EGE UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

(PhD THESIS)

CHIRAL METAL COMPLEXES AND THEIR PROPERTIES

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ÖZET

KİRAL METAL KOMPLEKSLERİ VE ÖZELLİKLERİ

DENİZALTI, Serpil

Doktora Tezi, Kimya Anabilim Dalı
Tez Danışmanı: Doç. Dr. Hayati TÜRKMEN
İkinci Tez Danışmanı: Prof. Dr. Bekir ÇETİNKAYA

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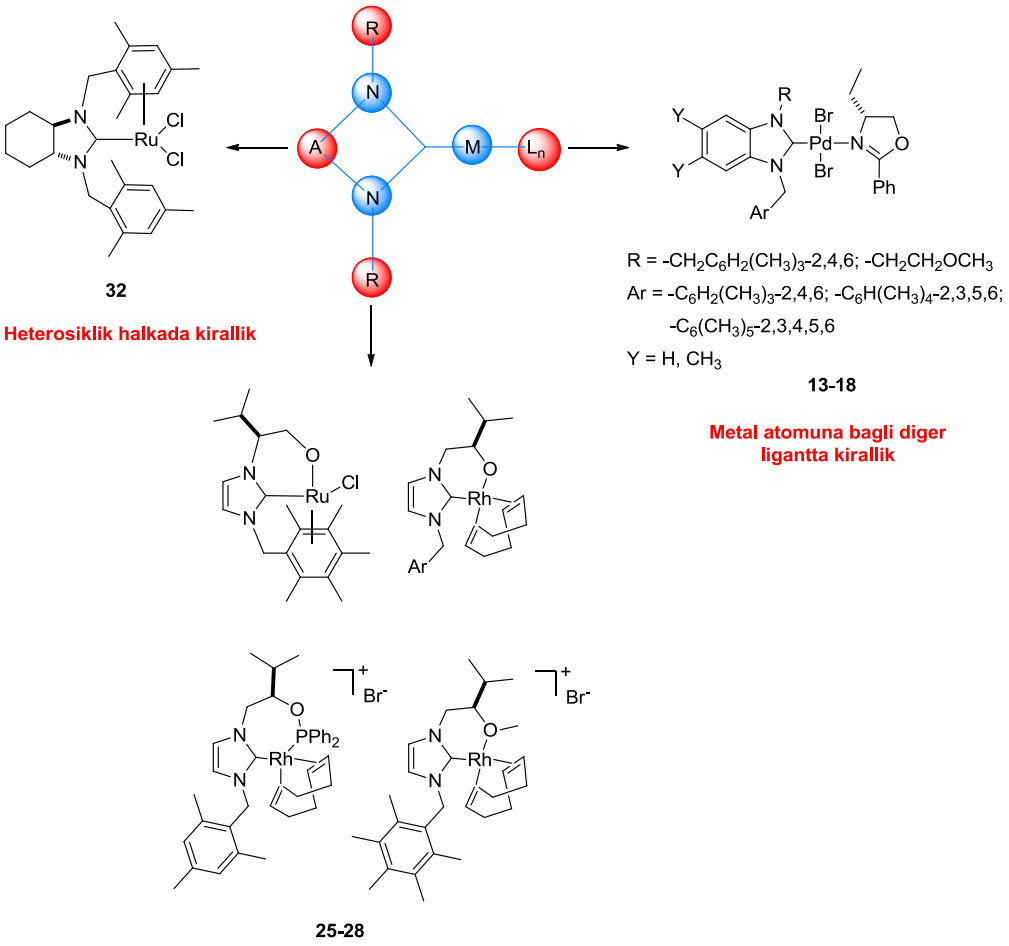
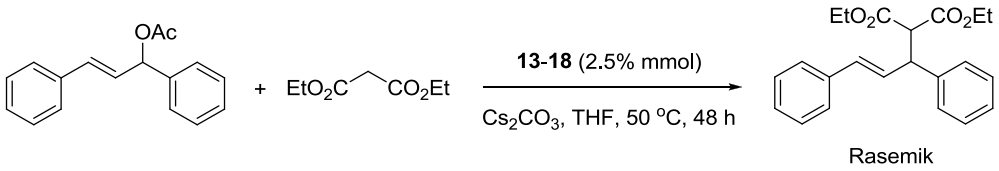
N-Heterosiklik karbenler (NHCs) güçlü σ-donörüdür ve metallerle kuvvetli bağ oluştururlar. Bu nedenle fosfin anologlarına göre ısıya, havaya ve neme karşı daha kararlı kompleksler meydana getirirler. Sahip oldukları bu özelliklerinden dolayı NHC kompleksleri, olefin metatezi, hidrosilasyon, hidrojenasyon, Heck ve Suzuki eşleşme gibi birçok tepkimede katalizör olarak kullanılmaktadır. Dolayısıyla, asimetrik katalizde bu ligantların kiral türevlerinin gelişimi de kaçınılmaz olmuştur. Asimetrik alken hidrojenasyonu, asimetrik alken metatezi gibi katalitik reaksiyonlarda iyi seçimlilik gösteren kiral NHC kompleksleri sentezlenmekle birlikte bunların sayısı sınırlıdır. Bu nedenle yüksek seçimlilik gösteren kiral katalizörlerin geliştirilmesine ihtiyaç duyulmaktadır.

Bu tez kiral NHC kompleksleri ile ilgilidir ve üç bölümden oluşmaktadır. Birinci bölümde, kirallik ve önemi, NHC hakkında temel bilgiler, kiral NHC ligantları ve komplekslerinin asimetrik katalizdeki uygulamalarına ilişkin çalışmalar özetlenmiştir. İkinci bölümde, deneysel çalışmalara yer verilmiştir. Üçüncü bölüm, kiral yardımcı ligant içeren NHC ve kiral NHC komplekslerinin sentezi, karakterizasyonu ve katalitik aktivitelerinin incelenmesini kapsamaktadır.

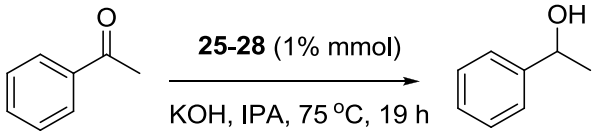


Kiral oksazolin ligandı içeren NHC-Pd(II) kompleksleri (**13-18**), sentezlenen dimerik NHC-Pd(II) komplekslerinin kiral oksazolin ligantı ile bölünmesi sonucu elde edilmiştir. Elde edilen bu kompleksler alilik alkilasyon reaksiyonunda katalizör olarak denenmiştir. Kompleksler aktivite göstermelerine rağmen elde edilen üründe seçimlilik gözlenmemiştir.

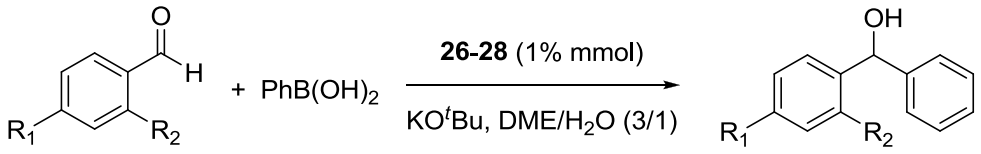


Kiralitenin azota bağlı sübstitüyentte olduğu, kiral NHC-Ru(II) ve Rh(I) kompleksleri (**25-28**) ile heterosiklik halkada kiraliteye sahip kiral NHC-Ru(II) kompleksi (**32**) sentezlendi. Elde edilen komplekslerin asetofenonun transfer

hidrojenasyondaki aktiviteleri araştırıldı. Transfer hidrojenasyonda en iyi sonuç katyonik rodyum komplekslerinden (**27**, **28**) alınmıştır.



Ayrıca rodyum kompleksleri aldehitlerin arilasyon reaksiyonunda da katalizör olarak kullanılmıştır. Arilasyon reaksiyonunda ise komplekslerin tamamının aktif olduğu ve 15 dakikada reaksiyonun tamamlandığı gözlenmiştir.



Anahtar kelimeler: Kiral N-heterosiklik karben, alilik alkilasyon, transfer hidrojenasyon, aldehitlerin arilasyonu.

ABSTRACT

CHIRAL METAL COMPLEXES AND THEIR PROPERTIES

DENİZALTI, Serpil

PhD Thesis in Chemistry
Supervisor: Assoc. Prof. Dr. Hayati TÜRKMEN
Co-Supervisor: Prof. Dr. Bekir ÇETİNKAYA

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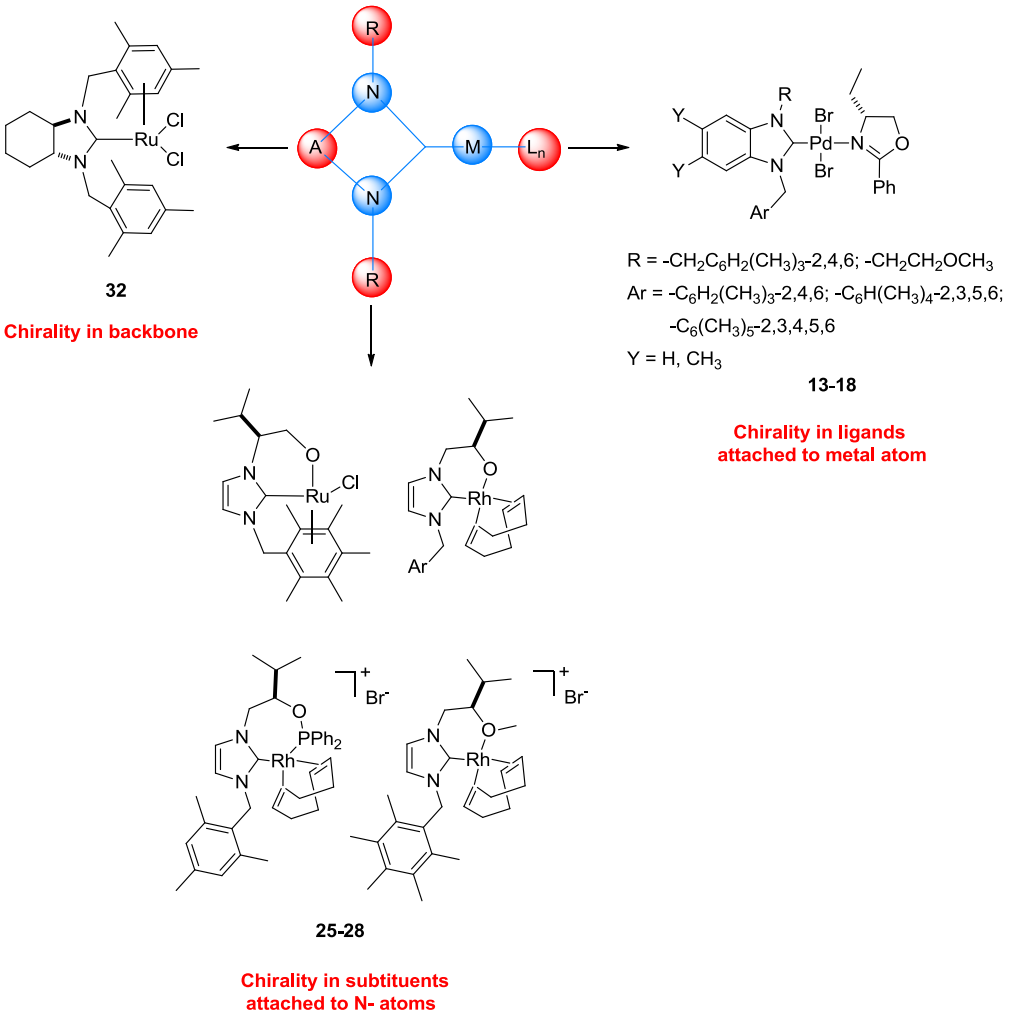
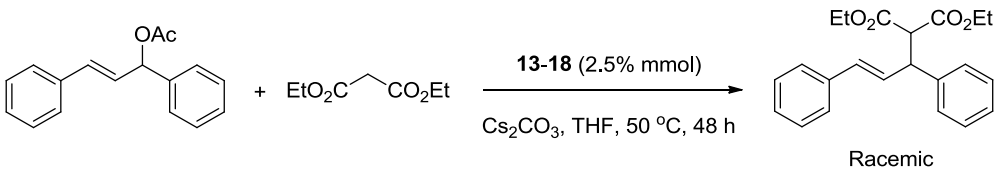
N-Heterocyclic carbenes (NHCs) are excellent σ-donors and form strong metal-carbon bonds, therefore these complexes have better thermal and air stability than phosphine analogues. N-Heterocylic carbene complexes have proved to be more effective catalysts in many catalytic reactions including olefin metathesis, hydrosilylation, hydrogenation, transfer hydrogenation, Heck and Suzuki C-C cross coupling reactions. Accordingly, development of chiral NHC ligands for enantioselective catalysis is a logical extension in this field. Although chiral NHC complexes, having good enantioselectivity in the asymmetric catalytic reactions such as hydrogenation, olefin metathesis were synthesized, the number of them is limited. Thus, it is still desirable to develop or find more active chiral catalysts and efficient catalytic systems for asymmetric catalysis.

This thesis is related with chiral NHC complexes and consists of three parts. The first part is a concise review about chirality and its importance, the applications of chiral NHC ligands and complexes in asymmetric catalysis. In part two, the experimental details were explained. Part three covers the synthesis, characterisation, and catalytic activities of NHC bearing chiral ligand and chiral NHC complexes.

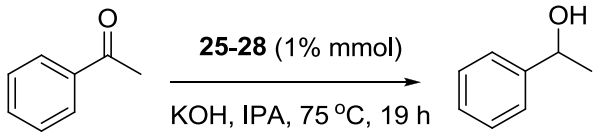


NHC-Pd(II) complexes bearing chiral oxazoline ligand (**13-18**) were obtained from dimeric NHC-Pd(II) complexes, which can readily be cleaved by chiral oxazoline. These palladium complexes were tested in the allylic alkylation reaction. All of the new palladium complexes were found to be active catalysts, however no enantioselectivity could be observed.

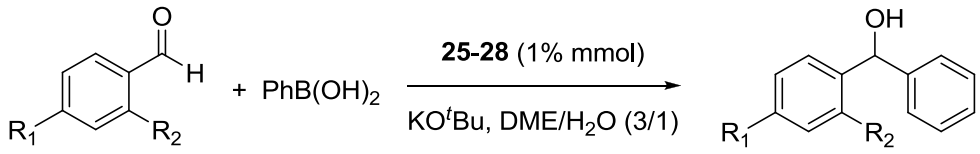


Chiral NHC-Ru(II) and Rh(I) complexes (**25-28**), which bear the chirality on the nitrogen atom, and chiral NHC-Ru(II) complex (**32**), in which the chirality is on the backbone, were prepared. All of the new rhodium and ruthenium

complexes were found to be effective catalysts for both reactions. Cationic rhodium complexes (**27**, **28**) gave the best result for the transfer hydrogenation of acetophenone.



In arylation reaction, it was observed that all complexes were active and the reaction was completed in 15 minutes.



Keywords: Chiral N-heterocyclic carbene, allylic alkylation, transfer hydrogenation, arylation of aldehydes.

This thesis is dedicated with love and gratitude to my wonderful family, especially…

*To my grandmother **Sare GÜVEN**, who has a very special place in my life;*

*To my parents **Aliye** and **Muhsin DENİZALTI**;*

*To my aunt **Emine DENİZALTI**;*

*To my sisters **Zeynep SEVİNÇ** and **Sibel DENİZALTI**;*

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ABBREVIATIONS

Abbreviation		Explanations
acac	:	Acetylacetonate
1-Ad	:	1-Adamantyl
Ar	:	Aryl
ATH	:	Asymmetric transfer hydrogenation
BARF	:	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
BINAM	:	1,1'-binaphthalenyl-2,2'-diamine
BINAP	:	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bn	:	Benzyl
BuOH	:	Buthanol
cat.	:	Catalyst
$CH(OEt)_3$	:	Triethyl orthoformate
COD	:	1,5-cyclooctadiene
Cy	:	Cyclohexyl
DIPAMP	:	Ethane-1,2-diylbis[(2-methoxyphenyl)phenylphosphane]
DiPP	:	N-(2,6-Diisopropylphenyl)imidazole
DME	:	1,2-Dimethoxyethane
DMF	:	N,N'-Dimethylformamide
DMSO	:	Dimethylsulfoxide
ee	:	Enantiomeric excess
Et	:	Ethyl
Et_2O	:	Diethylether
EtOH	:	Ethyl alcohol
GC	:	Gas chromatography
HPLC	:	High performance liquid chromatography
Hz	:	Hertz
IPA	:	Isopropyl alcohol
^{i}Pr	:	Isopropyl
$KN(SiMe_3)_2$	:	Potassium bis(trisilylmethyl)amide
L-DOPA	:	(*S*)-2-Amino-3-(3,4-dihydroxyphenyl)propanoic acid
mp	:	Melting point
Me	:	Methyl
MeCN	:	Acetonitrile

ABBREVIATIONS (Continue)

Abbreviation		Explanations
MeOH	:	Methanol
MS	:	Mass spectrometry
Mes	:	Mesityl (or 2,4,6-trimethylphenyl)
NHC	:	N-heterocyclic carbene
NMR	:	Nuclear magnetic resonance
NOESY	:	Nuclear overhauser effect spectroscopy
Nu	:	Nucleophile
OAc	:	Acetate
OMe	:	Methoxy
OTf	:	Triflate
Ph	:	Phenyl
PPh_3	:	Triphenylphosphine
PCy_3	:	Tricyclohexylphosphine
R	:	Alkyl
$SiMe_3$	:	Trimethylsilyl
^{t}Bu	:	*tert*-Butyl
THF	:	Tetrahydrofuran
TLC	:	Thin layer chromatography
X	:	Halogen
s	:	Singlet
d	:	Doublet
t	:	Triplet
m	:	Multiplet
br	:	Broad
α	:	Alpha
β	:	Beta

1. INTRODUCTION

1.1 Chirality

Chirality, also known as handedness, is used to describe an object that cannot be superimposable on its mirror image. In such a case, there are two possible forms of the same object. Two mirror images of a chiral molecule are named enantiomers or optical isomers (Figure 1.1) (Lin et al., 2001; Chirality, 2011).

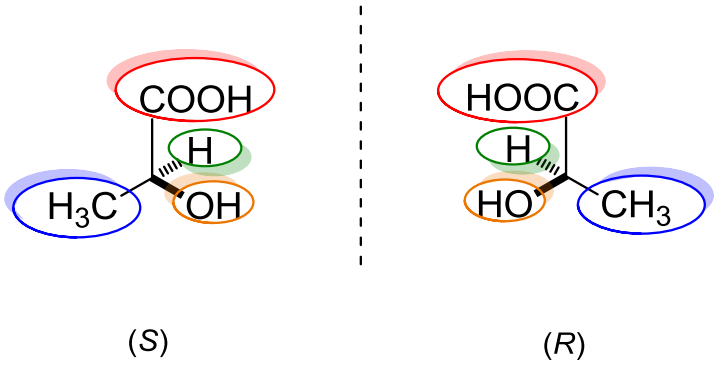


Figure 1.1. Enantiomers of lactic acid.

Enantiomers have the same chemical and physical properties. For example, they have the same melting point, chromatographic retention time, infrared spectroscopy and nuclear magnetic resonance. However, enantiomers interact differently in the presence of another chiral molecules and rotate plane polarized light in opposite direction. Enantiomer that rotates the plane of polarized light clockwise is denoted as dextrorotatory enantiomer (*d*) or (+). Its mirror image is denoted as levorotatory enantiomer (*l*) or (-). A mixture of equal amounts of enantiomers is called racemic that do not rotate plane polarized light (Lin et al., 2001; Chirality, 2011).

1.1.1 Importance of chirality

Chirality plays an important role for the existence of life. Many biologically active molecules are chiral, including proteins, sugars. Enzymes, which are biocatalysts in living organisms, are made from proteins. They distinguish between the two enantiomers of a chiral substrate. Enantiomers react with receptors in different ways, depending on their absolute configuration. One

enantiomer will fit inside and be bound, whereas the other enantiomer will not fit and is unlikely to bind (Figure 1.2) (Stereochemistry, 2011; Chirality, 2011).

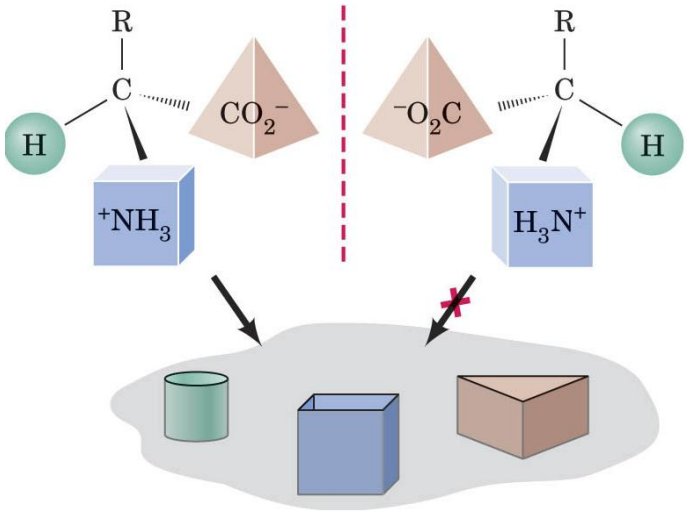


Figure 1.2. The binding specificity of a chiral receptor site for a chiral molecule.

The usage of enantiopure compounds is increasing especially in pharmaceutical industry. Drugs can exist as a pair of enantiomers. However, both enantiomers may not be biologically active. One enantiomer may have beneficial effect while the other may lead serious side effects or beneficial but definitely different effects. This showed that chirality plays an important role in biological systems. A well-known example of different biological activity of enantiomers is thalidomide disaster. Thalidomide was administered to women for treating morning sickness in pregnancy. Unfortunately, the (*R*)-enantiomer has the desired effect, whereas the (*S*)-enantiomer is teratogen, causing mutation in human embryos. Figure 1.3 presents a number of examples of different effects of enantiomers (Enantiopure drug, 2011).

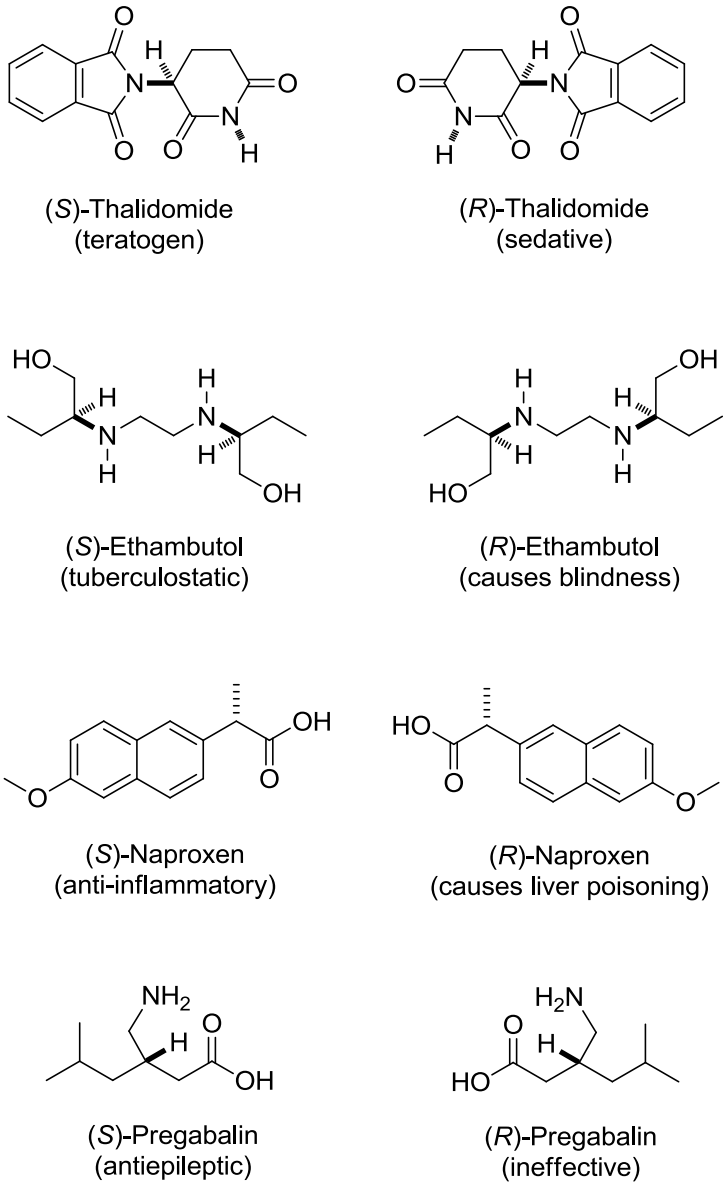
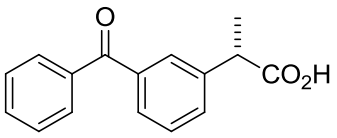
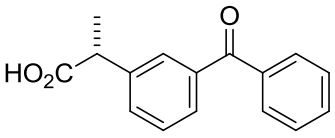


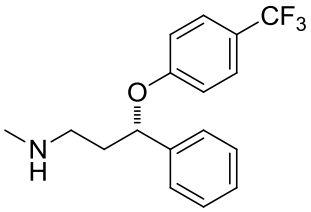
Figure 1.3. Examples of different effects of chiral drugs.



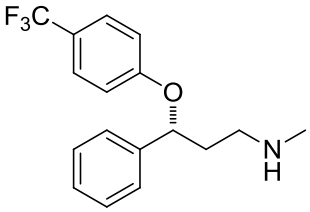
(*S*)-Ketoprofen
(toothpaste additive to prevent periodontal disease)



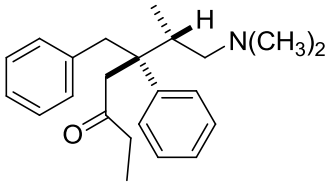
(*R*)-Ketoprofen
(analgesic)



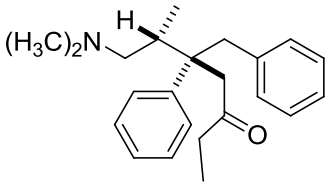
(*S*)-Fluoxetine
(treatment of migranes)



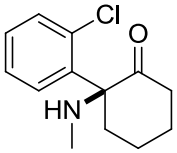
(*R*)-Fluoxetine
(treatment of depression)



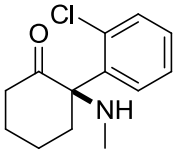
(*S*)-Propoxyphene
(cough suppressant)



(*R*)-Propoxyphene
(painkiller)



(*S*)-Ketamine
(anaesthetic)



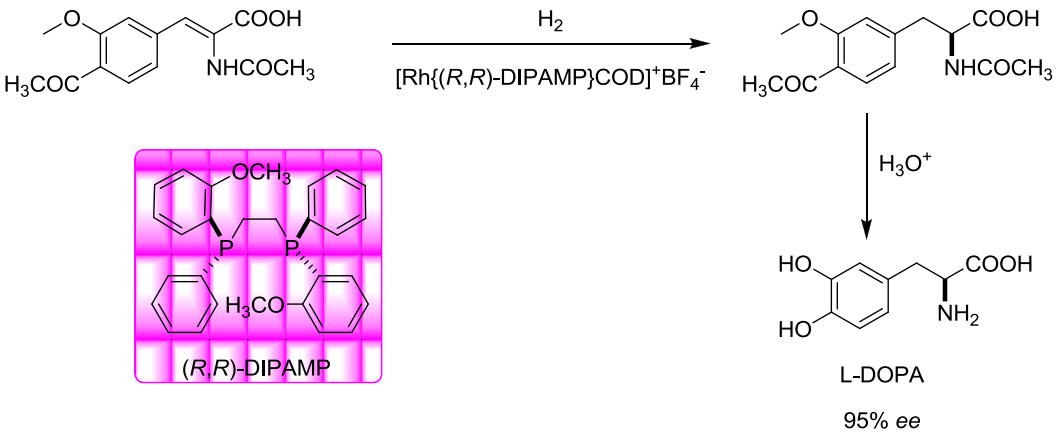
(*R*)-Ketamine
(halucinogen)

Figure 1.3. Examples of different effects of chiral drugs (continue).

1.1.2 Asymmetric Synthesis

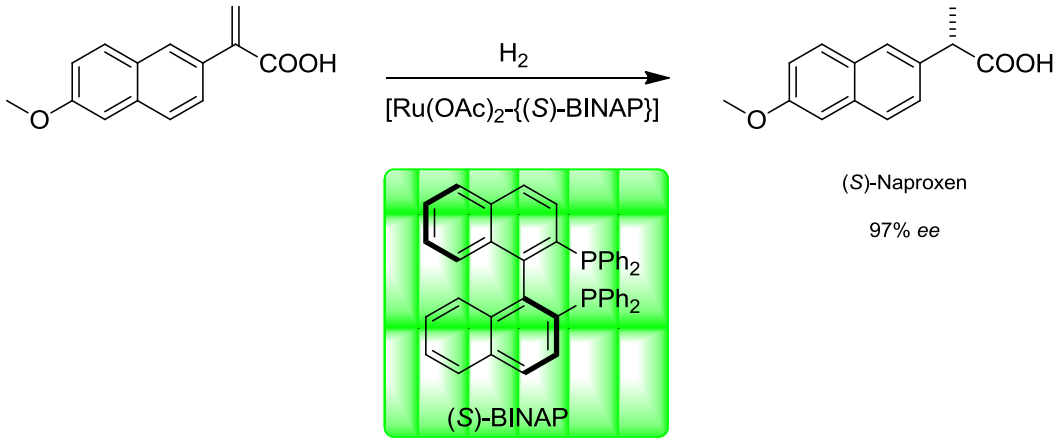
The chemists have tried to develop efficient synthetic methods to obtain pure enantiomer because the preparation of enantiomerically pure compounds has increased especially in pharmaceutical industry. There are three main ways to obtain enantiopure compounds: (i) resolution of racemates, (ii) chiral pool synthesis (includes the usage of chiral starting materials), (iii) asymmetric synthesis.

Asymmetric synthesis, also known as enantioselective or stereoselective synthesis, is the most frequently used method for obtaining chiral molecules. In this method, an achiral substrate is converted into a chiral substrate. The first methods were carried out by William S. Knowles and Ryoji Noyori. In 1968, Knowles developed chiral phosphine ligand modifying Wilkinson's catalyst. This catalyst was employed in Monsanto's production of L-DOPA, which is an important anti-Parkinson's drugs (Scheme 1.1) (Knowles et al., 1968; 2002).



Scheme 1.1. Synthesis of L-DOPA.

A few years later, Ryoji Noyori published a chiral BINAP ligand that was successfully used in enantioselective hydrogenation of C=C bonds and ketones (Scheme 1.2) (Miyashita et al., 1980; Ohta et al., 1987; Noyori et al., 1987; Tani, et al., 1984).



Scheme 1.2. Synthesis of (*S*)-Naproxen.

1.2 N-Heterocyclic Carbenes (NHCs) as Alternative to Phosphines

N-Heterocyclic carbenes (NHCs), also called Arduengo carbenes, are neutral compounds with a divalent carbon atom located between the two heteroatoms, at least one of which is typically a nitrogen in a position α to the carbene carbon (Roland and Mangeney, 2005; Schuster et al., 2009). The first isolation of a stable NHC was reported by Arduengo in 1991 (Arduengo et al., 1991). Since then, a wide range of NHCs have been synthesized (Figure 1.4) (Díez-González et al., 2009; Frémont et al., 2009).

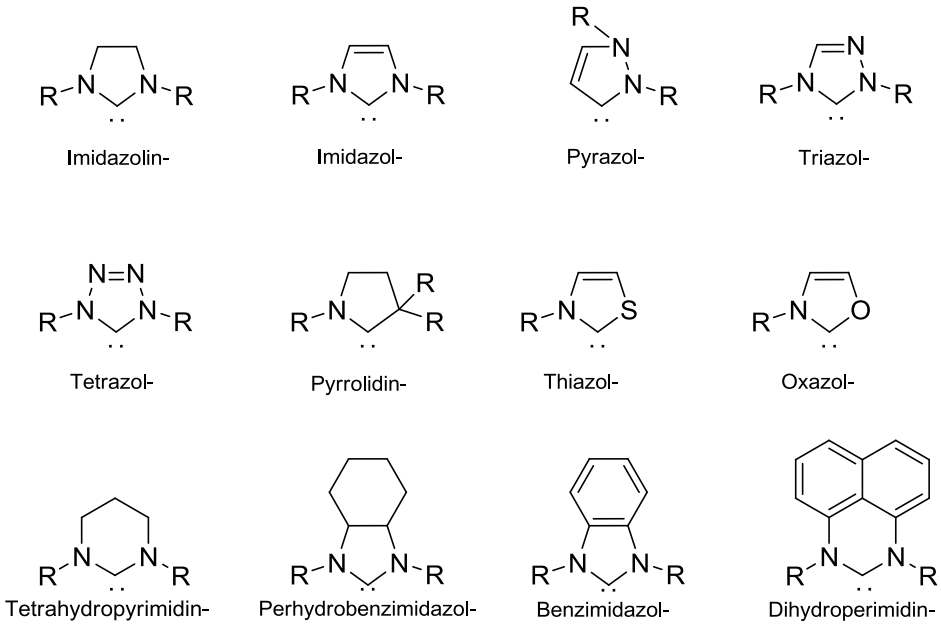
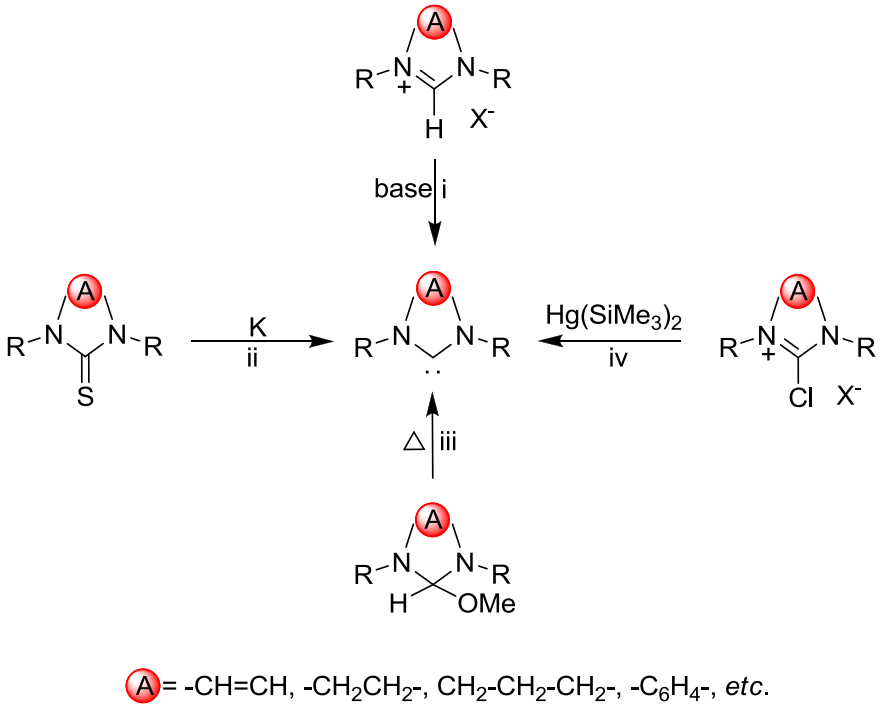


Figure 1.4. Structures of the most common NHCs.

There are several methods to allow the formation of free NHCs: i) deprotonation of an azolium salt, ii) desulfurization of thioureas with molten potassium, iii) vacuum pyrolysis under removal of volatiles, iv) treatment of chloro amidinum and azolium salts with bis(trimethylsilyl)mercury (Scheme 1.3) (Nair et al., 2004; Dröge and Glorius, 2010).



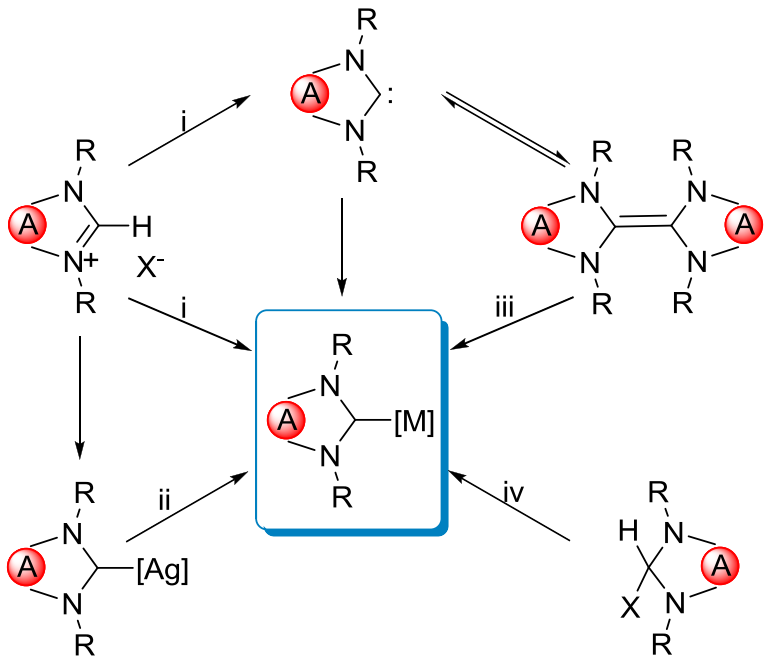
Scheme 1.3. Methods for the formation of free NHCs.

Due to the fact that NHCs are excellent σ-donors, which allows for very strong NHC-metal bonds and prevents decomposition of the catalyst, they have become the focus of intense study in organometallic chemistry (Cavallo et al., 2005; Díez-González et al., 2009; Jacobsen et al., 2009; Radius and Bickelhaupt, 2009).

1.3 NHC Complexes

N-Heterocyclic carbenes (NHCs) have been used as ligands for transition metal complexes by Wanzlik and Öfele in 1968 (Wanzlik, 1968; Öfele, 1968). In the early 1970s, Lappert and co-workers investigated their organometallic chemistry using electron-rich olefins *i.e.* the NHC dimers as precursors (Cardin et al., 1972; 1973; Çetinkaya et al., 1993; Çetinkaya et al., 1994; Lappert, 2005).

NHC complexes can be prepared by diverse methods (Scheme 1.4): i) the commonly used method is deprotonation of the azol(in)ium salts by a strong base such as NaH, KO^{t}Bu, KN(SiMe$_3$)$_2$ *etc*. to generate the carbene which is then transferred onto the metal precursor. In this method, free carbene can be used without being isolated (*in situ*) or isolated. The *in situ* complexation of the ligand has the advantage of not requiring to prepare and isolate the free NHC. Moreover, a base can be added directly to the reaction media or Brønstedt basic anions (such as OMe-, OAc-, acac-) on the metal precursor that can form the desired ligand *in situ* by deprotonation (Frémont et al., 2009); ii) the second method is transmetallation. Basic silver(I) oxide is a convenient precursor for silver(I)-NHC complexes (Wang and Lin, 1998; Bildstein et al., 1999). These complexes can be used as an attractive NHC transfer agents in the presence of an organometallic fragment bearing a metal more electronegative than silver. Also, these complexes do not have to be isolated during transmetallation reaction (Garrison and Youngs, 2005; Lin et al., 2009); iii) the third one is the cleavage of electron-rich olefins. They have been used as a source of carbene for transition metal complexes (Lappert et al., 1971; Çetinkaya et al., 1993; Çetinkaya et al., 1994); iv) the fourth method is oxidative addition of an azolium salt by activation of C2-X (X = Me, Halogen) bond.



Scheme 1.4. Synthetic pathways for the generation of transition metal–NHC complexes.

NHCs show many interesting properties that make them valuable as ligands. They are excellent σ-donors and form strong metal-carbon bonds, therefore these complexes have better air and thermal stability than phosphine analogues. N-Heterocylic carbene complexes have proved to be more effective catalysts in many catalytic reactions including olefin metathesis, C-C coupling reactions, hydrosilylation reactions (Perry and Burgess, 2003; Mauduit and Clavier, 2006; Nolan, 2006).

Development of chiral NHC ligands for enantioselective catalysis is a logical extension in this field. Asymmetric reactions using chiral NHCs are an efficient method to optically active compounds (Nair et al., 2004; Mauduit and Clavier, 2006). The first chiral carbene complexes were synthesized by Lappert in 1983 (Coleman et al., 1983). None of them, however, was tested in asymmetric catalysis. Several years later, in 1990s, Herrmann (Herrmann et al., 1996) and Enders (Enders et al., 1997) synthesized chiral NHC complexes for asymmetric catalysis. Later on, the first effective chiral NHC complex was synthesized by Burgess in 2001. The complex was used for asymmetric hydrogenation of alkenes which gave high stereoselectivity (Powell et al., 2001; Perry and Burgess, 2003) (Figure 1.5).

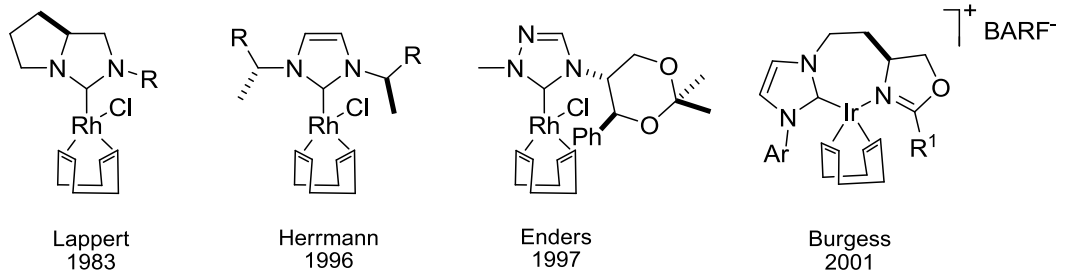


Figure 1.5. Chiral NHC complexes.

1.4 Classification of Chiral NHC Ligands

1.4.1 Chiral NHC ligands bearing chiral N-substituents and their applications

The method which was followed at first in the design of chiral NHCs was based on the introduction of N-substituents bearing a chiral center located on the carbon atoms adjacent to the nitrogen atoms within the ring. Their general

structure are showed in Figure 1.6 (César et al., 2004, Gade and Bellemin-Laponnaz, 2007).

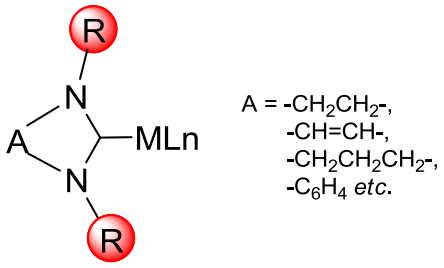
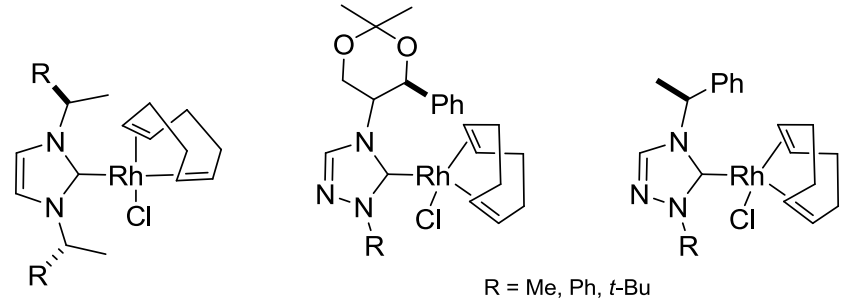


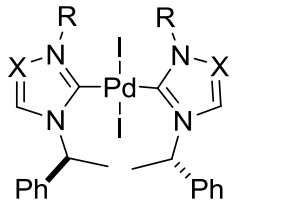
Figure 1.6. General structure of chiral NHC bearing chiral N-substituents.

The first chiral NHC ligand of this type were synthesized by Herrmann and Enders. Herrmann's group reported the usage of chiral NHC-Rh complexes in asymmetric hydrosilylation for the first time. Catalyst including naphthyl gave more than 90% conversion but low stereoselectivitiy (32% *ee*) in the hydrosilylation of acetophenone. It was stated that the optical induction is temperature-dependent. It decreases at higher temperatures (Herrmann et al., 1996). Enders and co-workers synthesized chiral triazolinylidene rhodium and palladium complexes. In the hydrosilylation of metyl ketones, they obtained the alcohols in 40-90% yield and up to 44% *ee* using rhodium complexes. Palladium complexes were tested for the Heck reaction which gave a product in only 8% *ee*. The reaction conditions were not specified (Enders et al., 1996; 1998). The group first prepared immobilised chiral carbene rhodium complexes (Enders and Gielen, 2001). The catalysts displayed good catalytic activities, although very low *ee* were obtained (24% *ee*).

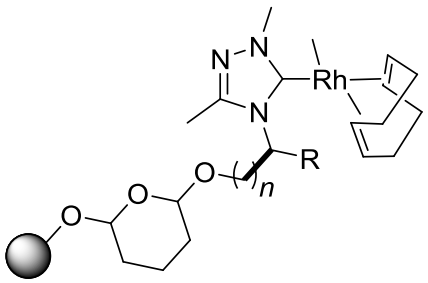


a: R = Ph
b: R = 1-Naphthyl

R = Me, Ph, *t*-Bu

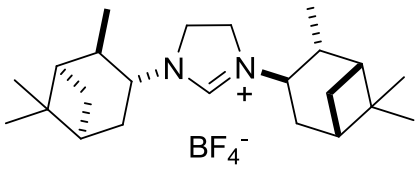


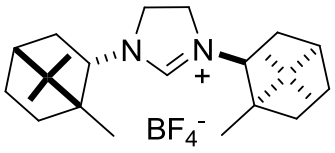
a: X = N, R = Ph
b: X = C, R = (*S*)-1-Phenylethyl



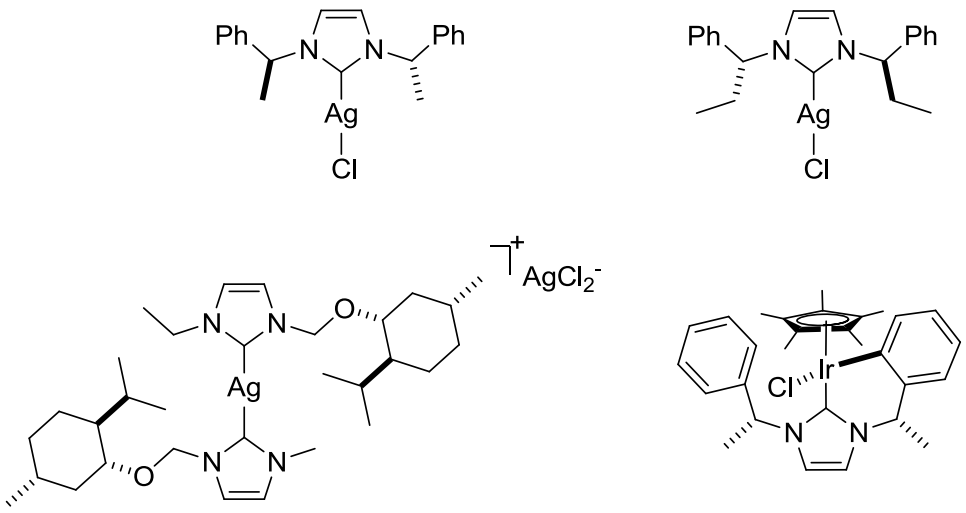
n = 1, R = ^{t}Bu
n = 4, R = H

Hartwing's group made an important contribution in the design of this type chiral NHC ligands. The imidazolinum salts were prepared from (-)-isopinocamphenylamine and (+)-bornylamine and used in the palladium catalyzed asymmetric oxindole reaction. They obtained 76% *ee* (Lee and Hartwing, 2001).

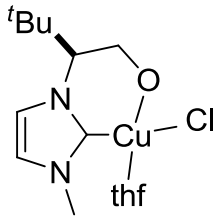




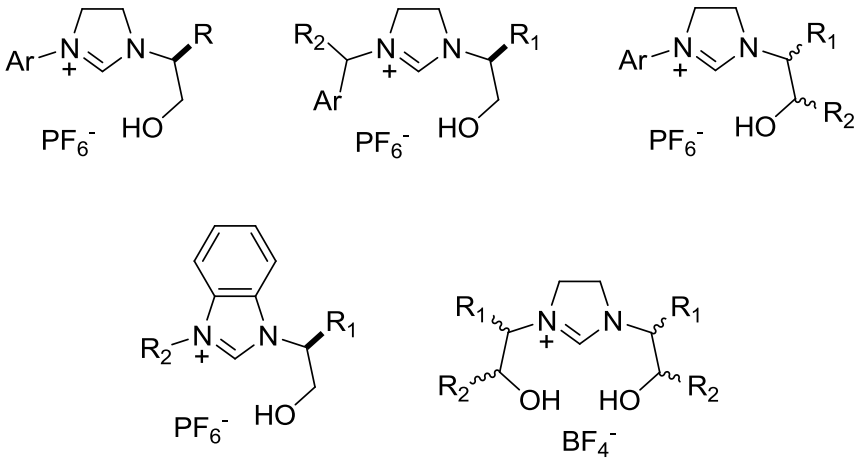
Peris, Fernández and co-workers developed chiral NHC-Ag and Ir complex (Ramírez et al., 2005; Corberán et al., 2006; 2007). These catalysts were applied in the catalytic diboration of olefins providing the products high yield with very low enatioselectivities (*ee*'s up to 10%).



Among the ligands of these types, polydentate ligands which combine the NHC unit with an anionic functional group have been developed recently. Thus, the rotation of the chiral substituents around the C-N axis is hindered (Gade and Bellemin-Laponnaz, 2007). Arnold's group reported the synthesis of the chiral copper complex. This complex was tested in the asymmetric conjugate addition of diethylzinc to cyclohexenone. They obtained moderate enantioselectivity (51% *ee*) (Arnold et al., 2004).



Afterwards, several groups prepared chiral alkoxy NHC ligands and their catalytic activities were investigated in the reactions catalyzed by copper such as asymmetric conjugate addition to cyclic enone, diethylzinc addition to aldehydes, asymmetric allylic alkylation and 1,4-addition of Grignard reagents to cyclic enones (Rix et al., 2005; Clavier et al., 2005; Jurčík et al., 2006; Gilani et al., 2008; Jennequin et al., 2010; Fengjun et al., 2011; Tissot et al., 2011).



Clavier et al. synthesized chiral imidazolinum salts bearing alkoxy group. These salts were tested in the copper catalyzed conjugate addition reaction. The place of the stereogenic center is of crucial role in this reaction (Figure 1.7). The stereogenic center in the alkoxymethylene side chain must be placed in the C2 position, near the NHC backbone (Clavier et al., 2005).

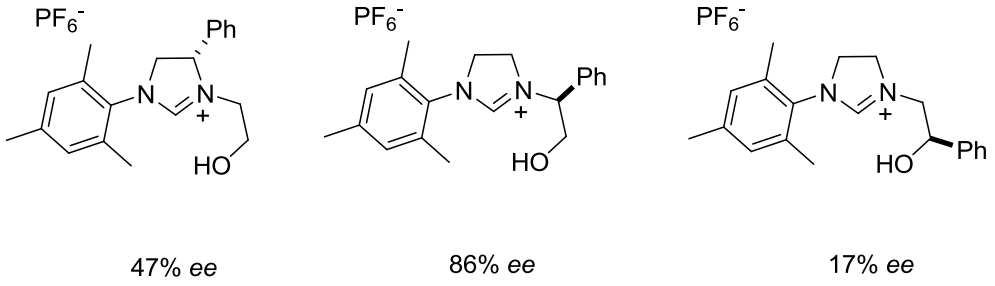
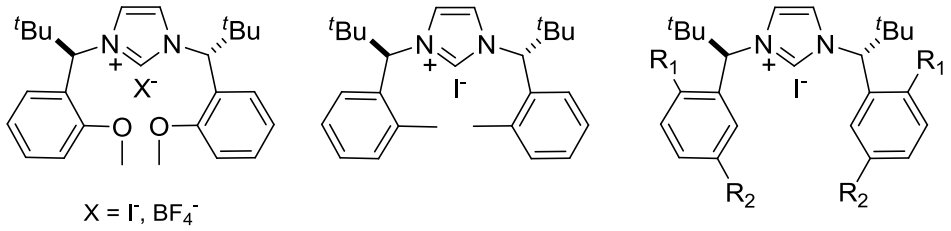
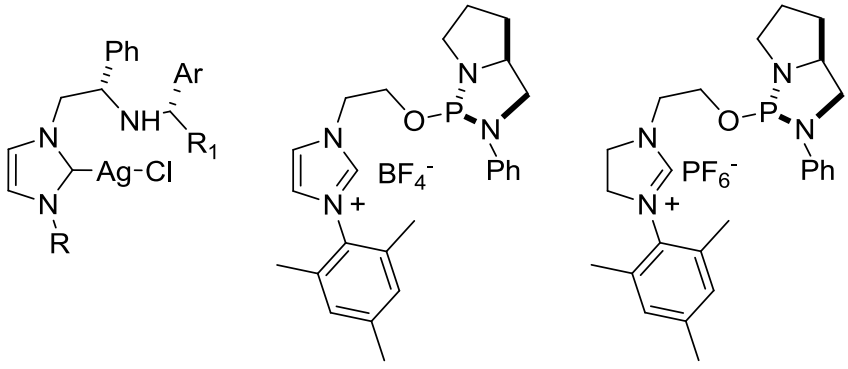


Figure 1.7. The importance of the position of the stereogenic center.

Chiral imidazolium ligands, prepared by Künding and co-workers, were tested in the Pd-catalyzed asymmetric α-arylation of amides (Künding et al., 2007). When the ligand bearing *ortho* methoxy substituent was used, the best enantioselectivity was gained (89% *ee*). Using the other ligand, which includes *ortho* methyl group, oxindoles were obtained in excellent enantioselectivities (95% *ee*). The authors further developed chiral NHC ligands and used them in the asymmetric intramolecular α-arylation of amide enolates containing heteroatom substituents to furnish optically active 3-alkoxy or 3-aminooxindoles, which are useful and important intermediates for the synthesis of biologically active chiral oxindoles, in high yields and enantioselectivities (97% *ee*) (Jia et al., 2008).

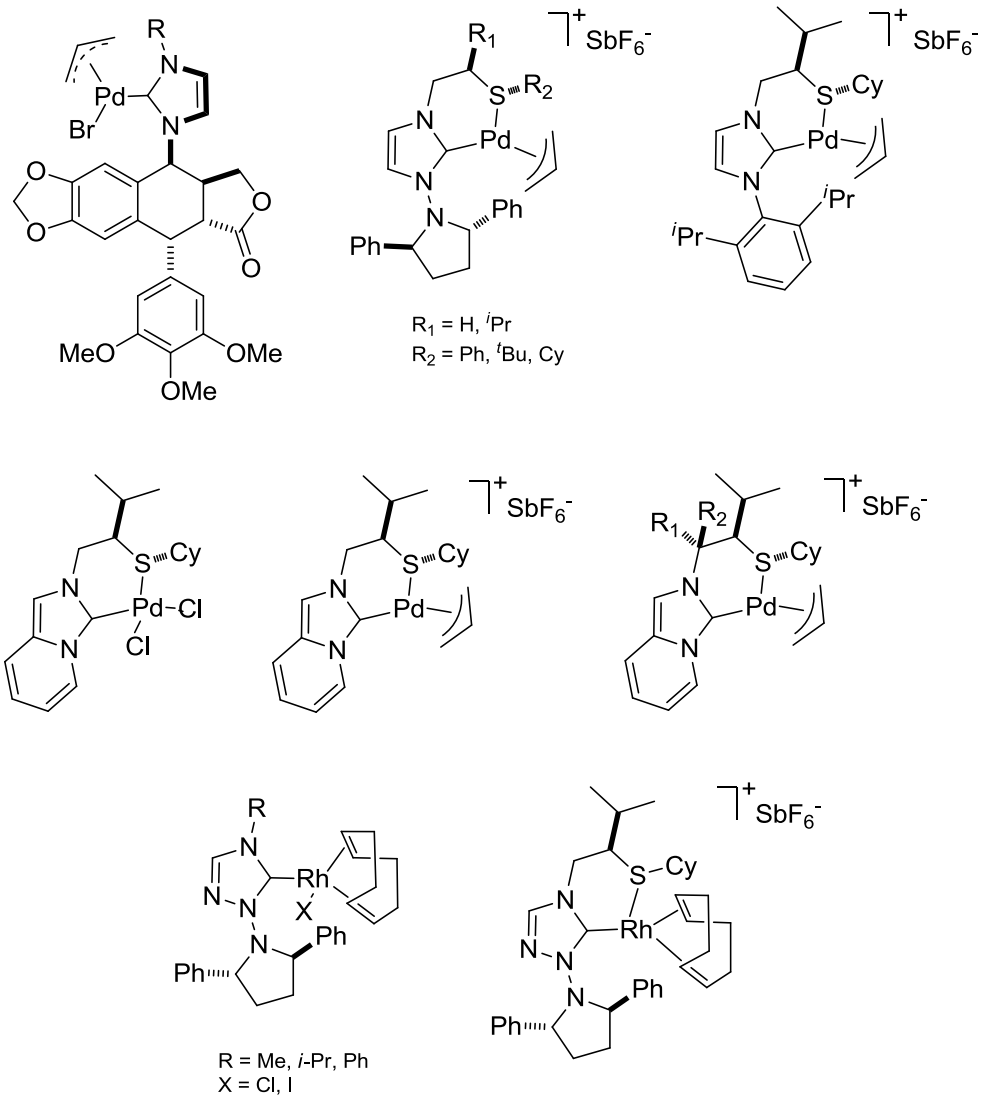


Roland's group developed chiral amino NHC-Ag(I) complexes and used them to generate *in situ* chelating NHC-amino palladium(II) complexes. These complexes were evaluated in the asymmetric allylic alkylation using (*E*)-1,3-diphenyl-3-en-yl acetate and dimethyl malonate (80% *ee*). They also investigated the effect of addition of PPh_3 to preformed NHC-amino palladium complexes in this catalytic reaction. In the absence of PPh_3, conversion was 33% with 76% *ee*. By adding PPh_3, the reaction was completed after 1 h with 10% *ee*. They assumed that decrease of the enantioselectivity could be due to the replacement of the chiral chelating amino side chain on the palladium by PPh_3 (Flahaut et al., 2006; 2007a; 2007b). Toselli et al. synthesized NHC ligands containing chiral 1,3,2-diazaphospholidenes and they investigated their catalytic activities in asymmetric allylic alkylation reaction. The association of a strong σ-donor ligand with chiral 1,3,2-diazaphospholidines led to an improvement of enantioselectivity (89% *ee*) (Toselli et al., 2008).



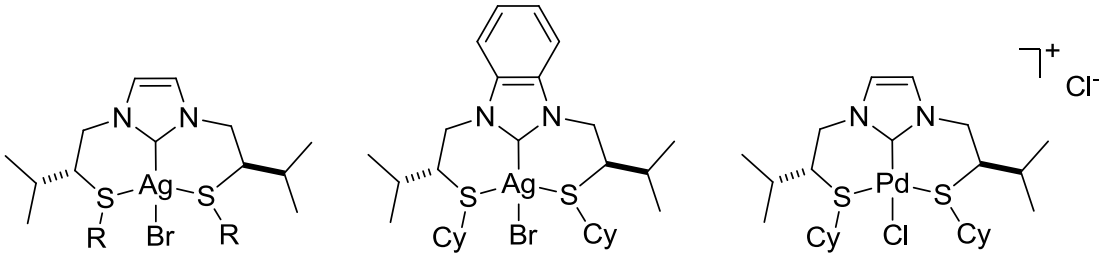
In 2006, Li et al. reported chiral NHC ligands derived from naturally occuring podophylotoxin (Li et al., 2006). These chiral ligands and their palladium allyl complexes were found to be active catalyst in the asymmetric alkylation of (*E*)-1,3-diphenyl-3-en-yl acetate with diethyl malonate which gave a product in high yield and enantioselectivities (87% *ee*). Fernández and co-workers published a family of thioether functionalized chiral NHC-Pd complexes (Ros et al., 2006; Roseblade et al., 2007). Studies on the catalytic behavior of the Pd complexes revealed that these complexes were suitable catalysts in the

asymmetric allylic alkylation (*ee*'s up to 91%). They also prepared Rh complexes of monodentate and bidentate NHC ligands. These complexes were active catalysts in the asymmetric hydrosilylation of acetophenone with diphenylsilane. When R was *i*-Pr and X was I in monodentate rhodium complex, it was obtained in modarete yield (40%) and low enantioselectivity (8% *ee*). The selectivity was slightly dependent on the nature of NHC and strongly dependent on the solvent and reaction temperature. The most active catalyst gave the desired product in 88% yield with 62% *ee* (Ros et al., 2009).



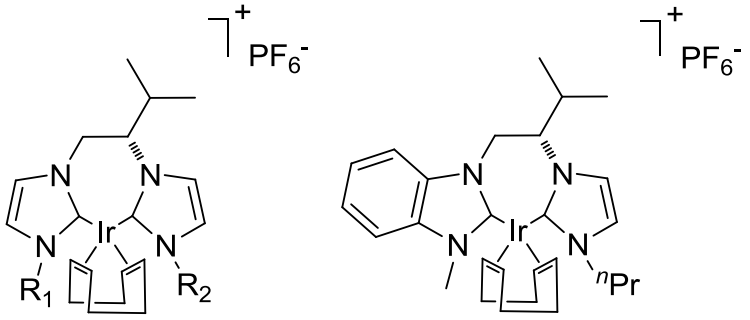
The authors have also published pincer type S/C(NHC)/S ligands and their silver and palladium complex (Iglesias-Sigüenza et al., 2009). Silver complexes

were used for the first time in the asymmetric 1,3-dipolar cycloaddition of iminoglycinates (*ee*'s up to 80%).



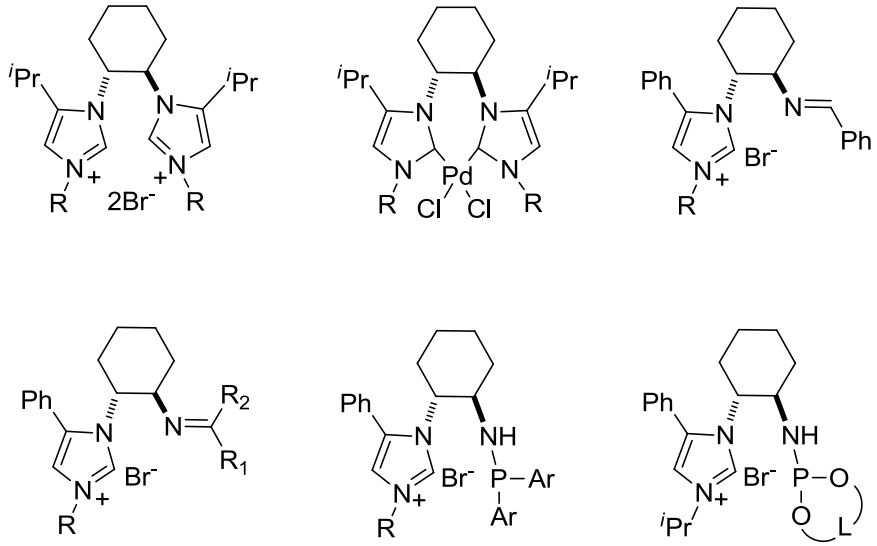
R = Cy, ^{t}Bu, Ph, Bn

Diez and Nagel described the synthesis of chiral bis(NHC) iridium(I) complexes and their application in the asymmetric transfer hydrogenation of ketones, affording the corresponding chiral alcohols in high yields and moderate to good enantioselectivities of up to 68% (Diez and Nagel, 2010).

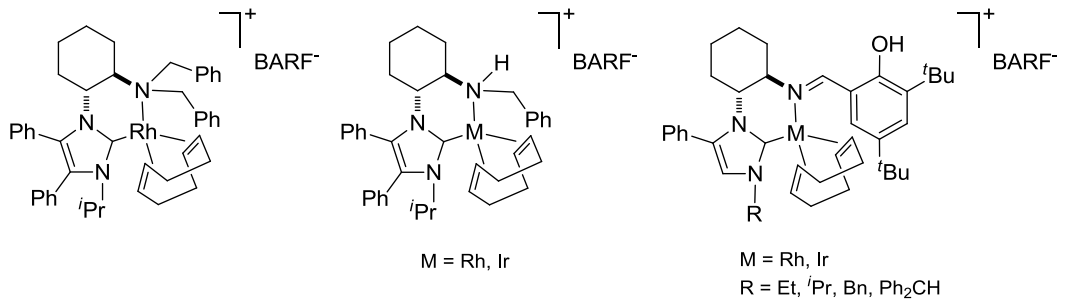


Douthwaite's group developed a series of chiral NHC ligands derived from *trans*-1,2-diaminocyclohexane and their complexes (Bonnet et al., 2003; Bonnet and Douthwaite, 2003; Bonnet et al., 2004; Hodgson and Douthwaite, 2005). Chiral di-NHC-Pd complexes were tested in the asymmetric intramolecular cyclization of amide. However, only 11% *ee* was observed (Bonnet et al., 2003). NHC-imine ligands were applied to asymmetric allylic alkylation reaction giving a maximum *ee* of 92% (Bonnet and Douthwaite, 2003). NHC-P ligands synthesized by this group were also used for the asymmetric allylic alkylation reaction (45% *ee*) and asymmetric transfer hydrogenation of acetophenone (*ee*'s up to 37%) (Hodgson and Douthwaite, 2005). Comparison with NHC-imine

ligands indicate that the presence of phosphine increases the yield of allylic alkylation reaction although NHC-P ligands displayed lower enantioselectivity.

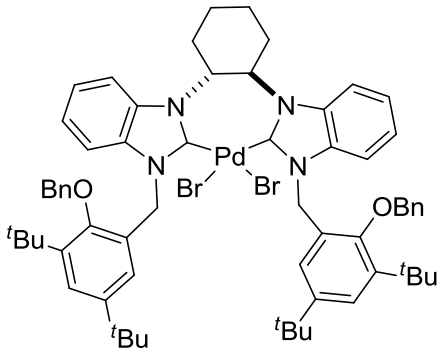


In 2009, Douthwaite's group reported the synthesis of NHC-amine- Rh and Ir complexes and investigation of their catalytic application to ATH (Dyson et al., 2008; 2009). Complexes of NHC-amines were found to be inactive catalysts for ATH (Dyson et al., 2009). The best result (56% *ee*) was obtained from Ir complex, when R is ^{i}Pr group. The enantioselectivity is sensitive to the N-substituent. When R is Et group, they could not observe *ee* value (Dyson et al., 2009).

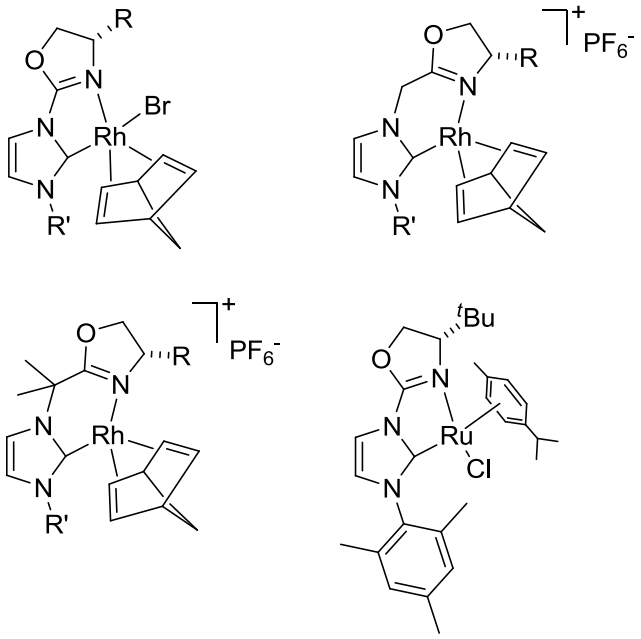


Very recently, Shigeng et al. synthesized palladium complex of chiral di-NHC ligand derived from chiral 1,2-cyclohexanediamine (Shigeng et al., 2012). This complex was used to catalyze the enantioselective Suzuki-Miyaura couplings

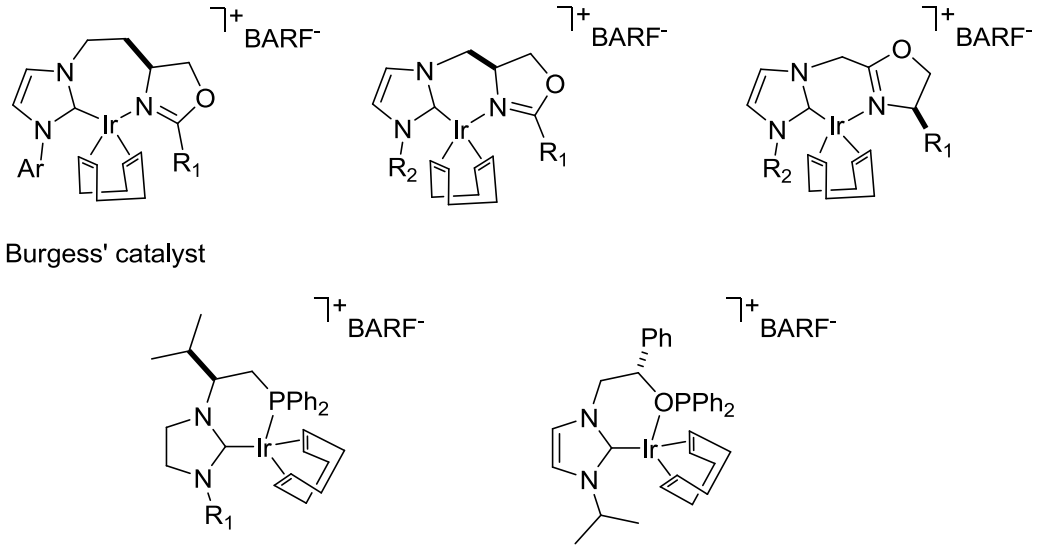
of aryl bromides with arylboronic acids in good yields and moderate enantioselectivities (up to 61% *ee*).



Gade, Bellemin-Lapponaz and co-workers reported the evaluation of NHC-Rh complexes bearing oxazoline units in the asymmetric hydrosilylation of ketones (Gade et al., 2004; César et al., 2005; Schneider et al., 2009). The best results were obtained at -60 ^{o}C giving 92% yield and 90% *ee* for the hydrosilylation of acetophenone in the presence of the first catalyst and a slight excess of $AgBF_4$. It is important the use of $AgBF_4$ since the same reaction performed without it gave both poor yield (53%) and enantioselectivity (13%). Although the other two systems were found to be active at room temperature they did not gave significant enantioselectivities. In comparison with the ligands in which the two heterocycles are connected by CH_2 or CMe_2 bridge, highly rigid type remains the most efficient system for the hydrosilylation reaction. This group also prepared chiral ruthenium complex and tested it in various asymmetric reactions such as transfer hydrogenation, hydrogenation of ketones or isomerization of allylic alcohols. This chiral complex did not show catalytic activity in none of these reactions (Poyatos et al., 2006).



Burgess' group synthesized several chiral NHC-Ir complexes containing oxazoline ligands (Powell et al., 2001). Their catalytic properties were investigated in asymmetric hydrogenations of alkenes. They obtained good enantioselectivities (98% *ee*). The substituent on the oxazoline ring (R_1) affected both enantioselectivity and yield of the reactions. The best yield and *ee* were gained from R_1 = 1-Ad. Other substituents, such as R_1 = Ph, $CHPh_2$ and ^{t}Bu, were also studied. The complexes, however, gave lower yield and selectivity than R_1 = 1-Ad. In 2006, Pfaltz's group developed NHC-oxazoline Ir complexes for asymmetric hydrogenation of alkenes which gave moderate to high enantioselectivities (Nanchen and Pfaltz, 2006). For catalysts, which oxazoline linked to NHC from 4-position, the choice of R_1 is crucial for activity as well as enantioselectivity. When R_1 = *tert*-butyl was replaced by an isopropyl group, enantioselectivity decrease. Complex which bears the least bulky substituent on the NHC ring, was the most selective catalyst. For other catalysts, enantioselectivity and activitiy strongly depend on the oxazoline substituent. High conversions were obtained for R_1 = *tert*-butyl and 1-adamantyl. Good enantioselectivities were obtained by catalysts with a smaller methyl or isopropyl group at the NHC moiety.



Nanchen and Pfaltz also prepared enantiomerically pure phosphino- and phosphinooxy-substituted NHC-Ir complexes (Nanchen and Pfaltz, 2006). Although they displayed low conversions for unfunctionalized olefins, these catalysts proved to be suitable for hydrogenation of the α,β-unsaturated ester, allylic alcohol and imine. However, they obtained moderate enantioselectivities. NMR analyses of Ir complexes showed fluxional behavior of the chelate ring (Figure 1.8). For this reason, asymmetric induction is effected such lack of rigidity (Nanchen and Pfaltz, 2006).

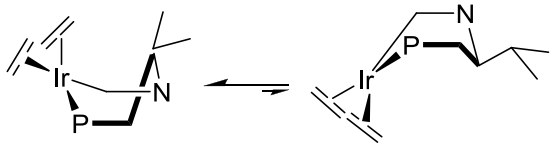
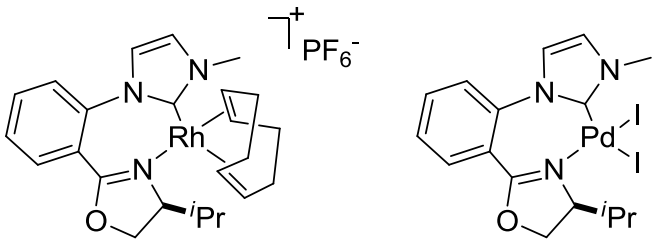
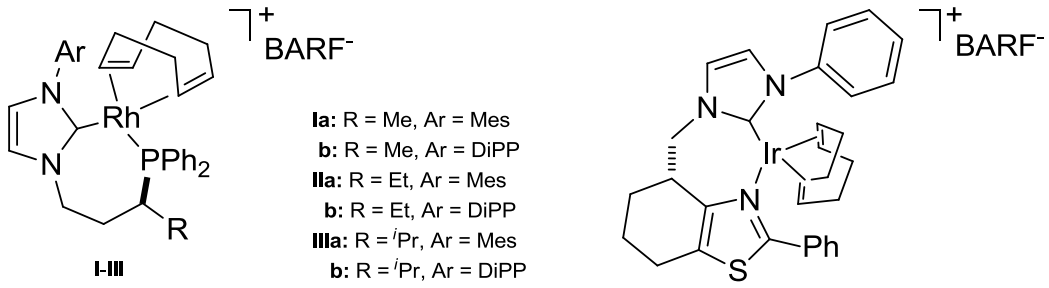


Figure 1.8. Two conformations of Ir complex.

Crudden's group reported the synthesis of chiral NHC-Rh and Pd complexes bearing oxazoline goup (Ren et al., 2004). The rhodium complex was investigated in the hydrosilylation of acetophenone and the hydroboration of styrene. However, they obtained poor enantioselectivities (< 10% *ee*).

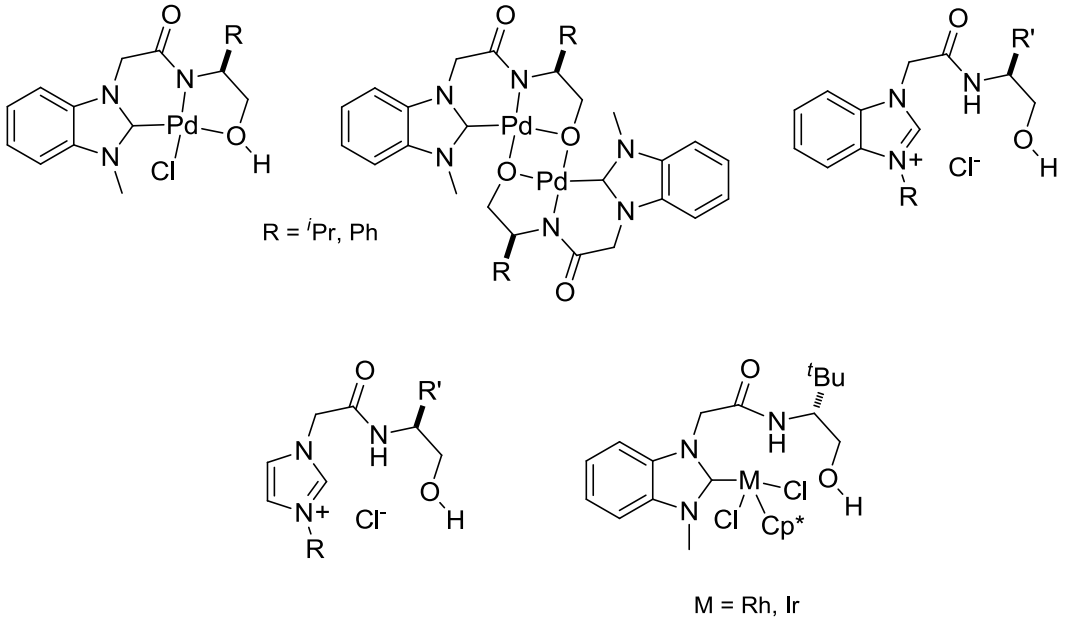


In 2011, Passays et al. synthesized chiral phosphine-carbene Rh complexes and investigated their catalytic properties in asymmetric hydrogenation of dehydroalanine and dehydrophenylalanine derivatives. Catalysts **Ib-IIIb** were totally inactive in the hydrogenation of dehydrophenylalanine however catalyst **IIIb** gave the product with 47% conversion and 60% *ee*. Catalysts containing DiPP (**Ib-IIIb**) led to lower conversions, but higher *ee*, than catalysts bearing mesityl (**Ia-IIIa**). Catalyst **IIIb** gave the product with 60% *ee* and 42% conversion, and catalyst **IIIa** gave 37% *ee* and 90% conversion (Passays et al., 2011). Källström and Andersson have developed chiral NHC-Ir complex bearing thiazole (Källström and Andersson, 2006). This complex evaluated in the asymmetric hydrogenation of olefins and is able to reduce various tri-substituted olefins with good enantioselectivities with *ee*'s ranging from 34% to 90%.

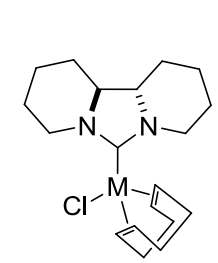


Yoo et al. reported chiral monomeric and dimeric tridentate NHC-Pd complexes tested in the asymmetric oxidative Heck-type reactions of aryl boronic acids with alkenes. Dimeric complexes gave higher enantioselectivity than the monomeric ones (*ee*'s up to 94%). It was implied that the ″counter axial groups″ (isopropyl and borate) effected the enantioselectivity (Yoo et al., 2010). Chiyojima and Sakaguchi synthesized chiral hydroxy-amide functionalized NHC ligands and Rh(III) and Ir(III) complex (Sakaguchi et al., 2010; Chiyojima and Sakaguchi, 2011). They used complexes in the asymmetric transfer hydrogenation of acetophenone using 4% mol catalyst at room temperature. After 20 h, they obtained 46% yield and 18% *ee* from Ir complex. In contrast to Ir complex, Rh complex did not showed any catalytic activities. They also tested

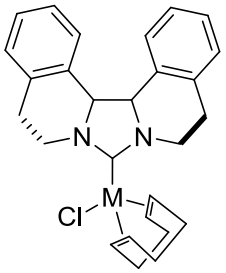
benzimidazolium salt (R = Me, R' = ^{t}Bu) in the same reaction and gained 41% yield and 18% *ee*. Therefore, they performed this reaction using chiral ligands without isolating complexes. They obtained 58% yield and 60% *ee* using KPF_6 as additive.



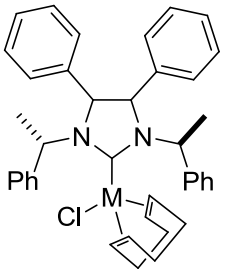
Herrmann and co-workers reported the synthesis of the chiral partially reduced biisoquinoline- or 2,2'-bipiperidine-based NHC ligands and their rhodium and iridium complexes (**IV**-**IX**) (Herrmann et. al., 2006; Baskakov et al., 2007). Complexes **IV**-**VI** were tested in asymmetric hydrosilylation and transfer hydrogenation of acetophenone giving the desired product with very low enantioselectivities (2-28% *ee*). However, complexes **VII**-**IX** were catalytically active in the asymmetric hydrogenation of methyl 2-acetamidoacrylate; iridium complexes gave moderate enantioselectivities (67% *ee*) (Baskakov et. al., 2007). Neutral and cationic iridium complexes bearing chiral phenanthroline-derived benzimidazolylidene ligands (**X**-**XII**) were synthesized by Metallinos and Du (Metallinos and Du, 2009). These complexes were tested hydrogenation of acetamidoacrylates, the best results were obtained using 2,9-diphenyl-substituted (**XI**), which afforded the desired product in 97% yield and 81% *ee*.



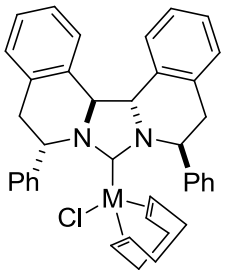
IV



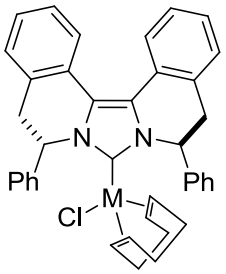
V



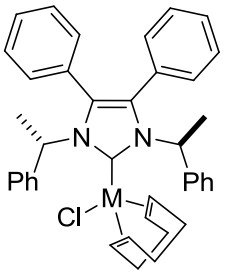
VI



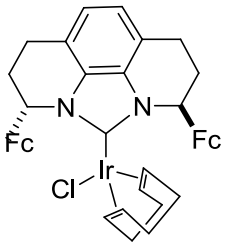
VII



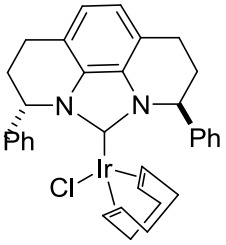
VIII



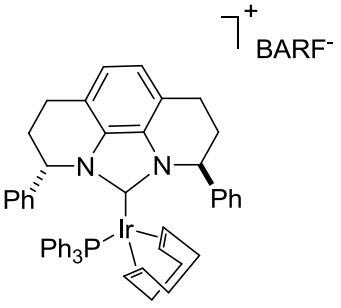
IX



X

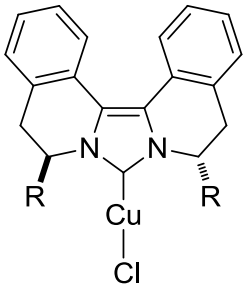


XI



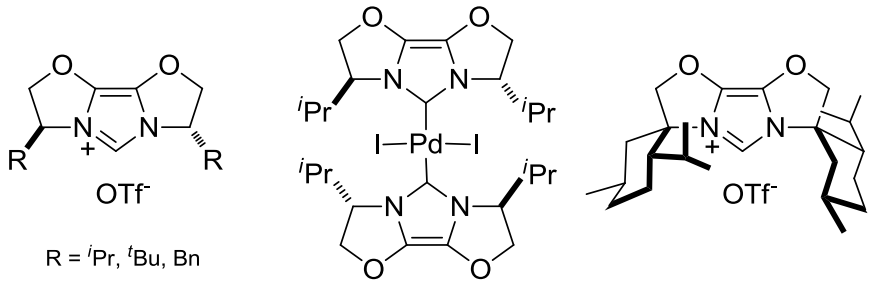
XII

Seo et al. designed chiral biisoquinoline-based NHC-Cu complexes (Seo et al., 2008) to evaluate them in the enantioselective allylic alkylation reaction. The corresponding products were obtained in moderate enantioselectivities (77% *ee*).



R = ^{i}Bu, ^{i}Pr, Cy

Glorius et al. designed imidazolium triflates and palladium complex prepared form bioxazolines and oxazolineimines (Glorius et al., 2002). These ligands and palladium complex were tested in the Pd-catalyzed intramolecular α-arylation of amides, giving oxindole in high yield with 43% *ee*. Glorius and co-workers further developed a highly sterically demanding chiral NHC ligand (Würtz et al., 2009). This ligand was applied to intramolecular α-arylation of bromides and chlorides, providing highly enantioselective formation of oxindoles in up to 99% *ee*.



1.4.2 Chiral NHC ligands bearing chiral elements within the heterocycle and their applications

The second strategy for the generation of chiral NHCs is to use imidazolinium salts containing substituents in the 4- and 5-position of the heterocycle (Figure 1.9).

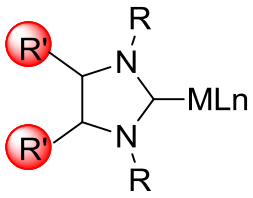
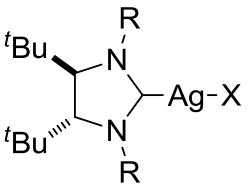


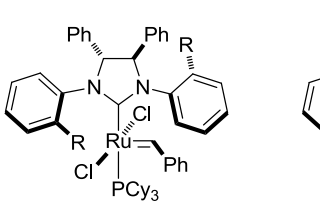
Figure 1.9. General structure of chiral NHC bearing chiral elements within the heterocycle.

The chiral NHC-Ag complexes prepared by Mangeney and Alexakis was used in the copper catalyzed asymmetric addition of diethylzinc to cyclohexenone (69% *ee*) (Pytkowicz et al., 2001; Guillen et al., 2001; Alexakis et al., 2003; Winn et al., 2005).



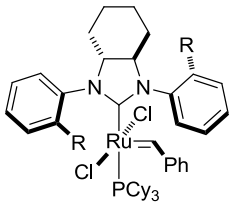
R = Me, Bn, Bn-*o*-OMe

Chiral imidazolinylidene-Ru complexes (**XIII**, **XIV**) have been also used by Grubbs and co-workers in the stereoselective ring-closing metathesis reaction and they obtained high enantioselectivity (91% *ee*) (Seiders et al., 2001). Replacement of the *o*-Me groups by the ^{i}Pr groups in the complex, the enantioselectivity was increased. Grubbs' group further prepared several chiral NHC-Ru complexes (**XV**-**XVII**) for improving enantioselectivity. These complexes were tested in asymmetric ring-closing metathesis reaction of (*E*)-trisubstituted olefins providing the corresponding products with five- to seven-membered rings in up to 92% *ee* (Funk et al., 2006). Fournier et al. synthesized Grubbs-type catalysts (**XVIII**) and evaluated them in triene desymmetrisation reaction with up to 94% *ee* (Fournier et al., 2006; 2008).

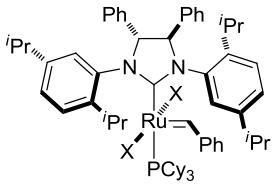


XIII

R = Me, ^{i}Pr

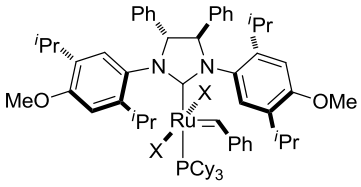


XIV



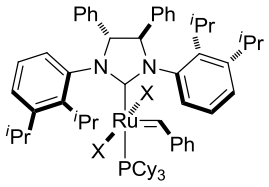
X = Cl, I

XV



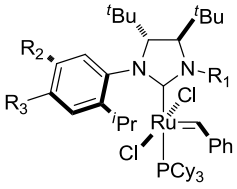
X = Cl, I

XVI



X = Cl, I

XVII

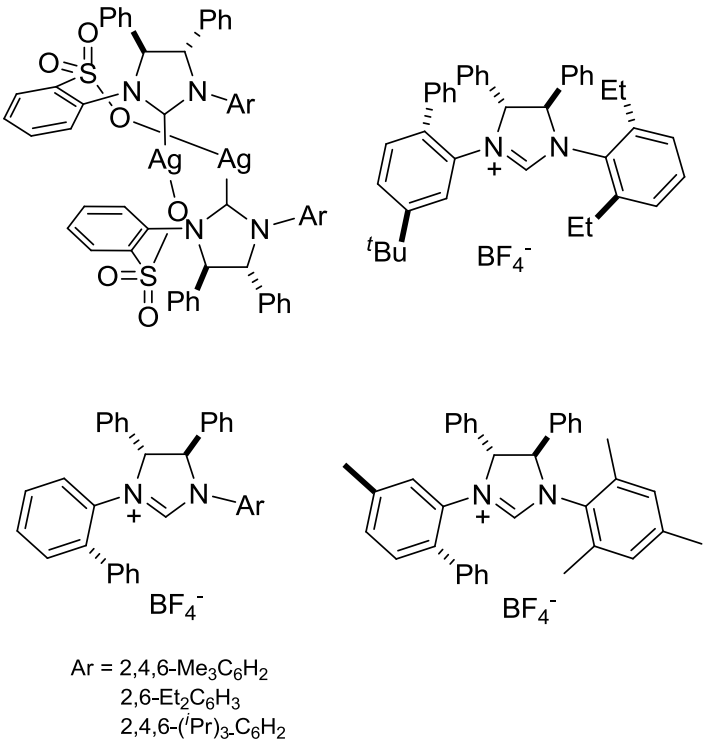


R_1 = Me, ^{n}Pr, Bn

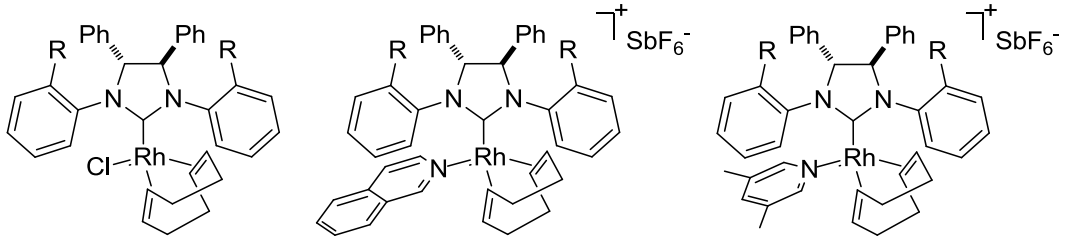
XVIII

Hoveyda and co-workers reported a series of chiral NHC-Ag complexes. They used them in allylic alkylation reaction using various vinyl reagents, aryl- and heteroaryllithium reagents affording the corresponding products in high enantioselectivities (Lee et al., 2008; Akiyama et al., 2010; Gao et al., 2010a; 2010b). Hoveyda's group has also synthesized chiral NHC ligands and investigated their catalytic activities such as enantioselective conjugate additions

of aryl and alkenyl groups to cyclic enones affording the desired β-aryl or β-vinylcycloalkanones in up to 98.5% *ee* (Lee and Hoveyda, 2009); and catalytic enantioselective conjugate boronate additions to cyclic and acylic α,β-unsaturated compounds (98% *ee*) (O'Brien et al., 2010).

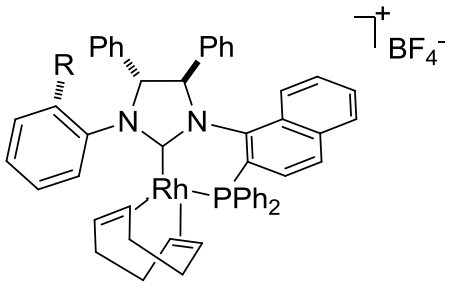


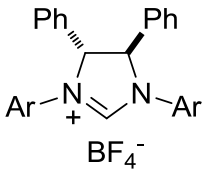
Faller and Fontaine reported neutral and cationic chiral NHC-Rh complexes (Faller and Fontaine, 2006). These complexes were active catalysts for hydrosilylation of acetophenone but the products were obtained with poor enantioselectivities (*ee*'s up to 58%).

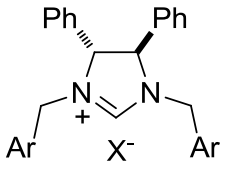


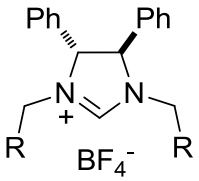
Becht et al. showed that NHC-Rh complexes were found to be active catalysts in the asymmetric conjugate addtion of arylboronic acids to α,β-unsaturated esters with up to 98% yield and 99% *ee* (Becht et al., 2005). Chiral

NHC ligands, as shown below, reported by several groups were tested in divers catalytic reactions. Alexakis' group published an efficient way to create all-carbon quaternary centers by applying the first asymmetric conjugate additions with Grignard reagents to trisubstituted enones using chiral ligands including aryl groups (Martin et al., 2006). Matsumoto et al. synthesized chiral NHC ligands derived from 1,2-diamino-1,2-diphenylethane, which aryl groups were directly linked to nitrogen atom or via methylene bridge, and examined their catalytic activities in the asymmetric conjugate additions of Grignard reagents to 3-substituted cyclohexenones, affording the products in good yield and up to 80% *ee* (Matsumoto et al., 2008). The last chiral NHC ligands illustrated below were developed by Arao et al. (Arao et al., 2006a; 2006b), which were used in both intramolecular α-arylation of amides (*ee*'s up to 67%) and asymmetric arylation of aldehydes with phenylboronic acid (*ee*'s up to 27%) (Arao et al., 2006b).

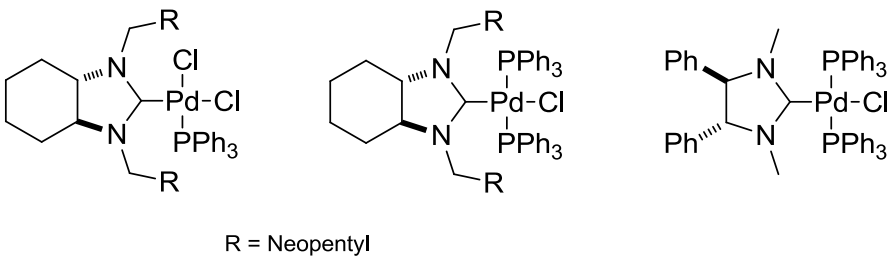






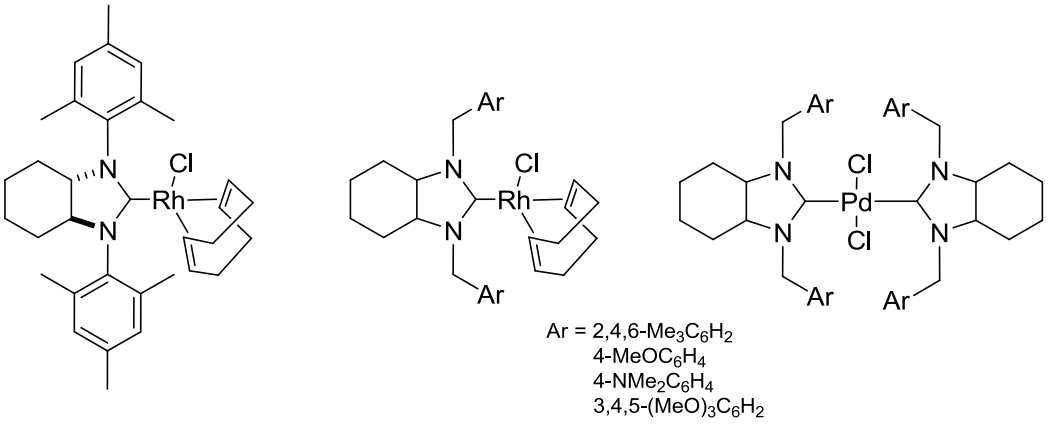


Fürstner's group synthesized chiral NHC-Pd complex containing *trans*-1,2-cyclohexanediamine backbone or phenyl group on the heterocycle (Fürstner et al., 2003; Kremzow et al., 2005), however, there has no application of this complex in any asymmetric catalytic reaction.

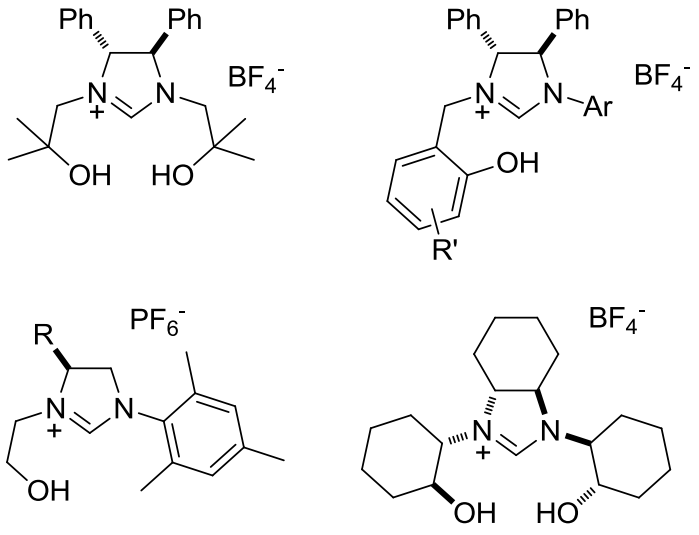


R = Neopentyl

Laï et al. has used chiral NHC-Rh complex in the asymmetric hydroformylation of styrene. However, enantioselectivity never excceeds 12.5% (Laï et al., 2009). Yiğit et al. synthesized 1,3-disubstituted-perhydrobenzimidazolium salts and their rhodium and palladium complexes derived from racemic cyclohexanediamine. Both ligands and complexes were tested various catalytic reactions such as hydrosilylation of acetophenone, arylation of benzaldehydes, Heck and Suzuki coupling reactions (Yiğit et al., 2005a; 2005b; Yiğit and Özdemir, 2007; Özdemir et al., 2006; Yiğit, 2009).



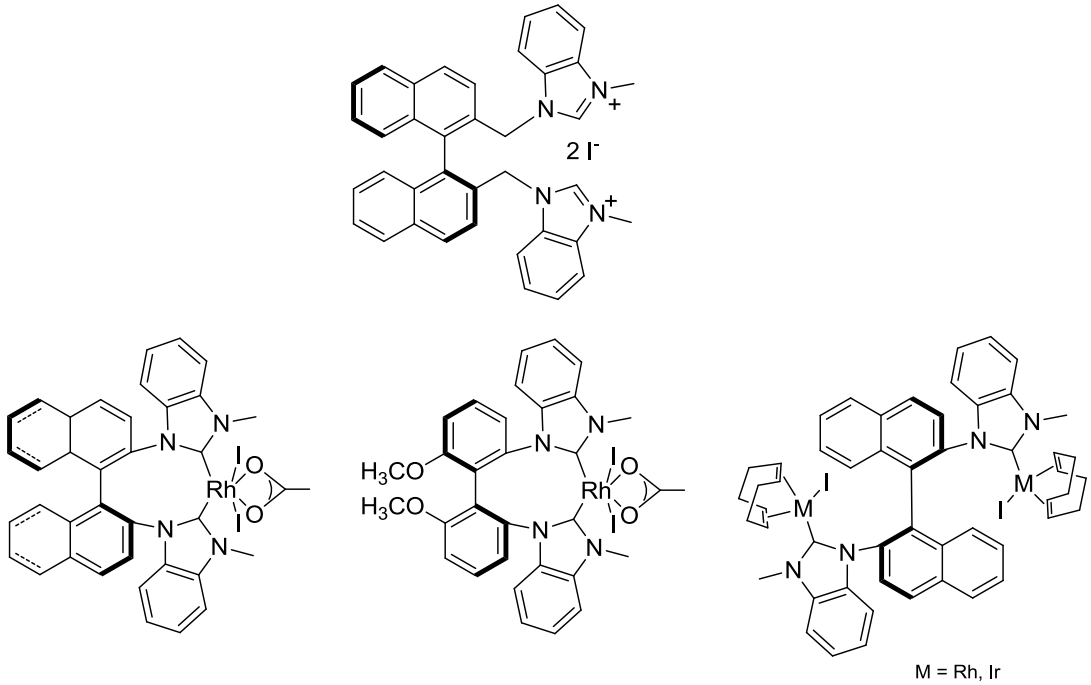
A series of chiral NHC bearing alkoxy ligands have been reported by several groups (Rix et al., 2005; Jurčík et al., 2006; Gilani et al., 2008; Uchida and Katsuki, 2009; Kehrli et al., 2010) and they was tested in the copper catalyzed asymmetric conjugate addition of dialkylzincs to acyclic enones (up to 97% *ee*), conjugate addition of dialkylzincs to enones (up to 66% *ee*), or diethylzinc addition to aldehydes (up to 66% *ee*).



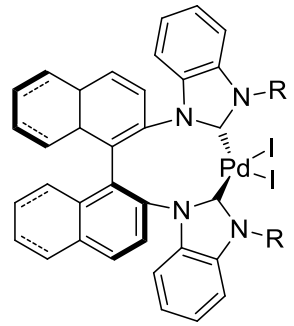
1.4.3 Chiral NHC ligands bearing an element of axial chirality and their applications

The term of axial chirality used to express a special case of chirality in which a molecule does not possess a stereogenic center but an axis of chirality-an axis about which a set of substituents is held in a spatial arrangement that is not superposable on its mirror image. This chirality is most commonly observed in atropisomeric biaryl compounds wherein the rotation about the aryl-aryl bond is restricted, for example, binaphthyls, biphenyls (Axial chirality, 2011). In asymmetric catalysis, the 1,1'-binaphthyl unit is one of the most widely used structural motifs in ligand design (Gade and Bellemin-Laponnaz, 2007).

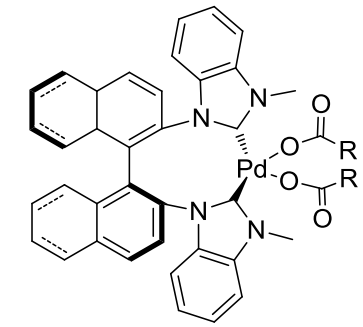
The first chiral NHC ligand containing a 1,1'-binaphthyl unit was published by Rajanbabu et al. (Rajanbabu et al., 2000). Shi and co-workers synthesized chiral NHC-Rh(III) derived from 1,1'-binaphthalenyl-2,2'-diamine (BINAM or H_8-BINAM) and 6,6'-dimethoxybiphenyl-2,2'-diamine. Differently from Rajanbabu's ligand, in this ligand, 1,1'-binaphthyl group was directly linked to NHC. These rhodium complexes were applied in the asymmetric hydrosilylation of methyl ketones (up to 98% *ee*) and 3-oxo-3-arylpropionic acid methyl or ethyl esters (up to 99% *ee*) (Duan et al., 2003; Xu et al., 2007; Chen et al., 2007a; Liu et al., 2009a). Shi and co-workers also prepared di-rhodium and iridium complexes but they not tested them in any catalytic reaction (Duan et al., 2003; Shi and Duan, 2005).



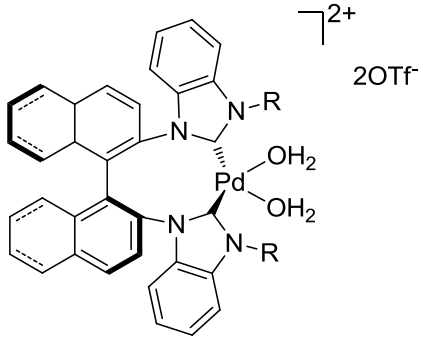
Shi's group has also developed a family of axially chiral bis(NHC)-Pd complexes bearing 1,1'-binaphthalenyl and 1,1'-biphenyl scaffold. These complexes displayed high chiral induction and catalytic activities in oxidative kinetic resolutions (94% *ee*) (Chen et al., 2007b; Liu et al., 2009b); conjugate addition of arylboronic acids to cyclic enones (97% *ee*) (Zhang and Shi, 2008a); and arylation of *N*-tosylimines with arylboronic acids (94% *ee*) (Ma et al., 2009). Neutral Pd(II) complexes synthesized from 1,1'-binaphthalenyl-2,2'-diamine (BINAM) or H_8-BINAM were used in the allylation of aldehydes with allyltributyltin to give the corresponding products in high yields (Zhang et. al., 2008b). Moreover, palladium complex synthesized from BINAM-bearing weakly coordinating acetate or trifluoroacetate counterions was tested in the in the allylic alkylation of (*E*)-1,3-diphenylprop-3-en-yl acetate. The reaction mixture was heated at 50 ^{o}C and stirred for 24 h. They found that complex was not effective in this reaction and the desired product was formed only in 13% yield with 7% *ee* (Zhang et al., 2008b). However the same complexes was also used in the enantioselective arylation of aldehydes and displayed moderate enantioselectivity (*ee*' up to 65%) (Zhang et al., 2010).



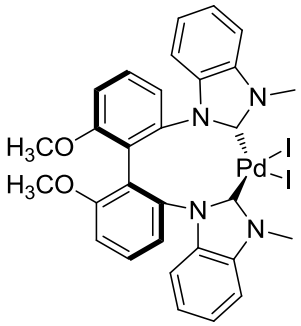
R = Me; Et; Bn; 3,5-dimethylbenzyl



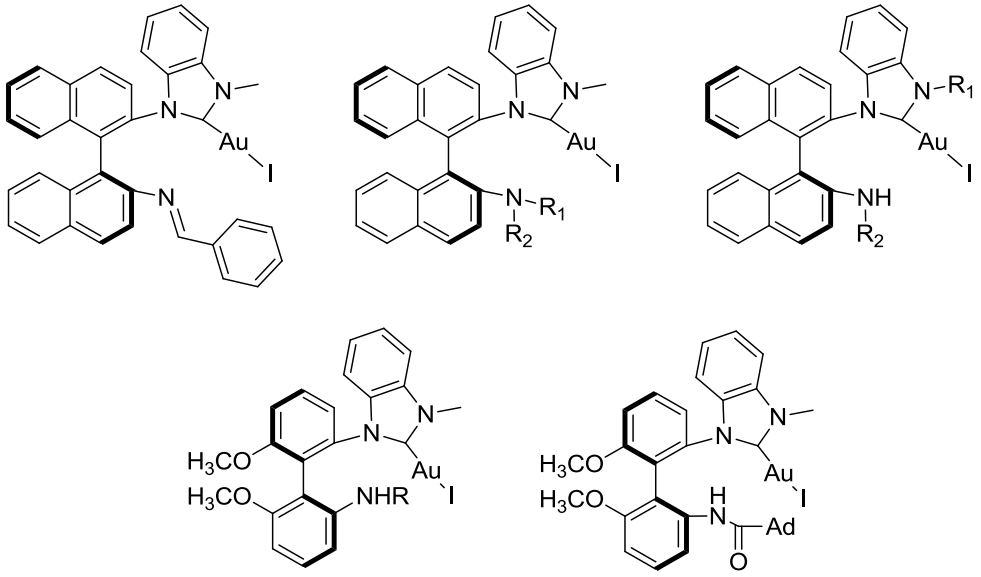
R = Me; CF_3



R = Me; Bn; 3,5-dimethylbenzyl

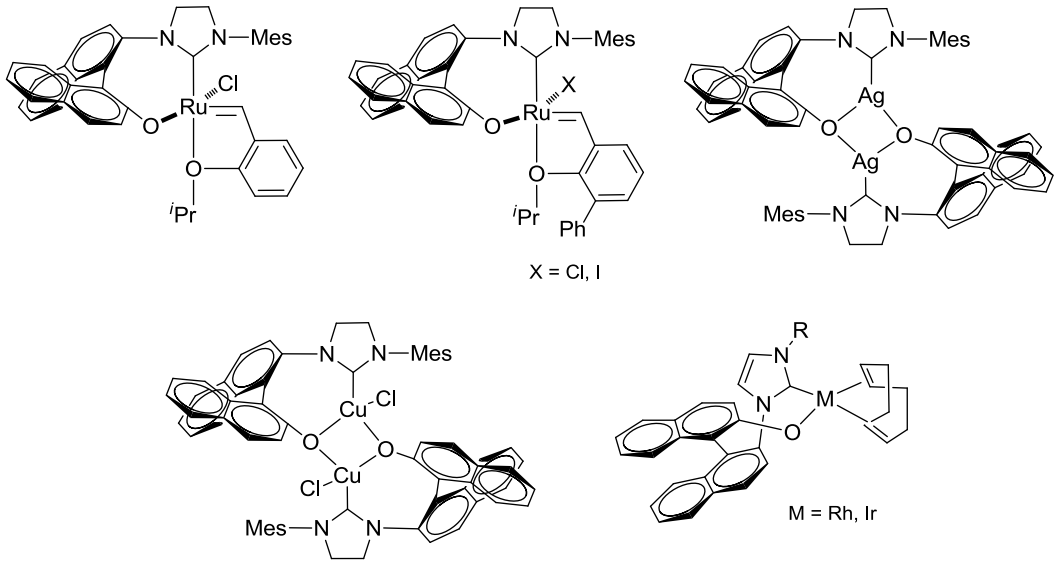


In recent years, Shi and co-workers reported chiral NHC-Au complexes using the same scaffold (Liu et al., 2011; Wang et al., 2011). These complexes have been used to catalyze asymmetric cyclization of 1,6-enynes or allene, giving the desired product in up to 70% *ee* and 44% *ee*, respectively.



Hoveyda's group has synthesized chiral ruthenium complexes (Van Veldhuizen et al., 2002; 2003; 2005). These complexes were tested ring opening

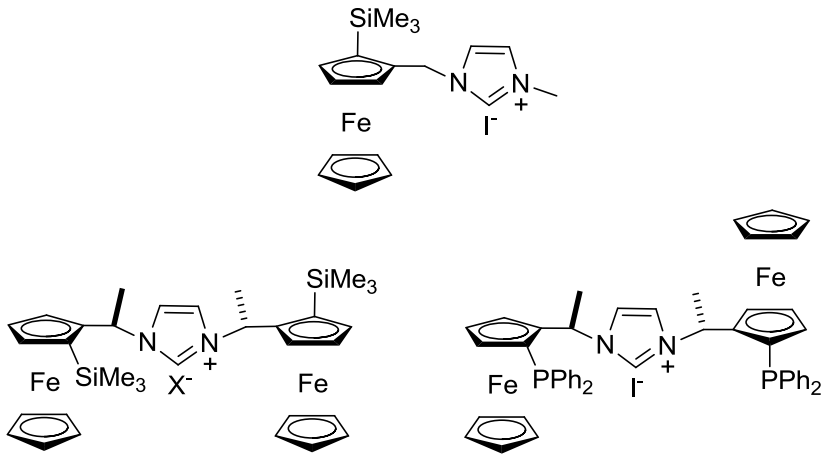
cross metathesis and the second complex, which X is Cl, was more active than the first complex. Hoveyda was also used this ligand in the copper catalyzed enantioselective formation of tertiary or quaternary carbon centers. Silver complex, containing this ligand, displayed good activity and enantioselectivity (98% *ee*) (Larsen et al., 2004). They also synthesized copper complex to gain insight to the identify of the active catalyst, which displayed highly effective catalytic activity. Moreover, Hoveyda and co-workers reported the first examples of copper-catalyzed asymmetric conjugate addition of alkyl- and arylzinc reagents to simple unactivated β-substituted cyclic enones using silver and copper complexes (Lee et al., 2006). They obtained the desired product in 67-98% yield and up to 98% *ee*. Chianese and Crabtree published chiral NHC rhodium and iridium complexes and applied these complexes in the asymmetric hydrosilylation of acetophenone (Chianese and Crabtree, 2005). Although rhodium complex gave low enantioselectivity, iridium complex displayed moderate enantioselectivity (60% *ee*).



1.4.4 Chiral NHC ligands bearing an element of planar chirality and their applications

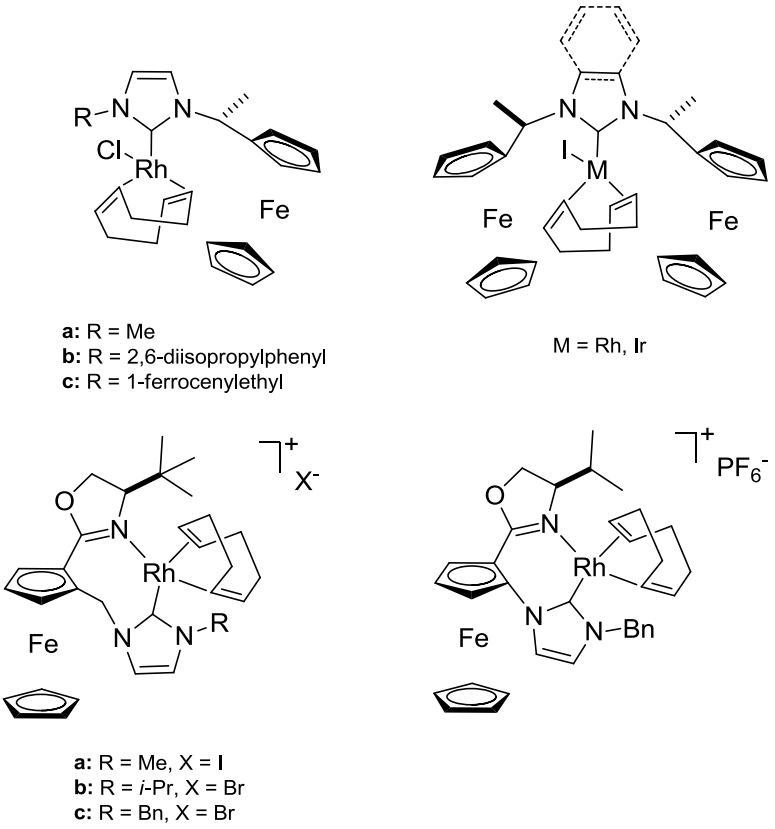
Planar chirality is used for chiral molecule lacking of an asymmetric carbon atom, but possessing two non-coplanar rings that are each dissymmetric and which cannot easily rotate about the chemical bond connecting them (Planar chirality, 2011). Ferrocene derivatives are the most encountered ones.

Bolm et al. reported the first planar chiral NHC ligand (Bolm et al., 2002). Its rhodium complex was tested in the hydrosilylation of ketones to give the corresponding alcohols, but it was only obtained racemic alcohols. Afterwards, Togni's group published chiral NHC bearing two ferrocenyl units linking to nitrogen atoms but they did not test this ligand in asymmetric catalysis (Broggini and Togni, 2002). In 2004, Gischig and Togni synthesized chiral tridentate PCP ligand and its palladium, ruthenium and copper complexes (Gischig and Togni, 2004; 2005).



Different ferrocene based chiral NHC complexes were prepared by several groups (Seo et al., 2003; Yuan et al., 2005; Jiang et al., 2009). In the hydrosilylation of 4'-metyl acetophenone, the racemic product was obtained in 55% yield using the imidazol-2-ylidene rhodium complex bearing 1-ferrocenylethyl substituent, which R is methyl group, after 72 h. Seo et al. also investigated the use of (benz)imidazol-2-ylidene Rh complexes bearing mono- and bis-ferrocenylethyl groups in the asymmetric transfer hydrogenation (ATH) reaction but they obtained low enantioselectivities. The best result was obtained from benzimidazolylidene Ir complex (Seo et al., 2003). Chelated ferrocene based-NHC complexes were also tested in the hydrosilylation of acetophenone. Although these complexes showed high catalytic activity, none of them displayed a significant enantioselectivity (up to 6% *ee*) (Yuan et al., 2005). The complex, which ferrocene substituent was directly linked to nitrogen atom, compared with Bolm's catalyst, the enantioselectivitiy increased (30-53% *ee*). It was suggested that this may be because of more rigid backbone of the ligand (Kuang et al.,

2009). This complex was also applied to ATH of acetophenone to give (*S*)-1-phenylethanol with 88% yield and 60% *ee* (Jiang et al., 2009).

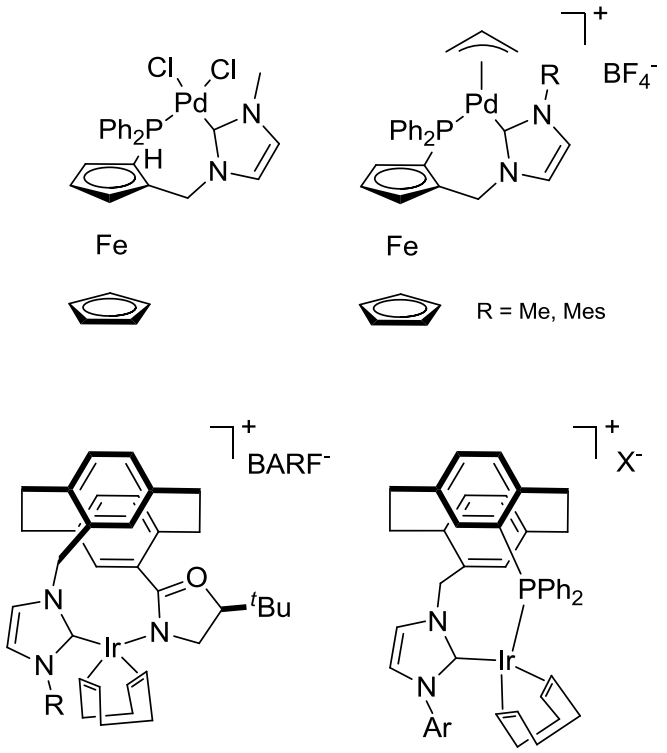


a: R = Me
b: R = 2,6-diisopropylphenyl
c: R = 1-ferrocenylethyl

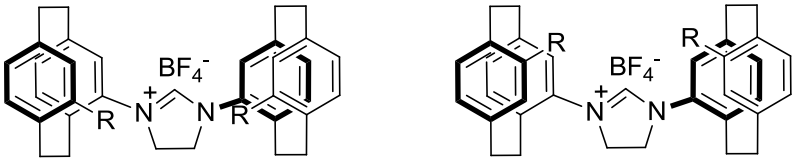
M = Rh, Ir

a: R = Me, X = I
b: R = *i*-Pr, X = Br
c: R = Bn, X = Br

In 2010, Debono et al. synthesized chiral ferrocenyl phosphine-imidazolium salts and their palladium complexes. They showed very good activites and moderate enantioselectivites (up to 42% *ee*) in the reaction of aryl bromides with arylboronic acids. This is the first example of asymmetric Suzuki-Miyaura reactions with NHC complexes. In this reaction, neutral palladium complexes showed better enantioselectivities than the cationic ones. Reducing temperature did not effect the enantioselectivity (Debono et al., 2010). Bolm et al. synthesized NHC-Ir complexes with a planar chiral [2.2] paracyclophane. These complexes have been applied as catalysts in the asymmetric hydrogenations of alkenes (Bolm et al., 2003).



Song et al. prepared chiral bis-paracyclophane NHC ligands (**XIX**) and tested them ruthenium catalyzed asymmetric hydrosilylation of ketones. They obtained 97% *ee* from the reactions performed using 1% mol catalyst in the presence of silver(I) triflate at room temperature (Song et al., 2005). In 2010, Ma et al. also reported a series of planar chiral NHC ligands (**XX-XXII**) (Ma et al., 2010). By using these ligands, they gained moderate enantioselectivities from the reaction of Rh-catalyzed 1,2-addition of arylboronic acids to aldehydes (*ee*'s up to 52%). The best result was obtained from **XXI** when R is Br and X is OTf^-. However, ligands **XX** showed very low yield and *ee* in this reaction.

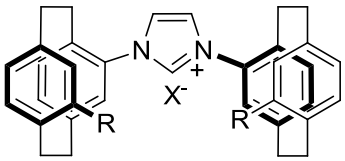


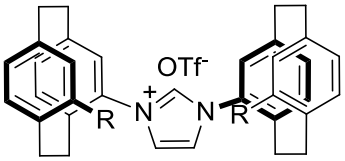
R = *o*-MeO-C_6H_5, Ph, H

XIX

R = Br, H

XX





R = Br, *o*-MeO-C_6H_5, Ph, *m*-MeO-C_6H_5, 1-Naphthyl, H

X = Cl^-, OTf^-

XXI **XXII**

1.4.5 NHC ligands bearing chiral ligands attached to metal and their applications

In other classification about chiral NHCs, chiralty is located in another ligand attached to metal atom instead of NHCs (Figure 1.10). There are a few reports in the literature in relation to this type of NHCs.

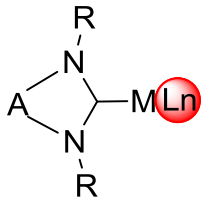
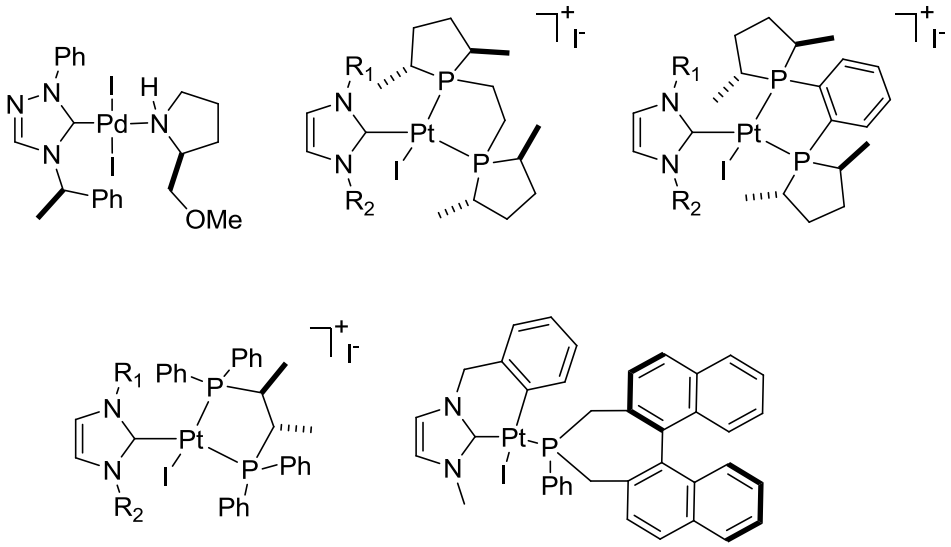


Figure 1.10. General structure of NHC bearing chiral ligand attached to metal atom.

Enders' group prepared triazolinylidene palladium complex that obtained by the addition of Lewis basic ligands to dimeric palladium complex (Enders et al., 1996). The palladium complex was used in asymmetric Heck type reaction but very low *ee* was obtained (< 8% *ee*). Marinettti and co-workers developed NHC-Pt complexes (Brissy et al., 2007; 2009a; 2009b). Their catalytic activities were examined in the asymmetric cycloisomerization reactions using allylpropargylamines, enynes affording the cycloisomerization product in good yields with up to 97% *ee*.



1.5 Aim of the Study

For the last decade, *N*-Heterocyclic carbenes (NHCs) have become the focus of intense study. These ligands have several valuable properties in catalysis, such as stronger σ-donors than their phosphines analogous, improving air and thermal stability of complexes. Because of these properties, NHC complexes have been used in catalytic reactions such as olefin metathesis, hydrosilylation, hydrogenation and C-C bond formation. Development of chiral NHC ligands for enantioselective catalysis become inevitable in asymmetric synthesis.

Chiral NHC ligands have been used in a large variety of metal asymmetric catalysed reactions, such as hydrogenation, olefin metathesis, conjugate addtition. However, transition-metal-catalyzed ATH of prochiral ketones or 1,2-addition of organoboronic acids to aldehydes using chiral NHCs as ligands has been limited so far and only a few examples have been reported. Generally, moderate to good conversions were obtained but with very poor enantioselectivities. Thus, it is still desirable to develop or find more active chiral catalysts and efficient catalytic systems for asymmetric catalysis.

In this thesis, our main aim was to synthesize chiral NHC complexes and to investigate their catalytic properties in asymmetric catalysis.

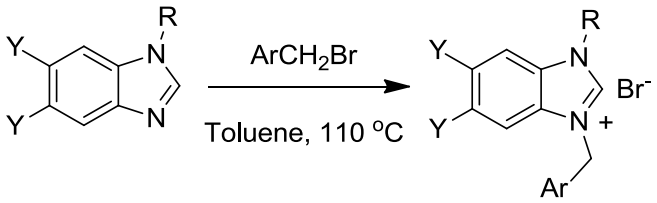
2. EXPERIMENTAL

Reactions involving air-sensitive components were performed by using Schlenk-type flasks under argon atmosphere and high vacuum-line techniques. The glass equipment was heated under vacuum in order to remove oxygen and moisture and then they were filled with argon. The solvents were analytical grade and distilled under argon atmosphere from sodium (toluene, diethyl ether, hexane, tetrahydrofuran) or diphosphorpentaoxide (dichloromethane).

Reagents: Toluene, tetrahydrofuran, dichloromethane, hexane, pentane, diethyl ether, ethanol, isopropylalcohol and methanol were obtained from J. T. Baker and Merck. Other chemicals were obtained from Aldrich, Acros Organics, Alfa Aesar, Fluka and Merck and used as received. $[RhCl(COD)]_2$ (Chatt and Venanzi, 1957), $[Rh(OMe)(COD)]_2$ (Uson *et al*., 1985), 2,4,6-trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, 2,3,4,5,6-pentamethylbenzyl (Van der Made, 1993), monosubstituted benzimidazoles (Özdemir et al., 2004; 2005a, Denizaltı, 2006), (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartarate salt (Larrow and Jacobsen et al., 1994), 1-[(2*R*)-1-(hydroxymethyl)-2-methylpropyl]imidazole (**20**) (Matsuoka et al., 2006), (*E*)-1,3-diphenyl-3-en-yl acetate (Leung et al., 2001) were synthesized according to previously published procedures. (4*R*)-4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazole synthesized by Mugesh (Mugesh et al., 1998) was prepared from (*R*)-2-amino-1-butanol according the known procedure (Chelucci et al., 1999; Mawo et al., 2008).

Instruments: ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 MHz. As solvent $CDCl_3$ was employed, *J* values are given in Hz. Melting points were determined by electrothermal melting point apparatus. Optical rotations were taken on a Rudolph Research Analytical Autopol I automatic polarimeter with a wavelength of 589 nm; the concentration 'c' has units of g/100 mL. The measurements for catalytic experiments performed by GC/MS (Thermo-Finnigan on a HP-5 capillary column and with a FID detector) in Ege University Department of Chemistry. The crystal of ruthenium complex mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER GADDS X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. MS analyses of rhodium and ruthenium complexes were performed using Bruker HCT Ultra Mass Spectrometry (ESI IONIZATION) Agilent 1200 Capillary HPLC. HPLC analyses were performed using chiralcel OD-H column and hexane/2-propanol systems.

2.1 General Procedure for the Synthesis of 1,3-disubstituted (5,6-dimethyl)benzimidazolium salts (1-6)



1-6

Table 2.1 Melting points and yields of the compounds **1-6**

Compound No	Y	R	Ar	m.p (°C)	Yield (%)
1	H	$-CH_2C_6H_2(CH_3)_3$-2,4,6	$C_6H_2(CH_3)_3$-2,4,6	145-148	70
2	H	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6	198-200	77
3	H	$-CH_2CH_2OCH_3$	$C_6H(CH_3)_4$-2,3,5,6	192-195	78
4	H	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6	202-203	70
5	CH_3	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6	210-214	98
6	CH_3	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6	109-110	80

1-Methoxyethyl-(5,6-dimethyl)benzimidazole or 1-(2,4,6-trimethyl)benzyl-benzimidazole (5.7 mmol) was dissolved in toluene and then 2,4,6-trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide or 2,3,4,5,6-pentamethylbenzyl bromide (5.7 mmol) was added. The mixture was refluxed for 4 h. The solid that separated out after cooling was filtered off and washed with diethyl ether (5 mL). The product was recrystallized from CH_2Cl_2/Et_2O.

2.1.1 Compound 1

^{1}H NMR : δ (ppm): 2.30 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.31 (s, 12 H, $CH_2C_6H_2(CH_3)_3$), 5.87 (s, 4 H, $CH_2C_6H_2(CH_3)_3$), 6.91 (s, 4H, $CH_2C_6H_2(CH_3)_3$), 7.20-7.22 (m, 2 H, Ar-*H*), 7.35-7.38 (m, 2 H, Ar-*H*), 10.78 (s, 1 H, NC*H*N).^{13}C NMR : δ (ppm): 20.3, 21.1, 47.6, 113.7, 125.1, 127.0, 130.2, 131.8, 137.9, 139.8, 143.2 (N*C*HN).

2.1.2 Compound 2

^{1}H NMR : δ (ppm): 2.30 (s, 3 H, $CH_2C_6H_2(CH_3)_3$), 2.32 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 3.30 (s, 3 H, OCH_3), 3.89 (t, *J* = 4.0 Hz, 2 H, CH_2), 4.93 (t, *J* = 4.0 Hz, 2 H, CH_2), 5.83 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 6.95 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 7.43-7.60 (m, 3 H, Ar-*H*), 8.01 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 10.40 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 20.3, 21.2, 47.3, 48.1, 59.1, 69.9, 113.7, 114.4, 125.1, 127.4, 130.4, 132.3, 138.2, 140.0, 142.5 (N*C*HN).

2.1.3 Compound 3

^{1}H NMR : δ (ppm): 2.24 (s, 6 H, $C_6H(CH_3)_4$), 2.27 (s, 6 H, $C_6H(CH_3)_4$), 3.29 (s, 3 H, OCH_3), 3.87 (t, *J* = 4.0 Hz, 2 H, CH_2), 4.94 (t, *J* = 4.0 Hz, 2 H, CH_2), 5.83 (s, 2 H, $CH_2C_6H(CH_3)_4$), 7.09 (s, 1 H, $C_6H(CH_3)_4$), 7.54-7.64 (m, 3 H, Ar-*H*), 8.01 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 10.04 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 16.3, 20.7, 47.7, 48.1, 59.1, 70.1, 113.6, 144.5, 127.4, 131.4, 132.4, 133.9, 135.6, 142.1 (N*C*HN).

2.1.4 Compound 4

^{1}H NMR : δ (ppm): 2.23 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.21 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.19 (s, 3 H, $CH_2C_6(CH_3)_5$), 3.22 (s, 3 H, OCH_3), 3.79 (t, *J* = 4.8 Hz, 2 H, CH_2), 4.87 (t, *J* = 4.4 Hz, 2 H, CH_2), 5.73 (s, 2 H, $CH_2C_6(CH_3)_5$), 7.49-7.58 (m, 3 H, Ar-*H*), 7.94 (d, *J* = 8.8 Hz, 1 H, Ar-*H*), 9.70 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 17.1, 17.2, 17.5, 48.1, 48.2, 59.1, 70.2, 113.6, 114.6, 124.8, 127.5, 131.4, 132.4, 133.8, 134.2, 137.6, 141.8 (N*C*HN).

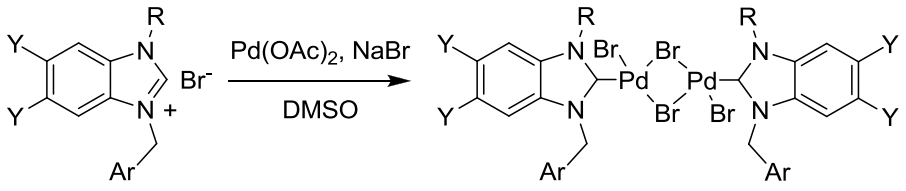
2.1.5 Compound 5

^{1}H NMR : δ (ppm): 2.31 (s, 3 H, $CH_2C_6H_2(CH_3)_3$), 2.32 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.35 (s, 3 H, C*H*$_3$-Ar), 2.42 (s, 3 H, C*H*$_3$-Ar), 3.30 (s, 3 H, OC*H*$_3$), 3.87 (t, *J* = 4.4 Hz, 2 H, C*H*$_2$), 4.83 (t, *J* = 4.8 Hz, 2 H, C*H*$_2$), 5.70 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 6.95 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 7.15 (s, 1 H, Ar-*H*), 7.64 (s, 1 H, Ar-*H*), 10.24 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 20.4, 20.8, 20.9, 21.3, 46.9, 47.8, 59.1, 70.1, 113.2, 113.8, 125.2, 129.9, 130.3, 130.9, 137.4, 137.5, 138.2, 140.0, 141.4 (N*C*HN).

2.1.6 Compound 6

^{1}H NMR : δ (ppm): 2.26 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.27 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.29 (s, 3 H, $CH_2C_6(CH_3)_5$), 2.41 (s, 3 H, C*H*$_3$-Ar), 2.45 (s, 3 H, C*H*$_3$-Ar), 3.27 (s, 3 H, OC*H*$_3$), 3.83 (t, *J* = 5.2 Hz, 2 H, C*H*$_2$), 4.87 (t, *J* = 4.8 Hz, 2 H, C*H*$_2$), 5.30 (s, 2 H, $CH_2C_6(CH_3)_5$), 7.42 (s, 1 H, Ar-*H*), 7.72 (s, 1 H, Ar-*H*), 9.49 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 17.1, 17.2, 17.5, 20.8, 20.9, 47.5, 48.0, 59.1, 70.3, 112.9, 114.0, 124.9, 129.9, 130.9, 133.7, 134.2, 137.5, 137.7, 140.4 (N*C*HN).

2.2 General Procedure for the Synthesis of Dimeric NHC-Pd(II) Complexes (7-12)



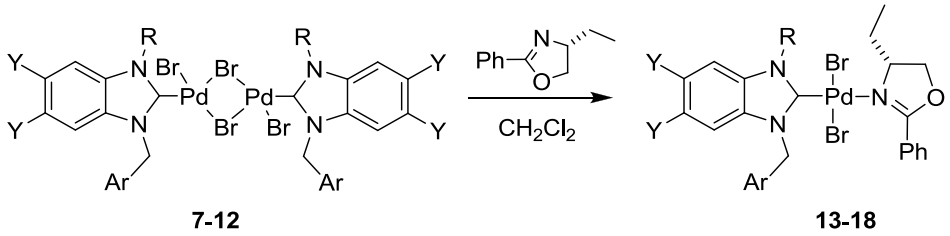
1-6 **7-12**

Table 2.2 Melting points and yields of the compounds **7-12**

Compound No	Y	R	Ar	m.p (°C)	Yield (%)
7	H	$-CH_2C_6H_2(CH_3)_3$-2,4,6	$C_6H_2(CH_3)_3$-2,4,6	322-325 (dec.)	76
8	H	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6	295-299 (dec.)	40
9	H	$-CH_2CH_2OCH_3$	$C_6H(CH_3)_4$-2,3,5,6	325-326 (dec.)	50
10	H	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6	310-313 (dec.)	60
11	CH_3	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6	296-298 (dec.)	61
12	CH_3	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6	300-304 (dec.)	64

A mixture of salt (**7-12**) (1.2 mmol), $Pd(OAc)_2$ (1.2 mmol) and NaBr (3.6 mmol) in DMSO was stirred at 90 ^oC for 24 h. The solvent was removed by vacuum distillation. The resulting residue was suspended in CH_2Cl_2 and H_2O then extracted. Drying of the organic phase over Na_2SO_4 followed by reduction of the solvent and addition of Et_2O afforded the orange solid.

2.3 General Procedure for the Synthesis of Mixed NHC-Oxazoline Pd(II) Complexes (13-18)



7-12 **13-18**

Table 2.3 Melting points, yields and optical rotations of the compounds **13-18**

Compound No	Y	R	Ar	m.p (°C)	Yield (%)	[α]
13	H	$-CH_2C_6H_2(CH_3)_3$-2,4,6	$C_6H_2(CH_3)_3$-2,4,5	119-122	45	-37.50 (c 0.16, 24.6 °C)
14	H	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6	173-177	40	-31.21 (c 0.26, 26.6 °C)
15	H	$-CH_2CH_2OCH_3$	$C_6H(CH_3)_4$-2,3,5,6	192-195	56	-35.81 (c 0.25, 26.9 °C)
16	H	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6	199-201	78	-38.46 (c 0.26, 26.8 °C)
17	CH_3	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6	174-176	79	-9.17 (c 0.11, 28.2 °C)
18	CH_3	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6	162-165	77	-8.77 (c 0.11, 26.8 °C)

A mixture of dimeric complex (**7-12**) (0.17 mmol) and (4*R*)-4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazole was suspended in CH_2Cl_2 (5 mL) and stirred at room temperature for 3 h. The yellow solid was obtained after the solution was removed. The product was washed with Et_2O and dried.

2.3.1 Compound 13

^{1}H NMR : δ (ppm): 1.11 (t, *J* = 8.0 Hz, 3 H, Ox-CH_2CH_3), 2.05-2.12 (m, 1 H, Ox-CH_2CH_3), 2.33 (s, 12 H, $CH_2C_6H_2(CH_3)_3$), 2.35 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.66-2.72 (m, 1 H, Ox-CH_2CH_3), 4.27 (m, 1 H, Ox-C*H*), 4.62-4.69 (m, 2 H, Ox-CH_2), 6.19 (s, 4 H, $CH_2C_6H_2(CH_3)_3$), 6.18-6.21 (m, 2 H, Ar-*H*), 6.70-6.73 (m, 2 H, Ar-*H*), 6.94 (s, 4 H, $CH_2C_6H_2(CH_3)_3$), 7.39-7.46 (m, 3 H, Ox-Ar-*H*), 8.82 (d, *J* = 8.0 Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR : δ (ppm): 10.0, 21.2, 21.3, 28.5, 51.6, 68.2, 72.9, 76.5, 76.9, 111.3, 122.7, 126.9, 127.8, 128.2, 129.8, 130.5, 132.7, 135.2, 138.9, 139.1, 166.1, 167.3 ($C_{carbene}$).

2.3.2 Compound 14

^{1}H NMR : δ (ppm): 1.10 (t, *J* = 7.6 Hz, 3 H, Ox-CH_2CH_3), 2.06-2.13 (m, 1 H, Ox-CH_2CH_3), 2.32 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.36 (s, 3 H, $CH_2C_6H_2(CH_3)_3$), 2.66-2.73 (m, 1 H, Ox-CH_2CH_3), 3.35 (s, 3 H, OCH_3), 4.15 (t, *J* = 6.0 Hz, 2 H, CH_2), 4.27 (t, *J* = 6.4 Hz, 1 H, Ox-C*H*), 4.62-4.68 (m, 2 H, Ox-CH_2), 5.02 (t, *J* = 6.0 Hz, 2 H, CH_2), 6.12 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 6.15 (d, *J* = 8.8 Hz, 1 H, Ar-*H*), 6.85 (t, *J* = 8.0 Hz, 1 H, Ar-*H*), 6.96 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 7.10 (t, *J* = 7.2 Hz, 1 H, Ar-*H*), 7.45-7.55 (m, 4 H, Ox-Ar-*H*, Ar-*H*), 8.76 (d, *J* = 7.6 Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR : δ (ppm): 10.1, 21.1, 21.3, 28.5, 48.8, 51.4, 59.4, 68.3, 71.5, 72.9, 111.2, 111.4, 122.8, 123.2, 126.8, 127.6, 128.3, 129.8, 130.4, 132.7, 134.7, 135.9, 139.1, 139.3, 165.6, 167.3 ($C_{carbene}$).

2.3.3 Compound 15

^{1}H NMR : δ (ppm): 1.12 (t, *J* = 7.2 Hz, 3 H, Ox-CH_2CH_3), 2.07-2.14 (m, 1 H, Ox-CH_2CH_3), 2.26 (s, 3 H, $CH_2C_6H(CH_3)_4$), 2.29 (s, 3 H, $CH_2C_6H(CH_3)_4$), 2.69-2.74 (m, 1 H, Ox-CH_2CH_3), 3.35 (s, 3 H, OCH_3), 4.16 (t, *J* = 5.6 Hz, 2 H, CH_2), 4.27 (t, *J* = 6.4 Hz, 1 H, Ox-C*H*), 4.62-4.69 (m, 2 H, Ox-CH_2), 5.03 (t, *J* = 5.6 Hz, 2 H, CH_2), 6.01 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 6.22 (s, 2 H, $CH_2C_6H(CH_3)_4$), 6.81 (t, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.09 (t, *J* = 8.4 Hz, 1 H, Ar-*H*), 7. 12 (s, 1 H, $CH_2C_6H(CH_3)_4$), 7.44-7.56 (m, 4 H, Ox-Ar-*H*, Ar-*H*), 8.78 (d, *J* = 7.2 Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR : δ (ppm): 10.1, 16.8, 20.7, 28.5, 48.8, 59.4, 68.3, 71.5, 72.9, 111.2, 111.6, 122.6, 123.1, 126.8, 128.3, 130.4, 130.5, 132.7, 132.9, 134.6, 134.9, 135.6, 135.9, 165.6, 167.2 ($C_{carbene}$).

2.3.4 Compound 16

^{1}H NMR : 1.11 (t, *J* = 7.2 Hz, 3 H, Ox-CH_2CH_3), 2.09-2.14 (m, 1 H, Ox-CH_2CH_3), 2.27 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.31 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.34 (s, 3 H, $CH_2C_6(CH_3)_5$), 2.68-2.73 (m, 1 H, Ox-CH_2CH_3), 3.36 (s, 3 H, OCH_3), 4.16 (t, *J* = 6.0 Hz, 2 H, CH_2), 4.29 (t, *J* = 6.8 Hz, 1 H, Ox-C*H*), 4.63-4.68 (m, 2 H, Ox-CH_2), 5.03 (t, *J* = 5.6 Hz, 2 H, CH_2), 6.06 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 6.23 (s, 2 H, $CH_2C_6(CH_3)_5$), 6.79 (t, *J* = 7.2 Hz, 1 H, Ar-*H*),7.08 (t, *J* = 7.2 Hz, 1 H, Ar-*H*), 7.44-7.55 (m, 4 H, Ox-Ar-*H*, Ar-*H*), 8.79 (d, *J* = 7.2 Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR : δ (ppm): 10.1, 17.1, 17.5, 17.8, 28.5, 48.7, 53.9, 59.4, 68.3, 71.4, 72.9, 111.1, 111.7, 122.6, 123.1, 126.8, 127.9, 128.3, 130.4, 132.7, 133.4, 134.9, 135.1, 136.5, 165.5, 167.2 ($C_{carbene}$).

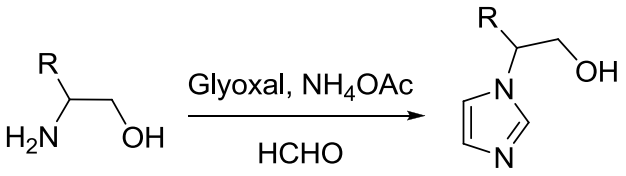
2.3.5 Compound 17

^{1}H NMR : δ (ppm): 1.14 (t, *J* = 7.6 Hz, 3 H, Ox-CH_2CH_3), 2.01 (s, 3 H, $CH_2C_6H_2(CH_3)_3$), 2.09-2.14 (m, 1 H, Ox-CH_2CH_3), 2.26 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.33 (s, 3 H, CH_3-Ar), 2.38 (s, 3 H, CH_3-Ar), 2.65-2.71 (m, 1 H, Ox-CH_2CH_3), 3.35 (s, 3 H, OCH_3), 4.13 (t, *J* = 6.4 Hz, 2 H, CH_2), 4.28 (t, *J* = 6.8 Hz, 1 H, Ox-C*H*), 4.62-4.70 (m, 2 H, Ox-CH_2), 4.94 (t, *J* = 6.0 Hz, 2 H, CH_2), 5.85 (s, 1 H, Ar-*H*), 6.04 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 6.95 (s, 2 H, $CH_2C_6H_2(CH_3)_3$), 7.19 (s, 1 H, Ar-*H*), 7.47-7.55 (m, 3 H, Ox-Ar-*H*), 8.77 (d, *J* = 8.0 Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR : δ (ppm): 10.1, 20.3, 20.6, 21.1, 21.3, 28.4, 48.5, 51.1, 59.4, 68.2, 71.5, 72.7, 111.3, 111.9, 126.9, 127.9, 128.2, 129.5, 130.4, 131.6, 131.7, 132.6, 133.3, 138.7, 139.4, 163.7, 167.1 ($C_{carbene}$).

2.3.6 Compound 18

^{1}H NMR : δ (ppm): 1.14 (t, *J* = 7.6 Hz, 3 H, Ox-CH_2CH_3), 1.96 (s, 3 H, $CH_2C_6(CH_3)_5$), 2.08-2.16 (m, 1 H, Ox-CH_2CH_3), 2.21 (s, 3 H, CH_3-Ar), 2.29 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.32 (s, 6 H, $CH_2C_6(CH_3)_5$), 2.38 (s, 3 H, CH_3-Ar), 2.68-2.74 (m, 1 H, Ox-CH_2CH_3), 3.37 (s, 3 H, OCH_3), 4.14 13 (t, *J* = 5.6 Hz, 2 H, CH_2), 4.28 (t, *J* = 6.8 Hz, 1 H, Ox-C*H*), 4.63-4.70 (m, 2 H, Ox-CH_2), 4.94 (t, *J* = 5.6 Hz, 2 H, CH_2), 5.76 (s, 1 H, Ar-*H*), 6.14 (s, 2 H, $CH_2C_6(CH_3)_5$), 7.18 (s, 1 H, Ar-*H*), 7.47-7.55 (m, 3 H, Ox-Ar-*H*), 8.79 (d, *J* = 7.2 Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR : δ (ppm): 10.1, 17.1, 17.5, 17.9, 20.3, 20.6, 28.4, 48.5, 52.6, 59.4, 68.3, 71.4, 72.7, 77.4, 111.2, 112.3, 126.9, 128.2, 130.4, 131.3, 131.4, 132.6, 133.0, 133.5, 134.6, 135.2, 136.1, 163.6, 167.1 ($C_{carbene}$).

2.4 Synthesis of 1-Subtituted Imidazoles (19, 20)



19 : R = Et
20 : R = ^{i}Pr

A methanol solution (6 mL) of glyoxal (40% w/v, 0.87 g, 6 mmol), ammonium acetate (0.46 g, 6 mmol), formaldehyde (36% w/v, 0.50 g, 6 mmol) and amino alcohol (3 mmol) was refluxed for 5 h. The reaction mixture was concentrated by distillation. The residue was treated with 2M KOH solution (100 mL) and extracted with CH_2Cl_2 (4 x 100 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuum.

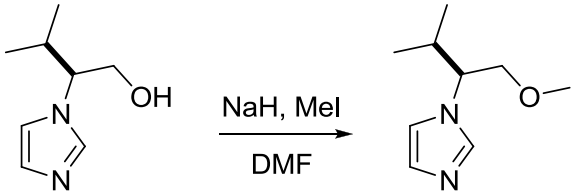
2.4.1 Compound 19

^{1}H NMR : δ (ppm): 0.86 (t, *J* = 7.6 Hz, 3 H, CHCH$_2$C*H*$_3$), 1.71-1.89 (m, 2 H, CHC*H*$_2$CH$_3$), 2.88 (s, 1 H, O*H*), 3.74-3.84 (m, 2 H, C*H*$_2$OH), 3.93-3.99 (m, 1 H, NC*H*), 6.92 (s, 1 H, imidazole-*H*), 6.97 (s, 1 H, imidazole-*H*), 7.43 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 10.7, 22.4, 24.8, 62.8, 64.6, 117.6, 127.9, 136.7 (N*C*HN). Yield: 42%.

2.4.2 Compound 20

^{1}H NMR : δ (ppm): 0.76 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.04 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 2.07-2.16 (m, 1 H, C*H*(CH$_3$)$_2$), 3.64-3.69 (m, 1 H, NC*H*), 3.89 (d, *J* = 5.2 Hz, 2 H, C*H*$_2$OH), 6.89 (s, 1 H, imidazole-*H*), 6.93 (s, 1 H, imidazole-*H*), 7.33 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 19.6, 20.2, 30.2, 63.2, 67.3, 118.1, 128.6, 136.9 (N*C*HN). Yield: 52%, m.p: 108-110.

2.5 Synthesis of (*S*)-1-(1-methoxy-3-methylbutan-2yl)-1*H*-imidazole (21)



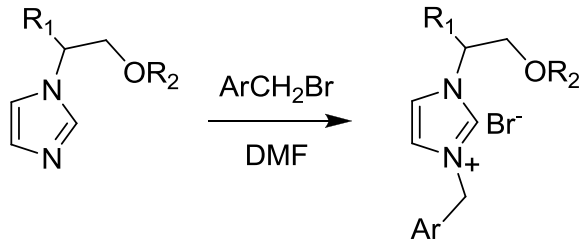
20 **21**

Synthesis of **21** was conducted according to the literature (Matsuoko et al., 2008).

To a DMF solution (10 mL) of **20** (0.2 g, 1.3 mmol) was added NaH (0.08 g, 3.3 mmol). After being stirred for 2 h at room temperature, the suspension was cooled to 0^{o}C, and iodomethane was added to the mixture. The mixture was allowed to warm to room temperature and stirred for 3 days. After adding aqueous HCl solution (30%, 0.8 mL), the mixture was concentrated in vacuum. To the residue was added water and washed with hexane (3x5 mL). And then the aqueous phase was treated with $NaHCO_3$ until the pH reached to 9, and extracted with CH_2Cl_2 (3x5 mL). The combined organic phases were washed with water (3x5 mL), dried over Na_2SO_4, concentrated in vacuo.

^{1}H NMR : δ (ppm): 0.74 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.00 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 2.06-2.15 (m, 1 H, C*H*(CH$_3$)$_2$), 3.32 (s, 3 H, OC*H*$_3$), 3.69-3.92 (m, 3 H, NC*H*, C*H*$_2$OCH$_3$), 6.92 (s, 1 H, imidazole-*H*), 6.98 (s, 1 H, imidazole-*H*), 7.46 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 19.4, 19.9, 30.4, 59.3, 64.5, 73.2, 118.4, 129.0, 137.3 (N*C*HN). Yield: 70%.

2.6 General Procedure for the Synthesis of 1,3-Disubstituted Imidazolium Salts (22-24)



19-21 **22-24**

Table 2.4 Melting points, yields and optical rotations of the compounds **22-24**

Compound No	R_1	R_2	Ar	m.p (°C)	Yield (%)	[α]
22a	Et	H	$C_6H_2(CH_3)_3$-2,4,6	101-105	60	-
22b	Et	H	$C_6(CH_3)_5$-2,3,4,5,6	175-178	68	-
23a	^{i}Pr	H	$C_6H_2(CH_3)_3$-2,4,6	215-216	90	-18.6 (c 0.24, 22.7 ^{o}C)
23b	^{i}Pr	H	$C_6(CH_3)_5$-2,3,4,5,6	181-182	95	-6.62 (c 0.15, 29.3 ^{o}C)
24	^{i}Pr	CH_3	$C_6(CH_3)_5$-2,3,4,5,6	172-175	89	-15.31 (c 0.20, 23.8 ^{o}C)

(*R*)-2-(1*H*-imidazol-1-yl)butan-1-ol (**19**), (*S*)-2-(1*H*-imidazol-1-yl)-3-methylbutan-1-ol (**20**) or (*S*)-1-(1-methoxy-3-methylbutan-2yl)-1*H*-imidazole (**21**) (1.8 mmol) was dissolved in DMF and then 2,4,6-trimethylbenzyl bromide or 2,3,4,5,6-pentamethylbenzyl bromide (1.8 mmol) was added. The mixture was stirred for 48 h at 25 ^{o}C. The solvent was removed under reduced pressure. The residue was recrystallized from CH_2Cl_2/Et_2O.

2.6.1 Compound 22a

^{1}H NMR : δ (ppm): 0.92 (t, *J* = 7.2 Hz, 3 H, CHCH$_2$C*H*$_3$), 1.89-1.96 (m, 2 H, CHC*H*$_2$CH$_3$), 2.29 (s, 3 H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$), 2.31 (s, 6 H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$), 3.81-3.97 (m, 2 H, C*H*$_2$OH), 4.53 (m, 1 H, NC*H*), 5.63-5.76 (m, 2 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 6.89 (s, 1 H, imidazole-*H*), 6.90 (s, 2 H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$), 7.47 (s, 1 H, imidazole-*H*), 9.83 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 10.6, 20.2, 21.3, 24.2, 48.2, 63.2, 64.3, 65.7, 120.7, 121.3, 126.0, 130.0, 136.7, 138.5, 139.7 (N*C*HN).

2.6.2 Compound 22b

^{1}H NMR : δ (ppm): 0.93 (t, *J* = 7.6 Hz, 3 H, CHCH$_2$C*H*$_3$), 1.84-1.97 (m, 2 H, CHC*H*$_2$CH$_3$), 2.23 (s, 6 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.26 (s, 6 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.27 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 3.78-4.02 (m, 2 H, C*H*$_2$OH), 4.58-4.60 (m, 1 H, NC*H*), 5.54-5.63 (m, 2 H, C*H*$_2$C$_6$(CH$_3$)$_5$), 6.90 (s, 1 H, imidazole-*H*), 7.32 (s, 1 H, imidazole-*H*), 9.64 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 10.6, 17.0, 17.1, 17.4, 24.2, 49.4, 63.3, 65.5, 120.9, 121.3, 125.9, 133.8, 133.9, 136.2, 137.2 (N*C*HN).

2.6.3 Compound 23a

^{1}H NMR : δ (ppm): 0.83 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 2.20-2.25 (m, 1 H, C*H*(CH$_3$)$_2$), 2.23 (s, 9 H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$), 3.94-4.10 (m, 2 H, C*H*$_2$OH), 4.26-4.32 (m, 1 H, NC*H*), 4.81 (t, *J* = 6.0 Hz, 1 H, CH$_2$O*H*), 5.57 (dd, *J* = 22.4 Hz, 2 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 6.87 (s, 1 H, imidazole-*H*), 6.93 (s, 2 H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$), 7.33 (s, 1 H, imidazole-*H*), 9.75 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 19.6, 19.7, 20.1, 21.3, 29.9, 48.3, 61.3, 70.1, 120.7, 122.0, 125.9, 130.1, 136.6, 139.9 (N*C*HN).

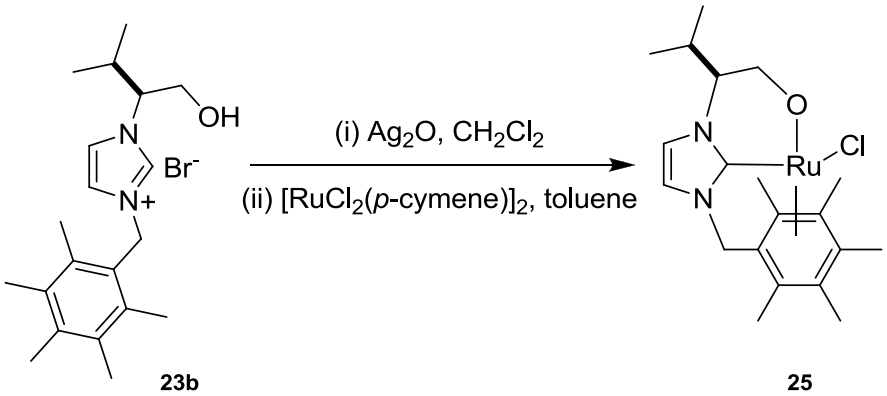
2.6.4 Compound 23b

^{1}H NMR : δ (ppm): 0.82 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 2.19-2.22 (m, 1 H, C*H*(CH$_3$)$_2$), 2.24 (s, 6 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.26 (s, 6 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.27 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 3.95-4.09 (m, 2 H, C*H*$_2$OH), 4.27-4.33 (m, 1 H, NC*H*), 5.65 (dd, *J* = 24.4 Hz, 2 H, C*H*$_2$C$_6$(CH$_3$)$_5$), 6.75 (s, 1 H, imidazole-*H*), 7.37 (s, 1 H, imidazole-*H*), 9.64 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 17.0, 17.1, 17.4, 19.5, 19.6, 25.6, 29.9, 49.5, 61.4, 70.0, 120.8, 121.8, 125.7, 133.9, 134.0, 136.3, 137.5 (N*C*HN).

2.6.5 Compound 24

^{1}H NMR : δ (ppm): 0.80 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.06 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.91-2.02 (m, 1 H, C*H*(CH$_3$)$_2$), 2.21 (s, 12 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.24 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 3.33 (s, 3 H, OC*H*$_3$), 3.69-3.92 (m, 2 H, C*H*$_2$OCH$_3$, NC*H*), 5.65 (dd, *J* = 19.6 Hz, 2 H, C*H*$_2$C$_6$(CH$_3$)$_5$), 6.81 (s, 1 H, imidazole-*H*), 7.38 (s, 1 H, imidazole-*H*), 10.61 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 16.9, 17.1, 17.4, 19.4, 19.5, 29.8, 49.3, 59.4, 67.2, 71.7, 120.6, 121.8, 125.7, 133.7, 133.9, 136.9, 137.5 (N*C*HN).

2.7 Synthesis of Ruthenium Complex (25)



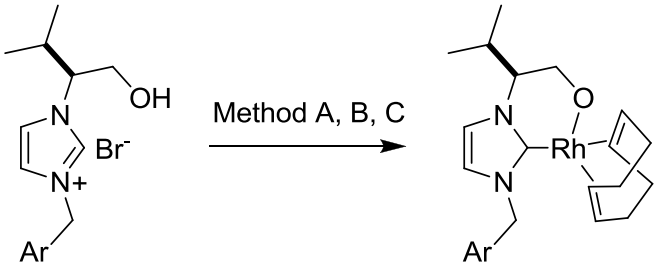
23b **25**

Compound **23b** (0.3 g, 0.8 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and Ag_2O (0.4 mmol) was added into the solution. The mixture was stirred in the dark at 25 ^{o}C for overnight under argon. Then the suspension was filtered through celite into the schlenk containing [$RuCl_2$(*p*-cymene)]$_2$ (0.2 g, 0.4 mmol). After the mixture was stirred at 25 ^{o}C for overnight, dry toluene was added. The mixture was heated to 90 ^{o}C for 16 h under argon. After cooling, toluene was removed in vacuum. The residue was crystallized from CH_2Cl_2/Et_2O.

^{1}H NMR : δ (ppm): 0.78 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 0.89 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.74-1.81 (m, 1 H, C*H*(CH$_3$)$_2$), 1.98 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 1.99 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.02 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.06 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.14 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 3.24-3.32 (m, 1 H, C*H*$_2$O), 3.95-3.99 (m, 1 H, C*H*$_2$O), 4.81-4.89 (m, 1 H, NC*H*), 4.93 (s, 2 H, C*H*$_2$C$_6$(CH$_3$)$_5$), 7.0 (d, *J* = 2.0 Hz, 1 H, imidazole-*H*), 7.17 (d, *J* = 2.0 Hz, 1 H, imidazole-*H*). ^{13}C NMR : δ (ppm): 15.0, 15.1, 15.2, 15.8, 19.5, 19.6, 30.9, 48.9, 64.3 (d, *J* = 46.5 Hz), 84.8,

85.9, 93.9, 97.3, 106.2, 106.4, 118.7, 119.3, 175.2 ($C_{carbene}$). Yield: 30%, m.p: 260 ^{o}C (dec.). [α] = +50.0 (c 0.2, 23.0 ^{o}C, in CH_2Cl_2).

2.8 Synthesis of Rhodium Complexes (26a, 26b)



23 **26**

a: $C_6H_2(CH_3)_3$-2,4,6
b: $C_6(CH_3)_5$-2,3,4,5,6

Method A: Imidazolium salt **23a** or **23b** (0.81 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and Ag_2O (0.45 mmol) was added into the solution. The mixture was stirred in the dark at 25 ^{o}C for overnight under argon. Then the suspension was filtered through celite into the schlenk containing $[RhCl(COD)]_2$ (0.41 mmol). After the mixture was stirred at 25 ^{o}C for overnight, CH_2Cl_2 was removed in vacuum. The residue was purified by column choromatography (eluent: CH_2Cl_2/hexane 9:1) to give yellow solid.

Method B: A mixture of **23a** or **23b** (0.27 mmol), LiO^{t}Bu (0.54 mmol) and $[RhCl(COD)]_2$ (0.14 mmol) in THF (8 mL) was heated at 70 ^{o}C for 16 h under argon. And then THF was removed in vacuum. The residue was purified by column choromatography (eluent: CH_2Cl_2/hexane 9:1) to give yellow solid.

Method C: Imidazolium salt **23a** or **23b** (0.27 mmol) and $[RhOMe(COD)]_2$ (0.14 mmol) were placed into the two-necked flask and 1,2-dichloroethane (8 mL) was added. The mixture was stirred for 4 h and then heated for overnight. The solvent was removed in vacuo. The residue was purified by column choromatography (eluent: CH_2Cl_2/hexane 9:1) to give yellow solid.

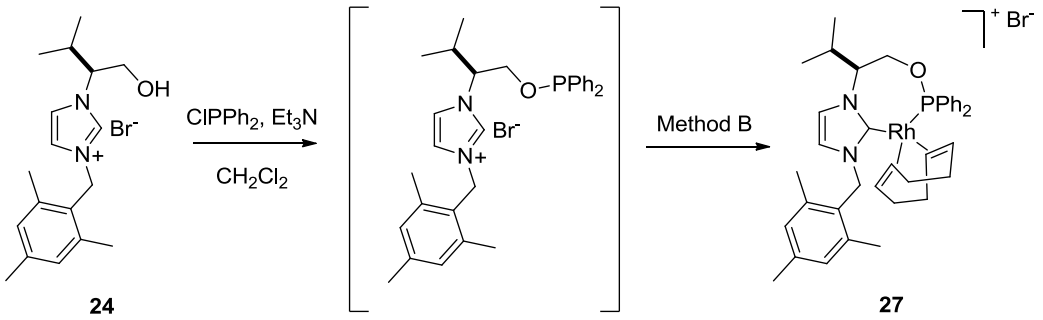
2.8.1 Compound 26a

^{1}H NMR : δ (ppm): 0.94 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.91-1.94 (m, 4 H, COD-C*H*$_2$), 2.08-2.17 (m, 1 H, C*H*(CH$_3$)$_2$), 2.11-2.17 (m, 1 H, C*H*(CH$_3$)$_2$), 2.26 (s, 3 H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$), 2.28 (s, 6 H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$), 2.36-2.46 (m, 4 H, COD-C*H*$_2$), 3.56-3.57 (m, 1 H, COD-C*H*), 3.62-3.64 (m, 1 H, COD-C*H*), 3.72-3.76 (m, 1 H, C*H*$_2$O), 4.14-4.18 (m, 1 H, C*H*$_2$O), 5.09-5.14 (m, 3H, COD-C*H*, NC*H*), 5.43 (d, *J* = 14.4 Hz, 1 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 5.82 (d, *J* = 14.0 Hz, 1 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 6.25 (s, 1 H, imidazole-*H*), 6.79 (s, 1 H, imidazole-*H*), 6.89 (s, 2 H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$). ^{13}C NMR : δ (ppm): 19.9, 20.4, 20.7, 21.2, 30.3, 32.8, 33.0, 49.2, 64.1, 68.5, 68.9, 69.5, (dd, *J* = 14.5 Hz, *C*H-cod), 97.9 (dd, *J* = 6.9 Hz, *C*H-cod), 117.9, 120.1, 129.5, 138.7, 181.2 (d, $J_{Rh,C}$ = 49.5 Hz, $C_{carbene}$). Yield: 53%, m.p: 104-106. [α] = -10.0 (c 0.2, 21.5 ^{o}C, in CH$_2$Cl$_2$).

2.8.2 Compound 26b

^{1}H NMR : δ (ppm): 0.92 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.16 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.89-1.98 (m, 4 H, COD-C*H*$_2$), 2.10-2.17 (m, 1 H, C*H*(CH$_3$)$_2$), 2.21 (s, 6 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.24 (s, 6 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.25 (s, 3 H, CH$_2$C$_6$(C*H*$_3$)$_5$), 2.30-2.46 (m, 4 H, COD-C*H*$_2$), 3.58-3.60 (m, 1 H, COD-C*H*), 3.64-3.67 (m, 1 H, COD-C*H*), 3.73-3.76 (m, 1 H, C*H*$_2$O), 4.14-4.17 (m, 1 H, C*H*$_2$O), 5.06-5.13 (m, 3H, COD-C*H*, NC*H*), 5.69 (d, *J* = 14.0 Hz, 1 H, C*H*$_2$C$_6$(CH$_3$)$_5$), 5.89 (d, *J* = 14.0 Hz, 1 H, C*H*$_2$C$_6$(CH$_3$)$_5$), 6.28 (d, *J* = 2.0 Hz, 1 H, imidazole-*H*), 6.76 (d, *J* = 2.0 Hz, 1 H, imidazole-*H*). ^{13}C NMR : δ (ppm): 17.0, 17.2, 19.9, 20.7, 29.3, 34.1, 50.4, 64.1, 67.3, 68.4, 69.5, (dd, *J* = 14.5 Hz, *C*H-cod), 97.9 (dd, *J* = 6.8 Hz, *C*H-cod), 117.7, 120.5, 128.6, 133.2, 134.4, 181.5 (d, $J_{Rh,C}$ = 50.3 Hz, $C_{carbene}$). Yield: 58%, m.p: 125-127. [α] = +20.0 (c 0.2, 22.5 ^{o}C, in CH$_2$Cl$_2$).

2.9 Synthesis of Rhodium Complex (27)



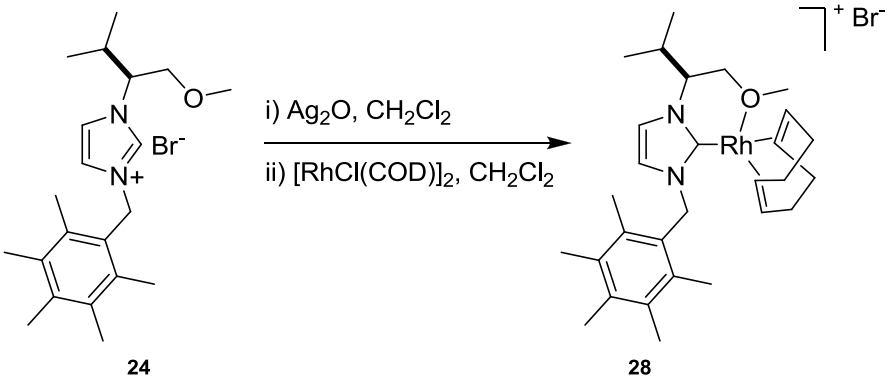
24 **27**

To a flask containing imidazolium salt **24** (0.4 g, 1.0 mmol) was added CH_2Cl_2 (2 mL), followed by triethylamine (0.21 mL, 1.5 mmol). The resultant mixture was cooled to -20 ^oC and then a solution of PPh_2Cl (0.18 mL, 1 mmol) in 2 mL of CH_2Cl_2 was slowly added to the mixture. The reaction mixture was stirred for 1 h and was then quenched with 5 N NaOH (0.5 mL), followed by water (1 mL). The aqueous layer was extracted with dichloromethane (2x5 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo (Iranpoor et al., 2006). The crude product (0.5 g, 0.90 mmol), LiO^tBu (0.11 g, 1.35 mmol) and $[RhCl(COD)]_2$ (0.22 g, 0.45 mmol) in THF (25 mL) were heated at 70 ^oC for 16 h under argon. And then THF was removed in vacuum. The residue was purified by column choromatography (eluent: CH_2Cl_2/hexane 9:1) to give yellow solid.

^{1}H NMR : δ (ppm): 0.88 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.01 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.06 (d, *J* = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.26 (d, *J* = 6.4 Hz, 3 H, CH(C*H*$_3$)$_2$), 1.73-2.03 (m, 8 H, COD-C*H*$_2$), 2.28; 2.30; 2.32 (s, 18 H, $CH_2C_6H_2$(C*H*$_3$)$_3$), 2.35-2.54 (m, 10 H, C*H*(CH$_3$)$_2$; COD-C*H*$_2$), 3.38-3.42 (m, 1 H, COD-C*H*), 3.49-3.53 (m, 2 H, COD-C*H*), 3.59-3.63 (m, 1 H, COD-C*H*), 3.64-3.68; 3.83-3.95 (m, 4H, C*H*$_2$OP(C_6H_5)$_2$), 4.99-5.05; 5.38-5.42 (m, 2 H, NC*H*), 5.08-5.17 m, 2 H, COD-C*H*), 5.47 (d, *J* = 14.0 Hz, 2 H, C*H*$_2C_6H_2$(CH$_3$)$_3$), 5.88 (dd, *J* = 14.4 Hz, 2 H, C*H*$_2C_6H_2$(CH$_3$)$_3$), 6.25 (s, 1 H, imidazole-*H*), 6.28 (s, 1 H, imidazole-*H*), 6.81 (s, 1 H, imidazole-*H*), 6.87 (s, 1 H, imidazole-*H*), 6.93; 6.95 (s, 4 H, $CH_2C_6H_2$(CH$_3$)$_3$, 7.35-7.75 (m, 30 H, P(C_6H_5)$_2$). ^{13}C NMR : δ (ppm): 19.2, 20.1, 20.3, 20.4, 21.1, 21.3, 27.7, 28.5, 29.2, 29.3, 30.1, 30.9, 32.3, 33.0, 33.8, 49.2, 49.5, 64.1 (d, *J* = 6.7 Hz, *C*H-cod), 65.9 (d, *J* = 7.3 Hz, *C*H-cod), 66.7 (d, *J* = 6.8 Hz, *C*H-cod), 68.5 (d, *J* = 14.3 Hz, *C*H-cod), 69.0 (dd, *J* = 15.1 Hz, *C*H-cod), 69.7 (dd, *J* = 14.0 Hz, *C*H-cod), 98.2-97.9 (m, *C*H-cod), 117.8, 119.0, 119.3, 119.6, 128.4, 128.5, 128.6, 128.8, 128.9, 129.1, 129.5, 129.6, 131.4, 131.5,

131.6, 131.7, 132.2, 132.3, 132.5, 132.7, 138.7. 182.6 (d, $J_{Rh,C}$ = 49.8 Hz, $C_{carbene}$), 182.9 (d, $J_{Rh,C}$ = 50.4 Hz, $C_{carbene}$). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm): 33.0, 33.8. Yield: 31%, m.p: 101-105. [α] = -50.0 (c 0.2, 22.6 ^{o}C, in CH_2Cl_2).

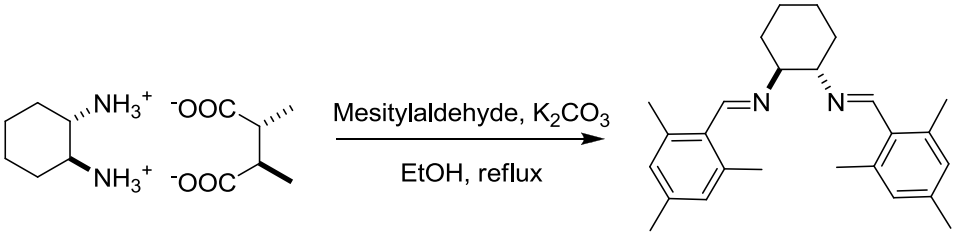
2.10 Synthesis of Rhodium Complex (28)



Complex **28** was synthesized using *Method A* as mentioned above.

^{1}H NMR : δ (ppm): 0.86 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.93 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 1.09 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 1.22 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 1.86-2.12 (m, 8 H, COD-CH_2), 2.24 (s, 12 H, CH_2C_6(CH_3)$_5$), 2.25 (s, 12 H, CH_2C_6(CH_3)$_5$), 2.27 (s, 6 H, CH_2C_6(CH_3)$_5$), 2.31-2.58 (m, 10 H, CH(CH$_3$)$_2$; COD-CH_2), 3.24 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 3.38-3.42 (m, 1 H, COD-CH), 3.49-3.53 (m, 2 H, COD-CH), 3.59-3.63 (m, 1 H, COD-CH), 3.64-3.68; 3.83-3.95 (m, 4 H, CH_2OCH$_3$), 4.96-5.00; 5.16-5.20 (m, 2 H, NCH), 5.03-5.09 (m, 2 H, COD-CH), 5.54 (dd, J = 14.4 Hz, 2 H, CH_2C_6(CH$_3$)$_5$), 6.00 (dd, J = 16.8 Hz, 2 H, CH_2C_6(CH$_3$)$_5$), 6.25 (s, 2 H, imidazole-H), 6.83 (d, J = 2.4 Hz, 1 H, imidazole-H), 6.85 (d, J = 1.6 Hz, 1 H, imidazole-H). ^{13}C NMR : δ (ppm): 17.0, 17.1, 17.2, 17.3, 19.6, 20.1, 20.6, 20.8, 28.0, 28.6, 29.0, 29.7, 30.8, 32.6, 33.1, 33.2, 33.9, 50.3 (d, J = 13.8 Hz, CH-cod), 59.4 (d, J = 11.5 Hz, CH-cod), 66.7, 67.2, 67.4 (d, J = 14.5 Hz, CH-cod), 67.9 (dd, J = 26.7 Hz, CH-cod), 68.5 (d, J = 14.5 Hz, CH-cod), 73.3, 73.7, 98.0 (d, J = 6.8 Hz, CH-cod), 98.4-98.2 (m, CH-cod), 117.9, 118.9, 119.1, 119.5, 128.8, 128.9, 133.2, 133.3, 134.3, 134.4, 135.8, 135.9, 181.3 (d, $J_{Rh,C}$ = 50.3 Hz, $C_{carbene}$), 182.0 (d, $J_{Rh,C}$ = 51.1 Hz, $C_{carbene}$). Yield: 89%, m.p: 106-110. [α] = -20.0 (c 0.2, 22.6 ^{o}C, in CH_2Cl_2).

2.11 Synthesis of (*R*,*R*)-1,3-bis(2,4,6-trimethylbenzyl)-1,2-cyclohexyldiimine (29)

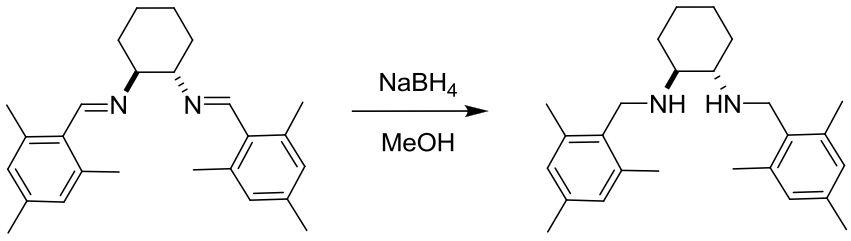


29

A two-necked flask was charged with (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartarate salt (1.0 g, 4.0 mmol), K_2CO_3 (1.1 g, 8.0 mmol) and distilled water (5 mL). The mixture was stirred until dissolution was achieved, and then EtOH (20 mL) was added. The mixture was heated to reflux, and 2,4,6-trimethylbenzaldehyde (1.1 mL, 8.0 mmol) was added. The slurry was stirred at reflux for 4 h. After cooling, EtOH was removed. And then aqueous phase was extracted with toluene (3x25 mL). After drying over Na_2SO_4, the solvent was removed under vacuum (Larrow and Jacobsen, 1994; Yiğit, 2002).

^{1}H NMR : δ (ppm): 1.51 (m, 2 H, NCH(C*H*$_2$)$_4$CHN), 1.82-1.88 (m, 6 H, NCH(C*H*$_2$)$_4$CHN), 2.24 (s, 6 H, CHC$_6$H$_2$(C*H*$_3$)$_3$), 2.26 (s, 12 H, CHC$_6$H$_2$(C*H*$_3$)$_3$), 3.39-3.42 (m, 2H, NC*H*(CH$_2$)$_4$C*H*N), 6.76 (s, 4 H, CHC$_6$*H*$_2$(CH$_3$)$_3$), 8.53 (s, 2 H, C*H*=N). ^{13}C NMR : δ (ppm): 20.8, 21.3, 24.8, 33.9, 75.9, 129.4, 131.5, 138.4, 160.5 (*C*H=N). Yield: 62%. m.p:114-117.

2.12 Synthesis of (*R*,*R*)-1,3-bis(2,4,6-trimethylbenzyl)-1,2-cyclohexyldiamine (30)



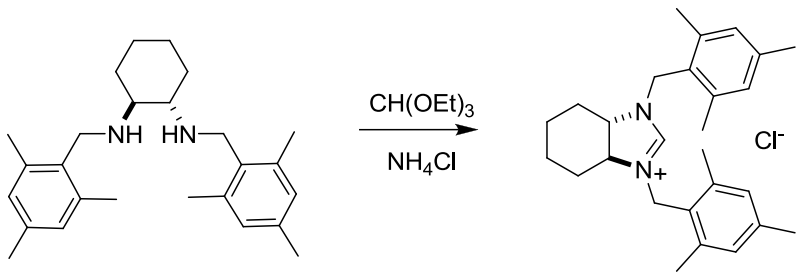
29 **30**

A solution of **29** in MeOH was added $NaBH_4$ in portions. After adding, the mixture was stirred at 25 ^{o}C for 3 h, and then refluxed for overnight. After

removing the solvent, the residue was dissolved in CH_2Cl_2 and washed with water. The organic phase was dried over Na_2SO_4 and then the volume reduced, and added hexane to the solution causing precipitation of the product (This compound was synthesized by Yiğit using a different procedure (Yiğit, 2002)).

^{1}H NMR : δ (ppm): 0.96-1.04 (m, 2 H, NCH(C*H*$_2$)$_4$CHN), 1.18-1.28 (m, 2 H, NCH(C*H*$_2$)$_4$CHN), 1.69-1.72 (m, 2 H, NCH(C*H*$_2$)$_4$CHN), 2.09-2.26 (m, 4 H, NCH(C*H*$_2$)$_4$CHN, NC*H*(CH$_2$)$_4$C*H*N), 2.16 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.20 (s, 12 H, $CH_2C_6H_2(CH_3)_3$), 3.40 (d, *J* = 11.6 Hz, 2 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 3.77 (d, *J* = 11.2 Hz, 2 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 6.70 (s, 4 H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR : δ (ppm): 19.7, 21.1, 25.4, 32.1, 45.3, 62.2, 129.1, 134.3, 136.4, 137.0. Yield: 86%.

2.13 Synthesis of (*R*,*R*)-1,3-bis(2,4,6-trimethylbenzyl)-1,2-cyclohexylimidazolidinium chloride (31)

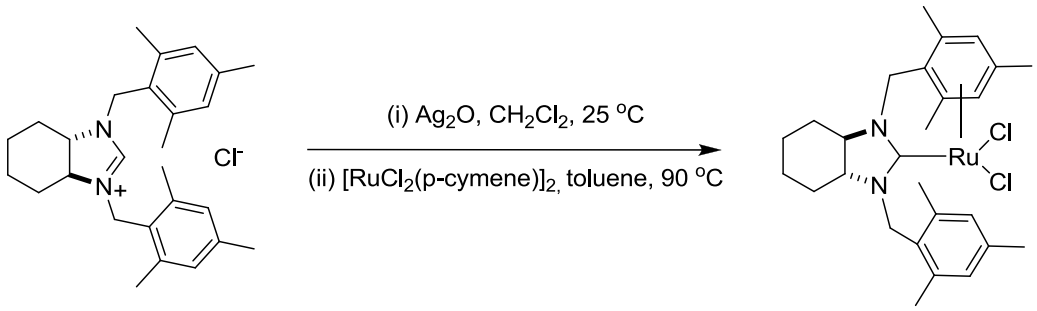


30 **31**

Compound **30** (4.8 g; 13.0 mmol), NH_4Cl (1.5 g, 26.0 mmol) and triethyl orthoformate (10 mL) were heated for 24 h until ethanol was removed by distillation. After volatiles were removed in vacuo, the residue was washed with ether and then was filtered off. The solid was recrystallized from CH_2Cl_2/Et_2O.

^{1}H NMR : δ (ppm): 1.17-1.26 (m, 2 H, NCH(C*H*$_2$)$_4$CHN), 1.34-1.44 (m, 2 H, NCH(C*H*$_2$)$_4$CHN), 1.74-1.89 (m, 4 H, NCH(C*H*$_2$)$_4$CHN), 2.25 (s, 6 H, $CH_2C_6H_2(CH_3)_3$), 2.31 (s, 12 H, $CH_2C_6H_2(CH_3)_3$), 3.45-3.47 (m, 2 H, NC*H*(CH$_2$)$_4$C*H*N), 4.89 (s, 4 H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$), 6.82 (s, 4 H, $CH_2C_6H_2(CH_3)_3$), 9.16 (s, 1 H, NC*H*N). ^{13}C NMR : δ (ppm): 20.4, 21.2, 28.0, 46.3, 68.8, 126.2, 129.9, 137.8, 138.9, 161.6 (NCHN) Yield: 80%, m.p: 238-240 ^{o}C (dec.).

2.14 Synthesis of Ruthenium Complex (32)



31 32

Compound **31** (0.5 g, 1.2 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and Ag_2O was added into the solution. The mixture was stirred in the dark at 25 ^oC for overnight under argon. Then the suspension was filtered through celite into the schlenk containing $[RuCl_2(p\text{-cymene})]_2$. After the mixture was stirred at 25 ^oC for overnight, dry toluene was added. The mixture was heated to 90 ^oC for 16 h under argon. After cooling, toluene was removed in vacuum. The residue was crystallized CH_2Cl_2/Et_2O.

^1H NMR : δ (ppm): 0.98-1.29 (m, 4 H, NCH(CH_2)$_4$CHN), 1.36-1.80 (m, 4 H, NCH(CH_2)$_4$CHN), 2.15, 2.20, 2.21, 2.22, 2.24, 2.29 (s, 18 H, $CH_2C_6H_2(CH_3)_3$), 2.96 (m, 1 H, NC*H*(CH$_2$)$_4$C*H*N), 3.15-3.22 (m, 1 H, NC*H*(CH$_2$)$_4$C*H*N), 3.89 (d, *J* = 12.0 Hz, 1 H, C$H_2C_6H_2(CH_3)_3$), 4.20 (d, *J* = 12.0 Hz, 1 H, C$H_2C_6H_2(CH_3)_3$), 5.09 (d, *J* = 16.0 Hz, 1 H, C$H_2C_6H_2(CH_3)_3$), 5.25 (d, *J* = 16.0 Hz, 1 H, C$H_2C_6H_2(CH_3)_3$), 5.41 (d, *J* = 16.0 Hz, 2 H, $CH_2C_6H_2(CH_3)_3$), 6.71 (d, *J* = 4.0 Hz, 1 H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR : δ (ppm): 16.7, 17.5, 20.4, 20.9, 24.4, 28.7, 29.4, 67.9, 68.6, 89.2, 90.8, 93.1, 97.2, 97.8, 103.7, 129.2, 129.4, 130.0, 136.5, 138.0, 206.3 ($C_{carbene}$). Yield: 30%. m.p: 260 ^oC (dec.). [α] = -28.57 (c 0.105, 24.8 ^oC, in CH_2Cl_2).

2.15 Catalytic Experiments

2.15.1 General procedure for the allylic alkylation reactions

To a solution of palladium complex (0.02 mmol, 2.5 mol%) and Cs_2CO_3 (0.84 mmol) in THF (1 mL) were added a solution of (*E*)-1,3-diphenyl-3-en-yl acetate (0.8 mmol) in THF (1 mL) followed by a solution of diethyl malonate in THF (1 mL). The mixture was heated to 50 ^oC for 48 h under argon. To the

mixture was added saturated NH_4Cl solution, and the organic layer was extracted with Et_2O. The combined organic layer washed with brine and dried over Na_2SO_4. After the solvent was evaporated in vacuo, the residue was analyzed by ^1H NMR and gas chromatography.

2.15.2 General procedure for the transfer hydrogenation reactions

To a solution of catalyst (1 mmol, 1mol%) and acetophenone (1 mmol) in IPA (4 mL) was added a solution of KOH (0.04 mmol) in IPA (1 mL). The mixture was stirred under argon in a two-necked flask at 75 ^oC for 19 h. After cooling to ambient temperature, the solvent was removed under vacuum. The product was purified by preperative TLC (pentane/Et_2O 6:3). Yields were determined by ^1H NMR. Enantiomeric excesses were determined by HPLC using chiral OD-H column.

2.15.3 General procedure for the arylation of aldehydes

Phenylboronic acid (2 mmol), rhodium complex (1 mmol, 1 mol%), (1 mmol) and KO^{t}Bu (1 mmol) were successively added to two-necked flask and the vessel was evacuated and flushed with argon three times. DME (3 mL) and H_2O (1mL) was syringed, and then benzaldehyde was added to the mixture. The mixture was heated to 80 ^oC for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with ethyl acetate (30 mL) and washed with water (5 mL). The organic phase was dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by preperative TLC (petrol ether/ethyl acetate 12:1). Yields were determined by ^1H NMR. Enantiomeric excesses were determined by HPLC using chiral OD-H column.

3. RESULTS AND DISCUSSION

The synthesis of three different types of chiral NHC ligands and their complexes (Figure 3.1) was targeted, and we also planned to test their catalytic activities in asymmetric allylic alkylation, transfer hydrogenation and arylation reactions.

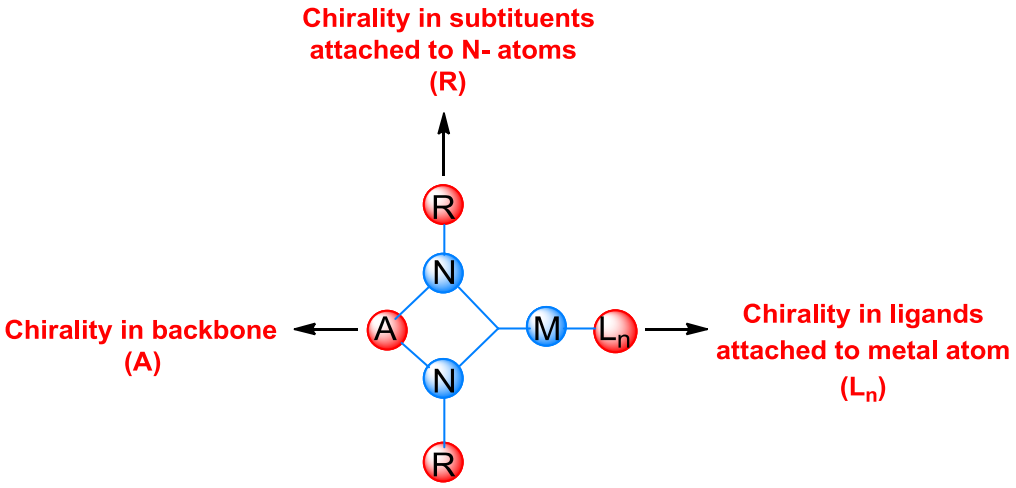


Figure 3.1. Possible chirality positions in a NHC complex.

In this section, the synthesis and characterization of NHC-Pd(II) complexes bearing a chiral ligand other than NHC were firstly described (Scheme 3.2). We prepared benzimidazolium salts and their dimeric palladium complexes to obtain NHC-Pd(II) complexes (Scheme 3.1 and 3.2). Chiral oxazolines are important chiral axuiliary or key elements in numurous ligands. Oxazolines or oxazoline containing compounds have been applied as ligands in asymmetric catalysis over the past decade (Västilä et al., 2004; Scwekendiek and Glorius, 2006). It is known that chiral NHC-oxazoline complexes displayed moderate to good enantioselectivities for asymmetric catalysis (Powell et al., 2001; Perry and Burgess, 2003; Gade et al., 2004; César et al., 2005; Nanchen and Pfaltz, 2006; Scheider et al., 2009). As a result, we decided to synthesize NHC complexes bearing a chiral oxazoline. The cleaveage of dimeric palladium complexes were performed by chiral oxazoline.

It has been noticed that the chiral induction of monodentate chiral NHC ligands was low, which is probably due to the rapid internal rotation of the chiral substituents around the C-N axis. However, polydentate chiral NHC ligands, in

which the NHC scaffold is linked to other coordinating units such as alkoxy, imino, oxazoline, phosphine or phosphinite, displayed better enantioselevtivity. For this reason, a secondary objective was to develop chelating chiral NHC ligands bearing functional groups such as hydroxyl group to increase the enantioselectivity.

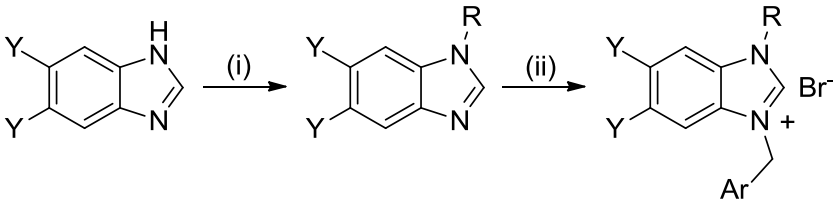
Besides, it has been shown that phosphine analogous containing NHCs give much superior asymmetric induction. Therefore, it was decided to devise the synthesis of phosphinite-NHC ligands.

3.1 NHC-Pd(II) Complexes Bearing Chiral Ligand Other Than NHC

3.1.1 Synthesis and characterization of (5,6-dimethyl)benzimidazolium bromides (1-6)

The (5,6-dimethyl)benzimidazolium salts were synthesized according to the steps illustrated in Scheme 3.1. At the first step, 1-substituted (5,6-dimethyl)benzimidazoles were prepared by treating (5,6-dimethyl)benzimidazole and appropriate alkyl or benzylic halide under basic conditions (Step (i)) (Özdemir et al., 2004; 2005a, Denizaltı, 2006). (5,6-dimethyl)benzimidazolium bromides (**1**-**6**) were obtained via alkylation of monosubstituted (5,6-dimethyl)benzimidazole with benzyl bromides in toluene (Step (ii)). These salts are air and moisture stable solids.

These benzimidazolium salts have been characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR chemical shifts were consistent with the proposed structures; the resonances for C_2 hydrogenes were observed as sharp singlets between 9.49-10.78 ppm. ^{13}C NMR of these salts showed the C_2 carbons at 140.4-143.2 ppm (Figure 3.2, 3.3).



1-6

Compound	Y	R	Ar
1	H	$-CH_2C_6H_2(CH_3)_3$-2,4,6	$C_6H_2(CH_3)_3$-2,4,6
2	H	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6
3	H	$-CH_2CH_2OCH_3$	$C_6H(CH_3)_4$-2,3,5,6
4	H	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6
5	CH_3	$-CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6
6	CH_3	$-CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6

Scheme 3.1. Synthesis of (5,6-dimethyl)benzimidazolium bromides (**1**-**6**). Reagents and conditions of reactions: (i) RX, KOH, toluene, EtOH or BuOH; (ii) $ArCH_2Br$, toluene, reflux.

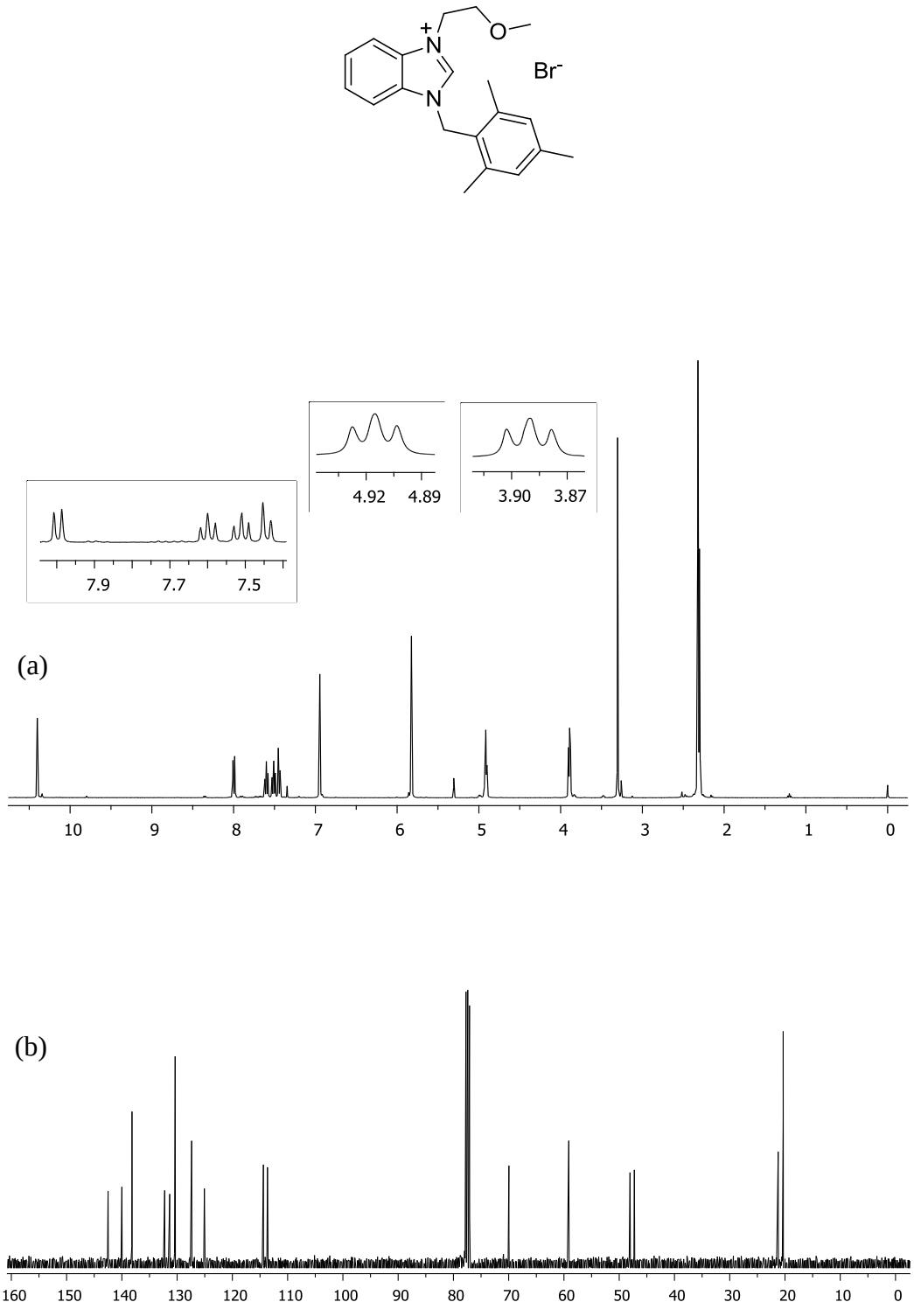


Figure 3.2. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **2** in $CDCl_3$.

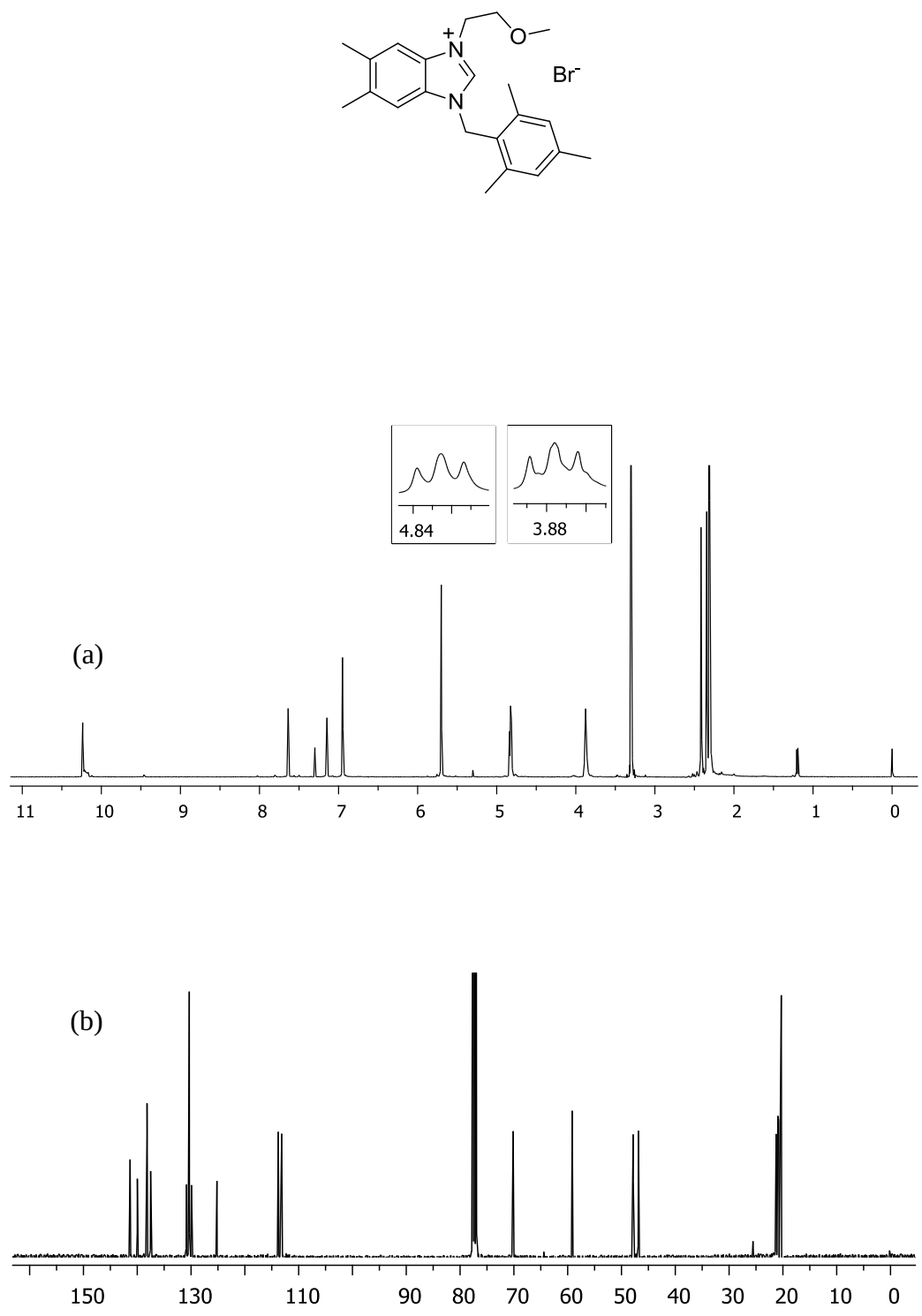


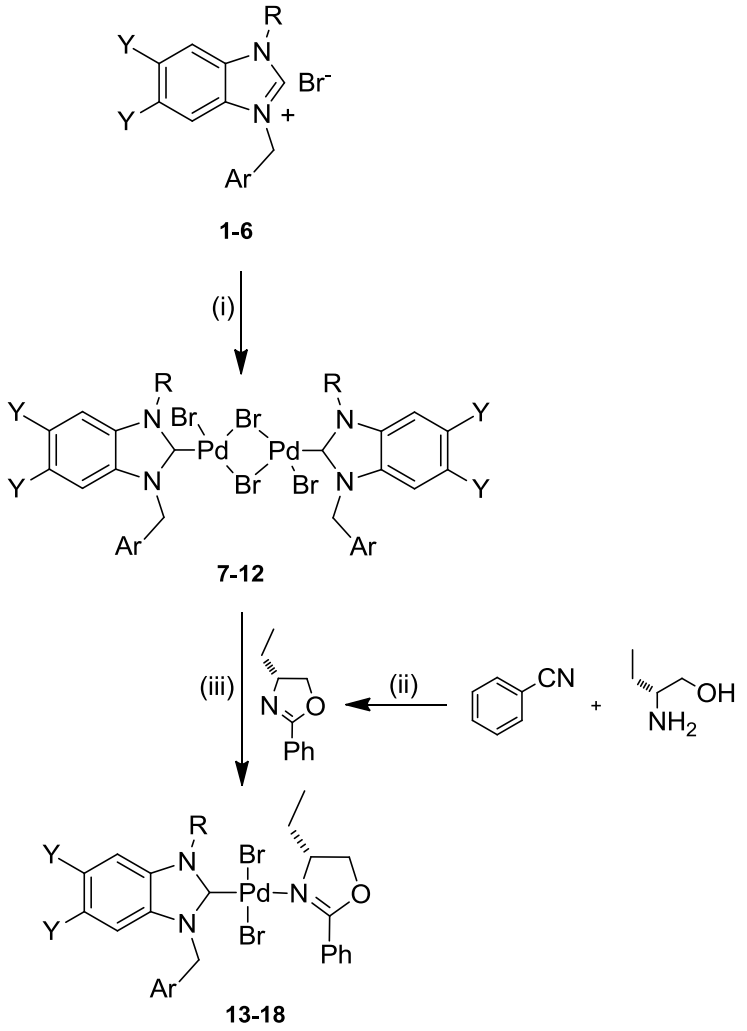
Figure 3.3. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **5** in $CDCl_3$.

3.1.2 Synthesis and characterization of NHC-Pd(II) complexes bearing chiral oxazoline ligand (13-18)

Dimeric NHC-Pd(II) carbene complexes cleaved by various nucleophiles to give mixed [Pd(NHC)(nuc)] complexes. NHC-Pd(II) complex containing chiral proline ligand synthesized using this method (Enders et al., 1996). Later, NHC-Pd(II) complexes containing N-donor ligands such as pyridine and azole derivatives have been reported (O'Brien et al., 2006; Yen et al., 2008; 2009a; 2009b; Türkmen et al., 2009). A similar methodology was followed for the synthesis of **13-18**.

The synthesis of dimeric NHC-Pd complexes by reaction of benzimidazolium salt with $Pd(OAc)_2$ in the presence of excess NaBr in DMSO has been reported by Huynh et al. (Huynh et al., 2006). Using a similar method the dimeric NHC-Pd(II) complexes (**7-12**) were synthesized in moderate yields (50%- 76%) as air stable orange solids slightly soluble in halogenated solvents (Scheme 3.2). However, it was known that coordinating solvents such as DMSO, THF, MeCN cleave the dimeric complex (Huynh et al., 2006). Dimeric complexes are sparingly soluble in $CDCl_3$. Additionally DMSO cleaves the dimeric complexes. Because of these properties, NMR spectra of dimeric complexes (**7-12**) have not been recorded.

Dimeric palladium complexes (**7-12**) and chiral oxazoline reacted in dichloromethane to give mixed NHC-oxazoline complexes of Pd(II) (**13-18**) as air-stable yellow solids soluble in halogenated solvents (Scheme 3.2). NMR analyses of the complexes showed that chiral oxazoline ligand coordinated to the palladium center. ^{13}C-NMR spectra of these complexes (**13-18**) showed $C_{carbene}$ resonance in 167.1-167.3 ppm range. C=N signal in the oxazoline ring was observed between 163.6 and 165.6 ppm. Optical rotations of these palladium complexes were also measured and given in the experimental section (Table 2.3).



Compound	Y	R	Ar
13	H	-$CH_2C_6H_2(CH_3)_3$-2,4,6	$C_6H_2(CH_3)_3$-2,4,6
14	H	-$CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6
15	H	-$CH_2CH_2OCH_3$	$C_6H(CH_3)_4$-2,3,5,6
16	H	-$CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6
17	CH_3	-$CH_2CH_2OCH_3$	$C_6H_2(CH_3)_3$-2,4,6
18	CH_3	-$CH_2CH_2OCH_3$	$C_6(CH_3)_5$-2,3,4,5,6

Scheme 3.2. Synthesis of NHC-Pd(II) complexes bearing chiral oxazoline ligand (**13**-**18**). Reagents and conditions of reactions: (i) $Pd(OAc)_2$, NaBr, DMSO, 90 ^oC; (ii) $ZnCl_2$, chlorobenzene; (iii) (4*S*)-4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazole, CH_2Cl_2, 25 ^oC.

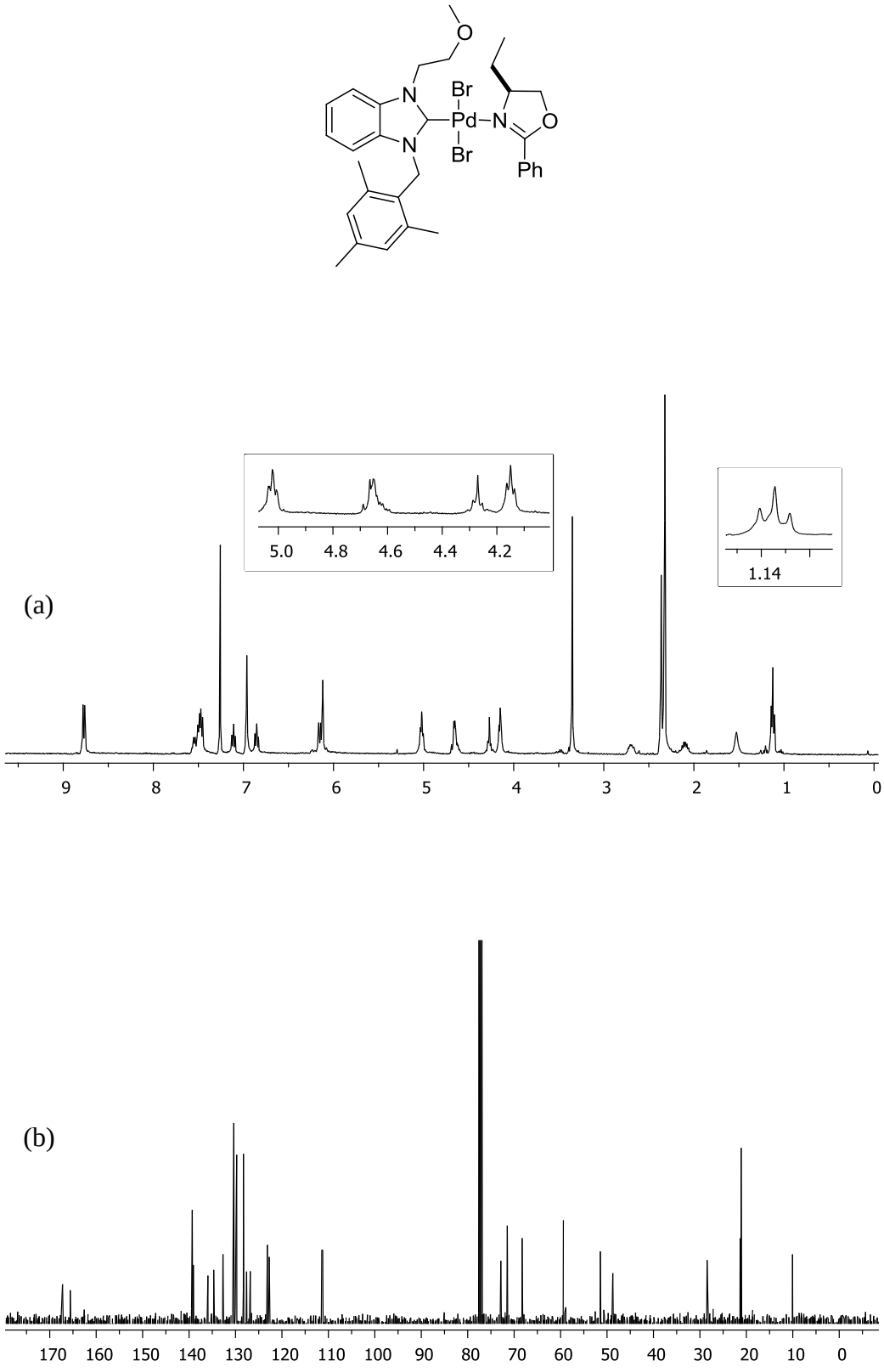


Figure 3.4. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **14** in $CDCl_3$.

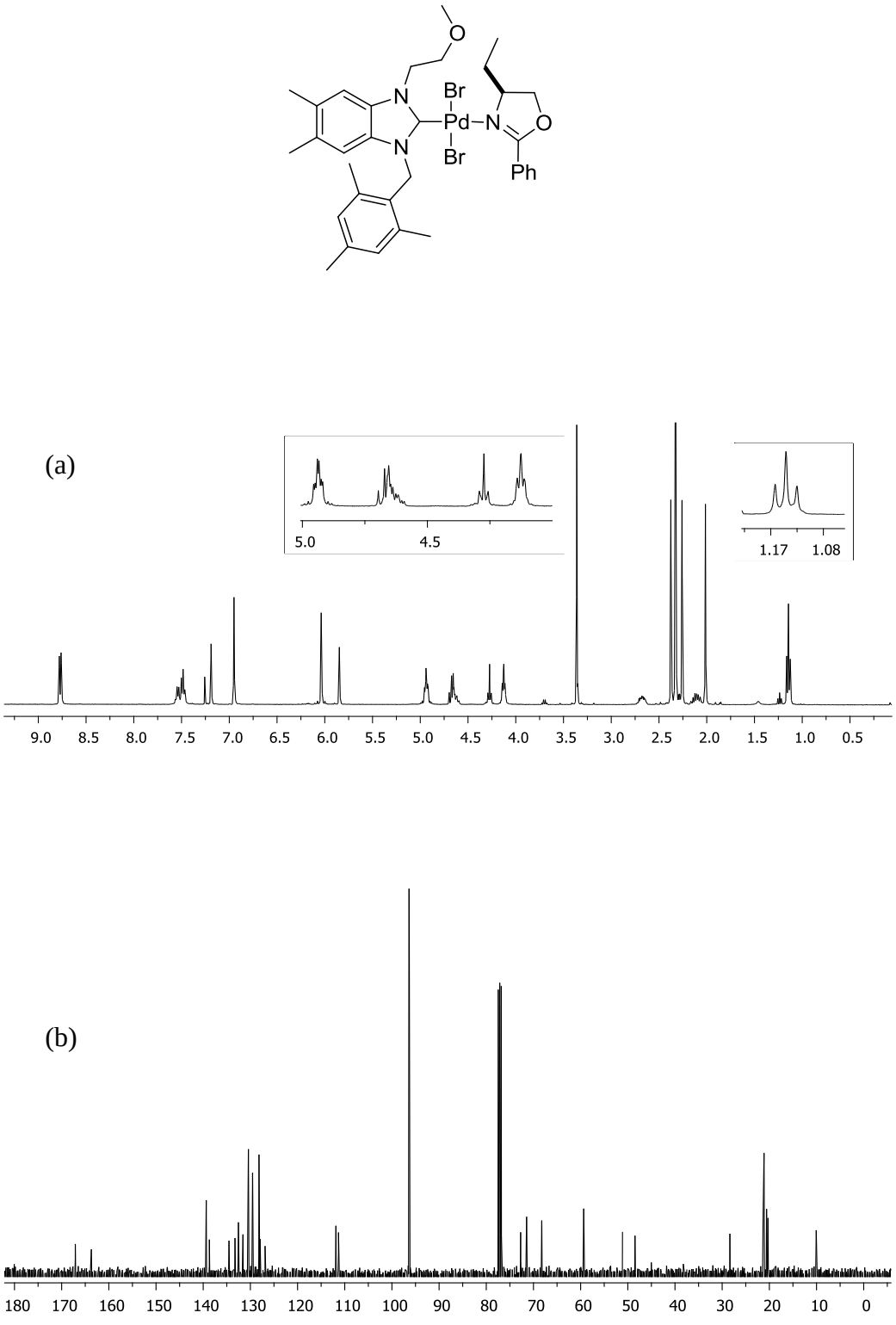
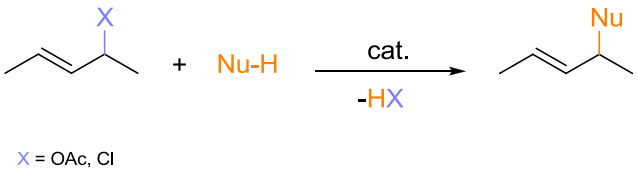


Figure 3.5. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **17** in $CDCl_3$.

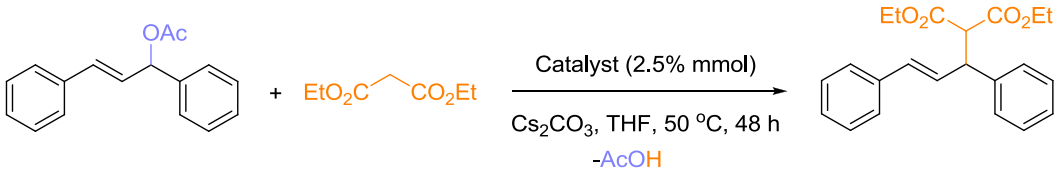
3.1.3 Allylic alkylation reactions with NHC-Pd(II) complexes bearing chiral oxazoline ligand (13-18)

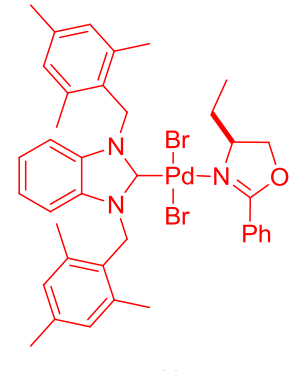
Palladium catalyzed allylic alkylation and its asymmetric variant are one of the most important carbon-carbon or carbon-heteroatom bond forming reactions (Scheme 3.3). The nucleophile can be carbon, nitrogen or oxygen based such as alcohols, enolates, phenols and enamines. The leaving group can for example be a halide or acetate. The first example of allylic alkylation catalyzed by NHC–palladium complexes was reported by Sato and Mori (Sato and Mori, 2003; Sato et al., 2005). Later on, several enantioselective versions using chiral NHC ligands have been published (Bonnet and Douthwaite, 2003; Hodgson and Douthwaite, 2005, Li et al., 2006; Flahaut et al., 2006; 2007a; 2007b; Toselli et al., 2008).



Scheme 3.3. Allylic alkylation reaction.

NHC-Pd(II) complexes **13-18** were screened as catalysts for allylic alkylation reaction of (*E*)-1,3-diphenyl-3-en-yl acetate using diethyl malonate as a nucleophile. The catalytic experiments were carried out using 2.5% mmol palladium complexes **13-18** as catalysts in the presence of Cs_2CO_3 in THF at 50 ^oC. The results were summarized in Figure 3.6. The complex **13** was found to be the most active catalyst among all of these complexes (Figure 3.6). The activities of these complexes would decrease in the order: **13** > **14** > **15** > **16** > **17** > **18**. Comparison of **14**, **17** and **16**, **18** showed that the methyl groups on the benzimidazole ring decrease the catalytic activity. The low reaction rate in the complexes could be explained that with the strong σ-donating effect of the NHC ligand which disfavors the nucleophilic addition step. These observations are consistent with the work of Flahaut (Flahaut et al., 2007a). Although the complexes **13-18** are chiral, no enantioselectivity could been observed. This result indicates that the chiral oxazoline ligand leaves the metal center early in the catalytic cycle. Clearly the development of chiral ligands independent of the NHC ligand for chiral induction in the allylic alkylation does not appear to be promising.





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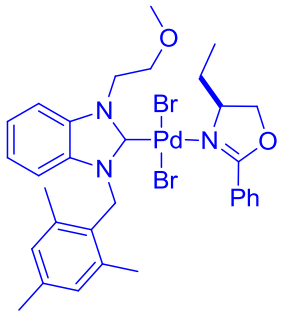

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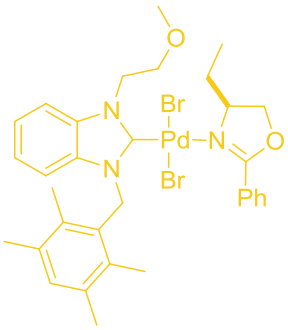

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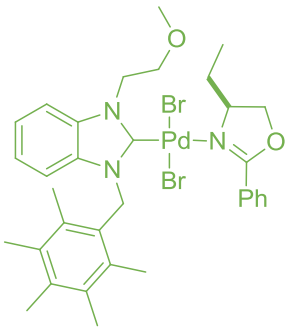

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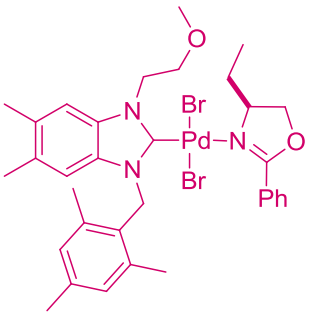

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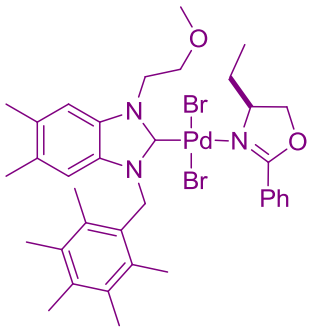

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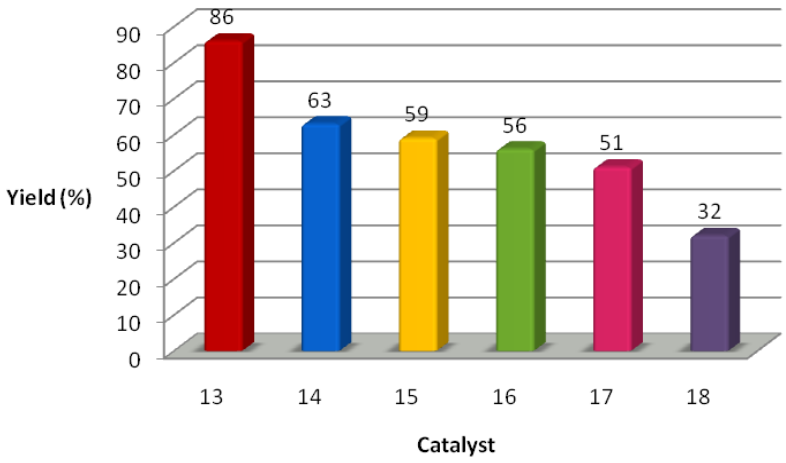


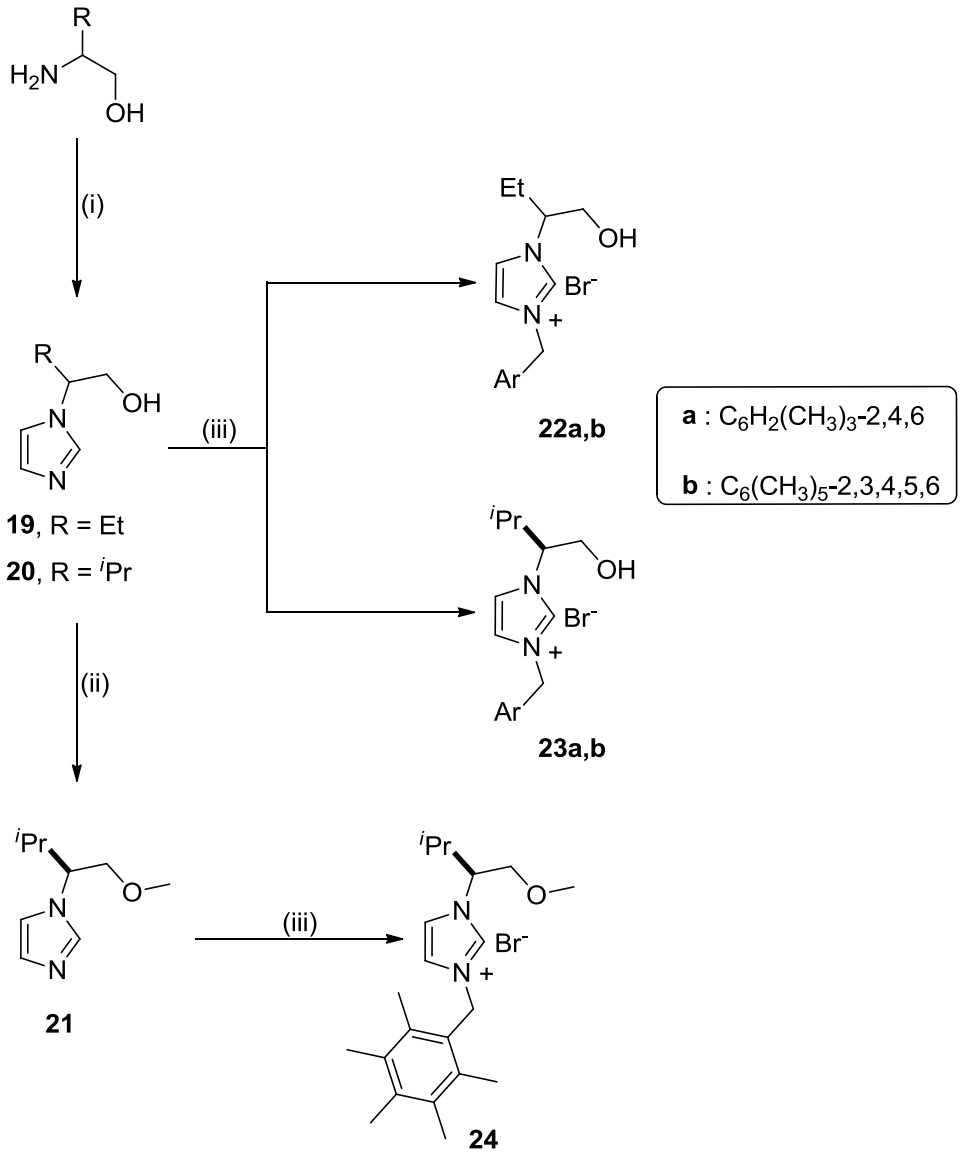
Figure 3.6. Allylic alkylation reaction of (*E*)-1,3-diphenyl-3-en-yl acetate catalyzed by NHC-Pd(II) complexes **13-18**.

3.2 Chiral NHC Ligands Bearing Chiral N-Substituents and Their Complexes

3.2.1 Synthesis and characterization of chiral imidazolium ligands (22-24)

Chiral imidazolium salts (**22**-**24**) were prepared according to the procedure indicated in Scheme 3.4 and described in the experimental section. These salts obtained from 1-substituted imidazoles (**19**, **20**) by the cyclocondensation of glyoxal, ammonium acetate, formaldehyde and chiral amino alcohol, which synthesized according to previously published procedure (Matsuoka et al., 2006). Compound **21** by methylation of hydroxyl group was prepared using MeI in the presence of NaH as a base. It is worth mentioning that imidazolium salts (**22**) derived from (*R*)-2-amino-1-butanol were achiral. It is assummed that ethyl group, which is smaller compared to the isopropyl group, rotates around the C-N axis.

These imidazolium salts have been characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR chemical shifts were consistent with the proposed structures; the resonances for C_2 hydrogenes were observed as sharp singlets between 9.63-10.61 ppm. ^{13}C NMR of these salts showed the C_2 carbons at 137.2-139.9 ppm (Figure 3.8, 3.11, 3.12).



Scheme 3.4. Synthesis of chiral imidazolium ligands (**22-24**). Reagents and conditions of reactions: (i) Glyoxal, HCOOH, NH_4OAc, MeOH, reflux, 5h; (ii) NaH, MeI, DMF; (iii) $ArCH_2Br$, DMF, 25 ^oC.

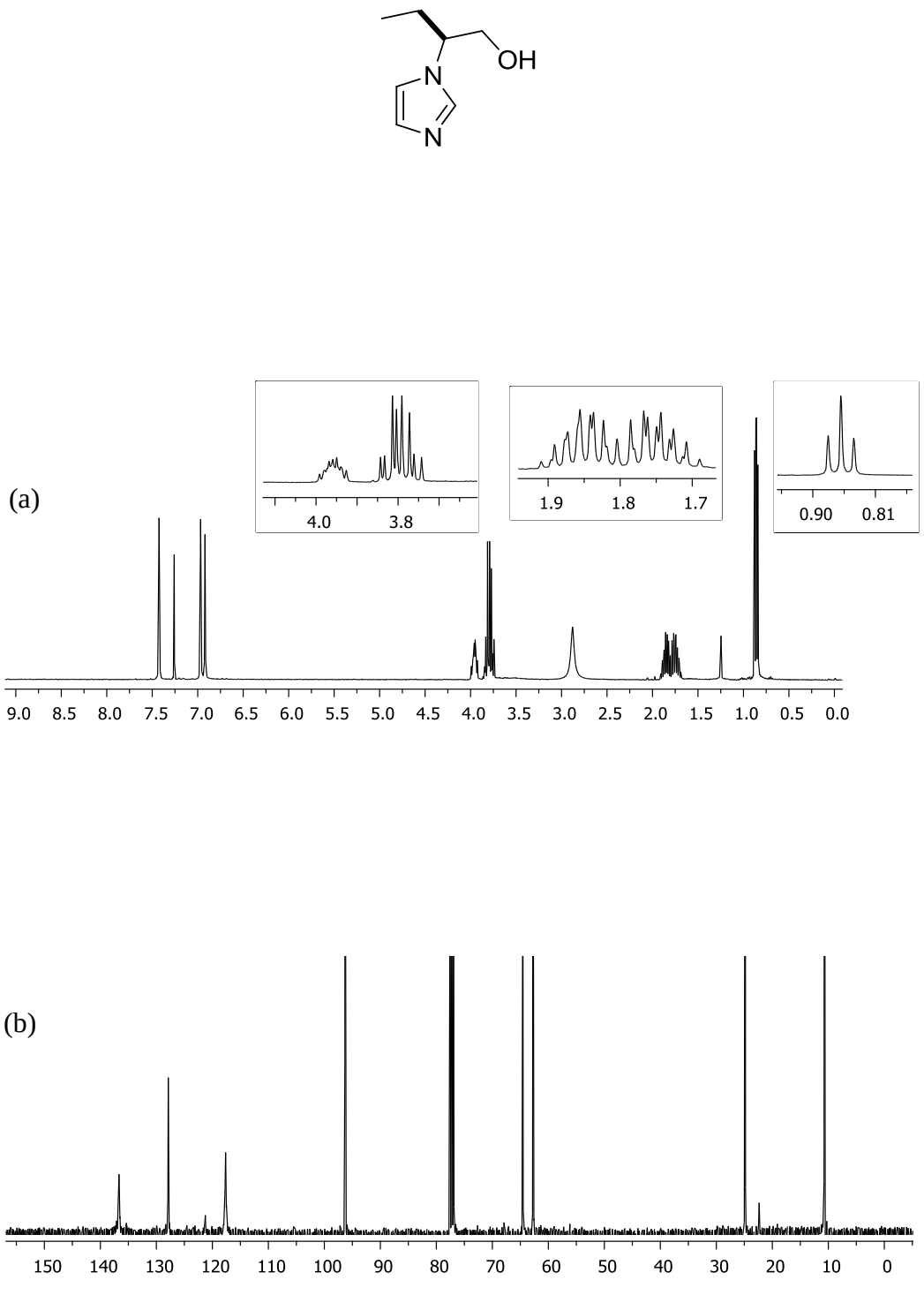


Figure 3.7. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **19** in $CDCl_3$.

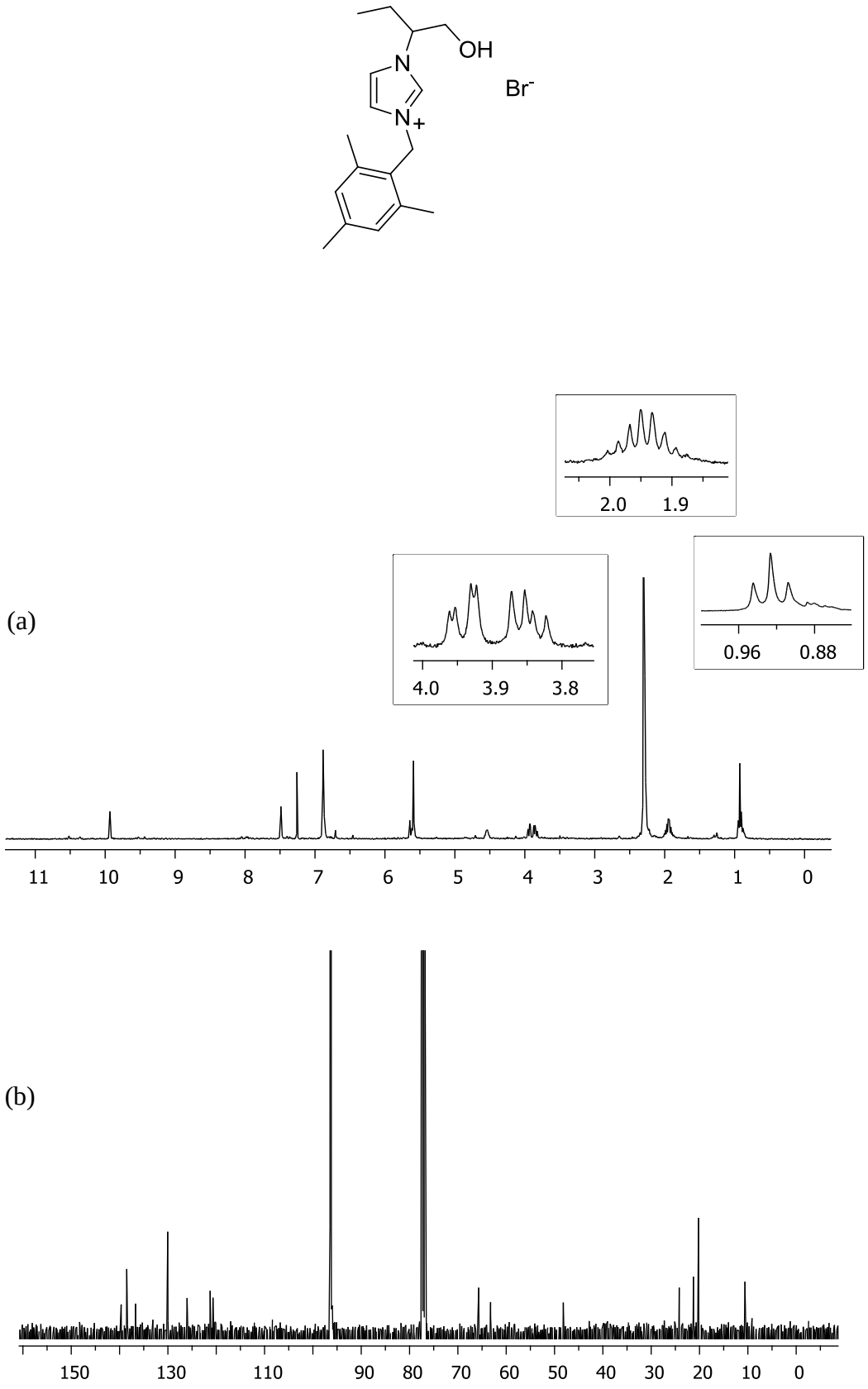
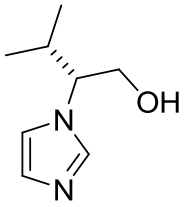


Figure 3.8. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **22a** in $CDCl_3$.



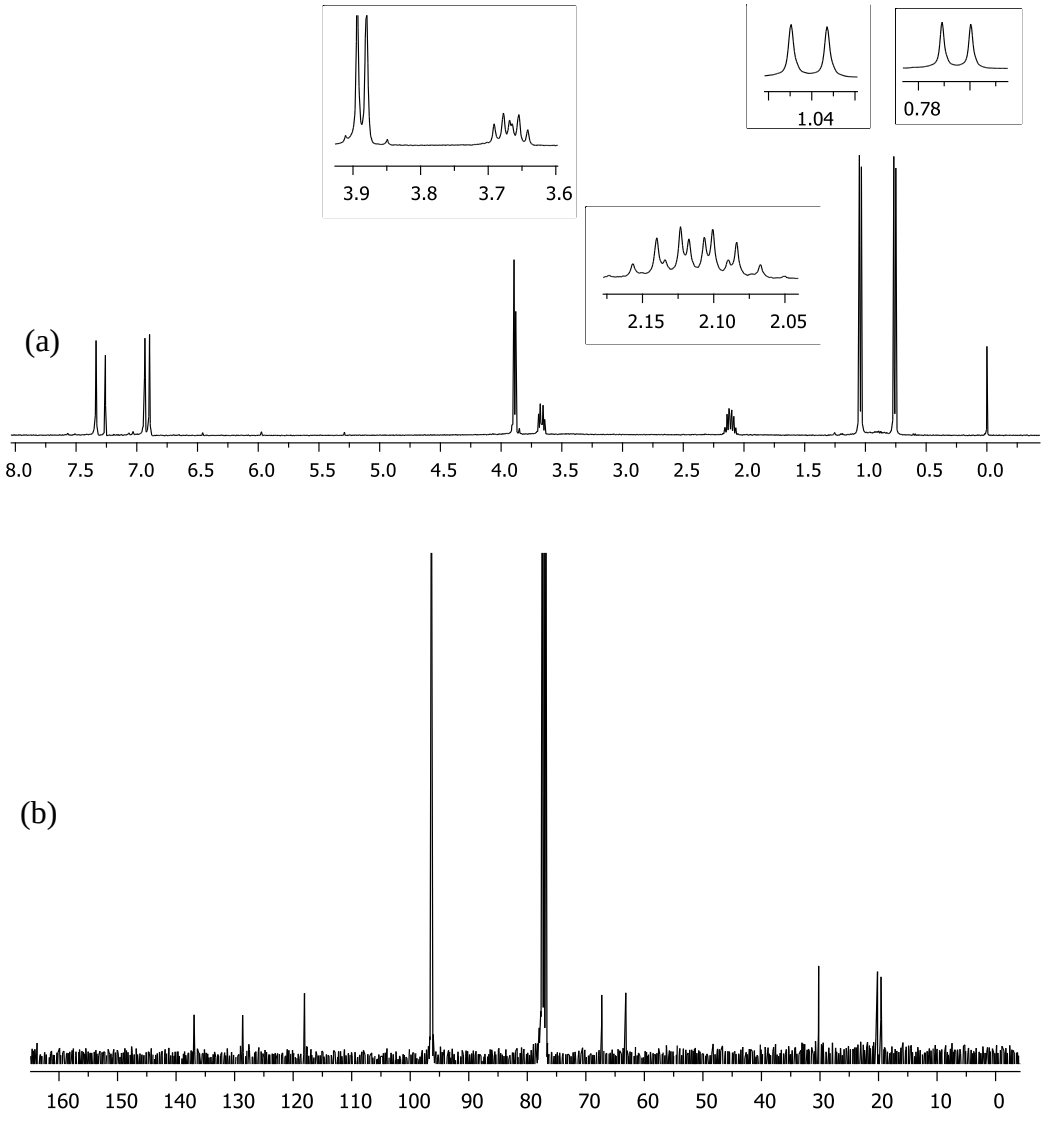


Figure 3.9. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **20** in $CDCl_3$.

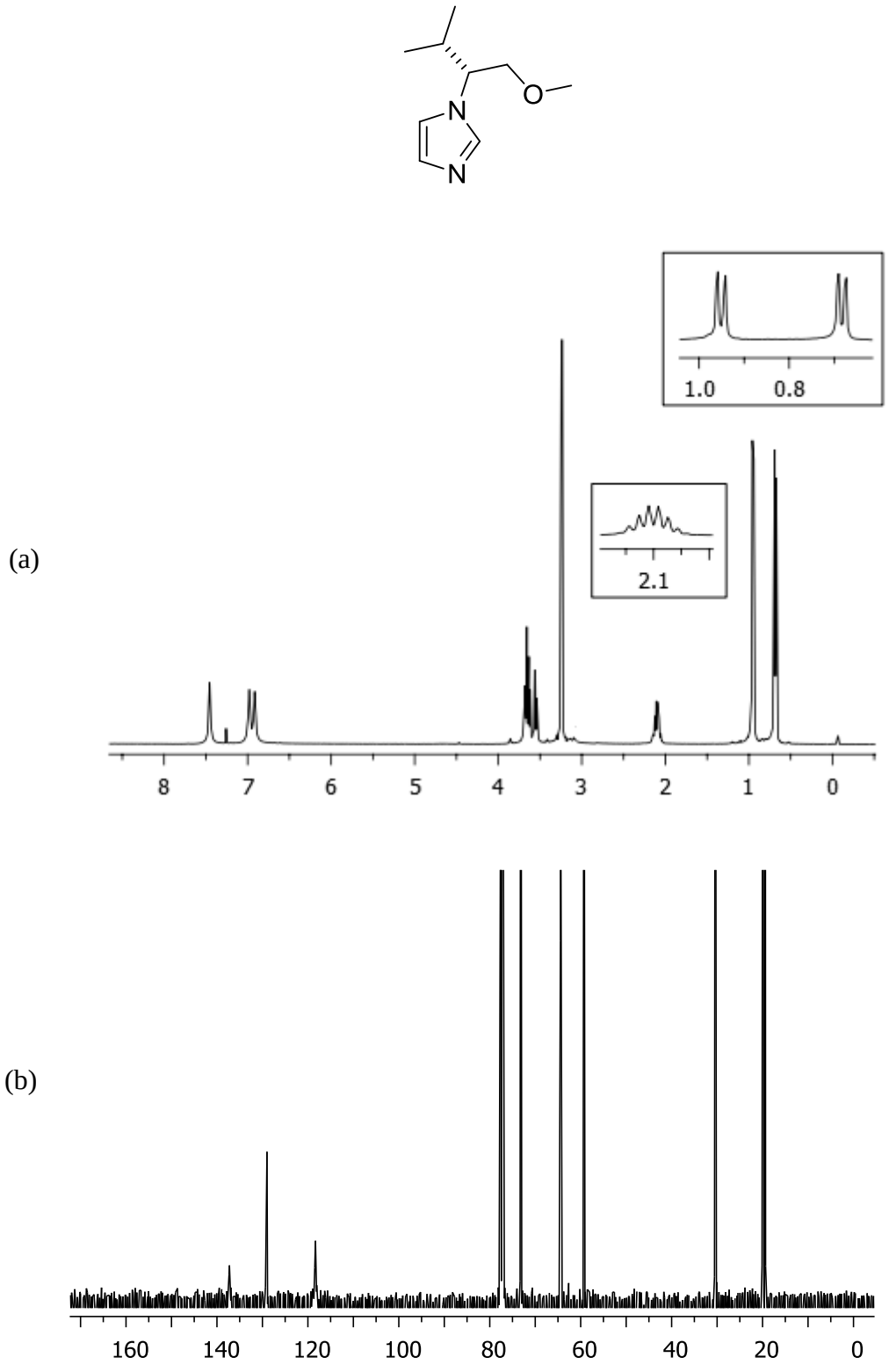
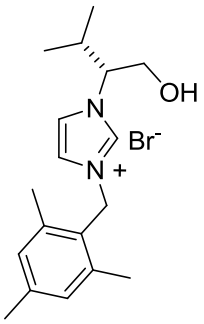
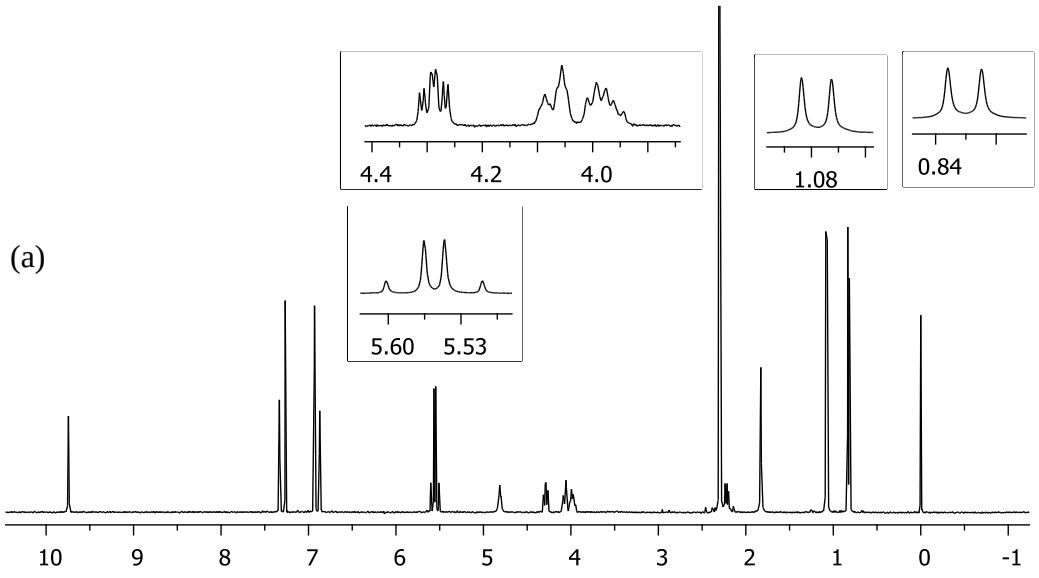


Figure 3.10. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **21** in $CDCl_3$.





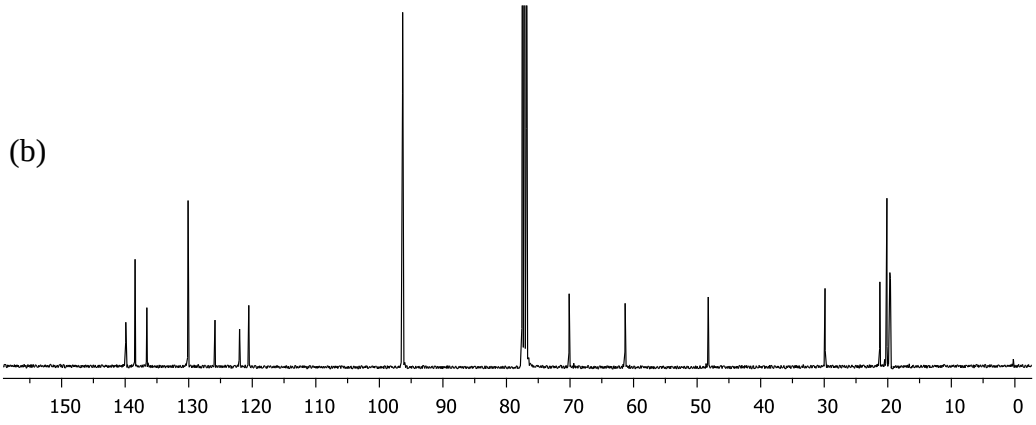


Figure 3.11. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **23a** in $CDCl_3$.

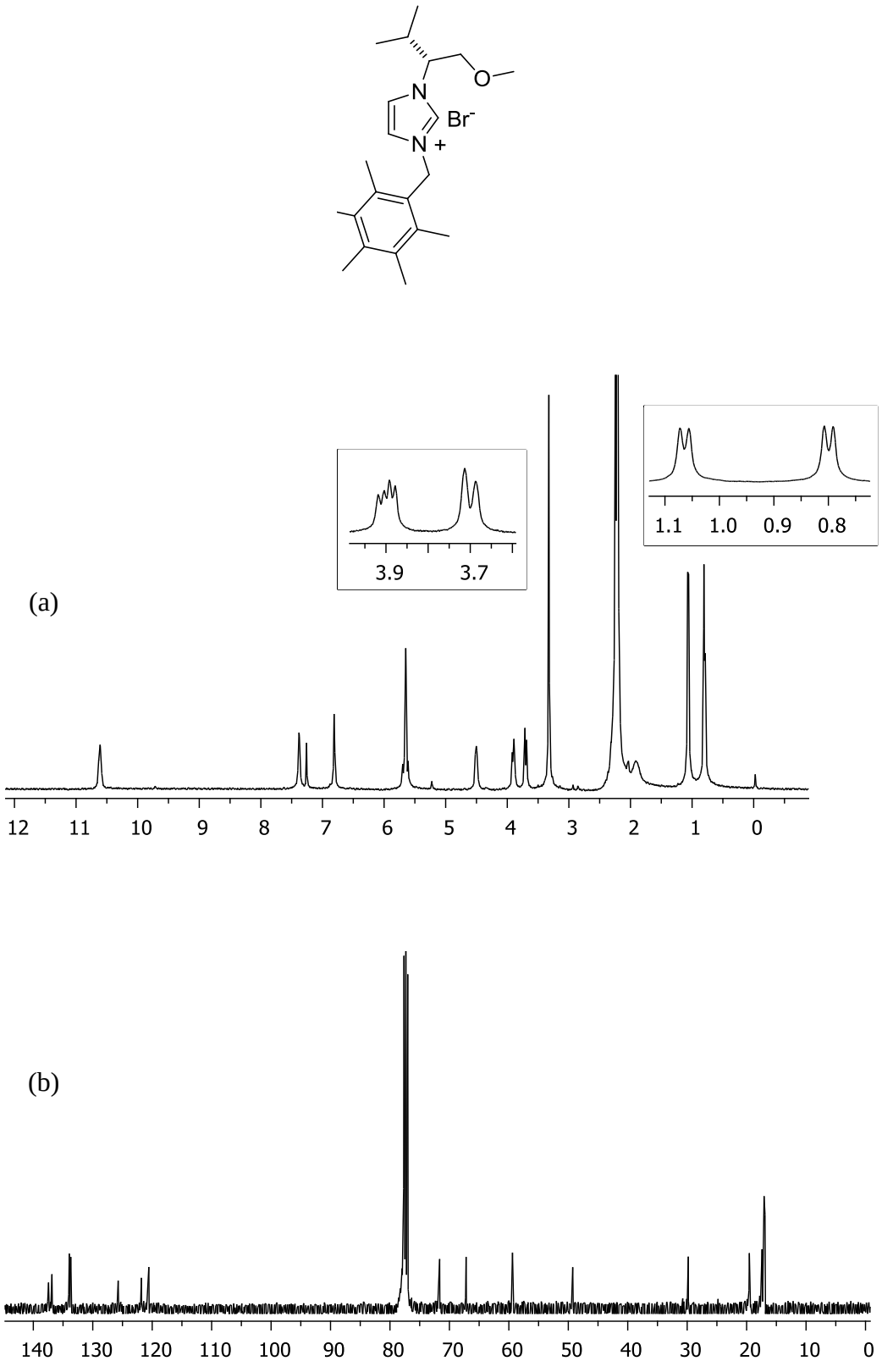


Figure 3.12. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **24** in $CDCl_3$.

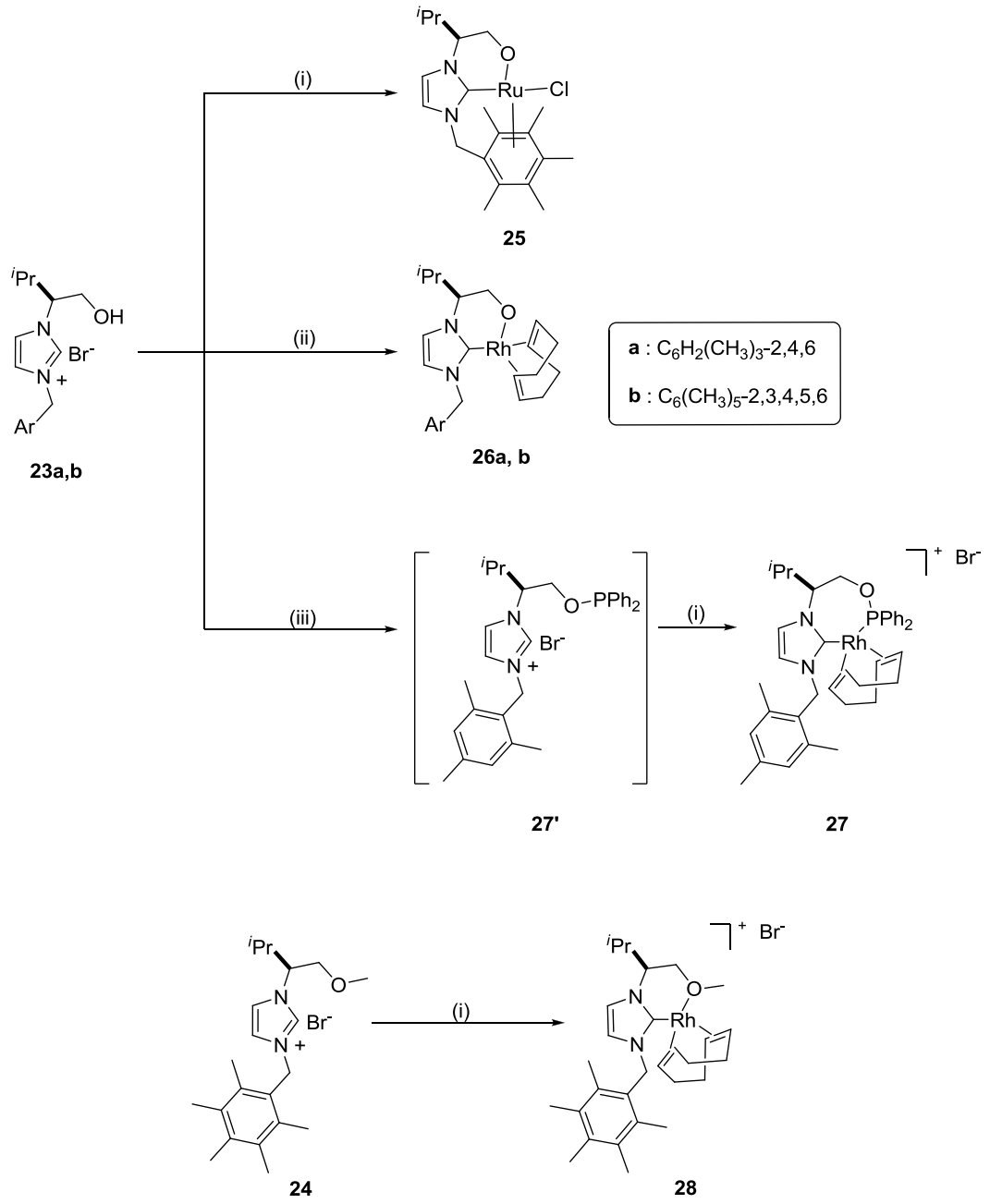
3.2.2 Synthesis and characterization of chiral NHC-Ru(II) and Rh(I) complexes (25-28)

Chiral NHC-Ru(II) complex (**25**) was synthesized by carbene-transfer reaction of *in situ* formed NHC-Ag species with $[RuCl_2(p\text{-cymene})]_2$ in dichloromethane at ambient temperature. The characteristic downfield signal for the C_2 hydrogen of imidazolium salt was not observed in the ^{1}H NMR spectrum of Ru complex. The ^{13}C NMR signal of the $C_{carbene}$ atom of complex **25** appeared at 175.2 ppm (Figure 3.13).

Chiral NHC Rh(I) complexes (**26**-**28**) could be synthesized in three different way: i) deprotonation of the imidazol(in)ium salts with a strong base such as LiO^tBu and subsequent reaction with $[Rh(COD)Cl]_2$, ii) using carbene-transfer reaction of *in situ* formed NHC-Ag species with $[RhCl(COD)]_2$ in dichloromethane at ambient temperature, iii) using $[RhOMe(COD)]_2$ which deprotonates and coordinates the desired ligand *in situ* (Scheme 3.5). However, it was known that rhodium(I) complexes formed by deprotonation of an imidazolinium salt with LiO^tBu and subsequent reaction with $[Rh(COD)Cl]_2$ affords achiral complex. This is supposed to be due to the basic conditions which results in the loss of chirality during the reaction (Zinner et al., 2008). For this reason, a different aproach was attempted by transmetallation reaction with a silver(I)–NHC complex leads to the corresponding rhodium(I) complexes (**26**-**28**) with the retention of chirality.

The rhodium complexes synthesized here were fully characterized by standard 2D-NMR techniques. In the ^{1}H NMR spectra of Rh complexes, OH proton was not observed. This behaviour was consistent with the literature (Edworthy et al., 2005). Silver alkoxide NHCs were prepared by Arnold's group. They reported that silver(I) oxide was sufficiently basic to deprotonate both the imidazolium and the alcoholic functionality (Edworthy et al., 2005). However, we also used two other methods to synthesize rhodium complexes. Both deprotonation of imidazolium salts with LiO^tBu and subsequent reaction with $[Rh(COD)Cl]_2$ or using of $[Rh(OMe)(COD)]_2$ and the corresponding salts leads to chiral NHC alkoxide Rh(I) complexes. The characteristic downfield signals for the C_2 hydrogens of the imidazolium salts were not observed in the ^{1}H NMR spectra of Rh(I) complexes. ^{13}C NMR spectra of Rh(I) complexes (**26**-**28**) showed $C_{carbene}$ resonance between δ 181.2-182.9 ppm and coupling constants $J(^{103}Rh–^{13}C)$ were between 49.5-50.4 Hz (Figure 3.15, 3.16).

NHC-phosphorus mixed ligands are good candidates for hemilable behavior since they combine a strong NHC donor with a more labile phoshorus donor. We envisioned that the alcohol functionality of **23** can be exploited. Therefore, we treated **23b** with $ClPPh_2$ in the presence of Et_3N. The resulting phosphinite ligand **27'** has not been isolated in view of air sensitivity of the product, instead the *in situ* procedure was followed (Scheme 3.5). ^{1}H NMR spectra of complexes **27** and **28** showed two sets of signals (1:1 ratio) at room temperature. Notably, two species were present in solution. These results were in accordance with the reference published by Nanchen and Pfaltz (Nanchen and Pfaltz, 2006). They indicated that the assumption of two conformers of Ir complex arise from a flip of the chelate ring was consistent with the NOSEY plot, which showed an NOE contact between the isopropyl group and the COD for one of the two conformers (Figure 1.8). Their ^{13}C NMR spectra also displayed two sets of signals of $C_{carbene}$ between 181.3 and 182.9 ppm and the coupling constants $J(^{103}Rh–^{13}C)$ were in the range of 49.8 and 51.0 Hz (Figure 3.18b, 3.19). ^{31}P NMR spectrum of complex **27** showed two signals (1:1 ratio) at 33.1 and 33.4 ppm indication of two conformers (Figure 3.18c).



Scheme 3.5. Synthesis of chiral NHC-Ru(II) and Rh(I) complexes (**25**-**28**). Reagents and conditions of reactions: (i) Ag_2O, CH_2Cl_2, 25 ^oC and then $[RuCl_2(p\text{-cymene})]_2$, toluene, 90 ^oC; ii) LiO^tBu, $[RhCl(COD)]_2$, 70 ^oC; or Ag_2O, CH_2Cl_2, 25 ^oC and then $[RhCl(COD)]_2$, CH_2Cl_2; or $[Rh(OMe)(COD)]_2$, DCE; iii) PPh_2Cl, Et_3N, CH_2Cl_2.

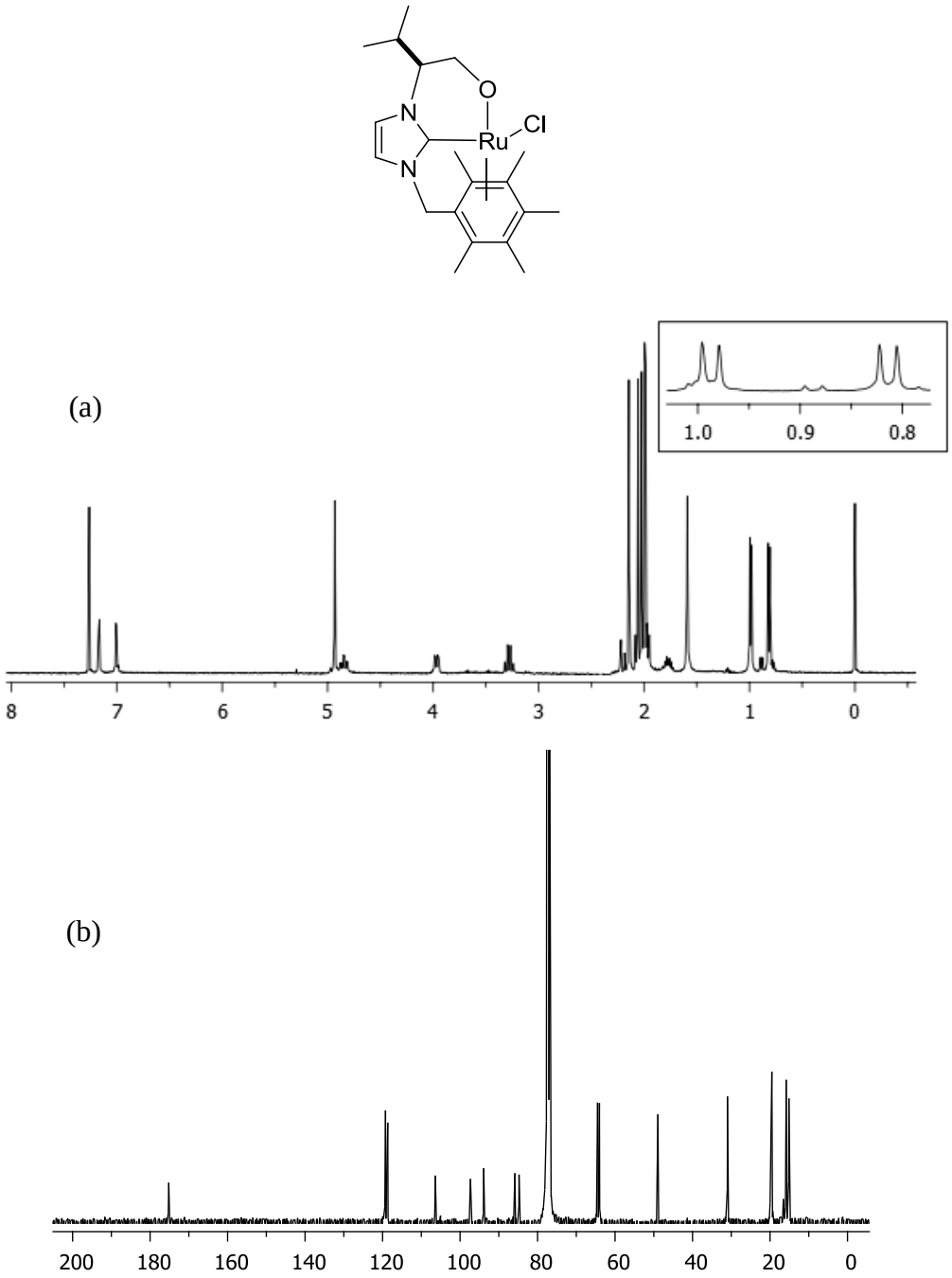


Figure 3.13. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **25** in $CDCl_3$.

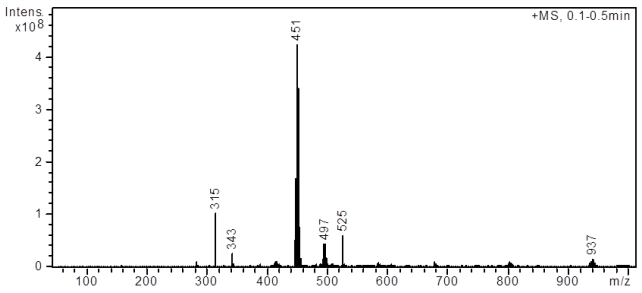
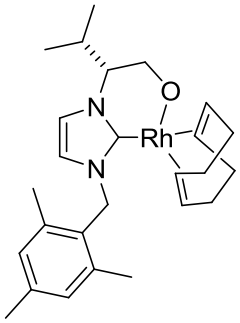
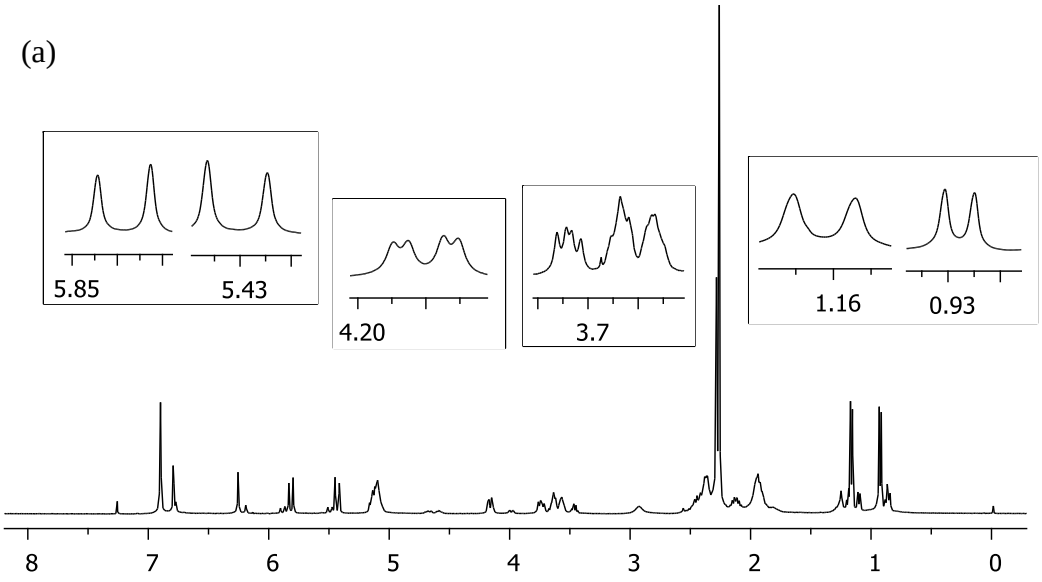


Figure 3.14. Electronspray ionization mass spectra of complex **25**.





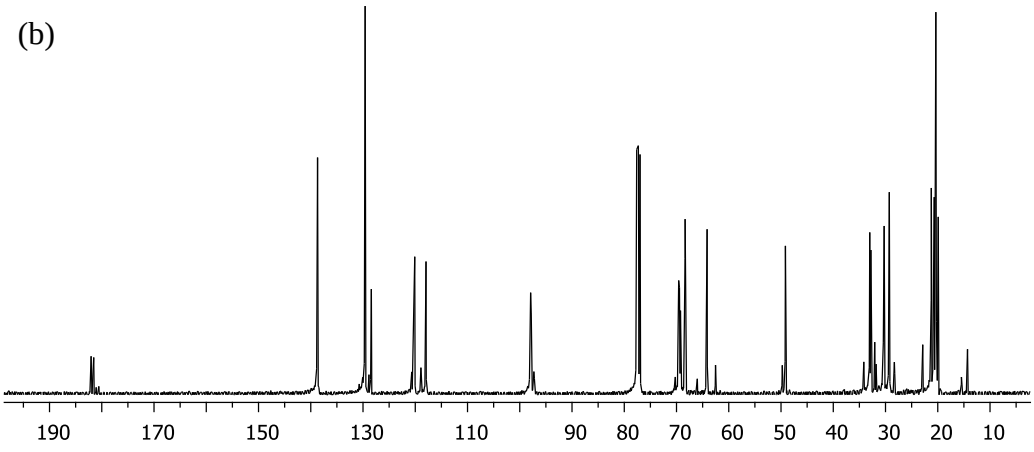


Figure 3.15. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **26a** in $CDCl_3$.

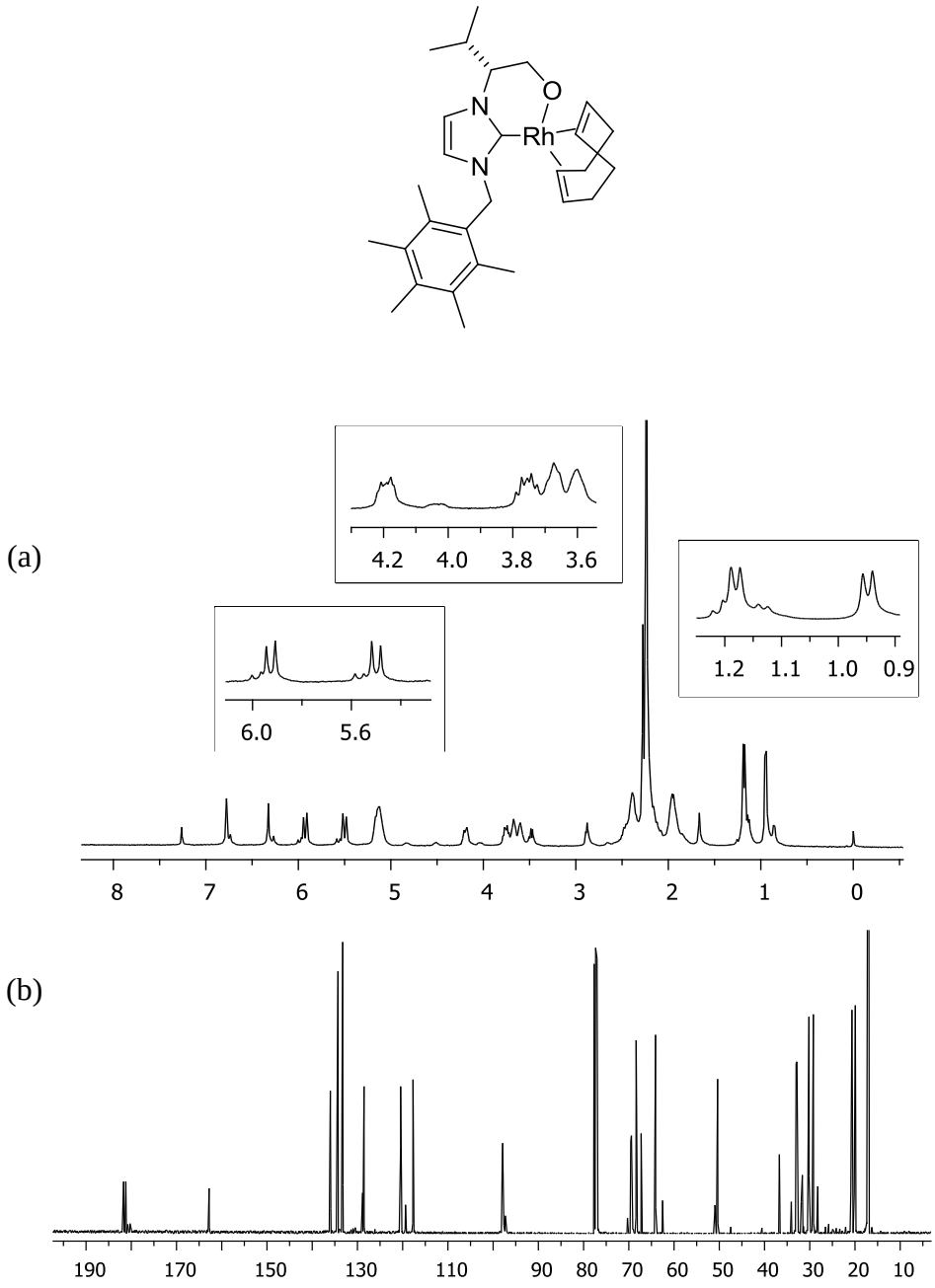


Figure 3.16. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **26b** in $CDCl_3$.

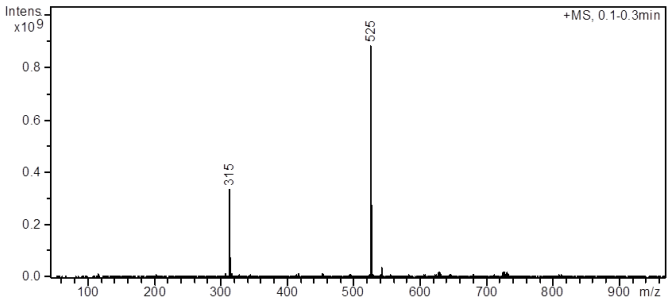


Figure 3.17. Electrospray ionization mass spectra of complex **26b**.

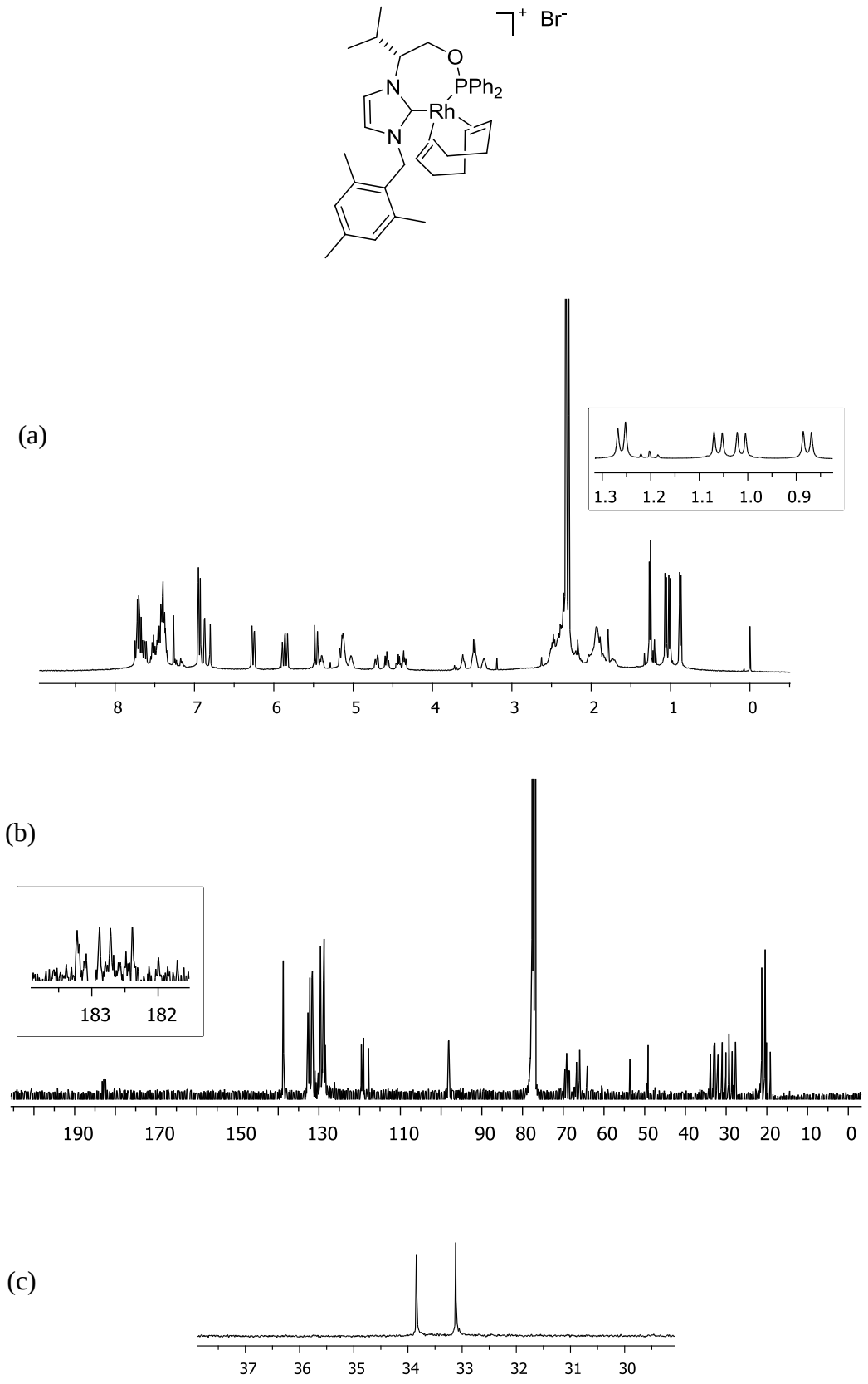
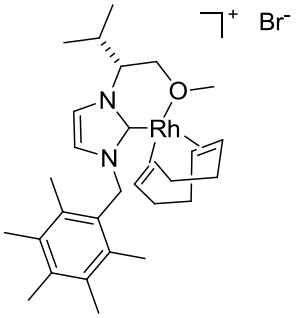
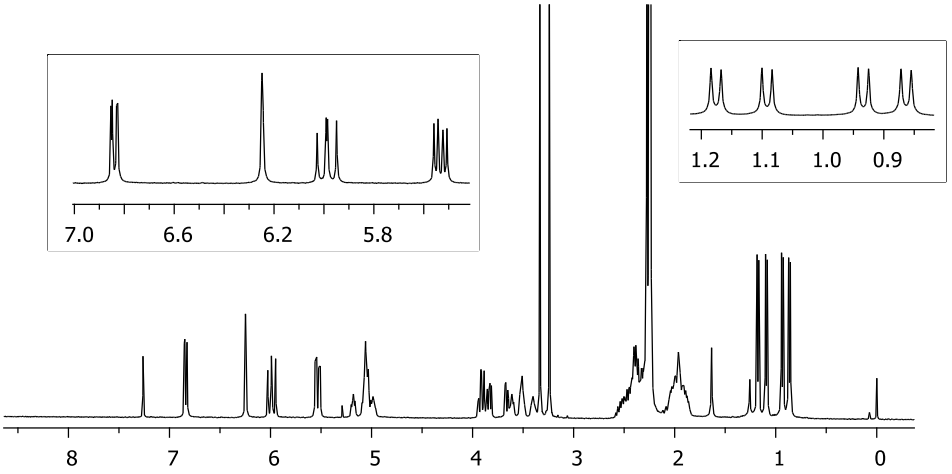


Figure 3.18. (a) ^{1}H NMR, (b) ^{13}C NMR, (c) ^{31}P NMR spectra of **27** in $CDCl_3$.



(a)



(b)

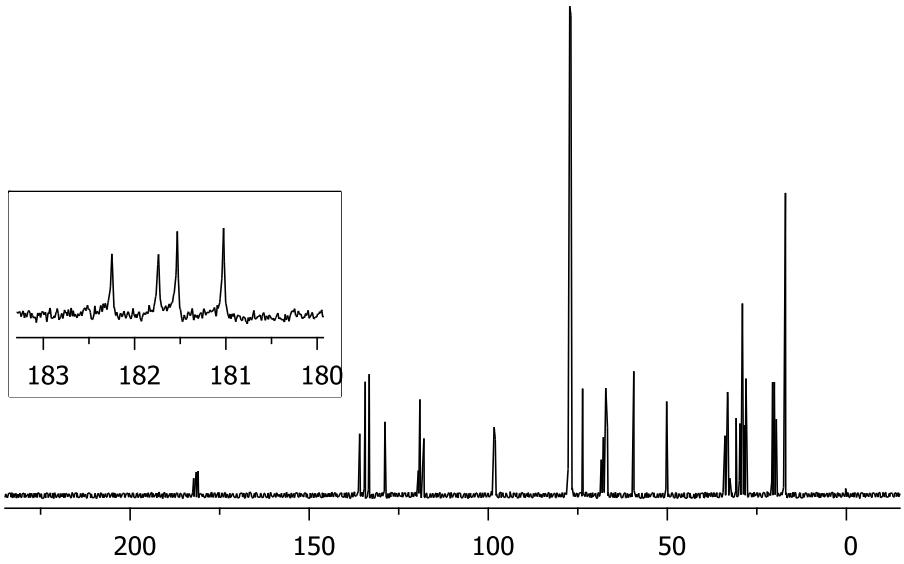


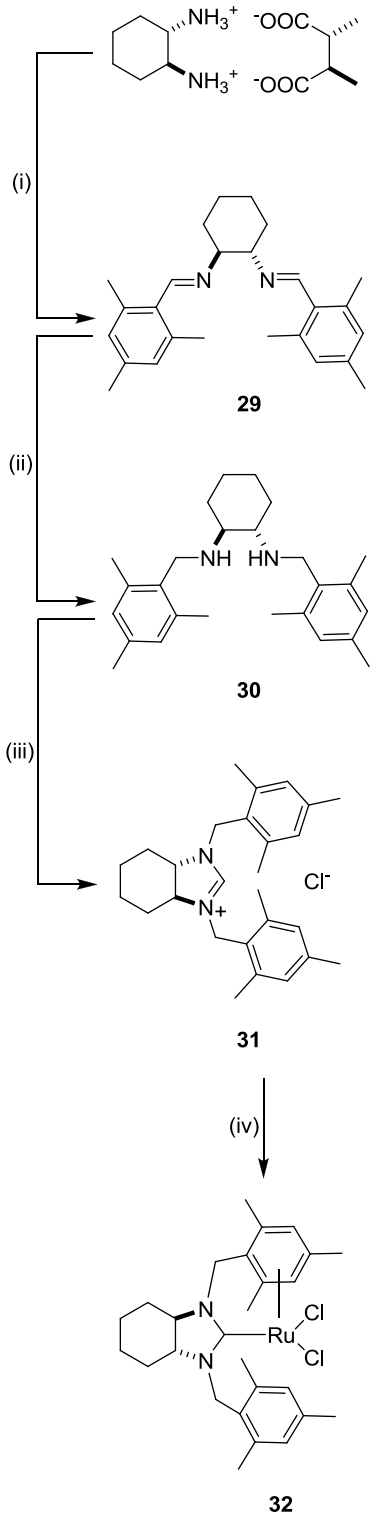
Figure 3.19. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **28** in $CDCl_3$.

3.3 Chiral NHC Ligand and Its Ru(II) Complex Bearing Chiral Elements within the Heterocycle

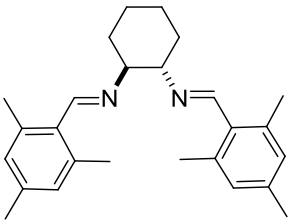
3.3.1 Synthesis and characterization of (*R*,*R*)-1,3-bis(2,4,6-trimethylbenzyl)-1,2-cyclohexylimidazolidinium chloride (31)

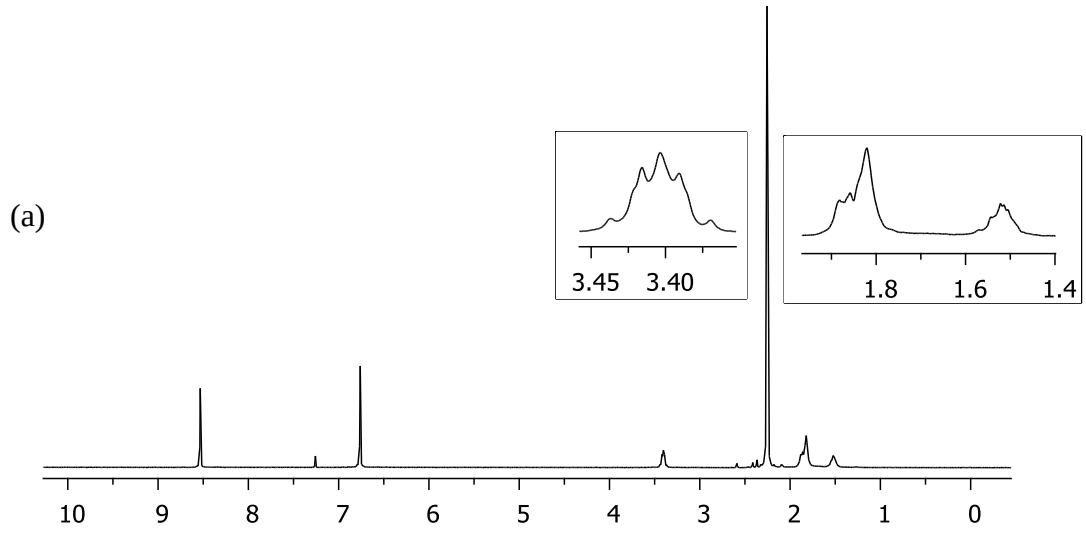
Chiral NHC ligand (**31**) was synthesized in three steps (Scheme 3.6). The first step involves Schiff base synthesis from (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartarate salt (Step (i)). In the second step, compound **30** prepared from Schiff base was reduced using $NaBH_4$. Finally, chiral NHC ligand (**31**) was obtained by cyclization of diamine with triethyl orthoformate in the presence of NH_4Cl. The compounds (**29**, **30**) were synthesized by Yiğit. The structures of **29** and **30** are consistent with the reference (Yiğit, 2002).

These compounds have been fully characterized by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR chemical shifts were consistent with the proposed structures; the resonance for C_2 hydrogen was observed as sharp singlet at 9.16 ppm. ^{13}C NMR of compound **31** showed the C_2 carbon at 161.6 ppm (Figure 3.22).



Scheme 3.6. Synthesis of chiral NHC-Ru(II) complex **32**. Reagents and conditions of reactions: (i) Mesitylaldehyde, K_2CO_3, EtOH, reflux; (ii) $NaBH_4$, MeOH; (iii) $CH(OEt)_3$, NH_4Cl; (iv) Ag_2O, CH_2Cl_2, 25 ^oC and then $[RuCl_2(p\text{-cymene})]_2$, toluene, 90 ^oC.





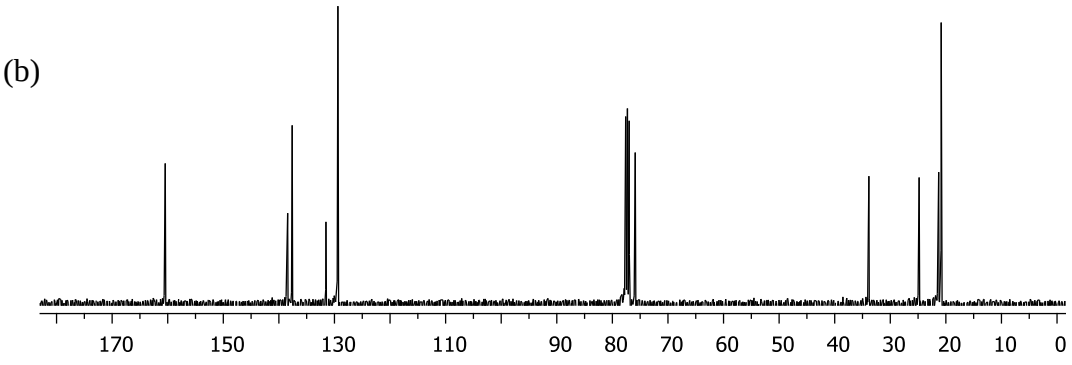


Figure 3.20. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **29** in $CDCl_3$.

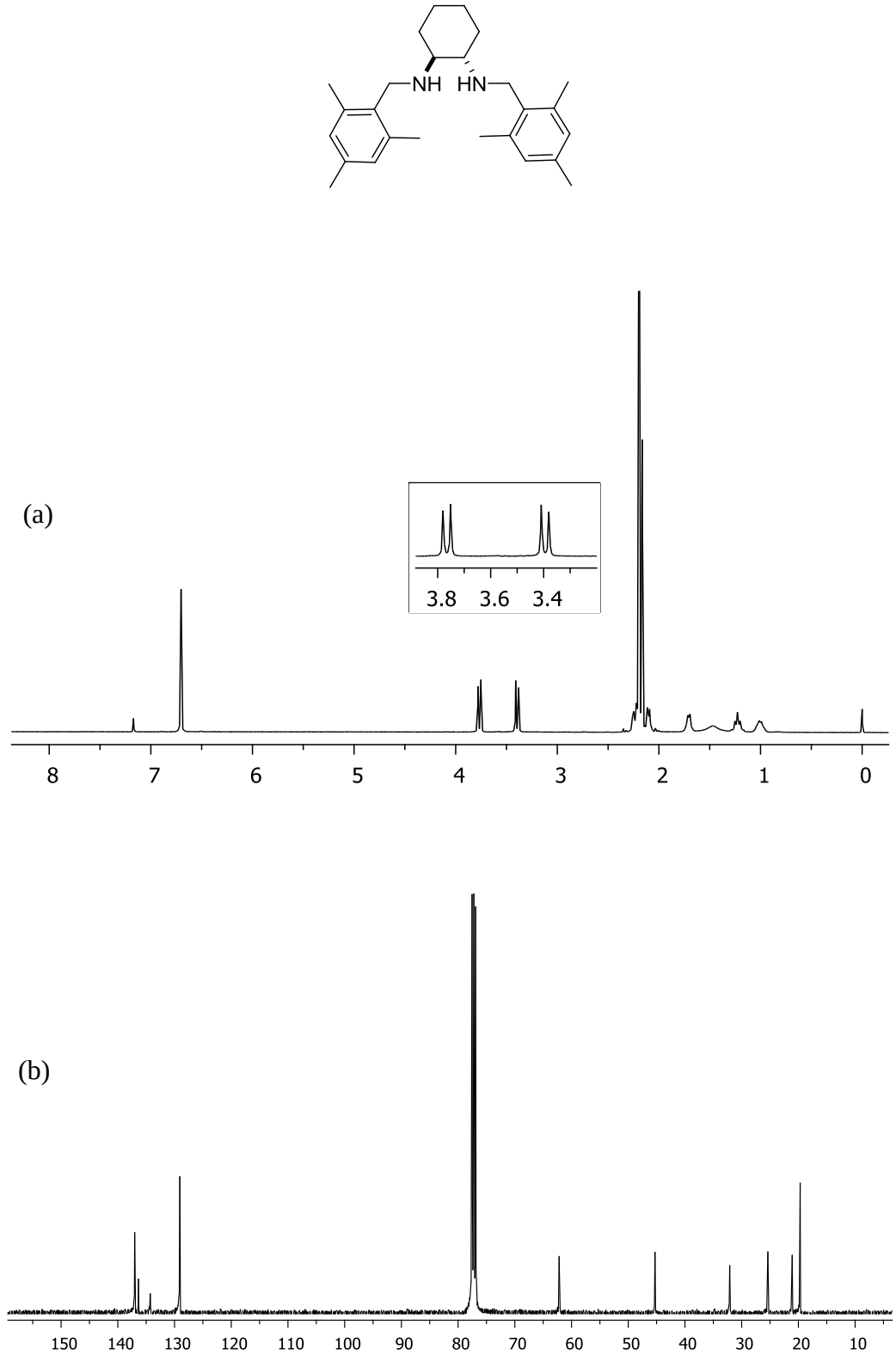


Figure 3.21. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **30** in $CDCl_3$.

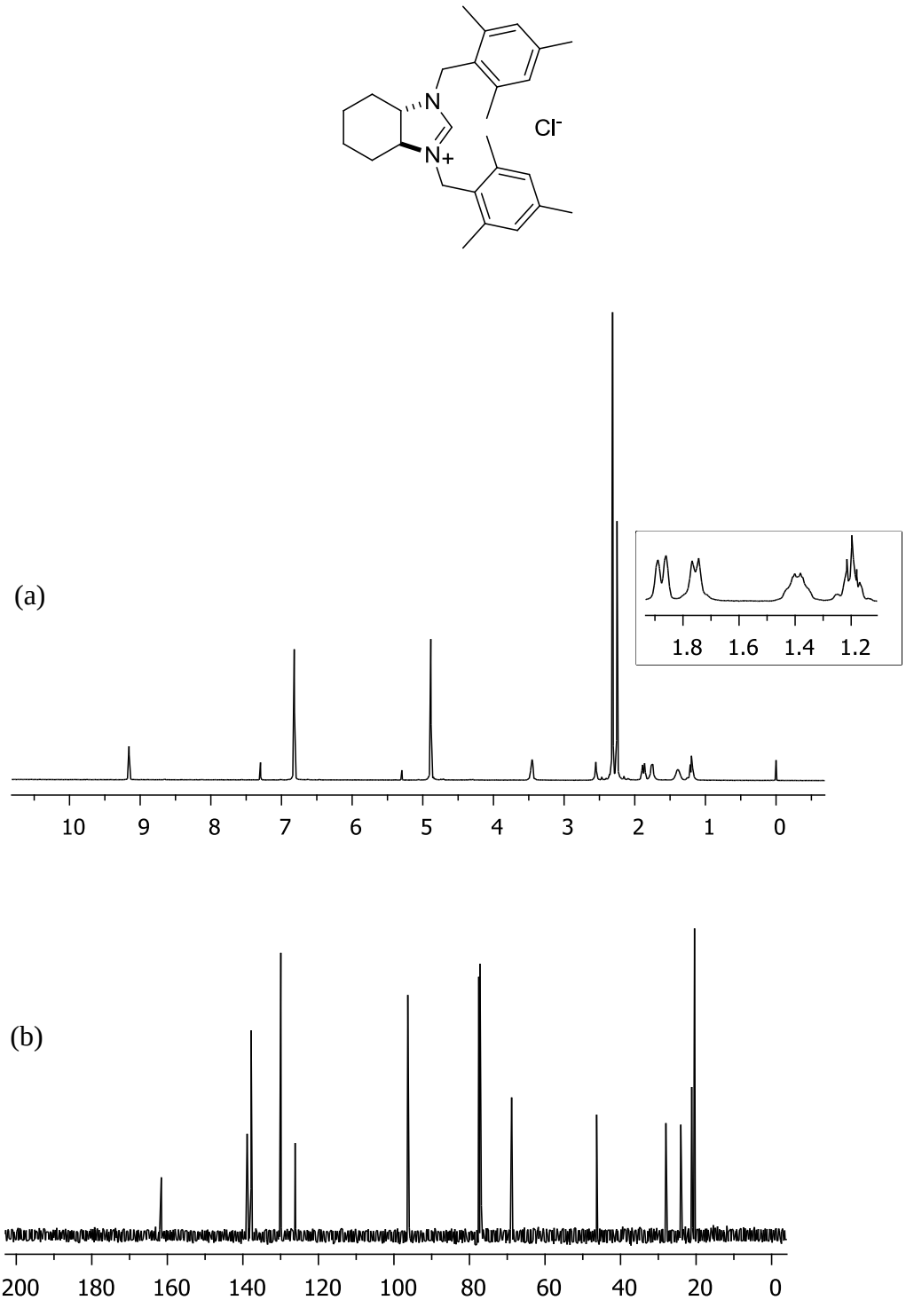
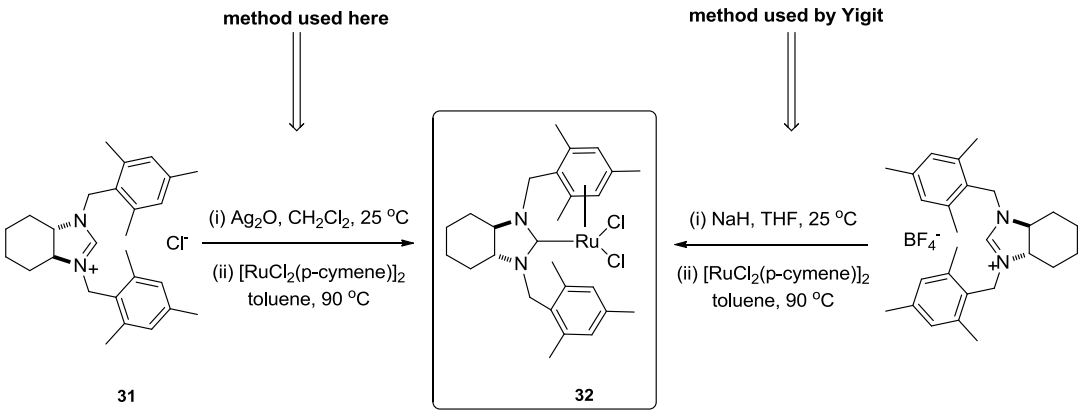


Figure 3.22. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **31** in $CDCl_3$.

3.3.2 Synthesis and characterization of chiral NHC-Ru(II) complex (32)

Chiral NHC-Ru(II) complex (**32**) was prepared by carbene-transfer reaction of *in situ* formed NHC-Ag species with $[RuCl_2(p\text{-cymene})]_2$ in dichloromethane at ambient temperature, and then the mixture was heated to 90 ^oC in toluene for 16 h under argon. The charactersitic downfield signal for the C_2 hydrogen of imidazolinium salt was not observed in the ^1H NMR spectrum of Ru complex. The ^{13}C NMR signal of the $C_{carbene}$ atom of complex **32** appeared at 206.3 ppm. The same complex (**32**) was prepared by Yiğit using a different procedure, which NaH and $[RuCl_2(p\text{-cymene})]_2$ were used (Yiğit, 2002) (Scheme 3.7). Complex **32** prepared by this route did not display optical rotation. Whereas the procedure used here exhibits optical rotation for complex **32** which was measured in CH_2Cl_2 as [α] = -28.57 (c 0.105, 24.8 ^oC). A single crystal data of **32** were given in Table 3.1. However, although the complex **32** has an optical rotation, it crystallized in centrosymmetric $P2_1/n$, implying that the co-crystallisation of both the *R* and the *S* stereoisomers, as a racemate.



Scheme 3.7. Two different methods used in the synthesis of complex **32**.

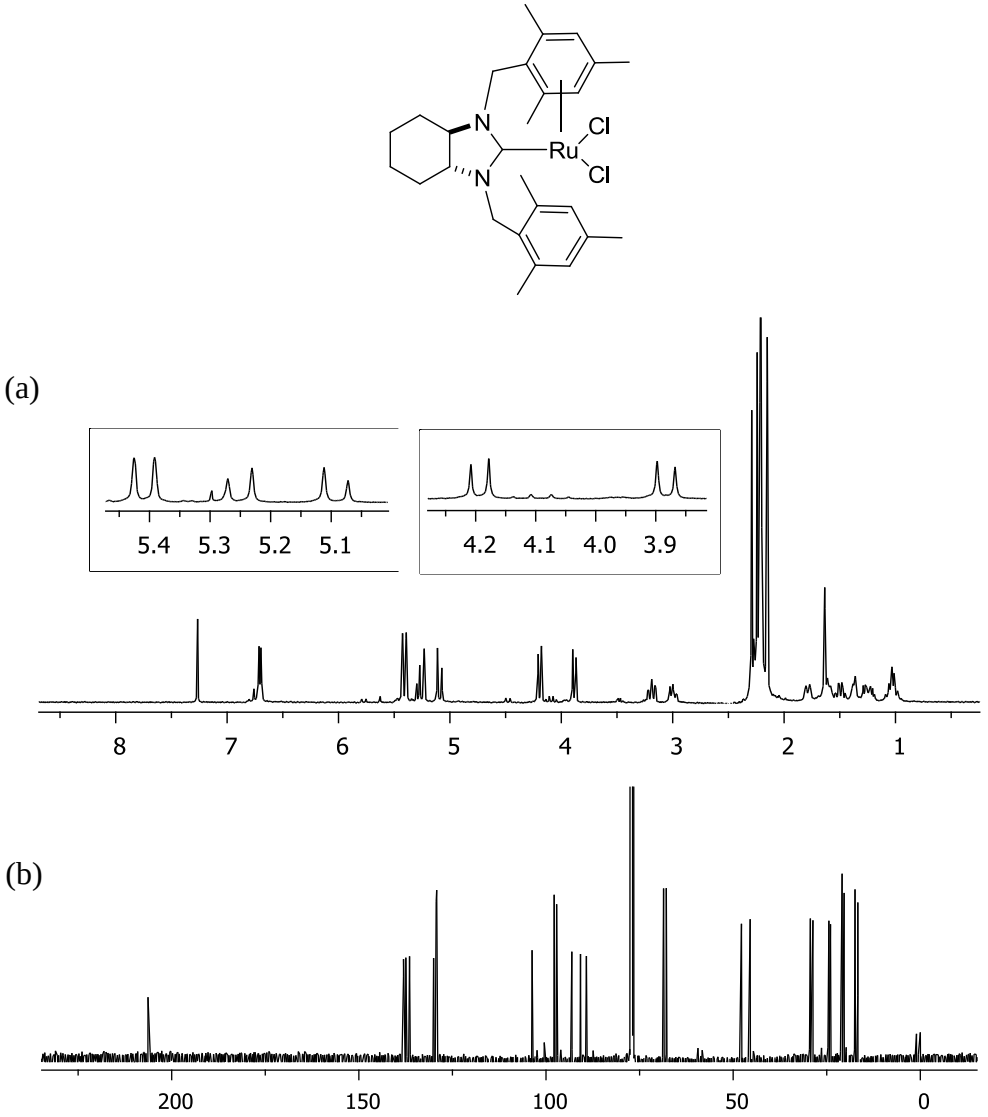


Figure 3.23. (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **32** in $CDCl_3$.

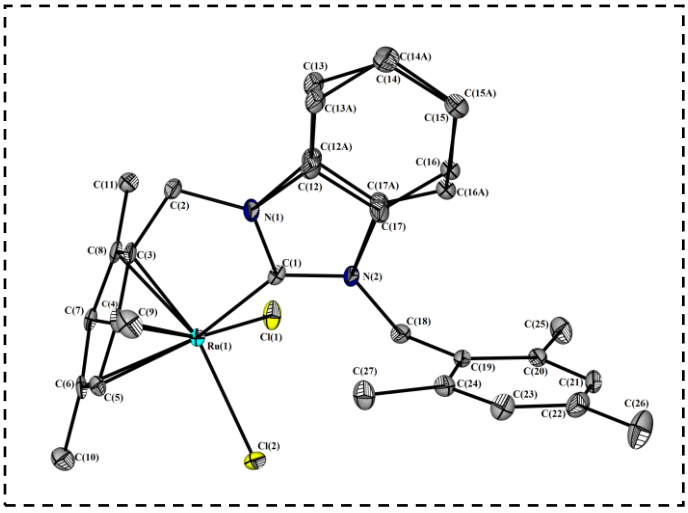


Figure 3.24. X-ray structure of complex **32**.

Table 3.1. Crystal data and structure refinement for **32**

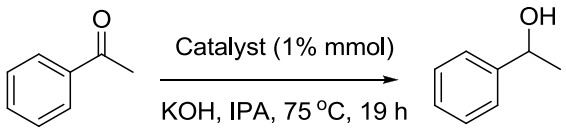
Identification code	**32**
Empirical formula	C27 H36 Cl2 N2 Ru
Formula weight	560.55
Temperature, K	110(2)
Wavelength, Å	1.54178
Crystal system	Monoclinic
Space group	P2(1)/n
a , Å	13.4890(7)
b, Å	13.9576(7)
c, Å	14.0217(7)
Volume, $Å^3$	2495.6(2)
Z	4
Density (calculated), Mg/m^3	1.492
Absorption coefficient, mm^{-1}	7.177
F(000)	1160
Crystal size, mm^3	0.30 x 0.18 x 0.13
Theta range for data collection	3.95 to 62.50°.
Reflections collected	43558
Independent reflections	3910 [R(int) = 0.0521]
Completeness to theta = 62.50°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4555 and 0.2220
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3910 / 72 / 308
Goodness-of-fit on F^2	1.250
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0742
R indices (all data)	R1 = 0.0350, wR2 = 0.0750
Largest diff. peak and hole	0.430 and -0.696 $e.Å^{-3}$

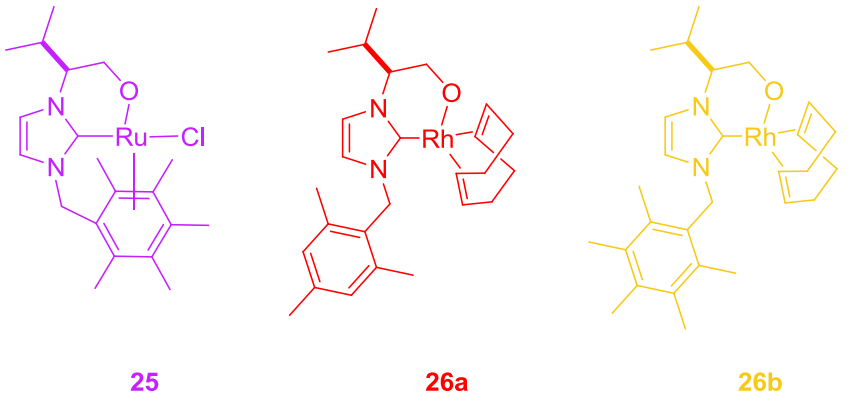
3.4 Transfer Hydrogenation Reactions with Chiral NHC-Rh(I) and Ru(II) Complexes (**25-28**, **32**)

Transfer hydrogenation is the addition of hydrogen to an unsaturated molecule from a reagent other than gaseous H_2. 2-Propanol (IPA) and $HCOOH/Et_3N$ are typically used as hydrogen donors with a strong base such as KOH. Whereas direct hydrogenation of unsaturated compounds is more widely applied, transfer hydrogenation is a powerfull alternative in view of its easy of handling, the easy availability of hydrogen donor, low cost of reducing agents and safety. Transition metal-catalyzed transfer hydrogenation of carbonyl compounds is one of the most important reactions in pharmaceutical and chemical industries. Many NHC ligands are known to be active catalysts for the transfer hydrogenation reaction (Hillier et al., 2001; Özdemir et al., 2005b; Jokić et al., 2011; Çetinkaya, 2011; Gürbüz et al., 2010; 2012). The asymmetric transfer hydrogenation (ATH) of prochiral ketones is highly efficient method to obtain enantiomerically enriched alcohols. However, there are very few report describing the use of chiral NHCs in asymmetric transfer hydrogenation. In general, moderate to good conversions were obtained but enantioselectivities were poor to moderate (Seo et al., 2003; Hodgson and Douthwaite, 2005; Herrmann et al., 2006; Jiang et al., 2009; Dyson et al., 2009; Diez and Nagel, 2010; Aupoix et al., 2011; Newman et al., 2011).

Chiral NHC-Ru(II) and Rh(I) complexes (**25-28**, **32**) were evaluated as catalysts for transfer hydrogenation of acetophenone. We started the catalytic experiments using complex **26a** with 4% mol KOH in IPA at 75 ^{o}C. After 19 h, the corresponding alcohol was obtained with 73% yield and 1.77% *ee*. When 10% mol base was used, yield was increased but enantioselectivity was lost. However, after 8 h, the product was obtained in 42% yield and 23.15% *ee* (Figure 3.25). As is seen from Table 3.2, the reaction did not proceed at 50 ^{o}C. We obtained the product in only 8% yield with 14.37% *ee* after 48 h. Under the determined reaction conditions, the catalytic experiments were carried out using 1 mmol of acetophenone, 0.01 mmol (1% mol) of rhodium or ruthenium complexes as catalysts and 0.04 mmol (4% mol) KOH as a base in IPA at 75 ^{o}C. The complex **27** was found to be the most active catalyst among all of these complexes tested. Cationic complexes (**27**, **28**) were shown to exhibit better activity than the neutral ones. After 3 h, they gave the desired alcohol in high yield (88-96%). We also tested ligand **23b** (1% mol) in the same reaction using $[Rh(OMe)(COD)]_2$ (0.5% mol) and KOH (4% mol). After 19 h, the reaction was completed but enantioselectivity could not been observed. Using complex **32**, the desired alcohol

was obtained in 96% yield and 5.11% *ee* after 8 h. Although the obtained yields were much better in comparison to the results described the literature (Mas-Marzá et al., 2005; Jiang et al., 2009; Jokić et al., 2011, Yiğit et al., 2012), the enantioselectivity was not also satisfactory with the references (Hodgson and Douthwaite, 2005; Herrmann et al., 2006; Jiang et al., 2009; Diez and Nagel, 2010; Newmann et al., 2011).





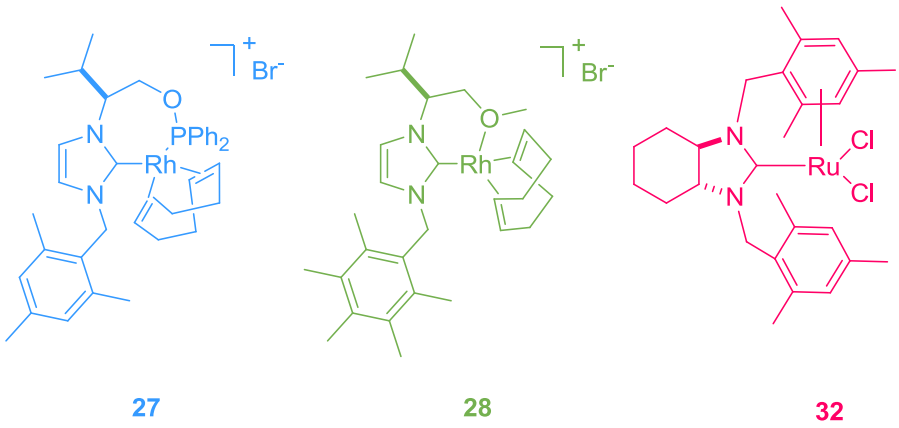
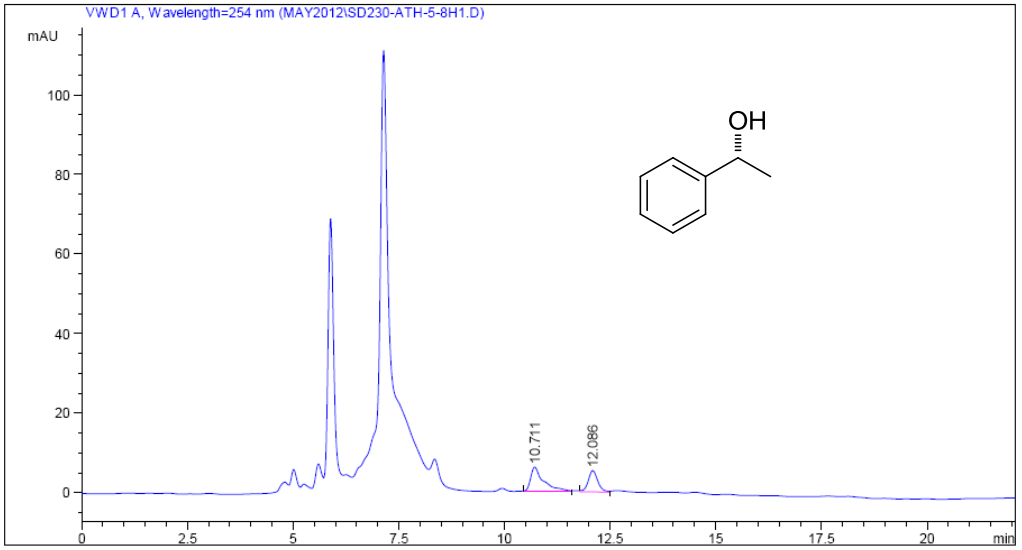


Table 3.2. The transfer hydrogenation reaction catalyzed by **25-28, 32**

Catalyst	Base (% mol)	Temp. (°C)	Yield (%)	ee (%)[e]
25	4	75	95	1.51(*R*)
26a	4	75	73	1.77(*R*)
26a	10	75	84	-
[a]**26a**	4	75	42	23.15(*R*)
26a	4	50	-	-
[b]**26a**	4	50	8	14.37(*R*)
26b	4	75	81	2.87(*S*)
26b	10	75	94	1.08(*S*)
[c]**27**	4	75	96	2.54(*S*)
[c]**28**	4	75	88	-
[d]**28**	4	75	92	-
[a]**32**	4	75	96	5.11(*R*)

a: 8h; b: 48h; c: 3h; d: 6h; e: Chiracel OD-H column, Hexane/IPA (95/5), flow rate 0.7 ml/min, 254 nm.

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  10.711 BB    0.3120  139.81520    6.21336  61.5806
   2  12.086 BB    0.2432   87.22885    5.41606  38.4194
```

Figure 3.25. HPLC analysis of the 1-phenylethanol after catalytic transfer hydrogenation reaction using complex **26a** (after 8 h, %23.15 *ee*).

3.5 Arylation Reactions with Chiral NHC-Rh(I) Complexes (26-28)

Diarylmethanols are important structural motives for the synthesis of biologically and pharmaceutically active compounds. The addition of organometallic reagents to aldehydes has been the general methods to obtain the diarylmethanols. Organolithium, organomagnesium, organozinc and organocopper compounds are most widely used. However, limitations to their use arise from the nature of the reagents, which are usually toxic and sensitive to air and moisture. In recent years, 1,2-addition of boronic acids to aldehydes catalyzed by rhodium complexes, especially NHC complexes, has become a very useful approach to prepare such compounds. With regard to the synthesis of chiral diarylmethanols, the asymmetric arylation of aldehydes with boronic acids in the presence of chiral NHC complexes has attracted much attention (Zhang et al., 2005; Arao et al., 2006; Ma et al., 2010; Zhang et al., 2010).

Chiral NHC-Rh(I) complexes were also tested in the 1,2-addition of phenylboronic acid to aldehydes. To survey the reaction parameters for the arylation reaction, a series of experiments have been performed with 4-isopropylbenzaldehyde and phenylboronic acid using complex **26b**. For the choice of solvent, we surveyed DMF/H_2O, 1,4-Dioxane/H_2O and DME/H_2O. We found that the reactions performed in DME/H_2O at 80 °C appeared to be best. We started our investigation with the 1,2-addition of phenylboronic acid to 4-isopropylbenzaldehyde in the presence of KO^{t}Bu as a base in DME at 80 °C. As can be seen from Table 3.3, the reaction catalyzed by both **26a** and **26b** was completed within 15 minutes. The cationic complexes **27** and **28** displayed lower catalytic activity, 85% and 84%, respectively. In general the enantioselectivity increases at lower reaction temperatures. Therefore, we decided to lower the reaction temperature to 60 ^oC. After 45 minutes, the product was obtained in > 99 yield, but no enantioselectivity was observed. And then, when the temperature was decrease to 40 ^oC, we obtained the product in 37% yield with no enantioselectivity, after 48 hours. In order to get the enantioselectivity, while the temperature of reaction was kept at 40 ^oC, rate of the catalyst was increased to 3% mol. Increasing the load of catalyst did not affect asymmetric induction. Finally, we tried to change the ratio of solvent from 3/1 (DME/H_2O) to 5/1 (DME/H_2O), but we failed to achieve the enantioselectivity. According the previously published results (Arao et al., 2006; Ma et al., 2010), the presence of an *ortho*-substituent in aromatic aldehydes resulted in slightly better asymmetric induction. In the light of this information, complex **26b** (1% mol) was also tested for the addition of benzeneboronic acid to 2-MeO-benzaldehyde, at 80 °C. After 15 minutes, 88% yield and 7.71% *ee* were obtained. The best enantioselectivity was obtained using complex **28** and 4-isopropylbenzaldehyde (32.10% *ee*) (Figure 3.26). Although we failed to achieve high asymmetric induction, the yields were comparable or even higher than reported values (Zhang et al., 2005; Özdemir et al., 2005c; Yiğit et al., 2005b; 2007; Arao et al., 2006b; Kılınçarslan et al., 2007; Ma et al., 2010; Trindade et al., 2010; He and Cai, 2011). To the best our knowledge, the best result for this reaction was obtained by Fürstner and Krause. Their ligands were tested in the addition of phenylboronic acid to 4-MeO-benzaldehyde using different metal salts such as $[RhCl(COD)]_2$, $RhCl_3.3H_2O$. They obtained the product in < 10% yield using $[RhCl(COD)]_2$ (3% mol) after 6.5 h, and 93% yield using $RhCl_3.3H_2O$ (1% mol) within 12 minutes (Fürstner and Krause, 2001). We also investigated ligand **23b** (1% mol) for this reaction using $[RhCl(COD)]_2$ (0.5% mol) and 4-MeO-benzaldehyde, affording the corresponding product in 90% yield after 15 minutes.

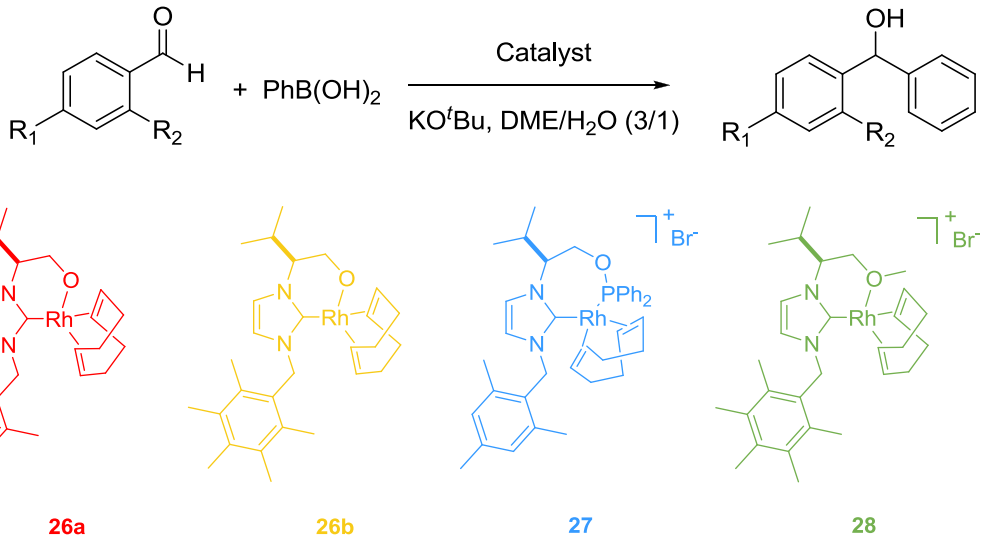
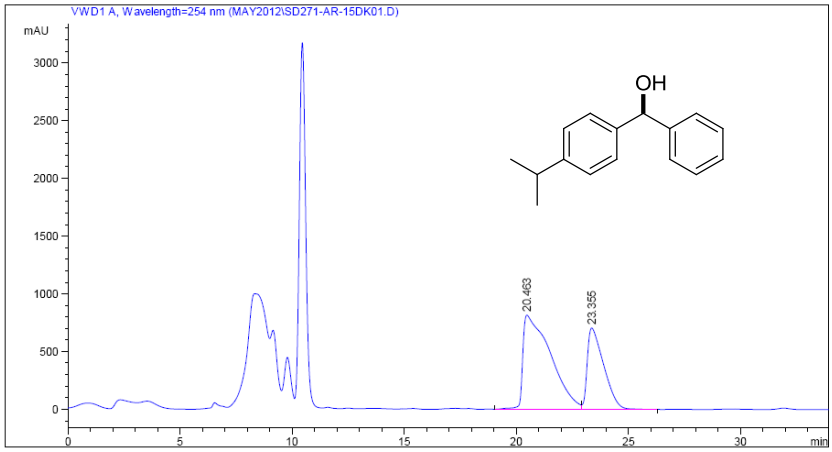


Table 3.3. The arylation reactions catalyzed by **26-28**

Catalyst	R_1	R_2	Temp.(°C)	Time	Yield (%)	ee (%)
26a	^{i}Pr	H	80	15 min	96	4.45(*R*)[d]
26b	^{i}Pr	H	80	5 min	54	-
26b	^{i}Pr	H	80	15 min	>99	-
26b	^{i}Pr	H	60	5 min	11	-
26b	^{i}Pr	H	60	15 min	56	-
26b	^{i}Pr	H	60	30 min	89	-
26b	^{i}Pr	H	60	45 min	>99	-
26b	^{i}Pr	H	40	48 h	37	-
[a]**26b**	^{i}Pr	H	40	8 h	84	-
[a]**26b**	^{i}Pr	H	40	10 h	>99	-
[a,b]**26b**	^{i}Pr	H	40	8 h	89	-
[a,b]**26b**	^{i}Pr	H	40	10 h	>99	-
26b	H	MeO	80	15 min	88	7.71(*S*)[e]
[c]**26b**	H	MeO	80	15 min	83	6.89(*S*)[e]
26b	MeO	H	80	5 min	28	-
26b	MeO	H	80	15 min	87	-
26b	Cl	H	80	5 min	>99	-
27	^{i}Pr	H	80	5 min	28	-
27	^{i}Pr	H	80	15 min	85	-
28	^{i}Pr	H	80	15 min	84	32(*S*).10[d]

a: 3% mol catalyst; b: DME/H_2O (5/1); c: 0.3% mol catalyst; d: Chiracel OD-H column, Hexane/IPA (95/5), flow rate 0.5 ml/min, 254 nm (for 4-^{i}Pr-benzaldehyde); e: Chiracel OD-H column, Hexane/IPA (90/10), flow rate 1.0 ml/min, 254 nm (for 2-MeO-benzaldehyde).

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=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  20.463 VV    1.0979 7.00376e4   816.82306  66.0508
   2  23.355 VB    0.7804 3.59984e4   705.32104  33.9492
```

Figure 3.26. HPLC analysis of (4-isopropyl)(phenyl)methanol after catalytic arylation reaction using complex **28** (%32.10 *ee*).

3.6 Conclusions

NHC-Pd(II) complexes bearing chiral oxazoline substituents (**13-18**) were synthesized, characterized and used for allylic alkylation reaction of (*E*)-1,3-diphenyl-3-en-yl acetate. The results are summarized in Figure 3.6. The complex **13** is the most active catalyst among the complexes tested. The complexes bearing electron donating methoxyethyl substituent were found to be less efficient. Catalytic activity decreased in the sequence: **13** > **14** > **15** > **16** > **17** > **18** (Figure 3.6). The results showed that electron donating groups on both the benzene ring or benzyl substituent decrease the catalytic activity. Unfortunately no enantioselectivity could be observed. The reason for this behavior is thought to be related with the oxazoline ligand. We may assume that the chiral oxazoline ligand departs the metal center early in the catalytic cycle.

Chiral NHC-Ru(II) and Rh(I) complexes (**25-28**, **32**) were prepared and characterized by spectroscopic techniques. Although the complex **32** has an optical rotation, X-ray data indicated that it crystallized as a racemate. Their

catalytic activities were evaluated for transfer hydrogenation of acetophenone. The complex **27** was found to be the most active catalyst among all of these complexes tested. Cationic complexes (**27**, **28**) showed better activity than the neutral ones. However, enantioselectivities are low (23.15% *ee*) (Figure 3.25). Increasing the amount of base has led to total loss of enantioselectivity.

Chiral NHC-Rh(I) complexes (**26**-**28**) were also tested for the arylation reaction of aldehydes. Among the complex screened **26a** and **26b** displayed better catalytic activities than the cationic ones (**27**, **28**). Nevertheless, we could not observe enantioselectivity. Our attempts to increase the enantioselectivity, by lowering the temperature, increasing catalyst loading or changing the ratio of solvent, failed. The best *ee* value was found to be 32.1% (Figure 3.26).

In summary, as part of a current research program directed to the design of chiral NHC ligands and their metal complexes, we presented here simple synthetic strategies for the construction of three types of chiral complexes: i) chirality in ligands other than the NHC attached to metal atom; ii) chirality in substituents attached to nitrogen atom; iii) chirality in backbone. As such, the derived Pd(II), Rh(I) and Ru(II) complexes were successfully synthesized and employed as catalysts for allylic alkylation, transfer hydrogenation and arylation reactions. Despite good conversions in these catalytic reactions, the new catalytic systems appeared to be inferior in enantioselectivity to the best results described in the literature (Flahaut et al., 2007a; Zhang et al., 2008b; Mas-Marzá et al., 2005; Jiang et al., 2009; Jokić et al., 2011, Yiğit et al., 2012; Zhang et al., 2005; Özdemir et al., 2005c; Yiğit et al., 2005b; 2007; Arao et al., 2006b; Kılınçarslan et al., 2007; Ma et al., 2010; Trindade et al., 2010; He and Cai, 2011).

Finally, it is hoped that this and earlier studies by other research groups cited in Part I of this thesis will draw growing attention on the chemistry of chiral NHCs. The experience, gained by this work can be used to improve the design of the chiral NHCs. Further efforts should be directed towards the synthesis of new chiral NHCs and their complexes bearing electron donating functionalities for the ATH and asymmetric arylation of aldehydes.

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PUBLICATIONS

1. Ertekin, K., Öter, Ö., Türe, M., **Denizaltı, S.**, Çetinkaya, E., 2009, A long wavelength excitable fluorophore; chloro phenyl imino propenyl aniline (CPIPA) for selective sensing of Hg (II), *Journal of Fluorescence*, 20, 533-540.
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SCIENTIFIC MEETINGS

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3. Derinkuyu, S., Ertekin, K., Öter, Ö., **Denizaltı, S.**, Çetinkaya, E., 2006, Fiber optic pH sensing with long wavelength excitable Schiff bases in the pH range of 7.5-11.5, Eighth European Conference on Optical Chemical and Biosensors, Poster Session, ALMANYA.
4. Derinkuyu, S., Ertekin, K., Öter, Ö., **Denizaltı, S.**, Çetinkaya, E., 2006, N,N-dimetil-4-(1*E*,3*E*)-3-[(4-nitrofenil)imino]-1-propenil anilin indikatörü ile etil selüloz matriks, 3. Ulusal Analitik Kimya Kongresi, ÇANAKKALE.

5. Türe, M., Ertekin, K., Öter, Ö., **Denizaltı, S.**, Çetinkaya, E., 2007, Yeni sentezlenmiş kloro fenil imino propenil anilin boyasının Hg^{2+} 'ye yanıtının spektroflorimetrik yöntemle incelenmesi, 10. Ulusal Spektroskopi Kongresi, Poster Sunum, URLA.
6. **Denizaltı, S.**, Türkmen, H., Çetinkaya, B., 2009, Dinükleer palladyum ve gümüş N-heterosiklik karben kompleksleri, 2. Ulusal Anorganik Kimya Kongresi, Poster Sunum, ELAZIĞ.
7. **Denizaltı, S.**, Çetinkaya, B., 2010, Kiral NHC-Pd kompleksleri ve katalik uygulamaları, 1. Organometalik Kimya ve Kataliz Çalıştayı, Poster Sunum, MALATYA.

RESEARCH PROJECTS

1. Assoc. Prof. Dr. Rafet KILINÇARSLAN, "Synthesis of Chiral N-Heterocyclic Carbene Complexes and Catalytic Applications" TÜBİTAK, 2005-2010.
2. Prof. Dr. Engin ÇETİNKAYA, "Transformation of Carbon Dioxide to Organic Products in the Presence of Catalyst", TÜBİTAK 106T364, 2006-2009.
3. Prof. Dr. Engin ÇETİNKAYA, "Bridged Bibenzimidazolium Bromides and Their Applications to Coupling Reactions", 05-FEN-009, 2005-2008.
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FELLOWSHIPS

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