SYNTHESIS CHARACTERIZATION AND APPLICATION OF SOME TRANSITION METAL COMPLEXES FOR CROSS COUPLING REACTIONS

Thesis
Submitted in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
by
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DECLARATION

I hereby *declare* that the Research Thesis entitled **“SYNTHESIS, CHARACTERIZATION AND APPLICATION OF SOME TRANSITION METAL COMPLEXES FOR CROSS COUPLING REACTIONS”** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy** in Chemistry is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

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CERTIFICATE

This is to *certify* that the Research Thesis entitled **“SYNTHESIS, CHARACTERIZATION AND APPLICATION OF SOME TRANSITION METAL COMPLEXES FOR CROSS COUPLING REACTIONS”** submitted by **Ansari Rasheeda Bano Maqbool Hasan (Register Number: 138027CY13F05)** as the record of the research work carried out by her, *is accepted as the Research Thesis submission* in partial fulfillment of the requirements for the award of degree of **Doctor of Philosophy**.

Research Guide

Chairman- DRPC

Date:

Dedicated to

my Family, Friends, & Teachers

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ABSTRACT

In recent years, transition metal based catalysts have gained large importance due to the inherent flexibility of the metals to be complex with different organic ligands. Schiff base which falls in the category of imines is a unique class of ligands with different donor atoms exhibiting fascinating coordination style to approach the numerous metals. Compounds with C-C bond have shown worldwide applications in various fields such as agrochemicals, pharmaceuticals, natural products, advanced materials and so on. The Suzuki-Miyaura reaction is one of the most frequently used reactions for the synthesis of biaryls using transition metal catalyst especially palladium. 3*d*-metal complexes act as an alternative to the high-cost palladium catalyst with comparable conversions.

In this study, Schiff bases were synthesized using 4-aminoacetophenone, 2-amino-5-bromopyridine, 2-aminophenol, and 1,2-phenylenediamine with different substituted aldehydes (Salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-napthaldehyde). Complexes of 3*d*-transition metal (Mn, Fe, Co, Ni, Cu) were synthesized using Schiff base ligands. Also, we have described the synthesis of nano-iron (II) and nickel (II) complex of a Schiff base ligand, namely 1-((pyridin-2-ylimino)methyl)naphthalen-2-ol using sonochemical method. The immobilization of Schiff base copper complex onto graphene oxide was carried out to synthesize heterogeneous and eco-friendly catalysts. The synthesized complexes were analyzed using elemental analysis, FTIR, UV-Vis, NMR, Mass, TGA and magnetic susceptibility. The synthesized complexes were examined for their C-C coupling efficiency in Suzuki cross-coupling between phenylboronic acid and para substituted aryl halides. These complexes had a better advantage over phosphine complexes. The mild reaction condition, low cost of the reagent and non-toxic by-products of the reaction makes it versatile.

Keywords: Schiff base, cross-coupling of aryl halides, transition metal complex, Suzuki-Miyaura coupling.

CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE SURVEY

CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF METAL SCHIFF BASE COMPLEXES (C-1 to C-27)

CHAPTER 4: APPLICATION OF METAL SCHIFF BASE COMPLEXES (C-1 to C-27) AS C-C COUPLING CATALYST

CHAPTER 5: SYNTHESIS CHARACTERIZATION AND CATALYTIC APPLICATION OF NANO Fe (II), Ni (II)-SCHIFF BASE COMPLEXES (C-28 & C-29)

CHAPTER 6: SYNTHESIS AND CHARACTERIZATION OF COPPER (II) SCHIFF BASE COMPOSITE WITH GRAPHENE OXIDE FOR SUZUKI-MIYAURA CROSS COUPLING REACTION

CHAPTER 7: SUMMARY AND CONCLUSIONS

NOMENCLATURE

DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
THF	Tetrahydrofuran
TMS	Tetramethylsilane
GC	Gas Chromatography
FTIR	Fourier Transform Infra-red Spectroscopy
UV-Vis	Ultraviolet Visible Spectroscopy
LMCT	Ligand to metal charge transitions
ILCT	Intra ligand charge transitions
TGA	Thermogravimetric Analysis
NMR	Nuclear Magnetic Resonance
ESIMS	Electron spray ionization mass spectra
SCXRD	Single Crystal X-ray Diffraction
SEM	Scanning electron microscope
TEM	Transmission electron microscopy

CHAPTER 1

INTRODUCTION

This chapter speaks about introduction of transition metal complexes and their application as a catalyst in the various coupling reactions. Also, the significance of transition metal complexes in catalysis is explained in brief.

1.1 CATALYSIS

1.1.1 Introduction to catalysis

A substance that can create a change in the rate of a chemical reaction without itself being consumed is called ‘catalyst’. The word catalysis was first invented by Berzelius in 1836.

1.1.2 Classification of the catalyst

A Catalyst can be broadly classified as:

(a) Positive catalyst: Positive catalyst enhances the rate of a chemical reaction. Example: Iron catalyst in the manufacturing ammonia (Haber’s process).

(b) Negative catalyst: Negative catalyst decreases the rate of the chemical reaction. Example: In the presence of sunlight, the rate of oxidation of chloroform to phosgene gas decreases due to ethanol.

(c) Homogenous catalyst: Catalyst and reactants present in a similar phase. Example: Oxidation of Sulfur dioxide (SO_2) to Sulfur trioxide (SO_3), catalyzed by Nitric oxide in Lead chamber process. Both catalyst and reactant are in gaseous phase.

(d) Heterogeneous catalyst: Catalyst and reactants are present in different phases. Example: The reaction between N_2 and H_2 over Iron surface. Here N_2 and H_2 are gases and Fe is solid.

1.1.3 History of catalysis

A substance which enhances the rate of a process is called as a "catalyst", and the term obtained from Greek word ‘Catal’, which means "to annul". The reactions which are speed up by the substances that remains unaffected after the completion of the reaction. Eilhard Mitscherlich worked for *contact* processes and Johann Wolfgang Döbereiner for *contact action*. Later Johann Wolfgang Döbereiner worked on hydrogen lighter and a platinum sponge and in the 1820s it became a huge commercial success. The use of platinum in catalysis was discovered by Humphry Davy. Wilhelm Ostwald (in 1880s) at Leipzig University initiated a system in which a systematic research for reactions which is catalyzed by acids and bases and he bring out the idea that chemical reactions occur at definite rates and later he got to know that these rates can be used to decide the tenacity of acid and base catalyst. For this work, he was awarded the 1909 Nobel Prize in Chemistry.

1.1.4 Technical perspective of catalysis

A Catalyzed reaction requires less free energy to reach the transition state without altering the total free energy of the reaction. Behavior of the catalyst may be altered by the presence of inhibitors (reduces the catalytic) or promoters (enhances the catalytic activity). However, the mechanism of the catalyzed reaction is very complicated. Catalysts favorably alter the reaction environment and also cause the dissociation of reagents.

The rate of a chemical reaction depends on the frequency at which the reactants come in contact during the rate-determining step. As per common occurrence, participation of the catalyst happens in the slowest step, and the rate of the reaction is defined by the amount of the catalyst and its "activity". In a heterogeneous catalysis, the rate determining step is dependent on the reagent’s diffusion onto the surface and product’s diffusion from the surface.

The inhibition and deactivation of the catalyst can happen by secondary processes. In the case of heterogeneous catalysis, a typical example of the secondary process is coking where the catalyst is covered by polymeric side products which deactivates the catalyst. The dissolution of heterogeneous catalysts in solid-liquid system and the sublimation of the same in solid-gas system also inhibit the catalytic activity.

1.1.5 Importance of Catalysis

The catalyst plays an important role in industrial processes. Such as, vanadium oxide used as a catalyst for the synthesis of sulfuric acid and the acid is used in lead acid batteries, for detergents synthesis and for dyes manufacturing. Also, they are very important in synthesis of explosive materials, plastics etc. Ammonia is a primary component of many fertilizers which is economically synthesized by use of iron oxide as a catalyst.

The global environment also gets affected by use of different catalyst. Catalytic converters are used to treat exhaust in many automobiles. The chemical conversion of noxious gases to more inert forms with the help of platinum and palladium catalyst which causes the decrease in the impact of combustion engines on our environment.

The effect of catalyst on life itself is very important impact. The enzymes are the important catalyst in biochemical reactions. They are mostly proteins which catalyze particular reactions inside the cells. Such as polymerases (for DNA and RNA synthesis), peptidases (to digest the protein) and ATP synthases for energy production which is used by different cell activities.

1.1.6 Characteristics of Catalysis

The following are the characteristics of catalytic reactions.

- A catalyst remains unaffected in mass and chemical composition.
- A small quantity of the catalyst is ample to catalyze the reactions.
- The catalyst cannot initiate the reaction: The main job of the catalyst is to change the reaction rate.
- The catalyst is typically specific in nature.
- The catalyst cannot alter the position of equilibrium: The catalyst catalyze both forward and backward reactions to the equal amount in a reversible reaction and thus have no effect on the equilibrium constant.

- Catalytic promoters: Materials which themselves are not catalysts, but when it is mixed with the catalysts, increase the efficiency of catalysts are known as promoters.
- Catalytic poison: Materials which destroys the activity of the catalyst is known as catalytic poison. The action of iron catalyst is destroyed due to presence of hydrogen sulfide or CO.
- The rate of catalytic reaction can alter due to change of temperature.

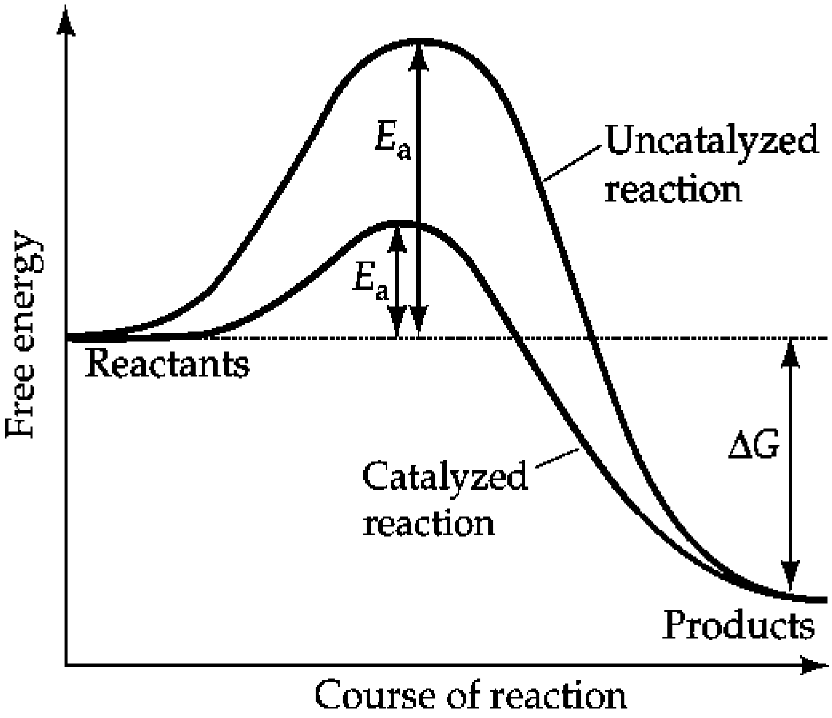


Figure 1.1 Generic potential energy diagram

- A positive catalyst decreases the activation energy. From collision theory, reaction happens due to effective collisions between the reacting molecules. It is essential for collision that the molecules must have a minimum amount of energy known as activation energy (E_a). After the collision, a molecule forms an activated complex which gets dissociated and yields the product. The catalyst supplies a new pathway includes lower amount of activation energy. Larger number of effective collisions occurs in the presence of a catalyst in comparison to effective collisions in absence of a catalyst at the same temperature. Hence, the reaction goes faster in the presence of a catalyst. Above figure shows that activation energy E_a, in absence of a catalyst is more than the activation energy E_a, in presence of a catalyst. The difference of the average energies of reactants and products gives the value of ΔG,

$\Delta G = E_R - E_P$

1.1.7 Types of catalysis

Catalysis can be divided into three main categories – homogeneous and heterogeneous and biocatalysis.

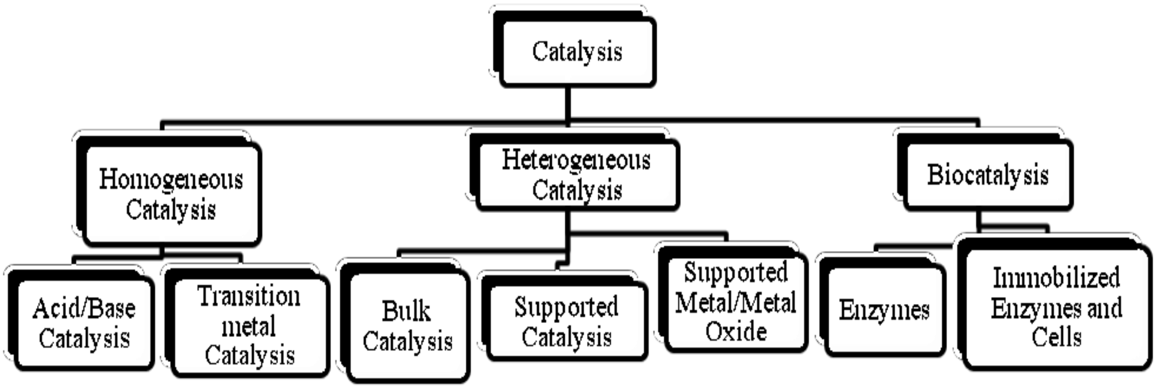


Figure 1.2 Types of Catalysis

1.1.7.1 Homogeneous catalysis

The catalysts and the reactant molecules react in same phase. Classically, in this system, the substrates and the catalysts are homogeneously mixed in a solvent medium. For example, in the synthesis of methyl acetate from acetic acid and methanol, the H^+ ion influences the esterification. Homogeneous catalysis is often regarded equally with organometallic catalysts. The types of homogeneous catalysis are as follows.

(a) Acid catalysis

The hydrogen proton is the most common homogeneous catalyst because water is the most universal solvent. Water produces protons by the process of self-ionization of water. Acids accelerate (catalyze) the esters hydrolysis:

$$CH_3COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + CH_3OH$$

Aqueous solutions of most esters do not hydrolyze in the absence of acids.

(b) Organometallic catalyst

A soluble organometallic complex falls under the homogeneous catalysis category. Hydroformylation and transfer hydrogenation, Ziegler-Natta polymerization and hydrogenation are well-known examples of homogeneous catalysis involve. It has also been used in different types of industrial processes like Wacker process, acetaldehyde synthesis as well as the Monsanto process and the Cativa process for the synthesis of acetic acid from MeOH and CO.

Other homogeneous catalysts are enzymes that are essential for life but are also exploited for industrial processes. A good example of enzyme catalyst is carbonic anhydrase, which catalyzes the release of CO_2 from the blood stream to the lungs.

(c) Theory of homogeneous catalysis

The catalyst forms an intermediate with the reactant molecules.

$$A + X \underset{K2}{\overset{K1}{\rightleftharpoons}} AX$$

Where ‘A’ is substrate, X is catalyst and AX is the intermediate compound.

AX then reacts with other reactant molecule (B) to give product and catalyst.

$$AX + B \overset{K3}{\rightleftharpoons} AB + X$$

This reaction is slow and is the rate determining step.

X is regenerated in last step. Thus, the rate of homogeneous catalytic reactions depends upon the concentration of X.

1.1.7.2 Heterogeneous catalysis

Reactants and catalysts react in different phase. Usually, heterogeneous catalysts are solids and it acts on substrates in a gaseous or liquid reaction mixture. Different mechanisms for heterogeneous reactions are known, it depends on how the adsorption happens on the surface (Eley-Rideal, Mars-van Krevelen and Langmuir-Hinshelwood). The reaction rate majorly depends on the surface area of total solid.

A heterogeneous catalyst has active sites for the reaction to occurs. The mechanism of the heterogeneous catalyst depends on, the active site may be an exposed planar metal surface, a crystal edge with flawed metal valence or a difficult combination of the two. To find out the quality of the active site needs a very tough research. Thus, great research for catalysis to find out new metal combinations continues.

Heterogeneous catalysts are typically deposited on the supported material. They are usually dispersed on other material which increases the affectivity and also minimizes the cost of the catalyst. Supporting materials such as alumina, zeolites or various kinds of activated carbon having different pore size, provide large surface area for reaction. Some specialized supports which include barium sulfate, calcium carbonate, titanium dioxide and silicon dioxide.

Between homogeneous and the heterogeneous catalysis, biocatalysis is a quite special case. Generally, the biocatalyst is an enzyme and they are greatly efficient catalysts. Conventionally used homogeneous and heterogeneous catalysts are ineffective and slow. Mild conditions of the reaction and shorter synthesis routes are few advantages of biocatalysis over “chemical catalysis”.

1.1.7.3 Comparison of Homogeneous and Heterogeneous Catalysis

In a heterogeneous catalytic system, the species are active only on the surface; the reactions often require relatively high temperature and low specificities. In addition, the study of mechanistic aspect of heterogeneous catalyst is difficult. However, the catalyst recovery is comparatively easy in heterogeneous catalysis. Whereas, by varying ligands, different types of homogeneous catalyst can be obtained. Homogeneous catalysis involves low temperatures and high specificities depending upon the catalyst being used. The mechanism of homogeneous catalysis can be accomplished more easily than the heterogeneous catalysis process.

1.1.8 Catalyst Deactivation

Loss in catalytic activity is called as catalyst deactivation. A catalyst made of organometallic complexes reduces its catalytic activity either by dimerization or oligomerization. Often, depending on the ligating groups attached the activity can be varied. The catalyst gets deactivated via side reactions, formation of additional phases, change of pH, oxidative degradation and temperature variation.

1.1.9 Transition metal as catalysts

Transition metal complexes have tremendous importance in catalysis, dye industry, analytical chemistry, agrochemical, food industry and biological activities. Transition metals and their compounds are often good catalysts. Transition metals and their metal oxides tend to be used as heterogeneous catalysts, their ions and complexes are usually employed as catalysts in homogeneous contexts.

A presence of incompletely filled d-orbitals is the typical general features in transition metals. Hence, they form compounds of variable oxidation states and as a result, transition metals find application in both homogeneous and heterogeneous catalysis process.

1.2 TRANSITION METAL COMPLEXES

1.2.1 Introduction to transition metal complexes

The bonding between transition metal and ligand in a transition metal complex can be understood by two approaches: “Crystal Field Theory” and “Molecular Orbital Theory”. Crystal Field Theory mainly focuses on the electrostatic attraction between the ligands and d-electrons of the metal ions, therefore is suitable to explain the spectral properties of the complex. On the other hand, molecular orbital theory explains the molecular structure of the complex and thereby giving a better insight to the physical properties of the system.

Since the electron pairs of the ligands can form saturated (18-electron) or unsaturated (16 or fewer electron) complexes with transition metal, they tend to form complexes with varying electronic properties which roots their importance in catalysis.

1.2.2 Basic properties of transition metal complexes

A transition metal atom or ion has degenerate *d*-orbitals in its free state. The *d*-orbitals of the metal atom interact with electron cloud of the ligands while forming complex which results in the loss of degeneracy of *d*-orbitals. Crystal field theory explains the distribution of energies among different *d*-orbitals and spatial distribution of *d*-electrons in a transition metal. When the transition metal absorbs electromagnetic radiation of sufficient energy, an electron excites from lower energy to higher energy due to the presence of incompletely filled *d*-orbitals. The geometry of the complex is dependent on splitting of the orbitals into different energy levels.

Transition metal complexes in general exhibit good thermal stability which is further improved by the use of chelating ligand. Additionally, transition metal complexes are stable in air and moisture, which mean that they are easy to handle and store. This important aspect provides a wide reaction scope of transition metal complexes.

1.3 COUPLING REACTIONS

A coupling reaction is in essence linking two hydrocarbon fragments together. This reaction is usually a metal catalyzed reaction as the energy requirement for reaching the transition state is very high for such reactions.

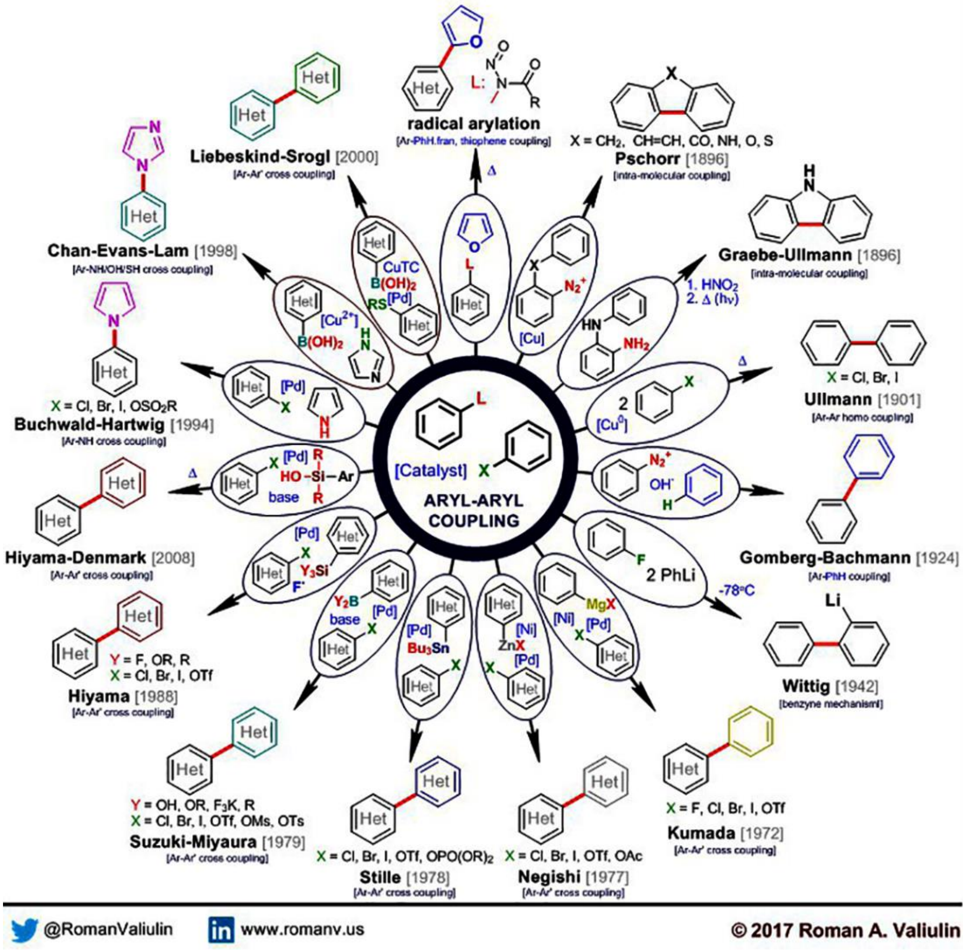


Figure 1.3 Common cross coupling reactions (© 2017 Roman A. Valiulin)

A coupling reaction can be primarily divided into two types:

- Homocoupling: A coupling of two identical partners, for example, the formation of biphenyl (Ph-Ph) from iodobenzene (PhI).
- Cross coupling: Involves a coupling of two different partners, for example formation of styrene ($PhCH=CH_2$) by the reaction between bromobenzene (PhBr) and vinyl chloride.

1.4 SUZUKI-MIYAURA COUPLING

A palladium-catalyzed coupling of aryl halide or vinyl (R_2X) with an organoborane (R_1-BY_2) to form product (R_1-R_2) with a new C-C bond is called the Suzuki reaction. This reaction is named after its inventor Akira Suzuki, who published his findings in 1979 and shared the Nobel Prize (2010) in Chemistry with Richard F. Heck and Ei-ichi Negishi for cross couplings in organic synthesis using palladium catalyst. The cross coupling is simply called as "Suzuki Coupling" or Suzuki-Miyaura reaction, and it is extensively used for the synthesis of styrenes, poly-olefins, and substituted biphenyls. The general Suzuki reaction is shown below.

$$\mathbf{R_1\text{-}BY_2} \;+\; \mathbf{R_2\text{-}X} \xrightarrow[\textbf{Base}]{\textbf{Pd catalyst}} \mathbf{R_1\text{-}R_2}$$

1.5 GENERAL MECHANISM FOR SUZUKI COUPLING REACTION

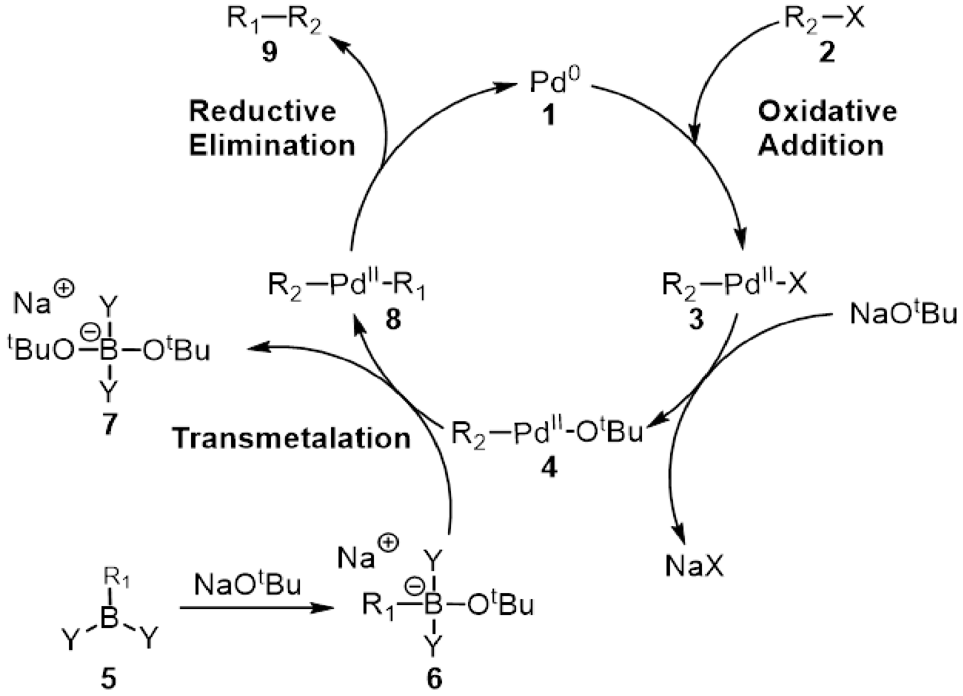


Figure 1.4 General mechanism of Suzuki-Miyaura cross coupling reaction

The mechanism of the Suzuki reaction can be studied using palladium catalyst. Figure 1.4 represents a pictorial flow of various steps involved in the Suzuki coupling reaction. The oxidative addition of palladium **(1)** to the aryl or alkyl halide **(2)** is the first step to form the organopalladium species **(3)**. The intermediate **(4)** obtained with the reaction of base, which via transmetalation with the boronate compound **(6)** gives the organopalladium species **(8)**. The final coupled product **(9)** obtained by reductive elimination and the original palladium catalyst **(1)** restored, which ends the catalytic cycle. The Suzuki reaction generally carried out in the presence of a base, though the role of the base was incompletely known. A trialkyl borate (R_3B-OR) was believed to form by presence of the base (reaction of alkoxide (RO^-) and trialkylborane (BR_3)). The trialkyl borate (R_3B-OR) considered as more nucleophilic and more reactive towards the palladium complex in the transmetalation step. Also, Duc and co-workers studied the importance of the base in the coupling mechanism and they understood that the base plays three important roles: Development of the palladium complex [$ArPd(OR)L_2$], formation of the trialkyl borate and it also accelerate the reductive elimination by reaction of the alkoxide with the palladium complex.

In this study, 3*d*-transition metal Schiff base complexes have been chosen for the Suzuki-Miyaura coupling reactions

CHAPTER 2

LITERATURE SURVEY

This chapter presents a brief examination on the literature with respect to the various synthesized transition metal shchiff base complexes and their application as catalysts for coupling reactions. The outline and main objectives of the present work conclude this chapter.

2.1 TRANSITION METAL COMPLEXES AND C-C COUPLING

Transition metal catalyzed formation of the carbon-carbon bond developed in the 1970s is of great importance in synthetic organic chemistry. The C-C coupling reactions are essential for the synthesis of new organic compounds having applications in diverse areas including pharmaceuticals, natural products, optical materials, liquid crystals, conductive polymers etc. The transition metal catalyzed coupling reactions are commonly used for the synthesis of biaryls, which are advantageous owing to their high selectivity, broad substrate scope, and mild reaction condition.

Gene et al. (1995) reported the coupling of esters or boronic acids using palladium (0) as a catalyst. The water-soluble catalyst in mild condition gave 60- 90% yield. Later, Reetz et al. (1996) reported the palladium and palladium/nickel bimetallic clusters as an effective catalyst for the Suzuki and Heck reactions. These clusters were stabilized by tetraalkylammonium salts or poly(vinylpyrrolidone) to retain their size and prevent further agglomeration.

A new palladium complex with salicylaldehyde N(4)-ethylthiosemicarbazone has been synthesized to catalyze the Heck coupling reaction of aryl bromides and styrene (Kovala-Demertzi et al. 2004). Korolev and Bumagin (2005) reported the $PdCl_2$-EDTA complex to be used to catalyze the Suzuki-Miyaura cross coupling reactions of aryl and heteroaryl halides with aryl (heteroaryl)boronic acids in aqueous media. In another report, palladium supported on hydrotalcite catalyst was used in Suzuki cross coupling reaction (Ruiz et al. 2006). Potassium carbonate was used as a base for the reaction. This report included a detailed study of the catalytic efficiency of different palladium salts, the influence of the base, and effect of temperature on the yield for Suzuki cross-coupling reaction. Another catalyst was reported where palladium synthesized from different palladium precursors were supported on Polyaniline (Kantam et al. 2007). They were characterized using different analysis. The catalytic activity was tested for the Suzuki-Miyaura coupling of bromo-and chloroarenes in water. The recovery of the catalyst was achieved by simple filtration and they were reused for several cycles without any significant reduction in the catalytic activity.

Iwasawa et al. (2008) synthesized palladium catalyst with pentaaryl benzene moiety for palladium-catalyzed Suzuki-Miyaura coupling of aryl chlorides and the synthesized catalyst achieved up to 5000 turnover numbers. Zhou et al. (2009) developed palladium catalyst with diimine ligands and applied for Suzuki coupling of arylbromide in different media.

An efficient immobilized MCM-41 palladium (0) catalyst was reported for C-C cross-coupling of different aryl halides with aryl borane and organotin (Jana et al. 2009). Zhou et al. (2010) cyclopalladated complexes with five- or six-member rings have been prepared using Schiff base ligands. Suzuki cross coupling reactions was carried out in aqueous solvents under mild conditions using prepared cyclopalladated complexes. Palladium catalyst from the reaction of $PdCl_2$(cod) with poly[(3-N-imidazolopropyl)methylsiloxane-co-dimethylsiloxane] was synthesized (Borkowski et al. 2011) and used as a catalyst for the coupling of aryl bromides with phenylboronic acid. The high yields of 2-methylbiphenyl with TOF up to 25,000 h^{-1} and eight number of run were passed with excellent results. Also, important role of the catalyst in the catalytic reaction was indicated by mercury poisoning test.

Palladium(II) complexes with square planar geometry was synthesized and characterized (Tamizh et al. 2013). The synthesized palladium (II) complexes shown good catalytic conversion in coupling of phenylboronic acid and 4-bromotoluene in N,N-dimethylacetamide (Suzuki coupling). Heterocyclic biaryls can also be synthesized using heterocyclic boronic acid and heterocyclic aryl bromides. $PdCl_2(CH_3CN)_2$ used as the catalyst for the synthesis of aryl-heteroaryl and heteroaryl-heteroaryl compounds through the Suzuki reactions of diazonium salts with potassium trifluoroborates in water and in the absence of ligand or base, additive (El Bakouri et al.2013). Also, it can be used for the Matsuda-Heck reaction between mono olefins with aryl diazonium salts. Suzuki-Miyaura cross-coupling of aryl bromides with phenylboronic acid was carried out with two palladium catalysts of $Pd(OAc)_2$ salt with differently substituted triazolylpolysiloxanes (Borkowskiet al. 2013). Recycling experiments were obtained with eight subsequent runs with very good results.

Leadbeater and Resouly (1999) reportedly used $NiCl_2$ to synthesize phosphine-free nickel complexes ($NiC1_2(NEt_3)_2$ and $NiCl_2$(bipy)). Catalytic property of these complexes was carried out in Suzuki-Miyaura reaction and the results show that the synthesized complexes were active catalyst for the above reaction. Inada and Miyaura (2000) studied $NiCl_2$.triphenylphosphine complexes for coupling of arylboronic acid with chloroarenes. $NiCl_2·6H_2O$ was also reported to have good yield for the coupling of aryl bromides and iodides with phenylboronic acid when used as a catalyst precursor (Zim and Monteiro 2002). Additionally, the influence of high pressure on the Suzuki-Miyaura cross-coupling reaction was demonstrated by Guo et al. (2008). Better yields were observed and palladium catalyst can be replaced with cheaper nickel, cobalt, and iron salts.

Hatakeyama et al. (2010) reported an iron catalyst for Suzuki-Miyaura coupling of nonactivated alkyl halides and arylboron compounds. Also, a nickel-catalyzed cross-coupling of aryl fluorides and aryl boronic esters was reported by Tobisu et al. (2011). Additionally, Suzuki-Miyaura cross coupling reaction of aryl halides and phenol-derivative with aryl boronic acids using nickel-catalyst in green solvents (2-Me-THF and tert-amyl alcohol) was reported (Ramgren et al. 2013). The high yield of biaryl obtained with this methodology and it can be used as a commercially available precatalyst, $NiCl_2(PCy_3)_2$. Later, Mieczyńska et al. (2014) developed a heterodinuclear macrocyclic Schiff base Pd(II)-Ni(II) complex for Suzuki and Heck cross-coupling reactions.

The complexes of Schiff base ligand with Ni(II), Cu(II), Co(II) and Pd(II) metal were synthesized (Kalita et al. 2015). All complexes were characterized by various analysis techniques. The synthesized palladium complex was used as catalyst for Suzuki reaction in open atmospheric conditions. Magano and Monfette (2015) reported the synthesis of NiCl(o-tolyl)(TMEDA) (TMEDA = tetramethylethylenediamine) and used it for coupling reactions. It was combined with an appropriate ligand, and applied to a wide range of transformations and reductive coupling reactions. The products obtained with these catalysts were superior in comparison with those obtained with common Ni sources. Moreover, the complex was stable for long time in air as a solid.

An efficient and recycled bifunctional Salen-Cu(II) catalyst was studied for N-arylation of imidazoles and Suzuki-Miyaura cross-coupling (Wang et al. 2015). The synthesis and characterization of new octahedral nickel(II) complex with monoanionic tridentate N,N,O-donor benzoylhydrazone ligand was reported by Suganthy et al (2016). The synthesized complex observed as an effective catalyst in the coupling of various aryl bromides with different arylboronic acids at optimized conditions. The yields of coupling obtained varied from moderate to excellent. A series of new pincer cobalt complexes were synthesized and their catalytic activity was carried out for Suzuki-Miyaura cross coupling reactions (Kumar and Bhat 2017). Also, Kumar et al. (2017) reported Fe (II) and Cu (II) PNP pincer complexes for Suzuki-Miyaura C-C cross coupling reactions.

2.2 SCHIFF BASE METAL COMPLEX

Schiff bases are the condensation products of amines with carbonyl compounds. Organic compounds containing azomethine group (>C=N) and have the general structure R-N=C-R' where R and R' are aryl, alkyl, cycloalkyl or heterocyclic groups. Since the mid nineteenth century the complexes of Schiff base ligands known (Schiff 1869) for their general preparation. Jorgensen and Werner in 1957 studied on Schiff base metal complexes and later theses complexes got important position in the coordination chemistry.

Transition metals that can form Schiff base complexes and bases have reported to be employed as chelating ligands for coordination chemistry. Their metal complexes are of significant research interest since many years. Also, N, O and S atoms play a vital role as active sites of many metallobiomolecules in the coordination of metals (Brown and Smith 1990).

These complexes have been extensively studied due to their importance in industrial, anticancer, antifungal, antibacterial, herbicidal and antiviral applications (Singh et al. 2007; Cozzi 2004; Chandra and Sangeetika 2004). Biologically importance and various catalytic applications of these complexes make them ideal.

The complexes of Schiff base having oxygen and nitrogen donor atom shows unusual configurations and structural labiality which is also sensitive to the molecular environment. The complexes of 2-hydroxy Schiff base ligands have been synthesized and their crystallographic, structural and magnetic properties were studied in detail (Yildiz et al. 1998; Sunatsuki et al. 2002; Sibous et al. 2010).

A large number of transition metal complexes with Schiff base ligands have been studied for their contemporary research (Di Bella et al. 1997). These ligands can be bind with metal in bidentate N,O-, tridentate N,O,O-, N,O,N-, N,O,S-, tetradentate N,N,O,O-, hexadentate N,N,O,O,S,S- fashion (Scheurer et al. 2005) etc.

Transition metal complexes (besides Pd) with Schiff base are applied for applications that includes polymer industry, dye industry, medicinal chemistry, agrochemical, and biological activities (Prakash and Adhikari 2011).

Schiff bases and their complexes have been reported to be widely employed for carrying out ample reactions in synthetic chemistry (Che and Huang 2003). Schiff bases have the potential to bind with different metals for formation of stable complexes (Jin et al. 2016; Shi et al. 2007) and also as intermediates in various organic reactions. Schiff base complexes pose to be superior as a catalyst for many reactions (Pouralimardan et al. 2007).

In addition, various Schiff bases have also been examined for their biological activities by researchers (Parashar et al. 1988; Akbar Ali et al. 2002; Neelakantan et al. 2008). Nickel and Copper complexes with ONNO asymmetric tetradentate Schiff base ligand were used in antimicrobial studies for DNA interaction (Abdel-Rahman et al. 2017).

Complexes mostly with palladium and a little with nickel, have been extensively used as an active catalysts in the cross coupling reactions. A greener approach in the domain of catalysis needs the application of catalysts using cheaper and environmentally affectionate metals. With this aim, use of non expensive metals like manganese, iron, cobalt, nickel, copper in the synthesis of metal complex and further its catalytic activity in cross coupling reactions needs an investigation.

2.3 SCOPE OF THE WORK

The synthesis of biaryls is of particular interest to the industry due to their wide-ranging application in multidisciplinary fields. The synthesis of these compounds demands more efficient and energy conserving methods. Transition metal complexes with Schiff base ligand possess distinctive metal bound structures which make them the most active catalyst in carbon-carbon coupling reactions. As discussed, the palladium and nickel Schiff base complexes are the extensively explored catalyst for the cross-coupling reactions. A greener approach in the area of catalysis needs the cheap and environmentally affectionate metals for catalytic applications.

The research work addresses the synthesis of Schiff base ligand (ON, ONN, OON, ONO and ONNO donor), its complexation with few 3*d*-transition metals, and their characterization followed by the investigation of their catalytic efficiency in cross coupling of aryl halides and organoborons. Thesis also describes the synthesis of nano-iron (II) and nickel complex of a Schiff base ligand, namely 1-((pyridin-2-ylimino)methyl)naphthalen-2-ol (NNO donor) using ultrasonic irradiation. These complexes were characterized and used for catalyzing the Suzuki-Miyaura cross coupling reactions. Lastly, this work presents a study of heterogeneous catalyst of copper Schiff base composite grafted onto graphene oxide (Cu-NH_2-GO). The catalytic performance of Cu-NH_2-GO was studied in the C-C cross coupling of aryl halides and phenylboronic acid.

2.4 OBJECTIVES

The main objectives of the proposed research work are as follows.

- To synthesize ligands and its complexes with 3*d*-transition elements.
- To synthesize the graphene oxide grafted copper catalyst.
- To characterize the synthesized ligands and complexes using UV-Vis, FTIR, ^{1}H-NMR, CHN, SCXRD, and mass spectral analysis.
- To study the catalytic activity of transition metal complexes in cross coupling reactions.
- To optimize the reaction condition with respect to solvent, time, base, and catalyst concentration.
- To study the scope of the catalytic system to different aromatic substrates and the effect of substituents in the activities of catalysts.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF METAL SCHIFF BASE COMPLEXES (C-1 to C-27)

The chapter details the information on the synthesis of ligands and metal complexes of Manganese, Iron, Cobalt, Nickel and Copper. This chapter also includes the experimental procedures for the catalytic studies performed using the synthesized complexes.

3.1 INTRODUCTION

Schiff base is a class of organic ligands containing imine skeleton with different donor atoms exhibiting fascinating coordination bonds towards the numerous metals (Gupta and Sutar 2008; Dhanraj et al., 2013). The chelation compatibility of the Schiff bases towards the transition metal ions is also applied in the preparation of respective metal complexes. Schiff base metal complexes are well known for their easy synthesis, stability and wide applications (Abu-Dief and Mohammad 2015; Alias et al. 2014). In addition to these, the metal complexes of Schiff base ligands also exhibit various properties, namely, their ability to bind with oxygen, photochromism, antibacterial & antifungal properties, catalytic activity in olefins hydrogenation, and complexing proficiency towards a few toxic metals (Malik et al. 2011; Raman et al. 2007).

In this chapter, we report the synthesis of O,N-; O,N,N-; O,O,N-; O,N,O-; and O,N,N,O-Schiff base ligands and their complexes using manganese, iron, cobalt, nickel, and copper as the active metals. Synthesized ligands and complexes have been characterized using relevant analytical techniques.

3.2 MATERIALS AND CHARACTERIZATION TECHNIQUES

3.2.1 Materials

All chemicals of Analytical Reagent (AR) grade were used without further purification. 4-aminoacetophenone, 3-methoxysalicylaldehyde, 2-amino-5-bromopyridine, 2-aminopyridine, salicylaldehyde, nickel acetate tetrahydrate, nickel chloride hexahydrate, 2-hydroxy-1-naphthaldehyde, 2-aminophenol, copper acetate monohydrate, cobalt acetate tetrahydrate, cobalt chloride hexahydrate, ferrous chloride hexahydrate, ferric chloride hexahydrate, manganese chloride tetrahydrate, potassium carbonate, and sodium carbonate were procured from Merck India. Acetonitrile (ACN), 1,4-dioxane, dimethylformamide (DMF), toluene, ethyl alcohol, diethyl ether, dichloromethane (DCM), tetrahydrofuran (THF), potassium tertiary butoxide, cesium carbonate, triethylamine, phenylboronic acid and aryl halides were purchased from Sigma-Aldrich.

3.2.2 Characterization techniques

(a) Magnetic Measurements

The magnetic susceptibilities of the complexes were done at room temperature on a Sherwood UK magnetic balance using ($HgCo(NCS)_4$) as solid calibrant. The solid compound was tightly packed into a weighed sample tube to appropriate length (*l*) and the sample weight (*m*) was noted. Then the packed sample tube was located into tube guide of the balance and the reading was noted (R). The mass susceptibility, χ_g, is calculated using the formula:

$$\chi_g = \frac{C_{bal} \times l \times (R\text{-}R_0)}{10^9 \times m}$$

Where, *l* = sample length in the tube (cm)

m = mass of the sample (g)

R = instrument measurement for the sample in tube

R_0 = instrument measurement for the empty tube

C_{bal} = calibration constant of the balance

The molar susceptibility was calculated as:

$$\chi_m = \chi_g \times \text{Molecular weight of complex}$$

The molar susceptibility was then corrected with diamagnetic contribution. The effective magnetic moment, μ_{eff}, was calculated using the formula:

$$\mu_{\mathrm{eff}} = 2.83\sqrt{T \times \chi_{\mathrm{m}}}$$

Where, χ_m is the molar susceptibility and *T* is temperature.

The theoretical magnetic moments were calculated using the formula

$$\mu_{\mathrm{eff}} = \sqrt{\mathrm{n}(\mathrm{n} + 2)}$$

with n being the number of unpaired electrons.

(b) Spectroscopic characterization

^{1}H-NMR spectra were recorded at 400 MHz using tetramethyl silane (TMS) as an internal standard on Bruker AV 400 instrument. FTIR spectra were recorded on a Bruker-Alpha ECO-ATR FTIR spectrophotometer within 400-4000 cm^{-1} after making KBr pellets of the samples. UV-Vis spectra of ligands and complexes were measured on Analytik Jena SPECORD S600 UV-Vis spectrophotometer.

(c) Thermo gravimetric analysis

Thermogravimetric measurements were performed on (EXSTAR-6000) using nitrogen as the carrier gas (flow rate: 50 mL/min). The heating rate was 10 °C/min.

(d) Mass spectra

Electron Spray Mass spectra of the ligands and complexes were recorded on Waters Q-ToF micro-mass spectrometer with an ESI source.

(e) Thermogravimetric analysis

Thermogravimetric measurements were performed on (EXSTAR-6000) using nitrogen as the carrier gas (flow rate: 50 mL/min) with heating rate 10 ˚C/min. The C, H and N contents of the compounds were determined using microanalysis Thermoflash EA1112 series analyzer.

(f) Electron microscopy

Scanning electron microscopy (SEM) analysis was carried out by JEOL-JSM-6360LV to investigate the morphology of the specimen. Transmission electron microscopy (TEM) analysis was carried out by JEM-2100Plus to investigate the morphology and size of the specimen.

(g) X-ray Diffraction analysis

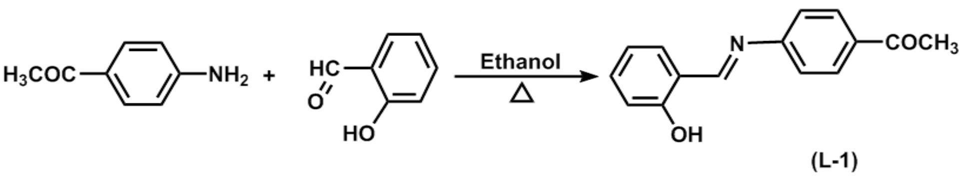
Powder X-ray diffraction (PXRD) was performed using Joel diffractometer with Cu-Kα (λ=1.542 Å) radiation. The Single crystal X-ray diffraction (SCXRD) analysis for crystals were completed on a Bruker APEX-II CCD diffractometer with Mo Kα radiation (λ_o = 0.71073 Å) at 296K. The structure was solved using SHELXL-2007/2014 software and refined by full matrix least square methods.

(h) Particle size measurement

Particle size measurement was carried out on Horiba particle size analyzer to investigate the size of the compound.

3.2.3 Synthesis of Schiff base ligand (L-1)

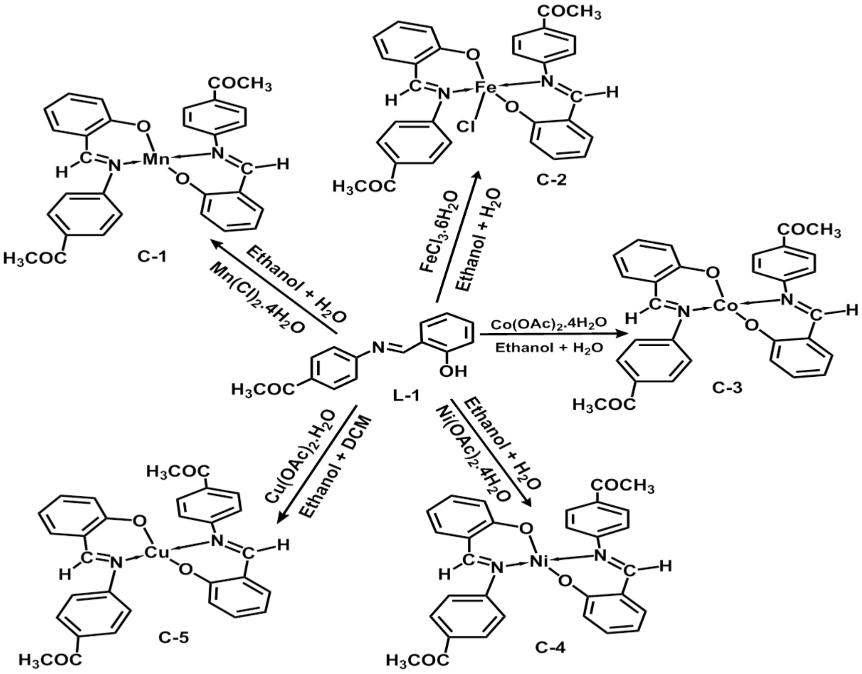
The solutions of 4-aminoacetophenone (0.135 g, 1.0 mmol) and salicylaldehyde (0.122 g, 1.0 mmol) in ethanol were taken in a 50 mL round bottom flask and heated to 60 ˚C. This mixture was further refluxed for 3 hours and filtered. The obtained compound was washed with diethyl ether and re-crystallized using small amount of ethanol followed by drying. A small portion of the synthesized compound was used for further characterization.



Scheme 3.1 Synthesis of ligand (L-1)

3.2.4 Synthesis of complexes (C-1 to C-5)

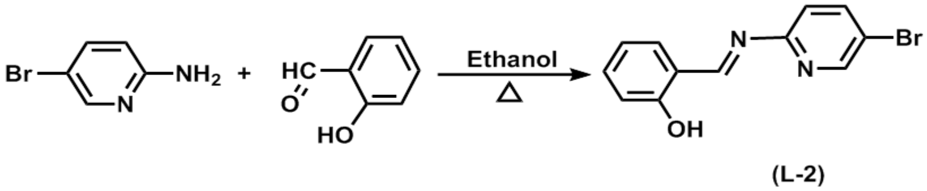
The complexes of transition metals ions, namely, Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) (C-1 to C-5) with Schiff base ligand were synthesized using simple reflux method. In a typical procedure, the solution of metal salt (1.0 mmol) and Schiff base ligand (L-1) (2.0 mmol) in 5 mL methanol was refluxed at 50 ˚C for 3 hours. The product was filtered and washed with cold methanol and dried.



Scheme 3.2 Synthesis of complexes (C-1 to C-5)

3.2.5 Synthesis of Schiff base ligand (L-2)

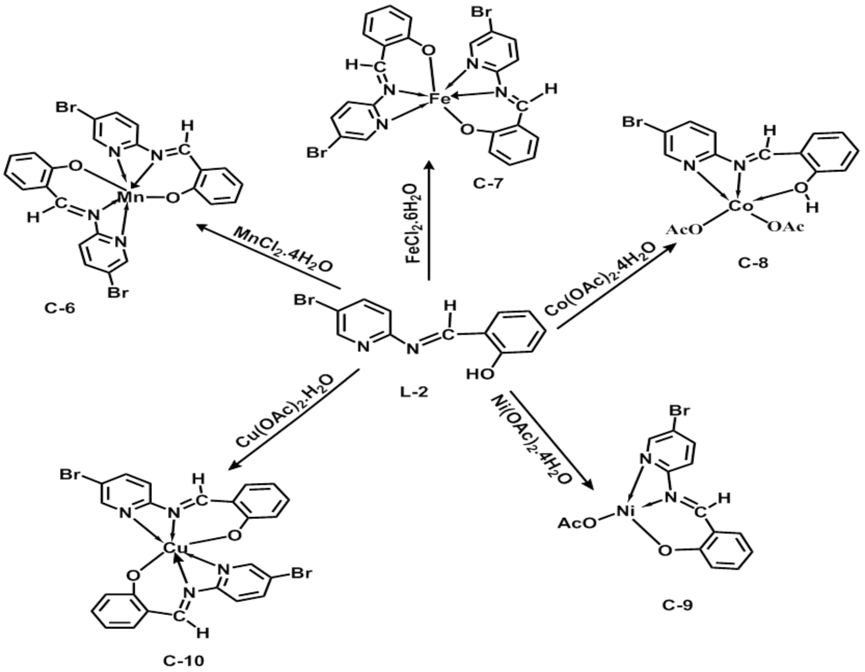
2-amino 5-bromo pyridine (0.277 g, 1.0 mmol) and salicylaldehyde (0.122 g, 1.0 mmol) dissolved in ethanol were taken in a 50 mL round bottom flask and heated to 60 ˚C. The reaction mixture was then refluxed for 3 hours and filtered. The obtained product then washed with diethyl ether, re-crystallized and dried.



Scheme 3.3 Synthesis of ligand (L-2)

3.2.6 Synthesis of complexes (C-6 to C-10)

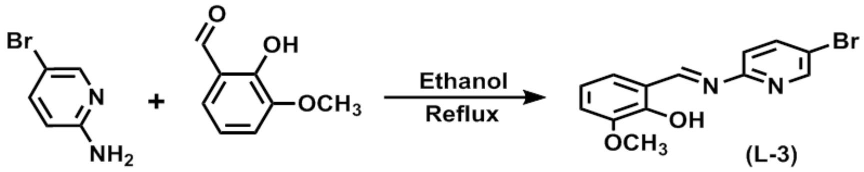
Schiff base complexes from C-6 to C-10 were synthesized using simple reflux method. A solution of metal salt (1.0 mmol) in 5 mL methanol was mixed with the ligand (L-2) (2.0 mmol). The resulting solution was then refluxed for 3 hours. The product was filtered and washed with cold methanol and dried.



Scheme 3.4 Synthesis of complexes (C-6 to C-10)

3.2.7 Synthesis of Schiff base ligand (L-3)

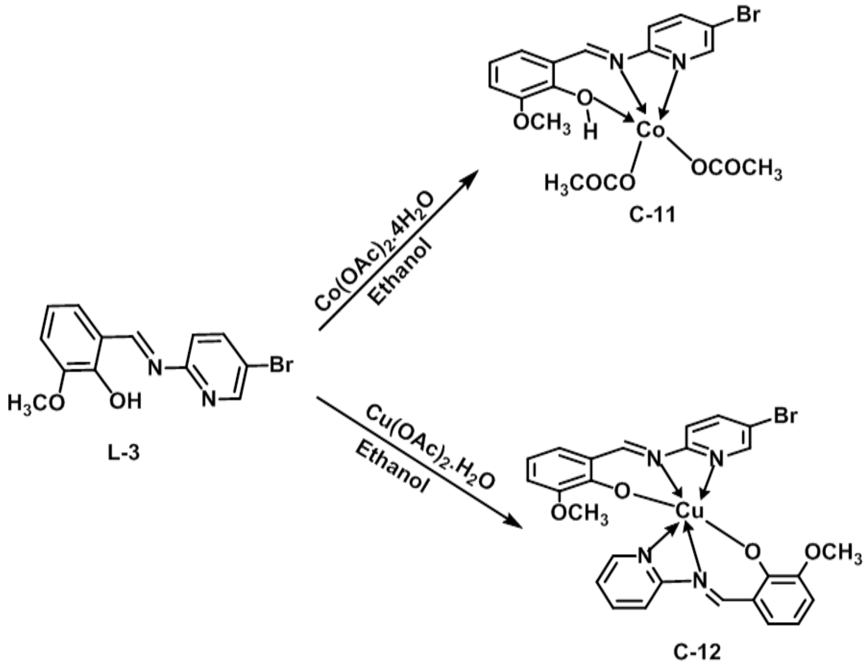
2-amino 5-bromo pyridine (0.173 g, 1.0 mmol) and 3-methoxysalicylaldehyde (0.152 g, 1.0 mmol) were dissolved in ethanol and heated to 60 ˚C in a 50 mL round bottom flask. The reaction mixture was then refluxed for 3 hours and filtered. The obtained product then washed with diethyl ether and re-crystallized from ethanol and dried.



Scheme 3.5 Synthesis of ligand (L-3)

3.2.8 Synthesis of complexes (C-11 & C-12)

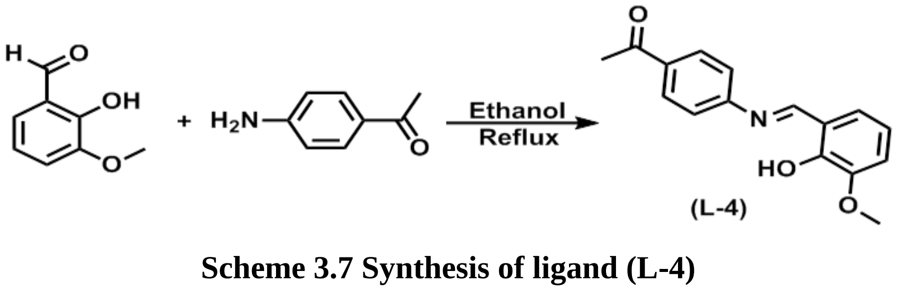
Schiff base complexes of cobalt and copper (C-11 & C-12) were synthesized using cobalt acetate and copper acetate. A solution of metal salt (1.0 mmol) in 5 mL ethanol was stirred with the ligand (L-3) (2.0 mmol) in 5 mL ethanol. The resulting solution was then refluxed for 3 hours. The product was filtered, washed with methanol and dried.



Scheme 3.6 Synthesis of complexes (C-11 & C-12)

3.2.9 Synthesis of Schiff base ligand (L-4)

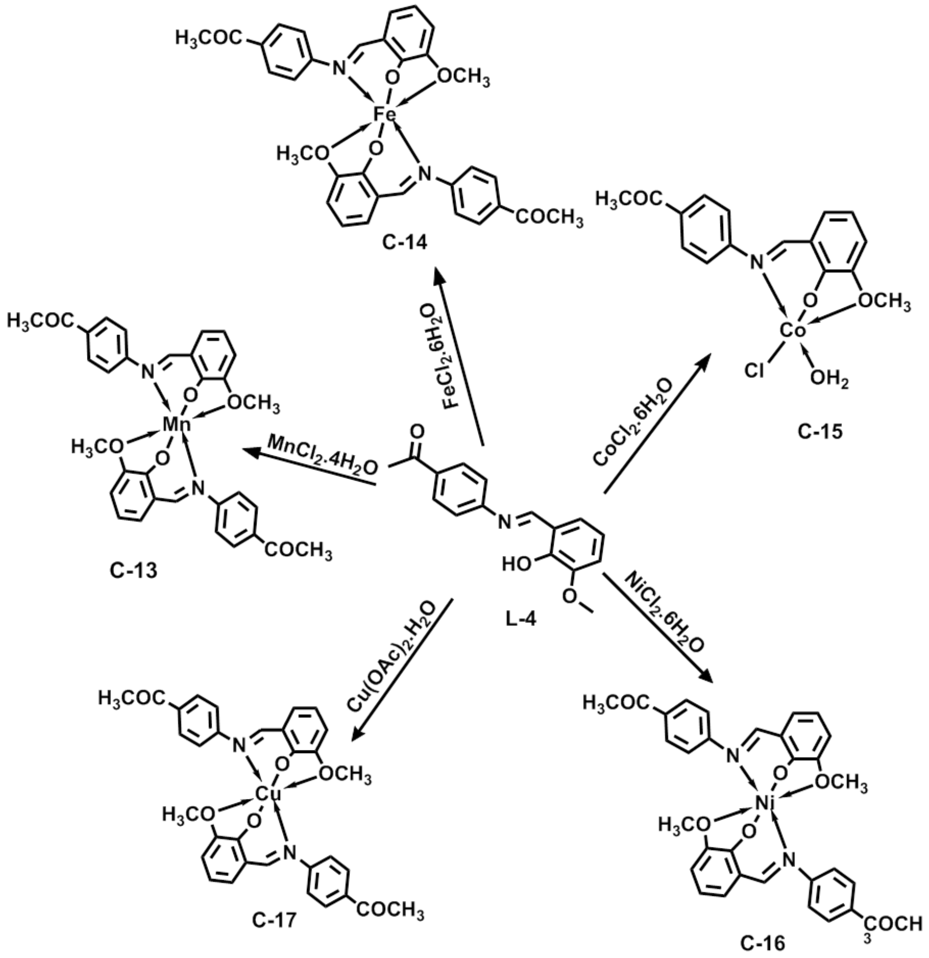
4-aminoacetophenone (0.135 g, 1.0 mmol) and 3-methoxysalicylaldehyde (0.152 g, 1.0 mmol) were dissolved in ethanol and heated to 60 ˚C in a 50 mL round bottom flask. The reaction mixture was refluxed for 3 hours and then filtered. The obtained product was then washed with diethyl ether and re-crystallized from ethanol and dried.



Scheme 3.7 Synthesis of ligand (L-4)

3.2.10 Synthesis of complexes (C-13 to C-17)

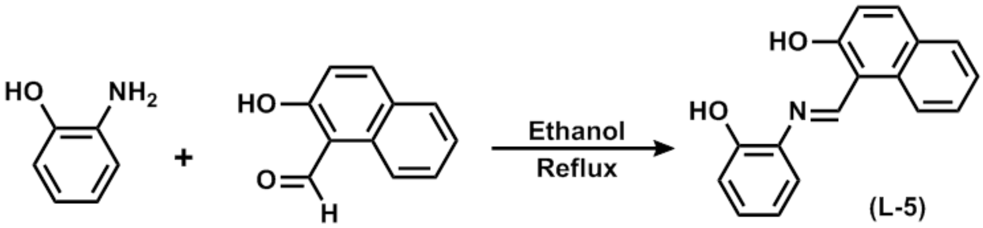
Schiff base complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) (C-13 to C-17) were synthesized using Schiff base ligand (L-4) and metal salt (Metal acetate or chloride). A solution of metal salt (1.0 mmol) in 5 mL ethanol was mixed with the ligand (L-4) (2.0 mmol) in 5 mL ethanol. The resulting mixture was then refluxed for 3 hours. The product was filtered and washed with methanol and dried in oven at 60 ˚C.



Scheme 3.8 Synthesis of complexes (C-13 to C-17)

3.2.11 Synthesis of Schiff base ligand (L-5)

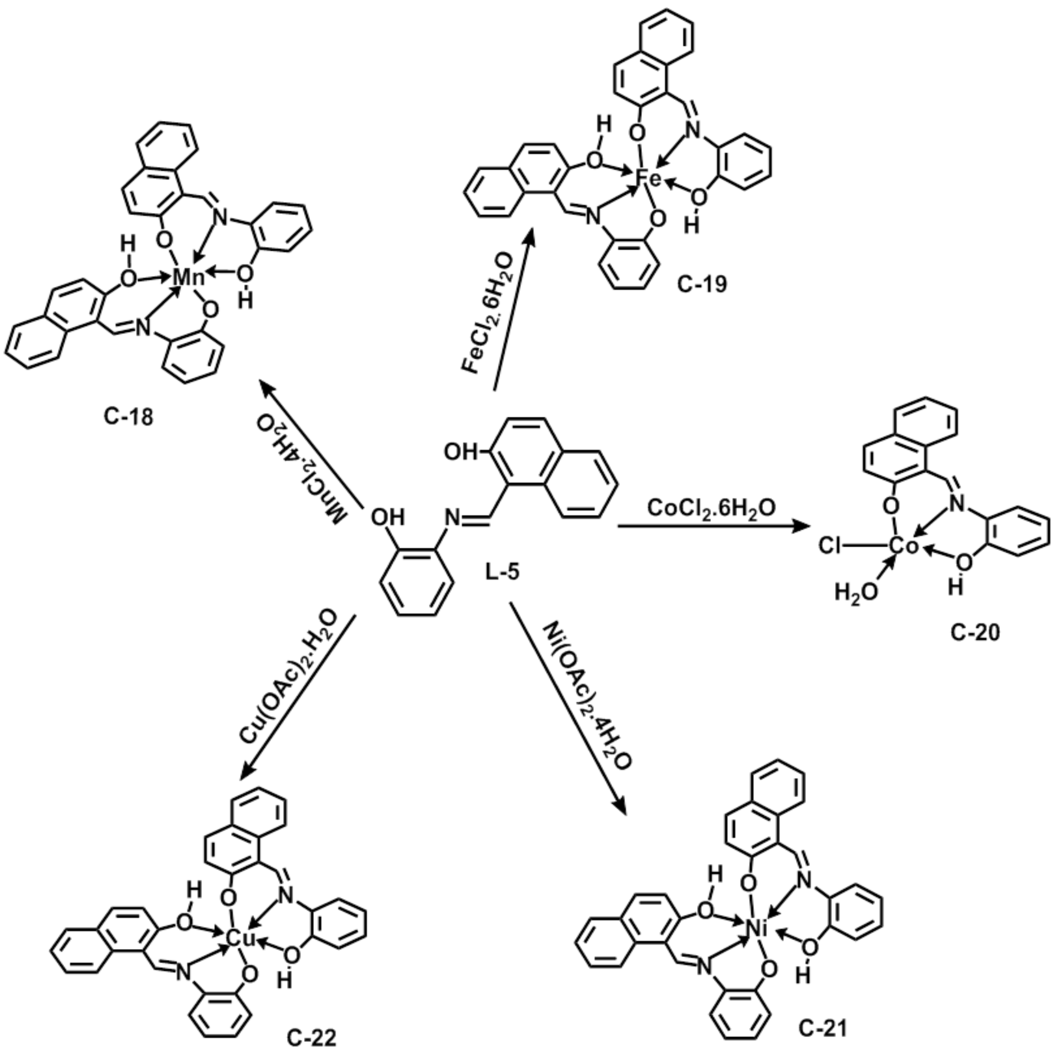
2-aminophenol (0.109 g, 1.0 mmol) and 2-hydroxy-1-naphthaldehyde (0.172 g, 1.0 mmol) were dissolved in ethanol and heated to 60 ˚C in a 50 mL round bottom flask. The reaction mixture was then refluxed for 3 hours and filtered. The obtained product then washed with diethyl ether and re-crystallized from ethanol and dried.



Scheme 3.9 Synthesis of ligand (L-5)

3.2.12 Synthesis of complexes (C-18 to C-22)

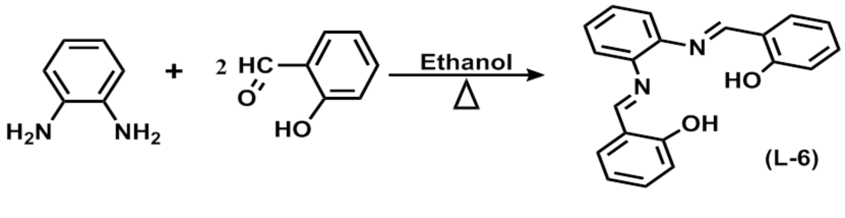
Five complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) (C-18 to C-22) were synthesized using simple reflux method. A solution of metal salt (1.0 mmol) in 5 mL ethanol was mixed with ligand (L-5) (2.0 mmol) in 5 mL ethanol. The resulting solution was then refluxed for 3 hours. The product was filtered and washed with cold methanol and dried.



Scheme 3.10 Synthesis of complexes C-18 to C-22

3.2.13 Synthesis of Schiff base ligand (L-6)

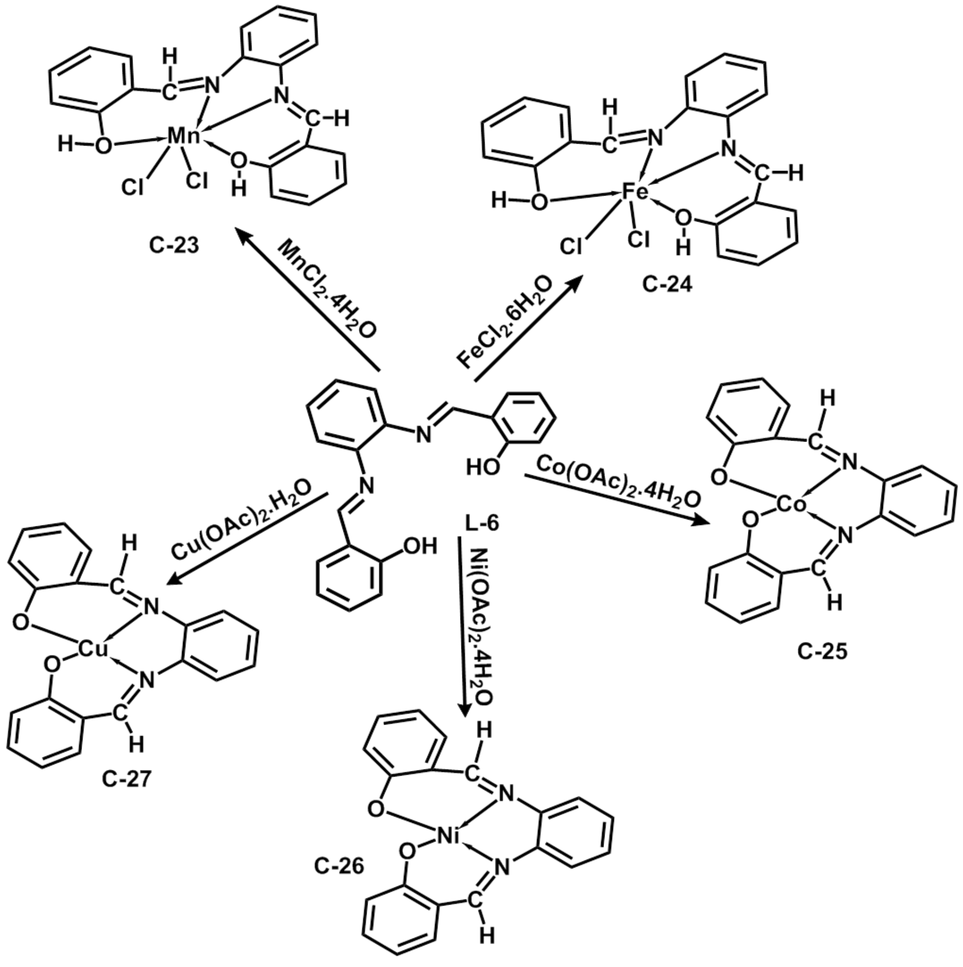
In a round bottom flask o-phenylenediamine (0.108 g, 1.0 mmol) and salicylaldehyde (0.244 g, 2.0 mmol) were taken in 5 mL of ethanol and refluxed for 3 hours. The product was filtered and washed with diethyl ether and dried at 60 ˚C.



Scheme 3.11 Synthesis of ligand (L-6)

3.2.14 Synthesis of complexes (C-23 to C-27)

Metal Schiff base complexes (C-23 to C-27) were prepared by using simple reflux method. The dissolved solution of metal salts (1.0 mmol) in ethanol (5 mL) was slowly added to the ligand (L-6) (0.316 g 1.0 mmol) solution in ethanol (10 mL) under constant stirring and refluxed for 2 hours. Reaction was monitored by color change and precipitate formation. The obtained precipitate was filtered, washed with ethanol and diethyl ether to remove unreacted Schiff base. Product was dried at 60 ˚C for 5 hours.



Scheme 3.12 Synthesis of complexes (C-23 to C-27)

3.3 RESULTS AND DISCUSSION

The synthesized ligands and their metal complexes were characterized by FTIR, mass spectra and elemental analysis. All the results found were in good agreement with the proposed structure. ^{1}H NMR spectral analysis of the ligands also validates the structures which are proposed for the ligands. Also, the TGA results of the complexes matches with structures of the complexes.

3.3.1 Physical and analytical studies

Analytical data and the physical properties of the ligands and the complexes are given in the (Table 3.1, 3.2, 3.3, 3.4, 3.5, 3.6 and 3.7). The elemental analysis (C, H and N) data were in good agreement with the proposed empirical formulae of the complexes.

Table 3.1 Physical properties and analytical data of ligands (L-1 to L-6).

Compounds	**Color**	**Yield (%)**	**Elemental analysis data Found (Calculated)**		
			C %	**H %**	**N %**
L-1	Light yellow	80	75.94 (75.30)	5.40 (5.48)	5.02 (5.85)
L-2	Dark Yellow	75	52.50 (52.01)	3.01 (3.27)	5.54 (5.77)
L-3	Red	80	75.94 (75.90)	5.40 (5.48)	5.50 (5.85)
L-4	Orange	84	59.92 (59.83)	4.35 (4.33)	4.45 (4.63)
L-5	Turmeric Yellow	82	77.40 (77.55)	4.77 (4.98)	5.02 (5.32)
L-6	Turmeric Yellow	82	75.22 (75.93)	4.90 (5.10)	8.74 (8.86)

Table 3.2 Physical properties and analytical data of Complex (C-1 to C-5).

Compounds	Color	Yield (%)	Elemental analysis data Found (Calculated) C %	H %	N %
C-1	Light orange	60	67.62 (67.80)	4.34 (4.55)	5.14 (5.27)
C-2	Dark purple	84	59.92 (59.83)	4.35 (4.33)	4.45 (4.63)
C-3	Orange	68	64.31 (64.43)	4.75 (4.90)	4.56 (4.70)
C-4	Bright green	78	67.00 (67.07)	4.81 (4.88)	5.11 (5.21)
C-5	Brown	80	66.68 (66.72)	4.40 (4.48)	5.17 (5.19)

Table 3.3 Physical properties and analytical data of complex (C-6 to C-10).

Compounds	Color	Yield (%)	Elemental analysis data Found (Calculated) C %	H %	N %
C-6	Light yellow	75	47.62 (47.48)	2.78 (2.66)	9.04 (9.23)
C-7	Dark purple	82	47.92 (47.41)	2.83 (2.65)	9.10 (9.21)
C-8	Orange	71	42.51 (42.32)	3.75 (3.33)	6.16 (6.17)
C-9	Bright green	76	42.78 (42.69)	2.94 (2.82)	7.42 (7.11)
C-10	Brown	81	47.00 (46.81)	2.77 (2.62)	9.17 (9.10)

Table 3.4 Physical properties and analytical data of complex (C-11 & C-12)

Compounds	Color	Yield (%)	Elemental analysis data Found (Calculated)		
			C %	**H %**	**N %**
C-11	Red	78	67.00 (67.07)	4.81 (4.88)	5.11 (5.21)
C-12	Brown	82	52.02 (52.32)	3.35 (3.55)	9.05 (9.39)

Table 3.5 Physical properties and analytical data of complex (C-13 to C-17)

Compounds	Color	Yield (%)	Elemental analysis data Found (Calculated)		
			C %	**H %**	**N %**
C-13	Red	60	64.88 (64.98)	4.47 (4.77)	4.64 (4.74)
C-14	Dark brown	64	64.50 (64.88)	4.75 (4.76)	4.52 (4.73)
C-15	Brown	68	64.31 (64.43)	4.75 (4.90)	4.56 (4.70)
C-16	Green	68	64.60 (64.57)	4.61 (4.74)	4.52 (4.71)
C-17	Brown	78	64.18 (64.04)	4.43 (4.70)	4.70 (4.67)

Table 3.6 Physical properties and analytical data of complex (C-18 to C-22).

Compounds	**Color**	**Yield (%)**	**Elemental analysis data** **Found** **(Calculated)**		
			C %	**H %**	**N %**
C-18	Light green	68	70.62 (70.47)	4.24 (4.17)	4.66 (4.83)
C-19	Light brown	74	70.12 (70.36)	4.30 (4.17)	4.85 (4.83)
C-20	Dark blue	80	54.54 (54.50)	3.82 (3.77)	3.68 (3.74)
C-21	Brown	78	70.00 (70.01)	4.11 (4.15)	4.71 (4.80)
C-22	Green	82	69.58 (69.44)	4.00 (4.11)	4.37 (4.46)

Table 3.7 Physical properties and analytical data of complex (C-23 to C-27)

Compounds	**Color**	**Yield (%)**	**Elemental analysis data** **Found** **(Calculated)**		
			C %	**H %**	**N %**
C-23	Light yellow	65	54.62 (54.32)	3.34 (3.62)	6.64 (6.34)
C-24	Dark purple	84	54.92 (54.21)	3.35 (3.64)	6.45 (6.32)
C-25	Brown	64	64.30 (64.35)	3.67 (3.78)	7.50 (7.50)
C-26	Maroon	78	64.20 (64.40)	3.55 (3.78)	7.40 (7.51)
C-27	Brown	82	63.68 (63.57)	3.64 (3.73)	7.37 (7.41)

3.3.2 FTIR spectra

The synthesized ligand (L-1) and complexes (C-1 to C-5) molecules were examined by the FTIR analysis and results are represented (Fig. 3.3). In addition, the individual FTIR spectra of ligand (L-1) as well as complex (C-1) have been presented in Fig. 3.1 and 3.2, respectively. FTIR spectra of the ligand (L-1) shows intense peak at 1577 cm^{-1} corresponds to an azomethine (CH=N) group and O-H peak appears at 3332 cm^{-1}. The peak in the region 1269 cm^{-1} is indicative of phenolic (-C-OH) ν(C-O) stretching. Thus, the ligand is bidentate in nature with N, O coordination sites. In the FTIR spectra of complexes, the appearance of a band for ν(CH=N) in the range of 1588-1606 cm^{-1} which indicates a shift to the higher frequencies by 10-19 cm^{-1} compared to ligand (L-1) indicating the complexion of ligand with metal atom through nitrogen atom. Phenolic ν(C-O) stretching in complexes is shifted by 10-15 cm^{-1} towards lower wave numbers compared to ligand indicating coordination of the phenolic oxygen of ligand to the metal ion (Kurup et al. 2011). The new bands in the range 580-672 cm^{-1} in complexes, tentatively assign coordination with oxygen atom. The bands which appear around 400-500 cm^{-1} in the spectra of complexes may be assigned to the coordination of metal with nitrogen atom.

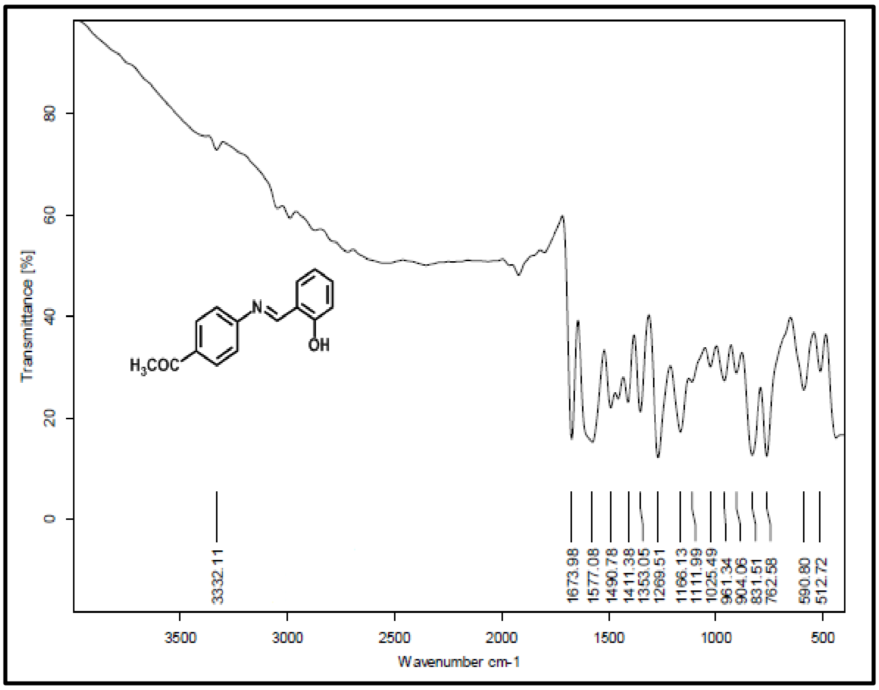


Figure 3.1 FTIR spectrum of ligand (L-1)

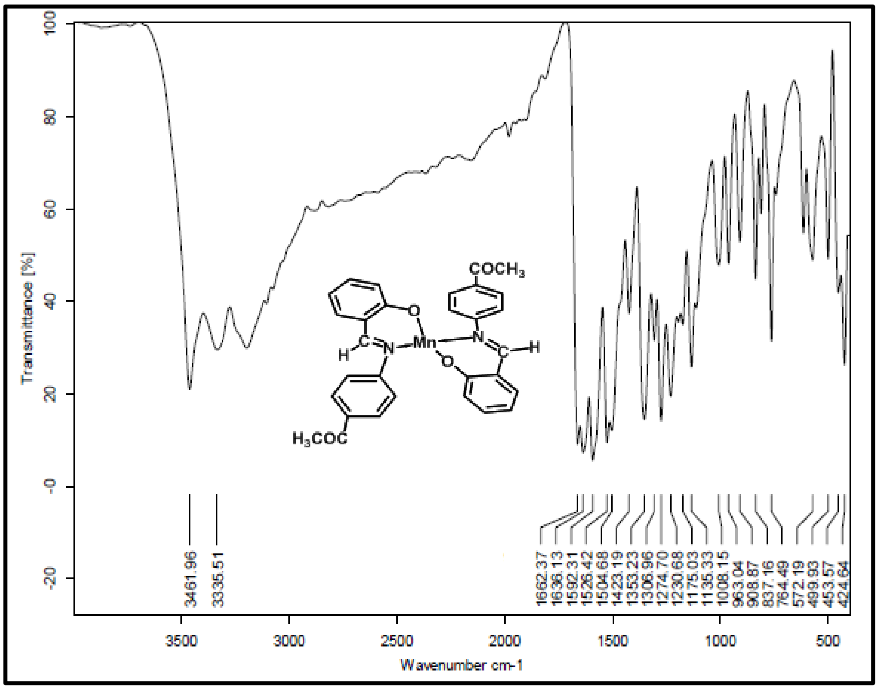


Figure 3.2 FTIR spectrum of complex (C-1)

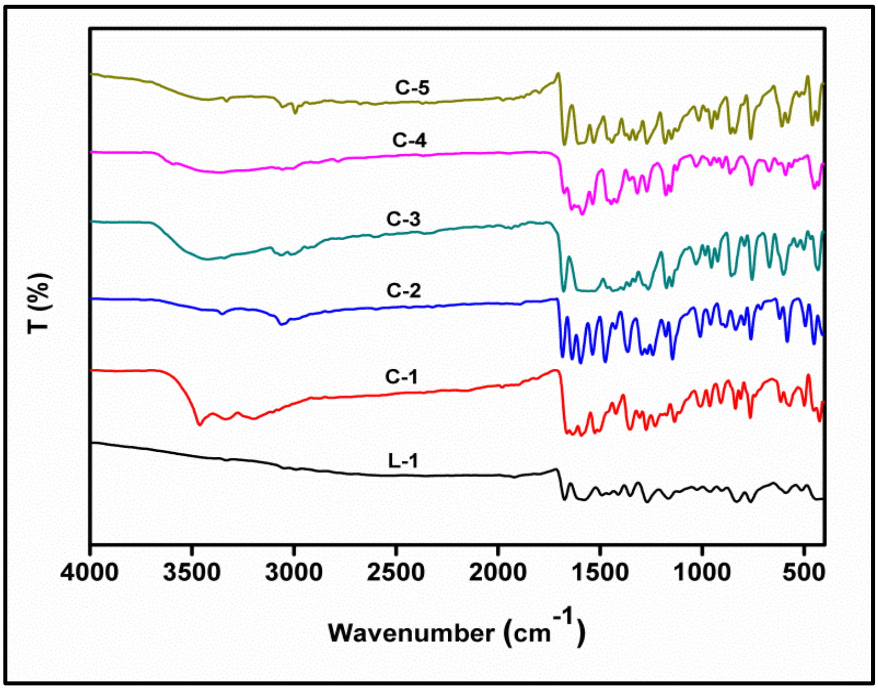


Figure 3.3 FTIR spectra of ligand (L-1) and complexes (C-1 to C-5)

FTIR spectra of ligand (L-2) and the complexes (C-6 to C-10) are shown in the Figure 3.6. Additionally, the individual FTIR spectra of ligand (L-2) as well as complex (C-6) have been presented in Fig. 3.4 and 3.5, respectively. The strong band in ligand at 1604 cm^{-1} assignable to azomethine ν(C=N) group. The peak in the region 1278 cm^{-1} is indicative of phenolic ν(C-O) stretching. Moreover, for complexes, the appearance of a band for ν(CH=N) in the range of 1607-1627 cm^{-1} indicates a shifting to the higher frequencies compared to ligand (L-2) indicating the complexion of ligand with metal atom through nitrogen atom has been formed. Phenolic ν(C-O) stretching in complexes is shifted from 1278 cm^{-1} to 1202-1185 cm^{-1} towards lower wave numbers indicating coordination of the phenolic oxygen of ligand to the metal ion.

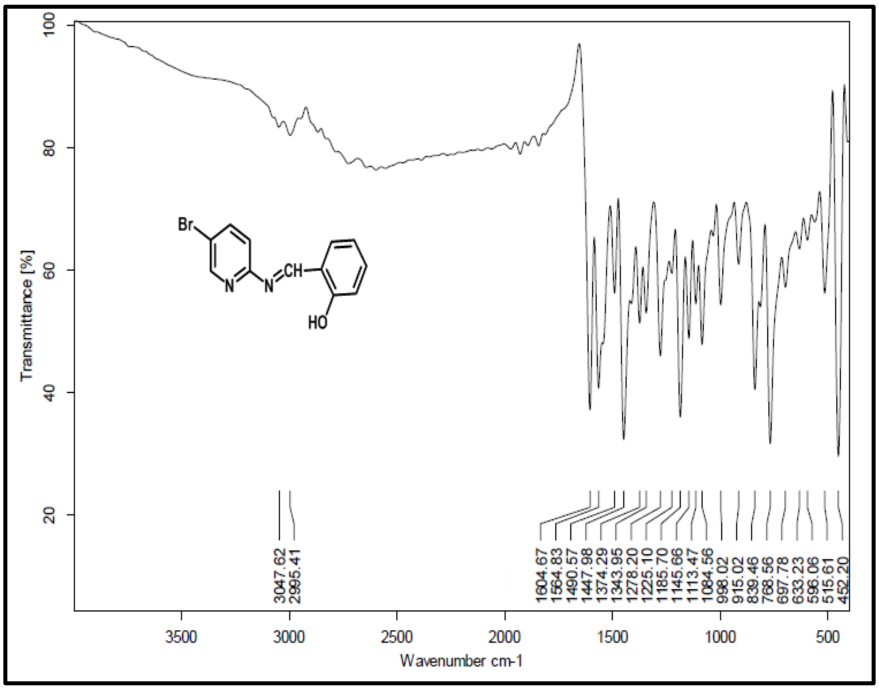


Figure 3.4 FTIR spectrum of ligand (L-2)

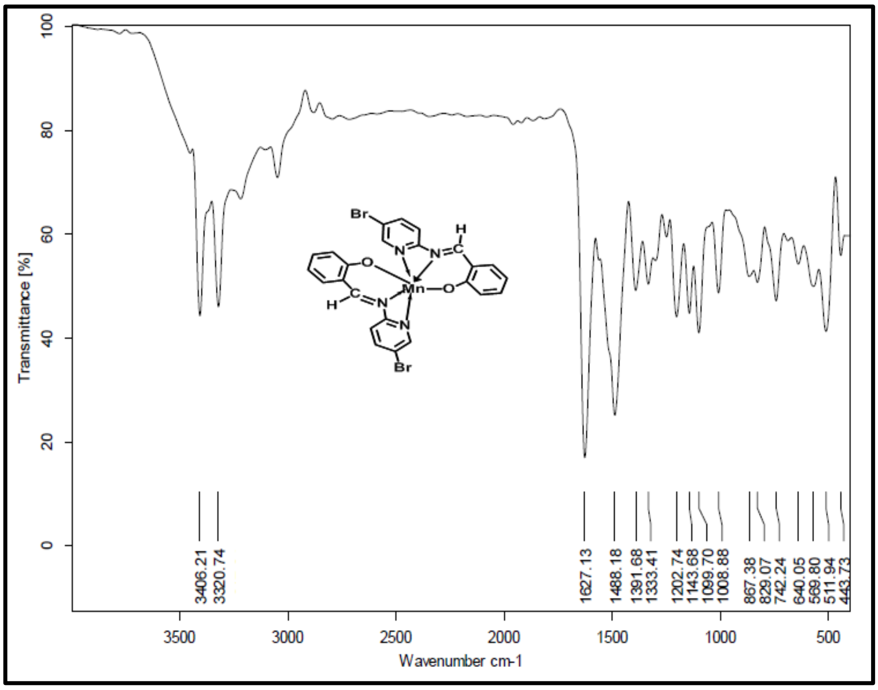


Figure 3.5 FTIR spectrum of complex (C-6)

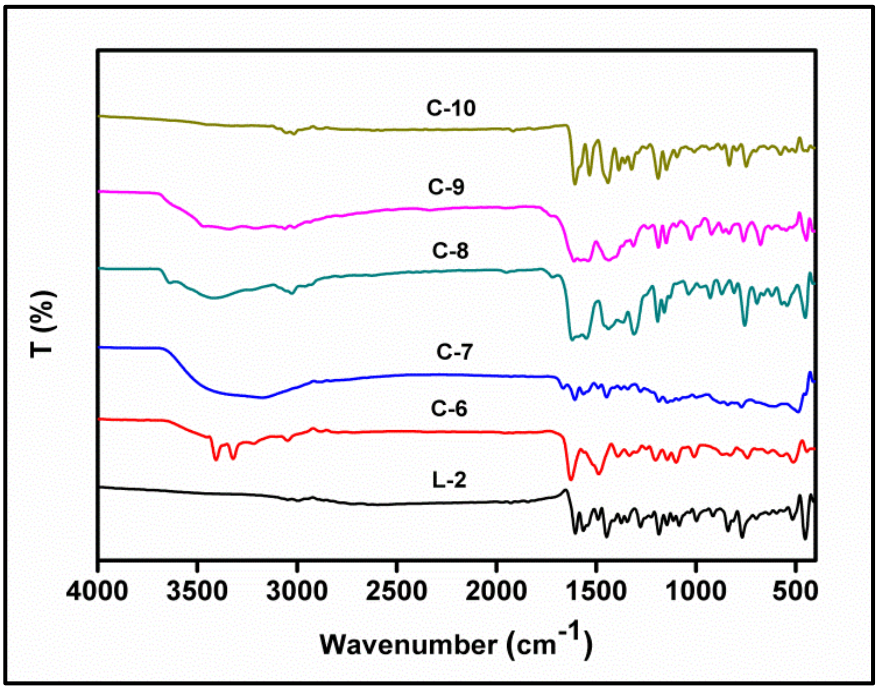


Figure 3.6 FTIR spectra of ligand (L-2) and complexes (C-6 to C-10)

FTIR spectra of ligand (L-3) and the complexes (C-11 & C-12) are shown in the Figure 3.7 to 3.9. The strong band in ligand at 1606.80 cm^{-1} assignable to azomethine ν(C=N) group and O-H peak appears at 3448.98 cm^{-1}. The peak in the region 1200 cm^{-1} is indicative of phenolic ν(C-O) stretching. Moreover, for complexes, the appearance of a band for ν(CH=N) in the range of 1604-1605 cm^{-1} indicates a shifting to the lower wave numbers compared to ligand (L-3) indicating the complexion of ligand with metal atom through nitrogen atom has been formed. Phenolic ν(C-O) stretching in complexes is shifted from 1200 cm^{-1} to 1193-1188 cm^{-1} towards lower wave numbers indicating coordination of the phenolic oxygen of ligand to the metal ion.

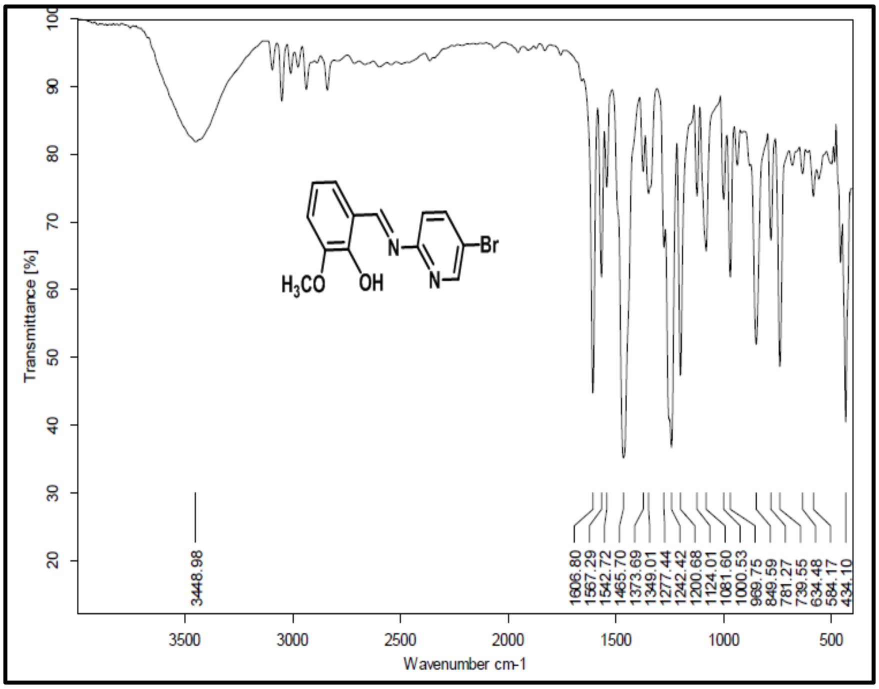


Figure 3.7 FTIR spectrum of ligand (L-3)

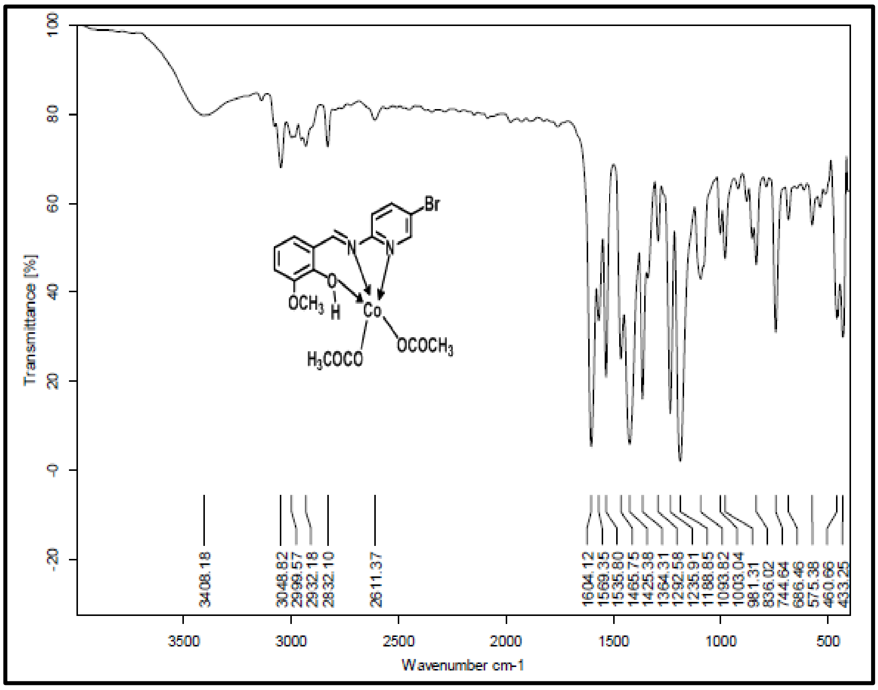


Figure 3.8 FTIR spectrum of complex (C-11)

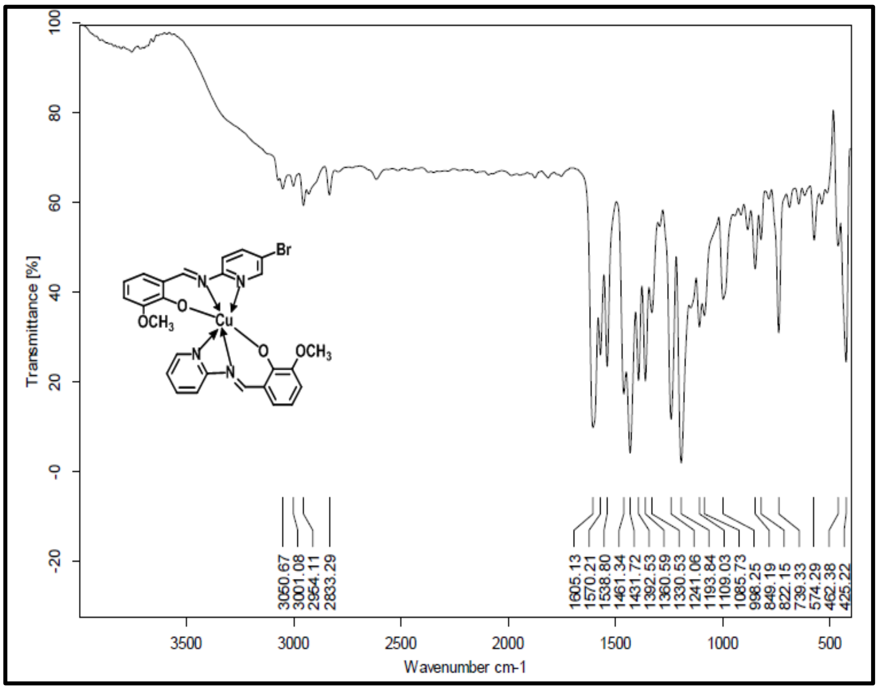


Figure 3.9 FTIR spectrum of complex (C-12)

The synthesized ligand (L-4) and complexes (C-13 to C-17) molecules were examined by the FTIR analysis and results are represented (Fig. 3.12). In addition, the individual FTIR spectra of ligand (L-4) as well as complex (C-14) have been presented in Fig. 3.10 and 3.11, respectively. FTIR spectra of the ligand (L-4) shows intense peak at 1588.62 cm^{-1} corresponding to an azomethine (CH=N) group and O-H peak appears at 3692 cm^{-1}. In the FTIR spectra of complexes, the appearance of a band for ν(CH=N) in the range of 1591.85-1593.46 cm^{-1} which indicates a shifting to the higher wave number compared to ligand indicating the complexion of the ligand with metal atom through a nitrogen atom. The peak in the region 1261.90 cm^{-1} is indicative of phenolic ν(C-O) stretching. Phenolic ν(C-O) stretching in complexes is shifted from 1261.90 cm^{-1} to 1235-1263.09 cm^{-1} indicating coordination of the metal ion to the phenolic oxygen of ligand. The new bands in the range 580-672 cm^{-1} in complexes, tentatively assign coordination of metal with oxygen atom ν(M-O) (Sravanthi et al. 2016). The bands which appear around 400-500 cm^{-1} in the spectra of complexes may be assigned to the coordination of metal with a nitrogen atom (More et al. 2017).

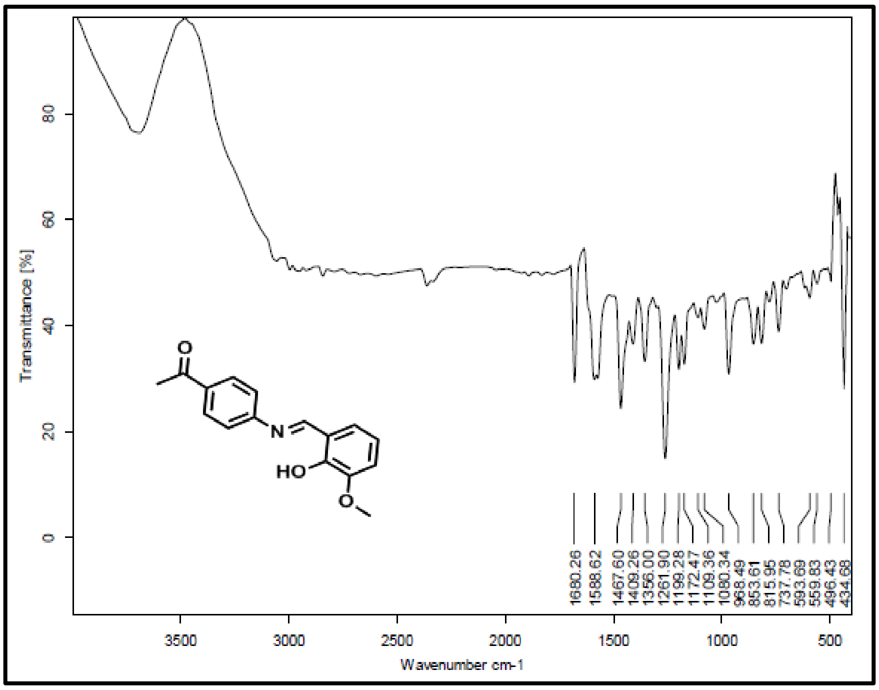


Figure 3.10 FTIR spectrum of ligand (L-4)

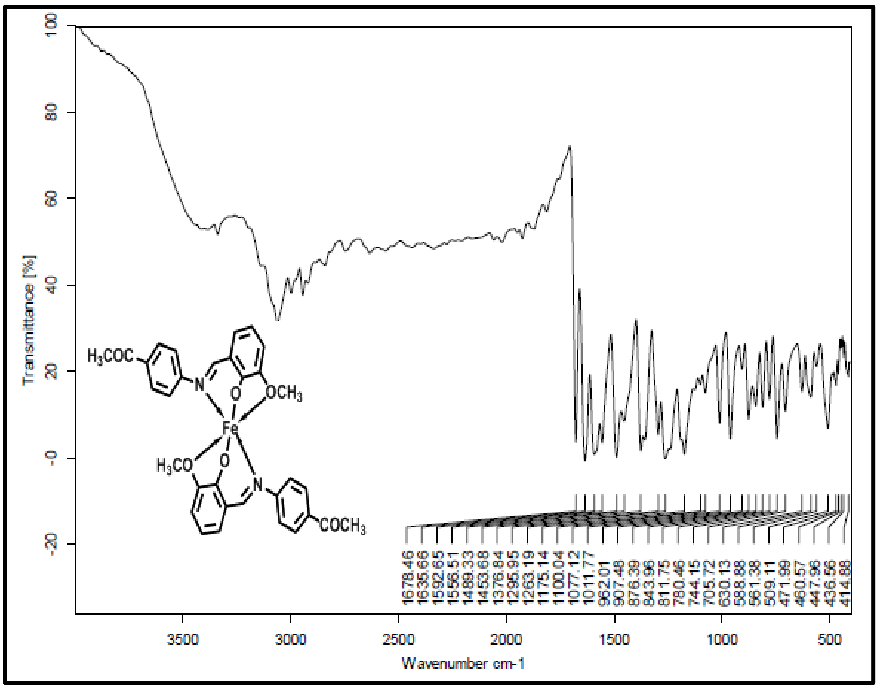


Figure 3.11 FTIR spectrum of complex (C-14)

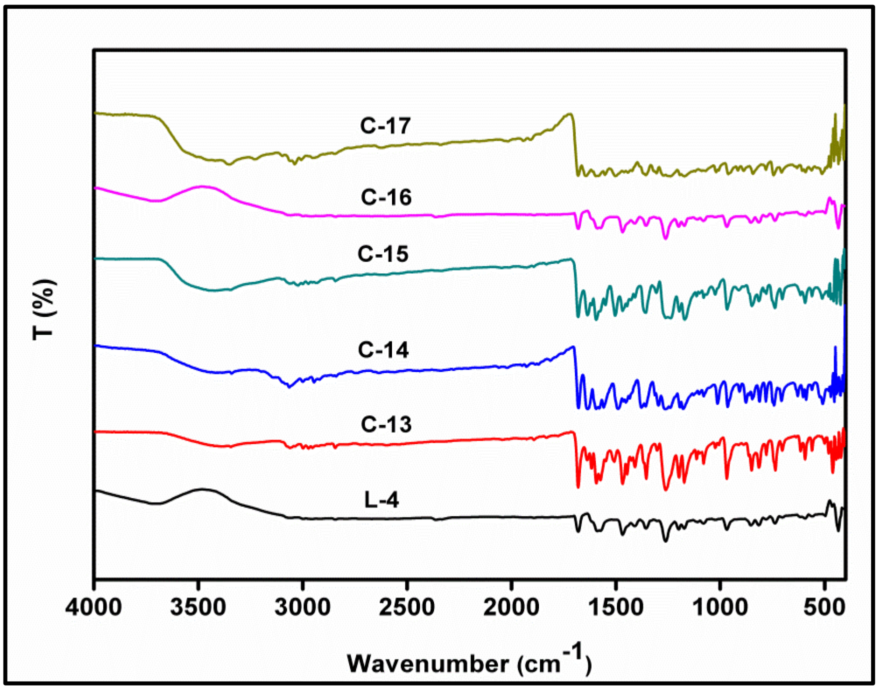


Figure 3.12 FTIR spectra of ligand (L-4) and complexes (C-13 to C-17)

FTIR spectra of ligand (L-5) and the complexes (C-18 to C-22) are shown in the Figure 3.15. In addition, the individual FTIR spectra of ligand (L-5) as well as complex (C-19) have been presented in Fig. 3.13 and 3.14, respectively. The strong band in ligand at 1630.01 cm^{-1} assignable to azomethine ν(C=N) group and O-H peak appears at 3448.98 cm^{-1}. The peak in the region 1240.32 cm^{-1} is indicative of phenolic ν(C-O) stretching. Moreover, for complexes, the appearance of a band for ν(CH=N) in the range of 1597-1628 cm^{-1} indicates a shifting to the lower wave numbers compared to ligand (L-5) indicating the complexion of ligand with metal atom through nitrogen atom has been formed. Phenolic ν(C-O) stretching in complexes is shifted from 1240.32 cm^{-1} to 1248-1359 cm^{-1} towards higher wave numbers indicating coordination of the phenolic oxygen of ligand to the metal ion.

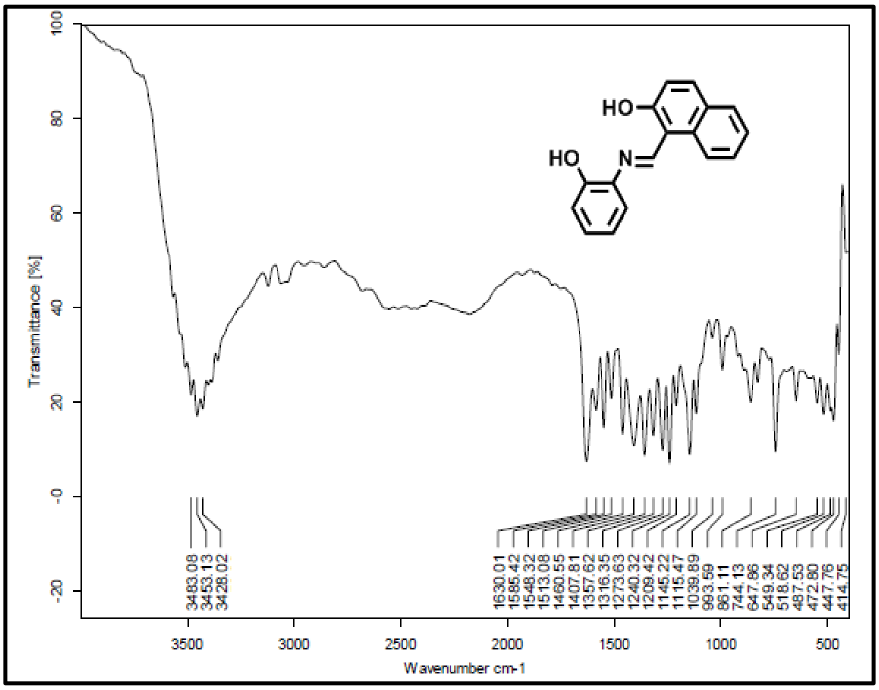


Figure 3.13 FTIR spectrum of ligand (L-5)

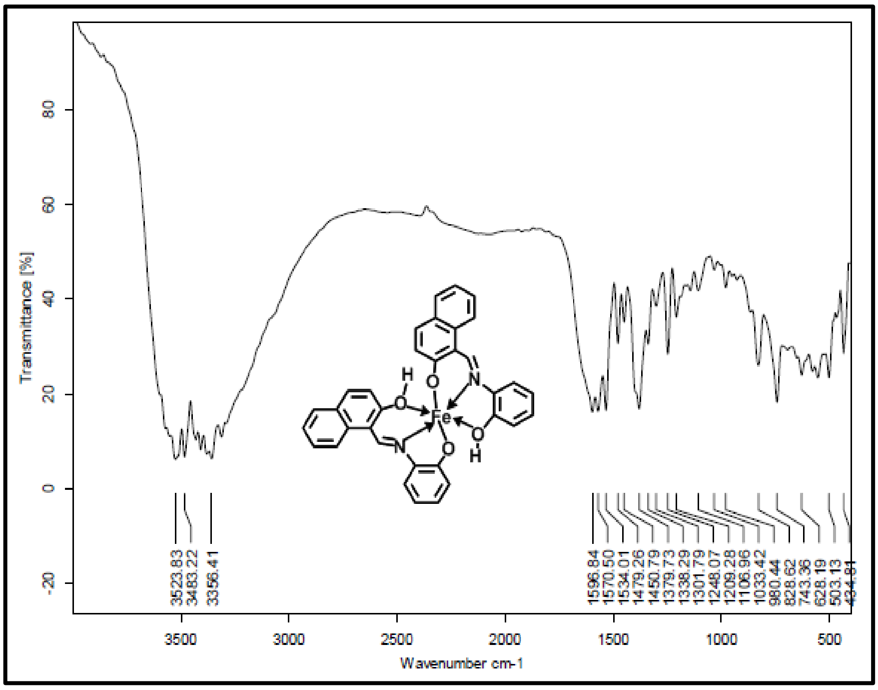


Figure 3.14 FTIR spectrum of complex (C-19)

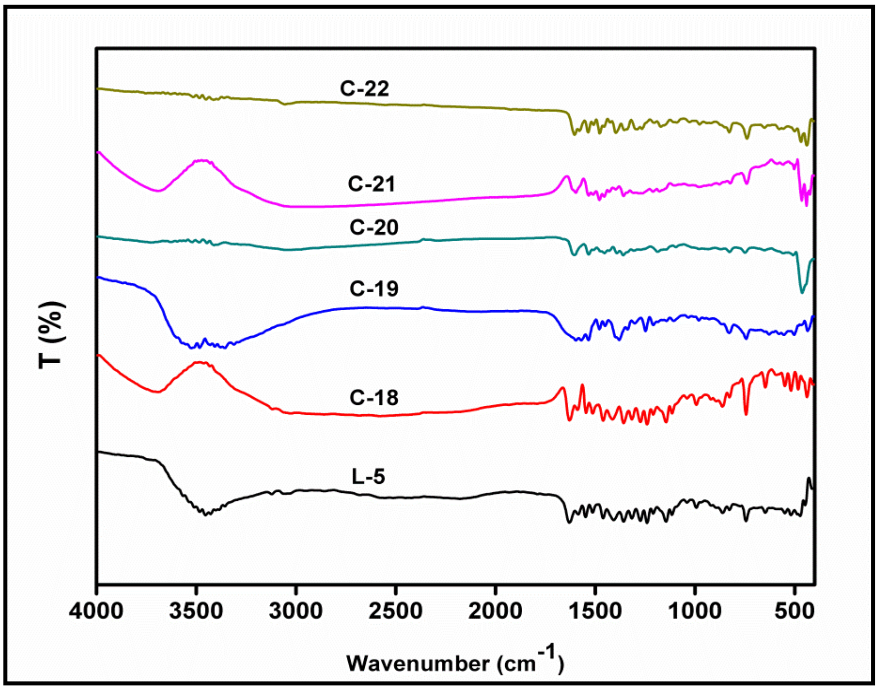


Figure 3.15 FTIR spectra of ligand (L-5) and complexes (C-18 to C-22)

FTIR spectra of ligand (L-6) and the complexes (C-23 to C-27) are shown in the Figure 3.18. In addition, the individual FTIR spectra of ligand (L-6) as well as complex (C-24) have been presented in Fig. 3.16 and 3.17, respectively. The strong band in ligand at 1615 cm^{-1} assignable to azomethine ν(C=N) group. The peak in the region 1275 cm^{-1} is indicative of phenolic ν(C-O) stretching. In the FTIR spectra of complexes, the appearance of a band for ν(CH=N) in the range of 1608-1599 cm^{-1} which indicates a shifting to the lower frequencies compared to ligand (L-6) indicating the complexion of ligand with metal atom through nitrogen atom (Garga et al. 2000). Phenolic ν(C-O) stretching in complexes is shifted from 1275 cm^{-1} to 1251-1245 cm^{-1} towards lower wave numbers indicating coordination of the phenolic oxygen of ligand to the metal ion. The new bands in the range 503-541 cm^{-1} in complexes, can be tentatively assigned to coordination of metal with oxygen atom. The coordination through azomethine N is further supported by the appearance of band at 420-455 cm^{-1} in metal complexes can be assigned to νM–N (Chandra and Kumar 2005).

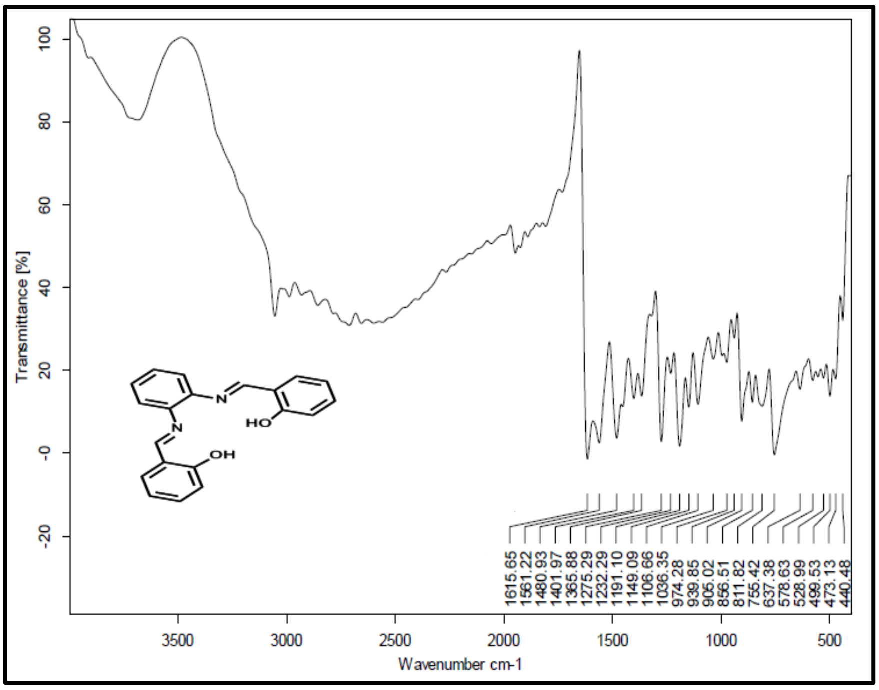


Figure 3.16 FTIR spectrum of ligand (L-6)

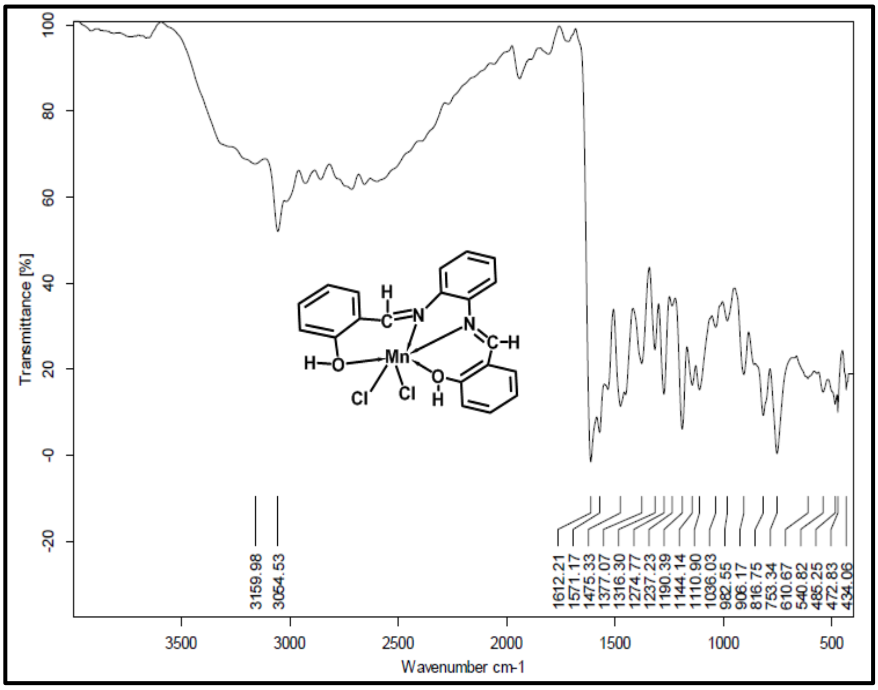


Figure 3.17 FTIR spectrum of complex (C-24)

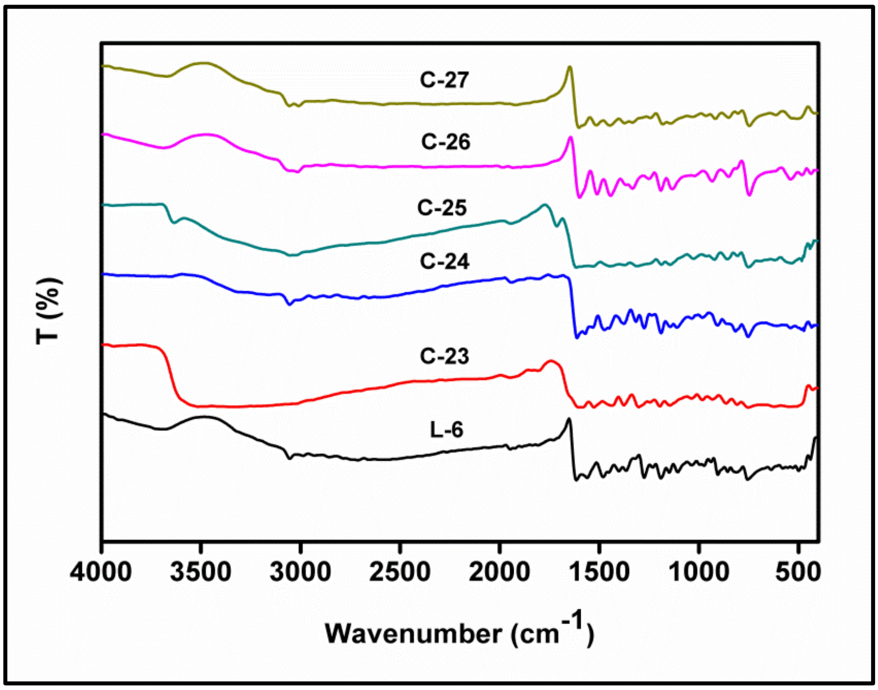


Figure 3.18 FTIR spectra of ligand (L-6) and complexes (C-23 to C-27)

3.3.3 UV-Vis spectra

UV-Vis spectra of the complexes along with their corresponding ligands were recorded as a confirmatory measure to imply the complex formation (Fig. 3.19 to 3.24). The UV-Vis spectra of synthesized ligand (L-1) and complexes (C-1 to C-5) were recorded in ethanol solvent (Fig. 3.19). Quartz cells with a 1 cm pathlength were employed in the 200-700 nm spectral range. In ligand (L-1), the peak in the region 218 nm is assigned to the π - π^* transitions of aromatic rings. The peak at 310-350 nm involves n - π^* transition of the CH=N group (Raman et al. 2007). Complexes (C-1 to C-5) show bands from 210 nm to 563 nm, which clearly indicates that the formation of the complex.

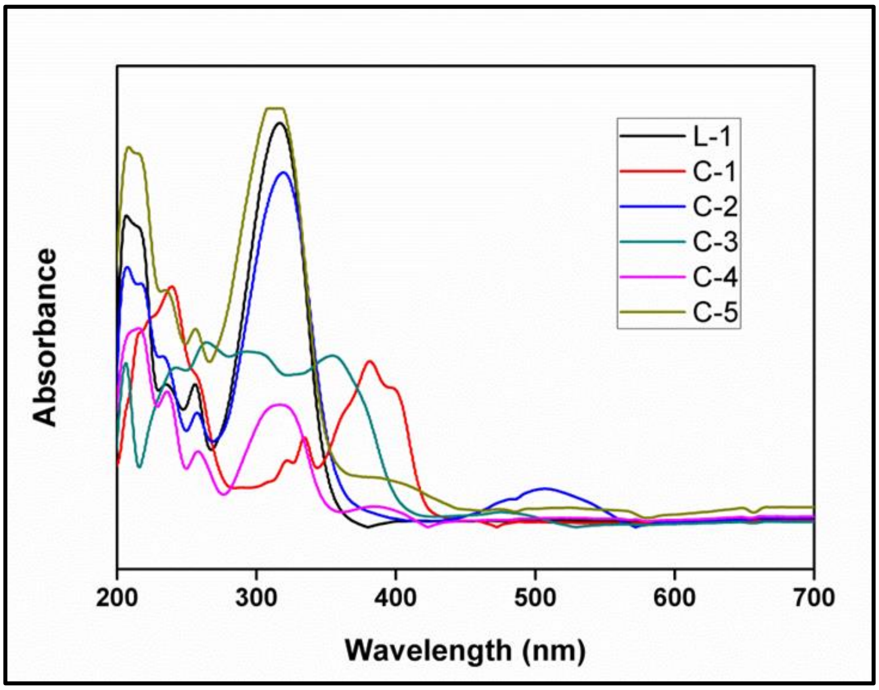


Figure 3.19 UV-Vis spectra of ligand (L-1) and complexes (C-1 to C-5)

UV-Vis spectra of the complexes (C-6 to C-10) along with ligand (L-2) were recorded as a confirmatory measure to imply the complex formation (Fig. 3.20). In all the spectra recorded, we observed the change in the absorption band from the ligand to the complex which clearly indicates that the formation of the complex. Moreover, the absorption bands which we observed in the free ligand spectrum have been shifted to lower energy region in the spectra of complexes because of the ligand coordination with a metal ion. These transitions are due to intra-ligand charge transfer transitions (ILCT) and ligand to metal charge transfer transitions (LMCT) (Kumar and Bhat 2017).

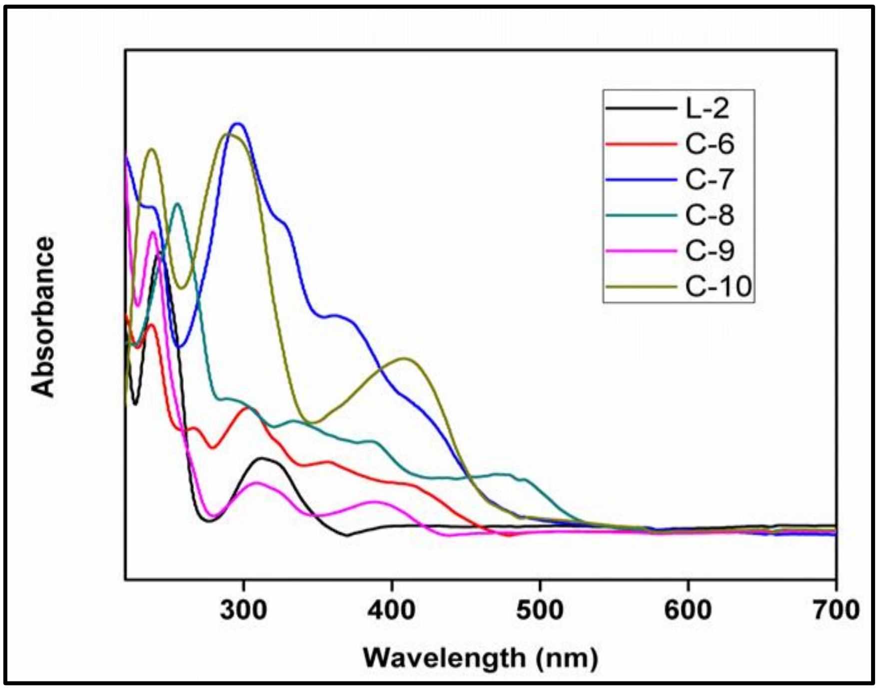


Figure 3.20 UV-Vis spectra of ligand (L-2) and complexes (C-6 to C-10)

Ligand (L-3) shows peaks at 261 nm and 327 nm which are due to π - π*, n - π* transitions, respectively (Abd El-Halim et al. 2017). In case of complexes, peaks at 281 nm, 310 nm, 403 nm (C-11) and 300 nm, 450 nm (C-12) were observed. In the spectra recorded, we observed the change in the absorption band from the ligand to the complex which clearly indicates that the formation of the complex (Fig. 3.21).

The peak in the region 222 nm in ligand (L-4) is assigned to the π - π* transitions of aromatic rings. The peak at 318 nm involves n - π* transition of the CH=N group. The complexes (C-13 to C-17) show bands from 220-500 nm which clearly indicates that the formation of the complex (Fig. 3.22).

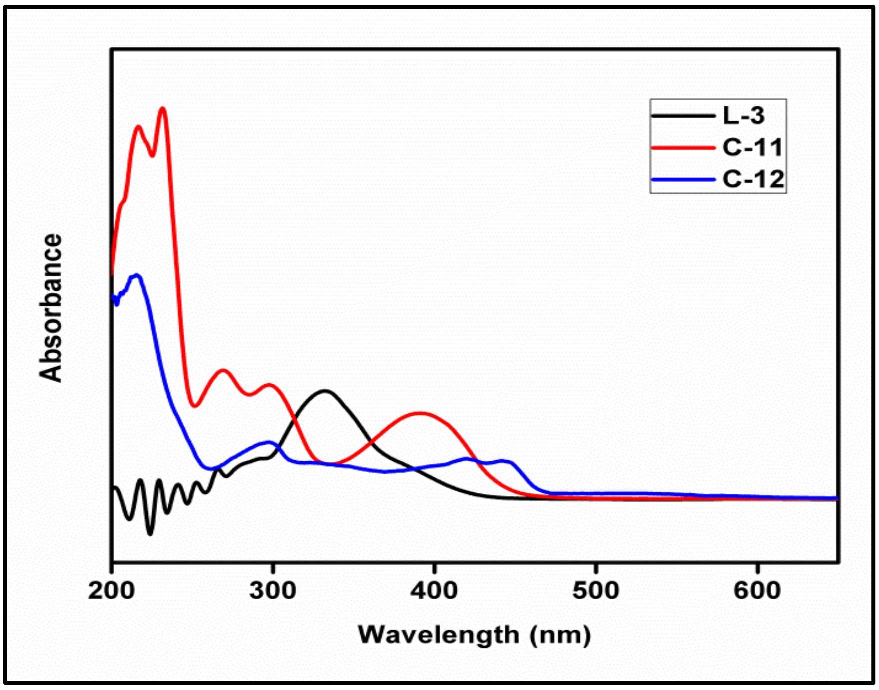


Figure 3.21 UV-Vis spectra of ligand (L-3) and complexes (C-11 & C-12)

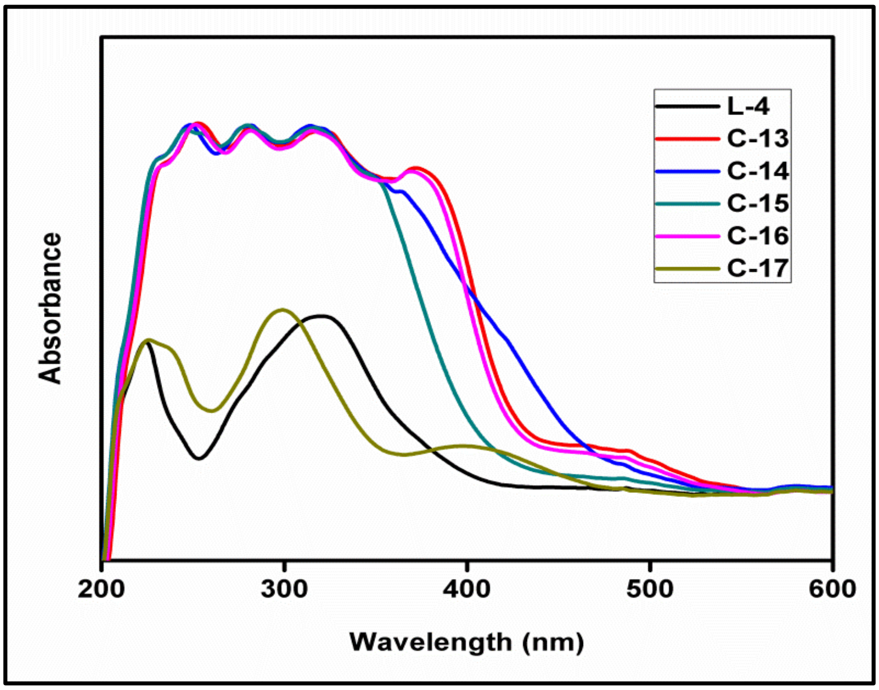


Figure 3.22 UV-Vis spectra of ligand (L-4) and complexes (C-13 to C-17)

UV-Vis spectra of the complexes (C-18 to C-22) along with ligand (L-5) were recorded as a confirmatory measure to imply the complex formation. In the spectra recorded (Fig. 3.23), we observed the change in the absorption band from the ligand to the complex which noticeably indicates that the formation of the complex.

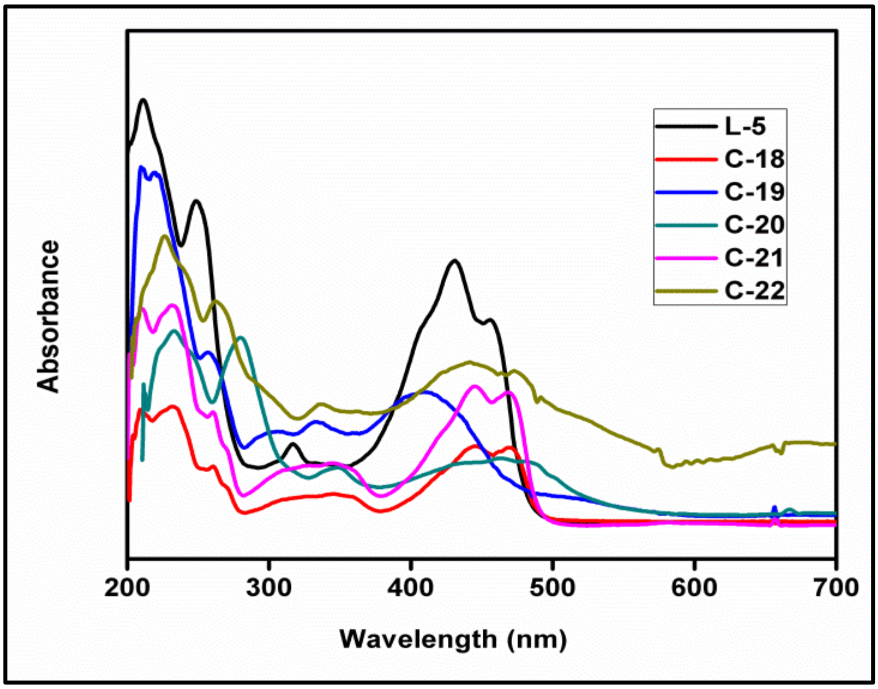


Figure 3.23 UV-Vis spectra of ligand (L-5) and complexes (C-18 to C-22)

The prepared complexes (C-23 to C-27) were confirmed by using UV-Vis absorption measurements in ethanol solvent. In the UV-Vis absorption spectrum of ligand (L-6), the molecule shows maximum wavelength values at 212 nm and 257 nm which are attributed to π - π^* transition. Similarly, 325 nm and 387 nm can be assigned to imino n - π^* transitions in ligand. Compared to the free ligand, the imine n - π^* transitions of the complexes were shifted to some extent, possibly the coordination of nitrogen atom of the ligand imine group to the metal ion (Temel and Şekerci 2001). Moreover, quite higher absorption intensity band at 484 nm (20,661.2 cm^{-1}) for complex (C-25) was observed, which confirms the square planar geometry of C-25. Similarly, absorption at 470 nm (21,276.5 cm^{-1}) in complex (C-26) indicates the square planar geometry of C-26 (Rashad et al. 2014).

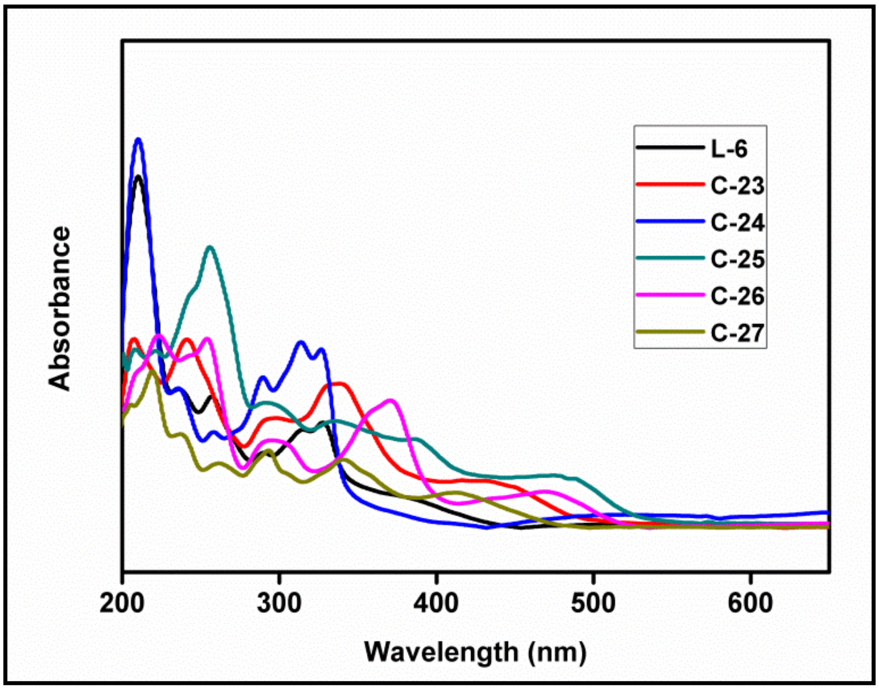


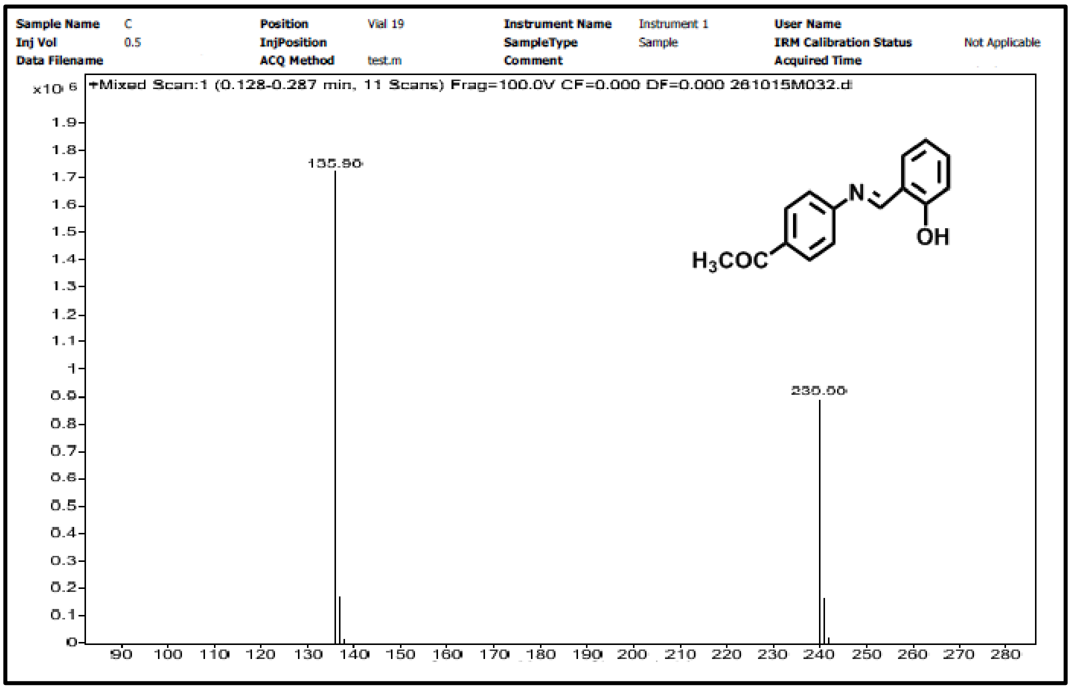
Figure 3.24 UV-Vis spectra of ligand (L-6) and complexes (C-23 to C-27)

3.3.4 Mass spectra

The electron impact mass spectra of the Schiff base ligand and metal complexes were recorded and investigated to confirm the molecular weight of the compounds. The important mass fragmentations of the ligands and complexes are shown in the spectra (Figs. 3.25 to 3.57). The expected molecular weight and the observed molecular weight of the ligands and complexes are given in the Table 3.8. From the table, it is confirmed that the observed molecular weight of the compounds is matches with expected molecular weight of the compounds.

Table 3.8 ESIMS data of ligands and complexes

Compound	Expected mass	Observed mass	Compound	Expected mass	Observed mass
L-1	239.00	239.09	**C-12**	594.00	594.55
L-2	277.12	277.00	**C-13**	591.13	592.00
L-3	306.00	306.10	**C-14**	592.13	592.52
L-4	269.11	269.09	**C-15**	380.01	380.10
L-5	263.09	263.00	**C-16**	594.13	594.24
L-6	316.12	317.10	**C-17**	599.12	599.60
C-1	531.11	531.00	**C-18**	579.11	579.61
C-2	567.08	568.10	**C-19**	580.11	580.44
C-3	535.11	535.90	**C-20**	374.00	374.70
C-4	534.11	535.85	**C-21**	582.11	582.00
C-5	539.10	539.00	**C-22**	587.10	587.90
C-6	606.90	607.00	**C-23**	441.00	441.05
C-7	607.90	607.55	**C-24**	441.99	442.25
C-8	452.95	452.50	**C-25**	373.04	373.00
C-9	391.93	391.80	**C-26**	372.04	373.10
C-10	612.89	612.30	**C-27**	377.04	378.00
C-11	482.96	482.85			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Comment
User Name
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Acquired Time

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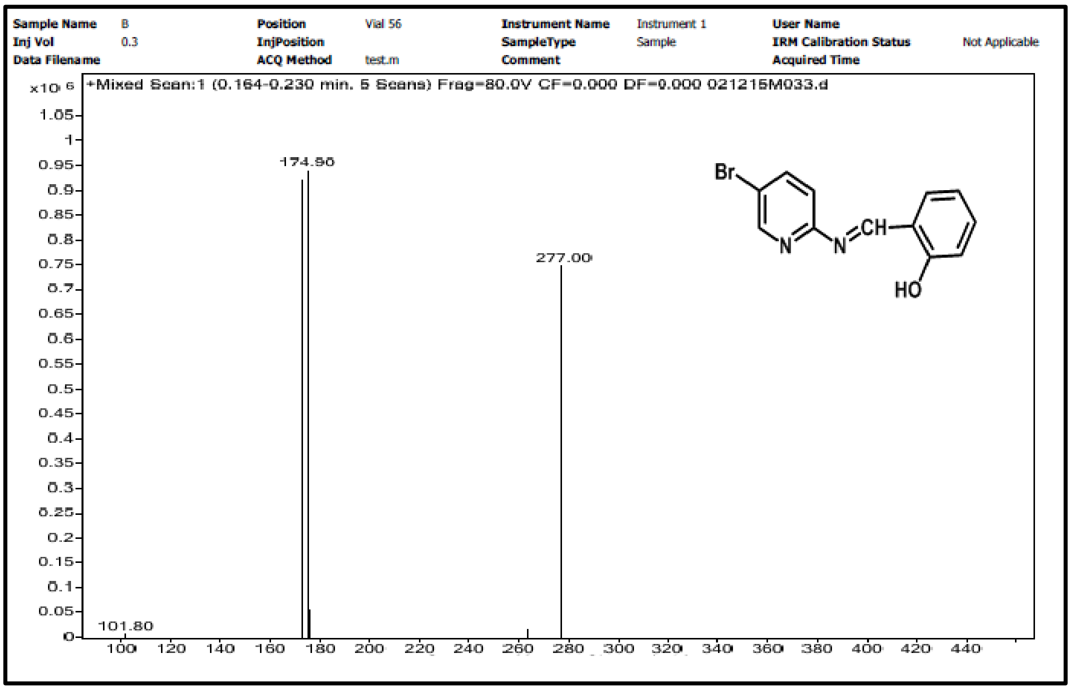
Figure 3.25 ESI mass spectrum of ligand (L-1)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Comment
User Name
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Acquired Time

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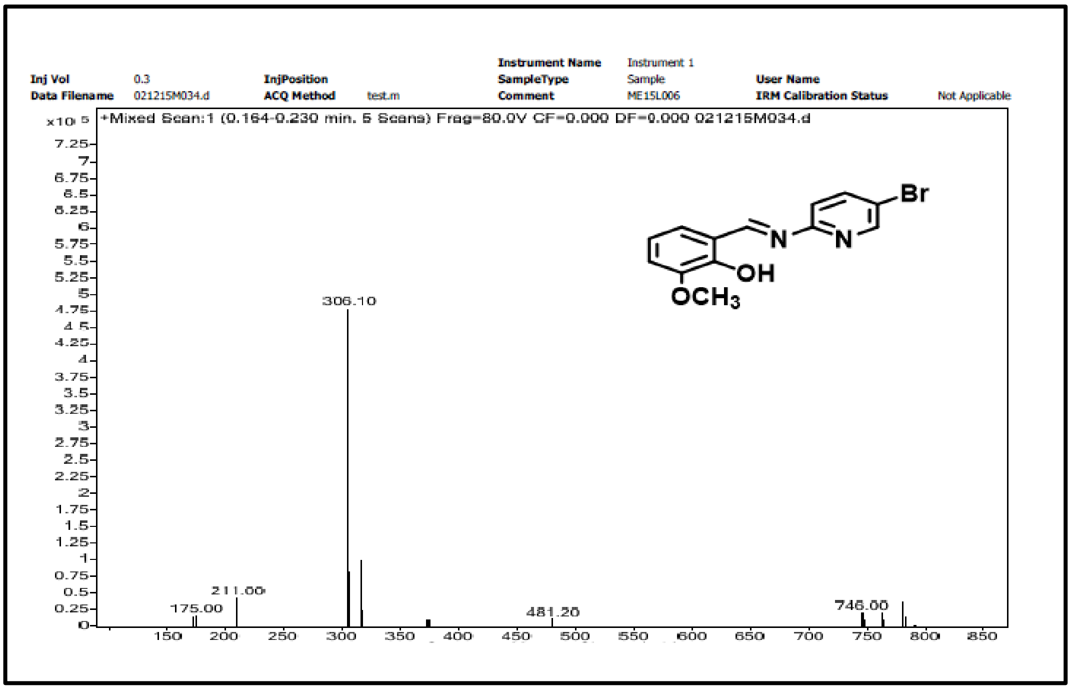
Figure 3.26 ESI mass spectrum of ligand (L-2)



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User Name
IRM Calibration Status Not Applicable

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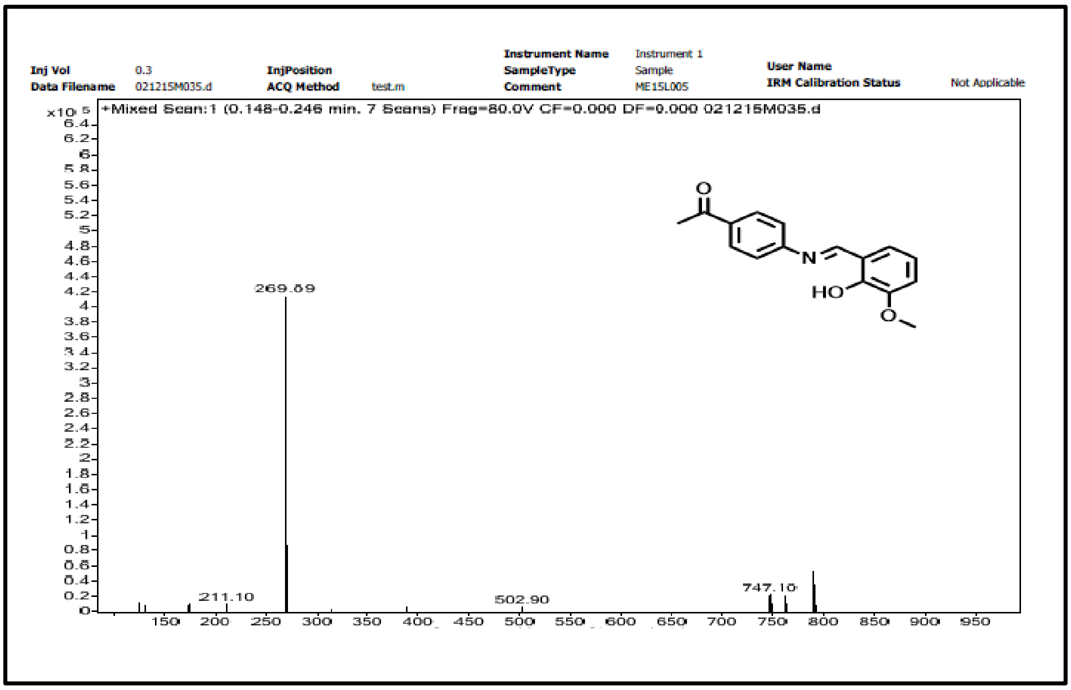
Figure 3.27 ESI mass spectrum of ligand (L-3)



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IRM Calibration Status Not Applicable

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Figure 3.28 ESI mass spectrum of ligand (L-4)

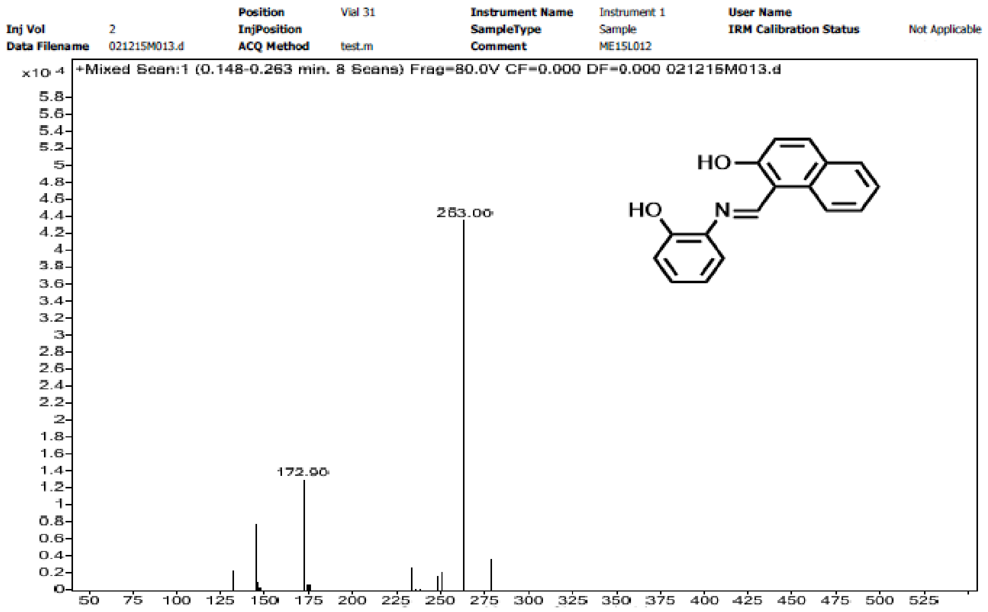


Figure 3.29 ESI mass spectrum of ligand (L-5)

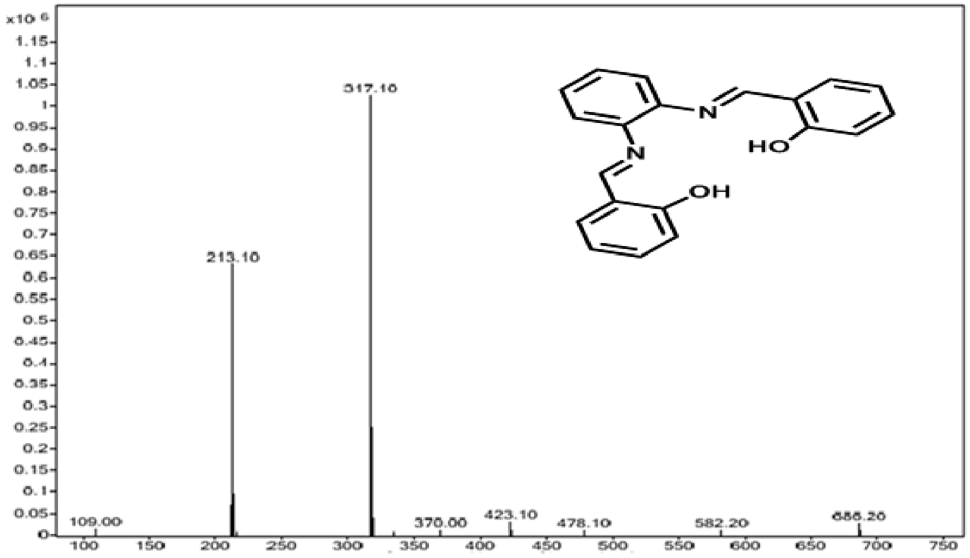


Figure 3.30 ESI mass spectrum of ligand (L-6)

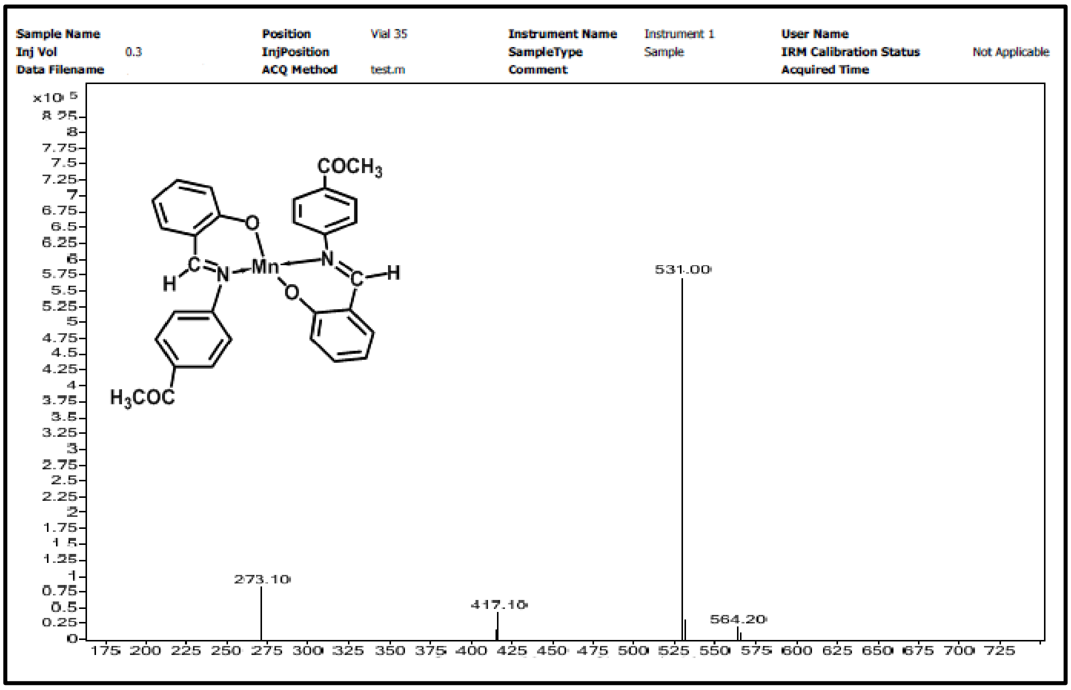


Figure 3.31 ESI mass spectrum of complex (C-1)

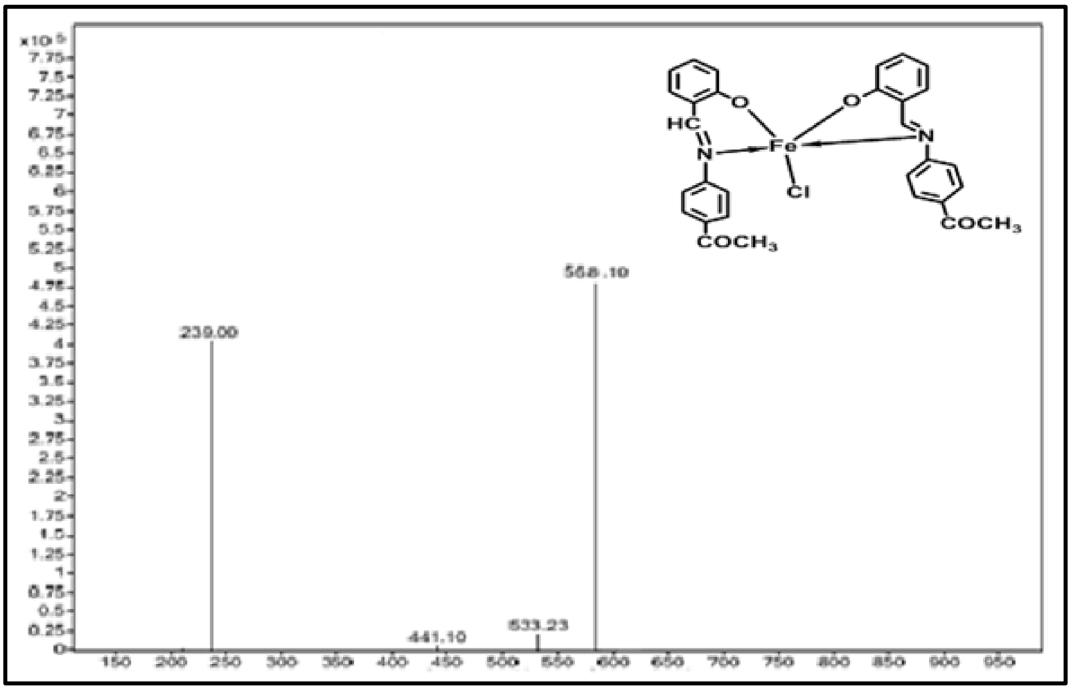


Figure 3.32 ESI mass spectrum of complex (C-2)

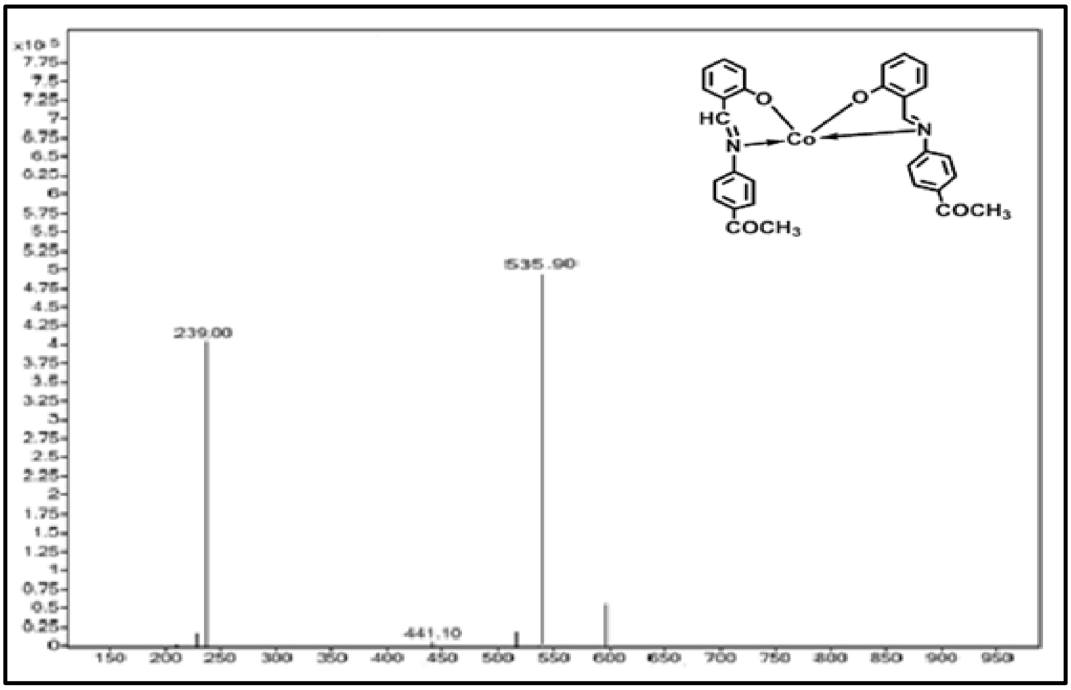


Figure 3.33 ESI mass spectrum of complex (C-3)

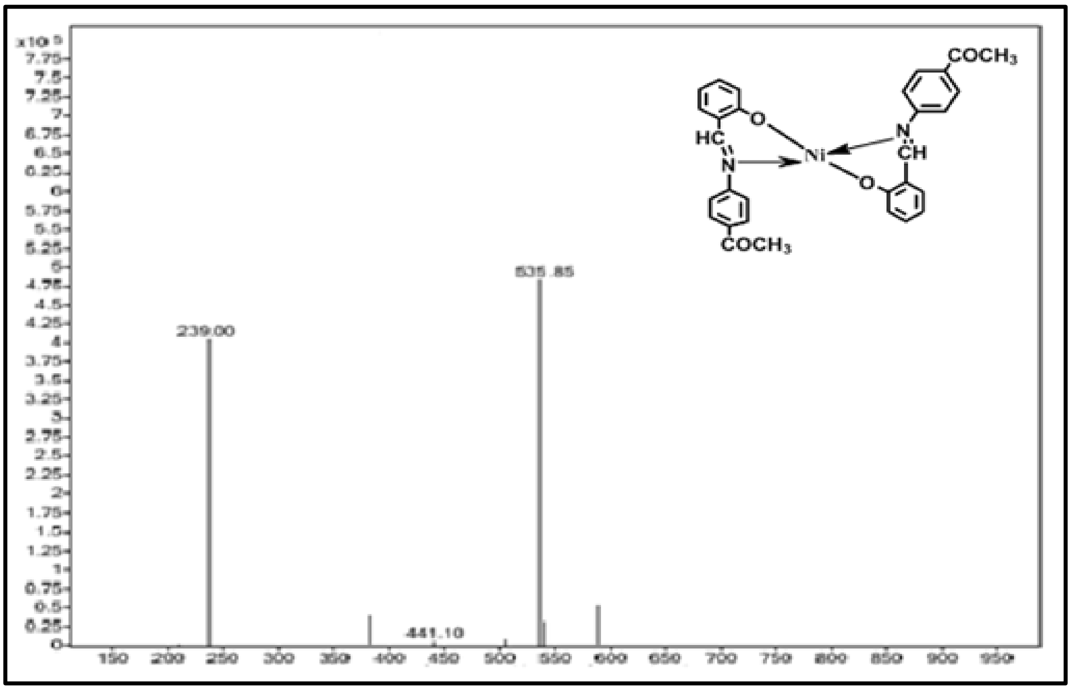


Figure 3.34 ESI mass spectrum of complex (C-4)

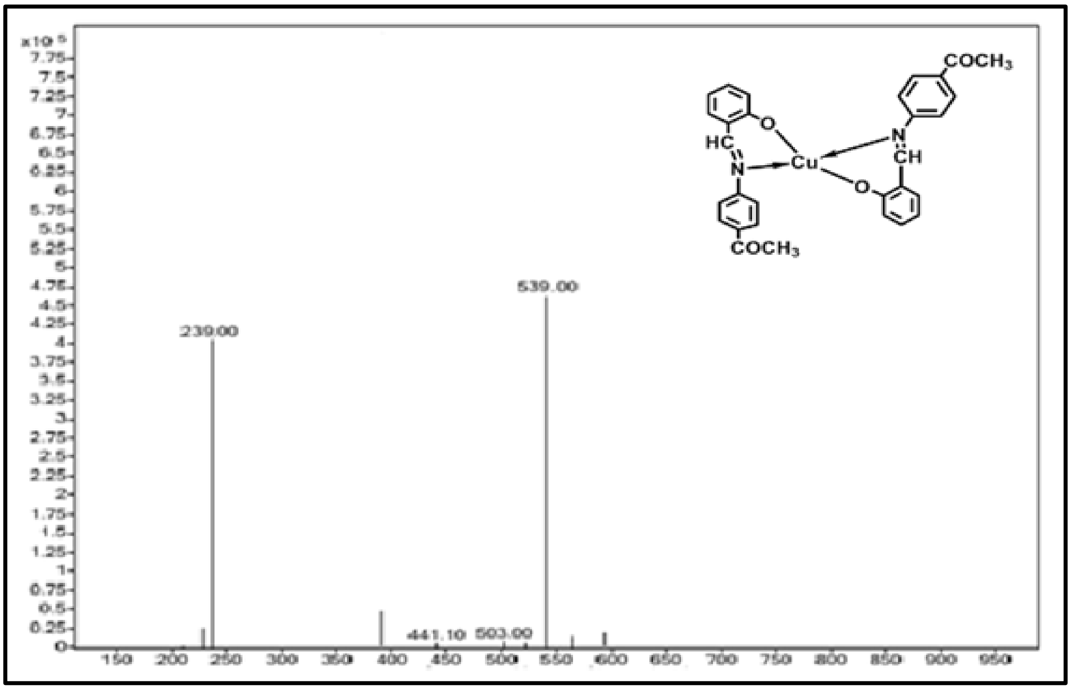
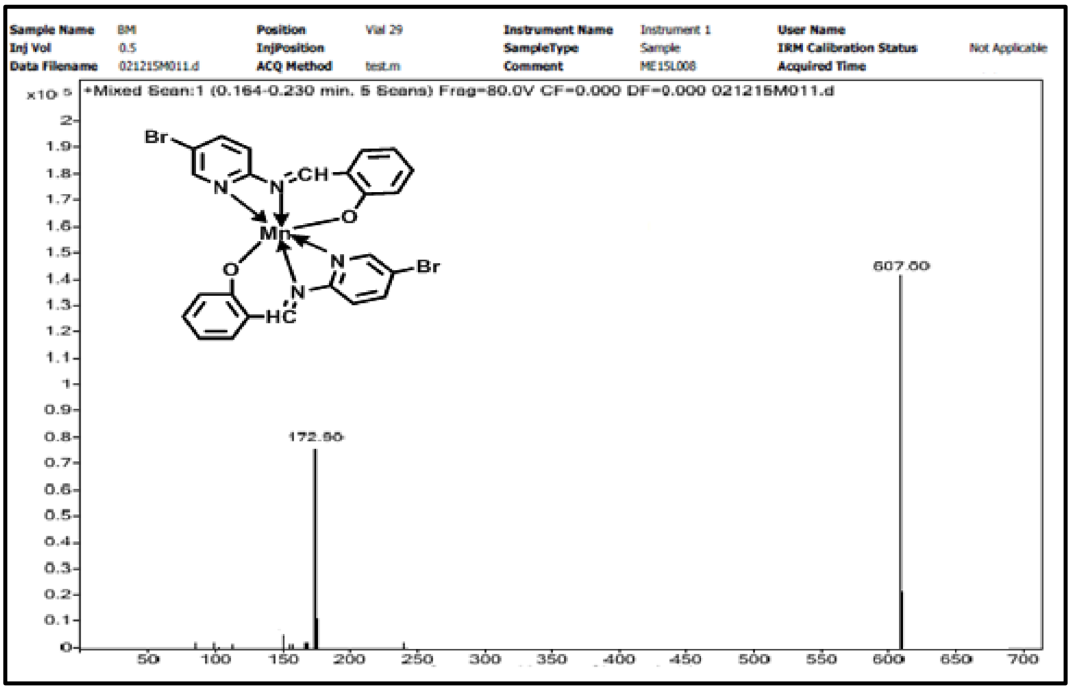


Figure 3.35 ESI mass spectrum of complex (C-5)



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Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Not Applicable
Data Filename	021215M011.d	**ACQ Method**	test.m	**Comment**	ME15L008	**Acquired Time**	

+Mixed Scan:1 (0.164-0.230 min. 5 Scans) Frag=80.0V CF=0.000 DF=0.000 021215M011.d

Figure 3.36 ESI mass spectrum of complex (C-6)

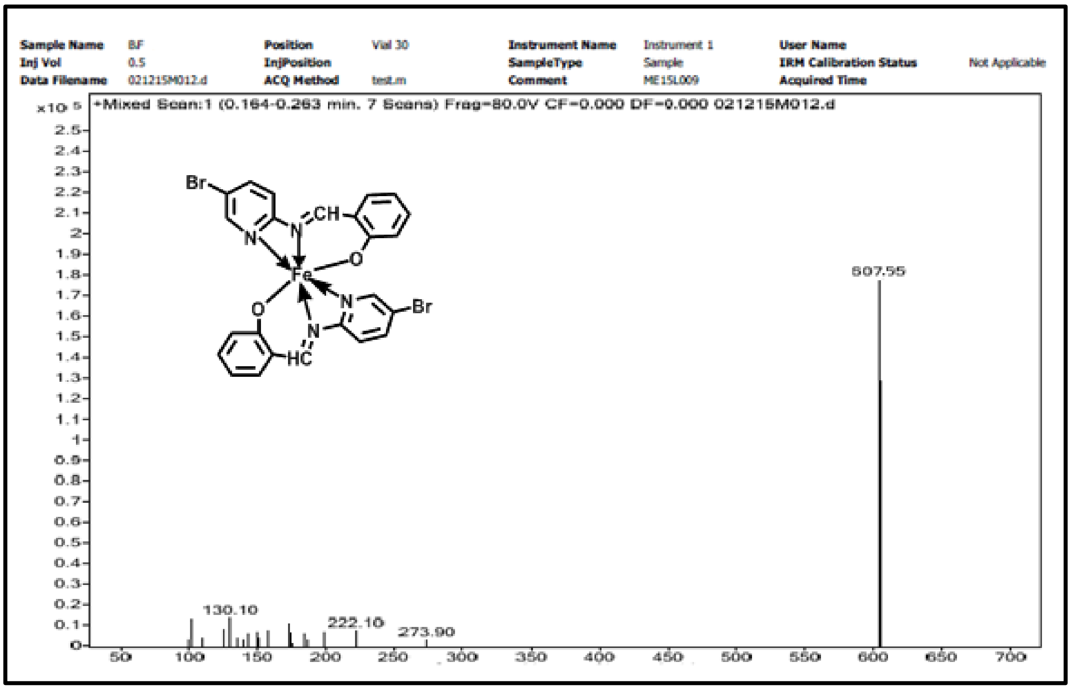

Sample Name BF
Inj Vol 0.5
Data Filename 021215M012.d
Position Vial 30
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment ME15L009
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.37 ESI mass spectrum of complex (C-7)

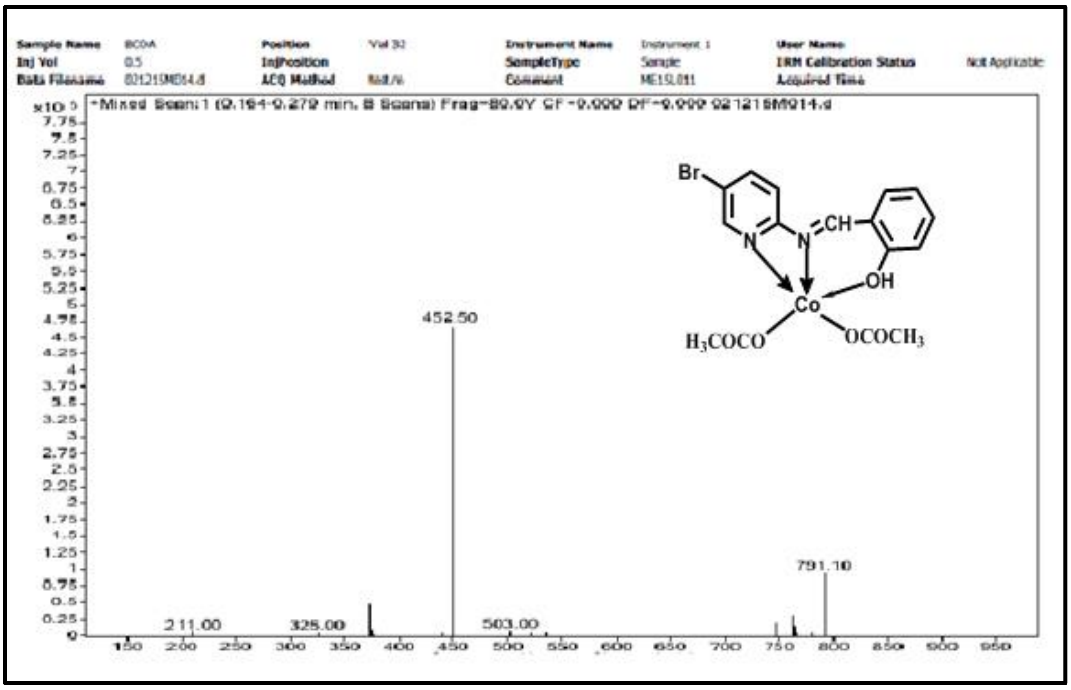
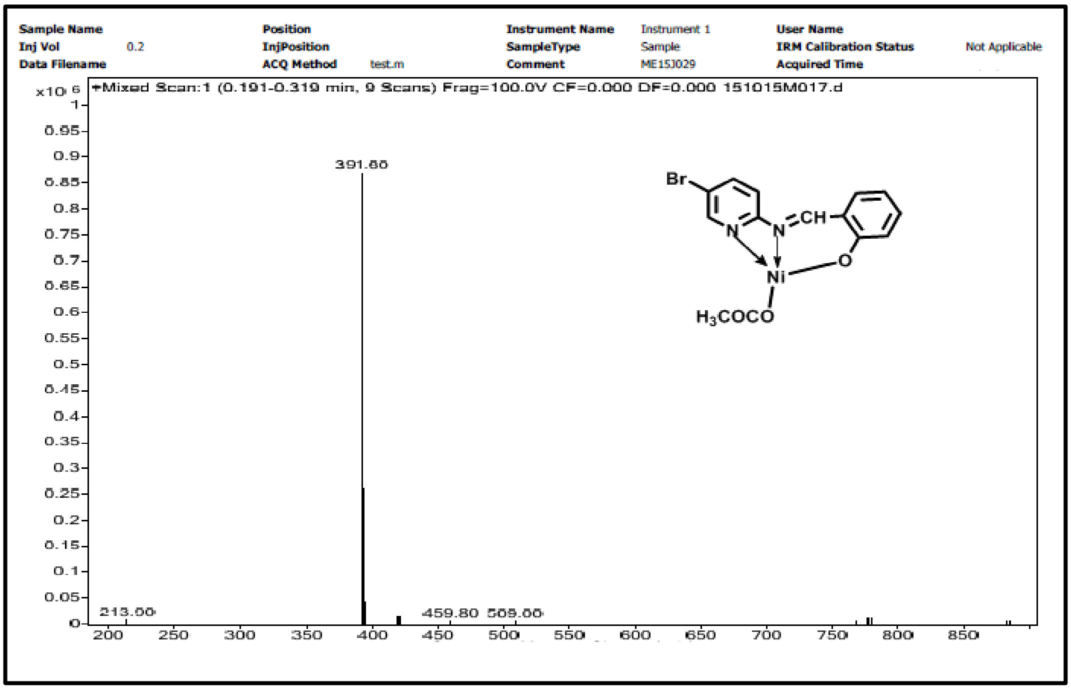
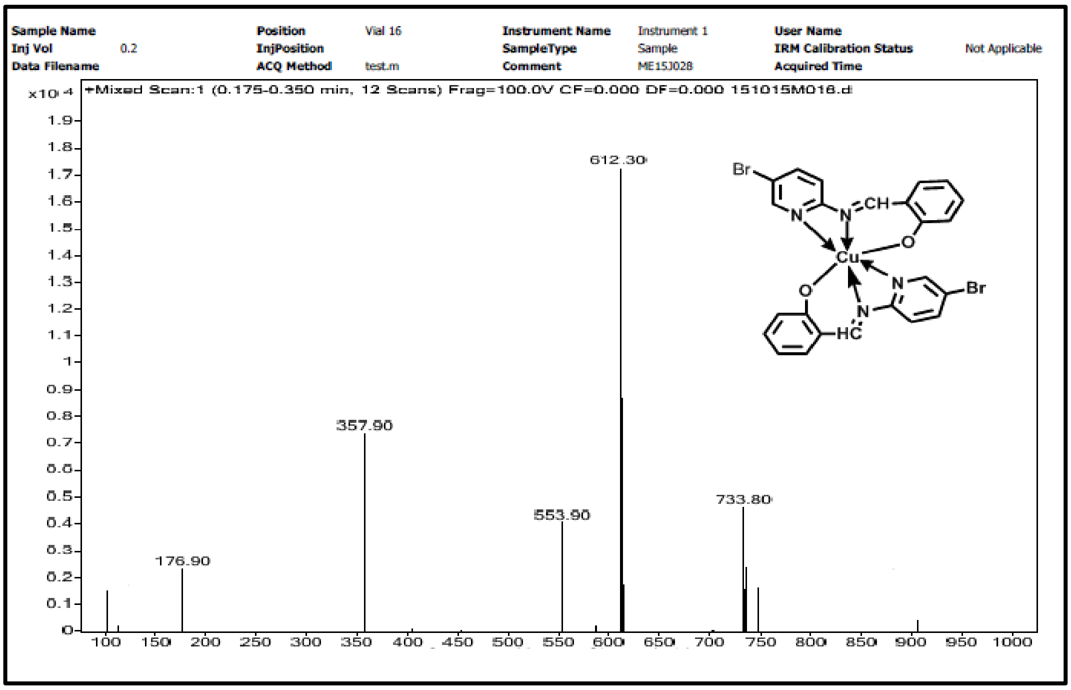

Sample Name BCOA
Inj Vol 0.5
Data Filename 021215M014.d
Position Vial 32
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment ME15L011
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.38 ESI mass spectrum of complex (C-8)



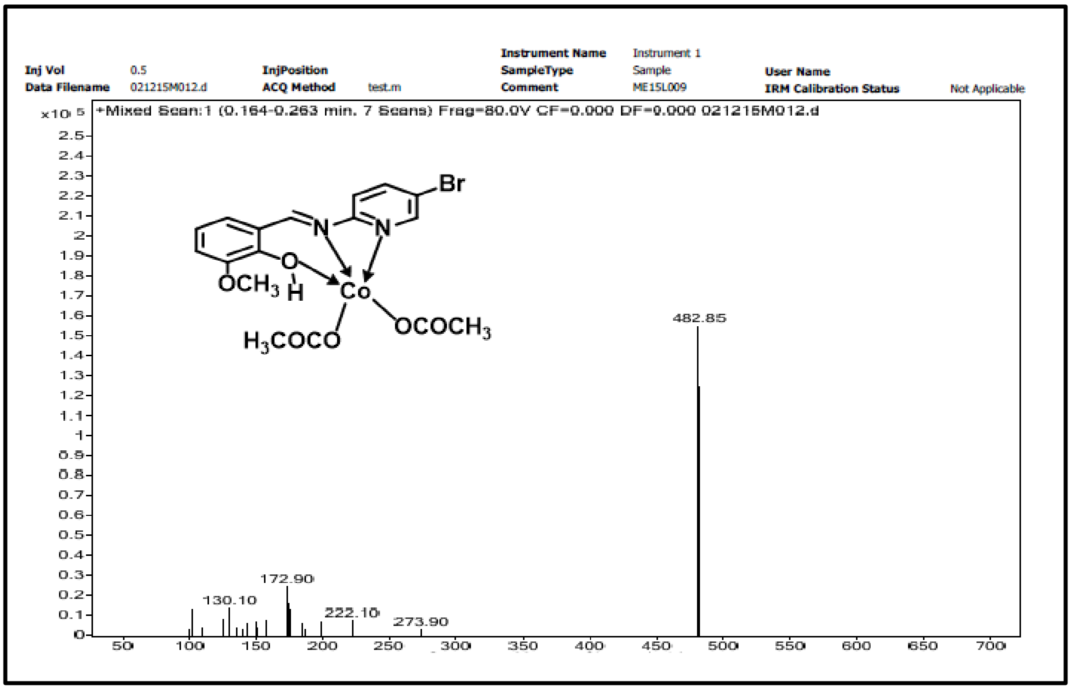
Sample Name
Inj Vol 0.2
Data Filename
Position
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment ME15J029
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.39 ESI mass spectrum of complex (C-9)



Sample Name
Inj Vol 0.2
Data Filename
Position Vial 16
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment ME15J028
User Name
IRM Calibration Status Not Applicable
Acquired Time

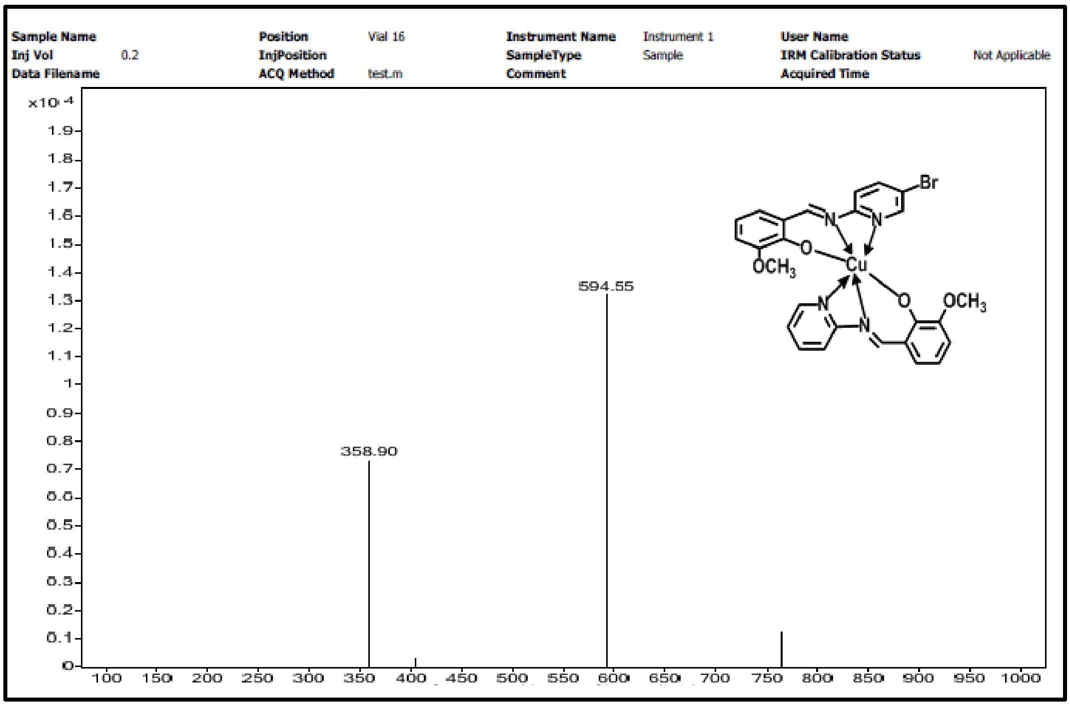
Figure 3.40 ESI mass spectrum of complex (C-10)



Instrument Name Instrument 1
Inj Vol 0.5
InjPosition
SampleType Sample
User Name
Data Filename 021215M012.d
ACQ Method test.m
Comment ME15L009
IRM Calibration Status Not Applicable

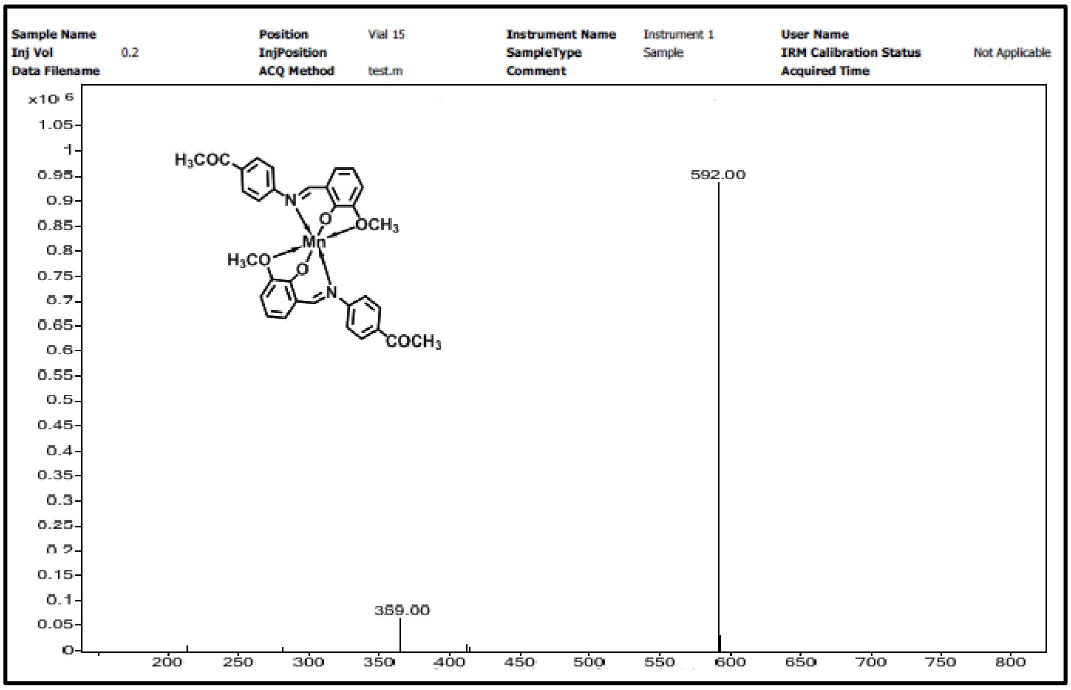
+Mixed Scan:1 (0.164-0.263 min. 7 Scans) Frag=80.0V CF=0.000 DF=0.000 021215M012.d

Figure 3.41 ESI mass spectrum of complex (C-11)



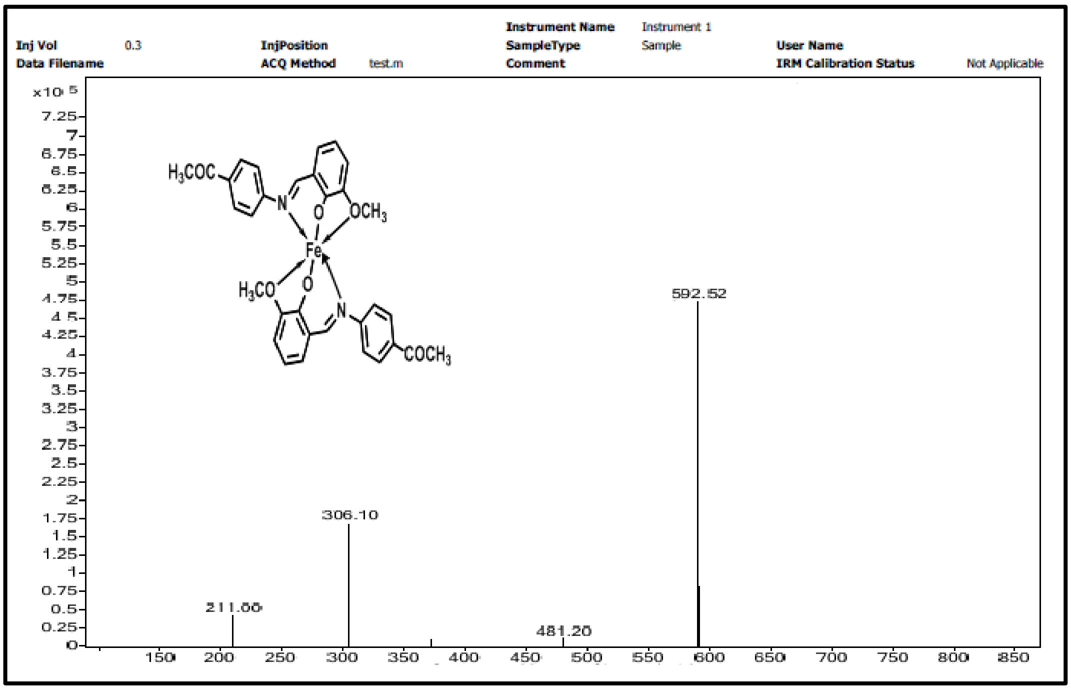
Sample Name
Position Vial 16
Instrument Name Instrument 1
User Name
Inj Vol 0.2
InjPosition
SampleType Sample
IRM Calibration Status Not Applicable
Data Filename
ACQ Method test.m
Comment
Acquired Time

Figure 3.42 ESI mass spectrum of complex (C-12)



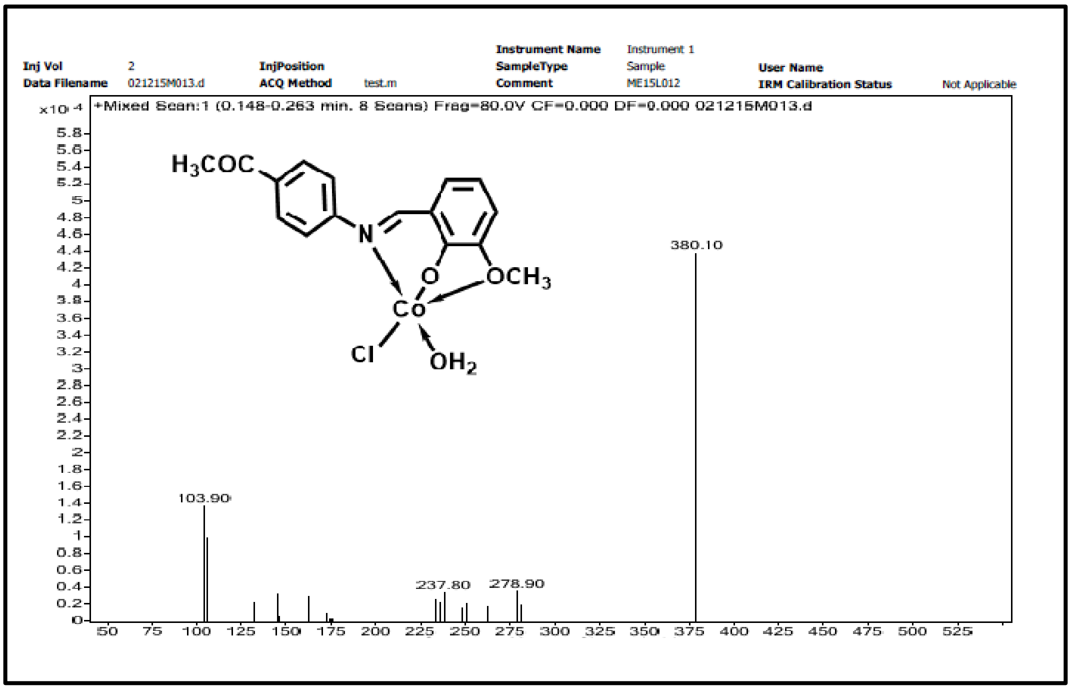
Sample Name
Inj Vol 0.2
Data Filename
Position Vial 15
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.43 ESI mass spectrum of complex (C-13)



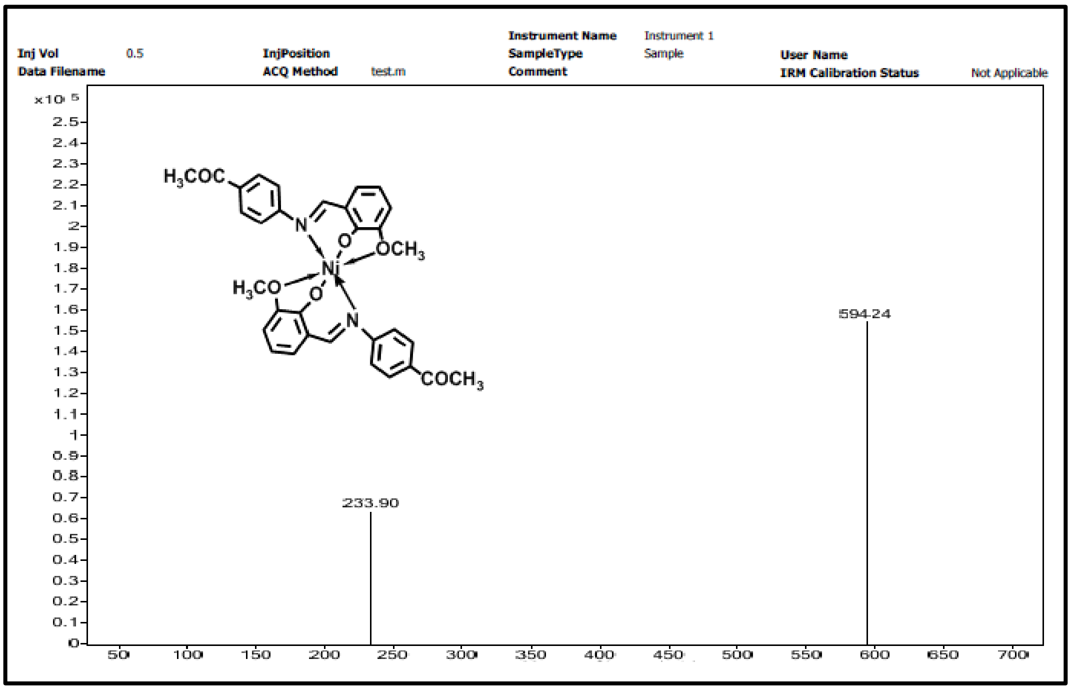
Inj Vol 0.3
Data Filename
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable

Figure 3.44 ESI mass spectrum of complex (C-14)



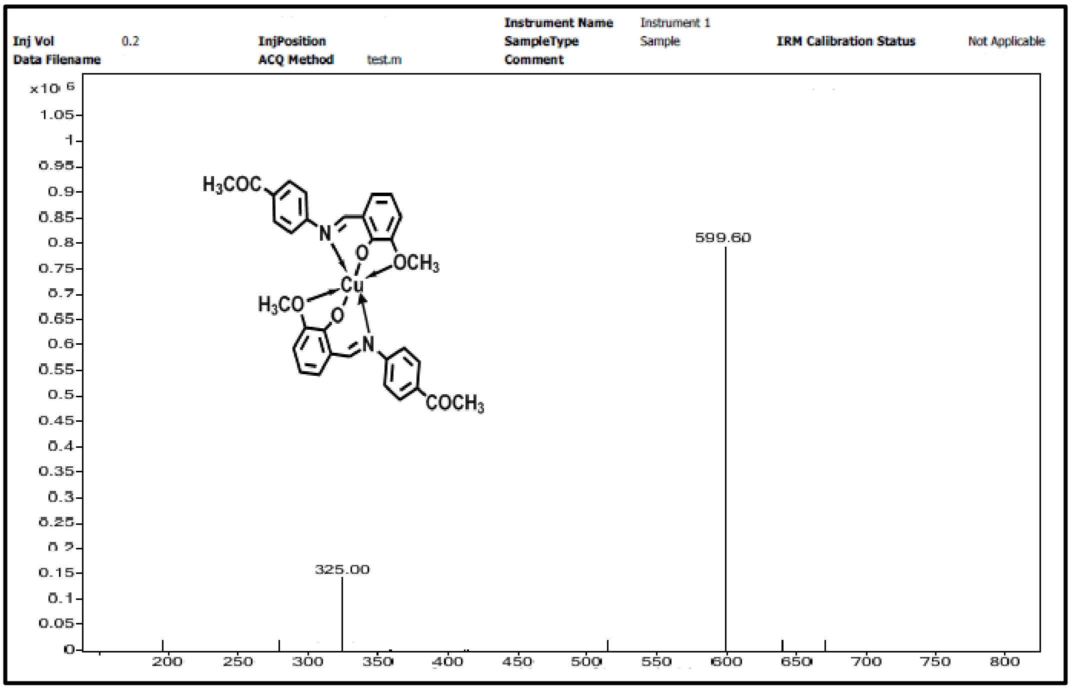
Inj Vol 2
Data Filename 021215M013.d
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment ME15L012
User Name
IRM Calibration Status Not Applicable

Figure 3.45 ESI mass spectrum of complex (C-15)



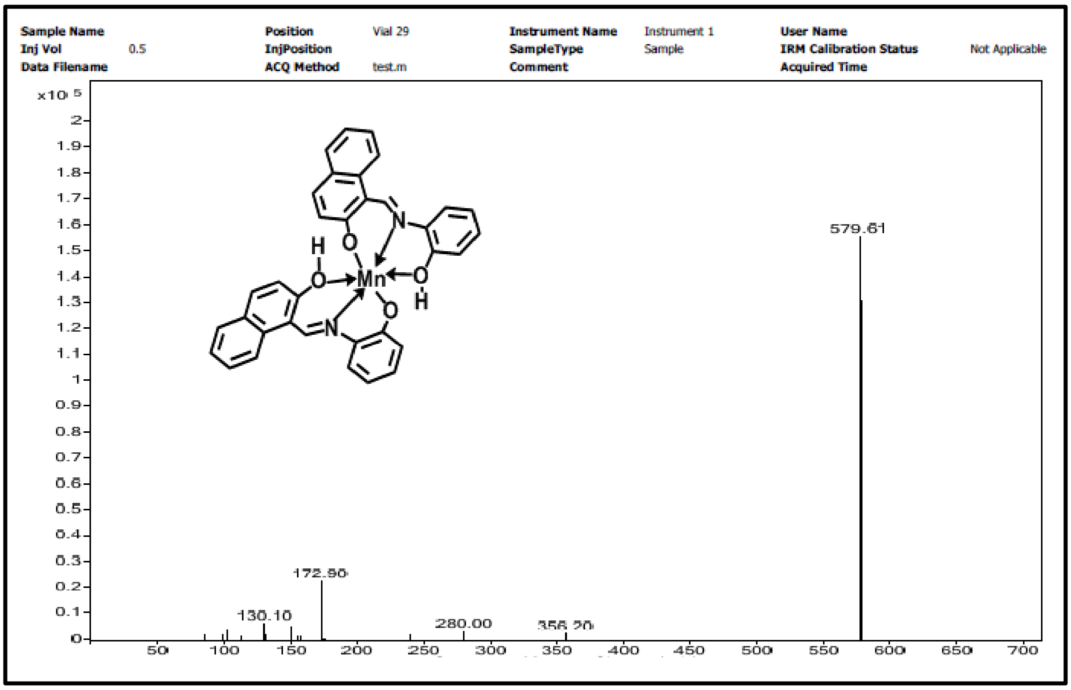
Inj Vol 0.5
Data Filename
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable

Figure 3.46 ESI mass spectrum of complex (C-16)



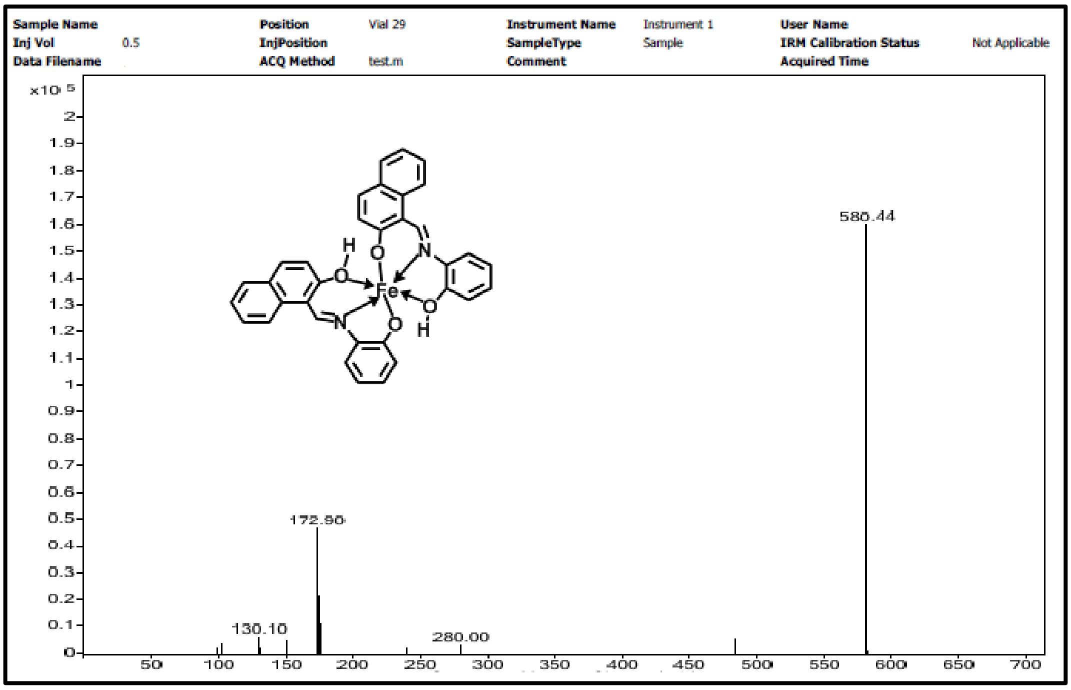
Instrument Name Instrument 1
Inj Vol 0.2 **InjPosition** **SampleType** Sample **IRM Calibration Status** Not Applicable
Data Filename **ACQ Method** test.m **Comment**

Figure 3.47 ESI mass spectrum of complex (C-17)



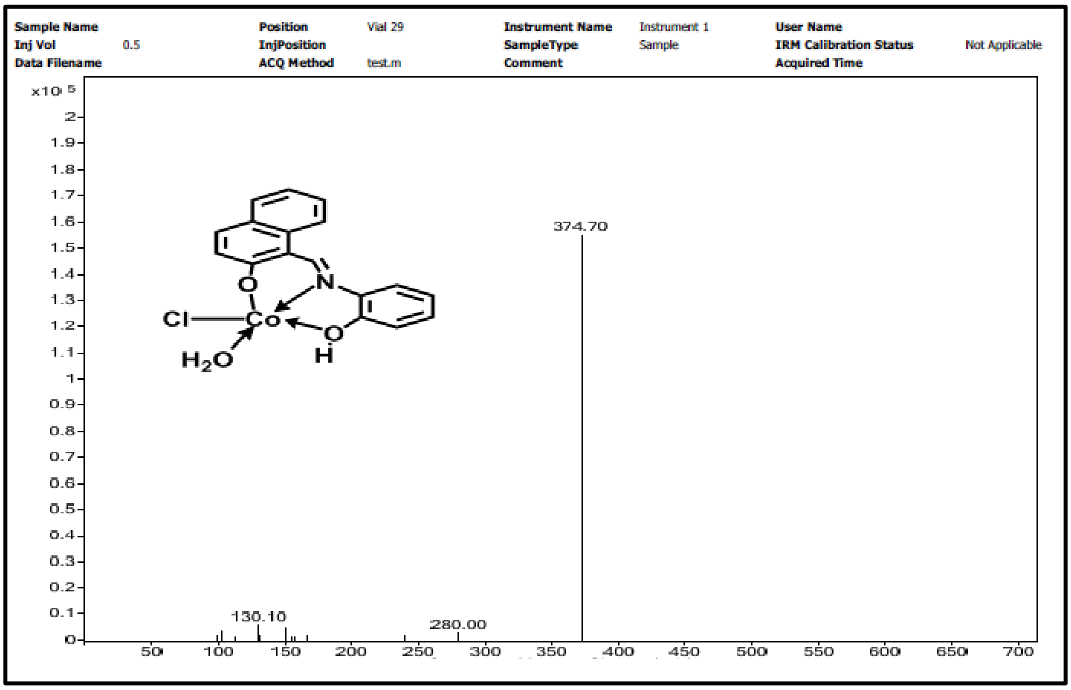
Sample Name **Position** Vial 29 **Instrument Name** Instrument 1 **User Name**
Inj Vol 0.5 **InjPosition** **SampleType** Sample **IRM Calibration Status** Not Applicable
Data Filename **ACQ Method** test.m **Comment** **Acquired Time**

Figure 3.48 ESI mass spectrum of complex (C-18)



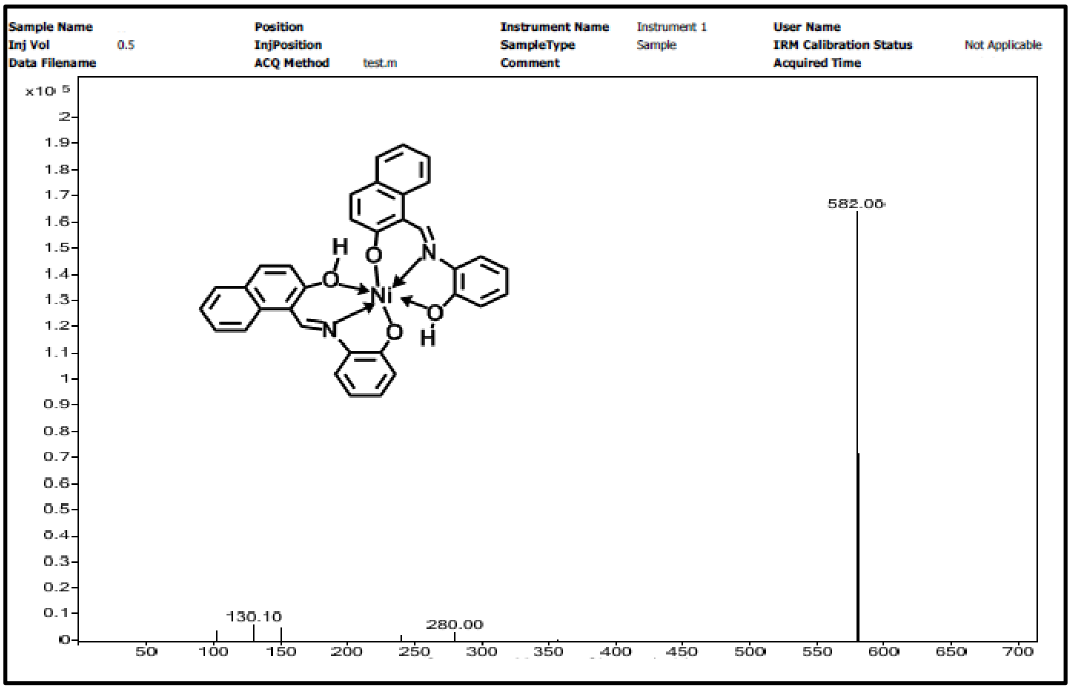
Sample Name
Inj Vol 0.5
Data Filename
Position Vial 29
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.49 ESI mass spectrum of complex (C-19)



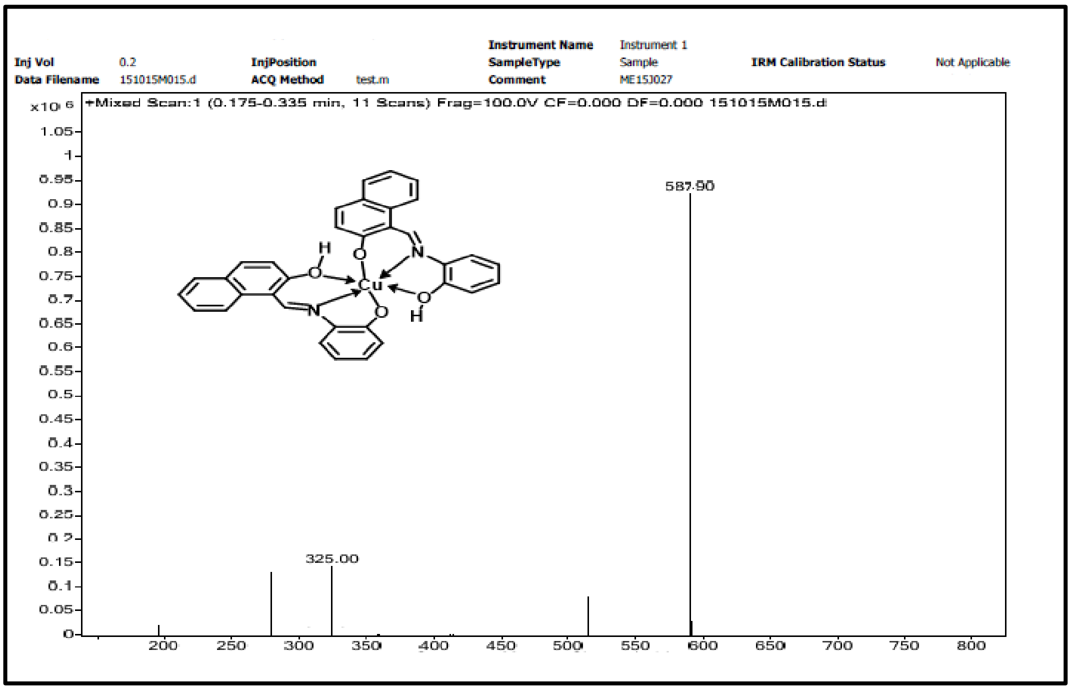
Sample Name
Inj Vol 0.5
Data Filename
Position Vial 29
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.50 ESI mass spectrum of complex (C-20)



Sample Name
Inj Vol 0.5
Data Filename
Position
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable
Acquired Time

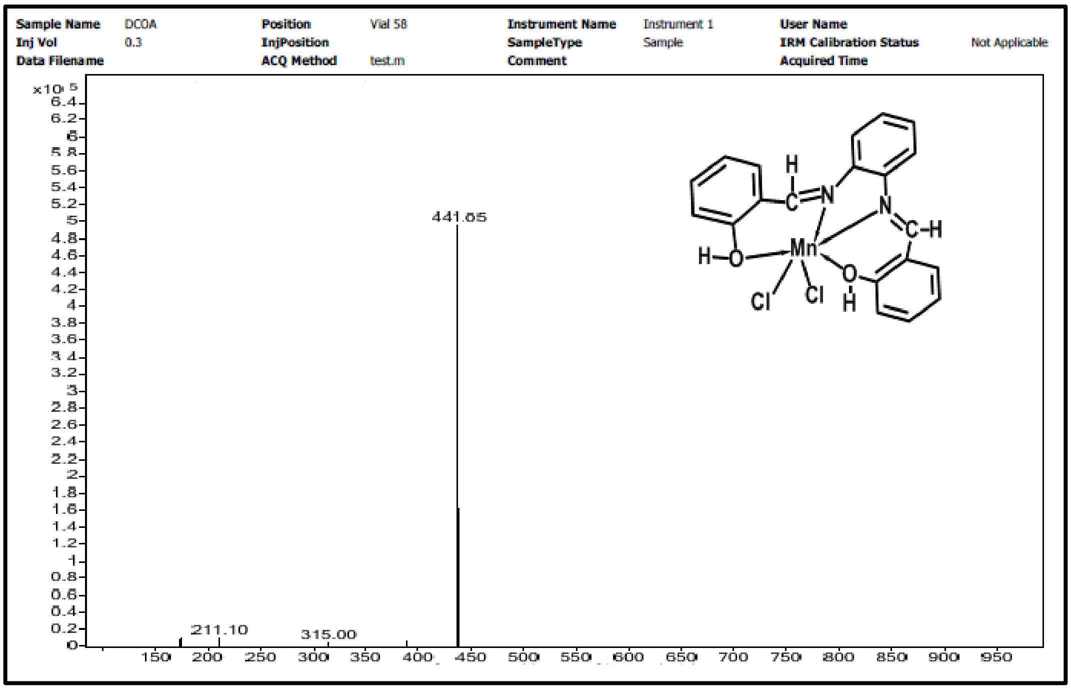
Figure 3.51 ESI mass spectrum of complex (C-21)



Inj Vol 0.2
Data Filename 151015M015.d
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment ME15J027
IRM Calibration Status Not Applicable

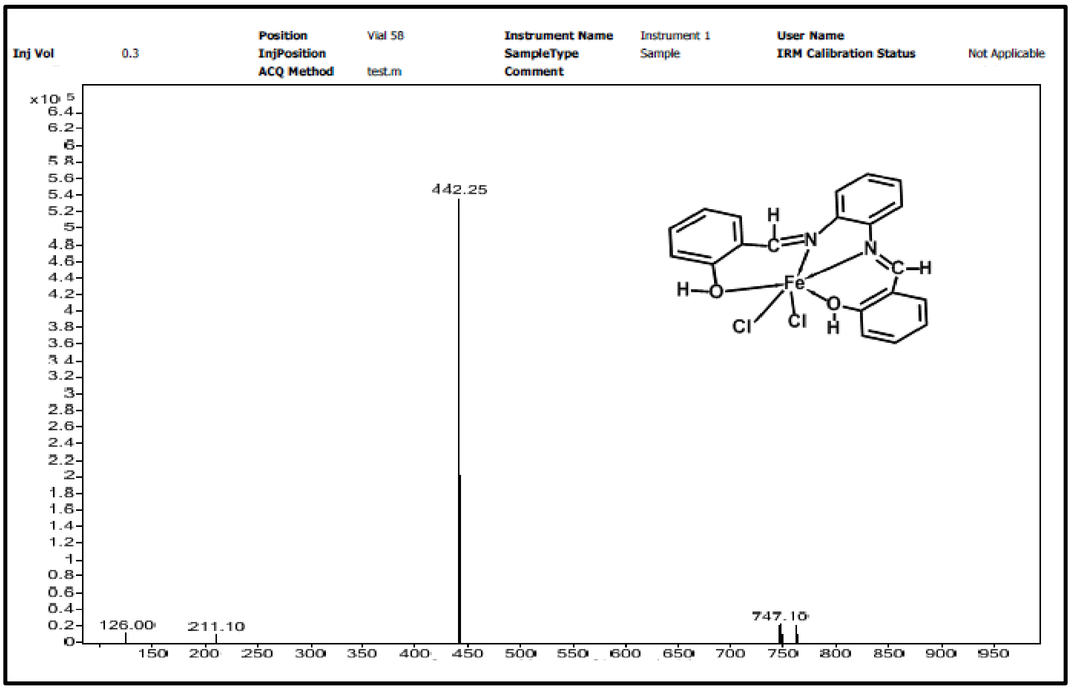
+Mixed Scan:1 (0.175-0.335 min, 11 Scans) Frag=100.0V CF=0.000 DF=0.000 151015M015.d

Figure 3.52 ESI mass spectrum of complex (C-22)



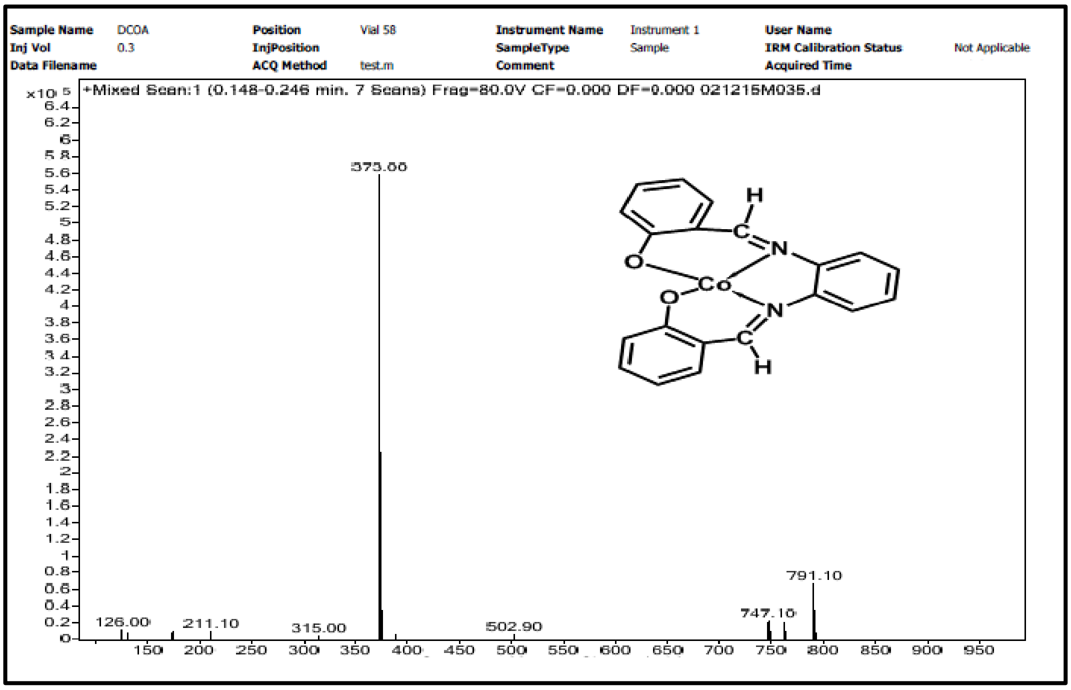
Sample Name DCOA
Inj Vol 0.3
Data Filename
Position Vial 58
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 3.53 ESI mass spectrum of complex (C-23)



Inj Vol 0.3
Position Vial 58
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable

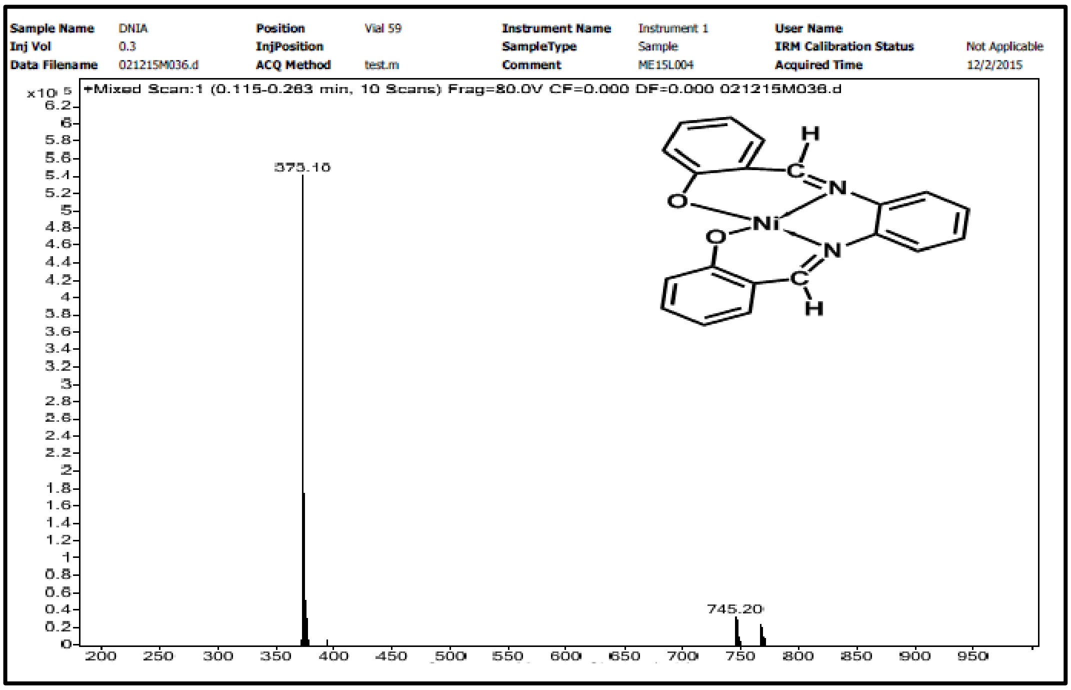
Figure 3.54 ESI mass spectrum of complex (C-24)



Sample Name	DCOA	**Position**	Vial 58	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Not Applicable
Data Filename		**ACQ Method**	test.m	**Comment**		**Acquired Time**	

+Mixed Scan:1 (0.148-0.246 min. 7 Scans) Frag=80.0V CF=0.000 DF=0.000 021215M035.d

Figure 3.55 ESI mass spectrum of complex (C-25)



Sample Name	DNIA	**Position**	Vial 59	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Not Applicable
Data Filename	021215M036.d	**ACQ Method**	test.m	**Comment**	ME15L004	**Acquired Time**	12/2/2015

+Mixed Scan:1 (0.115-0.283 min, 10 Scans) Frag=80.0V CF=0.000 DF=0.000 021215M036.d

Figure 3.56 ESI mass spectrum of complex (C-26)

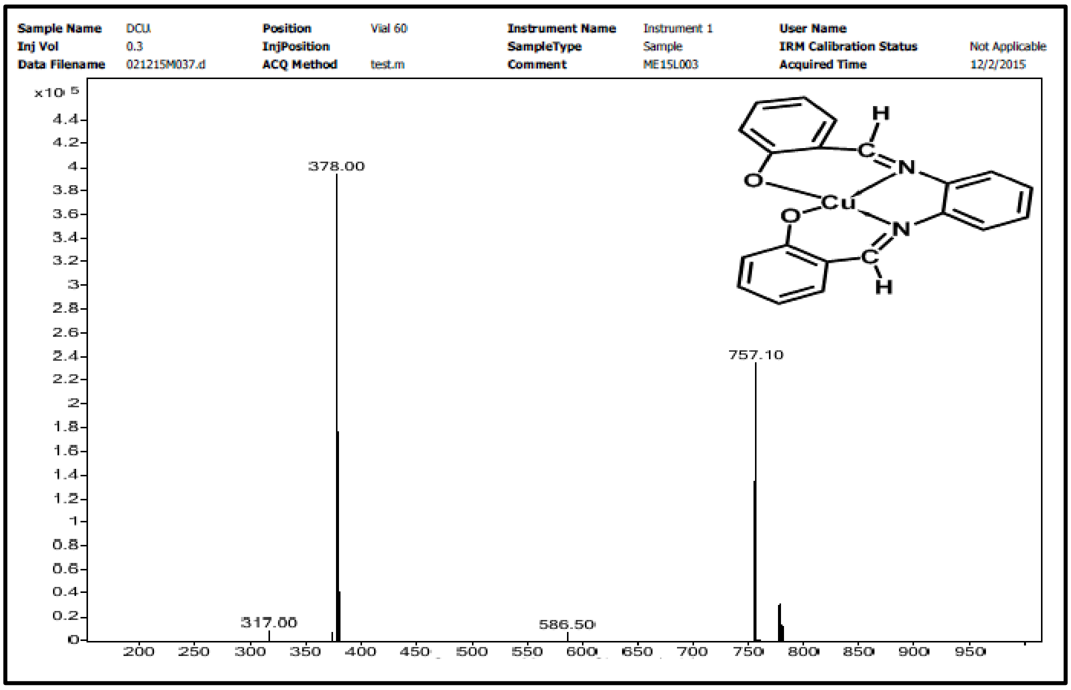


Figure 3.57 ESI mass spectrum of complex (C-27)

3.3.5 ^{1}H NMR spectrum of ligand and complex

^{1}H NMR spectra were recorded at 400 MHz for the ligand and complex which further provided their structural confirmation (Table 3.9). The ^{1}H NMR spectra of the ligands are represented in the figures (Figs 3.58 to 3.63).

The ^{1}H NMR spectrum of ligand (L-1) represents the singlet peak at δ 12.90 which corresponds to the phenolic proton (Fig. 3.58). The peak at δ 8.62 describes the characteristic peak of azomethine proton. The presence of a multiplet at δ 7.00-8.02 is due to the aromatic protons. The spectrum displays peaks at δ 2.60 due to methyl protons.

The ^{1}H NMR spectrum of ligand (L-2) represents the singlet peak at δ 12.60-12.80 which corresponds to the phenolic proton (Fig. 3.59). The peak at δ 9.40-9.50 describes the characteristic peak of azomethine proton. The presence of a multiplet at δ 6.90-8.65 is due to the aromatic protons.

The ^{1}H NMR spectrum of ligand (L-3) represents the singlet peak at δ 12.74-12.80 which corresponds to the phenolic proton (Fig. 3.60). The peak at δ 9.0-9.43

describes the characteristic peak of azomethine proton. The presence of a multiplet at δ 6.88-8.63 is due to the aromatic protons. The spectrum displays peaks at δ 3.81 due to methoxy protons (-OCH_3).

The ^1H NMR spectrum of ligand (L-4) represents the singlet peak at δ 12.80 which corresponds to the phenolic proton (Fig. 3.61). The peak at δ 9.02 describes the characteristic peak of azomethine proton. The presence of a multiplet at δ 6.93-8.07 is due to the aromatic protons. The methyl protons of $O=C-CH_3$ appears at δ 3.36 ppm and singlet of -OCH_3 appear at δ 3.85 ppm.

The ^1H NMR spectrum of ligand (L-5) represents the singlet peaks at δ 15.71-15.74 which corresponds to the phenolic proton of naphthalene ring (Fig. 3.62) and singlet peak at δ 10.35 which corresponds to the phenolic proton of benzene ring. The peak at δ 9.45-9.52 describes the characteristic peak of azomethine proton. The presence of a multiplet at δ 6.79-7.97 is due to the aromatic protons. Moreover, the shift of the peak at δ 15.71-15.74 in ligand (L-5) to δ 15.91 in the spectrum of complex (C-21) confirms the bonding between phenolic oxygen with nickel ions (Fig. 3.64). Also, the shift in the peak of azomethine proton (δ 9.97) as well as in aromatic protons (δ 6.65-8.67) was obsereved.

The ^1H NMR spectrum of ligand (L-6) portrays the well characteristic singlet peaks at δ 12.90 which corresponds to the phenolic proton (Fig. 3.63). Similarly, the peak at δ 8.9-9.0 represents the characteristic peak of azomethine proton. The presence of a multiplet at δ 6.95-7.65 is due to the aromatic protons (Ar-H). The spectrum displays all the characteristic peaks without any impure peak confirming the prepared Schiff base ligand (L-6).

Table 3.9 ^{1}H NMR shifts of ligands and complex

Compound	**Chemical shift (ppm)**
L-1	δ 12.90 (s, -OH), 8.62 (s, 1H), 7.00-8.02 (m, 8H), 2.60 (s, 3H)
L-2	δ 12.60-12.80 (s, -OH), 9.40-9.50 (s, 1H), 6.90-8.65 (m, 7H)
L-3	δ 12.74-12.80 (s, -OH), 9.0-9.43 (s, 1H), 6.88-8.63 (m, 7H), 3.81 (s, 3H)
L-4	δ 12.80 (s, -OH), 9.02 (s, 1H), 6.93-8.07 (m, 8H), 3.36 (s, 3H), 3.84 (s, 3H)
L-5	δ 15.71-15.74 (s, -OH), 10.35 (s, -OH), 9.45-9.52 (s, 1H), 6.79-7.97 (m, 10H)
L-6	δ 12.90 (s, -OH), 8.9-9.0 (s, 1H), 6.95-7.65 (m, 12H)
C-21	δ 15.91 (s, -OH), 9.97 (s, 1H), 6.65-8.67 (m, 10H)

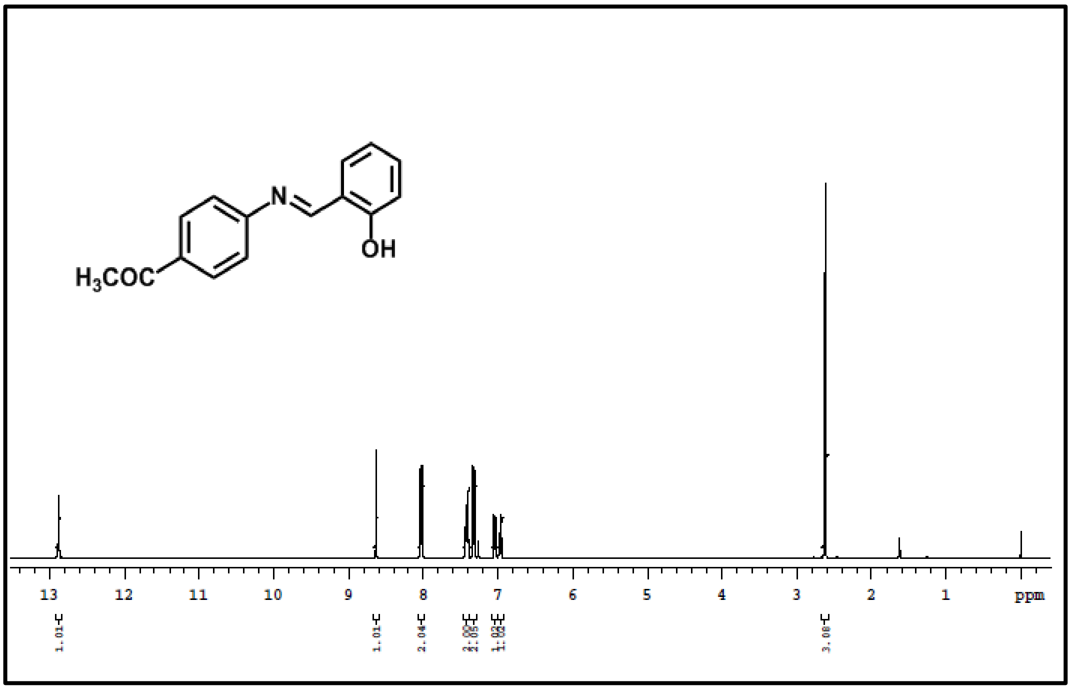


Figure 3.58 ^{1}H NMR of ligand (L-1)

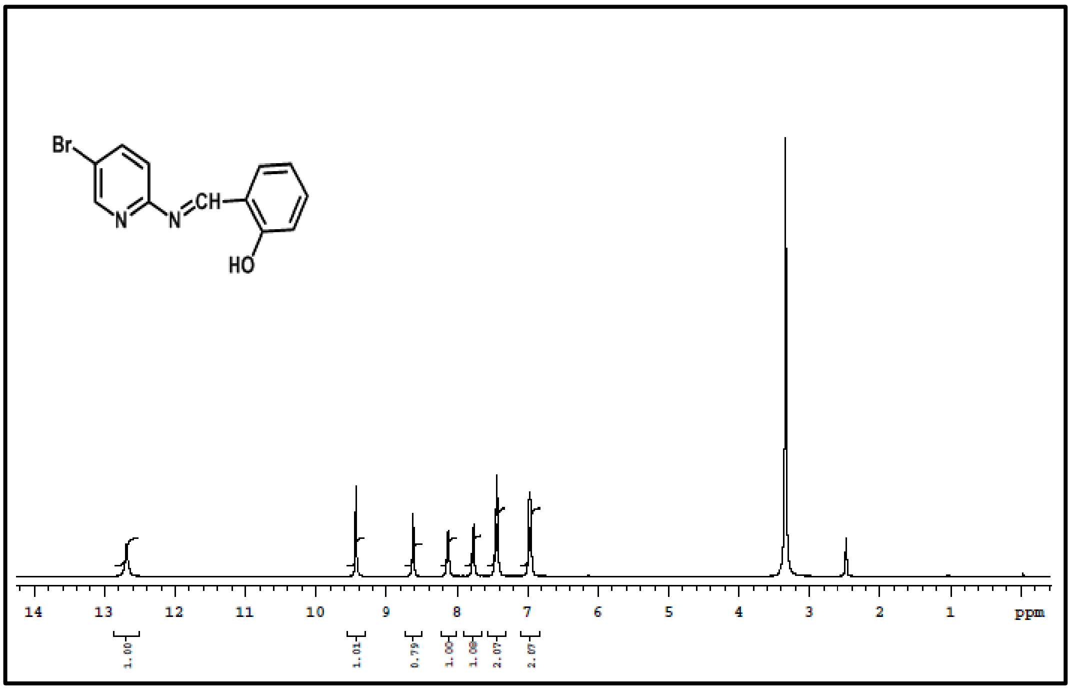


Figure 3.59 ^{1}H NMR of ligand (L-2)

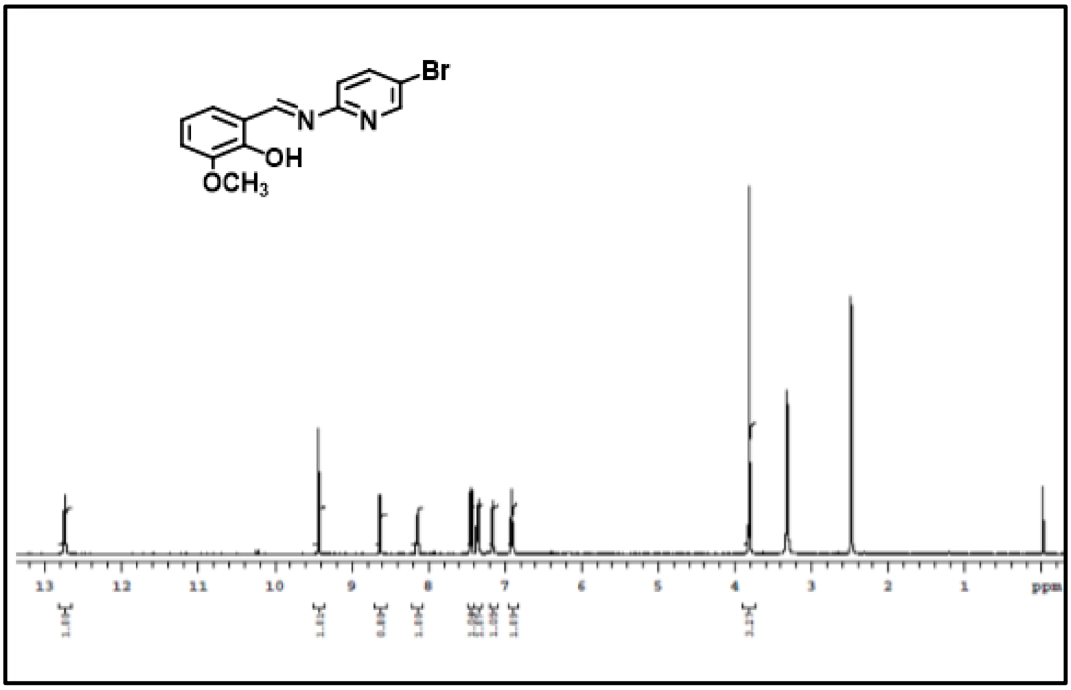


Figure 3.60 ^{1}H NMR of ligand (L-3)

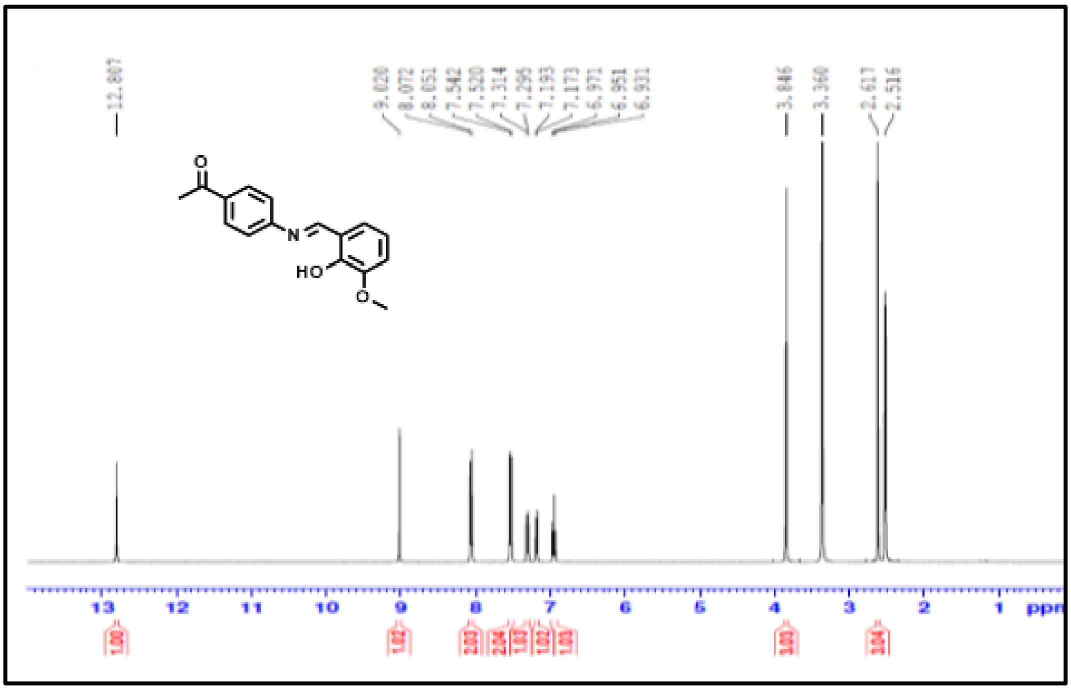


Figure 3.61 ^{1}H NMR of ligand (L-4)

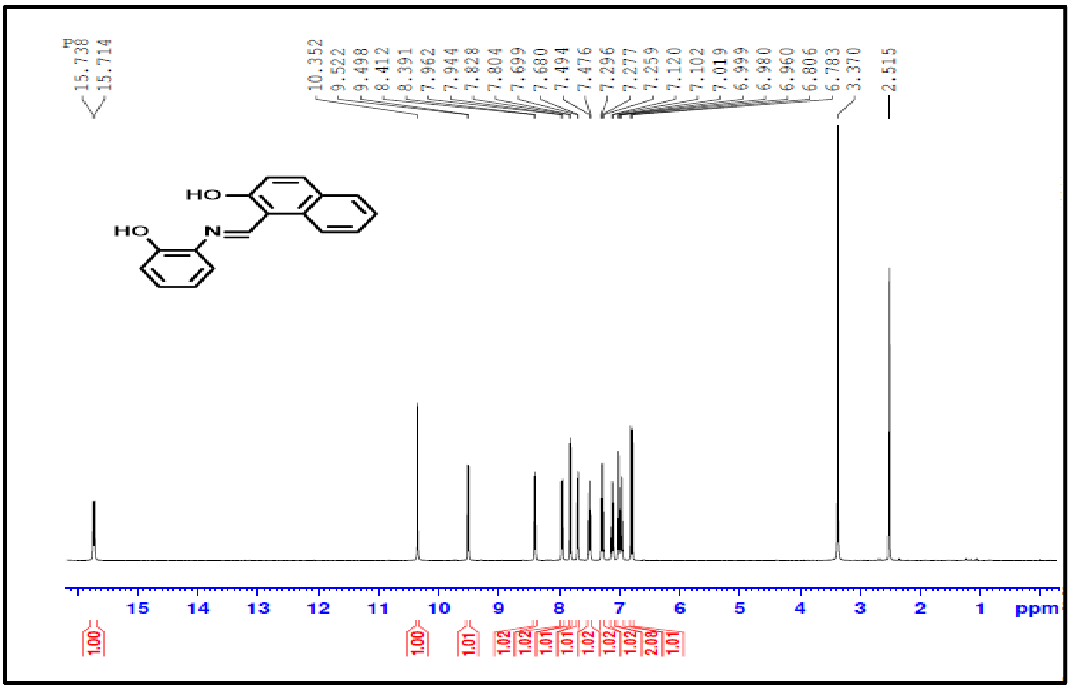


Figure 3.62 ^{1}**H NMR of ligand (L-5)**

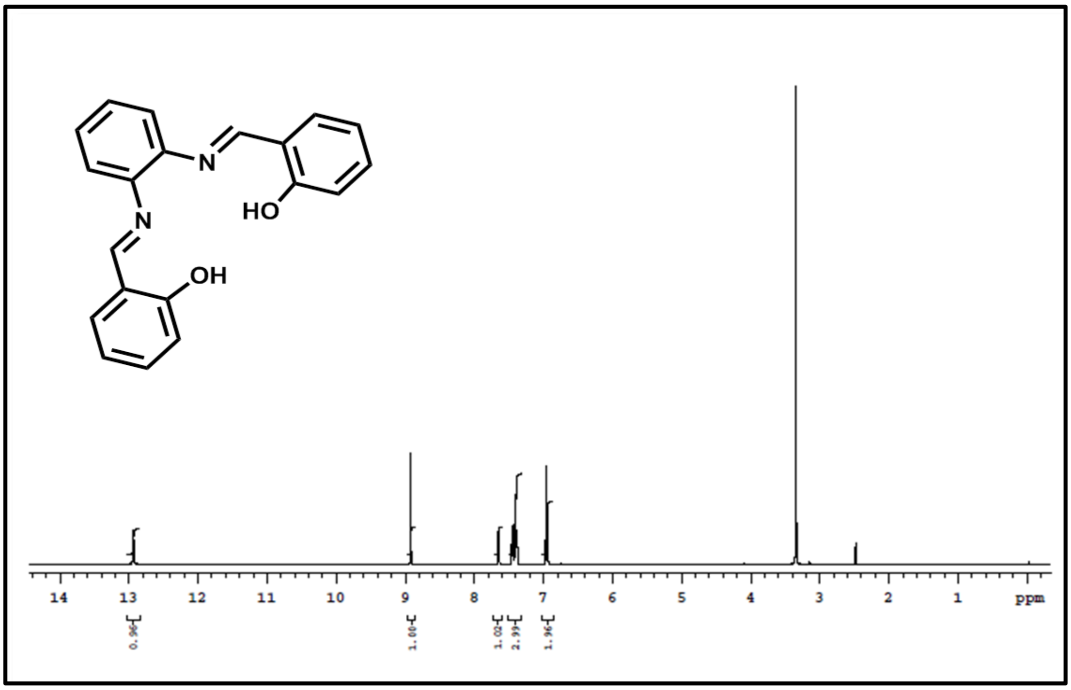


Figure 3.63 ^{1}**H NMR of ligand (L-6)**

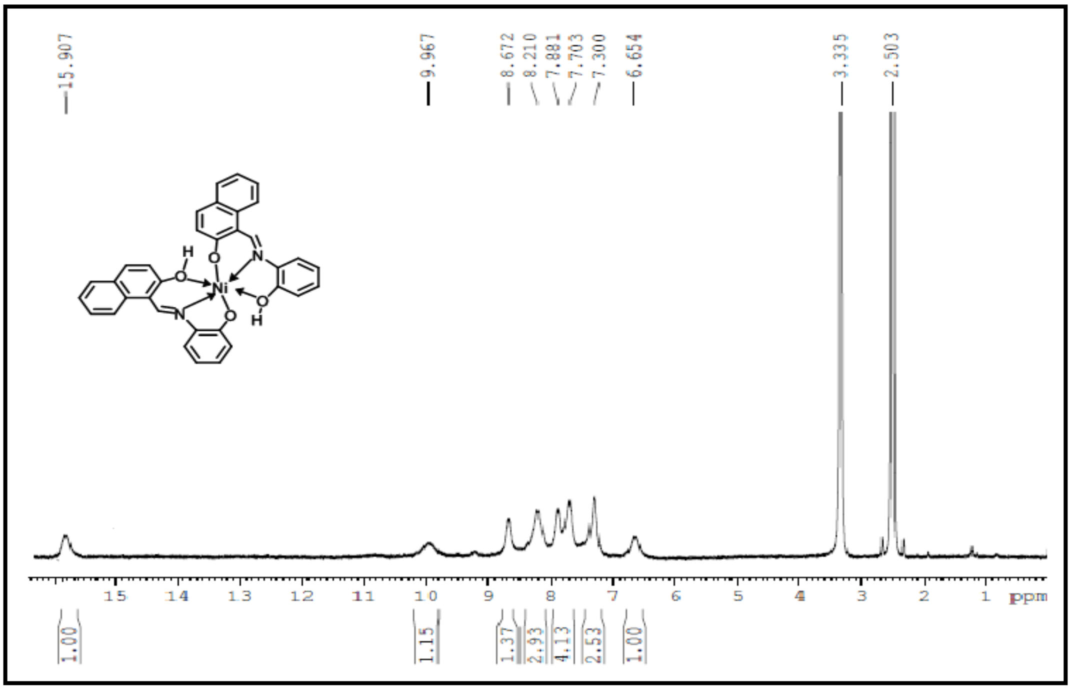


Figure 3.64 ^{1}H NMR of complex (C-21)

3.3.6 Thermogravimetric analysis

The purpose of thermal study is to confirm the course of the degradation and the presence of the hydrated water molecules in the complexes. Complexes were subjected to thermal analysis in order to interpret the stability as well as the structural information. C-2, C-3, C-4 and C-5 which are the complex of ligand L-1 show typical TGA curves (Fig. 3.65) representing single step dissociation of the complexes. The dissociation of the ligands is observed well near at temperature 500 ˚C indicating the stability of the complex formed.

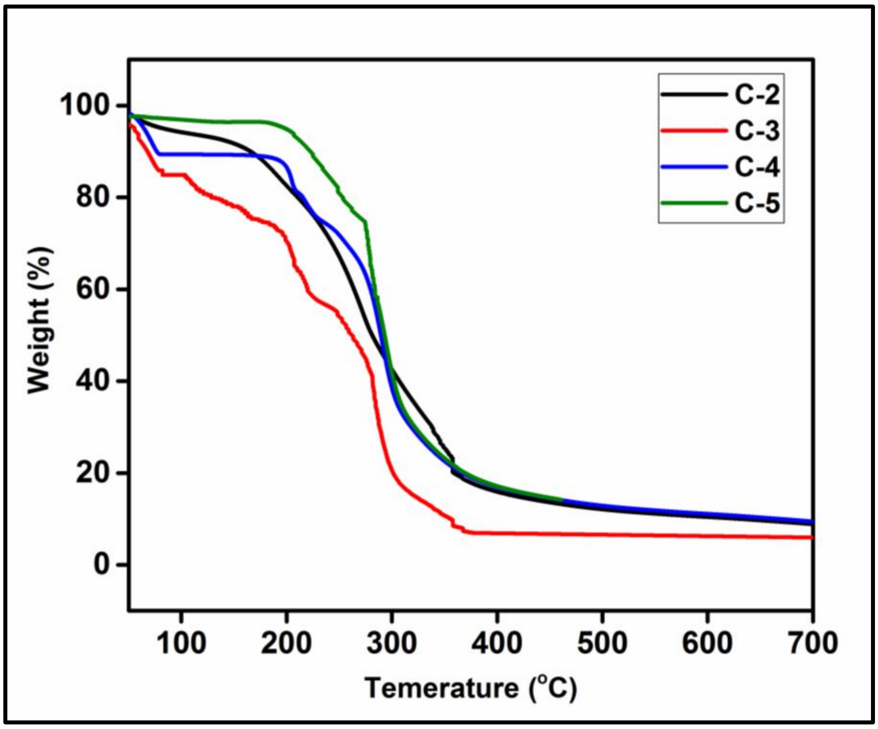


Figure 3.65 TGA curves of complexes (C-2 to C-5)

TGA curve for C-9 corresponding to cobalt complex of ligand L-2 is shown in Fig. 3.66. Complex C-9 was subjected to thermal analysis in order to interpret the stability as well as the structural information. The thermogravimetric analysis of complex proceeds in three steps with 16.90% mass loss due to acetate group decomposition. Further, 49.57% residual mass which can be attributed to the decomposition of ligand moiety. Decomposition of cobalt oxide can be seen with the remaining percentage mass loss. There is no peak observed from 100 to 200 °C which confirms that there is no coordinated water molecules present in the complex (Fasihizad et al. 2016). In case of complex (C-11) (Fig. 3.67), decomposition of complex was carried out with the ligand dissociation (31.40% and 35.53%). The remaining percentage mass loss can be assigned for cobalt oxide residue.

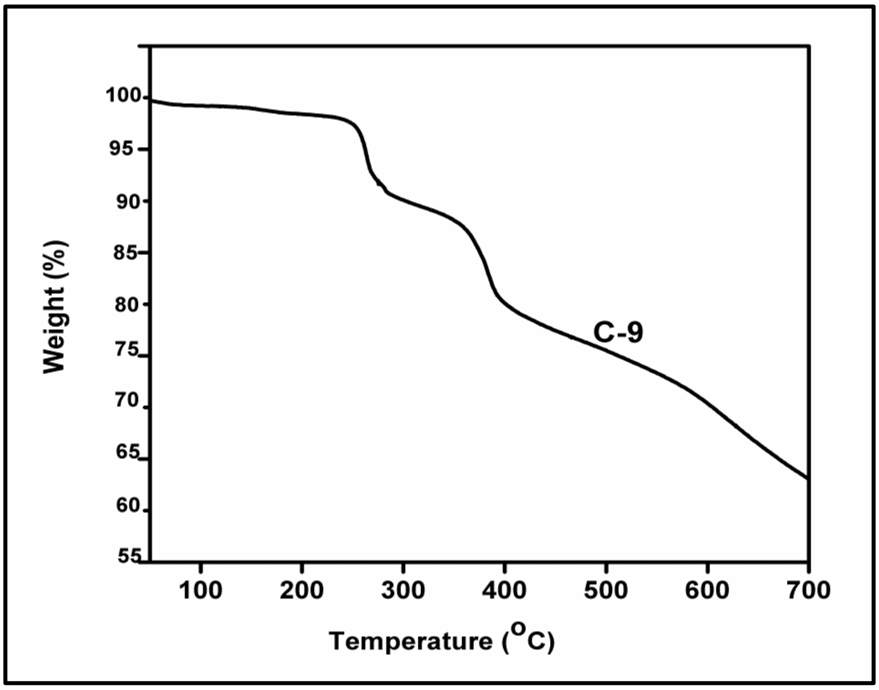


Figure 3.66 TGA curve of complex (C-9)

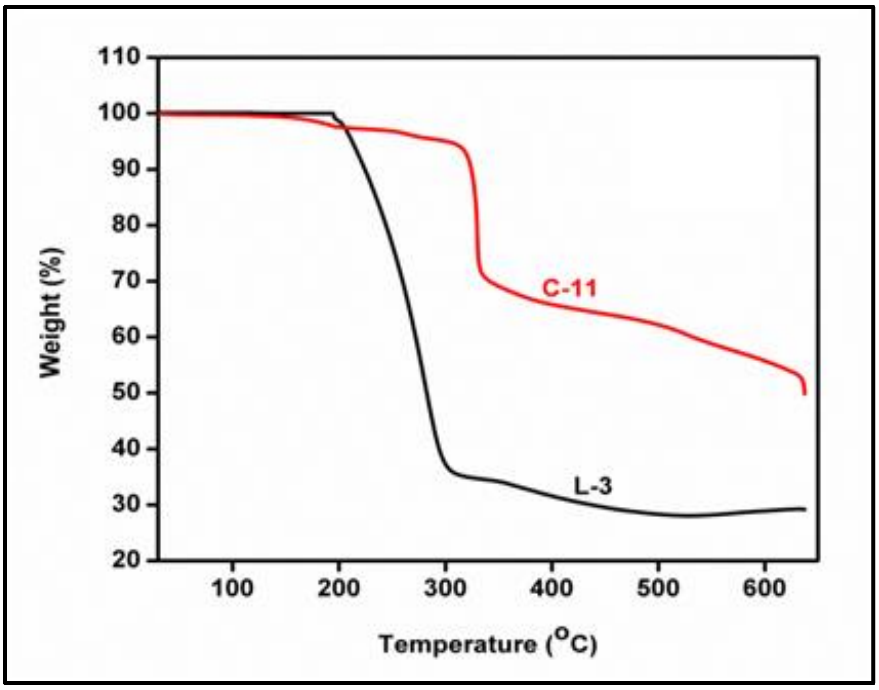


Figure 3.67 TGA curves of complex (C-11)

The thermogravimetric analysis of complex (C-15) proceeds in four steps with 4.21% mass loss due to water molecule. Decomposition of chloride ion can be seen with the 18.42 percentage mass loss. Further, 40.17% residual mass which can be attributed to the decomposition of half ligand moiety (Fig. 3.68). The other half part of ligand decomposed with 35.02% mass loss. Decomposition of cobalt oxide can be seen with the remaining percentage mass loss.

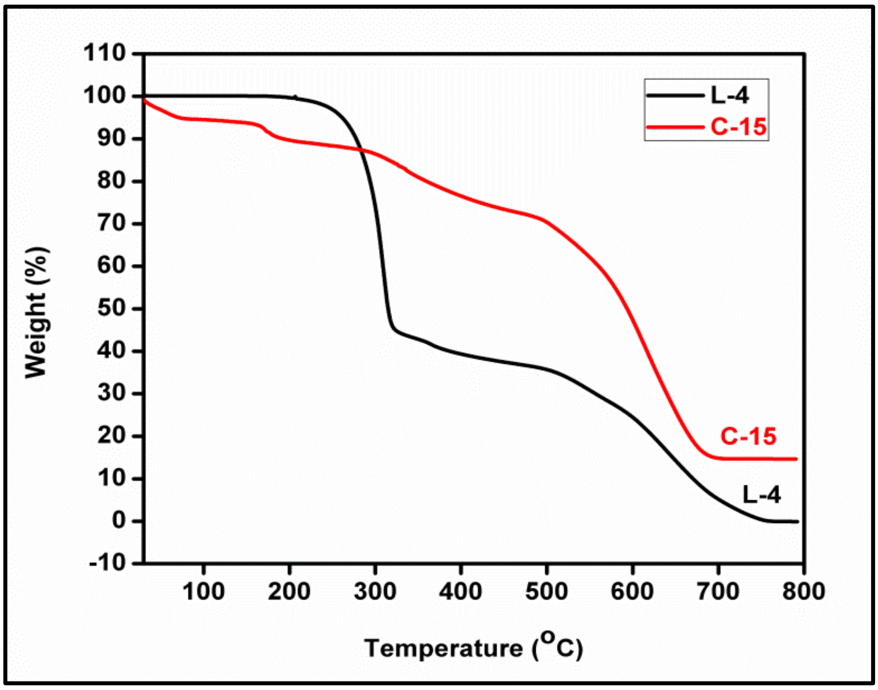


Figure 3.68 TGA curves of complex (C-15)

The thermogravimetric analysis of complex (C-18) proceeds in one step with decomposition of ligand molecule. Decomposition of ligand moiety can be seen with the 54.12 percentage mass loss. Decomposition of manganese oxide can be seen with the remaining percentage mass loss (Fig. 3.69). In case of C-19, the first weight loss of 11.88% in the temperature range 280 to 380 ˚C indicated by the thermogram is due to loss of loosely bound ligand moiety. The second loss of 18.50% in the temperature range of 400 to 496 ˚C is attributed to decomposition of ligand moiety. The third weight loss of 27.00% indicates removal of ligand. The thermogravimetric analysis of complex (C-21) indicates that removal of ligand (L-5) proceeds in single step with 64.00% mass loss with remaining 25.02% residual mass which can be attributed to formation of metal oxides (Fig. 3.96). Complex showed complete decomposition at ≥520 ˚C. Absence of peak from 100 to 200 ˚C confirms that no coordinated water molecule present in the complex (C-21). Losses of weight are in agreement with the calculated values.

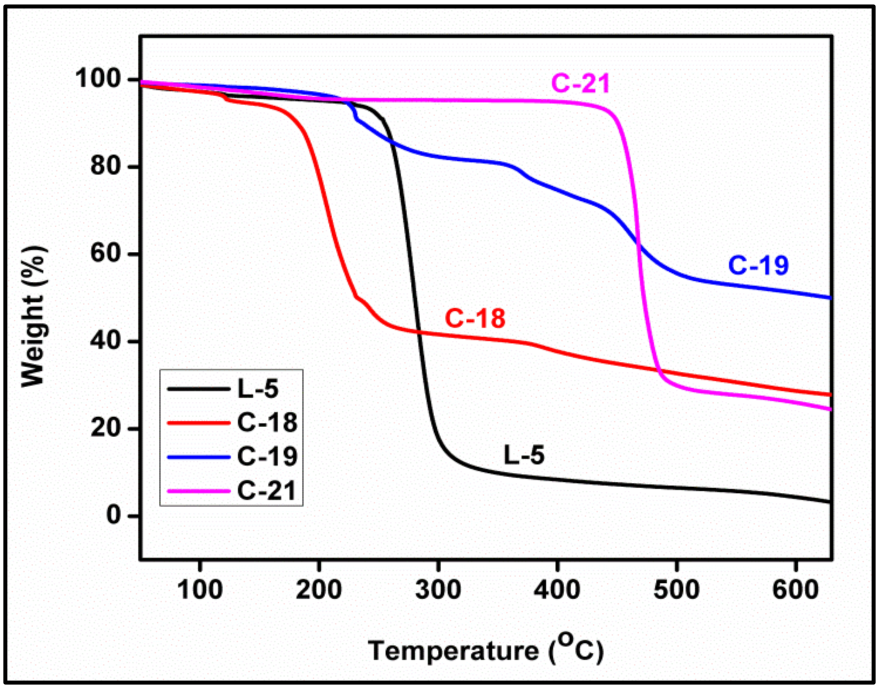


Figure 3.69 TGA curves of complexes (C-18, C-19 & C-21)

The thermal decomposition curves for the complex C-25 and C-26 at a temperature range from 30 ˚C to 700 ˚C are given in Fig. 3.70. The thermogravimetric analysis of complexes (C-25 & C-26) indicates that removal of ligand (L-6) proceeds in single step with 84.98% mass loss with remaining 15.02% residual mass which can be attributed to formation of metal oxides. Complexes showed complete decomposition at ≥450 ˚C. Absence of peak from 100 to 200 ˚C confirms that no coordinated water molecule present in both the complex. Losses of weight are in agreement with the calculated values.

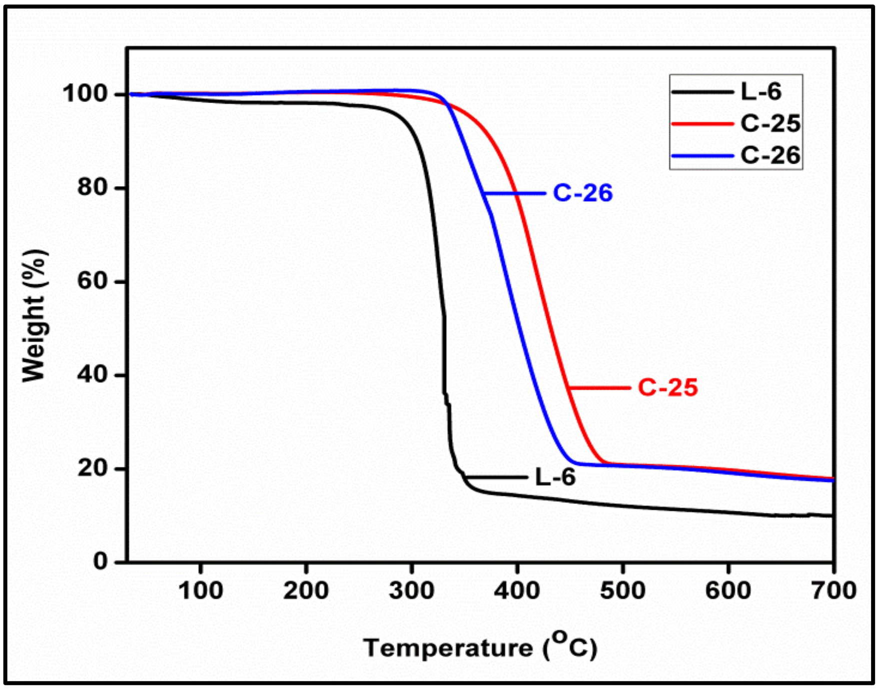


Figure 3.70 TGA curves of complexes (C-25 & C-26)

3.3.7 Magnetic Susceptibility Measurements

Room temperature magnetic moments of these complexes were found. Values obtained are shown in Table 3.10. The magnetic moment for manganese complex C-1, C-6, C-13, C-18 and C-23 was found in the range 1.35-1.80 BM, which indicates that one unpaired electron is present in the complex (low spin). The magnetic moment for iron complexes C-2 is 1.70 BM (paramagnetic). The magnetic moment for iron complex C-14, C-19 was found in the range 3.85-4.25 BM. Iron complexes (C-14 and C-19) are paramagnetic in nature with four unpaired electrons. Magnetic moment of iron complex C-7 and C-24 was found 0 BM, which indicates that no unpaired electron is present in both the complex. Cobalt complexes, C-3, C-8, C-11, C-15, C-20 and C-25 are paramagnetic low-spin complexes with magnetic moments in the range 1.09-1.75 BM suggesting the presence of Co^{2+}. Magnetic moment for the nickel complex (C-4) is 0 BM suggesting that diamagnetic complex. Similarly, the zero effective magnetic moment of nickel complex C-9, C-21 and C-26 clearly confirms the absence of unpaired electrons. Magnetic moment for the nickel complex C-16 is 2.23 BM suggesting that paramagnetic complex. The magnetic moment for copper complexes (C-5, C-10, C-12, C-17, C-22 and C-27) was observed in the range of 1.15-1.54 BM.

Table 3.10 Magnetic moment and proposed geometry of the complexes

Compound	**µ eff. (BM)**	**Geometry**	**Compound**	**µ eff. (BM)**	**Geometry**
C-1	1.80	Tetrahedral	**C-15**	1.26	Trigonal bipyramidal
C-2	1.70	Trigonal bipyramidal	**C-16**	2.23	Octahedral
C-3	1.73	Tetrahedral	**C-17**	1.15	Octahedral
C-4	Zero	Square planar	**C-18**	1.17	Octahedral
C-5	1.65	Tetrahedral	**C-19**	4.10	Octahedral
C-6	1.35	Octahedral	**C-20**	1.09	Trigonal bipyramidal
C-7	Zero	Octahedral	**C-21**	Zero	Octahedral
C-8	1.75	Trigonal bipyramidal	**C-22**	1.54	Octahedral
C-9	Zero	Square planar	**C-23**	1.80	Octahedral
C-10	1.40	Octahedral	**C-24**	Zero	Octahedral
C-11	1.08	Trigonal bipyramidal	**C-25**	1.23	Square planar
C-12	1.35	Octahedral	**C-26**	Zero	Square planar
C-13	1.75	Octahedral	**C-27**	1.45	Tetrahedral
C-14	4.25	Octahedral			

3.3.8 Crystal data

Ligands and complex crystal were obtained by recrystallization using 50% DCM in ethanol. The X-ray diffraction studies for these crystals were performed on a

Bruker APEX-II CCD diffractometer with Mo Kα radiation (λ_o = 0.71073 Å) at 296K. The structure was solved using SHELXL-2007/2014 software and refined by full matrix least square methods. The crystallographic data of the ligand and complex are shown in Table 3.11. The molecular structures of L-1, its complex C-5, and L-2 are shown in (Fig. 3.71, 3.72, and 3.73, respectively).

Table 3.11 Crystallographic data of the ligand L-1, its complex C-5, and ligand L-2

Compound	**L-1**	**C-5**	**L-2**
Chemical formula	$C_{15}H_{13}NO_2$	$C_{30}H_{24}CuN_2O_4$	$C_{12}H_9BrN_2O$
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 2_1/C	P c a 2_1	P 2_1/C
Unit cell dimensions			
a (Å)	14.7983 (4)	28.3587 (12)	5.79290(10)
b (Å)	7.4185 (2)	8.0006 (4)	8.9062(2)
c (Å)	11.5988 (3)	10.6118 (4)	21.6227(5)
α (˚)	90	90	90
β (˚)	106.877 (2)	90	93.0550(10)
γ (˚)	90	90	90
Z	2	4	4
T (K)	296	296	296
V (Å^3)	1218.49	2407.68	1113.99(4)
R-Factor (%)	4.64	5.51	3.94

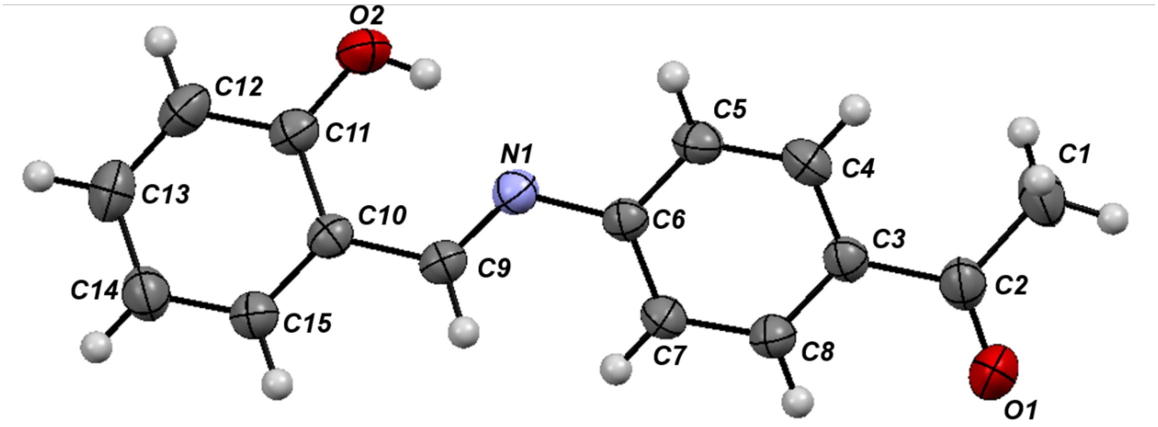


Figure 3.71 Single crystal structure of ligand L-1

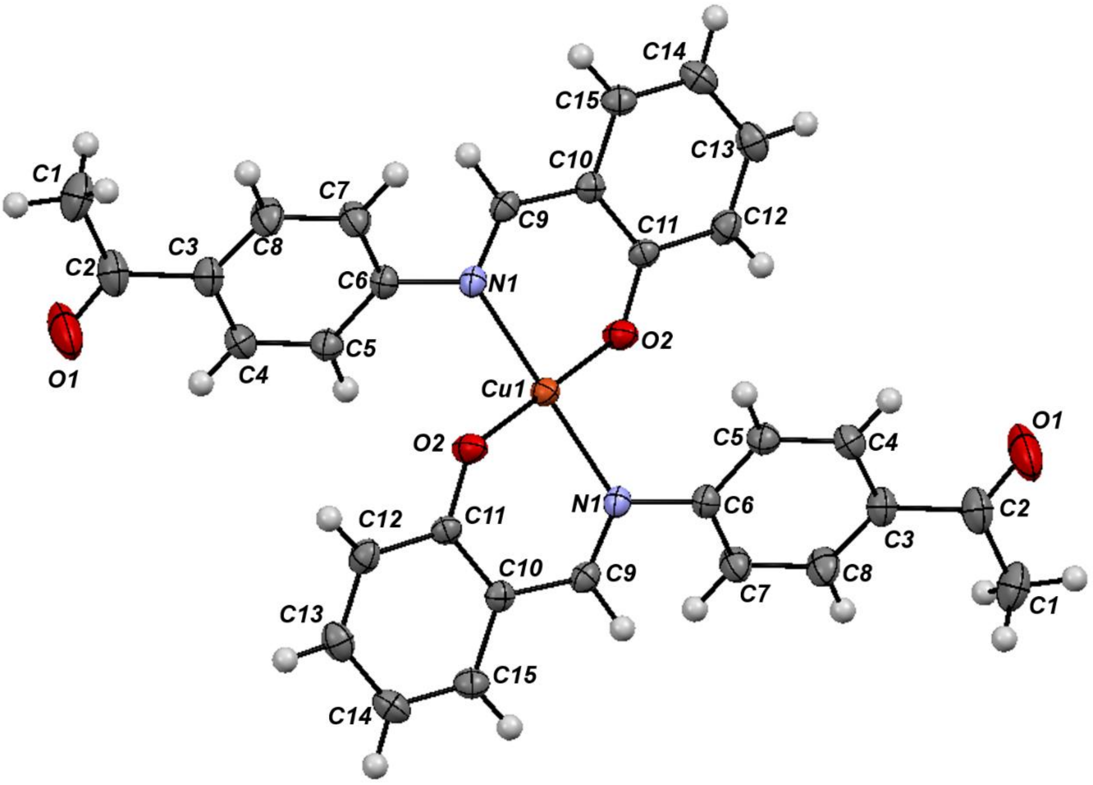


Figure 3.72 Single crystal structure of complex C-5

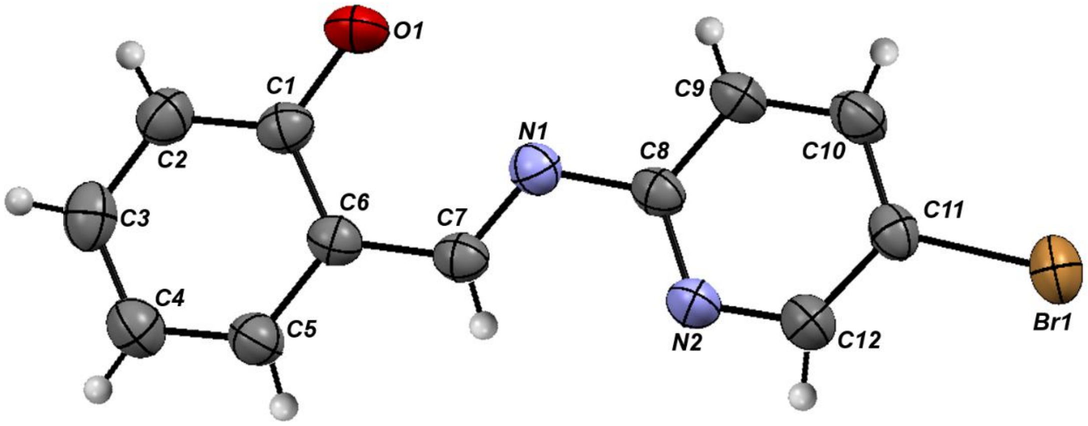


Figure 3.73 Single crystal structure of ligand L-2

Ligand L-4 crystal was obtained by slow evaporation method in ethanol. The crystallographic data of the ligand is shown in Table 3.12. The molecular structure of L-4 is shown in Fig. 3.74.

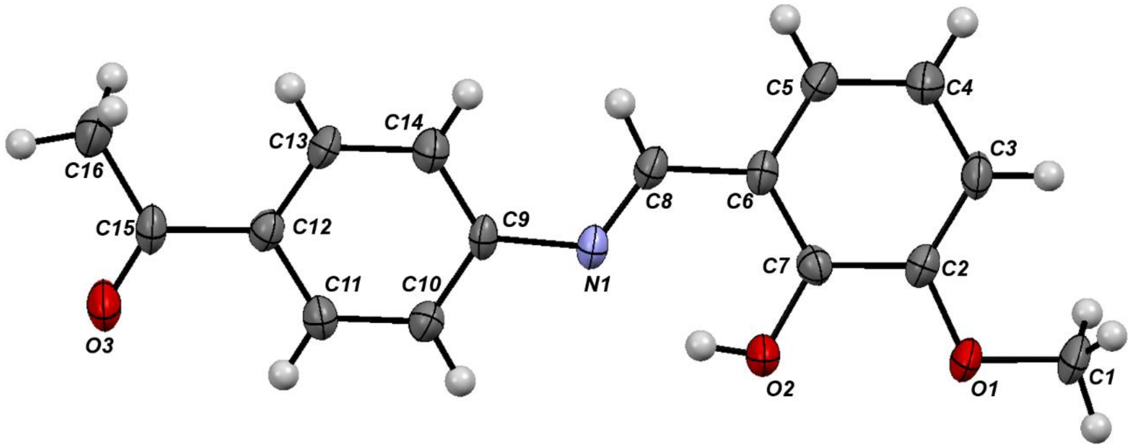


Figure 3.74 Single Crystal structure of ligand L-4

Table 3.12 Crystallographic data of the ligand (L-4)

Compound	**L-4**
Chemical formula	$C_{15}H_{15}NO_3$
Crystal system	Monoclinic
Space group	P 2_1/c
Unit cell dimensions	
a (Å)	14.932 (4)
b (Å)	6.913 (3)
c (Å)	13.973 (4)
α (°)	90
β (°)	113.530 (4)
γ (°)	90
Z	4
T (K)	296
Radiation (λ, Å)	Mo K_α (λ = 0.71073 Å) graphite monochromator
Number of reflections	2240
Number of refined parameters	184
Residual electron density (max/min), *e*/ Å^3	0.188/-0.200
V (Å^3)	1322.4 (7)
R-Factor (%)	8.17

The crystallographic data of complex (C-26 and C-27) is shown in Table 3.13. The molecular structure is shown in (Fig. 3.75 and 3.76). Selected interatomic distances (*d*) and bond angles (ω) in complex C-26 are given in Table 3.14 and 3.15 respectively. The crystallographic analysis of complex reveals that the unit cell contains two complex molecules. In complex molecule, metal atom is four-coordinated via two nitrogen atoms and two oxygen atoms from the deprotonated Schiff base ligand.

Table 3.13 Crystallographic data of the complex (C-26 and C-27)

Compound	**C-26**	**C-27**
Chemical formula	$C_{20}H_{14}N_2NiO_2$	$C_{20}H_{14}Cu\ N_2O_2$
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	5.4430 (3)	9.1346(5)
b (Å)	16.6157 (7)	18.0186(9)
c (Å)	17.2995 (8)	19.0127(9)
α (˚)	90	90
β (˚)	90	90
γ (˚)	90	90
Z	4	8
T (K)	296	296
V (Å^3)	1564.55	3129.4(3)
R-Factor (%)	3.17	3.1

Table 3.14 Selected Interatomic distances (*d*) in complex C-26

Bond	***d*, Å**	**Bond**	***d*, Å**
Ni1–O1	1.840	Ni1–N1	1.858
Ni1–O2	1.836	Ni1–N2	1.859

Table 3.15 Selected bond angles (ω) in complex C-26

Angle	ω, deg
O2 Ni1 O1	84.34 (7)
O2 Ni1 N2	94.74 (7)
O1 Ni1 N1	94.72 (7)
N2 Ni1 N1	86.20 (7)
O1 Ni1 N2	178.43 (7)
O2 Ni1 N1	179.03 (7)

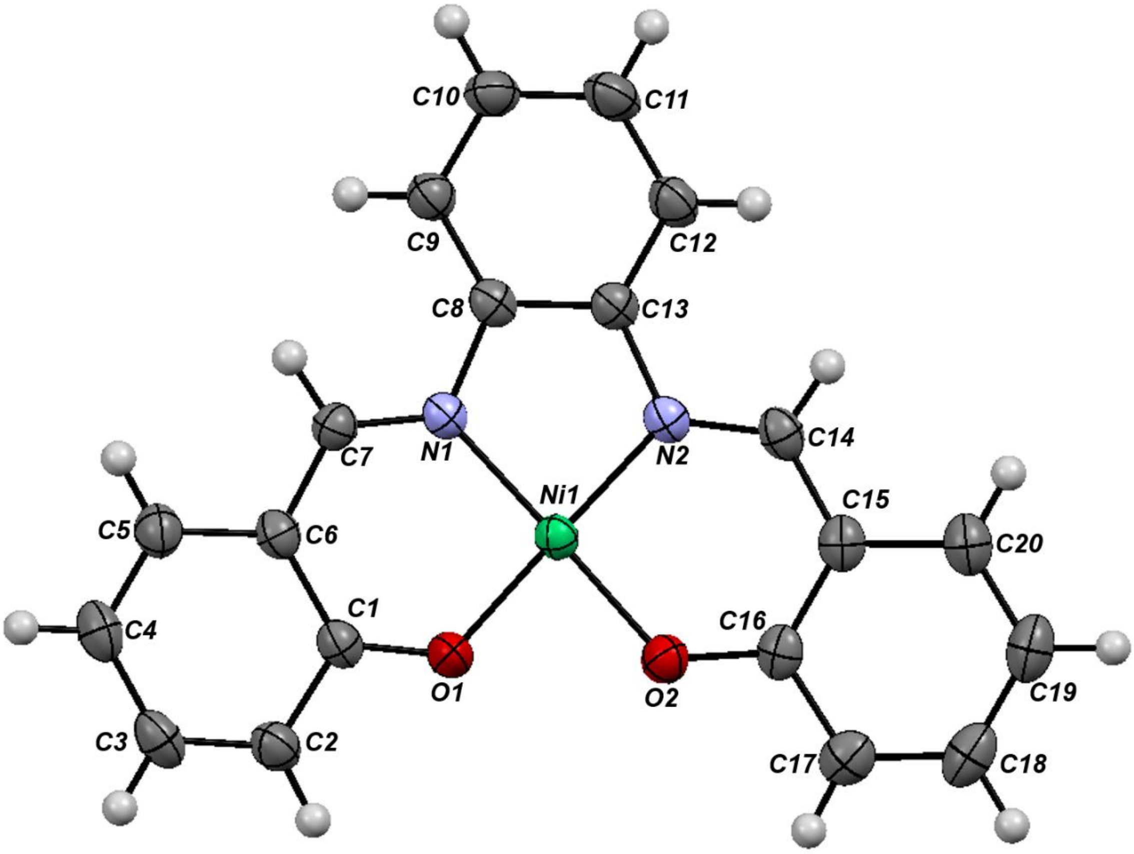


Figure 3.75 Single crystal structure of complex C-26

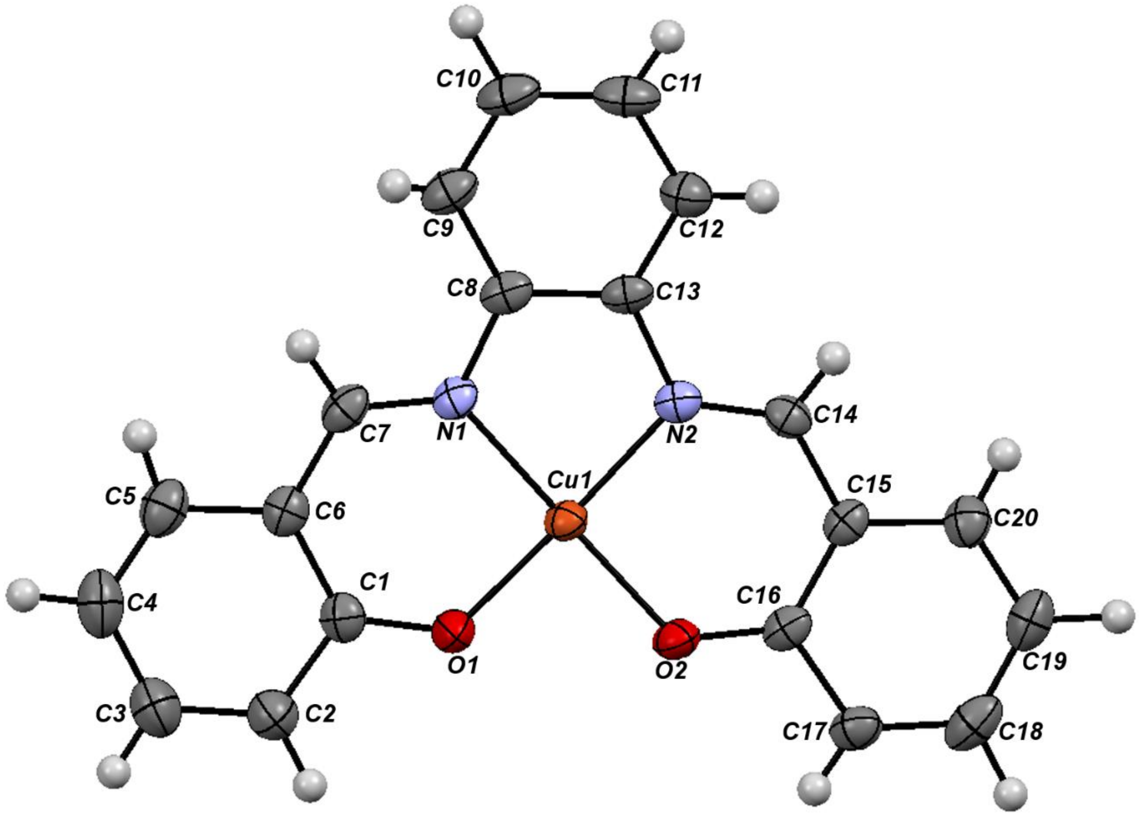


Figure 3.76 Single crystal structure of complex C-27

3.4 SUMMARY

Schiff base ligands (L-1, L-2, L-3, L-4, L-5 and L-6) were synthesized using 4-aminoacetophenone, 2-amino-5-bromopyridine, 2-aminophenol, and 1,2-phenylenediamine with different substituted aldehydes (salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-napthaldehyde). Complexes (C-1 to C-27) of few 3*d*-transition metals (Mn, Fe, Co, Ni, Cu) were synthesized using these six Schiff base ligands (L-1 to L-6). Synthesized ligands and complexes were characterized using relevant analytical techniques. All the results found were in good agreement with the proposed structure.

CHAPTER 4

APPLICATION OF METAL SCHIFF BASE COMPLEXES (C-1 to C-27) AS C-C COUPLING CATALYST

This chapter presents the catalytic activity of complexes (C-1 to C-27) in the Suzuki-Miyaura C-C Cross coupling of aryl halides and phenylboronic acid. Also, the effect of change of solvent, base, reaction time and concentration of the catalyst on the yield of cross coupling reaction has been described.

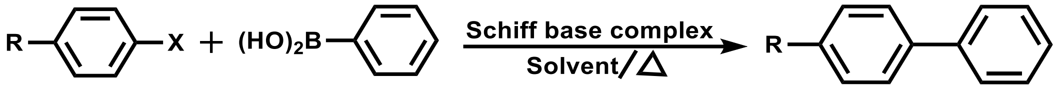
4.1 INTRODUCTION

The Suzuki cross-coupling reaction or simply Suzuki reaction is one of the most used cross-coupling reactions in modern organic synthesis, wherein a biphenyl molecule is being synthesized through coupling of an aryl halide or triflate to phenylboronic acid in the presence of a catalyst. High catalytic activity and selectivity has been achieved in C-C bond formation using palladium Schiff base complexes and to some with nickel and copper as the active metals. In practice, palladium (Pd) complexes are common catalyst for Suzuki coupling reactions, however, them being expensive and less abundant requires a search for more cost effective and eco-friendly catalysts. The research study aims to provide an alternative approach towards carrying out Suzuki reactions with Schiff base complexes of Mn, Fe, Co, Ni and Cu metal over the conventionally used palladium-phosphine ligand complexes which are not considered to be eco-friendly. The complexes are divided into 6 series namely, C-1 to C-5, C-6 to C-10, C-11 and C-12, C-13 to C-17, C-18 to C-22, and C-23 to C-27. This division is made on the basis of different ligands used to form metal complexes.

4.2 EXPERIMENTAL

4.2.1 General procedure for the Suzuki reaction

Aryl halide (1.0 mmol) was added to a mixture of phenylboronic acid (1.5 mmol), Schiff base complex (varied) and base (2.0 mmol) in 3 mL of solvent and heated to 80 ˚C for 16 hours. The mixture was then cooled to room temperature. Later, the organic layer was separated and analyzed by gas chromatography. Internal standard was used and calibrated against each and every one of the cross-coupling products.



4.2.2 Gas chromatography

The Gas Chromatography (GC) of the coupled product was done in GC2014 (Shimadzu, Japan) fitted with a 5% diphenyl and 95% siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector (FID). The temperature of the injection port was kept constant at 150 ˚C and 250 ˚C respectively during product analysis. After the injection of sample, the column temperature was increased from 60 ˚C to 150 ˚C at the rate of 10 ˚C/min and then further raised to 220 ˚C at the rate of 40 ˚C/min. Nitrogen gas was used as the carrier gas. The retention time for the products was determined by injecting the procured standards of the product under identical GC conditions.

4.3 RESULTS AND DISCUSSION

4.3.1 Catalytic activity studies of C-1 to C-5

The coupling of 4-bromobenzonitrile and phenylboronic acid was chosen as the model reaction to optimize the reaction conditions with synthesized catalyst.

The reaction conditions have been optimized with respect to

- Solvent and reaction temperature
- Base
- Catalyst concentration on the reaction
- Reaction time

(a) Effect of solvent and temperature

The catalytic activities of C-1 to C-5 were carried out in ethanol, toluene, THF, acetonitrile and 1,4-dioxane media (Fig. 4.1). Among the different solvents used, highest catalytic activity was observed with acetonitrile due to high polarity of the acetonitrile. Moderate catalyst activities were found in other solvents such as ethanol, THF, 1,4-dioxane and toluene. Acetonitrile was chosen as the optimum solvent for carrying out the reactions. With acetonitrile chosen as the solvent media, the other parameter considered for optimization is the reaction temperature. Reaction is found to work out best at its reflux temperature.

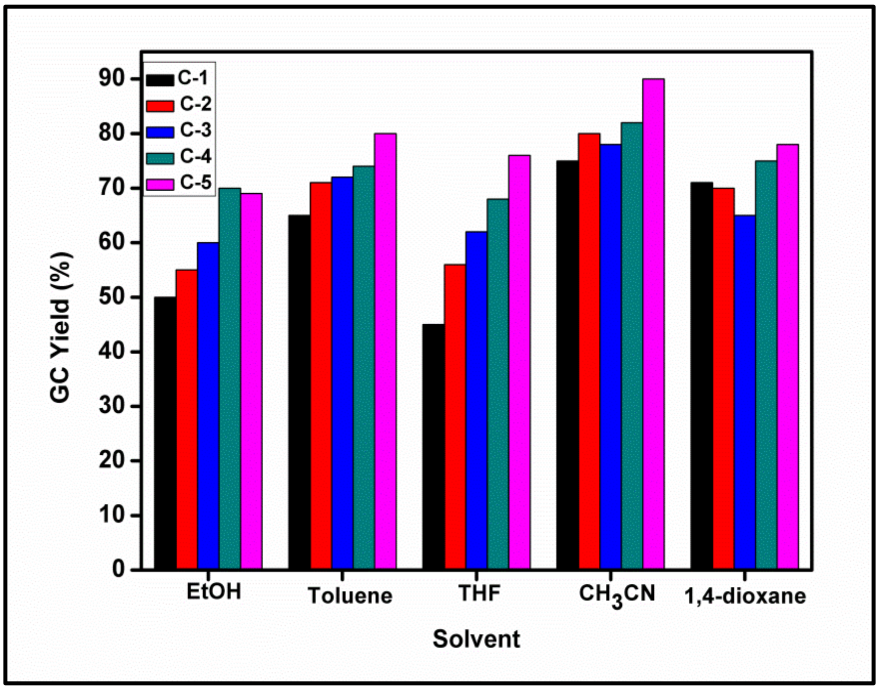


Figure 4.1 Effect of solvent on C-1 to C-5

(b) Effect of base on the reaction

The effect of bases on the product yield was examined for the coupling reaction. Et_3N was found to be the most effective base (Fig. 4.2). Slightly lower yields were obtained when Cs_2CO_3, K_2CO_3, Na_2CO_3, KOtBu were used as base.

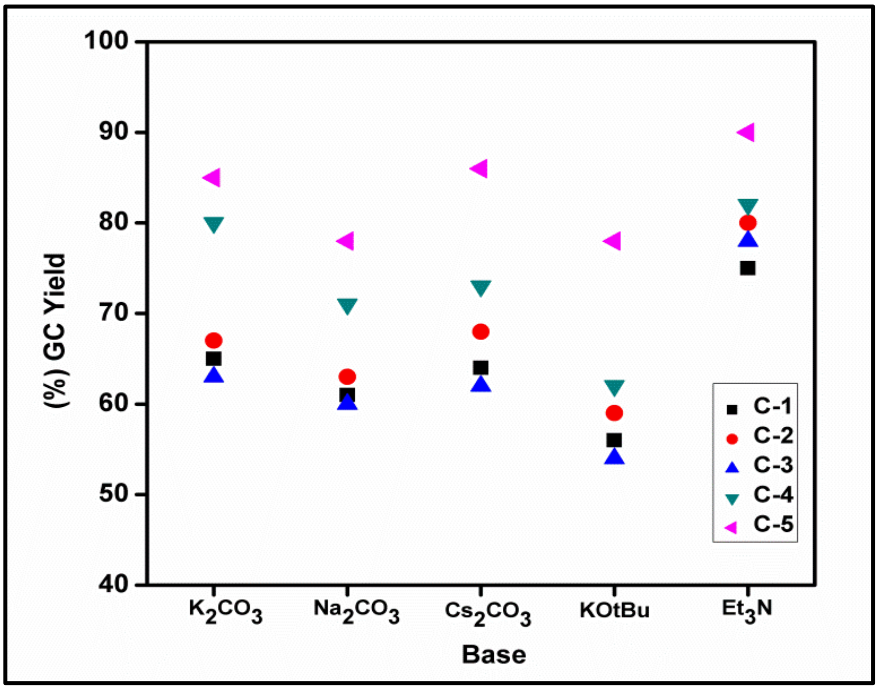


Figure 4.2 Effect of base on Suzuki coupling

(c) Effect of catalyst concentration on the reaction

Catalyst loading for the reaction was also considered for optimization. 0.02 mmol of the catalyst proved to be well efficient in catalyzing the reaction in acetonitrile media (Fig. 4.3).

(d) Effect of reaction time

The dependence of product yield on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time under similar conditions. Increase in yield was observed with increase in reaction time. Notable increase in the yield is observed up to 16 hours of reaction time, further which, there is no significant variation in the observed percentage yield (Fig. 4.4).

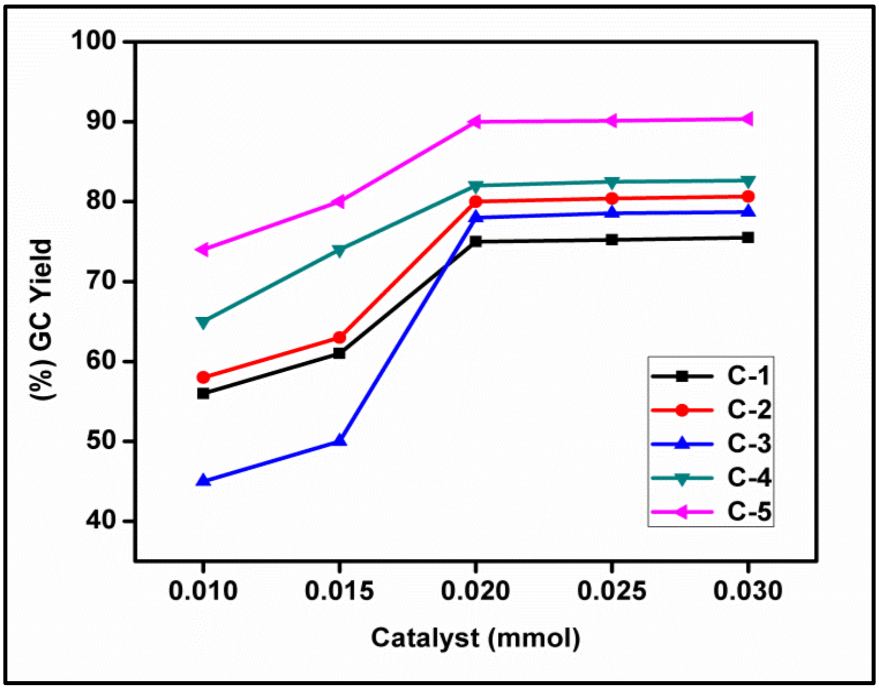


Figure 4.3 Effect of catalyst concentration for C-1 to C-5

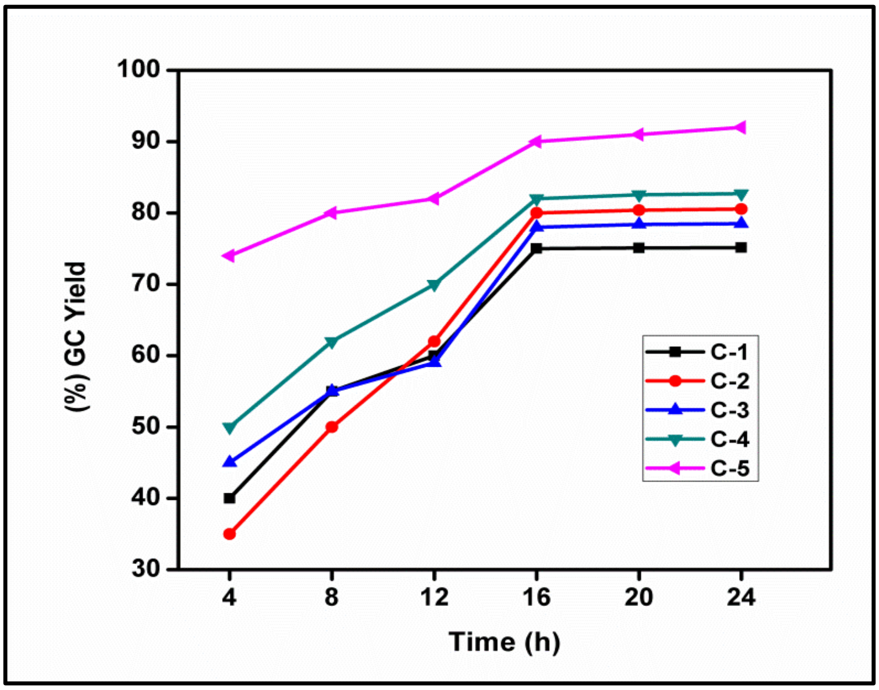


Figure 4.4 Effect of reaction time on C-1 to C-5

Further, different substituted aryl halides were used to extend the cross-coupling reaction with phenylboronic acid using the optimized reaction conditions. The results of different substituent are summarized in Table 4.1. All catalysts (C-1 to

C-5) were found to catalyze the coupling reactions very effectively. The conversion pattern different aryl halides with electron withdrawing groups accelerated the process of conversion to biaryls whereas presence of electron donating groups drop out the conversion (Bakherad et al. 2012). Iodide was observed to be a better leaving group than bromide.

Table 4.1 Catalytic activity study for complexes (C-1 to C-5).

Entry	**R**	**X**	**Yield**[a]				
			C-1	**C-2**	**C-3**	**C-4**	**C-5**
1	OCH_3	Br	58	64	60	64	65
2	H		45	55	50	52	62
3	CN		70	82	78	80	90
4	$COCH_3$		64	86	83	82	80
5	$NHCOCH_3$		65	75	74	73	72
6	OH		51	59	50	55	65
7	CH_3		46	61	54	60	62
8	F		42	46	40	42	50
9	OH	I	60	72	58	65	75
10	CN		72	86	79	81	91

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), Et_3N (2.0 mmol), catalyst (0.02 mmol), solvent (3 mL), 16 h.
[a] Yield determined by GC, average of 3 trials (Isolated yield).

4.3.2 Catalytic activity studies of C-6 to C-10

(a) Effect of solvent and temperature

The catalytic activities of C-6 to C-10 were carried out in DMF, THF, 1,4-dioxane, toluene and acetonitrile media (Fig. 4.5). The highest percentage conversion was observed with acetonitrile as the solvent media, closely followed by toluene and 1,4-dioxane. Acetonitrile was optimized as solvent media under reflux temperature for further reactions.

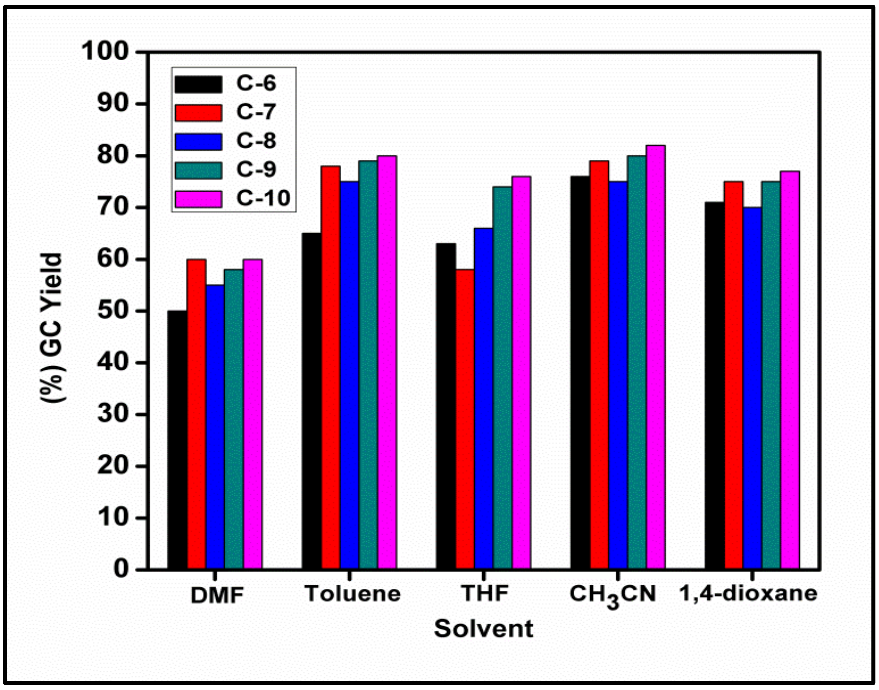


Figure 4.5 Effect of solvent on C-6 to C-10

(b) Effect of base

The effect of bases on the product yield was examined for the coupling reaction (Fig. 4.6). The highest percentage conversion was observed with base K_2CO_3 followed by the organic base Et_3N.

(c) Effect of catalyst concentration on the reaction

The effect of concentration of the catalyst on different substrate was studied at different substrate to catalyst ratios. The ratio was varied from total catalyst amount 0.01 mmol to 0.06 mmol. It was observed from the catalytic activity studies; the coupling yield increases with increase in catalyst loading. The yield of coupling product did not change much after 0.04 mmol concentrations (Fig. 4.7). 0.04 mmol of the catalyst proved to be well efficient in catalyzing the reaction in acetonitrile media.

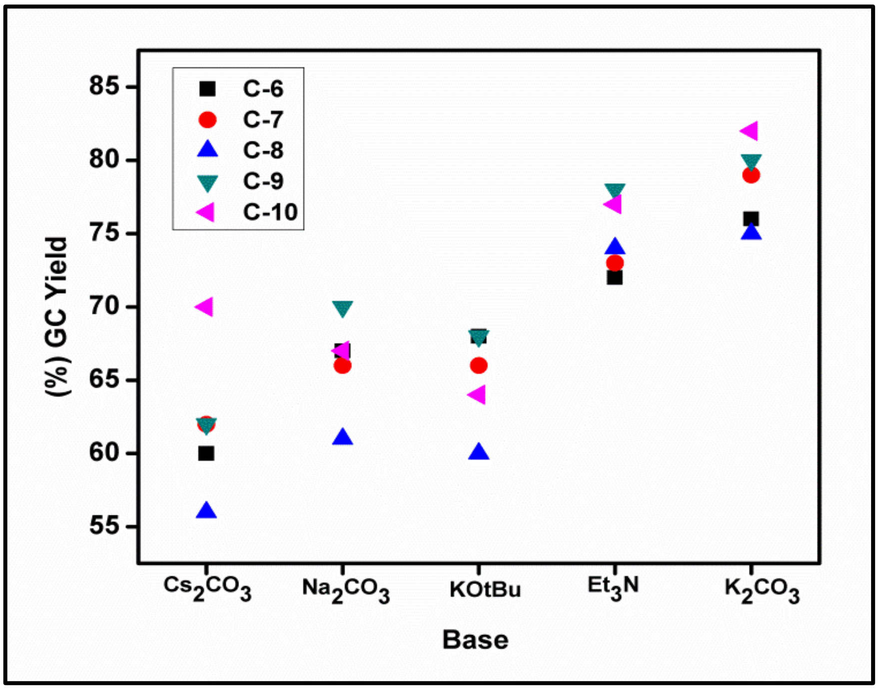


Figure 4.6 Effect of base on Suzuki coupling

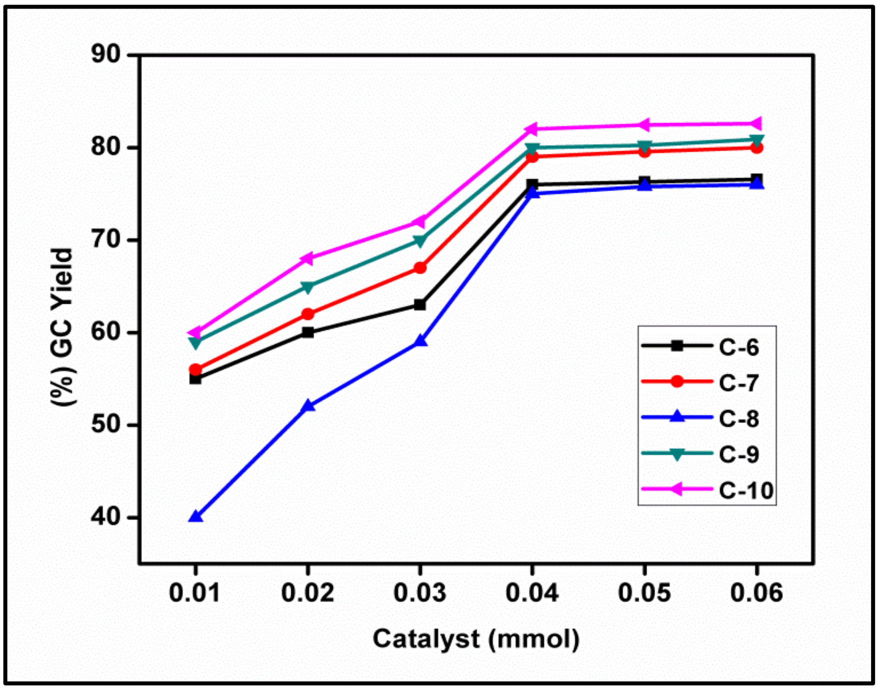


Figure 4.7 Effect of catalyst concentration for C-6 to C-10

(d) Effect of reaction time

Product yield dependence on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time. Product conversion was observed to increase with reaction time till the completion of 8 hours. The conversion remained almost insignificant after 8 hours (Fig. 4.8). Hence, optimized reaction time for coupling reaction was fixed at 8 hours.

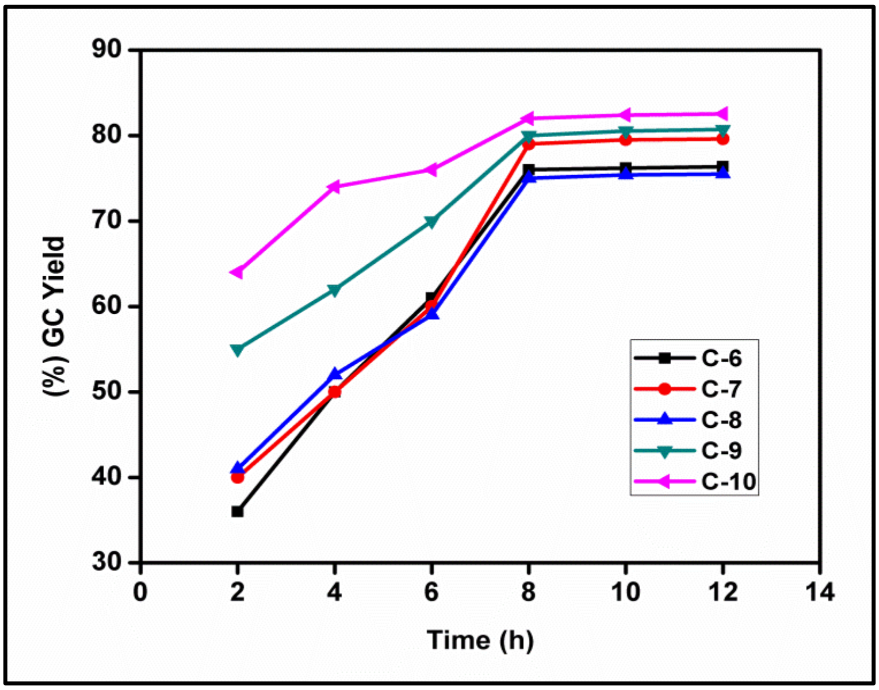


Figure 4.8 Effect of reaction time on C-6 to C-10

The cross-coupling reaction was extended to the coupling between phenylboronic acid and different aryl halides using the optimized reaction conditions. The results are summarized in Table 4.2. The catalysts (C-6 to C-10) were found to catalyze the coupling reactions effectively. The conversion pattern with different substituents on the aryl halides was different. Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas presence of electron donating groups brought about lesser conversion. Iodide was observed to be a better leaving group compared to bromide.

Table 4.2 Catalytic activity study for complexes (C-6 to C-10)

Entry	**R**	**X**	**Yield**[a]				
			C-6	**C-7**	**C-8**	**C-9**	**C-10**
1	OCH_3	Br	40	42	36	50	54
2	H		41	39	35	48	56
3	CN		80	79	75	81	85
4	$COCH_3$		67	69	65	75	78
5	$NHCOCH_3$		60	62	59	65	71
6	OH		53	54	48	57	62
7	CH_3		53	54	52	56	60
8	F		42	44	38	52	56
9	OH	I	63	64	58	67	72
10	CN		80.50	80	77	82	86

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.04 mmol), solvent (3 mL), 8 h.
[a] GC yields, average of 3 trials (Isolated yield).

4.3.3 Catalytic activity studies of C-11 & C-12

(a) Effect of solvent and temperature

The catalytic activities of C-11 & C-12 were carried out in 1,4-dioxane, toluene, DMF, THF and acetonitrile media (Fig. 4.9). The highest percentage conversion was observed with toluene as the solvent media, closely followed by 1,4-dioxane and acetonitrile. Toluene was optimized as solvent media under reflux temperature for further reactions.

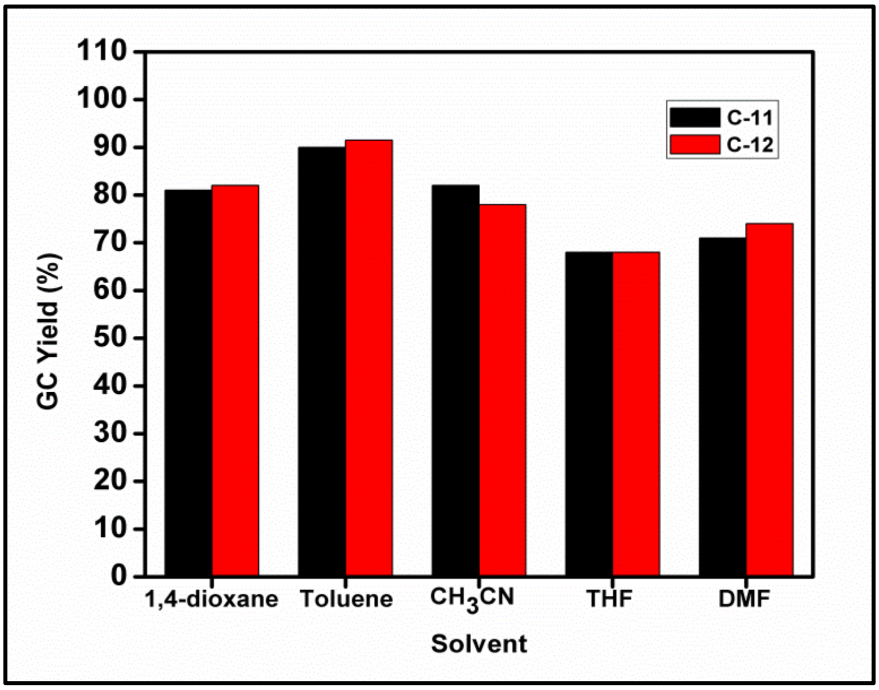


Figure 4.9 Effect of solvent on C-11 & C-12

(b) Effect of base

The effect of bases on the product yield was examined for the coupling reaction (Fig. 4.10). The highest percentage conversion was observed with base K_2CO_3 followed by the Cs_2CO_3 and organic base Et_3N.

(c) Effect of catalyst concentration on the reaction

The effect of concentration of the catalyst on different substrate was studied at different substrate to catalyst ratios. The ratio was varied from total catalyst amount 0.02 mmol to 0.14 mmol. It was observed from the catalytic activity studies; the coupling yield increases with increase in catalyst loading. The yield of coupling product did not change much after 0.1 mmol concentrations (Fig. 4.11). 0.1 mmol of the catalyst proved to be well efficient in catalyzing the reaction in toluene media.

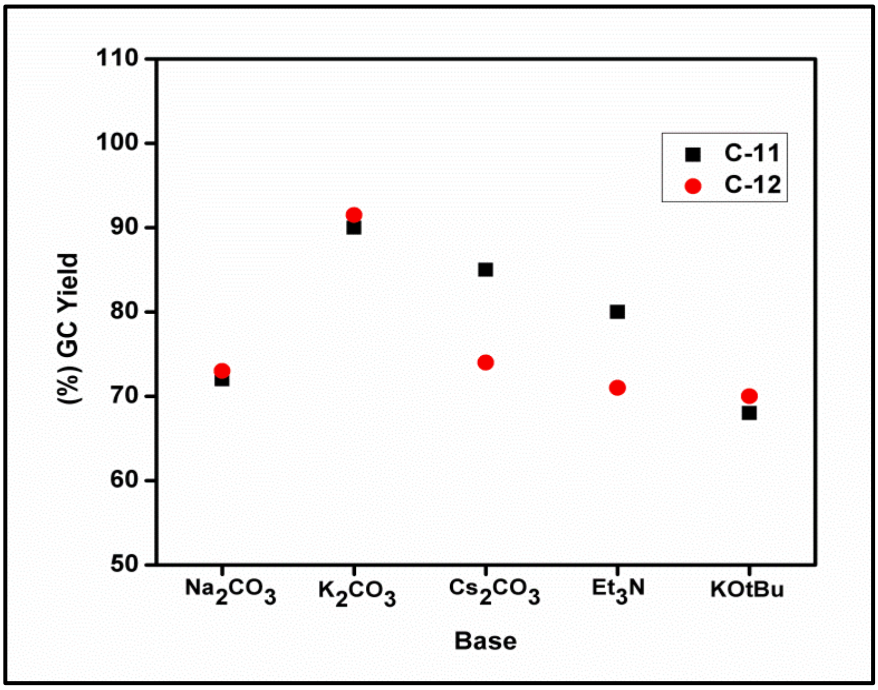


Figure 4.10 Effect of base on Suzuki coupling

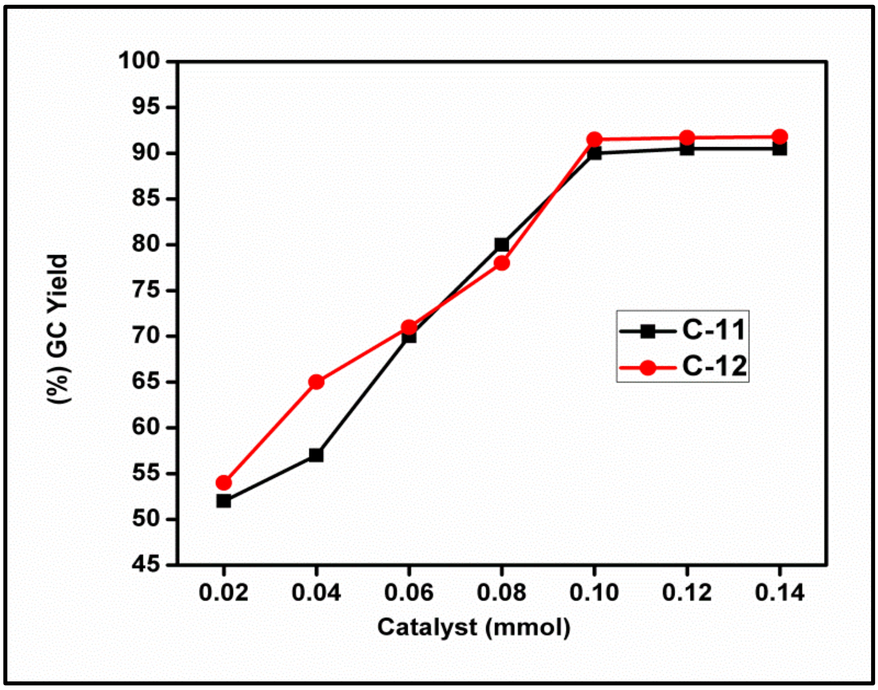


Figure 4.11 Effect of catalyst concentration for C-11 & C-12

(d) Effect of reaction time

Product yield dependence on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time. Product conversion was observed to increase with reaction time till the completion of 8 hours. The conversion remained almost insignificant after 8 hours (Fig. 4.12). Hence, optimized reaction time for coupling reaction was fixed at 8 hours.

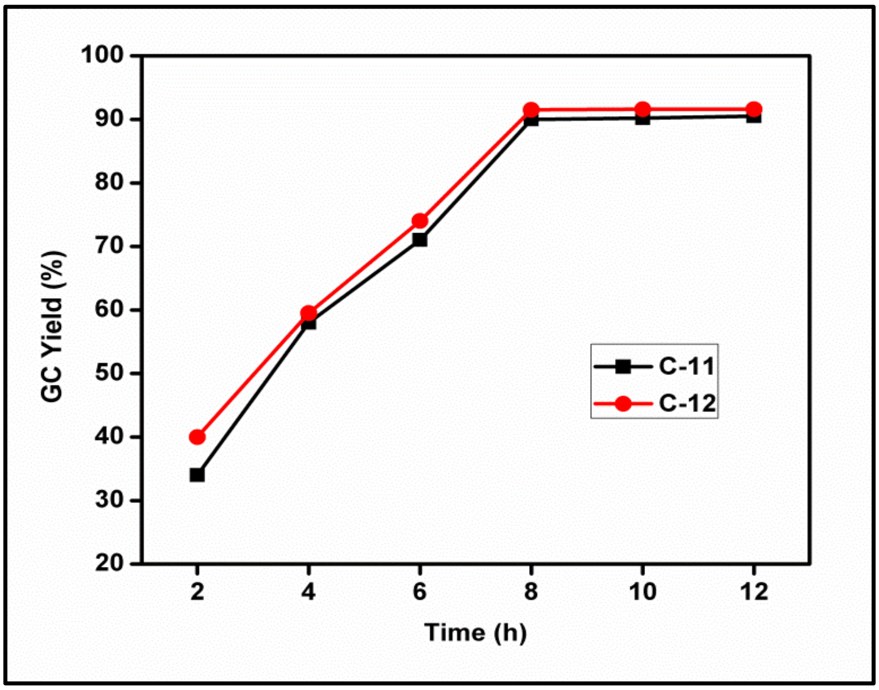


Figure 4.12 Effect of reaction time on C-11 & C-12

The cross-coupling reaction was extended to the coupling between phenylboronic acid and different aryl halides using the optimized reaction conditions. The results are summarized in Table 4.3. The catalysts (C-11 & C-12) were found to catalyze the coupling reactions effectively. The conversion pattern with different substituents on the aryl halides was different. Electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas presence of electron donating groups brought about lesser conversion.

Table 4.3 Catalytic activity study for complexes **(C-11 & C-12)**

Entry	**R**	**X**	**Yield[a]**	
			C-11	**C-12**
1	OCH_3	Br	64	65
2	H		48	51
3	CN		90	91.5
4	$COCH_3$		82	82
5	$NHCOCH_3$		71	71.5
6	OH		55	56
7	CH_3		44	51
8	F		53	55
9	OH	I	73	72
10	CN		91	92

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.1 mmol), solvent (3 mL), 8 h.
[a] GC yields, average of 3 trials (Isolated yield).

4.3.4 Catalytic activity studies of C-13 to C-17

(a) Effect of solvent and temperature

The catalytic activities of C-13 to C-17 were carried out in DMF, toluene, THF, acetonitrile and 1,4-dioxane media (Fig. 4.13). Among the different solvents used, highest catalytic activity was observed with toluene. Moderate catalyst activities were found in other solvents such as acetonitrile, THF, 1,4-dioxane and DMF. Toluene was chosen as the optimum solvent for carrying out the reactions. With toluene chosen as the solvent media, the other parameter considered for optimization is the reaction temperature. Reaction was carried out at reflux temperature of solvents.

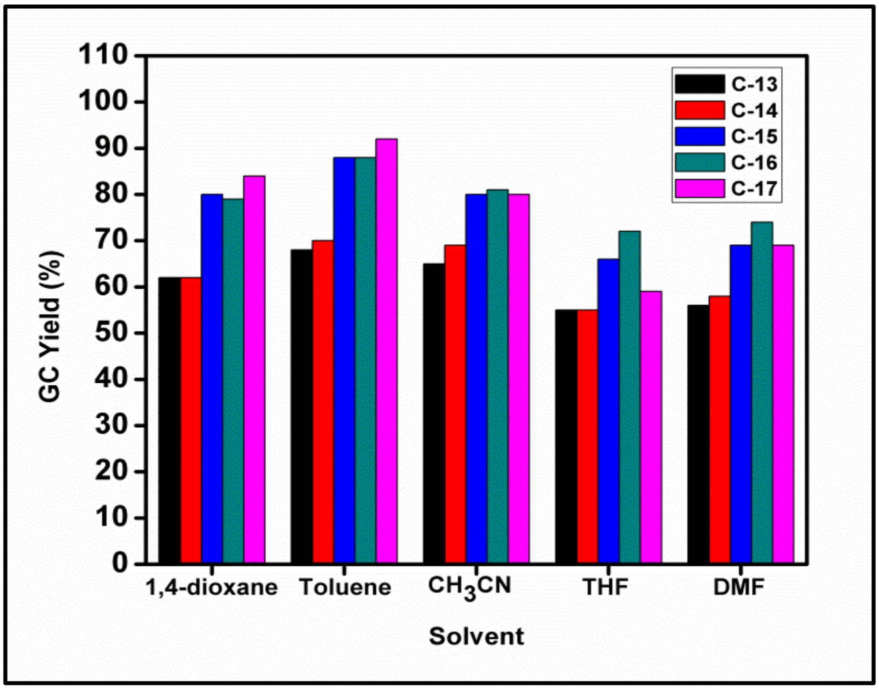


Figure 4.13 Effect of solvent on C-13 to C-17

(b) Effect of base on the reaction

The effect of bases on the product yield was examined for the coupling reaction. K_2CO_3 (mild base) was found to be the most effective base (Fig. 4.14). Slightly lower yields were obtained when Cs_2CO_3, Et_3N, Na_2CO_3, KOtBu were used as base.

(c) Effect of catalyst concentration on the reaction

Catalyst loading for the reaction was also considered for optimization. 0.1 mmol of the catalyst proved to be well efficient in catalyzing the reaction in toluene media (Fig. 4.15).

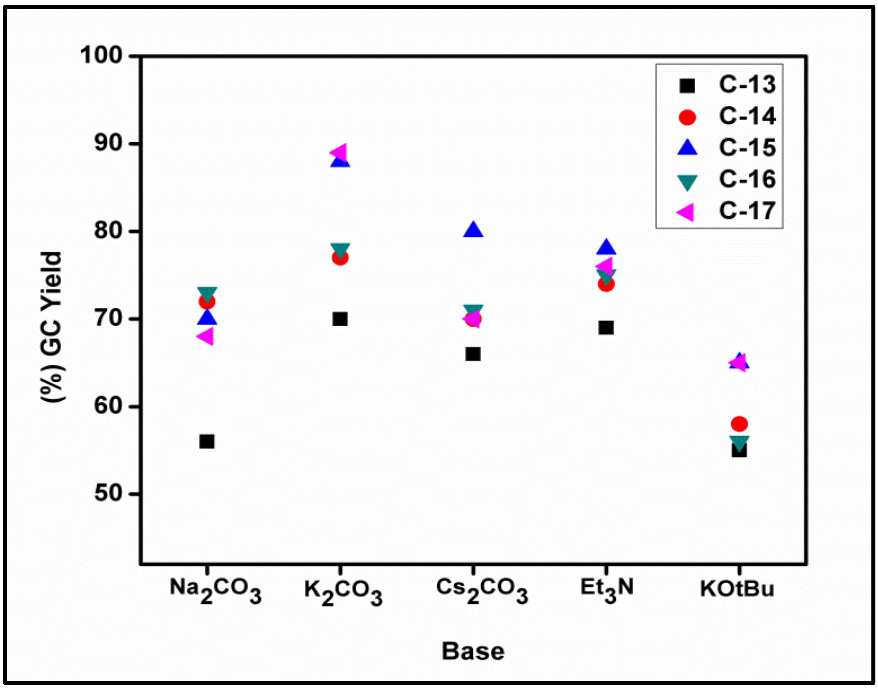


Figure 4.14 Effect of base on Suzuki coupling

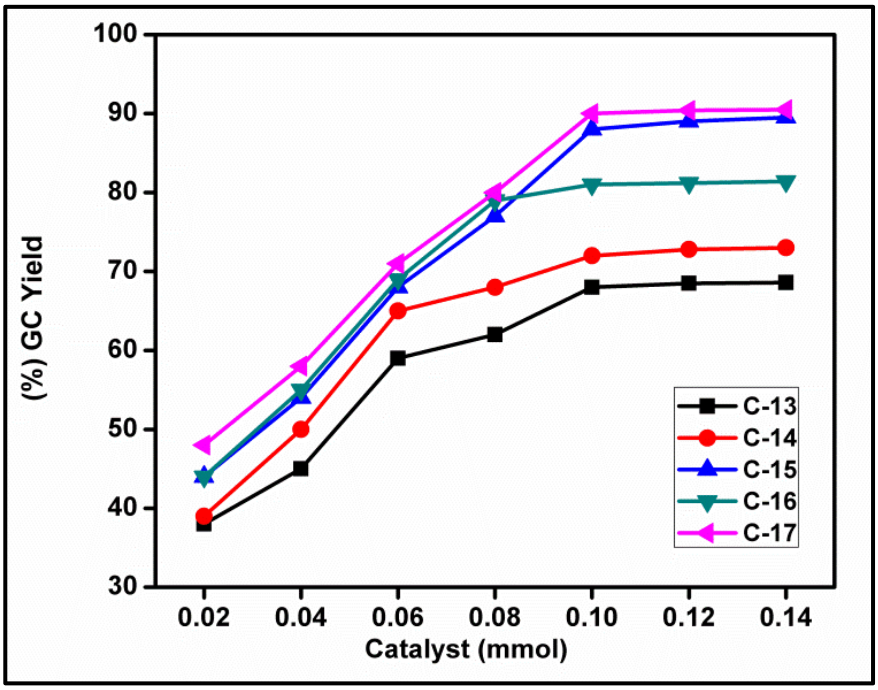


Figure 4.15 Effect of catalyst concentration for C-13 to C-17

(d) Effect of reaction time

The dependence of product yield on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time under similar conditions. Increase in yield was observed with increase in reaction time. Yield variance is apparent to a notable extent up to 8 hours of reaction time, further advance in reaction time no much effect on the percentage conversion of the product was observed (Fig. 4.16).

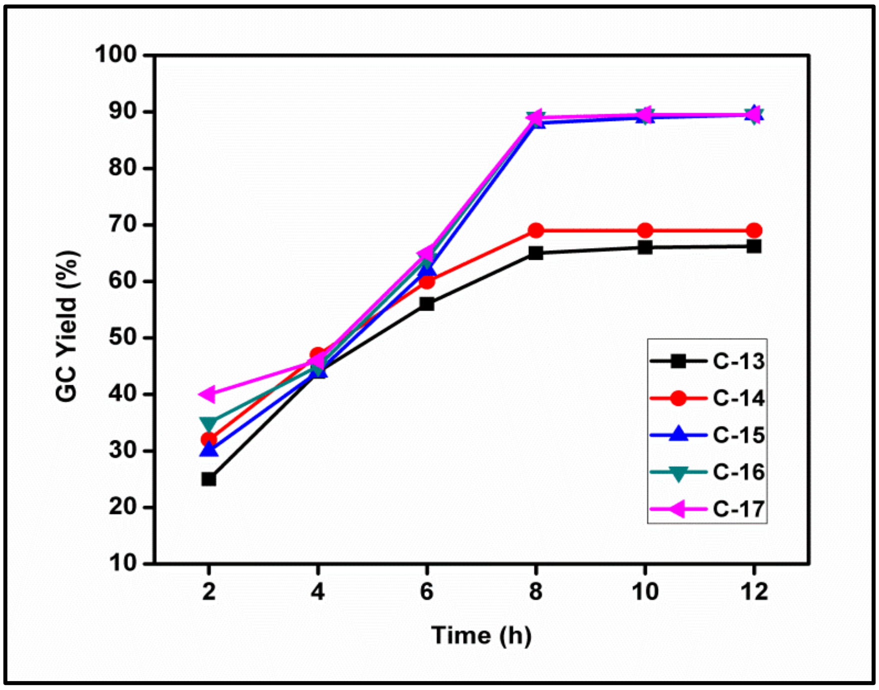


Figure 4.16 Effect of reaction time on C-13 to C-17

Further, different substituted aryl halides were used to extend the cross-coupling reaction with phenylboronic acid using the optimized reaction conditions. The results of different substituent are summarized in Table 4.4. All catalysts (C-13 to C-17) were found to catalyze the coupling reactions very effectively. The conversion pattern different aryl halides with electron withdrawing groups accelerated the process of conversion to biaryls whereas presence of electron donating groups drop out the conversion. Yield for coupling of substituted aryl iodide with phenylboronic acid was found to be more, since iodide is a better leaving group than bromide (Bakherad et al. 2013).

Table 4.4 Catalytic activity study for complexes **(C-13 to C-17)**

Entry	**R**	**X**	**Yield**[a]				
			C-13	**C-14**	**C-15**	**C-16**	**C-17**
1	OCH_3	Br	50	52	60	64	65
2	H		35	38	45	45	46
3	CN		68	70	88	88	92
4	$COCH_3$		77	79	80	81	82
5	$NHCOCH_3$		63	65	70	71	72
6	OH		49	50	51	59	61
7	CH_3		42	43	40	42	45
8	F		44	46	52	53	54
9	OH	I	66	68	69	70	73
10	CN		72	75	90	90	93

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.1 mmol), solvent (3 mL), 8 h.
[a] Yield determined by GC, average of 3 trials (Isolated yield).

4.3.5 Catalytic activity studies of C-18 to C-22

(a) Effect of solvent and temperature

The catalytic activities of C-18 to C-22 were carried out in 1,4-dioxane, toluene, DMF, THF and acetonitrile media (Fig. 4.21). Among the different solvents used, highest catalytic activity was observed with toluene. Moderate catalyst activities were found in other solvents such as acetonitrile, THF, 1,4-dioxane and DMF. Toluene was chosen as the optimum solvent for carrying out the reactions. With toluene chosen as the solvent media, the other parameter considered for optimization is the reaction temperature. Reaction was carried out at reflux temperature of solvents.

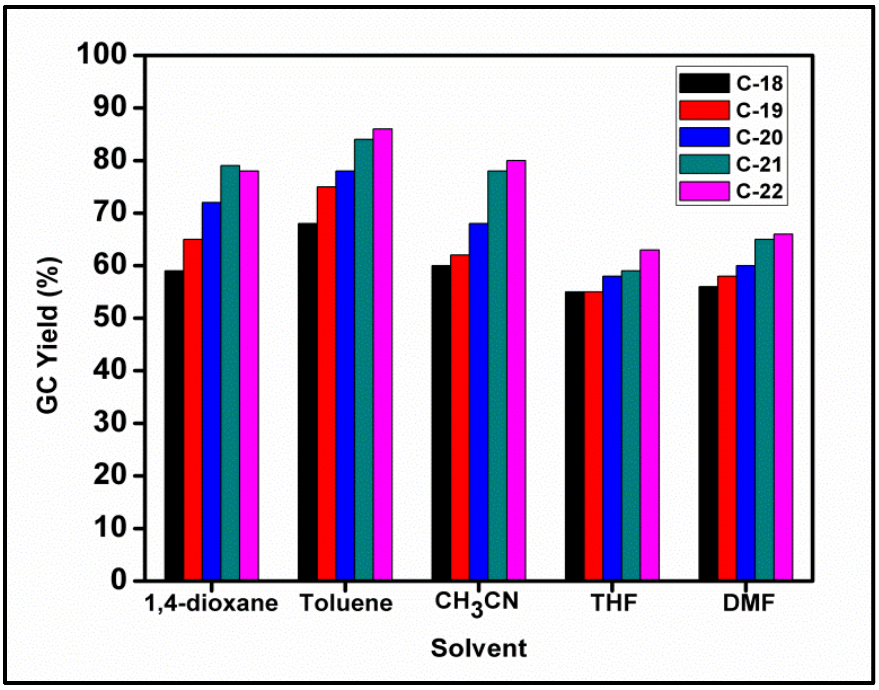


Figure 4.21 Effect of solvent on C-18 to C-22

(b) Effect of base on the reaction

The effect of bases on the product yield was examined for the coupling reaction. K_2CO_3 was found to be the most effective base (Fig. 4.22). Slightly lower yields were obtained when Et_3N, Cs_2CO_3, Na_2CO_3, KOtBu were used as base.

(c) Effect of catalyst concentration on the reaction

Catalyst loading for the reaction was also considered for optimization. 0.1 mmol of the catalyst proved to be well efficient in catalyzing the reaction in toluene media (Fig. 4.23).

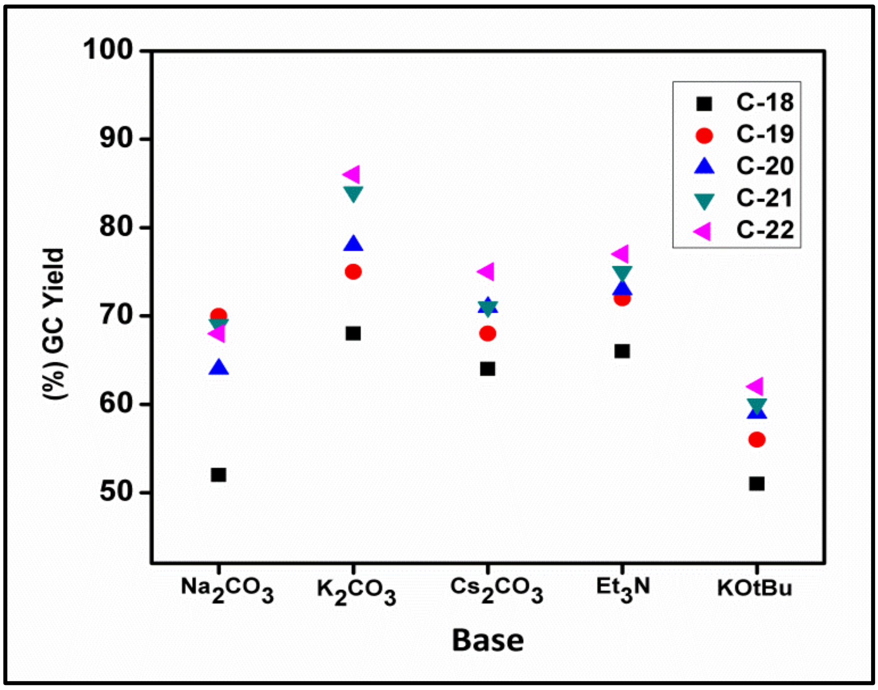


Figure 4.22 Effect of base on Suzuki coupling

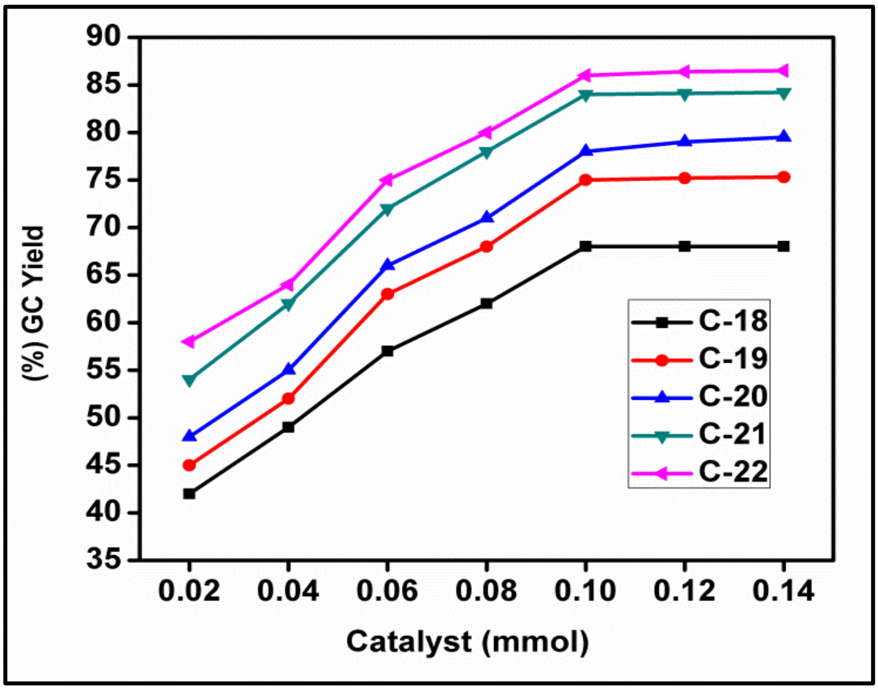


Figure 4.23 Effect of catalyst concentration for C-18 to C-22

(d) Effect of reaction time

The dependence of product yield on the reaction time was investigated by analyzing the reaction mixture at regular intervals of time under similar conditions. Increase in yield was observed with increase in reaction time. Yield variance is apparent to a notable extent up to 8 hours of reaction time, further advance in reaction time no much effect on the percentage conversion of the product was observed (Fig. 4.24).

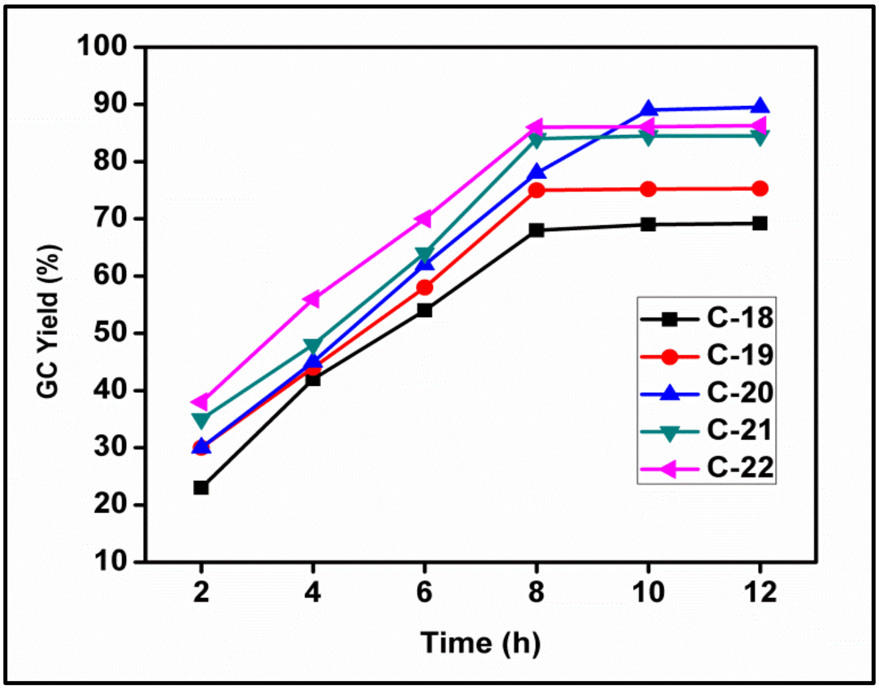


Figure 4.24 Effect of reaction time on C-18 to C-22

Further, different substituted aryl halides were used to extend the cross-coupling reaction with phenylboronic acid using the optimized reaction conditions. The results of different substituent are summarized in Table 4.5. All catalysts (C-18 to C-22) were found to catalyze the coupling reactions very effectively. The conversion pattern different aryl halides with electron withdrawing groups accelerated the process of conversion to biaryls whereas presence of electron donating groups drop out the conversion.

Table 4.5 Catalytic activity study for complexes **(C-18 to C-22)**

Entry	**R**	**X**	**Yield**[a]				
			C-18	**C-19**	**C-20**	**C-21**	**C-22**
1	OCH_3	Br	50	53	51	59	63
2	H		31	37	35	46	48
3	CN		69	76	79	85	87
4	$COCH_3$		68	75	78	84	86
5	$NHCOCH_3$		64	65	66	70	71
6	OH		47	48	49	57	59
7	CH_3		40	46	44	48	57
8	F		42	47	54	59	68
9	OH	I	52	53	55	61	63
10	CN		70	77	80	85.5	88

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.1 mmol), solvent (3 mL), 8 h.
[a] Yield determined by GC, average of 3 trials (Isolated yield).

4.3.6 Catalytic activity studies of C-23 to C-27

(a) Effect of solvent and temperature

The catalytic activities of C-23 to C-27 were carried out in DMF, toluene, THF, CH_3CN and 1,4-dioxane media (Fig. 4.25). Solvent optimization study indicates 1,4-dioxane to be the optimum solvent for coupling at 100 ˚C.

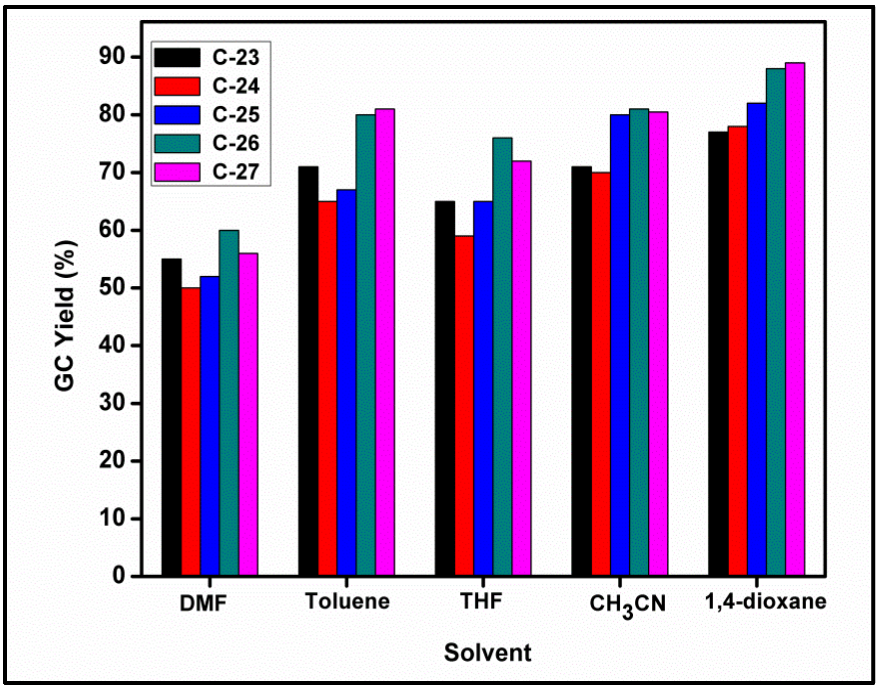


Figure 4.25 Effect of solvent on C-23 to C-27

(b) Effect of base

The effect of various bases in the coupling reaction of 4-bromobenzonitrile with phenylboronic acid was investigated in 1,4-dioxane media. It was found that K_2CO_3 the most effective base (Fig. 4.26). Other bases such as Na_2CO_3, Et_3N, Cs_2CO_3 and KO^tBu were less effective.

(c) Effect of catalyst concentration on the reaction

In order to study the effect of concentration of the catalyst with respect to substrate, the reaction was studied at different substrate to catalyst ratios. The ratio was varied from total catalyst amount 0.01 mmol to 0.04 mmol (Fig. 4.27). From the catalytic activity studies, it was observed that, increase in catalyst loading increases the coupling yield and after reaching the optimum concentration further increase of catalyst amount did not affect the yield of coupling product significantly and remained almost constant. 0.02 mmol of the catalyst proved to be well efficient in catalyzing the reaction.

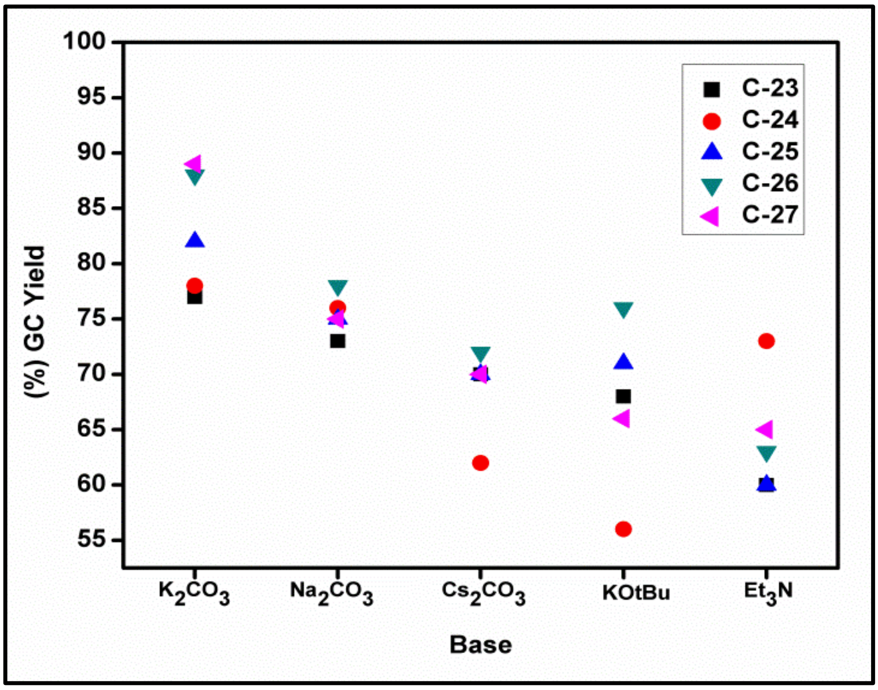


Figure 4.26 Effect of base on Suzuki coupling

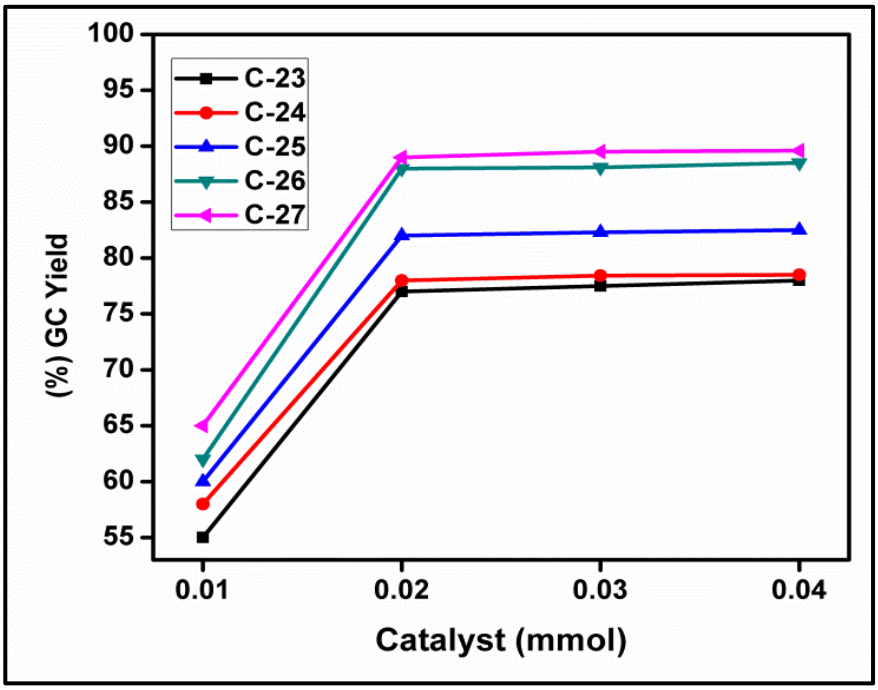


Figure 4.27 Effect of catalyst concentration for C-23 to C-27

(d) Effect of reaction time

The dependence of product yield on reaction time for the coupling of 4-bromobenzonitrile with phenylboronic acid was carried out by analyzing the reaction mixture at regular intervals of the time under same reaction condition. It could be analyzed that there was increase in the yield of product with time until 8 hours after which there was negligible change in the product yield (Fig. 4.28)

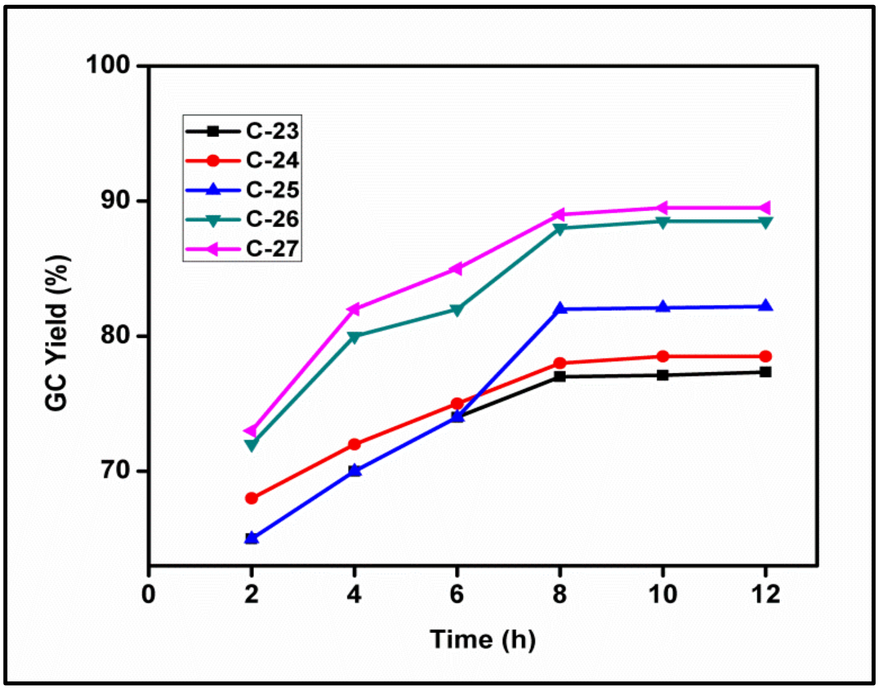


Figure 4.28 Effect of reaction time on C-23 to C-27

Based on the results, the reaction was extended to the cross coupling between different aryl halides and phenylboronic acid using the optimized reaction conditions. The results of these reactions are summarized in Table 4.6. The catalysts (C-23 to C-27) were found to catalyze the coupling reactions very effectively. The conversion pattern with different substituents on the aryl halides were similar to that of the earlier two series, i.e. electron withdrawing groups on the aryl halides accelerated the process of conversion to biaryls whereas presence of electron donating groups brought about lesser conversion. Among the halides, iodide was observed to be a better leaving group.

Table 4.6 Catalytic activity study for complexes (C-23 to C-27)

Entry	R	X	Yield^{a}				
			C-23	**C-24**	**C-25**	**C-26**	**C-27**
1	OCH_3	Br	64	64	60	64	65
2	H		32	34	35	45	46
3	CN		77	78	82	88	89
4	$COCH_3$		75	77	80	82	81
5	$NHCOCH_3$		65	68	70	71	72
6	OH		50	50	51	55	57
7	CH_3		40	42	44	44	43
8	F		43	43	50	58	59
9	OH	I	62	66	68	72	73
10	CN		78	80	85	90	91

Reaction conditions: Aryl halide (1.0 mmol), Phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.02 mmol), solvent (3 mL), 8 h.
[a] GC yields, average of 3 trials (Isolated yield).

4.4 PROPOSED MECHANISM FOR SUZUKI REACTION

The proposed mechanism is depicted in Fig. 4.13 for the synthesized metal Schiff base catalyzed reaction. The catalytic metal M(II) Schiff base complex getting reduced to M(0) (Beccalli et. al. 2007). It can be assume that the catalyst precursor (a) gets reduced to active M(0) species (b) in the presence of phenylboronic acid and base (K_2CO_3). The oxidative addition of metal complex to the aryl halide to forms the organometal species (c). Reaction with base gives intermediate (d), which via transmetalation with the phenylboronic acid forms the organometal species (e). Reductive elimination of the coupled product (f) brings back the original catalyst (b) which completes the catalytic cycle.

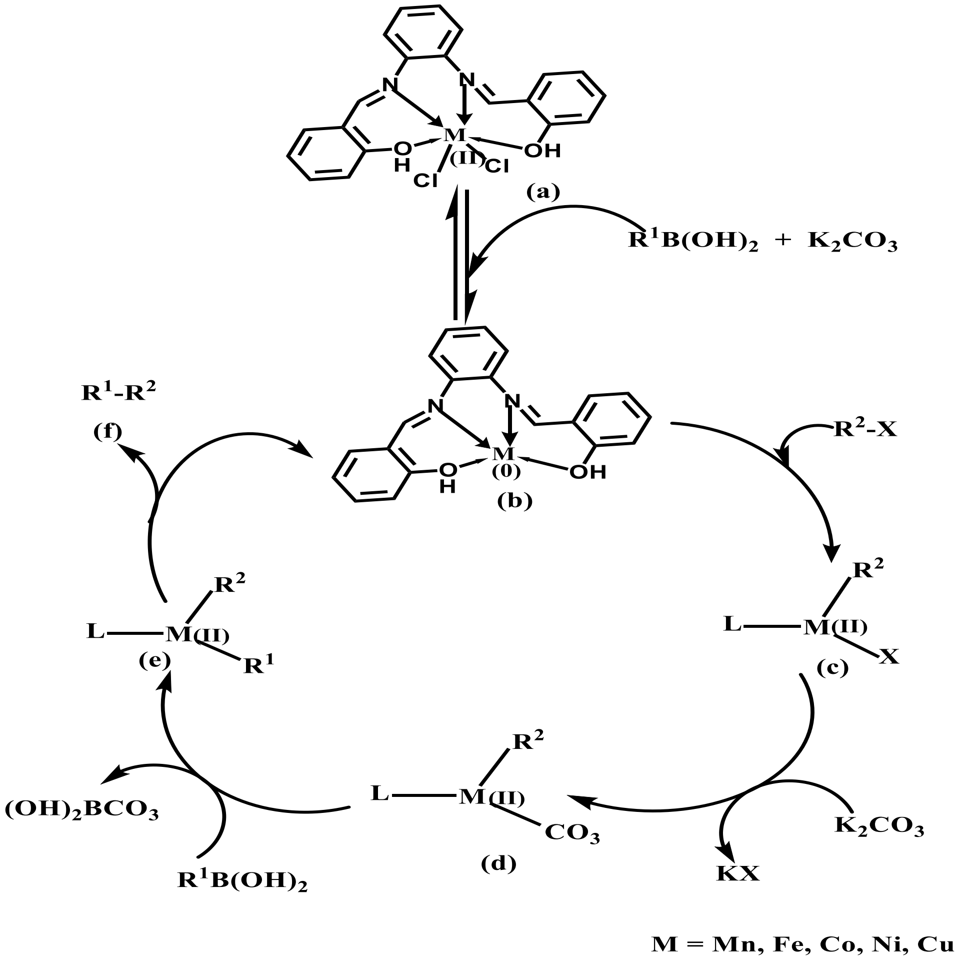


Figure 4.13 Proposed mechanism for Suzuki reaction

4.5 SUMMARY

The synthesized complexes (C-1 to C-27) were examined for their C-C coupling efficiency in Suzuki cross-coupling between phenylboronic acid and para substituted aryl halides. Effect of synthesized ligands on the catalytic activity of the complexes was explored based on the basis of coupling yields.

CHAPTER 5

SYNTHESIS CHARACTERIZATION AND CATALYTIC APPLICATION OF NANO Fe (II), Ni (II)-SCHIFF BASE COMPLEXES (C-28 & C-29)

In this chapter, a brief introduction of the nano-catalyst and their importance in the field of catalysis has been described. The synthesis of nano iron and nickel-Schiff base complex has been mentioned along with their catalytic studies in Suzuki-Miyaura coupling reactions.

5.1 INTRODUCTION

Formation of C-C bond by transition metal-catalyzed coupling reaction is understood to be a powerful tool for synthetic investigations. These complexes play a significant role in development of coordination chemistry in field of catalysis and enzymatic reactions, magnetism and molecular architectures, and liquid-crystal technology (Gingsberg 1971; Kagan 1972; Ohta et al. 1986; Siegbahn 2006). In addition, transition-metal nanoparticles for formation of carbon-carbon bonds are attractive to researchers (Moreno-Mañas and Pleixats 2003). Among, various catalytically active nanoparticles, palladium nanoparticles have gained considerable attention for the formation of C-C bonds (Dehbanipour et al. 2017). Nanoparticles have attained great interest in recent years as a result of their unique chemical and physical properties, which differ from their bulk materials, single atoms and can have potential applications in optoelectronics, catalysis, and ceramics etc. (Teranishi et al. 1998; Johnson 2003; Zhang et al. 2004).

Transition-metals like nickel, cobalt, copper, iron etc. have also been utilized for the formation of C-C bond (Nakamura and Yoshikai 2010). Recently, Fe_3O_4 nanoparticles (NPs) have been investigated as an efficient catalysts for C-C bond formation (Firouzabadi et al. 2011). However, the functional applications of Schiff bases and their metal complexes greatly rely on several properties, such as complexation ability towards metals, antibacterial activity (Raman et al. 2001) etc. On the other hand, the particle size plays important role on catalysis, so the synthesis of nano-sized compound has a basal role in many fields. In addition, the coupling of aryl halides with phenylboronic acids under mild condition is a subject of immense interest for both academicians and researchers.

In this chapter, we have described the synthesis of nano-iron (II) and nickel (II) complex of a Schiff base ligand, namely 1-((pyridin-2-ylimino)methyl)naphthalen-2-ol using sonochemical method. The complexes (C-28 & C-29) were characterized and their catalytic activity was investigated for Suzuki-Miyaura cross coupling reaction.

5.2 EXPERIMENTAL

5.2.1 Materials and methods

All chemicals used were of analytical reagent (AR) grade and used without any further purification. 2-aminopyridine, 2-hydroxy-1-naphthaldehyde, Nickel acetate and ferrous chloride (hydrated) were procured from Merck India.

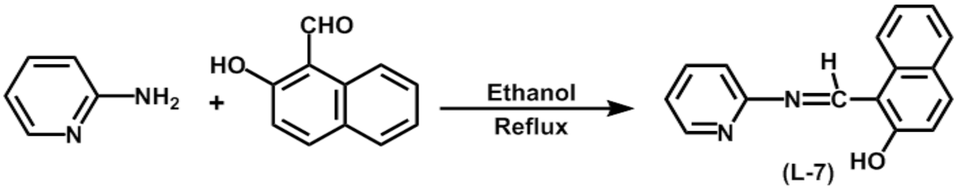
The analysis of synthesized compounds was done using different analysis techniques as described in chapter 3 (Section 3.2.2). The product biphenyl was analyzed using Gas Chromatography (GC) (Shimadzu 2014, Japan), siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector.

5.2.2 General procedure of Suzuki Miyaura reaction

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.02 mmol) and 1,4-dioxane (3 mL) were added to a 50 mL flask, and the mixture was stirred in parallel synthesizer for 8 hours at 110 ˚C. The progresses of the reactions were monitored by Gas chromatography.

5.2.3 Synthesis of ligand (L-7)

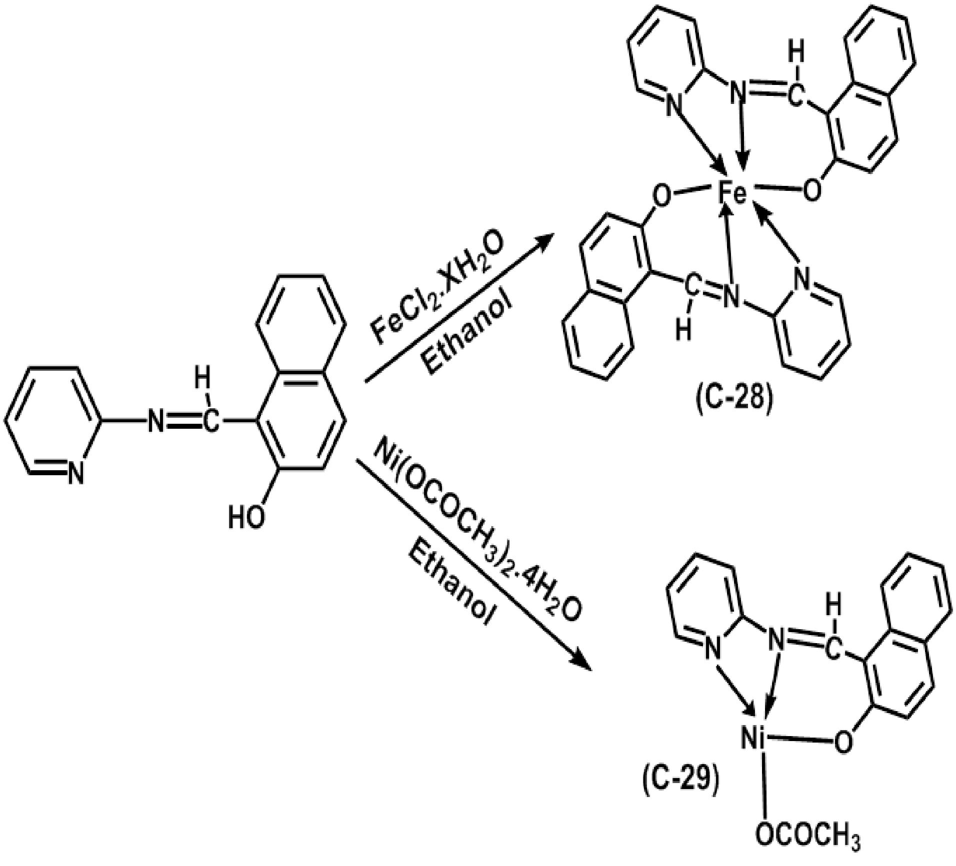
2-aminopyridine (0. 095 g, 1.0 mmol) and 2-hydroxy-1-naphthaldehyde (0.172 g, 1.0 mmol) were dissolved in ethanol and heated to 60 ˚C in a 50 mL round bottom flask. The reaction mixture was then refluxed for 3 hours and filtered. The obtained product then washed with diethyl ether and re-crystallized from ethanol and dried. Chemical Formula: $C_{16}H_{12}N_2O$; Melting point: 180 ˚C.



Scheme 5.1 Synthesis of ligand (L-7)

5.2.4 Synthesis of complex (C-28 & C-29)

A proper volume of ligand (0.496 gm, 2.0 mmol) solution in (ethanol) (5 mL) was added in dropwise manner under the ultrasonic irradiation to the prepared $FeCl_2.XH_2O$ (0.127 gm, 1.0 mmol) solution (5 mL) in ethanol. The mixture was irradiated under ultrasonic waves for one hour. The obtained solid was filtered, subsequently washed with cold methanol and dried. Similarly, complex C-29 was synthesized using $Ni(OCOCH_3)_2.4H_2O$ (0.248 gm, 1.0 mmol) with ligand (L-7) (0.496 gm, 1.0 mmol) in ethanol.



Scheme 5.2 Synthesis of complex (C-28 & C-29)

5.3 RESULTS AND DISCUSSION

5.3.1 ^{1}H NMR

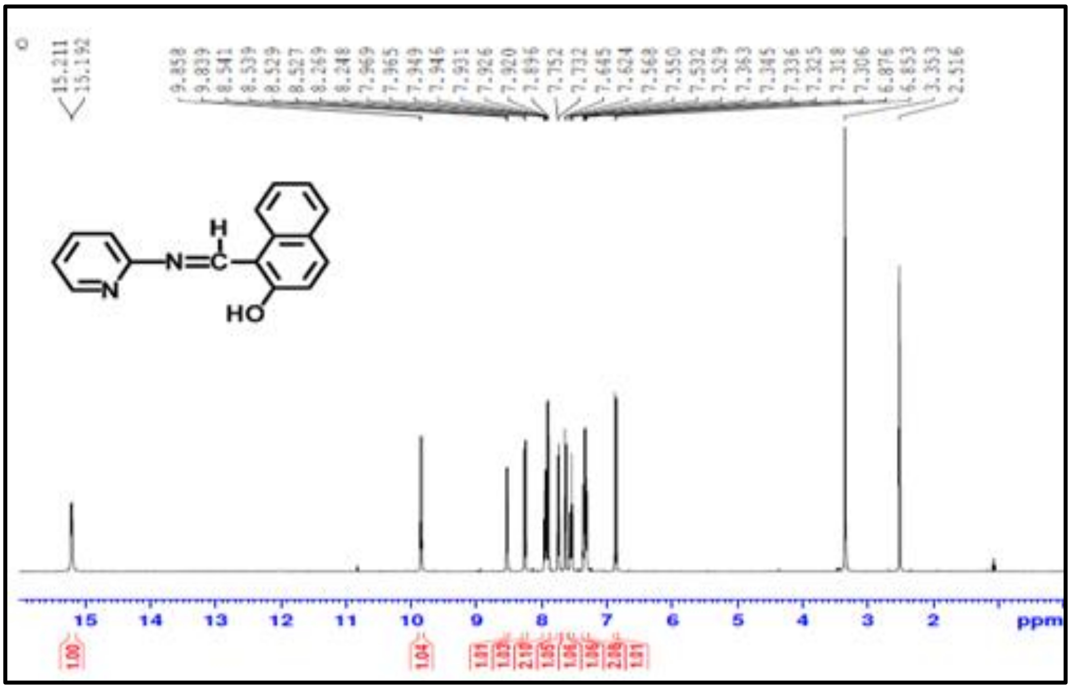


Figure 5.1 ^{1}H NMR of ligand L-7

The ^{1}H NMR spectrum of the ligand (L-7) was recorded in DMSO solvent to confirm the number of proton present in the molecule. The -OH peak was observed around 15.21 ppm. The peak at 9.85 ppm was observed for azomethine proton (Fig. 5.1).

5.3.2 Physical properties and analytical data of ligand and its complexes

Table 5.1 Physical properties and elemental analysis of ligand and its complexes (C-28 & C-29).

Compounds	**Color**	**Yield (%)**	**Elemental analysis data** **Found** **(Calculated)**		
			C %	**H %**	**N %**
L-7	Mehendi Yellow	80	77.45 (77.40)	4.75 (4.80)	11.00 (11.28)
C-28	Dark brown	80	77.45 (77.35)	4.78 (4.86)	9.72 (9.65)
C-29	Brown	74.50	59.13 (59.23)	4.02 (3.87)	7.55 (7.67)

5.3.3 FTIR spectra

FTIR spectra of ligand and the complex are shown in the Figure 5.2, 5.3 & 5.4. The strong band in ligand at 1618.59 cm^{-1} assignable to azomethine ν(C=N) group and and O-H peak appears at 3495.46 cm^{-1}. The peak in the region 1140.00 cm^{-1} is indicative of phenolic ν(C-O) stretching. Moreover, for complex, the appearance of a band for ν(CH=N) in the range of 1561.73 cm^{-1} to 1641.05 cm^{-1} indicates a shifting of bands compared to ligand suggesting the complexion of ligand with metal atom through nitrogen atom has been formed. Phenolic ν(C-O) stretching in complex is shifted to 1124.21 cm^{-1} (C-28) and 1183.80 cm^{-1} (C-29) indicating the coordination of the phenolic oxygen of ligand to the metal ion. The new band at 421.98 cm^{-1} (C-28) and 422.20 cm^{-1} (C-29) region, tentatively assign the coordination of metal with oxygen atom ν(M-O). The bands which appear around 515.10 cm^{-1} to 496.24 cm^{-1} in the spectrum of complexes may be assigned to the coordination of metal with a nitrogen atom (M-N) (Miyaura et al. 1981).

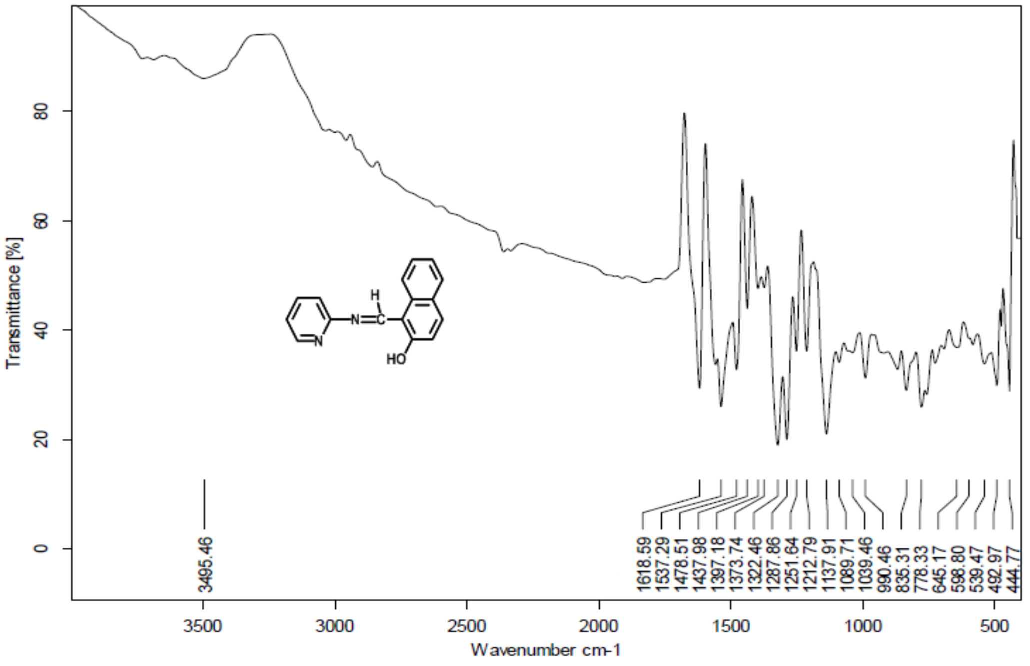


Figure 5.2 FTIR spectrum of ligand (L-7)

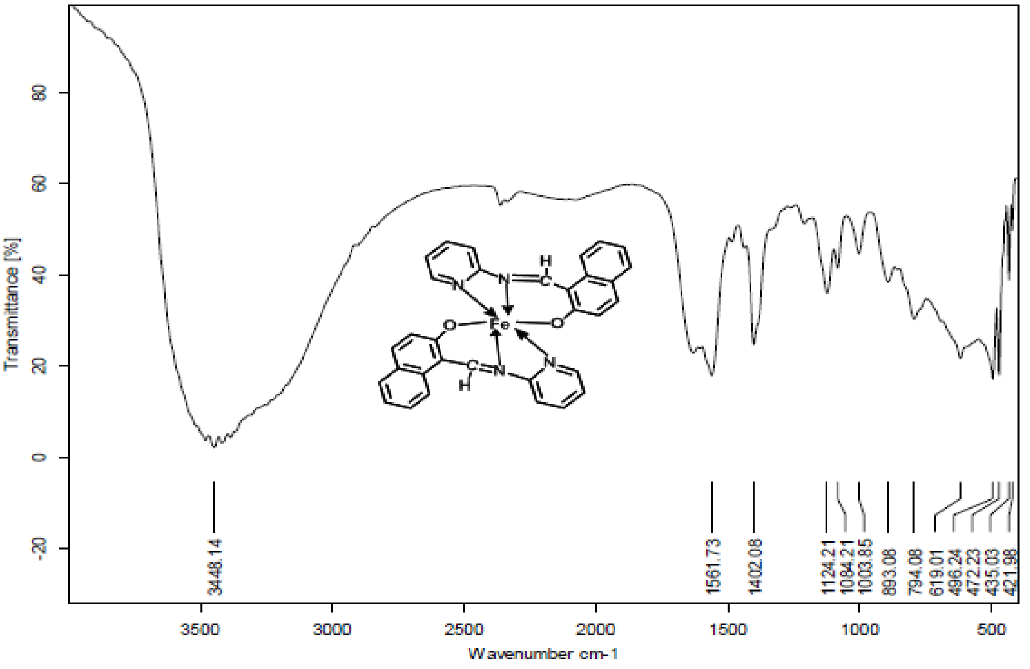


Figure 5.3 FTIR spectrum of complex (C-28)

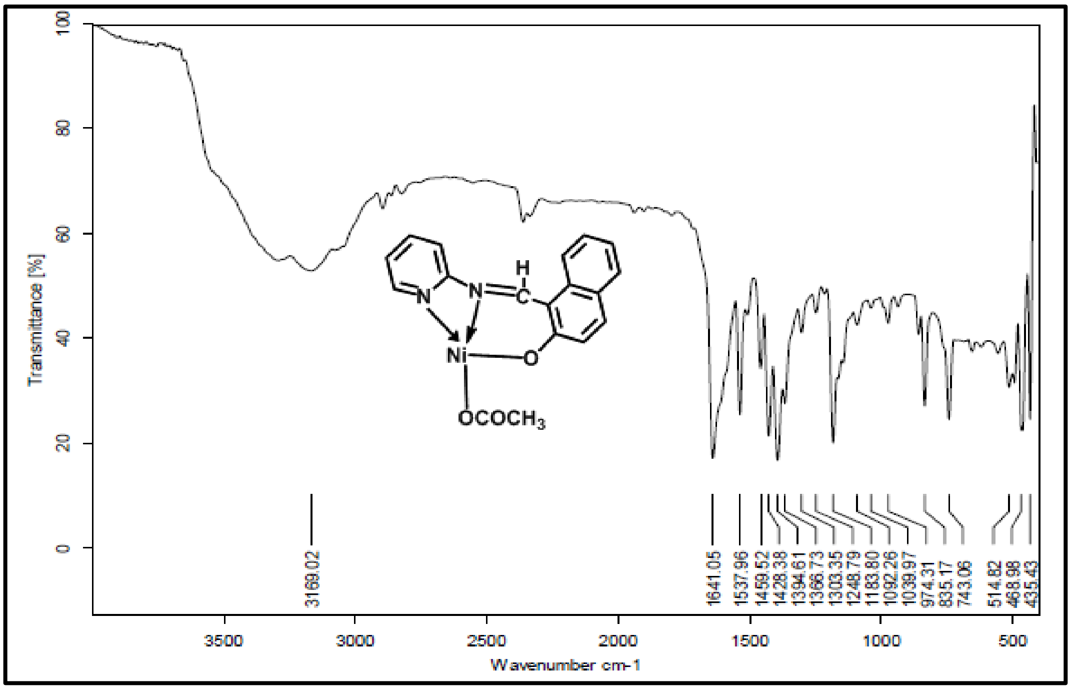


Figure 5.4 FTIR spectrum of complex (C-29)

5.3.4 UV-Vis spectra

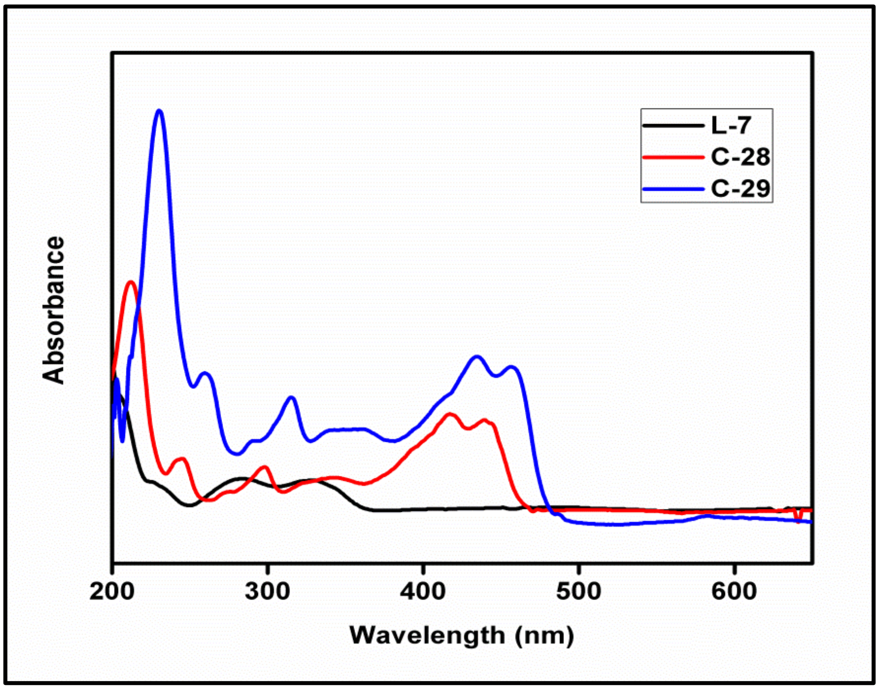
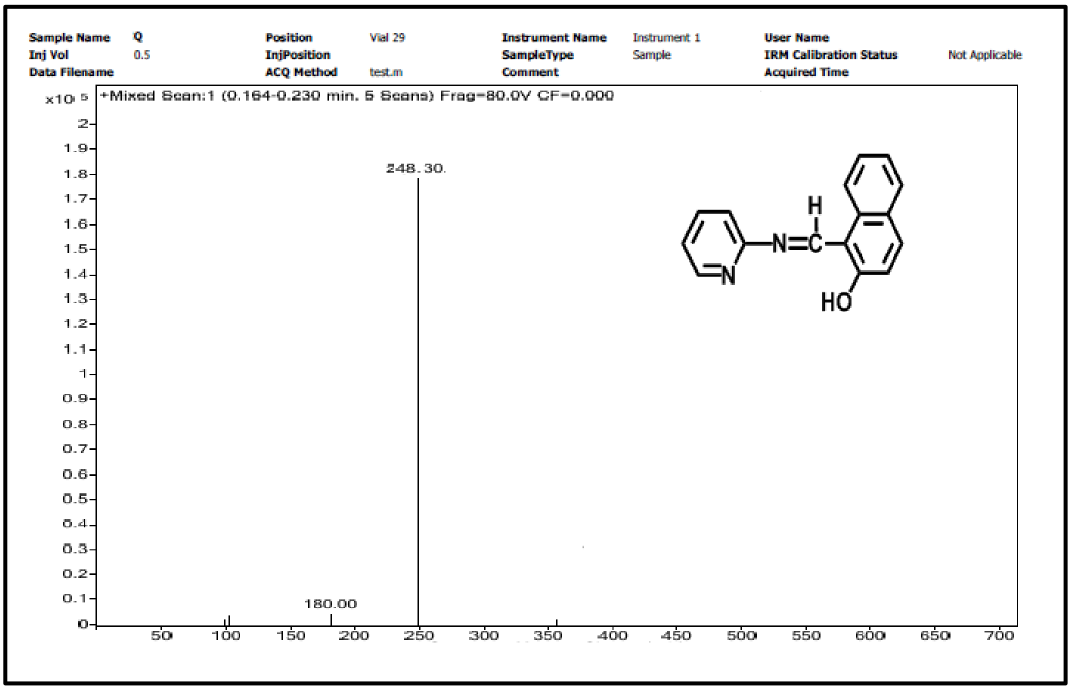


Figure 5.3 UV-Vis spectra of ligand and complexes (C-28 & C-29)

The UV-Vis spectra of synthesized ligand and complexes were recorded in methanol solvent (Fig. 5.3). The absorption bands which we observed in the free ligand spectrum have been shifted to lower energy region in the spectra of complexes because of the ligand coordination with a metal ion. These transitions are due to intra-ligand charge transfer transitions (ILCT) and ligand to metal charge transfer transitions (LMCT). Moreover, peaks at higher wavelength (≥400 nm) were observed due to d-d transition.

5.3.5 Mass spectra

The mass spectra of the ligand (L-7) and its nickel complex (C-29) were recorded at 50 eV of electron energy. The important mass fragmentations of the ligand and complex are shown in the spectra (Fig. 5.4 & 5.5).



Sample Name	Q	**Position**	Vial 29	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Not Applicable
Data Filename		**ACQ Method**	test.m	**Comment**		**Acquired Time**	

Figure 5.4 Mass spectrum of ligand (L-7)

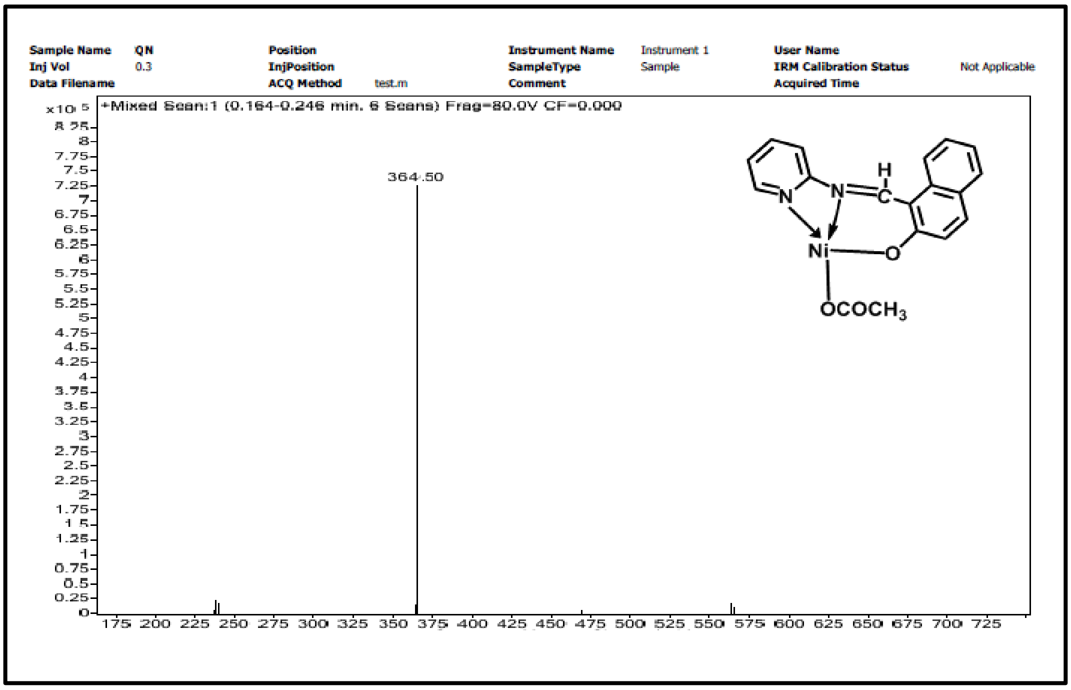

Sample Name QN
Inj Vol 0.3
Data Filename
Position
InjPosition
ACQ Method test.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Not Applicable
Acquired Time

Figure 5.5 Mass spectrum of complex (C-29)

5.3.6 Magnetic moment

The magnetic moment of both the synthesized Schiff base complex at room temperature have been investigated. The magnetic moment of complex (C-28) was found 4.10 BM, which indicates that 4 unpaired electron is present in the complex. The complex was found in octahedral geometrical shape and it is paramagnetic. The magnetic moment was found 2.2 BM for C-29, which indicates that 2 unpaired electron is present in the complex. The paramagnetic nature revealed tetrahedral geometry of the synthesized nickel complex.

5.3.7 Particle size analysis

The size of the catalyst particles was observed 47.5 nm and 22.9 nm for iron and nickel respectively (Fig. 5.6 (a & b)).

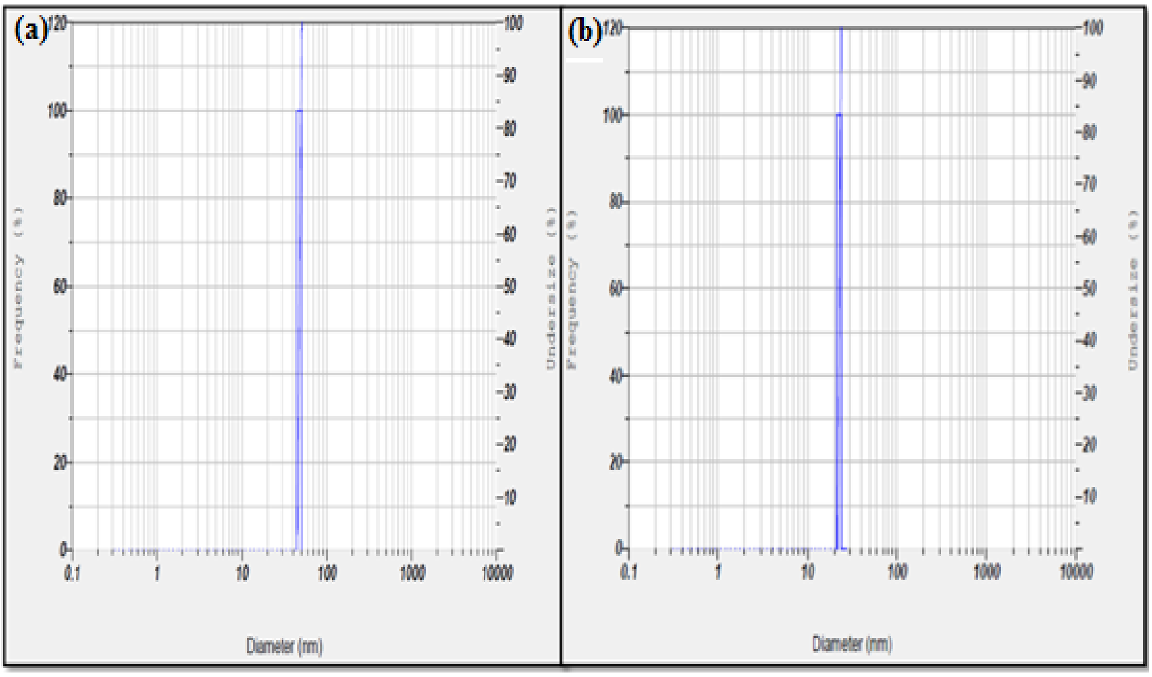


Figure 5.6 Particle size distribution of the synthesized complexes (C-28 & C-29)

5.3.8 SEM & TEM analysis

The morphology of the complex catalyst (C-28 & C-29) was studied by SEM images (Fig. 5.7 (a & b)). The tubular nanostructure of the nanotubes was found for both the complex.

TEM image of the complex C-29 is depicted in Fig. 5.8. The data imply that the nickel nanoparticles are almost tubular in shapes. Due to high surface area of the complex, catalytic properties of the catalyst can be improved.

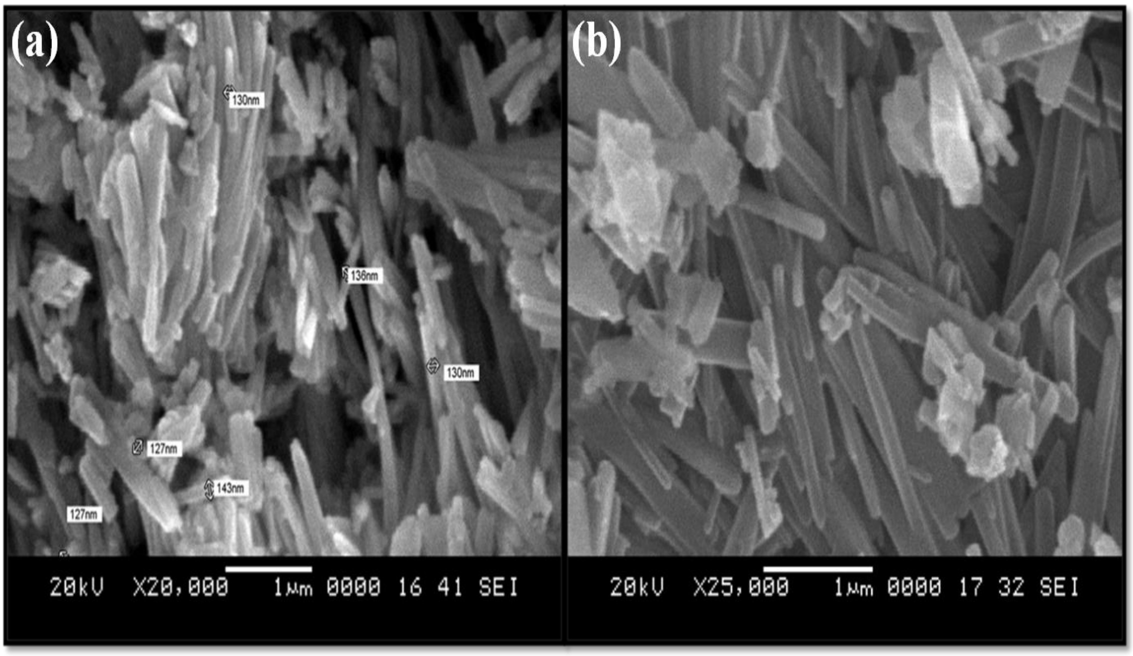


Figure 5.7 SEM micrographs of the complexes (C-28 & C-29)

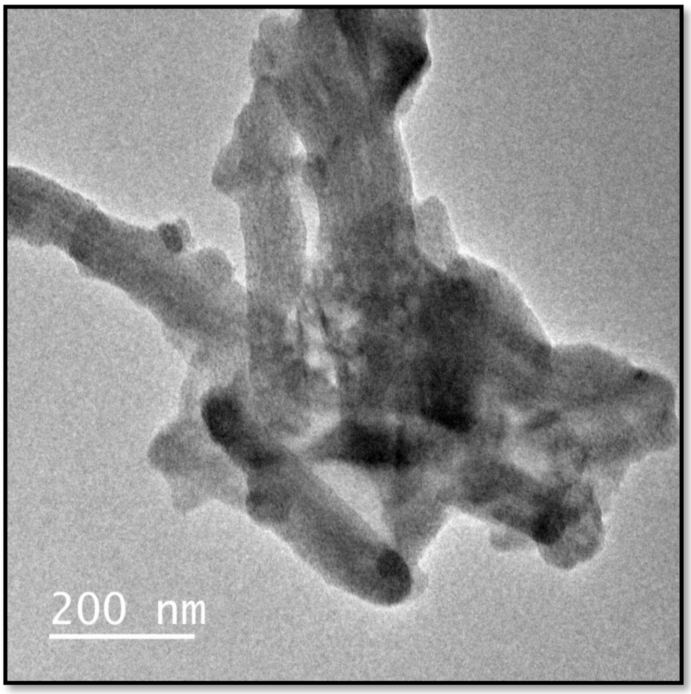


Figure 5.8 TEM micrograph of the complex (C-29)

5.3.9 Thermogravimetric analysis

The thermal behavior of the Schiff base ligand and its metal complexes was studied by using thermogravimetric techniques in the range of 30-650 ˚C in a nitrogen atmosphere. The TGA curves of the molecules are given in Fig. 5.9. The purpose of the thermal study is to confirm the course of the degradation and the presence of the hydrated water molecules in the compounds. In Figure 5.9, as can be seen, decomposition of the complex (C-28) was completed in a single step. The remaining percentage mass loss can be assigned for iron oxide residue. The absence of the peak around 200 ˚C confirms that no water molecule present in the complex. As can be seen in the figure 5.9, decomposition of the complex (C-29) was completed in a three steps. Moisture removal was observed at 120 ˚C. The second weight loss (20.50%) was due to acetate group from the complex. The ligand decomposition was observed with final percentage mass loss. The remaining percentage mass loss can be assigned for Ni-oxide residue.

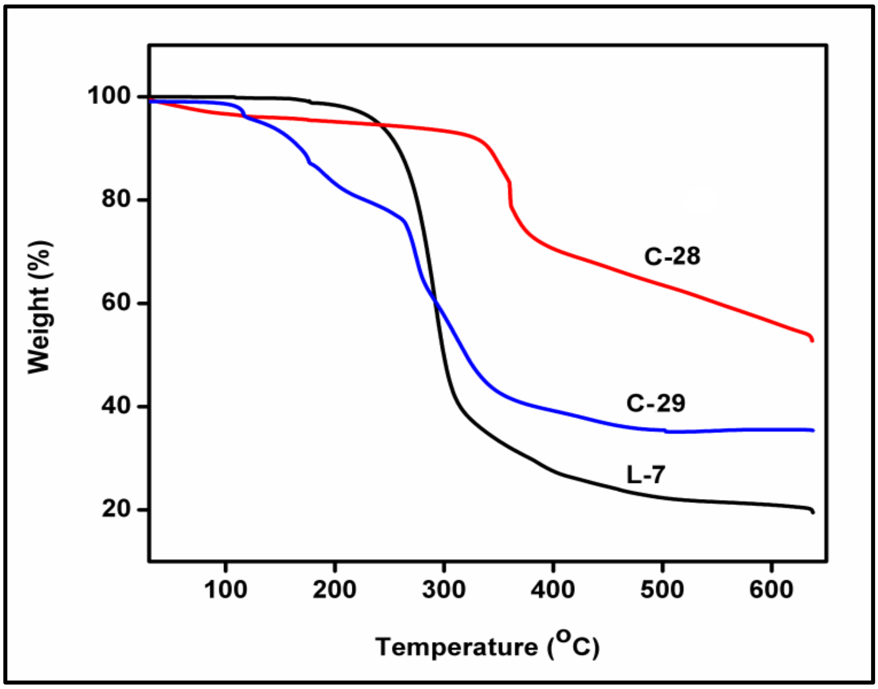


Figure 5.9 TGA of the complexes (C-28 & C-29)

5.3.10 Catalytic activity

The synthesized nano complexes (C-28 & C-29) used as a catalyst for the coupling of 4-bromobenzonitrile and phenylboronic acid as the model reaction to study the Suzuki-Miyaura coupling reaction. The effect of the base, solvent, time and concentration of the catalyst on the Suzuki coupling of the selected reactants were studied. The basic environment is essential for the Suzuki reaction. The impact of solvents on the reaction was also investigated and 1,4-dioxane (Fig. 5.10) gave the best result. Among the bases examined (Fig. 5.11), K_2CO_3 showed the best effect. Product yield dependence on the reaction period of time was investigated by analyzing the reaction mixture at particular intervals of time. Product conversion was observed to increase with reaction time till the completion of 8 hours. The conversion remained almost constant after 8 hours (Fig. 5.12). Hence, optimized reaction time for the coupling reaction was fixed at 8 hours.

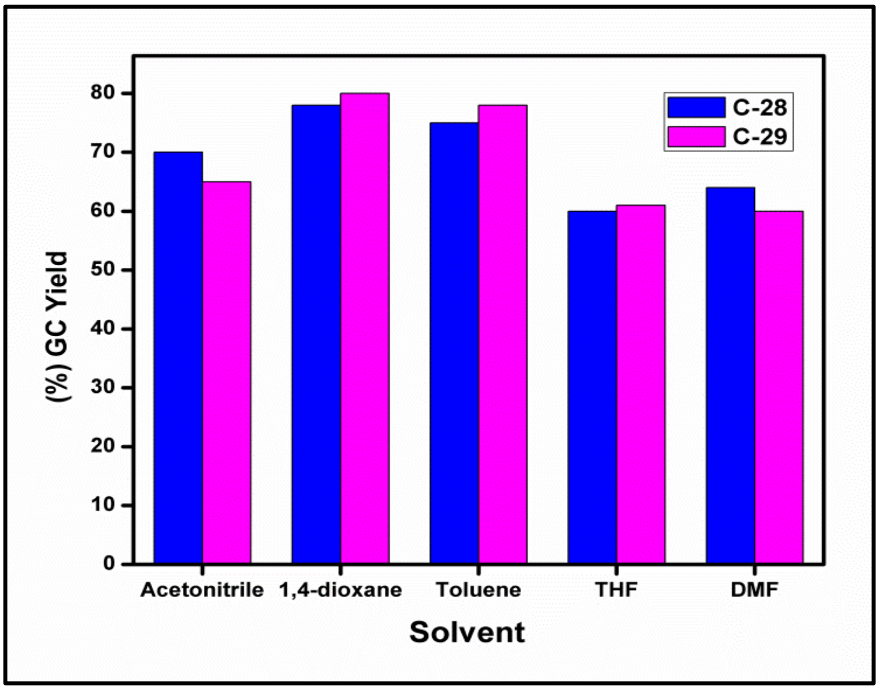


Figure 5.10 Optimization of solvent for Suzuki coupling reaction

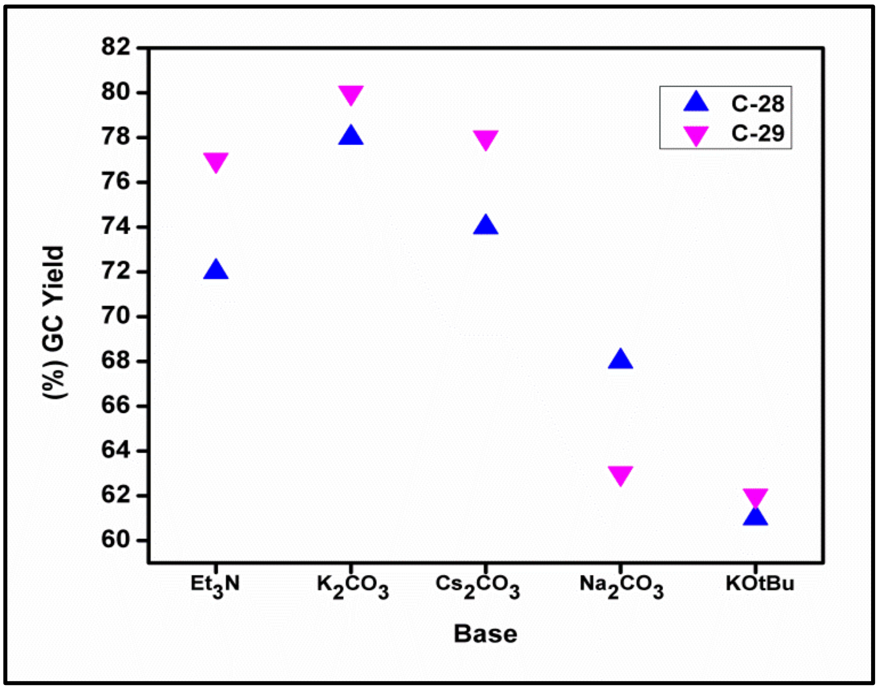


Figure 5.11 Optimization of base for Suzuki coupling reaction

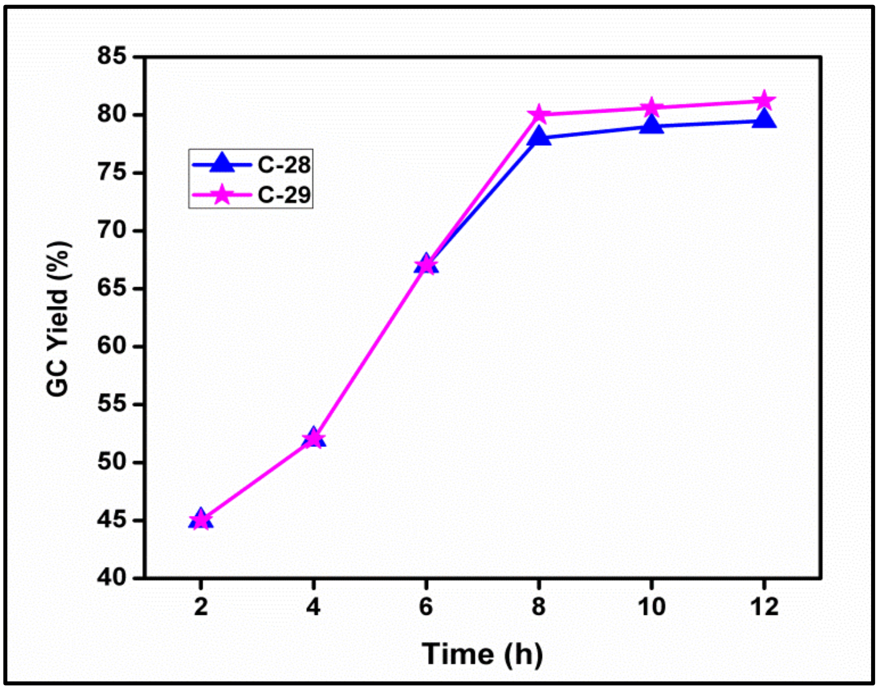


Figure 5.12 Optimization of effect of reaction time on coupling yield

The concentration effect of the catalyst (C-28 & C-29) on the conversion yield was investigated by carrying out the reaction mixture with different catalyst concentration from 0.005 mmol to 0.025 mmol (Fig. 5.13). The result showed almost constant yield with 0.02 and 0.025 mmol catalyst concentrations. Hence, 0.02 mmol concentration was taken for the further catalytic studies.

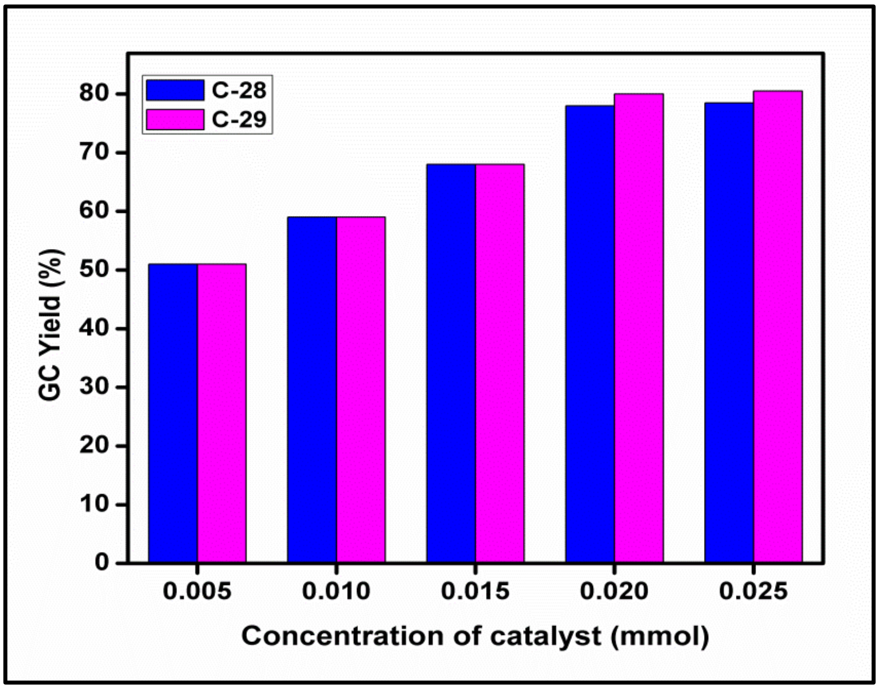
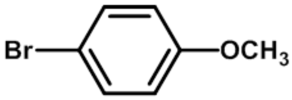
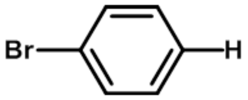
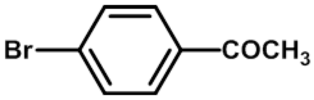
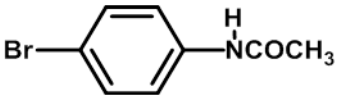
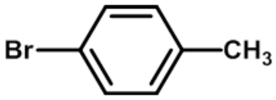
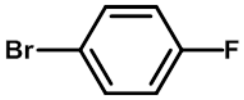
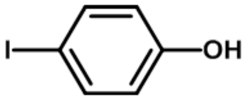
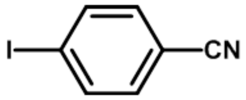


Figure 5.13 Optimization of catalyst loading for Suzuki-Miyaura coupling

Further, different substituted aryl halides were used to extend the cross-coupling reaction with phenylboronic acid using the optimized reaction conditions. The results of different substituent are summarized in Table 5.2. The catalysts were found to catalyze the coupling reactions effectively. The conversion pattern with different substituents on the aryl halides was different.

Table 5.2 Catalytic activity study for complex (C-28 & C-29)

Entry	Aryl halides	Yield[a]	
		C-28	**C-29**
1		50	51
2		38	40
3		78	80
4		79	79
5		67	68
6		50	52
7		46	48
8		57	59
9		58	62
10		80	82

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), catalyst (0.02 mmol), solvent (3 mL), 8 h.

[a] Yield determined by GC, average of 3 trials (Isolated yield).

5.4 SUMMARY

Nano iron (II) and nickel (II) Schiff base complexes have been synthesized via Ultrasonic irradiation and characterized. Suzuki cross-coupling of different aryl halides and phenylboronic acids was catalyzed with synthesized complexes. The synthesized complexes showed great potential in catalytic activity. The yields varied on the basis of substrates. Substrates having electron-donating groups showed lesser conversion whereas substrates having electron-withdrawing groups give comparatively better yield. It was concluded that the prepared catalysts is low-cost, highly catalytic active and stable, thus providing promising alternative for Suzuki-Miyaura carbon-carbon cross coupling reaction.

CHAPTER 6

SYNTHESIS AND CHARACTERIZATION OF COPPER (II) SCHIFF BASE COMPOSITE WITH GRAPHENE OXIDE FOR SUZUKI-MIYAURA CROSS COUPLING REACTION

In this chapter, we report the synthesis and characterization of copper Schiff base composite grafted onto graphene oxide (Cu-NH_2-GO). The catalytic performance of Cu-NH_2-GO was studied in the C-C cross coupling of aryl halides with phenylboronic acid. The catalysts showed high conversion, easy recovery and safer reuse.

6.1 INTRODUCTION

The isolation of homogeneous catalysts is a tedious process and in order to facilitate the isolation, heterogenisation of the catalyst is carried out. In this chapter, the copper Schiff base complex is grafted on graphene and the resulting catalyst is studied for Suzuki-Miyaura cross coupling reactions.

Graphene and its derivatives aptly suit as a solid substrate to immobilize the transition metal complexes owing to their large surface area. They find great application in the fields of composite materials, catalysis, drug delivery, sensors and photovoltaics due to their distinguishable nanostructures and attractive properties (Kaniyoor et al. 2009; Yang et al. 2009; Liu et al. 2010; Zhu et al. 2010; Yun et al. 2011; Nie et al. 2012). Graphene oxide (GO) obtained from graphene exhibits various advantages in comparison with graphene majorly because of the additional functional groups. The sheet edges having carbonyl and carboxyl groups, whereas the basal planes richly decorated with hydroxyl and epoxide groups makes graphene oxide heavily oxygenated (Park et al. 2008; Dreyer et al. 2010). These oxygenic groups present on the graphene oxide cause immobilization of metal complexes acting as active sites. Pd nanoparticles immobilized on graphene oxide was used for the Suzuki-Miyaura reactions. The Schiff base oxo-vanadium complex grafted onto graphene oxide has reportedly been used for the oxidation of alcohols (Mungse et al. 2012). As discussed in chapter 4, the catalytic activities reported for theses transition metal complexes have prompted the research of low-cost catalysts for the coupling reactions. Schiff base complexes with N, O donor atom have been widely reported for their catalytic and biological properties (Balasubramanian et al. 2006) and their activity profile in both homogenous and heterogeneous catalysis are comprehensively documented (Baleizão et al. 2003; Gupta and Sutar 2008).

Here, we have reported the synthesis and characterization of metal Schiff base composite grafted onto graphene oxide (Cu-NH_2-GO). The catalytic performance of Cu-NH_2-GO was studied in the C-C cross coupling of aryl halides with phenylboronic acid. The catalyst showed high conversion, easy recovery and safer reuse.

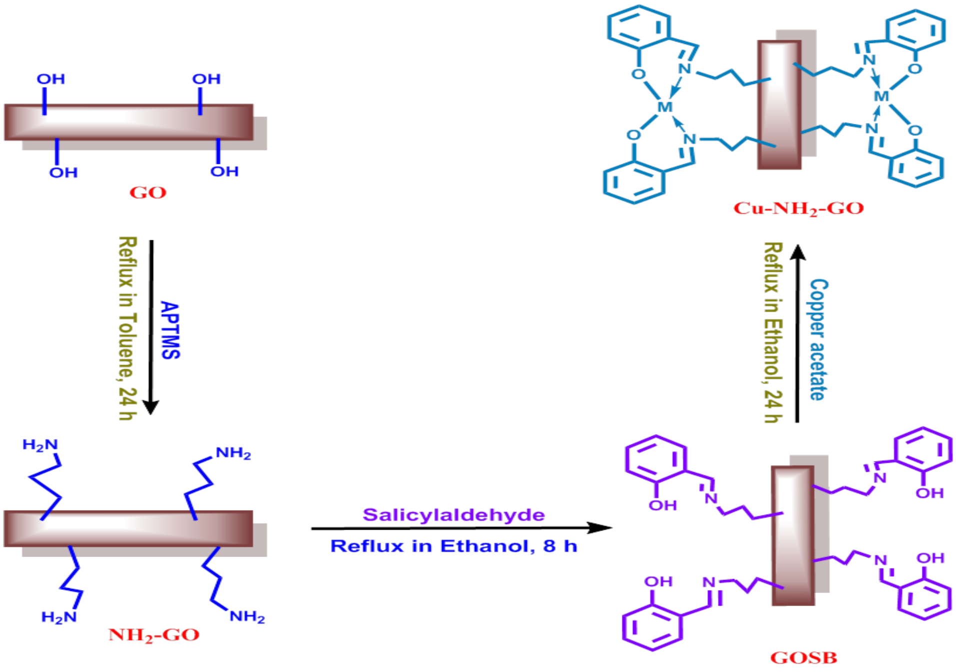
6.2 EXPERIMENTAL

6.2.1 Materials and methods

Salicylaldehyde, copper acetate monohydrate, 6% H_2O_2, H_2SO_4, and H_3PO_4 were procured from Merck India, while (3-aminopropyl)trimethoxysilane (APTMS) and graphite powder were obtained from Sigma-Aldrich. All chemicals were used as received. The analysis of synthesized compounds was done using different analysis techniques as described in chapter 3 (Section 3.2.2). The product biphenyl was analyzed using Gas Chromatography (GC) (Shimadzu 2014, Japan), siloxane Restek capillary column (30 m length and 0.25 mm diameter) and Flame Ionization Detector.

6.2.2 Synthesis of Cu-NH_2-GO

GO was prepared using improved Hummers method (Marcano et al. 2010). (3-aminopropyl) trimethoxysilane was grafted on graphene oxide (Lin et al. 2011). 0.1 g of GO was dispersed in 50 mL of toluene. To this dispersion, 2 mL of APTMS was added and refluxed at 110 ˚C for 24 hours in inert atmosphere. The obtained product was filtered and washed with toluene and ethanol. The APTMS coated GO nanosheets (NH_2-GO) was dried overnight at 70 ˚C. 0.05 g of functionalized graphene oxide (NH_2-GO) was weighed and dissolved in ethanol (10 mL). To this 0.122 g of salicylaldehyde was added (Scheme 6.1). Then it was refluxed for about 8 hours. The obtained precipitate was filtered and dried overnight. The obtained product was named as GOSB. 0.1 g of GOSB was dispersed in 5 mL ethanol, to this 0.2 g of metal salt was added and refluxed for 24 hours. The product was filtered and dried overnight. The obtained composite was named as Cu-NH_2-GO.



Scheme 6.1 Stepwise synthesis of Cu-NH_2-GO

6.2.3 Suzuki-Miyaura cross coupling

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), Cu-NH_2-GO (4.0 mg) and a base (2.0 mmol) was added in 3 mL of solvent and heated to 110 ˚C up to 12 hours. The organic layer was analyzed using gas chromatography.

6.3 RESULTS AND DISCUSSION

6.3.1 FTIR spectra

The obtained GO, NH_2-GO, GOSB and M-NH_2-GO were examined by the FTIR spectroscopy (Fig. 6.1). In the spectrum of GO. the broad peak at 3425 cm^{-1} corresponds to stretching of O-H bonds and sharp peak at 1690 cm^{-1} ν(C=O) was due to the presence of carbonyl, hydroxyl, and carboxylic acid groups (Khatri et al. 2014). The peak at 1195 cm^{-1} and 1048 cm^{-1} are indicative of the C-OH and C-O- groups, respectively. NH_2-GO shows additional peaks at 3441 cm^{-1} (N-H stretching) and 1600 cm^{-1} (N-H bending) is due to presence of -NH_2 groups. The peaks within 2850-3050 cm^{-1} are due to presence of methylene and methyl groups (Mungse et al. 2012). Peaks at 1128 cm^{-1} and 1026 cm^{-1} are the evidence for the formation of Si-O-Si and Si-O-C bonds, respectively. This shows successful grafting of APTMS on GO. The FTIR spectrum of GOSB shows a strong peak at 1616 cm^{-1} attributing to imine (C=N) stretching which is shifted to 1605 cm^{-1} in case of Cu-NH_2-GO sample. This confirms the formation of composite.

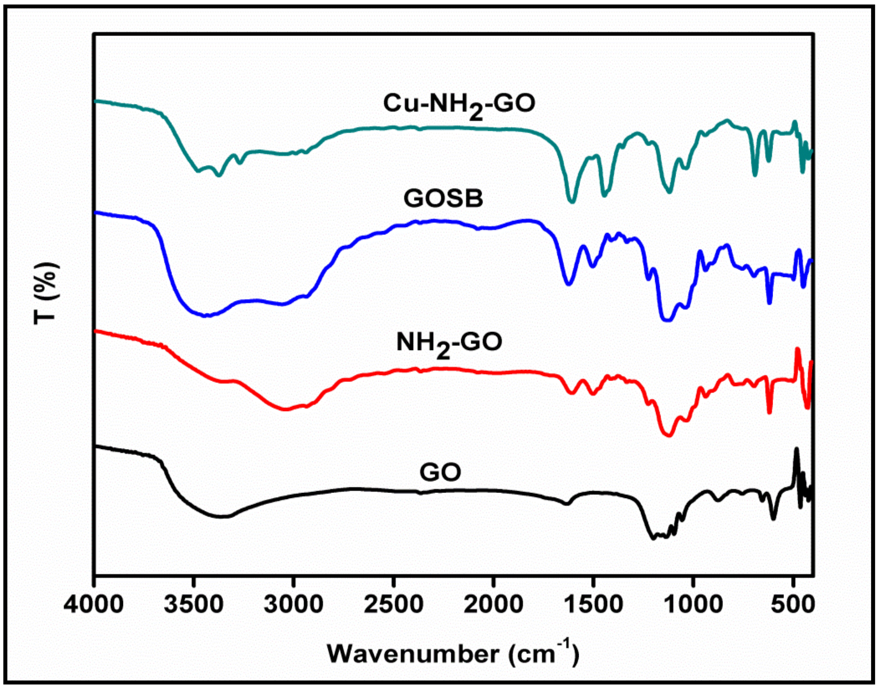


Figure 6.1 FTIR spectra of GO, NH_2-GO, GOSB and Cu-NH_2-GO

6.3.2 UV-Vis spectroscopy

The GO and Cu-NH_2-GO was analyzed by UV-Vis spectroscopy to investigate the chemical changes due to grafting of the complex on GO (Fig. 6.2). GO shows absorption at ~220 nm due to sp^2 bonded carbon atoms (Rayati et al. 2017). The presence of n-π* (~259 nm) peak in Cu-NH_2-GO supports the grafting of the catalyst on GO.

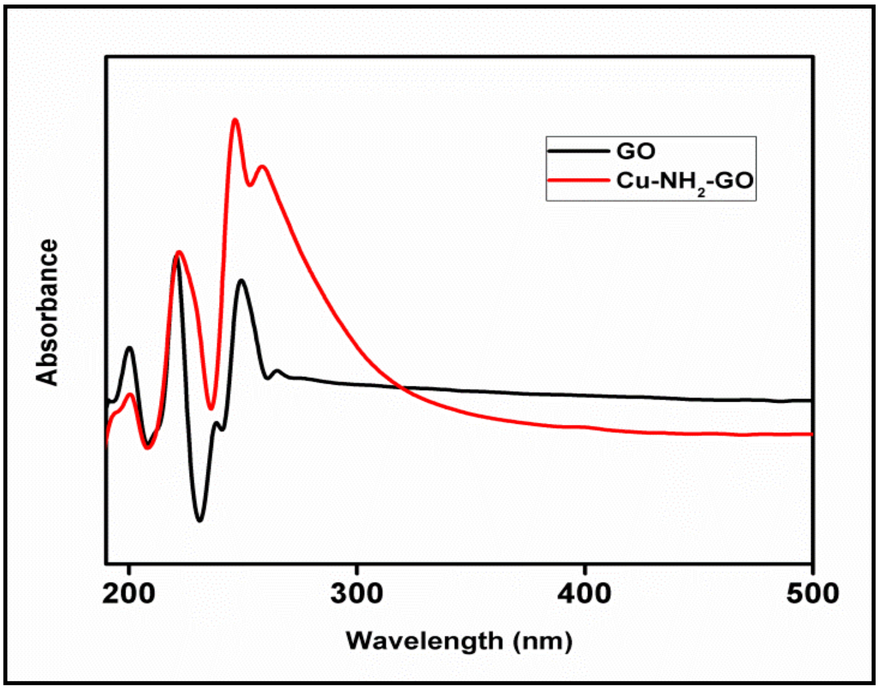


Figure 6.2 UV-Vis spectra of GO and Cu-NH$_2$-GO

6.3.3 X-ray diffraction analysis

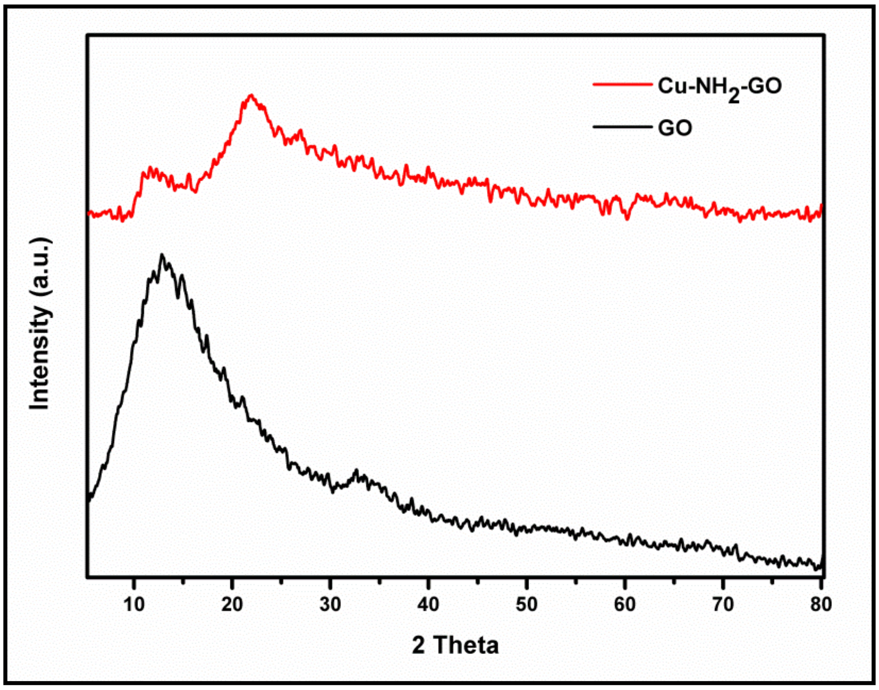


Figure 6.3 XRD patterns of GO and Cu-NH$_2$-GO

Figure 6.3 demonstrates the XRD of GO and Cu-NH_2-GO. GO shows a diffraction peak at 12.86° which corresponds to (002) plane (Mishra Praveen and Bhat B. Ramchandra 2017). The broad peak around 22° is observed due to reduced graphene oxide in Cu-NH_2-GO catalyst. The XRD pattern for Cu-NH_2-GO showed that the synthesized catalytic composite is amorphous, which is disclosed by broad peak (Gemeay et al. 2017).

6.3.4 SEM and TEM analysis

The SEM analysis was carried out to check the surface morphology of GO, NH_2-GO, GOSB and Cu-NH_2-GO (Fig. 6.4-6.7, respectively). It can be seen that SEM image of GO had sustained sheet-like structure and it became wrinkled with the reaction of APTMS (NH_2-GO) (Su et al. 2015). SEM image of GOSB showed well defined arrangement of organic molecules onto sheets. Moreover, different distinctive shape of Cu-NH_2-GO was identified and the SEM image was quite different from that of GOSB. TEM image of the Cu-NH_2-GO is shown in Fig. 6.8. The black dots in TEM image could confirm the immobilization of copper Schiff base complex onto graphene oxide sheets.

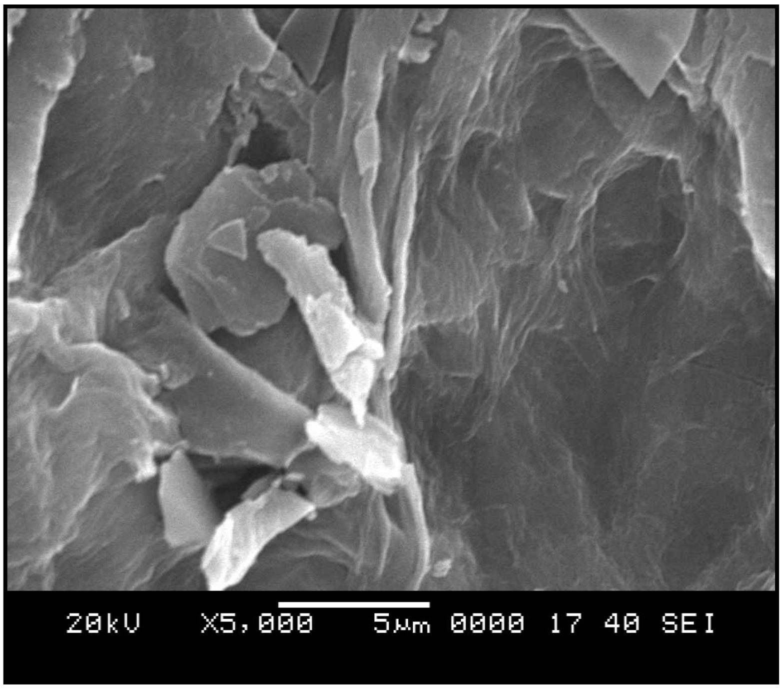


Figure 6.4 SEM images of GO

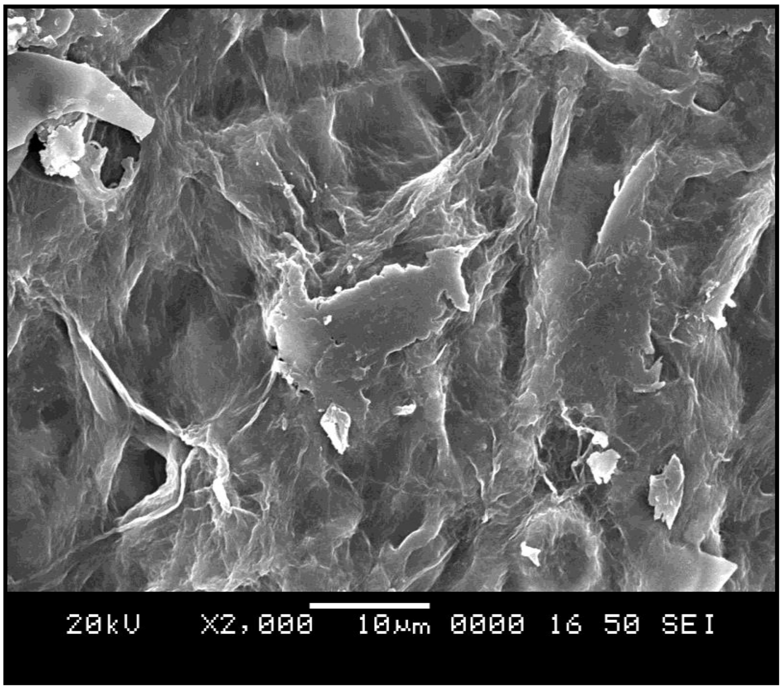


Figure 6.5 SEM images of NH_2-GO

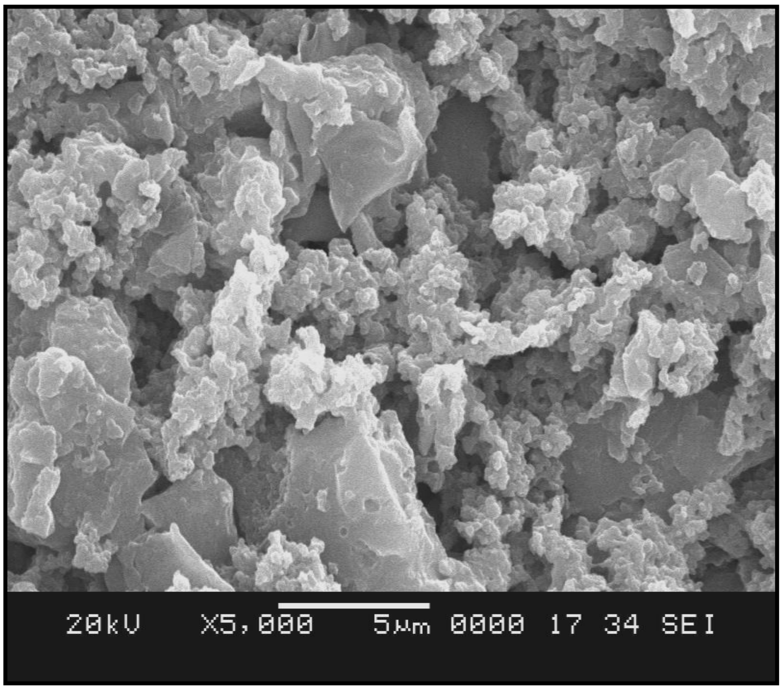


Figure 6.6 SEM images of GOSB

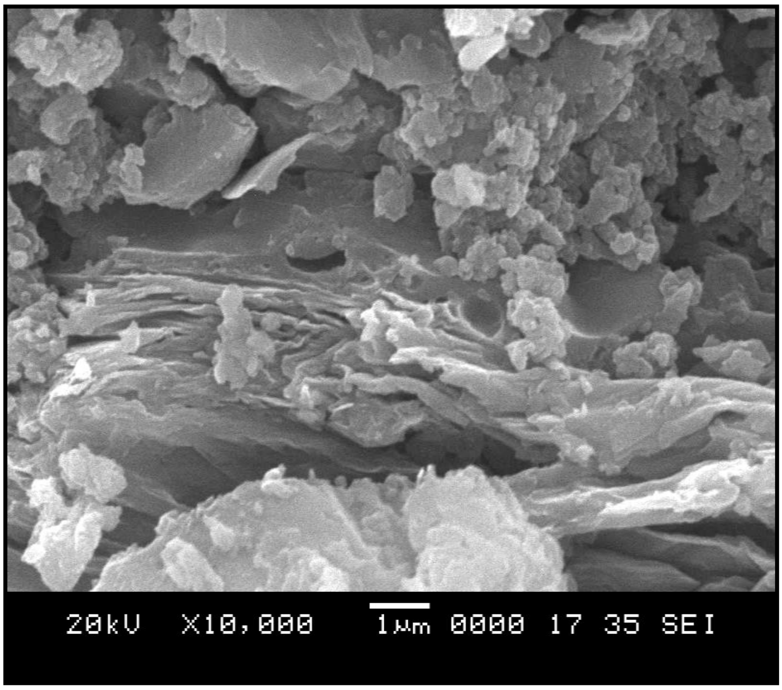


Figure 6.7 SEM images of Cu-NH_2-GO

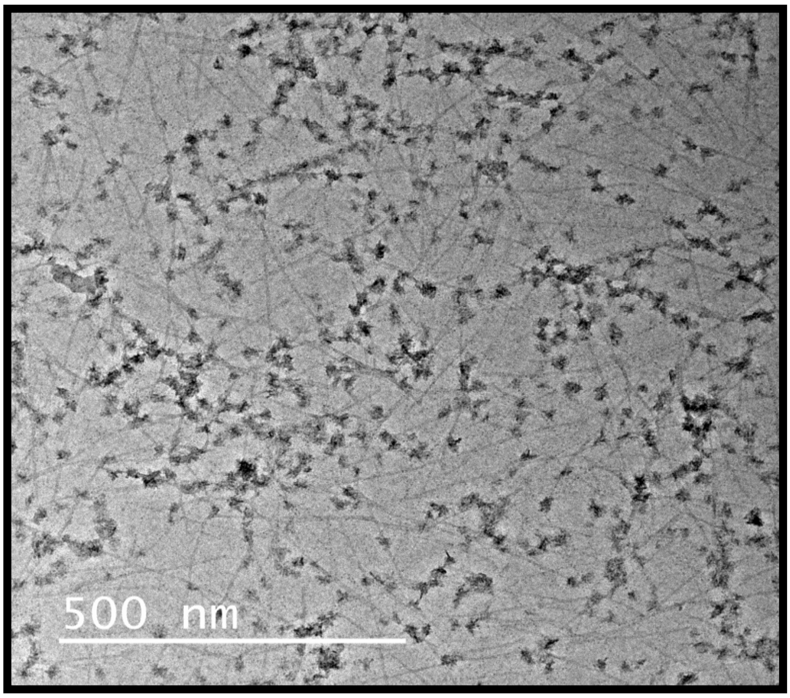


Figure 6.8 TEM image of Cu-NH_2-GO

6.3.5 Thermogravimetric analysis

The thermal behavior of the GO and Cu-NH_2-GO was examined by TGA. The first weight loss of GO in under 115 ˚C is due to the removal of trapped moisture. The second significant weight loss was noticed in the range of 250-330 ˚C, due to decomposition of oxygen moieties (Fig. 6.9) (Stankovich et al. 2007, Su et al. 2014). The Cu-NH_2-GO catalyst shows three weight losses up to 600 ˚C. The slight reduction in weight within 150-200 ˚C corresponds to the removal of water. The weight loss around 360 ˚C is due to the decomposition of complex on GO. The subsequent reduction in weight above 450 ˚C is attributed to the decomposition of the residual by products which resulted from the decomposition of complex.

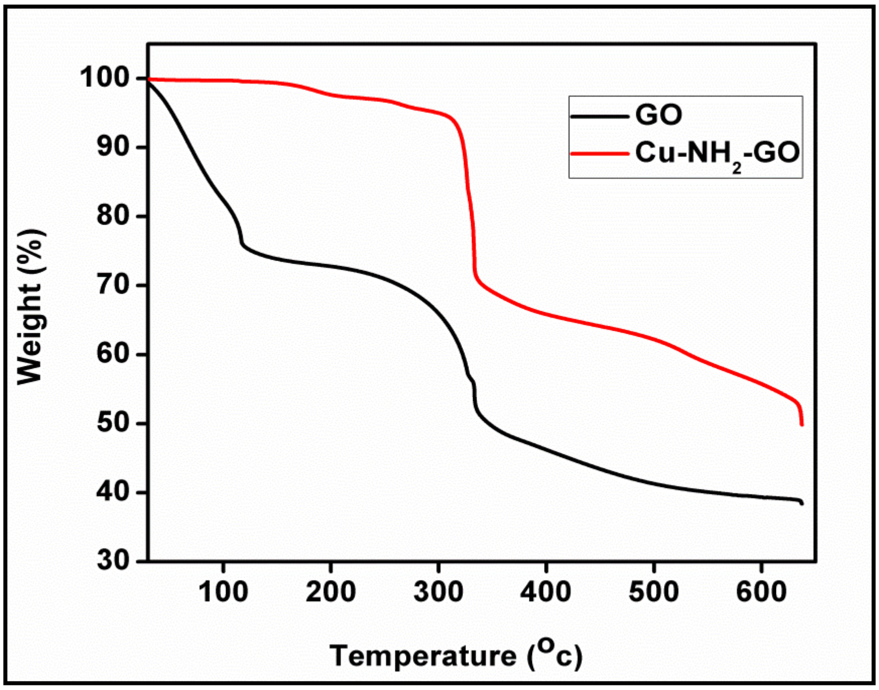


Figure 6.9 TGA of GO and Cu-NH_2-GO

6.3.6 Catalytic study

The catalyst Cu-NH_2-GO was examined for C-C cross coupling of 4-bromobenzonitrile with phenylboronic acid. Optimum reaction condition was studied using different parameters like base, solvent, catalyst concentration and reaction time on product yield. The catalytic activity of catalyst was carried out in acetonitrile, 1,4-

dioxane, toluene, THF and DMF solvent media at their reflux temperature (Table 6.1). Among different solvents chosen, highest catalytic activity was found in toluene, lightly lower yield by other solvents. Toluene was selected as solvent for further studies. The reaction was also examined for the effect of base on the yield of product. Among all the experimented bases, K_2CO_3 was found to be most active (Table 6.2). The effect of reaction time on the yield of product was established by examining the reaction mixture at different time intervals. The yield was observed to increase till 12 hours of reaction after which there was no further significant improvement (Fig. 6.10). The catalyst concentration effect on the reaction was analyzed with different catalyst concentration for coupling. An expected increase in yield was observed with increase in concentration till 4.0 mg catalyst concentration before reaching the plateau (Fig. 6.11). Further, different aryl halides were used to study the C-C coupling with phenylboronic acid. The yield obtained was different with various substituents. Presence of electron withdrawing group on the benzene ring facilitates the easy removal of halide group and thereby enhances the positivity on the para position favoring nucleophilic attack in the coupling reaction. The results are summarized in Table 6.3. Additionally, the catalyst was easily recovered and recycled without significant loss in its activity (Fig. 6.12).

Table 6.1 Effect of solvents on Suzuki-Miyaura cross coupling reaction.

Entry	Solvents	Base	Yield^a
1	Acetonitrile	K_2CO_3	76
2	Toluene		80
3	1,4-dioxane		75
4	THF		62
5	DMF		61

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), Cu-NH_2-GO (4.0 mg), solvent (3 mL), 12 h.
[a] Yield determined by GC.

Table 6.2 Effect of base on Suzuki-Miyaura cross coupling reaction.

Entry	**Bases**	**Solvent**	**Yield[a]**
1	Et_3N	Toluene	72
2	K_2CO_3		80
3	Cs_2CO_3		75
4	Na_2CO_3		69
5	KO^{t}Bu		60

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), Cu-NH_2-GO (4.0 mg), solvent (3 mL), 12 h.

[a] Yield determined by GC.

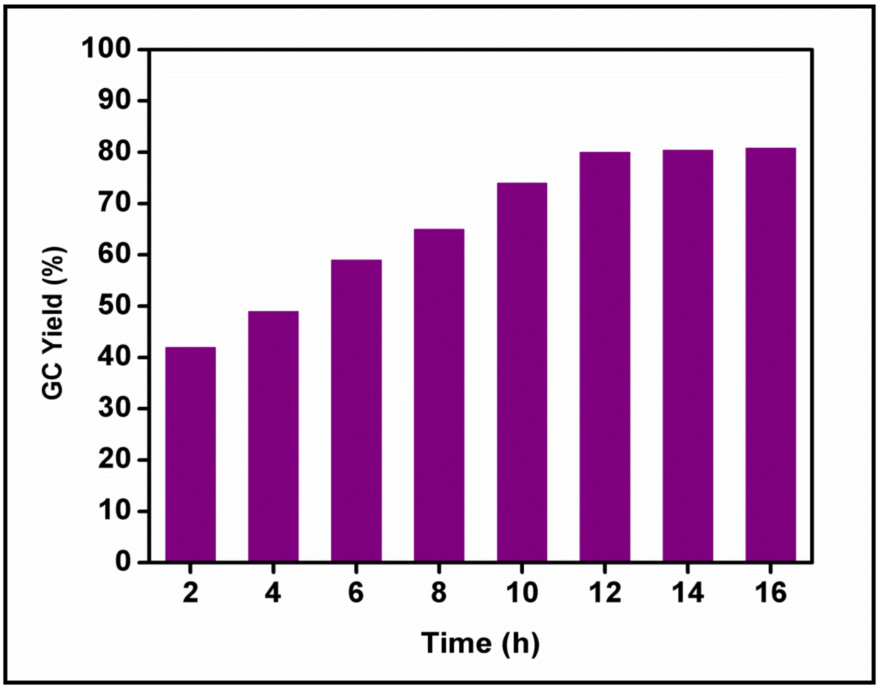


Figure 6.10 Effect of reaction time on coupling yield

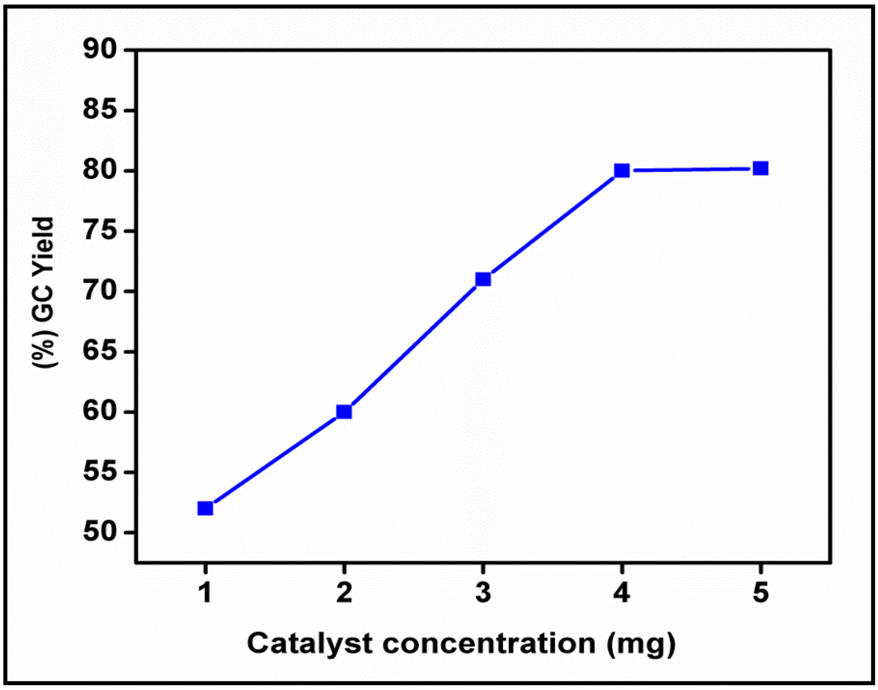


Figure 6.11 Effect of catalyst concentration on coupling yield

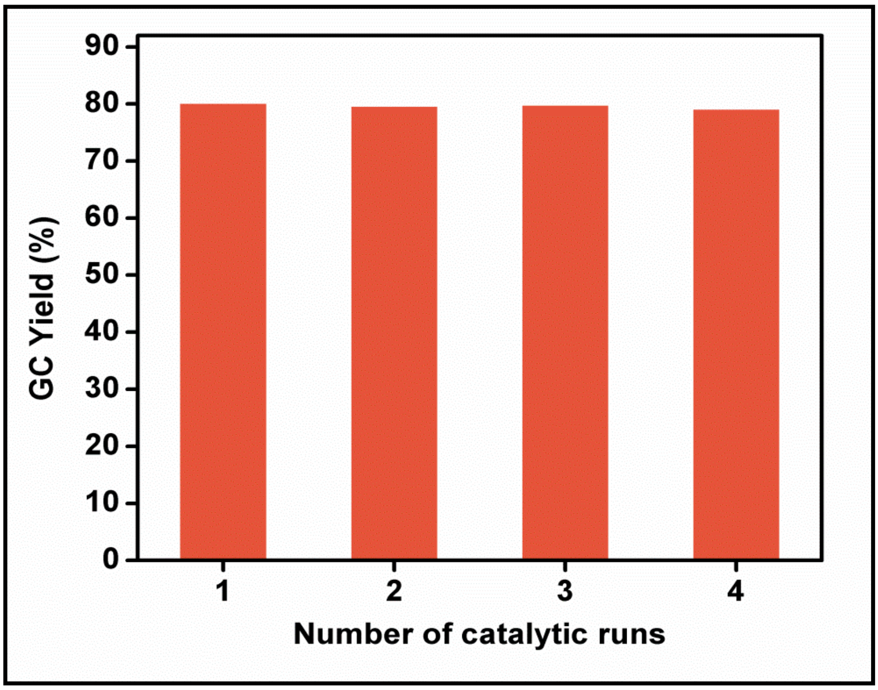
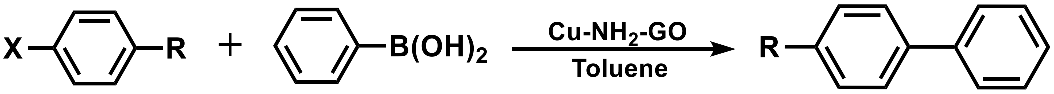


Figure 6.12 Recovery and reusability of the catalyst (Cu-NH_2-GO)

Table 6.3 Reaction yield for various aryl halides in Suzuki-Miyaura cross coupling reaction.



Scheme 6.2 Suzuki-Miyaura cross coupling reaction

Entry	**R**	**X**	**Yield[a]**
1	OCH_3	Br	55
2	H		50
3	CN		80
4	$COCH_3$		78
5	$NHCOCH_3$		75
6	OH		59
7	CH_3		44
8	F		52
9	OH	I	64
10	CN		84

Reaction conditions: Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), Cu-NH_2-GO (4.0 mg), toluene (3 mL), 12 h.

[a] Yield determined by GC.

6.4 SUMMARY

This work reports the immobilization of different chemical moieties on the graphene oxide and presents opportunities for designing high activity, heterogeneous, and eco-friendly catalysts. The catalytic activity of synthesized composite was studied in Suzuki-Miyaura reaction. Yield of Aryl halides with electron withdrawing groups fared better as compared to those with electron donating groups. Among the various aryl halides, iodide was found to be a better leaving group. The grafted catalyst was easy to recover and recycle with consistent activity (~80%, 4-bromobenzonitrile). Therefore, the developed GO based catalyst is viable heterogenous catalyst owing to its ease of synthesis and stability for the Suzuki-Miyaura reaction.

CHAPTER 7

SUMMARY AND CONCLUSIONS

This chapter discusses the summary of the work existing in the thesis and the important findings on synthesis, characterization, and application of some transition metal complexes for cross coupling reactions.

7.1 SUMMARY

In summary, the method used low cost, abundant, and environmentally benign metals in the synthesis of complexes and thereafter their efficient catalytic activity in Suzuki-Miyaura C-C cross coupling reaction. Six series of metal complexes which totals to 27 complexes were synthesized to study their catalytic activity in Suzuki-Miyaura coupling reactions. Schiff bases (L-1, L-2, L-3, L-4, L-5 and L-6) were synthesized using 4-aminoacetophenone, 2-amino-5-bromopyridine, 2-aminophenol, and 1,2-phenylenediamine with different substituted aldehydes (salicylaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2-hydroxy-1-napthaldehyde). Complexes (C-1 to C-27) of 3*d*-transition metal namely manganese, iron, cobalt, nickel, and copper were synthesized using these six Schiff base ligands (L-1 to L-6). The synthesized complexes were examined for their C-C coupling efficiency in Suzuki cross-coupling between phenylboronic acid and para substituted aryl halides. Effect of synthesized ligands on the catalytic activity of the complexes was explored based on the coupling yields. Further, we have described the synthesis of nano-iron (II) and nickel (II) complex of a Schiff base ligand (L-7), namely 1-((pyridin-2-ylimino)methyl)naphthalen-2-ol using sonochemical methods. The nano-complexes were characterized and their catalytic activity was investigated for Suzuki-Miyaura cross coupling reaction. Also, the immobilization of Schiff base copper complex onto graphene oxide was carried out to synthesize heterogeneous and eco-friendly catalysts for Suzuki-Miyaura cross coupling reaction.

The present study has led to the consideration of the role of ligands and their electron donating ability in enhancing the catalytic activity of a complex. Among all the complexes, copper complex catalyzed Suzuki reaction showed good yield with the reaction proceeding efficiently under mild condition. This catalytic system is more attractive because it is very cheap compared to more expensive palladium catalyst.

The absence of reducing agent and phosphine ligand in the catalytic system together are other advantages of this system as it leads to more ecofriendly catalyst. Also, the grafted copper catalyst was easy to recover and recycle with consistent activity (~80%, 4-bromobenzonitrile).

7.2 CONCLUSIONS

From the experimental results obtained in the presented research following conclusions were drawn:

- Presence of 3*d*-transition elements as the active metal center in the complexes resulted in satisfactory catalytic activity.
- Among the synthesized series, Copper Schiff base complexes (C-5, C-10, C-12, C-17, C-22 and C-27) showed best catalytic activity owing to the higher availability of electrons compared to other metals. Thus, exhibiting highest coupling efficiency.
- Presence of electron withdrawing substituents on the aryl halides enhances the coupling process. The electron donating substituents slightly reduces the biaryl conversion as evident from the higher yield obtained for aryl halides with electron withdrawing -CN group as compared to donating group like $-OCH_3$ group.
- Presence of iodide which is better leaving group among the halides leads to higher yield in Suzuki Miyaura cross coupling reaction. This indicates the importance of having good leaving group for better yield.
- Prepared iron and nickel nano-catalysts (C-28 & C-29) are low-cost, highly active, and stable, thus providing promising alternative for Suzuki-Miyaura carbon-carbon cross coupling reaction.
- The GO based copper catalyst ($Cu-NH_2-GO$) proved to be the viable heterogenous catalyst owing to its ease of synthesis and stability for the Suzuki-Miyaura coupling reaction.

SCOPE FOR THE FUTURE WORK

Based on the results obtained, it is planned to synthesize and characterize more Schiff base transition metal complexes, nano-metal Schiff base complexes and grafted metal composites. Their effect on C-C coupling will be carried out.

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RESEARCH PUBLICATIONS

(A) Research Papers in International Journals

1. **Rasheeda M. Ansari** and B. Ramachandra Bhat (2017) "Schiff base transition metal complexes for Suzuki-Miyaura cross-coupling reaction" *J. Chem. Sci*., 129, 1483–1490.
2. **Rasheeda M. Ansari**, Lolakshi M. K and B. Ramachandra Bhat (2018) "Air stable cobalt (II) and nickel (II) complexes with Schiff base ligand for catalyzing Suzuki Miyaura cross coupling reaction" *Russ. J. Coord. Chem.,* 44, 1-8.
3. **Rasheeda M. Ansari**, Lolakshi M. K and B. Ramachandra Bhat (2018) "Cobalt Schiff base Complexes: Synthesis Characterization and Catalytic Application in Suzuki-Miyaura Reaction" *Chin. J. Chem. Eng.* In press, (doi:10.1016/j.cjche.2018.05.002)

4. **Rasheeda M. Ansari** and B. Ramachandra Bhat (2018) "Synthesis Characterization and Catalytic activity of Nano-iron (II) Schiff base Complex in Suzuki-Miyaura Cross coupling reaction" *International Journal of Engineering & Technology*, 7 (4.5) 435-438.

5. **Rasheeda M. Ansari** and B. Ramachandra Bhat (2018) "Copper (II) Schiff base-graphene oxide composite as an efficient catalyst for Suzuki-Miyaura reaction" *Chemical Physics* (doi: 10.1016/j.chemphys.2018.09.018).

6. **Rasheeda M. Ansari** and B. Ramachandra Bhat "Nano-nickel (II) Schiff base Complex for Suzuki-Miyaura Cross coupling reaction" *Communicated to Chinese Journal of Chemical Engineering* (Under review)

7. **Rasheeda M. Ansari**, Lolakshi M. K and B. Ramachandra Bhat "Suzuki-Miyaura Cross-Coupling with Copper (II) Schiff base Complex" (Under preparation)

8. **Rasheeda M. Ansari** and B. Ramachandra Bhat "Nickel (II) Schiff base Complex for Suzuki-Miyaura Cross coupling reaction" (Under preparation)

(B) Papers Presented in Conferences

1. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2015). "Synthesis and catalytic application of Schiff base complexes in cross-coupling reactions." National Conference on Advances and Innovations in Chemical Sciences (NCAICS-2015). 12-13th February, 2015. University of Mumbai, Vidyanagri, Santacruz (E). Mumbai-400 098, India.
2. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2015). "Application of Nickel Schiff base complex in Suzuki-Miyaura cross-coupling reaction." International Conference on Multifunctional Materials for Future Applications (ICMFA- 2015). 27-29th October, 2015. Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, India.
3. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2015). "Copper Schiff base complex as a catalyst for Carbon-Carbon cross-coupling reaction." International Conference on Advances in Chemical Engineering (ICACE-2015). 20-22nd December, 2015. Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar-575025, Karnataka, India.
4. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2016). "Synthesis Characterization and Catalytic Application of Cobalt Schiff base Complex in Suzuki-Miyaura Cross-Coupling reaction." National Conference on Recent Trend in Chemical Sciences (NCRTCS-2016). 11-12th January, 2016. Department of Chemistry, Manipal Institute of Technology, Manipal-576104, Karnataka, India.
5. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2016). "Synthesis, Characterization and Catalytic Application of Iron Schiff base Complex in Suzuki-Miyaura Cross-Coupling reaction" International Conference on Impact of Chemical Research on Environment (ICRE-2016). 17-18th February, 2016.

Department of Chemistry and Research Centre, New Arts, Commerce and Science College, Parner-414302, Ahmednagar, Maharashtra, India.

6. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2017). "Synthesis, characterization and catalytic activity of nano-structured Fe(II) schiff base complex in Suzuki-Miyaura cross coupling reaction" International Conference on Emerging Trends in Nanomaterials Science and Technology (ICETNMST-2017). 4-6th January, 2017. Department of Science and Humanities, National Institute of Technology Nagaland, Dimapur-797103, Nagaland, India.
7. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2017). "Synthesis, Characterization and Catalytic Application of Iron Schiff base Complex in Suzuki-Miyaura Cross-Coupling Reaction" International Conference on Recent Trends in Chemical Science (ICRCS-2017). 12-13th January, 2017. Govt. Engineering College, Bikaner-334004, Rajasthan, India.
8. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2017). "Nano-Structured Fe(II) Schiff Base Complex: Synthesis, Characterization And Catalytic Activity" International Conference on Nanoscience and Nanotechnology (ICONN-2017). 9-11th August, 2017. Department of physics and Nanotechnology, SRM University, Kattankulanthur, Chennai-603203 Tamil Nadu, India.
9. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2018). "Synthesis Characterization and Catalytic activity of Nano-structured Co(II) Schiff base complex in Suzuki-Miyaura cross coupling reaction" International Conference on Science and Engineering of Materials (ICSEM-2018). 6-8th January, 2018. School of basic Sciences and Research, Sharda University, Greater Noida-201306 Delhi, India.
10. **Rasheeda M. Ansari** and Badekai Ramachandra Bhat (2018). "Synthesis Characterization and Catalytic activity of Nano-iron (II) Schiff base Complex in Suzuki-Miyaura Cross coupling reaction" International Conference on Recent Trends in Engineering and Sciences (ICRTES-2018). 20th-21st February, 2018. Visakhapatnam, Andhra Pradesh, India.

CURRICULUM VITAE

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❑ Educational Qualification

Ph.D. (Chemistry) :- **Pursuing (Joined in 2014)**

Thesis Title :- “Synthesis, Characterization and Application of Some Transition Metal Complexes for Cross Coupling Reactions”.

Institute :- National Institute of Technology, Mangalore, Karnataka

M.Sc. (Organic Chemistry) :- **2009-2011**

University :- University of Mumbai

Marks :- 63.50 %

B.Sc.(Chemistry) :- **2006-2009**

University :- University of Mumbai

Marks :- 75.00 %

❑ Work Experience

1. **In-plant Trainee** at Aarti Industries Ltd., Aarti Healthcare API Div. Unit I. Dombivli (Maharashtra) India. From June 2010 to July 2010.

❑ Teaching Experience

1. **Lecturer** at Aqsa Women's Degree College, 4th Millat Nagar, 4th Nizampur, Chavindra, Bhiwandi 421302, Thane (Maharashtra) India. From 13th June 2012 to 13th Jan 2014.

❑ Research Areas of Interest

1. Multistep organic synthesis.
2. Synthesis of Chromen, Pyrazole and Pyrimidine based active ingredient compounds for antibacterial and antifungal activity.
3. Synthesis of Schiff base ligand and their transition metal complexes for cross coupling reactions.
4. Development of nano-metal Schiff base catalysts for Suzuki-Miyaura cross coupling reaction.

❑ Research Papers in International Peer Reviewed Journals

1. **Rasheeda M. Ansari** and B. Ramachandra Bhat. Schiff base transition metal complexes for Suzuki-Miyaura cross-coupling reaction. *Journal of Chemical Sciences* **2017,** 129, 1483-1490.

2. **R. M. Ansari**, Lolakshi M. K and B. Ramachandra Bhat. Air stable cobalt (II) and nickel (II) complexes with Schiff base ligand for catalyzing Suzuki Miyaura cross coupling reaction. *Russian Journal of Coordination Chemistry* **2018**, 44, 1-8.

3. **Rasheeda M. Ansari**, Lolakshi M. K and B. Ramachandra Bhat (2018) "Cobalt Schiff base Complexes: Synthesis Characterization and Catalytic Application in Suzuki-Miyaura Reaction" *Chinese Journal of Chemical Engineering* (Accepted) (doi:10.1016/j.cjche.2018.05.002)

4. **Rasheeda M. Ansari**, Gawale YK, Bansode TN. Synthesis, Antibacterial and Antifungal Activity of Some New Pyrimidin-2 (5H) -One/Thione and 4H-Chromen-4-One Derivatives. *Pharmaceutical Chemistry Journal* **2011**, 45, 366-368.

5. **Rasheeda M. Ansari**, Gawale YK, Bansode TN. Synthesis and biological activity of some new pyrazole derivatives. *Journal of Pharmacy Research* **2012**, 1, 1141-1142.

☐ Presentations

1. **"National Conference on Advances and Innovations in Chemical Sciences (NCAICS-2015)"** organized by University of Mumbai Vidyanagri, Santacruz (E). Mumbai-400 098 (India) on 12-13th February, 2015.

2. **"International Conference on Multifunctional Materials for Future Applications (ICMFA- 2015)"** organized by Department of Chemistry Indian Institute of Technology (BHU) Varanasi (India) on 27-29th October 2015.

3. **"International Conference on Advances in Chemical Engineering (ICACE-2015)"** organized by Department of Chemical Engineering, National Institute of Technology Karnataka, Surathkal, Srinivasnagar-575025, Karnataka (India) on 20-22nd December 2015.

4. **"National Conference on Recent Trend in Chemical Sciences (NCRTCS-2016)"** organized by Department of Chemistry Manipal Institute of Technology, Manipal-576104, Karnataka (India) on 11-12th January 2016.

5. **"International Conference on Impact of Chemical Research on Environment (ICRE-2016)"** organized by Department of Chemistry and Research Centre, New Arts, Commerce and Science College, Parner-414302, Ahmednagar, Maharashtra (India) on 17-18th February, 2016.

6. **"International Conference on Emerging Trends in Nanomaterials Science and Technology (ICETNMST-2017)"** organized by Department of Science and Humanities, National Institute of Technology Nagaland, Dimapur-797103, Nagaland (India) on 4-6th January, 2017.
7. **"International Conference on Recent Trends in Chemical Science (ICRCS-2017)"** organized by Govt. Engineering College, Bikaner-334004, Rajasthan (India) on 12-13th January, 2017.

8. **"International Conference on Nanoscience and Nanotechnology (ICONN-2017)"** organized by Department of physics and Nanotechnology, SRM University, Kattankulanthur, Chennai-603203 Tamil Nadu (India) on 9-11th August, 2017.

☐ Conferences/ Workshops participated

1. **"6th Science Conclave: A Congregation of Nobel Laureates and Eminent Scientists"** organized by Indian Institute of Information Technology, Allahabad (India) on 8th to 14th December 2013.

Sophisticated Instrument Handled

1. SCXRD (Bruker APEX-II)
2. Freeze Dryer
3. UV-Visible Spectrophotometer (Analytik Jena SPECORD)

Analytical Instrument Handled

1. GC for Reaction Monitoring (Shimadzu 2014, Japan)
2. HPLC
3. FTIR (Bruker-Alpha)
4. DSC
5. TGA
6. Autolab
7. Magnetic balance (Sherwood UK)
8. Parallel Synthesize

Computer Programs

1. Chemdraw
2. Chemsketch
3. Chemcraft
4. Origin
5. Windows, MS Office 2013

Personal Details

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Marital Status : Single

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Languages known : English, Hindi, Marathi, Urdu

Nationality : Indian

Hobbies : Travelling, Singing.

References

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❑ Declaration

I hereby declare that the information mentioned above is correct up to my knowledge and I accept the responsibility for the correctness of the above-mentioned particulars.

Place: Mumbai (India)

(Ansari Rasheeda Bano Maqbool Hasan)