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EGE UNIVERSITY
Graduate School of Applied and Natural Science

SYNTHESIS OF NHC COMPLEXES CONTAINING NITRILE SUBSTUTIENT AND THEIR CATALYTIC APPLICATIONS

MSc THESIS

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Department of Chemistry

İzmir
2019

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Inorganic Chemistry Programme

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Sinem ÇAKIR tarafından **YÜKSEK LİSANS** tezi olarak sunulan "**Nitrilsubstitüentli NHC komplekslerinin sentezi ve katalitik uygulamaları**" başlıklı bu çalışma EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 10.06.2019 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Doktora Tezi olarak sunduğum ***"synthesis of NHC complexes containing nitrile substituent and their catalytic applications"*** başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

10/06/2019

Sinem ÇAKIR

ÖZET

NİTRİL SUBSTİÜENTLİ NHC KOMPLEKSLERİNİN SENTEZİ VE KATALİTİK UYGULAMALARI

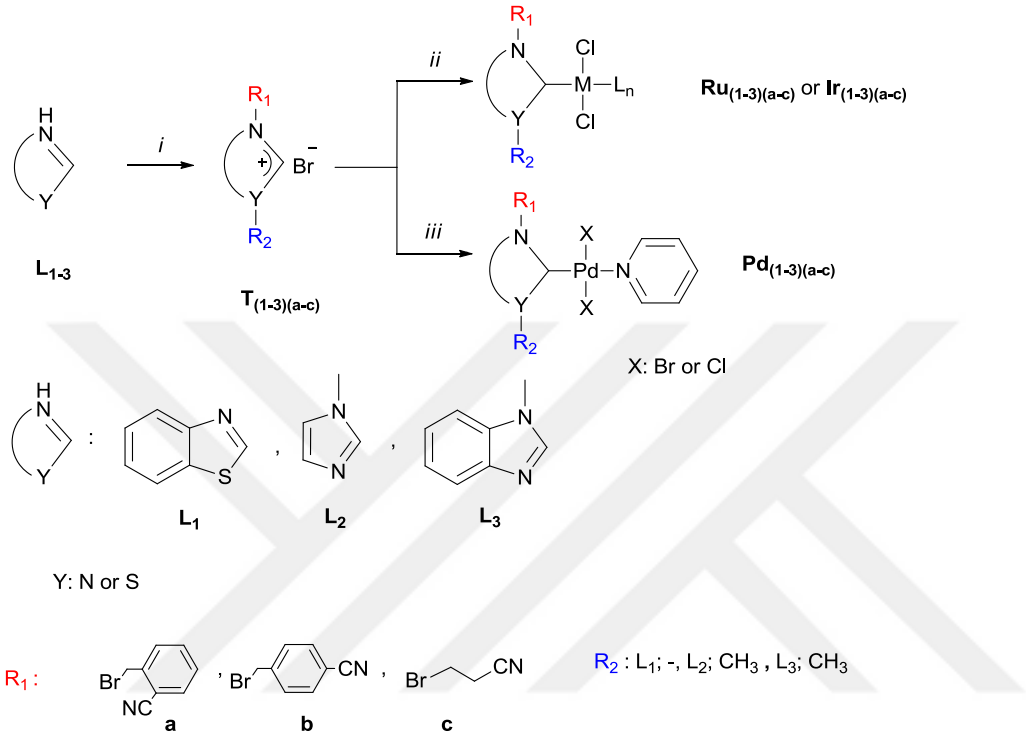
ÇAKIR, Sinem

Yüksek Lisans Tezi, Kimya Anabilim Dalı
Tez Danışmanı: Prof. Dr. Hayati TÜRKMEN
2019, 79 sayfa

Bu tez nitril fonksiyonlu NHC komplekslerinin sentezi ve katalitik aktivitelerinin araştırılması ile ilişkilidir. Nitrille fonksiyonelleştirilmiş NHC'ler ligand şelasyonu yoluyla arttırılmış stabiliteye sahip olan karben komplekslerine yol açabilen potansiyel çoklu-geçişli ligandlar olarak adlandırılmaktadır. Metallere karşı reaktiviteleri, özellikle şelasyon modu üzerinde ilginç ve ayrıca önemlidir. Son zamanlarda fonksiyonelleştirilmiş NHC kimyası, türetilmiş komplekslerin çok yönlü potansiyel uygulamaları nedeniyle şu anda büyük ilgi ve aktiviteye sahiptir.

Tez üç bölümden oluşmaktadır. Başlangıçta NHC bileşiklerinin özellikleri, sentez yöntemleri ve transfer hidrojenasyon ve suzuki çapraz bağlanma reaksiyonları ile ilgili literatür bilgisi kapsamaktadır. İkinci bölüm deneysel çalışmaları içermektedir. Üçüncü bölüm ise sentezlenen CN grubu içeren tuzlarının ve komplekslerinin sentezleri, karakterizasyonları ve yapılan katalitik çalışmaları ile ilgilidir.

Nitril grubuna sahip ligandların sentezlenmesinden yola çıkılarak Ru, Ir ve Pd metal tuzları ile reaksiyonu sonucu kompleksler sentezlenmiştir. Sentez adımları şema 1' de özetlenmiştir.



Şema 1. Reaksiyon ve koşulları: i) L (1 mmol), a, b or c (1 mmol), toluen, 110 °C, 24 s; ii) T (1 mmol), Ag_2O (2 mmol), $[RuCl_2(p\text{-cymene})]_2$ ya da $[IrCl_2Cp^*]_2$ (0.5 mmol), DCM, 39 °C, 6 s; iii) T (1 mmol), $Pd(OAc)_2$ (1 mmol), NaBr (3 mmol), Piridin, 80 °C, 24 s.

Sentezlenen Ru ve Ir kompleksleri tranfer hidrojenasyon reaksiyonunda , Pd kompleksleri Suzuki-Miyaura çapraz bağlama reaksiyonlarında katalitik aktiviteleri incelendi.

Anahtar kelimeler: N-heterosiklik karben, C-C bağlanma reaksiyonu, azot, kükürt donor ligand

ABSTRACT

SYNTHESIS OF NHC COMPLEXES CONTAINING NITRILE SUBSTITUENT AND THEIR CATALYTIC APPLICATIONS

ÇAKIR, Sinem

Master Thesis in Chemistry
Supervisor: Prof. Dr. Hayati TÜRKMEN
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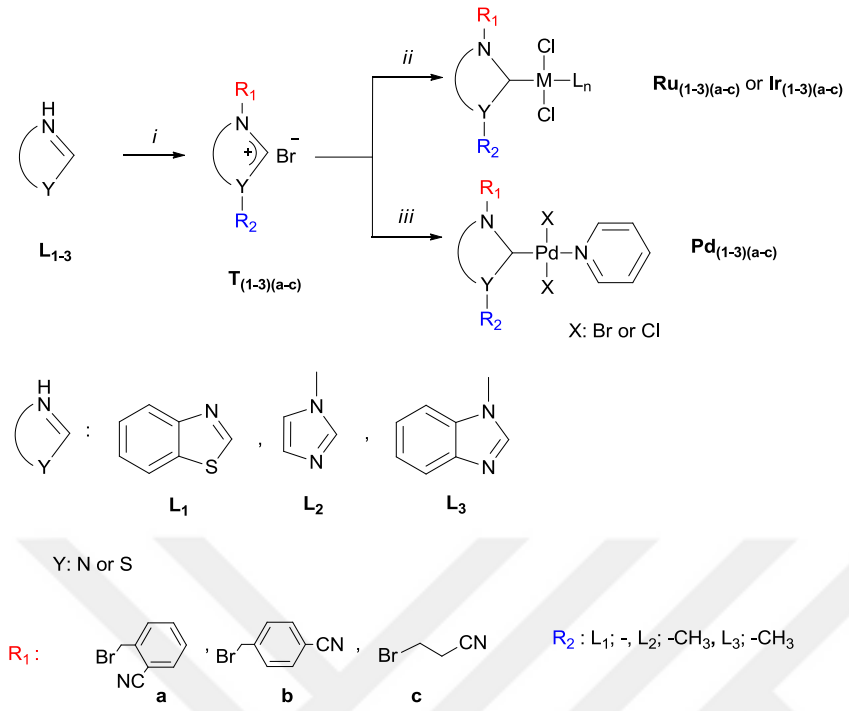
This thesis is related to the synthesis and catalytic activity of NHC complexes with nitrile function. Nitrile-functionalized NHCs are termed potential multi-pass ligands that can lead to carbene complexes with increased stability through ligand chelation. Their reactivity to metals is particularly interesting and especially important in chelation mode. Recently functionalized NHC chemistry currently has great interest and activity due to multilateral potential applications of derived complexes.

The thesis consists of three parts. The initial part consists of the properties of NHC compounds, synthesis methods, and transfer hydrogenation and Suzuki cross-coupling reactions are included in the literature. The second part includes experimental studies. The third part deals with the synthesis, characterization and catalytic studies of the synthesized CN group-containing salts and complexes.

Based on the synthesis of ligands having nitrile group, complexes were synthesized as a result of reaction with metal salts of Ru, Ir and Pd. The synthesis steps are summarized in Scheme 1.



Reaction Conditions: i) L (1 equiv.), a, b or c (1 equiv.), toluene, 110 °C, overnight; ii) T (1 equiv.), Ag_2O (2 equiv), $[RuCl_2(p\text{-cymene})]_2$ or $[IrCl_2Cp^*]_2$ (0.5 equiv.), DCM, 39 °C, 6 h; iii) T (1 equiv.), $Pd(OAc)_2$ (1 equiv.), NaBr (3 equiv.), Pyridine, 80 °C, 24 h.

Scheme 1. Synthesis of the Complexes

The synthesized Ru and Ir complexes were analyzed for their catalytic activity in the tranfer hydrogenation reaction and the catalytic activity of synthesized Pd complexes in Suzuki-Miyaura cross-coupling reactions was investigated.

Keywords: N-Heterocyclic carbene, C-C coupling reaction, nitrogen, sulfur donor ligand

PREAMBLE

In this thesis, it is desired to synthesize and develop catalytic activities of complexes with nitrile-substituted N, N- and N, S-donor ligand properties.

I would like to thank my dear Professor Prof.Dr.Hayati TÜRKMEN, who shaped his work in the light of his scientific background with his knowledge and experiences, who benefited from his vast knowledge and experience in his planning, research, implementation and formation.

İZMİR

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Adı-Soyadı

Sinem ÇAKIR

CONTENTS

Page

CONTENTS (continue)

Page

CONTENTS (continue)

Page

CONTENTS (continue)

Page

LIST OF SCHEMES

xx

LIST OF FIGURES

LIST OF FIGURES (continue)

Figure Page

LIST OF FIGURES (continue)

LIST OF TABLES

ABBREVIATIONS

Abbreviations		Explanations
^{13}C-NMR	:	Carbon Nuclear Magnetic Resonance Spectroscopy
^{1}H-NMR	:	Proton Nuclear Magnetic Resonance Spectroscopy
IPA	:	Isopropyl alcohol
DMSO	:	Dimethylsulfoxide
J	:	Coupling constant
L	:	Ancillary ligand (generally)
M	:	Transition metal (generally)
Me	:	Methyl
D	:	Doublet
S	:	Singlet
T	:	Triplet
M	:	Multiplet
Dd	:	Doublet of doublets
Cat.	:	Catalyst
X	:	Halogen (generally)
COD or cod	:	1,5-cyclooctadiene
Cp*	:	Pentamethylcyclopentadienyl
Hz	:	Hertz
η	:	Hapticity
A	:	Alpha
B	:	Beta
TH	:	Transfer Hydrogenation
Rt	:	Room Temperature
*P*cy	:	*p* – cymene
Pz	:	Pyrazine
Py	:	Pyridine

1. INTRODUCTION

1.1. Carbenes

Carbenes are divalent neutral carbon compounds bearing six electrons in the valence shell. Here X and Y demonstrate alkyl, aryl, H or heteroatom (Figure 1.1). In these compounds, there is an unpaired electron pair on the carbon atom. Free carbenes are electron deficient species and, for this reason, they are highly reactive. Also the geometry of the carbene can be planar or angular.

Figure 1.1 General show of carbene and metal-carbene complexes.

In general, carbenes are those containing carbon atoms with sp^2 hybrid orbital. Two of the three sp^2 hybrid orbitals of carbene carbon are covalently bonded with carbene substitutions. One of the other two orbital is sp^2 hybrid orbital and one is empty p orbital. If the remaining two electrons reside in the same 2 orbitals as opposite, it is named as singlet carbene. The carbene formed by the spinous settlement of electrons in parallel to different orbitals is called triplet carbene (Figure 1.2).

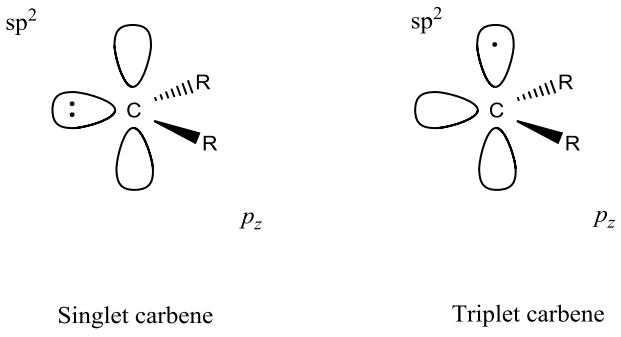


Figure 1.2 Schematic representation of singlets and triplet carbenes.

Since the structure of triplet and singlet carbene are different, their physical and chemical properties are different. In their chemical reactions, triplet carbenes exhibit radical behavior, while singlet carbenes exhibit nucleophilic and electrophilic behavior due to an electron pair and empty orbital (Table 1.1.).

NUCLEOPHILIC	ELECTROPHILIC
$CH_3\ddot{O}\ddot{C}OCH_3$	$Cl\ddot{C}Cl$
$CH_3O\ddot{C}N(CH_3)_2$	$Ph\ddot{C}Cl$
	$CH_3\ddot{C}Cl$
	$Br\ddot{C}COC_2H_5$

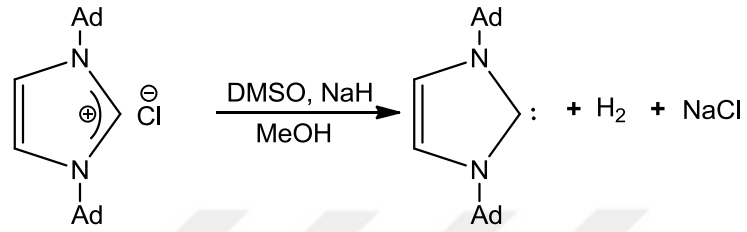
Table 1.1 Nucleophilic and electrophilic characteristics of various singlet carbenes.

There is also a difference in the angles between the singlet and triplet carbenes. According to the computation of molecular orbital theory, singlet carbenes have an angle of 105^o and triplet carbenes have an angle of 135^o. Therefore, bulky carbon substituents go for triplet carbenes due to their steric effects. The carbenes also differ in magnetic field; singlet carbenes show diamagnetic properties, whereas triplet carbenes show paramagnetic properties (Matzingerand et. al., 1995).

1.2. *N*-Heterocyclic Carbenes (NHCs)

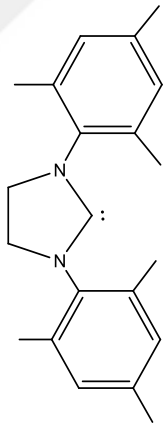
N-heterocyclic carbenes are the lewis bases presenting two electrons to the metal center and are singlet carbenes that can be complexed with all metals in the periodic table, notably transition metals. NHCs are cyclic structures and carbene carbon is bound to two nitrogen atoms by a sigma bond.

The first studies on NHCs were embarked by Ofele and Wanzlink in the 1960s. In the early 1971, Lappert synthesized Rh-NHC complex using rhodium metal as the transition metal. In 1991, the first stable, isolated NHC ligand was synthesized by Arduengo et al. The volumetric ligands bound on nitrogen have allowed the structure to be stable and counter its dimerization.



Ad: Adamantyle

In 1995, the first stable saturated N-heterocyclic carbene was synthesized by Arduengo et al.



NHCs could include to four nitrogen atoms. Among them five membered heterocycles imidazol-2-ylidene, its saturated analogue imidazolin-2-ylidene, and benzene annulated analogue benzimidazol-2-ylidene which contain two nitrogen atoms, are the most common NHCs and they are now accepted as normal NHCs. The most common subdivisions of NHCs are presented in Figure 1.3 (Diez-Gonzalez et al., 2009).

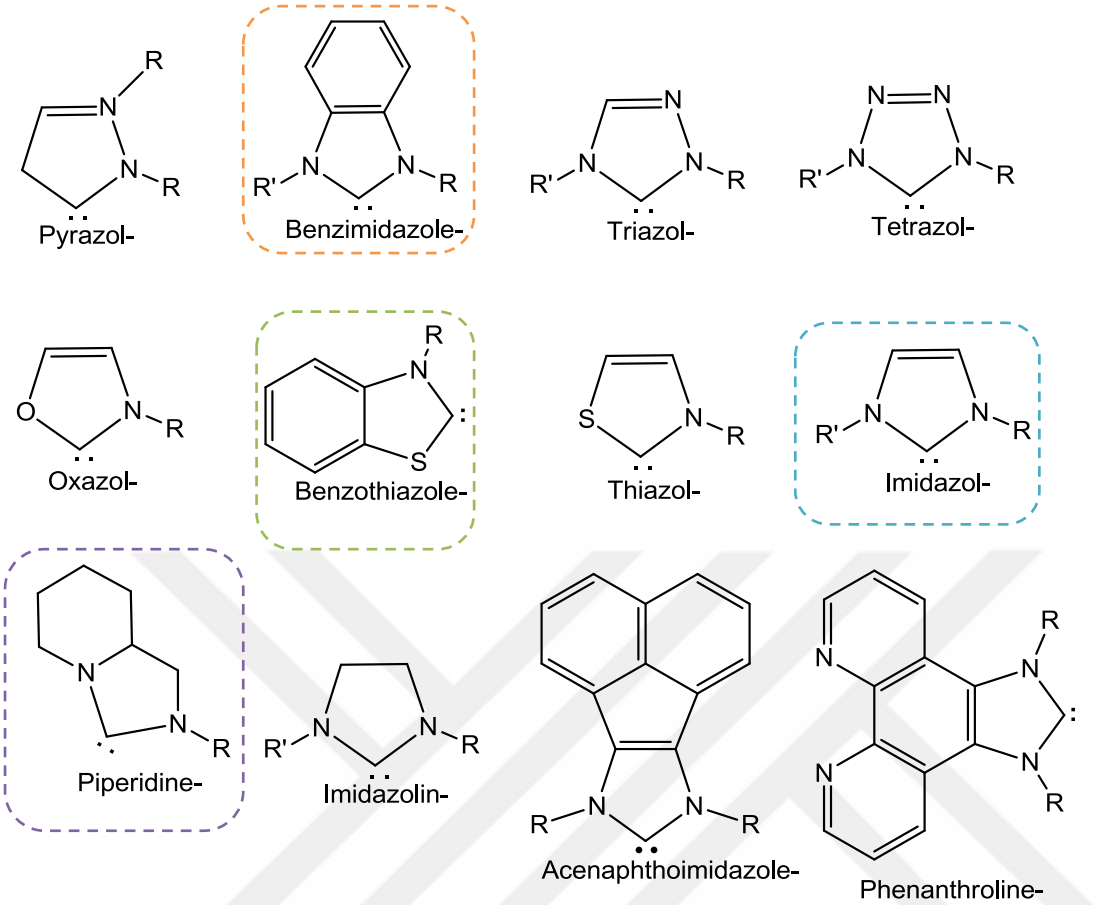


Figure 1.3 The ring structure of some NHCs. The representation does not imply that all of the NHCs are freely available.

Owing to its electronic structure, NHC is strong σ-donor yet weak π-acceptor ligand. NHCs are much more potent donor ligands than phosphines, and are strongly bound to most transition metals. These two properties make them favourable ligands in most catalytic reactions. Most NHC ligands are planar ligands as compared to cone-shaped phosphines. Bulk substituents in the imidazole ring can significantly rise the steric volume of NHC. Adjustable steric properties and specified structural and electronic properties provide a unique reactivity to the complexes of this class of ligands (Jacobsen et al., 2009).

1.2.1. Piperidine-Piperido

The piperidine, known as a saturated pyridine, is termed piperido when used as a ligand. Piperido is referred to as the name of the piperidine derivative radical derived from nitrogen by IUPAC in place of 1-piperidine**.** Piperidine is a ligand having the molecular formula $(CH_2)_5NH$. This heterocyclic amine involves a six-membered ring enclosing five methylene bridges ($-CH_2-$) an done amine bridge (-NH-). It is an uncolored liquid with an odor interpreted as abhorrent, like typical of amines. This name was given after genus name Piper, which means "pepper" in Latin. Piperidine is an extensively used reagent in the organic compound synthesis, including pharmaceuticals.

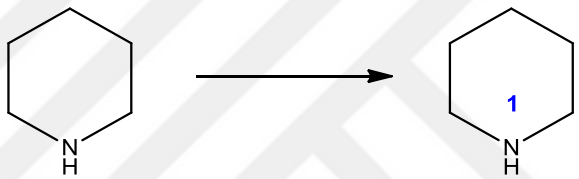


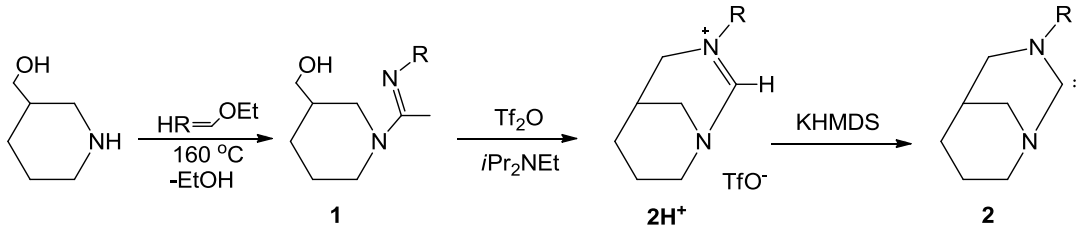
Figure 1.4 General demonstration of piperidine.

1.2.1.1. Piperidine Contaning NHCs Synthesis

Since NHC exploration, many studies have cope with the synthesis and usage of the stable carbenes. Latterly, certain methods have flourishingly been advanced for attuning their σ-donor features, which essentially related to the carbene substituents' σ effect (Dröge and Glorius, 2010). However, the regulation of the NHCs π-acceptor features is much more compulsioning, because of the fact that the high-energy LUMO is controlled by the forceful π donation of the two amino groups to the carbene bare orbital.

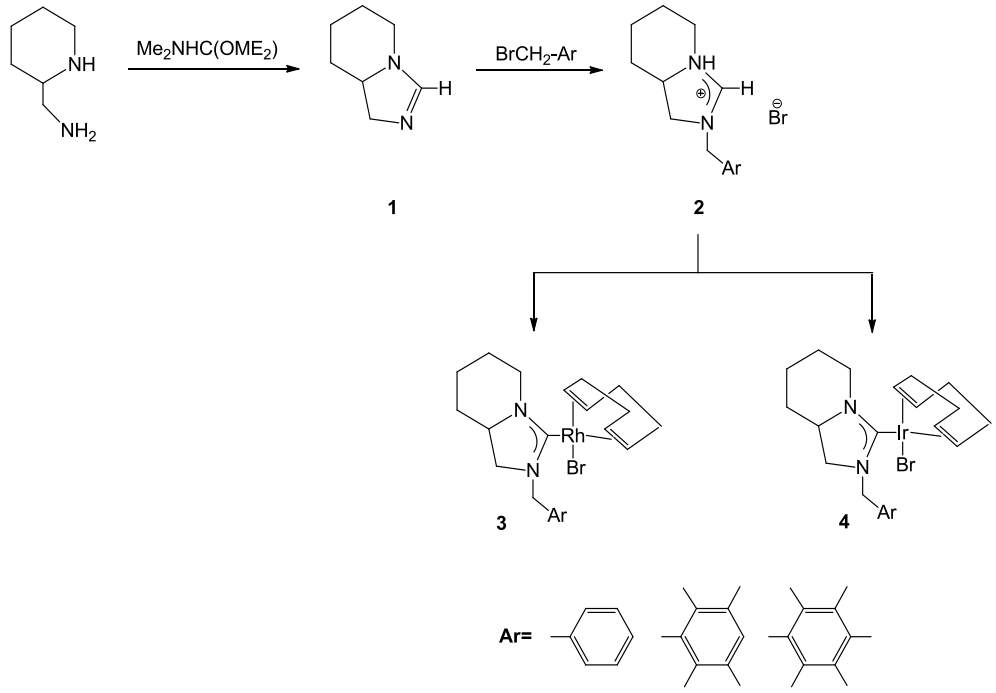
Martin et al., synthesized N-bridgehead amidinium salt **1** depend on commercially accessible piperidine methanol. Piperidine derivates of the carbene was synthesized by reaction from KHMDS and 2H+. They reported the cyclic diaminocarbene (2) which maintains a nucleophilicity on NHCs, synthesis and

single-crystal X-ray diffraction study for showing boosted electrophilicity (Martin et al., 2012).



Scheme 1.1 Synthesis of amıdınıum 2H+ and carbene 2.

This study which is performed by Türkmen et al., reported the synthesis, structure and catalytic efficiency in the catalytic transfer hydrogenations of RhI (3) and IrI (4) complexes involving piperidoimidazolidin-2-ylidenes as innovative carbene ligands (Scheme 1.2) (Türkmen et al., 2008).



Scheme 1.2 Synthesis of piperidoimidazol-2-ylidine carbene ligands and their complexes.

1.2.2. Benzothiazole

Benzothiazole is an aromatic heterocyclic compound, and its chemical formula is C_7H_5NS. Benzothiazole is a sallow liquid substance with a boiling point area of 227-228 ^{0}C. Benzothiazole ring is formed by thiazole ring fusion with benzene ring (Hisamoddin et al., 2014). The numbering of the ring starts from the sulfur atom, continues towards the other heteroatom (Figure 1.5).

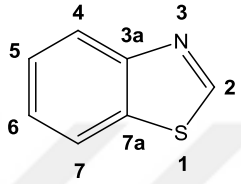


Figure 1.5 Numbering the benzothiazole ring.

Benzothiazoles are particularly interesting because of their different biological activities, such as antitumors, anticonvulsants and anti-inflammatory (Hutchison et al., 2002; Caryolle et al., 1990), and are shown as an important class in heterocyclic.

1.2.2.1 General Synthesis of Benzothiazole

Recently, various new procedures have been expressed, the most used methods for the synthesis of 2-substituted benzothiazole are as pursues; 2-substitued 1-mercapto benzothiazole (Figure 1.16) was first purchased by A. W. Hofmann an attack to make the disulfhydryl derivative of thiocarbanilide by the actuation of carbon disulfide on o-aminophenol. He achieved the same compound by the actuation of sodium hydro- sulfide on chlorophenyl mustard oil (1-chlorobenzothiazole). Thus, the product was obtained after recrystallization from alcohol. Its melting point is 179 ^{0}C and it was quickly oxidized to disulfide which melts at 180 ^{0}C. Besides, Hofmann indicated the formation of 2-

anilinobenzothiazole with the reaction of 2- aminothiophenol and phenyl isothiocyanate (Hofmann et al., 1887).

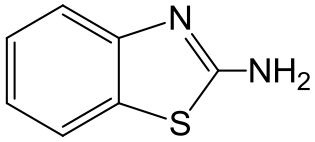
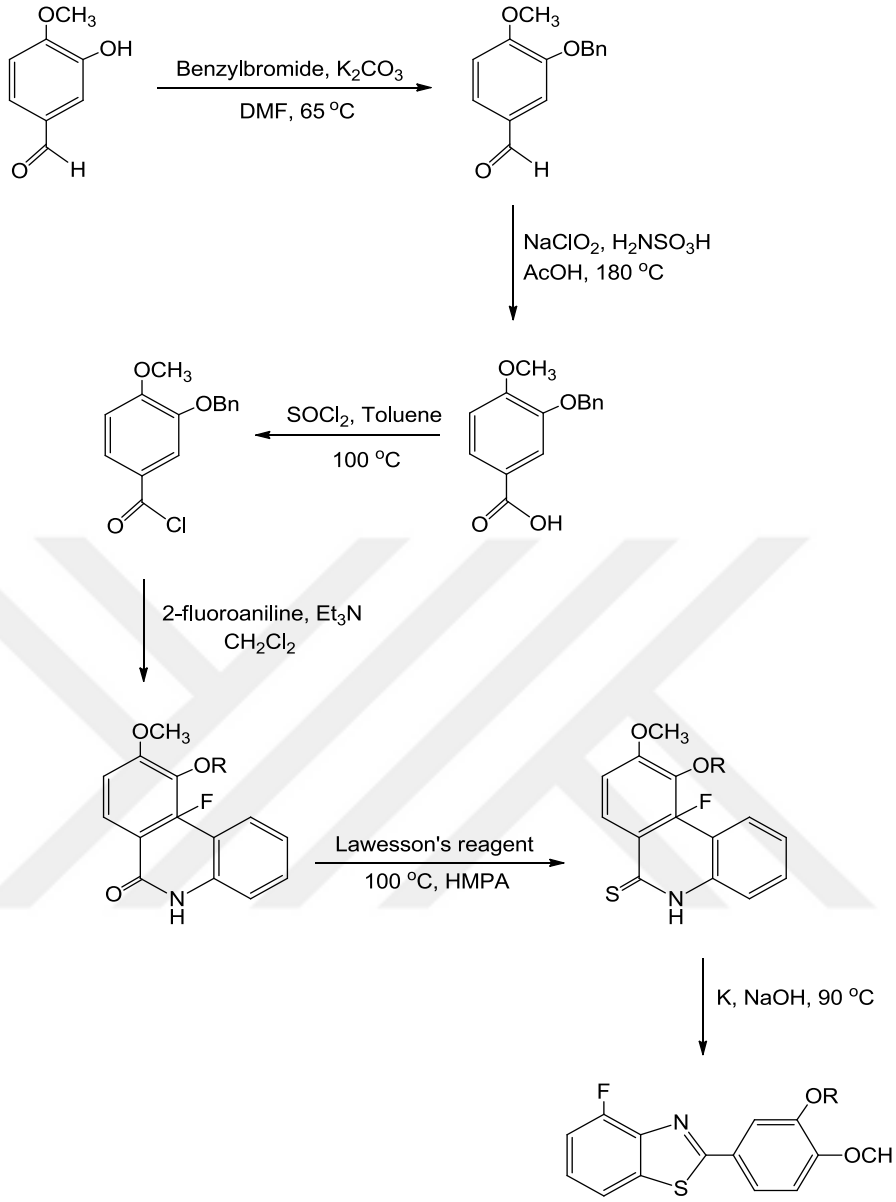


Figure 1.6 2-substituted benzothiazole**.**

Min Wang synthesized 4-fluorinated 2-phenylbenzothiazoles (Scheme 1.3) which involves the benzylation of the initiation compound 3-hydroxy-4-methoxybenzaldehyde. This was accomplished by the phenolic hydroxyl group protection using benzyl bromide to implement 3-benzloxy-4-methoxybenzaldehyde. This compound's oxidation with the usage of sodium chlorite provided 3-benzloxy-4-methoxybenzoic acid that interacted with thionyl chloride to obtain 3-benzloxy-4-methoxybenzoyl chloride. 2-fluorobenzamides N-(2-fluorophenyl)-3,4-dimethoxybenzamide and N-(2-fluorophenyl)- 3-benzloxy-4-methoxybenzamide were produced by condensation of 3-benzloxy-4-methoxybenzoylchloride, or 3,4-dimethoxybenzoyl chloride with 2-fluoroaniline which is commercially available starting material. The benzamides were transformed to their thiobenzamides N-(2-fluorophenyl)-3,4-dimethoxythiobenzamide and N-(2-fluorophenyl)-3-benzloxy-4-methoxythiobenzamide with Lawesson's reagent in HMPA (hexamethylphosphoramide). Cyclization of thiobenzamides via a customized procedure of Jacobson thioanilide radical cyclization with potassium ferricyanide and aqueous sodium hydroxide allowed the formation of 4-fluorobenzothiazoles-4-fluoro-2-(3-benzloxy-4-methoxyphenyl) benzothiazole (Min Wang et al., 2006).



Scheme 1.3 Synthesis of 4-fluorobenzothiazoles-4-fluoro-2-(3-benzloxy-4-methoxphenyl) benzothiazole.

1.2.3. Benzimidazole

Benzimidazole, also known as 1,3-benzodiazole and benzoglyoxalin, is a heteroaromatic ring system formed by coupling the imidazole ring from the 4 and

5 positions to benzene. Naming in the compound is done starting from imino hydrogen.

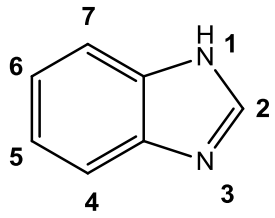


Figure 1.7 Numbering the benzimidazole ring.

The benzimidazole ring structure carries two different nitrogen atoms. The nitrogen carrying the hydrogen atom is called “imino nitrogen” or “pyrrole nitrogen” while the other nitrogen in the tertiary structure is called “pyridine nitrogen” or “tertiary nitrogen”. The hydrogen atom of the imino nitrogen is also called “imino hydrogen”.

Benzimidazoles containing free imino hydrogen are tautomeric systems. Because of this situation, two different benzimidazole derivatives are obtained in the synthesis of the non-substituted benzimidazole derivatives from position 1 (Wright et al., 1951).

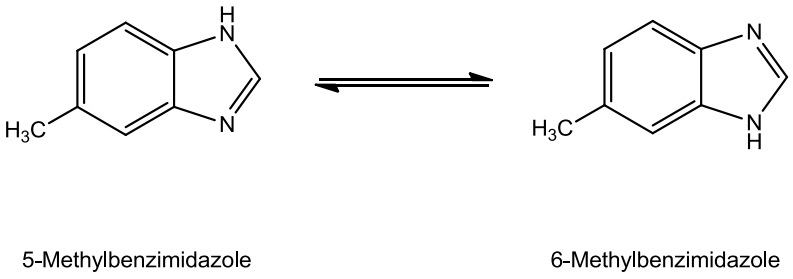


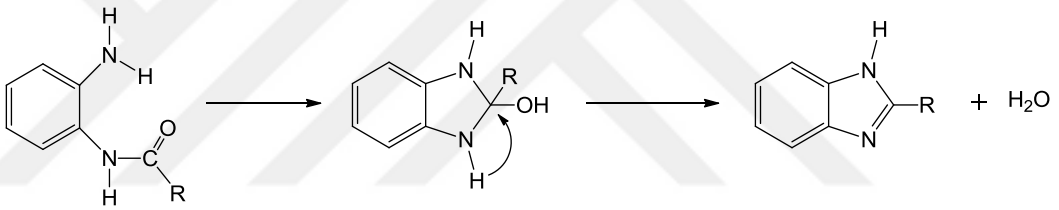
Figure 1.8 Tautomer in benzimidazoles.

Benzimidazoles are generally high melting point solids. In addition, the basic properties of the acid are more effective than the properties of amphoteric compounds. The benzimidazole ring is highly stable. Conjugation in the benzimidazole ring increases the stability of the molecule. This increased stability

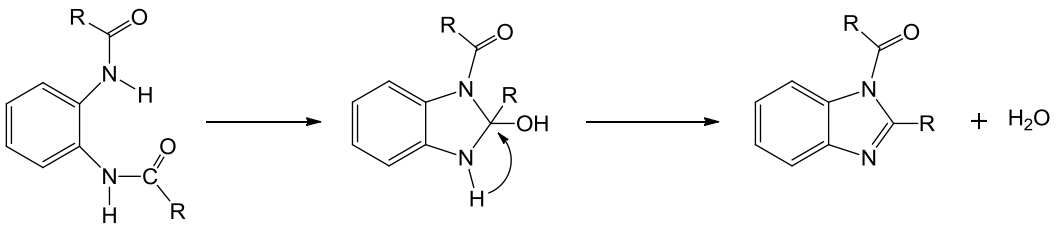
also causes the basicity to be lower than the imidazoles. Benzimidazoles are highly resistant to acids and bases, and are not easily affected by oxidizing compounds (Elderfield et al., 1957).

1.2.3.1. Synthesis methods of benzimidazoles

Benzimidazole is widely obtained by heating *o*-phenylenediamine with formic acid or triethylorthoformate. The monoacyl derivatives are obtained by heating the monoacyl derivatives of o-phenylenediamine solely. Monoacyl derivatives are readily available and thus are proper for the preparation of these benzimidazoles. In this method the monoacyl derivative of diamine is heated in a nitrogen atmosphere to block oxidation and the product is obtained in good yield (Kelly et. Al. 1945).

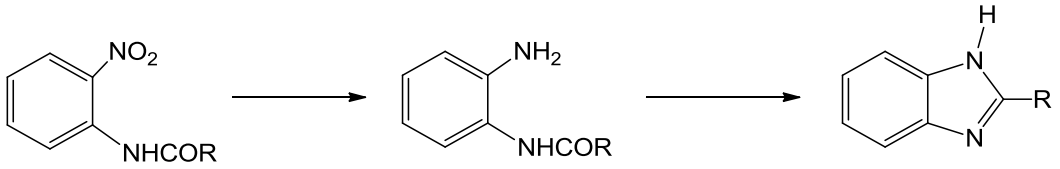


Also, o-phenylenediamines diacyl derivatives are changed to benzimidazoles. This requires high temperatures. High temperature causes the production of by-products and decline in efficiency (Deniz, 2009).



If o-diamino compounds cannot be easily obtained, acyl derivatives of the corresponding 1-amino-2-nitro compounds can be used. These derivatives are reduced with metals such as tin and zinc and hydrochloric acid, which are converted into the corresponding benzimidazoles. The amine intermediate could

be isolated when the nitro compounds are hydrogenated with Pt and Pd. The amino derivatives are converted to the corresponding benzimidazoles when diluted with dilute HCl or back-cooled alone.



1.2.4. Imidazole

The imidazole is a diazole with two nitrogen. It is a highly stable, colorless and odorless solid compound. Imidazole is dissolved in water and organic solvents such as other 1,3 diazoles, but it is a base that is stronger than other diazoles in terms of basicity. The precise numeration of the imidazole ring is displayed in the figure below (Figure 1.9). The imino nitrogen takes position 1 and follows the ring by assigning the smallest conceivable number to the third row of nitrogen created as the numbering location 3. The substituted nitrogen represents the embarking point for the numbering of N-substituted imidazoles (Hofmann et al., 1953).

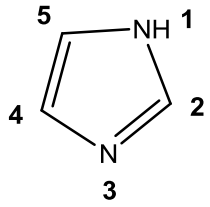


Figure 1.9 Imidazole (1, 3 diazole).

The solubility of the imidazole is high in polar solvents and low in apolar solvents. N-substituted imidazoles are generally much more dissolve in apolar solvents than free imino hydrogenated imidazoles. Imidazole is a monoacidic base capable of forming crystalline salts with acids. The basic structure of the

imidazoles is due to the skill of a pyridine nitrogen to accept a proton. Addition of methyl groups to the imidazole ring raises its basic firmness. This can be elucidated by the fact that the methyl groups, which tend to ascend the electron density around the pyridine nitrogen, exhibit electron release properties. Imidazole is an abnormally basic compound for a compound having a nitrogen atom of sp^2 hybrid. The high basicity of the imidazole is presumably a result of the symmetry of the conjugate acid and resonance stability (Streitwieser et al., 1985).

The N-H proton in the imidazole ring is free and forms strong hydrogen bonds between molecules. Due to this feature of imidazole boiling point is higher than expected (Joule et al., 2000). For imidazole, the following tautomeric forms are possible:

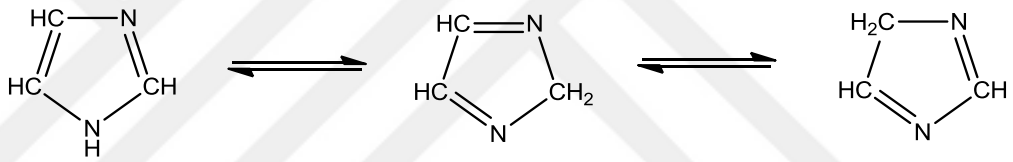
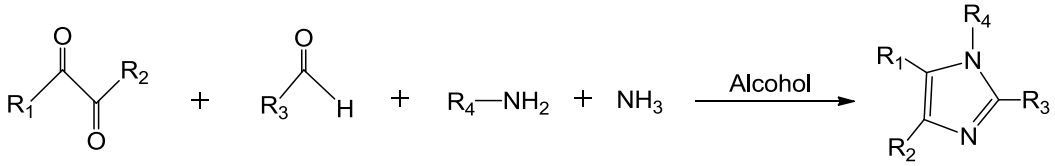


Figure 1.10 Tautomeric forms of the imidazole.

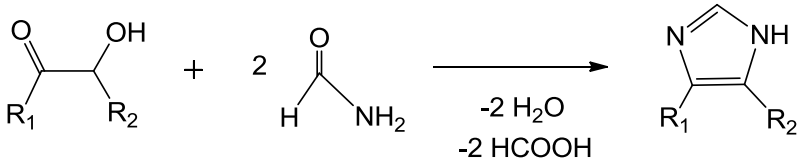
1.2.4.1. General Synthesis of Imidazole

Imidazole was first synthesized by Heinric Debus in 1858 but this reaction fully enhanced by Radziszewski starting in 1882 and further adjusted by Weidenhagen in 1882 and further adjusted by Weidenhagen in 1935 (Debus, 1858; Weidenhagen, 1935).

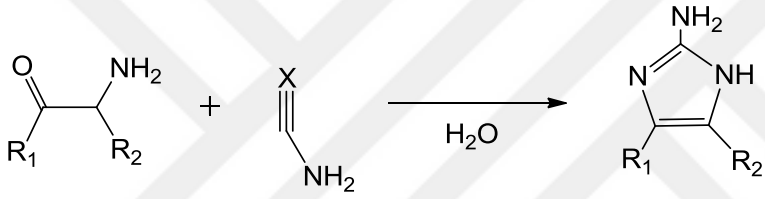


This reaction proceeds to accord imidazole ring by the condensation of an aldehyde, α-dicarbonyl compound (such as glyoxal) and two equiv. of dry

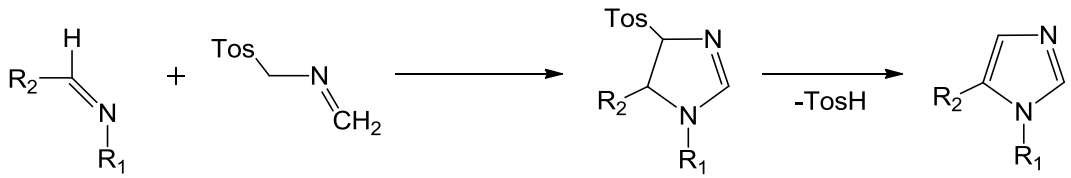
ammonia in alcohol. The other synthesis of imidazole is Bredereck Synthesis. According to this route imidazoles are obtained from α-hydroxyketones and formamide which are free of substitution at the 2-position of the ring.



α-Amino ketones may be condensed with cyanamide to form 2-aminoimidazoles. Marckwald Synthesis is the name for this imidazole synthesis type (Eicher and Hauptmann, 2003).



Aldimines react with tosylmethylisocyanide (TosMIC) in the presence of K_2CO_3.



1.3. NHC Complexes

NHCs are stable singlet carbene that could complex with all metals in the periodic table thanks to two donor electrons and heterocyclic compounds involving nitrogen atoms in it. The Lewis-specific N-heterocyclic carbenes (NHC)

form a strong sigma bond, giving two donor electrons on the carbene carbon to the metal center. The unbound electrons on the nitrogen atoms in the heterocyclic ring are transmitted to the carbene carbon through the π bond, while the metal atom π back-bonding contributes to the strengthening of the metal-NHC bond.(kühl et al, 2010). Besides, the steric and electronic effects of the nitrogen atom-linked functional groups in the heterocyclic structure evolve many properties such as synthetic flexibility to N-heterocyclic carbenes (Figure 1.11).

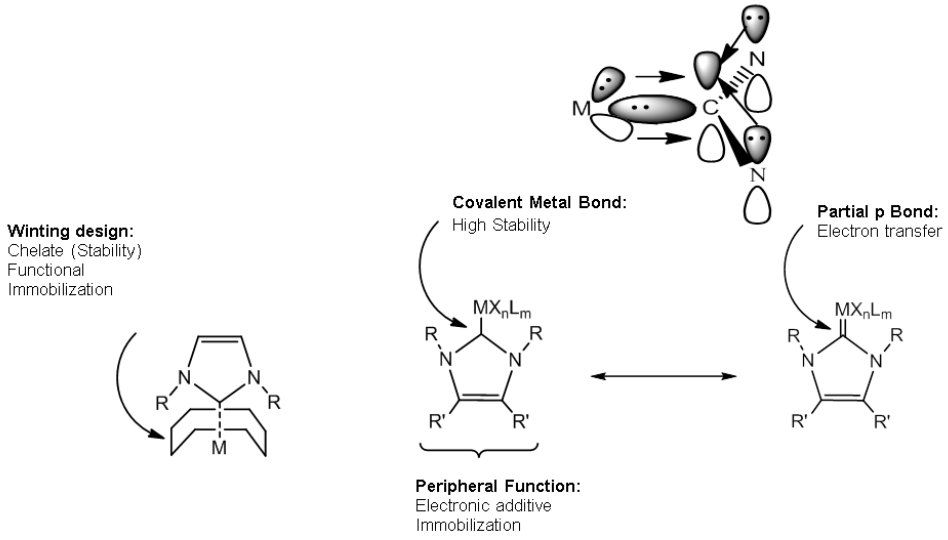


Figure 1.11 Structural properties of metal-carbene complexes.

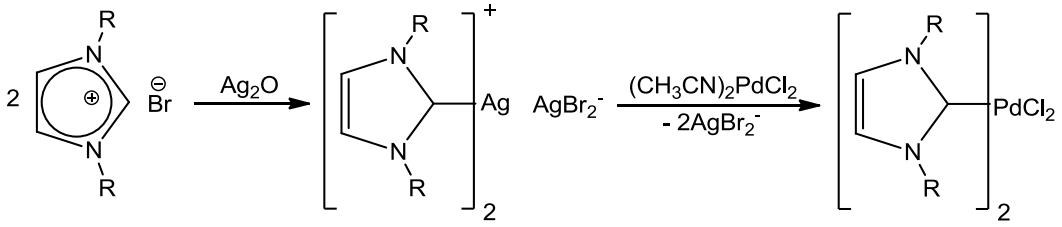
Notably used methods for the preparation of NHC metal complexes can be summarized as pursues (Weskamp 2000);

1) In-situ Deprotonation of Ligand Precursors: The complexization of the ligand in-situ eliminates the stage of NHC free preparation and provides practicality for administration. Deprotonation can be done in four different ways: deprotonation by basic methalates, deprotonation by basic anions, deprotonation with external bases and elimination of small molecules from neutral ligand initiator. Basic silver (I) oxide is an remarkably and proper precursor of silver (I) bis NHC complexes. The reaction is carried out in methylene chloride under room

conditions and the cationic complex is precipitated off. The resulting structure is commonly used as a suitable NHC transfer agent (Bildstein et al. 1999).

2) Complexation of free NHCs: Phosphines and other ligands could be replaced by NHCs. Many phosphines are easily replaced by NHCs even at temperatures below room temperature. This method is crucial for NHC complex formations. In some instances, complex complexes of NHC-phosphine may form in pure form. Both phosphine ligands in the dichlorobis (tricyclohexylphosphine) benzylidene ruthenium (II) complexes, an important catalyst for olefin metathesis, are replaced by NHC. The use of bulk NHCs allows mixed phosphine-NHC complexes forming.

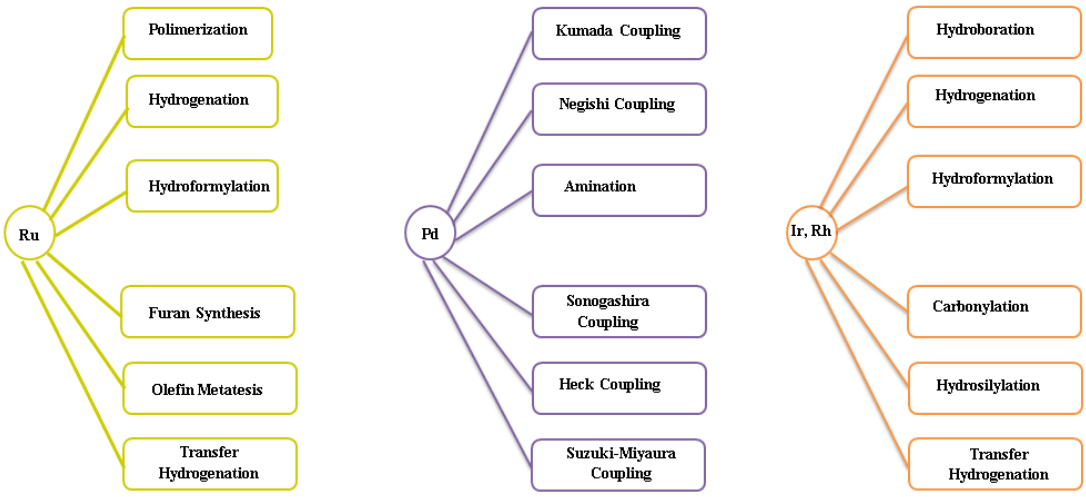
3) Opening of Electron Rich Olefins: The olefinic complexes exhibit nucleophilic properties and undergo thermal expansions by transition metal complexes. Electroluminescent tetraaminoethylenes are formed in the toluene with complex precursors such as Mn, Fe, Ru, Co and Ni carbonyls and corresponding NHC complexes are formed.Different metal-NHC complexes can be synthesized by ligand exchange over silver (I) complexes (Scheme 1.4). This method is very significant (Lin and Vasam 2004)



Scheme 1.4 Synthesis of different metal-NHC complexes by ligand exchange through silver (I) complexes

1.4. Catalytic Applications of NHC Complexes

After the isolation of free N-heterocyclic carbenes by Arduengo in 1991, a wide variety of NHCs were synthesized (Fortman et al., 2011). NHC complexes with stable metal carbon bonds show better activity than phosphin ligands owing to strong σ-donor, weak π acceptor traits. Furthermore, the bonds they form with metals are stronger than phosphines. Because of these properties, NHCs have become attractive ligands in organometallic and inorganic coordination chemistry. In especially, this catalytic activity of NHC complexes over the last two decades has been observed to be more efficient than the commonly used phosphine complexes. The reactions in which these complexes are used as catalysts are seen in scheme 1.5.



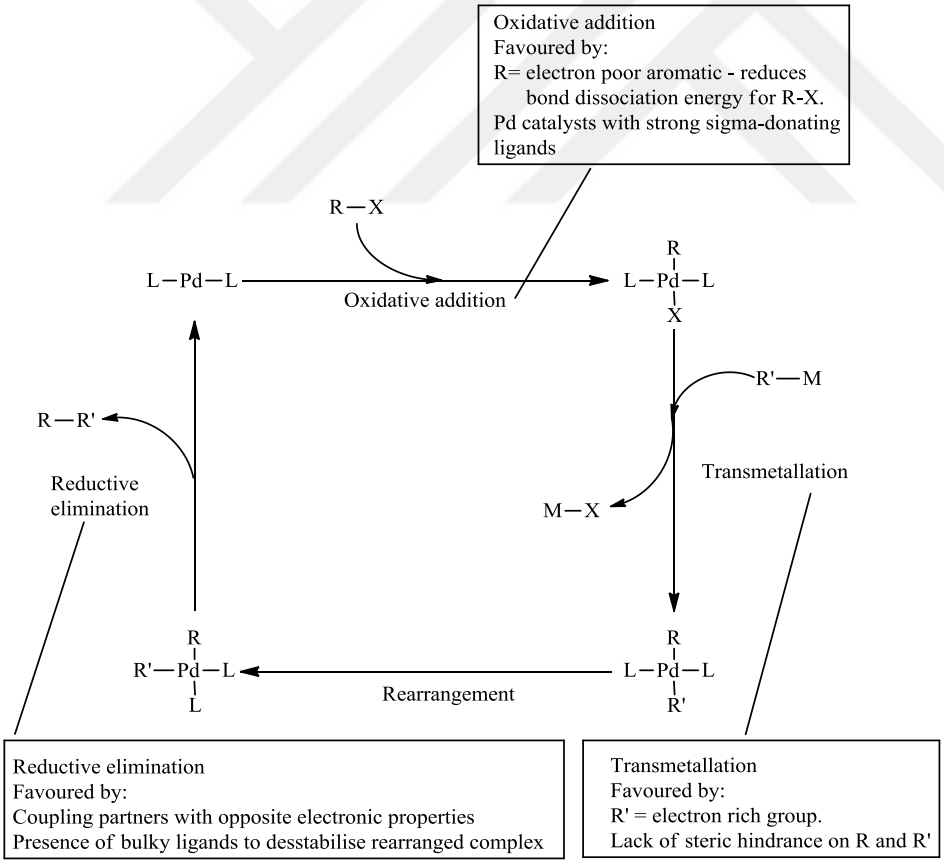
Scheme 1.5 The different type catalytic reactions using metal-NHC complexes.

1.4.1. Suzuki – Miyaura coupling Reaction

The Suzuki-Miyaura cross-coupling reaction is the most widely used cross-coupling reaction. Suzuki-Miyaura coupling is the reaction with

organoborane derivatives of aryl halides with the palladium catalyst and biaryl derivatives in the presence of a base (Bellina et al., 2004).

In other words, it combines chemically differentiated parts which are comprised in different processes electronically with the metal catalyst. Oxidative additives are formed by formaldehyde electrophilic organic groups, thereby electron donation oxidized palladium to form the novel Pd-C bond. Nevertheless, the transmetalization takes place as it is shown in Scheme 1.6. via the formal nucleophilic organic groups transfer from boron to palladium. This complimentary reactivity chain between transmetalation and oxidative addition permits two very much alike, yet different, components to be cross-coupled, by this way forming the cornerstone of this important methodology.

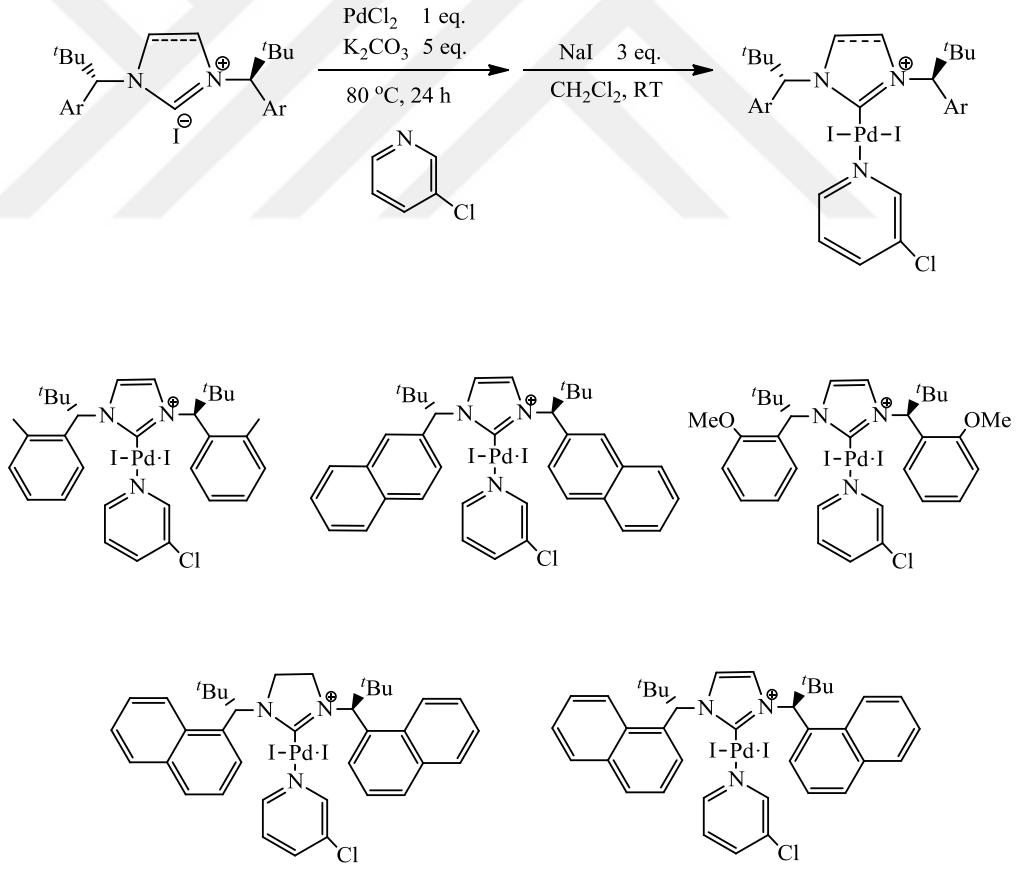


Scheme 1.6 General mechanism of Suzuki coupling reactions.

1.4.1.1. Pd-catalyzed Suzuki – Miyaura Coupling Reaction

In the 21st century, researches on Pd catalysts for cross-couplings have particularly goaled the Suzuki reaction and have included new investigations on the reaction mechanism and the development of catalytic systems displaying exceptional high catalytic performances.

Benhamou et al. In 2014, they synthesized chiral volume NHC ligands containing 2,2-dimethyl-1-(o-substitutedaryl)-propane 1-amine and chiral PEPPSI complexes containing these ligands. They analyzed the catalytic activity of chiral PEPPSI complexes in the Suzuki-Miyaura reaction (Benhamou et al., 2014) (Scheme 1.7).



Scheme 1.7 Synthesis of chiral NHC-containing PEPPSI complexes.

Türkmen et al. stated the use of benzimidazolylidene ligands and pyridine carboxylic acids as ligands, giving stable palladium complexes which are resplendently catalyzed Suzuki−Miyaura crosscoupling in aqueous solution (Turkmen et al. 2009).

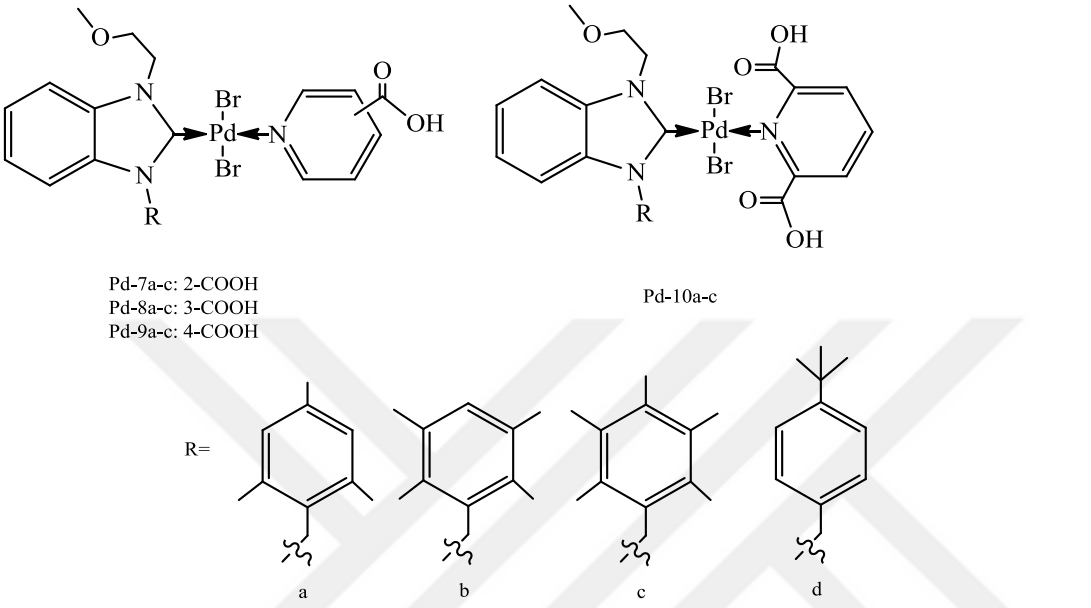


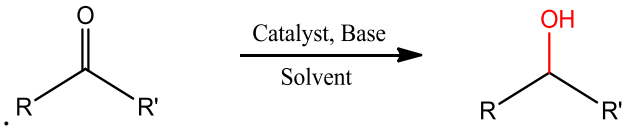
Figure 1.12 Palladium nhc complexs with group.

Complexes Pd-7 and Pd-10, which have a carboxylic acid group in the ortho position, provided slightly superior yields than Pd-8 and Pd-9, para and meta positions substituted, suggested that the carboxy group might be interacting positively with the metal (Figure 1.12).

1.4.2. Transfer Hydrogenation (TH)

Transfer hydrogenation (TH) is a useful technique to add hydrogen to a molecule by eliminating the danger of explosion using a reagent other than the H 2 molecule. For practical application, the two compounds that are commonly utilized as hydrogen donors for transfer hydrogenation are isopropanol and formic acid (Gladiali et al., 2006). It is also used in combination with Ru, Rh or Ir catalyst and a strong base such as KOH (Scheme 1.8). TH produces few by-products, abstain from dangerous reagents, and utilizes readily available and

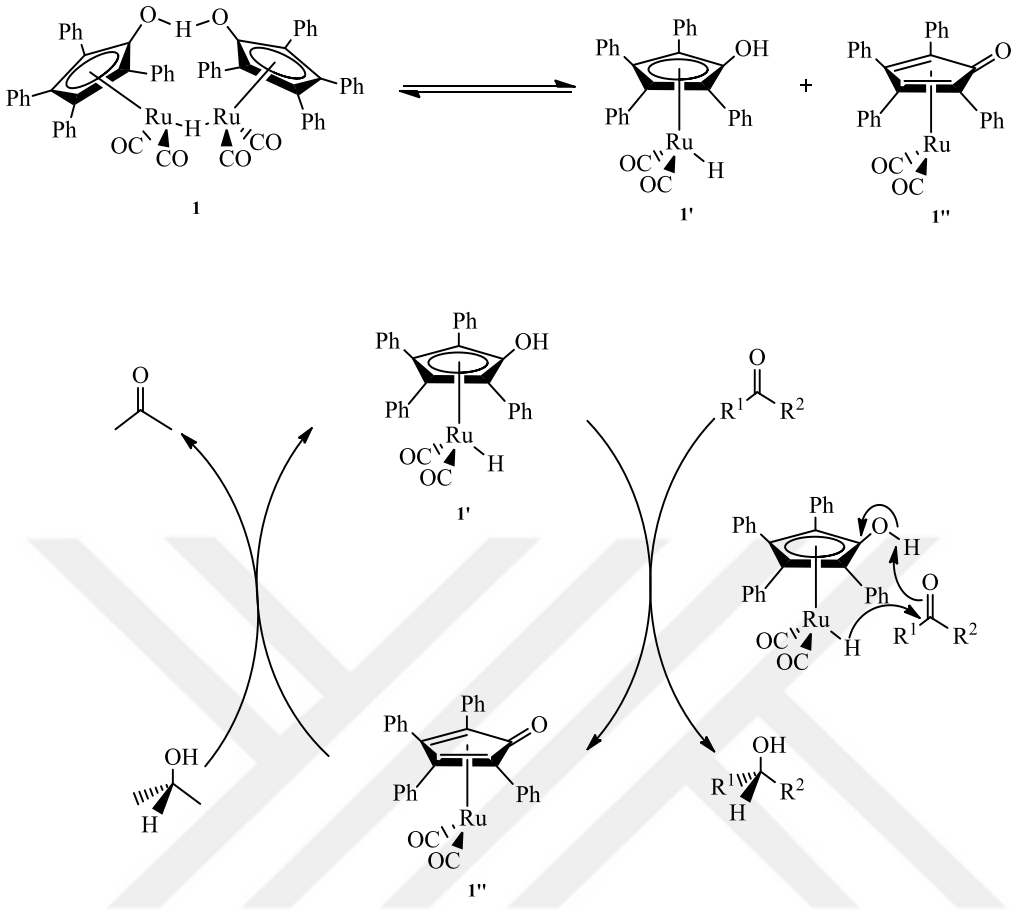
benign embarking materials such as carbonyl compounds, imines, alkynes and alkenes.



Scheme 1.8 Transfer Hydrogenation Reaction.

1.4.2.1. Ru-catalyzed Transfer Hydrogenations

Ruthenium-based catalysts are the most widely used to mediate transfer hydrogenation. In 1986, Shvo's group reported the synthesis of the ruthenium complex 1, that originally found to be very efficient in direct hydrogenation of ketones, was later appling in transfer hydrogenation reaction (Conley et al, 2010). The dinuclear complex 1 dissociates upon heating into the active reduced form 1' and the coordinatively unsaturated and therefore, highly reactive species 1". The complex 1' operated through an outer sphere mechanism involving a simultaneous transfer of hydride from the ruthenium center and proton from the hydroxyl group on cyclopentadienyl ligand to the carbonyl group of the ketone substrate. 1" upon dehydrogenation of the hydrogen donor isopropanol, the active transfer hydrogenation catalyst is regenerated. This Shvo catalyst was first presented instance of bifunctional metal-ligand catalyst.



Scheme 1.9 Transfer hydrogenation mediated by Shvo's catalyst.

Various types of half-sandwich ruthenium complexes which contain cyclopentadienyl, indenyl or arene have been intensively investigated in transfer hydrogenation (Wang et al 2015). These metal complexes containing C, N, O, P, S elements in ligands with very different forms such as half-sandwich and multidentate metal complexes and also, metal-N-hetereocyclic carbenes may the most used and popular catalysts for transfer hydrogenation. These are shown in figüre 1.13.

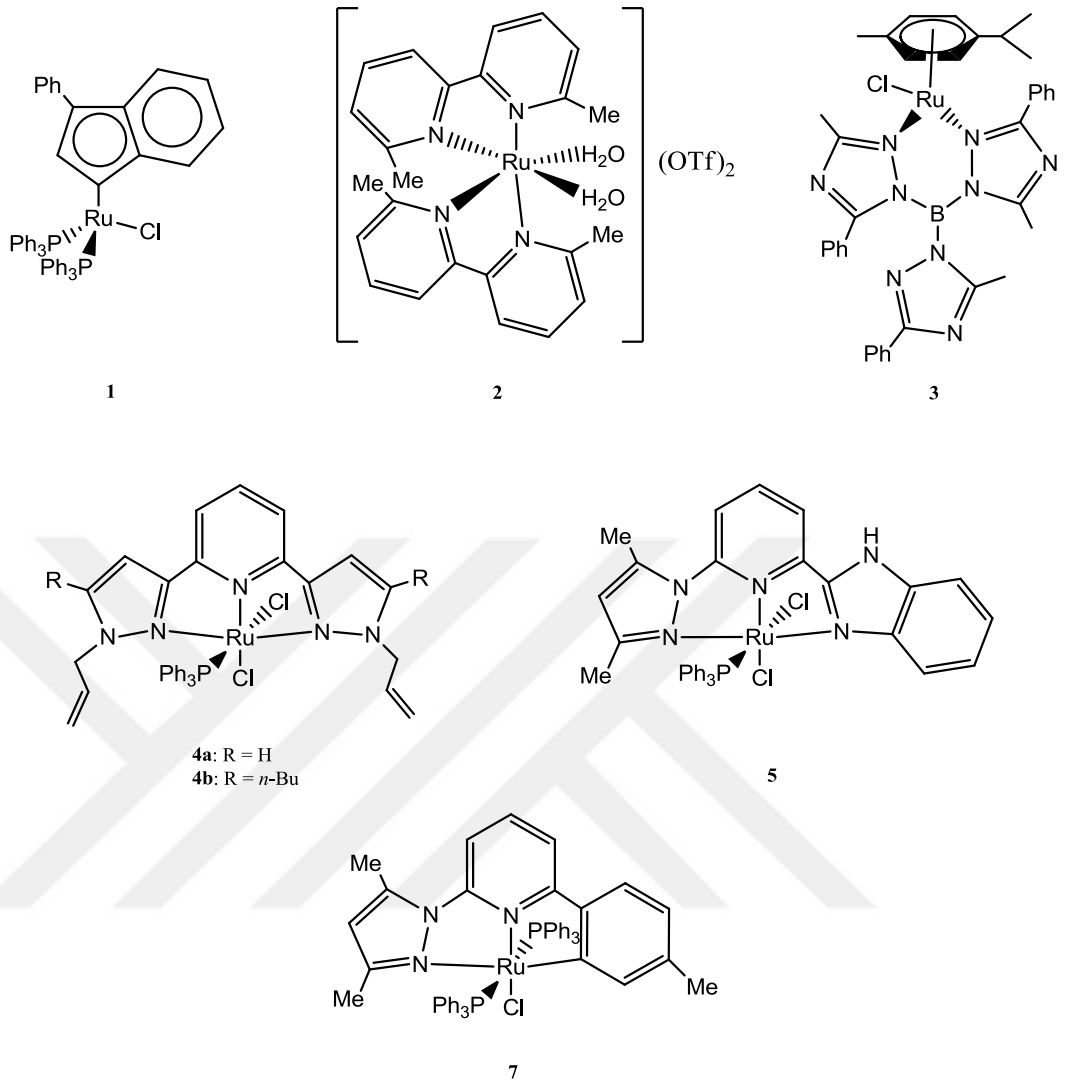


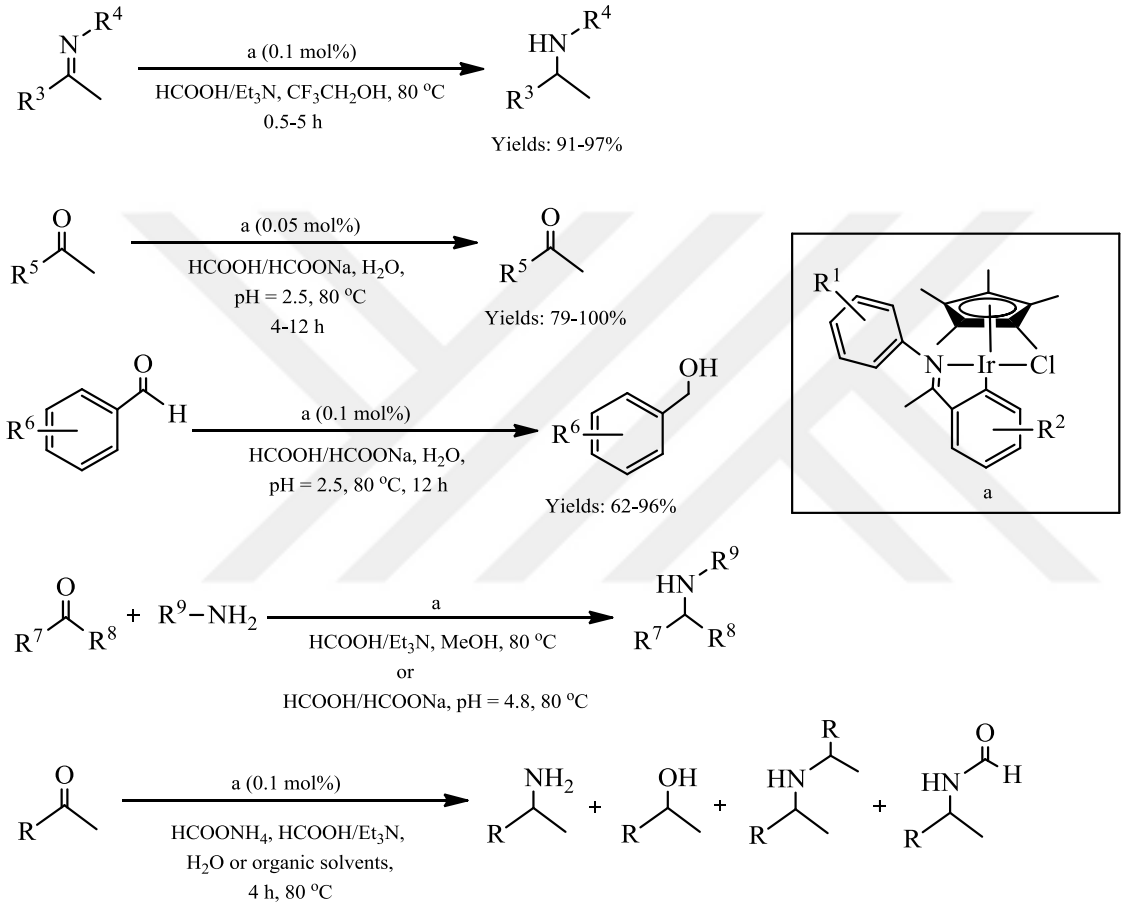
Figure 1.13 Selected ruthenium-based transfer hydrogenation catalysts.

1.4.2.2. Ir-catalyzed Transfer Hydrogenations

Iridium complexes are among the most important class to catalyze transfer hydrogenation reactions. And it also showed that its catalytic activities are very high compared to other transition metals and that focus is always on complexes due to this large yield.

Wang's group illuminated the catalytic efficiency of a branch of iridium complexes which are cyclometalated containing Cp* unit in assorted TH

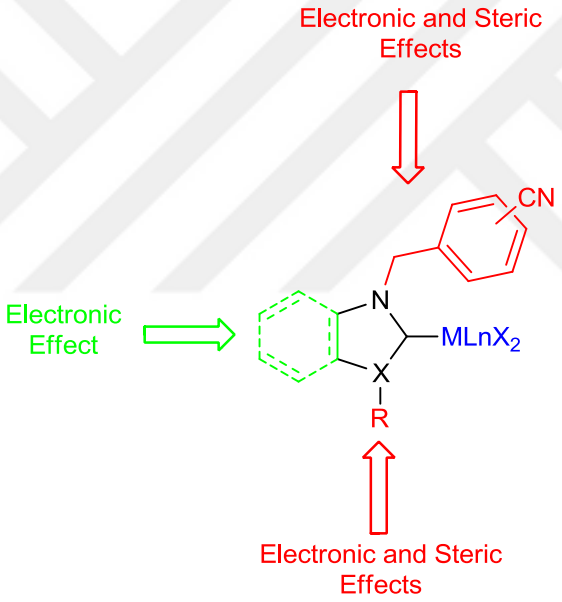
processes. These complexes have been identified as versatile catalysts. They allowed the efficient and selective TH with a range of substrates including imines to amines,ketones and aldehydes to alcohols,and TH for reductive amination of ketones to secondary and primary amines using safe and inexpensive formate as hydrogen donor (Wang et al , 2010)(Scheme 1.10).



Scheme 1.10 Half-sandwich Cyclometalated Ir Complexes as TH Catalysts.

1.5. Aim of the Study

Homogeneous catalysts are the catalysts that become more important in industry particularly in the area of pharmaceutical and polymer industry and have greater selectivity and milder conditions compared with heterogeneous catalysts. Homogeneous catalysis is that the catalyst mixes into the reaction mixture, allowing a very high degree of interaction between catalyst and reactant molecules. Ligands also play an important role in homogeneous catalysis.That also, the NHC ligands generally contain the 1,3-diorganylimidazole ring, the substituents on the N atoms play an important role in catalytic activity and selectivity.



In this respect, the importance of electron withdrawing and acceptor group in complexes is increasing. Therefore, different complexes containing nitrile substituent were synthesized. Catalytic properties were investigated in Suzuki-Miyaura and transfer hydrogenation reactions.

2. EXPERIMENTAL

Unless otherwise stated, all reactions, including catalytic reactions were performed under inert atmosphere. The solvents were used as received and if necessary dried according to the common methods. The glass equipment was heated under vacuum in order to remove oxygen and moisture then they were filled with argon.

Solvents, dichloromethane, acetonitrile, diethyl ether, ethanol and other starting components like carboxylic acid derivatives and metal salts were purchased from Merck, Sigma Aldrich and Alfa Aesar. $[RuCl_2(p\text{–cymene})_2]_2$ (Benett and Smith, 1974) and $[Cp^*IrCl_2]_2$ (1990) were synthesized according to literature.

^1H NMR and ^{13}C NMR spectra were taken with Varian as 400 Mercury instrument operating at 399.88 MHz (^1H), 100.56 (^{13}C). As solvent DMSO–d_6 and $CDCl_3$ was employed. Chemical shifts (δ) are given in ppm relative to TMS; coupling constants (*J*) in Hz.

FTIR spectra were recorded on Perkin Elmer Spectrum 100 series.

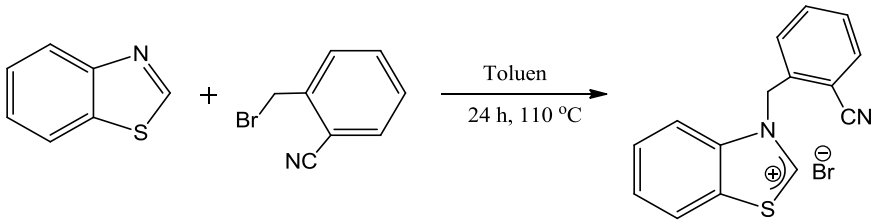
The yields of catalytic experiments were measured by GS Agilent brand (7890A series GS model) on a HP-5 capillary column and with a FID detector in Ege University in Faculty of Science at Department of Chemistry.

X-Ray diffraction analysis were performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic Mo-Kα radiaton, Dr. Onur Şahin, Sinop University, Scientific and Technological Research Application and Research Center, Sinop, Turkey.

Melting points were determined by electro thermal melting point detection apparatus.

2.1. General Synthesis of Ligands

2.1.1 Compound T_{1a}

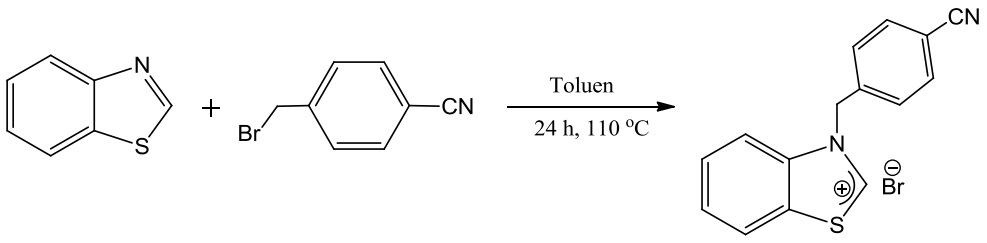


T_{1a}

Benzothiazole (1.00 g, 7.39 mmol) was dissolved in 5 ml of toluene and 2-bromobenzonitrile (1.45 g, 7.39 mmol) was added to boil under reflux for 24 h. The precipitate is then filtered off and washed with diethyl ether. Dried under vacuum to yield.

Yield = 81%, 1.98 g. ^{1}H NMR (400 MHz, DMSO–d_6): δ 10.8 (s, 1 H, S-*CH*-N), 8.59 (d, 1 H, J = 2 Hz, Ar-*H*), 8.17 (d, J = 1.6 Hz, 1 H, Ar-*H*), 7.99 (d, J = 7.6 Hz, 1 H, Ar-*H*), 7.86 (m, 2 H, Ar-*H*), 7.69 (t, J = 8 Hz, 1 H, Ar-*H*), 7.60 (t, J = 7.6 Hz, 1 H, Ar-*H*) , 7.31 (d, J = 7.6 Hz, 1 H, Ar-*H*), 6.40 (s, 2 H, N-CH_2). ^{13}C NMR (100 Hz, DMSO – d_6): δ 194.4, 140.7, 136.5, 134.5, 134.4, 132.2, 130.3, 130.1, 128.9, 126.1, 117.5, 111.1, 54.1. IR, νmax (cm^{-1}) (CH_2Cl_2): 3367, 3091, 3021, 2978, 2939, 2897, 2221, 1987, 1682, 1594, 1577, 1493, 1462, 1448, 1426, 1293, 1209, 1175, 1094, 1080, 1032, 900, 834, 792, 774, 760, 751, 730, 643, 597, 581, 512, 452, 425, 404. Anal. Calcd for $C_{15}H_{11}BrN_2S$ (M: 329,98): C, 54.39; H, 3.35; N, 8.46 %; Found: C, 4.39; H, 3.34; N, 8.44%.

2.1.2. Compound T_{1b}

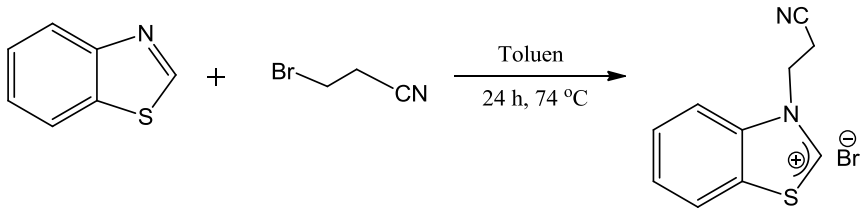


T_{1b}

Prepared according to procedure T_{1a} using 4-bromobenzonitrile (1.45 g, 7.39 mmol).

Yield = 58%, 1.42 g. ^{1}H NMR (400 MHz, DMSO–d_6): δ 10.9 (s, 1 H, S-*CH*-N), 8.56 (d, 1 H, *J* = 8 Hz, Ar-*H*), 8.21 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.85 (m, 4 H, Ar-*H*), 7.67 (d, 2 H, *J* = 8 Hz, Ar-*H*), 6.28 (s, 2 H, N-CH_2). ^{13}C NMR (100 Hz, DMSO– d_6): δ 166.6, 140.4, 138.8, 132.3, 134.4, 130.2, 129.5, 128.9, 126.0, 117.7, 112.1, 54.9. IR, νmax (cm^{-1}) (CH_2Cl_2): 3473, 3032, 2998, 2861, 2226, 1779, 1611, 1592, 1578, 1506, 1463, 1451, 1430, 1378, 1342, 1329, 1308, 1283, 1228, 1208, 1188, 1160, 1120, 1090, 1046, 1019, 984, 972, 945, 900, 885, 830, 815, 773, 745, 705, 658, 637, 579, 549, 508, 498, 427. Anal. Calcd for $C_{15}H_{11}BrN_2S$ (M: 329,98): C, 54.39; H, 3.35; N, 8.46 %; Found: C, 54.36; H, 3.32; N, 8.48%.

2.1.3. Compound T_{1c}

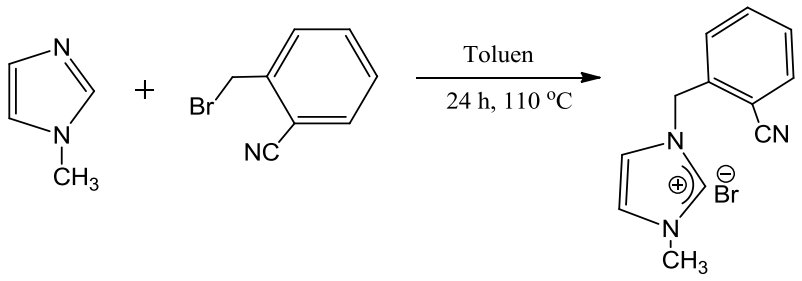


T_{1c}

Prepared according to procedure T_{1a} using 3-bromopropionitrile (0.99 g, 7.39 mmol).

Yield = 35%, 0.699 g. ^{1}H NMR (400 MHz, DMSO – d_6): δ 10.7 (s, 1 H, S-*CH*-N), 8.54 (dd, 2 H, *J* = 8 Hz, Ar-*H*), 7.89 (dt, *J* = 8 Hz, 2 H, Ar-*H*), 5.23 (t, *J* = 8 Hz, 2 H, N-CH_2), 3.37 (t, *J* = 4 Hz, 2 H, N-CH$_2$CH_2). ^{13}C NMR (100 Hz, DMSO – d_6): δ 166.7, 140.4, 131.9, 130.1, 128.9, 125.9, 118.0, 117.7, 47.8, 18.5. IR, νmax (cm^{-1}) (CH_2Cl_2): 3415, 2895, 2253, 1771, 1616, 1579, 1518, 1455, 1354, 1263, 1090, 1020, 925, 763, 635, 425. Anal. Calcd for $C_{10}H_9BrN_2S$ (M: 267,97): C, 44.62; H, 3.37; N, 10.41 %; Found: C, 44.63; H, 3.34; N, 10.44%.

2.1.4. Compound T_{2a}

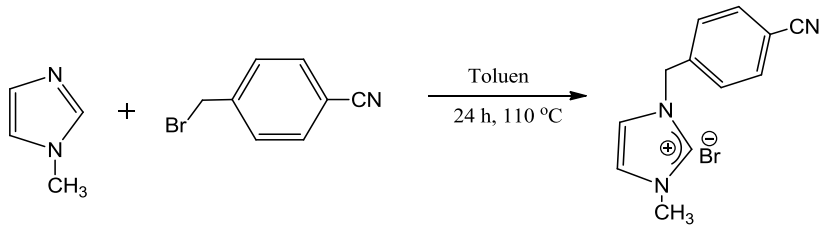


T_{2a}

Prepared according to procedure T_{1a} using 1-methylimidazole (1.00 g, 12.0 mmol) and 2-bromobenzonitrile (2.38 g, 12.0 mmol).

Yield = 89%, 3.02 g. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.2 (s, 1 H, NC*H*N), 7.92 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.71 (s, 1 H, Ar-*H*), 7.59 (m, 2 H, Ar-*H*), 7.51 (s, 1 H, NC*H*CHN), 7.43 (t, *J* = 7.6 Hz,1 H, NCHC*H*N), 5.80 (s, 2 H, N-C*H*$_2$) , 4.00 (s, 3 H, N-C*H*$_3$). ^{13}C NMR (100 Hz, $CDCl_3$): δ 137.4, 136.5, 134.3, 133.4, 131.1, 130.1, 124.3, 122.3, 117,0, 112.0, 50.8, 37.0. IR, νmax (cm^{-1}) (CH_2Cl_2): 3487, 3136, 3084, 3030, 2950, 2919, 2885, 2843, 2407, 2227, 2000, 1740, 1657, 1599, 1572, 1561, 1490, 1451, 1366, 1339, 1298, 1285, 1212, 1169, 1162, 1095, 1082, 962, 887, 866, 824, 775, 652, 622, 557, 477, 447, 404. Anal. Calcd for $C_{12}H_{13}BrN_3$ (M:278,03): C, 51.63; H, 4.69; N, 15.05 %; Found: C, 51.60; H, 4.70; N, 15.05%.

2.1.5. Compound T_{2b}

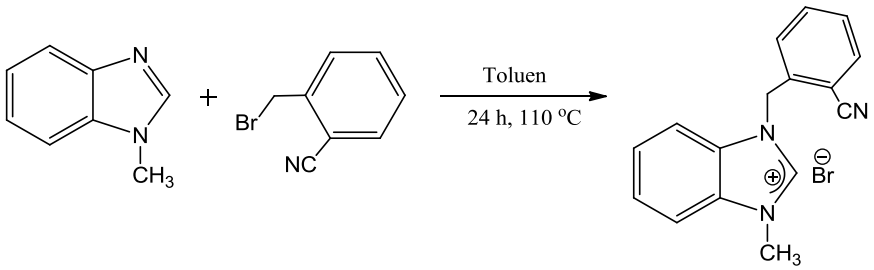


T_{2b}

Prepared according to procedure T_{1a} using 1-methylimidazole (1.00 g, 12.0 mmol) and 4-bromobenzonitrile (2.38 g, 12.0 mmol).

Yield = 62%, 2.10 g. ^{1}H NMR (400 MHz, DMSO–d_6): δ 9.33 (s, 1 H, NC*H*N), 7.89 (d, J = 8 Hz, 2 H, Ar-*H*), 7.83 (s, 1 H, NC*H*CHN), 7.76 (s, 1 H, NC*H*CHN), 7.60 (d, J = 8 Hz, 2 H, Ar-*H*), 5.57 (s, 2 H, N-CH_2) , 3.86 (s, 3 H, N-CH_3). ^{13}C NMR (100 Hz, DMSO – d_6): δ 140.6, 137.5, 133.3, 129.7, 124.5, 122.8, 118.9, 111.8, 54.4, 36.5. IR, νmax (cm^{-1}) (CH_2Cl_2): 3439, 3354, 3158, 3121, 3088, 3032, 2975, 2229, 1610, 1570, 1558, 1505, 1554, 1419, 1362, 1331, 1287, 1210, 1190, 1163, 1026, 977, 864, 843, 826, 765, 758, 694, 652, 621, 552, 423. Anal. Calcd for $C_{12}H_{13}BrN_3$ (M:278,03): C, 51.63; H, 4.69; N, 15.05 %; Found: C, 51.62; H, 4.72; N, 15.03%.

2.1.6. Compound T_{3a}



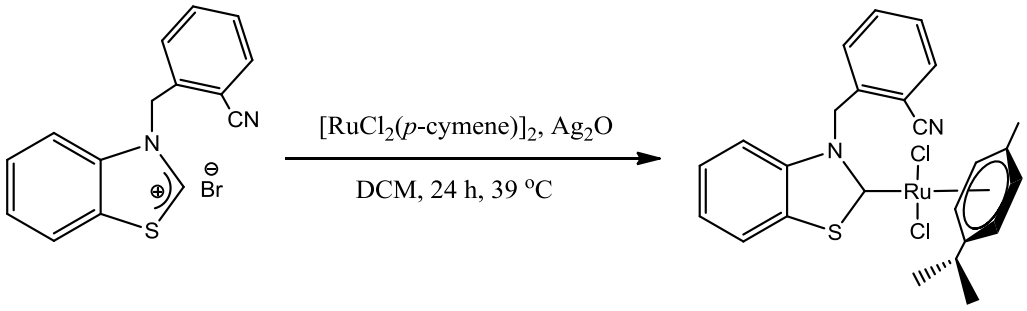
T_{3a}

Prepared according to procedure T_{1a} using 1-methylbenzimidazole (1.00 g, 7.56 mmol) and 2-bromobenzonitrile (1.48 g, 7.56 mmol).

Yield = 78%, 1.92 g. ^{1}H NMR (400 MHz, DMSO–d_6): δ 9.84 (s, 1 H, NC*H*N), 8.08 (d, J = 8 Hz, 1 H, Ar-*H*), 7.98 (d, J = 8 Hz, 1 H, Ar-*H*), 7.88 (d, J = 8 Hz, 1 H, Ar-*H*), 7.66 (m, 4 H, Ar-*H*), 7.45 (d, J = 8 Hz, 1 H, Ar-*H*), 6.03 (s, 2 H, N-CH_2), 4.13 (s, 3 H, N-CH_3).^{13}C NMR (100 Hz, DMSO–d_6): δ 144.0, 137.5, 134.4, 134.2, 131.2, 129.9, 129.4, 127.4, 127.2, 117.4, 114.4, 113.3, 111.3, 48.6, 33.9. IR, νmax (cm^{-1}) (CH_2Cl_2): 3422, 3006, 2223, 1615, 1570, 1483, 1443, 1366, 1215, 1128, 1089, 747, 609. Anal. Calcd for $C_{16}H_{14}BrN_3$ (M:327,04): C, 58.55; H, 4.30; N, 12.80 %; Found: C, 58.56; H, 4.26; N, 12.83 %.

2.2. General Synthesis of Complexes

2.2.1 Complex Ru_{1a}

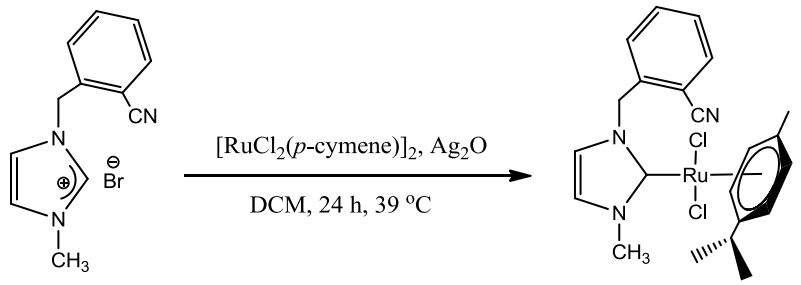


T_{1a} Ru_{1a}

In balloon, T_{1a} (1.00 g, 3.03 mmol) under argon gas was dissolved in 5 mL dry DCM. $[RuCl_2(p\text{-cymene})_2]_2$ (0.93 g, 1.52 mmol) and Ag_2O (1.40g, 6.06 mmol) was added over and the riflaks overnight protected from light. The solid residue remained was washed with diethyl ether. Then dried under vacuum.

Yield = 36%, 0.62 g. m.p =243.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8 Hz, 1 H, Ar-*H*), 7.38 (m, 2H, Ar-*H*), 7.33 (d, J = 8 Hz, 1 H, Ar-*H*) 7.29 (d, J = 8 Hz, 1 H, Ar-*H*), 7.13 (d, J = 8 Hz, 1 H, Ar-*H*), 6.98 (t, J = 4 Hz, 1 H, Ar-*H*), 6.51 (s, 2 H, N-CH_2), 5.47 (d, J = 4 Hz, 2 H, *p*-cymene-Ar-*H*), 5.30 (d, J = 8 Hz, 2 H, *p*-cymene-Ar-*H*) 2.87 (m, 1 H, *p*-cymene-C*H*), 2.17 (s, 3 H, *p*-cymene-CH_3), 1.26 (d, J = 8 Hz, 6 H, *p*-cymene-(CH_3)$_2$). ^{13}C NMR (100 Hz, $CDCl_3$): δ 229.2, 143.8, 139.3, 136.4, 133.4, 132.9, 128.3, 126.4, 125.0, 121.6, 117.1, 114.2, 110.1, 107.5, 100.8, 87.0, 65.8, 55.8, 30.7, 22.3, 18.3, 15.2. IR, vmax (cm^{-1}) (CH_2Cl_2): 3789, 3682, 3662, 3638, 3517, 3040, 2962, 2221, 1598, 1456, 1379, 1316, 1206, 1113, 1054, 903, 780, 752, 551. Anal. Calcd for $C_{26}H_{28}Cl_2N_2RuS$ (M:572,04): C, 54.54; H, 4.93; N, 4.89 %; Found: C, 54.56; H, 4.91; N, 4.89 %.

2.2.2. Complex Ru_{2a}

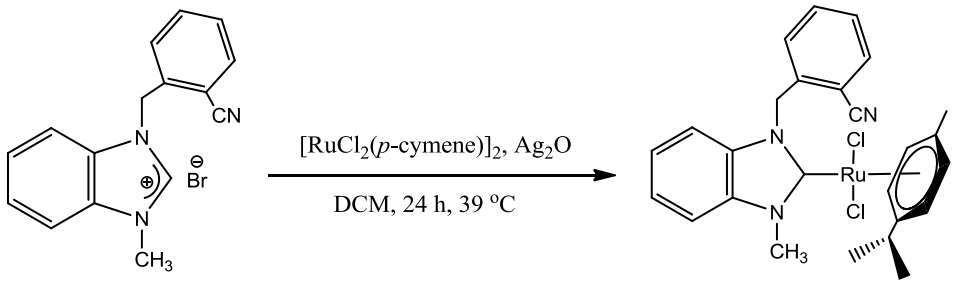


T_{2a} Ru_{2a}

In balloon, T_{1a} (1.00 g, 3.60 mmol) and Ag_2O (1.67 g, 7.19 mmol) under argon gas was suspend in DCM (5 mL) and stirred at 39 °C for 5 h protected from light. Then, $[RuCl_2(p\text{-cymene})_2]_2$ (1.10 g, 1.80 mmol) was added over and the riflaks 6 h. The solid residue remained was washed with diethyl ether. Then dried under vacuum.

Yield = 60%, 1.13 g. m.p = 230.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (t, *J* = 8 Hz, 2 H, Ar-*H*), 7.52 (t, *J* = 4 Hz, 1 H, Ar-*H*), 7.39 (t, *J* = 8 Hz, 1 H, Ar-*H*), 6.98 (d, *J* = 8 Hz, 1 H, N-C*H*CH-N), 6.67 (d, *J* = 4 Hz, 1 H, N-CHC*H*-N), 5.47 (d, *J* = 4 Hz, 2 H, *p*-cymene-Ar-*H*), 5.21 (d, *J* = 4, 2 H, *p*-cymene-Ar-*H*), 4.04 (s, 3 H, N-C*H*$_3$), 2.95 (m, 1 H, *p*-cymene-C*H*), 2.10 (s, 3 H, *p*-cymene-C*H*$_3$), 1.28 (d, *J* = 4 Hz, 6 H, *p*-cymene-(C*H*$_3$)$_2$). ^{13}C NMR (100.6 Hz, $CDCl_3$): δ 177.7, 133.5, 132.3, 131.0, 128.6, 124.4, 121.9, 109.0, 99.0, 52.5, 39.8, 30.9, 18.7. IR, vmax (cm^{-1}) (CH_2Cl_2): 3414, 3090, 2959, 2222, 1617, 1549, 1450, 1384, 1232, 1084, 865, 769, 689, 618, 468. Anal. Calcd for $C_{23}H_{31}Cl_2N_3Ru$ (M:521,09): C, 52.97; H, 5.99; N, 8.06 %; Found: C, 52.95; H, 5.94; N, 8.09 %.

2.2.3. Complex Ru_{3a}

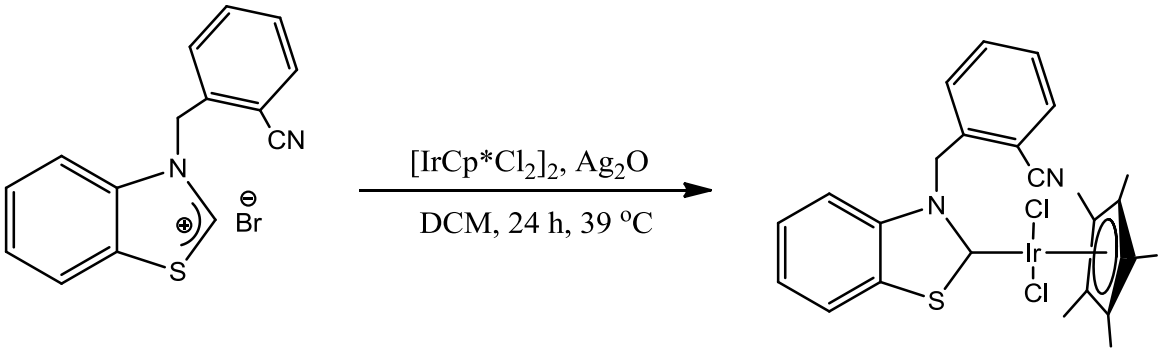


T_{3a} Ru_{3a}

Prepared according to procedure Ru_{1a} using T_{3a} (1.00 g, 3.05 mmol), Ag_2O (1.42g, 6.09 mmol) and $[RuCl_2(p\text{-cymene})_2]_2$ (0.932 g, 1.52 mmol).

Yield = 56%, 0.97 g. m.p = 248.4 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8 Hz, 1 H, Ar-*H*), 7.35 (m, 5 H, Ar-*H*), 7.13 (m, 2 H, Ar-*H*), 6.79 (d, J = 8 Hz, 2 H, N-CH_2), 5.54 (d, J = 4 Hz, 2 H, *p*-cymene-Ar-*H*), 5.23 (d, J = 8, 2 H, *p*-cymene-Ar-*H*), 4.29 (s, 3 H, N-CH_3), 2.99 (m, 1 H, *p*-cymene-C*H*), 2.09 (s, 3 H, *p*-cymene-CH_3), 1.26 (d, J = 4 Hz, 6 H, *p*-cymene-$(CH_3)_2$). ^{13}C NMR (100.6 Hz, $CDCl_3$): δ 191.5, 140.5, 136.2, 134.5, 133.2, 132.3, 129.4, 127.9, 123.4, 117.6, 110.8, 110.2, 99.2, 86.5, 83.6, 51.7, 36.8, 30.9, 29.7, 22.5, 18.8. IR, vmax (cm^{-1}) (CH_2Cl_2): 3446, 3379, 3039, 2958, 2221, 1887, 1600, 1461, 1378, 1350, 1265, 1193, 1127, 1089, 1030, 973, 925, 842, 752, 564, 558, 442. Anal. Calcd for $C_{27}H_{31}Cl_2N_3Ru$ (M:569,09): C, 56.94; H, 5.49; N, 7.38 %; Found: C, 56.95; H, 5.44; N, 7.39 %.

2.2.4.Complex Ir_{1a}

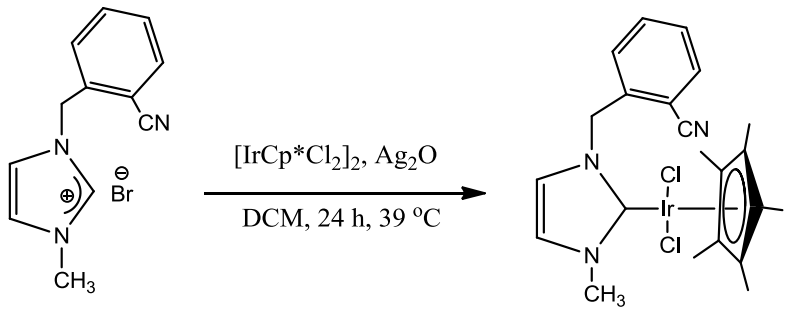


T_{1a} Ir_{1a}

Prepared according to procedure Ru_{1a} using T_{1a} (1.00 g, 3.03 mmol), Ag_2O (1.40g, 6.06 mmol) and $[IrCp^*Cl_2]_2$ (1.21 g, 1.52 mmol).

Yield = 62%, 1.25 g. m.p = 290.3 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.70 (d, *J* = 2.8 Hz, 1 H, Ar-*H*), 7.34 (m, 2 H, Ar-*H*), 7.29 (m, 2 H, Ar-*H*), 7.14 (m, 2 H, Ar-*H*), 1.69 (s, 15 H, $C_5(CH_3)_5$).^{13}C NMR (100 Hz, $CDCl_3$): δ 203.3, 143.6, 139.1, 136.6, 133.4, 132.3, 128.8, 128.3, 126.6, 125.3, 121.9, 117.3, 114.5, 109.9, 91.1, 55.3, 8.6. IR, νmax (cm^{-1}) (CH_2Cl_2): 3418, 3060, 2965, 2910, 2221, 1599, 1510, 1483, 1454, 1379, 1357, 1314, 1284, 1270, 1207, 1141, 1116, 1053, 1029, 982, 913, 793, 762, 718, 674, 604, 552, 450, 432. Anal. Calcd for $C_{26}H_{29}Cl_2N_2SIr_2$ (M:664,11): C, 46.98; H, 4.40; N, 4.21 %; Found: C, 46.95; H, 4.40; N, 4.21 %.

2.2.5. Complex Ir_{2a}

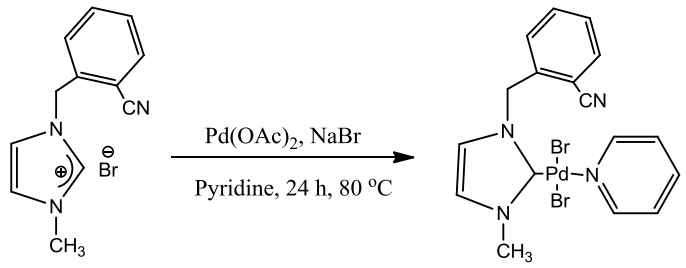


T_{2a} Ir_{2a}

Prepared according to procedure Ru_{2a} using T_{2a} (1.00 g, 3.60 mmol), Ag_2O (1.67g, 7.19 mmol) and $[IrCp^*Cl_2]_2$ (1.43 g, 1.80 mmol).

Yield = 68%, 1.49 g. m.p = 281.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.66 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.55 (t, *J* = 8 Hz, 1 H, Ar-*H*), 7.39 (t, *J* = 8 Hz, 1 H, Ar-*H*), 6.94 (d, *J* = 4 Hz, 1 H, N-C*H*CH-N), 6.66 (d, *J* = 4 Hz, 1 H, N-CHC*H*-N), 4.03 (s, 3 H, N-CH_3), 1.67 (s, 15 H, $C_5(CH_3)_5$).^{13}C NMR (100 Hz, $CDCl_3$): δ 157.9, 140.4, 133.6, 132.1, 130.9, 128.5, 123.9, 121.5, 117.6, 111.7, 90.6, 89.1, 51.8, 9.3. IR, νmax (cm^{-1}) (CH_2Cl_2): 3414, 2955, 2912, 2219, 1656, 1603, 1403, 1379, 1301, 1241, 1191, 1116, 1077, 1030, 824, 763, 729, 692, 617, 415. Anal. Calcd for $C_{23}H_{30}Cl_2N_3Ir_2$ (M:611,14): C, 45.17; H, 4.94; N, 6.87 %; Found: C, 45.15; H, 4.94; N, 6.89 %.

2.2.6. Complex Pd_{2a}

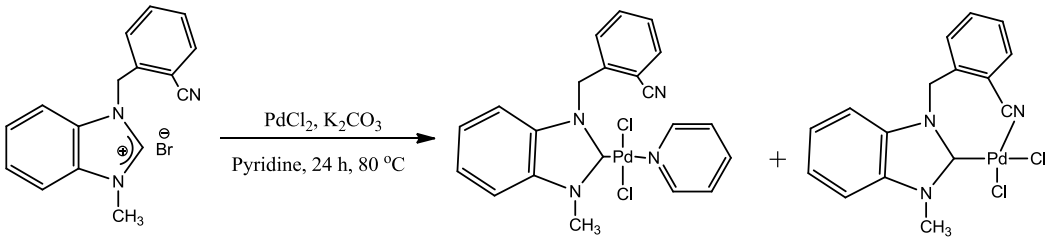


T_{2a} Pd_{2a}

In balloon, T_{2a} (1.00 g, 3.60 mmol) under argon gas was pyridine (5 mL) dissolved. Then, $Pd(OAc)_2$ (0.81 g, 3.60 mmol) and NaBr (0.73 g, 7.19 mmol) was added over and the riflaks overnight. The solid residue remained was washed with diethyl ether. Then dried under vacuum.

Yield = 70%, 1.36 g. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (d, J = 4 Hz, 2 H, Py-*H*), 8.89 (d, J = 4 Hz, 1 H, Ar-*H*), 7.95 (d, J = 8 Hz, 1 H, Ar-*H*), 7.74 (m, 2 H, Py-*H*) 7.60 (t, J = 4 Hz, 1 H, Py-*H*), 7.44 (t, J = 8 Hz, 1 H, Ar-*H*), 7.33 (m, 1 H, Ar-*H*), 6.97 (d, J = 4 Hz, 1 H, N-C*H*CH-N), 6.95 (d, J = 4 Hz, 1 H, N-CHC*H*-N), 5.98 (s, 2 H, N-CH_2), 4.14 (s, 3 H, N-CH_3). ^{13}C NMR (100 Hz, $CDCl_3$): δ 199.1, 154.3, 152.5, 150.1, 139.0, 138.4, 137.9, 133.3, 128.9, 124.7, 123.9, 122.2, 112.2, 52.4, 38.7. IR, νmax (cm^{-1}) (CH_2Cl_2): 3441, 3283, 3173, 3095, 3063, 3030, 3003, 2990, 2860, 2837, 2823, 2325, 1962, 1704, 1640, 1606, 1597, 1570, 1498, 1477, 1450, 1413, 1338, 1269, 1238, 1224, 1209, 1189, 1161, 1082, 1050, 1024, 969, 926, 801, 794, 766, 713, 697, 656, 544, 525, 472, 461. Anal. Calcd for $C_{17}H_{17}Br_2N_4Pd$ (M: 540,89): C, 37.56; H, 3.15; N, 10.31 %; Found: C, 37.56; H, 3.12; N, 10.33 %.

2.2.7. Complex Pd_{3a}



T_{3a} Pd_{3a} Pd_{3a}'

In balloon, T_{3a} (1.00 g, 3.05 mmol) under argon gas was pyridine (5 mL) dissolved. Then, $PdCl_2$ (0.54 g, 3.05 mmol) and K_2CO_3 (2.11 g, 15.24 mmol) was added over and the riflaks overnight. The solid residue remained was washed with diethyl ether. Then dried under vacuum.

Pd_{3a} : Yield = 56%, 0.85 g. m.p = 293.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, *J* = 4 Hz, 2 H, Py-*H*), 7.79 (m, 1 H, Py-*H*), 7.72 (d, *J* = 8 Hz, 2 H, Py-*H*), 7.38 (m, 2 H, Ar-*H*) 7.21 (m, 1 H, Ar-*H*), 7.10 (m, 2 H, Ar-*H*), 6.36 (s, 2 H, N-C*H*$_2$), 4.40 (s, 3 H, N-C*H*$_3$). ^{13}C NMR (100 Hz, $CDCl_3$): δ 164.8, 152.6, 151.9, 138.5, 138.1, 135.4, 133.9, 133.4, 132.9, 129.5, 128.7, 124.6, 123.6, 117.3, 111.4, 110.7, 110.3, 50.4, 35.5. IR, νmax (cm^{-1}) (CH_2Cl_2): 3527, 3444, 3379, 3059, 2926, 2222, 1691, 1601, 1541, 1499, 1447, 1401, 1341, 1295, 1254, 1210, 1191, 1154, 1128, 1100, 1068, 1013, 920, 796, 761, 744, 692, 658, 442. Anal. Calcd for $C_{21}H_{19}Br_2N_4Pd$ (M: 503,00): C, 49.97; H, 3.79; N, 11.10 %; Found: C, 49.96; H, 3.82; N, 11.13 %.

Pd_{3a}' : Yield = 32%, 0.41 g. m.p = 298.9 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8 Hz, 1 H, Ar-*H*), 7.48 (t, *J* = 4 Hz, 1 H, Ar-*H*), 7.37 (t, *J* = 8 Hz, 2 H, Ar-*H*), 7.10 (m, 3 H, Ar-*H*) 7.93 (d, *J* = 4 Hz, 1 H, Ar-*H*), 5.31 (s, 2 H, N-C*H*$_2$), 3.49 (s, 3 H, N-C*H*$_3$). ^{13}C NMR (100 Hz, $CDCl_3$): δ 154.5, 140.1, 132.9, 130.1, 128.2, 124.9, 121.6, 117.3, 111.3, 107.7, 42.7, 27.4. IR, νmax (cm^{-1}) (CH_2Cl_2): 3381, 3059, 2926, 2223, 1692, 1603, 1539, 1499, 1446, 1403, 1343, 1295, 1258, 1190, 1153, 1126, 1098, 1070, 1011, 919, 803, 760, 744, 691, 668, 558, 439. Anal. Calcd for $C_{16}H_{14}Br_2N_3Pd$ (M: 423,96): C, 45.15; H, 3.32; N, 9.87 %; Found: C, 45.16; H, 3.28; N, 9.89 %.

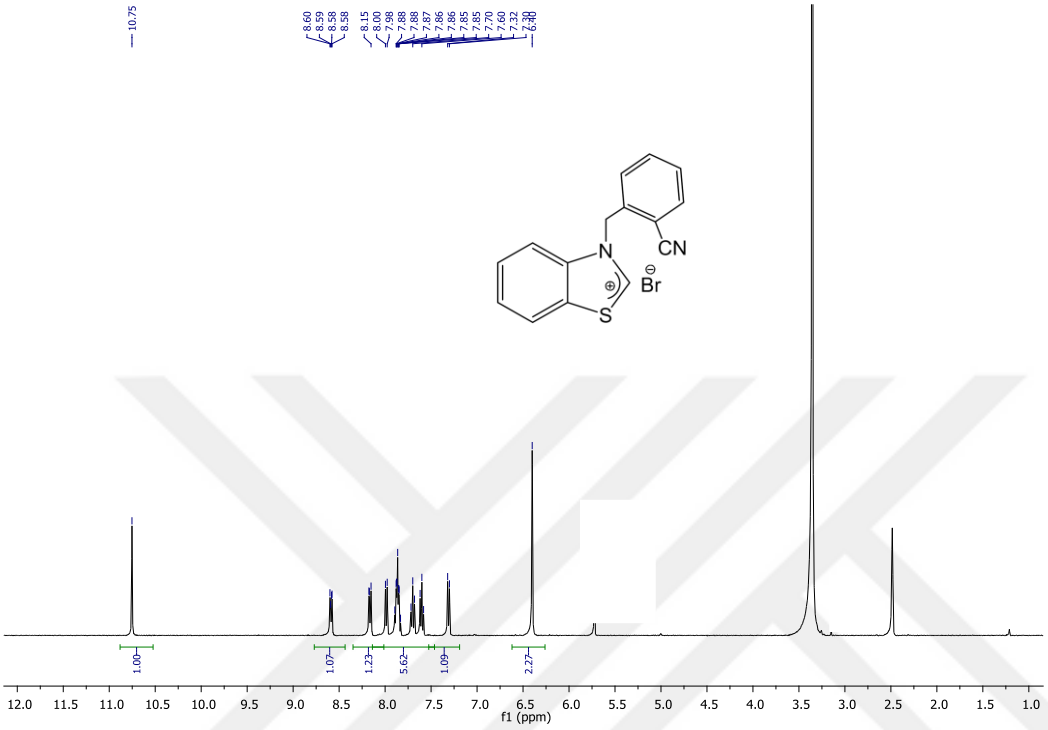
3. RESULTS AND DISCUSSION

A series of azolium salts (imidazolium, benzimidazolium and benzothiazolium) with benzlylic and aliphatic group bearing nitrile substituted and their NHC metal complexes were synthesized. The difficulty of carbene formation and subsequent coordination to the Ru(II) or Ir(I) center can be attributed to competing processes such as (i) nonselective coordination of the hard nitrogen of nitrile group, (ii) competing deprotonation of C_4/C_5 on imidazol or benzylic protons. So, the alternative and milder Ag-carbene transfer method was investigated. Two equivelent of azolium salts were treated with Ag_2O in CH_2Cl_2, and the resulting Ag-carbene species were added into CH_2Cl_2 solution of $[RuCl_2(p\text{-cymene})]_2$ or $[IrCl_2Cp^*]_2$. The Pd complex (**Pd_{2a}**) was synthesized with azolium salt (**T_{2a}**), NaBr and $Pd(OAc)_2$ in neat pyridine. The other Pd complexes (**Pd_{3a}, $Pd_{3a'}$**) were synthesized azolium salt (**T_{3a}**), K_2CO_3 and $PdCl_2$ in neat pyridine. The synthesized complexes are red or yellow colored, stable to air and moisture. The solubility of the complexes in polar and apolar solvents are soluble.

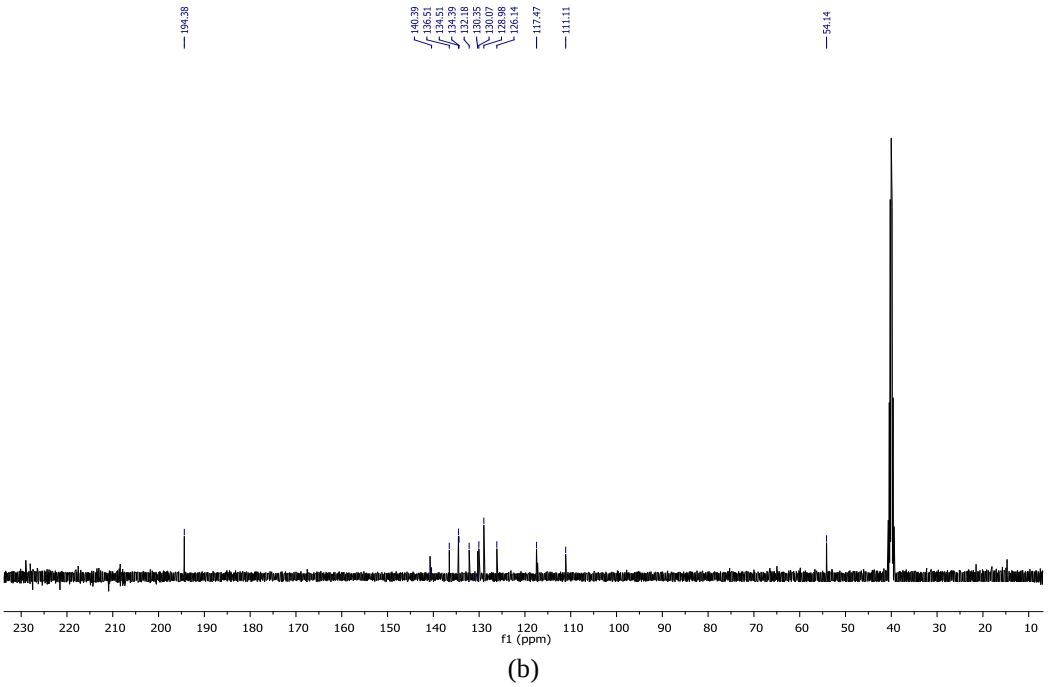
The characteristic C_2-H protons of salt are 10.75 ppm (**T_{1a}**), 10.90 ppm (**T_{1b}**), 10.71 ppm (**T_{1c}**), 10.22 ppm (**T_{2a}**), 9.33 ppm (**T_{2b}**) and 9.84 ppm (**T_{3a}**) respectively. The related C_2-C carbons in the salts are 194.4, 166.6, 166.7, 137.4, 140.6 and 144.0 ppm, respectively. In the ^{1}H-NMR of the complexes, the CH_2 protons of the benzylic group attached to the nitrogen atom were observed at 5.06-5.09 ppm in the **Ir_{2a}** complex as 2 dublets while a single singlet was observed in the **Pd_{2a}** complex at 5.98 ppm. Interestingly, these peaks do not appear in the spectrum in the **Ru_{2a}** complex. In the **Ru_{1a}** complex, these protons are observed as siglet in 6.51 ppm whereas in **Ir_{2a}** complex these peaks do not appear again. Nitrogen-bounded methyl peaks for metal complexes of **T_{2a}** in ^{1}H-NMR are seen in 4.05, 4.03 and 4.14 ppm for **Ru_{2a}**, **Ir_{2a}** and **Pd_{2a}**, respectively. The chemical shifts of these peaks in ligands and complexes supports the complex formation.

3.1. Characterization

3.1.1. Characterization of the Ligands

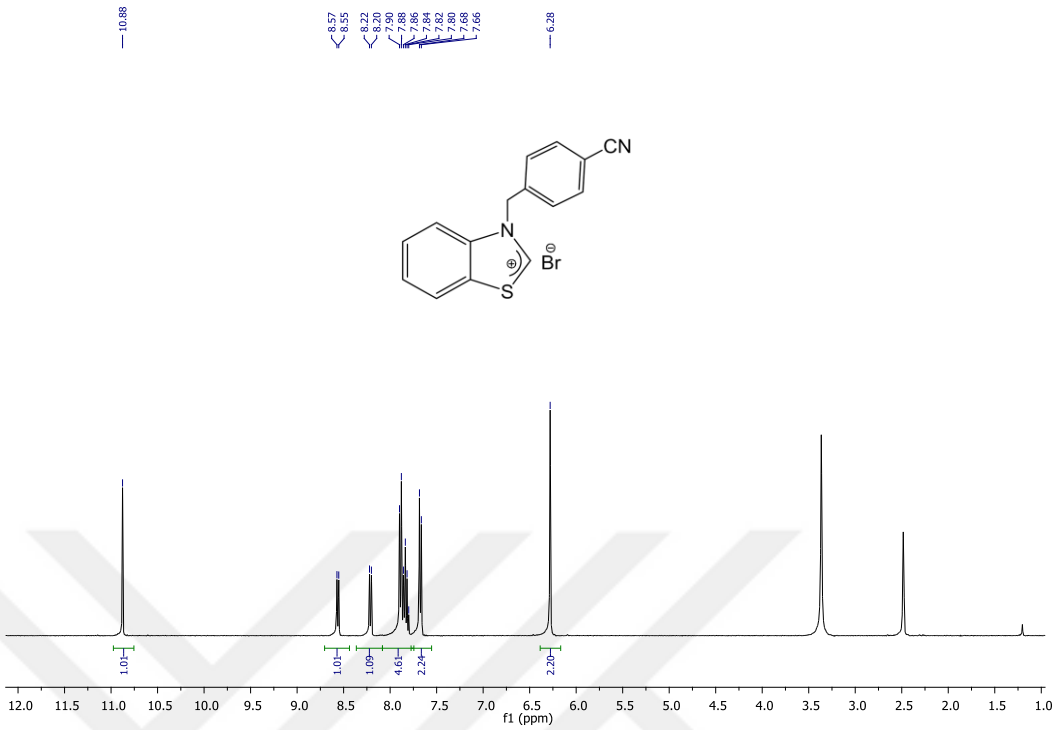


(a)

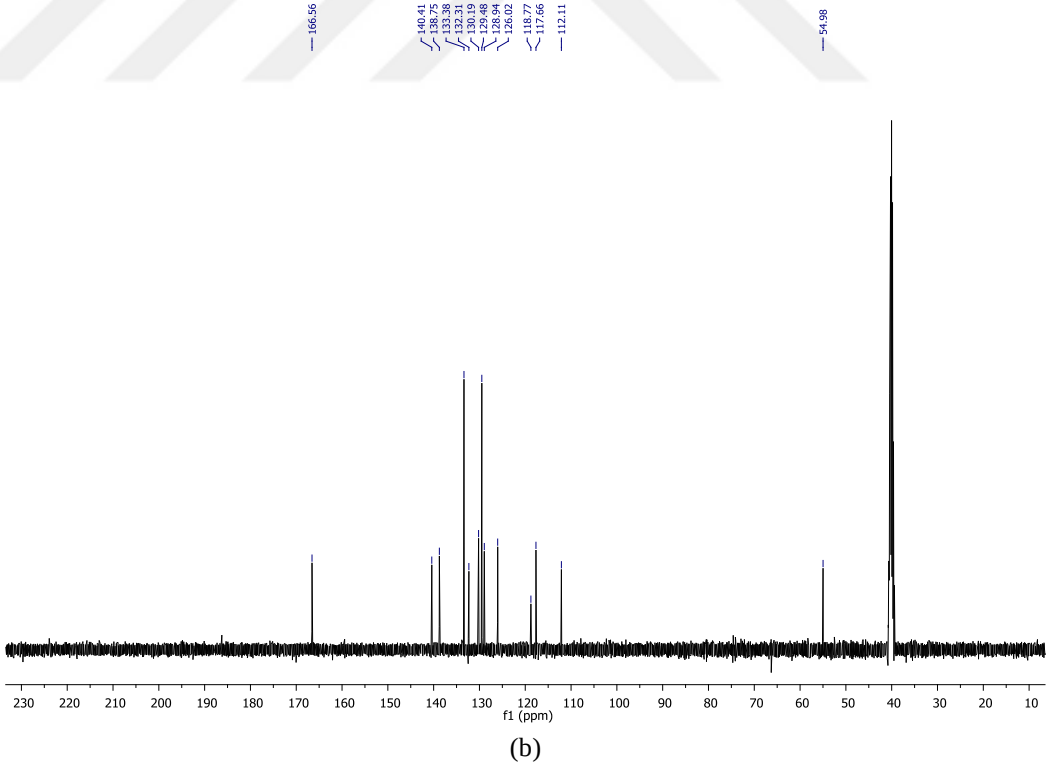


(b)

Figure 3.1 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of $\mathbf{T_{1a}}$.



(a)



(b)

Figure 3.2 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of $\mathbf{T_{1b}}$.

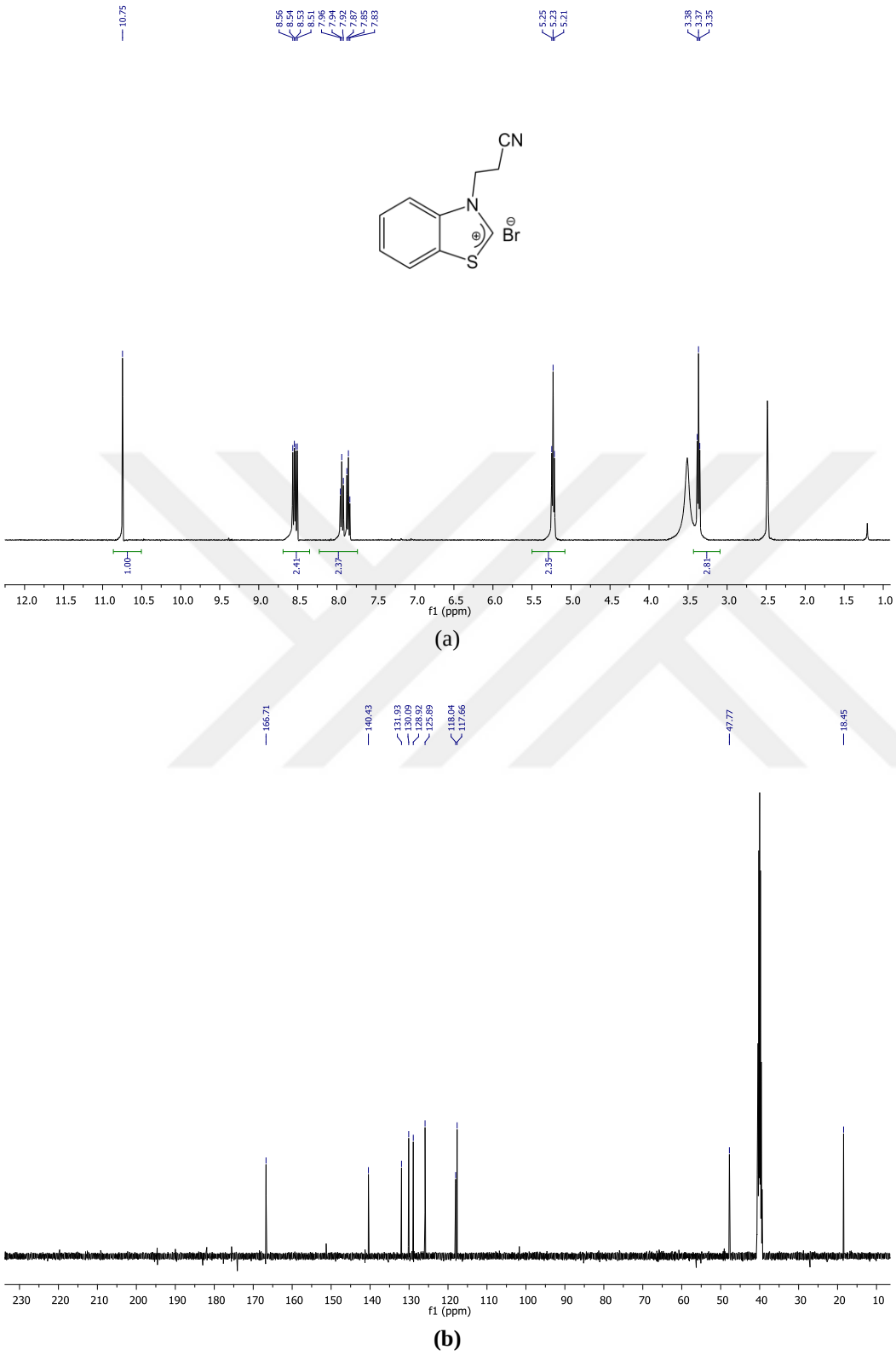
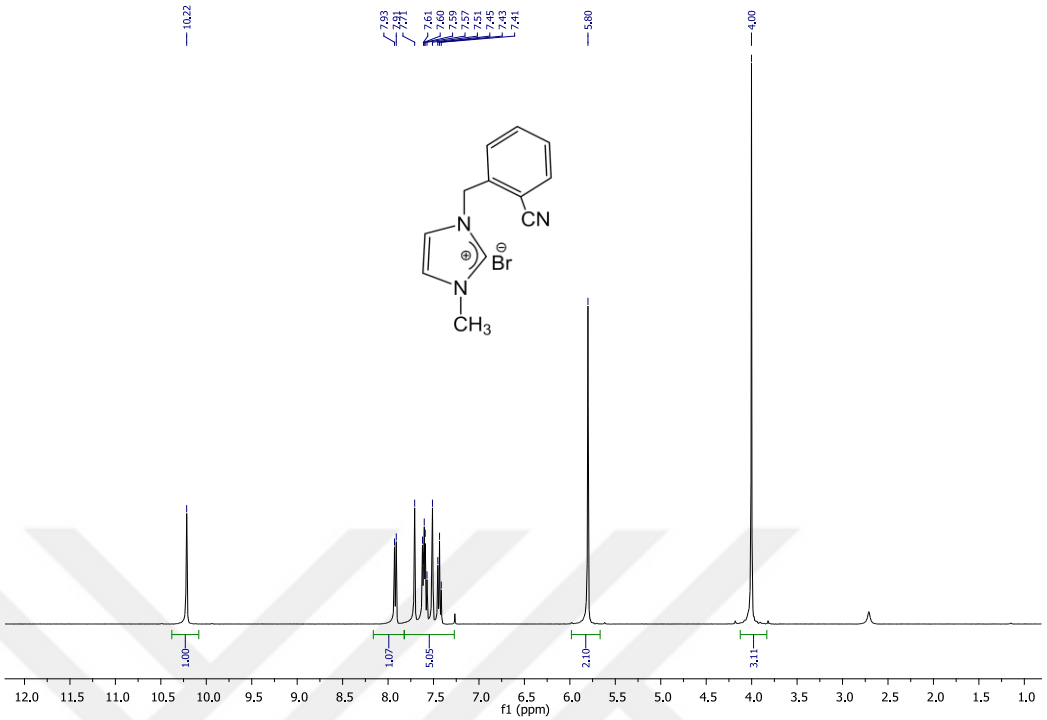
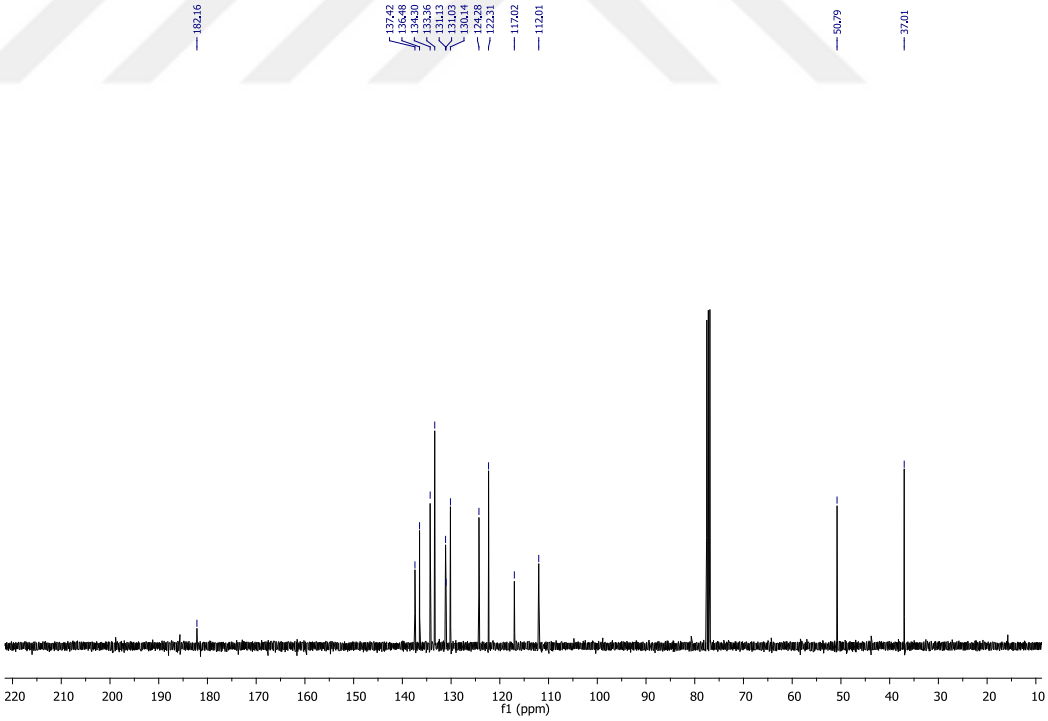


Figure 3.3 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of $\mathbf{T_{1c}}$.

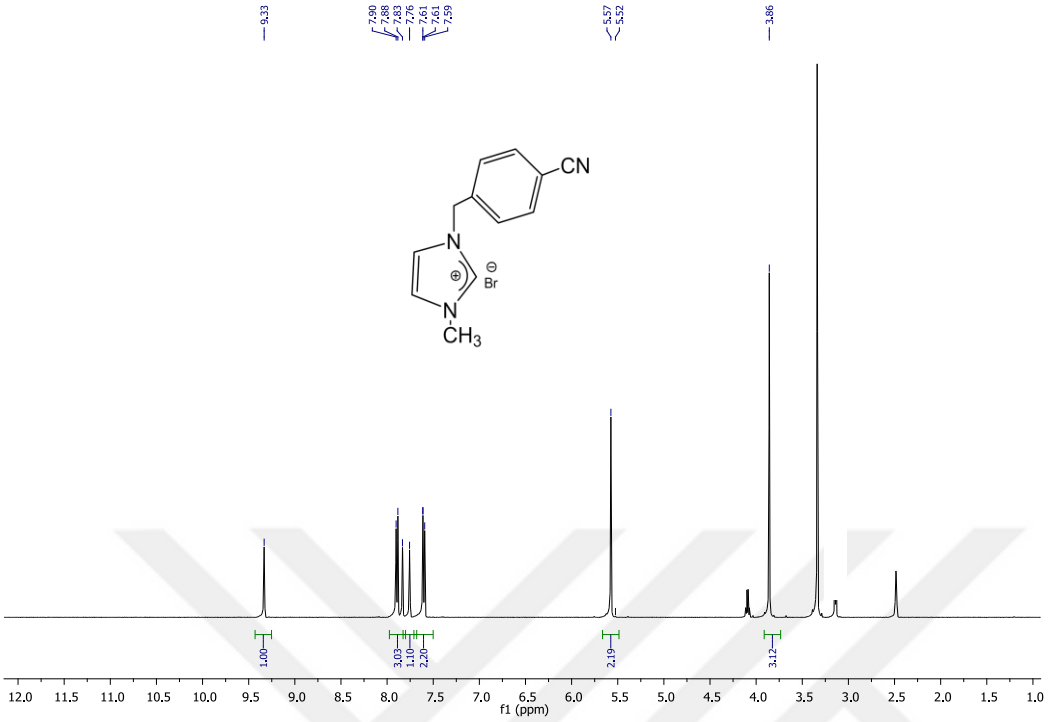


(a)

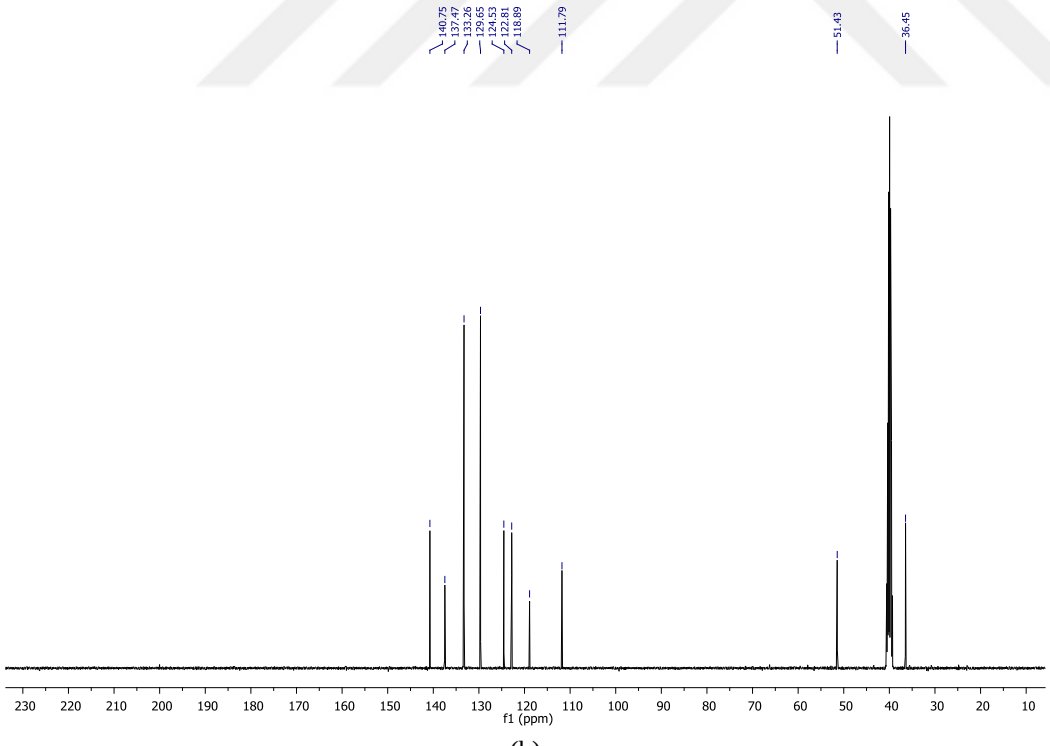


(b)

Figure 3.4 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of $\mathbf{T_{2a}}$.

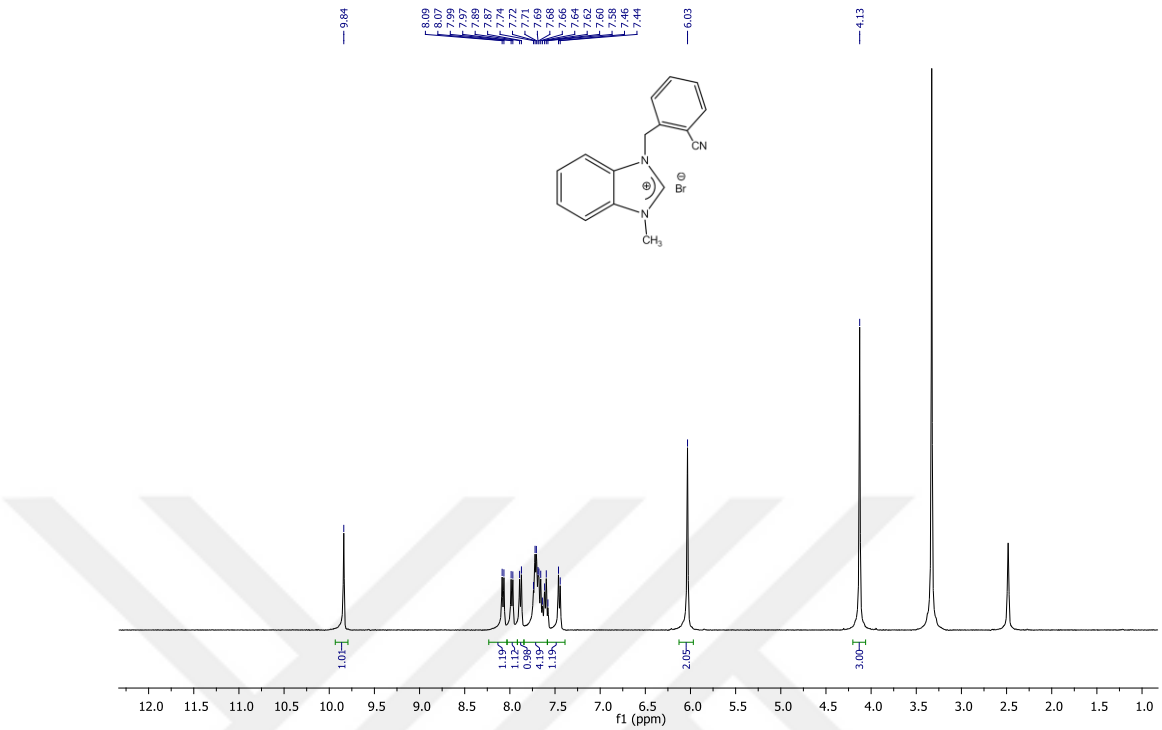


(a)

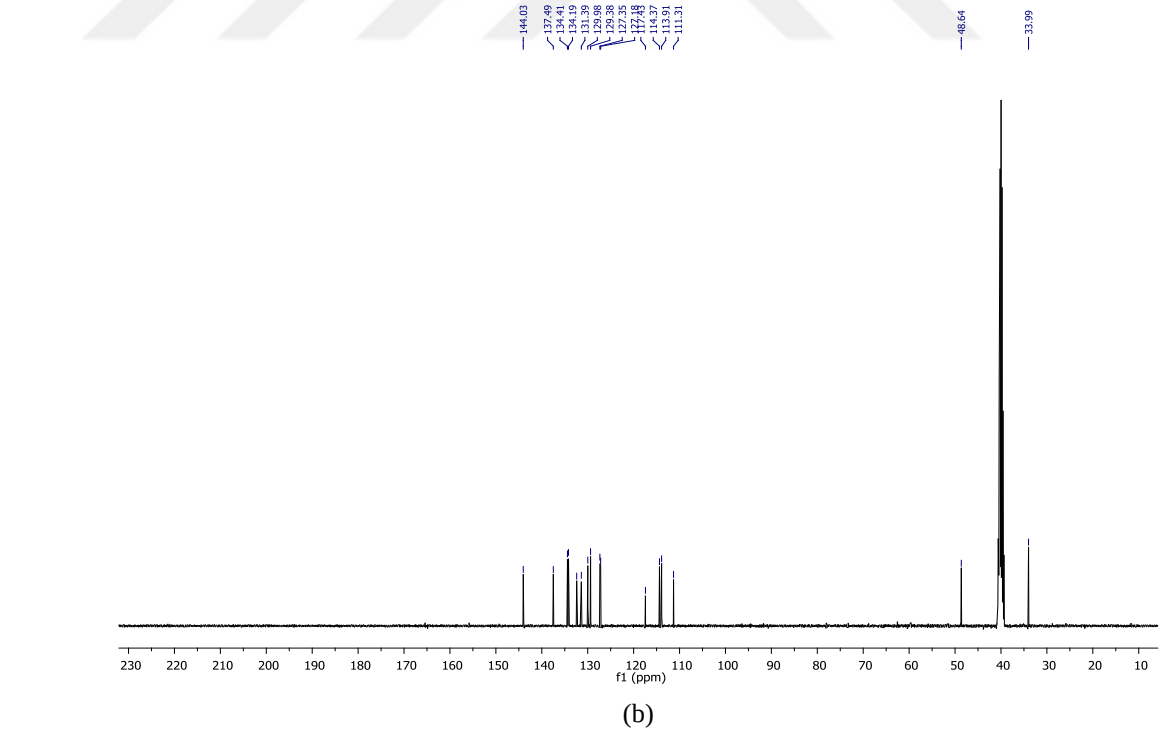


(b)

Figure 3.5 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **T_{2b}.**



(a)



(b)

Figure 3.6 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of $\mathbf{T_{3a}}$.

3.1.2. Characterization of the Complexes

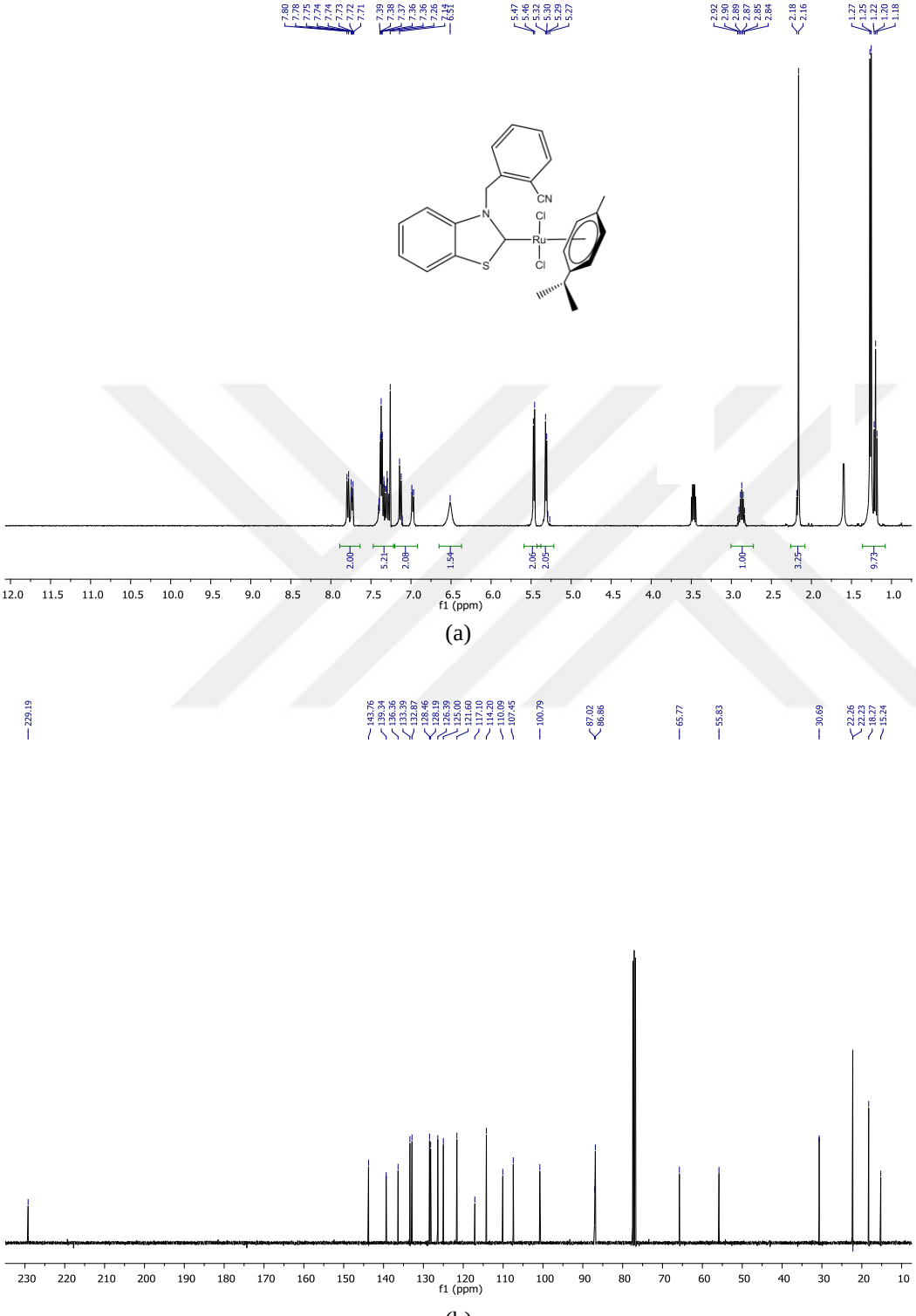


Figure 3.7 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Ru_{1a}**.

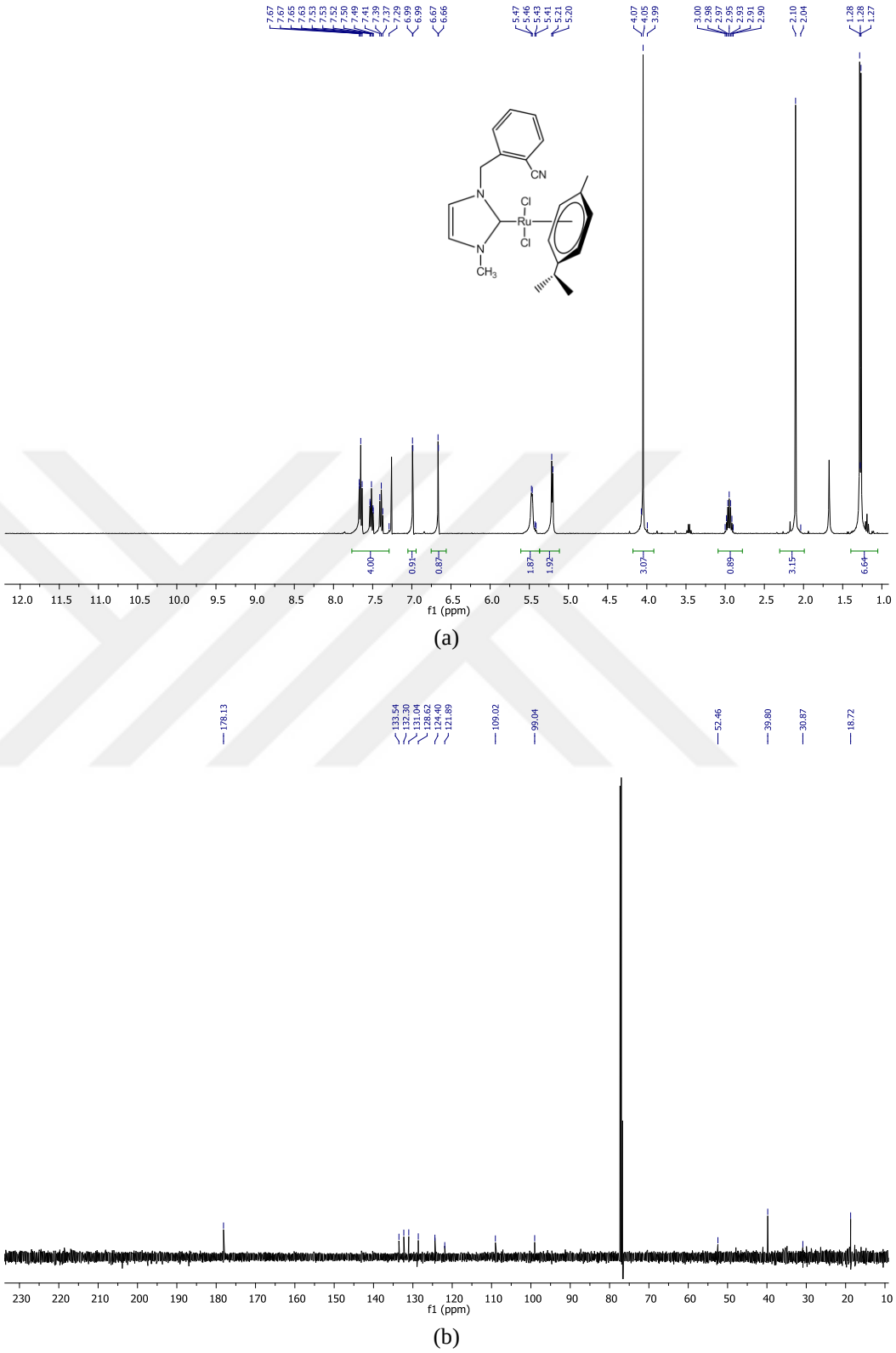
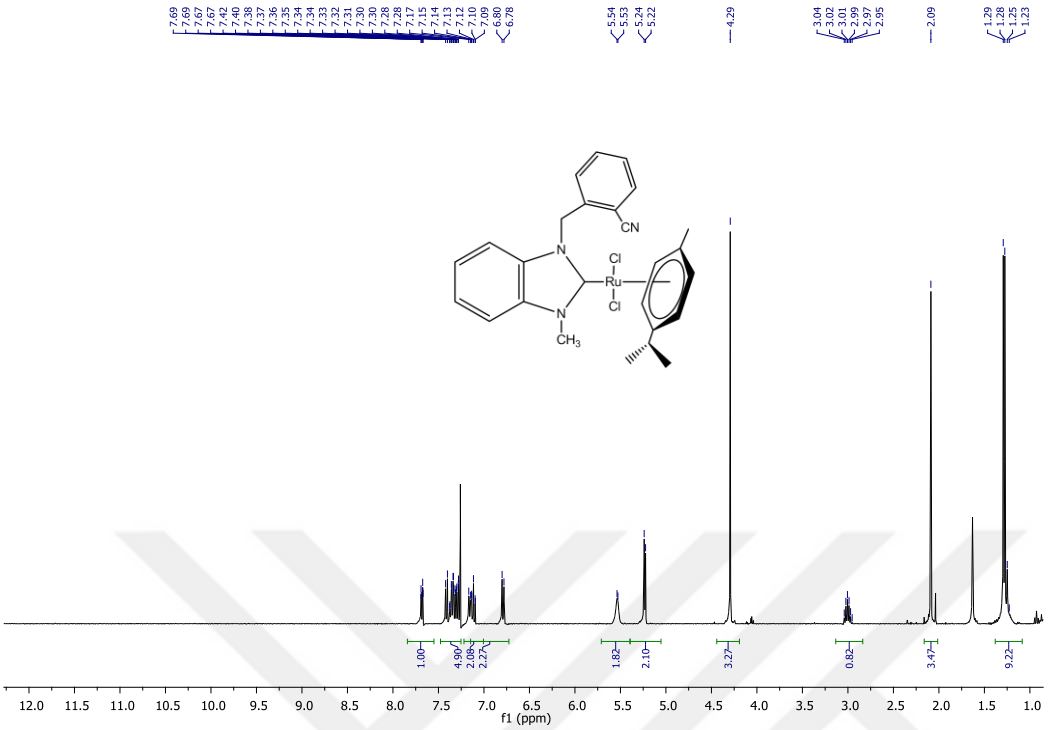
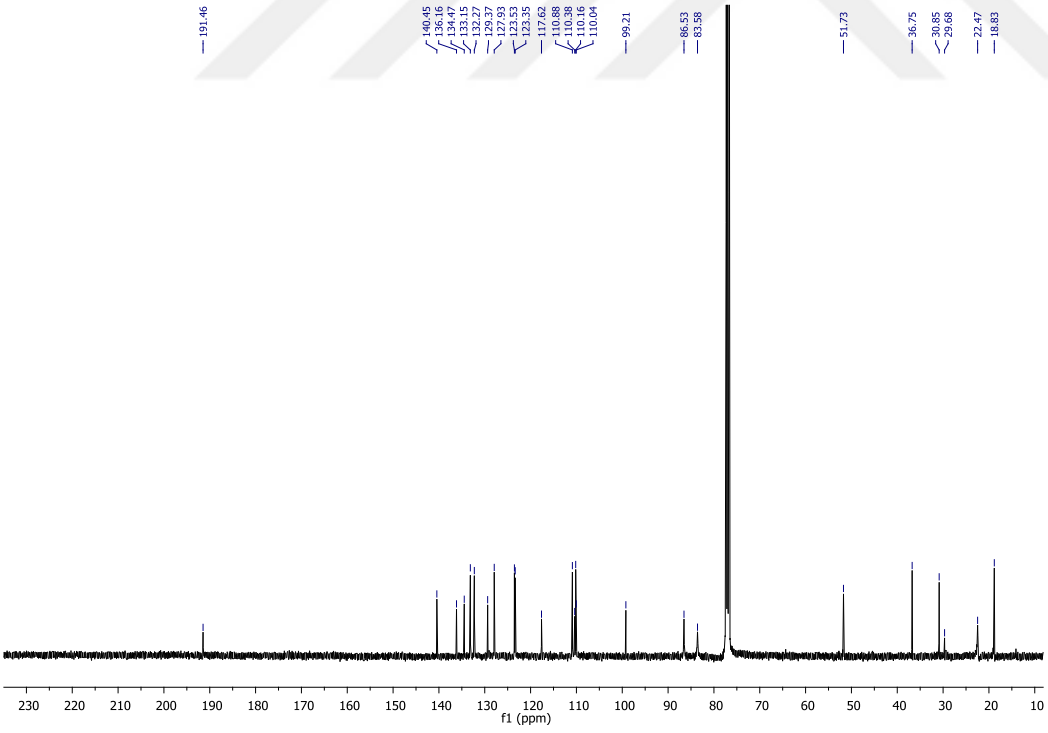


Figure 3.8 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Ru_{2a}**.

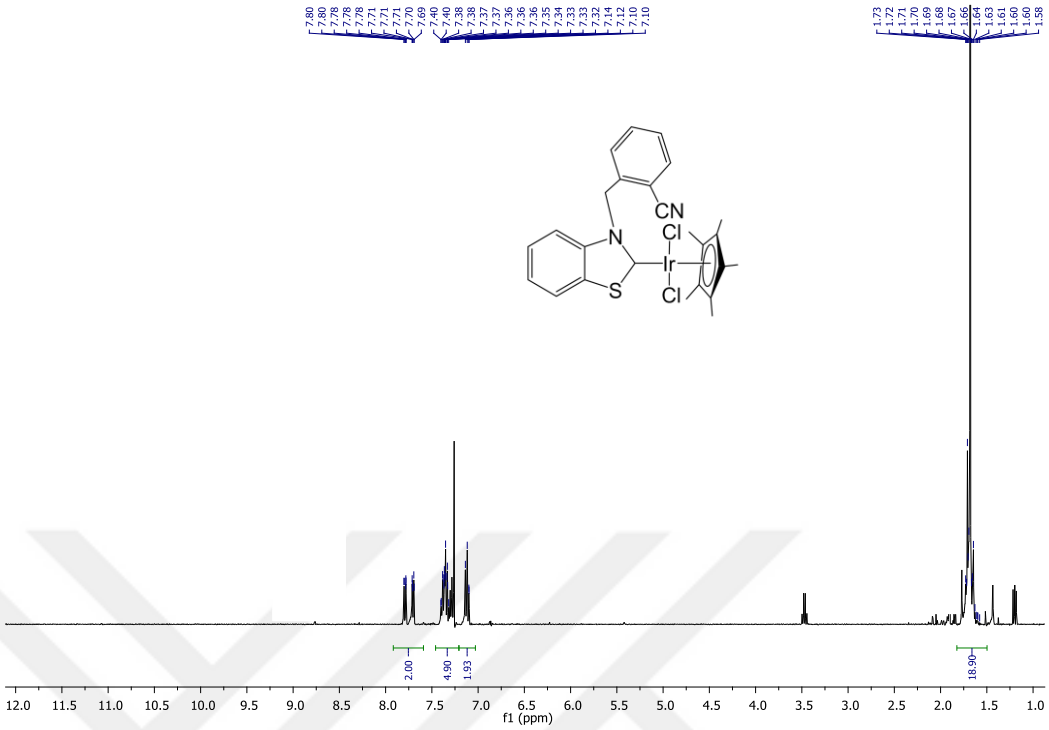


(a)

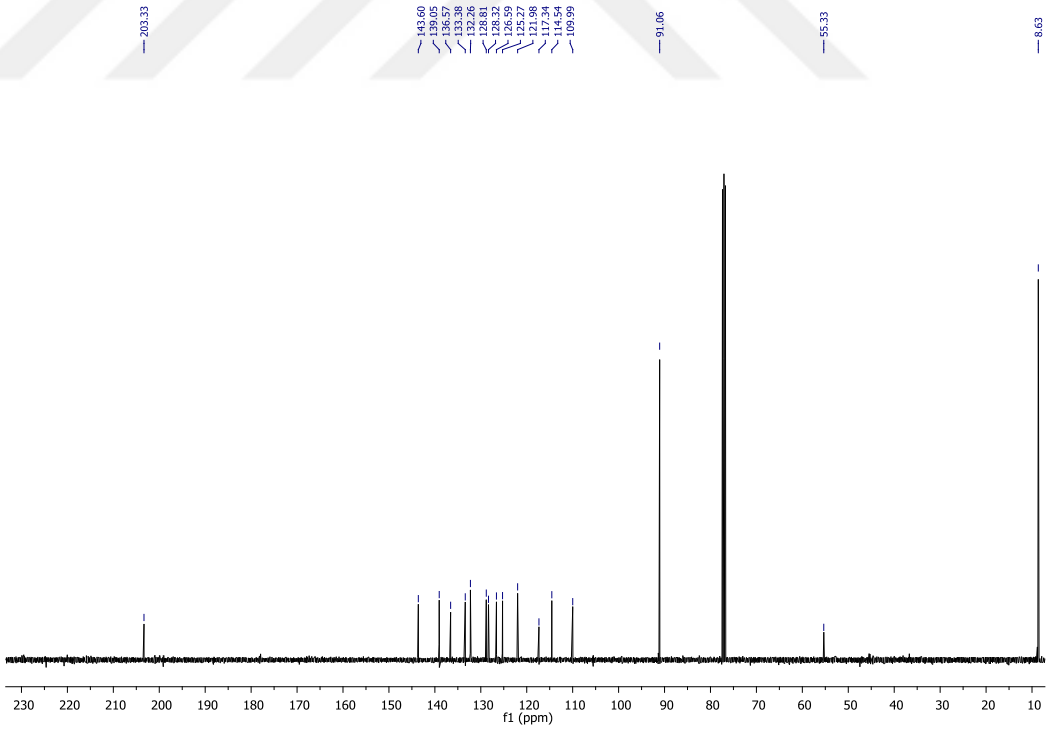


(b)

Figure 3.9 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Ru_{3a}**.

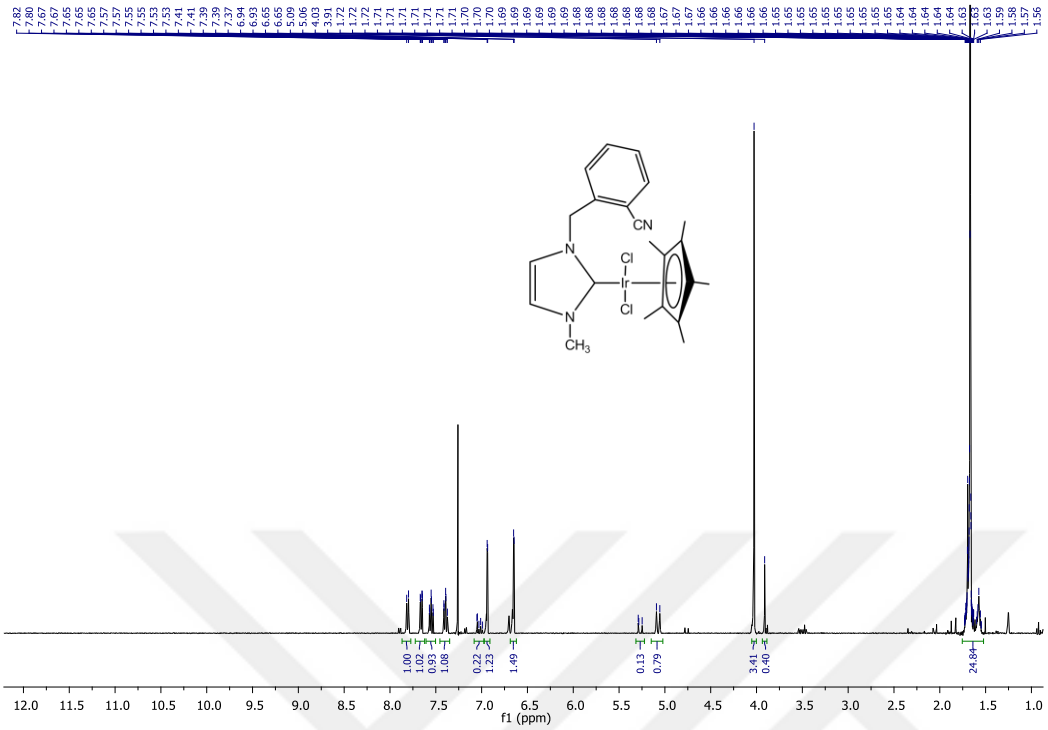


(a)

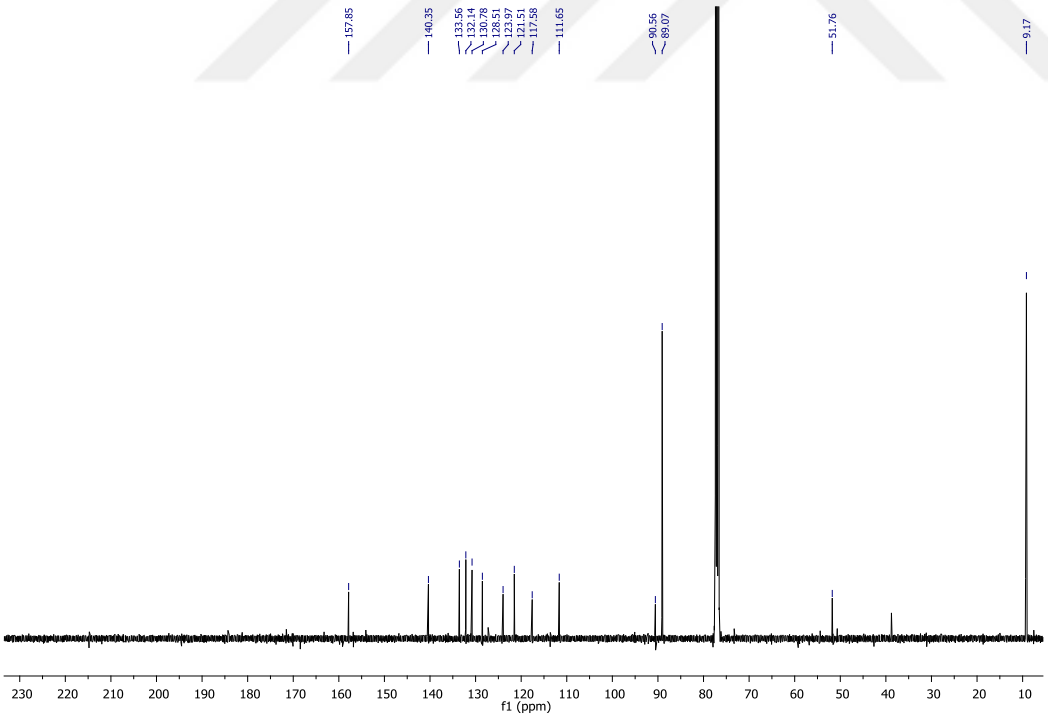


(b)

Figure 3.10 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Ir_{1a}**.

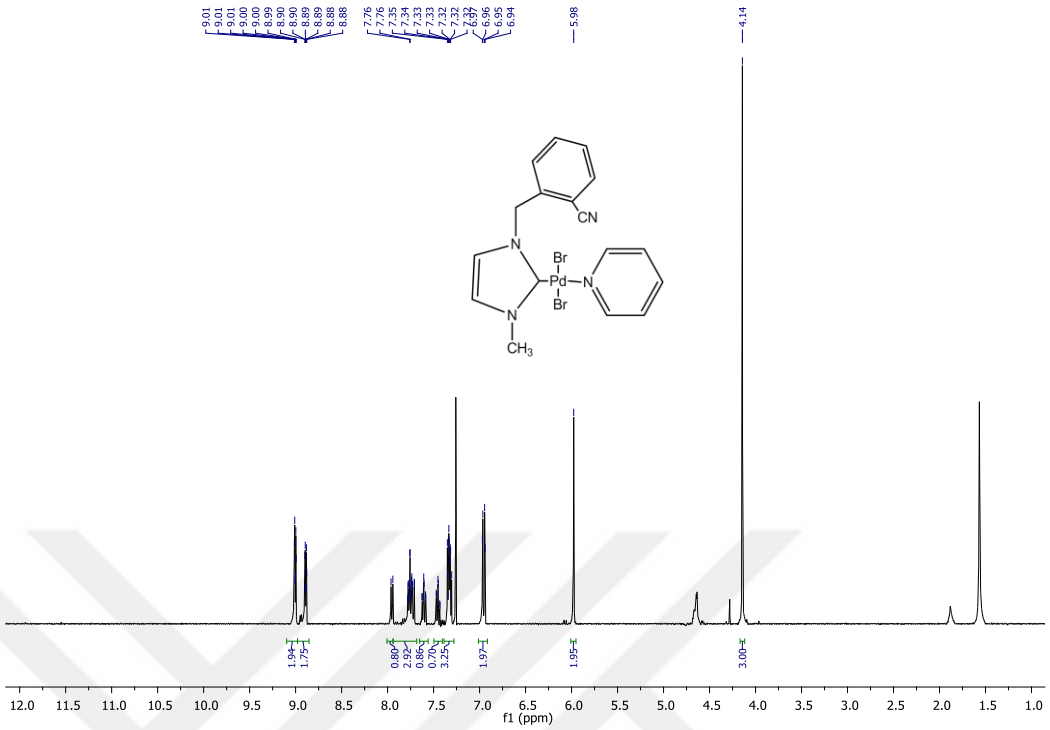


(a)

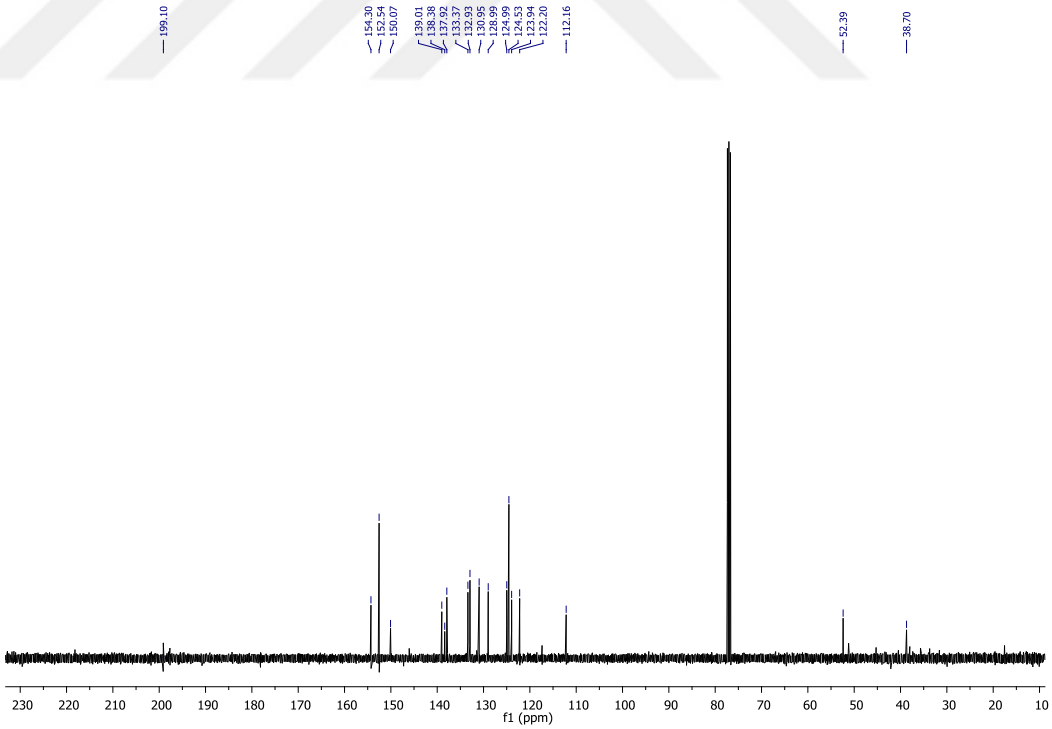


(b)

Figure 3.11 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Ir_{2a}**.

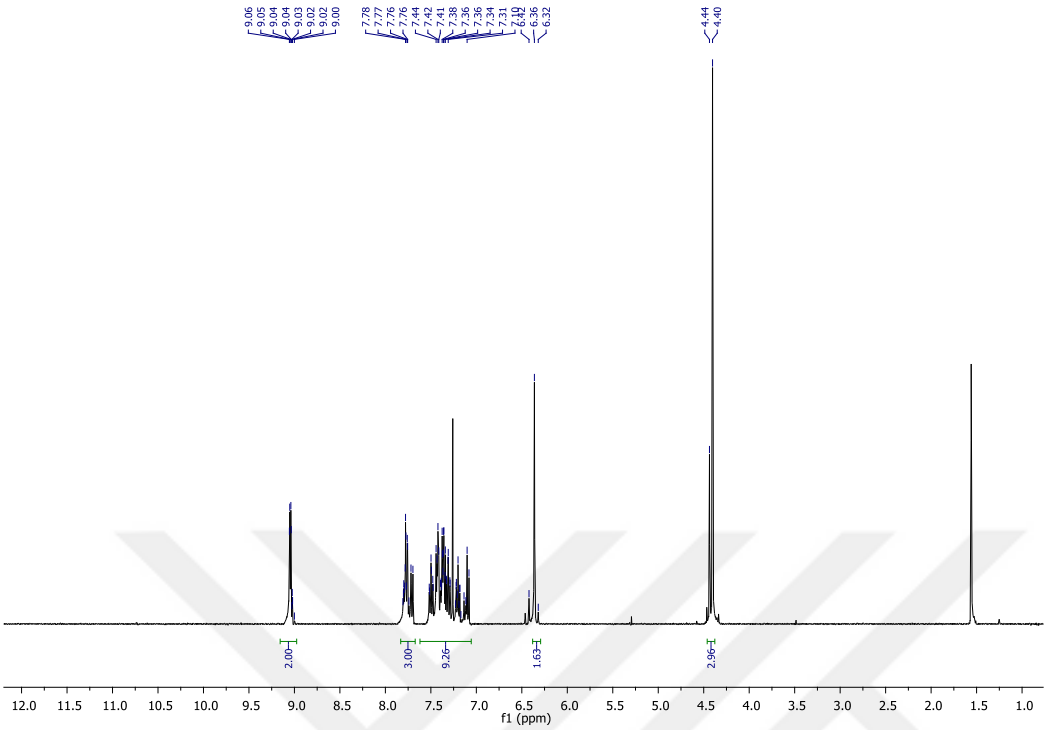


(a)

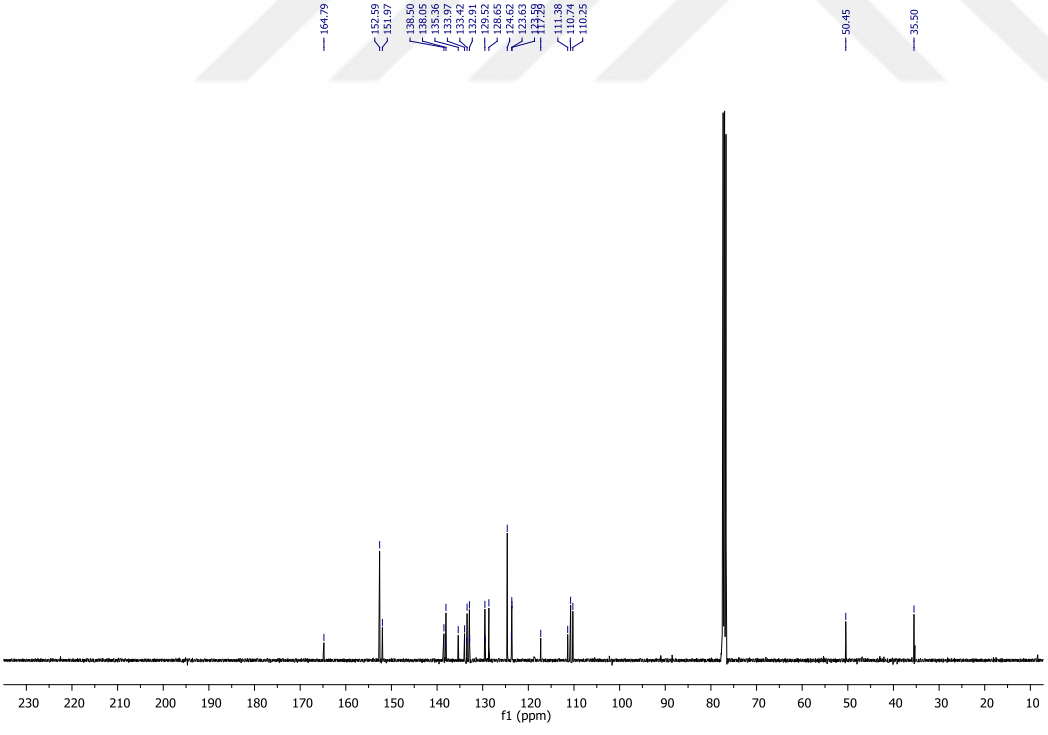


(b)

Figure 3.12 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Pd_{2a}**.

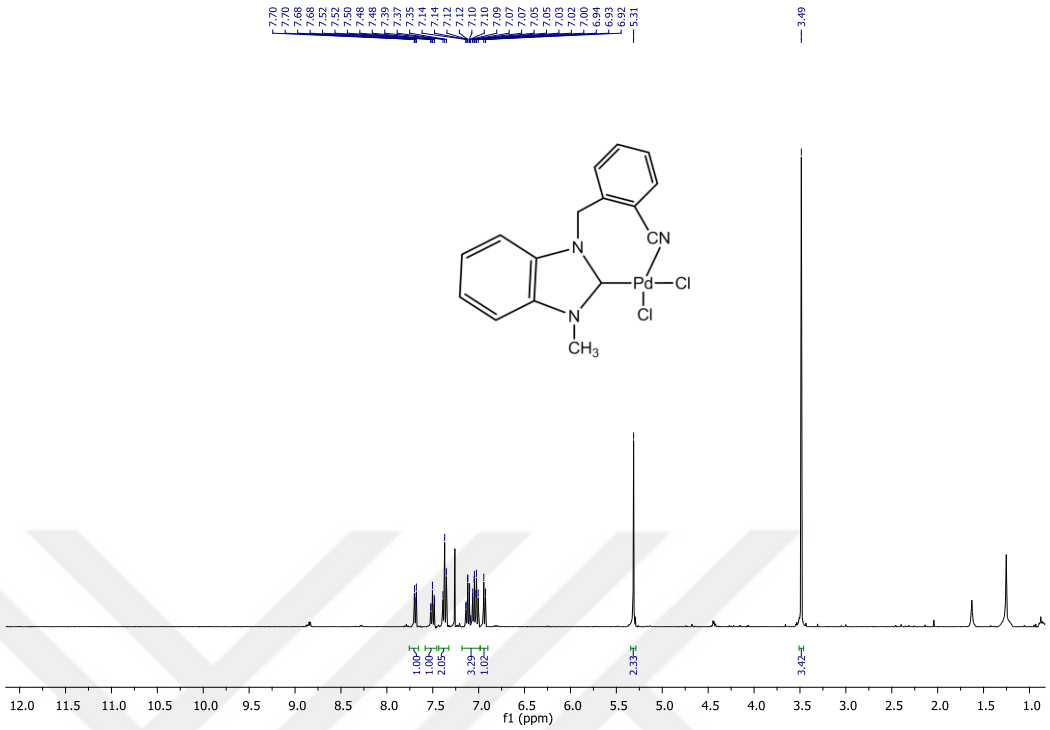


(a)

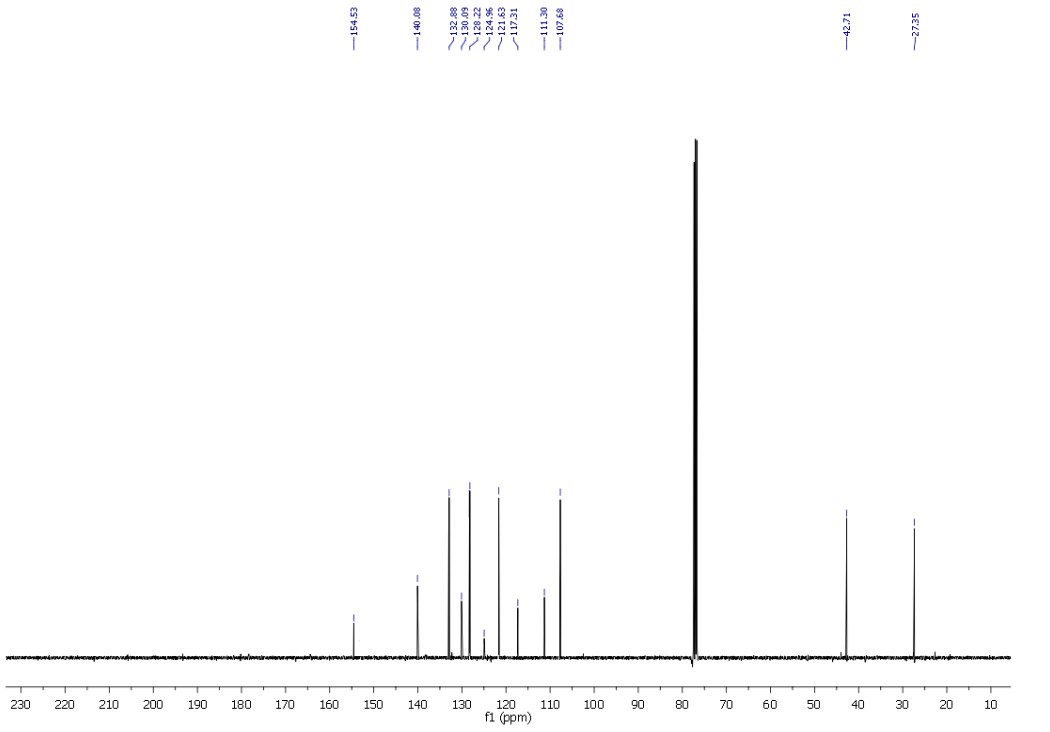


(b)

Figure 3.13 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Pd_{3a}**.



(a)



(b)

Figure 3.14 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **Pd_{3a}'**.

3.2. FT-IR Spectrums

Infrared spectra were registered on Perkin Elmer Spectrum 100 IR spectrometer as using KBr pellet. Analyzes were made between 400 – 4000 cm^{-1}.

3.2.1 FT-IR Spectrums of the Ligands

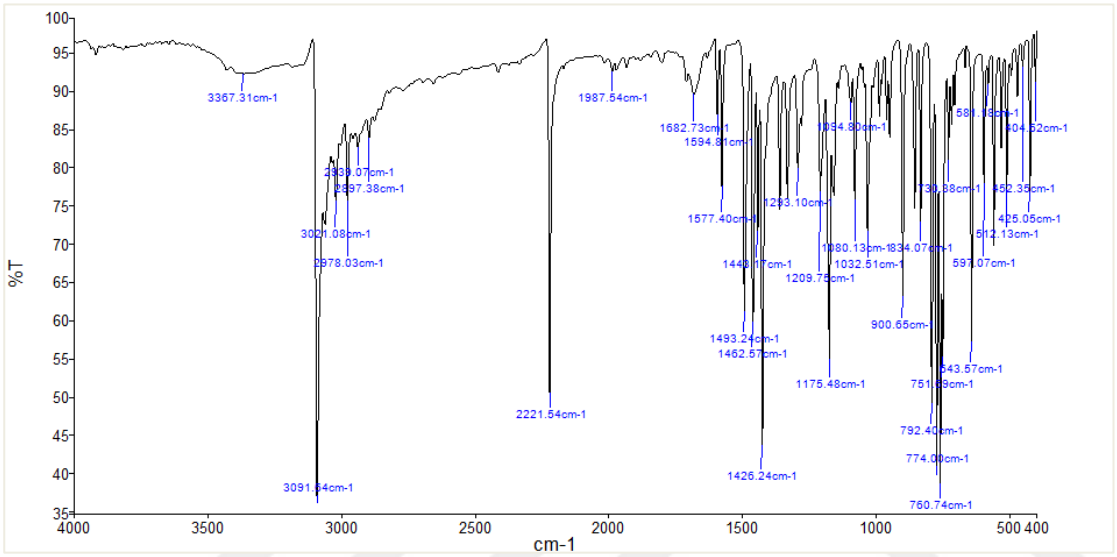


Figure 3.15 IR Spectrum of $\mathbf{T_{1a}}$.

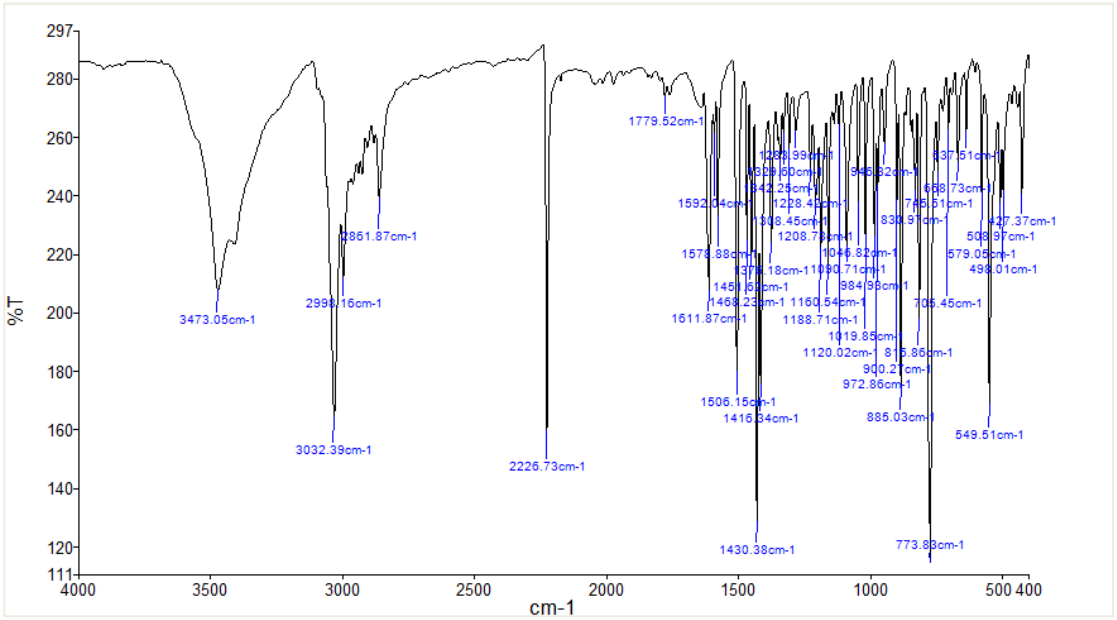


Figure 3.16 IR Spectrum of $\mathbf{T_{1b}}$.

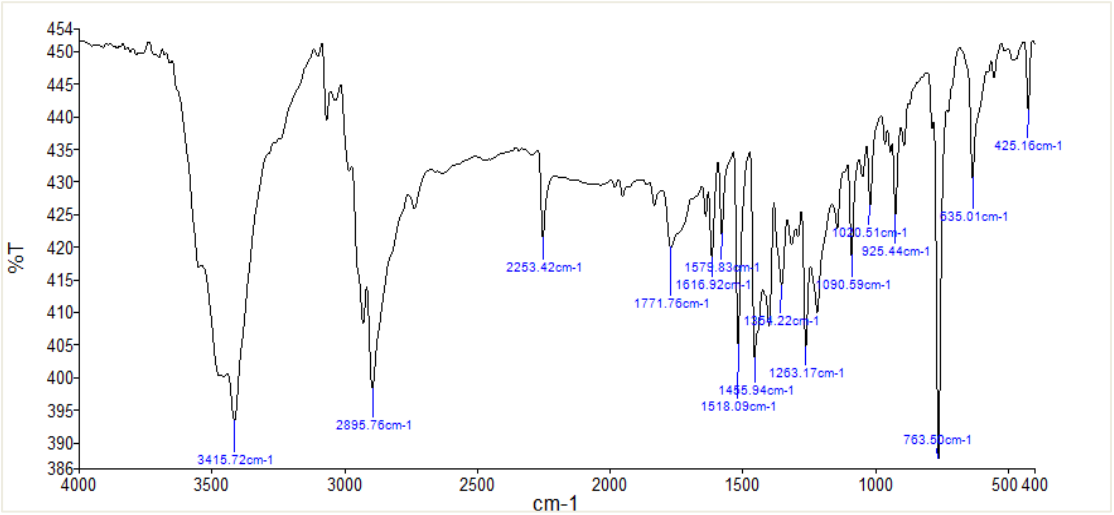


Figure 3.17 IR Spectrum of $\mathbf{T_{1c}}$.

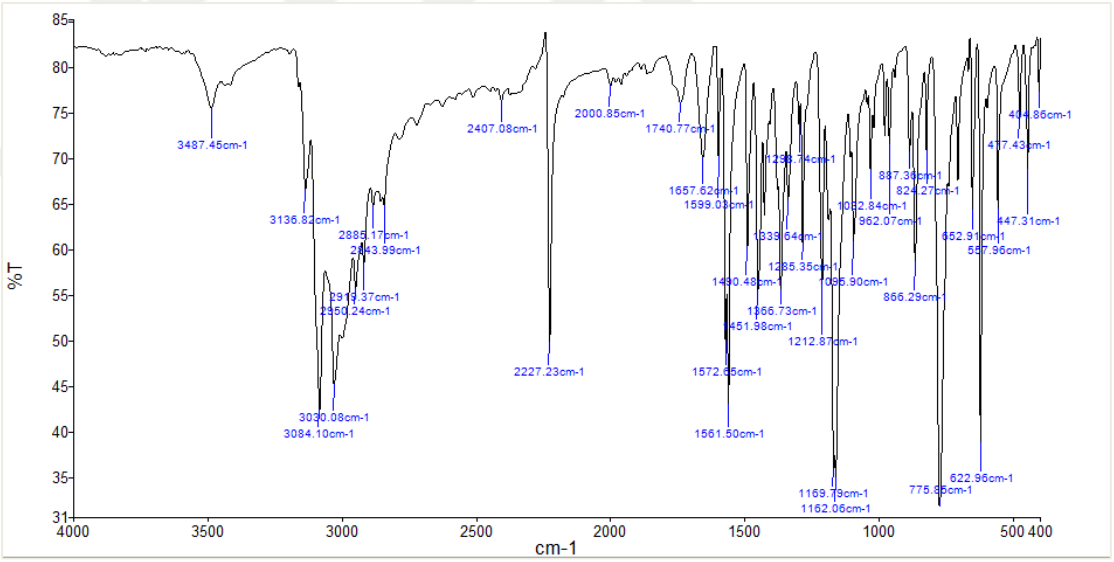


Figure 3.18 IR Spectrum of $\mathbf{T_{2a}}$.

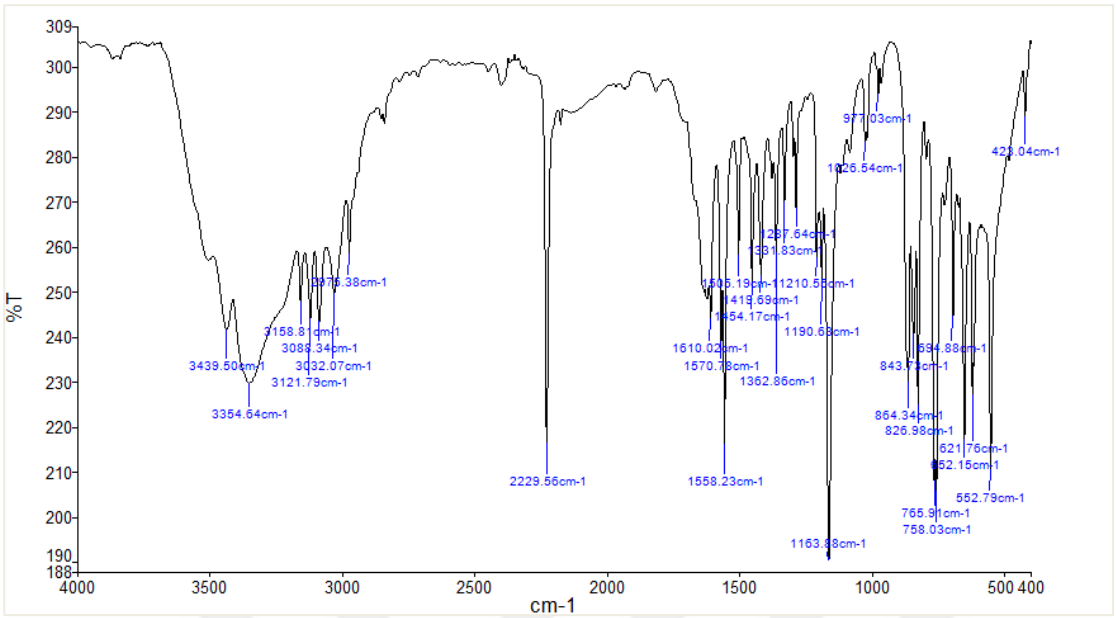


Figure 3.19 IR Spectrum of $\mathbf{T_{2b}}$

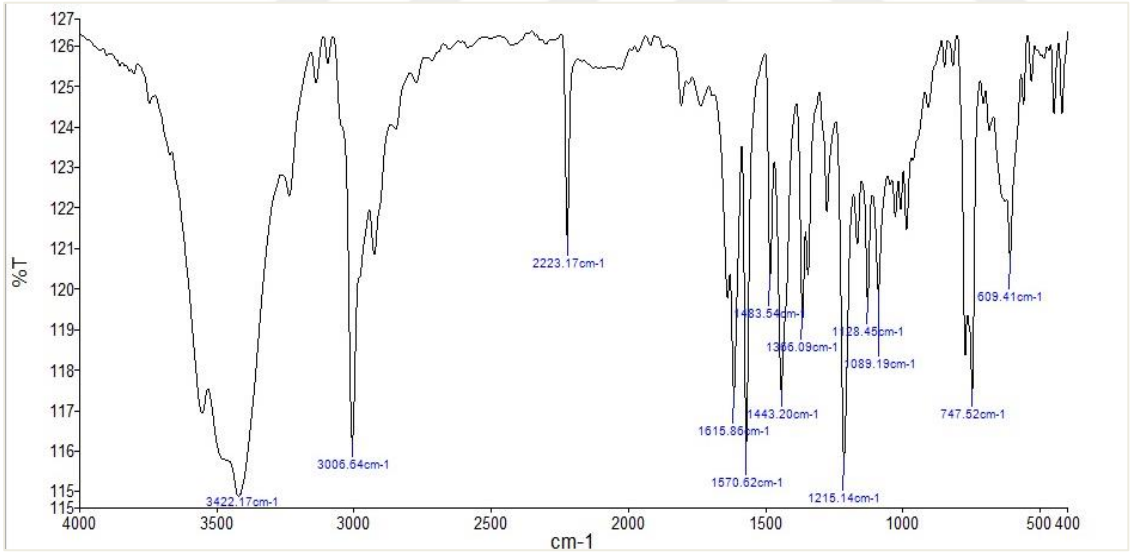


Figure 3.20 IR Spectrum of $\mathbf{T_{3a.}}$

Complex	$\nu_{C\equiv N}$	ν_{C-H} (Aromatic, Aliphatic)	$\nu_{C=C}$ (Aromatic)
T_{1a}	1682	3021,2939,2978	1577
T_{1b}	1611	3032,2861,2998	1578
T_{1c}	1616	2895	1518
T_{2a}	1657	3084,2919,2950	1572
T_{2b}	1610	3088,2975	1570
T_{3a}	1615	3006	1570

Table 3.1 IR frequencies of ligands.

The spectra of the ligands were similar. In the spectra, C≡N stretching vibration frequencies was observed at 1600-1700 cm^{-1}. Aromatic C-H stretching vibration frequencies were viewed between 3000-3100 cm^{-1}. Also, aliphatic C-H stretching vibration frequencies between 2850-3000 cm^{-1} were seen. Finally, The peaks in the 1500-1600 cm^{-1} frequency range in the spectrum indicated the C=C stretching frequencies in the ring.

3.2.2. FT-IR Spectrums of the Complexes

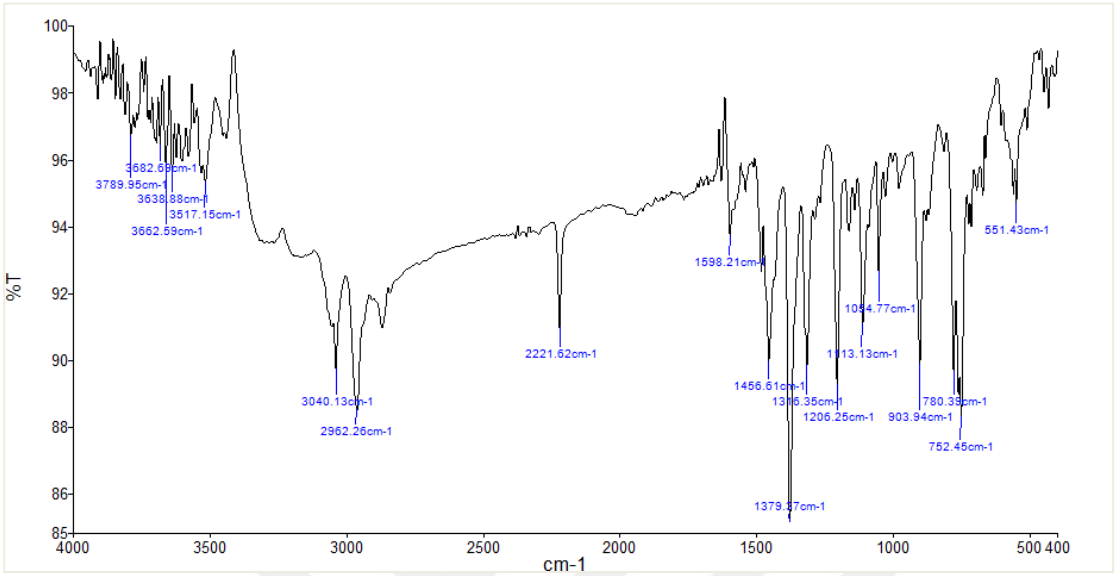


Figure 3.22 IR Spectrum of **Ru_{1a}.**

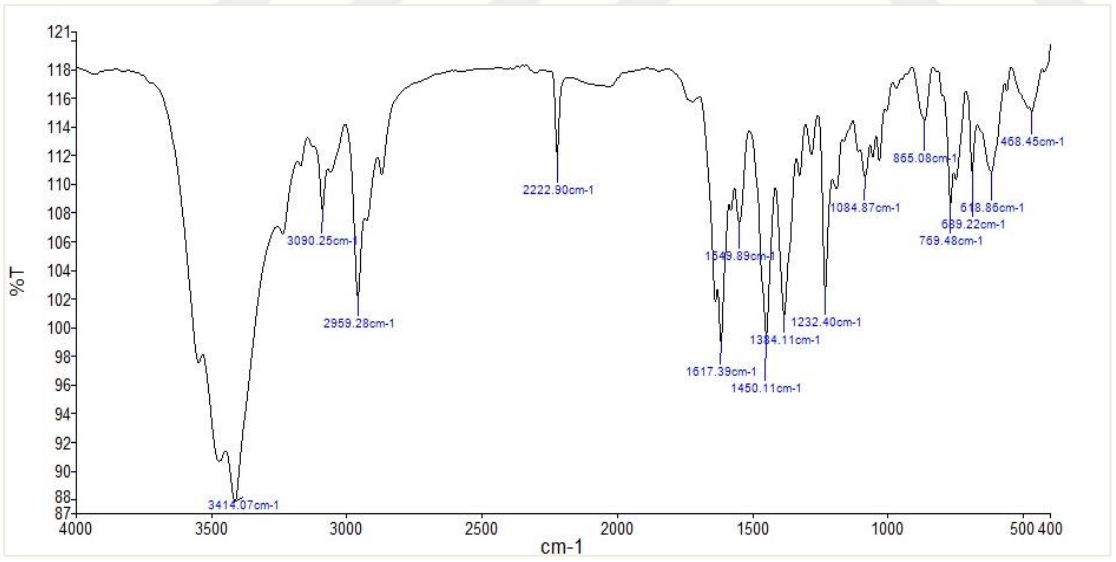


Figure 3.23 IR Spectrum of **Ru_{2a}.**

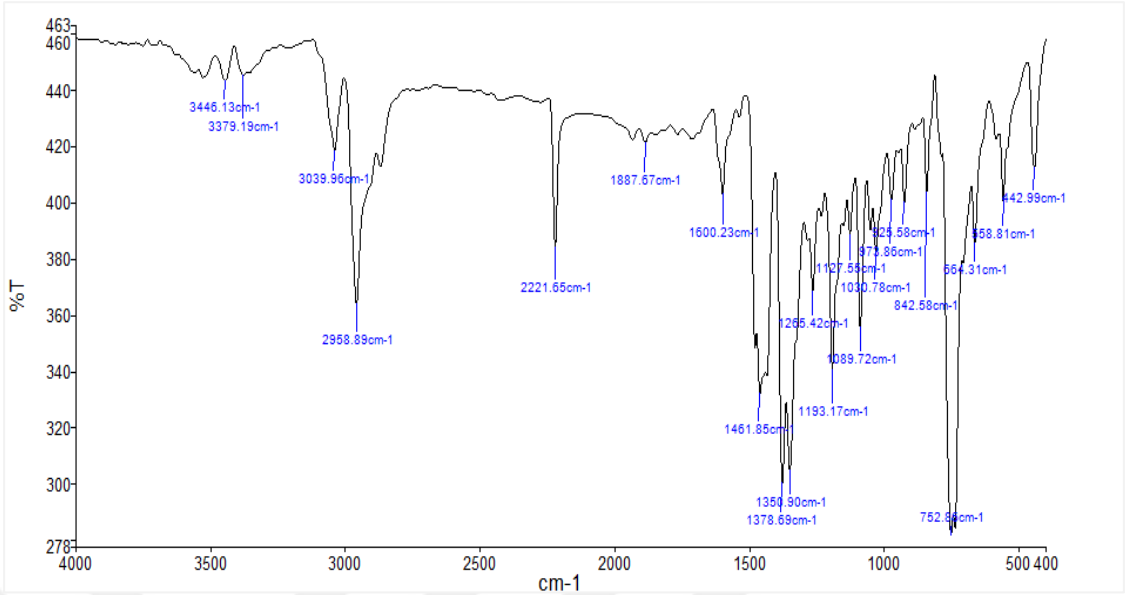


Figure 3.24 IR Spectrum of **Ru_{3a}.**

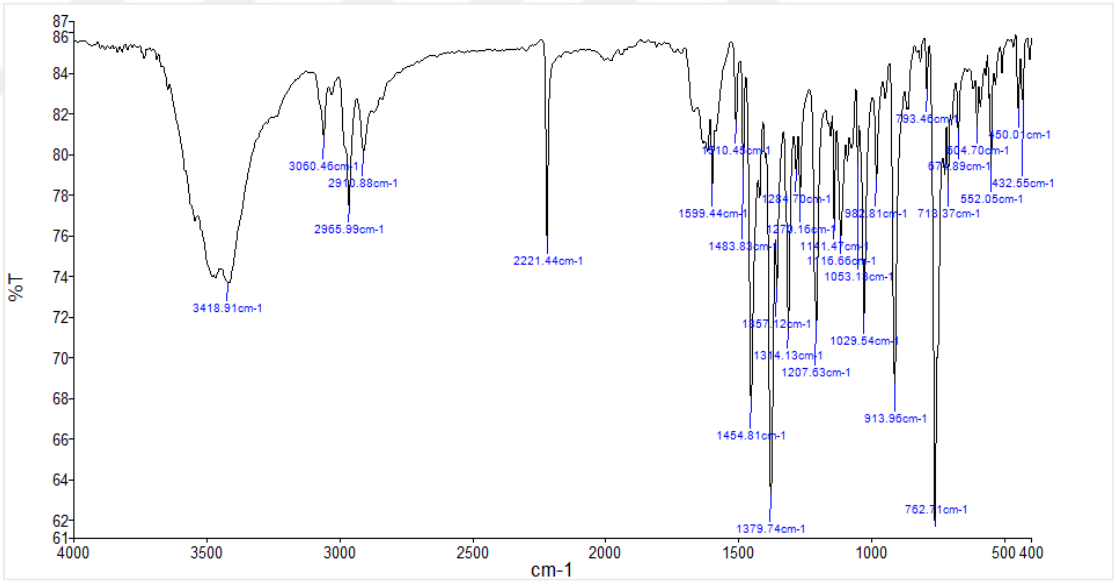


Figure 3.25 IR Spectrum of **Ir_{1a}.**

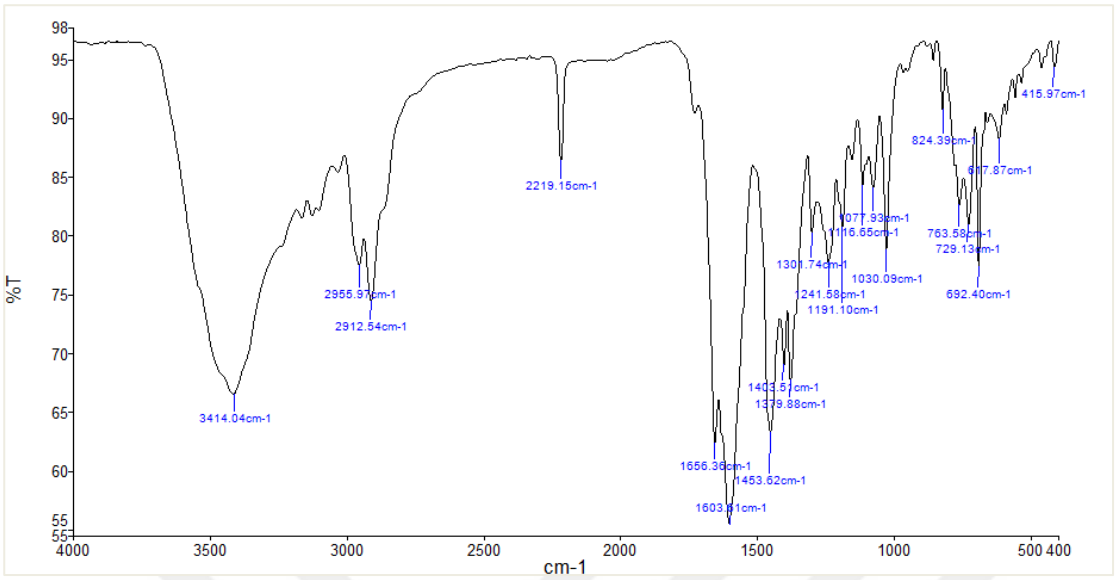


Figure 3.26 IR Spectrum of **Ir_{2a}.**

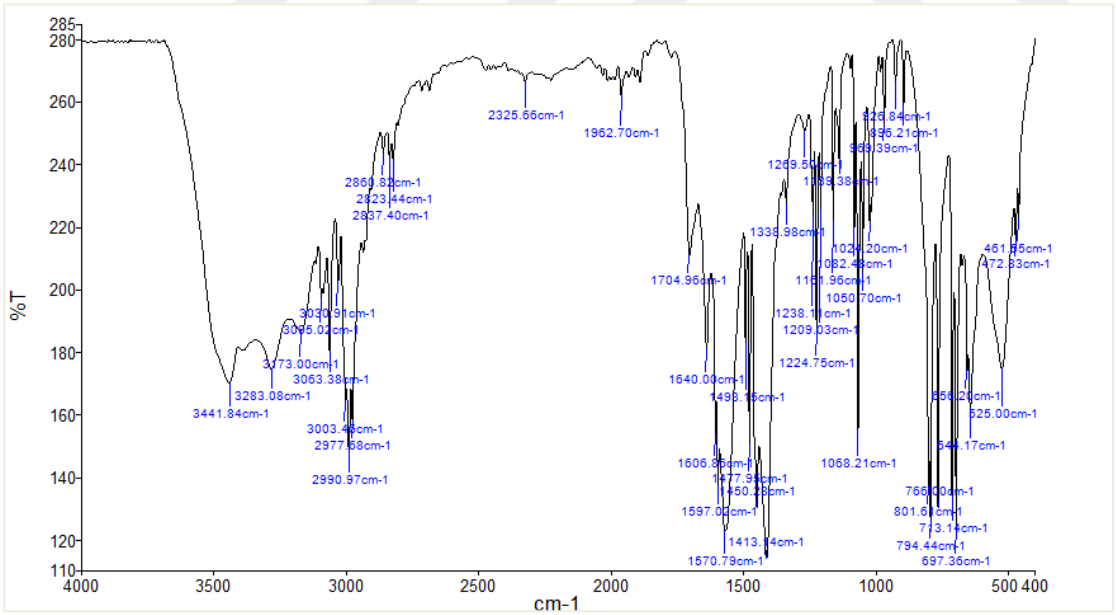


Figure 3.27 IR Spectrum of **Pd_{2a}.**

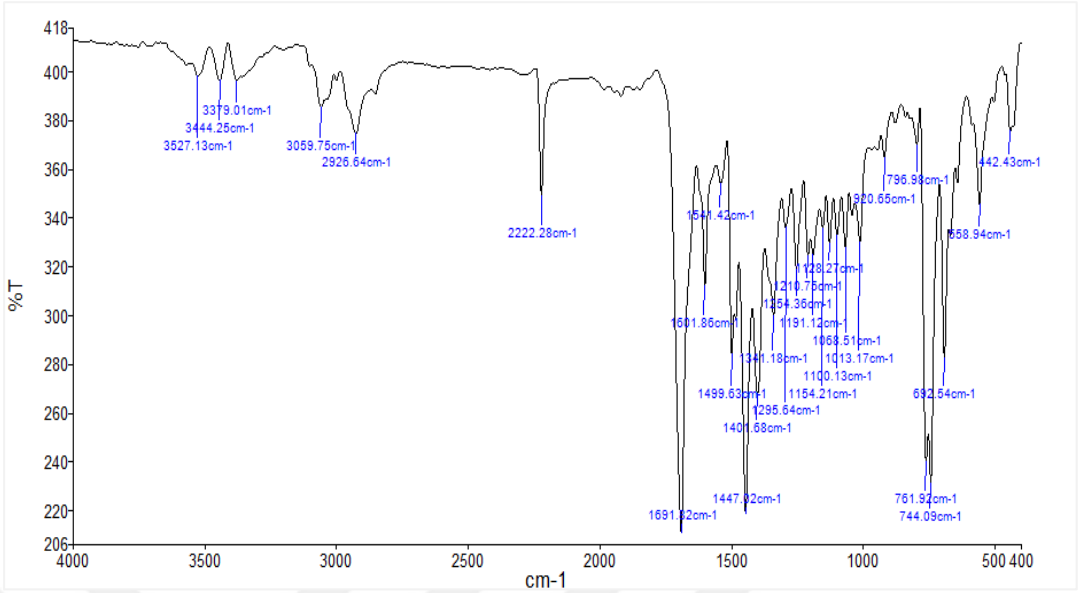


Figure 3.28 IR Spectrum of **Pd_{3a}**.

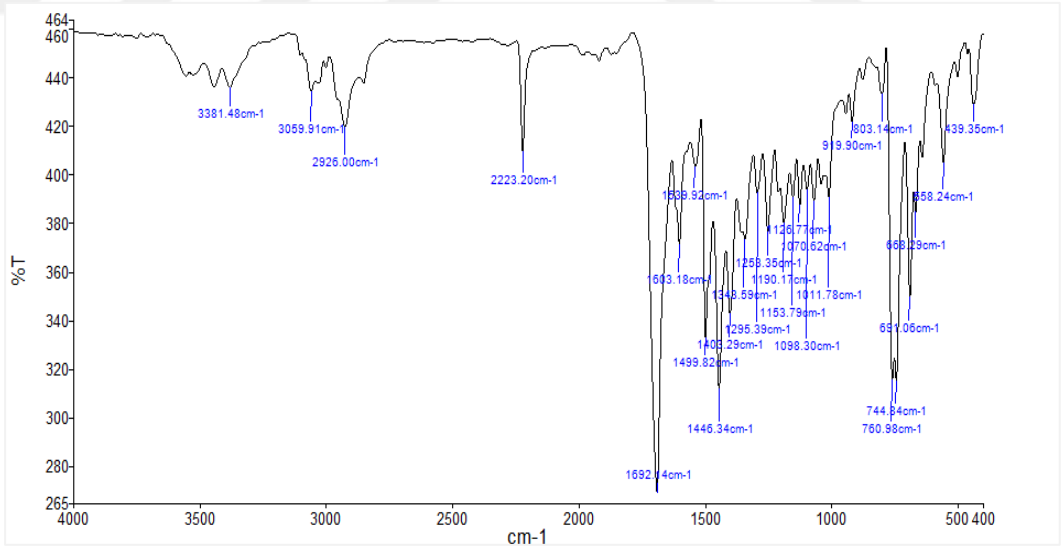


Figure 3.29 IR Spectrum of **$Pd_{3a'}$**.

Complex	$\nu_{C\equiv N}$	ν_{C-H} (Aromatic, Aliphatic)	$\nu_{C=C}$ (Aromatic)
$\mathbf{Ru_{1a}}$	1598	3040, 2962	1456
$\mathbf{Ru_{2a}}$	1549	3090, 2959	1450
$\mathbf{Ru_{3a}}$	1600	3039, 2958	1461
$\mathbf{Ir_{1a}}$	1599	3060, 2910	1510
$\mathbf{Ir_{2a}}$	1603	3414, 2912	1403
$\mathbf{Pd_{2a}}$	1640	3003, 2990	1570
$\mathbf{Pd_{3a}}$	1691	3059, 2926	1541
$\mathbf{Pd_{3a}}$,	1692	3039, 2926	1539

Table 3.2 IR frequencies of complexes.

The IR data of the complexes are summarized in Table 3,2. In the spectra, C≡N stretching vibration frequencies are observe at 1850-1650 cm^{-1}. Aromatic C-H stretching vibration frequencies are viewed between 3000-3100 cm^{-1}. Also, aliphatic C-H stretching vibration frequencies between 2900-3000 cm^{-1} are seen. Finally, The peaks in the 1400-1575 cm^{-1} frequency range in the spectrum indicate the C=C stretching frequencies in the ring.

3.3. X-Ray Diffraction Analysis

Different solvent systems such as dichlorometane – diethyl ether, acetonitrile – diethyl ether and chloroform – pentane have been tried to obtaine the crystals of the synthesized complexes . The crystal of the monometallic **Ru_{1a}** has been obtained from the dichloromethane – diethyl ether solvent system.

Complex **Ru_{1a}**

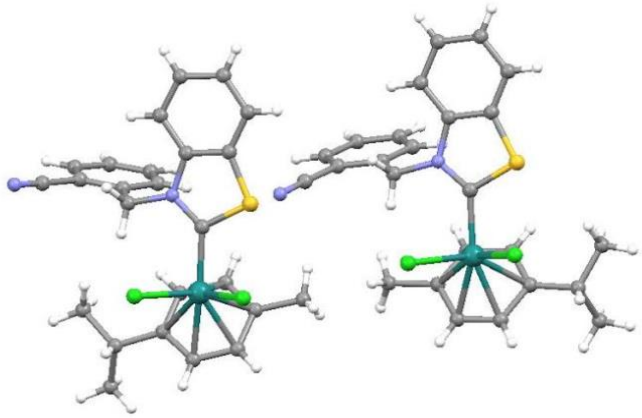


Figure 3.30 The molecular structure of complex Ru_{1a} showing the atom numbering scheme.

3.4. Catalytic Experiments

3.4.1. Catalytic Trasfer Hyrogenation Reaction with Ru/Ir-NHC Complexes

The catalytic behavior of the complexes (**Ru_{1a}, Ru_{2a}, Ru_{3a}, Ir_{1a}, Ir_{2a}**) was studied at 82 °C for 1.5 hours under argon atmosphere with acetophenone (1 mmol), KOH (0.5 mmol) and isopropyl alcohol (1 mL). The conversions were determined by GC. Iridium complexes (**Ir_{1a}, Ir_{2a}**) were found to be more active than ruthenium complexes (**Ru_{1a}, Ru_{2a}, Ru_{3a}**). Although activities were close to each other, the most active catalyst was found to be **Ir_{2a}** (Figure 3.31). In the transfer hydrogenation reaction, optimization studies showed that low solvent

volumes were positively affected by catalytic activity. In the same manner, the reaction did not occur well in lower temperatures than 82 °C such as 60 °C and RT. When the survey was performed **Ir_{2a}**, the best result is determined by KOH. The catalytic activity of **Ir_{2a}** was investigeted indifferent solvents, the best result was given to IPA.

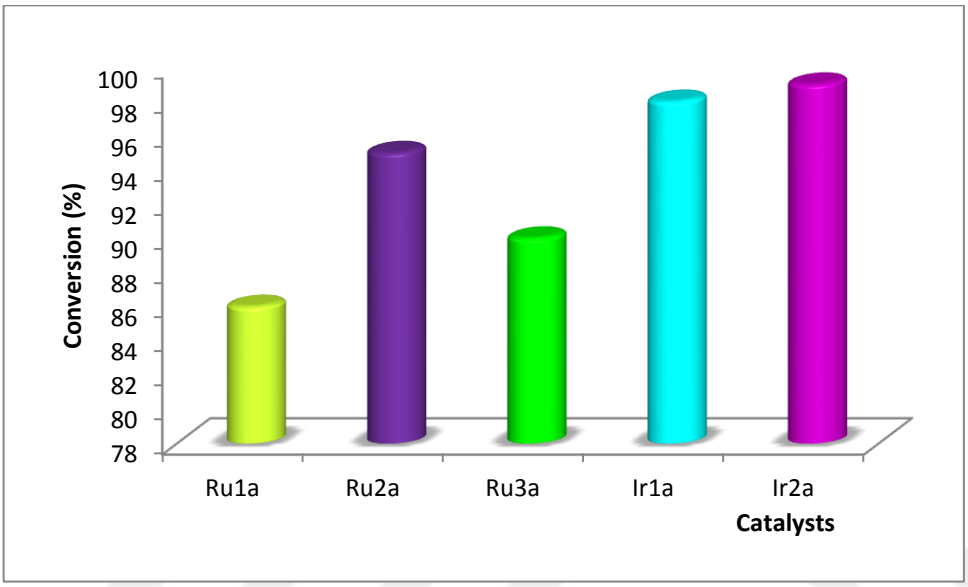
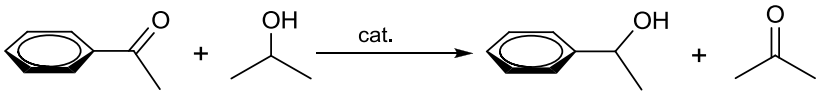


Figure 3.31 Transfer Hydrogenation results in the scale of time.

Table 3.3 Screening of reaction conditions in the transfer hydrogenation reaction.



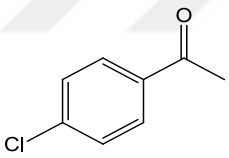
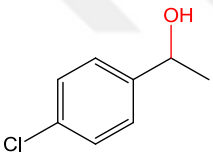
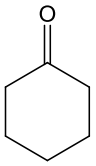
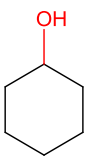
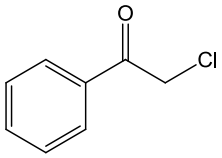
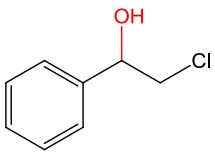
Entry	Cat. (mol%)/ Base (mmol)	Base	Solvent	Time	Yield (%)
1	1/0.5	KOH	IPA	1.5	99
2	1/0.25	KOH	IPA	1.5	10
3	0.5/0.5	KOH	IPA	1.5	52
4	0.2/0.5	KOH	IPA	4	96
5	1/0.5	$HCOOH/NaOCOO^-$	H_2O	1.5	Trace
6	1/0.5	$NaHCO_3$	IPA	1.5	24
7	1/0.5	NaOH	IPA	1.5	62

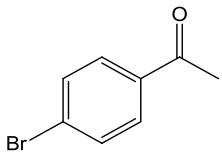
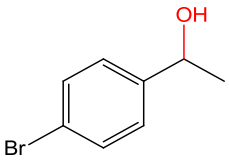
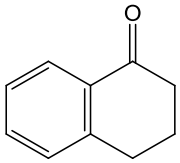
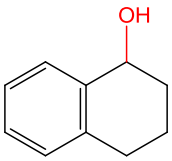
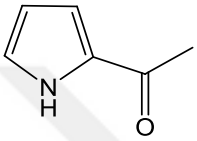
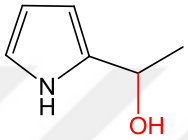
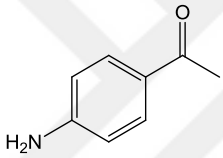
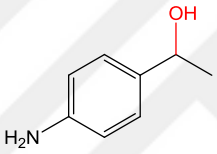
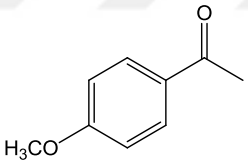
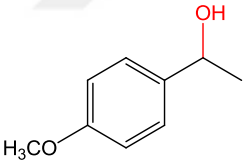
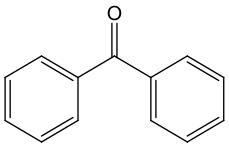
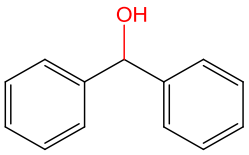
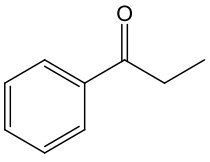
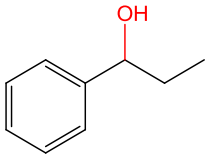
8	-/0.5	KOH	IPA	1.5	14
9	1/-	-	IPA	4	87
10[b]	1/0.5	KOH	IPA	1.5	Trace
11[c]	1/0.5	KOH	IPA	1.5	54

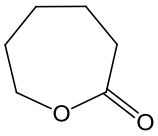
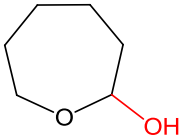
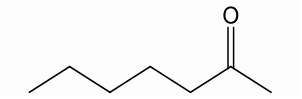
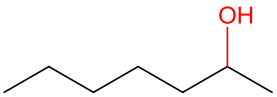
Catalytic conditions: substrate (1 mmol), solvent (1 mL).[b] T= 25 °C,[c] T= 60 °C.

Using the most active catalyst **Ir$_{2a}$**, the scope of the catalytic transfer hydrogenation was studied with ketones corresponding l alcohols in excellent yields (51−98%) (Table 3,4). The aryl ketones were chosen to explore the effects of electronic and variations on the substrate backbone. The position of the substituents on the phenyl ring causes significant changes in the reduction rate. The reduction of aliphatic ketones by catalyst **Ir$_{2a}$** resulted in the quantitative formation of aliphatic alcohols (entries 2,12).

Table 3.4 The effects of subsrate for the transfer hydrogenation reaction

Entry	Substrate	Product	Yield (%)
1			96
2			54
3			84

4			90
5			54
6			51
7			63
8			85
9			79
10			72

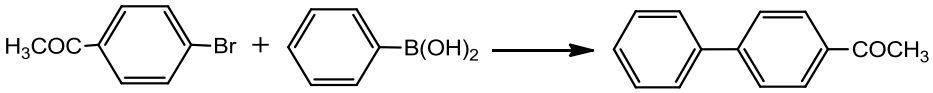
11			98
12			59

Catalytic conditions: Substrate (1 mmol), base (0.5 mmol), cat.(%1), solvent (1 mL), T= 82 ^{o}C.

3.4.2. Catalytic Suzuki-Miyaura Reactions with Pd-NHC Complexes

A model reaction was generated using 4-bromoacetophenone (1 mmol), phenyl boronic acid (1.5 mmol) and KOH (0.5 mmol) to investigate the effect of the Pd-NHC complexes on the Suzuki-Miyaura crosscoupling reaction. The conversions were determined by GC. Among the Pd complexes (**Pd_{2a}**, **Pd_{3a}**, **$Pd_{3a'}$**), the activity of the **Pd_{2a}** complex was slightly better than the other complex. In the optimization studies, the appropriate solvent system was determined as 2 mL (1:1, IPA-H_2O). The role of IPA in this catalytic cycle is to dissolve aryl bromides while the role of water is to activate phenyl boronic acid and base although weak bases such as $NaHCO_3$ and K_2CO_3 were used, the reaction was carried out efficiently. Although KO^tBu was a strong base, the reaction did not yield effectively. The best yields Cs_2CO_3 and NaOH took place. However, due to the price of Cs_2CO_3, substrate trials were performed with NaOH.

Tablo 3.5 Screening of reaction conditions in the Suzuki-miyaura coupling reaction.

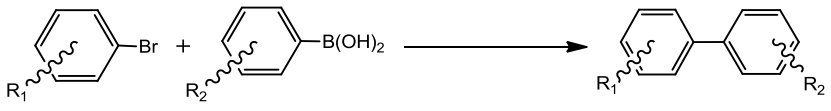


Entry	Cat.	Cat. (mol%)	Solvent	Base	Yield (%)
1	Pd_{2a}	0.5	IPA	NaOH	76
2	Pd_{3a}	0.5	IPA	NaOH	61
3	$Pd_{3a'}$	0.5	IPA	NaOH	65
4	Pd_{2a}	0.2	IPA	NaOH	54
5	Pd_{2a}	0.5	IPA–H_2O	NaOH	88
6	Pd_{2a}	0	IPA–H_2O	NaOH	trace
7	Pd_{2a}	0.5	IPA–H_2O	KOH	66
8	Pd_{2a}	0.5	IPA–H_2O	K_2CO_3	75
9	Pd_{2a}	0.5	IPA–H_2O	Cs_2CO_3	95
10	Pd_{2a}	0.5	IPA–H_2O	Na_2CO_3	35
11	Pd_{2a}	0.5	IPA–H_2O	$NaHCO_3$	67
12	Pd_{2a}	0.5	IPA–H_2O	KO*t*-Bu	55

Reaction condition: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.0 mmol), base (0.5 mmol), IPA-H_2O = 1:1 (2.0 ml), 82^oC, 30 min. Analyzed by GC.

When the substrate was screened with different aryl bromides, the results were close to each other and the best result was 4-bromoacetophenone.

Table 3.6 The effects of subsrate for Suzuki-Miyaura cross coupling.



Entry	R_1	R_2	Yield (%)
1	4-Me	H	64

2	4-COMe	H	65
3	4-NO_2	H	63
4	4-CHO	H	59
5	4-COMe	4-Me	69
6	4-COMe	4-Br	59
7	4-COMe	2-Me	57
8	4-COMe	3-Me	60
9	4-COMe	4-CF_3	77
10	4-COMe	2-CF_3	71
11	4-COMe	2,5-Me	73
12	4-COMe	4-F,3-COH	47
13	4-COMe	4-t-Bu	65

Reaction condition: Aryl bromide (1.0 mmol), Phenylboronic acid (1.0 mmol), cat. Pd_{2a} (0.5 mol %), NaOH (0.5 mmol), IPA-H_2O=1:1 (2.0 ml), 82^oC, 30 min.

4. CONCLUSIONS

In this study, the NHC ligands with nitrile substituted and their NHC metal complexes were prepared from methyl imidazole, metylbenzimidazole and benzothiazole. The synthesized complexes were characterized by spectroscopic methods (NMR, IR, elemental analysis). The new synthesized complexes as a catalyst were investigated in transfer hydrogenation and Suzuki-miyaura reactions.

The Ru(NHC) and Ir(NHC) complexes transformed the corresponding ketone derivative into alcohols in the presence of KOH in IPA within 1.5 hours in the transfer hydrogenation reaction. Ir(NHC) complexes were found to be more active in both skeletal structures (methylimidazole and benzothiazole). The most active catalyst was **Ir_{2a}** in TH reaction.

The Pd(NHC) complexes gave good conversions in a short time with the low base and catalyst in the mixture of IPA and H_2O in Suzuki-Miyaura cross-coupling reaction. The most active catalyst is **Pd_{2a}**. Substrate screening was performed by **Pd_{2a}** with different aryl bromides. Catalytic reactions were carried out in short time and with a low catalyst under air atmosphere without the use of stoichiometric amount bases and excess substrate.

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