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"Synthesis and (co)polymerization of (co)monomers containing different helical shaped units"

Master´s Thesis

Molecular Chemistry and Homogeneous catalysis

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A mis padres,

porque todo lo bueno que hay en mi es gracias a ellos

Gratitudes

To begin I would like to thank professor Stefano Menichetti, for allowed me to perform my master´s thesis in his laboratory, for his confidence, for listening my proposals and for his help during this months.

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I can not forget all the workmates that have made my stay here much easier and they have made me feel at home, thank you Kristian Vasa, Sara Rocchi, Michela Lupi, Sara Piantini, Lorenzo Tofani and Mekhala De Silva.

Synthesis and (co)polymerization of (co)monomers containing different helical shaped units

Resumen:

Los helicenos son unos compuestos únicos debido a su estructura y a las propiedades que derivan de dicha estructura, así como de su disposición electrónica. El término heliceno comprende una gran variedad de compuestos dependiente del esqueleto de la molécula, podemos estudiar diferentes heterohelicenos como thia[n]helicenos, aza[n]helicenos or oxa[n]helicenos. A parte de por su peculiar estructura los helicenos destacan por el gran número de usos que pueden tener: desde ligandos en catálisis asimétrica hasta fármacos capaces de interaccionar con la doble hélice de ADN pasando por sustancias electroactivas útiles en el almacenamiento de información o en la fabricación de baterías. Vinculado con este último punto, recientemente diversos grupos han estudiado la idea de sintetizar polímeros con cadenas laterales que contengan distintos grupos electroactivos para el almacenamiento de energía u otras aplicaciones relacionadas.

En este trabajo de fin de máster se ha buscado obtener distintos monómeros que contengan unidades heteroheliceno los cuales permitan obtener polímeros y copolímeros con ramificaciones laterales que posean diferentes helicenos terminales. Una vez obtenidos dichos polímeros helicénicos se estudiará la formación de los correspondientes radicales.

Para el proceso de polimerización se han utilizado dos reacciones diferentes: una de ellas es la polimerización RAFT, la cual se basa en una polimerización radicalaria controlada. Además de homopolímeros permite obtener copolimeros bloque en nuestro caso un bloque de PEG hidrófilo y otro de polimetacrilato con unidad heliceno hidrófobo. El otro tipo de polimerización realizada es la Ring Opening Metathesis Polymerization, esta reacción se basa en el uso del catalizador de Grubbs, un complejo organometálico de Rutenio que permite polimerizar dobles enlaces presentes en anillos como es el caso del norborneno, el ciclopenteno o el ciclohexeno.

Synthesis and (co)polymerization of (co)monomers containing different helical shaped units

Abstract:

Helicenes are unique compounds due to their structure and the properties that derive from said structure, as well as their electronic arrangement. The term helicene comprises a great variety of compounds dependent on the skeleton of the molecule, we can study different heterohelicenes such as thia[n]helicenes, aza[n]helicenes or oxa[n] helicenes. In addition to its peculiar structure, helicenes are notable for the large number of uses they can have: from ligands in asymmetric catalysis to drugs capable of interacting with the double helix of DNA, passing through electro active substances useful in the storage of information or in manufacturing of batteries. Linked to this last point, recently several groups have studied the idea of synthesizing polymers with side chains containing different electroactive groups for the storage of energy or other related applications.

In this master's thesis, we have sought to obtain different monomers containing heterohelicene units which are able to polymerize and obtain chains with lateral branches that have different terminal helicenes. Once said helicenic polymers were obtained, study the formation of the corresponding radicals.

Two different reactions have been used for the polymerization process: one of them is the RAFT polymerization, which is based on a controlled radical polymerization. In addition to homopolymers it is possible to obtain block copolymers in our case a block of hydrophilic PEG and another of polymethacrylate with hydrophobic helicen. The other type of polymerization carried out is the Ring Opening Metathesis Polymerization, this reaction is based on the use of the Grubbs catalyst, a ruthenium organometallic complex that allows the polymerization of double bonds present in rings such as norbornene, cyclopentene or cyclohexene.

Abbreviations used

ABCN: 1,1'-Azobis(cyclohexanecarbonitrile)

AcOEt: ethyl acetate

ADMET: acyclic diene metathesis

AIBN: 2,2'-azobis(2-metilpropionitrilo)

ATRP: atom transfer radical polymerization

CRP: controlled radical polymerization

CTA: chain transfer agent

DCM: dichlorometane

DFT: density functional theory

DIC: N,N'-Diisopropylcarbodiimide

DMF: N, N´-dimethylformamide

DMAP: 4-Dimethylaminopyridine

DMSO: dimethylsulfoxide

DNA: desoxyribonucleic acid

eV: electronvolt

IR: infrared

NBS: N-bromosuccinimide

NHC: N-heterocyclic carbene

NMR: nuclear magnetic resonance

PEG: polyethylene glycol

RAFT: reversible addition-fragmentation chain transfer

ROMP: ring opening metathesis polymerization

SeAr: aromatic electrophilic substitution

TS: transition state

TLC: thin layer chromatography

UV: ultraviolet

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1. Introduction

1.1 Helicenes: general proprieties.

Helicenes are polyciclic aromatic and heteroaromatic compounds with a non-planar screw-shaped backbone. This non-planar structure provides them an interesting property: chirality. They also show other important proprierties related with their chemical structural features.[1] Carbohelicenes can be described as orto-fused benzenes while heterohelicenes incorporate at least one heteroatom in the structure.

The first helicenes were synthesised by Meisenheimer and Witte[2] in 1903 after that discovery Newman and co-workers described the synthesis and resolution of hexahelicenes. They proposed a differet nomenclature method to simplify the IUPAC nomenclature, introducing the name hexahelicenes or hexa[6]helicene for phenanthro[3,4-c]phenanthrene in 1956.[3] If the aromatic rings are thiophenes, pyrroles, pyridines or furans they are called thia[n]helicenes, aza[n]helicenes or oxa[n]helicenes respectively.[4]

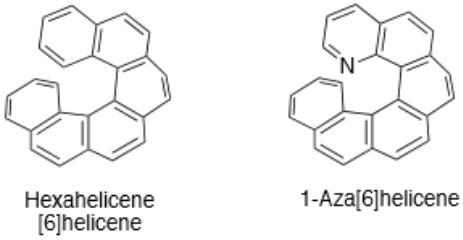

Figure 1.1. Carbohelicen and heterohelicen

The most important characteristic of the helicenes is their chirality, indeed because of the steric hindrance of terminal rings, helicenes show a helical structure where the skeleton can wind in opposite direction forming a pair of enantiomers. In according to the rule suggested by Cahn, Ingold and Prelog in 1966 left handed helix is denoted by "minus" (M); while helicenes denoted by "plus" (P) are right hended.[5]

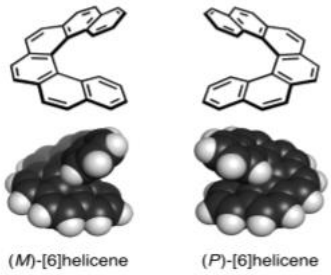

Figure 1.2. Left handed (M) and right handed (P) helix

[1] Chen, C.F.; Shen, Y. *Chem. Rev*. 2012, **112**, 1463.
[2] Meisenheimer, J.; Witte, K. Chem. Ber. 1903, **36**, 4153
[3] Lednicer, D. J.; Newman, M. S. *Am. Chem. Soc*. 1956, **78**, 4765.
[4] Martin, R. H. Angew. *Chem., Int. Ed. Engl*. 1974, **13**, 649
[5] Cahn, R.S.; Ingold, C.; Prelog, V. Angew. *Chem. Int. Ed*. 1966, **5**, 385.

Although helicenes share common propierties their specific values can change from one to other for example the torsion of the helical backbone increases from the structures with four benzene rings, [4]helicene (26.7º) to the six aromatic rings [6]helicene (58.5º) and decrease when the structure extends further. Up to now we only have spoken about aromatic rings but the presence of substituents on the terminal rings modify the distorsion of the helix, enlarging the interplanar angle.[6]

The presence of substituents also has impact in other property: the racemization barrier, to understand this process two different transition states have been sugested (Figure 3). As we can see in the Figure 1.3 one transition state has a planar structure with C2v simmetry however the other transition state is not planar becasue the rings bent to the same side with Cs symmetry. If we think to unsubstituted pentahelicene it can be transformed to the Cs-TS with the same probability without taking into account if is M or P configuration. Also we can confirm that the barrier of racemization[7] increases with the size of the helicen for this reason we can isolate the two enantiomers of [6]helicene but it is imposible for [4]carbohelicenes.

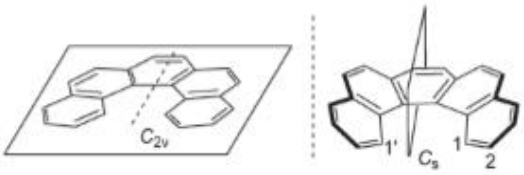

Figure 1.3. C2v and Cs symmetry for transition states of helicene racemization

The presence of substituents in steric hindered position, for example in 1,1´-, can greatly increase the racemization energy. [8]

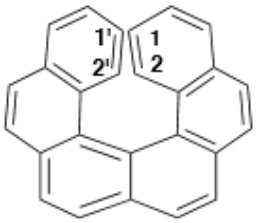

Figure 1.4. Steric hindered positions

Helicenes have an unique π-conjugation system because of their non planar skeleton like the other polycyclic aromatic compounds. This fact explains some of the physico-chemical features for example their high chiro-optical propierties.[9] Their unique structure determinates a magnetic coupling that explains how the largest helicenes suffer an increase in the aromaticity of the terminal rings. An analogous correlation is

[6] Laarhoven, W. H.; Prinsen, W. J. C. Top Curr. *Chem*. 1984, **125**, 63
[7] Grimme, S.; Peyerimhoff, S. D. *Chem. Phys*. 1996, **204**, 411
[8] Martin, R. H.; Marchant, M. J.; *Tetrahedron Lett*. 1972, **13**, 3707.
[9] Rajca, A.; Pink, M.; Xiao, S.; Miyasaka, M.; Rajca, S.; Das, K.; Plessel, K. *J. Org. Chem*. 2009, **74**, 7504

well established for achiral π-systems for which optical properties are significantly enhanced with increased electron delocalization.[10] Recient studies of density functional teory (DFT) in gas phase have demonstrated that conjugated systems thia[n]helicenes with alternating thiophene and benzene rings posses the lowest, Eg ≈ 2.4 eV, HOMO-LUMO gap conversely cross-conjugated carbo-sulfur [n]helicenes posses the highest band gap Eg ≈ 3.5 eV.[11]

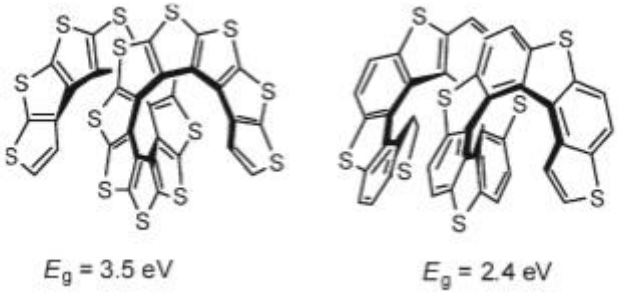

Figure 1.5. Band gap

1.2 Applications of helicenes

The main important applications of helicenes derive from their special properties (structure, optical and spectral), for them they are used in various fields. For example, one of the most useful applications of helicenes is in asymmetric synthesis, they can be a very good chiral ligands in this field (P,P)-HELOL (Figure 1.6) stand out with an important role in the reduction of aldehydes to alcohols giving enantiopure alcohols with a high yield and enantioselectivity.[12]

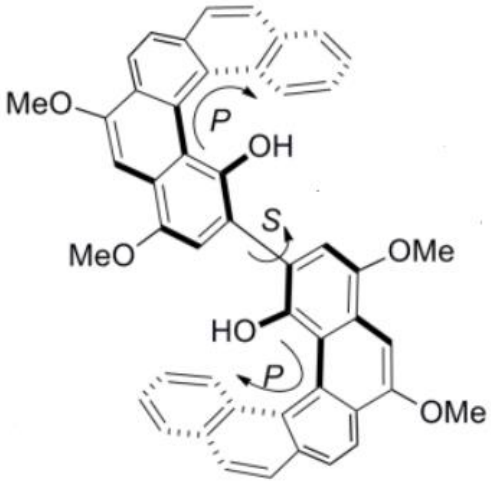

Figure 1.6 Helicen Ligand

[10] Klessinger, M.; Michl, J. Excited States and Photochemistry of Organic Molecules; VCH: New York, 1995; Chapter 2, pp 63-137.
[11] Rajca, A.; Pink, M.; Xiao, S.; Miyasaka, M.; Rajca, S.; Das, K.; Plessel, K. *J. Org. Chem*. 2009, **74**, 7504
[12] Bao, J. M.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc*. 1993, **115**, 3814.

Regarding to the optically pure helicenes they are a fantastic ligand for enantioselective reactions, Martin and co-workers have used a [7]helicene as a chiral reagent in several diasteroselective reactions incluiding epoxidation of an olefin, hydrogenation…

The most promising application is the production of *dye materials* using the magnetic, optical and conductive propierties of helicenes to convert solar energy in electric energy. In 1991 Grätzel and O'Regan reported the first DSSCs, *dye-sensitized solar cells.*[13] DSSCs are highly conjugated system, called donor-acceptor conjugated dyes (D-π-A) that generally consist of photoactive compounds linked to a layer of TiO_2. Harima and co-workers synthesized a series of D-π-A using a heterohelicene as building block. The π-π interaction between π-conjugated systems is responsible for the performance of the cell, thus the helicene plays a peculiar role in the production of dye material. A helicene with ciano group as electron acceptor and a carboxyl group as a linking group has built to evaluate electron interaction between the surface and the dye and enhance the performance of the cell.

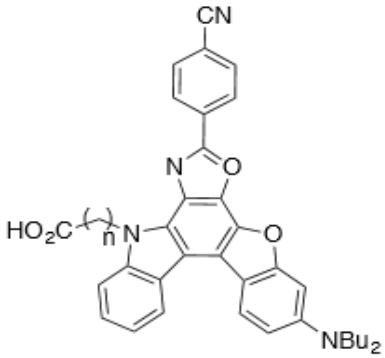

Figure 1.7 Helicene for DSSCs

Helicenes also can be used with biological purposes owing to their winded structure are capable to interact with the DNA helix-shape. Recently a great number of molecules are used in medical diagnostic and therapy against many diseases for example cancer, one of the most powerful drug is the cis platino (Figure 1.8). Helicenes have their analogous in our case the windend structure favor the interaction with the DNA.[14]

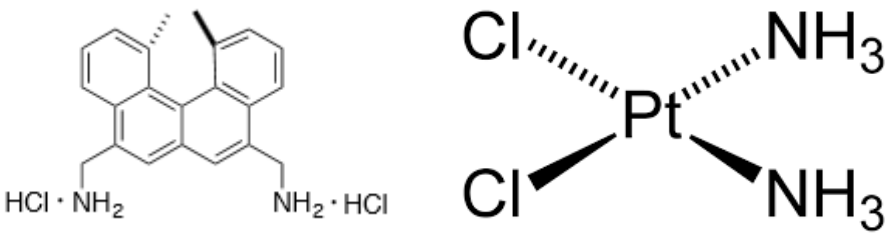

Figure 1.8 cisplatino (right) and its analogous helicen (left)

[13] Katz,T.J.; Schulman,J. *J. Am. Chem. Soc*. 1964, **86**, 3169

[14] Honzawa, S.; Okubo, H.; Anzai, S.; Yamaguchi, M.; Tsumoto, K.; Kumagai, I. Bioorg. & Med. *Chem*. 2002, **10**, 3213-3218

The presence of helicenes in the biological applications it is not just about the interaction with the DNA, nowadays there are studies focus in the demostrating that a (M)-thia[7]helicene (Figure 10) is able to bind quadruplex super helical structure of telomeres, in contrast to its enantiomer.[15] Moreover this bind causes the inhibition of telomerase, a ribonucleoprotein involved in various tumor processes, for these reasons helicenes have a high potential in biological and medical applications.

1.3 Redox polymers for new materials

Nowadays the chemistry of polymers has experienced a great interest by many reasons: their mechanical properties (films are prepared easily), great flexibility in the molecular design… One of the new materials prepare with polymers is electro-active polymers with redox active pendant groups such as triphenylamine, carbazole and nitroxide.[16] These redox active materials has renewed attention in energy-storage and opto/electro applications,[17] among the great variety of pendant groups the phenothiazine unit has been proposed as a key constituent of this polymers due to its electronic characteristics. Phenothizaine can be oxidized and leads to the formation of stable radical cation compounds and their π-π stacking results in enhanced electric conductivity,[18] moreover both compounds are very stable more than 50 hours.

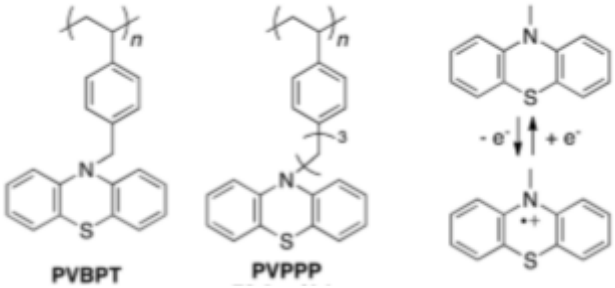

Figure 1.9 Phenothiazine polymers and radical[19]

Regarding to the uses of polyphenothiazine compounds it has been demostrated that a thin film of poly-3-vinylbenzylphenothiazine can be used as a bias-responsive bistable media for data storage.[20] Such long stability of radical cations can be used in redox process supported in presence of electrolytes, Nishide[21] and co workers have checked that the phenothiazine polymer its appropiate for rechargeable battery in this field phenothiazine is a promising candidate because it has a more positive oxidation potential which leads to higher cell voltage.

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[15] Shinohara, K.; Sannohe, Y.; Kaieda, S.; Tanaka, K.; Osuga, H.; Tahara, H.; Xu, Y.; Kawase, T.; Bando, T.; Sugiyama, H. *J. Am. Chem. Soc*. 2010, **132**, 3778-3782

[16] Ali A. G.; Takeo, S.; Hiroyuki, O.; Rudiger, B.; *RSC Adv*., 2015,**5**, 22947–22950

[17] H. Nishide and K. Oyaizu, *Science*, 2008, **319**, 737.

[18] Z. Zhou, A. W. Franz, M. Hartmann, A. Seifert, T. J. J. Muller and W. R. Thiel, *Chem, Mater.,* 2008, **20**, 4986

[19] Ali A. G.; Takeo, S.; Hiroyuki, O.; Rudiger, B.; *RSC Adv*., 2015,**5**, 22947–22950

[20] A. A. Golriz, T. Kaule, J. Heller, M. B. Untch*, Nanoscale*, 2011, **3,** 5049

[21] T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu and H. Nishide, *Adv. Mate. 2011,* **23**, 751

Attending to the polymerization ways, controlled free radical polymerizations (CRPs) are one of the most recent innovations in the polymers chemistry being useful to obtain functionalized polymers with well defined structure and architecture also has the advantage to know the degree of polymerization.

There are two techniques of CRPs which stand out of the rest: one is the ATRP (atom transfer radical polymerization) is one of the most used and operates via a redox equilibrium process mediated by a ligated metal catalyst (Cu[I], Fe[II], Ru[II]). An important limitation of ATRP is metal contamination and ambitious solution for this problem would be a metal-free catalyst system for example with an organic photocatalyst.[22]

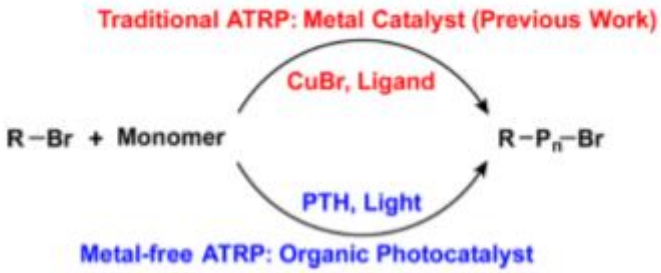


Figure 1.10 Traditional ATRP and Metal free ATRP (ref. 22)

The other important polymerization is RAFT polymerization (Reversible Addition–Fragmentation chain Transfer). It is a radical controlled polymerization discovered by Rizzardo, Moad y Thang[23] it can be applied in a great among of functionalized monomers for this reaction its necessary a substance which generates a great amount of radicals in the solution and a chain transfer.

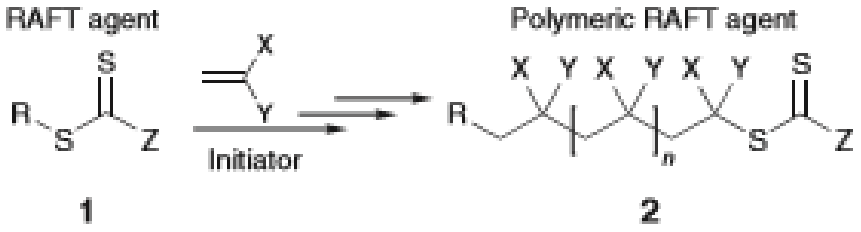


Figure 1.11 Overall reaction in RAFT polymerization[24]

In the field of polymerization reactions there is also non-radical studies, there have been described several polymerizations using metathesis reaction via catalysts with carbenes, *Ring Opening Metathesis Polymerization (ROMP)* and *Polymerization by Acyclic Metathesis of Dienes (ADMET).* In both cases the catalyst is the key of the reaction, a large number of polymerizations have been described using the Grubbs catalyst,[25] it is

[22] Nicolas J. Treat,† Hazel Sprafke,† John W. Kramer,‖ Paul G. Clark,‖ Bryan E. Barton,‖ Javier Read de Alaniz, § Brett P. Fors,*,‡ and Craig J. Hawker*J. Am. Chem. Soc*. 2014, **136**, 16096−16101
[23] G. Moad, E. Rizzardo, S. H. Thang, Aust. *J. Chem*. 2005, **58**, 379-410
[24] G. Moad, E. Rizzardo, S. H. Thang, Aust. *J. Chem*. 2005, **58**, 379-410
[25] R. H. Grubbs, *Tetrahedron* 2004, **60**, 7171

about an organometallic compound with a heterocyclic carbene (NHC). The development of these grubbs catalysts is due to the facility to be modified their ligands, initially they had phospine ligands but the substitution for NHC carbenes demonstrated that the time of the reaction was reduced.[26] Typically heterocyclic precursors are easily accessible from commercial reagents many of the existing carbenes are stable enough to be isolated; however, their in situ generation and subsequent reaction with the desired metal source is more straightforward and, consequently, more popular. The most common methods for the generation of free heterocyclic carbene ligands is the deprotonation of imidazolium or imidazolinium salts with a strong base, such as potassium hexamethyldisilazane (KHMDS) or potassium tert-butoxide (KOt-Bu), afford the corresponding free NHCs.[27]

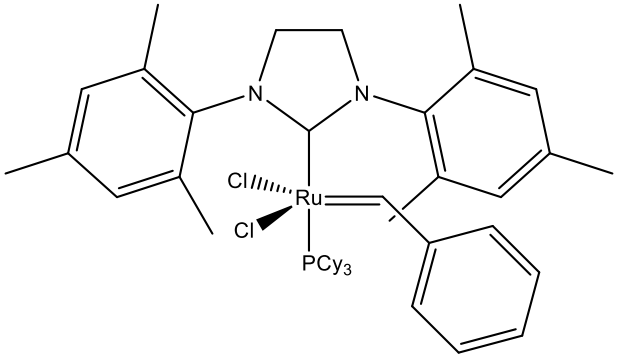


Figure 1.12 Grubbs catalyst 2 Generation

2. Objectives

The main objectives of this master final work were: i) the synthesis of polymers and copolymers containing different helicene units, ii) to study the formation of radical cations both in polymers and monomers; iii) to study the redox and spectropic propierties of radical cations both in polymers and monomers. I also analyzed polymerization methods and helicenes functionalizations. To obtain the polymers, I developped the following specific tasks:

- Synthesis of different helicene units derivates from a triarylamine which allows to obtain monomers and their corresponding radical cations, via different reactions.

[26] M. S. Sanford, J. A. Love, R. H. Grubbs*, J. Am. Chem. Soc*. 2001, **123**, 6543
[27] G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev*. 2010**, 110**, 1746–1787

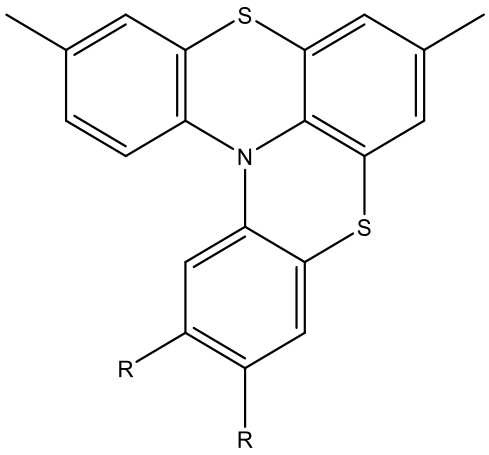


Figure 2.1. General Helicene structure

- Synthesis of a methacrylate monomer derived from helicene. This monomer appears as a perfect precursor to obtain hydrophobic polymers via doble bond reaction, for example using RAFT polimerization.

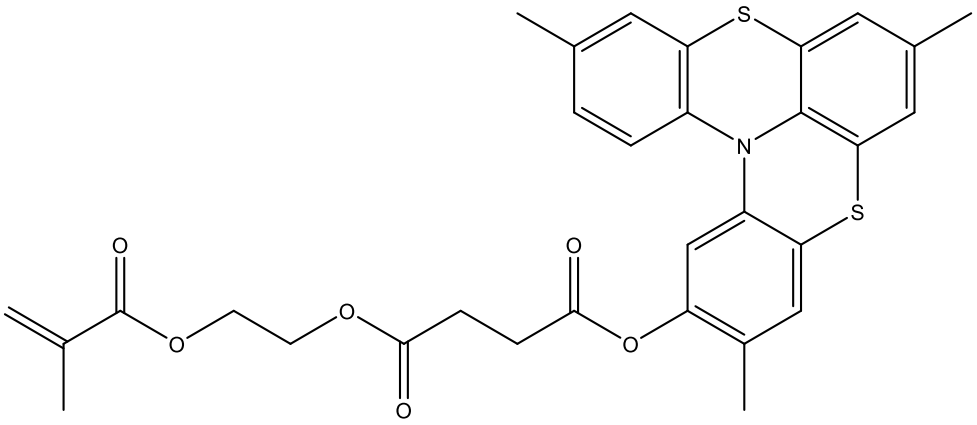


Figure 2.2 Hydrophobic monomer with helicene unit

- Functionalization of the helicene unit with norborneno mojety (via Heck reaction) to get a suitable monomer to be used in a ROMP (ring opening metathesis polymerization) process:

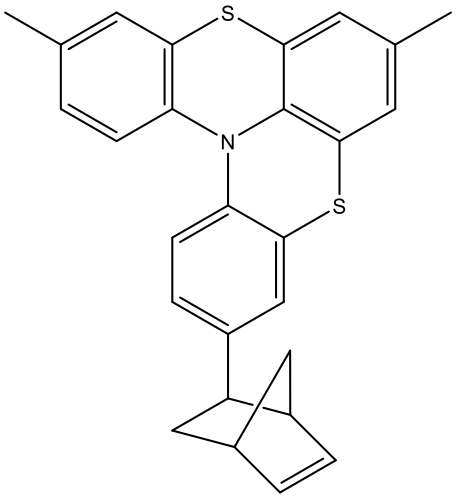


Figure 2.3 Monomer for ROMP with helicene unit

- Studying the formation of different polymers and copolymers with several polymerization procedures for example RAFT or ROMP.

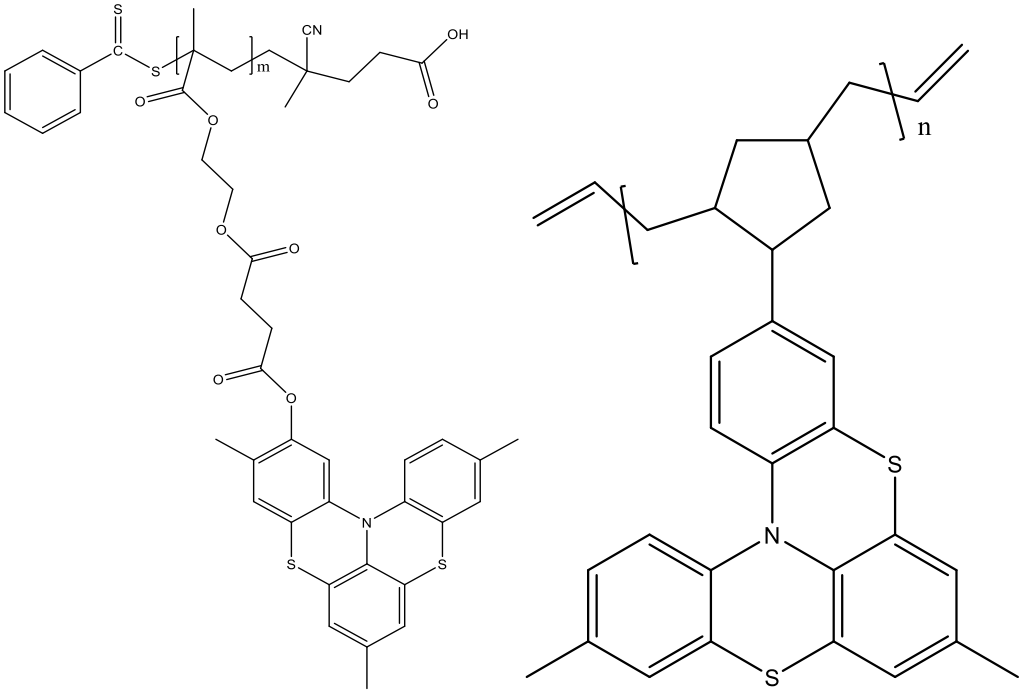


Figure 2.4 Polymer of norbornene (right) and polymer of metacrilate (left)

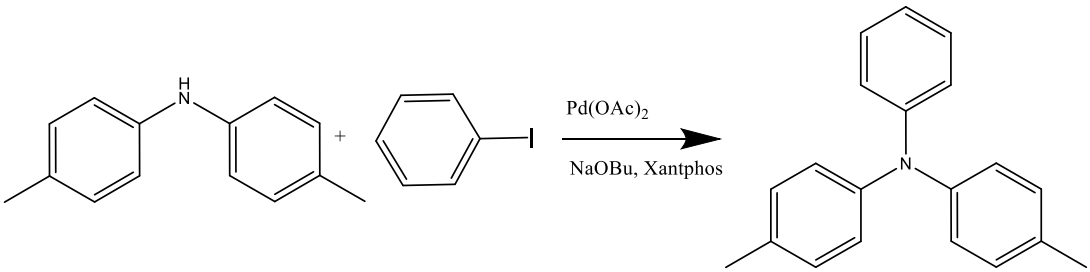
- Preparation and caracterization of radical cations: the main objective of this work is to verify the formation of stable radical cations both in the monomers and (co)polymers and to study these redox processes.

3. Results and discussion

In this chapter, the steps related to the synthesis of the different molecular and macromolecular helicenes and radical cations as well as the consideration on their structural features and properties will be discussed.

3.1 Bromo-Helicene

To begin this work I tried to obtain a helicene which could be easily functionalized for example with the insertion of an olefinic mojety, perhaps via Heck reaction, to prepare a suitable (co)monomer. So, to start with the synthesis I run a Buchwald-Hartwig reaction to get a triarylamine. In particular, I reacted di-p-tolaylamine (in a bit excess), iodobenzene, Xantphos, sodium tert-butoxide and the catalyst: Pd(OAc)2. The reaction took place in dry toluene at 100ºC during 18 hours after that time I checked the formation of the triarylamine by thin layer chromatography also I saw in the TLC the excess of iodotoluene. The product was purified by flash chromatography then was characterized by NMR.



Reaction 1 Formation of triarylamine

The Buchwald-Hartwig is an amination reaction catalyzed by Pd[28], for this reaction is also necessary the use of a base and a phosphine ligand their function is explained through the mecanism of the reaction:

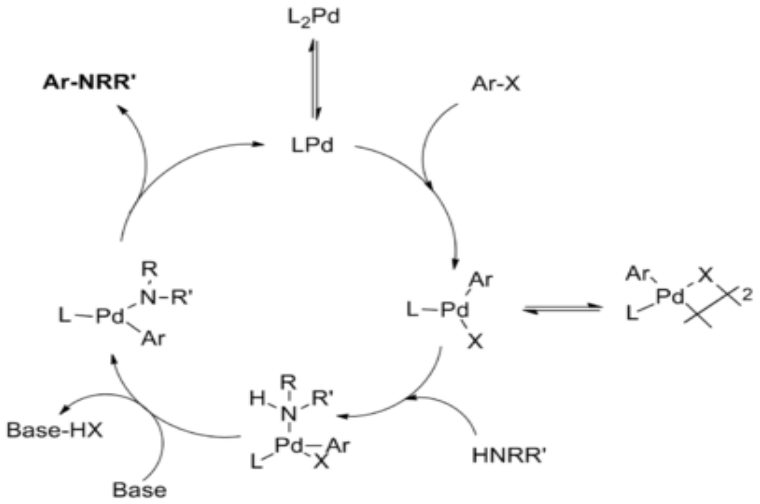


Figure 3.1 Mecanism of the Bochwald-Hartwig reaction

The reaction begins with the formation of a specie of Palladium (0) then this complex can be oxidate by the aryl halide resulting a specie of Pd (II) by oxidative adittion, after that the amine can attack the metal due to the pair of electrons of the N. In that moment the base desprotonates the amine followed by a reductive elimination generating the desired product (Ar-NRR´) and regenerating the catalyst. The Pd(II) catalyst is reduced in situ by the phosphine (Figure 3.2), the precursors of Pd(0) are more inestable and sometimes due to the high temperature of this reactions (around 100º C) is formed black palladium. If we attend to the phosphine ligand it has been demonstrated that a bidentate ligand with a small bite angle accelerates the rate of the reaction[29] in general phosphines are good ligands because they are electronically rich ligands.

[28] Y. Kanazawa et al. / *Tetrahedron* **71** (2015) 1395-1402
[29] Espinet, Echavarren Angew. *Chem*. 2004, **43**, 4704

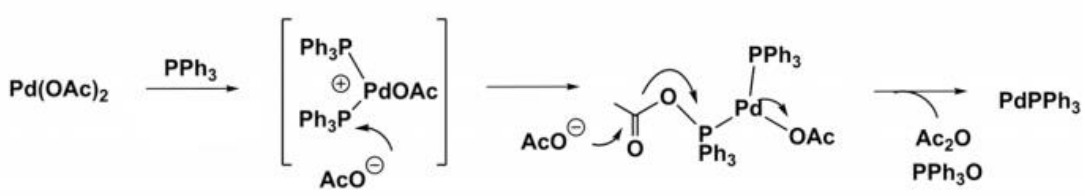
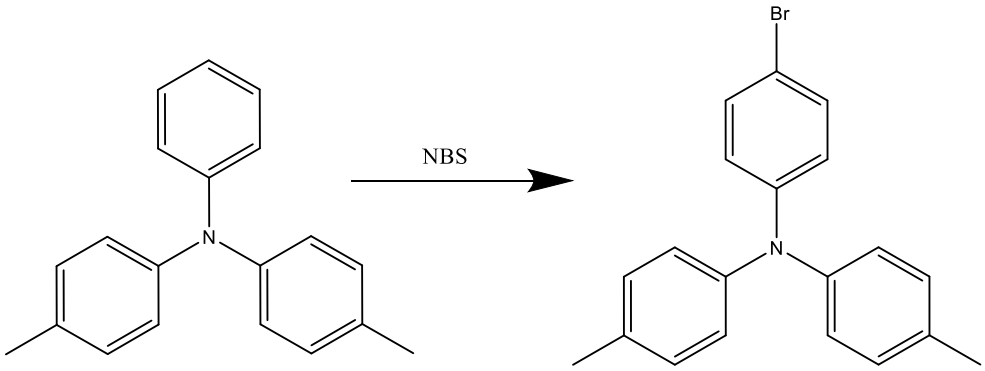


Figure 3.2 Formation of the catalyst

For the introduction of a bromine atom in the triarylamine skeleton a reaction with N-bromosuccinimide was carried out.[30] The reaction took place in dry DCM at room temperature for two hours:



Reaction 2. Formation of bromo-triarylamine

The N-bromosuccinimide is a source of bromo ideal for S_EAr reaction. The substitution in the benzene ring by the NArAr´ directs the reaction to para and orto positions (Figure 3.3), as we can see the amine group is an excellent donor group by resonance that is the reason of its strong activation. Regarding the Figure 3.3 there is a negative charge in para and orto which attracts the bromo although the bromo has a great electronegativity in the molecule of NBS the bromo has a partially positive charge due to the great attraction of electronic density made by the nitrogen and the ring. In my case I obtained only the para position probably due to the big size of the bromo, after the reaction the product was characterized by NMR.

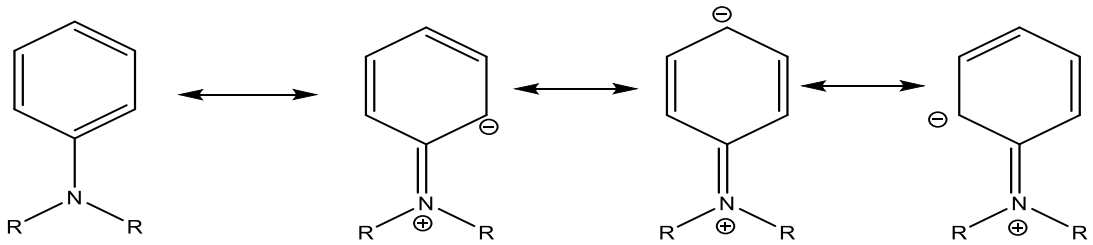


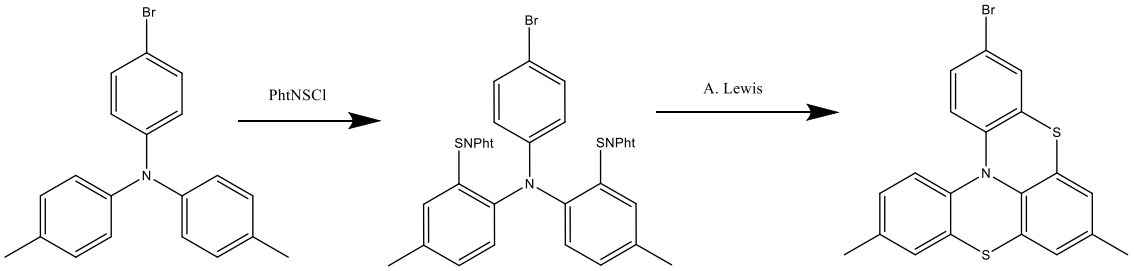
Figure 3.3 EDG effect in triarylamine

In the past, several different methods to obtain heterehelicenes have been studied. Our research group recently described a method to synthesized thia-bridge triarylamine heterohelicenes through a one-pot procedure,[31] which includes four consecutive inter-

[30] H.-Y. Wang et al. / *Dyes and Pigments*, 2011, **88**, 358-365

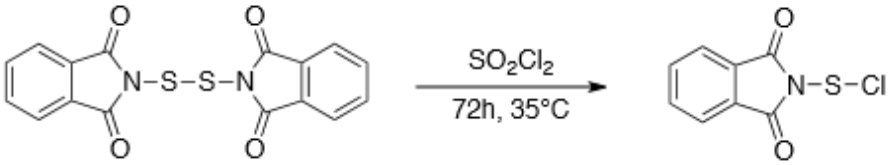
[31] Lamanna, G.; Faggi, C.; Gasparrini, F.; Ciogli, A.; Villani, C.; Stephens, P. L.; Devlin, F. L.; Menichetti*, S. Chem. Eur. J*. 2008, **14**, 5747

and intramolecular electrophilic regioselective aromatic sulfenylation of a triarylamine. I used this procedure to obtain the bromo-thiahelicen:



Reaction 3 Formation of helicene

Previously to this reaction it is necessary the synthesis of the ftalimidesulfenyl chloride ($PhtNSCl$) which provides us the sulfur atoms in the final compounds. It is a yellow solid which can be conserved under nytrogen atmosphere in the fridge for several weeks. It is prepared by chlorination of the corresponding disulfide with sulfuryl chloride (SO_2Cl_2). This reagent has the particular characteristic of a very electrophilic S-Cl bond and a less electrophilic N-S bond. In any case the positive charge on the sulfur atom is quite high.



Reaction 4 Formation of ftalimidesulfenyl chloride

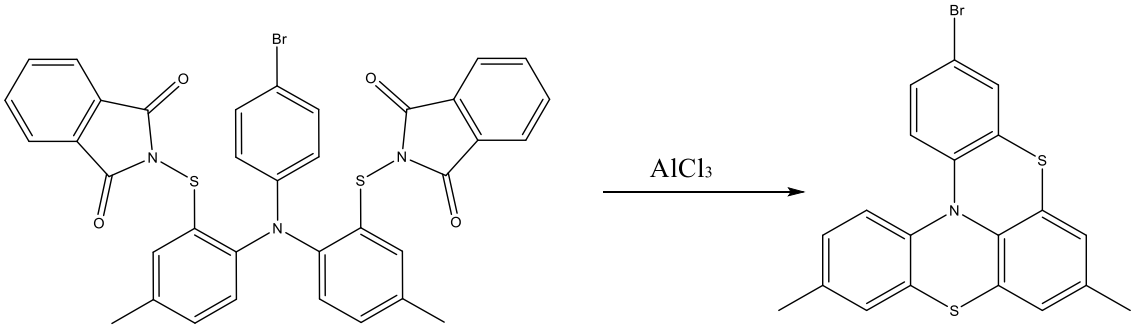
The electrophile character of the sulfur atom and the ability of the Phthalimide residue to act as a leaving group are the main features of this reactive and they have convert it in a fantastic reactive to make S_EAr reactions.

In my case the reaction was followed by TLC and two products were isolated after the sulfenylation, the mono and the bis sulfenilated derivate, both were characterized by NMR. I tried to improve the yield of the reaction adding a base to avoid the protonation of the amine. The base should be a non-nucleophilic one, because it could react with the sulfur atom instead. So, I added 4-methyl-2,6-ditercbutylpyridine, which is very impeded by the two tercbutyl groups, but it was not effective, so it did not desprotonate the amine and I did not get anything of the bisulfenilated product.

Then I tried to sulfenilated the monosulfenilated product using the same conditions of the sulfenilation of the triarylamine, but this reaction is not useful because I did not obtain anything of bisulfenilated product.

For the synthesis of the helicen it was made a reaction with the bisulfenilated product and $AlCl_3$ in dry DCM during four hours at room temperature (Reaction 5). In the TLC we can see two plots: the helicen and the ftalimide liberated after the cyclization so they

are separated by flash chromatography column. Then the helicene was characterized by the usual techniques.



Reaction 5. Intramolecular cyclization

This reaction consists in a double intramolecular S_EAr, the atom of sulfur has a very electrophilic character for the presence of two aromatic rings moreover the presence of a Lewis acid[32] increases its electrophilia so the cyclization in orto position lead to the formation of bromo-helicene and it occurs with good yield.

3.2 Mono-Norbornene-Helicene

Once I obtained the bromo-helicene the next step was its functionalization to get a monomer easily to polymerize. I performed a Heck reaction with the bromo-helicene, norbornadiene, trifenylphosphine, palladium (II) acetate and ammonium formate in dry DMF during 24 hours at 90ºC. The Heck reaction has four important steps, regarding to the Figure 3.5 the first one (A) is the oxidative addition of the aryl bromide, in our case the bromo-helicene, generating a specie of palladium (II) Then the double bond (norbornadiene) it is approximated to the coordination sphere (B) forming a π-complex when the interaction happens between the double bond and the palladium, the double bond is inserted (syn insertion) in the bond Pd-Aryl. Finally, we obtain the final product with a reductive elimination (β-elimination) (D)

[32] G. Lamanna, S. Menichetti, Adv. Synth. Catal. 2007, 349, 2188– 2194; b) G. Capozzi, F. de Sio, S. Menichetti, C. Nativi, P. L. Pacini, Synthesis 1994, 521–525

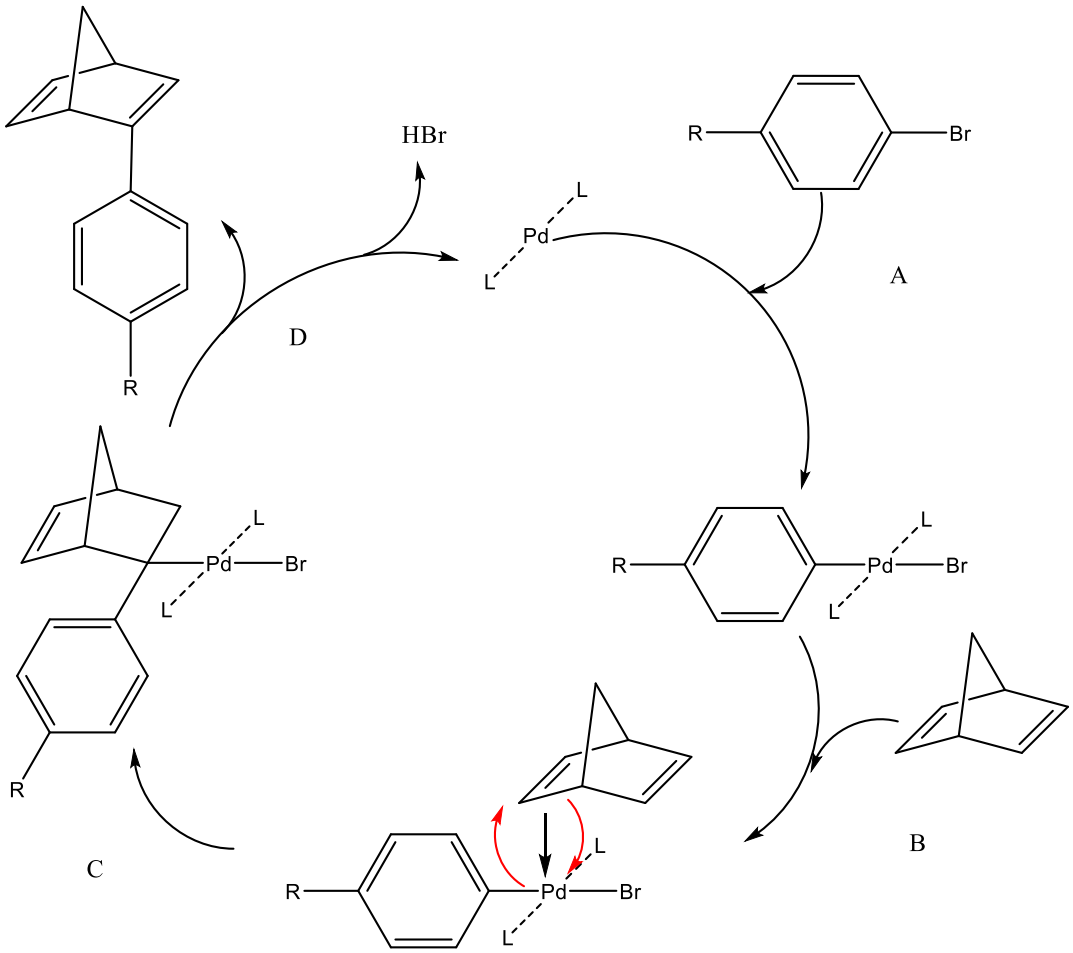
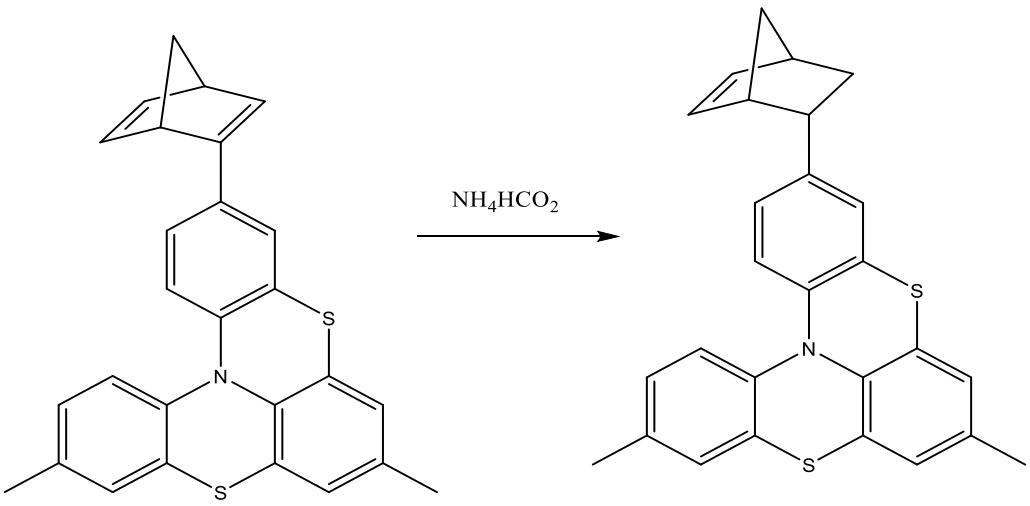


Figure 3.4 Heck Mecanism

In our reaction also is necessary the addition of ammonium formate to reduce the double bond which is trisubstituted (Reaction 6). As it happened in the Bochwald-Hartwig reaction the catalyst is generated in the reaction medium as from the precursor of Pd(II) and the triphenylphosphine.

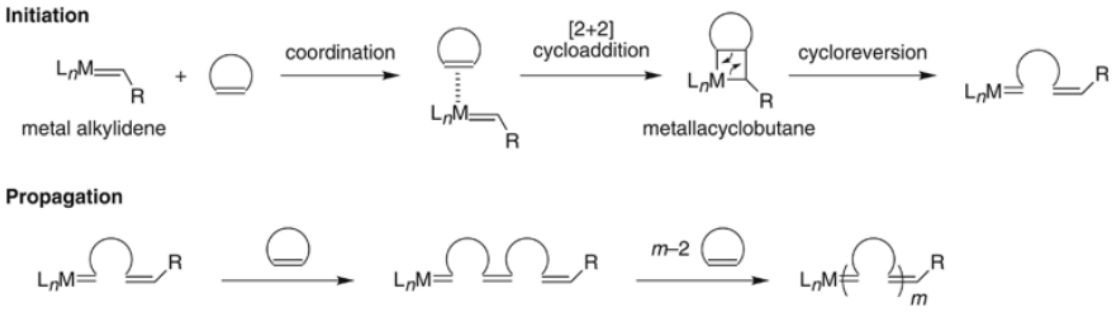


Reaction 6. Double bond reduction

To finish with the discussion of this reaction is remarkable to say that after the reaction three products were obtained: the starting material, the product searched and a subproduct generated in the mecanism. This mix of products lead to a regular yield, 20%, that could be improved searching a better solvent since it was a problem disolved the starting material in DMF and may be changing the conditions (temperature, time, ligand…), we could avoid the formation of subproducts.

3.3 PNorbornene-Helicene

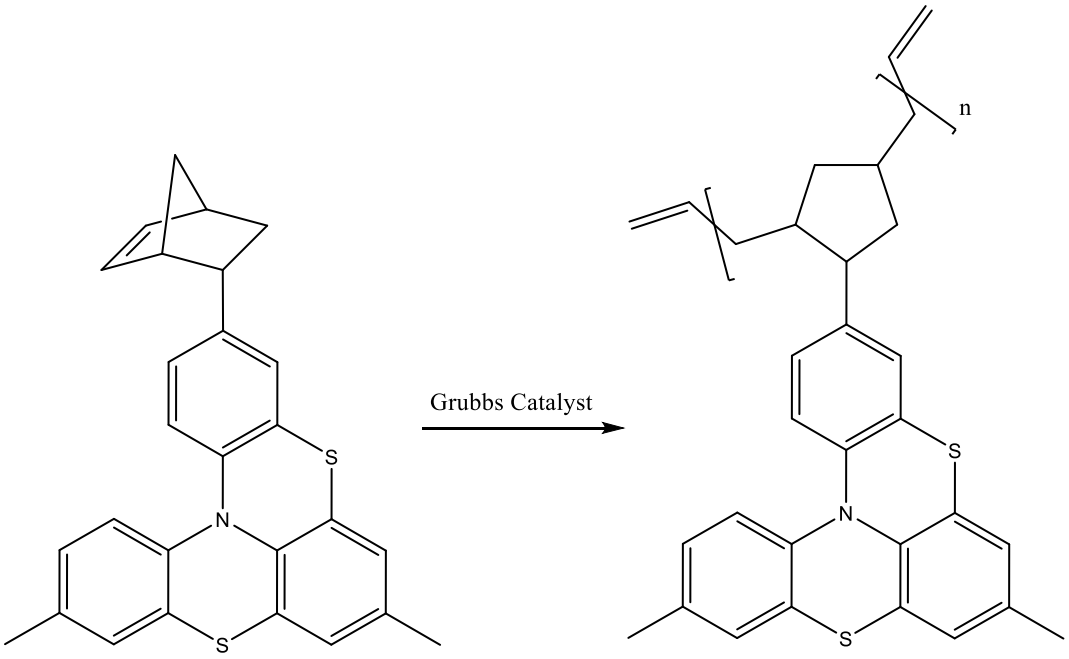
The polymerization proposed for this monomer was a Ring Opening Metathesis Polymerization (ROMP), the reactions of metathesis are catalyzed by different metal complexes and have sundry mechanisms. ROMP has been described[3334] for monomers which contain norbornene because its high tension in their structure, ROMP is more efective for norbornene than for cyclopentene and more efective for cyclopentene than for cyclohexene. Attending to the catalyst used in this kind of reactions, the most efficient catalyst are complexes of ruthenium and molybdenum, these last ones have the desadvantage of being sensitive to functional groups in the substrates. The deep studies in the mechanism have permitted a great develop in the knowledge of the paper of the ligands in the catalyst, for example in the case of Grubbs catalyst (catalyst of Ru) is necessary that the active species has two coordinating vacancies[35] since one is necessary for the coordination of the olefin and the second to avoid the cycloreversion of the metalacycle because this would regenerate the starting products.
The Grubbs catalyst have been studied and improved, for example the first modification from the Grubbs catalyst was change a phosphine ligand for a N-heterocyclic carbene ligand (NHC).[36] This changed was made with the idea of bring on easily the descoordination of the phosphine in trans position to the NHC (because the NHC has a bigger trans effect than a phosphine) however the initation step was slower than the phosphine complex but surprisingly the propagation step was faster and the global speed raised with the change of a phosphine for a NHC.
The proposed mechanism for the ROMP is the following: in the initiation step the olefin is approaching to the metal complex to coordinate the metal alkylidene immediately a cycloaddition 2+2 happens to form a four-center cycle (metallacyclobutane) the presence of a second vacance allows the formation of the propagatin species. In the propagation this step is repeated m times until the monomer is finished either other substance in the solution induces the enf of the polymerization.



[33] Y. Nishihara, Y. Inoue, Y. Nakayama, T. Shiono and K. Takagi. *Macromolecules* 2006, **39**, 7458-7460
[34] S. T. Nguyen and R. H. Grubbs. *J. Am. Chem. SOC*. 1993,**115**, 9858-9859
[35] R. Castarlenas. (2011). *Rev. Real Academia de Ciencias*. Zaragoza. **66**: 7-29
[36] M. S. Sanford, J. A. Love, R. H. Grubbs, J. Am. Chem. Soc. 2001, 123, 6543

Figure 3.5 ROMP mechanism

To make the ROMP it was disolved the monomer in dry DCM and it was added the Grubbs catalyst (second generation) the reaction took place during 24 hours at room temperature.



Reaction 7. ROMP of MNorbornene-Helicen

Unfortunately, the polymer could not be characterized due to its low solubility in all solvents, a goal in the future could be the synthesis of copolymers which contains this monomer and other block, may be the presence of other polymer in the same chain allows to dissolve all chain.[37]

3.4 Study of radical cations

They were prepared the radical cation of the bromo-helicen and the Mono-Norbornene-helicene with the same procedure: over the solution of the helicen in dry DCM it was added $AgSbF_6$, after the addition a great change in the color of the solution occured. The radical cation is a solid that can be isolated for a long time in solid state. Then I prepared a solution of the Bromo-Helicene, MNorbornene-Helicen and the radical cation of the MNorbornene-Helicen all of them were 0.02 M in dry DCM and I measured the absorbance for all wavelenghts (Figure 3.7). The curves of the radical cations present a maximum of absorbance around 575 cm^{-1} this fact has its origin in the loss of an

[37] I. Trito, L. Boggioni, J. C. Jansen, K. Thorshaug, M. C. Sacchi and D. R. Ferro, *Macromolecules*, **2002**, *35* (3), pp 616–623

electron which is taken by the $AgSbF_6$. This lack of electron produces an absorption in the visible spectrum because the different between the HOMO-LUMO gap now is shorter than in the normal molecule. Regarding to the electron our molecule has a great electronity density due to the benzene rings but the most likely the electron will proceed from the pair of electrons of the nitrogen atom and owing to that electronic offshoring the radical cations are very stable. We can also talk about the color of the solution, the color we see is the mix of all wavelengths except the wavelength that the radical cation absorbs.

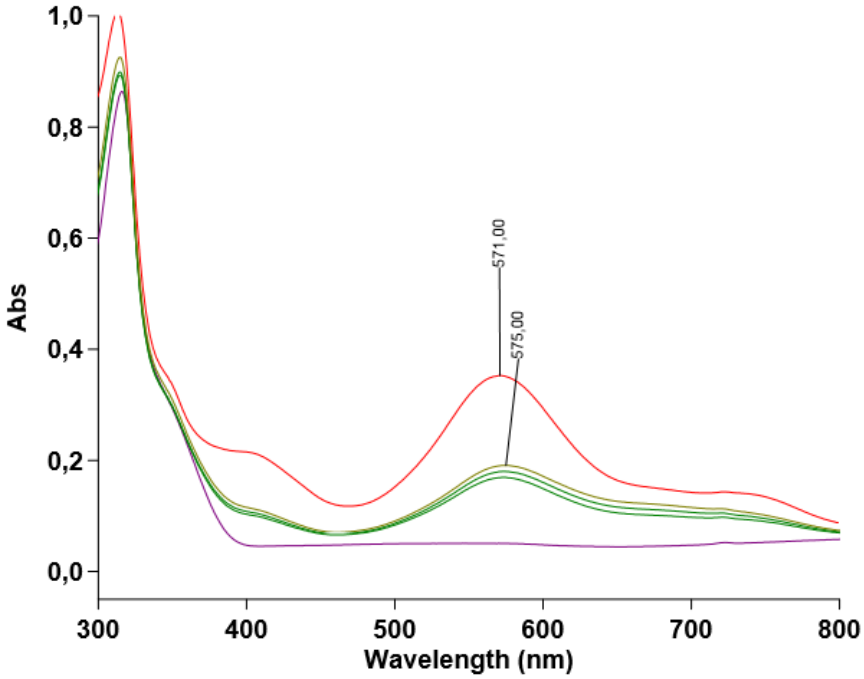
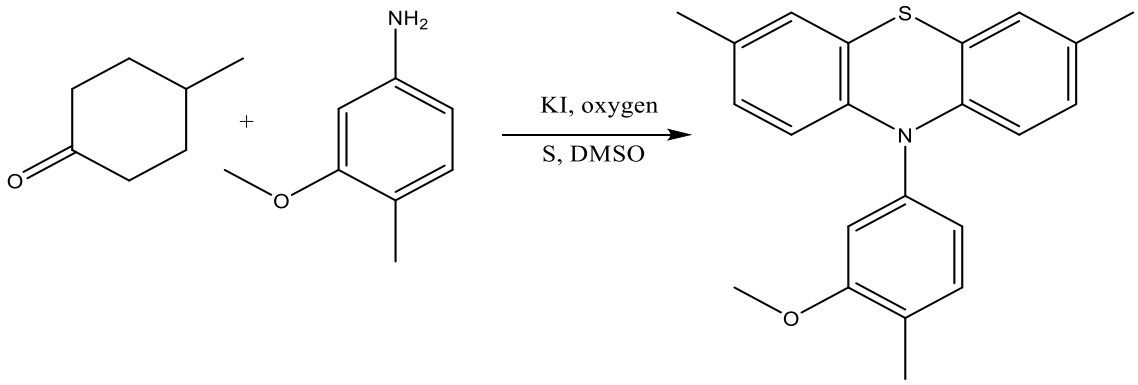


Figure 3.6 Spectrum of helicene (purple), radical helicene (green) and radical Mnorbornene-helicen (red)

3.5 Methoxy Helicene

To begin this synthesis was proposed a one plot reaction to obtain a N-substituted phenothiazine under transition metal free conditions,[38] for this reaction was used 4-methylcyclohexanone, 3-metoxi-4-methylanyline, potassium iodide, dimethylsulfoxide and sulfur all were disolved in dry toluene under an oxygen atmosphere at 150ºC.

[38] Jinjin C., Guozheng L., Yanjun X., Yunfeng L., Fuhong X.,and Guo-Jun D. *Org. Lett*. 2015, **17**, 5870−5873



Reaction 8. One plot reaction

The reaction was followed by TLC where I could see three products then I made a flash chromatography column to isolate them. Surprisingly I isolated the diarylamine which supposedly did not form in the mecanism of the reaction,[39] attending to the Figure 3.6 we can see that there are only two signals corresponding to methyls with an integration of three protons each one instead of three signals of three protons. So, we can affirm that the diarylamine is one of the intermediates of the reaction.

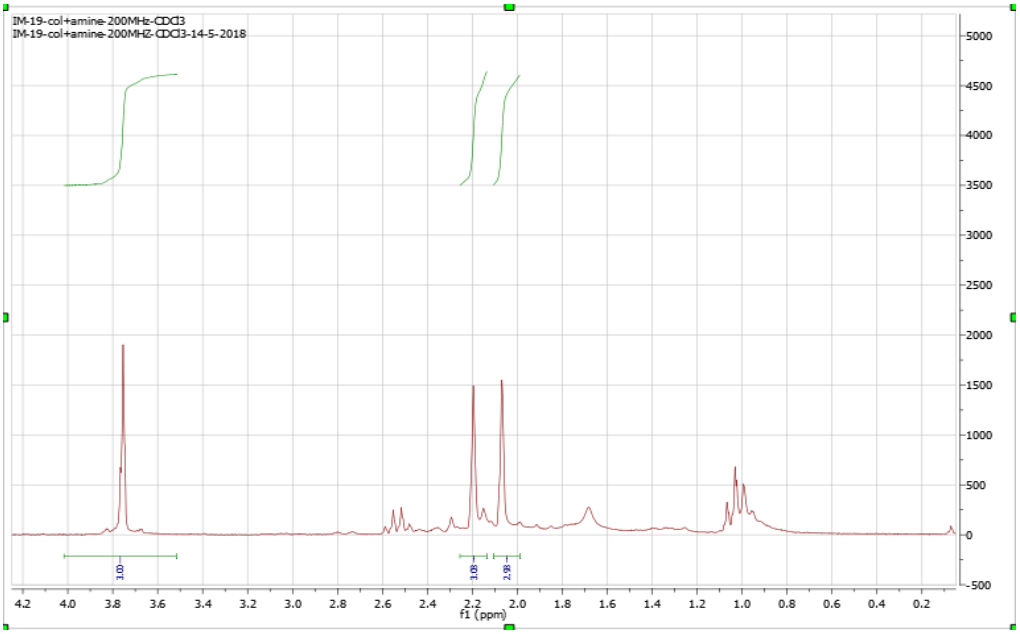
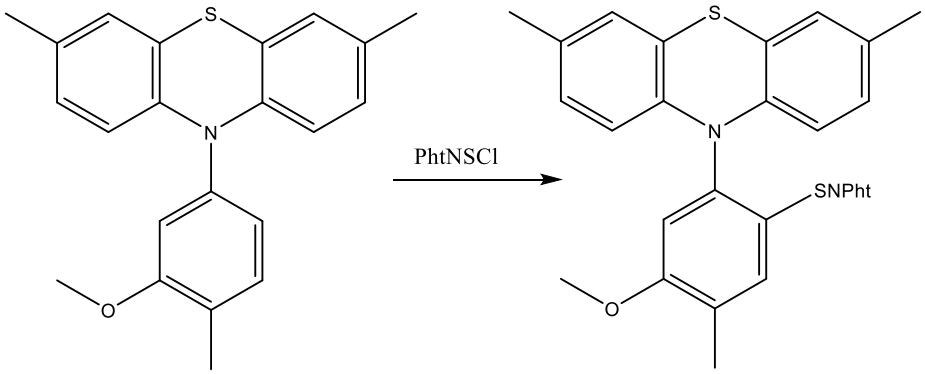


Figure 3.7 NMR extension

The phenothiazine was isolated and characterized by NMR, IR and melting point, to improve this reaction I repeated the reaction with a longer time trying to not obtain diarylamine however it was obtained anyway.

Continuing with the synthesis of the metoxihelicen it was made a sulfenilation reaction of the phenothiazine, again was used ftalimidesulfenyl chloride to develop this reaction:

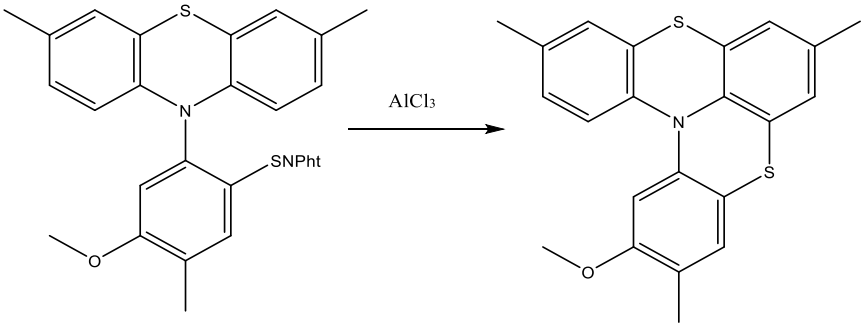
[39] Jinjin C., Guozheng L., Yanjun X., Yunfeng L., Fuhong X., and Guo-Jun D. *Org. Lett*. 2015, **17**, 5870−5873



Reaction 9. Sulfenilation of phenothiazine

The phenothiazine was disolved in dry DCM and after was added the PhtNSCl, the reaction took place in two hours under nytrogen atmosphere at room temperature. The reaction was followed by TLC where I observed three plots, the excess of ftalimidesulfenyl chloride, the final product and one subproduct possibly the sulfenilation in other position due to the fact that the Rf of the product and the impurity are very similar. As it happened in the triarylamine is a S_EAr reaction but in this case the presence of the metoxy group leads the sulfenilation to its para position because it is a great donor group by resonance, this allows to obtain very good yields for this reaction (around 75%) compared with the sulfenilation in the previous synthesis (around 30%). After the purification by flash chromatography column the product was characterized by H-NMR, C-NMR, IR and melting point.

Finally, the methoxy helicene was obtained in a S_EAr intramolecular cyclization, the sulfenilated phenothiazine was disolved in dry DCM and then $AlCl_3$ was added to the solution the reaction occurred under nytrogen atmosphere, at room temperature during two hours.



Reaction 10. Intramolecular cyclization

After the reaction it was made a flash chromatography column to separate the product and the ftalimide liberates after the cyclization, then it was characterized (H-NMR, C-NMR, IR and melting point). In the spectrum of H-NMR we can see that the signal of the ftalimide group dissapears also in the IR is appreciated that the double bond C=O of the ftalimide does not exist (Figure 3.9) the black spectrum has a peak in 1731 cm-1 corrresponding to the C=O and in the red spectrum it does not exist.

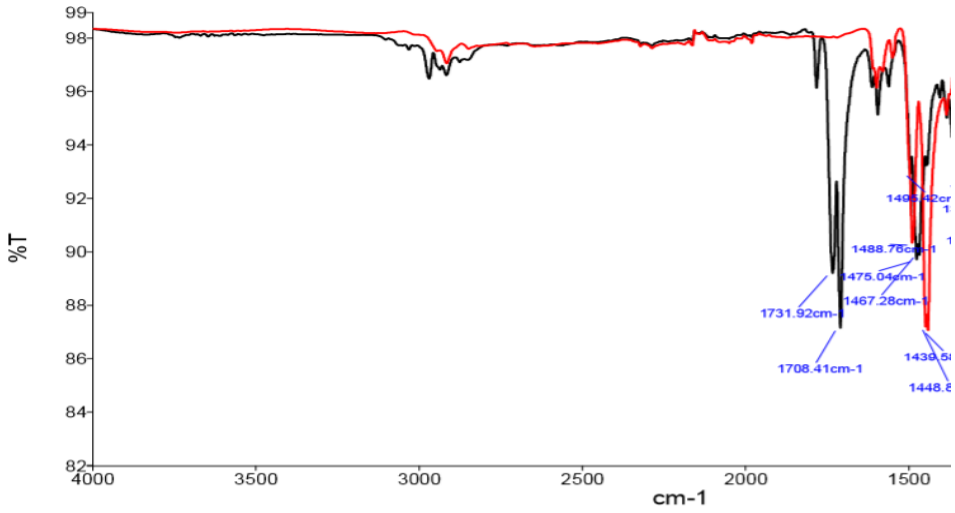
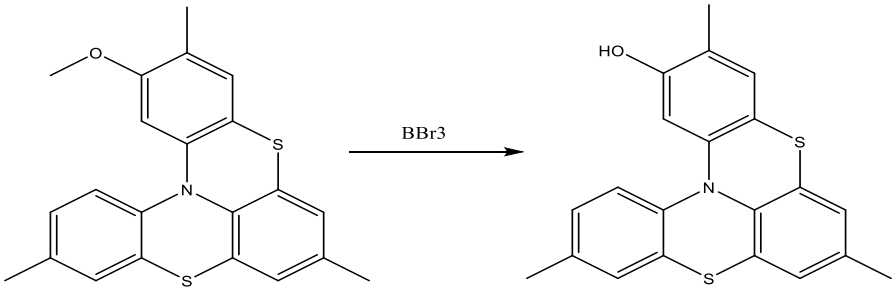


Figure 3.8 IR of helicen (red spectrum) vs IR of ftalimidephenothiazine (black spectrum)

3.6 Phenolic Helicene

After getting the methoxy helicene I tried to desprotect the methoxy group to generate a phenolic helicene which could be interesting to continue the synthesis of the polymer. So with that purpose I made the following reaction:



Reaction 11. Desprotection reaction

Over a solution of methoxy helicene in dry DCM it was added BBr_3, the reaction took place during 6 hours at 25ºC under a nytrogen atmosphere. After that time it was characterized, using the ^1H-NMR we could see that the signal of the methoxy group disappears and it appears a signal which integrates by one proton corresponding to the alcohol. Regarding the IR we have a wide signal around 3000 cm^{-1}(Figure 3.10).

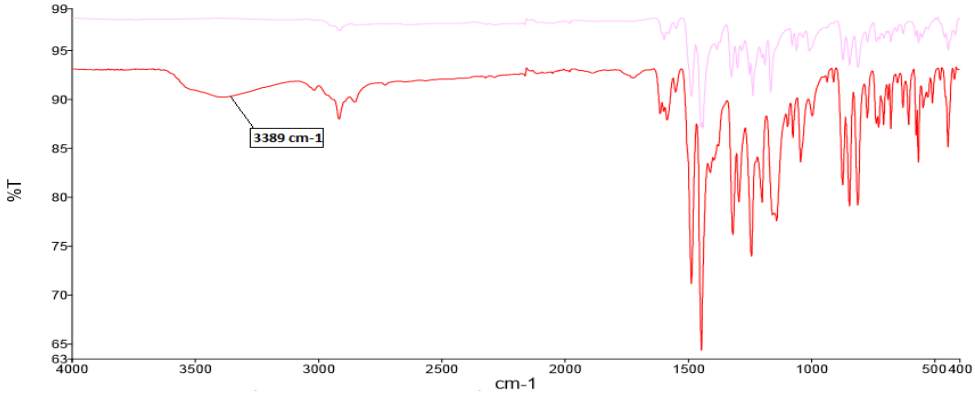
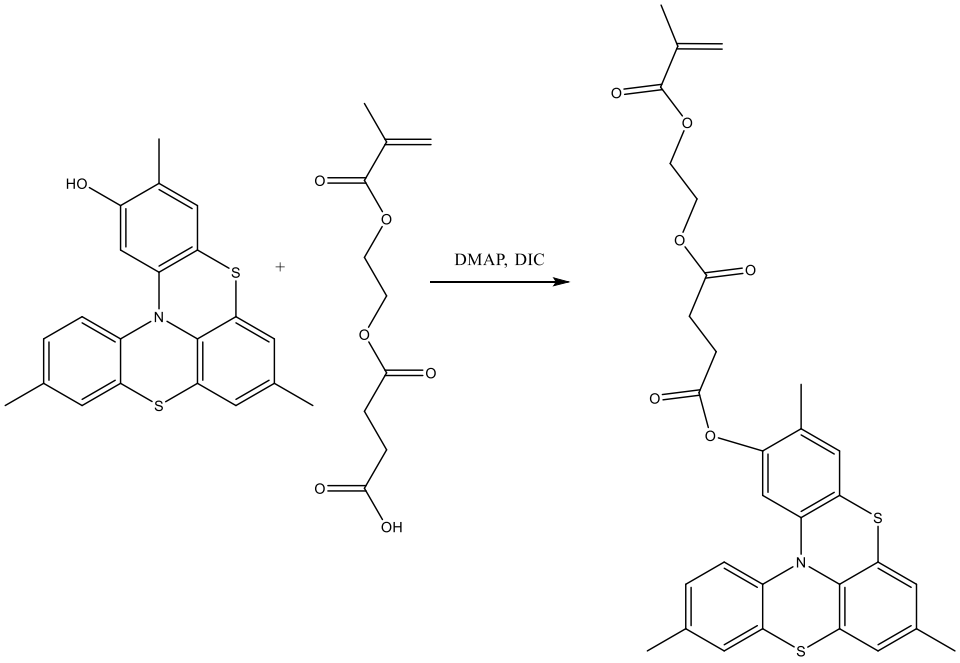


Figure 3.9 IR of alcohol helicene (red curve) and methoxy helicene (pink curve)

3.7 Mono-MethacrylateHelicene

For the synthesis of the monomer it was carried out a sterification of Steglich[40] regarding to the Reaction 9 it was made with the phenolic helicene and mono-2-methacryloyloxyethylsuccinate in dry DCM under nytrogen atmosphere at room temperature during 18 hours.



Reaction 12. Sterification of Steglich

In this kind of reaction is necessary activate the carboxylic acid for this reason is used carbodiimides, there are a great variety of commercially available, in our case I used DIC (N,N´-diisopropylcarbodiimide). In another way the DMAP plays an important role as a catalyst in the sterification reactions. Moreover, in the process of obtaining the monomer, adequate precautions were taken to prevent the monomer from unintentionally polymerizing; for this it was protected from light and distilled under vacuum in the rotavapor without heating.

The reaction was followed by TLC where there were three products, after the 18 hours I isolated them by flash chromatography and I made them characterization. The first compound was the starting material so maybe it would be necessary a longer time of reaction, the second one was the product that I wanted to obtain and the third one was an intermediate of the reaction between the carbodiimide and the carboxylic acid. It is clear in the H-NMR (Figure 3.10) of the intermediate product that the reaction between the acid and the carbodiimide takes place, we can see a signal which integrates by twelve protons corresponding to the isopropyl groups at 1.38 ppm also the two signals of the double bond at 6.14 ppm and 5.60 ppm.

[40] J. C. Kim, J. Jung, Y. Rho, M. Kim Biomacromolecules 2011, 12, 2822-2833

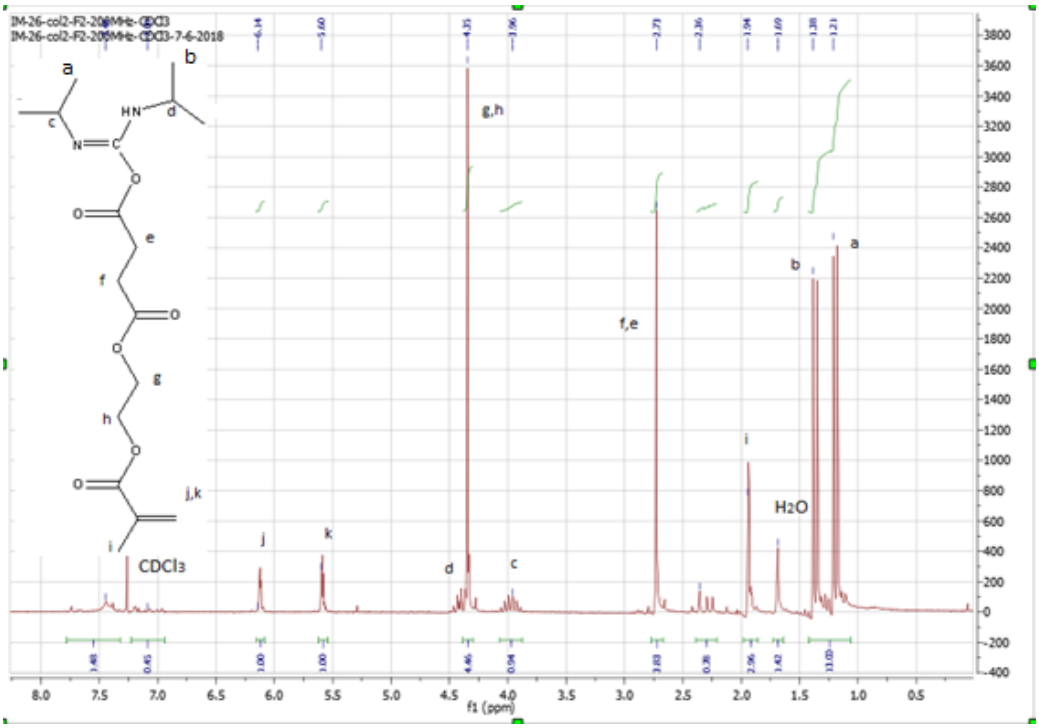


Figure 3.10 Carbodiimide intermediate

3.8 Block copolymer PMHelicene-b-PEG (10000)

The synthesis of the block copolymers was carried out by RAFT polymerization: radical polymerization, addition, fragmentation and chain transfer (Reversible Addition-Fragmentation chain Transfer, RAFT). The RAFT polymerization is a controlled radical polymerization, first described by the group of Rizzardo, Moad and Thang,[41] which can be applied to a wide variety of different functional monomers. It is based on the transfer of the growing chain to sulfur derivatives, generally dithioesters, for this reason the concentration of macroradicals is low all time, which in turn minimizes chain termination.

As in a traditional radical polymerization, polymerization begins with a peroxide or an aliphatic azo compound (such as AIBN) which have labile bonds that break homolytically upon heating. Furthermore, in this type of polymerization, a chain transfer agent (CTA) containing xanthate, dithioester, dithiocarbonate, etc. groups is necessary. The choice of the CTA is marked by the type of monomer that we are going to polymerize, since the advance of a controlled form of the polymerization process, and therefore the dispersity and molecular mass, depend on the chosen CTA. In fact, there is already a good offer of commercial CTAs with a recommendation of choice based on the type of polymer.[42]

The first and last step (initiation and ending) in this type of polymerization happen in the same way as in a traditional radicalary. In fact as happens in a conventional thermal polymerization is used an initiator, the active species of the initiator is formed and after that a propagation radical is formed $Pn\bullet$ which reacts with the chain transfer agent and causes the break of the RX bond (X is generally an atom of S). After this step we obtain a living polymer in the sense that it can continue reacting through the reactive end, even

[41] G. Moad, E. Rizzardo, S. H. Thang, Aust. *J. Chem*. 2005, **58**, 379-410

[42] http://www.sigmaaldrich.com/technical-documents/articles/materials-science/polymer-science/raft-polymerization.html

though it is desactivated. We also obtain a new radical, (R •), which will be in charge of continuing with the polymerization when reacting with the monomer, producing again propagation radicals Pm •. A rapid equilibrium is then established between the two propagating radicals and the polymer bound to the CTA. This balance leads to polymers with very little polydispersity. The termination stage can not be avoided but it is minimized because there is a low concentration of macroradicals in the medium. At the end of the polymerization, many chains still retain the CTA group as a terminal group and can be isolated as stable compounds. These macromolecules with a terminal CTA can be used as transfer agents in subsequent processes, which makes them a perfect reagent for obtaining block copolymers by polymerization of other monomers. In this case they are called macro-CTA. An outline of the RAFT process is shown in Figure 3.11.

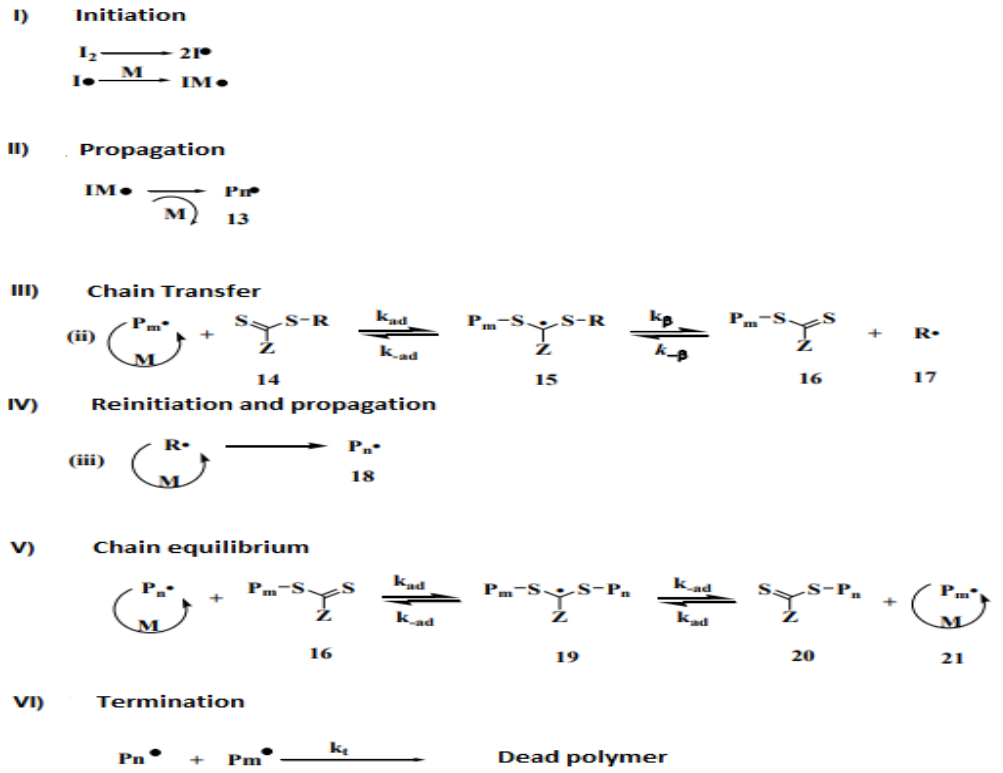
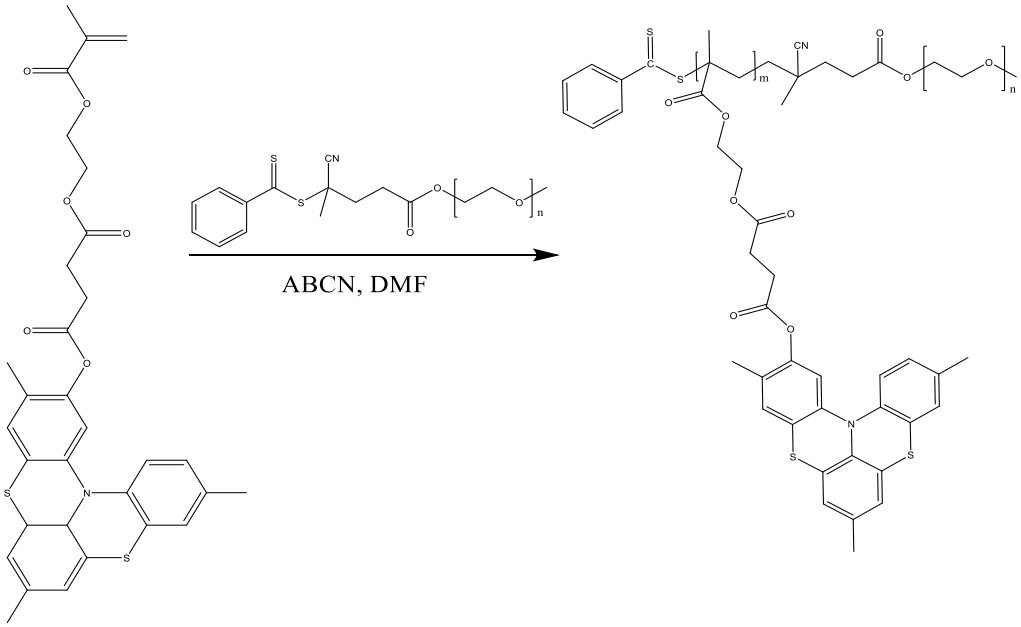


Figure 3.11 Raft mechanism[43]

To synthesize the block copolymer PMHelicene-PEG(10000) the following reaction was made during 24 hours at 80ºC:

[43] Grande. C. and Zuluaga. F. *Rev. Iberoam. Polim*., **11**(6), 339-359(2010)



Reaction 13. Raft polymerization

The crude was dissolved in DCM and then centrifuged after the centrifugation the DMF was removed and the solution of DCM was dried during a night. The solid obtained was dissolved in 1 ml of DCM and precipitated in diethyl ether. Once is obtained the solid it was characterized by H-NMR. As the mass of the PEG(10000) is known we know its degree of polymerization therefore we can relate its relative integration with the integration of the methacrylate block and find the degree of polymerization of our polymer. The polymerization degree of the PEG(10000) is 227 so is integration is 227 $*$ 4 = 908 protons, now we can know the number of repetitive units of the methacrylate block because they are related, in this way I obtained a degree of polymerization of 29.

Over a solution of PMHelicene-b-PEG(10000) was added a solution of HBF_4 in diethyl ether after some hours it was observed the formation of a precipitate and a great change in the color, this suggests the formation of the radical cation. Then I studied the absortion of the radical at different pHs: we can see that the modification in the pH produces the reversibility of the radical formation reaction. At pH=1 (grey curve) we have the radical cation with a maximum of absorbance at 556 nm (0.971) (as happened with the Norbornene-helicen radical) however when I added to the solution a bit of triethylamine the pH changes to 3 (blue curve) and the absorbance is reduced to 0.338 at 556 nm. Finally when the pH arrives to 7 (red curve) there is no absorbance at 556 nm so we can affirm that the addition of the base recover the original compound.

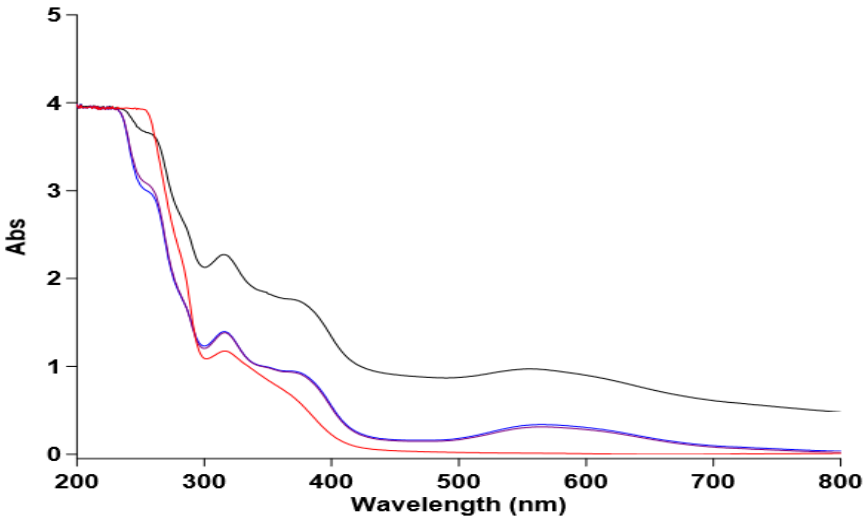


Figure 3.12 Absortion of radical at pH 1 (grey), 3 (blue) and 7 (red)

4. Conclusions

In this master´s thesis I have obtained two monomers capable of being polymerized, one polymer and one copolymer derivated of norbornene and a methacrylate monomer respectively, the formation of radical cations has also been studied in helicenes, monomers and polymers. The main finding obtained during the synthesis of these compounds are:

- We can obtain different triarylamines through a Buchwald-Hartwig reaction using a Pd catalyst showing great results with the $Pd(OAc)_2$ catalyst. These triarylamines react with ftalimidesulfenyl chloride ($PhtNSCl$) getting the helicenes.
- The helicenes can be functionalized with norbornadiene via Heck reaction obtaining a monomer capable to polymerize using a Grubbs catalyst in a ROMP (Ring Opening Metathesis Polymerization) however the solubility of this polymer is very bad in all the solvents and is not possible to characterize.
- The radical cation of the Bromo-Helicene and the radical cation of the Mono-Norbornene-Helicene absorb in the same region of the UV spectrum, both are synthesized with $AgSbF_6$.
- The one plot reaction to obtain 10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine is a good match point to start the synthesis of the helicene because the methoxy group leads the sulfenilation to its para position with a very good yield. Also, the cyclization with $AlCl_3$ happens with a good yield.
- The phenolic helicen is capable to react with a carboxylic acid with a good yield via Steglich esterification to synthesize helicenes with long chains. In our case is also useful to act as a monomer in a polymerization reaction.
- The RAFT polymerization allows to obtain block copolymers such as PMHelicene-b-PEG(10000).
- The formation of the radical cation in the PMHelicene-b-PEG(10000) with HBF_4 happens in a reversible way as we could demonstrated changing the pH.

5. Experimental procedure

5.1. Synthesis of 4,4´-dimethyltriphenylamine

A schlenk is dried in the oven and then its added di-p-tolylamine (1000 mg, 4.92 mmol), $\mathrm{Pd(OAc)_2}$ (9.00 mg, 0.04 mmol), Xantphos (23 mg, 0.04 mmol) and NaOBu (580 mg, 6.05 mmol) after this I made 3 cycles of nitrogen-vacuum. Then I added 5 ml of dry toluene with a syringe and finally iodobenzene (823 mg, 4 mmol). The mix is stirred at 100ºC during 18 hours. After this time the mix is disolved in water (75 ml) and extracted with diethyleter (3x50ml), the organic phase is dried with Na_2SO_4, filtrated and evaporated I obtein a mix of the starting material and the final product. The final product is purified by flash chromatography in a mix of Eter petroleum 9:1 DCM getting 705 mg (2.58 mmol) of a white solid with a 78% of yield.

^{1}H NMR (200 MHz, CDCl3) δ 7.04 ppm (13H, m), 2.31 ppm (6H, s).

5.2. Synthesis of 4-bromo-*N, N*-di-p-tolylaniline

A solution of N-bromosuccinimide (502 mg, 2.82 mmol) its prepared in dry DCM (5 ml) under an atmosphere of nitrogen in a round-bottom flask. Another solution of 4,4´-dimethyltriphenylamine (700 mg, 2.56 mmol) is prepared in dry DCM (5 ml) under nytrogen atmosphere in a round-bottom flask. Then both solutions are added in a schlenk with a syringe, the schlenk contains a stir barr and its under a nitrogen atmosphere. The mix is stirred during two hours at room temperature. After this time the mix is disolved in 100 ml of DCM and is extracted four times with water (4x100 ml) is dried over Na_2SO_4, filtrated and evaporated. The final product is purified by flash chromatography with an eluyent mix of éter petroleum 20:1 DCM getting 650 mg with a 75% of yield.

^{1}H NMR (200 MHz, CDCl3) δ 7.28 (2H, m), 6.98 (10H, m), 2.31 ppm (6H, s).

5.3. Synthesis of bisulfenilated-4-bromo-*N, N*-di-p-tolylaniline

A solution of 4-bromo-*N, N*-di-p-tolylaniline (700 mg, 1.99 mmol) was prepared in 9 ml of $CHCl_3$ in a round-bottom flask with two necks, over this solution is added PhtNSCl (940 mg, 4.38 mmol) with a dropwise. The mix is stirred at room temperature during 64 hours under a nitrogen atmosphere. After this time, I dissolve the mix in 150 ml of DCM then is extracted with $NaHCO_3$ (3x150ml), dry with Na_2SO_4 the organic layer, filtrated and concéntrate in vacuum. The final product is purified by flash chromatography with a eluyent mix of DCM 2:1 Eter petroleum getting 400 mg, 0.57 mmol of the bisulfenilated product with a yield of 29%.

^{1}H NMR (200 MHz, CDCl3) δ 7.85 ppm (8H, ddd), 7.55 ppm (2H, J=8 Hz, d), 7.27 ppm (2H, m), 7.05 ppm (2H, J=8Hz, d), 6.83 ppm (2H, s), 6.57 ppm (2H, J=10), 2.16 ppm (6H, s).

5.4. Synthesis of Bromo-Helicene

In a round-bottom flask a solution of bisulfenilated-4-bromo-N,N´-di-p-tolylaniline (300 mg, 0.43 mmol) in dry DCM (22 ml) its prepared after I add $AlCl_3$ (230 mg, 1.70 mmol). The mix is stirred at room temperature during four hours under a nitrogen atmosphere. Then is diluited in 150 ml of DCM and washed with $NaHCO_3$ (3x150ml), dry with Na_2SO_4 the organic layer, filtrated and concentrated to vacuum. To purificate the product a flash chromatography is made with an eluyent mix of eter petroleum 4:1 DCM getting 96 mg of the final product with a yield of 57%.

^{1}H NMR (200 MHz, $CDCl_3$) δ 7.31 ppm (1H, J=2 Hz, d), 7.21 ppm (1H, J=8 Hz J=2 Hz, dd), 6.98 ppm (4H, m), 6.79 ppm (2H, J=2 Hz, dm), 2.28 ppm (3H, s), 2.21 ppm (3H, s)

5.5. Synthesis of Mono-Norbornene-Helicene

A dry schlenk is charged with PPh_3 (6.10 mg, 0.023 mmol), $Pd(OAc)_2$(2.62 mg, 0.012 mmol) and NH_4HCO_2(60.18 mg, 0.96 mmol), then is evacuated and refilled with nitrogen three times. After a solution of Bromo-Helicene (96 mg, 0.23 mmol) in dry DMF and norbornadieno (107.18 mg, 1.17 mmol) is added with a syringe and stirred at 90ºC during 24 hours. Then the mix is disolved in 200 ml of DCM, washed with HCl 0.1 M (2x150ml), washed with H_2O (3x150ml), dried the organic layer with Na_2SO_4, filtrated and evaporated the solvent to vacuum. To purificate the product I make a flash chromatography with an eluyent mix of eter petroleum 15:1 DCM, I isolate 20 mg of the final product with a yield of 20%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 ppm (5H, m), 6.91 ppm (2H, m), 6.77 ppm (1H, s), 6.24 (2H, J=32 Hz, dm), 2.96 ppm (1H, s), 2.86 ppm (1H, s), 2.62 ppm (1H, m), 2.28 ppm (3H, s), 2.20 (3H, s), 1.68 ppm (2H, m), 1.44 ppm (2H, m)
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.45 ppm, 140.37 ppm, 140.09 ppm, 137.39 ppm, 137.17 ppm, 134.38 ppm, 134.06 ppm, 128.06 ppm, 128.00 ppm, 126.73 ppm, 126.60 ppm, 126.50 ppm, 125.93 ppm, 125.32 ppm, 120.18 ppm, 120.10 ppm, 119.95 ppm, 48.33 ppm, 45.77 ppm, 43.07 ppm, 42.23 ppm, 33.62 ppm, 20.59 ppm, 20.35 ppm

5.6 Synthesis of PNorbornene-Helicene

In a dry Schlenk I added a solution of Grubbs II catalyst (3 mg, 0.03 mmol) in 750 µL of dry DCM then I make three cycles of nitrogen-vacuum, in other Schlenk are introduced 320 mg, 0.75 mmol of Mono-Norbornene-Helicene and its made three cycles of nitrogen-vacuum after is dissolved in 1.74 of dry DCM and added drop by drop over the solution of the catalyst. The mix is stirred at room temperature during 21 hours under a nitrogen atmosphere. The solid is washed with DCM and filtered with a buchner obtaining 110 mg of a brown solid.

5.7. Synthesis of radical MNorbornene-Helicene

Over a solution of Mono-Norbornene-Helicene (20 mg, 0.047 mmol) in dry DCM (2 ml) in a round-bottom flask its added a solution of AgSbF6 (25mg, 0.075 mmol) in 1 ml of

dry DCM with a syringe drop by drop. The mix is stirred at room temperature under a nitrogen atmosphere during 1 hour. After this time the solvent is evaporated, then the solid is disolved in 1 ml of dry DCM and precipitated in 3 ml of hexane by last is filtrated with a buchner and washed with hexane.

5.8. Synthesis of 10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine

In a dry schlenk I add the solids reactives 3-methoxy-4-methylaniline (480 mg, 3.50 mmol), KI (116.25 mg, 0.70 mmol) and S (672 mg, 21 mmol), after this I make three cycles of vacuum-nitrogen and add the DMSO (0.6 ml) with a syringe, I make three cycles of vacuum oxygen and add 3 ml of dry toluene and 4-methylciclohexanone (1180 mg, 10.5 mmol). The mix is stirred at 150ºC during 48 hours under a oxygen atmosphere. After this the mix its disolved in 200 ml of DCM, extracted with 100 ml of water, 100ml of $Na_2S_2O_3$ and 100 ml of NaCl. To finish the organic layer is dried with Na_2SO_4, filtrated and evaporated. To purificate the product I make a flash chromatography with an eluyent mix of eter pretroleum 7:3 DCM, 420 mg of product are isolated with a yield of 35%.

^{1}H NMR (200 MHz, CDCl3) δ 7.33 ppm (1H, J=8Hz, d), 6.88 ppm (1H, J=8 Hz J=2Hz, dd), 6.83 ppm (2H, J=2 Hz, d), 6.80 ppm (1H, J=2 Hz, d), 6.64 ppm (2H, J=8 Hz J=2 Hz, dd),6.15 ppm (2H, J=8 Hz, d), 3.79 ppm (3H, s), 2.28 ppm (3H, s), 2.16 ppm (6H, s)

^{13}C NMR (100 MHz, CDCl3) δ: 159.45 ppm, 142.05 ppm, 139.84 ppm, 131.85 ppm, 131.50 ppm, 127.20 ppm, 126.98 ppm, 126.48 ppm, 122.45 ppm, 119.46 ppm, 115.55 ppm, 111.95 ppm, 55.46 ppm, 20.11 ppm, 16.08 ppm.

IR υ (cm-1): 1500.92 cm-1, 1476.08 cm-1, 1454.99 cm-1(C=C Ar), 1273 cm-1 (C-O).

Melting point: 123.3ºC

5.9. Synthesis of sulfenilated-10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine

Over a solution of 10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine (400 mg, 1.15 mmol) in dry DCM (6 ml) in a round-bottom flask, I added a solution of PhtNSCl (295 mg, 1.38 mmol) with a dropwise. The mix is stirred at room temperature under a nitrogen atmosphere during 2 hours. After this time the mix is disolved in 200 ml of DCM, extracted with $NaHCO_3$ (3x150ml) and the organic layer is dried with Na_2SO_4, filtrated and the solvent is evaporated to vacuum. To purificate the product I make a flash chromatography in a mix of DCM 1:1 eter pretoleum, 450 mg of product are isolated with a yield of 74%.

^{1}H NMR (200 MHz, CDCl3) δ 7.74 ppm (4H, dm), 7.49 ppm (1H, s), 6.74 ppm (1H, s), 6.62 ppm (2H, J=1.6 Hz d), 6.40 ppm (2H, J=8 Hz J=1.6 Hz, dd), 5.80 ppm (2H, J=8 Hz, d), 3.76 ppm (3H, s), 2.25 ppm (3H, s), 2.03 ppm (6H, s)
^{13}C NMR (100 MHz, CDCl3) δ: 167.18 ppm, 160.31 ppm, 139.52 ppm, 134.03 ppm, 133.92 ppm, 131.98 ppm, 131.39 ppm, 128.55 ppm, 127.10 ppm, 126.56 ppm, 126.47

ppm, 123.49 ppm, 118.26 ppm, 114.68 ppm, 113.55 ppm, 55.79 ppm, 20.04 ppm, 16.15 ppm.
IR υ (cm-1): 1731 cm-1 (C=O), 1495 cm-1, 1475 cm-1, 1467 cm-1(C=C Ar), 1277 cm-1 (C-O)
Melting point: 240.9ºC

5.10. Synthesis of 2-methoxy-3,7,11-trimethylbenzo[5,6][1,4]thiazinophenothiazine

In a round-bottom flask 400 mg, 0.76 mmol sulfenilated-10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine are dissolved in 28 ml of dry DCM after I added $AlCl_3$ (152 mg, 1.14 mmol) the reaction takes place during 3 hours at room temperature under a nitrogen atmosphere. Then is diluted in 200 ml of DCM, washed with $NaHCO_3$(3x150ml), the organic layer was dried over Na_2SO_4, filtered and concetrated in vacuum. The crude was purified by flash chromatography with an eluyent mix of eter pretoleum 10:1 DCM to give 210 mg of the product with a 73% of yield.

^{1}H NMR (400 MHz, CDCl3) δ: 7.09 ppm (1H, J=8 Hz, d), 7.02 ppm (1H, J=1.6 Hz, d), 6.92 ppm (2H, J=8 Hz J=1.6 Hz, dd), 6.77 ppm (2H, s), 6.64 ppm (1H, s), 3.65 ppm (3H, s), 2.28 ppm (3H, s), 2.20 ppm (3H, s), 2.14 ppm (3H, s)
^{13}C NMR (100 MHz, CDCl3) δ: 157.39 ppm, 141.24 ppm, 140.22 ppm, 137.26 ppm, 134.33 ppm, 133.98 ppm, 128.95 ppm, 128.10 ppm, 127.94 ppm, 126.54 ppm, 125.93 ppm, 125.79 ppm, 125.22 ppm, 123.35 ppm, 120.21 ppm, 116.46 ppm, 103.35 ppm, 55.61 ppm, 20.59 ppm, 20.34 ppm, 15.59 ppm.
IR υ (cm-1): 1488.76 cm-1, 1448.80 cm-1, 1440.58 cm-1 (C=C Ar), 1237.41 cm-1 (C-O)
Melting point: 165.3ºC

5.11. Synthesis of: 3,7,11-trimethylbenzo[5,6][1,4]thiazinophenothiazin-2-ol

In a flask with two necks a solution of 2-methoxy-3,7,11-trimethylbenzo[5,6][1,4]thiazinophenothiazine (190 mg, 0.5039 mmol) is prepared in 6 ml of dry DCM then I add drop by drop BBr_3(251 mg, 1.0079 mmol) at 0ºC. After the addition I left the reaction at room temperature under nitrogen atmosphere during six hours then I disolved the crude in DCM (100 ml), washed with $NaHCO_3$(2x100ml) and H_2O (1x100ml), the organic layer its dried with Na_2SO_4, filtered and concentrate to vacuum. 90 mg of the product are isolated with a yield of 49%.

^{1}H NMR (200 MHz, CDCl3) δ: 7.09 ppm (1H, J=8 Hz, d), 6.99 ppm (1H, s), 6.92 ppm (2H, J=8.2 Hz, d), 6.77 ppm (2H, s), 6.61 ppm (1H, s), 4.64 ppm (1H, s), 2.27 ppm (3H, s), 2.20 ppm (3H, s), 2.17 ppm (3H, s)
^{13}C NMR (100 MHz, CDCl3) δ: 153.42 ppm, 141.92 ppm, 139.72 ppm, 137.11 ppm, 134.35 ppm, 134.14 ppm, 129.36 ppm, 128.03 ppm, 127.98 ppm, 126.75 ppm, 125.93 ppm, 125.79 ppm, 125.08 ppm, 124.41 ppm, 122.92 ppm, 120.57 ppm, 120.50 ppm, 117.01 ppm, 107.79 ppm, 20.59 ppm, 20.34 ppm, 15.14 ppm.
IR υ (cm-1): 3389 cm-1 (-OH), 1487.76 cm-1, 1446.80 cm-1, 1410.58 cm-1 (C=C Ar)
Melting point: 128ºC

5.12. Synthesis of Mono-Methacrylate-Helicene

In a flask with two necks are added 2-methacrylolyoxyethyl succinate (60mg, 0.2640 mmol) and DMAP (2.68 mg, 0.022 mmol), three cycles of nitrogen vacuum are realized then its added a solution of 3,7,11-trimethylbenzo[5,6][1,4]thiazinophenothiazin-2-ol (80 mg, 0.2200 mmol) in dry DCM (6 ml) with a syringe finally the reaction begins with the addition of DIC (45 µl, 0.2640 mmol). The reaction takes place under nitrogen atmosphere at room temperature during 18 hours after that time the mix is disolved in DCM (100 ml), washed with NH_4Cl (2x100 ml), washed with $NaHCO_3$ (1x100ml), washed with Na_2CO_3 (2x100 ml), then the organic layer is dried with Na_2SO_4, filtered and concéntrate to vacuum. The crude was purified by flash chromatography with an eluyent mix of DCM 6:1 AcOEt to give 50 mg of the product with a yield of 35%.

^{1}H NMR (400 MHz, CDCl3) δ: 7.09 ppm (1H, J=8 Hz, d), 7.02 ppm (1H, s), 6.99 ppm (1H, J=1.2 Hz, d), 6.93 ppm (1H, J=8 Hz J=2.4 Hz, dd), 6.81 ppm (1H, s), 6.77 ppm (2H, J=2.4 Hz J=1.2 Hz, dd), 5.58 ppm (1H, m), 4.33 ppm (4H, s), 2.83 ppm (4H, m), 2.27 ppm (3H, s), 2.20 ppm (3H, s), 2.09 ppm (3H, s), 1.92 ppm (3H, s)

^{13}C NMR (100 MHz, CDCl3) δ: 171.73 ppm, 170.23 ppm, 167.04 ppm, 150.32 ppm, 148.46 ppm, 141.47 ppm, 139.57 ppm, 136.78 ppm, 135.80 ppm, 134.59 ppm, 134.34 ppm, 129.32 ppm, 128.20 ppm, 128.06 ppm, 126.62 ppm, 126.27 ppm, 126.11 ppm, 126.01 ppm, 125.92 ppm, 125.28 ppm, 125.16 ppm, 124.05 ppm, 120.17 ppm, 113.76 ppm, 62.33 ppm, 62.51 ppm, 28.87 ppm, 20.93 ppm, 20.57 ppm, 18.22 ppm, 15.53 ppm.

5.11. Synthesis of block copolymer PMHelicene-b-PEG(10000)

In a dry schlenk I add the solids reactives Mono-Methacrylate-Helicene (50mg, 0.0869 mmol), PEG(10000) (17.40 mg, 0.001739 mmol) and ABCN (0.15mg, 0.0006083 mmol) and I make three cycles of nitrogen-vacuum. After that are disolved in 1.5 ml of dry DCM, the solvent is frozen in liquid nitrogen and three cycles of nitrogen vacuum are made. The reaction takes place during 24 hours at 80ºC. After that time the crude is precipitated in DCM and centrifugate then the DMF is removed and I left evaporated the DCM one night. Once is evaporated I dissolved it in 1 ml of DCM and is precipitated in diethyl eter, I removed the solution of DCM with a pipet and dry the solid.

^{1}H NMR (200 MHz, CDCl3) δ: 6.98 ppm (198H, m), 4.24 ppm (109H, m), 3.64 ppm (909H, s), 2.81 ppm (116H, m), 2.25 ppm (177H, m), 2.07 ppm (83H, s), 1.25 ppm (52H, s)

Annexes A-K: Spectrum (IR, H-NMR, C-NMR)

4,4´-dimethyltriphenylamine:

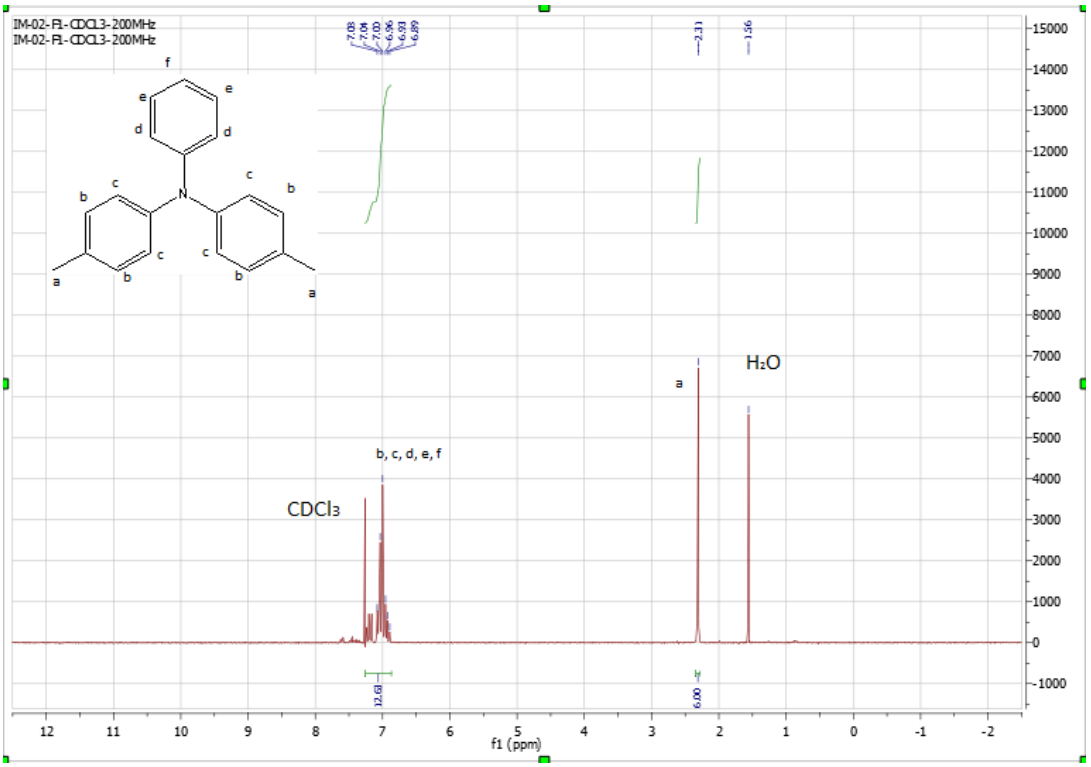


Figure A.1 ^{1}H-RMN spectrum (CDCl3, 200MHz) δ (ppm)

4-bromo-*N, N*-di-p-tolylaniline:

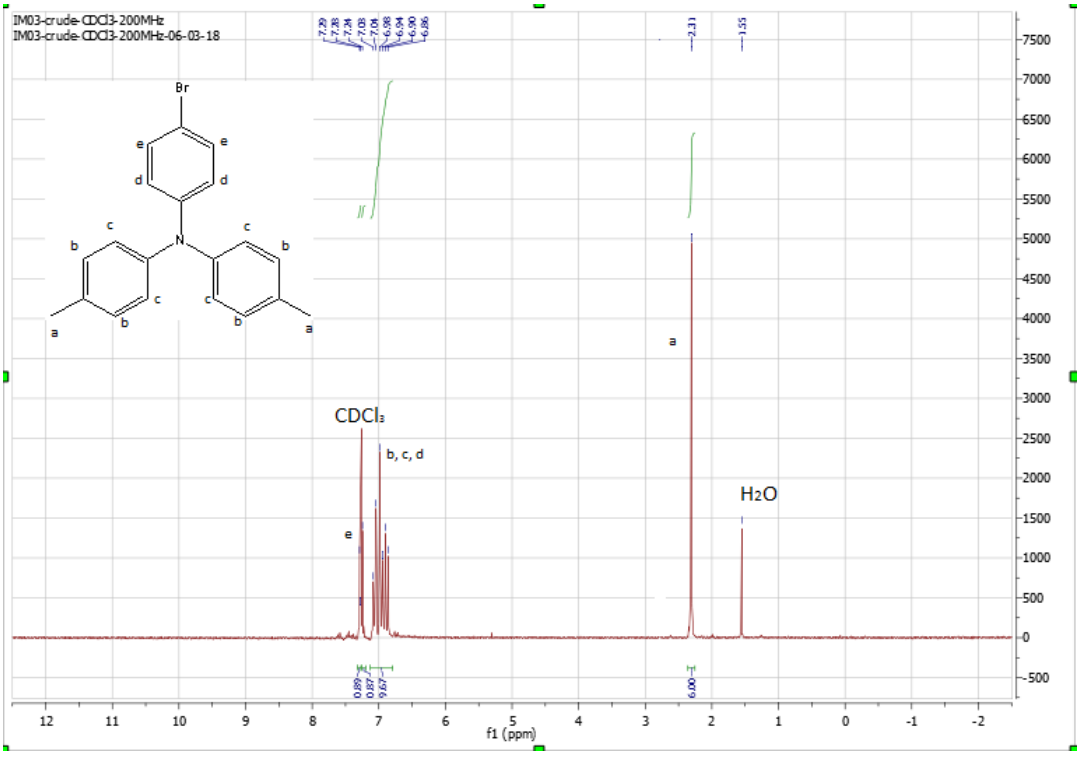


Figure B.1 ^{1}H-RMN spectrum (CDCl3, 200MHz) δ (ppm)

Bisulfenilated-4-bromo-*N, N*-di-p-tolylaniline:

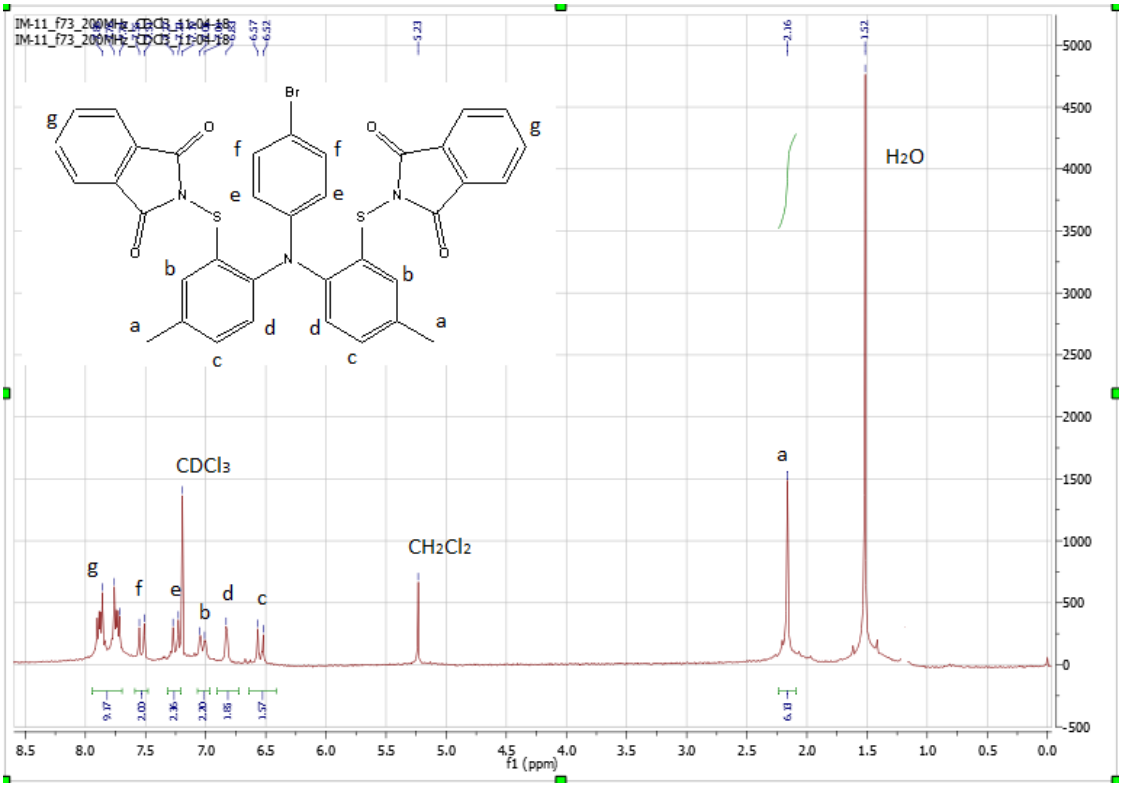


Figure C.1 ^{1}H-RMN spectrum (CDCl3, 200MHz) δ (ppm)

Bromo-Helicene:

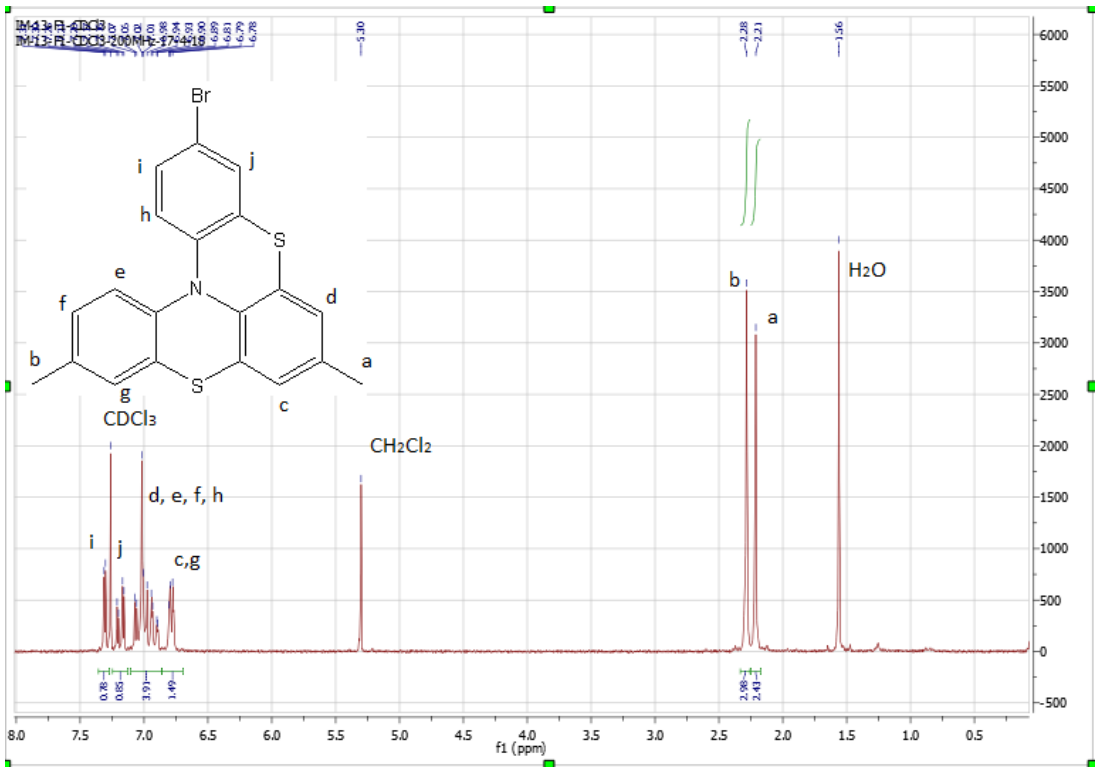


Figure D.1 ^{1}H-RMN spectrum (CDCl3, 200MHz) δ (ppm)

Mono-Norbornene-Helicene:

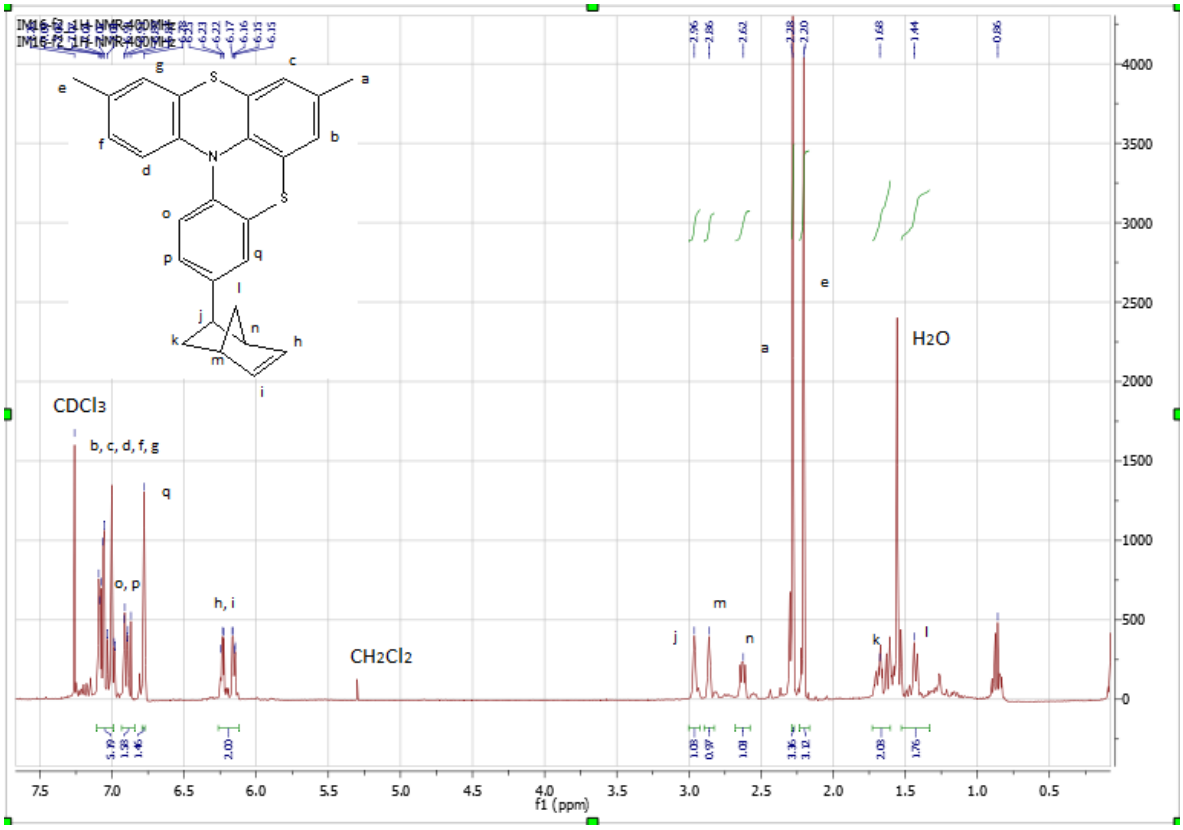


Figure E.1 ^{1}H-RMN spectrum (CDCl3, 400MHz) δ (ppm)

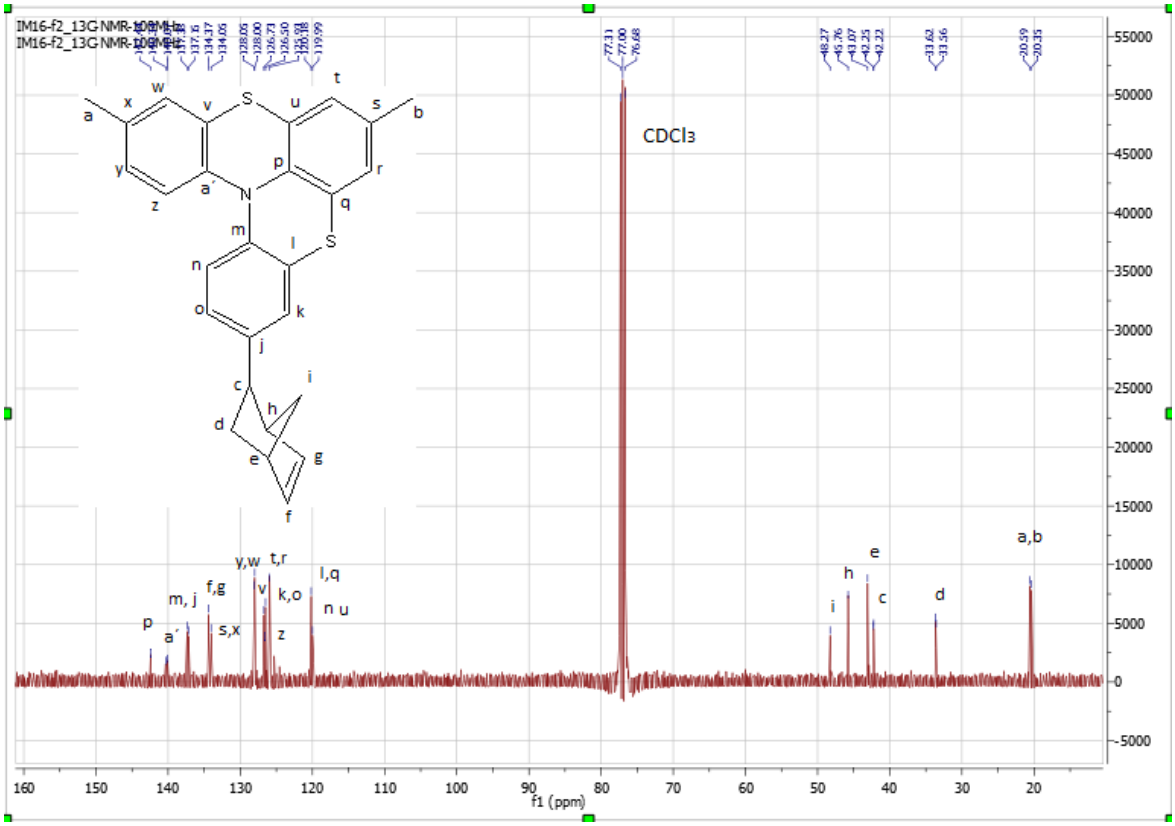


Figure E.2 ^{13}C-RMN spectrum (CDCl3, 100MHz) δ (ppm)

10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine:

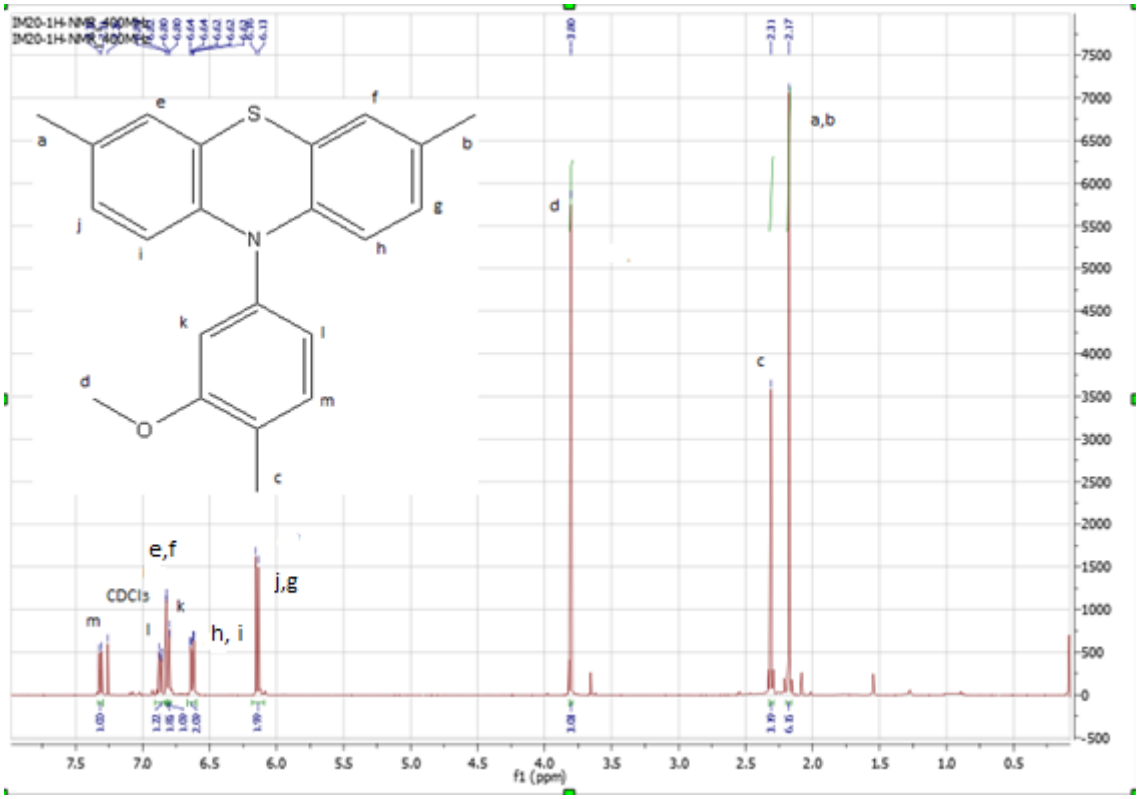


Figure F.1 ^{1}H-RMN spectrum (CDCl3, 400MHz) δ (ppm)

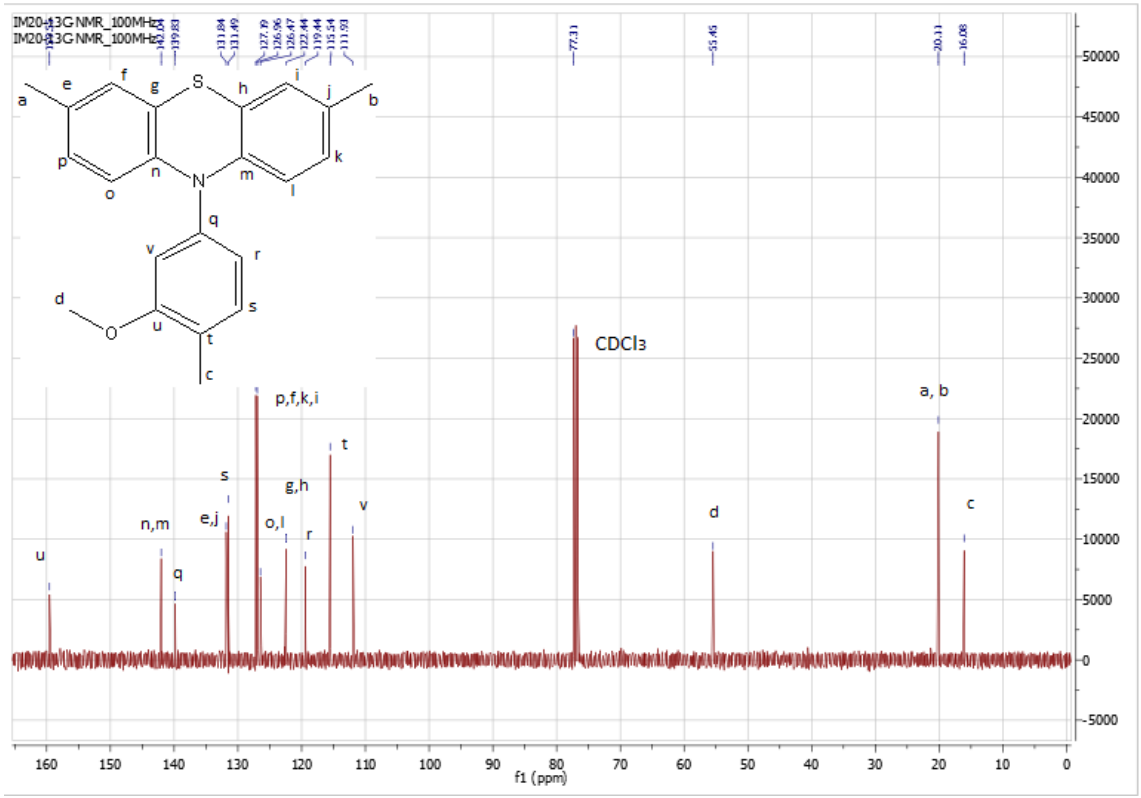


Figure F.2 ^{13}C-RMN spectrum (CDCl3, 100MHz) δ (ppm)

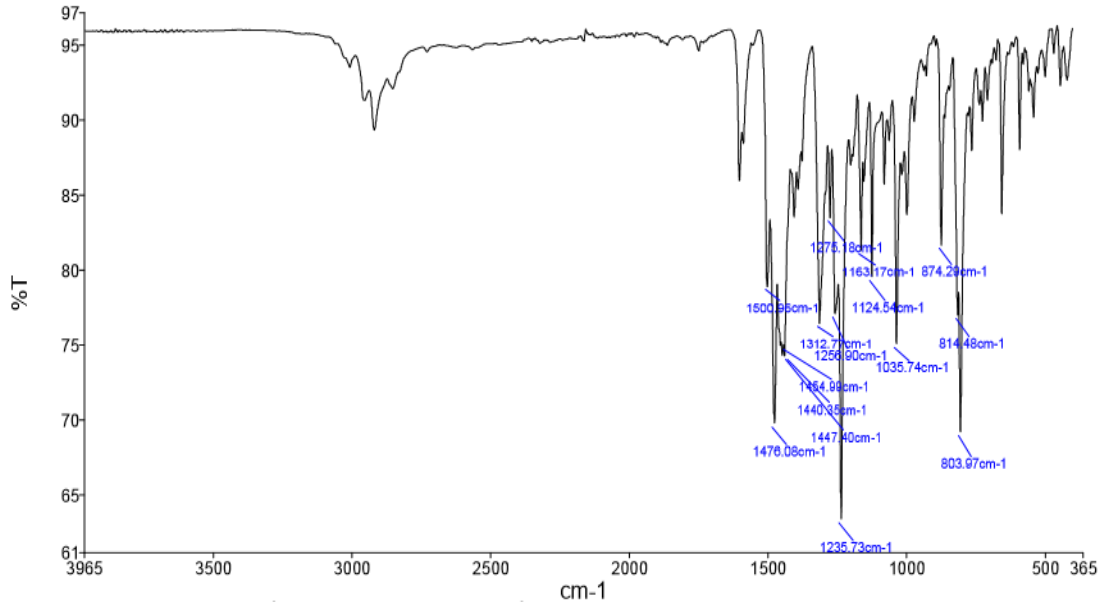


Figure F.3. IR spectrum (cm-1)

Sulfenilated-10-(3-methoxy-4-methylphenyl)-3,7-dimethyl-10-phenothiazine:

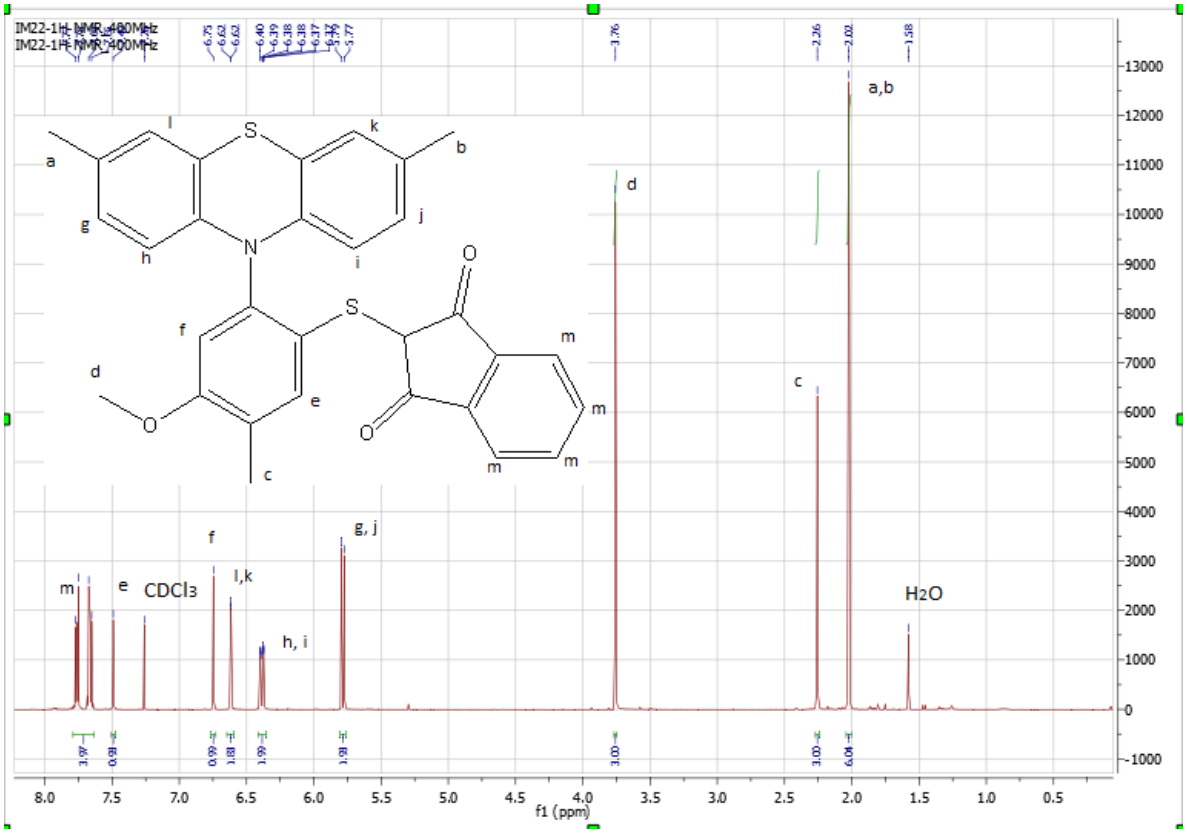


Figure G.1 ^{1}H-RMN spectrum (CDCl3, 400MHz) δ (ppm)

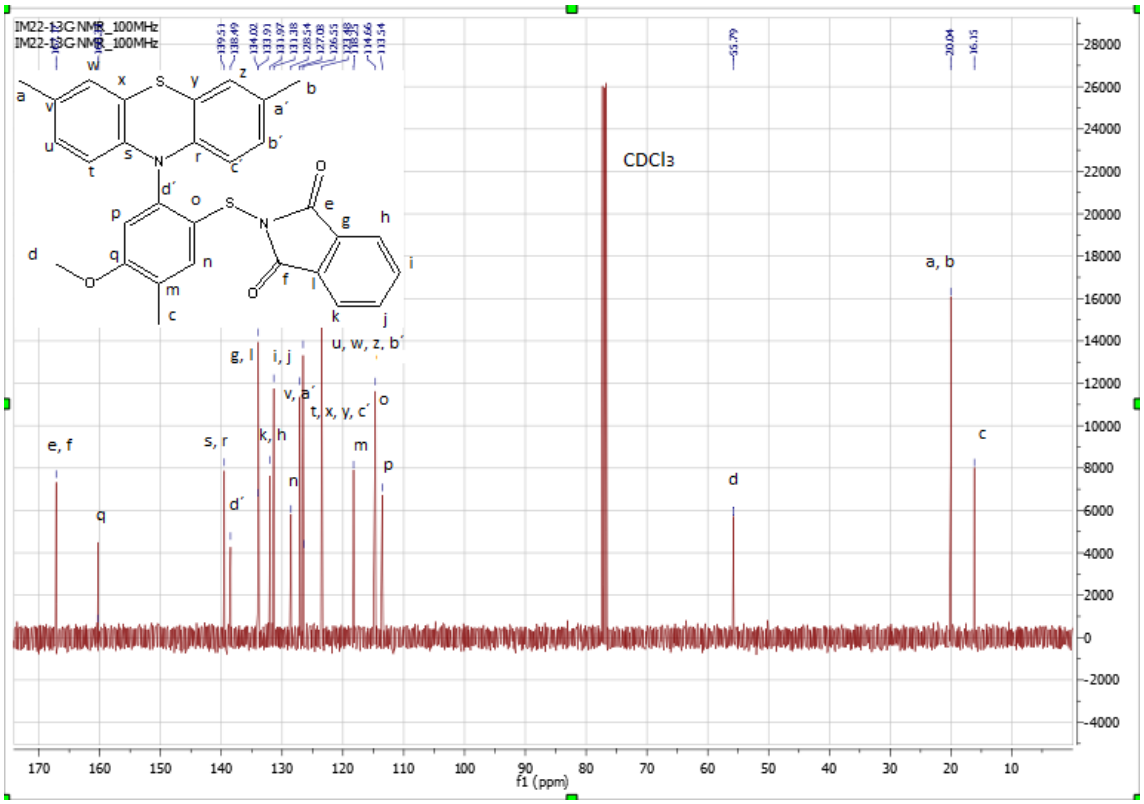


Figure G.2 ^{13}C-RMN spectrum (CDCl3, 100MHz) δ (ppm)

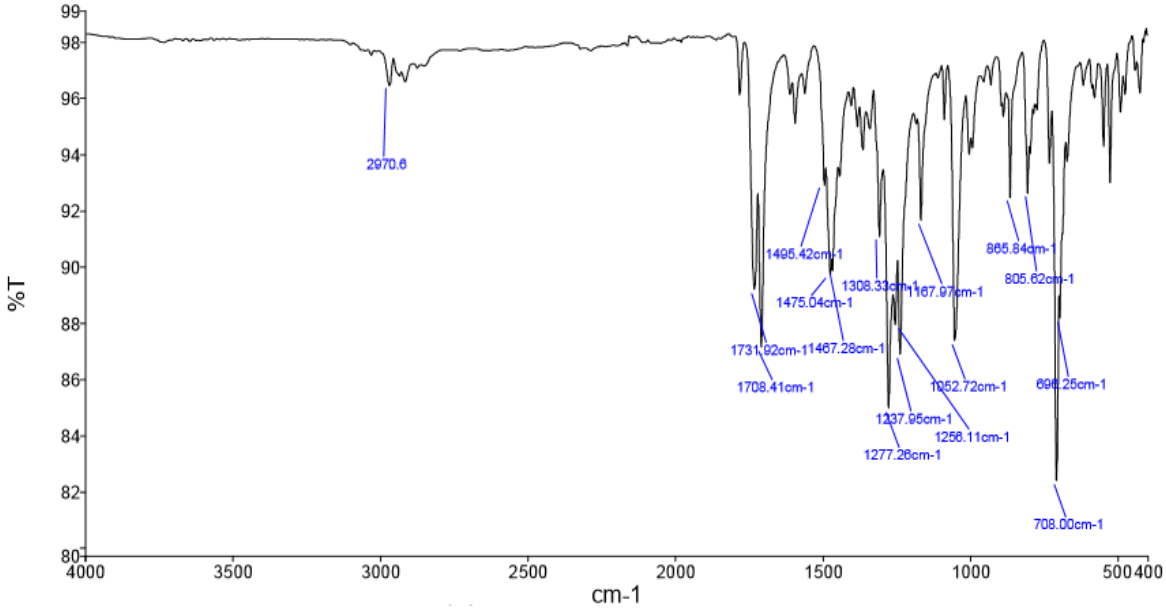


Figure G.3 IR spectrum (cm-1)

2-methoxy-3,7,11-trimethylbenzo[5,6][1,4]thiazino-phenothiazine:

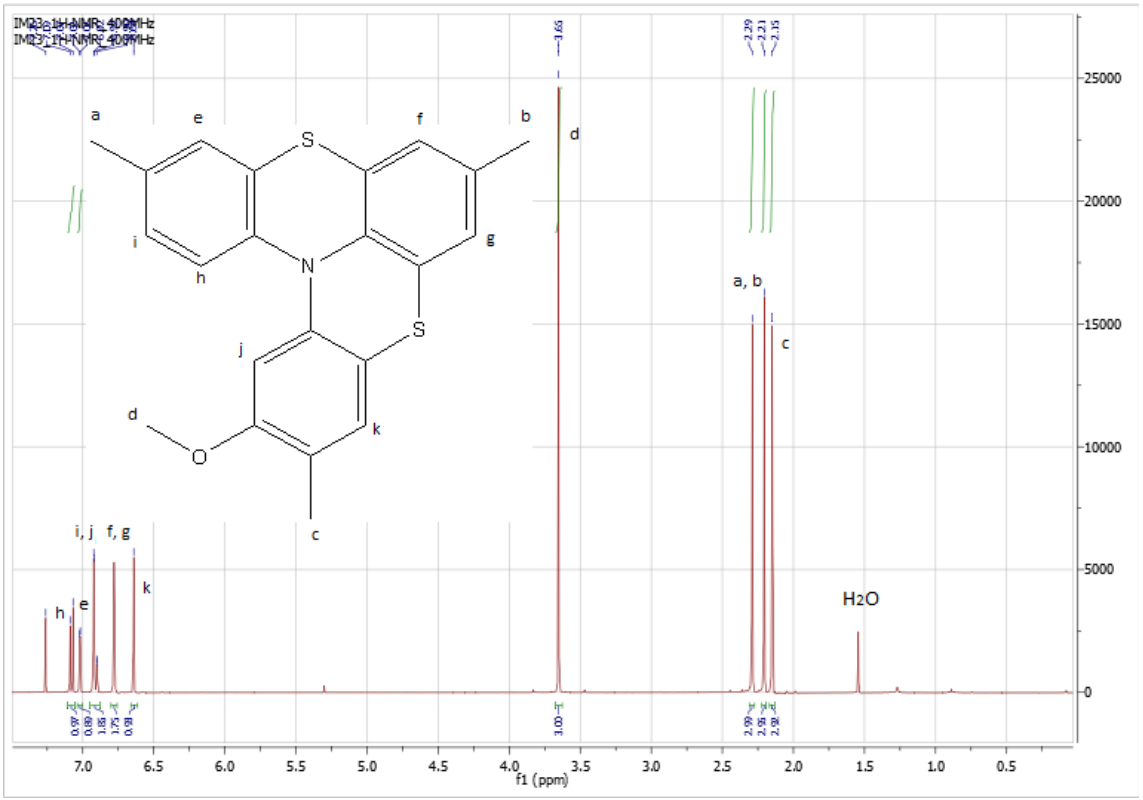


Figure H.1 ^{1}H-RMN spectrum (CDCl3, 400MHz) δ (ppm)

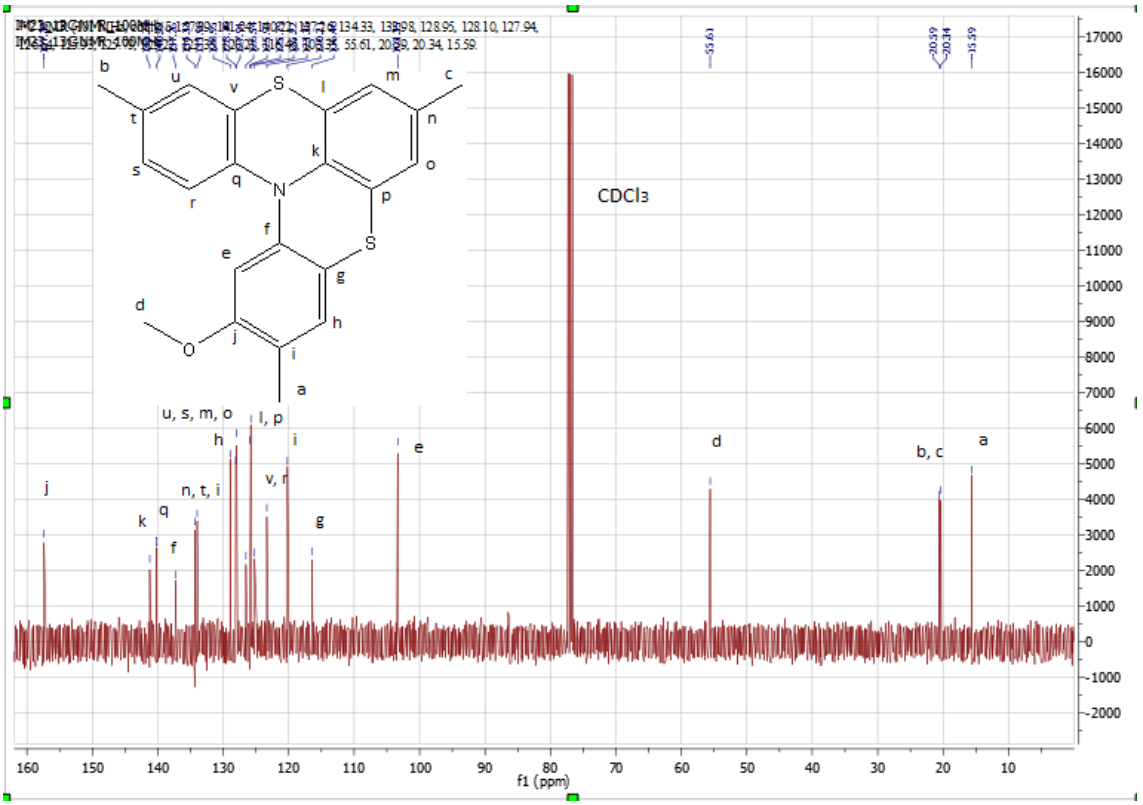


Figure H.2 ^{13}C-RMN spectrum (CDCl3, 100MHz) δ (ppm)

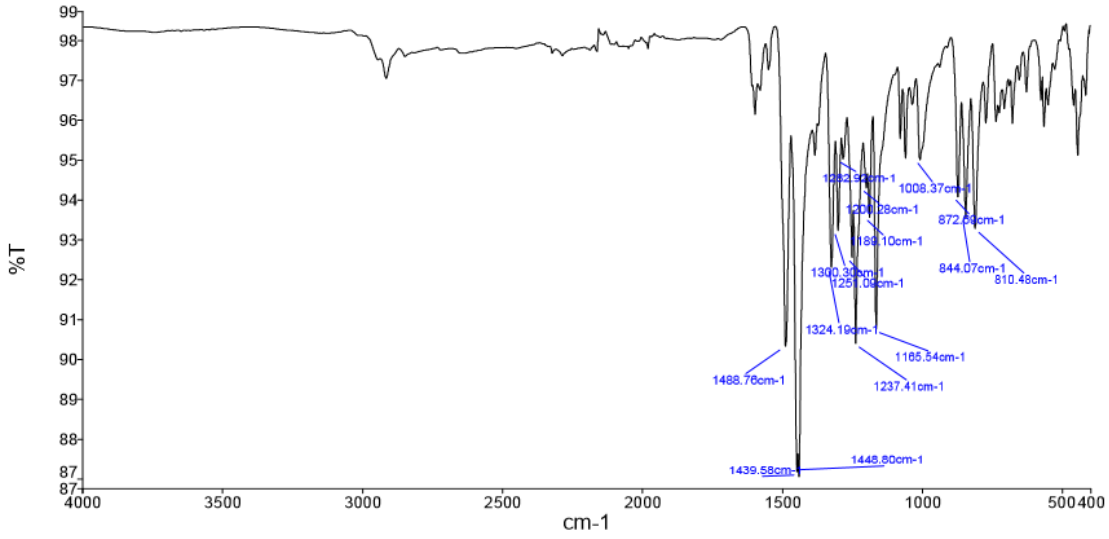


Figure H.3. IR spectrum (cm-1)

3,7,11-trimethylbenzo[5,6][1,4]thiazinophenothiazin-2-ol:

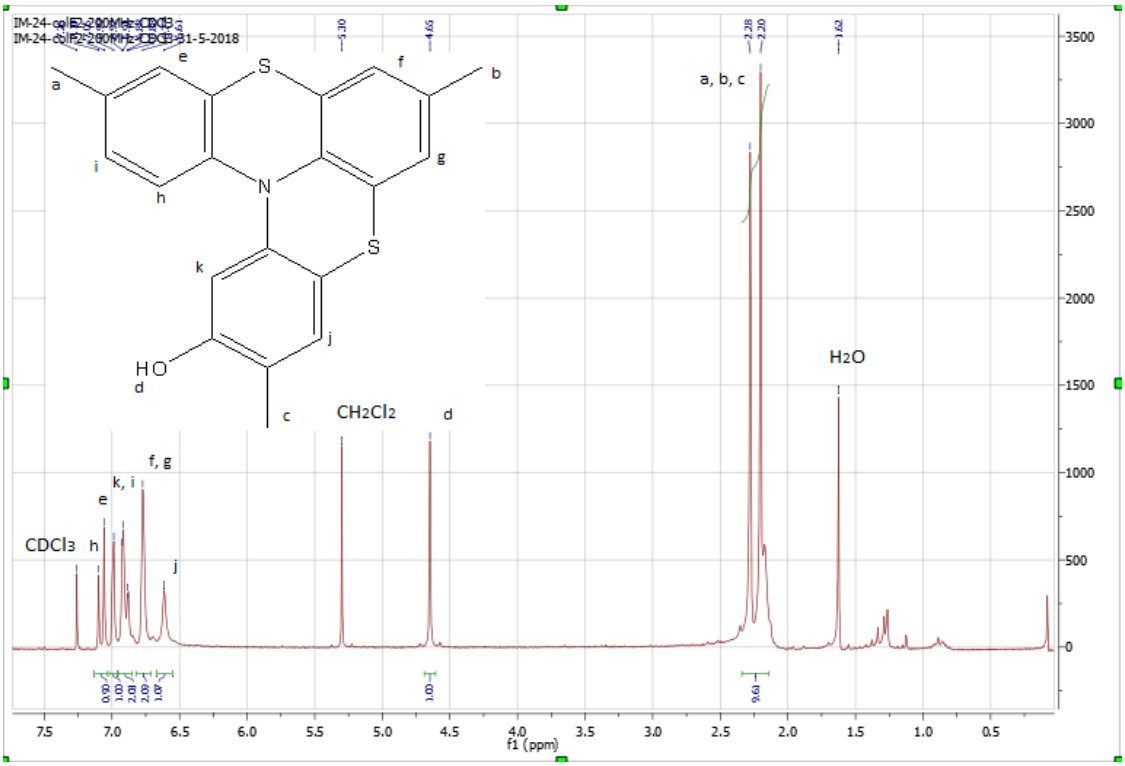


Figure I.1 ^{1}H-RMN spectrum (CDCl3, 400MHz) δ (ppm)

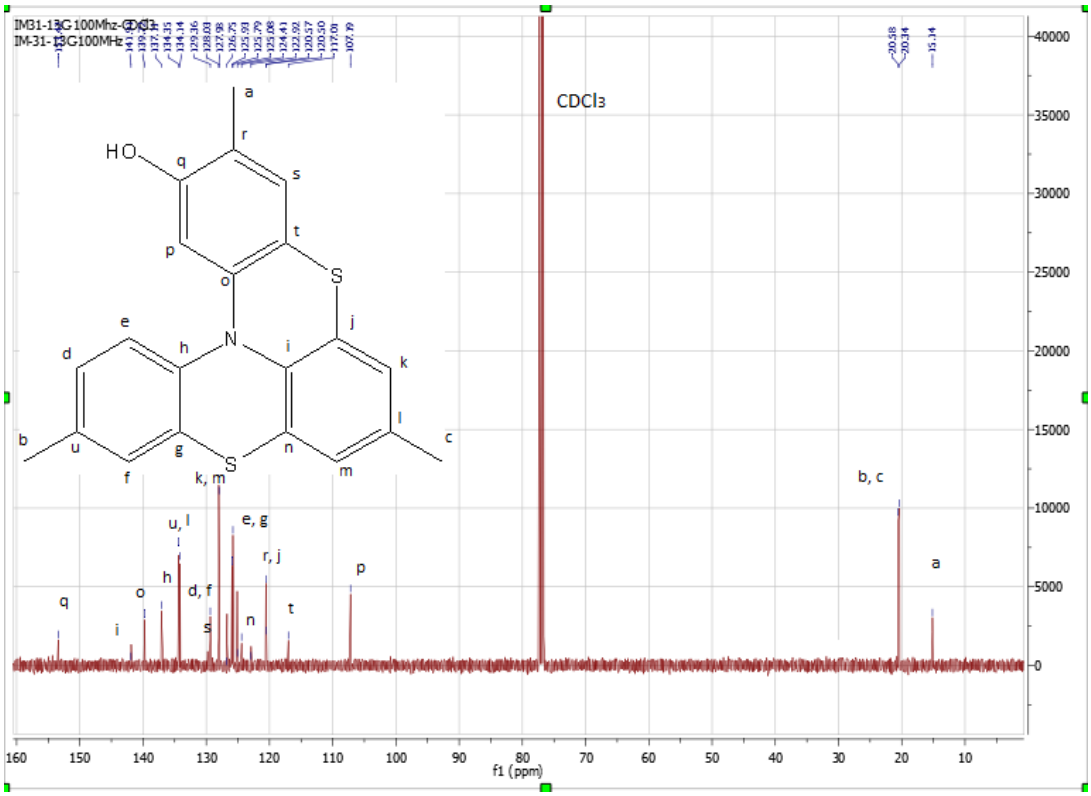


Figure I.2 ^{13}C-RMN spectrum (CDCl3, 100MHz) δ (ppm)

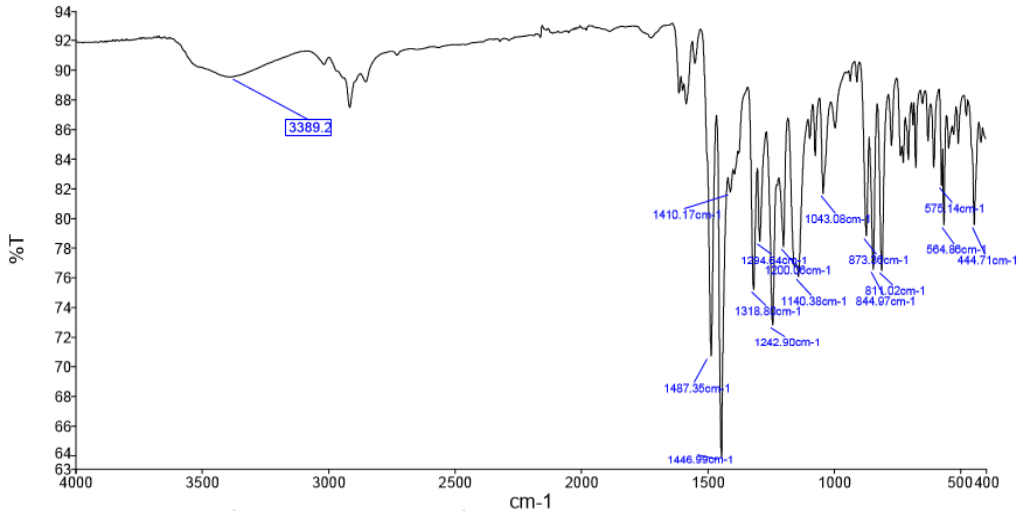


Figure I.3 IR spectrum (cm-1)

Mono-Methacrylate-Helicene:

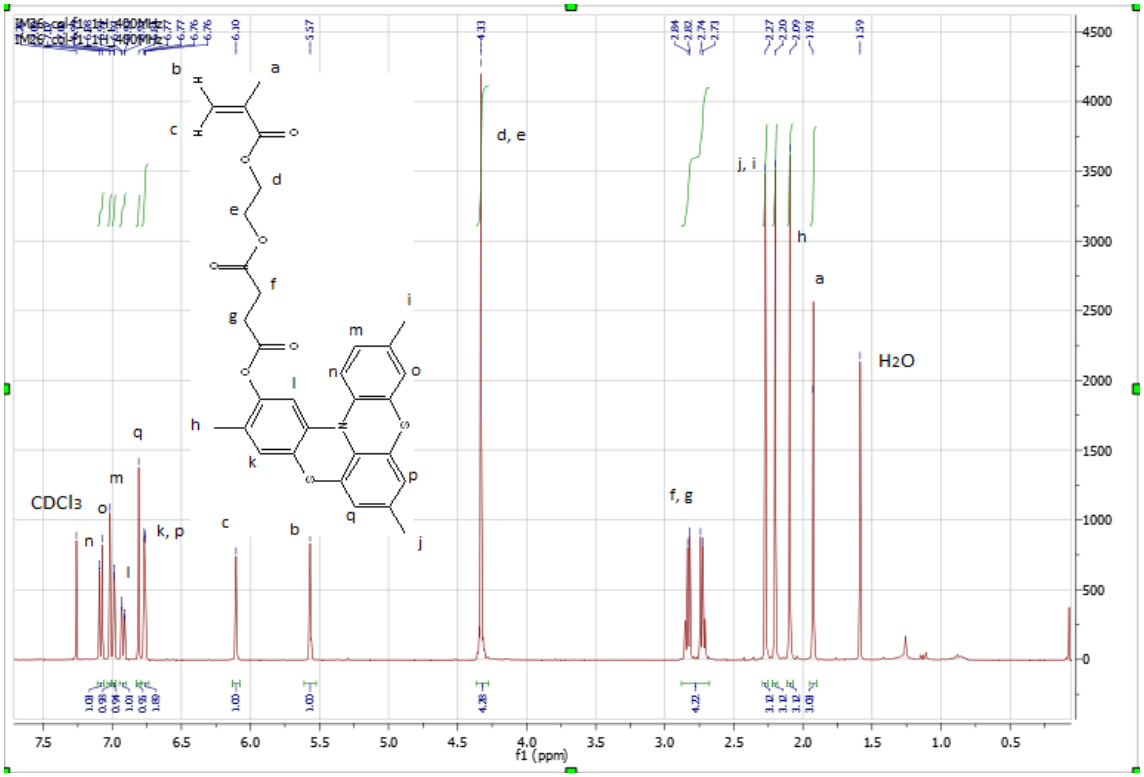


Figure J.1 ^{1}H-RMN spectrum (CDCl3, 400MHz) δ (ppm)

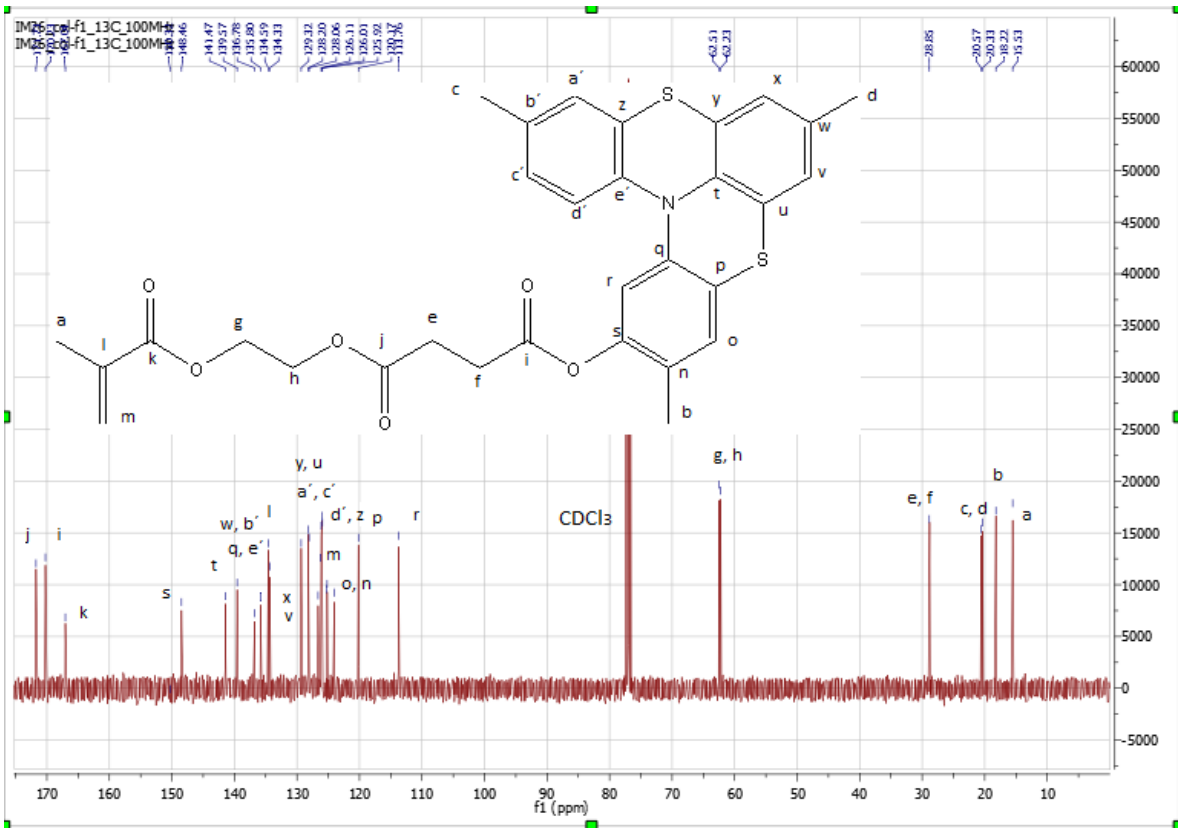


Figure J.2 ^{13}C-RMN spectrum (CDCl3, 100MHz) δ (ppm)

PMHelicene-b-PEG(10000)

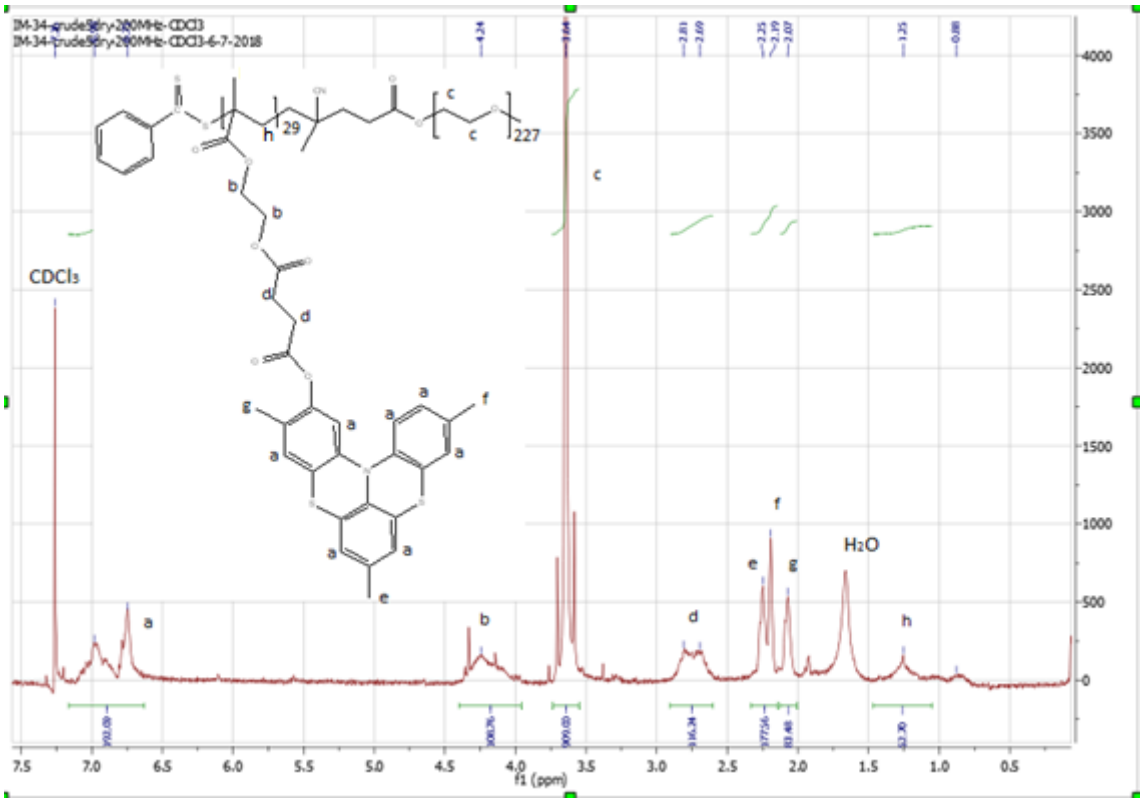


Figure K.1 ^{1}H-RMN spectrum (CDCl3, 200MHz) δ (ppm)