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Grau de Química

Treball Final de Grau

Activation of CH bonds of N-donor ligands by palladium compounds.

Activació d'enllaços CH de lligands nitrogenats amb compostos de pal·ladi.

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Si no conozco una cosa, la investigaré.

Louis Pasteur

Als meus pares, pel seu incondicional suport, ara i sempre. A tothom que m'han fet costat durant aquest temps. Als meus companys de laboratori i amics, Marc-Ricard Batten, Oriol Serra i Mònica Solé, per fer les hores de treball més amenes i resoldrem dubtes estúpids. A la Dra. Margarita Crespo per les seves classes d'Organometàl·lics i Química Supramolecular i per tot l'ajud que m'ha donat tot i no ser la meva tutora. I sobretot, al Dr. Jaume Granell, per la seva direcció, per totes les hores de dedicació i per tot el que he pogut aprendre al seu costat durant aquest treball. Sense cap d'ells aquest camí hauria estat molt més difícil.

Moltes gràcies a tots.

REPORT

CONTENTS

1. SUMMARY

Some cyclometallated palladium(II) compounds have been synthesized from the *ortho*- and *para*-chloro isomers of the imine [$ClC_6H_4CHNCH_2C_6H_5$]. The C-H bond aryl activation was performed by the metallation agent $Pd(AcO)_2$ and the expected acetate-bridged cyclometallated compounds [Pd{μ-AcO}{$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ have been obtained.

Some reactions of [Pd{μ-AcO}{$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ were performed and three type of compounds have been obtained; the bridged dinuclear, the neutral mononuclear and the ionic mononuclear. The respective halogen-bridged analogues [Pd{μ-X}{$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ were formed after reacting acetate-bridged compounds with LiBr or LiCl. Splitting reaction took place, when acetate-bridged compounds react with phosphines, but depending of the nature of the phosphine different products could be formed. Neutral mononuclear cyclometallated compounds were obtained by reacting with PPh_3, whereas ionic mononuclear cyclometallated compounds were obtained by reaction with diphosphine dppe ($Ph_2PCH_2CH_2Ph$).

The products were characterized by ^1H and ^{31}P NMR, IR and MS-ESI$^+$. It has been found some tendencies through the products: i) the *ortho*-chloro atoms show an interaction with the imine proton in all the compounds obtained; ii) monodentated phosphines or pyridines adopt a *trans* arrangement with the imine nitrogen that tend to shield the nearest proton of the metallated aryl ring; iii) dinueclear compounds are more rigid than mononueclear compounds.

Keywords: Palladium, Cyclometallation, C-H bond activation, Imine ligands, Phosphines.

2. RESUM

En aquest treball s'han sintetitzat compostos de pal·ladi(II). A partir dels dos isòmers de la imina [$ClC_6H_4CHNCH_2C_6H_5$] amb els àtoms de clor en posicions *orto*- i *para*-, s'han obtingut els compostos ciclometal·lats amb pont acetat de pal·ladi [$Pd\{\mu\text{-}AcO\}\{ClC_6H_3CHNCH_2C_6H_5\}]_2$, per l'activació de l'enllaç aril C-H mitjançant l'agent metal·lant $Pd(AcO)_2$.

S'han obtingut tres tipus de compostos a partir de les reaccions amb $[Pd\{\mu\text{-}AcO\}\{ClC_6H_3CHNCH_2C_6H_5\}]_2$, els compostos dinuclears amb lligands pont, i els compostos mononuclears neutres i mononuclears iònics. De la reacció dels compostos amb pont acetat amb LiBr o LiCl s'obtenen els respectius derivats amb pont halogen $[Pd\{\mu\text{-}X\}\{ClC_6H_3CHNCH_2C_6H_5\}]_2$. Quan els compostos pont-acetat es fan reaccionar amb fosfines, es produeix una reacció de dissociació. Es poden formar diferents compostos en funció de la naturalesa de la fosfina, en reaccionar amb PPh_3 s'obtenen compostos neutres mononuclears, en canvi en reaccionar amb la difosfina dppe ($Ph_2PCH_2CH_2Ph$) s'obtenen compostos iònics.

Els productes han estat caracteritzats per RMN de ^1H i ^{31}P, IR i MS-ESI$^+$. S'han observat les següents tendències entre els productes: i) els àtoms de clor en posició *orto*- presenten una interacció amb el protó de la imina en tots els productes obtinguts; ii) les fosfines monodentades o les piridines en posició *trans*- respecte del nitrogen de la imina tendeixen apantallar el protó més proper de l'anell aromàtic metal·lat; iii) els compostos dinuclears son mes rígids que els compostos mononuclears.

Paraules clau: Pal·ladi, Ciclometal·lació, Activació de l'enllaç C-H, Ligands Iminics, Fosfines.

3. INTRODUCTION

In the last decades, organometallic chemistry has growth such as a scientific discipline and as an interesting area of research and applications. Over all kinds of transition-metal complexes, organopalladium compounds have a very rich chemistry due to their ease interchanging between the two stable Pd(II)/Pd(0) oxidation states. Moreover, their compatibility with most functional groups also differentiates them from many other transition-metal complexes [1]. One of the most popular classes of organopalladium derivatives is cyclopalladated compounds or palladacycles. These compounds have an organic moiety with at least one Pd-C bond intramoleculary stabilized with at least one donor atom (N, P, As, O, Se, or S). Since the first isolation and characterization in the 1960's a plethora of research and application has been studied, such as their synthesis, structural aspects, and applications in organic synthesis and organometallic catalysis [2].

3.1. TYPES OF PALLADACYCLES

There is a difference between those palladacycles with an organic moiety that can act as a C-anionic four-electron donor ligand or as a C-anionic six-electron donor ligand abbreviated as CY and YCY respectively (see Figure 1). CY-type palladacycles usually exist as halogen or acetate bridged dimers that lead two geometrical isomers, *cisoid* and *transoid* conformations (see Figure 2). These compounds can be neutral (bis-cyclopalladated or monomeric) or ionic

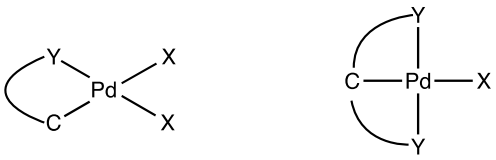


Figure 1. Anionic four-electron donor (CY) and aniònic six-electron donor (YCY) palladacycle.

(cationic or anionic), depending on the nature of the ligand X. The Pd-C bond is usually with an aromatic sp^2 carbon and less common with a sp^3 carbon or an sp^2 vinylic carbon [3]. Ligands usually have nitrogen as donor atom, such as azobenzenes, amines, imines and pyridines, phosphor such as phosphines or oxygen such as amides and ethers. The most common palladacycles are derived from tertiary amines and imines whereas compounds derived from

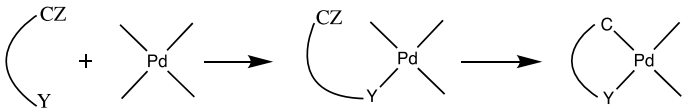
Cisoid-palladacycle Transoid-palladacycle

Figure 2. CY dimer geometrical isòmers (X=Cl, Br, I, OAc, etc.)

primary amines are quite rare [3]. Five- or six-members rings usually stabilize the CY-type compounds even though the number of members can vary. YCY-type palladacycles are usually symmetrical with two rings, or unsymmetrical with mixed rings [1].

3.2. METHODS OF PREPARATION

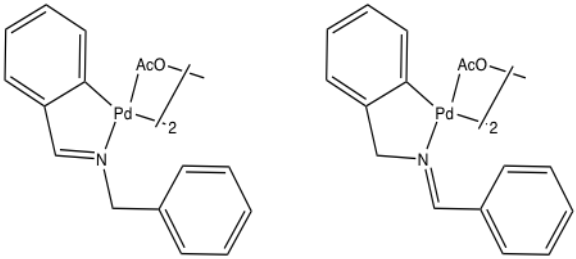
There are several methods for the synthesis of palladacycles, mostly for the formation of five- or six-membered chelate. In these processes a stable Pd-C bond is formed by the assistance of a two-electron donor ligand that previously coordinated the metal (see Scheme 1).



Scheme 1. Resume for the formation of a chelate where Y= NR_2, SR, PR_2, etc. and CZ= CH, CX, CM, C=C, C≡C

3.2.1. C-H Bond Activation

This is the more direct and simple method for the formation of palladacycles. It consists in the coordination of an assistant donor atom to facilitate an intramoleculary electrophilic attack of the metal at the carbon atom, preferentially for the formation of a five- or six-membered ring and the activation of aromatic C-H bonds versus other possible C-H [4]. The more commons methods are mixing Pd^{2+} salts with a base, or palladium acetate with acetic acid. The cyclopalladation of imines or oxazolines is highly regioselective because the *endo* product is mostly formed [5]. The *endo*- descriptor is used to refer to the structural isomers which contain the C=N inside the metallacycle and the *exo*- descriptor to refer to the structural isomers which contain the C=N outside the metallacycle (see Figure 3) [6]. This method can also be used for the synthesis of macrocycles [7].



endo-palladacycle exo-palladacycle

Figure 3. Exemples of endo- and exo-isomers

3.2.2. Oxidative Addition

Another very useful method that complements the C-H bond activation is the oxidative addition. Some palladacycles cannot be obtained directly, and the oxidative addition of aryl halides or alkyl halides can be a useful strategy. The more common starting materials are $[Pd_2(dba)_3]$ or $[Pd(PPh_3)_4]$ which generate dimeric halogen-bridged palladacycles, neutral YCY-type palladacycle or PPh_3-Pd bonded monomers. This is a good procedure for the formation of three- and four-membered rings pallacycles that are not easily accesible by C-H activation. Also it is a important method for the generation of palladacycles with reactive funcionalities. A disadvantage of these method is the accesibility of halide starting materials, because a multistep syntesis is needed [1].

3.2.3. Transmetalation

The transmetalation is a very common reaction and in most cases organolithium or organomercurial reagents are used for the generation of palladacycles. Organolithum compounds could be done by direct selective lithiation or by Li/halogen exchange [8]. Organomercurial compounds are good reagents for the generation of planar chiral cyclopalladed complexes with $Cr(CO)_3$ moiety [9]. Both methods are useful for the preparation of bis-cyclopalladated compounds. From these bis-cyclopalladated compounds and using $[PdCl_2(SMe)_2]$ it is possible obtaining halogen dimer palladacycles that are not accessible through others methods [1].

3.2.4. Alkoxy- and Carbopalladation of Alkenes and Halopalladation of Akynes

These reaction goes through the coordination of both the donor group and the C=C bond to the electrophilic Pd^{2+} followed by nucleophilic addition to the unsatured carbon atom leading to

the more stable palladacyclic ring, five-membered over six-membered rings [10]. Terminal allyl or homoallyl alkenes are better than internal alkenes. Hard nucleophiles tend to attack the metal center forming metallic palladium. Otherwise, estabilized carbanions lead to palladacycles by addition to the C=C bond [1].

3.3. STRUCTURAL ASPECTS

The Pd-C bond distance depends on various structural and electronic aspects such as the nature of the carbon bonded to the metal, the nature of the donor group, the size of the ring, etc. The distance may vary from 1.985 to 2.295 Å [11]. Dimeric pallacycles usually adopt two isomeric forms, *cisoid* and *transoid*, that are in equilibrium in solution [12]. For halogen dimer palladacycles, the *transoid* geometry is the more stable. The bond Pd-Halogen in *trans* is longer than the bond Pd-Halogen in *cis* because the trans influence of the carbon bonded to the metal is stronger than the *trans* inlfuence cause by the heteroatom bonded to the metal [13]. Acetate-

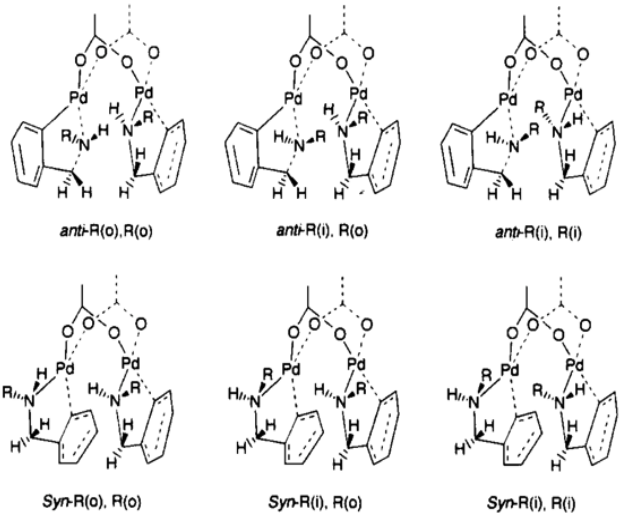


Figure 4. Possible isomers for aceto-bridged dinuclear complexes of Palladium.. R groups situated outside or inside the dihedral angle are representated by "in" or "out". (figure extracted by Y. Fuchita et al. ref. 14)

bridged palladacycles adopt an "open-book" structure that lead to three more structural isomers, besides the *cisoid* and the *transoid* conformations; *in-in, out-in* and *out-out,* that depend on the nature of the ligand [14]. The monomeric palladacycles that are formed through the bridge

splitting reaccion with L-type ligands such as pyridine or phosphines, most of them have the L ligand located in *cis* with the Pd-C bond, more stable isomer, because of the thermodinamic control of the reaction.

3.4. APPLICATIONS

There are many areas of research of cyclopalladated compounds that have promoted into some interesting applications including organic synthesis, homogeneous catalysis, the design of new metallomesogenses and antitumor drugs.

Various applications of cyclopalladated compounds to organic synthesis are the reactions with alkenes, alkynes, carbon monoxide, isocyanides, halogens, organolithiums, Grignard reagents, etc, that provide routes to a variety of *ortho*-disubstituted aromatic molecules, heterocycles and other products [15]. Cyclopalladated compounds are usually used for these reactions because Pd^{2+} is by far the most efficient metal for intramoleculary C-H activation of a great variety of ligands. Also Pd is one of the most versatile metals for C-C and C-Y bond synthesis [16].

The use of palladacycles as catalyst precursors started with the hydrogenation of C=C bonds and it was followed by the selective reduction of nitro-aromatic compounds, nitro-alkenes, nitriles, alkynes, alkenes and aromatic carbonyl compounds [17]. But the most interesting subject is the possibility of C-C coupling reactions such as Heck- and Suzuki-type, besides other cross-couplings reactions and oxidation chemistry. Although palladacycles are used, they just act as a precursor, being Pd(0) the real active specie. Most of catalytic reactions follow a cyclic model mechanism[1].

Mesogenic palladacycles interest has been arising over the last years due their promising properties [18]. The ease of being able to coordinate a great varity of ligands to palladium makes possible to improve desired properties. These palladium liquid crystals, in the majority of cases, are dimeric or monomeric five-membered orthopalladated complexes derivates from aromatic imines, phenylpyridine or phenylpyrimidine. These new compounds have high termal stability and a variety of geometries [1]. Halogen-bridged compounds present better mesogenic proprieties than acetate-bridged compounds because of their “open-book” structure, which is bad for anisotropy [19]. Even so, no practical applications have yet been reported, in particular due to the melting point being so distant from room temperature.

The discovery of biological propieties of cisplatin (*cis*-$PtCl_2(NH_3)_2$) was one of the most important achievements for cancer chemotherapy. The cytotoxicity of cisplatin is originated by platinum-DNA monoaducts and intra- and interstrand adducts in the nucleus of cells. The success of platinum drugs has inspired the search for other cancer metallodrugs, specifically for metal complexes that do not behave like cisplatin [20]. In general most palladium complexes have little or no antitumor activity relative to platinum complexes. It has been attributed to the high lability of the palladium(II) species [21]. Whereas platinum compounds maintain their structure, palladated compounds undergo rapid hydrolysis, substitution and isomeration reactions. The anticancer activity of palladium complexes can be modulated by modifying their structure to get more stable coordination compounds [12]. Particularly cyclopalladated compounds display cytotoxic proprieties toward several tumor cells lines, and some of them are also effective against cells that are resistant to cisplatin. Although some cyclopalladated complexes have been reportd to interect with DNA to kill tumor cells, there are also other cellurar sites interactions like mithocondrial membrane or inhibition of some enzymes implicated in some diseases, than contribute in cytotoxic activity [20]. Even though platinum complexes are better anticancer treatment at the moment, is important to investigate on new palladium complexes due to the possibility to modulate their properties.

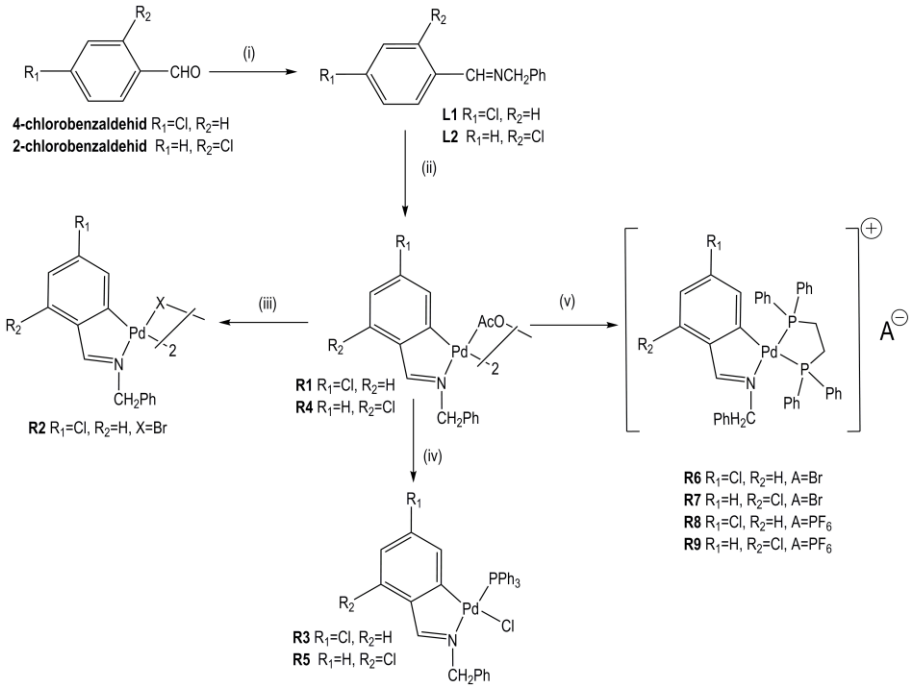
4. OBJECTIVES

The aim of this work is the preparation and characterization of some metallacycles of palladium. The specific objectives are:

- The synthesis of aromatic imines as ligands from aldehydes and primary amines by a condensation reaction.
- The synthesis of the acetate-bridged cyclopalladated compounds by C-H aryl bond activation from palladium acetate as metalation agent and the imines prepared before.
- The synthesis of halogen-bridged cyclopalladated compounds though substitutions reactions of acetate-bridged compounds.
- The synthesis of neutral mononuclear cyclopalladated compounds by splitting reactions of acetate-bridged compounds with phosphines.
- The synthesis of ionic mononuclear cyclopalladated compounds by splitting reaction of acetate-bridged compounds with chelating diphosphines.
- To improve purity of products done by column chromatography or recrystallization.
- To characterize products by IR spectra, ^{1}H and ^{31}P NMR spectra and MS-ESI^{+}.

5. RESULTS AND DISCUSSION

Several cyclopalladated compounds derivated from imines have been synthetized and characterized. Starting from *ortho*- and *para*-chlorobenzaldehid and benzylamine, the respective imines were obtained. Then mixing the imines with $Pd(AcO)_2$ the cyclometallation took place by the activation of the C-H aryl bond, and the *otro*- and *para*-chloro isomers of acetate-bridged cyclopalladated complex $[ClC_6H_4CHNCH_2C_6H_5]$ were obtained. From here and on it was possible to obtain different derivates such as other bridged dinuclear complexes and neutral or ionic mononuclear complexes (see Scheme 2).



Scheme 2. Resume for the synthesis. (i) NH_2CH_2Ph, in ethanol refluxing 1h; (ii) $Pd(AcO)_2$, in acetic acid refluxing 45 min; (iii) LiBr, in acetone at room temperature; (iv) PPh_3, LiCl, in acetone; (v) dppe, in acetone with LiBr for **R6-R7** and KPF_6 for **R8-R9**.

5.1. IMINE LIGANDS

The *para*- and *ortho*-isomers of chlorobenzaldehid reacted with benzylamine in refluxing ethanol for 1 hour to give the corresponding [p-$ClC_6H_4CHNCH_2C_6H_5$] (**L1**) and [o-$ClC_6H_4CHNCH_2C_6H_5$] (**L2**) over 90% yield. The compound **L1** is a white solid at room temperature whereas **L2** is an oily material.

^1H NMR was done to verify the structure of compounds **L1** and **L2**. There are two interesting signals in the ^1H NMR spectra, the signal from -CH=N- proton and the signal from -CH_2N- proton. The imine proton has a signal at δ 8.35 ppm (1H) for **L1** and δ 8.85 ppm (1H) for **L2**, this difference in shifts can be explain by the position of the chlorine group in the coordinated aryl ring. A N=CH···Cl interaction between the imine proton and the chlorine atom takes place, that interaction reinforces the planarity of the compound and produces a downfield shift of the imine proton [22]. Only the *ortho*-compound (**L2**) has this interaction, because the imine proton and the chlorine are close enough in the space. In both isomers the -CH_2N- protons appear as an A_2 system that produces a single signal between 4.90-4.80 (2H). The other signals are just multiplets from aromatic protons. The NMR spectrums of both compounds are in accord with previous examples in the literature [23].

5.2. BRIDGED DINUCLEAR COMPLEXES

The imine ligands (**L1** and **L2**) reacted with palladium(II) acetate in acetic acid refluxing during 1 hour to give the corresponding acetate-bridged dinuclear cyclopalladated complexes [Pd{μ-AcO}{p-$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ (**R1**) and [Pd{μ-AcO}{o-$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ (**R4**). These acetate-bridged complexes can afford the conversion into the halogen-bridged analogues [Pd{μ-X}{$ClC_6H_3CHNCH_2C_6H_5$}]$_2$, by substitution reaction with LiBr for **R1** and LiCl for **R4**. Only a single characterizable compound [Pd{μ-Br}{p-$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ (**R2**) was isolated, the chloride-bridged could not been charateritzated by its insolubility. Both acetate-bridged and bromo-bridged compounds are yellow solids and were isolated in a high-yield. The mechanism of cyclopalladation reaction of imines in acetic acid is a complex process but it has been reported that takes place by an initial coordination to the palladium through the N-donor atom of imine, followed by the C-H bond activation to form the acetato-bridged dimer specie.[4] The halogen-bridged compounds go through a substitution pathway.

Compounds **R1**, **R2** and **R4** afforded IR, MS-ESI$^+$ and ^{1}H NMR spectra which were consistent with the structures proposed. In IR spectrum the C=O symmetric and asymmetric stretching appear at 1581 and 1414 cm^{-1} for **R1** and 1586 and 1405 cm^{-1} for **R4** suggesting a bidentate bridging coordination of acetate [24]. The C=N stretching band of **R1** may be overlap by the symmetric carboxilato stretching but for **R4** and **R2** appear at 1610 and 1612 cm^{-1} respectively [6]. The products were characterized by MS-ESI$^+$ and **R1** and **R4** afforded the same pattern of fragmentation but only the [M/2-AcO]$^+$ peak was observed. That result is characteristic of acetate-bridged palladacycles because they are quite labile. **R2** has a different pattern of fragmentation and none fragments can be assigned. ^{1}H NMR spectres of **R1**, **R2** and **R4** presented a singlet signal at δ 7.09, 7.69 and 7.61 ppm, respectively, which was assigned to the imine proton -CH=N-. The difference between **R1** and **R4** shifts can be explain by the position of the chlorine group in the coordinated aryl ring such in free imines [22]. **R1**, **R2** and **R4** also present a set of signals at lower δ values characteristic of an AB spin system, corresponding to the -CH_2N- protons. The results indicated that these cyclopalladeted bridged compounds adopted a rigid dinuclear structure.

Few drops of pyridine-d^5 were added to a $CDCl_3$ solution of **R1** and the ^{1}H NMR spectrum was recorded. A splitting reaction takes place and pyr-d^5 was coordinated as a ligand, so a mononuclear complex **R1'** was formed. ^{1}H NMR spectra of **R1'** does not have same signals for

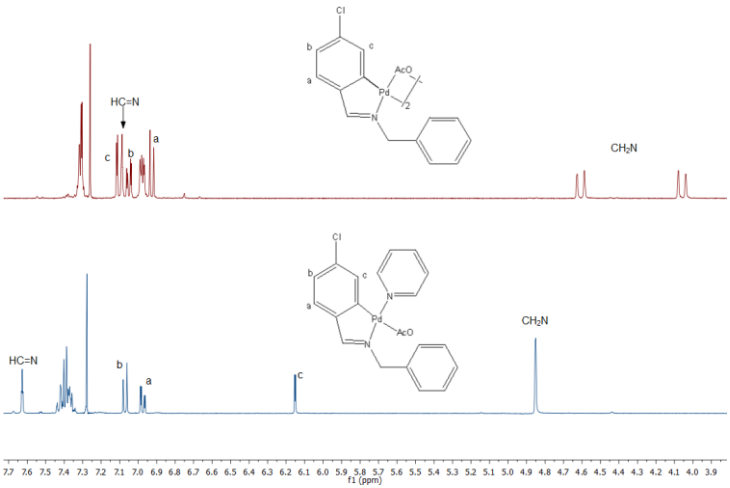


Figure 5. Comparison of the ^{1}H NMR spectrums of compounds **R1** (up) and **R1'** (down).

-HC=N- , -CH_2N-, and aromatic aryl chelated protons that was assigned previously from **R1**. There are differences between those products shown in Figure 5. The imine proton shows a downfield shift. The system -CH_2N- passed form an AB to an A_2 spin system, it only has a singlet (2H) instead of two doublets (1H). Finally the more interesting fact is that proton "c" from the aryl was upfield shifted due the interaction caused by the π-system from the pyridine, justifying that pyr-d^5 is in *cis* in relation to the coordinated aryl, and the metallation reaction has taken place [14].

Product **R1** was eluted by a column chromatography with silica gel and a solution of 100:1 CH_2Cl_2/MeOH as eluent and followed by TLC, in order to purify it. The ^{1}H NMR spectrum was not as the expected. The product was not the same as before the column, so it would have reacted within the column that was supposed to be inert. The spectrum seems to be like the halogen-bridged spectra so it may has been a substitution because the acetate group is too labile. To confirm this fact the product of the column was reacted with triphenylphosphine in acetone and the product of the reaction characterized by ^{1}H NMR. The evidences were clear and the final product has the same spectrum that product **R3** (see next headland), so **R1** reacted with the column and a substitution of the acetate-bridged ligand by chloride anion took place.

5.3. NEUTRAL MONONUCLEAR COMPLEXES

The acetate-bridged complexes (**R1**) and (**R4**) reacted with triphenilphosphine and lithium chloride in excess in acetone during 1 hour to give the mononuclear cyclopalladated complexes [PdCl{PPh_3}{p-$ClC_6H_3CHNCH_2C_6H_5$}] (**R3**) and [PdCl{PPh_3}{o-$ClC_6H_3CHNCH_2C_6H_5$}] (**R5**) respectively as white solids. This is a process that involves two reactions, a substitution of the acetate-bridged group for a halide-bridged group and the splitting reaction of the dinuclear complex with the coordination of the PPh_3 to the palladium center, to form a neutral mononuclear cyclopalladated complex.

IR, MS-ESI$^+$ and ^{1}H and ^{31}P NMR spectra of compounds **R3** and **R5** were consistent with the structures proposed. In IR spectrum the PPh_3 signals appears at 1434 and 1096 cm^{-1} for **R3** and 1435 and 1102 cm^{-1} for **R5** [24]. The C=N stretching band appear at 1618 and 1615 cm^{-1} for **R3** and **R5** respectively. Both compounds present a signal of MS-ESI$^+$ at 596.05 associated to the fragment [M-Cl]$^+$. Moreover **R5** present signals at 335.96 and 263 associated to [M-PPh_3-Cl]$^+$ and [PPh_3]$^+$ fragments. Signals present the expected isotopic distribution. ^{1}H NMR

spectrum of **R3** and **R5** present imine proton at δ 7.85 and 8.46 ppm, the different between shifts can be explain because the N=CH···Cl interaction of the *ortho*-chloro derivate. Both compounds have a set of signals at low δ values associated to -CH_2N- protons such previous products, but now that the dimer has been broken there is free rotation, the AB spin system has passed to an A_2 spin system. Moreover, there is a displacement to lower δ values for proton "c" in both compounds **R3** and **R5** compared with their acetate-bridged analogues respectively, same fact has been observed in ^{1}H NMR of pyr-d^5 derivate (see before). This fact can be explain by the anisotropic magnetic interaction produced by the phenyls of the PPh_3, and indicates a *trans* arrangement between the phosphine and the nitrogen atom [25]. In ^{31}P NMR spectra **R3** have a single signal at δ 41.13 ppm, within the range of coordinated phosphorous for PPh_3 that also confirm the *trans* arrangement between the PPh_3 and the imine nitrogen [25]. **R5** ^{31}P NMR spectrum presents a broad signal at δ 42.15 ppm, also in ^{1}H NMR there is a broad signal at δ 7.68 ppm. This may suggest that there is a dynamic equilibrium with the PPh_3. When the ^{1}H NMR was recorded in the presence of an excess of PPh_3 the signal at δ 7.6-7.8 ppm appears as a well-defined multiplet (see Figure 6). It seems that in solution there is a process of descoordination/coordination of PPh_3.

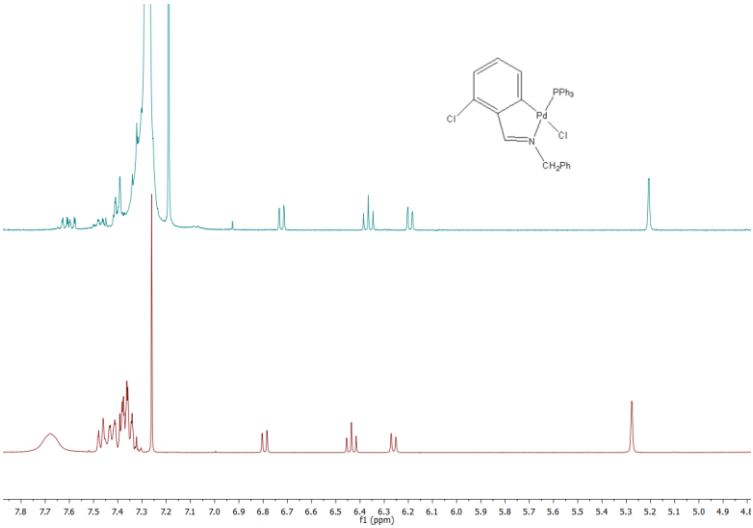


Figure 6. Comparison of the ^{1}H NMR spectrums of **R5** with excess of PPh_3 (up) and **R5** (down).

5.4. IONIC MONONUCLEAR COMPLEXES

The acetate-bridged complexes (**R1**) and (**R4**) reacted with dppe and lithium bromide in acetone during 1 hour to give the respectively cyclopalladated ionic complexes [Pd{dppe}{p-$ClC_6H_3CHNCH_2C_6H_5$}]Br (**R6**) and [Pd{dppe}{o-$ClC_6H_3CHNCH_2C_6H_5$}]Br (**R7**). When the same reaction was performed with potassium hexafluorophosphate ionic complexes [Pd{dppe}{p-$ClC_6H_3CHNCH_2C_6H_5$}]PF_6 (**R8**) and [Pd{dppe}{o-$ClC_6H_3CHNCH_2C_6H_5$}]PF_6 (**R9**) were obtained. All four compounds were yellow crystalline solids. This process involves a substitution of the acetate by diphosphine and the corresponding splitting reaction to form a cationic mononuclear complex with the respective contra ion.

IR, MS-ESI$^+$ and ^{1}H and ^{31}P NMR spectra were recorded for compounds **R6** and **R7** whereas only ^{1}H and ^{31}P NMR were recorded for compounds **R8** and **R9**. In IR spectrum it is possible to assigned the bands for the coordinated PPh_3 at 1435 and 1102 cm^{-1} for **R6** and 1434 and 1102 cm^{-1} for **R7**, and the band for C=N streching at 1618 and 1617 cm^{-1} respectively. MS-ESI$^+$ of both compounds present a signal at 732 associated to the fragment [M-Br]$^+$. The attempt of purify these compounds by recrystallization was unsuccesfull. In ^{1}H NMR it is possible to assigned -CH_2N- as a singlet, A_2 spin system, at δ value 4.45 for compounds **R6** and **R7** and 4.41 for compounds **R8** and **R9**. Moreover between δ values 2.4-3.0 there are multiplets in all compounds corresponding to the -CH_2CH_2- system of dppe. In some spectrum it is possible to recognize the aryl chelated protons as well as the imine proton, but it there are clearly several set of signals in each spectrum so the products are not pure. ^{31}P NMR present more evidences of impurities in all compounds. The four compounds present doublets at δ values 43 and 59 ppm meaning that the diphosphine is coordinated somehow, but also there are others nearby signals that implies that other products has been formed. The difference between coordinated phosphorous δ values of same diphosphine could be caused by the *trans* influence of the atom bonded to the metal. At higher δ values there are the signals of phosphorous in *trans* with C, and in lower δ values there are the siganls in *trans* with the N [26]. In ^{31}P NMR of **R8** and **R9** there is also a multiplet at δ -142.09 and -142.07 ppm respectively, that shown the coupling with the fluoro atoms.

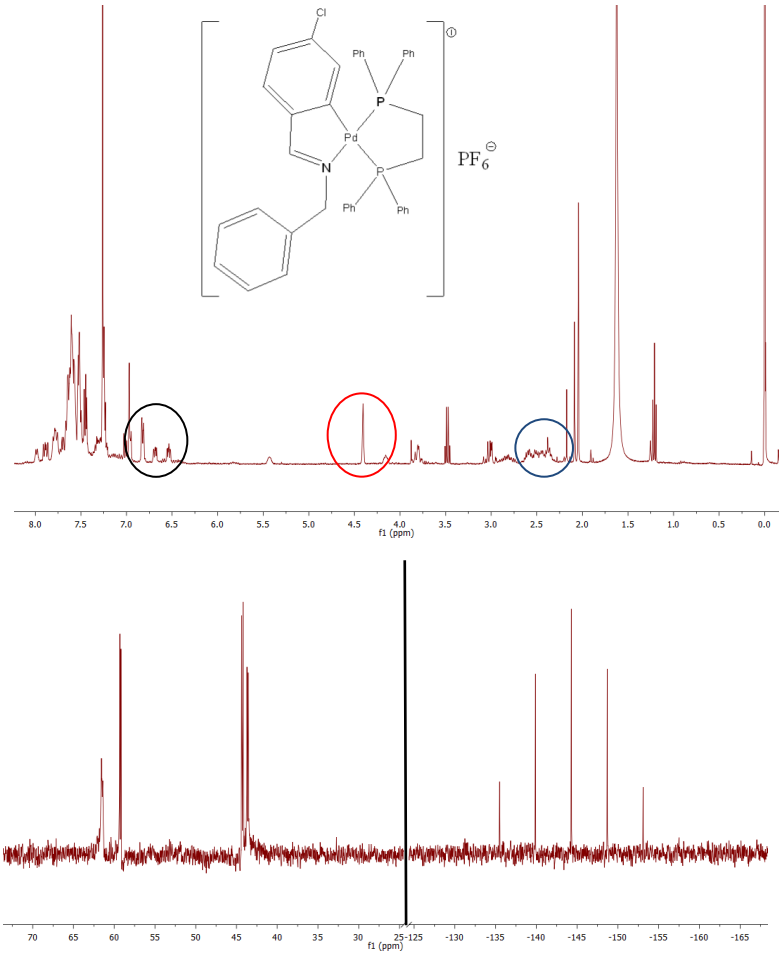


Figure 7. ^{1}H NMR (up) and ^{31}P NMR (down) of **R8** as example. ^{31}P NMR has been cut from 30 to -125 ppm. Indicated signals in ^{1}H NMR are aryl protons (black), $-CH_2N-$ protons (red) and $-CH_2CH_2-$ protons of dppe (blue). In both NMR spectrum could be seen that there are impurities.

As it was seen the reactions did not occur as expected and even though the main products seem to be formed some other subproducts of the reactions are observed. It has been proposed reasonable structures for those subproducts according to the information of the characterization (see Figure 8). Diphosphine can be coordinated either at the same complex or being a bridge between two complexes. In the first case it is possible that when the second phosphorous of the

diphosphine attacks the metal center, one way or the other the anion or the nitrogen leave and

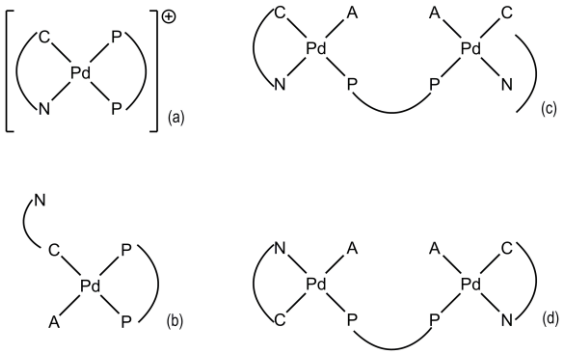
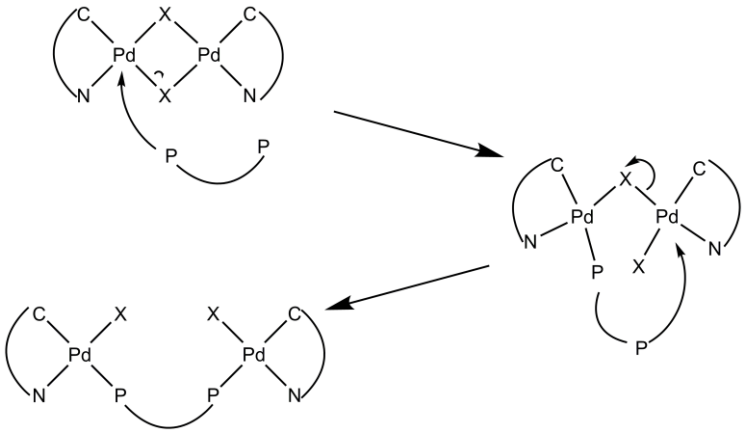


Figure 8. Possible products of reaction (v); (a) ionic mononuclear compound, (b) neutral mononuclear compound, (c) *cisoid* dinuclear compound, (d) *transoid* dinuclear compound.

two possible species could be form. Specie (a) is a cationic mononuclear complex whereas specie (b) is a neutral mononuclear complex with the imine ligand unchelated. If the anion is big enough the first specie it is more stable and should be formed. On the other case, after the coordination of the first phosphorous, the second phosphorous could have attack the bridging metalled center and form two possible dinuclear complexes, *cisoid* (c) and *transoid* (d) at is shown in Scheme 3 [27].



Scheme 3. Proposed mechanism for dppe attak on a cyclopalladated complex, as a subproduct of reaction (v). Example for *cisoid* comformation.

6. EXPERIMENTAL SECTION

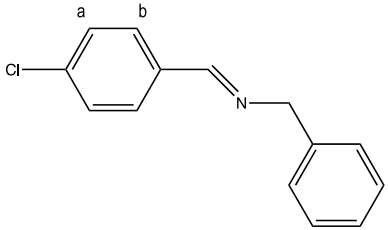
6.1. MATERIALS AND METHODS

IR, NMR and mass spectroscopy were used for characterisation of the compounds. NMR spectra were recorded in $CDCl_3$ (at 298 K). Chemical shifts are given in δ values (ppm) relative so TMS, and coupling constants are given in Hz. Multiplicity is expressed as: s (singlet), d (doublet), t (triplet), and m (multiplet). IR spectra were recorded in KBr dispersion. Band values are given in (cm^{-1}). MS-ESI$^+$ spectra were recorded in acetonitrile. Signal values are given in (m/z).

6.2. PREPARATION OF THE COMPOUNDS

6.2.1. Preparation of [p-$ClC_6H_4CHNCH_2C_6H_5$] - L1

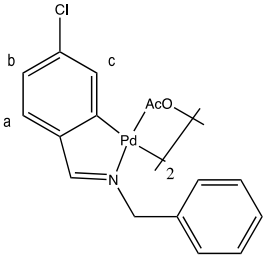
Compound [p-$ClC_6H_4CHNCH_2C_6H_5$] was obtained after refluxing for 1 hour a solution containing 294 mg (2.75 mmol) of [NH_2CH_2Ph] and 406 mg (2.89 mmol) of [p-ClC_6H_4CHO] in 20 ml of ethanol. The solvent was evaporated and a yellow liquid was obtained. Yield: 611 mg (97%)



^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.35 (s, 1H, HC=N), 7.72 (d, $^3J_{H-H}$=8.5, 2H, H^b), 7.39 (d, $^3J_{H-H}$=8.6, 2H, H^a), 7.36-7.24 (m, 5H, H^{ar}), 4.82 (s, 2H, CH_2N)

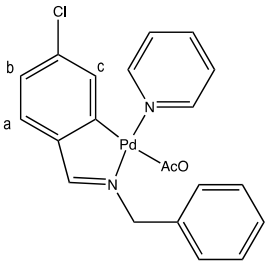
6.2.2. Synthesis of [Pd{μ-AcO}{p-$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ - R1

Compound [Pd{μ-AcO}{p-$ClC_6H_3CHNCH_2C_6H_5$}]$_2$ was obtained after stirring at 100ºC for 45 minutes a solution containing 202 mg (0.879 mmol) of [o-$ClC_6H_4CHNCH_2C_6H_5$] and 201 mg (0.895 mmol) of $Pd(AcO)_2$ in 20 ml of acetic acid. The residue was filtered and the solvent was evaporated. Then it was treated with ethanol and the precipitation of a brown solid was observed. The solid was filtered and dried under vacuum. Yield: 228 mg (66%)



^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.32 (d, $^4J_{H-H}$=1.6, 1H, H^{ar}), 7.30 (d, $^3J_{H-H}$=2.2, 2H, H^{ar}), 7.11 (d, $^4J_{H-H}$=2, 1H, H^c), 7.09 (t, $^4J_{H-H}$=1.6, 1H, HC=N), 7.05 (dd, $^3J_{H-H}$=8, $^4J_{H-H}$= 2 1H, H^b), 7.00-6.98 (m, 2H, H^{ar}) , 6.93 (d, $^3J_{H-H}$=8, 1H, H^a), 4.61 (d, $^3J_{H-H}$=15.9, 1H, CH_2N), 4.06 (d, $^3J_{H-H}$=15.8, 1H, CH_2N), 2.18 (s, 2H, H^{AcO})
IR: υ= 1581 (acetate), 1414 (acetate)
MS-ESI$^+$: $[M/2\text{-Aco}]^+$= 335

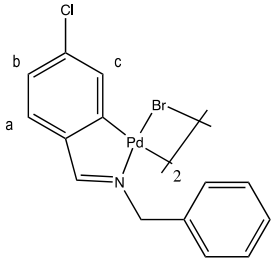
A little part of product was also treated with Pyr-d5 in NMR tube and then characterised by NMR.



^{1}H NMR ($CDCl_3$, 400 MHz): δ=8.62 (s, $H^{pyr\text{-}d5}$), 7.63 (t, $^4J_{H-H}$=1.5, 1H, HC=N), 7,39 (m, 5H, H^{ar}), 7.07 (d, $^3J_{H-H}$=8, 1H, H^a), 6.98 (dd, $^3J_{H-H}$=8, $^4J_{H-H}$=2, 1H, H^b), 6.15 (d, $^4J_{H-H}$=1.5, 1H, H^c), 4.85 (s, 2H, CH_2N), 2.23 (s, 2H, H^{AcO})

6.2.3. Synthesis of $[Pd\{\mu\text{-}Br\}\{p\text{-}ClC_6H_3CHNCH_2C_6H_5\}]_2$ - R2

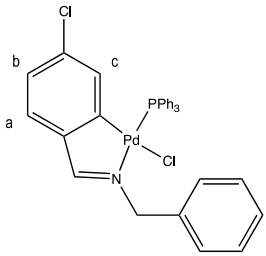
Compound $[Pd\{\mu\text{-}Br\}\{C_6H_4CHNCH_2C_6H_5\}]_2$ was obtained after stirring at room temperature for 1 hour a solution containing 101 mg (0.128 mmol) of $[Pd\{\mu\text{-}AcO\}\{p\text{-}ClC_6H_3CHNCH_2C_6H_5\}]_2$ and excess of LiBr, 60 mg (0.677 mmol), in 20 ml of acetone. The residue was filtered and the solvent was evaporated. A yellow solid was obtained then it was treated with ethanol and filtrated under vacuum. Yield 62 mg (58%)



^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.69 (s, 1H, HC=N), 7.51 (s. br., 1H, H^c), 7.39 (m, 5H, H^{ar}), 7.08 (d, $^3J_{H-H}$=7.9, 1H, H^a), 7.04 (dd, $^3J_{H-H}$=8.1, $^4J_{H-H}$=1.8, H^b), 3.73 (d, $^3J_{H-H}$=8, 1H, CH_2N), 3.72 (d, $^3J_{H-H}$=8, 1H, CH_2N)
IR: υ= 1612 (C=N)

6.2.4. Synthesis of [PdCl{PPh_3}{p-$ClC_6H_3CHNCH_2C_6H_5$}] - R3

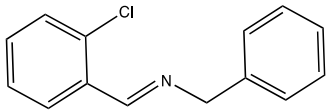
Compound [PdCl{PPh_3}{p-$ClC_6H_3CHNCH_2C_6H_5$}] was obtained after stirring at room temperature for an hour a solution containing 102 mg (0.129 mmol) of [Pd{μ-AcO}{p-$ClC_6H_3CHNCH_2C_6H_5$}]$_2$, 68 mg (0.259 mmol) of PPh_3 and excess of LiCl, 35 mg (0.642 mmol), in 20 ml of acetone. The white suspension was filtered under vacuum and the mother liquor was evaporated. Then a white solid was obtained after the addition of ether, and it was filtered under vacuum. Yield: 62 mg (38%)



^{1}H NMR ($CDCl_3$, 400 MHz): δ= 7.85 (s, 1H, HC=N), 7.73 (t, $^3J_{H-H}$=9.8, 6H, H^{ar}), 7.46 (dd, $^3J_{H-H}$=7.5, $^4J_{H-H}$=1.9, 2H, H^{ar}), 7.42-7.35 (m,10H, H^{ar}), 7.06 (d, $^3J_{H-H}$=8, 1H, H^a), 6.84 (dd, $^3J_{H-H}$=8, $^4J_{H-H}$=1.9, 1H, H^b), 6.24 (s, 1H, H^c), 5.25 (s, 2H, CH_2)
^{31}P NMR ($CDCl_3$, 161.98 MHz): δ= 41.13 (s, 1P, PPh_3)
IR: υ= 1618 (C=N), 1434 (PPh_3), 1096 (PPh_3)
MS-ESI$^+$: $[M-Cl]^+$= 596

6.2.5. Preparation of [o-$ClC_6H_4CHNCH_2C_6H_5$] - L2

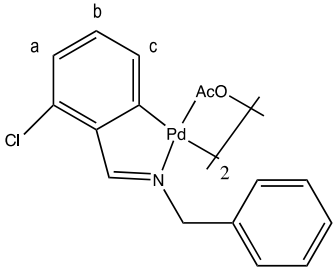
Compound [o-$ClC_6H_4CHNCH_2C_6H_5$] was obtained after refluxing for 1 hour a solution containing 310 mg (2,89 mmol) of [NH_2CH_2Ph] and 404 mg (2,87 mmol) of [o-ClC_6H_4CHO] in 20 ml of ethanol. The solvent was evaporated and a yellow liquid was obtained. Yield: 619 mg (94%)



^{1}H NMR ($CDCl_3$, 400 MHz): δ= 8.85 (d, J_{H-H}=1.6, 1H, HC=N), 8.09 (dd, $^3J_{H-H}$=7.9, $^4J_{H-H}$=1.9, 1H, H^{ar}), 7.33 (m, 8H, H^{ar}), 4.87 (d, $^4J_{H-H}$=1.5, 2H, CH_2N)

6.2.6. Synthesis of $[Pd\{\mu\text{-}AcO\}\{o\text{-}ClC_6H_3CHNCH_2C_6H_5\}]_2$ - R4

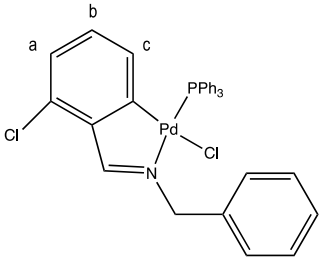
Compound $[Pd\{\mu\text{-}AcO\}\{o\text{-}ClC_6H_3CHNCH_2C_6H_5\}]_2$ was obtained after stirring at 100ºC for 45 minutes a solution containing 207 mg (0.901 mmol) of $[o\text{-}ClC_6H_4CHNCH_2C_6H_5]$ and 202 mg (0.900 mmol) of $Pd(AcO)_2$ in 20 ml of acetic acid. A suspension was observed. The solid was filtered under vacuum and the solvent was evaporated. Then it was treated with ethanol and it was filtered and dried under vacuum. Yield: 237 mg (67%)



^1H NMR ($CDCl_3$, 400 MHz): δ= 7.61 (t, $^3J_{H\text{-}H}$=1.5, 1H, HC=N) 7.31 (m, 3H, H^{a+b+c}), 7.03 (m, 5H, H^{ar}), 4.52 (d, $^3J_{H\text{-}H}$=15.1, 1H, CH_2), 3.92 (d, $^3J_{H\text{-}H}$=16.3, 1H, CH_2).
IR: υ= 1610 (C=N), 1586 (acetate), 1405 (acetate)
MS-ESI$^+$: $[M/2\text{-}AcO]^+$= 335

6.2.7. Synthesis of $[PdCl\{PPh_3\}\{o\text{-}ClC_6H_3CHNCH_2C_6H_5\}]$ - R5

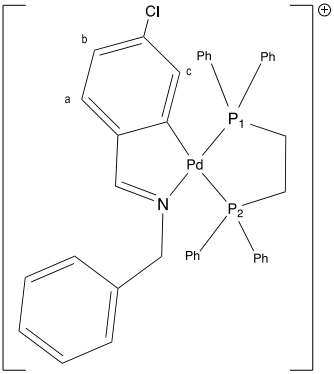
Compound $[PdCl\{PPh_3\}\{o\text{-}ClC_6H_3CHNCH_2C_6H_5\}]$ was obtained in two steps. After stirring at room temperature for 45 min a solution containing 116 mg (0.147 mmol) of $[Pd\{\mu\text{-}AcO\}\{\{o\text{-}ClC_6H_3CHNCH_2C_6H_5\}]_2$ and 31mg (0.736 mmol) of LiCl in 20 ml of acetone, to obtain $[Pd\{\mu\text{-}Cl\}\{o\text{-}ClC_6H_3CHNCH_2C_6H_5\}]_2$. The solid was filtered dried under vacuum and the solvent was evaporated obtaining 75mg (0.101 mmol). The yellow solid was added into a solution with 53 mg (0.202 mmol) of PPh_3 and 20 ml of acetone. After stirring 45 min at room temperature, the solution was filtered and the solvent was evaporated. The solid obtained was treated with ether and then filtered under vacuum and the solvent was evaporated. Yield: 77 mg (42 %)



^1H NMR ($CDCl_3$, 400 MHz): δ= 8.46 (s, 1H, HC=N), 7.71 (s br., 6H, H^{ar}), 7.28 (m, 16H, H^{ar}), 6.79 (d, $^3J_{H\text{-}H}$=8.2, 1H, H^a), 6.44 (t, $^3J_{H\text{-}H}$=7.9, 1H, H^b), 6.27 (d, $^3J_{H\text{-}H}$=7.8, 1H, H^c), 5.28 (s, 2H, CH_2N)
^{31}P NMR ($CDCl_3$, 161.98 MHz): δ= 42.17 (s, 1P, PPh_3)
IR: υ= 1615 (C=N), 1435 (PPh_3), 1102 (PPh_3)
MS-ESI$^+$: $[M\text{-}Cl]^+$= 596, $[M\text{-}PPh_3\text{-}Cl]^+$=336, $[PPh_3]^+$=263

6.2.8. Synthesis of [Pd{dppe}{p-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]Br – R6

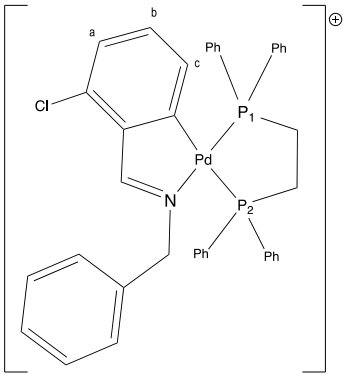
Compund [Pd{dppe}{p-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]Br was obtained after stirring at room temperature for 1 hour a solution containing 102 mg (0.129 mmol) of [Pd{μ-AcO}{{p-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]$_2$ in 20 ml of acetone and adding 106 mg (0.266 mmol) of dppe and 67 mg (0.779 mmol) of LiBr. The solution was filtered and the solvent was evaporated. A yellow solid was obtained and treated with ether, then filtered under vacuum and the solvent was evaporated. Yield: 251 mg (119%)



^{1}H NMR (CDCl$_3$, 400 MHz): 8.17 (d, $^nJ_{H-H}$=6.4, 1H, HC=N), 7.80 (m, 4H, H) 7.68 (m, 3H, H), 7.53 (m, 10H, H), 7.36 (d, $^3J_{H-H}$=8.2, 1H, H^a), 7.24 (m, 3H, H), 7.01 (dd, $^3J_{H-H}$=8, $^4J_{H-H}$=2, 1H, H^b), 6.83 (m, 2H, H), 6.58 (t, $^3J_{H-H}$=6.5, 1H, H^c), 4.45 (d, 2H, CH$_2$), 2.60 (m, CH$_2^{dppe}$)
^{31}P NMR (CDCl$_3$, 161.98 MHz): 60.75 (d, 1P, P$_2$), 43.51 (d, 1P, P$_1$)
IR: υ= 1617 (C=N), 1435 (PPh$_3$). 1102 (PPh$_3$)
MS-ESI$^+$: [M-Br]$^+$= 732

6.2.9. Synthesis of [Pd{dppe}{o-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]Br – R7

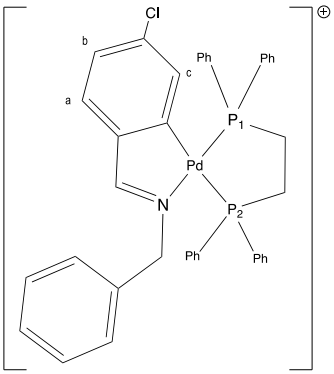
Compund [Pd{dppe}{o-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]Br was obtained after stirring at room temperature for 1 hour a solution containing 102 mg (0.129 mmol) of [Pd{μ-AcO}{{o-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]$_2$ in 20 ml of acetone and adding 104 mg (0.261 mmol) of dppe and 68 mg (0.783 mmol) of LiBr. The solution was filtered and the solvent was evaporated. The solid obtained was treated with ether and then filtered under vacuum and the solvent was evaporated. Yield: 250 mg (119%)



^{1}H NMR ($CDCl_3$, 400 MHz): 8.49 (d, $^{n}J_{H\text{-}H}$=6.6, 1H, HC=N), 7.89 (dd, $^{3}J_{H\text{-}H}$=12.4, $^{4}J_{H\text{-}H}$=7.5, 8H, H^{ar}), 7.67 (dd, $^{3}J_{H\text{-}H}$=11.4, $^{4}J_{H\text{-}H}$=7.6, 6H, H^{ar}), 7.52 (m, 15H, H^{ar}), 7.32 (m, 1H, H^{ar}), 7.26 (m, 7H, H^{ar}), 6.96 (d, $^{3}J_{H\text{-}H}$= 7.9, 2H, H^{ar}), 6.84 (dd, $^{3}J_{H\text{-}H}$=7.3, $^{4}J_{H\text{-}H}$=2.1, 5H, H^{ar}), 6.75 (m, 1H, H^{ar}), 6.60 (q, $^{3}J_{H\text{-}H}$=7, 2H, H^{ar}), 4.44 (s, 2H, CH_2N), 3-2.5 (m, 4H, CH_2^{dppe})
^{31}P NMR ($CDCl_3$, 161.98 MHz): 61.75 (d, 1P, P_2), 43.99 (d, 1P, P_1)
IR: υ= 1616 (C=N), 1434 (PPh_3), 1102 (PPh_3)
MS-ESI^{+}: $[M\text{-}Br]^{+}$= 732

6.2.10. Synthesis of [Pd{dppe}{p-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]PF$_6$ – R8

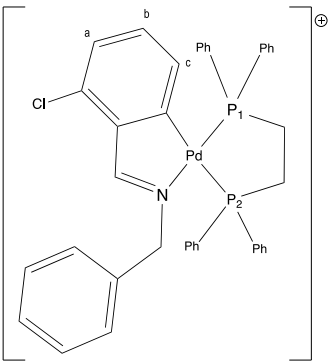
Compund [Pd{dppe}{p-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]PF$_6$ was obtained after stirring at room temperature for 1 hour a solution containing 100 mg (0.127 mmol) of [Pd{μ-AcO}{{p-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]$_2$ in 20 ml of acetone and adding 112 mg (0.281 mmol) of dppe and 48 mg (0.261 mmol) of KPF_6. The solution was filtered and the solvent was evaporated. The resin obtained was treated with ether and then filtered under vacuum and the solvent was evaporated. Yield: 200 mg (90%)



^{1}H NMR ($CDCl_3$, 400 MHz): 7.99 (d, $^{n}J_{H\text{-}H}$=7.5, 1H, HC=N), 7.89 (dd, $^{3}J_{H\text{-}H}$=11.9, $^{4}J_{H\text{-}H}$=7.3, 2H, H^{ar}), 7.78 (t, $^{3}J_{H\text{-}H}$=10, 2H, H^{ar}), 7.70 (m, 7H, H^{ar}), 7.61 (m, 6H, H^{ar}), 7.52 (m, 12H, H^{ar}), 7.45 (m, 3H, H^{ar}), 7.16 (m, 5H, H^{ar}), 7.02 (dd, $^{3}J_{H\text{-}H}$=8, $^{4}J_{H\text{-}H}$=2, 1H, H^{ar}), 6.97 (m, 3H, H^{ar}), 6.82 (dd, $^{3}J_{H\text{-}H}$=7.4, $^{4}J_{H\text{-}H}$=2, 2H, H^{ar}), 6.69 (m, 1H, H^{ar}), 6.54 (m, 1H, H^{ar}), 4.41 (s, 2H, CH_2N), 3-2.5 (m, 4H, CH_2^{dppe})
^{31}P NMR ($CDCl_3$, 161.98 MHz): 59.24 (d, 1P, P_2), 43.64 (d, 1P, P_1)

6.2.11. Synthesis of [Pd{dppe}{o-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]PF$_6$ – R9

Compund [Pd{dppe}{o-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]PF$_6$ was obtained after stirring at room temperature for 1 hour a solution containing 100 mg (0.127 mmol) of [Pd{μ-AcO}{{o-ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}]$_2$ in 20 ml of acetone and adding 111 mg (0.279 mmol) of dppe and 47 mg (0.255 mmol) of KPF$_6$. The solution was filtered and the solvent was evaporated. The solid obtained was treated with ether and then filtered under vacuum and the solvent was evaporated. Yield: 190 mg (85%)



$PF_6^{\ominus}$

^{1}H NMR (CDCl$_3$, 400 MHz): 7.97 (m,2H, H^{ar}), 7.86 (m, 1H, H^{ar}), 7.64 (m, 11H, H^{ar}), 7.48 (m, 18H, H^{ar}), 7.31 (m, 5H, H^{ar}), 7.23 (m, 11H, H^{ar}), 6.99 (m, 2H, H^{ar}), 6.93 (m, 2H, H^{ar}), 6.80 (m, 3H, H^{ar}), 6.68 (m, 4H, H^{ar}), 4.41 (s, 2H, CH$_2$N), 3-2.5 (m, 4H, CH$_2^{dppe}$)

^{31}P NMR (CDCl$_3$, 161.98 MHz): 59.35 (d, 1P, P$_2$), 43.48 (d, 1P, P$_1$)

7. CONCLUSIONS

Two aromatic imines have been synthesized. The metallation of the ligans were done and the acetate-bridged cyclopalladatd compounds, [*p*-$ClC_6H_4CHNCH_2C_6H_5$] (**R1**) and [*o*-$ClC_6H_4CHNCH_2C_6H_5$] (**R4**) has been synthesized (over 60% yield) and characterized by spectroscopic techniques. Moreover bromo-bridged compound [Pd{μ-Br}{$C_6H_4CHNCH_2C_6H_5$}]$_2$ (**R2**) and mononuclear neutral compounds [PdCl{PPh_3}{$ClC_6H_3CHNCH_2C_6H_5$}] (**R3**) and (**R5**) have been synthesized and fully characterized by ^1H and ^{31}P NMR and MS-ESI$^+$. On the other hand ionic compounds [Pd{dppe}{$ClC_6H_3CHNCH_2C_6H_5$}]A (A=Br, 2-Cl, **R6**; A=Br, 4-Cl, **R7**; A= PF_6, 2-Cl, **R8**; A= PF_6, 4-Cl, **R9**) could not be pure isolated and characterization shown that other by-products of the reaction have been formed. *Ortho-chloro* products have a N=CH···Cl interaction between the imine proton and the chlorine atom. This interaction reinforces the planarity of the compound producing a downfiled shift of iminic proton HC=N. Dimeric compounds have a rigid structure making the -CH_2N- group a AB spin system, whereas monomeric compounds have free rotation and the -CH_2N- group appears a A_2 spin system. Monodentated phosphines or pyridines in *trans* arrangement with imine nitrogen, produce an upshift of the *ortho* proton in relation to C-Pd bond, due the magnetic field induced. Acetate-bridged compounds could not have purified by a chromatographic column because they are very labile and have reacted with the column.

8. REFERENCES AND NOTES

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9. ACRONYMS

AcO - Acetate Gruop

ar - aromatic

br - broad signal

d - doublet

dba - Dibenzylideneacetone

dd - doublet of doublets

DNA - Desoxyribonucleic Acid

dppe – 1,2-Bis(diphenylphosphino)ethane

MS-ESI$^+$ - Electrospray ionization time-of-flight mass spectrometry

IR - Infrared spectroscopy

J_{A-B} - Coupling constant between atom A and B

L - Neutral Ligand

m - multiplet

NMR - Nuclear Magnetic Ressonace

pyr-d5 – pyridine pentadeuterated

q - quadruplet

s - singulet

t - triplet

TLC – Thin-layer chromatography

TMS – Tetramethylsilane

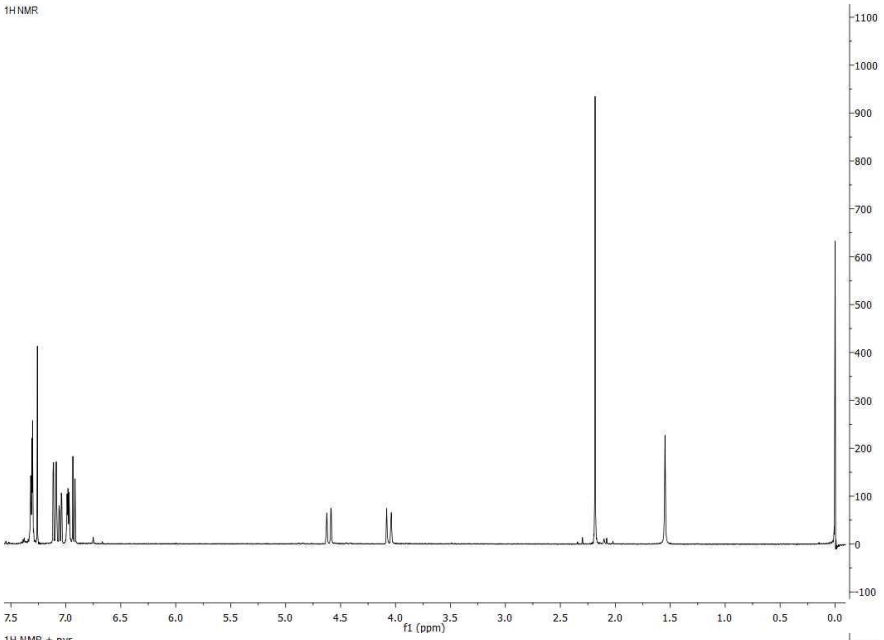
X - Halogen Group

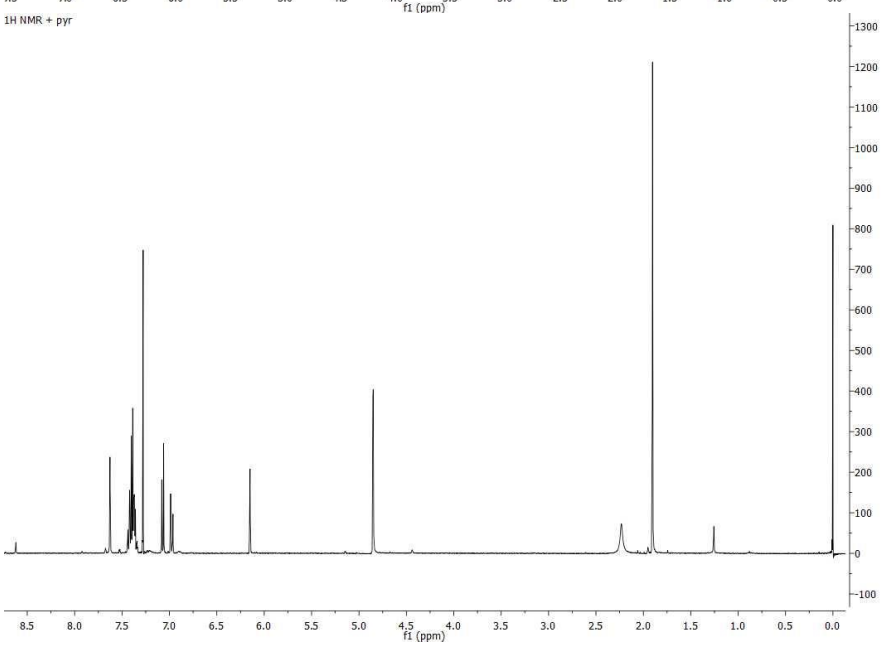
δ – chemical shift

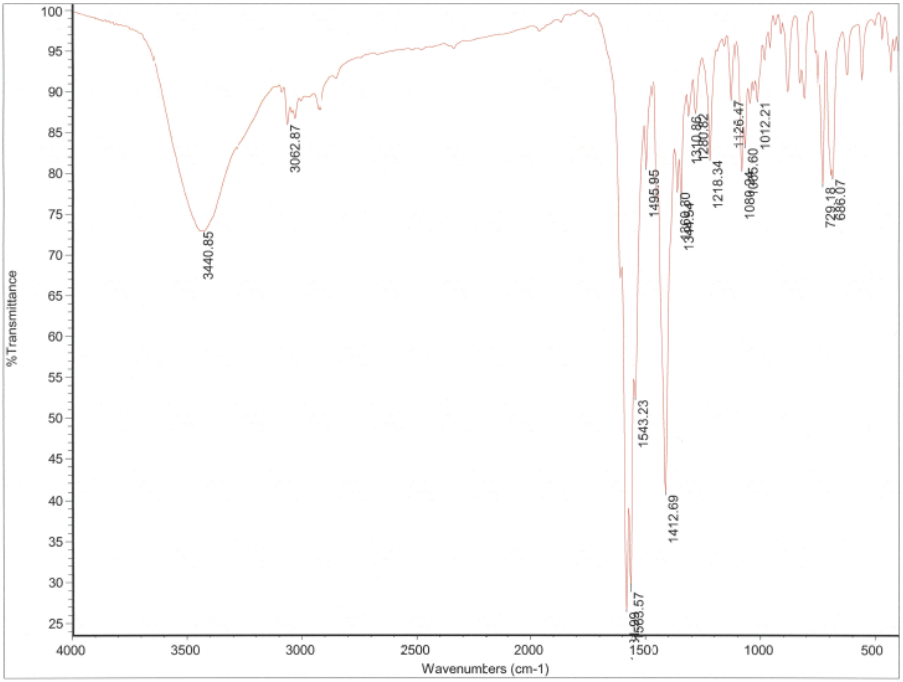
μ - Bridged ligand

APPENDICES

APPENDIX 1: SPECTRA DATA OF R1



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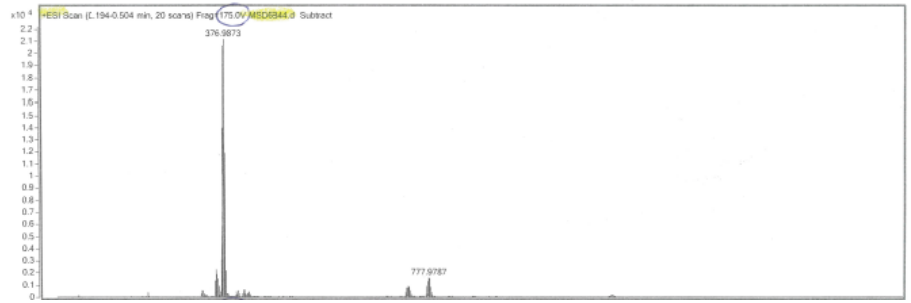
729.18
686.07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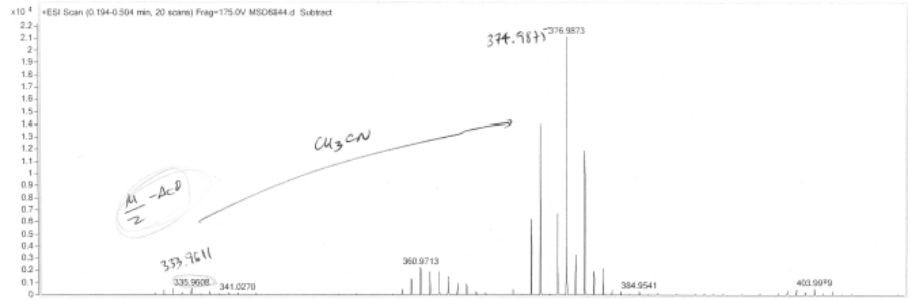
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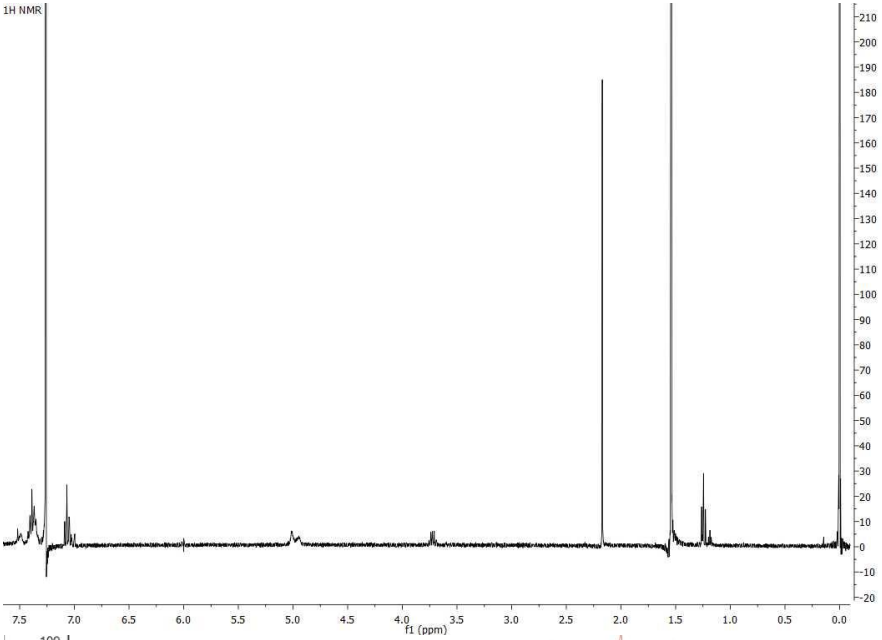

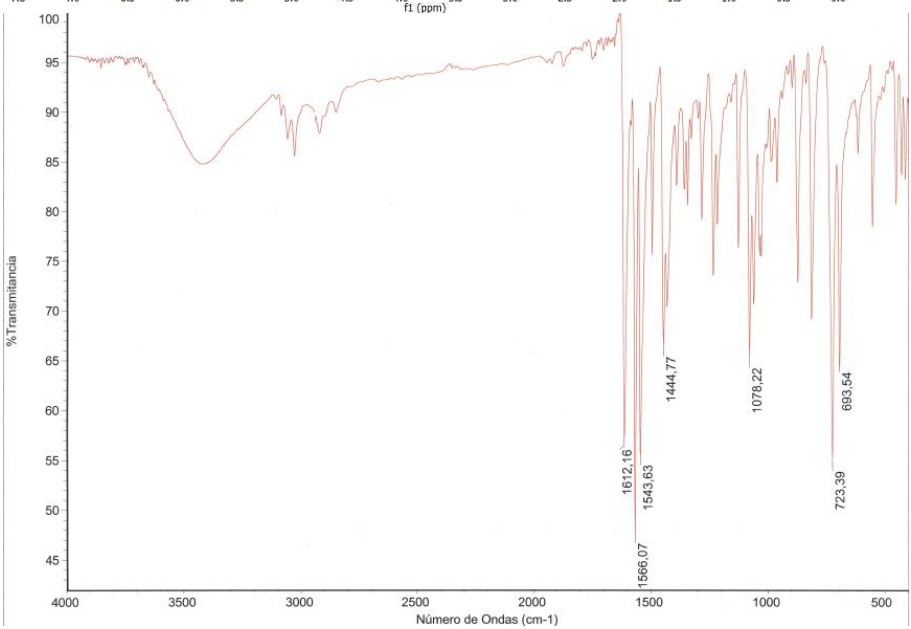

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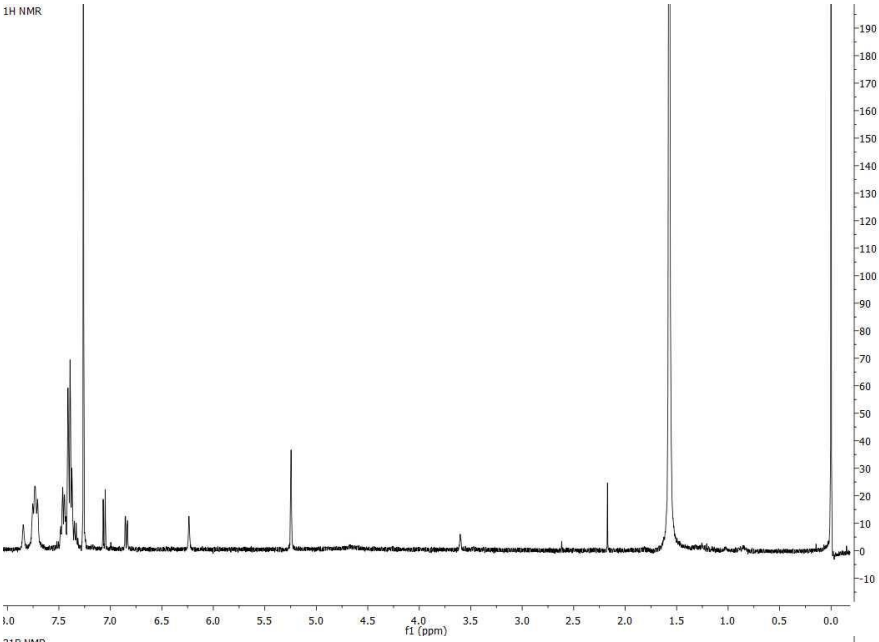

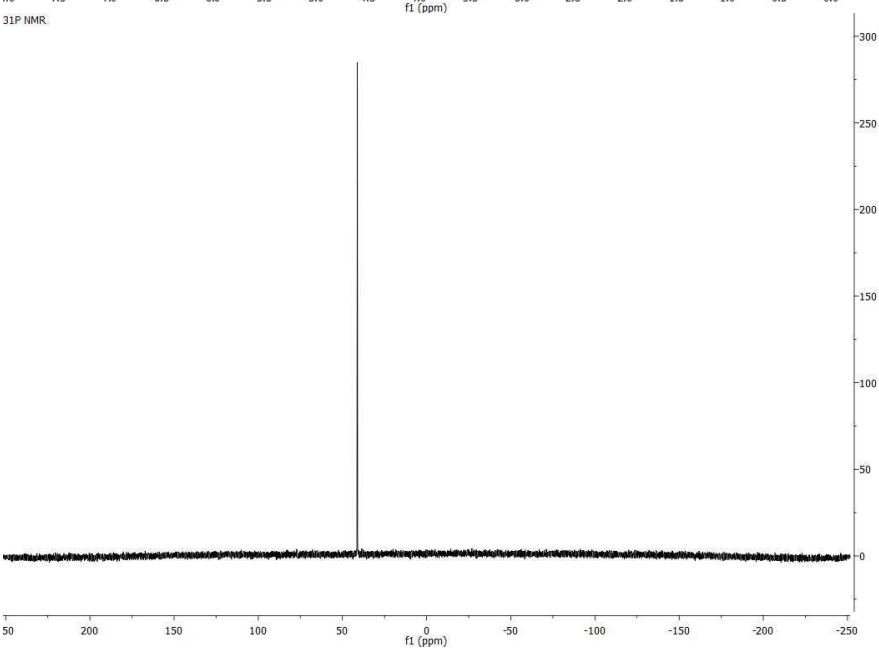

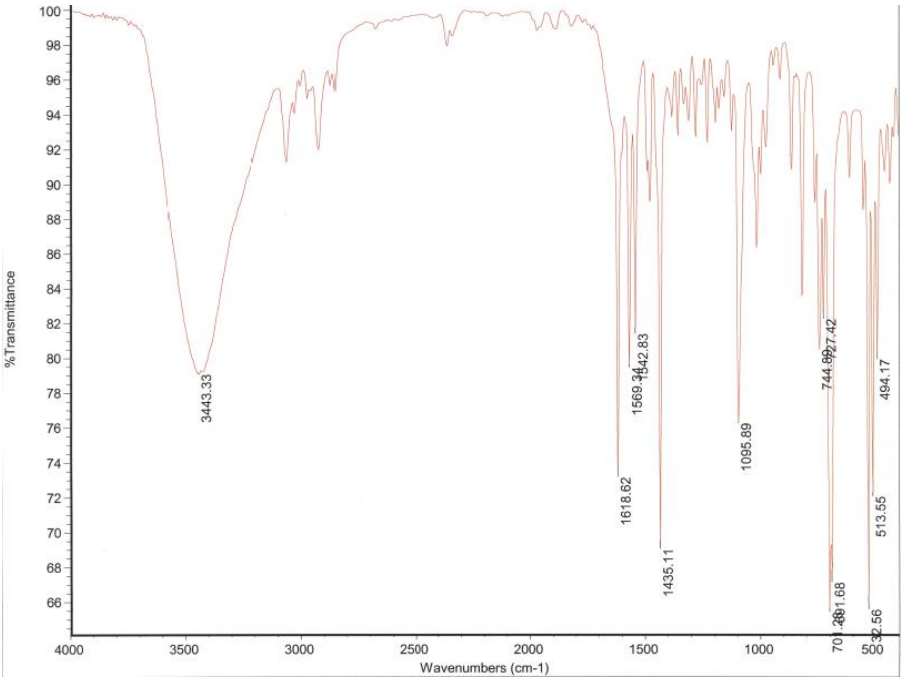
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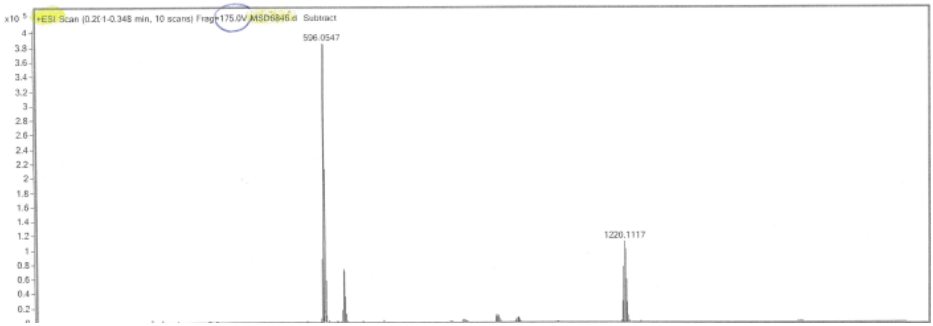
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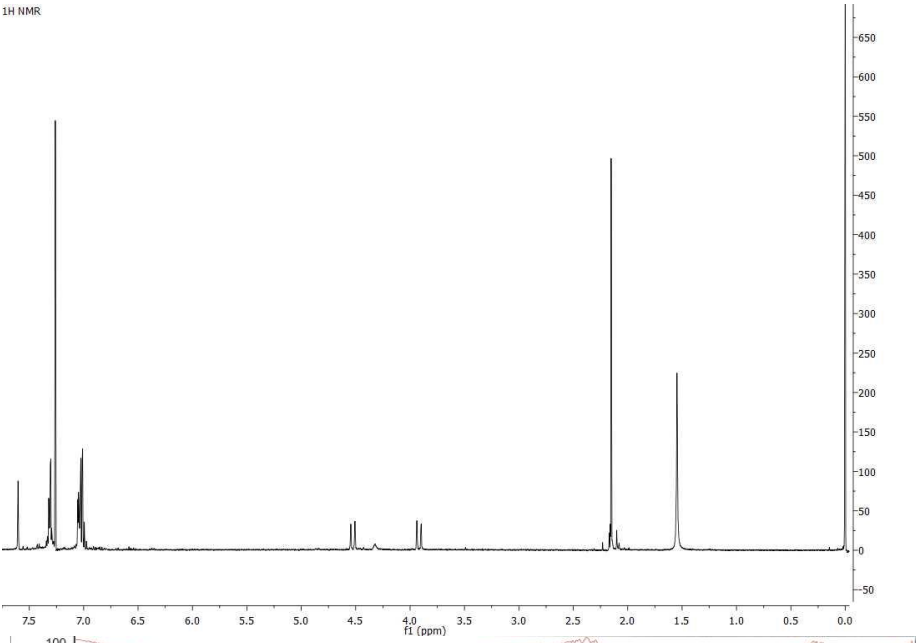

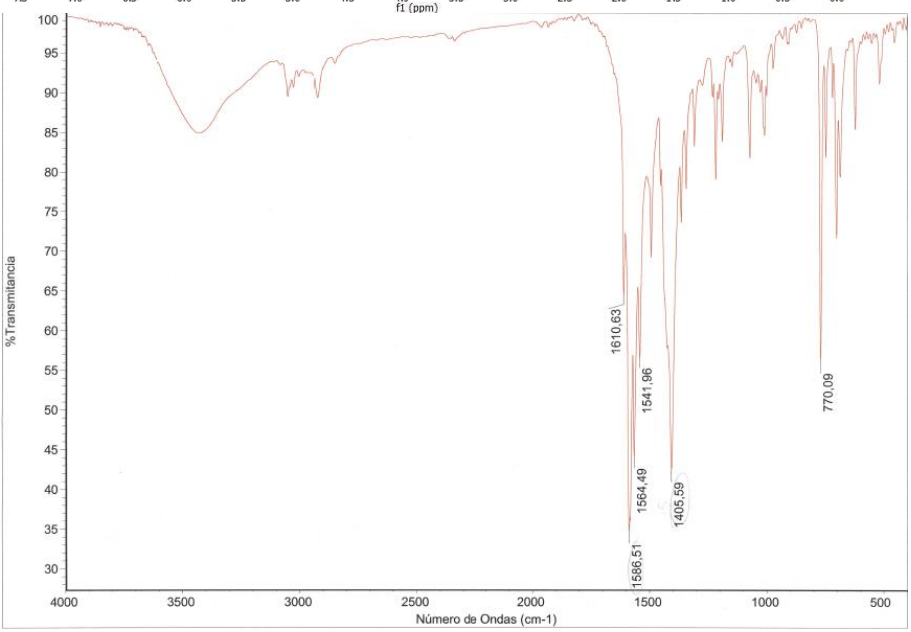

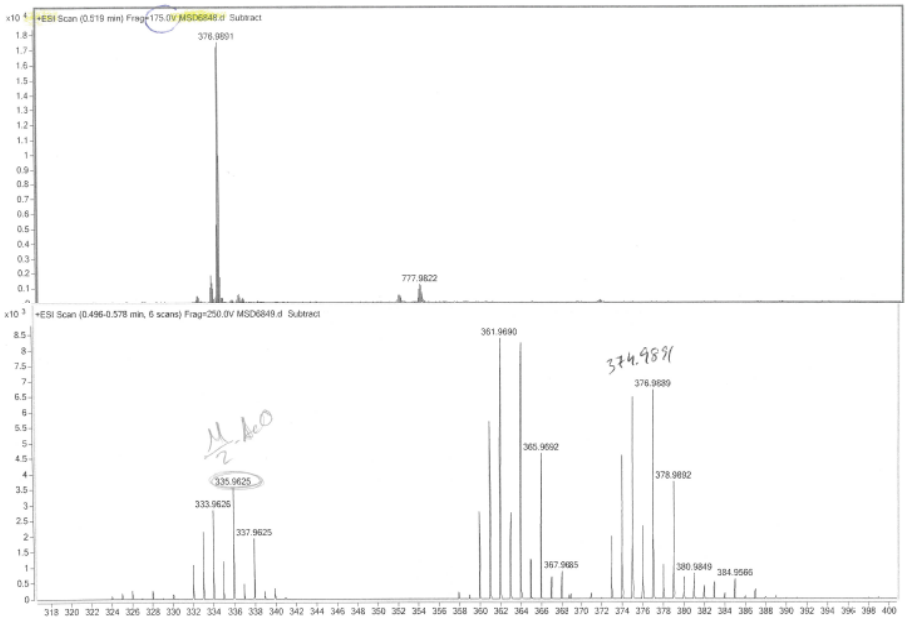
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374.9891
376.9889
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380.9849
384.9566

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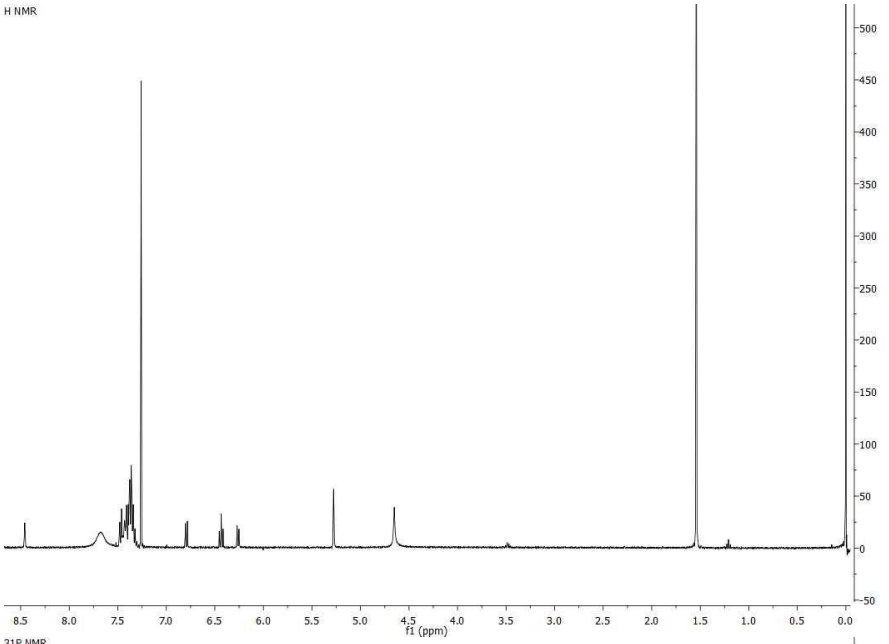

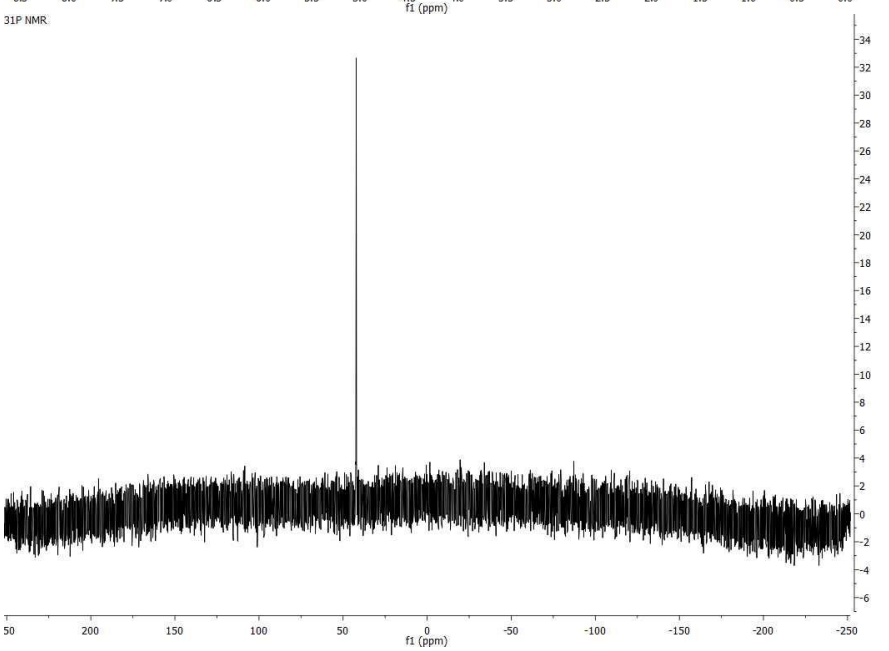

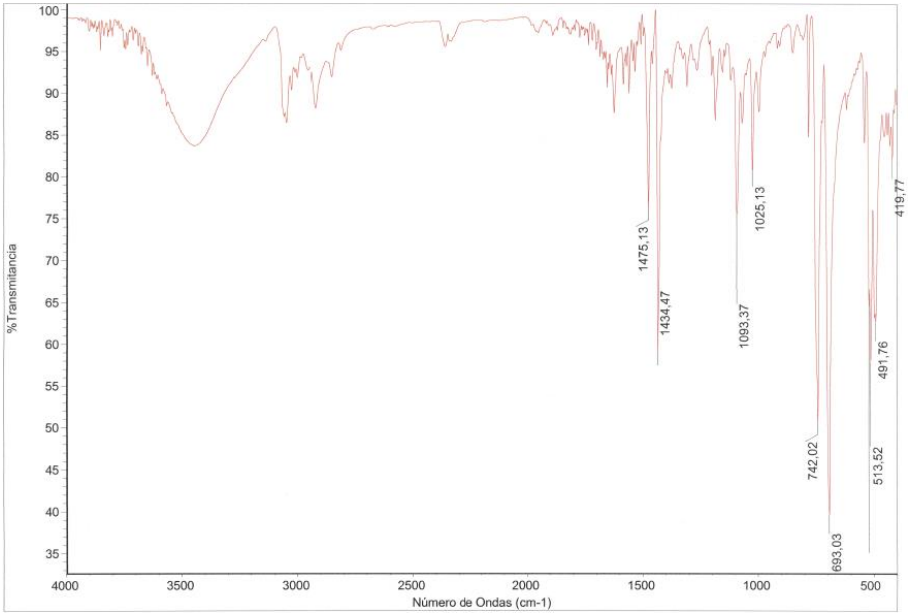
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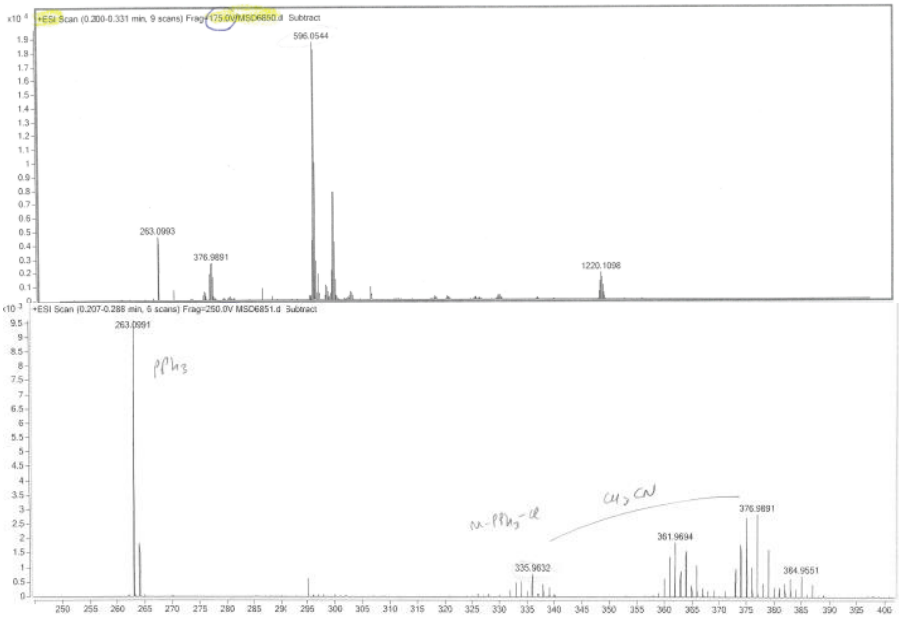
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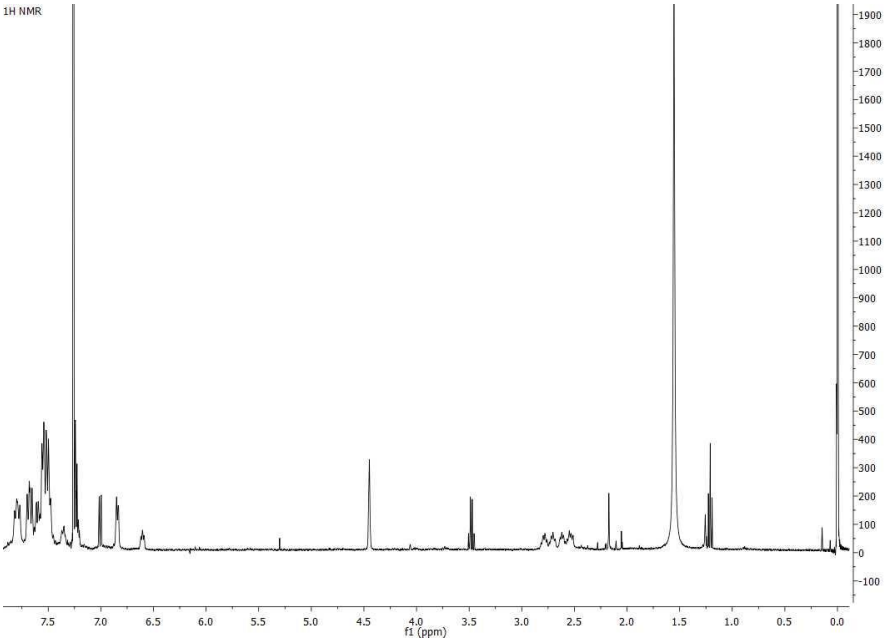

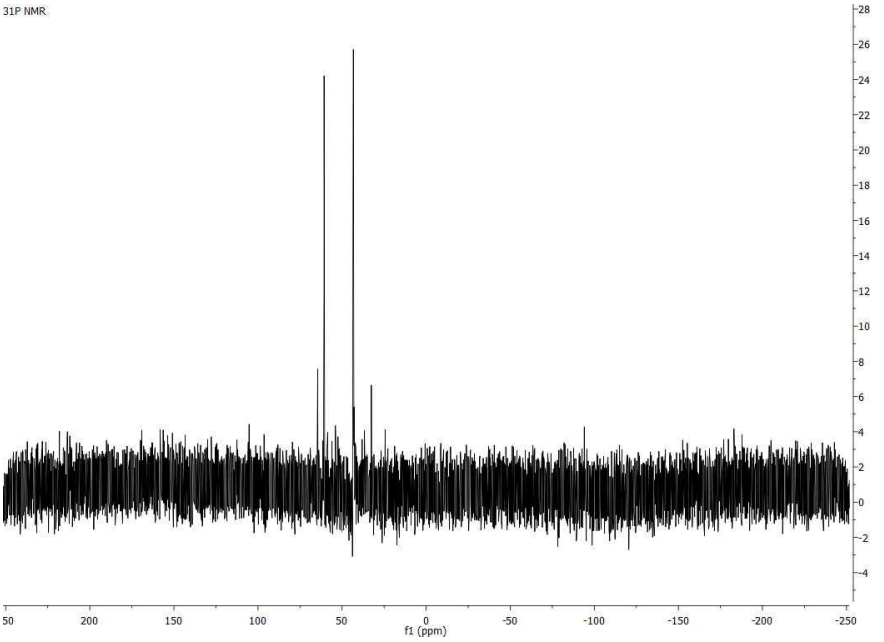

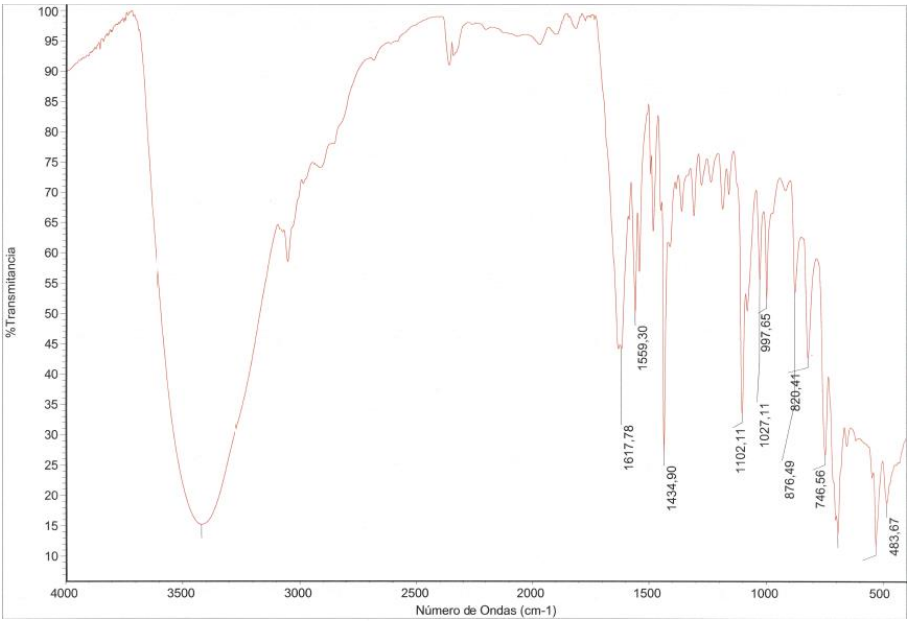
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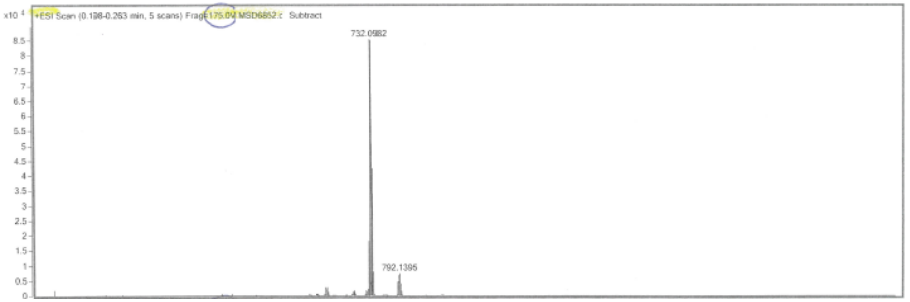
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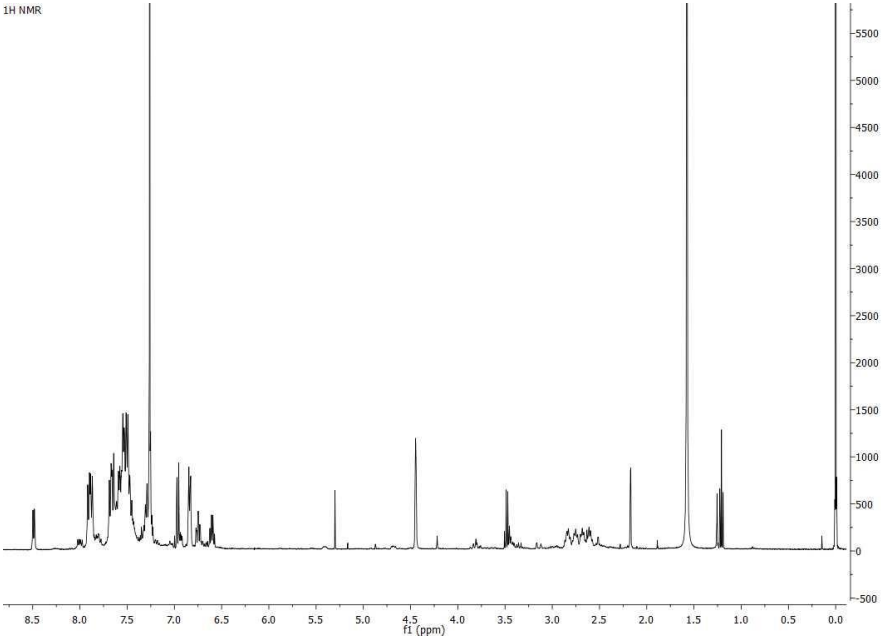

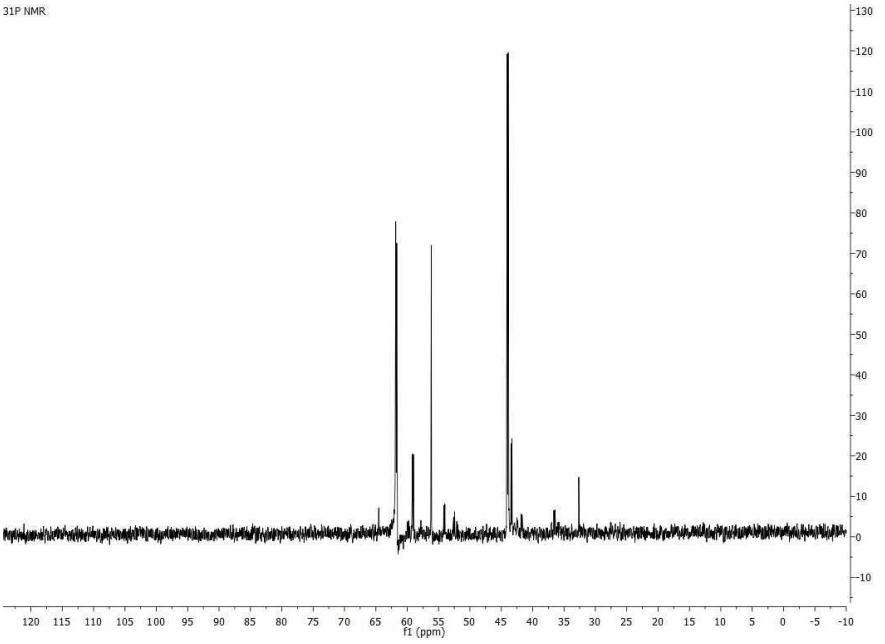

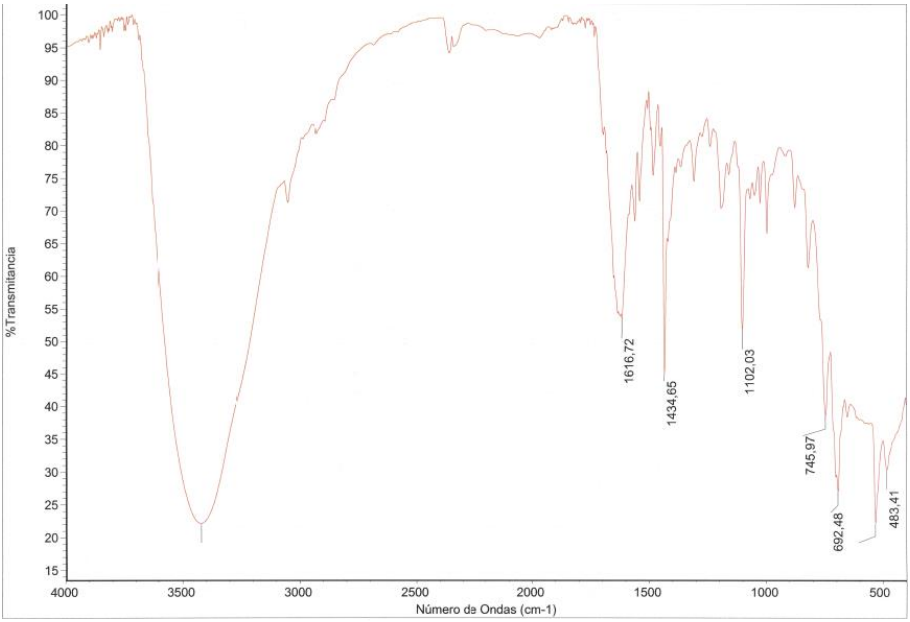
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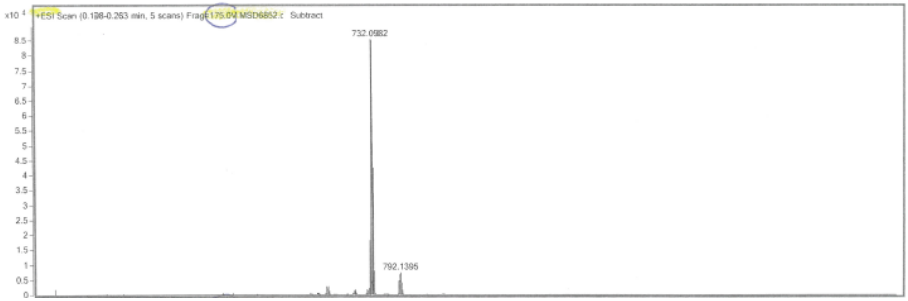
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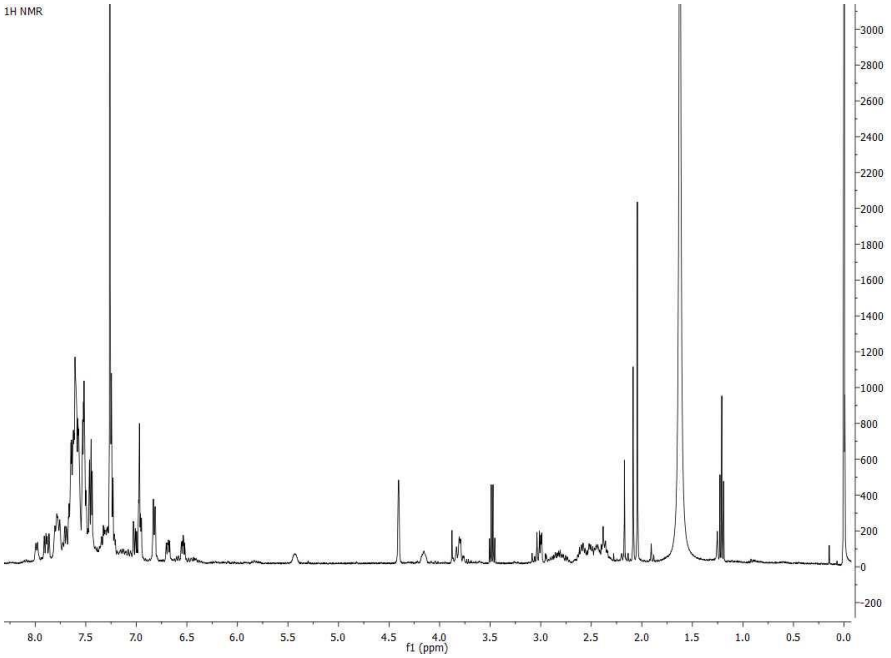
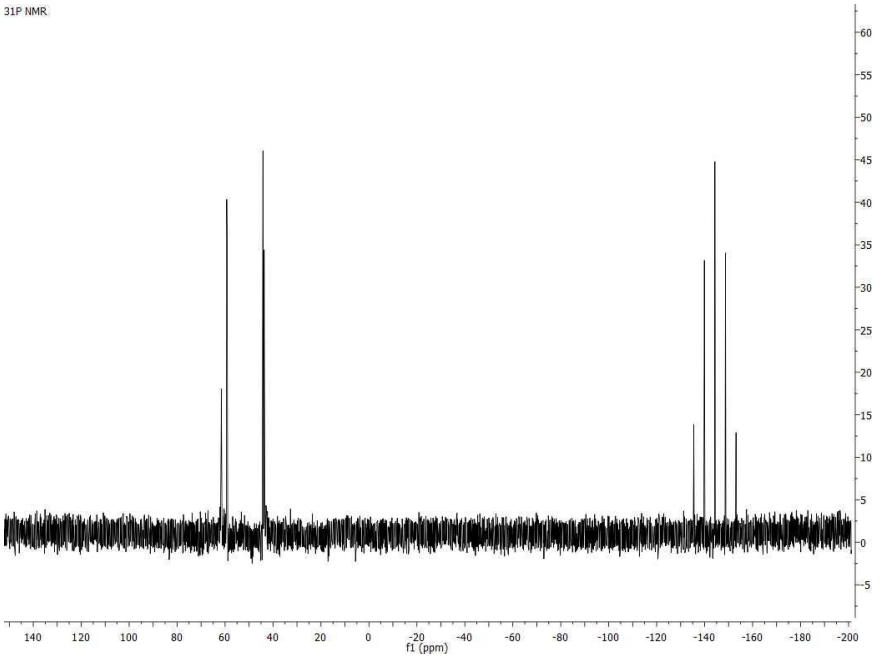
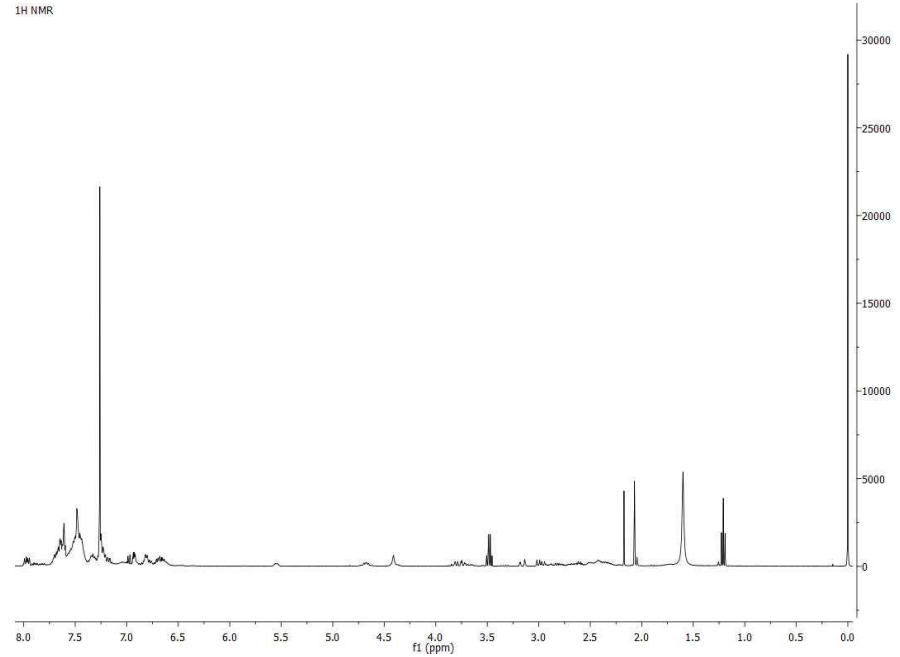
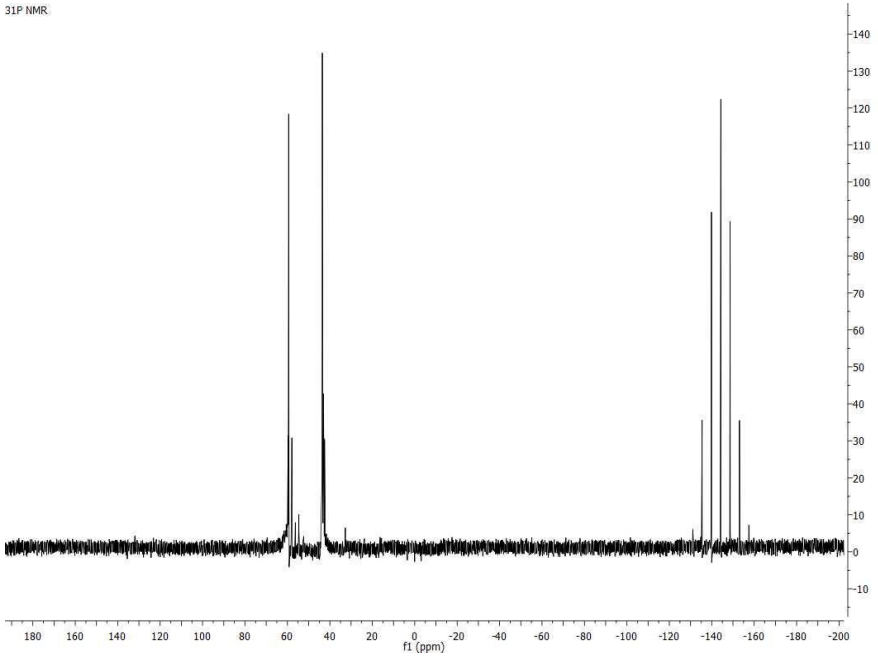
APPENDIX 8: SPECTRA DATA OF R8





APPENDIX 9: SPECTRA DATA OF R9





APPENDIX 10: SPECTRA DATA OF L1AND L2