Thiolate Bridged Gold(I) NHC Catalysts: New Approach for Catalyst Design and its Application Trapping Catalytic Intermediates

Renso Visbal,[a,b] Raquel P. Herrera*[c] and M. Concepción Gimeno*[a]

Dedicated to Professor Pablo Espinet on the occasion of his 70th birthday

Abstract: Novel dinuclear *N*-heterocyclic gold complexes with bridging thiolate ligands have been designed to be catalytic precursors with desired properties such as stability, recyclability and the no necessity of additives. The dinuclear compounds [(AuNHC)$_2$(μ-SC$_6$F$_5$)]OTf could slowly release the active catalytic species [Au(NHC)]$^+$ and the precursor [Au(SC$_6$F$_5$)(NHC)] in solution, which means that both species would maintain stable during all catalytic cycle and the pre-catalyst could easily be recovered. These properties shown by the complexes have been taken advantage to get new insights in the gold catalyzed hydroalkoxylation of alkynes, with the aim of clarifying all the steps of the catalytic cycle, together with the characterization of intermediates and final products. Isolation and characterization of the pure final spiroketals and the thermodynamic intermediate have been achieved for the first time. Moreover, the kinetic intermediate has been also detected for the first time.

Introduction

Gold catalysis has attracted great interest in organic synthesis and it is considered one of the most powerful catalytic tool for electrophilic activation of alkynes.[1] Gold compounds exhibit high carbophilicity, which provides strong Lewis acids for the easy C–C multiple bonds activation towards the nucleophilic attack, showing in addition high functional group tolerance under mild reaction conditions.[1] Numerous gold(I) complexes have been developed, which are precursors of the active species in different catalytic reactions. Silver-mediated halide abstraction from gold(I) complexes of the form [L-Au-Cl] produces the *in situ* generation of the catalytically active cationic and neutral species of the form [L-Au-L']X or [L-Au-X], depending on the coordinating nature of the anion X.[2] However, the implication and influence of silver salts in gold catalysis is not totally insignificant, and there is some evidence that the catalytic activity of gold species generated *in situ* by the addition of silver salts can be affected if they are filtered through Celite.[3] These results suggest that the presence of Ag$^+$ cations in solution promotes the formation of different complexes by combination with the [LAu]$^+$ species. Studies on several catalytic systems revealed a long-overlooked "silver effect" in gold catalysis that show a significant difference in the reactivity with and without silver. The addition of different silver salts to promote the chloride abstraction of the well-known [AuCl(JohnPhos)] complex, which is widely used as a catalytic precursor in many organic transformations, has been reported to afford the corresponding chloride-bridged gold(I) complexes (Figure 1, **I**) together with the desired [Au(JohnPhos)]$^+$ species.[4] More recent studies have supported the controversy in the so called "silver effects"[3,5] showing that silver can interact with key intermediates such as the vinyl gold species, giving compounds such as those shown in Figure 1 (**II**).

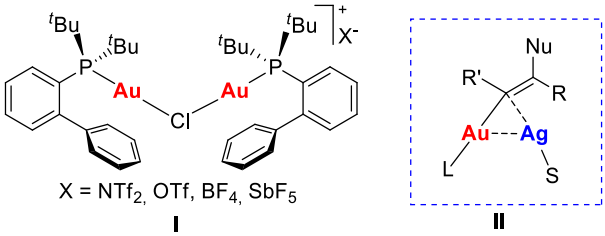

Figure 1. Synthesis of chloride-bridged digold complexes as a consequence of the incomplete abstraction of the chloride ligand (**I**) and proposed catalytic intermediate in the presence of silver (**II**).

This effect may have important implications in studies where the *in situ* generation of the gold(I) active species was made through a silver-promoted chloride abstraction, considering that the digold species probably present different reactivity as catalysts, or the formation of the catalytic intermediate may hinder the protodeauration step, key in the catalytic cycle, among other properties. Then, the biggest problem in the use of gold(I) catalysts generated by the *in situ* addition of silver salts is the difficulty in determining which species is acting as catalyst. In addition, silver salts are very hygroscopic and light sensitive, and in catalytic amounts, are very difficult to weigh and keep under nonacidic reaction medium. Therefore, some research groups have focused their attention on the design of new silver-free protocols that allow the preparation of air-stable precursors and the identification of the final active species. Thus, Gagosz and co-workers described the synthesis of gold(I) complexes **III** (Figure 2) containing a weakly coordinating counteranion (NTf$_2$ = bis(trifluoromethanesulfonyl)imide).[6] Additionally, Echavarren and coworkers prepared the acetonitrile solvate of the JohnPhos

[a] Dr. R. Visbal, Prof. Dr. M. C. Gimeno
Departamento de Química Inorgánica
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH)
CSIC-Universidad de Zaragoza
C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain
E-mail: gimeno@unizar.es
[b] Dr. R. Visbal
Departamento de Química
Facultad de Ciencias Naturales y Exactas. Universidad del Valle
A.A. 25360, Cali, Colombia
[c] Dr. R. P. Herrera
Departamento de Química Orgánica. Laboratorio de Organocatálisis Asimétrica
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH)
CSIC-Universidad de Zaragoza
C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain
E-mail: raquelph@unizar.es

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IV,[7] or Nolan and co-workers prepared the air-stable hydroxide bridged Au(I)-NHC complex **V** (Figure 2).[8]

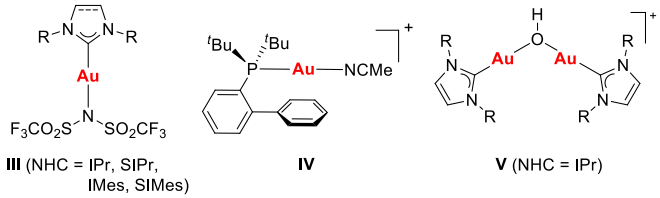


Figure 2. Air-stable NHC-Au(I) complexes **III-V** used as catalysts.

The catalytic activity of **V** was tested in several nitrile hydration reactions and compared to those found for the [(NHC)AuNTf$_2$], with better results observed for the dinuclear species.[8] In another study, the existence of the [{(IPr)Au}$_2$(μ-OH)]BF$_4$ (**V**) has been proposed as a combination of the [(NHC)AuBF$_4$] and [(NHC)AuOH] species, although the latter has not been obtained. Investigations on the hydrophenoxylation of alkynes pointed to a synergistic effect as a consequence of a dual activation pathway promoted by the dissociation of the digold-hydroxide complex (**V**).[9] In both of the previously commented cases, there are two important aspects to be considered: the need for highly stable catalyst precursors, and the efficiency of releasing the catalytically active species [Au(NHC)]$^+$.

Taking into account all these considerations, we aimed to prepare new thiolate bridged gold(I)-NHC catalysts, since to the best of our knowledge, this motif has been overlooked in the literature so far. This pre-catalyst should also be stable enough in solid state and solution to release the catalytically active species and then, be regenerated. Figure 3 summarizes this pivotal idea.

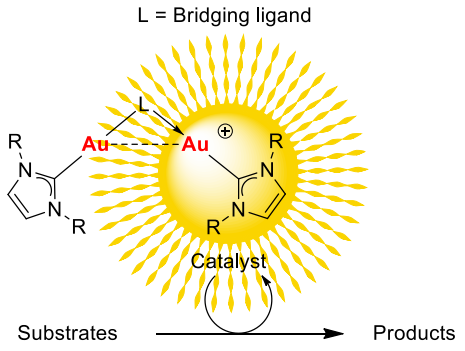
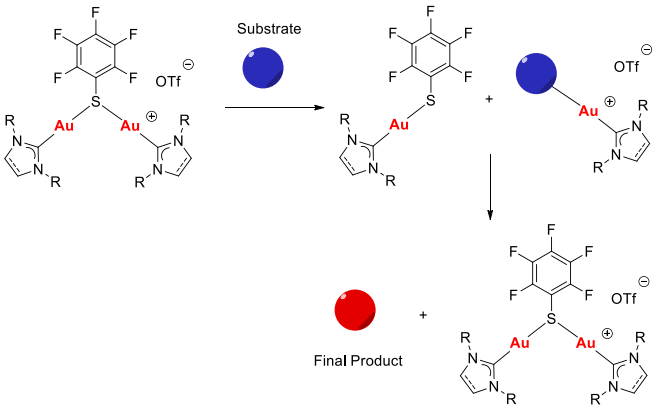


Figure 3. Original idea for the design of the pre-catalyst.

The only precedents for dinuclear thiolate bridging gold complexes were described in 2012 when Gray and Sadighi reported the formation of a novel trigold monocation containing an NHC ligand, [(AuNHC)$_3$]$^+$. The exploration of its reactivity towards oxidative cleavage with different oxidants showed a mixture formation of the cationic [{(IPr)Au}$_2$(μ-SPh)]OTf species as well as the formation of the neutral derivative of the form [(IPr)AuSPh] and the release of hydrogen, but the compounds were neither isolated nor characterized.[10] Independently, Maier's group described the second example of a thiolate bridging gold complex.[11] The same year, Lee and co-workers reported another bridging thiolate complex precatalyst of type [{Au(L)}$_2$(μ-SR)][SbF$_6$] (with L = PR$_3$),[12a] that they isolated and fully characterized in a subsequent article.[12b] However, in the catalytic studies the presence of residual H$^+$ was required to generate the active catalyst in solution.

Herein, we report on the synthesis of stable gold complexes with the pentafluorophenyl thiolate ligand. The less donating properties of this thiolate ligand could give rise to excellent catalyst precursors for the release of the catalytically active species. In addition, the stability of the precursor and easy recovery of the pre-catalyst could help to the study of several catalytic reactions, including the characterization of intermediate reactions (Scheme 1).



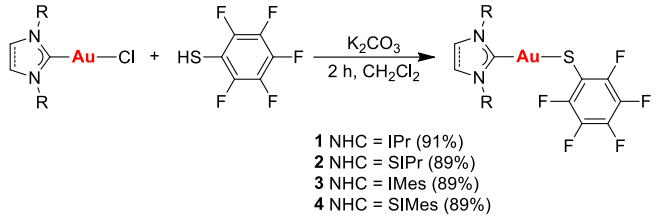
Scheme 1. Release of the catalytic NHC-Au(I) species and cyclic recovery of the pre-catalyst.

In order to prove the viability of this interesting idea, we have tried these catalysts in the gold catalyzed hydroalkoxylation of alkynes, with the aim to shed more light in the intermediate species involved on it.

Results and Discussion

Synthesis of the Thiolate-Gold-NHC Complexes

Thiolate ligands are known for their good σ- and π-donor capabilities, and hence the selection of the appropriate ligand takes an important relevance. The presence of an electron-withdrawing group at the S atom should reduce its electron density, which may cause an enhancement in the lability of the Au-S bond. The good electron-withdrawing properties of the pentafluorophenyl group[13] and the different coordination modes of the [SC$_6$F$_5$]$^-$ fragment make this ligand a possible candidate for this purpose. Following the same procedure as previously reported,[14] the thiolate precursors **1**-**4** were prepared from the corresponding [(NHC)AuCl] complexes and thiol HSC$_6$F$_5$ in the presence of K$_2$CO$_3$ (Scheme 2).



Scheme 2. Synthesis of thiolate gold(I)-NHC complexes **1**-**4**. IPr: 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene; SIPr: 1,3-Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene; IMes: 1,3-Dimesitylimidazol-2-ylidene; SIMes: 1,3-Dimesitylimidazolin-2-ylidene.

All complexes were obtained as white solids and in good yields (89-91%). The ^{1}H NMR spectra of the complexes are very similar to those reported for the gold chloride NHC precursors. However, in the ^{13}C{^{1}H}-APT spectra the signals corresponding to the C_{carb} are downfield showing resonances around 183 and 203 ppm for the unsaturated and saturated derivatives, respectively. This shifting could be rationalized as a consequence of the higher π-donor capacity of the chloride ligand compared to S-C_6F_5 group. As expected, in the ^{19}F NMR spectra three groups of signals around -132, -164 and -165 ppm corresponding to the *o*-, *p*- and *m*-C_6F_5, respectively, are observed. In addition, the peaks observed in the mass spectra associated to the $[M]^+$ species confirmed the presence of the complexes **1**-**4** in solution.

Furthermore, the molecular structure of complex **3** was obtained by single crystal X-ray diffraction analysis. As shown in Figure 4, complex **3** crystallizes in the monoclinic space group $P2_1/c$ with one molecule occupying the asymmetric unit. The X-ray crystal structure shows a clear linear disposition around the gold center with a C1-Au1-S1 bond angle of 178.09(6)°. The Au1-C1 of 2.003(2) and Au1-S1 of 2.2948(7) Å bond distances are also in agreement with those reported for other thiolate gold(I) complexes containing NHC ligands.[12b]

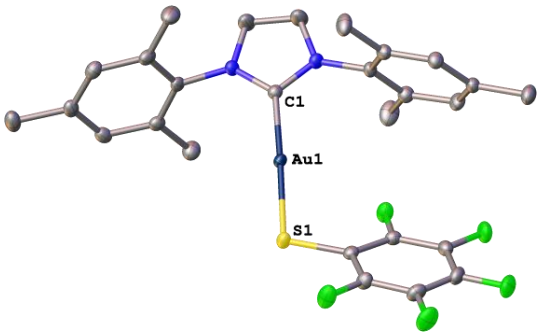
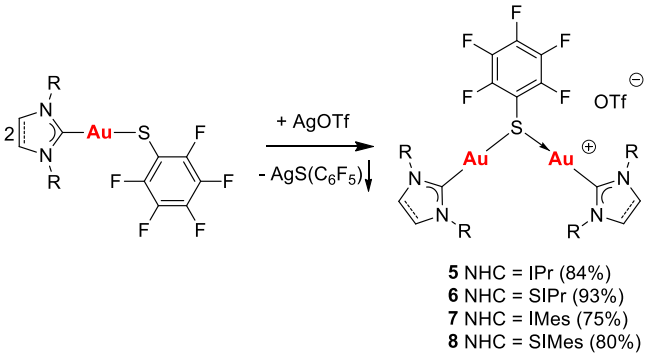


Figure 4. Molecular structure of complex **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au1-C1 2.003(2), Au1-S1 2.2948(7), S1-C22 1.764(2), N1-C1 1.353(3), N2-C1 1.347(3), C1-Au1-S1 178.09(6), C22-S1-Au1 106.62(8).

After the preparation of the precursors **1**-**4**, the next goal was the synthesis of the corresponding thiolate-bridged gold(I)-NHC complexes **5**-**8**. For this purpose, there are two convenient methods. The first one involves the addition of one equivalent of the [(NHC)AuX] (X = non-coordinating anion) to the corresponding precursor. However, isolation of such species is not easy due to the marked instability that complexes of the form [(NHC)AuX] present under ambient conditions. On the other hand, the second method does not require the isolation of the desired [(NHC)AuX] species, which can easily be prepared by *in situ* generation after addition of 0.5 equiv. of the corresponding silver salt. Fortunately, this was rapidly corroborated and, as shown in Scheme 3, the addition of 0.5 equivalents of AgOTf to a solution of the complexes **1-4** in dichloromethane, protected from light, gave the corresponding thiolate-bridged gold(I)-NHC complexes **5**-**8**.



Scheme 3. Synthesis of bridging thiolate digold(I)-NHC complexes **5**-**8**.

All complexes were isolated with hexane after filtration over Celite in good yields as beige solids, and have demonstrated to be very stable even for months. All complexes were fully characterized by the conventional spectroscopic techniques. Suitable crystals for X-ray diffraction analysis were obtained for complex **5** (Figure 5). The complex crystallizes in the monoclinic space group $P2_1/n$ with one molecule occupying the asymmetric unit. As expected, the thiolate group presents a distorted tetrahedral geometry with the lone pair of electrons in one of the apical positions and appears bonded to two gold(I) centers. The Au1-S1 and Au2-S1 bond distances of 2.303(2) and 2.311(2) Å are slightly longer than those found for the precursor, while the bond angles (C-Au-S) are a little more deviated from linearity, especially the C7-Au1-S1 bond angle, that presents a value of 173.4(3)°. The Au-C bonds are 1.995(9) and 2.014(9) Å, which are dissimilar but in a similar range to those found in the mononuclear precursor. The long bond distance between the gold centers (3.903 °A) confirms the absence of aurophilic interactions, which is in agreement with the wide Au1-S1-Au2 angle of 115.57(10)° and other similar structures with phosphines.[14]

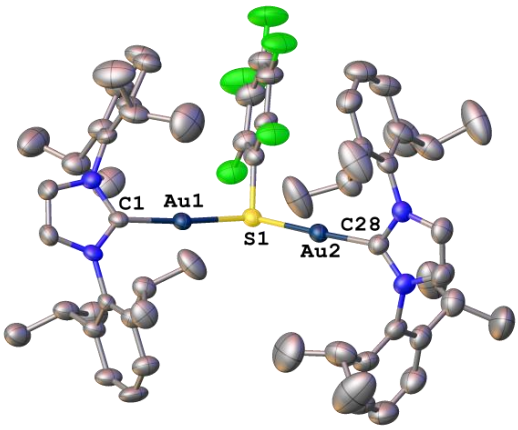
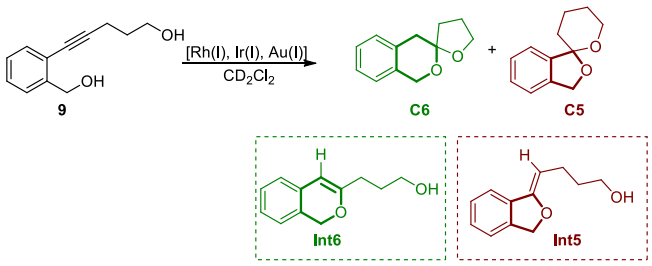


Figure 5. Depiction of the molecular structure of complexes **5** and a summary of its most relevant bond lengths (Å) and angles (°). Complex **5**: Au1-S1 2.303(2), Au1-C7 1.995(9), Au2-S1 2.311(2), Au2-C34 2.014(9), S1-C1 1.789(9); C7-Au1-S1 173.4(3), C34- Au2-S1 177.3(3), Au1-S1-Au2 115.57(10).

Catalytic Study

In order to evaluate the catalytic activity of the synthesized thiolate-bridged gold(I)-NHC complexes **5-8**, the dihydroalkoxylation of alkyne diol **9** for the synthesis of spiroketals, depicted in Scheme 4, was explored.



Scheme 4. Dihydroalkoxylation of alkyne diols **9**.

The cyclization of **9** to give spirocycles **C6** and **C5** has been firstly investigated by Messerle and co-workers using Rh and/or Ir complexes as catalysts.[15] However, in none of these previous reported examples the final products were isolated. Moreover, the intermediates **Int6** and **Int5** have been only invoked by these authors and proposed in the mechanism for the synthesis of spiroketals **C6** and **C5** as a result of the initial electrophilic activation of the alkyne through π bonding of the metal center and subsequent attack of the OH group.[15] The authors also concluded that the first addition of alcohol to the alkyne is likely to be the rate determining step. Nevertheless, intermediates **Int6** and **Int5** have never been purified by any author. Very recently, Hashmi and co-workers have described several highly efficient gold catalysts for this system,[16] achieving very low TONs using low catalyst loadings. But in no case the products were isolated. Moreover, in other of the scarce example where a gold complex has been used in this model reaction, Shue, Li and co-workers postulated the implication of the gold atom in both steps of the reaction mechanism.[17] Therefore, to the best of our knowledge neither the spirocycles **C6** and **C5** nor the intermediates **Int6** and **Int5** have never been isolated and moreover, the intermediates **Int6** and **Int5** have only been invoked but not detected. With this background in mind, and the challenging task to obtain and to characterize these spiroketals and intermediates for the first time, this reaction was selected to test the catalytic activity of our gold complexes **5-8**.

Firstly, we monitored the reaction by NMR using IPr complex derivative **5** with different catalyst loading and the results are reported in Table 2.

Table 2. Screening of gold complex **5**.[a]

Entry	Cat. (mol%)	Time (h)	yield (%)[b]	C6: C5: Int6: Int5
1	7	0.17	>99	0 : 0 : 27 :73
2	5	0.25	>99	0 : 0 : 29 : 71
3	1	0.50	>99	0 : 75: 25: 0
4	0.1	2.50	>99	33 : 67 : 0 : 0

[a] All reactions were carried out in an NMR tube (0.1 mmol of **9** in CD_2Cl_2 500 µL) at 40 °C and were monitored by ^1H NMR spectroscopy. [b] Yields determined by NMR experiments using TTBB (1,3,5-tri-*tert*butylbenzene) as internal standard.

As shown in Table 2, a complete conversion of the substrate **9** was observed in all cases and the major products are also in agreement with the Baldwin's rules,[18] as expected. The reactions were stopped when total conversion of diol **9** into the products was observed. Therefore, increasing amount of catalyst affords shorter reactions times. It is wort noting that the selectivity obtained in the proofs is very interesting. These results support our initial hypothesis, since it is also important to remark that with our catalyst **5** was not necessary the use of an additional additive (such as silver compounds).

A comparison of the selectivity reveals significant differences between catalyst **5** and those catalysts previously used. The rhodium and iridium complexes showed a marked tendency to stabilize the formation of compound **C6** over **C5** in almost all cases,[15a,d] while the gold(I) catalysts described by Hashmi and co-workers did not show any selectivity, affording a **C6**: **C5** ratio close to 1:1.[16] In contrast, in our case spirocycle **C5** is obtained doubled the quantity of **C6** (entry 4) and the same occurs with the intermediate **Int5** over **Int6** (entries 1 and 2). This fact means that the five-membered cycle is preferably formed against the initial six-membered ring (present in **C6** and **Int6**).

Another interesting feature that can be observed in Table 2 is that a total conversion of the reaction occurs in 2.5 h for a 0.1 mol% of catalyst loading, giving rise a mixture of **C6**: **C5** of 1:2 (entry 4). However, an increase in the amount of catalyst produces a mixture of the five-membered spiroketal **C5** and the detection of intermediate **Int6** (entry 3), and a further increase affords only intermediates **Int6** and **Int5**, being the latter the most abundant (entries 1 and 2). It seems that if the reaction is really fast, 17-25 min for a 7-5 mol% catalyst loading, we are able to detect the intermediates of the reaction, in the first reaction step.

Interestingly, the transformation into the spirocycle occurs faster from the intermediate **Int5** to final product **C5** (see for instance entry 3, where all intermediate **Int5** has been already transformed into **C5**, while intermediate **Int6** still remains). Moreover, it is the first time that intermediates **Int6** and **Int5** are detected and obtained as the major products of theses

reactions. This would be opposite to the previous hypothesis invoked by Messerle and co-workers, where the first step was proposed as the rate limiting step. In contrast, the accumulation of intermediates **Int6** and **Int5** would be in agreement with the second cyclization being the rate limiting step using gold as catalyst. Since with more catalyst the intermediates and **Int5** remain unaltered (entries 1 and 2), this could be in agreement with the lack of participation of the gold center in the second step of the reaction, as in these cases (with higher amount of catalyst) more products **C6** and **C5** should be expected. These surprising observations encouraged us to go more in depth in the study of this interesting reaction.

At this point, we decided to change several variables in the experiments, mainly the solvent, temperature or gold catalyst in order to gain insight about the mechanism operating in this process. It is interesting to note that these reactions have been only studied in chlorinated solvents (CD_2Cl_2, $CDCl_3$ and $CDCl_2CDCl_2$). Then, in the first place, the activity in other non-chlorinated solvent, such as CD_3CN, was evaluated (Table 3).

Table 3. Screening of gold complexes **5-8** (1 mol%) in CD_3CN.[a]

Entry	Cat.	T (ºC)	Time (h)	C6: C5: Int6: Int5
1	**5**	40	<0.5	0:0:**54**:**46**
2	**5**	r.t	2	0:0:**51**:**49**
3	**5**	5	7	0:0:**48**:**52**
4	**6**	40	<0.5	0:0:**56**:**44**
5	**6**	r.t.	2	0:0:**53**:**47**
6	**6**	5	7	0:0:**51**:**49**
7	**6**	-20	27[b]	0:0:**48**:**52**
8	**7**	40	5[c]	**40**:**39**:**21**:0
9	**7**	r.t.	5[d]	0:**44**:**56**:0
10	**8**	40	3	0:**37.5**:**62.5**:0
11	**8**	r.t.	5[e]	0:**23**:**61**:**16**

[a] To a mixture of diol **9** (0.05 mmol) in 150 µL of CD_3CN, gold complex **5-8** (0.0005 mmol) in 100 µL of CD_3CN is added at the desired temperature. [b] 78% conversion. [c] 65% conversion. [d] 50% conversion. [e] 90% conversion.

Surprisingly, when the reaction was performed in the presence of CD_3CN with **5**, it seems that the major products are the intermediates **Int6** and **Int5** at 40 °C (compare entry 1 in Table 3, against entry 3 in Table 2). The same occurs at room temperature and a 5 ºC (entries 2 and 3, Table 3). When the temperature of the reaction is decreased for a catalyst (see catalysts **5** and **6**) the amount of intermediate **Int5** slightly increases in comparison with **Int6** (entries 1 to 7, Table 3). For catalysts **7** and **8**, when the temperature increases intermediate **Int5** is rapidly transformed in product **C5** while intermediate **Int6** remains (entries 8-11, Table 3). On the base of these results, we could affirm that the intermediate **Int5** is the kinetic one and **Int6** is the thermodynamic.

Because of the mixture of both spiroketal products **C6** and **C5** or intermediates **Int6** and **Int5** are difficult to separate by column chromatography, we used the mixture of spirocycle **C5** and intermediate **Int6** obtained with catalyst **7** (entry 9, Table 3) or catalyst **8** (entry 10, Table 3) in order to isolate these compounds. These mixtures of products allowed us the isolation and characterization of these compounds **C5** and **Int6** for the first time in the literature.

Moreover, and in order to support the plausible active specie of our process, we have compared the activity of dinuclear complexes **6** and **8** against the activity of their mononuclear complexes **2** and **4**, respectively, under the same reaction conditions at 40º C, r.t and 5 ºC (see supporting information for the details). As expected, the mononuclear complexes **2** and **4** did not promote the reaction after the same reaction time. These interesting results could support the hypothesized mode of activation proposed for our catalysts in Scheme 1.

Since we were convinced that the second cyclization step can occur in the total absence of gold (or other metal) and that traces of acid present in chlorinated solvent could be responsible of the second step,[19] we performed the ^{1}H NMR spectrum of a sample of pure intermediate **Int6**, using $CDCl_3$, and the transformation into **C6** was instantaneous (Figure 6).

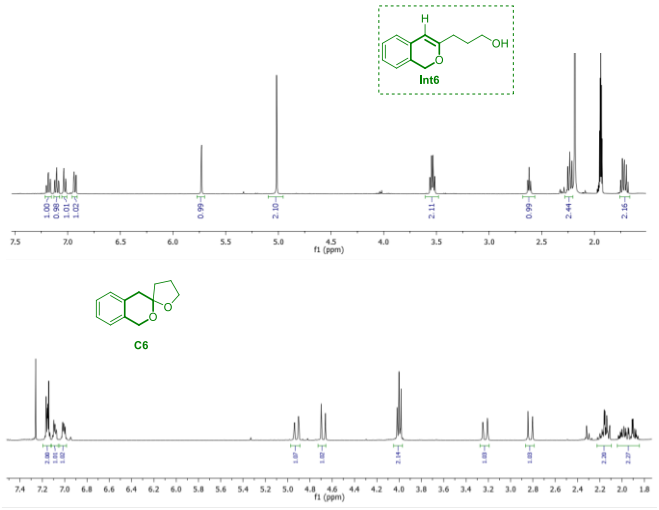
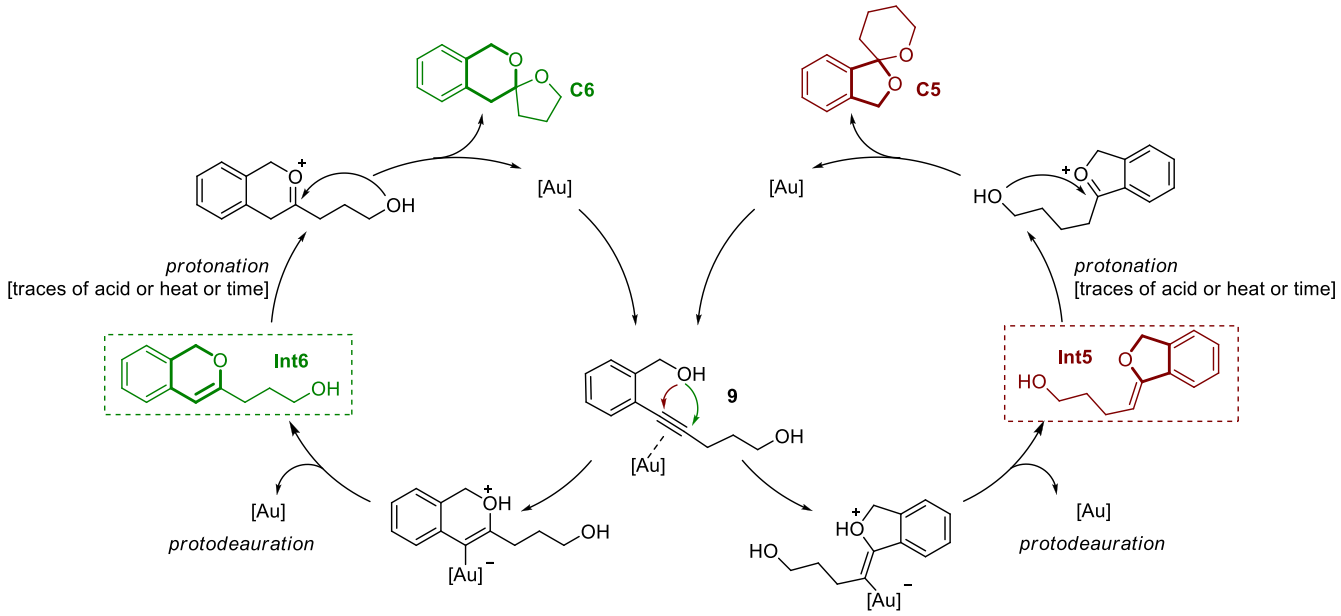


Figure 6. Transformation of **Int6** into spirocycle **C6** in $CDCl_3$ in the absence of catalyst.

The ^{1}H NMR experiment supports our hypothesis about the second step of the reaction and this approach also lets us to isolate **C6** for the first time.

At this point, we haven't been able to isolate intermediate **Int5**, since it is very reactive and in the column chromatography is transformed in the final spirocycle **C5**. Interestingly, we report in the supporting information a spectrum of a mixture of **Int6**:**Int5** in order to proof the capture of both intermediates.

On the base of these results, a plausible mechanism is envisioned and depicted in Scheme 5.



Scheme 5. Proposed catalytic cycle.

The reaction would initiate by the formation of a π-coordinated alkyne–Au complex, which would enhance the electrophilicity of the triple bond in **9**. This would favor an intramolecular addition of the hydroxyl group to the triple bond giving rise to a first 5-exo-dig or 6-endo-dig cyclization. The resulting enol vinylgold intermediate would suffer a protodeauration with the subsequent release of the gold atom to start the cycle and affording to intermediates **Int6** and **Int5**. As demonstrated, it is possible to stop the process at this step in the absence of protons, since the gold atom is not involved in the subsequent catalytic pathway. In contrast, if there are acidic protons in the medium, products **Int6** and **Int5** would evolve to the corresponding spiroketals **C6** or **C5**, respectively, after a tautomerization and final cyclization. We have also observed that the temperature (see table 3) and the time (see supporting information for a spectrum) could transform intermediate **Int6** and **Int5** in the corresponding spiroketals **C6** or **C5**, especially in the case of intermediate **Int5**. The oxonium ion generated from **Int5** could be expected to be more electrophilic in comparison with that generated from **Int6**, which would favor the subsequent attack of the OH group giving rise to spiroketal **C5** faster.

Conclusions

In conclusion, we have developed a series of novel dinuclear *N*-heterocyclic gold complexes with bridging thiolate ligands. These novel complexes can slowly release the active catalytic species $AuNHC^+$ and the precursor $[Au(SC_6F_5)(NHC)]$ in the reaction medium, in the absence of any silver additive, and both species maintain stable during the whole catalytic cycle. We have taken advantage of these excellent properties to shed light into the gold catalyzed hydroalkoxylation of alkynes, with the aim of clarifying all the steps of the catalytic cycle, together with the characterization of intermediates and final products. Interestingly, we have isolated and characterized the pure final spiroketals and the thermodynamic intermediate of this process for the first time. Moreover, the kinetic intermediate has been also detected for the first time. This new family of catalysts opens the door for further exploration of new processes without the necessity of using any additive. Additionally, the exploration of new reactivities using gold complexes could be envisioned.

Experimental Section

Instrumentation. C, H, and N analysis were carried out with a PERKIN-ELMER 2400 microanalyzer. Mass spectra were recorded on a BRUKER ESQUIRE 3000 PLUS, with the electrospray (ESI) technique. ^1H and $^{13}C\{^1H\}$-APT and ^{19}F NMR, including 2D experiments, were recorded at room temperature on a BRUKER AVANCE 400 spectrometer (^1H, 400 MHz, ^{13}C, 100.6 MHz; ^{19}F, 376.5 MHz) or on a BRUKER AVANCE II 300 spectrometer (^1H, 300 MHz, ^{13}C, 75.5 MHz; ^{19}F, 282.3 MHz), with chemical shifts (δ, ppm) reported relative to the solvent peaks of the deuterated solvent.

Crystallography. Crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of an Xcalibur Oxford Diffraction (**3**) or a Smart Apex Duo diffractometer (**5**) equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ = 0.71073 Å). Scan type: ω. Absorption corrections based on multiple scans were applied with the program SADABS,[20] or using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm.[21] The structures were solved with the ShelXS structure solution program using direct methods and by using Olex2 as the graphical interface.[22] All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were included in calculated positions and refined using a riding model. Refinements were carried out by full-matrix least-squares on F^2 for all data. Further details of the data collection and refinement are given in the supporting information. CCDC Deposition Number 1922320 (**3**)-1922321 (**5**) contains the crystallographic information.

Starting Materials. All reactions were performed under air atmosphere and solvents were used as received without further purification or drying. [AuCl(tht)][23] and the unsaturated imidazolium salts[24] were prepared according to published procedures. The saturated imidazolium salts,

HS−C_6F_5 and K_2CO_3 are commercially available from Aldrich and PANREAC. The chloride complexes of the form [(NHC)AuCl] were prepared according to published procedures.[25] Diol **9** was prepared following the procedure reported in the literature.[15a]

General procedure for the synthesis of complexes 1-4. To a mixture of the corresponding gold(I) complex of the form [(NHC)AuCl] (0.30 mmol) and [(C_6F_5)−SH] (0.30 mmol) in CH_2Cl_2 (15 mL) was added K_2CO_3 (7 mmol) and stirred for 2 h. Then, the mixture was filtered through Celite and the solvent was removed in vacuo until 2 mL (*c.a.*). The product was precipitated with hexane (20 mL) and washed (3 x 5 mL) to give a white solid.

[(IPr)Au(SC_6F_5)] (**1**). Yield: 0.2147 g (91%). ^{1}H NMR ($CDCl_3$, 300 MHz, 294 K): δ 7.48 (t, J_{H-H} = 7.8 Hz, 2H, Ph), 7.24 (d, J_{H-H} = 7.8 Hz, 4H, Ph), 7.16 (s, 2H, Im), 2.52 (hept, J_{H-H} = 6.7 Hz, 4H, CH−$(CH_3)_2$), 1.27 (d, J_{H-H} = 6.9 Hz, 12H, CH_3), 1.20 (d, J_{H-H} = 6.9 Hz, 12H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 294 K) δ 184.0 (Im_{carb}), 145.8 (Ph), 134.1 (Ph), 130.7 (Ph), 124.2 (Ph), 123.0 (Im), 28.9 (CH−(CH3)$_2$), 24.3 (CH_3), 24.2 (CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz, 294 K): δ -132.37 (m, *o*-C_6F_5), -164.12 (t, J_{F-F} = 21.1 Hz, *p*-C_6F_5), -165.19 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 785.1 [M]$^+$. Anal. Calcd. (%) for $C_{33}H_{36}N_2F_5SAu$: C, 50.51; H, 4.62; N, 3.57. Found: C, 50.67; H, 4.35; N, 3.39.

[(SIPr)Au(SC_6F_5)] (**2**). Yield: 0.2089 g (89%). ^{1}H NMR ($CDCl_3$, 300 MHz, 294 K): δ 7.38 (t, J_{H-H} = 7.8 Hz, 2H, Ph), 7.17 (d, J_{H-H} = 7.8 Hz, 4H, Ph), 4.04 (s, 4H, Im), 3.01 (hept, J_{H-H} = 6.7 Hz, 4H, CH−$(CH_3)_2$), 1.34 (d, J_{H-H} = 6.9 Hz, 12H, CH_3), 1.31 (d, J_{H-H} = 6.9 Hz, 12H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 294 K) δ 203.7 (Im_{carb}), 146.8 (Ph), 134.1 (Ph), 129.9 (Ph), 124.5 (Ph), 53.7 (Im), 29.1 (CH−$(CH_3)_2$), 24.9 (CH_3), 24.4 (CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz, 294 K): δ -132.23 (m, *o*-C_6F_5), -163.98 (t, J_{F-F} = 21.1 Hz, *p*-C_6F_5), -165.13 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 787.0 [M]$^+$. Anal. Calcd. (%) for $C_{33}H_{38}N_2F_5SAu$: C, 50.38; H, 4.87; N, 3.56. Found: C, 50.61; H, 4.47; N, 3.37.

[(IMes)Au(SC_6F_5)] (**3**). Yield: 0.1866 g (89%). ^{1}H NMR ($CDCl_3$, 400 MHz, 294 K): δ 7.09 (s, 2H, Im), 6.96 (s, 4H, Ph), 2.33 (s, 6H, CH_3), 2.09 (s, 12H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 101 MHz, 294 K) δ 182.0 (Im_{carb}), 139.7 (Ph), 134.7 (Ph), 134.6 (Ph), 129.2 (Ph), 122.0 (Im), 21.0 (CH_3), 17.7 (CH_3). ^{19}F NMR ($CDCl_3$, 377 MHz, 294 K): δ -132.66 (m, *o*-C_6F_5), -164.24 (t, J_{F-F} = 21.0 Hz, *p*-C_6F_5), -165.35 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 700.9 [M]$^+$. Anal. Calcd. (%) for $C_{27}H_{24}N_2F_5SAu$: C, 46.29; H, 3.45; N, 4.00. Found: C, 46.56; H, 3.82; N, 3.89.

[(SIMes)Au(SC_6F_5)] (**4**). Yield: 0.1880 g (89%). ^{1}H NMR ($CDCl_3$, 400 MHz, 294 K): δ 6.90 (s, 4H, Ph), 3.98 (s, 4H, Im), 2.30 (s, 12H, CH_3), 2.28 (s, 6H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 101 MHz, 294 K) δ 202.8 (Im_{carb}), 139.0 (Ph), 135.7 (Ph), 134.7 (Ph), 129.6 (Ph), 50.9 (Im), 21.0 (CH_3), 18.0 (CH_3). ^{19}F NMR ($CDCl_3$, 377 MHz, 294 K): δ -132.60 (m, *o*-C_6F_5), -164.05 (t, J_{F-F} = 21.0 Hz, *p*-C_6F_5), -165.29 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 702.9 [M]$^+$. Anal. Calcd. (%) for $C_{27}H_{26}N_2F_5SAu$: C, 46.16; H, 3.73; N, 3.99. Found: C, 46.46; H, 3.72; N, 3.91.

General Procedure for the Synthesis of Complexes 5-8. To a solution of the corresponding thiolate gold(I) complex [(NHC)Au(SC_6F_5)] (0.127 mmol) in a mixture of CH_2Cl_2/MeOH (20 mL) was added AgOTf (0.64 mmol) and stirred for 1 h. Then, the mixture was filtered through Celite and the solvent was removed in vacuo until 2 mL (*c.a.*). The product was precipitated with hexane (20 mL) and washed (3 x 5 mL) to give a beige solid.

[{(IPr)Au}$_2$(μ-SC_6F_5)]OTf (**5**). Yield: 0.0853 g (84%). ^{1}H NMR ($CDCl_3$, 300 MHz, 294 K): δ 7.45 (t, J_{H-H} = 7.6 Hz, 2H, Ph), 7.34 (s, 4H, Im), 7.16 (d, J_{H-H} = 7.7 Hz, 4H, Ph), 2.34 (hept, J_{H-H} = 6.0 Hz, 8H, CH−$(CH_3)_2$), 1.17 (d, J_{H-H} = 6.9 Hz, 24H, CH_3), 1.02 (d, J_{H-H} = 6.9 Hz, 24H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 294 K) δ 176.9 (Im_{carb}), 145.6 (Ph), 133.5 (Ph), 130.9 (Ph), 124.6 (Im), 124.1 (Ph), 28.8 (CH−$(CH_3)_2$), 24.5 (CH_3), 24.1 (CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz, 294 K): δ -78.10 (s, OTf^-), -129.19 (m, *o*-C_6F_5), -155.08 (t, J_{F-F} = 21.5 Hz, *p*-C_6F_5), -160.01 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 1369.5 [M]$^+$. Anal. Calcd. (%) for $C_{61}H_{72}N_4F_8O_3S_2Au_2$: C, 48.22; H, 4.78; N, 3.69. Found: C, 48.35; H, 4.51; N, 3.40.

[{(SIPr)Au}$_2$ (μ-SC_6F_5)]OTf (**6**). Yield: 0.0903 g (93%). ^{1}H NMR ($CDCl_3$, 300 MHz, 294 K): δ 7.33 (t, J_{H-H} = 7.8 Hz, 4H, Ph), 7.07 (d, J_{H-H} = 7.8 Hz, 8H, Ph), 4.12 (s, 8H, Im), 2.87 (hept, J_{H-H} = 6.8 Hz, 8H, CH−$(CH_3)_2$), 1.27 (d, J_{H-H} = 6.8 Hz, 24H, CH_3), 1.07 (d, J_{H-H} = 6.8 Hz, 24H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 294 K) δ 197.7 (Im_{carb}), 146.7 (Ph), 133.5 (Ph), 130.1 (Ph), 124.4 (Ph), 54.1 (Im), 28.9 (CH−$(CH_3)_2$), 25.1 (CH_3), 24.2 (CH_3). ^{19}F NMR ($CDCl_3$, 282 MHz, 294 K): δ -78.26 (s, OTf^-), -129.00 (m, *o*-C_6F_5), -155.25 (t, J_{F-F} = 21.0 Hz, *p*-C_6F_5), -159.89 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 1373.5 [M]$^+$. Anal. Calcd. (%) for $C_{61}H_{76}N_4F_8O_3S_2Au_2$: C, 48.10; H, 5.03; N, 3.68. Found: C, 47.92; H, 4.77; N, 3.49.

[{(IMes)Au}$_2$ (μ-SC_6F_5)]OTf (**7**). Yield: 0.0642 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz, 294 K): δ 7.28 (s, 4H, Im), 6.94 (s, 8H, Ph), 2.36 (s, 12H, CH_3), 2.02 (s, 24H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 101 MHz, 294 K) δ 174.9 (Im_{carb}), 140.1 (Ph), 134.7 (Ph), 134.3 (Ph), 129.4 (Ph), 123.6 (Im), 21.2 (CH_3), 17.8 (CH_3). ^{19}F NMR ($CDCl_3$, 377 MHz, 294 K): δ -78.09 (s, OTf^-), -129.28 (m, *o*-C_6F_5), -155.44 (m, *p*-C_6F_5), -161.18 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 1201.3 [M]$^+$. Anal. Calcd. (%) for $C_{49}H_{48}N_4F_8O_3S_2Au_2$: C, 43.56; H, 3.58; N, 4.15. Found: C, 43.67; H, 3.72; N, 4.01.

[{(SIMes)Au}$_2$(μ-SC_6F_5)]OTf (**8**). Yield: 0.0685 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz, 294 K): δ 6.87 (s, 8H, Ph), 4.10 (s, 8H, Im), 2.30 (s, 12H, CH_3), 2.24 (s, 24H, CH_3). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 294 K) δ 197.0 (Im_{carb}), 139.1 (Ph), 135.6 (Ph), 134.2 (Ph), 129.6 (Ph), 51.3 (Im), 21.1 (CH3), 18.0 (CH_3). ^{19}F NMR ($CDCl_3$, 377 MHz, 294 K): δ -78.09 (s, OTf^-), -129.17 (m, *o*-C_6F_5), -155.62 (m, *p*-C_6F_5), -161.14 (m, *m*-C_6F_5). ESI$^+$-MS, *m/z*: 1205.1 [M]$^+$. Anal. Calcd. (%) for $C_{49}H_{52}N_4F_8O_3S_2Au_2$: C, 43.43; H, 3.87; N, 4.13. Found: C, 43.86; H, 3.70; N, 3.96.

Catalysis. To a mixture of diol **9** (0.05 mmol) in 150 μL of CD_3CN, gold complex **5-8** (0.0005 mmol) solved in 100 μL of CD_3CN is added at the desired temperature. The resulting reaction mixture was monitored by thin-layer chromatography. After the indicated reaction time in Table 3, the conversions are given by ^{1}H NMR and the corresponding spiroketals **C6** or **C5** or intermediate **Int6** were isolated by column chromatography (SiO_2, using Hex/Et_2O 95:5-80:20).

4,5-dihydro-3*H*-spiro[furan-2,3'-isochroman] (**C6**). ^{1}H NMR ($CDCl_3$, 400 MHz, 294 K): δ 7.19-7.12 (m, 2H, Ph), 7.11-7.05 (m, 1H, Ph), 7.05-6.97 (m, 1H, Ph), 4.92 (d, J_{H-H} = 14.7 Hz, 1H, CH_2), 4.68 (d, J_{H-H} = 14.8 Hz, 1H, CH_2), 4.00 (dd, J_{H-H} = 9.7, 4.0 Hz, 2H, CH_2), 3.23 (d, J_{H-H} = 16.4 Hz, 1H, CH_2), 2.82 (d, J_{H-H} = 16.3 Hz, 1H, CH_2), 2.21-2.09 (m, 2H, CH_2), 2.04-1.83 (m, 2H, CH_2). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 101 MHz, 294 K) δ 133.8, 132.0, 128.9, 126.6, 126.1, 124.0, 105.3, 68.1, 62.6, 37.3, 36.2, 23.9.

3',4',5',6'-tetrahydro-3*H*-spiro[isobenzofuran-1,2'-pyran] (**C5**). ^{1}H NMR (CD_3CN, 400 MHz, 294 K): δ 7.39-7.27 (m, 4H, Ph), 5.05 (d, J_{H-H} = 12.0 Hz, 1H, CH_2), 4.95 (d, J_{H-H} = 12.0 Hz, 1H, CH_2), 3.97 (ddd, J_{H-H} = 12.4, 11.2, 2.7 Hz, 1H, CH_2), 3.72-3.66 (m, 1H, CH_2), 2.14-2.08 (m, 1H, CH_2), 2.02-1.95 (m, 1H, CH_2), 1.85-1.54 (m, 4H, $2CH_2$). ^{13}C- NMR (CD_3CN, 101 MHz, 294 K) δ 143.1, 141.2, 129.7, 128.3, 122.7, 122.2, 108.7, 71.4, 63.7, 34.5, 26.0, 20.4.

3-(1*H*-isochromen-3-yl)propan-1-ol (**Int6**). ^{1}H NMR (CD_3CN, 400 MHz, 294 K): δ 7.23-7.15 (m, 1H, Ph), 7.10 (td, J_{H-H} = 7.4, 1.3 Hz, 1H, Ph), 7.06-7.00 (m, 1H, Ph), 6.94-6.90 (m, 1H, Ph), 5.73 (s, 1H, CH), 5.02 (s, 2H, CH_2), 3.54 (dd, J_{H-H} = 11.8, 6.4 Hz, 2H, CH_2), 2.62 (t, J_{H-H} = 5.4 Hz, 1H, OH), 2.27-2.20 (m, 2H, CH_2), 1.72 (ddt, J_{H-H} = 8.5, 7.4, 6.5 Hz, 2H, CH_2). ^{13}C- NMR (CD_3CN, 101 MHz, 294 K) δ 159.7, 133.0, 129.1, 128.4, 126.8, 124.7, 123.2, 101.8, 69.3, 61.9, 31.1, 30.7.

4-(isobenzofuran-1(3*H*)-ylidene)butan-1-ol (**Int5**). ^{1}H NMR (CD_3CN, 400 MHz, 294 K): δ 7.52-7.43 (m, 1H, Ph), 7.37-7.27 (m, 3H, Ph), 5.29 (s, 2H, CH_2), 5.00 (t, J_{H-H} = 7.5 Hz, 1H, CH), 3.54 (dd, J_{H-H} = 12.0, 6.0 Hz, 2H, CH_2), 2.56 (t, J_{H-H} = 5.5 Hz, 1H, OH), 2.30-2.20 (m, 2H, CH_2), 1.66-1.56 (m, 2H, CH_2). ^{13}C NMR (CD_3CN, 75 MHz, 294 K) δ 156.3, 140.6, 134.7, 129.2, 128.8, 122.5, 120.4, 95.5, 74.3, 62.2, 33.9, 22.1.

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