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Treball Final de Grau

Study of the Suzuki-Miyaura cross-coupling reactions with NHC palladium carbenes in MOF structures and Natural Deep Eutectic Solvents.

Estudi de les reaccions d'acoblament creuat Suzuki-Miyaura amb carbens NHC de pal·ladi en estructures tipus MOF i dissolvents eutèctics d'origen natural.

Lluís Batlle Sabio

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UNIVERSITAT DE BARCELONA

B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

“Si no conec una cosa, la investigaré.”
Louis Pasteur

Primer de tot agrair al meu tutor Dani per haver estat dirigint-me i ensenyant-me durant tot el treball de forma tant agradable, aconsellar-me en l’escriptura de la memòria, a més de fer-me millorar com a futur químic.

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Per últim, agrair a la meva família per el seu suport i acompanyament durant tot el transcurs del treball i durant tota l’etapa com estudiant.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (ODS)

The main objective of this project is study the catalytic properties of the N-heterocyclic carbene (NHC) ligands through Suzuki-Miyaura cross-coupling reactions in MOF structures with NADES solvent, therefore this project can be classified within the class **planet** within the five broad areas (known as the 5Ps) into which the ODS can be classified. This fact is due the use of catalysis allows the reduction of times, increase of speeds in previously known reactions, reducing waste generated and its environmental impact, thus allowing a substantial improvement of quality.

The ONU has developed the Sustainable Development Goals, which attempt to be a model to achieve a better and more sustainable future, aimed at fighting challenges such as poverty, inequality, climate change, environmental degradation, peace, and justice. Within these seventeen objectives, this project can be identified with:

- **Goal 12:** Ensure sustainable consumption and production patterns.

  All the waste generated during the experimentation part has been correctly deposited in this corresponding container (halogenated/non-halogenated).
- **Goal 13:** Take urgent action to combat climate change and its impacts

  Catalytic reactions are carried out in solvents of NADES class, these solvents can be recycled and reused, and are considered nontoxic solvent.

All these actions allow a responsible use of substances with the minimum production of residues, with the aim of having a minimum environmental impact.

CONTENTS

1. SUMMARY

The construction of large organometallic networks formed by the union of ligands through a metal atom, is great interest in the chemistry as it allows the synthesis of large supramolecular complexes, which can encapsulate other compounds, giving it a wide variety of applications. In this way, the study of synthesis of MOFs (Metal-Organic Frameworks) has a great interest, as these materials formed by metal nodes and organic ligands, have many applications, such can it be use as sensors, gas storage, or in the case that interests us, the use in catalysis, all this thanks to the porous character that presents.

Since the isolation of an N-heterocyclic carbene (NHC) from Arduengo in 1991, the use of this ligand for the synthesis of MOFs has increased, due to its neutral and strong σ-donor character, some ideal characteristics inside the world of organometallics and catalysis, allowing the formation of a strong bond between the ligands and metal centers.

In this context, it is tried to synthesize star-shaped ligands NHC carbene from the triphenyl precursor, and their catalytic properties are studied through Suzuki–Miyaura cross-coupling reaction (usually catalyzed by palladium), creating metal-organic frameworks with different metals. These reactions are kinetically followed by gas chromatography, and it carry out in low toxicity natural solvents with a low eutectic point (NADES).

Keywords: Suzuki–Miyaura cross-coupling, homogeneous catalysis, MOF, NADES, NHC carbenes, palladium, nickel, copper, star-shaped ligands.

2. RESUM

La construcció de grans xarxes organometàl·liques formades per la unió entre lligands a través d'un àtom metàl·lic, té un gran interès dins del món de la química ja que permet la síntesi de grans complexos supramoleculars, els quals són capaços d'encapsular altres compostos, donant-li així una gran varietat d'aplicacions. En aquest sentit, l'estudi de la síntesi de MOFs (Fragments Metàl·lics Orgànics) té un gran interès ja que aquests materials, formats per nodes metàl·lics i lligands orgànics, presenten un gran nombre d'aplicacions, com pot ser l'ús com a sensors, emmagatzematge de gasos, o en el cas que ens interessa en el nostre cas, l'ús en catàlisi, tot això gràcies al caràcter porós que presenta.

Des de l'aïllament d'un carbè N-heterocíclic (NHC) d'Arduengo el 1991, ha augmentat el ús d'aquest lligand per a la síntesi de MOFs, gràcies al seu caràcter neutre i σ-donador fort, unes característiques idònies dins del món de l'organometàl·lica i la catàlisi, permeten la formació d'un enllaç fort entre el lligands i centres metàl·lics.

En aquest context, s'intenta preparar lligands de carbens NHC en forma d'estrella, partint del precursor trifenil, i s'estudien les seves propietats catalítiques a traves de reaccions d'acoblament de Suzuki-Miyaura (generalment catalitzades per pal·ladi), creant MOFs amb diferents metalls. Aquestes reaccions son cinèticament seguides mitjançant la cromatografia de gasos, i realitzades en dissolvents d'origen natural de baixa toxicitat que presenten un baix punt eutèctic (NADES).

Paraules clau: Acoblament creuat Suzuki-Miyaura, catàlisi homogènia, MOF, NADES, carbens NHC, pal·ladi, níquel, coure, lligands en forma d'estrella.

3. INTRODUCTION

Over the last decades, the chemistry that involving the combination of metals with bridging organic ligands forming different assemblies of different sizes and shapes, has become a very important due to their wide range of application. These applications include stabilization of reactive species, drugs delivery, molecular encapsulation, supramolecular catalysis, and many others [1]. The name to refer to this chemistry is metallosupramolecular chemistry. That chemistry is dominated by use of O-, N-, and P-donor Werner-type polydentate ligands, while only a little example is bearing a carbon donor ligand. But even considering this fact, over the last years the organometallics ligands have allowed preparation of a lot of different supramolecular organometallic coordination complexes (SOC), and that term is gaining space in organometallic metallosupramolecular chemistry.

During the last ten years, the use of multidentate N-heterocyclic carbene (NHC) ligands, has been impulse due to efficiency of these ligand in metal catalyst [2]. The number of SOC has increased in the last years due their use for host-guest chemistry in catalysis, where the carbon-metal bond is structurally very important for the formation of the architecture of the final SOC. While the formation of highly reactive metal catalysts is facilitated by the type of poly-NHC, the bridge of poly-NHC is utilized in different molecular structures, that go from one, three-dimensional molecular cages, to molecular cages, and organometallic polymers [3]. These poly-NHCs containing supramolecules as active catalyst in homogeneous and heterogeneous catalysis.

The term of metal-organic frameworks (MOF) is use in coordination polymers, for preparation structures of one-, two, and three-dimensional structures. This material has a lot of number of applications, ranging from catalyst to sensors, and gas stores [4]. The main characteristic of this structure is for coordination compounds exhibiting porosity. For the preparation of MOF, N-heterocyclic carbenes have excellent scaffold, because have stability, well coordination versatility, and possibility to enable communication between the metal d_π orbitals and empty π orbitals of the ligand through metal-to-ligand π backdonation.

The cross-coupling reactions is a term used to denote a σ-bond metathesis reaction between a nucleophilic and electrophilic reagent, and thus can be regarded as a generalization of nucleophilic substitution, where is generated a new carbon-carbon bond [5]. This type of reaction is closely associated with palladium catalyst and the final product is generally bigger than precursors. One perfect form to test the MOF synthesized is use them as catalyst in Suzuki-Miyaura cross-coupling.

3.1. N-HETEROCYCLIC CARBENE

The research on divalent carbon species stabilized within the nitrogen-heterocyclic has shown big steps in organic and organometallic catalyzes since the isolation of Arduengo carbene in decade 1990 [3]. It was in 1991 when Arduengo synthesized and crystallographically characterized the first NHC. During last years, it has been interested in designing poly-NHC ligands connected by polycyclic aromatic hydrocarbons, aiming to facilitate the preparation of homogeneous metal-based catalysts, with interesting catalytic properties that attributed to substrate-ligand supramolecular interactions. These ligands are still far from being full explored and can be show very good potential in homogeneous catalysis, organocatalysis, design metal-based drugs and other applications [9].

The ligand has become an important ligand for do organometallics complexes due to their strong σ-donating properties and faculty to tunable steric forms, NHC ligands are two-electron σ-donor with little π-accepting ability, that's make an advantageous for forming strong bonds to metal center, with a little tendency of dissociation, perfect to use the ligand in organometallic catalysts.

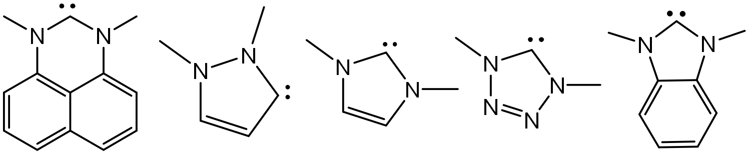


Figure 1. Examples NHC

The easy preparation, his great chemical stability and coordination versatility has allowed a lot of possibility to the researchers for create a news organometallic compounds with variety of geometries [9]. The most common method for the preparation is deprotonation of the corresponding azolium salt under anhydrous conditions [7]. Most NHC based supramolecular organometallic complexes are based on polydentate NHC ligands bound on group 11 metals, because these metals often allow linear coordination modes that facilitate trans coordination of the ligands, forming assemblies that metal atoms are sandwiched between the two polydentate NHC ligands [1]. The bond ligand-metal are usually labile, which allows the formation of the thermodynamic most stable assemblies from mixtures of the metal precursor. Due to the application in carbon-carbon coupling reactions, the chemistry of Pd(II)-NHC complex has become an area of quite interest and it's in continuous development, because is considered as a new generation of catalysts for such organic transformation, alternative to the phosphines. Since the preparation of the first Pd(II) complex with biscarbene ligand and great application in carbon-carbon coupling reaction such as Heck and Suzuki, many of others applications have been described in to organic transformations.

There are different examples of ligand NHC (Figure 1) with different constitution, who varies the σ-donor strength, and considering poly-NHC ligands composition, can be classified as bis-, tris-, and tetra-NHC. For compare the electronic properties of ligands, we can use the valor of pKa (high value indicates strong donor), or techniques IR spectroscopy (σ-basic carbene ligand is related to low stretching frequency) and X-ray diffraction [6]. The control steric and electronic properties of ligands is very important to improve the catalytic performance of the transition metal complexes that bear them. The binding constants increase exponentially with the number of π electrons of the guest as a consequence of the enhancement of the host-guest face-to-face overlap.

3.2. METAL-ORGANIC FRAMEWORKS

Metal-organic frameworks (MOFs) are a class of micro-/mesoporous crystalline solid with unique properties. This material is characterized for having large surface, high porosity, and content transition metals. Since the first use for term coordination polymers, the preparation of one-, two-, and three-dimensional MOFs has provided a lot of applications, how they can be fabrication of chemical sensors, materials with interesting optoelectronic properties, and catalysis [4][10]. MOFs are especially suitable as catalysts, because that material has possibility to be designed and modified during the synthesis. These types of materials are also known as porous coordination polymers, owing to nature of interactions between the metallic nodes and organic linkers [8].

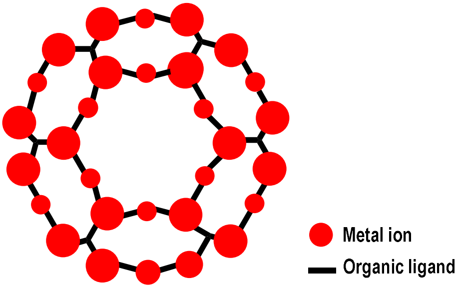
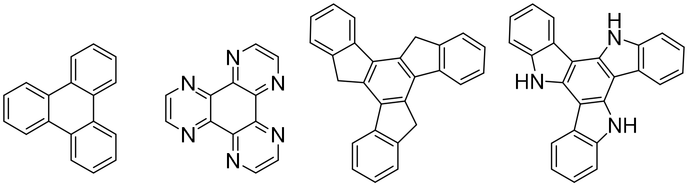


Figure 2. Concept of MOF. Crystalline network through metal-ligand coordination bonds

The network of the MOFs is generated by connecting metallic nodes constituted by metal cations or clusters of a few metal ions with rigid organic linkers having two or more coordination positions. There are a lot of examples of MOF, because there is high variety in structures and binding groups of the organic linkers, the most commons MOF are nitrogenated heterocycles and aromatic polycarboxylates. That solid can act as host to include guest and can be used to anchor to the lattice some active sites. In some cases, can be used as solid Lewis acids and can act as general catalysts for those reactions. The general properties of MOF are their large specific surface area and high porosity, what make have a high internal area, lowest framework density, and high content of active sites. The most challenges in the synthesis of polymeric materials are the capacity to predict the network geometry while avoiding interpenetration of a second polymer in to the first, which may result in filling of potential cavities. Choice of both adequate ligands and metal fragments connectors, are the key to successful MOF design. A great feature of MOF is possibility to design isostructural materials and predict the pore geometry and dimensions of a MOF with the relative dimensions of the ligands.

3.2.1. Star-shaped ligands

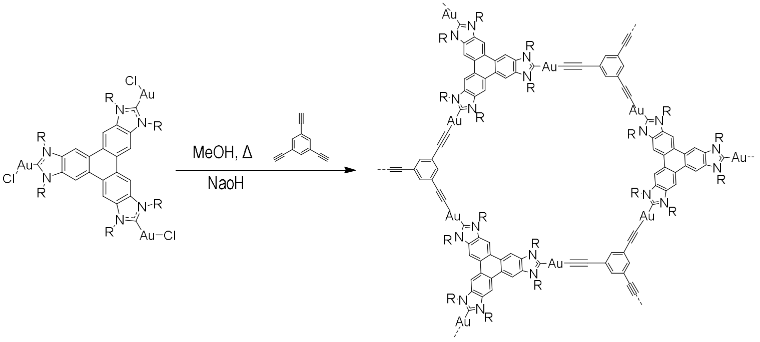
Polycyclic aromatic hydrocarbons (PAHs) are usually considered as two-dimensional graphite segments and have conjugated aromatic system, with excellent self-assembling and optoelectronic properties. Star-shaped PAHs, one class of polycyclic aromatic hydrocarbons, have planar rigidity character that makes it possible form three dimensional packed structures due to intermolecular strong π-π interactions. Generally, the star-shaped PAHs contain triphenylene (**1**), trinaphthylenes, N-hetero-triphenylenes, starphenes, truxene and triazatruxenes (Figure 3) [10]. There are different synthetic pathways for the synthesis of each of these ligands. These star-shaped polycyclic aromatic hydrocarbons (specially π-conjugated systems) can create tall ordered columnar structures by self-assembly, and such ordered configuration promotes their applications, how they can be molecular recognition, nano materials, or optoelectronic materials.



triphenylene N-hetero-triphenylenes truxene triazatruxenes

Figure 3. Star-shaped PAHs

N-heterocyclic carbenes have been as excellent scaffolds for synthesis of electronically active organometallic polymers, owing to combine high stability, great coordination versatility, and possibility to enable communication between the metal dπ orbitals and the empty π orbitals of the ligand thought metal-to-ligand π backdonation [4][15]. We can use the star-shaped ligand for a preparation of MOF and study his catalytic properties. One example is on the literature [4], where from triphenylene based tris-NHC, that have the advantage of having three carbenes connected by π-delocalized polyaromatic system, what does convert into perfect potential building block, they can prepare a triphenylene-based tris-NHC-gold-acetylide MOF and study their catalytic applications in Strecker reaction (Scheme 1).



Scheme 1. Example of synthesis [4]

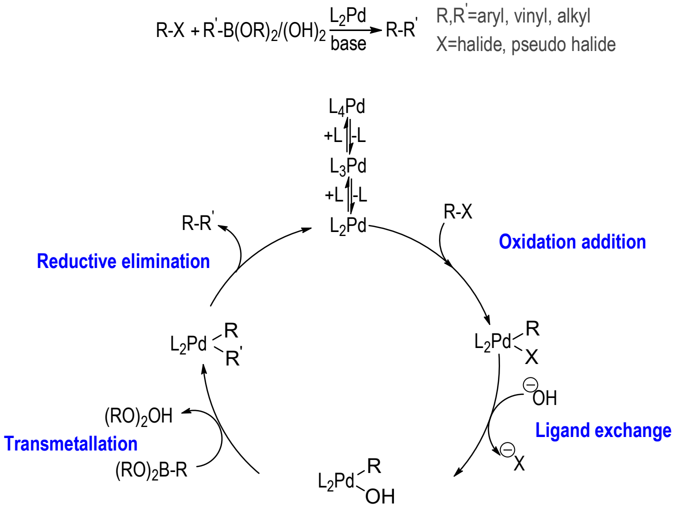
3.3. CROSS-COUPLING REACTIONS

The cross-coupling reactions involve the formation of carbon-carbon bond in presence of a transition metal catalyst (usually palladium). These types of reaction allow the substitution of an aryl, vinyl and alkyl halide/ pseudohalide by a range of a different carbon nucleophiles, how they can be an aryl, vinyl and alkyl derivates of magnesium (Kumada-Corriu), zinc (Negishi), boron (Suzuki-Miyaura), silicon (Hiyama), tin (Stille-Migita-Kosugi), and reactions that involve the construction of carbon-heteroatom bond.

The cross-coupling reactions have very important for synthesis of natural products and other biologically active molecules in pharmaceutical and other industries. These reactions facilitate the construction of building blocks form supramolecular chemistry and organic materials or polymers [12]. There are three steps in the reaction: oxidation addition, transmetallation and reductive elimination.

3.3.1. Suzuki–Miyaura cross-coupling reaction

The Suzuki-Miyaura cross-coupling reaction as one of the most important reactions for forming carbon-carbon bonds. That reaction allows the coupling of aryl, vinyl and alkyl halides/pseudohalides with organoboron compounds in basic solution with presence of palladium catalyst (Scheme 2). The vinyl halide keeps the double bond configuration [11][12].



Scheme 2. Mechanism for Suzuki–Miyaura cross-coupling reaction

- *Oxidation addition*: Palladium catalyst is inserted between the carbon (R) and the halogen (X).
- *Ligand exchange*: Hydroxide ion displaces the halide ion.
- *Transmetallation*: The group R' is moved from boron to palladium. The hydroxide ion is moved from palladium to boron.
- *Reductive elimination*: The catalyst is regenerated, a new C-C bond is formed and the palladium is eliminated.

The Suzuki-Miyaura cross-coupling reaction usually is catalyzed by palladium metal due to its good catalytic efficiency, but palladium has its own limitations to bringing about the coupling of some electrophiles. For that reason, other transitions metals are being used to try to overcome this limitation, although in less quantity (Figure 4).

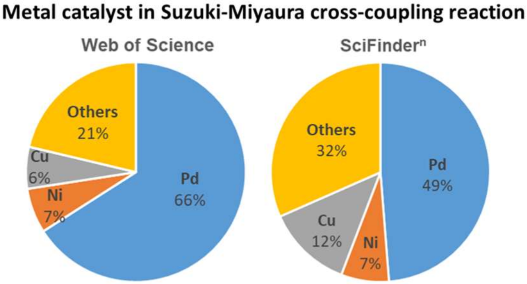


Figure 4. Graph of documents about catalyst metals in Suzuki-Miyaura cross-coupling reaction; Web of Science. *Clarivate Analytics PLC.* https://www.webofscience.com.sire.ub.edu/ (9 June 2022); SciFinder^n–CAS. *American Chemical Society.* https://scifinder-n-cas-org.sire.ub.edu/ (9 June 2022)

3.4. NATURAL DEEP EUTECTIC SOLVENTS

Natural Deep Eutectic Solvents (NADES) are a new class of Deep Eutectic Solvents (DES), which are eutectic mixtures of an ammonium salt and another compound capable of forming hydrogen bonds. These solvents are characterized by mixture presenting melting point significantly lower than those of precursors compounds. NADES is when the precursors are amino acids, organic acids sugars or choline derivatives originating from natural sources [13]. One example is ChCl:Gly (1:2), where the precursor has melting point of 305ºC (choline chloride) and 20ºC (glycerol), but the NADES has melting point of 17.8ºC [21].

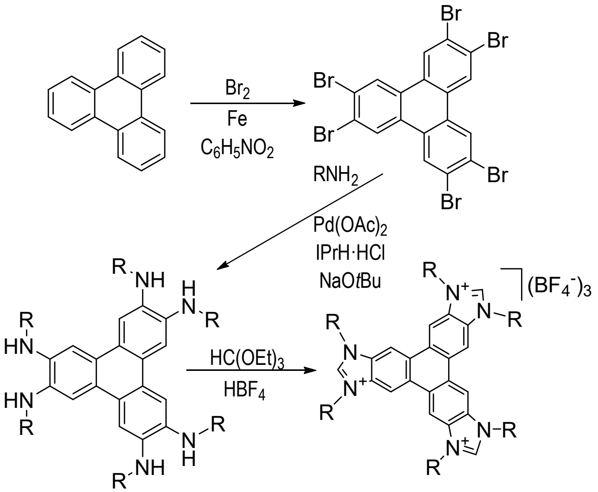
This solvent is characterized for present melting points low, higher viscosity, biodegradability, sustainability, simple synthesis, and stabilization of the solute. This solvent is formed by hydrogen bonding between receptors and donor compounds with other intermolecular interactions weak. NADES appears by the fact of having constant effort to develop of a new sustainable solvent for substitution organic solvent considered toxic and flammable, that offer lower toxicity, faster synthesis, lower reagent consumption, and safety for analysis, accordance with green analytical chemistry.

NADES can be synthesized from combination of choline or derivates and compounds how they can be glucose, xylitol, ribitol, citric acid, malic acid, oxalic acid, tartaric acid, fructose and propanoic acids. The stability of this solvent depends on the structures of the precursors and their molar ratio. The main methods for synthesis of that sustainable solvent are based on stirring and heating, freeze drying, evaporation, and microwave-assisted synthesis. The stirring and heating method consist in presence of water, mixing two compounds together by stirring and heat solution until formation transparent solution. The evaporation method consists in dissolved and evaporated in water. The freeze method consists in freezing and drying the solution until obtaining a viscous liquid. The microwave-assisted method consists in irradiated at controlled temperature the precursors [13]. NADES can be analyzed and characterized by mass spectrometry, infrared spectroscopy and NMR methods [14]. The properties of NADES (viscosity, density, and polarity) are related for intermolecular interactions and the chemical natures of the components. The physicochemical properties can be modified by addition of water (decrease viscosity owing to weakening of the hydrogen bonds between the precursors) and increasing the temperature (decrease density owing to increases of molecular movement and the molar volume of the solution).

NADES in their determinate application, these solvents can be recycled and reused, and as considerate nontoxic solvent. This solvent can dissolve synthetic chemicals of lower water solubility and thanks of his biodegradability can are alternative for some organic solvents and ionic liquids. It can used as extraction media, as chromatography media, and replace some toxic solvents such as DMSO as dissolving media in biological assays.

4. OBJECTIVES

The main objective of this project is the synthesis of the N-heterocyclic carbene (NHC) ligands from triphenylene and characterized by Nuclear Magnetic Resonance spectroscopy (NMR) ^{1}H and FTIR-ATR.



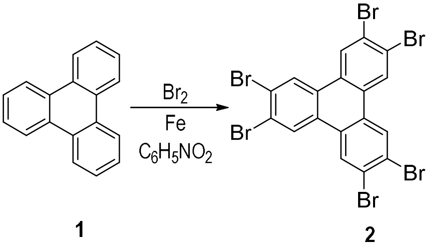
Scheme 3. Synthesis plan

The second objective is to use the ligands synthesized to study their catalytic properties through Suzuki–Miyaura cross-coupling reactions in low toxicity natural solvents, NADES, and to use them to create a metal-organic frameworks.

5. RESULTS AND DISCUSSION

5.1. 2,3,6,7,10,11-HEXABROMOTRIPHENYLENE

2,3,6,7,10,11-hexabromotriphenylene **2** (HBTP) has been synthesized starting of triphenylene and bromo reactive. HBTP polyhalogenated polyaromatic hydrocarbons received considerable attention because as precursor is one of the most common and readily available building blocks for the synthesis of star-shaped molecules, discotic liquid crystals and two-dimensional π-conjugated MOF [16]. Triphenylene **1** was utilized for the synthesis of the compound **2** using the method indicated in the bibliography [16]. The reaction consists of a bromination of triphenylene, catalyzed by Fe and nitrobenzene (Scheme 4).



Scheme 4. Synthesis of 2,3,6,7,10,11-hexabromotriphenylene

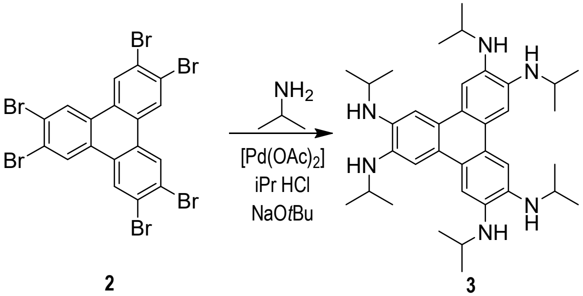
The final light gray solid was obtained in 86% yield. The ^{1}H-NMR spectrum showed presence of wished product but presence of little impurities as there are unknown peaks in 9.56(s), 8.65(d) and 8.61(s)ppm (Appendix 2, Figure H1).

5.2. AMINATION OF 2,3,6,7,10,11-HEXABROMOTRIPHENYLENE

The reaction consists of amination of 2,3,6,7,10,11-hexabromotriphenylene, a Buchwald-Hartwig cross-coupling reaction. It is a reaction that allows the formation of C-N bond between amines and aryl halides catalyzed by palladium complex and this type of reaction have a lot of interest in organic chemistry for synthesis new materials, pharmaceuticals and natural products [22]. The catalyst complex was formed *in situ* by palladium precursor [Pd(OAc)$_2$] and the ligand 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, where NaO*t*Bu as a base.

5.2.1. 2,3,6,7,10,11-hexakis(isopropylamine)triphenylene

2,3,6,7,10,11-hexakis(isopropylamine)triphenylene **3** has been tried to synthesize starting with 2,3,6,7,10,11-hexabromotriphenylene **2** and isopropylamine. HBTP **2** was utilized for try to synthesis the compound **3** using the method indicated in the bibliography [3][18], but using isopropylamine as amine source (Scheme 5).



2 **3**

Scheme 5. Synthesis of 2,3,6,7,10,11-hexakis(isopropylamine)triphenylene

Different methods have been used to try the synthesis of compound **3** because a lot of unwished precipitate solid was formed, and the product wanted to form appeared together with other unwanted compounds due to possibly an incomplete animation of all bromines and its photosensitive proprieties what made that amine decomposed. Finally, it was not possibility to obtain the product **3**. The tried attempts are summarized below (Table 1):

5.2.1.1. Method A

2,3,6,7,10,11-hexakis(isopropylamine)triphenylene **3** has been tried to synthesize using the method indicated by reference [18], but using isopropylamine as amine source. In this case, it was obtained a lot of brown solid, that was tried to be dissolved in mixture of acetone and toluene, and concentrated under reduced pressure but it was not work. The ^{1}H-NMR of the brown resin showed many unwanted signals and a TLC analysis showed the presence of different products. The FTIR-ATR of the solid showed possible presence of amine since it showed signal to 3400cm^{-1}(NH stretching).

5.2.1.2. Method B

In this case, it was used the same procedure than *Method A*, but the final mixture was heating over reflux double of the theorical time that needed, owing suspicion of need more time to complete a reaction. The ^{1}H-NMR and FTIR-ATR showed the same results as the previous case.

5.2.1.3. Method C

In this case, it was used another reference [3], and the catalyst mixture was heating 30min at 100ºC, not 10min at room temperature, for tried to activate the catalyst. The analysis of filtered solid showed again presence of amine, therefore incomplete reaction, and multiple unwanted signals in the resin.

5.2.1.4. Method D

In this case, the reaction was made in closed reactor under inert atmosphere with excess of isopropylamine, due to suspicion of possibly the isopropylamine is lost on heating, although the condenser should prevent this. To try to work in inert conditions has been worked with argon gas (Figure 5), because it is denser than oxygen (ρ_{Ar} =1.784 g/l (0ºC); ρ_{Oxygen} = 1,429 g/l (0ºC)). The ^{1}H-NMR and TLC analysis of resin showed presence of the amine with other products.

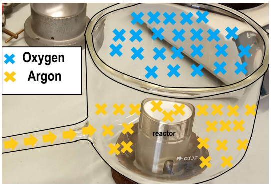


Figure 5. Work with Argon

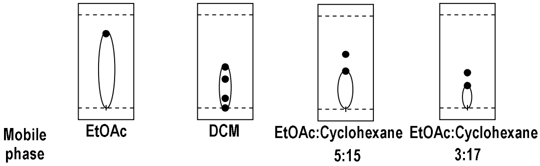


Figure 6. TLC decreasing polarity to the right

To try to separate the desired amine, it was realized a HPLC with mixture of EtOAc and cyclohexane as mobile phase (Figure 6). The resulting yellow resin showed photosensitivity and the analysis not showed practically difference compared to previous product before separation (Figure 7).

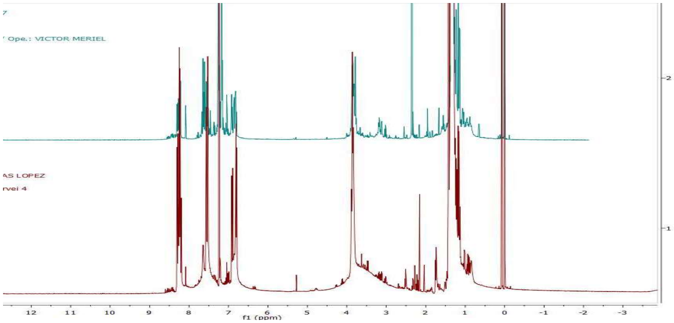


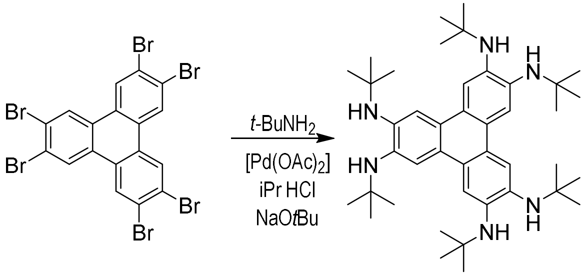
Figure 7. ^{1}H-NMR: Top pre-purification; Down post-purification

		Method A[1]	Method B[2]	Method C[2]	Method D[3]
Brown solid	**(g)**	0.0313[4]	0.7953	0.7885	0.1761
Brown resin	**(g)**	0.2862	0.1	-	0.0818
	Yield (%)	35	24	-	40

Table 1. Compared results. [1] starting from 1.0g of **2**; [2] starting from 0.5g of **2**; [3] starting from 0.25g of **2**; [4] solid has been lost when dissolving

5.2.2. 2,3,6,7,10,11-hexakis(tertbutylamine)triphenylene

2,3,6,7,10,11-hexakis(tertbutylamine)triphenylene **4** has been synthesized starting of HBTP **2,** using the method indicated in the bibliography [18]. The reaction consists of a multifold amination of 2,3,6,7,10,11-hexabromotriphenylene under inert conditions, catalyzed by [Pd(OAc)$_2$], 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride and NaO*t*Bu (Scheme 6).



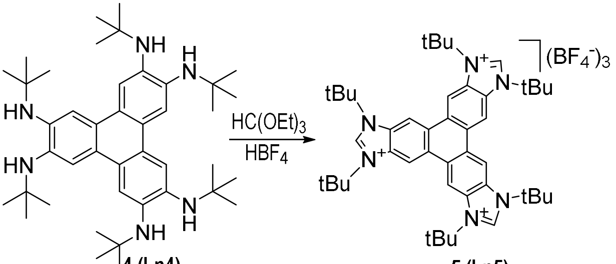
2 **4 (Ln4)**

Scheme 6. Synthesis of 2,3,6,7,10,11-hexakis(tertbutylamine)triphenylene

The final dark red solid was obtained in 69% yield, a bit lower than expected according to the reference. The ^{1}H-NMR spectrum showed great purity of product obtained but it was not possible to obtain a satisfactory characterization due to the light sensitive nature of the compound (Appendix 2, Figure H2).

5.3. TRIPHENYLENE-BASED TRIS(AZOLIUM) SALT

The triphenylene-based tris(azolium) salt **5** has been synthesized starting of **4** and HBF$_4$, using the method indicated in the bibliography [18]. The reaction consists in trisannulation with triethylorthoformate in presence of HBF$_4$ under aerobic conditions (Scheme 7).



4 (Ln4) **5 (Ln5)**

Scheme 7. Synthesis of triphenylene-based tris(azolium) salt

The ^{1}H-NMR of brown solid showed presence of impurities, so it was decided to recrystallize the product with a mixture of CH_3CN/Et_2O. The final light tan solid was obtained in 89% yield. In the final product obtained, the ^{1}H-NMR spectrum showed good purity (Appendix 2, Figure H3).

5.4. CATALYSIS

The Suzuki–Miyaura cross-coupling reaction was carried out to measure the catalytic efficiency of a complex formed from the ligand with a metal.

The reactions were performed under nitrogen atmosphere, using K_3PO_4 as base, 1% molar of catalyst, NADES as a solvent, at 80ºC and 400RPM. The reaction was followed by GC-MS after 1, 2 and 24h.

The Suzuki cross-coupling reaction is usually catalyzed by palladium metal, for that reason that metal was used, and other metals such as nickel and copper is also used for compared. The catalyst mixture was synthesized *in situ* with stoichiometric quantities of metal precursor complex and ligand to form the tri-metal NHC complex. For create a metal-organic framework *in situ* with the metal, it was used as a ligand the previously synthesized azolium salt **5** (Ln5) (Figure 8) and amine **4** (Ln4) (Figure 9). For compared the result, it also used another ligand that can also form a MOF, the 2,3,6,7,10,11-hexahydroxytriphenylene **6** (Ln6) (Figure 10). To evaluate the efficiency of metal-organic framework complex with the ligand, the entry 10 and 11, it had been done without metals, and to evaluate the efficiency of metal palladium, the entry 12 it had been done without ligand. The kinetic of reaction was followed by GC-MS.

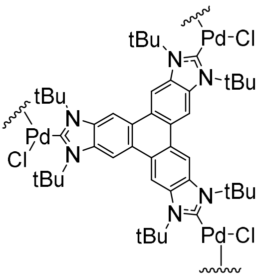


Figure 8. Example of MOF with palladium and **5**

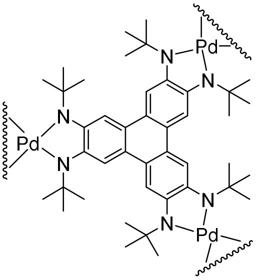


Figure 9. Example of MOF with palladium and **4**

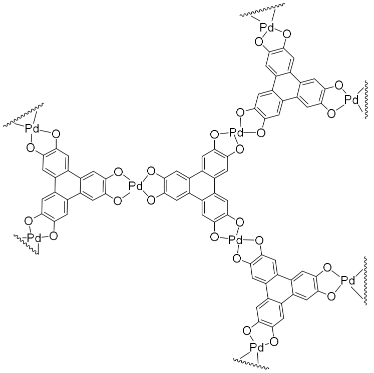
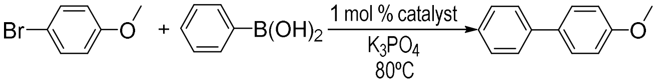


Figure 10. Example of MOF with palladium and **6**

To study this Suzuki–Miyaura cross-coupling reaction between phenylboronic acid **7** and 4-bromoanisole **8**, it was carried out using different catalysts complexes, using the NADES solvent ChCl:Gly (1:2).



Scheme 8. The Suzuki–Miyaura cross-coupling reaction

Entry	**Catalyst**	**Yield (%)** **1 hour**	**Yield (%)** **2 hours**	**Yield (%)** **24 hours**
1	Pd + Ln5	87.0	97.0	98.2
2	Pd + Ln4	78.3	95.9	98.4
3	Pd + Ln6	90.9	96.7	98.8
4	Ni + Ln5	0.0	0.0	0.0

5	Ni + Ln4	8.5	18.6	89.6
6	Ni + Ln6	0.0	0.0	0.0
7	Cu + Ln5	0.0	0.0	0.0
8	Cu + Ln4	14.6	29.5	84.7
9	Cu + Ln6	0.0	0.0	0.0
10	Ln5	0.0	0.0	0.0
11	Ln4	0.0	0.0	0.0
12	Pd	1.4	3.2	12.2

Table 2. Result catalyst A

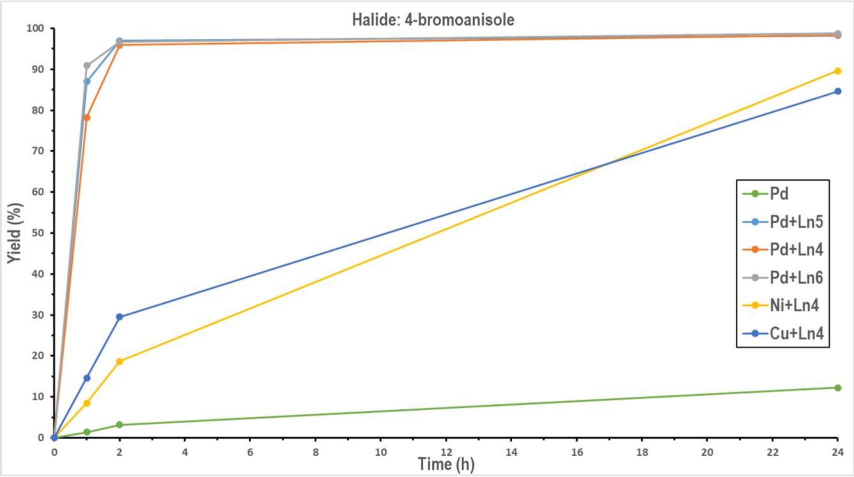


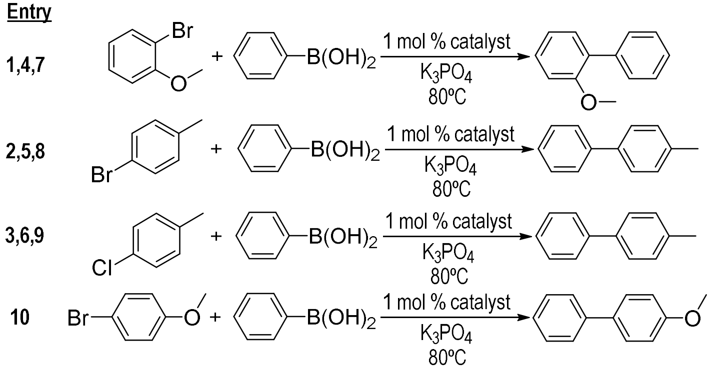
Figure 11. Graph of halide 4-bromoanisole

The palladium metal showed great results with all three ligands, showing conversions of almost 90% after 1 hour with ligands **5** and **6**, and conversions close to 97% in only 2 hours. The palladium precursor with all three ligands showed very similar conversions after 24 hours, very close to 99%. On the other hand, the metal precursor alone, without the presence of ligand, showed very low conversions than with presence of ligand, not reaching 15% in 24 hours.

The nickel and copper metal precursor only showed conversions with amine ligand **4.** In the two cases, presented low conversions in first hour, but after 24 hours achieved much higher conversions, reaching values higher than 85%, showing that the catalytic complex with these metals needs more time to be active.

The ligands **5** and **4** without metal, not showed any reactions, demonstrating that the carbene and amine ligands by itself doesn't work as a catalyst.

Another catalytic series was made with another halides in order study the good efficiency previously obtained with the complex palladium-carbene and nickel/copper-amine. It was used a substrate with an electron-withdrawing substituent at orto-position (2-bromoanisole **10**), a substrate with an electron-donating group at para-position (4-bromotoluene **8**), and a substrate with an electron-donating group at para-position but with another halogen (4-chlorotoluene **12**).



Scheme 9. The Suzuki–Miyaura cross-coupling reactions

Entry	Halide	Catalyst	Yield (%) 1 hour	Yield (%) 2 hours	Yield (%) 24 hours
1	2-bromoanisole	Pd + Ln5	75.7	76.9	88.2
2	4-bromotoluene	Pd + Ln5	44.3	44.5	87.4
3	4-chlorotoluene	Pd + Ln5	0.0	0.0	0.0
4	2-bromoanisole	Ni + Ln4	0.0	3.5	41.0
5	4-bromotoluene	Ni + Ln4	0.0	0.0	30.7
6	4-chlorotoluene	Ni + Ln4	0.0	0.0	0.0
7	2-bromoanisole	Cu + Ln4	0.0	7.9	21.4
8	4-bromotoluene	Cu + Ln4	0.0	8.1	29.0

9	4-chlorotoluene	Cu + Ln4	0.0	0.0	0.0

Table 3. Result catalyst B

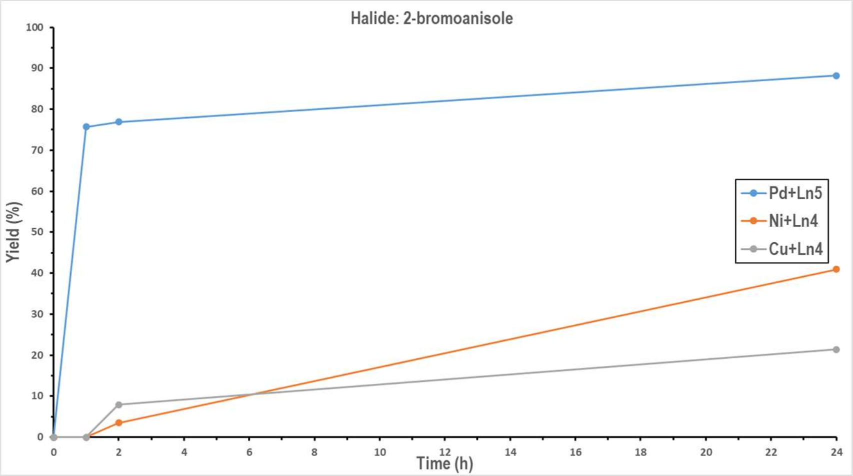


Figure 12. Graph of halide 2-bromoanisole

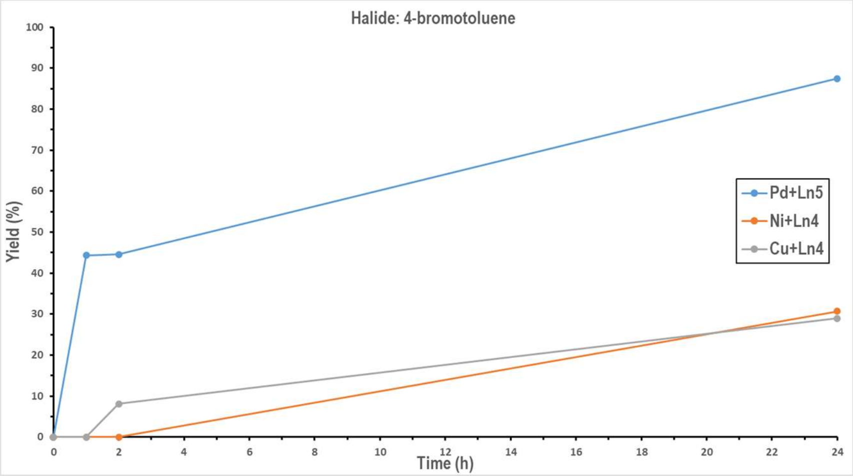


Figure 13. Graph of halide 4-bromotoluene

Of the 3 metals precursors studied, the palladium showed very good catalytic properties in NADES. The palladium metal with carbene **5** ligand showed great catalytic efficiency for 4-bromoanisole, 2-bromoanisole and 4-bromotoluene, especially for 4-bromoanisole (Table 2) where in this case showed conversions above 85% during the first hours of reaction. For 2-

bromoanisole and 4-bromotoluene (Table 3), although it showed a slower start of reaction than 4-bromoanisole, reached conversions close to 90% after 24 hours.

The entries 4 to 9 showed (Table 3) for the nickel and copper precursor with the amine ligand, conversions close to 30% after 24 hours with the same halides than palladium. As well as in the previous catalytic series (Table 2), the catalyst mixture of Ni or Cu with ligand, needed more time to be active than Pd catalyst. Also like palladium, nickel and copper obtained the best results with halide 4-bromoanisole. This result is very interesting because only few samples of the Suzuki–Miyaura cross-coupling reaction are described in the literature with Ni or Cu catalysts and always with organic solvents (Figure 4).

On the other hand, no one of the three metals precursors showed activity with 4-chlorotoluene, showing greatest difficulty in producing this cross-coupling reaction with a smaller halogen.

6. EXPERIMENTAL SECTION

6.1. MATERIALS AND METHODS

For word in inert conditions, it has been done working with $N_{2(g)}$ and $Ar_{(g)}$.

^1H NMR spectra was recorded at 293K on Varian Mercury 400 referenced to solvent peaks. The spectra were compared with the references [17][19][20].

Fourier Transform Infrared Spectroscopy (FTIR) were recorded on a Nicolet iS5 ID7-ATR Thermo Scientific spectrometer.

Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} plates and analyzed by UV.

High performance liquid chromatography (HPLC) was performed in Interchim puriFlash XS 420 using puriFlash silica IR-50SI-F0012 flash column and puriFlash dry load empty PF-DLE-F0004.

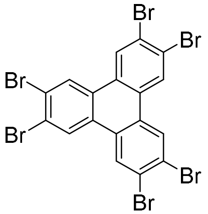
The catalysis has been done in Carousel 12 Plus Reaction Station at 80ºC and 400RPM.

The gas chromatography (GC) analysis was determined with an Agilent Technology 6890 instrument using helium as carried gas, with a flame ionization detector and HP-5 capillary column, $T_{injector}$ = 250ºC, $T_{detector}$ = 275ºC, T_{column} = 100ºC (2 min) and 100-250 ºC (10ºC min^{-1}).

The mass spectrometry (MS) analysis was performed in an Agilent Technologies 7820A instrument with a Agilent Technologies detector 5975.

6.2. SYNTHESIS OF 2,3,6,7,10,11-HEXABROMOTRIPHENYLENE

Fe powder (0.3774g) (previously attacked with HCl 1%) was added into mixture of triphenylene (4.0045g, 17mmol) and dissolved in nitrobenzene (160mL) at room temperature. Followed by dropwise addition of bromine (8mL, 150mmol) and stirred during 22h at room temperature. The next day, the reaction mixture was heated under reflux (205ºC) during 2h, and later diethyl ether was added (300mL), and the precipitate was filtered off. The light gray solid was washed with acetone and drying with help of vacuum line. Yield: 10.5842g (86%).



Light gray. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.71 (s, 6H, Ar-H). (Appendix 2, Figure H1)
FTIR-ATR: ν_{max} (cm^{-1}) = 2600, 2150, 2050, 1600, 1550, 1450, 1375, 1100, 975, 650. (Appendix 3, Figure I1)

6.3. AMINATION OF 2,3,6,7,10,11-HEXABROMOTRIPHENYLENE

6.3.1. Synthesis of 2,3,6,7,10,11-hexakis(isopropylamine)triphenylene

6.3.1.1 Method A

Catalyst Buchwald-Hartwig coupling was prepared mixing [Pd(OAc)$_2$] (0.024g, 0.1mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) (0.0917g, 0.2mmol) and NaO*t*Bu (0.0312g, 0.3mmol), dissolved in toluene (10mL) at room temperature during 10min. After this time, the resulting mixture was added into another flask containing **2** (1.0005g, 1mmol) and NaO*t*Bu (0.9911g, 10mmol) dissolved in toluene (20mL), over via dried cannula. The isopropylamine (0.88mL, 1mmol) was added, and the resulting dissolution was refluxed for 20h under inert conditions. The next day, the solution was filtered over Celite at room temperature and the dissolution was concentrated under reduced pressure.

Solid	Brown. FTIR-ATR: ν_{max} (cm^{-1}) = 3366, 2963, 2867, 1600, 1455, 1363, 1325, 1244, 1172, 1122, 805, 756.
Resin	Brown. FTIR-ATR: ν_{max} (cm^{-1}) = 3365, 2961, 2866, 1608, 1455, 1381, 1325, 1256, 1173, 1120, 1091, 800, 754.

6.3.1.2. Method B

Same procedure of *Method A*, but using 0.0129g [Pd(OAc)$_2$], 0.0461g 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) and 0.0162g NaO*t*Bu dissolved in toluene (10mL) for catalyst Buchwald-Hartwig. The reactive mixture was 0.5045g of **2** and 0.4960g of NaO*t*Bu, dissolved in 20mL of toluene, and using 0.44mL isopropylamine. The mixture was refluxed for 46h. The filtered solution was concentrated under reduced pressure using line of $N_{2(g)}$ at room temperature.

Solid	Brown. FTIR-ATR: ν_{max} (cm^{-1}) = 3500, 2957, 2935, 2873, 1583, 1500, 1399, 1363, 1226, 1117, 1042, 862, 878, 765.
Resin	Brown.

6.3.1.3. Method C

Same procedure of *Method B*, but catalyst Buchwald-Hartwig was stirred at 100ºC during 30min. The final mixture refluxed at 100ºC for 3 days.

Solid	Brown. FTIR-ATR: v_{max} (cm^{-1}) = 3405, 2029, 1625, 1425, 1405, 1363, 1334, 1116, 1031, 970, 861, 829, 768, 654.
Resin	Brown. FTIR-ATR: v_{max} (cm^{-1}) = 2957, 2935, 2873, 1583, 1500, 1399, 1363, 1226, 1117, 1042, 862, 878, 765.

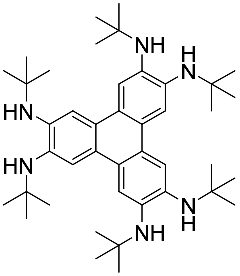
6.3.1.4. Method D

[Pd(OAc)$_2$] (0.0096g, 0.4mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) (0.0315g, 0.7mmol), and NaO*t*Bu (0.0111g, 0.1mmol) were dissolved in toluene (5mL) at room temperature. The solution was added over dried cannula in closed reactor (inert atmosphere with Argon gas) with **2** (0.2510g, 0.3mmol), and NaO*t*Bu (0.2580g, 20mmol), dissolved in toluene (10mL). Isopropylamine (0.8mL, 1mmol) was added, and the mixture was heating in furnace at 80ºC for 2 days. The solution was filtered and concentrated under reduced pressure. The resin was dissolved in DCM and three 3 times of its weight of celite added and concentrated under reduced pressure. The resulting solid was purified by HPLC with mixture cyclohexane and EtOAc (17:3). The resulting product showed photosensitivity.

Solid	Brown. FTIR-ATR: v_{max} (cm^{-1}) = 3432, 1637, 1584, 1550, 1467, 1363, 1281, 1116, 861, 700, 654.

6.3.2. Synthesis of 2,3,6,7,10,11-hexakis(tertbutylamine)triphenylene

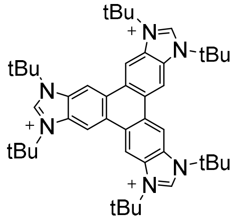
Catalyst Buchwald-Hartwig coupling was prepared mixing [Pd(OAc)$_2$] (0.0488g, 0.2mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl) (0.1823g, 0.4mmol) and NaO*t*Bu (0.0625g, 0.6mmol), dissolved in toluene (20mL), at room temperature during 10min. After this time, the resulting mixture was added into another flask containing **2** (2.0048g, 3mmol) and NaO*t*Bu (1.9871g, 20mmol), dissolved in toluene (40mL), over via dried cannula. The resulting mixture was added tert-butylamine (2.2mL, 10mmol) and it was refluxed for 22h under inert conditions. The cooled solution was filtered over celite, and then concentrated under reduced pressure, obtaining the dark red solid. Yield: 1.3026g (69%).



Dark red. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 7.71 (s, 6H, Ar-H), 3.52 (s, 6H, NH), 1.36 (s, 54H, $C(CH_3)_3$).(Appendix 2, Figure H2) FTIR-ATR: ν_{max} (cm^{-1}) = 3308, 2960, 2866, 1610, 1518, 1427, 1385, 1270, 1216, 1200, 1024, 870, 835, 694. (Appendix 3, Figure I2)

6.4. SYNTHESIS OF TRIPHENYLENE-BASED TRIS(AZOLIUM) SALT

A mixture of compound **4** (1.3026g, 2mmol), HBF_4 (0.91mL, 7mmol) and triethylorthoformate (60mL) was refluxed 21h under aerobic conditions. The cooled solution was added Et_2O (80mL), and the light tan solid was collected by filtration. For to purify the solid, it was dissolved in CH_3CN (60mL) and recrystallized with Et_2O. The light tan solid was obtained by filtration. Yield: 1.6863g (89%).



Light tan. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.20 (s, 6H, Ar-H), 9.17 (s, 3H, N-CH-N), 2.04 (s, 54H, C-$(CH_3)_3$).
(Appendix 2, Figure H3)
FTIR-ATR: ν_{max} (cm^{-1}) = 3206, 2990, 1632, 1547, 1471, 1398, 1378, 1308, 1201, 1010, 851, 810, 782, 598. (Appendix 3, Figure I3)

6.5. CATALYSIS: SUZUKI–MIYAURA CROSS-COUPLING REACTION

The samples were prepared mixing phenylboronic acid (0.18g, 1.5mmol) and 4-bromoanisole or 2-bromoanisole or 4-bromotoluene or 4-chlorotoluene (1mmol), K_3PO_4 (0.42g, 2mmol) and 1mol % catalyst, dissolved in ChCl:Gly (1:2) (4mL) and H_2O (Milli-Q) (1mL). The catalyst mixture was synthesized *in situ* with stoichiometric quantities of metal precursor complex ([Pd(cinnamyl)Cl]$_2$, $Ni(OAc)_2$ or $Cu(OAc)_2$) and ligand (**4**,**5** or **6**). The reaction was carried out at 80ºC and 400RPM in a Carousel 12 Plus Reaction Station under inert atmosphere. After 1,2 and 24h, aliquots of 0.5mL samples was taken off, and the separation of NADES and products was made adding 0.5mL pentane and 0.5mL water. The phases were separated with helped of centrifuge, and the organic phases were analyzed with GC-MS.

Reagent	Retention Time (minutes)
4-chlorotoluene (**12**)	2.3
1-bromo-4-methoxybenzene (**7**)	4.6
2-bromoanisole (**10**)	4.7
4-bromotoluene (**8**)	4.9
4-methyl-1,1'-biphenyl (**14**)	8.6
2-methoxy-1,1'-biphenyl (**13**)	9.5
4-methoxy-1,1'-biphenyl (**9**)	10.7

Table 4. Retentions times of GC

6.6. SYNTHESIS OF CHCL:GLY (MOLAR RATIO 1:2)

The NADES solvent was prepared mixing choline chloride (69.8g, 500mmol) and glycerine (92.1g, 1000mmol). The mixture was heated at 80ºC for 20min. The homogeneous liquid was cooled at room temperature.

7. CONCLUSIONS

The main objective of synthesizing of an N-heterocyclic carbene (NHC) ligands from the triphenylene compound as a precursor has been achieved using tert-butylamine as a reagent, but it was not possible with isopropylamine. All the synthesized compounds were characterized by ^{1}H-NMR and FTIR-ATR.

The amination of 2,3,6,7,10,11-hexabromotriphenylene **2** with isopropylamine was not possible due to its photosensitive proprieties.

The preparation of compound **4** from the amination of 2,3,6,7,10,11-hexabromotriphenylene **2** using tert-butylamine has been successfully completed with high yields.

The triphenylene-based tris(azolium) salt **5** was synthesized from compound **4** with high yield and characterized by ^{1}H-NMR and FTIR-ATR.

The study of the catalytic Suzuki–Miyaura cross-coupling reactions, with the ligands and precursors metals of palladium, nickel, and copper creating *in situ* the active species, using NADES solvents, give very good results with the palladium and the ligands **4** and **5,** especially in the reaction of phenylboronic acid **7** and 4-bromoanisole **8**. Instead, the nickel and copper precursors with the ligand **4** are less active during the first hours, needing more time to be active.

No one of the three metals studied showed Suzuki–Miyaura cross-coupling reaction between boronic acid **7** and 4-chlorotoluene **12**.

8. REFERENCES AND NOTES

1. Ibáñez, S.; Poyatos, M.; Peris, E. N-Heterocyclic Carbenes: A Door Open to Supramolecular Organometallic Chemistry. *Accounts of Chemical Research*, **2020**, 53(7), 1401–1413.
2. Bidal, Y. D.; Lesieur, M.; Melaimi, M.; Nahra, F.; Cordes, D. B.; Athukorala Arachchige, K. S.; Slawin, A. M. Z.; Bertrand, G.; Cazin, C. S. J. Copper(I) Complexes Bearing Carbenes beyond Classical N-Heterocyclic Carbenes: Synthesis and Catalytic Activity in "click Chemistry." *Advanced Synthesis and Catalysis*, **2015**, 357(14), 3155–3161.
3. Wang, Y. T.; Chang, M. T.; Lee, G. H.; Peng, S. M.; Chiu, C. W. Planar tris-N-heterocyclic carbenes. *Chemical Communications*, **2013**, 49(65), 7258–7260.
4. Gonell, S.; Poyatos, M.; Peris, E. Main-chain organometallic microporous polymers bearing triphenylene-tris(N- heterocyclic carbene)-gold species: Catalytic properties. *Chemistry-A European Journal*, **2014**, 20(19), 5746–5751.
5. Beletskaya, I. P.; Cheprakov, A. Copper in cross-coupling reactions: The post-Ullmann chemistry. *Coordination Chemistry Reviews*, **2004**, 248(21), 2337–2364.
6. Frey, G. D.; Herdtweck, E.; Herrmann, W. Structural investigations of metalcarbonyl complexes with acyclic diamino carbenes. *Journal of Organometallic Chemistry*, **2006**, 691(11), 2465–2478.
7. Roselló, M. Complejos de metales de transición conteniendo ligandos de tipo carbeno N-heterocíclico de 5 y 6 miembros. Síntesis y estudios de reactividad. *Tesis Doctoral*, **2013**, 21-27.
8. Dhakshinamoorthy, A.; Li, Z.; Garcia, H. Catalysis and photocatalysis by metal organic frameworks. *Chemical Society Reviews*, **2018**, 47(22), 8134-8172.
9. Poyatos, M.; Mata, J. A.; Peris, E. Complexes with poly(N-heterocyclic carbene) ligands: Structural features and catalytic applications. *American Chemical Society*, **2009**, 109(8), 3677–3707.
10. Zhang, H.; Wu, D.; Liu, S. H.; Yin, J. Star-Shaped Polycyclic Aromatic Hydrocarbons: Design and Synthesis of Molecules. *Current Organic Chemistry*, **2012**, 16, 2124-2158.
11. Bruice, P. Organic Chemistry, Global Edition [EBook]. *Pearson Education Limited*, **2016**, 8th, 552-556.
12. Noêl, T.; Buchwald, S. L. Cross-coupling in flow. *Chemical Society Reviews*, **2011**, 40(10), 5010-5029.
13. Santana, A. P. R.; Mora-Vargas, J. A.; Guimarães, T. G. S.; Amaral, C. D. B.; Oliveira, A.; Gonzalez, M. H. Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods. *Journal of Molecular Liquids*, **2019**, 293, 111452.
14. Liu, Y.; Friesen, J.; McAlpine, J. B.; Lankin, D. C.; Chen, S. N.; Pauli, G. F. Natural Deep Eutectic Solvents: Properties, Applications, and Perspectives. *American Chemical Society*, **2018**, 81(3), 679-690.
15. Ibáñez, S.; Poyatos, M.; Peris, E. A D 3h-symmetry hexaazatriphenylene-tris-N-heterocyclic carbene ligand and its coordination to iridium and gold: Preliminary catalytic studies. *Chemical Communications*, **2017**, 53(26), 3733–3736.
16. Goryunkov, A.; Asfandiarov, N.; Muftakhov, M.; Ioffe, I.; Solovyeva, V. A.; Lukonina, N. S.; Markov, V. Y.; Rakhmeyev, R. G.; Pshenichnyuk, S. Dissociative Electron Attachment to 2,3,6,7,10,11-Hexabromotriphenylene. *Journal of Physical Chemistry A*, **2020**, 124(4), 690–694.
17. Hirose, T.; Miyazaki, Y.; Watabe, M.; Akimoto, S.; Tachikawa, T.; Kodama, K.; Yasutake, M. Trialkylsilylethynyl-substituted triphenylenes and hexabenzocoronenes: Highly soluble liquid crystalline materials and their hole transport abilities. *Tetrahedron*, **2015**, 71(29), 4714–4721.

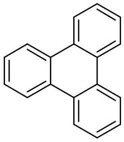
18. Gonell, S.; Poyatos, M.; Peris, E. Triphenylene-based tris(N-heterocyclic carbene) ligand: Unexpected catalytic benefits. *Angewandte Chemie - International Edition*, **2013**, 52(27), 7009–7013.
19. Binev, Y.; Marques, M. M.; Aires-de-Sousa, J. Tools for NMR spectroscopists. http://www.nmrdb.org/ (*31 May 2022*)
20. National Institute of Advanced Industrial Science and Technology. Spectral Database for Organic Compounds SDBS. https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi (*31 May 2022*)
21. Zhang, Q.; Oliveira, K.; Royer, S.; Jérôme, F. Deep eutectic solvents: Syntheses, properties and applications. *Chemical Society Reviews*, **2012**, 41(21), 7108–7146.
22. Heravi, M.; Kheilkordi, Z.; Zadsirjan, V.; Heydari, M.; Malmir, M. Buchwald-Hartwig reaction: An overview. *Journal of Organometallic Chemistry,* **2018,** 861, 17–104.

9. ACRONYMS

ATR	Attenuated Total Reflection
$CDCl_3$	Deuterated chloroform
ChCl:Gly	Choline Chloride : Glycerol
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography - Mass Spectrometry
HBTP	2,3,6,7,10,11-hexabromotriphenylene
HPLC	High Performance Liquid Chromatography
Ln	Ligand
MOF	Metal Organic Framework
NADES	Natural Deep Eutectic Solvents
NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance
*t*Bu	Tert-butyl
TLC	Thin Layer Chromatography
s	singlet
d	doublet
t	triplet
q	quartet
quint	quintet
sex	sextet
m	multiplet

APPENDICES

APPENDIX 1: LIST OF COMPOUNDS



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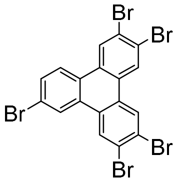

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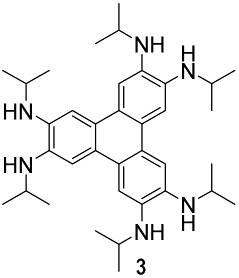

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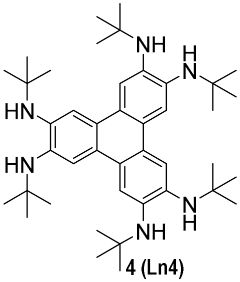
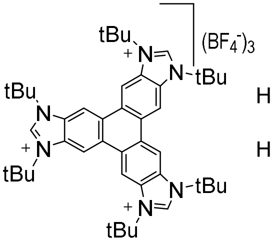
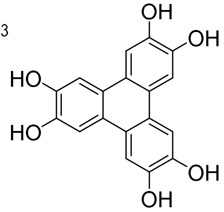


4 (Ln4)



5 (Ln5)



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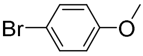

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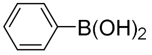

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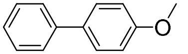

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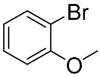

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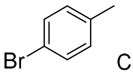

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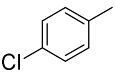

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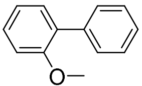

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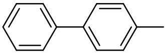

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APPENDIX 2: ^{1}H-NMR OF COMPOUNDS

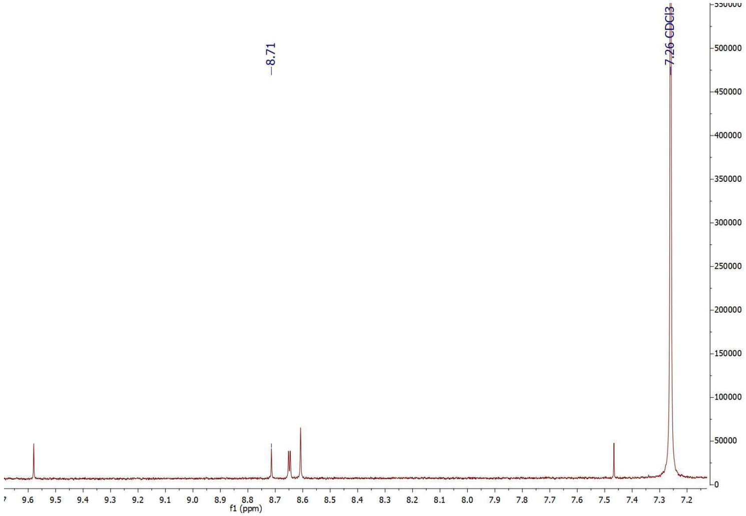

Figure H1. ^{1}H NMR of **2**

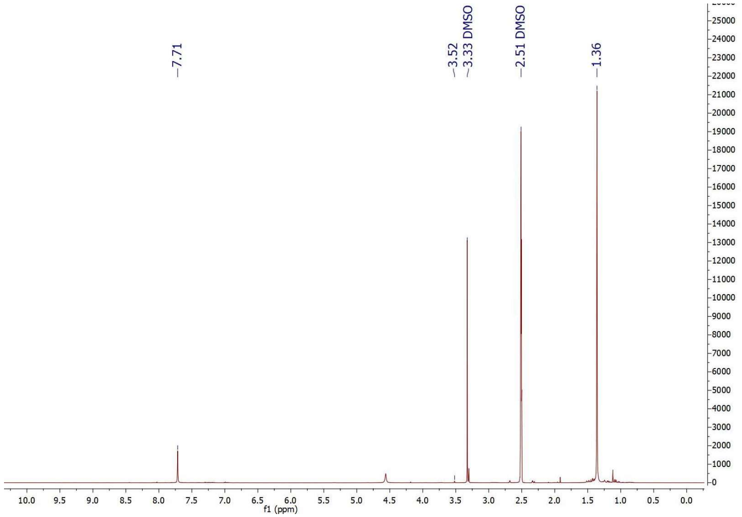

Figure H2. ^{1}H NMR of **4 (Ln4)**

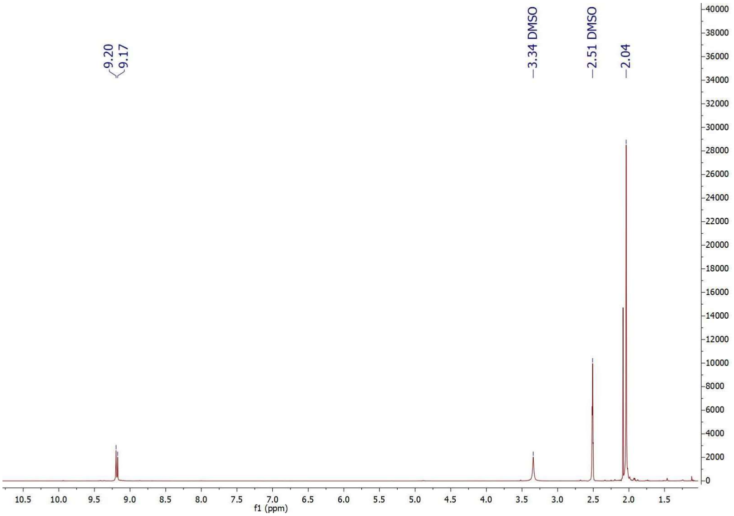

Figure H3. ^{1}H NMR of **5 (Ln5)**

APPENDIX 3: FTIR-ATR OF COMPOUNDS

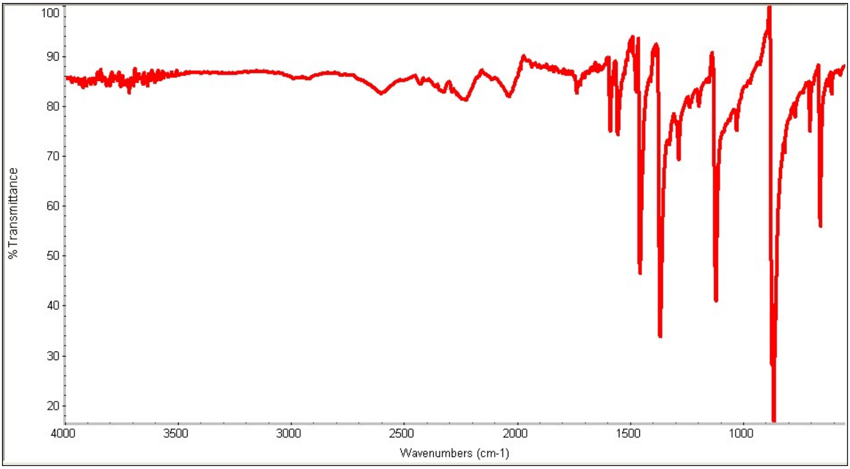

Figure I1. FTIR-ATR of **2**

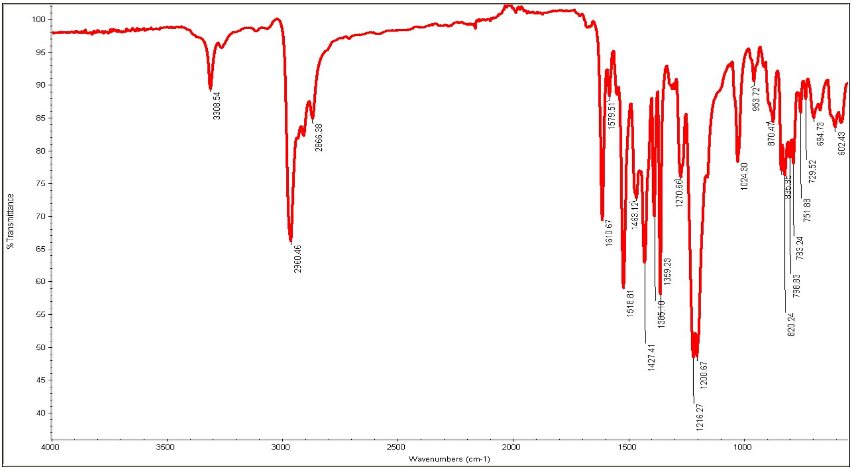

Figure I2. FTIR-ATR of **4 (Ln4)**

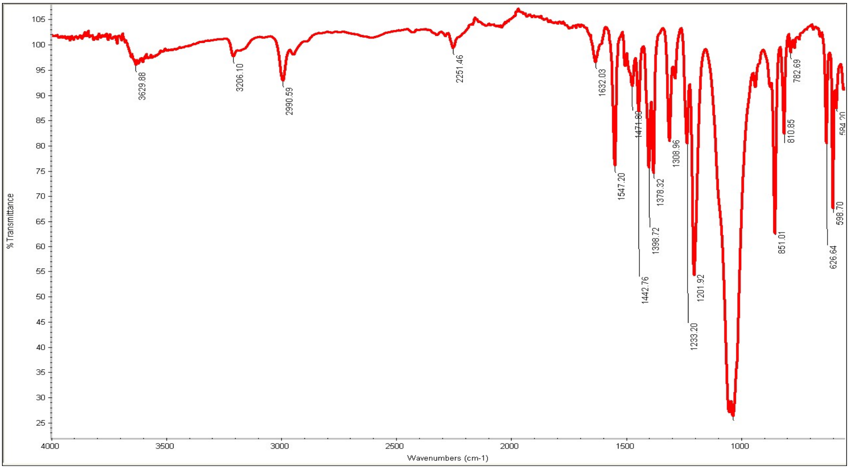

Figure I3. FTIR-ATR of **5 (Ln5)**