Tutor

Dr. Daniel Sainz García
Departament de Química Inorgànica i Orgànica, Secció de Química Inorgànica

Grau de Química

Treball Final de Grau

Synthesis and characterization of polynuclear silver N-heterocyclic carbenes using star-shaped imidazol based ligands.

Síntesi i caracterització de carbens N-heterocíclics de plata utilitzant lligands en forma d'estrella basats en imidazol.

Marc Camats Gangonells

June 2017

UNIVERSITAT DE BARCELONA

B:KC Barcelona Knowledge Campus
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I am always looking, for the wonders I am going to find,

maybe not every time,but every once in a while .

Richard Feynman

Primer de tot vull agrair al Daniel per donar-me la llibertat creativa que tota ment científica necessita i per la seva simpatia natural sense la qual aquest treball hauria estat molt mes feixuc.

Gràcies a l'Albert i l'Arnald pel seu humor particular, per estar sempre disposats a ajudar i per donar emoció a les nostres vides fent "química de veritat".

Thanks to Kseniia for always keeping a great mood, even when things were not of a "well-defined shape".

Gràcies també als meus pares i la meva germana per donar-me suport després de les llargues jornades al laboratori i per, a pesar de la complexitat de la química, interessar-se pel meu treball.

REPORT

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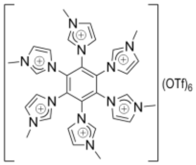
1. SUMMARY

This work is focused on the synthesis of new polynuclear silver N-heterocyclic carbenes using star-shaped imidazole based ligands. These silver carbenes can be used in the fields of homogeneous catalysis and supramolecular chemistry.

The ligands prepared in this work are:



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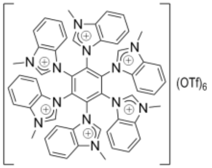

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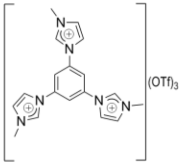

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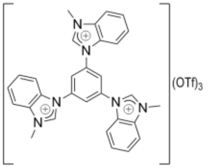
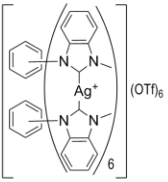


L4

And the silver NHC synthetic targets are:

S1



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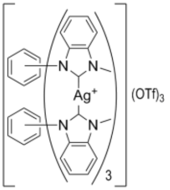

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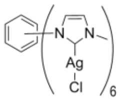

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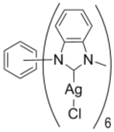

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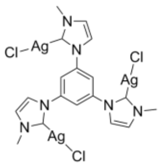

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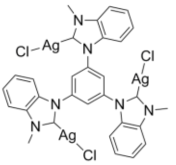

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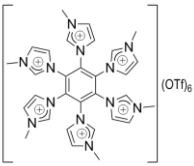
Keywords: Silver N-heterocyclic carbenes, star-shaped ligands, homogeneous catalysis, supramolecular chemistry.

2. RESUM

Aquest treball està centrat en la síntesi de nous carbens N-heterocíclics de plata polinuclears utilitzant lligands en forma d’estrella basats en imidazol. Aquests carbens de plata poden tenir utilitat en els camps de catàlisi homogènia i química supramolecular.

Aquests són els lligands utilitzats en aquest treball:



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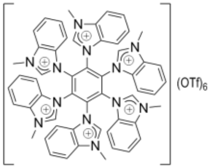

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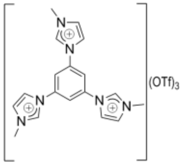

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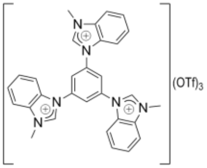

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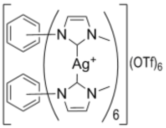
Els objectius sintètics (carbens N-heterociclics de plata) d’aquest treball són:



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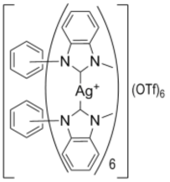

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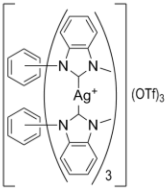

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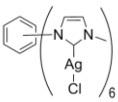

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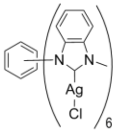

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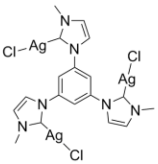

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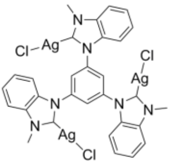

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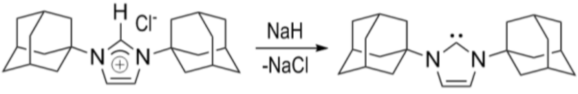
Paraules clau: Carbens N-heterocíclics de plata, lligands en forma d’estrella, catàlisi homogènia, química supramolecular.

3. INTRODUCTION

3.1. N-HETEROCYCLIC CARBENES (NHCS)

N-heterocyclic carbenes are the largest group of persistent carbenes, a type of particularly stable carbenes discovered in 1991 by Arduengo[1], who isolated the first free NHC (Scheme 1):



Scheme 1. Formation of Arduengo's first free carbene

This discovery was followed by a rapid growth of interest in this kind of molecules, foremost in their use as ligands. Soon, they were shown to have an equal or even higher ability to bind to a wide variety of metals in comparison to phosphines. Nowadays numerous metal-NHC systems have been described including complexes with nearly all transition metals.

The generation of these carbenes is generally achieved by deprotonation of imidazolium cations, although imidazolinium, tetrahydropyrimidonium and triazolium cations can also be used.

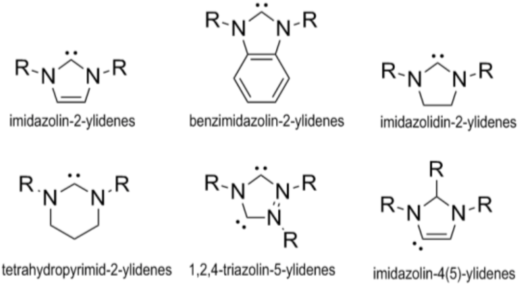


Figure 1. Types of NHCs.

As ligands, NHCs are classified as a different kind of carbenes apart from the classical Fisher and Schrock carbenes. The major reason for this is the difference in the π character of the metal-carbon bond, which is considerably important in Fisher and Schrock carbenes but was considered to be negligible in NHCs due to their weak π-backbonding. However, recent theoretical studies and structural evidence suggest that π-back-donation plays a more important role than it was previously thought[2,3].

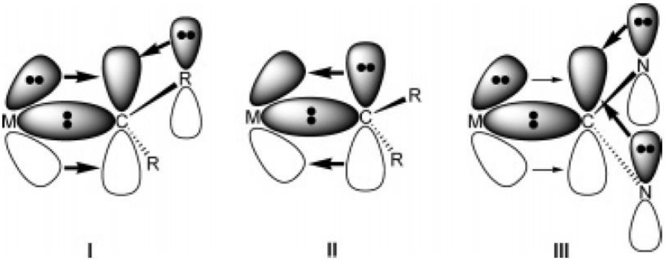


Figure 2. Electronic systems of Fisher (I), Shrock (II) and N-Heterocyclic (III) carbenes.

(image from Garrison ref. 4)

The versatility of NHCs as ligands makes them very helpful in the preparation of a vast collection of catalysts with an extensive variety of uses depending on the metal center these include hydrogenation, metathesis and isomerization among others. These reactions have important uses in pharmaceutical and petrochemical industries.

The particular structure of NHCs and the various metals that can bind to these ligands has already proved their importance as targets for the preparation of smart catalysts[5], these are switchable, multifunctional, adaptable and/or tunable catalysts. Two examples of this kind are shown in Figure 3.

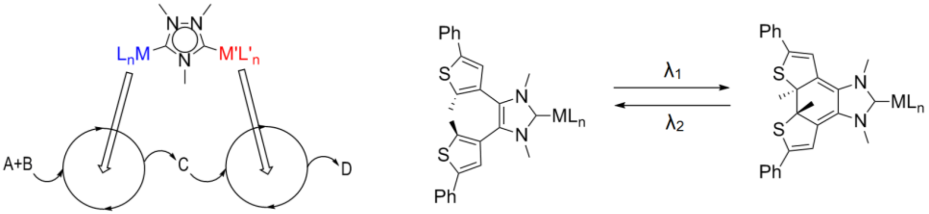


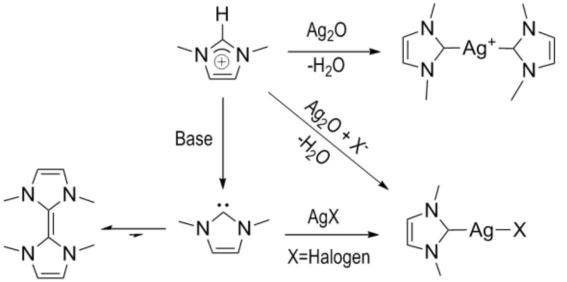
Figure 3. General examples of a multifunctional catalyst (left) and a photo-switchable catalyst (right).

The diversity of metals capable of binding to these ligands, as well as the enormous variety of NHC systems, makes them also useful in building complex architectures, such as molecular cages[6,7], which can have applications in the field of supramolecular chemistry.

Nowadays, the study of NHCs has become a major area of research, especially in the field of homogeneous catalysis where the catalytic properties of phosphine analogue NHCs, along with many other complexes, have received an intense interest[5].

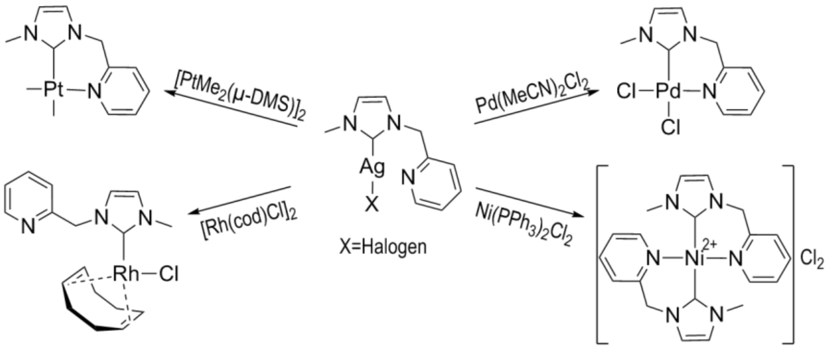
3.2. SILVER N-HETEROCYCLIC CARBENES

Silver NHCs are among the most important complexes of the type. These carbenes are often used as precursors in the synthesis of various metal-NHC compounds via transmetallation reaction in the so-called "Silver oxide route". Some methods of silver metallation involving the use of silver salts and an external base have also been reported[8]. This silver intermediate is often necessary because free NHCs are stable only when the carbene position is very sterically protected, otherwise they easily dimerize. The use of silver (I), especially silver oxide, allows the rapid metallation of the carbene, preventing dimerization reactions from happening (Scheme 2).

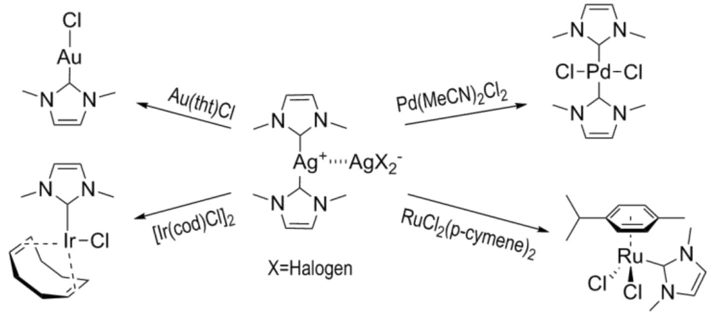


Scheme 2. Simplified reactivity of non-hindered NHCs.

Silver NHCs are classified in two main types, the mono-NHCs (silver-halide carbenes) where silver bonds to a NHC on one side and to a halogen in the other, and the di-NHCs where both coordinating positions of the silver atom are occupied by carbenes. Many metals easily occupy the carbene position by removal of silver via halide precipitation or reduction (Schemes 3 and 4).



Scheme 3. Some known examples of silver halide carbene transmetallations[4].

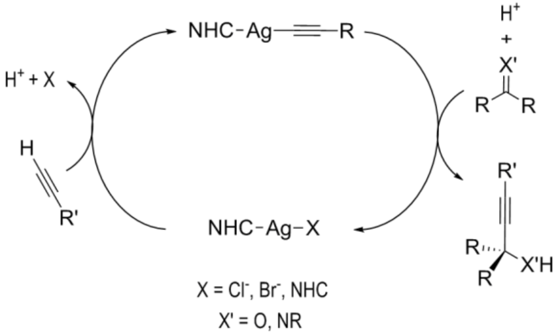


Scheme 4. Some known examples of silver di-NHC transmetallations[4].

3.3. SILVER CATALYSIS

Silver NHCs have also proven to be useful alkyne transfer catalysts which have important applications in synthesis. Some groups have studied the catalytic properties of silver NHCs in reactions with pharmaceutical interest obtaining good results[9,10].

Scheme 5 shows a general mechanism for the silver alkyne transfer catalysis, functional groups play an important role in the proton exchange that has been omitted for clarity. This general mechanism is based on the mechanisms suggested by the groups of Larzeg[9] and Li[10].



Scheme 5. General mechanism for silver catalysis.

The catalytic properties of polynuclear silver carbenes have not been studied and may allow a notable increase in the catalytic activity per mol of catalyst.

4. OBJECTIVES

This work focuses on the preparation of two kinds of silver carbenes (mono-NHCs and di-NHCs) using star-shaped polycoordinating N-heterocyclic ligands.

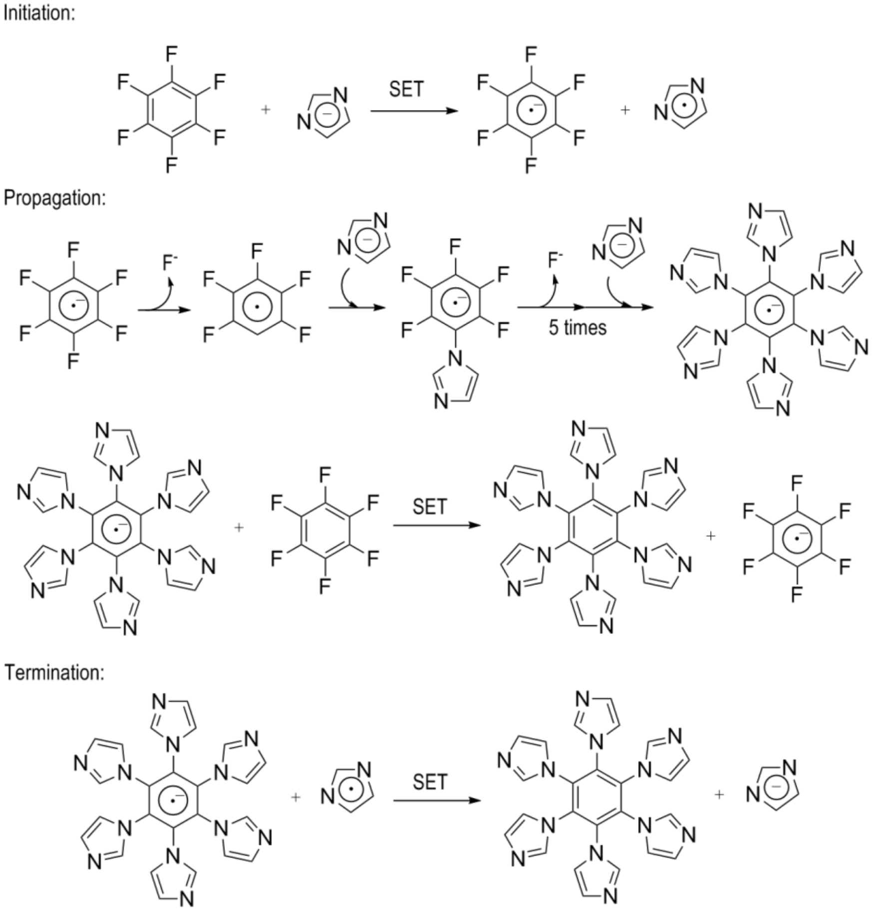
To achieve this, the first goal is to prepare four different star-shaped imidazole based ligands and characterize them using ^{1}H and ^{13}C NMR and ESI-MS, some of these synthesis have not been described by other groups.

The main goal is to synthesize and characterize polynuclear silver N-heterocyclic carbenes using tris- and hexakis(3-methylimidazol-1-ylidene)benzenes and tris- and hexakis(3-methylbenzimidazol-1-ylidene)benzenes as ligands. These complexes can be used as a precursor (carbene transfer agent) to obtain various other polynuclear metallic carbenes as well as to study their catalytic activity as alkyne transfer agents.

5. PREPARATION OF THE LIGANDS

5.1. SYNTHESIS OF THE HEXACARBENE LIGANDS

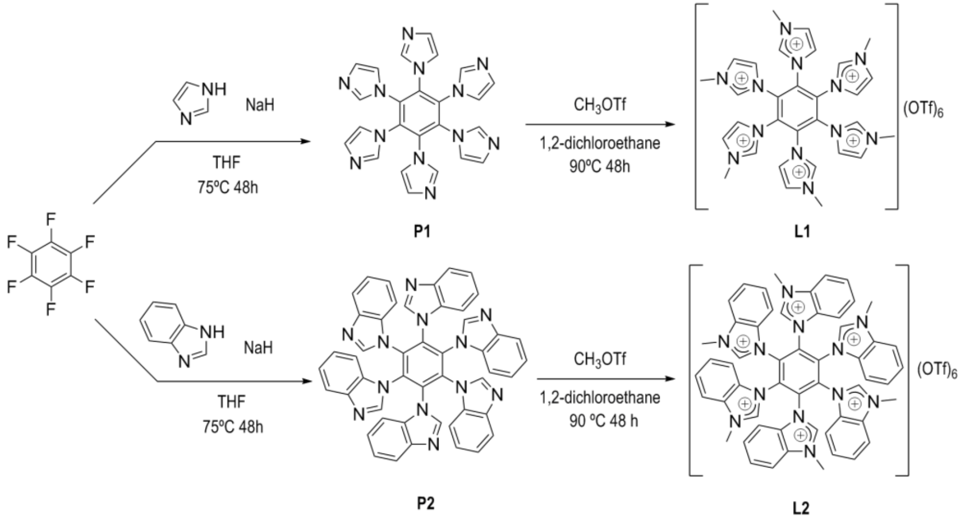
The hexacarbene ligands were obtained in a two-step synthesis. The first step is the construction of the hexakis(imidazole-1-yl)benzene **P1** or hexakis(benzimidazole-1-yl)benzene **P2** by following a procedure based on the study of Henrie and Yeager[11]. The mechanism of this reaction is shown in Scheme 6.



Scheme 6. Mechanism of the formation of hexakis(imidazol-1-yl)benzene.

In this reaction, hexafluorobenzene reacts with imidazolate anions through radical-nucleophilic aromatic substitution $S_{RN}1$ mechanism. This pathway results in a large preference for the hexasubstituted product over the rest. Using this method the precursors **P1** and **P2** are obtained.

Once these precursors were obtained, the next step was the methylation of the six outer nitrogen atoms. This was achieved by using methyl triflate to yield the desired ligand salts (Scheme 7).



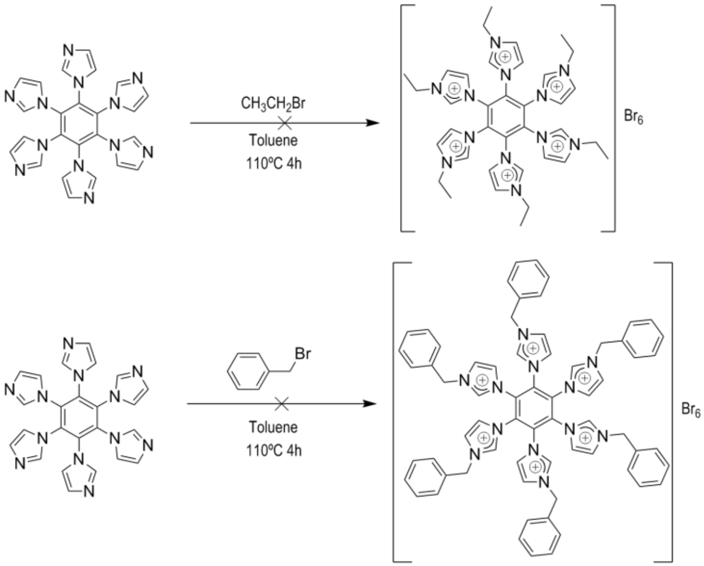
Scheme 7. Overall reaction for the synthesis of **L1** and **L2**

Following this procedure, two ligand salts have been obtained, hexakis(3-methylimidazol-1-ylium)benzene triflate **L1** and hexakis(3-methylbenzimidazol-1-ylium)benzene triflate **L2**.

L1 and **L2** have very different properties; the most important is the difference in the sterical interaction between substituents. While imidazole substituents do not present important hindrance at room temperature, benzimidazole substituents do. This has shown to strongly affect the reactivity of **L2**.

According to the studies of Cornago[12], the conformers of **P2** can be slowly interconverted. The isolation of one conformer was reported, proving a notable difference in physical properties between conformers. The study of these systems is complex and is not an objective of this work. This will be discussed later in the section 7.

A general procedure[13] for the preparation of imidazolium salts has been attempted with **P1** using ethyl bromide and benzyl bromide as alkylating agents (Scheme 8). Unfortunately, most of the starting material remains unreacted under these conditions. The use of imidazolium halides in silver metallation reactions normally leads to the formation of silver halide carbenes, which was the initial intention for using alkyl halides as alkylating agents. A better methodology for the synthesis of these halide salts remains a subject of further development.

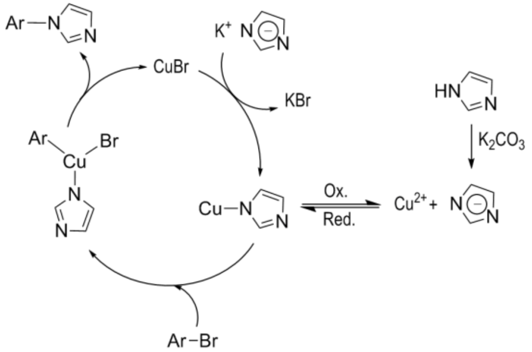


Scheme 8. Attempted reactions with **P1** using ethyl bromide and benzyl bromide.

5.2. SYNTHESIS OF THE TRICARBENE LIGANDS

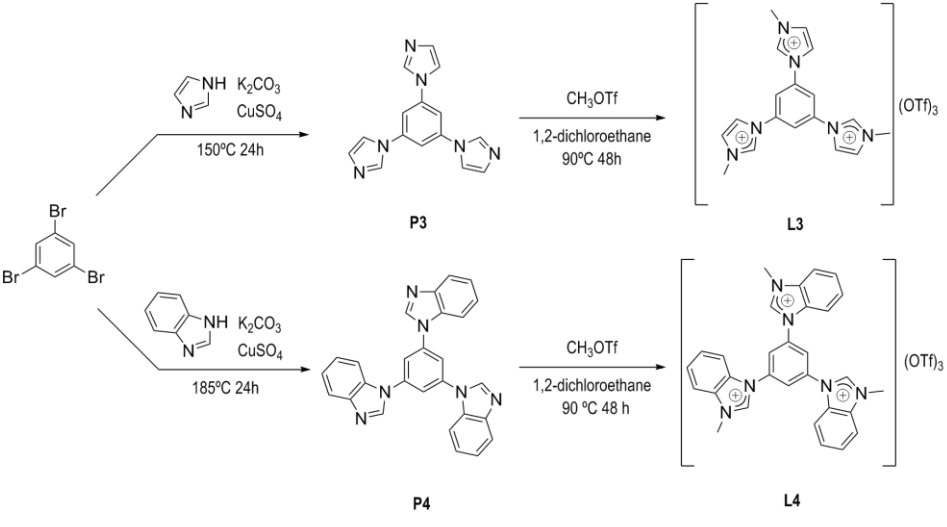
The synthesis of the tricarbene ligands was carried out by following a two-step synthesis, the first step is a variation of an Ullmann's coupling, this reactions were performed using a procedure based on the work of Rit[7] using 1,3,5-tribromobenzene, potassium carbonate and copper (II) sulfate as a catalyst.

In this variation, the copper source is copper (II) sulfate. As the mechanism of Ullmann's coupling is based on copper (I) catalysis, this case is unusual. The most plausible explanation seems to be the possible reduction of copper (II) to copper (I) by imidazolate anions. An example of these anions acting as reducers is the initiation of the mechanism of hexa(imidazol-1-yl)benzene previously discussed in this work. A plausible mechanism complying with the well-known Ullmann's cycle is proposed in Scheme 9.



Scheme 9. Plausible mechanism for the copper (II) sulfate Ullman's coupling variation.

Notably, the reaction is performed under free-solvent conditions. Since all the reagents are solid at room temperature, it is necessary to maintain a high temperature (150ºC for imidazole and 190ºC for benzimidazole) in the entire reaction flask to avoid solidification of the corresponding imidazole. In this reaction, the organic reagents remain melted, acting as a solvent (Scheme 10).



Scheme 10. Overall reactions to obtain trisubstituted ligand salts.

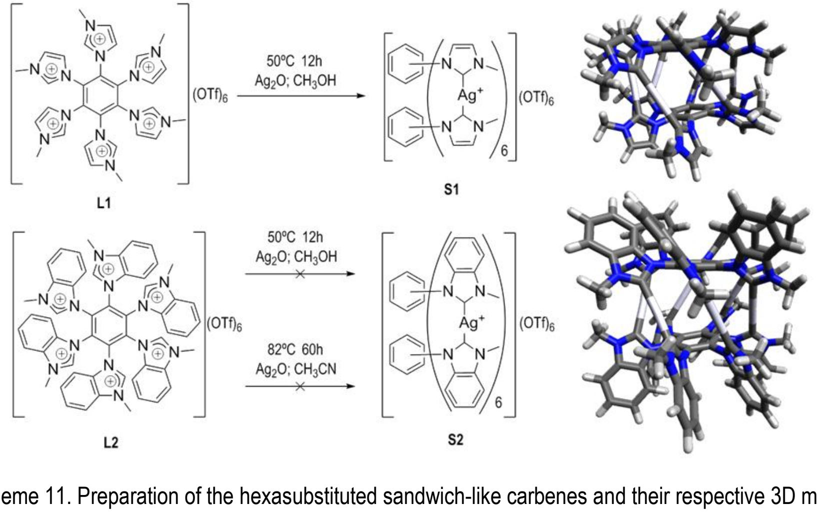
Using this reaction, two molecules have been prepared: 1,3,5-tris(imidazol-1-ylium)benzene **P3** and 1,3,5-tris(benzimidazol-1-ylium)benzene **P4**. These molecules were methylated using a similar procedure as the one used in their hexasubstituted analogues to obtain 1,3,5-tri(3-methylimidazol-1-yl)benzene triflate **L3** and 1,3,5-tri(3-methylbenzimidazol-1-yl)benzene triflate **L4**.

In this case, **L4** is not as affected by sterical interactions as its hexasubstituted analogue **L2**, this has very important implications in its reactivity and characterization.

6.PREPARATION OF SILVER CARBENES

6.1. SYNTHESIS OF SANDWICH-LIKE CARBENES

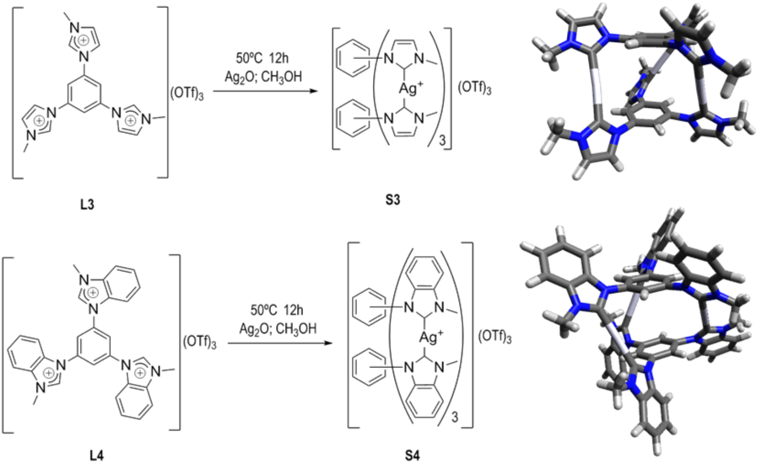
The first synthetic goal in this work was to prepare **S2**. This was first approached using the conditions reported by Peris[6] for the preparation of **S1**. These conditions did not lead to the formation of the synthetic target, but yielded a tar-like substance. The most plausible hypothesis for this was that the used conditions do not allow the rapid interconversion between conformers.



Scheme 11. Preparation of the hexasubstituted sandwich-like carbenes and their respective 3D models.

A similar reaction was successfully performed by Rit[7], using tri- and tetrasubstituted 3-butylimidazol-1-yl benzenes as ligands in acetonitrile. This solvent allows higher reaction temperatures the same reaction was performed acetonitrile reflux (82ºC) during a longer period of time in an attempt to overcome the rotational barrier (Scheme 11). These conditions also lead to a tar-like substance.

The preparation of trisubstituted sandwich-like carbenes **S3** and **S4** has been performed using the same conditions as Peris[6]. These conditions formed easily the expected carbenes (Scheme 12).



Scheme 12. Preparation of the trisubstituted sandwich-like carbenes and their respective 3D models.

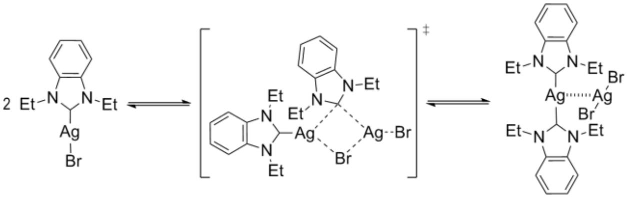
S3 has shown to be much more unstable than **S4** and **S1**. This could be explained by a combination of factors, in the case of **S4,** the lone electron pairs on the nitrogen atoms are delocalized through the aromatic ring of benzimidazole, this may enhance the π-back-bonding by reducing the electron density on the carbene carbon. In the case of **S1** there is no such stabilization but the carbene position is sterically protected by the other substituents. The yield for the preparation of **S3** improves notably when the reaction is performed at room temperature during longer times.

6.2. SYNTHESIS OF SILVER CHLORIDE CARBENES

The major difficulty in the formation of sandwich-like carbenes is the need for an adequate conformation of the two NHC ligand molecules, in the case of **L1, L3** and **L4** this is not an issue in contrast to the case of **L2** where this becomes much more important due to the rotational barrier.

The formation of silver chloride carbenes has the advantage of a low dependence on the conformation of the ligand to form a stable complex. This type of carbenes is widely known and has shown to be remarkably stable in a variety of solvents, in some cases even in water[4]. This might be explained by enhancement of the silver-carbene π-back-bonding by halide ligands through π-donation.

According to several sources[4,7,8], silver halide carbenes, especially bromides, can undergo a dimerization reaction to form a silver di-NHC cation and a dihalogenosilver anion held together by an argentophylic bond.



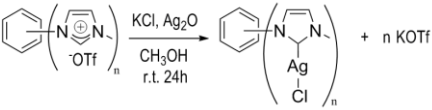
Scheme 13. Mechanism proposed by Lin[8] for the dimerization of silver bromide carbenes.

In the work of Lin[8], this equilibrium is thought to cause a fluxional behaviour (Scheme 13) in this silver bromide carbene removing the $^{107/109}$Ag-^{13}C coupling in NMR-^{13}C. The ligands used in this work may have different behaviour, favouring one of the two arrangements and could be useful to improve the understanding of this process.

This type of systems may be also useful in silver catalysis since the silver anion may also present catalytic activity.

An unusual method was used by Lin[8] to obtain 1,3-diethylbenzimidazole-2-ylidene silver bromide in very good yield (94%) using a biphasic H_2O:CH_2Cl_2 reaction mixture with AgBr as a silver source and an aqueous solution of NaOH as a base along with $[NBu_4]Br$ as a phase transfer catalyst at room temperature. The success of this reaction seems to indicate that the formation of insoluble silver halides might not compromise the yield of the reaction in the way that would be reasonable to expect.

Knowing this, an alternative method for the preparation of silver halide complexes was attempted (Scheme 14):



Scheme 14. Proposed method for preparing silver chloride carbenes with polyimidazolium benzenes

The goal of these reactions was to obtain the following polysubstituted silver chloride carbenes:

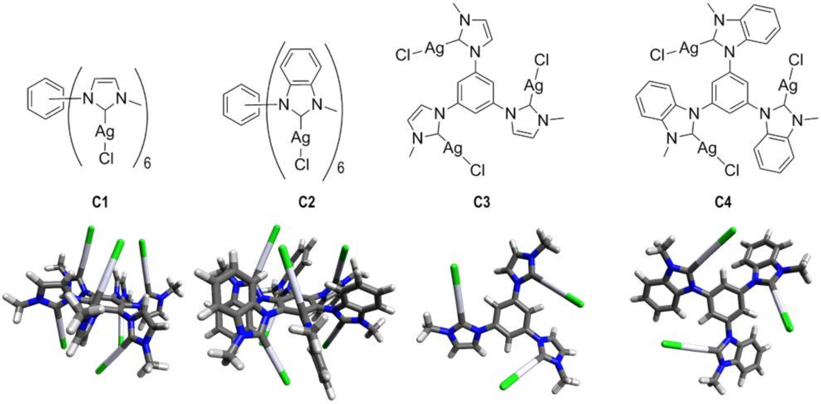


Figure 4. Expected silver chloride NHCs **C1**, **C2**, **C3** and **C4** and their respective 3D models.

The attempts of making **C1**, **C3** and **C4** have led to the generation of sandwich-like carbenes but with important differences in ^{1}H and ^{13}C NMR compared to **S1, S3** and **S4,** these sandwich-like compounds will be called **S1'**, **S3'** and **S4'**.Only in the case of **C2** and **C3** some results agree with the expected silver chloride carbenes:

The attempt of preparing **C2** and dichloromethane as a solvent instead of methanol leads to the formation of a yellow solid with very different properties compared to **L2**, the main one is the large increase in solubility in dichloromethane, this is a reasonable behaviour for **C2** since it is expected to be neutral, the final product also presents a notable change in color (intense yellow). Performing the same reaction using **L3** and methanol as a solvent leads to a mixture of two complexes. ^{1}H-NMR results indicate that the mixture contains **S3'** and a second compound, ESI-MS results suggest the presence of the expected silver halide carbene. Unfortunately, their isolation has been unsuccessful; therefore, its characterization is unclear. These results will be discussed in section 7.

7. CHARACTERIZATION DISCUSSION

The characterization was a major issue in this work. It was performed mainly with the use of ^{1}H and ^{13}C NMR and ESI-MS. However, for some compounds, the characterization with the mentioned techniques was complicated. In this section only the most complex characterizations will be discussed.

7.1. CHARACTERIZATION OF HEXAKIS(BENZIMIDAZOL-1-YL)BENZENES

P2 **L2**

Figure 5. Molecules of **P2** and **L2**.

Hexakis(benzimidazol-1-yl)benzene systems have been the most challenging molecules to characterize in this work due to the generation of a mixture of 8 possible conformers, according to the studies of Cornago[12], the major conformers are C, F and G (see Figure 6) although other conformers can be also observed in ^{1}H-NMR in important proportions.

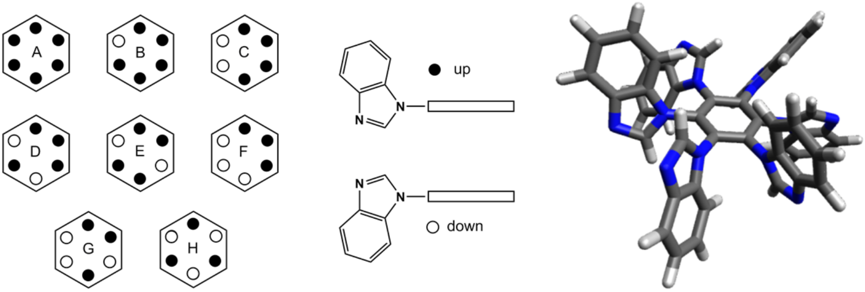


Figure 6. Possible conformers for hexakis(benzimidazol-1-yl)benzenes and 3D model of H

This behaviour makes their characterization more complicated than for their imidazole analogue and is crucial to understand the difference in their chemical properties. All attempts of ^{13}C-NMR experiments have been unsuccessful due to the low intensity of the signals.

The methylation reaction is controlled by tracking the most deshielded signals, which move around 1.8 ppm in ^{1}H-NMR, a group of signals also appears around 4 ppm related to the methyl groups. This same deshielding of the NCHN proton is also observed in the other methylation reactions performed in this work.

Precursor	**NCHN ^{1}H-NMR shift (ppm)**	**Ligand triflate**	**NCHN ^{1}H-NMR shift (ppm)**	**Δppm**
P1	7.43	**L1**	9.14	1.71
P2	7.65-8.33	**L2**	9.5-10.1	1.8 (av.)
P3	8.56	**L3**	9.82	1.26
P4	8.86	**L4**	10.32	1.46

Table 1. Shifts of the NCHN ^{1}H-NMR(DMSO-d_6; 400MHz; 293K).

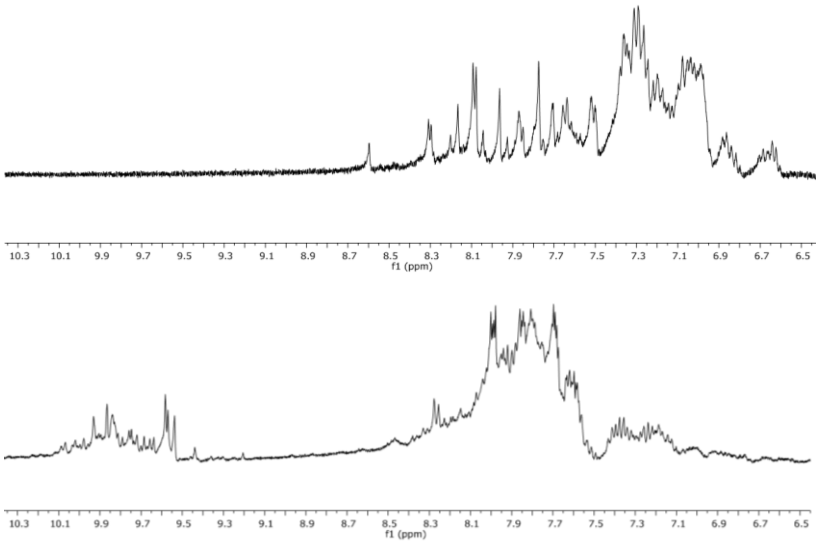


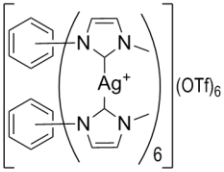
Figure 7. ^{1}H-NMR(DMSO-d_6; 400MHz; 293K) of **P2** and **L2**

Another factor that contributes to the complexity of the spectra of **P2** is the presence of important couplings between the protons of benzimidazole substituents that can be easily observed in **P3** ^{1}H-NMR as two doublets and a broad multiplet.

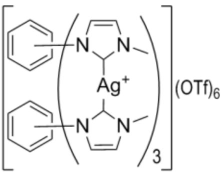
The combination of these important couplings along with the conformational mixture in **P2** explains the complex ^{1}H-NMR of these systems.

The characterization with mass spectrometry of **L1** and **L2** is also problematic. Hexasubstituted cations have shown to easily break under the conditions used in the mass spectrometer (ESI 175V H_2O:CH_3CN (1:1)) and no molecular peaks (caused by the loss of one or more anions) are observed, the main peak matches a methylimidazole fragment in **L1** and a methylbenzimidazole fragment in **L2**. The mass spectra of hexakis(benzimidazol-1-yl)benzene **P2** is fairly easy and the molecular peak mass ($C_{48}H_{31}N_{12}^+$ m/z calc. 775.2789 found 775.2782) corresponds to the expected molecule.

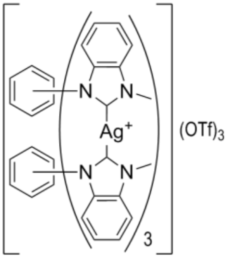
7.2. CHARACTERIZATION OF SANDWICH-LIKE CARBENES



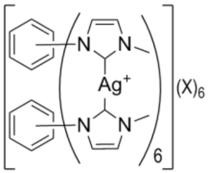
S1



S3

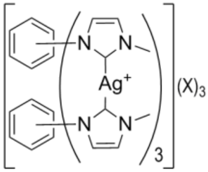


S4



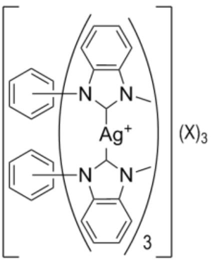
X = $AgCl_2^-$ or Cl^- or TfO^-

S1'



X = $AgCl_2^-$ or Cl^- or TfO^-

S3'



X = $AgCl_2^-$ or Cl^- or TfO^-

S4'

Figure 8. Obtained sandwich-like carbenes.

Sandwich-like carbenes present a very high symmetry which leads to a simple NMR spectrum. This symmetry turns out to be useful in ^{13}C-NMR where the presence of 6 (in trisubstituted ligands) or 12 (in hexasubstituted ligands) equivalent carbons bonded to silver facilitates the detection of this quaternary carbon, nonetheless, the intensity of the signal is low and requires long ^{13}C-NMR experiments to be detected. This carbon signal is key to detect the C-Ag bond, the reason for this is that the 2 major isotopes of silver (^{107}Ag (51.84%) and ^{109}Ag (48.16%)) have both spin ½, this creates a very distinct pattern resembling a doublet of doublets caused by the different coupling constants that depend on the silver isotope.

Silver complex	**NCN ^{13}C-NMR shift**	$^{1}J_{C\text{-}Ag107}$	$^{1}J_{C\text{-}Ag109}$
S1	179.7 ppm	182 Hz	211 Hz
S4	188.8 ppm	187 Hz	213 Hz

Table 2. Shifts of the carbene position ^{13}C-NMR(DMSO-d_6; 100MHz; 293K) in **S1** and **S4**. **S3** carbene signal has not been observed due to its low stability.

In the case of **S3** the carbene signal has not been detected, this it's probably caused by the easy decomposition of the compound. Nonetheless, it can be probably detected using anhydrous DMSO-d_6 and protecting the sample from light.

When using as ligands **L1** and **L4**, and methanol as a solvent, sandwich-like arrangement prevails over the silver halide arrangement when the halide is added from an external source and **S1'** and **S4'** are formed, only in the case of using **L3** a mixture of **S3** and "**C3**" is obtained. The ESI-MS results confirm that the generated species **S1'**, **S3'** and **S4'** are sandwich-like carbenes but clearly different from **S1**, **S3** and **S4** in ^{1}H and ^{13}C NMR:

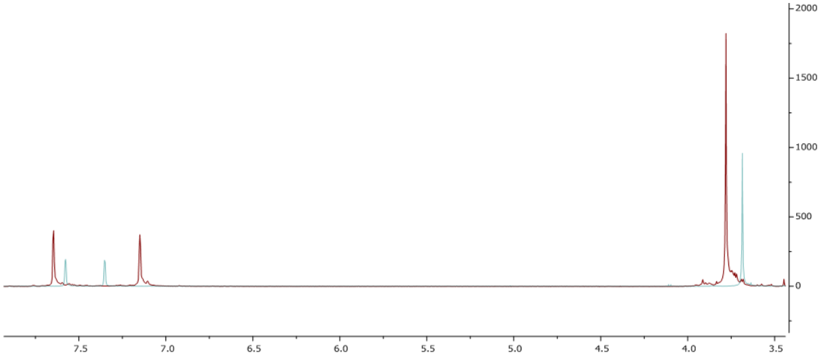


Figure 9. ^{1}H-NMR(DMSO-d_6; 100MHz; 293K) of **S1**(red) and **S1'**(blue)

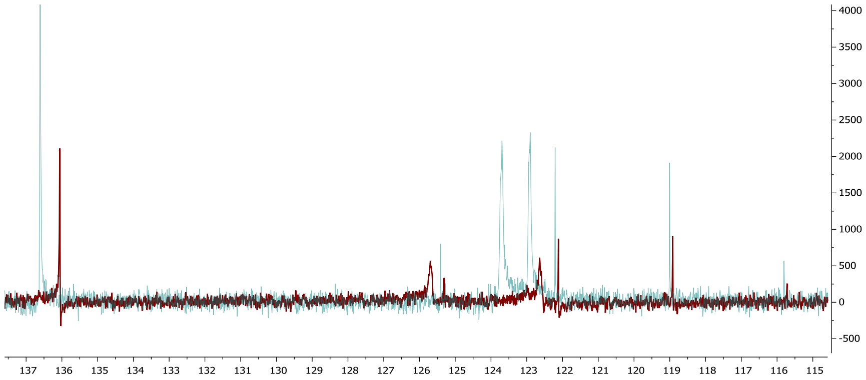


Figure 10. ^{13}C-NMR(DMSO-d$_6$; 100MHz; 293K) of **S1**(red) and **S1'**(blue)

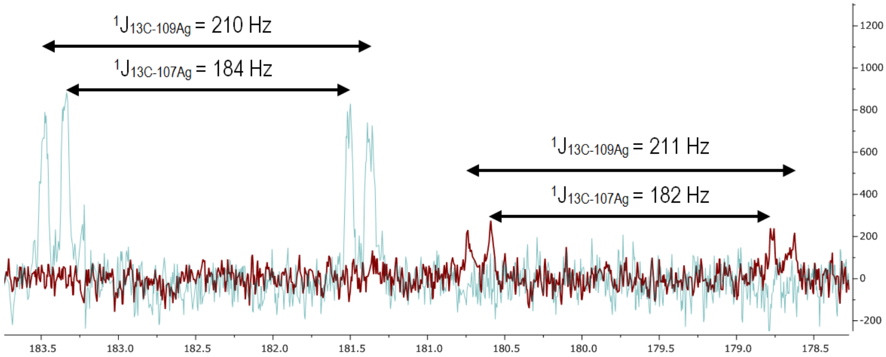


Figure 11. ^{13}C-NMR(DMSO-d$_6$; 100MHz; 293K) carbene signal of **S1**(red) and **S1'**(blue)

The same behaviour is observed in ^{1}H-NMR of **S3'** and **S4'**. Clearly the presence of KCl affects the product of this reaction.

There are several hypotheses for this shift in the NMR signals. One possibility is the formation of dihalogenosilver anions that bind to the silver atoms in the molecule by argentophylic bonds. Numerous cases of this phenomenon have been described in a variety of silver NHCs[4]. This type of interactions are normally considered very weak but in this case are enhanced by an electrostatic attraction between the positively charged silver of the di-NHC system and the negative charge of the dihalogenosilver anion, this hypothesis is supported by the studies of Wang and Lin[8] where this interaction is shown to be remarkably important in solution.

Another plausible possibility would be a supramolecular interaction with the chloride anion.

Unfortunately, no monocrystals of this sandwich-like carbenes have been obtained. The work-up procedure for these reactions is not adequate to remove the triflate anions and these can be seen in the final mixture in ^{13}C-NMR.

ESI-MS has also been used in the characterization of sandwich-like carbenes. This technique is remarkably useful in the characterization of these complexes for two reasons:

The first one is the easy detection of peaks, given the cationic nature of sandwich-like complexes, it is not necessary to generate charges in the molecule, the cationic fragments observed with this technique are generated by the loss of one or more triflate anions with a general formula $[M\text{-}nOTf]^{+n}$.

The second reason is that the isotopic distribution of silver can be easily identified; this distribution depends on the number of silver atoms and is a faster and easier method than ^{13}C-NMR to detect the silver in the complex.

In the complexes **S1'**, **S3'** and **S4'** several combinations of anions are observed and the assignment of peaks becomes much harder, nonetheless, the corresponding isotopic distribution of silver is observed in all three compounds.

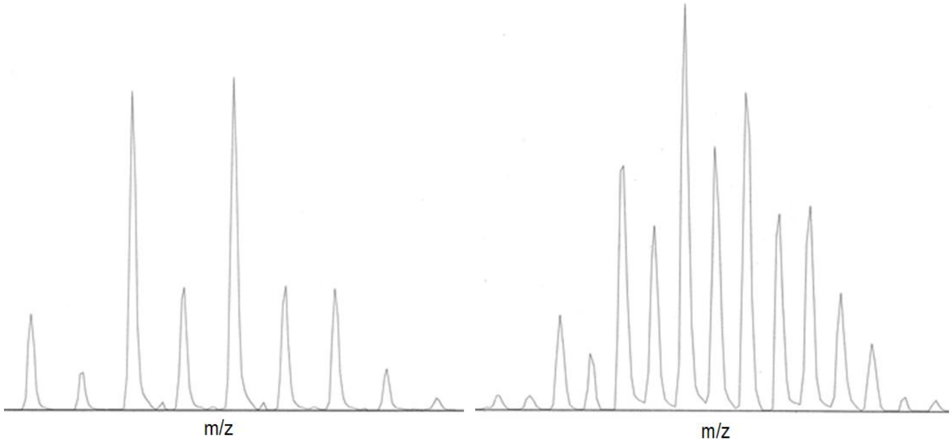


Figure 12. Isotopic distribution observed ESI-MS in **S3** (left; $C_{37}H_{36}N_{12}Ag_3F_3O_3S^{2+}$) and **S1'** (right; $C_{60}H_{60}N_{24}Ag_6Cl^{5+}$). For detailed distribution, see *APPENDIX 2.*

7.3. CHARACTERIZATION OF SILVER CHLORIDE CARBENES

The formation of silver chloride carbenes in the used conditions is unclear due to difficulties in the characterization; nonetheless, some observations indicate that a reaction has occurred.

ESI-MS (175V) has failed in characterizing “**C2**” and the molecular peak is not observed, only light fragments are detected and these cannot be assigned. ^{1}H-NMR in $CDCl_3$ has not been possible to record since these substance forms a resin in this solvent. A qualitative analysis using X-ray fluorescence has detected the presence of silver in this compound.

In the mixture of **S3’**+“**C3**” the ^{1}H-NMR results show the presence of two different compounds. Mass spectrometry results have detected a presence of a possible $C_{18}H_{18}N_6Ag_3Cl_2^+$ fragment (m/z calc. 711.8358 found 712.8095) that matches the expected silver chloride carbene and has the expected isotopic distribution.

8. EXPERIMENTAL SECTION

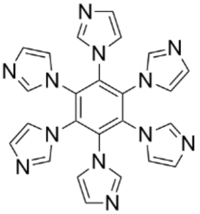
8.1. MATERIALS AND METHODS

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 at 293K using the solvent peak as a reference. IR spectra were recorded in a Nicolet Avatar 330 FT-IR and ESI-MS were recorded on a LC/MSD-TOF G1969A with a 175V fragmentor and a flux of H_2O:CH_3CN (1:1).The X-ray fluorescence spectroscopy was performed using a Fisherscope X-ray system XDAL.

8.2. PREPARATION OF LIGAND SALTS

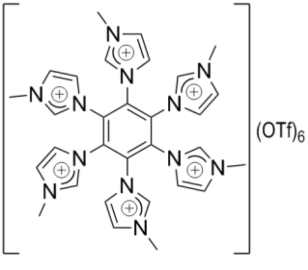
8.2.1. Preparation of L1

2.31 g (34.0 mmol) of imidazole are dissolved in 50 mL of THF under nitrogen. 1.36 g of NaH (34.0 mmol; 60% dispersion in mineral oil) are added and the mixture is refluxed during 1 h. The solution is cooled to room temperature and 0.66 mL (5.7 mmol) of hexafluorobenzene are added. The reaction is then heated to reflux during 48 h. The solvent is removed to dryness and the solid is washed with water and filtered yielding to 1.13 g (42%) of **P1**.



White powder. Soluble in CH_3CN and CH_3OH. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 7.43 (s, 6H), 6.94 (s, 6H), 6.85 (s, 6H).

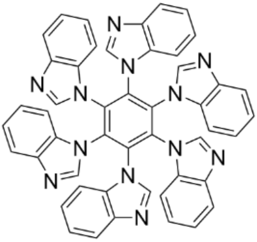
0.24 g (0.5 mmol) of **P1** are dissolved under nitrogen in 20 mL of 1,2-dichloroethane. 0,68 mL (6 mmol) of CH_3OTf are added and the solution is refluxed during 48 h, the mixture is filtered and the solid is washed with diethyl ether yielding to 0.59 g (80%) of **L1**.



White powder. Soluble in CH_3CN and CH_3OH. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 9.14 (m, 6H) , 8.03 (m, 6H), 7.57 (m, 6H), 3.90 (s, 18H).

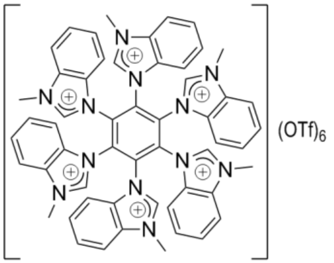
8.2.2. Preparation of L2

1.00 g (8.5 mmol) of benzimidazole is dissolved under nitrogen in 40 mL of THF, 0.34 g of NaH (8.55 mmol; 60% dispersion in mineral oil) are added and the mixture is refluxed during 1h. The solution is cooled to room temperature while adding 20 mL of THF. Once the solution is cooled, 0,17 mL (1.4 mmol) of hexafluorobenzene are added. The reaction is then heated to reflux during 24-48 h. The solvent is removed to dryness and the solid is washed with 40 mL of water, filtered and washed with 40 mL of THF yielding to 0.93 g (92%) of **P2**.



White powder. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.65-8.33 (m, 6H), 6.50-7.65 (m, 24H). ESI-MS(175V): m/z calc. for $C_{48}H_{31}N_{12}^+$ [M+H]$^+$ 775.2789; found 775.2782.

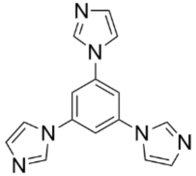
0.4 g (0.52 mmol) of **P2** are dissolved under nitrogen in 20 mL of 1,2-dichloroethane. 0.7 mL (6.24 mmol) (of CH_3OTf are added and the solution is refluxed during 48h, during the reaction the solution gets darker and a resin-like material is formed in the walls. After this, the solvent is evaporated to dryness. 30mL of diethyl ether are added and with strong stirring the resin slowly becomes a white/yellowish powder. The mixture is then filtered and the solid is washed with diethyl ether yielding to 550 mg (80%) of **L2**.



White/brownish powder. Soluble in CH_3CN. IR (KBr): 3066, 1256, 1171, 1032, 640 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ (ppm) 9.5-10.1 (m, 6H), 7.1-8.4 (m, 24H), 3.45-4.15 (m, 18H).

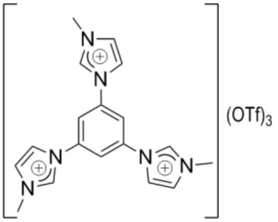
8.2.3. Preparation of L3

A 100 mL teflon reactor is charged with 2.52 g (8.0 mmol) of 1,3,5-Tribromobenzene, 2.42 g (32.0 mmol) of K_2CO_3, 3.26 g (48.0 mmol) of imidazole, and 0.05 g (0.2 mmol) $CuSO_4$ and the mixture is heated for 24 h to 150 °C under argon atmosphere. The mixture is then allowed to cool to room temperature. The solid mixture is suspended in water, filtered and washed with water until the solution is colourless. The floating solids are also removed The residue is washed with 20mL dichloromethane and dried under vacuum yielding to 1.95 g (88%) of **P3**.



White powder. ^{1}H-NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 8.56 (s,3H), 8.05 (s, 3H), 7.97 (s, 3H), 7.20 (s,3H).

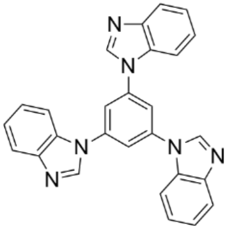
0.36 g (1.3 mmol) of **P3** are dissolved under nitrogen in 20 mL of 1,2-dichloroethane. 0.9 mL (7.9 mmol) of CH_3OTf are added and the solution is refluxed during 48 h. After this, the solid is filtered, washed with diethyl ether and dried under vacuum yielding to 0.85 g (85%) of **L3**.



White powder. IR (KBr): 3116, 1627, 1171, 1029, 637 cm^{-1}. ^{1}H-NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 9.82 (s, 3H), 8.48 (s, 3H), 8.37 (m, 3H), 8.09 (m, 3H), 4.05 (s,9H). ^{13}C-NMR (DMSO-d$_6$, 100 MHz): δ (ppm) 136.5 (C$_{arom}$), 136.4 (C$_{arom}$), 125.2 (NCHN), 120.9 (CH$_{imz}$), 115.9 (CH$_{imz}$), 120.6 (q, $^1J_{C-F}$ = 320 Hz, $CF_3SO_3^-$).

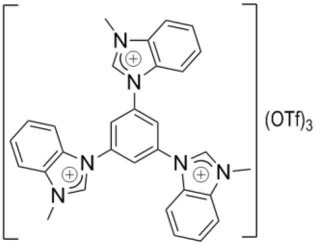
8.2.3. Preparation of L4

2.52 g (8.0 mmol) of 1,3,5-Tribromobenzene, 2.42 g (32.0 mmol) of K_2CO_3, 5.67 g (48.0 mmol) of benzimidazole, and 0.05 g (0.2 mmol) $CuSO_4$ are added to a 100 mL flask and the mixture is heated for 24 h to 190 °C under nitrogen atmosphere. The mixture is allowed to cool to room temperature. 30 mL of dichloromethane are added to the flask and it is sonicated to slowly soften the solid, after several hours, this leads to a suspension. The suspension is allowed to settle and the clear solution is transferred to a 100 mL Schlenk flask, the solid is washed two times with 15 mL of dichloromethane and the clear solution is added to the flask. The solution is concentrated to 25 mL and 0.2 g of NaH (60% dispersion in mineral oil) are added. The mixture is stirred under nitrogen atmosphere for 18 h. The solids are removed by filtration and the solvent is concentrated to 5 mL, 20 mL of pentane are added and the mixture is filtered yielding to 0.37g (11%) of **P4**.



White powder. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 8.86 (s,3H), 8.17 (s, 3H), 7.98 (dd, ^3J = 6.8 Hz, ^4J = 1.6 Hz, 3H), 7.82 (dd, ^3J = 7.2 Hz, ^4J = 2.0 Hz 3H), 7.37(m, 6H).

0.32 g (0.75 mmol) of **P4** are dissolved under nitrogen in 20 mL of 1,2-dichloroethane. 0,6mL (5.3 mmol) of CH_3OTf are added and the solution is refluxed during 48 h. After this, the solid is filtered and washed with diethyl ether and dried under vacuum yielding to 0.63 g (91%) of **L4**.

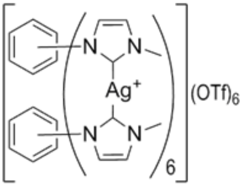


White powder. IR (KBr): 3085, 1574, 1260, 1153, 637 cm^{-1}. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 10.32 (s, 3H), 8.69 (s, 3H), 8.25 (m, 6H), 7.89 (t, ^3J = 7.3 Hz, 3H), 7.84 (t, ^3J = 7.3 Hz, 3H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ (ppm) 143.7(NCHN), 135.7 (C$_q$), 131.9 (C$_q$), 130.4 (C$_q$), 127.8 (C$_{bzimz}$), 127.5 (C$_{bzimz}$), 123.2 (C$_{benzene}$) , 120.6 (q, $^1J_{C-F}$ = 320 Hz, $CF_3SO_3^-$), 114.35 (C$_{bzimz}$), 113.65(C$_{bzimz}$).

8.3. PREPARATION OF SILVER CARBENES

8.3.1. Preparation of S1

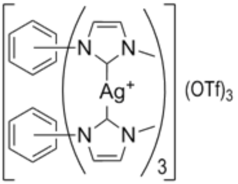
0.2 g (0.137 mmol) of **L1** are dissolved under nitrogen in 20mL of methanol. 0.12 g (0.5 mmol) of Ag_2O are added and the mixture is heated to 50ºC during 12h. After this, the mixture is filtered through Celite obtaining a colorless solution. The solution is concentrated to 5mL and 20mL of diethyl ether are added. The white precipitate is filtered, washed with diethyl ether and dried under vacuum yielding to 0.096 g (60%) of **S1**.



White powder. Photosensitive. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 7.65 (s,12H), 7.15 (s, 12H), 3.78 (s, 36H). ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ (ppm) 179.68 (dd, $^1J_{C-Ag107}$ = 182 Hz, $^1J_{C-Ag109}$ = 211 Hz, NCN), 136.06 (C$_{q,arom}$), 125.67 (CH$_{imz}$), 122.63 (CH$_{imz}$), 120.51 ($^1J_{C-F}$ = 320 Hz, $CF_3SO_3^-$).

8.3.2. Preparation of S3

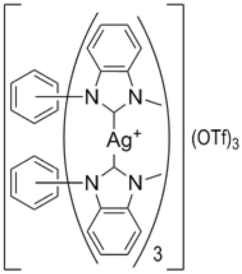
0.3 g (0.4 mmol) of **L3** is dissolved under nitrogen in 20 mL of methanol. 0.15 g (0.6 mmol) of Ag_2O are added and the mixture is stirred at room temperature during 48 h. After this, the mixture is filtered through Celite obtaining a colorless solution. The solution is concentrated to 5 mL and 20 mL of pentane are added. The white precipitate is filtered, washed with pentane and dried under vacuum to yield 0.08 g (29%) of **S3**.



White powder. Highly photosensitive. ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.94 (s, 6H), 7.79 (d, ^3J=1.6Hz, 6H), 7.79 (d, ^3J=1.6Hz , 6H), 3.96 (s, 3H). ESI-MS(175V): m/z calc. for $C_{37}H_{36}N_{12}Ag_3F_3O_3S^{2+}$ [M-2OTf]$^{2+}$ 552.9924; found 554.9927.

8.3.3. Preparation of S4

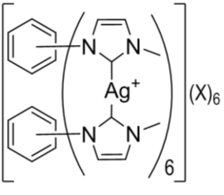
0.25 g (0.3 mmol) of **L4** is dissolved under nitrogen in 20 mL of methanol. 0.11 g (0.5 mmol) of Ag_2O are added and the mixture is heated to 50 ºC during 12 h. After this, the mixture is filtered through Celite obtaining a colorless solution. The solution is concentrated to 5 mL and 20 mL of pentane are added. The white precipitate is filtered, washed with pentane and dried under vacuum yielding 0.065 g (28%) of **S4**.



White powder. Photosensitive. ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 8.40 (s, 6H), 7.91 (d, ^3J=8.3Hz, 6H), 7.71 (d, ^3J=8.3Hz, 6H), 7.57 (t, ^3J=8.1Hz, 6H), 7.45 (t, ^3J=8.1Hz, 6H), 4.22 (s, 18H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 188.8 (dd, $^1J_{C\text{-}Ag107}$ = 187 Hz, $^1J_{C\text{-}Ag109}$ = 213 Hz, NCN), 139.8, 133.9, 133.5, 120.7 ($^1J_{C\text{-}F}$ = 320 Hz, $CF_3SO_3^-$), 125.0, 124.2, 112.8, 112.4, 36.2. ESI-MS(175V): m/z calc. for $C_{61}H_{48}N_{12}Ag_3F_3O_3S^{2+}$ [M-2OTf]$^{2+}$ 703.0393; found 705.0401.

8.3.4. Preparation of S1’

0.3 g (0.2 mmol) of **L1** are dissolved under nitrogen in 20 mL of methanol. 0.12 g (1.6 mmol) of KCl and 0.185 g (0.8 mmol) of Ag_2O are added and the mixture is stirred at room temperature during 24 h. After this, the mixture is filtered through Celite obtaining a colorless solution. The solution is concentrated to 2 mL and 20 mL of pentane are added. The white precipitate is filtered, washed with pentane and dried under vacuum yielding to 0.132 g of **S1'**.



X = $AgCl_2^-$ or Cl^- or TfO^-

White powder. Photosensitive. ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.58 (s,12H), 7.35 (s, 12H), 3.69 (s, 18H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 182.4 (dd, $^1J_{C\text{-}Ag107}$ = 184 Hz, $^1J_{C\text{-}Ag109}$ = 210 Hz, NCN), 136.6, 123.7, 122.9, 120.6 (q, $^1J_{C\text{-}F}$ = 320 Hz, $CF_3SO_3^-$), ~40 (CH_3; overlapping with DMSO signal). ESI-MS(175V): m/z calc. for $C_{60}H_{60}N_{24}Ag_6Cl^{5+}$ 358.5885; found 359.7883.

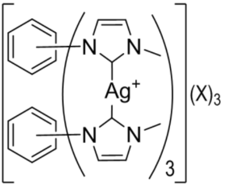
8.3.5. Preparation of "C2"

0.28 g (0.2 mmol) of **L2** are suspended under nitrogen in 20 mL of dichloromethane. 0.075 g (1.0 mmol) of KCl and 0.12 g (0.5 mmol) of Ag_2O are added and the mixture is stirred at room temperature during 24 h. After this, the mixture is filtered through Celite obtaining a yellow solution. The solution is concentrated to 2 mL and 20 mL of pentane are added. The yellow precipitate is filtered, washed with pentane and dried under vacuum yielding to 0.103 g of **"C2"**.

8.3.6. Preparation of S3' + "C3"

0.3 g (0.4 mmol) of **L3** are added under nitrogen to 20 mL of methanol. 0.095 g (1.3 mmol) of KCl and 0.155 g (0.7 mmol) of Ag_2O are added and the mixture is stirred at room temperature during 24 h. After this, the mixture is filtered through Celite obtaining a colorless solution. The solution is concentrated to 5 mL and 20 mL of pentane are added. The white precipitate is filtered, washed with pentane and dried under vacuum to yield 0.12 g of a mixture.

The ESI-MS results suggest the presence of **S3'** and **C3** but the assignment of the peaks in ^1H-NMR remains unclear, the following data has been assigned using **S3** as a reference for the sandwich-like complex, nonetheless, the compounds have not been successfully isolated.

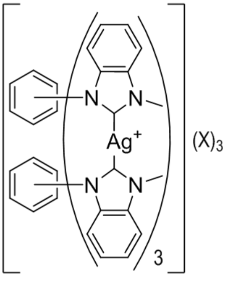


X = $AgCl_2^-$ or Cl^- or TfO^-

White powder. Highly photosensitive. ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.95 (s,18H), 7.81 (d, ^3J = 1.8Hz, 6H), 7.70 (d, ^3J = 1.8Hz, 6H), 3.97 (s, 6H). *These values are detected in a mixture of S3'+"C3".* ESI-MS(175V): m/z calc. for $C_{36}H_{36}N_{12}Ag_3^{3+}$ 319.0113; found 319.6776

8.3.7. Preparation of S4’

0.27 g (0.3 mmol) of **L4** are added under nitrogen to 20 mL of methanol. 0.075 g (1.0 mmol) of KCl and 0.125 g (0.6 mmol) of Ag_2O are added and the mixture is stirred at room temperature during 24 h. After this, the mixture is filtered through Celite obtaining a colorless solution. The solution is concentrated to 5mL and 20mL of pentane are added. The white precipitate is filtered, washed with pentane and dried under vacuum to yield 0.14 g of **S4’**.



X = $AgCl_2^-$ or Cl^- or TfO^-

White powder. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 8.49 (s, 6H), 7.87 (d, ^3J = 8.2 Hz, 6H), 7.66 (d, ^3J = 8.2Hz, 6H), 7.54 (t, ^3J = 7.5 Hz, 6H), 7.41 (t, ^3J = 7.5 Hz, 6H), 4.22 (s, 18H). ESI-MS(175V): m/z calc. for $C_{60}H_{48}N_{12}Ag_3^{3+}$ 419.0426; found 420.3766

9. CONCLUSIONS

Compound **S2** has not been possible to obtain although the success in the preparation of **S4** indicates that benzimidazol-1-yl substituents are capable of producing sandwich-like carbenes when the steric interactions between them are less important. The use of the adequate conformer of **L2** may lead to the formation of **S2**. Unfortunately, a methodology for isolating or selectively obtaining the adequate conformer is needed.

Two new sandwich-like carbenes (**S3** and **S4**) have been successfully prepared and characterized by ESI-MS, ^{1}H and ^{13}C NMR.

The silver metallation in presence of KCl generates sandwich-like carbenes (**S1'** and **S4'**) but these are notably different in ^{1}H and ^{13}C NMR compared to the ones prepared in absence of chloride. ESI-MS results indicate that the only difference compared to **S1** and **S4** are the anions of the salt. The reason for this difference in NMR shifts is at this point unknown although the described behaviour of this kind of compounds suggests that the presence of dihalogenosilver anions may be the reason behind these results. A supramolecular interaction of chloride anions with the cationic complex is also a plausible hypothesis.

The preparation of **S3'** in the same conditions used to prepare **S1'** and **S4'** is not selective and yields a mixture of compounds, the results of ^{1}H-NMR suggest that the mixture contains two compounds. By comparing the data with **S3**, **S3'** can be identified.

The only cases where the preparation of silver chloride carbenes has given some results have been the attempts of preparing **C2** and **C3** but in both cases the characterization of the compounds is unclear. In the case of **C2** it is not possible to perform NMR experiments in chloroform due to the low solubility of the product and mass spectrometry results only show small fragments. The results on **C3** are unclear because this compound has not been successfully isolated and is mixed with **S3'**. Nonetheless, an increase on the amount of KCl in the reaction might lead to the generation of a single product.

10. REFERENCES AND NOTES

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11. ACRONYMS

NHC: N-Heterocyclic Carbene

THF: tetrahydrofuran

DMSO-d_6: hexadeuterated dimethylsulfoxide

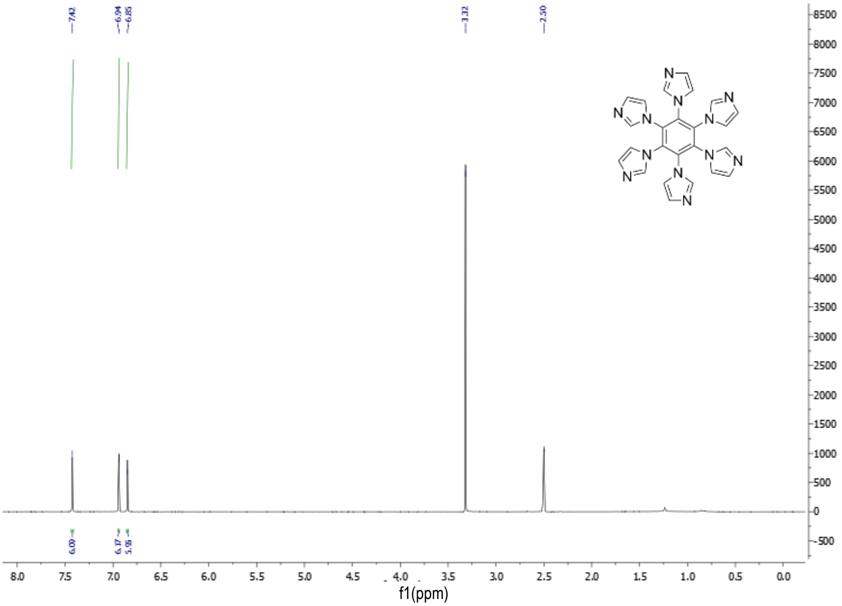
NMR: Nuclear magnetic ressonance

ESI-MS: Electrospray ionization mass spectrometry

APPENDICES

APPENDIX 1: ^{1}H AND ^{13}C NMR

^{1}H-NMR of **P1**:



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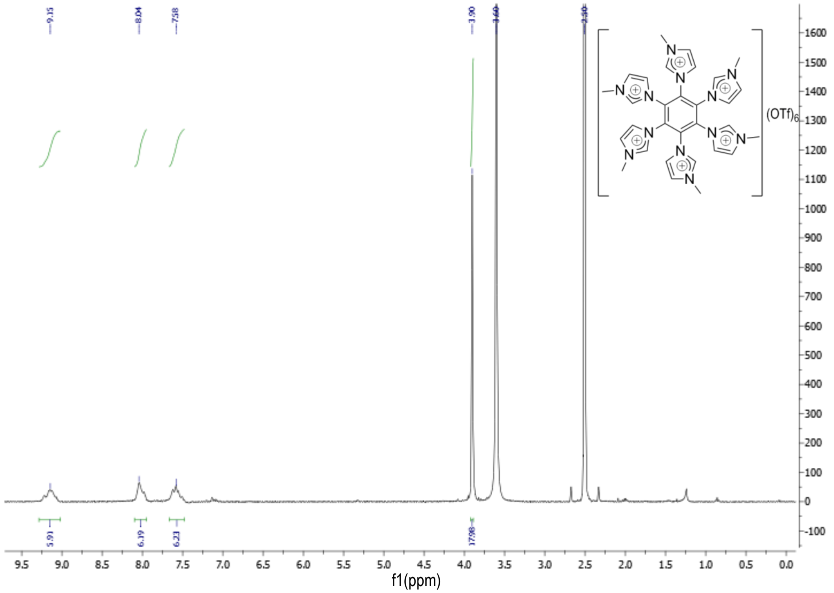

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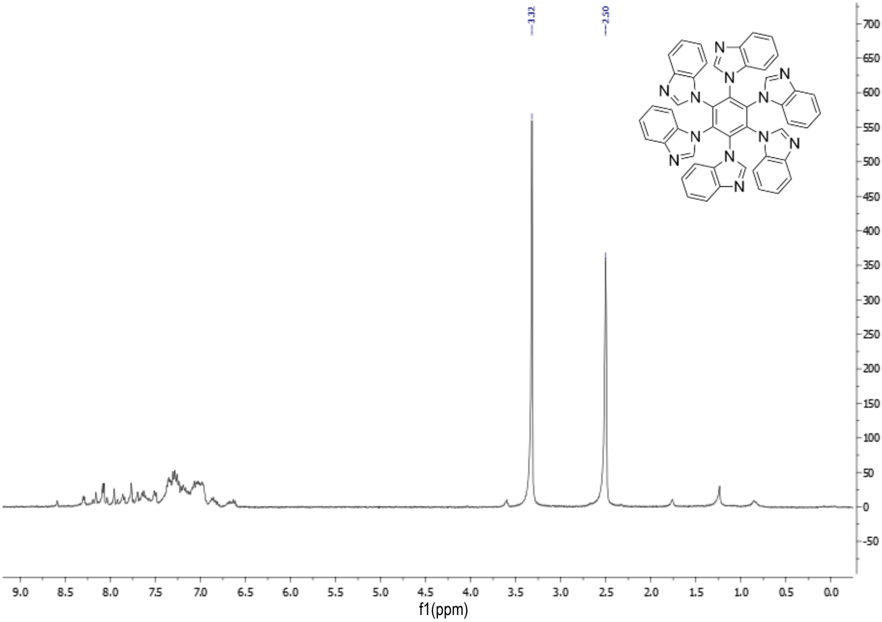
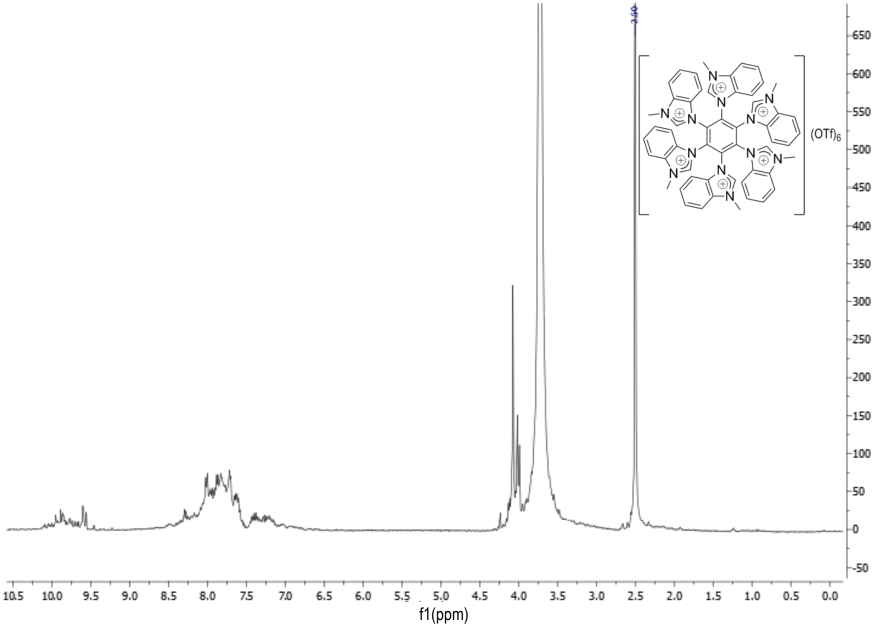


^{1}H-NMR of **L2**:



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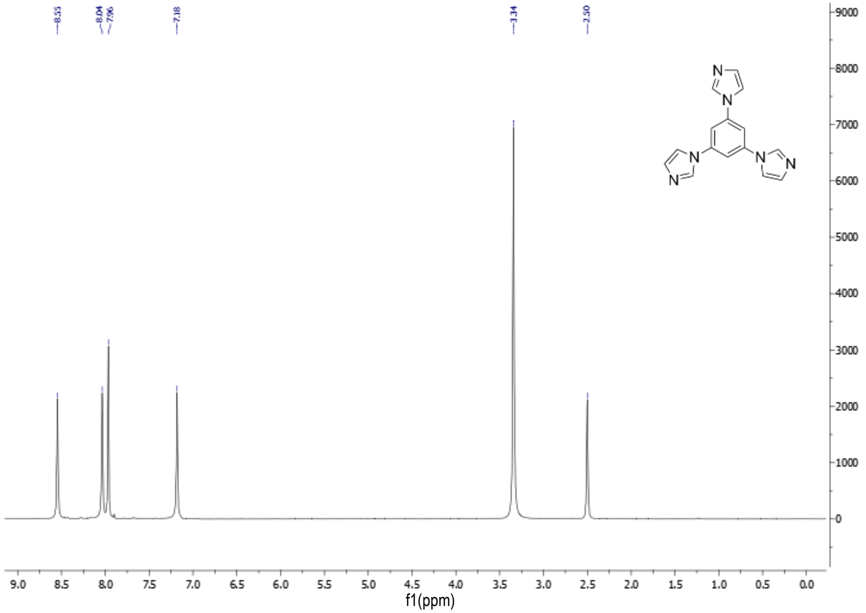
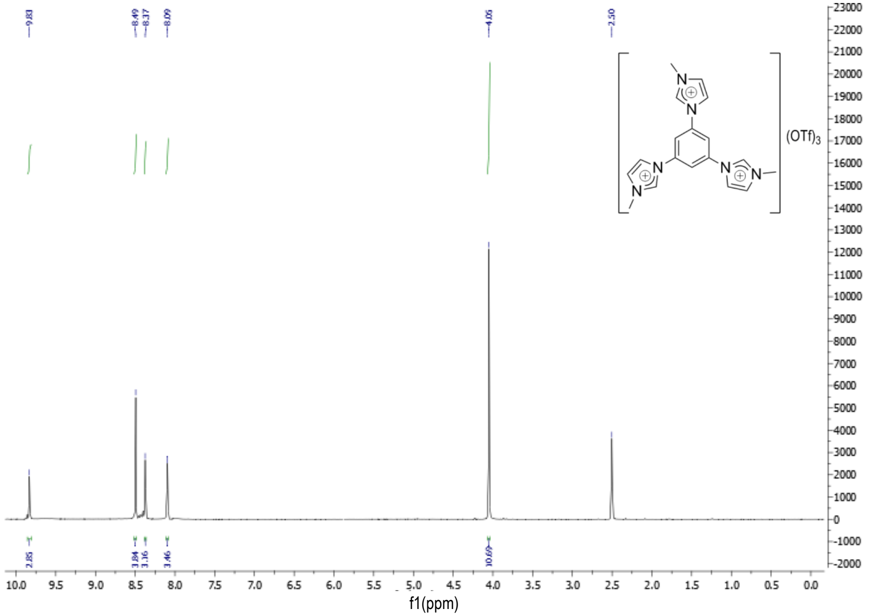
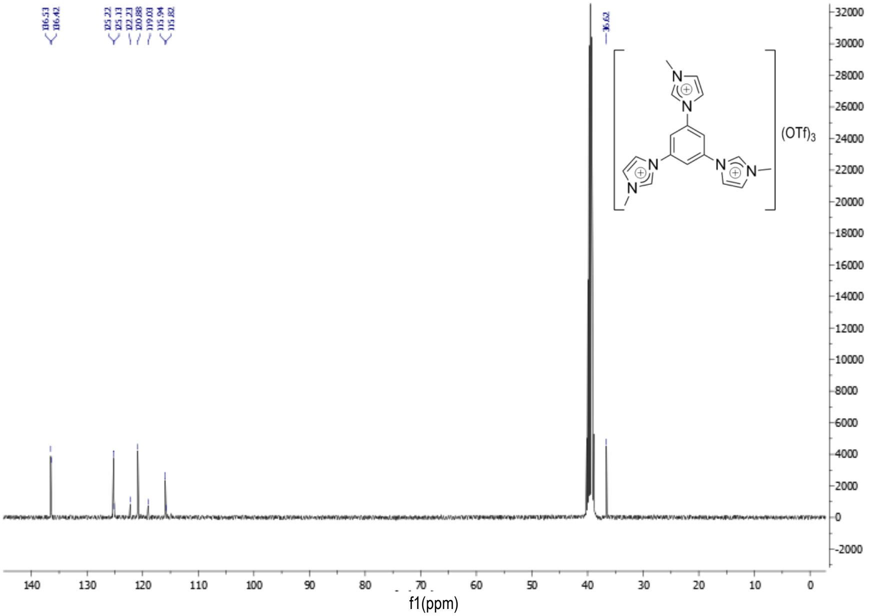


^{1}H-NMR of **L3**:



^{13}C-NMR of **L3**:



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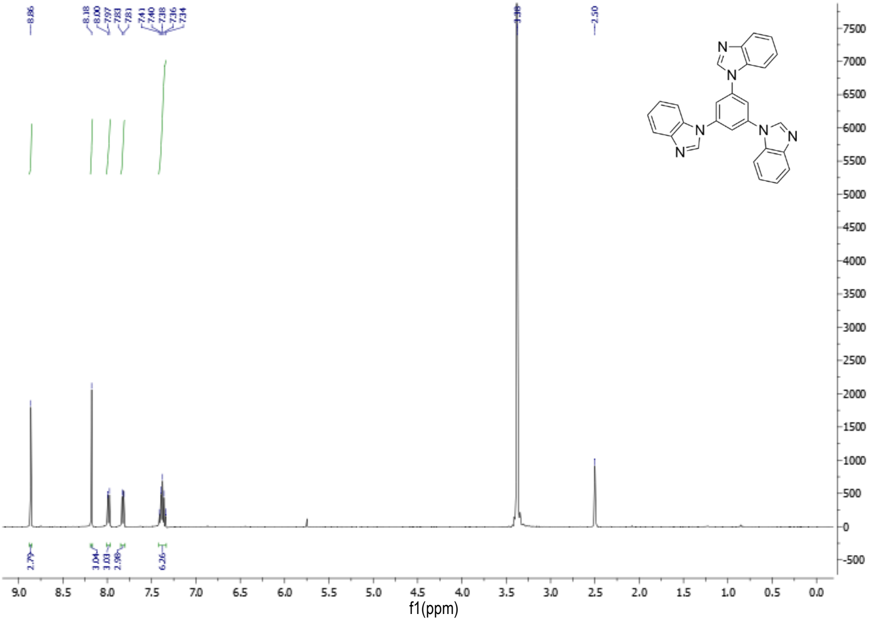

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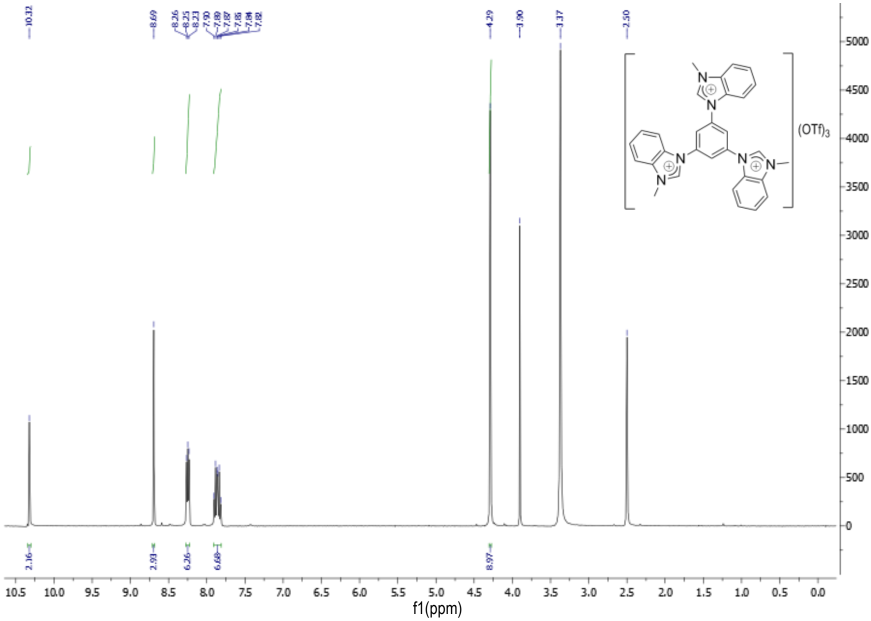

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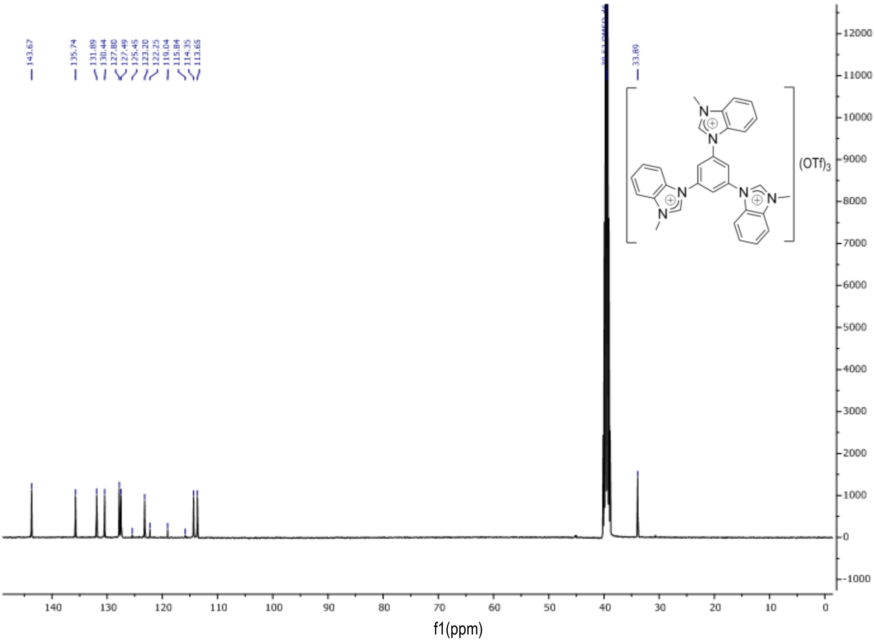

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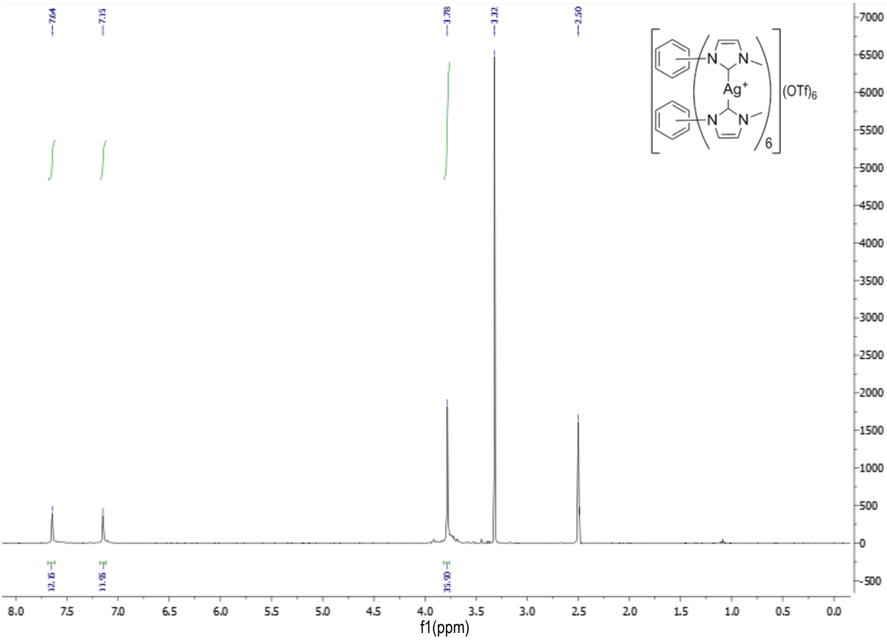

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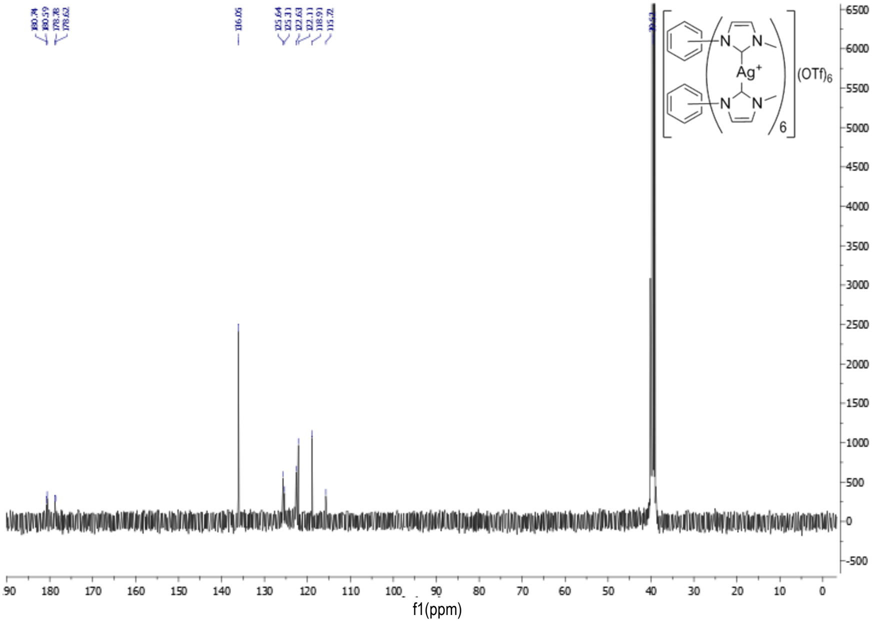

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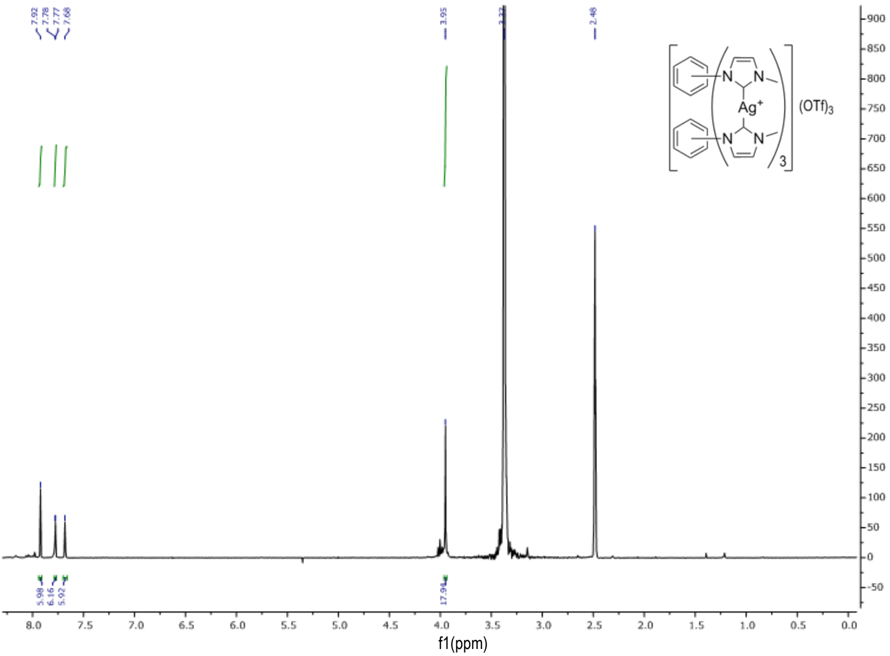

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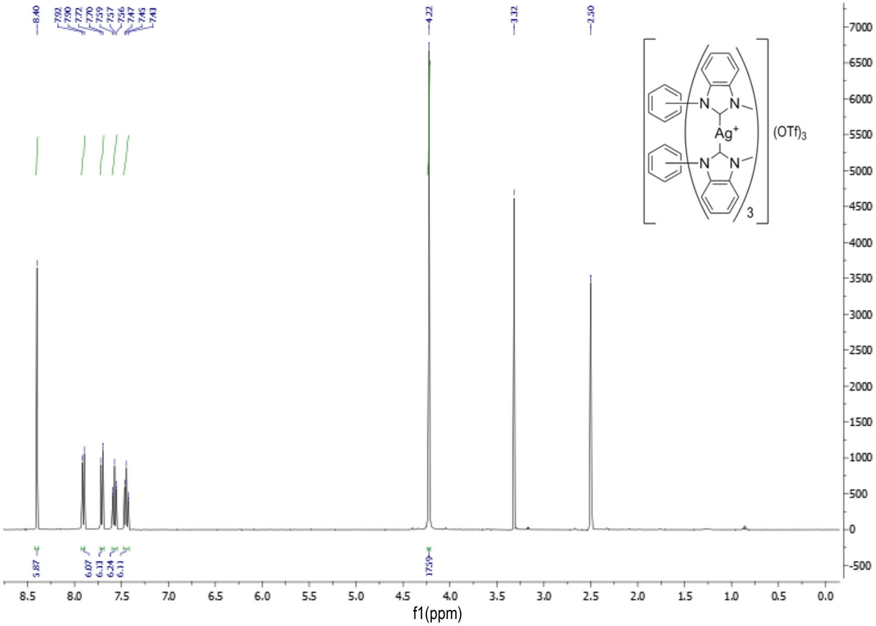
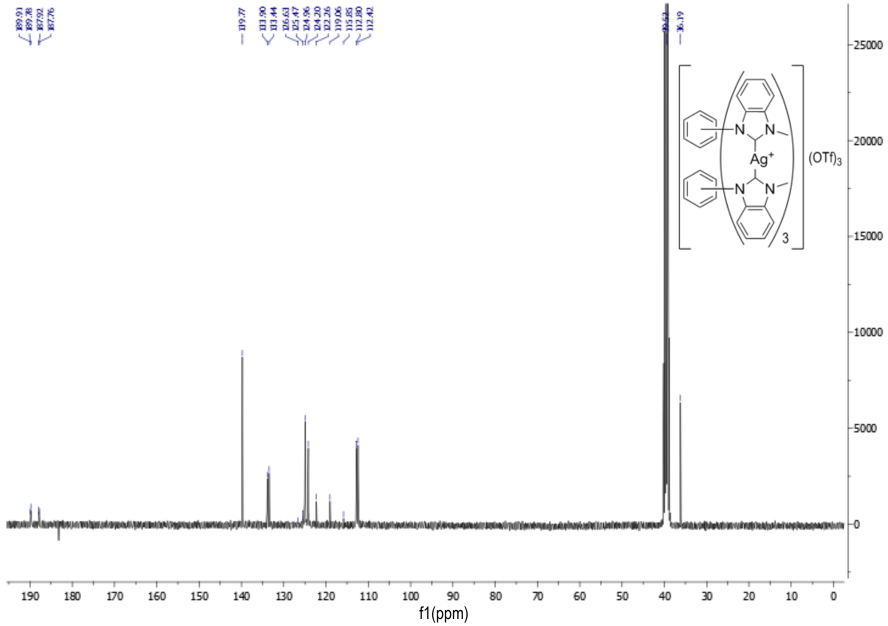
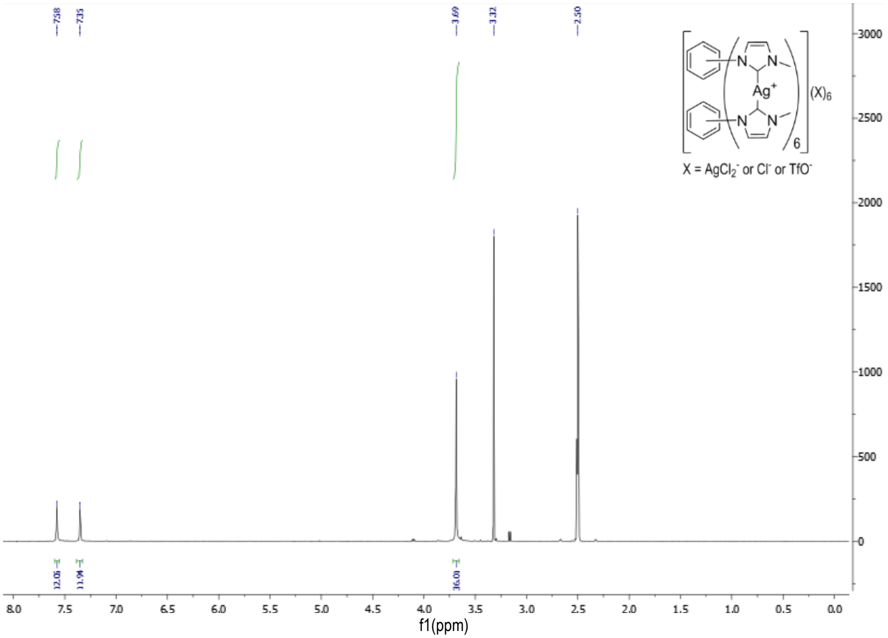


^{13}C-NMR of **S4**:



^{1}H-NMR of **S1'**:



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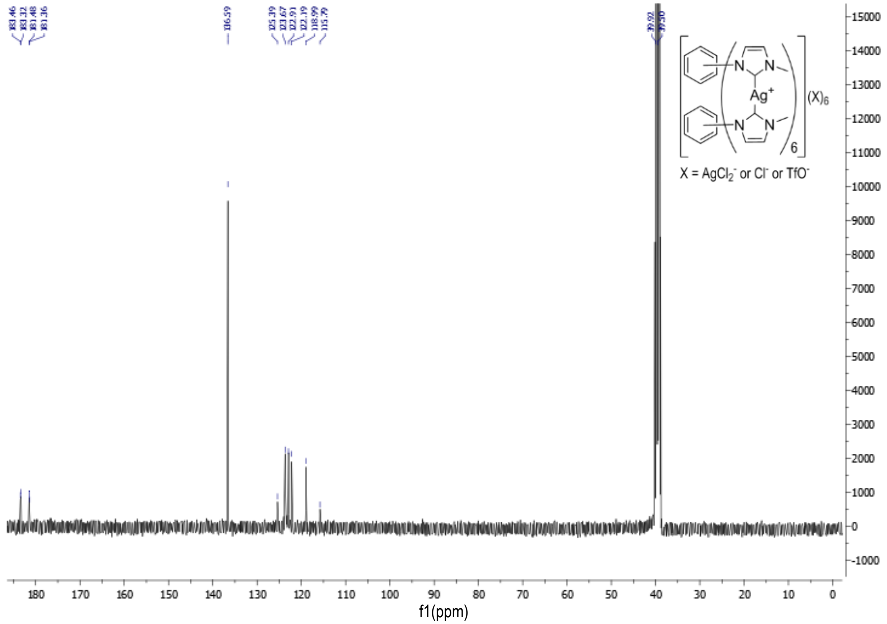
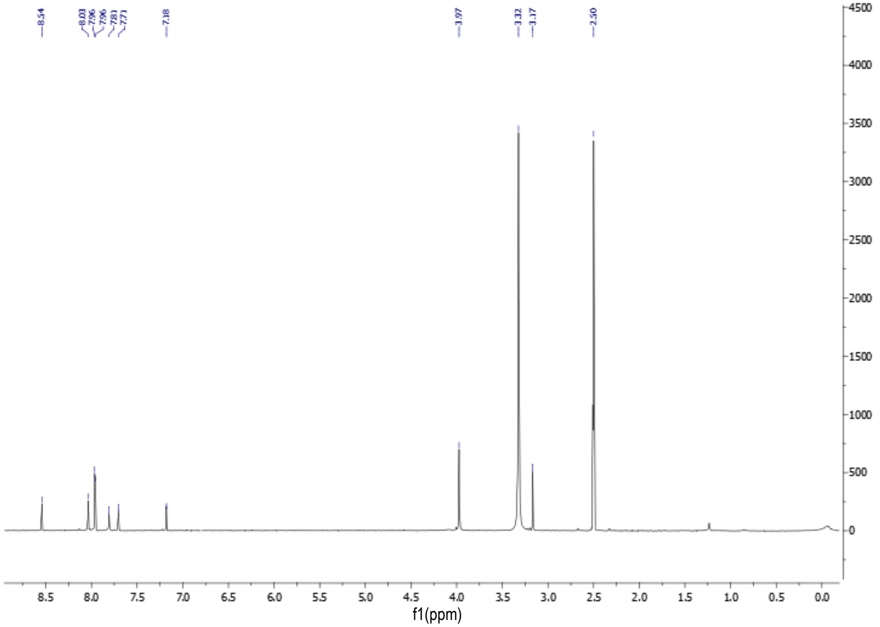
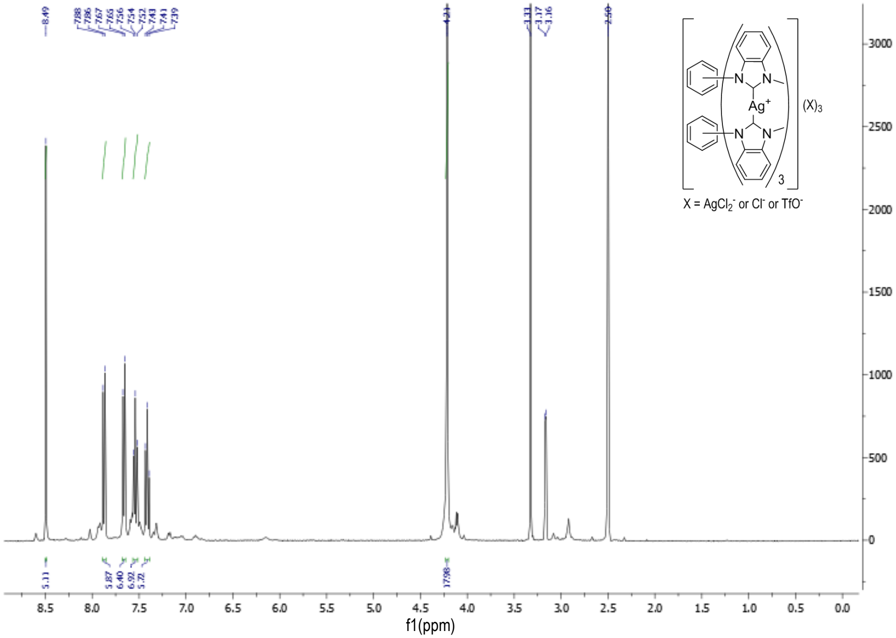


^{1}H-NMR of **S3’+”C3”**:



^{1}H-NMR of **S4’**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7.88
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7.65
7.56
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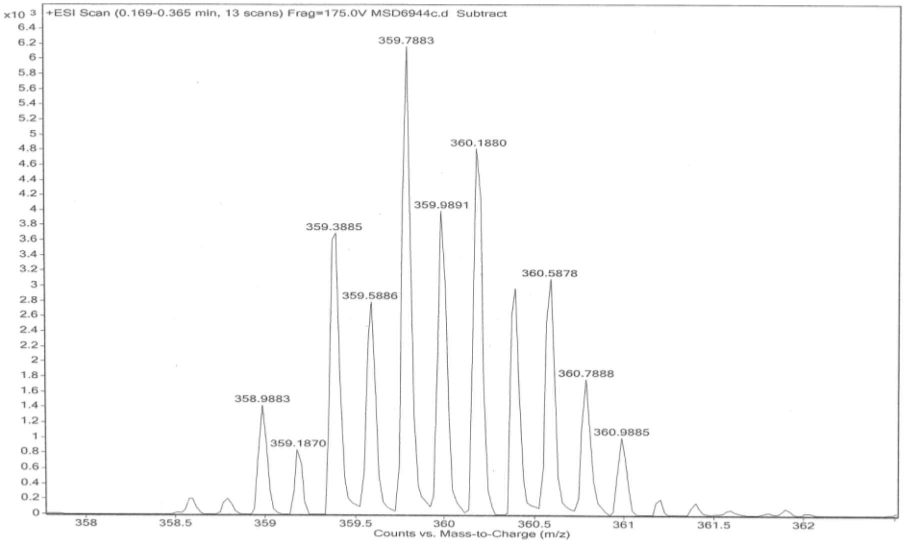
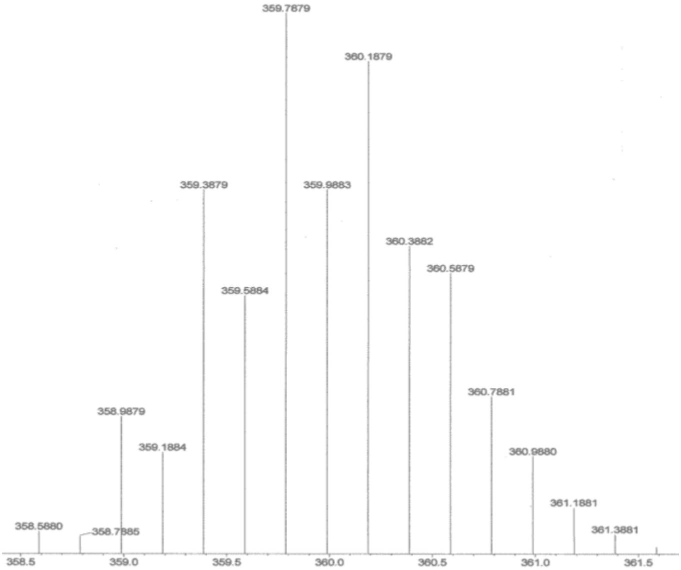
7.52
7.43
7.41
7.39
4.21
3.33
3.17
3.16
2.50
5.11
5.87
6.40
6.92
5.72
17.98
N
N
Ag+
N
N
(X)3
3
X = AgCl2- or Cl- or TfO-
3000
2500
2000
1500
1000
500
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1(ppm)

APPENDIX 2: MS

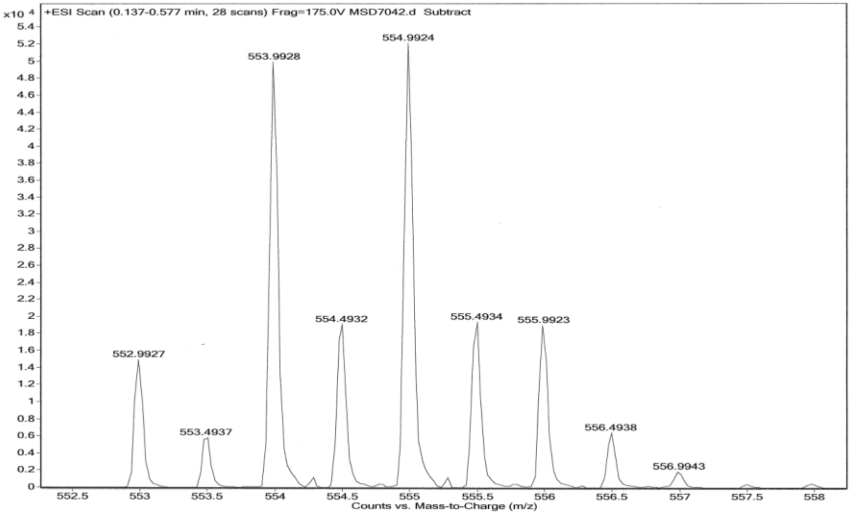
ESI-MS of **S1’**: Isotopic distribution in peak $C_{60}H_{60}N_{24}Ag_6Cl^{5+}$:



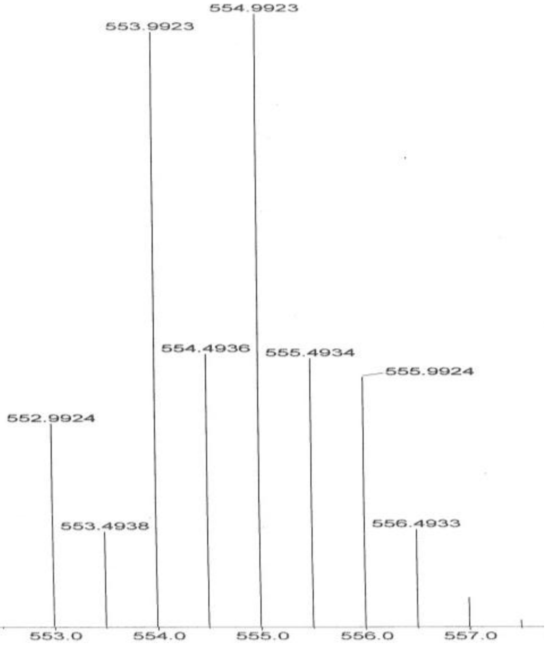
Calculated isotopic distribution:



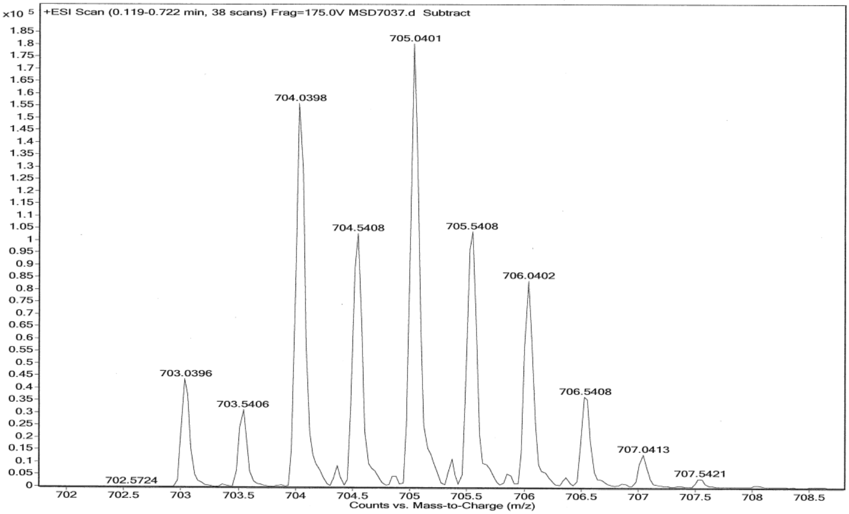
ESI-MS of **S3**: Isotopic distribution in peak $C_{37}H_{36}N_{12}Ag_3F_3O_3S^{2+}$



Calculated isotopic distribution:



ESI-MS of **S4**: Isotopic distribution in peak $C_{61}H_{48}N_{12}Ag_3F_3O_3S^{2+}$



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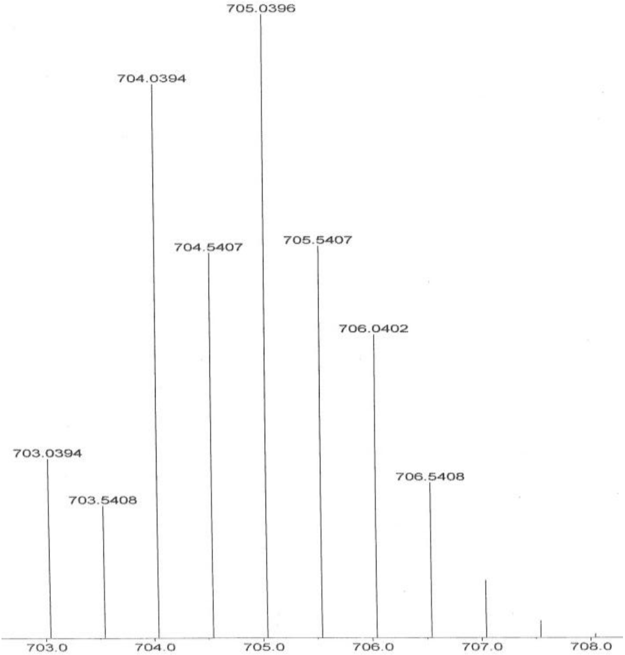
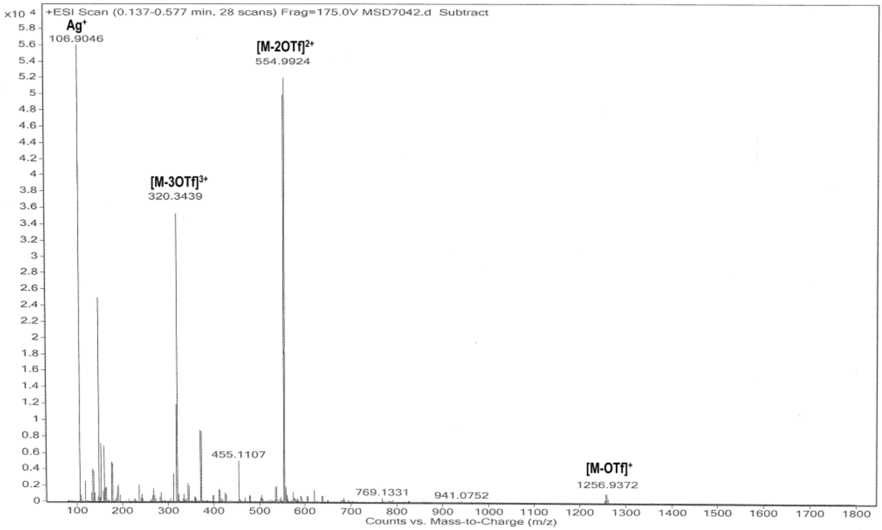


ESI-MS of **S3**:



ESI-MS of **S4:**