ANALYSIS OF CATALYTIC ACTIVITY OF CHROMIUM AND COPPER COMPLEXES DERIVED FROM TRIDENTATE LIGANDS

A DISSERTATION

Submitted in partial fulfilment of the

requirements for the award of the degree

of

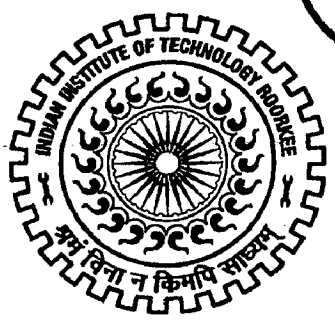
MASTER OF TECHNOLOGY

in

ADVANCED CHEMICAL ANALYSIS

By

ISHA GOYAL



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE

ROORKEE - 247 667 (INDIA)

JUNE, 2011

To

My parents and friends

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE, ROORKEE

Certificate

This is certified that the Dissertation report entitled **"ANALYSIS OF CATALYTIC ACTIVITY OF CHROMIUM AND COPPER COMPLEXES DERIVED FROM TRIDENTATE LIGANDS"** is the result of work carried out during the period of **July, 2009** to **June, 2011** by Isha Goyal, Department of Chemistry, Indian Institute of Technology Roorkee, under my supervision. Her work neither in part nor in whole has been submitted for any other degree or any other academic award anywhere before.

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"ANALYSIS OF CATALYTIC ACTIVITY OF CHROMIUM AND COPPER COMPLEXES DERIVED FROM TRIDENTATE LIGANDS"** in partial fulfilment of the requirements for the award of the Degree of **MASTER OF THECHNOLOGY** and submitted in the **Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee,** is an authentic record of my own work carried out during a period from **July, 2009** to **June, 2011** under the supervision of **Dr. Kaushik Ghosh, Assistant Professor, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee.**

The matter embodies in this project work has not been submitted for the award of any other degree.

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ISHA GOYAL

Preface

The work embodied in this thesis entitled "Analysis of catalytic activity of chromium and copper complexes derived from tridentate ligands" was initiated August, 2010.

The thesis consists of a preamble of the present work and two chapters. Synthesis, characterization and catalytic activity studies of new mononuclear Cr(III) complexes derived from tridentate ligands is described in chapter 1. In chapter 2, Catalytic activity studies on mononuclear complexes of copper will be described.

All the ligands and complexes described in this thesis were characterized by spectral analysis.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made of the findings of other investigators. I must take the responsibility of any unintentional oversights and error which might have crept in.

Publications

1. Journal Publications

Kaushik Ghosh, Pramod Kumar, **Isha Goyal** "Synthesis and characterization of chromium(III) complexes derived from tridentate ligands and their applications in catalytic oxidation of olefins" (Submitted to *J. Mol. Catal. A: Chem.)*.

2. Seminars

Participated in seminar, 4th Recent Trends in Instrumental Methods of Analysis, organized by Department of Chemistry, IIT Roorkee, Feb 2011.

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Chapter-1: Synthesis on catalytic activity of chromium complexes derived from tridentate ligands

Introduction and literature review

Abstract

In this chapter the preamble of the work and literature review will be described. The chemical systems reported in the present study are briefly introduced. The various chemical methods and equipments used are summarized.

1. Introduction and literature review:

Catalysis is the key to chemical transformations. Most industrial synthesis and nearly all biological reactions require catalysts. However, the systematic scientific development of catalysis only began about 200 years ago, and its importance has grown up to the present day. The term "catalysis" was introduced as early as 1836 by Berzelius in order to explain various decomposition and transformation reactions.[1] He assumed that catalysts possess special powers that can influence the affinity of chemical substances.[2]

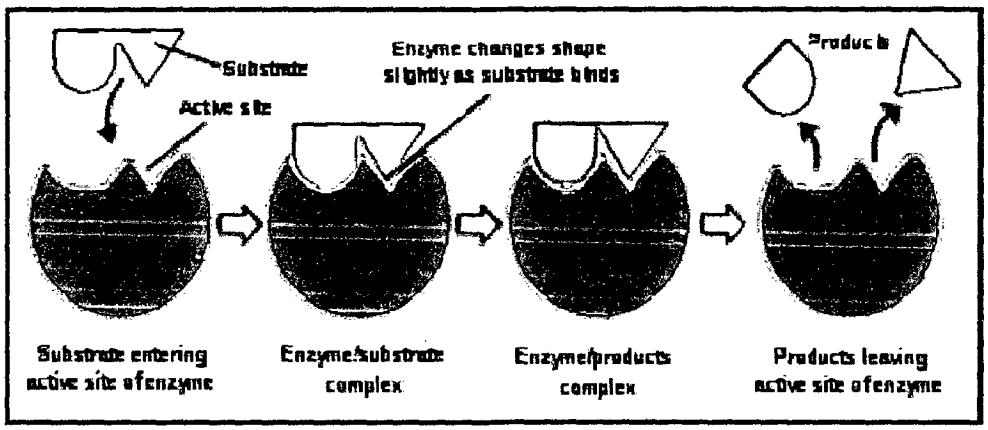


Fig. 1.1. The induced fit hypothesis of enzyme action.

A definition that is still valid today is due to Ostwald (1895): "A catalyst accelerates a chemical reaction without affecting the position of the equilibrium." Ostwald recognized catalysis as a ubiquitous phenomenon that was to be explained in terms of the laws of physical chemistry.[3] Thus catalysis is a cyclic process: the reactants are bound to one form of the catalyst, and the products are released from another, regenerating the initial state.[4]

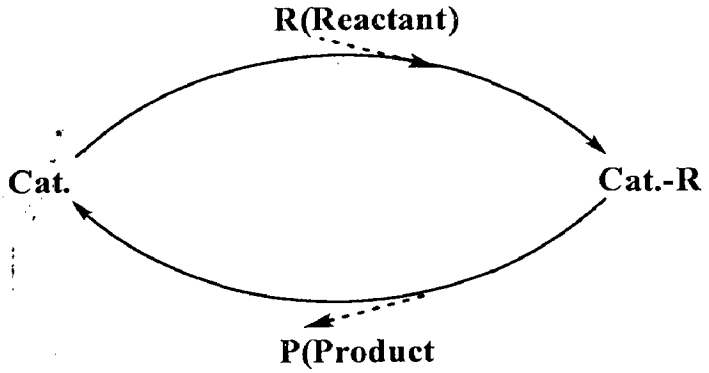


Fig. 1.2. Conversion of reactant in to product by catalytic cycle.

Research into the application of transition metal complexes in chemical processes has attracted much interest over the last century. Reasons are the novelty of the chemistry involved, its great potential and, as proven in numerous examples, the practical applications. All kinds of inorganic and organometallic compounds are used as catalysts or as reactants in the vast number of chemical reactions. Some of the important processes include hydrogenation of alkenes (Wilkinson catalyst), hyroformylation (cobalt and rhodium catalyst, oxo process), alkene oxidation (Wacker process), polymerization (Zeigler-Natta catalyst) and alkene isomerization (nickel catalyst).[5]

The oxidation of alkenes to epoxides, aldehydes, ketones and glycols is a large and growing part of homogeneous catalysis with direct industrial applications.[6,7] The oxidation of organic substrates by direct oxygen atom transfer from transition metal complexes is of fundamental importance and has been investigated extensively. Reasons for this interest are the necessity for functionalization of lower alkenes, interest in understanding reactions of biological importance, the need for partial selective oxidation and the preparation of compounds with a specific spatial structure. The transition metal complexes seem to fulfil some of these requirements and many different systems are available that can utilize a variety of oxygen sources for these oxidation reactions.

Due to the selectivity and activity of homogeneous catalysts under mild reaction conditions is unbeaten by their heterogeneous counterparts. Unfortunately, the problem of separating the single-site-catalysts from the reaction media is still an important drawback which blocks large scale applications in industry. Only a few processes are applied nowadays in industry, such as the production of adiponitrile by Dupont, acetic acid by Monsanto and butanal by Celanese (former Ruhr Chemie).[8] In each case an individual solution was developed to solve the problem of catalyst separation and recovery. A general toolbox for this has to be filled. In Table 1, the advantages and disadvantages of homogeneous versus heterogeneous catalysis are shown. In this way the major problem of homogeneous catalysis becomes obvious.

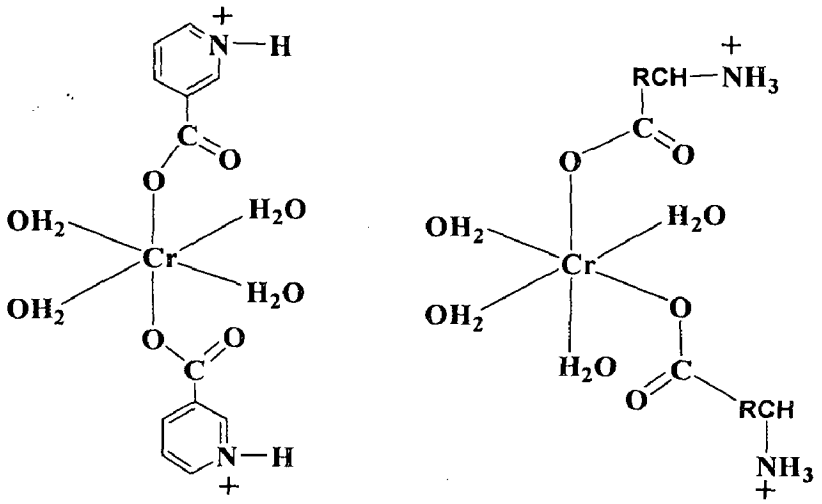
Table 1.1 Homogeneous versus heterogeneous catalysis

Characteristics	Homogeneous	Heterogeneous
Activity	+++	-
Selectivity	+++	+
Catalyst Description	++	–
Catalyst Recycling	-	+++
TON	+	+++
Quantity of Catalyst	++	+++

A number of potential methods for homogeneous catalyst separation and recovery have been or are presently being developed.[9,10] Therefore, the search for concepts that enable the combination of the advantages of both homogeneous and heterogeneous catalysis continues as it potentially could lead to the development of highly active and selective recyclable catalytic systems.

Among first row transition elements, we have chosen chromium and copper for present investigation because these two elements play crucial roles in several processes eg. catalytic oxidation reactions[11-13] and in biosystem.[14-18] Since chromium and copper, both metals can swap easily between various oxidation states and their catalytic properties go hand in hand

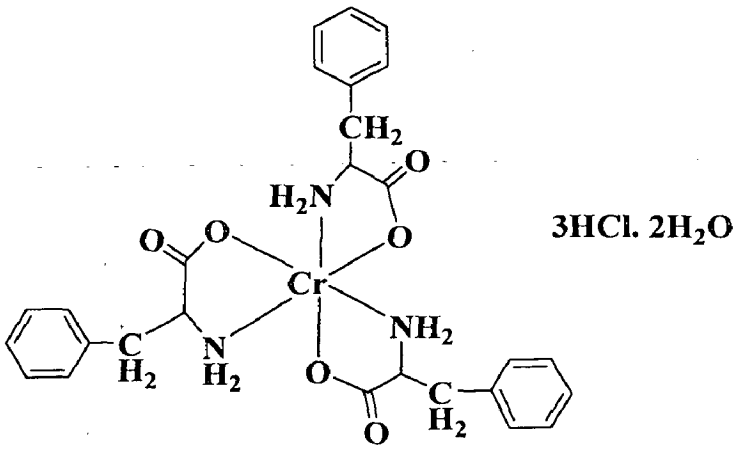
activity of the synthetic mixture must therefore be attributed to the O-coordinated chromium-dinicotinic acid complex[26] although there will also be a contribution from the green, polymeric chromium-glycine-nicotinic acid.



$[Cr(nic)_2(H_2O)_6]^{-3}$ $[Cr(gly)_2(H_2O)_6]^{-3}$

Scheme 1.1 Structures of biologically-active chromium(III) complexes

Another example of biologically active chromium compound i.e., chromium (phenylalanine)$_3$ [Cr(D-phe)$_3$] (where D-phe stands for phenylalanine) which synthesized by chelating chromium(III) with D-phenylalanine ligand in aqueous solution to improve the bioavailability of chromium, and reported that Cr(D-phe)$_3$ improved insulin sensitivity.[27]



$3HCl.\ 2H_2O$

Scheme 1.2 Structure of [Cr((D-phe)$_3$]

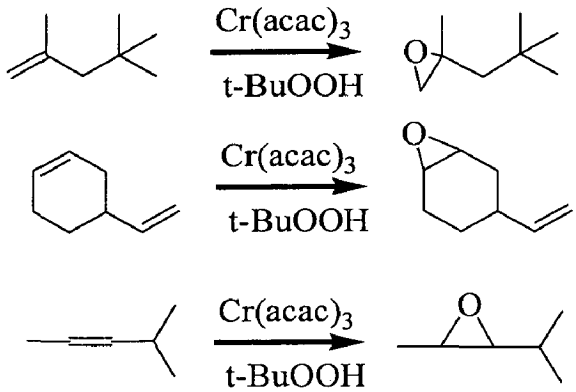
Interestingly, schiff base complexes of chromium(III) such as N,N_0-ethylene bis(salicylidene-iminate)diaquochromium(III)chloride, $[Cr(salen)(H_2O)_2]Cl$ (where salen are Schiff bases containing two phenolato functions) used as a new model of GTF, was also shown to reduce the symptoms of diabetes like, hyperglycemia and cholesterol in diabetic rats.[29,30] The use of organic chromium complexes has been found to give superior results when compared to inorganic salts.[28] Since the exact structure of this complex is not known the activity of this species does not lead to any conclusions about the possible mechanism of GTF.

1.3. Role of chromium as an oxidation catalyst:

Chromium-catalyzed oxidation reactions have been studied in several literatures. A plethora of catalytic processes involve chromium in the formal oxidation state (III) as a starting catalyst. Chromium(III) oxide has been used since the beginning of chromium-catalyzed oxidations and has been associated almost exclusively with oxygen. Many experiments thereafter have been carried out with chromium acetylacetonate or chromium esters in conjunction with oxygen or hydroperoxide.[31-33] Recently, chromium porphyrins and more generally, metalloporphyrins have been subjected to intensive investigation since they mimic the cytochrome P-450 monooxygenases. A large variety of oxygen sources have been tested with the chromium porphyrins.[34,35]

The first use of chromium(III) oxide as a catalyst occurred more than a half century ago during screening of heavy metal oxides to attempt to accelerate oxidations of benzylic methylene and methyl groups to the corresponding ketones and acids, at high temperatures, under a stream of oxygen.[36] In studies with alkenes, it was claimed that Cr_2O_3 acted as the initiator of a radical chain reaction rather than as a catalyst.[37] Recently, chromium(III) oxide has also been used as an additive to improve a catalytic system containing copper and cobalt which performed the dehydrogenation of ethyl alcohol to acetaldehyde at 275-300 °C.[38]

The first use of tris(acetylacetonato)chromium as an oxidation catalyst was probably encountered in the course of studies directed toward the epoxidation of olefins by tert-butyl hydroperoxide.[39] The epoxidation was provided fair yields at room temperature and low catalyst concentrations when oxygen was excluded from the medium.



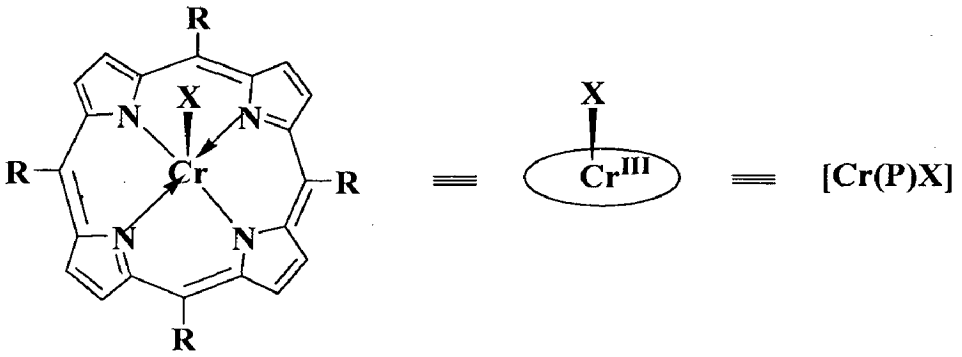
Scheme 1.3 Conversion of alkene to epoxides in presence of $Cr(acac)_3$ along with t-BuOOH

$Cr(acac)_3$-catalyzed oxidations with oxygen have also been investigated. Alkanes provided the corresponding ketones and alcohols with a ketone/alcohol ratio >1.[40]

Chromium esters have often been examined with the objective soluble in organic media. With this aim, a cheap fatty acid has been generally employed for the ester part, the catalyst most considered being chromium(III) stearate.[41] The efficiency of chromium(III) acetate has been less investigated. Chromium esters have been used mainly in conjunction with oxygen. When they were employed with ozone to oxidize cyclohexane to cyclohexanone, they were less efficient than $Cr(CO)_6$.[33]

Chromium(III) halides have been primarily used to promote the decomposition of primary and secondary alkyl hydroperoxides to the corresponding acids[42] and ketones.[43] Chromium(III) bromide seems to be one of the best additives for improving the autooxidation of alkenes under aqueous conditions in the presence of a phase-transfer catalyst.[44] Recently, chromium(III) chloride has been employed as a cocatalyst.[45]

Chloro(tetraphenylporphyrinato)chromium(III) [(TPP)CrCl] has been the main chromium catalyst employed to mimic the biological activity of cytochrome P-450. Cytochrome P-450 is a hemeprotein, used by enzymes known as monooxygenases, and is able to catalyze selective monooxygenations by molecular oxygen under very mild conditions in living organisms.[34,35]

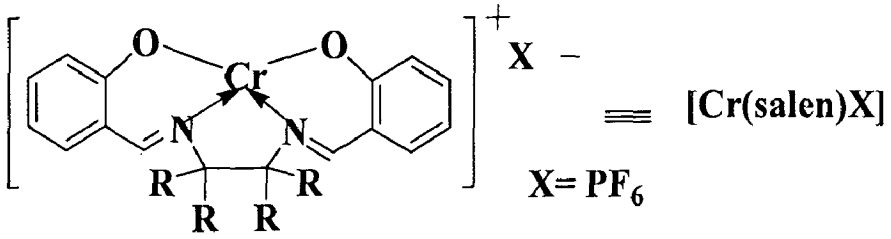


(TPP)CrX: R = Ph
(TFPP)CrX: R = C_6F_5
(TTP)CrX: R = p-melhylphenyl
(2, 6-CI-P)CrX: R = 2, 6-dichlorophenyl

Scheme 1.4 [Cr^{III}(P)X] complexes

Modifications of the porphyrin ligand (P) have been undertaken to increase the stability, selectivity, and efficiency of the catalyst. The use of phthalocyanine instead of porphyrin as ligand coordinated to chromium has been briefly mentioned for benzylic autooxidations.

Like the preceeding [Cr^{III}(P)X] complexes, the [Cr^{III}(salen)X] ones are principally employed to mimic the monooxygenase model systems and they have been mainly used to catalyze the oxidation of alkenes by PhIO. [46,47] The rate of oxidation was accelerated by the addition of a promoter which played the role of a donor ligand such as pyridine[46] or pyridine N-oxide[47] in dichloromethane or acetonitrile respectively.



≡ [Cr(salen)X]

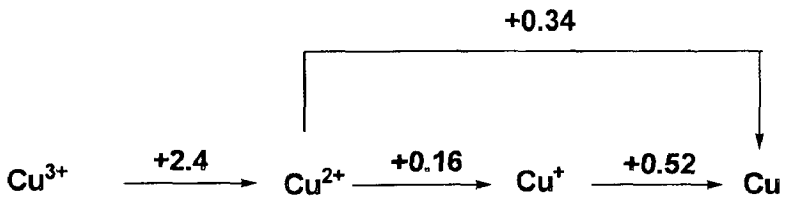
(salen)CrX: R = H
(m-salen)CrX: R = Me

Scheme 1.5 [Cr(salen)X] complexes

Another two chromium salts CrO_3 and $K_2Cr_2O_7$, having Cr(VI) oxidation state has also been used for oxidations under stoichiometric[48,50] and catalytic conditions.[49]

1.4. Copper: A general chemistry

Copper is moderately abundant and is the twenty-fifth most abundant element in the earth's crust, have been found in soil and biological materials.[19]



The transition element copper (Cu) belongs to Group IB of the Periodic Table and has an atomic weight of 63.5. Copper can exist mainly in +1 to +3 oxidation state. Although copper forms compounds in any of four different oxidation state, only the +2 state enjoys much stability. The +3 state is generally too strong an oxidizing agent, though Cu(III) has been found in biological systems. The free +1 ion will spontaneously disproportionate (+0.52V > +0.16V).[5]

1.5. Role of copper in biosystem:

Copper is biologically important in various oxidase enzymes, as an oxygen carrier in invertebrates and in photosynthesis. Azurins, plastocyanins and laccases are involved in electron transfer reactions. Tyrosinases and ascorbate oxidases are used in oxygenation reactions.[5]

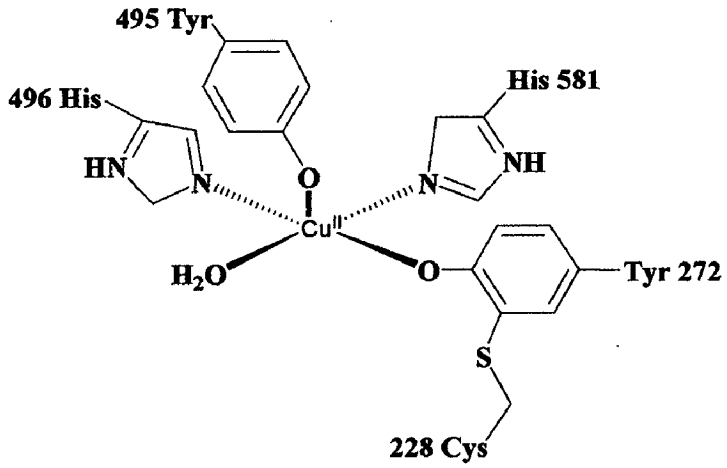
In Nature, many enzymes are present which are capable of catalysing oxidation reactions.[51] In a number of these reactions copper containing enzymes are involved. These enzymes are frequently studied by using model complexes which provide information on the nature and reactivity of the active site and about possible reaction mechanisms.[51] Based on these copper containing enzymes and the related model complexes, various oxidation catalysts have been evaluated.[52]

1.5.1. Galactose Oxidase (GO):

Galactose Oxidase (GO) from filamentous *heat-rot* fungus *Fusarium ssp.* was first isolated in 1959,[53] that selectively catalyzes the aerial oxidation of primary alcohols to the corresponding aldehydes with concomitant reduction of molecular oxygen to hydrogen peroxide.[54]

$$RCH_2OH + O_2 \xrightarrow{\text{Galactose oxidase}} RCHO + H_2O_2$$

Galactose oxidase is a single polypeptide with a molecular mass of 68.5 kDa, and is unusual because, in contrast to most copper proteins that affect multi-electron redox reactions by using multinuclear active sites, galactose oxidase uses an isolated single copper center to carry out the required two-electron redox chemistry.



Scheme 1.6 Schematic diagram of galactose oxidase

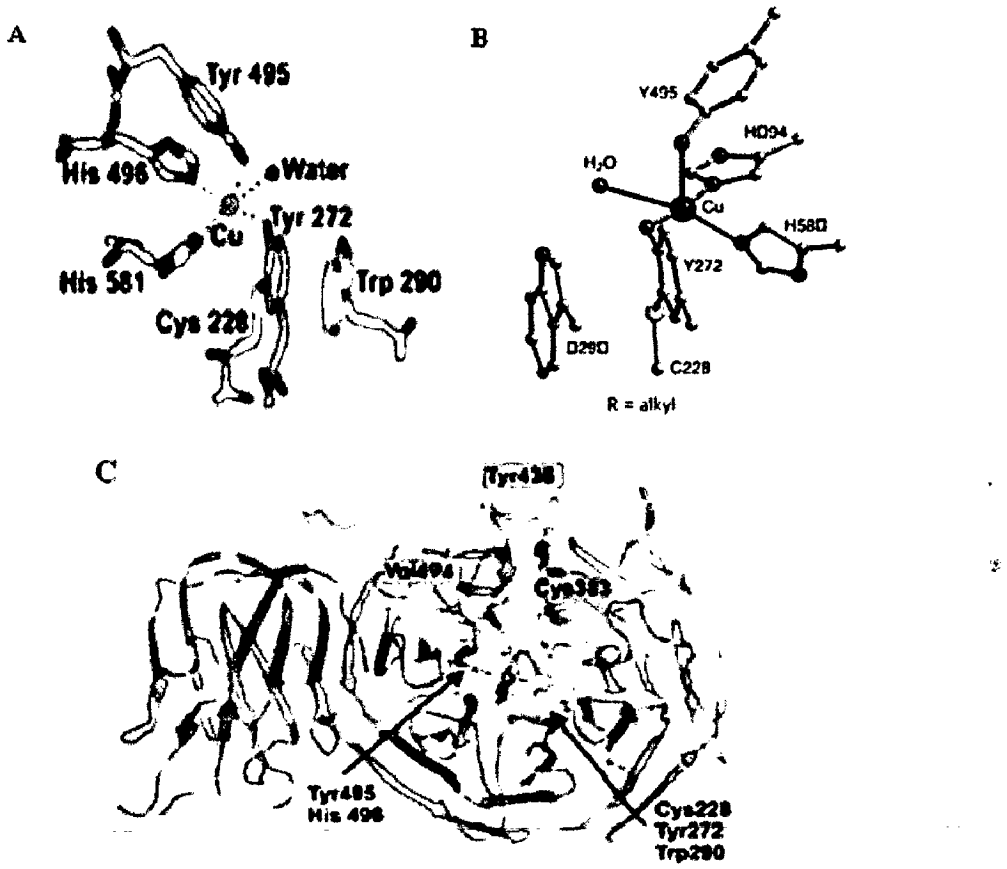


Fig. 1.7. Structure of galactose oxidase. (A and B) The active site showing the copper ligands (C) An overview of the galactose oxidase monomer showing the locations of the residues Cys383, Tyr436 and Val 494 (shown in mauve and highlighted by yellow labels), which form the basis of the present study. The active site residues are shown in atom colouring and are labelled by arrows. Non-covalent bond interactions are shown as dotted lines.

The active site of galactose oxidase consists of a mononuclear copper ion in a square pyramidal coordination geometry and a tyrosine 272 radical.[55-59] Hence, two redox sites are

present in the active form of this mononuclear metalloenyzme. In this enzyme, at pH 7, the copper ion is coordinated to two histidine residues (His496, His581), a tyrosinate residue (Tyr272), a water molecule in the equatorial plane and to another tyrosinate (Tyr495) in the apical position.[60] This catalytic cycle starts with the binding of the substrate by replacing a H_2O molecule at the metal centre.[61]

The mechanism of galactose oxidase is now well established (Fig. 1.7).[57] As a first step of the catalytic process, an alcoholate is formed through the deprotonation of the substrate by the axial tyrosinate ligand. In the next reaction step, a hydrogen atom is abstracted from the substrate to the equatorial tyrosine 272 radical and subsequently or simultaneously the copper center is reduced to Cu(I) by the single electron transfer from the ketyl radical. The catalytic cycle is closed by recovering the initial copper oxidation state under concomitant reduction of molecular oxygen to hydrogen peroxide.

Very recently, a few structural and functional models of galactose oxidase have appeared in literature[62-64] which uses a phenol containing tripodal ligand. The models mimics the native enzyme structurally and also the functional aspect by oxidizing primary alcohols to the corresponding aldehydes with moderate turnover numbers.

1.5.2. Glyoxal oxidase :

Glyoxal oxidase[65] from the wood-rot fungus *Phanerochaete chrysosporium* is a secreted enzyme that functions as an extracellular factory for production of hydrogen peroxide, fueling peroxidases (lignin peroxidase) that are responsible for microbial lignin degradation.[65-67] Glyoxal oxidase catalyzes the oxidization of aldehydes to carboxylic acids, coupled to reduction of dioxygen to hydrogen peroxide,

$$\mathbf{RCHO + O_2 + H_2O \xrightarrow{Glyoxal\ oxidase} RCO_2H + H_2O_2}$$

The enzyme has fairly broad specificity for the reducing substrate. However, there is biological evidence that *P. chrysosporium* specifically secretes simple dicarbonyls (glyoxal and methylglyoxal) to drive this reaction. Further metabolism of the glyoxylic acid product leads to formation of oxalic acid.[68]

Previous studies of glyoxal oxidase[69] have demonstrated that it is a copper metalloenzyme containing an unusual free radical-coupled copper active site similar to that found in galactose oxidase,[70,71] forming a class of enzymes known as *radical copper oxidases*. Glyoxal oxidase is isolated as an inactive, reduced form lacking the free radical, and requires treatment with a strong oxidant (*e.g.* Ir(IV) or Mo(V)) for activation.[69]

1.6. Role of copper as an oxidation catalyst:

The search for low molecular weight Cu(II) complexes as functional models for galactose oxidase which would mimic this reactivity had a promising start in 1996[61] reported a stoichiometric oxidation by a phenoxyl radical complex. In the same year Wang and Stack[72] reported the first truly catalytic system, which in presence of a base and an oxidizing agent oxidizes benzyl alcohol to benzaldehyde with up to 10 turnovers. A different system was described by Pierre and co-workers in 1998.[73] They showed that the electrochemically one electron oxidized phenoxyl radical complex electrocatalyzes, in the presence of KOH (where > 30 turnovers were observed).

Some of the functional models of galactose oxidase involve salen-type ligands and exhibit interesting catalytic activity only with activated alcohols as substrates. These model complexes do true galactose oxidase chemistry but are not, strictly speaking, structural models. The best results have been obtained by Wieghardt *et al.*[74-76] with a set of complexes

in which the redox chemistry during the catalytic cycle is ligand based and the proposed mechanism is similar to the mechanism proposed for galactose oxidase itself.

Copper(II) Schiff-base complexes, upon immobilization into microporous or mesoporous aluminosilicates, are capable of catalyzing olefin epoxidations and/or oxidations.[77-79] However, the activity of Schiff-base copper(II) complexes towards catalytic oxidation in a homogeneous medium is not well documented in the literature. So far only a few copper(II) Schiff-base complexes are reported to be catalytically active towards olefin oxidation.[80]

2. Aim and scope of the present work:

The aim of this work is two fold: (i) to gain deeper insight into the electronic structure of the metal core and the ligand surrounding of these radical-containing complexes and (ii) to explore the oxidation chemistry of well-characterized metal complexes, which is expected to provide the basis for new catalytic oxidation systems for synthetic and industrial processes of olefins.

To produce radical containing metal complexes, which will act as functional model complexes of some radical containing metalloenzymes, e.g. Galactose Oxidase, Glyoxal Oxidase etc. (which will change their redox property in the presence of metal ion and oxygen) ligands have been synthesized.

Chapter-1

Studies on catalytic activity of chromium complexes derived from tridentate ligands

Abstract

Tridentate planar ligands PhimpH (2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)phenol), N-PhimpH (2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)napthalen-1-ol) and Me–PhimpH (2-(1-(2-phenyl-2-(pyridine-2-yl)hydrazono)ethyl)phenol) where H stands for dissociable proton, were synthesized and characterized. Mononuclear chromium (III) complexes ($[Cr(Phimp)_2](ClO_4)$ (**1**), $[Cr(N–Phimp)_2](ClO_4)$ (**2**), and $[Cr(Me–Phimp)_2](ClO_4)$ (**3**)) of these ligands were synthesized and characterized by UV-visible, IR spectral and magnetic moment measurement studies. Redox property of the metal centre was examined and phenoxyl radical complexes were generated in solution and were characterized by UV-Vis spectrophotometer. We investigated catalytic studies of these complexes by GC and GC-MS studies.

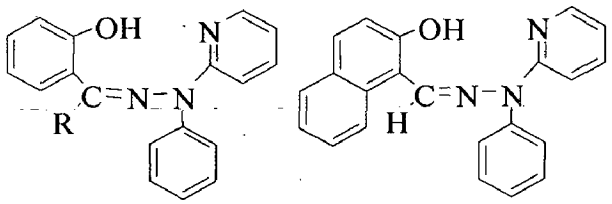
1. Introduction:

Catalysis is known to play a key role in modern chemical technologies. Now a days it is generally agreed that the key role in catalytic reactions is played by intermediate chemical interaction of reactive molecules with definite functional groups (active sites) of homogeneous, heterogeneous or biological (enzyme) catalysts.[81] Oxidation of hydrocarbons under mild and environmental friendly conditions, is an important research field, since industrial processes, especially in pharmaceutical industry, for synthesizing synthons from readily available olefins.[82] However, selective oxidation of alkanes under mild conditions, is a difficult task due to their chemical inertness. In this regard, use of coordination complexes of transition metals as catalysts is of abiding importance,[83,84] as it offers an effective possibility for synthesis of pure compounds. Although transition metal Schiff base complexes of bear resemblance to enzymatic catalysts and are eye-catching since they provide advantages due to their relatively easy synthesis and versatile coordination structures. Among the various transition metal complexes reported.[85-93] In this regard, first row transition metals namely vanadium, chromium, iron and copper complexes are preferred because of their versatile coordination chemistry in different oxidation states.[94] Moreover, these transition metal-catalyzed oxidation reactions are chemical models for several metalloenzymes namely, monooxygenase, cytochrome P-450 enzymes etc.[95,96]

Hence chromium is an important metal for catalytic studies because chromium exhibited variable oxidation states, spin states, coordination numbers and redox properties in different chromium complexes.[5] However, chromium(III) is an essential nutrient that is involved in the glucose tolerance factor (GTF) in maintenance of normal carbohydrate and lipid metabolism.[97,98] Schiff base complexes of chromium(III) such as N,N$_0$-ethylene bis(salicylidene-iminate)diaquochromium(III)chloride, [Cr(salen)(H_2O)$_2$]Cl used as a new model of GTF.[29,30] Chromium(salen) complexes are well-known catalysts, both in

heterogeneous and homogeneous systems. Other applications of theses complexes are reported, such as, the alkene epoxidations[47,99] and alcohol oxidations.[100] There is a wide range of chromium complexes[83,84] that are known to be capable of catalyzing asymmetric oxidation of unfunctionalized olefins as well as other organic molecules in presence of terminal oxidants, however, reports on the use of chromium complexes are sparse in the literature.[101-104]

Herein we report the synthesis and characterization of chromium complexes $[Cr(Phimp)_2](ClO_4)$ (**1**), $[Cr(N–Phimp)_2](ClO_4)$ (**2**), and $[Cr(Me–Phimp)_2](ClO_4)$ (**3**) derived from tridentate ligands PhimpH, N–PhimpH, Me–PhimpH respectively having NNO donors (Scheme 1). The complexes were characterized by UV-visible, IR, magnetic moment and Conductivity measurement studies. Redox property was also investigated for the stabilization of Cr(III) oxidation states. Phenoxyl radical complexes are important intermediates in the catalytic oxidation of primary alcohol to aldehyde and aldehyde to carboxylic acid by galactose oxidase (GO)[105-107]and glyoxal oxidase[108] enzymes respectively. Due to the presence of phenolato donor in the ligand frame we have explored the generation of phenoxyl radical complexes. The catalytic oxidation chemistry of the chromium complexes was examined.



PhimpH, R= H
Me-PhimpH, R= Me

N-PhimpH

Scheme 2.1 Tridentate ligands with abbreviations

2. Experimental:

2.1. Materials and method:

All the solvents used were reagent grade. Removal of all solvents was carried out under reduced pressure. Toluene, diethyl ether and dimethylformamide (DMF) were purified by distillation over 4Å molecular sieves and stored over sieves. Analytical grade reagents phenyl hydrazine and hydrogen peroxide (S. D. Fine, Mumbai, India), salicylaldehyde, o-hydroxyacetophenone (SRL, Mumbai, India), 2-hydroxy-1-napthaldehyde (Sigma Aldrich, Steinheim, Germany), $CrCl_3.6H_2O$ (Loba Chemie, Mumbai, India), styrene (Avra, Hyderabad, India), *trans*-stilbene (Lancaster, Eastgate, England), sodium hydride, 2-chloropyridine, *cis*-cyclooctene (Acros organics, USA), sodium perchlorate (Himedia Laboratories Pvt. Ltd, Mumbai, India) were used as obtained. Solvent used for spectroscopic studies were HPLC grade and purified by standard procedures before use.[109]

2.2. Synthesis of ligands and metal complexes

2.2.1. Synthesis of ligands:

2.2.1.1. Synthesis of 2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methylphenol, [PhimpH]

Salicyaldehyde (122.0 mg, 1.00 mmol) and 2-(1-phenylhydrazinyl)pyridine (185.0 mg, 1.00 mmol) were dissolved in 10 mL of methanol. The reaction mixture was stirred at room temperature. Within 30 min a white solid began to separate out and stirring was continued for another 2 h. The mixture was stirred for about 2 h, white precipitate was filtered, washed thoroughly with methanol, diethylether and then dried in vacuum. PhimpH was recrystallized from dichloromethane. Yield: 145 mg, (50%). GC-MS (dichloromethane, m/z): 289 M^+ (7.3%), 169 (100%), 196 (28%).

2.2.1.2. Synthesis of 2-((2-phenyl-2-(pyridin-2-yl)hydrazono)methyl)napthalen-1-ol, [N-PhimpH]

2-Hydroxy-1-napthaldehyde (172.0 mg, 1.00 mmol) was dissolved in 30 mL of methanol completely by heating and 2-(1-phenylhydrazinyl)pyridine (185.0 mg, 1.00 mmol) was added to this reaction mixture with continuous stirring. The reaction mixture was refluxed for 2 h and yellow solid separated out which was filtered washed with methanol and dried in vacuum. Yield: 180.9 mg, (54%).

2.2.1.3. Synthesis of 2-(1-(2-phenyl-2-(pyridine-2-yl)hydrazono)ethyl)phenol, [Me-PhimpH]

o-Hydroxyacetophenone (136.0 mg, 1.00 mmol) and 2-(1-phenylhydrazinyl)pyridine (185.0 mg, 1.0 mmol) were dissolved in 15 mL of methanol with one drop of concentrated HCl and this reaction mixture was stirred for 12 h at room temperature. After 12 h a yellow solid was separated out. This solid mass was filtered and washed with small amount of methanol and dried in vacuo. Yield: 203 mg, (67%). GC-MS (dichloromethane, m/z): 303 M^+ (7.8%), 169 (100%), 210 (44%).

2.2.2. Metal complexes synthesis:

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and handled with proper protection.

2.2.2.1. Synthesis of [Cr (Phimp)$_2$](ClO$_4$) (1)

A batch (0.289 g, 1.0 mmol) of PhimpH was dissolved in 10 mL of ethanol. The solution of $CrCl_3.6H_2O$ (0.135 g, 0.5 mmol) in 10 mL of ethanol was added dropwise, the

color of solution was turned from green to dark brown. After 4 h of stirring, sodium perchlorate (0.070 g, 0.5 mmol) was added to the reaction mixture. Red-brown solid was precipitated out within 30 min. The stirring was continued for another 2 h. The reaction mixture was filtered and washed with excess of ethanol and dried in *vacuo*. **1** crystallized in dichloromethane: methanol mixture. Yield: (40%) (0.15 g, 0.2 mmol). Anal. Calculated for $C_{36}H_{28}N_6O_6ClCr$ (728.1): C 59.39, H 3.88, N 11.54; Found: C 59.34, H 3.93, N 11.49.

2.2.2.2. Synthesis of [Cr (N–Phimp)$_2$] (ClO_4) (2)

To a 30 mL of ethanolic solution of ligand (N–PhimpH) (0.339 g, 1.0 mmol), a batch of $CrCl_3.6H_2O$ (0.135 g, 0.5 mmol) with 10 mL of ethanol was added dropwise. The color of solution was changed to dark brown. The mixture was stirred for 4 h. Now a batch of sodium perchlorate (0.070 g, 0.5 mmol) was added to the reaction mixture. Dark brown solid was precipitated out within 30 min. The reaction mixture was stirred continuously for 2 h. After that the mixture was filtered to obtain dark brown solid. It was washed with excess of ethanol and was dried in vacuo. Yield: (36%) (0.07 g, 0.18 mmol). Anal. Calculated for $C_{44}H_{32}N_6O_6ClCr$ (828.1): C 63.81, H 3.89, N 10.15; Found: C 63.85, H 3.86, N 10.20.

2.2.2.3. Synthesis of [Cr (Me–Phimp)$_2$] (ClO_4) (3)

This complex was prepared in a similar procedure as for **1** and **2**. Yield: (37%) (0.14 g, 0.18 mmol). Anal. Calculated for $C_{38}H_{32}N_6O_6ClCr$ (756.1): C 60.36, H 4.27, N 11.11; Found: C 60.38, H 4.30, N 11.18.

2.3. Generation of the phenoxyl radical complexes:

The phenoxyl radical species of the chromium complexes were generated *in situ* by adding $(NH_4)_2[Ce^{IV}(NO_3)_6]$ (CAN, 2.0 x 10^{-4}M) into the acetonitrile solution of these phenolate complexes (1.0 x 10^{-4}M) at 0°C. The decomposition rate of in situ generated phenoxyl radical metal complexes was monitored by a time dependent study at a λ value.

2.4. Catalytic activity studies:

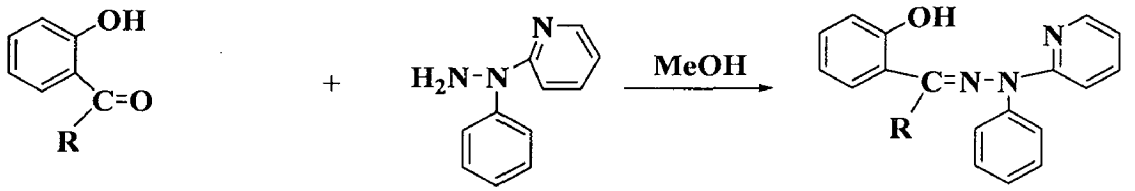
The catalytic activity measurements were carried out in a 50 mL double-necked flask fitted with a water condenser. Styrene (0.208 g, 2.0 mmol) and the catalyst (complex **1**, **2** or **3**) for the activity test (0.01 mmol) were mixed in 2.0 mL of acetonitrile and the reaction mixture was heated with continuous stirring on an oil bath maintained at 90°C. 30% aqueous H_2O_2 (0.453 g, 4.0 mmol) was added to the reaction mixture and the reaction was carried out for 6 h. The catalyst was separated by extraction with hexane and the hexane layer was analyzed after 1 h, 2 h and at the end, the products were analyzed quantitatively by a TRACE GC ULTRA gas chromatograph having RT-10523 column (30 m × 0.25 mm) and FID detector. The products were identified by GC–MS (Perkin-Elmer Clasus 500 column; 30 m × 60 mm). An amount of *cis*-cyclooctene (0.220 g, 2.0 mmol) or *trans*-stilbene (0.364 g, 2.0 mmol) and the catalyst (complex **1**, **2** or **3**) (0.01 mmol) was taken in 2.0 mL of acetonitrile and heated at 90°C. After addition of H_2O_2 (0.453 g, 4.0 mmol), the reaction was carried out for 6 h and the products were analyzed by the procedure as mentioned previously.

3. Results and discussion:

3.1. Synthesis and characterization of ligand:

The tridentate ligands PhimpH was prepared by stirring 2-(1-phenylhydrazinyl)pyridine with salicylaldehyde whereas N-PhimpH has been prepared by

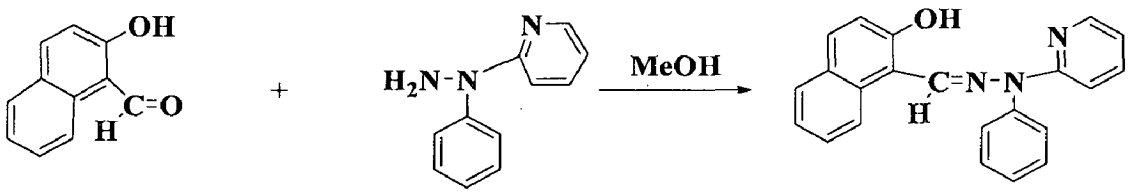
refluxing 2-(1-phenylhydrazinyl)pyridine with 2-hydroxy-1-napthaldehyde in methanol. Me-PhimpH was prepared by stirring 2-(1-phenylhydrazinyl)pyridine with o-hydroxyacetophenone in presence of few drops of concentrated HCl in methanol. Synthetic preparations of these ligands are shown in Scheme 3.1. These ligands were soluble in several organic solvent like dichloromethane, methanol, acetonitrile, dimethylformamide and acetone.[110]



Salicyaldehyde, R = H
o-Hydroxyacetophenone, R = Me

2-(1-phenylhydrazinyl)pyridine

PhimpH, R = H
Me-PhimpH, R = Me



2-Hydroxy-1-napthaldehyde

2-(1-phenylhydrazinyl)pyridine

N-PhimpH

Scheme 2.2 Synthetic pathways of the ligands

A characterization of this ligand was performed by UV–visible, FT-IR, GC-MS spectrometry and NMR (^1H and ^{13}C) spectroscopic studies.[110] All the spectral data were tabulated in Table 2.1. The IR-spectrum of Schiff base ligand, PhimpH showed a band at 1607 cm^{-1} which was designated as $\nu_{-HC=N}$ for the Schiff base ligand. The corresponding band for N-PhimpH and Me-PhimpH was found to be at 1620 and 1598 cm^{-1} respectively. UV-visible spectra of ligands PhimpH, N-PhimpH and Me-PhimpH showed bands near 339, 332 and 350 nm respectively. However, N-PhimpH has two extra peaks near 371 and 385 nm. All these bands were assigned as intramolecular π-π^* or n-π^* transitions. Characterization of PhimpH, N-PhimpH and Me-PhimpH were also established unambiguously by NMR and

GC-MS spectrometry studies. The characteristic peak for -OH in all ligands came around δ = 12.0-13.0 ppm. ^{1}H NMR spectrum of Me-PhimpH is shown in Fig. 2.1. MS spectra of ligands PhimpH and Me-PhimpH showed molecular ion (M^+) peak at 289 (7.3%) and 303 (7.7%) respectively and base peak at 169 (100%). The base peak at 169 was due to N-phenylpyridylamine cation (mass spectra of ligands PhimpH, Me-PhimpH and probable fragmentation patterns of Me-PhimpH are shown in Fig. 2.2-2.3 and Scheme 2.3). NMR data for all ligands are listed in Table 2.2.

^{1}H NMR spectrum of Me-PhimpH

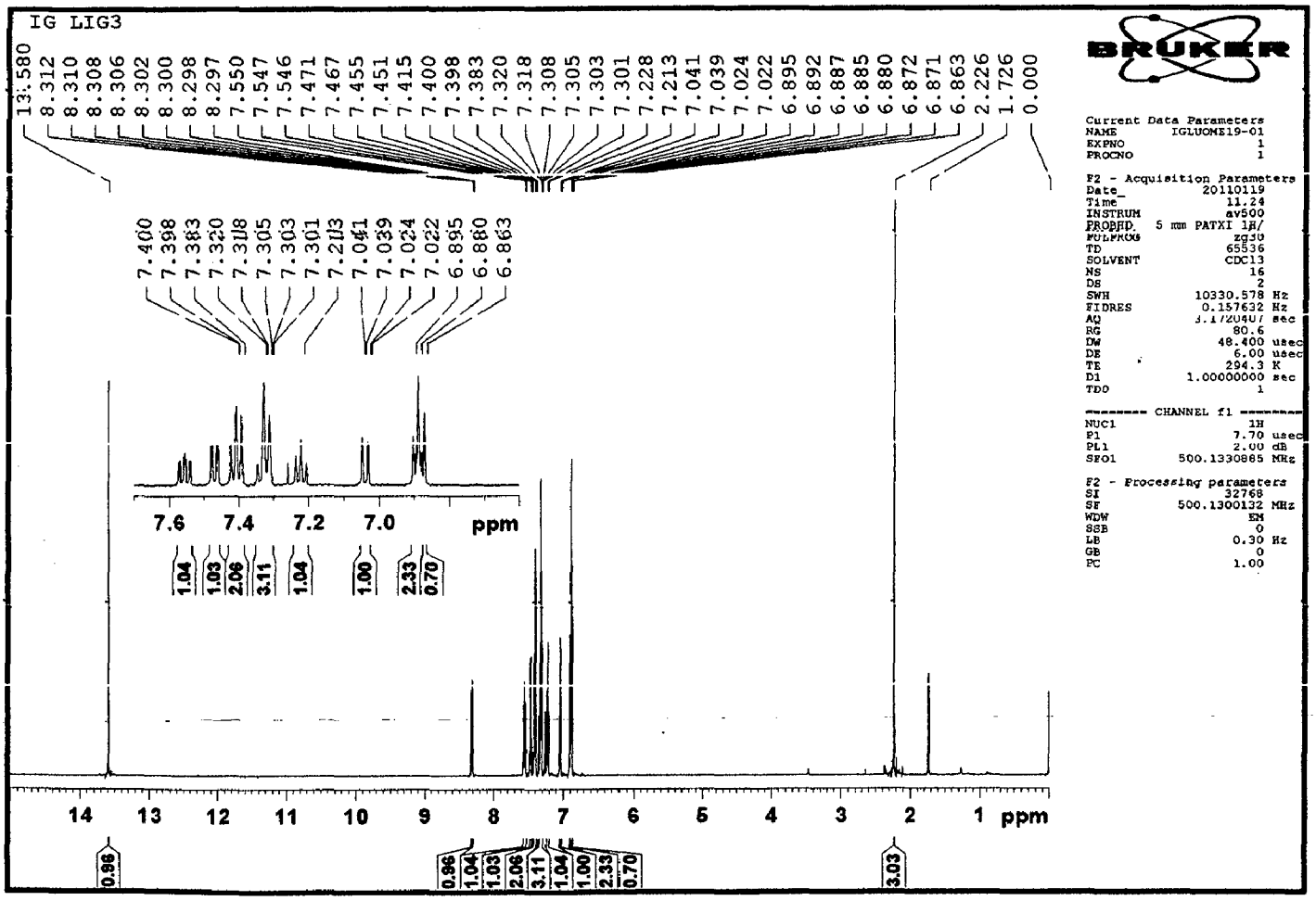


Fig. 2.1. ^{1}H NMR spectrum of selected proton of Me-PhimpH in $CDCl_3$.

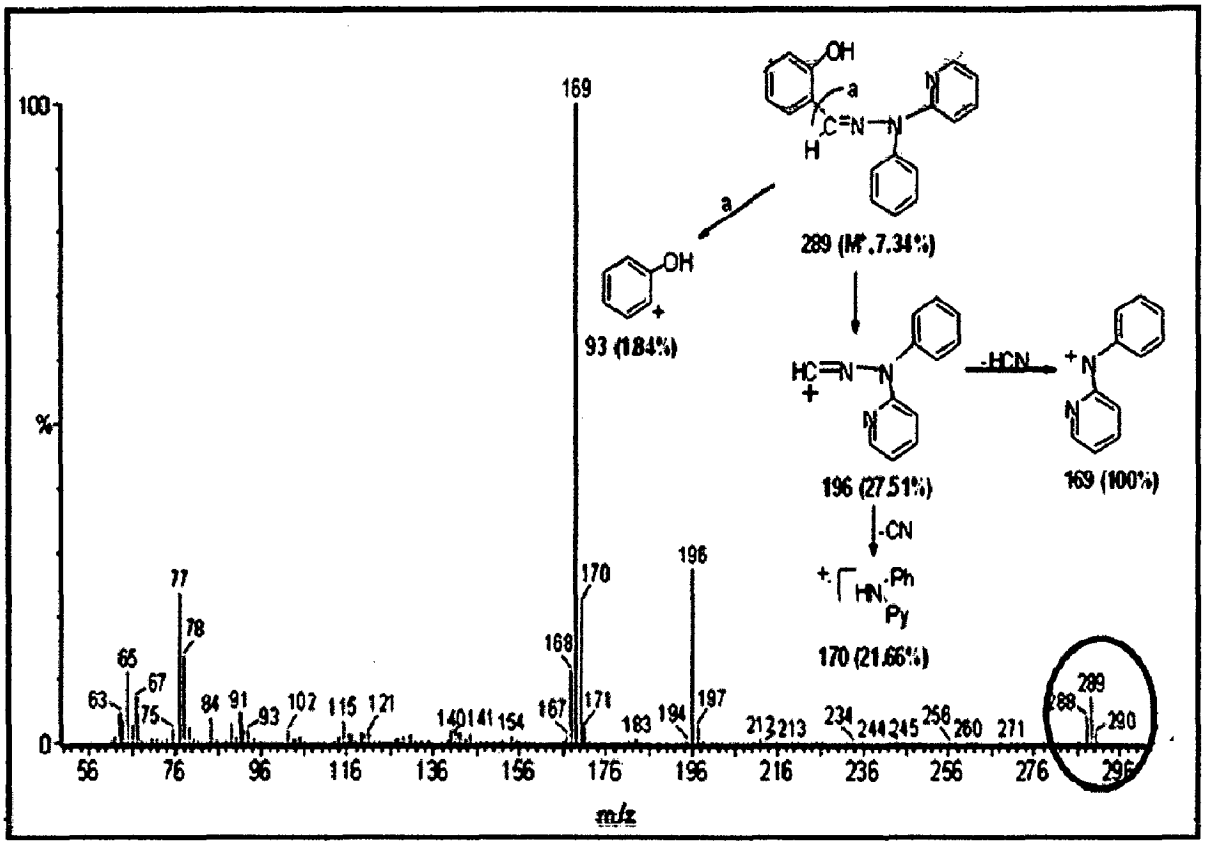


Fig. 2.2. Mass-spectrum and fragmentation pattern for ligand PhimpH.

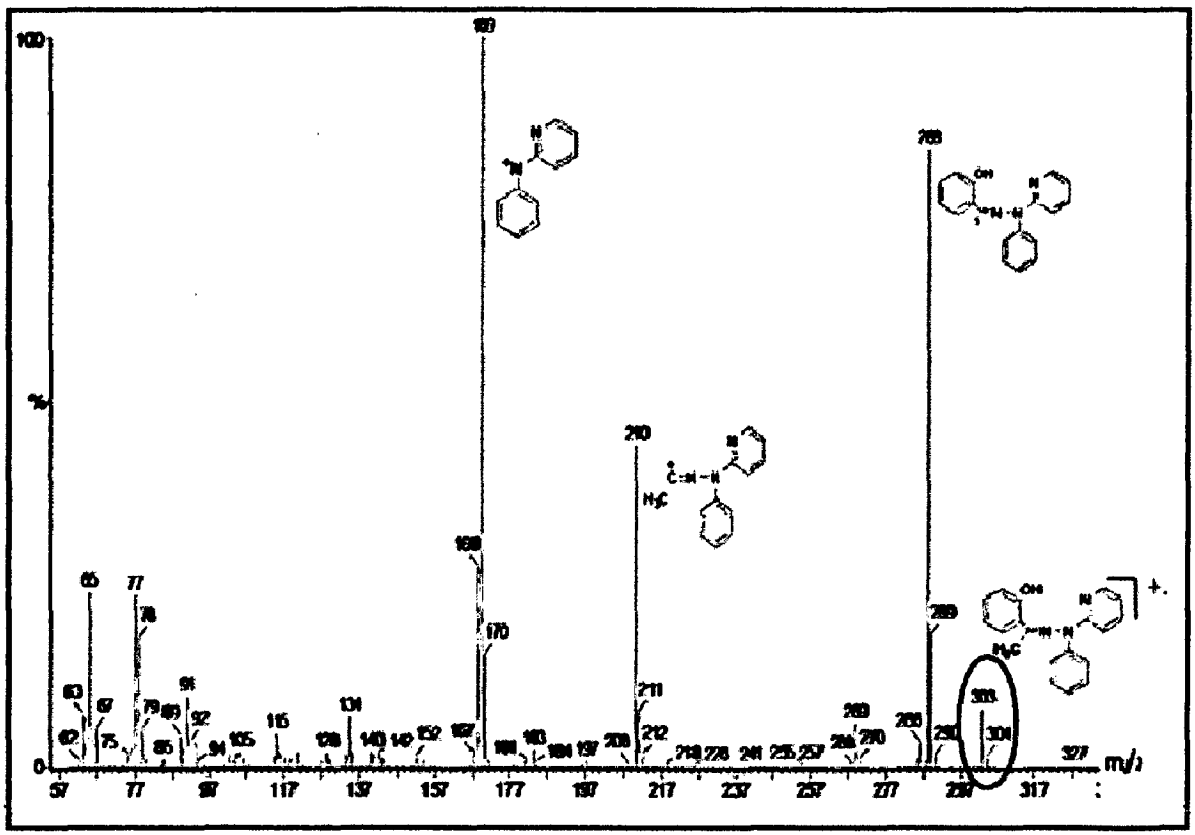
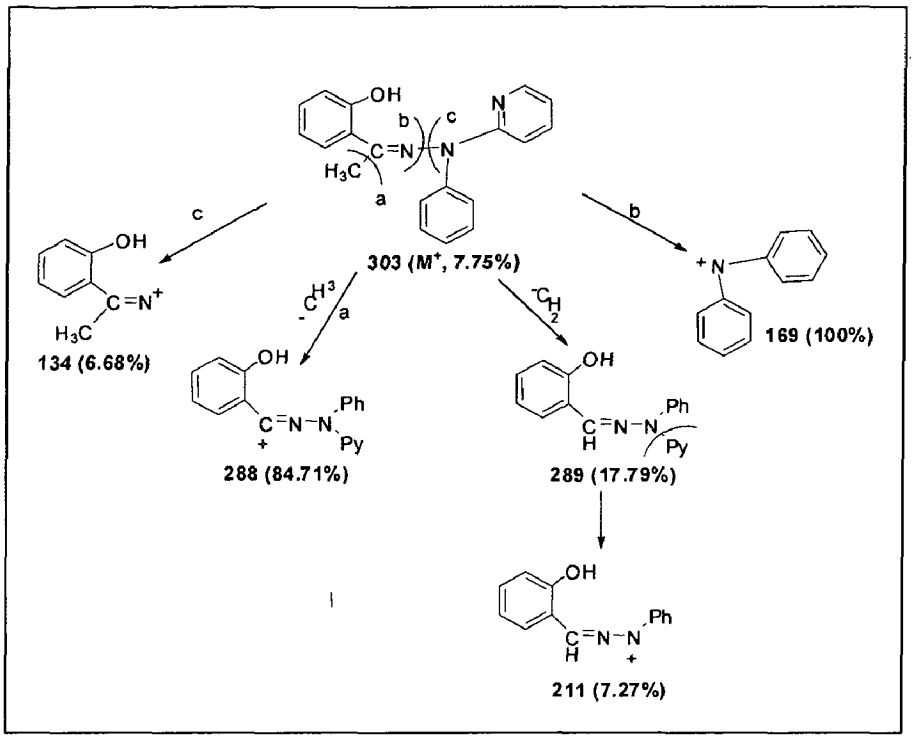


Fig. 2.3. Mass-spectrum for ligand Me-PhimpH.



Scheme 2.3 Fragmentation pattern for ligand Me-PhimpH

Table 2.1 Selected spectral data of ligands*

Ligand	IR data (cm^{-1})[a]			UV-visible data (λ_{max}/nm, ε/$M^{-1}cm^{-1}$)[b]
	ν_{OH}	$\nu_{-CH=N}$	ν_{-C-OPh}	
PhimpH	3441	1607	1269	238 (33,133), 310 (27,956), 339 (40,163)
N-PhimpH	3437	1620	1282	250 (37,990), 320 (15,980), 332 (21,560), 371 (32,400), 385 (30,450)
Me-PhimpH	3433	1598	1272	258 (20,012), 290 (15,131), 349 (12,359)

[a]using KBr pellets, [b]UV-visible data recorded in dichloromethane.

**Spectra are shown in appendices A_1- A_6.*

Table 2.2 ^{1}H NMR and ^{13}C NMR spectral data of ligands*

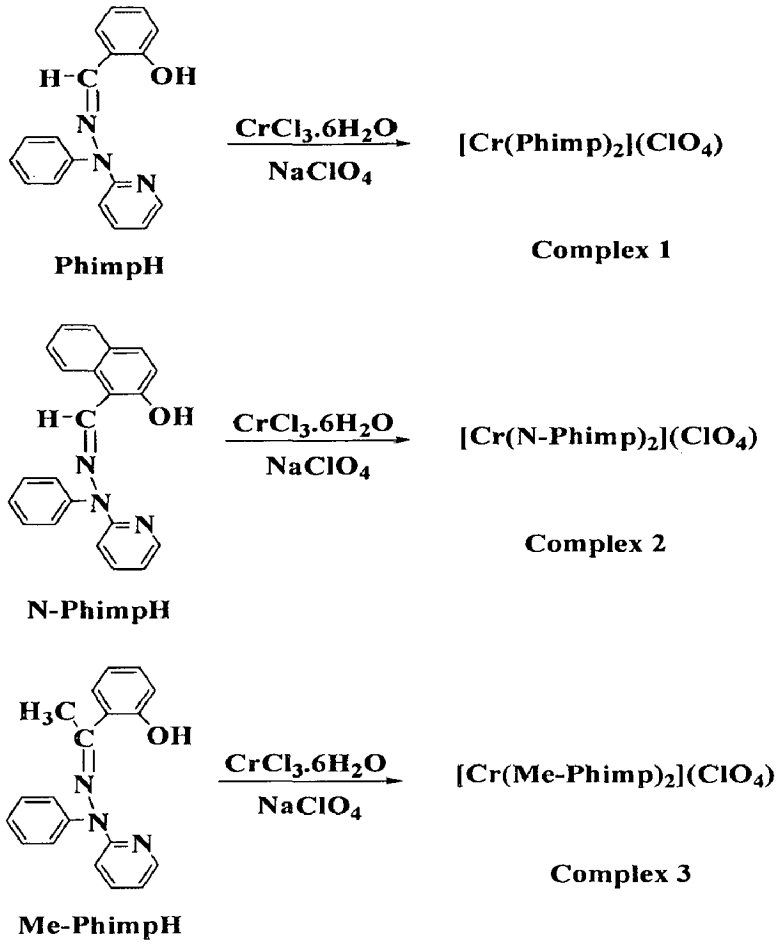
Ligand	^{1}H NMR, $CDCl_3$ δ (ppm from TMS), J/Hz	^{13}C NMR δ (ppm from TMS)
PhimpH	6.84-6.87 (m, 2H), 6.96-6.99 (m, 2H), 7.01-7.03 (d, J = 8.00 Hz, 1H), 7.20-7.24 (td, J = 6.75 Hz, 2.00 Hz, 1H), 7.29-7.31 (d, J = 7.50 Hz, 2H), 7.40 (s, 1H), 7.52-7.56 (t, J = 7.00 Hz, 1H), 7.57-7.61 (td, J = 6.75 Hz, 2.00 Hz, 1H), 8.27-8.28 (d, J= 5.0 Hz, 1H), 11.73 (s, 1H).	108.73, 116.51, 116.68, 118.76, 119.06, 129.10, 129.81, 129.97, 130.01, 130.71, 137.54, 137.71, 141.11, 148.22, 156.57, 157.32.
N-PhimpH	6.88-6.89 (m, 1H), 6.96-6.98 (m, 1H), 7.26-7.28 (m, 2H), 7.37-7.38 (m, 1H), 7.38-7.40 (dd, J = 1.0 Hz, 8.5 Hz, 2H), 7.50-7.52 (m, 1H), 7.58-7.61 (m, 2H), 7.69-7.74 (m, 3H), 8.33-8.34 (d, J = 2.0 Hz, 2H), 13.03 (s, 1H).	108.85, 109.26, 116.62, 119.31, 119.79, 123.15, 126.92, 128.25, 129.03, 129.46, 130.02, 131.08, 131.37, 131.83, 137.71, 137.82, 137.87, 148.44, 156.60, 157.19.
Me-PhimpH	2.23 (s, 3H), 6.86-6.90 (m, 3H), 7.02-7.04 (dd, J = 7.0 Hz, 1.25 Hz, 1H), 7.21-7.24 (td, J = 6.25, 1.00 Hz, 1H), 7.30-7.32 (m, 3H), 7.34-7.42 (t, J = 6.25 Hz, 2H), 7.46-7.48 (dd, J = 6.50 Hz, 1.50 Hz, 1H), 7.54-7.57 (td, J = 6.75, 2.00 Hz, 1H), 8.30-8.32 (d, 6.50 Hz, 1H), 13.58 (s, 1H).	16.92, 110.82, 117.14, 117.95, 118.53, 119.51, 125.32, 125.64, 128.44, 129.40, 132.05, 137.67, 145.33, 148.17, 158.62, 160.27, 171.79.

Solvent was used $CDCl_3$; [s]singlet, [d]doublet, [t]triplet, [m]multiplet;

**NMR spectra of ^{1}H and ^{13}C are shown in appendices A_{10}-A_{15}.*

3.2. Synthesis and characterization of metal complex:

The tridentate ligands PhimpH, N-PhimpH and Me-PhimpH were synthesized by the reported procedure.[110] Complexes were synthesized by the stirring of ligands with chromium(III) salt ($CrCl_3.6H_2O$) in ethanol for 6 h. Bis complexes were obtained even though reaction was started by 1:1 ratio of ligand and salts or 2:1. Details of the syntheses are summarized in Scheme 2.4.



Scheme 2.4 Synthetic pathways of Chromium complexes

3.2.1. IR spectral studies:

The characteristic band of azomethine ($\nu_{\text{-HC=N}}$) group in IR spectra of the ligands were observed near 1598-1620 cm^{-1}.[111,112] Coordination of the nitrogen to the metal centre reduced the electron density in the azomethine moiety and thus lowered the ($\nu_{\text{-HC=N}}$) frequency. Decrease in stretching frequencies for ($\nu_{\text{-HC=N}}$) in complexes **1, 2** and **3** clearly indicated the ligation of azomethine nitrogen (-HC=N-) to metal centre.[113,114] The bands near 1090 cm^{-1} together with a band at 623 cm^{-1} were found in all chromium(III) complexes **1-3** which showed the presence of perchlorate ion. The lack of splitting of these two bands suggested the presence of non-coordinated perchlorate ion to the metal centre (Fig. 2.4).[115] A high intensity band near 1300 cm^{-1} in the Schiff's bases can be assigned as phenol C-O ($\nu_{\text{C-OPh}}$) stretching freqency. Shift of $\nu_{\text{C-O}}$ to higher frequency supported deprotonation and the formation of

metal oxygen bond.[116] It was further supported by disappearance of the broad $\nu_{O\text{-}H}$ band in IR spectra of all metal complexes (Table 2.3).

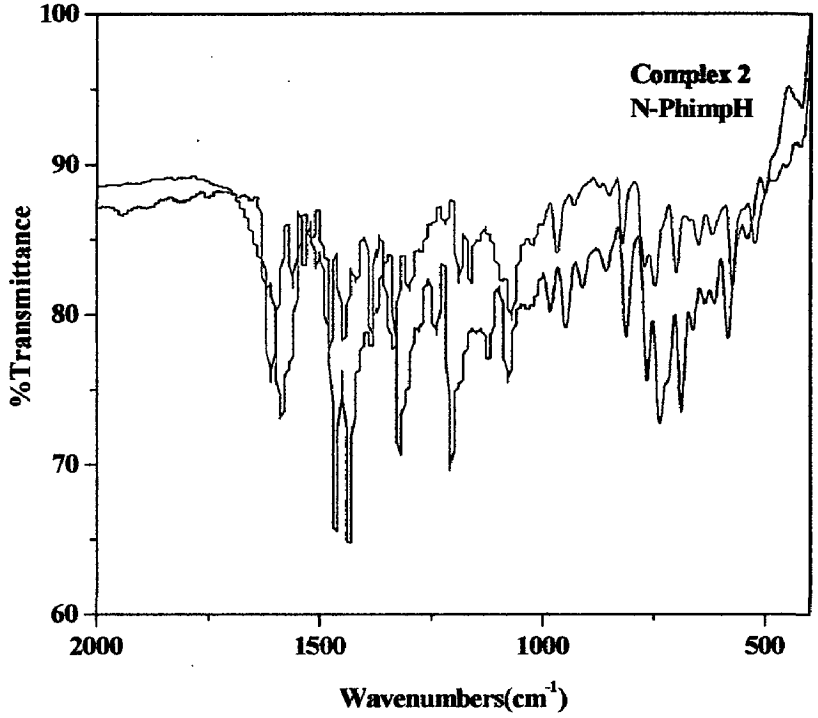


Fig. 2.4. IR spectra of ligand **N-PhimpH** and complex **2.**

3.2.2. Conductivity studies:

Experimental data for molar conductivity are tabulated in Table 2.3. The molar conductivity measurements in dimethylformamide at *ca.* 10^{-3}M determined at 298 K for complexes were found to be 48-59 $\Omega^{-1}cm^2mol^{-1}$. These values confirmed the uni-univalent (1:1) electrolyte behaviour in solution.[118]

3.2.3. Magnetic moment studies:

For complexes magnetic moments were measured at room temperature (300 K). The magnetic moment values for **1**, **2** and **3** were 3.94, 3.98 and 3.94 BM respectively, which were paramagnetic in nature and predicting the stabilization of $3d^3$ system.[119] (Table 2.3).

Table 2.3 Data for IR, conductivity and magnetic moment of complexes **1-3***

Complex	IR data (cm^{-1})[a]			Conductivity data ($\Omega^{-1}cm^2mol^{-1}$)[b]	μ_{eff} (μ_B)[c]
	$\nu_{-HC=N}$	ν_{C-Oph}	ν_{ClO4^-}		
1	1606	1306	1091, 621	52.0	3.94
2	1610	1300	1100, 620	48.0	3.98
3	1611	1299	1094, 621	59.0	3.94

[a]Using KBr pellets, [b]Solvent: dimethylformamide, [c]recorded at 300 K

**Spectra are shown in appendices A_{16}- A_{18}.*

3.2.4. Electronic spectral studies:

The absorption spectra of complexes were recorded in acetonitrile at room temperature (Fig. 2.5). The transition band near 235-245 nm was designated as π-π^* transition in ligand as well as in complexes (Table 2.4). The band near 420 nm for complexes **1**, **2** and **3** was assigned as ligand-to-metal charge transfer (LMCT) transition of phenolato oxygen to chromium(III).[117] However, in addition **2** possesses one absorption band ~450 nm which was also of charge transfer type.

Table 2.4 Electronic spectra of complexes **1-3** and radical species*

Complex [a]	λmax/nm (ε/M^{-1} cm^{-1})]
1	427(8,700), 338 (18,200), 302 (21,400), 244 (37,900).
[1]$^{\bullet+}$	601(420), 551(720), 422(8,800), 336(18,280), 300(22,600), 246(36,800)
2	484 (4,300), 445 (7,900), 426 (7,400), 350 (16,600), 257 (32,400), 244 (34,600).
[2]$^{\bullet+}$	805(600), 672(360), 444(12020), 424(11940), 349(24040).
3	409 (7,300), 354 (10,300), 308 (15,800), 235 (42,300).
[3]$^{\bullet+}$	740(100), 560(420), 399(6,100), 311(14,140), 268(23,960).

[a] All complexes in parentheses are radical species, [b]Solvent: acetonitrile.

**Spectra are shown in appendices A_{19}- A_{27}.*

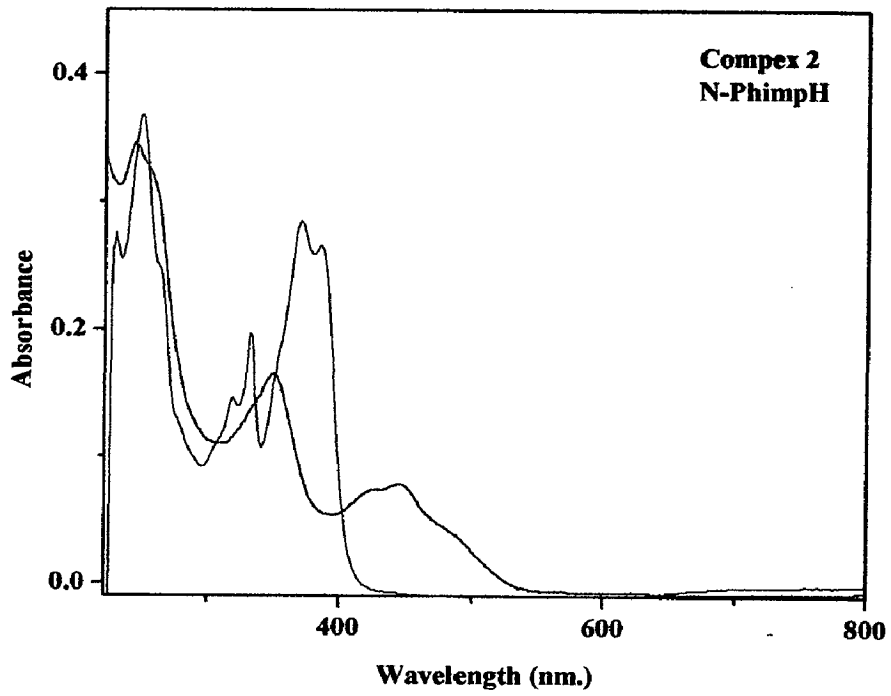


Fig. 2.5. UV-visible spectra of ligand **N-PhimpH** and complex **2.**

3.2.5. Cyclic voltammetry studies:

The redox potentials of complexes **1-3** are described in Table 2.5 and representative voltammograms are shown in appendices.

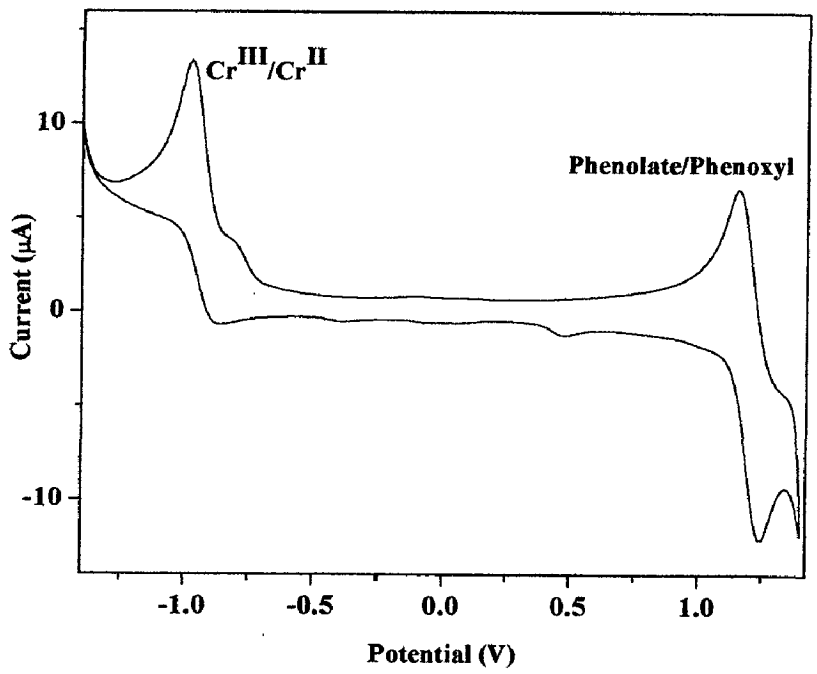


Fig. 2.6. Cyclic voltammogram of complex **2.**

The neutral uncomplexed ligands did not show any cyclic voltammogram over the range from 0.0 to 1.1 V; hence all the curves were attributed to the redox activity of our complexes. For **1** and **2** showed quasi-reversible peaks and from the Table 3, it has been shown that one electron is involved in this redox process. The wave detected at 0.12-0.92 V vs $Ag^+/AgCl$ has been considered as one-electron-redox process attributed to the reduction of $[Cr^{III}L_2]^+$ to $[Cr^{II}L_2]$ (where L = $Phimp^-$, $N\text{-}Phimp^-$, $Me\text{-}Phimp^-$) indicating Cr(III)/Cr(II) redox couple. Whereas **3** showed irreversible peak at –1.3 V. Interestingly, cyclic voltammogram of 2 afforded a reversible peak ~ 1.2 V due to ligand centered oxidation (Fig. 2.6). The $E_{1/2}$ and ΔE values were found to be +1.20 V and 0.093 V respectively vs $Ag^+/AgCl$ and was described as phenoxyl radical redox couple.[120,121]

Table 2.5 Cyclic voltammetric redox potentials for complexes **1-3** at 298 K. Conditions: solvent DCM; supporting electrolyte, TBAP (0.1 M); working electrode glassy carbon; reference electrode, Ag/AgCl; scan rate 0.1 V/s, concentration ~10^{-3} M*

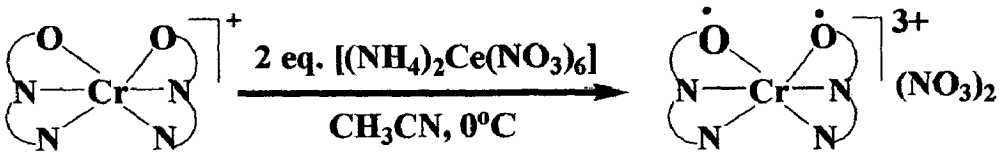
Complex	[Cr(III)/Cr(II)]	
	$E_{1/2}$[a]/V	ΔE[b]/mV
1	0.123	64
2	0.92, 1.20	112, 93
3	-	-

[a]$E_{1/2} = 0.5(E_{pa} + E_{pc})$ where E_{pa} , E_{pc} are anodic and cathodic peak potential.
[b]$\Delta E = (E_{pa} - E_{pc})$.

**Voltammograms are shown in Appendices A_{28}- A_{30}.*

3.2.6. Generation of phenoxyl radical complexes

Generation of phenoxyl radical complexes through the ligand centered oxidation of phenolato chromium(III) complexes **1-3** by addition of two equivalents of the CAN afforded the corresponding phenoxyl radical complexes at 0°C (Scheme 2.5).



Scheme 2.5 Schematic drawing for generation of phenoxyl radical complexes

The formation of the phenoxyl radical complexes of **1-3** showed dark reddish brown color and have been confirmed by the characteristic peaks in UV-visible spectra for phenoxyl radical complexes (Table 2.4.)[122,124] Upon addition of CAN, the LMCT band for the complex **2** near 484 nm readily disappeared together with the concomitant appearance of the new bands at 672 and 805 nm which indicated the formation of phenoxyl radical complex (Fig. 2.7). A similar absorption spectrum (422nm, 551 nm and 601 nm) of **1** and (405 nm, 560 nm and 740 nm) **3** were also obtained during the oxidation in the same procedure given as above. Redish brown color and characterstics peaks in UV-visible spectra showed the phenoxyl radical complexes of **1-3**.

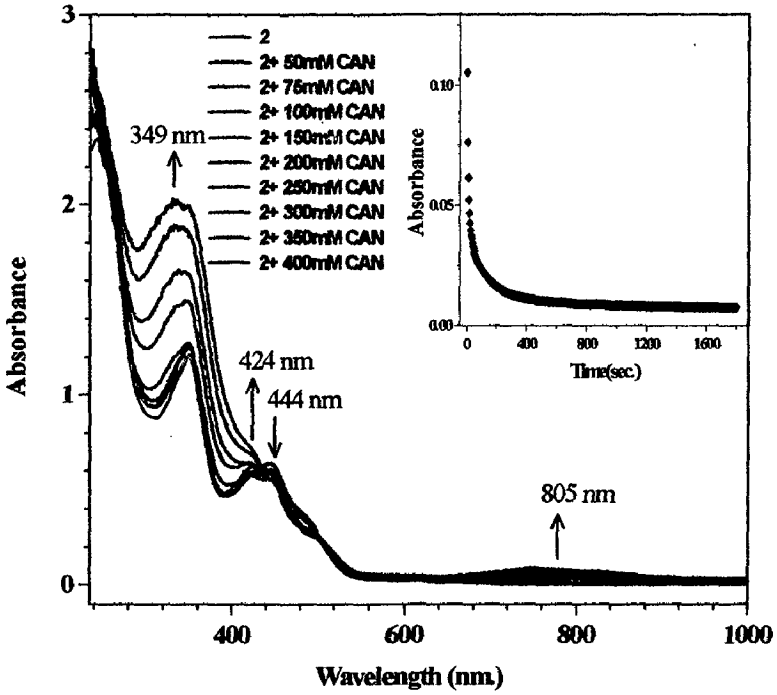


Fig. 2.7. UV-visible spectra of generated phenoxyl radical complex of **2** (50 μM) in acetonitrile by CAN (50-400 μM) at 0 °C, Inset: Decomposition of generated phenoxyl radical complex of **2** monitored by 805 nm at 0°C.

During our studies on the synthesis of phenoxyl radical complexes, we found that the radicals were unstable and gradually decomposed within very short time (2-5 min) because of the participation of oxygen or solvent for the regeneration of the precursor complex.[123] The decomposition rate of radical complexes of **1-3** was monitored by a time dependent study at λ values of 601nm, 805 nm and 740 nm. It is reported in the literature that stability of the phenoxyl radical complexes increase with the increase in λ value of the lowest energy transition,[125] hence, the stability order of the phenoxyl radical complexes was **2** >**3** > **1**. The higher stability of phenoxyl radical complex of **2** may be due to engagement of *ortho* and *para* position of phenolato function in naphthol ring. We have generated and characterized the phenoxyl radical complexes, however the catalytic activity of these radical complexes (conversion of primary alcohol to aldehydes) are under progress.

3.2.7. Thermal studies:

In the present investigation, the heating rates were suitably controlled at 10°C min^{-1} under nitrogen atmosphere and the weight loss was measured from ambient temperature up to ~ 800°C. These data was necessary to check the thermal stability of the complexes **1** -**3** before we proceed to investigate the catalytic activity of metal complexes.The results of the thermogravimetric analysis of the complexes are not very conclusive in terms of the loss of specific group(s) on increasing the temperature under nitrogen atmosphere. However, it is clear from the thermogravimetric profiles that these complexes are stable up to 260°C (Table 2.6). Complex **1** loses weight in three steps. A weight loss of 31.5% was observed in the up to 310°C in the first two overlapping steps followed by a weight loss of 68.3% in a sharp and narrow temperature range of 310-420°C. The total weight loss of complex **1** is 99.8%. Similarly, complex **2** and **3** lose the maximum weight of 63.6% and 45.7% in the third, a sharp narrow step (between 360°C and 440°C) and in the second step (between 257-267°C)

respectively. Finally, the remaining loss of 4.6% for **2** and 12.4% for **3** is in the range of 400-770°C. The initial decomposition and inflection temperatures have been used as an indication on the thermal stability of complexes.[126]

Table 2.6 Data for TGA/DTA of complexes **1-3***

Complex	Temperature Range (°C)	Loss (wt%)[a]	Types of loss
1	20-270	7.7	Exothermic
	270-310	31.5	Exothermic
	310-420	99.8	Exothermic
2	20-275	4.9	Exothermic
	275-360	28.3	Exothermic
	360-440	91.9	Exothermic
	440-770	96.5	Exothermic
3	20-257	6.3	Exothermic
	257-267	52.0	Exothermic
	267-404	85.6	Exothermic
	404-480	95.6	Exothermic
	480-772	98.0	Exothermic

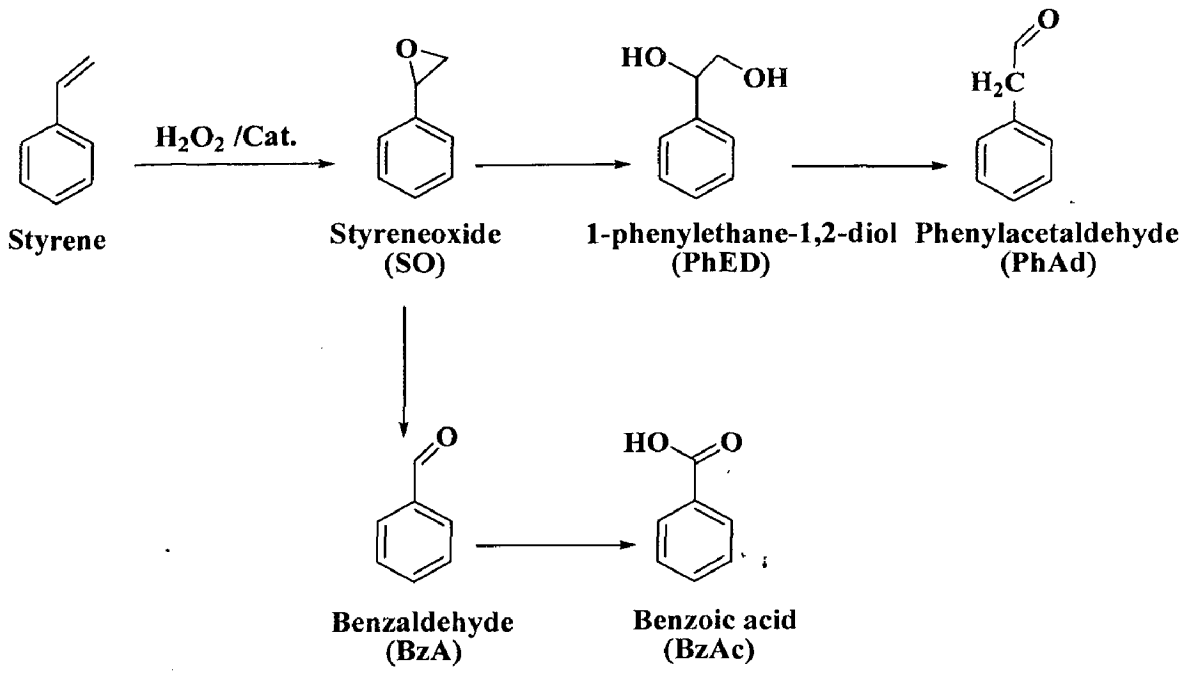
[a]Rate:10°C/min, Gas:Nitrogen(200 ml/min, Reference:Alumina Powder.

**DTA-TGA curves are shown in appendices A_{31}- A_{33}.*

3.3. Catalytic activity studies:

3.3.1. Oxidation of styrene:

Oxidation of styrene has been investigated by several workers using homogeneous as well as heterogeneous catalysts and major oxidation products generally obtained are styreneoxide, benzaldehyde, benzoic acid, phenyl acetaldehyde and 1- phenylethane-1,2-diol.[127-132] We have found that Cr(III) complexes **1, 2** and **3** satisfactorily catalyse the oxidation of styrene using H_2O_2 as oxidant and gives styreneoxide, benzaldehyde, 1-phenylethane-1,2-diol and benzoic acid along with some unidentified products in homogeneous conditions (Scheme 2.6).



Scheme 2.6 Various oxidation products of styrene

In order to get the maximum oxidation of styrene, effect of time on the oxidation of styrene reaction has been studied in detail. Carrying out this reaction in 2.0 mL acetonitrile at 90°C with 30% aqueous H_2O_2 under these reaction conditions (i.e. 1:2, substrate to oxidant ratio) gave 80-90% conversion after 6 h but the recovery of the catalyst from the reaction mixture became very difficult due to partial decomposition as well as blending of the complexes with solvent. Thus, under the above reaction conditions (i.e. styrene (0.208 g, 2.0 mmol), catalyst (0.01 mmol) and 30% aqueous H_2O_2 (0.453 g, 4.0 mmol), acetonitrile (2.0 mL), temperature (90°C) and time (6 h)), catalytic activity of all the three complexes **1**, **2** and **3** was analyzed (Fig. 2.8).

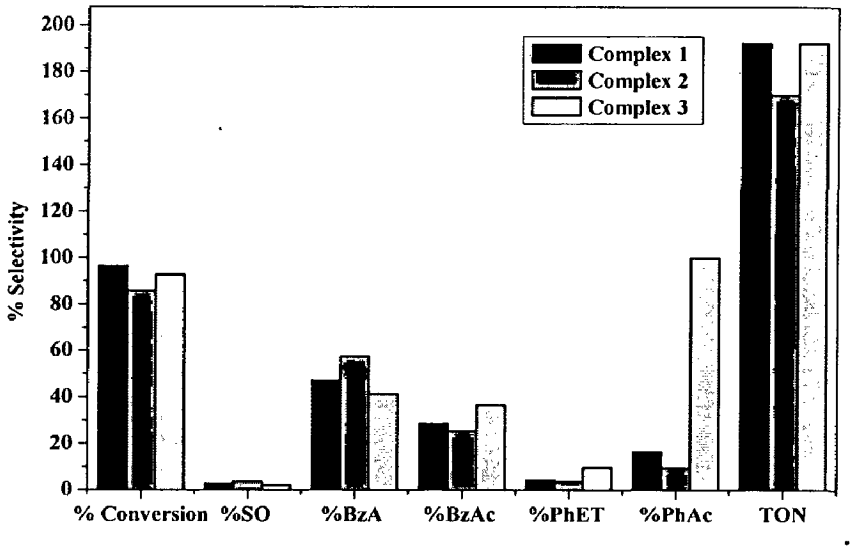


Fig. 2.8. Bar diagram showing conversion of styrene and selectivity of products in 6h.

The percent conversion of styrene was found to be 96.5%, 92.7% and 86.0% for **1**, **3** and **2** respectively. Moreover, the formations of styreneoxide were 2.7, 2.2 and 3.6%, respectively (Table 2.7).

Table 2.7 Effect of time on the oxidation of styrene and the product selectivity[a]

Catalyst	Time	Percent of conversion	Percent of product selectivity					TON
			SO[b]	BzA[c]	BzAc[d]	PhED[e]	[f]PhAc	
1	1	34. 5	15.1	80.7	-	4.2	-	-
	2	38.1	3.1	91.9	-	5.0	-	-
	6	96. 5	2.7	47.3	28.6	4.4	17.0	192.5
2	1	29.4	1.7	95.0	-	3.3	-	-
	2	47.0	2.2	93.2	-	4.6	-	-
	6	86.0	3.6	57.8	25.4	3.6	9.6	170.0
3	1	39.6	1.2	90.5	2.6	-	5.7	-
	2	50.4	1.4	88.5	2.5	1.0	6.6	-
	3	92.7	2.2	41.5	36.7	9.6	10.0	192.3

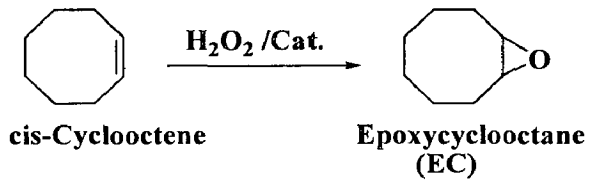
[a]Reaction conditions: styrene (0.208g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453g, 4.0 mmol), temperature (90°C) and acetonitrile (2 mL).[b]Styrene oxide, [c]Benzaldehyde, [d]Benzoic acid, [e]1-Phenylethane-1,2-diol, [f]Phenylacetaldehyde.

Thus, turns over number (TON: moles of substrate converted per mole of metal in the solid catalyst) of the three catalysts are ~192.2 (for **1**and **3**) and 170.0 (for **2**). However, in all cases, the selectivity of various products follows the order: benzaldehyde > benzoic acid >

Phenylacetaldehyde > 1-phenylethane- 1,2-diol > styreneoxide. The highest formation of benzaldehyde is probably due to a nucleophilic attack of H_2O_2 to styreneoxide. Benzaldehyde formation may also be facilitated by direct oxidative cleavage of the styrene side chain double bond via radical mechanism. Other products, e.g. benzoic acid formation through benzaldehyde is rather slow in all reactions. Water present in H_2O_2 as well as formed during the reaction if any, is probably responsible for partial hydrolysis of styreneoxide to 1-phenylethane-1,2-diol.

3.3.2. Oxidation of cis-cyclooctene:

Oxidation of *cis*-cyclooctene catalysed by complexes **1**, **2** and **3** gave epoxycyclooctane (Scheme 2.7)[133] along with some unidentified products.



Scheme 2.7 Oxidation product of cis- Cyclooctene

Catalytic activity of all the three complexes **1**, **2** and **3** was analyzed at reaction conditions (i.e. *cis*-cyclooctene (0.220 g, 2.0 mmol), catalyst (0.01 mmol) and 30% aqueous H_2O_2 (0.453 g, 4.0 mmol), acetonitrile (2.0 mL), temperature (90°C) and time (6 h)), (Fig. 2.9).

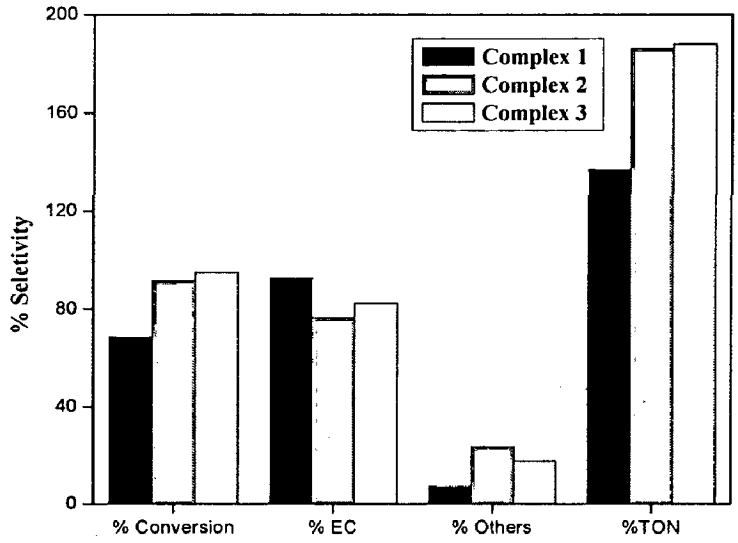


Fig. 2.9. Bar diagram showing conversion of *cis*-Cyclooctene and selectivity of products in 6h.

As 90°C was found an ideal temperature to run the homogeneous catalytic reaction, achieve the maximum oxidation of *cis*-cyclooctene using complexes **1**, **2** and **3** as a representative catalyst. The oxidation of *cis*-cyclooctene after 6 h of the reaction time is illustrated in Table 2.8.

Table 2.8 Effect of time on the oxidation of *cis*-Cyclooctene and the product selectivity[a]

Catalyst	Time	Percent of conversion	Percent of product selectivity		TON
			EC[b]	Others	
1	1	5.7	100	-	-
	2	56.8	92.7	7.3	-
	6	68.7	90.4	9.6	137.0
2	1	34.4	92.1	7.9	-
	2	74.5	86.9	13.1	-
	6	91.8	76.4	23.5	186.3
3	1	40.8	88.6	11.4	-
	2	58.0	85.4	14.6	-
	3	95.0	82.4	17.6	188.1

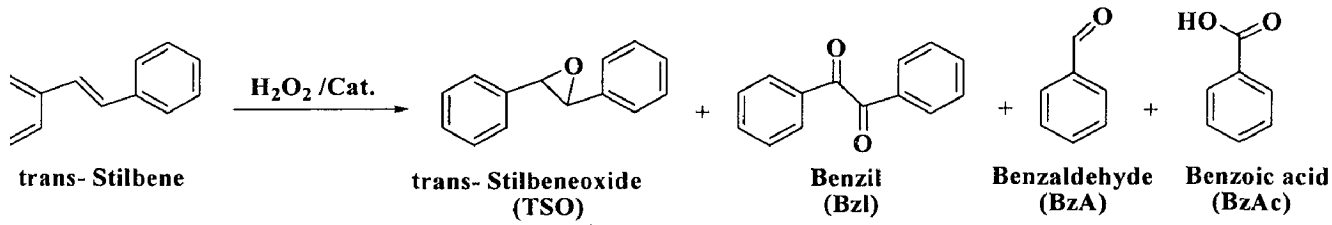
[a]Reaction conditions: *cis*-Cyclooctene (0.22g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453g, 4.0 mmol), temperature (90°C) and acetonitrile (2 mL). [a]Epoxycyclooctane.

The percent conversion of *cis*-Cyclooctene was found to be 95.0%, 92.7% and 68.7% for **3, 2** and **1** respectively. Moreover, the formations of epoxycyclooctane are 82.4, 76.4 and

90.4%, respectively. Thus, turns over number of the three catalysts are ~188.1 (for **2**and **3**) and 137.0 (for **1**). However, in all cases, the selectivity of epoxycyclooctane is appreciable.

3.3.3. Oxidation of trans-stilbene:

Complexes were also tested for the oxidation of *trans*-stilbene where *trans*-stilbeneoxide, benzaldehyde, benzoic acid and 1,2- diphenylethanedione (benzil) were obtained as major oxidation products (Scheme 2.8).[134]



Scheme 2.8 Various oxidation products of trans- Stilbenene

All reactions were carried out by the above procedure which followed in the oxidation of styrene and cis-cyclooctene. Complexes **1**, **2** and **3** were used as a representative catalyst.

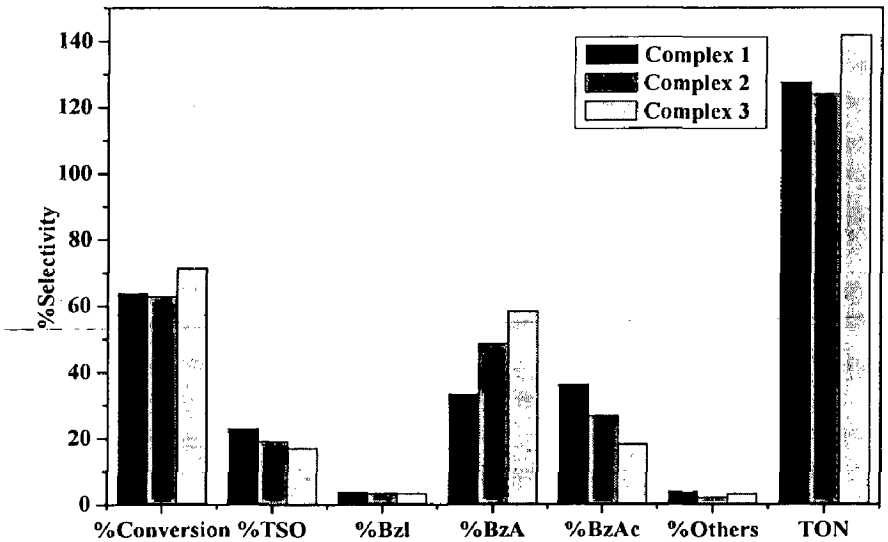


Fig.2.10. Bar diagram showing conversion of *trans*-stilbene and selectivity of products in 6 h.

Results presented in Table 4 shows that time of reaction plays an important role in that increasing the oxidation of *trans*-stilbene. However, the selectivity of epoxide increases

from ~0.4 to 23%. A considerably lower formation of *trans*-stilbeneoxide is probably due to further reaction of *trans*-stilbeneoxide with H_2O_2 to give benzil which in turn converted into benzaldehyde due to hydrolysis. The percentage conversion of all three catalysts along with the selectivity of oxidation products are presented as bar diagrams in Fig. 2.10.

Table 2.9 Effect of time on the oxidation of *trans*-Stilbene and the product selectivity[a]

Catalyst	Time	Percent of Conversion	Percent of product selectivity					TON
			TSO[b]	Bzl[c]	BzA[d]	BzAc[e]	Others	
1	1	14.6	0.4	12.8	83.7	-	3.1	-
	2	15.3	13.0	11.8	56.2	10.7	8.3	-
	6	64.0	22.9	3.9	33.3	36.2	3.8	127.6
2	1	19.5	2.6	8.9	78.7	-	9.8	-
	2	40.7	3.7	4.0	88.3	1.5	2.5	-
	6	62.9	19.0	3.4	48.7	26.8	2.1	124.0
3	1	16.2	2.7	9.5	81.0	1.6	5.3	-
	2	34.8	8.5	7.6	75.1	3.3	5.6	-
	3	71.3	17.0	3.3	58.3	18.2	3.2	141.8

[a]Reaction conditions: *trans*-Stilbene (0.364g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453g, 4.0 mmol), temperature (90 ^{0}C) and acetonitrile (2 ml). [b]*trans*-Stilbene oxide, [c]Benzil, [d]Benzaldehyde, [e]Benzoic acid.

Thus, turns over number of the three catalysts are ~127.0 (for **1** and **2**) and 141.8 (for **3**) (Table 2.9). However, unidentified products are further oxidation products of benzil as indicated by GCMS, but these are only in trace amounts and in the frame of the present study, no efforts were undertaken to separate them.

4. Conclusion:

A new family of mononuclear chromium complexes derived from tridentate ligands have been synthesized and characterized. Investigations of UV-visible, IR spectral studies and magnetic moment data confirmed the formation of this family of complexes **1-3**. The ligands stabilized the Cr(III) complexes which were found to paramagnetic in nature. The TGA profile of the **1, 2** and **3** was indicating that these complexes were thermally stable up to 260°C. The complexes **1**, **2** and **3** described in this report showed a good oxidation catalytic activity comparable to that of a large number of Cr(III) complexes already reported in the literature. The results of the catalytic studies revealed that oxidation of various unfunctionalized alkenes is achievable in the presence of either **1, 2** or **3** using with 30% H_2O_2 as a precursor oxidant, though **2** is comparatively less efficient. We examined the ligand centered oxidation of complexes **1-3** in relevance with the active site modeling of Galactose Oxidase and phenoxyl radical complexes were generated in solution at 0°C. Oxidation *via* phenoxyl radical complexes and related works are under process.

Chapter-2

Studies on catalytic activity of copper complexes derived from tridentate ligands

Abstract

Mononuclear copper (II) complexes ([$Cu(Phimp)_2$] (4) and [$Cu(N\text{-}Phimp)_2$]) of the ligands PhimpH and N-PhimpH were synthesized and characterized by UV-visible, IR, magnetic moment and Conductivity measurements studies. These data were compared with reported results. We investigated catalytic studies of these copper complexes by GC and GC-MS and compared the data with the same derived from chromium complexes.

1. Introduction:

Copper(II) complexes with tetradentate or tridentate Schiff-base ligands are of considerable interest due to their structural and magnetic properties, in addition to being potential models for a number of important biological systems.[135] Several copper(II) Schiff-base ligands complexes exhibit antimicrobial, anti-inflammatory and antipyretic activities,[136] together with an activity similar to super-oxide dismutase.[137] Schiff-base metal complexes are important systems in asymmetric catalysis[138] and can often mimic biological sites. Because of the versatility of the steric and electronic properties, which can be fine-tuned by choosing the appropriate amine precursors and ring substituents, metal complexes of Schiff-bases derived from aromatic carbonyl compounds have received a great deal of attention in connection with studies on asymmetric catalysis and metalloprotein modeling.[139-144] Catalytic epoxidation of alkenes is an important industrial reaction for the production of a wide variety of fine chemicals[145] as they are derived directly from alkenes, a primary petrochemical source. Thus olefin epoxidations/ oxidations catalyzed by a metal complex have now become an important research topic in both organic synthesis and bioinorganic modelling of oxidase. Schiff-base complexes of chromium(III)[147], ruthenium(III)[146] and ruthenium(II)[148] are used as potential catalysts for olefin oxidation.

However, the activity of Schiff-base copper(II) complexes towards catalytic oxidation in a homogeneous medium is not well documented in the literature. So far only a few copper(II) Schiff-base complexes are reported to be catalytically active towards olefin oxidation.[149] There are some reports of molecular oxygen catalyzed oxidation, and 30% hydrogen peroxide is usually considered an environmental friendly oxidant. Herein we report the catalytic studies of copper complexes derived from PhimpH and N-PhimpH.

2. Experimental:

2.1. Materials and methods:

All the solvents used were reagent grade. Purification of solvents was done as mentioned in the ***chapter 1***. $Cu(ClO_4)_2$ (Acros organics, USA) were used as obtained. Other reagents, those were used same as in ***chapter 1*** also.

2.2. Synthesis:

2.2.1. Synthesis of metal complexes:

The ligands have been synthesized by the procedure reported in the previous chapter (***chapter 1***).[110]

2.2.1.1. Synthesis of [Cu(Phimp)$_2$] (4)

A batch (0.289 g, 1.0 mmol) of PhimpH was dissolved in 8 mL acetonitrile and the solution was stirred with (0.024 g, 1.0 mmol) sodium hydride for 30 min. A solution of $Cu(ClO_4)_2.6H_2O$ (0.111 g, 0.3 mmol) in 3 mL acetonitrile was added dropwise to the deprotonated ligand solution. After 15 min of stirring microcrystalline greenish-yellow compound was precipitated. The solid was separated by filtration after 3 h of stirring, washed with acetonitrile and diethyl ether and then dried in *vacuo*. Yield: 73%. Anal. Calculated for $C_{36}H_{28}N_6O_2Cu$ (640.1): C 67.54, H 4.41, N 13.13; Found: C 67.51, H 4.39, N 13.10.

2.2.1.2. Synthesis of [Cu(N-Phimp)$_2$] (5)

This complex was prepared in a similar procedure as for **4**. Yield: 62%. Anal. Calculated for $C_{44}H_{32}N_6O_2Cu$ (740.3): C 71.39, H 4.36, N 11.35; Found: C 71.35, H 4.32, N 11.30.

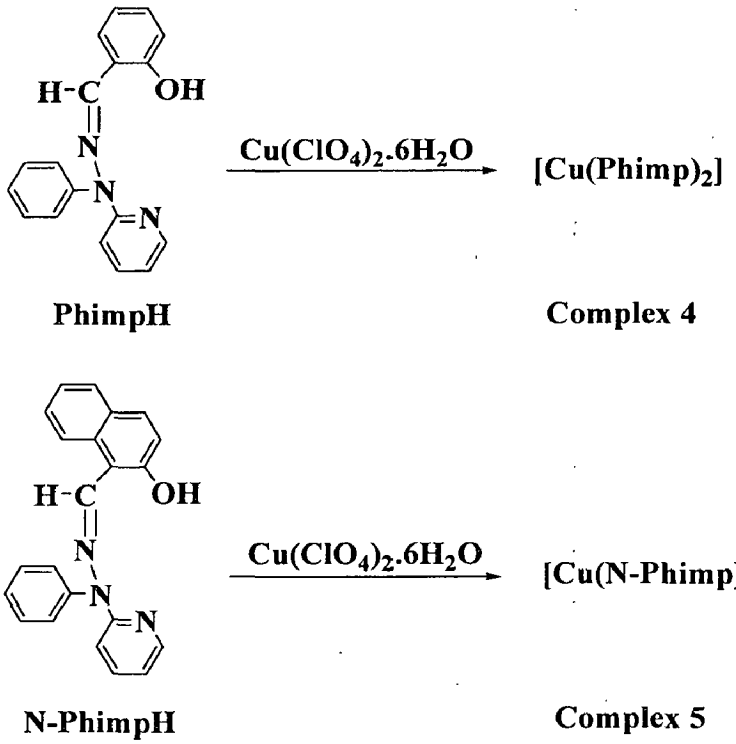
2.3. Catalytic activity studies

General procedure for catalytic oxidation of alkenes with hydrogen peroxide catalyzed by [Cu(Phimp)$_2$] and [Cu(N-Phimp)$_2$] was taken from the previous chapter (**chapter 1**). All reactions were carried out in a 100 ml double-necked flask equipped with a reflux condenser in oil bath. In a typical experiment, 0.01 mmol catalyst, 2.0 mL acetonitrile, 2.0 mmol alkene and 4.0 mmol hydrogen peroxide (30%) were mixed and stirred at 90°C for 6 h. The catalyst was separated by extraction with hexane and the hexane layer was analyzed after 1 h, 2 h and at the end, the products were analyzed quantitatively. The progress reaction of was monitored by GC.

3. Results and discussion:

3.1. Synthesis and characterization of metal complexes:

Ligand PhimpH was prepared according to the reported procedure.[110] Reaction of the deprotonated ligand (Phimp$^-$) and Cu(ClO$_4$)$_2$.6H$_2$O in acetonitrile (3:1, ligand to metal-salt ratio) afforded [Cu(Phimp)$_2$] (**4**). On replacing ligand Phimp$^-$ by deprotonated ligand N-Phimp$^-$, the similar reaction with 1:3 of metal-salt to ligand ratio resulted [Cu(N-Phimp)$_2$] (**5**). Complexes were isolated with a very good yield of 60-65% and their synthesis were summarized in Scheme 3.1.[122]



Scheme 3.1 Synthetic pathways of copper complexes

3.1.1. IR spectral studies:

In IR, the characteristic band of azomethine ($\nu_{HC=N}$) and phenol C-O (ν_{C-OPh}) group in free ligand was observed near 1615 and 1275 cm^{-1} respectively. On the other hand, in the copper complexes the bands were shifted to 1600-1610 cm^{-1} and 1300 cm^{-1} respectively, indicating the coordination of the azomethine nitrogen (-HC=N-) to the metal centre and formation of metal oxygen bond. Coordination of the nitrogen with the metal centre was expected to reduce the electron density in the azomethine moiety and thus lowered the ($\nu_{HC=N}$) frequency[150] and shift of ν_{C-O} to higher frequency supported deprotonation (Fig.3.1). It was further supported by disappearance of the broad ν_{O-H} band in IR spectra of all metal complexes. All values are tabulated in table 3.1.

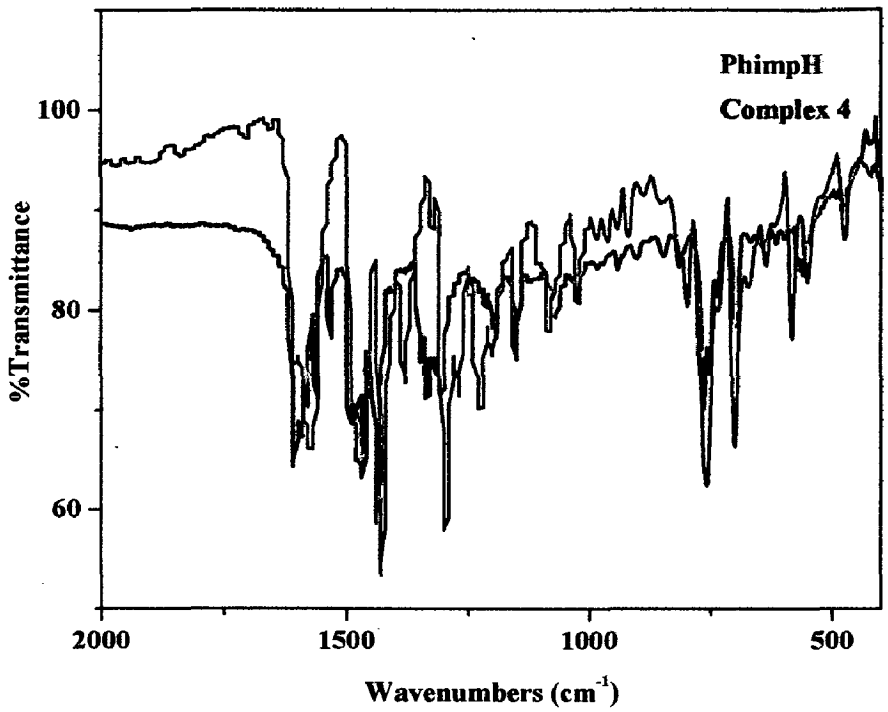


Fig. 3.1. IR spectra of ligand **PhimpH** and complex **4.**

3.1.2. Conductivity studies:

Experimental data for molar conductivity are tabulated in Table 3.1. The molar conductivity measurements in dimethylformamide at *ca.* 10^{-3} M determined at 298 K for complexes **4** and **5** were in the range of 15-35 $\Omega^{-1}cm^2mol^{-1}$ confirming neutral electrolytic behaviour[152] in solution.

3.1.3. Magnetic moment studies:

For complexes **4** and **5**, room temperature (298 K) magnetic moments were 1.95 and 1.99 μ_B respectively, which were expected for the stabilization of $3d^9$ copper(II) ion and paramagnetic nature (Table 3.1).

3.1.4. Electronic spectral studies:

The absorption spectra of complexes were recorded in dichloromethane solution at room temperature. The band near 240-245 nm was designated as π-π^* transition in ligand as

well as in complexes. The absorption band 387-401 nm for both complexes in different solvents shows a strong charge transfer transition. These bands are probably due to phenolate/Cu(II) ligand-to-metal charge transfer (LMCT)[151] The electronic spectral data are depicted in Table 3.1 and spectra were shown in Fig. 3.2. It is noteworthy that complex 4 has been studied as a possible galactose oxidase model in an earlier study and showed remarkable phenoxyl radical activity.[122]

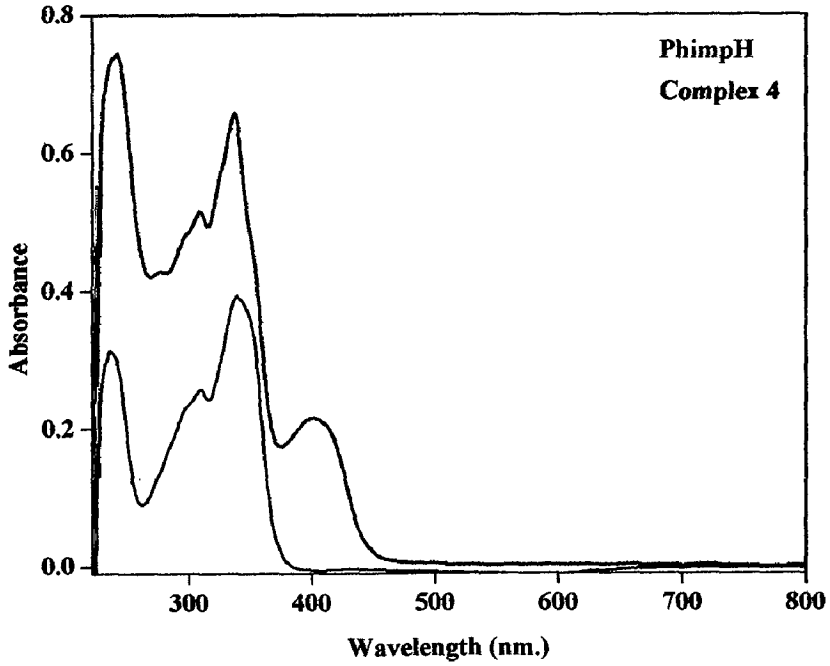


Fig. 3.2. UV-visible spectra of ligand **PhimpH** and complex **4.**

Table 3.1 Data for IR, UV-visible, conductivity and magnetic moment of complex **4-5***

Complex	IR data (cm^{-1})[a]			UV-visible data (λ_{max}/nm, $\varepsilon/M^{-1}cm^{-1}$)[b]	Conductivity data ($\Omega^{-1}cm^2mol^{-1}$)[c]	μ_{eff} (μ_B)[d]
	$\nu_{HC=N}$	ν_{C-Oph}	ν_{ClO4^-}			
4	1608	1307	-	401(21,500), 337(65,800), 309(51,600), 278(42,900), 242(74,400)	14.0	1.95
5	1605	1302	-	542(800), 437(16,000), 387(30,300), 332(32,900), 244(66,000)	35.0	1.99

[a]Using KBr pellets, [b]Solvent: dichloromethane, [c]Solvent: DMF, [d]Recorded at 298 K.

**Spectra are shown in appendices* A_{34}- A_{37}.

3.1.5. Cyclic voltammetry studies:

Both the complexes show quasi-reversible cyclic voltammogram having ΔE values in between 87-200 mV.[122] The $E_{1/2}$ values for CuII/CuI couple were found to be in the potential range -0.50 to -0.65 V vs. Ag/AgCl. Phenolato oxygen stabilizes higher oxidation states and the negative potentials are consistent with the data reported.[153]

3.1.6. Thermogravimetry studies:

The TGA data of the catalysts along with the weight percentage loss at different steps and their probable assignments are presented in Table 3.2. The TGA profile of the catalyst was indicating that these complexes were thermally stable up to 100°C. The thermal decomposition of both the catalysts occurs in three to four steps. The weight loss of these catalysts occurs in two major stages in the temperature range (0°C - 100°C). In complex **4**, first stage weight loss starts 250-150°C (47.1%) and second stage weight loss starts 430-550°C (31.3%). The total weight loss of complex **4** is 98.1%. The decomposition of complex **5**, in the first stage occurs at 162-300°C with the weight loss of 39.3%, and after a small weight loss of 12.5% in the range of 300-470°C, the second stage starts immediately with the weight loss of 39.8% up to 600°C. Complete decomposition of complex **5** was ~600°C.

Table 3.2 Data for TGA/DTA of complexes **4** and **5***

Complex	Temperature Range (^{0}C)	Loss (wt %)[a]	Types of loss
4	20-250	7.2	Exothermic
	250-280	47.1	Exothermic
	280-430	12.5	Exothermic
	430-550	31.3	Exothermic
5	100-162	8.4	Exothermic
	162-300	39.3	Exothermic
	300-470	12.5	Exothermic
	470-600	39.8	Exothermic

[a]Rate:10°C/min, Gas:Nitrogen(200 ml/min, Reference:Alumina Powder.

**DTA-TGA curve are shown in appendices A_{38} and A_{39}.*

3.2. Catalytic activity studies:

Aromatic and aliphatic alkenes react with 30% aqueous H_2O_2 to produce the corresponding oxides and/or epoxides in good yield, with moderate selectivity, in acetonitrile when catalyzed by the Cu Schiff-base complexes. The results of the catalytic oxidation of different olefins substrates are given in Table 3.3-3.5.

3.2.1. Oxidation of styrene:

The oxidation of styrene with 30% aqueous H_2O_2 gave styrene oxide in moderate amount (from 44.0% to 0.6% for **4** and from 3.8% to 1% for **5**) (Fig. 3.3.) under the homogeneous conditions in reaction time period along with this a good yield of benzaldehyde and benzoic acid was also detected (Table 3.3). A turnover number of 171.0-196.0 has been attained in the styrene oxidation reaction (Scheme 2.6, in ***chapter 1***).

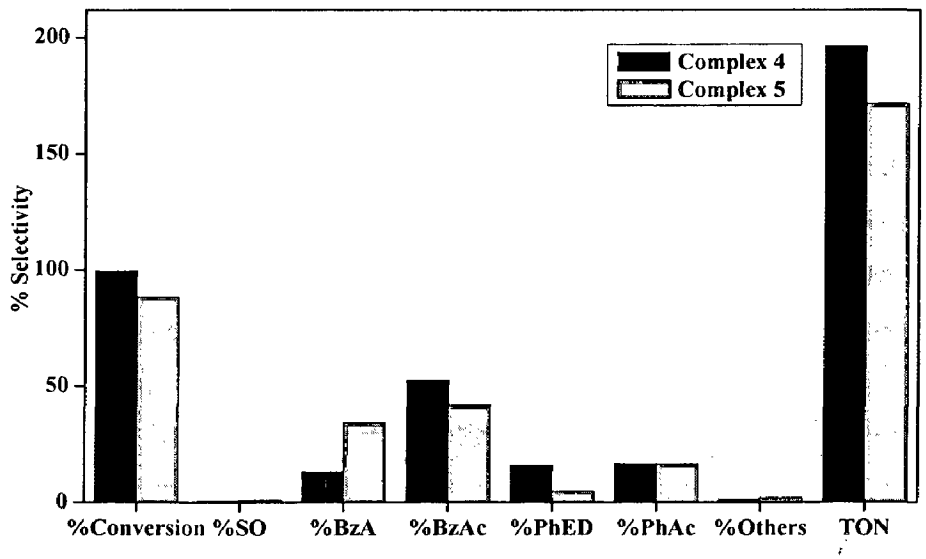


Fig. 3.3. Bar diagram showing total conversion of styrene and selectivity of various products.

Das et al. have obtained a moderate yield of olefin epoxides using a copper(II) Schiff-base complex as a catalyst in the presence of 2-methylpropanal and molecular oxygen under

homogeneous conditions[154(a)], while a maximum yield of *ca.* 15% of styrene epoxide has been achieved with iodosylbenzene using Schiff-base copper complexes.[154]

Table 3.3 Effect of time on the oxidation of styrene and the product selectivity[a]

Catalyst	Time	Percent of conversion	Percent of product selectivity						TON
			SO[b]	BzA[c]	BzAc[d]	PhED[e]	PhAd[f]	Others	
4	1	4. 4	43.4	56.6	-	-	-	-	-
	2	36.2	3.7	75.1	2.6	2.9	14.6	1.1	-
	6	99. 5	0.6	13.0	52.4	16.0	16.7	1.4	196.0
5	1	17.7	17.4	66.5	16.1	-	-	-	-
	2	36.6	3.8	78.0	18.2	-	-	-	-
	6	88.1	1.0	34.2	41.7	4.6	16.5	2.0	171.4

[a]Reaction conditions: styrene (0.208g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453g, 4.0 mmol), temperature (90 ^{0}C) and acetonitrile (2 ml).[b]Styrene oxide, [c]Benzaldehyde, [d]Benzoic acid, [e]1-Phenylethane-1,2-diol, [f]Phenylacetaldehyde.

3.2.2. Oxidation of cis-cyclooctene:

The main product observed during the oxidation of *cis*-cyclooctene with 30% aqueous H_2O_2 under the preset conditions was epoxycyclooctane and some minor products (Scheme 2.7., in ***chapter 1***). Complex **5** is an outstanding catalyst performing significantly better than the other **4** under study (Fig. 3.4.).

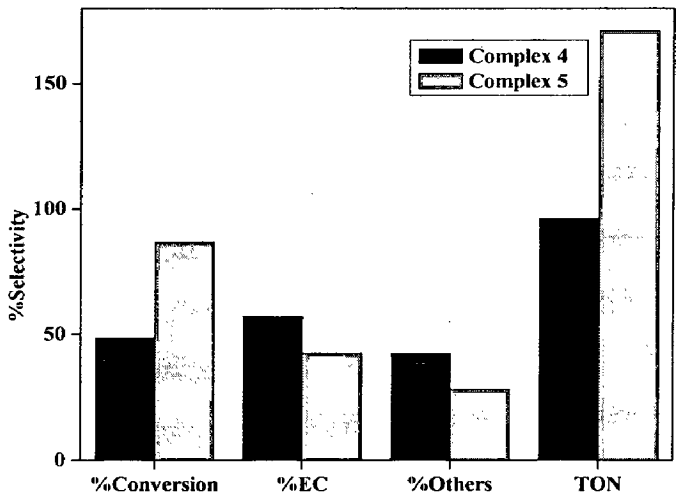


Fig. 3.4. Bar diagram showing total conversion of cis-cyclooctene and selectivity of various products.

The effect of time was investigated. It is observed that the increment of time from 1 h to 6 h increases the conversion from 10% to 49% for **4** and 15% to 87% for **5** (Table 3.4).

Table 3.4 Effect of time on the oxidation of *cis*-Cyclooctene and the product selectivity[a]

Catalyst	Time	Percent of Conversion	Percent of product selectivity EC[b]	Others	TON
4	1	10.6	72.6	27.4	-
	2	12.1	70.3	29.7	-
	6	48.8	57.4	42.6	96.1
5	1	14.8	100	-	-
	2	24.2	91.8	8.2	-
	6	86.7	71.9	28.1	171.1

[a]Reaction conditions: *cis*-Cyclooctene (0.22g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453g, 4.0 mmol), temperature (90 ^{0}C) and acetonitrile (2 ml).[b]Epoxycyclooctane.

3.2.3. Oxidation of trans-stilbene:

The above optimized reaction conditions could be applied to the oxidation reaction of other olefins by Cu(II) catalysts and the results are shown in Fig. 3.5. Reactions were performed at 90°C in acetonitrile containing alkene, oxidant and catalyst. This catalyst efficiently converts olefins to their corresponding oxidation products (Scheme 2.8., in ***chapter 1***).

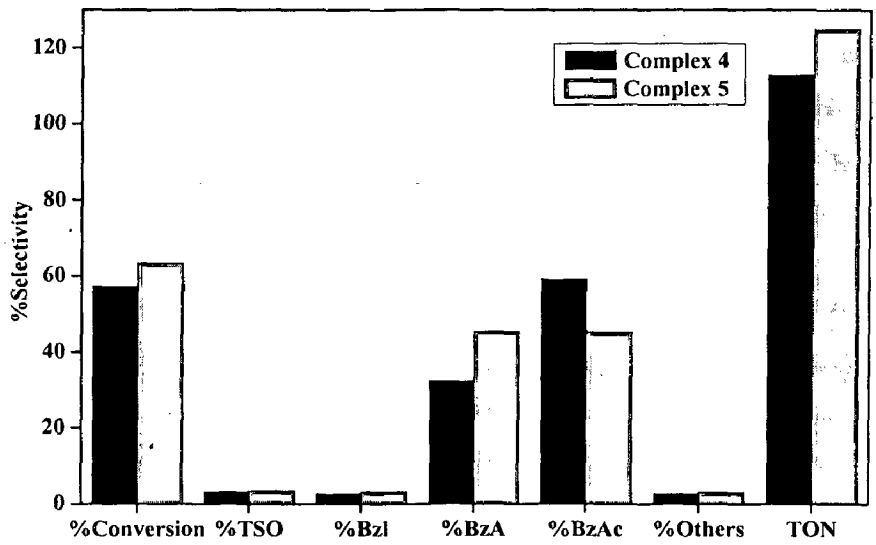


Fig. 3.5. Bar diagram showing conversion of *trans*-stilbenene and selectivity of products.

Table 3.5 Effect of time on the oxidation of *trans*-stilbene and the product selectivity[a]

Catalyst	Time	Percent of conversion	Percent of product selectivity					TON
			TSO[b]	Bzl[c]	BzA[d]	BzAc[e]	Others	
4	1	20.7	0.5	6.3	84.2	2.0	7.0	-
	2	39.2	1.2	4.7	76.8	10.5	6.8	-
	6	57.3	2.6	3.2	32.4	59.1	2.7	112.8
5	1	23.2	0.8	6.7	83.4	3.8	5.3	-
	2	32.9	2.7	4.4	78.8	10.8	3.3	-
	6	63.3	3.1	3.4	45.3	45.2	3.0	124.9

[a]Reaction conditions: *trans*-stilbene (0.364g, 2.0 mmol), catalyst (0.01 mmol), oxidant (0.453g, 4.0 mmol), temperature (90 ^{0}C) and acetonitrile (2 ml). [b]*trans*-stilbene oxide, [c]Benzil, [d]Benzaldehyde, [e]Benzoic acid.

trans-Stilbene gives benzaldehyde as major product with benzoic acid having good selectivity, benzil and *trans*-Stilbene epoxide with minimum selectivity (Table 3.5).

4. Conclusion:

The synthesis and characterization of two reported copper complexes (**4** and **5**) have been described. The TGA profile of the **4** and **5** was indicating that these complexes were thermally stable up to 100°C. The complexes **4** and **5** were tested as oxidation catalysts in the epoxidation of alkenes in this report showed a good oxidation catalytic activity comparable to that of a large number of Cu(II) complexes already reported in the literature..

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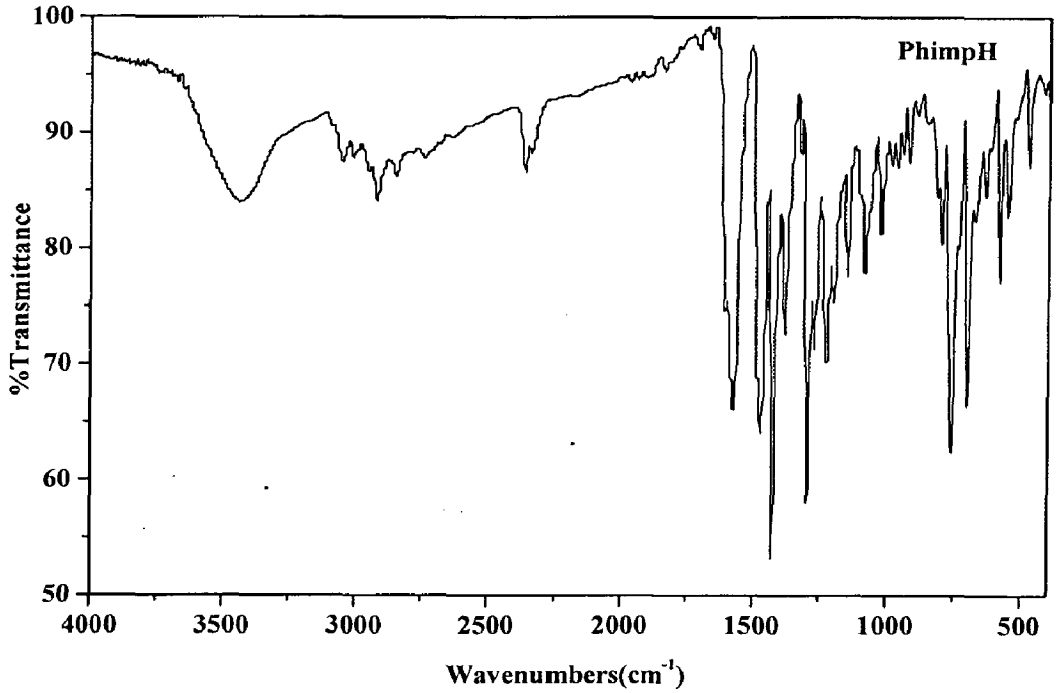
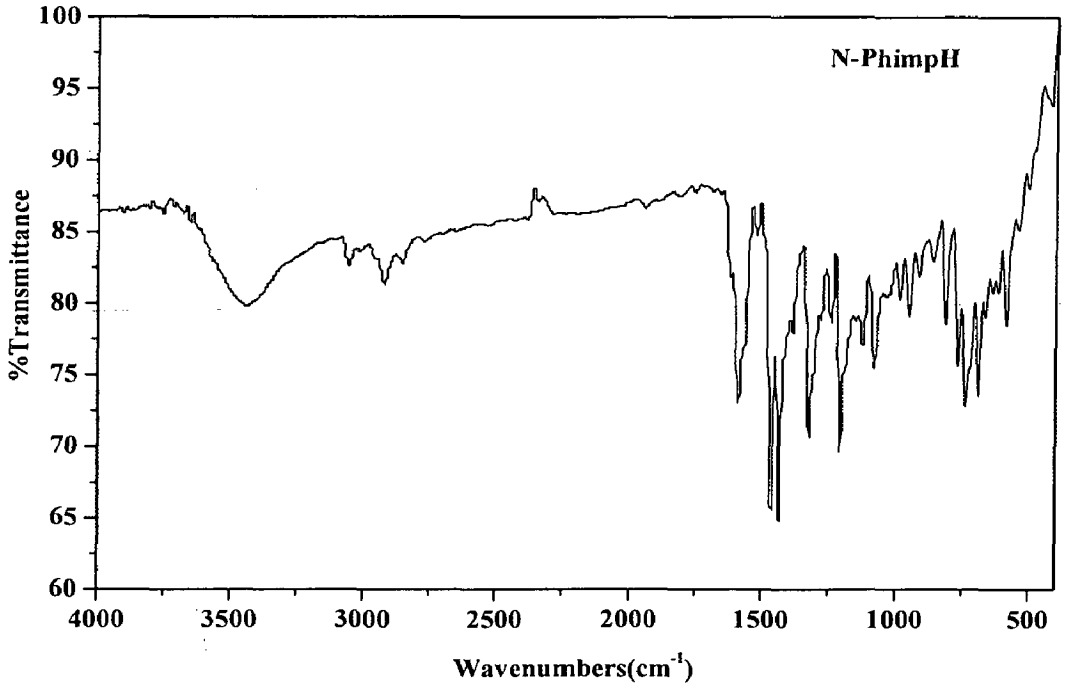
Appendices

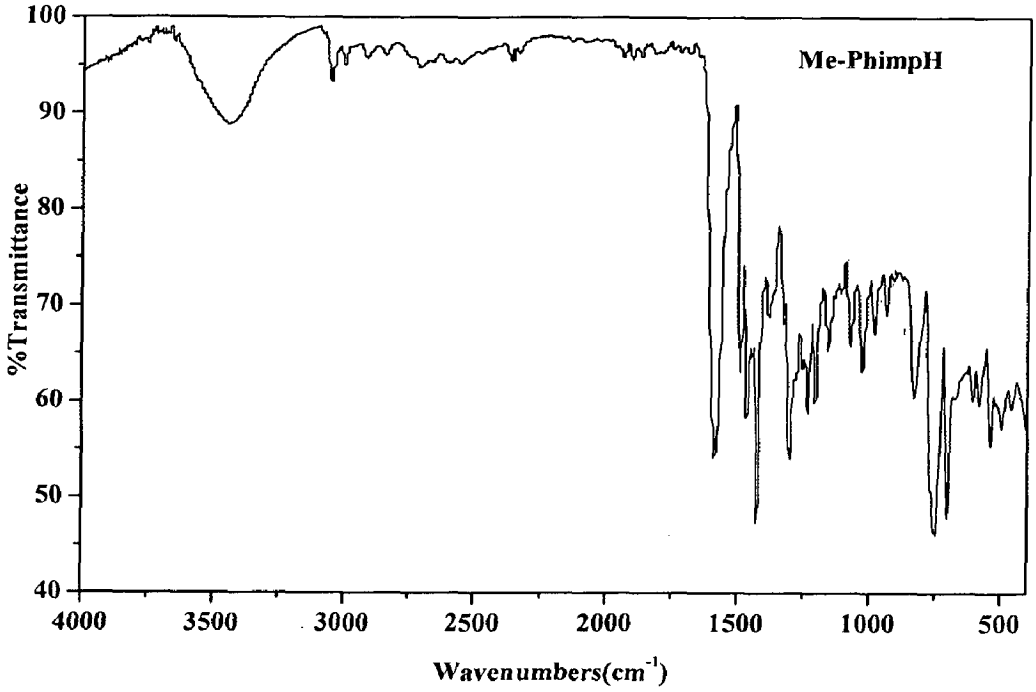
Appendix A_1: IR spectra of ligand PhimpH



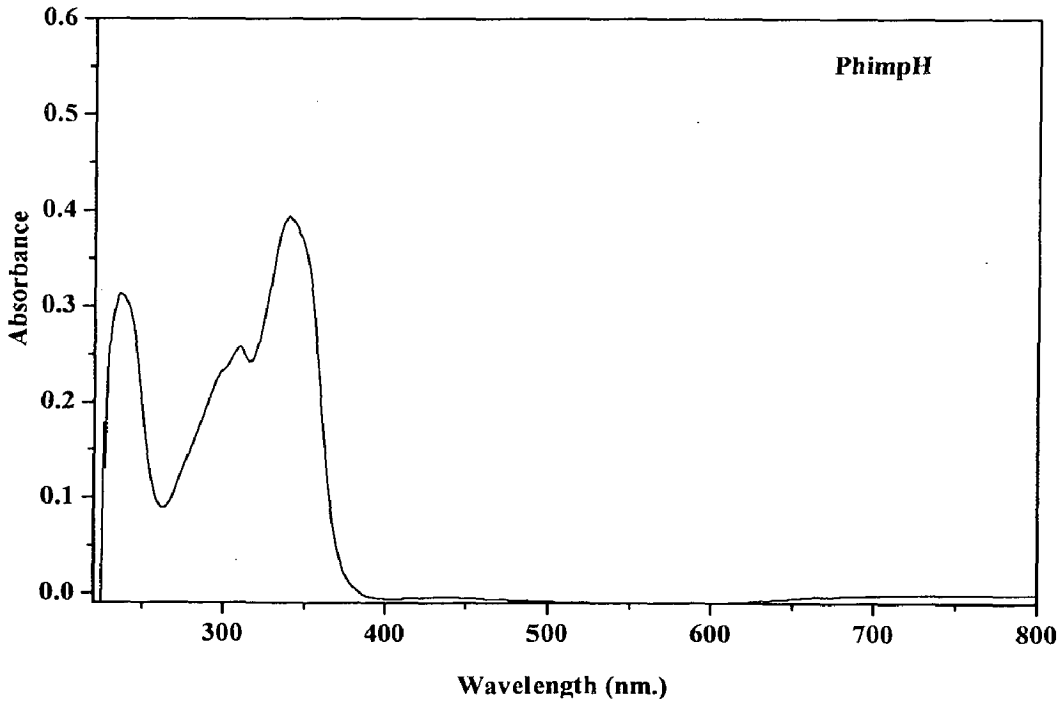
Appendix A_2: IR spectra of ligand N-PhimpH



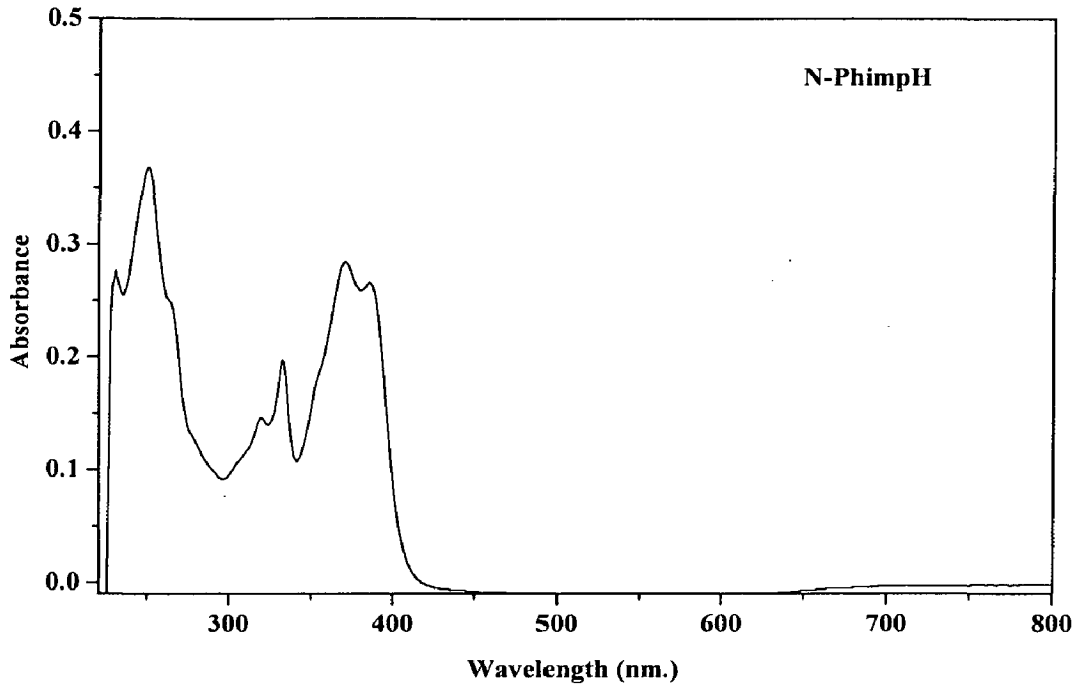
Appendix A_3: IR spectra of ligand Me-PhimpH



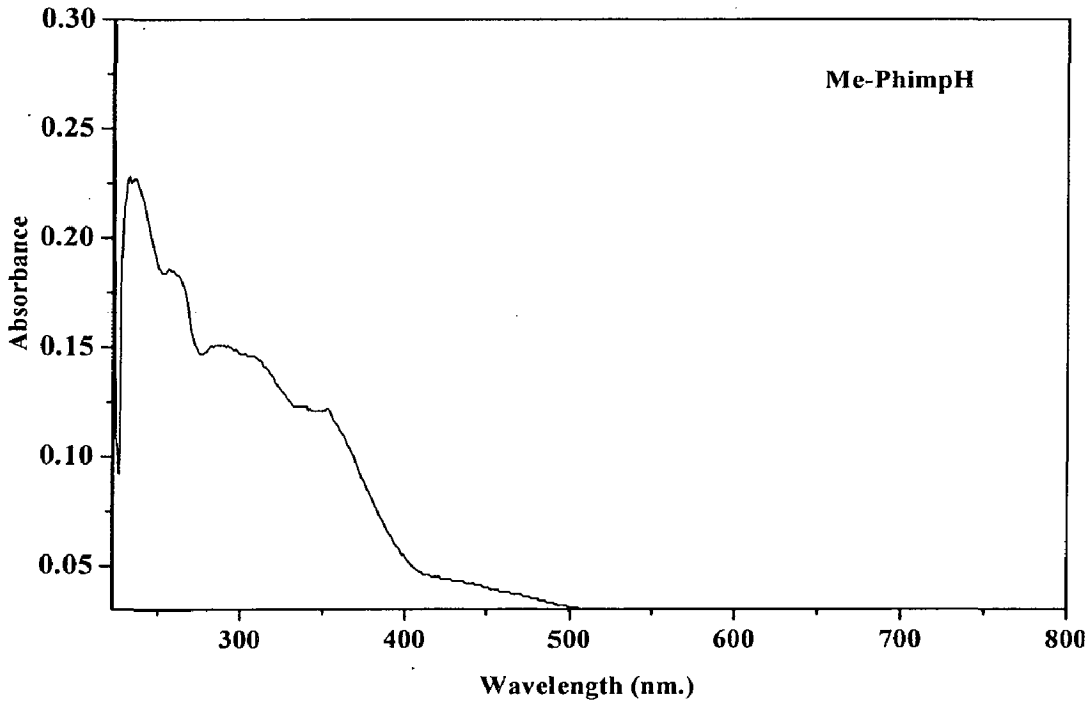
Appendix A_4: UV-visible spectra of ligand PhimpH



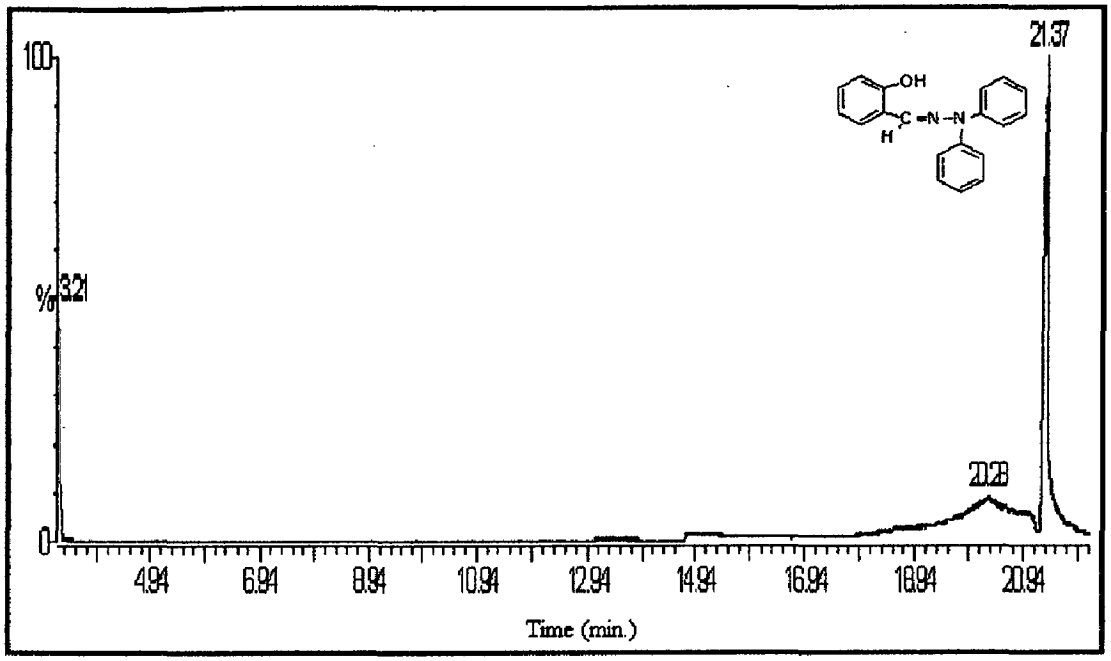
Appendix A_5: UV-visible spectra of ligand N-PhimpH



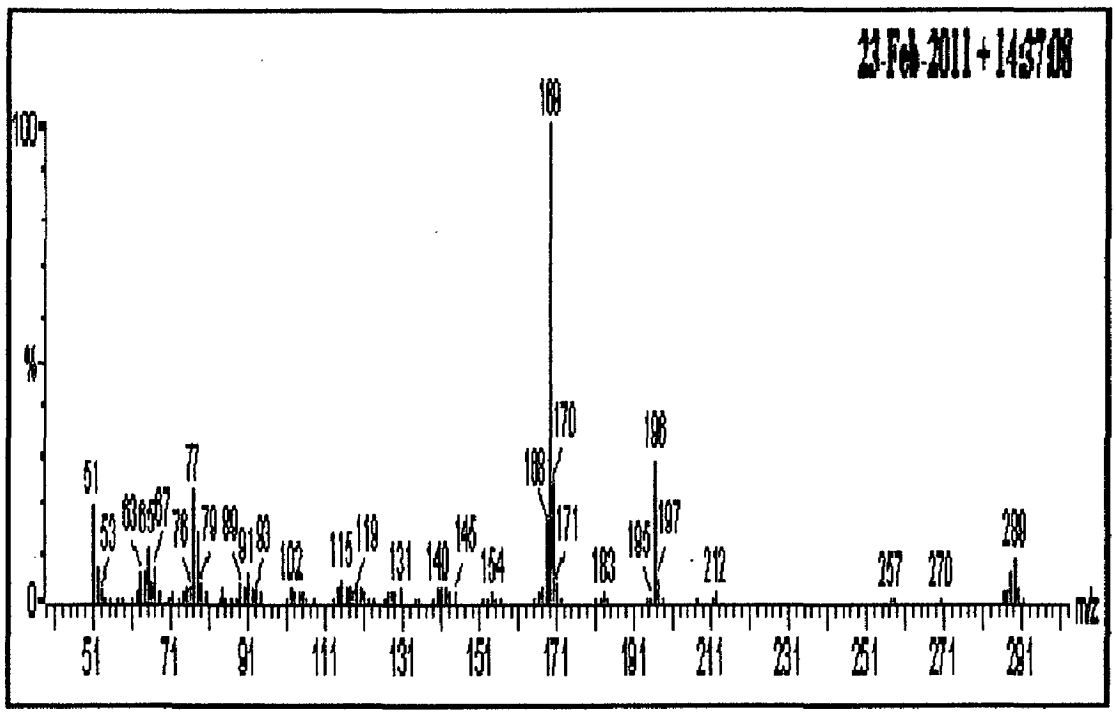
Appendix A_6: UV-visible spectra of ligand Me-PhimpH



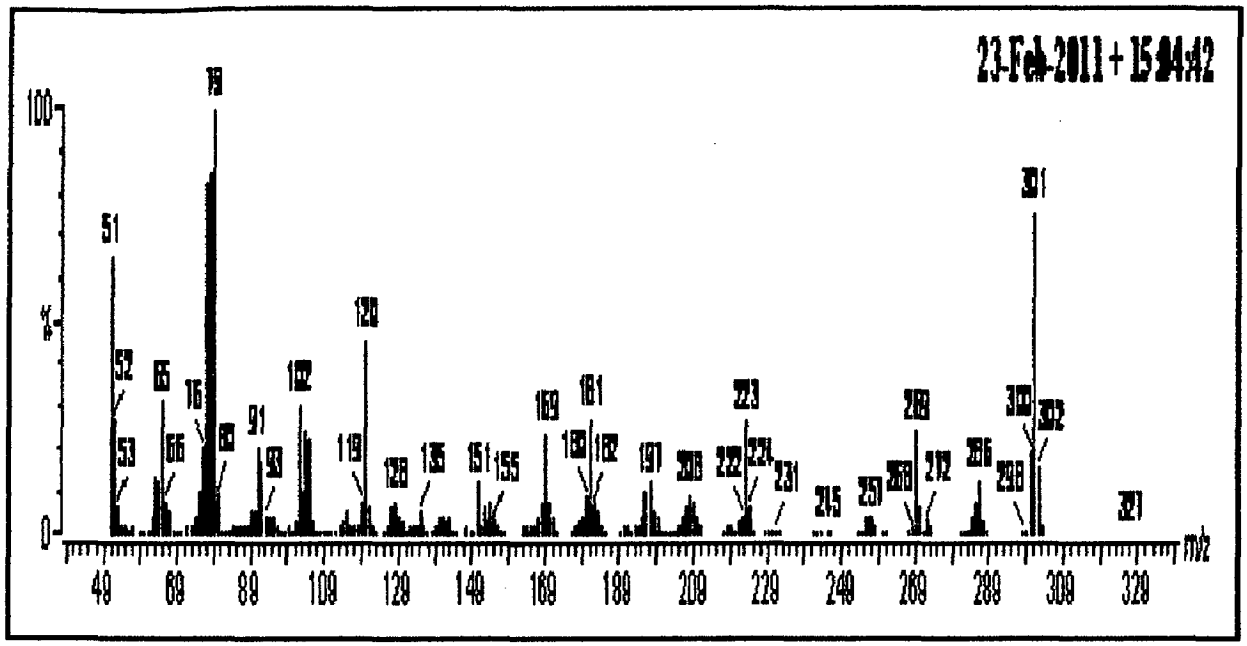
Appendix A_7: Gas chromatograph of ligand PhimpH



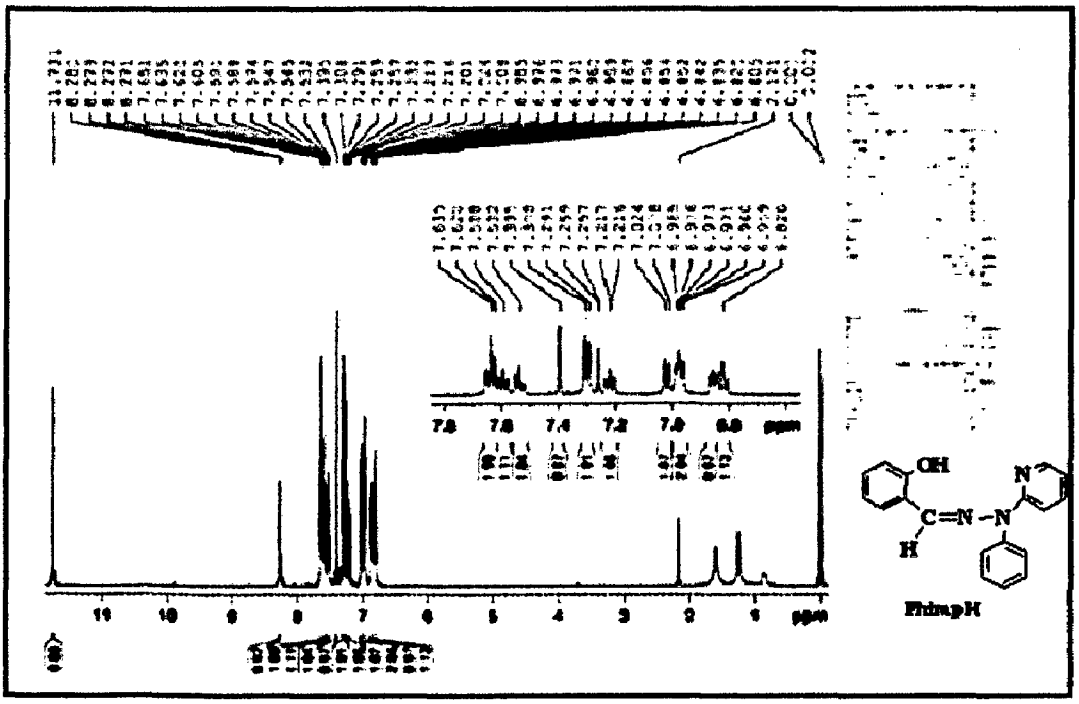
Appendix A_8: Mass spectra of ligand PhimpH



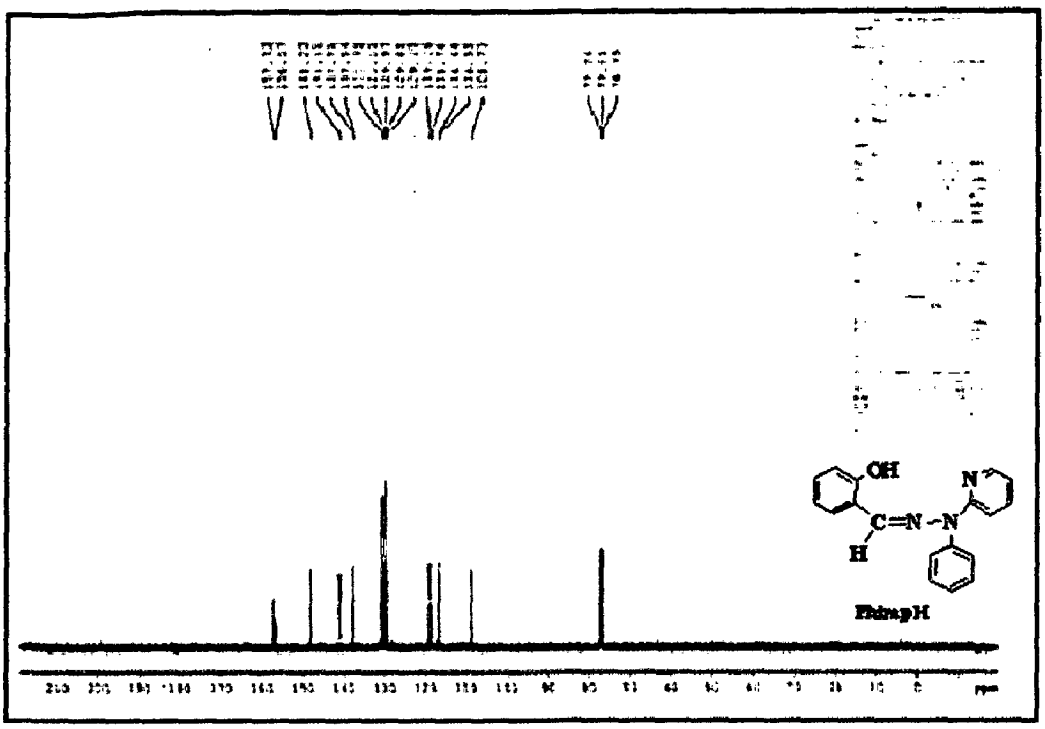
Appendix A_9: Mass spectra of ligand Me-PhimpH



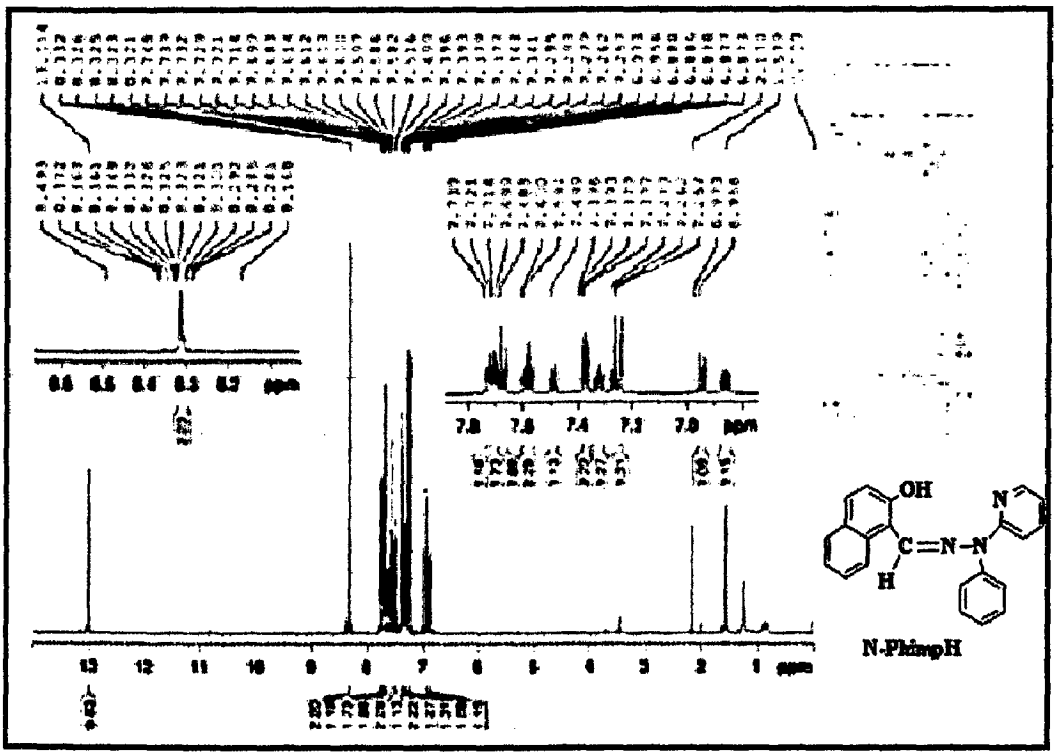
Appendix A_{10}: ^{1}H NMR of PhimpH



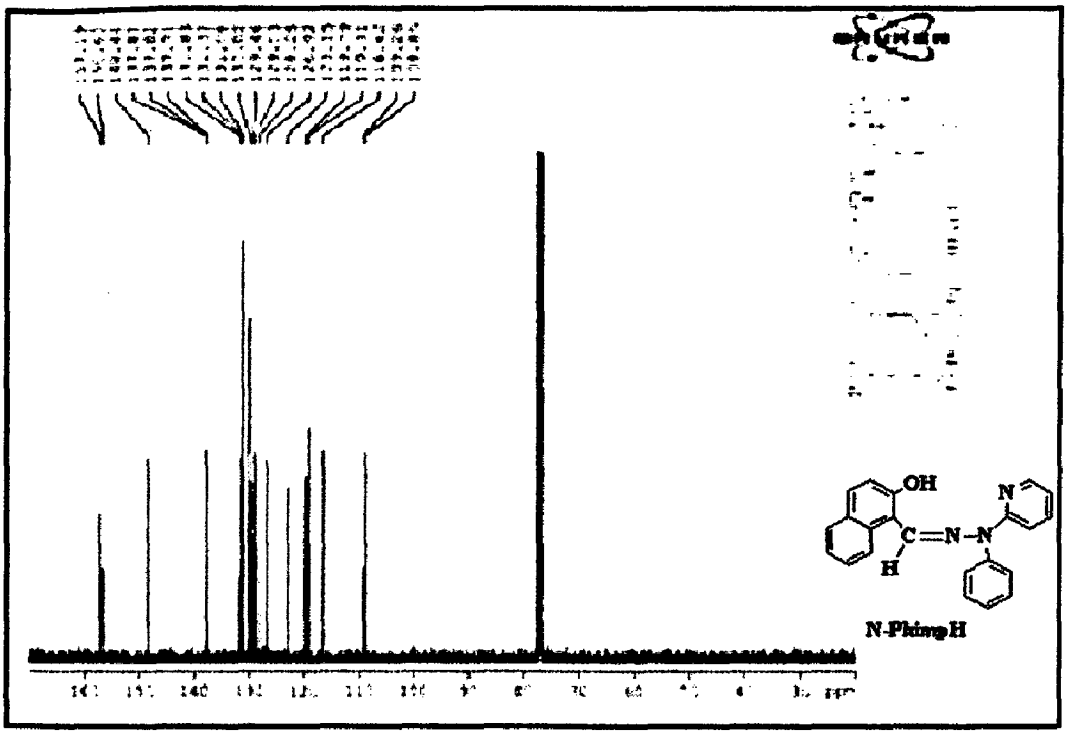
Appendix A_{11}: ^{13}C NMR of PhimpH



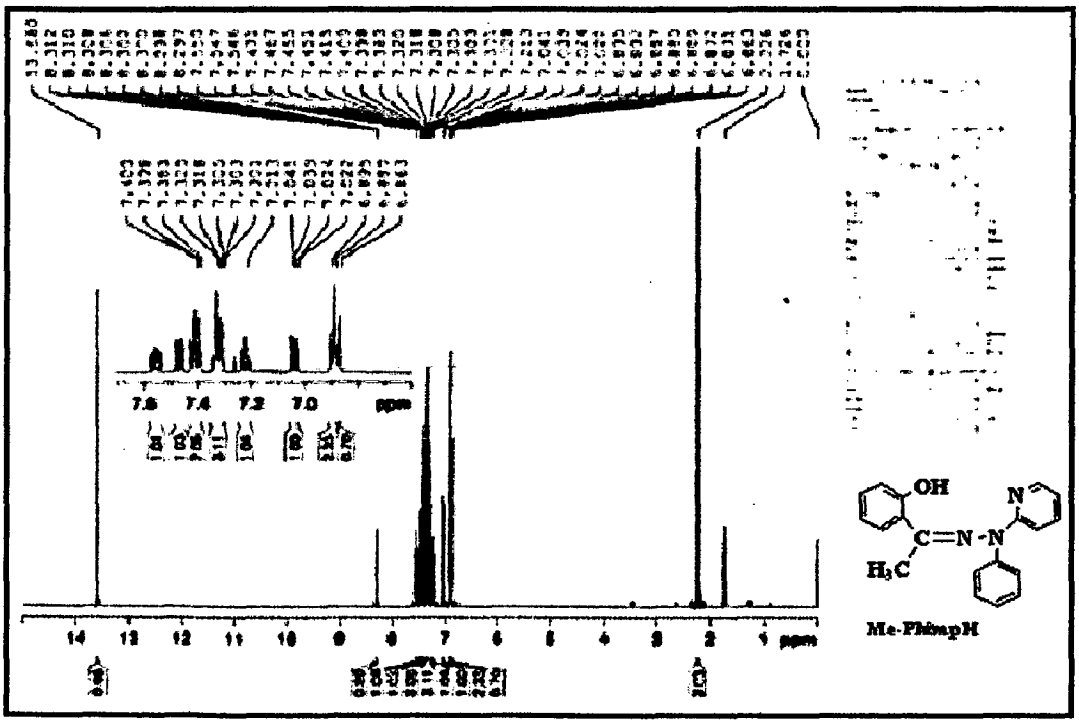
Appendix A_{12}: ^{1}H NMR of N-PhimpH



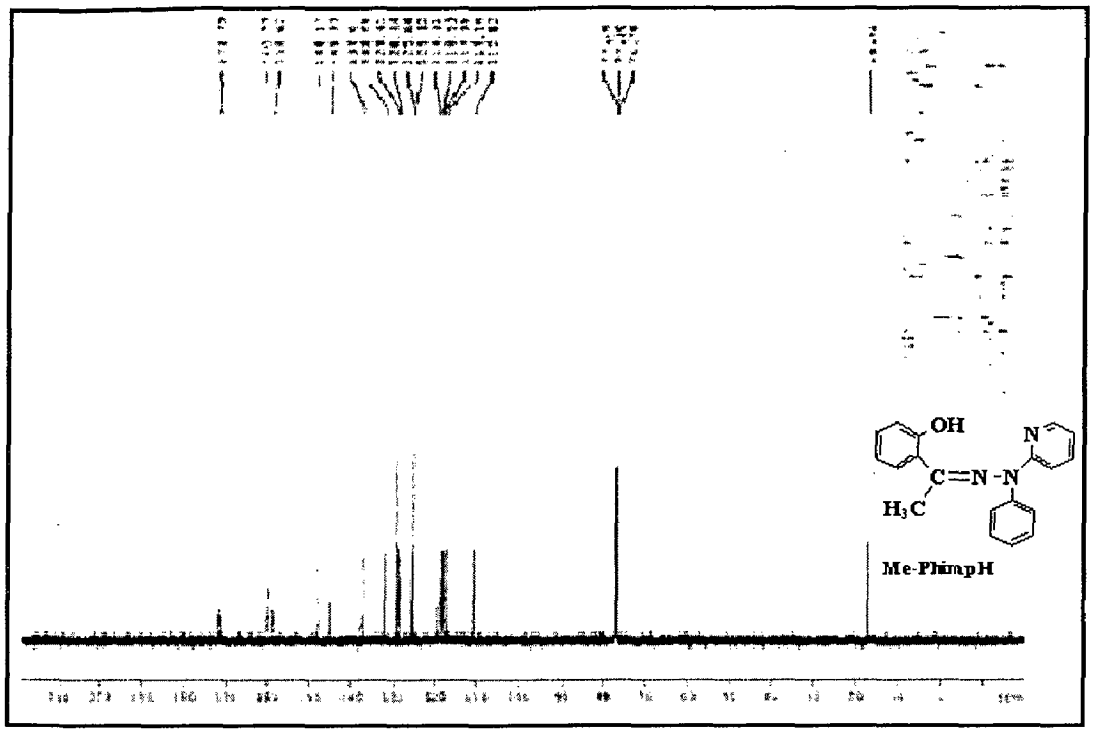
Appendix A_{13}: ^{13}C NMR of N-PhimpH



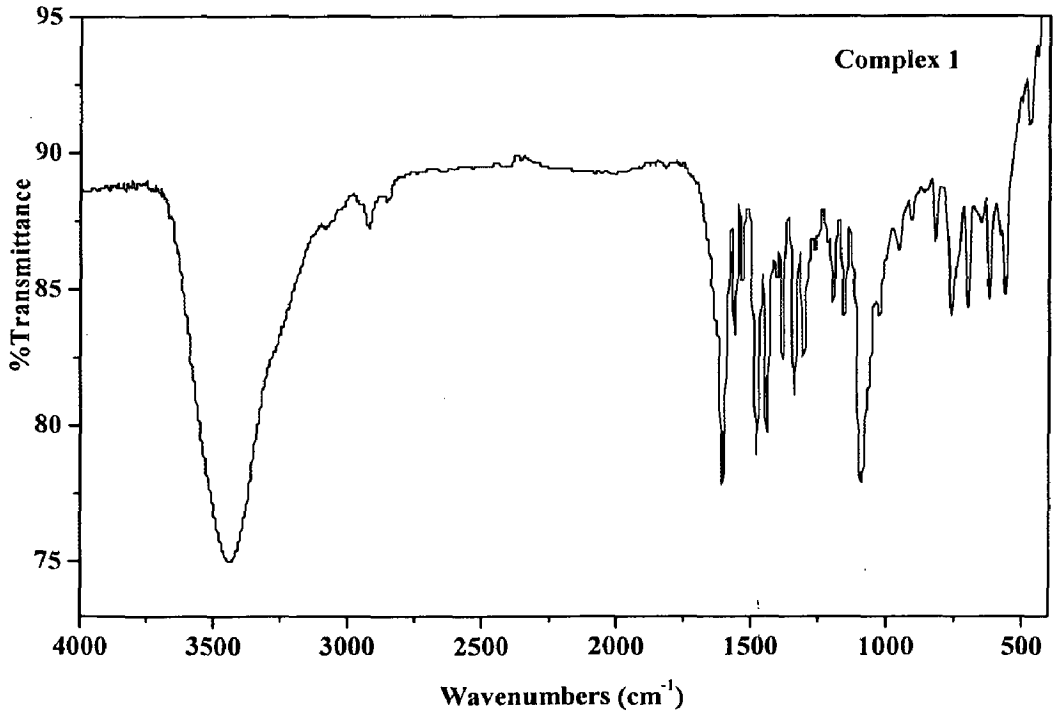
Appendix A_{14}: ^{1}H NMR of Me-PhimpH



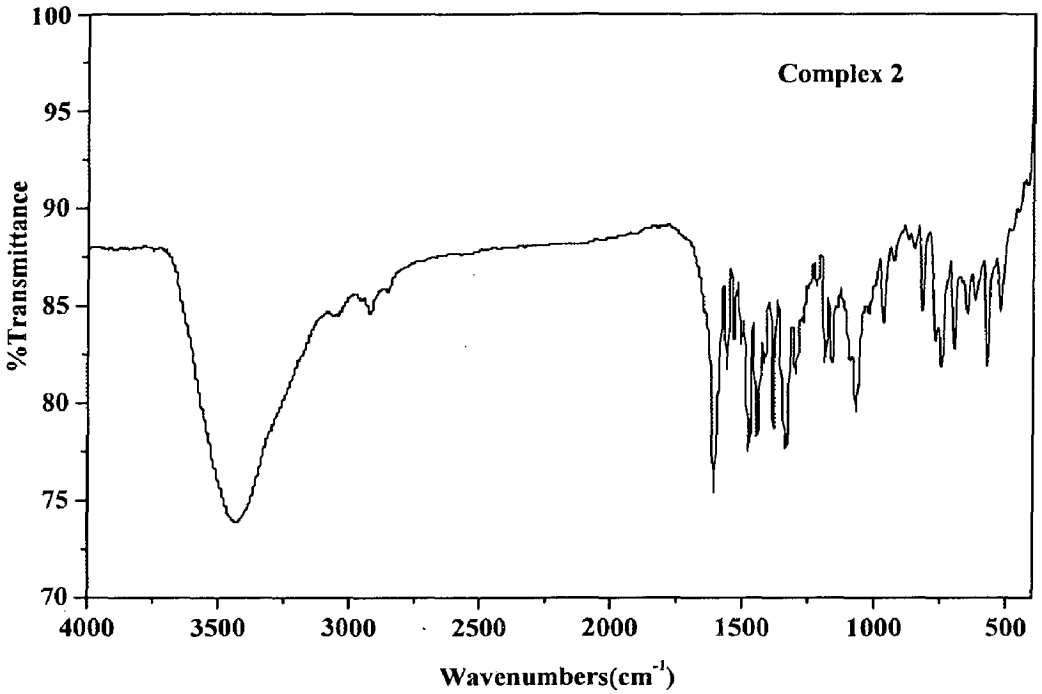
Appendix A_{15}: ^{13}C NMR of Me-PhimpH



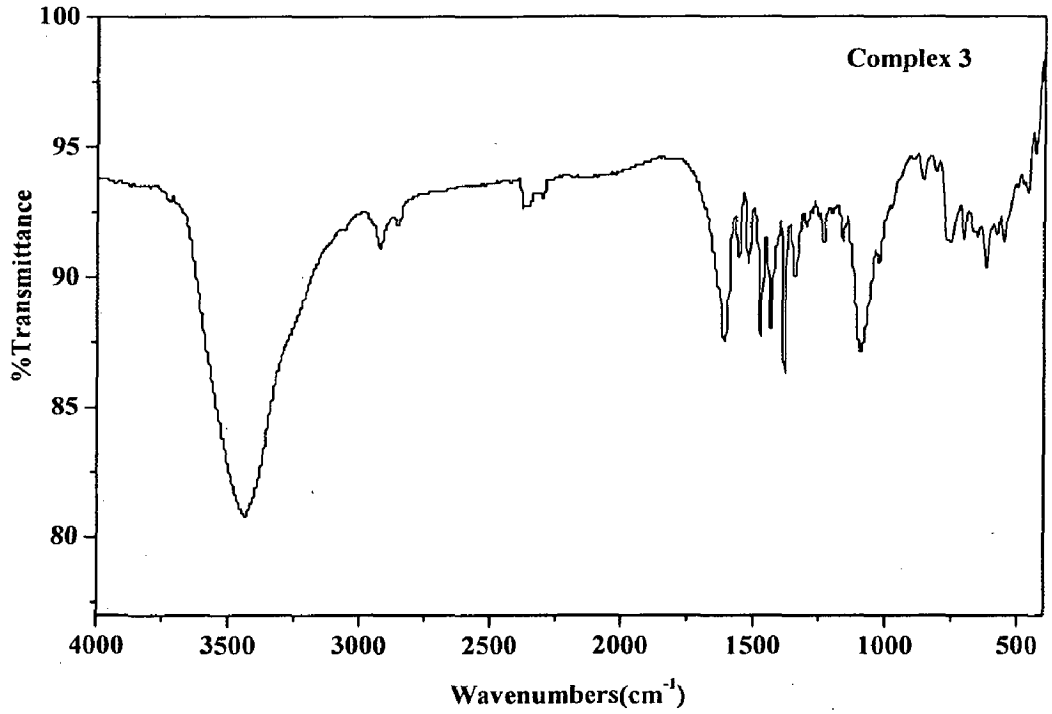
Appendix A_{16}: IR spectra of complex $[Cr(Phimp)_2](ClO_4)$ (**1**)



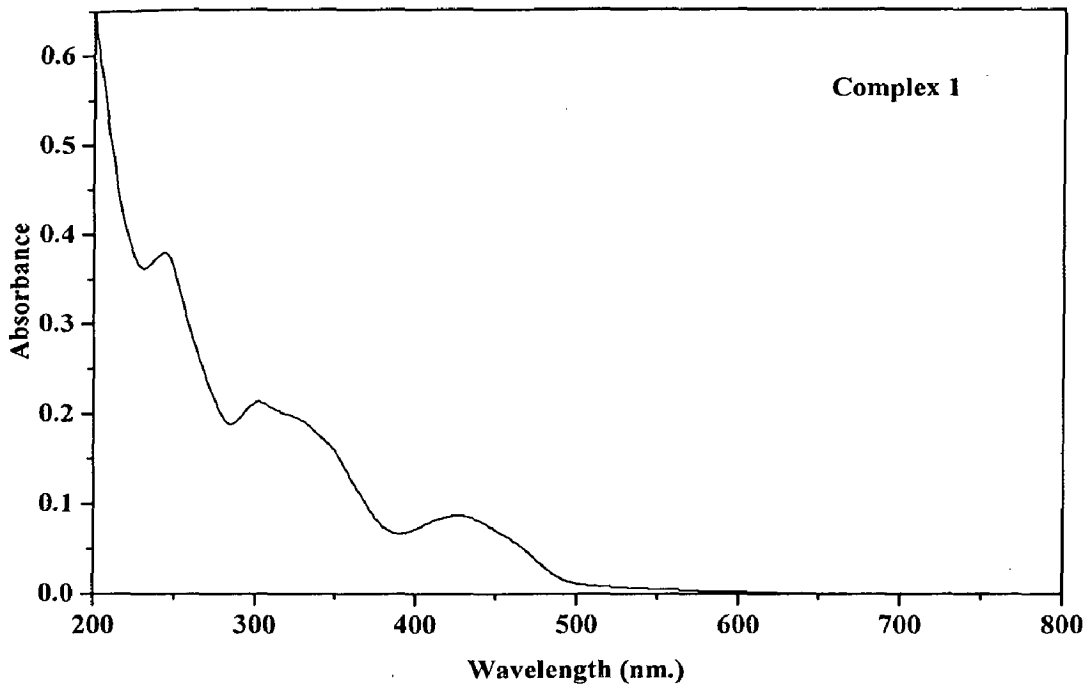
Appendix A_{17}: IR spectra of complex $[Cr(N\text{-}Phimp)_2](ClO_4)$ (**2**)



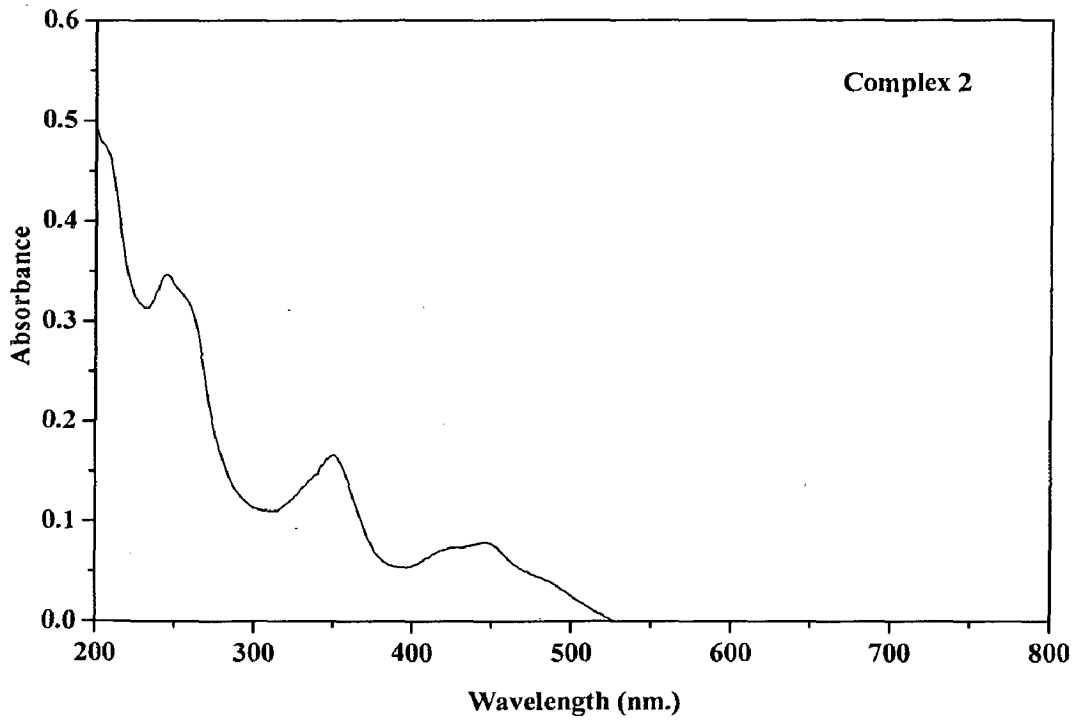
Appendix A_{18}: IR spectra of complex $[Cr(Me\text{-}Phimp)_2](ClO_4)$ (**3**)



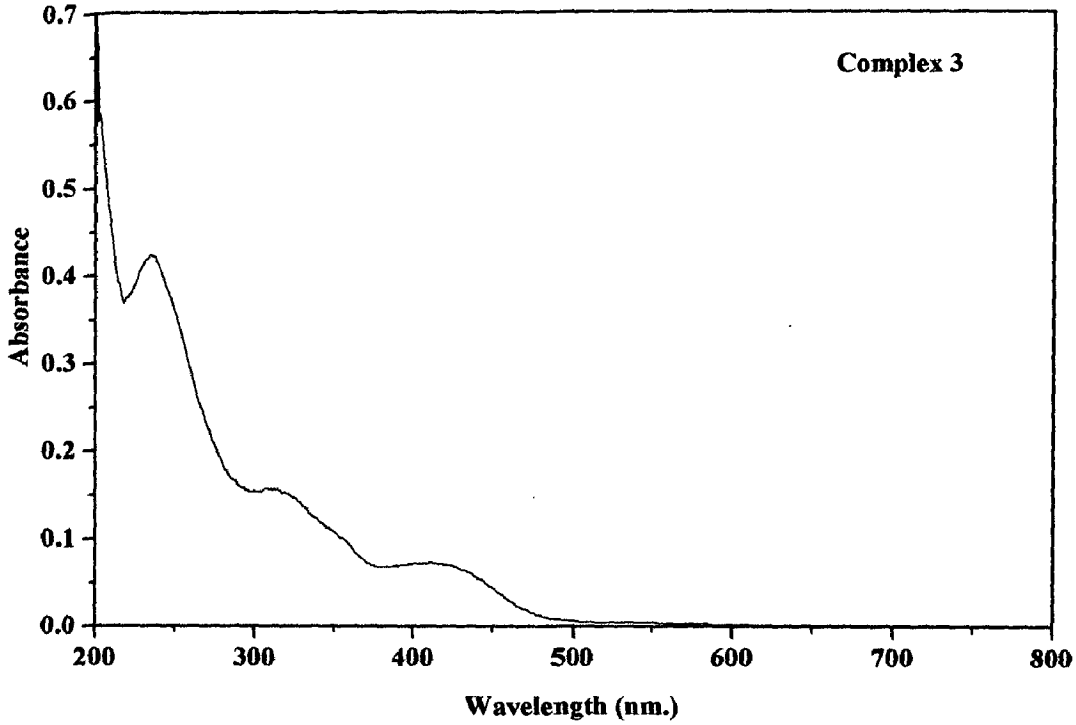
Appendix A_{19}: UV-visible spectra of complex $[Cr(Phimp)_2](ClO_4)$ (**1**)



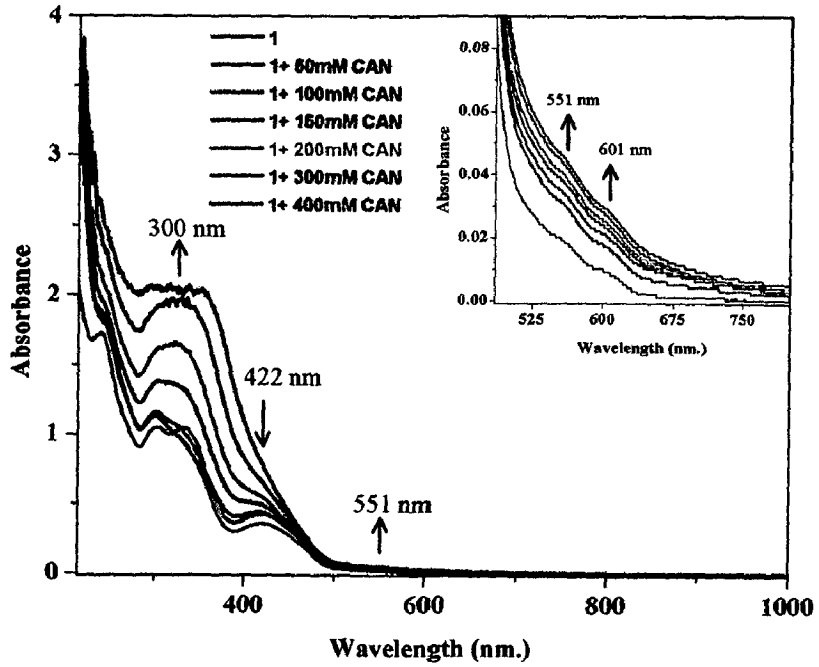
Appendix A_{20}: UV-visible spectra of complex $[Cr(N\text{-}Phimp)_2](ClO_4)$ (**2**)



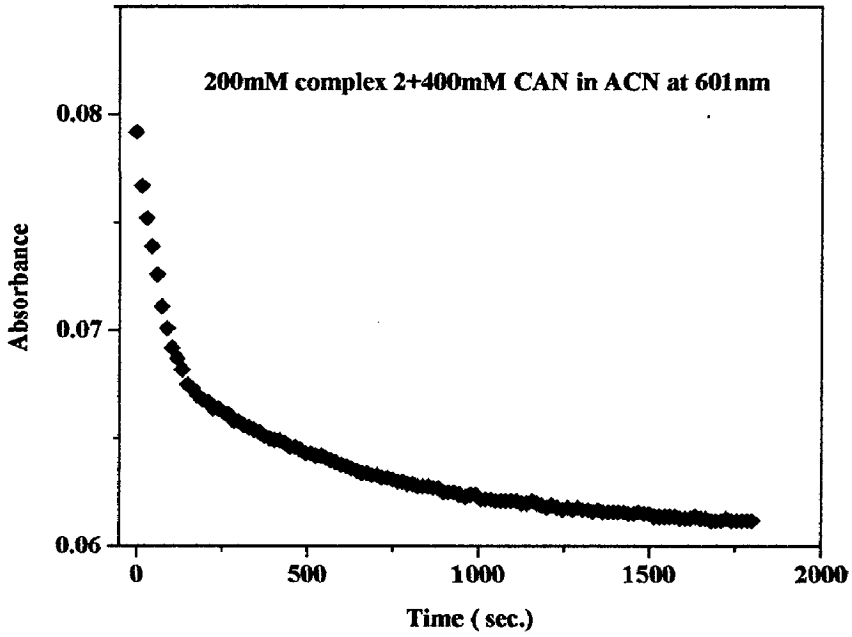
Appendix A_{21}: UV-visible spectra of complex $[Cr(Me\text{-}Phimp)_2](ClO_4)$ (**3**)



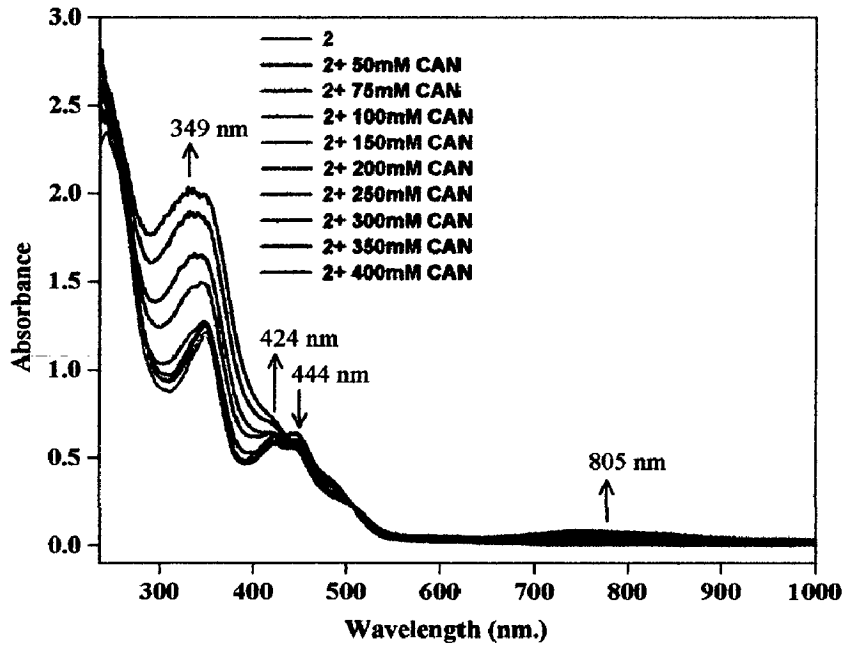
Appendix A_{22}: UV-visible spectra of phenoxyl radical complex $[1]^{\bullet 2+}$



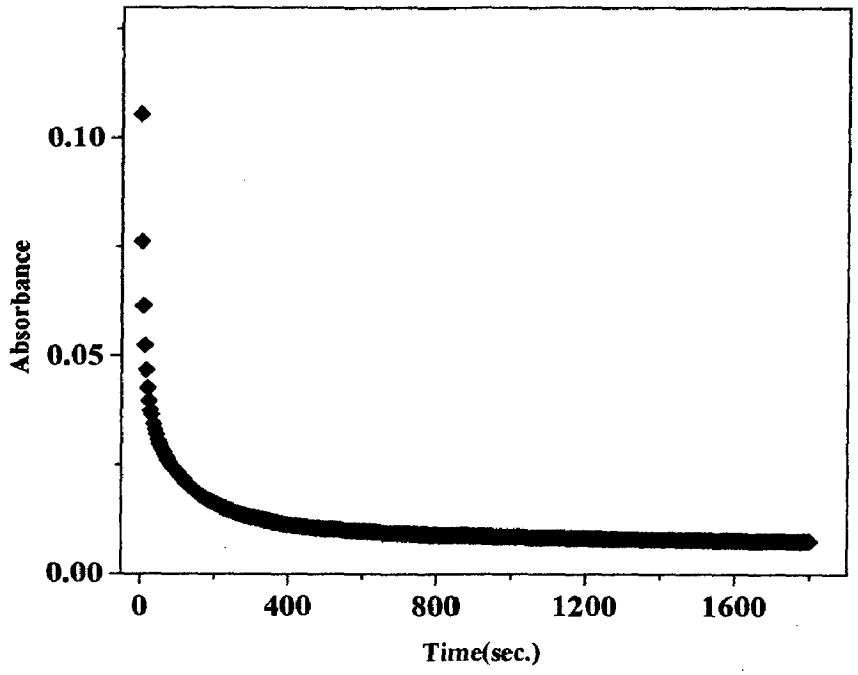
Appendix A_{23}: UV-visible spectra of the kinetics of phenoxyl radical complex $[1]^{\bullet+}$



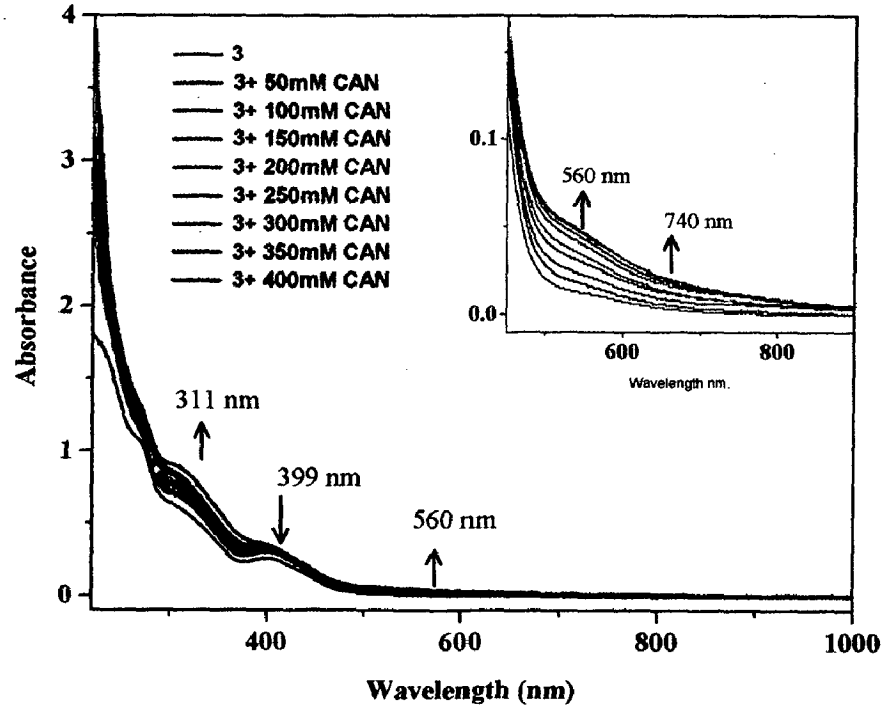
Appendix A_{24}: UV-visible spectra of phenoxyl radical complex $[2]^{\bullet+}$



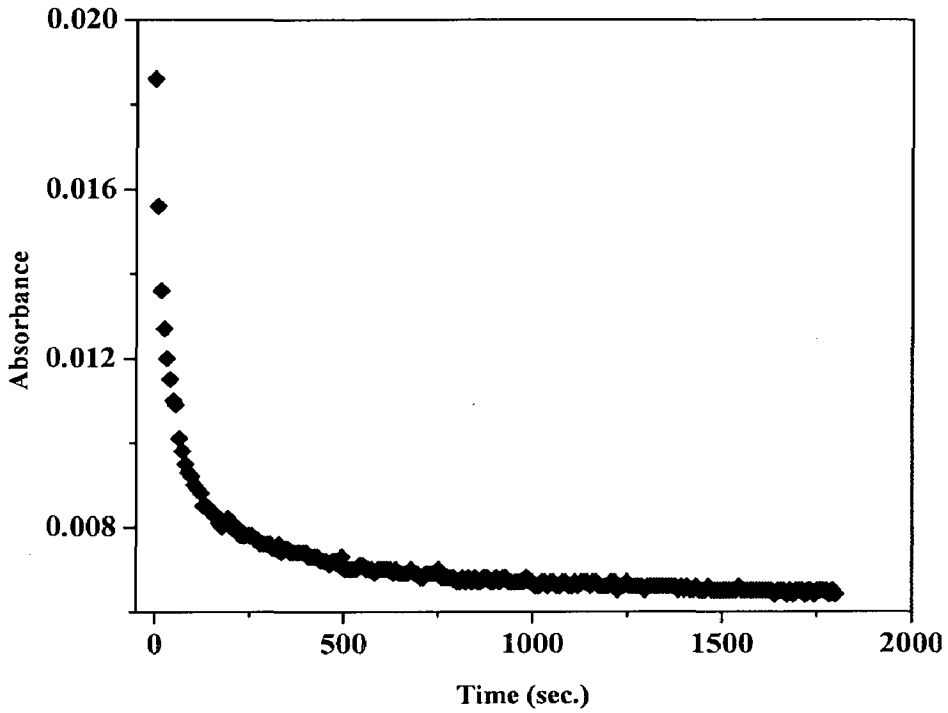
Appendix A_{25}: UV-visible spectra of the kinetics of phenoxyl radical complex $[2]^{\bullet+}$



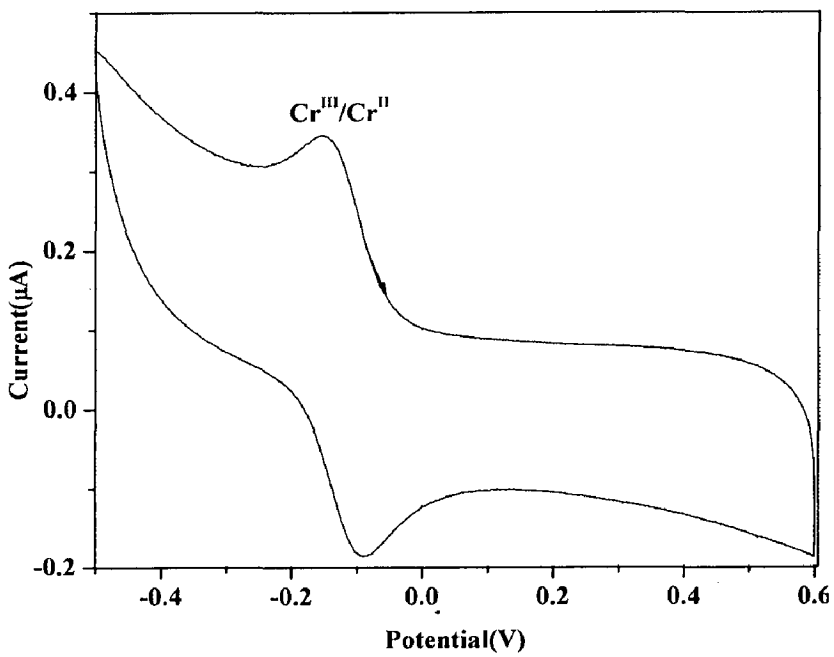
Appendix A_{26}: UV-visible spectra of phenoxyl radical complex $[3]^{\bullet+}$



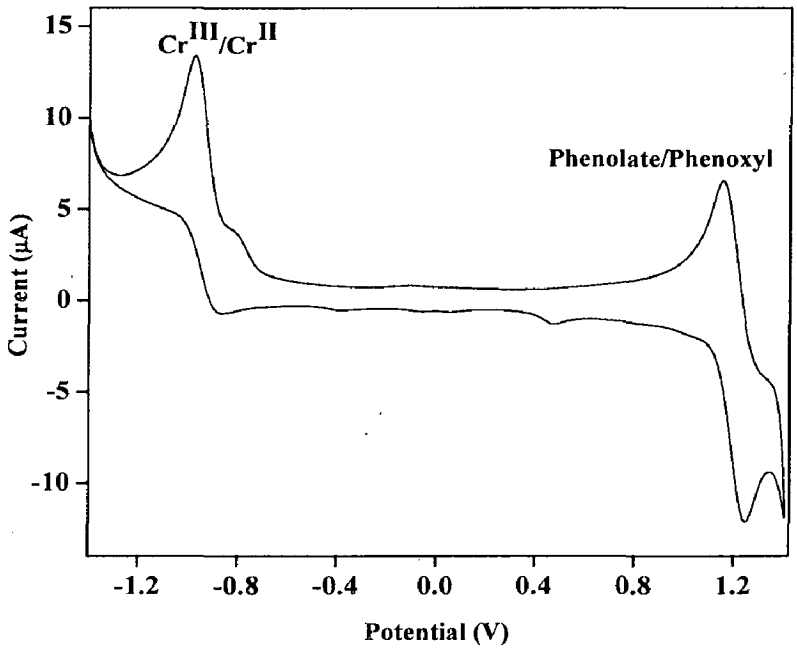
Appendix A_{27}: UV-visible spectra of the kinetics of phenoxyl radical complex **[3]**$^{\bullet+}$



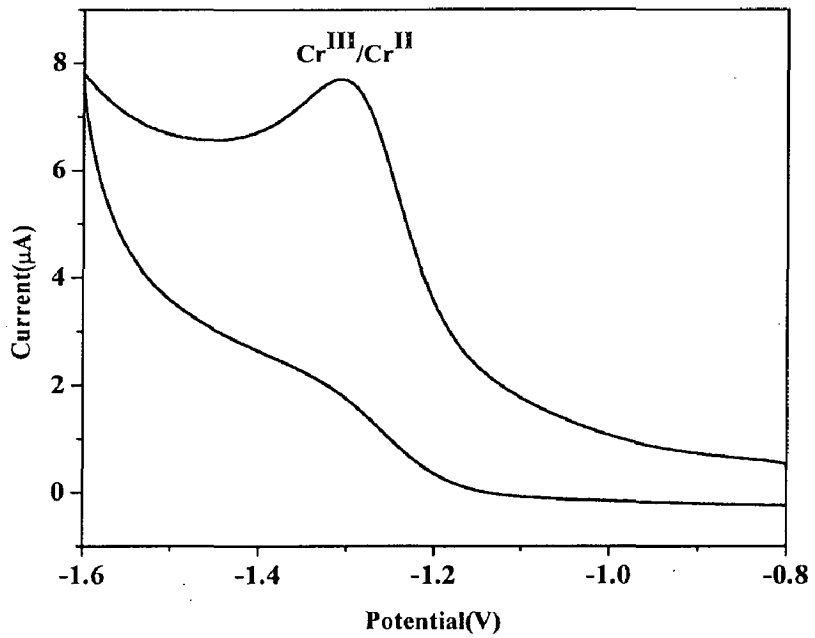
Appendix A_{28}: Cyclic Voltammogram of complex $[Cr(Phimp)_2](ClO_4)$ (1)



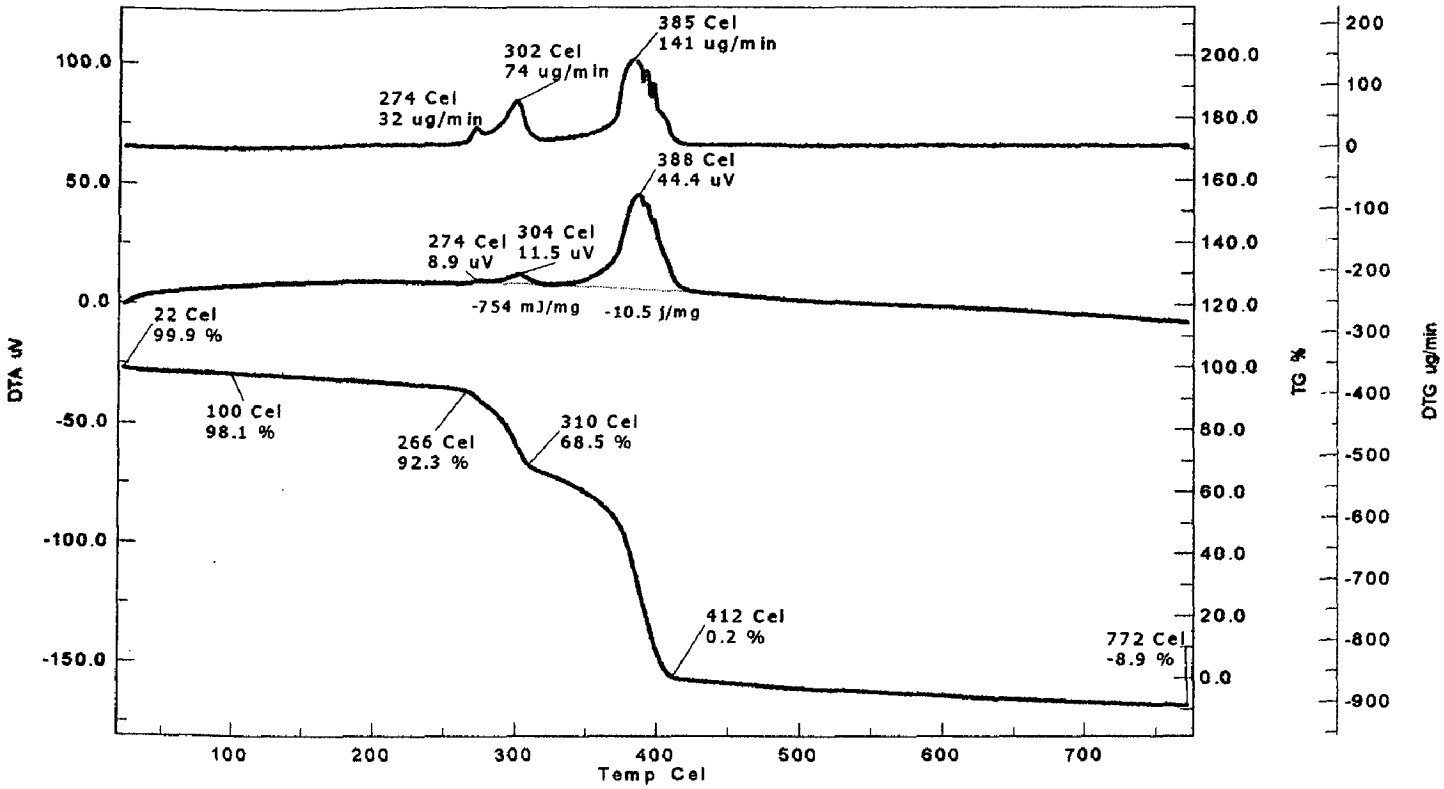
Appendix A_{29}: Cyclic Voltammogram of complex $[Cr(N\text{-}Phimp)_2](ClO_4)$ (**2**)



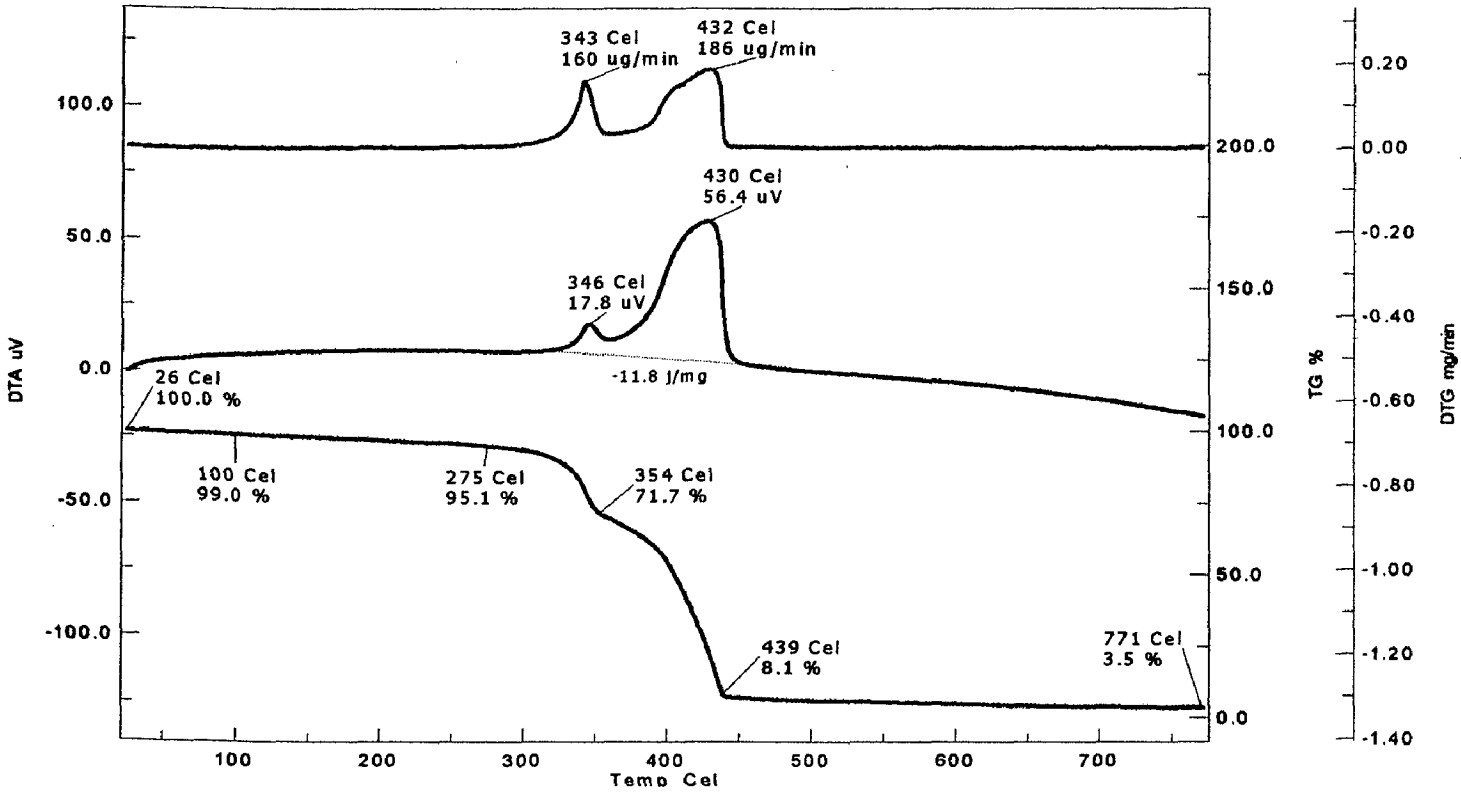
Appendix A_{30}: Cyclic Voltammogram of complex $[Cr(Me\text{-}Phimp)_2](ClO_4)$ (**3**)



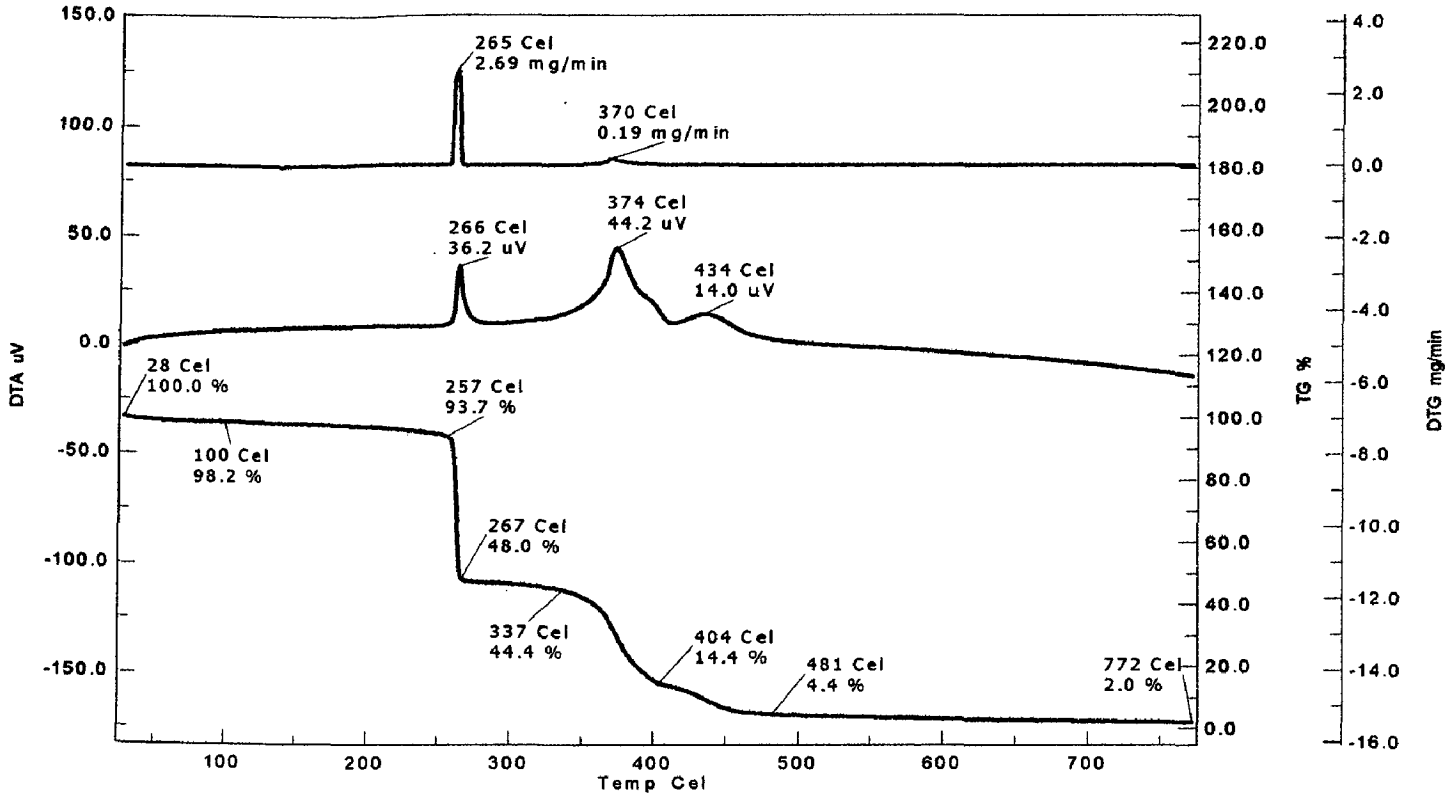
Appendix A_{31}: TGA-DTA curve of complex $[Cr(Phimp)_2](ClO_4)$ **(1)**



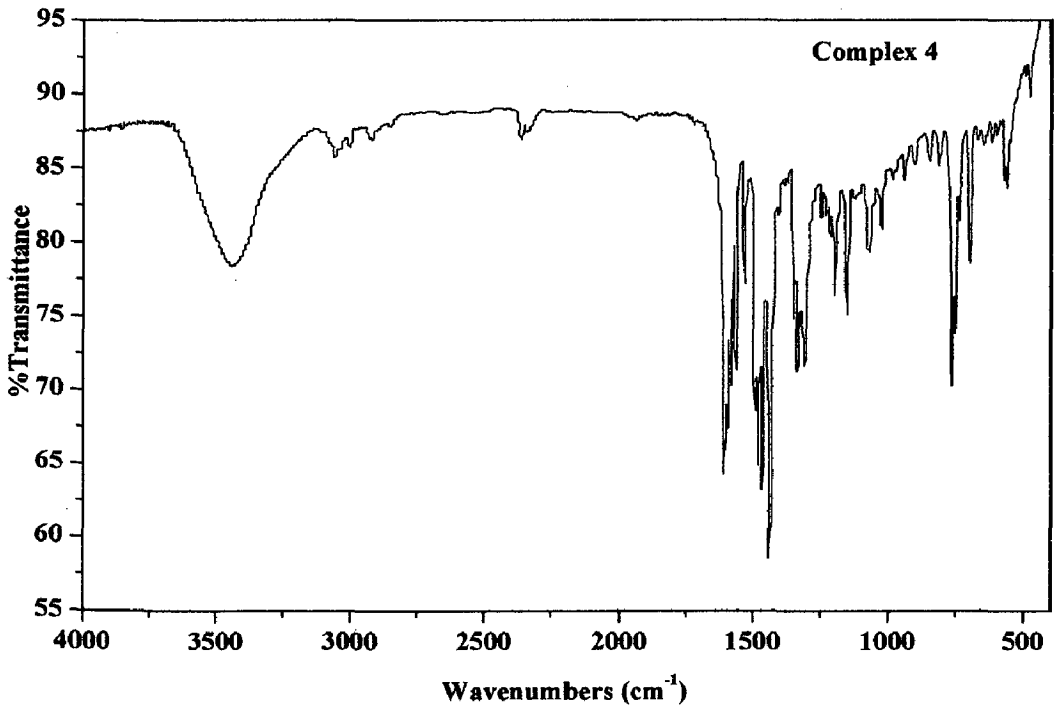
Appendix A_{32}: TGA-DTA curve of complex $[Cr(N\text{-}Phimp)_2](ClO_4)$ **(2)**



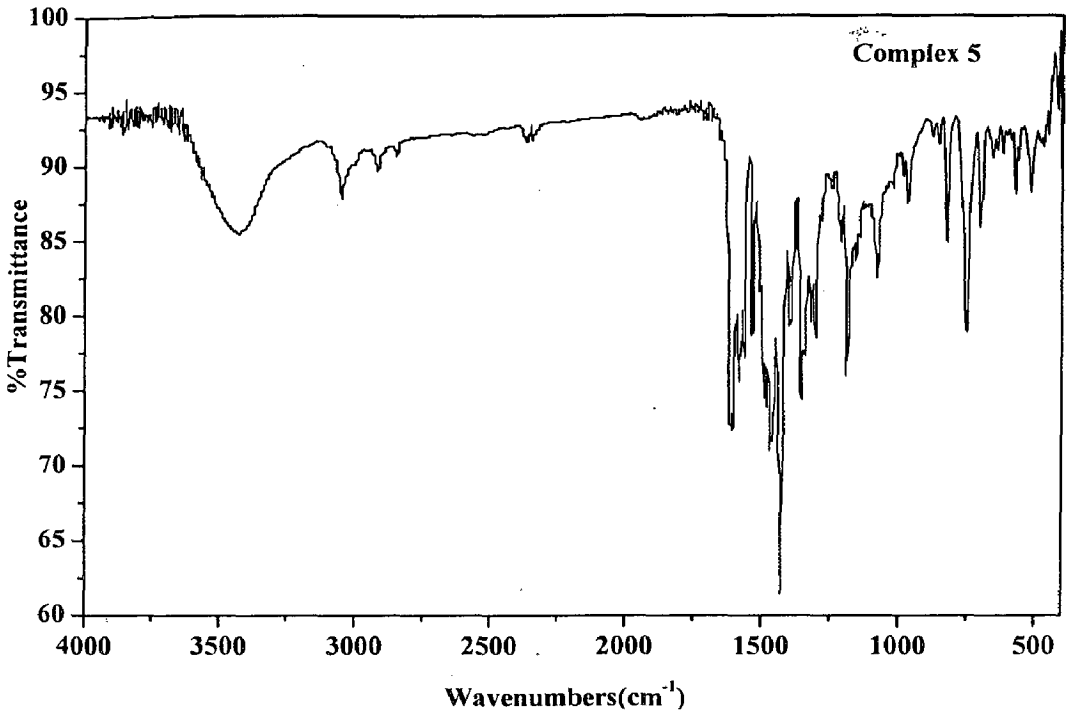
Appendix A_{33}: TGA-DTA curve of complex $[Cr(Me\text{-}Phimp)_2](ClO_4)$ (**3**)



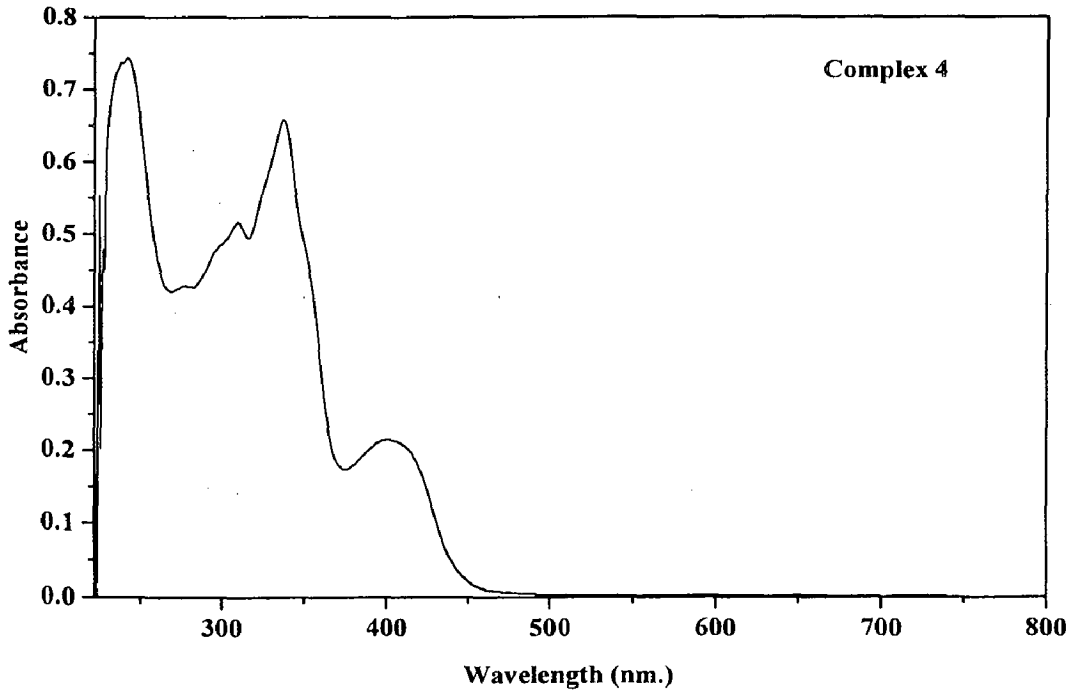
Appendix A_{34}: IR spectra of complex $[Cu(Phimp)_2]$ (**4**)



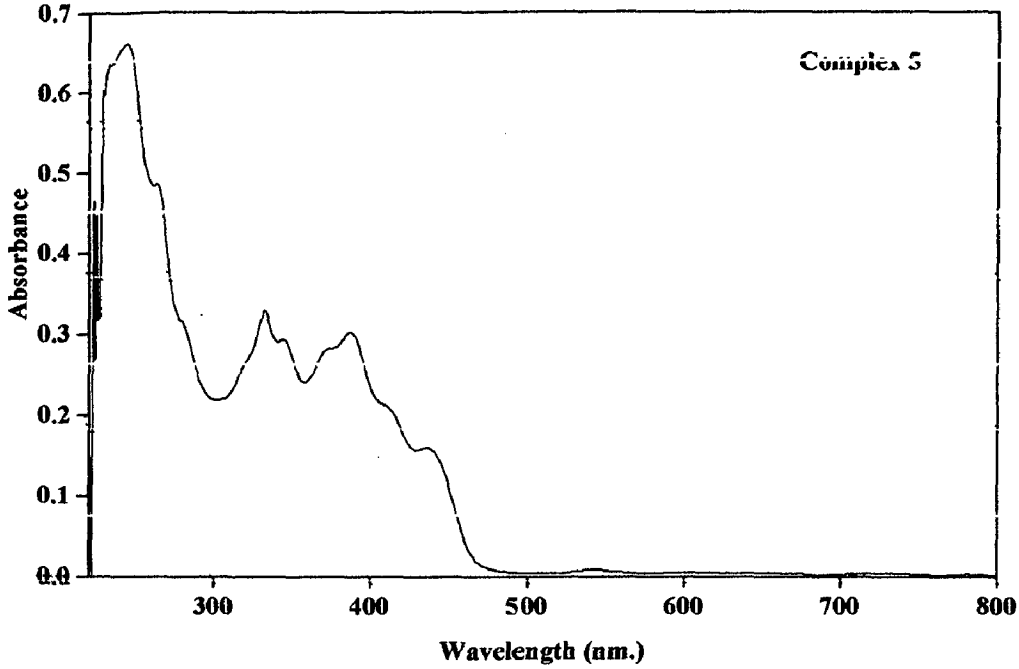
Appendix A_{35}: IR spectra of complex $[Cu(N\text{-}Phimp)_2]$ **(5)**



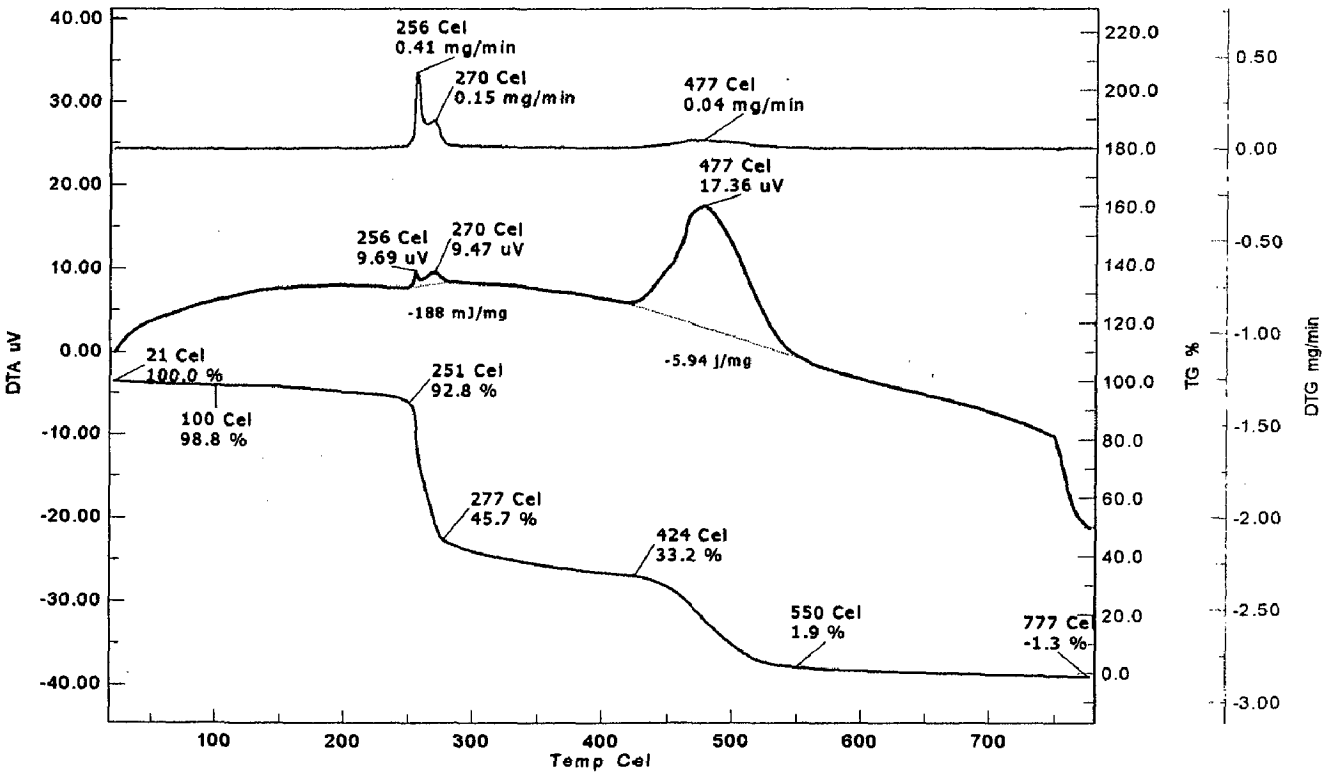
Appendix A_{36}: UV-visible spectra of complex $[Cu(Phimp)_2]$ **(4)**



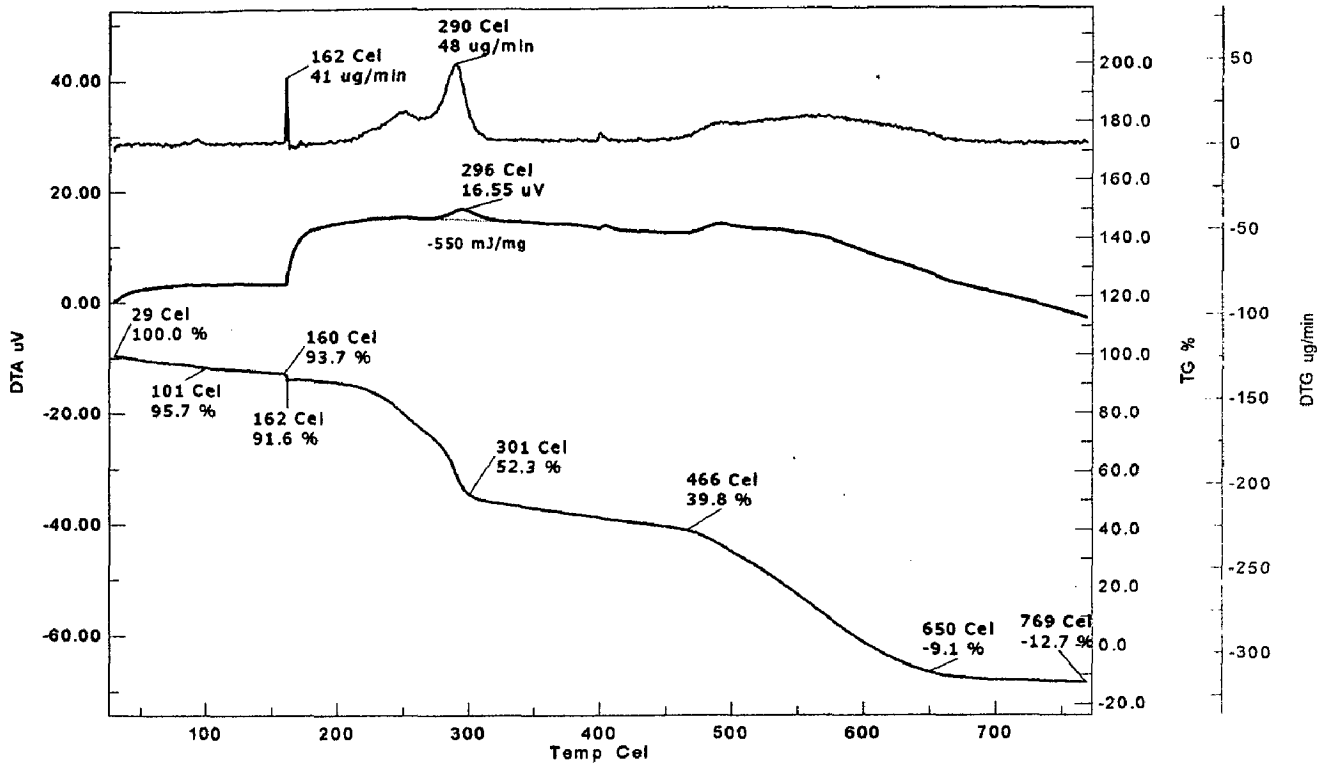
Appendix A_{37}: UV-visible spectra of complex $[Cu(N\text{-}Phimp)_2]$ (5)



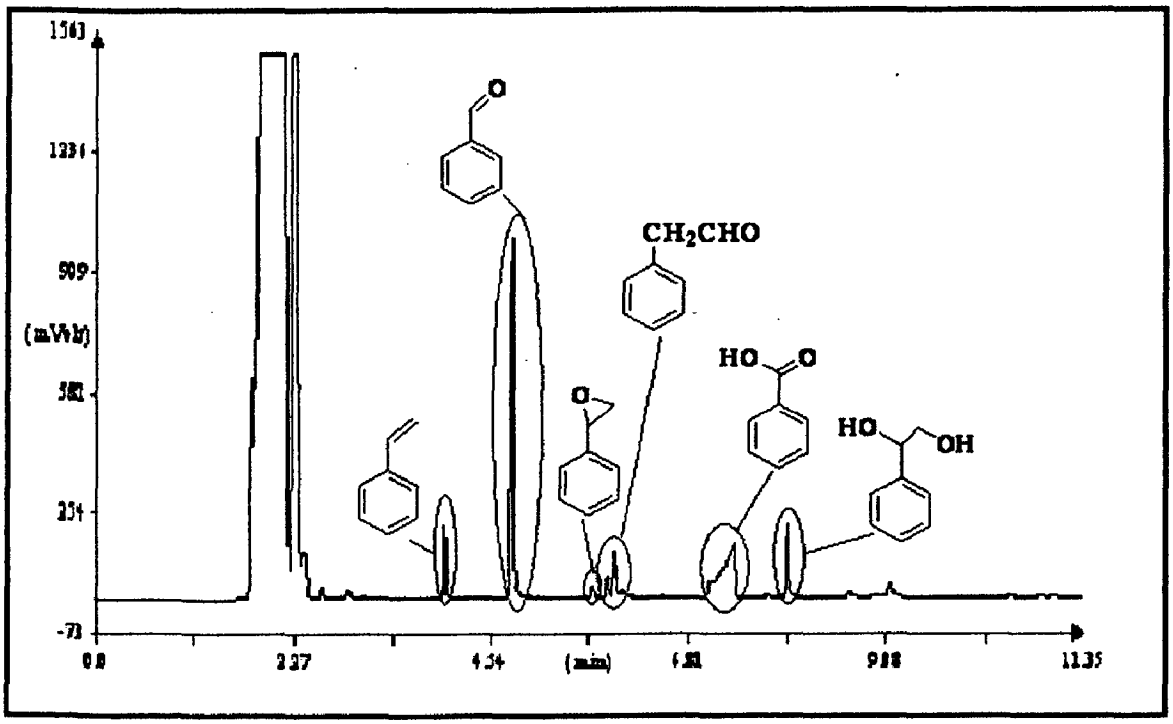
Appendix A_{38}: TGA-DTA curve of complex $[Cu(Phimp)_2]$ (4)



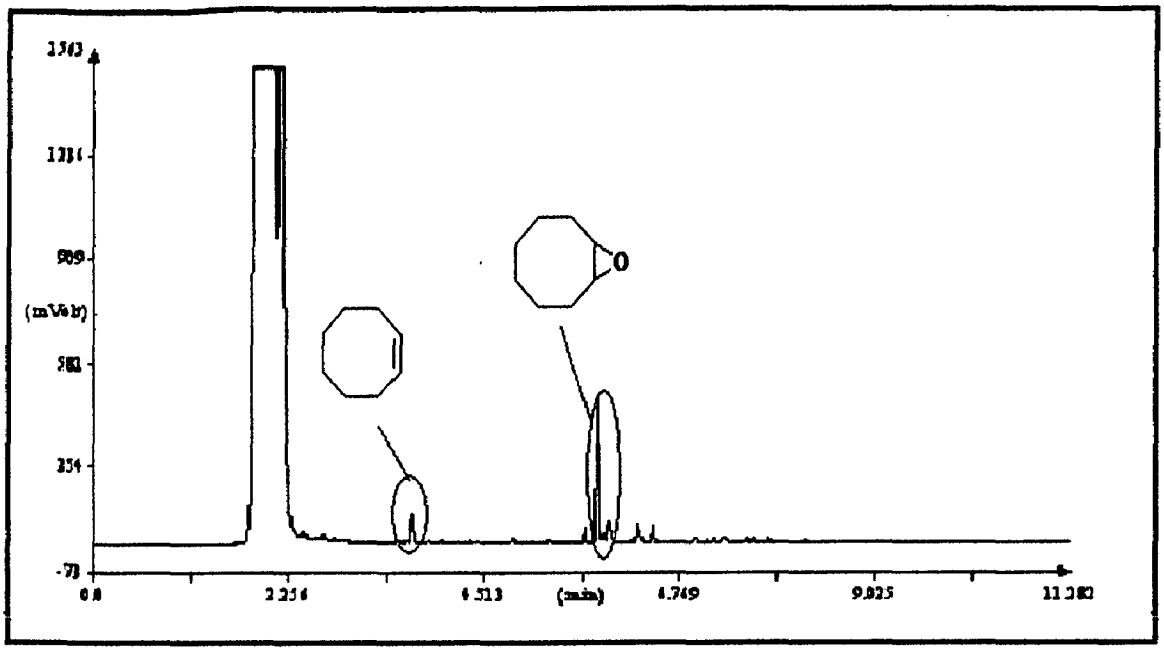
Appendix A_{39}: TGA-DTA curve of compiex $[Cu(N\text{-}Phimp)_2]$ (5)



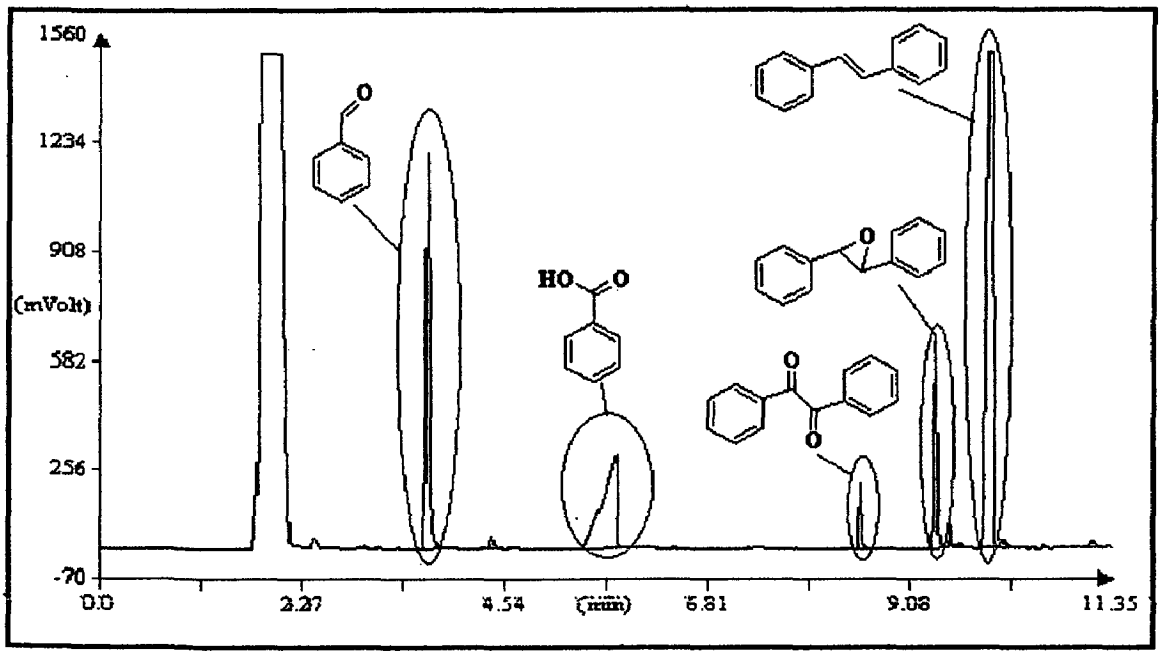
Appendix A_{40}: Gas Chromatogram pattern of oxidation products of styrene



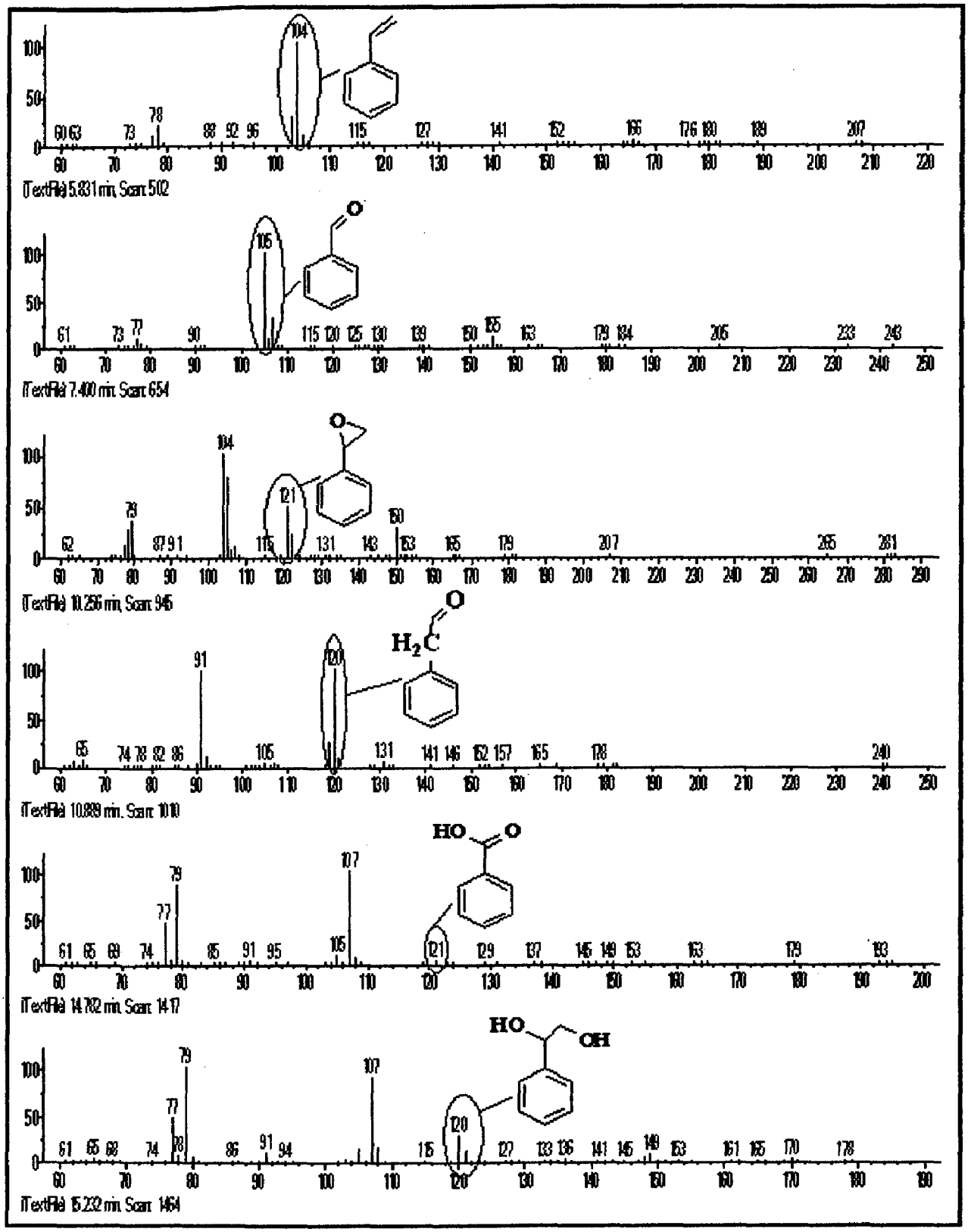
Appendix A_{41}: Gas Chromatogram pattern of oxidation products of *cis*-cyclooctene



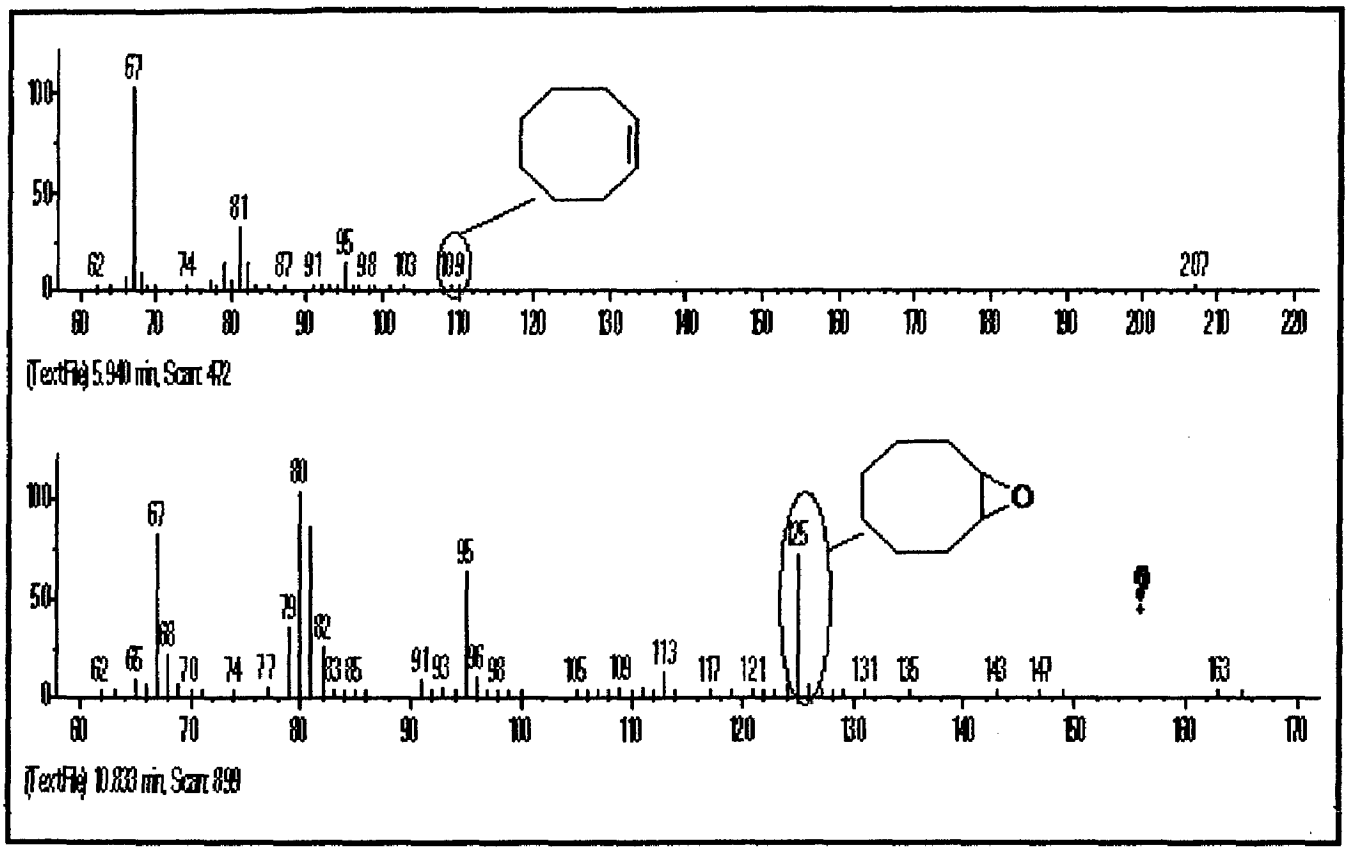
Appendix A_{42}: Gas Chromatogram pattern of oxidation products of *trans*-stilbene



Appendix A$_{43}$: Mass pattern of oxidation products of styrene



Appendix A$_{44}$: Mass pattern of oxidation products of *cis*-cyclooctene



Appendix A$_{45}$: Mass pattern of oxidation products of *trans*-stilbene