

**NOVEL TITANIUM AND ZIRCONIUM COMPLEXES OF SCHIFF BASE
LIGANDS LINKED TO FURAN AND THIOPHENE**

**M.Sc. Thesis by
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Date of submission : 20 December 2010

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December 2010

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**FURAN VE TİYOFENE BAĞLI YENİ SCHIFF BAZLARININ TİTANYUM
VE ZİRKONYUM KOMPLEKSLERİ**

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FOREWORD

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December 2010

Kerem Kaya

Department of Chemistry

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ABBREVIATIONS

ATR	: Attenuated Total Reflectance
CH₂Cl₂	: Dichloromethane or Methylenechloride
E	: Entgegen isomer
Et₂O	: Diethylether
FT	: Fourier transform
g	: Gram(s)
HDPE	: High Density Polyethylene
Hf	: Hafnium
HPLC	: High Performance Liquid Chromatography
Hz	: Hertz
HSAB	: Hard and Soft Acid and Bases
IR	: Infrared
J	: Coupling constant
LLDPE	: Linear Low Density Polyethylene
M	: Metal
MAO	: Methylaluminoxane
mmol	: Milimol (10 ⁻³ mol)
μ-oxo	: Oxygen bridged
NMR	: Nuclear Magnetic Resonance
Ppm	: Particules per million
W	: Tungsten
Sc	: Scandium
THF	: Tetrahydrofuran
Ti	: Titanium
Vacuo	: Vacuum
Z	: Zusammen isomer
Zr	: Zirconium

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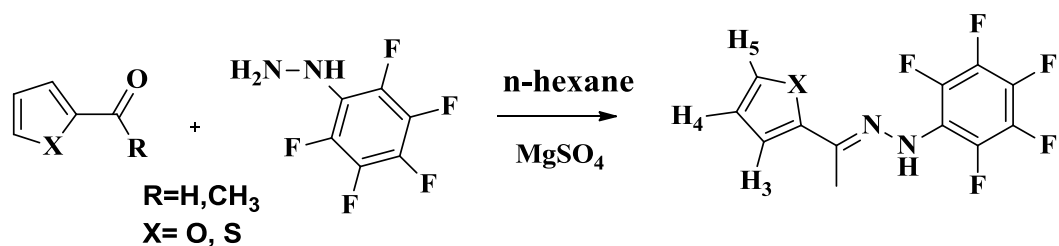
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NOVEL TITANIUM AND ZIRCONIUM COMPLEXES WITH SCHIFF BASE LIGANDS LINKED TO FURAN AND THIOPHENE

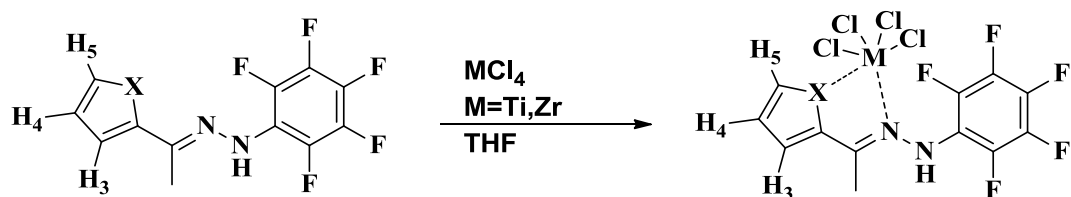
SUMMARY

The design and synthesis of new transition-metal catalyst precursors is a very important subject that can provide high catalytic activity with low cocatalyst-to-catalyst precursor (pre-catalyst) ratios and allows unprecedented control over the polymer microstructure, producing new polymers with improved polymer properties [1,2]. The catalytic activity of transition metal Schiff base complexes became compelling in synthesis of commercially important polymers. Schiff base complexes of especially early transition metal ions (Ti, Zr) are efficient catalysts both in homogeneous and heterogeneous reactions, the activity of these complexes varied with the type of ligands, coordination sites and metal ions [3]. The non-metallocene complexes of titanium and zirconium so called “post-metallocene” complexes, such as the titanium and zirconium phenoxyimine complexes, bisimido pyridyl complexes and recently some Schiff Base complexes bearing heterocycle donors such as furan, thiophene and pyrrole are showing high efficiency in olefin polymerization [4].

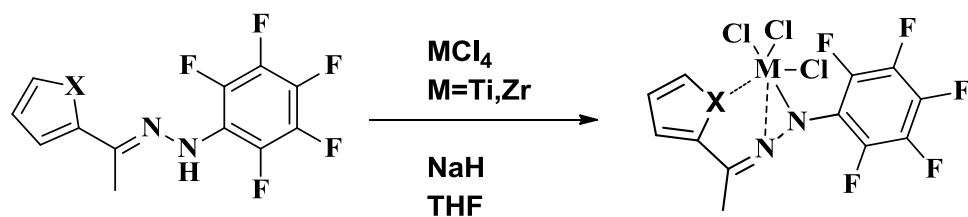
A series of new Schiff base ligands were synthesized by reacting the heterocyclic (furan and thiophene) ketones and aldehydes with perfluorophenyl hydrazine in *n*-hexane. The ligands formed have all the desired electronic and steric properties, coordination sites to metal center to obtain an efficient non-metallocene transition metal olefin polymerization catalyst.



The syntheses of novel titanium and zirconium complexes of Schiff base derivatives linked to furan and thiophene were achieved first by the reaction of the Schiff bases with THF adducts of titanium tetrachloride ($\text{TiCl}_4(\text{THF})_2$) and zirconium tetrachloride ($\text{ZrCl}_4(\text{THF})_2$)



and secondly by reacting the Group 4 metal halides with the sodium salt of the new Schiff base ligands obtained by the addition of excess amount of NaH (sodium hydride) in THF to the Schiff base ligands:

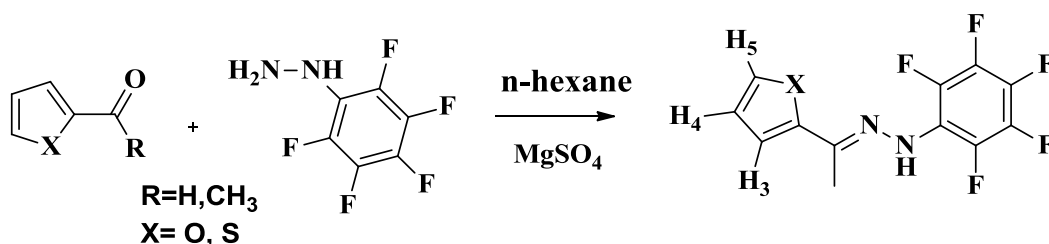


FURAN VE TİYOFENE BAĞLI YENİ SCHIFF BAZLARININ TİTANYUM VE ZİRKONYUM KOMPLEKSLERİ

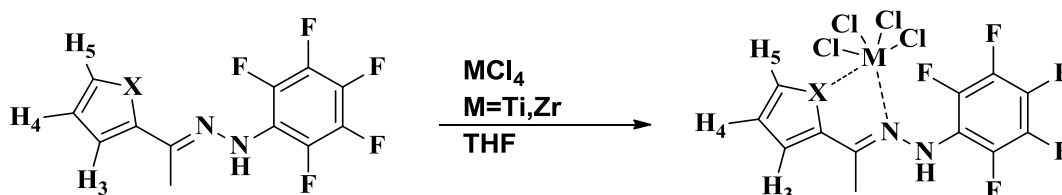
ÖZET

Günümüzde yeni geçiş metali katalizörlerinin tasarlanması ve sentezlenmesi yüksek katalitik aktivite gösterebilen ve düşük kokatalizör-katalizör oranına ihtiyaç duyan katalizörlerin elde edilebilmesi açısından büyük önem taşımaktadır. Bu katalizörler sayesinde polimerin mikroyapısı üzerinde kontrol sağlanıp gelişmiş özelliklere sahip polimerler elde edilebilir [1,2]. Son zamanlarda Schiff bazlarının geçiş metali kompleksleri ticari açıdan önem taşıyan polimerlerin elde edilmesinde yüksek katalitik aktivite göstermektedirler. Özellikle erken geçiş metallerinin Schiff baz kompleksleri (Ti, Zr) hem homojen hem de heterojen reaksiyonlarda yüksek katalitik aktivite göstermektedirler. Bu komplekslerin katalitik aktiviteleri içerdikleri ligandların cinsine, elektronik ve sterik özelliklerine, koordinasyon mevkilerine ve metal iyonuna göre farklılık göstermektedirler [3]. Titanyum ve zirkonyumun metalosen olmayan ve “post-metalosen” adı verilen kompleksleri fenoksiimin, bisimido piridil kompleksleri ve yakın zamanda furan, tiyofen, ve pirol gibi heterosiklik yapılar içeren Schiff bazı kompleksleri olefin polimerizasyonunda yüksek katalitik aktivite göstermektedirler [4].

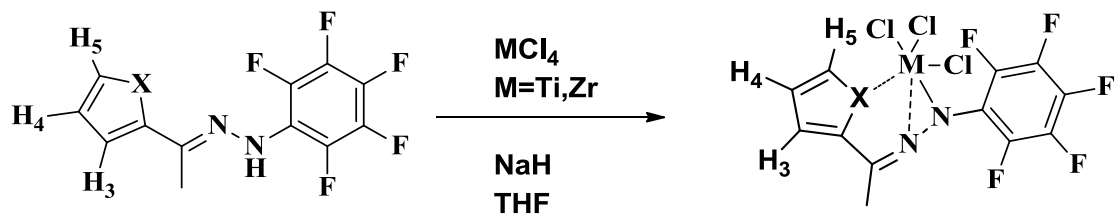
Bir seri yeni Schiff bazı ligandları heterosiklik (furan ve tiyofen) keton ve aldehitlerin perflorofenil hidrazinle n-hekzan çözüsünde tepkimeye sokulması sonucu sentezlenmiştir.



Sentezlenen ligandların titanyum ve zirkonyum kompleksleri Schiff bazlarının ilk olarak titanyum tetraklorür ve zirkonyumun tetraklorürün THF birleşikleriyle ($\text{TiCl}_4(\text{THF})_2$), ($\text{ZrCl}_4(\text{THF})_2$)



daha sonraysa Schiff bazlarının aşırı miktarda sodyum hidrür (NaH) kullanılarak elde edilen tuzlarının THF çözücüsünde metal klorürlerle tepkimeye sokulması elde edilmiştir:



1. INTRODUCTION

1.1 Polyolefins

Polyolefins are polymers made from simple alkenes as monomers like ethylene, propylene or styrene. An equivalent term is polyalkene, although most of the people prefer the term polyolefin. They are the most widely used synthetic polymers. They represent approximately 50% of all commodity polymers and 90% by weight of the global polymer production. There are hundreds of polyolefins grades available with different properties and different applications [1].

Polyolefinic materials, as represented by polyethylenes (PEs), polypropylenes (PPs), ethylene/ α -olefin amorphous copolymers, and ethylene/propylene/diene elastomers (EPDMs) are not only huge molecules, but they are also manufactured and consumed in huge amounts. Their worldwide consumption exceeded 100 million tons in the year 2008, and this is predicted to increase at an average annual growth rate of more than 5% [2].

There is an incredible variety of properties for polyolefins. Polyolefins from ultra-rigid thermosets stiffer than steel to high-performance elastomers. Moreover, these materials are cost-effective and, furthermore, possess good chemical inertness and recyclability. The applications include plastic shopping bags, food packages, shampoo and detergent bottles, containers, storage boxes, toys, disposable diapers, sneakers, bullet-proof vests, and automotive interior and exterior parts (e.g., instrument panels, glass run channels, door trim, fuel tanks, bumpers [1] (Figure 1.1). Thus, they have become indispensable materials for modern living and directly impact our daily lives in countless beneficial ways. But looking at the chemical compositions polyolefins are so few; polyethylenes, polypropylenes and some copolymers of polyethylenes with an α -olefin. The key reason behind this contradiction is the molecular control of the polymerization process by the modern transition based metal catalysts. Transition metal catalysts makes it possible to

produce olefins with precisely defined properties by controlling the molecular weight, molecular weight distribution, and the tacticity [3].



Figure 1.1:Examples of polyolefin application.

1.2. Transition Metal Catalysts for Olefin Polymerization

In the past, the term “Ziegler–Natta catalysts” was used as a general expression that describes a variety of catalysts based on transition metal compounds and capable of polymerizing and copolymerizing alkenes and dienes. However, the development of numerous new catalysts for alkene polymerization in the last 20 years called for separation of all transition metal-based polymerization catalysts into several groups [5].

1.2.1 Ziegler-Natta catalysts

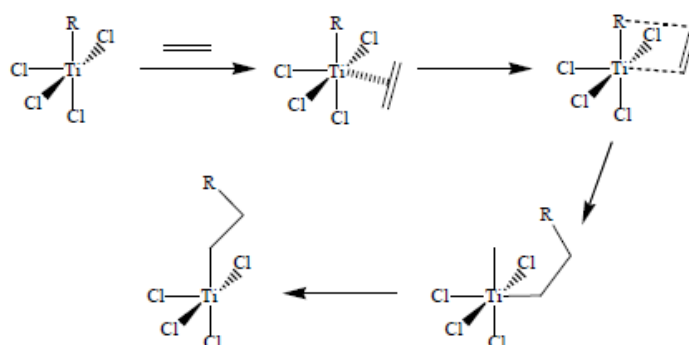


Figure 1.2:Monometallic Ziegler-Natta polymerization mechanism.

The first group, which includes mostly titanium and vanadium-based catalysts, has retained the name “Ziegler–Natta catalysts.” These catalysts are named after Karl Ziegler (Germany) and Giulio Natta (Italy). In the early 1950s, these chemists discovered the first catalytically active compositions for alkene polymerization, determined principles of their action, and investigated the structures and properties of polymers produced with the catalysts. The monumental contributions of Ziegler and Natta received universal recognition and these scientists were jointly awarded the

Nobel Prize in chemistry in 1963. Ziegler–Natta catalysts have been used in the commercial manufacture of various polymeric materials since 1956 [5].

1.2.2 Phillips catalysts

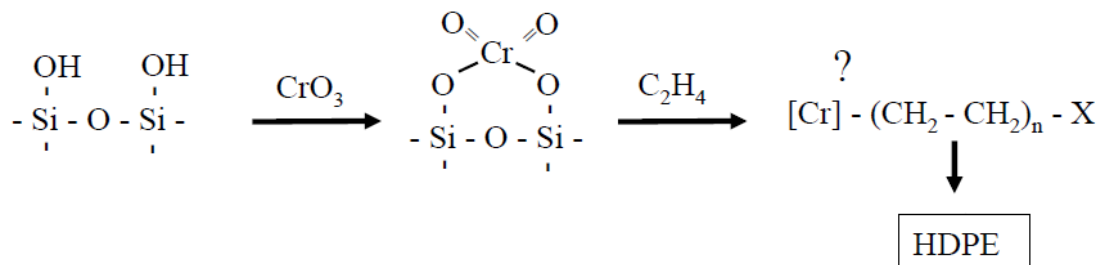


Figure 1.3:Chromium based Phillips catalysts.

The second group constitutes chromium-based catalysts. Historically, chromium oxide catalysts were the first transition metal catalysts used for alkene polymerization; J. P. Hogan and R. L. Banks (USA) discovered them in the early 1950s. Phillips Petroleum Company extensively used these catalysts for the polymerization of ethylene to high molecular, highly crystalline ethylene homopolymers. Later, researchers at Phillips Petroleum Company have found that the same type of catalyst, after modification, is suitable for the polymerization of other alkenes and for alkene copolymerization reactions [5].

1.2.3 Metallocene catalysts

The third catalyst group are commonly called “metallocene polymerization catalysts.” D. Breslow (USA) and G. Natta discovered first metallocene catalysts for alkene polymerization soon after the original discovery of the Ziegler–Natta catalysts. The early metallocene catalysts had relatively low activity and were regarded as most suitable for academic research [6]. However, German scientists W. Kaminsky and H. Sinn in 1976 discovered a new class of metallocene catalyst systems that exhibit extremely high activity [5]. A large number of metallocene complexes can be used in Kaminsky–Sinn catalysts. They usually belong to the following classes:

- Bis(cyclopentadienyl) complexes Cp_2MX_2 , where M is Titanium, Zirconium, or Hafnium, and X are halogen atoms, H, or small alkyl groups. The cyclopentadienyl groups can carry various alkyl substituents.

- Bis-metallocene complexes in which one or both ligands are indenyl groups C_9H_7 , tetrahydroindenyl groups, C_9H_{11} , or fluorenyl groups, $C_{13}H_9$.
- Bridged metallocene complexes with cyclopentadienyl, indenyl, tetrahydroindenyl, and fluorenyl ligands. The bridges connect two cyclopentadienyl rings. The most frequently used bridges are $-CH_2-CH_2-$, $WSiMe_2$, WCM_2 , $WSiPh_2$, and $-CHPh-CHPh-$ [5].

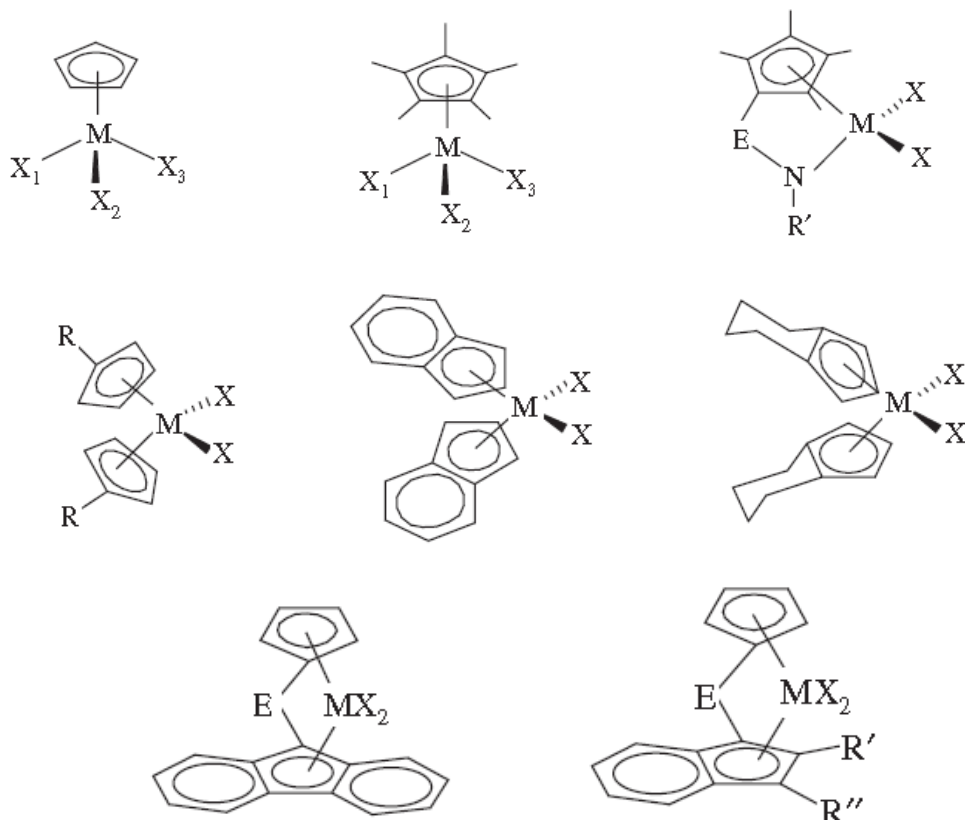


Figure 1.4: Structures of different type of metallocene catalysts.

The structures of these metallocene complexes are shown in Figure 1.4. Among metallocene complexes of this type, zirconium complexes are usually preferred because of their high activity. When polymerization reactions with Kaminsky–Sinn catalysts are carried out in solution, either in an aromatic or in an aliphatic solvent, the $[MAO]:[Zr]$ ratio is usually high, 1,000–2,000, although much lower ratios are employed under commercial conditions. Kaminsky–Sinn catalysts, when used for ethylene polymerization in toluene solutions at sufficiently high $[Al]:[Zr]$ ratios, exhibit exceptionally high activity. Many commercial polymerization processes require preparation of supported Kaminsky–Sinn catalysts. Nowadays, two types of metallocene complexes are widely used as components of catalyst systems. The first

type of the metallocene complex contains two cyclopentadienyl rings attached to a transition metal atom (usually Zr, Ti, rarely Hf) and the second type contains one cyclopentadienyl ring. Both types of metallocene complexes were the subjects of an enormous volume of research, both in academia and in industry. These catalysts and their subsequent modifications presently compete with Ziegler–Natta catalysts for many applications [6].

In spite of the success of metallocene catalysts in polymerization reactions, they also exhibit some disadvantages. These catalysts need a large amount of MAO or expensive fluorinated borate activators to obtain adequate polymerization activity, which causes concern over the high cost of metallocene catalysts and the high ash (Al_2O_3) content of the product polymers. Consequently, there is a great need to develop new catalyst systems that can provide high catalytic activity with no need for a large amount of expensive cocatalysts [3].

1.2.4 Post-Metallocene catalysts

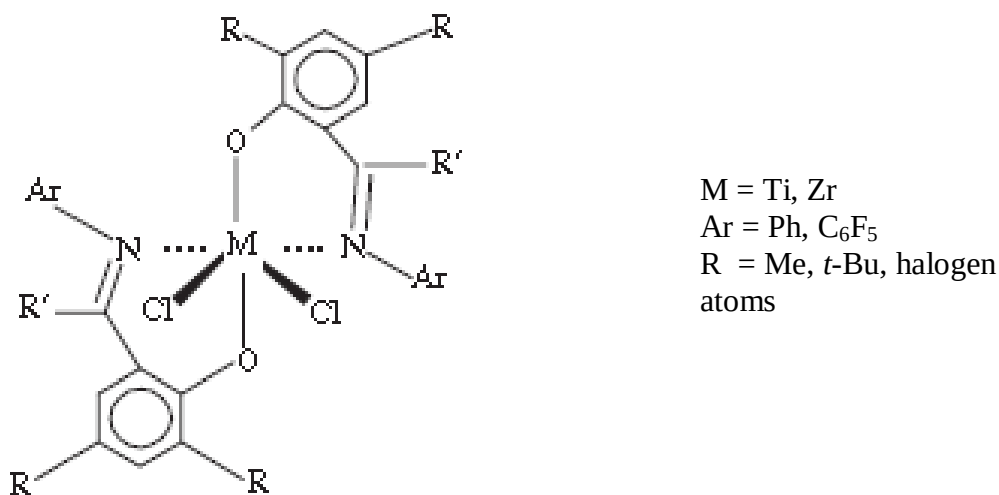


Figure 1.5:Example of a Post-Metallocene catalyst.

The fourth group includes polymerization catalysts based on hydrocarbon-soluble non-metallocene transition metal complexes. M. Brookhart (USA) in 1995 discovered the first catalysts of this type. In the past several years this field underwent a rapid development and now encompasses well-defined complexes of many early-period and late-period transition metals in the Periodic Table.[6] At the present time, the development of homogeneous catalyst systems based on non-metallocene complexes of various transition metals is the leading research area in the

field of alkene polymerization catalysis. A large variety of multidentate complexes of early- and late-period transition metals are being explored. Some of these catalysts are relatively stable in a polar environment. They also provide the best route to the synthesis of alkene copolymers with polar vinyl compounds. The family of non-metallocene homogeneous catalysts utilizes a variety of complexes of various metals, ranging from d^0 metals (Sc) to lanthanoid and actinoid metals, and a large variety of monodentate, bidentate, and multidentate ligands containing oxygen, nitrogen, phosphorus, and sulfur as metal-coordinating atoms. The complexes are usually isolated and are well characterized by the single crystal X-ray method. They are transformed into polymerization catalysts using the same cocatalysts as those in metallocene catalysis, MAO or ion-forming activators under mild conditions [5].

1.3 Single-Site catalysts

The definition of a single type of active center in a catalytic polymerization reaction can be formulated on the basis of its kinetic and stereochemical properties. Active centers of a single type have the following common characteristics:

- 1) The value of the propagation rate constant in a polymerization reaction of a particular alkene, as well as the rate constants of all chain transfer reactions, is the same for all the centers. These kinetic features lead to a particular type of the molecular weight distribution of any polymer produced with uniform active centers.
- 2) The stereospecificity of all the centers of a given type (represented, e.g., by the probability of steric errors in homopolymer chains) is the same. This characteristics leads to a very narrow stereoregularity distribution of alkene homopolymers.
- 3) In copolymerization reactions of two alkenes, relative reactivities of the alkenes are the same for all the centers of a given type. This characteristics leads to a narrow compositional distribution of alkene copolymers [2].

While the multi-sited heterogeneous Ziegler–Natta catalysts represented by $MgCl_2$ - supported $TiCl_4$ catalysts currently dominate the market, molecular catalysts (single-site catalysts) represented by group 4 metallocene catalysts and post-metallocene catalysts are gaining an increasing presence in the market. Benefits of the single-site catalysts include the ability to produce polymers with controlled molecular weight,

specific tacticity, improved molecular weight distribution, and better comonomer distribution and content [8]. With these advantages, the single site catalysts have allowed the preparation of a wide variety of new or differentiated polyolefinic materials, which include high-performance LLDPE (linear low-density polyethylene), polyolefinic elastomers, cyclic olefin copolymers, ethylene/styrene copolymers, highly isotactic and syndiotactic PPs (iPPs and sPPs), and highly syndiotactipolystyrenes (sPPs) [7].

Additionally, recently emerging non-metallocene or so-called “post-metallocene” single-site catalysts (Figure 1.3) have enabled synthesizing distinctive polymers such as hyperbranched PE’s, ethylene/polar monomer copolymers and higher α -olefin-based block copolymers, which are difficult or virtually impossible to produce using group 4 metallocene catalysts. Moreover, the post-metallocene catalysts have provided systematic opportunities to study the mechanisms of the initiation, propagation, and termination steps of coordination (insertion) polymerization and the mechanisms of stereospecific polymerization [8]. This has significantly contributed to advances in the rational design of catalysts for the controlled copolymerization of olefinic monomers. Altogether, the development of high performance post-metallocene catalysts has made a dramatic impact on polymer synthesis and catalysis chemistry. There is thus great interest in the development of new non-metallocene catalysts for olefin polymerization with a view to achieving unique catalysis and distinctive polymer synthesis [9].

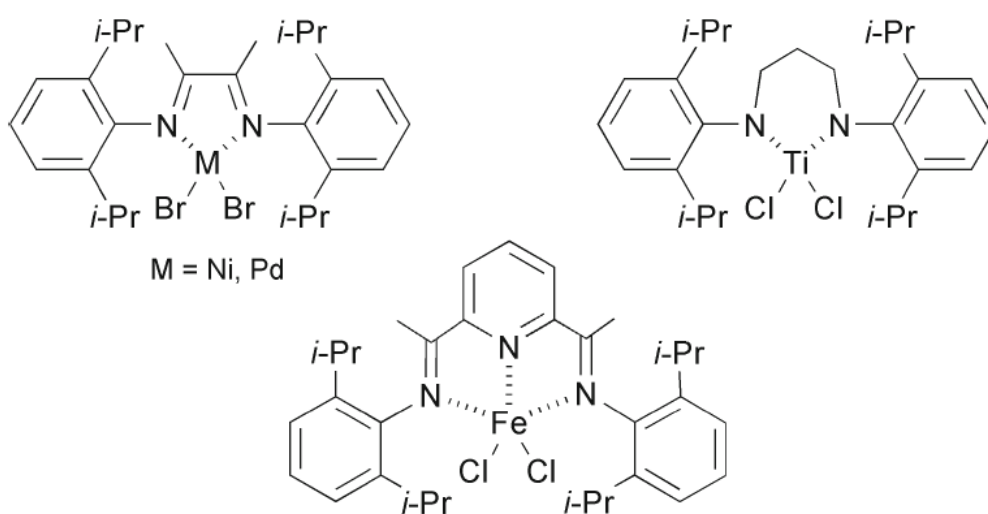


Figure 1.6: Examples of post-metallocene single site catalysts.

1.4 Coordination or Insertion Polymerisation

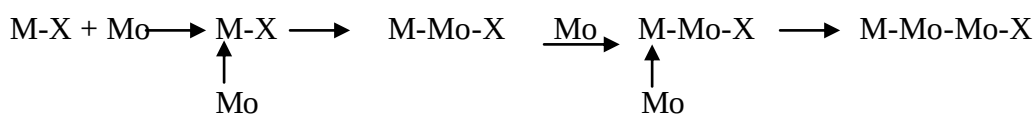


Figure 1.7:Coordination of a monomer (Mo) to a metal (M).

Polymerisation carried out in the presence of a coordination catalyst is referred to as “coordination polymerisation” or “insertion polymerisation”, when each step involves the complexation of monomer before its enchainment at the active site of the catalyst. The active site in each coordination catalyst comprises the metal atom (M) surrounded with ligands’ one of which (X) forms a covalent active bond (M-X) with this metal atom. This implies that the growing polymer chain is covalently bound to the metal atom. A characteristic feature of coordination polymerisation is the mutual activation of the reacting bonds of both the monomer (Mo) and the active site (M-X) through the complexation of the monomer with the metal atom at this site, which results in the cleavage of these bonds in the concerted reaction [10].

The coordination step proposed in many polymerisation systems with coordination catalysts has not been fully established. Thus, the more general term ‘insertion polymerisation’ has been used for these polymerisations systems to imply a hindered propagation site and to avoid implying the unproven coordination aspect.

1.5 Activation of Catalysts

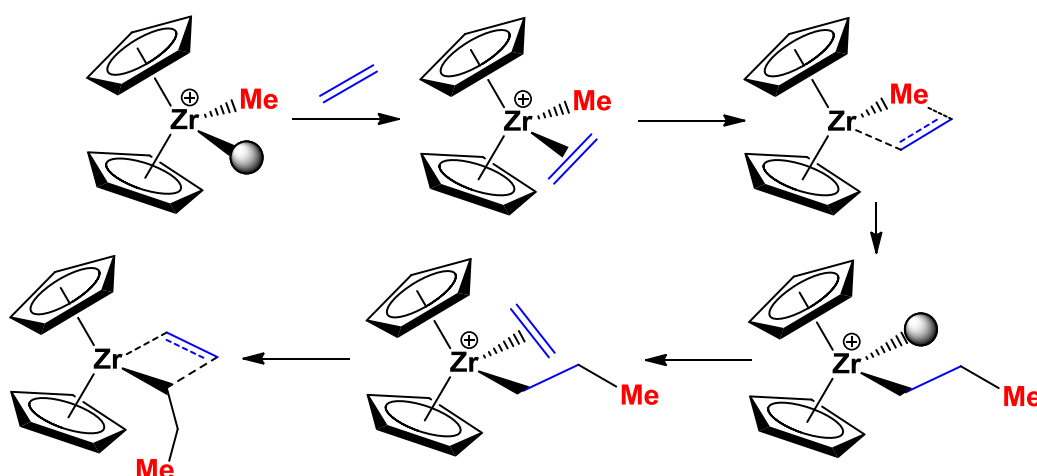


Figure 1.8:Activation of a metallocene precatalyst by MAO.

The activation of polymerization catalysts based on coordination complexes consists of generating an equilibrium concentration of a coordinatively unsaturated species,

usually cationic, that contains a reactive metal-alkyl bond and is capable of binding an olefin in such a manner that transfer of the alkyl ligand to the monomer can occur.

MAO is the most widely employed activator in the industry of group 4 polymerization catalysts. Methylalumoxane activates metallocene catalysts by virtue of Lewis acidic sites on some of the complex structures present in MAO [11].

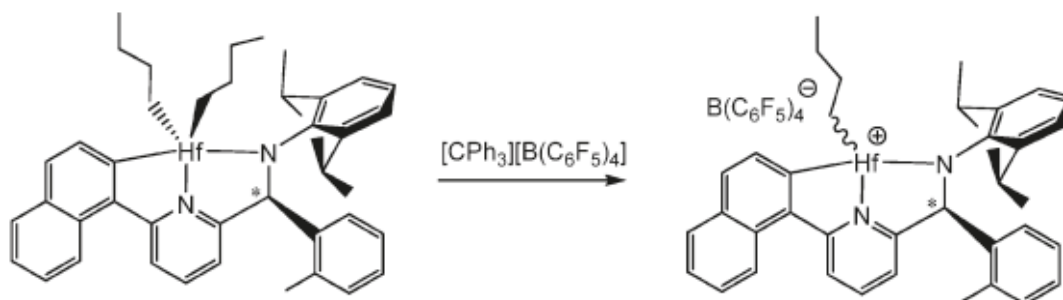


Figure 1.9: Activation of a Post-Metallocene precatalyst by borate cocatalyst.

This activation can also be achieved by reacting metal dialkyl complexes, usually the metal dimethyls LnMMe_2 ($\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$), ($\text{Ln}=\text{Ligand}$) with suitable Lewis acids such as $\text{B}(\text{C}_6\text{F}_5)_3$ and triphenylmethyl (“trityl”) salts of noncoordinating anions, or Brønsted acids capable of generating weakly coordinating counteranions. Among the last class of activators, anilinium salts such as $[\text{HNR}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{Me}, \text{Et}$) have been widely used [11].

1.6 Termination of Polymerization

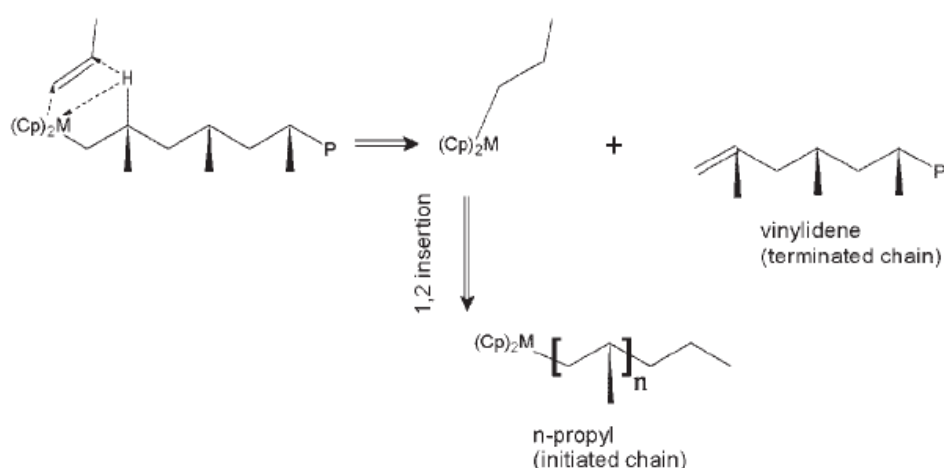


Figure 1.10: Beta-Hydrogen elimination.

One of the most important properties of a polymer is its average chain length. For metal-catalyzed olefin polymerization, the degree of polymerization is determined by

the ratio between the rate of propagation and those of all possible chain termination mechanisms. There are many potential chain termination reactions. The most important ones are hydrogen elimination (BHE) and hydrogen transfer to monomer (BHT) [12].

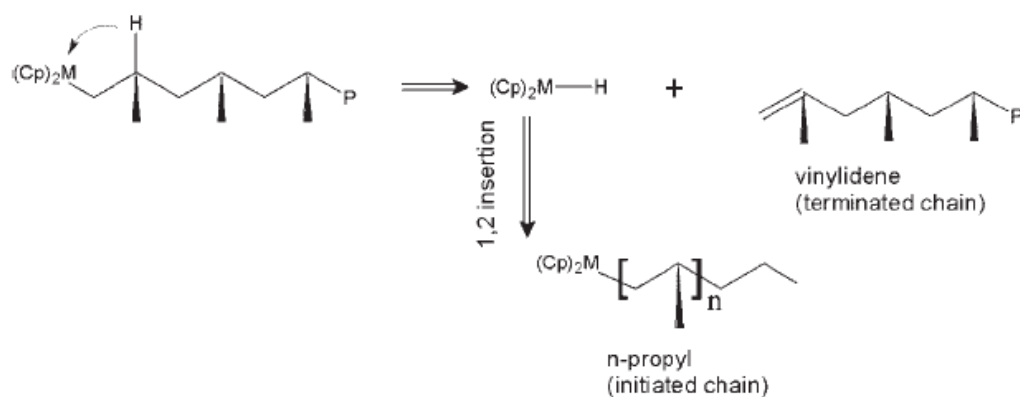


Figure 1.11: Beta-Hydrogen transfer to monomer.

2. SCHIFF BASES

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in 1864. Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily-tunable electronic and steric effects thus being versatile. Schiff bases are compounds having a formula $RR'C=NR''$ where R is an aryl group, R' is a hydrogen atom or methyl group and R'' is either an alkyl or aryl group. However, usually compounds where R'' is an alkyl or aryl group and R' is an alkyl or aromatic group are also counted as Schiff bases. The Schiff base class is very versatile as compounds can have a variety of different substituents and they can be unbridged or bridged. Most commonly Schiff bases have NO or N₂O₂-donor atoms but the oxygen atoms can be replaced by sulphur, nitrogen, or selenium atoms.

2.1 Syntheses of Schiff Bases

There are several reaction pathways to synthesize Schiff bases. The most common is an acid catalysed condensation reaction of amine and aldehyde or ketone under refluxing conditions. The first step in this reaction is an attack of nucleophilic nitrogen atom of amine on the carbonyl carbon, resulting in a normally unstable carbinolamine intermediate. The reaction can reverse to the starting materials, or when the hydroxyl group is eliminated and a C=N bond is formed an imine can be formed. Many factors affect the condensation reaction, for example the pH of the solution as well as the steric and electronic effects of the carbonyl compound and amine. As amine is basic, it is mostly protonated in acidic conditions and thus cannot function as a nucleophile and the reaction cannot proceed. Furthermore, in very basic reaction conditions the reaction is hindered as sufficiently protons are not available to catalyse the elimination of the carbinolamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reaction centre of aldehyde is sterically less hindered than that of ketone. Furthermore, the extra carbon of ketone donates electron density and thus makes the

ketone less electrophilic compared to aldehyde. The presence of dehydrating agents normally favours the formation of Schiff bases. [13]

Magnesium sulfate (MgSO_4) is commonly employed as a dehydrating agent. The water produced in the reaction can also be removed from the equilibrium using a Dean Stark apparatus, when conducting the synthesis in toluene or benzene. Finally, ethanol, at room temperature or in refluxing conditions, is also a valuable solvent for the preparation of Schiff bases. Degradation of the Schiff bases can occur during the purification step. Chromatography of Schiff bases on silica gel can cause some degree of decomposition of the Schiff bases, through hydrolysis. In this case, it is better to purify the Schiff base by crystallization. If the Schiff bases are insoluble in hexane or cyclohexane, they can be purified by stirring the crude reaction mixture in these solvents, sometimes adding a small portion of a more polar solvent (Et_2O , CH_2Cl_2), in order to eliminate impurities. In general, Schiff bases are stable solids and can be stored without precautions. [13]

2.2 Schiff Base Complexes of Transition Metals

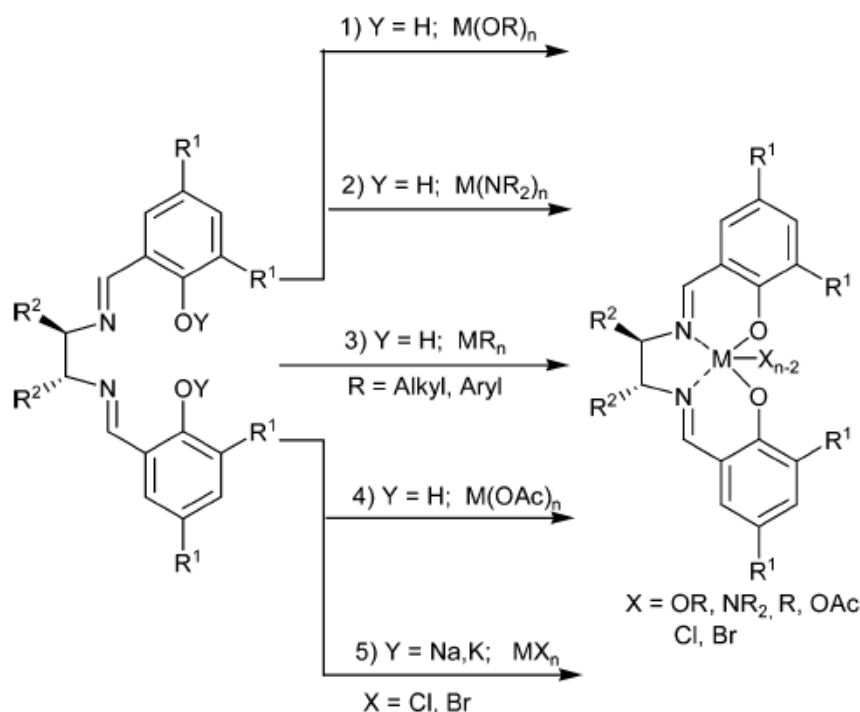


Figure 2.1: Preparation of salen type Schiff base complexes.

Schiff base ligands are able to coordinate metals through imine nitrogen and also other possible donor atoms. Modern chemists still prepare Schiff bases, nowadays

furan and thiophene derivatives of Schiff base ligands are considered “privileged ligands”. In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations. Schiff bases are also able to transmit chiral information to produce nonracemic products through a catalytic process; chiral aldehydes or chiral amines can be used. From a practical point of view, the aspects involved in the preparation of Schiff base metal complexes are spread out in the literature.[13,14]

In many catalytic applications of Schiff base metal complexes are prepared in situ by producing a reaction between the Schiff base and commercially available metal complexes. This approach is clearly simple and suitable for catalytic applications. Essentially, four different synthetic routes can be identified for the preparation of Schiff base metal complexes. [13]

Route 1 involves the use of metal alkoxides ($M(OR)_n$). For early transition metal alkoxide ($M = Ti, Zr$) derivatives are commercially available and easy to handle, while the use of other metal alkoxide derivatives is more problematic, particularly in the case of highly moisture-sensitive derivatives of lanthanides. The introduction of a bulky group in the Schiff bases can control the stability of the complex, by shifting the equilibrium towards the formation of a single product. Metal alkoxides are sensitive to hydrolysis and the presence of adventitious water can result in the formation of μ -oxo species. Additionally, metal Schiff bases bearing alkoxide groups as ligands, are sensitive to traces of water, producing various μ -oxo species. The presence of adventitious water is difficult to control, especially when the reaction between the Schiff bases and the metal alkoxide is performed in situ. The formation of μ -oxo species can cause difficulties in reproducing the results of catalytic reactions. [13]

Route 2 involves the reaction of metal amides $M(NMe_2)_4$ ($M = Ti, Zr$) which are also highly suitable precursors for the preparation of Schiff base metal complexes of early transition metals. The reaction occurs via the elimination of the acidic proton of the Schiff base, occurring at the same time as the formation of volatile $NHMe_2$. [13]

In route 3, a Schiff base metal complex can be prepared in a clean and effective way using metal alkyl complexes as precursors. Various metal alkyls in the main group of metals ($AlMe_3$, $GaMe_3$, $InMe_3$) are commercially available and can be used in the

preparation of Schiff bases by a direct exchange reaction. Alkyl titanium and zirconium tetrabenzyl complexes are used in the preparation of Schiff base metal complexes, that are active as polymerization catalysts. These alkyl reagents are obtained from titanium and zirconium halides by the reaction of a benzyl Grignard reagent. [13]

In route 4, many Schiff base metal complexes can be obtained by the treatment of the Schiff base with the corresponding metal acetate, normally by heating the Schiff base in the presence of the metal salt under reflux conditions. Copper, cobalt and nickel Schiff bases are prepared using the corresponding acetate $M(OAc)_2$ ($M = Ni, Cu, Co$). (route 4) [13]

In route 5, instead of using acetate, a direct reaction with metal halides is also possible. In fact, early transition Schiff bases are sometimes prepared by direct reaction with $TiCl_4$ or $ZrCl_4$. [13]

2.3 Goal of the Thesis

Main purpose of this thesis is to synthesize and characterize a series of novel post-metallocene catalysts by the reaction between metal tetrachlorides ($M = Ti, Zr$) and newly designed furan and thiophene derivatives of Schiff base ligands. The design of such Schiff bases which have unique electronic and steric features was inspired by combining all the information about efficient precatalysts for olefin polymerization. [12-21] The general requirements for a highly active polymerization precatalyst are:

- A catalyst must have high olefin-insertion ability.
- A catalyst must have two available *cis*-located sites for polymerization.
- A catalyst must be stable enough under usual polymerization conditions [15]

Bulky substituents in the backbone of the ligand are generally considered to be necessary for olefin polymerization catalysts. [16] Electron-withdrawing substituents are routinely incorporated to enhance the electrophilicity of the metal center, giving improved activities.[17] In comparison with the dihalide complexes only a few of the trihalide (or trialkyl) non-metallocene precursors were found to be active for olefin polymerization. One of the reasons is probably that the space of the central metal in the trichloride complex is more open than in the similar dichloride species because the chlorine atom is small, influencing the chain-transfer process of

polymerization.[19,20] Electron-withdrawing, fluorinated aryl groups are expected to provide highly electrophilic, reactive metal centers. [21] The presence of fluorine interaction with the central metal ion is sometimes possible which renders the complex more active. [18] The presence of Schiff base ligands with heteroatom donors renders the complex more electrophilic, a requirement for an active olefin polymerization catalyst. [14] In addition to that, highly fluorous Group4 metal complexes exhibit increased robustness over the non-fluorinated analogues and can survive even at high temperatures (over 100°C) which could be necessary for a good catalytic activity. [17]

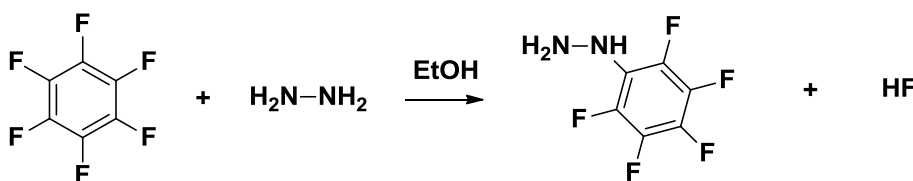
Considering the different electronic properties and spaces of the reactive sites between trichloride and dichloride complexes, we designed trichloride complexes bearing perfluorophenyl hydrazone group linked to furan or thiophene which should combine all the necessary properties (explained above) of an efficient olefin polymerization catalyst.

3. EXPERIMENTAL PART

3.1 General

All the manipulations for the titanium and zirconium complexes were carried out in an inert (Nitrogen) atmosphere using standard Schlenk techniques or in a Innovative Glovebox with O₂ level below 5 ppm and H₂O level below 1 ppm. All the solvents used were HPLC grade solvents distilled prior to use in a Innovative Solvent Purification System with special molecular sieves and catalysts (activated alumina) which eliminates trace amount of water. Melting points were measured on a Buchi B540 instrument and are uncorrected. Proton ¹H-NMR spectra used in the characterization of products were recorded on Bruker 250 MHz AC Aspect 3000 spectrometer with tetramethylsilane as internal reference. Gas Chromatography-Mass analyses were taken on a Thermo Finnigan Trace DSQ GC and Perkin Elmer Clarus 500 spectrometers. Infrared Spectra of ligands were taken in a Perkin Elmer Spectrum-One FT-IR instrument with ATR accesory, for highly air-sensitive metal complexes the infrared spectra were taken either on a sealed liquid cell with NaCl windows or on a mull cell using nujol between CsI cells. All the chemicals were used as they were purchased. The deuterated solvents were taken into glovebox, opened inside the box and stored with 4A molecular sieves to eliminate trace amount of water.

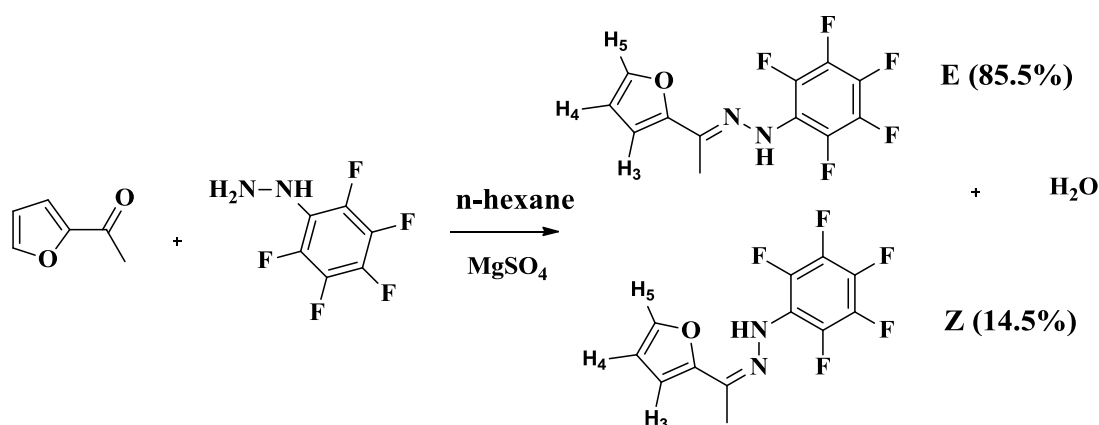
3.2 Synthesis of Perfluorophenyl Hydrazine



Perfluorophenyl hydrazine was prepared according to literature.[24]. 12,7 ml (0,1mol) of hexafluorobenzene was added to 20 ml (0,4mol) of hydrazine monohydrate in 30ml of THF. The mixture was refluxed for 2 days and the crude

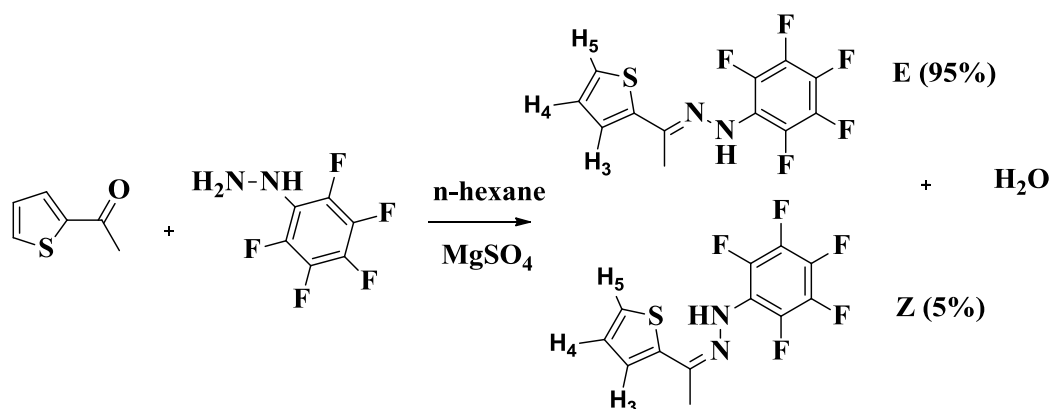
product was poured in water for the extraction of organic phase and the organic phase was evacuated in vacuo and washed with water. Perfluorophenyl hydrazine was purified by column chromatography in silica gel 60 (0,063-0,200 mesh) using hexane as the eluent. Light yellow product of perfluorophenyl hydrazine was obtained after the removal of solvent in vacuo with 51% yield. Melting Point: 74-75°C. IR(ATR): $\nu(\text{NH})$: 3344, $\nu(\text{NH}_2)$: 3248, $\nu(\text{C}=\text{C})_{\text{aromatic}}$: 2980-2966 cm^{-1} .

3.3 Synthesis of Ligand a



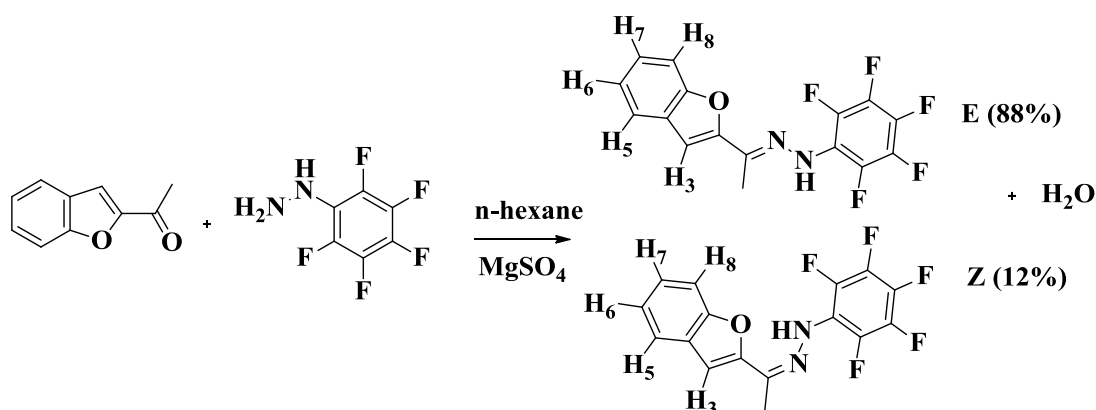
A procedure was adopted by combining the information from a review explaining the general synthesis methods of Schiff bases [12]. 1ml (10mmol) of 2-acetyl furan and 2,97g (15mmol) of pentafluorophenyl hydrazine together with a small amount of magnesium sulfate were refluxed in 25ml of n-hexane for 6 hours. The magnesium sulfate was filtered from the residue and the residue was two times crystallized from n-hexane solution. The desired product was obtained as a mixture of E and Z isomers, as dark yellow crystals with 68% yield. Melting point was detected as 103,5°C-104,5°C. IR(ATR): $\nu(\text{N-H})$ 3374 cm^{-1} , $\nu(\text{C-H})$ 3154-3119 cm^{-1} , $\nu(\text{C}=\text{N})$ 1664 cm^{-1} , $\nu(\text{C}=\text{C}_{\text{Furan}})$ 1570 cm^{-1} . $^1\text{H-NMR}$ (250MHz, CDCl_3) : δ 2.24 (s, 3 H, CH_3), δ 6.45 (dd, $J=4\text{Hz}$, 1 H, C(4) H), δ 6.69 (d, $J=4\text{Hz}$, 1 H, C(3) H), δ 6.78 (s, 1 H, N- H), δ 7.49 (d, $J=4\text{Hz}$, 1 H, C(5) H). MS (EI) m/z (%): 290.13 (60), 222.09 (10), 181.08 (50), 155.08 (30), 131.07 (10), 117.01 (15), 108.06 (100), 93.04 (20), 80.07 (15), 65.01 (20), 53.00 (45), 51.00 (10).

3.4 Synthesis of Ligand b



A similar procedure for the synthesis of compound a was applied to obtain 62% of 2-acetyl thiophene perfluorophenyl hydrazone as white crystals. M.P.: 126-127°C. IR(ATR): $\nu(\text{N-H})$ 3365 cm⁻¹, $\nu(\text{C-H})$ 3121-2962 cm⁻¹, $\nu(\text{C=N})$ 1664 cm⁻¹, $\nu(\text{C=C}_{\text{Thiophene}})$ 1591 cm⁻¹. ¹H-NMR (250MHz, CDCl₃) : δ 2.30 (s, 3 H, CH₃), δ 6.81 (s, 1 H, N-H), δ 7.00 (dd, J=2Hz, 1 H, C(4)H), δ 7.23 (d, 1 H, J=2Hz, C(3)H), δ 7.29 (d, J=2Hz, 1 H, C(5)H). MS (EI) *m/z* (%): 307.1 (10), 306 (80), 222 (15), 182 (15), 181 (65), 155 (30), 124 (100), 97.1 (45), 69.1 (20), 45.1 (35), 39.1 (60).

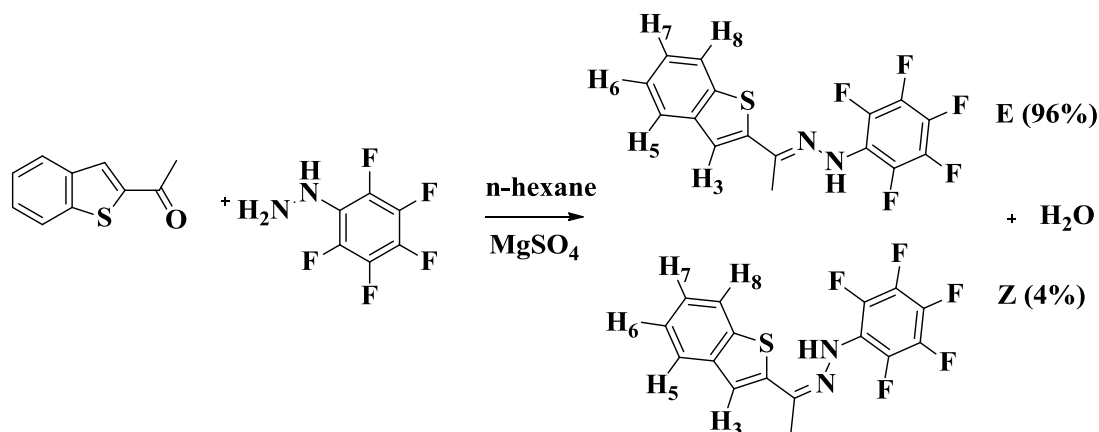
3.5 Synthesis of Ligand c



With a 58% yield yellow crystals of compound c was obtained. M.P.= 216-217°C. IR(ATR): $\nu(\text{N-H})$ 3365 cm⁻¹, $\nu(\text{C-H})$ 3100-3041 cm⁻¹, $\nu(\text{C=N})$ 1660 cm⁻¹, $\nu(\text{C=C}_{\text{Benzofuran}})$ 1654 cm⁻¹. ¹H-NMR (250MHz, CDCl₃) : δ 2.35 (s, 3H, CH₃) δ 6.98

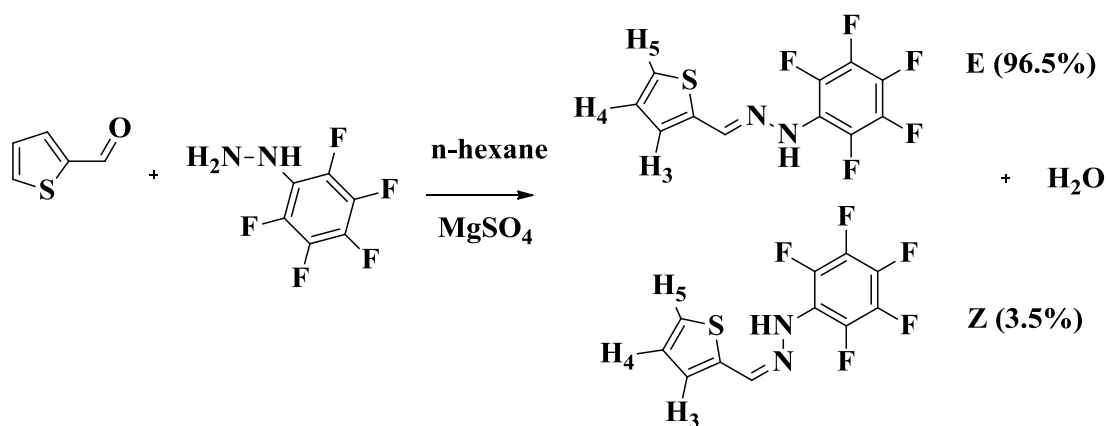
(s, 1H, N-H) δ 7.04 (s, 1H, , C(3)H) 7.32 (dd, 1H, J=5Hz, , C(6)H), δ 7.35(dd, J=5Hz, , C(7)H), 7.53 (J=7.8Hz, dd, 1H, , C(5)H) 7.58(J=7.8Hz ,d, 1H, , C(8)H). MS (EI) m/z (%): 341 (5), 340 (55), 222 (5), 181 (45), 158 (95), 155 (20), 143 (25), 131 (30), 118 (15), 115 (45), 103 (5), 89 (100), 63 (40), 51 (10) .

3.6 Synthesis of Ligand d



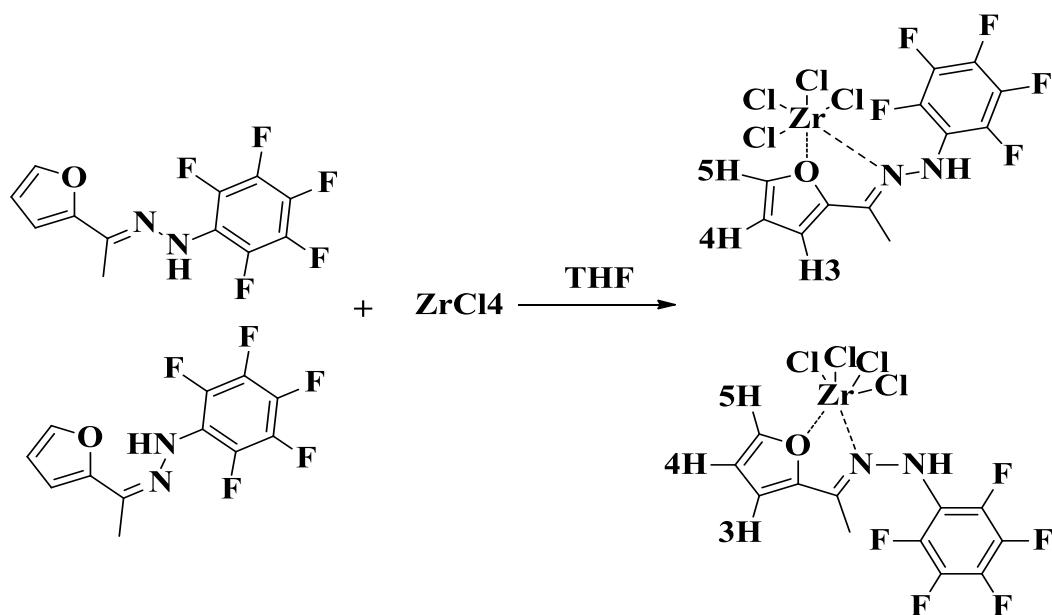
With a 52% yield yellow crystals of 2-acetyl benzothiophene perfluorophenyl hydrazone was obtained. M.P.= 232-233°C. IR(ATR): $\nu(\text{N-H})$ 3345 cm⁻¹, $\nu(\text{C-H})$ 3246-3007 cm⁻¹, $\nu(\text{C=N})$ 1663 cm⁻¹, $\nu(\text{C=C}_{\text{thiophene}})$ 1583 cm⁻¹. ¹H-NMR (250MHz, CDCl₃) : δ 2.35 (s,3H, CH₃), δ 6.98 (s,1H, N-H), δ 7.315 (dd, 1H, J=3.8Hz, C(6)H)), δ 7.335 (dd, 1H, J=3.8Hz, C(7)H)), δ 7.43 (s, 1H, Thiophene), δ 7.73 (d, 1H, J=3.1Hz, C(5)H)) δ 7.75 (d, 1H, J=3.1Hz, C(6)H)). MS (EI) m/z (%): 358 (5), 357 (10), 356 (45), 355 (20), 295 (10), 281(20), 222(20), 221 (45), 181 (40), 174 (75), 159 (40), 147(70), 133(45), 115 (15), 89 (80), 78 (25), 73 (100), 69 (10), 63 (10).

3.7 Synthesis of Ligand e



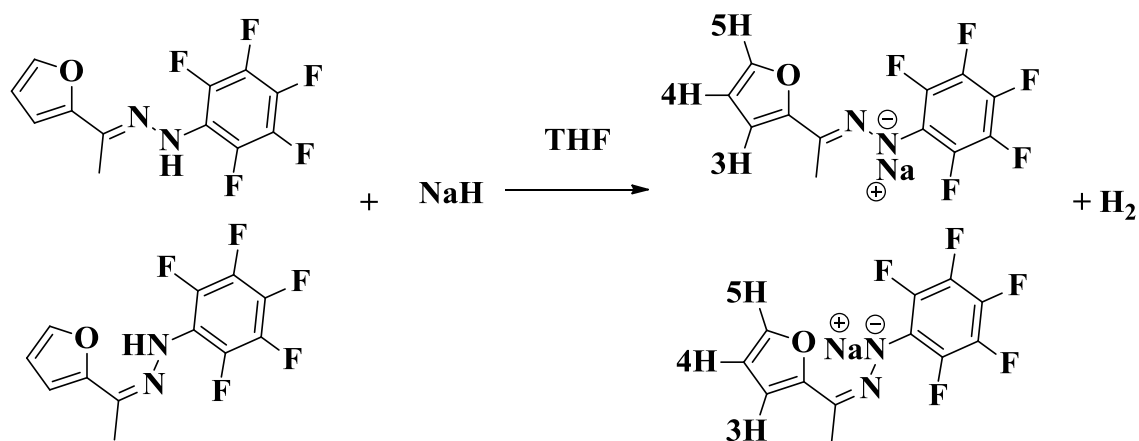
1,12 ml of thiophene 2-carboxaldehyde (10mmol) and 2,97g (15mmol) of perfluorophenyl hydrazine were refluxed in 25 ml n-hexane with a small portion of magnesium sulfate. The residue was two times crystallised from n-hexanes. Brown-yellow crystals were obtained with 68% yield. M.p.=140-141°C. IR(ATR): $\nu(\text{N-H})$ 3329 cm^{-1} , $\nu(\text{C-H})$ 3117-2985 cm^{-1} , $\nu(\text{C=N})$ 1659 cm^{-1} , $\nu(\text{C=C}_{\text{Thiophene}})$ 1510 cm^{-1} . $^1\text{H-NMR}$ (250MHz, CDCl_3) : δ 7.04 (dd, 1 H, $J=3.8\text{Hz}$, C(3) H), δ 7.18 (d, 1 H, $J=3.8\text{Hz}$, C(4) H), δ 7.18 (s, 1H, N-H), 7.34 (d, 1 H, $J=3.8\text{Hz}$, C(5) H), 8.00 (s, 1 H, CH). MS (EI) m/z (%): 292.07 (80), 207.10 (30), 183.07 (50), 155.01 (40), 117.04 (10), 110.01 (100), 83.01 (35), 73.05 (30), 68.99 (45), 56.99 (15).

3.8 Synthesis of Complex 2a



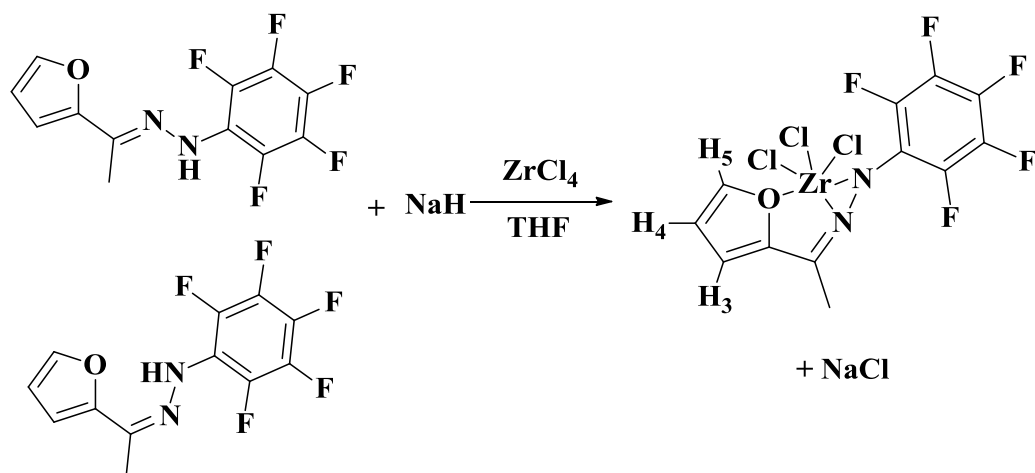
1,45 g (5mmol) of 2-acetyl furan perfluorophenyl hydrazone was added to 10ml THF solution of 1,16g (5mmol) zirconium tetrachloride and the mixture was stirred inside glovebox in a Schlenk tube for 24 hours. THF was removed in vacuum and the residue was washed with n-hexane. The orange zirconium complex was obtained with 60% yield. IR(Mull Cell): $\nu(\text{C-H})$ 2943-2869 cm^{-1} , $\nu(\text{C=N})$ 1628 cm^{-1} . $^1\text{H-NMR}$ (250MHz, CDCl_3) : δ 2.23 (s, 3 H, CH_3), δ 6.55 (dd, $J=4\text{Hz}$, 1 H, NH), δ 6.77 (s, 1 H, C(4) H), δ 7.70 (d, $J=4\text{Hz}$, 1 H, C(4) H), δ 8.74 (d, $J=2\text{Hz}$, 1 H, C(5) H).

3.9 Synthesis of Salt aNa



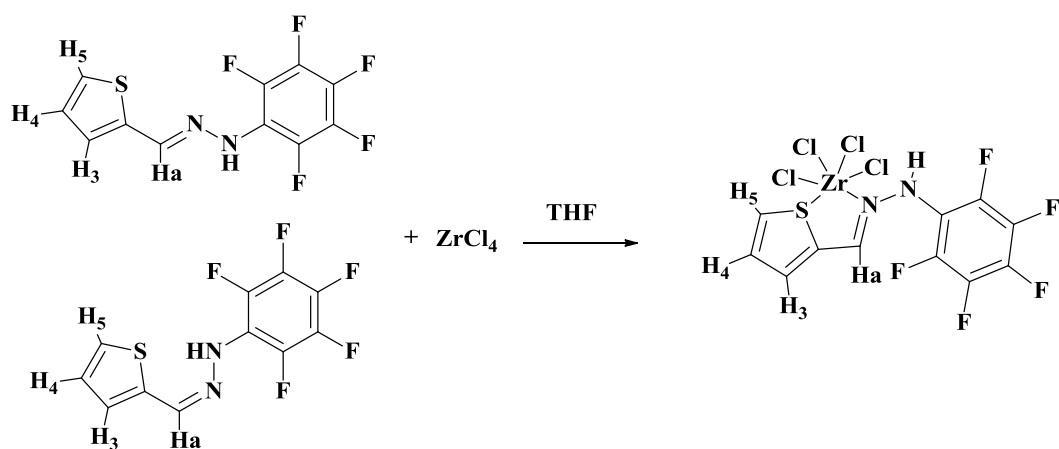
0,39g (1,35mmol) of was slowly added to a 0,12g (5mmol) of NaH in THF. The resulting product was washed with n-hexane, then THF was removed in vacuum. The resulting white salt was obtained with 78% yield. ¹H-NMR (250MHz, CDCl₃) : δ 2.25 (s, 3H, CH₃), δ 6.45(dd, 1H, J=3Hz, C(4)H), δ 6.68 (d,1H, J=3Hz, C(3)H), δ 7.47 (d,1H, J=3Hz, C(5)H).

3.10 Synthesis of Complex 2a3Cl



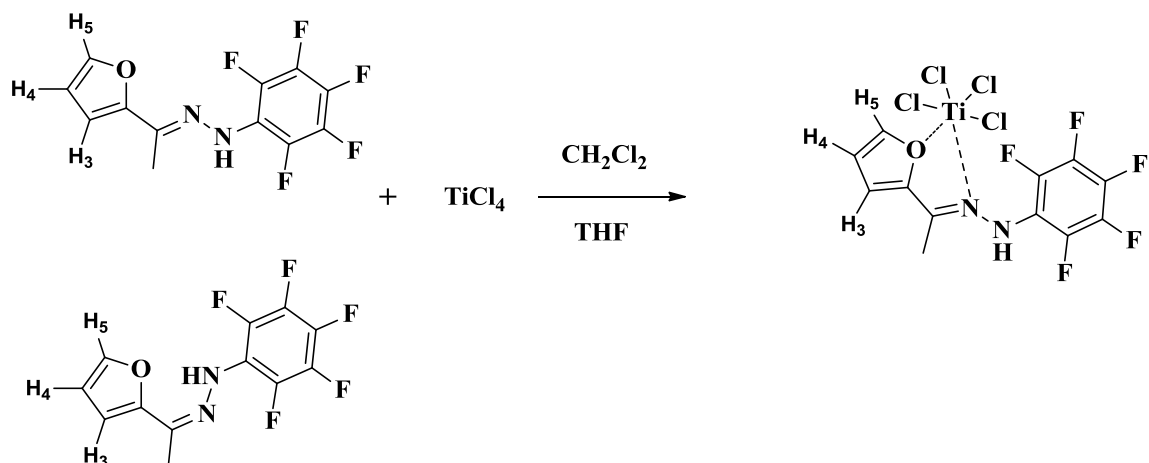
0,39g (1,35mmol) of **1** was slowly added to a 0,12g (5mmol) of NaH in THF. Then 0,314g of 10 ml THF solution of ZrCl₄ was slowly added to this mixture. The precipitation of white NaCl was observed. The NaCl was filtered using Celite 545 and the solvent of the resulting mixture was removed in vacuo. Yellow single crystals of **2** were obtained with 45% yield. ¹H-NMR (250MHz, CDCl₃) : δ 2.57 (s, 3H, CH₃), δ 6.84-7.01(dd, 1H, C(4)*H*), δ 7.13-7.41 (d, 1H, C(3)*H*), δ 7.70 (d, 1H, C(3)*H*).

3.11 Synthesis of **2e**



0,56 g (5mmol) of 2-formyl thiophene perfluorophenyl hydrazone was added to 10ml THF solution of 1,16g (5mmol) zirconium tetrachloride and the mixture was stirred inside glovebox in a Schlenk tube for a day. THF was removed in vacuum and the residue was washed with n-hexane. The turquoise zirconium complex was obtained with 63% yield. IR (Mull Cell): $\nu(\text{C}=\text{N})1632\text{ cm}^{-1}$, $\nu(\text{C}=\text{C}_{\text{thiophene}})1520\text{ cm}^{-1}$. ¹H-NMR (250MHz, CDCl₃) : δ 7.51 (dd, 1 H, J=3.8Hz, C(3)*H*), δ 7.67 (d, 1 H, J=3.8Hz, C(4)*H*), δ 8.48 (s, 1H, N-H), δ 8.48 (d, 1 H, J=3.8Hz, C(5)*H*), 9.41 (s, 1 H, CH).

3.12 Synthesis of Complex 1a



0,292g (1mmol) of ligand **a** was dissolved in 10ml of dichloromethane. To a 10 ml hexane solution of 0.1ml (1mmol) TiCl_4 was added 15ml of THF. Then to $\text{TiCl}_4(\text{THF})_2$ was slowly added dichloromethane solution of ligand **a**. The reaction's color turned immediately from yellow to red and left out in stirring for 24 hours. Then the solvent was removed in vacuo and possible non-reacted ligand **a** was removed by washing with n-hexane. Red solid was obtained with 40% yield. ^1H -NMR (250MHz, CDCl_3) : δ 2.85 (s, 3H, CH_3), δ 6.81 (s, 1H, N-H), δ 6.92(dd, 1H, C(4)H), δ 7.85 (d, 1H, C(3)H), δ 8.22 (d, 1H, C(5)H)

4. RESULTS AND DISCUSSION

4.1 Characterization of the Schiff Base Ligands

Most of the Schiff base ligands, especially those which lack bulky substituents around C=N bond show stereoisomerism around C=N bond. Most of the time the E (entgegen) isomer, sometimes referred as anti-product, is the dominant product since it is sterically favored over the Z (zusammen). [25,26] Although it is difficult to differentiate the two isomers without using 2D-NMR techniques, GC-MS was also a very easy and efficient method for both qualitative and quantitative determination of the synthesized Schiff base isomers. GC-MS method was used for the isomer characterization of all the synthesized Schiff base ligands. According to the results of GC-MS data, thiophene derivatives of Schiff bases have higher percentage of E isomers than furan analogues due to the larger atomic radius of sulphur. The Z isomers of thiophene derivative of Schiff bases distort the planarity of the molecule because of the closeness of large perfluorophenyl group to thiophene ring. On the other hand, the formation percentages of the two isomers were not so much affected by the condensation of benzene ring to either furan or thiophene.

4.2 Characterization of the Metal Complexes

According to ^1H -NMR and FT-IR data, it is clear that the nitrogen of the imine group bonded to the metal by coordinative covalent bond since there is a significant decrease ($20\text{-}30\text{cm}^{-1}$) in the C=N stretching bands in complexes compared to that of ligands. [27] Another phenomenon occurring in the complexation is the coordination of the electronegative heteroatoms (oxygen and sulphur) of the heterocycles to titanium and zirconium resulting in significant changes in the chemical shifts of the heterocycle's protons. Referring to the study done by the C. Parrado *et al.* [28] the chemical shifts of all the complexes are typical consequences of the coordination of heterocycles to a Lewis acidic center. It is also possible to detect the chelation of ring oxygen or ring sulphur to the metal atom using FT-IR: C=C stretching bands of the heterocycles shift to lower energies due to chelation. Also a band near $1200\text{-}1210\text{cm}^{-1}$

belongs to (C-O-C) or (C-S-C) should shift to $10\text{-}30\text{cm}^{-1}$ lower energies due to chelation. [26] Unfortunately, the complex fingerprint region of all the ligands (especially $1200\text{-}1250\text{cm}^{-1}$ region) makes it nearly impossible to assign these stretching bands. Coordination of THF oxygen to zirconium and titanium centers also resulted in down field shifts in CH_2 and OCH_2 protons of THF. To summarize all the complexes showed chelation through both azomethine ($\text{C}=\text{N}$) and heterocycles which was proved by FT-IR and ^1H -NMR techniques.

4.3 Complex 2a

Looking to the proton-NMR the ring (furan) protons shifted to the down-field with the proton closer to oxygen atom showing the greatest shift which is reasonable due to decrease of the inductive effect of the ring oxygen due to chelation. The proton attached to the nitrogen of hydrazone group didn't show a significant change (only 0.1 ppm) which means that there is no interaction between second Nitrogen and the metal center. Also the methyl protons remained in 2.23ppm. FT-IR data shows the chelation through imine nitrogen since there is a decrease of 36cm^{-1} .

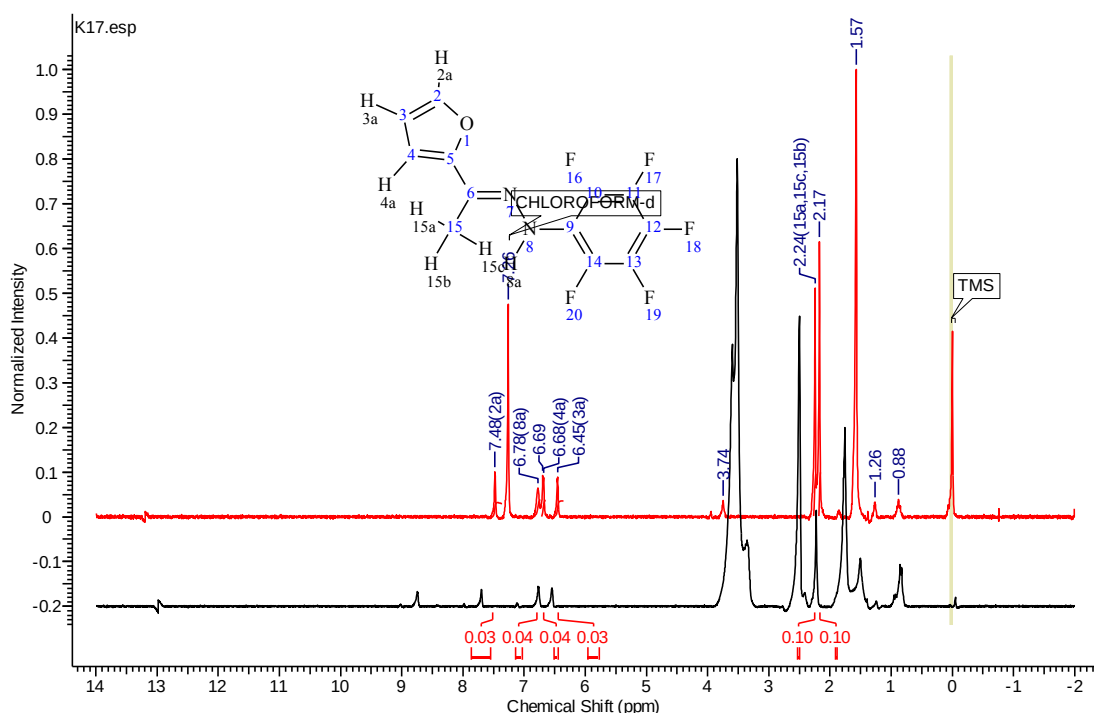


Figure 4.1: Proton-NMR spectra of ligand **a** and complex **2a**.

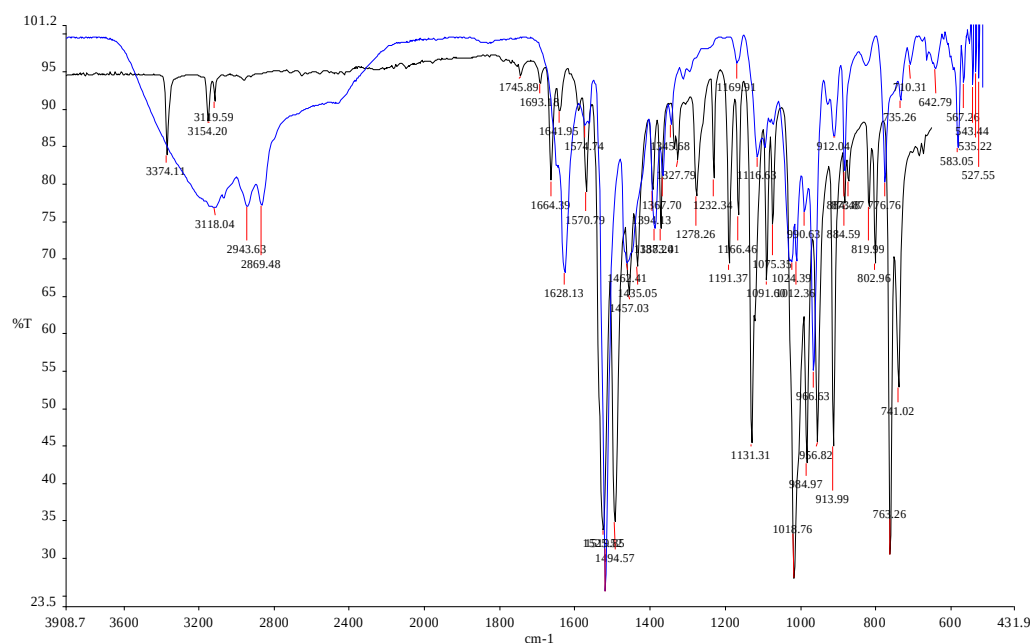


Figure 4.2: FT-IR spectra of ligand **a** and complex **2a**.

4.4 Complex **2a**3Cl

To investigate the possible tridentate complex, previously synthesized and characterized sodium salt of the compound **aNa** mixed with THF solution of ZrCl_4 . Disappearance of the N-H proton is a sign of sigma bonding between nitrogen and zirconium.

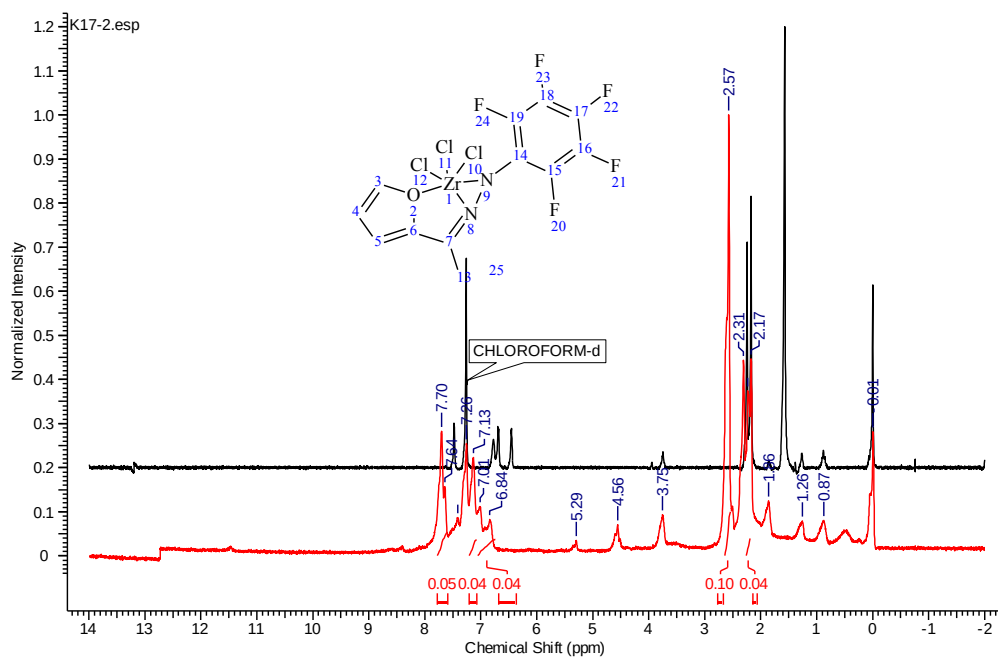


Figure 4.3: Proton-NMR spectra of ligand **a** and complex **2a**3Cl.

4.5 Complex 2e

¹H NMR spectrum of compound **1** in CDCl₃. The spectrum shows peaks at 9.41, 8.48, 7.67, 7.53, 7.27, 4.60, 3.76, 2.07, 1.87, 1.25, 0.85, and 0.06 ppm. Integration values are shown below the peaks. A chemical structure of the compound is shown above the spectrum.

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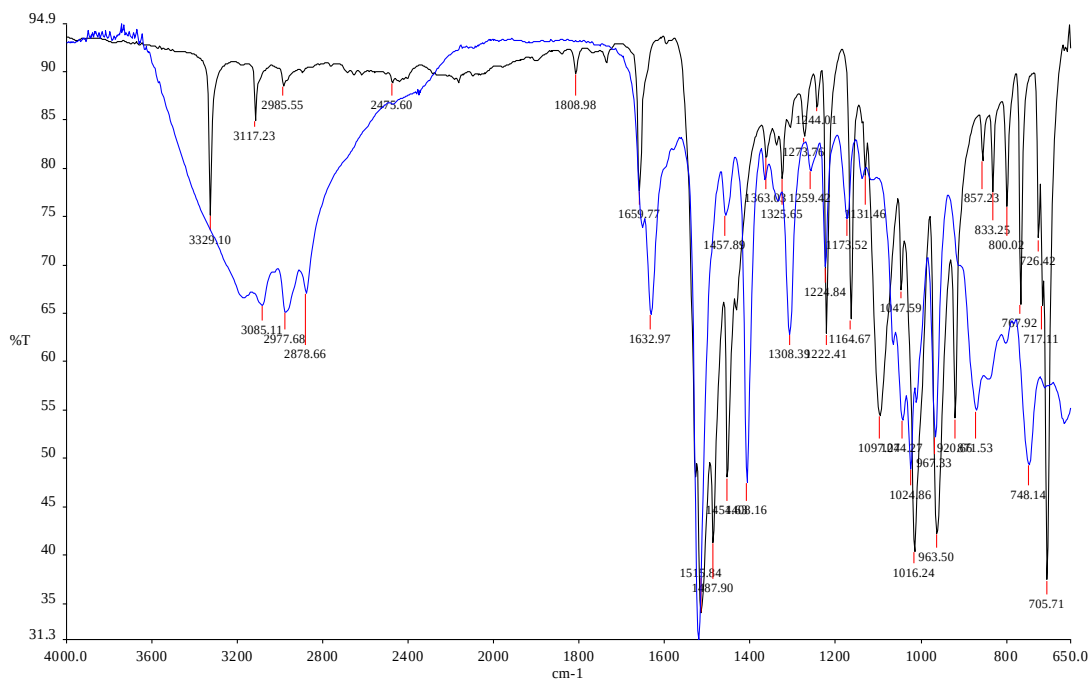


Figure 4.5: FT-IR spectra of ligand **e** and complex **2e**.

4.6 Complex 1a

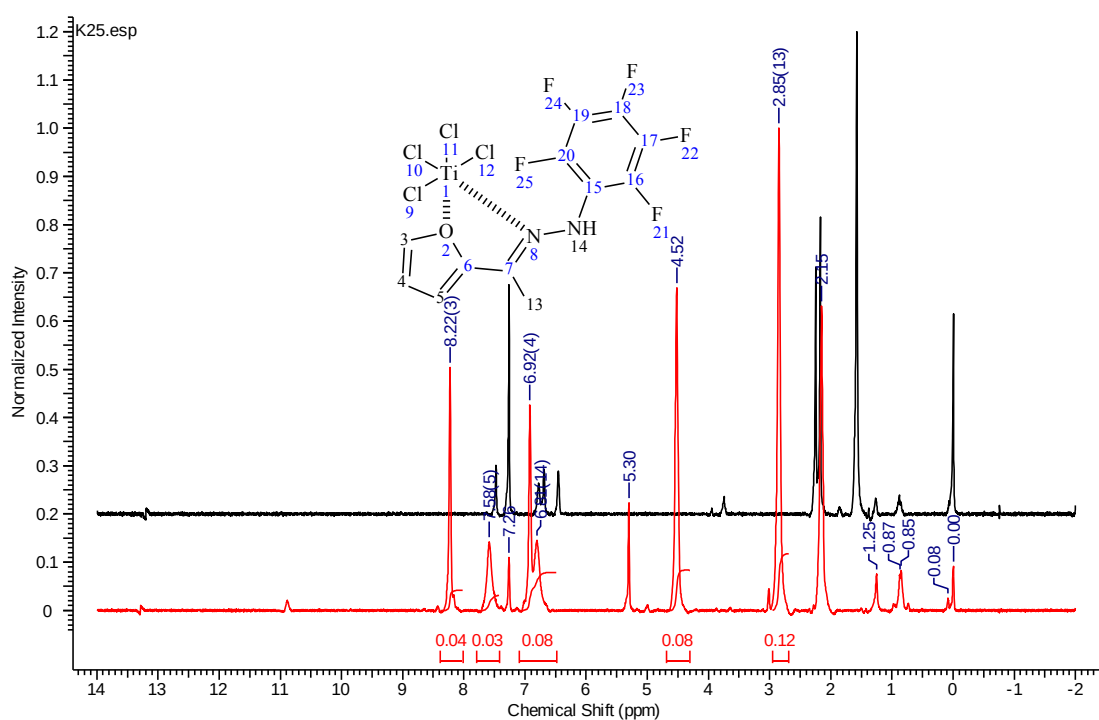


Figure 4.6: Proton-NMR spectra of ligand **a** and complex **2a**.

In complex **1a** the main difference was that the methyl protons shifted greater to down field compared with methyl protons of the other metal complexes. The chemical shifts of the furan protons are slightly smaller than the shifts of the

complex **2a** which means that the interaction of zirconium with the ligand is slightly stronger than the interaction of titanium which can also be explained by HSAB Theory.

5. CONCLUSION

To conclude, novel Schiff base ligands with unique steric and electronic features and their titanium and zirconium complexes were synthesized and characterized. The insulating nitrogen atom between the highly electron-withdrawing perfluorophenyl moiety and heterocycles could electronically be crucial in the catalytic activity of the synthesized tridentate complexes. All the spectroscopic evidences prove the chelation by imine nitrogen and ring heteroatoms. (O,S). THF coordination is very common among Group 4 metal complexes and can be removed by refluxing the complex in either benzene or toluene but is most of the time unnecessary. Except complex **2a3Cl** the molecular structures of the metal complexes are easy to predict without single crystal X-Ray analysis. The newly designed and synthesized complexes, especially the tridentate complex **2a3Cl** is a candidate for an efficient olefin polymerization precatalyst.

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APPENDICES

APPENDIX A.1 : GC-MS DATA

APPENDICES

A.1. GC-MS Data:

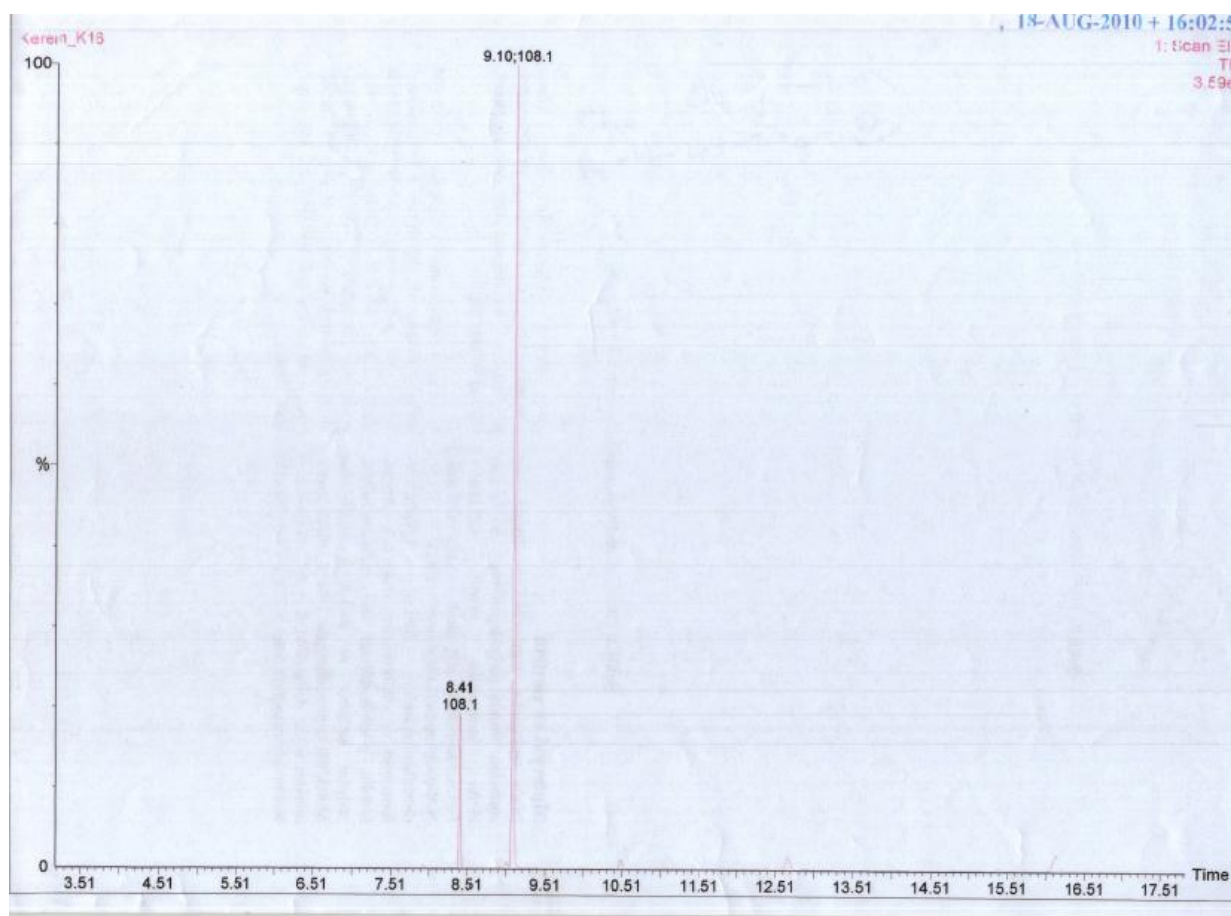


Figure A.1. Gas Chromatogram of ligand **a**

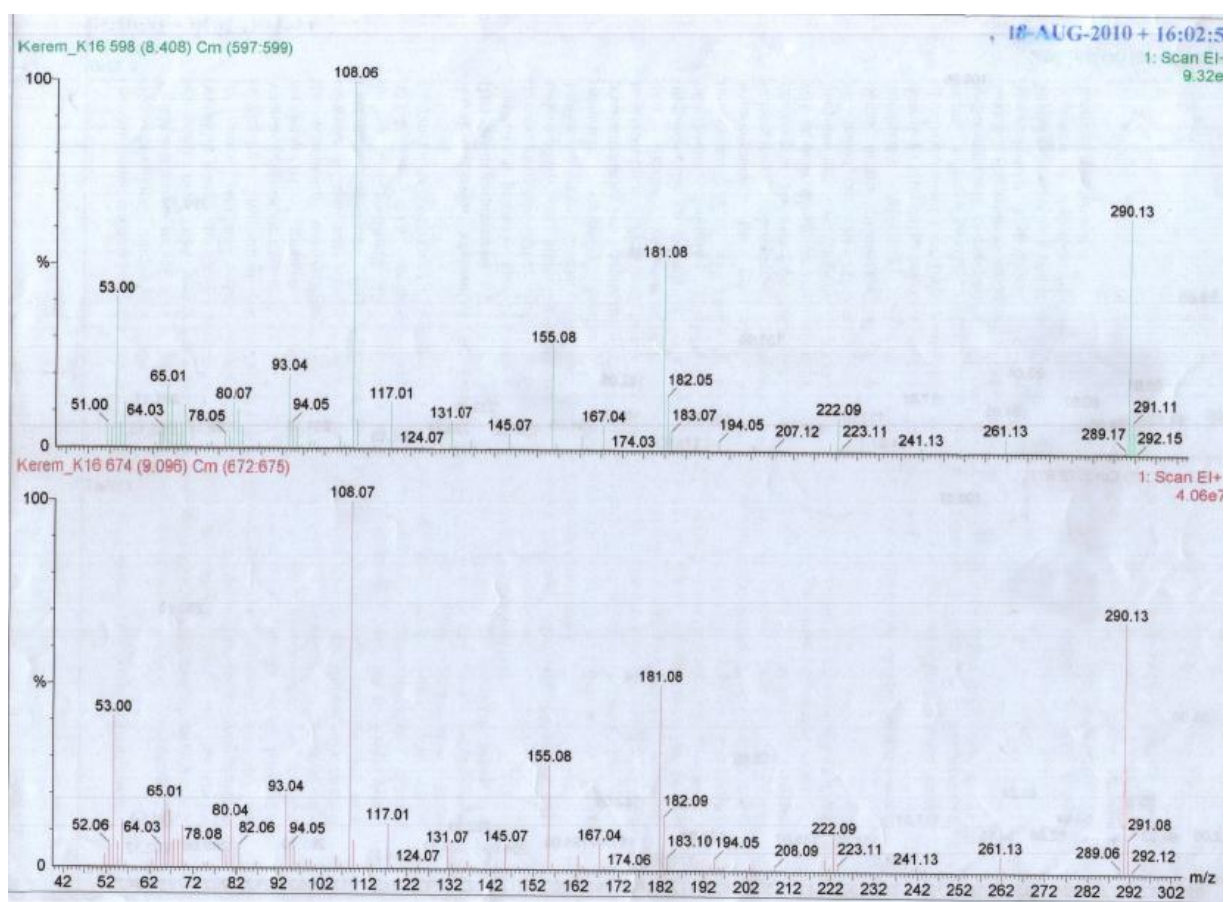


Figure A.2. Mass Spectrum of ligand **a**

RT: 7.96 - 11.24

NL:
3.27E7
TIC F: MS
K3-B

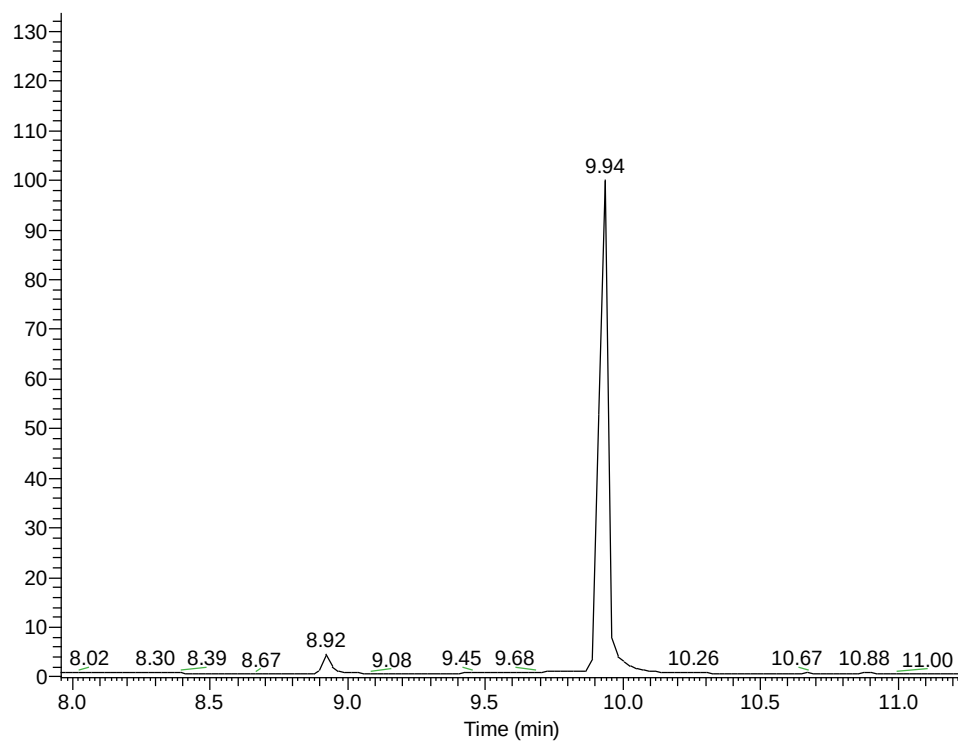
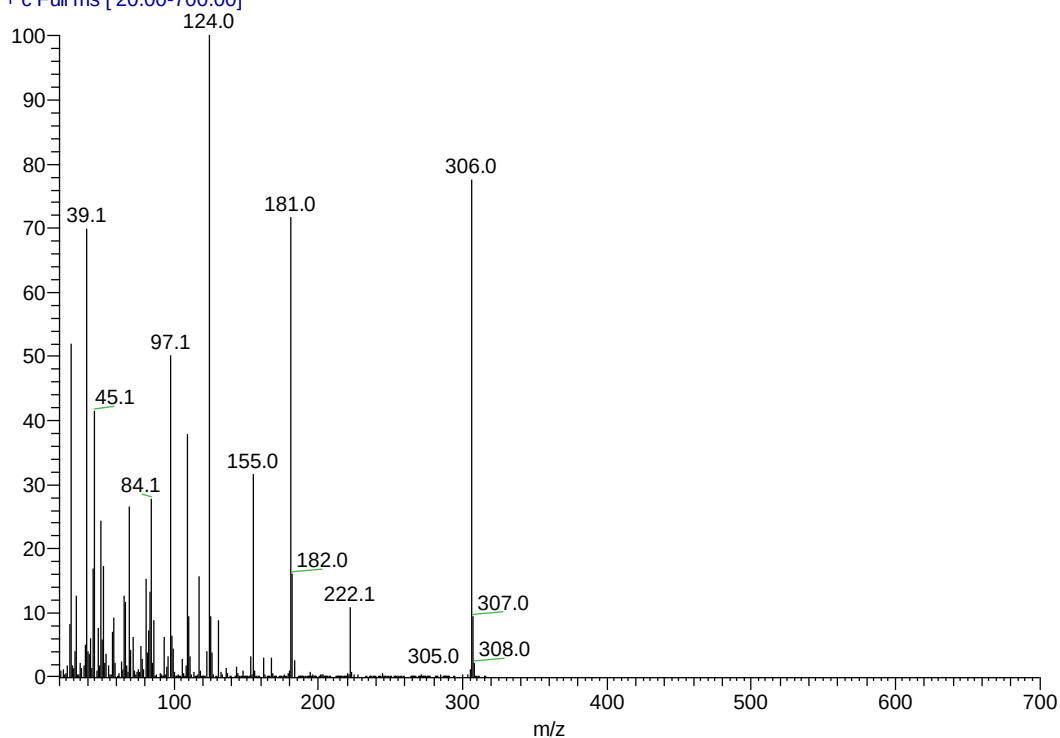


Figure A.3. Gas Chromatogram of ligand **b**

K3-B #258 RT: 8.92 AV: 1 NL: 1.49E5
T: + c Full ms [20.00-700.00]



K3-B #302 RT: 9.94 AV: 1 NL: 3.78E6
T: + c Full ms [20.00-700.00]

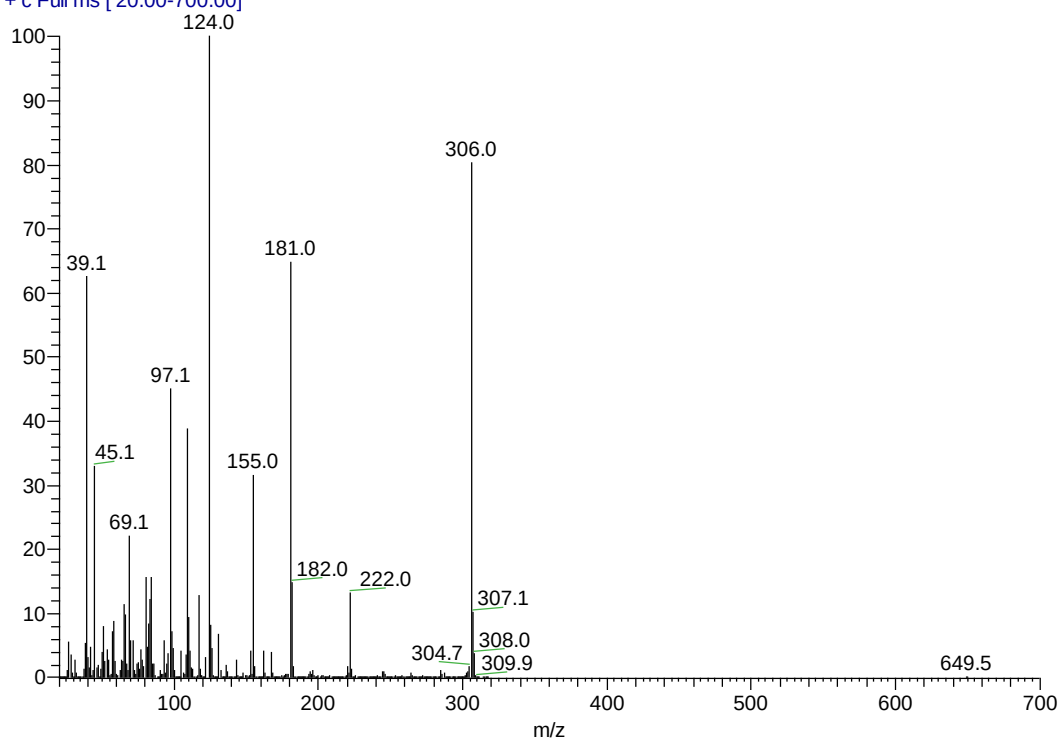


Figure A.4. Mass Spectrum of ligand **b**

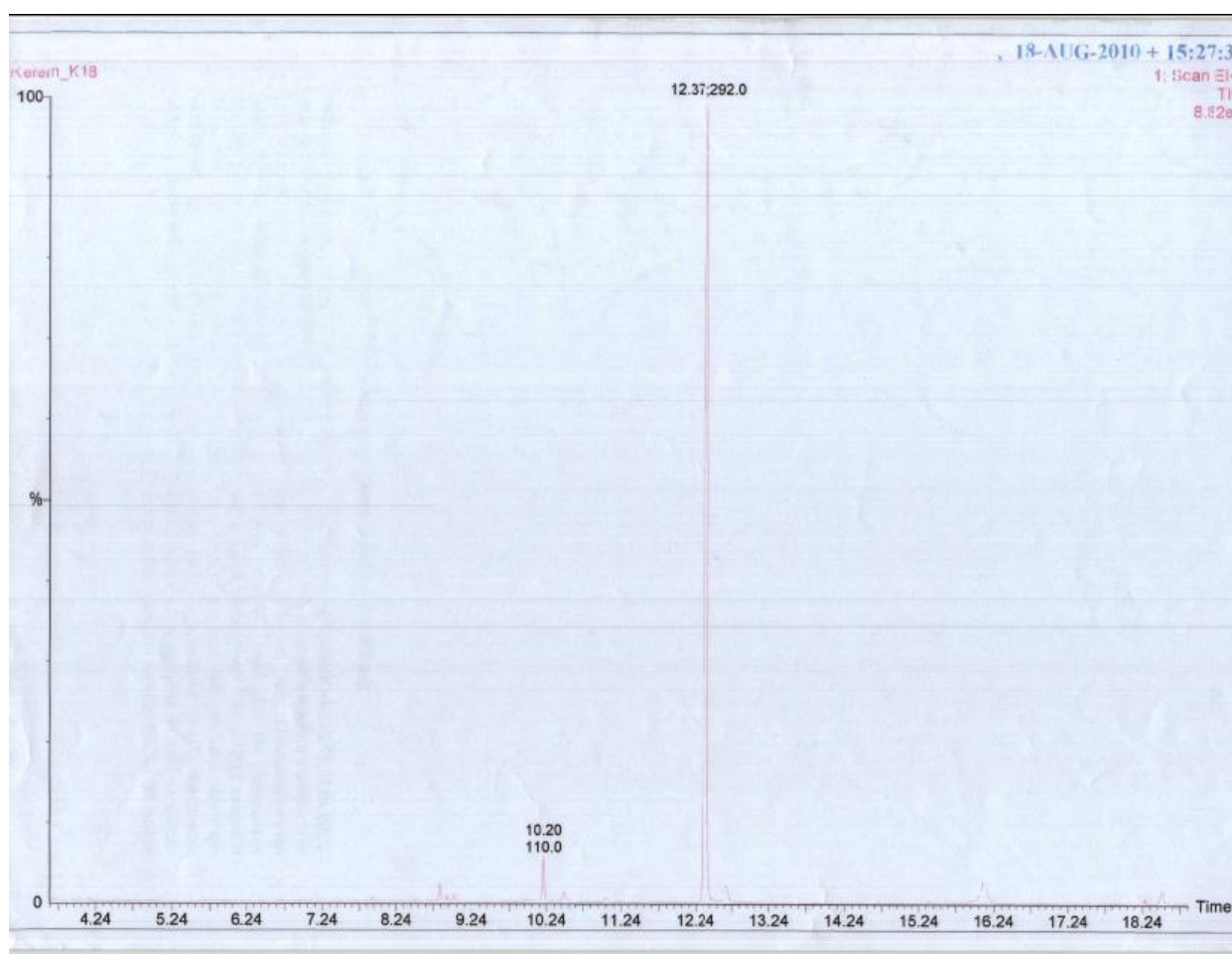


Figure A.5. Gas Chromatogram of ligand **e**

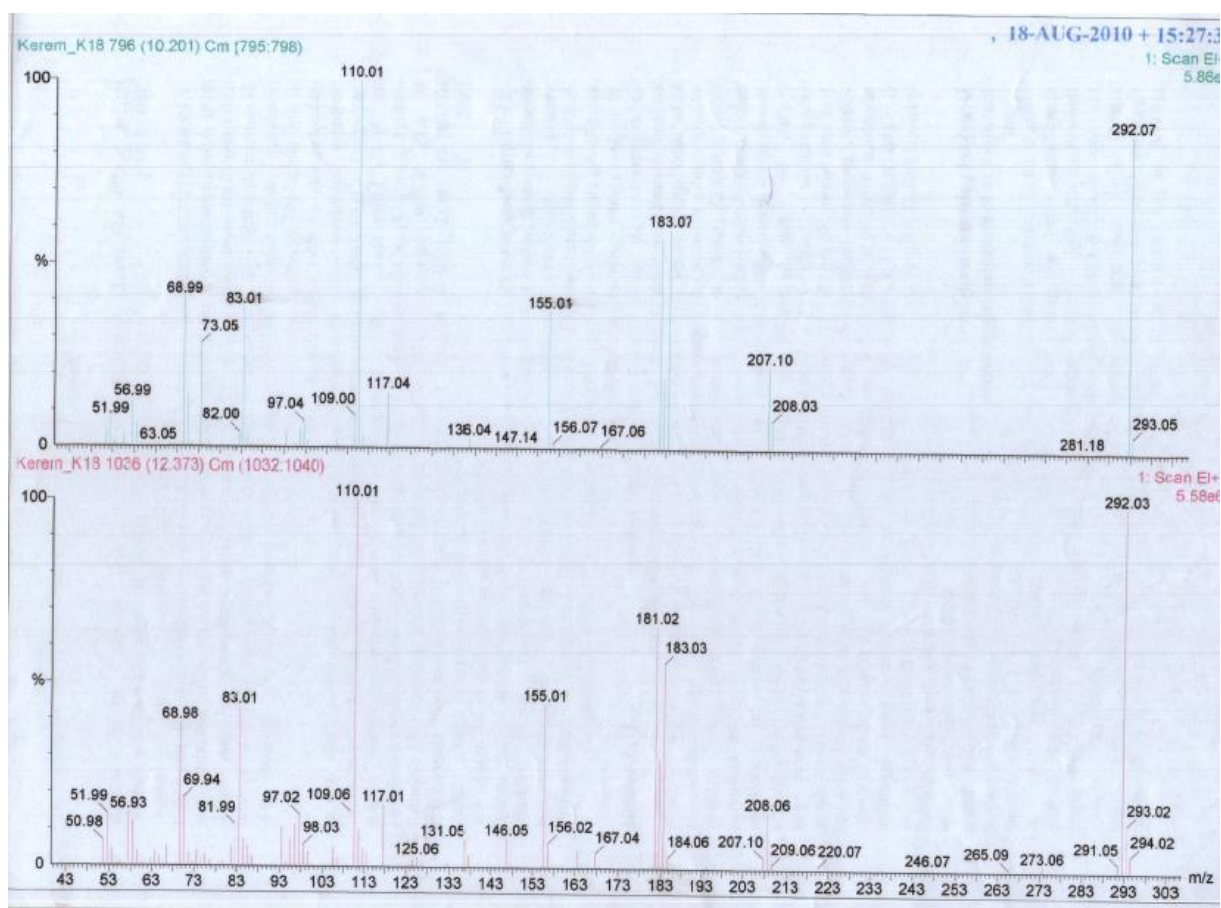


Figure A.6. Mass Spectrum of ligand e

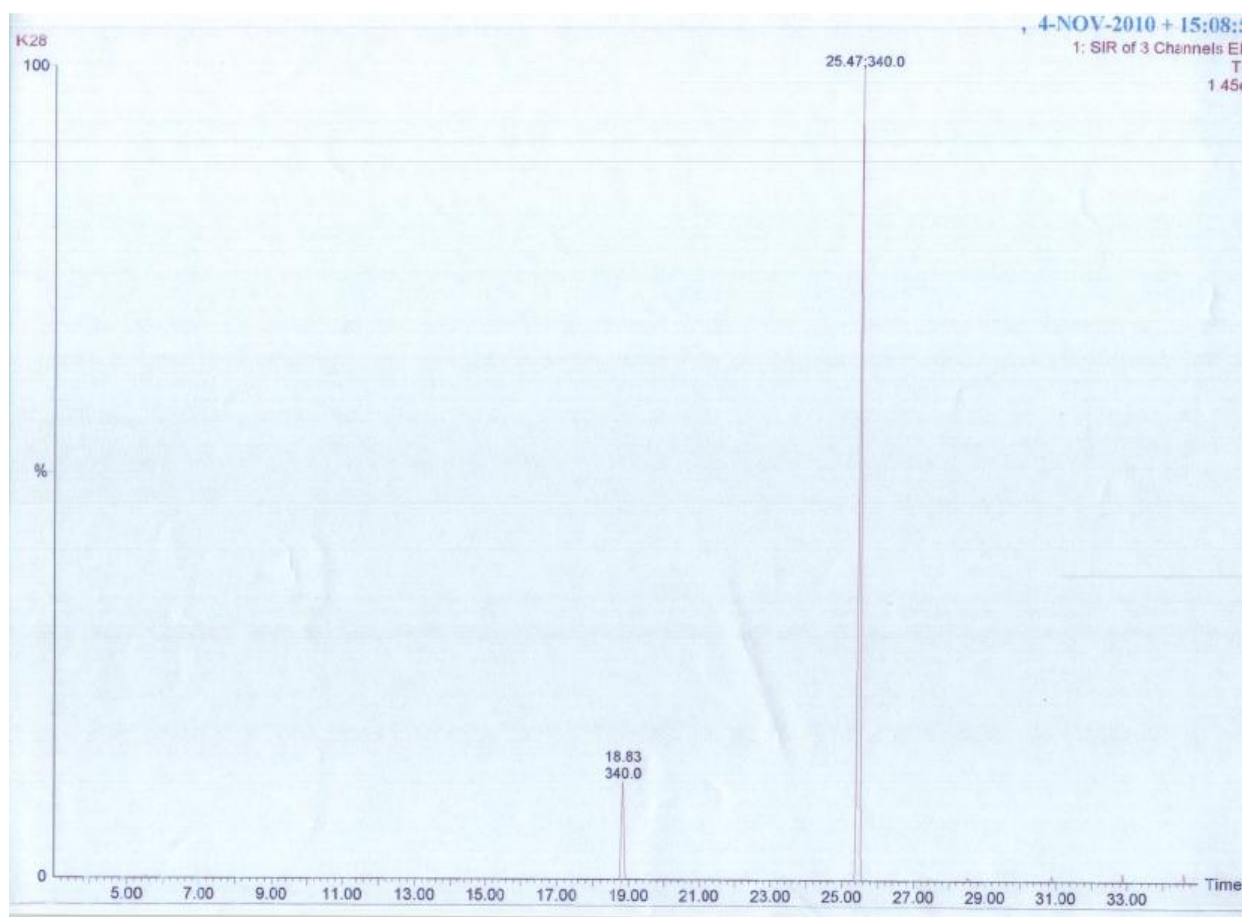


Figure A.7. Gas Chromatogram of ligand **c**

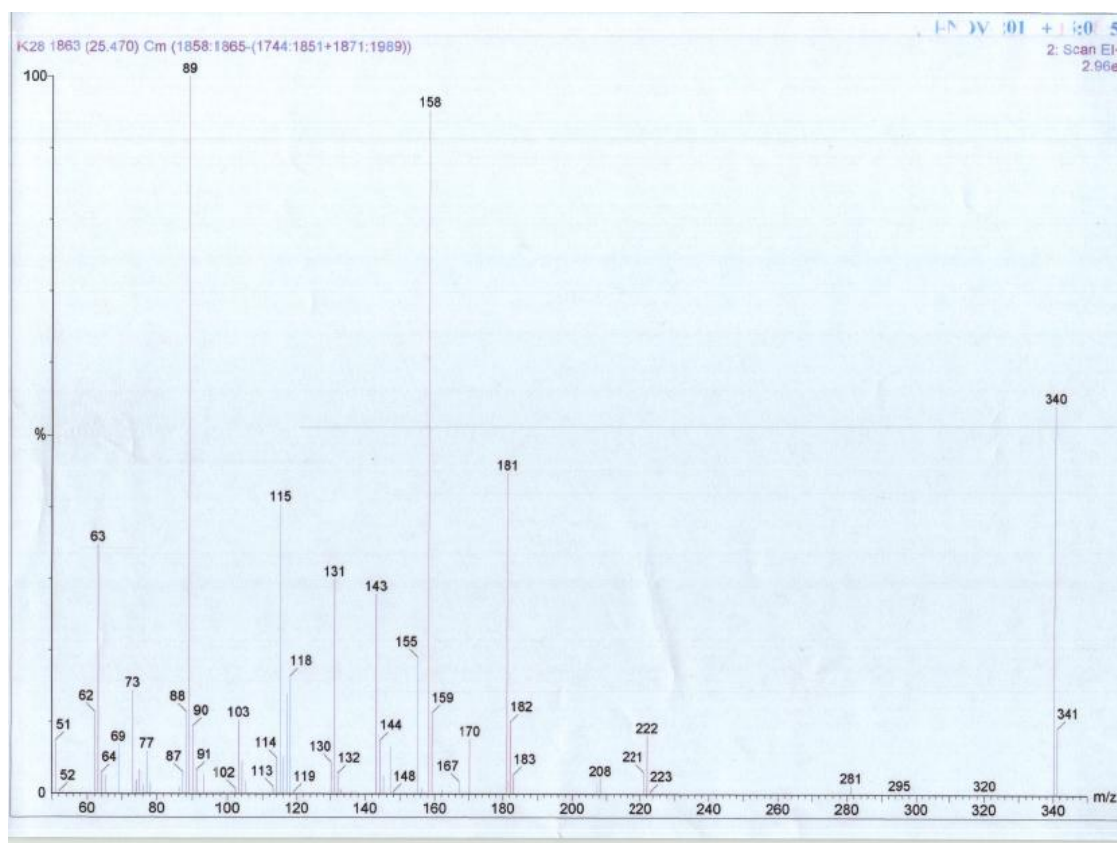


Figure A.8. Mass Spectrum of ligand **c**

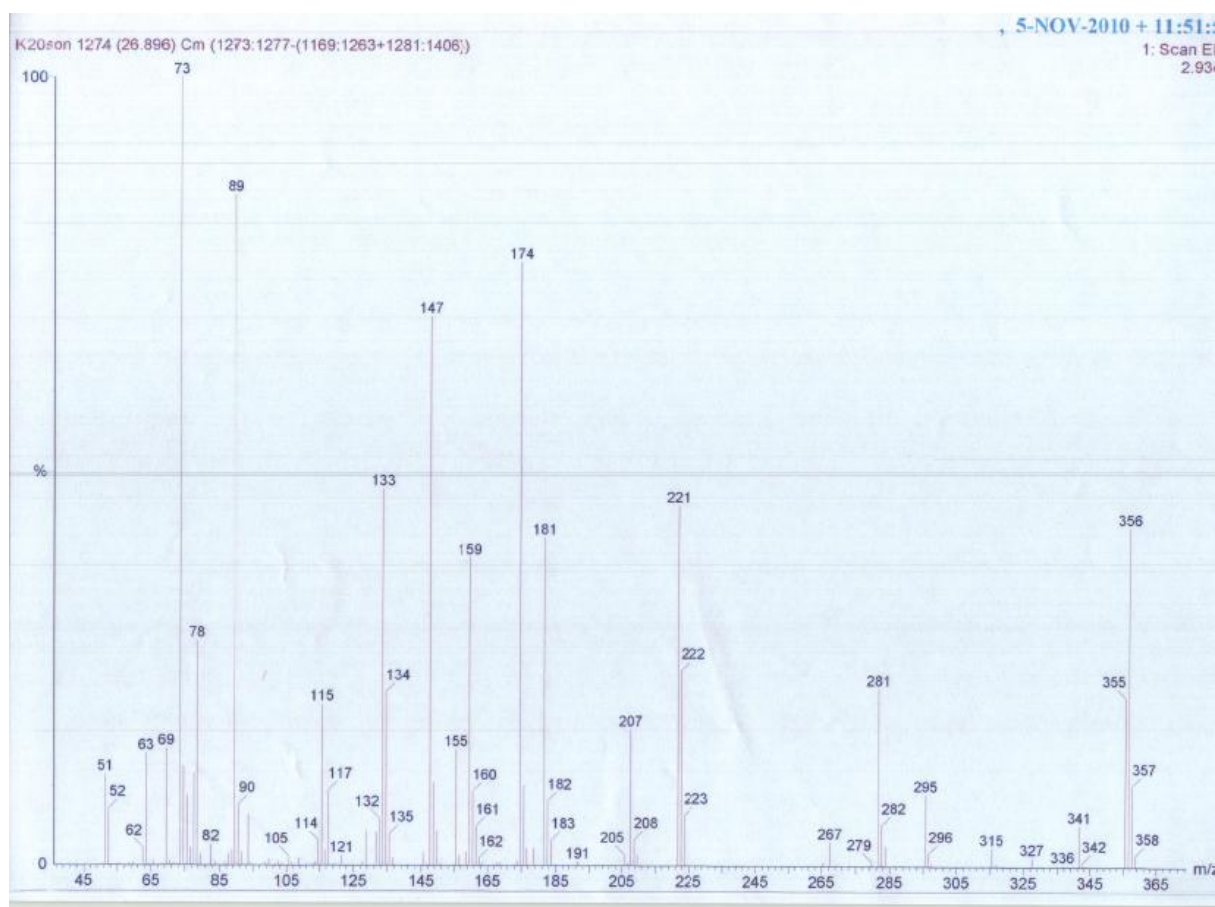


Figure A.9. Mass Spectrum of ligand **d**

A.2. Proton NMR Spectra:

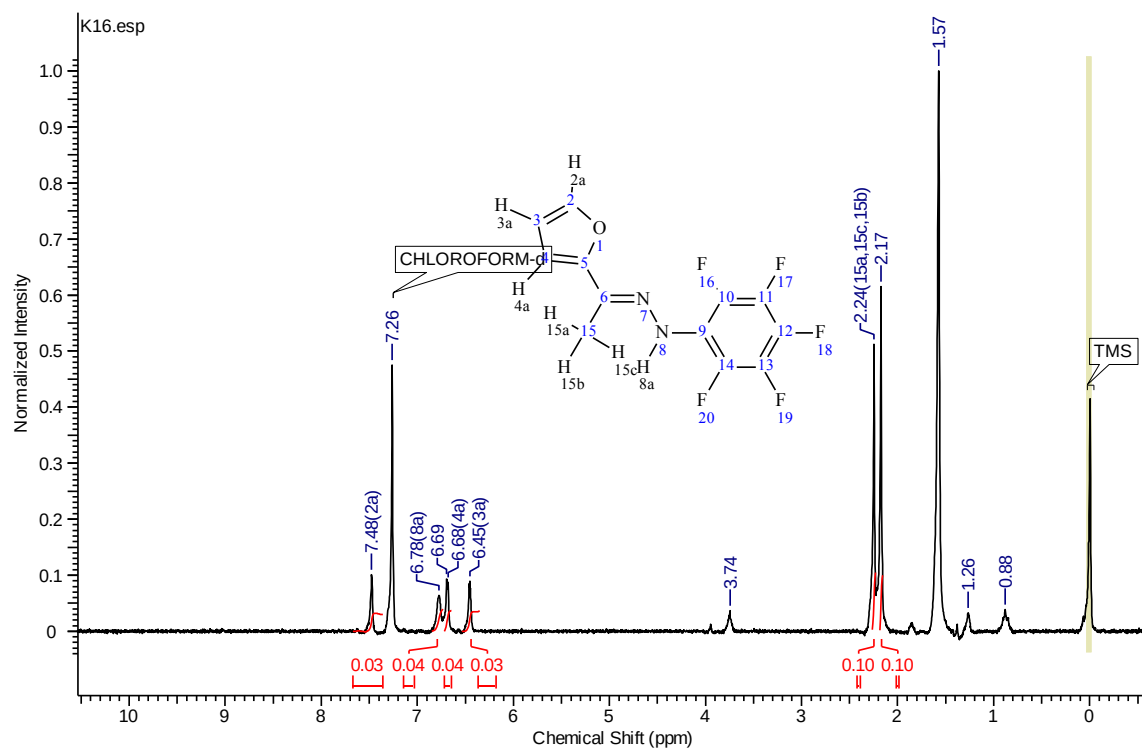


Figure A.10. Proton NMR Spectrum of ligand **a**

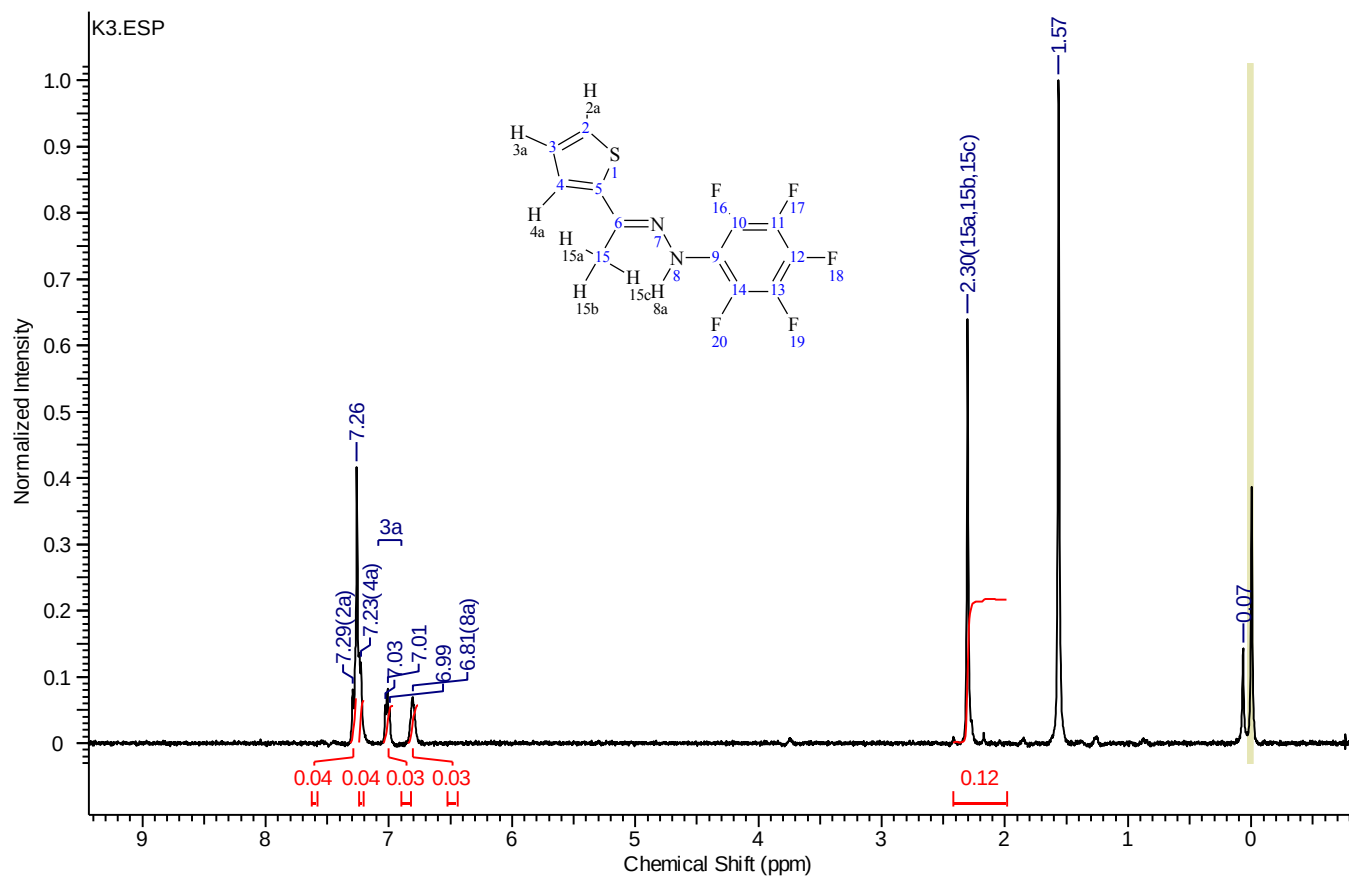


Figure A.11. Proton NMR Spectrum of ligand **b**

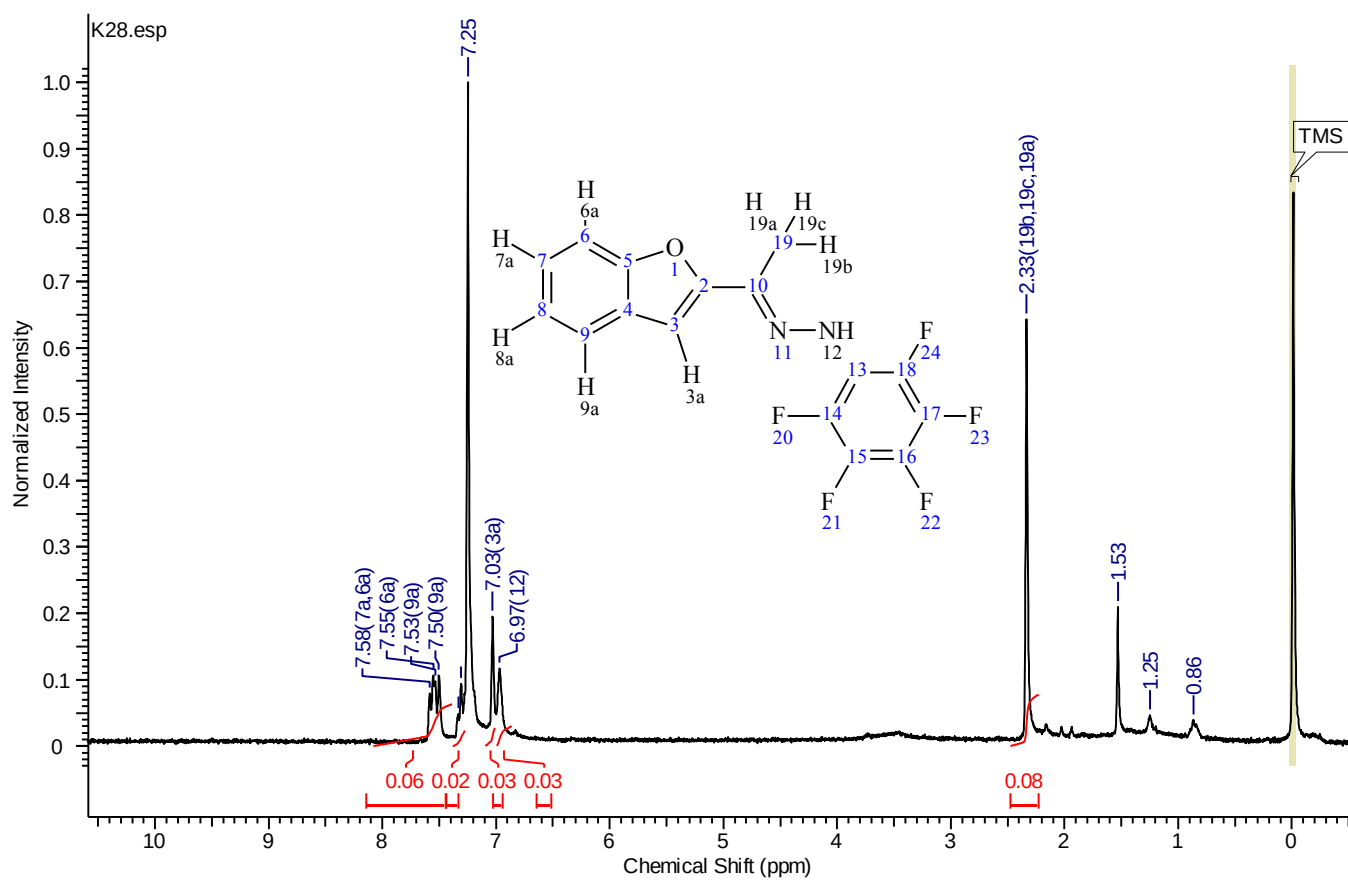


Figure A.12. Proton NMR Spectrum of ligand **c**

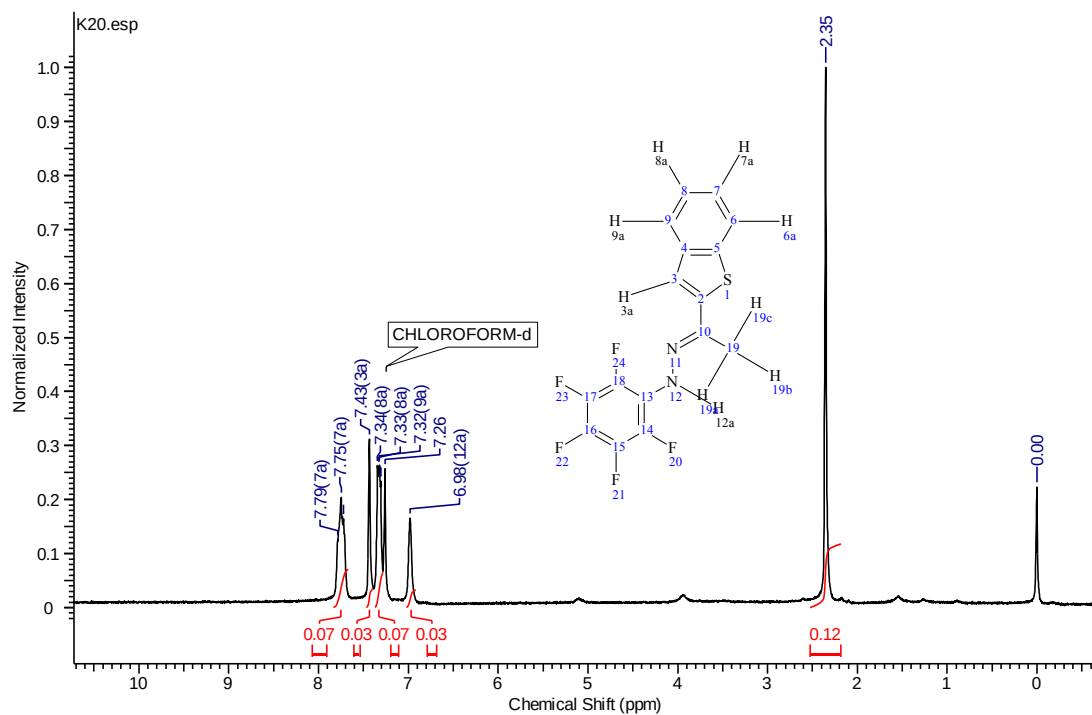


Figure A.13. Proton NMR Spectrum of ligand **d**

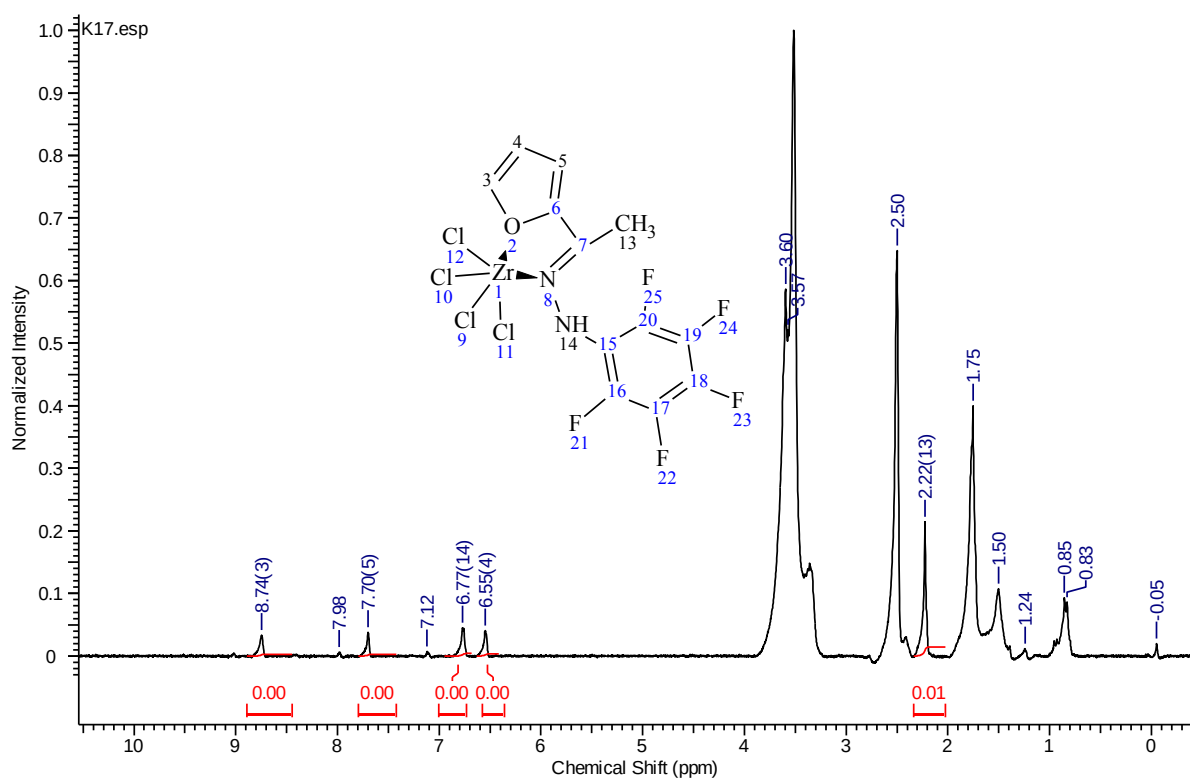


Figure A.15. Proton NMR Spectrum of complex 2a

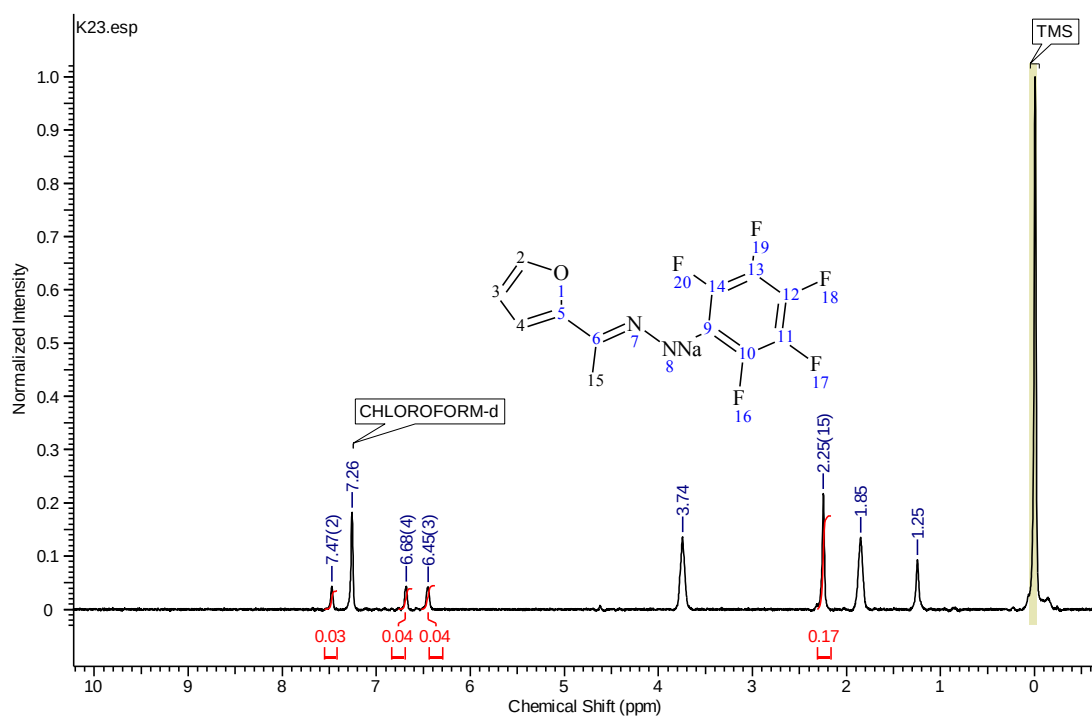


Figure A.16. Proton NMR Spectrum of **1aNa**

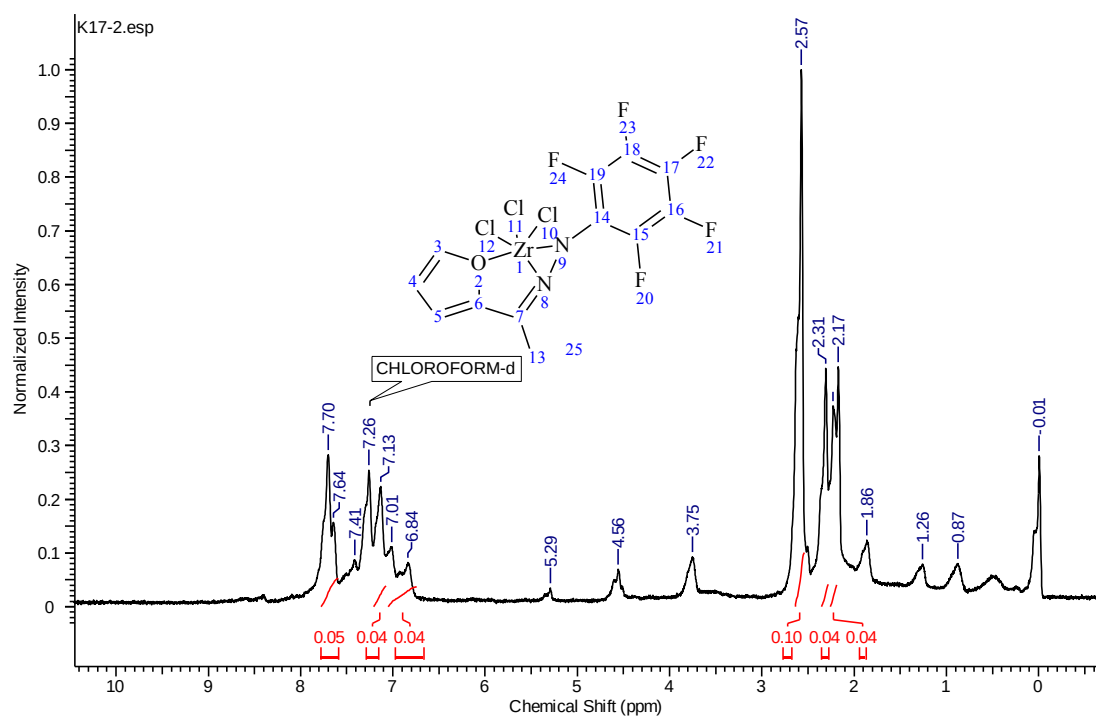


Figure A.17. Proton NMR Spectrum of complex 2a3Cl

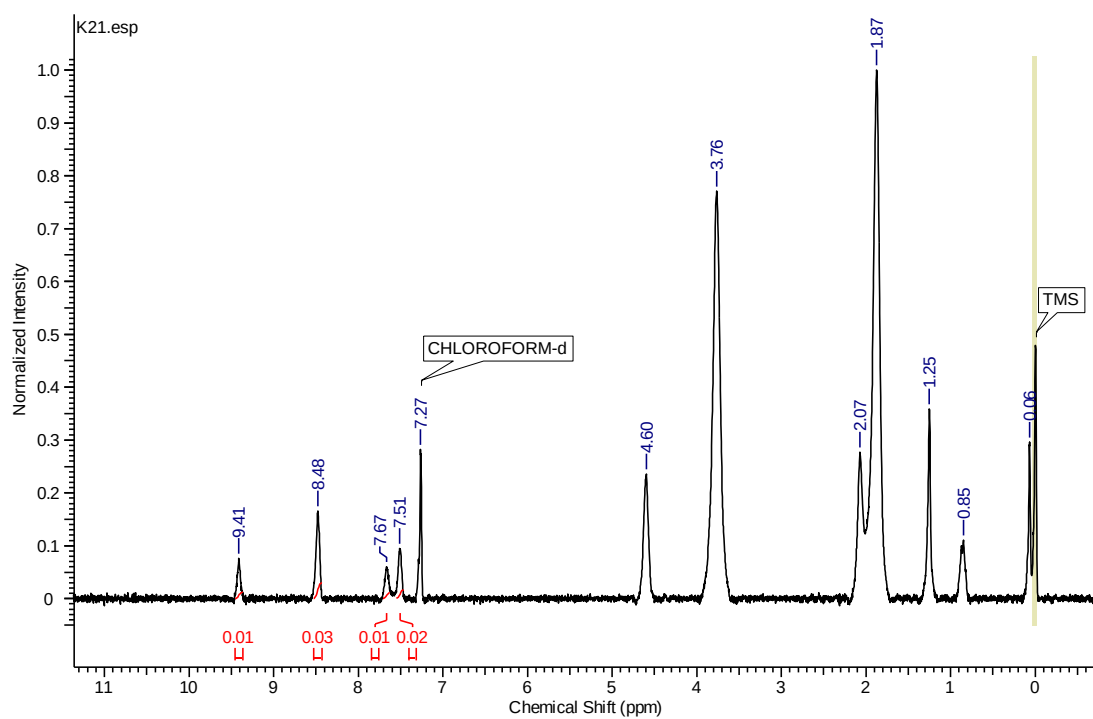


Figure A.18. Proton NMR Spectrum of complex **2e**

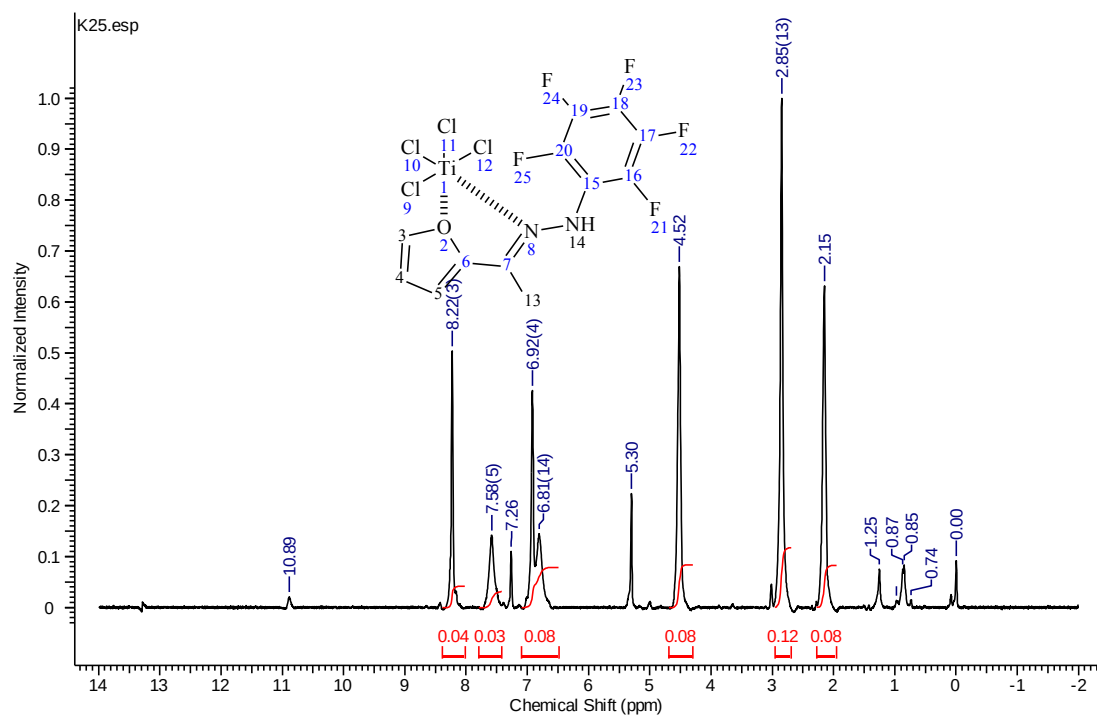


Figure A.19. Proton NMR Spectrum of complex **1a**

A.3. FT-IR Spectra:

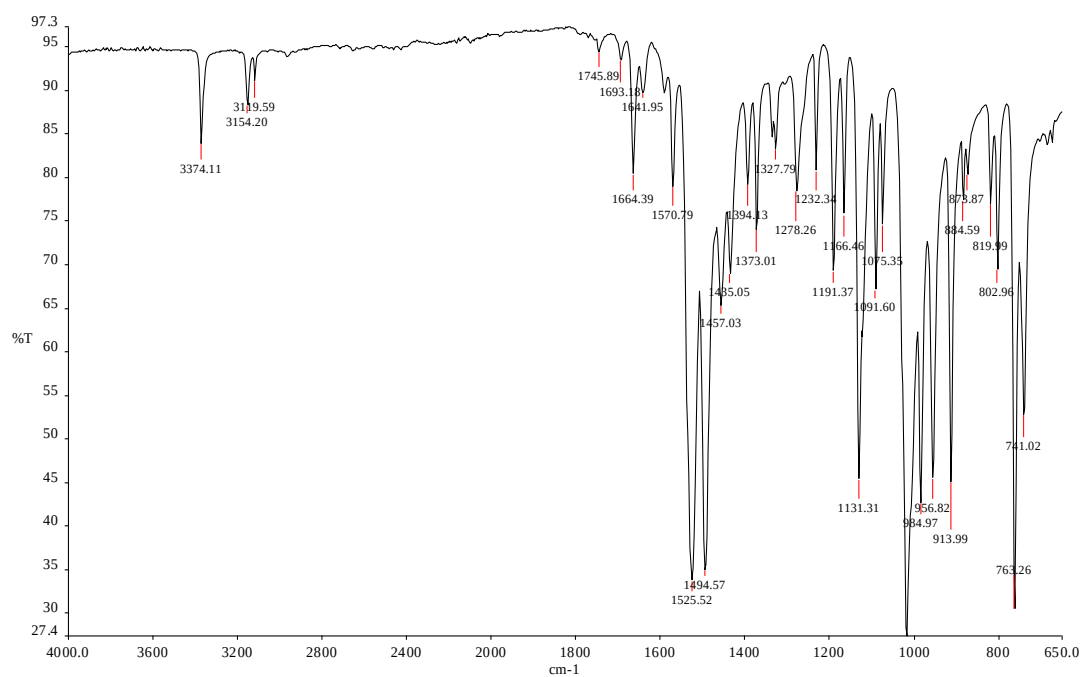


Figure A.20. Infrared Spectrum of **a**

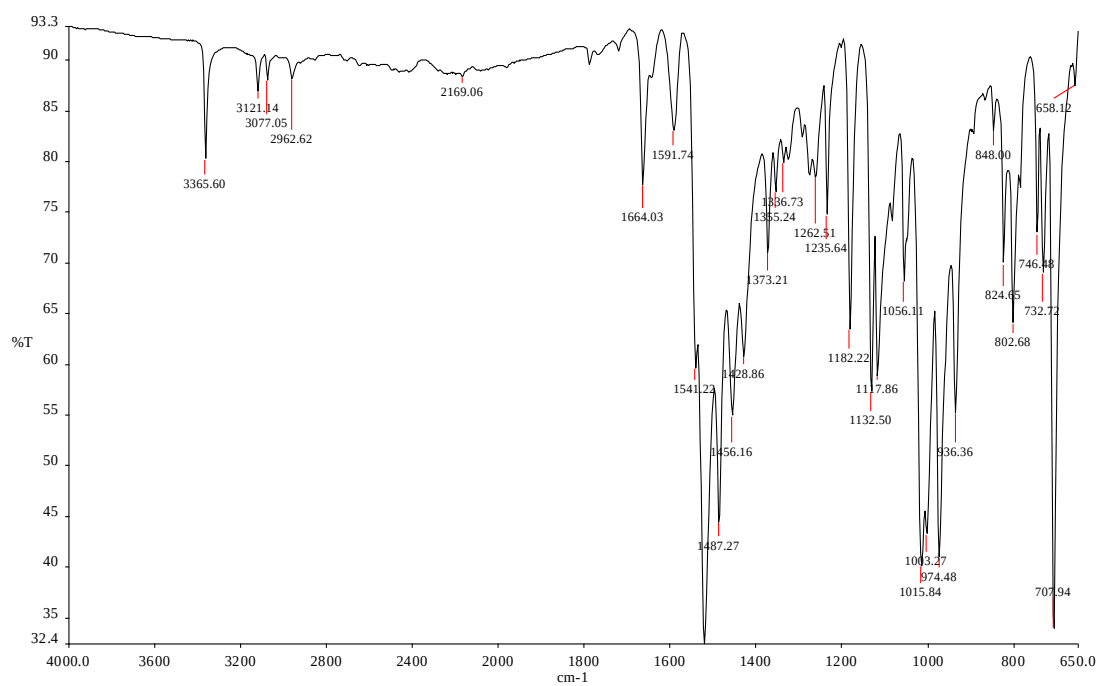


Figure A.21. Infrared Spectrum of b

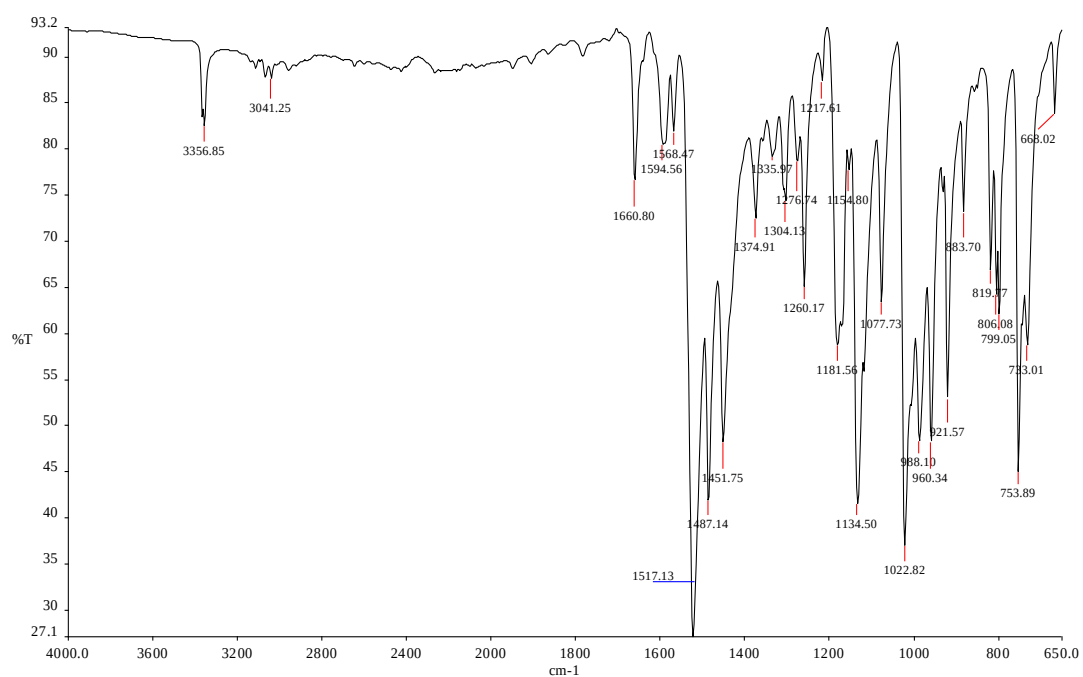


Figure A.22. Infrared Spectrum of c

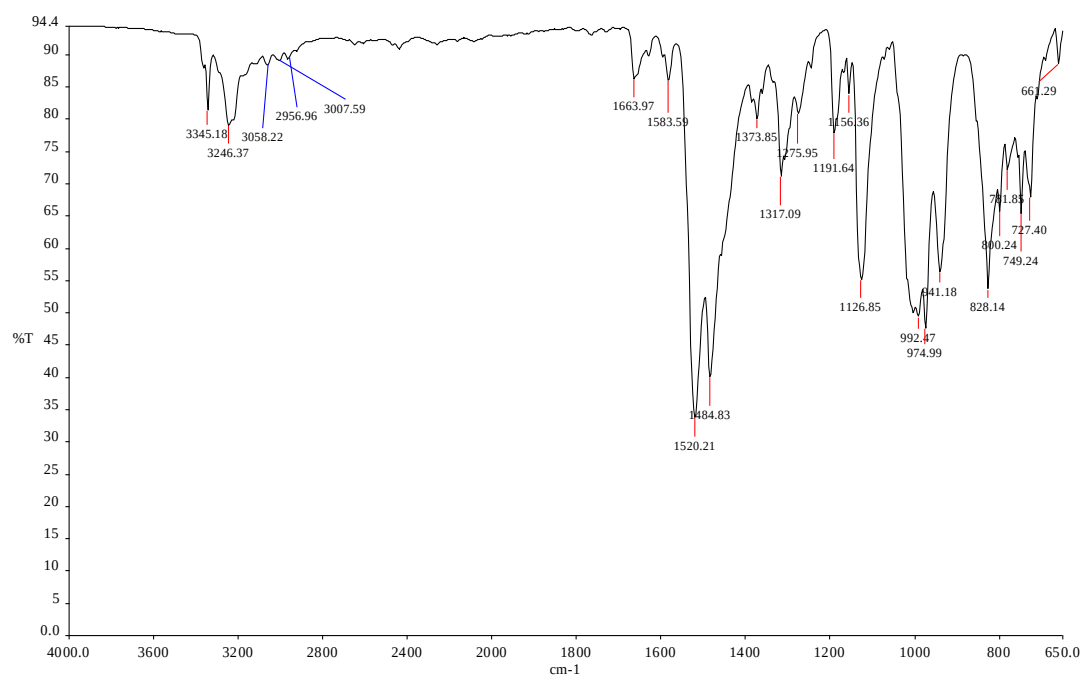


Figure A.23 Infrared Spectrum of **d**

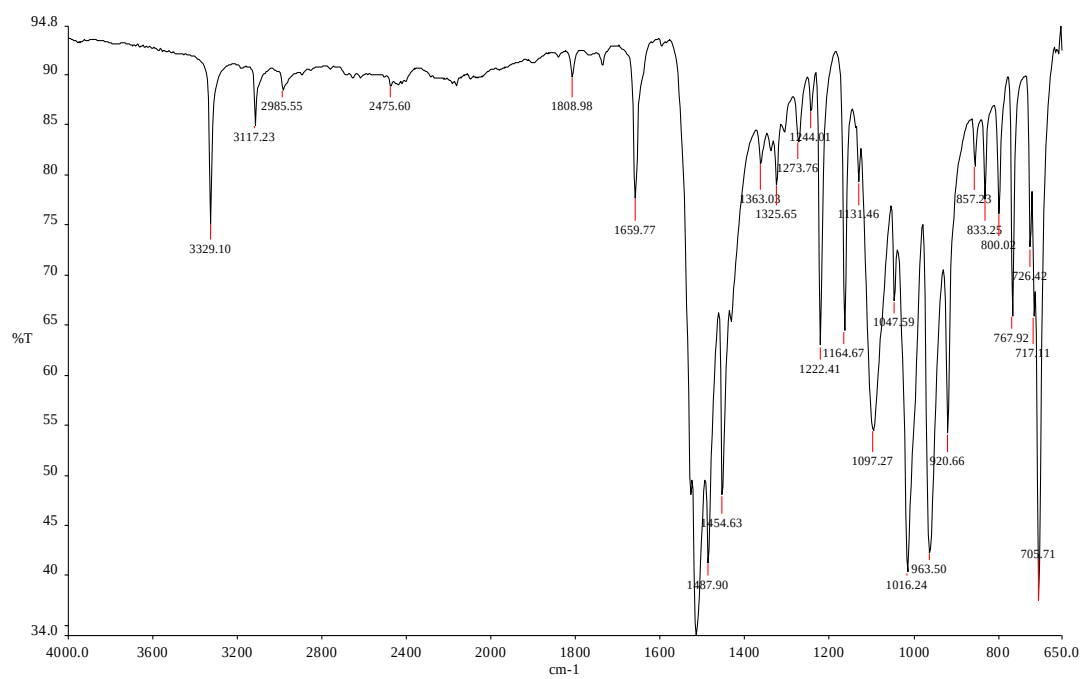


Figure A.24 Infrared Spectrum of **e**

CURRICULUM VITAE



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