Synthesis and Photophysical Studies of *a*NHC Supported Coinage Metal Complexes

A Thesis submitted to

Indian Institute of Science Education and Research (IISER), Pune

In partial fulfilment of the requirements for the BS-MS Dual Degree Programme

by

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Under the guidance of

Dr. Shabana Khan

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We state that the affair incorporated in the thesis given which named as **"Synthesis and Photophysical Studies of *a*NHC Supported Coinage Metal Complexes"** is the outcomes of the work performed by me (Rahul Verma) at the "Department of Chemistry, Indian Institute of Science Education and Research, Pune," under the guidance of **Dr. Shabana khan** and the related work is not been introduced in any other thesis for completion of any degree.

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I devoted my thesis to my beloved parents

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I express my sincere thanks where it is due

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Rahul Verma

20161119

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List of Abbreviations

Notation	Full Name
NHC	N-heterocyclic carbene
*a*NHC	Abnormal N-heterocyclic carbene
THF	Tetrahydrofuran
DCM	Dichloromethane
hrs	Hours
SCXRD	Single crystal X-ray Diffraction
δ	Chemical shift
rt	Room temperature
ppm	Parts per million
ml	Milliliter
mg	Milligram
mmol	Millimole
°C	Degree Celsius
NMR	Nuclear magnetic resonance
gm	gram
H	Hydrogen
m	Multiplet
sept	Septet
s	Singlet
d	Doublet

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1. Abstract

For 160 years, carbene as a ligand has played a powerful role in organometallic chemistry, but carbene is first considered a fugitive species. Arduengo and co-workers synthesize the first stable carbene known as NHCs (N-Heterocyclic carbenes). This indication that carbene is no longer a fugitive species helps provide a diaspora in this field. NHCs show strong σ-donating and π-accepting properties that are utilized to make a strong bond with the metal center. cAAC (cyclic (alkyl)(amino)carbenes), *a*NHC (abnormal N-heterocyclic carbene, MAC (Monoamido-amino carbene), and DAC (Diamidocarbene) are other well-explored carbenes. The energy gap of NHCs is 4.8 eV, aNHC is 4.6 eV and cAAC is 3.3 eV. NHCs and cAAC with coinage metal are well explored from the photophysical aspects. Still, *a*NHC for the same is not documented despite having better σ-donating properties than NHCs. A detailed study on the structural, electrochemical, and photophysical behavior of previously reported two-coordinated coinage metal (copper and silver) complexes with *a*NHC and two new compounds by inserting carbazolide as an anionic ligand in the place of halide were scrutinized. Previously reported Cu and Ag complexes show emissions in the range of 380-420nm (blue emissive) and provide excitation-dependent emission. The electrochemical study reveals the redox-active behavior of ligand and metal complexes.

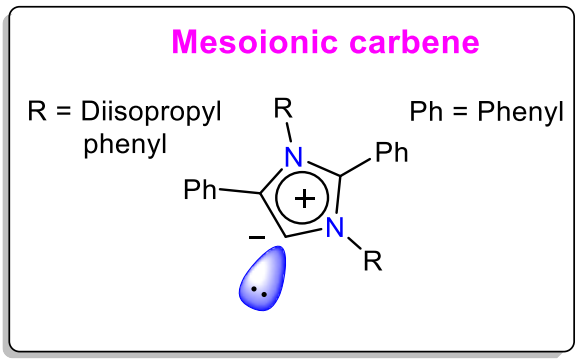


Figure 1: Schematic representation of Abnormal NHC

2. Introduction

A carbene is a divalent species that contains a neutral carbon atom with two unshared valence electrons. The hierarchy of carbene includes two basic types. The first is singlet carbene, which has an opposite spin of two unshared valence electrons in the sp^2 orbital. The other is a triplet with the parallel spin of unshared electrons, one in p orbital and another in sp^2 orbital.[1a]

For years, carbenes have been considered short-lived intermediate species that are difficult to isolate. Then Arduengo, 1991, first isolated the stable carbene, known as the NHC. This discovery opened a new domain for researchers. NHCs are electron-rich nucleophilic compounds that show strong σ-donating and π-accepting behavior utilized to make a strong bond with the metal center. NHCs are easy to isolate because of their intrinsic stability.[1b] cAAC (cyclic (alkyl)(amino)carbenes), *a*NHC (abnormal N-heterocyclic carbene, MAC (Monoamido-amino carbene), and DAC (Diamidocarbene) are other well-explored carbenes. NHC, cAAC, MAC, and DAC binds metal *via* the C2 carbene center of the ring. Later, some carbenes also show donations from C4/C5 position to the metal center, which is known as abnormal binding, and these carbenes are called *a*NHCs.[2] The HOMO-LUMO gap for the classical NHC ligand is 4.8 eV, *a*NHC ligand is 4.6 eV, cAAC is 3.3 eV, MAC is 4.37 eV, and DAC is 4.27 eV. The HOMO-LUMO gap of *a*NHCs is less than NHCs, which means it will show better donor ability.[2c]

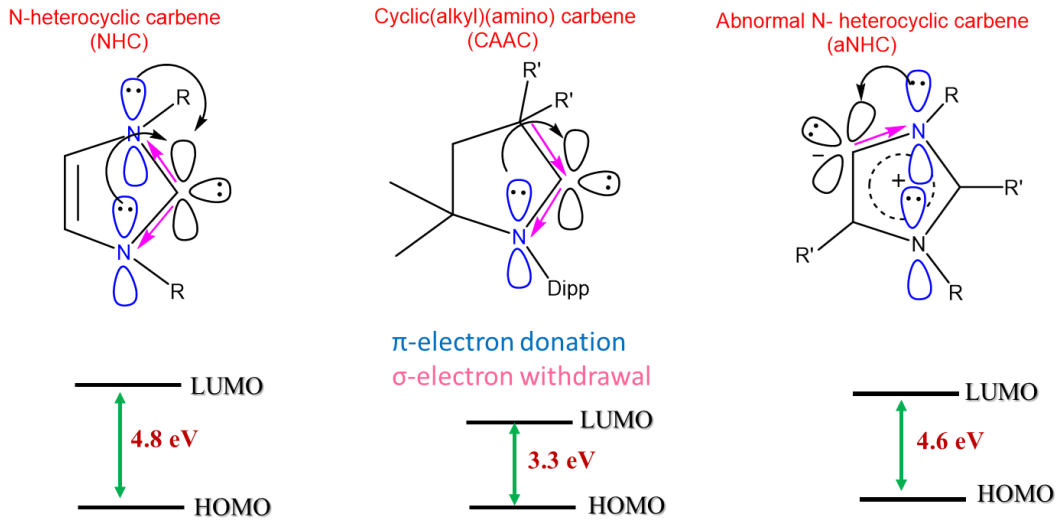


Figure **2:** Electronic distribution of NHC, cAAC, and *a*NHC.[2c]

Crabtree and co-workers[3] (2001) synthesized iridium complex imidazole-5-ylidine, which was bounded at C5 and not on C2. Since then, few other transition metal complexes have been prepared with abnormal binding.[2] In these types of carbenes, ligand-bound through a backbone C4/C5 carbon and hydrogen migration happen from the backbone to C2.[4] Bertrand and co-workers first isolated these carbenes.[5] They synthesized *a*NHC imidazolium salt by protecting the C2 position with the aryl/alkyl group and reacted with a strong base,

Many *a*NHC transition metal complexes have been reported earlier through the trans-metalation procedure, but synthesizing the free *a*NHC is challenging owing to its lower thermal stability and higher reactive nature than NHCs.[2] A range of catalysts is synthesized using *a*NHCs by engaging with transition metal-based precursors. These catalysts were further exploited for different organic transformations such as the Suzuki–Miyaura cross-coupling reaction,[6] dehydrogenative coupling,[7] C–H bond activation,[8] click reaction,[9] the migratory insertion of carbenes hydro-heteroarylation,[5] and hydrosilylation reaction[10]. In this work, to synthesize free *a*NHC, the C2 position of the imidazolium salts has been protected by the alkyl/aryl group because the proton of C2 is more acidic than C4/C5. [11]

Many transition metal -NHC and -cAAC complexes have been studied for their photophysical properties in past years, but transition metal-*a*NHCs have not been studied before. Transition metal -NHC and –cAAC complexes with carbazole moiety attached to it are also synthesized and looked at from their photophysical aspect. Some selected examples are mentioned in Chart 1.

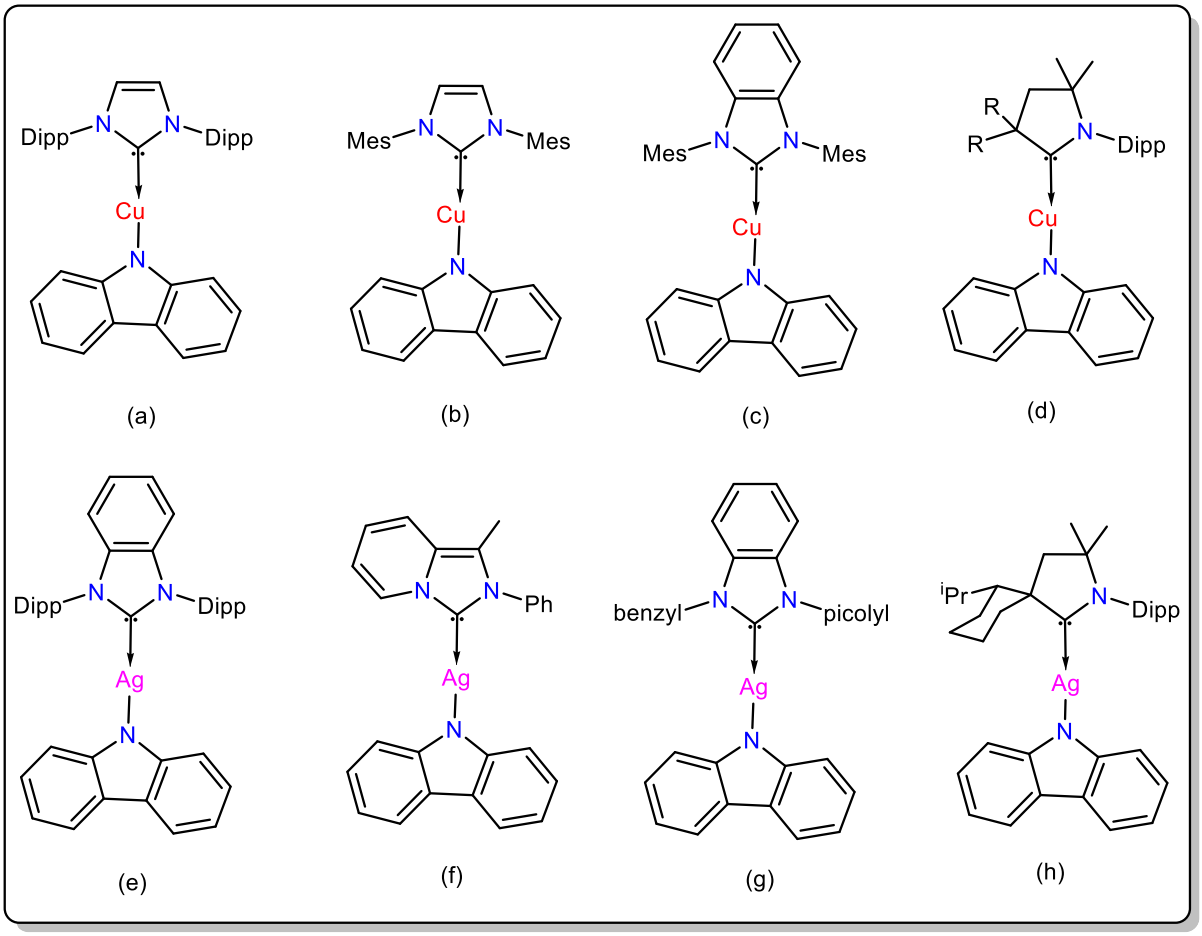


Chart **1**: Selected NHC and cAAC; copper and silver complexes examples.

The luminescence properties give them the full potential for fabricating organic light-emitting diodes (OLED).[12a] Luminescence can be altered by varying electrophilicity of the backbone. As they have excellent photophysical properties so they are ideal candidates for application in dye-sensitized solar cells,[13] biosensing,[14] and photocatalysis,[15] and as dopants in OLEDs.[16] For their short radiative lifetimes, the small energy separation between their lowest singlet and triplet excited states (ΔE_{ST}) and spin-orbit coupling via the metal ion are the responsible factors. Still, they can be altered using a ligand system.[7] These complexes also show solvatochromism, depending upon the polarity of the solvents. More polar solvents produce bathochromic shifts or redshifts where the λ_{max} value increases ($\pi \rightarrow \pi^*$) transitions. In the case of $n \rightarrow \pi^*$ changes, polar solvents have hypsochromic shifts or blueshifts in which the λ_{max} value decreases.[17]

Herein, we have synthesized the copper and silver *a*NHC complexes with halide and carbazole as anionic counterparts. And we have studied the structural, photophysical, and electrochemical behavior of these complexes. We have also tried to elucidate the role of the *a*NHC and the metal ion in the excited-state properties. Solvatochromic effect and excitation-dependent emission are also studied.

3. Experimental

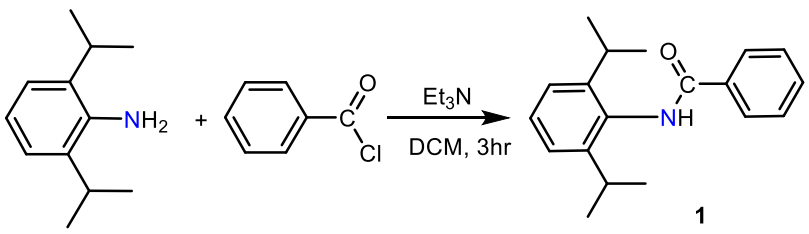
3.1 General

Without otherwise stated, reactions were carried out under atmosphere using standard Schlenk techniques or vacuum line and in a dinitrogen-filled MBRAUN MB 150-G1 glovebox. The solvents used were distilled and dried in "MBRAUN MB SPS-800" except for THF and hexane, dried manually. Crystal structure of complexes was done using "BRUKER Smart Apex Duo diffractometer" at 100 K using Molybdenum K_α radiation (λ = 0.71073 Å). All other chemicals purchased from Sigma Aldrich, Alfa Aesar, and RANKEM were used without further purification. At ambient temperature, all the NMR spectra were recorded on a 400 MHz BRUKER/JEOL NMR spectrophotometer.

3.2 Synthesis of Benzamide. [18]

2,6-diisopropylaniline (5.7 ml, 0.033 mol) and triethylamine (4.6 ml, 0.033 mol) were added to the flask with 50 ml DCM. After that, benzoyl chloride (3.48 ml, 0.003 mol) was added dropwise using a syringe. The mixture was stirred for 3 hrs (Scheme 1). After stirring for 3 hrs, workup was done, and the product was extracted in DCM and dried over sodium sulphate (Na_2SO_4). DCM was evaporated by using a rota. A white solid compound **1** was obtained. Yield = 8.05 g (94.7%).

Compound **1** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.31 (s, 1H), 7.51 (t, 8H), 3.15 (m, 2H), 1.23 (t, 12H)

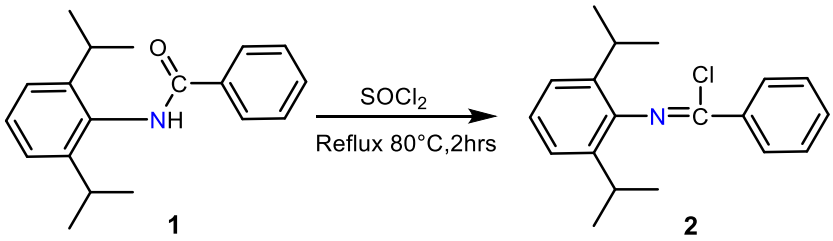


Scheme 1: Synthesis of Benzamide

3.3 Synthesis of imidoyl chloride. [18]

Compound **3** (3 gm, 10.66 mmol) was weighed in a 100 ml Schlenk flask and dried under vacuum on the Schlenk line. Then thionyl chloride (in excess) was added. The reaction mixture was put on reflux for 2 hrs at 80 °C. To maintain the inert atmosphere, an Argon-filled balloon was attached on top of the reflux condenser (Scheme 2). The orange color oily mixture was observed after 2 hrs of refluxing. The excess thionyl chloride was evaporated under a vacuum. Solid yellow color compound **2** was obtained. Yield = 3.10 gm (97%)

Compound **2** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.85 (m, 3H), 7.45 (m, 5H), 2.74 (s, 2H), 1.11 (t, 12H)



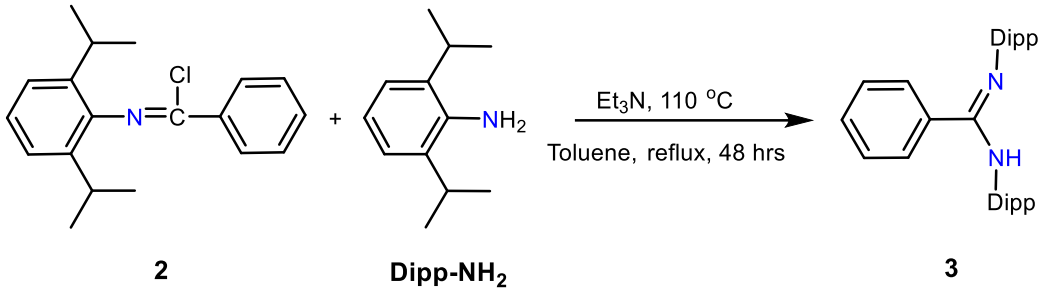
Scheme 2: Synthesis of imidoyl chloride

3.4 Synthesis of bis(2,6-diisopropylphenyl)benzamidine.[18]

In the Schlenk flask containing **2** (3 gm, 10 mmol), toluene (50 ml) was added. 2,6-diisopropylaniline (1.89 ml, 0.01066 mol) and triethylamine (1.63 ml, 0.01172 mol) were added to the Schlenk flask. In addition, the red-colored solution was observed (Scheme 3). A reflux condenser was attached to the flask with Argon filled balloon to maintain an inert atmosphere. The reaction was refluxed for 48 hrs. After 48 hrs of reflux, the reaction mixture was filtered using a celite pad to remove $(C_2H_5)_3N.HCl$ and solvent were evaporated under a vacuum. A solid orange compound was obtained.

Recrystallization was done using pentane. Bis(2,6-diisopropylphenyl)benzaminide(**3**) obtained as colourless crystals. Yield = 4.1 gm (87.42 %)

Compound **3** ^{1}H NMR (400 MHz $CDCl_3$): δ (ppm) = 7.32 (m, 2H), 7.18 (m, 7H), 6.92 (m,2H), 5.62 (s,1H), 3.18 (sept, 2H), 3.09 (sept, 2H), 1.29 (d, 6H), 1.17 (d, 6H), 0.92 (d,6H), 0.82 (d, 6H)



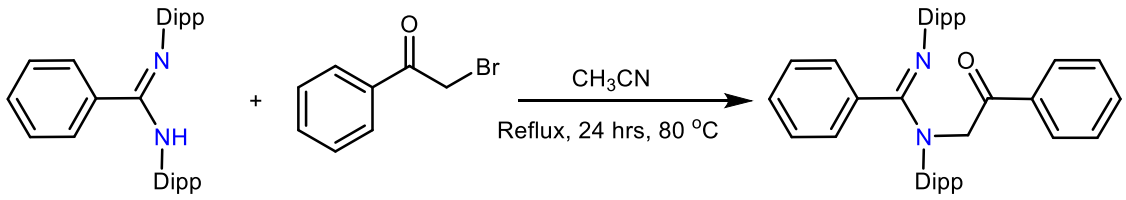
2 **Dipp-NH$_2$** **3**

Scheme 3: Synthesis of bis(2,6-diisopropylphenyl)benzamidine

3.5 Synthesis of N,N'-bis(2,6-diisopropylphenyl)-N-(2-oxo-2-phenylethyl)benzimidamide.[5][19]

In a 250 ml RB flask, take **3**(1 gm, 2.27 mmol)**,** 2-bromoacetophenone (0.49 gm, 2.5 mmol), and potassium bicarbonate (0.54 gm, 5.45 mmol) and add distilled acetonitrile (80 ml) in it (**Scheme 4**). Put the reaction mixture on reflux for 24 hrs (the color of the reaction mixture changes from white to yellow). The column used 2% ethyl acetate in pet ether mixture to give **4** as yellow crystalline solid. Yield = 0.8 gm (63.49%)

Compound **4** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.96 (m, 6H), 7.29 (m, 5H), 6.92 (m, 5H), 5.62 (s, 2H), 3.08 (sept, 4H), 1.29 (d, 5H), 1.17 (d, 11H), 0.92 (d, 6H), 0.80 (d,2H)



3 **4**

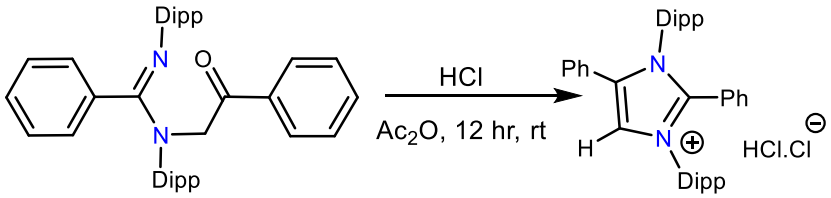
Scheme 4: Synthesis of N,N'-bis(2,6-diisopropylphenyl)-N-(2-oxo-2-phenylethyl)benzimidamide

3.6Synthesis of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium. [5]

At 0 °C, to a suspension of **4** (3.5 g, 6.23 mmol) in acetic anhydride (16 ml), HCl (12.1 M in water) was added dropwise. The mixture was then removed from 0 °C and stirred overnight at ambient temperature. Water was added to the reaction

mixture until a white precipitate formed. The workup for the suspension was done in DCM. The organic part was extracted using a separating funnel and dried with anhydrous magnesium sulphate, filtered, and dried under a vacuum. In the residue, diethyl ether (30 ml) was added, stirred for 45min and then filtered (Scheme 5). After that, washing of diethyl ether was given to the solid to afford white-colored imidazolium salt **5** (3.20 gm, 83.55 %).

Compound **5** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.05 (s, 1H), 7.66 (m, 2H), 7.40 (m, 6H), 7.33 (m, 4H), 7.22 (m, 2H), 6.95 (m, 2H), 2.54 (sept, 2H), 2.44 (sept, 2H), 1.39 (d, 6H), 1.02 (d, 6H), 0.87 (d, 6H)



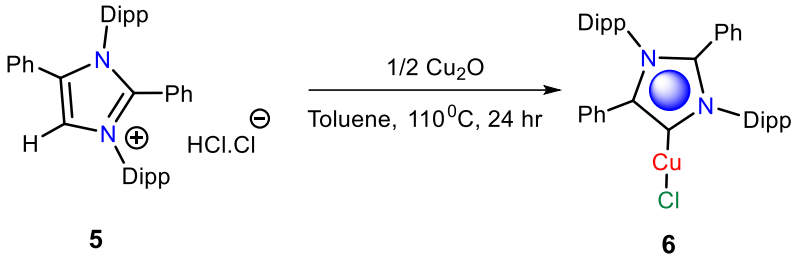
4 **5**

Scheme 5: Synthesis of 1,3-bis(2,6-diisopropylphenyl)-2, 4-diphenyl imidazolium

3.7 Synthesis of copper complex of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium. [19]

In a glove box, a 100 ml Schlenk flask was charged with **5** (1 mmol, 613.71 mg) and copper(I) oxide (0.7 6mmol,108.72 mg) and 30 ml toluene. The reaction mixture was then refluxed for 24 hrs. The reaction mixture became light green (Scheme 6). Using a celite pad, the resulting mixture was filtered and evaporated to dryness. Recrystallization was done in DCM and pentane. After some time, transparent crystals were formed. Yield = 424 mg (66.45%)

Compound **6** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.41 (5H, m), 7.19 (7H, m), 7.01 (2H, m), 6.78 (2H, m), 2.54 (2H, sept), 2.51 (2H, sept),1.36 (7H, d), 0.90 (5H, d), 0.74 (12H, d)



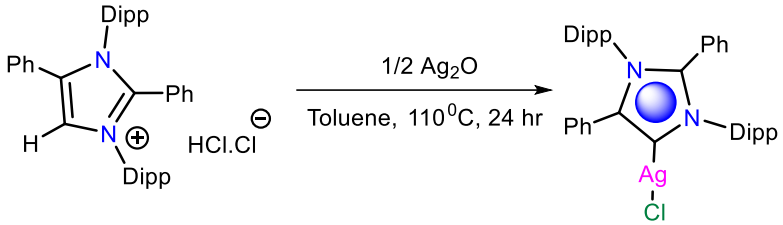
5 **6**

Scheme 6: Synthesis of copper complex of 1,3-bis(2,6diisopropylphenyl)-2, 4-diphenyl imidazolium

3.8 Synthesis of silver complex of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium. [11]

In a glove box, a 100 ml Schlenk flask was charged with **5** (1 mmol, 613.71 mg) and Silver(I) oxide (0.76 mmol,176.11 mg) and 30 ml toluene. The reaction mixture was then put on reflux for 24 hrs. The reaction mixture became light orange (Scheme 7). Using a celite pad, the reaction mixture was filtered, and all the volatiles were removed under vacuum. The brown color solid was formed. Yield = 201 mg (59.29 %)

Compound **7** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.62 (2H, m), 7.47 (2H, m), 7.32 (2H, m), 7.17 (8H, m), 7.05 (2H, m), 6.96 (1H, m),6.87 (2H, d), 2.65 (2H, sept), 2.56 (2H, sept), 1.38 (7H, d), 1.00 (6H, d), 0.93 (4H, d), 0.78 (7H, d)



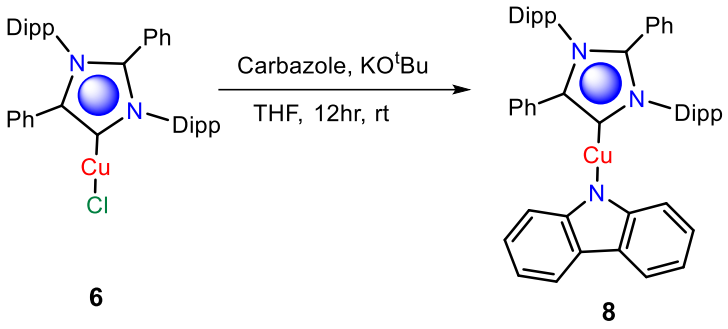
5 **7**

Scheme 7: Synthesis of silver complex of 1,3-bis(2,6diisopropylphenyl)-2, 4-diphenyl imidazolium

3.9 Synthesis of copper complex of1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium with carbazole moiety

The complex was prepared from complex **6** (639.7 mg, 1 mmol), carbazole (167.21 mg, 1 mmol), and KO^{t}Bu (112.21 mg, 1mmol) in THF (Scheme 8) and isolated as a colorless powder **8** (244 mg, 31.26 %). Crystallization was tried in ether and acetonitrile.

Compound **8** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.21 (2H, m), 7.5 (10H, m), 7.23 (6H, m), 7.19 (2H, m), 7 (2H, m), 2.65 (2H, sept), 2.60 (2H, sept), 1.45 (6H, d), 1 (6H, d), 0.96 (12H, d)



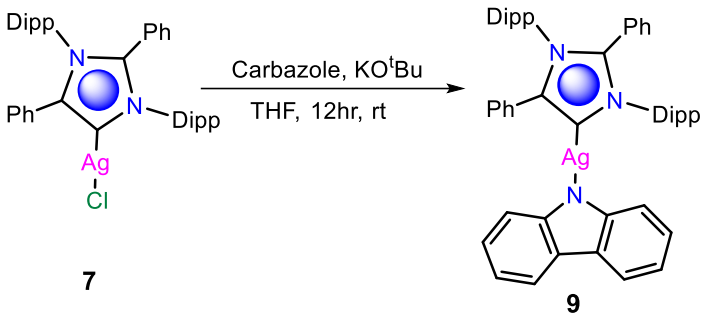
6 **8**

Scheme 8: Synthesis of silver complex of 1,3-bis(2,6diisopropylphenyl)-2, 4-diphenyl imidazolium with carbazole moiety

3.10 Synthesis of silver complex of1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium with carbazole moiety

The complex was prepared from complex **7** (684 mg, 1 mmol), carbazole (167.21 mg, 1 mmol), and KO^{t}Bu (112.21 mg, 1 mmol) in THF (Scheme 9) and isolated as a colorless powder **8** (276.3 mg, 33.29%). Crystallization was tried in diethyl ether and acetonitrile.

Compound **9** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (2H, m), 7.54 (5H, m), 7.16(8H, m), 6.95 (9H, m), 2.65 (2H, sept), 2.61 (2H, sept), 1.34 (6H, d), 0.94 (6H, d), 0.79 (12H, d)



7 **9**

Scheme 9: Synthesis of the copper complex of 1,3-bis(2,6diisopropylphenyl)-2, 4-diphenyl imidazolium with carbazole moiety

4. Results and Discussion

Synthesis

We followed Liu et al.,[18] Ung and G.Bertand,[5] Aldeco-Perez*et al*,[19] and Bidal *et al.*[20] during the ligand synthesis. During our synthesis process, we faced some problems with the published procedure, and by making some changes in the reported method, we successfully reached the abnormal NHC ligand. We are mentioning the changes we made in the documented methodology in some steps.

i) During the synthesis of benzamide, following the published procedure, we did not find the pure compound, so organic layer separation was done in DCM and water.

ii) Following the reported procedure, we could not isolate the crystal of compound **3**. We modified the recrystallization and used pentane instead of ethanol/water.

iii) During the synthesis of compound **4**, following the published procedure, we did not get pure compound and got the mixture. We did the column in 2% ethyl acetate for the purified compound in pet ether.

iv) During the synthesis of compound **6**, recrystallization was done in the DCM and diethyl ether in the published procedure, but we got the crystals using DCM and pentane.

X-ray analysis

Molecular structures of complexes **6** and **7** (Figure: 4) are previously reported, so other parameters are not discussed.[11,20] From this structure, it is clear that metals (Cu and Ag) are attached to the C5 carbon and coordinated linearly with the ligand.

Carbazolide substituted copper and silver complexes with *a*NHC are also synthesized. We will study the bonding parameter and coordination geometry with NHCs and cAAC, where carbazolide is present as an anionic counterpart, and compare it with complexes **8** and **9**. But so far, we cannot isolate the crystal of complex **8** and **9.**

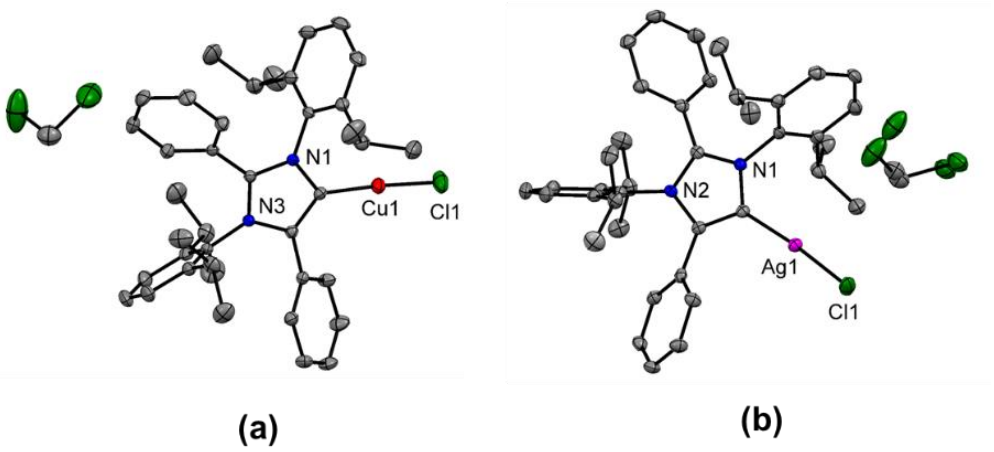


Figure 4: Molecular structure of complex **6** (a) and complex **7** (b).

Photophysical Studies

As shown in Figure **4**, absorbance and emission spectra were recorded for complexes **6** and **7** in three different solvents to study their solvatochromism effect. We used acetonitrile, toluene, and DCM for the solvatochromism, with other polarity indexes below (Table 1). From the table, we can conclude that acetonitrile is more polar than DCM, which is more polar than toluene.

Solvent	Polarity Index
Toluene	2.4
DCM	3.1
Acetonitrile	5.8

Table1: Used solvent in solvatochromism and their polarity index [15]

We used 0.5 µM solutions of the complexes in the solvents for the photophysical studies. The UV visible spectra show a shorter wavelength (280 nm) corresponds to the π→π* transition, and a longer wavelength (410 nm) represents the n→π* transition. [21]

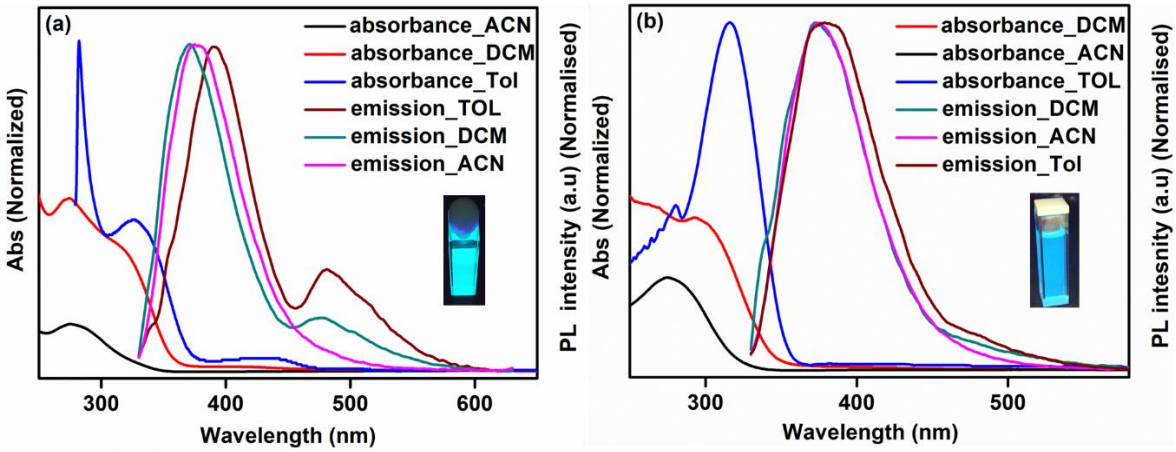


Figure 5: Absorption (black, red, and blue line) and emission (brown, green, and pink line) plot for complex **6** (a) and complex **7** (b).

In complex **6,** a peak appeared at 282 nm could be due to of π→π* transition. Another peak observed at 310 nm might be due to n→π*, surpassed by π→π*.[21,22] Tailing is also observed in the visible region due to charge transfer. This trend remains the same in toluene and DCM, but acetonitrile charge transfer is missing. Complex 7 shows only π→π* transition at a lower wavelength.

Both complexes **6** and **7** show excitation-dependent emission, as shown in Figure **5**. The emission peak almost changed with the variation of excitation wavelength in the range of 320–480 nm.[23.24] The photoluminescence intensity in the region 380-400 nm shows different intensities at different excitation. With the increment in the excitation wavelength, another peak at 500-600 nm is prominent because of intersystem crossing. [25,26]

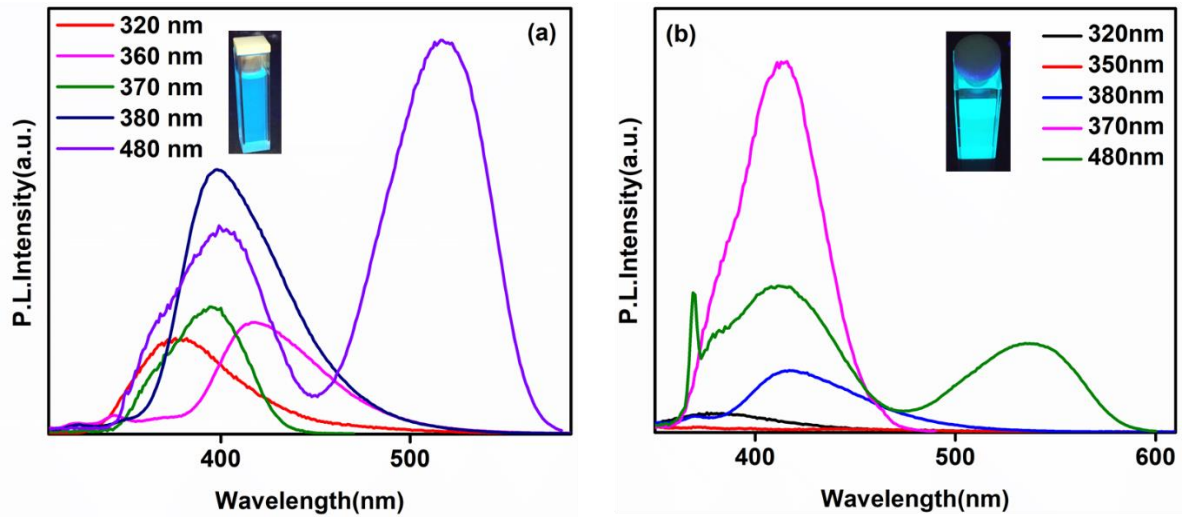


Figure 6: Emission spectra forcomplex **6** (a) and complex **7** (b).

Electrochemical studies

Redox property of the ligand and complexes was explored by performing cyclic voltammetry. We used a nonaqueous medium, and THF was used as a solvent. A platinum electrode is used as a pseudo reference and counter electrode, whereas glassy carbon is used as a working electrode. The potential window of 3 to -3 V was used, and the scan rate was kept at 50 mV s^{-1}.

We performed the CV of salt and all the metal complexes. Complex **5,** *a*NHC chloride salt, shows the redox-active properties (figure 6(a)), which is continued in all the metal complexes. In figure 6(b), for complex **6**, an anodic peak at E_{pa} = 1071 mV was observed and can be attributed to Cu(I) →Cu(II) for the linear Cu(I) center. This reversible peak shows Cu(II) →Cu(I) at E_{pc} = 138 mV. Other peaks correspond to the redox-active ligand.[27] In the case of complex **7,** ligand peaks are present, and Ag(I) is getting reduced to Ag(0). It shows reversible peak at E_{pa} = 560 mV for oxidation of Ag(0)→Ag(I) and E_{pc} = 416 mV for reduction of Ag(I)→Ag(0).[28] In the case of complexes **8** and **9,** carbazole is present as an anionic counterpart which is also redox-active. These complexes will be linearly coordinated where oxidation and reduction will be spread over *a*NHC, and carbazole contains oxidation only.[24]In complex **8**, E_{pa} = 1117 mV was observed and can be attributed to Cu(I) →Cu(II). This peak is also reversible and shows Cu(II) →Cu(I) at E_{pc} = 596 mV both the peaks

are positively shifted compared to the complex **6**, a similar trend was observed for complex **9**.

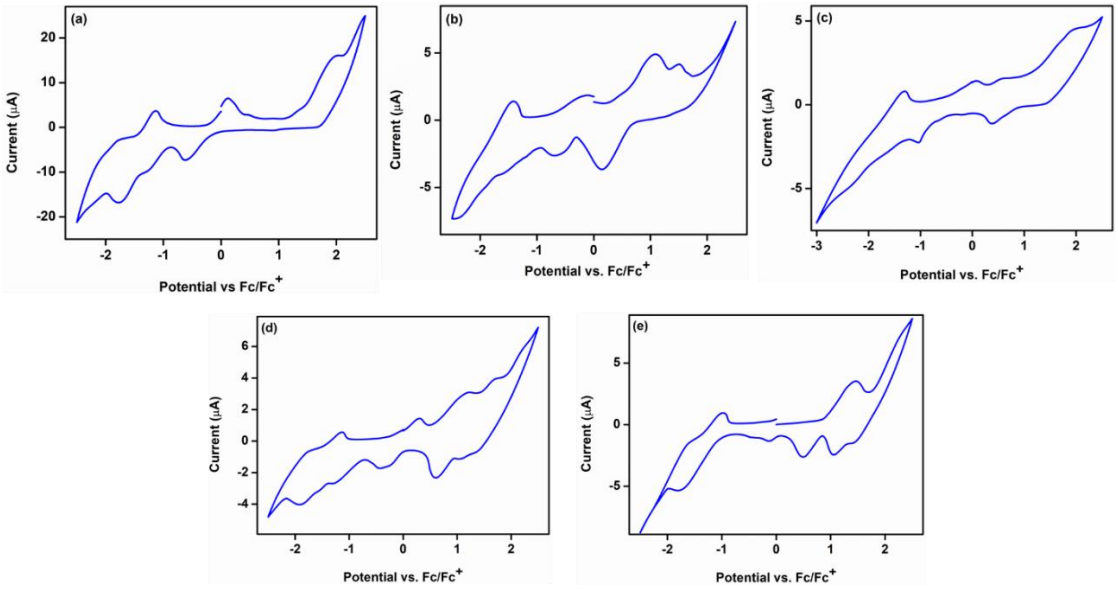


Figure7: Cyclic voltammogram of complex **5** (a), **6** (b), **7** (c), **8** (d) and **9** (e) in THF for with 0.05 M *t*-butyl-ammonium-hexafluorophosphate. All potentials were referenced to the Fc/Fc^{+} couple. Scan rate = 50 mV s^{-1}.

4. Spectroscopic and characterization data

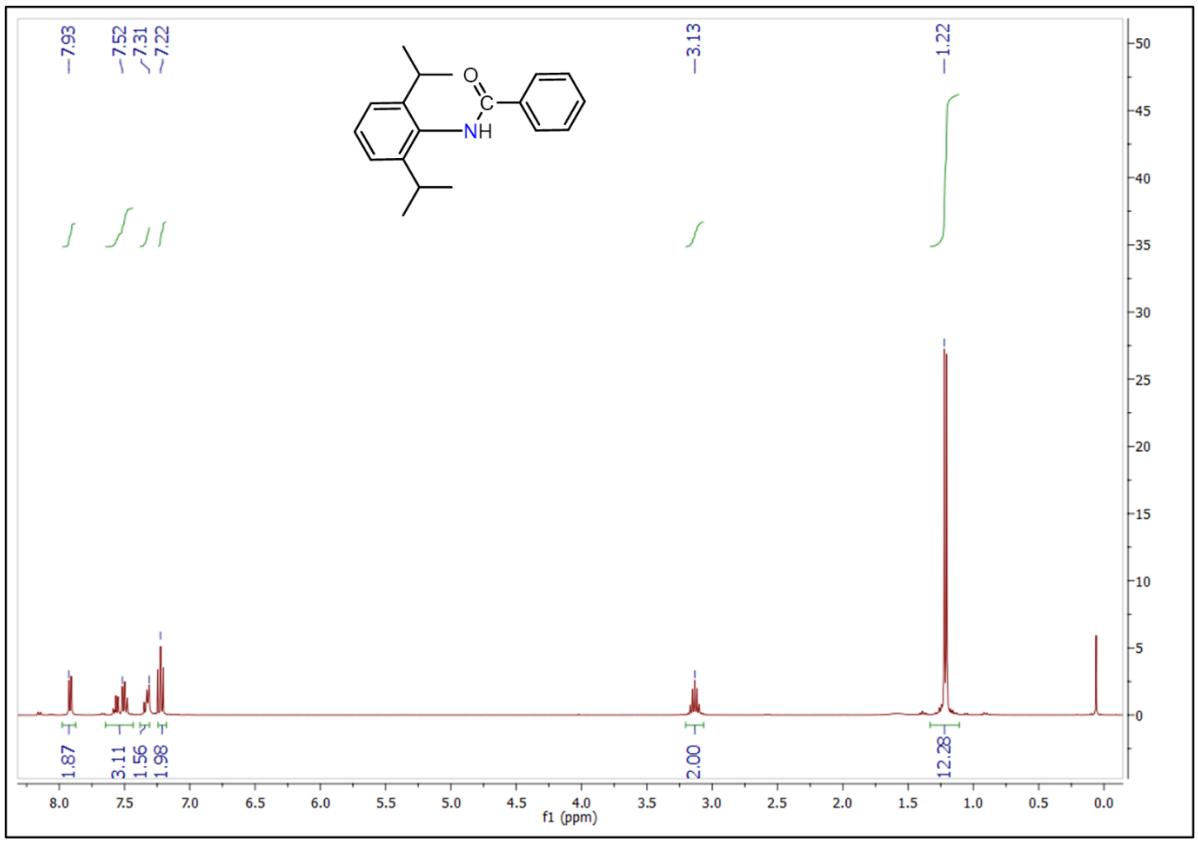


Figure 8: ^{1}H NMR of Compound **1**

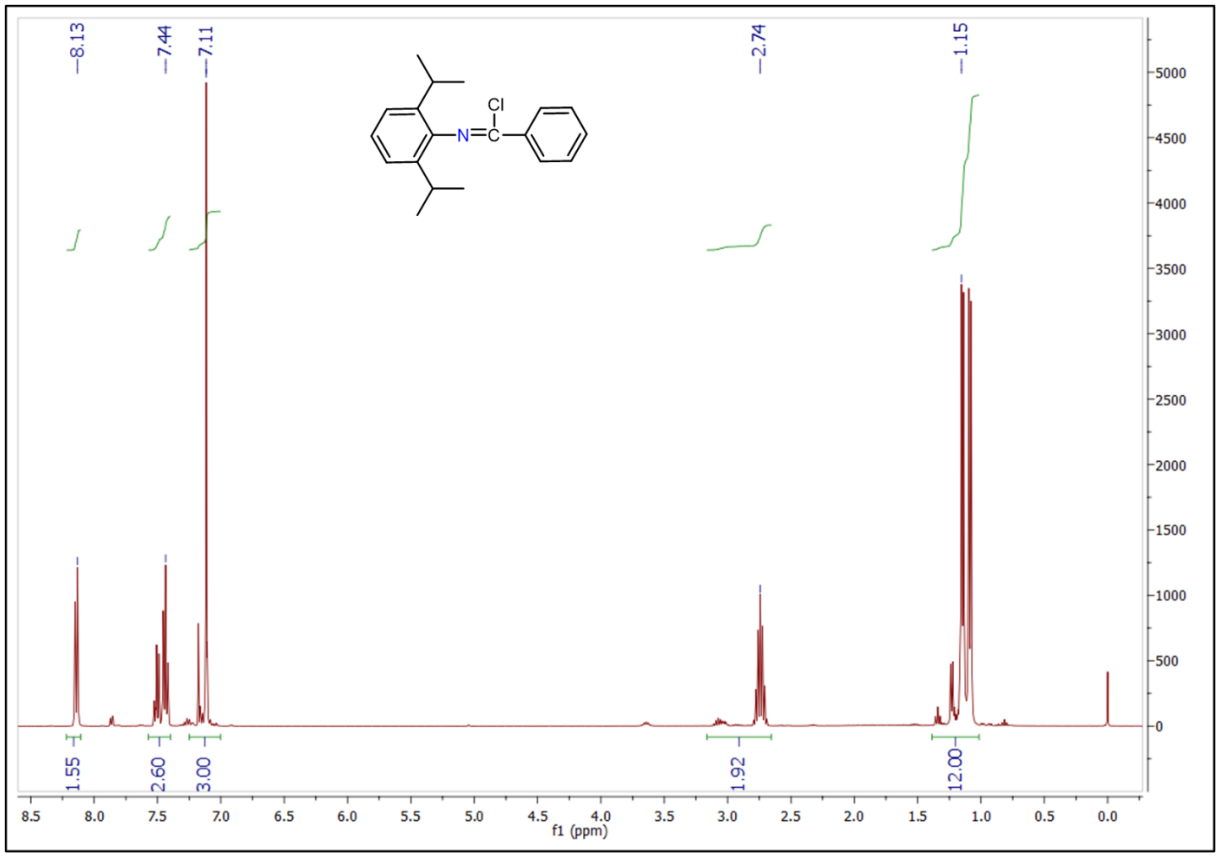


Figure 9: ^{1}H NMR of Compound **2**

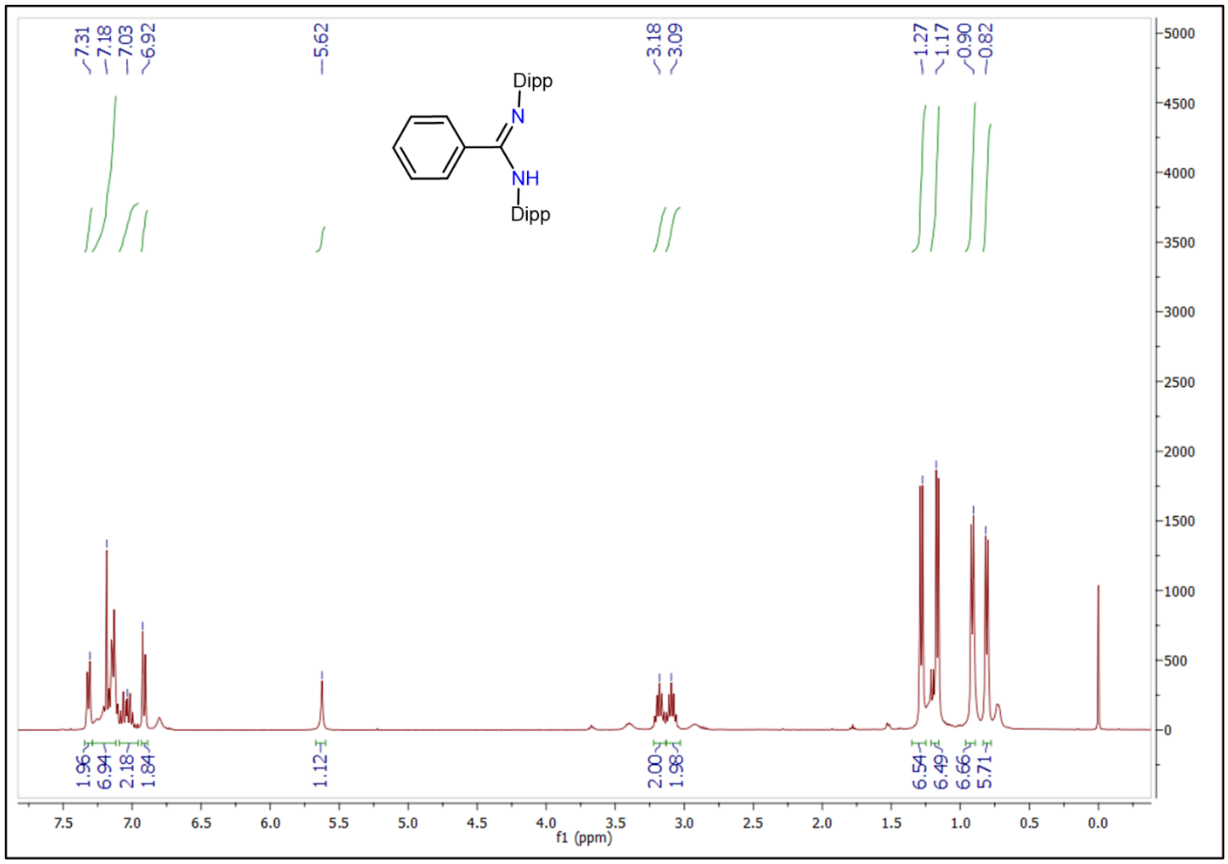


Figure 10: ^{1}H NMR of Compound **3**

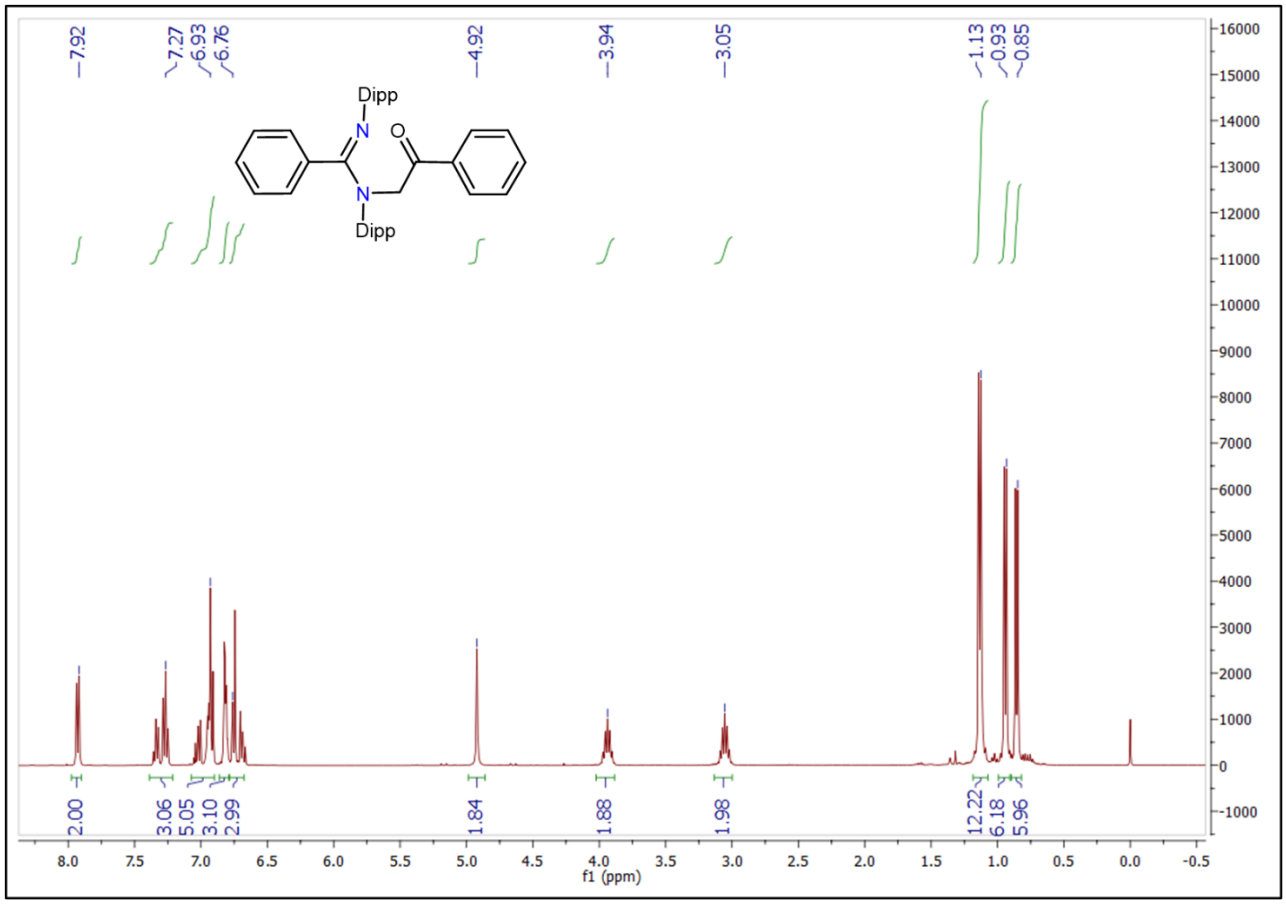


Figure 11: ^{1}H NMR of Compound **4**

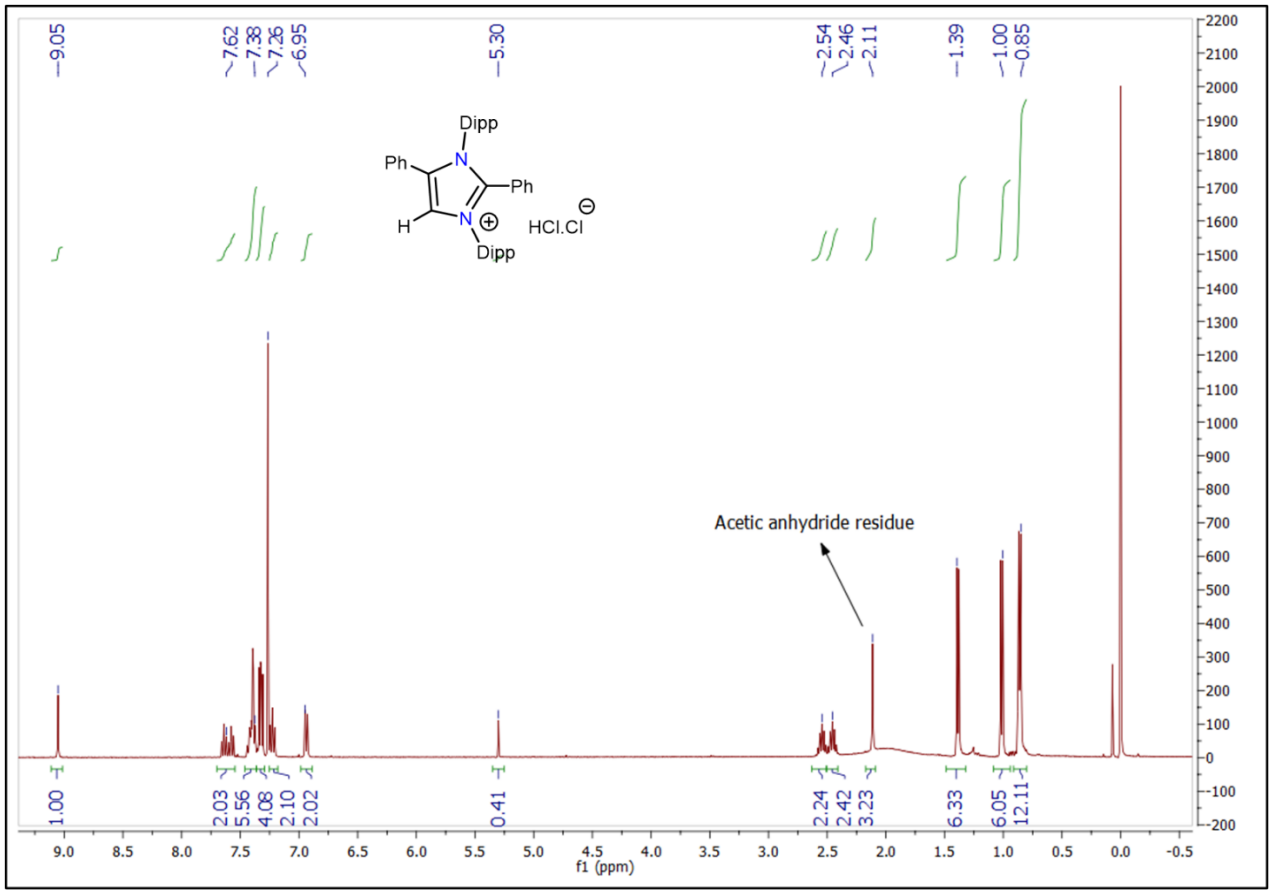


Figure 12: ^{1}H NMR of Compound **5**

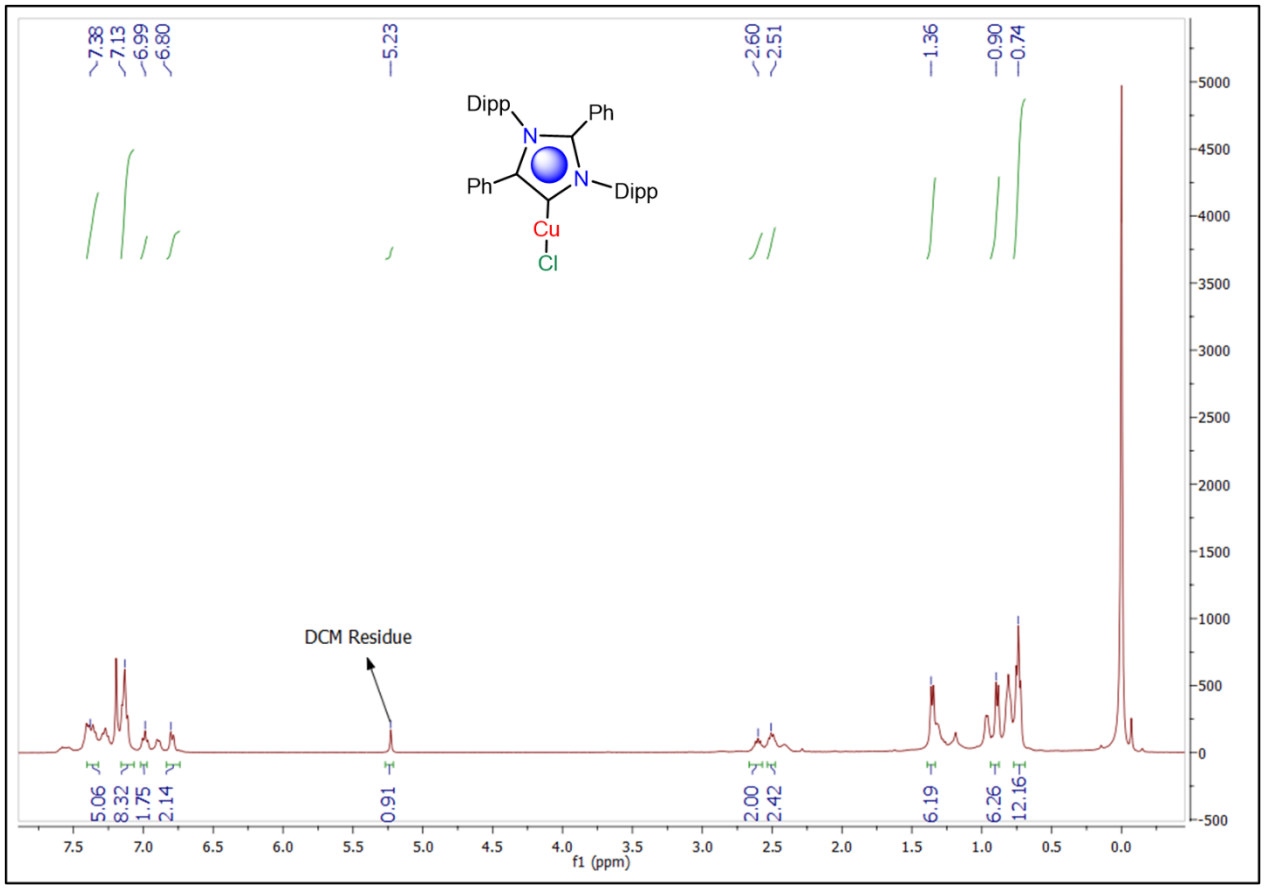


Figure 13: ^{1}H NMR of Compound **6**

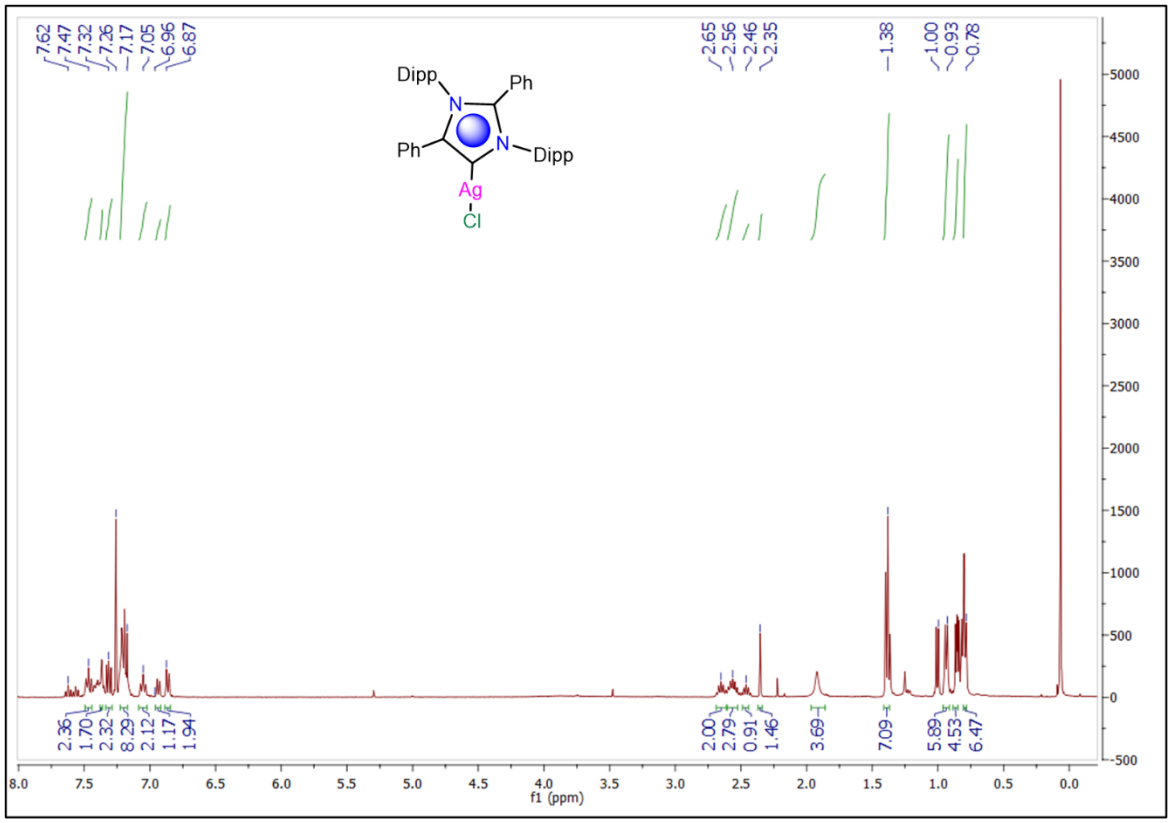


Figure 14: ^{1}H NMR of Compound **7**

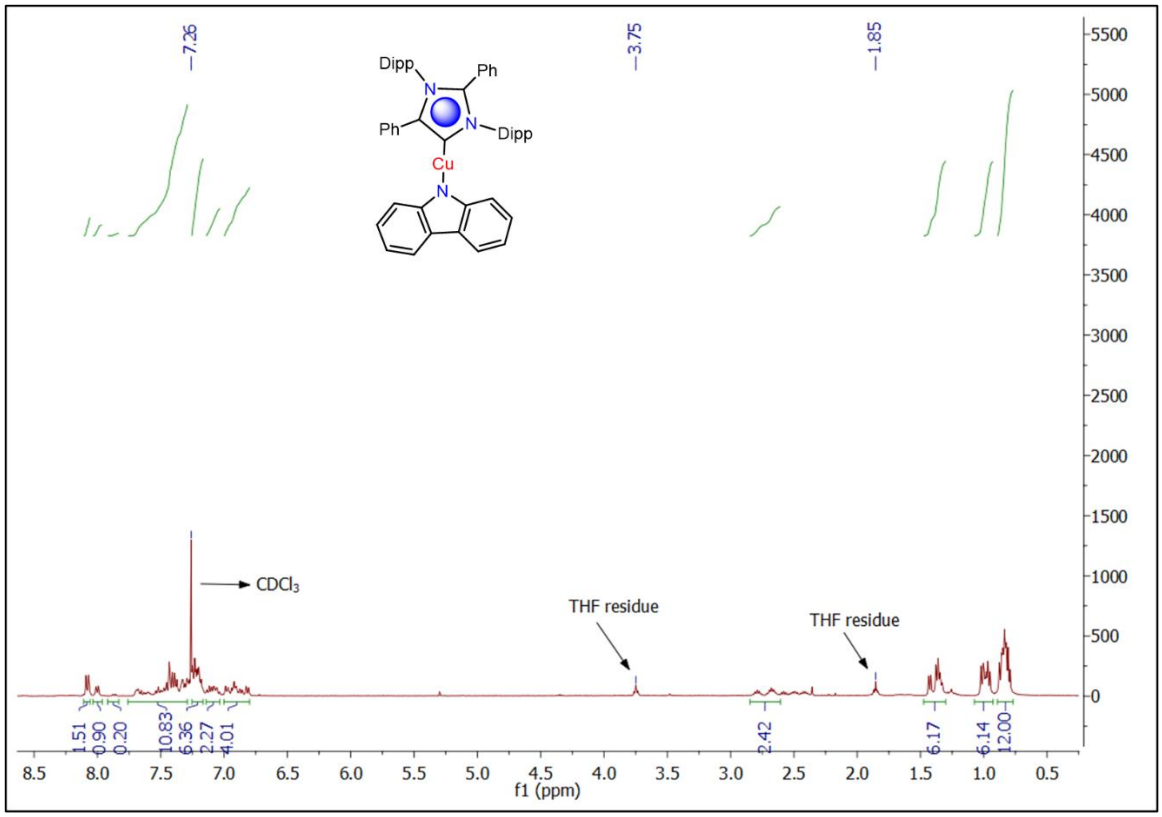


Figure 15: ^{1}H NMR of Compound **8**

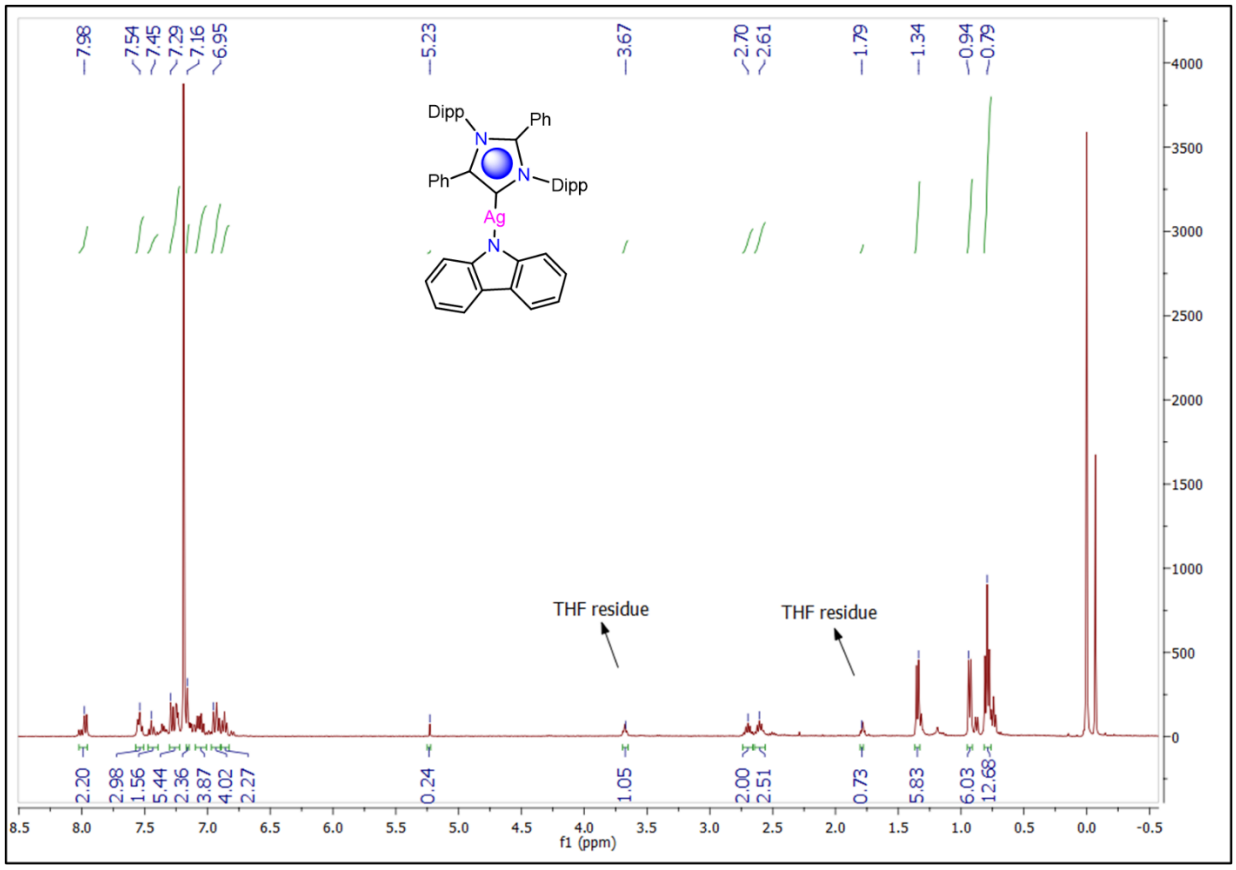


Figure 16: ^{1}H NMR of Compound **9**

5. Conclusion

Carbene-metal-amide (CMA) complexes with coinage metals are alluring in interest for device fabrication. We have prepared copper and silver two-coordinated complexes with halide precursors and their amide precursors. We have done structural, electrochemical, and photophysical studies in detail in this work. Complex **6** and **7** show solvatochromic effect and excitation-dependent emission. Electrochemical studies reveal that complexes and salt are both redox-active, meaning redox potential is independently controlled by ligand, and ligand is showing non-innocent behavior. In the future, we will try to isolate the crystal structure of complexes **8** and **9**. All the complexes have potential properties that can be further utilized for OLED fabrication. We will also try to modify the properties of the complexes by changing the arm of *a*NHC and carbazole moiety.

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