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(MASTER OF SCIENCE THESIS)

SYNTHESIS AND PROPERTIES OF PERIMIDINE DERIVATIVES

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ÖZET

PERİMİDİN TÜREVLERİNİN SENTEZİ VE ÖZELLİKLERİ

AKINCI, Pakize Arzu

Yüksek Lisans Tezi, Kimya Bölümü
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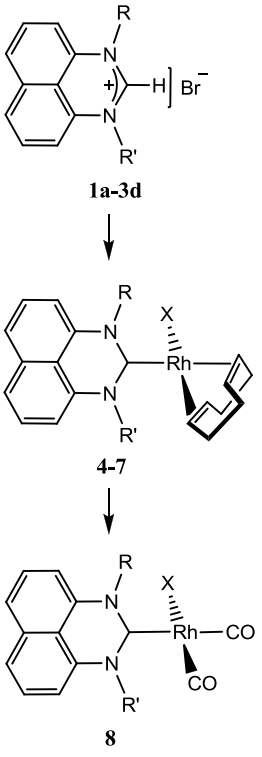
Bu çalışmanın amacı perimidin-2-iliden metal komplekslerinin sentezi ve sentezlenen komplekslerin organik tepkimelerde katalizör rolü oynayıp oynamadığını saptamaktır. Bu tez üç bölümden oluşmaktadır.

Birinci bölümde perimidin, perimidin türevleri ve NHC' lere ait temel bilgiler, önemi ve kullanım alanları özetlenmiştir. İkinci bölümde deneysel çalışmalar açıklanmıştır. Üçüncü bölümde, sentezlenmiş simetrik ve asimetrik perimidinyum tuzlarının (LHX: **1a-3d**) ve rodyum komplekslerinin (**4-7**) yapıları aydınlatılarak, sentezlenen komplekslerin katalitik aktiviteleri incelendi. Kompleks **8**, perimidin-2-iliden ligandının *σ*-verici özelliğini belirlemek için sentezlendi ve yapısı aydınlatıldı.



LHX	R	R'
1a	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$
1b		$-CH_2C_6H(CH_3)_4$
1c		$-CH_2C_6(CH_3)_5$
2a	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
2b		$-CH_2C_6H(CH_3)_4$
2c		$-CH_2C_6(CH_3)_5$
2d		$-CH_2CH_2CH_2CH_3$
3a	$-CH_2CH_2CH_2CH_3$	$-CH_2C_6H_2(CH_3)_3$
3b		$-CH_2C_6H(CH_3)_4$
3c		$-CH_2C_6(CH_3)_5$
3d		$-CH_2CH_2CH_2CH_3$

Compound No	R	R'
4	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$
5	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
6	$-CH_2CH_2OCH_3$	$-CH_2CH_2CH_2CH_3$
7	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$
8	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$

Bu çalışmada, üç seri halinde 1,3-disübstitüye perimidinyum tuzları (**1a-3d**) ve bunların rodyum kompleksleri (**4-8**) sentezlendi. Perimidinyum tuzlarının deprotonasyon çalışmaları sonucu NHC yerine, düşük verimle dimerleşmiş ürünler ve karakterize edilemeyen bir madde oluştu. [RhX(NHC)(COD)] yapısına uyan rodyum(I) kompleksleri (NHC: perimidin-2-iliden), [Rh(μ-OMe)COD]$_2$ ve karşılık gelen perimidinyum tuzlarının reaksiyonu sonucu sentezlendi. NHC ligantlarının σ-verici/π-alıcı özelliklerini belirlemek amacıyla, bu komplekslerden biri (**4**) ile [RhX(NHC)(CO)$_2$] yapısındaki rodyum kompleksi (**8**) sentezlendi. IR spektroskopisi veri sonuçları, trisiklik NHC ligantlarının σ-verici özelliğinin, N^1 ve N^3 atomlarının üzerindeki sübstitüentlere bağlı olduğunu gösterdi. Bu nedenle, literatürde bilinen ^{i}Pr ve *m*-xylene sübstitüye 2-iliden'lerin aksine, 2,4,6-trimetilbenzil sübstitüye perimidin-2-iliden yapısında yüksek ν(CO) değeri bulundu. Bu sonuç, -CH_2Ar sübstitüentinin asidik protonlarına bazın saldırısından kaynaklanmış olabilir. Ayrıca, C_2 karbonunun pozitif karakterinin bu asitliğe katkıda bulunduğu söylenebilir.

Anahtar kelimeler: Perimidin, perimidinyum tuzları, Rh(I) kompleksleri, katalitik aktivite, σ-verici özellik.

ABSTRACT

SYNTHESIS AND PROPERTIES OF PERIMIDINE DERIVATIVES

AKINCI, Pakize Arzu

Master of Science Thesis in Chemistry
Supervisor : Prof. Dr. Engin ÇETİNKAYA
Co-Supervisor : Dr. Süleyman GÜLCEMAL
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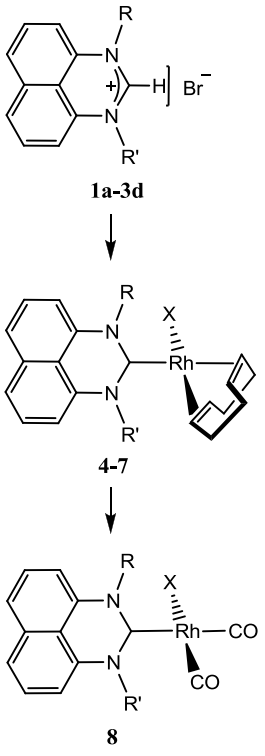
The aim of this study is to synthesize metal complexes of perimidin-2-ylidene and to establish whether these complexes play role in organic reactions. This thesis consist of three parts.

The first part is a concise review about perimidine, perimidine derivatives and NHCs with their importance and usage. In part two the experimental details explained broadly. Part three covers the characterization series of synthesized symmetrical and unsymmetrical perimidinium halides (LHX: **1a**-**3d**) and rhodium complexes (**4**-**7**) and results of catalytic properties of rhodium complexes were presented. Complex **8** was prepared to determine the σ-donor strength of the perimidin-2-ylidene ligand.



LHX	R	R'
1a **1b** **1c**	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$ $-CH_2C_6H(CH_3)_4$ $-CH_2C_6(CH_3)_5$
2a **2b** **2c** **2d**	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$ $-CH_2C_6H(CH_3)_4$ $-CH_2C_6(CH_3)_5$ $-CH_2CH_2CH_2CH_3$
3a **3b** **3c** **3d**	$-CH_2CH_2CH_2CH_3$	$-CH_2C_6H_2(CH_3)_3$ $-CH_2C_6H(CH_3)_4$ $-CH_2C_6(CH_3)_5$ $-CH_2CH_2CH_2CH_3$

Compound No	R	R'
4	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$
5	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
6	$-CH_2CH_2OCH_3$	$-CH_2CH_2CH_2CH_3$
7	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$
8	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$

In this study, three series of 1,3-disubstituted perimidinium salts (**1a**-**3d**) and their rhodium complexes (**4**-**8**) were synthesized. Attempted synthesis to deprotonate the perimidinium salts failed to generate the NHC cleanly, instead dimerized products formed in low yields with some unidentifed compound. Rhodium(I) complexes of the type [RhX(NHC)(COD)] where NHC: variously substituted perimidin-2-ylidene were synthesized by the reaction of $[Rh(\mu\text{-OMe})(COD)]_2$ with the corresponding perimidinium salts. One of these complexes (**4**) was converted to $[RhX(NHC)(CO)_2]$ complex (**8**) in order to obtain the relative σ-donor/π-acceptor properties of those NHC ligands. IR spectroscopy data reveals that the σ-donor ability of these tricyclic NHC ligands are dependent on the substitution pattern of the N^1, N^3 atoms. Thus, the 2,4,6-trimethylbenzyl substituted perimidin-2-ylidene presents very high ν(CO) value in contrast to the ^{i}Pr and *m*-xylene substituted ylidene which are from the literature. This may be due to the attack of the base to the acidic protons of -CH_2Ar substituent. Positive character of the C_2 carbon may contribute to this acidity.

Keywords: Perimidine, perimidinium salts, Rh(I) complexes, catalytic activity, σ-donor strength.

DEDICATION

I dedicate this work to my wonderful parents, Gülay and Ilgaz AKINCI, who have always been there for me. If it were not their support, words of encouragement and continuous love, I would not have made it.

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ABBREVIATIONS

Abbreviation		Explanations
Ar	:	Aryl
cat.	:	Catalyst
$CDCl_3$	:	Deuteriochloroform
COD	:	1,5-cyclooctadiene
DMF	:	*N,N*'-Dimethylformamide
DMSO	:	Dimethylsulfoxide
e.r.o.	:	Electron-rich-olefin
Et_2O	:	Diethylether
EtOH	:	Ethyl alcohol
FT-IR	:	Fourier Transformation Infrared
Hz	:	Hertz
IPA	:	Isopropyl alcohol
IR	:	Infrared Spectroscopy
^{i}Pr	:	Isopropyl
KO^{t}Bu	:	Potassium *tert*-butoxide
m.p.	:	Melting point
Me	:	Methyl
MeOH	:	Methanol
Mes	:	Mesityl, 2,4,6-trimethylphenyl
NHC	:	N-heterocyclic carbene
NMR	:	Nuclear Magnetic Resonance
R	:	Alkyl
rt	:	Room temperature
TH	:	Transfer hydrogenation
THF	:	Tetrahydrofuran
X	:	Halogen
s	:	Singlet
d	:	Doublet
t	:	Triplet
m	:	Multiplet
br	:	Broad
δ	:	Delta
μ	:	Bridge ligand

1. INTRODUCTION

1.1 Perimidines

Perimidines a heterocyclic system that comprises of three rings fusion which has been known since the beginning of the 20th century. It has two nitrogen atoms at nonadjacent positions. These N-atoms are situated in the 1- and 3-positions (Figure 1.1). At present time the name “perimidine” has been confirmed by IUPAC rules (Nikol’skii, 1968), but other names can also be encountered in the literature; 1*H*-1,3-diazaphenalene, 1*H*-benzo[*d*,*e*]quinazoline, 1*H*-naphtho-[1,8-*d*,*e*]pyrimidine and perinaphth-imidazole.

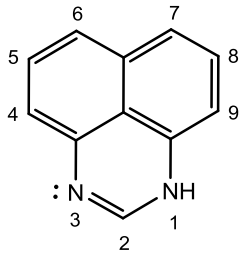


Figure 1.1 Perimidine ring with numbering scheme

Perimidine derivatives have received wide interest because of their diverse biological activities and chemical application. Perimidine ring is present in many alkaloids, antibiotics and antimicrobial compounds. Therefore these systems find wide use in medicine, agriculture and industry.

1.2 Usage of Perimidines

1.2.1 Dyes

Perimidine derivatives have been used as dye intermediates and coloring materials for polymers and polyester fibers. A lot of patents for the synthesis and use of alkyl-, aryl-, azo-, sulpho- and acyl-derivatives of perimidines as dyes appeared in literature. N-aroylperimidones (Kobrakov et al., 2006), 6(7)-azoperimidines (Allam and About-Zeid, 1972), the amides of perimidine-6,7-dicarboxylic acid (Christman, 1968; Krasovitskii, 1965), (9-acridinyl)-substitue-2,3-dihydroperimidine (Suzuki et al., 2001), (Figure 1.2) have been proposed as dyes for synthetic fibres.

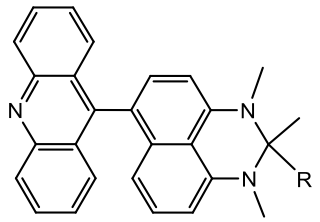


Figure 1.2 The structure of (9-acridinyl)-2,3-dihydroperimidines

Azodyes are any of a large class of synthetic organic dyes that contain nitrogen as the azo group −N=N− as part of their molecular structures. “Sudan Black B” which contains perimidine skeleton is a fat-soluble diazo dye used for staining of neutral triglycerides and lipids on frozen sections and some lipoproteins on paraffin sections (Figure 1.3). It has the appearance of a dark brown to black powder with maximum absorption at 596-605 nm and melting point 120-124 °C. It stains blue-black.

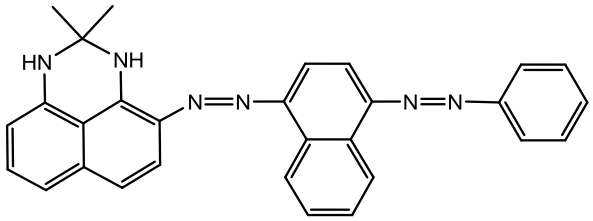


Figure 1.3 The structure of Sudan Black B

Acid dye is a dye, in chemical regard a sodium salt of a sulfonic, carboxylic or phenol organic acid. “Acetonsaeureblau” (acetone acid blue) is a kind of acid dyes which is effective on protein fibers particularly animal hair fibers such as wool, alpaca and mohair. They are also useful for dyeing silk. Its IUPAC name is 2,3-dihyro-2,2-dimethyl-4,9-bis(4-nitrophenyl)diazene-5,8-perimidine disulphonic acid (Figure 1.4).

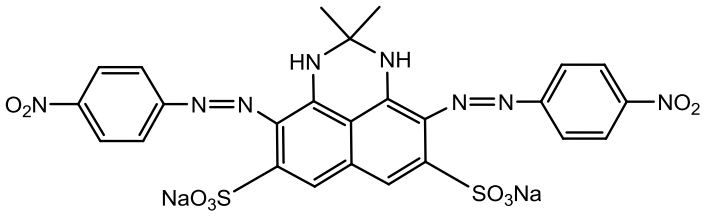


Figure 1.4 The structure of “acetone acid blue”

The use of perimidine derivatives as a coupler substance for the preparation of oxidation dyestuffs and also to hair colouring compositions which comprise perimidine derivatives have been reported in U.S. Pat. No. 5,922,086, which are incorporated herein by reference. Hair colorants based on perimidine derivatives disclosed in these patent and applications are of the general formula as shown in Figure 1.5, R_1 and R_2 are hydrogen or organic groups, R_3 is (C_1-C_6)-alkyl, chlorine or bromine and n is 0,1 or 2 (Bauer et al., 1998).

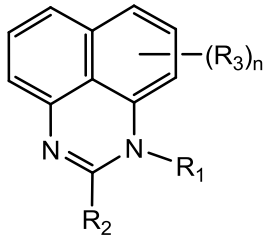
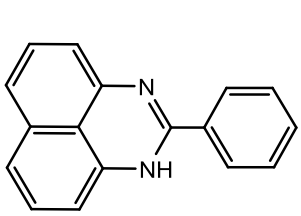


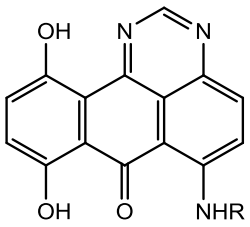
Figure 1.5 General structrure of perimidine derivatives used for hair colorants

1.2.2 Pharmaceutical importance of perimidines

A number of communications have been devoted to the biological activity of perimidines. Various 1- and 2-substituted perimidines have been proposed as highly effective antiulcer (Paragamian et al., 1970), antibacterial (Pande et al., 2009), antifungal (Pozharskii et al., 1976), antitumor (Garnier-Suillerot et al., 2001), antihelminic (Krotov et al., 1976; Bekhli et al., 1979) agents, cytotoxic effects (Figure 1.6), (Korkmaz, 2005; İncesu, 2008) and neurotropic preparations.



2-Phenyl-1*H*-perimidine



Benzoperimidine derivatives

Figure 1.6 Some of perimidine derivatives which have cytotoxic activity

Furyl substitued perimidine derivatives are useful to inhibit gastric acid secretion, for that reason they are antiulcer agents and neurotropic preparations (Paragamian et al., 1970). It has been described in U.S. Pat. No.3956496 (Figure 1.7).

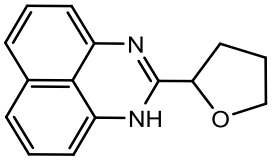


Figure 1.7 2-(Tetrahydrofuryl)perimidine

Moreover, perimidine and its analogs have been described as DNA-intercalating and antitumoral agents agains several carcinogenic cell lines (Figure 1.8), (Popp et al., 1966; Denny et al., 1987; Deady et al., 2001).

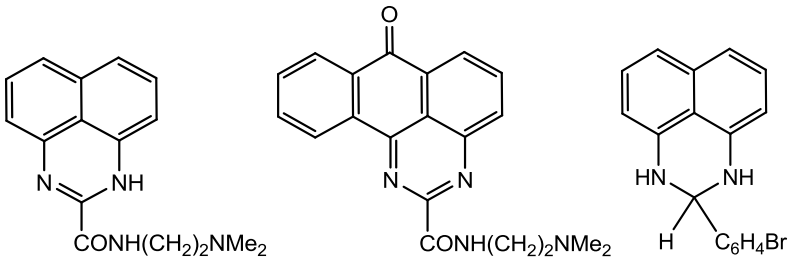


Figure 1.8 Some of perimidine derivatives which have antitumoral activity

1.3 Physical Properties of Perimidines

1.3.1 Melting point and decomposition degree

Perimidine is a tricyclic heterocycle consisting of a dihydropyrimidine ring *ortho*- and *peri*-fused to naphthalene. It is olive-green solid and soluble in polar solvents especially ethanol. On heating the substance in a capillary tube obvious decomposition progresses around 225 °C. The nearly black mass appeares to be holly liquid at 233 °C to 238 °C, with brown oily droplets on the walls of the tube (Wagner, 1939).

1.3.2 Colour and electronic spectra of perimidines

The electronic spectra of perimidines consist of three absorption bands at 400, 330 and 235 nm. The long wavelength absorption band of perimidines is the π-electron transfer from the naphthalene ring to the heteroring. Thus this band is due to charge transfer between the π-donor and π-acceptor components of the perimidine system and explains qualitatively the influence of certain substituents on the colour of perimidines. When strong π-acceptors are present in the 2-position in perimidine, the corresponding compounds are deeply coloured (Pozharskii and Dalnikovskaya, 1981).

1.3.3 Fluorescent properties of substituted perimidines

The fluorescence of perimidine and some of its derivatives has been studied (Minkin et al., 1967). It has been noted that the fluorescence of perimidines is less intense than naphtoimidazoles (Yoshida et al.,1952). Otherwise, 1,8-naphthylene-diamines, 2,3-dihyroperimidines and some of 2-substituted perimidines (Figure 1.9) have showed fluorescence properties (Yusuff et al., 2010).

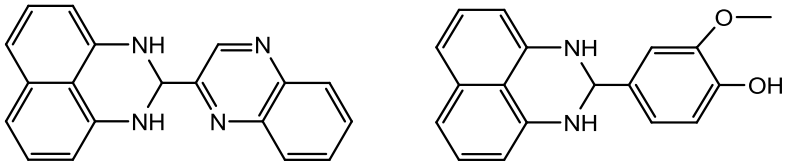
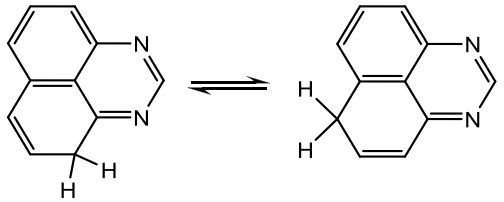


Figure 1.9 Some of 2-substituted perimidine derivatives which have fluorescent properties

1.3.4 Tautomeric character of perimidine

Tautomerism with migration of the proton to the 4(9)- and 6(7)-positions is theoretically possible for perimidines. Also 4*H*-perimidine and 6*H*-perimidine derivatives can show tautomeric forms (Figure 1.10).



4*H*-perimidine 6*H*-perimidine

Figure 1.10 Tautomeric character of perimidine

Tautomerism occurs with 2-amino derivatives of perimidine (Figure 1.11). The great facility of transfer of a proton of the NH_2 group to an intracyclic N atom to form an imine (Pozharskii, 1971).

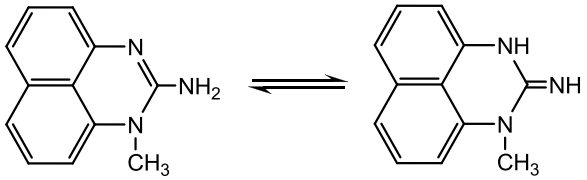


Figure 1.11 Tautomeric character of 2-amino derivatives of perimidine to imine form

1.3.5 Quantum-mechanical calculations and aromaticity of perimidines

The perimidine molecule is a 14π-electron system, but one pair of its electrons is not delocalised, which leads to a decrease of aromaticity. The distribution of electron density in perimidine is so non-uniform it can be represented as consisting of two parts: the μ-carbon atom with an unusually high positive charge and the negatively charged 1,8-naphthylenediamine residue.

The transfer of π-electron density from the heteroring to the naphthalene system takes place. The maximum negative charge in molecule is concentrated in the 4- and 9-positions (the *ortho*-positions relative to the heteroring) and in the 6- and 7-positions (*para*-positions), while in the 5- and 8-positions (*meta*-positions) it is vitually zero and shown in Figure 1.12 (Pozharskii and Dalnikovskaya, 1981; Garnovskii et al., 1967).

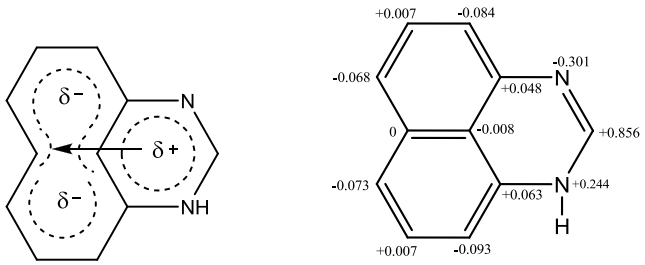


Figure 1.12 Calculated electron density of perimidine ring

1.4 Chemical Properties of Perimidines

1.4.1 Oxidation

As a result of their high π-donor capacity, perimidines are sensitive to the action of oxidants. 2-Substituted perimidine derivatives are oxidized by Fremy's salt ($Na_2NO(SO_3)_2$) under mild condition (Figure 1.13). Oxidants converts compound to mixture of 4- and 6-perimidone derivatives. These are also formed on oxidation of 4(9)- and 6(7)-hydroxyperimidines by atmospheric oxygen (Cameron et al., 1976).

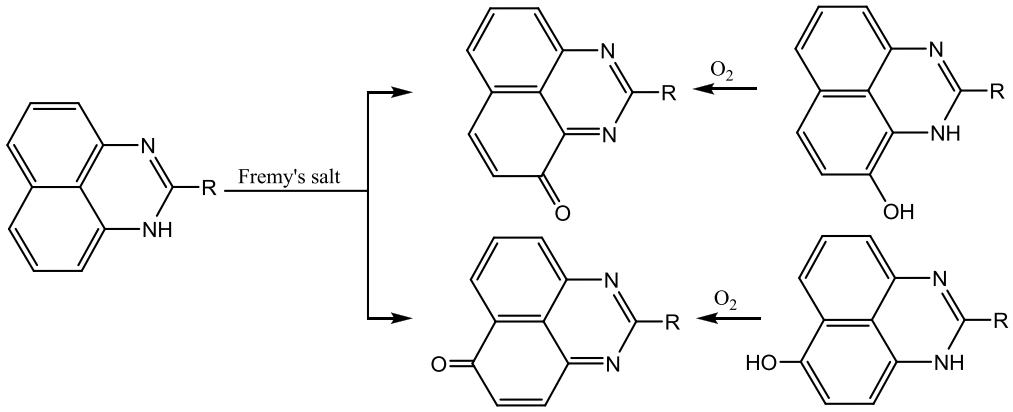


Figure 1.13 Oxidation reaction of 2-substituted perimidine derivatives

1.4.2 Reduction

The reduction of 1-substitued perimidines can be carried out by Birch procedure (Li or Na in liquid NH_3) and is shown in Figure 1.14. These conditions let 1-R-2,3-dihydroperimidine compounds occur (Pozharskii et al., 1977).

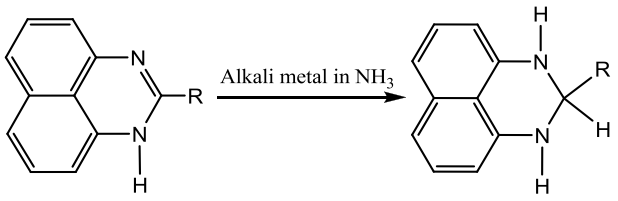


Figure 1.14 Reduction of perimidine derivatives

1.4.3 Nucleophilic substitution reactions of perimidines

Reactions with nucleophiles are extremely characteristic of N-substituted perimidines (Figure 1.15). They all involve μ-carbon atom on which a high positive charge is concentrated. Thus 1-alkyl-, 1-benzyl-, 1-phenyl-, 1-methoxymethyl- and 1-dialkylaminoalkyl- perimidines undergo amination by sodium amide with formation of high yields of the amines and hydroxylation by alkali with formation of high yields of the perimidones (Pozharskii et al., 1970, 1971).

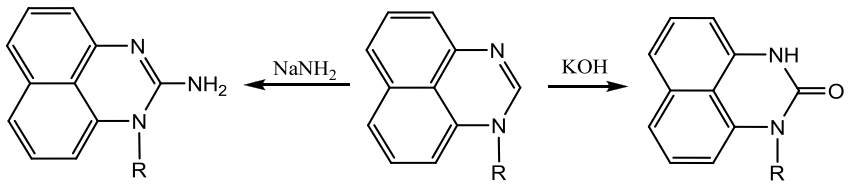


Figure 1.15 Reactions of nucleophiles with perimidine derivatives

1.4.4 Electrophilic substitution reactions of perimidines

Perimidine is one of the most active heterocycles in relation to electrophiles, which can be explained by its high π-donor capacity and high negative π-electron change in the *ortho*- and *para*-positions of the naphthalene ring. Electrophilic substitution reactions involve precisely these positions and they can be seen in Figure 1.16.

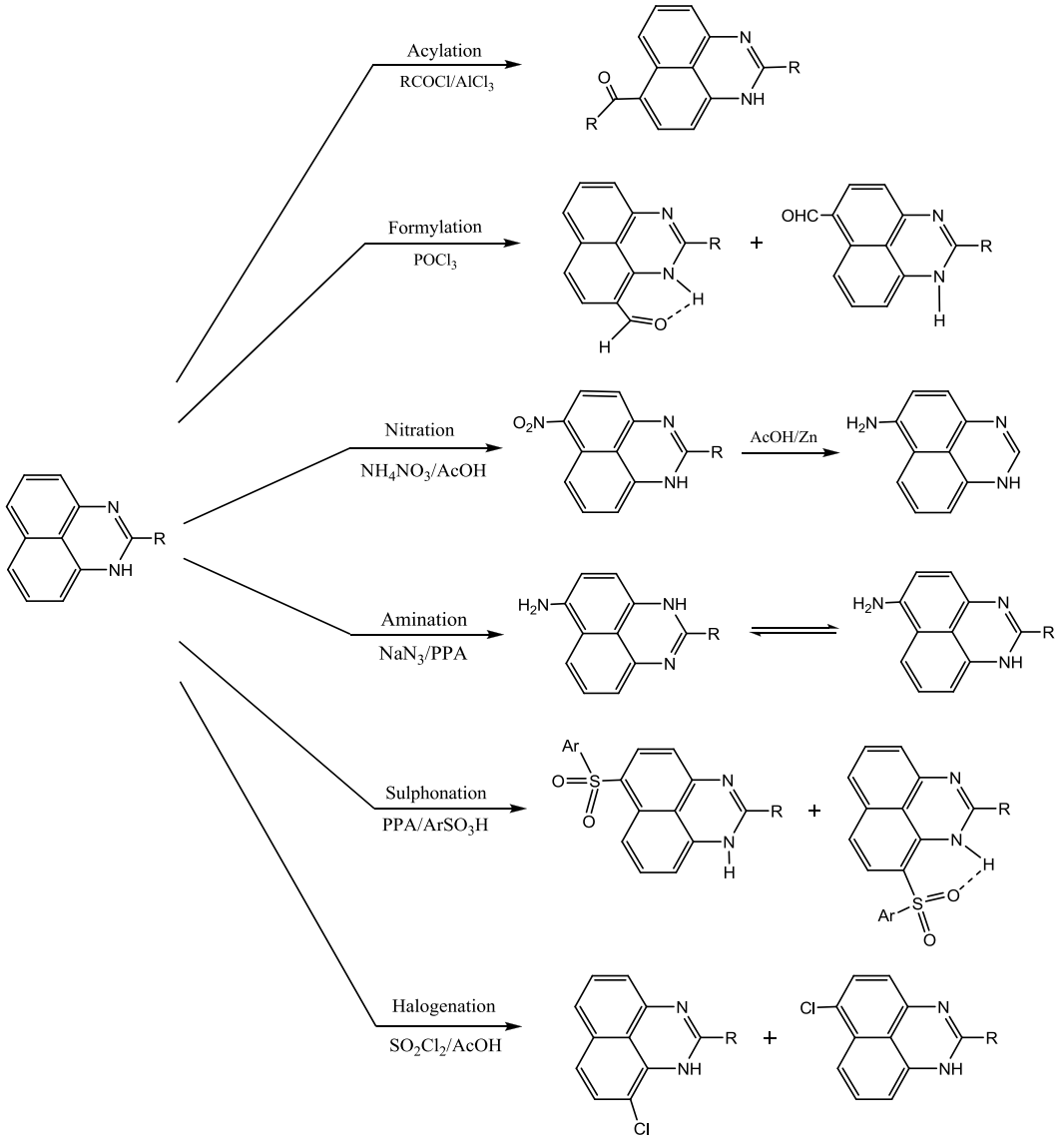


Figure 1.16 Electrophilic reactions of 2-substituted perimidine derivatives

Acylation

6(7)-Acylperimidines are synthesized by the effect of acyl chlorides on perimidine in polar solvent in presence of excess $AlCl_3$. The reaction proceeds selectively at C-6(7) in the perimidine system, which eliminates the necessity of separating the 4(9)- and 6(7)-isomers (Figure 1.16).

The direct acylation of 2,3-dihydroperimidines is possible by carboxylic acids in polyphosphoric acid (PPA) to obtain 4-acetylperimidine (Figure 1.17), (Borovlev and Demidov, 2009).

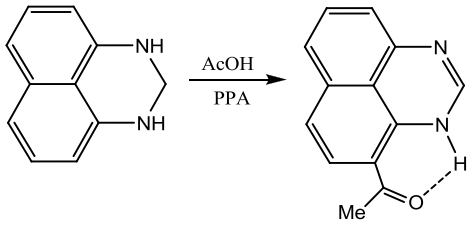


Figure 1.17 Acylation of dihyroperimidines

Unsubstituted perimidone is acylated by aroyl chloride without a catalyst at 180^{o}C. The reaction product is the 4-(9)-aroyl derivative is shown in Figure 1.18 (Christman, 1965).

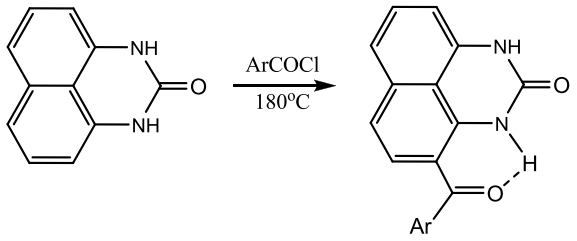


Figure 1. 18 Wolff-Kishner reactions of perimidones

Intramolecular acylation reaction can ocur in the presence of polyphosphoric acid (PPA) in the series of perimidines and perimidones; the resulting ketones can be converted by the Wolff-Kishner reaction into bridged systems as shown in Figure 1.19 (Pozharskii et al., 1981).

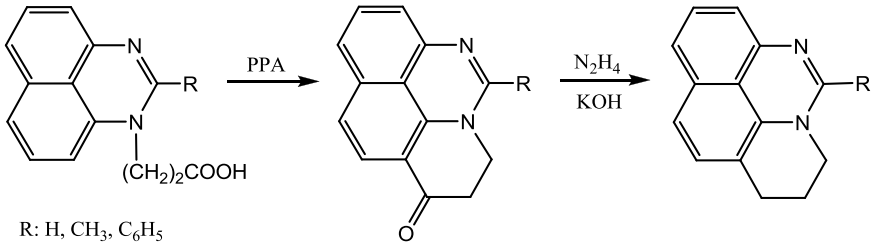


Figure 1. 19 Wolff-Kishner reactions of perimidines

Formylation

The formylation of perimidine, its 2- and 3-alkyl derivatives and 1,3-dialkylperimidones has been studied under conditions of the Vilsmeier reaction (Filatova et al., 2006; Vistorobskii et al., 1999).

The Vilsmeier reaction is the chemical reaction of a substituted amide with phosphorus oxychloride and an electron rich arene to produce an aryl aldehyde or ketone (Figure 1.20).

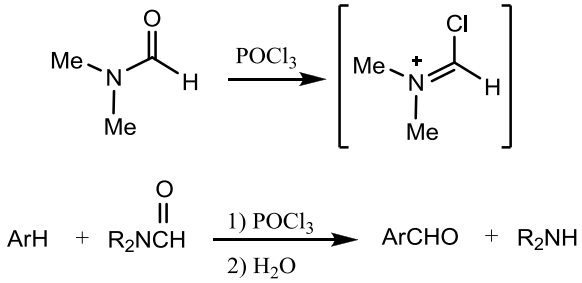


Figure 1.20 The reagent and reaction of the Vilsmeier reaction

The basic products of Vilsmeier reaction from perimidines were 4(9)- and 6(7)-carbaldehydes shown in Figure 1.16 and the yields of each of which did't exceed 10 % (Filatova et al., 2006).

Nitration

The initial nitration ways of perimidines is using nitric acid. When 2-methylperimidine was treated with nitric acid in glacial acetic acide, only dinitro-2-metylperimidine derivatives were obtained, but their structure was not established and yields which is written in the article is too low (Whitehurst, 1951). It is shown that satisfactory results are obtain refluxing perimidines with NH_4NO_3 with glacial acetic acid. The precipitate is named 6(7)-nitroperimidine. The treatment of the reaction mixture with zinc powder gave 6(7)-aminoperimidine derivatives (Figure 1.16), (Aksenov et al., 2011).

Amination

A disadvantage of the method reported by Pozharskii et al. (1976) for the synthesis of 6(7)-amino-2-alkylperimidines involving the reduction of 2-methyl-6(7)-nitroperimidine was the low yield of the nitro compounds. A one-step synthesis of these compounds using a new reagent combination which is NaN_3/PPA and the reaction is shown in Figure 1.16 (Aksenov et al., 2009).

Sulphonation

2-Substituted perimidines can be direct sulfonated by arenesulfonic acids in PPA under more rigid conditions (Figure 1.16). The observed products 4(9)- and 6(7)-substituted varieties, has been separated based on their different mobilities. 4(9)-Isomers are mobile in low polarity solvents because of the intramolecular hydrogen bond (Borovlev et al., 2002).

Halogenation

It is known that chlorination of perimidines, perimidones and dihydroperimidines is possible in the presence of sulfuryl chloride (SO_2Cl_2) in acetic acid. There is an important point while observing this process, regarding proportion of SO_2Cl_2. The more SO_2Cl_2 concentration, the more chloro-derivatives of perimidine are formed. One mole of SO_2Cl_2 leads to formation of the 6(7)- and 4(9)-chloro derivatives (Figure 1.16). Two moles of SO_2Cl_2 results in the formation of a complex mixture of mono-, di- and tri-chloro perimidines, while treatment of three moles of SO_2Cl_2 gives rise to 4,6,7-trichloro perimidine. Tetrachloro derivatives can be formed by excess of SO_2Cl_2 (Kuz'menko et al., 1978). Bromination of perimidines is known very little. When 2-methylperimidine was treated with bromine in acetic acid, only the mono and di-bromo derivatives were obtained, but their structures were not established (Whitehurst, 1951).

1.4.5 Preparation of oligomers containing perimidine skeleton

An oligomer is a molecule that consist of a few monomer units, in contrast to a polymer that, consist of an unlimited number of monomers. A series of oligomeric polyaminals based on 1,8-bis(methylamino)naphthalene was obtained by condensation of polyketones with 1,8-bis(methylamino)naphthalene and also the simple monomer 2,2-diethyl-1,3-dimethyl-2,3-dihydro-1*H*-perimidine was calculated for the tetramer and hexamer in the presence of *p*-toluenesulphonic acid (PTSA), (Figure 1.21), (Alder et al., 2009).

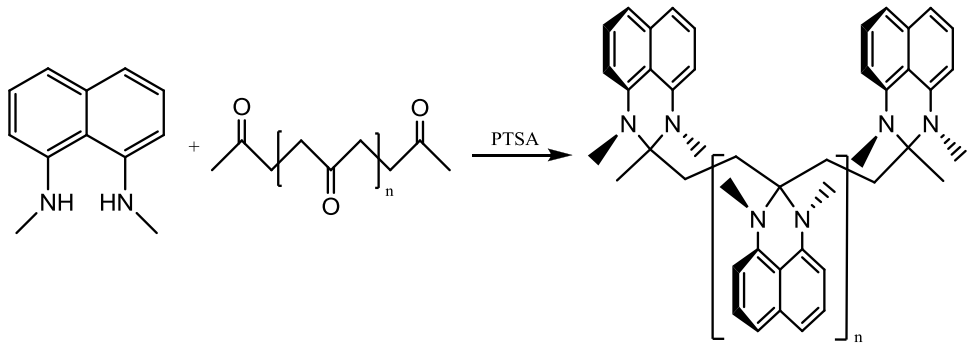


Figure 1.21 Preparation of oligomeric aminals containing 1,8-DAN units

1.4.6 Annulation of perimidines

As shown in Figure 1.22-1.23, interaction of 1,3-diketone (**II**) and aromatic nitriles (**IV**) in PPA with 1,8-DAN (1,8-Diaminonaftalene) leads to closure of the perimidine ring and corresponding 2,6,8-trialkyl-1,3-diazapyrenes (**III**) and 2,6,8-triaryl-1,3,7-triaza- pyrenes (**V**) (Borovlev et al., 2007; 2008).

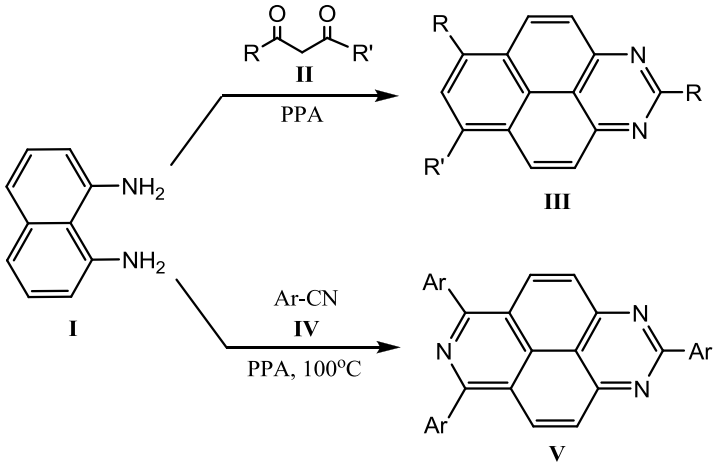


Figure 1.22 Annulation reaction of 1,8-DAN

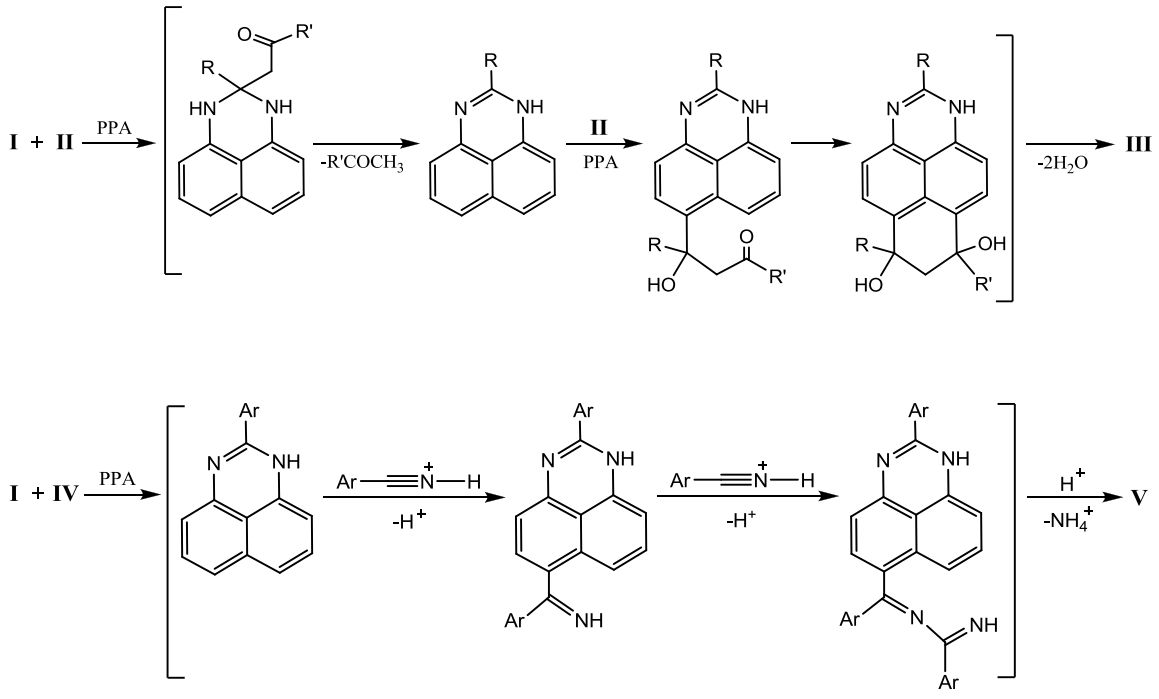


Figure 1.23 Mechanism of the annulation reactions of 1,8-DAN

1.4.7 The "proton sponge"

1,8-Bis(dimethylamino)naphthalene is a chemical compound which is often referred by the trade name "proton sponge" shown in Figure 1.24. This compound is a diamine in which the two dimethylamino groups are attached on the same side or peri position of a naphthalene system. Proton sponge is one of the strongest Bröensted bases in organic chemistry (pK_a of 12.1), (Alder et al. ,1968).

The high basicity is attributed to the relief of strain upon protonation and/or the strong interaction between the nitrogen lone pairs (Rettig et al., 2001; Alder, 1989). However, the molecule is sterically hindered, making it a weak nucleophile. Because of this combination of properties, it has been used in organic synthesis as a highly selective non-nucleophilic base.

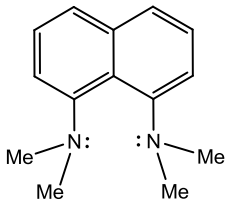


Figure 1.24 1,8-Bis(dimethylamino)naphthalene, "proton sponge"

It is synthesed that perimidine skeleton which has 1,8-bis(dimethylamino) naphthalene (proton sponge) structure containing the N-substituted methyl groups shown in Figure 1.25 (Pozharskii et al., 2001).

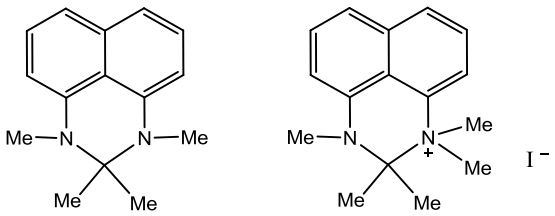


Figure 1.25 Proton sponge of the perimidine skeleton

1.5 Synthesis of Perimidine Derivatives

Perimidine was first obtained and described in detail by Franz Sachs in 1909. Several classical synthetic methods have been reported for synthesis of perimidine derivatives. The most widely used method for preparation of perimidine is the cyclocondensation reaction of 1,8-diaminonaphthalene with carboxylic acid under reflux condition (Sachs, 1909; Denny et al., 1987).

The alternative facile method for the synthesis of perimidine is using moleculer sieve as a catalyst and shown in Figure 1.26 (Heravi et al., 2009).

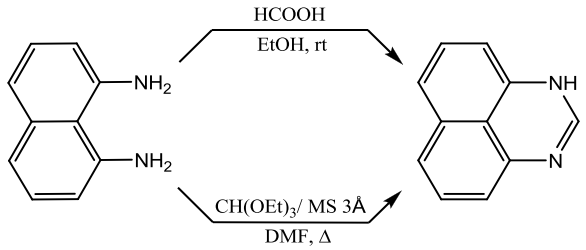


Figure 1.26 Synthesis of perimidine presence of catalysts

The use of hydrogen halides is the most convenient method for synthesis of 2-substituted and 1,2-disubstituted perimidines. The reaction proceeds via the formation of the monoacyl derivative. The formation of a certain amount of N,N'-diacyl derivatives of 1,8-DAN which can be separated from compounds. On the other hand, it has been reported that aromatic and aliphatic aldehydes react with 1,8-DAN in ethanol or benzene to give the corresponding dihydroperimidines (Figure 1.27), (Pozharskii and Dalnikovskaya, 1981; Hendrickson and Hussoin, 1987; Paragamian et al., 1968).

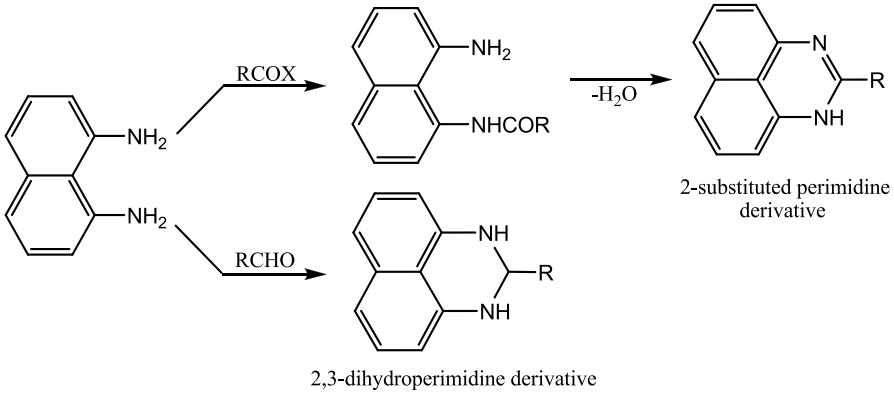


Figure 1.27 Synthesis of 2-substituted and 2,3-dihydroperimidine

There are other methods to develop reactions in the presence of a catalyst (Figure 1.28). The use of solid catalysts in organic synthesis is important, because of their suitable acidity, low cost, recoverability. They also provide eco-friedly conditions, short reaction time and high yields. Nano-silica sulfuric acid (NSSA) and cupper nitrate have been used as an efficient catalyst for synthesis of perimidine derivatives (Mobinikhaledi et al., 2009, 2010).

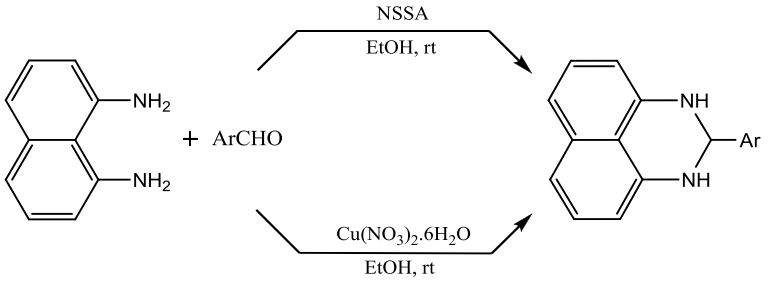


Figure 1.28 Synthesis of perimidine derivatives via different catalysts

1.6 Synthesis 1,3-Dialkylperimidinium Salts

The hydrogen in the 1-position of perimidines has an asidic character. Therefore 1,3-dialkylperimidinium salts are more difficult to obtain than 2-substituted derivatives (Figure 1.29). Firstly 1-substituted product is synthesized in the presence of a strong base such as NaH, KOH, after that, 1,3-disubstituted perimidinium halides are prepared via addition of alkyl halide to the 1-substituted derivatives (Karaaslan, 2003; Özdemir et al., 2004; Mashima et al., 2010).

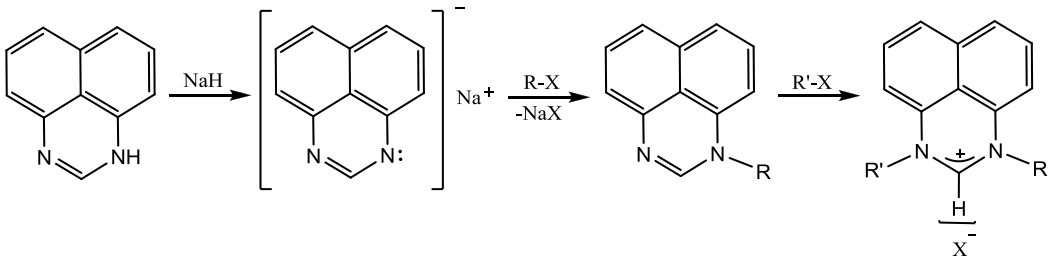


Figure 1.29 Synthesis of 1,3-dialkylperimidinium salts

Another method for the synthesis of the dialkylperimidinium salts is ring closure of the N,N'-di(alkyl)-1,8-diaminonaphthalene dihydrochloride in the presence of triethyl orthoformate as shown in Figure 1.30 (Alıcı et al., 2003).

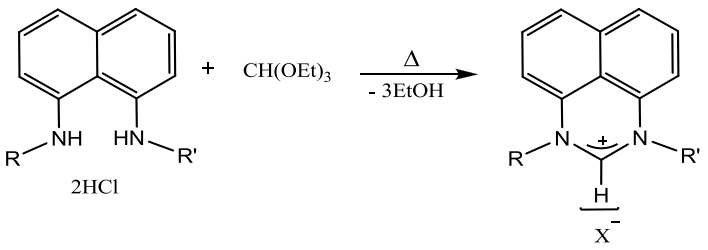


Figure 1.30 Synthesis of dialkylperimidinium salts with $CH(OEt)_3$

Lutidine-bridged bis-perimidinium dibromide salt was synthesized in quantitative yield by N-alkylation of N-butylperimidine with 2,6-bis(bromomethyl)pyridine in a sealed tube is shown in Figure 1.31 (Tu et al., 2009). This study focused on the role of a strong *σ*-donor in a 6-membered heterocycle on the catalytic activity and compared between the lutidine-bridged bis-perimidinium dibromide and its imidazole and benzimidazole analogues. The bis-perimidinium salt was an efficient precatalyst in combination with palladium acetate for Heck and Suzuki cross-coupling reactions under aerobic conditions.

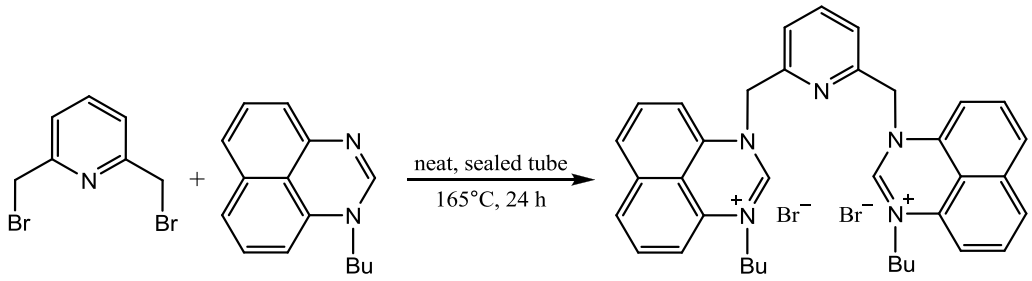


Figure 1.31 Synthesis of lutidine-bridged bis-perimidinium dibromide

Compared neutral perimidines with perimidinium salts exhibit a still greater reactivity in relation to nucleophiles. The most important and interesting reactions of perimidinium salts are those under the influence of alkali agents. 1,3-dimethylperimidinium (**VI**) and 1,3-dimethylaceperimidinium (**VII**) salts are almost quantitatively converted with aqueous alkali solution into a mixture of the corresponding perimidone (**IX**) and 2,3-dihydro-1,3-dimethylperimidine (**X**). The reaction proceeds through a step involving the formation of a carbinol pseudo base (**VIII**), which then apparently undergoes redox reaction with the starting quaternary salt or itself undergoes disproportionation (Figure 1.32), (Pozharskii and Kashparov, 1972).

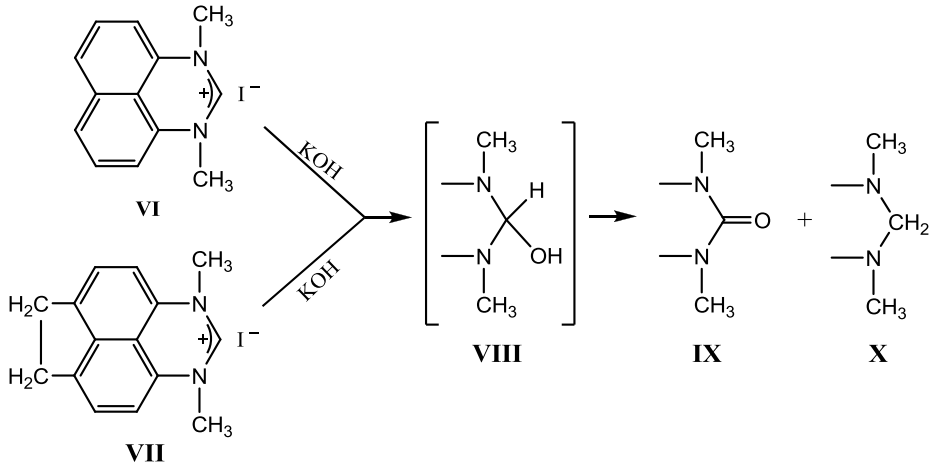


Figure 1.32 The interaction of perimidinium salts with nucleophiles

1.7 Carbenes

The word “carbene” derives from the name given to free, disubstituted carbon compounds with general structure :CXY, where X and Y may be H, alkyl, or heteroatoms (O, N, S, halogens). Since the central carbon atom does not possess an octet of electrons, free carbenes are electron deficient and extremely reactive. Disubstituted carbon atoms may bind directly to a transition metal (M) producing a formal double bond between the metal and the carbon. Complexes containing these divalent carbon ligands are called *metal-carbene* complexes. Metal-carbene complexes have the general structure L_nM = CXY. Here, L_n represents all ligands except carbene and M is transition metal (Figure 1.33).

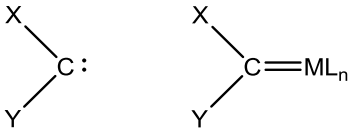


Figure 1.33 General demonstration of carbene and metal-carbene complexes

One of the best methods for generating carbenes is the alpha-elimination route in organic chemistry (Figure 1.34).

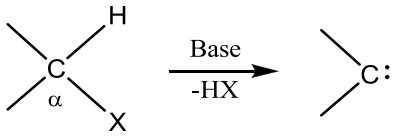


Figure 1.34 General demonstration of alpha elimination reaction

Chloroform is weakly acidic (pK_a = 25) and when treated with a strong base such as potassium *tert*-butoxide, is deprotonated, giving trichloromethanide anion, $^{-}$**:**CCl_3. This anion is unstable and expels a chloride ion, yielding dichlorocarbene (Figure 1.35).

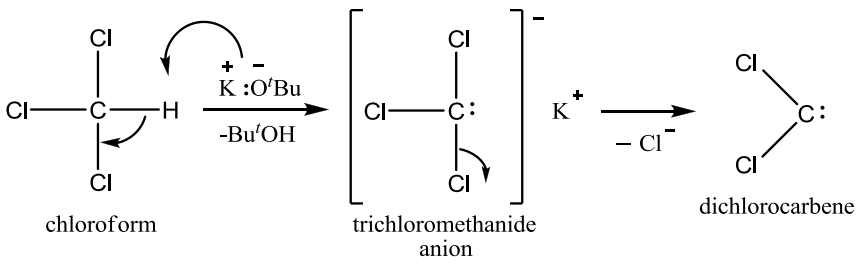


Figure 1.35 Mechanism of the formation of dicholorocarbene from chloroform

Carbens take place in many organic reactions. Olefin cyclopropanation, hydrosilanation and furanisation may be given as examples for the above mentioned organic reactions, which is a synthetically useful transformation (McMurry, 1984; Sykes, 1975).

1.7.1 N-heterocyclic carbenes (NHCs)

"N-heterocyclic carbenes (NHCs) are ring compounds bearing at least one α-amino substituent" (Diez-Gonzalez et al., 2009). NHCs could contain one to four nitrogen atoms (Figure 1.36).

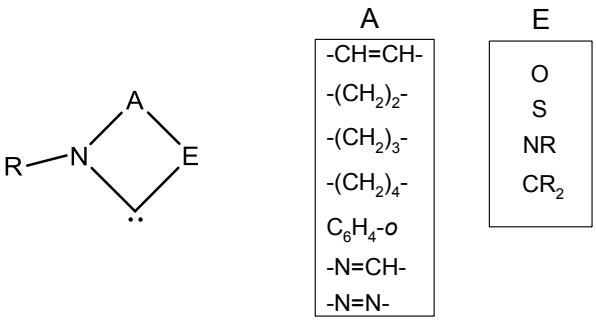
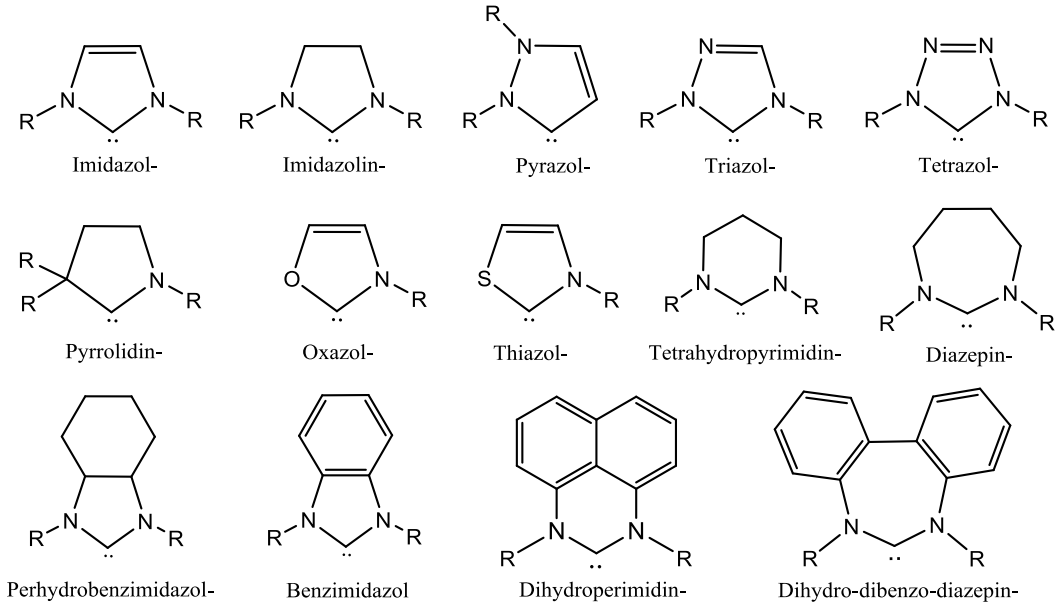


Figure 1.36 General demonstration of NHC

Most of the N-heterocyclic carbenes and their metal complexes reported in the literature have been composed of 5-membered rings which include imidazole, imidazoline, benzimidazole, triazole and their saturated analogues. The most common subclasses of NHCs are presented in Scheme 1.1 (Diez-Gonzalez et al., 2009).



Scheme 1.1 The ring structure of some NHCs; the most common 5-membered ring compounds are shown with abbreviations. IUPAC nomenclature requires -ylidene ending to represent proper naming e.g. imidazol-2-ylidene.

NHCs are strong σ-donors with a low capacity for π-acceptance (Herrmann, 1996, 2002; Lammertsma et al., 2003) and these properties make them effective stabilizing ligands in organometallic chemistry and important ligands in some forms of catalysis. Therefore, there has been widespread attention in this area and the coordination chemistry and catalytic applications of NHC complexes have been covered by a number of review articles (Nolan et al., 2009; Herrmann et al., 2002; Lappert et al., 2005; Bourissou et al., 2000; Jacobsen et al., 2009; Cavell, 2008; Glorius and Dröge, 2010).

1.7.2 Importance of ring size

The ylidenes **A** and **B** represent the typical skeleton of stable nucleophilic singlet carbenes. These species have been largely restricted to 5-membered heterocyclic rings possess the 6π-electron structure expected for aromatic systems (Liu et al., 1999; Hahn et al., 2000; Heinemann et al., 1996; Boehme et al., 1996; Alder et al., 1999; Guillen et al., 2001). The carbene center in a 6-membered ring, which has significant implications on the steric impact of the R substituents and leaves the divalent carbon as part of a formally 7π-electron, 6-membered heterocyclic ring (Figure 1.37), (Richeson et al., 2003).

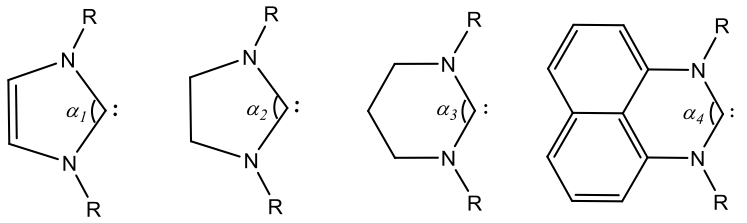


Figure 1.37 Demonstration of the NCN bond angle of carbenes

The ring-expanded NHCs display enhanced donor properties due to the widening of the N-$C_{carbene}$-N bond angle (Cavell et al., 2005; Whittlesey et al., 2010). That angles observed for isolated carbenes of type **A** was 101,4^o (Arduengo et al., 1992), type **B** was 104,7^o (Arduengo et al., 1995), type **C** was 114,6^o (Cavell et al., 2008), type **D** was 115,3^o (Richeson et al., 2003) , while R was mesityl except for **D** (R: ^{i}Pr for type D).

The N-$C_{carbene}$-N angle of the 6-membered heterocyclic rings in **C** and **D** were larger than the analogous angles observed for isolated carbenes of type **A** and **B**.

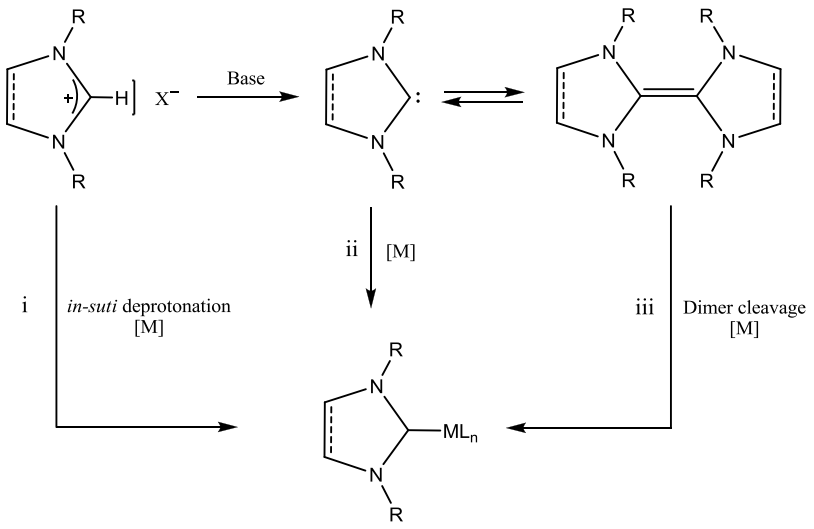
Extended aromatic heterocyclic ring feature modulates the donor properties of the carbene center and imposes geometric constraints on the N-substituents, influencing their steric impact. Especially, perimidine scaffold directs the N-bound groups closer to the carbene atom, increasing N-$C_{carbene}$-N bond angle, decreasing the R-N-$C_{carbene}$ angle and increasing the steric pressure on both the carbene and a coordinated metal.

1.8 General Synthesis of Transition Metal-NHC Complexes

It is known that the discovery of transition metal complexes of NHCs have been in 1968 by Wanzlick, by Öfele and in 1971 by Lappert (Wanzlick and Schöenherr, 1968; Öfele, 1968; Lappert et al., 1971). Transition metal complexes incorporating 1,3-disubstituted NHC have attracted a great interest (Herrmann et al., 1997; Bourissou et al., 2000; Alder et al., 1999). Many of the transition metal-NHC complexes and NHCs have been used as catalysts in various organic reactions.

Therefore, plenty of efforts has been focused on the improvement of known structural NHC motifs. Generally NHC complexes can be prepared by three major methods as examplified by imidazol(in)-2-ylidenes (Scheme 1.2):

i. the *in situ* deprotonation of ligand precursors,
ii. complexation of free N-heterocyclic carbenes,
iii. the cleavage of electron-rich olefins (e.r.o.)



Scheme 1.2 Major synthetic pathways for the generation of transition metal–NHC complexes

NHC complexes can be obtained by *in situ* deprotonation of the diazol(in)ium salts in the presence of metal precursors under basic conditions. The *in situ* complexation of the ligand has the advantage of not having to prepare and isolate the free NHC which are air and moisture sensitive. If metal precursors with basic ligands are available, e.g. $Pd(OAc)_2$, deprotonation could be the method of choice to introduce selectively only one NHC moiety into the product.

L^R_2 type (R = Me, Et, CH_2Ph, Ph) tetraaminoalkenes, described as e.r.o. are source of ligand which create carbene as shown in Figure 1.38 (Çetinkaya et al., 1971; Lappert et al., 1984).

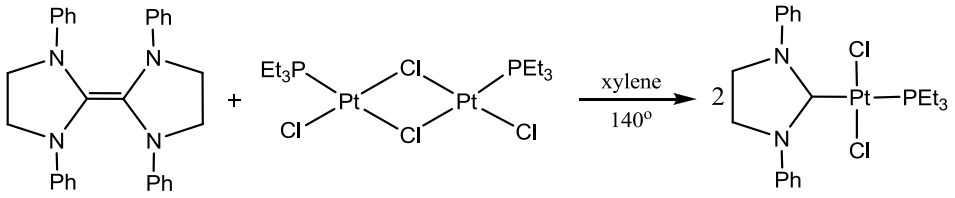


Figure 1.38 The synthesis of the carben complexes formed by cleavage of e.r.o.

As expected, deprotonation of 1,3-disubstituted perimidinium halides with NaH in the presence of catalytic amount of potassium *tert*-butoxide in dry THF resulted in the formation of the tetraaminoalkene derivatives. As shown in Figure 1.39. However, the e.r.o. obtained, was found to be surprisingly inert to electrophiles such as O_2 or S_8 (Alıcı et al., 2003). It is worth nothing that this observed inertness is in contrast to conventional e.r.o.s derived from imidazolidines or hexahydropyrimidin-2-ylidenes which are spontaneously inflamable in air (Çetinkaya et al., 1992).

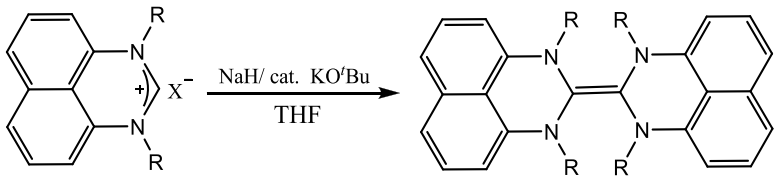


Figure 1.39 The synthesis of the e.r.o. as a result of deprotonation reaction

1.8.1 Metal complexes derived from monosubstituted perimidines

The N-coordinated palladium and ruthenium complexes of perimidine scaffolds were synthesized (Figure 1.40) and their catalytic activities in C-C bond formation and transfer hydrogenation (TH) reactions were investigated (Alıcı et al., 2005; Özdemir et al., 2005).

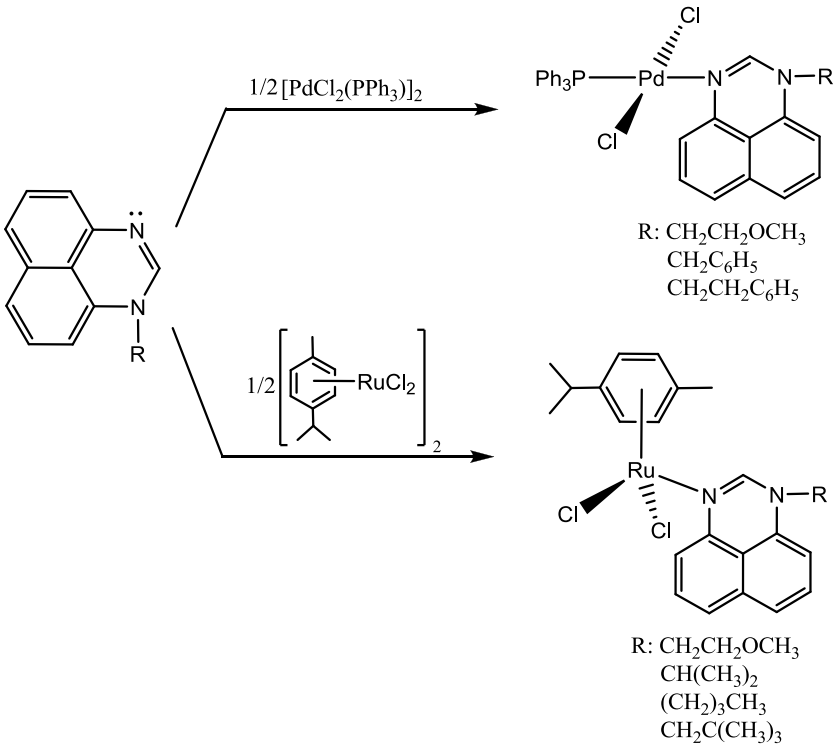


Figure 1.40 The synthesis of 1-alkylperimidine complexes

1.8.2 Ylidene complexes derived from perimidinium salts

N,N'-disubstituted perimidinium salts were prepared as precursors of NHC complexes (Figure 1.41). The Ir complexes were formed by changing the bases and silver salts (Mashima, 2010).

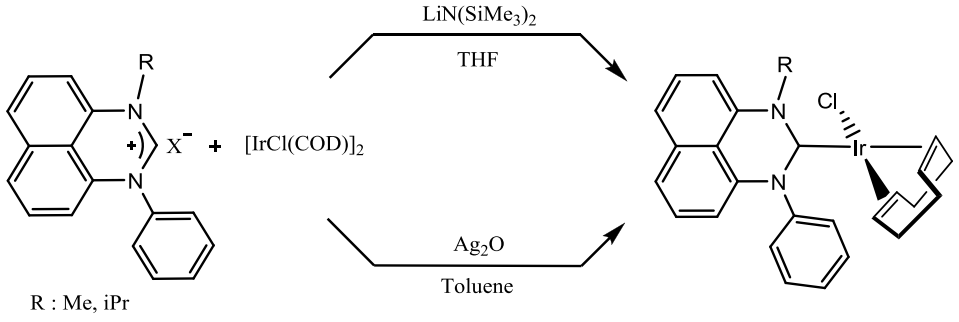


Figure 1.41 The synthesis of the Ir complexes from perimidinium salts

Richeson et al. first synthesized free neutral carbene 1,3-diisopropyl-perimidin-2-ylidene, and characterized it by a single-crystal X-ray diffraction. It exhibits the planar geometry around the N atoms as seen in Figure 1.42. Other neutral carbene structures of perimidine architecture and its complexes have been described in PCT Number WO2005/030782 A2.

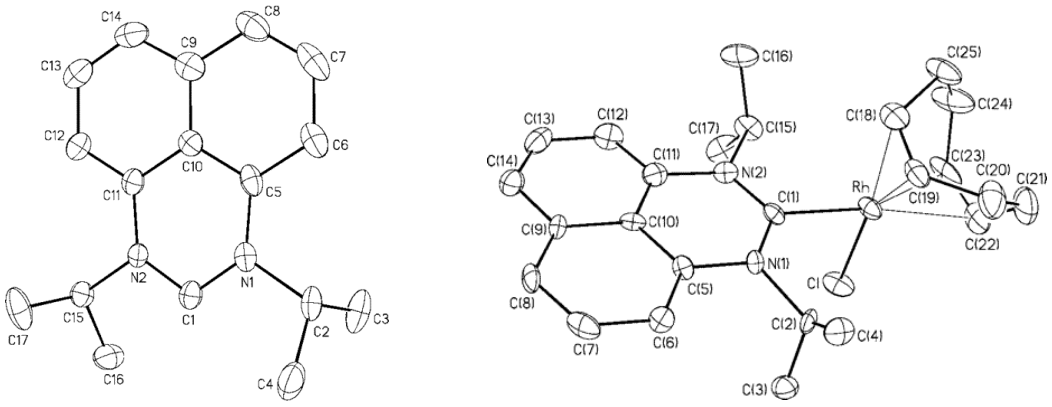


Figure 1.42 Molecular structure and atom-numbering scheme for 1,3-diisopropyl-perimidin-2-ylidene and its Rh complex

The Rh complexes were prepared by the reaction of $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ with neutral carbene which was synthesized by deprotonation with $LiN(SiMe_3)_2$ (Figure 1.43).

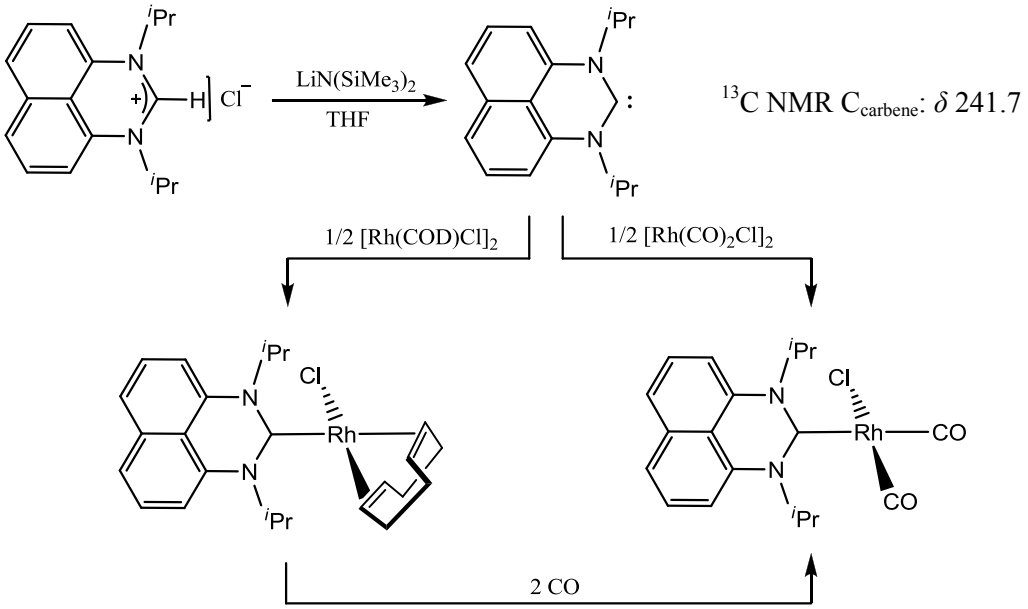


Figure 1.43 The synthesis of the Rh complexes by deprotonation of perimidinium salts

In another study, 1,3-dimethylperimidin-2-ylidene rhodium complex was prepared and its electronic properties, e.g. the σ-donor/π-acceptor property have been investigated (Figure 1.44), (Herrmann et al., 2006).

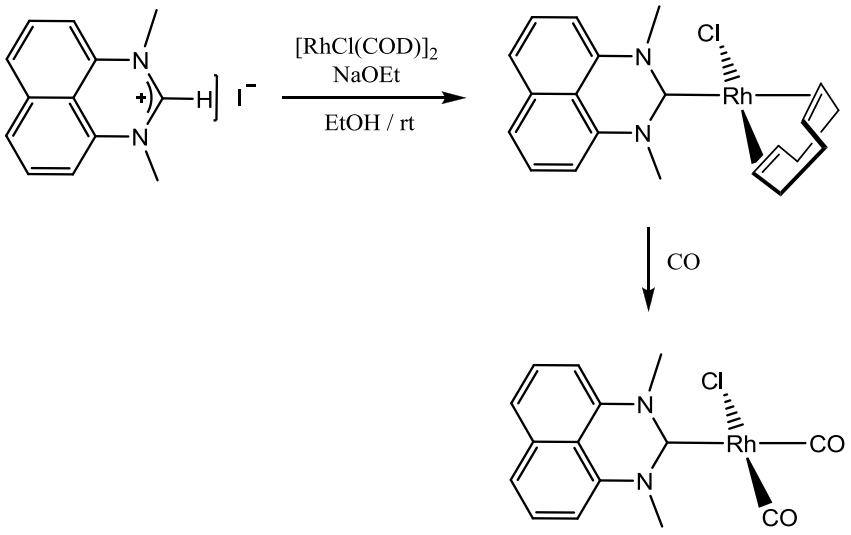


Figure 1.44 The synthesis of the Rh complexes from perimidinium salts

The measurement of the CO-stretching frequencies were determined for perimidine-2-ylidene as one of the strongest *σ*-donor of known NHCs (Herrmann et al., 1997).

1.9 The Aim of This Study

Transition metal complexes of NHC ligands have been used as catalysts for a number of organic reactions (Türkmen et al., 2010; Türkmen et al., 2008; Yiğit et al., 2006; Çetinkaya et al., 2010; Nolan et al., 2009; Gülcemal et al., 2009; Whittlesey et al., 2010; Glorius and Akkattu, 2010). Imidazol-2-ylidenes and dihydroimidazol-2-ylidenes are strong *σ*-donors which serve as standard ligands in coordination chemistry and catalysis due to their stabilyzing properties and ease of preparation (Çetinkaya et al., 1997; Türkmen et al., 2009; Özdemir et al., 2005, 2007; Herrman et al., 2006). Furthermore, they can be modified in various ways. In comparison the most common 5-membered (**XI-XII**), 6- (**XIII**) and 7- (**XIV**) membered NHCs are more basic (Figure 1.45).

On the other hand, the construction of bicyclic and tricyclic systems by annulation is another strategy (Arduengo and Iconaru, 2009). Selected examples of annulation is given by **XI'-XIV'**. Naphtalene-annulated tricyclic system (Figure 1.46) which is dihydroperimidin-2-ylidene (**XV**) and their corresponding complexes are rare. To the best of our knowledge, there are a few example of dihydroperimidin-2-ylidene complex have been reported so far (Richeson et al., 2003; Herrmann et al., 2006).

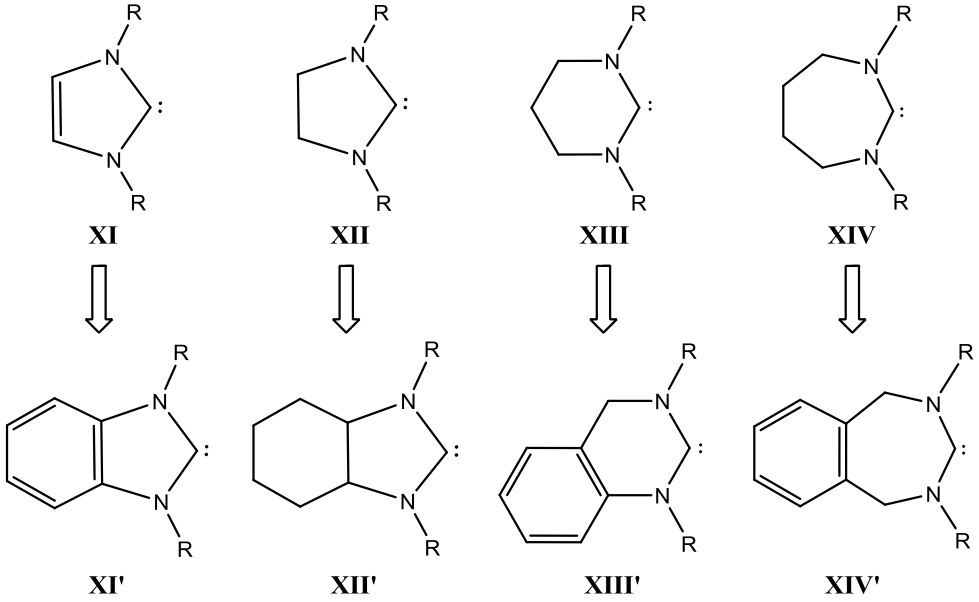


Figure 1.45 Examples of annulated 5-,6- and 7-membered NHCs

As demonstrated previously, the annulation and the substituent(s) R (R') offers new possibilities for the electronic and steric modulation of the NHC ligand. For example, obtained by deprotonation of 1,3-dibutylperimidinium salt has been reported to give tetraaminoalkene (or e.r.o.) be surprisingly inert to the electrophiles such as O_2 or S_8 (Alıcı et al., 2003).

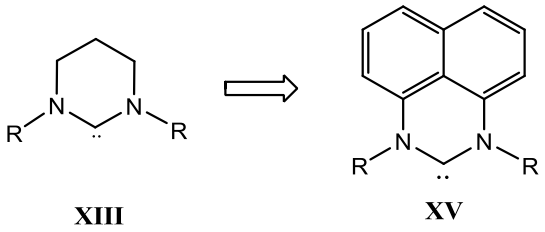


Figure 1.46 4,6-Annulation of dihydropyrimidine-2-ylidene to produce dihydroperimidin-2-ylidene

On the contrary, σ-donation of perimidin-2-ylidenes (R = Me or $CHMe_2$) were found to be extremely strong. This property was contributed to the lone pair residing on nitrogen atom which takes part in the perimidine π-systems imparts an unusual property to the three-condensed system. It is expected that this donor property is reflected in the catalytic activity.

These facts prompted us to pay more attention to investigate synthesis, characterization and properties of new perimidine derivatives bearing methylated benzyl and long-chain alkyl substituents on the N^1 and N^3 atoms and catalytic properties of their complexes.

2. EXPERIMENTAL

Unless otherwise noted all manipulations were performed in air. Reactions involving air-sensitive components were performed by using Schlenk-type flask 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).

Reagents: Toluene, tetrahydrofuran, dichloromethane, ethanol, hexane, pentane, diethyl ether and methanol were obtained from Aldrich, J. T. Baker and Merck. All commercially available chemicals were obtained from Aldrich, Acros, Alfa Aesar, Fluka and Merck. $[Rh(\mu\text{-OMe})(COD)]_2$ (Uson et al., 1995), 2,4,6-trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide and 2,3,4,5,6-pentamethylbenzyl bromide (Van der Made, 1993) were synthesized according to previously published procedure. N-(2,4,6-trimethylbenzyl)perimidine, N-(methoxyethyl)perimidine, N-butylperimidine and 1,3-dialkylperimidinium salts were prepared according to a slightly modified procedure from reference (Karaaslan, 2003). By the way 1,3-dibutylperimidinium bromide and 1,1',3,3'-tetrabutyl-2,2'-biperimidinylidene were sytnthesized before by Alıcı in 2003 (Alıcı et al., 2003) however, there is no information about 1,3-dibutylperimidin-2-ylidene rhodium complex.

Representative protocol was given for the same class of compounds bearing different substituents and data were presented in Tables.

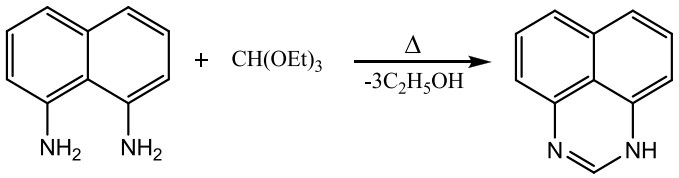
Instruments: ^1H and^{13}C NMR spectra were recorded on a Varian AS400 Mercury at Ege University. As solvent $CDCl_3$ and d_6-DMSO were employed, *J* values were in Hz.

FTIR Spectra were recorded on a Perkin Elmer Spectrum 100 series.

Melting points were recorded with Gallenkamp electrothermal melting point apparatus.

^1H, ^{13}C NMR and IR spectra of known compounds were shown in experimental part. Whereas, spectra (^1H, ^{13}C NMR and IR) of new compounds will be shown in Result and Discussion part.

2.1 Synthesis of 1*H*-Perimidine (Sachs, 1909)



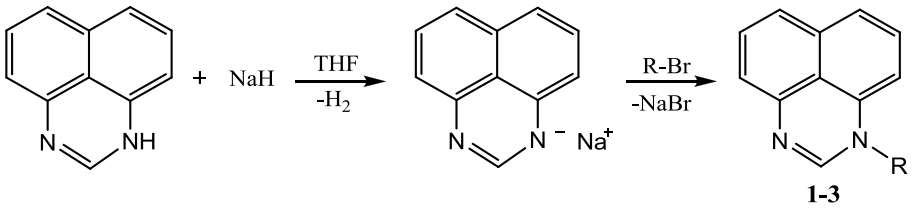
1,8-DAN (10.0 g; 63.21 mmol) was heated with $CH(OEt)_3$ (12.6 mL; 75.85 mmol) on steam bath for 2 h in order to distill EtOH formed. Then the mixture was heated to 110 ^oC on oil bath for 1 h. After that volatiles were removed under vacuo, residue was crystallized from $EtOH/H_2O$. Yield: 9.46 g; 89 %; mp: On heating the substance in a capilary tube obvious decomposition was in progress around 225 ^oC.

^1H NMR (d_6 DMSO) δ (ppm): 6.36 (d, 2H, *J* 7.6 Hz); 6.96 (d, 2H, *J* 8.0 Hz); 7.06 (t, 2H, *J* 8.4 Hz); 7.29 (s, *H*-2); 10.52 (b, -N*H*)

^{13}C NMR (d_6 DMSO) δ (ppm): 108.3; 119.2; 123.7; 129.0; 136.0; 141.7; 147.1

v (C-N) cm^{-1}: 3193-3111 (NH), 3045-2705 (Ar C-H), 1635-1377 (C=C and C=N), 1207-1026 (C-N)

2.2 Synthesis of Monosubstituted Perimidines (1-3) (Alıcı, 2003; 2005)



1-3

This reaction was carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods.

Perimidine (5.0 g; 29.73 mmol) was dissolved in dry THF (approximately 60 mL). NaH (0.86 g; 35.67 mmol), washed with dried hexane and dried under vacuo beforehand, was added in dribs and drabs to the above solution, while vigorous H_2 evolution was observed and the resulting mixture was refluxed for 24 h.

After evoluation of H_2 gas, 2,4,6-trimethylbenzyl bromide (7.6 g; 35.67 mmol) was added and the mixture was refluxed for 24 h. Then volatiles were removed under vacuo. The oily residue was treated with ethyl acetate and filtered off. Then volatiles were removed with distillation and the residue was dissolved in CH_2Cl_2. Purification by column chromatography on silica gel using CH_2Cl_2-MeOH as the eluent (v/v = 49:1 mL) gave a yellow solid.

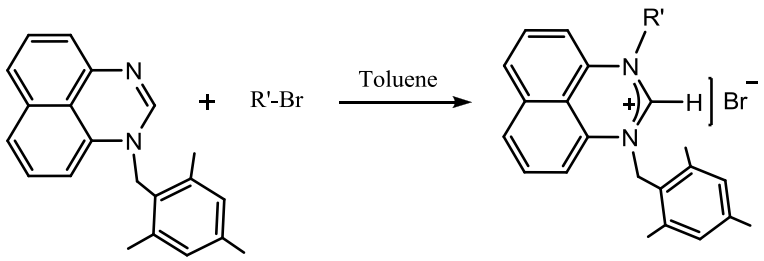
The rest of 1-alkylperimidines were synthesized with the same method as mentioned above. Melting points, yields, C=N vibrations are given in Table 2.1, ^1H and ^{13}C NMR data of the compouns **1-3** in Tables 3.1 and 3.2 repectively.

Table 2.1 Melting points, yields and C=N vibrations of the compounds **1-3**

Compound No	R	Yield (%)	m.p. (^oC)	υ (C=N) cm^{-1}
1	$-CH_2C_6H_2(CH_3)_3$	67	158-160	1627.9
2*	$-CH_2CH_2OCH_3$	91	99-101	1624.6
3	$-CH_2CH_2CH_2CH_3$	80	61-63	1627.2

* Reported to be as liquid (Karaaslan, 2003).

2.3 Synthesis of 1,3-Disubstituted perimidinium Bromides (1a-c)



1 **1a-c**

1-(2,4,6-Trimethylbenzyl)-1*H*-perimidine (1.0 g; 3.33 mmol) was dissolved in toluene (10 mL) and 2,4,6-trimethylbenzyl bromide (0.85 g; 4.00 mmol) was added. The mixture was stirred for 2 h at 25 ^oC and then refluxed for 12 h. Following the completion of the process the solid formed was filtered off and precipitate was recrystallized from CH_2Cl_2/Et_2O (v/v = 2:10 mL) as yellow solid.

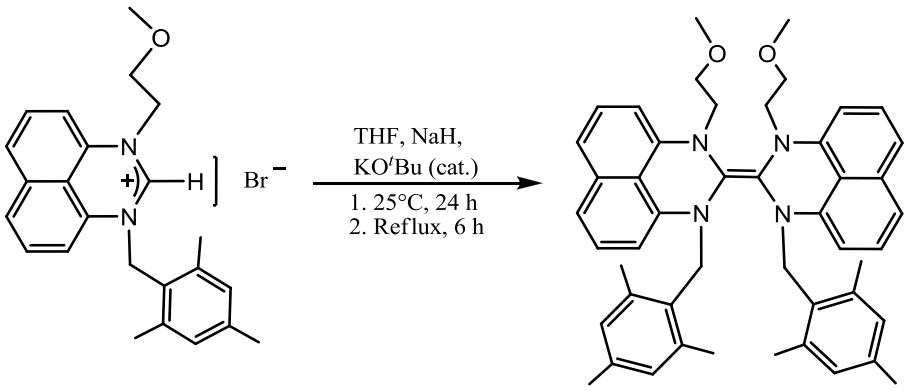
The bromides **2a-d** were synthesized from N-(methoxyethyl)perimidine with alkyl bromides, **3a-d** synthesized from N-butylperimidine with alkyl bromides using the same procedure.

Their selected physical properties (melting points, yields, C=N vibrations data) are given in Table 2.2 and their ^{1}H, ^{13}C NMR data in Tables 3.3 and 3.4 respectively.

Table 2.2 Melting points, yields and C=N vibrations of the compounds **1a-3d**

LHX	R	R'	Yield(%)	m.p.°C	υ(C=N) cm^{-1}
1a	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$	86	217-218	1663.7
1b		$-CH_2C_6H(CH_3)_4$	64	232	1664.5
1c		$-CH_2C_6(CH_3)_5$	56	241	1663.6
2a	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$	76	208-210	1658.7
2b		$-CH_2C_6H(CH_3)_4$	77	227-229	1656.4
2c		$-CH_2C_6(CH_3)_5$	68	221-223	1657.8
2d		$-CH_2CH_2CH_2CH_3$	53	229	1660.7
3a	$-CH_2CH_2CH_2CH_3$	$-CH_2C_6H_2(CH_3)_3$	87	176-178	1656.4
3b		$-CH_2C_6H(CH_3)_4$	73	219	1655.2
3c		$-CH_2C_6(CH_3)_5$	88	208-209	1656.6
3d		$-CH_2CH_2CH_2CH_3$	76	213-215	1659.2

2.4 Synthesis of 1,1'-Di(methoxyethyl)-3,3'-di(2,4,6-trimethyl-benzyl)-2,2'-biperimidinylidene (2a', 3d')



2a **2a'**

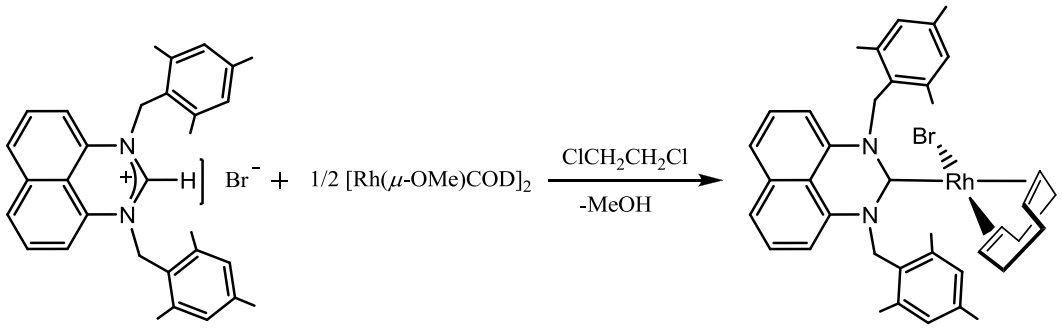
A suspension of **2a** (1.0 g; 2.28 mmol), NaH (0.11 g; 4.55 mmol) and KO^{t}Bu (catalytic amount) in dry THF (20 mL) was stirred at 25 °C for 24 h. H_2 evolution and colour change from yellow to cream was observed and then the mixture was refluxed for 6 h. The resultant mixture was cooled to room temperature and undissolved part was filtered off with cannula under argon atmosphere. The volatiles were removed in vacuo. The residue was crystallized from CH_2Cl_2/*n*-hexane (v/v = 2:10 mL).

Compound **3d'** was synthesized using the same procedure and their physical properties (yields, melting points, C=N vibrations data) are given in Table 2.3 and their ^{1}H, ^{13}C NMR data in Tables 3.5 and 3.6, respectively.

Table 2.3 Melting points and yields of the compounds **2a'** and **3d'**

Compound	R	R'	Yield (%)	m.p. (°C)	υ(C=N) cm^{-1}
2a'	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$	49	121	1650.7
3d'	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$	42	201	1655.1

2.5 Rhodium Complexes with N,N'-Disubstituted Perimidine-2-ylidene Ligands (4-7)



1a LHX **4**

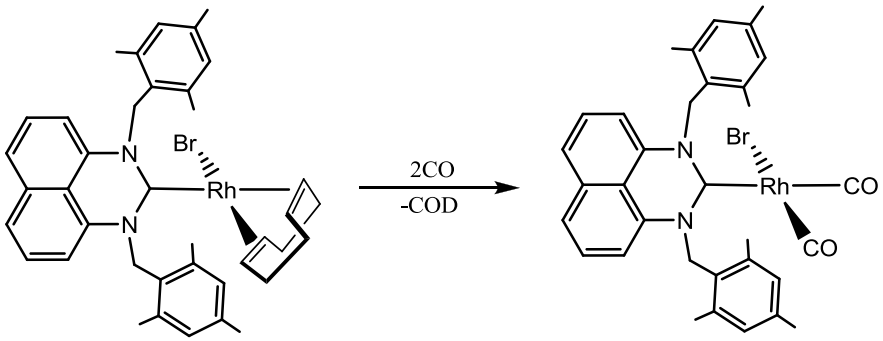
[Rh(μ-OMe)COD]$_2$ (121 mg; 0.25 mmol) was added to 1,3-bis(2,4,6-trimethylbenzyl)perimidinium bromide salt (256.75 mg; 0.5 mmol) which was dissolved in 1,2-dicholoroethane (10 mL) under argon atmosphere. The reaction mixture was stirred 1 h at 25^{o}C and then refluxed for 48 h. Meanwhile the reaction progress was controled with thin layer chromatography. After removal of the solvent under vacuo, the rhodium compound was purified by column chromatography on silica gel using CH_2Cl_2/CH_3COCH_3 as the eluent (v/v = 49:1) to give a yellow solid. The residue was recrystallized from $CH_2Cl_2/(C_2H_5)_2O$ (v/v = 4:10 mL).

Other rhodium complexes (**5**, **6**, **7)** were synthesized from the corresponding perimidinium salts (**2a**, **2d**, **3d**) using the same procedure. Their melting points and yields were listed below in Table 2.4. Their ^{1}H and ^{13}C NMR data are given in Tables 3.7 and 3.8, respectively.

Table 2.4 Melting points and yields of the compounds **4-7**

Complex	LHX	R	R'	Yield (%)	m.p. (°C)
4	**1a**	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$	46	219
5	**2a**	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$	56	206
6	**2d**	$-CH_2CH_2OCH_3$	$-CH_2CH_2CH_2CH_3$	87	225
7	**3d**	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$	84	231

2.6 *Cis*-Bromodicarbonylbis(1,3-bis(2,4,6-trimethylbenzyl) perimidin-2-ylidenerhodium(I) (8)



4 **8**

Compound **4** (72 mg ; 0.1 mmol) was dissolved in 10 mL of CH_2Cl_2 and carbon monoxide was bubbled 4 h through the solution. The volatile was removed in vacuo and the residue washed three times with 5 mL of *n*-pentane. The residue was crystallized from CH_2Cl_2/Et_2O (v/v = 4:10 mL) as yellow solid. Yield : 83 (%) ; m.p.: 247 °C (decompose); ν_{CO} (cm^{-1}) : 2006, 2086.

Its ^1H and ^{13}C NMR data are given in result and discussion part.

2.7 Catalytic Experiments

2.7.1 General procedure for the TH reaction

A mixture of acetophenone (10 mmol), the catalyst (0.1 mmol) and propan-2-ol (19 mL) were stirred at 82 ºC for 10 minutes. 1 mL of 0.1 M KOH (1 mmol) solution in propan-2-ol was added. The solution was stirred at the refluxing temperature. At the desired reaction times, aliquots were withdrawn from reaction vessel. The reaction progress was monitored by ^1H NMR. The yields were recorded for an average of two runs.

2.7.2 General procedure for rhodium-carbene catalyzed addition of phenylboronic acid to aldehydes

Phenylboronic acid (1.20 g, 9.8 mmol), KO^{t}Bu (4.9 mmol), the aromatic aldehyde (4.9 mmol), rhodium–carbene catalyst (1 mol %) and DMF (15 mL) were introduced into a schlenk tube and then water (5 mL) was added. The resulting mixture was heated at 80 ºC for 4 h under an argon atmosphere, cooled to ambient temperature and extracted with CH_2Cl_2 (20 mL). After drying over $MgSO_4$ the organic phase was evaporated. The conversion was monitored by ^{1}H NMR.

3. RESULTS AND DISCUSSION

In this part of the thesis, the characterization of 1,3-disubstituted perimidinium salts and some of their rhodium complexes were described. Their chemical and physical properties were examined. The most frequently used method to synthesis of NHCs and their metal complexes involve the preparation of the corresponding salts. The required perimidinium salts (**1a-3d**) were synthesized in three steps from 1,8-diaminonaphthalene as shown in Scheme 3.1.

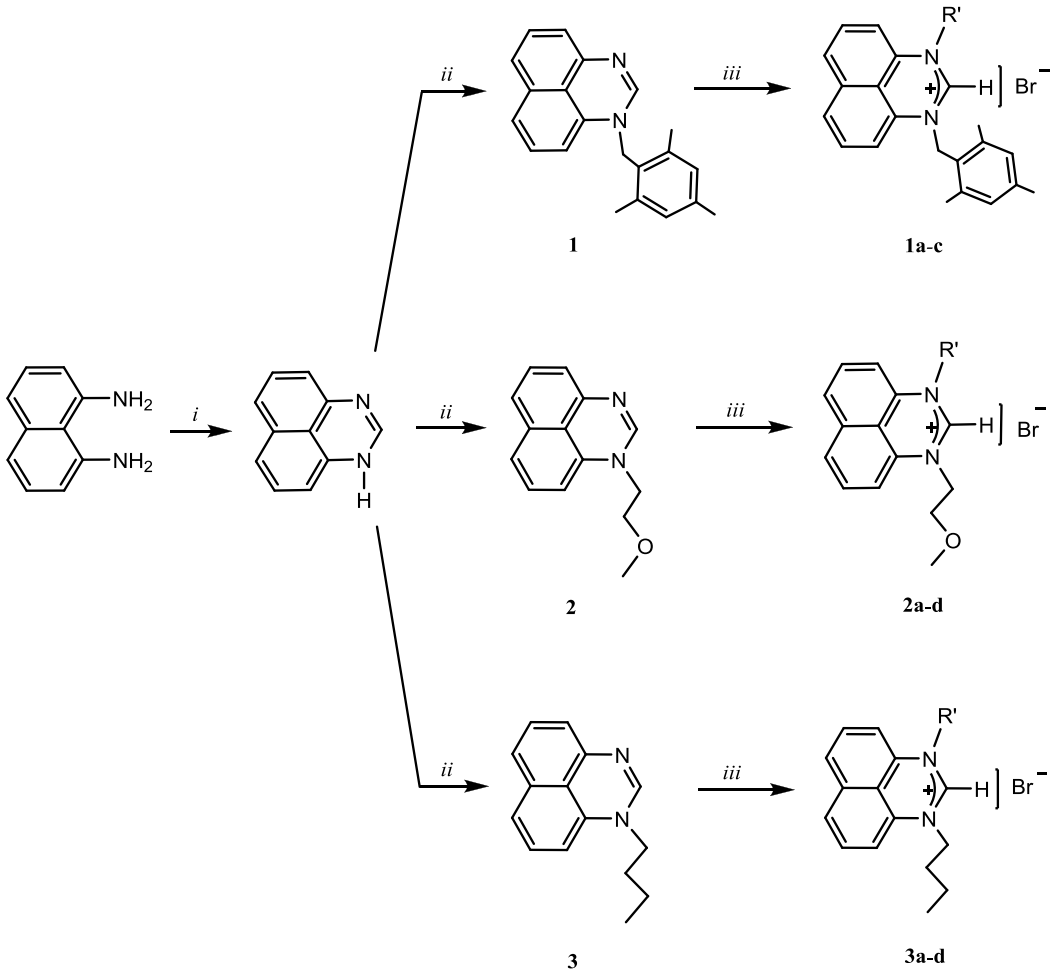
3.1 Synthesis and Characterization of Perimidinium Salts Bearing Alkyl Substituents on the Nitrogen Atoms (1a-3d)

The synthesis of the desired salts involve three steps. The first step involves perimidine synthesis from ring closing of 1,8-diaminonaphthalene (Step(*i*)). Monosubstituted perimidine derivatives (**1**, **2**, **3**) were prepared with strong base (NaH) from perimidine via alkyl halides (Step (*ii*)). These products are air stable and yellow-light brown solids. It is worth mentioning that N-(methoxyethyl)perimidine (**2**) is a solid, but not liquid as reported previously (Karaaslan, 2003). The compound **1-3** were synthesized by the method used by Alıcı, their structure are coherent with the reference (Alıcı et al., 2003, Karaaslan, 2003).

Perimidinium salts were obtained by treating monosubstituted products with different alkyl bromides (Step (*iii*)).

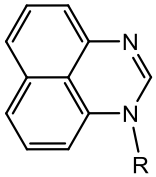
These perimidinium salts are air and moisture stable and yellow solids. The IR data for these salts (**1a-3d**) clearly indicate the presence of the –C=N– group with a υ (C=N) vibrations between 1656-1664 cm^{-1}.

Synthesized perimidinium salts have been characterized by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of these salts were consistent with the proposed structures; C_2-*H* resonance at δ = 6.69-10.82 ppm as sharp singlets. The formation of the salts were also supported by a resonance at δ = 145-153 ppm in the ^{13}C NMR spectrum for the C_2-H carbon atom.



LHX	R	R’
1a **1b** **1c**	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$ $-CH_2C_6H(CH_3)_4$ $-CH_2C_6(CH_3)_5$
2a **2b** **2c** **2d**	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$ $-CH_2C_6H(CH_3)_4$ $-CH_2C_6(CH_3)_5$ $-CH_2CH_2CH_2CH_3$
3a **3b** **3c** **3d**	$-CH_2CH_2CH_2CH_3$	$-CH_2C_6H_2(CH_3)_3$ $-CH_2C_6H(CH_3)_4$ $-CH_2C_6(CH_3)_5$ $-CH_2CH_2CH_2CH_3$

Scheme 3.1 Reagents and conditions of reactions: (*i*) $CH(OEt)_3$, Δ; (*ii*) NaH, R-X, THF, reflux; (*iii*) R’-Br, toluene, reflux.



1,2,3

Compound No	R
1	$-CH_2C_6H_2(CH_3)_3$
2	$-CH_2CH_2OCH_3$
3	$-CH_2CH_2CH_2CH_3$

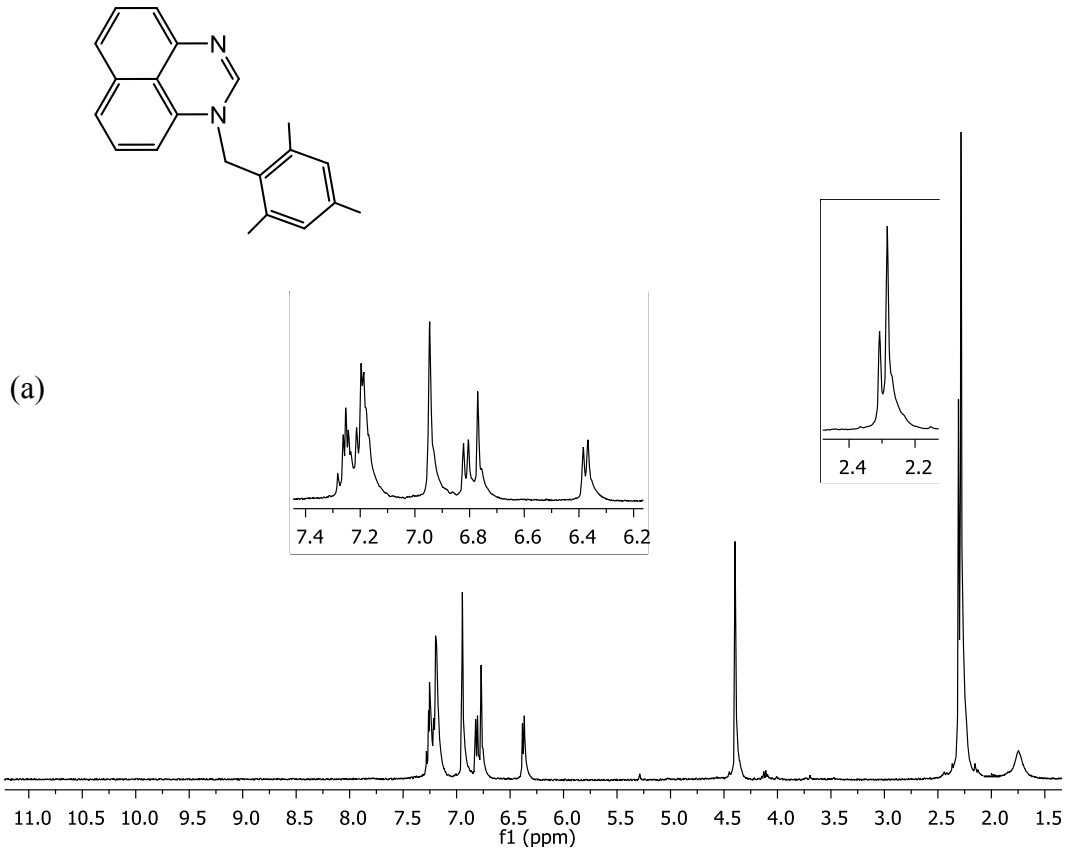
Table 3.1 ^{1}H NMR data for **1-3**

Compound No	H^2(s)	Aromatics	Others
1	6.77	6.37 (d, *J* 6.8 Hz, 1H); 6.81 (d, *J* 6.8Hz, 1H,); 7.16-7.28 (m, 4H)	2.28; 2.31 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.39 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.94 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6)
2*	7.10	6.10-6.15 (m, 1H); 6.83 (d, *J* 7.6 Hz, 1H); 7.11-7.26 (m, 4H)	3.36 (s, 3H, $CH_2CH_2OCH_3$); 3.61 (t, *J* 5.2 Hz, 2H, $CH_2CH_2OCH_3$); 3.70 (t, *J* 5.2 Hz, 2H, $CH_2CH_2OCH_3$)
3*	7.19	6.13; 6.14 (dd, *J* 6.4 Hz, 1.6 Hz, 1H); 6.81 (d, *J* 7.2 Hz, 1H); 7.07-7.26 (m, 4H)	0.98 (t, *J* 7.6 Hz, 3H, $CH_2CH_2CH_2CH_3$); 1.39-1.46 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.66-1.74 (m, 2H, $CH_2CH_2CH_2CH_3$); 3.48-3.52 (m, 2H, $CH_2CH_2CH_2CH_3$)

Table 3.2 ^{13}C NMR data for **1-3**

Compound No	2-*C*H	Aromatics	Alkyl
1	145.3	100.3; 115.4; 120.0; 120.5; 123.2;126.0; 127.7; 129.1; 129.9; 135.7; 138.4; 139.1; 139.3; 143.6	19.9; 21.3 (2,4,6-$CH_2C_6H_2(CH_3)_3$) 46.6 (2,4,6-$CH_2C_6H_2(CH_3)_3$)
2*	149.3	100.6; 115.2; 119.6; 120.6; 123.3; 127.6; 129.0; 135.9; 137.6; 143.4	48.6 ($CH_2CH_2OCH_3$); 59.2 ($CH_2CH_2OCH_3$) 67.8 ($CH_2CH_2OCH_3$)
3*	148.7	100.8; 115.2; 119.5; 120.6; 123.5; 127.6; 129.0; 135.9; 137.8; 143.8	13.9 ($CH_2CH_2CH_2CH_3$); 20.0 ($CH_2CH_2CH_2CH_3$), 28.4 ($CH_2CH_2CH_2CH_3$); 49.0 ($CH_2CH_2CH_2CH_3$)

* **2** was synthesized by Karaaslan in 2003 and **3** was synthesized by Alıcı, 2003, 2005 (Alıcı et al, 2003, 2005)



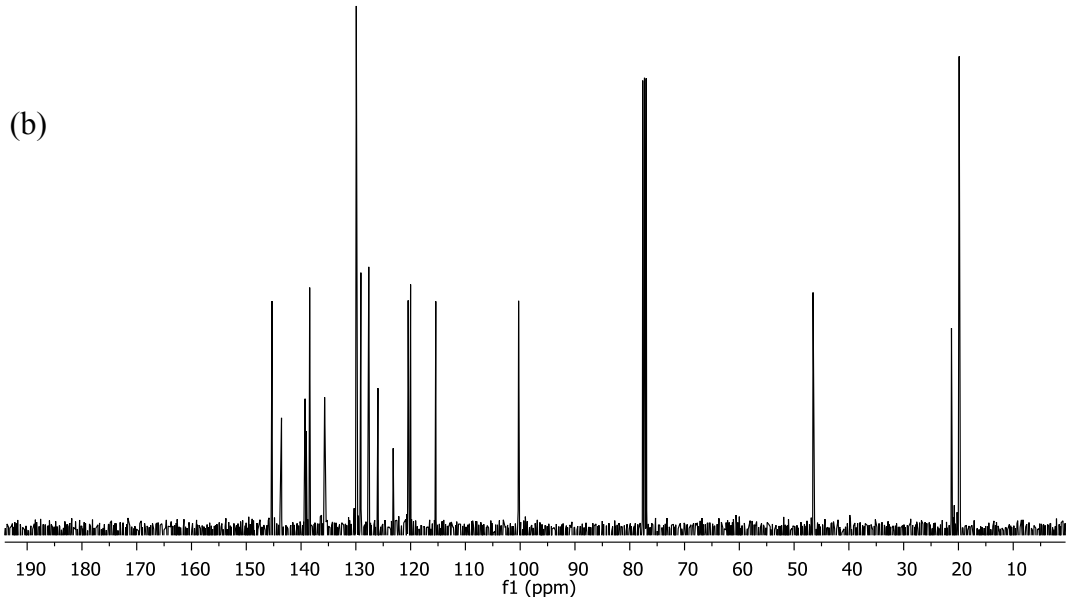
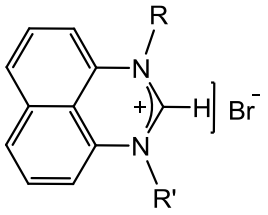


Figure 3.1 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **1**



LHX

LHX	R	R'
1a	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$
1b		$-CH_2C_6H(CH_3)_4$
1c		$-CH_2C_6(CH_3)_5$
2a	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
2b		$-CH_2C_6H(CH_3)_4$
2c		$-CH_2C_6(CH_3)_5$
2d		$-CH_2CH_2CH_2CH_3$
3a	$-CH_2CH_2CH_2CH_3$	$-CH_2C_6H_2(CH_3)_3$
3b		$-CH_2C_6H(CH_3)_4$
3c		$-CH_2C_6(CH_3)_5$
3d		$-CH_2CH_2CH_2CH_3$

Table 3.3 ^{1}H NMR data for **1a-3d**

Compound No	H^2(s)	Aromatics	Others
1a	6.69	7.39 (d, *J* 7.2 Hz, 2H); 7.53-7.6 (m, 4H)	2.11; 2.32 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.92 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.73 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6)
1b	6.72	6.56 (d, *J* 6.0 Hz, 1H); 6.69 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.92 (d, *J* 6.0 Hz, 1H); 7.42-7.59 (m, 7H)	1.96; 2.02 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.15; 2.28 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 4.91 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 4.96 (s, 2H,$CH_2C_6H_2(CH_3)_3$-2,4,6)
1c	6.66	6.75 (s, 2H; $CH_2C_6H_2(CH_3)_3$-2,4,6); 7.39 (d, *J* 6.8 Hz, 1H); 7.45-7.56 (m, 1H); 7.56-7.62 (m, 4H)	1.99, 2.02, 2.04 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 2.26, 2.27 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.93 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6)
2a	8.57	6.93 (d, *J* 7.6 Hz, 1H); 7.07 (d, *J* 7.6 Hz, 1H); 7.37-7.50 (m, 4H); 6.97 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6)	2.31; 2.44 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 3.23 (s, 3H, $CH_2CH_2OCH_3$); 3.73 (t, *J* 5.2 Hz, 2H, $CH_2CH_2OCH_3$); 4.44 (t, *J* 4.4 Hz, 2H, $CH_2CH_2OCH_3$); 5.13 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6)

Table 3.3 ^{1}H NMR data for **1a-3d** (Continue)

Compound No	C_2-*H* (s)	Aromatics	Others
2b	8.05	7.00 (d, *J* 7.6 Hz, 1H); 7.04 (d, *J* 7.6 Hz, 1H); 7.45-7.56 (m, 4H); 7.13 (s, 1H, $CH_2C_6H(CH_3)_4$-2,3,5,6)	2.31; 2.32 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 3.19 (s, 3H, $CH_2CH_2OCH_3$); 3.71 (t, *J* 2.2 Hz, 2H, $CH_2CH_2OCH_3$); 4.46 (t, *J* 2.2 Hz, 2H, $CH_2CH_2OCH_3$); 5.05 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6)
2c	7.72	7.08 (d, *J* 7.6 Hz, 1H); 7.16 (d, *J* 7.2 Hz, 1H); 7.44-7.56 (m, 4H)	2.28; 2.31; 2.32 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 3.15 (s, 3H, $CH_2CH_2OCH_3$); 3.70 (t, *J* 4.8 Hz, 2H, $CH_2CH_2OCH_3$); 4.41 (t, *J* 4.8 Hz, 2H, $CH_2CH_2OCH_3$); 5.00 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6)
2d	10.18	6.81 (d, *J* 7.2 Hz, 1H); 6.94 (d, *J* 7.2 Hz, 1H); 7.38-7.48 (m, 4H)	1.02 (t, *J* 7.2 Hz, 3H, CH_2CH_2 CH_2CH_3); 1.54-1.59 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.88-1.92 (m, 2H, $CH_2CH_2CH_2CH_3$); 3.42 (s, 3H, $CH_2CH_2OCH_3$); 3.83 (t, *J* 5.2 Hz, 2H, $CH_2CH_2OCH_3$); 4.28 (t, *J* 7.2 Hz, 2H, $CH_2CH_2CH_2CH_3$); 4.55 (t, *J* 4.8 Hz, 2H, $CH_2CH_2OCH_3$)
3a	10.07	6.70 (d, *J* 7.6 Hz, 1H); 6.85 (d, *J* 7.2 Hz, 1H); 6.90 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 7.29 (t, *J* 8 Hz, 1H); 7.40-7.50 (m, 3H)	0.97 (t, *J* 7.6 Hz, 3H, $CH_2CH_2CH_2CH_3$); 1.44-1.50 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.82-1.87 (m, 2H, $CH_2CH_2CH_2CH_3$); 2.27; 2.48 (s, 9H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 4.32 (t, *J* 6.8 Hz, 2H, $CH_2CH_2CH_2CH_3$); 5.3 (s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6);
3b	9.07	6.84 (d, *J* 8.4 Hz, 1H); 6.86 (d, *J* 8.4 Hz, 1H); 7.07 (s, 1H); 7.34-7.50 (m, 4H)	0.91 (t, *J* 7.2 Hz, 3H, $CH_2CH_2CH_2CH_3$); 1.20-1.37 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.77 (m, 2H, $CH_2CH_2CH_2CH_3$); 2.27, 2.36 (s, 12H, $CH_2C_6H(CH_3)_4$-2,3,5,6); 4.27 (t, *J* 6.8 Hz, 2H, $CH_2CH_2CH_2CH_3$); 5.27 (s, 2H, $CH_2C_6H(CH_3)_4$-2,3,5,6)
3c	8.68	6.88 (d, *J* 8 Hz, 1H); 6.96 (d, *J* 7.2 Hz, 1H); 7.38-7.51 (m, 4H)	0.88 (t, *J* 7.2 Hz, 3H, $CH_2CH_2CH_2CH_3$); 1.27-1.33 (m, 2H, $CH_2CH_2CH_2CH_3$); 1.73-1.77 (m, 2H, $CH_2CH_2CH_2CH_3$); 2.26; 2.28; 2.38 (s, 15H, $CH_2C_6(CH_3)_5$-2,3,4,5,6); 4.24 (t, *J* 6.8 Hz, 2H, $CH_2CH_2CH_2CH_3$); 5.21 (s, 2H, $CH_2C_6(CH_3)_5$-2,3,4,5,6)
3d	10.82	6.81 (d, *J* 7.2 Hz, 2H); 7.42-7.52 (m, 4H)	1.02 (t, *J* 7.6 Hz, 6H, $CH_2CH_2CH_2CH_3$); 1.53-1.63 (m, 4H, $CH_2CH_2CH_2CH_3$); 1.87-1.94 (m, 4H, $CH_2CH_2CH_2CH_3$); 4.32 (t, *J* 7.6 Hz, 4H, $CH_2CH_2CH_2CH_3$)

Table 3.4 ^{13}C NMR data for **1a-3d**

Compound No	2-*C*H	Aromatics	Others
1a	145.7	109.2; 121.2; 122.7; 125.2; 129.0; 129.9; 132.4; 134.9;138.4; 140.4	19.7; 21.4 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 49.9 ($CH_2C_6H_2(CH_3)_3$-2,4,6)
1b	146.0	108.9; 109.1; 121.2; 122.3; 125.4; 129.1; 129.5; 132.3; 133.6; 133.7; 133.9; 134.1; 135.0; 137.5; 138.6	16.7; 16.9 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 17.6;19.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 50.6 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 51.2 ($CH_2C_6H(CH_3)_4$-2,3,5,6)
1c	145.3	109.2; 109.4; 121.0; 122.2; 125.1; 125.3; 129.0; 129.7; 129.9; 132.3; 133.8; 134.1; 134.8; 135.1; 135.2; 138.3; 140.5	15.6; 15.7 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 19.6; 20.5; 21.4 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 50.0 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 50.6 ($CH_2C_6(CH_3)_5$-2,3,4,5,6)
2a	151.2	108.2; 108.6; 121.6; 123.3; 124.6; 124.9; 128.5; 128.7; 130.6; 131.4; 132.6; 135.2; 138.6; 140.3	20.6; 21.3 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 50.8 ($CH_2CH_2OCH_3$); 52.0 ($CH_2CH_2OCH_3$); 58.9 ($CH_2CH_2OCH_3$); 66.5 ($CH_2C_6H_2(CH_3)_3$-2,4,6)
2b	151.7	108.3; 110.7; 117.3; 121.2; 123.5;128.6; 129.2; 131.4; 133.9; 134.2; 135.2; 136.0; 141.0; 142.4	16.8; 21.1 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 50.9 ($CH_2CH_2OCH_3$); 52.4 ($CH_2CH_2OCH_3$); 59.1 ($CH_2CH_2OCH_3$); 67.5 ($CH_2C_6H(CH_3)_4$-2,3,5,6)

Table 3.4 ^{13}C NMR data for **1a-3d** (Continue)

Compound No	2-*C*H	Aromatics	Others
2c	151.5	108.5; 110.7; 117.2; 121.3; 123.6; 128.7; 129.2; 132.7; 133.8; 133.9; 134.5; 136.8; 140.9; 142.6	16.8; 17.2; 18.0 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 51.0 ($CH_2CH_2OCH_3$); 53.2 ($CH_2CH_2OCH_3$); 60.0 ($CH_2CH_2OCH_3$); 67.0 ($CH_2C_6(CH_3)_5$-2,3,4,5,6)
2d	153.2	107.8; 108.1; 121.8; 124.5; 124.6; 128.4; 128.5; 131.6; 131.6; 135.4	13.8 ($CH_2CH_2CH_2CH_3$); 19.5 ($CH_2CH_2CH_2CH_3$); 28.3 ($CH_2CH_2CH_2CH_3$); 50.8 ($CH_2CH_2OCH_3$); 51.6 ($CH_2CH_2OCH_3$); 59.3 ($CH_2CH_2OCH_3$); 66.9 ($CH_2CH_2CH_2CH_3$)
3a	151.9	108.2; 108.5; 121.7; 124.2; 124.7; 124.8; 128.4; 128.5; 130.8; 131.3; 132.2; 135.2; 137.74; 139.6	13.7 ($CH_2CH_2CH_2CH_3$); 19.5 ($CH_2CH_2CH_2CH_3$); 21.0; 21.1 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 28.4 ($CH_2CH_2CH_2CH_3$); 51.7 ($CH_2CH_2CH_2CH_3$); 52.2 ($CH_2C_6H_2(CH_3)_3$-2,4,6)
3b*	149.7	108.9; 109.0; 122.0; 124.5; 124.8; 127.0;129.0; 129.1; 132.3; 133.6; 133.9; 134.8; 135.0; 135.6	13.9 ($CH_2CH_2CH_2CH_3$); 19.1 ($CH_2CH_2CH_2CH_3$); 16.2; 20.8 ($CH_2C_6H(CH_3)_4$-2,3,5,6); 28.0 ($CH_2CH_2CH_2CH_3$); 50.7 ($CH_2CH_2CH_2CH_3$); 51.6 ($CH_2C_6H(CH_3)_4$-2,3,5,6)
3c*	149.6	108.9; 109.0; 122.0; 124.2; 124.4; 124.8;129.0; 129.1; 132.4; 133.6; 133.8; 135.0; 135.2; 137.4	14.0 ($CH_2CH_2CH_2CH_3$); 19.1 ($CH_2CH_2CH_2CH_3$); 17.3; 17.4; 17.8 ($CH_2C_6(CH_3)_5$-2,3,4,5,6); 28.1 ($CH_2CH_2CH_2CH_3$); 51.2 ($CH_2CH_2CH_2CH_3$); 51.5 ($CH_2C_6(CH_3)_5$-2,3,4,5,6)
3d	152.1	107.9; 121.7; 124.6; 128.5; 131.3; 135.3	13.8 ($CH_2CH_2CH_2CH_3$); 19.6 ($CH_2CH_2CH_2CH_3$); 28.4 ($CH_2CH_2CH_2CH_3$); 51.3 ($CH_2CH_2CH_2CH_3$)

*^{13}C NMR spectrums were analysed in DMSO

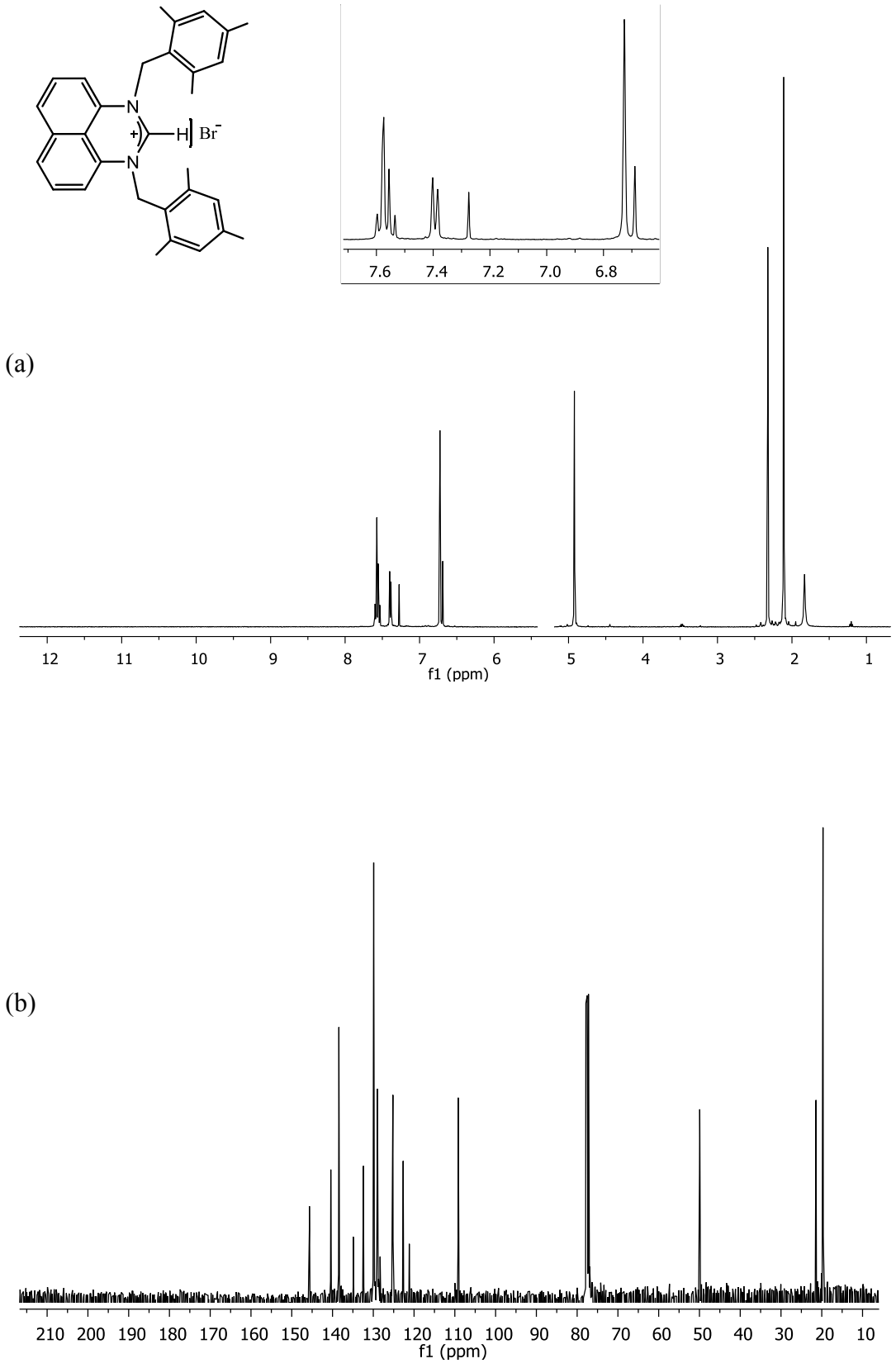


Figure 3.2 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **1a**

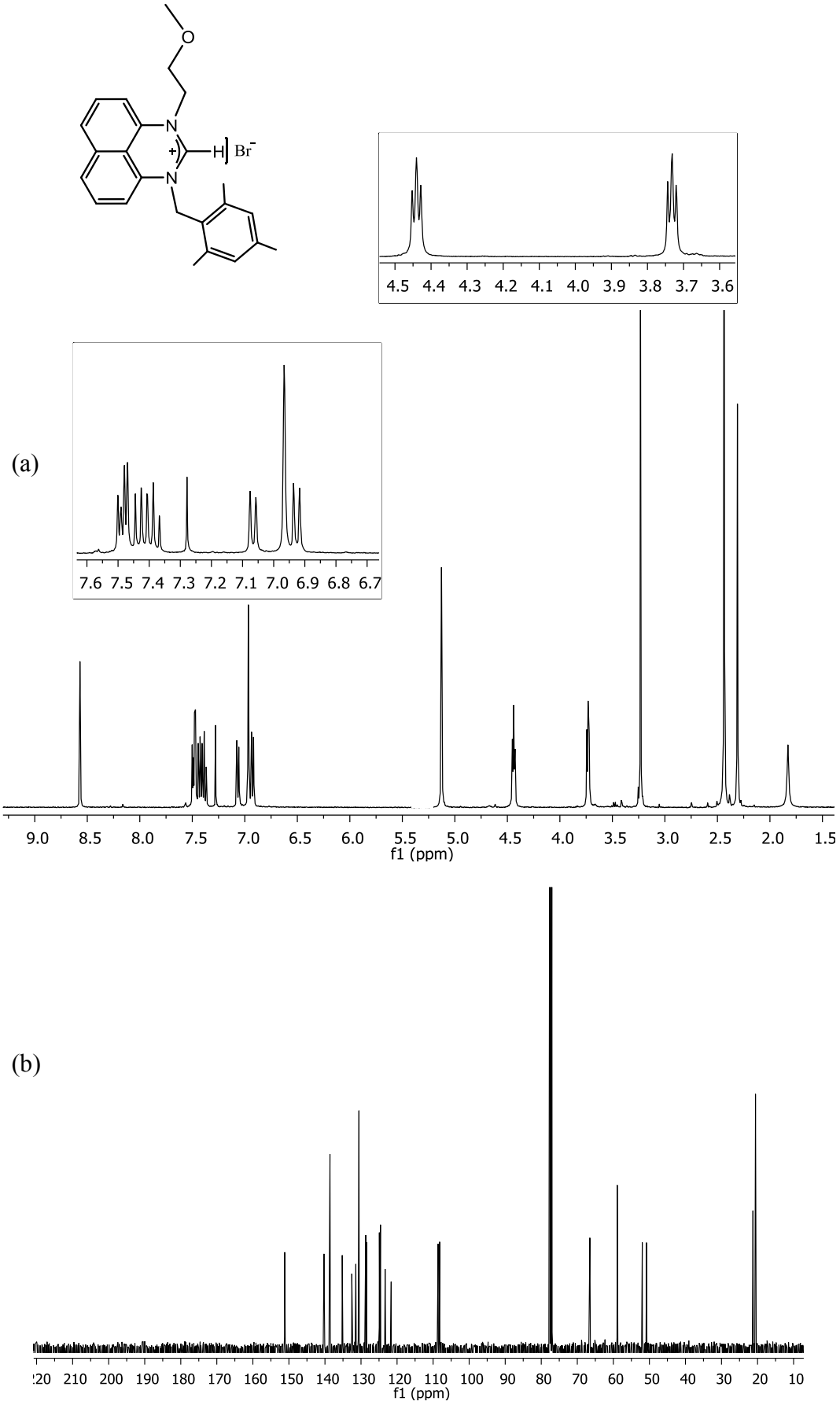


Figure 3.3 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **2a**

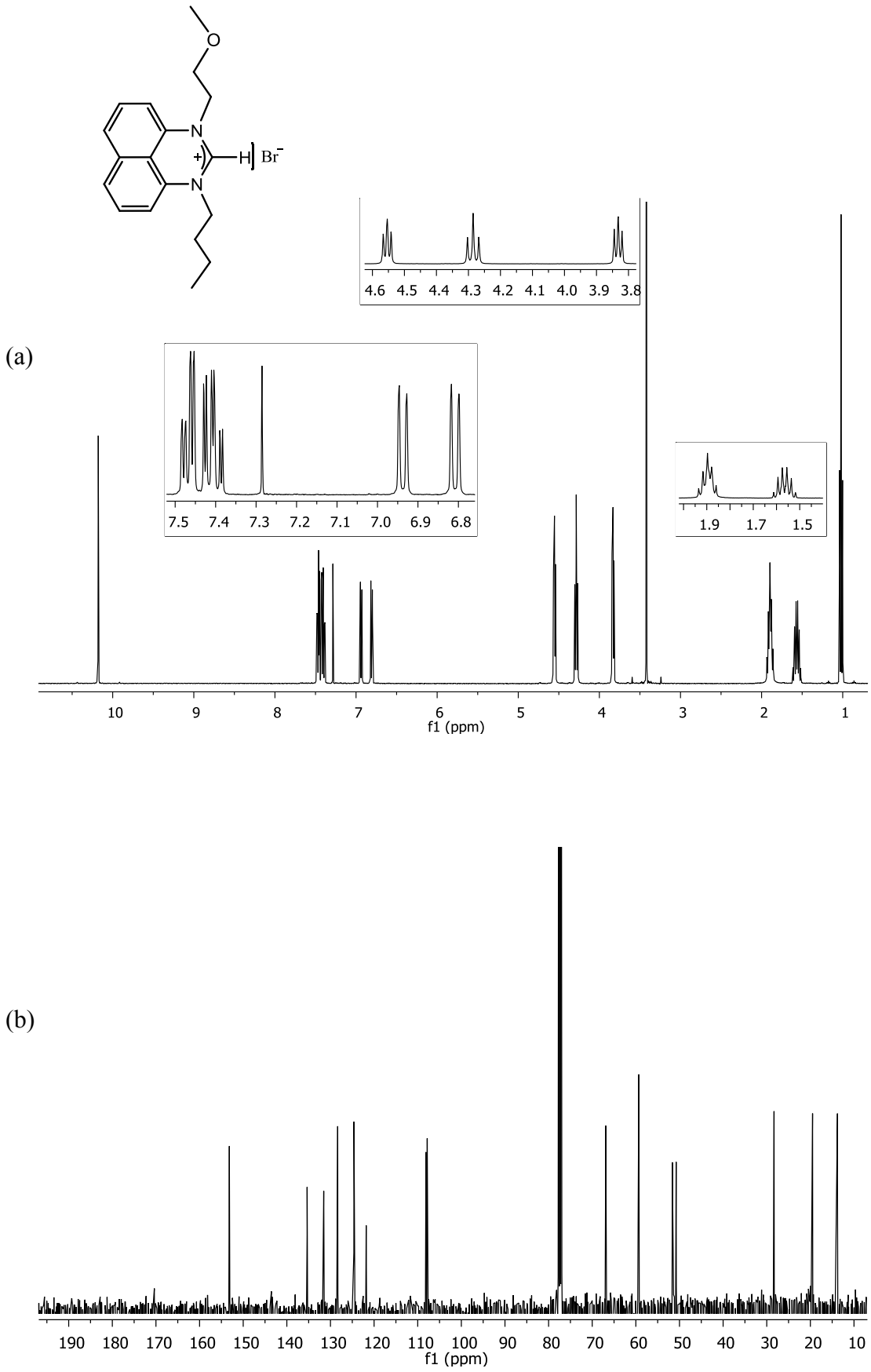


Figure 3.4 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **2d**

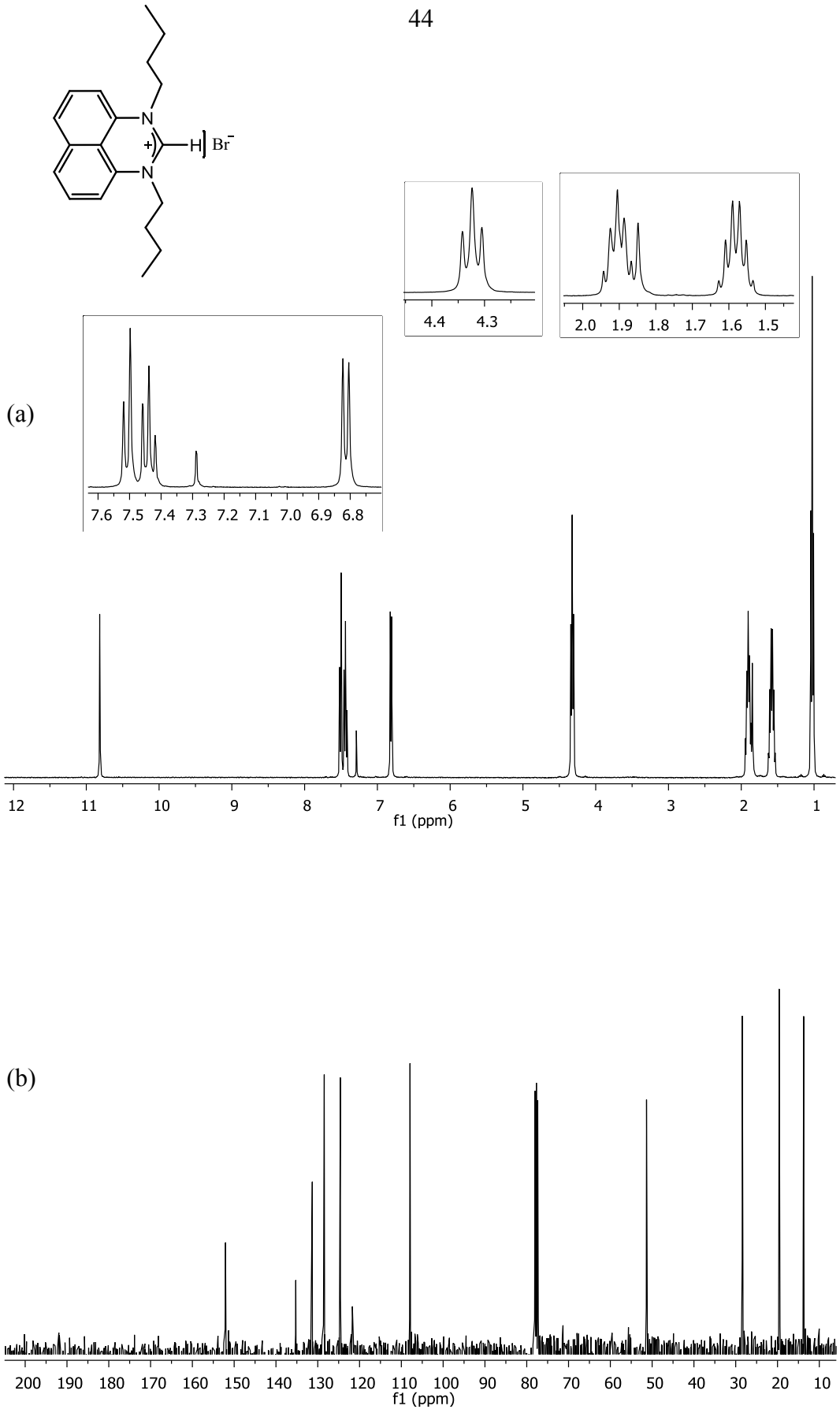


Figure 3.5 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **3d**

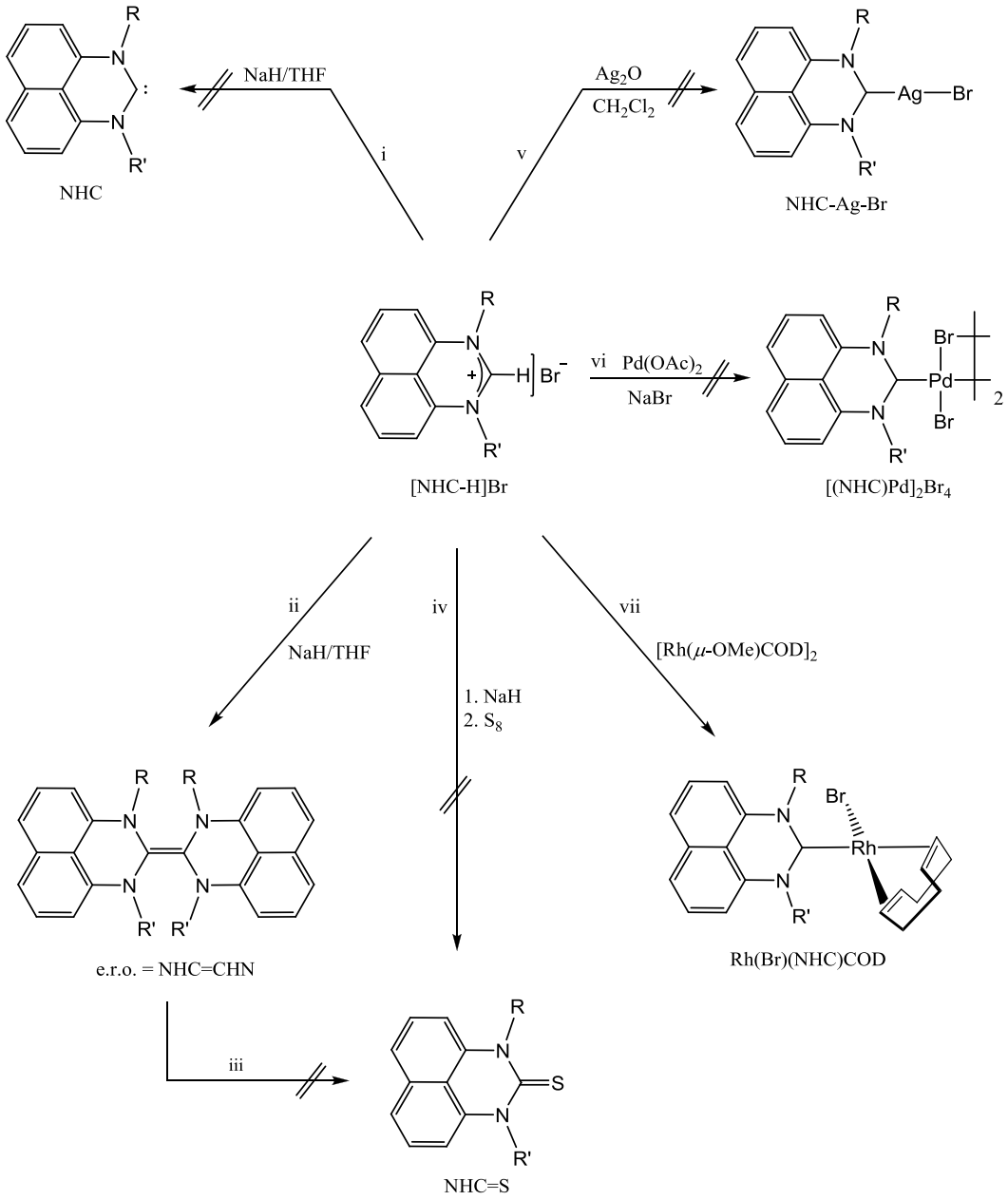
3.2 Attempted Deprotonation Reactions of Perimidinium Salts with Various Bases

The most NHCs studied so far have been obtained by deprotonation of azol(in)ium salts (Herrmann et al., 1998, 1999; Türkmen et al., 2008; Diez-Gonzalez and Nolan, 2008; Lin and Vasam, 2007; Yiğit et al., 2005). The reaction can be performed in ammonia or in non-protic solvents such as THF or ethers. The deprotonation requires anhydrous conditions and the use of strong bases such as NaH, KH with a catalytic amount of *tert*-butoxide, KO^{t}Bu itself, potassium hexamethyldisilazane (KHMDS) etc..

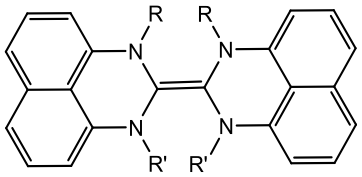
Electron-rich olefins (tetraaminoalkenes) derived from deprotonation of certain [NHC-H]X salts are convenient precursors to a variety of transition-metal complexes. There are plenty of communications concerning electron-rich olefins and their metal complexes (Winberg et al., 1965; Lappert et al., 1984; Çetinkaya et al., 1992; Çetinkaya et al., 1994; Yun et al., 2004; Alder et al., 2004; Özdemir et al., 2005). Therefore, tetraaminoalkenes (e.r.o.) have attracted considerable attention, due to their ease of oxidation and chemiluminescent reactions. The ultimate oxidation product of tetraaminoalkenes with air is urea and also sulfur reacts similarly to form the corresponding thioanalog (Karaaslan, 2003). Alıcı et al. worked with 1,3-dibutylperimininium bromide and 1,3-bis(2-methoxyethyl)-perimidinium chloride salts and synthesized the tetraaminoalkene derivatives. While 1,1',33'-tetra(2-methoxyethyl)-2,2'-biperimidinylidene was air sensitive and faded as the perimidine-2-one via chemiluminescence; 1,1',33'-tetrabutyl-2,2'-biperimidine-2-ylidene was resistant to oxidation by dioxygen (Alıcı et al., 2003). In other words, deprotonation of perimidinium salts can give free carbene (perimidin-2-ylidene) or its dimer (e.r.o.) unless there is an electrophile such as O_2, S_8 in situ.

Our initial attempts to generate the free carbene (i) and thioderivative (iv) under standard conditions with NaH, KO^{t}Bu failed, but instead tetraaminoalkene derivatives (ii) was observed as can be seen from Scheme 3.2.

When we treated tetraaminoalkene derivatives with sulfur, it was observed that the alkene derivatives were extremely unreactive (iii). The deprotonation reactions with Ag_2O (v) and $Pd(OAc)_2$ (vi) gave a mixture of unidentified products. However, change of the metal precursors, resulted in the deprotonation of the perimidinium salts with $[Rh(\mu\text{-OMe})(COD)]_2$ was successfully afforded the [RhBr(NHC)COD] (vii), (Scheme 3.2).



Scheme 3.2 Attempted deprotonation reactions



2a',3d'

Compound	R	R'
2a'	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
3d'*	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$

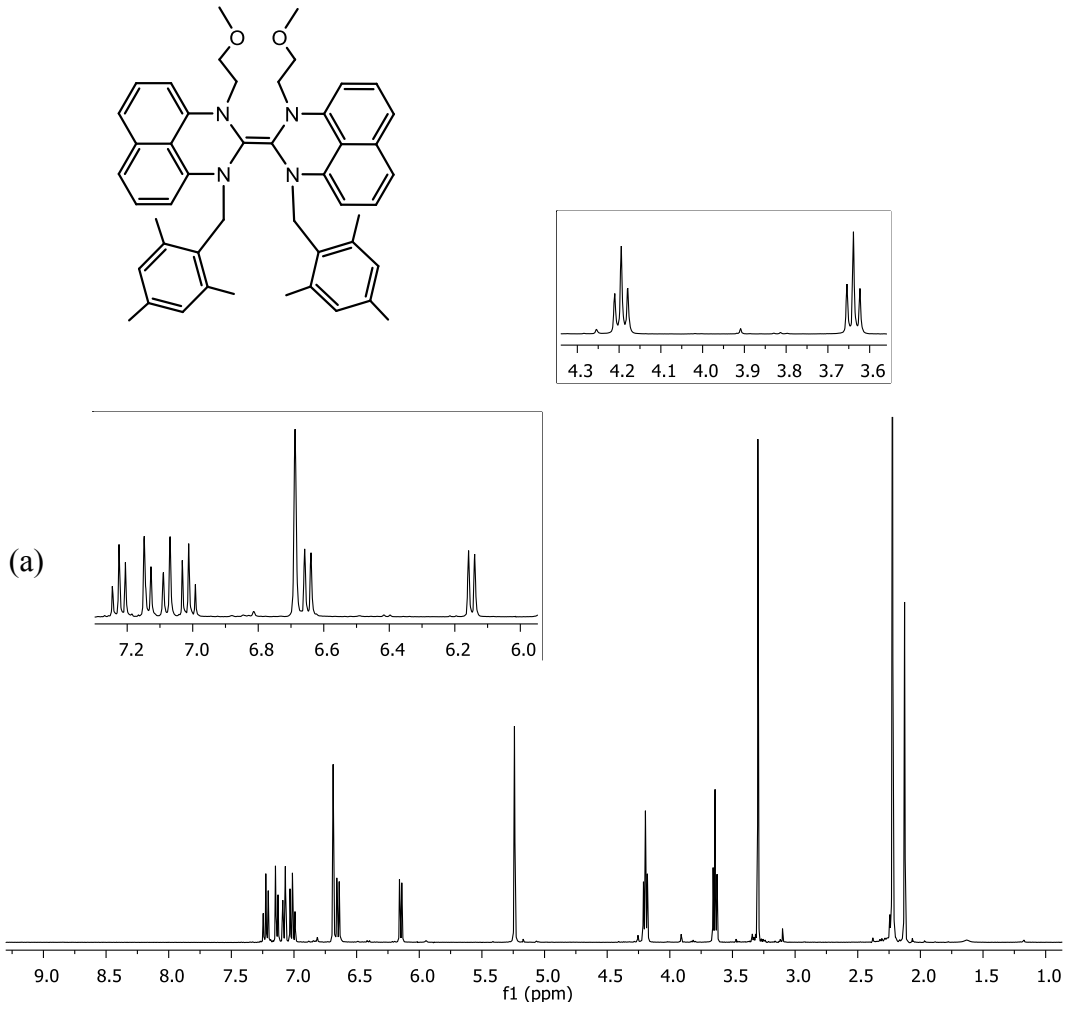
* **3d'** were synthesized by Özdemir, 2003 (Özdemir et al., 2003)

Table 3.5 ^{1}H NMR data for **2a'**, **3d'**

Compound No	Aromatics	Others
2a'	6.15 (d, *J* 7.6 Hz, 2H); 6.65 (d, *J* 7.6 Hz, 2H); 6.69 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.99-7.24 (m, 8H)	2.13; 2.22 (s, 18H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 3.30 (s, 6H, $CH_2CH_2OCH_3$); 3.64 (t, *J* 6 Hz, 4H, $CH_2CH_2OCH_3$); 4.20 (t, *J* 6 Hz, 4H, $CH_2CH_2OCH_3$); 5.24 (s, 4H, $CH_2C_6H_2(CH_3)_3$-2,4,6)
3d'	6.58 (d, *J* 7.2 Hz, 4H); 7.14 (d, *J* 7.6 Hz, 4H); 7.30 (t, *J* 7.6 Hz, 4H)	0.71 (t, *J* 7.6 Hz, 12H, $CH_2CH_2CH_2CH_3$); 1.13-1.21 (m, 8H, $CH_2CH_2CH_2CH_3$); 1.32-1.39 (m, 4H, $CH_2CH_2CH_2CH_3$); 1.51-1.60 (m, 4H, $CH_2CH_2CH_2CH_3$); 3.36-3.44 (m, 4H, $CH_2CH_2CH_2CH_3$); 3.66-3.73 (m, 4H, $CH_2CH_2CH_2CH_3$)

Table 3.6 ^{13}C NMR data for **2a'**, **3d'**

Compound No	C_{alkene}	Aromatics	Others
2a'	150.4	136.0; 135.5; 135.2; 134.9; 133.6; 129.2; 128.3; 126.5; 126.4; 118.4; 118.3; 114.1; 104.2; 103.3	19.3, 19.7 ($CH_2C_6H_2(CH_3)_3$-2,4,6); 42.3 ($CH_2CH_2OCH_3$); 42.9 ($CH_2CH_2OCH_3$); 58.0 ($CH_2CH_2OCH_3$); 68.0 ($CH_2C_6H_2(CH_3)_3$-2,4,6)
3d'	142.3	135.8; 127.2; 126.2; 117.4; 117.2; 104.9	14.0 ($CH_2CH_2CH_2CH_3$); 20.7 ($CH_2CH_2CH_2CH_3$); 30.1 ($CH_2CH_2CH_2CH_3$); 49.8 ($CH_2CH_2CH_2CH_3$)



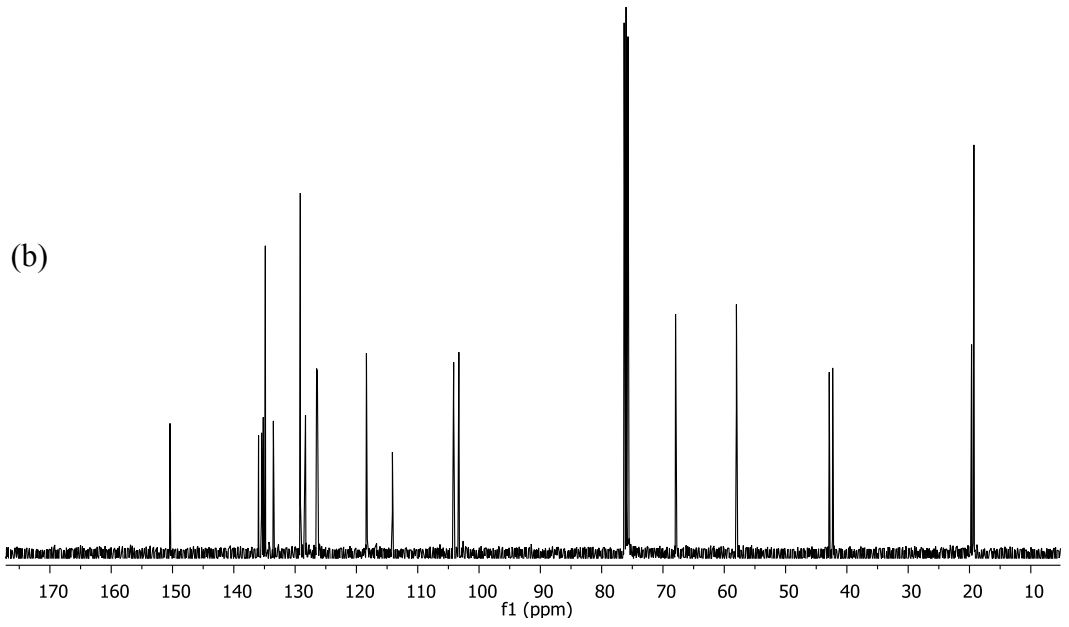
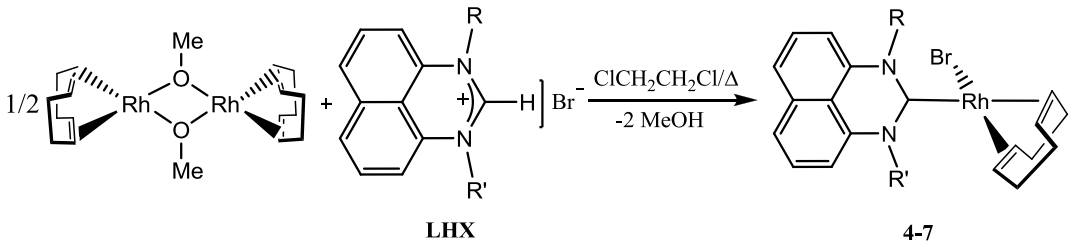


Figure 3.6 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **2a'**

3.3 Synthesis and Characterization of Rh(I)-NHC Complexes (4-7)

All attempts to prepare perimidin-2-ylidene complex from Ag_2O for transmetalation and a dimeric Pd(II) complex from $Pd(OAc)_2$ have not been successsfull. Therefore, we enuisaged that deprotonation of $[Rh(\mu\text{-OMe})(COD)]_2$ could be the method of choice. Furthermore, previous studies have shown that Rh-NHC complexes can be used as catalysts in a variety of different organic reactions including TH, hydrosilylation and arylation of carbonyl compounds. Therefore, we have synthesized complexes of the formula *cis*-[RhBr(NHC)COD] (**4**-**7**).

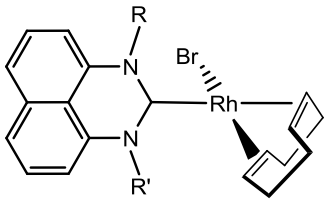
Rh(I)-NHC complexes (**4**-**7**) were prepared by deprotonation of two equivalents of perimidinium salt (**1a**, **2a**, **2d**, **3d**) with $[Rh(\mu\text{-OMe})COD]_2$ in 1,2-dicholoroethane under argon atmosphere as illustrated in Scheme 3.3. The complexes are air stable and yellow solids; **6** and **7** were obtained in higher yields than **4** and **5**.



Complex	LHX	R	R'
4	**1a**	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$
5	**2a**	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
6	**2d**	$-CH_2CH_2OCH_3$	$-CH_2CH_2CH_2CH_3$
7	**3d**	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$

Scheme 3.3 Synthesis of Rh(I)- NHC complexes

Complexes **4**-**7** have been fully identified by spectroscopic techniques. The characteristic signals for the C_2-*H* proton of the perimidinium salts (**1a**, **2a**, **2d**, **3d**) disappeared in the ^1H NMR spectra of Rh(I)-NHC complexes. Values of δ ($^{13}C_{carbene}$) were in the 210-215 ppm range and coupling constants J ($^{103}Rh–^{13}C$) were in the range 47.5-49.1 Hz for the new Rh(I) complexes **4**-**7** and these values were similar to those found for other perimidin-2-ylidene rhodium(I) complexes (Richeson et al., 2003; 2007).



Compound	R	R’
4	$-CH_2C_6H_2(CH_3)_3$	$-CH_2C_6H_2(CH_3)_3$
5	$-CH_2CH_2OCH_3$	$-CH_2C_6H_2(CH_3)_3$
6	$-CH_2CH_2OCH_3$	$-CH_2CH_2CH_2CH_3$
7	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$

Table 3.7 ^{1}H NMR data for **4-7**

Compound No	Aromatics	Others
4	6.40 (d, *J* 8.0 Hz, 2H) 6.85 (d, *J* 4.8 Hz, 4H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6); 6.92 (d, *J* 8.0 Hz, 4H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$-2,4,6); 7.10 (t, *J* 8.0 Hz, 2H); 7.26 (d, *J* 8.4 Hz, 2H)	1.84-1.90 (m, 4H, COD-C*H*$_2$); 2.10-2.22 (br, 4H, COD-C*H*$_2$); 2.28 (s, 6H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6); 2.34 (s, 6H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6); 2.52 (s, 6H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6); 3.62 (s, 2H, COD-C*H*); 5.08 (s, 2H, COD-C*H*)
5	6.20 (d, *J* 8.0 Hz, 1H); 6.38 (d, *J* 16.4 Hz, 1H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6); 6.49-6.65 (br, 1H, C*H*$_2$CH$_2$OCH$_3$); 6.72 (s, 1H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$-2,4,6); 6.80 (s, 1H, CH$_2$C$_6$*H*$_2$(CH$_3$)$_3$-2,4,6); 6.91 (d, *J* 7.2 Hz, 1H); 7.04-7.12 (m, 2H); 7.23 (d, *J* 15.2 Hz, 1H, C*H*$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6); 7.30-7.37 (m, 2H)	1.88-1.99 (m, 4H, COD-C*H*$_2$); 2.22 (s, 3H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6); 2.30 (s, 3H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6); 2.33 (s, 3H, CH$_2$C$_6$H$_2$(C*H*$_3$)$_3$-2,4,6); 2.36-2.51 (m, 4H, COD-C*H*$_2$); 3.39-3.47 (m, 2H, COD-C*H*); 3.52 (s, 3H, CH$_2$CH$_2$OC*H*$_3$); 3.82-3.88 (m, 1H, CH$_2$C*H*$_2$OCH$_3$); 4.21-4.30 (m, 1H, CH$_2$C*H*$_2$OCH$_3$); 4.65-4.88 (br, 1H, C*H*$_2$CH$_2$OCH$_3$); 5.07 (s, 2H, COD-C*H*)
6	6.06-6.23 (br, 2H, C*H*$_2$CH$_2$OCH$_3$); 6.40-6.50 (br, 2H, C*H*$_2$CH$_2$OCH$_3$); 6.54 (d, *J* 6.8 Hz, 1H); 6.72 (d, *J* 6.8 Hz, 1H); 7.18-7.26 (m, 4H)	1.04 (t, *J* 6.8 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$); 1.48-1.60 (m, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$); 1.74-1.97 (m, 4H, COD-C*H*$_2$); 2.10-2.17 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$); 2.72-2.42 (m, 4H, COD-C*H*$_2$); 3.23-3.31 (m, 2H, COD-C*H*); 3.41 (s, 3H, CH$_2$CH$_2$OC*H*$_3$); 3.62-3.67 (m, 1H, CH$_2$C*H*$_2$OCH$_3$); 4.09-4.15 (m, 1H, CH$_2$C*H*$_2$OCH$_3$); 4.26-4.49 (br, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$); 5.05-5.08 (m, 2H, COD-C*H*)
7	5.93-6.17 (br, 2H, C*H*$_2$CH$_2$OCH$_3$); 6.50 (d, *J* 7.2 Hz, 2H); 7.14-7.21 (m, 4H)	1.02 (t, *J* 7.2 Hz, 6H, CH$_2$CH$_2$CH$_2$C*H*$_3$); 1.50-1.58 (m, 4H, COD-C*H*$_2$); 1.69-1.91 (m, 6H, CH$_2$CH$_2$C*H*$_2$CH$_3$); 2.08-2.18 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$); 2.26-2.33 (m, 4H, COD-C*H*$_2$); 3.25 (s, 2H, COD-C*H*); 4.20-4.45 (br, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$); 5.04 (s, 2H, COD-C*H*)

Table 3.8 ^{13}C NMR data for **4-7**

Compound No	$C_{carbene}$	Aromatics	Others
4	214.8 (d, *J* 49.07 Hz)	104.1; 104.7; 118.4;118.8; 120.2; 126.4; 126.6; 127.1, 128.6; 129.0; 129.6; 129.7; 133.1; 133.3; 133.5; 135.0;135.2; 135.3; 135.5; 135.7	19.5; 19.7; 20.0 (s, $CH_2C_6H_2(CH_3)_3$-2,4,6); 27.7; 31.50 (s, COD-CH_2); 58.4 (s, $CH_2C_6H_2(CH_3)_3$-2,4,6); 69.9 (d, *J* 13.7 Hz, COD-*C*H); 96.8 (d, *J* 6.9 Hz, COD-*C*H)
5	215.2 (d, *J* 49.07 Hz)	105.6, 105.9; 120.3; 121.3; 121.6; 127.5; 127.9; 127.9; 130.7; 131.2; 133.8; 133.9; 134.7; 136.5; 136.5	21.0; 21.2; 21.5 (s, $CH_2C_6H_2(CH_3)_3$-2,4,6); 29.0 (d, *J* 9.1 Hz, COD-CH_2); 32.8 (d, *J* 7.6 Hz, COD-CH_2); 54.3 (s, $CH_2CH_2OCH_3$); 58.5 (s, $CH_2C_6H_2(CH_3)_3$-2,4,6); 59.5 (s, $CH_2CH_2OCH_3$); 68.6 (s, $CH_2CH_2OCH_3$); 71.2 (d, *J* 14.6 Hz, COD-*C*H); 71.5 (d, *J* 14.6 Hz, COD-*C*H); 98.3 (d, *J* 6.9 Hz, COD-*C*H); 98.8 (d, *J* 6.9 Hz, COD-*C*H)
6	213.0 (d, *J* 47.56 Hz)	105.3; 105.5; 120.8; 121.2;121.2; 127.9; 128.0; 133.6; 134.0; 134.9	14.0 (s, $CH_2CH_2CH_2CH_3$); 20.6 (s, $CH_2CH_2CH_2CH_3$); 27.0 (s, $CH_2CH_2CH_2CH_3$); 29.3 (d, *J* 65.1 Hz, COD-CH_2); 32.6 (d, *J* 57.5 Hz, COD-CH_2); 53.8 (s, $CH_2CH_2CH_2CH_3$); 55.2 (s, $CH_2CH_2OCH_3$); 59.3 (s, $CH_2CH_2OCH_3$); 67.7 (s, $CH_2CH_2OCH_3$); 71.7 (d, *J* 14.6 Hz, COD-*C*H); 71.2 (d, *J* 14.6 Hz, COD-*C*H); 97.5 (d, *J* 6.9 Hz, COD-*C*H); 97.7 (d, *J* 6.9 Hz, COD-*C*H)
7	210.6 (d, *J* 47.56 Hz)	104.0; 119.6; 119.8; 126.6; 132.7; 133.7	12.8 (s, $CH_2CH_2CH_2CH_3$); 19.4 (s, $CH_2CH_2CH_2CH_3$); 25.8 (s, $CH_2CH_2CH_2CH_3$); 28.1 (s, COD-CH_2); 31.4 (s, COD-CH_2); 54.0 (s, $CH_2CH_2CH_2CH_3$); 70.4 (d, *J* 13.7 Hz, COD-*C*H); 95.8 (d, *J* 6.8 Hz, COD-*C*H);

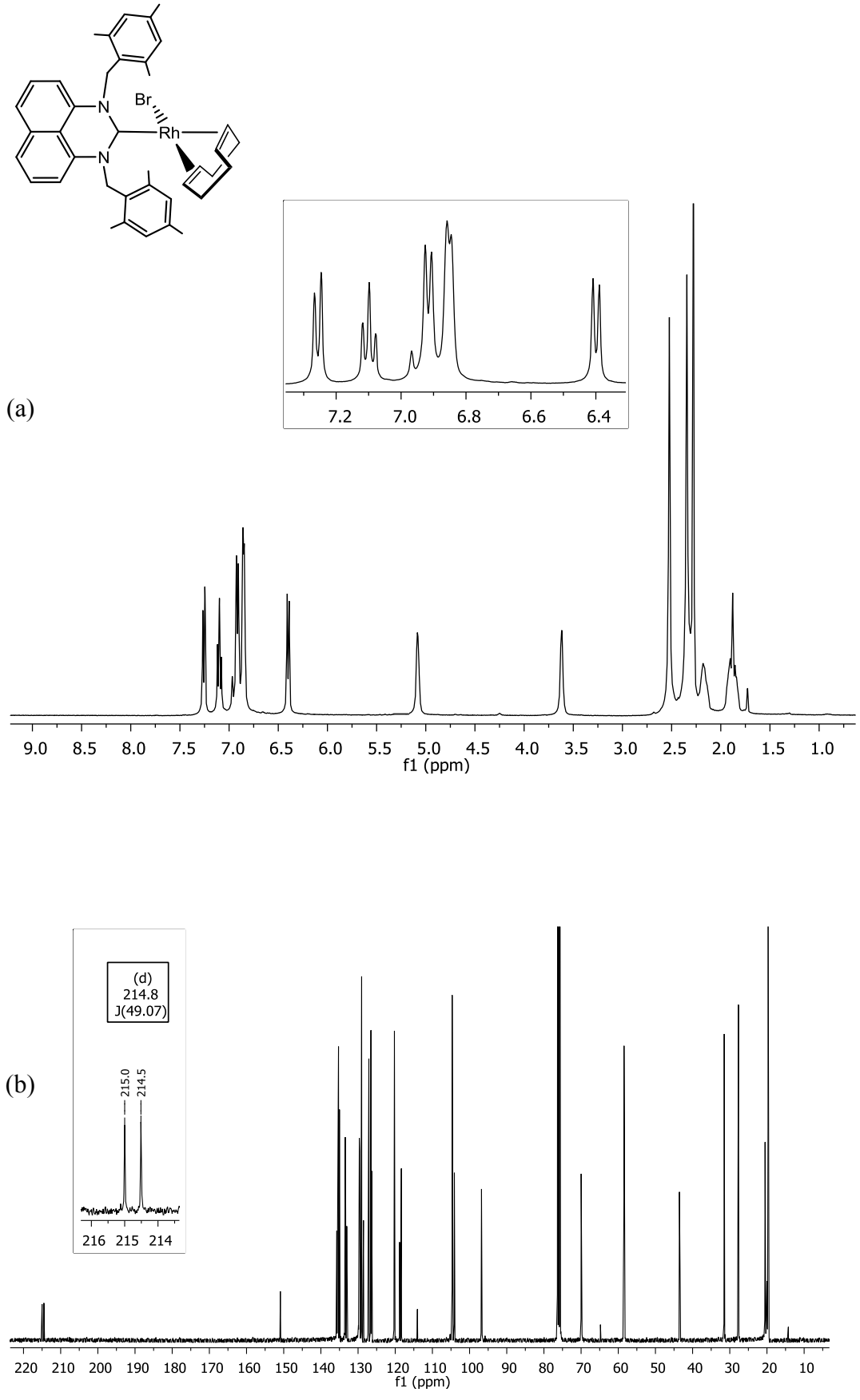
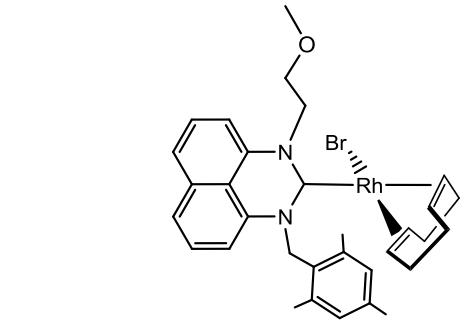
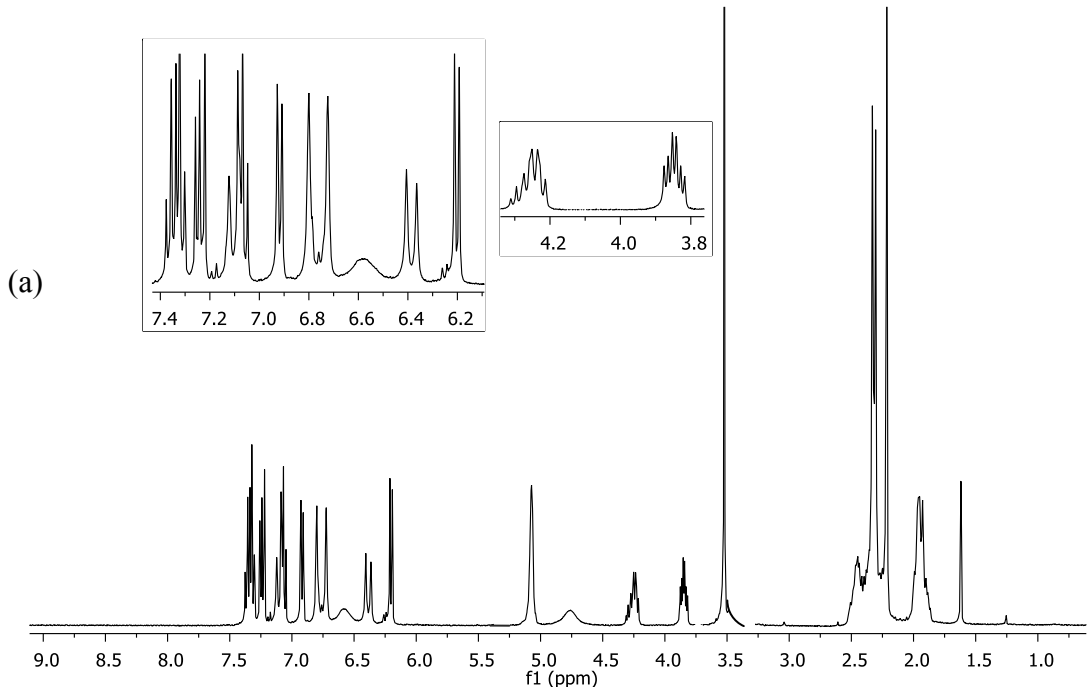


Figure 3.7 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **4**



(a)



(b)

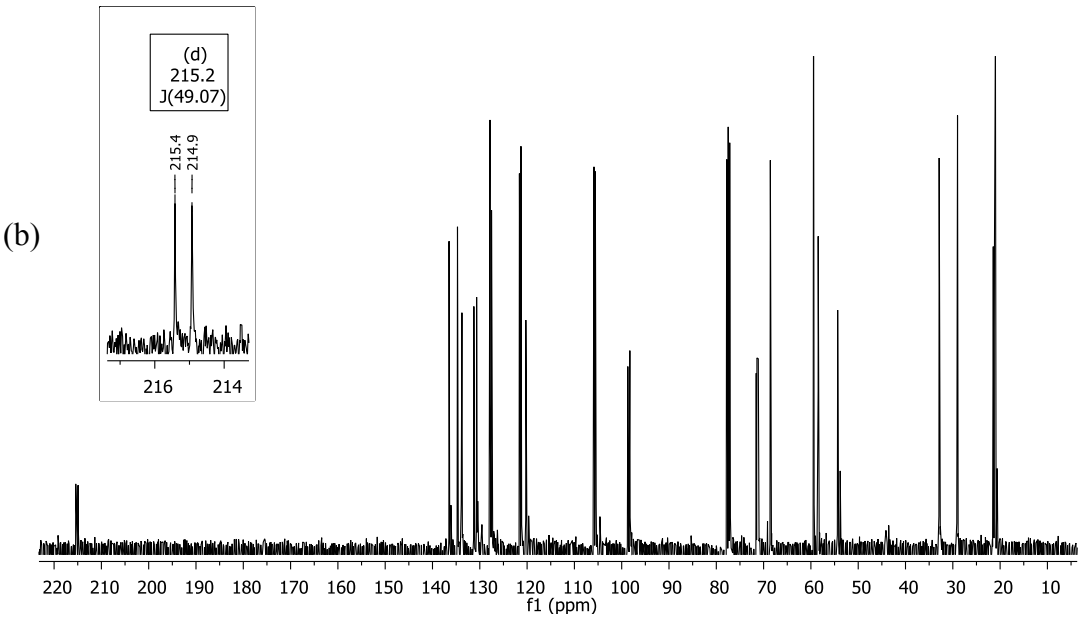
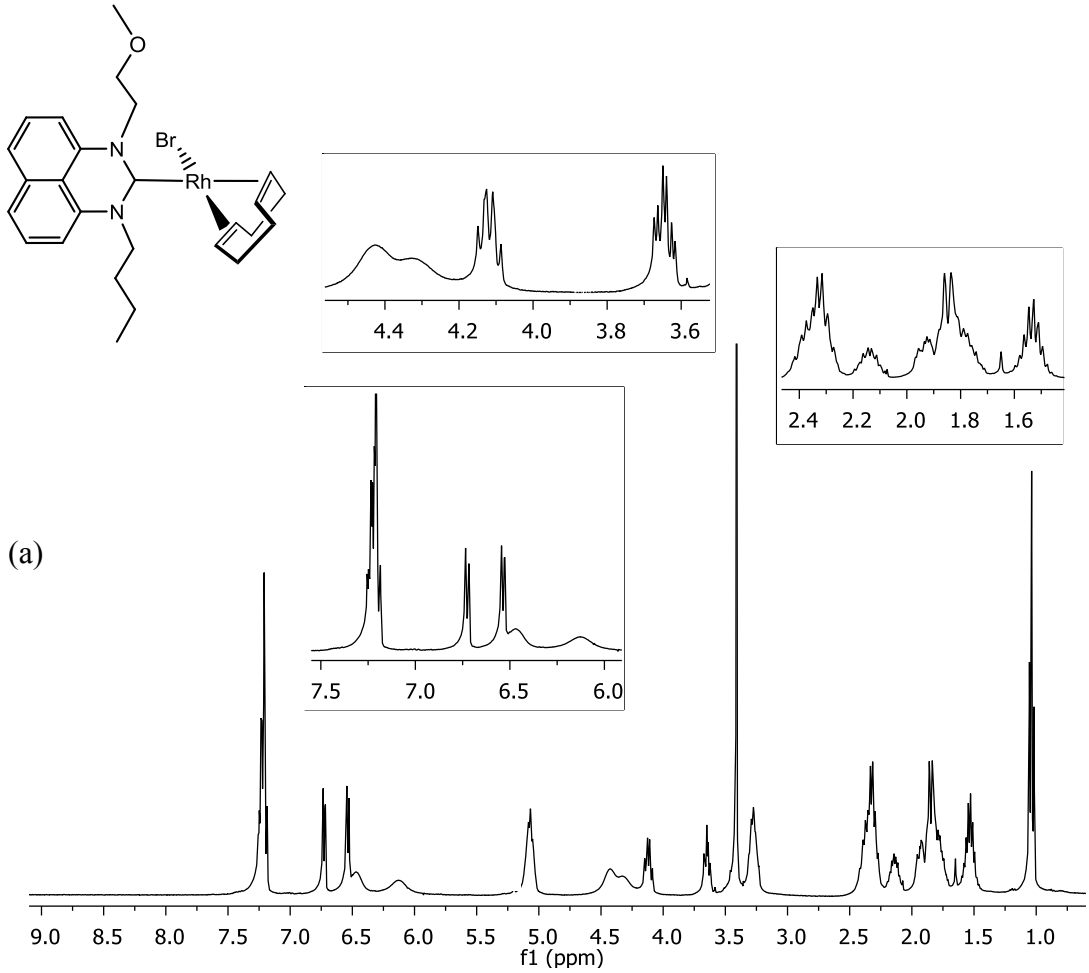


Figure 3.8 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **5**



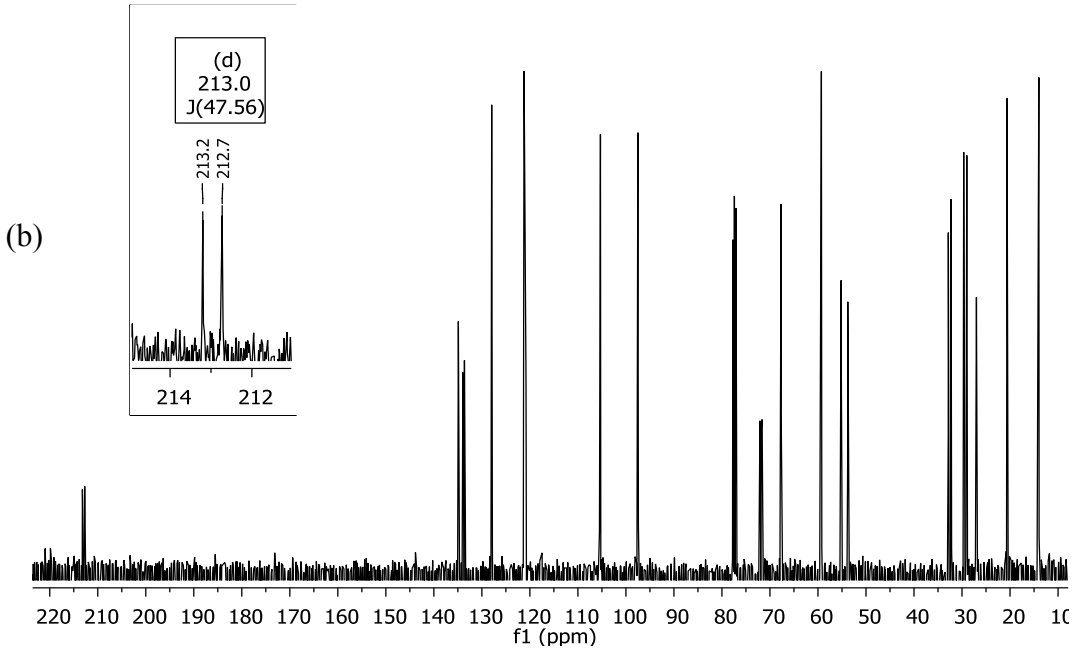
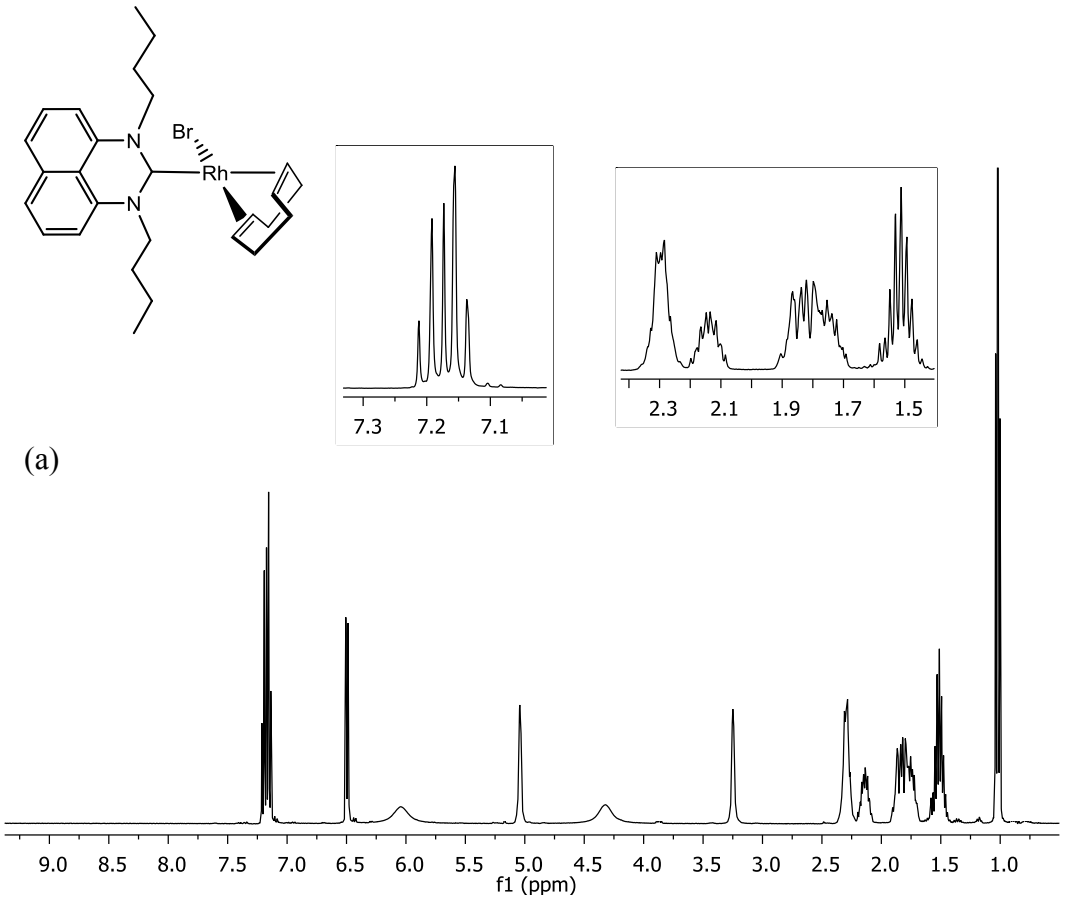


Figure 3.9 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **6**



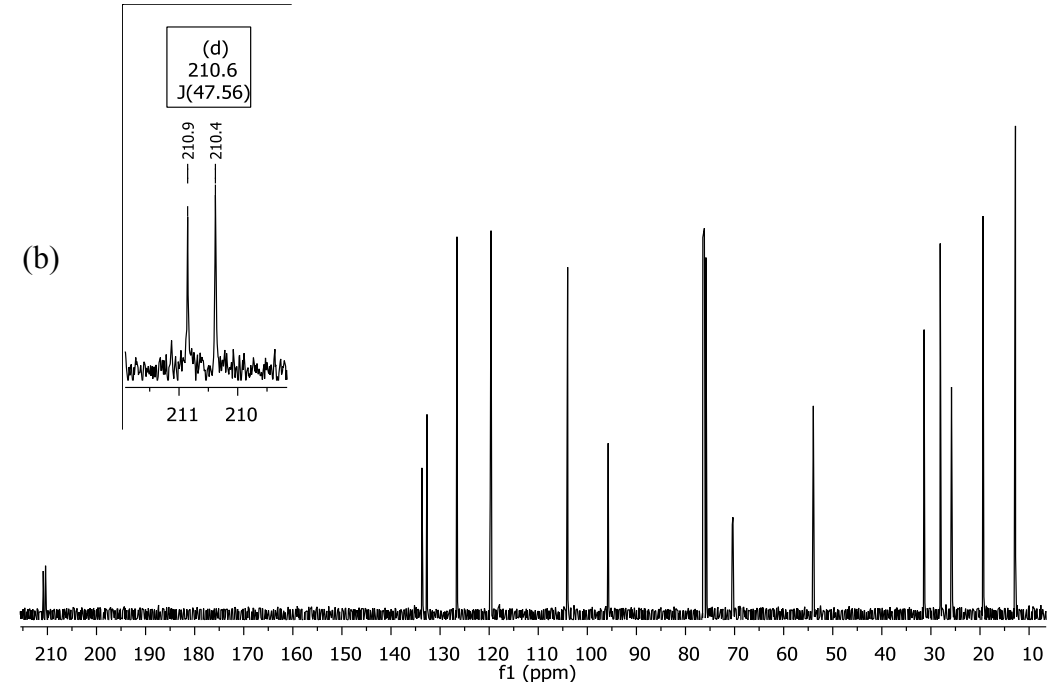


Figure 3.10 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **7**

3.4 Synthesis and Characterization of Rh(I)-CO NHC Complex (8)

A simple and relatively precise method is the measurement of the σ-donor strength by IR. The basicity of a carbene ligand is evaluated by the comparison of the ν(CO) infrared data in $Rh(CO)_2X$ carbene complexes (Herrmann et al., 2002). For the experimental determination of σ-donor strength the rhodium carbonyl complexes were synthesized by passing carbon monoxide through a solution in dichloromethane at room temperature or reacted with $[Rh(CO)_2Cl]_2$ (Richeson et al., 2007).

Treatment of **4** with CO at 1 atm at 25 °C afforded Rh(I)-CO NHC complex **8** as a yellow crystalline solid.

Complex **8** have been fully identified by spectroscopic techniques. The characteristic signals for the COD protons of the $[Rh(\mu\text{-OMe})COD]_2$ disappeared in the ^{1}H NMR spectra of $Rh(CO)_2Br$ NHC complex. The C_{NHC} and C_{CO} atoms gave rise doublets at 205.55 ($J_{Rh–C}$ 42.7 Hz), 185.45 ($J_{Rh–C}$ 54.2 Hz), 182.57 ($J_{Rh–C}$ 75.5 Hz), respectively in the ^{13}C NMR spectra. The two bands at 2008 and 2086 cm^{-1} [$\nu_{av(CO)}$ 2047 cm^{-1}] in CH_2Cl_2 can be considered for as measurement the σ-donor strength of complex **8**.

Full data for ^{1}H and ^{13}C NMR data of the compound **8** were listed below:

^{1}H NMR ($CDCl_3$) δ (ppm): 2.25 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.29-2.40 (br, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 2.40-2.56 (br, 6H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 5.69 (d, *J* 4.22 Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.39 (d, *J* 2.01 Hz, 2H, *H*Ar), 6.71(d, *J* 4.22 Hz, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.75-6.82(br, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 6.82-6.93 (br, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6); 7.09 (t, *J* 2.11 Hz, 2H, *H*Ar); 7.27 (d, *J* 2.11 Hz, 2H, *H*Ar)

^{13}C NMR ($CDCl_3$) δ (ppm): 21.0; 20.7 (s, $CH_2C_6H_2(CH_3)_3$-2,4,6); 59.8 (s, $CH_2C_6H_2(CH_3)_3$-2,4,6); 107.4; 121.1; 122.4; 127.5; 127.7; 130.8; 133.8; 134.6; 136.4; 137.3 (C_{arom}); 182.6 (d, J_{Rh-C} 75.92 Hz, *C*O); 185.4 (d, J_{Rh-C} 54.4 Hz, *C*O); 205.6 (d, J_{Rh-C} 42.94 Hz, N*C*N)

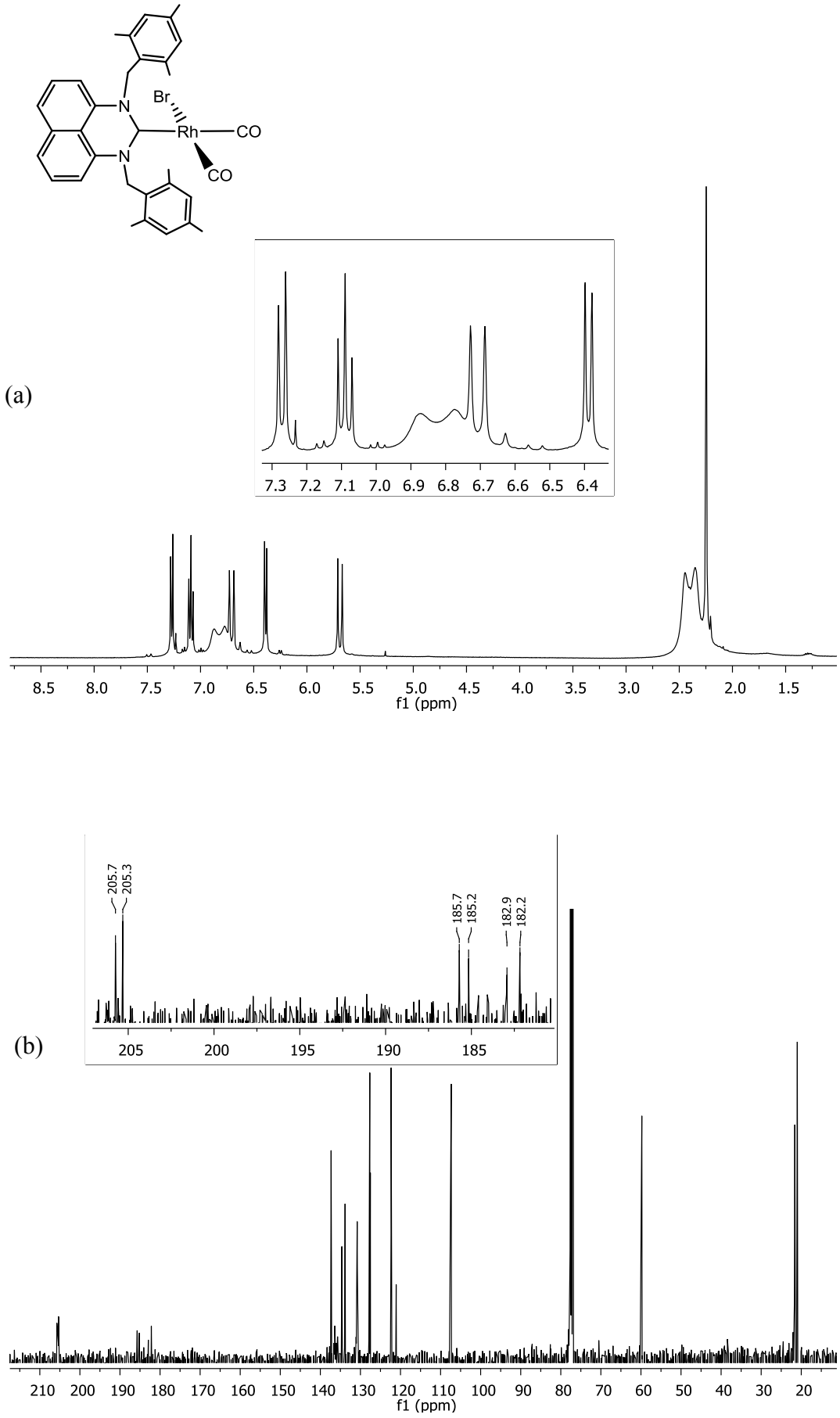


Figure 3.11 (a) ^{1}H NMR, (b) ^{13}C NMR spectra of **8**

The CO stretching frequencies some of 5- and 6-membered $Rh(CO)_2X$ carbene complexes in CH_2Cl_2 solution were listed in Figure 3.11 for comparison:

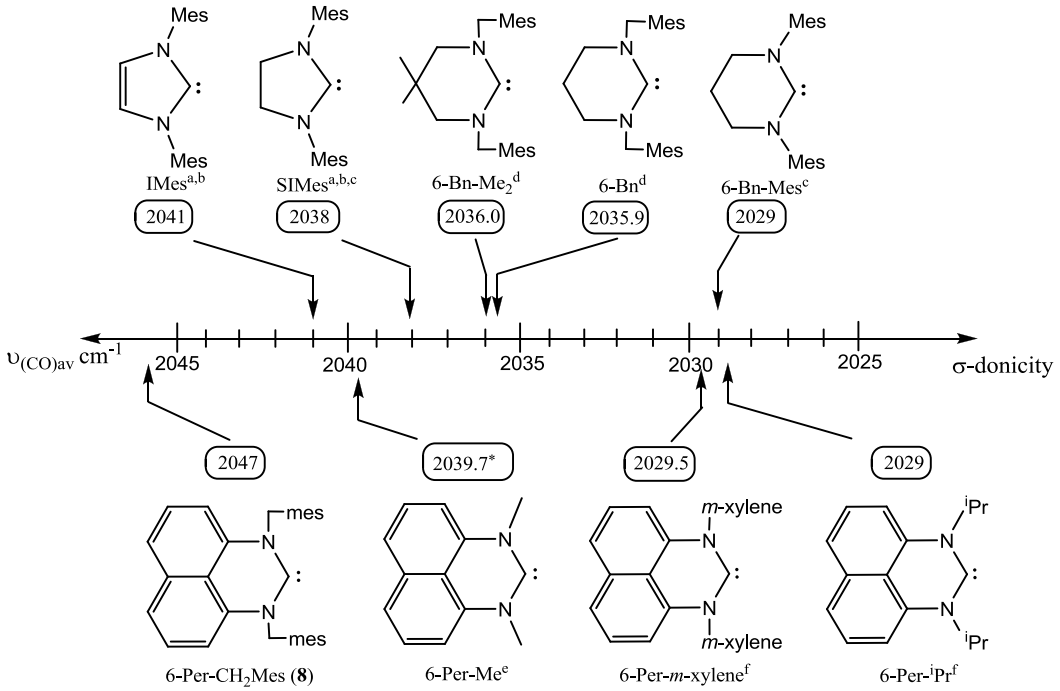


Figure 3.12 Comparison of σ-donor ability of some 5- and 6-membered NHC ligands. Data taken from literature ([a]Wolf and Plenio, 2009; [b]Herrman et al., 2002; [c]Cavell et al., 2009; [d]Mercan et al., 2011; [e]Herrman et al., 2006; *There is an inconsistence of ν_{CO}(cm^{-1}) values in literature; [f]Richeson et al., 2003, 2007).

Althought steric and electronic influences are not same from $Rh(CO)_2X$ carbene complexes in Figure 3.11, it can be possible to compare each complexes with one another thereby considering substituents.

The relevant IR data differ by 20-25 wavenumbers. The carbene ligands in 6-membered ligands are among the strongest σ-donors of this comparison, whereas 5-membered ligands represents weaker donor property. On the other hand, σ-donating ability of the NHCs derived from the naphtylen-annulated backbone substituted hexahydropyrimidin-2-ylidens covers a rather broad range (2029-2047 cm^{-1}) and strongly depends on N^1, N^3-substituents. As can be seen from Figure 3.12, 6-Per-Mes is the poorest σ-donor as compared to other tricyclic NHC ligands; ^{i}Pr, *m*-xylene and methyl substituted perimidin-2-ylidene presents low $\nu_{CO(av)}$ in contrast to the 2,4,6-trimethylbenzyl substituted ylidene. The reason behind this unexpected high ν_{CO} value is not known at this stage. However, the steric bulk of the N-substituents may play important role.

3.5 Catalytic TH Reactions with Rh(I) Complexes

Rhodium(I)-NHC complexes of type **4**-**7** were screened as catalysts for TH of acetophenone to 1-phenylethanol using 2-propanol as hydrogen donor in the presence of KOH. The catalytic experiments were carried out using 10.0 mmol of acetophenone, 0.1 mmol (1 mol %) of rhodium complexes **4**-**7** as catalyst, 1.0 mmol of KOH, 20 mL of 2-propanol with a catalyst/base/substrate ratio of 1:10:100. The catalyst was added to a solution of 2-propanol containing acetophenone and KOH, which was kept at 82 °C for 30 min.

Percentage conversion was determined by comparing the methyl proton signals of acetophenone (s, δ 2.50 ppm) and 1-phenylethanol (d, δ 1.50 ppm, J = 6.8 Hz) in the ^{1}H NMR spectrum of the crude product in $CDCl_3$ and the time-dependent conversions were followed (Figure 3.13).

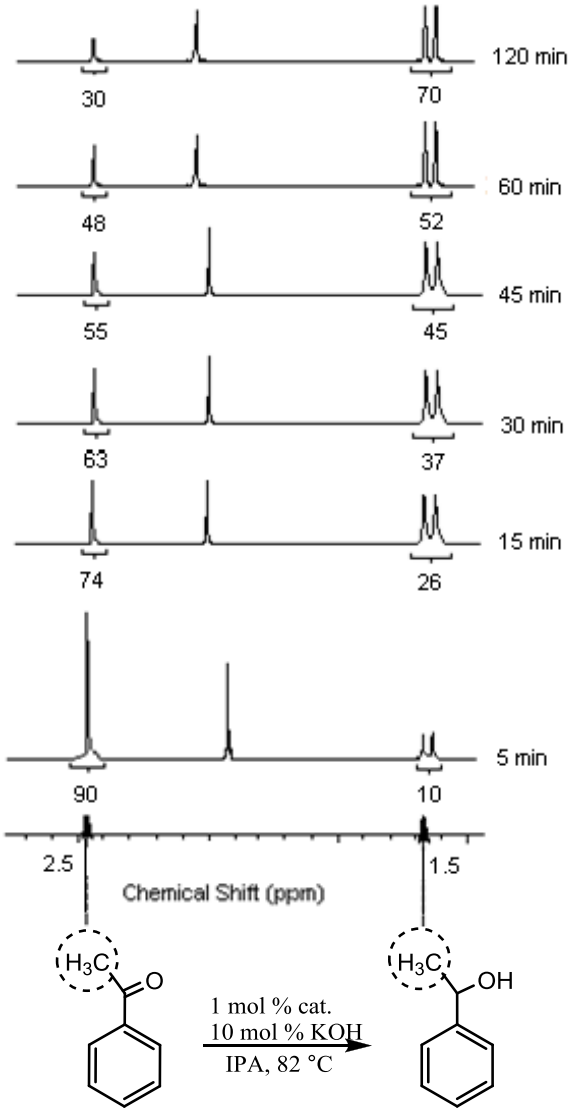


Figure 3.13 ^{1}H NMR monitoring of time-dependent of TH of acetophenone catalyzed by the complex **5**. The yields were obtained by integration areas of methyl peaks assigned to acetophenone (x) and recemic 1-phenylethanol (y) $\left\{\text{Yield \%} = \frac{y}{x+y} \times 100\right\}$.

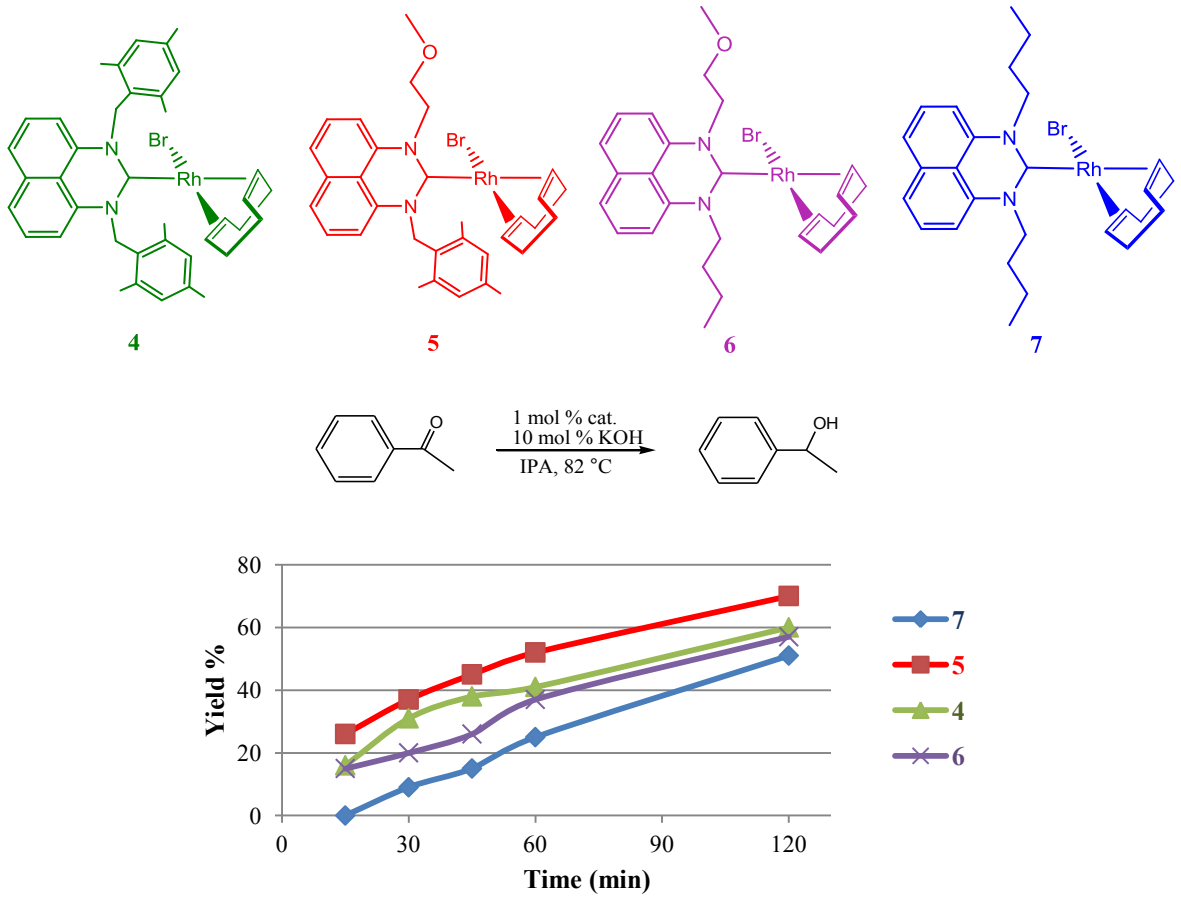


Figure 3.14 Time dependency of the catalytic TH of acetophenone catalyzed by the complexes **4**-**7**. Reactions were carried out at 82ºC using acetophenone (10.0 mmol) with Rh(I) complexes (0.1 mmol), KOH (1.0 mmol) in 2-propanol (20 mL).

The complex **5** was found to be the most active catalyst among all of these complexes tested. The sequence of the activity is **5** > **4** > **6** > **7** (Figure 3.14). However, after 120 min, only 70 % conversion was achieved by using complex **5**. When compared with the previously published results (Türkmen et al., 2008a; 2008b; Gülcemal et al., 2009), we can conclude that there is significant difference between Rh(I) complexes of 5-membered ring with perimidine derived systems.

3.6 Catalytic Arylation Reactions with Rh(I) Complexes

Rh(I)-NHC complexes of type **4** and **5** were evaluated as catalysts for 1,2-addition of phenylboronic acid to aldehydes. The catalytic experiments were carried out using 1.0 mmol 3,4,5-trimethoxybenzaldehyde as aromatic aldehyde, 2.0 mmol of phenylboronic acid, 0.01 mmol (1 mol %) of rhodium complexes **4** and **5** as catalyst, 1.0 mmol of KO^{t}Bu, 3 mL N,N-dimethylformamide and 1 mL water, with a catalyst/base/substrate ratio of 1:100:100.

The mixture was heated at 80 °C under an argon atmosphere from 4 h to 24 h. At the desired reaction times, aliquots were withdrawn from reaction mixture, cooled to ambient temperature and extracted with CH_2Cl_2 (10 ml). After drying over $MgSO_4$ the organic phase was evaporated.

Percentage conversion was calculated by comparing the proton signals of 3,4,5-trimethoxybenzaldehyde (s, δ 9.81 ppm) and phenyl(3,4,5-trimethoxy-phenyl)methanol (s, δ 6.05 ppm) in the ^{1}H NMR spectrum of the crude product in $CDCl_3$ and the time-dependent conversions were followed (Figure 3.15).

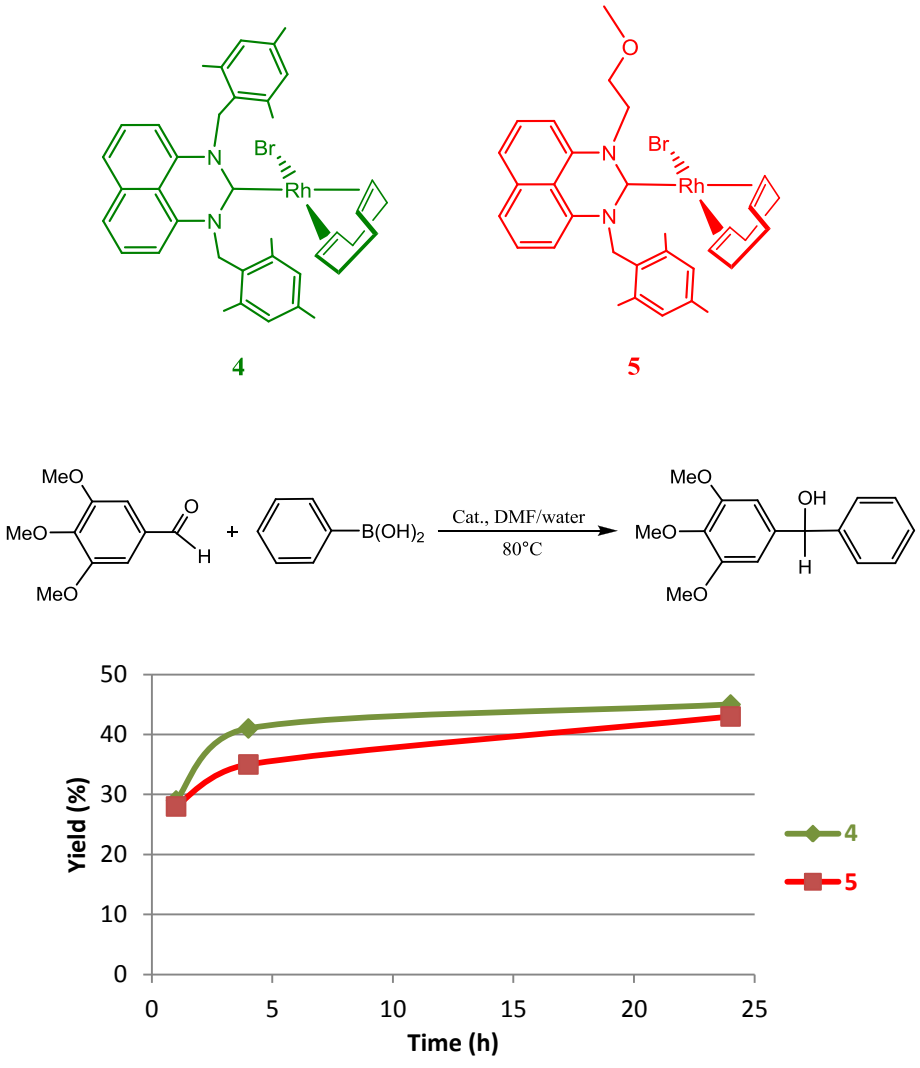


Figure 3.15 Time dependency of the addition of phenylboronic acid to aldehydes catalyzed by the rhodium-carbene complexes **4** and **5**. Reaction conditions 3,4,5-trimethoxy benzaldehyde (1.0 mmol), phenylboronic acid (2.0 mmol), rhodium-carbene (0.01 mmol), KO^{t}Bu, (1.0 mmol), N,N-dimethylformamide (3 mL), water (1 mL).

The complexes **4** and **5** were found to be less active than known catalyst (Figure 3.15). Thus, even after 24 h, only 41-45 % conversion were achieved for the synthesis of phenyl(3,4,5-trimethoxyphenyl)methanol by using complex **4** or **5**. When compared with the previously published results (Çetinkaya et al., 2005), we can conclude that there is significant difference between Rh(I) complexes of perimidine ring with tetrahydropyrimidine ring systems. Thus, while rhodium-1,3-bis(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene complex as a catalyst, after 4 h, 87 % conversion was achieved for the conversion of the product, 41 % conversion was achieved by using complex **4**. Based on their findings, the catalytic activity of rhodium-1,3-dialkyl-3,4,5,6-tetrahydropyrimidin -2-ylidene complexes are more active than rhodium-1,3-dialkyl-perimidin-2-ylidene complexes. It is important that influence of the alkyl substituents to catalytic activity.

3.7 Conclusion

6-Membered NHCs are known to be better σ-donors than 5-membered NHCs. However, the hexahydropyrimidin-2-ylidene architecture with 1,8-diaminonaphthalene (perimidin-2-ylidenes) has not been explored in detail. Therefore, this study was devoted to such species.

With the exception of **3d**, eleven perimidinium salts (**1a-1c**, **2a-2d**, **3a-3d**) bearing alkyl substituents on N^1, N^3 atoms of naphthylene-annulated backbone hexahydropyrimidine (perimidine) have been synthesized in good yields by three steps from commercially available 1,8-DAN and characterized by spectroscopic techniques. Despite the acidity of C_2-*H* (δ = 6-10 ppm), perimidinium architecture has a dramatic effect on the deprotonation behavior and is base selective. Thus, the standard base NaH did gave e.r.o., not the free carbene. Deprotonation in the presence of S_8 did not afford the expected thion but gave a low yield of the corresponding e.r.o. On the other hand, the palladation reaction with $Pd(OAc)_2$ and transmetallation with Ag_2O gave mixtures of unidentified products.

The deprotonation/coordination was successfully achived only by $[Rh(\mu\text{-OMe})(COD)]_2$ in $ClCH_2CH_2Cl$. In this context four Rh(I)-NHC complexes (**4-7**) of symmetrical and unsymmetrical perimidin-2-ylidene ligands bearing alkyl substituents on N^1, N^3 atoms have been synthesized and characterized by spectroscopic techniques.

One of the Rh(I)-NHC complexes (**4**), (NHC = 1,3-bis(2,4,6-trimethylbenzyl)perimidin-2-ylidene) has been converted to [RhBr(NHC)$(CO)_2$] (**8**), in order to determine relative σ-donor/π-acceptor properties of NHC ligand. In CH_2Cl_2 solution compound **8** displaced very high CO stretching frequencies. In view of the previous studies on PerNMe_2 (Herrmann et al., 2006), PerN^{i}Pr_2 (Richeson et al., 2003) this observed value of $\nu_{(CO)}$ is very high.

The catalytic activities for rhodium(I) complexes **4**-**7** were evaluated for TH reaction of acetophenone and in another reaction **4** and **5** were evaluated for arylation of arylaldehydes. The catalytic efficiency for TH and arylation reactions were low, however, consistent with σ-donor/π-acceptor property determined by IR spectroscopy of the perimidin-2-ylidene ligand studied here. It is worth nothing that the more bulky substituted perimidin-2-ylidenes bearing ^{i}Pr on nitrogen atoms exhibit stronger σ-donor properties.

In summary, as part of a current research program directed to the design of perimidine derivatives and their NHC-metal complexes, we presented here simple synthetic strategies for the construction of new type of 1,3-disubstituted perimidine salts and perimidin-2-ylidenes incorporating alkyl groups containing methoxyethyl, butyl, 2,4,6-trimethylbenzyl, 2,3,5,6-tetramethylbenzyl, 2,3,4,5,6-pentamethylbenzyl as N substituents. As such, the derived Rh(I) complexes were successfully synthesized and employed as catalyst for TH and arylation reactions.

Finally, it is hoped that this and earlier studies by other research groups cited in Part I of this thesis will draw some attention on the rich chemistry of perimidine and perimidine derivatives. The experience, gained by this work can be used to improve the catalytic activity of 1,3-disubstituted perimidine ligands. Future researchers should be more cautious chosing the N^1, N^3 substituents. Further efforts should be directed towards the synthesis of new NHCs bearing different but bulkier substituents on N^1, N^3 atoms which should exhibit σ-donor strength.

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