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Grau de Química

Treball Final de Grau

Effect of the substituents on the resulting luminescent properties.
Efecte dels substituents en les resultants propietats luminescents.

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Vull agrair a la meva tutora, Laura Rodríguez Raurell, i a tot el grup de recerca pel temps que han dedicat per ajudar-me sempre que ho he necessitat.

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REPORT

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1. SUMMARY

There is a great interest in research on the study of gold(I) complexes with alkynyl and coumarin ligands. These compounds have a wide range of applications, like in medicine or as luminescent sensors.

Alkynyl and coumarin ligands have been prepared in this project. Luminescent gold(I) compounds with phosphine and coumarin ligands have been synthesized. The obtained products have been characterized using techniques like ^{1}H, ^{31}P and ^{13}C NMR, IR spectroscopies and mass spectrometry.

The luminescent properties of these compounds have been studied by recording the absorption and emission spectra. The properties obtained have been compared to the ones from some gold(I) complexes that contain a similar coumarin ligand.

Keywords: Luminescence, Au(I), alkynyl, coumarin.

2. RESUM

Hi ha un gran interès a la recerca en l'estudi dels complexos d'or(I) que contenen lligands alquinil i cumarina. Aquests compostos tenen un ampli ventall d'aplicacions com, per exemple, en medicina o com a sensors luminescents.

En aquest projecte s'han preparat diversos lligands alquinil i cumarina. També s'han sintetitzat compostos d'or(I) luminescents que contenen lligands fosfina i cumarina. Aquests productes han sigut caracteritzats mitjançant tècniques com espectroscòpies IR, RMN ^{1}H, ^{31}P i ^{13}C i espectrometria de masses.

Les propietats luminescents dels compostos sintetitzats s'han estudiat enregistrant els espectres d'absorció i emissió. Aquestes propietats s'han comparat amb les de compostos d'or(I) similars que contenen un lligand cumarina diferent.

Paraules clau: Luminescència, Au(I), alquinil, cumarina.

3. INTRODUCTION

For the last years there has been an increasing interest in organometallic complexes due to their prospective applications in several fields in chemistry, like molecular electronics, material science and chemical sensors. Gold(I) derivatives have been particularly interesting to study because of their luminescent properties. These properties come from both the structure of the ligands and the interactions that can be established between two gold(I) atoms[1], also known as aurophilic interactions. The fact that gold(I) has a d^{10} electronic configuration makes the d-d transitions not possible, making the luminescent studies more challenging[2].

The term luminescence refers to the emission in the optical range of the visible, ultraviolet, or infrared light after the transference of any kind of external input to the molecule[3]. The luminescent property of a substance is inherent, and it can be found in any aggregate state. There are several ways to induce luminescence. The difference between them is the method of excitation of the molecule. These can be using light (photoluminescence), ionizing radiation (radioluminescence), heat (thermoluminescence), chemical reactions (chemiluminescence), mechanical influences (triboluminescence) and ultrasounds (sonoluminescence). The two most studied photoluminescent phenomena are the fluorescence and the phosphorescence[4]. The first one occurs when the radiation decays rapidly after the excitation, resulting from the allowed transitions between levels of identical multiplicity (see figure 1). The second phenomenon is the prolonged luminescence that lasts after the excitation. In this case an intersystem crossing occurs. The intersystem crossing provokes a transition of electrons from an excited singlet state to a triplet stated. This luminescence comes from the transition from the triplet state to the ground state that is forbidden by quantum rules (see figure 1).

In gold complexes, the presence of a metal center favors the spin-orbit coupling, which at the same time promotes the access to the triplet excited state with an intersystem crossing[2]. These complexes have been studied using different types of ligands, such as alkynyl, phosphine and thiolate.

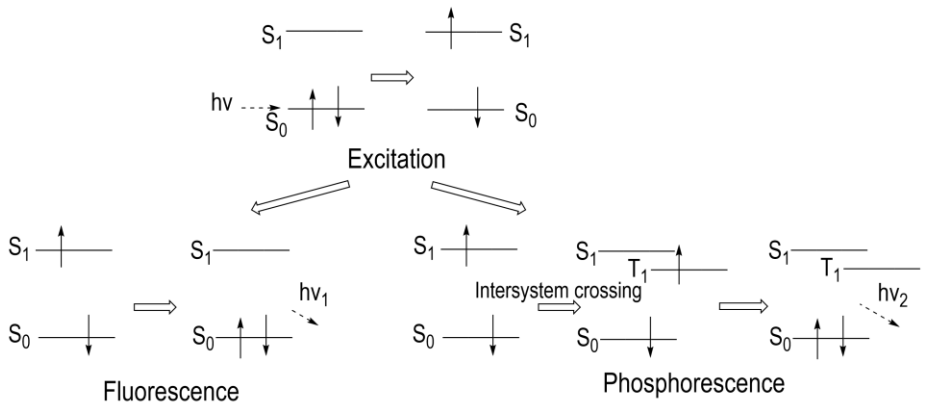
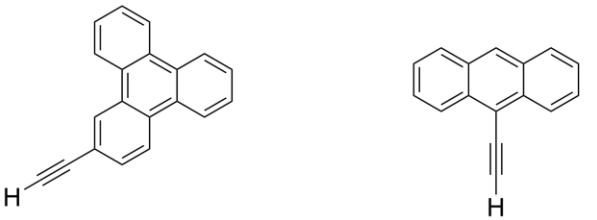


Figure 1. Representation of luminescent properties: fluorescence and phosphorescence[4].

The linearity of the alkynyl ligands makes them interesting to bond with a gold(I) atom. These ligands when coordinate with a gold(I) derivative form a linear geometry that interacts with the π-unsaturated nature of the acetylide group. That group at the same time interacts with the π-system of the aromatic moiety[5]. The alkynyl fragments are useful in the building of numerous organometalic compounds. These compounds can establish a M···π(C≡C) interaction[6]. These interactions generate and modify the luminescent properties of the molecules. The fluorescence found in these compounds is assigned to the π→π* (C≡C) transition[6] of the alkynyl moiety.

In this work two alkynyl ligands have been synthesized and can be seen in the figure 2. These have been chosen by the research group to amplify the chromofors studied. These ligands are known for their high photoluminescence and quantum yields[7] [8]. Once synthesized and bonded with a gold(I) complex, the ligands will improve their luminescent properties, having better quantum yields and phosphorescence.



2-ethynyltriphenylene

1

9-ethynylanthracene

2

Figure 2. Alkynyl ligands synthsized in this work.

Another ligands used are different coumarin compounds. These ligands are found in a lot of natural plants, with a high concentration in the leaves, fruits, roots and seeds. A coumarin has a base structure that consists on a benzene ring fused to an α-pyrone[9], as it can be seen in the figure 3. The different positions where it can be substituted makes the coumarin derivatives a very wide family of compounds. Depending on the different structures, these compounds have differents applications. One of the most important fields used is the medical field and are gaining importance in the drug research. The coumarin compounds have a variety of uses in biological processes, such as inhibitors or modulators of target structures, like derivatives with anticoagulat properties[9].

Another important use is as luminescent proves[10]. These type of compounds have a chromophore group from the π-system of the benzene moiety and the α-pyrone, that makes them ideal for luminescent studies and fluorescent sensors.

As seen in previous studies[11-13], the substituents have a big effect on the properties of the cumarin molecule. These effects include a change in the permanent dipolar moment, the solubility in organic solvents or the intensity and wavelenght of the absorption and fluorescence bands. There have been numerous studies on the luminescent properties of cumarin compounds. Depending on the position and type of substituent, the wavelenght of absorption can change from 200 nm to 520 nm[11]. The emission bands are also dependent on the substituents attached to the molecule, seeing values from 322 nm to 483 nm[12]. There have been evidences[11] that with an increase of electron donating ability from the substituents, the walenght of the fluorescent bands shifts bathochromically.

These absorption bands are assigned to the π→π* transitions[11 12]. However, this assignment is not always correct[14]. The coumarin molecule can have a lowest lying state $^1(n,\pi^*)$. In some cases with the coumarin excitation and resulting relaxation, the $^1(n,\pi^*)$ state is populated before the $^1(\pi,\pi^*)$ state. These two states have a small difference in their energy, making the substituents and solvents very important variables in the study of the photoluminescent properties.

The compounds studied in this work are substituted in the forth and the seventh positions, marked in the figure 3.

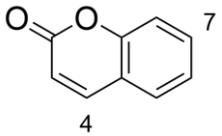


Figure 3. Base structure of a coumarin.

These ligands can have diffents subtituents like a thiol, that with a desprotonation can coordinate to a gold(I) atom, or an alcohol that with the proper reaction, can become alkynyl ligands. As seen before, these ligands can form numerous luminescent compounds with gold(I) complexes.

Some reports[15] have shown that the gold(I) coumarin complexes have highs quantum yields. This fact makes the coumarin derivatives a very interesant ligands to study.

With these ligands we will synthesize new coumarin compounds, which have not been described previously in the literature. We will also synthesize the resulting gold(I) complexes and study their luminescent properties.

4. OBJECTIVES

The goal of this project is the synthesis of luminescent gold(I) compounds. To achieve this goal, different chromophore ligands will be synthesized. The synthesis of the gold(I) precursors and the corresponding gold(I) complexes will be carried out. These compounds will be characterized through different spectroscopic techniques and mass spectrometry. The luminescent properties of those compounds will be measured.

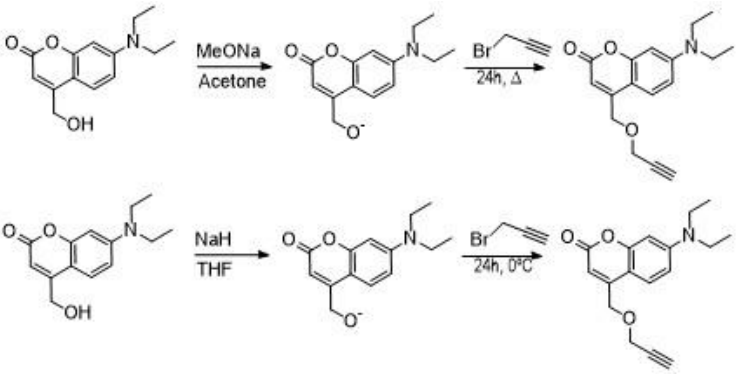
5. RESULTS AND DISCUSSION

5.1. SYNTHESIS AND CHARACTERIZATION

5.1.1. Synthesis of alkynyl ligands

There are two different reactions that have been used to prepare the alkynyl ligands, the propargylation of an hydroxycoumarin and the Sonogashira cross coupling of the 2-bromotriphenylene and the 9-bromoanthracene.

For the propargylation it was followed a two steps procedure from the literature[9]. The first one was an extraction of the proton from the alcohol with a base, as it can be seen in scheme 1. The literature procedure used K_2CO_3 as base, but it was changed for sodium methoxide due to the more acidity of the alcohol been reacted. The second step was the reaction with propargyl bromide. After a couple of days of stirring at 50ºC, the reaction was followed with ^{1}H NMR and the signal from the -CH_2- attached to the alcohol had not changed, it was a doublet at 4.7 ppm (see figure 4), and the rest of the signals were at the same shift. That means that the reaction was not successful. It was tried again changing the conditions[16], using tetrahydrofurane (THF) as solvent and stirring at 0ºC, and the base for a stronger one, NaH. These changes did not work either as it can be seen in the ^{1}H NMR (see figure 4). The propargylation was not possible, so it was left to try again in another time.



Scheme 1. Procedures for the different attempts of the propargylation reaction.

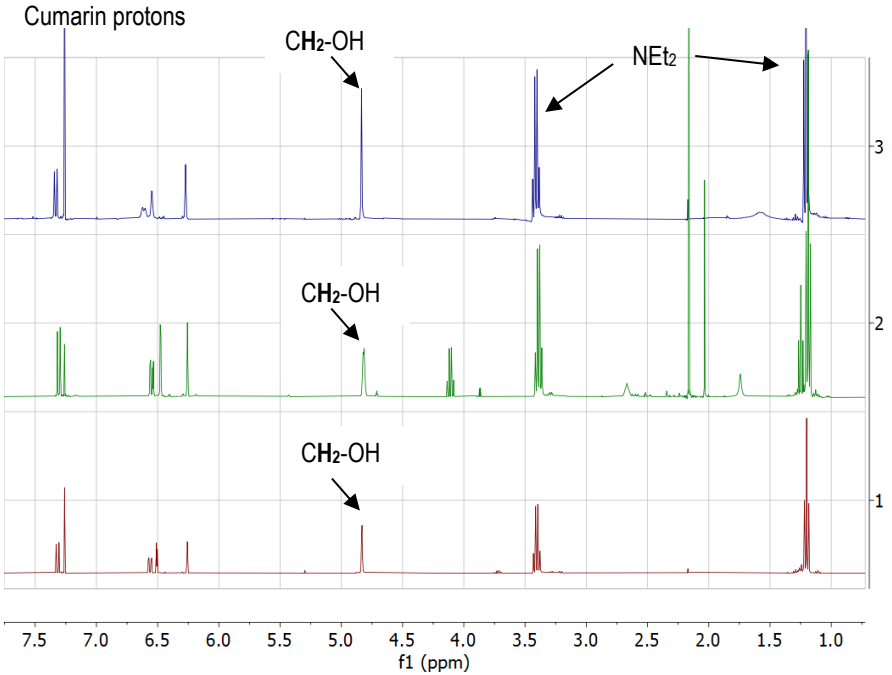


Figure 4. ^{1}H NMR spectra of the propargylation reaction attempts. Initial reactant in red, first reaction in green and second reaction in blue.

The second type of alkynylation was using the Sonogashira cross coupling. This reaction follows a catalytic cycle, with $Pd^{(0)}$ as catalyst and CuI as co-catalyst. It is common to use $[PdCl_2(PPh_3)_2]$ as pre-catalyst because $Pd^{(II)}$ is less reactive than $Pd^{(0)}$ and it can be stored for longer periods of time. The $Pd^{(0)}$ species can be obtained from the $[PdCl_2(PPh_3)_2]$ in situ, by losing the two chloride atoms. The mechanism of the cycle follows 4 steps[17], that are described in the figure 5. The first step of the mechanism is an oxidative addition of the aryl bromide precursor to the $Pd^{(0)}$ catalyst. In this reaction the atom of $Pd^{(0)}$ is oxidized to $Pd^{(II)}$ with the addition of the bromide precursors. The next part of the cycle is the transmetalation, where the trimethylsilylacetyene is exchanged with the bromide atom of the palladium complex. For the trimethylsilylacetylene to be able to be exchanged, there is a secondary reaction with the co-catalyst CuI, which enhances the reactivity of this compound. For the final step to be possible, first there must be a trans/cis isomerization between one of the phosphine ligands and the aryl group. Once all the previous steps are completed, there is the reductive elimination of the arylacetylene compound. This reaction has a reduction of the $Pd^{(II)}$ to $Pd^{(0)}$ when the aryl and the acetylene groups are oxidized and eliminated from the complex, returning the catalyst to the initial form.

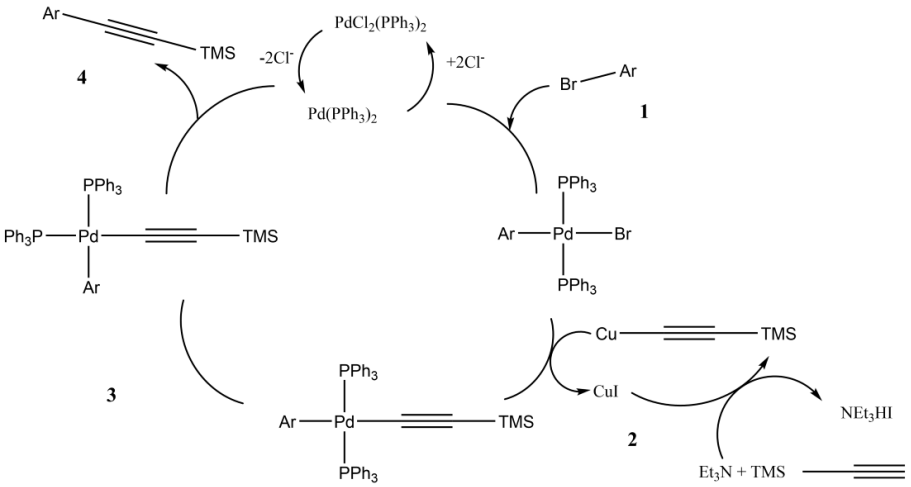
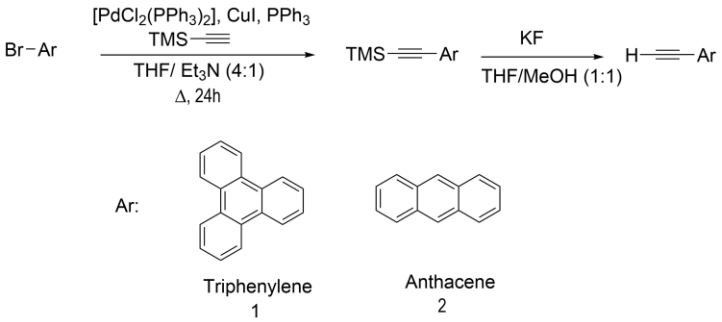


Figure 5. Sonogashira cross coupling mechanism

For the synthesis of the 2-ethynyltriphenylene and the 9-ethynylanthracene, there was a second reaction. The ethynyl group was obtained after the deprotection of the TMS group. This reaction used KF in a methanol/THF mixture, as described in the scheme 2.



Scheme 2. Procedure of the alkynylation for 2-ethynyltriphenylene (1) and 9-ethynylanthracene (2).

The success of the reaction can be seen in the ^{1}H NMR. The appearance of the signal from the terminal proton from the ethynyl group in both cases, and the corresponding peaks for the protons of the aromatic rings (see figure 6) confirmed it. The aromatic protons from 1 and 2 closest to the alkynyl group appeared slightly downfield shifted comparing with the bromo-derivative, about 0.07 ppm. Meanwhile, the farthest ones did not change their position. By looking at the IR spectra from both compounds, this success can be confirmed. There was the appearance of the C≡C-H band at 3200 cm^{-1}, and the aromatic bands from the aryl moiety.

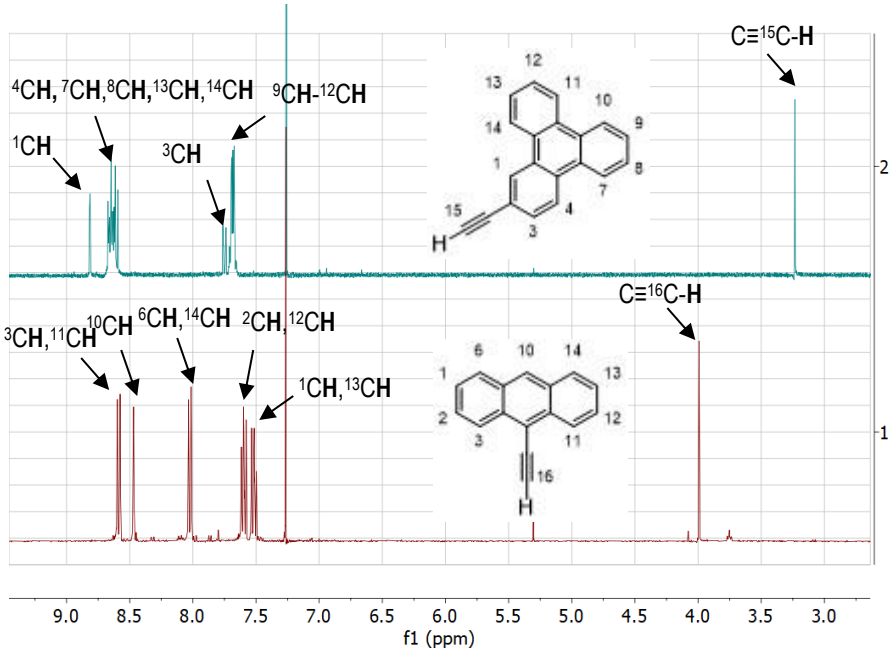
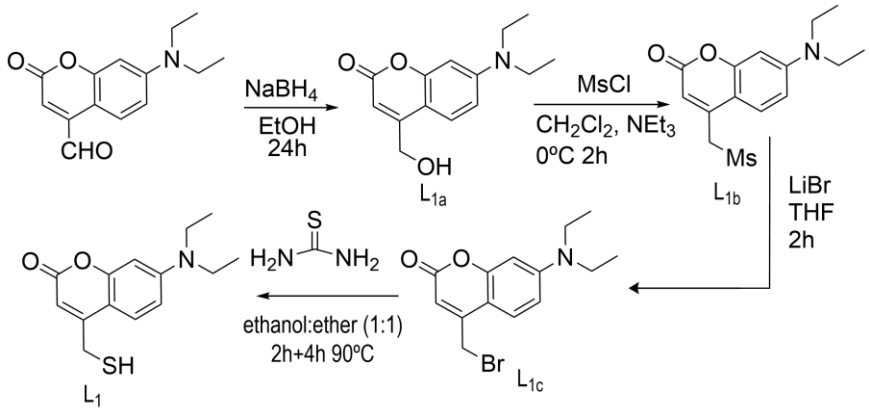


Figure 6. ^{1}H NMR spectra of 2-ethynyltriphenylene (1) (blue) and 9-ethynylanthracene (2) (red).

5.1.2. Synthesis of 7-(diethylamino)-4-(mercaptomethyl)-2H-chromen-2-one (L_1).

The synthesis of the L_1 ligand followed 4 steps[18-20]. The first one started with the coumarin with an aldehyde that was reduced using $NaBH_4$ to the alcohol. Then this alcohol was exchanged for a mesyl group with mesyl chloride. Reacting the mesyl compound with lithium bromide it was obtained the bromide coumarin. Finally, with thiourea the L_1 was obtained (see scheme 3).



Scheme 3. Synthesis of L_1.

Every step of the synthesis was followed using ^{1}H NMR. To confirm that the reactions were happening correctly, the signal from the protons of the aldehyde carbon were studied. The spectra of the L_{1a} showed a doublet signal at 4.7 ppm that corresponded with the protons of the C**H**$_2$-OH (see figure 7). The next reaction was a success as it can be seen in the spectra of the figure 7, because there were the signals from the C**H**$_2$-Ms this time at 5.3 ppm, and the methyl from the mesyl group at 3.1 ppm. The L_{1c} spectra had also the signal from the C**H**$_2$-Br, but this time was upfield shifted, 4.4 ppm and the methyl signal was not visible. Finally, the L_1 spectra (see figure 7) confirmed that the synthesis was successful due to the presence of the doublet signal from the C**H**$_2$-SH at 3.7 ppm and the triplet signal at 1.8 ppm from the S**H**. The rest of the protons from the aromatic part also changed with the reactions, but the ones from the diethylamino group did not changed. From L_{1a} to L_{1b}, the protons were found upfield shifted with decreases from 0.03 to 0.09 ppm. From L_{1b} to L_{1c} the signal from the ^{5}CH was found downfield shifted for 0.16 ppm. The ^{6}CH and ^{8}CH protons were at 0.02 ppm downfield shifted. The ^{3}CH proton was found at 0.04 ppm

upfield. In the last reaction the L_1 protons were found upfield shifted with changes from 0.01 to 0.07 ppm.

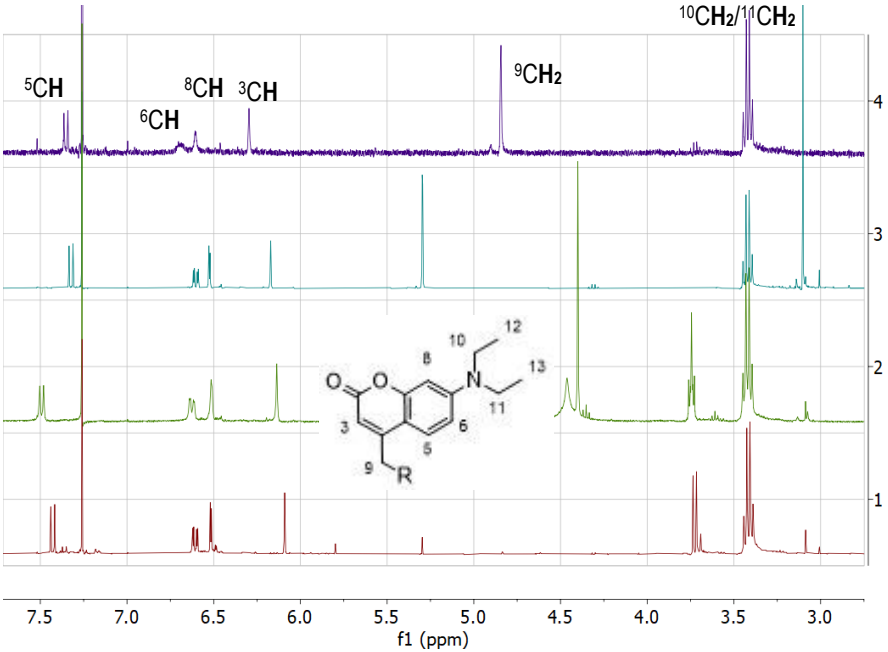
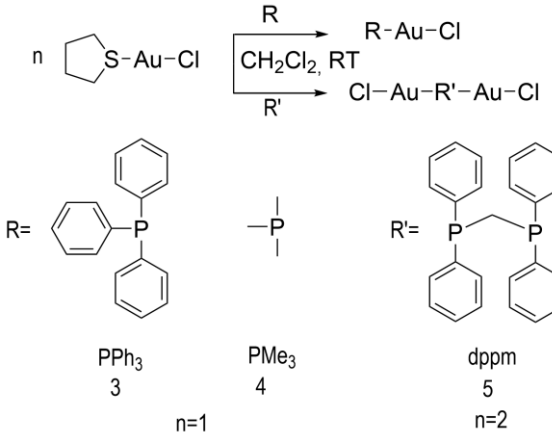


Figure 7. ^{1}H NMR of L_{1a} (purple), L_{1b} (blue), L_{1c} (green) and L_1 (red).

5.1.3. Synthesis of gold(I) chloride complexes

For the synthesis of some of the gold(I) L_1 complexes it was necessary to prepare the gold(I) chloride phosphines first. In this reaction, as it can be seen in the scheme 4, the tetrahydrothiophene (tht) from the [AuCl(tht)] was substituted by the corresponding phosphine[21].

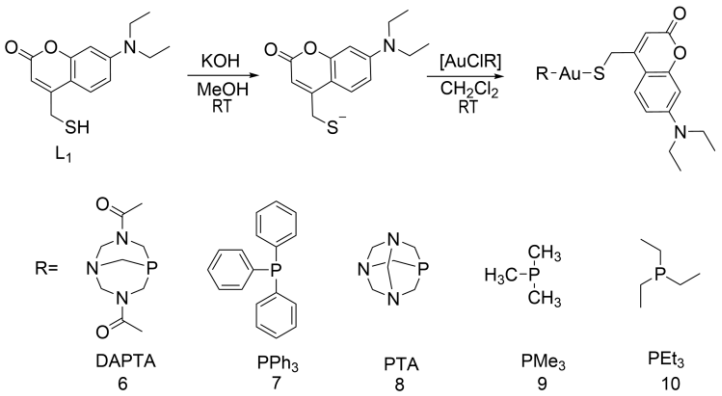


Scheme 4. Synthesis of [AuClR] (3-5).

The success of the reactions was confirmed with ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR and compared with the free phosphines. The compounds had just one signal in the $^{31}P\{^{1}H\}$ NMR which was found downfield shifted than the free phosphine. These increases had values that went from 15 to 50 ppm.

5.1.4. Synthesis of monophosphine gold(I) L_1 complexes

These complexes have all been synthesized following the same procedure [21], described in the scheme 5. Firstly, there was the deprotonation of the thiol in presence of a strong base, in this case KOH. Then the corresponding gold(I) chloride phosphine complex was added, and the chloride was replaced by the deprotonated L_1.



Scheme 5. Synthesis of [AuL_1R] (6-10) complexes.

The compound 6 was recrystallized due to some impurities seen on the ^{1}H NMR, but the rest were obtained in pure form. Both 6 and 8 had a moderate yield over 50%, but 7 had a 30% yield which was lower than expected.

Using the ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, IR and ES-MS spectra the compounds have been characterized. For the case of the compound 6, the integration of the signals (see figure 8) showed that the compound produced was the dinuclear, $[(AuDAPTA)_2L_1]$, where two gold atoms were attached to the same sulfur from the L_1 (see figure 8). This was confirmed with the molecular peak in the corresponding mass spectrum.

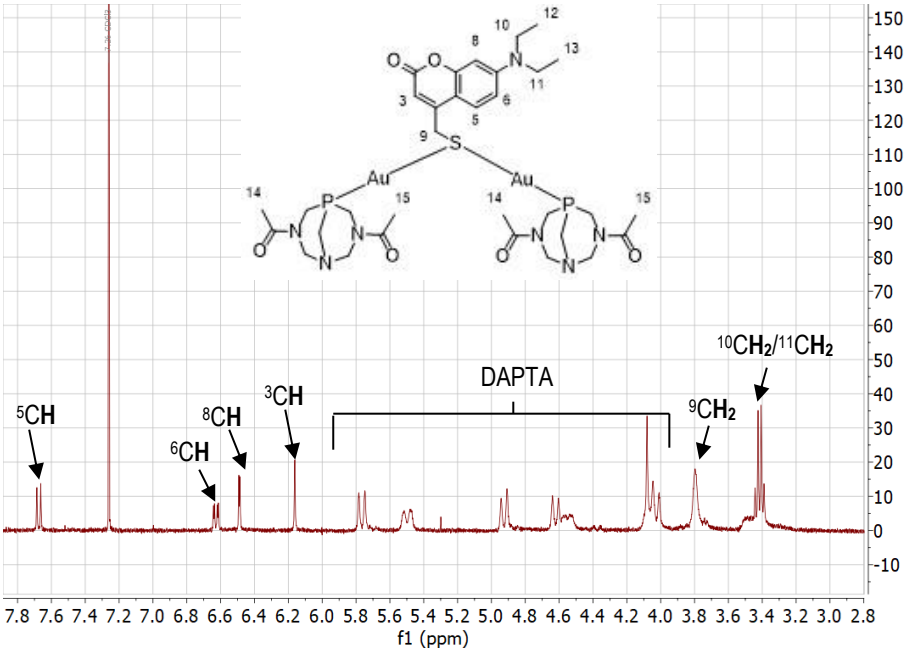


Figure 8. ^{1}H NMR spectra from $[(AuDAPTA)_2L_1]$ (6).

With the HSQC spectra of this compound, the assignment of the carbons from the compound 6 can be easily made. There was the correlation of the 2 protons from the same carbon, as it can be seen in the figure 9.

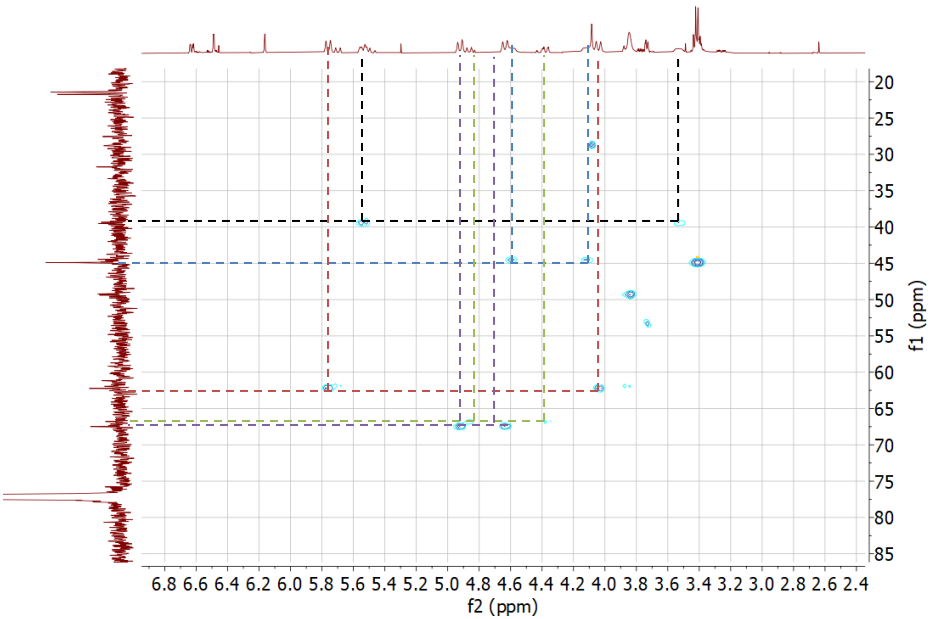


Figure 9. HSQC spectra of $[(AuDAPTA)_2L_1]$ (3).

The compound 7 was successfully synthesized as it can be known by looking at the ^1H NMR (see figure 10). There was presence of the L_1 protons and the ones from the phenyl groups of the PPh_3. The same result was seen for the compound 8, where there was the quadruplet and the singlet from the PTA group, and the L_1 protons (see figure 10) in the correct respective integration. In both cases the signals from the L_1 protons closest to the gold(I) atom, $^9CH_2$, ^3CH and ^5CH, were downfield shifted. The farthest ones, ^6CH, ^8CH, $^{10}CH_2/^{11}CH_2$ and $^{12}CH_3/^{13}CH_3$, were upfield shifted for the compound 7 and downfield shifted for the compound 8, compering with the free ligand. This difference is because the PPh_3 group provokes a bigger deshieldment of the closest protons than the PTA group. For the compound 7 the shift increase of the protons was of 0.48, 0.16 and 0.45 ppm, while the shift decreases were 0.07, 0.03, 0.02 and 0.03 ppm respectively. The compound 8 had an increased shift of the closest protons of 0.38, 0.11 and 0.31, and for the farthest protons of 0.07, 0.04, 0.05 and 0.04 ppm respectively. As it can be seen, the coordination with the gold(I) atom has a bigger effect on the protons near the thiol group than the ones close to the diethylamino moiety.

Two more compounds, 9 and 10 were tried to synthesize following the same procedure, but the reactions were not successful, and the expected signals of the ^{1}H NMR could not be found.

The $^{31}P\{^{1}H\}$ NMR spectra of the compound 6, 7 and 8 showed that the reaction was successful. For the 3 compounds there was one signal that was downfield shifted. These changes were 6.4 ppm for the compound 6, 5 ppm for compound 7 and 32 ppm for compound 8.

With the ES-MS we can see the molecular peaks from the compounds 6, 7 and 8, which confirms the correct formation of the complexes.

The IR spectra was also used to characterize the compounds. For the compounds 6, 7 and 8 there was the C=O, C=C and C-O bands from the L_1 ligand. In the compound 6 spectra it was visible the C=O and the C-N bands from the DAPTA group. The compound 7 spectra had the aromatic (C=C) bands from the phenyl groups. In the compound 8 spectra there was the bands C-N from the PTA ligand. Most importantly was the lack of the S-H vibration of the L_1

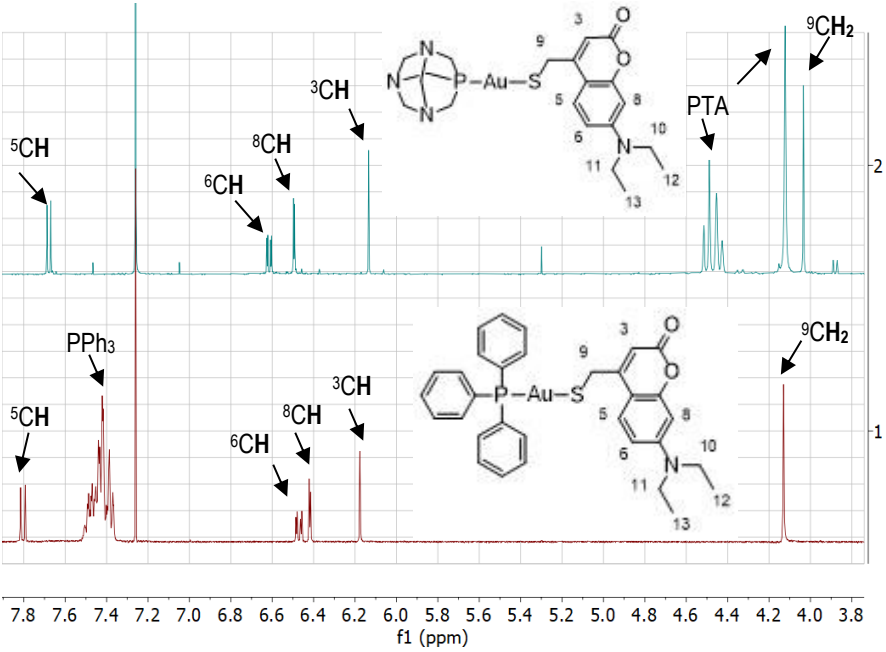
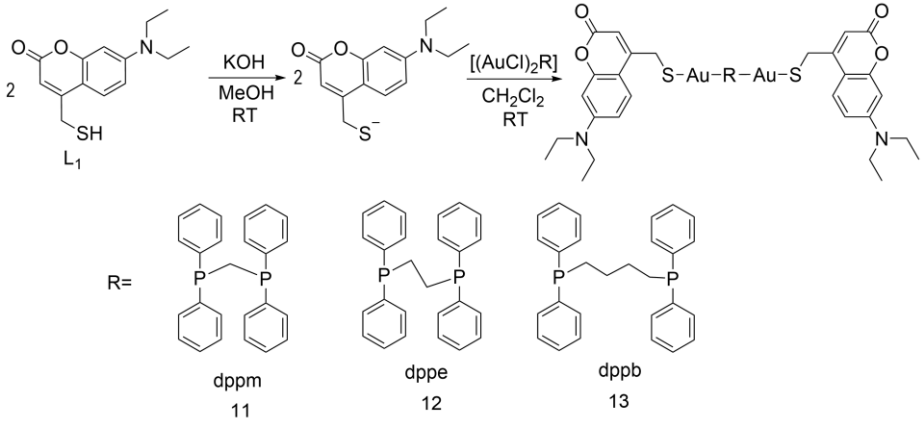


Figure 10. ^{1}H NMR of $[AuL_1(PPh_3)]$ (7) (red) and $[AuL_1(PTA)]$ (8) (blue).

5.1.5. Synthesis of (diphosphine)$(AuL_1)_2$ complexes

The dinuclear complexes were synthesized using the same reaction from the monophosphines, but with a ratio of 2 equivalents of L_1 for 1 equivalent of the corresponding $[(AuCl)_2R]$ (R =dppm, dppe, dppb). In the second step of the reaction, as it can be seen in the scheme 6, two L_1 substituted the two chloride atoms[21].



Scheme 6. Synthesis of $[(AuL_1)_2R]$ (11-13) complexes

The resulting solids 11 and 13 were almost not soluble in $CDCl_3$, so the NMR spectra were done in dmso-*d6* instead. Nevertheless, from the NMR data it can be said that it was not possible to synthesize these compounds. In both cases on the ^1H NMR it was not possible to identify the protons from the L_1 or the ones from the diphosphine groups. The ^1H NMR of the compound 12, as it can be seen in figure 11, had the signals from the aromatic protons of the diphosphine and the L_1. The intensity of the signals was very low, and the integration was not the expected. This fact meant that it could not be confirmed that the product obtained was the desired one. It was suspected that there was a mixture of the compound where only one chloride was substituted and the expected one. This mixture could be because the reaction time was not enough for the complete substitution to occur. The reaction was prepared a second time leaving it stirring for two days. With the help of the ^1H NMR it was not possible to determine that the reaction was a success. The ^1H NMR of the second attempt had only the signals from the phenyl groups, and the ones from the L_1 moiety were not possible to identify.

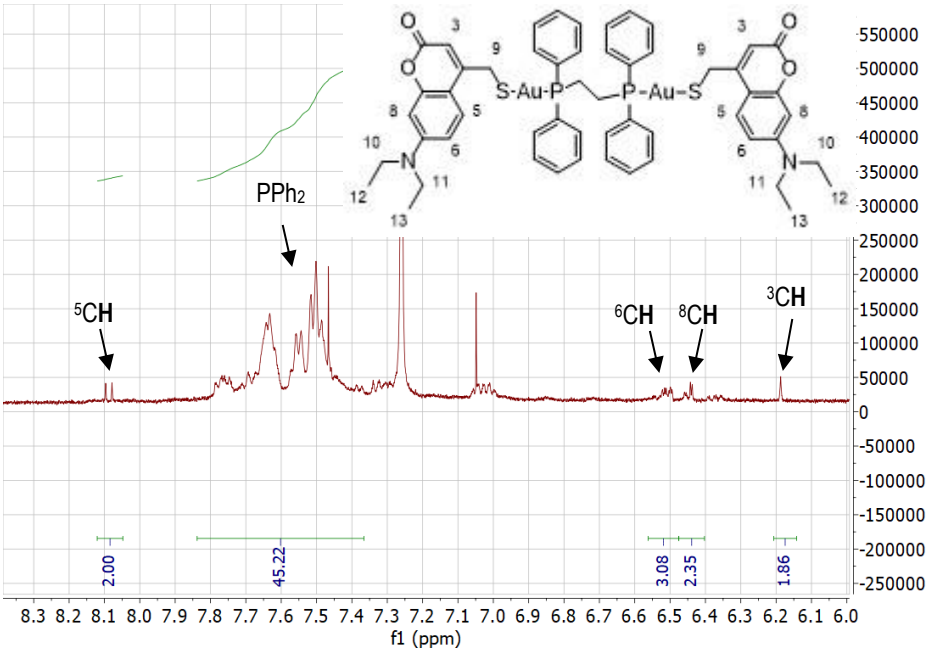


Figure 11. ^{1}H NMR of [$(AuL_1)_2$dppe] (12) of the first attempt.

5.2. LUMINESCENT STUDIES

5.2.1. Gold(I) L_1 complexes

The absorption and emission spectra have been recorded to study the effect of the phosphine ligand on the gold(I) L_1 complexes synthesized. The recording of the spectra was done in CH_2Cl_2 solution at room temperature, air-equilibrated and N_2-saturated. The results are summarized in table 1.

As it can be seen in the figure 12, the maximum of absorption was at a wavelength of 386nm. This band was assigned to the π → π* transition[11 12]. Using the absorption from the L_1 as reference, the compound 6 had a higher absorption, and the compounds 8 and 7 had lower values, respectively.

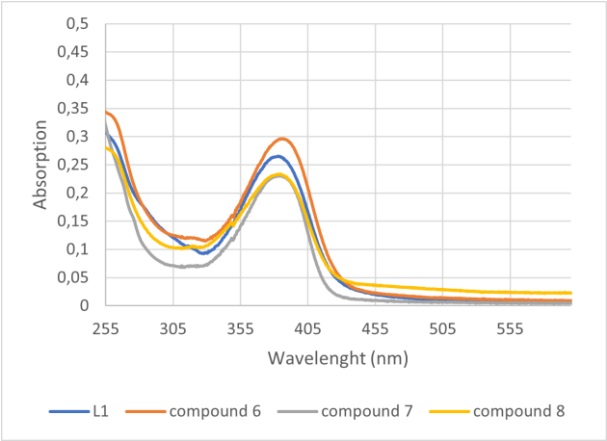


Figure 12. Absorption spectra of L_1, [AuL_1(DAPTA)] (6), [$AuL_1(PPh_3)$] (7) and [AuL_1(PTA)] (8) in CH_2Cl_2 at $1.66 \cdot 10^{-5}$ M.

To measure the fluorescence of the samples, they were excited at 386 nm. The emission spectra of the free ligand L_1 showed a band at 447 nm. The spectra of the gold(I) complexes showed a lower intensity of fluorescence than the L_1, as it can be seen in the figure 13. The gold(I) atom makes it easier for the triplet excited state to fill. The triplet is a non-emissive state, making the intensity to decrease, comparing with the free ligand[2]. The complex 6 had a maximum emission intensity at 449 nm, while the complexes 7 and 8 had it at 445 nm (see figure 13). The absence of an extra band at higher wavelengths, indicated that there were not phosphorescent properties at room temperature.

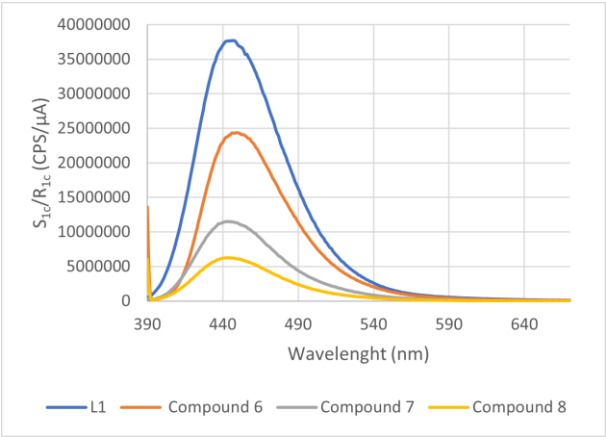


Figure 13. Spectra of emission of L_1, [AuL_1(DAPTA)] (6), [$AuL_1(PPh_3)$] (7) and [AuL_1(PTA)] (8).

5.2.2. Comparison between different coumarins

The effect of the different substituents on a coumarin have also been studied in this project. The absorption and emission spectra of the L_1 and $[(AuDAPTA)_2L_1]$ have been compared to ones from a similar coumarin, L_2. The structures from the L_2 compounds are described on figure 14.

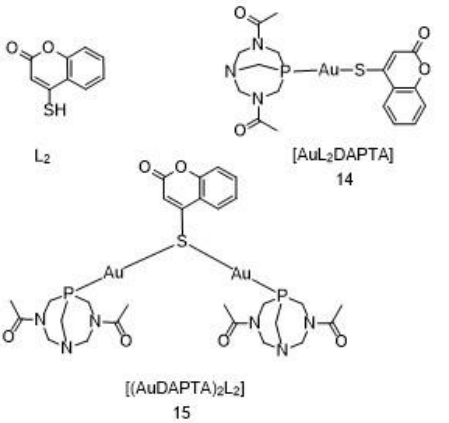


Figure 14. Structure of L_2, $[AuL_2DAPTA]$ (14) and $[(AuDAPTA)_2L_2]$ (15).

The same concentration was used for the L_2, 14 and 15 compounds. There was a big difference between the 5 samples. The absorption of the L_2 compounds had 4 bands between 250 nm and 350 nm (see figure 15). The studied band (321 nm) was 61 nm blue shifted in relation to the L_1 compounds (see table 1). The changes on the aspect of the spectra is due to the CH_2 that difference the compounds.

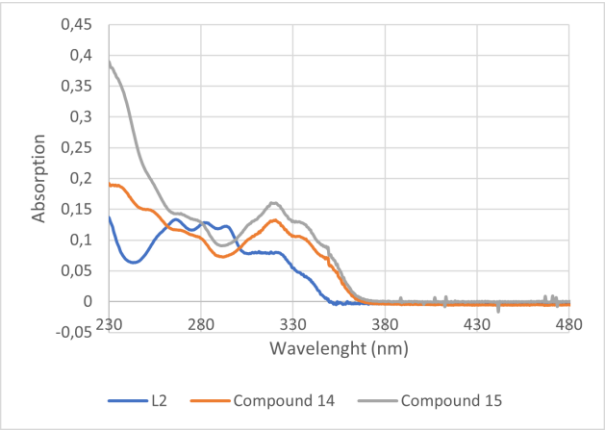


Figure 15. Absorption spectra of L_2, $[AuL_2DAPTA]$ (14) and $[(AuDAPTA)_2L_2]$ (15)) in CH_2Cl_2 at $1.66 \cdot 10^{-5}$ M.

The emission spectra for the L_2 compounds were recorded at 321 nm (see figure 16). It was seen that the L_2 compounds had lower intensity of emission than the L_1 compounds. The L_2 ligand had an emission band at 390 nm while for the L_1 ligand was at 447 nm. The difference of intensity between the L_1 and the L_2 compounds was due to the diethylamino moiety of the L_1 ligand [11 13]. This ligand has a non-bonding par of electrons that modifies the charge distribution of the molecule. In both cases, there was no phosphorescent band visible.

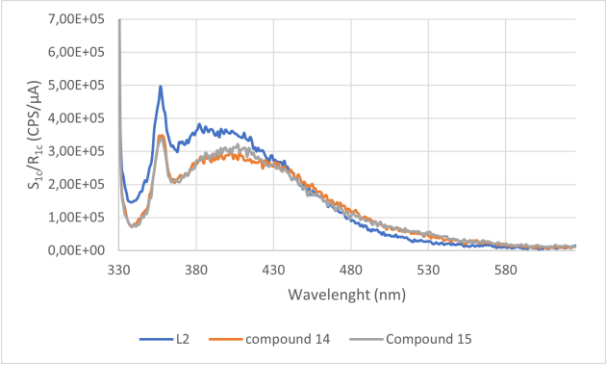


Figure 16. Emission spectra of L_2, [AuL_2DAPTA] (14) and [(AuDAPTA)$_2L_2$] (15).

Compound	Absorption wavelenght [nm] (ε)	Emission wavelenght [nm]
L_1	383 ($1.60 \cdot 10^5$)	447
[(AuDAPTA)$_2L_1$] (6)	386 ($1.79 \cdot 10^5$)	449
[AuL_1(PPh_3)] (7)	385 ($1.40 \cdot 10^5$)	443
[AuL_1(PTA)] (8)	385 ($1.41 \cdot 10^5$)	444
L_2	321 ($4.85 \cdot 10^4$)	390
[AuL_2(DAPTA)] (14)	350 ($3.41 \cdot 10^4$)	412
[(AuDAPTA)$_2L_2$] (15)	349 ($5.33 \cdot 10^4$)	410

Table 1. Summery of luminescent properties obtained.

6. EXPERIMENTAL SECTION

6.1. MATERIALS AND METHODS

General procedures:

All the preparations have been done under argon atmosphere, using Schlenk techniques. Dry solvents were dispensed from a solvent purification system *(Innovativen Technologies; Newburyport, MA, USA*). The deuterated solvents were obtained from Aldrich, the dmso-d_6 was used as received but the chloroform was filtered through alumina and under argon atmosphere. The $[PdCl_2(PPh_3)_2]$, L_1, [AuCl(DAPTA)], $[(AuCl)_2dppe]$, $[(AuCl)_2dppb]$ and dppm were previously synthesized at the laboratory by the research group members. Literature methods were used to prepare [AuCl(tht)][22], $[AuCl(PPh_3)]$[21] and $[(AuCl)_2dppm]$[21]. Commercial reagents 9-bromoanthracene (Aldrich, 94%), 2-bromotriphenylene (Fluorochem), triphenylphosphine (PPh_3, Aldrich, 99%), copper (I) iodide (Aldrich), trimethylsilylacetylene (Fluorochem), potassium fluoride (Carlo Erba), tetrahydrothiophene (tht, Merck- Schuchardt) and trimethylphosphine (PMe_3, Aldrich, 1M) were used as received.

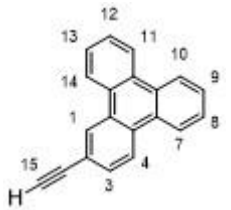
Physical measurements:

IR spectra were recorded with a *Thermo Scientific Nicolet iS5* with an *iD7* ATR. ^{1}H-NMR (δ(TMS)=0.00), ^{13}C-NMR and $^{31}P\{^1H\}$-NMR spectra were recorded with a *Varian Mercury 400* and *Bruker 400*. ElectroSpray-Mass Spectra were measured with a *Fision VG Quatro* spectrophotometer. Absorption spectra were recorded with UV-visible *Varian Cary 100 Bio* spectrophotometer. Emission spectra were recorded with *Nanolog-Horiba Jobin Yvon* spectrofluorimeter.

6.2. SYNTHESIS OF ALKYNYL LIGANDS WITH TRIMETHYLSILYLACETYLENE

6.2.1. Synthesis of 2-ethynyltriphenylene (1)

2-bromotriphenylene (500 mg, 1.6 mmol), $[PdCl_2(PPh_3)_2]$ (114 mg, 0.16 mmol) and PPh_3 (21.1 mg, 0.08 mmol) were dissolved in THF (8 mL) and NEt_3 (2 mL). This solution was stirred at 40ºC for 2h. CuI (31 mg, 0.16 mmol) was added and stirred for 15min. The addition of trimethylsilylacetylene (1.4 mL, 9.8 mmol) caused a change in the color of the solution, from yellow to black. The reaction was stirred at 60ºC overnight, and then for another 4h at 85ºC. When the solution cooled to room temperature, the solvent was removed under reduced pressure, and the product obtained was purified by column chromatography with an eluent of hexane and dichloromethane (9:1, v/v). The desired product was dissolved in THF (5 mL) and MeOH (5 mL). KF (128 mg, 2.2 mmol) was added and stirred overnight at room temperature. The solvent was removed under reduced pressure and extracted with 10 mL of dichloromethane and 5x15 mL of water. The organic phase was dried with $MgSO_4$, and the solvent was removed. The obtained product was purified by column chromatography with hexane and dichloromethane (7:3, v/v).

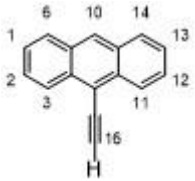


White solid. Yield: η= 33% (0.1983g). IR: 3283 (C≡C-H), 2103 (C≡C), 1492+1429 (C=C aromatic) 757 (out of plane =C-H bending) cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ 8.82 (d, J=9.5Hz, 1H, ^1CH), 8.69-8.59 (m, 5H, ^3CH + ^7CH + ^8CH + ^{13}CH + ^{14}CH), 7.75 (dd, J=52.9/9.5Hz, 1H, ^{17}CH), 7.71-7.65 (m, 4H, ^9CH + ^{10}CH + ^{11}CH + ^{12}CH), 3.23 (s, 1H, ^{15}CH) ppm.

6.2.2 Synthesis of 9-ethynylanthracene (2)

9-bromoantracene (300 mg, 1.1 mmol), CuI (22.2 mg, 0.12 mmol), PPh_3 (15.1 mg, 0.058 mmol) and $[PdCl_2(PPh_3)_2]$ (81.9 mg, 0.12 mmol) were dissolved in THF (5 mL) and NEt_3 (5 mL) and heated until reached 60ºC, then waited for 5min. Trimethylsilylacetylene was added to the solution (1 mL, 7.02 mmol) and stirred at 80ºC overnight. The solution changed from yellow to black. The solution was cooled to room temperature and 15 mL of dichloromethane were added. The suspension generated was filtered and the solution extracted with water (3x50 mL). The organic phase was dried with $MgSO_4$, and the solvent was removed under reduced pressure. The product obtained was purified by column chromatography with hexane as eluent. The compound

was dissolved in 5 mL of THF and 5 mL of MeOH, and KF (111.2 mg, 1.91 mmol) was added. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and extracted with dichloromethane (15 mL) and water (5x15 mL). The organic phase was dried with $MgSO_4$, and the solvent removed.

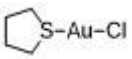


Red solid. Yield: η= 30% (70.3 mg) IR: 3278 (C≡C-H), 3052 (C_{sp2}-H), 1444+1521 (C=C aromatic), 732 (out of plane =C-H bending) cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ 8.59 (d, J=54.25Hz, 2H, ^3CH + ^{14}CH), 8.47 (s, 1H, ^{10}CH), 8.02 (d, J=54.25Hz, 2H, ^6CH + ^{14}CH), 7.61-7.57 (m, 2H, ^2CH + ^{12}CH), 7.53-7.49 (m, 2H, ^1CH + ^{13}CH), 3.99 (s, 1H, ^{16}CH) ppm.

6.3. SYNTHESIS OF GOLD(I) CHLORIDE COMPLEXES

6.3.1. Synthesis of [AuCl(tht)]

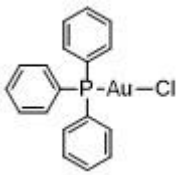
[$HAuCl_4$] (5 g, 16.7 mmol) was dissolved in a mixture of H_2O-EtOH (6.5 mL/ 32 mL). Then was added dropwise 1.8 mL (20.4 mmol) of tht and a yellow precipitate was formed. The suspension was stirred for 50min, filtered with a glass disc, and washed first with EtOH and then with Et_2O. The white solid was dried under vacuum[22].



White solid. Yield: η=50% (2.645 g). IR: 2959 (C_{sp3}-H), 2854 (S-C) cm^{-1}. ^1H NMR (400MHz, $CDCl_3$): δ 3.42 (s, 4H, S-CH_2), 2.20 (s, 4H, C-CH_2) ppm.

6.3.2. Synthesis of [AuCl(PPh_3)] (3)

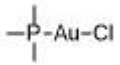
[AuCl(tht)] (350 mg, 1.09 mmol) was dissolved in dichloromethane (15 mL) and PPh_3 (286.4 mg, 1.09 mmol) was added. The solution was stirred for 1h at room temperature. The mixture obtained was concentrated almost to dryness, precipitated with hexane, and left in the freezer overnight. The solid was filtered under Ar[21].



White solid. Yield: η=51% (0.2743 g). ^1H NMR (400MHz, $CDCl_3$): δ 7.56-7.44 (m, 15H, Ph_3) ppm. $^{31}P\{^1H\}$ NMR (162MHz, $CDCl_3$): δ 33.2 ppm.

6.3.2. Synthesis of [AuCl(PMe$_3$)] (4)

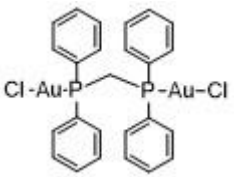
Same procedure of [AuCl(PPh$_3$)] was followed but starting with 100mg (0.31mmol) of [AuCl(tht)] and adding 23.7mg (0.31mmol) of PMe$_3$.



White solid. Yield: η=83% (0.0798 g). ^{1}H NMR (400MHz, $CDCl_3$): δ 0.49 (d, 9H, P-CH_3) ppm. $^{31}P\{^1H\}$ NMR (162MHz, $CDCl_3$): δ -10.34 ppm

6.3.3. Synthesis of [(AuCl)$_2$dppm] (5)

Same procedure of [AuCl(PPh$_3$)] was followed but starting with 100mg (0.31mmol) of [AuCl(tht)] and adding 60mg (0.16mmol) of dppm, with a 2:1 ratio.

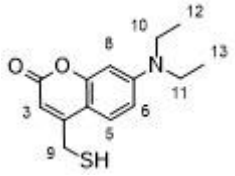


White solid. Yield: η=91% (0.1211 g). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.70-7.40 (m, 20H, Ph), 3.60 (t, 2H, P-CH_2-P) ppm.

6.4. SYNTHESIS OF L$_1$.

L$_1$-CHO (0.530 g, 2.14 mmol) was dissolved in EtOH absolute (65 mL) and $NaBH_4$ (80 mg, 2.11 mmol), was added[18]. The solution was stirred overnight at room temperature. Then, an excess of a solution of HCl 1M (6mL, 6 mmol) was added and the red solution changed to turbid yellow. Water (25 mL) was added to dissolve and extractions with CH_2Cl_2 (3x50 mL) were carried out. The combined organic layers were washed with water, dried with $MgSO_4$ anhydrous and the solvent was removed under pressure. The oily orange solid that was obtained was dissolved in CH_2Cl_2 (30 mL) and NEt_3 (0.53 mL, 3.80 mmol)[19]. The mixture was cooled in an ice bath and MsCl (0.23 mL, 3.01 mmol) was added. It was stirred at 0ºC for 2h. The solution was extracted with a saturated $NaHCO_3$ (2x50 mL). The organic layer was dried with $MgSO_4$ anhydrous, and the solvent evaporated. The mesyl derivative was obtained and dissolved in THF (30 mL). An excess of LiBr (0.670 g, 7.71 mmol) was added. It was stirred at room temperature for 2h and almost all the solvent was evaporated. CH_2Cl_2 (50 mL) was added and washed with brine (50 mL). The aqueous layer was washed with CH_2Cl_2 (10 mL) The organic layers were combined and dried using $MgSO_4$ anhydrous and the solvent was removed under vacuum. The yellow solid obtained

was dissolved in a mixture of ethanol:ether (1:1) and thiourea (0141 g, 1.86 mmol) was added[20]. The solution was stirred at room temperature for 2h and a change of color was visible, from orange to a turbid red. It was heated to 90ºC and stirred with reflux for 4h. Half of the volume was evaporated, NaOH (5%, 30 mL) was added and then it was neutralized with HCl 1M. A brown precipitate was obtained. The product was extracted with CH_2Cl_2 (3x50 mL) and the organic layer was washed with water (10 mL), dried with $MgSO_4$ anhydrous, and evaporated to dryness. A red solid was obtained.

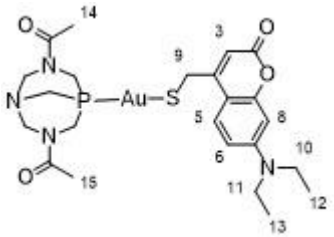


Red solid. Yield: η=67% (0.3828 g). IR: 2970 (C_{sp3}-H), 1718 (C=O), 1598+1415 (C=C aromatic), 1261 (C-O), 1078 (C-N) cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.36 (d, J=56Hz, 1H, ^{5}CH), 6.54 (dd, J=56/17Hz, 1H, ^{6}CH), 6.45 (d, J=17Hz, 1H, ^{8}CH), 6.02 (s, 1H, ^{3}CH), 3.65 (d, J=49.5Hz, 2H, $^9CH_2$), 3.35 (q, J=44.5Hz, 4H, $^{10}CH_2/^{11}CH_2$), 1.80 (t, J=49.5Hz, 1H, SH), 1.16 (t, J=44.5Hz, 6H, $^{12}CH_3/^{13}CH_3$) ppm.

6.5. SYNTHESIS OF GOLD(I) COUMARIN (L_1) COMPLEXES.

6.5.1. Synthesis of [AuL_1(DAPTA)] (6)

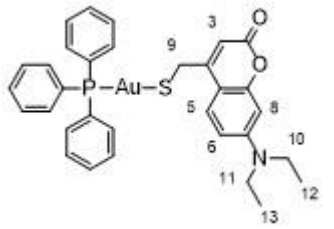
L_1 (44.2 mg, 0.17 mmol) was dissolved in 10 mL of MeOH, and KOH (18.8 mg, 0.34 mmol) was added. The solution was stirred for 30min. A suspension of [AuCl(DAPTA)] (77.5 mg, 0.17 mmol) in dichloromethane (10 mL) was prepared, added and the resulting solution was stirred overnight at room temperature. A change in the color was visible, from yellow to orange. The solution was concentrated almost to dryness and the product was precipitated with Et_2O and left in the freezer overnight. The solid obtained was filtered under Ar and recrystallized in dichloromethane/hexane[21].



Yellow solid. Yield: η=59% (0.1107 g) IR: 2967 (C_{sp3}-H), 1610 (C=O), 1528+1413 (C=C), 1334 (P-C), 1228 (N-C), 1053 (C-O) cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.67 (d, J=56.8Hz, 1H, ^{5}CH), 6.62 (dd, J=56.5/15Hz, 1H, ^{6}CH), 6.48 (d, J=15Hz, 1H, ^{8}CH), 6.16 (s, 1H, ^{3}CH), 5.76 (d, J=88Hz, 2H, N-CH_2-N), 5.50 (d, J=84Hz, 2H, P-CH_2-N), 4.92 (d, J=88Hz, 2H, N-CH_2-N), 4.64-4.50 (m, 4H, P-CH_2-N + N-CH_2-N), 4.10-3.98 (m, 6H, P-CH_2-N + N-CH_2-N + P-CH_2-N), 3.80 (s, 2H, $^{9}CH_2$), 3.41 (q, J=44Hz, 4H, $^{10}CH_2$ + $^{11}CH_2$), 1.59 (s, 12H, $^{14}CH_3$ + $^{15}CH_3$), 1.20 (t, J=44Hz, 6H, $^{12}CH_3$ + $^{13}CH_3$) ppm. $^{31}P\{^{1}H\}$ NMR (162MHz, $CDCl_3$): δ 1.5 ppm. ^{13}C NMR ($CDCl_3$): δ 170.24 (Cq), 169.84 (Cq), 138.33 (Cq), 126.73 (^{5}C), 108.81 (^{6}C), 107.34 (^{3}C), 97.84 (^{8}C), 67.49 (N-CH_2-N), 62.24 (N-CH_2-N), 49.22 ($^{9}CH_2$), 44.91 ($^{10}CH_2$/$^{11}CH_2$), 44.47 (P-CH_2-N), 27.53 (P-CH_2-N), 21.75 (Cq), 14.27 (Cq), 12.66 ($^{12}CH_3$/$^{13}CH_3$) ppm ES-MS: 230.1057 (DAPTA+H), 264.106 (L_1+H), 459.2051 (2DAPTA+H), 527.2038 (2L_1+H), 689.1608 ([AuL_1(DAPTA)]).

6.5.2. Synthesis of [AuL_1(PPh_3)] (7)

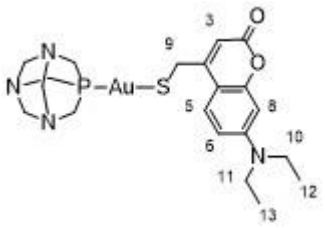
The same procedure as [AuL_1(DAPTA)] was followed using 40.4 mg (0.15 mmol) of L_1, 17.2 mg (0.31 mmol) of KOH and 75.8 mg (0.15 mmol) of [AuCl(PPh_3)].



Yellow solid. Yield: η=30% (0.0326 g) IR: 3059 (C_{sp2}-H), 2967 (C_{sp3}-H), 1712 (C=O), 1597+1422 (C=C aromatic), 1127 (C-N), 1099 (C-O) cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.81 (d, J=56Hz, 1H, ^{5}CH), 7.52-7.36 (m, 15H, Ph), 6.47 (dd, J=56/16Hz, 1H, ^{6}CH), 6.42 (d, J=16HZ, 1H, ^{8}CH), 6.18 (s, 1H, ^{3}CH), 4.13 (s, 2H, $^{9}CH_2$), 3.33 (q, J=44Hz, 4H, $^{10}CH_2$ + $^{11}CH_2$), 1.13 (t, J=44Hz, 6H, $^{12}CH_3$ + $^{13}CH_3$) ppm. $^{31}P\{^{1}H\}$ NMR (162MHz, $CDCl_3$): δ 38.1 ppm. ^{13}C NMR ($CDCl_3$): δ 163.08 (Cq), 161.44 (Cq), 156.95 (Cq), 150.50 (Cq), 134.30-129.31 (Ph), 127.02 (^{5}C), 108.58 (^{6}C), 107.69 (^{3}C), 107.21 (Cq), 97.86 (^{8}C), 44.83 (^{10}C/^{11}C), 28.76 (^{9}C), 12.66 (^{12}C/^{13}C) ppm. ES-MS: 721.1466 ([Au(PPh_3)$_2$]), 722.1539 ([AuL_1(PPh_3)]+H), 1180.2048 ([Au$_2$(L1)$_2$(PPh_3)]+H).

6.5.3. Synthesis of [AuL$_1$(PTA)] (8)

The same procedure as [AuL$_1$(DAPTA)] was followed using 27.7 mg (0.11 mmol) of L$_1$, 11.8 mg (0.21 mmol) of KOH and 64.9 mg (0.11 mmol) of [AuCl(PTA)].



Yellow solid. Yield: η=51% (0.0334 g) IR: 2970 (C_{sp3}-H), 1709 (C=O), 1598+1415 (C=C aromatic), 1131 (C-N), 1016 (C-O) cm^{-1}. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.67 (d, J=55.5Hz, 1H, ^{5}CH), 6.61 (dd, (J=55.5/16Hz, 1H, ^{6}CH), 6.49 (d, J=16Hz, 1H, ^{8}CH), 6.13 (s, 1H, ^{3}CH), 4.47 (q, J=80.75Hz, 6H, N-CH_2-N), 4.12 (s, 6H, N-CH_2-P), 4.03 (s, 2H, ^{9}CH), 3.42 (q, J=44Hz, 4H, $^{10}CH_2$ + $^{11}CH_2$), 1.20 (t, J=44Hz, 6H, $^{12}CH_3$ + $^{13}CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162MHz, $CDCl_3$): δ -49.3 ppm. ^{13}C NMR ($CDCl_3$):163.10 (Cq), 161.86 (Cq), 156.57 (Cq), 150.68 (Cq), 126.55 (^{5}C), 108.60 (^{6}C), 107.36 (^{3}C), 97.64 (^{8}C), 73.40 (N-C-N), 52.7 (P-C-N), 44.7 (^{10}C/^{11}C), 26.15 (^{9}C), 12.64 (^{12}C/^{13}C) δ ppm. ES-MS: 158.0841 (PTA+H), 264.1055 (L$_1$+H), 617.142 ([AuL$_1$PTA]).

7. CONCLUSIONS

By looking at the obtained results, it can be confirmed that the Sonogashira cross coupling is a correct method to prepare alkynyl ligands. Also, that the propargylation with the conditions used is not useful to prepare an alkynyl ligand from an hydroxycoumarin.

The synthesis of the gold(I) complexes showed that the synthetic method was successful in preparing three of the five monophosphine gold(I) L_1 compounds. The same reaction with similar conditions was used to prepare the diphosphine $(gold(I)L_1)_2$ compounds. The differences in the conditions affected the accomplishment of the reaction, making it impossible to synthesize the diphosphine compounds.

The successfulness of these reactions was confirmed by using ^{1}H, ^{31}P and ^{13}C RMN and IR spectroscopies and mass spectrometry, that presented the characteristic features of each compound in every technique.

The luminescent studies showed that by bonding the coumarin moiety to a gold(I) phosphine complex, the gold(I) atom affects the intersystem crossing making the emission intensity to decrease. This luminescence is due to the $\pi \rightarrow \pi^*$ transition, that with the gold(I) bond populates the triplet state, which is not emissive. The effect of the substituents of the coumarin ligand were studied by comparing two thiolate coumarins. It was seen that a CH_2 group at the fourth position and an amino substituent at the seventh, affect at the wavelength of the absorption and emission bands. These amino substituents are electron donative groups and increase the wavelength of the bands. The study also showed that the mononuclear and the dinuclear compounds of the same coumarin, have the same absorption and emission bands, with almost the same intensity.

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9. ACRONYMS

Tht: tetrahydrothiophene

DAPTA: 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.31]nonane

PTA: 1,3,5-traiza-7-phosphaadamantane

Dppm: 1,1-Bis(diphenylphosphino)methane

Dppe: 1,2-Bis(diphenylphosphino)ethane

Dppb: 1,4-Bis(diphenylphosphino)butane

IR: Infrared

NMR: nuclear magnetic resonance

HSQC: heteronuclear single quantum correlation

ES-MS: ElectroSpray-Mass Spectra

APPENDICES

APPENDIX 1: HSQC SPECTRA OF [AUL$_1$(PPH$_3$)]

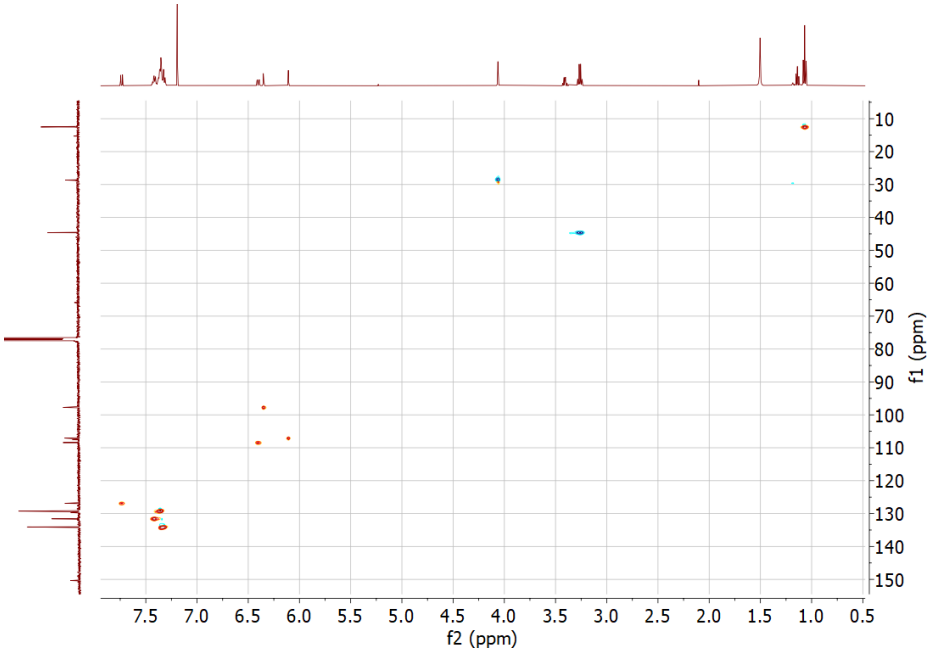

Figure I. HSQC spectra of [AuL$_1$(PPh$_3$)]

APPENDIX 2: ES-MS SPECTRA OF MONOPHOSPHINE GOLD(I) L_1 COMPLEXES

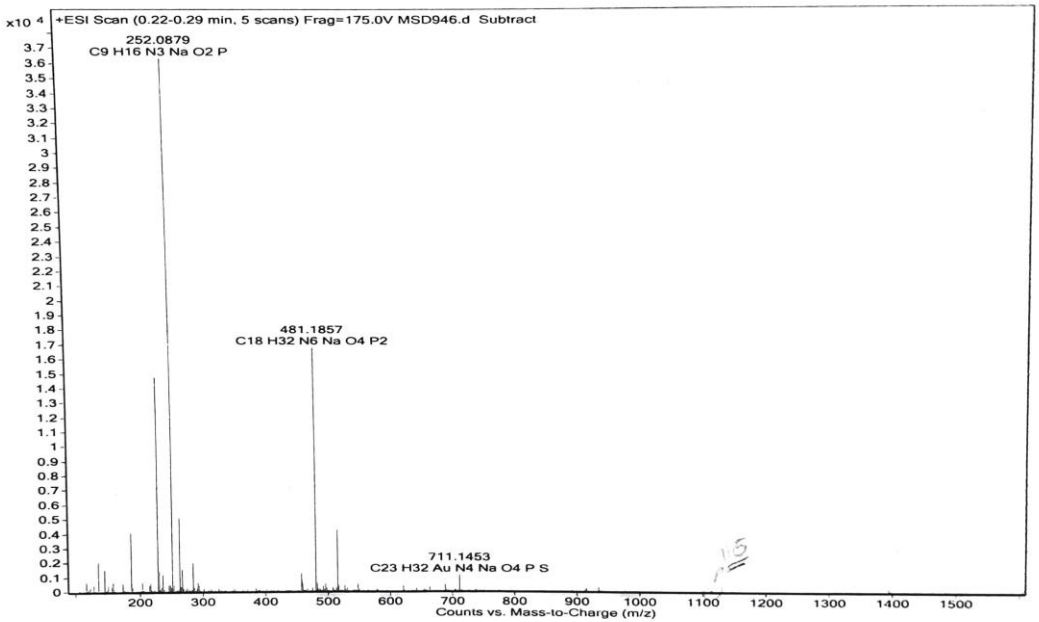

Figure II. ES-MS of $[(AuDAPTA)_2L_1]$

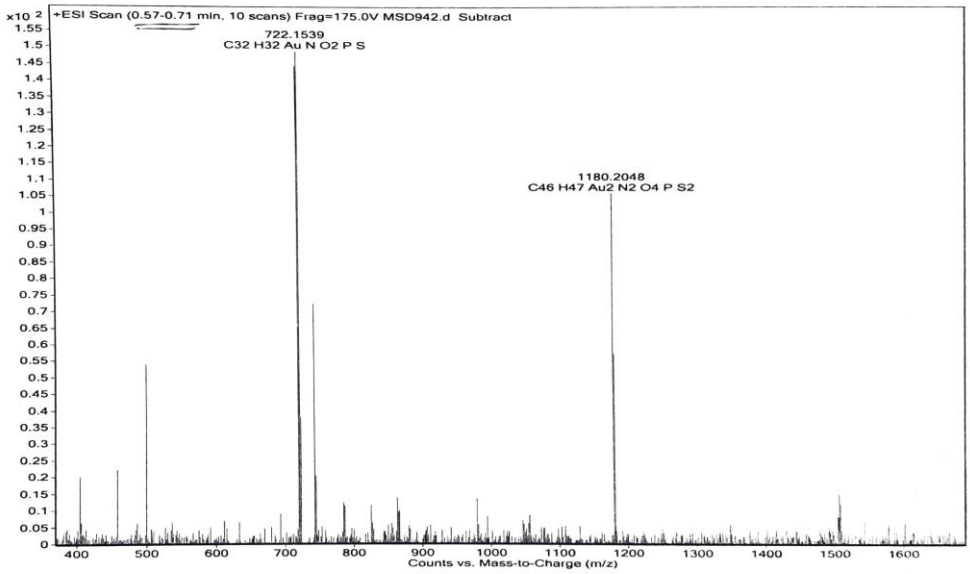

Figure III. ES-MS of [$AuL_1(PPh_3)$]

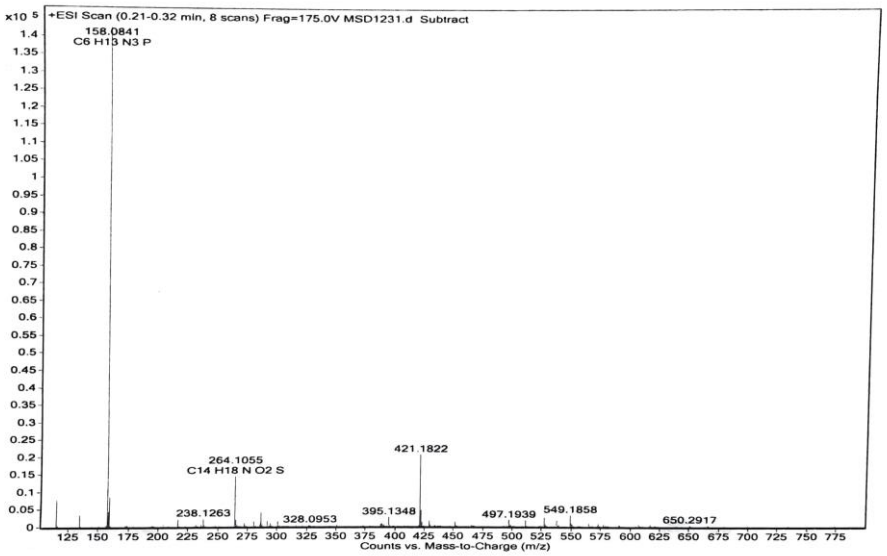

Figure IV. ES-MS of [$AuL_1(PTA)$]