ATTEMPT SYNTHESIS OF IR (I) METAL COMPLEXES FOR CATALYTIC CONVERSION OF GLYCEROL TO LACTIC ACID

Final Degree Project

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LIST OF ABBREVIATIONS

Approx.	approximately
Cat	catalyst
calcd	calculated
$CDCl_3$	deuterated chloroform
CD_2Cl_2	deuterated dichloromethane
CD_3CN	deuterated acetonitrile
COD	1,5-Cyclooctadiene
DCE	1,2-Dichloroethane
DCM	dichloromethane
Dipp	2,6-Diisopropylphenyl
ESI-TOF-MS	Electrospray Ionization-Time of Flight-Mass Spectrometry
g	gram
GAL	glyceraldehyde
h	hour
HR-MS	High Resolution Mass Slectrometry
i-bitz	bis-triazolyilidene ligand
LA	Lactic Acid
LC	Liquid Chromatography
Mes	mesityl
min	minute
mL	mililiter
mmol	milimol
NaOBu	sodium *tert*-butoxide
NHC	N-Heterocyclic Carbene
aNHC	abnormal N-Heterocyclic Carbene
nNHC	normal N-Heterocyclic Carbene
rNHC	remote N-Heterocyclic Carbene
MIC	Mesoionic Carbene

NMR		Nuclear Magnetic Resonance
	alk	alkylation
	arom	aromatic
	d	doblet
	m	multiplet
	MHz	MegaHertz
	ppm	parts per millons
	quat	quaternary
	s	singlet
	trz	triazole
	δ	cheimcal shift
PAL		pyruvaldehyde
QOMCAT		Organometallic Chemistry and Homogeneous Catalysis Group at the Universitat Jaume I
rt		room temperature
SPS		Solven Purification Systems
TfO^-		triflate
THF		tetrahydrofuran
TMS		trimethylsilyl
°C		degree Celsius

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1. INTRODUCTION

The development that the industry has experienced during the last decades had significant beneficial impact in the society. However, it has also brought some negative consequences such as pollution, climate change, greenhouse effect, depletion of the ozone layer, acid rain, etc.[1] As a result, the population has become more concerned of the importance of protecting the environment only recently. Our task as chemists is the design and development of more sustainable chemical transformations to be used for industrial applications agriculture or energy sources among others.

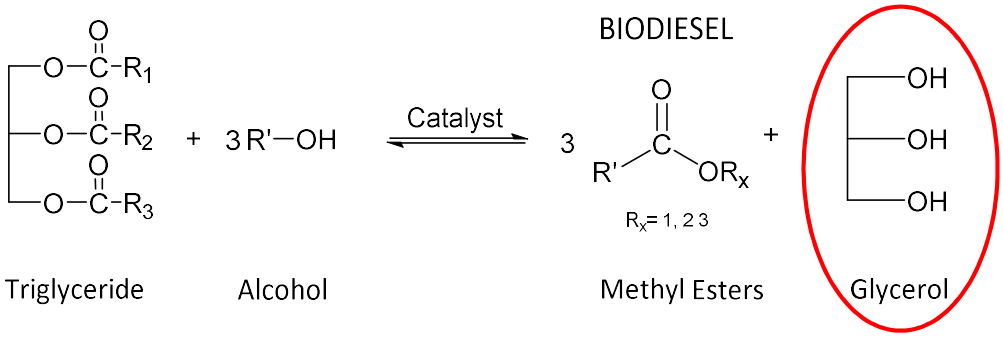
A few decades ago the concept of 'Green Chemistry', was developed by Anastas and Warner, which has 12 postulates and advocates for the design of chemical products or chemical synthesis that reduce or eliminate the generation of toxic products, the use of catalysts to have more selective reactions or avoid the use of solvents.[2]

One of the biggest challenges at the present time is the substitution of products derived from the limited fossil resources for analogous products using renewable feedstock, both in the production of energy, commodity chemicals and greener.

Currently, fossil fuels are the largest source of energy at the industrial and human level. Their extended use is causing significant environmental and health problems to human beings. To begin with, they are a non-renewable source of energy, so they will not last forever, but the principal problem associated to them is the environmental pollution. To obtain energy from these fuels it is necessary to burn them, that produces the emission of large amount of CO_2, in addition to other gases, which cause the greenhouse effect and global warming, among others.

One of the alternatives to fossil fuels is the use of a renewable feedstock such as biodiesel, which is obtained from vegetable oils or animal fats through a transterification process forming glycerol as a by-product (Scheme 1.1). Although It applicability has been known for quite some time, it has been only during the last decades when the process has been optimized and are emerging large biodiesel production plants.[3]

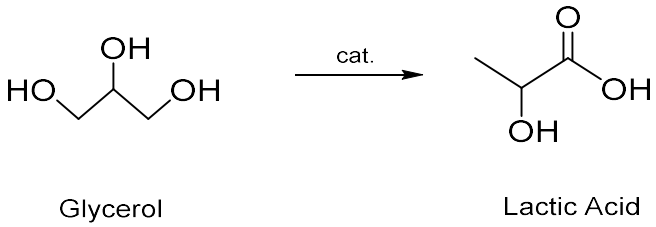
However, one of the downsides of the increment of biodiesel production directly implies a rise in the amount of crude glycerol produced. It is estimated that glycerol production is 10% w /w of the total production of biodiesel.



Scheme 1.1. Synthesis of Biodiesel and glycerol

This by-product contains a certain amount of impurities depending on the process from which it is obtained. As a consequence, it is not possible to use it as it is in conventional industries where glycerine is used. It has to be passed previously through a refining stage, which would greatly increase its price and would not be profitable.

It is important for the biodiesel industry to convert said crude glycerol into added value chemicals or biofuels (H_2), both for economical and environmental reasons. This is why there are different research platforms trying to obtain the maximum potential of this by-product.[4] For instance, glycerol as can be used as a feedstock, to produce chemicals such as 1,3-propanediol or citric acid via biological conversion (fermentation). More recently, the transition metal based catalytic transformation of glycerol into lactic acid (LA) has merged as a potential alternative (Scheme 1.2).[5, 6]



Scheme 1.2. Conversion of Glycerol to Lactic acid (LA)

Interestingly, despite the number of applications of LA, its production from glycerol, as feedstock is one of the least explored. The LA can be seen as a chemical platform for the production of different chemicals such as biodegradable polyesters as well as green solvents having a less negative impact for the environment. In addition, it can use in the pharmaceutical or food industry.[6] Currently, 90% (approx.) of LA production is obtained from sugar fermentation (Figure 1.1), a process that present serious drawbacks such as low conversion or complicated purification steps.[6,7,8]

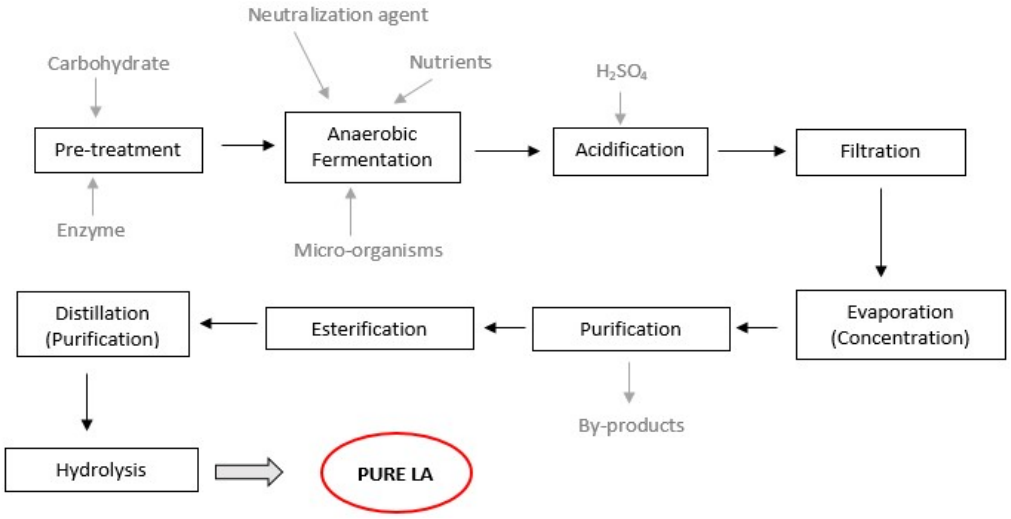


Figure 1.1. Conventional method for producing lactic acid

Herein, the development of a more sustainable synthetic alternative is highly desirable. In this context, in line with one of the twelve principles of "green chemistry", the catalytic synthesis of LA is considered a promising avenue of research, overcoming some of the current disadvantages.[6]

In this line, Sharninghausen, Campos *et al.,* recently reported the catalytic conversion of glycerol to lactic acid, along with H_2 using a family of homogeneous catalysts based on iridium containing N-heterocyclic carbene ligands (NHCs). This process involves the iridium catalysed dehydrogenation of glycerol to form glyceraldehyde (GAL), a dehydration step to form pyruvaldehyde (PAL) and a rehydration step before the lactic acid is formed (Figure 1.2).

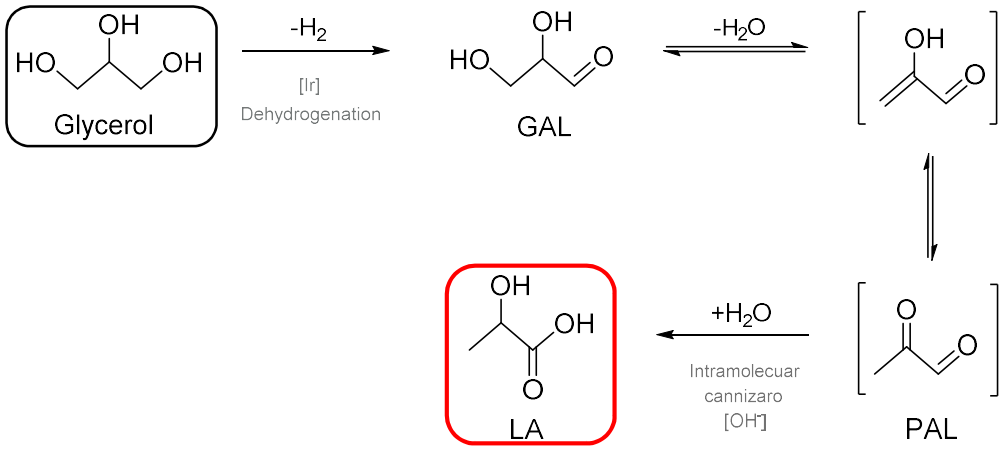
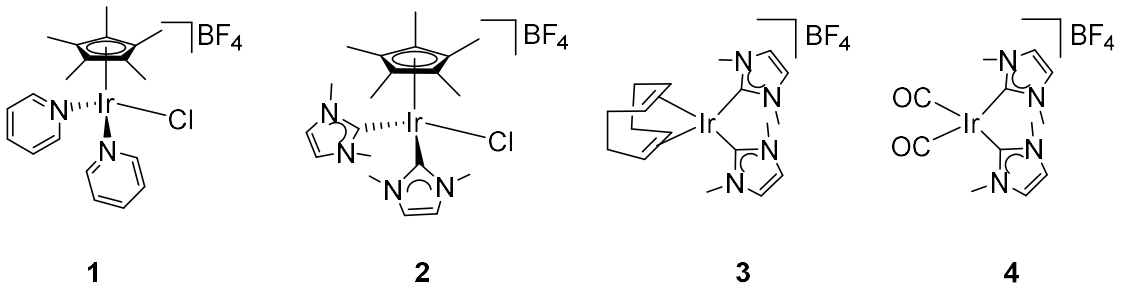


Figure 1.2. Mechanism for the conversion of glycerol to lactic acid

Significantly one of the great advantages of this synthetic strategy complementary to the high selectivity observed, is the hydrogen gas production that could be employed for further applications reducing production costs.

Some of the reported examples in the literature, employed catalysts based on Au-Pt / TiO_2 although, only low yields were obtained. In contrast, Sharninghausen, Campos *et al.* have recently reported a more efficient catalytic system based on iridium.

They initially explored several Cp*Ir(III) complexes featuring different substituents (anionic, cationic, neutral, monodentate or chelating) (e.g. 1 and 2). It was concluded that the one with a remarkable activity was $[Cp^*Ir(NHC)_2Cl]^+ BF_4^-$ (2). From these data, it was observed that one of the factors of this great activity was the presence of the two NHC (N-heterocycles Carbenes) substituents in the complex, in addition, it was demonstrated that the Pentamethylcyclopentadienyl ligand (Cp*) was unnecessary. In view of this results, two iridium (I), $[Ir(NHC)_2(cod)]^+ BF_4^-$ (3) and $[Ir(NHC)_2(CO)_2]^+ BF_4^-$ (4) were prepared (Scheme 1.3). Both gave a great result, better than the previous ones studied, especially the complex with bis-carbonyl.[6]

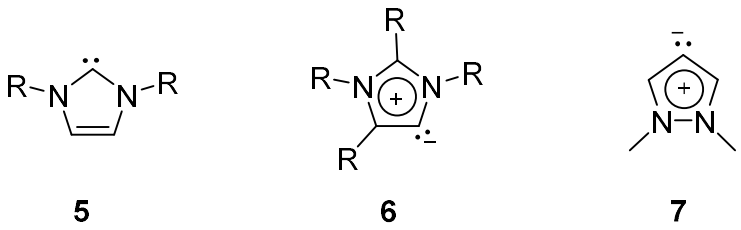


Scheme 1.3. Different proposed complexes of Ir (I) and Ir(III)

In this case, the choice of the use of iridium (I) complexes was due to the fact that it normally forms planar square complexes, so it has coordination vacancies that allow it to coordinate with glycerol to bind with protons in order to release H_2 in the dehydrogenation process. The Ir(I) complexes contained two N-Heterocyclic carbene ligands (NHCs). They possess a strong sigma-electron donating character, so they bind strongly with the metal providing higher stability to the catalyst.[9]

They present some advantages, such as the possibility of being synthesized from convenient and inexpensive salt precursors. Other important advantages of these types of ligand is the possibility of small changes in their structure, their electronic donor properties can be modified widely or it is also possible to impose steric restrictions by introducing very bulky substituents. [10]

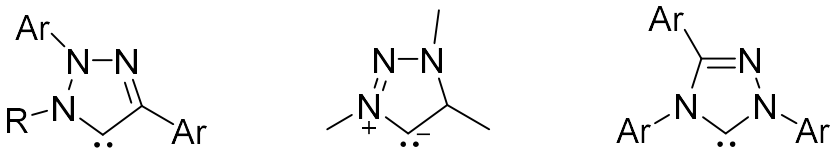
You can differentiate three types of NHC ligands, normal (nNHC) (5), abnormal (aNHC) (6) (also called mesoionic (MIC)) and remote (rNHC) (7).



Scheme 1.4. Representation of the different types of NHC [11,12,13]

The nNHC are cyclic compounds that have a carbene, at least one nitro group in α-position and that has no formal charge. The aNHC o mesoionic carbene ligands display a positive and a negative charge in their structure and they cannot be represented by a unique resonance form. They have a stronger σ-donor character than the nNHC. The rNHC are those NHC in which the carbon carbene is not in α-position to any heteroatom, it can be both nNHC and aNHC.[14]

Within the family of NHC ligands, there is a class of compounds known as triazolylidenes (five-membered rings with three nitrogens in their structure). Three types can be distinguished (Scheme 1.5). Two of them are 1,2,3-triazolidenes (8 and 9) and the other is 1,3,4-triazolidene (10). The different substitution pattern in compounds 8 and 9, make 8 an nNHC, while 9 is a MIC. [15,16,17]



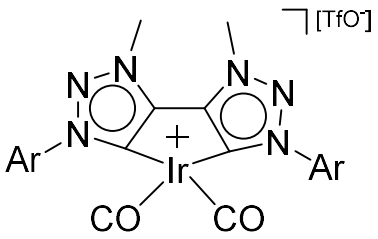
8 **9** **10**

Scheme 1.5. Representation of the different types of triazolylidenes

In some cases, the incorporation of mesoionic triazolylidenes (9), that present stronger σ-donating character could offer better catalytic results in the conversion of glycerol to LA.

Therefore, we decided to attempt the synthesis of Ir(I) bis carbonyl complexes containing a bistriazolyilidene ligand that could resemble to those reported by Sharninghausen, Campos *et al.* To design both complexes we have based on a complex described in the bibliography [18], but the metal has been replaced by Ir.

Based on the "state of the art", this work was devoted to attempt the synthesis of two iridium (I) complexes containing a mesoionic bis-triazolylidene ligand bearing different substituents.



Scheme 1.6. Proposed complex

Based on these precedents it is at this point where our work is focused, since it is intended to synthesize a metallic catalyst capable of converting glycerol into lactic acid, and also follow the principles of green chemistry.

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2. OBJECTIVES

The aim of this research work is the synthesis of two novel iridium complexes containing mesoionic triazolylidene ligands. The ultimate goal would imply the evaluation of their performance in a very challenging transformation such as the catalytic conversion of glycerol to lactic acid.

The synthesis of the iridium complexes involves the synthesis of the ligand salt precursors that will afford the desired corresponding metal complexes after deprotonation. Herein, two bis-triazolium salts will be prepared. They are ready available after alkylation of the related bis-triazole that can be obtained on big scale from ready available compounds.

To acquire new skills through the search and use scientific articles from different resources that can be used for the design and synthesis of compounds that have not been described in the literature.

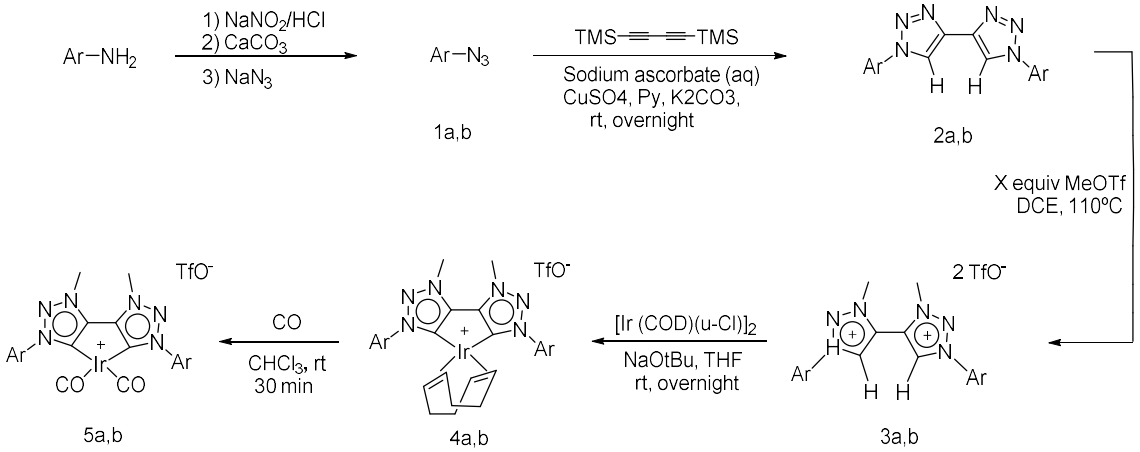
On the other hand, there are other types of objectives in the realization of this research work, such as gaining experience in a research laboratory, learning the use of some of the most commonly used techniques in an Organometallic laboratory. Among them, is the use of Schlenk techniques working with a glass manifold that allows to work under strict inert conditions, but also the use of liquid nitrogen to carry out reactions at very low temperature.

To get familiar with the use of characterization techniques such as NMR and HR-MS spectroscopy. In addition, improve skills in interpreting the results obtained in NMR spectroscopy and mass spectroscopy.

3. RESULTS AND DISCUSSION

The synthetic procedures and characterization of the compounds synthesized during this work will be described in this section.

As it has been already mentioned in the introduction, our main target was to obtain the synthesis of two Ir(I) complexes **5a,b** of formula $[Ir(i\text{-}bitz)CO_2]^+ X^-$ with (i-bitz = bis-triazolyilidene ligand), with the ultimate goal of evaluating their catalytic activity towards the conversion of glycerol to LA. To accomplish this task, a combination of several reported synthetic procedures for related metal complexes were followed.



Scheme 3.1. The general procedure for the preparation of complexes **4a,b** and **5a,b**.

A schematic representation of the proposed synthesis for both iridium complexes **5a,b** $[Ir(i\text{-}bitz)(CO)_2]^+ X^-$ is depicted in Scheme 3.1. The first part of the synthesis is devoted to the preparation of the ligand salt precursor **3a,b.** Initially, two aryl amines (**a** Ar=2,4,6-trimethylphenyl and **b** Ar= 2,6-diisopropylphenyl) are converted in the corresponding aryl azides **1a,b**[1,2], that were transformed into the corresponding bis-triazoles **2a,b** by means of a double copper catalysed [3+2] cycloaddition "click chemistry".[3]

Finally, further alkylation of **2a,b** afforded the desired ligand salt precursors **3a,b**.[4] The following step involves the coordination studies, that will allow us the preparation of complexes **4a,b** $[Ir(i\text{-}bitz)(cod)]^+ X^-$ using $[Ir(cod)Cl]_2$ as a metal precursor (cod = 1,5-Cyclooctadiene). Finally **4a,b** complexes will be further converted into the biscarbonyl derivatives **5a,b** $[Ir(i\text{-}bitz)(CO)_2]^+ X^-$.[5]

3.1. Synthesis and characterization of azides (1a,b)

As early mentioned, in this research work the synthesis of several iridium complexes with two different ligands was attempted. Both ligands present the same structure, which is a bistriazolylidene, differing only of the aryl substituents.

The first step in the synthesis of the ligand salt precursors **3a,b** (Scheme 3.1) involves the preparation of aryl azides **1a,b** (**a** Ar=2,4,6-trimethylphenyl, **b** Ar= 2,6-diisopropylphenyl), bearing two different substituents. The reaction involves the conversion of the NH_2 functionality into the corresponding azide (N_3). However, two different synthetic routes, were employed for the preparation of **1a** and **1b**.

In the case of **1a**, diazotization of the primary amine (2,4,6-Trimethylphenylamine) was obtained with an aqueous solution of $NaNO_2$ in HCl that produces the diazonium salt $(Ar\text{-}N_2)^+ Cl^-$. Further addition of an aqueous solution of NaN_3 generated the aryl azide ($Ar\text{-}N_3$).[1]

For the synthesis of **1b**, the aryl azide was produced by reacting the primary amine (2,6-Diisopropylphenylamine) with ^tBuONO followed by Me_3SiN_3. In this case, the reaction is carried out in acetonitrile.[2]

3.1.1 Characterization:

The two aryl azides **1a,b** were characterized by ^1H RMN and ^{13}C NMR of **1a,b**. Despite our attempts to characterize the two compounds by mass spectroscopy, satisfactory results could not be obtaining, probably due to the limited stability of the azides.

- Characterization of **1a**:

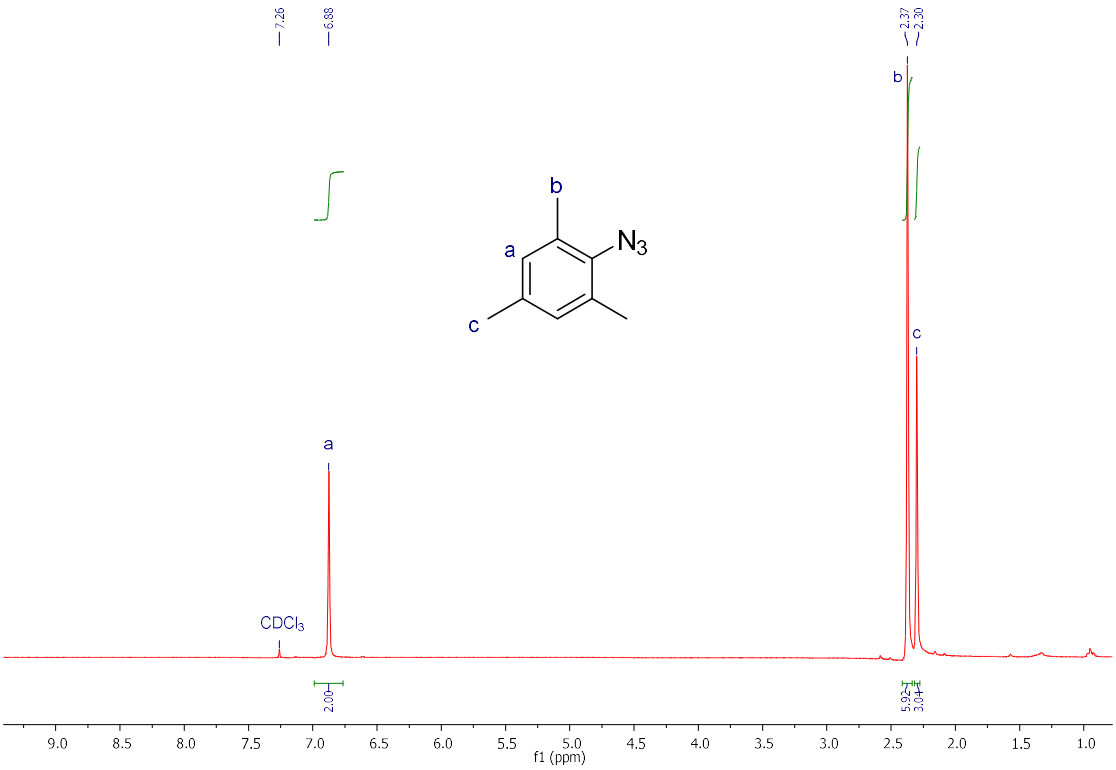


Figure 3.1. ^1H NMR spectrum of **1a** in $CDCl_3$

Figure 3.1 shows the ^{1}H NMR spectrum of **1a** in $CDCl_3$ (7.26 ppm). The singlet at 6.88 ppm correspond to the aromatics protons of the aromatic ring, **a**. Two singlets are observed at upper field, at 2.37 and 2.30 ppm integrating as six protons and three protons respectively. The signal at 2.37 ppm corresponds to the two methyl substituents in *-ortho* position **b**, while the signal at 2.30 ppm correspond to the methyl group in *-para* position, **c**.

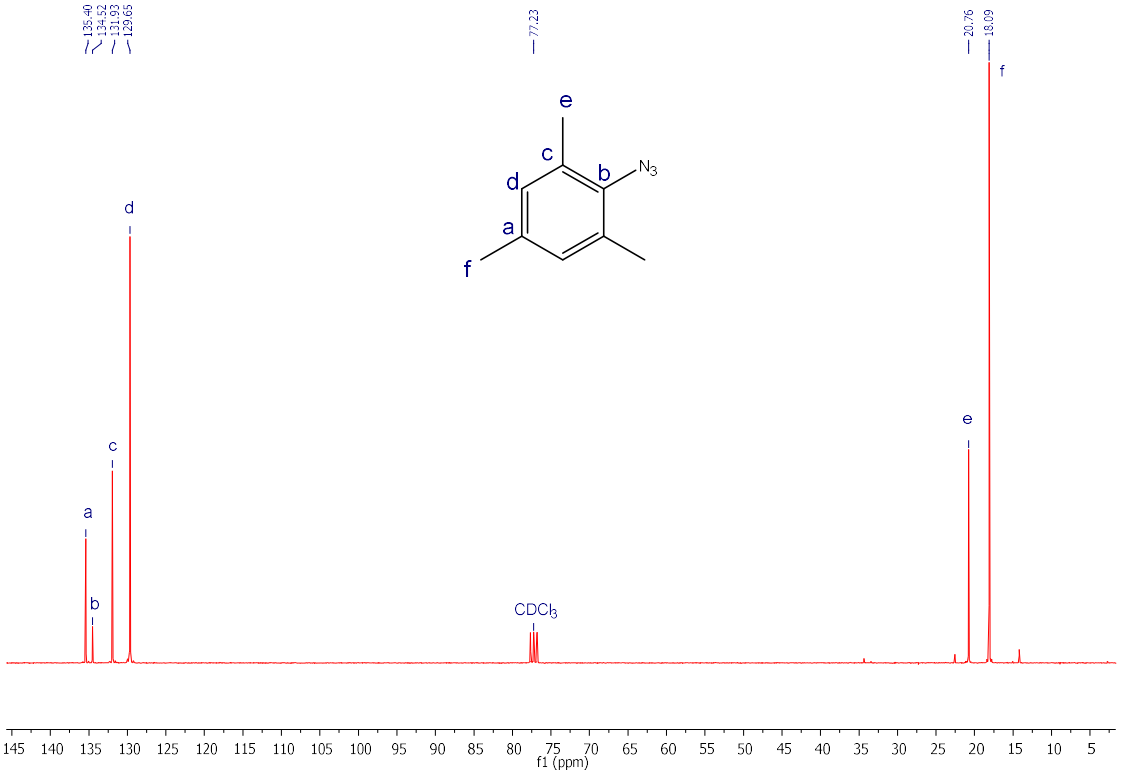


Figure 3.2. ^{13}C NMR spectrum of **1a** in $CDCl_3$

Figure 3.2 shows the ^{13}C NMR spectrum of **1a** in $CDCl_3$ (77.23 ppm). The signals at lower field are due to the carbons of the aromatic ring. The signals (**a**, **b** and **c**) at (135.40, 134.52 and 131.93 ppm respectively) are assigned to the quaternary carbons. The signal at 129.65 ppm corresponds to the tertiary carbon **d**. Finally, the signals at upper field are due to the CH_3 groups attached to the aromatic ring **e** and **f** respectively, the signal at 20.76 ppm corresponds to the methyl substituents at the *-ortho* position, while the signal at 18.09 ppm corresponds to the CH_3 at the *-para* position.

- Characterization of **1b**:

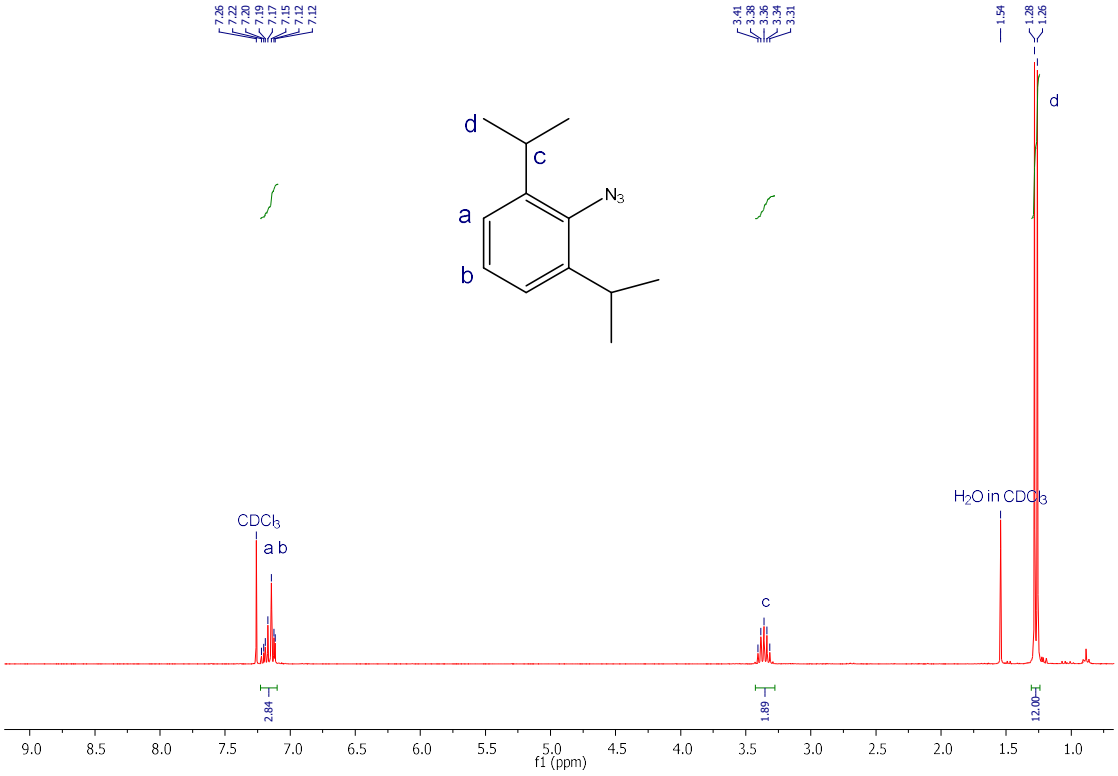


Figure 3.3. ^{1}H NMR spectrum of **1b** in $CDCl_3$

Figure 3.3 shows the ^{1}H NMR spectrum of **1b** in $CDCl_3$ (7.26 ppm). The multiplet observed at 7.17 ppm integrating as three protons corresponds to the three aromatics protons **a** and **b**. The multiplet at 3.36 ppm integrating as two protons corresponds to the CH, **c**. Finally, the doublet at 1.27 ppm integrating as twelve corresponds to the protons of the CH_3 **d**.

Figure 3.4 displays the ^{13}C NMR spectrum of compound **1b** in $CDCl_3$ (77.23 ppm). The signals at lower field are due to the carbons constituting the aromatic ring. The signals **a** and **b** at (143.34 and 135.64 ppm respectively) are due to the quaternary carbons. The signals **c** and **d** at 127.05 and 124.15 respectively are assigned to the tertiary carbons of the aromatic ring.

The signals at upper field are due to isopropyl substituents of the aromatic groups, the signal **e**, at 29.06 ppm corresponds to the CH, while the signal **f**, at 23.70 ppm, corresponds to the CH_3 groups. In addition, there are three additional peaks in the aliphatic region that may be due to the pentane, a solvent that used during the workup.

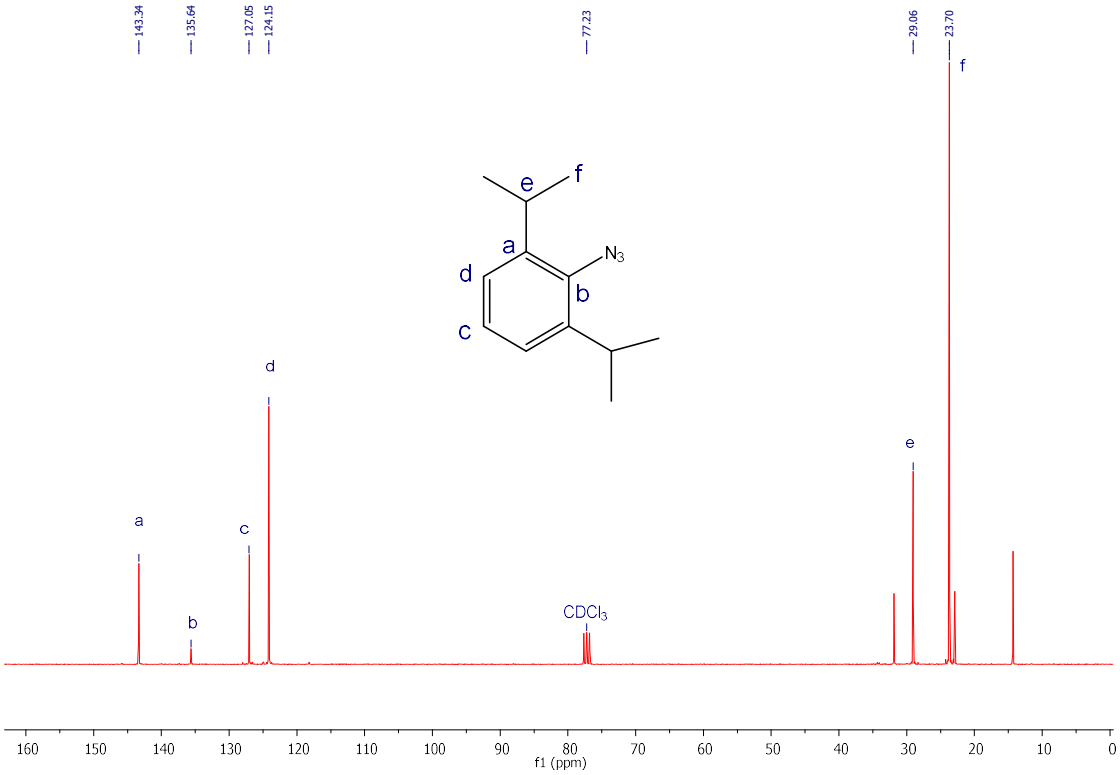


Figure 3.4. ^{13}C NMR spectrum of **1b** in $CDCl_3$

3.2 Synthesis and characterization of bis(triazoles) (2a,b)

The next synthetic step involves the preparation of bis-triazoles **2a,b** by means of a regioselective copper catalyzed Huisgen 1,3-dipolar cycloaddition between, a terminal bis-alkyne and the corresponding aromatic azides prepared in the previous section.

However, butadiyne would be the ideal starting material for this reaction is not used, because it is a flammable gas under ambient conditions and therefore less practical for our purpouse. Instead, the commercially available 1,4-bis (trimethylsilyl)butadiene, which is a solid was employed. As early mentioned, the reaction occurs between an azide and a terminal alkyne. Therefore, the trimethylsilyl (TMS) protecting group needs to be removed using a base. The addition of K_2CO_3 and pyridine together with the reaction conditions $tBuOH/H_2O$, promote the deprotection of the alkyne without interfering with the 1,3-dipolar Huisgen cycloaddition catalyzed by Cu.

The catalyst is prepared in situ by reduction of Cu (II) to Cu (I) salt in aqueous solution, in this case $CuSO_4 \cdot 5H_2O$ as a source of Cu^{II} and sodium ascorbate as reducing agent.

It is important to mention, that subsequently, a large number of extractions with 9/1 DCM/NH_4OH is necessary to be able to eliminate all the copper from the organic phase.[4]

3.2.1 Characterization:

In this section de ^{1}H RMN, ^{13}C NMR and mass spectrum of **2a**-**b** will be described.

- Characterization of **2a**:

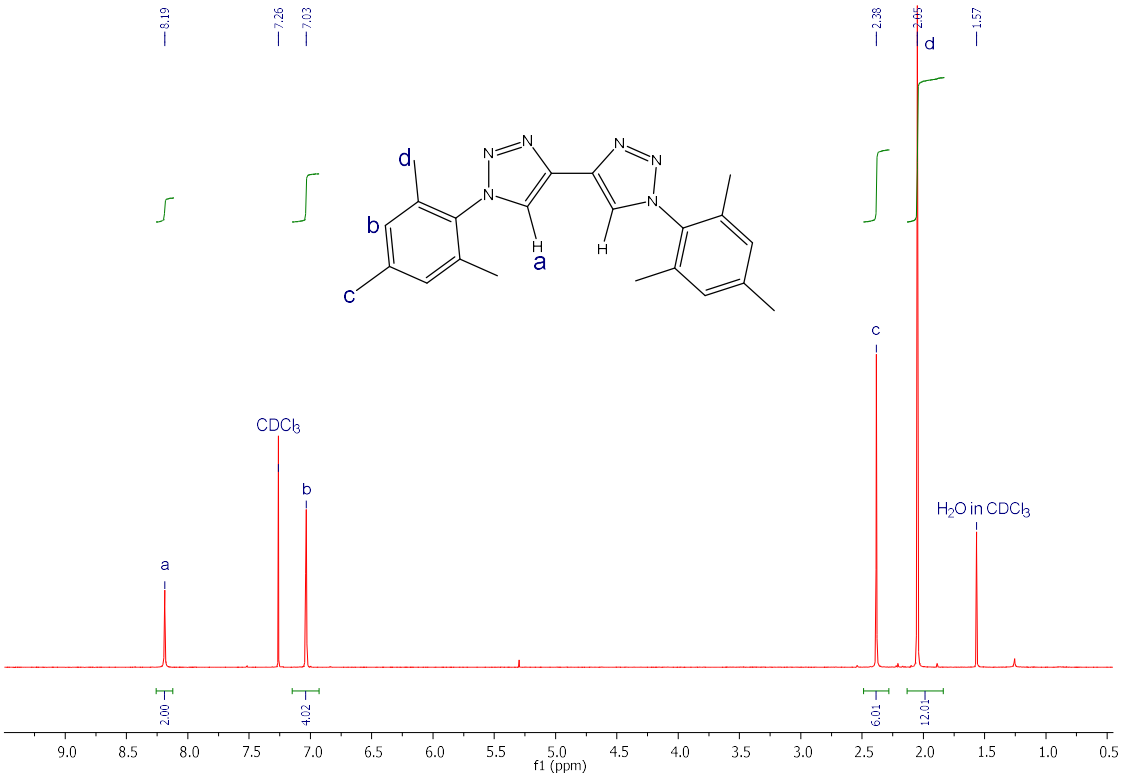


Figure 3.5. ^{1}H NMR spectrum of **2a** in $CDCl_3$

Figure 3.5 shows the ^{1}H NMR spectrum of **2a** in $CDCl_3$ (7.26 ppm). The singlet at 8.19 ppm corresponds to **a**, the acidic proton of the triazole. The signals due to the protons of the aromatic ring **b**, appear at 7.03 ppm as a singlet. The last two singlets, **c** at 2.38 and **d** 2.05 ppm corresponds to the methyl group in -*para* and in -*ortho* position respectively.

Figure 3.6 shows the ^{13}C NMR spectrum of **2a** in $CDCl_3$ (77.23 ppm). The signals at 140.48 and 133.56 ppm are assigned to the quaternary carbons of the aromatic ring **a, b** and **d**. Although we may expect two different peaks for **a** and **b**, in this case they are overlapped.

The peaks at 135.34 ppm and 129.46ppm, are assigned to **c** and **e**, that corresponds with the tertiary carbons of the bistriazole and those of aromatic ring respectively. The signal at 122.96 ppm corresponds to quaternary carbon **f** of the bistriazole. Finally, the two peaks **g** and **h** that corresponds to the methyl substituents attached to the aromatic ring were found at 21.35 and 17.55 ppm respectively.

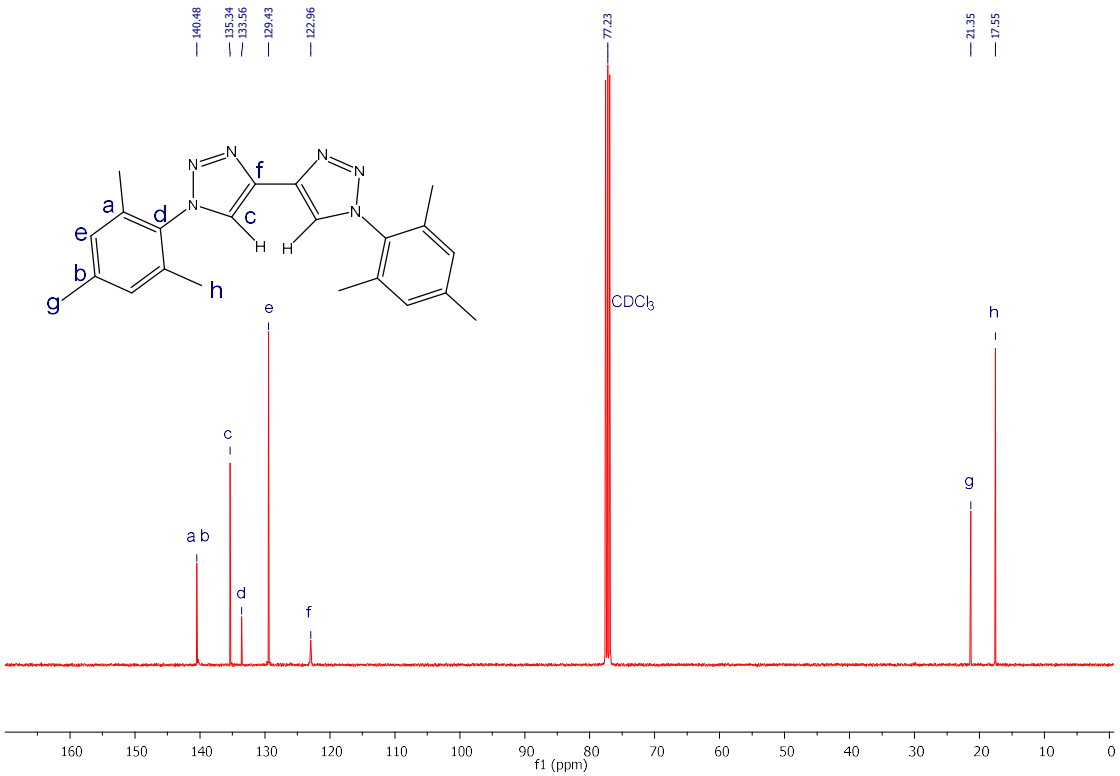


Figure 3.6. ^{13}C NMR spectrum of **2a** in $CDCl_3$

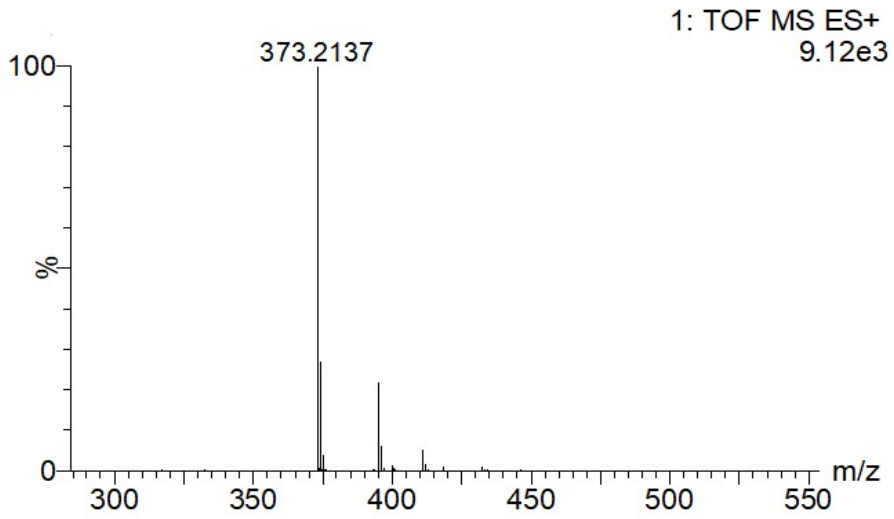


Figure 3.7. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **2a**

Figure 3.7 corresponds to the ESI-TOF-MS spectrum of **2a**, the characteristic peak at m/z 373.2137, matches perfectly with [M + H]. The existence of this peak confirms the presence of compound **2a** as a major compound and therefore confirm that the desired product has been obtained.

- Characterization of **2b**:

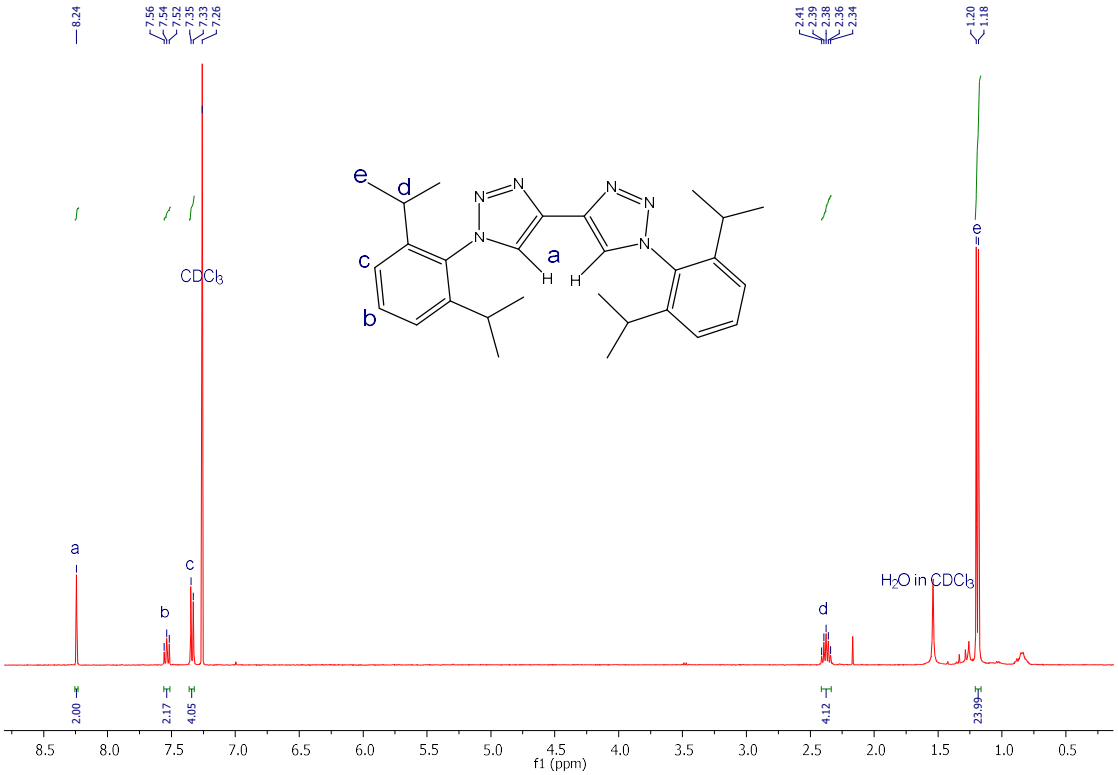


Figure 3.8. ^{1}H NMR spectrum of **2b** in $CDCl_3$

Figure 3.8 shows the ^{1}H NMR of compound **2b**, in $CDCl_3$, (7.26 ppm). The peak **a** observed at 8.24 ppm is a singlet and corresponds to the acidic proton of the triazole, Then the triplet **b** at 7.54 ppm and the doublet **c** at 7.34 ppm corresponds to the protons of the aromatic ring at -*para* position, and -*meta* position, respectively. Finally, the multiplet **d** at 2.38 ppm and the doublet **e** at 1.19 ppm are assigned to the CH and the methyls of the isopropyl group.

Figure 3.9 shows the ^{13}C NMR spectrum of **2b** in $CDCl_3$ (77.23 ppm). The peaks **a**, and **e** at 146.32 and 124.13 ppm are due to the tertiary carbons constituting the aromatic ring and the signals **b**, and **c** at 140.07 and 133.14 ppm are assigned to the quaternary carbons of the aromatic ring Then the peak at signal **d** and **f** at 124,13 and 123.88 ppm correspond to the tertiary and quaternary carbon of the triazole. Finally, the signals **g** at 28.65 ppm are due to CH the isopropyl group and the two peaks **h** and **i** at 24.47 and 24.26 ppm, corresponds to the methyl groups, the isopropyl group.

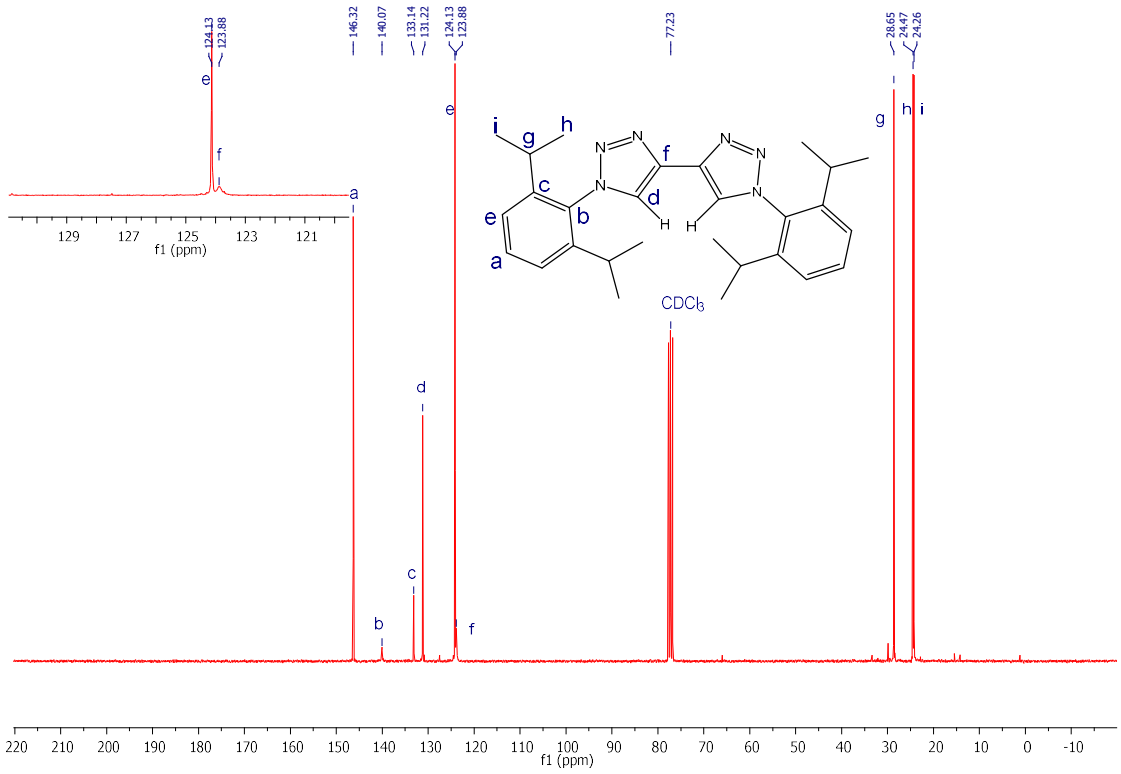


Figure 3.9. ^{13}C NMR spectrum of **2b** in $CDCl_3$

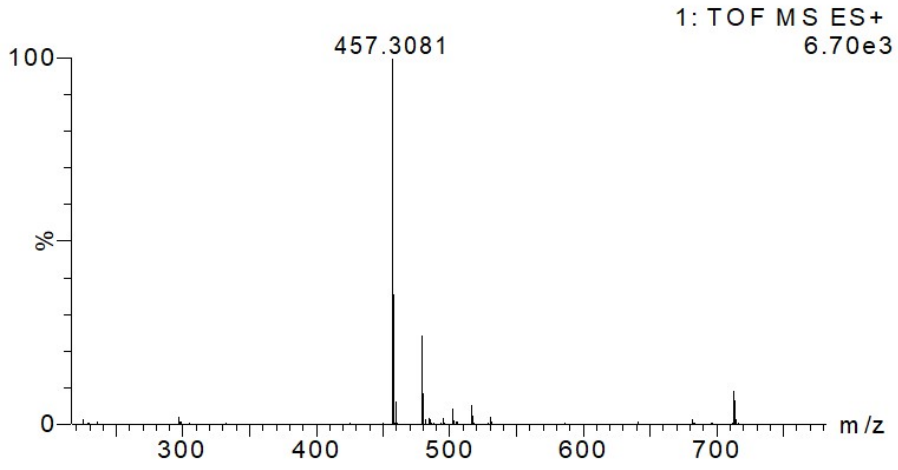


Figure 3.10. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **2b**

Figure 3.10 corresponds to the ESI-TOF-MS spectrum of **2b**, the characteristic peak at m/z 457.3081, matches perfectly with [M + H]. The existence of this peak confirms the presence of compound **2b** as a major compound and therefore confirm that the desired product has been obtained.

3.3 Synthesis and characterization of Bis(triazolium) Salts (3a,b)

Compounds **3 a,b** were prepared by alkylation of the bistriazoles using methyl trifluoromethanesulfonate as the alkylating agent. The synthesis of both ligand salt precursors **3a-b** were carried out in an inert atmosphere and require at least one night of reaction. While compound **3b** only needs one night at room temperature, compound **a**, needed longer reaction times, at least 48 h and higher temperatures, 100 ° C.[5]

3.3.1 Characterization:

In this section de ^{1}H RMN, ^{13}C NMR and mass spectrum of **3 a**,**b** will be described.

- Characterization of **3a**:

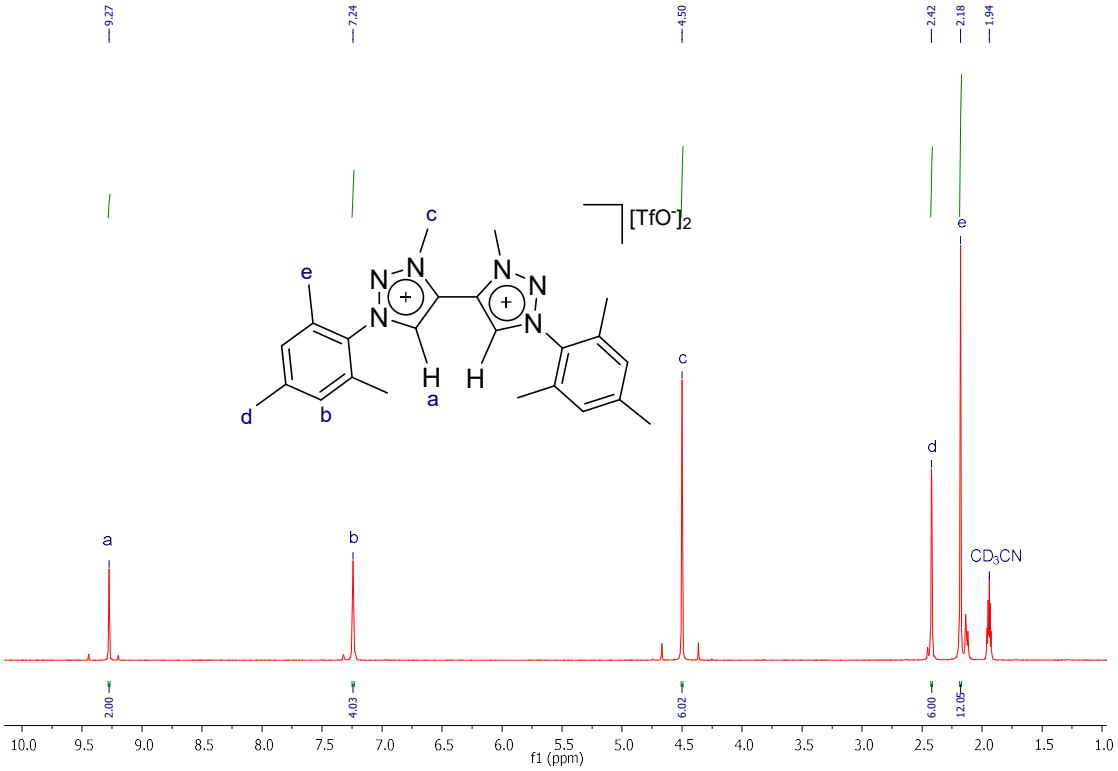


Figure 3.11. ^{1}H NMR spectrum of **3a** in CD_3CN

Figure 3.11 shows the ^{1}H NMR of compound **3a** in $CDCl_3$ (1.94 ppm). The peak **a** observed at 9.27 ppm is a singlet and corresponds to the acidic proton of the triazole. The signal due to the protons of the aromatic ring **b**, appear at 7.24 ppm as singlet. The peak **c** at 4.50 ppm is a singlet correspond to CH_3 from the alkylation. Finally, the singlets **d** and **e** at 2.42 and 2.18 ppm corresponds to the methyl group of the aromatic ring at *-para* position and *-ortho* position, respectively.

Figure 3.12 shows the ^{13}C NMR spectrum of **3a** in CD_3CN (118.69 and 1.39 ppm). Can be observed nine carbon signals, which perfectly matches the number of inequivalent carbons present in the molecule.

The peaks **a, c** and **e** at 144.55, 131.99 and 128.62 ppm are due to the quaternary carbons constituting aromatic rings and the signal **d** at 131.04 ppm are assigned to the tertiary carbon of the aromatic ring. The peak **b** and **f** at 135.87 and 118.03 ppm correspond to the tertiary and quaternary carbon of the triazole, respectively. The peak **g** at 41.59 ppm correspond to the methyl from alkylation. The signals **h** and **i** at 21.37 and 17.61 ppm, correspond to the methyl substituents attached to the aromatic ring.

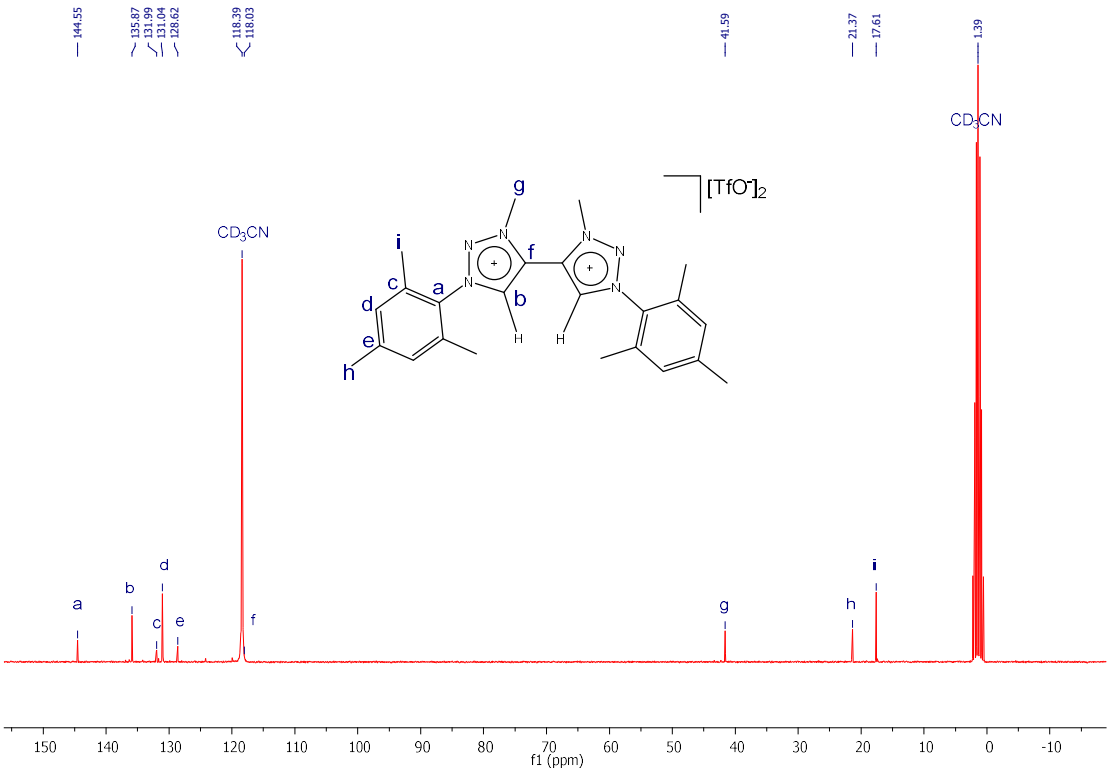


Figure 3.12. ^{13}C NMR spectrum of **3a** in CD_3CN

Figure 3.13 correspond to the ESI-TOF-MS spectrum of **3a**, the main peak at m/z 551.2054 and 201.1246 can be assigned to $[M + TfO]^+$ and a $[M]^{2+}$ respectively. The appearance of these peaks confirms the identity of the product obtained, it also reflects a high purity of the product obtained, due to the low % of peaks of unidentified compounds.

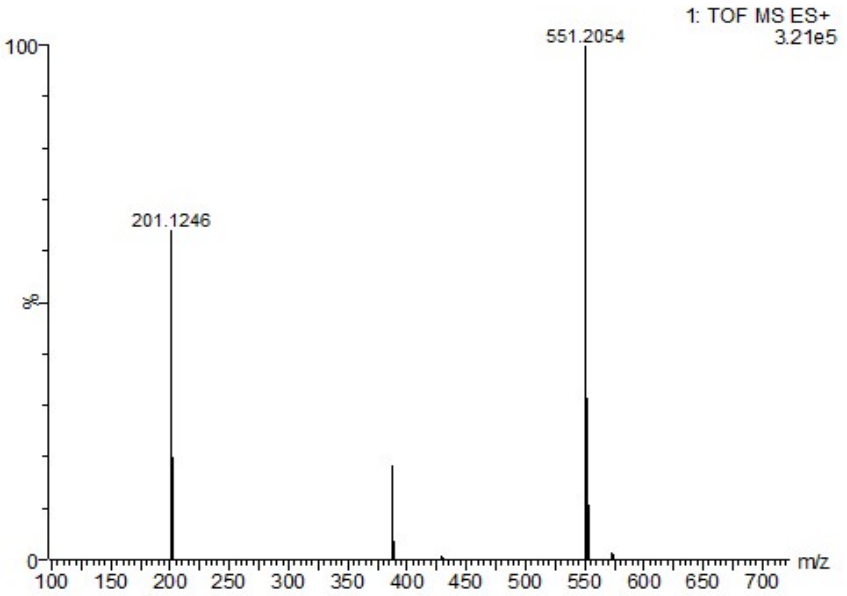


Figure 3.13. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **3a**

- Characterization of **3b:**

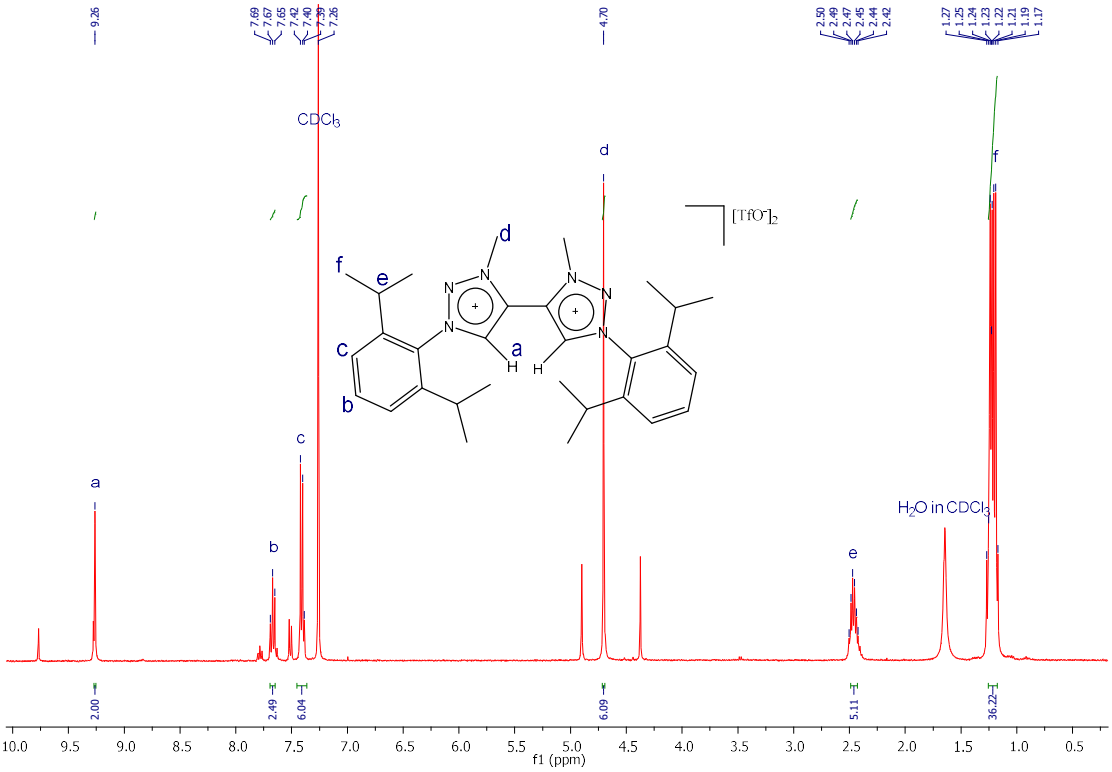
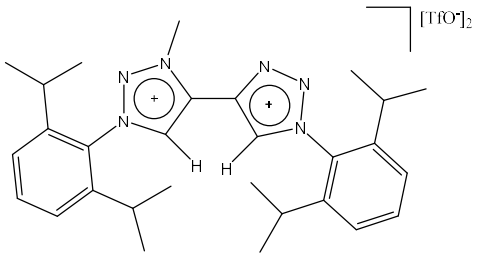


Figure 3.14. ^{1}H NMR spectrum of **3b** in $CDCl_3$

Figure 3.14 shows the ^{1}H NMR spectrum of compound **3b** in $CDCl_3$ (7.26 ppm). The peak **a** observed at 9.26 ppm is a singlet and correspond to the acid proton of the triazoles. Then, the triplet **b** at 7.67 ppm and the doublet **c** at 7.40 ppm correspond to the protons of the aromatic ring at -*para* and -*meta* position respectively. The peak **d** at 4.70 ppm correspond to the methyl from alkylation. Finally, the multiplets **e** and **f** at 2.46 and 1.22 ppm are assigned to the CH and the methyls of the isopropyl group respectively.

Figure 3.14 also shows signals that do not correspond to **3b**, that indicates the presence of an impurity or by-product. These signals appear very close to the correct ones, therefore, the compound must be very similar to **3b**. It is proposed that the by-product formed is represented in Scheme 2.



Scheme 3.2. Possible by-product

This means, that the correct alkylation has not occurred in the entire compound. Therefore, there is a part of the compound in which only one nitrogen has been methylated instead of both, and the product obtained is a mixture of both, so it would cease to be a symmetric molecule and each side of the molecule would come out to a chemical displacement similar, but not the same.

Despite this, the spectrum shows that the desired product has been obtained as a major compound, so perhaps, it would be possible to obtain the product by performing a more extensive purification or by making a crystallization.

Figure 3.15 shows the ^{13}C NMR spectrum of compound **3b** in $CDCl_3$ (77.23 ppm). The peaks **a** and **e** at 146.40 and 129.11 ppm are due to the quaternary carbons constituting the aromatic ring and the signals **c** and **d** at 133.72 and 130.57 ppm, are assigned to the tertiary carbons of the aromatic ring. The peaks **b** and **f** at 134.25 and 125.15 ppm correspond to the tertiary and quaternary carbons of the triazole. The peak **g** at 40.95 ppm is due to the methyl group from alkylation. Finally, the signal **h** at 28.80 is due to CH the isopropyl group and the two signals **i** and **j** at 24.46 and 23.94 ppm, correspond to the methyl groups, the isopropyl group.

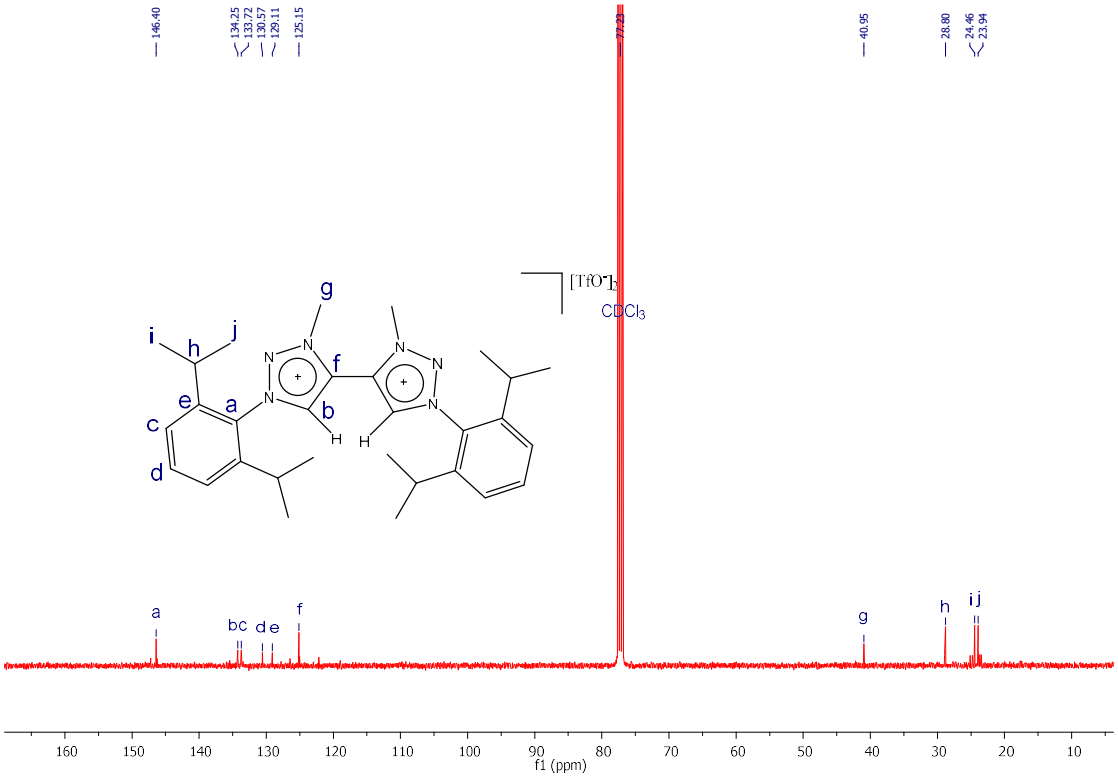


Figure 3.15. ^{13}C NMR spectrum of **3b** in $CDCl_3$

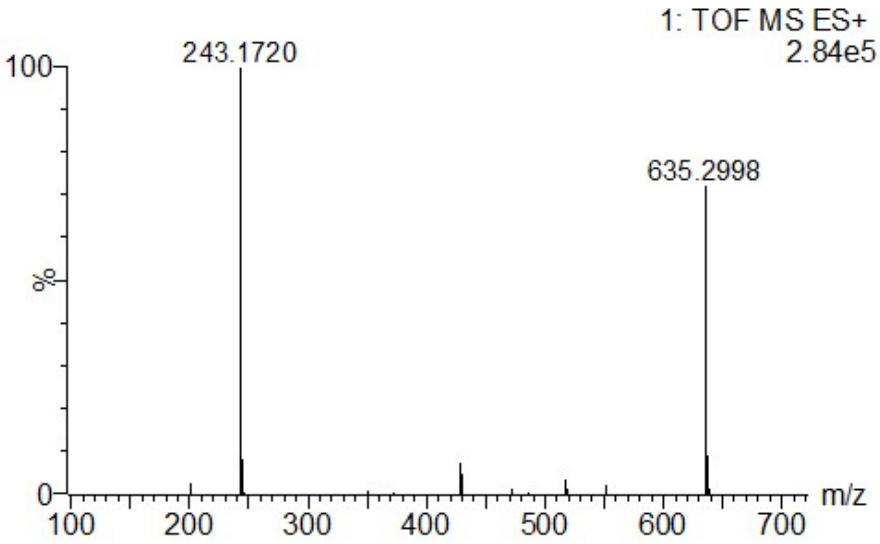


Figure 3.16. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **3b**

Figure 3.16 correspond to the ESI-TOF-MS spectrum of **3b**, the main peaks at m/z 635.2998 and 243.1720 can be assigned to $[M + TfO]^+$ and a $[M]^{2+}$ respectively. The presence of these peaks confirms, that the desired compound was obtained.

3.4 Synthesis of complexes with Iridium (4a,b)

As earlier mentioned, none of the targeted complexes had been previously described in the literature. Herein, we adapted the synthetic procedure described for a related metal complex.

The [Ir (cod)(μ-Cl)]$_2$ complex was used as iridium precursor and NaO^{t}Bu as base dry THF is used as the solvent. The reaction was carried out in a Schlenk flask, under nitrogen atmosphere at -78 ° C.

As it can be observed in the NMR spectrum, the synthesis of the iridium complex was not successful, or at least to achieve it with a minimum purity. In both cases it was purified several times, dissolving in ether or DCM and filtering it later. Even so, no improvement was obtained. It could be possible the necessity of changing some of the conditions of the reaction to be able to obtain the desired product, but in this case there was not enough time to be able to carry it out.

3.4.1 Characterization:

^{1}H NMR of **4a**:

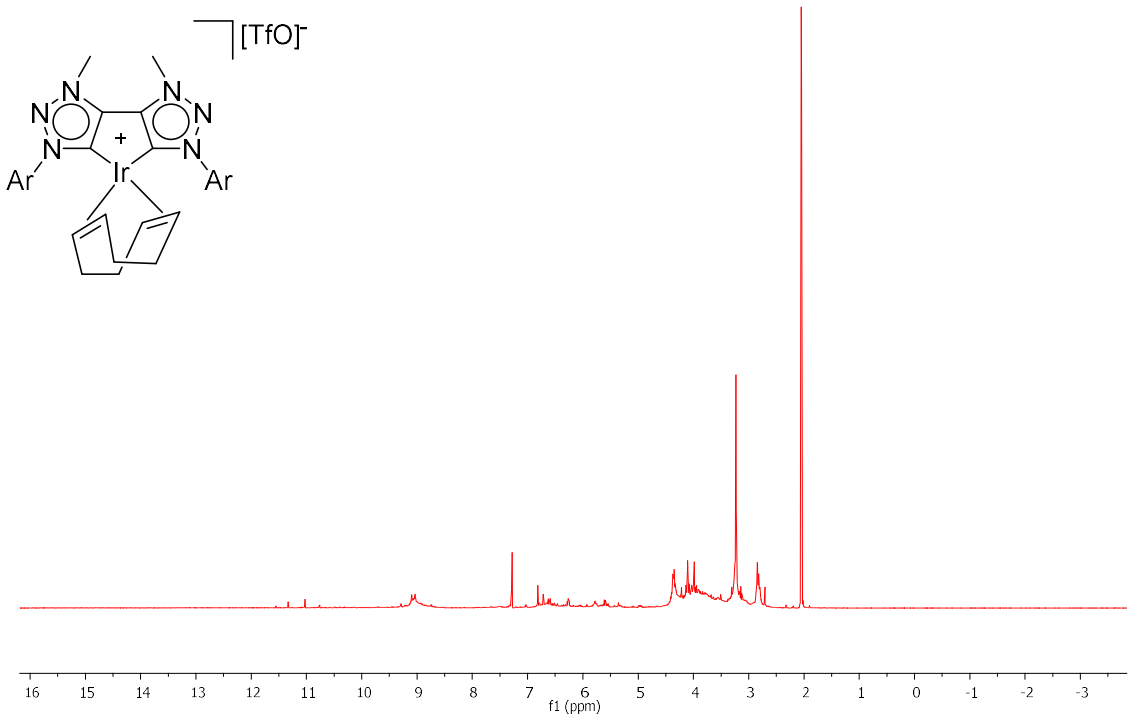


Figure 3.17. ^{1}H NMR spectrum of the crude mixture from the attempted synthesis of **4a** in CD_2Cl_2

^{1}H NMR of **4b**:

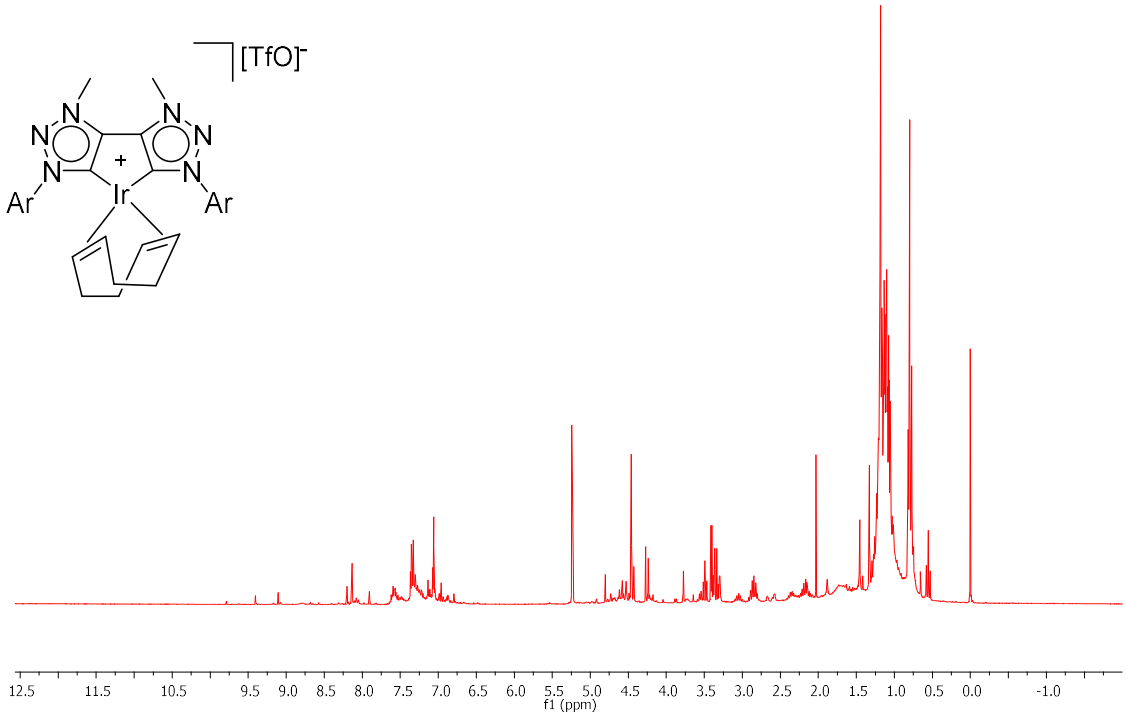


Figure 3.18. ^{1}H NMR spectrum of the crude mixture from the attempted synthesis of **4b** in CD_2Cl_2

Subsequently, it should be bubbled with CO to replace the COD ligand with the CO ligand and thus form the compound **5**, but since the satisfactory synthesis of the complex **4** has not been achieved, the synthesis was not carried forward.

References

1. Ugi, I., Perlinger, H. & Behringer, L. *Chem. Ber*. **1958**, 91, 2330-2336.

2. Guisado-Barrios, G., Bou, J., Donnadieu, B. & Bertrand, G. *Angew. Chem.* **2010**, 122, 4869 -4872

3. Fletcher, J. T., Bumgarner, B. J., Engels, N. D. & Skoglund, A. *Organometallics* **2008**, 27, 5430-5433

4. Guisado-Barrios, G., Bouffard, Jean., Donnadie, B. & Bertrand, G. *Organometallics*, **2011**, 30, 6017-6021

5. Brill, M., Marrwitz, D., Rominger, F. & Hofmann, P. *J. Org. Chem.* **2015**, 75, 137-151

4. CONCLUSIONS

During my stay at the Group of Organometallic Chemistry and Homogenous Catalysis (QOMCAT) at the Jaume I University, I had the opportunity to see from the inside, how it works in a research laboratory and how is the process in the synthesis of a novels compounds.

The news compounds consist of an Ir (I) catalyst linked to a bis (1,2,3-triazol-5-ylidene) (i-bitz) ligand and also to two carbonyls, to study its properties and activity in the catalytic conversion of glycerol from the production of biodiesel in lactic acid. To this end, the corresponding azides, Bis (triazoles) and Bis (triazolium) alts have been synthesized, to be subsequently complexed.

The desired complex has not been obtained. Being a novel catalyst, the procedure for the synthesis of an analogous compound has been followed, in which the structure of the NHC ligand varied. It is therefore reasonable to think that it would be necessary some modification in said procedure to be able to obtain the desired package.

All the synthesized compounds were characterized by the usual characterization techniques, ^{1}H NMR, ^{13}C NMR and Mass Spectrometry. The azides were decomposed and the mass spectrum was not obtained. On the other hand, the final compounds **5a**,**b**, as observed, did not give a clear spectrum, so it can be said that the complexation was not achieved and therefore neither ^{13}C NMR nor mass spectrum were performed.

5. EXPERIMENTAL SECTION

5.1 General comments

In this research, all the reactions were carried out under an inert atmosphere unless otherwise stated. It was necessary to use anhydrous solvents, which were dispensed by the solvent purification system (SPS) M BRAUN. The reagents and other non-anhydrous solvents that were used were received by the commercial house.

The NMR spectra equipment that was used for the analysis was the Bruker spectrometers operating at 400 MHz (^{1}H NMR), 300 MHz (^{1}H NMR) and 100.8 MHz (^{13}C NMR), and were used as solvents $CDCl_3$, CD_3CN and CD_2Cl_2.

Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas.

All the reagents were obtained from commercial available suppliers. Compound **1a** was synthesized according to Behringer *et al*.[1], while compound **1b** followed the procedure according to Bertrand *et al*.[2] Azides are potentially dangerous compounds, since they can decompose explosively, for this reason they should not be prepared on a large scale.

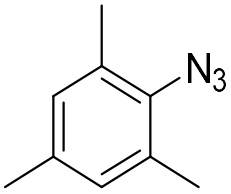
The **2a,b** and **3a,b** compounds were all synthesized by adapting a reported procedure by Bertrand *et al.*[3]. Whereas the synthesis of bistriazoles **2a,b**, was carried out under aerobic conditions, the preparation of **3a,b**, the alkylation, required the use of inert atmosphere.[3]

For the complexation studies, the attempted synthesis of **4a,b** was carried out adapting a reported method in the literature[4], that required the use of Schlenk techniques and to work under intert atmosphere. The iridium precursor $[Ir(cod)(\mu\text{-}Cl)]_2$ was prepared according to a literature procedure.[5]

5.2 Synthesis and characterization

5.2.1 Synthesis of azides.

- Synthesis of **1a.**



To a stirred solution of $MesNH_2$ (13.5 g, 99.9 mmol) in 20 mL HCl conc., 60 mL H_2O and 60 mL of ice at 0°C, was added, dropwise, an aqueous solution containing 7.38 g $NaNO_2$ (7.38 g, 107.0 mmol) in 38 mL H_2O. The reaction mixture was cold and stirring for 20 min. Afterward, $CaCO_3$ (12 g, 119.9 mmol) was added. Then, the ice bath was removed and NaN_3 (7.54 g, 116.0 mmol) in 30 mL H_2O was added to the solution. The reaction solution was allowed to warm up to room temperature and stirred for 30 min. After this period of time The product was extracted from the aqueous phase with pentane (3x 50 mL). The organic phase was passed through a pad of silica and the volatiles were removed to yield a yellow oil (12.4 g, 77.02%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 (s, 2H, CH_{arom}), 2.37 (s, 6H, $CH_{3\ ortho}$), 2.30 (s, 3H, $CH_{3\ para}$). ^{13}C NMR (100.8 MHz, $CDCl_3$): δ 135.4 ($C_{quat.\ arom}$), 134.5 (CN_{arom}), 131.9 ($C_{quat.\ arom}$), 129.7 (CH_{arom}), 20.8 ($CH_{3\ ortho}$), 18.1, ($CH_{3\ para}$).

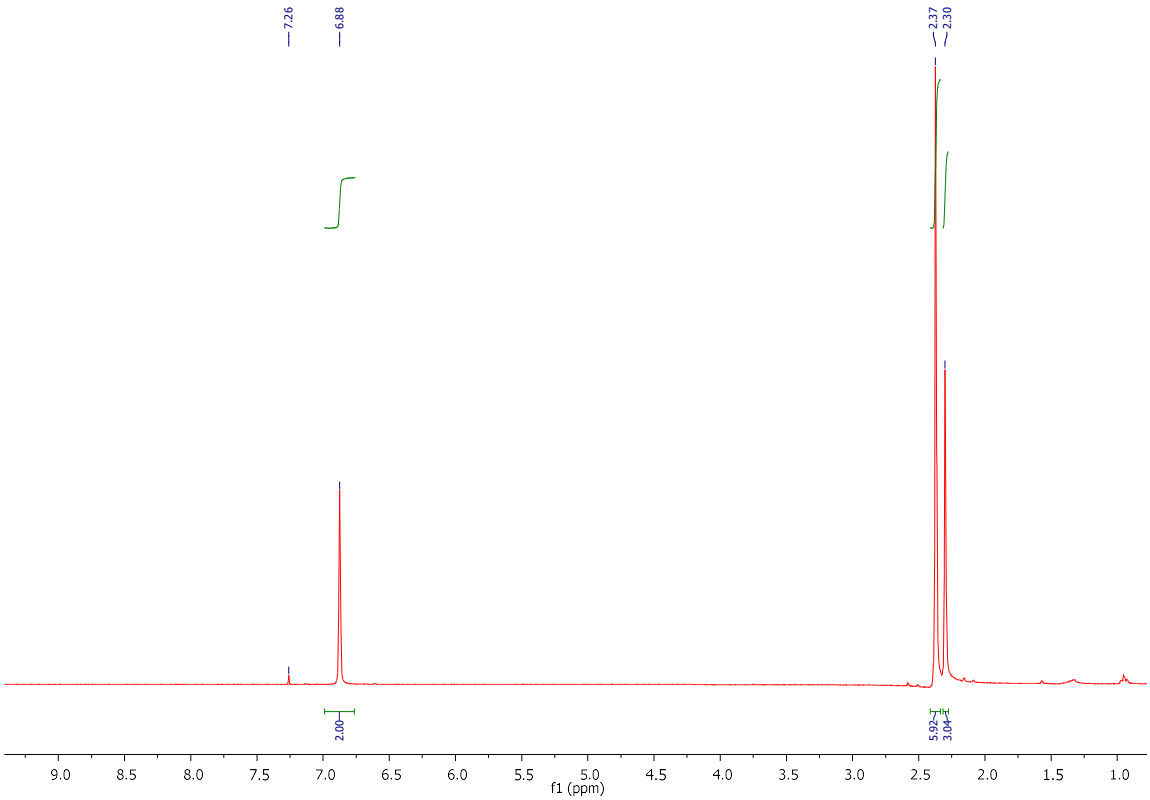


Figure 5.3. ^{1}H NMR spectrum of **1a** in $CDCl_3$

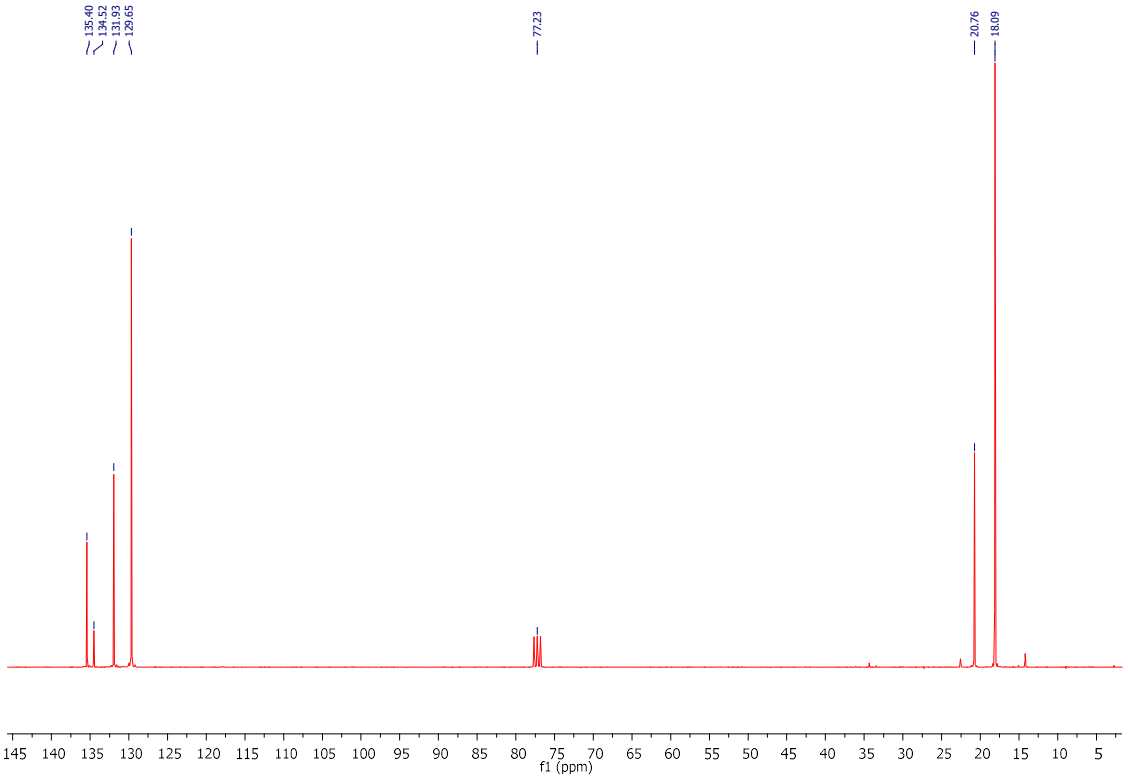
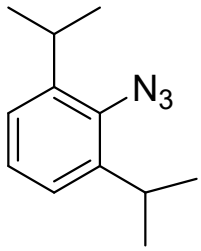


Figure 5.4. ^{13}C NMR spectrum of **1a** in $CDCl_3$

- Synthesis of **1b.**



To a stirred solution of 2,6 Diisopropylaniline (2.76 g, 15.6 mmol) in CH_3CN (10 mL) at 0°C, were added first *tert*-butyl nitrite (2.42 g, 23.5 mmol), then Me_3SiN_3 (2.17 g, 18.8 mmol) was added dropwise at 0°C in an ice bath. The reaction mixture was warmed to room temperature, while stirring was maintained for 1 h. The solvent was evaporated. The crude mixture was purified by column chromatography, the mobile phase used was hexane. The solvent was evaporated again to yield a yellow oil (3.87 g, 122.35%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (m, 3H, CH_{arom}), 3.36 (m, 2H, CH), 1.27(d, 12H, CH_3). ^{13}C NMR (100.8 MHz, $CDCl_3$): δ 143.3 ($C_{quat\ arom}$), 135.6 (CN), 127.0 and 124.2 (CH_{arom}), 29.1 (CH) and 23.7 (CH_3).

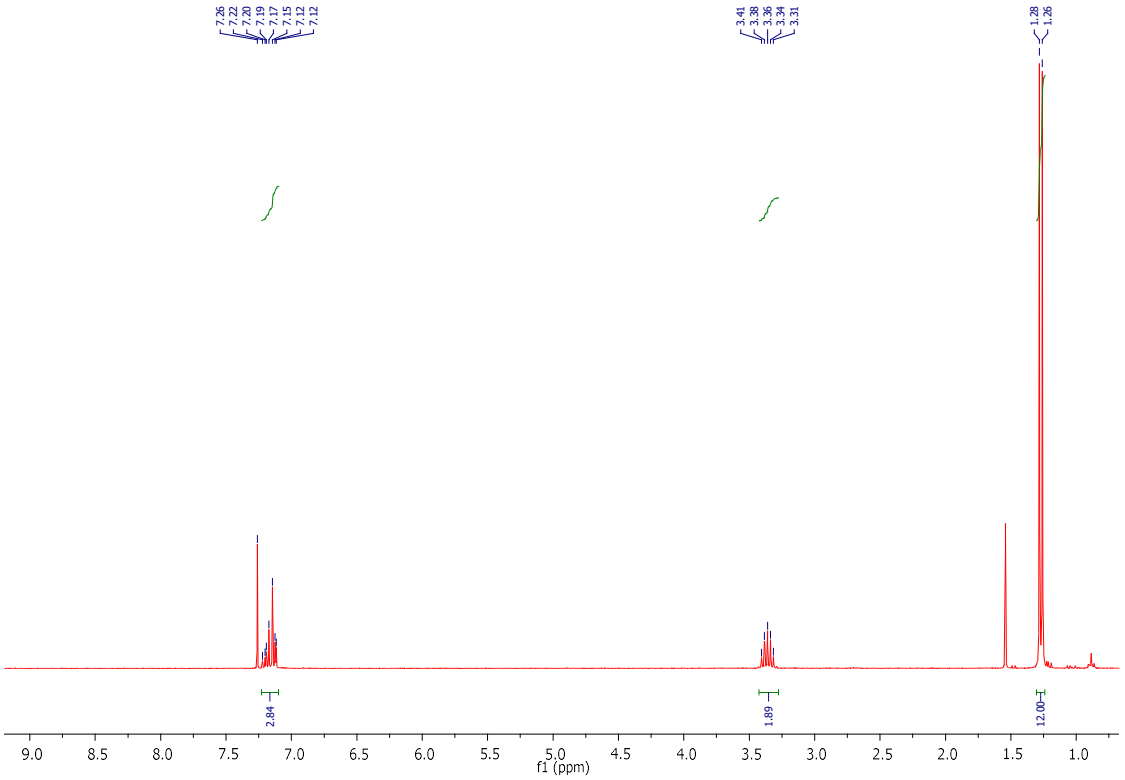


Figure 5.5. ^{1}H NMR spectrum of **1b** in $CDCl_3$

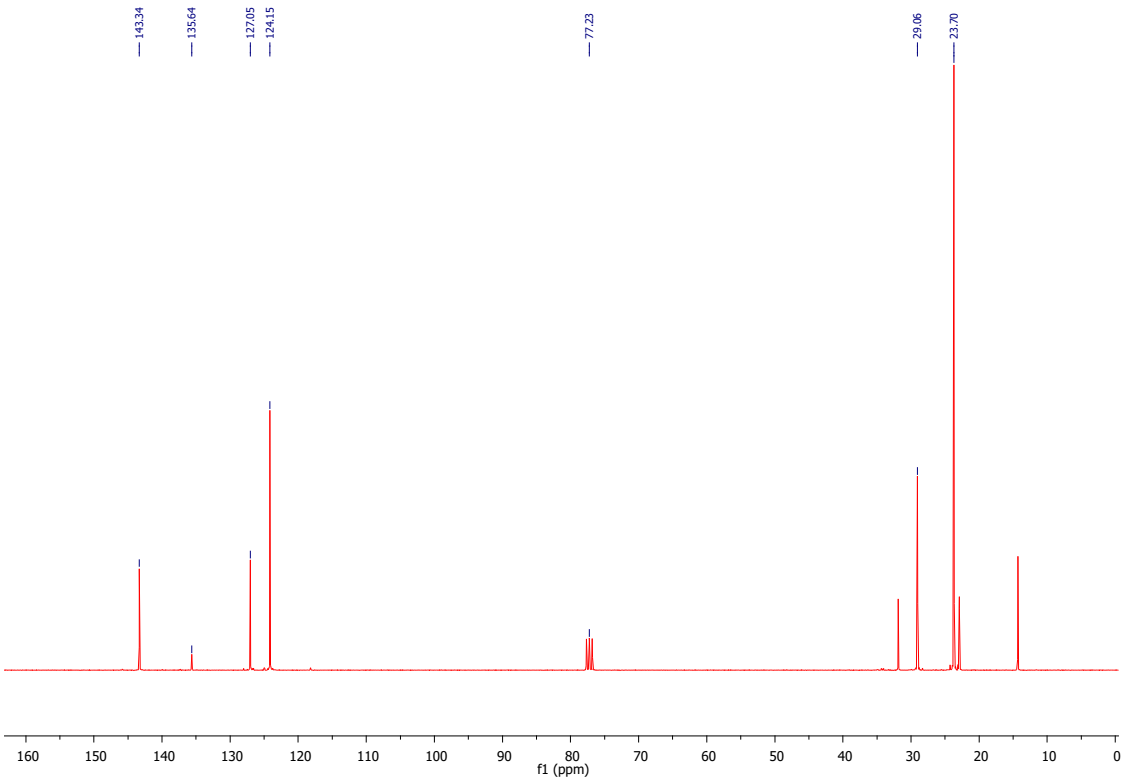
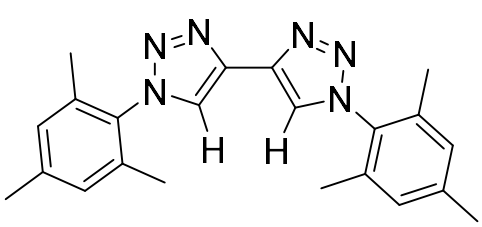


Figure 5.6. ^{13}C NMR spectrum of **1b** in $CDCl_3$

5.2.2 Synthesis of Bis(triazoles)

- Synthesis of **2a**



To a 60 mL approx. of a mixture 1/1 tert-butyl alcohol/H_2O, were added 2-azido-1,3,5-trimethylbenzene (5.0 g, 31.0 mmol), 1,4-bis(trimethylsilyl)buta-1,3diyne (3.01 g, 15.5 mmol), $CuSO_4 \cdot 5H_2O$ (1.44 g, 5.8 mmol), sodium ascorbate (2.46 g, 12.4 mmol) and K_2CO_3 (4.01 g, 29.0mmol). The mixture was stirred 2 days at room temperature.

The solution was washed with 9/1 DCM/NH_4OH as many times as necessary until the blue colour of the aqueous phase was eliminated, this was due to the presence of copper. Once all the Cu was removed, the solvent and pyridine that could remain were evaporated. Pentane was added and filtered. The precipitate was dissolved with ether and filtered again.

The solid was washed with 9/1 DCM/NH_4OH again and the organic phase was dried over magnesium sulphate, and the solvent was evaporated. To the crude mixture was added THF and filtered to yield a crystalline white solid (2.67 g, 46%).^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 2H, H_{trz}), 7.03 (s, 4H, CH_{arom}), 2.38 (s, 6H, $CH_{3\ para}$), 2.05 (s, 12H, $CH_{3\ ortho}$). ^{13}C NMR (100.8 MHz, $CDCl_3$): δ 140.5 ($C_{quat.\ arom}$), 135.3 (NHC), 133.6 (CN), 129.4 (CH_{arom}), 123.0 (CN_{trz}), 21.4 ($CH_{3\ para}$), 17.6 ($CH_{3\ ortho}$). ESI-TOF-MS (positive mode): $[M+H]^+$ calcd 373.2141 found 373.2137 (1.1 ppm).

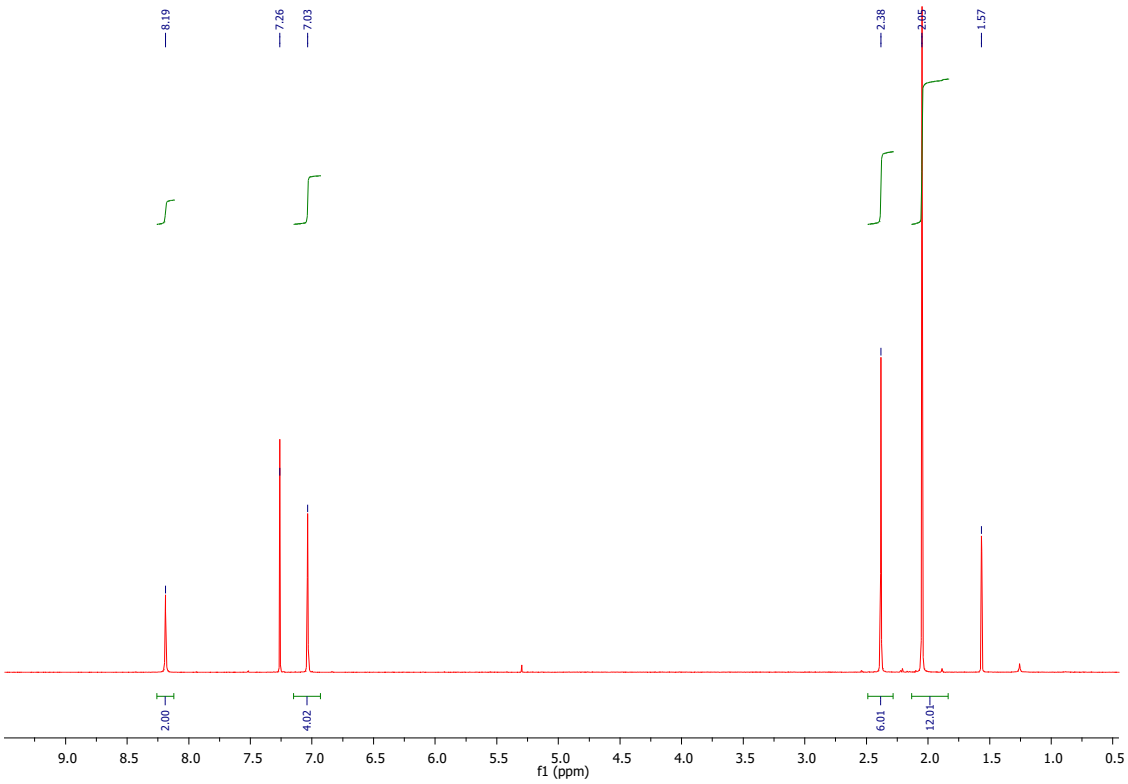


Figure 5.7. ^{1}H NMR spectrum of **2a** in $CDCl_3$

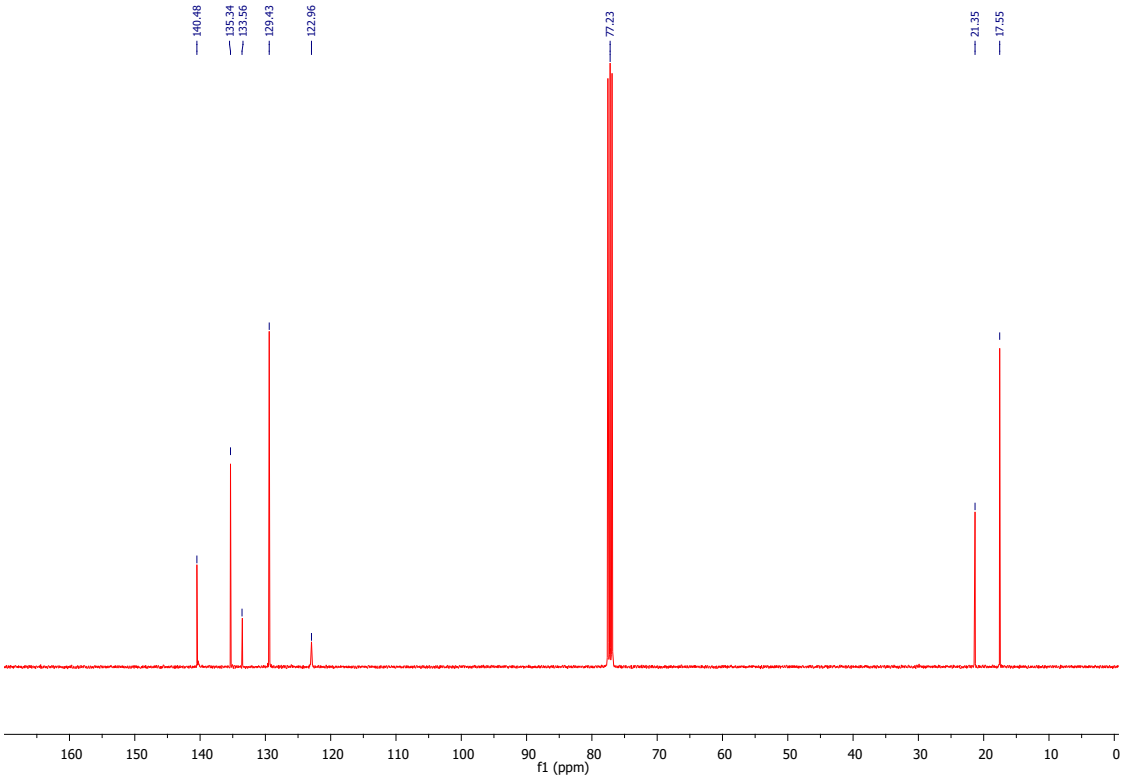


Figure 5.8. ^{13}C NMR spectrum of **2a** in $CDCl_3$

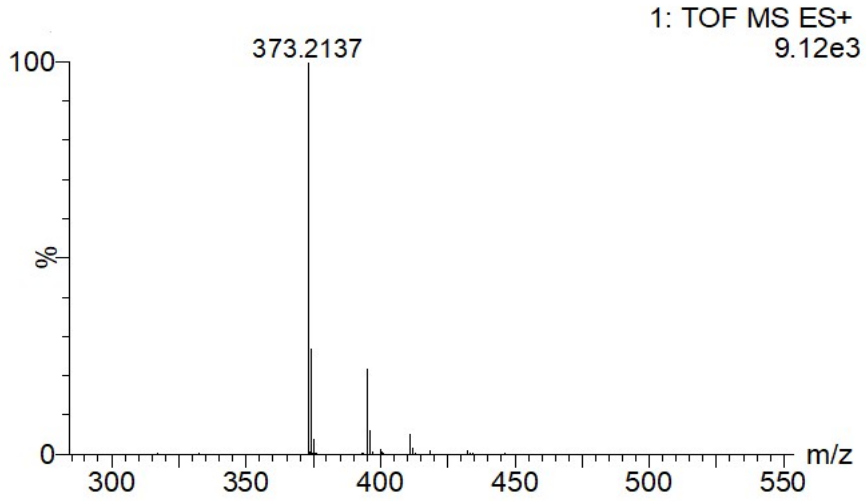
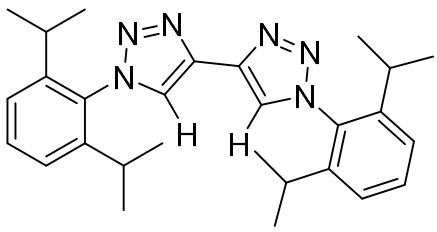


Figure 5.9. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **2a**

- Synthesis of **2b.**



In a 3 neck round flask was added 1b (2.0 g, 9.8 mmol), 40 mL of CH_3CN, 1,4-bis(trimethylsilyl)buta-1,3diyne (0.88 g, 4.5 mmol) pyridine (3.54 g, 44.80 mmol), an aqueous solution containing $CuSO_4 \cdot 5H_2O$ (0.29 g, 1.2 mmol) and sodium ascorbate (0.71 g, 3.6 mmol) in H_2O (40 mL) and last K_2CO_3 (1.24 g, 9.0 mmol). The mixture was stirred 3 days at room temperature.

The white precipitate was washed with pentane and ether in a filter plate. A second wash was carried out, the resulting solution was evaporated and a white crystalline solid, the compound, is obtained (0.05 g, 0.10 mmol, 1.99%). The non-dissolved precipitate was subjected to a purification process. It was washed with DCM, and washed again with CH_3CN.

Both were purified by column chromatography, silica compacted whit DCM and as phase mobile 95:5 DCM/ MeOH. Afterwards, the solvent was dissolved to yield a whitish solid. (0.32 g, 0.69 mmol, 14.03%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 2H, H_{trz}), 7.54 (t, 2H, $CH_{arom\ para}$), 7.34 (d, 4H, $CH_{arom\ metha}$), 2.38 (m, 4H, CH), 1.19 (d, 24H, CH_3). ^{13}C NMR (100.8 MHz, $CDCl_3$): δ 146.3 ($CH_{arom\ para}$), 140.1 (CN_{arom}), 133.1 ($C_{quat\ arom}$), 131.22 (NHC), 124.1 (CH_{arom}), 123.9 (CN_{trz}), 28.7 (CH), 24.5 and 24.3 (CH_3). ESI-TOF-MS (positive mode): $[M+H]^+$ calcd 457.3081 found 373.3080 (0.2 ppm).

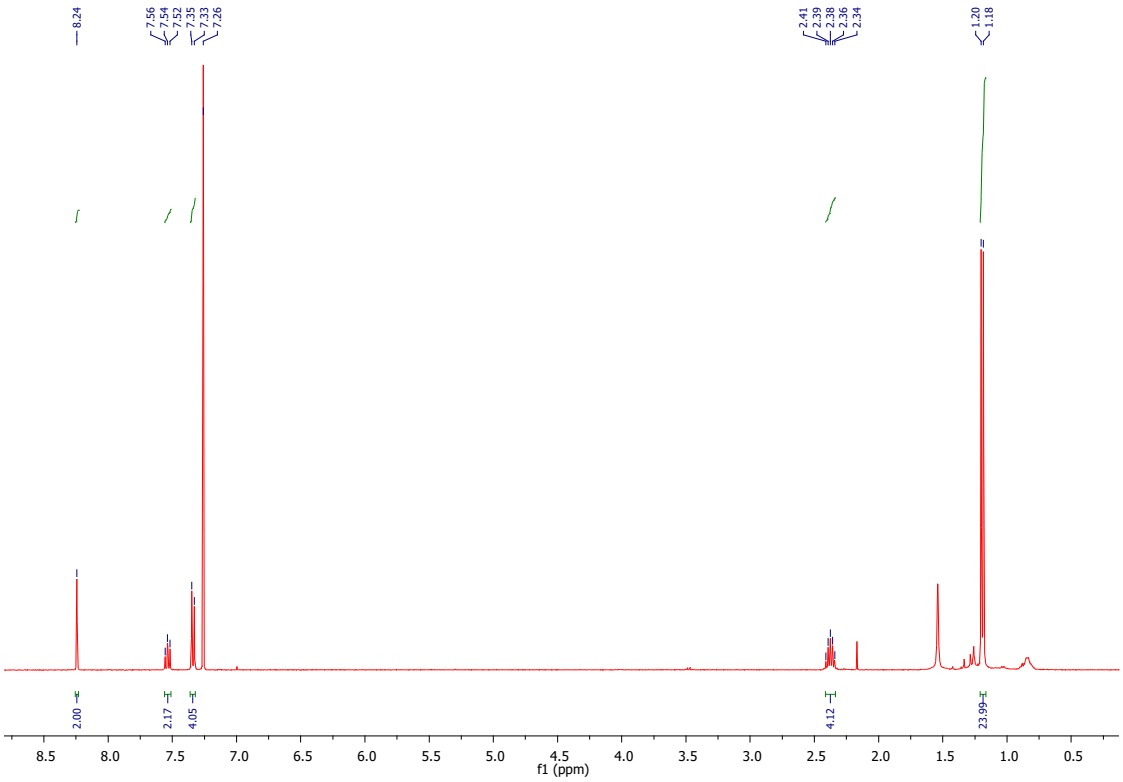


Figure 5.10. ^{1}H NMR spectrum of **2b** in $CDCl_3$

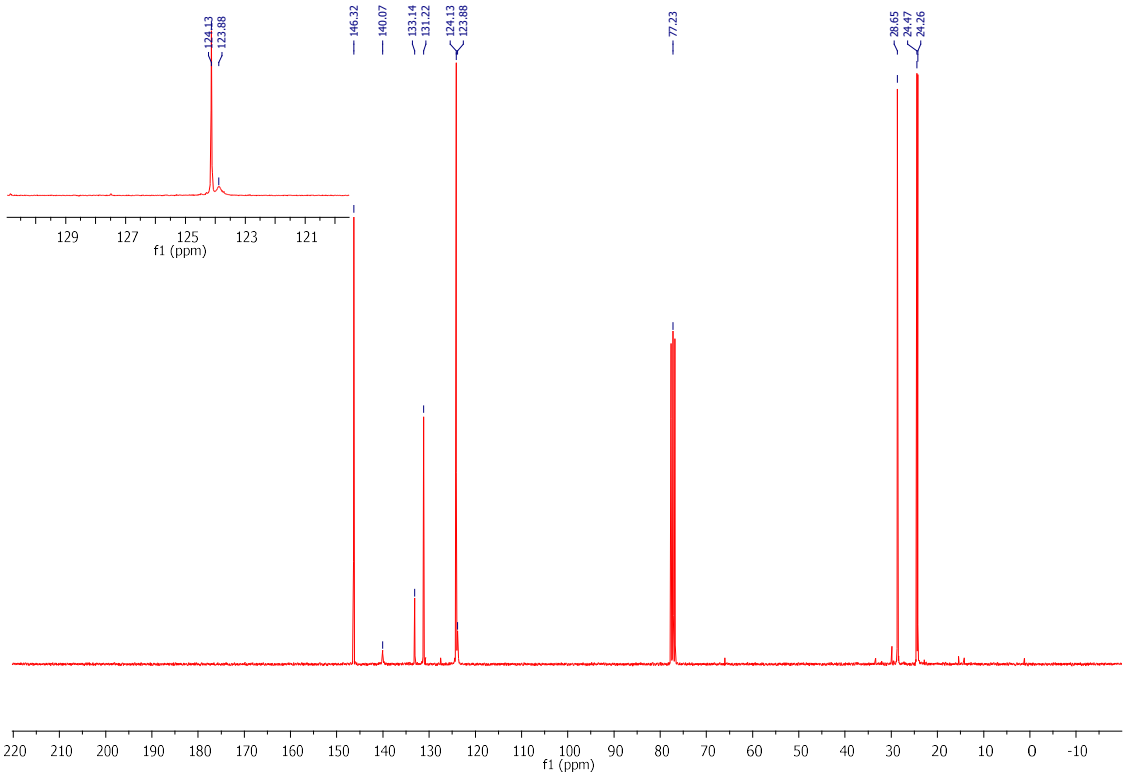


Figure 5.11. ^{13}C NMR spectrum of **2b** in $CDCl_3$

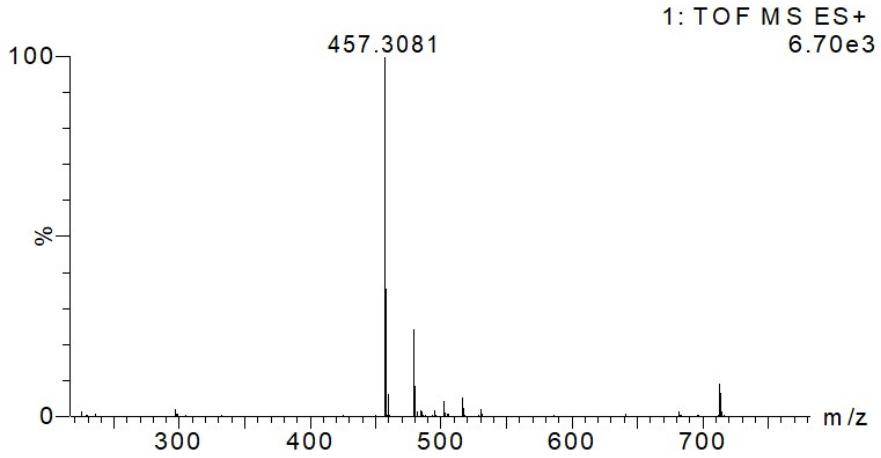
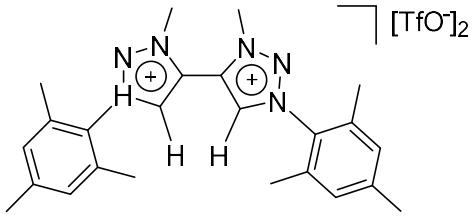


Figure 5.12. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **2b**

5.2.3 Synthesis of Bis(triazolium) Salts

- Synthesis of **3a**



To a stirred solution of 2a (1.20 g, 3.20 mmol) in DCE (20 mL) was added methyl trifluoromethanesulfonate (1.17 g, 7.10 mmol). The reaction was heated to 100°C in a sealed Schlenk flask for 48 h.

The mixture was filtered and the precipitated washed with ether to yield a white solid (1.17 g, 52 %).^{1}H NMR (300 MHz, CD_3CN): δ 9.27 (s, 2H, H_{trz}), 7.24 (s, 4H, CH_{arom}), 4.50 (s, 6H, $CH_{3\ alk}$), 2.42 (s, 6H,$CH_{3\ para}$), 2.18 (s, 12H, $CH_{3\ ortho}$). ^{13}C NMR (100.8 MHz, CD_3CN): 144.6 (CN), 135.9 (NHC), 132.0 ($C_{quat\ arom}$), 131.0 (CH_{arom}), 128.6 ($C_{quat\ arom}$), 118.03 (CN_{trz}), 41.6 ($CH_{3\ alk}$), 21.4 and 17.7 (CH_3). ESI-TOF-MS (positive mode): $[M+TfO]^+$ calcd 551.2052, found 551.2054 (0.4 ppm).

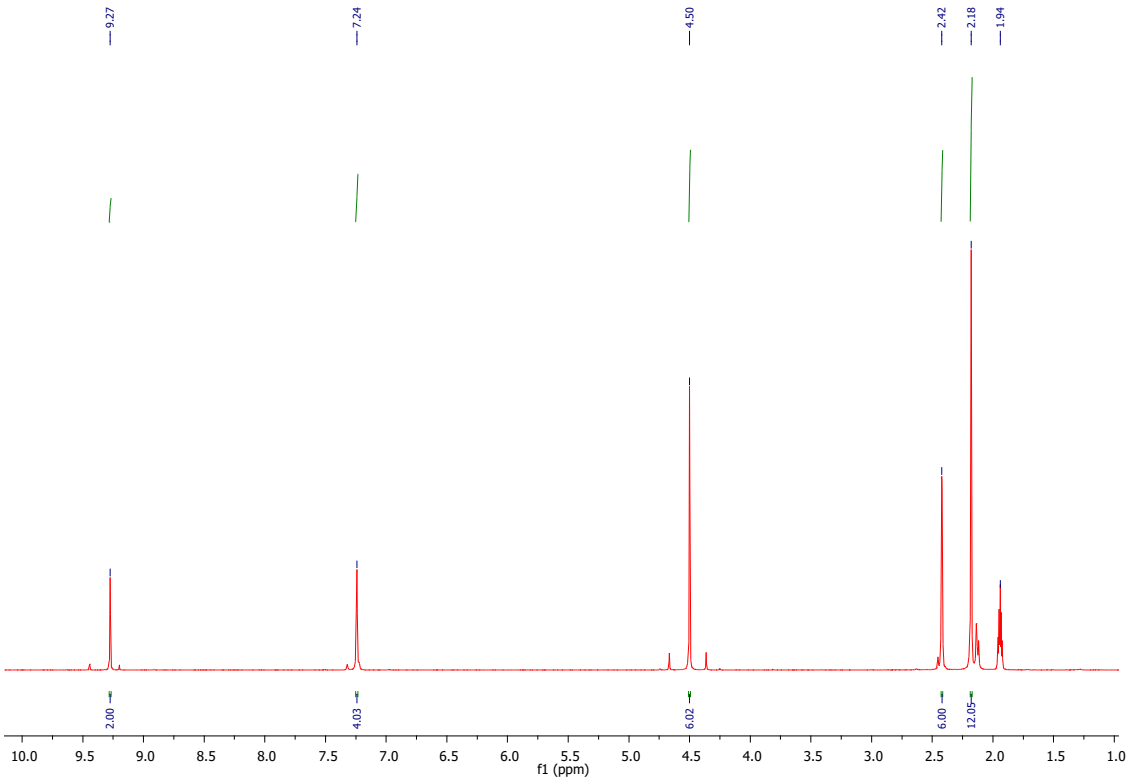


Figure 13: ^{1}H NMR spectrum of **3a** in CD_3CN

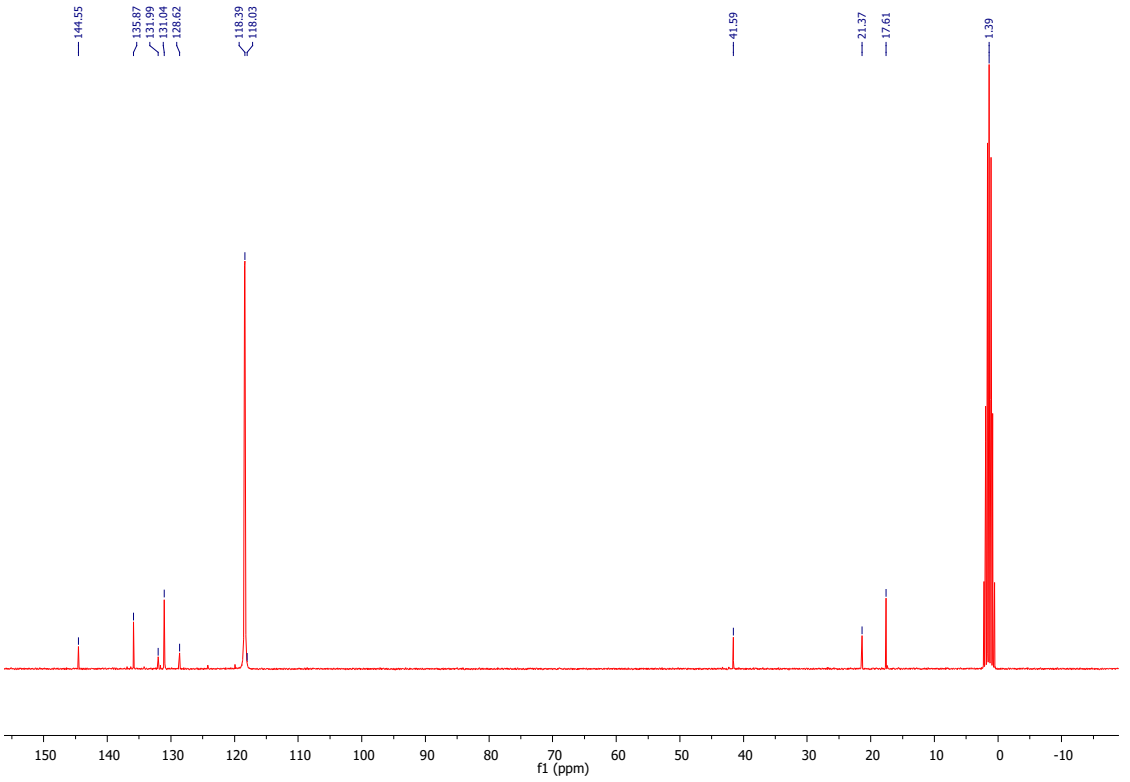


Figure 14: ^{13}C NMR spectrum of **3a** in CD_3CN

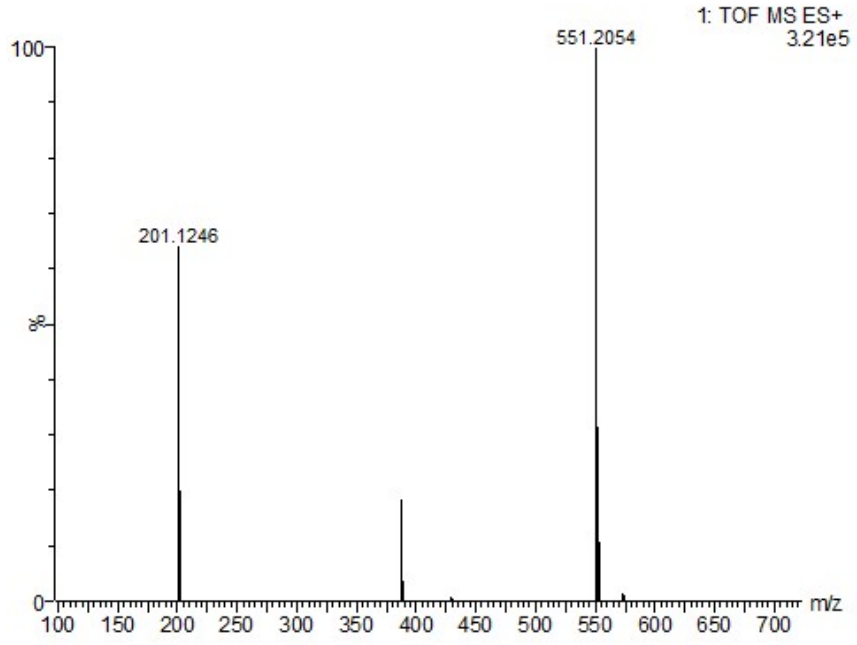
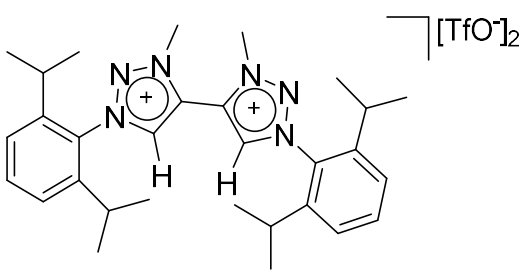


Figure 15: Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **3a**

- Synthesis of **3b**



To a stirred solution of **2b** (0.30 g, 0.66 mmol) in DCE (20 mL), previously cooled to -78°C, was added methyl trifluoromethanesulfonate (0.24 g, 1.50 mmol). The reaction mixture was warmed to room temperature, and stirring was maintained overnight. The solvent was evaporated and ether was added stirring the crude mixture for 30 min. More ether was added and filtered the mixture. Afterwards, the precipitated was washed with hexane.

The product was purified in column chromatography, the silica was compacted with DCM and as mobile phase 95:5 DCM/MeOH. Afterwards, the solvent was dissolved to yield a white solid (0.249 g, 48 %).^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (s, 2H, NHC), 7.67 (m, 2H, $CH_{arom\ para}$), 7.41 (d, 4H, $CH_{arom\ meta}$), 4.70 (s, 6H, $CH_{3\ alk}$), 2.46 (m, 4H, CH_{Dipp}), 1.22 (d, 24H, CH_3). ^{13}C NMR (100.8 MHz, $CDCl_3$): δ 146.4 (CN), 134.3 (NHC), 133.7 ($CH_{arom\ meta}$), 130.6 ($CH_{arom\ para}$), 129.11 ($C_{quat\ arom}$), 125.2 (CN_{trz}), 41.0 ($CH_{3\ alk}$), 28.8 (CH_{Dipp}), 24.5 and 23.9 ($CH_{3\ Dipp}$). ESI-TOF-MS (positive mode): $[M+TfO]^+$ calcd 635.2991, found 635.2998 (1.1 ppm).

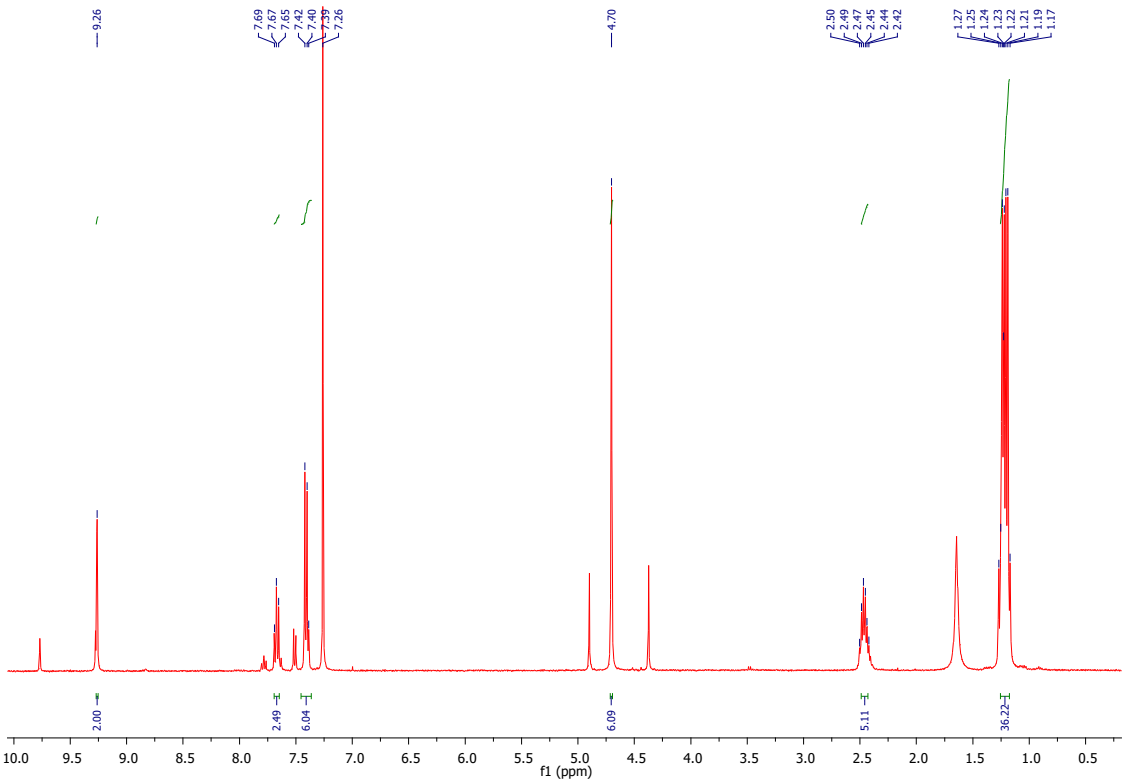


Figure 5.16. ^{1}H NMR spectrum of **3b** in $CDCl_3$

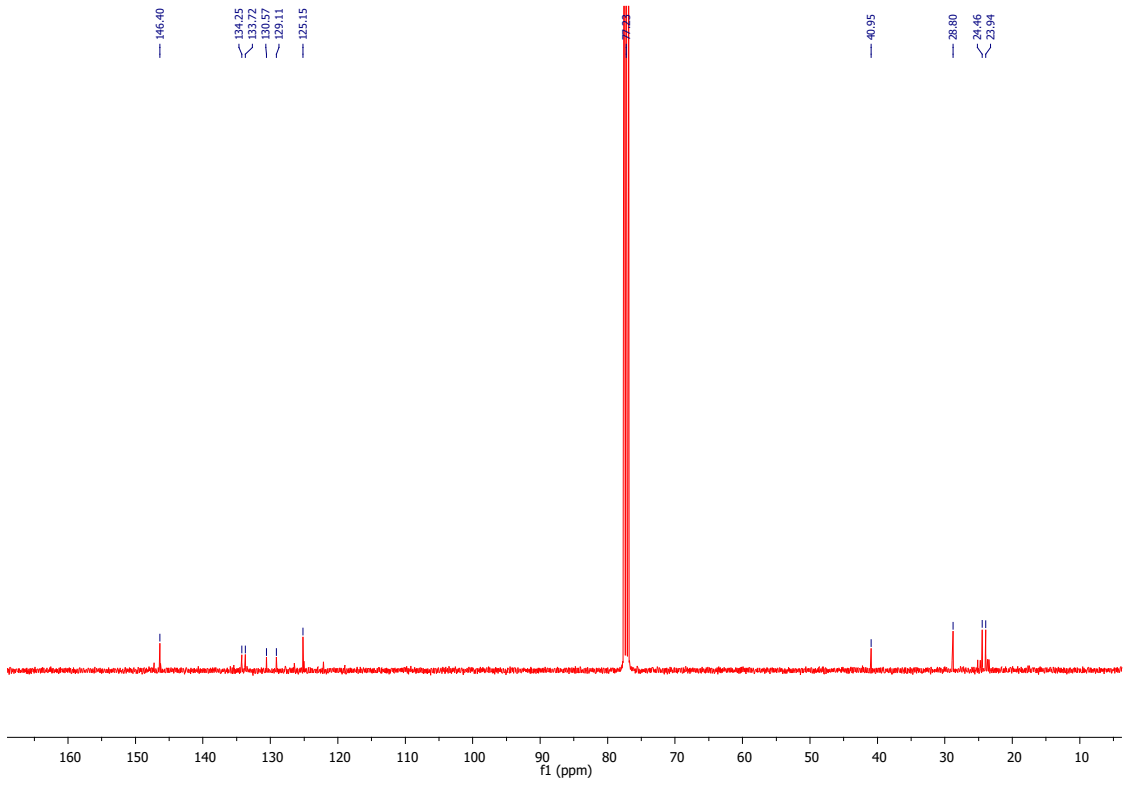


Figure* 5.17.** *^{13}C NMR spectrum of* ***3b *in $CDCl_3$*

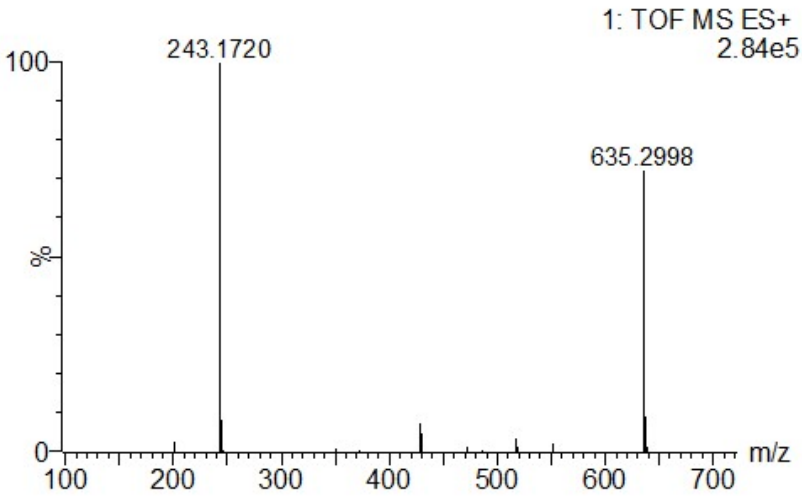
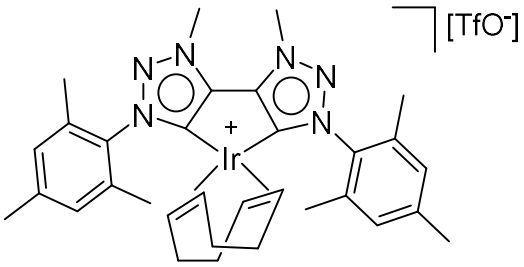


Figure 5.18. Electrospray Ionization-Time of Flight-Mass Spectrometry (ESI-TOF-MS) of compound **3b**

5.2.4 Synthesis of Iridium Complexes

All our attempts to obtain the desired metal complexes were unfruitful. The crude NMR for both complexes were analysed by ^{1}H NMR using CD_2Cl_2 as solvent but it could be observed that the desired compound was not obtained, so the characterization part is not added.

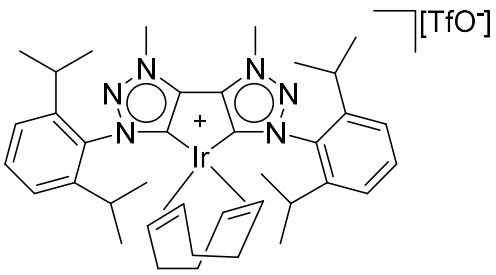
- Synthesis of **4a**



In a sealed Schlenk, $[Ir(cod)(\mu\text{-}Cl)]_2$ (0.03 g), **3a** (0.08 g) was added. At -78°C, was added 4 mL of THF and NaOtBut (0.12 mL approx.) was carefully added dropwise. The mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum and the crude dissolved with DCM. The mixture was filtered and the solvent of solution was evaporated.

The product mixture was purified by column chromatography, the silica was compacted with DCM and as mobile phase 90:10 DCM/MeOH. The solvent was evaporated to yield an orange solid, which did not correspond with the product.

Synthesis of **4b**



In a sealed Schlenk, $[Ir(cod)(\mu\text{-}Cl)]_2$ (0.03 g), **3b** (0.98 g) was added. At -78°C, was added 4 mL of THF and NaOtBut (0.12 mL approx.) was carefully added dropwise. The mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum. Dry DCM (10 mL) was added to the crude mixture, afterwards, filtration via cannula and evaporated the solvent.

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