9762123507
H	0	0.6045166063	-2.4102031011	0.9745564790
C	0	2.1259645055	-2.0865612176	-0.4708731211
H	0	1.7406220940	-2.8376656750	-1.1668154715
C	0	3.4138465669	-1.3733160609	-0.8047039623
H	0	3.5473022733	-1.2903365664	-1.8948494250
H	0	4.2577952374	-1.9963653150	-0.4423149362
C	0	3.4847488895	0.0150436058	-0.1538048672
H	0	2.8483176370	0.7243243129	-0.7227019639
H	0	4.5096921614	0.4133790823	-0.2164779833

C251c

0 1

C	0	0.7269450000	-0.9965000000	0.0072420000
C	0	1.5409690000	0.0853810000	-0.0375380000
C	0	-0.7272250000	-0.9962500000	-0.0044710000
H	0	-1.1853910000	-1.9890570000	-0.0455050000
C	0	-1.5409700000	0.0859670000	0.0372570000
H	0	1.0847530000	1.0787370000	-0.1031210000
H	0	-1.0846570000	1.0794300000	0.1004420000
H	0	1.1846770000	-1.9893190000	0.0513300000
C	0	-3.0028180000	0.0907750000	0.0163090000
C	0	-3.6813490000	1.3235670000	0.1044450000
C	0	-3.7820540000	-1.0815370000	-0.0885800000
C	0	-5.0746590000	1.3873750000	0.0914360000
H	0	-3.0969760000	2.2440590000	0.1852490000
C	0	-5.1726460000	-1.0182720000	-0.1010050000
H	0	-3.2929200000	-2.0544540000	-0.1636240000
C	0	-5.8287030000	0.2158190000	-0.0109330000
H	0	-5.5742610000	2.3566670000	0.1615860000
H	0	-5.7541090000	-1.9399110000	-0.1832230000
H	0	-6.9201560000	0.2609650000	-0.0218040000
C	0	3.0028630000	0.0903410000	-0.0167210000
C	0	3.6810390000	1.3233800000	-0.1042520000
C	0	3.7825050000	-1.0817860000	0.0873080000
C	0	5.0743270000	1.3876470000	-0.0910990000
H	0	3.0963820000	2.2437340000	-0.1845570000
C	0	5.1730710000	-1.0180650000	0.0998790000
H	0	3.2937850000	-2.0549860000	0.1612450000
C	0	5.8287480000	0.2162920000	0.0106690000
H	0	5.5736060000	2.3571460000	-0.1606840000
H	0	5.7548220000	-1.9395860000	0.1813800000
H	0	6.9201860000	0.2617760000	0.0216040000

C251d

0 1

C	0	-1.4161940000	0.1556420000	-0.1004250000
C	0	-1.4847470000	1.5015780000	-0.0953730000
C	0	-2.5917280000	-0.7356710000	-0.1857960000
H	0	-0.5980450000	2.1298640000	-0.0110150000
H	0	-2.3625890000	-1.7302230000	-0.5833630000
C	0	-3.8401360000	-0.4403440000	0.1958340000
H	0	-4.6506920000	-1.1638460000	0.0790000000
H	0	-2.4494130000	1.9998220000	-0.1862130000
H	0	-4.0945470000	0.5252950000	0.6419360000
O	0	-0.2631490000	-0.5595350000	-0.0468390000
Si	0	1.3664520000	-0.0834160000	0.0211950000
C	0	2.2977390000	-1.7069260000	0.0404630000

H	0	2.0818840000	-2.2943290000	-0.8661790000
H	0	3.3857430000	-1.5353170000	0.0856670000
H	0	2.0107440000	-2.3132860000	0.9142900000
C	0	1.6817660000	0.8813580000	1.6015260000
H	0	1.1372260000	1.8373210000	1.6256590000
H	0	1.3684440000	0.2928320000	2.4789590000
H	0	2.7571910000	1.1013610000	1.7075630000
C	0	1.8016070000	0.9167490000	-1.5080480000
H	0	2.8795090000	1.1496580000	-1.5184240000
H	0	1.5703420000	0.3435990000	-2.4204220000
H	0	1.2492160000	1.8670370000	-1.5585580000

aa-PR1

0 1

H	0	1.0865406709	-2.4066164390	0.8536832496
C	0	1.1319440685	-1.3911842275	0.4573329570
H	0	2.4818639468	0.4783264578	-1.5075659259
C	0	2.5187336707	-0.7904602923	0.3645864034
C	0	1.4975320446	-0.2428785802	1.3474597076
H	0	3.3864502157	1.1450994161	-0.1063606104
C	0	2.5320488650	0.5220271122	-0.4080560021
C	0	0.0391458702	-1.0021424766	-0.5346592633
H	0	3.3870116173	-1.4236441202	0.5595730805
C	0	0.0133383247	0.5611924480	-0.4701269199
H	0	1.4797756163	-0.2326255846	2.4365170161
C	0	1.2417133495	0.9352403412	0.3674162046
H	0	1.2085925507	1.9579449831	0.7620038830
H	0	0.0754335294	1.0013341046	-1.4745946681
C	0	0.3674649054	-1.4350021657	-1.9767581054
O	0	1.4500213938	-1.7909547106	-2.3589733661
O	0	-0.6882509933	-1.2370922096	-2.7837750405
C	0	-0.5250988122	-1.6658490382	-4.1345093447
H	0	-1.4549731439	-1.4045367976	-4.6540383700
H	0	0.3335516336	-1.1640127860	-4.6045713014
H	0	-0.3613297261	-2.7533961782	-4.1660610711
N	0	-1.2824432629	-1.5103235573	-0.1420400770
C	0	-2.2568345284	-0.6162303898	0.4794799023
C	0	-1.6438346621	-2.7580855916	-0.5652627910
H	0	-3.1949002613	-0.6762815177	-0.0980255592
S	0	-1.5922299765	1.0854706828	0.2351609486
C	0	-2.6292503762	-0.9023797954	1.9702266996
H	0	-2.7211176643	-2.9774406881	-0.4091981823
O	0	-0.8805613352	-3.5515232936	-1.0801554478
C	0	-3.2613380014	-2.2990451751	2.1008333750
C	0	-3.6790074731	0.1436880097	2.3857340584
C	0	-1.4150820430	-0.8201584268	2.8983413257
H	0	-2.5355233842	-3.1021277525	1.9062709462
H	0	-3.6336074770	-2.4396503567	3.1274310057
H	0	-4.1170416082	-2.4284531174	1.4182325595
H	0	-4.0160933365	-0.0449615704	3.4164942944
H	0	-3.2670477824	1.1634059325	2.3479622177
H	0	-4.5648795221	0.1061831248	1.7303608517
H	0	-0.9455282522	0.1714939808	2.8465650715
H	0	-1.7252183428	-1.0036367280	3.9389411240
H	0	-0.6618761380	-1.5733465672	2.6298410343

aa-PR2

0 1

H	0	-3.8709311536	-1.3521854199	1.0972136735
C	0	-2.8233275360	-1.6360472898	1.0175580349
H	0	0.3796803124	-1.5188891305	2.0187945270
C	0	-1.6595600690	-0.7858085390	1.5146705441

C	0	-2.3091942612	-2.7079900284	0.3976266916
H	0	-0.9522448215	-2.5390182539	2.6617831681
C	0	-0.6319969139	-1.8950949311	1.8314780314
C	0	-0.9605538330	-0.1358697631	0.2650826594
H	0	-1.8901529353	-0.0469131622	2.2870962863
C	0	-0.4469917236	-1.3939887427	-0.5086995083
H	0	-2.8496734958	-3.4830474331	-0.1483251093
C	0	-0.7941569624	-2.5751869871	0.4579933865
H	0	-0.2077452005	-3.4816654853	0.2615944176
H	0	-0.9579962977	-1.5088118098	-1.4723918016
C	0	-1.8180125738	0.7380878110	-0.6634521591
O	0	-1.3279101755	1.4257929616	-1.5265838633
O	0	-3.1302387180	0.6301646415	-0.4574474236
C	0	-3.9628694175	1.4431179060	-1.2847183099
H	0	-3.7384198972	2.5068894176	-1.1187682399
H	0	-4.9954246837	1.2186050291	-0.9919502517
H	0	-3.8025670329	1.2100952361	-2.3477255766
N	0	0.2018055639	0.6864101981	0.6554015717
C	0	1.4686487113	0.4931415535	-0.0724420264
C	0	-0.1167479973	1.9089848911	1.1915557345
H	0	1.5170580379	1.2200344308	-0.9006923626
S	0	1.3297227643	-1.1823043244	-0.8381367785
C	0	2.8002692504	0.6031362803	0.7427847049
H	0	0.7417149858	2.5981921068	1.2787544975
O	0	-1.2389052356	2.2263957785	1.5370687597
C	0	3.9434222939	0.1790879573	-0.2031778917
C	0	3.0972080979	2.0546356533	1.1742007713
C	0	2.7893308970	-0.2971327245	1.9834100450
H	0	3.8590781693	-0.8755228689	-0.5034013647
H	0	4.9128016754	0.3043846797	0.3026159371
H	0	3.9568866462	0.7969392086	-1.1157056273
H	0	4.1499562765	2.1319014786	1.4871314274
H	0	2.4909341269	2.3753642228	2.0322199450
H	0	2.9436510204	2.7674510957	0.3480390751
H	0	1.9831629419	-0.0092713118	2.6743982602
H	0	3.7449604772	-0.2060945204	2.5228803999
H	0	2.6497053964	-1.3513869721	1.7066358746

aa-PR3

0 1

H	0	0.4546564531	-1.1548128765	2.1057467709
C	0	0.7016517193	-0.4275874988	1.3315754908
H	0	2.5760830645	0.7285754583	-1.2084386707
C	0	1.5032145890	-0.7402489420	0.0769385088
C	0	0.2780869844	0.8407238743	1.2404679085
H	0	2.8424496168	0.9435084336	0.5582580089
C	0	2.1202173085	0.6430204763	-0.2128619673
C	0	0.4690086568	-0.8318932661	-1.1339368340
H	0	2.1630781757	-1.6085446907	0.1106364005
C	0	-0.0652090259	0.6483120360	-1.1903316453
H	0	-0.3925393327	1.3674899932	1.9210970183
C	0	0.7737143402	1.3817824400	-0.0910716120
H	0	0.7766444744	2.4730860953	-0.2089859455
H	0	-1.1392864469	0.6974482691	-0.9878084856
C	0	-0.5839119118	-1.9113997641	-0.8678859145
O	0	-0.5055712112	-3.0434179770	-1.2741931629
O	0	-1.5973014579	-1.4728580150	-0.1059384929
C	0	-2.5847068260	-2.4423804191	0.2461232791
H	0	-2.1269998960	-3.2830723449	0.7878004402
H	0	-3.3090959863	-1.9214942813	0.8833278042
H	0	-3.0785287099	-2.8363321540	-0.6547289767
N	0	1.1145881302	-1.1155019802	-2.4173880977
C	0	0.6464929209	-0.3438672493	-3.5598150281

C	0	2.1503805910	-2.0035707984	-2.5760036623
H	0	1.4994415675	-0.2183522639	-4.2437687965
S	0	0.2819561529	1.3221549361	-2.8636991357
C	0	-0.5177111872	-0.9453788364	-4.4104383391
H	0	2.5275146427	-1.9911906968	-3.6255281502
O	0	2.6397617175	-2.7121980491	-1.7260753560
C	0	-1.8768709072	-0.9240480142	-3.6956462167
C	0	-0.1630079907	-2.3937639416	-4.7853583537
C	0	-0.6165685792	-0.0904327533	-5.6854903842
H	0	-2.1240092853	0.0863458797	-3.3394507699
H	0	-2.6652767920	-1.2383911366	-4.3971989910
H	0	-1.9081523339	-1.6217364617	-2.8506510597
H	0	-0.9327122973	-2.8056279139	-5.4567437151
H	0	0.8010306417	-2.4510467037	-5.3164302321
H	0	-0.1112508150	-3.0351721372	-3.8937438388
H	0	0.3306130171	-0.0993053449	-6.2495726125
H	0	-1.4054014930	-0.4791122640	-6.3475091466
H	0	-0.8616715387	0.9554690429	-5.4433839966

aa-PR4

0 1

H	0	1.5520519564	-2.0955843014	-1.8627358674
C	0	1.5978114320	-1.2137625835	-1.2247176585
H	0	2.1139043207	0.3009689493	1.7338071732
C	0	1.4287230033	-1.2471740190	0.2824494008
C	0	1.6734796173	0.0733353343	-1.5935307476
H	0	3.3267025633	-0.1476577921	0.4799087514
C	0	2.2571717629	-0.0080988175	0.6901770419
C	0	-0.0480259827	-0.7085322017	0.5741835661
H	0	1.6346707521	-2.2017231175	0.7734350794
C	0	0.0929423300	0.8028466227	0.1865989921
H	0	1.7055239589	0.4694853775	-2.6084382096
C	0	1.5632595000	0.9153466082	-0.3319258976
H	0	1.9165589432	1.9522205925	-0.4018545830
H	0	-0.0415163565	1.4284440364	1.0768835500
C	0	-0.3214506938	-0.8866851381	2.0699189888
O	0	0.0943475076	-0.1514735936	2.9339730472
O	0	-1.0275497939	-1.9937671951	2.3237847013
C	0	-1.2620982827	-2.2942724032	3.6994591930
H	0	-1.8061215746	-3.2457463443	3.7130086449
H	0	-1.8608370697	-1.5004606776	4.1713986778
H	0	-0.3107036633	-2.3850852549	4.2434429119
N	0	-1.0922020899	-1.2971031914	-0.2573198507
C	0	-2.0826492975	-0.3846105827	-0.8119143447
C	0	-1.0758506928	-2.6131735877	-0.6364082215
H	0	-2.3513298473	-0.7548112674	-1.8134446461
S	0	-1.1799719611	1.2052990135	-1.0642656282
C	0	-3.4174520986	-0.2272613630	-0.0186159030
H	0	-1.8822124066	-2.8367017016	-1.3729950920
O	0	-0.2936479100	-3.4553734513	-0.2536668472
C	0	-4.3658071211	0.6092325033	-0.8936877615
C	0	-4.0277046749	-1.6201270821	0.2084722182
C	0	-3.2328335166	0.4719662738	1.3348272363
H	0	-3.9573343648	1.6161214792	-1.0696812555
H	0	-5.3436591963	0.7210264439	-0.4006247836
H	0	-4.5352656860	0.1312796364	-1.8726997614
H	0	-5.0072834934	-1.5253634060	0.7026339325
H	0	-3.3831627070	-2.2380750453	0.8502752454
H	0	-4.1878631809	-2.1542979582	-0.7421761761
H	0	-2.6630039724	-0.1474904740	2.0378082251
H	0	-4.2160490228	0.6597069872	1.7937308591
H	0	-2.7222625004	1.4384980718	1.2181163087

aa-TS1

0 1

H	0	1.6013965841	-2.0680893222	1.7552826824
C	0	1.8185753970	-1.1753400187	1.1692733233
H	0	2.3290502574	0.5172318416	-1.5944469594
C	0	2.1116696526	-1.1647157181	-0.1960590647
C	0	1.7100567646	0.1494721075	1.6222423169
H	0	3.6506715334	0.2840302433	-0.4195157260
C	0	2.5524838013	0.2230652444	-0.5620785308
C	0	-0.1140027739	-0.4909837058	-0.8351824085
H	0	2.2800418419	-2.0509412993	-0.8039497934
C	0	-0.0324512377	0.8435117814	-0.3807173666
H	0	1.3998686158	0.4503435169	2.6230699730
C	0	1.8814455832	1.0224088045	0.5282901589
H	0	2.0012637101	2.1031846093	0.6344479920
H	0	0.1469914906	1.6318316747	-1.1123692401
C	0	0.0378726068	-0.7707511376	-2.2802392560
O	0	0.7757765051	-0.1612745090	-3.0294737290
O	0	-0.7720635350	-1.7580345366	-2.6987656375
C	0	-0.6348171783	-2.1453292435	-4.0614621035
H	0	-1.3515088989	-2.9602328099	-4.2204460831
H	0	-0.8536971225	-1.3028914501	-4.7350631260
H	0	0.3885723810	-2.4954801818	-4.2641411249
N	0	-0.9920606751	-1.2885521521	-0.0376916787
C	0	-2.0738941992	-0.5011880190	0.5745532417
C	0	-0.8220574094	-2.6482517173	0.0586756125
H	0	-2.8536672046	-0.3298803834	-0.1887605274
S	0	-1.2735761181	1.1644088079	0.8622854287
C	0	-2.7788207747	-1.0134882576	1.8613249923
H	0	-1.6086090383	-3.1404841057	0.6566449573
O	0	0.0879243756	-3.2740017448	-0.4433559354
C	0	-3.7864297621	-2.1366651675	1.5333413219
C	0	-3.6154899766	0.1611878193	2.4168573605
C	0	-1.7748256799	-1.4554336290	2.9366360111
H	0	-3.3202399799	-3.0746840869	1.2065585864
H	0	-4.3807530428	-2.3686492697	2.4305627920
H	0	-4.4848896828	-1.8166061813	0.7439185540
H	0	-4.2350024972	-0.1901468272	3.2556904154
H	0	-2.9795995987	0.9761857336	2.7923190677
H	0	-4.2893004412	0.5743762635	1.6494549359
H	0	-1.0509134207	-0.6532066147	3.1390645217
H	0	-2.3073888921	-1.6869134985	3.8721685630
H	0	-1.2095078006	-2.3516563908	2.6467713627

aa-TS2

0 1

H	0	-3.4223588284	-1.0973583536	1.9460112128
C	0	-2.5134542706	-1.5283238476	1.5258192819
H	0	0.7206646704	-1.8962717239	1.1314054893
C	0	-1.2237463308	-1.2852235750	1.9907730818
C	0	-2.4408833712	-2.2830316513	0.3441261125
H	0	-0.2699116719	-3.1843127151	1.8445233931
C	0	-0.3048786507	-2.2285284856	1.2837923800
C	0	-0.7133620263	0.3364962442	-0.0904112682
H	0	-0.9668578353	-0.6882025107	2.8652088011
C	0	-0.5011501165	-0.8047259905	-0.9139533995
H	0	-3.2901649751	-2.5553765031	-0.2829476855
C	0	-1.0703456691	-2.4602477412	0.0015564297
H	0	-0.7511135044	-3.2233555645	-0.7135993030
H	0	-1.1491747391	-0.9495445157	-1.7787816061
C	0	-2.0436822668	0.9084287869	0.2137048116
O	0	-2.3209545018	1.6485327978	1.1262083555

O	0	-2.9653263711	0.4368012661	-0.6660741610
C	0	-4.2962050570	0.8943879802	-0.4552396472
H	0	-4.6646007553	0.5976047034	0.5389627728
H	0	-4.9083889052	0.4345650685	-1.2411511612
H	0	-4.3413609923	1.9912170657	-0.5246591884
N	0	0.4103408077	1.2103921058	0.0232602381
C	0	1.7036613633	0.6179993827	-0.3418427444
C	0	0.2490757034	2.5460764493	-0.3734157972
H	0	2.1644639872	1.2641909453	-1.1033484385
S	0	1.2598918880	-0.9456039328	-1.2716997730
C	0	2.7776138356	0.5069824963	0.7788622412
H	0	1.2267440704	3.0749785602	-0.3983537482
O	0	-0.7872971048	3.0824700419	-0.6697544158
C	0	4.0109081642	-0.1907315739	0.1848196251
C	0	3.1611520482	1.9454611167	1.1815577608
C	0	2.3143839050	-0.2282115618	2.0395890639
H	0	3.7756379915	-1.2235828892	-0.1147332578
H	0	4.8230039453	-0.2295636114	0.9272044686
H	0	4.3911018737	0.3455795620	-0.7003151448
H	0	3.9890443005	1.9224381664	1.9067083865
H	0	2.3163647798	2.4677421844	1.6551141184
H	0	3.4945484061	2.5382024995	0.3144917858
H	0	1.3277435573	0.1281327526	2.3679332648
H	0	3.0304180463	-0.0463326023	2.8558692770
H	0	2.2728313597	-1.3135679766	1.8871484976

aa-TS3

0 1

H	0	0.4322340020	-1.0622294840	2.2597306160
C	0	0.7988771381	-0.3831179867	1.4898896183
H	0	2.3686104639	0.4519439843	-1.2772535821
C	0	1.7075234805	-0.7188680762	0.4842997014
C	0	0.3302143792	0.9194486666	1.2690942660
H	0	2.9665373822	0.9890516912	0.3049630297
C	0	2.0955503763	0.5477409310	-0.2190555889
C	0	0.0673186499	-0.8749966236	-1.3569879222
H	0	2.2436407849	-1.6598953405	0.3891696044
C	0	-0.2987724097	0.4969989300	-1.3519825637
H	0	-0.4532974203	1.4134311736	1.8460252858
C	0	0.8838746317	1.4076499597	0.0609743053
H	0	0.8344714915	2.4584078537	-0.2355399735
H	0	-1.2741229542	0.7764963784	-0.9582120428
C	0	-0.7837166179	-1.9230465032	-0.7762480754
O	0	-0.8097326877	-3.0820469465	-1.1249813253
O	0	-1.5926529737	-1.4268880665	0.1935793092
C	0	-2.4332322294	-2.3751617315	0.8403896932
H	0	-1.8355871897	-3.1512103669	1.3431318061
H	0	-3.0211637748	-1.8125075912	1.5763752046
H	0	-3.0988403564	-2.8702692453	0.1172614001
N	0	0.8501822663	-1.2185058753	-2.4976606301
C	0	0.6065679536	-0.3724721329	-3.6609888279
C	0	1.8724772332	-2.1405553275	-2.4965522351
H	0	1.5520185923	-0.2341473675	-4.2066236244
S	0	0.1652739863	1.2717054819	-2.9111297825
C	0	-0.4548849340	-0.9111449605	-4.6606691843
H	0	2.3795406320	-2.1822229751	-3.4882384066
O	0	2.2153398491	-2.8241275699	-1.5602290639
C	0	-1.8290910946	-1.0968463170	-4.0024528260
C	0	0.0294671956	-2.2708148295	-5.1939172126
C	0	-0.5559881223	0.0880497950	-5.8234833303
H	0	-2.1882557175	-0.1582816166	-3.5555603619
H	0	-2.5627484418	-1.4136352472	-4.7602742548
H	0	-1.7957783780	-1.8747433497	-3.2273346561

H	0	-0.6694256804	-2.6420691865	-5.9594111616
H	0	1.0248626340	-2.1948778894	-5.6617279474
H	0	0.0740605386	-3.0219886466	-4.3917773686
H	0	0.4195452193	0.2301402162	-6.3177687835
H	0	-1.2649887975	-0.2794091701	-6.5811061359
H	0	-0.9111083305	1.0701935119	-5.4758229123

aa-TS4

0 1

H	0	1.4485806307	-2.1582961360	-1.7809750246
C	0	1.6766399945	-1.2983300022	-1.1519174226
H	0	2.1240467608	0.2718240329	1.6966033557
C	0	1.8839628677	-1.3500617616	0.2284389359
C	0	1.6760109813	0.0430970549	-1.5632735631
H	0	3.4928172684	-0.0089632669	0.5887351639
C	0	2.3867706433	-0.0059603861	0.6688937432
C	0	-0.3406270969	-0.5144846292	0.7656579453
H	0	1.9575162221	-2.2651512923	0.8130079373
C	0	-0.1250851358	0.8197935197	0.3455601771
H	0	1.4427030140	0.3945597050	-2.5684218426
C	0	1.8292136624	0.8696851069	-0.4280429925
H	0	2.0341630075	1.9410599853	-0.4927617315
H	0	0.0571104204	1.5797366824	1.1067012566
C	0	-0.2541554766	-0.8668107246	2.1943892833
O	0	0.4395469079	-0.2929115862	3.0116269646
O	0	-1.0640957816	-1.8924783859	2.5184629919
C	0	-0.9964661085	-2.3420045444	3.8676629887
H	0	-1.6883716590	-3.1896908382	3.9405024871
H	0	-1.2921756565	-1.5424411603	4.5637720683
H	0	0.0256016604	-2.6620280952	4.1196644103
N	0	-1.2277242195	-1.2117230043	-0.1033156756
C	0	-2.1644642566	-0.3524289461	-0.8213301648
C	0	-1.1153633962	-2.5473640919	-0.4090435721
H	0	-2.2991477710	-0.7465840679	-1.8399213868
S	0	-1.2581008235	1.2622094649	-0.9745885337
C	0	-3.5678495628	-0.2139721456	-0.1648915335
H	0	-1.8424481158	-2.8457836594	-1.1990948172
O	0	-0.3327784370	-3.3255716568	0.0873178043
C	0	-4.4207318626	0.6956427813	-1.0628163471
C	0	-4.2144409047	-1.6082314623	-0.0933901015
C	0	-3.4839967626	0.3712669909	1.2513416885
H	0	-3.9926746225	1.7076601707	-1.1259012567
H	0	-5.4402876226	0.7844970740	-0.6572876338
H	0	-4.5001699937	0.2908245767	-2.0855200957
H	0	-5.2398599813	-1.5252444720	0.2990762780
H	0	-3.6546786619	-2.2768527232	0.5769624318
H	0	-4.2765948515	-2.0809239184	-1.0873783358
H	0	-2.9353062223	-0.3015883315	1.9242592583
H	0	-4.4979055934	0.5028819867	1.6608002038
H	0	-2.9878849844	1.3525075057	1.2480251571

ab-PR1

0 1

H	0	1.8601605996	-2.2027262834	0.6781980782
C	0	1.7012112567	-1.2124994538	0.2547325602
H	0	2.2506621156	0.6256120718	-2.0903912314
C	0	2.9436461310	-0.5344625075	-0.2781069835
C	0	2.2298477573	0.0052260265	0.9536325882
H	0	3.4833931281	1.4227979012	-1.0526303168
C	0	2.6269083864	0.7334550147	-1.0622392486
C	0	0.3346404186	-0.9407665650	-0.3792808100
H	0	3.8748178889	-1.1021801468	-0.3371288732

C	0	0.2131941994	0.6032520635	-0.2866352014
H	0	2.5333075131	0.0722184720	1.9989152780
C	0	1.6102929931	1.1116806345	0.0554013940
H	0	1.6182173322	2.1538963300	0.3993667058
H	0	-0.2578018889	1.0844978597	-1.1563323628
C	0	0.2316046671	-1.4191950687	-1.8365535273
O	0	1.1587053757	-1.5755792670	-2.5855385270
O	0	-1.0548211892	-1.5673235247	-2.1990151861
C	0	-1.2807492526	-2.0226356768	-3.5338277053
H	0	-2.3688340589	-2.0650380138	-3.6623682572
H	0	-0.8327793735	-1.3305205606	-4.2620177737
H	0	-0.8377741885	-3.0192901577	-3.6758423935
N	0	-0.7651536027	-1.5225907621	0.4240654124
C	0	-1.8675279147	-0.6169947225	0.7162286456
C	0	-0.8135044889	-2.8915691298	0.4617476460
H	0	-2.4200489877	-0.3602384104	-0.2061045816
S	0	-0.9591191144	0.9893920271	1.0962384735
C	0	-2.8761558915	-0.9765806024	1.8379835797
H	0	-1.6612631441	-3.3012567178	1.0378064300
O	0	0.0098251605	-3.6034136476	-0.0789929701
O	0	-1.8041240063	2.1483540096	0.6228368807
C	0	-3.9052627796	-2.0115701262	1.3341675900
C	0	-3.6831496697	0.2943482753	2.1888843394
C	0	-2.1571942868	-1.4642007202	3.1062972662
H	0	-3.4754854248	-2.9921002911	1.0929958048
H	0	-4.6710640822	-2.1744107863	2.1083255313
H	0	-4.4154208255	-1.6389323216	0.4322178113
H	0	-4.5011103795	0.0210403073	2.8722869561
H	0	-3.0712824342	1.0593913359	2.6862153771
H	0	-4.1169232557	0.7619875915	1.2930976296
H	0	-1.3981368351	-0.7339268859	3.4264855660
H	0	-2.8825841947	-1.5786055983	3.9262628106
H	0	-1.6548734937	-2.4318795228	2.9718642847

ab-PR2

0 1

H	0	3.8718855496	-1.0254771740	-0.8854757406
C	0	2.8983593091	-1.4619975510	-0.6724120868
H	0	-0.2924493341	-2.1497696116	-1.4765094186
C	0	1.5851813073	-0.9698441382	-1.2707551802
C	0	2.6077145329	-2.4274007228	0.2109273040
H	0	1.1958456612	-3.0361794512	-1.9563319388
C	0	0.7797293385	-2.2872323158	-1.2693262909
C	0	0.8231906212	-0.1817626443	-0.1380335075
H	0	1.6595778525	-0.4031782887	-2.2012210544
C	0	0.5147617086	-1.3207197042	0.8839451572
H	0	3.2923992091	-2.9472893663	0.8824989728
C	0	1.0960759191	-2.5944452164	0.2106133811
H	0	0.7050428877	-3.5273083743	0.6376575433
H	0	0.8690023666	-1.1320006504	1.9049740241
C	0	1.5602904155	0.9960051017	0.5157787763
O	0	1.0144651536	1.7342526198	1.3015093522
O	0	2.8314163801	1.1234880215	0.1423850405
C	0	3.5407352552	2.2358904702	0.6914626522
H	0	3.0702541497	3.1783146552	0.3755659935
H	0	4.5625426349	2.1674356897	0.3002787689
H	0	3.5416995537	2.1916407168	1.7903319666
N	0	-0.4827436117	0.3509092281	-0.5961681657
C	0	-1.5547574346	0.2477045840	0.3948393942
C	0	-0.4333160290	1.3068788341	-1.5824571403
H	0	-1.3175704994	0.8741341377	1.2721056681
C	0	-3.0259843698	0.4838795174	-0.0367840250
H	0	-1.4237785970	1.6905466499	-1.8824224296

O	0	0.5943604262	1.6908033538	-2.1036239310
C	0	-3.9470683818	-0.0479708646	1.0857776592
C	0	-3.3285782864	1.9940728124	-0.1532877470
C	0	-3.3602446095	-0.2625279111	-1.3378239994
H	0	-3.9178787259	-1.1432372264	1.1719469806
H	0	-4.9851671388	0.2416908791	0.8639252779
H	0	-3.6701159041	0.3617717303	2.0676928986
H	0	-4.4063273715	2.1390285804	-0.3257556325
H	0	-2.8012292087	2.4978609903	-0.9731173711
H	0	-3.0652491302	2.5120983626	0.7817748533
H	0	-2.8063829334	0.1190065571	-2.2068615186
H	0	-4.4340759599	-0.1663076179	-1.5602345934
H	0	-3.1327293254	-1.3353041255	-1.2382703837
S	0	-1.3215504719	-1.4803920275	1.0993372304
O	0	-1.6072110791	-1.4107968697	2.5798211101

ab-PR3

0 1

H	0	0.4581130970	-1.1699423332	2.1030365241
C	0	0.7014047064	-0.4491148518	1.3217638957
H	0	2.5936674146	0.7188546071	-1.2034450091
C	0	1.5137929120	-0.7644423184	0.0747647847
C	0	0.2719681868	0.8171059432	1.2203443264
H	0	2.8387595525	0.9230575033	0.5684797279
C	0	2.1318536497	0.6173184483	-0.2147133813
C	0	0.4885755311	-0.8553930095	-1.1445075207
H	0	2.1740370370	-1.6323104781	0.1137921101
C	0	-0.0471568212	0.6136654385	-1.1963719825
H	0	-0.4046625992	1.3454063604	1.8939086963
C	0	0.7824466256	1.3588533397	-0.1060577207
H	0	0.7958185408	2.4473739767	-0.2351215694
H	0	-1.1287291476	0.6834033521	-1.0404780376
C	0	-0.5547439257	-1.9463105304	-0.8928439802
O	0	-0.4616818876	-3.0764379350	-1.3010263773
O	0	-1.5807613164	-1.5178091050	-0.1412750114
C	0	-2.5577868678	-2.4996880954	0.2088987382
H	0	-2.0931129644	-3.3255048035	0.7671119288
H	0	-3.2990719371	-1.9833772736	0.8299992698
H	0	-3.0313948590	-2.9126006600	-0.6942840059
N	0	1.1407744609	-1.1099185118	-2.4326515736
C	0	0.6400470211	-0.3539916833	-3.5619784744
C	0	2.2060497617	-1.9647565248	-2.6054330588
H	0	1.4749317811	-0.1671526131	-4.2523413377
S	0	0.2911588405	1.3602426728	-2.8884692117
C	0	-0.5554790679	-0.9270233151	-4.3772537217
H	0	2.5782157056	-1.9257830224	-3.6563855795
O	0	2.7143222153	-2.6685888759	-1.7651191459
O	0	1.6248299201	2.0716106866	-2.8399257703
C	0	-1.9080388997	-0.7718512812	-3.6588714154
C	0	-0.2948974677	-2.4129064098	-4.6695386005
C	0	-0.6106559662	-0.1405276792	-5.6993063166
H	0	-2.1331141766	0.2831079461	-3.4370129479
H	0	-2.7136192309	-1.1475491218	-4.3083206850
H	0	-1.9589961038	-1.3419846709	-2.7243295677
H	0	-1.0952805469	-2.8115059362	-5.3126773040
H	0	0.6590065843	-2.5544220063	-5.2023796228
H	0	-0.2679259090	-3.0055712224	-3.7445879239
H	0	0.3217102903	-0.2615040696	-6.2733511839
H	0	-1.4416135762	-0.5012126396	-6.3245673209
H	0	-0.7646407933	0.9361369026	-5.5250370937

ab-PR4

0 1

H	0	1.6167940093	-2.1193772781	-1.8240665305
C	0	1.6306437759	-1.2286436331	-1.1977479430
H	0	2.0853388995	0.3291128914	1.7463886473
C	0	1.4338037303	-1.2451312144	0.3035665485
C	0	1.6884202190	0.0538912422	-1.5855450571
H	0	3.3111016830	-0.1126508583	0.5004753321
C	0	2.2387986099	0.0114795461	0.7063473486
C	0	-0.0554667805	-0.7187627875	0.5762611801
H	0	1.6443037093	-2.1894165874	0.8129733962
C	0	0.0831453299	0.7834263171	0.2014378655
H	0	1.7402306767	0.4423207967	-2.5991381677
C	0	1.5422609086	0.9152189736	-0.3367760702
H	0	1.8790400204	1.9557816991	-0.4192562254
H	0	-0.0665598357	1.4209657836	1.0819525480
C	0	-0.3530633846	-0.9135649644	2.0642533931
O	0	0.0336023808	-0.1742043570	2.9387247244
O	0	-1.0457464320	-2.0326129836	2.2979675582
C	0	-1.2932417766	-2.3525867322	3.6678093904
H	0	-1.8260234390	-3.3104001600	3.6631718696
H	0	-1.9062468324	-1.5716845197	4.1427888832
H	0	-0.3469449916	-2.4393932659	4.2210708031
N	0	-1.0868272804	-1.2899980616	-0.2842760526
C	0	-2.0836988897	-0.3726482444	-0.8000602992
C	0	-1.0656078258	-2.5981418121	-0.6980296322
H	0	-2.3251961530	-0.6539689645	-1.8355372093
S	0	-1.2163536676	1.2837078600	-1.0385284604
C	0	-3.4071501775	-0.2130665222	0.0013466183
H	0	-1.8620954168	-2.7998871232	-1.4518631666
O	0	-0.2899650272	-3.4475001445	-0.3222000950
O	0	-0.6121842323	1.2703493117	-2.4221769328
C	0	-4.3931895288	0.5580974167	-0.8935818574
C	0	-3.9786962031	-1.6052713141	0.3115802725
C	0	-3.2129997345	0.5597178220	1.3175077913
H	0	-4.0155313298	1.5613010692	-1.1450163431
H	0	-5.3581765689	0.6829412239	-0.3789546482
H	0	-4.5795439990	0.0199000224	-1.8365575718
H	0	-4.9447308752	-1.5057698542	0.8310570720
H	0	-3.2994559226	-2.1788617896	0.9577754540
H	0	-4.1544710969	-2.1838158918	-0.6092605180
H	0	-2.5854556973	0.0138064440	2.0318183634
H	0	-4.1888960391	0.7187088301	1.8016255039
H	0	-2.7669117847	1.5520542140	1.1487788169

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0 1

H	0	1.6249244920	-2.0884549277	1.7345133474
C	0	1.8215827562	-1.1848088904	1.1580811570
H	0	2.3242985516	0.5358730120	-1.5823729559
C	0	2.1622506435	-1.1557896201	-0.1897210482
C	0	1.6523113977	0.1350778415	1.6200623565
H	0	3.6324513164	0.3650494861	-0.3804433082
C	0	2.5415758189	0.2501153961	-0.5462240647
C	0	-0.1499260681	-0.4912830871	-0.8761081296
H	0	2.3639422731	-2.0298718440	-0.8049969643
C	0	-0.0355574619	0.8305136663	-0.4326149808
H	0	1.3275004811	0.4211042399	2.6209133670
C	0	1.8219051551	1.0211405331	0.5348926265
H	0	1.9077498154	2.1039871013	0.6524968583
H	0	0.0966274917	1.6535740877	-1.1366940579
C	0	0.0237766809	-0.8096213061	-2.3114104695
O	0	0.7848050604	-0.2228541057	-3.0539637996
O	0	-0.7954270501	-1.7893521590	-2.7200615612

C	0	-0.6531349602	-2.2021773519	-4.0761329404
H	0	-1.3839672449	-3.0054789296	-4.2281313548
H	0	-0.8503443023	-1.3661214044	-4.7637873824
H	0	0.3654872006	-2.5746665354	-4.2616842993
N	0	-0.9875739424	-1.2926329785	-0.0429000475
C	0	-2.0374155406	-0.5010289163	0.5953905263
C	0	-0.7916563562	-2.6512160439	0.0647472348
H	0	-2.7779364043	-0.1861705946	-0.1620035181
S	0	-1.2325164734	1.2091165274	0.9000238524
C	0	-2.7681955804	-1.0084017918	1.8578378642
H	0	-1.5541086919	-3.1491877420	0.6888625482
O	0	0.1173062326	-3.2618177473	-0.4549365786
O	0	-2.2258936654	2.2086558778	0.3597316833
C	0	-3.7833923901	-2.1151063588	1.4983935974
C	0	-3.5959698909	0.1694527084	2.4233915010
C	0	-1.7821736738	-1.4751262596	2.9414278285
H	0	-3.3235762482	-3.0407146076	1.1291341414
H	0	-4.3717221025	-2.3780320235	2.3911751789
H	0	-4.4842565969	-1.7585734667	0.7276440797
H	0	-4.2423402122	-0.1986853320	3.2341594790
H	0	-2.9605004008	0.9635426109	2.8414729818
H	0	-4.2302858434	0.6294532625	1.6517962716
H	0	-1.0614393819	-0.6771728852	3.1761138582
H	0	-2.3292974231	-1.7183139930	3.8652472294
H	0	-1.2115973012	-2.3673329689	2.6499266121

ab-TS2

0 1

H	0	-3.2309301907	-1.2971984130	1.9292321674
C	0	-2.3235592887	-1.6569624570	1.4437956480
H	0	0.9101185061	-1.8440298660	0.8869881768
C	0	-1.0287691792	-1.3481218319	1.8466240001
C	0	-2.2763643768	-2.3771148199	0.2372289158
H	0	0.0103639074	-3.1885023097	1.5990044402
C	0	-0.0990317491	-2.2236894964	1.0639662527
C	0	-0.7472113549	0.3783818030	-0.1283926538
H	0	-0.7591191332	-0.7756604166	2.7322918320
C	0	-0.5351824637	-0.6885719146	-1.0280966317
H	0	-3.1413462834	-2.6753535790	-0.3552223086
C	0	-0.9249879051	-2.4705895642	-0.1789729884
H	0	-0.5951055126	-3.1649588341	-0.9557088263
H	0	-1.1787917827	-0.8439424663	-1.8950390217
C	0	-2.0804661866	0.9011500002	0.2629076422
O	0	-2.3218618982	1.5806205837	1.2301923444
O	0	-3.0276685455	0.4501539206	-0.5914365540
C	0	-4.3593544091	0.8630069770	-0.3003679006
H	0	-4.6727244842	0.5100002032	0.6943617380
H	0	-4.9945957249	0.4240815326	-1.0794408454
H	0	-4.4334716048	1.9602148294	-0.3160857797
N	0	0.3621118108	1.2588180397	0.0499037153
C	0	1.6464935252	0.6726143509	-0.2972209434
C	0	0.1877078754	2.6046060599	-0.3065051071
H	0	2.1268477389	1.2889420749	-1.0705833261
S	0	1.2429291410	-0.8049749626	-1.4637058523
C	0	2.6849119606	0.4969440225	0.8511478968
H	0	1.1601809630	3.1451301546	-0.3059789063
O	0	-0.8571335155	3.1305422130	-0.5884013874
O	0	1.4175877875	-0.2551056143	-2.8575442198
C	0	3.7356518895	-0.5457773897	0.4393498300
C	0	3.3831477843	1.8670911454	1.0040104069
C	0	2.0667070238	0.1467799061	2.2125447149
H	0	3.3116065202	-1.5601303464	0.3974681603
H	0	4.5650651463	-0.5563812094	1.1631467757

H	0	4.1581639018	-0.3192000446	-0.5534124653
H	0	4.1736222481	1.8067159135	1.7678941489
H	0	2.6727873534	2.6446571904	1.3243513031
H	0	3.8464921477	2.1909373308	0.0587832365
H	0	1.1841297059	0.7710683442	2.4133138814
H	0	2.8052845025	0.3321297330	3.0072201342
H	0	1.7753370395	-0.9065352928	2.2894904663

ab-TS3

0 1

H	0	0.4344360543	-0.9876518781	2.2887824291
C	0	0.8040224488	-0.3396472107	1.4938640468
H	0	2.3824925398	0.4069680988	-1.2936354012
C	0	1.7244078338	-0.7092523593	0.5156788034
C	0	0.3495650646	0.9642410958	1.2347269245
H	0	2.9893854929	0.9779674996	0.2615553240
C	0	2.1118408349	0.5225792607	-0.2396453084
C	0	0.0268745431	-0.8974803381	-1.3648333368
H	0	2.2509494998	-1.6583828371	0.4525342032
C	0	-0.3253708848	0.4651025407	-1.3172935037
H	0	-0.4306626271	1.4820775148	1.7949353802
C	0	0.9225859464	1.4176378615	0.0247722023
H	0	0.8949097135	2.4496002940	-0.3267388925
H	0	-1.2932017238	0.7579796227	-0.9130816656
C	0	-0.7986657345	-1.9696985120	-0.7854775425
O	0	-0.8221800296	-3.1181416163	-1.1670037032
O	0	-1.5898942285	-1.5041737121	0.2106228566
C	0	-2.4224794105	-2.4713033440	0.8414441428
H	0	-1.8174094463	-3.2633389440	1.3087234629
H	0	-2.9963748222	-1.9309658159	1.6045173786
H	0	-3.1012616787	-2.9418638754	0.1141398861
N	0	0.8345259104	-1.2225629885	-2.4919894810
C	0	0.5919699745	-0.3727671144	-3.6418442090
C	0	1.8751151002	-2.1263575863	-2.4779443084
H	0	1.5350565338	-0.1403090448	-4.1579236508
S	0	0.0972620111	1.3051218930	-2.9159484955
C	0	-0.4549744710	-0.8985647810	-4.6561767070
H	0	2.3968905403	-2.1554826491	-3.4621971982
O	0	2.2119755907	-2.8045333236	-1.5365561011
O	0	1.3689039403	2.1132988688	-2.7811160097
C	0	-1.8509928357	-1.0264264782	-4.0236434049
C	0	-0.0083467666	-2.2854793169	-5.1488786872
C	0	-0.4994368711	0.0780893937	-5.8428967356
H	0	-2.2095891960	-0.0659735826	-3.6214479758
H	0	-2.5734327567	-1.3557066408	-4.7866380889
H	0	-1.8555619887	-1.7729202930	-3.2179800565
H	0	-0.7073594392	-2.6503808401	-5.9174964077
H	0	0.9963903730	-2.2516976098	-5.6001751787
H	0	-0.0014735599	-3.0161654875	-4.3270772185
H	0	0.4899443506	0.1743758643	-6.3184355799
H	0	-1.2060329284	-0.2837961416	-6.6053553765
H	0	-0.8266831073	1.0829407031	-5.5344292658

ab-TS4

0 1

H	0	1.4625393337	-2.2968437942	-1.6763901800
C	0	1.6736060094	-1.3898423747	-1.1108128433
H	0	2.1805398668	0.3485193724	1.6121706083
C	0	1.9974141427	-1.3522266943	0.2358611248
C	0	1.5547160710	-0.0726506243	-1.6008927235
H	0	3.5052291841	0.1290138293	0.4410298767
C	0	2.4084837884	0.0466246097	0.5826759759

C	0	-0.3849853607	-0.4892552096	0.8610904380
H	0	2.1421559971	-2.2203175347	0.8767426667
C	0	-0.0884952728	0.8139353965	0.4407332228
H	0	1.2505181580	0.2179450014	-2.6032424580
C	0	1.7386964199	0.8288600197	-0.5296012514
H	0	1.8903508249	1.8988324312	-0.6855054918
H	0	0.1654616969	1.5630313329	1.1929209091
C	0	-0.2451910423	-0.8976228576	2.2678207625
O	0	0.5157332652	-0.3812423322	3.0629245309
O	0	-1.0983487546	-1.8843172509	2.6017873800
C	0	-0.9745652245	-2.4001874789	3.9233037982
H	0	-1.7219388208	-3.1979634644	4.0099779539
H	0	-1.1599884362	-1.6149036079	4.6715593345
H	0	0.0348885242	-2.8063519370	4.0867165571
N	0	-1.2391418172	-1.1779716643	-0.0406667213
C	0	-2.1397728814	-0.3084506809	-0.7764407073
C	0	-1.1158766124	-2.5149907152	-0.3490652161
H	0	-2.1719892770	-0.5857651825	-1.8407078800
S	0	-1.3007280608	1.3965679354	-0.8147791893
C	0	-3.5745409282	-0.2013704432	-0.1987813592
H	0	-1.8104132120	-2.8077757593	-1.1693790204
O	0	-0.3529802922	-3.2915880061	0.1773533077
O	0	-0.6680383133	1.5704484505	-2.1738449320
C	0	-4.3975222472	0.7135849338	-1.1206895275
C	0	-4.2147571099	-1.5996358025	-0.1751144716
C	0	-3.5546258724	0.3582726009	1.2333135750
H	0	-3.9895856327	1.7351806908	-1.1579128674
H	0	-5.4345585158	0.7823458037	-0.7580367165
H	0	-4.4247006919	0.3222570986	-2.1504320538
H	0	-5.2570183080	-1.5252939170	0.1724283053
H	0	-3.6827578885	-2.2746732233	0.5109122922
H	0	-4.2287451708	-2.0571375871	-1.1774402558
H	0	-2.9993946913	-0.3074324244	1.9084769437
H	0	-4.5838749809	0.4461248839	1.6146818327
H	0	-3.0987448063	1.3596885555	1.2733610803

ac-PR1

0 1

H	0	1.8538577700	-1.9863015508	2.0550696587
C	0	1.9013529522	-1.1259958800	1.3872598279
H	0	2.6286490294	0.3308983109	-1.5495831532
C	0	1.8961257861	-1.2105893027	-0.1269761400
C	0	1.8426388855	0.1716445939	1.7214965723
H	0	3.7175256727	0.0306962279	-0.1465516431
C	0	2.6725012680	0.0770986262	-0.4826105697
C	0	0.4262293029	-0.8110450426	-0.5721982789
H	0	2.2246253151	-2.1496911018	-0.5752728160
C	0	0.4360896490	0.7202162216	-0.2781134767
H	0	1.7383555980	0.6021473182	2.7151838828
C	0	1.8040742429	0.9723519367	0.4274496392
H	0	2.0538706060	2.0375391026	0.4996302042
H	0	0.3314887973	1.3252498703	-1.1865722050
C	0	0.2147767270	-1.0798710224	-2.0680157753
O	0	1.0737072799	-0.9693226810	-2.9049993636
O	0	-1.0564832903	-1.4035520038	-2.3459808475
C	0	-1.3500752056	-1.6828924277	-3.7177599529
H	0	-2.4220597358	-1.9078840219	-3.7592834981
H	0	-1.1118525175	-0.8141701186	-4.3485127673
H	0	-0.7616067523	-2.5446540875	-4.0641756821
N	0	-0.6397234415	-1.4360726245	0.2347200113
C	0	-1.8062461060	-0.6024339166	0.5014031867
C	0	-0.6466782482	-2.8087178949	0.2598585357
H	0	-2.3869847102	-0.4628566871	-0.4261519419

S	0	-1.0583450652	1.0995799778	0.6876095021
C	0	-2.7826851677	-0.9639800469	1.6549636960
H	0	-1.4813723873	-3.2422163260	0.8372493891
O	0	0.1931367684	-3.4957216956	-0.2838984334
O	0	-0.6865148455	1.3995667938	2.0815511637
O	0	-1.8954871485	2.0430142910	-0.0655511941
C	0	-3.7641627415	-2.0625088947	1.1898603994
C	0	-3.6487275744	0.2814678783	1.9591622029
C	0	-2.0341870214	-1.3863242083	2.9287131493
H	0	-3.2928528618	-3.0356394275	1.0015725688
H	0	-4.5258739958	-2.2192143325	1.9688204185
H	0	-4.2855989407	-1.7566632628	0.2691804426
H	0	-4.4476477952	-0.0024087993	2.6599656755
H	0	-3.0646478204	1.0859102336	2.4228380119
H	0	-4.1192397336	0.6792778170	1.0475645555
H	0	-1.3267580090	-0.6058486807	3.2370846460
H	0	-2.7575641880	-1.5439461288	3.7434904111
H	0	-1.4756269670	-2.3237955232	2.7971775080

ac-PR2

0 1

H	0	3.8715704232	-1.0706782065	-0.8907547554
C	0	2.8915314957	-1.4898380266	-0.6718029895
H	0	-0.3161832199	-2.1284897827	-1.4556495081
C	0	1.5821818229	-0.9716127121	-1.2574707461
C	0	2.5921015965	-2.4643492290	0.1988607584
H	0	1.1612800813	-3.0229351019	-1.9518654374
C	0	0.7532332915	-2.2727512676	-1.2616112351
C	0	0.8347324738	-0.1770659416	-0.1197289367
H	0	1.6615590213	-0.3970147421	-2.1824922590
C	0	0.5697048296	-1.3132644641	0.9195874215
H	0	3.2737987853	-3.0070910853	0.8553206330
C	0	1.0762477831	-2.6029816346	0.2111773402
H	0	0.6564151515	-3.5230104035	0.6331712238
H	0	1.0206594685	-1.1337320805	1.9015472346
C	0	1.5707970807	1.0124509659	0.5133776226
O	0	1.0147154130	1.7808559437	1.2627336276
O	0	2.8541844527	1.1012107294	0.1788675300
C	0	3.5721729951	2.2140040719	0.7184687790
H	0	3.1320226543	3.1564092086	0.3618417373
H	0	4.6031579889	2.1117563994	0.3605513863
H	0	3.5390266845	2.2003530703	1.8175437241
N	0	-0.4849217125	0.3447662056	-0.5723184693
C	0	-1.5621629824	0.2861000564	0.4194378983
C	0	-0.4323743399	1.3076688687	-1.5540849993
H	0	-1.3447141461	0.9932239416	1.2369399063
C	0	-3.0438928376	0.4515138097	-0.0240867688
H	0	-1.4213812219	1.7004217668	-1.8464867189
O	0	0.5969087618	1.6874987995	-2.0732471768
C	0	-3.9485090658	-0.0953821575	1.1050952285
C	0	-3.3848625656	1.9522202781	-0.1587005980
C	0	-3.3497122809	-0.3078993950	-1.3244082045
H	0	-3.8722058871	-1.1858072609	1.2017012174
H	0	-4.9952691352	0.1497930296	0.8721622069
H	0	-3.6993116152	0.3534692128	2.0779001882
H	0	-4.4639898948	2.0620476098	-0.3458366373
H	0	-2.8633803740	2.4585739677	-0.9812376301
H	0	-3.1488163379	2.4919524589	0.7716177008
H	0	-2.7862043267	0.0816561068	-2.1841002600
H	0	-4.4205110723	-0.2101732079	-1.5606277839
H	0	-3.1150928704	-1.3745126264	-1.2136135884
S	0	-1.2285624862	-1.3386483300	1.2487120918
O	0	-1.4644471703	-1.2050254060	2.6910583867

O	0	-1.8415626630	-2.4539337596	0.5028317694

ac-PR3

0 1

H	0	0.4456546135	-1.1913239430	2.1049042930
C	0	0.7041016605	-0.4585920727	1.3398838683
H	0	2.6347417512	0.7126558236	-1.1540400187
C	0	1.5111754258	-0.7650986866	0.0861757270
C	0	0.3048952693	0.8190915249	1.2672184598
H	0	2.8680736144	0.8829660930	0.6190988967
C	0	2.1583812364	0.6086514237	-0.1726584710
C	0	0.4795028858	-0.8145450848	-1.1293603938
H	0	2.1524192628	-1.6470518279	0.1086514388
C	0	-0.0312771041	0.6608422350	-1.1406426883
H	0	-0.3563773635	1.3513532256	1.9523378576
C	0	0.8245210363	1.3752528832	-0.0505832855
H	0	0.8486327398	2.4655132519	-0.1618912797
H	0	-1.1101998015	0.7571105522	-0.9908060816
C	0	-0.5718414912	-1.8982386647	-0.8811312756
O	0	-0.4522032089	-3.0397622644	-1.2469275934
O	0	-1.6205062038	-1.4466807048	-0.1810097713
C	0	-2.6151556115	-2.4143008481	0.1624982626
H	0	-2.1724888998	-3.2297050017	0.7526869943
H	0	-3.3707902784	-1.8784110576	0.7483634640
H	0	-3.0645925802	-2.8428075602	-0.7455453192
N	0	1.1224450238	-1.0637925653	-2.4347999965
C	0	0.5978233531	-0.3431229112	-3.5808951188
C	0	2.2041202557	-1.9021465885	-2.6131906002
H	0	1.4291927577	-0.1435535412	-4.2716426515
S	0	0.2835295021	1.3252740972	-2.8244978637
C	0	-0.5698142395	-0.9615805408	-4.4016140625
H	0	2.5687968665	-1.8568691070	-3.6656700362
O	0	2.7289670251	-2.5955811355	-1.7765074137
O	0	-0.9309132575	1.9873807064	-3.3256975884
O	0	1.5638000181	2.0497789568	-2.8513987228
C	0	-1.9277642523	-0.9725768128	-3.6774428316
C	0	-0.1792711507	-2.4084304255	-4.7498458006
C	0	-0.6884320990	-0.1321630187	-5.6942004550
H	0	-2.2283404558	0.0316742298	-3.3543832185
H	0	-2.6962980161	-1.3444668925	-4.3723404135
H	0	-1.9282747566	-1.6534889638	-2.8188585539
H	0	-0.9494489833	-2.8479567801	-5.4023870635
H	0	0.7779657695	-2.4520402252	-5.2937630183
H	0	-0.1007064462	-3.0320913424	-3.8475798164
H	0	0.2550192743	-0.1510879530	-6.2639824373
H	0	-1.4766000349	-0.5507331959	-6.3381752361
H	0	-0.9434571170	0.9138220626	-5.4749321148

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0 1

H	0	-2.7485798134	-0.3009142097	2.3123671579
C	0	-2.7055806765	-0.2002140269	1.2289763862
H	0	-2.5742738039	-1.4867079093	-1.8757282689
C	0	-2.1327452548	-1.2528470863	0.3014389348
C	0	-3.0144716707	0.8712999054	0.4851934228
H	0	-4.0171986725	-1.1931416821	-0.8373318381
C	0	-2.9504550885	-0.9733361136	-0.9806602859
C	0	-0.6962754126	-0.7243405462	-0.1669965539
H	0	-2.0948308900	-2.2741477934	0.6884814102
C	0	-1.1031491486	0.4602742863	-1.0853106075
H	0	-3.3653005022	1.8418574472	0.8288511815
C	0	-2.6550219736	0.5438423329	-0.9578756859

H	0	-3.1140761794	1.1688144252	-1.7330533450
H	0	-0.7879711874	0.2943813136	-2.1214275334
C	0	-0.0223853686	-1.8505905803	-0.9553903832
O	0	-0.2168090456	-2.0697263191	-2.1268856768
O	0	0.7545018152	-2.6058053325	-0.1756536064
C	0	1.3644220144	-3.7412131417	-0.7936685177
H	0	1.9166720111	-4.2568323520	0.0001178149
H	0	2.0472497799	-3.4219074711	-1.5953344717
H	0	0.5994482753	-4.4020439630	-1.2261155289
N	0	0.1574541826	-0.1999886126	0.9078243823
C	0	0.9469671433	0.9866655780	0.6265761958
C	0	0.1538053245	-0.7342155901	2.1751901466
H	0	0.9520527314	1.6244911035	1.5222028883
S	0	-0.1753652669	1.9333259167	-0.5309324834
C	0	2.4155885935	0.8030346922	0.1511332155
H	0	0.7569448018	-0.1158017326	2.8788045558
O	0	-0.4276775616	-1.7367962084	2.5184135933
O	0	0.5362713963	2.5089517299	-1.6829575010
O	0	-1.0151793358	2.8036051505	0.3035873579
C	0	3.0704302615	2.1969640826	0.1421446238
C	0	3.1347271076	-0.0865067050	1.1806086439
C	0	2.5457366450	0.1523158414	-1.2360380444
H	0	2.5826157606	2.8638157094	-0.5809637739
H	0	4.1327174654	2.1095549638	-0.1321530695
H	0	3.0197142012	2.6632858476	1.1397708939
H	0	4.1969369089	-0.1782000472	0.9060568988
H	0	2.7048222622	-1.0984203533	1.2092700333
H	0	3.0905743779	0.3423723979	2.1944658178
H	0	2.2067390284	-0.8903448518	-1.2236074707
H	0	3.6070370659	0.1377627188	-1.5282029586
H	0	1.9950156987	0.7073401855	-2.0048749505

ac-TS1

0 1

H	0	1.7599493402	-2.1503940142	1.6327591223
C	0	1.9294565854	-1.2202319834	1.0912514976
H	0	2.3204993035	0.6199130663	-1.5852622544
C	0	2.2311472070	-1.1290863687	-0.2599797834
C	0	1.7567351125	0.0769691373	1.6159243089
H	0	3.6695832665	0.4189547319	-0.4402437855
C	0	2.5748465811	0.2970812290	-0.5687680824
C	0	-0.1404815261	-0.4735763674	-0.8475329230
H	0	2.4137997388	-1.9718088314	-0.9235183590
C	0	0.0035908018	0.8444055255	-0.4088369324
H	0	1.4456729531	0.3181044972	2.6298134461
C	0	1.8929123591	1.0128820745	0.5747533424
H	0	1.9577976520	2.0898815824	0.7401567868
H	0	0.1562685313	1.6560280672	-1.1200159041
C	0	0.0087431927	-0.7986469652	-2.2854278852
O	0	0.7528562027	-0.2120744809	-3.0438421793
O	0	-0.8166928072	-1.7814877392	-2.6719456214
C	0	-0.6980455336	-2.2054125543	-4.0277142457
H	0	-1.4302400866	-3.0108462547	-4.1597792866
H	0	-0.9086504946	-1.3749128110	-4.7179248492
H	0	0.3177360935	-2.5780250027	-4.2274159411
N	0	-0.9710446486	-1.2747538664	0.0005030316
C	0	-2.0636498036	-0.5082792299	0.6035135000
C	0	-0.7686554487	-2.6345112029	0.1067204834
H	0	-2.8077174472	-0.2728092510	-0.1763062016
S	0	-1.2755987184	1.1947892871	0.8081748122
C	0	-2.8067860965	-1.0013422112	1.8673867737
H	0	-1.5294825996	-3.1350491819	0.7303259909
O	0	0.1428798656	-3.2373600018	-0.4146896871

O	0	-0.7333909513	1.4143865193	2.1604955948
O	0	-2.1974363191	2.1885316517	0.2417822739
C	0	-3.8019867519	-2.1192783612	1.4860239716
C	0	-3.6574186793	0.1792910408	2.3933972882
C	0	-1.8470056841	-1.4641272664	2.9760619439
H	0	-3.3227923703	-3.0429568921	1.1360074222
H	0	-4.4070638775	-2.3815479425	2.3673678939
H	0	-4.4900664909	-1.7775709643	0.6968943953
H	0	-4.3146583571	-0.1821305356	3.1980780181
H	0	-3.0338743371	0.9839961591	2.8025933461
H	0	-4.2914414614	0.6041214647	1.6004160853
H	0	-1.1407966585	-0.6645121743	3.2328922576
H	0	-2.4263730873	-1.7161626927	3.8775917289
H	0	-1.2731211705	-2.3580993772	2.6949861457

ac-TS2

0 1

H	0	-3.6152120770	-1.1280879386	1.7741252064
C	0	-2.6479789273	-1.5272464886	1.4680240702
H	0	0.6186285225	-1.7310430987	1.4160558046
C	0	-1.4258115147	-1.1908538622	2.0376798968
C	0	-2.4271842879	-2.3594931826	0.3561250739
H	0	-0.3590834607	-3.0312427183	2.0969869377
C	0	-0.3954564801	-2.1124822461	1.4773652681
C	0	-0.7407626090	0.3292758043	-0.0901408578
H	0	-1.2805820146	-0.5162102264	2.8808565728
C	0	-0.5579630251	-0.8498889894	-0.8488688021
H	0	-3.1987658121	-2.7146899286	-0.3276628539
C	0	-1.0267358255	-2.4879702460	0.1550544852
H	0	-0.5848580054	-3.2581747457	-0.4802091249
H	0	-1.1790739822	-1.0456306871	-1.7236172438
C	0	-2.0699254030	0.9377469207	0.1742625192
O	0	-2.3458752577	1.6985199354	1.0686646412
O	0	-2.9750720823	0.4712167708	-0.7188993852
C	0	-4.3023173452	0.9614266843	-0.5547687574
H	0	-4.7007699529	0.6957929290	0.4365851506
H	0	-4.9022394806	0.4949155525	-1.3456891510
H	0	-4.3216928326	2.0567568058	-0.6516947649
N	0	0.4054664949	1.1732120390	0.0845840442
C	0	1.6950097720	0.5931228586	-0.3047870763
C	0	0.2672816977	2.5256238592	-0.2976591675
H	0	2.1084357645	1.1889534773	-1.1309127294
S	0	1.2024965280	-0.9531789718	-1.2612206980
C	0	2.8296856104	0.4764858489	0.7471963214
H	0	1.2352138370	3.0630918813	-0.2241539098
O	0	-0.7441345607	3.0526329979	-0.6760579651
O	0	1.3727296565	-0.6640621585	-2.6895861037
O	0	1.8247245128	-2.1609850930	-0.6900031238
C	0	4.0809594230	-0.0527922790	0.0214338287
C	0	3.1208033623	1.9013037166	1.2594413977
C	0	2.5092334765	-0.4072201937	1.9560390353
H	0	3.9224902342	-1.0691768409	-0.3625466052
H	0	4.9328109977	-0.0769016344	0.7179864847
H	0	4.3576330142	0.5999755419	-0.8223846672
H	0	3.9783836823	1.8730004313	1.9488112408
H	0	2.2624123244	2.3175269998	1.8074780245
H	0	3.3801364181	2.5874040647	0.4375155754
H	0	1.5652245671	-0.1045820834	2.4320682361
H	0	3.3087125808	-0.2988191950	2.7047950325
H	0	2.4605024599	-1.4659633111	1.6749161393

ac-TS3

0 1

H	0	0.3863954839	-1.0301307797	2.2868057890
C	0	0.7847389273	-0.3691075089	1.5171426115
H	0	2.4326487711	0.4084640455	-1.2183108853
C	0	1.7153578218	-0.7309335217	0.5456713788
C	0	0.3596019005	0.9493716665	1.2827843056
H	0	3.0158037130	0.9372883487	0.3618975319
C	0	2.1405564043	0.5124981535	-0.1691529653
C	0	0.0538625943	-0.8527755924	-1.3638748337
H	0	2.2247647781	-1.6877962834	0.4625309661
C	0	-0.2868985504	0.5092016874	-1.2908472837
H	0	-0.4191715591	1.4693606439	1.8428195256
C	0	0.9632713048	1.4232380497	0.0966949478
H	0	0.9488272660	2.4651381746	-0.2266081228
H	0	-1.2614797967	0.8302861799	-0.9290395526
C	0	-0.7770177550	-1.9302400172	-0.7986637254
O	0	-0.7741153987	-3.0808290424	-1.1710880275
O	0	-1.5949211619	-1.4636926650	0.1726611363
C	0	-2.4374095790	-2.4318219406	0.7912234304
H	0	-1.8383712780	-3.2146961784	1.2810165179
H	0	-3.0347100787	-1.8882654434	1.5334741486
H	0	-3.0930973129	-2.9124856194	0.0498880274
N	0	0.8490281130	-1.1679941542	-2.5125496137
C	0	0.5695556253	-0.3519812235	-3.6874990152
C	0	1.8961767444	-2.0673109032	-2.5111145164
H	0	1.5019281622	-0.1368083519	-4.2282308972
S	0	0.1620411825	1.2859417607	-2.8700729433
C	0	-0.4898739246	-0.9085885412	-4.6701642789
H	0	2.3938327586	-2.1098468088	-3.5063391836
O	0	2.2597650187	-2.7268803060	-1.5677160001
O	0	-1.0357141876	1.9452905241	-3.4115227302
O	0	1.4217558847	2.0417717740	-2.7870957544
C	0	-1.8734961137	-1.0780926014	-4.0204286287
C	0	-0.0016118122	-2.2898716749	-5.1447706215
C	0	-0.5661764956	0.0453872112	-5.8754353225
H	0	-2.2633054920	-0.1262983108	-3.6375240522
H	0	-2.5814544438	-1.4540790704	-4.7752019702
H	0	-1.8398929407	-1.8174194618	-3.2084758384
H	0	-0.6956761701	-2.6795919979	-5.9051318389
H	0	0.9983995248	-2.2351904877	-5.6048723468
H	0	0.0276949965	-3.0130405127	-4.3167291306
H	0	0.4172786496	0.1430850574	-6.3643429234
H	0	-1.2710400639	-0.3521743861	-6.6214741810
H	0	-0.9088455113	1.0447874480	-5.5769150626

ac-TS4

0 1

H	0	1.5010672113	-2.2918512203	-1.6688503766
C	0	1.7222873858	-1.3915624569	-1.0968751495
H	0	2.1786914115	0.3439840725	1.6414187601
C	0	1.9805969976	-1.3594144060	0.2664795732
C	0	1.6775329105	-0.0736438754	-1.5920298910
H	0	3.5400650882	0.0536341406	0.5306701290
C	0	2.4356602598	0.0230537812	0.6248692640
C	0	-0.3578542820	-0.4661936414	0.8043317936
H	0	2.0673243976	-2.2315747756	0.9120853650
C	0	-0.0501385741	0.8332080465	0.3869201155
H	0	1.4233326830	0.2172004051	-2.6086625737
C	0	1.8512233823	0.8236332538	-0.5184718595
H	0	2.0313832913	1.8914670795	-0.6581079461
H	0	0.1507899442	1.6193474008	1.1150622638
C	0	-0.2422541053	-0.8613171913	2.2218830759
O	0	0.4923434338	-0.3214378437	3.0244101316

O	0	-1.0754763969	-1.8642452162	2.5427078209
C	0	-0.9911693686	-2.3483109769	3.8807331747
H	0	-1.7109345373	-3.1723117753	3.9510638061
H	0	-1.2412583009	-1.5545004946	4.6003632169
H	0	0.0250588783	-2.7096736193	4.0972267836
N	0	-1.2408515639	-1.1450145858	-0.0887357479
C	0	-2.1913313893	-0.2879875687	-0.7904345935
C	0	-1.1319065592	-2.4848182218	-0.3982084046
H	0	-2.2657140128	-0.5882581651	-1.8451188694
S	0	-1.2399745901	1.3322642132	-0.8804424211
C	0	-3.6072665697	-0.1964198073	-0.1672648772
H	0	-1.8516744265	-2.7784320865	-1.1946986157
O	0	-0.3538270004	-3.2606515295	0.1047248739
O	0	-1.9863545638	2.4808572485	-0.3422450312
O	0	-0.6734958096	1.4303346558	-2.2320352867
C	0	-4.4652131430	0.7200039225	-1.0581601591
C	0	-4.2199250009	-1.6095243151	-0.1719225332
C	0	-3.5733436943	0.3144449560	1.2825416674
H	0	-4.0741232328	1.7453009273	-1.0781046687
H	0	-5.4961188528	0.7530670785	-0.6738116373
H	0	-4.5066780896	0.3390076930	-2.0920467212
H	0	-5.2584987578	-1.5556674020	0.1890030688
H	0	-3.6734099722	-2.2933405134	0.4939528988
H	0	-4.2420157035	-2.0445817622	-1.1842723162
H	0	-2.9922221428	-0.3655050398	1.9209968484
H	0	-4.5997599979	0.3477107768	1.6797609749
H	0	-3.1500843082	1.3242275690	1.3470402338

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0 1

H	0	-0.4081702015	-1.3151501568	3.0468554962
C	0	-0.7524740774	-1.4585976395	2.0203387485
C	0	-0.2400560389	-2.3636898582	1.1773262093
C	0	-1.2811597740	0.1120083835	0.1983041306
C	0	-0.8108061118	-0.9668324507	-0.8199900410
H	0	0.5730048493	-3.0460501070	1.4318559966
C	0	-0.8916990956	-2.3769018590	-0.1818757813
H	0	-0.4350837842	-3.1087846426	-0.8625862880
H	0	-1.4771075744	-0.9582904292	-1.6946650360
C	0	-2.3185664036	1.0060165272	-0.5129994759
O	0	-3.5144604951	0.8714313864	-0.4820879438
O	0	-1.7037717364	1.9243158989	-1.2794229087
C	0	-2.5586103131	2.8198144497	-1.9890938537
H	0	-1.8994496084	3.4699796158	-2.5766092166
H	0	-3.2423076903	2.2660418084	-2.6492302982
H	0	-3.1557148878	3.4151313916	-1.2825076298
N	0	-0.1196415943	0.9461931659	0.5779079726
C	0	1.1000379407	0.8922765323	-0.2440381513
C	0	-0.4264431700	2.1100904467	1.2355803776
H	0	1.1481161507	1.8103397959	-0.8539762711
S	0	0.8390258351	-0.4925042308	-1.4324741520
C	0	2.4737448286	0.7648553890	0.4917532837
H	0	0.4145587020	2.8279007860	1.2836445132
O	0	-1.5174953374	2.3616143410	1.7099043406
C	0	2.7453395378	1.9880008300	1.3867897583
C	0	3.5586574785	0.7377706522	-0.6028437875
C	0	2.5736055046	-0.4994187783	1.3493652390
H	0	2.0938860095	2.0082437981	2.2720032764
H	0	3.7834136728	1.9476750893	1.7516245351
H	0	2.6251375378	2.9365032903	0.8382945039
H	0	4.5580583930	0.7059233581	-0.1427830357
H	0	3.4599977016	-0.1473674663	-1.2490524306
H	0	3.5097250065	1.6360818428	-1.2400457226

H	0	2.4199164319	-1.4021033724	0.7435064547
H	0	3.5707450483	-0.5550938846	1.8141879298
H	0	1.8193730784	-0.4957387215	2.1465665035
C	0	-2.4029683601	-2.6647386271	0.0155685722
H	0	-2.9142199382	-2.6035065015	-0.9590639155
H	0	-2.5317413121	-3.6932599388	0.3826490532
C	0	-2.9849358496	-1.6315854251	1.0093899158
H	0	-3.3458679524	-2.1306239520	1.9202629205
H	0	-3.8265127212	-1.0842405800	0.5739301284
C	0	-1.8745770699	-0.6341341408	1.4397076245
H	0	-2.2674209396	0.1125661330	2.1366350452

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0 1

H	0	-3.3750373905	-2.9242624831	1.2101325408
C	0	-2.3824719263	-2.7134756970	0.8108854723
C	0	-1.4540868574	-1.7438130433	1.5063737636
C	0	-1.8758755848	-3.2765613001	-0.2928208585
C	0	-1.1023091448	-0.5955725363	0.5092823203
H	0	-1.9037685697	-1.3030003905	2.4006653091
C	0	-0.6232821892	-1.2482424607	-0.8236979427
H	0	-2.4043536927	-4.0069169450	-0.9097876334
C	0	-0.4903876069	-2.7851466145	-0.6423006491
H	0	-0.1092151828	-3.2276178458	-1.5736831602
H	0	-1.3705127599	-1.0692041027	-1.6068723325
C	0	-2.3678240935	0.2306109010	0.2082569649
O	0	-3.4995798868	-0.1381668072	0.3748330659
O	0	-2.0436800352	1.4108006592	-0.3523055785
C	0	-3.1369406632	2.2719582927	-0.6690265474
H	0	-3.8335334403	1.7783633462	-1.3626525959
H	0	-2.6998199723	3.1639794861	-1.1335230562
H	0	-3.6845026771	2.5437479358	0.2456051643
N	0	-0.0414840264	0.3055288929	1.0106332165
C	0	1.0076815581	0.7478976811	0.0729264033
C	0	-0.4314999372	1.1557748590	2.0172519322
H	0	0.7365723791	1.7466333300	-0.3098360768
S	0	0.9074211490	-0.4102227080	-1.3583305077
C	0	2.4779146079	0.8422967863	0.6019846077
H	0	0.2749557658	1.9865423817	2.1965520238
O	0	-1.4611571541	1.0399255946	2.6521562528
C	0	2.9877083907	-0.4876206195	1.1664359224
C	0	3.3517657612	1.2675206768	-0.5956610984
C	0	2.6326797783	1.9275940389	1.6853160613
H	0	2.3570214307	-0.8333387373	1.9976052206
H	0	4.0123767913	-0.3634061938	1.5497226623
H	0	3.0050642873	-1.2674309032	0.3940000443
H	0	4.3949819316	1.4005928542	-0.2710829317
H	0	3.0073438409	2.2229706638	-1.0238414284
H	0	3.3455633221	0.5114503354	-1.3947461523
H	0	2.1790340062	2.8842491728	1.3794711769
H	0	3.7037900426	2.1119235270	1.8611386194
H	0	2.1996993645	1.6240747615	2.6486134803
C	0	-0.1546140900	-2.5113662763	1.8417875030
H	0	0.5522511023	-1.8373674426	2.3435816868
H	0	-0.4012044301	-3.3094185009	2.5563064012
C	0	0.4515975495	-3.0940750512	0.5430914985
H	0	0.5834294538	-4.1829233713	0.6193886880
H	0	1.4384492982	-2.6609799870	0.3367253471

ba-PR3

0 1

H	0	4.0312365511	0.8429143591	0.1651184325

C	0	3.2186857582	0.1187390153	0.0758797185
C	0	2.0971845894	0.0728670311	1.0873504266
C	0	3.1303733613	-0.7941501775	-0.8981291357
C	0	0.7384575241	0.3106392130	0.3190425569
H	0	2.1932494920	0.8271166203	1.8718441203
C	0	0.6688753317	-0.7523267170	-0.8341182307
H	0	3.8596818142	-0.9072896456	-1.7035372018
C	0	1.9130887166	-1.6807791522	-0.7912793783
H	0	1.8520815688	-2.4046178821	-1.6165923809
H	0	0.6484338192	-0.2390987167	-1.8000234204
C	0	0.7488016824	1.7675050183	-0.1787586636
O	0	0.2991492850	2.6926866933	0.4492885010
O	0	1.3470405824	1.9115038403	-1.3697349514
C	0	1.4633084293	3.2479814753	-1.8588015926
H	0	2.0170458175	3.8747148509	-1.1446504502
H	0	2.0031762810	3.1776574435	-2.8104437847
H	0	0.4682229034	3.6914815205	-2.0132546662
N	0	-0.4488561652	0.1297671333	1.1612103567
C	0	-1.6086784795	-0.4798564372	0.5244593971
C	0	-0.5209014054	0.4905999596	2.4844032503
H	0	-2.1404332450	-1.0561417998	1.2965333686
S	0	-0.8948483624	-1.7059473474	-0.6440806517
C	0	-2.6686201741	0.4691521802	-0.1253972461
H	0	-1.5016277077	0.1927083168	2.9237449825
O	0	0.3387035337	1.0307031829	3.1427052503
C	0	-2.1862623790	1.1378827144	-1.4212633779
C	0	-3.0620684450	1.5554134984	0.8888248444
C	0	-3.8941295190	-0.4034416533	-0.4480084755
H	0	-1.8147183355	0.3932786483	-2.1397158607
H	0	-3.0258323430	1.6728403821	-1.8918964137
H	0	-1.4030779841	1.8812689701	-1.2330557127
H	0	-3.8672403380	2.1806307322	0.4720896783
H	0	-3.4386033475	1.1183102858	1.8277158524
H	0	-2.2106412435	2.2108479589	1.1223586852
H	0	-4.2953099659	-0.8841258382	0.4594098816
H	0	-4.6965622615	0.2095249717	-0.8861339880
H	0	-3.6386512376	-1.1942139718	-1.1705291950
C	0	1.9789392607	-2.4055466608	0.5749529920
H	0	1.0821942681	-3.0279470695	0.6977918224
H	0	2.8517374626	-3.0743349373	0.5784875045
C	0	2.0758446807	-1.3500842040	1.6993098825
H	0	1.2398441456	-1.4395956742	2.4042766761
H	0	2.9968702200	-1.4757376107	2.2861613770

ba-PR4

0 1

H	0	2.4023062275	-0.7006034348	2.7549184611
C	0	2.2815359565	-0.7932092173	1.6738484739
C	0	2.1696672476	0.4300031479	0.7994116228
C	0	2.2034833705	-1.9531161845	1.0105249045
C	0	0.7586157538	0.3600643884	0.0901843029
H	0	2.2293145702	1.3566178495	1.3736956959
C	0	0.7185544592	-0.9735086803	-0.7260109771
H	0	2.2612297806	-2.9349006264	1.4845176992
C	0	2.0060403050	-1.7971352499	-0.4785703014
H	0	1.9216763085	-2.7646741442	-0.9935578238
H	0	0.6436954636	-0.7323026408	-1.7929426257
C	0	0.6582450307	1.5671122468	-0.8523997458
O	0	1.0139541334	1.5697023690	-2.0065490244
O	0	0.1922157940	2.6496849299	-0.2208471279
C	0	0.1383429625	3.8563586237	-0.9818675643
H	0	-0.2237804518	4.6308374789	-0.2960049075
H	0	-0.5482111961	3.7447342340	-1.8348062433

H	0	1.1350343094	4.1162168310	-1.3672797354
N	0	-0.3533010033	0.3340502286	1.0514936507
C	0	-1.4880739204	-0.5157093147	0.7115885418
C	0	-0.3366712147	0.9460120905	2.2799786600
H	0	-1.8820352007	-0.9284913819	1.6527499411
S	0	-0.7602266017	-1.9275656767	-0.2099934482
C	0	-2.6956716540	0.1623842479	-0.0106518711
H	0	-1.2262737351	0.6478270586	2.8823684983
O	0	0.4998817485	1.7074630431	2.7127553765
C	0	-3.8274376816	-0.8782466658	-0.0574899201
C	0	-3.1537662942	1.3769777983	0.8131700055
C	0	-2.3723188351	0.6143773595	-1.4407247291
H	0	-3.5322659195	-1.7567947418	-0.6513700134
H	0	-4.7285131673	-0.4442036777	-0.5173463074
H	0	-4.0984280769	-1.2229698983	0.9540949082
H	0	-4.0483718297	1.8264236480	0.3543412699
H	0	-2.3716599457	2.1490600536	0.8556596050
H	0	-3.4187583158	1.0937604302	1.8446567251
H	0	-1.6860270744	1.4692527189	-1.4544978888
H	0	-3.2959141008	0.9369790247	-1.9461180431
H	0	-1.9316998845	-0.2030741862	-2.0288569377
C	0	3.1793681878	-0.9702449339	-1.0575142405
H	0	2.9916260286	-0.7738182810	-2.1241183044
H	0	4.1086153826	-1.5540984126	-0.9879310944
C	0	3.2879628374	0.3550078189	-0.2696717025
H	0	3.2394177169	1.2187597938	-0.9460877735
H	0	4.2478846883	0.4190601752	0.2621659380

ba-TS1

0 1

H	0	-0.5107840524	-1.0684620536	2.8743174832
C	0	-1.0656286919	-1.4919509708	2.0335773155
C	0	-0.4690067516	-2.4659110687	1.2155350802
C	0	-0.9893770901	0.1924981683	-0.3545709072
C	0	-0.5385209892	-0.9603006109	-1.0324525389
H	0	0.5394737317	-2.8197539748	1.4398023695
C	0	-1.0403413757	-2.7255996965	-0.0364581448
H	0	-0.5239249706	-3.4344153212	-0.6933286155
H	0	-1.0775785520	-1.2517037601	-1.9359771314
C	0	-2.1716907498	0.9041940151	-0.8621487895
O	0	-3.0983554000	0.3696983402	-1.4443788424
O	0	-2.1093238078	2.2320876554	-0.6552106546
C	0	-3.2508747860	2.9823996042	-1.0511567208
H	0	-3.0274396886	4.0284662426	-0.8082922184
H	0	-3.4441243783	2.8701888027	-2.1289426277
H	0	-4.1452461008	2.6502551151	-0.5022263236
N	0	0.0650219708	0.8924850455	0.3059093332
C	0	1.3596212296	0.7450865100	-0.3835631861
C	0	-0.1580163039	1.6725933799	1.4153687368
H	0	1.3801734653	1.4466516027	-1.2363261703
S	0	1.2482159073	-0.9640054175	-1.1272702206
C	0	2.6893806002	0.9205978020	0.4049054925
H	0	0.7502995530	2.1979655479	1.7564265362
O	0	-1.2187549965	1.7949636135	1.9902443774
C	0	3.0080678405	2.4128092484	0.6439929191
C	0	3.8242995907	0.3857058742	-0.4982006433
C	0	2.6902566183	0.1274792201	1.7203165807
H	0	2.3405423565	2.9053716548	1.3621234555
H	0	4.0306633740	2.5089760136	1.0402625362
H	0	2.9619263342	2.9786524406	-0.3000595927
H	0	4.7985893629	0.6040970671	-0.0357238555
H	0	3.7597966223	-0.7032102189	-0.6374112318
H	0	3.8077549259	0.8627182017	-1.4911320408

H	0	2.4439167869	-0.9274721787	1.5323875461
H	0	3.6879358032	0.1733983548	2.1839047691
H	0	1.9670997600	0.5160643624	2.4504657450
C	0	-2.5482707539	-2.6783837080	-0.1893162043
H	0	-2.8135329032	-2.4605056337	-1.2353129880
H	0	-2.9346613692	-3.6893662317	0.0231148397
C	0	-3.2203762440	-1.6470740168	0.7496273103
H	0	-3.9343442227	-2.1581203721	1.4216350642
H	0	-3.8156100544	-0.9295911482	0.1694907926
C	0	-2.2586397817	-0.9190953518	1.6383696603
H	0	-2.6235301389	-0.0383199886	2.1662882853

ba-TS2

0 1

H	0	-3.9523351833	1.1801534534	-0.9729146963
C	0	-2.9223569823	1.5198069862	-0.8387329077
C	0	-1.9729664373	1.1932296046	-1.7789694526
C	0	-2.5318698135	2.0789614950	0.3911494219
C	0	-0.6236719461	-0.5342613396	0.1843715153
H	0	-2.2443856324	0.5324854706	-2.6058284587
C	0	-0.4814528072	0.5169897918	1.1395075940
H	0	-3.2586874762	2.1762088406	1.2006574653
C	0	-1.1452483677	2.2342890760	0.6390015217
H	0	-0.8861660741	2.7698462544	1.5597331944
H	0	-1.0971926539	0.4221863681	2.0343681931
C	0	-1.9166719047	-1.1538309706	-0.1498778552
O	0	-2.1970487147	-1.8198093363	-1.1205104308
O	0	-2.8191019207	-0.8711432030	0.8370645243
C	0	-4.1266671460	-1.3826939610	0.6211802549
H	0	-4.5606135232	-0.9823691042	-0.3085913077
H	0	-4.7269265515	-1.0725054938	1.4860079408
H	0	-4.1063563245	-2.4797287755	0.5407779476
N	0	0.5817858490	-1.1450947223	-0.2487494770
C	0	1.8310385035	-0.5953906316	0.3517840027
C	0	0.6246511946	-2.5588185036	-0.3361516395
H	0	2.2522126273	-1.3807199982	0.9996054840
S	0	1.2684754119	0.7386758194	1.5157582643
C	0	3.0170732939	-0.1777677996	-0.5708653937
H	0	1.6270496669	-2.9087024908	-0.6525886917
O	0	-0.2685043931	-3.3167976371	-0.0712206173
C	0	2.6840348288	0.9052853389	-1.5959842828
C	0	4.1361807675	0.3275087432	0.3602207185
C	0	3.5397582021	-1.4118708747	-1.3295436889
H	0	1.9486249113	0.5463194071	-2.3280080900
H	0	3.5950354248	1.1791015803	-2.1502986977
H	0	2.2985273725	1.8132265535	-1.1166052038
H	0	5.0439020916	0.5449143829	-0.2229024931
H	0	4.3985867976	-0.4244974313	1.1222876929
H	0	3.8407041313	1.2528342121	0.8779474704
H	0	3.8117392758	-2.2318057905	-0.6457536774
H	0	4.4436821253	-1.1397949986	-1.8961155212
H	0	2.7996258366	-1.7870288846	-2.0516630524
C	0	-0.6182583731	1.8280563573	-1.8193188060
H	0	0.1335903445	1.0430733889	-1.9659178730
H	0	-0.5468622280	2.4609262403	-2.7238182935
C	0	-0.3313837626	2.6780736540	-0.5689085312
H	0	-0.5999459803	3.7289105914	-0.7648203226
H	0	0.7371305399	2.6678903370	-0.3196557442

ba-TS3

0 1

H	0	4.0065088947	0.9898697132	-0.0098886009

C	0	3.3806190286	0.1076442047	0.1413518659
C	0	2.5728747216	0.0171404622	1.2638325156
C	0	3.1891044006	-0.7985964689	-0.9103702314
C	0	0.4525830756	0.5101349974	-0.0115654730
H	0	2.5578820449	0.8243980230	1.9962072510
C	0	0.4673332125	-0.5277431784	-0.9804960088
H	0	3.6595614426	-0.6121283491	-1.8793365914
C	0	2.1693334731	-1.7538901837	-0.7865090505
H	0	1.9874603962	-2.4239953940	-1.6338047144
H	0	0.6825577127	-0.2587670601	-2.0124456294
C	0	0.8334004634	1.8869985567	-0.3615127043
O	0	0.4164820639	2.8937816771	0.1654732312
O	0	1.6937324427	1.9080973906	-1.4117269230
C	0	2.1570509236	3.1945486826	-1.8036955742
H	0	2.7156457241	3.6760625770	-0.9859941171
H	0	2.8136709775	3.0341800854	-2.6680341627
H	0	1.3168050542	3.8502390830	-2.0774261260
N	0	-0.5639127643	0.3323850823	0.9651573938
C	0	-1.6954804923	-0.4750577306	0.5154870732
C	0	-0.4870500896	0.7767537784	2.2680195346
H	0	-2.0468474820	-1.0991511406	1.3509343514
S	0	-0.9435368282	-1.6162015733	-0.7458589860
C	0	-2.9047666102	0.3346635574	-0.0344779490
H	0	-1.3779951153	0.4581969148	2.8560418413
O	0	0.4193279008	1.4141768305	2.7508428002
C	0	-2.5066862891	1.2184126483	-1.2247885495
C	0	-3.4507904469	1.2326353129	1.0894581423
C	0	-3.9912804782	-0.6673593873	-0.4547470652
H	0	-2.0699411420	0.6201339065	-2.0377534873
H	0	-3.3976641664	1.7297411422	-1.6216114372
H	0	-1.7869174521	1.9911189192	-0.9206768650
H	0	-4.3571077384	1.7520657988	0.7416281267
H	0	-3.7252053932	0.6485727226	1.9832426272
H	0	-2.7217016433	2.0022852253	1.3820288505
H	0	-4.2962334198	-1.3074729575	0.3899131364
H	0	-4.8854613703	-0.1321939096	-0.8092303851
H	0	-3.6414892565	-1.3181239857	-1.2704942597
C	0	1.9437124732	-2.3577184188	0.5831847805
H	0	0.9829465949	-2.8917349839	0.6022837286
H	0	2.7302558585	-3.1159799178	0.7351575572
C	0	2.0013311196	-1.3004387097	1.7083382638
H	0	1.0115951175	-1.1485473161	2.1604344113
H	0	2.6334571812	-1.6656360964	2.5369821885

ba-TS4

0 1

H	0	2.0686488173	-0.5942868125	2.7269083329
C	0	2.3837186439	-0.6752095665	1.6838454119
C	0	2.7601026588	0.4599513605	0.9917753299
C	0	2.1973309010	-1.8765834191	0.9812272598
C	0	0.4376239626	0.4209425674	-0.2150961362
H	0	2.7176069105	1.4252016567	1.4972287329
C	0	0.5136953262	-0.8316694741	-0.8658674822
H	0	1.7559000969	-2.7382103833	1.4865321821
C	0	2.2742748108	-1.8485667232	-0.4180412899
H	0	2.0593065092	-2.7782314254	-0.9565096681
H	0	0.7222040289	-0.8298276501	-1.9378356021
C	0	0.7320913538	1.6552447346	-0.9480442895
O	0	1.4538913582	1.7248032157	-1.9263270809
O	0	0.0854756798	2.7244738357	-0.4406546356
C	0	0.3597398447	3.9749847047	-1.0616365367
H	0	-0.2349845045	4.7203177096	-0.5198213019
H	0	0.0782021695	3.9572522931	-2.1255181746

H	0	1.4302535558	4.2197629171	-0.9899496818
N	0	-0.4823789048	0.4056360677	0.8710437128
C	0	-1.5684251835	-0.5588864872	0.7131208629
C	0	-0.3264243808	1.0888567788	2.0543210645
H	0	-1.8074600290	-0.9890642095	1.6972753312
S	0	-0.8111707545	-1.9112244132	-0.3063216581
C	0	-2.8788659669	0.0190812889	0.1056503347
H	0	-1.1203024394	0.8116029267	2.7855691896
O	0	0.5460810136	1.8858546059	2.3136500978
C	0	-3.9069326561	-1.1208560240	0.0348404142
C	0	-3.4074552043	1.1225562027	1.0384164492
C	0	-2.6523806193	0.6120892903	-1.2916135674
H	0	-3.5661638270	-1.9232658457	-0.6369799007
H	0	-4.8680310666	-0.7444871373	-0.3479050521
H	0	-4.0902332986	-1.5594052905	1.0299240495
H	0	-4.3750484465	1.4943052956	0.6669573955
H	0	-2.7171039397	1.9777486252	1.0814344759
H	0	-3.5665838634	0.7493062036	2.0634156396
H	0	-1.9786038820	1.4785288679	-1.2485057843
H	0	-3.6117915318	0.9531748743	-1.7113506915
H	0	-2.2270185768	-0.1348148813	-1.9772800202
C	0	3.2787172622	-0.9295599617	-1.0864047422
H	0	2.9417090986	-0.6808839790	-2.1043947113
H	0	4.2188290825	-1.4944846101	-1.2013809752
C	0	3.5385350407	0.3702714315	-0.2855839540
H	0	3.3477914548	1.2519993883	-0.9115230326
H	0	4.6048916752	0.4296316610	0.0003256420

bb-PR1

0 1

H	0	-0.3891066091	-1.5077941935	2.9926305838
C	0	-0.7599958425	-1.6031141488	1.9698908190
C	0	-0.3205411347	-2.5218223690	1.0984157746
C	0	-1.2568041643	0.0404495979	0.2018713751
C	0	-0.7547389165	-1.0237102475	-0.8079451165
H	0	0.4496526927	-3.2627130028	1.3228296619
C	0	-0.9855391599	-2.4468047991	-0.2569716673
H	0	-0.5817917177	-3.1829407950	-0.9665922903
H	0	-1.2029956071	-0.8978964668	-1.8035456642
C	0	-2.2780176442	0.9249741540	-0.5429974584
O	0	-3.4733179837	0.7873712985	-0.5508336438
O	0	-1.6345218268	1.8275093276	-1.3023817146
C	0	-2.4562144688	2.6971509661	-2.0819606523
H	0	-1.7696886070	3.3255868448	-2.6611407077
H	0	-3.1070226183	2.1178079529	-2.7529399841
H	0	-3.0849428672	3.3154910331	-1.4245248539
N	0	-0.1086985977	0.8851611545	0.6169435861
C	0	1.1180827802	0.8200195585	-0.1754438909
C	0	-0.4491780194	2.0393228113	1.2792526964
H	0	1.0959574238	1.5564545272	-0.9975816964
S	0	1.0461551324	-0.7811429282	-1.1615692737
C	0	2.4865153811	0.8818619164	0.5667682203
H	0	0.3862333554	2.7528458258	1.3912610448
O	0	-1.5661918548	2.2813586772	1.6934025048
O	0	1.1954320493	-0.3906824092	-2.6118076306
C	0	2.7412016616	2.2511173721	1.2288466098
C	0	3.5926554020	0.6863452687	-0.4922654014
C	0	2.5778467721	-0.2134253866	1.6385308523
H	0	3.7994437231	2.3154352583	1.5259119842
H	0	2.5393552473	3.0845352875	0.5372119800
H	0	2.1481968942	2.3969952924	2.1419418509
H	0	4.5798015129	0.7638122873	-0.0123216890
H	0	3.5411611134	-0.2939772104	-0.9872610331

H	0	3.5319801003	1.4542661856	-1.2790288525
H	0	2.4818141760	-1.2162000605	1.1981491439
H	0	3.5491552082	-0.1569050827	2.1540081928
H	0	1.7817817563	-0.0989953411	2.3879371619
C	0	-2.5155266989	-2.6224739001	-0.0828974127
H	0	-3.0082328258	-2.4187939329	-1.0470426263
H	0	-2.7348915633	-3.6676639810	0.1793563726
C	0	-3.0162112192	-1.6488239856	1.0072460278
H	0	-3.3357644568	-2.2014061887	1.9026016872
H	0	-3.8657354365	-1.0570509131	0.6544746375
C	0	-1.8556988339	-0.7110021327	1.4366938095
H	0	-2.2005120380	0.0310550677	2.1630102923

bb-PR2

0 1

H	0	4.1199572855	-1.1480325906	-0.8011205116
C	0	3.1056618692	-1.3770663447	-0.4738495173
C	0	1.9086617938	-0.8765548009	-1.2499140067
C	0	2.8080971974	-2.0949411874	0.6155070097
C	0	1.0576739796	0.0162889572	-0.2892235188
H	0	2.2004047834	-0.2837142788	-2.1198967438
C	0	0.7270393329	-0.8328901781	0.9716311923
H	0	3.5479579387	-2.5338686107	1.2882256034
C	0	1.3252589081	-2.2535302628	0.8480074289
H	0	1.0978041278	-2.8223343730	1.7609686644
H	0	1.0490274044	-0.3434618728	1.8999330503
C	0	1.8737371145	1.2583125683	0.1174413184
O	0	3.0657793831	1.3767926846	0.0240782749
O	0	1.0715316940	2.1971058531	0.6498333304
C	0	1.7092484446	3.4031205885	1.0743697048
H	0	2.4773228430	3.1889303017	1.8318403101
H	0	0.9182945385	4.0336340036	1.4972186353
H	0	2.1866116043	3.9033641800	0.2190715753
N	0	-0.2280511427	0.4511469397	-0.8856018267
C	0	-1.3695199174	0.5126963140	0.0283574314
C	0	-0.1395414823	1.2525599805	-1.9987771926
H	0	-1.2668006348	1.3642790463	0.7232628010
S	0	-1.1103091187	-0.9177995503	1.2150832045
C	0	-2.8130802289	0.4799860716	-0.5539932902
H	0	-1.1182472127	1.5885581300	-2.3826545462
O	0	0.9033785630	1.5667224340	-2.5350074755
O	0	-1.4046894542	-0.3840267830	2.5973916465
C	0	-3.7886660473	0.1092098002	0.5881086618
C	0	-3.2539216415	1.8774171956	-1.0438762038
C	0	-2.9344844431	-0.5662817191	-1.6712876907
H	0	-3.6768341834	-0.9362328840	0.9096063967
H	0	-4.8226462498	0.2358727487	0.2344030272
H	0	-3.6404463062	0.7432255497	1.4740920463
H	0	-4.3284568283	1.8587556391	-1.2824153287
H	0	-2.7355766799	2.2228818052	-1.9473031138
H	0	-3.0995999286	2.6309952710	-0.2558539219
H	0	-2.3304675422	-0.3144687787	-2.5543989014
H	0	-3.9827519785	-0.6511155063	-1.9965172841
H	0	-2.6116124954	-1.5568382436	-1.3144648592
C	0	1.0533830977	-2.1000272211	-1.6569476092
H	0	0.1358875442	-1.7575379297	-2.1567120733
H	0	1.6177997708	-2.6907991511	-2.3916791390
C	0	0.7208503078	-2.9440035861	-0.4023574749
H	0	1.1411991423	-3.9565308581	-0.4809128358
H	0	-0.3660761527	-3.0592403518	-0.2764122486

bb-PR3

0 1

H	0	3.9754418118	0.9061384086	0.2611830123
C	0	3.1826916963	0.1652062086	0.1374628952
C	0	2.0750776713	0.0239654382	1.1576868638
C	0	3.0923011795	-0.6669574319	-0.9068443840
C	0	0.7211412446	0.2880196424	0.3938057718
H	0	2.1562693929	0.7339426082	1.9837508816
C	0	0.6404900773	-0.7637242845	-0.7565877395
H	0	3.8028162081	-0.6945799359	-1.7362291070
C	0	1.9265124574	-1.6277235281	-0.8225036238
H	0	1.8740095579	-2.3006213876	-1.6900465205
H	0	0.4977556164	-0.2623231922	-1.7203602836
C	0	0.7480939112	1.7507582819	-0.0911610495
O	0	0.3825656851	2.6805079224	0.5824158868
O	0	1.2430666081	1.8933887675	-1.3302112868
C	0	1.3698720511	3.2343234544	-1.8065500730
H	0	2.0184864408	3.8202692829	-1.1394036384
H	0	1.8108058242	3.1611316316	-2.8075284860
H	0	0.3848220479	3.7224086985	-1.8532448714
N	0	-0.4821277088	0.1137619832	1.2164392152
C	0	-1.6354160262	-0.4474450974	0.5438071893
C	0	-0.5654268852	0.4169632130	2.5571825411
H	0	-2.1971559406	-1.0506517527	1.2706991053
S	0	-0.9366619456	-1.7756909694	-0.5738863453
C	0	-2.6366001269	0.5038205662	-0.1756383973
H	0	-1.5619274276	0.1243688712	2.9649264792
O	0	0.2951595072	0.9090740831	3.2472879884
O	0	-0.7223928466	-2.9630942353	0.3377887648
C	0	-2.1300360710	1.0113520415	-1.5367443768
C	0	-2.9381865742	1.7003895867	0.7401551057
C	0	-3.9240250818	-0.3075380466	-0.4087963735
H	0	-1.9207303440	0.1796312245	-2.2274918668
H	0	-2.9038696255	1.6383086194	-2.0056773605
H	0	-1.2267420887	1.6257038365	-1.4526096873
H	0	-3.7042617219	2.3406781230	0.2751674357
H	0	-3.3309732020	1.3701975004	1.7149030352
H	0	-2.0407692947	2.3096308259	0.9171432822
H	0	-4.3581871904	-0.6478393486	0.5446113035
H	0	-4.6774684085	0.3084670444	-0.9229342701
H	0	-3.7349622285	-1.1961490442	-1.0317934607
C	0	2.1397229405	-2.4230523743	0.4939433778
H	0	1.3860597854	-3.2092456104	0.5907859207
H	0	3.1329574146	-2.8922739044	0.4378753255
C	0	2.0559352747	-1.4368629568	1.6767847625
H	0	1.1302226866	-1.6095117288	2.2411590870
H	0	2.8925213979	-1.5702080953	2.3768855911

bb-PR4

0 1

H	0	2.4535189391	-0.6341240382	2.7349369307
C	0	2.3191673391	-0.7366921836	1.6568711257
C	0	2.1815763276	0.4768562779	0.7762352573
C	0	2.2246636344	-1.9028780602	1.0073535016
C	0	0.7571376361	0.3848068132	0.0902595042
H	0	2.2405762952	1.4101535391	1.3405045073
C	0	0.7317647366	-0.9325055651	-0.7305712141
H	0	2.2761544179	-2.8820103298	1.4819704059
C	0	2.0081386962	-1.7658228032	-0.4820683748
H	0	1.9179290708	-2.7410499768	-0.9787026587
H	0	0.6251814281	-0.7059829336	-1.7993426578
C	0	0.6113595906	1.6034350325	-0.8299030849
O	0	0.9240697506	1.6233105206	-1.9969611527
O	0	0.1545165789	2.6704314620	-0.1682372050

C	0	0.0656976152	3.8904915287	-0.9060645671
H	0	-0.2773895685	4.6498874371	-0.1941559821
H	0	-0.6494433007	3.7890028669	-1.7363009656
H	0	1.0469035952	4.1638204036	-1.3204129532
N	0	-0.3432703749	0.3077685459	1.0628615247
C	0	-1.4686981321	-0.5299450805	0.6961926842
C	0	-0.3238728838	0.8733106081	2.3163242893
H	0	-1.8390384535	-1.0310681106	1.6018474184
S	0	-0.7615296420	-1.9665371433	-0.2738668750
C	0	-2.6757921823	0.1296298493	-0.0328723109
H	0	-1.2030564256	0.5359172568	2.9140803553
O	0	0.5045161311	1.6324275744	2.7640563436
O	0	-0.3335057542	-3.0058849326	0.7353794872
C	0	-3.8392400085	-0.8764514178	0.0238578430
C	0	-3.0728419685	1.4145364270	0.7100427372
C	0	-2.3804525261	0.4640699198	-1.5051326239
H	0	-3.5869443723	-1.8175795158	-0.4891537650
H	0	-4.7316241015	-0.4570689408	-0.4653866319
H	0	-4.1058880274	-1.1188939508	1.0648382558
H	0	-3.9612513871	1.8610962911	0.2364714274
H	0	-2.2614616902	2.1556079778	0.6860357210
H	0	-3.3242931461	1.2114950440	1.7630799354
H	0	-1.6180062838	1.2433857110	-1.6182815660
H	0	-3.2960194805	0.8371215541	-1.9895731969
H	0	-2.0514280770	-0.4227829448	-2.0684531991
C	0	3.1772306090	-0.9410698479	-1.0761055350
H	0	3.0006794872	-0.7745420451	-2.1497680592
H	0	4.1077675850	-1.5189937529	-0.9802558689
C	0	3.2732625432	0.4052096577	-0.3204833339
H	0	3.1872034017	1.2513588635	-1.0156664224
H	0	4.2448533079	0.5036371716	0.1837468691

bb-TS1

0 1

H	0	-0.6288097829	-1.0056749123	2.9095305466
C	0	-1.1241613215	-1.4540251807	2.0452806364
C	0	-0.4236613124	-2.3644469614	1.2289058280
C	0	-1.0062256490	0.2454477564	-0.3947713631
C	0	-0.5988841388	-0.9162587334	-1.0592121882
H	0	0.6038821798	-2.6424067317	1.4761324733
C	0	-0.9586694028	-2.6803217436	-0.0258882311
H	0	-0.3844864733	-3.3567084865	-0.6688264829
H	0	-1.0959731945	-1.2151460799	-1.9845886908
C	0	-2.1819198267	0.9952381880	-0.8606736264
O	0	-3.1264263141	0.4886711293	-1.4382021337
O	0	-2.0845792683	2.3137533932	-0.6261008757
C	0	-3.2100941292	3.1021912885	-0.9977089582
H	0	-2.9577400552	4.1364423433	-0.7343884045
H	0	-3.4117526328	3.0172998103	-2.0762182854
H	0	-4.1079457933	2.7797860990	-0.4489222165
N	0	0.0482958391	0.8800296419	0.3236480000
C	0	1.3352292142	0.7151977835	-0.3531877241
C	0	-0.1839045401	1.6109540449	1.4687633204
H	0	1.3445939087	1.3185392650	-1.2787037087
S	0	1.2333035272	-1.0103416525	-1.1683099176
C	0	2.6723261112	0.8981449071	0.3997233285
H	0	0.7294550059	2.0902372451	1.8614997331
O	0	-1.2581103091	1.7279777387	2.0161095288
O	0	1.6267595348	-0.7804466753	-2.6069213660
C	0	2.9714098295	2.3937851198	0.6424438173
C	0	3.8005141052	0.3793590251	-0.5230449791
C	0	2.7054868020	0.0942511269	1.7096978330
H	0	2.2788900687	2.8819241624	1.3399558657

H	0	3.9836740280	2.5021049001	1.0617722624
H	0	2.9400302324	2.9514160303	-0.3064837244
H	0	4.7756939404	0.6316585306	-0.0803842784
H	0	3.7675317362	-0.7125549893	-0.6490671505
H	0	3.7452683963	0.8278557739	-1.5256523380
H	0	2.4926450224	-0.9677907459	1.5144176132
H	0	3.7060022860	0.1594721957	2.1642702331
H	0	1.9794174263	0.4508476004	2.4529501806
C	0	-2.4670473354	-2.7695247256	-0.1637564624
H	0	-2.7569875109	-2.7126852103	-1.2234265266
H	0	-2.7558146746	-3.7769131096	0.1823745536
C	0	-3.2159126439	-1.6925288375	0.6553443487
H	0	-4.0358476849	-2.1602020910	1.2301474869
H	0	-3.7020635906	-0.9637168532	-0.0097115131
C	0	-2.3474890342	-0.9709777520	1.6374309128
H	0	-2.7853608955	-0.1283254679	2.1738862230

bb-TS2

0 1

H	0	-3.6955390123	-2.2743078460	0.8608964200
C	0	-2.6114504471	-2.3288957287	0.7328130532
C	0	-1.7923549139	-1.8973720804	1.7504113344
C	0	-2.0805078079	-2.6336279284	-0.5346792370
C	0	-0.8452808321	0.3120390900	0.0530376085
H	0	-2.2393839428	-1.4394136180	2.6360475408
C	0	-0.4959005062	-0.5469218618	-1.0191697430
H	0	-2.7489919181	-2.8031407718	-1.3813432927
C	0	-0.6964657128	-2.4231805022	-0.7368968724
H	0	-0.2926709158	-2.7681897840	-1.6960649778
H	0	-1.0787669716	-0.4802044661	-1.9391046997
C	0	-2.2470969199	0.6039379439	0.4150769891
O	0	-2.6688215342	1.0564296015	1.4545967739
O	0	-3.0542273135	0.2756042070	-0.6314609818
C	0	-4.4453480834	0.4588362264	-0.4042609772
H	0	-4.7903033640	-0.1569913049	0.4412380956
H	0	-4.9515406102	0.1551649276	-1.3290771420
H	0	-4.6666692334	1.5110654571	-0.1721051113
N	0	0.2176734789	0.9602968532	0.7225878398
C	0	1.5218368623	0.8412425678	0.0150612499
C	0	0.0012453899	2.3051972345	1.1578796704
H	0	1.6652521000	1.7563817376	-0.5838646404
S	0	1.2918902275	-0.3704795067	-1.4225797543
C	0	2.8454858676	0.5812385658	0.7876090276
H	0	0.8520149550	2.6790369835	1.7555779981
O	0	-0.9494300561	2.9826319549	0.8853920263
O	0	1.4185483572	0.4525664283	-2.6784293259
C	0	2.9645170472	-0.8336793964	1.3679507279
C	0	3.9815765672	0.8006704570	-0.2330868227
C	0	3.0303747667	1.5867581501	1.9373264127
H	0	2.1570912882	-1.0505230689	2.0788895211
H	0	3.9184536370	-0.9286906939	1.9085519896
H	0	2.9602148005	-1.5950110766	0.5763023165
H	0	4.9556536899	0.6137113319	0.2434844101
H	0	3.9800636050	1.8327428224	-0.6164917398
H	0	3.8973152823	0.1286891484	-1.1008067213
H	0	2.9889408203	2.6285865579	1.5847578675
H	0	4.0189828430	1.4338740695	2.3971401253
H	0	2.2742009220	1.4460008548	2.7238858367
C	0	-0.3168136912	-2.1387271415	1.7716677989
H	0	0.1936843345	-1.1870695313	1.9966202446
H	0	-0.0689673950	-2.7998863934	2.6221879023
C	0	0.1787533339	-2.7775425577	0.4616590757
H	0	0.1491534348	-3.8754063284	0.5574414736

H	0	1.2254929307	-2.5191837746	0.2670590294

bb-TS3

0 1

H	0	4.0483333500	0.9040716622	-0.0644132102
C	0	3.3996401183	0.0477837593	0.1325217595
C	0	2.6199829900	0.0271537454	1.2769771864
C	0	3.1763642056	-0.8980920220	-0.8806410894
C	0	0.4637417522	0.5438444200	-0.0709352719
H	0	2.6469951890	0.8666495707	1.9725859794
C	0	0.5421662373	-0.5055409243	-1.0128975946
H	0	3.6335653075	-0.7542685843	-1.8633064737
C	0	2.1376578332	-1.8247077617	-0.7012891431
H	0	1.9144421025	-2.5317638931	-1.5057623147
H	0	0.8195965142	-0.2503787944	-2.0345264747
C	0	0.8544188784	1.9262855430	-0.4064846509
O	0	0.3852731191	2.9281447575	0.0835251731
O	0	1.7697154642	1.9519338884	-1.4055767768
C	0	2.2141462345	3.2446084609	-1.8028873502
H	0	2.7079911235	3.7624365787	-0.9662676939
H	0	2.9244344104	3.0857411199	-2.6237700602
H	0	1.3702482402	3.8647578292	-2.1407437350
N	0	-0.5522474209	0.3640653700	0.9015798630
C	0	-1.6647721881	-0.4612858752	0.4596670484
C	0	-0.4709901380	0.8271215599	2.2004300652
H	0	-1.9298960922	-1.2136874237	1.2181234549
S	0	-0.9971603682	-1.5169372804	-0.9724123094
C	0	-2.9242883361	0.3195671920	-0.0013312956
H	0	-1.3461620128	0.4971445612	2.8035651458
O	0	0.4303820955	1.4888403819	2.6583680085
O	0	-0.7831898004	-2.9228252453	-0.4639125275
C	0	-2.5890249255	1.2537769788	-1.1761081000
C	0	-3.4647053122	1.1691525438	1.1614488619
C	0	-3.9971093773	-0.7032932693	-0.4116811050
H	0	-2.1955514266	0.6966271132	-2.0406121731
H	0	-3.4985524255	1.7789287241	-1.5064988312
H	0	-1.8523030890	2.0128671784	-0.8772546961
H	0	-4.4025224416	1.6576673135	0.8543440078
H	0	-3.6843741794	0.5538734153	2.0487656420
H	0	-2.7594619751	1.9627806760	1.4472779802
H	0	-4.2498453579	-1.3739081470	0.4253702485
H	0	-4.9173513135	-0.1822537978	-0.7169000930
H	0	-3.6727432282	-1.3274005324	-1.2582652450
C	0	1.9294040270	-2.3520962559	0.7049007548
H	0	0.9884758869	-2.9087328644	0.7537413636
H	0	2.7470479275	-3.0728564868	0.8788466005
C	0	1.9841423683	-1.2389455985	1.7699467552
H	0	0.9843863539	-1.0307254510	2.1756090910
H	0	2.5665773794	-1.5792091858	2.6444908356

bb-TS4

0 1

H	0	2.1015350779	-0.3459872382	2.7501805627
C	0	2.3893098719	-0.5371914410	1.7143880663
C	0	2.9166844286	0.4868063809	0.9639176399
C	0	2.0244985864	-1.7528886033	1.0985603839
C	0	0.4059689154	0.5023016816	-0.3384100730
H	0	3.0003467362	1.4789195207	1.4129910583
C	0	0.5948516049	-0.7333979637	-0.9740155454
H	0	1.4535640434	-2.5081715064	1.6397478114
C	0	2.1668505982	-1.8703238110	-0.2904344889
H	0	1.8692700670	-2.8232653355	-0.7358054440

H	0	0.8984037714	-0.7247169584	-2.0237445350
C	0	0.7222959024	1.7712862875	-0.9894524805
O	0	1.4981525595	1.8917764680	-1.9222364809
O	0	0.0245402957	2.8065639212	-0.4793020109
C	0	0.3344296222	4.0915269865	-1.0061979308
H	0	-0.3130655988	4.8016123638	-0.4777591918
H	0	0.1455667734	4.1303858470	-2.0897409850
H	0	1.3918168515	4.3394288661	-0.8283655950
N	0	-0.4739358919	0.4213255010	0.7711347992
C	0	-1.5248449900	-0.5671265765	0.6056652182
C	0	-0.2942552104	1.0792850242	1.9691648367
H	0	-1.6593297504	-1.1569174012	1.5246906520
S	0	-0.8392380287	-1.8482429680	-0.6128955975
C	0	-2.8861266206	-0.0123085702	0.1124949736
H	0	-1.0466670618	0.7533013307	2.7232103088
O	0	0.5637352159	1.8967170744	2.2076955180
O	0	-0.4266943733	-3.0584121971	0.1923434204
C	0	-3.8805929192	-1.1826795022	0.0342252234
C	0	-3.4066525111	1.0233912906	1.1235080261
C	0	-2.7452004810	0.6640127320	-1.2611539577
H	0	-3.5627458016	-1.9457098987	-0.6926234765
H	0	-4.8707378485	-0.8173705801	-0.2785795517
H	0	-3.9953440363	-1.6753251423	1.0131678576
H	0	-4.4046565437	1.3730855196	0.8164425282
H	0	-2.7480851474	1.9025989595	1.1754120723
H	0	-3.4995893059	0.5939553335	2.1339830310
H	0	-2.0703957268	1.5293256089	-1.2069742564
H	0	-3.7285916076	1.0219172456	-1.6037775334
H	0	-2.3615525229	-0.0335371582	-2.0216802858
C	0	3.3312180829	-1.1450753902	-0.9402046071
H	0	3.2005799938	-1.1009150713	-2.0322247420
H	0	4.2239001077	-1.7700961580	-0.7637816051
C	0	3.5593813926	0.2722182008	-0.3695999525
H	0	3.2081810055	1.0442485437	-1.0729075429
H	0	4.6420413936	0.4605535538	-0.2518302079

bc-PR1

0 1

H	0	-1.1442547494	-1.4274533792	3.1488523779
C	0	-1.2864174108	-1.6265387789	2.0852079431
C	0	-0.7008427538	-2.6227671640	1.4103558935
C	0	-1.1936031050	-0.1073563851	0.1480005491
C	0	-0.6983864780	-1.3063702127	-0.7079185549
H	0	-0.0196695176	-3.3520998961	1.8499388424
C	0	-1.0488471996	-2.6604486364	-0.0579609826
H	0	-0.5324971059	-3.4684698670	-0.5921953076
H	0	-1.1083024859	-1.2479612283	-1.7224364538
C	0	-1.9650049494	0.8741126748	-0.7504290040
O	0	-2.7477693968	0.5273946618	-1.6017481410
O	0	-1.6854179116	2.1506049525	-0.4754294504
C	0	-2.4130134695	3.1337149975	-1.2169430356
H	0	-2.0524352344	4.1067369572	-0.8643500955
H	0	-2.2288563522	3.0171226567	-2.2948866607
H	0	-3.4920821769	3.0327369867	-1.0307652520
N	0	-0.0064925388	0.5560776895	0.7402692274
C	0	1.1211779878	0.6200369250	-0.1790528512
C	0	-0.1105736556	1.3459227879	1.8636395336
H	0	0.8561279021	1.2402197050	-1.0552555417
S	0	1.0937082375	-1.0827778243	-0.9370390806
C	0	2.5401921731	1.0466228487	0.2933021541
H	0	0.8431154068	1.8353501400	2.1208402880
O	0	-1.1045779238	1.5064034672	2.5369060959
O	0	1.8264329281	-2.0556147119	-0.1069750043

O	0	1.3883768931	-0.9721117172	-2.3727229638
C	0	2.6085888252	2.5851023854	0.4104494380
C	0	3.5427871470	0.6512748902	-0.8169271310
C	0	2.9731605486	0.3573591728	1.6000060255
H	0	1.9452809639	3.0070490553	1.1766907340
H	0	3.6365745148	2.8836142914	0.6671287392
H	0	2.3530933519	3.0590711807	-0.5504393929
H	0	4.5244334876	1.0869048089	-0.5791197964
H	0	3.6669150767	-0.4369506473	-0.8891664994
H	0	3.2307130900	1.0248679289	-1.8032065881
H	0	2.8619921349	-0.7310394061	1.5167268729
H	0	4.0329918584	0.5857026003	1.7912051936
H	0	2.4055153768	0.6948910482	2.4773261275
C	0	-2.5868095650	-2.7827007222	-0.1923375918
H	0	-2.8632720267	-2.7733960955	-1.2578297846
H	0	-2.9082307242	-3.7480448287	0.2239597353
C	0	-3.2401552111	-1.5980348429	0.5562162611
H	0	-3.9100499046	-1.9568181737	1.3504522159
H	0	-3.8436558769	-0.9871374078	-0.1267059163
C	0	-2.1552701804	-0.7284653911	1.2396110868
H	0	-2.6027193304	0.0790986837	1.8202693352

bc-PR2

0 1

H	0	-3.7869422647	-2.2873707984	1.6970164583
C	0	-2.7500156842	-2.3263363749	1.3619068522
C	0	-1.7526824737	-1.2779647513	1.8028823646
C	0	-2.2468183593	-3.2823814386	0.5711641681
C	0	-1.1709614787	-0.5785768547	0.5318609681
H	0	-2.2037260347	-0.5165136271	2.4439647015
C	0	-0.7454380368	-1.6956780506	-0.4543375709
H	0	-2.8200207312	-4.1233996881	0.1750421249
C	0	-0.7864029874	-3.0815823913	0.2324539243
H	0	-0.3918317443	-3.8399014515	-0.4554066699
H	0	-1.3886445100	-1.7086386490	-1.3419571011
C	0	-2.2602500004	0.2703703670	-0.1483549370
O	0	-3.4437466596	0.1101021781	-0.0184375483
O	0	-1.7069033773	1.1598931161	-0.9880835438
C	0	-2.6124116028	1.9814890067	-1.7280719280
H	0	-3.3069229839	1.3606656967	-2.3122163060
H	0	-1.9931030198	2.5944340021	-2.3929996510
H	0	-3.1934048220	2.6171317914	-1.0438956791
N	0	0.0107670758	0.2822220795	0.8346053577
C	0	1.1401532575	0.3019353401	-0.1034419714
C	0	-0.2945934086	1.4348285949	1.5273792367
H	0	0.9892670356	1.0938269702	-0.8539518240
S	0	0.8648893319	-1.2158651243	-1.1643456018
C	0	2.5955687007	0.4072590619	0.4438393704
H	0	0.5279540195	2.1705697007	1.5512852133
O	0	-1.3662613802	1.6474761189	2.0544817002
O	0	0.6702448696	-0.7369887858	-2.5380273877
O	0	1.8411738660	-2.2900302547	-0.9079697784
C	0	3.5454032519	0.2989239291	-0.7697538038
C	0	2.8467260512	1.7911219923	1.0806932996
C	0	2.9172517420	-0.6704421702	1.4886067221
H	0	3.4803387036	-0.6776848375	-1.2642274298
H	0	4.5836387429	0.4353167848	-0.4320818443
H	0	3.3278345761	1.0827094970	-1.5127935867
H	0	3.9301841382	1.9218281367	1.2233640545
H	0	2.3836548738	1.8922638673	2.0719755179
H	0	2.4958677898	2.6139207075	0.4373053494
H	0	2.2002427769	-0.6341223489	2.3220632824
H	0	3.9209264742	-0.4907698305	1.9034904610

H	0	2.9033636480	-1.6742547180	1.0498031385
C	0	-0.5990034427	-2.0170937089	2.5179599027
H	0	0.1541657025	-1.2930944015	2.8567611236
H	0	-1.0076982031	-2.5002813696	3.4163627938
C	0	0.0183261248	-3.0583331602	1.5552893976
H	0	-0.0119146024	-4.0665321568	1.9920063919
H	0	1.0692961853	-2.8382888565	1.3382773677

bc-PR3

0 1

H	0	3.9812489045	0.9037212297	0.2523107161
C	0	3.1968911588	0.1526269622	0.1381120455
C	0	2.0762415367	0.0307573051	1.1476289864
C	0	3.1324130195	-0.7145489297	-0.8791854194
C	0	0.7307666373	0.2660363649	0.3605092355
H	0	2.1422651502	0.7641093858	1.9537824219
C	0	0.6905323863	-0.8016867686	-0.7730376600
H	0	3.8563314333	-0.7649194942	-1.6954283632
C	0	1.9689334494	-1.6772730932	-0.7855534480
H	0	1.9240555916	-2.3717191406	-1.6354797912
H	0	0.5612222176	-0.3277790966	-1.7504846364
C	0	0.7538473154	1.7213402652	-0.1449280212
O	0	0.3979672939	2.6570967424	0.5246508707
O	0	1.2389119749	1.8407703636	-1.3871212168
C	0	1.3582761023	3.1718531274	-1.8938806297
H	0	2.0097343508	3.7736623651	-1.2439665279
H	0	1.7916010634	3.0774360291	-2.8962179206
H	0	0.3709047043	3.6544655988	-1.9446366742
N	0	-0.4892110352	0.0947202958	1.1784806383
C	0	-1.6649210981	-0.4357517250	0.5114339697
C	0	-0.5739686118	0.4064256415	2.5202044672
H	0	-2.2257030579	-1.0419382603	1.2365906352
S	0	-0.8880455643	-1.7299936459	-0.5671442016
C	0	-2.6684775673	0.5364451451	-0.1745556137
H	0	-1.5710755465	0.1186419030	2.9276547706
O	0	0.2866983220	0.8986431890	3.2078771545
O	0	-1.5265582190	-1.8774986370	-1.8845521707
O	0	-0.7273253344	-2.9171897698	0.2865079699
C	0	-2.1545375754	1.1817766287	-1.4732152263
C	0	-3.0109367897	1.6477707578	0.8323188279
C	0	-3.9313068271	-0.2888713532	-0.4864899906
H	0	-1.8609911129	0.4293271891	-2.2155072314
H	0	-2.9625948405	1.7873120236	-1.9115287571
H	0	-1.3172103273	1.8640492729	-1.2900633208
H	0	-3.7829277303	2.3047286532	0.4025827640
H	0	-3.4139316935	1.2367015125	1.7716091140
H	0	-2.1311829456	2.2644908750	1.0669766996
H	0	-4.3618489158	-0.7165529382	0.4336629457
H	0	-4.6967435426	0.3535787192	-0.9475058533
H	0	-3.7079386987	-1.1098712770	-1.1820289605
C	0	2.1584720063	-2.4341298827	0.5555345955
H	0	1.4044578354	-3.2186789250	0.6657798335
H	0	3.1475350815	-2.9134226773	0.5240592426
C	0	2.0730899022	-1.4136002868	1.7099074542
H	0	1.1608199138	-1.5752615050	2.2982677802
H	0	2.9205107026	-1.5158670894	2.4019794862

bc-PR4

0 1

H	0	2.4303246748	-0.5925089142	2.7669125871
C	0	2.3193650180	-0.7105617746	1.6877791191
C	0	2.1645581372	0.4901507665	0.7908197603

C	0	2.2807698925	-1.8853065722	1.0487912623
C	0	0.7620398807	0.3576362478	0.0738345967
H	0	2.1889570503	1.4298279952	1.3457053862
C	0	0.7961538482	-0.9693746667	-0.7274615593
H	0	2.3574756472	-2.8571020124	1.5364387512
C	0	2.0852141396	-1.7700822823	-0.4447416003
H	0	2.0238068817	-2.7490129948	-0.9385476911
H	0	0.6807447034	-0.7759460402	-1.8000567387
C	0	0.6150016942	1.5581779365	-0.8701563346
O	0	0.9237206888	1.5504970456	-2.0370365449
O	0	0.1740207551	2.6381512336	-0.2209536771
C	0	0.0826112832	3.8464261212	-0.9795821961
H	0	-0.2636121500	4.6162842423	-0.2807521009
H	0	-0.6311178596	3.7276371210	-1.8084755563
H	0	1.0639881848	4.1148417218	-1.3966559606
N	0	-0.3686027563	0.2766865853	1.0280592515
C	0	-1.5101477819	-0.5381210497	0.6490997408
C	0	-0.3652313971	0.8404104055	2.2861537511
H	0	-1.8889580808	-1.0404351514	1.5503133122
S	0	-0.6901051716	-1.9337217682	-0.2634120325
C	0	-2.7159382379	0.1391084353	-0.0628651745
H	0	-1.2465127457	0.4947703052	2.8744526304
O	0	0.4520332940	1.6046030960	2.7416932832
O	0	-1.4051709285	-2.3367949878	-1.4851251968
O	0	-0.3457922958	-2.9535474203	0.7374687300
C	0	-3.8517239112	-0.9003827280	-0.1097414249
C	0	-3.1576774706	1.3354693438	0.7977838401
C	0	-2.4117475300	0.6392919315	-1.4845116772
H	0	-3.5692786567	-1.7731395035	-0.7135333901
H	0	-4.7528599935	-0.4511601333	-0.5540762385
H	0	-4.1142311408	-1.2449407252	0.9039619967
H	0	-4.0522339480	1.7971448823	0.3519737199
H	0	-2.3721907067	2.1033369451	0.8536620303
H	0	-3.4193893882	1.0284364950	1.8228777405
H	0	-1.7116273686	1.4825403255	-1.4776916130
H	0	-3.3434018405	1.0051945319	-1.9427223628
H	0	-2.0141225414	-0.1567092428	-2.1255276594
C	0	3.2383169009	-0.9173219764	-1.0298087097
H	0	3.0698331485	-0.7638750256	-2.1063710859
H	0	4.1836397533	-1.4670862891	-0.9179340012
C	0	3.2827435458	0.4357608526	-0.2816482949
H	0	3.1924926704	1.2751195603	-0.9844345204
H	0	4.2390910886	0.5623901017	0.2446318222

bc-TS1

0 1

H	0	-0.8376628749	-0.9973855412	2.9594030908
C	0	-1.2819735816	-1.4664975277	2.0790902694
C	0	-0.5260244322	-2.3799767855	1.3142901694
C	0	-0.9820710179	0.2182998873	-0.3772522711
C	0	-0.6063638247	-0.9624993410	-1.0220213111
H	0	0.4953475970	-2.6258069317	1.6055087918
C	0	-0.9898402158	-2.7452422024	0.0492810019
H	0	-0.3642376253	-3.4156674287	-0.5460922863
H	0	-1.1203237690	-1.2633185748	-1.9361565538
C	0	-2.1345177686	0.9972643212	-0.8519116788
O	0	-3.0701854322	0.5208432707	-1.4680546863
O	0	-2.0233461783	2.3068611532	-0.5781713962
C	0	-3.1257929260	3.1239815743	-0.9593386536
H	0	-2.8653046239	4.1459198239	-0.6588891807
H	0	-3.2965453596	3.0727316472	-2.0452183348
H	0	-4.0439439652	2.8001599451	-0.4463560041
N	0	0.0801744698	0.8341480668	0.3561329323

C	0	1.3629730650	0.7240133587	-0.3441770773
C	0	-0.1522603195	1.5428670622	1.5174882822
H	0	1.3379003021	1.3773318601	-1.2325861444
S	0	1.1959746362	-0.9568507814	-1.1838538901
C	0	2.7166885834	0.9236705801	0.3774381648
H	0	0.7609571504	2.0173762673	1.9161589745
O	0	-1.2260072215	1.6441838393	2.0662708726
O	0	1.8426604729	-2.0377550816	-0.4169799933
O	0	1.5365008135	-0.7908579328	-2.6033328971
C	0	2.9657062946	2.4303522140	0.6103929841
C	0	3.8275023368	0.4424198713	-0.5863556902
C	0	2.8155628046	0.1330164055	1.6927144124
H	0	2.2688455770	2.8934011240	1.3211541633
H	0	3.9807440424	2.5715583447	1.0121488815
H	0	2.8997549078	2.9883244129	-0.3368534234
H	0	4.8082271295	0.7114191104	-0.1669037543
H	0	3.8069665162	-0.6456754882	-0.7256447786
H	0	3.7375625806	0.9182063253	-1.5747212711
H	0	2.6483757780	-0.9364808979	1.5132828527
H	0	3.8236821271	0.2579837136	2.1170365165
H	0	2.0967372240	0.4753603343	2.4500453399
C	0	-2.4867385881	-2.8347296683	-0.1698573920
H	0	-2.7207158039	-2.8265766419	-1.2451543197
H	0	-2.7978999689	-3.8264058134	0.2018286521
C	0	-3.2778871858	-1.7241588469	0.5598435271
H	0	-4.1579895684	-2.1585154780	1.0677657976
H	0	-3.6869995197	-0.9955150632	-0.1565332481
C	0	-2.4820393401	-0.9999316545	1.5985938171
H	0	-2.9502026177	-0.1464106722	2.0920603225

bc-TS2

0 1

H	0	-4.0708408436	-1.3746082872	0.8397670502
C	0	-3.0002177557	-1.5945253474	0.8404186772
C	0	-2.2141992005	-1.1051885259	1.8557689436
C	0	-2.4223113108	-2.2022359185	-0.2920650369
C	0	-0.6977845306	0.5721492773	-0.2220992658
H	0	-2.6575267624	-0.4360385368	2.5973924549
C	0	-0.5335416195	-0.5645766698	-1.0606096318
H	0	-3.0443194423	-2.4330949257	-1.1600065598
C	0	-1.0071308341	-2.2425543866	-0.3847554589
H	0	-0.5926071528	-2.8521211680	-1.1943861169
H	0	-1.1205097309	-0.5826559667	-1.9807929219
C	0	-2.0160760524	1.1647770510	0.0687072986
O	0	-2.3120679046	1.8742750414	1.0031278733
O	0	-2.8978392576	0.8013326496	-0.9024880392
C	0	-4.2260752940	1.2746430930	-0.7209622670
H	0	-4.6563759627	0.8868000042	0.2159141591
H	0	-4.8022389680	0.9153168547	-1.5826416640
H	0	-4.2440365446	2.3734654209	-0.6760144826
N	0	0.4705614561	1.2046666139	0.2770714368
C	0	1.7541552304	0.6957073650	-0.2588930856
C	0	0.4669551546	2.6335017438	0.3250765868
H	0	2.1537131957	1.4550175662	-0.9477669354
S	0	1.2234466195	-0.5958419655	-1.5148410133
C	0	2.9335855944	0.3175395527	0.6810734743
H	0	1.3975292489	3.0221831809	0.7798006301
O	0	-0.3996437897	3.3435544393	-0.0997642437
O	0	1.3721672051	0.0121676747	-2.8411956993
C	0	2.6936039664	-0.8861537945	1.5972013813
C	0	4.1451688068	0.0373870774	-0.2315817158
C	0	3.2626112776	1.5336801884	1.5677956471
H	0	1.8017878007	-0.7439278369	2.2210787287

H	0	3.5542645516	-0.9963488351	2.2743411099
H	0	2.5988005056	-1.8134819668	1.0227609062
H	0	5.0289887140	-0.1845689442	0.3852395188
H	0	4.3842524410	0.9111172260	-0.8589131867
H	0	3.9651148978	-0.8246509572	-0.8879336767
H	0	3.4834047396	2.4329221677	0.9716824545
H	0	4.1571308294	1.3096944935	2.1685289023
H	0	2.4418992605	1.7613538048	2.2643711346
C	0	-0.7918055632	-1.5187114636	2.0610840707
H	0	-0.1665811014	-0.6148313048	2.1552826731
H	0	-0.7018516310	-2.0220818822	3.0414040681
C	0	-0.3060895260	-2.4655531556	0.9516391990
H	0	-0.5364932813	-3.5040443130	1.2410587413
H	0	0.7761216413	-2.4183421046	0.8243973011
O	0	1.8354839226	-1.9103802300	-1.2569914207

bc-TS3

0 1

H	0	3.9302587596	1.0621705241	0.0488578358
C	0	3.3544850887	0.1430103759	0.1774346236
C	0	2.5738514805	-0.0238122031	1.3110677735
C	0	3.1952863002	-0.7333249252	-0.9071773318
C	0	0.4298027438	0.4598839277	0.0065857553
H	0	2.5263579148	0.7648698020	2.0616759682
C	0	0.5078366262	-0.5951160291	-0.9279610349
H	0	3.6104454482	-0.4681339789	-1.8827036366
C	0	2.2738893942	-1.7823544492	-0.7767306480
H	0	2.0992720372	-2.4377929314	-1.6353630863
H	0	0.6543336992	-0.3743276904	-1.9831517066
C	0	0.8030343637	1.8437902675	-0.3396576618
O	0	0.4001311300	2.8406851525	0.2135472134
O	0	1.6260730647	1.8718620214	-1.4146262269
C	0	2.0713881252	3.1627100139	-1.8203363694
H	0	2.6541547136	3.6434901517	-1.0195368425
H	0	2.6987071071	3.0058298886	-2.7063359271
H	0	1.2183247299	3.8130088128	-2.0643147455
N	0	-0.5987210053	0.2851218018	0.9795581763
C	0	-1.7634848649	-0.4594759854	0.5113294096
C	0	-0.5186861043	0.7119142657	2.2924143521
H	0	-2.1347923357	-1.1227395407	1.3051482907
S	0	-0.9479190662	-1.6477708007	-0.6877157114
C	0	-2.9295276353	0.3876339034	-0.0575141889
H	0	-1.4290145171	0.4254247059	2.8649294760
O	0	0.4091343058	1.3024533654	2.7889738348
O	0	-1.6344827734	-1.7541793336	-1.9840106182
O	0	-0.6757735156	-2.8759421738	0.0731424404
C	0	-2.5121718634	1.2224655799	-1.2799736853
C	0	-3.4015371594	1.3497631890	1.0483954438
C	0	-4.0792371563	-0.5713811631	-0.4154215659
H	0	-2.1476149787	0.5906779845	-2.0997457162
H	0	-3.3852791002	1.7831887829	-1.6480512681
H	0	-1.7425758957	1.9586424653	-1.0096489123
H	0	-4.2840203219	1.9038332980	0.6934465941
H	0	-3.6942980161	0.8112805626	1.9642433742
H	0	-2.6266865485	2.0878614383	1.3020186343
H	0	-4.4024539304	-1.1464792998	0.4680425390
H	0	-4.9461823883	0.0043698696	-0.7737302353
H	0	-3.7856956742	-1.2768931549	-1.2035002736
C	0	2.1971755729	-2.4219820001	0.5950016998
H	0	1.3957438813	-3.1644792278	0.6376755416
H	0	3.1551479191	-2.9524324404	0.7361476810
C	0	2.0218961967	-1.3664385809	1.6983618558
H	0	0.9633760297	-1.2785612211	1.9856791322

H	0	2.5363392187	-1.6903920211	2.6194407469

bc-TS4

0 1

H	0	2.1441448941	-0.3369649641	2.7394941548
C	0	2.4416192043	-0.5284145294	1.7066828024
C	0	2.9036616348	0.5118014312	0.9346157433
C	0	2.1423276067	-1.7692700244	1.1085132774
C	0	0.4189815446	0.4443335247	-0.3047100521
H	0	2.9280151944	1.5152992033	1.3645774592
C	0	0.6159538008	-0.7877559090	-0.9370403736
H	0	1.6181665759	-2.5406065490	1.6731852544
C	0	2.2699073561	-1.8948051297	-0.2785713337
H	0	1.9959446662	-2.8545992622	-0.7256851980
H	0	0.8644458275	-0.8168697456	-1.9992089899
C	0	0.7194796623	1.7121467264	-0.9751893020
O	0	1.4658517693	1.8176347927	-1.9315457914
O	0	0.0489059786	2.7514937126	-0.4466441682
C	0	0.3197171151	4.0285934186	-1.0162655749
H	0	-0.2954743234	4.7456185259	-0.4598410819
H	0	0.0594287929	4.0448260938	-2.0853148381
H	0	1.3855483397	4.2814630679	-0.9127876768
N	0	-0.4911379416	0.3688438086	0.7900310901
C	0	-1.5842110882	-0.5818420081	0.6090937679
C	0	-0.3256790502	1.0280745949	1.9915256504
H	0	-1.7612369756	-1.1387764057	1.5398138721
S	0	-0.7797348646	-1.8662326918	-0.5026504392
C	0	-2.9181005100	0.0104938298	0.0880776066
H	0	-1.1037817275	0.7252748474	2.7275382732
O	0	0.5465274968	1.8232968043	2.2483374563
O	0	-1.5288943690	-2.1239059329	-1.7432657505
O	0	-0.4150048331	-3.0068949448	0.3502174243
C	0	-3.9409535794	-1.1351007257	-0.0185068881
C	0	-3.4218551625	1.0315466669	1.1254525097
C	0	-2.7496773187	0.7294520693	-1.2604812163
H	0	-3.6333132431	-1.8833530633	-0.7602036616
H	0	-4.9194126918	-0.7326728256	-0.3221933788
H	0	-4.0740218924	-1.6374875078	0.9539443584
H	0	-4.4105620466	1.4044237127	0.8167937243
H	0	-2.7509200147	1.8996678059	1.2031465382
H	0	-3.5336466450	0.5810040586	2.1250187438
H	0	-2.0570976247	1.5772796863	-1.1656159705
H	0	-3.7236732886	1.1298794701	-1.5820901694
H	0	-2.3862583205	0.0493741451	-2.0404079407
C	0	3.3751047106	-1.1172212261	-0.9663445918
H	0	3.1932748148	-1.0645341337	-2.0503255114
H	0	4.2982533952	-1.7086446825	-0.8398504978
C	0	3.5734654457	0.3028287606	-0.3861822874
H	0	3.2308391210	1.0705278906	-1.0967614900
H	0	4.6503115636	0.5035366135	-0.2397855327

ca-PR1

0 1

H	0	1.4740110000	-3.3908870000	0.2605850000
C	0	0.9079880000	-2.5339410000	0.6325820000
C	0	-0.3422970000	-2.6936420000	1.0657000000
C	0	0.6958690000	0.0158800000	0.7212060000
C	0	-0.4779100000	-0.2201290000	1.7066080000
H	0	-0.8021050000	-3.6851430000	1.0277330000
C	0	-1.2422750000	-1.5807840000	1.5444350000
H	0	-0.0603690000	-0.1773190000	2.7195040000
C	0	1.5952790000	1.1400590000	1.2943940000

O	0	1.8918950000	1.2179910000	2.4608270000
O	0	2.0909910000	1.9383640000	0.3456210000
C	0	3.0499080000	2.9091730000	0.7694660000
H	0	3.2745950000	3.5179340000	-0.1139670000
H	0	2.6413600000	3.5299150000	1.5797450000
H	0	3.9617040000	2.4082540000	1.1253100000
N	0	0.0325930000	0.4850300000	-0.5129780000
C	0	-0.7647040000	1.6754420000	-0.1914870000
C	0	-0.1196940000	-0.2441680000	-1.6550930000
H	0	-0.0560770000	2.4912190000	-0.0098310000
S	0	-1.4972360000	1.2911040000	1.5040650000
C	0	-1.8099370000	2.2760980000	-1.1700180000
H	0	-0.7496870000	0.2736580000	-2.3962200000
O	0	0.3582140000	-1.3357270000	-1.8911370000
C	0	-1.1013060000	2.8232220000	-2.4272970000
C	0	-2.4047120000	3.4964840000	-0.4297390000
C	0	-2.9713930000	1.3413260000	-1.5335960000
H	0	-0.6859820000	2.0399210000	-3.0750930000
H	0	-1.8177680000	3.4006220000	-3.0318950000
H	0	-0.2753510000	3.4974670000	-2.1502160000
H	0	-3.0740180000	4.0492760000	-1.1057860000
H	0	-2.9947680000	3.1897490000	0.4465400000
H	0	-1.6174050000	4.1888120000	-0.0910720000
H	0	-3.4283910000	0.9188500000	-0.6294400000
H	0	-3.7432380000	1.9101140000	-2.0753980000
H	0	-2.6764020000	0.5022010000	-2.1746970000
C	0	1.6499870000	-1.2303890000	0.7397490000
H	0	1.9715670000	-1.1944870000	1.7946210000
H	0	-1.5573210000	-1.8344180000	2.5716040000
C	0	2.9626590000	-1.1219620000	-0.0313450000
C	0	3.1525630000	-1.6217640000	-1.3274850000
C	0	4.0664630000	-0.5460550000	0.6230220000
C	0	4.3964390000	-1.5162210000	-1.9566100000
H	0	2.3156360000	-2.0774000000	-1.8499170000
C	0	5.3066290000	-0.4312100000	-0.0070280000
H	0	3.9542640000	-0.1913140000	1.6503670000
C	0	5.4757240000	-0.9133890000	-1.3072300000
H	0	4.5195280000	-1.9120070000	-2.9679780000
H	0	6.1462360000	0.0214710000	0.5266970000
H	0	6.4454450000	-0.8324680000	-1.8045680000
C	0	-2.5371260000	-1.5669550000	0.7333580000
C	0	-3.7300590000	-1.1290030000	1.3300600000
C	0	-2.5883500000	-2.0411480000	-0.5840130000
C	0	-4.9350400000	-1.1455280000	0.6276610000
H	0	-3.7125250000	-0.7673380000	2.3608590000
C	0	-3.7956950000	-2.0649810000	-1.2898120000
H	0	-1.6760260000	-2.3940040000	-1.0646400000
C	0	-4.9723290000	-1.6148600000	-0.6898570000
H	0	-5.8505820000	-0.7970040000	1.1119550000
H	0	-3.8117810000	-2.4391300000	-2.3165630000
H	0	-5.9158160000	-1.6337570000	-1.2407160000

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0 1

H	0	3.6939540715	-1.5036425734	-1.1778736471
C	0	2.6968267841	-1.4838215926	-0.7357933004
C	0	1.6718179244	-0.5079479696	-1.2574472591
C	0	2.3304467381	-2.3164121921	0.2428982847
C	0	1.0530542866	0.2890770554	-0.0552451349
C	0	0.6272565601	-0.7066661210	1.0837936194
H	0	3.0095322621	-3.0658198072	0.6554499390
C	0	0.9254514771	-2.2041919715	0.7900551917
H	0	1.1908361712	-0.4558418150	1.9901858511

C	0	2.0981477289	1.2122133940	0.6053911443
O	0	3.2899351937	1.1210155567	0.4633970773
O	0	1.5123871080	2.0317911602	1.4889539233
C	0	2.3697089375	2.9732967248	2.1315393101
H	0	3.1873600941	2.4618293826	2.6603386044
H	0	1.7402685572	3.5264636858	2.8388098302
H	0	2.7996059037	3.6574711819	1.3848838458
N	0	-0.1290861260	1.0631409116	-0.4604744967
C	0	-1.4471616778	0.6624901694	0.0290498817
C	0	0.0481358733	2.3434645710	-0.9246553222
H	0	-1.9502015477	1.5680670623	0.4033035094
S	0	-1.1238649503	-0.3745476624	1.5134026996
C	0	-2.4303468288	0.0215674216	-0.9987850504
H	0	-0.9138768080	2.8875266904	-1.0449456647
O	0	1.1200255144	2.8528293167	-1.1676056267
C	0	-3.7830831046	-0.1414989486	-0.2839792025
C	0	-2.6061245972	0.9773367121	-2.1908760842
C	0	-1.9683383369	-1.3459241959	-1.5103280541
H	0	-3.7003067268	-0.8307434648	0.5703269316
H	0	-4.5352231456	-0.5487120177	-0.9768991396
H	0	-4.1587787325	0.8249883947	0.0901291060
H	0	-3.3482521462	0.5680950569	-2.8937945121
H	0	-1.6652284137	1.1188812902	-2.7419505240
H	0	-2.9684702713	1.9665944290	-1.8676718081
H	0	-1.0298705134	-1.2722368138	-2.0756968432
H	0	-2.7265783391	-1.7706615728	-2.1859372151
H	0	-1.8205426990	-2.0482322706	-0.6780753421
H	0	0.2189224880	-2.5316004883	0.0100166463
H	0	0.8218821005	-1.1147566053	-1.6024822367
C	0	0.6727164296	-3.0345335517	2.0294547760
C	0	-0.4752647647	-3.8294246664	2.1401079425
C	0	1.5630860840	-2.9860047262	3.1131641811
C	0	-0.7275250715	-4.5644120822	3.3015087834
H	0	-1.1797166531	-3.8694904509	1.3061288059
C	0	1.3145029598	-3.7179213011	4.2756728312
H	0	2.4629764366	-2.3684491321	3.0447681616
C	0	0.1668891136	-4.5107467666	4.3730910851
H	0	-1.6271714252	-5.1809307341	3.3689582356
H	0	2.0196615494	-3.6700759756	5.1090787842
H	0	-0.0286750151	-5.0848790595	5.2818806398
C	0	2.0947153113	0.3189959796	-2.4548393910
C	0	1.2093581985	0.4457450856	-3.5347430446
C	0	3.3415173448	0.9548940364	-2.5368646385
C	0	1.5405528840	1.2089978409	-4.6564713141
H	0	0.2451977717	-0.0665156339	-3.5014668651
C	0	3.6786021781	1.7122185710	-3.6591772908
H	0	4.0343275180	0.8817093288	-1.7000499186
C	0	2.7792366106	1.8495456856	-4.7201818000
H	0	0.8317507046	1.2960805716	-5.4837566470
H	0	4.6516801754	2.2078766386	-3.7013065816
H	0	3.0453337301	2.4487026375	-5.5944329073

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H	0	4.0894264672	-0.1608074182	1.1055800605
C	0	3.1298308785	-0.4288699888	0.6558682926
C	0	1.8995631591	0.1971428034	1.2597268830
C	0	3.0843349580	-1.3444142613	-0.3143498249
C	0	0.7273041310	0.2737830537	0.2236416576
C	0	0.5487300667	-1.1170254377	-0.4247732642
H	0	4.0091270780	-1.8046915480	-0.6740959326
C	0	1.8210875986	-1.7746664053	-1.0061447633

H	0	-0.1759039589	-1.0029301256	-1.2341321758
C	0	0.8281591026	1.2900654238	-0.9288910996
O	0	-0.0650645786	1.4491232600	-1.7231772805
O	0	2.0138398936	1.8915572263	-1.0130301193
C	0	2.1349728564	2.8747800907	-2.0417385358
H	0	1.3987161864	3.6753567043	-1.8818051579
H	0	3.1552287781	3.2696866558	-1.9655587099
H	0	1.9658228170	2.4204064741	-3.0286373988
N	0	-0.5429594655	0.5117493498	0.9269658386
C	0	-1.3606521706	-0.6565454073	1.2817325992
C	0	-0.8393397521	1.7824442481	1.3405447010
H	0	-1.5168111467	-0.6748136921	2.3734930002
S	0	-0.2741731845	-2.1026562817	0.8889675410
C	0	-2.7687922405	-0.7477255474	0.6051764611
H	0	-1.6762112564	1.8202273259	2.0682033322
O	0	-0.2511843277	2.7764724666	0.9673895554
C	0	-2.6778925361	-0.8398932991	-0.9244396878
C	0	-3.6208553755	0.4827360330	0.9664350906
C	0	-3.4664528881	-1.9971478141	1.1693019988
H	0	-2.1854641716	-1.7718882359	-1.2385260342
H	0	-3.6910632670	-0.8401293731	-1.3556229695
H	0	-2.1267784949	0.0145134794	-1.3435992120
H	0	-4.6525302637	0.3241972579	0.6162477803
H	0	-3.6642288520	0.6509734484	2.0549208449
H	0	-3.2534162503	1.3985922502	0.4822476589
H	0	-3.5736367970	-1.9370073787	2.2653248181
H	0	-4.4751700612	-2.0947250849	0.7397529682
H	0	-2.9037292466	-2.9111154325	0.9291500814
H	0	1.5173084950	-0.5577877784	1.9676563935
H	0	1.7063719113	-2.8647859688	-0.8689843306
C	0	2.1682817989	1.4246529050	2.1061598849
C	0	1.5286715552	1.5385841864	3.3490253365
C	0	3.0553036895	2.4382988675	1.7200746940
C	0	1.7304083652	2.6513199908	4.1671493730
H	0	0.8580149322	0.7395259262	3.6776729329
C	0	3.2682542559	3.5483856920	2.5386971159
H	0	3.5724496763	2.3601680984	0.7647221580
C	0	2.5999299490	3.6654230688	3.7605677773
H	0	1.2140238806	2.7223711836	5.1276761549
H	0	3.9600339588	4.3316649360	2.2184571498
H	0	2.7638057676	4.5386409548	4.3965976893
C	0	1.8778227562	-1.5417988350	-2.5158245830
C	0	1.0526724388	-2.2979420353	-3.3617929625
C	0	2.6953232762	-0.5556071518	-3.0803281754
C	0	1.0370663249	-2.0689577678	-4.7378588917
H	0	0.4109776967	-3.0733414393	-2.9326591188
C	0	2.6834540729	-0.3248511168	-4.4593980806
H	0	3.3359847134	0.0418974636	-2.4305678187
C	0	1.8536146331	-1.0778719552	-5.2921734580
H	0	0.3872798387	-2.6669307304	-5.3814455777
H	0	3.3274464421	0.4494610906	-4.8840641500
H	0	1.8433137356	-0.8964097647	-6.3694555802

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H	0	-4.2951275550	-0.5721720467	0.9147245366
C	0	-3.3740452486	-0.3683650939	0.3606566936
C	0	-2.2764247707	-1.3750829818	0.5749179367
C	0	-3.3146593162	0.6994516987	-0.4361360030
C	0	-1.0045510536	-1.1109890155	-0.3262151899
C	0	-0.8375330261	0.3563229682	-0.7724958679
H	0	-4.1890125132	1.3476161612	-0.5425326351
C	0	-2.1174376595	1.0366371687	-1.2778805783

H	0	-0.0993059568	0.3827875765	-1.5818277560
C	0	-1.1302175608	-1.9499973317	-1.6116811962
O	0	-2.1688862932	-2.3848412824	-2.0378504946
O	0	0.0385136457	-2.0370524254	-2.2644647319
C	0	0.0372843910	-2.8498602822	-3.4375655001
H	0	1.0508279975	-2.7892473857	-3.8516743758
H	0	-0.7012360806	-2.4855306973	-4.1666760740
H	0	-0.2070744699	-3.8891758706	-3.1730374434
N	0	0.2404886036	-1.4205892213	0.3814366656
C	0	0.9860959226	-0.3047051573	0.9801883824
C	0	0.4890982400	-2.7261856346	0.6806803755
H	0	1.0192559272	-0.4388806590	2.0743710748
S	0	-0.0655494502	1.1821739543	0.6739282990
C	0	2.4497481319	-0.1110057786	0.4660561120
H	0	1.2910619344	-2.8683738874	1.4317238276
O	0	-0.1172285377	-3.6585582683	0.1833232456
C	0	3.0653518575	1.0514334955	1.2636277973
C	0	3.2926609963	-1.3721107803	0.7270619795
C	0	2.4896657457	0.2021758167	-1.0360080185
H	0	2.5098712077	1.9862968928	1.0990545416
H	0	4.1085146650	1.2152751044	0.9525203353
H	0	3.0669827872	0.8373861867	2.3452971140
H	0	4.3483089902	-1.1586291648	0.4980540131
H	0	2.9878762187	-2.2145042812	0.0896568645
H	0	3.2415289392	-1.6911826596	1.7807769096
H	0	2.0095127270	-0.5988895421	-1.6161786186
H	0	3.5344480218	0.2921583913	-1.3721306795
H	0	1.9836891407	1.1538003989	-1.2555611687
H	0	-2.2972663856	0.6121468133	-2.2837167473
H	0	-2.6735661295	-2.3357165520	0.2184595294
C	0	-1.8799688664	2.5253407161	-1.4653870683
C	0	-2.1850004932	3.4438690928	-0.4514903881
C	0	-1.2785261626	2.9951344278	-2.6412440856
C	0	-1.8921806995	4.8009607179	-0.6095262038
H	0	-2.6489669393	3.0908650502	0.4718756054
C	0	-0.9840149953	4.3502238430	-2.8021192120
H	0	-1.0397827995	2.2876834018	-3.4407844526
C	0	-1.2900574183	5.2583015816	-1.7840986512
H	0	-2.1354679295	5.5042418064	0.1906248418
H	0	-0.5176990616	4.6997197505	-3.7265127593
H	0	-1.0624300220	6.3196785742	-1.9081386909
C	0	-2.0003844465	-1.5589608141	2.0649377533
C	0	-1.9170789571	-0.4665325700	2.9413194161
C	0	-1.8718767875	-2.8507897598	2.5973071731
C	0	-1.6699651201	-0.6576483515	4.3025453151
H	0	-2.0388083202	0.5414436064	2.5465003978
C	0	-1.6269917675	-3.0459239271	3.9593416062
H	0	-1.9450599366	-3.7113944949	1.9308161750
C	0	-1.5167671779	-1.9487353922	4.8167187771
H	0	-1.6039309707	0.2079049149	4.9667605659
H	0	-1.5263274722	-4.0613267644	4.3506202489
H	0	-1.3249946103	-2.0985133470	5.8821408910

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H	0	1.2433964351	-0.6258714341	-2.6396763312
C	0	0.8449908355	-1.0986553629	-1.7393059890
C	0	-0.5331199035	-1.2425096268	-1.6139664269
C	0	0.5106175937	0.1907899623	0.9074322616
C	0	-0.7717134439	-0.4231069193	0.9758180481
H	0	-1.1715934965	-0.8524835859	-2.4094485279
C	0	-1.1275982910	-1.7556516805	-0.4286508397
H	0	-0.9265852493	-1.0982638459	1.8197591959

C	0	1.5539412578	-0.1938591062	1.8618407217
O	0	1.6077995614	-1.2833611583	2.4080564261
O	0	2.4413864321	0.7904438005	2.0861441171
C	0	3.5508101010	0.4730340697	2.9210574930
H	0	4.0865915117	1.4161914030	3.0846684795
H	0	3.2150465559	0.0483884097	3.8786239590
H	0	4.2124087882	-0.2494561196	2.4213747925
N	0	0.4575125062	1.4817258190	0.3150069653
C	0	-0.7934973981	2.2007952302	0.6276755805
C	0	1.5010864409	2.0268749894	-0.3975880262
H	0	-0.6962978977	2.6441698828	1.6345447478
S	0	-2.0452791976	0.8307263852	0.7708269110
C	0	-1.3154425946	3.3139399423	-0.3310648657
H	0	1.3216848011	3.0809086012	-0.6690260322
O	0	2.5137336814	1.4479531141	-0.7179889806
C	0	-0.5502572363	4.6413325203	-0.1352847559
C	0	-2.7777529893	3.6101082061	0.0760407043
C	0	-1.2925172284	2.8626681488	-1.7989982415
H	0	0.4800518140	4.6277414129	-0.5126761190
H	0	-1.0739545512	5.4469509352	-0.6725266744
H	0	-0.5151307870	4.9198647613	0.9300181795
H	0	-3.1499495941	4.4766939879	-0.4907819860
H	0	-3.4442679600	2.7621842291	-0.1373686949
H	0	-2.8562641388	3.8503221761	1.1484485082
H	0	-1.8144828811	1.9010790572	-1.9106325367
H	0	-1.8004747062	3.6094838525	-2.4288207562
H	0	-0.2727078486	2.7380031021	-2.1886810471
C	0	1.7148111763	-1.4695794713	-0.7146358677
H	0	1.3119559836	-2.0692581154	0.0988220068
H	0	-0.5369730301	-2.5226181568	0.0794761374
C	0	3.1678802491	-1.4412162304	-0.7333244688
C	0	3.8600463679	-2.1220488734	0.2910330197
C	0	3.9242406611	-0.7993636973	-1.7366952950
C	0	5.2542238105	-2.1609566567	0.3124882788
H	0	3.2855162123	-2.6065788312	1.0820971771
C	0	5.3129597692	-0.8491161635	-1.7201986016
H	0	3.4160984455	-0.2327651836	-2.5158771279
C	0	5.9862449143	-1.5270906419	-0.6946311189
H	0	5.7706279939	-2.6925442922	1.1155309606
H	0	5.8819100199	-0.3440980977	-2.5043996323
H	0	7.0785396658	-1.5580431094	-0.6835389103
C	0	-2.5816436753	-2.0333569348	-0.3364550085
C	0	-3.0398412175	-2.9728714429	0.6047554198
C	0	-3.5364512821	-1.3529363446	-1.1131889562
C	0	-4.4011400092	-3.2357440907	0.7582565712
H	0	-2.3109517933	-3.5061800388	1.2216987727
C	0	-4.8984037881	-1.6180376047	-0.9645977491
H	0	-3.2135955090	-0.6035446724	-1.8362948020
C	0	-5.3375237113	-2.5585638518	-0.0284461284
H	0	-4.7325839161	-3.9728587462	1.4935777092
H	0	-5.6234585059	-1.0809378190	-1.5809877819
H	0	-6.4046177547	-2.7617400927	0.0885741352

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H	0	1.0150811376	-3.2110060960	-1.4124947625
C	0	0.5316373395	-2.2315680948	-1.3748190196
C	0	1.3253680174	-1.0858108445	-1.3447907356
C	0	-0.8465058498	-2.1940582134	-1.2098439288
C	0	0.4146633217	-0.1918092406	0.9580623977
C	0	-0.9948188436	-0.2225119556	0.7270994135
H	0	-1.3820767794	-3.1421113636	-1.1200232026
C	0	-1.5620552528	-0.9830206743	-0.9895346490

H	0	-1.5584770853	-0.9389290147	1.3230092945
C	0	1.1383727684	-1.3931962690	1.4057944847
O	0	2.3280640590	-1.5455676733	1.5535202327
O	0	0.2388094058	-2.4045149702	1.6183982390
C	0	0.8079245498	-3.6622897828	1.9497520973
H	0	-0.0327530582	-4.3362145545	2.1583272753
H	0	1.4624156669	-3.5793390840	2.8297894683
H	0	1.4061173301	-4.0571996961	1.1130538124
N	0	0.9633906435	1.1089313278	1.0937098932
C	0	0.0359299681	2.2105108220	0.7529643011
C	0	1.8362998791	1.4235647452	2.1563806103
H	0	0.0581163916	2.9183726421	1.5935271456
S	0	-1.6563513622	1.4439725146	0.7998398028
C	0	0.3113317034	3.0880254525	-0.5049398782
H	0	2.1191774305	2.4994198861	2.1174622857
O	0	2.2214761413	0.6815569451	3.0164369451
C	0	0.0979791496	2.3763423551	-1.8425402863
C	0	-0.6704236680	4.2723638805	-0.4252758508
C	0	1.7515142299	3.6206578704	-0.4236645907
H	0	0.8531027195	1.6033508554	-2.0239174875
H	0	0.1751971263	3.1006747586	-2.6676066396
H	0	-0.8991680574	1.9165073793	-1.8893164202
H	0	-0.4877319851	4.9753681584	-1.2521688166
H	0	-0.5575176375	4.8276731791	0.5200252661
H	0	-1.7142685830	3.9292866074	-0.4986234385
H	0	1.9063634666	4.2286136774	0.4821617209
H	0	1.9687071979	4.2610080138	-1.2927326753
H	0	2.4820522930	2.7993488158	-0.4116084225
H	0	-1.2041484252	-0.1272802591	-1.5656356628
H	0	0.8419381809	-0.1349762419	-1.5380719232
C	0	-3.0430351025	-1.0247327570	-0.8763629269
C	0	-3.8325835433	-0.0365191753	-1.4857769212
C	0	-3.6832503882	-2.0143255218	-0.1095950093
C	0	-5.2228282313	-0.0495713609	-1.3550138026
H	0	-3.3475338250	0.7472328511	-2.0715090910
C	0	-5.0718502261	-2.0283285122	0.0230836506
H	0	-3.0828979438	-2.7739010587	0.3981585599
C	0	-5.8478475225	-1.0464955841	-0.6017619301
H	0	-5.8205397258	0.7245304860	-1.8423353280
H	0	-5.5518933178	-2.8051857558	0.6232055603
H	0	-6.9351905511	-1.0557964515	-0.4959690601
C	0	2.7726564111	-1.0504290771	-1.2974950198
C	0	3.4443252634	0.1736267526	-1.5051228228
C	0	3.5527418561	-2.1882941073	-0.9988083773
C	0	4.8320560342	0.2581154229	-1.4297471229
H	0	2.8628097994	1.0657647615	-1.7384591328
C	0	4.9397291119	-2.1054902679	-0.9305222061
H	0	3.0655059989	-3.1424449558	-0.7989395778
C	0	5.5870159375	-0.8833165836	-1.1423055718
H	0	5.3283456244	1.2173308624	-1.5952765876
H	0	5.5235773461	-2.9976591429	-0.6927236154
H	0	6.6757934644	-0.8203756828	-1.0777569631

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H	0	-1.5923749961	-3.4184425232	0.8403857615
C	0	-1.0583480388	-2.7341438432	0.1773194662
C	0	-1.8058676230	-1.8323235917	-0.5789427351
C	0	0.3263271363	-2.7698677734	0.2542020363
C	0	-0.3972062152	0.4045636170	0.2441990923
C	0	0.7929043786	-0.2000940265	0.7413694352
H	0	0.7667484134	-3.5076991866	0.9309516580
C	0	1.2003350623	-1.7908380755	-0.2968487404

H	0	0.7578778168	-0.6018230731	1.7542920369
C	0	-1.6431616965	0.5830285940	0.9706958265
O	0	-2.5195149391	1.3657283650	0.6533081368
O	0	-1.7179286615	-0.1888275736	2.0868703852
C	0	-2.8690599639	0.0179723609	2.8990172340
H	0	-2.8400572209	-0.7595145077	3.6731375192
H	0	-2.8412938657	1.0145902510	3.3681962798
H	0	-3.7909101913	-0.0671127812	2.3084149652
N	0	-0.0789767661	1.3572182932	-0.7747198579
C	0	1.1200878503	2.1311373248	-0.4671055989
C	0	-0.6126370761	1.3953378353	-2.0331974461
H	0	1.6321859986	2.3720848183	-1.4100329181
S	0	2.1967334431	0.9109949382	0.4356156538
C	0	0.8905206274	3.4597792206	0.3024083724
H	0	-0.1589560953	2.2090511382	-2.6439038388
O	0	-1.4614896186	0.6531200965	-2.4821178190
C	0	0.2418821543	3.2454542186	1.6772491710
C	0	-0.0266113201	4.3511219963	-0.5521431044
C	0	2.2613546619	4.1346531185	0.4697343089
H	0	0.8014520837	2.5072820857	2.2704885124
H	0	0.2361673526	4.1956085478	2.2343387207
H	0	-0.7995166058	2.9130911370	1.5778873528
H	0	-0.1617497389	5.3292382864	-0.0648118711
H	0	0.3994705401	4.5340172392	-1.5526874118
H	0	-1.0203505336	3.8943142265	-0.6696552378
H	0	2.7489366711	4.3059575469	-0.5044157866
H	0	2.1472613428	5.1113238480	0.9645607527
H	0	2.9352630510	3.5210688370	1.0877880866
H	0	0.8964462053	-1.3577811778	-1.2546597036
H	0	-1.3544865635	-1.3100181546	-1.4207770444
C	0	-3.2369938729	-1.6410013584	-0.4112352386
C	0	-3.9204792623	-0.7356990890	-1.2534739935
C	0	-3.9783488601	-2.2977748970	0.5996390793
C	0	-5.2880797683	-0.5133286456	-1.1011989523
H	0	-3.3508308147	-0.1975541862	-2.0089092777
C	0	-5.3432663753	-2.0776568392	0.7428275173
H	0	-3.4803418660	-2.9817509627	1.2874154834
C	0	-6.0062868667	-1.1829992629	-0.1084956289
H	0	-5.7948218186	0.1960112054	-1.7594176778
H	0	-5.8978703131	-2.5998165270	1.5262976189
H	0	-7.0783712518	-1.0075309562	0.0096663917
C	0	2.6671974754	-2.0260114180	-0.2073848412
C	0	3.4901146253	-1.7765185683	-1.3165681186
C	0	3.2685539174	-2.4558089987	0.9876287777
C	0	4.8694110202	-1.9744133327	-1.2447633071
H	0	3.0374336891	-1.4215614675	-2.2455454764
C	0	4.6487781749	-2.6464855400	1.0648797191
H	0	2.6523932114	-2.6274373966	1.8739098606
C	0	5.4547459664	-2.4100392242	-0.0527139503
H	0	5.4918176954	-1.7809183803	-2.1217832635
H	0	5.0988734414	-2.9760450368	2.0044815737
H	0	6.5354667932	-2.5582437711	0.0077260540

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H	0	-1.2269378183	-1.8495123468	-2.4117692138
C	0	-0.7937839607	-1.8863608337	-1.4096906500
C	0	-1.6255727888	-1.7738958819	-0.2974310350
C	0	0.5895193852	-1.9755985824	-1.2830445851
C	0	-0.3380120363	0.4256693450	0.4448621023
C	0	0.9667759500	-0.1071713542	0.6588929188
H	0	1.1953768421	-1.9824240079	-2.1915592560
C	0	1.2339561748	-1.9203100223	-0.0163544303

H	0	1.2213989186	-0.3406287993	1.6951547441
C	0	-1.3313594881	0.4356488550	1.5147715215
O	0	-1.3222153396	-0.3251820952	2.4682726359
O	0	-2.2591467134	1.3987059106	1.3446054823
C	0	-3.3113430165	1.4517171288	2.3037357097
H	0	-3.8748764627	2.3666901423	2.0838247606
H	0	-2.9093733274	1.4820967111	3.3270885313
H	0	-3.9683571051	0.5763430434	2.2016695205
N	0	-0.3576587363	1.3538748746	-0.6256432615
C	0	0.8881960096	2.1022988728	-0.7730099193
C	0	-1.3419606213	1.4717425347	-1.5803772287
H	0	1.0626648338	2.2910877438	-1.8427190119
S	0	2.1868689089	0.9105583333	-0.2111103359
C	0	0.9242728260	3.4686738785	-0.0306997875
H	0	-1.0508564887	2.2070481654	-2.3657420563
O	0	-2.3879424221	0.8692538846	-1.6067659765
C	0	2.2827170863	4.1236109496	-0.3264985909
C	0	-0.2026550662	4.3575326435	-0.5842880280
C	0	0.7376807269	3.3084816399	1.4841800576
H	0	3.1115978524	3.5160659333	0.0675367276
H	0	2.3376862053	5.1172222141	0.1442730577
H	0	2.4378471358	4.2562166986	-1.4102393350
H	0	-0.1522827899	5.3567703100	-0.1244396173
H	0	-1.1932443186	3.9361083332	-0.3580576936
H	0	-0.1193191596	4.4898040468	-1.6756032537
H	0	-0.2634713846	2.9245438701	1.7218040719
H	0	0.8474457698	4.2869237246	1.9778524240
H	0	1.4897947688	2.6272736258	1.9077644951
H	0	-1.1888785339	-1.9666170366	0.6801588091
H	0	0.6633064797	-2.3672486636	0.8021329024
C	0	-3.0778587527	-1.7389196765	-0.2743412453
C	0	-3.7258994405	-1.9273588135	0.9655653541
C	0	-3.8757004418	-1.5631896164	-1.4249032015
C	0	-5.1176727608	-1.9422906578	1.0532933446
H	0	-3.1177302837	-2.0470386846	1.8639646257
C	0	-5.2625673106	-1.5884531410	-1.3365979143
H	0	-3.4012681249	-1.3734637345	-2.3866492279
C	0	-5.8916145070	-1.7754713288	-0.0980919240
H	0	-5.5998011462	-2.0894505340	2.0228368144
H	0	-5.8645034973	-1.4476926175	-2.2374448336
H	0	-6.9824266294	-1.7892837432	-0.0343878605
C	0	2.6894243669	-2.1717917406	0.1331121660
C	0	3.1785891516	-2.6298546134	1.3697450619
C	0	3.6147416336	-1.9189794085	-0.8950540918
C	0	4.5422550021	-2.8430258506	1.5715188954
H	0	2.4722903821	-2.8252248272	2.1817366168
C	0	4.9790446531	-2.1349704512	-0.6958114525
H	0	3.2679119057	-1.5384587390	-1.8561936057
C	0	5.4493625111	-2.5969883736	0.5366597408
H	0	4.8983731191	-3.2037989219	2.5394584232
H	0	5.6814717145	-1.9350346951	-1.5086172409
H	0	6.5182281590	-2.7626646203	0.6906563490

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H	0	-3.5315965020	-0.9619928254	2.2839141717
C	0	-2.9493489716	-0.9083105722	1.3614498229
C	0	-2.7373859733	-2.0110662965	0.6430192716
C	0	-1.2705250208	0.4185531896	-0.0383459632
C	0	-1.4912699179	-0.6623380568	-1.1255737990
H	0	-3.1314586131	-2.9691229213	0.9934325713
C	0	-1.9104184443	-2.0753708055	-0.6164164290
H	0	-2.2218794026	-0.2883549644	-1.8528067013

C	0	-1.3170763791	1.8114907492	-0.7240099792
O	0	-2.1849753248	2.1140099368	-1.5022118844
O	0	-0.3846143275	2.6521132422	-0.2759790431
C	0	-0.4270801220	3.9776406216	-0.8121985528
H	0	0.4404350363	4.5004164700	-0.3932165054
H	0	-0.3746368369	3.9446961730	-1.9097271052
H	0	-1.3570613514	4.4793414588	-0.5085298000
N	0	0.0856133516	0.1286088143	0.4799611936
C	0	1.0181751153	0.1441331570	-0.6370737423
C	0	0.3785710522	-0.4159376249	1.6991346503
H	0	1.0252455575	1.1546800841	-1.0616444741
S	0	0.0986441924	-0.6816801043	-2.1114471134
C	0	2.4979463063	-0.2909728072	-0.5375216166
H	0	1.4568649198	-0.6183864699	1.8087797990
O	0	-0.4026314702	-0.6715073296	2.5915095377
O	0	0.0245319334	0.4452095399	-3.1210605531
C	0	3.2542579880	0.6405600929	0.4334788673
C	0	3.1029994471	-0.0565292873	-1.9419206658
C	0	2.7052830496	-1.7712276554	-0.1835196771
H	0	2.9574277290	0.5156701503	1.4833200312
H	0	4.3347753088	0.4379104187	0.3719833076
H	0	3.0918413978	1.6959153182	0.1647643240
H	0	4.1859374002	-0.2474992236	-1.9075750896
H	0	2.6710369503	-0.7287749364	-2.6973906723
H	0	2.9426861558	0.9754318462	-2.2875254753
H	0	2.1410498054	-2.4207156077	-0.8670710554
H	0	3.7721103814	-2.0259214060	-0.2810971701
H	0	2.4005741374	-2.0284070347	0.8378909616
C	0	-2.5210158489	0.4607313645	0.9124824634
H	0	-3.2930441540	0.7606627281	0.1843214494
H	0	-2.5574661969	-2.4736466734	-1.4165391313
C	0	-2.5648458572	1.5709736201	1.9608565847
C	0	-2.2386939028	1.3798114847	3.3113371070
C	0	-3.0304158197	2.8393117616	1.5681491752
C	0	-2.3398666750	2.4315642235	4.2264724851
H	0	-1.8864259392	0.4073378875	3.6437587997
C	0	-3.1218382173	3.8932307363	2.4785835856
H	0	-3.3427411624	3.0001670630	0.5344827860
C	0	-2.7699854955	3.6947228727	3.8157432021
H	0	-2.0781732233	2.2567833929	5.2731574474
H	0	-3.4862111538	4.8676322088	2.1434014554
H	0	-2.8452180620	4.5143879741	4.5345501341
C	0	-0.7930540766	-3.1143907402	-0.4630084985
C	0	-0.3319589318	-3.8188139112	-1.5873721518
C	0	-0.2559724493	-3.4374222667	0.7909281005
C	0	0.6538422692	-4.7990860090	-1.4673451670
H	0	-0.7537280796	-3.5988718887	-2.5710174344
C	0	0.7248910078	-4.4258757750	0.9155265239
H	0	-0.6113362149	-2.9144130141	1.6785326747
C	0	1.1874057653	-5.1067840452	-0.2115928955
H	0	0.9990942821	-5.3324599154	-2.3562373004
H	0	1.1281008872	-4.6625703551	1.9032222961
H	0	1.9544670604	-5.8786784977	-0.1143467333

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H	0	3.7043851109	-1.4929343146	-1.1734837398
C	0	2.7037118001	-1.4763248226	-0.7395090230
C	0	1.6807634806	-0.5020203621	-1.2685953245
C	0	2.3357011886	-2.3073192819	0.2397222449
C	0	1.0500263664	0.2837177855	-0.0649314487
C	0	0.6082404628	-0.7135865867	1.0510754550
H	0	3.0134605625	-3.0529505937	0.6609379544

C	0	0.9273597557	-2.2052108385	0.7852671892
H	0	1.0595949401	-0.4286997211	2.0087189278
C	0	2.0883114174	1.2014651169	0.6180378066
O	0	3.2818603583	1.1078715437	0.4896073494
O	0	1.4864519698	2.0056519984	1.4970631520
C	0	2.3212264418	2.9221228653	2.2015271911
H	0	3.1337075407	2.3911473758	2.7186479148
H	0	1.6710622979	3.4295865773	2.9234682870
H	0	2.7572068783	3.6468610314	1.4977709704
N	0	-0.1338901146	1.0607458980	-0.4674751890
C	0	-1.4497069863	0.6463142619	-0.0022067287
C	0	0.0398633506	2.3489538034	-0.9171050618
H	0	-1.9495596858	1.5060342041	0.4684597093
S	0	-1.1889927589	-0.4568790636	1.4940463445
C	0	-2.4274428641	0.0159905998	-1.0328765170
H	0	-0.9247333757	2.8906331282	-1.0294177750
O	0	1.1102439038	2.8623257366	-1.1533306162
O	0	-1.2186264575	0.4448144069	2.7003455743
C	0	-3.8024681092	-0.0984686918	-0.3503494876
C	0	-2.5513032208	0.9405668249	-2.2547114427
C	0	-1.9776560989	-1.3764115875	-1.4973314405
H	0	-3.7684966013	-0.7614634933	0.5278060562
H	0	-4.5426996938	-0.5105899376	-1.0530434281
H	0	-4.1647466378	0.8867083314	-0.0164153785
H	0	-3.2716165157	0.5170138166	-2.9719192076
H	0	-1.5900432811	1.0609261193	-2.7739615367
H	0	-2.9158682396	1.9397909897	-1.9687553875
H	0	-1.0144121886	-1.3379357720	-2.0228247790
H	0	-2.7167799622	-1.7981125568	-2.1953853950
H	0	-1.8857771743	-2.0749607905	-0.6515468046
H	0	0.2343708042	-2.5634592766	0.0040578720
H	0	0.8371080891	-1.1104535996	-1.6273861482
C	0	0.6847254326	-3.0271452188	2.0336302457
C	0	-0.3950942471	-3.9149292773	2.1130687043
C	0	1.5242323249	-2.8856741443	3.1487843289
C	0	-0.6330676301	-4.6489331030	3.2782795798
H	0	-1.0582798871	-4.0318464362	1.2519959535
C	0	1.2903778580	-3.6168579371	4.3141467597
H	0	2.3703959263	-2.1945558551	3.1029770679
C	0	0.2093003710	-4.5012042895	4.3822770458
H	0	-1.4804553615	-5.3371627643	3.3230885553
H	0	1.9530326716	-3.4945679959	5.1741435492
H	0	0.0239512991	-5.0721880704	5.2950310537
C	0	2.1113807105	0.3337347510	-2.4564253819
C	0	1.2417023258	0.4494750266	-3.5501646749
C	0	3.3493069706	0.9892232229	-2.5159483031
C	0	1.5785409045	1.2215934582	-4.6641936907
H	0	0.2864824839	-0.0806388291	-3.5350981722
C	0	3.6919561345	1.7554628666	-3.6304292381
H	0	4.0295843384	0.9239626141	-1.6682557524
C	0	2.8076017100	1.8821307940	-4.7053495097
H	0	0.8822246692	1.2998683606	-5.5028327549
H	0	4.6574434723	2.2667367186	-3.6553335492
H	0	3.0781556496	2.4885343642	-5.5731501957

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H	0	4.1854262778	0.1910293591	0.7769396298
C	0	3.2223263672	-0.1996454001	0.4403251537
C	0	1.9879204026	0.2337192281	1.1855042711
C	0	3.1676723404	-1.0820617975	-0.5586327004
C	0	0.7898370169	0.3710095093	0.1828248483
C	0	0.6129854748	-0.9726913862	-0.5447226976

H	0	4.0826686298	-1.4229824599	-1.0502921661
C	0	1.8850091504	-1.6858813767	-1.0699768505
H	0	-0.0879804885	-0.8179442396	-1.3716197469
C	0	0.8847627015	1.4633349573	-0.9064118419
O	0	-0.0020144095	1.6451144324	-1.7052562489
O	0	2.0467471561	2.1100124672	-0.9291389769
C	0	2.1346454364	3.1970363701	-1.8515804307
H	0	1.3808152136	3.9574589930	-1.6018394986
H	0	3.1459097229	3.6065808796	-1.7433823758
H	0	1.9650695500	2.8464933290	-2.8800319922
N	0	-0.4764171669	0.5836486410	0.9036543237
C	0	-1.3483216922	-0.5619331434	1.1386032059
C	0	-0.7487293510	1.8321967059	1.4031817251
H	0	-1.4794543369	-0.7344384616	2.2196510979
S	0	-0.3468989030	-2.0616280670	0.6128126740
C	0	-2.7477823846	-0.5568606461	0.4450976409
H	0	-1.5709954027	1.8333751226	2.1479863598
O	0	-0.1577231335	2.8396921192	1.0765457780
O	0	0.5470203213	-2.4500123369	1.7715323167
C	0	-2.6302033621	-0.5904062115	-1.0877285600
C	0	-3.5439692473	0.6999022377	0.8373639504
C	0	-3.5171289185	-1.7916804612	0.9482732836
H	0	-2.1936631338	-1.5362376136	-1.4455070822
H	0	-3.6319507915	-0.5094503592	-1.5368297456
H	0	-2.0191760790	0.2456183885	-1.4580544380
H	0	-4.5690925061	0.6125481405	0.4452912191
H	0	-3.6155443657	0.8187292799	1.9301685632
H	0	-3.1105943114	1.6148630035	0.4093761110
H	0	-3.6413550531	-1.7668065561	2.0430535937
H	0	-4.5204943746	-1.8202220096	0.4969764401
H	0	-3.0059969936	-2.7298360497	0.6855117172
H	0	1.6861323777	-0.6370910621	1.7883311570
H	0	1.8535663652	-2.7265161555	-0.6982466143
C	0	2.1825128325	1.3577607330	2.1788635612
C	0	1.5501487627	1.2504001277	3.4266313180
C	0	2.9660744470	2.4904118000	1.9230997068
C	0	1.6595003784	2.2649119044	4.3798925457
H	0	0.9669542266	0.3526273728	3.6493550445
C	0	3.0865167705	3.5018217599	2.8769713176
H	0	3.4696776677	2.5874022073	0.9622119690
C	0	2.4260654742	3.3991980703	4.1046144123
H	0	1.1541003898	2.1639283703	5.3436601460
H	0	3.6967773282	4.3818446383	2.6584183865
H	0	2.5170433973	4.1960808499	4.8467034432
C	0	1.8389058744	-1.7432415238	-2.5894534447
C	0	1.2938303908	-2.8567379379	-3.2413515331
C	0	2.2786632360	-0.6567911425	-3.3590210857
C	0	1.1856969370	-2.8855333862	-4.6343514078
H	0	0.9506149089	-3.7105016925	-2.6500209760
C	0	2.1714107199	-0.6825594759	-4.7507833650
H	0	2.7099063517	0.2120599309	-2.8570994112
C	0	1.6234186532	-1.7968910430	-5.3930789960
H	0	0.7614253913	-3.7629508918	-5.1285751719
H	0	2.5172610878	0.1718437155	-5.3377364328
H	0	1.5403395248	-1.8175801172	-6.4822491904

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H	0	-4.1292397358	-0.2106557503	1.3354079516
C	0	-3.2902519759	-0.1019724060	0.6427065471
C	0	-2.2923295157	-1.2305316323	0.6831943493
C	0	-3.2525273728	0.9470058070	-0.1789492935
C	0	-1.0117058252	-0.9777785764	-0.2155189858

C	0	-0.8658899932	0.4650373543	-0.7334839789
H	0	-4.0577871771	1.6854780369	-0.1617495427
C	0	-2.1588549559	1.1466202739	-1.1928497190
H	0	-0.1437750416	0.4608399302	-1.5613373324
C	0	-1.1150064060	-1.8631271756	-1.4781097379
O	0	-2.1424749518	-2.3230986571	-1.9043000490
O	0	0.0609735149	-1.9522737548	-2.1179619080
C	0	0.0839020820	-2.8036626936	-3.2640875846
H	0	1.0993266813	-2.7373178420	-3.6726662494
H	0	-0.6558919094	-2.4772215371	-4.0094150230
H	0	-0.1424373688	-3.8377786952	-2.9658358135
N	0	0.2429943396	-1.2443696978	0.4954804086
C	0	1.0296434872	-0.1163530906	0.9852263054
C	0	0.5042041415	-2.5424787188	0.8380244704
H	0	1.0240201913	-0.0885374212	2.0871613804
S	0	0.0775880593	1.4502906642	0.5312501782
C	0	2.4947475743	0.0076431150	0.4606500512
H	0	1.2965730868	-2.6532701049	1.6038858957
O	0	-0.0846336311	-3.4919516020	0.3582916371
O	0	-0.8008792373	1.8355385443	1.6981249459
C	0	3.1572557232	1.1779825862	1.2102612392
C	0	3.3048232031	-1.2666781528	0.7547859635
C	0	2.5252050167	0.2597848119	-1.0561719151
H	0	2.6376683550	2.1309187325	1.0306019964
H	0	4.1989685385	1.2982448106	0.8760166454
H	0	3.1702731408	0.9975915549	2.2971334149
H	0	4.3602756490	-1.0895434839	0.4958520385
H	0	2.9640395302	-2.1231952567	0.1562004572
H	0	3.2662665010	-1.5424077121	1.8204380755
H	0	1.9941132404	-0.5378057485	-1.5947125615
H	0	3.5670680114	0.2820233546	-1.4109887850
H	0	2.0721788257	1.2285160790	-1.3190741497
H	0	-2.4583985667	0.6160259112	-2.1165373165
H	0	-2.7971110611	-2.0789122813	0.1990936375
C	0	-1.8985151831	2.5919323025	-1.5866576544
C	0	-2.0033348019	3.6375689147	-0.6571826854
C	0	-1.4923966349	2.8891374824	-2.8954457838
C	0	-1.7072477104	4.9498830303	-1.0347206582
H	0	-2.2848466968	3.4155855009	0.3729153555
C	0	-1.1948875213	4.2000547026	-3.2732125624
H	0	-1.4153499308	2.0813235970	-3.6294255346
C	0	-1.3028216215	5.2360835362	-2.3411265094
H	0	-1.7905718766	5.7536397020	-0.2991927123
H	0	-0.8846203105	4.4141515368	-4.2988923136
H	0	-1.0737385624	6.2636814458	-2.6334222411
C	0	-2.0120659627	-1.6700105242	2.1143956067
C	0	-1.6192484600	-0.7563791831	3.1039678402
C	0	-2.1819355503	-3.0159547652	2.4685256252
C	0	-1.3784928228	-1.1893692565	4.4110322352
H	0	-1.4922280877	0.2948845946	2.8377727632
C	0	-1.9501564071	-3.4476805395	3.7763907184
H	0	-2.4750885413	-3.7362667585	1.7021680873
C	0	-1.5413766876	-2.5351383823	4.7525209404
H	0	-1.0697511672	-0.4650532646	5.1694364198
H	0	-2.0857625765	-4.5016450470	4.0312377705
H	0	-1.3571819246	-2.8707825107	5.7762990595

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H	0	1.2827888709	-0.6743670895	-2.6661829956
C	0	0.8746971417	-1.1429100039	-1.7680437192
C	0	-0.5088322393	-1.2840186072	-1.6634770097
C	0	0.4952520304	0.1930723390	0.8682192239

C	0	-0.7625078207	-0.4446427198	0.9180578003
H	0	-1.1318433466	-0.8988773114	-2.4736562469
C	0	-1.1227383452	-1.7911508834	-0.4884936968
H	0	-0.9944957113	-1.0676728646	1.7845813221
C	0	1.5453451039	-0.1552385855	1.8327016294
O	0	1.6122965881	-1.2321798712	2.3984235922
O	0	2.4143378585	0.8471984479	2.0352321327
C	0	3.5232587835	0.5691975354	2.8864492388
H	0	4.0485415022	1.5226358084	3.0205612507
H	0	3.1854797590	0.1742370056	3.8557621930
H	0	4.1932735467	-0.1639117402	2.4141440794
N	0	0.4341134474	1.4677706443	0.2343029774
C	0	-0.8174368189	2.1597931880	0.5579673626
C	0	1.4649709923	1.9952746057	-0.5126953065
H	0	-0.8177120190	2.4374448127	1.6269470987
S	0	-2.1101552324	0.7699539625	0.5916510493
C	0	-1.3283009020	3.3492335130	-0.2897084580
H	0	1.2676455281	3.0332754523	-0.8312539085
O	0	2.4810911943	1.4137512425	-0.8139062121
O	0	-2.8778796468	0.9592736389	1.8757001366
C	0	-0.5297690052	4.6358124924	0.0118388255
C	0	-2.7843993295	3.6381332158	0.1481970706
C	0	-1.3312476774	3.0186865510	-1.7921893864
H	0	0.5220123956	4.5959025969	-0.2992015718
H	0	-0.9915539597	5.4860848026	-0.5137260863
H	0	-0.5511485665	4.8569447647	1.0903348335
H	0	-3.1264246497	4.5687557084	-0.3289633081
H	0	-3.4785750072	2.8389070069	-0.1485659374
H	0	-2.8662935183	3.7537784564	1.2387200012
H	0	-1.8754267906	2.0796827389	-1.9776351435
H	0	-1.8393440125	3.8199214471	-2.3506637506
H	0	-0.3226761681	2.9103152883	-2.2134092721
C	0	1.7353976239	-1.5093915337	-0.7375739665
H	0	1.3241482514	-2.0868284743	0.0880602728
H	0	-0.5330040514	-2.5400993939	0.0459962222
C	0	3.1875100249	-1.4719950349	-0.7388537993
C	0	3.8702678953	-2.1212737003	0.3122447892
C	0	3.9523196170	-0.8461350098	-1.7461664827
C	0	5.2640885045	-2.1450644478	0.3556228713
H	0	3.2889150885	-2.5923612597	1.1064454463
C	0	5.3410077080	-0.8804633840	-1.7068276579
H	0	3.4509771295	-0.3048550351	-2.5474366184
C	0	6.0048024395	-1.5270753122	-0.6551491619
H	0	5.7735788111	-2.6519680075	1.1786867949
H	0	5.9170934193	-0.3884377166	-2.4939864561
H	0	7.0970130208	-1.5462708229	-0.6266927433
C	0	-2.5778202434	-2.0707933001	-0.3965522085
C	0	-3.0421518250	-2.8990995591	0.6404163488
C	0	-3.5260976215	-1.5005092028	-1.2645214418
C	0	-4.4025442028	-3.1613025095	0.8004849466
H	0	-2.3199965292	-3.3431341912	1.3313145064
C	0	-4.8865432757	-1.7647504579	-1.1093121000
H	0	-3.2019929716	-0.8371811791	-2.0675159411
C	0	-5.3313550068	-2.5945442423	-0.0759175515
H	0	-4.7388046620	-3.8075024684	1.6144904777
H	0	-5.6062386774	-1.3132770012	-1.7962475945
H	0	-6.3981494427	-2.7939703447	0.0483562390

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H	0	-1.6420505204	-3.2348262567	0.7945625519
C	0	-1.0973748179	-2.6059022168	0.0867274919
C	0	-1.8368529750	-1.7532015614	-0.7213050939

C	0	0.2905897562	-2.6720778563	0.1877738203
C	0	-0.4167421355	0.5278685911	0.0476708005
C	0	0.8341134379	-0.0379751269	0.3665193865
H	0	0.6786877265	-3.3624094799	0.9425271104
C	0	1.2398490281	-1.8257723184	-0.4350047674
H	0	1.0569251141	-0.2968546735	1.4021719628
C	0	-1.5689053718	0.6165159566	0.9406281018
O	0	-2.5306880486	1.3361571747	0.7640016360
O	0	-1.4242249421	-0.1612956566	2.0457645093
C	0	-2.4718368659	-0.0643562195	3.0064932288
H	0	-2.2690419223	-0.8370319973	3.7590260094
H	0	-2.4753126122	0.9298134029	3.4810886010
H	0	-3.4514061265	-0.2303885822	2.5380415833
N	0	-0.3047000901	1.5491499281	-0.9581949750
C	0	0.8885283438	2.3378182306	-0.7426390477
C	0	-0.8516856054	1.5035940907	-2.2165892187
H	0	1.2082575665	2.7842354430	-1.6938285591
S	0	2.1778388400	0.9835871826	-0.4891355421
C	0	0.8464775718	3.4301597920	0.3502865086
H	0	-0.5264816535	2.3743738581	-2.8299173309
O	0	-1.5997987954	0.6539856797	-2.6447342396
O	0	2.3360694694	0.4597690088	-1.9031153881
C	0	0.8764925422	2.8783247387	1.7872525716
C	0	-0.4337111347	4.2563477196	0.1431442166
C	0	2.0893290243	4.3134121971	0.1398422614
H	0	1.7648869587	2.2511186597	1.9643123755
H	0	0.9226489278	3.7188713665	2.4970835309
H	0	-0.0138306617	2.2875142542	2.0324356205
H	0	-0.4574756536	5.0987207955	0.8523672591
H	0	-0.4770981099	4.6744498144	-0.8759531872
H	0	-1.3298790874	3.6387363801	0.2989177282
H	0	2.0832469120	4.7810791250	-0.8576041196
H	0	2.1202591299	5.1178378317	0.8903867226
H	0	3.0188628191	3.7293293658	0.2353060796
H	0	1.0388269110	-1.4674448627	-1.4491923470
H	0	-1.3777915790	-1.2615211397	-1.5777481449
C	0	-3.2734855937	-1.5648539460	-0.5689583714
C	0	-3.9889924928	-0.8124387585	-1.5259815519
C	0	-3.9902623264	-2.0877190312	0.5329222656
C	0	-5.3616697787	-0.6097210579	-1.3944133083
H	0	-3.4440302667	-0.3750281045	-2.3598597588
C	0	-5.3599596490	-1.8838674285	0.6600634742
H	0	-3.4683974662	-2.6519682108	1.3063834213
C	0	-6.0541822794	-1.1433830140	-0.3051808237
H	0	-5.8939953429	-0.0229565138	-2.1466191044
H	0	-5.8929868502	-2.2989530540	1.5189540539
H	0	-7.1297203024	-0.9804804516	-0.2019695768
C	0	2.6805070109	-2.0736096332	-0.1381680284
C	0	3.6372885860	-2.0841835640	-1.1673256686
C	0	3.1139722142	-2.2910986097	1.1819961667
C	0	4.9807080665	-2.3313406698	-0.8849016059
H	0	3.3198333999	-1.8751364285	-2.1885292016
C	0	4.4595856693	-2.5304221078	1.4656002779
H	0	2.3907478082	-2.2649760645	2.0015587604
C	0	5.3982825622	-2.5550545609	0.4307130834
H	0	5.7095605664	-2.3417421028	-1.6988683500
H	0	4.7763300267	-2.6932204776	2.4986742289
H	0	6.4527170673	-2.7399808494	0.6494099105

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H	0	-1.1981701938	-1.9127755316	-2.4704500483
C	0	-0.7769956565	-1.9130047711	-1.4623579670

C	0	-1.6234987459	-1.7972437335	-0.3706992778
C	0	0.6169285291	-1.9807841785	-1.3358765147
C	0	-0.3437380326	0.5178795065	0.4000851473
C	0	0.9578099681	-0.0156575172	0.5088185318
H	0	1.2193449515	-2.0149169358	-2.2422849161
C	0	1.2571060676	-1.8824790223	-0.0768080220
H	0	1.3508484325	-0.1907103186	1.5136862235
C	0	-1.2754798393	0.4788644889	1.5229891532
O	0	-1.2116904349	-0.3295150503	2.4345842227
O	0	-2.2075391706	1.4499904089	1.4557168638
C	0	-3.2223793811	1.4363039186	2.4559604584
H	0	-3.7860594856	2.3685724607	2.3290761338
H	0	-2.7826735221	1.3838154953	3.4625960730
H	0	-3.8906809199	0.5753611388	2.3100792947
N	0	-0.4697150575	1.4608238977	-0.6542829497
C	0	0.7492655520	2.2121360870	-0.8757090746
C	0	-1.5167556150	1.5498786296	-1.5437556353
H	0	0.8612272334	2.4438966794	-1.9441286420
S	0	2.1121433619	0.9465688168	-0.6071863454
C	0	0.9184637421	3.5016189812	-0.0365597070
H	0	-1.3092837193	2.3130932111	-2.3301821307
O	0	-2.5360600715	0.9051922641	-1.5050535766
O	0	2.2121562294	0.2532027192	-1.9503259832
C	0	2.1918979409	4.2132544807	-0.5235101305
C	0	-0.3045948864	4.4006671881	-0.2837851770
C	0	1.0295473613	3.2127492212	1.4696834176
H	0	3.0889474162	3.5952381130	-0.3637233289
H	0	2.3335108188	5.1575839972	0.0240980594
H	0	2.1306880926	4.4514845642	-1.5975991098
H	0	-0.1845410642	5.3547042166	0.2529915524
H	0	-1.2258331796	3.9199338417	0.0760614465
H	0	-0.4262330496	4.6317325276	-1.3544155432
H	0	0.1059548835	2.7687331017	1.8630567277
H	0	1.2070712698	4.1538509139	2.0134483751
H	0	1.8679460728	2.5361687980	1.6979977336
H	0	-1.1942578922	-1.9150549429	0.6222747952
H	0	0.6557124001	-2.2376038206	0.7634505833
C	0	-3.0759826230	-1.7814372968	-0.3670809495
C	0	-3.7364785074	-1.8989351644	0.8741969356
C	0	-3.8600727637	-1.6807951703	-1.5351790284
C	0	-5.1290514769	-1.9165123293	0.9469023950
H	0	-3.1369818179	-1.9641156201	1.7845722745
C	0	-5.2476406692	-1.7078149131	-1.4618423236
H	0	-3.3747839662	-1.5503524725	-2.5022888332
C	0	-5.8899970958	-1.8235489015	-0.2214209110
H	0	-5.6223726010	-2.0082771387	1.9176723572
H	0	-5.8399093363	-1.6248444635	-2.3761349664
H	0	-6.9813609343	-1.8395367732	-0.1695163904
C	0	2.7000213984	-2.1615207323	0.1503998912
C	0	3.1098293297	-2.4847678078	1.4573301138
C	0	3.6769893512	-2.1042122582	-0.8596223668
C	0	4.4481204100	-2.7489092621	1.7510070403
H	0	2.3607828677	-2.5369699877	2.2531102213
C	0	5.0138665062	-2.3735643890	-0.5663379524
H	0	3.3930135459	-1.8096038884	-1.8680902501
C	0	5.4073038505	-2.6956615115	0.7365908736
H	0	4.7410463462	-3.0009353448	2.7730634905
H	0	5.7585880375	-2.3248510105	-1.3645641664
H	0	6.4567637424	-2.9023754095	0.9596688318

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H	0	-2.2261387551	-1.0412326245	3.0889741503

C	0	-2.0765685002	-1.0870616939	2.0119944885
C	0	-1.8824465913	-2.2379715170	1.3593513337
C	0	-0.7778495312	0.2389929168	0.3055864161
C	0	-0.7362737026	-1.0723749879	-0.5623241950
H	0	-1.8719734932	-3.1987488353	1.8752312251
C	0	-1.7235070804	-2.1896464741	-0.1387029170
H	0	-0.9008034793	-0.8282266380	-1.6179971950
C	0	-0.9917686737	1.4463782908	-0.6285783679
O	0	-1.7075920073	1.4030470959	-1.6000425368
O	0	-0.3629201007	2.5411022042	-0.2056475418
C	0	-0.6502655389	3.7527534694	-0.9100112462
H	0	0.0199593234	4.5117359665	-0.4907820205
H	0	-0.4751058977	3.6267398649	-1.9879017548
H	0	-1.6989262277	4.0389960699	-0.7444449369
N	0	0.5532075382	0.3692236714	0.9519553280
C	0	1.5547164380	0.1109070337	-0.0726225247
C	0	0.8560152221	0.1420744272	2.2763177811
H	0	1.2679309140	0.6942954463	-0.9595411346
S	0	1.0272912515	-1.6105963487	-0.5214045077
C	0	3.0731319978	0.3571139347	0.1118601360
H	0	1.9469465736	0.0844874088	2.4303306654
O	0	0.0839168969	0.0415700384	3.1997380642
O	0	1.2716331955	-2.4606659957	0.6592053068
O	0	1.4793117850	-2.0286911233	-1.8551612129
C	0	3.2772124907	1.7489017814	0.7390448736
C	0	3.6557068134	0.3767374948	-1.3201635804
C	0	3.8293007463	-0.7287592174	0.9014528558
H	0	2.9945254640	1.7849051941	1.8001412887
H	0	4.3393169643	2.0296126927	0.6676049530
H	0	2.6835913882	2.5101848229	0.2100301154
H	0	4.7458752116	0.5167864559	-1.2773182743
H	0	3.4435308335	-0.5623055784	-1.8499040071
H	0	3.2307173039	1.2052005679	-1.9093195376
H	0	3.7255902274	-1.7143024695	0.4284104207
H	0	4.8985945262	-0.4677544055	0.9219701977
H	0	3.4939620880	-0.8347574961	1.9410816844
C	0	-2.0790178401	0.1835344258	1.2020364711
H	0	-2.8343271613	0.0367953277	0.4107451997
H	0	-2.6878084372	-1.8287706618	-0.5445982800
C	0	-2.5081430220	1.4844023501	1.8690599107
C	0	-2.1650216382	1.8582155349	3.1757464744
C	0	-3.3372488755	2.3482099852	1.1301249107
C	0	-2.6177468472	3.0671657430	3.7122140344
H	0	-1.5261076318	1.2082027258	3.7672601980
C	0	-3.7821829974	3.5600537019	1.6609859272
H	0	-3.6423254516	2.0638625126	0.1202325748
C	0	-3.4189549753	3.9275398054	2.9589520615
H	0	-2.3372400339	3.3365677951	4.7335669140
H	0	-4.4264278481	4.2098519514	1.0633165532
H	0	-3.7685146365	4.8716408596	3.3838885685
C	0	-1.4363667724	-3.4981849778	-0.8553228783
C	0	-1.8821304568	-3.6551725505	-2.1760696856
C	0	-0.7109810669	-4.5396507082	-0.2624140166
C	0	-1.6131074034	-4.8222683674	-2.8912488097
H	0	-2.4513599058	-2.8498024229	-2.6499014554
C	0	-0.4455028243	-5.7118662760	-0.9744794354
H	0	-0.3233011514	-4.4234548096	0.7488578186
C	0	-0.8927428525	-5.8574902627	-2.2892396983
H	0	-1.9687294128	-4.9247969069	-3.9192360041
H	0	0.1239859941	-6.5134117984	-0.4980657363
H	0	-0.6794689961	-6.7739368597	-2.8446450103

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H	0	3.5255688527	-1.6436100517	-1.3319631342
C	0	2.5566937126	-1.5897888539	-0.8333877383
C	0	1.5512200476	-0.5652626871	-1.2956645280
C	0	2.2269153968	-2.4228055351	0.1556286210
C	0	0.9731848237	0.1894054892	-0.0505791825
C	0	0.5286235753	-0.8252994903	1.0488384719
H	0	2.9105688409	-3.1978369945	0.5083178591
C	0	0.8703501606	-2.3164548361	0.8202378132
H	0	0.9394115556	-0.5157823806	2.0149712035
C	0	2.0510241269	1.0460481900	0.6556249554
O	0	3.2372763269	0.9303982202	0.4968061731
O	0	1.4891588376	1.8101155058	1.5991427406
C	0	2.3662074855	2.6776314632	2.3174893628
H	0	3.1752518401	2.1056533140	2.7944519239
H	0	1.7478678970	3.1755347246	3.0732685564
H	0	2.8044267114	3.4158270769	1.6297285958
N	0	-0.1897649651	1.0368785342	-0.4101891300
C	0	-1.5420720340	0.6294105841	-0.0633978844
C	0	0.0399107923	2.3454553018	-0.7737636795
H	0	-2.0398667182	1.4651024514	0.4498662653
S	0	-1.2684375695	-0.5503276377	1.3511178492
C	0	-2.4986681325	0.1362418252	-1.1878853844
H	0	-0.8993221073	2.9316716195	-0.8633194065
O	0	1.1332514490	2.8262994811	-0.9632816617
O	0	-1.4148094168	0.2189588097	2.5902448431
O	0	-2.0216553604	-1.8032892953	1.1686330309
C	0	-3.8976939065	-0.0204006428	-0.5607186839
C	0	-2.5678561812	1.2299730831	-2.2693327776
C	0	-2.0708276860	-1.1834392662	-1.8469687736
H	0	-3.9081646869	-0.7963217110	0.2154933741
H	0	-4.6240499090	-0.3025128145	-1.3378577807
H	0	-4.2382404710	0.9279215045	-0.1138621160
H	0	-3.2858154290	0.9273282010	-3.0469247091
H	0	-1.5961256773	1.3918681977	-2.7570129789
H	0	-2.9141693421	2.1906288167	-1.8561060217
H	0	-1.1057854541	-1.0828086356	-2.3594449272
H	0	-2.8124531157	-1.4654389307	-2.6097946035
H	0	-2.0059948698	-1.9995431553	-1.1180306602
H	0	0.1103785906	-2.7347980660	0.1389961103
H	0	0.6826720100	-1.1309772211	-1.6647110841
C	0	0.8028810812	-3.0737748736	2.1351847683
C	0	-0.2127869255	-4.0006657865	2.3946612746
C	0	1.7736230881	-2.8386563859	3.1210869978
C	0	-0.2551147910	-4.6835271986	3.6132880453
H	0	-0.9874207154	-4.1692548520	1.6454632312
C	0	1.7319188325	-3.5171053581	4.3398445508
H	0	2.5748843858	-2.1187597082	2.9295486470
C	0	0.7153891611	-4.4443752498	4.5886485015
H	0	-1.0559903621	-5.4022752747	3.8023510961
H	0	2.4953350470	-3.3226807535	5.0969841793
H	0	0.6792358290	-4.9764804181	5.5422264896
C	0	2.0000511704	0.3166290391	-2.4462636902
C	0	1.1243698849	0.5387662885	-3.5184114278
C	0	3.2691238423	0.9120159081	-2.4903125398
C	0	1.4852129109	1.3568492866	-4.5915738130
H	0	0.1454156559	0.0569126710	-3.5236855197
C	0	3.6353693233	1.7246348859	-3.5637014814
H	0	3.9592115473	0.7625602270	-1.6618275614
C	0	2.7444494286	1.9582743917	-4.6147934629
H	0	0.7825475966	1.5161265419	-5.4132115468
H	0	4.6255977629	2.1866094142	-3.5746322833
H	0	3.0334101255	2.6002143964	-5.4504545990

cc-PR3

0 1

H	0	4.1640335519	0.0052933530	0.8852998810
C	0	3.1968772870	-0.3228713021	0.4973211945
C	0	1.9651915254	0.1779934088	1.2075188717
C	0	3.1441723431	-1.1990161637	-0.5073128840
C	0	0.7727111984	0.3159351602	0.1992132097
C	0	0.6063029769	-1.0120986345	-0.5565744385
H	0	4.0656409390	-1.5844283862	-0.9517180079
C	0	1.8653066990	-1.7204306272	-1.1027148638
H	0	-0.1063332242	-0.8480484218	-1.3720313971
C	0	0.8707198481	1.4147930581	-0.8834622129
O	0	-0.0294836092	1.6326739950	-1.6559190439
O	0	2.0592955742	2.0067415929	-0.9403602795
C	0	2.1854829680	3.0534722768	-1.9055537952
H	0	1.4655289050	3.8543699173	-1.6849287735
H	0	3.2136049977	3.4239779475	-1.8180549496
H	0	1.9952817808	2.6667708763	-2.9171996190
N	0	-0.5106923124	0.5113640978	0.9201422474
C	0	-1.4382322523	-0.6060224568	1.0975865878
C	0	-0.7683956353	1.7593784253	1.4364326588
H	0	-1.6064992956	-0.7961787421	2.1697815075
S	0	-0.3634104903	-2.0447919462	0.5782069788
C	0	-2.8161890846	-0.5347301828	0.3670692025
H	0	-1.5999085435	1.7665134053	2.1694263153
O	0	-0.1482981635	2.7549087222	1.1337471661
O	0	-1.0597009696	-3.0836419914	-0.1958972436
O	0	0.4286530259	-2.4500009915	1.7505793670
C	0	-2.6784841345	-0.5264239322	-1.1648269065
C	0	-3.5589436528	0.7493680130	0.7810142346
C	0	-3.6497015981	-1.7405375947	0.8411580055
H	0	-2.2848607839	-1.4789723881	-1.5427395358
H	0	-3.6714435943	-0.3770845024	-1.6156351171
H	0	-2.0298439707	0.2969093646	-1.4974080615
H	0	-4.5814760870	0.7089504548	0.3758138322
H	0	-3.6419939775	0.8485903916	1.8751094400
H	0	-3.0865220142	1.6552234353	0.3751388485
H	0	-3.8096608624	-1.7042592945	1.9315902528
H	0	-4.6386300443	-1.7187061248	0.3588332861
H	0	-3.1689195760	-2.6939450818	0.5889797194
H	0	1.6431105958	-0.6582479630	1.8446336745
H	0	1.7799373654	-2.7889452837	-0.8337173850
C	0	2.2005305900	1.3237456610	2.1696468940
C	0	1.5834995175	1.2674615989	3.4280469899
C	0	3.0219848465	2.4200445413	1.8776387082
C	0	1.7428232071	2.2980622127	4.3561626271
H	0	0.9687227830	0.3988276336	3.6801957200
C	0	3.1920167323	3.4478593315	2.8062484215
H	0	3.5191914743	2.4743079223	0.9101980333
C	0	2.5456964247	3.3972259817	4.0444729835
H	0	1.2475536743	2.2372204630	5.3284118397
H	0	3.8319428038	4.2989277752	2.5599189396
H	0	2.6761725160	4.2065255274	4.7668643638
C	0	1.8436382719	-1.6476087585	-2.6249072270
C	0	1.0776521840	-2.5719786922	-3.3488789014
C	0	2.5096241241	-0.6263984373	-3.3135882951
C	0	0.9853900726	-2.4810013795	-4.7388320414
H	0	0.5383662477	-3.3572998544	-2.8114724425
C	0	2.4179857755	-0.5347563081	-4.7053245146
H	0	3.0974043666	0.1024918779	-2.7517485453
C	0	1.6572026904	-1.4619071831	-5.4214994919
H	0	0.3869041251	-3.2088727920	-5.2919135550
H	0	2.9430104523	0.2659401429	-5.2321538367

H	0	1.5859262648	-1.3905645084	-6.5093517069

cc-PR4

0 1

H	0	-2.5680135354	0.4923705264	2.8421180619
C	0	-2.3514568232	0.5393657371	1.7755085044
C	0	-1.9358000403	-0.6922485886	1.0230640841
C	0	-2.4263917609	1.6765720236	1.0736334672
C	0	-0.5117108694	-0.3975609449	0.3371945520
C	0	-0.7169588398	0.8727595185	-0.5594805282
H	0	-2.7167250571	2.6245601431	1.5261281060
C	0	-2.0801149002	1.6025166999	-0.3913077321
H	0	-0.5594859210	0.6214266198	-1.6140680911
C	0	-0.2584269628	-1.6235275160	-0.5468614780
O	0	-0.7519148688	-1.7641890645	-1.6406684199
O	0	0.4847843434	-2.5398980281	0.0691873295
C	0	0.6569955595	-3.7913002153	-0.6012500287
H	0	1.3919145055	-4.3506538252	-0.0114248387
H	0	1.0167386104	-3.6341267489	-1.6280105228
H	0	-0.2982120878	-4.3341892192	-0.6294732470
N	0	0.6572048929	-0.1134131899	1.2060066123
C	0	1.6913752943	0.7409585144	0.6399688645
C	0	0.7535591818	-0.3771663607	2.5531596628
H	0	2.1504163356	1.2921869166	1.4704788186
S	0	0.6439257493	2.0377396942	-0.1420334808
C	0	2.8505152198	0.1466104277	-0.2072242435
H	0	1.6931577948	0.0538800798	2.9701022514
O	0	-0.0313877679	-0.9819356752	3.2367089063
O	0	1.2110504496	2.6191689210	-1.3667263792
O	0	0.2383411077	2.9116134315	0.9708690043
C	0	3.9088022623	1.2617190115	-0.3275176885
C	0	3.4424151717	-1.0331072522	0.5816808256
C	0	2.4582709693	-0.3106070604	-1.6221570033
H	0	3.5063724310	2.1361839245	-0.8571465941
H	0	4.7815237926	0.8914620085	-0.8863536876
H	0	4.2590186789	1.5847453895	0.6664178379
H	0	4.3135903793	-1.4384580703	0.0439542926
H	0	2.7063715321	-1.8376870415	0.7104349615
H	0	3.7870265826	-0.7167425649	1.5794769891
H	0	1.7839105200	-1.1730953037	-1.6201974985
H	0	3.3668624676	-0.6215224261	-2.1603633656
H	0	1.9957444590	0.5036102547	-2.1947593023
H	0	-2.8000376891	0.9065152267	-0.8600312863
H	0	-2.5463027932	-0.7067638631	0.1055251542
C	0	-2.1505077731	2.8771780857	-1.2153578331
C	0	-1.9729486512	4.1544393917	-0.6689178012
C	0	-2.3793141043	2.7622509609	-2.5952235866
C	0	-2.0296721356	5.2874436361	-1.4847470987
H	0	-1.7547040043	4.2664789311	0.3919042873
C	0	-2.4288112937	3.8911239781	-3.4126802175
H	0	-2.5241456930	1.7706166287	-3.0346030947
C	0	-2.2548439885	5.1616255477	-2.8567195170
H	0	-1.8863482216	6.2759787774	-1.0420451210
H	0	-2.6074279225	3.7792586719	-4.4847383272
H	0	-2.2933374338	6.0497231794	-3.4920003930
C	0	-2.2544530066	-2.0517444791	1.6363788756
C	0	-2.4180748584	-2.2703713187	3.0110744204
C	0	-2.5440673819	-3.1174829896	0.7659558607
C	0	-2.8089226458	-3.5194231517	3.4975468263
H	0	-2.2214037997	-1.4685121538	3.7168302660
C	0	-2.9178270686	-4.3733588147	1.2486427112
H	0	-2.4973715914	-2.9601774942	-0.3134511085
C	0	-3.0460486446	-4.5823432791	2.6230128173

H	0	-2.9252072686	-3.6611129567	4.5747653425
H	0	-3.1313147036	-5.1820247079	0.5450030604
H	0	-3.3464150535	-5.5595438638	3.0087841709

cc-TS1

0 1

H	0	1.1256134485	-0.9188299345	-2.7843774636
C	0	0.7555841514	-1.3089821102	-1.8333517873
C	0	-0.6238914915	-1.4810670512	-1.6878667910
C	0	0.3836900504	0.2416830916	0.8031695300
C	0	-0.9015147705	-0.3441932619	0.7468433801
H	0	-1.2714806269	-1.1908294908	-2.5154425773
C	0	-1.2059247486	-1.8719916936	-0.4579662840
H	0	-1.2706423072	-0.8587568221	1.6357606552
C	0	1.3310333784	-0.1910409182	1.8337625236
O	0	1.3091795791	-1.3003238832	2.3411916390
O	0	2.2133958362	0.7631392124	2.1680549401
C	0	3.2368550204	0.3978921720	3.0900736164
H	0	3.7564850559	1.3278070543	3.3511209900
H	0	2.8091083724	-0.0720015548	3.9875203960
H	0	3.9423622379	-0.3022518695	2.6191384409
N	0	0.4570980792	1.5429866632	0.2145787571
C	0	-0.7751655396	2.3036295558	0.4358903918
C	0	1.5907602204	2.0126744894	-0.4137791521
H	0	-0.8782775525	2.5043733605	1.5165250104
S	0	-2.0505257835	0.9564331209	0.1969336531
C	0	-1.0944378276	3.6080617993	-0.3357100113
H	0	1.5169581255	3.0802959289	-0.6842904565
O	0	2.5743411404	1.3512825198	-0.6480674941
O	0	-2.3655379730	0.8422944923	-1.2393108532
O	0	-3.1332189685	1.0912289754	1.1775641231
C	0	-0.2722202039	4.7654133768	0.2704982650
C	0	-2.5851779715	3.9353109703	-0.0857056747
C	0	-0.8701208397	3.5054892260	-1.8559681976
H	0	0.8134901614	4.6338442822	0.1672193379
H	0	-0.5395775092	5.7068772714	-0.2336467165
H	0	-0.4945009520	4.8832558427	1.3427458215
H	0	-2.8011669769	4.9409891868	-0.4758684216
H	0	-3.2496512246	3.2251803490	-0.5954554033
H	0	-2.8328154309	3.9225154572	0.9862102806
H	0	-1.3912755115	2.6326805293	-2.2671918490
H	0	-1.2726544278	4.4103783163	-2.3369960913
H	0	0.1904482402	3.4385494524	-2.1321449763
C	0	1.6526049074	-1.5665637821	-0.8049843723
H	0	1.2772274986	-2.0614929105	0.0884263586
H	0	-0.5629150303	-2.4931964934	0.1701076460
C	0	3.1007870345	-1.4916774721	-0.8550628313
C	0	3.8293730714	-2.0043404948	0.2388441682
C	0	3.8171312349	-0.9565858063	-1.9458787456
C	0	5.2234932518	-1.9823490062	0.2440424268
H	0	3.2814153322	-2.4114092386	1.0911286019
C	0	5.2064523824	-0.9440980843	-1.9434385981
H	0	3.2773283032	-0.5247441150	-2.7890337957
C	0	5.9170060044	-1.4539975016	-0.8479964135
H	0	5.7713214794	-2.3837353037	1.1000578178
H	0	5.7465291343	-0.5231673023	-2.7946670090
H	0	7.0095533912	-1.4374556910	-0.8492052329
C	0	-2.6346308348	-2.2512774611	-0.2982081155
C	0	-2.9896142506	-3.0235129772	0.8225842282
C	0	-3.6487694656	-1.8640770651	-1.1904265332
C	0	-4.3126246450	-3.4039463556	1.0468896599
H	0	-2.2106949042	-3.3327046007	1.5259448089
C	0	-4.9707254330	-2.2489892614	-0.9693773939

H	0	-3.4091848595	-1.2354666340	-2.0462353396
C	0	-5.3100150590	-3.0174731988	0.1483056784
H	0	-4.5645725972	-4.0040792479	1.9243529239
H	0	-5.7459864640	-1.9373739046	-1.6733389219
H	0	-6.3484949426	-3.3105441976	0.3194674331

cc-TS2

0 1

H	0	1.0208652767	-3.2769630259	-1.0167624272
C	0	0.5563244770	-2.2923980857	-1.1122481816
C	0	1.3741901645	-1.1686174987	-1.1699735671
C	0	-0.8290755087	-2.2309487470	-1.0221441230
C	0	0.3750488622	-0.0617854384	1.0129983200
C	0	-1.0081936221	-0.1101746666	0.7012819976
H	0	-1.3664066541	-3.1650416124	-0.8430661578
C	0	-1.5780507733	-1.0227558452	-0.9741033730
H	0	-1.6531146074	-0.7071641758	1.3459547125
C	0	1.0568980576	-1.2235172849	1.6190858907
O	0	2.2389742342	-1.3686405497	1.8173588641
O	0	0.1339538758	-2.1852391804	1.9068059113
C	0	0.6613111137	-3.4025802338	2.4183205232
H	0	-0.2022613383	-4.0323656452	2.6654302322
H	0	1.2737825990	-3.2189667108	3.3129379768
H	0	1.2901997374	-3.9037872345	1.6655488805
N	0	0.9827870403	1.2272461371	1.0443455396
C	0	0.1515178967	2.3269435758	0.5384672549
C	0	1.7598577609	1.6010426977	2.1703288210
H	0	0.0835565907	3.0900381734	1.3256708930
S	0	-1.5776962430	1.6026292590	0.6212970617
C	0	0.5388219928	3.0832911588	-0.7617861021
H	0	2.1489263670	2.6351811652	2.0462758920
O	0	1.9664102081	0.9345319875	3.1437733124
O	0	-2.1394800449	1.9566425095	1.9287537768
C	0	0.3887546216	2.2807674200	-2.0605588817
C	0	-0.3630195688	4.3321810476	-0.8336704112
C	0	2.0024141971	3.5369036465	-0.6114077018
H	0	1.1025693737	1.4517653274	-2.1125404895
H	0	0.6026528271	2.9367368132	-2.9179835876
H	0	-0.6297816847	1.8929798319	-2.1799125998
H	0	-0.0745637481	4.9496106241	-1.6977920478
H	0	-0.2551125702	4.9521174621	0.0711178238
H	0	-1.4202653156	4.0576120525	-0.9443868864
H	0	2.1301856233	4.2079572760	0.2528692599
H	0	2.3127351560	4.0921732444	-1.5100310952
H	0	2.6802869814	2.6811946504	-0.4844424643
O	0	-2.3362953427	1.9041715576	-0.6033543802
H	0	-1.2405134141	-0.2167124093	-1.6306692255
H	0	0.9197614843	-0.2314511739	-1.4725142476
C	0	-3.0582793784	-1.1314115948	-0.8563608553
C	0	-3.9089414231	-0.3822319586	-1.6830343461
C	0	-3.6306232553	-1.9928648794	0.0956757741
C	0	-5.2942897024	-0.5104625877	-1.5785006452
H	0	-3.4777905558	0.3130495959	-2.4040646280
C	0	-5.0161340579	-2.1157755558	0.2065846508
H	0	-2.9814243061	-2.5654186455	0.7641281961
C	0	-5.8529770653	-1.3767241942	-0.6344518500
H	0	-5.9423406493	0.0776905508	-2.2324581497
H	0	-5.4440399115	-2.7854732713	0.9563254488
H	0	-6.9381723701	-1.4685682533	-0.5476118083
C	0	2.8197884830	-1.1669682878	-1.0624643822
C	0	3.5420154989	0.0043408488	-1.3759524222
C	0	3.5474887277	-2.2883274611	-0.6077923120
C	0	4.9281529902	0.0535361696	-1.2518119929

H	0	3.0046746115	0.8817565572	-1.7345149606
C	0	4.9324286701	-2.2412446543	-0.4892173458
H	0	3.0208195997	-3.1993953122	-0.3247676999
C	0	5.6302094304	-1.0707858386	-0.8072239001
H	0	5.4639950537	0.9718773666	-1.5029772410
H	0	5.4744565483	-3.1188884349	-0.1299181660
H	0	6.7171829783	-1.0347802590	-0.7040933577

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H	0	-1.2814691325	-3.3786411968	0.7669019358
C	0	-0.8285504688	-2.6982757113	0.0425834744
C	0	-1.6704243554	-1.8567572907	-0.6739087360
C	0	0.5633744710	-2.6876486661	0.0271873922
C	0	-0.3210027174	0.4582375827	0.1019556453
C	0	0.9714305977	-0.0655440152	0.3110308251
H	0	1.0583586923	-3.3726987629	0.7218729423
C	0	1.3998057667	-1.7608797777	-0.6446183276
H	0	1.2851767691	-0.3528750223	1.3139409592
C	0	-1.4189418788	0.4513564368	1.0647355620
O	0	-2.4180700709	1.1350727137	0.9758963615
O	0	-1.1783338900	-0.3754729204	2.1131175602
C	0	-2.1590817250	-0.3619615871	3.1472050911
H	0	-1.8870219073	-1.1710382627	3.8368167345
H	0	-2.1497079596	0.6025154247	3.6792987526
H	0	-3.1646504095	-0.5264072807	2.7371596347
N	0	-0.3177334742	1.5392920488	-0.8549362623
C	0	0.8104810467	2.4352715662	-0.6574859893
C	0	-0.9540575346	1.5289693029	-2.0709668490
H	0	1.0656621560	2.9181686018	-1.6101535318
S	0	2.1385077150	1.1348243027	-0.4747614998
C	0	0.6984209026	3.5098386921	0.4458721453
H	0	-0.7475360571	2.4598602021	-2.6461451616
O	0	-1.6576777689	0.6441851891	-2.5031673900
O	0	3.2175590207	1.4620618349	0.4665763004
O	0	2.4452031148	0.7482017382	-1.8614605360
C	0	0.6822225851	2.9500566416	1.8794194131
C	0	-0.6093865203	4.2790517212	0.1878802460
C	0	1.9095481544	4.4458158323	0.2790934600
H	0	1.5716155989	2.3402954684	2.0866165631
H	0	0.6795469099	3.7924497189	2.5884188619
H	0	-0.2185217233	2.3574024964	2.0794613441
H	0	-0.6944320884	5.1157690818	0.8985638036
H	0	-0.6343407697	4.7019546533	-0.8301274798
H	0	-1.4825060928	3.6227410081	0.3154831268
H	0	1.9181199692	4.9099074420	-0.7207837269
H	0	1.8670571810	5.2547405122	1.0241150036
H	0	2.8535911376	3.8996471619	0.4173251593
H	0	1.0633434611	-1.3843166482	-1.6142320450
H	0	-1.3022061287	-1.3099693536	-1.5406897941
C	0	-3.0978113193	-1.7465919591	-0.4105783423
C	0	-3.9112227777	-0.9766706908	-1.2708338337
C	0	-3.7094006079	-2.3615065362	0.7070216903
C	0	-5.2776534521	-0.8439504289	-1.0319648674
H	0	-3.4469640815	-0.4707643684	-2.1151074816
C	0	-5.0734665268	-2.2275856642	0.9410132302
H	0	-3.1099427258	-2.9434576685	1.4075713903
C	0	-5.8656577628	-1.4675510623	0.0709707421
H	0	-5.8874535423	-0.2419071761	-1.7094179387
H	0	-5.5255231734	-2.7131219766	1.8092210050
H	0	-6.9366370448	-1.3597360971	0.2587317835
C	0	2.8741309713	-1.9477187229	-0.5280018936
C	0	3.6924896174	-1.9159502958	-1.6681540322

C	0	3.4748882424	-2.1530809506	0.7250451123
C	0	5.0682985262	-2.1130930350	-1.5604218189
H	0	3.2422499115	-1.7203777382	-2.6421181987
C	0	4.8531119512	-2.3412512903	0.8353841372
H	0	2.8609632518	-2.1524640224	1.6295456628
C	0	5.6542716478	-2.3257814722	-0.3088406176
H	0	5.6895849998	-2.0892662882	-2.4587400755
H	0	5.3035637400	-2.4902160861	1.8194461428
H	0	6.7342565782	-2.4678963491	-0.2248337644

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H	0	-1.2044095034	-1.9652519006	-2.4625903016
C	0	-0.7829856198	-1.9617733861	-1.4547880095
C	0	-1.6260140568	-1.8022019216	-0.3621012618
C	0	0.6040486467	-2.0649626455	-1.3219795235
C	0	-0.3308674149	0.4809243714	0.3538726070
C	0	0.9637618095	-0.0711634567	0.4832753400
H	0	1.2072655764	-2.1181697142	-2.2283731600
C	0	1.2515268317	-1.9505459720	-0.0671378882
H	0	1.3789267122	-0.2063456513	1.4837818073
C	0	-1.2681778168	0.4706881494	1.4749826949
O	0	-1.2098315898	-0.3200719705	2.4012273541
O	0	-2.1955635237	1.4411406655	1.3813819013
C	0	-3.1937950240	1.4765025029	2.3987878356
H	0	-3.7568575348	2.4036926936	2.2379160920
H	0	-2.7355622066	1.4703441399	3.3983816217
H	0	-3.8659273792	0.6115891450	2.3054302157
N	0	-0.4221420147	1.4478749746	-0.6931513537
C	0	0.7889499092	2.2359833736	-0.8757109686
C	0	-1.4529020583	1.5496482581	-1.6020980169
H	0	0.9126111787	2.4873895990	-1.9377907161
S	0	2.0636089880	0.9049049328	-0.6061002564
C	0	0.9160502561	3.5168933630	-0.0174845530
H	0	-1.2430815735	2.3386518567	-2.3608759960
O	0	-2.4606443156	0.8872768016	-1.6035920199
O	0	3.2475964378	1.3311463714	0.1523284381
O	0	2.2248949188	0.2783673203	-1.9283766698
C	0	2.1847618423	4.2592836502	-0.4735865041
C	0	-0.3215659132	4.3865734072	-0.3028808547
C	0	0.9822962960	3.2285372502	1.4916243934
H	0	3.0847130611	3.6534113807	-0.3024058313
H	0	2.2901433099	5.2011506085	0.0862610192
H	0	2.1311238649	4.5109656236	-1.5456625592
H	0	-0.2312073960	5.3436098924	0.2338132227
H	0	-1.2431486494	3.8915159564	0.0363850102
H	0	-0.4200760730	4.6151665836	-1.3765876503
H	0	0.0572373235	2.7570245872	1.8490190567
H	0	1.0986350552	4.1789794539	2.0353801110
H	0	1.8378018849	2.5889005534	1.7453133158
H	0	-1.1994425795	-1.9302909391	0.6307416744
H	0	0.6546627569	-2.2869902824	0.7841194522
C	0	-3.0764043273	-1.7487692847	-0.3596707078
C	0	-3.7406872822	-1.8527418643	0.8813092021
C	0	-3.8558912940	-1.6283590854	-1.5293560964
C	0	-5.1330930657	-1.8391188689	0.9518731919
H	0	-3.1442850186	-1.9342020705	1.7922317030
C	0	-5.2437312985	-1.6237978147	-1.4575990300
H	0	-3.3664804783	-1.5073825784	-2.4952788852
C	0	-5.8894964339	-1.7267243329	-0.2178879711
H	0	-5.6301085057	-1.9219313367	1.9214447036
H	0	-5.8330005126	-1.5260822943	-2.3722422309
H	0	-6.9809860478	-1.7180966251	-0.1674259535

C	0	2.6957234334	-2.2281209893	0.1479640345
C	0	3.1202204140	-2.5427814010	1.4515852991
C	0	3.6603196208	-2.1662156715	-0.8722085573
C	0	4.4628560817	-2.7963184617	1.7312271562
H	0	2.3805517171	-2.5934000231	2.2561383444
C	0	5.0020075571	-2.4247124471	-0.5934253001
H	0	3.3663104982	-1.8838046180	-1.8816493160
C	0	5.4104255556	-2.7390237964	0.7061800414
H	0	4.7693524265	-3.0398944801	2.7512009245
H	0	5.7381952543	-2.3700060751	-1.3988276967
H	0	6.4640042893	-2.9342425068	0.9194450759

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C	0	-1.3624581216	-1.5874329804	1.6959862341
C	0	-1.8511346390	-0.2315944527	1.2706497967
C	0	-1.0890927109	-2.5229302062	0.7725311281
C	0	-1.1791040073	0.3351482593	-0.0034806454
H	0	-1.7299181745	0.4874298899	2.0894410652
C	0	-0.6656031263	-0.7681464262	-0.9834167071
H	0	-0.7431222033	-3.5208234299	1.0423925242
C	0	-1.2473644535	-2.1547551769	-0.6767633807
H	0	-0.7677186409	-2.8986027535	-1.3306661296
H	0	-0.9334569390	-0.4825696388	-2.0085942549
C	0	-2.2394837321	1.1165697311	-0.8191808663
O	0	-3.4281026094	0.9517660362	-0.7247347874
O	0	-1.6638286544	1.8912510770	-1.7493845388
C	0	-2.5507057058	2.6969347198	-2.5238052062
H	0	-1.9240130740	3.2357604415	-3.2446199092
H	0	-3.2916190686	2.0739196316	-3.0460693224
H	0	-3.0791542097	3.4068819387	-1.8703259077
N	0	-0.0443963539	1.2163504985	0.3101122018
C	0	1.3268420899	0.7753567525	0.0566006734
C	0	-0.3174280330	2.5085271417	0.6540262923
H	0	1.8160788147	1.5239912132	-0.5896950052
S	0	1.1680603939	-0.7794461076	-0.9154578809
C	0	2.2447972919	0.5798991123	1.3070620242
H	0	0.5838848551	3.1553031569	0.6795628085
O	0	-1.4339786719	2.9305931110	0.8898126198
C	0	2.4632620618	1.9208632469	2.0296642595
C	0	3.6097008647	0.0833696718	0.7966599897
C	0	1.6565347197	-0.4270099936	2.2982607142
H	0	1.5473038310	2.2827779447	2.5186415583
H	0	3.2205089744	1.7924283355	2.8186635728
H	0	2.8280418983	2.7038702402	1.3446758339
H	0	4.3159358586	-0.0125780079	1.6355734893
H	0	3.5255093262	-0.9029030496	0.3158537657
H	0	4.0468476356	0.7857970946	0.0677807885
H	0	1.4816094792	-1.3992653294	1.8208997754
H	0	2.3505316134	-0.5694045679	3.1419048443
H	0	0.7006377481	-0.0768926604	2.7102927830
H	0	-2.3138776929	-2.1315515589	-0.9735293137
H	0	-2.9316110716	-0.2908821568	1.0668307341
O	0	-1.2790512126	-1.7312484909	3.0380126411
Si	0	-0.9900407018	-3.1055525321	3.9979020625
C	0	-2.3042317537	-4.3968136705	3.6374170600
C	0	-1.1379834232	-2.4555277295	5.7463616283
C	0	0.7383449538	-3.7721152893	3.6842759862
H	0	-3.3101889018	-3.9775211358	3.8002028823
H	0	-2.2537820163	-4.7583823227	2.5992446316
H	0	-2.1858370854	-5.2653079833	4.3064506903
H	0	-0.9748605351	-3.2607368700	6.4812926622
H	0	-0.3930083018	-1.6658421379	5.9338538839

H	0	-2.1376845388	-2.0278172556	5.9225278786
H	0	1.4953805651	-3.0001516195	3.8920397960
H	0	0.9375539577	-4.6308773839	4.3469695171
H	0	0.8766976413	-4.1079132874	2.6455335282

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C	0	-2.2790473870	1.4999666602	-1.1720193484
C	0	-1.5436137752	0.2107586516	-0.9457228325
C	0	-2.1368636178	2.5777473871	-0.3858746199
C	0	-0.9968088562	0.0552275710	0.4770378535
H	0	-2.2024432853	-0.6350771827	-1.1798302368
C	0	-0.3927009268	1.3651340621	1.0248909524
H	0	-2.6691696596	3.4969795126	-0.6402321720
C	0	-1.2901037243	2.5907008239	0.8553990710
H	0	-1.9376738795	2.6537686904	1.7499013014
H	0	-0.1954421400	1.2016450844	2.0921533092
C	0	-2.0743712927	-0.3694900770	1.5050956694
O	0	-1.8689623494	-0.3754235489	2.6935609716
O	0	-3.2633581633	-0.6138349939	0.9511489316
C	0	-4.2684415224	-1.1019725667	1.8391685045
H	0	-3.9579371013	-2.0755313682	2.2459413738
H	0	-5.1807995321	-1.2052706574	1.2407860508
H	0	-4.4288985333	-0.4007050140	2.6708971620
N	0	0.1326710654	-0.8982436245	0.5201359987
C	0	1.4877098453	-0.3305060528	0.3618735161
C	0	-0.0741748122	-2.1859187400	0.9193724554
H	0	2.0470304840	-0.5022759214	1.2979552737
C	0	2.3672855224	-0.8789340858	-0.8077035891
H	0	0.8664241357	-2.7290298451	1.1440892645
O	0	-1.1681103192	-2.7046754719	1.0383194269
C	0	3.6673012057	-0.0515491294	-0.8242820405
C	0	2.7510746234	-2.3505235140	-0.5641024192
C	0	1.6665104507	-0.7724997460	-2.1675107125
H	0	3.4769154909	1.0045485510	-1.0679761703
H	0	4.3576874179	-0.4491555994	-1.5837475687
H	0	4.1796062684	-0.0893797478	0.1507421824
H	0	3.5123034654	-2.6560771141	-1.2985807295
H	0	1.8967559545	-3.0309815198	-0.6859267080
H	0	3.1788094364	-2.5018633761	0.4403173831
H	0	0.7486759992	-1.3781106368	-2.1886695267
H	0	2.3321904885	-1.1468496339	-2.9606864682
H	0	1.4042885483	0.2684643930	-2.4033446676
S	0	1.2224967247	1.4917517971	0.1836865270
H	0	-0.6693910544	3.5026158598	0.8912224125
H	0	-0.7077296175	0.1715791722	-1.6553192552
O	0	-3.0398486001	1.4821423858	-2.3000780679
Si	0	-4.6982666745	1.8150379263	-2.4412064071
C	0	-5.0140746261	3.6667372091	-2.3667666999
H	0	-4.8323146205	4.0722637220	-1.3590798533
H	0	-4.3627147241	4.2038214866	-3.0750584821
H	0	-6.0609586146	3.8895673500	-2.6331074239
C	0	-5.5875054747	0.9284067244	-1.0469226450
H	0	-6.6722892538	1.1216096428	-1.0763045882
H	0	-5.4238925506	-0.1584398058	-1.1156856575
H	0	-5.2006309336	1.2640195928	-0.0724380250
C	0	-5.1615748806	1.1395632343	-4.1240704247
H	0	-4.9573544893	0.0587069204	-4.1827416952
H	0	-6.2323280961	1.2989826667	-4.3320540368
H	0	-4.5830070884	1.6378134362	-4.9184977002

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C	0	-3.0608037280	1.1086452531	-0.4489940583
C	0	-2.1118466510	0.5320592190	0.5616172765
C	0	-2.7507547780	1.2487774718	-1.7439331552
C	0	-1.0337536704	-0.3808830620	-0.0495665367
H	0	-2.6625068535	-0.0189685398	1.3306638668
C	0	-0.4386532687	0.2302763452	-1.3336269983
H	0	-3.4864337180	1.6994140520	-2.4148464944
C	0	-1.4653913581	0.7560174331	-2.3395817064
H	0	-1.6859012219	-0.0630121158	-3.0502011116
H	0	0.1715286073	-0.5360358609	-1.8211322550
C	0	-1.5264474279	-1.8007366500	-0.3804106815
O	0	-0.7888090568	-2.6876455180	-0.7327487449
O	0	-2.8557254229	-1.9268581706	-0.3093498019
C	0	-3.3739550787	-3.2348610911	-0.5582321221
H	0	-2.9916731433	-3.9392646093	0.1946599259
H	0	-4.4641931949	-3.1476224205	-0.4850480760
H	0	-3.0790722599	-3.5857781320	-1.5576761053
N	0	0.1020403769	-0.4964438757	0.8829186152
C	0	1.2788559561	0.3433669432	0.6256898173
C	0	-0.1254971032	-1.1035710241	2.0822065484
H	0	1.4807053840	0.9616195559	1.5156878892
S	0	0.7152920670	1.5101666612	-0.6917095083
C	0	2.5962650967	-0.4220080796	0.2847595555
H	0	0.6901188196	-0.9475955213	2.8202364574
O	0	-1.1245831379	-1.7511603462	2.3359802267
C	0	2.4791190500	-1.2447534271	-1.0050654540
C	0	2.9556584418	-1.3730754911	1.4403308030
C	0	3.7141456220	0.6237267334	0.1433923981
H	0	2.3284347528	-0.5924705596	-1.8780289420
H	0	3.4098980879	-1.8094114662	-1.1706670387
H	0	1.6485413369	-1.9631272544	-0.9444732212
H	0	3.9465609844	-1.8162147222	1.2562680866
H	0	3.0047018023	-0.8459904845	2.4073243630
H	0	2.2391041319	-2.2026448844	1.5273199537
H	0	3.8394375363	1.2061441844	1.0715118710
H	0	4.6733379935	0.1290065460	-0.0733253568
H	0	3.4987614251	1.3260368948	-0.6754171254
H	0	-1.5982179841	1.3651590281	1.0681581985
H	0	-0.9900283551	1.5385088875	-2.9568846299
O	0	-4.2446919158	1.5492406715	0.0610480905
Si	0	-5.6365187321	0.6053884479	0.3055190524
C	0	-6.9782808594	1.8492608253	0.6990274727
C	0	-5.3766282086	-0.5767362341	1.7419338454
C	0	-5.9893181327	-0.3394036175	-1.2788952240
H	0	-6.7207157264	2.4301416058	1.5991664015
H	0	-7.1164587743	2.5568597950	-0.1338118821
H	0	-7.9405225881	1.3441101683	0.8841052401
H	0	-6.2980860331	-1.1484060040	1.9438764277
H	0	-4.5673258931	-1.2924962572	1.5330916981
H	0	-5.1145281215	-0.0270527555	2.6603483017
H	0	-5.1062045204	-0.9300492493	-1.5671818469
H	0	-6.8423978223	-1.0264760334	-1.1539264046
H	0	-6.2216039423	0.3473937744	-2.1084623112

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C	0	2.6583398739	-1.5514781633	0.8606787090
C	0	2.4240681016	-0.1984370289	0.2388019240
C	0	2.2433420648	-2.6148910169	0.1533635087
C	0	0.9161214876	-0.0325644441	-0.1282288365
H	0	2.7272432787	0.6208927819	0.8886008523
C	0	0.4551989006	-1.2604774921	-0.9892514376

H	0	2.3346105038	-3.6289777975	0.5439251726
C	0	1.5606912610	-2.3270187735	-1.1560130929
H	0	1.1187710141	-3.2358285326	-1.5905646154
H	0	0.1436406986	-0.8977034604	-1.9759851313
C	0	0.8610262483	1.2488295139	-0.9712010192
O	0	1.1215518706	1.2857337406	-2.1487224505
O	0	0.5873890622	2.3313970252	-0.2346695857
C	0	0.6214234414	3.5862693341	-0.9158777025
H	0	0.4209733844	4.3495890726	-0.1552714356
H	0	-0.1451101195	3.6172850032	-1.7048947424
H	0	1.6062357405	3.7486462954	-1.3774291734
N	0	0.0569423888	0.0357575453	1.0627452096
C	0	-1.2534778697	-0.5984807223	0.9548969791
C	0	0.4316603547	0.5548102368	2.2721238811
H	0	-1.5027083706	-1.0032420680	1.9473423194
S	0	-0.9776936730	-2.0393217955	-0.1401047619
C	0	-2.4514936331	0.3117718540	0.5345099739
H	0	-0.3324189115	0.3380533591	3.0524477377
O	0	1.4454532762	1.1722589712	2.5322717294
C	0	-3.7298675449	-0.5185595366	0.7411995705
C	0	-2.4914592290	1.5465973669	1.4492983334
C	0	-2.3859343504	0.7632822293	-0.9309452016
H	0	-3.7273912242	-1.4132948832	0.0999495997
H	0	-4.6198006537	0.0782170583	0.4889469277
H	0	-3.8304056107	-0.8472033127	1.7887253742
H	0	-3.3757950216	2.1595582072	1.2146950327
H	0	-1.5985276218	2.1735730481	1.3137188089
H	0	-2.5601486033	1.2634632581	2.5121427722
H	0	-1.5561693981	1.4568300555	-1.1113806573
H	0	-3.3125477793	1.2954993232	-1.1968143035
H	0	-2.2831992070	-0.0971589082	-1.6072805995
H	0	2.9753113177	-0.1166525605	-0.7109991010
H	0	2.2739643327	-1.9442618096	-1.9102385717
O	0	3.1750205141	-1.6438960257	2.0993060390
Si	0	4.3008562037	-0.8336409186	3.0743798429
C	0	4.8894308747	0.7815344883	2.3148316305
C	0	5.7427414017	-2.0224105493	3.2632940310
C	0	3.4451720317	-0.5320416317	4.7100304508
H	0	5.2598628325	0.6493973209	1.2856895130
H	0	4.0828740567	1.5297589963	2.3128850633
H	0	5.7222418291	1.1784200628	2.9196488778
H	0	6.5054992927	-1.6164673078	3.9484813567
H	0	5.4006870936	-2.9888017190	3.6671381439
H	0	6.2265207005	-2.2151018274	2.2917449088
H	0	3.0233727425	-1.4670446624	5.1122248120
H	0	4.1492862890	-0.1255207054	5.4547976733
H	0	2.6286992271	0.1922013952	4.5663582007

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C	0	1.3893362019	0.1600117604	1.4531432340
C	0	0.5058259296	-0.3761273323	2.4213215325
C	0	-0.9557754117	1.3365544529	0.2387830018
C	0	-1.7416516534	0.9122917922	1.3228805897
C	0	-0.4911951124	0.3933170592	3.0017994441
H	0	-1.2049177176	-0.0881577499	3.6757471745
H	0	-2.2946373462	1.6650777435	1.8851767494
C	0	-0.9268047546	2.7844558685	-0.0706708979
O	0	-0.8706826054	3.6525955958	0.7755273613
O	0	-1.0181019709	3.0347123147	-1.3863166318
C	0	-0.9052544263	4.4006231602	-1.7728920609
H	0	-0.9768070715	4.4149900626	-2.8671996722
H	0	-1.7097902437	5.0042806364	-1.3263990415

H	0	0.0617476694	4.8149839316	-1.4501707202
N	0	-0.8382842211	0.3435948407	-0.7793309179
C	0	-1.9392376509	-0.6456134577	-0.7996547025
C	0	0.1589318245	0.3727810430	-1.7198045658
H	0	-2.7455578382	-0.2600933571	-1.4491519463
S	0	-2.5906832404	-0.6071693779	0.9456898061
C	0	-1.6453382418	-2.1169210725	-1.2303808882
H	0	0.0577155843	-0.4308107765	-2.4656446301
O	0	1.0753588413	1.1707862594	-1.7633341804
C	0	-1.4358842526	-2.2528286253	-2.7579907538
C	0	-2.9163426317	-2.9326677785	-0.9023771935
C	0	-0.4490139242	-2.7009008703	-0.4684448662
H	0	-0.4085614069	-2.0363966969	-3.0790259727
H	0	-1.6396152996	-3.2909514435	-3.0614893342
H	0	-2.1220404701	-1.6021694853	-3.3237521782
H	0	-2.7834501375	-3.9721043658	-1.2376397088
H	0	-3.1240550410	-2.9586065730	0.1770602222
H	0	-3.8012465669	-2.5231219757	-1.4164027478
H	0	-0.6484942856	-2.7166328790	0.6122008736
H	0	-0.2604062174	-3.7333985242	-0.8021737634
H	0	0.4680579142	-2.1167011870	-0.6181216594
C	0	1.3037838410	1.4926306469	1.1021533331
H	0	1.8699259174	1.8908837845	0.2677270315
H	0	0.8555323621	2.2127629091	1.7797132951
H	0	-0.3330973391	1.4567427813	3.1857642794
H	0	0.4818469373	-1.4648136641	2.5099103383
O	0	2.1170406373	-0.7380192970	0.7424599031
Si	0	3.6042105155	-0.7343722070	-0.0775393438
C	0	4.2409321100	0.9889122133	-0.4513402438
H	0	4.3463785340	1.6015954774	0.4573471823
H	0	5.2357818963	0.9093191203	-0.9214797416
H	0	3.5665766737	1.5017163921	-1.1534274108
C	0	4.8024797682	-1.6589440719	1.0347071065
H	0	5.7854149777	-1.7790804809	0.5496821341
H	0	4.9562205192	-1.1167981529	1.9821023105
H	0	4.4163521694	-2.6617595705	1.2784501758
C	0	3.2900674989	-1.6805496009	-1.6647630466
H	0	2.6318360103	-1.0946397781	-2.3244886697
H	0	4.2347161332	-1.8658233805	-2.2020481307
H	0	2.8157626120	-2.6540481139	-1.4635994582

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C	0	-1.7789290424	-0.7237379482	0.3957660630
C	0	-0.7348221915	-0.5410994345	1.2844877717
C	0	-1.5357760811	-1.2789023495	-0.8772988728
C	0	0.8013007522	0.8310041575	-0.1506948521
H	0	-0.8845308101	0.0527127180	2.1854718868
C	0	0.9263106796	0.0197217196	-1.3103182991
C	0	-0.2454469145	-1.6545688655	-1.2690903042
H	0	-0.1074158670	-2.0327972108	-2.2859916359
H	0	0.4680489211	0.3845709628	-2.2281041669
C	0	-0.3101363730	1.7932355636	0.0556177052
O	0	-0.5319700849	2.4552513727	1.0394932555
O	0	-1.1103899416	1.8039415330	-1.0417058293
C	0	-2.2735606608	2.6201865065	-0.9308788064
H	0	-2.8703831785	2.3159640917	-0.0602135614
H	0	-2.8391193788	2.4700047412	-1.8589331059
H	0	-1.9935899605	3.6783101829	-0.8207903519
N	0	2.0270294616	1.0312071615	0.5528554983
C	0	3.1010094158	0.0879185532	0.1991939353
C	0	2.4918914974	2.3479315610	0.7472759059
H	0	4.0069299188	0.6815026011	0.0119806135

S	0	2.6064513497	-0.5802526308	-1.4723706143
C	0	3.5426897730	-0.9767362285	1.2415461999
H	0	3.4906713225	2.3383929102	1.2399213190
O	0	1.9349837323	3.3612334595	0.4246882366
C	0	2.4666226908	-1.9984462480	1.6086141985
C	0	4.7520362372	-1.7129255001	0.6383474024
C	0	3.9820261325	-0.2292347390	2.5125052438
H	0	1.6680101420	-1.5405463599	2.2054331213
H	0	2.9070883138	-2.8027671379	2.2176834706
H	0	2.0325572592	-2.4606643644	0.7100830963
H	0	5.1727278566	-2.4188988423	1.3705457355
H	0	5.5514647357	-1.0099467794	0.3518610937
H	0	4.4626913540	-2.2855857992	-0.2563845684
H	0	4.8079817340	0.4707323254	2.3060287100
H	0	4.3346274578	-0.9447554581	3.2715611906
H	0	3.1459431835	0.3410636457	2.9443418097
H	0	0.4131970145	-2.1313319647	-0.5428982772
H	0	0.1372707661	-1.1733433461	1.2254401428
O	0	-2.9771361643	-0.1506907160	0.6863179320
H	0	-2.3125625759	-1.1676800503	-1.6369440868
Si	0	-4.5587904162	-0.6333097559	0.3085360017
C	0	-5.0276457578	-0.0646350404	-1.4218898427
H	0	-4.4348023044	-0.5630453070	-2.2045973771
H	0	-6.0904431896	-0.2850473786	-1.6176379476
H	0	-4.8850889372	1.0221968391	-1.5275383065
C	0	-4.6673180289	-2.5009002489	0.4574737185
H	0	-5.6923464915	-2.8510625498	0.2522841129
H	0	-3.9890218547	-3.0005985452	-0.2518089772
H	0	-4.3923328392	-2.8260076056	1.4737722359
C	0	-5.6153946859	0.2409967944	1.5809329428
H	0	-6.6842862417	0.0180949324	1.4297800269
H	0	-5.3385334586	-0.0703023368	2.6005114843
H	0	-5.4820222710	1.3326454082	1.5135897226

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C	0	1.9770107302	1.3930018527	-0.1954470612
C	0	1.2573564508	0.7177743164	-1.1648238574
C	0	1.3858886357	2.4707535518	0.4991402201
C	0	-0.5787021274	-0.0199689328	0.2077030754
H	0	1.6330039863	-0.1864217325	-1.6331658061
C	0	-1.1450844782	1.1823972593	0.6895784662
C	0	0.0794811214	2.8699279902	0.2397346935
H	0	-0.3629324899	3.6535058166	0.8616698024
H	0	-1.0998336880	1.3905292434	1.7565009577
C	0	0.2366294457	-0.8587981924	1.1103580385
O	0	0.3324676076	-2.0635582355	1.0766189233
O	0	0.8483797827	-0.0828067768	2.0350497550
C	0	1.7124318399	-0.7370977150	2.9558381885
H	0	2.6310707816	-1.0695595518	2.4518712225
H	0	1.9628456744	0.0066169451	3.7220879603
H	0	1.2178958928	-1.6095421394	3.4068384751
N	0	-1.3808532415	-0.6547977674	-0.7841120347
C	0	-2.7815193029	-0.2303029758	-0.7732377514
C	0	-0.9188568486	-1.4991131684	-1.7671547711
H	0	-3.1504632422	-0.1858292188	-1.8087051350
S	0	-2.6970037746	1.5159031636	-0.1525714976
C	0	-3.7337611615	-1.1470673195	0.0469527181
H	0	-1.7376848458	-1.7883644326	-2.4641965713
O	0	0.2167117902	-1.8937489475	-1.9073745327
C	0	-3.3117034223	-1.2430907732	1.5197710881
C	0	-3.7119640990	-2.5579053985	-0.5677342156
C	0	-5.1537199949	-0.5701544709	-0.0607015630

H	0	-3.2946670664	-0.2522730151	1.9962771738
H	0	-4.0293763861	-1.8711691735	2.0704371329
H	0	-2.3197978693	-1.7061871695	1.6199625212
H	0	-4.4427374904	-3.1990267804	-0.0509684936
H	0	-3.9816871931	-2.5426759070	-1.6364874331
H	0	-2.7248484102	-3.0311928450	-0.4612446879
H	0	-5.4814496871	-0.5036377376	-1.1115755203
H	0	-5.8682348363	-1.2157021114	0.4725786079
H	0	-5.2093129296	0.4362418570	0.3806355507
H	0	0.4454437281	1.2168256959	-1.6873684796
H	0	-0.3196171325	2.8312560229	-0.7744505683
H	0	1.9039495431	2.8142653776	1.3980732889
O	0	3.1574727235	0.9308306068	0.2841908664
Si	0	4.2169174969	-0.2375831059	-0.3703886628
C	0	4.6880466386	0.2845721583	-2.1122137337
C	0	5.6922436140	-0.1496554050	0.7810094395
C	0	3.4600281638	-1.9530636040	-0.3480672664
H	0	5.0957883495	1.3083012763	-2.1148780300
H	0	5.4590598717	-0.3908155076	-2.5187389724
H	0	3.8259726138	0.2592043222	-2.7960282021
H	0	6.1355901287	0.8587436069	0.7805779521
H	0	5.3973171854	-0.3901339519	1.8150612676
H	0	6.4707160071	-0.8678112813	0.4755177591
H	0	3.2475380375	-2.2898933478	0.6779445315
H	0	2.5162969655	-2.0313183826	-0.9083336699
H	0	4.1791059114	-2.6646179884	-0.7891721591

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C	0	1.8560146880	-0.6064788057	-1.1739724996
C	0	1.5811271257	0.7115368723	-1.4895966682
C	0	1.1658686549	-1.6505559820	-1.8330494263
C	0	-0.7764392386	0.5998452971	-0.7993299334
H	0	1.9948994276	1.5271580712	-0.9065333447
C	0	-1.3312660474	-0.4475546025	-1.5645034882
C	0	0.1482033913	-1.3900055033	-2.7438634845
H	0	-0.4044807329	-2.2337828088	-3.1668113011
H	0	-1.9396984149	-0.1829361737	-2.4305192560
C	0	-0.9174108587	1.9879651923	-1.2704045839
O	0	-0.9512942741	2.3053751937	-2.4421747834
O	0	-1.0263246806	2.8696624523	-0.2592986763
C	0	-1.0814256487	4.2436618092	-0.6304845259
H	0	-1.1272869926	4.8106048558	0.3070597015
H	0	-1.9687006781	4.4487715706	-1.2483157044
H	0	-0.1855943400	4.5261806602	-1.2034301980
N	0	-0.6785714104	0.2632999096	0.5811957706
C	0	-1.6371032421	-0.7533381711	1.0176568228
C	0	0.2960217858	0.6916562316	1.4471350944
H	0	-1.1450692697	-1.4098603232	1.7505592877
S	0	-1.9358181110	-1.7632772333	-0.5043876616
C	0	-2.9357279521	-0.1884250378	1.6615187069
H	0	0.2491913164	0.1376546112	2.4106676203
O	0	1.1288819146	1.5464374892	1.2335302635
C	0	-3.8092430486	-1.3813614826	2.0800607020
C	0	-2.5560900316	0.6242913530	2.9116906444
C	0	-3.7076347092	0.7167128871	0.6917935110
H	0	-4.1097491116	-1.9801856751	1.2070051667
H	0	-4.7242744430	-1.0273399112	2.5792406350
H	0	-3.2765061683	-2.0420979203	2.7841028826
H	0	-3.4680634750	0.9645580451	3.4263185579
H	0	-1.9704541581	1.5182307969	2.6510603104
H	0	-1.9751374707	0.0223058842	3.6295226596
H	0	-3.1201149049	1.6071758238	0.4289352513

H	0	-4.6424080610	1.0574713284	1.1641125024
H	0	-3.9690039656	0.1787601989	-0.2308994709
H	0	0.1969826679	-0.5115179915	-3.3893322021
H	0	1.1439820762	0.9623346888	-2.4511697574
H	0	1.2795701092	-2.6514667296	-1.4098661412
O	0	2.5890509442	-0.9623005081	-0.0921433224
Si	0	3.9831726537	-0.3763364580	0.6824638065
C	0	5.3639115553	-1.5527066689	0.1937631780
H	0	5.1041931935	-2.5911951444	0.4550688024
H	0	5.5480114215	-1.5138829155	-0.8924093123
H	0	6.3060194101	-1.2968316508	0.7064954871
C	0	3.6164783102	-0.4886349856	2.5156084177
H	0	4.5314250130	-0.3326018359	3.1104804065
H	0	2.8858721018	0.2859145027	2.7947487777
H	0	3.2047168956	-1.4768577956	2.7759688442
C	0	4.4117249421	1.3822155136	0.1906258225
H	0	3.6352337280	2.0787553160	0.5403282218
H	0	5.3674741759	1.6648959782	0.6635588144
H	0	4.5295529370	1.4941777815	-0.8984169281

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C	0	-1.4728100858	-1.8835297909	1.3980251366
C	0	-2.1707240578	-0.6201964504	0.9831512730
C	0	-0.9178267509	-2.6514046838	0.4478766272
C	0	-1.3277181428	0.1900149674	-0.0277679961
H	0	-2.3914239761	0.0261359248	1.8391655398
C	0	-0.9173109604	-0.7045844430	-1.2349370480
C	0	-1.0307883816	-2.2287204634	-0.9905830516
H	0	-0.2799961531	-2.7615446602	-1.5887120259
H	0	-1.5786401312	-0.4652019398	-2.0779966069
C	0	-2.1918486437	1.3341266112	-0.5998415765
O	0	-3.3865463109	1.2670849377	-0.7407937323
O	0	-1.4499891844	2.3715594998	-1.0090745882
C	0	-2.1675620895	3.4823620893	-1.5447278701
H	0	-1.4115492776	4.2110622724	-1.8605151672
H	0	-2.7852167220	3.1715641890	-2.4001436797
H	0	-2.8225435580	3.9177245576	-0.7754988145
N	0	-0.1003718145	0.7374553734	0.5835234943
C	0	1.1686962784	0.6445837785	-0.1493878558
C	0	-0.2708137330	1.7676344092	1.4737837394
H	0	1.5029315933	1.6662512065	-0.3959467638
S	0	0.7400275918	-0.1282852501	-1.7636077618
C	0	2.3612074444	-0.0552084030	0.5744971508
H	0	0.6735922610	2.3005523934	1.7089506025
O	0	-1.3358950477	2.0972363328	1.9566565736
C	0	2.6972619186	0.6816886724	1.8827694678
C	0	3.5777094464	0.0429511471	-0.3630287682
C	0	2.0711402236	-1.5205928951	0.8998215305
H	0	1.8921639648	0.5855638552	2.6258436886
H	0	3.6055035946	0.2455867979	2.3270425223
H	0	2.8940039317	1.7531422812	1.7147008119
H	0	4.4652955337	-0.3933642266	0.1203792393
H	0	3.4028218402	-0.5024966115	-1.3025457585
H	0	3.8116597026	1.0914899519	-0.6117822285
H	0	1.8361552571	-2.0985239423	-0.0036824669
H	0	2.9518241558	-1.9790346785	1.3770457855
H	0	1.2215933648	-1.6061941253	1.5871846661
H	0	-2.0202047416	-2.5514841543	-1.3627885731
H	0	-3.1361033601	-0.8252863069	0.4911649639
H	0	-1.4172683120	-2.1429469659	2.4559490093
O	0	-0.2535729423	-3.8158881988	0.6256633082
Si	0	-0.1579365948	-4.8417575363	1.9802732872

C	0	-1.8947839069	-5.3161670791	2.5101672358
C	0	0.7850213599	-4.0116212719	3.3773305976
C	0	0.7918326653	-6.3217568217	1.3402115549
H	0	-2.4781537158	-4.4408886882	2.8338998584
H	0	-2.4359421478	-5.7938518740	1.6775502003
H	0	-1.8612400489	-6.0318028148	3.3483366897
H	0	0.9013690329	-4.7139030179	4.2197829818
H	0	1.7906758566	-3.7115648806	3.0444969050
H	0	0.2728064694	-3.1145508646	3.7567619643
H	0	1.7889850333	-6.0201514519	0.9816564876
H	0	0.9275986808	-7.0754640340	2.1330352629
H	0	0.2592145998	-6.7983472640	0.5019993275

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C	0	-1.9805164388	1.5780945653	-1.7961011267
C	0	-1.1159932955	0.3502427704	-1.7142092232
C	0	-1.7552232348	2.5705697476	-0.9208324152
C	0	-0.9647200730	-0.1774086683	-0.2632500973
H	0	-1.4983592081	-0.4627248233	-2.3401312470
C	0	-0.8428091293	0.9998329225	0.7575406844
C	0	-0.6566761231	2.3743173500	0.0931600134
H	0	-0.7005963526	3.1646636873	0.8541342884
H	0	-1.7741222563	1.0524455359	1.3382275908
C	0	-2.1825183911	-1.0102608730	0.2001159281
O	0	-2.1568985270	-1.7487114797	1.1502982667
O	0	-3.2848237229	-0.7553613403	-0.5163355740
C	0	-4.4506051887	-1.4908975508	-0.1427658942
H	0	-4.2696386253	-2.5699632383	-0.2538234739
H	0	-5.2479944694	-1.1625856294	-0.8200588389
H	0	-4.7233365953	-1.2836565147	0.9024766510
N	0	0.2205389753	-1.0390299269	-0.1224633480
C	0	1.2279959403	-0.7278973121	0.8893430731
C	0	0.1328860273	-2.2998992312	-0.6491379794
H	0	1.3668138124	-1.6163581285	1.5269501875
C	0	2.6384474603	-0.3303609308	0.3534901591
H	0	0.9566505065	-2.9693289664	-0.3221839439
O	0	-0.7552753721	-2.6692428077	-1.3915862720
C	0	3.5568136287	-0.1346254646	1.5713980039
C	0	3.2038319393	-1.4706383905	-0.5111103876
C	0	2.6057737882	0.9534034042	-0.4802646760
H	0	3.1950449340	0.6810724290	2.2153112547
H	0	4.5772337543	0.1176456866	1.2442261201
H	0	3.6160230036	-1.0521489195	2.1797470520
H	0	4.2402021213	-1.2375698847	-0.8007277702
H	0	2.6270130456	-1.6086497819	-1.4375026164
H	0	3.2206605401	-2.4279338997	0.0345115258
H	0	1.9255072881	0.8532571719	-1.3391659533
H	0	3.6099758051	1.1746065777	-0.8736889499
H	0	2.2827997230	1.8101651171	0.1269976927
S	0	0.4478128416	0.5395311942	1.9723991123
H	0	0.3294623572	2.4292628228	-0.3885427881
H	0	-0.0951985285	0.5700359057	-2.0705839044
H	0	-2.7743325572	1.6306122164	-2.5411110743
O	0	-2.4589917788	3.7245289156	-0.8107455411
Si	0	-4.1477338921	3.9084561263	-0.9383825462
C	0	-4.9419168472	2.5297445859	0.0584686516
C	0	-4.6902508766	3.8575410951	-2.7364454664
C	0	-4.4773493364	5.5992859162	-0.2071289831
H	0	-4.5685972774	1.5502983724	-0.2781852041
H	0	-4.7009229516	2.6357495650	1.1288209569
H	0	-6.0391037113	2.5400293826	-0.0461897866
H	0	-5.7428772660	4.1742573707	-2.8268031569

H	0	-4.0782370101	4.5411835006	-3.3467873594
H	0	-4.6066123225	2.8481935628	-3.1681071415
H	0	-3.9524422321	6.3823429876	-0.7775324724
H	0	-5.5548481592	5.8315369684	-0.2235385248
H	0	-4.1313393920	5.6504430686	0.8373949439

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C	0	-3.0828462466	1.1737916962	0.5383282113
C	0	-1.9066495432	0.7247976698	1.3568584439
C	0	-2.8492887642	1.8930101507	-0.5698994125
C	0	-0.7815193492	0.0973213596	0.4701692491
H	0	-2.1947407877	0.0073130763	2.1304276730
C	0	-0.4533282075	1.0601105869	-0.7270659403
C	0	-1.4240245656	2.2486144843	-0.8922435059
H	0	-1.3646053395	2.6406590902	-1.9165350202
H	0	-0.4564183778	0.4778296338	-1.6550446513
C	0	-1.2591287374	-1.2758752982	-0.0409418360
O	0	-0.8712819726	-2.3367170403	0.3790149741
O	0	-2.1745842233	-1.1668843779	-1.0161902564
C	0	-2.6985376609	-2.3948996640	-1.5248217024
H	0	-3.1693000067	-2.9778017872	-0.7198715061
H	0	-3.4409180235	-2.1175333002	-2.2815182001
H	0	-1.8975525069	-3.0019563702	-1.9723715453
N	0	0.4600266752	-0.1056583262	1.2267279631
C	0	1.7061209292	0.2716902350	0.5743273123
C	0	0.4869077667	-0.5767036268	2.5156702763
H	0	2.3866978082	0.6482253322	1.3532071497
S	0	1.2394954447	1.7235432291	-0.4438392581
C	0	2.4863774109	-0.8407206883	-0.1982059391
H	0	1.5230872469	-0.5554291716	2.9274210019
O	0	-0.4565539211	-0.9598045616	3.1703025625
C	0	1.8104745852	-1.2632521722	-1.5108359186
C	0	2.6377788915	-2.0719999578	0.7101521702
C	0	3.8747179941	-0.2626044242	-0.5204879240
H	0	1.6694086170	-0.4020337963	-2.1798223698
H	0	2.4479541242	-1.9937087706	-2.0330434912
H	0	0.8441089867	-1.7511842911	-1.3340813666
H	0	3.2608516787	-2.8297950807	0.2096739971
H	0	3.1323414059	-1.8169331295	1.6613617339
H	0	1.6609725040	-2.5254957485	0.9305570439
H	0	4.4160333652	0.0173639351	0.3982634311
H	0	4.4850601094	-1.0057015226	-1.0562175564
H	0	3.7929690373	0.6326847917	-1.1563158257
H	0	-1.4278785380	1.5713173483	1.8819120613
H	0	-1.0988295850	3.0562678527	-0.2141775516
H	0	-4.0861314174	0.8709234195	0.8383791252
O	0	-3.7593945444	2.3607557948	-1.4529959928
Si	0	-5.4109510238	1.9864745125	-1.6198225889
C	0	-6.3695726433	2.5972511321	-0.1253747987
C	0	-5.5886206153	0.1318869170	-1.8579087101
C	0	-5.9231305024	2.9187631242	-3.1593064956
H	0	-6.1127086334	2.0491078614	0.7935658677
H	0	-6.1656730048	3.6658068810	0.0509900948
H	0	-7.4533821609	2.4836185385	-0.2947283958
H	0	-6.6460605488	-0.1447473076	-2.0014920847
H	0	-5.0272383579	-0.1892051184	-2.7500595951
H	0	-5.2007200486	-0.4270173730	-0.9935520971
H	0	-5.3320040490	2.5943300902	-4.0304261211
H	0	-6.9884426839	2.7482552941	-3.3855809233
H	0	-5.7715343803	4.0023663576	-3.0306474211

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C	0	3.3324343573	-0.5673182206	-0.1280499348
C	0	2.6028724420	0.6264267322	-0.6679347220
C	0	3.0124336706	-1.7558673003	-0.6676049338
C	0	1.0561401904	0.3816318087	-0.6054796844
H	0	2.8468528958	1.5398278936	-0.1209709999
C	0	0.7307650481	-0.9751685426	-1.3249396423
C	0	1.9895575018	-1.7456860484	-1.7733881046
H	0	1.7254008632	-2.7731163980	-2.0579406944
H	0	0.1027342583	-0.7661542757	-2.1987219733
C	0	0.4367574246	1.5469553127	-1.3853271311
O	0	0.3335357915	1.5700799613	-2.5877613943
O	0	0.1151126019	2.5743119324	-0.5911244719
C	0	-0.3640131482	3.7517280828	-1.2416572264
H	0	-0.5299793385	4.4901436264	-0.4487947726
H	0	-1.3030178750	3.5421783029	-1.7761491904
H	0	0.3760929561	4.1215165985	-1.9660900568
N	0	0.5527329868	0.2900563876	0.7718905131
C	0	-0.5308074257	-0.6542400433	1.0089472114
C	0	1.1038042844	0.9301442490	1.8543843989
H	0	-0.3965641506	-1.0564588409	2.0245474636
S	0	-0.1975863004	-2.0386167919	-0.1448340852
C	0	-1.9907975309	-0.1039324912	0.9411697675
H	0	0.6455572778	0.5639507922	2.8028464511
O	0	1.9695271225	1.7771309334	1.8525466771
C	0	-2.9091416464	-1.2195396552	1.4684546713
C	0	-2.1030417990	1.1264969631	1.8557430269
C	0	-2.4327869898	0.2737593977	-0.4791795540
H	0	-2.8485087716	-2.1156130389	0.8317304153
H	0	-3.9566030776	-0.8812485356	1.4794417262
H	0	-2.6382641907	-1.5102368696	2.4968690119
H	0	-3.1442302867	1.4847030764	1.8778976634
H	0	-1.4677919089	1.9488527177	1.4966804961
H	0	-1.8134738744	0.8903863655	2.8924923416
H	0	-1.8953661274	1.1515559917	-0.8563375449
H	0	-3.5040834786	0.5284137082	-0.4791684777
H	0	-2.2834869676	-0.5613566021	-1.1783589729
H	0	2.8287616724	0.7932954160	-1.7349142355
H	0	2.3949684961	-1.2482019813	-2.6710164929
H	0	4.0276761701	-0.4535935367	0.7041224363
O	0	3.4627423005	-2.9701263314	-0.2878305568
Si	0	3.8480398567	-3.4817389734	1.2927500687
C	0	2.5793913827	-2.7823234572	2.4869294846
C	0	5.5909659819	-2.9341492241	1.7271092095
C	0	3.7454521756	-5.3481115294	1.1943479112
H	0	2.6757082684	-1.6914691522	2.5926083468
H	0	1.5651563613	-2.9982102948	2.1159726640
H	0	2.6990756821	-3.2370013844	3.4841459797
H	0	5.8975863281	-3.3519397445	2.7006602651
H	0	6.3085344620	-3.2836007826	0.9672153366
H	0	5.6729729074	-1.8379288505	1.7912101775
H	0	4.4326502250	-5.7375194878	0.4261805303
H	0	4.0145939061	-5.8104151279	2.1581745409
H	0	2.7249331184	-5.6692937176	0.9318353066

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H	0	-0.5095892262	-1.0672456209	-2.7175738714
C	0	-0.2775120981	-1.6390642839	-1.8151222374
C	0	-1.2015205611	-1.5248749444	-0.7442724364
C	0	1.7291913853	-0.7548415061	0.3052656811
C	0	0.6326521114	-0.8742530536	1.1867365231

C	0	-0.8824894411	-2.0338379646	0.5264622592
H	0	-1.6167112272	-1.9266321068	1.3282096442
H	0	0.7892313311	-1.4842978780	2.0783039129
C	0	2.8791177321	-1.6384309295	0.4956892721
O	0	2.7814703032	-2.7865657701	0.8969380029
O	0	4.0581715254	-1.0529570670	0.2185597482
C	0	5.1992687310	-1.9003469817	0.2501948575
H	0	6.0564093404	-1.2699161968	-0.0170631269
H	0	5.3415951377	-2.3376528463	1.2502845791
H	0	5.0940608777	-2.7210903440	-0.4758415101
N	0	1.8042357143	0.5060736562	-0.3470477739
C	0	1.1717223357	1.6067509682	0.4041095260
C	0	2.4359982671	0.6505885659	-1.5594739260
H	0	1.9105588184	2.0326937985	1.1059893324
S	0	-0.1014719135	0.7367361643	1.4580106959
C	0	0.5151955471	2.7890533454	-0.3749116830
H	0	2.4702557110	1.6985886916	-1.9024919792
O	0	2.9214927821	-0.2529407533	-2.2081217931
C	0	1.5747761153	3.8037650007	-0.8580145548
C	0	-0.3760749664	3.5592612609	0.6261802065
C	0	-0.3568441599	2.2923376828	-1.5375821374
H	0	2.2055735276	3.4361188714	-1.6770105241
H	0	1.0703871950	4.7094980129	-1.2284484444
H	0	2.2368854272	4.1059523780	-0.0308154947
H	0	-0.7523194185	4.4792277140	0.1542266678
H	0	-1.2475069717	2.9657808802	0.9377504604
H	0	0.1859132552	3.8498293324	1.5284885364
H	0	-1.0733237260	1.5317497623	-1.1961235256
H	0	-0.9203949316	3.1357904215	-1.9666439304
H	0	0.2381218429	1.8479651403	-2.3477128365
C	0	0.9262591060	-2.2730652740	-1.6870257018
H	0	1.6573908756	-2.2314099704	-2.4924337166
H	0	1.1548167191	-2.9446881519	-0.8614190422
H	0	-0.3043218687	-2.9572471710	0.5679834565
O	0	-2.2471754590	-0.7046247802	-0.9530703847
Si	0	-3.7877147711	-0.5824969145	-0.2292544701
C	0	-3.6920401197	0.2048447734	1.4707676055
C	0	-4.7156036091	0.5314723645	-1.4111188136
C	0	-4.5292705183	-2.3038496849	-0.1475079512
H	0	-3.1723834741	1.1735359785	1.4236797411
H	0	-4.7123428950	0.3766946661	1.8534467231
H	0	-3.1602247676	-0.4222917322	2.2021254719
H	0	-4.2206256728	1.5131226612	-1.4850531086
H	0	-4.7505046162	0.0919863546	-2.4204001235
H	0	-5.7507679962	0.6962942510	-1.0704091111
H	0	-4.5740121969	-2.7568888751	-1.1508301950
H	0	-3.9376465992	-2.9708213829	0.4988726987
H	0	-5.5545875098	-2.2653625129	0.2559588011

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H	0	-2.2255087397	2.0859628405	2.2345189245
C	0	-1.4728302341	1.3005296955	2.1280901617
C	0	-0.2206146739	1.4831297523	2.6092546270
C	0	-1.8739754142	0.1752609748	1.3389658672
C	0	0.9478514562	0.7922357356	-0.3101159690
H	0	0.0621403960	2.4214460232	3.0893287268
C	0	0.1624752376	-0.3892418425	-0.4421748812
C	0	-0.9690943026	-0.8588820493	1.0009669821
H	0	-1.4137100922	-1.7708085198	0.5955484994
H	0	-0.6437498214	-0.3463261874	-1.1753753565
C	0	0.3771387581	2.1296184412	-0.2961218348
O	0	0.9171413147	3.1791207705	-0.0271116534

O	0	-0.9566320901	2.0494934434	-0.6323968292
C	0	-1.6749069094	3.2701908138	-0.5643838389
H	0	-1.5162924328	3.7686756014	0.4037782695
H	0	-2.7347256764	3.0120435833	-0.6907359443
H	0	-1.3509480290	3.9599907473	-1.3592428147
N	0	2.3499156364	0.5993949653	-0.4493887760
C	0	2.7857987294	-0.7832842940	-0.2784923448
C	0	3.0608856440	1.3547140590	-1.3902930571
H	0	3.5070647231	-1.0178932026	-1.0746686760
S	0	1.2626288291	-1.7946742764	-0.6835335209
C	0	3.4910844633	-1.1343883641	1.0571956279
H	0	4.1129961027	0.9927158159	-1.4708168456
O	0	2.6295704893	2.2723047672	-2.0374641208
C	0	2.6343197981	-0.8007085819	2.2766253804
C	0	3.8348736594	-2.6313435544	1.0447607714
C	0	4.7915555497	-0.3128261431	1.1192812025
H	0	2.4246565136	0.2765509635	2.3150084617
H	0	3.1614929186	-1.0772936496	3.2027646381
H	0	1.6849610994	-1.3550438512	2.2553741422
H	0	4.4107247097	-2.8986964610	1.9442294128
H	0	4.4454480255	-2.8955791261	0.1653969424
H	0	2.9238610430	-3.2483955809	1.0263529903
H	0	5.4525543811	-0.5388849107	0.2667599091
H	0	5.3450251895	-0.5459752191	2.0422532812
H	0	4.5794115956	0.7666385325	1.1140212053
H	0	-0.2117207431	-1.0743426784	1.7524390432
H	0	0.5428454799	0.7140371299	2.5430045108
O	0	-3.1021428565	0.2601177850	0.8190251271
Si	0	-4.0354067496	-0.6827396531	-0.2585762306
C	0	-5.5996624297	0.3238186675	-0.4398421093
H	0	-5.3810314385	1.3093006615	-0.8810955759
H	0	-6.3230425960	-0.1893995948	-1.0942141882
H	0	-6.0783860066	0.4872593956	0.5385608513
C	0	-3.1412807994	-0.8478880304	-1.8993885109
H	0	-2.7259242810	0.1244339201	-2.2078422693
H	0	-2.3175281996	-1.5770436085	-1.8573309941
H	0	-3.8435069263	-1.1849256719	-2.6799152259
C	0	-4.3796529765	-2.3509538279	0.5284883993
H	0	-3.4663198470	-2.9529837190	0.6533156918
H	0	-4.8428177060	-2.2255219315	1.5203096595
H	0	-5.0769457715	-2.9295865561	-0.1000317392

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H	0	-2.2757975095	2.7004799088	-1.1944393533
C	0	-1.6692794006	1.8618749631	-1.5456733607
C	0	-0.4295652490	2.0794948224	-2.0691229681
C	0	-2.1519135385	0.5669583238	-1.2161691954
C	0	0.8779736117	0.7510536560	-0.1158132891
H	0	-0.0218376348	3.0834474927	-2.1764030328
C	0	0.1682499554	-0.4739479662	-0.1244076228
C	0	-1.3494921198	-0.5691546865	-1.4288298199
H	0	-1.7762550100	-1.5511487506	-1.2097562961
H	0	-0.4422608098	-0.7002099424	0.7479038658
C	0	0.5591835035	1.8141325482	0.8258259994
O	0	1.3033974994	2.6831055239	1.2247947613
O	0	-0.7327680901	1.6901635743	1.2611225957
C	0	-1.1989204744	2.7246826587	2.1144251962
H	0	-0.6087895533	2.7719187859	3.0425269773
H	0	-1.1325272023	3.7041496882	1.6157702136
H	0	-2.2467760498	2.4873986857	2.3397643410
N	0	2.1791888153	0.6527065785	-0.6728841357
C	0	2.7547417547	-0.6815621344	-0.5669566751

C	0	2.7947415604	1.6359066396	-1.4150565322
H	0	3.3683417435	-0.8828879197	-1.4577814779
S	0	1.2696323858	-1.8004394745	-0.6696021948
C	0	3.6319656131	-0.9147215874	0.6944314625
H	0	3.7778149858	1.2876565424	-1.8097588588
O	0	2.3550031536	2.7403858824	-1.6348686125
C	0	2.8501879365	-0.6663505929	1.9919383591
C	0	4.8237849591	0.0573198547	0.6368212213
C	0	4.1509338294	-2.3599724495	0.6553232620
H	0	1.9638723007	-1.3148200084	2.0536503695
H	0	3.4920668167	-0.8867160449	2.8594425623
H	0	2.5314688050	0.3826927721	2.0690785831
H	0	5.5020737958	-0.1321701615	1.4831757511
H	0	5.4064606770	-0.0669433861	-0.2908301228
H	0	4.4917681161	1.1036353450	0.7043590688
H	0	4.7216109332	-2.5572638049	-0.2675617382
H	0	4.8199035067	-2.5478685357	1.5091635972
H	0	3.3223983499	-3.0824526469	0.7076340341
H	0	0.1556517900	1.2845208316	-2.5275335497
H	0	-0.7061236624	-0.5639189055	-2.3077394401
O	0	-3.2890618675	0.5346254190	-0.5048750423
Si	0	-4.0839700040	-0.6561970702	0.4188507764
C	0	-2.9002941141	-1.3633844986	1.6940145267
C	0	-5.4645378050	0.2987555578	1.2420009996
C	0	-4.7594949847	-1.9844484736	-0.7219476576
H	0	-2.3404096895	-0.5516592136	2.1845499697
H	0	-3.4614834713	-1.9123556907	2.4682080568
H	0	-2.1747013420	-2.0629514018	1.2514645240
H	0	-5.0584146173	1.0865271848	1.8964174073
H	0	-6.1102387516	0.7809365927	0.4910961508
H	0	-6.0920073836	-0.3667437199	1.8570561521
H	0	-5.4054266422	-1.5392349099	-1.4956611947
H	0	-3.9601781588	-2.5458052040	-1.2301236213
H	0	-5.3649332622	-2.7074606518	-0.1502659927

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H	0	-1.3297425680	-2.4407960033	1.8722612582
C	0	-1.0128671214	-2.4957472058	0.8272318139
C	0	0.1288137665	-3.1567252768	0.4913929747
C	0	-1.7629154341	-1.7038471029	-0.0919235898
C	0	1.3300551763	-0.8460430081	-0.4637833716
H	0	0.7247988970	-3.6457506478	1.2606374227
C	0	0.3102395328	-0.3832415561	-1.3243878339
C	0	-1.3261943015	-1.5381258969	-1.4168174791
H	0	-1.9598278001	-0.9748591464	-2.1025872350
H	0	0.4945655526	-0.4690854022	-2.3973997108
C	0	2.3790573166	-1.7151176361	-0.9638036098
O	0	2.2466586281	-2.4632595261	-1.9201221415
O	0	3.5374195611	-1.5948334381	-0.2776412898
C	0	4.5712325258	-2.5022305179	-0.6360493115
H	0	5.4171876367	-2.2794177666	0.0259192901
H	0	4.8644095554	-2.3744473170	-1.6893143759
H	0	4.2432330013	-3.5431270698	-0.4919681685
N	0	1.4202962814	-0.1021358765	0.7390822751
C	0	1.0021263268	1.2870370510	0.6002635679
C	0	1.6758582136	-0.6402784169	1.9790038727
H	0	0.4826396404	1.6003300685	1.5183147321
S	0	-0.2695196168	1.2289205917	-0.7557721929
C	0	2.1555826582	2.2908489563	0.3220327304
H	0	1.5557537815	0.1213049273	2.7839951803
O	0	1.9940630564	-1.7862838391	2.2032496316
C	0	1.5447838390	3.6945774622	0.1927985292

C	0	3.1188967939	2.2639582140	1.5215572931
C	0	2.9312488189	1.9287860399	-0.9518174162
H	0	0.8589428804	3.7533975635	-0.6660566875
H	0	2.3376284280	4.4436589515	0.0439757379
H	0	0.9848715151	3.9745190374	1.1008607451
H	0	3.9089380159	3.0184330874	1.3839078836
H	0	3.6080459501	1.2840632249	1.6221409610
H	0	2.5998736767	2.4939737850	2.4666191155
H	0	3.4207052550	0.9500175879	-0.8523238066
H	0	3.7124097701	2.6824314646	-1.1390998498
H	0	2.2666899706	1.9030304984	-1.8277436418
O	0	-2.7539869489	-0.9903209230	0.4464562149
Si	0	-3.9030019711	0.2149773994	0.0963776300
C	0	-5.5483065521	-0.5760510996	0.5204818624
H	0	-5.7578866292	-1.4336986391	-0.1390284632
H	0	-5.5506665345	-0.9398047114	1.5602619748
H	0	-6.3727233346	0.1476894120	0.4097476502
C	0	-3.5168621799	1.6351805257	1.2528032576
H	0	-2.5375212739	2.0722103799	1.0068979269
H	0	-4.2819267951	2.4252696301	1.1752854220
H	0	-3.4888374328	1.2868902477	2.2975548247
C	0	-3.8926542128	0.7656943899	-1.6987487492
H	0	-2.9378557546	1.2313744659	-1.9842870602
H	0	-4.1035590481	-0.0674542188	-2.3877010165
H	0	-4.6870442857	1.5186202595	-1.8379776704
H	0	-0.8056554464	-2.3801218396	-1.8735162598
H	0	0.4458212197	-3.3056971396	-0.5396248474

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C	0	-1.4469523847	-1.5447814180	1.7114089383
C	0	-1.8282091575	-0.1428696902	1.3221981065
C	0	-1.2790098805	-2.4909606780	0.7696598626
C	0	-1.1708532551	0.3655325928	0.0167378706
H	0	-1.5968113058	0.5495574933	2.1401681621
C	0	-0.6843515248	-0.7685225937	-0.9139498410
H	0	-1.0449491543	-3.5240794484	1.0272467503
C	0	-1.3966495085	-2.0980503492	-0.6808595760
H	0	-0.9523487031	-2.8618738078	-1.3373541662
H	0	-0.7153616850	-0.4429259776	-1.9629621653
C	0	-2.2240143403	1.1352700571	-0.8190957025
O	0	-3.4142725523	1.0117577705	-0.6882626268
O	0	-1.6442726552	1.8363704884	-1.8004411720
C	0	-2.5184351306	2.6248282042	-2.6079057684
H	0	-1.8873354787	3.0947744222	-3.3714399907
H	0	-3.2897870990	1.9966693177	-3.0767827365
H	0	-3.0081719184	3.3914793351	-1.9894427444
N	0	-0.0010760145	1.2243987195	0.2838413590
C	0	1.3403012859	0.6979203516	0.0732367808
C	0	-0.2294430152	2.5432523988	0.5576279772
H	0	1.8531331796	1.2420043703	-0.7375049840
S	0	1.1470036503	-1.0142967928	-0.6897869944
C	0	2.2695665694	0.5943192697	1.3181666237
H	0	0.6920784754	3.1602526247	0.5493166900
O	0	-1.3324761828	3.0112685925	0.7646580293
O	0	1.7669345081	-0.9618410889	-2.0646439964
C	0	2.5271817119	1.9741541520	1.9476509988
C	0	3.6206518897	0.0306040295	0.8382453303
C	0	1.6542842871	-0.3259957383	2.3818032934
H	0	1.6267668369	2.3911091081	2.4208879206
H	0	3.2896665613	1.8766513517	2.7361752839
H	0	2.9043778230	2.6985701703	1.2080976589
H	0	4.3170021625	-0.0492199772	1.6868186511

H	0	3.5232794002	-0.9704395225	0.3921215728
H	0	4.0791207864	0.6866741898	0.0814910447
H	0	1.4840051213	-1.3384814123	1.9910769844
H	0	2.3295924060	-0.4054650263	3.2479916340
H	0	0.6916225884	0.0603573831	2.7435365344
H	0	-2.4507042937	-1.9922050689	-0.9999187431
H	0	-2.9187489806	-0.1021405326	1.1766488567
O	0	-1.3547088666	-1.7190941136	3.0469969949
Si	0	-1.0511417575	-3.1121001867	3.9797629904
C	0	-2.4050514594	-4.3745461306	3.6707653633
C	0	-1.1059904076	-2.4777442077	5.7384565852
C	0	0.6492118016	-3.7974037218	3.5693110560
H	0	-3.3951538093	-3.9297641567	3.8609341407
H	0	-2.3977550489	-4.7515228968	2.6369345894
H	0	-2.2858393793	-5.2375682319	4.3467401657
H	0	-0.9189373058	-3.2929013310	6.4564972287
H	0	-0.3418693502	-1.7002772031	5.8975695624
H	0	-2.0900788111	-2.0389633307	5.9674080738
H	0	1.4309457539	-3.0551475930	3.7938383193
H	0	0.8519874822	-4.6960157612	4.1754615128
H	0	0.7438763453	-4.0771003655	2.5092291808

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C	0	-2.8595344024	1.5504472007	0.0736852459
C	0	-1.9374069105	0.5818298386	-0.6159567855
C	0	-2.8586472719	1.7616093950	1.3979091336
C	0	-1.1978877224	-0.3894270723	0.3223573082
H	0	-2.4817792641	-0.0131054799	-1.3586995376
C	0	-0.8433146722	0.2624564136	1.6596840883
H	0	-3.5517994786	2.5018100893	1.8039645441
C	0	-1.9724556993	1.0113940601	2.3475932432
H	0	-2.5624853075	0.2828564575	2.9359749541
H	0	-0.4025249809	-0.4878482771	2.3323895158
C	0	-1.9944140940	-1.6650489058	0.6589986402
O	0	-1.5128067550	-2.5992603261	1.2463936612
O	0	-3.2848219445	-1.5644233615	0.3304698416
C	0	-4.0977142409	-2.6996921512	0.6334881777
H	0	-3.7464946335	-3.5760277955	0.0695174413
H	0	-5.1172904793	-2.4316006949	0.3330199815
H	0	-4.0565993974	-2.9290432155	1.7081582741
N	0	0.1002385091	-0.7826525788	-0.2722694910
C	0	1.2928633632	-0.1562782335	0.2947511259
C	0	0.0480972370	-1.6848207566	-1.2928193497
H	0	1.7172110429	-0.7529802575	1.1226307648
C	0	2.4329429103	0.2843398997	-0.6657330504
H	0	1.0353851560	-2.0005690511	-1.6746471116
O	0	-0.9964896094	-2.1214784980	-1.7427441681
C	0	3.3603728173	1.2569729866	0.0972282180
C	0	3.3096146464	-0.9180308686	-1.0764595077
C	0	1.8686026860	0.9969875252	-1.9034623654
H	0	2.8719139576	2.2154233232	0.3230381145
H	0	4.2448754005	1.4719758120	-0.5208414124
H	0	3.6978858520	0.8321943925	1.0539375145
H	0	4.2036574369	-0.5554214719	-1.6067693589
H	0	2.8057607538	-1.6224045598	-1.7510594052
H	0	3.6496797792	-1.4769502166	-0.1906135123
H	0	1.2566089150	0.3334646520	-2.5313797707
H	0	2.6926812055	1.3765946372	-2.5265555300
H	0	1.2467995971	1.8571960707	-1.6100815802
S	0	0.5965694228	1.3363173360	1.2428418658
O	0	1.4035762611	1.4940957949	2.5080188402
H	0	-1.5241221911	1.6858468629	3.0981425217

H	0	-1.1914952528	1.1636356419	-1.1831619308
O	0	-3.6521306657	2.2880320164	-0.7445123598
Si	0	-4.5939010101	1.8430309461	-2.0863802097
C	0	-5.5397284391	0.2768636121	-1.6671407436
H	0	-4.8486931157	-0.5510922903	-1.4486157917
H	0	-6.1715246662	0.4338164494	-0.7779803679
H	0	-6.1910507081	-0.0265379306	-2.5031587848
C	0	-3.5030089677	1.5988229053	-3.5983592246
H	0	-4.1255445953	1.4935282098	-4.5026879363
H	0	-2.8436724561	2.4699692357	-3.7443474480
H	0	-2.8710666600	0.7006746979	-3.5217964678
C	0	-5.7321798518	3.3059981348	-2.3405959493
H	0	-5.1521226186	4.2240973344	-2.5264815616
H	0	-6.3972526310	3.1420919098	-3.2042954951
H	0	-6.3593093065	3.4755276917	-1.4510659882

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C	0	-3.5672632590	-0.7265228333	-0.5443160237
C	0	-2.5369032487	-1.0062751935	0.5095452011
C	0	-3.3146246228	-0.6631575973	-1.8572371201
C	0	-1.1137956246	-1.3146104379	-0.0116965557
H	0	-2.8896081114	-1.8267570144	1.1462467794
C	0	-0.8448881996	-0.6460712880	-1.3671185769
H	0	-4.1362513147	-0.4532099845	-2.5447206832
C	0	-1.9339789391	-0.8237912599	-2.4161110278
H	0	-1.7985862030	-1.8180568033	-2.8847457821
H	0	0.1143963382	-1.0099962278	-1.7541970032
C	0	-0.8161306974	-2.8144498154	-0.1907145871
O	0	0.2956561294	-3.2524327138	-0.3637250671
O	0	-1.9256387102	-3.5482382433	-0.2310166145
C	0	-1.7495578074	-4.9547474630	-0.4075732691
H	0	-1.2027447100	-5.3771888210	0.4481125275
H	0	-2.7572897126	-5.3816298856	-0.4680574946
H	0	-1.1830647445	-5.1621292728	-1.3272406310
N	0	-0.1025672615	-0.7465405802	0.8973579668
C	0	0.5557290196	0.4932223702	0.5005909942
C	0	-0.0757040181	-1.2209683872	2.1795522257
H	0	0.3670991935	1.2793997855	1.2491531945
S	0	-0.4518209505	1.1250128287	-0.9586979651
C	0	2.0855385213	0.4283673130	0.2185873708
H	0	0.5403212373	-0.6025231846	2.8675776034
O	0	-0.6698596571	-2.2164315632	2.5409535484
O	0	-1.6672086113	1.8012874272	-0.3603455519
C	0	2.4295669079	-0.4887434513	-0.9651330049
C	0	2.8089744102	-0.1062436387	1.4672139774
C	0	2.5721249233	1.8610161439	-0.0597505580
H	0	2.0535799643	-0.0847329127	-1.9185040903
H	0	3.5229811457	-0.5722693810	-1.0617820536
H	0	2.0209484550	-1.4990286892	-0.8154556939
H	0	3.8973454959	-0.0528002776	1.3098926960
H	0	2.5728792362	0.4889227574	2.3638152499
H	0	2.5566918196	-1.1579171839	1.6648563192
H	0	2.3630984204	2.5278376276	0.7924690800
H	0	3.6594378604	1.8654447489	-0.2305299670
H	0	2.0903804692	2.2893483618	-0.9515825289
H	0	-2.4730257849	-0.1131463003	1.1448816745
H	0	-1.7620904438	-0.0988197227	-3.2311901038
O	0	-4.8082225088	-0.4936893798	-0.0360199844
Si	0	-5.3921845187	1.0710025771	0.3220964533
C	0	-4.4379731086	1.7770891196	1.7767703540
C	0	-7.1959896154	0.7896545845	0.7396557342
C	0	-5.1537517197	2.1761360822	-1.1736460720

H	0	-4.4301037653	1.0839376496	2.6332734040
H	0	-3.3999375296	1.9833896744	1.4703969619
H	0	-4.8894442057	2.7264284858	2.1107612517
H	0	-7.6888575343	1.7386169258	1.0075340986
H	0	-7.7351592831	0.3532123604	-0.1162483468
H	0	-7.2977843506	0.0998853723	1.5928143501
H	0	-5.6550670621	1.7750981569	-2.0688953612
H	0	-5.5589364372	3.1826697632	-0.9758905369
H	0	-4.0762544859	2.2745554310	-1.3807531719

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C	0	3.3365193264	-0.0511909684	0.5860284619
C	0	2.5438737332	1.1174178402	0.0696023016
C	0	3.3196817972	-1.1789992238	-0.1401454978
C	0	1.0722863871	0.6747450994	-0.2127614103
H	0	2.5582573925	1.9432611391	0.7844652632
C	0	1.0760022080	-0.5965038665	-1.1133846448
H	0	3.8244830435	-2.0909888721	0.1755166622
C	0	2.4773100167	-1.1748922444	-1.3866196956
H	0	2.3808328633	-2.1892310692	-1.7992417302
H	0	0.5606597938	-0.3800449343	-2.0579095267
C	0	0.4439567465	1.8517035556	-0.9739265641
O	0	0.5477134639	2.0070090591	-2.1665174186
O	0	-0.1553887717	2.7228209174	-0.1575773048
C	0	-0.6675005894	3.9125881129	-0.7613083763
H	0	-1.0764242219	4.5155055088	0.0574933926
H	0	-1.4538069621	3.6676007018	-1.4911522079
H	0	0.1348199230	4.4573762823	-1.2794416254
N	0	0.3346217884	0.3360641246	1.0142724519
C	0	-0.6420867487	-0.7305180672	0.9072326756
C	0	0.5325665508	0.9146419670	2.2476051004
H	0	-0.6424311861	-1.2978805473	1.8489578347
S	0	0.0689369423	-1.9586854175	-0.3032657953
C	0	-2.1147566575	-0.3601114941	0.5593738182
H	0	-0.0626624848	0.3838159405	3.0258684767
O	0	1.2388878770	1.8593131625	2.5149226134
O	0	0.9990694189	-2.8627684630	0.4740066830
C	0	-2.9716194768	-1.6065048877	0.8453932320
C	0	-2.5730392545	0.7927140134	1.4657348064
C	0	-2.3026461196	0.0433160748	-0.9133663983
H	0	-2.6654224524	-2.4617878751	0.2232464932
H	0	-4.0310283991	-1.3986252582	0.6310458165
H	0	-2.8934272970	-1.9099730171	1.9014859340
H	0	-3.6314517968	1.0241579799	1.2680556054
H	0	-1.9830475930	1.7017340078	1.2846077035
H	0	-2.4850128150	0.5278912986	2.5312328994
H	0	-1.7696292450	0.9665769685	-1.1686618480
H	0	-3.3702520682	0.2228695101	-1.1131773388
H	0	-1.9722763029	-0.7503784877	-1.6010310723
H	0	2.9439141771	1.4650830263	-0.8960207696
H	0	2.9311787271	-0.5547953738	-2.1813646872
O	0	3.9551086102	0.1462785051	1.7682634667
Si	0	4.0705422576	-0.9066412138	3.1024247712
C	0	5.4567371656	-2.1401667268	2.8034124436
C	0	2.4299382078	-1.7795978840	3.3522402112
C	0	4.4754241140	0.2429575340	4.5222048872
H	0	5.2005475298	-2.8550524047	2.0055518937
H	0	6.3850269970	-1.6220821589	2.5131086213
H	0	5.6629943216	-2.7201934602	3.7185650892
H	0	2.5531163047	-2.6263595385	4.0479155466
H	0	1.6940590859	-1.0905940237	3.7957029056
H	0	2.0246724258	-2.1711715289	2.4043202073

H	0	3.6860776124	1.0067126259	4.6107256434
H	0	4.5415860466	-0.3048785190	5.4764899229
H	0	5.4337374570	0.7604944606	4.3562306162

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C	0	1.3944056230	0.1379482668	1.4278947651
C	0	0.4943542729	-0.4628677394	2.3445388605
C	0	-0.9511397105	1.3478898489	0.2401416650
C	0	-1.7294299217	0.9572687600	1.3299818765
C	0	-0.5066679622	0.2660636174	2.9673159240
H	0	-1.2288788439	-0.2568397250	3.5999476191
H	0	-2.2988432093	1.6907718170	1.9022474152
C	0	-0.8920047987	2.7882512279	-0.1204936745
O	0	-0.8042605631	3.6806509713	0.6939653846
O	0	-1.0135984016	2.9863338521	-1.4397077447
C	0	-0.9090508168	4.3368744628	-1.8834817562
H	0	-1.0179311558	4.3083956410	-2.9742033915
H	0	-1.6966256869	4.9594070025	-1.4334012927
H	0	0.0702244254	4.7570594236	-1.6093036968
N	0	-0.7915659800	0.3174886116	-0.7313011211
C	0	-1.8993840988	-0.6472290622	-0.7385622649
C	0	0.2435783032	0.3187780633	-1.6334990971
H	0	-2.7645719940	-0.2084957125	-1.2670922747
S	0	-2.6204759118	-0.6052701945	1.0266217986
C	0	-1.6850397487	-2.1094756475	-1.2032594484
H	0	0.2067656937	-0.5403046019	-2.3207368650
O	0	1.1299950042	1.1477054631	-1.6884140321
O	0	-4.0813687444	-0.2863541978	0.8274879174
C	0	-1.5016513440	-2.2165360938	-2.7362497631
C	0	-2.9851550781	-2.8824743288	-0.8781994094
C	0	-0.5071948939	-2.7601781374	-0.4628877458
H	0	-0.4845515692	-1.9845349290	-3.0779360990
H	0	-1.7060571976	-3.2502591313	-3.0540700845
H	0	-2.2050341569	-1.5586363098	-3.2704735006
H	0	-2.8973547811	-3.9124245349	-1.2546559579
H	0	-3.1834592018	-2.9421828930	0.2012975214
H	0	-3.8626532113	-2.4145063969	-1.3493396956
H	0	-0.7071775262	-2.7974302153	0.6185798136
H	0	-0.3640567182	-3.7933641073	-0.8155589684
H	0	0.4355377106	-2.2136253282	-0.5996469788
C	0	1.3174640311	1.4892650769	1.1594818592
H	0	1.9055561509	1.9380554286	0.3666985731
H	0	0.8391917201	2.1681972292	1.8586236628
H	0	-0.3439230342	1.3124687272	3.2268122682
H	0	0.4752226648	-1.5552161296	2.3656540772
O	0	2.1283097295	-0.7181948611	0.6775914572
Si	0	3.6446021124	-0.6830855897	-0.0947757090
C	0	4.2797098790	1.0547841147	-0.3918477584
H	0	4.3700349564	1.6320544781	0.5413259826
H	0	5.2817791619	0.9971320569	-0.8495719273
H	0	3.6138377297	1.5917204666	-1.0836692054
C	0	4.8084320700	-1.6344049383	1.0304060133
H	0	5.8096827778	-1.7295002283	0.5785069959
H	0	4.9223990479	-1.1229507585	2.0002122640
H	0	4.4240746990	-2.6483472734	1.2260312778
C	0	3.3769080382	-1.5846093950	-1.7150143012
H	0	2.7616143404	-0.9685543731	-2.3884723925
H	0	4.3388376429	-1.7826073567	-2.2156535830
H	0	2.8721694756	-2.5507104172	-1.5551142528

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C	0	1.9520571877	1.3901844123	-0.1655252582
C	0	1.2136641661	0.7514502298	-1.1462569589
C	0	1.3804110722	2.4497266710	0.5770801776
C	0	-0.5611367249	-0.0622995217	0.2306627337
H	0	1.5916745194	-0.1276534372	-1.6596015597
C	0	-1.1426204424	1.1254490769	0.7100291247
C	0	0.0900151898	2.8930037829	0.3404898308
H	0	-0.3414934241	3.6327308235	1.0214611115
H	0	-1.1608527673	1.3523467615	1.7736755554
C	0	0.2532309545	-0.9057144211	1.1389312925
O	0	0.3357029793	-2.1105343628	1.1064928574
O	0	0.8633736268	-0.1329415518	2.0619963799
C	0	1.7234315342	-0.7912315311	2.9856479106
H	0	2.6217199159	-1.1648249405	2.4740840542
H	0	2.0083477484	-0.0363826311	3.7282340333
H	0	1.2100393133	-1.6366058555	3.4663330191
N	0	-1.3383918371	-0.7105358806	-0.7726949131
C	0	-2.7262984076	-0.2730899852	-0.8021044032
C	0	-0.8543031398	-1.5534858861	-1.7484653090
H	0	-3.0756841475	-0.1928827256	-1.8414558536
S	0	-2.6433763481	1.5255041701	-0.2603126191
C	0	-3.7178772635	-1.1260302282	0.0286043104
H	0	-1.6643168619	-1.8614483531	-2.4473491958
O	0	0.2879653975	-1.9304415923	-1.8746161571
O	0	-2.2150772698	2.2855371069	-1.5036755266
C	0	-3.3845257160	-1.1062384054	1.5295387602
C	0	-3.6537243007	-2.5808240557	-0.4682765173
C	0	-5.1324955962	-0.5693867705	-0.2041798841
H	0	-3.4297194424	-0.0894951473	1.9488688261
H	0	-4.1141262060	-1.7234116617	2.0766314555
H	0	-2.3856743122	-1.5215781973	1.7230054826
H	0	-4.4024899772	-3.1878302718	0.0639081437
H	0	-3.8713473017	-2.6520900825	-1.5460004367
H	0	-2.6660877081	-3.0261181424	-0.2790348882
H	0	-5.4000700497	-0.5938310867	-1.2728764864
H	0	-5.8728558572	-1.1738007516	0.3417855509
H	0	-5.2237611052	0.4704865169	0.1443509330
H	0	0.3753250043	1.2600370029	-1.6153285386
H	0	-0.3497286543	2.8903234824	-0.6585601761
H	0	1.9149617707	2.7470830041	1.4828852805
O	0	3.1346276175	0.9109708806	0.2828824115
Si	0	4.1949466756	-0.2374587881	-0.4092602949
C	0	4.6195580515	0.3071792272	-2.1554140939
C	0	5.6935144000	-0.1401188474	0.7105847606
C	0	3.4517122816	-1.9571144543	-0.3813458470
H	0	5.0073974594	1.3385861951	-2.1583578209
H	0	5.3960345507	-0.3500484865	-2.5809030135
H	0	3.7461092919	0.2697588427	-2.8239216545
H	0	6.1262877765	0.8728410739	0.7067582588
H	0	5.4233139673	-0.3899336402	1.7491988321
H	0	6.4727489620	-0.8481229240	0.3840548512
H	0	3.2701865975	-2.3037932347	0.6475423385
H	0	2.4946215357	-2.0330628282	-0.9186946142
H	0	4.1622623133	-2.6610675810	-0.8476052556

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C	0	1.8234628501	-0.6386897464	-1.1292689461

C	0	1.6185317989	0.6471722008	-1.5851269077
C	0	1.0718557229	-1.7219048011	-1.6515466225
C	0	-0.8243631035	0.6415875295	-0.8784787963
H	0	2.0832057668	1.4979063446	-1.0971775833
C	0	-1.3557171852	-0.3679598954	-1.6916583996
C	0	0.1031754464	-1.5449392691	-2.6309147073
H	0	-0.4839906066	-2.4137857428	-2.9328461311
H	0	-1.8810838446	-0.0792617496	-2.6041585689
C	0	-0.8830183789	2.0542493071	-1.2997656969
O	0	-0.8587219396	2.4169640022	-2.4571719423
O	0	-1.0146805349	2.8958363889	-0.2582046261
C	0	-0.9888952669	4.2859634306	-0.5687862776
H	0	-1.0760266835	4.8136090217	0.3884903770
H	0	-1.8219093233	4.5556161433	-1.2352201089
H	0	-0.0440554510	4.5524785261	-1.0656062105
N	0	-0.7046868796	0.2485532396	0.4808932851
C	0	-1.6691860381	-0.7593152010	0.8930407165
C	0	0.2943397223	0.6432821959	1.3400833904
H	0	-1.1772954390	-1.5557083456	1.4709439438
S	0	-2.1972975072	-1.6599431155	-0.6837794530
C	0	-2.9060677863	-0.2135143902	1.6532534576
H	0	0.2819489096	0.0437555111	2.2761403052
O	0	1.1099560037	1.5146996872	1.1339650086
O	0	-1.4618539066	-2.9777006174	-0.7123753420
C	0	-3.7862014608	-1.4090885042	2.0548310042
C	0	-2.4468482087	0.5183697457	2.9258901906
C	0	-3.7014240057	0.7684233299	0.7769629372
H	0	-4.1578117243	-1.9604052162	1.1778248475
H	0	-4.6612473969	-1.0598980387	2.6240290257
H	0	-3.2303848956	-2.1179889337	2.6893575593
H	0	-3.3265317894	0.8407997796	3.5044117323
H	0	-1.8601789424	1.4178284632	2.6886006884
H	0	-1.8417391982	-0.1345870543	3.5750300182
H	0	-3.0893243945	1.6398025394	0.5054146792
H	0	-4.5831507006	1.1315140490	1.3275863822
H	0	-4.0605218742	0.2896056781	-0.1471592329
H	0	0.2303766232	-0.7699093615	-3.3887594739
H	0	1.1440947114	0.8262474270	-2.5448482350
H	0	1.1029856648	-2.6610668118	-1.0967421158
O	0	2.5511531453	-0.9180555272	-0.0236784100
Si	0	3.9554425729	-0.3129677322	0.7177604135
C	0	5.3321673446	-1.4973975732	0.2391965775
H	0	5.0787997677	-2.5299362521	0.5284682667
H	0	5.5017291982	-1.4838760524	-0.8499527582
H	0	6.2803357221	-1.2265464555	0.7327168613
C	0	3.6004294221	-0.3874072778	2.5547361265
H	0	4.5163484266	-0.2080711319	3.1413606815
H	0	2.8623345171	0.3849334024	2.8202784311
H	0	3.2009034273	-1.3740567565	2.8388371404
C	0	4.3802099686	1.4356641247	0.1875430065
H	0	3.5834184386	2.1314013450	0.4897948498
H	0	5.3156294450	1.7439243226	0.6845815104
H	0	4.5360548497	1.5170398179	-0.8994118681

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C	0	-1.4638537984	-1.9931585327	1.0642957926
C	0	-1.8170795973	-0.5781653183	0.6878120191
C	0	-1.0387288128	-2.8641278162	0.1324257592
C	0	-0.9103795746	0.0423248464	-0.4098860764
H	0	-1.7907170578	0.0817557793	1.5645164935
C	0	-0.1062224384	-1.0103421583	-1.1997954133
C	0	-0.7849444723	-2.3726345658	-1.2710143370

H	0	-0.1412685581	-3.0891369983	-1.8010303822
H	0	0.1753047790	-0.6212797899	-2.1881908154
C	0	-1.7826476387	0.7492928295	-1.4754982551
O	0	-2.9518834921	0.5252939813	-1.6532439931
O	0	-1.0381593477	1.5264936106	-2.2730551966
C	0	-1.7490812749	2.2688366618	-3.2635458177
H	0	-0.9914137621	2.8141854566	-3.8386872651
H	0	-2.3225477244	1.5970944865	-3.9187933993
H	0	-2.4417034125	2.9720489724	-2.7778800330
N	0	0.0827446775	0.9823171034	0.1499383383
C	0	1.4706739015	0.5563341500	0.2770688585
C	0	-0.3185009641	2.2690764855	0.3705251083
H	0	2.1232339911	1.0929271493	-0.4330736431
S	0	1.5549825905	-1.2039937097	-0.3939412055
C	0	2.0971244814	0.5751397200	1.7023346849
H	0	0.5174349415	2.9597706380	0.5991328006
O	0	-1.4748867686	2.6388945913	0.2984173465
O	0	2.5867080734	-1.2102400714	-1.4947335232
C	0	2.2192247436	2.0070591123	2.2548744293
C	0	3.5213853364	-0.0052788605	1.5943474149
C	0	1.2503598060	-0.2629789977	2.6708615523
H	0	1.2437438258	2.4434590712	2.5106156605
H	0	2.8143758039	1.9889911305	3.1811501406
H	0	2.7294211277	2.6768390881	1.5440847325
H	0	4.0133789442	0.0304284190	2.5780734060
H	0	3.5274034685	-1.0523888001	1.2579437413
H	0	4.1342257804	0.5716125931	0.8840886626
H	0	1.1536330434	-1.3014390151	2.3259720360
H	0	1.7146605707	-0.2750672472	3.6689559041
H	0	0.2384047837	0.1553756133	2.7731108830
H	0	-1.7254934815	-2.2866983395	-1.8428693440
H	0	-2.8501680420	-0.5355818873	0.3090350404
H	0	-1.6337811819	-2.3095986834	2.0948065226
O	0	-0.7495078299	-4.1698161761	0.3151773456
Si	0	-0.5009113144	-5.0718487852	1.7376237325
C	0	0.7955185724	-4.2094706047	2.7880939001
C	0	0.1220044789	-6.7186628034	1.1068139807
C	0	-2.1237614540	-5.2767109726	2.6591377122
H	0	1.6627176597	-3.9286477829	2.1692009632
H	0	0.4073487557	-3.2964963462	3.2628336999
H	0	1.1488825566	-4.8816708725	3.5874155497
H	0	0.3070335952	-7.4150093276	1.9410315164
H	0	-0.6142591613	-7.1831903544	0.4316913730
H	0	1.0635976701	-6.5944595272	0.5487232831
H	0	-2.8886450937	-5.7189268364	2.0005614255
H	0	-1.9920285437	-5.9489910910	3.5233991606
H	0	-2.5150361515	-4.3187987579	3.0346098799

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C	0	-3.0356466176	0.5130580334	-1.1908403582
C	0	-2.0645221166	-0.6174539655	-1.0034923328
C	0	-3.1565703033	1.5641465021	-0.3680875739
C	0	-1.2445861441	-0.5728342531	0.3095303788
H	0	-2.5733100255	-1.5887482106	-1.0651940644
C	0	-1.0835784671	0.8536819023	0.8373304476
C	0	-2.3430140095	1.6891019225	0.8912861162
H	0	-2.9522859784	1.3971102798	1.7656087145
H	0	-0.5766359000	0.8365870174	1.8132345077
C	0	-1.8503363015	-1.3843487508	1.4701171857
O	0	-1.2559592945	-1.6050243860	2.4947145497
O	0	-3.1290124244	-1.6949147612	1.2550818681
C	0	-3.7771160079	-2.4331778965	2.2918793288

H	0	-3.2945044931	-3.4139117622	2.4143092946
H	0	-4.8191220432	-2.5546467411	1.9737410726
H	0	-3.7231422709	-1.8907251425	3.2471769354
N	0	0.1455252151	-1.0348648807	0.0773761302
C	0	1.1819013697	-0.0038764652	0.0334583301
C	0	0.3182572165	-2.3826139454	-0.0509066901
H	0	1.6047058099	0.2012668074	1.0340567729
C	0	2.3363702535	-0.1464050223	-0.9973514553
H	0	1.3708542209	-2.6993776436	-0.1629507565
O	0	-0.6047510421	-3.1749416242	-0.0313337037
C	0	3.0334085913	1.2261161346	-1.1326323791
C	0	3.4118069889	-1.1319276979	-0.4929036179
C	0	1.8019653598	-0.5751073261	-2.3716934289
H	0	2.3918901122	1.9802574205	-1.6100947332
H	0	3.9348267491	1.1140800301	-1.7534197393
H	0	3.3328420782	1.6291792550	-0.1538731014
H	0	4.2900336699	-1.0860940916	-1.1552111496
H	0	3.0798605344	-2.1781243602	-0.4777950544
H	0	3.7440313590	-0.8647652851	0.5225136063
H	0	1.3652874457	-1.5839748378	-2.3596527070
H	0	2.6195921475	-0.5756068063	-3.1085556047
H	0	1.0297983492	0.1248183681	-2.7270963083
S	0	0.1758924685	1.5713921785	-0.2966391424
O	0	0.8072913057	2.7314754231	0.4413347300
H	0	-2.0506101065	2.7358586126	1.0706154015
H	0	-1.3460474356	-0.6079378848	-1.8414273020
H	0	-3.6681393358	0.4862072215	-2.0821554555
O	0	-4.0583114113	2.5545139955	-0.5988866254
Si	0	-3.7197252943	4.2064144907	-0.8433785312
C	0	-1.9889503479	4.3747706954	-1.5533016483
C	0	-3.8883082739	5.1169368825	0.7910373041
C	0	-5.0296929878	4.7863631313	-2.0482821382
H	0	-1.1968415708	4.1249371256	-0.8293178114
H	0	-1.8654844470	3.7171912212	-2.4290328513
H	0	-1.8165889538	5.4125828178	-1.8840522901
H	0	-3.7834470300	6.2045386225	0.6418743655
H	0	-4.8776549699	4.9303829574	1.2393658478
H	0	-3.1212797492	4.8048241684	1.5172266574
H	0	-6.0377707488	4.5870990238	-1.6505447406
H	0	-4.9447261856	5.8695293520	-2.2346123751
H	0	-4.9367106071	4.2630449078	-3.0131994553

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C	0	-2.8927286205	1.3833155423	0.4485015410
C	0	-1.8580343347	0.5704627873	1.1646588650
C	0	-2.7250290154	1.8427724644	-0.7971810583
C	0	-0.9182448698	-0.1917387571	0.2070718274
H	0	-2.3324142830	-0.1535364897	1.8378658757
C	0	-0.4400010715	0.7023075296	-0.9489636377
C	0	-1.5040148592	1.5646909609	-1.6243145148
H	0	-1.8364010780	1.0725189715	-2.5548589298
H	0	0.0580839038	0.0704773749	-1.6935792663
C	0	-1.5397304836	-1.4633806326	-0.4094827120
O	0	-0.9029086858	-2.2350961508	-1.0869375133
O	0	-2.8430326072	-1.5868652479	-0.1694333476
C	0	-3.4611763706	-2.7775110850	-0.6595420056
H	0	-3.0311867648	-3.6566028008	-0.1575795518
H	0	-4.5281113233	-2.6849213704	-0.4259780230
H	0	-3.3101550460	-2.8761734670	-1.7442289067
N	0	0.3147767648	-0.5955276516	0.9119953601
C	0	1.5303614108	0.1736622701	0.6748470146
C	0	0.1967622814	-1.4772470641	1.9491352860

H	0	1.8939689421	0.6092545380	1.6194510777
S	0	0.9609645888	1.7052270327	-0.2560868621
C	0	2.7105501209	-0.5582940119	-0.0316925105
H	0	1.1104223128	-1.5408512507	2.5787480979
O	0	-0.8033047625	-2.1299869385	2.1741419478
O	0	0.4055492931	2.6653488918	0.7677638541
C	0	2.3610041059	-0.9805634753	-1.4674550378
C	0	3.0883379309	-1.8202944426	0.7629408286
C	0	3.9150318557	0.3991075739	-0.0385644508
H	0	2.2084035848	-0.1086077857	-2.1231561215
H	0	3.1925515616	-1.5618955548	-1.8947515326
H	0	1.4576462811	-1.6076383696	-1.4881595071
H	0	3.9879013199	-2.2747125671	0.3195224248
H	0	3.3173704469	-1.5891720566	1.8154986095
H	0	2.2904788322	-2.5762207936	0.7329502510
H	0	4.2035106646	0.6868419698	0.9854249783
H	0	4.7834193413	-0.0876857270	-0.5080976572
H	0	3.7010861653	1.3197510630	-0.6020309705
H	0	-1.2226442741	1.2353620538	1.7705466589
H	0	-1.0724556990	2.5293274372	-1.9445951896
H	0	-3.8088455991	1.6260384491	0.9901420995
O	0	-3.6417040286	2.5797344391	-1.4834848475
Si	0	-5.3091129312	2.2749912315	-1.6145934388
C	0	-6.2191318679	2.8819106505	-0.0871367780
C	0	-5.5331645586	0.4248815459	-1.8513858587
C	0	-5.8407645390	3.2551765786	-3.1182829081
H	0	-6.0124020159	2.2564662902	0.7951977754
H	0	-5.9258355599	3.9166827581	0.1528429985
H	0	-7.3085835085	2.8693335925	-0.2586345366
H	0	-6.6002031090	0.1492787875	-1.8675785615
H	0	-5.0803409928	0.0945279080	-2.8003967588
H	0	-5.0428931825	-0.1242954053	-1.0328153669
H	0	-5.2939909775	2.9270398091	-4.0165106936
H	0	-6.9195468620	3.1311191230	-3.3082163690
H	0	-5.6427522172	4.3294759606	-2.9740896076

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C	0	3.3014428394	-0.0718265159	0.9713788465
C	0	2.4891884833	1.1437813645	0.6446118034
C	0	3.4483504365	-0.9902989591	0.0026433610
C	0	1.1064859423	0.7366328522	0.0364247145
H	0	2.3252533528	1.7745311203	1.5214543549
C	0	1.3431897699	-0.2242037511	-1.1681883119
C	0	2.7978514875	-0.7033444981	-1.3305597648
H	0	2.8438016101	-1.5998981844	-1.9622496355
H	0	0.9995412087	0.2575513840	-2.0923994403
C	0	0.4925472935	2.0545907026	-0.4518908482
O	0	0.6938252416	2.5287525708	-1.5438415229
O	0	-0.2127160095	2.6636984171	0.5064818152
C	0	-0.7237609775	3.9609980025	0.1931820772
H	0	-1.2247734718	4.3164528076	1.1008596324
H	0	-1.4363894332	3.9039194073	-0.6434522958
H	0	0.0940983808	4.6397225210	-0.0886594326
N	0	0.2394053162	0.0270495954	0.9883751510
C	0	-0.6640471203	-0.9499287750	0.4190278039
C	0	0.3079263599	0.1281397419	2.3611309310
H	0	-0.7757460479	-1.7765626258	1.1350330137
S	0	0.2813248366	-1.7568119422	-0.9697771488
C	0	-2.0899889143	-0.4997113532	-0.0147799140
H	0	-0.3227016979	-0.6568082760	2.8416268406
O	0	0.9386205258	0.9292243362	3.0095030060
O	0	1.1352584490	-2.8273510562	-0.3208728977

C	0	-2.9165324837	-1.7813633770	-0.2257643565
C	0	-2.7121754884	0.3316732314	1.1172130804
C	0	-2.1025384075	0.3129590262	-1.3206715202
H	0	-2.4886098170	-2.4144806207	-1.0187916162
H	0	-3.9462625438	-1.5273517715	-0.5198447249
H	0	-2.9664386334	-2.3807369808	0.6971538899
H	0	-3.7455599665	0.6077312702	0.8549381219
H	0	-2.1412851136	1.2537018912	1.2928832018
H	0	-2.7490084360	-0.2368388265	2.0601071331
H	0	-1.6070840009	1.2850784894	-1.2215826631
H	0	-3.1429539722	0.5121412293	-1.6203346764
H	0	-1.6255466488	-0.2346799442	-2.1484341802
H	0	2.9738360374	1.7584212361	-0.1346930644
H	0	3.3489962720	0.0978224930	-1.8524606365
H	0	3.7211609563	-0.1997209116	1.9690573675
O	0	4.1487771372	-2.1318029630	0.0953315548
Si	0	3.9927183888	-3.4403593220	1.1801613536
C	0	5.6990622515	-3.6600495468	1.9351842087
C	0	3.5225955531	-4.9370478858	0.1592573197
C	0	2.7087314228	-3.0591946430	2.4931697929
H	0	6.4583405878	-3.8126188935	1.1510619985
H	0	5.9908518502	-2.7733280264	2.5209445533
H	0	5.7242434621	-4.5351935717	2.6058179164
H	0	3.4753557953	-5.8463388435	0.7814050703
H	0	2.5383147327	-4.7648675229	-0.3011759225
H	0	4.2615864500	-5.1092422635	-0.6401302561
H	0	1.7679053554	-2.7935544047	1.9903110773
H	0	2.5367701310	-3.9553045497	3.1126503697
H	0	3.0078923463	-2.2355018641	3.1586107085

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H	0	-0.6910852003	-1.5876925346	-2.6732579441
C	0	-0.2938078833	-1.9910778410	-1.7374873155
C	0	-1.1492208756	-1.8607677216	-0.5967515950
C	0	1.7440106803	-0.5964847294	0.3980497288
C	0	0.5930015810	-0.7384752739	1.1854409719
C	0	-0.6854757203	-2.1802929920	0.6897160866
H	0	-1.3962836747	-2.1399029827	1.5156275562
H	0	0.6767634898	-1.0841384011	2.2185768521
C	0	2.9121192138	-1.4277608023	0.6552811121
O	0	2.8352564813	-2.5419870270	1.1497548250
O	0	4.0766753664	-0.8421061405	0.3276206978
C	0	5.2372768099	-1.6581864008	0.4274044426
H	0	6.0809573320	-1.0300663421	0.1159862873
H	0	5.3840353413	-2.0144869526	1.4582840074
H	0	5.1537655937	-2.5332737432	-0.2352738534
N	0	1.7551325219	0.5603967776	-0.4286670184
C	0	0.9992091935	1.6574380468	0.1746437087
C	0	2.3581995219	0.5556667921	-1.6663888184
H	0	1.5434987371	2.0507069758	1.0519344649
S	0	-0.4391231484	0.7680565280	1.0418631612
C	0	0.4581015639	2.8244365685	-0.6830855033
H	0	2.3421320244	1.5421465902	-2.1607723445
O	0	2.8718611628	-0.4167922558	-2.1784166712
O	0	-0.5829283815	1.3706623710	2.4241416375
C	0	1.5969268745	3.7855360283	-1.0836694171
C	0	-0.5088755207	3.6436439240	0.2034480596
C	0	-0.3180598309	2.3182036249	-1.9129778465
H	0	2.3472465261	3.3340573143	-1.7453011965
H	0	1.1758183275	4.6552384158	-1.6116440684
H	0	2.1203031659	4.1569920675	-0.1889029197
H	0	-0.8151749072	4.5509318208	-0.3382679132

H	0	-1.4202419454	3.0859413676	0.4624979201
H	0	-0.0361749226	3.9451051056	1.1497707049
H	0	-1.0721671452	1.5710744522	-1.6233435097
H	0	-0.8435994136	3.1585022221	-2.3922002421
H	0	0.3295345358	1.8597942839	-2.6719239781
C	0	0.9757963608	-2.4724527409	-1.6823588326
H	0	1.6066018276	-2.4667946109	-2.5699096550
H	0	1.3960408453	-2.9357220920	-0.7903856058
H	0	0.0614387536	-2.9698685898	0.7747084755
O	0	-2.3093137278	-1.2390431530	-0.8220308773
Si	0	-3.7073653787	-0.7055047547	0.0112038926
C	0	-3.5426859439	-0.6684941948	1.8798675067
C	0	-4.0076254840	1.0133760947	-0.6650249010
C	0	-5.0542621572	-1.9006626690	-0.5066443603
H	0	-2.7310538494	-0.0163965548	2.2378100455
H	0	-4.4874040187	-0.2636151591	2.2826048240
H	0	-3.4131334988	-1.6730610654	2.3121951235
H	0	-3.2197347651	1.7068422048	-0.3343683805
H	0	-4.0187072120	1.0057210418	-1.7662567774
H	0	-4.9761015617	1.4055563418	-0.3140222254
H	0	-5.1482062057	-1.9361098701	-1.6035405453
H	0	-4.8337963015	-2.9204115655	-0.1514689520
H	0	-6.0288761580	-1.5997527994	-0.0882398245

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H	0	-2.3238217977	2.1388274783	2.1946008941
C	0	-1.5431933243	1.3765290602	2.1272730709
C	0	-0.3187891648	1.6070431049	2.6550714309
C	0	-1.8874080094	0.2233003000	1.3462535126
C	0	0.9505881490	0.9035023992	-0.3143391397
H	0	-0.0886069905	2.5580393455	3.1381040539
C	0	0.1107707326	-0.2250259042	-0.4318291844
C	0	-0.9475487278	-0.7869573076	1.0563846363
H	0	-1.3435285127	-1.7214338616	0.6531227192
H	0	-0.7309060069	-0.1628388867	-1.1229881247
C	0	0.4418283536	2.2734378574	-0.2516364761
O	0	1.0367262129	3.2731968032	0.0781213564
O	0	-0.8813571045	2.2750983908	-0.6049751816
C	0	-1.5387673254	3.5277254104	-0.4976481600
H	0	-1.4256318565	3.9455115424	0.5147631936
H	0	-2.5978848077	3.3390643236	-0.7153927412
H	0	-1.1217629860	4.2517140777	-1.2143137821
N	0	2.3427318528	0.6550950567	-0.4453667544
C	0	2.7000392598	-0.7458391245	-0.3191047113
C	0	3.0872361814	1.4046766600	-1.3703727197
H	0	3.3479193144	-1.0385805893	-1.1583552542
S	0	1.1212793345	-1.7115313453	-0.7936546278
C	0	3.3920678384	-1.1762641313	0.9950713480
H	0	4.1205028139	0.9976490804	-1.4653412557
O	0	2.6914999743	2.3570370418	-1.9869732960
O	0	1.1448339732	-1.8566183550	-2.2968408094
C	0	2.5820748447	-0.7913817124	2.2345907264
C	0	3.6293322211	-2.6944064487	0.9605897695
C	0	4.7508915630	-0.4524256705	1.0511110527
H	0	2.3723821560	0.2872215821	2.2392274955
H	0	3.1465211137	-1.0329093059	3.1482380344
H	0	1.6321158115	-1.3433643604	2.2849380273
H	0	4.2120998128	-3.0078996256	1.8404153487
H	0	4.1934985203	-2.9907731012	0.0614354367
H	0	2.6825620044	-3.2550109303	0.9647935932
H	0	5.3771296038	-0.7076068903	0.1814311470
H	0	5.2997359509	-0.7464675928	1.9594500470

H	0	4.6179660821	0.6392753392	1.0726530708
H	0	-0.1862413572	-0.9496706346	1.8167837195
H	0	0.4799609654	0.8697819694	2.6198231022
O	0	-3.0823807929	0.2718602581	0.7519399197
Si	0	-3.9581073984	-0.7924962500	-0.2703664198
C	0	-5.5560105130	0.1348483790	-0.5479639176
H	0	-5.3656367992	1.0985107540	-1.0466572269
H	0	-6.2417247523	-0.4479716012	-1.1842404648
H	0	-6.0648174248	0.3395433205	0.4071834656
C	0	-3.0485639588	-1.0541416123	-1.8894321817
H	0	-2.7670275096	-0.0862977604	-2.3343714103
H	0	-2.1370282698	-1.6647591655	-1.8025343545
H	0	-3.7183812794	-1.5655517866	-2.6013682393
C	0	-4.2478265744	-2.4031181650	0.6481891826
H	0	-3.3183886801	-2.9673945014	0.8203089857
H	0	-4.7184245174	-2.2143574767	1.6263935088
H	0	-4.9250951991	-3.0498204378	0.0659325838

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H	0	-2.1863929451	2.6588270529	-1.3830280680
C	0	-1.5879163901	1.7863148680	-1.6572351997
C	0	-0.3427386051	1.9394293997	-2.1825803569
C	0	-2.1071123981	0.5230742121	-1.2525992455
C	0	0.8973063919	0.7257900874	-0.0599238570
H	0	0.0754835626	2.9260663206	-2.3748070727
C	0	0.2093800577	-0.4991789177	-0.1327497627
C	0	-1.3567934429	-0.6504949958	-1.4214104210
H	0	-1.8100591780	-1.5983957171	-1.1207070751
H	0	-0.3699689824	-0.8320742887	0.7282691837
C	0	0.5302638329	1.7684791792	0.8928301509
O	0	1.2575442590	2.6199382921	1.3532919209
O	0	-0.7804079709	1.6371828273	1.2523893214
C	0	-1.2887642668	2.6396737743	2.1218193682
H	0	-1.1769343337	3.6383247446	1.6728045886
H	0	-2.3516085170	2.4078670481	2.2672204486
H	0	-0.7594946129	2.6347938640	3.0870891449
N	0	2.2074548063	0.6998447316	-0.6024883700
C	0	2.8044585852	-0.6181468682	-0.5695542385
C	0	2.7989389813	1.7379880854	-1.2909501613
H	0	3.4150272351	-0.7858546147	-1.4686728999
S	0	1.3494986033	-1.7871403531	-0.8504467211
C	0	3.6231387117	-0.9539155453	0.7014140269
H	0	3.8039850095	1.4456561551	-1.6747898246
O	0	2.3167806519	2.8312557569	-1.4695964311
O	0	1.1466839295	-1.8202420707	-2.3531364573
C	0	2.7561150343	-0.9341418190	1.9713221402
C	0	4.7360832096	0.0980736172	0.8476305464
C	0	4.2506524206	-2.3448297006	0.5133448641
H	0	1.9332532444	-1.6644555107	1.9193268686
H	0	3.3746587870	-1.1952617384	2.8442646501
H	0	2.3295851899	0.0627227956	2.1484168692
H	0	5.3739578822	-0.1499940629	1.7102570553
H	0	5.3798115218	0.1328803838	-0.0460434599
H	0	4.3149695695	1.1000535833	1.0150090713
H	0	4.8909735729	-2.3760609443	-0.3829644918
H	0	4.8758123611	-2.6004475082	1.3825710668
H	0	3.4838174748	-3.1277710629	0.4094901167
H	0	0.2477040630	1.0905207108	-2.5249581711
H	0	-0.7106701081	-0.7383283496	-2.2961777242
O	0	-3.2468108102	0.5693773693	-0.5485157574
Si	0	-4.0854564218	-0.5542417649	0.4217729489
C	0	-2.9177228448	-1.2820320323	1.7014588669

C	0	-5.4024097281	0.4927754956	1.2373223787
C	0	-4.8397841402	-1.8771288243	-0.6730714586
H	0	-2.2854360420	-0.4897976499	2.1314791482
H	0	-3.4934393565	-1.7482609667	2.5179856857
H	0	-2.2605363822	-2.0557776049	1.2755767202
H	0	-4.9479855348	1.2707463836	1.8714639560
H	0	-6.0282237757	0.9938918203	0.4820438682
H	0	-6.0591462602	-0.1242908334	1.8719900448
H	0	-5.4874866267	-1.4227071431	-1.4398454146
H	0	-4.0737528480	-2.4760116731	-1.1896111050
H	0	-5.4570034269	-2.5663009985	-0.0729402752

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H	0	-1.1481666679	-2.5576264625	1.5237579773
C	0	-0.9322332016	-2.5256364903	0.4528483860
C	0	0.0710459088	-3.2859563882	-0.0548039569
C	0	-1.6153970769	-1.5046056925	-0.2828794611
C	0	1.4519440253	-0.9483061874	-0.7829122028
H	0	0.6363130155	-3.9499308381	0.5997519890
C	0	0.5366510270	-0.5288151957	-1.7549368556
C	0	-1.3519220819	-1.3047134538	-1.6476231492
H	0	-1.9201701479	-0.5434146359	-2.1789339963
H	0	0.7469672642	-0.7889594067	-2.7948514063
C	0	2.5725088275	-1.8327665489	-1.0969814239
O	0	2.5873197723	-2.6147810486	-2.0293439409
O	0	3.6212302575	-1.6458946909	-0.2693435405
C	0	4.7139095897	-2.5415579902	-0.4341592121
H	0	5.4575568428	-2.2589615674	0.3209381881
H	0	5.1425133546	-2.4619225973	-1.4447061112
H	0	4.3893903467	-3.5810623405	-0.2743921787
N	0	1.3289850507	-0.2383533702	0.4375574468
C	0	0.8568079156	1.1286992376	0.2835279796
C	0	1.3996074442	-0.8280261803	1.6836191295
H	0	-0.0299740282	1.3190378247	0.9076480938
S	0	0.1955269227	1.2539604032	-1.4929379350
C	0	1.9318951163	2.2254538853	0.5011742875
H	0	1.0585175774	-0.1309497078	2.4810520492
O	0	1.7682528314	-1.9569472230	1.9104667646
O	0	-1.2856793544	1.5671645518	-1.4341548071
C	0	1.2753184574	3.5954272092	0.2590872386
C	0	2.4441801560	2.1756127587	1.9508759958
C	0	3.1181774844	2.0086823485	-0.4523809126
H	0	0.8984245978	3.7021532943	-0.7696056867
H	0	2.0071217417	4.4000592215	0.4280554081
H	0	0.4281414546	3.7570213061	0.9450371422
H	0	3.1348839421	3.0151387553	2.1257996722
H	0	2.9963879352	1.2478185257	2.1585127323
H	0	1.6204499985	2.2639032606	2.6774107155
H	0	3.5664196996	1.0156499955	-0.3010543178
H	0	3.8932399037	2.7687480401	-0.2684931476
H	0	2.8108360172	2.0923756647	-1.5059132600
O	0	-2.3343771371	-0.6647180468	0.4601444856
Si	0	-3.6659344258	0.4056927433	0.3013015442
C	0	-4.9917906292	-0.4167964573	1.3492460477
H	0	-5.2805550608	-1.3941050692	0.9291553114
H	0	-4.6345099207	-0.5829223541	2.3781925927
H	0	-5.8976740874	0.2100542905	1.4003472757
C	0	-3.1293985555	2.0195845927	1.0793275170
H	0	-2.3877287880	2.5105241068	0.4339366610
H	0	-3.9935055918	2.6918465078	1.2096786193
H	0	-2.6875859735	1.8411925692	2.0732889746
C	0	-4.2679749062	0.5824567882	-1.4625099231

H	0	-3.5371862071	1.1364100923	-2.0676970034
H	0	-4.4578251762	-0.3989314343	-1.9258644629
H	0	-5.2207799063	1.1383746516	-1.4605233994
H	0	-1.0830866467	-2.1916378346	-2.2207197796
H	0	0.3257730927	-3.3161584129	-1.1131931544

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C	0	-0.6817953132	-2.4722791167	1.3057156671
C	0	-1.7361880981	-1.4332519598	1.0317170008
C	0	-0.0387810338	-3.0189745902	0.2629274477
C	0	-1.2244306187	-0.3779108729	0.0313017663
H	0	-2.0612849361	-0.9071857398	1.9338876179
C	0	-0.6014168262	-1.0500334694	-1.2205273687
H	0	0.7476640650	-3.7580633809	0.4167265330
C	0	-0.4096113307	-2.5707263718	-1.1202413557
H	0	0.3466787943	-2.8763888868	-1.8560545330
H	0	-1.1791903148	-0.8015054521	-2.1199251211
C	0	-2.4133331227	0.4592799335	-0.4871163680
O	0	-3.5454381667	0.0548126607	-0.5394669619
O	0	-1.9974639326	1.6261224628	-0.9849790180
C	0	-2.9989056415	2.4728321022	-1.5510767811
H	0	-2.4650268534	3.3289756224	-1.9789643684
H	0	-3.5606024132	1.9389094870	-2.3310224481
H	0	-3.6990256661	2.8034007578	-0.7696864252
N	0	-0.2172189819	0.5159321092	0.6702886080
C	0	1.1013693823	0.7243251942	0.0804442266
C	0	-0.7214246760	1.4643029184	1.5234605011
H	0	1.1872921811	1.7678966190	-0.2594990146
S	0	0.9710040896	-0.1557136956	-1.5573264976
C	0	2.3607401083	0.3899635013	0.9322589452
H	0	0.0066336654	2.2584525230	1.7807500120
O	0	-1.8578096694	1.4563416829	1.9557363473
O	0	2.0552382439	-1.1259458279	-1.7778828384
O	0	0.7015146267	0.8773877473	-2.5647909640
C	0	2.3362808643	1.2366363923	2.2189060254
C	0	3.5921264201	0.8130174822	0.1070673412
C	0	2.4604938568	-1.0858676009	1.3374882742
H	0	1.5170600032	0.9440621610	2.8913932893
H	0	3.2783401874	1.0790694991	2.7657881038
H	0	2.2537749735	2.3149477607	2.0071344387
H	0	4.5053485295	0.6564667489	0.7007449182
H	0	3.6828521783	0.2278022000	-0.8166901600
H	0	3.5444503692	1.8823133646	-0.1572774117
H	0	2.5150401153	-1.7430794795	0.4629103861
H	0	3.3744116802	-1.2306911180	1.9347991877
H	0	1.6060161003	-1.3935170144	1.9531438944
H	0	-1.3660084162	-3.0230165926	-1.4440718583
H	0	-2.6353975521	-1.8901463861	0.5907217447
O	0	-0.3704597377	-2.7967798510	2.5781254108
Si	0	-1.0477411525	-2.4572771538	4.1000994958
C	0	-2.8866151228	-2.8372007214	4.0789180593
C	0	-0.7131191441	-0.6708939212	4.5695504840
C	0	-0.1324600165	-3.6214708132	5.2440370071
H	0	-3.4511928598	-2.1463234437	3.4341922490
H	0	-3.0674526355	-3.8641375083	3.7222131555
H	0	-3.3015277068	-2.7560543528	5.0974479062
H	0	-1.0098960905	-0.4979616503	5.6176846507
H	0	0.3637084511	-0.4501869487	4.4879039982
H	0	-1.2635950361	0.0478876357	3.9444144242
H	0	0.9519805910	-3.4306426093	5.2096205350
H	0	-0.4691201823	-3.4944538657	6.2859495472
H	0	-0.3014190189	-4.6706081312	4.9540107640

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C	0	-2.8934214657	1.5279912724	0.1516856920
C	0	-1.8841802037	0.6297083776	-0.5081962164
C	0	-2.8600072183	1.8186624892	1.4599314369
C	0	-1.1935721766	-0.3282908195	0.4680575217
H	0	-2.3483900672	0.0221453154	-1.2933750050
C	0	-0.8150570760	0.3385850831	1.7977987124
H	0	-3.6082233711	2.5106706888	1.8530291913
C	0	-1.8736853820	1.2406865243	2.4300769069
H	0	-2.4029147453	0.6457077028	3.1961818600
H	0	-0.4904129602	-0.4470671614	2.4941028016
C	0	-2.0646979962	-1.5483623606	0.8579536688
O	0	-1.6726972979	-2.4017931361	1.6133561633
O	0	-3.2968842920	-1.4846726540	0.3610154979
C	0	-4.1512084143	-2.5902042113	0.6570457760
H	0	-3.7329350857	-3.5106458708	0.2243588408
H	0	-5.1191208310	-2.3551105827	0.1999129971
H	0	-4.2544663631	-2.7197844099	1.7440693991
N	0	0.0863239431	-0.8298370915	-0.1059255281
C	0	1.3342512995	-0.1872299453	0.3080699862
C	0	0.0190517799	-1.8994056207	-0.9513605865
H	0	1.8843612167	-0.8203061735	1.0243500246
C	0	2.3293451588	0.3137621911	-0.7848016110
H	0	1.0075188951	-2.2968061683	-1.2493644379
O	0	-1.0267044078	-2.3890470138	-1.3337855302
C	0	3.3366816338	1.2731855872	-0.1129627345
C	0	3.1441156212	-0.8724079257	-1.3437908858
C	0	1.6059563516	1.0277083786	-1.9355734813
H	0	2.8606279537	2.2024703412	0.2245599436
H	0	4.1182540111	1.5416815378	-0.8390795220
H	0	3.8257769516	0.8029648076	0.7539537935
H	0	3.9845001254	-0.4837697932	-1.9388378020
H	0	2.5591058297	-1.5193698894	-2.0112774617
H	0	3.5653848321	-1.4924224454	-0.5363771044
H	0	0.8804495125	0.3646430251	-2.4306665930
H	0	2.3415223656	1.3391446547	-2.6929888247
H	0	1.0786491742	1.9210027356	-1.5780946487
S	0	0.7299570229	1.1956077475	1.4114606273
O	0	1.5937594589	1.2810070312	2.5936418583
O	0	0.4306075606	2.4087092337	0.6322760562
H	0	-1.3615451378	2.0392024648	2.9970168835
H	0	-1.1221005856	1.2589277528	-0.9893066806
O	0	-3.8114328414	2.1137734552	-0.6527794221
Si	0	-4.4516407313	1.7209873808	-2.1732536115
C	0	-5.1770847891	-0.0114827230	-2.1267887819
H	0	-4.4045715534	-0.7759175179	-1.9554532102
H	0	-5.9181832399	-0.0913223150	-1.3149043735
H	0	-5.6858598374	-0.2431211015	-3.0772542238
C	0	-3.1281445866	1.8757591114	-3.5003461526
H	0	-3.5867184847	1.8203823669	-4.5018538040
H	0	-2.6121875477	2.8461986407	-3.4187444235
H	0	-2.3704718789	1.0802177326	-3.4356491938
C	0	-5.7852674002	3.0076971140	-2.4315586022
H	0	-5.3572300095	4.0226700465	-2.4154926130
H	0	-6.2885557596	2.8636719874	-3.4016667078
H	0	-6.5467430108	2.9485156924	-1.6377800453

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C	0	-3.1475887862	1.0600823361	-0.7890031376

C	0	-2.3664844458	0.2403454734	0.1978882078
C	0	-2.5943227913	1.6215046977	-1.8723243495
C	0	-1.0677616159	-0.3638012994	-0.3680149543
H	0	-2.9762343595	-0.5799590166	0.5865756785
C	0	-0.3245365115	0.6237374235	-1.2789742560
H	0	-3.2250740112	2.2329337355	-2.5212995164
C	0	-1.1618098769	1.4347086973	-2.2661064215
H	0	-1.1043961612	0.9270793984	-3.2463851217
H	0	0.4756060197	0.0901389904	-1.8044352455
C	0	-1.2931864337	-1.6631741523	-1.1687377968
O	0	-0.3893500149	-2.3752441420	-1.5313743483
O	0	-2.5732384627	-1.8657099508	-1.4685211465
C	0	-2.8722223575	-3.0503929798	-2.2100374475
H	0	-2.5819340818	-3.9401127387	-1.6327428547
H	0	-3.9551562770	-3.0362369575	-2.3765493058
H	0	-2.3301284121	-3.0536293495	-3.1667342724
N	0	-0.1255638923	-0.6749661358	0.7418876310
C	0	1.0533515958	0.1598495594	0.9490819665
C	0	-0.5516323416	-1.5728663051	1.6812424204
H	0	1.0463038355	0.5688389264	1.9713929482
S	0	0.6093342818	1.6423891434	-0.0923236496
C	0	2.4454401458	-0.4786711177	0.6684246074
H	0	0.0892526607	-1.6025706606	2.5875265474
O	0	-1.5379338723	-2.2701542576	1.5479894502
O	0	1.7580368545	2.2630553277	-0.7664228578
O	0	-0.3002401697	2.4723549969	0.7090011378
C	0	2.6562657480	-0.8361289736	-0.8118140022
C	0	2.5699963278	-1.7709255901	1.4956630339
C	0	3.5164720276	0.5187266007	1.1456524093
H	0	2.6890302856	0.0629794964	-1.4420982099
H	0	3.6207926746	-1.3542826264	-0.9249327137
H	0	1.8672127104	-1.5136351169	-1.1694651397
H	0	3.5900668587	-2.1694433702	1.3857524767
H	0	2.4003835714	-1.5923804376	2.5697026839
H	0	1.8743247555	-2.5492815565	1.1497843798
H	0	3.4108063821	0.7256849066	2.2235584411
H	0	4.5190752818	0.0944289153	0.9842649915
H	0	3.4534734161	1.4690537337	0.6000037166
H	0	-2.1015738749	0.8865270112	1.0480563097
H	0	-0.6584747382	2.4058161036	-2.4261781621
O	0	-4.4488244938	1.2853855918	-0.4913239169
Si	0	-5.5895996897	0.4434079463	0.4416011248
C	0	-7.1752010577	1.3918100025	0.1451398446
C	0	-5.1236253427	0.4925895117	2.2622476882
C	0	-5.7264110231	-1.3258933554	-0.1765259900
H	0	-7.0705456150	2.4387681829	0.4716650493
H	0	-7.4365800823	1.3952762462	-0.9249565904
H	0	-8.0131714943	0.9417268568	0.7022264515
H	0	-5.9710088971	0.1471759492	2.8779667383
H	0	-4.2598505099	-0.1492528429	2.4929013114
H	0	-4.8792971537	1.5217056550	2.5718154487
H	0	-4.7986383899	-1.8906201492	-0.0009518306
H	0	-6.5495351988	-1.8508675211	0.3360446007
H	0	-5.9344792070	-1.3383717729	-1.2587794677

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C	0	3.3323945902	-0.0526020837	0.6073608768
C	0	2.5140204772	1.1044856046	0.1022104344
C	0	3.3520459883	-1.1699272525	-0.1356237050
C	0	1.0575260856	0.6456446660	-0.2182314677
H	0	2.5026050510	1.9183093445	0.8299645759
C	0	1.1098714816	-0.6114896271	-1.1329763331

H	0	3.8886329124	-2.0684462989	0.1665418321
C	0	2.5202357132	-1.1717827566	-1.3892414270
H	0	2.4312953744	-2.1826088298	-1.8130659497
H	0	0.5867565925	-0.4174254977	-2.0761434586
C	0	0.4356168354	1.8241044800	-0.9827788898
O	0	0.5333588201	1.9689369257	-2.1762061757
O	0	-0.1374174900	2.7066338253	-0.1620390737
C	0	-0.6462496569	3.8994522704	-0.7646393247
H	0	-1.0308940169	4.5132049108	0.0576866385
H	0	-1.4503860358	3.6576216021	-1.4756707431
H	0	0.1526538866	4.4290605136	-1.3031941426
N	0	0.2830430083	0.2878618089	0.9939859890
C	0	-0.7293398470	-0.7459409052	0.8615556703
C	0	0.4785267575	0.8324594595	2.2466152638
H	0	-0.7568751681	-1.3207872547	1.7980061489
S	0	0.1044729750	-1.9108269739	-0.3105533147
C	0	-2.1894341734	-0.3396544170	0.5075987218
H	0	-0.1298295728	0.2886828424	3.0047138080
O	0	1.1929914933	1.7601108508	2.5433307544
O	0	-0.8055837494	-2.5178936335	-1.2945907574
O	0	0.9607962854	-2.7917287081	0.4985436244
C	0	-3.0633501217	-1.5907997089	0.7170292900
C	0	-2.6254927366	0.7567913737	1.4946154840
C	0	-2.3741519427	0.1796020409	-0.9282454836
H	0	-2.7662519028	-2.4027592604	0.0396321684
H	0	-4.1188429599	-1.3481459291	0.5214311254
H	0	-2.9898710517	-1.9549682748	1.7548740070
H	0	-3.6805178287	1.0138742065	1.3132217427
H	0	-2.0262375364	1.6703357611	1.3721635590
H	0	-2.5424212766	0.4215701659	2.5406722943
H	0	-1.8508867988	1.1284243741	-1.0932020201
H	0	-3.4434571440	0.3742391633	-1.1030160429
H	0	-2.0423425804	-0.5526087743	-1.6743936476
H	0	2.9230177805	1.4766121048	-0.8507521392
H	0	2.9714062527	-0.5438477115	-2.1790103600
O	0	3.9496872421	0.1512651800	1.7871547555
Si	0	4.1081595238	-0.8993493897	3.1196349540
C	0	5.4709650435	-2.1469721811	2.7787195572
C	0	2.4670554571	-1.7551107271	3.4231992445
C	0	4.5671069096	0.2496232171	4.5217500616
H	0	5.1762394207	-2.8735192607	2.0051023935
H	0	6.3897328323	-1.6408800645	2.4409970546
H	0	5.7121665402	-2.7134798612	3.6937689709
H	0	2.5967774558	-2.5916810028	4.1296008839
H	0	1.7469417669	-1.0510519108	3.8681909262
H	0	2.0410166168	-2.1586676515	2.4912737813
H	0	3.7850869661	1.0166320074	4.6405793240
H	0	4.6657069427	-0.2991193822	5.4726656674
H	0	5.5212693820	0.7625405199	4.3213434123

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C	0	1.4551083248	0.3057067733	1.4643298538
C	0	0.5922406594	-0.2619055217	2.4388575181
C	0	-0.9682707485	1.2953506184	0.2060763591
C	0	-1.6972375951	0.9395959043	1.3406994426
C	0	-0.4234598653	0.4612853934	3.0357087874
H	0	-1.1202072204	-0.0555346803	3.6978186216
H	0	-2.3114950237	1.6745174625	1.8606521221
C	0	-0.9828513660	2.7125819441	-0.2396949928
O	0	-0.9551649421	3.6539170186	0.5218569533
O	0	-1.0953013670	2.8246004573	-1.5693885051
C	0	-1.0509571267	4.1500441759	-2.0938841532

H	0	-1.1412824472	4.0499891456	-3.1819840519
H	0	-1.8752317238	4.7578350137	-1.6921440695
H	0	-0.0979205929	4.6341705690	-1.8334640277
N	0	-0.7720082911	0.2191689672	-0.7159730307
C	0	-1.8691409871	-0.7590258915	-0.7134668629
C	0	0.2770337510	0.2058093058	-1.6059703125
H	0	-2.7269517641	-0.3271002587	-1.2557161082
S	0	-2.5076544385	-0.6369108947	1.0516051554
C	0	-1.6580506159	-2.2179802994	-1.1929538264
H	0	0.2854992627	-0.6962281660	-2.2367848653
O	0	1.1268957606	1.0660909268	-1.7019541333
O	0	-1.9872975154	-1.7137221248	1.9119020227
O	0	-3.9593480270	-0.4207470791	0.9897020467
C	0	-1.6029827731	-2.2744046274	-2.7376811684
C	0	-2.9171585491	-3.0213337126	-0.7863934455
C	0	-0.4101784463	-2.8640141811	-0.5687533397
H	0	-0.6773511909	-1.8753578747	-3.1719385402
H	0	-1.6761178781	-3.3243007634	-3.0593653246
H	0	-2.4499079119	-1.7294047731	-3.1839041891
H	0	-2.8502166291	-4.0316067685	-1.2162817966
H	0	-3.0086545246	-3.1244217628	0.3013649507
H	0	-3.8354736806	-2.5496402835	-1.1687872381
H	0	-0.5086097634	-2.9138969751	0.5225515862
H	0	-0.2965594065	-3.8883563493	-0.9560349107
H	0	0.5124556449	-2.3127592029	-0.7938010613
C	0	1.3261717880	1.6287104787	1.0996972206
H	0	1.8847403416	2.0394814098	0.2659704368
H	0	0.8155268977	2.3350476332	1.7470490318
H	0	-0.3208329837	1.5346667741	3.1978160573
H	0	0.5993979472	-1.3499463944	2.5223678032
O	0	2.2052607529	-0.5755004320	0.7643169685
Si	0	3.7254832273	-0.5525966622	-0.0007013048
C	0	4.2951588881	1.1782650971	-0.4402590095
H	0	4.3617761851	1.8325691235	0.4427959011
H	0	5.2995418264	1.1224855717	-0.8930392231
H	0	3.6105845011	1.6319990043	-1.1722914949
C	0	4.9165362069	-1.3603052654	1.2044151979
H	0	5.9235481489	-1.4554083748	0.7655007905
H	0	5.0051541630	-0.7648004568	2.1277834937
H	0	4.5686746607	-2.3676733742	1.4840149540
C	0	3.5005400506	-1.5956218558	-1.5399229918
H	0	2.8582368762	-1.0682621653	-2.2617727508
H	0	4.4711494911	-1.7900759349	-2.0249676382
H	0	3.0405080387	-2.5669066619	-1.2982999085

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C	0	-1.7748082970	-0.7570291508	0.4461567316
C	0	-0.7424504121	-0.5338099236	1.3371018732
C	0	-1.5184208561	-1.3531152720	-0.8103807539
C	0	0.7736933112	0.8492614238	-0.1449258811
H	0	-0.9108095883	0.0764445395	2.2233630721
C	0	0.8311815128	0.0388669359	-1.2970263110
C	0	-0.2292711281	-1.7297272674	-1.1883272248
H	0	-0.0636893881	-2.1246613125	-2.1930019364
H	0	0.3430765715	0.3712549051	-2.2121467055
C	0	-0.3298231098	1.8170167857	0.1165278180
O	0	-0.5059052425	2.4579419919	1.1219776093
O	0	-1.1613117174	1.8514785878	-0.9497750100
C	0	-2.3130066276	2.6789734616	-0.7923053326
H	0	-2.9017091796	2.3474534340	0.0740875031
H	0	-2.8912706954	2.5715579570	-1.7179507411
H	0	-2.0161144295	3.7275106888	-0.6453302820

N	0	2.0084695107	1.0280927918	0.5561605384
C	0	3.0801686930	0.1014526937	0.1843655803
C	0	2.4754824749	2.3528049940	0.7465357282
H	0	3.9690647266	0.6927187065	-0.0739146756
S	0	2.5452369442	-0.4565471749	-1.5312918376
C	0	3.5589478957	-0.9793185384	1.1869537019
H	0	3.4551878170	2.3485332769	1.2731644351
O	0	1.9282202237	3.3551188449	0.3836574267
O	0	3.1717172903	0.4500594768	-2.5005218358
C	0	2.5387676669	-2.0773791577	1.5049227289
C	0	4.8296981158	-1.6141526493	0.5891168252
C	0	3.9246733722	-0.2484441457	2.4919155022
H	0	1.6902136216	-1.6818398923	2.0774288117
H	0	3.0158367596	-2.8437812997	2.1345364923
H	0	2.1812605480	-2.5736630106	0.5937722859
H	0	5.2620923952	-2.3289291651	1.3055654603
H	0	5.5942491156	-0.8487737284	0.3781214899
H	0	4.6082870409	-2.1506172165	-0.3431121745
H	0	4.7092222548	0.5075943366	2.3274335551
H	0	4.3096473391	-0.9714178617	3.2275874651
H	0	3.0474320996	0.2511758763	2.9292171006
O	0	2.6813226011	-1.9126586159	-1.7076680028
H	0	0.4472733212	-2.1530287512	-0.4479549058
H	0	0.1513411293	-1.1375049147	1.2911309153
O	0	-2.9793007051	-0.1962021929	0.7112761545
H	0	-2.2919096804	-1.2708177415	-1.5768953471
Si	0	-4.5580751543	-0.6603474325	0.2812588047
C	0	-4.9573205991	-0.0963484400	-1.4670508881
H	0	-4.3521223135	-0.6113143873	-2.2291403113
H	0	-6.0176976774	-0.2984635176	-1.6931625787
H	0	-4.7923712399	0.9868442425	-1.5762547999
C	0	-4.6939135380	-2.5240864215	0.4428836045
H	0	-4.4525497941	-2.8438130460	1.4693383158
H	0	-5.7180485908	-2.8611181572	0.2127786671
H	0	-4.0053238244	-3.0416730851	-0.2432507666
C	0	-5.6367223150	0.2410072653	1.5142063772
H	0	-5.4899936503	1.3303401937	1.4379154906
H	0	-6.7034367296	0.0280256113	1.3361785559
H	0	-5.3918088689	-0.0615945516	2.5444596815

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C	0	3.4232198967	-0.6687872232	-0.7860027742
C	0	2.6839953155	-0.8935142475	0.3622448383
C	0	2.9592804442	-1.1433645198	-2.0372941093
C	0	0.6965856784	0.2761109319	-0.2732278008
H	0	2.9658816537	-0.4542768555	1.3142690100
C	0	0.2691480010	-0.4472528484	-1.3976393581
C	0	1.7842673810	-1.8623202629	-2.1563588418
H	0	1.4055208641	-2.1008352086	-3.1538844928
H	0	0.1669122416	0.0072816432	-2.3795018367
C	0	1.3042073473	1.6200733353	-0.4466991474
O	0	1.2141357799	2.5421008154	0.3272668296
O	0	1.9408973115	1.6852672225	-1.6326187745
C	0	2.6110596373	2.9043754283	-1.9392844370
H	0	3.4851388247	3.0354883573	-1.2860691910
H	0	2.9376561445	2.8180315390	-2.9823011896
H	0	1.9374278222	3.7638826527	-1.8114227296
N	0	-0.0986801595	0.0473811506	0.8970893948
C	0	-1.4357823199	-0.4819897712	0.6336413835
C	0	0.3394490750	0.1873815979	2.1973973037
H	0	-1.7031244744	-1.2227128174	1.4000386589
S	0	-1.0699763120	-1.5159720579	-0.8734030281

C	0	-2.5636398245	0.5703122600	0.4899069537
H	0	-0.4538671462	-0.1046668036	2.9205237348
O	0	1.4321700974	0.5632093932	2.5512710946
O	0	-2.1408442741	-1.5297319681	-1.8790000147
O	0	-0.5389978519	-2.7895602224	-0.3536959757
C	0	-2.3505785532	1.5031998915	-0.7143293857
C	0	-2.5859831965	1.4250767406	1.7703766757
C	0	-3.8984890436	-0.1843736722	0.3595710913
H	0	-2.3449153789	0.9485607828	-1.6618569125
H	0	-3.1736215236	2.2332187502	-0.7553151497
H	0	-1.4143345124	2.0711622003	-0.6170428670
H	0	-3.4340891951	2.1252533935	1.7242833386
H	0	-2.7159462782	0.8071493206	2.6734387826
H	0	-1.6671759995	2.0200748147	1.8774534252
H	0	-4.0803769339	-0.8170023519	1.2440141664
H	0	-4.7286712954	0.5346884618	0.2870320454
H	0	-3.9139737007	-0.8218009181	-0.5341023360
H	0	1.9828076896	-1.7228643478	0.4066784175
H	0	1.4421069923	-2.5343612962	-1.3701625169
H	0	3.4490463800	-0.7277339390	-2.9214958096
O	0	4.4738080573	0.1782934945	-0.8187769100
Si	0	5.4145508724	0.8269303963	0.4562026817
C	0	6.0632585086	-0.5898148640	1.5029993156
C	0	6.8045037895	1.6866868432	-0.4575555540
C	0	4.4267083721	2.0490246573	1.4760594492
H	0	6.5952836437	-1.3247363086	0.8776769928
H	0	6.7708269690	-0.2104076810	2.2587959296
H	0	5.2559248500	-1.1154934808	2.0350908061
H	0	7.3784260817	0.9725955430	-1.0691075237
H	0	6.4097454826	2.4672165581	-1.1276380010
H	0	7.4985909593	2.1682527162	0.2505101628
H	0	4.1074852550	2.9144799143	0.8754686516
H	0	3.5197800550	1.6185552068	1.9260958478
H	0	5.0647009396	2.4296569631	2.2920495957

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C	0	2.6252493257	-1.1976420632	1.2796155917
C	0	2.9077889099	-0.0323286923	0.5975852817
C	0	2.1794526838	-2.3519767307	0.5832891381
C	0	0.5609669562	0.2127274146	-0.2991542144
H	0	3.1133997497	0.8928996789	1.1259004364
C	0	0.4177638464	-0.9362556095	-1.0792930779
C	0	1.9890644272	-2.3658671549	-0.7881993237
H	0	1.5603756190	-3.2584731270	-1.2486393983
H	0	0.5120318074	-0.8878641359	-2.1641017952
C	0	1.0247360987	1.4731246403	-0.9177030442
O	0	1.7582911628	1.5152514244	-1.8820202819
O	0	0.5141649007	2.5591854915	-0.3171076626
C	0	0.9623311223	3.8192906753	-0.8119235096
H	0	0.4773870926	4.5799099901	-0.1888992643
H	0	0.6802456048	3.9474138684	-1.8675516560
H	0	2.0564868249	3.8980799925	-0.7296261242
N	0	-0.2303486760	0.1843205393	0.8888914538
C	0	-1.4698757401	-0.5850293966	0.7896953425
C	0	0.1398752512	0.7262117595	2.0995285754
H	0	-1.6135034116	-1.1853132165	1.6987459515
S	0	-1.0141052206	-1.8682913115	-0.4968329304
C	0	-2.7478166444	0.2398499334	0.4912216826
H	0	-0.5530840747	0.4149686460	2.9105612880
O	0	1.0965820215	1.4401704859	2.2982013039
O	0	-1.9675663768	-1.9523625271	-1.6150598168
O	0	-0.6761526265	-3.0958870433	0.2352609976

C	0	-3.9447909487	-0.7280603108	0.4679000256
C	0	-2.9481058704	1.2483660714	1.6379287782
C	0	-2.6405357321	1.0189205301	-0.8300830018
H	0	-3.8526893781	-1.4647069685	-0.3404365132
H	0	-4.8766803647	-0.1629813944	0.3135410175
H	0	-4.0352907674	-1.2663042888	1.4259102247
H	0	-3.8994363512	1.7815954099	1.4883538633
H	0	-2.1484069071	2.0031209667	1.6650822831
H	0	-2.9974430533	0.7504221480	2.6197830307
H	0	-1.8041577529	1.7311797869	-0.7964488502
H	0	-3.5641346724	1.5976812818	-0.9862967828
H	0	-2.5108006082	0.3465851656	-1.6870199226
H	0	2.6144760947	-1.7545134447	-1.4400207458
H	0	3.1231334414	-0.0548044674	-0.4661894473
H	0	1.7573030887	-3.1529014267	1.1923181801
O	0	2.5201899936	-1.2556870197	2.6237532004
Si	0	3.3102203361	-0.5497430532	3.9566672423
C	0	4.4859988994	-1.8664234742	4.5958609899
H	0	3.9426078070	-2.7949701183	4.8335312272
H	0	5.2543154988	-2.1076138607	3.8431170518
H	0	5.0021377680	-1.5288372403	5.5099144432
C	0	1.9500701714	-0.1911018439	5.1913219813
H	0	2.3717488123	0.0802202811	6.1730285392
H	0	1.3359407949	0.6494681636	4.8338575793
H	0	1.3023901643	-1.0714580463	5.3301390562
C	0	4.2495062624	1.0110149393	3.5103398902
H	0	3.5560294310	1.7936155070	3.1686310583
H	0	4.7739739196	1.3820270906	4.4071497872
H	0	5.0059599384	0.8344313042	2.7299070101

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C	0	-1.7964632058	-2.0892143876	1.3641675250
C	0	-2.2425510098	-0.6994071875	1.0076251451
C	0	-1.4685892156	-2.9251335206	0.3657317718
C	0	-1.2948542002	0.0035085625	0.0025709094
H	0	-2.3553825658	-0.0623788268	1.8894342823
C	0	-0.8378873507	-0.9953561528	-1.0988377830
C	0	-1.4963912372	-2.3771851256	-1.0389778954
H	0	-0.9854808372	-3.0692371587	-1.7224439255
H	0	-0.9402617931	-0.5569121817	-2.0996372562
C	0	-2.0456615882	1.1345101813	-0.7275755095
O	0	-3.2299640590	1.1498360005	-0.9340014825
O	0	-1.1876057549	2.0491143173	-1.2105261986
C	0	-1.7707189613	3.1461518212	-1.9180067119
H	0	-0.9347173751	3.7663758593	-2.2619263340
H	0	-2.3624714305	2.7865833027	-2.7723631684
H	0	-2.4266698488	3.7214975406	-1.2486600072
N	0	-0.0869075840	0.5552550928	0.6801753572
C	0	1.2007423391	0.4123035273	0.0055877261
C	0	-0.3244391836	1.5915766428	1.5514409473
H	0	1.2871567494	1.1438798799	-0.8166661963
S	0	0.9787765624	-1.1624433824	-0.9419373677
C	0	2.5165822177	0.4283614346	0.8449145980
H	0	0.5913224382	2.0143144536	1.9989305626
O	0	-1.4303524209	2.0138280904	1.8214760517
O	0	1.3024613537	-2.3404189809	-0.1195747005
O	0	1.5940123659	-1.0133915918	-2.2669303390
C	0	2.9730545235	1.8831538620	1.0946475807
C	0	3.6420462204	-0.2298064591	0.0118226817
C	0	2.3452348441	-0.3300441752	2.1688959182
H	0	2.3254945300	2.4456609244	1.7796325162
H	0	3.9771694041	1.8723719892	1.5450639780

H	0	3.0377225583	2.4445236862	0.1491266786
H	0	4.5991714554	-0.0899678502	0.5353545789
H	0	3.4840763700	-1.3073207149	-0.1175783789
H	0	3.7282538962	0.2268181987	-0.9853895225
H	0	1.9943594057	-1.3534313805	1.9880040273
H	0	3.3123510215	-0.3789951728	2.6924914725
H	0	1.6283376146	0.1627247820	2.8411141719
H	0	-2.5351189876	-2.2656706173	-1.3951173825
H	0	-3.2310563902	-0.7107482118	0.5198996347
H	0	-1.7762596726	-2.3976426497	2.4098118635
O	0	-1.0922018760	-4.2112923134	0.4554564789
Si	0	-0.4614401068	-5.0901595237	1.7722398980
C	0	-1.8600803175	-5.4885660480	2.9628226182
C	0	0.9031038500	-4.1136981175	2.6058747704
C	0	0.2020781952	-6.6478606846	0.9761571609
H	0	-2.2791976861	-4.5806860294	3.4240878156
H	0	-2.6784673132	-6.0101720586	2.4406840417
H	0	-1.5034903949	-6.1445617141	3.7745156299
H	0	1.3870984484	-4.7260494507	3.3847881272
H	0	1.6563371050	-3.8206905427	1.8600395346
H	0	0.5239798631	-3.1957529450	3.0791195080
H	0	1.0006999693	-6.4034134089	0.2578795454
H	0	0.6179397555	-7.3324419314	1.7334900482
H	0	-0.5937266802	-7.1821871935	0.4330501540

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C	0	-2.8838581941	0.7434198319	-1.0806285465
C	0	-1.8166457987	-0.3064083195	-1.0031274067
C	0	-3.0843858037	1.6803294240	-0.1456972188
C	0	-1.2248981291	-0.5049571620	0.4024596751
H	0	-2.1836417481	-1.2782635491	-1.3594025093
C	0	-1.1469357958	0.7935518248	1.2215988430
C	0	-2.3660462745	1.6988044452	1.1758375136
H	0	-3.0698240320	1.3960903083	1.9708309704
H	0	-0.8778230736	0.5304542994	2.2541617429
C	0	-2.0356354596	-1.4750322618	1.2990688294
O	0	-1.7063311876	-1.7278589046	2.4315629776
O	0	-3.1644117390	-1.8811406929	0.7294888100
C	0	-3.9506940579	-2.8029040667	1.4859994459
H	0	-3.3911944353	-3.7391485936	1.6279259170
H	0	-4.8585845301	-2.9820150319	0.8985235842
H	0	-4.2010515879	-2.3831805654	2.4710997171
N	0	0.1810351978	-0.9944677582	0.3266178663
C	0	1.2671519396	-0.0195042442	0.4428354053
C	0	0.3823369323	-2.3437127856	0.2460579882
H	0	1.7571616073	-0.0941738012	1.4282866465
C	0	2.3718791738	0.0280758762	-0.6579541917
H	0	1.4451096894	-2.6404715692	0.3347578947
O	0	-0.5147819795	-3.1513174710	0.1080312394
C	0	3.1616702723	1.3438643715	-0.4839961045
C	0	3.3707368855	-1.1305140603	-0.4533906200
C	0	1.7808458550	-0.0549853268	-2.0719756715
H	0	2.5511347173	2.2261533214	-0.7148472773
H	0	4.0213005072	1.3430244771	-1.1704318954
H	0	3.5469702770	1.4512949681	0.5417424011
H	0	4.2531184170	-0.9615327189	-1.0892098418
H	0	2.9568243702	-2.1065129328	-0.7406598613
H	0	3.7179666811	-1.1901608216	0.5905673874
H	0	1.2163226092	-0.9884462160	-2.2158248898
H	0	2.5967401964	-0.0420943696	-2.8108433150
H	0	1.1161045712	0.7936247190	-2.2755865743
S	0	0.3498849129	1.5999486318	0.6081875701

O	0	0.9775027437	2.4124699676	1.6558633176
O	0	0.0767411983	2.2046383611	-0.7102279031
H	0	-2.0660845323	2.7281732692	1.4286251350
H	0	-0.9951173046	-0.0177453574	-1.6758315710
H	0	-3.4793609546	0.7900244787	-1.9952715677
O	0	-4.0015130292	2.6793649395	-0.2817161422
Si	0	-3.6586575212	4.1287168940	-1.1168422722
C	0	-3.2705693553	3.7289730340	-2.9086139320
C	0	-2.1818393052	4.9627273599	-0.3127758735
C	0	-5.2251213833	5.1374617002	-0.9444221719
H	0	-2.3657637628	3.1043970774	-2.9728325829
H	0	-4.1011936058	3.1894142442	-3.3912592126
H	0	-3.0855336263	4.6535260727	-3.4804239967
H	0	-1.9492452394	5.9108288554	-0.8259121778
H	0	-2.3743671407	5.1950005275	0.7473085151
H	0	-1.2889624047	4.3200211712	-0.3764433495
H	0	-5.4556517097	5.3278908227	0.1159239397
H	0	-5.1215964108	6.1108439772	-1.4512760706
H	0	-6.0836422923	4.6099660893	-1.3898891650

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C	0	-2.9022109781	1.3906153670	0.4244499401
C	0	-1.8742950391	0.5711078603	1.1432362991
C	0	-2.7522152614	1.8313734611	-0.8306629829
C	0	-0.9143305104	-0.1852394744	0.1987409092
H	0	-2.3573740800	-0.1601303642	1.8015790773
C	0	-0.4807514959	0.6817920980	-0.9941733197
C	0	-1.5542390184	1.5196739265	-1.6779256611
H	0	-1.9050522389	0.9869682760	-2.5784160500
H	0	0.0318414097	0.0475980022	-1.7265741493
C	0	-1.5006833377	-1.4946132461	-0.3712304633
O	0	-0.8366385204	-2.2926532894	-0.9869206224
O	0	-2.8120643723	-1.6080677737	-0.1755200899
C	0	-3.4162518855	-2.8138491202	-0.6487927763
H	0	-3.0150635158	-3.6760918854	-0.0965037228
H	0	-4.4917125791	-2.7063374713	-0.4669024645
H	0	-3.2167338052	-2.9527619693	-1.7210775977
N	0	0.3456263665	-0.5300304876	0.9119349066
C	0	1.5715309485	0.2098267748	0.6302645647
C	0	0.2376762003	-1.3713122531	1.9859677283
H	0	1.9534006757	0.6713179622	1.5545651133
S	0	0.8885636404	1.6683426028	-0.3109588139
C	0	2.7309650308	-0.5607552389	-0.0693553845
H	0	1.1535457378	-1.4079015151	2.6128031464
O	0	-0.7607430139	-2.0144312074	2.2381450313
O	0	1.7555343260	2.1338724178	-1.4025653544
O	0	0.3870270354	2.6316700946	0.6777518187
C	0	2.3725002584	-1.0176963479	-1.4928928382
C	0	3.0691265945	-1.8113070981	0.7624123488
C	0	3.9607288711	0.3652296922	-0.0851356655
H	0	2.2342226827	-0.1619185818	-2.1674319619
H	0	3.1960383935	-1.6268094937	-1.8958699243
H	0	1.4650605815	-1.6392109351	-1.4891403696
H	0	3.9594734707	-2.2952481641	0.3328086153
H	0	3.3034212480	-1.5611320186	1.8095960941
H	0	2.2548671101	-2.5502031157	0.7463502561
H	0	4.2605860211	0.6399670438	0.9398115626
H	0	4.8111044956	-0.1533187935	-0.5534306736
H	0	3.7661460121	1.2855008335	-0.6506303929
H	0	-1.2575588465	1.2255101513	1.7788646568
H	0	-1.1131791330	2.4589702915	-2.0544349429
H	0	-3.8041755337	1.6569167161	0.9786511662

O	0	-3.6719999413	2.5678784121	-1.5090395970
Si	0	-5.3446184147	2.2715954503	-1.6162138927
C	0	-6.2277776496	2.8930714520	-0.0792614391
C	0	-5.5771347109	0.4202595591	-1.8354448169
C	0	-5.8892737566	3.2436068843	-3.1193537447
H	0	-6.0132389280	2.2711955941	0.8037713302
H	0	-5.9247731339	3.9273812651	0.1503399102
H	0	-7.3195706572	2.8866769467	-0.2353531691
H	0	-6.6451645902	0.1481334454	-1.8323458795
H	0	-5.1414052574	0.0817390339	-2.7895422025
H	0	-5.0762617750	-0.1255848640	-1.0208079145
H	0	-5.3552242941	2.9065254259	-4.0218532950
H	0	-6.9709256841	3.1238938619	-3.2950361578
H	0	-5.6838765421	4.3177532962	-2.9849628049

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C	0	2.7370792782	-0.0612488760	2.1134590683
C	0	2.1303835621	1.1300548187	1.4340591392
C	0	3.0902429627	-1.1064983613	1.3477725074
C	0	0.9313548398	0.7366618742	0.5060874305
H	0	1.7943029511	1.8867728598	2.1465860040
C	0	1.3428224960	-0.4951903197	-0.3482729268
C	0	2.7713397985	-1.0060864054	-0.1278013713
H	0	2.8885675050	-1.9673858946	-0.6448914489
H	0	1.1684034655	-0.3018172292	-1.4123074904
C	0	0.7165170623	1.9434623961	-0.4167796428
O	0	1.3503932206	2.1224845907	-1.4286087485
O	0	-0.1817582111	2.8023460798	0.0673869184
C	0	-0.3679477235	4.0125160993	-0.6710258357
H	0	-1.0966642347	4.6031931226	-0.1044479427
H	0	-0.7485291631	3.7928105305	-1.6797641106
H	0	0.5830486267	4.5562967500	-0.7642366807
N	0	-0.2975828215	0.3714712686	1.2495962028
C	0	-1.1323242723	-0.6781192166	0.6937718684
C	0	-0.6582191330	0.9021010471	2.4714623994
H	0	-1.5816747521	-1.2375945967	1.5264155516
S	0	0.1625852013	-1.8371880581	0.0725048653
C	0	-2.2650136019	-0.2997209201	-0.3020232947
H	0	-1.5234024066	0.3447147126	2.9009725133
O	0	-0.1515844402	1.8387172951	3.0405493886
O	0	-0.1977799360	-2.5677782089	-1.1546397672
O	0	0.6324398576	-2.5903707033	1.2433184109
C	0	-3.1469751717	-1.5506289732	-0.4724133171
C	0	-3.0916554565	0.8285511534	0.3377018323
C	0	-1.7637681831	0.1593030877	-1.6815643696
H	0	-2.5730768874	-2.3877351974	-0.8931439244
H	0	-3.9845062497	-1.3313489542	-1.1519329438
H	0	-3.5727168951	-1.8680900220	0.4934508334
H	0	-3.9517616620	1.0655299700	-0.3074140333
H	0	-2.4936747446	1.7420545452	0.4636085528
H	0	-3.4880152532	0.5336196421	1.3223970706
H	0	-1.1616763785	1.0743825901	-1.6247209321
H	0	-2.6303870650	0.3895079766	-2.3200438302
H	0	-1.1804963586	-0.6242891985	-2.1818597092
H	0	2.8598481188	1.6095570642	0.7573355121
H	0	3.4544094477	-0.2961998945	-0.6247261792
H	0	2.8881833393	-0.0743971591	3.1931577925
O	0	3.6834527555	-2.2047076352	1.8383624935
Si	0	4.2169965558	-3.6776416311	1.1801445299
C	0	5.5620712106	-3.3128036155	-0.0854981832
C	0	2.8203743661	-4.6690565652	0.4168314491
C	0	4.9258949422	-4.5727518433	2.6621412772

H	0	5.1718859360	-2.7897971246	-0.9730608938
H	0	6.3543758995	-2.6871795519	0.3564926598
H	0	6.0258647499	-4.2512438982	-0.4327320110
H	0	3.1985651617	-5.6649428001	0.1293191028
H	0	2.0009614751	-4.7938838608	1.1395166822
H	0	2.3826716060	-4.2024141079	-0.4783836906
H	0	4.1441368721	-4.7466441194	3.4185710161
H	0	5.3426361675	-5.5503503780	2.3694257721
H	0	5.7286296503	-3.9827811341	3.1320616730

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H	0	-1.0452121371	-0.3104960235	3.5605929082
C	0	-1.5605046237	-0.5878383268	2.6369339939
C	0	-1.1701532285	-1.8464727804	2.0705189551
C	0	-0.8417766212	0.4400095216	-0.2899780522
C	0	-0.8230408547	-0.9263046951	-0.5805541138
C	0	-1.6293945058	-2.2320089567	0.8003115286
H	0	-1.3314831707	-3.2027378612	0.4073539945
H	0	-1.4294617800	-1.2991738587	-1.4071457775
C	0	-1.8945938618	1.2930768608	-0.8458337079
O	0	-3.0086866419	0.8853860073	-1.1211902322
O	0	-1.4907339582	2.5560455302	-1.0593545284
C	0	-2.4933472026	3.4688604740	-1.4928388301
H	0	-1.9967055493	4.4410754675	-1.5980309217
H	0	-2.9266689714	3.1524708329	-2.4535951615
H	0	-3.3026060247	3.5354811031	-0.7498418347
N	0	0.3727054316	0.9529990578	0.2552226399
C	0	1.5548365738	0.3137595994	-0.3206393703
C	0	0.3699715585	1.9782201387	1.1783239607
H	0	1.6989097932	0.6819897853	-1.3503438444
S	0	0.9103488956	-1.4218834943	-0.7004030191
C	0	2.9177549319	0.3123690457	0.4120393995
H	0	1.3855576552	2.2995240044	1.4663663071
O	0	-0.6265669209	2.4933224206	1.6342121154
O	0	1.2777623264	-2.4014935661	0.3427100294
O	0	1.2337593091	-1.7317856625	-2.0989164204
C	0	3.6003477092	1.6875263327	0.2426554895
C	0	3.8324521801	-0.7121912144	-0.3011129184
C	0	2.7838288295	-0.0654676194	1.8979886128
H	0	3.0532323525	2.5171456796	0.7088903596
H	0	4.5994526742	1.6550873798	0.7037941596
H	0	3.7308503231	1.9293719858	-0.8238369819
H	0	4.8580981166	-0.6052626887	0.0818071493
H	0	3.5106930407	-1.7454915357	-0.1241561288
H	0	3.8561409499	-0.5416187432	-1.3883351921
H	0	2.1857585527	-0.9765086830	2.0220327927
H	0	3.7837057179	-0.2512194087	2.3194953641
H	0	2.3215645814	0.7320891203	2.4955787284
C	0	-2.4051955008	0.2885320130	2.0379107977
H	0	-2.5819460931	1.2682550323	2.4796112389
H	0	-2.9877362588	0.0431985390	1.1507686795
H	0	-2.6335491729	-1.9092223679	0.5276600946
O	0	-0.2439901049	-2.5033792506	2.7562045051
Si	0	0.4390206880	-4.0749558654	2.8519167653
C	0	0.0557137276	-5.1698020397	1.3800499810
C	0	2.2743388708	-3.8076899081	3.0761461977
C	0	-0.3321992071	-4.7919490786	4.4066960755
H	0	0.4623648005	-4.7367623622	0.4554447874
H	0	0.5330845022	-6.1510877873	1.5429222414
H	0	-1.0248178092	-5.3456974405	1.2603207397
H	0	2.7214970876	-3.4290652399	2.1463431510
H	0	2.4672259341	-3.0804502757	3.8805763258

H	0	2.7682775478	-4.7554810975	3.3467449513
H	0	-0.1375146208	-4.1458042639	5.2774660387
H	0	-1.4242521852	-4.8936204946	4.2969904867
H	0	0.0798820634	-5.7913673022	4.6241026699

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H	0	4.1634247761	-1.3672936808	-1.4246802658
C	0	3.0702624697	-1.3666316720	-1.4489678300
C	0	2.4117342168	-0.5463188117	-2.2972940128
C	0	2.4428826346	-2.2120233693	-0.4664585070
C	0	0.6637347957	0.4960467316	0.5264472858
H	0	2.9572280392	0.1341268495	-2.9534149000
C	0	0.6321166572	-0.8436961115	0.9600961790
C	0	1.0501939244	-2.2384743926	-0.2786045758
H	0	0.6231334397	-3.0747216831	0.2758158381
H	0	1.3406670246	-1.1542983884	1.7311147646
C	0	1.9060736105	1.2226220279	0.2669034324
O	0	2.0393848436	2.2427017893	-0.3687574976
O	0	2.9498611192	0.5539192956	0.8397489799
C	0	4.2345343159	1.1017274539	0.5874629833
H	0	4.4355716175	1.1455098036	-0.4946708337
H	0	4.9548562004	0.4373174732	1.0813137275
H	0	4.3110073840	2.1223985366	0.9915289065
N	0	-0.5856914170	1.1825185543	0.4602473645
C	0	-1.7594257329	0.3320533749	0.5122302860
C	0	-0.6996177684	2.4340745230	1.0889465914
H	0	-2.4748425956	0.7440899653	1.2377799102
S	0	-1.0886655610	-1.1556652918	1.4536840056
C	0	-2.5177810168	0.0769162859	-0.8126871395
H	0	-1.7526356046	2.7969490026	1.0606606603
O	0	0.2017401466	3.0495828507	1.5900804123
O	0	-1.2127975142	-0.8696272585	2.8882157873
C	0	-1.6806396026	-0.6735039205	-1.8524887594
C	0	-3.8036418823	-0.7046126563	-0.4936020877
C	0	-2.8906385795	1.4608358972	-1.3773923066
H	0	-0.7239607626	-0.1590978041	-2.0272351162
H	0	-2.2200031757	-0.7070431034	-2.8112489979
H	0	-1.4929868100	-1.7075192030	-1.5363170255
H	0	-4.3863656778	-0.8591842236	-1.4146996855
H	0	-4.4388905029	-0.1455708447	0.2128999158
H	0	-3.5787455849	-1.6864992743	-0.0567282995
H	0	-3.4901841957	2.0426835437	-0.6589237982
H	0	-3.4927686880	1.3380432982	-2.2908225966
H	0	-1.9938314573	2.0444631359	-1.6314499249
O	0	-1.5831113826	-2.4416238629	0.9251895305
H	0	0.4500987964	-1.9628673993	-1.1400943804
H	0	1.3237869006	-0.5140790950	-2.3569179307
O	0	3.2739094402	-2.8180175419	0.3830632947
Si	0	3.0317299758	-4.0780813328	1.5342386412
C	0	4.7611800773	-4.3845130880	2.1686375942
H	0	5.1685777989	-3.4789183370	2.6455950383
H	0	4.7645273506	-5.1938830898	2.9167113673
H	0	5.4374114621	-4.6725534546	1.3484307637
C	0	1.8991526999	-3.5203281765	2.9213686889
H	0	2.2665172556	-2.5931712403	3.3896075071
H	0	0.8561475320	-3.3591814364	2.6107672538
H	0	1.8881513602	-4.2993866519	3.7025684123
C	0	2.3409246915	-5.5615271856	0.6203083170
H	0	1.3350526686	-5.3704885893	0.2160951485
H	0	2.9986152912	-5.8453304392	-0.2167689935
H	0	2.2674319058	-6.4245447726	1.3025194371

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H	0	4.4053189186	1.2164189973	-0.1270593862
C	0	3.7100090061	0.5070846117	0.3286814653
C	0	2.9594841176	0.8673274203	1.4009809880
C	0	3.5166872555	-0.7152389012	-0.3887528323
C	0	0.5355557922	0.5984089823	-0.0526681040
H	0	3.0354934063	1.8584770468	1.8477420848
C	0	0.8252746420	-0.6339229212	-0.6485411510
C	0	2.4966483470	-1.6064358398	-0.0298282633
H	0	2.4094899161	-2.5567301972	-0.5588095861
H	0	1.0334168802	-0.6819373256	-1.7152494646
C	0	0.8411270143	1.8780990393	-0.6826999899
O	0	0.3202650099	2.9426321076	-0.4324511167
O	0	1.7794505391	1.7173484944	-1.6573298554
C	0	2.1868795476	2.9036019769	-2.3262483578
H	0	2.6134168551	3.6272200577	-1.6144477478
H	0	2.9467917967	2.5979717458	-3.0564107611
H	0	1.3373090487	3.3832815977	-2.8359096054
N	0	-0.4680229507	0.5298552721	0.9600613495
C	0	-1.4998063157	-0.4620772479	0.7005979452
C	0	-0.3943577062	1.1872583115	2.1705020739
H	0	-1.8179086984	-0.9357976476	1.6399648513
S	0	-0.4690795688	-1.8012319333	-0.1194280183
C	0	-2.7353437808	0.0338997251	-0.0874298761
H	0	-1.2650212375	0.9400908141	2.8206549473
O	0	0.4892447366	1.9376281484	2.5089552066
O	0	-1.0721329322	-2.3892467628	-1.3277983389
O	0	-0.0027923321	-2.6874123030	0.9585149551
C	0	-2.3725159107	0.5670442213	-1.4834368814
C	0	-3.3656881068	1.1796570611	0.7259167081
C	0	-3.7361907215	-1.1301976886	-0.1905212109
H	0	-1.8960166573	-0.2049284712	-2.1018204468
H	0	-3.2919377571	0.8907721138	-1.9957045699
H	0	-1.7101766879	1.4409737857	-1.4122204473
H	0	-4.2925729760	1.5112622051	0.2331705756
H	0	-3.6277218407	0.8594882579	1.7475468952
H	0	-2.6899701241	2.0449976122	0.7889796487
H	0	-4.0238276891	-1.4933055231	0.8101033489
H	0	-4.6522643997	-0.7912586093	-0.6980181809
H	0	-3.3184487311	-1.9709571896	-0.7599731094
H	0	2.3147021867	0.1669112828	1.9270061886
H	0	2.2018158374	-1.6657364031	1.0153667591
O	0	4.2009057260	-0.8283807222	-1.5300609894
Si	0	4.1537481529	-1.9712524005	-2.8106798894
C	0	2.4381062288	-1.9990239219	-3.5715712169
C	0	5.4073928231	-1.2872307583	-4.0152169723
C	0	4.6724922825	-3.6497972651	-2.1564602892
H	0	2.1091891042	-0.9745386774	-3.8099780813
H	0	2.4669858545	-2.5672941799	-4.5163813054
H	0	1.6738438745	-2.4663853265	-2.9322085936
H	0	5.1120171141	-0.2836779719	-4.3603516197
H	0	6.4007723444	-1.2074900617	-3.5461269941
H	0	5.4975229235	-1.9395588580	-4.8990281148
H	0	5.6492169835	-3.5841447889	-1.6507764957
H	0	3.9472188272	-4.0695204401	-1.4429920015
H	0	4.7709944012	-4.3639291617	-2.9908980260

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H	0	2.5152537091	-0.2605273696	3.5051643699

C	0	2.6484791915	-0.1733297147	2.4233010580
C	0	2.6944526032	1.0466454833	1.8350162277
C	0	2.6577144859	-1.4216153404	1.7086514899
C	0	0.4070383663	0.6041626030	0.1133800040
H	0	2.5930621770	1.9512838797	2.4334245916
C	0	0.7615660801	-0.6842555788	-0.2979691209
C	0	2.5917605652	-1.4458602164	0.3070905074
H	0	2.6341745333	-2.4102697071	-0.1993029812
H	0	1.0089789218	-0.8765107116	-1.3428988822
C	0	0.8575084409	1.7745049253	-0.6277856173
O	0	1.8640563228	1.7857439512	-1.3160716804
O	0	0.0324883867	2.8312854374	-0.4995927631
C	0	0.4650675297	4.0416775256	-1.1124511011
H	0	-0.3079655756	4.7879964017	-0.8932803683
H	0	0.5795543246	3.9141520123	-2.1994007244
H	0	1.4313832540	4.3626165498	-0.6950023415
N	0	-0.6523586163	0.6495749229	1.0649946185
C	0	-1.6276855582	-0.4158162362	0.9091340082
C	0	-0.6662017103	1.4785688576	2.1659265984
H	0	-1.9832116786	-0.7537039841	1.8926145767
S	0	-0.4968850911	-1.8065416669	0.3682262029
C	0	-2.8315851423	-0.1057754177	-0.0119871413
H	0	-1.5424951685	1.2714967598	2.8220940720
O	0	0.1513226075	2.3360157416	2.4048481731
O	0	-1.0167482738	-2.6472234826	-0.7230538470
O	0	-0.0527550867	-2.4552492444	1.6139739414
C	0	-3.7849751483	-1.3129524603	0.0248675730
C	0	-3.5463578301	1.1275092232	0.5701322295
C	0	-2.4055415517	0.2062006067	-1.4559300880
H	0	-3.3040355051	-2.2174250729	-0.3704879923
H	0	-4.6778465710	-1.1030564626	-0.5836628030
H	0	-4.1228442059	-1.5174873730	1.0543277659
H	0	-4.4549714819	1.3357515500	-0.0154984545
H	0	-2.9048804944	2.0197449535	0.5276335339
H	0	-3.8540370827	0.9649602002	1.6159254307
H	0	-1.7569142623	1.0923256786	-1.4938820874
H	0	-3.3011599125	0.4216012920	-2.0592675915
H	0	-1.8846673816	-0.6432566477	-1.9173746702
O	0	2.6101491813	-2.5022479531	2.4668648220
Si	0	2.4056526730	-4.2031322476	2.3374206747
C	0	4.0817035154	-4.8752335441	2.8521702129
H	0	4.8685713361	-4.5674580719	2.1444119495
H	0	4.3627712516	-4.5091428761	3.8524513555
H	0	4.0677940943	-5.9773775538	2.8841695354
C	0	1.0908139960	-4.6465814496	3.5868562972
H	0	0.1224266904	-4.2292564438	3.2773699637
H	0	0.9980016996	-5.7415558200	3.6772576631
H	0	1.3477812124	-4.2417805573	4.5786163800
C	0	1.9875441618	-4.8087662539	0.6106046968
H	0	1.0725991591	-4.3494320451	0.2130381581
H	0	2.8145702647	-4.6484342629	-0.0991418713
H	0	1.8181760007	-5.8977628662	0.6686407126
H	0	3.0690980276	-0.6245692450	-0.2265802398
H	0	2.9005100155	1.1827584921	0.7740409925