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CHEMISTRY DEPARTMENT

DIOGO MANUEL DA CONCEIÇÃO COSTA

BSc in Applied Chemistry

HETEROLEPTIC COPPER(I) COMPLEXES BASED ON NHC CARBENES AS CATALYSTS FOR THE SYNTHESIS OF IMINES AND PROPARGYLAMINE DERIVATIVES

MASTER IN BIOORGANIC CHEMISTRY

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DEPARTAMENTO DE QUÍMICA

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Orientador: Vitor Rosa, Researcher,
NOVA School of Science and Technology

Co-orientadores: Clara Gomes, Auxiliary Researcher,
NOVA School of Science and Technology

Júri:

Presidente: Luísa Ferreira, Assistant Professor with Habilitation,
NOVA University Lisbon

Arguentes: Maria Manuel Marques, Assistant Professor with Habilitation,
NOVA University Lisbon

MASTER IN BIOORGANIC CHEMISTRY

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Heteroleptic Copper(I) Complexes Based on NHC Carbenes as Catalysts for the Synthesis of Imines and Propargylamine Derivatives

I just want to shine to the world, have the sky as the limit, sing with all the stars and dance with them one by one.
Mário Cotrim

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Finally, I want to thank to everybody that passed through our laboratory during this last year, because I also learned things with them and I hope I was also able to pass a little bit of my knowledge to them.

ABSTRACT

Throughout the last decades, researchers have been working on new methodologies to develop more sustainable processes to produce relevant chemical compounds. One of the main focuses of these research were on catalytic systems, that can be improved by: reducing the amount of catalyst used, a lesser quantity of solvent, decreasing the reaction's temperature, and avoiding harsh conditions or toxic reagents.

Therefore, in this work several copper(I) complexes were synthesized, and their catalytic activity was tested on two main reactions: (1) imine formation via direct aerobic oxidation of an alcohol and an amine and (2) coupling of an aldehyde, an amine and an alkyne for the synthesis of propargylamines, that are precursors for a wide variety of biologically active compounds, highly relevant in pharmaceutic and medicinal chemistry. Since the product of the first reaction, an imine, is the intermediate of the second one, a parallel between both reactions can be established, allowing to compare a complex's catalytic activity in both reactions.

Among the complexes synthesized, the highlight goes to heteroleptic copper(I) complexes, where the copper centre is coordinated by a bis(imino)acenaphthene (BIAN) ligand and a N-heterocyclic carbene, with or without the acenaphthene backbone. The NHCs have been employed as ligands with great success over the last years, due to their unique behaviour when bonding with transition metals, as well as BIANs, thanks to the properties that their structure grants them. The choice on copper relies on its low toxicity and cost, in addition to its chemical properties.

All the compounds, complexes and their precursors synthesized in this work were characterized by ^{1}H NMR. The ones that were not reported in literature were additionally characterized by ^{13}C NMR, IR, EA and X-ray diffraction crystallography, when suitable single crystals were obtained.

Keywords: Copper(I), BIAN, NHC, Heteroleptic complexes, Imines, Propargylamines

RESUMO

Ao longo das últimas décadas, investigadores têm trabalhado em novas metodologias para desenvolver processos mais sustentáveis para produzir compostos químicos relevantes. Um dos principais focos desta investigação foram os sistemas catalíticos, que podem ser melhorados através de: redução da quantidade de catalisador utilizado, menor quantidade de solvente, diminuição da temperatura da reação, e evitando condições adversas ou reagentes tóxicos.

Assim, neste trabalho foram sintetizados vários complexos de cobre(I) e testada a sua atividade catalítica em duas reações principais: (1) formação de iminas a partir de um álcool e uma amina por reação de oxidação aeróbia direta e (2) acoplamento de um aldeído, uma amina e um alcino para a síntese de propargilaminas, que são precursores de uma grande variedade de compostos biologicamente ativos, de grande relevância na química farmacêutica e medicinal. Uma vez que o produto da primeira reação, uma imina, é o intermediário da segunda, é possível estabelecer um paralelo entre ambas as reações, permitindo comparar a atividade catalítica de um complexo em ambas as reações.

Entre os complexos sintetizados, destacam-se os complexos de cobre(I) heterolépticos, onde o centro de cobre é coordenado por um ligando bis(imino)acenafteno (BIAN) e um carbeno N-heterocíclico, com ou sem acenafteno. Os NHCs têm sido utilizados como ligandos com grande sucesso nos últimos anos, devido ao seu comportamento único na ligação com metais de transição, bem como os BIANs, graças às propriedades que a sua estrutura lhes confere. A escolha do cobre deve-se à sua baixa toxicidade e custo, para além das suas propriedades químicas.

Todos os compostos, complexos e seus precursores sintetizados neste trabalho foram caracterizados por ^{1}H RMN. Os que não foram relatados na literatura foram adicionalmente caracterizados por ^{13}C RMN, IV, AE e cristalografia de raios-X, quando cristais únicos adequados foram obtidos.

Palavras-chave: Cobre (I), BIAN, NHC, Complexos heterolépticos, Iminas, Propargilaminas

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SYMBOLS AND ABREVIATIONS

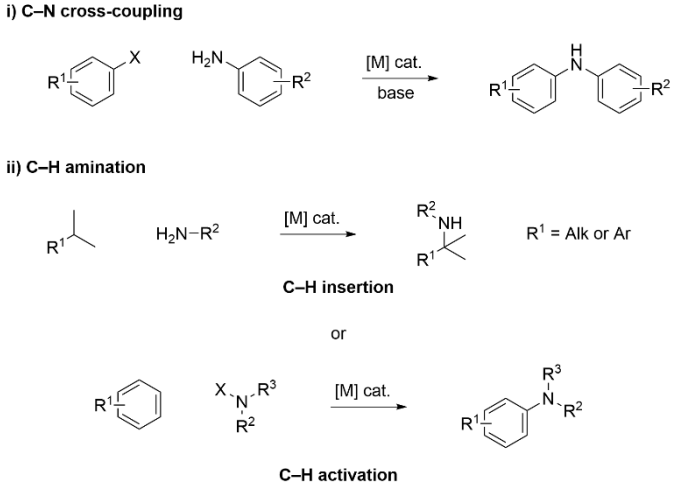
Å	Angstrom
A^3	Aldehyde-Amine-Alkyne
ABNO	9-Azabicyclo[3.3.1]nonane *N*-oxyl
Alk	Alkyl
Ar	Aromatic
BIAN	Bis(imino)acenaphthene
br s	Broad singlet
BTMAH	Benzyltrimethylammonium hydroxide
Bu	Buthyl
COSY	Correlation Spectroscopy
d	Duplet
DCM	Dichloromethane
dd	Doublet of duplets
Dip	Diisopropyl
DMAP	4-Dimethylaminopyridine
DMSO	Dimethyl sulfoxide
eq.	Equivalents
g	Grams
h	Hour(s)
hept	Heptet
HMBC	Heteronuclear Multiple Bond Correlation
HSQC	Heteronuclear Single Quantum Coherence
Hz	Hertz
IR ATR	Infrared Attenuated Total Reflectance
J	Coupling Constant
K	Kelvin
m	Multiplet
MAO-B	Monoamine oxidase B
Me	Methyl
Mes	Mesityl
MHz	Megahertz
mL	Millilitre
mM	Millimolar
mm	Millimole
mmol	Millimole

NHC	N-Heterocyclic Carbene
NMR	Nuclear Magnetic Resonance
NOESY	Nuclear Overhauser Effect Spectroscopy
º	Degree
ºC	Celsius degrees
Tf	Triflyl
Ph	Phenyl
ppm	Parts per million
Pr	Propyl
r.t.	Room temperature
s	Singlet
t	Triplet
T	Temperature
TBA	Tetrabutylammonium
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
THF	Tetrahydrofuran
Δ	Reflux
δ	Chemical shift
λ	Wavelength
υ	Wavenumber

1. INTRODUCTION

In chemistry, organic molecules are seen as carbon-based skeletons with functional groups formed by heteroatoms. One of the most common heteroatoms that allows the existence of countless organic compounds and its derivatives like amines, imines, enamines, amides, azides, N-heterocycles, among many others is nitrogen. These compounds have an enormous importance in medicinal and pharmaceutical chemistry due to their biologic activity, since nitrogen is a versatile atom, having a lone pair with a basic character, the capacity to carry a positive charge and the ability to donate a hydrogen bond in the case of the NH group.[1]

Generally, carbon-nitrogen bonds are covalent bonds stronger than carbon-carbon ones,[2] and just like them, they can be simple, double, or triple. C–N bond formation has been one of the most studied research subjects due to its relevance and there are two main methods to synthesize nitrogen-containing compounds: C–N cross-coupling reactions (**Scheme 1**, **i**), that consists of the reaction of an amine with aryl halides, and C–H amination (**Scheme 1**, **ii**), which can be via C–H insertion for sp^3 carbons or via C–H activation for sp^2 carbons (and also sp^3).[3] Generally, these reactions are carried out in the presence of a metal catalyst, since metal-free methodologies usually required several steps and harsh conditions, even though, with the recent advances, more sustainable procedures have been developed.



Scheme 1 - C-N bond formation methods.

This dissertation was essentially focused on the synthesis of a family of copper (I) complexes to be tested as catalysts for the synthesis of imines and propargylamines, due to their relevance. In the next chapters, some background on these two compounds, on copper complexes and ligands is given in order to offer some historical and theoretical context, and then the synthesis, characterization and application of the complexes formed is presented.

1.1. Imines

Imines are compounds that contain in their structure (RN=CR'R'') a double bond between a carbon atom and a nitrogen atom and are therefore considered analogues of aldehydes and ketones. Imines can be: aldimines (**Figure 1**, **a**), if one of the substituents attached to the carbon atom is hydrogen, ketoimines (**Figure 1**, **b**), if both groups attached to that carbon are other than hydrogen, and Schiff bases (**Figure 1**, **c**), if the substituent group attached to the nitrogen atom is not hydrogen.

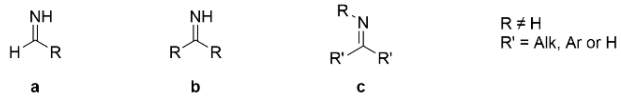


Figure 1 - Types of imines.

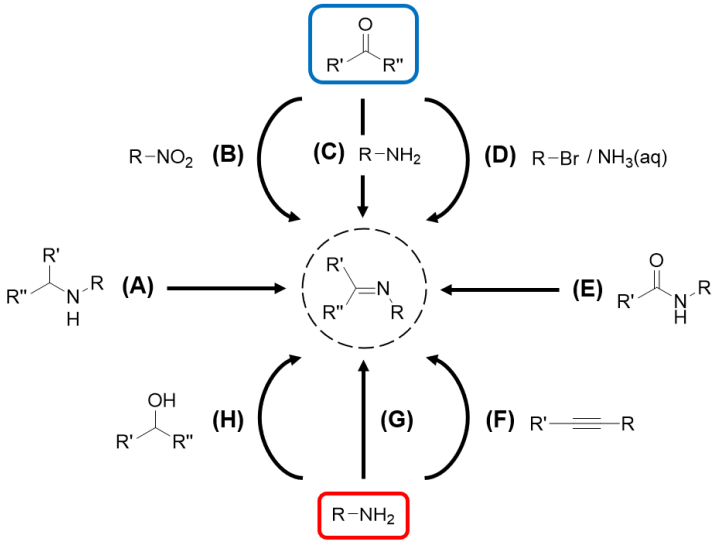
1.1.1. Synthesis

Among the several existing methods for the synthesis of imines, the most common are shown in **Scheme 2**.

One of the methods is the dehydrogenation of secondary amines (**A**), which consists on the removal of the hydrogen attached to the nitrogen of the amine with the formation of a C=N double bond, using hypervalent iodine reagents,[4] through a Swern-type[5] oxidation or via a metal-oxidizing catalytic system, for example rhodium and t-BuOOH.[6] The major negative aspect of this method is the lack of mild reaction conditions, and when they do apply, the variety of possible substrates to be used is limited.

Another method is by coupling compounds with nitro groups to aldehydes or ketones (**B**), using heterogeneous catalysts, in which hydrogen is formed *in situ*, reducing the nitro group to an amine, followed by its condensation with the carbonyl group to form an imine.[7] The main disadvantages are the formation of secondary products in significant quantities and the high cost of the catalytic system.

The traditional and most common method for synthesizing imines is the direct condensation of aldehydes or ketones with amines (**C**), which consists of the nucleophilic attack of the amine on the carbonyl, with the formation of the hemiaminal, which is converted into the imine with the elimination of one water molecule. These two steps are usually catalysed by a metallic catalytic system (copper,[8] magnesium,[9] among others), which acts as a Lewis acid to facilitate nucleophilic attack and to irreversibly bind to water, causing its removal. Although it is probably the most widely used method, the need of harsh conditions for the reaction to take place, such as high temperatures, do not make it the most desirable method.



Scheme 2 - Methods for the synthesis of imines.

A less conventional method for the synthesis of imines is through the addition of ammonia in aqueous solution and alkyl bromides to aldehydes[10] (**D**) which, despite showing excellent yields, is quite limited in terms of the diversity of substrates that can be used.

Another less-used method is the chemoselective reduction of secondary amides (**E**) using triflate anhydride and a reducing agent such as triethylsilane.[11] Again, the major disadvantage of this method is the limitation in terms of substrates.

The hydroamination of alkynes (**F**) is another way of synthesizing imines, a reaction that follows Markovnikov's rule, in which an amine is added to an alkyne in the presence of a homogeneous (Au,[12] Pd,[13] Rh,[14] Ti,[15] etc.) or heterogeneous (Zn,[16] among others) metal catalyst, and a majority of Markovnikov or anti-Markovnikov's product can be formed. This method turns out not to be the most suitable for the synthesis of imines, since unwanted isomers are often formed, in addition to the unfavourable reaction conditions.

It is also possible to form imines from the oxidative coupling reaction of amines (**G**), using metallic catalytic systems (copper,[17] vanadium,[18] manganese,[19] among others), organocatalysts[20] or even by photocatalysis.[21] Almost all the protocols that apply, this method use oxidants or even oxygen itself, which makes this type of reaction unsafe.

Finally, the method used in this thesis for the investigation of the catalytic activity of some families of copper catalysts in the synthesis of imines is the direct aerobic oxidation of alcohols and amines (**H**).

1.1.2. Oxidative Coupling of Alcohols with Amines

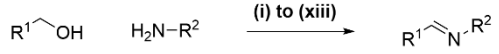
During the last years, efforts have been made in the development of a method to synthesize imines from alcohols and amines. Since alcohols are a desirable starting material, because of their availability and price, the goal is to turn this methodology as *green* as possible, avoiding the use of high temperatures and other harsh reaction conditions. As an addition, the only byproduct of this reaction is water.

This reaction usually requires an oxygen source and a catalyst, metallic or not, to occur and so several catalytic systems have already been tested. Iron catalysts are a good choice due to their low-cost and low toxicity. Zhang *et al* developed a $Fe(NO_3)_3$/(2,2,6,6-

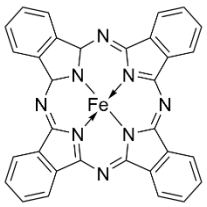
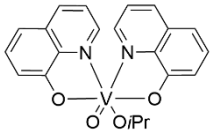
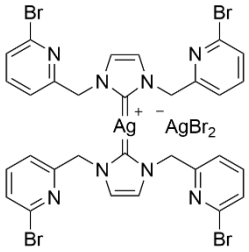
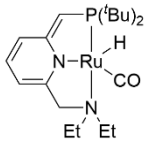
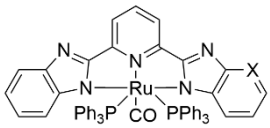
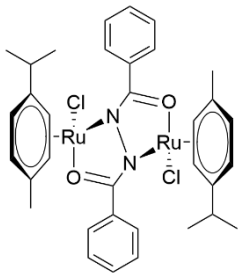
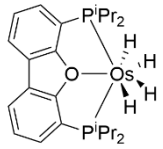
tetramethylpiperidin-1-yl)oxyl system for the aerobic synthesis of imines from anilines and substituted benzyl alcohols in toluene at 80 ºC in the presence of a base, potassium hydroxide (KOH), with moderate to excellent yields.[22] They found electron-rich anilines to be better substrates comparing to electron-deficient ones. Good results with similar reaction conditions were also achieved by Bala *et al*, using an iron phthalocyanine catalyst, that doesn't need a co-catalyst, and sodium *tert*-butoxide (NaO*t*Bu) as a base, under a nitrogen atmosphere.[23] A vanadium(V) catalyst successfully employed by Wang *et al* through identical conditions, using dichloroethane as solvent.[24] Jiang *et al* studied the activity of a $Pd(OAc)_2$ catalyst by coupling substituted benzyl alcohols with primary aliphatic and aromatic amines at room temperature.[25] Despite not needing heating, which is an improvement, this method has the downside of a long reaction time. Another protocol, where heating was not necessary, was the one developed by Han *et al*, using a silver(I) *N*,*N*'-pyridyl NHC catalyst and benzyltrimethylammonium (BTMAH) as a base in toluene, in which very good to excellent yields were obtained from benzyl alcohols with primary aromatic and aliphatic amines.[26] Rigoli *et al* reported a procedure for the synthesis of imines from aromatic alcohols with aromatic and aliphatic amines using a PNN pincer ruthenium catalyst in toluene under reflux with good results.[27] Another catalyst from the same family was designed Sindhuja *et al*, who managed to decrease the temperature required for this reaction to achieve high yields from 110 ºC to 70 ºC.[28] The reaction is actually possible at room temperature, with good to excellent yields, using a diruthenium(II) catalyst and potassium *tert*-butoxide (*t*BuOK) as a base in tetrahydrofuran (THF), as reported by Saranya *et al*.[29] As an alternative to ruthenium, Esteruelas *et al* reported the synthesis of imines from aromatic and aliphatic alcohols and amines with moderate to excellent yields, using a POP-type osmium pincer complex and KOH as a base in toluene under reflux.[30] With copper being one of the cheapest and most available alternatives, this metal has also been explored in order to catalyse this reaction. Kang *et al* reported the synthesis of imines from benzyl alcohol with aromatic and aliphatic amines using a $Cu(ClO_4)_2$ catalyst using KOH as a base at 70 ºC in toluene, under an oxygen atmosphere, with moderate to excellent yields.[31] This reaction was also studied at room temperature using a catalytic system of copper(I) iodide, 2,2'-bipyridine and TEMPO in acetonitrile, achieving excellent results.[32]

A few metal-free methods to imine formation via aerobic oxidation of alcohols and amines have also been developed. Wan *et al* reported a procedure starting from aromatic alcohols and anilines in toluene at 80 ºC, using ABNO-KOH as the catalytic system, obtaining excellent yields.[33] A solvent-free protocol was reported by Donthiri *et al*, catalysed by sodium hydroxide (NaOH) at 100 ºC with very good to excellent yields. [34]

Table 1 - Procedures for the synthesis of imines via oxidative coupling of alcohols with amines.



Procedure	Catalyst	Conditions	Reference
(i)	10 mol% $Fe(NO_3)_3$	TEMPO, KOH Toluene, air 80 ºC, 24 h	22

(ii)	1 mol% 	NaO*t*Bu Toluene, N_2 80 °C, 12 h	23
(iii)	5 mol% 	DCE, air 80 °C, 18 h	24
(iv)	1 mol% $Pd(OAc)_2$	neat, air 25 °C, 3 d	25
(v)	0.1 mol% 	BTMAH Toluene, air 25 °C, 12 h	26
(vi)	1 mol% 	Toluene, N_2 111 °C, 24 h	27
(vii)	1 mol% 	Toluene, air 70 °C, 12 h	28
(viii)	1 mol% 	*t*BuOK THF, air 25 °C, 24 h	29
(ix)	2 mol% 	KOH Toluene, Ar 150 °C, 24 h	30
(x)	5 mol% $Cu(ClO_4)_2.6H_2O$	KOH Toluene, O_2 70 °C, 19 h	31

(xi)	1:1 mol% CuI:bpy	TEMPO CH_3CN, air 25 ºC, 12 h	32
(xii)	3 mol% ABNO	KOH Toluene, air 80 ºC, 8 h	33
(xiii)	-	NaOH neat, air 100 ºC, 20 h	34

1.1.3. Applications

Imines can act as electrophiles in reductions, condensations, additions and cycloadditions and are very versatile intermediates in the formation of N-heterocyclic compounds, which are very important, especially in the pharmaceutical industry, because they can have biological activity. In addition, the nitrogen atom of imines can easily coordinate with various metals, due to their non-bonding electron pair, and they can be used as ligands in homogeneous catalysis.[35]

1.2. Propargylamines

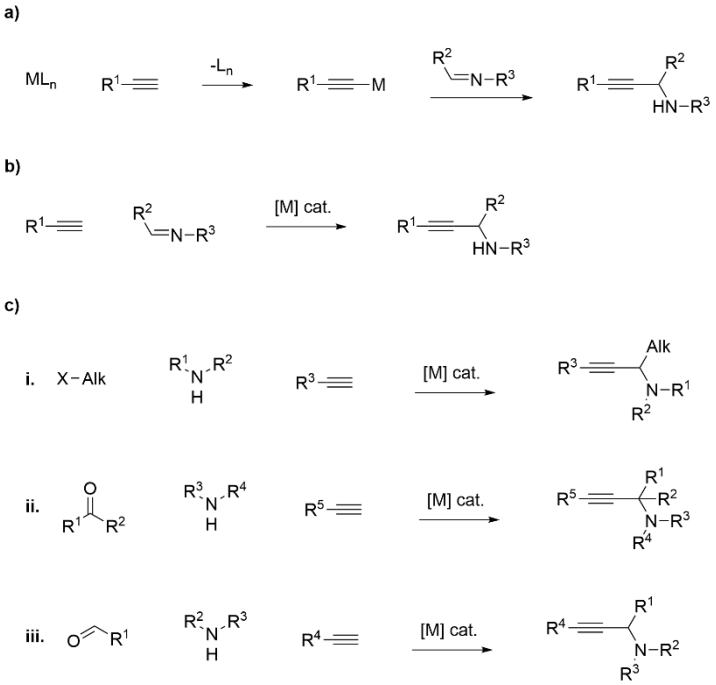
Propargylamines are an important family of compounds with varied applications. They are precursors to a wide range of molecules, that being the reason for the importance to develop efficient and sustainable ways of synthesizing them. The unique structure of these compounds makes them one of the most versatile classes of organic compounds, susceptible to a wide variety of chemical transformations, as they comprise an amine group, that can undergo nucleophilic reactions, and an alkyne moiety, that can behave either as an electrophilic or nucleophilic group.[36] The various compounds in this category differ in the latter functional group and in the substituents on the respective amine and propargyl groups.

1.2.1. Synthesis

There are a couple of ways to synthesize propargylamines, starting by the addition of a metal acetylide to an imine (**Scheme 3**, **a**), which is an unattractive process since it requires the use of stoichiometric amounts of the organometallic reagent, which, in addition, can be toxic. Another method is the reaction of a terminal alkyne with an imine (**Scheme 3**, **b**), using a metal catalyst (Zn,[37] Cu,[38] Ag,[39] among others). The most common approach to the synthesis of propargylamines is the three-component coupling of amines, alkynes, and alkyl halides (**Scheme 3**, **c**, **i**), ketones (**Scheme 3**, **c**, **ii**) or aldehydes (**Scheme 3**, **c**, **iii**). This past method is called A^3 coupling, and it is the one used in this work to test the catalytic activity of some families of copper catalysts in the synthesis of propargylamines.

1.2.2. A^3 Coupling

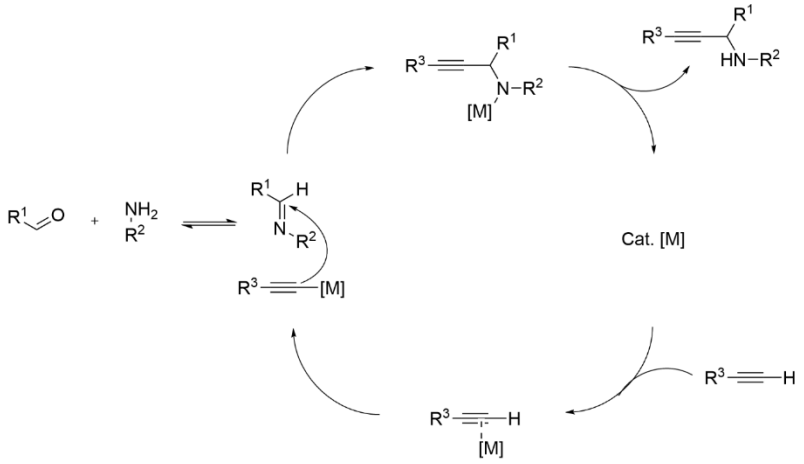
The coupling of aldehydes, amines and alkynes is the most attractive method to synthesize propargylamines, due to the simplicity and availability of these substrates, and because this reaction has a high atom economy, moreover it is environmentally friendly.[40] Neverthe-



Scheme 3 - Methods for the synthesis of propargylamines.

less, researchers keep developing more sustainable procedures, by designing catalysts that allow the decrease of the reaction's temperature and the use of greener solvents and milder reaction conditions.

The mechanism of this reaction is slightly different, depending on the catalyst used. Generally, using a metal catalyst, it relies on the cleavage of the C-H bond of the alkyne by the metal complex, forming the metal acetylide intermediate, which reacts with the imine originated in situ by the aldehyde and amine, resulting in the desired propargylamine (**Scheme 4**).

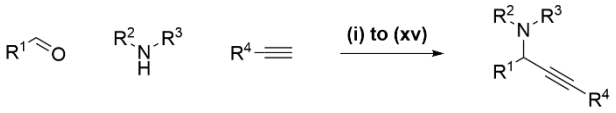


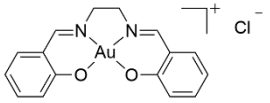
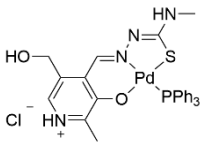
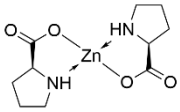
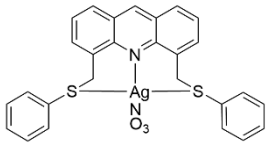
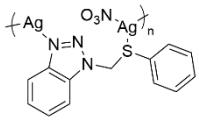
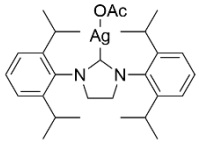
Scheme 4 - Mechanism for the metal-catalysed synthesis of propargylamines via A^3 coupling.

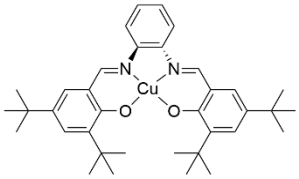
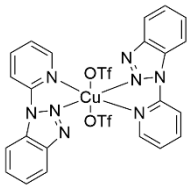
The majority of propargylamine synthesis procedures via A^3 coupling starts from secondary amines, since the iminium intermediate formed in the reaction's first step is more stable than the one formed with primary amines. Usually, the reaction requires a metallic catalytic system, and several metals were already studied in this reaction. Wei *et al* reported a procedure using $AuBr_3$ in water at 100 ºC from various aldehydes, secondary amines and a short scope of alkynes, achieving mostly excellent yields.[41] A gold(III) salen complex also in water showed very good results as well, starting from hexanal or benzaldehyde, pyrrolidines and phenylacetylene at 40 ºC under nitrogen atmosphere, as reported by Lo *et al*.[42] A procedure using $NiCl_2$ in toluene at 111 ºC under argon atmosphere reported by Samai *et al* showed moderate to excellent results starting from a wide range of aldehydes, primary and secondary amines and some alkynes.[43] A palladium(II) complex was successfully applied to this reaction, by coupling phenylacetylene, some secondary amines and aromatic aldehydes in a ionic liquid at 80ºC, as reported by Manikandan *et al*.[44]. Since most of amines and alkynes, two of the three substrates, are liquid at room temperature, there are some solvent-free A^3 coupling procedures in the literature, like the one reported by Afraj *et al*, where the reaction between several aldehydes, some secondary amines and a short range of alkynes at 90 ºC is catalysed by $MnCl_2$.[45] Similar procedures without the use of a solvent, using $Zn(OTf)_2$[46] and [$Zn(L\text{-}proline)_2$],[47] were also reported with good to excellent yields. Meanwhile, silver and copper catalysts seem to be the go-to, since, in general, those are the metals that allow these kinds of reactions to take place under lower temperatures than the other metals. Prakash *et al* synthesized two silver pincer catalysts that showed good to excellent yields on coupling phenylacetylene, piperidine or pyrrolidine and a variety of aromatic aldehydes at 60 ºC in dichloromethane under nitrogen atmosphere.[48] Using the same substrates and at the same temperature, Sharma *et al* developed another two polymeric silver complexes with equally successful results.[49] One of the few A^3 coupling reactions at room temperature was reported by Chen *et al*, using a NHC-AgCl complex, starting from secondary amines, aliphatic and aromatic aldehydes and some alkynes in methanol.[50] A procedure using a ionic liquid and CuI as the catalyst at 50 ºC starting from pyrrolidine, a panoply of aromatic aldehydes and some alkynes was reported by Zhu *et al* with great results.[51] Sampani *et al* designed a copper(II) salen complex managing to successfully synthesize propargylamines from various secondary amines, aliphatic and aromatic aldehydes and some alkynes at room temperature in dichloromethane by two different methods, one using microwave irradiation and the other without it.[52] Later, the same group of investigators built another copper(II) catalyst that under the same conditions was able to catalyse the reaction between the same aldehydes, alkynes and primary amines, something that is extremely difficult and rare, for the reason already mentioned above.[53]

Some metal-free procedures have already been developed too, for example, Singh *et al* reported an A^3 coupling method where the catalyst is tetrabutylammonium idodide (TBAI) using secondary amines, aromatic aldehydes and alkynes as substrates in acetonitrile at 75 ºC with good to excellent yields.[54] A base-catalysed procedure using tetrabutylammonium hydroxide (TBAOH) was also reported by Patil *et al*, starting from phenylacetylene, aromatic aldehydes and secondary amines in dimethyl sulfoxide (DMSO) at room temperature.[55]

Table 2 - Procedures for the synthesis of propargylamines via A^3 coupling.



Procedure	Catalyst	Conditions	Reference
(i)	1 mol% $AuBr_3$	H_2O, N_2 100 °C, 12 h	41
(ii)	1 mol% 	H_2O, N_2 40 °C, 24 h	42
(iii)	5 mol% $NiCl_2$	Toluene, Ar 111 °C, 8 h	43
(iv)	1 mol% 	[emim]BF_4 80 °C, 8 h	44
(v)	10 mol% $MnCl_2$	neat 90 °C, 12 h	45
(vi)	5 mol% $Zn(OTf)_2$	neat 100 °C, 12 h	46
(vii)	1 mol% 	neat 80 °C, 6 h	47
(viii)	0.5 mol% 	DCM, N_2 60 °C, 5 h	48
(ix)	2 mol% 	DMSO 60 °C, 6 h	49
(x)	1 mol% 	MeOH 25 °C, 20 min	50
(xi)	2.5 mol% CuI	[MEA][H_2PO_4] 50 °C, 1 h	51

(xii)	2 mol% 	DCM 25 ºC, 72 h	52
(xiii)	1.5 mol% 	DCM 25 ºC, 24 h	53
(xiv)	10 mol% TBAI	CH_3CN 75 ºC, 6 h	54
(xv)	10 mol% TBAOH	DMSO 25 ºC, 30 min	55

1.2.3. Applications

Propargylamines are relevant compounds, especially in the pharmaceutical industry, due to the fact that they have a nucleophilic amine and an alkyne in their scaffold, which makes them precursors to a huge variety of natural biological products, namely heterocycles and alkaloids that inhibit MAO-B, the enzyme responsible for the oxidative degradation of dopamine, a reaction that contributes to the development of neurodegenerative diseases such as Parkinson's, Alzheimer's and Huntington's diseases.[56]

A wide range of heterocycles can be synthesized from propargylamines using catalytic systems with or without metal. Among these heterocycles are quinolines (**Figure 2**, **A**), used mainly to treat malaria,[57] which are formed through an oxidation step after the propargylamine cyclization process, using copper, silver, iron, ytterbium, yttrium, zinc, niobium and molecular iodine catalytic systems.[58] Aminoindolizino[8,7-*b*]indoles (**Figure 2**, **B**), precursors of some compounds with sedative and antinociceptive properties,[59] can be synthesized from N-substituted 1-formyl-9H-β-carbolines, secondary amines and substituted alkynes, in toluene at 90 ºC, using a copper catalyst.[60] With the same substrates, but with a methoxy group on the benzyl ring of the formylcarboline, in the presence of $MeSO_3H$ and under an inert atmosphere, it is possible to form polycyclic β-carbolines (**Figure 2**, **C**), which have anticancer and antiparasitic properties.[61] From *o*-phenylenediamines, ethylglyoxalates and terminal alkynes, using a copper catalyst without ligands, furoquinoxalines (**Figure 2**, **D**) can be synthesized,[62] compounds with important luminescent properties.[63] Several imidazole-benzothiazoles (**Scheme 5**, **E**), which have anthelmintic properties and are used in parasiticides, can be synthesized from benzaldehyde, aminothiazoles and alkynes in the presence of a Cu(I) or Cu(II) catalyst.[64] Using a gold catalyst and amides instead of amines, oxazoles (**Figure 2**, **F**) are obtained, compounds that have antibacterial, anti-inflammatory, antidepressive, anticancer, antimicrobial, antidiabetic, antioxidant and analgesic properties.[65] By forming an azide followed by cyclization of the propargylamine formed from γ-chloro amines, using CuBr as the catalyst, it is possible to synthesize diazepine derivatives (**Figure 2**, **G**), commonly used in the treatment of anxiety and epilepsy.[66] Propargylamines treated with isocyanides, in the

presence of AgOTf or acetic acid in acetonitrile, form imidazole salts (**Figure 2**, **H**), which are used as ligands in palladium complexes for Suzuki reactions[67] and have antiparasitic properties against sleeping sickness and Chagas' disease.[68]

The alkaloids, obtained from hydroxypropargylamines, are synthesized by N-debenzylation and reduction of the triple bond, followed by cyclization. These five and six membered cyclic alkaloids (**Figure 2**, **I**) are used in the food industry and have shown relevant biological activity against Alzheimer's disease.[69]

Non-heterocyclic compounds can also be synthesized from propargylamines, such as chalcones (**Figure 2**, **J**), compounds that have shown interesting properties such as anticancer, anthelmintic, antibacterial, anti-allergic, anti-inflammatory, anti-malarial, antiviral, antifungal, germicidal, herbicidal and insecticidal capabilities.[70]

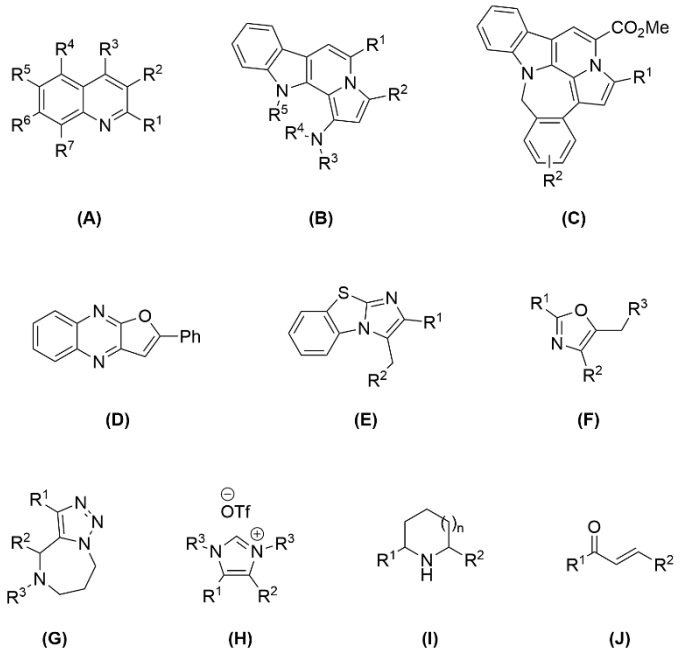


Figure 2 - Relevant propargylamines' derivatives.

1.3. Catalysis

1.3.1. Copper

Copper (Cu), the 29th element of the periodic table and the 25th most abundant in earth's crust, has two natural stable isotopes, ^{63}Cu and ^{65}Cu, with isotopic abundances of approximately 69 and 31%, respectively. Its atomic weight is 63.54 and the electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$. The main oxidation states of copper are 0, +1, that is not usually stable in solution, and +2, being the most common. Cu(I) is easily oxidized to Cu(II).[71]

Copper has a wide range of practical applications, being used in wires, electricity cables, tubes, vessels, containers and as a building material. It is also an alloying metal, combined with zinc, to make brass, tin, to make bronze and nickel to make a coinage material. Some copper-based alloys can also have medicinal applications, as in dental bridges and crowns and intrauterine contraceptive devices.[72]

From a chemical perspective, copper is one of the most attractive metals for catalysis. Due to its low toxicity, high functional group tolerance and low cost (it is one of the transition metals with the lowest price per mol),[73] copper is the second most used metal in catalysts for organic reactions, only losing to palladium (**Figure 3**). This high appreciation for copper has to do with some interesting properties like the capacity to activate terminal alkynes and its variable and interchangeable oxidation state, turning its redox chemistry valuable.[74]

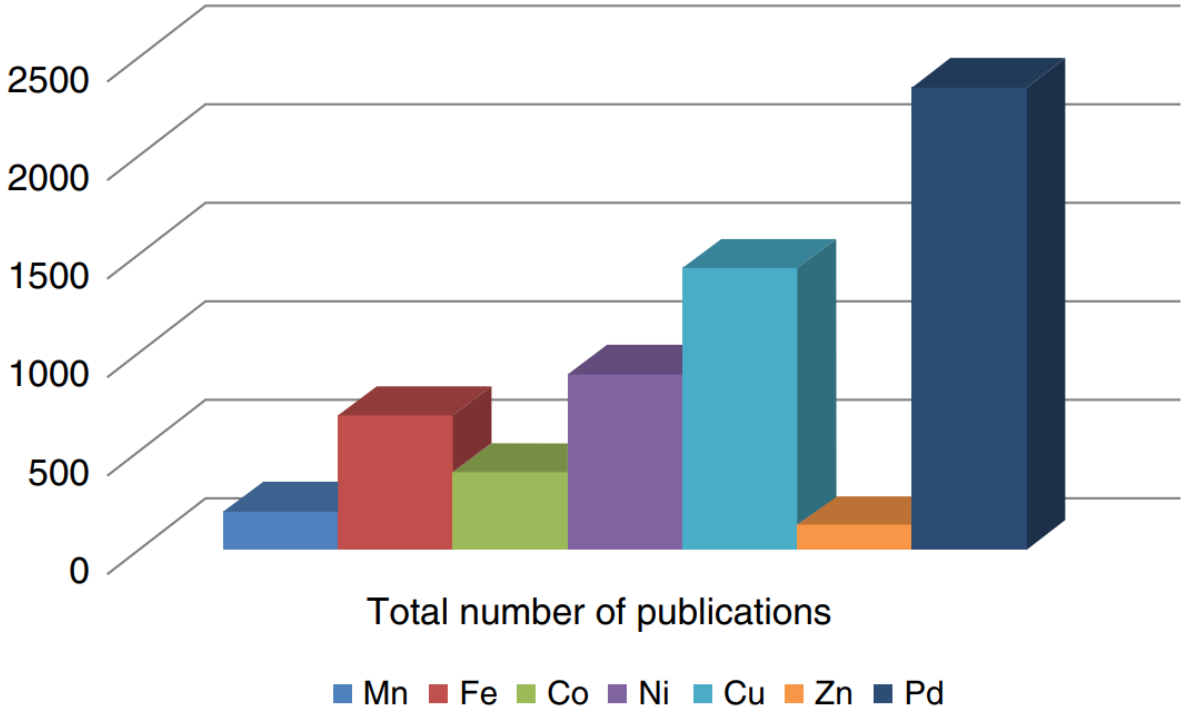


Figure 3 - Total number of publications using different metal catalysts until 2019. Adapted from [75]

Catalysis by copper is extremely versatile, since several reactions have been successfully applied in organic chemistry, like amination, C–H activation, aziridination, hydrosilylation, additions to carbonyl compounds, "click chemistry", heterocyclic synthesis, and many other multicomponent reactions.[75]

As this dissertation is focused on copper-catalysed direct aerobic oxidation of alcohols with amines and coupling of aldehydes, amines and alkynes, it is important to note that for the first case, in addition to the ability of copper to coordinate to heteroatoms, promoting amination reactions, its rich redox chemistry under aerobic conditions can catalyse the oxidation of the alcohol and then the condensation of the aldehyde with the amine to form the imine.[76] In fact, copper is present in the active site of metalloenzymes found in nature, mediating several aerobic oxidation processes, like the oxidation of organic substrates by oxidases and the formation of C–O bonds by oxygenases. Regarding the A^3 coupling reaction, since copper is a metal with a high affinity for π-bonds, especially in alkynes, it allows the addition of the respective metal acetylide to electrophilic carbons, promoting the formation of propargylamine.[77]

1.3.2. N-Heterocyclic Carbenes

Carbenes are compounds with a divalent carbon with six valence electrons, four of them bonding and two non-bonding. When a carbene is attached to at least a nitrogen atom within

a heterocycle, it is called N-Heterocyclic Carbene. However, NHCs are very special carbenes, having a particular difference from regular ones, that are generally electrophilic: since they are stabilized by the π-electron-donating and the π-electron-withdrawing character of the nitrogen(s) atom(s), they end up being nucleophilic.[78]

Due to these properties, NHCs form stronger bonds with metal centres rather than most classical ligands. In fact, initially they were compared to phosphines but then it was found that NHCs make even stronger and shorter metal-ligand bonds, as they are more electron-donating, in addition to the better steric protection of the metal centre, provided by the nitrogen-substituents that create a fan- or umbrella-shaped shield, instead of the cone formed by a phosphine (**Figure 4**).[79]

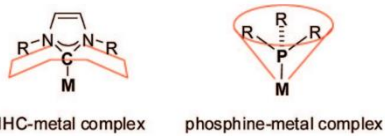
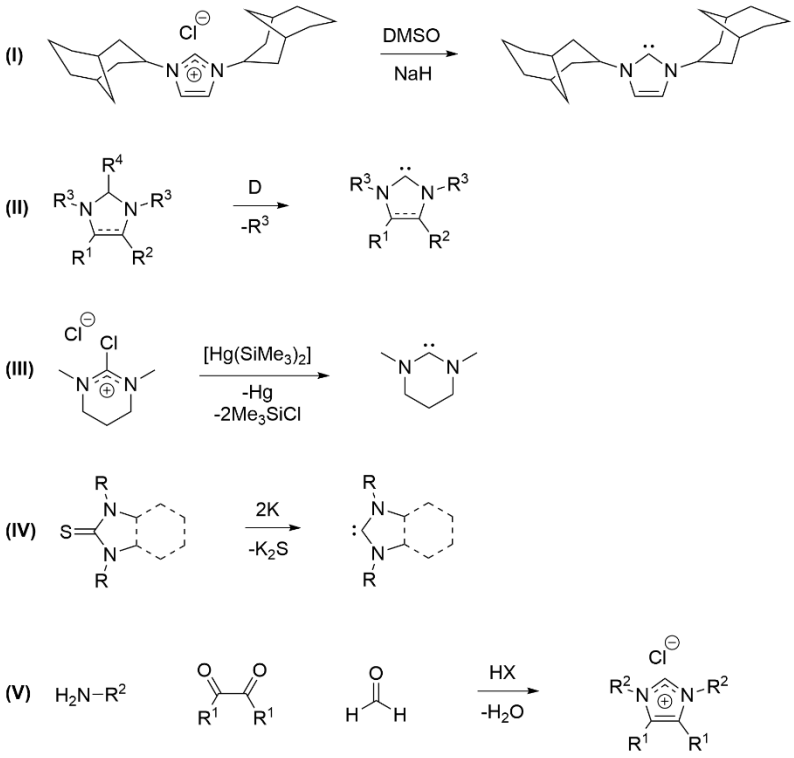


Figure 4 - Shape formed by NHCs and phosphine ligands. Adapted from [114]

The first isolation of a N-Heterocyclic Carbene dates back to 1991, when Arduengo *et al* managed to synthesize an adamantyl N-substituted NHC by deprotonation of N-di-adamantylimidazolium chloride with DMSO in THF at room temperature, in the presence of sodium hydride (**Scheme 5, I**).[80] Since these ligands had attracted so much attention because of their unique properties, there were developed another methodologies for their synthesis and researchers have been trying hard on its improvement. NHCs can also be synthesized by α-elimination by thermal induction (**Scheme 5, II**),[81] or α-dehalogenation of imidazolinium salts (**Scheme 5, III**).[82] Imidazole thiones can be desulfurized by reduction with potassium in THF to form NHCs (**Scheme 5, IV**).[83] The most common route to synthesize NHCs is probably by condensation of a dialdehyde or a diketone with two equivalents of substituted primary amines and an halogen ion source (**Scheme 5, V**),[84] which is the method used in this thesis.

NHC-metal complexes have been used to catalyse a wide variety of organic reactions such as Sonogashira coupling,[85] Suzuki-Miyaura coupling,[86] dehydrogenation of alcohols to carboxylic acids,[87] amide formation from alcohols and amines,[88] alcohol oxidation,[89] N-alkylation of amines,[90] among others. Imine formation from amines and alcohols and A^3 coupling reactions mediated by these types of metal complexes have already been studied previously as well. Furthermore, NHC complexes coordinated to several transition metals like copper, silver, gold, platinum, palladium, ruthenium, rhodium and iridium were found to have biological applications, due to their antibacterial and anticancer properties.[91]



Scheme 5 - Synthetic routes to NHCs.

1.3.3. Bis(imino)acenaphthene

BIANs are a family of compounds consisting of two imines connected by an acenaphthene structure. Due to their extended π-system and rigid structure, in addition to strong π-electron-donating and π-electron-accepting that they grant, the N-substituents are pulled closer to the metallic centre, increasing the steric control and stability over it. Additionally, the more electron-donating the N-substituents are, the stronger is the stabilization of the metal complex.[92]

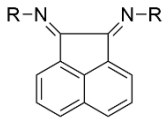


Figure 5 - General structure of bis(imino)acenaphthene.

There are two main routes for the synthesis of BIAN compounds: condensation of acenaphthoquinone with an amine under acidic conditions and the template method, in which the condensation occurs in the presence of $ZnCl_2$ or $NiBr_2$, resulting in a BIAN-metal complex and subsequently removed.

BIANs can display until four consecutive oxidation states, by accepting electrons and through their delocalization in the π-system. This induces radical reactivity and electron-reservoir behavior, so that they become excellent ligands to build metal complexes capable of catalyse a wide variety of organic reactions,[93] like Suzuki coupling, Negishi coupling, Murahashi coupling, Sonogashira coupling, Buchwald-Hartwig coupling, Suzuki-Miyaura, esters amidation, alkynylation of imines, amination, cyclization reactions, among others.[94]

1.4. Aims and Goals

In this work, four families of copper(I) catalysts were synthesized using Ar-BIANs and NHCs (with or without an acenaphthene backbone) as ligands. Among these catalysts, there are heteroleptic copper complexes composed by a NHC or an Ar-BIAN-NHC ligand and an Ar-BIAN ligand, copper chloride NHC and Ar-BIAN-NHC complexes, dimeric copper Ar-BIAN complexes and BIAN copper complexes. The objective of their synthesis was to study their catalytic activity on the imine formation via direct aerobic oxidation of alcohols and amines and the coupling of aldehydes, amines and alkynes, in an attempt to soften the reaction conditions already reported in the existing literature, by decreasing some parameters as much as possible, like the temperature, the amount of catalyst needed and the reaction time. As part of a green chemistry laboratory, the will is always to perform reactions using mild reaction conditions, in the most sustainable way possible, causing a minimal impact on the environment on each chemical process.

This dissertation is structured in a way that presents the discussion of the results obtained, where firstly a comparison is made between the various synthetic procedures and the structural characterization of the complexes synthesized and then their catalytic activity is evaluated from the conversion rates obtained in the catalytic studies. In the following section, synthetic procedures are described, and the characterization is presented. Finally, some conclusions are stated, and future perspectives are made about work that was still left to do and improvements that could have been made.

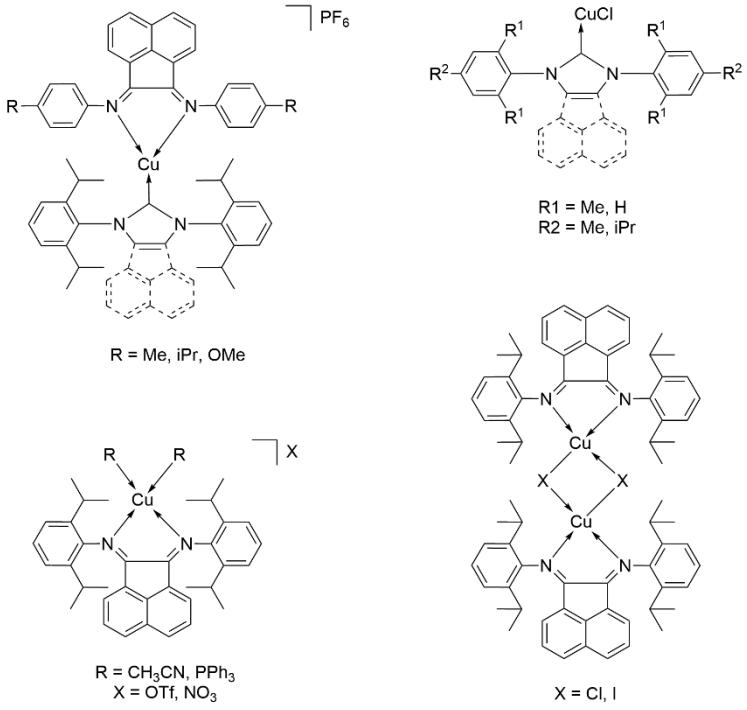


Figure 6 - Families of copper(I) complexes synthesized in this dissertation.

2. RESULTS AND DISCUSSION

In this section of the dissertation, the results of all the synthesis are presented and discussed. The reaction steps are explained, the yields are justified and the ^{1}H NMR, ^{13}C NMR and IR spectra of the products are analysed, in order to take conclusions.

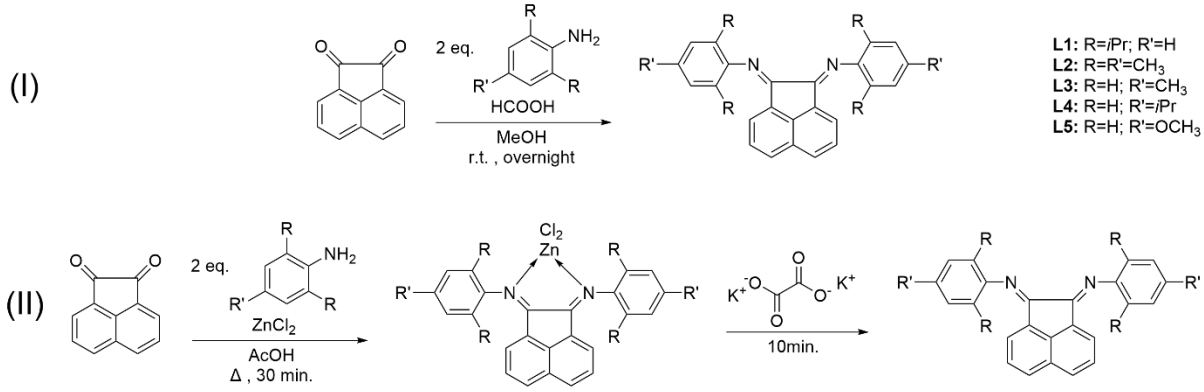
In the first subchapters, the BIAN and NHC ligands are disclosed and then the heteroleptic copper(I) complexes. Finally, the results of the studies on the catalytic activity of the complexes synthesized via aerobic oxidation of alcohols and amines and via A^3 coupling are given.

2.1. Bis(imino)acenaphthene (BIAN) ligands

Three bis(imino)acenaphthene compounds with different N-aryl groups were synthesized to be used as ligands in heteroleptic copper(I) complexes and as precursors to the synthesis of bis(imino)acenaphthene-N-heterocyclic carbenes.

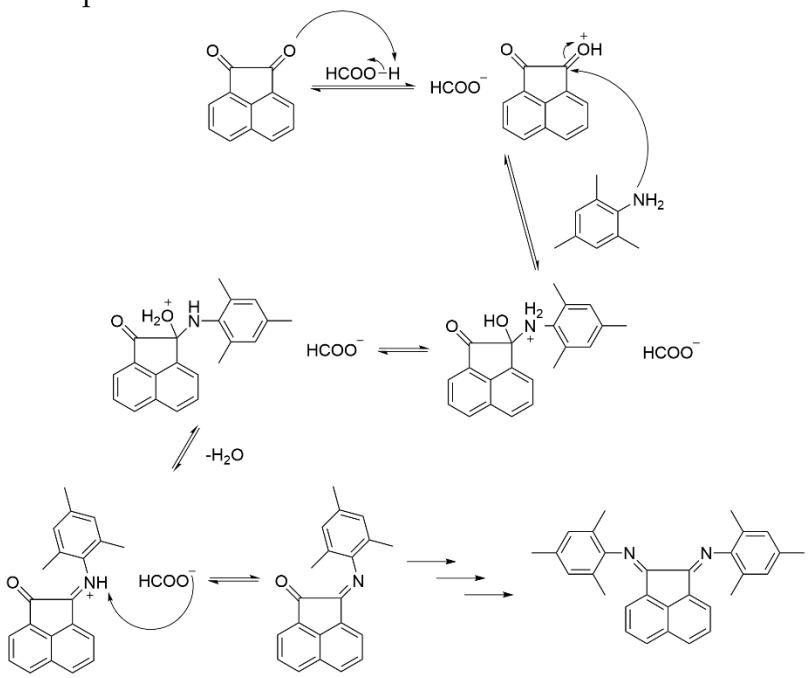
2.1.1. Synthesis

The synthesis of these compounds was performed through two different methods, as described in **Scheme 6**.



Scheme 6 - Methods for the synthesis of the BIAN ligands, (I) classic and (II) template.

L2 was obtained via the classic method, with 95 % yield, synthesized by acid-catalysed condensation of acenaphthene quinone with two equivalents of 2,4,6-trimethylaniline, overnight at room temperature, using a catalytic amount of formic acid, and methanol, a protic solvent that enhances this protonation step. As shown in **Scheme 7**, the amine's nucleophilic nitrogen attacks the carbonyl's carbon and then the C=N double bond is formed with the elimination of a water molecule. **L1** was already available in the laboratory, previously synthesized by the same procedure.



Scheme 7 - Mechanism for the formation of the diimine via acid-catalysed condensation of acenaphthene quinone with 2,4,6-trimethylaniline.

L4 and **L5** were obtained with 83 and 80 % yield, respectively, using the *template* method, where a mixture of acenaphthene quinone and the corresponding aniline were reacted with metal salt, in this case zinc(II) chloride, under reflux with acetic acid for half an hour, followed by demetallation with a solution of potassium oxalate. **L3** was already available in the laboratory, previously obtained by the same method.

Comparing both methods, better yields were achieved using the first one, because boiling in aqueous potassium salts may lead to decomposition resulting in a mixture of the BIAN ligand and the metal-BIAN complex. In addition, the first method can be considered more sustainable, since it does not require heating and uses only a catalytic quantity of acid, even though the *template* method is faster.

2.1.2. Characterization

All the BIAN ligands synthesized and available in the laboratory were already reported in the literature,[95] so the formation of the desired products was confirmed by ^{1}H NMR.

From the analysis of the ^{1}H NMR spectra of **L4** vs **L4ZnCl$_2$** and **L5** vs **L5ZnCl$_2$** (**Figure 7**), it was possible to confirm that the demetallation occurred, since almost every peak was shifted upfield, especially the one corresponding to the *ortho* protons (3) of the acenaphthene.

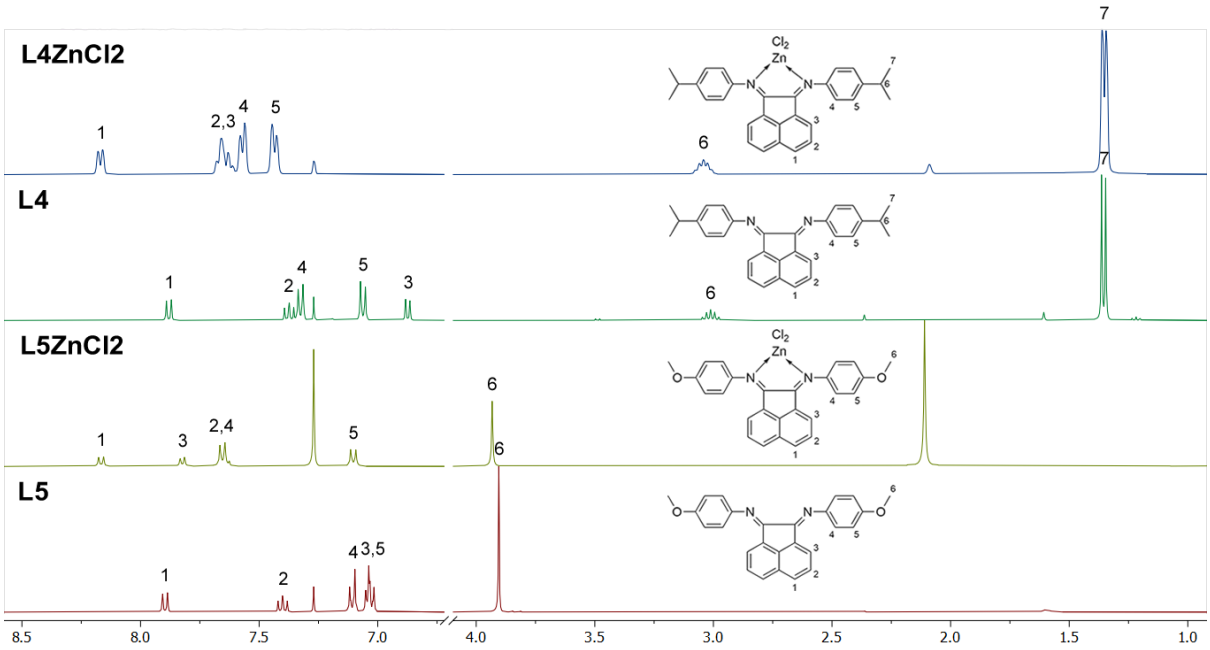


Figure 7 - Expansion of the stacked ^{1}H NMR spectra of **L4**, **L4ZnCl2**, **L5** and **L5ZnCl2** in $CDCl_3$.

This can suggest an adjustment in the tridimensional position of the N-aryl groups, due to an increase of the deshielding effect when the N atoms are coordinated to zinc.

Analysing the ^{1}H NMR spectra of the ligands **L1**, **L2**, **L3**, **L4** and **L5** (**Figure 8**), it is possible to notice that the *para* (1) and *meta* (2) protons of the acenaphthene have similar chemical shifts, around 7.90 and 7.40 ppm, respectively. On the other hand, the *ortho* protons (3) suffer from different shielding effects according to the substituents on the N-aryl groups, reinforcing the fact these groups can adopt different spatial positions, depending on how bulky they are and on the existing heteroatoms. As can be seen, when the N-aryl groups don't have substituents in the *para* position, like in **L1**, the peak corresponding to the *ortho* protons of the acenaphthene are shifted upfield in comparison to the other ligands. Apparently, the methoxy group in the *para* position is the one that causes the most deshielding effect on the acenaphthene's *ortho* protons (around 7.00 ppm), followed by methyl (6.94 ppm), then isopropyl (6.87 ppm) and finally methyl with also methyl groups in *ortho* positions (6.78 ppm). Comparing the distance between *ortho* (4) and *meta* (5) protons' peaks of the N-Aryl groups in the ligands with a substituent in the *para* position of the ring, it was observed that when that substituent is isopropyl those peaks are the most far from each other, followed by methyl, with them being closer in the methoxy case. Regarding the characteristic heptets displayed by the C-H of isopropyl groups (6) in **L1** and **L4**, the difference between the shifts of the protons in *ortho* and *para* is insignificant, though the nuclei of these protons in *ortho* position (3.04 ppm) are more deshielded than in *para* (3.01 ppm). As for the methyl groups, the highlight is in **L5**, where the CH_3 protons are highly deshielded by the oxygen atom (3.90 ppm). The *o*-methyl groups' protons are less deshielded than the *p*-methyl's, in addition to the fact that these last ones are slightly more deshielded when there are no substituents in the *ortho* position of the ring, as witnessed in **L2** and **L3** spectra. This effect can also be spotted on the isopropyl's methyl groups, which are the least deshielded of all. On **L1** spectra it was also observed that isopropyl's CH_3 signals were split in two (7 and 8), meaning they have two different chemical environments.

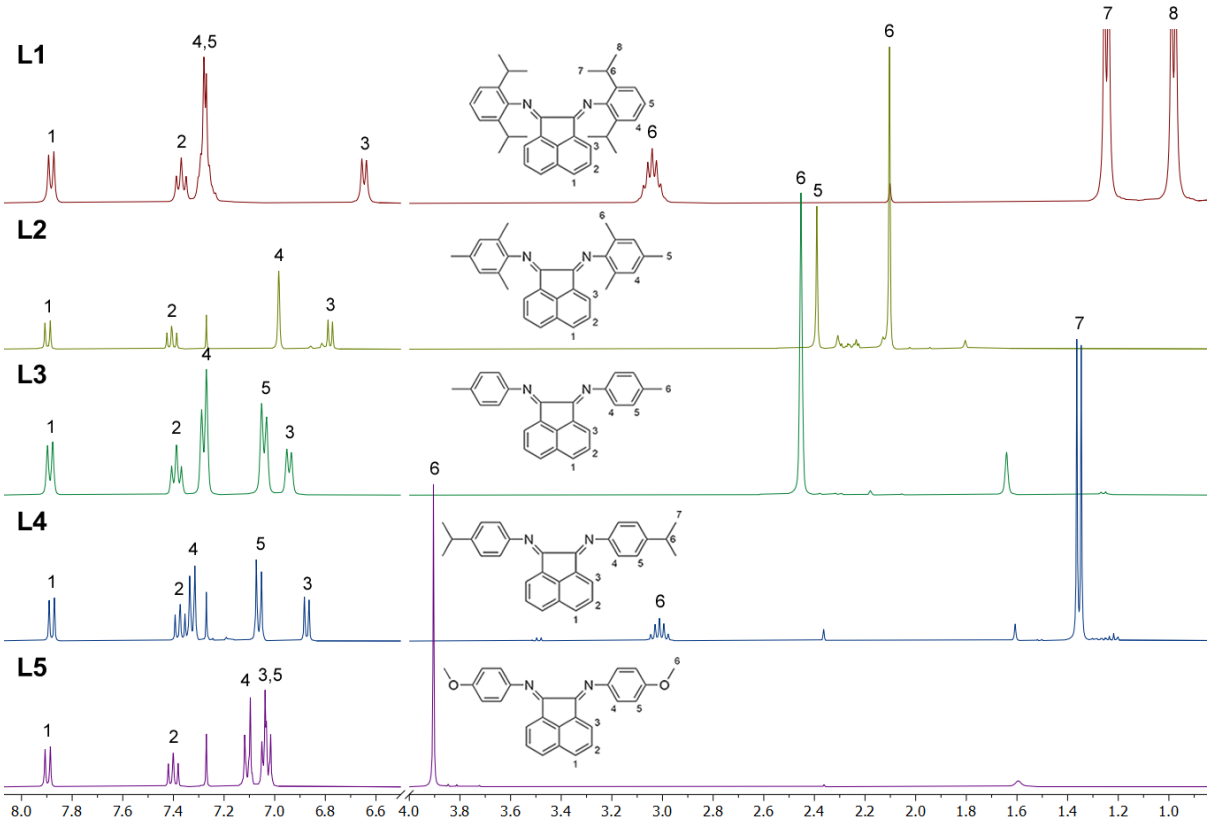


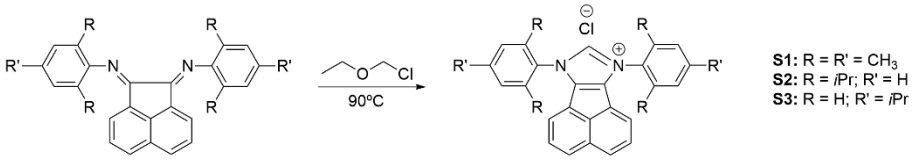
Figure 8 - Expansion of the stacked ^{1}H NMR spectra of **L1**-**L5** in $CDCl_3$.

2.2. Bis(imino)acenaphthene (BIAN) imidazolium chlorides

Three bis(imino)acenaphthene imidazolium chlorides with different N-aryl groups were synthesized from the BIAN ligands, to be used as precursors in the synthesis of the BIAN-NHC Copper(I) complexes.

2.2.1. Synthesis

The salts **IMesBIANCl** (**S1**), **IDipBIANCl** (**S2**) and **I*p*-iPrBIANCl** (**S3**) were obtained with yields of 96 %, 73 % and 92 % respectively, by mixing ethoxy(methyl)chloride with the desired bis(imino)acenaphthene at 90 ºC overnight (**Scheme 8**). The addition of the reagents and the reaction itself were performed under inert atmosphere (argon), since ethoxy(methyl)chloride easily hydrolyses with water, that exists in the atmosphere. At the end of the reaction time, the product instantly precipitated with the addition of diethyl ether, and the filtration and the washes with this solvent allowed the removal of the starting materials. The relatively low yield in the synthesis of **S2** may be explained by the loss of a considerable amount of product in the workup steps, since the literature[96] reports higher yields on the formation of this compound, following the same procedure.



Scheme 8 - Method for the synthesis of the BIAN-NHC salts.

2.2.2. Characterization

S1 and **S2** were already reported in the literature,[96,97] so the formation of the desired products was confirmed by ^{1}H NMR. **S3** was not reported yet, so it was characterized by ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, IR and EA.

Comparing the ^{1}H NMR of **S1**, **S2** and **S3** (**Figure 9**), it was immediately perceptible that the N-aryl substituents arrange themselves in space in a way that a huge effect is produced on the carbenic protons shifts, since in **S2,** isopropyl groups in *ortho* positions highly deshields their nucleus (11.99 ppm) in relation to an isopropyl group in *para* position, like in **S3** (11.35 ppm) or methyl groups in *ortho* and *para* positions **S1** (11.31 ppm). The *meta* and *para* protons of the acenaphthene seemed to not be much influenced by the modification of these substituents, but when looking at the *ortho* ones, it was observed that they were much more shifted downfield when there is a *p*-isopropyl group in the N-aryl rings, like in **S3** (7.88 ppm), rather than methyl groups in *ortho* and *para* positions, like in **S1** (7.30 ppm) or isopropyl groups in *ortho* positions, like in **S2** (7.23 ppm). In the case of the CH_3, it is possible to note that just like in the diimines precursors of these Imidazolium salts, the methyl groups in *ortho* and *para* positions of the N-aryl in **S1** (2.33 and 2.43 ppm) are way more deshielded than the methyls in isopropyl groups in **S2** (1.40 and 1.17 ppm) and **S3** (1.35 ppm). The signal of the heptet corresponding to the C-H protons is also more downfield in **S3** (3.07 ppm) than in **S2** (2.73 ppm), which means that, in these compounds, the nucleus of these hydrogens is more deshielded when having an isopropyl in *para* position rather than isopropyls in *ortho* positions.

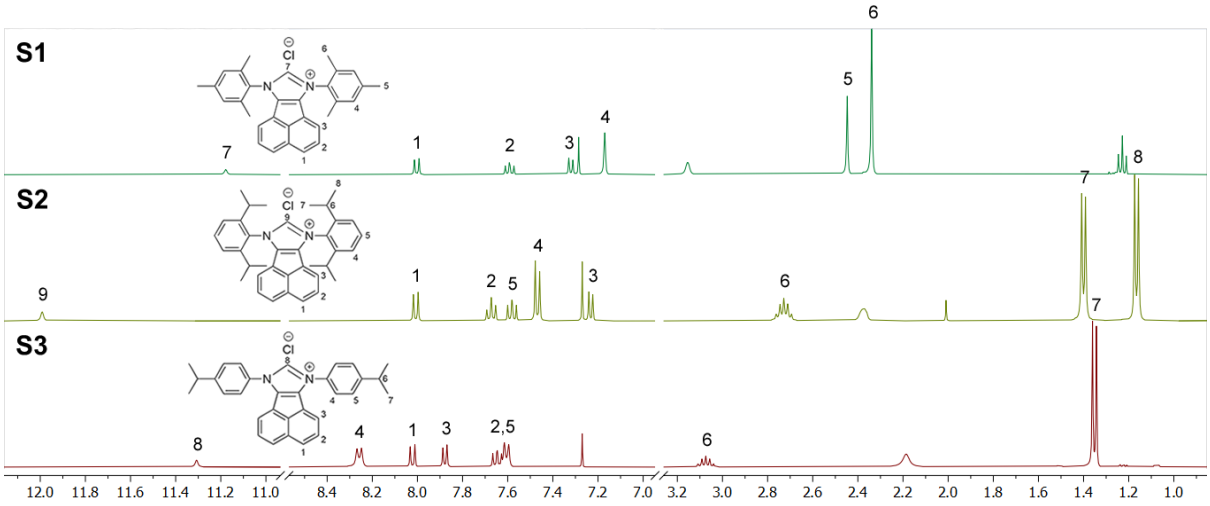


Figure 9 - Expansion of the stacked ^{1}H NMR spectra of **S1**-**S3** in $CDCl_3$.

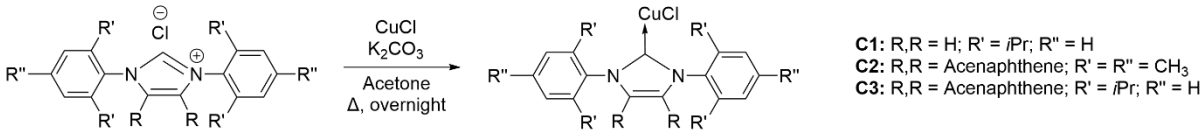
In the $^{13}C\{^{1}H\}$ NMR spectrum (**Annex 9**) it was possible to identify the carbenic carbon, at 138 ppm. There are other carbons that deserve the highlight, like the ones near the nitrogen atom, at 136 and 132 ppm, corresponding to the one that belongs to the acenaphthene and the one that belongs to the N-aryl, respectively. The most deshielded signal was the one corresponding to the quaternary carbons near the isopropyl groups, at 152 ppm. The isopropyl's C-H and CH_3 were spotted at 34 and 24 ppm, respectively.

2.3. N-Heterocyclic Carbene Copper(I) complexes

Three N-heterocyclic carbene copper(I) complexes with different N-aryl groups were synthesized starting from the corresponding imidazolium chloride. These complexes belong to two different families of N-heterocyclic carbenes, one with a bis(imino)acenaphthene backbone and the other without it, even though all these complexes were synthesized by the same procedure, using the weak base method, developed by Nolan *et al.*[98]

2.3.1. Synthesis

The complexes **[Cu(IDip-NHC)Cl]** (**C1**), **[Cu(IMesBIAN-NHC)Cl]** (**C2**) and **[Cu(IDip-BIAN-NHC)Cl]** (**C3**) were obtained with yields of 83 %, 61 % and 80 % respectively, by mixing the respective imidazolium chloride with copper(I) chloride and an excess of potassium carbonate under reflux (60 ºC) in acetone overnight (**Scheme 9**). The addition of the reagents and the reaction itself were carried under inert atmosphere since K_2CO_3 is hygroscopic and copper(I) chloride in contact with water slowly undergoes disproportionation forming Cu(0) and copper(II) chloride. After the reaction time, filtration allowed the removal of unreacted starting material, especially the excess of K_2CO_3. The yields obtained are similar to the ones reported in literature, except for the complex (**C2**) where the loss of product during the workup steps may be a reason for the significative lower yield obtained.



Scheme 9 - Method for the synthesis of the NHC copper(I) complexes.

2.3.2. Characterization

These three complexes were already reported in the literature,[99,100,101] so the formation of the desired products was confirmed by ^{1}H NMR.

The formation of compounds **C1**, **C2** and **C3** was confirmed by the absence of the signals of the carbenic protons at around 11-12 ppm observed in the imidaziolium chlorides precursors.

Comparing the ^{1}H NMR spectra of **C1** and **C3** (**Figure 10**), complexes where the only structural difference is the presence/absence of the acenaphthene backbone, it can be noted that its presence causes the deshielding of the triplet and the doublet of the N-Aryl groups protons and also of the heptet's protons corresponding to C-H of the isopropyl groups. In the case of CH_3 protons, one of the signals is more deshielded and the other is less deshielded.

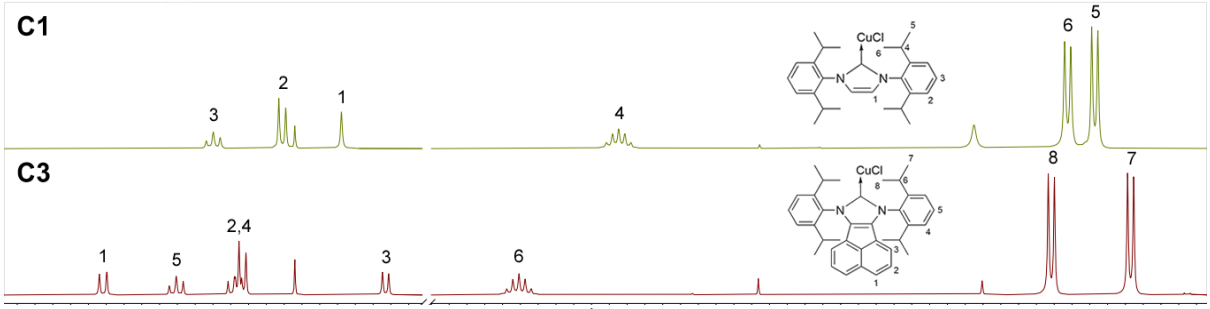


Figure 10 - Expansion of the stacked ^{1}H NMR spectra of **C1** and **C3** in $CDCl_3$.

2.4. Heteroleptic Copper(I) complexes

Combining copper(I) complexes with bis(imino)acenaphthene ligands, a variety of heteroleptic copper(I) complexes were synthesized in order to be tested in the synthesis of imines and propargylamines.

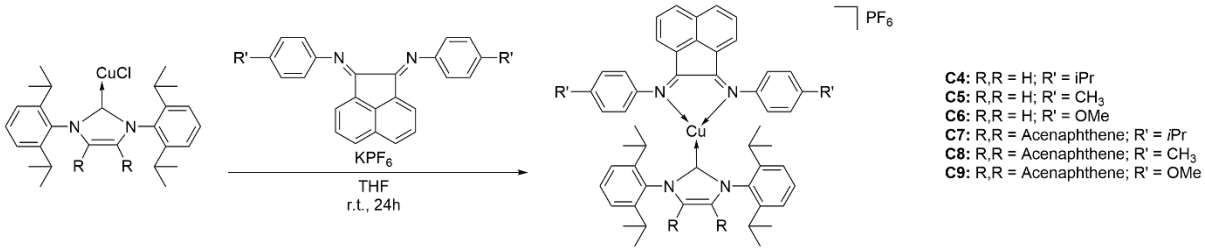
This was the probably the most important section of the dissertation, where the focus relied on two families of complexes, where the diimine ligands were the same, with the difference being whether the N-Heterocyclic Carbene ligand had the bis(imino)acecnaphthene backbone or not.

The synthesis of another family of copper(I) heteroleptic complexes was also attempted, but without success. Similarly, to the previous ones, these complexes would have a N-Heterocyclic carbene ligand and two triphenylphosphines coordinated to the copper atom.

To finish off this section, two other copper(I) heteroleptic complexes, **[Cu(*p*-*i*PrBIAN)(PPh$_3$)$_2$]NO$_3$** (**C13**) and **[Cu(DipBIAN)(CH$_3$CN)$_2$]OTf** (**C14**) were synthesised. The reason behind the choice of these specific complexes was that they had shown excellent catalytic activity among their respective families in two reactions that may be related with the catalysis studied in this thesis. **C13** obtained the best results in the addition of an azide to an alkyne (reaction that share some features with the alkynylation step of the A^3 coupling) and **C14** granted great conversion rates on the aerobic oxidation of alcohols (which is the first step of the imine formation via aerobic oxidation of alcohols and amines). Bearing that in mind, these two complexes were synthesized so that their behaviour could be tested on the catalytic imine formation and A^3 coupling.

2.4.1. Synthesis

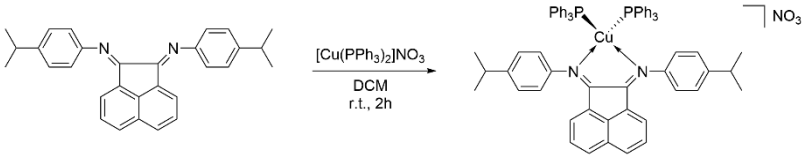
Complexes **[Cu(IDip-NHC)(*p*-*i*PrBIAN)]PF$_6$** (**C4**), **[Cu(IDip-NHC)(*p*-*i*PrBIAN)]PF$_6$** (**C5**), **[Cu(IDip-NHC)(*p*-MeBIAN)]PF$_6$** (**C6**), **[Cu(IDipBIAN-NHC)(*p*-OMeBIAN)]PF$_6$** (**C7**), **[Cu(IDipBIAN-NHC)(*p*-MeBIAN)]PF$_6$** (**C8**) and **[Cu(IDipBIAN-NHC)(*p*-OMeBIAN)]PF$_6$** (**C9**) were obtained by mixing the respective [Cu(NHC)]Cl with the desired diimine ligand in the presence of an excess of KPF$_6$ in THF at room temperature for 24 hours, under argon atmosphere (**Scheme 10**), with yields of 45, 63, 60, 66, 56 and 35 % respectively. These moderate to good yields can be considered positive results, having in mind this was the first time most these compounds were synthesized, and the synthetic process was not optimized yet. If the reaction time and/or temperature were higher, probably better yields could have been achieved. The filtrations allowed the removal of unreacted starting materials, especially the excess of KPF$_6$.



Scheme 10 - Method for the synthesis of the [Cu(NHC)(BIAN)]PF$_6$ complexes.

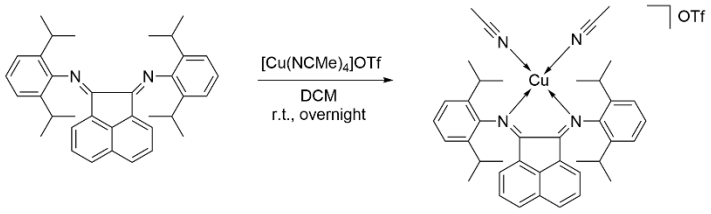
The attempt of synthesizing complexes **[Cu(IMesBIAN)(PPh3)2]NO3** (**C10**), **[Cu(IDip-BIAN)(PPh3)2]NO3** (**C11**) and **[Cu(*p*-*i*PrBIAN)(PPh3)2]NO3** (**C12**) consisted in adding the desired bis(imino)acenaphthene imidazolium chloride to $Cu(PPh_3)_2NO_3$ in the presence of an excess of K_2CO_3 in dry dichloromethane at 40 ºC overnight, under argon atmosphere, since phosphines are sensitive to atmospheric oxygen, oxidizing very easily. As referred before, the products obtained were not the expected.

Complex **C13** was synthesized by mixing bis[N-(4-isopropylphenyl)imino]acenaphthene with $[Cu(PPh_3)_2]NO_3$ in dry dichloromethane at room temperature for 2 hours, under argon atmosphere (**Scheme 11**), by the same reason mentioned earlier bearing the phosphine ligands. The filtrations removed successfully undesired starting materials, obtaining the pure product with a yield of 84 %.



Scheme 11 - Method for the synthesis of $[Cu(p\text{-}iPrBIAN)(PPh_3)_2]NO_3$.

Complex **C14** was obtained with 84 % yield as well, by adding bis[N-(2,6-diisopropylphenyl)imino]acenaphthene to $[Cu(CH_3CN)_4]OTf$ in dry dichloromethane at room temperature overnight, under argon atmosphere (**Scheme 12**), because this copper complex is very unstable under non-inert atmosphere due to the high lability of acetonitrile ligands. The filtration through celite allowed the removal of non-coordinated copper.



Scheme 12 - Method for the synthesis of $[Cu(DipBIAN)(CH_3CN)_2]OTf$.

2.4.2. Characterization

Complexes **C4** and **C5** were already reported in the literature,[102] so their formation was confirmed by ^1H NMR. Complexes **C6**, **C7**, **C8** and **C9** were not reported yet, so they were totally characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR, IR and EA.

Comparing the ^1H NMR spectra of these six complexes (**Figure 11**), it was possible to observe that the NHC ligand proton's nucleus do not suffer much interference from the BIAN ligand, since the shifts are very similar. In the case of the BIAN ligand, the methoxy groups in *para* positions of N-aryl groups caused the most deshielding of the *ortho* protons of the acenaphthene (6.72 ppm, in **C6**, and 6.71 ppm, in **C9**), followed by methyl groups (6.63 ppm, in **C5**, and 6.64 ppm, in **C8**) and finally isopropyl groups (6.56 ppm, in **C4**, and 6.61 ppm, in **C7**), while the opposite happened to *ortho* protons of N-aryl groups, with isopropyl groups in *para* positions deshielding the most (7.22 ppm, in **C4**, and 7.24 ppm, in **C7**), followed by methyl groups (7.16 ppm, in **C5**, and 7.19 ppm, in **C8**) and finally methoxy groups (6.90 ppm,

in **C6**, and 6.92 ppm, in **C9**). When looking at the differences between the complexes with a NHC ligand and a BIAN-NHC ligand, it was spotted that when having the acenaphthene backbone, the NHC's N-aryl *para* protons and C-H proton's signals were shifted downfield.

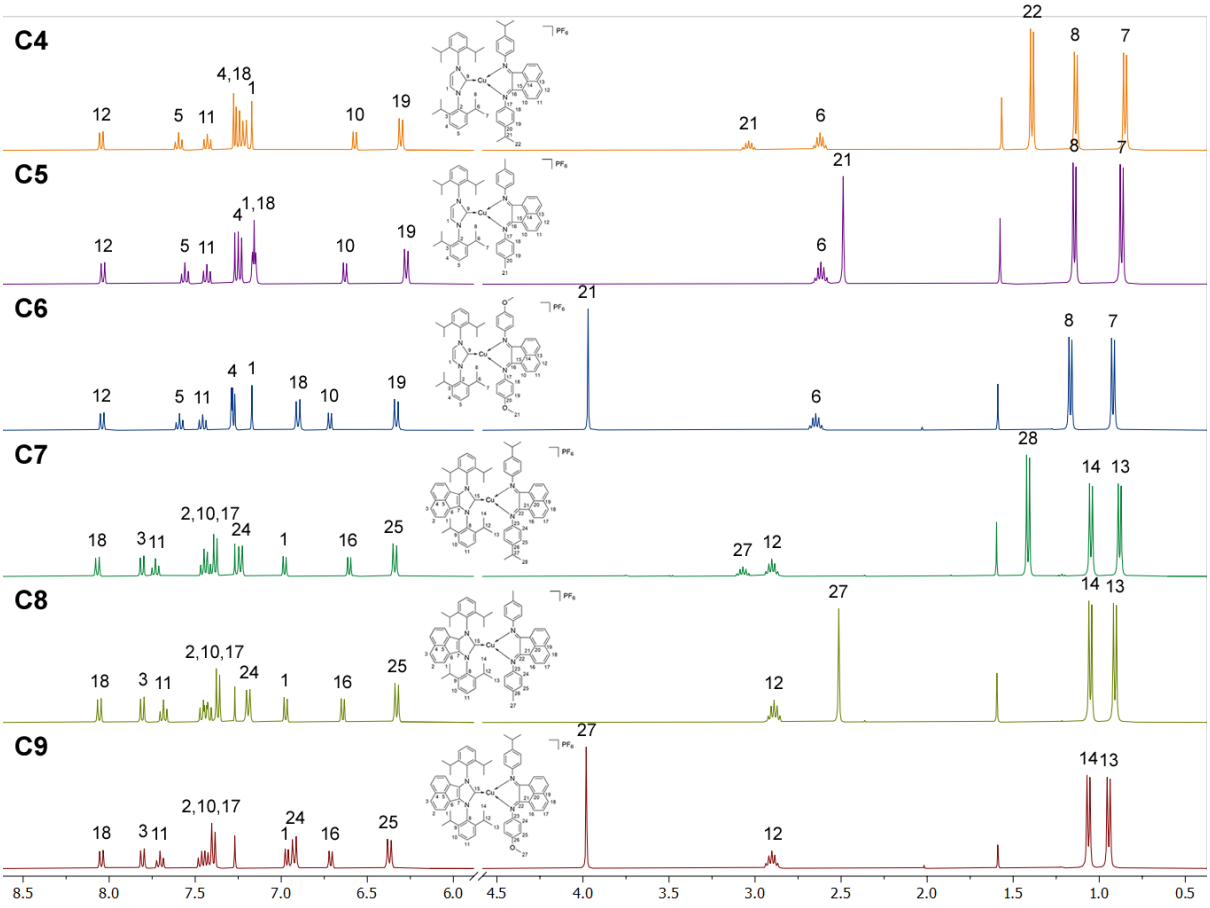


Figure 11 - Expansion of the stacked ^{1}H NMR spectra of **C4**-**C9** in $CDCl_3$.

Single crystals suitable for X-ray crystallography of the complexes **C6**-**C9** were obtained by liquid-liquid diffusion. Complexes **C6**, **C7**, **C8** and **C9** crystallized in monoclinic, triclinic, monoclinic and monoclinic systems with $P2_1/n$, $P\bar{1}$, $C2/c$ and $C2/c$ space groups, respectively.

The data for selected bond lengths and dihedral angles are described in **Table 1**. The explanation of dihedral angles is discriminated in **Figure 12**.

Complex **C6**'s asymmetric unit was composed by two molecules of the complex, cations and anions, and three molecules of co-crystalized dichloromethane. Complex **C7**'s asymmetric unit was composed by one molecule of the complex, cation and anion, and three molecules of co-crystalized dichloromethane. On the other hand, complex **C8** asymmetric unit was composed by only half molecule of the complex, cation and anion, and two molecules of co-crystalized dichloromethane, and complex **C9** by half molecule of the complex, cation and anion, without any co-crystallized solvent molecules. The cations' molecular structures are represented in **Figure 13**, with copper, nitrogens and carbenic carbon atoms properly identified.

All complexes present distorted trigonal planar geometries, with C-Cu-N angles of around 140º, since the angle between BIAN's chelating nitrogen atoms and the copper centre is around 80º in all the derivatives.

It was possible to verify that the C-N, Cu-N and Cu-C bond lengths do not have significant differences between complexes. In fact, the C-N bond lengths in the BIAN ligands are similar to a common C=N bond (1.279 Å) and the C-N bond lengths in the NHC ligands are analogous to a common N-heterocyclic C-N bond (1.370 Å).[103] The most notorious difference in the angle between the N-aryl groups of the BIAN ligand, since the complex without the acenaphthene backbone (**C6**) shows a wider ω angle than the ones observed in complexes with a BIAN-NHC ligand.

Table 3 - Data for the selected bond lengths and dihedral angles of complexes **C4**-**C9**.

C	C-N (BIAN) [Å]	Cu-N [Å]	C-N (NHC) [Å]	Cu-C [Å]	N-Cu-N [°]	ω [°]	φ_1 φ_2 [°]	τ [°]	ρ_1 ρ_2 [°]	θ [°]
6	1.283(6) 1.284(6)	2.097(4) 2.072(4)	1.362(6) 1.360(6)	1.897(5)	80.5(2)	49.6(2)	51.4(1) 78.0(1)	52.6(2)	66.8(2) 79.3(2)	56.5(1)
	1.279(6) 1.281(6)	2.068(4) 2.082(4)	1.387(6) 1.392(6)	1.891(4)	81.1(1)	47.5(2)	77.1(4) 78.9(4)	49.0(2)	65.0(2) 78.5(2)	47.9(2)
7	1.242(14) 1.267(13)	2.104(9) 2.040(9)	1.399(12) 1.376(11)	1.900(9)	79.4(4)	27.0(4)	70.2(3) 83.7(3)	50.3(4)	72.1(3) 73.6(3)	53.2(2)
8*	1.273(5) 1.273(5)	2.074(4) 2.074(4)	1.379(5) 1.379(5)	1.894(5)	80.9(2)	24.9(2)	78.5(1)	51.2(2)	72.0(1)	51.2 (1)
9**	1.273(5) 1.273(5)	2.071(4) 2.071(4)	1.390(5) 1.390(5)	1.888(5)	80.7(2)	27.7(2)	76.9(1)	51.3(2)	72.0(1)	52.1(1)

ω - angle between the planes containing the BIAN ligand's N-aryl groups; φ_1 and φ_2 - angle between the plane containing the BIAN ligand's N-aryl groups and the plane of the acenaphthene backbone; τ - angle between the planes containing the NHC ligand's N-aryl groups; ρ - angle between the plane of the NHC ligand's N-aryl groups and plane containing the imidazole ring; θ - angle between BIAN and NHC ligands; *Half molecule is generated by the symmetry operation 1-*x*,*y*,1/2-*z*; **Half molecule is generated by the symmetry operation 1-*x*,*y*,3/2-*z*.

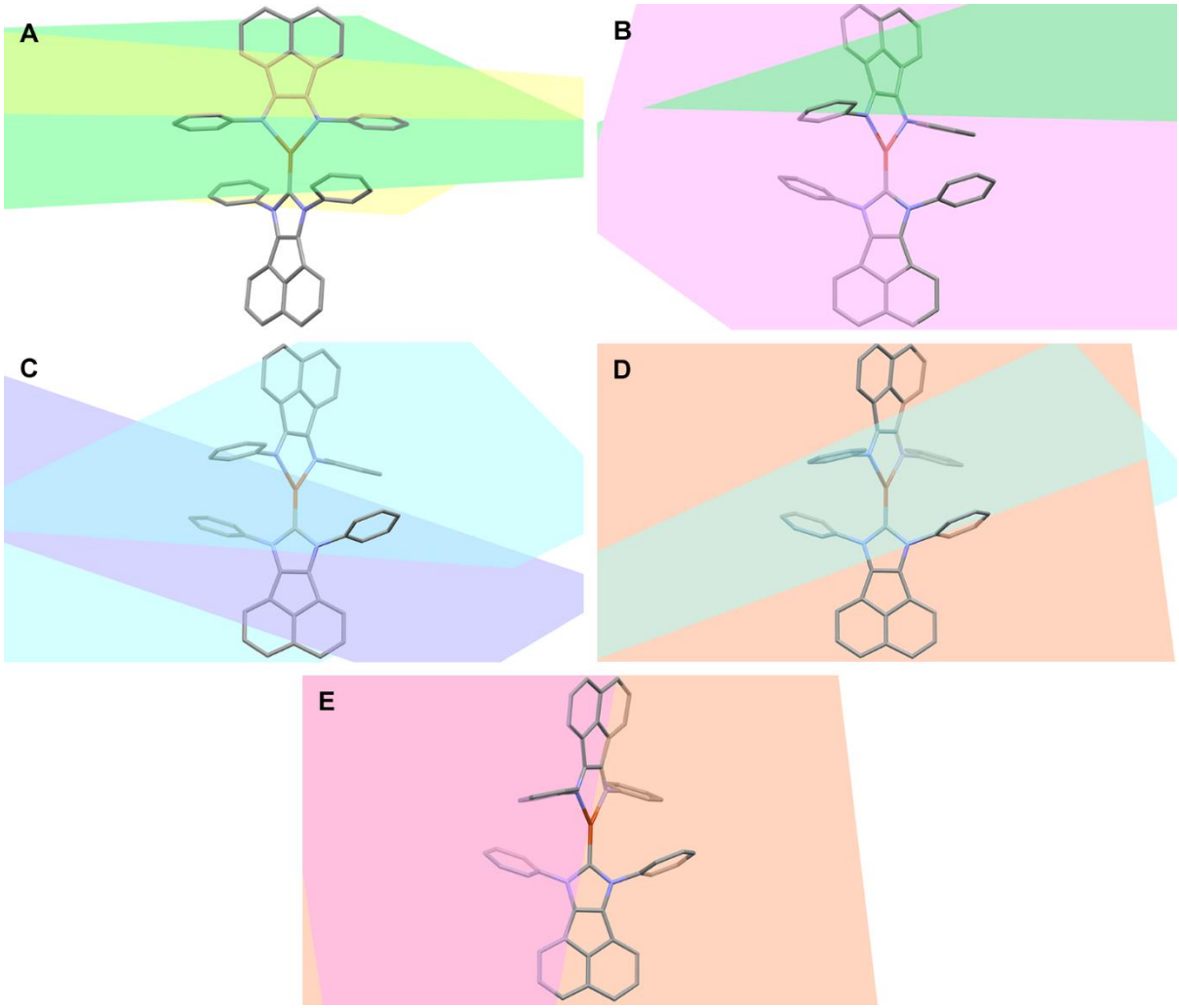


Figure 12 - (A) Dihedral angle ω, between BIAN ligand's N-aryl groups; (B) Dihedral angle , between BIAN ligand's N-aryl groups and acenaphthene; (C) Dihedral angle, between NHC ligand's N-aryl groups; (D) Dihedral angle ρ, between NHC ligand's N-aryl groups and imidazole ring; (E) Dihedral angle θ, between BIAN and NHC ligands.

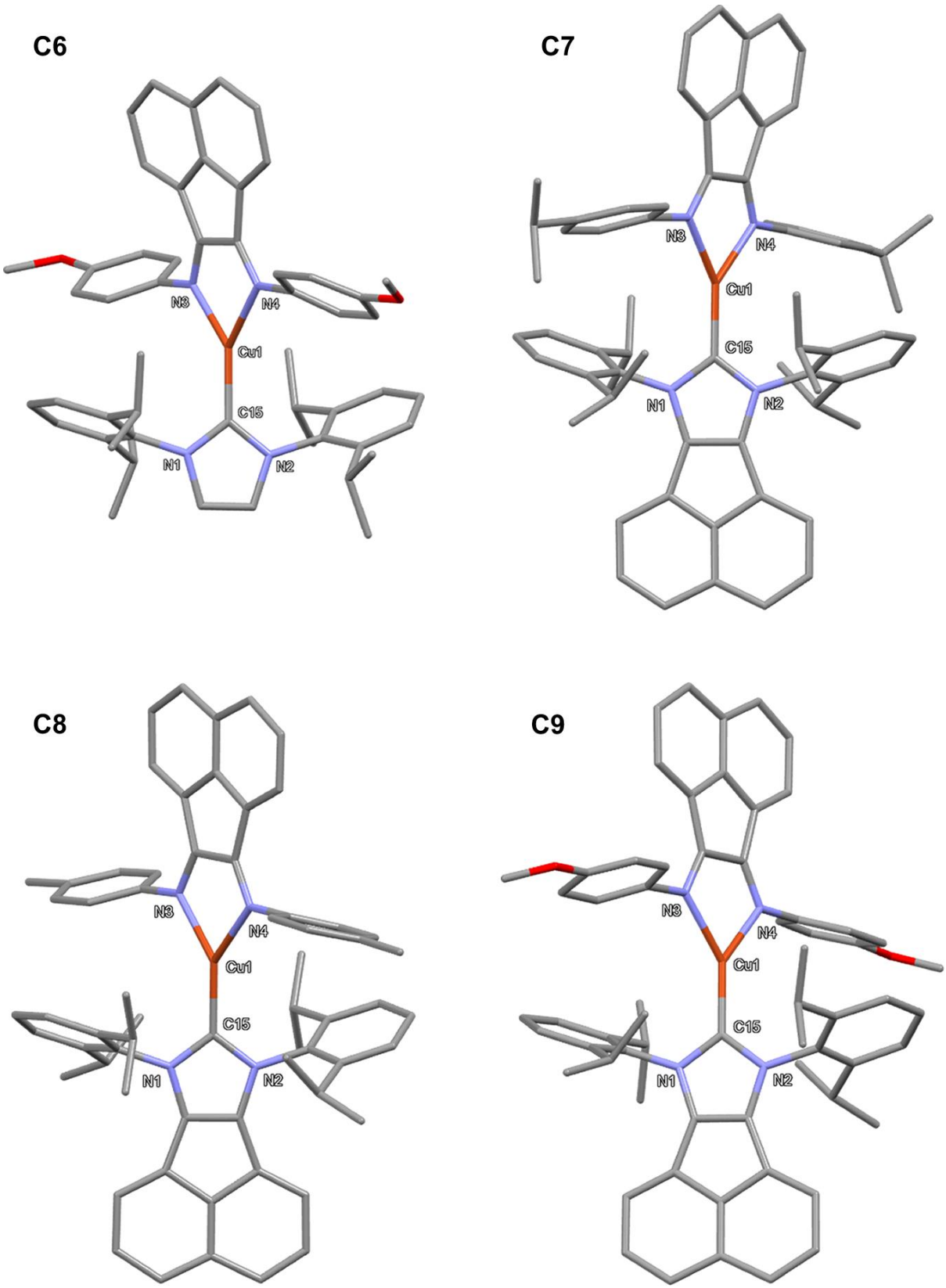


Figure 13 - *Mercury* representation of the 3D structures of complexes **C6-C9**. Hydrogen atoms, the anion and solvent molecules were omitted for clarity.

Comparing the IR spectra of complexes **C6**, **C7** and **C8**, it is possible to spot two differences between **C6** spectrum and the others, the appearance of a peak, at 1244 cm^{-1} corresponding to the C-O stretching of the methoxy group, and another one at 1504 cm^{-1}, corresponding to the C=C stretching of the NHC, which is more intense in the absence of the acenaphthene backbone.

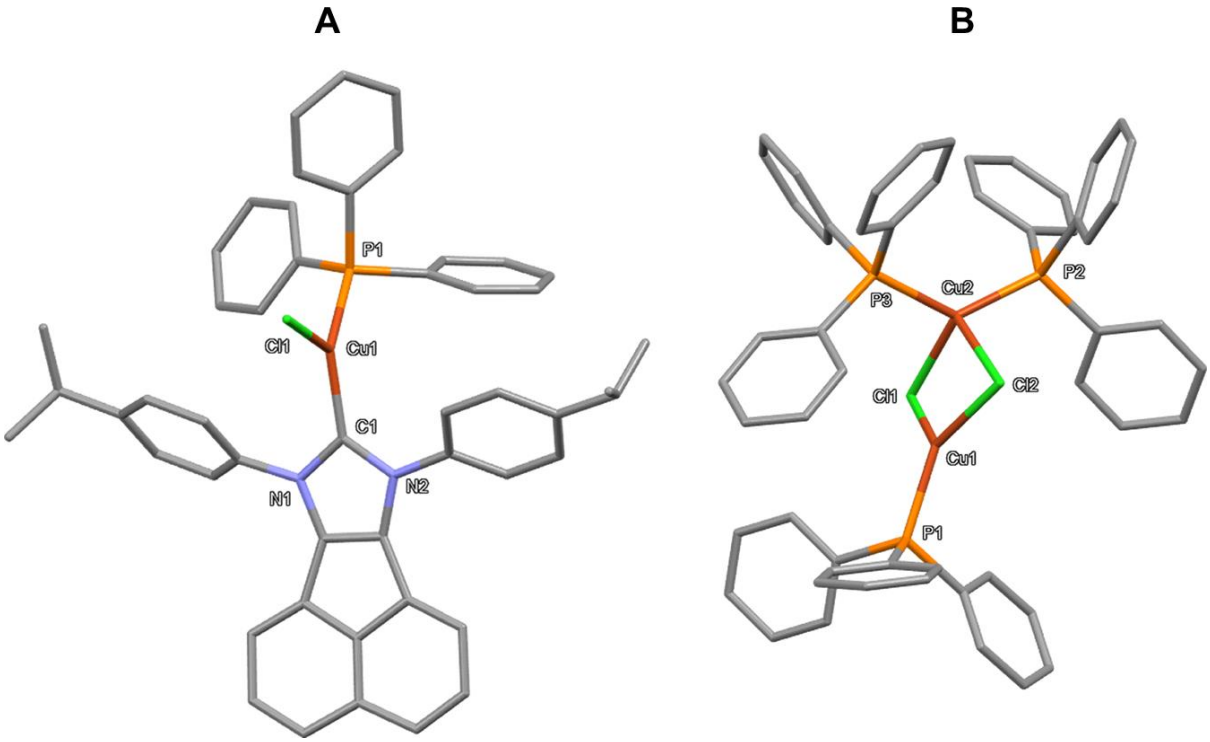


Figure 14 - Mercury representation of the 3D Structures of complexes [Cu(p-iPrBIAN)(PPh_3)(Cl)]NO_3 (A) and [Cu(PPh_3)][Cu(PPh_3)$_2$]Cl_2 (B); anion and solvent molecules were omitted.

In relation to the attempts of synthesizing [Cu(BIAN)(PPh_3)$_2$]NO_3 complexes, the ^{1}H NMRs obtained were always a mixture of compounds, so the analysis was not possible. Nevertheless, the sample obtained from the attempted synthesis of **C12** was recrystallized, and a mixture of two different single crystals suitable for X-ray crystallography were obtained. The structures are presented in **Figure 14**, where it is possible to observe that one of the products obtained was [Cu(*p*-iPrBIAN)(PPh_3)(Cl)]NO_3 (A), almost the product desired, but a chlorine atom from the imidazolium salt bonded to the copper, hindering the second triphenylphosphine to coordinate to the metallic centre. The other crystal (B) corresponded to a double copper centred complex with the formula [Cu(PPh_3)][Cu(PPh_3)$_2$]Cl_2.

Complexes **C13** and **C14** were already reported in the literature,[104,105] so the formation of the desired products was confirmed by ^{1}H NMR. The formation of both complexes was also proven by comparing the ^{1}H NMR of the free diimines ligands with the products obtained (**Figure 15**). In both complexes, the aliphatic protons' signals do not suffer much influence after the coordination. Looking at the aromatic protons, in **C14** all the protons are shifted downfield when the complex is formed, but in **C13** this only happens to the acenaphthene protons, since the signals of the N-aryl protons are shifted upfield after the coordination.

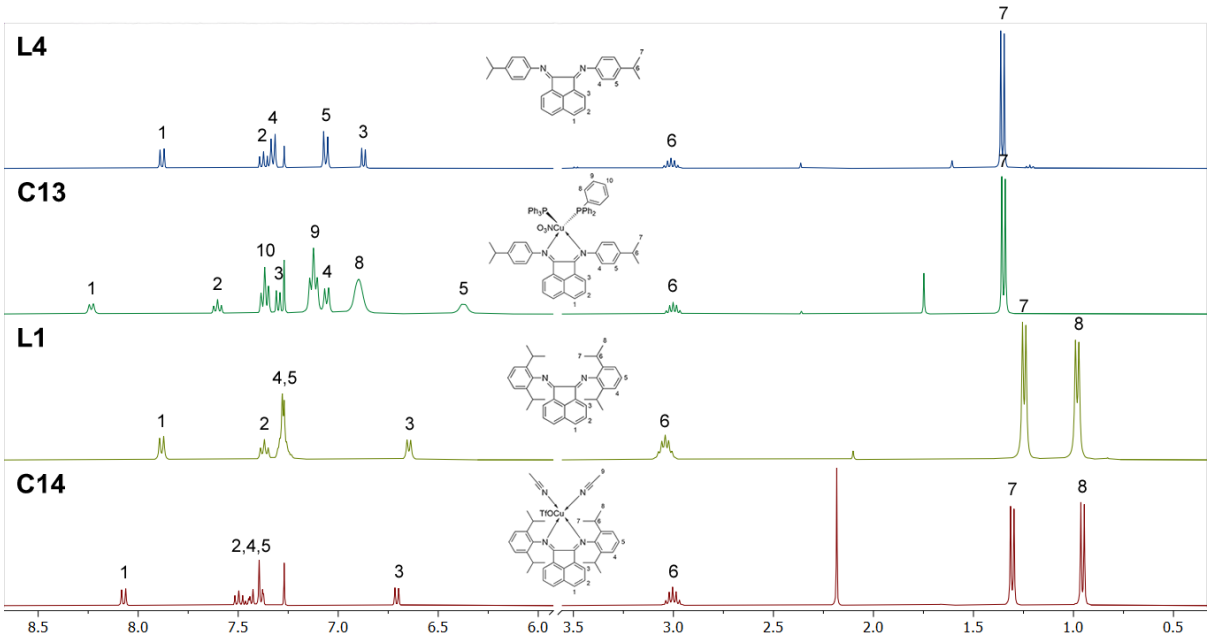


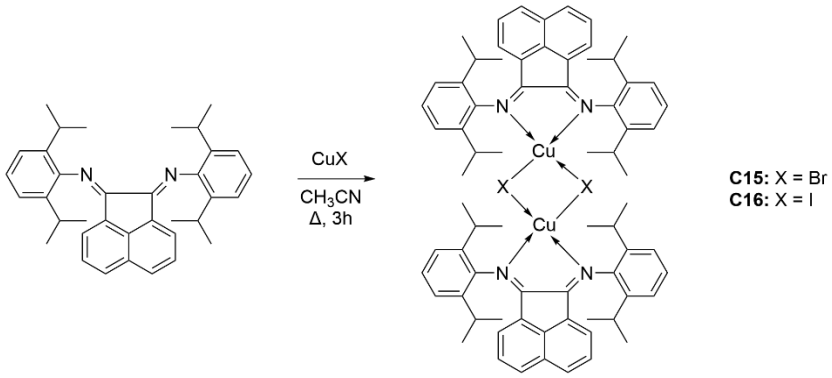
Figure 15 - Expansion of the stacked ^{1}H NMR spectra of **L4**, **C13**, **L1** and **C14** in $CDCl_3$.

2.5. Dimeric Copper(I) complexes [Cu(Ar-BIAN)X]$_2$

Two dimeric copper(I) complexes with the formula [{Cu(IDipBIAN)X}$_2$] were synthesized, aiming to test their catalytic activity in the synthesis of imines and propargylamines, since complexes of this family were tested in addition of alkynes to azides with good results.

2.5.1. Synthesis

Complexes **[Cu(IDipBIAN)Br]$_2$** (**C15**) and **[Cu(IDipBIAN)I]$_2$** (**C16**) were obtained with yields of 76 % and 44 % respectively, by reacting IDipBIAN with the respective copper(I) halide under reflux in acetonitrile for 3 hours (**Scheme 13**). The addition of the reagents and the reaction itself were carried under inert atmosphere since, as reported previously, copper(I) chloride disproportionates to Cu(0) and $CuCl_2$ in contact with water. After the reaction time, the eventual presence of remaining starting materials was removed by washing the product with pentane and diethyl ether. Both complexes were obtained in moderate to good yields.



Scheme 13 - Method for the synthesis of $[Cu(Ar\text{-}BIAN)X]_2$ complexes

2.5.2. Characterization

These two dimeric complexes were already reported in the literature,[106] so the formation of the desired products was confirmed by ^1H NMR.

Comparing the ^1H NMR spectra of **C15** and **C16** (**Figure 16**), it was possible to see that almost all the protons are more deshielded when a bromine is coordinated to the copper centre rather than a iodine, with this being more evident in the signals of *para* and *ortho* protons of the acenaphthene (at 8.01 and 6.72 ppm for **C16** versus 8.05 and 6.80 ppm for **C15**, respectively) and in the peaks corresponding to the methyl protons of the isopropyl groups (at 0.96 and 1.29 ppm for **C16** versus 1.03 and 1.36 ppm for **C15**). The exception to this effect was the heptet, which protons' nucleus were more deshielded in **C16** (3.18 ppm) than in **C15** (3.07 ppm).

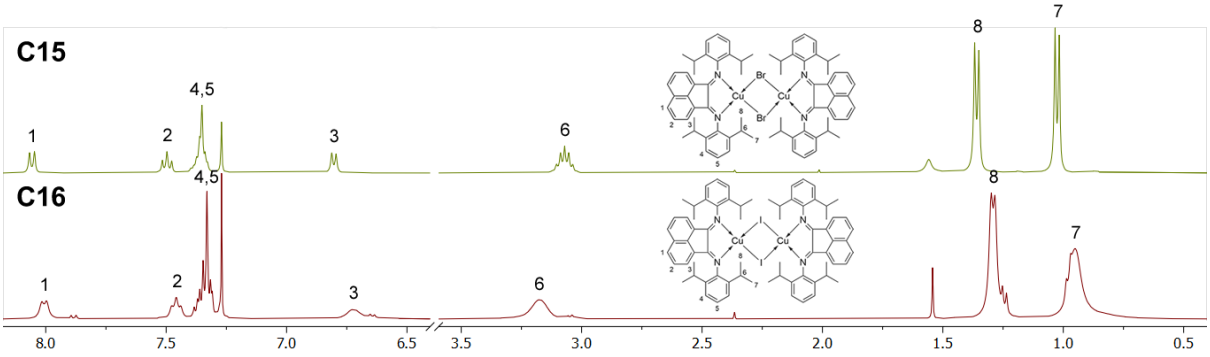


Figure 16 - Expansion of the stacked ^1H NMR spectra of **C15** and **C16** in $CDCl_3$.

2.6. Substrates

Benzaldehyde was synthesized following the Stahl procedure, to be used as substrate in the A^3 coupling.

It was synthesized via oxidation of the benzyl alcohol catalysed by complex **C14**, using a procedure reported in the literature.[107]

The reaction takes place with the copper catalyst and a co-catalyst (TEMPO) that induces the oxidation step, in the presence of a base (DMAP). The conversion rate was 100 % and the yields was near quantitative, being 99 %. The extraction process allowed the removal of remaining catalyst, co-catalyst and base.

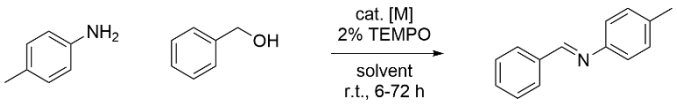
The formation of the desired product was confirmed via ^{1}H NMR (**Annex 26**). It was possible to observe a singlet at 10.06 ppm integrating for one proton, corresponding to the CHO proton, a doublet at 7.92 ppm integrating for two protons, corresponding to the *ortho* proton, and two triplets at 7.66 and 7.57 ppm integrating for one and two protons, corresponding to the *para* and *meta* protons, respectively.

2.7. Catalytic studies

The study of the catalytic activity of the synthesised complexes was split into two reactions: imine formation via direct aerobic oxidative coupling of alcohols and amines and coupling of aldehydes, amines and alcohols, noting that the first one is the first step of the second, with the particularity that it starts from an alcohol instead of an aldehyde, since it is a more accessible substrate.

2.7.1. Catalysis of Imines via Direct Aerobic Oxidative Coupling of Alcohols and Amines

Following a procedure reported in literature,[32] the reactions were carried out using *p*-toluidine and benzyl alcohol as substrates in the presence of the catalyst and the co-catalyst (TEMPO in a concentration of 2 %), as shown in **Scheme 14**.



Scheme 14 - Synthesis of benzal-*p*-toluidine via direct aerobic oxidative coupling of alcohols and amines catalysed by copper(I) complexes.

After testing some solvents and even the reaction under neat conditions, it was stated that the use of acetonitrile afforded the highest conversion rates for this reaction, using **C15** (2 mol%) as a catalyst (**Table 2**).

Table 4 - Solvent selection for the synthesis of benzal-*p*-toluidine via direct aerobic oxidative coupling of alcohols and amines catalysed by copper(I) complexes.

Entry	Time (h)	Solvent	Conversion (%)
1	24	CH_3CN	90
2	24	DCM	55
3	24	MeOH	30
4	24	neat	49

Reactions were carried out using 1.00 mmol *p*-toluidine and 1.10 mmol benzyl alcohol at 25ºC with 2 mol% TEMPO and 2 mol% catalyst.

The same catalyst (**C15**) was used in the optimization of the reaction conditions, where different catalyst concentrations and reaction times were tested, in order to find the perfect balance between these two parameters, so that the reaction matches in the best way possible the *green chemistry* principles (**Table 3**). The reaction was first tested at two different temperatures, 25 and 50 ºC, and it was determined that no heating was required, since the conversion rates were exactly the same at both temperatures. Different catalyst concentrations were experimented, from 1 to 5 mol%, and it was observed that when doubling from 1 to 2 mol%, the

conversion rates almost double as well, but higher concentrations than 2 mol% do not significantly increase the product formation. It was also detected that no matter how high the catalyst concentration was, the product formation was capped at 97 %, reaching a *plateau*, and conversion rates of 100 % were not possible to achieve. It was also observed that the reaction does not occur at all in the absence of a catalyst and, in the absence of TEMPO it occurs in an almost stoichiometric way in relation to the catalyst concentration. When increasing the reaction time from 24 to 72 hours, the conversion rates actually decrease, indicating that when the *plateau* is reached, if the reaction is extended for too much time, the imine may start to hydrolyse, reversing to amine and aldehyde. It was attempted to increase the catalyst concentration to 3 mol % and decrease the reaction time to 6 hours, obtaining a good result, but it was considered that having a lower catalyst loading even though a little higher reaction time was preferable being a more sustainable option. Having that said, it was determined that the optimal conditions for this reaction were 2 mol% of catalyst at 25 ºC for 24 hours, and the catalyst screening was undertaken (**Table 4**).

Table 5 - Optimization of the reaction conditions for the synthesis of benzal-*p*-toluidine via direct aerobic coupling of alcohols and amines catalysed by copper(I) complexes.

Entry	Catalyst mol %	Time (h)	Temperature (ºC)	Conversion (%)
1	1	24	25	53
2	1	24	50	53
3	2	24	25	90
4[a]	2	24	25	0
5[b]	2	24	25	3
6[c]	2	24	25	0
7	2	72	25	83
8	3	24	25	94
9	3	6	25	85
10	4	24	25	97
11	5	24	25	97

Reactions were carried out using 1.00 mmol *p*-toluidine and 1.10 mmol benzyl alcohol with 2 mol % TEMPO in acetonitrile; [a] No catalyst was added; [b] No TEMPO was added; [c] No catalyst and no TEMPO were added.

Complexes **C2**-**C9** and **C13**-**C16** were tested as catalysts in the imine formation via direct aerobic oxidative coupling of alcohols and amines. As observed, complexes from the BIAN-NHC copper(I) chloride family showed high conversion rates, the new [Cu(NHC)(BIAN)]PF_6 family was a disappointment with conversion rates near 0 %, **C13**'s was indeed null, **C14**'s product formation was low, showing only traces of the target compound, and the [Cu(Ar-BIAN)X]$_2$ dimers family presented very different conversion rates, with one being excellent and the other very poor.

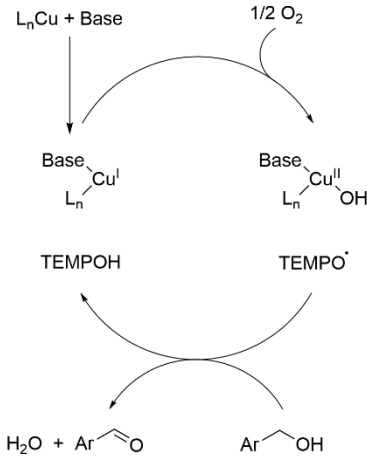
Table 6 - Catalyst screening for the synthesis of benzal-*p*-toluidine via direct aerobic oxidative coupling of alcohols and amines catalysed by copper(I) complexes.

Entry	Catalyst	Catalyst mol %	Conversion (%)
1	C2	2	70
2	C3	2	67
3	C4	2	4

4	C5	2	3
5	C6	2	2
6	C7	2	4
7	C8	2	5
8	C9	2	1
9	C13	2	0
10	C14	2	39
11	C15	2	90
12	C16	2	18

Reactions were carried out using 1.00 mmol *p*-toluidine and 1.10 mmol benzyl alcohol at 25 ºC with 2 mol% TEMPO and 2 mol% catalyst in acetonitrile for 24 hours.

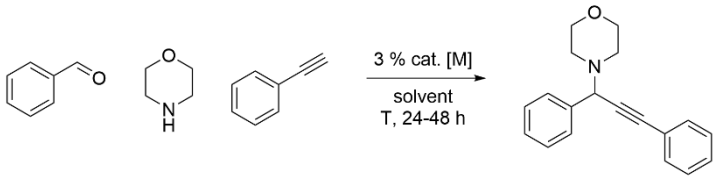
All these complexes have the acenaphthene backbone in one or both ligands, maybe granting them higher stability, but also enhancing the way substrates bond to the catalytic centre, which is very important for a catalyst to be ideal. Analysing these results, it was clear that, in this case, where there is an oxidation of the alcohol to aldehyde with its further condensation with the amine to form the imine, beyond the stability of the complex, the ligand's lability is also something that cannot be forgotten. Most authors think that the activity of the catalyst in this reaction occurs mainly during the first step, and having in mind the mechanism suggested by Stahl *et al* (**Scheme 15**),[108] it can be suggested that the [Cu(NHC)(BIAN)]PF_6 type complexes (**C4-C9**) have their ligands so strongly coordinated to the copper centre that the atmospheric oxygen, which is the oxidant, is barely able to bond to the catalytic centre, preventing the oxidation of alcohol to aldehyde, and consequently the formation of the final product, the imine. Unfortunately, due to the conversion rates being so low and similar to each other, an analysis on the influence of the presence/absence of an acenaphthene backbone in the NHC ligand and the different N-aryl groups could not be done. In the case of complex **C13**, the phosphine ligands are very sensitive to oxidation so, instead of oxidating the alcohol, oxygen oxidates them, resulting in a null conversion rate. Complex **C14** achieved low conversions conversion rates that can be justified by the fact that CH_3CN molecules are too labile, interfering with the complex's stability, that ends up decomposing in the reaction medium. BIAN-NHC copper(I) chloride complexes (**C2** and **C3**) showed good results, due to chlorine being a good leaving group but at the same time stabilizing the copper centre, since it is a halogen that forms strong ionic bonds with metals. The conversion rates obtained with complexes **C15** and **C16** were surprising and no explanation could be given to justify the huge difference between them, since further tests needed to be carried out.



Scheme 15 - Mechanism for the oxidation of alcohols to aldehydes catalysed by copper.

2.7.2. A^3 Coupling

The catalytic tests on the coupling of aldehydes, amines and alkynes followed a procedure reported in the literature.[109] The reactions were carried out using benzaldehyde, morpholine and phenylacetylene as substrates in the presence of the catalyst (3 mol%) (**Scheme 16**).



Scheme 16 - Synthesis of 1,3-diphenyl-3-morpholino-1-propyne via A^3 coupling catalysed by copper(I) complexes.

Firstly, some parameters like temperature and solvent were tested in order to achieve optimal reaction conditions, with the aim of, again, fitting the *green chemistry* principles in the best way possible (**Table 5**). Three different temperatures were tested (25, 40 and 70 ºC) and it was observed that this reaction requires heating, since no product was found for these trials at room temperature. There was an increasing of product formation when the temperature is increased from 40 to 70 ºC, but it was established that it was better to use a lower temperature, since the conversion rate at 40 ºC is relatively good, allowing to save energy, which is more sustainable according to the principles of *green chemistry*. After the solvent screening, even though the reaction in chloroform also achieved moderate conversion rates (54 %), dichloromethane was determined to be the ideal solvent, since it presented the highest conversion rates (60 %) and its boiling point is lower, making the workup procedures easier and more sustainable. Surprisingly, the reaction under neat conditions also showed moderate conversion rates (50 %) but dichloromethane was the solvent chosen, due to a better solubilization of the catalyst and ability to work with a wider range of substrates. It was also tested if the reaction could occur in the absence of a catalyst and the answer was negative.

Table 7 - Optimization of the reaction conditions for the synthesis of 1,3-diphenyl-3-morpholino-1-propyne via direct A^3 coupling catalysed by copper(I) complexes.

Entry	Solvent	Temperature (ºC)	Conversion (%)
1	DCM	70	85
2	DCM	40	60
3	DCM	25	0
4	CH_3CN	40	17
5	$CHCl_3$	40	54
6	THF	40	15
7	Toluene	40	11
8	MeOH	40	4
9	neat	40	50
10[a]	DCM	40	0

Reactions were carried out using 1.00 mmol benzaldehyde, 1.10 mmol morpholine and 1.10 mmol phenylacetylene with 3 mol% catalyst for 24 hours; [a] No catalyst was added.

Complexes **C2-C9** and **C13-C16** were tested as catalysts in the propargylamine formation via coupling of aldehydes, amines and alkynes. Analysing the results, it was possible to observe that **C13** showed almost no catalytic activity, that can be explained by the fact that the reactions were not carried out under an inert atmosphere, and since phosphines are sensitive to air, they oxidized, causing the decomposition of the catalyst in the reaction medium. When comparing the conversion rates achieved by the NHC-BIAN copper(I) chloride complexes, it was detected that for this family it preferrable that the N-aryl groups have less bulky substituents, since the product's formation was way higher with **C2** than with **C3**. It was also observed that, in a general way, conversion rates for this reaction were higher in the presence of a acenaphthene backbone in the NHC ligand for complexes of the $[Cu(NHC)(BIAN)]PF_6$ type, although, in this case, it was not possible to state the influence of the different N-aryl groups. Complex **C14** showed a relatively positive result for the A^3 coupling, despite the poor catalytic activity on the imine formation, and one possible reason for this is that the solvent being dichloromethane instead of acetonitrile, the liability of CH_3CN molecules is slightly decreased, avoiding a little more the catalyst decomposition. Again, the dimers of the $[Cu(Ar\text{-}BIAN)X]_2$ family showed a completely different catalytic activity, with complex **C15** being the best catalyst, with the highest product's formation. The complexes whose conversion rates were above 30 %, were tested on the same conditions but with the reaction time being 48 instead of 24 hours, and most of the conversions almost double, with complex **C15** achieving an almost quantitative conversion rate.

Table 8 - Catalyst screening for the synthesis of 1,3-diphenyl-3-morpholino-1-propyne via A^3 coupling catalysed by copper(I) complexes.

Entry	Catalyst	Time (h)	Conversion (%)
1	C2	24	37
2	C2	48	65
3	C3	24	2
4	C4	24	15
5	C5	24	17
6	C6	24	18

7	C7	24	32
8	C7	48	51
9	C8	24	29
10	C9	24	23
11	C13	24	3
12	C14	24	37
13	C14	48	55
14	C15	24	60
15	C15	48	95
16	C16	24	21

Reactions were carried out using 1.00 mmol benzaldehyde, 1.10 mmol morpholine and 1.10 mmol phenylacetylene at 40 ºC with 3 mol% catalyst in dichloromethane.

3. EXPERIMENTAL

3.1. General procedures

The reactions were carried out in air unless otherwise stated. The reagents and solvents used were purchased from *Sigma-Aldrich*, *Alfa Aesar*, *TCI*, *Scharlau*, *Fluka*, *Riedel-de Haën*, *Carlo Erba* and *LaborSpirit*. In the case of syntheses involving the use of Schlenk techniques, solvents previously dried in a distillation assembly with the respective drying agent were used (sodium for diethyl ether, pentane and tetrahydrofuran; calcium hydride for acetonitrile and dichloromethane). The petroleum ether used has a boiling point of between 40-60 ºC. The silica used was Silica gel 60 (0.040-0.063 mm), with a grain size of 230-400 mesh.

The IR spectra were acquired on a *Perkin-Elmer FT-IR Spectrum Two* using the ATR module without prior sample preparation. The intensity of the IR bands is described by the abbreviations w (weak), m (medium) and s (strong). The FTIR characterization is shown by: wavenumber of the transmittance maximum (band intensity, assignment).

The $^{13}C\{^{1}H\}$ NMR and 2D mono- and heteronuclear spectra were acquired on a Bruker Avance III 500 spectrometer, the $^{31}P\{^{1}H\}$ NMR spectra on a Bruker Avance III 400 spectrometer and the ^{1}H NMR spectra on both, at 25 ºC, using deuterated $CDCl_3$ as the solvent in the sample preparation, except in specific cases indicated in the characterization below. Chemical shifts are reported in ppm at low field relative to TMS using the $CDCl_3$ signal as a reference, at 7.27 ppm for ^{1}H NMR and at 77.16 ppm for $^{13}C\{^{1}H\}$ NMR.The multiplicities of the signals are abbreviated as s (singlet), d (duplet), t (triplet), hept (heptet), m (multiplet), dd (duplet of duplets) and br s (broad singlet). The coupling constants shown in the ^{1}H NMR are of the $^{3}J_{HH}$ type. The complete assignment of signals was confirmed by COSY, HSQC, HMBC and NOESY for the new compounds, which were not previously reported in the literature. The NMR characterization is presented by chemical shift (multiplicity, [coupling constant], integration, assignment) in the case of ^{1}H NMR, and chemical shift (assignment) in the other cases.

Mass spectrometry was carried out using LC Agilent 1200 Series equipment with binary pump / MS Agilent 6130B Single Quadrupole with ESI source. The LC/MS characterisation is presented by: corresponding ion m/z peak, for positive mode and negative mode with identification of the base peak by (100 %).

The elemental analysis was determined using the *Thermo Finnigan-CE Instruments Flash EA 1112 CHNS series*. EA characterization is presented by molecular formula: expected composition; obtained composition.

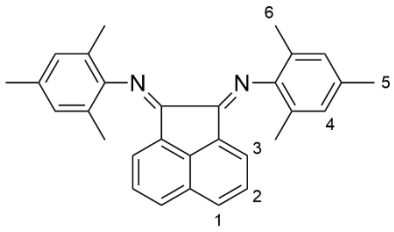
The crystal structures were determined at the Small Molecule Crystallography Service of LAQV-REQUIMTE (Chemistry Department). The single crystals were selected, coated with Fomblin oil and mounted in a nylon loop. The data were collected at 110(2) K on a *Bruker D8 Venture* diffractometer equipped with a *Photon II* detector using monochromatic Mo-K radiation (λ = 0.71073 Å) and an *Oxford Cryosystems* cold system. Crystal data and structure refinement for complexes **C6**, **C7**, **C8**, **C9** and **A** are presented in **Table 7**.

3.2. Bis(imino)acenaphthene (BIAN) ligands

The compound **bis[N-(2,6-diisopropylphenyl)imino]acenaphthene** (**L1**), already available in the laboratory, was synthesized by a procedure reported in the literature.[110] The compound **bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene** (**L2**) was synthesized following the same procedure, with slight modifications.

Bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene (L2):

To a stirred solution of acenaphthene quinone (1.60 g, 8.80 mmol) and 2,4,6-trimethylaniline (2.60 mL, 18.49 mmol, 2.10 eq.) in methanol (25 mL) was added formic acid (1 mL). The mixture was stirred overnight at room temperature. The resulting solution was extracted with water (25 mL) and dichloromethane (3 x 25 mL), the organic phases were combined, dried over anhydrous sodium sulphate, filtered and the solvents were removed by rotary evaporation. The product was obtained as an orange solid (3.49 g, 8.38 mmol, 95 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.90 (d, *J* = 8.3 Hz, 2H, 1), 7.41 (dd, *J* = 8.3, 7.2 Hz, 2H, 2), 6.98 (s, 4H, 4), 6.78 (d, *J* = 7.2 Hz, 2H, 3), 2.39 (s, 6H, 5), 2.10 (s, 12H, 6).

The compound **bis[N-(4-methylphenyl)imino]acenaphthene (L3)** was already available in the laboratory and synthesized by a procedure reported in the literature.[111] The compounds **bis[N-(4-isopropylphenyl)imino]acenaphthene** (**L4**) and **bis[N-(4-methoxyphenyl)imino]-acenaphthene (L5)** were synthesized following the same procedure, with slight modifications.

General procedure for the synthesis of BIAN ligands:

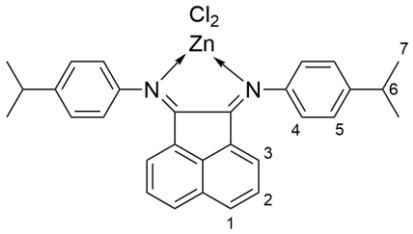
1st step: Preparation of the Zinc complex – A mixture of $ZnCl_2$ and acenaphthene quinone in acetic acid were heated to 60 ºC. Then, the desired aniline was added, and the mixture was heated under reflux (118 ºC) for half an hour. The mixture was cooled to the room temperature and filtered off, washing with acetic acid and diethyl ether.

2nd step: Demetallation – A solution of potassium oxalate in water was added to another solution of the complex **[Zn(BIAN)Cl_2]** obtained in the first step, in dichloromethane, and

stirred for 10 minutes at room temperature. The resulting suspension was extracted with water and the organic phases were combined, dried over anhydrous sodium sulphate, filtered and the solvent was removed by rotary evaporation.

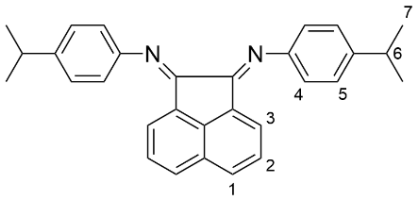
Bis[N-(4-isopropylphenyl)imino]acenaphthene (L4):

1st step: Following the general procedure, 4-isopropylaniline (2.48 mL, 18.11 mmol, 2.20 eq.) was added to $ZnCl_2$ (1.68 g, 12.35 mmol, 1.50 eq.) and acenaphthene quinone (1.50 g, 8.23 mmol) in acetic acid (7 mL). The complex **[Zn((*p*-*i*Pr-C$_6$H$_4$)$_2$BIAN)Cl$_2$]** (**L4ZnCl$_2$**) was obtained as a light-orange solid (3.60 g, 6.51 mmol, 79 % yield).



^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 8.17 (d, *J* = 2.2 Hz, 2H, 1), 7.70 – 7.60 (m, 4H, 2 and 3), 7.57 (d, *J* = 2.5 Hz, 4H, 4), 7.43 (d, *J* = 2.5 Hz, 4H, 5), 3.04 (hept, 2H, 6), 1.35 (d, *J* = 2.5 Hz, 12H, 7).

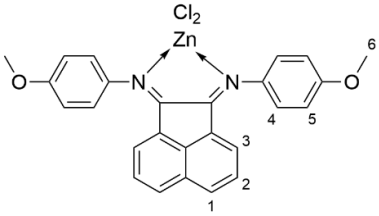
2nd step: A solution of potassium oxalate (1.11 g, 6.69 mmol) in water (10 mL) was added to another solution of the complex [Zn((*p*-*i*Pr-C$_6$H$_4$)$_2$BIAN)Cl$_2$] (2.00 g, 3.62 mmol) in dichloromethane (100 mL). The product was obtained as an orange solid (1.25 g, 2.99 mmol, 83 % yield).



^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 7.88 (d, *J* = 8.3 Hz, 2H, 1), 7.37 (dd, *J* = 8.3, 7.3 Hz, 2H, 2), 7.33 (d, 4H, 4), 7.06 (d, 4H, 5), 6.87 (d, *J* = 7.2 Hz, 2H, 3), 3.01 (hept, *J* = 6.9 Hz, 2H, 6), 1.35 (d, *J* = 6.9 Hz, 12H, 7).

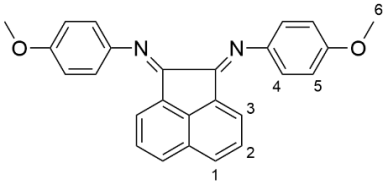
Bis[N-(4-methoxyphenyl)imino]acenaphthene (L5):

1st step: Following the general procedure, 4-methoxyaniline (1.46 mL, 11.47 mmol, 2.20 eq.) was added to $ZnCl_2$ (1.07 g, 7.82 mmol, 1.50 eq.) and acenaphthene quinone (1.00 g, 5.21 mmol) in acetic acid (5 mL). The complex **[Zn((*p*-OMe-C$_6$H$_4$)$_2$BIAN)Cl$_2$]** (**L5ZnCl$_2$**) was obtained as an orange solid (2.73 g, 5.16 mmol, 99 % yield).



^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 8.17 (d, *J* = 8.2 Hz, 2H, 1), 7.82 (d, *J* = 7.4 Hz, 2H, 3), 7.69 – 7.60 (m, 6H, 2 and 4), 7.10 (d, *J* = 8.8 Hz, 4H, 5), 3.93 (s, 6H, 6).

2nd step: A solution of potassium oxalate (1.06 g, 3.78 mmol) in water (10 mL) was added to another solution of the complex [Zn((*p*-OMe-C$_6$H$_4$)$_2$BIAN)Cl$_2$] (2.00 g, 3.78 mmol) in dichloromethane (100 mL). The product was obtained as a dark-orange solid (1.18 g, 3.01 mmol, 80 % yield).



^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 7.90 (d, *J* = 8.3 Hz, 2H, 1), 7.40 (dd, *J* = 8.3, 7.2 Hz, 2H, 2), 7.11 (d, *J* = 8.8 Hz, 4H, 4), 7.07 – 6.98 (m, 6H, 3 and 5), 3.90 (s, 6H, 6).

3.3. Bis(imino)acenaphthene (BIAN) imidazolium chlorides

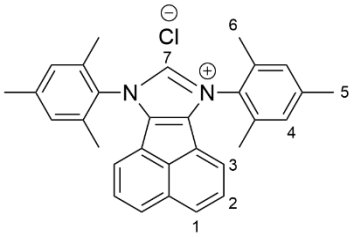
The compounds **bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene imidazolium chloride** (**S1**), **bis[N-(2,6-diisopropylphenyl)imino]acenaphthene imidazolium chloride** (**S2**) and **bis[N-(4-isopropylphenyl)imino]acenaphthene imidazolium chloride** (**S3**) were synthesized following a procedure reported in the literature,[96] with slight modifications.

General procedure for the synthesis of BIAN imidazolium chlorides:

To an argon-flushed ACE Pressure Tube containing the desired diimine, ethoxy(methyl)chloride was added, under an argon atmosphere. The mixture was stirred at 90 ºC overnight. The resulting solution was cooled to room temperature and diethyl ether was added to from a precipitate, that was filtered off, washed with diethyl ether, and dried under vacuum.

Bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene imidazolium chloride (S1):

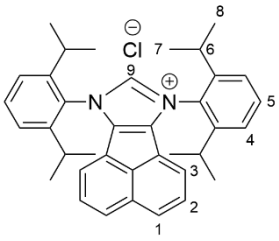
Following the general procedure, methoxy(methyl)chloride (4.65 mL, 59.05 mmol, 20.00 eq.) was added to bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene (1.23 g, 2.95 mmol). **IMesBIANCl** was obtained as a greenish-yellow solid (1.32 g, 2.83 mmol, 96 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 11.35 (s, 1H, 7), 7.98 (d, *J* = 8.3 Hz, 2H, 1), 7.57 (t, 2H, 2), 7.30 (d, *J* = 7.0 Hz, 2H, 3), 7.15 (s, 4H, 4), 2.43 (s, 6H, 5), 2.33 (s, 12H, 6).

Bis[N-(2,6-diisopropylphenyl)imino]acenaphthene imidazolium chloride (S2):

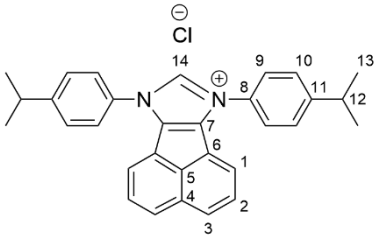
Following the general procedure, methoxy(methyl)chloride (3.18 mL, 40.34 mmol, 20.00 eq.) was added to bis[N-(2,6-diisopropylphenyl)imino]acenaphthene (1.01 g, 2.02 mmol). **IDipBIANCl** was obtained as a yellow solid (0.81 g, 1.48 mmol, 73 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 11.99 (s, 1H, 8), 8.01 (d, *J* = 8.3 Hz, 2H, 1), 7.67 (t, *J* = 7.8 Hz, 2H, 2), 7.58 (dd, *J* = 8.3, 7.0 Hz, 2H, 5), 7.47 (d, *J* = 7.9 Hz, 4H, 4), 7.23 (d, *J* = 7.0 Hz, 2H, 3), 2.73 (hept, *J* = 6.7 Hz, 4H, 6), 1.40 (d, *J* = 6.8 Hz, 12H, 7), 1.17 (d, *J* = 6.8 Hz, 12H, 8).

Bis[N-(4-isopropylphenyl)imino]acenaphthene imidazolium chloride (S3):

Following the general procedure, methoxy(methyl)chloride (3.79 mL, 48.16 mmol, 20.00 eq.) was added to bis[N-(4-isopropylphenyl)imino]acenaphthene (1.00 g, 2.41 mmol). **I*p*-*i*PrBIANCl** was obtained as a greenish-brown solid (1.03 g, 2.22 mmol, 92 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 11.31 (s, 1H, 14), 8.26 (d, *J* = 8.0 Hz, 4H, 9), 8.02 (d, *J* = 8.2 Hz, 2H, 3), 7.88 (d, *J* = 7.1 Hz, 2H, 1), 7.69 – 7.57 (m, 6H, 2 and 10), 3.07 (hept, *J* = 7.0 Hz, 2H, 12), 1.35 (d, *J* = 6.9 Hz, 12H, 13).

^{13}C{^{1}H} RMN (126 MHz, $CDCl_3$) δ (ppm): 152.12 (11), 138.39 (14), 135.54 (8), 131.70 (7), 130.66 (6), 130.45 (3), 129.94 (5), 128.70 (10), 127.94 (2), 123.80 (1), 123.46 (4), 123.41 (9), 34.06 (12), 23.83 (13).

IR ATR υ (cm^{-1}): 2958 (w, C-H); 1531 (m, C=N); 1506 (m, C=N); 1418 (m, C-N); 820 (s); 767 (s); 557 (s).

Elemental Analysis (%) for $C_{31}H_{29}ClN_2.3/5CH_2Cl_2$: calcd. C 73.56, H 5.90, N 5.43; found C 73.97, H 6.30, N 5.46.

LC/MS (CH_3CN/H_2O) *m/z*: Positive mode: 429.2 [**S3**-Cl]$^+$ (100%).

3.4. N-Heterocyclic Carbene (NHC) Copper(I) complexes

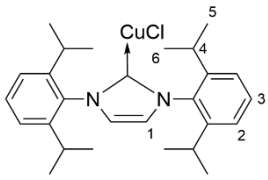
The compounds **[Cu(IDip-NHC)]Cl (C1), [Cu(IMesBIAN-NHC)]Cl (C2)** and **[Cu(IDip-BIAN-NHC)]Cl (C3)** were synthesized following a procedure reported in the literature,[101] with slight modifications.

General procedure for the synthesis of [Cu(NHC)Cl] complexes:

Using Schlenk techniques, bis(imino)acenaphthene imidazolium chloride was added to an argon-flushed Schlenk flask containing CuCl and K_2CO_3. The mixture was heated under reflux (60 ºC) in acetone overnight. Then the resulting solution was filtered off and washed with dichloromethane. Hexane was added and the solution was cooled to 0 ºC. The solid precipitate was filtered to collect the desired product, that was dried under vacuum.

[Cu(IDip-NHC)]Cl (C1):

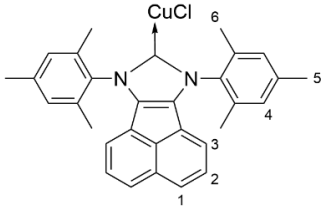
Following the general procedure, bis[N-(2,6-diisopropylphenyl)] imidazolium chloride (1.00 g, 2.35 mmol) was added to CuCl (0.23 g, 2.35 mmol, 1.00 eq.) and K_2CO_3 (0.65 g, 4.69 mmol, 2.00 eq.) in acetone (8 mL), obtaining **[Cu(IDip-NHC)Cl]** as a white solid (0.95 g, 1.95 mmol, 83 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.50 (t, *J* = 7.8 Hz, 2H, 3), 7.31 (d, *J* = 7.8 Hz, 4H, 2), 7.14 (s, 2H, 1), 2.57 (hept, *J* = 6.8 Hz, 4H, 4), 1.31 (d, *J* = 6.9 Hz, 12H, 6), 1.24 (d, *J* = 6.9 Hz, 12H, 5).

[Cu(IMesBIAN-NHC)]Cl (C2):

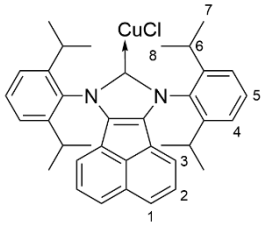
Following the general procedure, bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene imidazolium chloride (0.50 g, 1.08 mmol) was added to CuCl (0.11 g, 1.08 mmol, 1.00 eq.) and K_2CO_3 (0.30 g, 2.15 mmol, 2.00 eq.) in acetone (4 mL), obtaining **[Cu(IMesBIAN-NHC)Cl]** as a dark-brown solid (0.34 g, 0.65 mmol, 61 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.80 (d, *J* = 8.3 Hz, 2H, 1), 7.43 (dd, *J* = 8.3, 7.0 Hz, 2H, 2), 7.11 (s, 4H, 4), 7.07 (d, *J* = 7.3 Hz, 2H, 3), 2.43 (s, 6H, 5), 2.23 (s, 12H, 6).

[Cu(IDipBIAN-NHC)]Cl (C3):

Following the general procedure, bis[N-(2, 6-diisopropylphenyl)imino]acenaphthene imidazolium chloride (0.50 g, 0.91 mmol) was added to CuCl (0.09 g, 0.91 mmol, 1.00 eq.) and K_2CO_3 (0.25 g, 1.82 mmol, 2.00 eq.) in acetone (4 mL), obtaining **[Cu(IDipBIAN-NHC)Cl]** as a solid (0.44 g, 0.73 mmol, 80 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.81 (d, *J* = 8.3 Hz, 2H, 1), 7.60 (t, *J* = 7.8 Hz, 2H, 5), 7.48–7.38 (m, 6H, 2 and 4), 7.01 (d, *J* = 7.0 Hz, 2H, 3), 2.85 (hept, *J* = 6.9 Hz, 4H, 6), 1.36 (d, *J* = 6.9 Hz, 12H, 8), 1.13 (d, *J* = 6.8 Hz, 12H, 7).

3.5. Heteroleptic Copper(I) complexes

3.5.1. [Cu(NHC)(BIAN)]PF_6

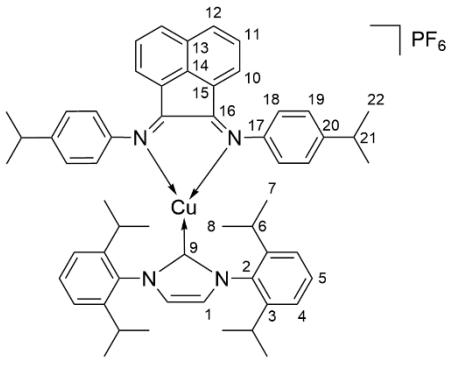
The compounds **[Cu(IDip-NHC)(*p*-*i*PrBIAN)]PF_6 (C4)**, **[Cu(IDip-NHC)(*p*-MeBIAN)]PF_6 (C5)**, **[Cu(IDip-NHC)(*p*-OMeBIAN)]PF_6 (C6)**, **[Cu(IDipBIAN-NHC)(*p*-*i*PrBIAN)]PF_6 (C7)**, **[Cu(IDipBIAN-NHC)(*p*-MeBIAN)]PF_6 (C8)** and **[Cu(IDipBIAN-NHC)(*p*-OMeBIAN)]PF_6 (C9)** were synthesized following a procedure reported in the literature,[112] with slight modifications.

General procedure for the synthesis of [Cu(NHC)(BIAN)]PF_6 complexes:

To an argon-flushed Schlenk flask containing KPF_6 was added the [Cu(NHC)Cl] complex and the diimine ligand, using Schlenk techniques. The mixture was stirred under argon atmosphere in THF at room temperature for 24 hours. Then the solution was filtered through Schlenk techniques to another Schlenk flask and the THF was evaporated. Dried dichloromethane was added and again the solution was filtered to another Schlenk, and dried pentane was added, letting the compound precipitate. Finally, the solvents were evaporated, and the solid precipitate was dried under vacuum.

[Cu(IDip-NHC)(*p*-*i*PrBIAN)]PF_6 (C4):

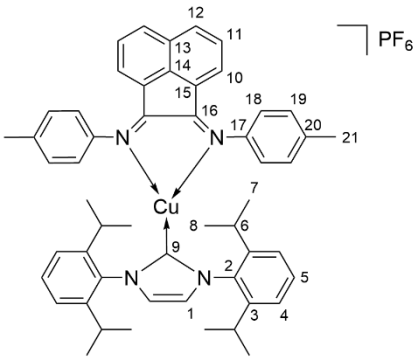
Following the general procedure, [Cu(IDip-NHC)Cl] (0.20 g, 0.41 mmol) and bis[N-(4-isopropylphenyl)imino]acenaphthene (0.17 g, 0.41 mmol, 1.00 eq.) were added to KPF_6 (0.75 g, 4.10 mmol, 10.00 eq.) in THF (10 mL), obtaining **[Cu(IDip-NHC)(*p*-*i*PrBIAN)][PF_6]** as a dark-green solid (0.19 g, 0.19 mmol mmol, 45 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.04 (d, *J* = 8.2 Hz, 2H, 12), 7.59 (t, *J* = 7.8 Hz, 2H, 5), 7.42 (dd, *J* = 8.3, 7.3 Hz, 2H, 11), 7.26 – 7.18 (m, 8H, 4 and 18), 7.16 (s, 2H, 1), 6.56 (d, *J* = 7.3 Hz, 2H, 10), 6.29 (d, *J* = 8.3 Hz, 4H, 19), 3.05 (hept, *J* = 7.0 Hz, 2H, 21), 2.63 (hept, *J* = 6.9 Hz, 4H, 6), 1.40 (d, *J* = 6.9 Hz, 12H, 22), 1.14 (d, *J* = 6.8 Hz, 12H, 8), 0.85 (d, *J* = 6.9 Hz, 12H, 7).

[Cu(IDip-NHC)(*p*-MeBIAN)]PF_6 (C5):

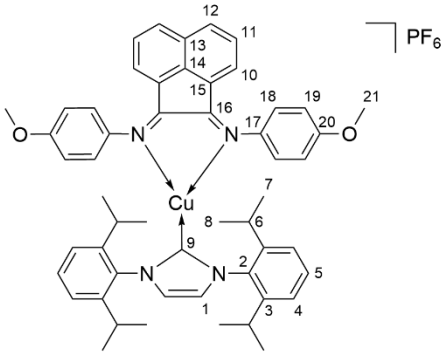
Following the general procedure, [Cu(IDip-NHC)Cl] (0.20 g, 0.41 mmol) and bis[N-(4-methylphenyl)imino]acenaphthene (0.15 g, 0.41 mmol, 1.00 eq.) were added to KPF_6 (0.75 g, 4.10 mmol, 10.00 eq.) in THF (10 mL), obtaining **[Cu(IDip-NHC)(*p*-MeBIAN)][PF_6]** as a dark-green solid (0.25 g, 0.26 mmol, 63 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.04 (d, *J* = 8.2 Hz, 2H, 12), 7.56 (t, *J* = 7.8 Hz, 2H, 5), 7.43 (dd, *J* = 8.3, 7.4 Hz, 2H, 11), 7.24 (d, *J* = 7.8 Hz, 4H, 4), 7.15 - 7.17 (m, 6H, 1 and 18), 6.63 (d, *J* = 7.3 Hz, 2H, 10), 6.27 (d, *J* = 8.1 Hz, 4H, 19), 2.62 (hept, *J* = 7.0 Hz, 4H, 6), 2.49 (s, 6H, 21), 1.14 (d, *J* = 6.8 Hz, 12H, 8), 0.87 (d, *J* = 6.9 Hz, 12H, 7).

[Cu(IDip-NHC)(*p*-OMeBIAN)]PF_6 (C6):

Following the general procedure, [Cu(IDip-NHC)Cl] (0.15 g, 0.30 mmol) and bis[N-(4-methoxyphenyl)imino]acenaphthene (0.12 g, 0.30 mmol, 1.00 eq.) were added to KPF_6 (0.55 g, 2.97 mmol, 10.00 eq.) in THF (10 mL), obtaining **[Cu(IDip-NHC)(*p*-OMeBIAN)][PF_6]** as a dark-green solid (0.18 g, 0.18 mmol, 60 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.04 (d, *J* = 8.3 Hz, 2H ,12), 7.59 (t, *J* = 7.8 Hz, 2H, 5), 7.46 (dd, *J* = 8.3, 7.4 Hz, 2H, 11), 7.29 (d, *J* = 2.5 Hz, 4H, 4), 7.17 (s, 2H, 1), 6.90 (d, *J* = 8.7 Hz, 4H, 18), 6.72 (d, *J* = 7.3 Hz, 2H, 10), 6.33 (d, *J* = 8.8 Hz, 4H, 19), 3.97 (s, 6H, 21), 2.65 (hept, *J* = 7.0 Hz, 4H, 6), 1.17 (d, *J* = 6.9 Hz, 12H, 8), 0.92 (d, *J* = 6.9 Hz, 12H, 7).

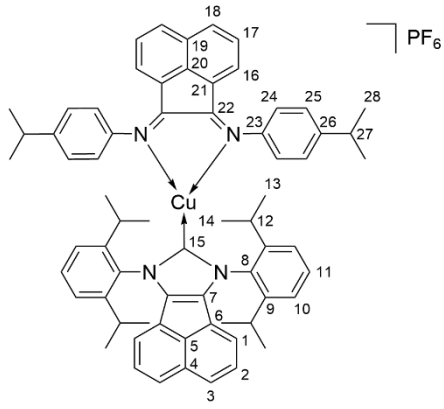
IR ATR υ (cm^{-1}): 2962 (w, C-H); 1575 (w, C=N); 1504 (m, C=C); 1465 (w, C-N); 1445 (w, C-N); 1244 (m, C-O); 837 (s, C-H); 761 (m, C-H); 557 (m, P-F).

Elemental Analysis (%) for $C_{53}H_{56}CuF_6N_4O_2P.1/4CH_2Cl_2$: calcd. C 63.28, H 5.63, N 5,54; found C 63.32, H 5.80, N 5.48.

LC/MS (CH_3CN/H_2O) *m/z*: Positive mode: 843.3 [**C7**-PF_6]$^+$ (20%); 393.1 [**L5**+H]$^+$ (25%).

[Cu(IDipBIAN-NHC)(*p*-*i*PrBIAN)]PF_6 (C7):

Following the general procedure, [Cu(IDipBIAN-NHC)Cl] (0.15 g, 0.25 mmol) and bis[N-(4-isopropylphenyl)imino]acenaphthene (0.1 g, 0.25 mmol, 1.00 eq.) were added to KPF_6 (0.45 g, 2.45 mmol, 10.00 eq.) in THF (10 mL), obtaining **[Cu(IDip-BIAN-NHC)(*p*-*i*PrBIAN)][PF_6]** as a dark-green solid (0.19 g, 0.16 mmol, 66 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.07 (d, *J* = 8.3 Hz, 2H, 18), 7.81 (d, *J* = 8.3 Hz, 2H, 3), 7.73 (t, *J* = 7.8 Hz, 2H, 11), 7.48 – 7.41 (m, 4H, 2 and 17), 7.38 (d, *J* = 7.8 Hz, 4H, 10), 7.24 (d, *J* = 8.3 Hz, 4H, 24), 6.98 (d, *J* = 6.9 Hz, 2H, 1), 6.61 (d, *J* = 7.3 Hz, 2H, 16), 6.34 (d, *J* = 8.0 Hz, 4H, 25), 3.07

(hept, *J* = 6.9 Hz, 2H, 27), 2.90 (hept, *J* = 6.9 Hz, 4H, 12), 1.41 (d, *J* = 6.9 Hz, 12H, 28), 1.05 (d, *J* = 6.8 Hz, 12H, 14), 0.88 (d, *J* = 6.9 Hz, 12H, 13).

$^{13}C\{^{1}H\}$ RMN (126 MHz, $CDCl_3$) δ (ppm): 187.08 (15), 167.21 (22), 147.78 (7), 145.31 (23), 145.12 (8), 144.06 (9), 138.57 (26), 133.99 (5), 131.98 (18), 131.10 (20), 130.73 (24), 130.43 (4), 129.84 (11), 128.62 (19), 128.58 (3) 128.38 (17), 127.85 (2), 125.77 (16), 125.38 (21), 125.27 (6), 125.00 (10), 120.97 (1), 119.23 (25), 33.85 (27), 28.62 (12), 24.26 (28), 23.89 (13), 23.11 (14).

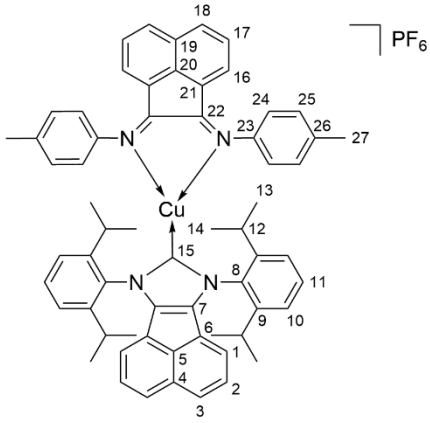
IR ATR υ (cm^{-1}): 2962 (w, C-H); 1581 (w, C=N); 1463 (w, C-N); 1441 (w, C-N); 838 (s, C-H); 771 (m, C-H); 556 (m, P-F).

Elemental Analysis (%) for $C_{67}H_{68}CuF_6N_4P$ (1136.44): calcd. C 70.73, H 6.02, N 4.92; found C 70.24, H 6.05, N 4.84.

LC/MS (CH_3CN/H_2O) *m/z*: Positive mode: 991.4 $[C7\text{-}PF6]^+$ (30%); 616.3 [**C3**+MeCN-Cl]$^+$ (100%); 417.2 [**L4**+H]$^+$ (42%).

[Cu(IDipBIAN-NHC)(*p*-MeBIAN)]PF_6 (C8):

Following the general procedure, [Cu(IDipBIAN-NHC)Cl] (0.14 g, 0.23 mmol) and bis[N-(4-methylphenyl)imino]acenaphthene (0.08 g, 0.23 mmol, 1.00 eq.) were added to KPF_6 (0.42 g, 2.29 mmol, 10.00 eq.) in THF (10 mL), obtaining **[Cu(IDipBIAN-NHC)(*p*-MeBIAN)][PF_6]** as a dark-green solid (0.14 g, 0.13 mmol, 56 % yield).



^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.06 (d, *J* = 8.3 Hz, 2H, 18), 7.81 (d, *J* = 8.3 Hz, 2H, 3), 7.68 (t, *J* = 7.8 Hz, 2H, 11), 7.53 – 7.39 (m, 4H, 2 and 17), 7.37 (d, *J* = 7.8 Hz, 4H, 10), 7.19 (d, *J* = 7.9 Hz, 4H, 24), 6.97 (d, *J* = 7.0 Hz, 2H, 1), 6.64 (d, *J* = 7.3 Hz, 2H, 16), 6.33 (d, *J* = 8.2 Hz, 4H, 25), 2.89 (hept, *J* = 6.9 Hz, 4H, 12), 2.58 (s, 6H, 27), 1.05 (d, *J* = 6.8 Hz, 12H, 14), 0.91 (d, *J* = 6.9 Hz, 12H, 13).

$^{13}C\{^{1}H\}$ RMN (126 MHz, $CDCl_3$) δ (ppm): 186.98 (15), 167.20 (22), 145.02 (23), 144.01 (8), 138.63 (9), 136.77 (26), 133.91 (5), 131.93 (18), 131.07 (20), 130.92 (24), 130.75 (4), 130.43 (11), 129.84 (19), 128.59 (3), 128.57 (17), 127.82 (2), 125.85 (16), 125.39 (21), 125.26 (6), 125.02 (10), 121.02 (1), 119.27 (25), 28.65 (12), 23.94 (13), 23.25 (14), 21.15 (27).

IR ATR υ (cm^{-1}): 2962 (w, C-H); 1579 (w, C=N); 1461 (w, C-N); 1443 (w, C-N); 829 (s, C-H); 773 (m, C-H); 556 (m, P-F).

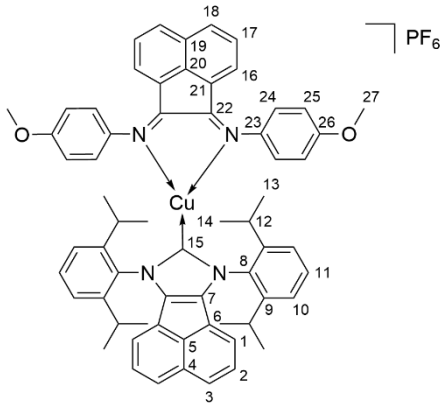
Elemental Analysis (%) for $C_{63}H_{60}CuF_6N_4P$ (1080.38): calcd. C 69.95, H 5.59, N 5.18; found C 69.96, H 5.64, N 5.11.

LC/MS (CH_3CN/H_2O) *m/z*: Positive mode: 935.4 [**C8**-PF_6]$^+$ (30%); 616.3 [**C3**+MeCN-Cl]$^+$ (100%); 361.1 [**L3**+H]$^+$ (32%). Negative mode: 145.0 (100 %) $[PF_6]^-$.

[Cu(DipBIAN-NHC)(*p*-OMeBIAN)]PF_6 (C9):

Following the general procedure, [Cu(IDipBIAN-NHC)Cl] (0.10 g, 0.16 mmol) and bis[N-(4-methoxyphenyl)imino]acenaphthene (0.06 g, 0.16 mmol, 1.00 eq.) were added to KPF_6 (0.30 g, 1.63 mmol, 10.00 eq.) in THF (10 mL), obtaining **[Cu(IDipBIAN-NHC)(*p*-OMeBIAN)][PF_6]** as a dark-green solid (0.06 g, 0.06 mmol, 35 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.05 (d, *J* = 8.3 Hz, 2H, 18), 7.81 (d, *J* = 8.3 Hz, 2H, 3), 7.70 (t, *J* = 7.8 Hz, 2H, 11), 7.50 – 7.36 (m, 8H, 2, 10 and 17), 6.97 (d, *J* = 6.9 Hz, 2H, 1), 6.92 (d, *J* = 8.8 Hz, 4H, 24), 6.71 (d, *J* = 7.3 Hz, 2H, 16), 6.37 (d, *J* = 8.7 Hz, 4H, 25), 3.98 (s, 6H, 27), 2.90 (hept, *J* = 6.8 Hz, 4H, 12), 1.06 (d, *J* = 6.8 Hz, 12H, 14), 0.95 (d, *J* = 6.9 Hz, 12H, 13).



^{13}C{^{1}H} RMN (126 MHz, $CDCl_3$) δ (ppm): 186.97 (15), 167.41 (22), 158.52 (7), 145.05 (23), 143.89 (8), 140.59 (9), 138.66 (26), 133.94 (5), 131.81 (18), 131.08 (20), 130.76 (4), 130.52 (11), 129.84 (19), 128.60 (3), 128.57 (17), 127.83 (2), 125.71 (16), 125.54 (21), 125.27 (6), 125.07 (10), 121.02 (1), 120.82 (24), 115.62 (25), 55.93 (27), 28.68 (12), 23.99 (13), 23.23 (14).

Elemental Analysis (%) for $C_{63}H_{60}CuF_6N_4O_2P$ (1112.36): calcd. C 67.94, H 5.43, N 5.03; found C 67.62, H 5.50, N 4.99.

LC/MS (CH_3CN/H_2O) *m/z*: Positive mode: 967.3 [**C9**-PF_6]$^+$ (12%); 616.3 [**C3**+MeCN-Cl]$^+$ (100%); 393.2 [**L5**+H]$^+$ (30%). Negative mode: 145.0 (100 %) [PF_6]$^-$.

3.5.2. [Cu(BIAN-NHC)(PPh_3)$_2$]NO_3

The compounds **[Cu(IMesBIAN-NHC)(PPh_3)$_2$]NO_3 (C10)**, **[Cu(IDipBIAN-NHC)(PPh_3)$_2$]NO_3 (C11)** and **[Cu(I*p*-*i*PrBIAN-NHC)(PPh_3)$_2$]NO_3 (C12)** were tried to synthesize following a procedure similar to the one used in the synthesis of NHC copper(I) complexes, with slight modifications.

General procedure for the synthesis of [Cu(BIAN-NHC)(PPh_3)$_2$]NO_3 complexes:

Using Schlenk techniques, the desired bis(imino)acenaphthene imidazolium chloride was added to an argon-flushed Schlenk flask containing Cu(PPh_3)$_2NO_3$ and K_2CO_3. The mixture was left stirring at 40 ºC dry dichloromethane overnight. Then the resulting solution was filtered to another Schlenk, and pentane was added in order to precipitate. The solution was filtered again, collecting the solid precipitate, that was dried under vacuum.

Attempt of [Cu(IMesBIAN-NHC)(PPh_3)$_2$]NO_3 (C10):

Following the general procedure, bis[N-(2,4,6-trimethylphenyl)imino]acenaphthene imidazolium chloride (0.10 g, 0.22 mmol) was added to Cu(PPh_3)$_2NO_3$ (0.14 g, 0.22 mmol, 1.00 eq.) and K_2CO_3 (0.06 g, 0.43 mmol, 2.00 eq.) in dry dichloromethane (1 mL). The product obtained was a mixture of other compounds than the desired one, as explained in the discussion, so the characterization was not made.

Attempt of [Cu(IDipBIAN-NHC)(PPh_3)$_2$]NO_3 (C11):

Following the general procedure, bis[N-(2,6-diisopropylphenyl)imino]acenaphthene imidazolium chloride (0.10 g, 0.18 mmol) was added to Cu(PPh_3)$_2NO_3$ (0.12 g, 0.18 mmol, 1.00 eq.) and K_2CO_3 (0.05 g, 0.36 mmol, 2.00 eq.) in dry dichloromethane (1 mL). The product obtained was a mixture of other compounds than the desired one, as explained in the discussion, so the characterization was not made.

Attempt of [Cu(I*p*-*i*PrBIAN-NHC)(PPh_3)$_2$]NO_3 (C12):

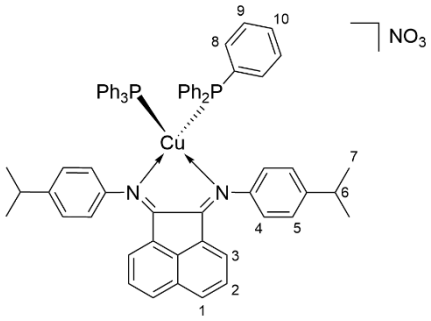
Following the general procedure, bis[N-(4-isopropylphenyl)imino]acenaphthene imidazolium chloride (0.09 g, 0.19 mmol) was added to Cu(PPh_3)$_2NO_3$ (0.12 g, 0.19 mmol, 1.00 eq.) and K_2CO_3 (0.05 g, 0.37 mmol, 2.00 eq.) in dry dichloromethane (1 mL). The product obtained was a mixture of other compounds than the desired one, as explained in the discussion, so the characterization was not made.

3.5.3. [Cu(DipBIAN)(PPh_3)$_2$]NO_3

The compound **[Cu(*p*-*i*PrBIAN)(PPh_3)$_2$]NO_3 (C13)** was synthesized following a procedure reported in the literature,[104] with slight modifications.

Using Schlenk techniques, bis[N-(4-isopropylphenyl)imino]acenaphthene (0.10 g, 0.24 mmol) was added to [Cu(PPh_3)$_2$]NO_3 (0.16 g, 0.24 mmol, 1.00 eq.) in an argon-flushed Schlenk flask in dichloromethane (4 mL). The mixture was left stirring at room temperature for 2 hours and then was filtered to another Schlenk. Dry pentane was added in order to precipitate. After filtration, **[Cu(*p*-*i*PrBIAN)(PPh_3)$_2$]NO_3** was obtained as a reddish-brown solid (0.22 g, 0.20 mmol, 84 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.23 (d, *J* = 8.3 Hz, 2H, 1), 7.60 (t, *J* = 7.8 Hz, 2H, 2), 7.37 (t, *J* = 7.5 Hz, 6H, 10), 7.30 (d, *J* = 7.3 Hz, 2H, 3), 7.12 (t, *J* = 7.6 Hz, 12H, 9), 7.06 (d, *J* = 8.0 Hz, 4H, 4), 6.90 (br s, 12H, 8), 6.37 (br s, 4H, 5), 3.00 (hept, *J* = 7.0 Hz, 2H, 6), 1.35 (d, *J* = 6.9 Hz, 12H, 7).

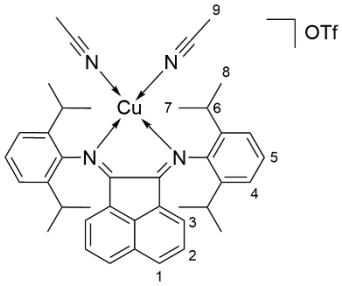


3.5.4. [Cu(DipBIAN)(CH_3CN)$_2$]NO_3

The compound **[Cu(DipBIAN)(CH_3CN)$_2$]OTf (C14)** was synthesized following a procedure reported in the literature,[105] with slight modifications.

Using Schlenk techniques, bis[N-(2,6-diisopropylphenyl)imino]acenaphthene (0.30 g, 0.60 mmol) was added to an argon-flushed Schlenk flask containing a suspension of [Cu(CH_3CN)$_4$]OTf (0.23 g, 0.60 mmol, 1.00 eq.) in dichloromethane (10 mL). The mixture was left stirring at room temperature overnight and then filtered through activated celite, washing with pentane. The solution was concentrated, and dry pentane was added in order to induce precipitation. After filtration, **[Cu(DipBIAN)(CH_3CN)$_2$]OTf** was obtained as a brown solid (0.40 g, 0.50 mmol, 84 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.07 (d, *J* = 8.2 Hz, 2H, 1), 7.54 – 7.35 (m, 8H, 2; 4 and 5), 6.71 (d, *J* = 7.2 Hz, 2H, 3), 3.00 (hept, *J* = 6.9 Hz, 4H, 6), 2.18 (s, 6H, 9), 1.31 (d, *J* = 6.8 Hz, 12H, 7), 0.95 (d, *J* = 6.9 Hz, 12H, 8).



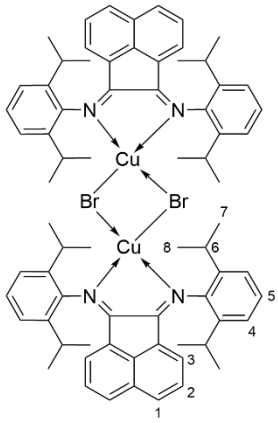
3.6. Dimeric Copper(I) complexes [Cu(Ar-BIAN)X]$_2$

The compounds **[Cu(DipBIAN)Br]$_2$ (C15)** and **[Cu(DipBIAN)I]$_2$ (C16)** were synthesized following a procedure reported in the literature,[113] with slight modifications.

General procedure for the synthesis of [{Cu(IDipBIAN)X}$_2$] complexes:

To an argon-flushed Schlenk flask containing CuX was added the diimine, using Schlenk techniques. The mixture was heated under reflux and stirred under argon atmosphere in acetonitrile for 3 hours. Then, the solvent was evaporated, and the solid obtained was washed with pentane and diethyl ether and dried under vacuum.

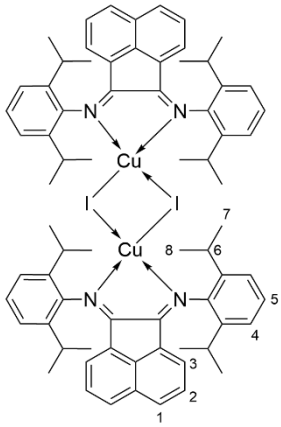
[Cu(DipBIAN)Br]$_2$ (C15):



Following the general procedure, bis[N-(2,6-diisopropylphenyl)imino]acenaphthene (0.40 g, 0.80 mmol) was added to CuBr (0.11 g, 0.80 mmol, 1.00 eq.) in acetonitrile (25 mL), obtaining **[{Cu(DipBIAN)Br}$_2$]** as a dark-purple solid (0.40 g, 0.63 mmol, 79 % yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 8.06 (d, *J* = 8.3 Hz, 4H, 1), 7.50 (t, *J* = 7.8 Hz, 4H, 2), 7.41 – 7.31 (m, 12H, 4 and 5), 6.80 (d, *J* = 7.2 Hz, 4H, 3), 3.07 (hept, *J* = 6.9 Hz, 8H, 6), 1.36 (d, *J* = 6.7 Hz, 24H, 8), 1.03 (d, *J* = 6.8 Hz, 24H, 7).

[Cu(DipBIAN)I]$_2$ (C16):



Following the general procedure, bis[N-(2,6-diisopropylphenyl)imino]acenaphthene (0.30 g, 0.60 mmol) was added to CuI (0.11 g, 0.60 mmol, 1.00 eq.) in acetonitrile (20 mL), obtaining **[{Cu(IDipBIAN)I}$_2$]** as a dark-blue solid (0.18 g, 0.26 mmol, 44 % yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 8.01 (d, *J* = 8.3 Hz, 4H, 1), 7.46 (t, *J* = 7.9 Hz, 4H, 2), 7.41 – 7.29 (m, 12H, 4 and 5), 6.72 (br s, 4H, 3), 3.18 (br s, 8H, 6), 1.29 (d, *J* = 6.7 Hz, 24H, 8), 0.95 (d, *J* = 9.3 Hz, 24H, 7).

3.7. Substrates for the catalytic tests

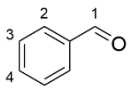
3.7.1. Benzaldehyde

Benzaldehyde was synthesized following a procedure reported in the literature,[107] with slight modifications.

A flask was charged with benzyl alcohol (0.96 mL, 9.25 mmol), TEMPO (0.07 g, 0.46 mmol, 0.05 eq.) and [Cu(DipBIAN)(MeCN)$_2$]OTf (0.07 g, 0.09 mmol, 0.01 eq.) in dry acetonitrile (10 mL). Then, DMAP (0.11 g, 0.92 mmol, 0.10 eq.) was added to the reaction mixture, and it was left stirring for 3 hours. The resulting solution was extracted with water and pen-

tane, combining the organic layers, which were dried over anhydrous sodium sulphate, filtered and the solvent was removed by rotary evaporation, affording **benzaldehyde** as an orange oil (0.97 g, 9.12 mmol, 99 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 10.06 (s, 1H), 7.92 (d, 2H), 7.66 (t, 1H), 7.57 (t, J = 7.5 Hz, 2H).



3.8. Catalytic tests

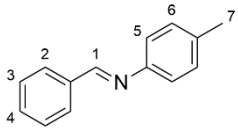
3.8.1. Catalysis of Imines via Direct Aerobic Oxidative Coupling of Alcohols and Amines

The catalytic tests for the synthesis of imines via direct aerobic oxidative coupling of alcohols and amines were carried out following a procedure reported in the literature.[32]

General procedure for the catalytic synthesis of imines from alcohols and amines:

A catalysis tube was charged with *p*-toluidine (0.10 g, 1.00 mmol) and benzyl alcohol (0.11 mL, 1.10 mmol, 1.10 eq.) in a determined solvent (0.25 mL). Then TEMPO (2 mol%) and the catalyst were added. The solution was left stirring at room temperature for a certain reaction time and, after that, the resulting mixture was filtered through activated aluminium oxide, previously washed with triethylamine (0.10 mL), washing with a solvent mixture of petroleum ether:ethyl acetate 10:1 and then the solvents were rotary evaporated. The conversion rate of the reactions was determined via ^{1}H NMR, even though the product was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.49 (s, 1H, 1), 7.92-7.68 (m, 2H, 2), 7.50-7.40 (m, 3H, 4 and 5), 7.35 (d, J = 8.4 Hz, 2H, 6), 7.23 (d, J = 8 Hz, 2H, 3), 2.42 (s, 3H, 7).



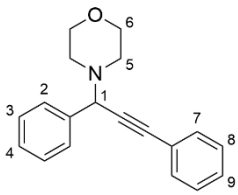
3.8.2. Catalysis of Propargylamines via A^3 Coupling

The catalytic tests for the synthesis of propargylamines via coupling of aldehydes, amines and alkynes were carried out following a procedure reported in the literature.[109]

General procedure for the catalytic synthesis of propargylamines from aldehydes, amines and alkynes:

A catalysis tube was charged with benzaldehyde (0.05 mL, 0.50 mmol), morpholine (0.05 mL, 0.55 mmol, 1.10 eq.) and phenylacetylene (0.06 mL, 0.55 mmol, 1.10 eq.) in a determined solvent (0.25 mL). Then the catalyst (3 mol%) was added and the solution was left stirring at an established temperature for a selected reaction time. After that, the resulting mixture was filtered through silica, washing with a solvent mixture of petroleum ether:ethyl acetate 3:2 and then the solvents were rotary evaporated. The conversion rate of the reactions was determined via ^{1}H NMR, even though the product was not isolated.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.66 (d, J = 7.5 Hz, 2H, 7), 7.59–7.49 (m, 2H, 2), 7.42–7.31 (m, 6H, 3; 4; 8 and 9), 4.81 (s, 1H, 1), 3.82–3.68 (m, 4H, 6), 2.71-2.60 (m, 4H, 5).



4.

CONCLUSIONS AND FUTURE PERSPECTIVES

Several copper(I) complexes were synthesized in this work, including NHC copper chlorides, BIAN complexes (dimeric and monomeric) and a whole family of heteroleptic complexes with four completely new compounds that were not published yet, having a NHC ligand and a BIAN ligand. These novel complexes were obtained with yields that are not ideal but considering this was the first time they were tried to synthesize, they can be seen as moderate to good. In a future perspective, in order to increase these yields, the synthesis of these complexes could be carried out for longer reaction times or maybe using higher temperatures to increase the unbounding of chlorine to the copper atom, so the BIAN ligand coordination is increased.

These copper(I) complexes all had their catalytic activity tested on two reactions: the imine formation via direct aerobic oxidation of alcohols and amines and the propargylamine formation via coupling of aldehydes, amines and alkynes. The activity of the $[Cu(NHC)(BIAN)]PF_6$ family whose complexes were the focus of this thesis was disappointing since the conversion rates were low. The complex that ended up being the most effective in both reactions was $[Cu(DipBIAN)Br]_2$, allowing us to speculate if they could be carried out in only one-pot reaction starting from the alcohol, amine and alkyne to form the propargylamine, since a bridge can be made between them, because the formation of an imine is the intermediate step of the synthesis of a propargylamine via A^3 coupling.

Finally, both reaction systems could be optimized, exploring the different parameters, combining different temperatures, reaction times and catalyst concentrations, studying what solvents better solubilize which solvents, in order to find the perfect balance and comply as much as possible with the principles of *green chemistry*, so the laboratory work is the most sustainable possible. Another future perspective is to use different substrates, varying their substituents so a wide range of compounds with relevance and interest can be synthesized. Another important thing is to optimize and develop a better workup system, in order to isolate the products as pure as possible, since in this work only conversion rates were obtained because it was not possible to isolate them.

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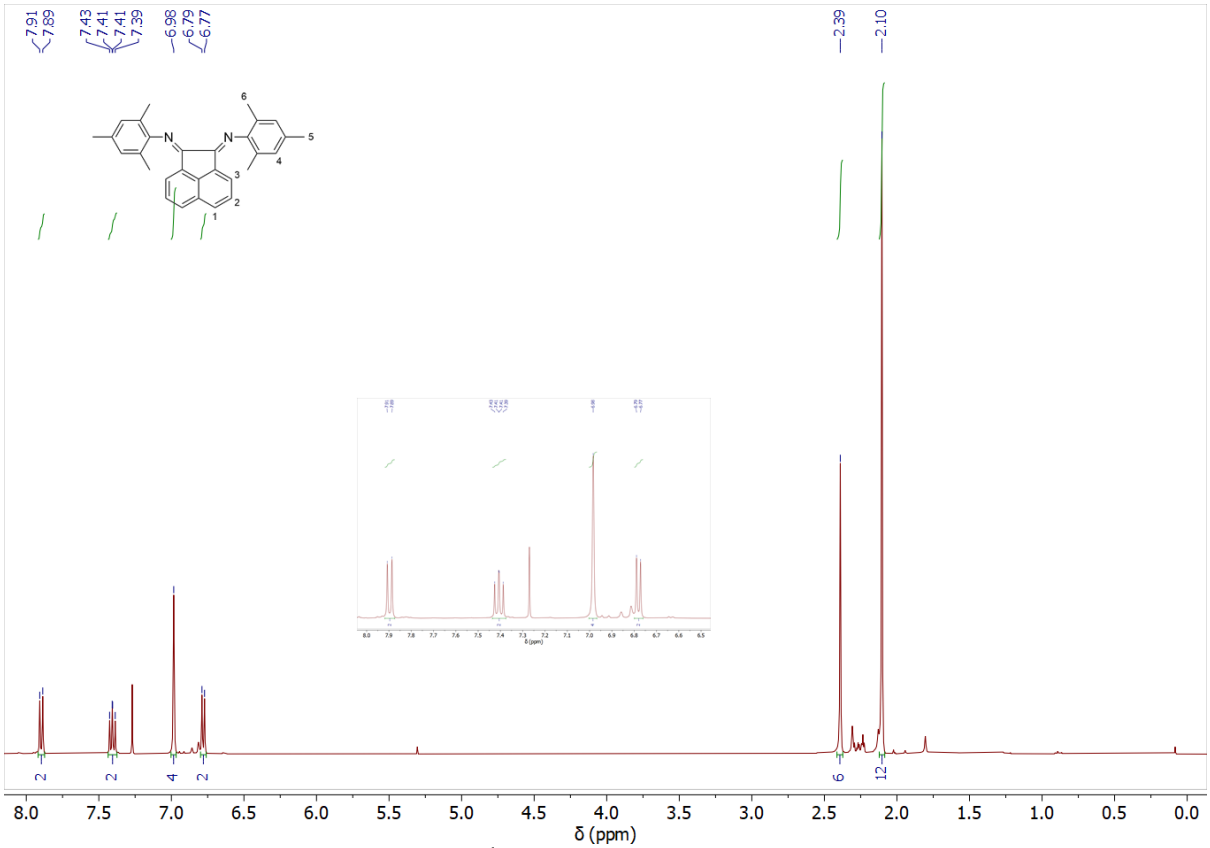
A.

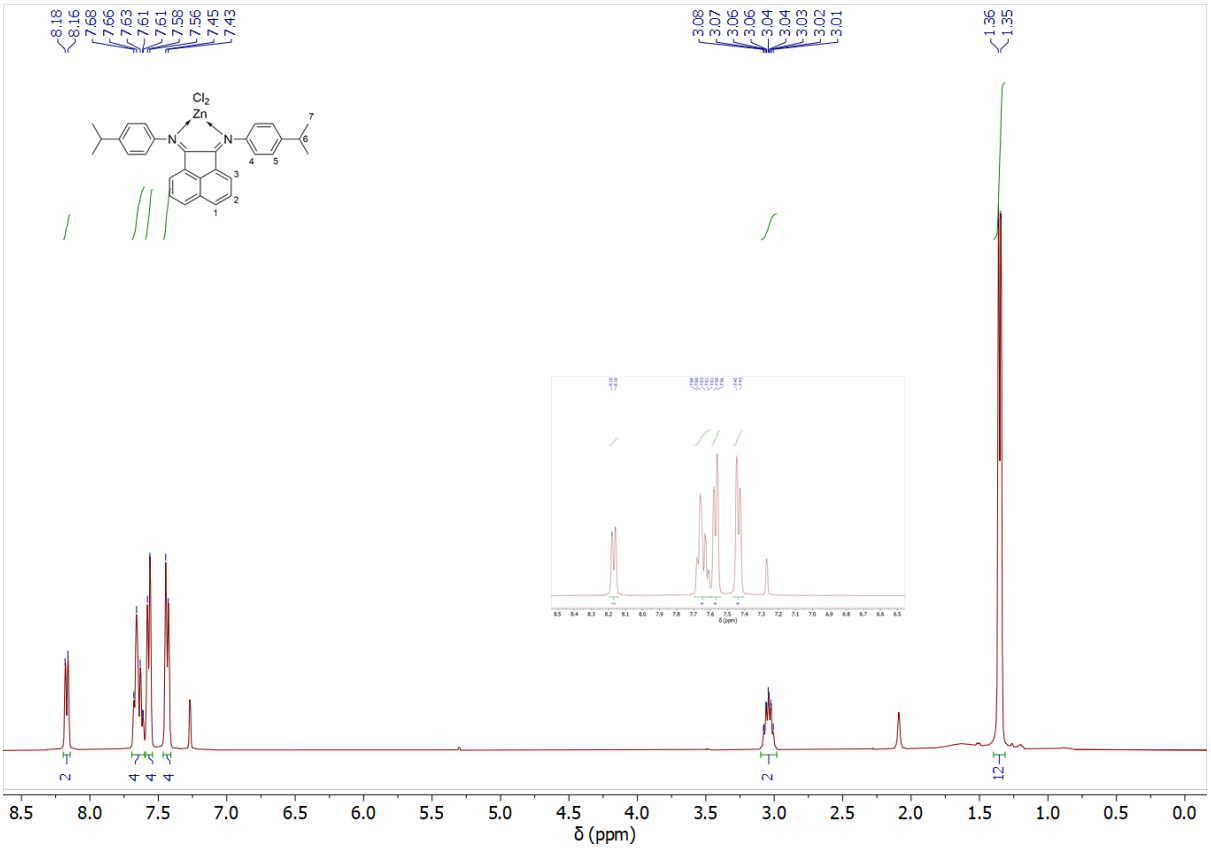
APPENDIX

	C6	**C7**	**C8**	**C9**	**A**
Formula	$C_{109}H_{118}Cl_6Cu_2F_{12}N_8O_4P_2$	$C_{70}H_{74}Cl_6CuF_6N_4P$	$C_{67}H_{68}CuF_6N_4P$	$C_{63}H_{60}CuF_6N_4O_2P$	$C_{49}H_{43}ClCuN_2P$
M	2233.83	1392.54	1421.37	1113.66	789.81
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	110(2)	110(2)	110(2)	110(2)	110(2)
crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$
Crystal description	Prism	Block	Needle	Prism	Plate
Crystal colour	Green	Bronze	Bronze	Bronze	Orange
a (Å)	19.586(3)	14.148(5)	23.107(6)	23.638(3)	9.1702(8)
b (Å)	25.216(4)	16.998(5)	23.871(6)	23.832(3)	10.2598(10)
c (Å)	22.317(3)	17.151(6)	14.012(3)	14.0714(17)	21.779(2)
α (deg)	90	88.882(11)	90	90	96.036(3)
β (deg)	99.125(5)	68.809(11)	119.355(7)	120.026(5)	98.303(3)
γ (deg)	90	69.801(11)	90	90	91.320(3)
V (Å3)	10882(3)	3583(2)	6737(3)	6863.1(16)	2014.8(3)
Z	4	2	4	4	2
ρ_{calc} (g cm^{-3})	1.363	1.291	1.401	1.078	1.302
μ (mm^{-1})	0.643	0.608	0.725	0.397	0.685
θ_{max} (deg)	27.149	26.359	27.911	25.681	26.002
total data	371372	182086	187408	133905	130378
unique data	24012	13942	8046	6518	7904
R_{int}	0.2136	0.3624	0.1649	0.0825	0.1102
R [I>3σ(I)]	0.0982	0.1295	0.0933	0.0821	0.0551
wR2	0.1974	0.3269	0.2390	0.2216	0.1425
Goodness of fit	1.008	1.216	1.100	1.055	1.085
ρ min	-0.945	-1.105	-1.661	-1.159	-0.510
ρ max	0.979	2.339	2.289	2.932	0.599

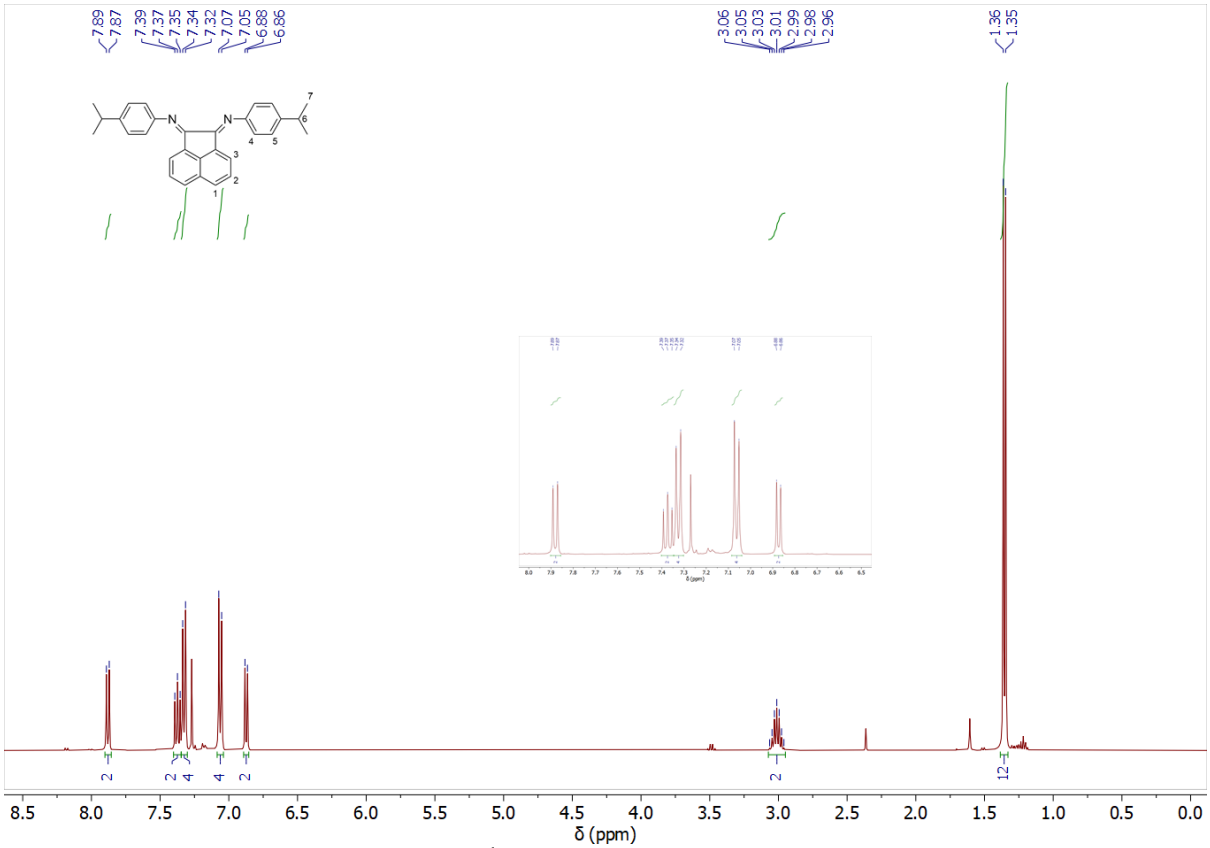
Table 6. Crystal data and structure refinement for complexes **C6**, **C7**, **C8**, **C9** and **A**.



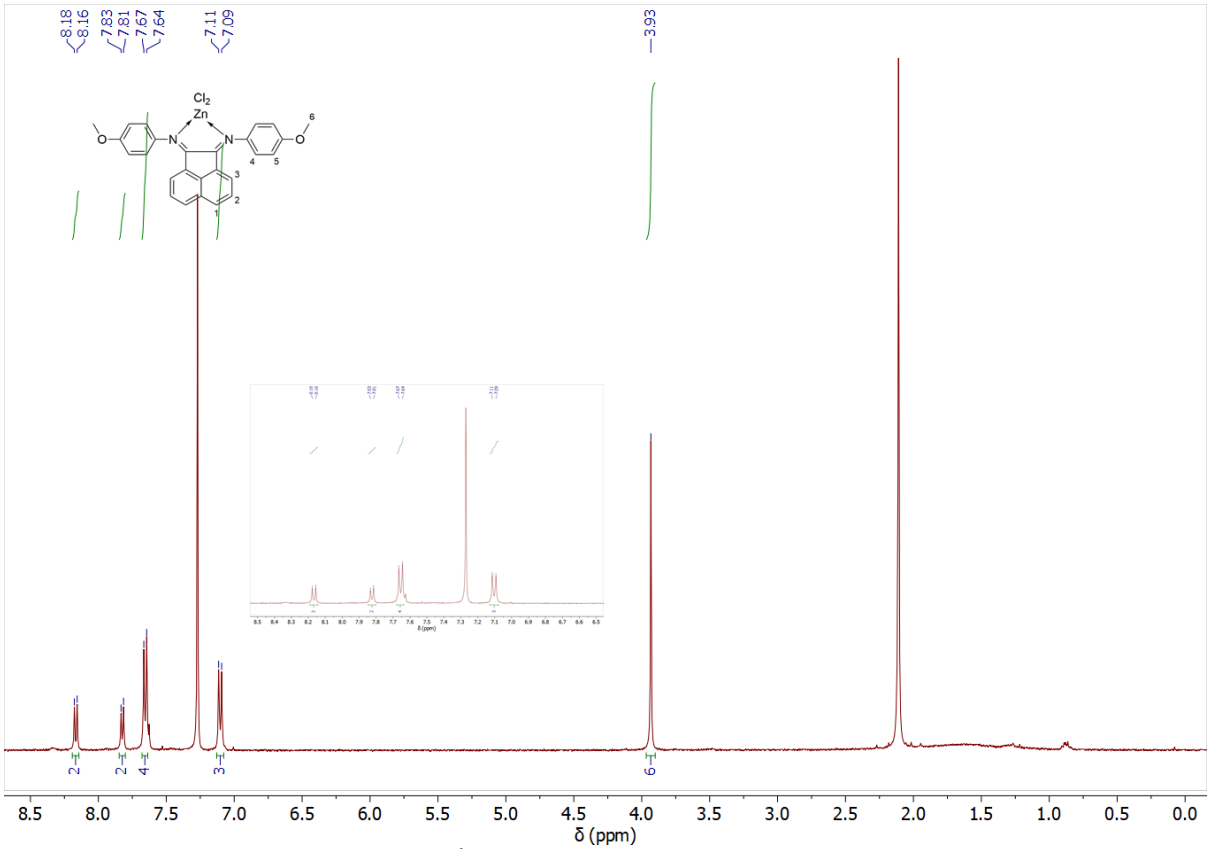
Annex 1 - ^{1}H NMR spectra of **L2** in $CDCl_3$.



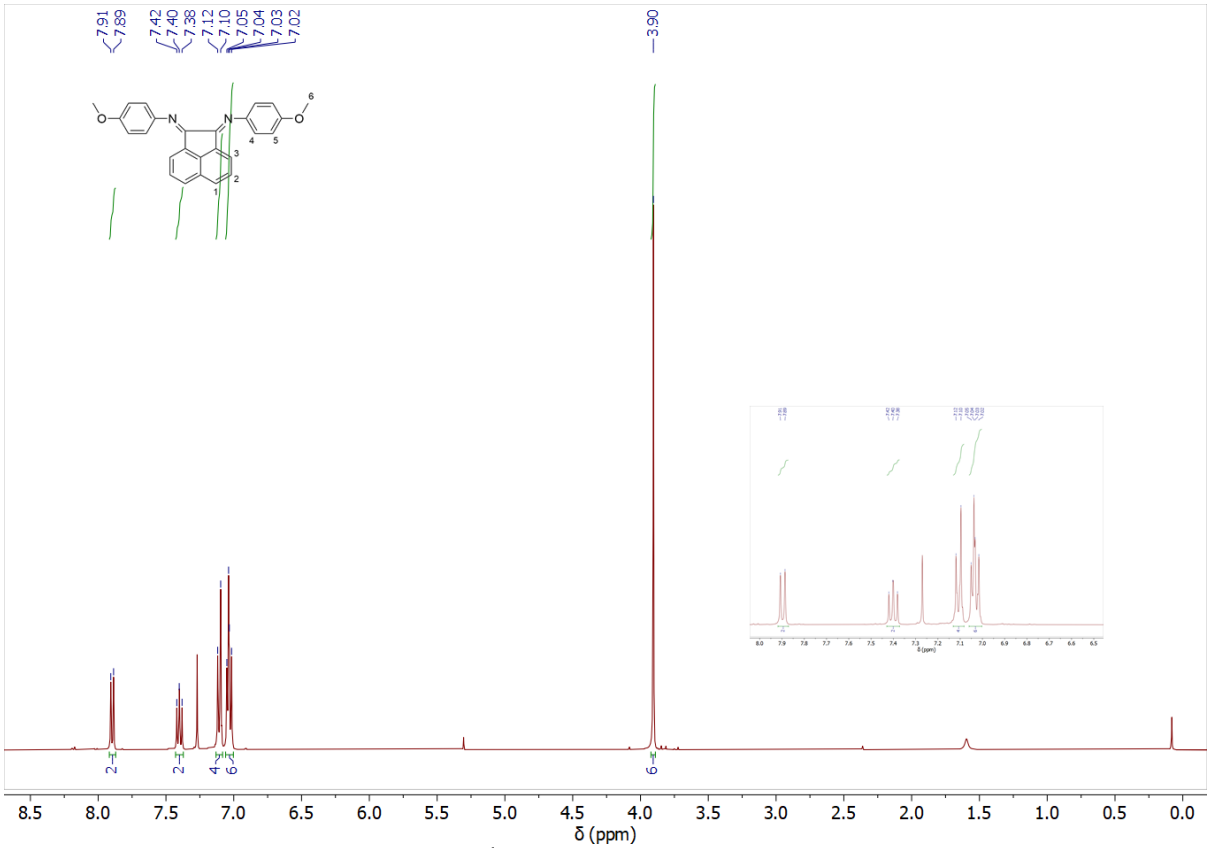
Annex 2 - ^{1}H NMR spectra of **L4ZnCl₂** in $CDCl_3$.



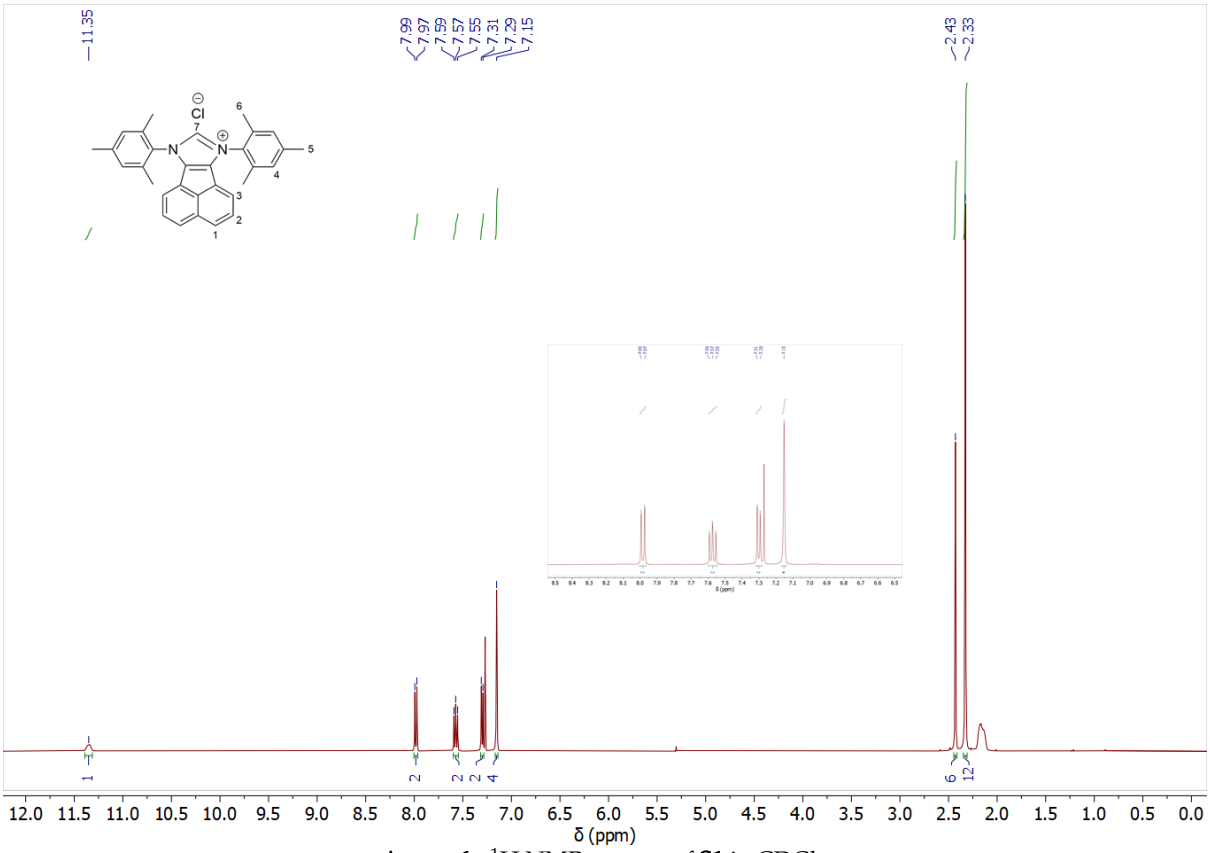
Annex 3 - ^{1}H NMR spectra of **L4** in $CDCl_3$.



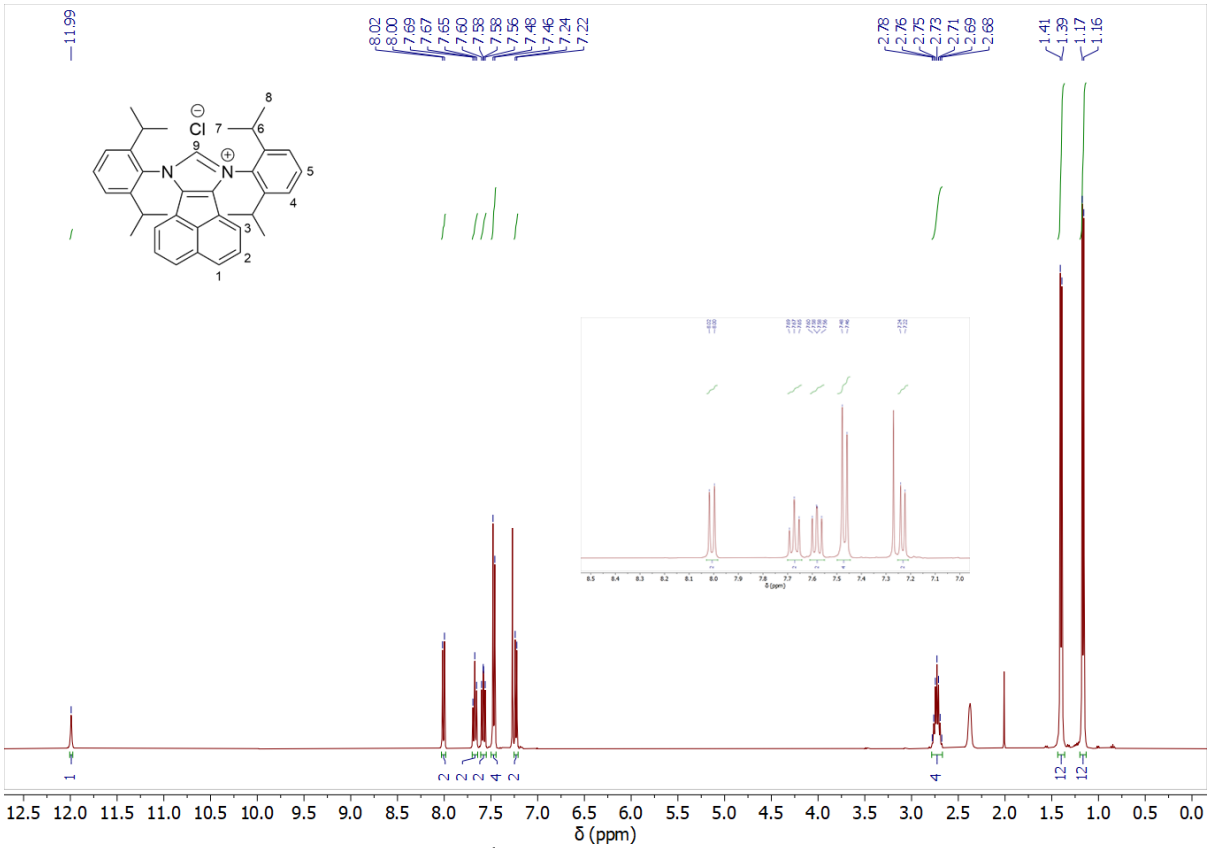
Annex 4 - ^{1}H NMR spectra of **L5ZnCl2** in $CDCl_3$.



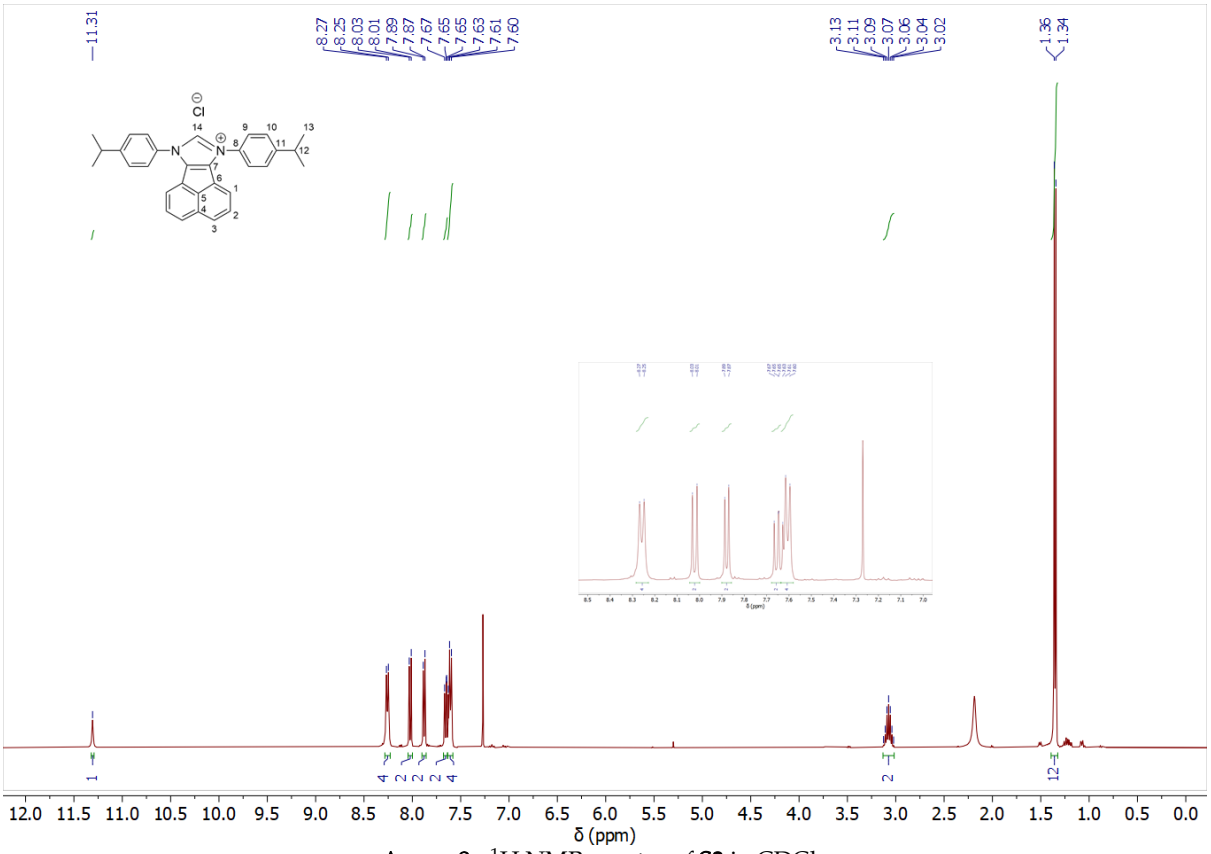
Annex 5 - ^{1}H NMR spectra of **L5** in $CDCl_3$.



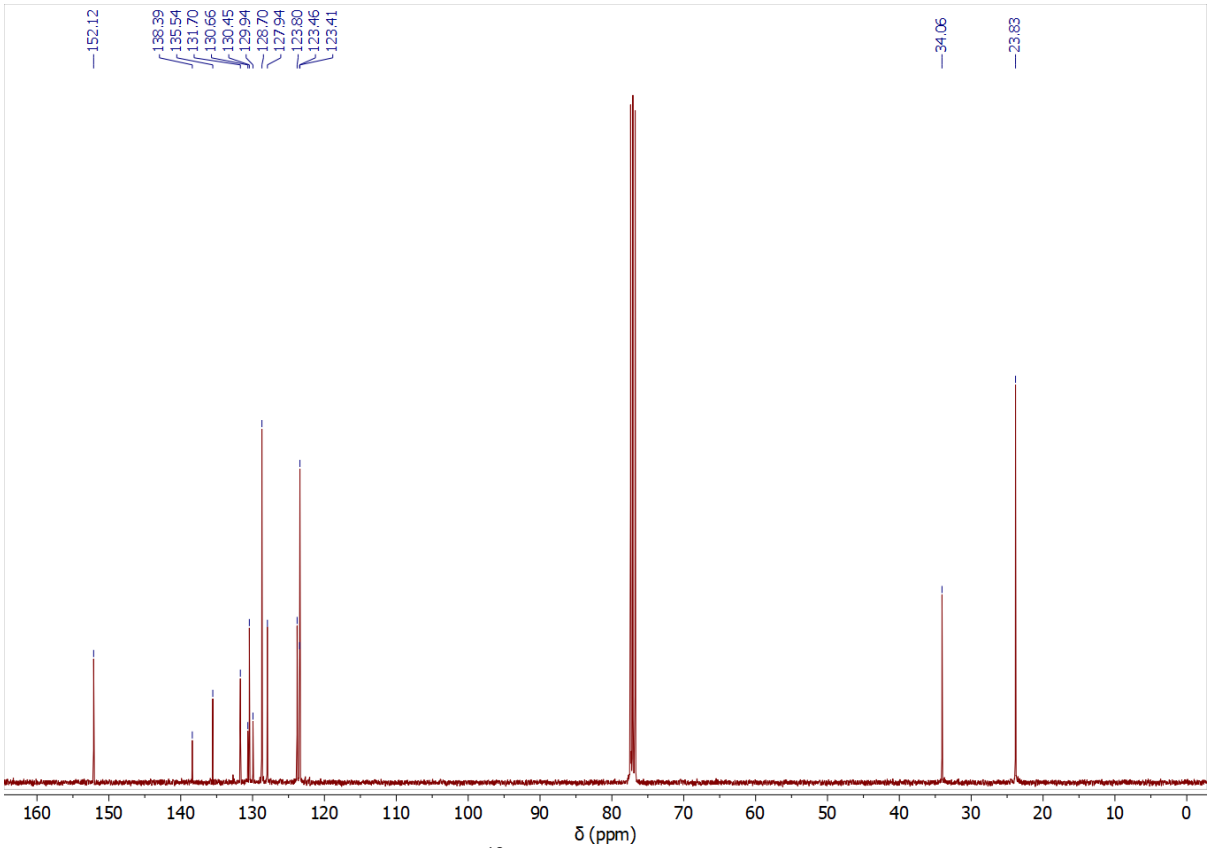
Annex 6 - ^{1}H NMR spectra of **S1** in $CDCl_3$.



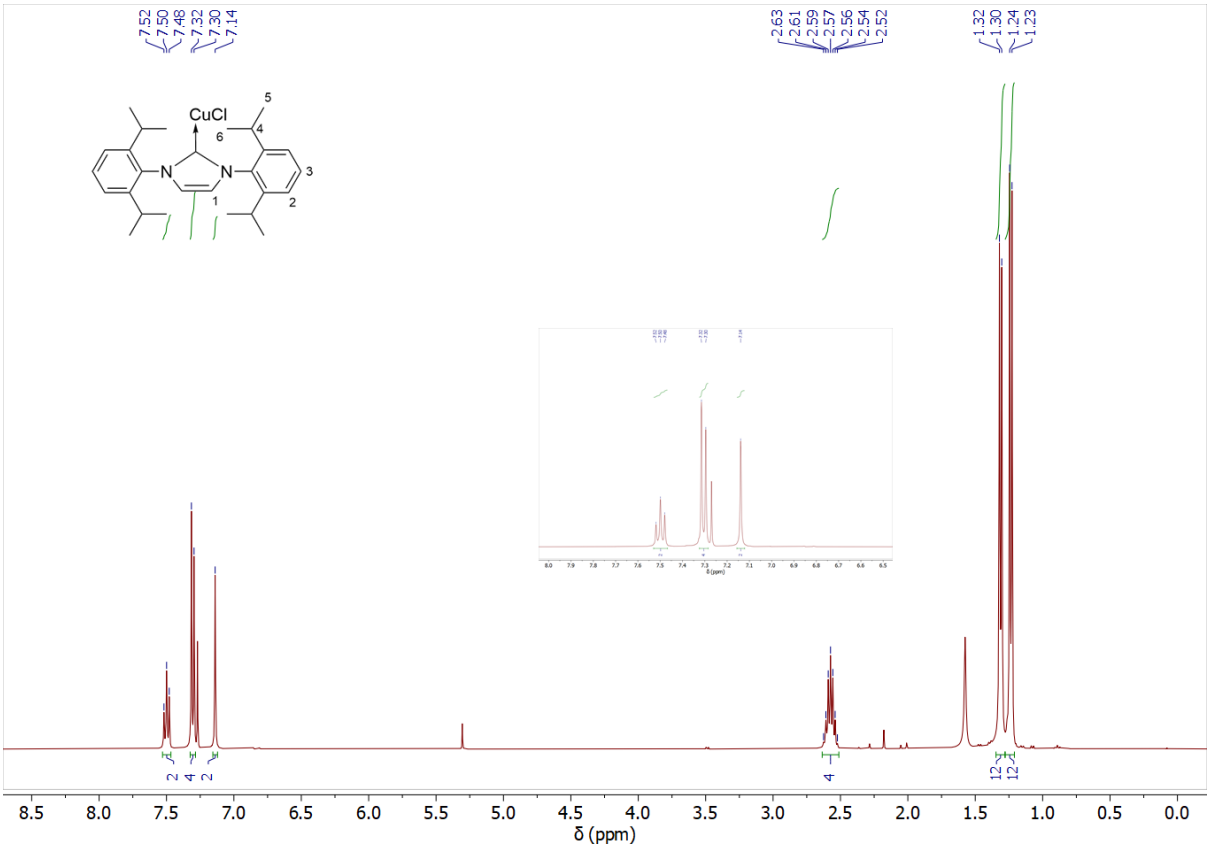
Annex 7 - ^{1}H NMR spectra of **S2** in $CDCl_3$.



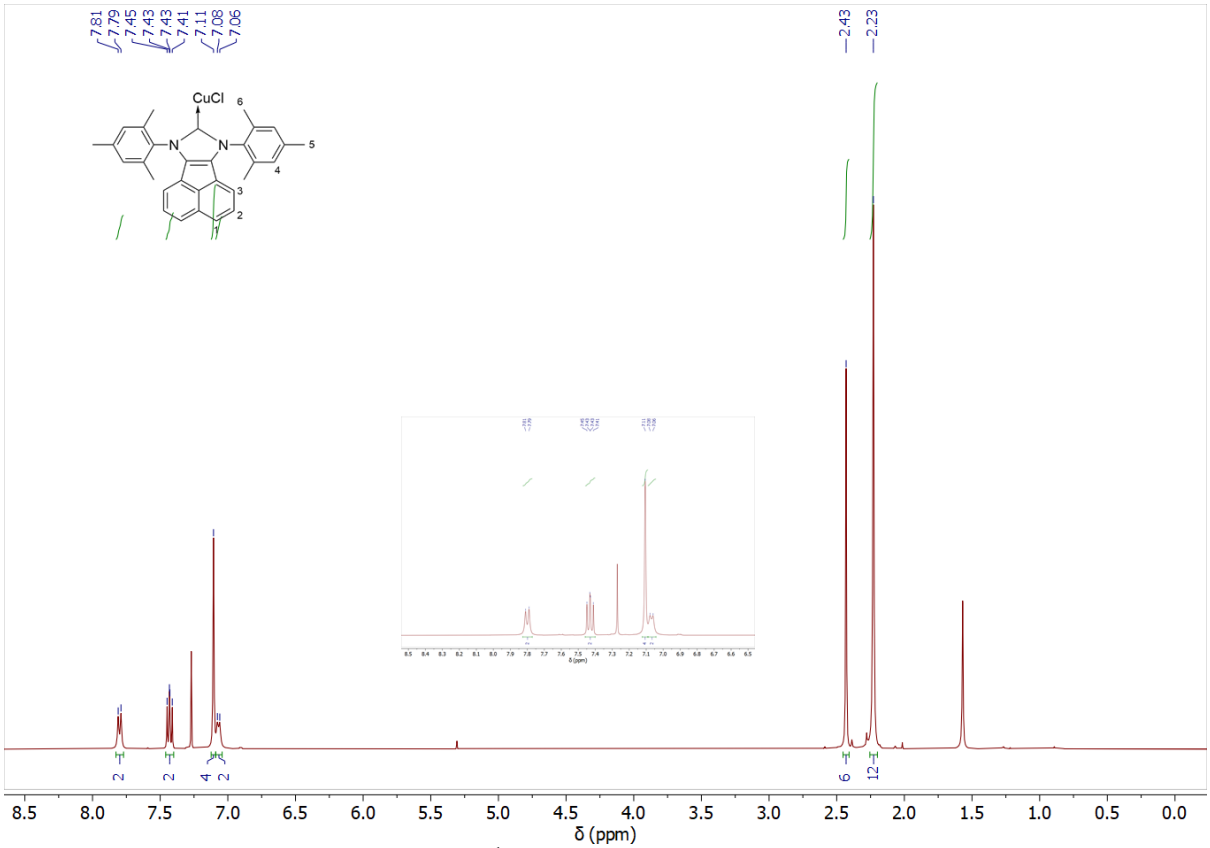
Annex 8 - ^{1}H NMR spectra of **S3** in $CDCl_3$.



Annex 9 - ^{13}C NMR spectra of **S3** in $CDCl_3$.

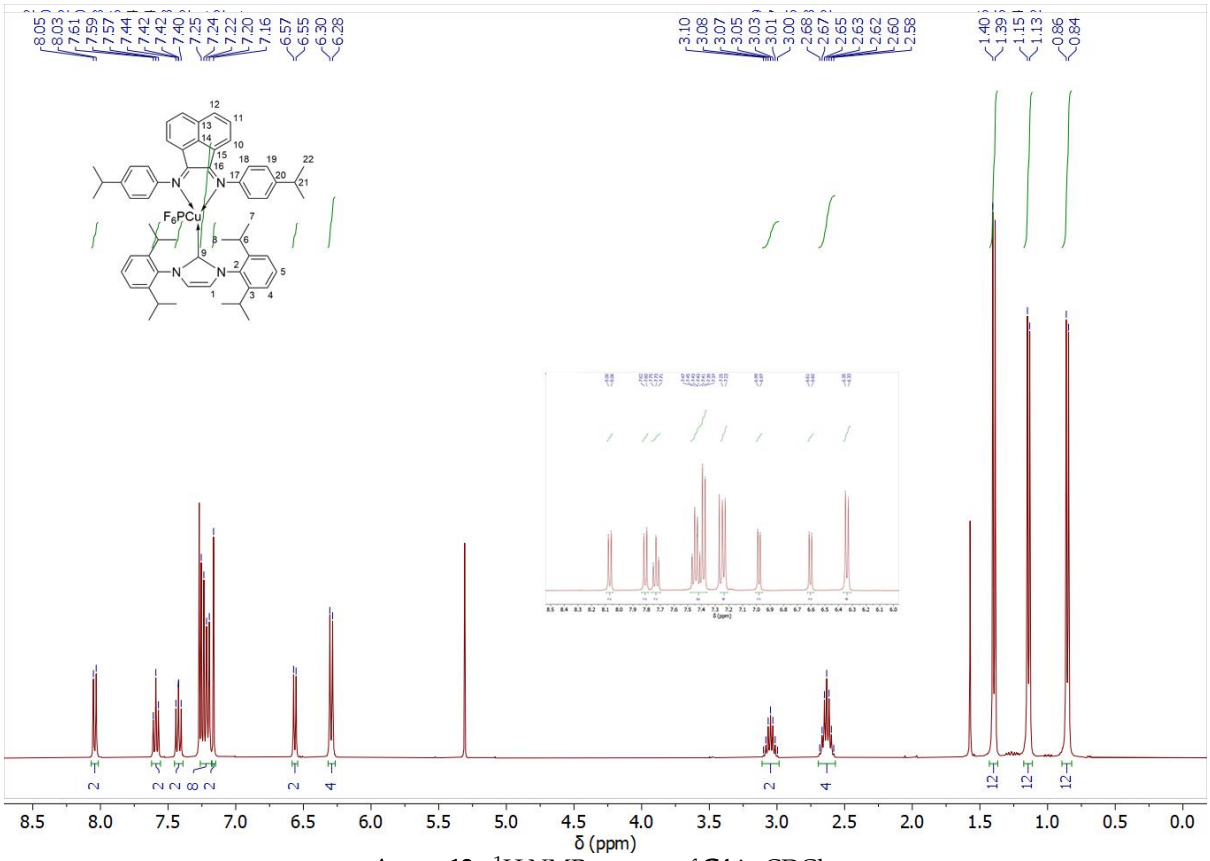


Annex 10 - ^{1}H NMR spectra of **C1** in $CDCl_3$.

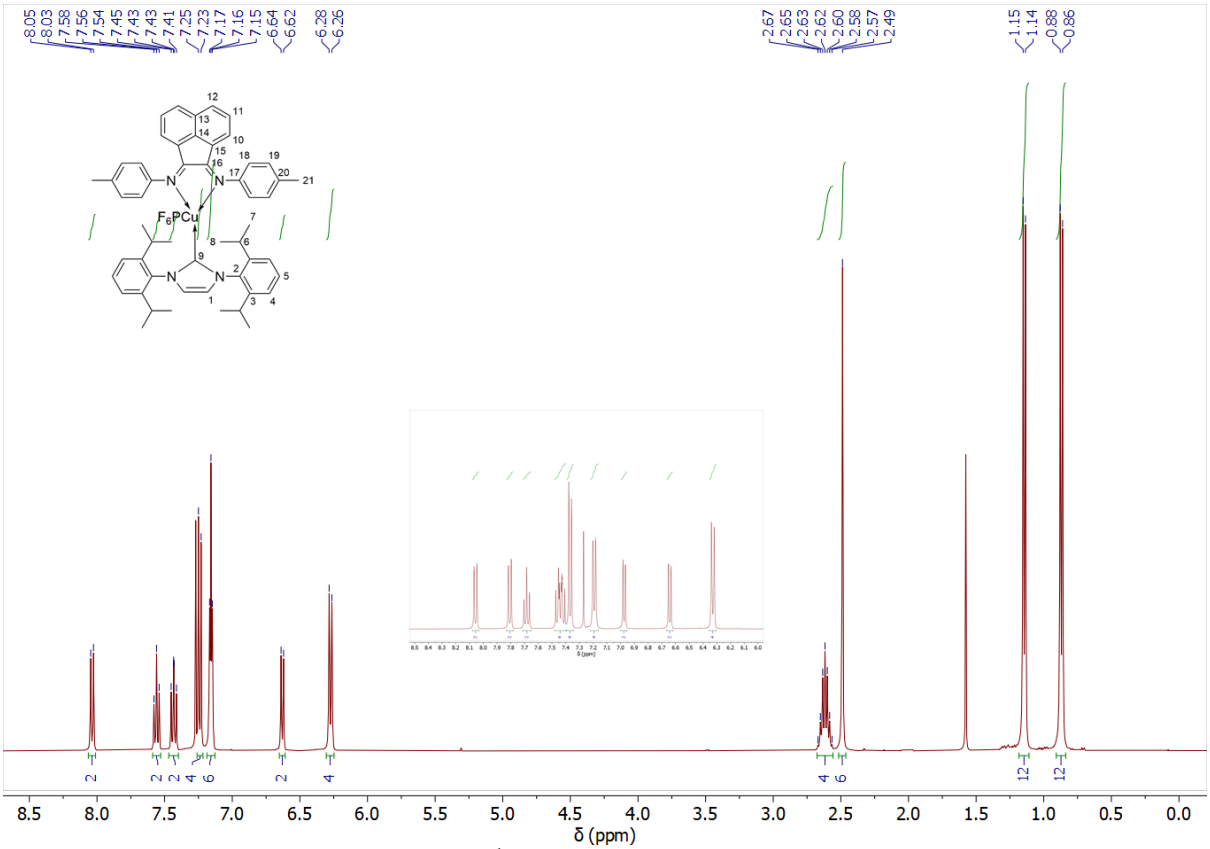


Annex 11 - ^{1}H NMR spectra of **C2** in $CDCl_3$.

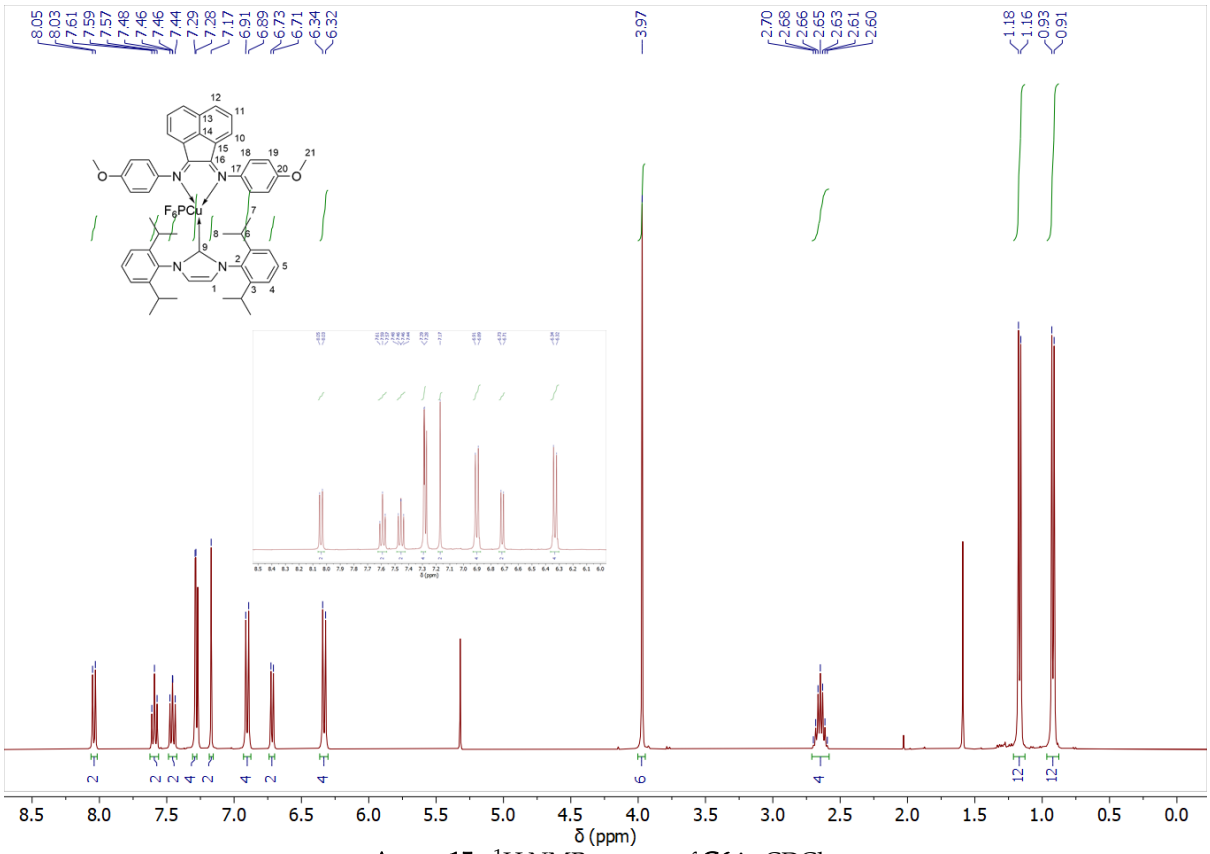
Annex 12 - ^{1}H NMR spectra of **C3** in $CDCl_3$.



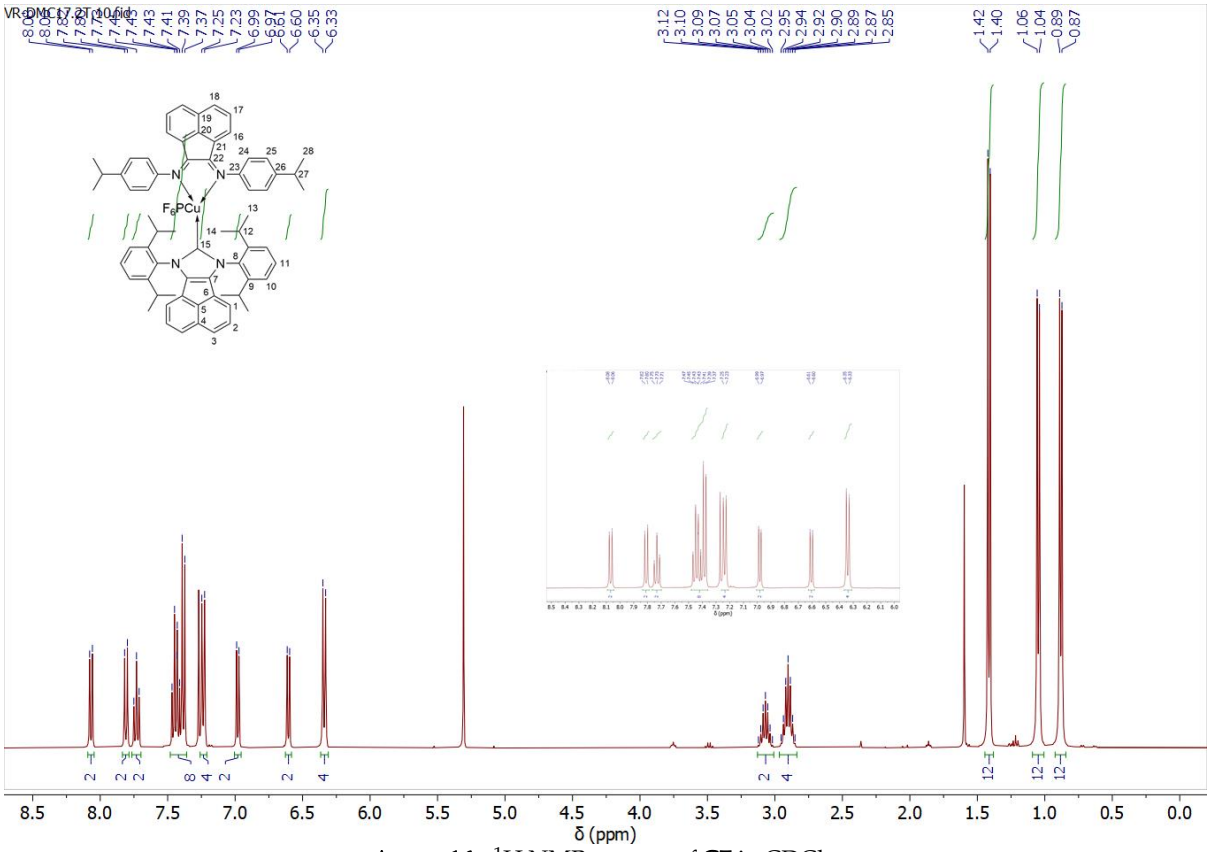
Annex 13 - ^{1}H NMR spectra of **C4** in $CDCl_3$.



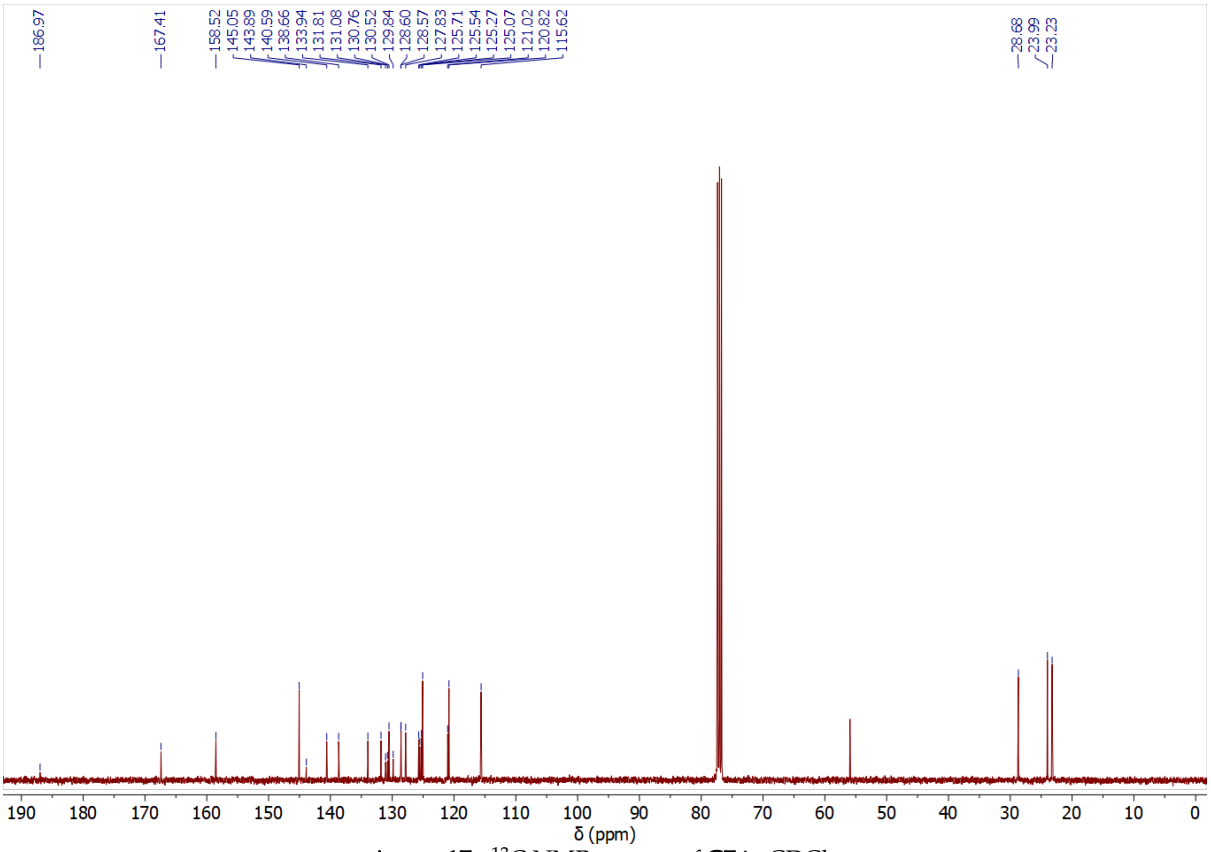
Annex 14 - ^{1}H NMR spectra of **C5** in $CDCl_3$.



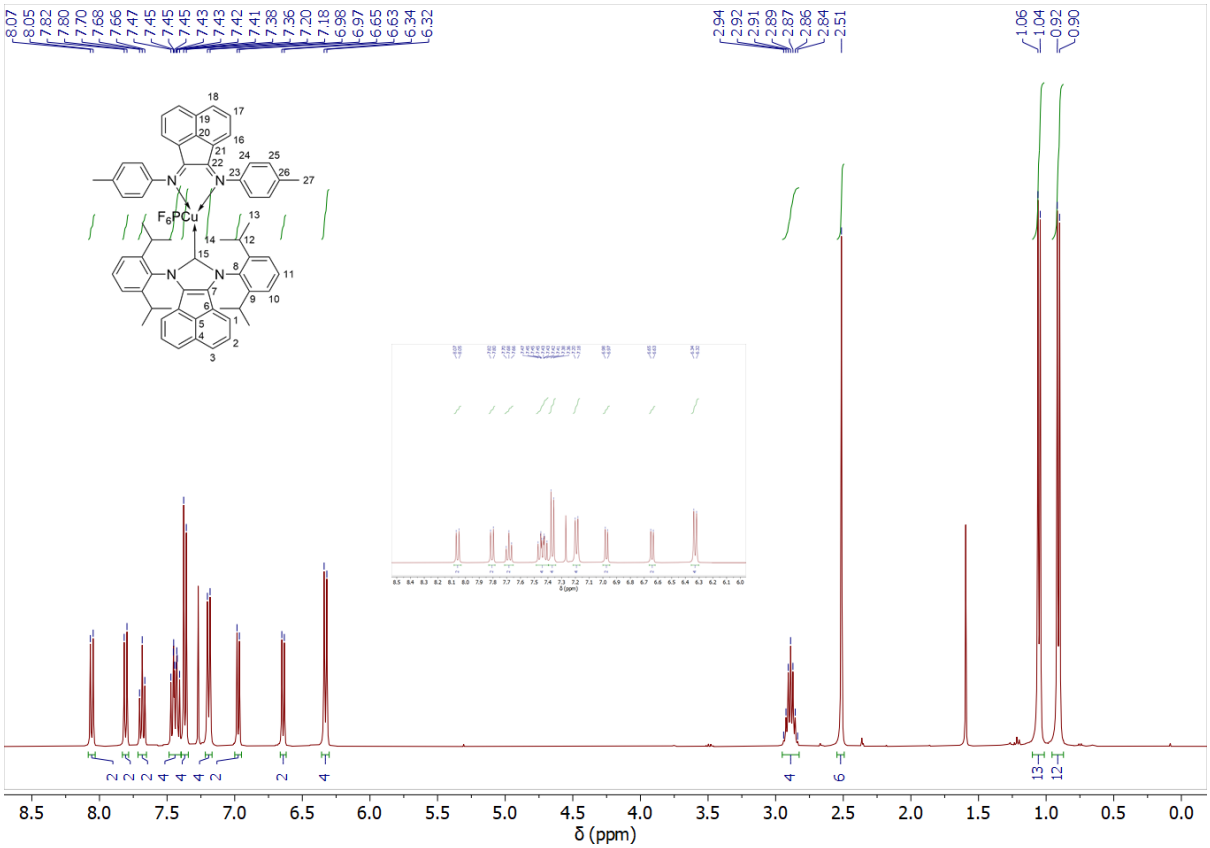
Annex 15 - ^{1}H NMR spectra of **C6** in $CDCl_3$.



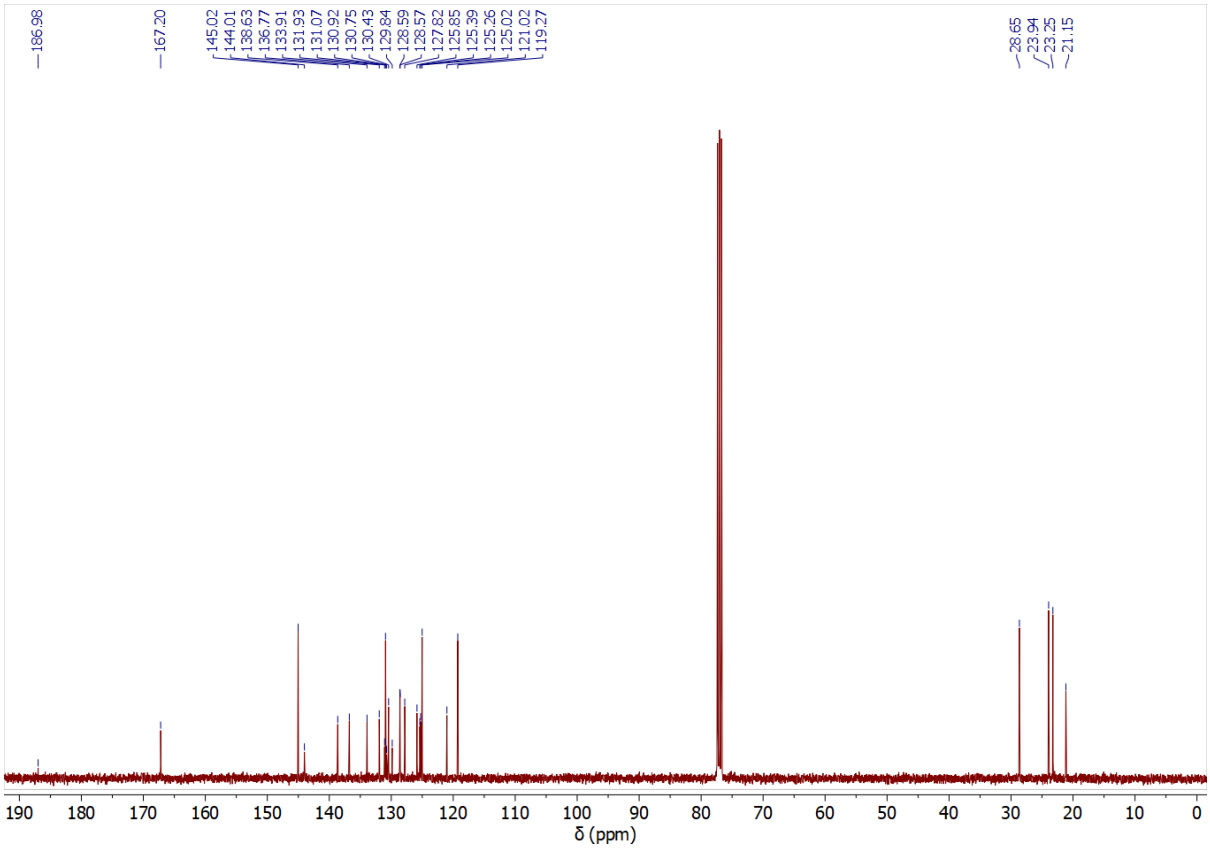
Annex 16 - ^{1}H NMR spectra of **C7** in $CDCl_3$.



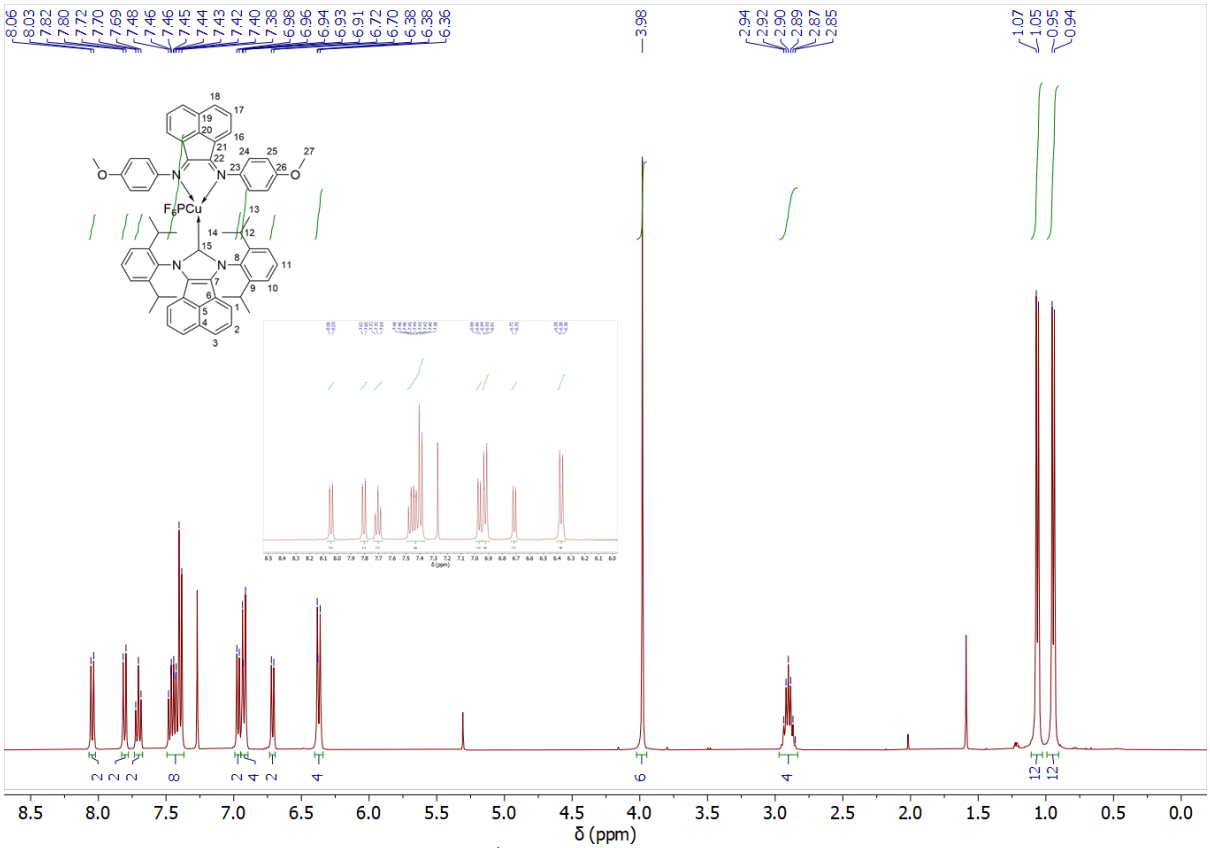
Annex 17 - ^{13}C NMR spectra of **C7** in $CDCl_3$.



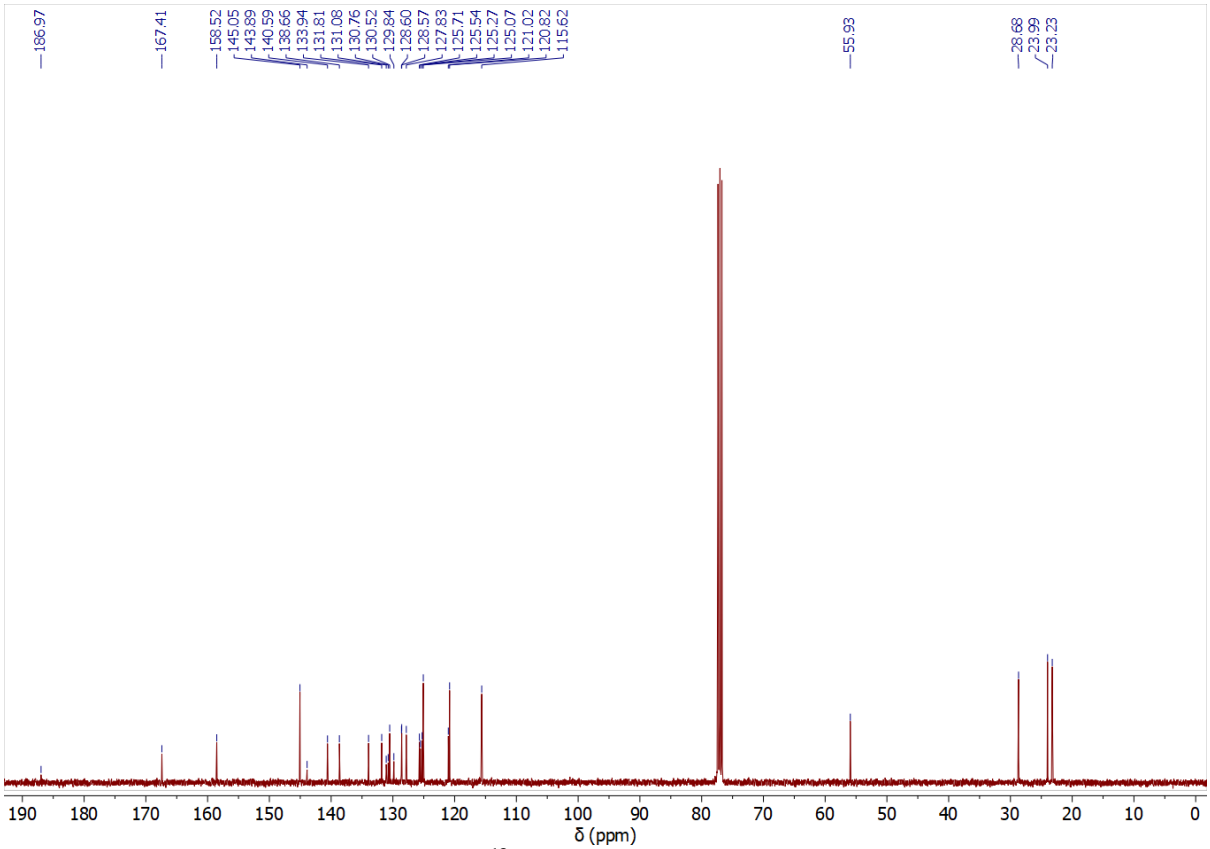
Annex 18 - ^{1}H NMR spectra of **C8** in $CDCl_3$.



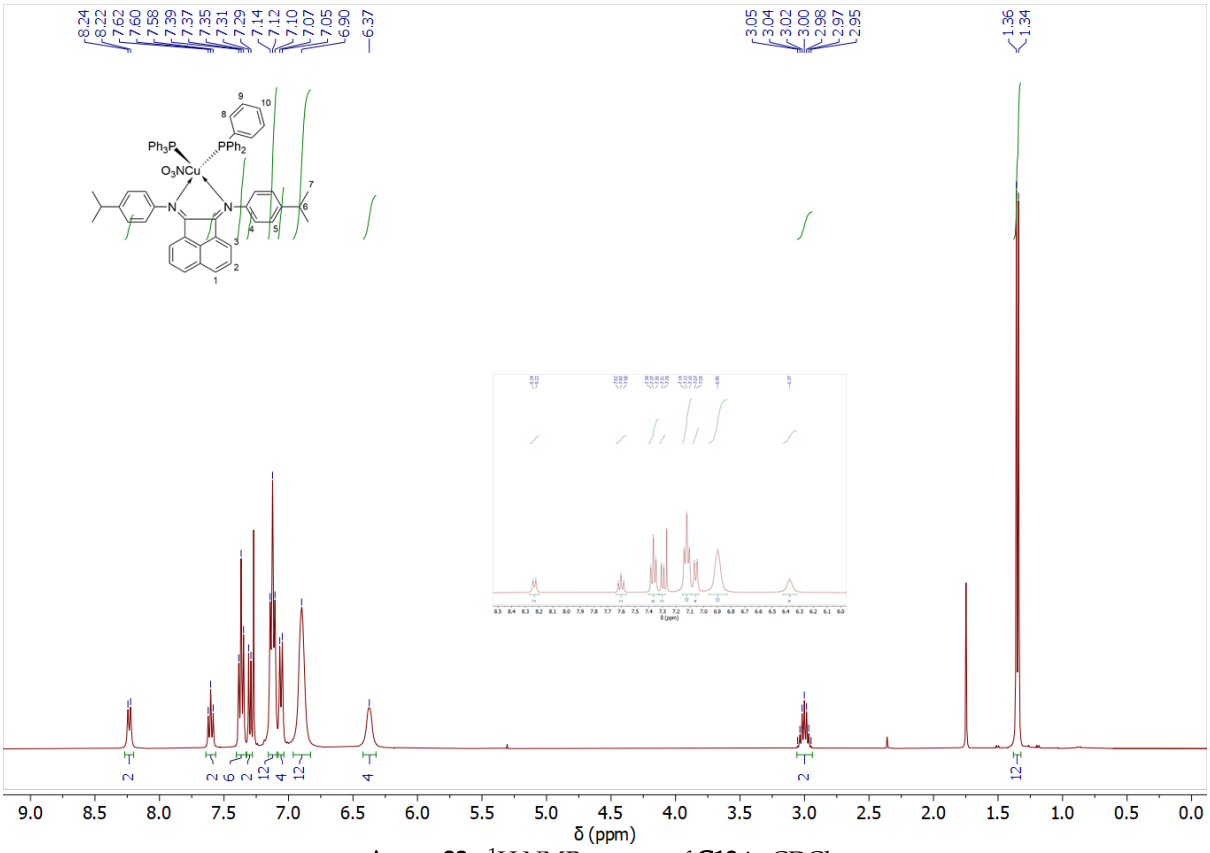
Annex 19 - ^{13}C NMR spectra of **C8** in $CDCl_3$.



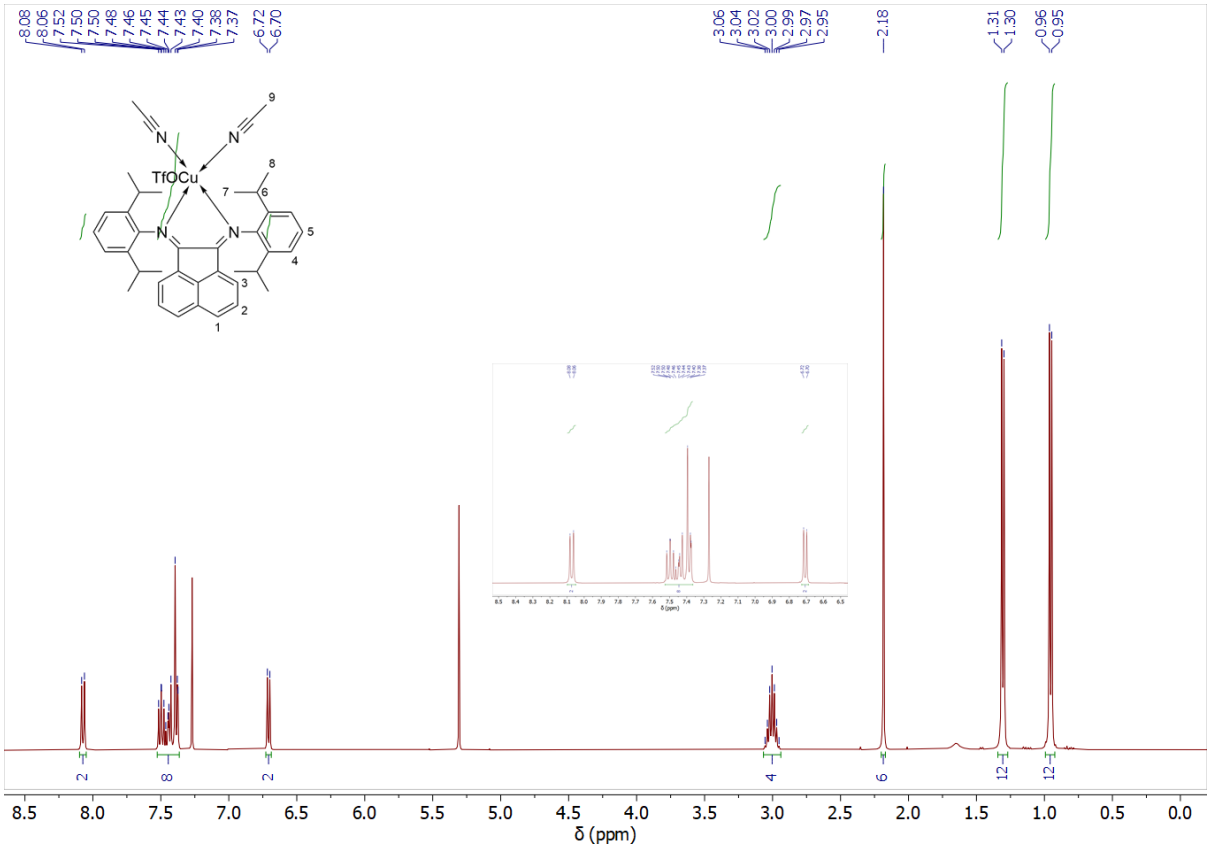
Annex 20 - ^{1}H NMR spectra of **C9** in $CDCl_3$.



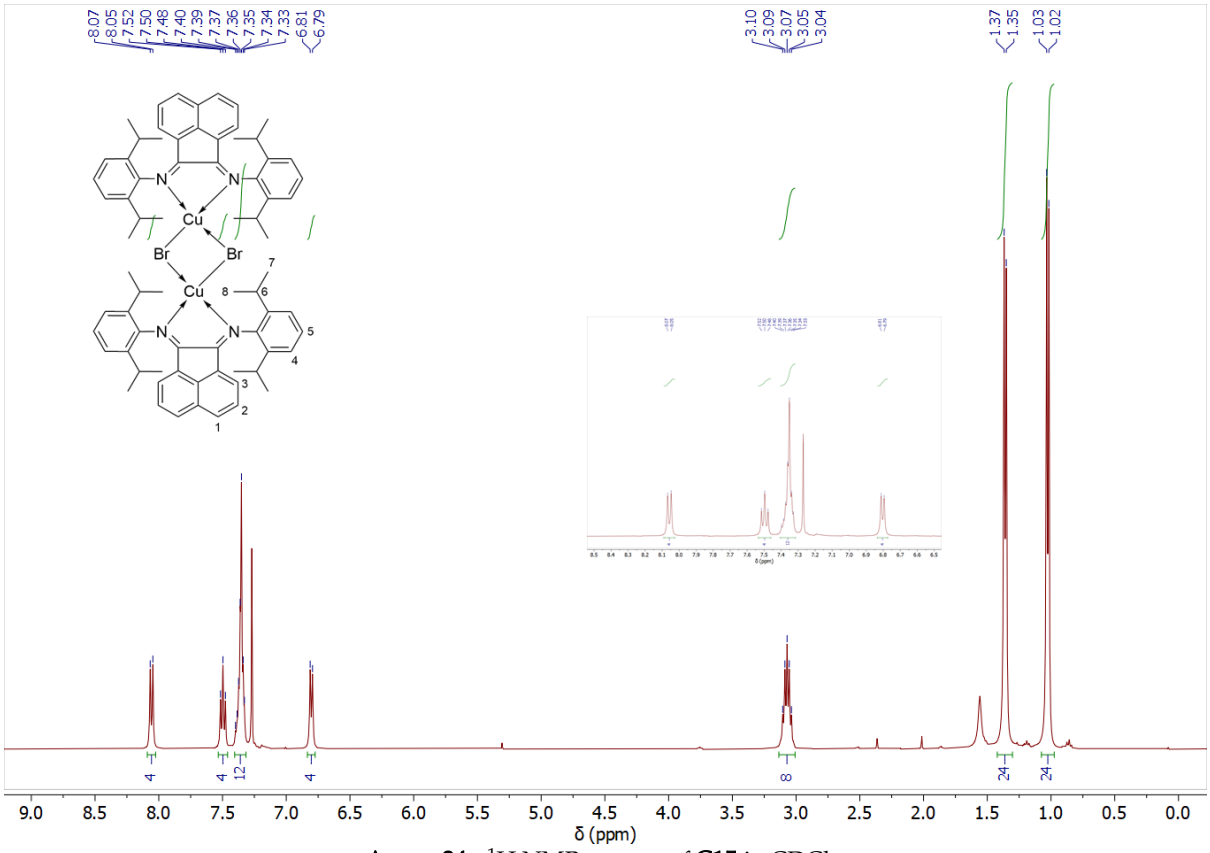
Annex 21 - ^{13}C NMR spectra of **C9** in $CDCl_3$.



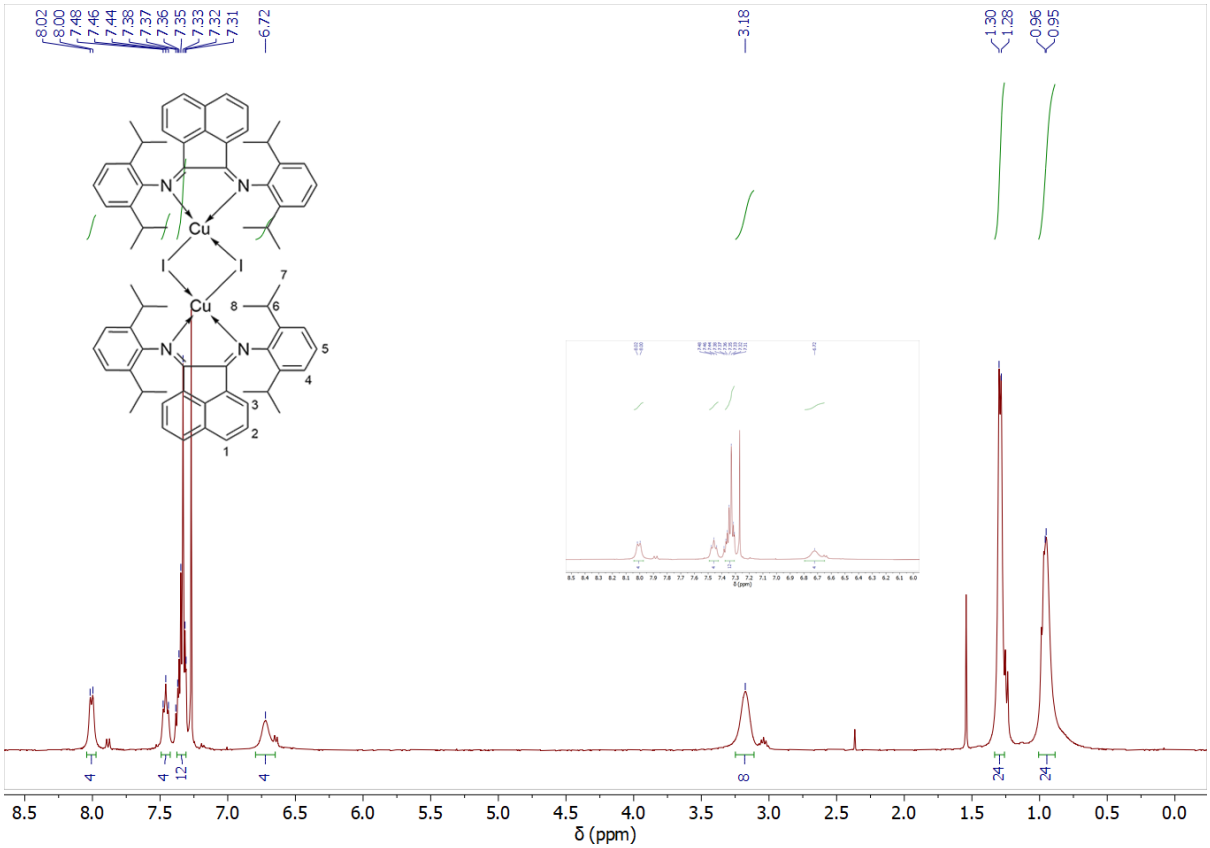
Annex 22 - ^{1}H NMR spectra of **C13** in $CDCl_3$.



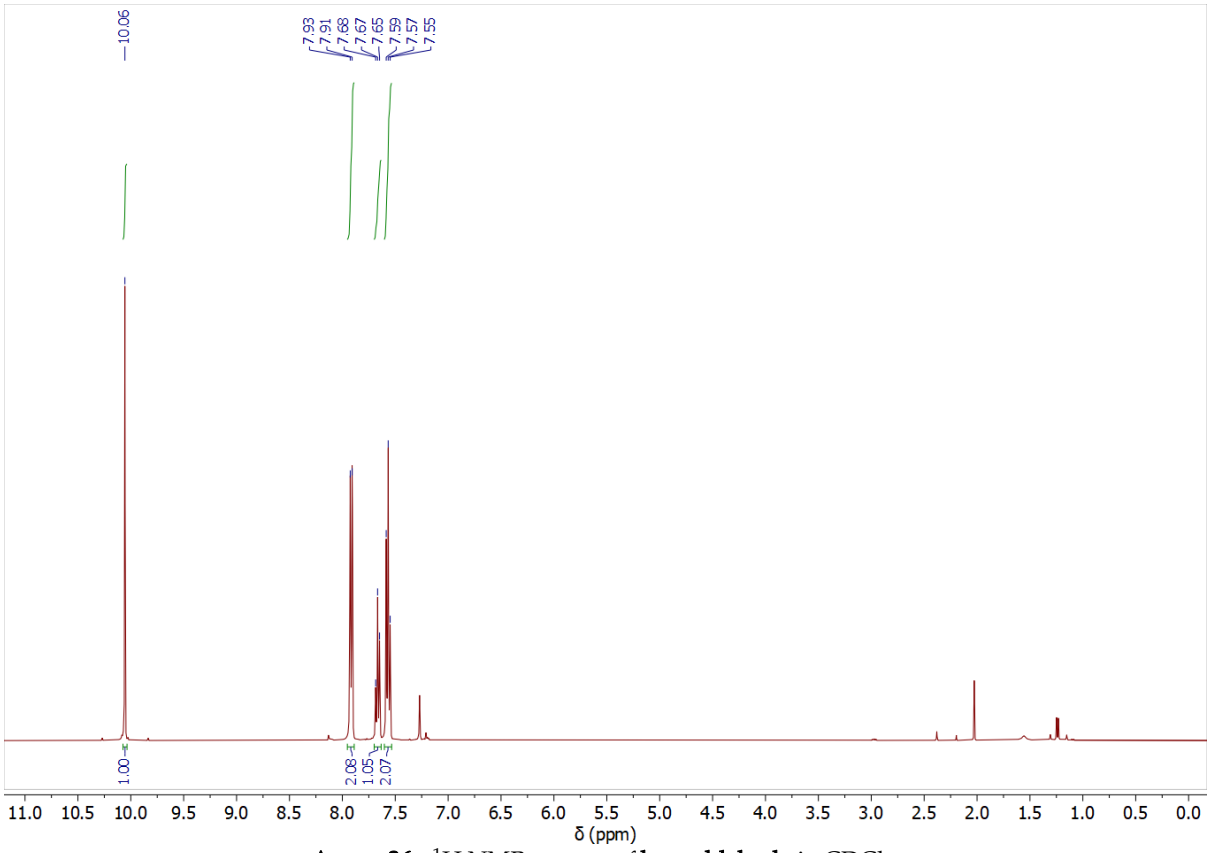
Annex 23 - ^{1}H NMR spectra of **C14** in $CDCl_3$.



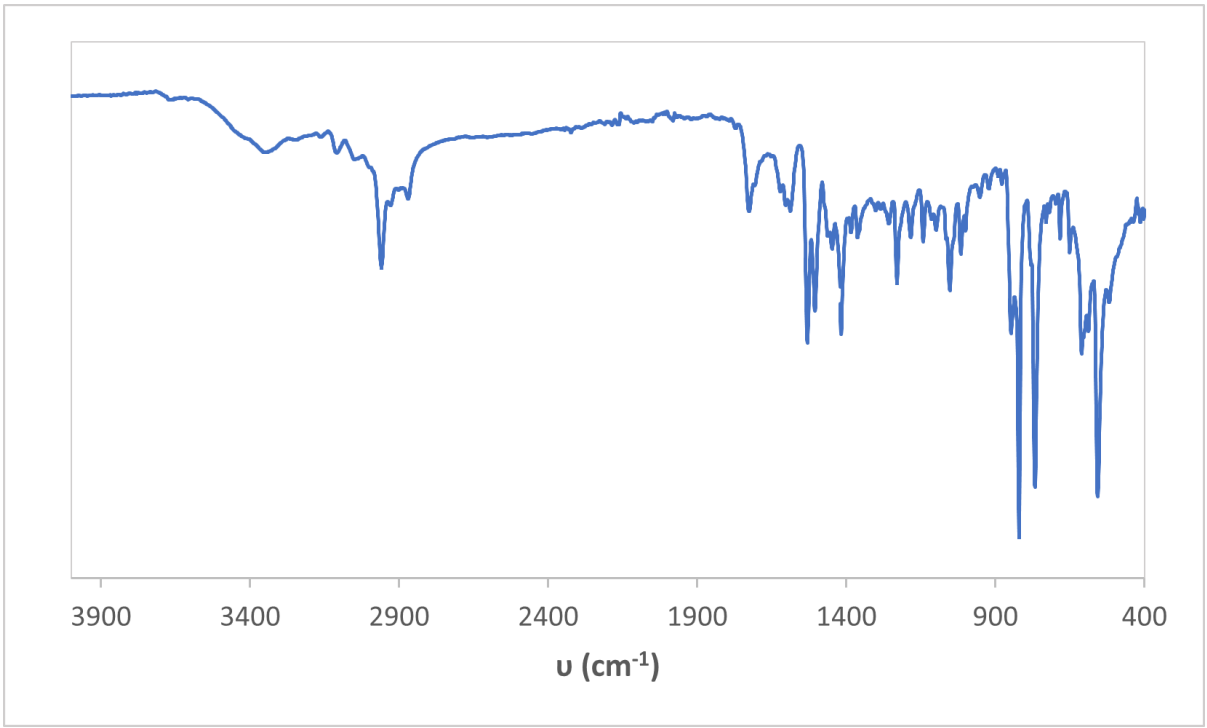
Annex 24 - ^{1}H NMR spectra of **C15** in $CDCl_3$.



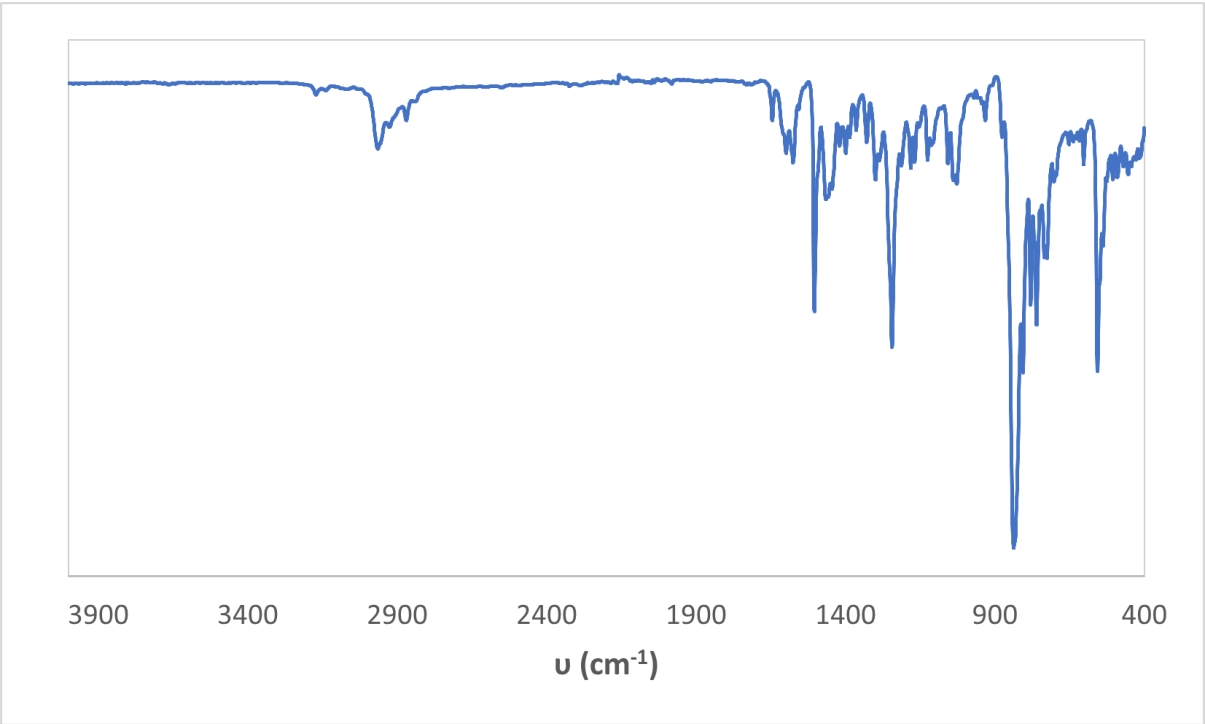
Annex 25 - ^{1}H NMR spectra of **C16** in $CDCl_3$.



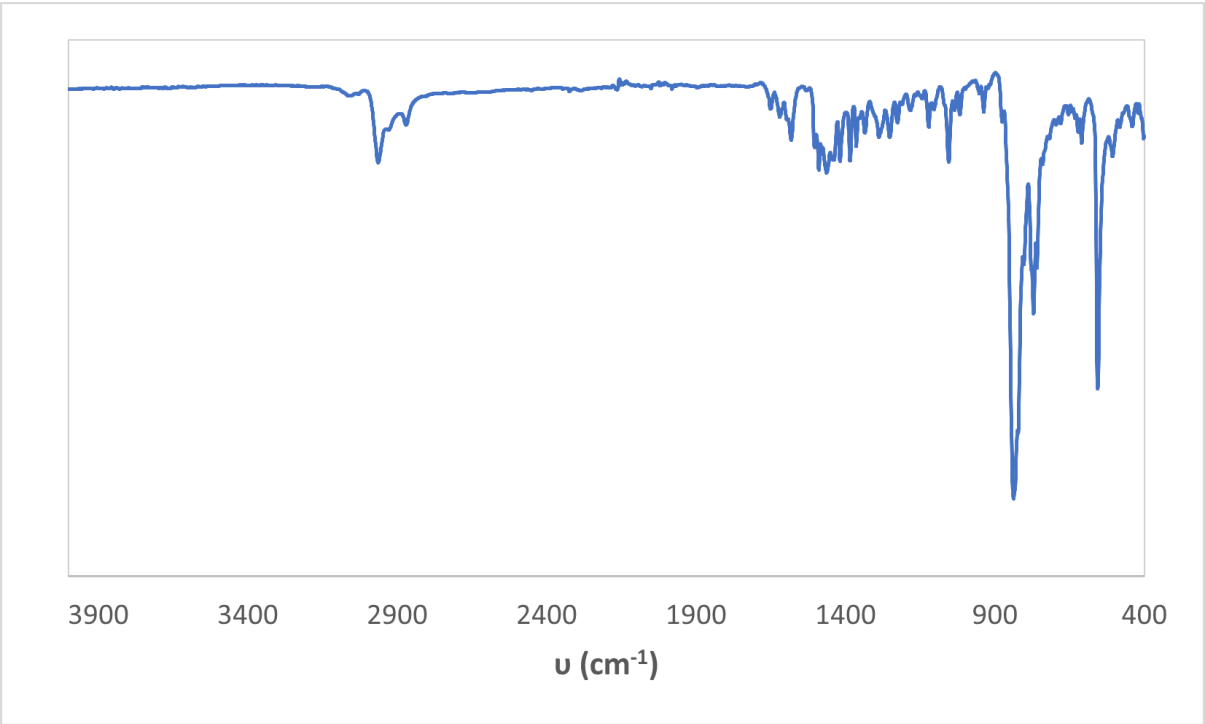
Annex 26 - ^{1}H NMR spectra of **benzaldehyde** in $CDCl_3$.



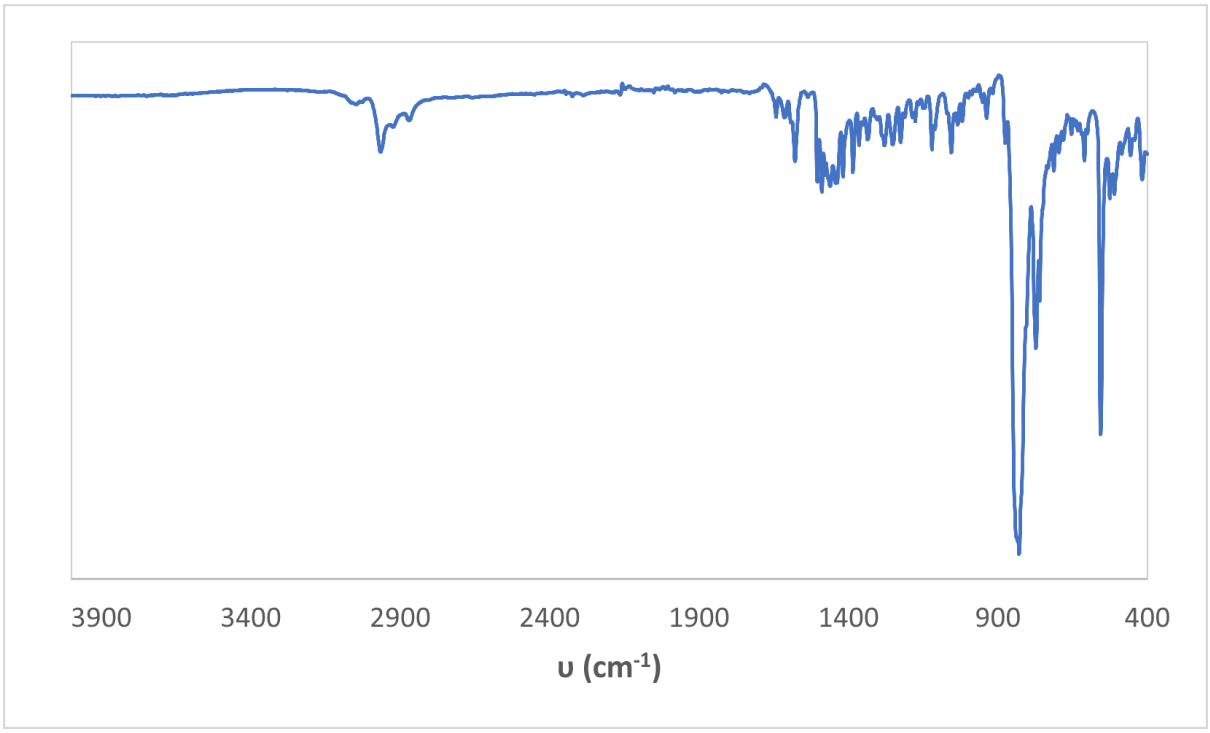
Annex 27 - IR spectra of **S3**.



Annex 28 - IR spectra of **C6**



Annex 29 - IR spectra of **C7**.



Annex 30 - IR spectra of **C8**.

2023

DIOGO MANUEL DA CONCEIÇÃO COSTA

HETEROLEPTIC COPPER(I) COMPLEXES BASED ON NHC CARBENES AS CATALYSTS FOR THE SYNTHESIS OF IMINES AND PROPARGYLAMINE DERIVATIVES

NOVA SCHOOL OF SCIENCE & TECHNOLOGY