Some Aspects of the Oxidation of Organic Substrates and Synthesis of Stereoregular Chiral Polymers

by

SUBBARAYAN VELUSAMY

Department of Chemistry
Indian Institute of Technology Guwahati
Guwahati-781039
May 2006

Some Aspects of the Oxidation of Organic Substrates and Synthesis of Stereoregular Chiral Polymers

A
Thesis Submitted
In Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

SUBBARAYAN VELUSAMY

Roll No: 03612206

Department of Chemistry
Indian Institute of Technology Guwahati
Guwahati 781039
May 2006

Dedicated

To

My Parents

And Sisters

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Guwahati, India under the supervision of Dr. T. Punniyamurthy.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

I.I.T. Guwahati S. Velusamy

May, 2006

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

CERTIFICATE

This is to certify that Mr. S. Velusamy has been working under my supervision since July, 2003. I am forwarding his thesis entitled "*Some Aspects of the Oxidation of Organic Substrates and Synthesis of Stereoregular Chiral Polymers*" being submitted for the Ph.D. degree of this Institute. I certify that he has fulfilled all the requirements according to the rules of this Institute, and regarding the investigations embodied in his thesis and this work has not been submitted elsewhere for a degree.

I.I.T. Guwahati
May, 2006

Dr. T. Punniyamurthy
Supervisor

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

COURSE CERTIFICATE

This is to certify that Mr. S. Velusamy has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

CHM 603	Supra Molecules: Concept and Applications
CHM 611	Bio Inorganic Chemistry
CHM 627	Newer Reagents in Organic Synthesis
CHM 630	A Molecular Approaches in Physical Chemistry

Mr. S. Velusamy has successfully completed his Ph.D. qualifying examination in November 2004.

Prof. A. T. Khan	Dr. Anil Kumar Saikia
Head	Secretary
Department of Chemistry	Departmental Post Graduate Committee
I.I.T. Guwahati	Department of Chemistry
	I.I.T. Guwahati

ACKNOWLEDGEMENT

I am extremely grateful to my guide Dr. T. Punniyamurthy for his expert guidance, encouragement and suggestions in interesting research topics throughout my research carrier. His unfounding enthusiasm and zeal for research has inspired me immensely and has been a pleasure for me to have the benefit of this invaluable training in the art of organic synthesis. For these and his many contributions, I shall ever remain profoundly indebted to him.

I wish to thank I owe my sincere thanks to my lab colleagues, Laxmider, Suribabu and Vijyakumar for there pleasant company.

I am also thankful to my all friends for their support and encouragement.

I acknowledge to the Indian Institute of Technology, Guwahati for providing institute fellowship for the entire period of the Ph.D. programme.

Finally my heartful thanks go to my parents and sisters for their sustained help and encouragement in all my academic endeavors. I feel deeply indebted to them for whatever I have achieved so far.

S. Velusamy

Abstract

The thesis has four chapters. The first chapter describes the oxidation of alcohols with molecular oxygen in the presence of recyclable polyaniline supported vanadium and molybdenum catalysts. In the second chapter, the oxidation of alcohols, alkanes and sulfides is demonstrated with copper(II) salan in the presence of 30% aqueous H_2O_2. The third chapter focuses on the selective oxidation of primary alcohols to aldehydes and sulfides to sulfoxides by the combined use of copper(II) salan and TEMPO. Molecular oxygen and 30% aqueous H_2O_2 have been employed as the terminal oxidants. The final chapter describes the synthesis and application of a chiral main chain polymer with optically active (1*R*,2*R*)-1,2-diamidocyclohexane for the asymmetric desymmetrization of cyclohexene oxide.

1. Polyaniline Supported Vanadium and Molybdenum Catalyzed Oxidation of Alcohols with Molecular Oxygen

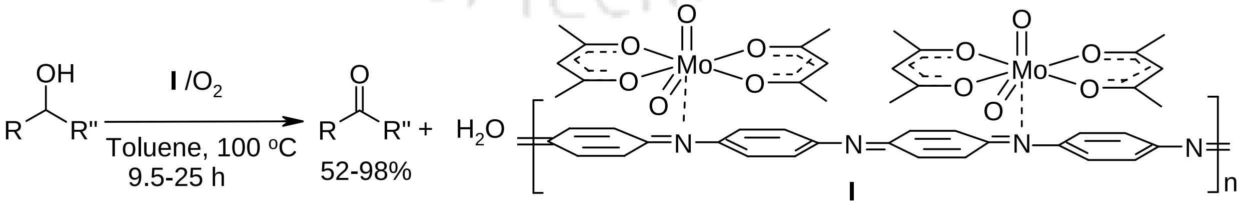
The oxidation of alcohols to aldehydes and ketones is one of the most important and fundamental functional transformations in organic chemistry. The world wide annual production of carbonyl compounds is about 10^7 tones and many of these compounds are produced from the oxidation of alcohols. Traditionally, the oxidation of alcohols is carried out with stoichiometric amount of inorganic reagents such as chromate and permanganate. These reagents generate significant amount of inorganic salt containing effluent along with the target molecules and demand laborious work-up procedure. Therefore, in view of the increasing global concern on environmental problem, the chemists both in academic institutions and industries are forced to replace these antiquated technologies by cleaner catalytic alternatives. A clean methodology should involve a catalytic system with atom efficient oxidant such as molecular oxygen and hydrogen peroxide, which can generate only water as by-product. The use of heterogeneous catalysts in the liquid phase offers several advantages over homogeneous ones, such as ease of recovery and recycling, atom utility and enhanced stability.

First part of this chapter describes the polyaniline supported molybdenum catalyzed oxidation of alcohols to aldehydes and ketones using atmospheric oxygen. In the second part of the chapter, vanadium catalyzed aerobic oxidation of alcohols to aldehydes and ketones in the presence of molecular oxygen has been discussed. The reactions are clean technological processes and the catalysts are recyclable without loss of activity.

1.1 Oxidation of Alcohols

Polyaniline-$MoO_2(acac)_2$ Catalyzed Reactions

The polyaniline supported molybdenum complex **I** was prepared by reacting a 1:1 (wt/wt) mixture of polyaniline and $MoO_2(acac)_2$ in acetonitrile at ambient temperature. Whose catalytic activity has been evaluated for the oxidation of aliphatic, aromatic and allylic alcohols with atmospheric oxygen (Scheme 1). The oxidation of primary alcohols was found to be greater in comparison to secondary alcohols. The reactions did not involve additives and generate only water as the by-product.

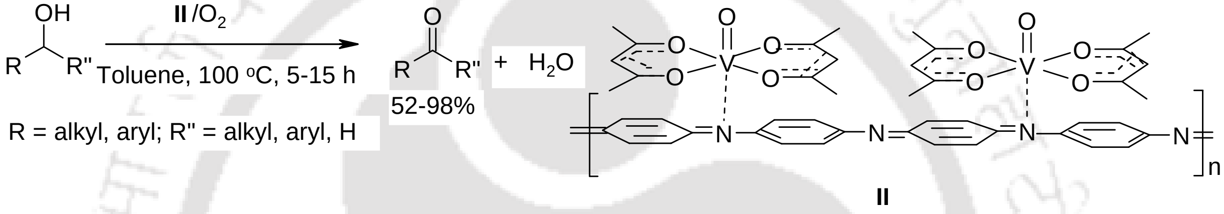


R = alkyl, aryl; R" = alkyl, aryl, H

Scheme 1

Polyaniline-VO(acac)$_2$ Catalyzed Reactions

The polyaniline supported vanadium complex **II** was prepared, as described for the polyaniline-molybdenum complex **I,** in dichloromethane. The oxidation of aliphatic, aromatic and allylic alcohols has been studied to the corresponding aldehydes and ketones with high yields. In this system, the secondary alcohols were more reactive in comparison to primary alcohols. The reactions were found to be efficient under oxygen balloon. More recently the catalyst **II** has been commercialized by Sigma-Aldrich.



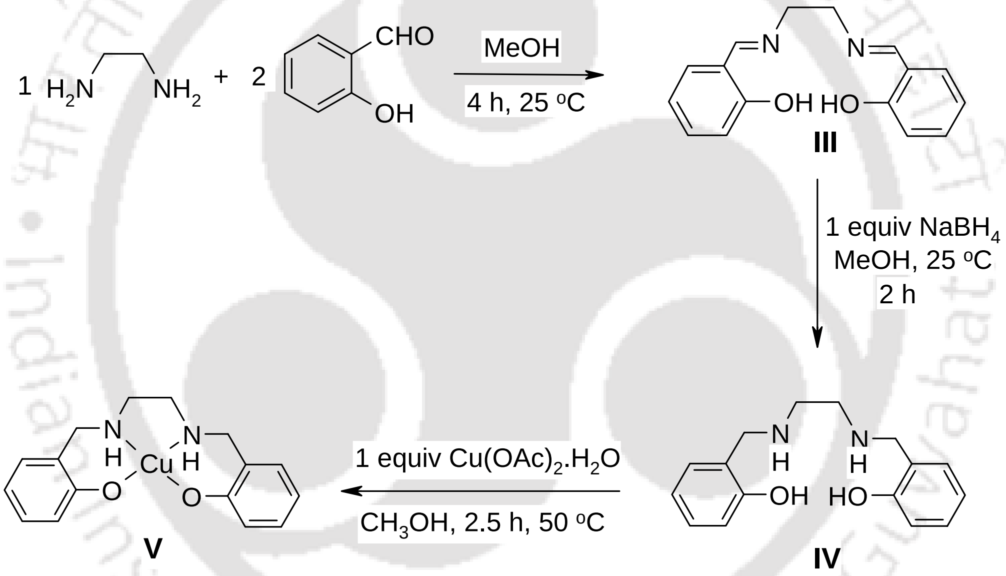
Scheme 2

2. Copper(II) Catalyzed Oxidation of Organic Compounds with Aqueous 30% H$_2$O$_2$

H_2O_2 is a very attractive oxidant for liquid-phase reactions. It can oxidize the organic compounds with atom efficiency of 47%. It is relatively cheap, <0.7 US dollar Kg^{-1} (100%, H_2O_2), and about 2.4 million metric tons are produced for use, mainly as bleach. It should be noted that H_2O_2 can be ideal and waste-avoiding oxidant only when it is used in a controlled manner. The H_2O_2 oxidation is particularly useful for the synthesis of high-value fine chemicals, pharmaceuticals or agrochemicals, and electronic materials which require high chemical purity. It may also be used for improving the environment by oxidative removal of very small amounts of toxic compounds. We foresee that H_2O_2

and O_2 (or air) will be complementary useful clean oxidants in practical chemical synthesis.

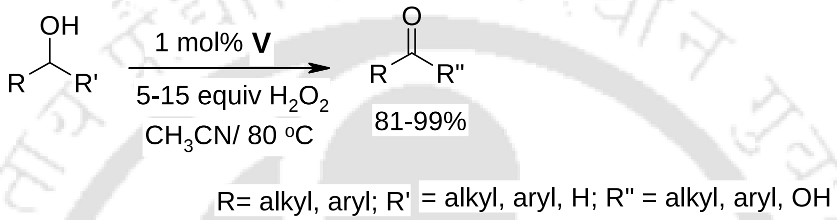
In this chapter, the oxidation of alcohols, alkanes and sulfides with copper(II) complex **V** in the presence of 30% aqueous H_2O_2 has been described. Reaction of ethylenediamine with salicylaldehyde provides the corresponding Schiff base **III** which could be reduced by $NaBH_4$ in methanol to afford **IV** as a colorless solid. The latter could be readily reacted with $Cu(OAc)_2$ in methanol to yield copper(II) complex **V** as a green powder in high yield.



Scheme 3

2.1 Oxidation of Alcohols to Carboxylic Acids and Ketones

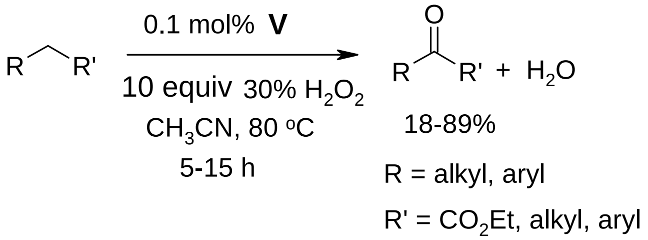
The oxidation of alcohols to carboxylic acids and ketones is a routinely used functional transformation in both laboratories and industries. Traditionally these reactions are carried out with stoichiometric amount of chromium and manganese based reagents. Removal of traces of these reagents from the reaction mixtures is difficult and demands laborious work-up procedure. Thus development of catalytic systems for this process will be quite useful. This section describes the oxidation of alcohols to carboxylic acids with copper(II) complex **V** in the presence of 30% aqueous H_2O_2 (Scheme 4). Aromatic and aliphatic alcohols were oxidized to the corresponding carbonyl compounds in high yields. The compounds with carbon-carbon double bond underwent oxidative cleavage to provide the corresponding carboxylic acids.



Scheme 4

2.2 Oxidation of Alkylbenzenes and Cyclohexane

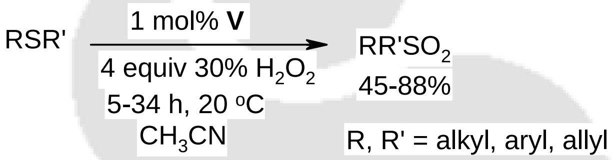
Functionalization of hydrocarbons to alcohols and carbonyl compounds is an important process in view of its synthetic and industrial aspects. The success of this process depends upon the nature of the metal catalyst and oxidizing reagent employed. Most of the reported procedures are modeled on metalloenzymes that perform the oxidation of hydrocarbons in natural systems. This section demonstrates the oxidation of hydrocarbons with copper(II) complex **V** in the presence of 30% aqueous H_2O_2 in high yields (Scheme 5).



Scheme 5

2.3 Oxidation of Sulfides to Sulfones

Organic sulfoxides and sulfones are useful synthetic intermediates for the construction of various chemically and biologically active molecules. They often play an important role as therapeutic agents such as anti-ulcer (proton pump inhibitor), antibacterial, antifungal, anti-atherosclerotic, anthelmintic, antihypertensive and cardiotonic agents. This section focuses on the oxidation of a series of aryl alkyl sulfides to the corresponding sulfoxides and sulfones in the presence of copper(II) complex **V** and 30% aqueous H_2O_2 (Scheme 6).



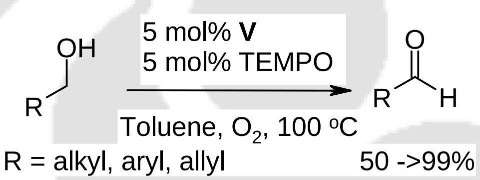
Scheme 6

3. Copper(II) complex and TEMPO Catalyzed Selective Oxidation of Primary Alcohols to Aldehydes and Sulfides to Sulfoxides

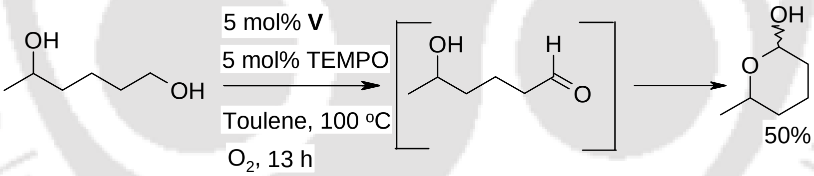
The selective oxidation of primary alcohols to aldehydes and sulfides to sulfoxides are important process in fine chemical industries. The first part of the chapter describes the oxidation of a series of primary alcohols to aldehydes by the combined use of copper(II) complex **V** and TEMPO in the presence of atmospheric oxygen. The second part of the chapter focuses on the selective oxidation of sulfides to sulfoxides with copper(II) complex **V** and TEMPO in the presence of 30% aqueous H_2O_2.

3.1.1 Oxidation of Primary Alcohols to Aldehydes with Atmospheric Oxygen

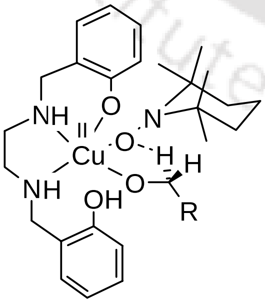
The selective oxidation of primary alcohols to aldehydes using molecular oxygen in the presence of secondary hydroxyl group is a valuable functional transformation. So far only few studies have been reported for this purpose. This section deals with the catalytic oxidation of primary alcohols to aldehydes covering aromatic, allylic and aliphatic alcohols to aldehydes with atmospheric oxygen in high yields (Scheme 7-8). The combination of copper(II) complex **V** and TEMPO is essential for this process.



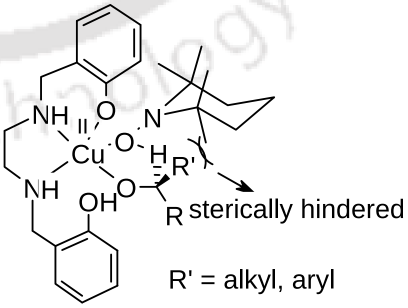
Scheme 7



Scheme 8



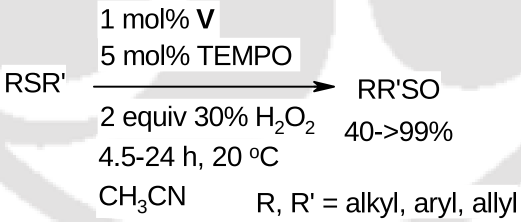
a



b

3.2.1 Copper(II) Complex Catalyzed Selective Oxidation of Sulfides to Sulfoxides with 30% H_2O_2

Synthetic building blocks containing sulfoxide functional groups are particularly useful for the construction of various important compounds. These derivatives are usually prepared by oxidation of sulfides. Generally, it is important to stop the oxidation at the sulfoxide stage by controlling the electrophilic character of the oxidant, but this requirement is often hard to meet and failure results in over oxidation to sulfones. Thus, there is still considerable interest in the development of selective oxidants for this transformation. This section describes the selective oxidation of sulfides to sulfoxides with 30% H_2O_2 in the presence of copper(II) complex **V** and TEMPO at ambient temperature. The presence of TEMPO is essential in its absence the oxidation occurred to provide a mixture of sulfoxides and sulfones. The substrates having double bonds are compatible with this protocol (Scheme 9).

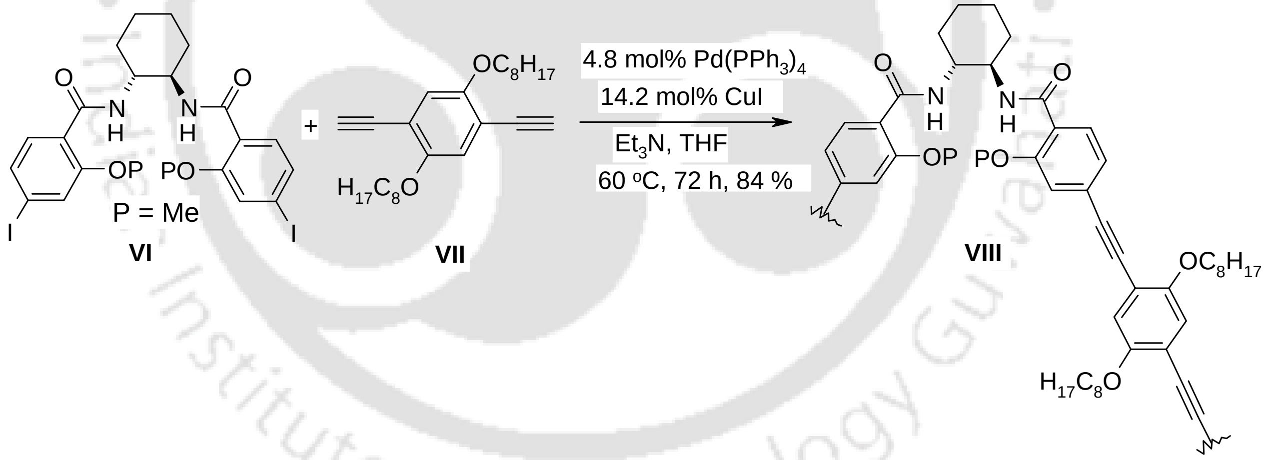


Scheme 9

4. New Chiral Main Chain Polymers for Asymmetric Synthesis

Extensive studies in the field of asymmetric synthesis have led to the discovery of many highly enantioselective catalysts. Since these optically active catalysts are often quite expensive, their recovery and reuse are highly desirable. Thus, much attention has been recently focused on the design and development of chiral macromolecular catalysts. They can be broadly divided into three groups: (i) monomeric chiral compounds anchored to stereoirregular polymers, (ii) chiral main chain polymers and (iii) chiral dendrimers. Of these, the chiral main chain polymers are usually found to be efficient material since the microenvironment of the chiral monomeric units can be preserved.

This chapter focuses on the palladium catalyzed synthesis of stereoregular chiral main chain polymer **VIII** from (1*R*,2*R*)-1,2-diamidocyclohexane **VI** and conjugate segment, 1,4-diethynyl-2,5-bis(octyloxy)benzene **VII**, in high yield (Scheme 10). The polymer **VIII** has shown an enhanced enantioselectivity in comparison to its chiral monomer in the asymmetric desymmetrization of cyclohexene oxide with aniline and 4-methoxybenzyl alcohol in the presence of Sc(OTf)$_3$.



Scheme 10

Contents

Polyaniline Supported Vanadium and Molybdeunm Catalyzed Aerobic Oxidation of Alcohols

Transition-metal-catalyzed oxidation reactions are among the most fundamental reactions in nature; they are responsible for the activation and reactions of molecular oxygen (O_2) in living species on the earth's surface and fundamental for the chemical industry in modern society.

In industry, transition-metal-catalyzed oxidation reactions, cover a variety of different reactions and are used for the production of bulk chemicals, which are building blocks for the formation of a variety of products. Moving further up in the hierarchy in the complexity of organic molecules, transition-metal-catalyzed oxidation reactions are also basic for the synthesis of complex organic molecules, such as pharmaceutical products where the stereochemistry is of utmost importance. The industrial use of transition-metal-catalyzed oxidations for the production of bulk chemicals is primarily based on heterogeneous catalysis with molecular oxygen as the terminal oxidant, while the homogeneous catalysis mainly used for the preparation of fine chemicals with a variety of different terminal oxidants.

1.1 Oxidation of Alcohols

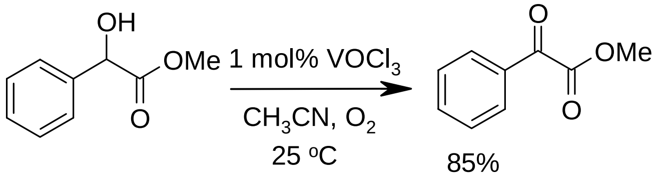
The oxidation of alcohols to aldehydes and ketones is one of the most important reactions in organic chemistry, both for fundamental research and industrial manufacturing.[1-3] The world-wide annual production of carbonyl compounds is over 10^7 tones and many of these compounds are produced from the oxidation of alcohols.[4] The oxidation of alcohols is traditionally carried out with stoichiometric amounts of oxidants such as chromate,[5-9] permanganate,[10,11] ruthenium(VIII) oxide,[12-13] TPAP/NMO (*tetra*-*N*-propylammonium perruthenate/*N*-methyl-morpholine-*N*-oxide),[14-15] activated dimethyl sulfoxide (DMSO)[16] and Dess–Martin periodinane.[17] Some of these processes generate equal amounts of metal wastes along with the target molecules demanding laborious work-up procedure. Furthermore, most of these reactions are usually carried out in halogenated solvents, typically chlorinated hydrocarbons, which are environmentally undesirable. Therefore, development of green, selective and efficient catalytic system for the oxidation of alcohols, that can use air or pure dioxygen (O_2) as oxidant, is more desirable for both economic and environmental reasons (Scheme 1).[18]

$$\text{R-CH}_2\text{OH} \xrightarrow[\text{O}_2]{\text{Catalyst}} \text{RCHO} + \text{H}_2\text{O}$$

Scheme 1

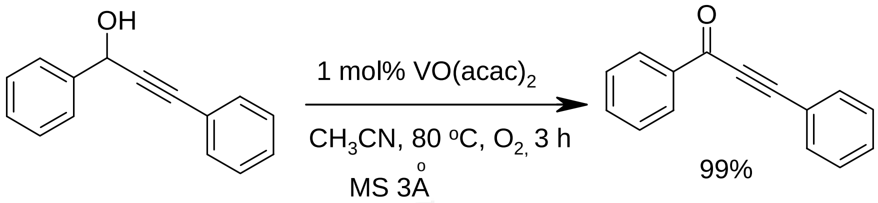
1.1.1 Vanadium Catalysts

α-Hydroxy carbonyl compounds have been oxidized to the corresponding α-dicarbonyl compounds in high yields in the presence of $VO(OEt)Cl_2$ as well as $VOCl_3$ under oxygen atmosphere (Scheme 2).[19-20] The presence of α-carbonyl group is essential in its absence no reaction is observed.



Scheme 2

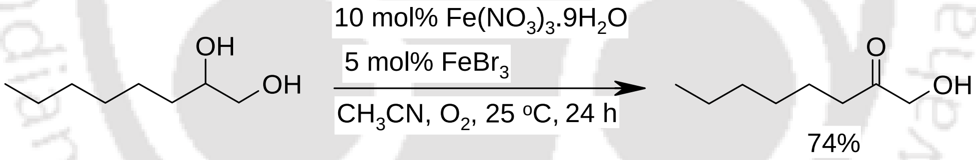
The oxidation of propargylic alcohols to the corresponding ketones is reported in high yields in the presence of $VO(acac)_2$ under atmospheric oxygen (Scheme 3).[21]



Scheme 3

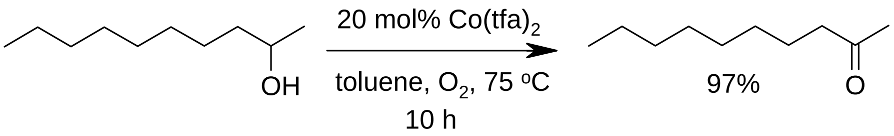
1.1.2 Iron Catalysts

By the combined use of $Fe(NO_3)_3$–$FeBr_3$ the oxidation of alcohols to aldehydes and ketones is reported with atmospheric oxygen at ambient temepratura.[22] The reactivity of secondary alcohols is found to be greater in comparison to primary alcohols (Scheme 4).



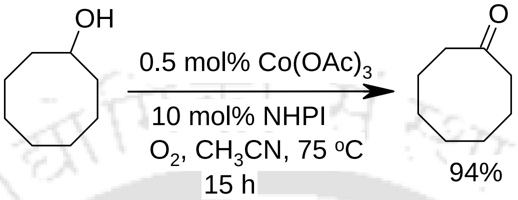
Scheme 4

Yamada and Mukaiyama employed $Co(tfa)_2$ for the oxidation of secondary alcohols to ketones with atmospheric oxygen at 75 °C in toluene (Scheme 5).[23]



Scheme 5

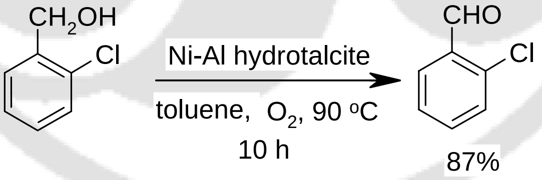
The catalytic system having NHPI and $Co(OAc)_3$ catalyzes the oxidation of alcohols to ketones and carboxylic acids under atmospheric oxygen (Scheme 6).[24] The reactivity of secondary alcohols is found to be greater in comparison to primary alcohols.



Scheme 6

1.1.3 Nickel Catalyst

Ni-Al hydrotalcite has been shown to catalyze the oxidation of alcohols to aldehydes and ketones under atmospheric oxygen (Scheme 7).[25] The catalyst is recyclable without loss of activity up to six runs.

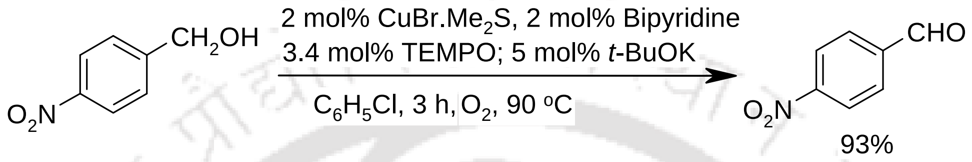


Scheme 7

1.1.4 Copper Catalysts

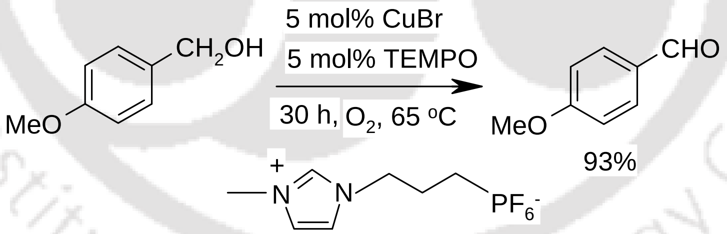
Copper based catalysts have been considerably studied for the oxidation of alcohols to aldehydes and ketones with molecular oxygen. Knochel and co-workers reported the oxidation of alcohols using perfluoroalkyl substituted bipyridine-$CuBr{\cdot}Me_2S$ and

TEMPO in a fluorous biphasic system of chlorobenzene and perfluorooctane under oxygen atmosphere (Scheme 8).[26] To demonstrate the recyclability of the catalyst, the fluorous phase containing the catalyst has been reused several times for further reaction runs without a significant decrease in yield and in rate.



Scheme 8

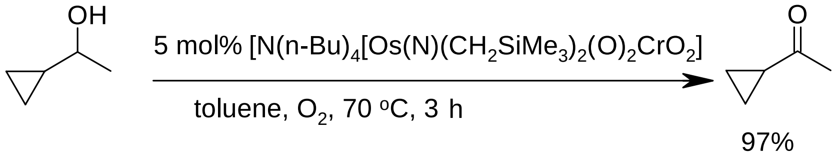
CuCl has been shown to catalyze the oxidation of alcohols in the presence of TEMPO in ionic liquid [bmim][PF_6] (Scheme 9).[27] Under these conditions aliphatic and cyclic alcohols are found to be less reactive and no oxidation is observed when the solubility of alcohols in the ionic solvent is poor.



Scheme 9

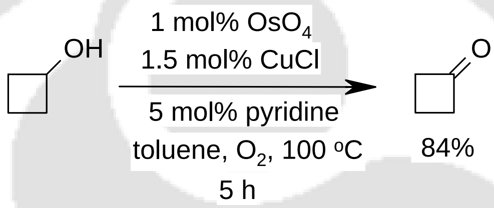
1.1.5 Osmium Catalysts

Os-Cr complex, [*N*(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$(μ-O)$_2$$CrO_2$], has been shown to catalyze the oxidation of alcohols to aldehydes and ketones with atmospheric oxygen (Scheme 10).[28] The oxidation of primary alcohols is found to be greater in comparison to secondary alcohols.



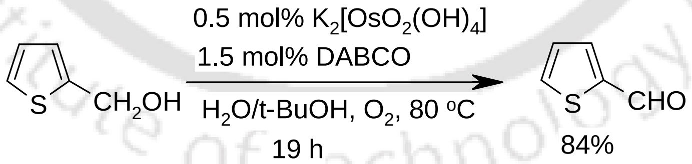
Scheme 10

By the combined use of OsO_4 and CuCl, the oxidation of alcohols to aldehydes and ketones has been studied with molecular oxygen (Scheme 11).[29]



Scheme 11

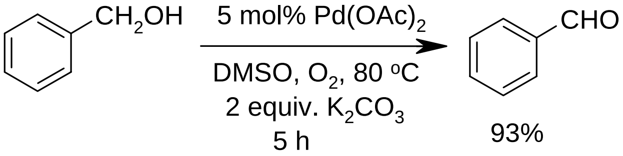
$K_2[OsO_2(OH)_4]$ has been used for the oxidation of alcohols with 1 bar molecular oxygen in the presence of DABCO (Scheme 12).[30] Secondary aliphatic alcohols need a larger amount of catalyst and/or higher reaction temperatures in order to obtain sufficient conversion.



Scheme 12

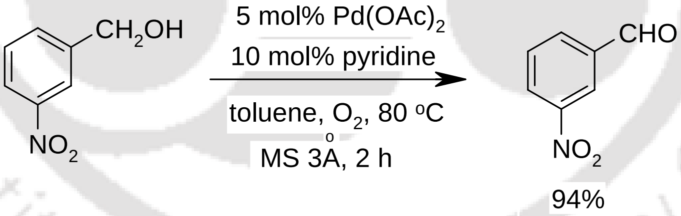
1.1.6 Palladium Catalysts

Palladium based catalysts have been extensively studied for the oxidation of alcohols with molecular oxygen. $Pd(OAc)_2$ has been employed for the oxidation of alcohols in the presence of base such as $NaHCO_3$ and K_2CO_3 (Scheme 13).[31]



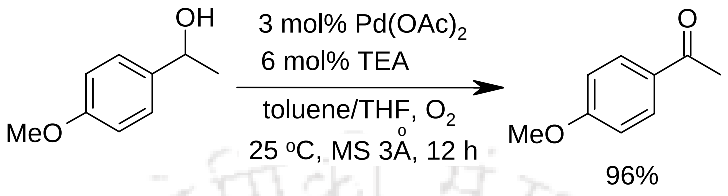
Scheme 13

Subsequently, $Pd(OAc)_2$ has been shown to catalyze the oxidation of alcohols with molecular oxygen in the presence of pyridine and MS 3Å in toluene.[32] All major classes of alcohols like primary, secondary, benzylic, and allylic alcohols are oxidized under these conditions. Substrates bearing alkene functionality, especially allylic alcohols, require the use of excess of pyridine (500 mol%) to prevent palladium metal precipitation (Scheme 14). Several alcohol-protecting groups are compatible with the reaction conditions, including tetrahydropyranyl, *tert*-butyldimethylsilyl, and benzyl ethers. Alcohols bearing vicinal heteroatom functionality (amines, ethers) appear to be ineffective substrates, possibly reflecting substrate chelation.



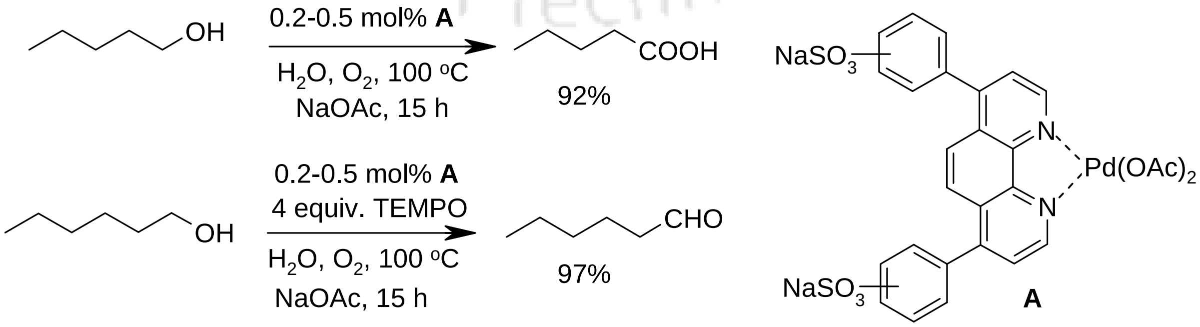
Scheme 14

Sigman and co-workers studied the oxidation of alcohols in the presence of $Pd(OAc)_2$ at ambient temperature.[33] This procedure is found to be efficient in the presence of triethylamine (TEA) and activated MS 3Å. Both aliphatic and aromatic alcohols are oxidized in high yields (Scheme 15). But allylic alcohols are not the candidates for the reaction. This may be due to complex formation with palladium salt leading to inhibition of the oxidation processes.



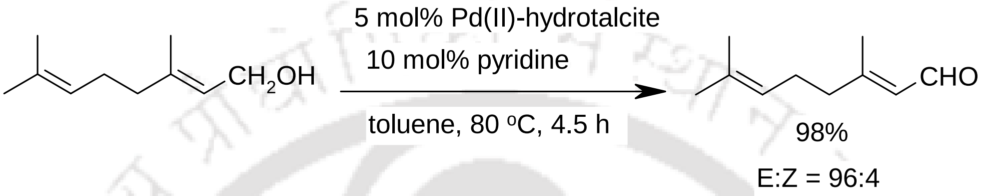
Scheme 15

The oxidation of alcohols with 30 bar air has been studied in the presence of Pd catalyst **A** and 10 mol% NaOAc in aqueous solution at 100 °C.[34] Catalytic rates (up to 100 $\mathrm{TOh^{-1}}$) and turn over numbers (200-400) of this system are significantly higher than those reported for previous catalytic systems. Aliphatic primary alcohols are oxidized into carboxylic acids under the reaction conditions, but in the presence of 2% TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxy) (4 equiv relative to Pd), the reaction can be stopped after oxidation into aldehyde (Scheme 16). Amine, sulfide, and polyether functionalities present in the alcohol substrate appear to inhibit turnover by coordination to palladium.



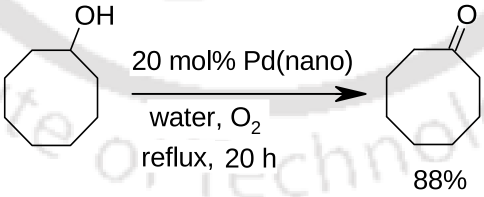
Scheme 16

Palladium(II)-hydrotalcite has been used as a reusable catalyst for the oxidation of alcohols in the presence of pyridine under atmospheric oxygen (Scheme 17).[35] Both aromatic and aliphatic alcohols could be oxidized to the corresponding carbonyl compounds in high yields.



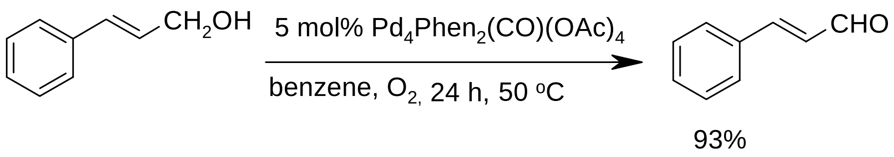
Scheme 17

Uozumi and Nakao studied the oxidation of alcohols to aldehydes using palladium nano particles under molecular oxygen in aqueous medium.[36] Sterically hindered alcohol such as cyclooctanol has been oxidized smoothly but required longer reaction time (Scheme 18). Aliphatic primary alcohols are converted to carboxylic acids after 40 h in the presence of 0.2 M K_2CO_3 solution.



Scheme 18

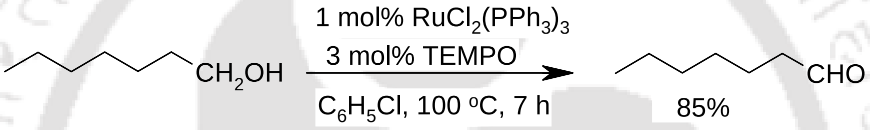
The oxidation of allylic alcohols has been accomplished using Pd-cluster, $Pd_4(CO)_4(OAc).2AcOH$ (PCA), in the presence of molecular oxygen (Scheme 19).[37] $Pd(OAc)_2$, Pd/C and $PdCl_2$ were less reactive compared to pd-cluster.



Scheme 19

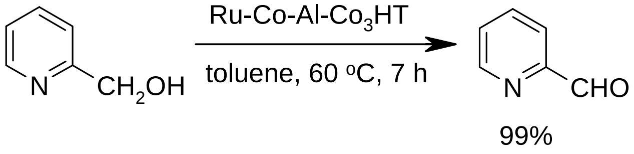
1.1.7 Ruthenium Catalysts

The combination of $RuCl_2(PPh_3)_3$ and TEMPO has been shown to catalyze the aerobic oxidation of alcohols in good yields (Scheme 20).[38]



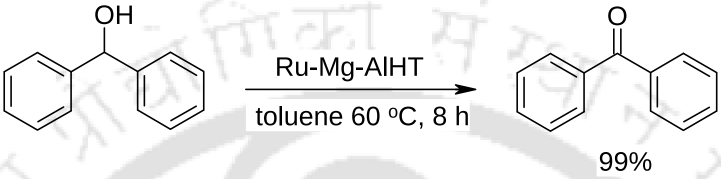
Scheme 20

The ruthenium hydrotalcite having cobalt cations, Ru-Co-Al-CO_3 HT, has been demonstrated as an effective heterogeneous catalyst for the oxidation of alcohols in the presence of molecular oxygen.[39] In the case of benzylic alcohols, the corresponding aldehydes were obtained in high yields (Scheme 21). A secondary saturated alcohol, octan-2-ol, was smoothly converted into the corresponding ketone while primary saturated alcohols such as octan-1-ol showed extremely low reactivity for this oxidation.



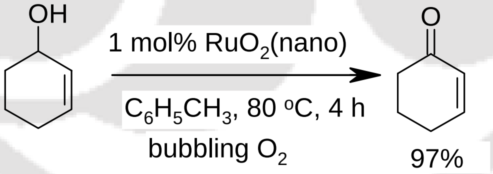
Scheme 21

The oxidation of allylic and benzylic alcohols has been carried out using molecular oxygen in the presence Ru-Al-Mg hydrotalcites.[40] Under these conditions, secondary alcohols are efficiently oxidized to the corresponding ketones in quantitative yields (Scheme 22).



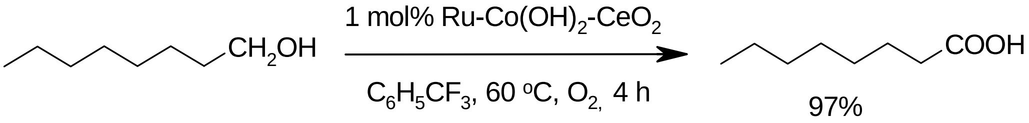
Scheme 22

Zeolite-confined nano-RuO_2 has been shown to catalyze the aerobic oxidation of alcohols in high yields.[41] In this system benzyl alcohol was oxidized in 99% with 13 TON. Aliphatic alcohol like heptanol oxidized to heptanal in quantitative yield (Scheme 23).



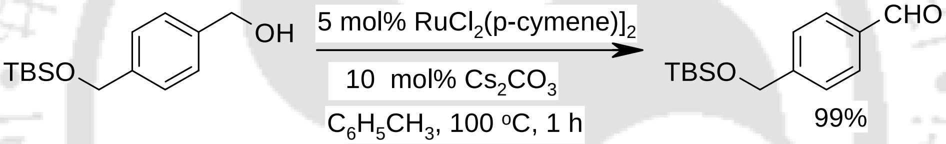
Scheme 23

Ru cation combined with cobalt hydroxide and cerium oxide, Ru–$Co(OH)_2$–CeO_2, has been found to be an effective heterogeneous catalyst for the oxidation of various alcohols to carbonyl compounds under atmospheric pressure of oxygen (Scheme 24)[42]. Notably, the present catalyst showed high activity for the oxidation of primary aliphatic alcohols to carboxylic acids.



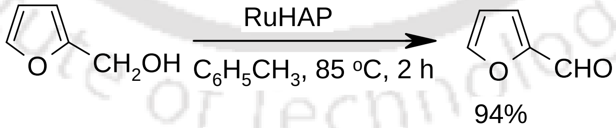
Scheme 24

Lee and Chang employed [$RuCl_2$(*p*-cymene)]$_2$:Cs_2CO_3 for the oxidation of activated alcohols to the corresponding carbonyl compounds under molecular oxygen.[43] Primary alcohols are smoothly oxidized to the corresponding aldehydes in excellent yields. Common protecting groups such as silyl ether or acetate are tolerant under these conditions (Scheme 25).



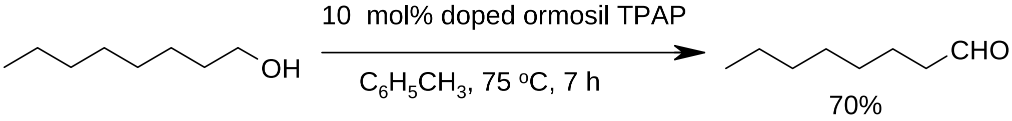
Scheme 25

Ru^{3+}-exchanged hydroxyapatite (RuHAP) has been shown to efficiently catalyze the the oxidation of various alcohols using molecular oxygen (Scheme 26).[44]



Scheme 26

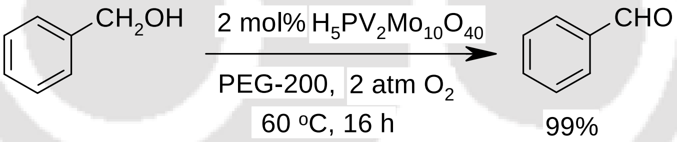
Pagliaro and Criminna reported the aerobic oxidation of alcohols to aldehydes and ketones with recyclable sol-gel ormosils doped TPAP (*tetra*-*n*-propyl ammonium perruthenate) (Scheme 28).[45]



Scheme 27

1.1.8 Polyoxometalate Catalyst

Polyoxometalate, $H_5PV_2Mo_{10}O_{40}$, has been shown to catalyze the oxidation of alcohols with molecular oxygen in the presence of polyethylene glycol (Scheme 28).[46] Analysis of the reaction mixture by GC and GC-MS revealed that for PEG-200, primary benzylic alcohols yielded only benzaldehydes as reaction products. For a secondary alcohol, 1-phenylethanol, selectivity towards oxidation is low. Here, acid catalyzed dehydration to styrene (some of which was oxidized to benzaldehyde) is the major reaction pathway. The advantage of the system is the solvent-catalyst phase can be recovered and recycled.



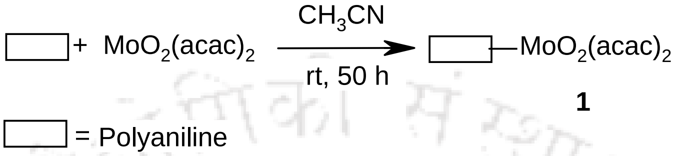
Scheme 28

1.2 Present Study

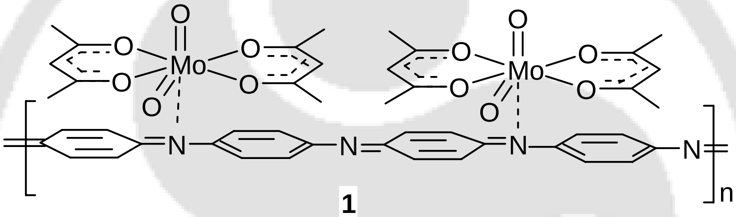
The use of heterogeneous catalysts in the liquid phase offers several advantages over homogeneous ones, such as ease of recovery and recycling, atom utility and enhanced stability. Furthermore, the development of catalytic systems with less toxic, inexpensive and readily accessible metal salts will be quite useful. In this context, we have prepared polyaniline supported $VO(acac)_2$ and $MoO_2(acac)_2$ catalysts and studied their activity in the aerobic oxidation of alcohol.

Polyaniline-$MoO_2(acac)_2$ Catalyzed Reactions

The preparation of polyaniline supported $MoO_2(acac)_2$ **1** was carried out by stirring a 1:1 (wt/wt) mixture of polyaniline and $MoO_2(acac)_2$ in acetonitrile for 50 h at ambient temperature (Scheme 30).



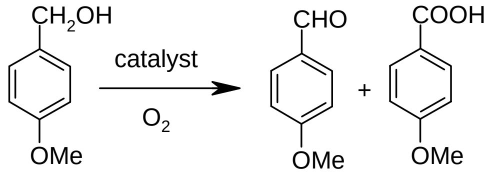
Scheme 29



1

Figure 1. Proposed Structure for Polyaniline Supported $MoO_2(acac)_2$ **1**.

Having the catalyst **1** in hand, we investigated the oxidation of 4-anisyl alcohol as a standard substrate under atmospheric oxygen (Scheme 31). We were pleased to find that the reaction occurred efficiently to afford 4-anisaldehyde in high yield when the reaction was allowed to stir in the presence of 3 mol% of **1** in toluene at 100 ^{o}C. This is a clean technology process where compound formed free from any contaminated by-product. This is the first example for the activation of molecular oxygen using a polymer supported molybdenum catalyst. Furthermore, it is noteworthy that the corresponding homogenous reaction was less effective providing a mixture of 4-anisaldehyde and 4-anisic acid in moderate yield (Scheme 30).



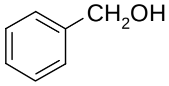
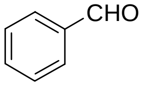
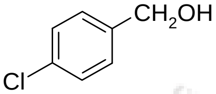
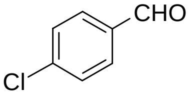
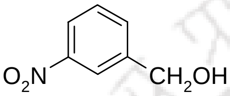
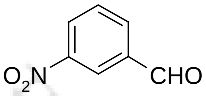
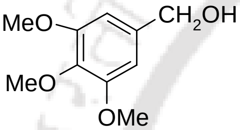
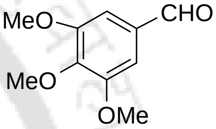
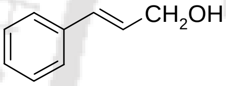
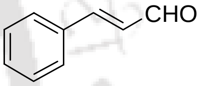
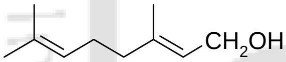
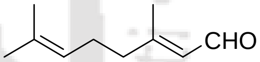
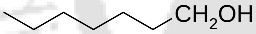
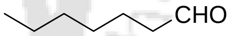
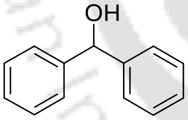
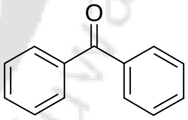
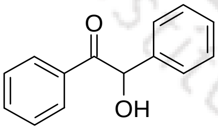
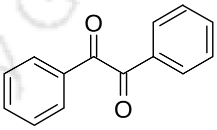
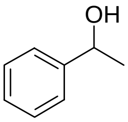
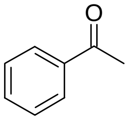
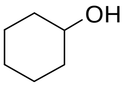
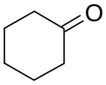
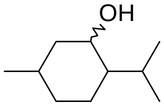
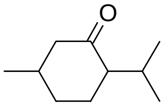
1 (3 mol% equiv Mo)	96%	-
$MoO_2(acac)_2$ (3 mol%)	58%	13%

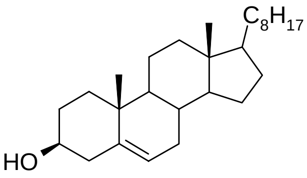
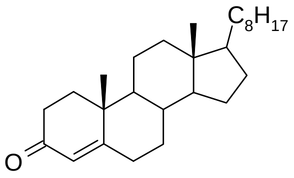
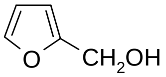
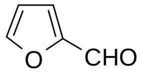
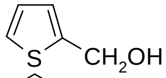
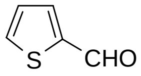
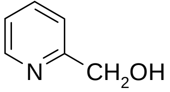
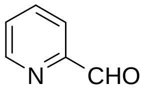
Scheme 30

To study the scope of the procedure, the oxidation of other alcohols was next studied using **1** as catalyst (Table 1, entries 1-16). Benzyl alcohol was oxidized to benzaldehyde in 92% conversion and 98% selectivity. A similar reactivity was observed with the substrates having electron withdrawing and donating groups in the aromatic ring, i.e., 4-chloro-, 3-nitro- and 3,4,5-trimethoxybenzyl alcohols. Allylic alcohols, geraniol and cinnamyl alcohol, were oxidized to the corresponding aldehydes along with 5-10% of unidentified by-products. Secondary alcohols, phenylethanol, diphenylmethanol, benzoin, cyclohexanol and (±)-menthol, required slightly longer reaction time in comparison to primary alcohols to afford the corresponding ketones (Figure 2). In the case of cholesterol, the carbon-carbon double bond migrated to give 4-cholesten-3-one in 72% yield. 2-Furfurol, 2-thiophenemethanol and 2-pyridinemethanol were oxidized to the corresponding aldehydes in high yields.

The catalyst **1** could be filtered and recycled without loss of activity (Table 2). For an example, the oxidation of 4-methoxybenzyl alcohol was performed up to 3 runs with no loss of activity. To study the leaching of the metal complex, catalyst **1** was stirred at 100 °C for 10 h and the filtrate was used for the oxidation of 4-methoxybenzyl alcohol and no reaction was observed indicating that leaching of the metal complex has not involved.

Table 1: Polyaniline Supported Molybdenum(VI) Catalyzed Oxidation of Alcohols to Aldehydes and Ketones with Atmospheric Oxygen[a]

Entry	Substrate	Time (h)	Yield (%)[b]	Selectivity (%)[h]	Product
1		12	86(92)[c]	>98	
2		13	85	>99	
3		12	69	100	
4		10	89	>99	
5[d]		16	75	86	
6[d]		19	77	77	
7[e]		17	80(86)[c]	100	
8		18	85	100	
9		14	90	99	
10		18	80(89)[c]	100	
11		15	59(68)[c]	100	
12		21	52	100	

13[f,g]		25	72	100	
14		11	98	99	
15		11	88	99	
16		20	72	99	

[a] Substrate (1 mmol) and catalyst **1** (22 mg, 3 mol% eq. Mo) were stirred at *ca.* 100 °C under oxygen balloon for the appropriate time.

[b] Isolated yield.

[c] GC yield.

[d] Accompanied 5-10% of unidentified products.

[e] Catalyst **1** (44 mg, 6 mol% eq. Mo) used.

[f] 1,2-Dichloroethane was employed as solvent.

[g] Catalyst **1** (66 mg, 9 mol% eq. Mo) used.

[h] Determined by GC (except entry 13).

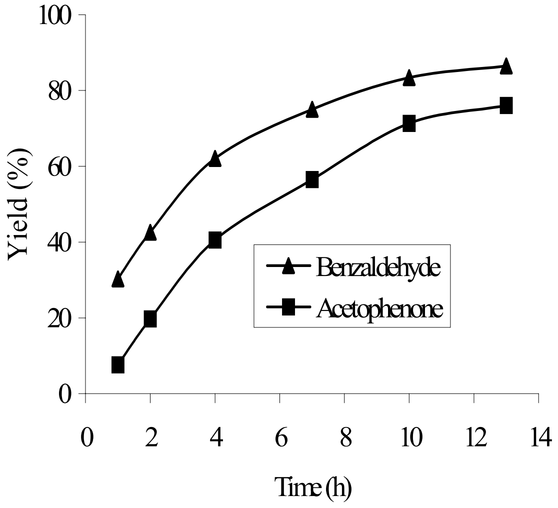
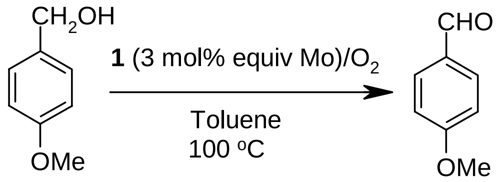


Figure 2. Oxidation Profile of Benzyl alcohol and Phenyl ethanol

Table 2: Recycling of the Catalyst



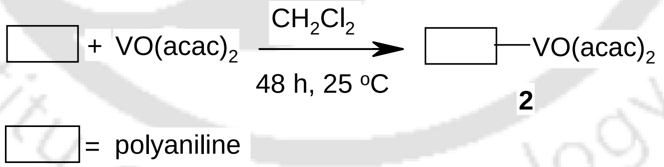
Run[a]	Recovery (%)	Product (%, yield)[b]
1.	>99	96
2.	>98	95
3.	>97	94

[a] Substrate (1 mmol) and catalyst **1** (22 mg, 3 mol% eq. Mo) were stirred at *ca.*100 °C for 9.5 h under oxygen balloon.

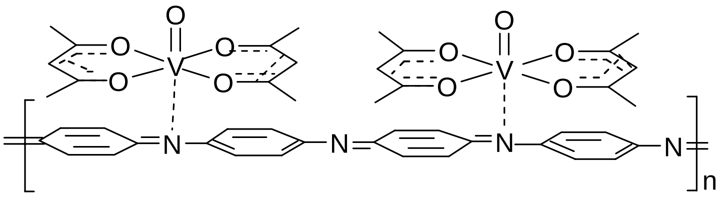
[b] Determined by GC.

Polyaniline-VO(acac)$_2$ Catalyzed Reactions

After the above observation, we have prepared the polyaniline supported VO(acac)$_2$ **2** as shown in Scheme 31 by stirring a 1:1 (wt/wt) mixture of VO(acac)$_2$ and polyaniline in CH_2Cl_2 at room temperature for 48 h.



Scheme 31

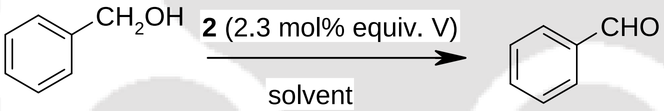


2

Figure 3. Proposed Structure for Polyaniline Supported VO(acac)$_2$ **2**

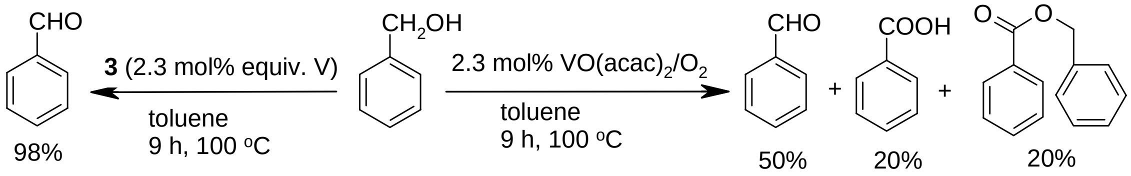
The catalyst **2** was then investigated for the oxidation of benzyl alcohol under molecular oxygen in acetonitrile, toluene and *p*-xylene as solvents at 80 °C for 15 h. As expected oxidation took place to afford benzaldehyde in 68%, 91% and 45% yields, respectively (Table 3). Alternatively, the reaction could be driven to completion to give a 98% yield of benzaldehyde by stirring the reaction mixture at *ca.* 100 °C in toluene for 9 h (Scheme 32). The corresponding homogeneous reaction using 2.3 mol% $VO(acac)_2$ provided a 2.5:1:1 mixture of benzaldehyde, benzoic acid and benzyl benzoate (Scheme 32). This may due to acidic nature (pH 4.3) of the reaction medium that could lead to over oxidation to carboxylic acids and esters.

Table 3: The Oxidation of Benzyl Alcohol



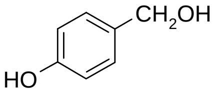
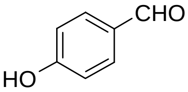
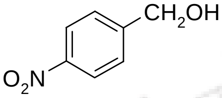
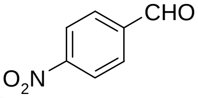
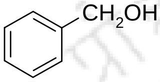
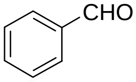
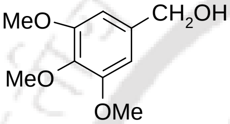
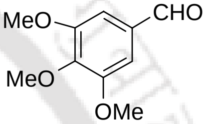
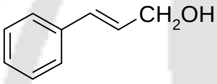
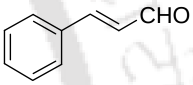
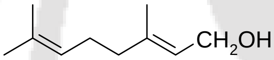
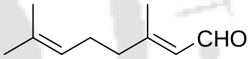
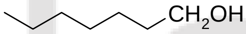
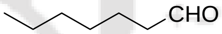
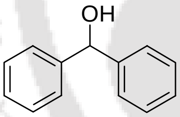
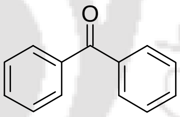
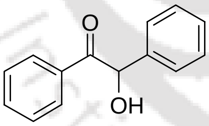
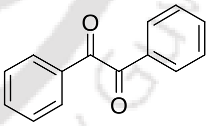
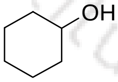
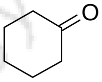
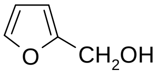
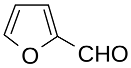
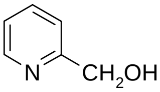
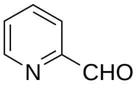
Entry	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	CH_3CN	80	15	68
2	Toluene	80	15	91
3	Xylene	80	15	45
4	Toluene	100	9	98

[a]GC yield.



Scheme 32

Table 4: Polyaniline Supported Vanadium(IV) Catalyzed Oxidation of Alcohols to Aldehydes and Ketones with Molecular Oxygen

Entry	Substrate	Time (h)	Yield (%)	Product[b]
1[c]		15	91	
2		12	97	
3		9	98	
4		9	97	
5		7	98	
6		9	85	
7[c]		15	55	
8		5	99	
9		5	99	
10		7	99	
11		9	92	
12		12	88	

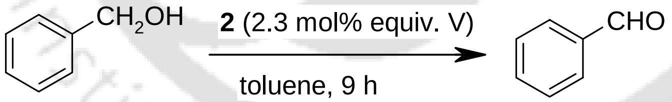
[a] Catalyst 1 (20 mg, 2.3 mol% equiv V) and the substrate (1 mmol) were stirred in toluene (3 ml) at *ca.* 100 °C under an oxygen balloon.

[b] Isolated yield.

[c] 40 mg was used.

To evaluate the scope of this catalytic system, the oxidation of other aromatic and aliphatic alcohols was further studied (Table 4, entries 1–12). Substrates having both electron donating and electron withdrawing groups in the aromatic ring, 4-methoxy-, 4-nitro-, 4-hydroxy- and 3,4,5-trimethoxy-benzyl alcohols, oxidized to the corresponding aldehydes in high yields. A similar reactivity was observed with the allylic alcohols, geraniol and cinnamyl alcohol. The saturated alcohol, heptan-1-ol was less reactive, providing the corresponding aldehyde in moderate yield. Secondary alcohols, diphenylmethanol, benzoin and cyclohexanol, underwent oxidation to provide the corresponding ketones in quantitative yields. Furfurol and pyridine-2-methanol could be oxidized to the respective aldehydes in high yields. Unlike the polyaniline-$MoO_2(acac)_2$ catalyzed process where the oxidation of primary alcohol was greater in comparison to secondary alcohol, the polyaniline-$VO(acac)_2$ catalyzed the oxidation of secondary alcohol faster in comparison to primary alcohol.

Table 5: Recycling of the Catalyst



Run[a]	Benzaldehyde (%)[b]	Recovery of **3** (%)
1	98	99
2	96	96
3	95	94

[a]Benzyl alcohol (1 mmol) and complex **2** (20 mg for 1st run) were stirred under an oxygen balloon in toluene (3 ml) at *ca.* 100 °C for 9 h. [b]Determined by GC.

In summary, the recyclable polyaniline supported vanadium and molybdenum catalysts **1** and **2** efficiently catalyze the aerobic oxidation of alcohols to aldehydes and ketones with high yields. In comparison to the homogeneous reactions, the heterogeneous reactions using catalyst **1** and **2** are highly selective and more reactive. These are clean technological processes generating only water as-product.

Experimental Section

General. Alcohols were purchased from Aldrich, Fluka and Lancaster. Polyaniline, emaralidine base (Mw *ca.* 65,000) was obtained from Aldrich. NMR spectra were recorded on DRX-300 (300 MHz for ^{1}H and 75.5 MHz for ^{13}C) spectrophotometer using $CDCl_3$ as a solvent and Me_4Si as internal standard. IR spectra were recorded on Nicolet impact 410 spectrophotometer. GC analysis was performed on HP-6890 chromatography with a FID detector. Elemental analysis was conducted using Perkin Elmer 2400 series II CHNS analyzer. Column chromatography was performed on silica gel (60-120 mesh) using ethyl acetate (or diethyl ether) and hexane as eluent.

Preparation of Polyaniline-$MoO_2(acac)_2$ 1. A mixture of polyaniline (300 mg) and $MoO_2(acac)_2$ (300 mg) was stirred in acetonitrile (15 ml) for 50 h at ambient condition. The solid was filtered and dried under vacuum after washing with acetonitrile (3 x 5 ml) to afford **1** as black powder (549 mg). The filtrate was concentrated in vacuum to provide 42 mg of unsupported $MoO_2(acac)_2$.

Data for the supported catalyst **1**:

UV/Vis (Solid): λ_{max} 318, 294, 206 nm.

IR (KBr): 1598, 1496, 1375, 938, 907, 837, 799, 641, 513, 420 cm^{-1}.

General Procedure for the Oxidation Alcohol using Catalyst 1

Alcohol (1 mmol) and catalyst **1** (22 mg, 3 mol% equiv., Mo) were stirred at *ca.* 100 ^{o}C in toluene (3 ml) under atmospheric oxygen for the appropriate time (Table 1). After filtering the catalyst **1**, the filtrate was analyzed by GC and passed through a short pad of silica gel using ethyl acetate and hexane (1:19) as eluent or distilled to provide the analytically pure aldehydes and ketones.

Benzaldehyde. Benzyl alcohol (5 mmol, 540 mg) and complex **1** (3 mol% Mo equiv., 110 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 12 h to afford benzaldehyde in 86% (460 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 7.5-7.9 (m, 5H), 10.2 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 129.7, 128.9, 134.4, 136.5, 192.2.

IR (neat): 1695 cm^{-1}.

Anal Calcd for C_7H_6O: C, 79.23; H, 5.70. Found: C, 79.19; H, 5.73.

4-Methoxybenzaldehyde. 4-Methoxybenzyl alcohol (1 mmol, 138 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the above described reaction conditions for 9.5 h to afford 4-methoxybenzaldehyde in 96% (133 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.9 (s, 3H), 7.0 (d, 2H, J = 8.2 Hz), 7.8 (d, 2H, J = 8.2 Hz), 9.9 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 55.5, 114.3, 130.0, 131.9, 164.6, 190.6.

IR (neat): 1682 cm^{-1}.

Anal Calcd for $C_8H_8O_2$: C, 70.58; H, 5.92. Found: C, 70.52; H, 5.90.

4-Methoxybenzoic acid. 4-Methoxybenzyl alcohol (1 mmol, 138 mg) and $MoO_2(acac)_2$ (3 mol%, 13.6 mg) were subjected to the above described reaction conditions for 9 h to afford 4-methoxybenzoic acid in 13% (20 mg) yield as a colorless solid.

Mp: 182 °C.

^{1}H NMR ($CDCl_3$-DMSO-d_6): δ 3.8 (s, 3H), 7.0 (d, 2H, J = 8.0 Hz), 7.9 (d, 2H, J = 8.0 Hz).

^{13}C NMR ($CDCl_3$-DMSO-d_6): δ 55.1, 113.4, 123.1, 131.3, 162.8, 167.3.

IR (KBr): 1683, 3025 cm^{-1}.

Anal Calcd for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.10; H, 5.32.

3-Nitrobenzaldehyde. 3-Nitrobenzyl alcohol (1 mmol, 153 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the above described reaction conditions for 12 h to afford 3-nitrobenzaldehyde as a yellow solid in 69% (104 mg) yield.

Mp: 58 °C.

^{1}H NMR ($CDCl_3$): δ 7.8 (t, 1H, J = 8.0 Hz), 8.3 (d, 1H, J = 8.0 Hz), 8.5 (d, 1H, J = 8.0 Hz), 8.8 (s, 1H), 10.3 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 124.4, 128.5, 130.5, 134.7, 137.5, 149.1, 190.0.

IR (KBr): 1678 cm^{-1}.

Anal Calcd for $C_7H_5O_3N$: C, 55.64; H, 3.33; N, 9.27. Found: C, 55.69; H, 3.29; N, 9.24.

4-Chlorobenzaldehyde. 4-Chlorobenzyl alcohol (1 mmol, 143 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 13 h to afford 4-chlorobenzaldehyde as a colorless solid in 85% (119 mg) yield.

Mp: 50 ^{o}C.

^{1}H NMR ($CDCl_3$): δ 7.5 (d, 2H, *J* = 8.4 Hz), 7.8 (d, 2H, *J* = 8.4 Hz), 10.1 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 129.4, 130.9, 137.8, 140.9, 190.7.

IR (KBr): 1705 cm^{-1}.

Anal Calcd for C_7H_5OCl: C, 59.81; H, 3.59. Found: C, 59.82; H, 3.53.

3,4,5-Trimethoxybenzaldehyde. 3,4,5-Trimethoxybenzyl alcohol (1 mmol, 198 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 10 h to afford 3,4,5-trimethoxybenzaldehyde as a pale yellow solid in 89% (175 mg) yield.

Mp: 74^{o} C.

^{1}H NMR ($CDCl_3$): δ 3.9 (s, 9H), 7.1 (s, 2H), 9.9 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 56.3, 60.9, 106.8, 131.7, 143.7, 153.6, 190.9.

IR (KBr): 1682 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.30; H, 6.19.

Cinnamaldehyde. Cinnamyl alcohol (1 mmol, 134 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 16 h to afford cinnamaldehyde as a yellow liquid in 75% (99 mg) yield.

^{1}H NMR (CDCl$_3$): δ 6.5-6.7 (m, 2H), 7.4-7.5 (m, 5H), 9.7 (d, 1H, J = 7.7 Hz).

^{13}C NMR (CDCl$_3$): δ 128.3, 128.4, 129.0, 131.1, 133.8, 152.6, 193.4.

IR (neat): 1681 cm^{-1}.

Anal Calcd for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.82; H, 6.16.

Geranial. Geraniol (1mmol, 154 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 19 h to afford geranial as a colorless liquid in 77% (117 mg) yield.

^{1}H NMR (CDCl$_3$): δ 1.6 (s, 3H), 1.7 (s, 3H), 1.9 (s, 3H), 2.1-2.2 (m, 4H), 4.8-4.9 (m, 1H), 5.8 (d, 1H, J = 8.1 Hz), 9.9 (d, 1H, J = 8.1 Hz).

^{13}C NMR (CDCl$_3$): δ 17.4, 17.5, 25.5, 25.6, 40.5, 122.4, 127.2, 132.9, 163.5, 191.0.

IR (neat): 1678 cm^{-1}.

Anal Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.95; H, 10.61.

Heptanal. Heptanol (5 mmol, 580 mg) and complex **1** (6 mol% Mo equiv., 220 mg) in toluene (10 ml) were subjected to the reaction conditions described in the general procedure for 17 h to afford heptanal in 80% (455 mg) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 0.9 (t, 3H, J = 6.0 Hz), 1.1-1.6 (m, 8H), 2.4-2.5 (m, 2H), 9.8 (t, 1H, J = 7.3 Hz).

^{13}C NMR (CDCl$_3$): δ 13.9, 22.1, 22.5, 28.8, 31.6, 43.9, 202.7.

IR (neat): 1724 cm^{-1}.

Anal Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.69; H, 12.39.

Benzophenone. Diphenylmethanol (1 mmol, 182 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 18 h to afford benzophenone as a colorless solid in 85% (155 mg) yield.

^{1}H NMR (CDCl$_3$): δ 7.41-7.60 (m, 6H), 7.71-7.83 (m, 4H).

^{13}C NMR (CDCl$_3$): δ 128.2, 129.9, 132.3, 137.5, 196.6.

IR (KBr): 1661 cm^{-1}.

Anal Calcd for $C_{13}H_{10}O$: C, 80.00; H, 6.66. Found: C, 80.02; H, 6.68.

Benzil. Benzoin (1 mmol, 212 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 14 h to afford benzil as a yellow solid in 90% (189 mg) yield.

Mp: 95 °C.

^{1}H NMR (CDCl$_3$): δ 7.3-7.5 (m, 4H), 7.6-7.7 (m, 2H), 7.8-8.0 (m, 4H).

^{13}C NMR (CDCl$_3$): δ 129.6, 130.4, 133.6, 135.4, 195.1.

IR (KBr): 1671 cm^{-1}.

Anal Calcd for $C_{14}H_{10}O_2$: C, 79.99; H, 4.79. Found: C, 79.89; H, 4.80.

Acetophenone. Phenylethanol (1 mmol, 122 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 18 h to afford acetophenone as a colorless liquid in 80% (96 mg) yield.

^{1}H NMR ($CDCl_3$): δ 2.6 (s, 3H), 7.3-7.6 (m, 3H), 7.8-8.0 (m, 2H).

^{13}C NMR ($CDCl_3$): 26.5, 128.2, 128.5, 133.0, 137.2, 197.9;

IR (film): 1683 cm^{-1}.

Anal Calcd for C_8H_8O: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.70.

Cyclohexanone. Cyclohexanol (2 mmol, 196 mg) and complex **1** (3 mol% Mo equiv., 44 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 15 h to afford cyclohexanone in 59% (116 mg) yield.

^{1}H NMR ($CDCl_3$): δ 1.7-1.9 (m, 6H), 2.3-2.4 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 25.0, 27.1, 41.9, 211.7.

IR (neat): 1717 cm^{-1}.

Anal Calcd for $C_6H_{10}O$: C, 73.43; H, 10.21. Found: C, 73.46; H, 10.25.

(±)-Menthone. (±)-Menthol (1 mmol, 156 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 21 h to afford (±)-menthone as a colorless liquid in 52% (81 mg) yield.

^{1}H NMR ($CDCl_3$): δ 0.7-1.0 (m, 9H), 1.4-1.6 (m, 2H), 1.7-2.1 (m, 6H), 2.2-2.4 (m, 1H).

^{13}C NMR ($CDCl_3$): δ 18.7, 21.1, 22.2, 25.9, 27.8, 33.6, 35.3, 50.8, 55.7, 212.0.

IR (neat): 1714 cm^{-1}.

Anal Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.85; H, 12.00.

4-Cholesten-3-one. Cholesterol (1 mmol, 387 mg) and complex **1** (9 mol% Mo equiv., 66 mg) in $(CH_2Cl)_2$ (5 ml) was stirred at 80 ^oC for 25 h under oxygen atmosphere. The reaction mixture was cooled to room temperature and the catalyst **1** was filtered. The filtrate was concentrated on a rotary evaporator under reduced pressure to afford a residue which was passed through a short pad of silica gel using ethyl acetate and hexane (1:9) as eluent to provide 4-cholesten-3-one as a colorless solid in 72% (277 mg) yield.

Mp: 80 ^oC.

^1H NMR ($CDCl_3$): δ 0.7 (s, 3H), 0.9-2.5 (m, 40 H), 5.7 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 12.0, 17.4, 18.7, 21.1, 22.6, 22.8, 23.8, 24.2, 28.1, 28.2, 32.1, 32.9, 34.0, 35.7, 35.8, 36.2, 38.6, 39.6, 39.7, 42.4, 53.4, 55.9, 56.2, 123.7, 171.5, 199.4.

IR (KBr): 1677 cm^{-1}.

Anal Calcd for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.28; H, 11.51.

Furfural. Furfurol (1 mmol, 98 mg) and complex **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 11 h to afford furfural as colorless liquid in 98% (94 mg) yield.

^1H NMR ($CDCl_3$): δ 6.6 (s, 1H), 7.3 (s, 1H), 7.7 (s, 1H), 9.7 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 121.1, 112.6, 148.1, 152.9, 177.8.

IR (neat): 1681 cm^{-1}.

Anal Calcd for $C_5H_4O_2$: C, 62.50; H, 4.20. Found: C, 62.47; H, 4.23.

2-Thiophenecarboxaldehyde. 2-Thiophenemethanol (1 mmol, 114 mg) and catalyst **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 11 h to afford 2-thiophenecarboxaldehyde as a yellow liquid in 88% (99 mg) yield.

^{1}H NMR (CDCl$_3$): δ 7.2-7.3 (m, 1H), 7.6-7.9 (m, 2H), 9.9 (s, 1H).

^{13}C NMR (CDCl$_3$): δ 128.6, 135.4, 136.7, 144.1, 183.1.

IR (neat): 1714 cm^{-1}.

Anal Calcd for C_5H_4SO: C, 53.55; H, 3.60. Found: C, 53.52; H, 3.59.

2-Pyridinecarboxaldehdye. 2-Pyridinemethanol (1 mmol, 109 mg) and catalyst **1** (3 mol% Mo equiv., 22 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 20 h to afford 2-pyridinecarboxaldehyde as a yellow liquid in 72% (78 mg) yield.

^{1}H NMR (CDCl$_3$): δ 7.5-7.6 (m, 1H), 7.9-8.0 (m, 2H), 8.8-8.9 (m, 1H), 10.1 (s, 1H).

^{13}C NMR (CDCl$_3$): δ 121.8, 128.0, 137.2, 150.2, 152.7, 193.3.

IR (neat): 1680 cm^{-1}.

Anal Calcd for C_6H_5NO: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.30; H, 4.73; N, 13.00.

Preparation of Polyaniline-VO(acac)$_2$ 2. A mixture of polyaniline (200 mg) and VO(acac)$_2$ (200 mg) was stirred in CH_2Cl_2 (10 ml) under atmospheric oxygen at room temperature for 48 h. The polyaniline supported VO(acac)$_2$ **2** was filtered and washed with dichloromethane until the filtrate was colorless. The catalyst **2** was then dried under vacuum to provide a black powder (322 mg). Concentration of the combined filtrate provided 75 mg of unsupported VO(acac)$_2$.

Data for the supported catalyst **2**:

UV/Vis (Solid): λ_{max} 276, 327, 334, 383 nm.

IR (KBr): 1593, 1501, 1306, 1148, 1025, 999, 943, 835 cm^{-1}.

General Procedure for the Oxidation of Alcohol using Catalyst 2

The alcohol (1 mmol) and catalyst **2** (2.3 mol% V equiv., 20 mg) were stirred under an oxygen balloon in toluene (3 ml) at *ca.* 100 ^{o}C for the appropriate time. The catalyst was filtered and the filtrate, after GC analysis, passed through a short pad of silica gel using a mixture of diethyl ether and hexane as eluent or distilled to provide the analytically pure carbonyl compound.

4-Hydroxybenzaldehyde. 4-Hydroxybenzyl alcohol (1 mmol, 124 mg) and complex **2** (2.3 mol% V equiv., 20 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 15 h to afford 4-hydroxybenzaldehyde in 91% (111 mg) yield as a colorless solid.

Mp: 118 ^{o}C.

^{1}H NMR (CDCl$_3$): δ 7.0 (d, 2H, *J* = 8.2 Hz), 7.7 (d, 2H, *J* = 8.2 Hz), 9.8 (s, 1H), 10.6 (s, 1H).

^{13}C NMR (CDCl$_3$): δ 115.8, 128.5, 131.8, 163.7, 190.2.

IR (KBr): 1682 cm^{-1}.

Anal Calcd for $C_7H_6O_2$: C, 63.64; H, 4.54. Found: C, 63.66; H, 4.57.

4-Nitrobenzaldehyde. 4-Nitrobenzyl alcohol (1 mmol, 153 mg) and complex **2** (2.3 mol% V equiv., 20 mg) in toluene (3 ml) were subjected to the reaction conditions described in the general procedure for 12 h to afford 4-nitrobenzaldehyde in 97% (147 mg) yield as a yellow solid.

Mp: 107 °C.

^{1}H NMR ($CDCl_3$): δ 8.0 (d, 2H, *J* = 8.3 Hz), 8.3 (d, 2H, *J* = 8.3 Hz), 10.3 (s, 1H).

^{13}C NMR ($CDCl_3$): δ 124.3, 130.4, 140.1, 151.1, 190.2.

IR (KBr): 1678 cm^{-1}.

Anal Calcd for $C_7H_5NO_3$: C, 55.63; H, 3.30, N, 9.27, Found: C, 55.65; H, 3.33, N, 9.30.

Benzoic acid. Benzyl alcohol (5 mmol, 540 mg) and $VO(acac)_2$ (2.3 mol%, 100 mg) in toluene (10 ml) were subjected to the reaction conditions described in the general procedure for 9 h to afford benzoic acid in 20% (122 mg) yield as a colorless solid

Mp: 123 °C;

^{1}H NMR ($CDCl_3$): δ 7.31-7.80 (m, 5H).

^{13}C NMR ($CDCl_3$): δ 128.4, 129.3, 130.17, 133.7, 172.6.

IR (KBr): 1679 cm^{-1}.

Anal Calcd for $C_7H_6O_2$: C, 68.85; H, 4.92. Found: C, 68.88; H, 4.94.

Benzyl benzoate. Benzyl alcohol (5 mmol, 540 mg) and $VO(acac)_2$ (2.3 mol%, 100 mg) in toluene (10 ml) were subjected to the reaction conditions described in the general procedure for 9 h to afford benzyl benzoate in 20% (106 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 5.4 (s, 2H), 7.3-7.6 (m, 8H), 8.0-8.2 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 66.6, 128.1, 128.2, 128.3, 128.5, 129.6, 130.1, 132.9, 136.0, 166.3.

IR (neat): 1719 cm^{-1}.

Anal Calcd for $C_{14}H_{12}O_2$: C, 79.25; H, 5.66. Found: C, 79.30; H, 5.70.

1.3 References

1. Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.
2. *Comprehensive Organic Synthesis;* Trost, B. M., Fleming I., Eds.; Pergamon Press: Oxford, 1991; Vol. 7.
3. Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1999; pp 1234.
4. Weissermel, K.; Arpe, H.-J. *In Industrial Organic Chemistry*, 3rd ed; Lindley, C. R., Ed.; VCH: New York, 1997.
5. Holum, J. R. *J. Org. Chem.* **1961**, *26*, 4814.
6. Lee, D. G.; Spitzer, U. A. *J. Org. Chem.* **1970**, *35*, 3589.
7. Cainelli, G.; Cardillo, G. *Chromium Oxidants in Organic Chemistry*; Springer: Berlin, 1984.
8. Ley, S. V.; Madin, A. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ley, S. V., Eds.; Pergamon: Oxford, 1991; Vol. 7, pp 251.
9. Muzart, J. *Chem. Rev.* **1992**, *92*, 113.
10. Regen, S. L.; Koteel, C. *J. Am. Chem. Soc.* **1977**, *99*, 3837.
11. Menger, F. M.; Lee, C. *Tetrahedron Lett.* **1981**, *22*, 1655.
12. Berkowitz, L. M.; Rylander, P. N. *J. Am. Chem. Soc.* **1958**, *80*, 6682.
13. Griffith, W. P. *Chem. Soc. Rev.* **1992**, *21*, 179.

14. Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc., Chem. Commun*. **1987**, 1625.

15. Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639.

16. Lee, T. V. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ley, S. V., Eds.; Pergamon: Oxford, 1991; Vol. 7, pp 291.

17. Dess, D. B.; Martin, J. C. *J. Org. Chem*. **1983**, *48*, 4155.

18. (a) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57,* 157; (b) Muzart, J. *Tetrahedron* **2003**, *59,* 5789; (c) Mahadevan, V.; Gebbink, R. J. M. K.; Stack, T. D. P. *Curr. Opin. Chem. Biol*. **2000**, *4,* 228, and references therein. (d) Sheldon, R. A.; Arends, I. W. C. E. *Catal. Met. Complexes* **2003**, *26,* 123.

19. Kirihara, M.; Ochiai, Y.; Takizawa, S.; Takahata, H.; Nemoto, H. *Chem. Commun.* **1999**, 1387.

20. Kirihara, M.; Takizawa, S.; Momose, T. *J. Chem. Soc., Perkin Trans. 1,* **1998**, 7.

21. (a) Maeda, Y.; Kakiuchi, N.; Matsumura, S.; Nishimura, T.; Uemura, S. *Tetrahedron Lett.* **2001**, *42*, 8877; (b) Maeda, Y.; Kakiuchi, N.; Matsumura, S.; Nishimura, T.; Kawamura, T.; Uemura, S. *J. Org. Chem*. **2002**, *67*, 6718.

22. Martin, S. E.; Suarez, D. F. *Tetrahedron Lett*. **2002**, *43*, 4475.

23. Yamada, T.; Mukaiyama, T. *Chem. Lett*. **1989**, 519.

24. Iwahama, T.; Yoshino, Y.; Keitoku, T.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2000**, *65*, 6502.

25. Choudary, B. M.; Kantam, M. L.; Rahman, R.; Reddy, C. V.; Rao, K. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 763.

26. Ragagnin, G.; Betzemeier, B.; Quici, S.; Knochel, P. *Tetrahedron* **2002,** *58,* 3985.

27. Ansari, I. A.; Gree, R. *Org. Lett.* **2002**, *4,* 1507.

28. Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool, D. H.; Liang, H.-C. *J. Am. Chem. Soc.* **2000**, *122*, 1079.

29. (a) Coleman, K. S.; Coppe, M.; Thomas, C.; Osborn, J. A. *Tetrahedron Lett.* **1999**, *40,* 3723; (b) Lorber, C. Y.; Smidt, S. O.; Osborn, J. A. *Eur. J. Inorg. Chem.* **2000**, *4,* 655.

30. Dobler, C.; Mehltretter, G. M.; Sundermeier, U.; Eckert, M.; Militzer, H.-C.; Beller, M. *Tetrahedron Lett.* **2001**, *42,* 8447.

31. Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1998**, *63*, 3185.

32. (a) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **1998**, *39*, 6011; (b) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750.

33. Schultz, M. J.; Park, C. C.; Sigman, M. S. *Chem. Commun.* **2002**, 3034.

34. (a) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000**, *287,* 1636; (b) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Adv. Synth. Catal.* **2002**, *344,* 355.

35. Matsushita, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **1999**, 265.

36. Uozumi, Y.; Nakao, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 194.

37. Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2002**, *124,* 11572.

38. Dijksman, A; Marino-Gonzalez, A; Mairata, A; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123,* 6826.

39. Kaneda, K.; Yamashita, T.; Matsushita, T.; Ebitani, K. *J. Org. Chem.* **1998**, *63*, 1750.

40. Matsushita, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **1999**, 265.

41. Zhan, B.-Z.; White, M. A.; Sham, T.-K.; Pincock, J. A.; Doucet, R. J.; Rao, K. V. R.; Robertson, K. N.; Cameron, T. S. *J. Am. Chem. Soc.* **2003**, *125,* 2195.

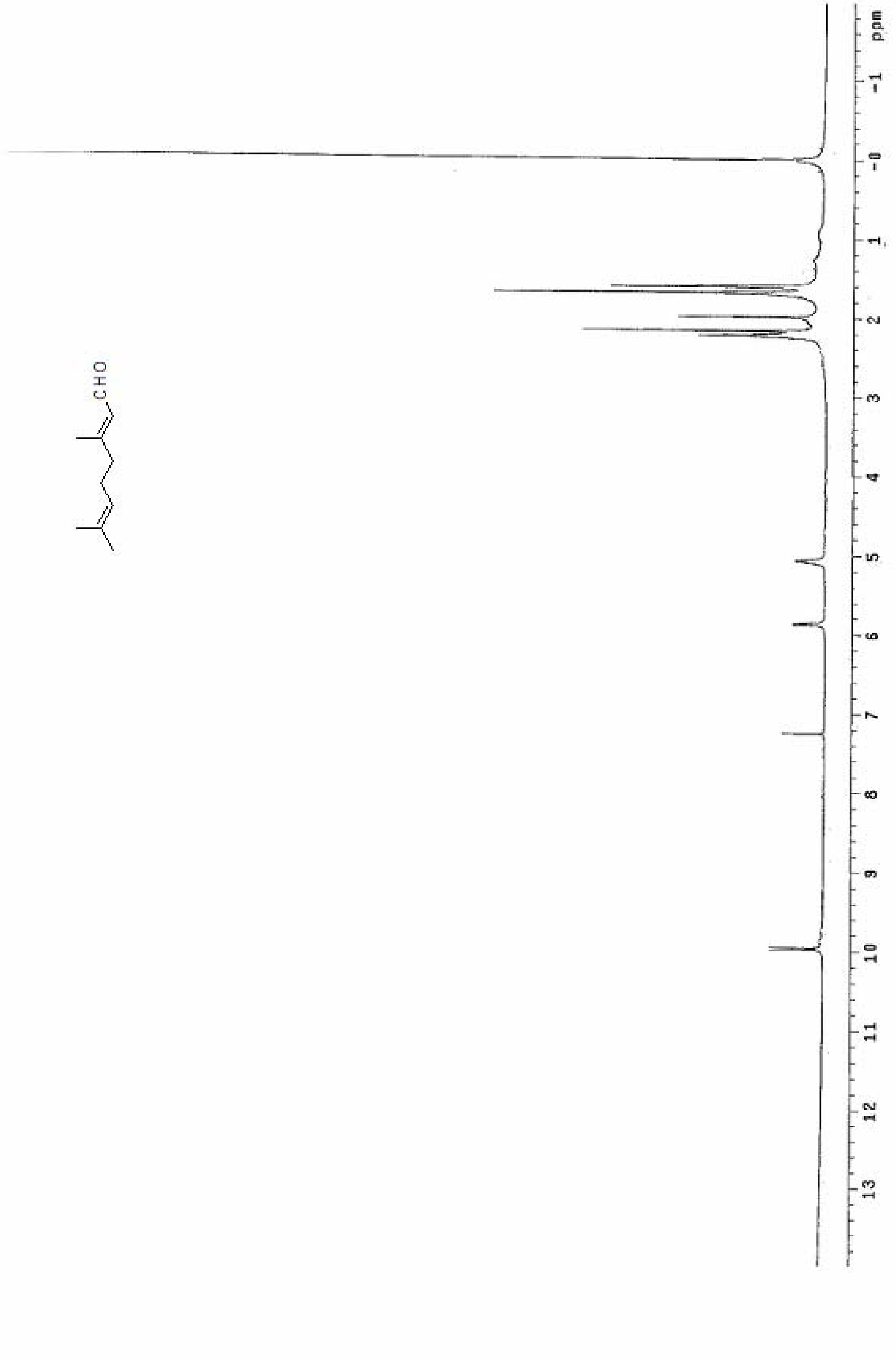
42. Ji, H-B.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2002**, *43,* 7179.

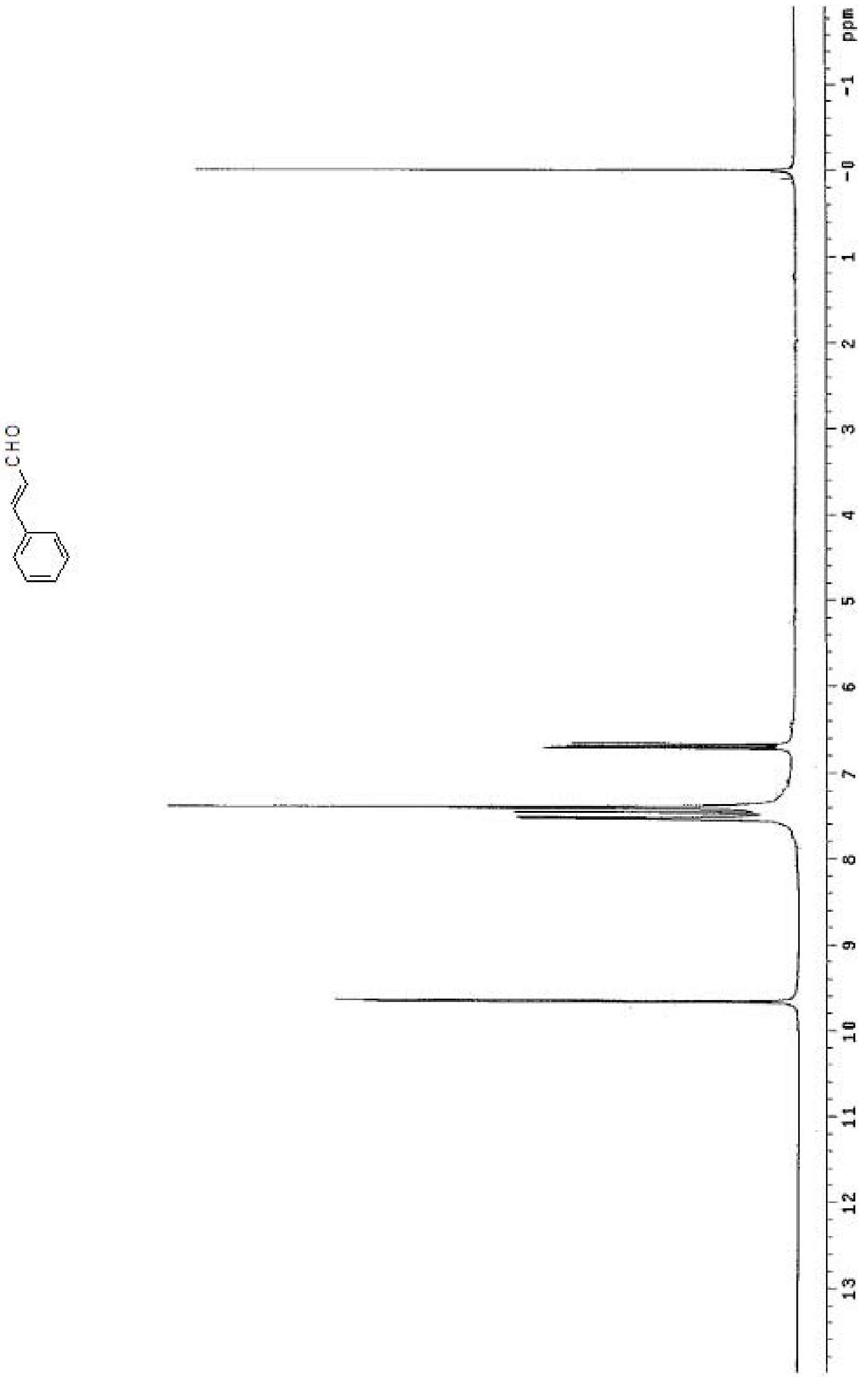
43. Lee, M.; Chang, S. *Tetrahedron Lett.* **2000**, *41*, 7507.

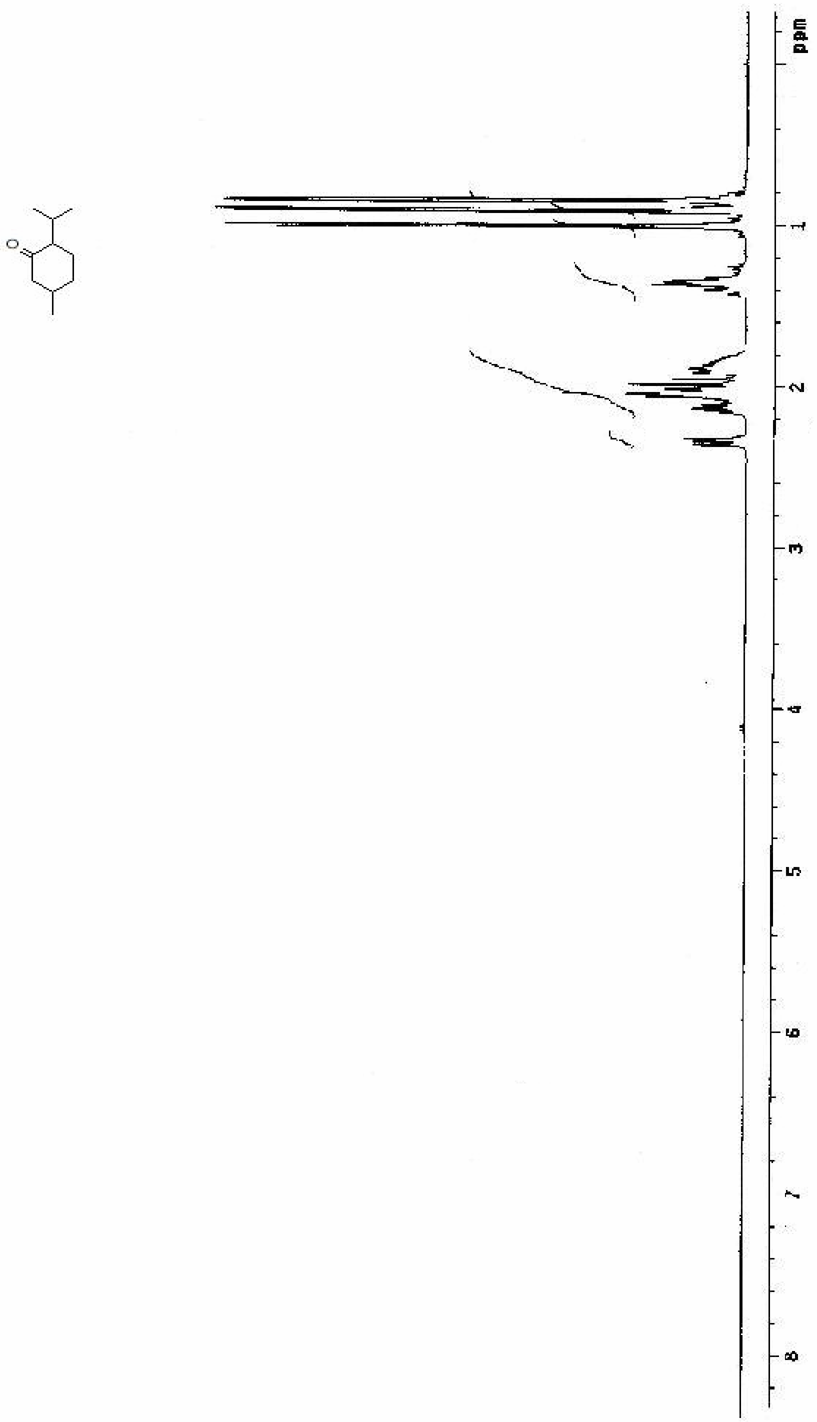
44. Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2000**, *122,* 7144.

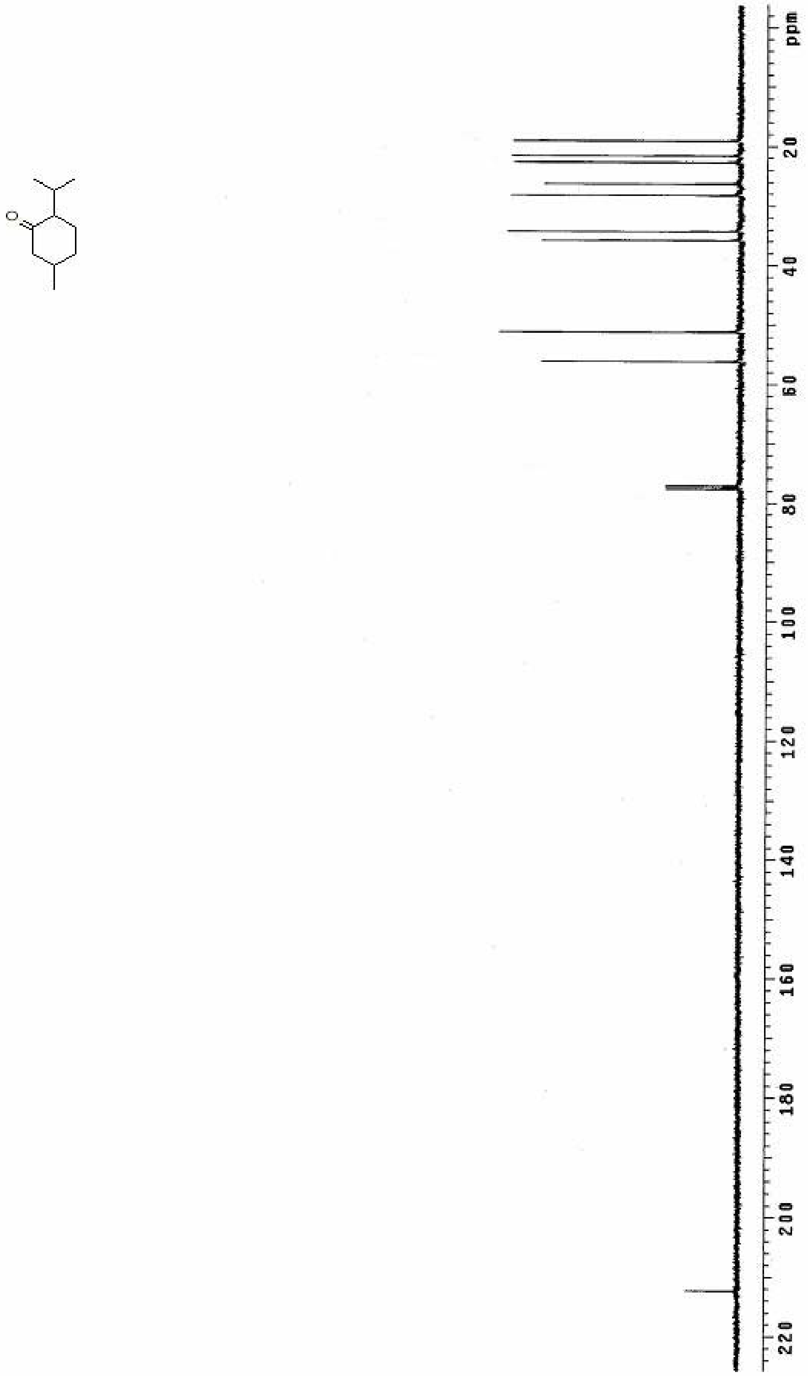
45. Pagliaro, M.; Ciriminna, R. *Tetrahedron Lett.* **2001**, *42*, 4511.

46. Haimov, A.; Neumann, R. *Chem. Commun.* **2002**, 876.


CHO
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13


CHO
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13


ppm
1
2
3
4
5
6
7
8


O
ppm
20
40
60
80
100
120
140
160
180
200
220

Chapter 2

Copper(II) Catalyzed Oxidation of Organic Compounds with Aqueous 30% Hydrogen Peroxide

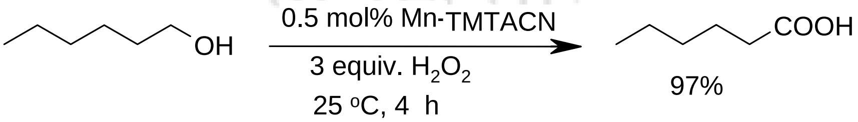
Hydrogen peroxide, H_2O_2, is a very attractive oxidant for liquid-phase reactions.[1] H_2O_2 is an adduct of H_2 and O_2 that is also viewed as an adduct of an O atom and an H_2O molecule. It can oxidize organic compounds with atom efficiency of 47% generating water as the only co-product. It is relatively cheap, <0.7 US dollar Kg^{-1} (100%, H_2O_2), and about 2.4 million metric tons are produced for use, mainly as bleach.[2] It should be noted that H_2O_2 can be ideal, waste-avoiding oxidant only when it is used in a controlled manner. Thus, the discovery of an efficient catalyst and the choice of reactions conditions are the keys to realizing an ideal oxidation procedure. The reaction should be achieved with H_2O_2 concentration of <60%. Because the use, storage and transportation of higher concentration of H_2O_2 are not desirable for safety reasons.[3] The H_2O_2 oxidation is particularly useful for the synthesis of high-value fine chemicals, pharmaceuticals, agrochemicals and electronic materials which require high chemical purity. It may also be used for improving the environment by oxidative removal of very small amounts of toxic compounds. However, despite a sustained effort in industry, the current cost of H_2O_2 still does not allow for the economical production of inexpensive compounds in large quantities. There will be significant changes depending on the development of low cost H_2O_2 production, demand for high product quality, stringent environmental regulations, and changes in public opinion, legislation, and taxation policy regarding environment protection. In fact, there is a trend to use H_2O_2 as an oxidant for large volume processes such as caprolactam synthesis and propylene oxidation. H_2O_2 oxidation methods may switch to *in situ* or on-site technology using H_2 and O_2. Since the structures of chemical substances are diverse and reaction volumes variable depending on whether the purpose is research or production, no synthetic methods can be universal. One of the major advantages of the H_2O_2 oxidation is the high tenability of the reaction parameters. We foresee that H_2O_2 and O_2 (or air) will be complementary useful clean oxidants in practical chemical synthesis.

2.1 Oxidation of Alcohols

The oxidation of alcohols is a fundamental and routinely used functional transformation in organic synthesis. During the recent years effort has been made to develop catalytic systems for this process with aqueous H_2O_2 to reduce the environment impact of the process (E-factor).

2.1.1 Manganese Catalyst

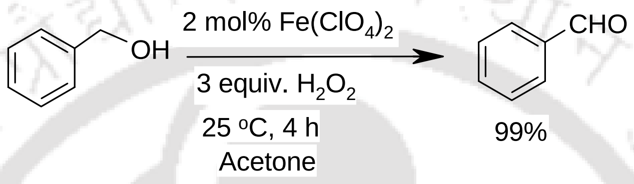
The oxidation of primary alcohols to carboxylic acids has been accomplished using Mn-TMTACN (TMTACN=1,4,7-trimethyl-1,4,7-triazacyclononane) in the presence of H_2O_2 (Scheme 1).[4]



Scheme 1

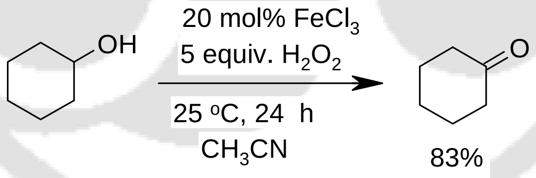
2.1.2 Iron Catalysts

Feringa and co-workers reported the oxidation of alcohols with $Fe(ClO_4)_2$ in the presence H_2O_2 (Scheme 2).[5] The oxidation of primary alcohol could be stopped at aldehyde stage without over oxidation to carboxylic acid. However, secondary alcohols are less reactive under these conditions. For an example, cyclohexanol oxidized to cyclohexanone in 20% yield.



Scheme 2

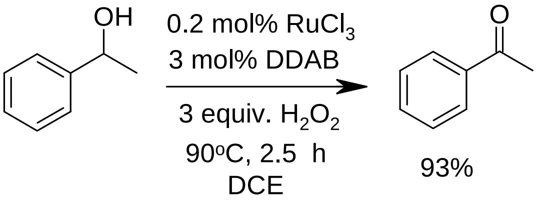
FeCl₃ has been shown to catalyze oxidation of alcohols to aldehydes and ketones in the presence of H_2O_2 at ambient temperature (Scheme 3).[6] Long chain alcohol like decanol is inert under these reaction conditions.



Scheme 3

2.1.3 Ruthenium Catalyst

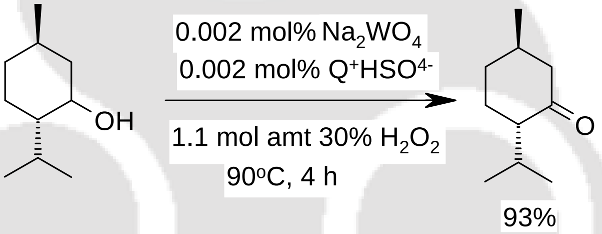
Sasson and co-workers studied the oxidation of alcohols to aldehydes and ketones using $RuCl_3$ in the presence of didecyldimethylammoniumbromide(DDAB) and H_2O_2 (Scheme 4).[7]



Scheme 4

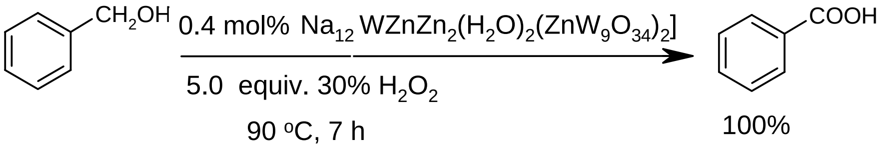
2.1.4 Tungsten Catalysts

The combined system of sodium tungstate (Na_2WO_4) and methyl-trioctylammonium hydrogen sulfate [CH_3 (n-C_8H_{17})$_3$ N^+ HSO_4^- ($Q^+HSO_4^-$)] has been reported to catalyze the oxidation of alcohols with 30% H_2O_2 in high yields (Scheme 5).[8]



Scheme 5

The water soluble polyoxometalate, $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$, has been used for the oxidation of alcohols to carboxylic acids and ketones in the presence of H_2O_2 (Scheme 6).[9] Under these conditions, carbon-carbon double bonds undergo oxidative cleavage to give carbonyl compounds.



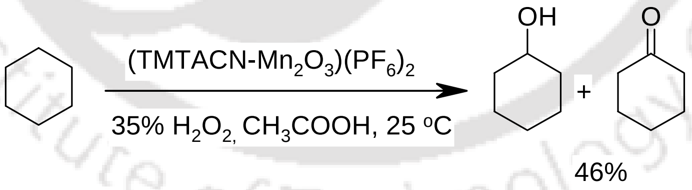
Scheme 6

2.2 Oxidation of Alkanes

Functionalization of hydrocarbons to alcohols and carbonyl compounds is an important process in view of its synthetic and industrial aspects.[10,11] Most of the studies for this process are modeled on metalloenzymes that perform the oxidation of hydrocarbons in natural systems with molecular oxygen.[12] Only few studies have been so far studied with H_2O_2.

2.2.1 Managanese Catalyst

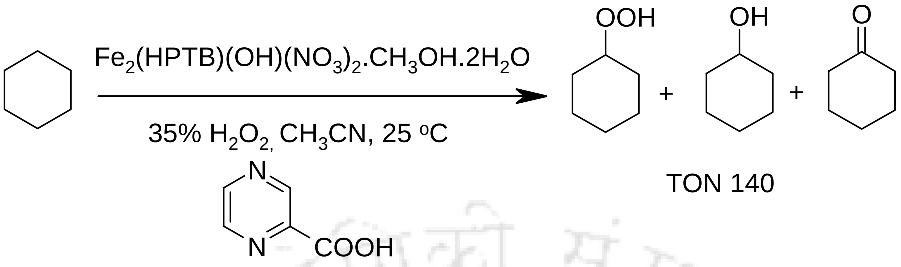
The oxidation of unactivated alkanes (cyclohexane, *n*-pentane, *n*-heptane, methylbutane, 2- and 3-methylpentanes, 3-methylhexane, *cis*- and *trans*-decalins) has been carried out with manganese(IV) salt $[L_2Mn_2O_3](PF_6)_2$ (L = 1,4,7-trimethyl-1,4-7-triazacyclononane) in the presence of 35% H_2O_2.[13] The reactions are found to be effective in the presence of acetic acid and turnover numbers up to 3300 has been reported for cyclohexane oxidation. The oxidation affords initially alkyl hydroperoxide which undergoes decomposition to provide the corresponding ketone and alcohol (Scheme 7).



Scheme 7

2.2.2. Iron Catalyst

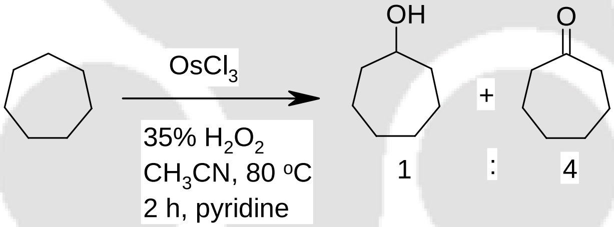
Binuclear iron(III) complex, $[Fe_2(HPTB)(m\text{-}OH)(NO_3)_2](NO_3)_2\cdot CH_3OH\cdot 2H_2O$ [HPTB = N,N,N’,N’-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane], has been shown to catalyze the oxidation of cyclohexane into a mixture of cyclohexylperoxide, cyclohexanol and cyclohexanoe with up to 140 turnovers in the presence of 35% H_2O_2 at room temperature (Scheme 8).[14]



Scheme 8

2.2.3 Osmium Catalyst

The oxidation of cyclooctane to a mixture of the corresponding alcohol and ketone is reported with $OsCl_3$ in the presence of 35% H_2O_2 at 80 °C in acetonitrile (Scheme 9).[15]



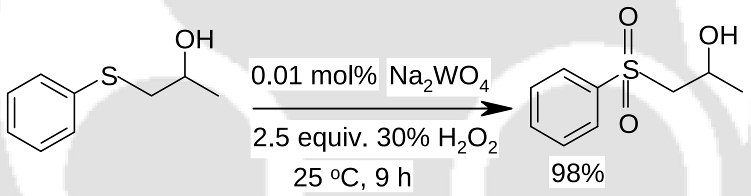
Scheme 9

2.3 Oxidation of Sulfides

The oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides and sulfones, both of which are important as commodity chemicals and, in some cases, as pharmaceuticals. Conventional oxidants include, among others, $NaBO_3$,[16] $NaOCl$,[17] $Ca(ClO)_2$,[18] $H_5IO_6/[Mn^{IV}\text{-}Mn^{IV}\text{-}(\mu\text{-}O)_3L_2](PF_6)_2$,[19] $KHSO_5$,[20-21] HNO_3,[22] $(NH_4)_2Ce(NO_3)_6$,[23] $NaIO_4$,[24,25] MnO_2,[26] $KMnO_4$,[27] RuO_4,[28] CF_3CO_3H,[29] dimethyldioxirane,[30-31] $t\text{-}C_4H_9O_2H$,[32] 4-methylmorpholine oxide with OsO_4,[33] 3-$ClC_6H_4CO_3H$,[34] and $[(n\text{-}C_4H_9)_4N]\text{-}HSO_5$.[35-36] Singlet oxygen[37] or molecular oxygen[38] combined with $CH_3CH(CH_3)CHO$ or $CH_3CH(CH_3)CH_2CHO$ and $Co(acac)_2$[39] have also been used. Unfortunately, most of these reagents are not satisfactory for medium to large scale synthesis because of the low content of effective oxygen, the formation of environmentally unfavorable co-product along with the target molecules. Thus, the development of alternative methods for this process with atom efficient oxidant such as H_2O_2 will be quite valuable.

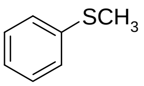
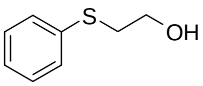
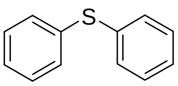
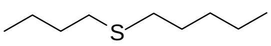
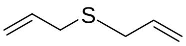
2.3.1 Tungsten Catalysts

Nayori and co-workers reported the oxidation of sulfides to sulfones with high yields in the presence of aqueous H_2O_2 (Scheme 10 and Table 1).[40] Hydroxy groups don't undergo oxidation under these conditions.



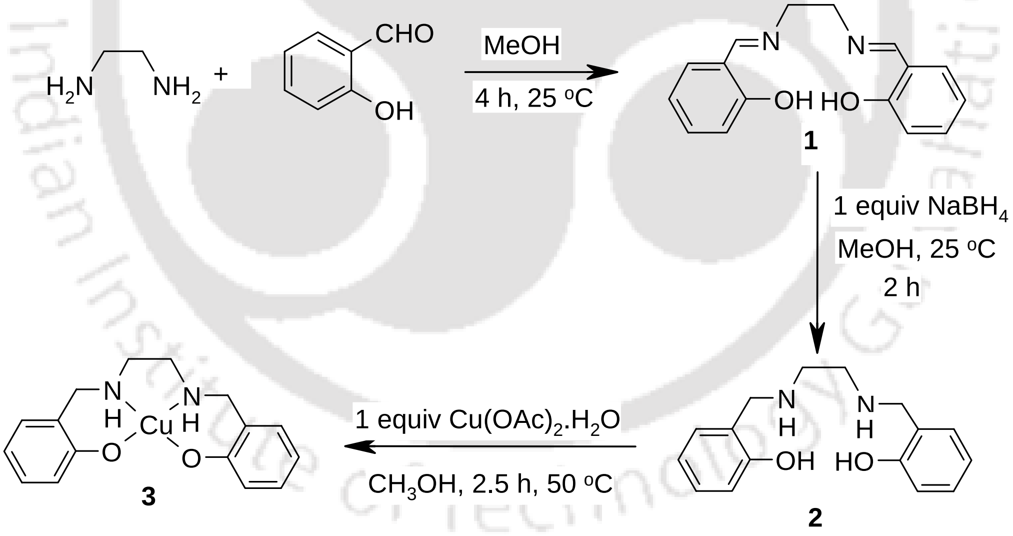
Scheme 10

Table 1: Tungstan Catalyzed Oxidation of Sulfides to Sulfones with 30% H_2O_2

Sulfide	H_2O_2 (equiv)	Catalyst (equiv)	Temp (° C)	Time (h)	Yield of Sulfone (%)
	2.5	0.01	50	2	97
	2.5	0.01	25	6	91
	2.5	0.54	50	2	96
	2.5	0.01	50	1	95
	2.5	0.01	25	2	93

2.4 Present Study

Copper is an abundant element and less expensive in comparison to many other metals. Thus, design and development of copper based catalysts will be quite useful for the oxidation of organic compounds with aqueous H_2O_2. The copper(II) complex **3** has been prepared from the readily available ethylenediamine and salicylaldehyde as shown in Scheme 11. Reaction of ethylenediamine with salicylaldehyde provided the Schiff base **1** as yellow solid which could be reacted with $NaBH_4$ to give **2** with 72% yield as a colorless solid. The latter underwent reaction with $Cu(OAc)_2{\cdot}H_2O$ to provide copper(II) complex **3** (hereafter referred as Cu^{II}salan) as a green powder. The catalyst **3** is soluble in water as well as in common organic solvents such as acetonitrile, acetone and THF.



Scheme 11

Oxidation of Alcohols

Having **3** in hand, we first studied the oxidation of alcohols to carboxylic acids and ketones in the presence of aqueous 30% H_2O_2. To standardize the reaction conditions the oxidation of 4-chlorobenzyl alcohol was studied at ambient conditions (Table 2). We were pleased to find 4-chlorobenzyl alcohol was oxidized to a 2:1 mixture of 4-cholorobenzaldehyde and 4-chlorobenzoic acid with 30% yield in the presence of 1 mol% of **1** and 10 equiv. of H_2O_2. The reaction could be driven to completion with 92% yield of 4-chlorobenzoic acid by heating at 80 ^{o}C for 4.5 h. Acetonitrile was found to be the solvent of choice for this process. Control experiments without complex **1** showed no oxidation. Similarly, no significant oxidation was observed with molecular oxygen as a terminal oxidant. $Cu(OAc)_2$ and Cu^{II}salen were also examined, but they were less effective in comparison to **3** providing a mixture of carboxylic acid and aldehyde in moderate yields (entries 3 and 4).

Table 2: Cu^{II}salan Catalyzed Oxidation of 4-Chlorobenzyl Alcohol with 30% H_2O_2

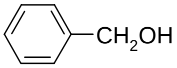
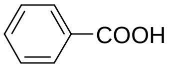
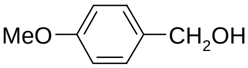
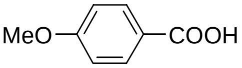
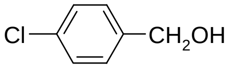
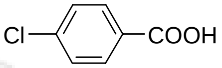
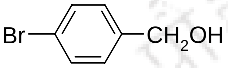
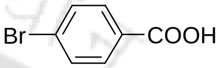
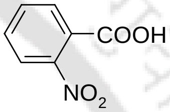
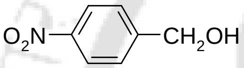
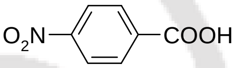
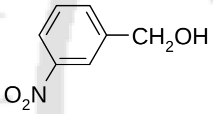
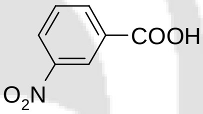
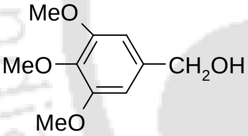
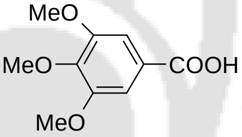
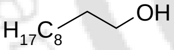
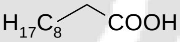
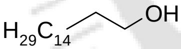
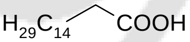
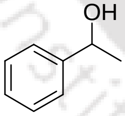
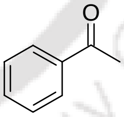
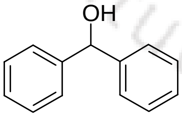
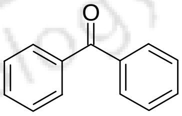
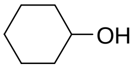
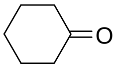
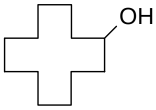
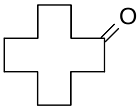
Entry	Catalyst 1 mol%	Time (h)	Conversion (%)[b]	Selectivity [b]
1	3	4.5	93	99
2	None	16	-	-
3	$Cu(OAc)_2$	4.5	30	16
4	Cu^{II}salen	4.5	65	99

[a] A solution of the catalyst **3** (1 mol%), alcohol (2 mmol) and 30% H_2O_2 (2.26 ml, 20 mmol) in acetonitrile (2 ml) was stirred under atmospheric oxygen at *ca.* 80 °C.

[b] Determined by GC.

To evaluate the scope of the protocol, the oxidation of other alcohols was further studied (Table 3). Benzylic alcohols having 4-bromo, 4-nitro, 3-nitro, 2-nitro, 4-methoxy and 3,4,5-trimethoxy substituents in the aromatic ring were oxidized to the corresponding carboxylic acids in high yields (entries 1-8). The oxidation of aliphatic alcohols, decyl

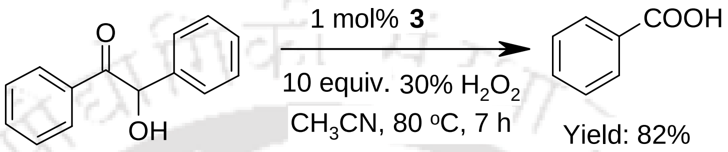
Table 3: Copper(II) Catalyzed Oxidation of Alcohols with 30% H_2O_2

Entry	Substrate	Time (h)	Product	Yield (%)[a,b]
1		5		92
2		3		93
3		4.5		93
4		4		94
5		8		83
6		8		82
7		7		89
8		2		93
9		8		93
10		9		90
11		0.5		99
12		0.5		98
13		4		99
14		4		81

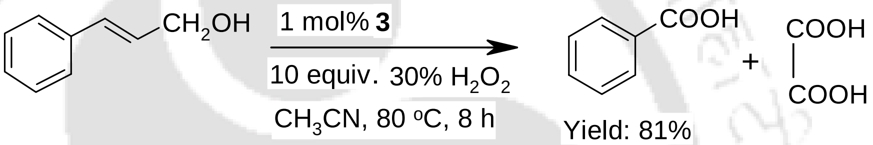
[a] Catalyst **3** (1 mol%), alcohol (2 mmol) and 30% H_2O_2 (10-30 mmol) in acetonitrile (2 ml) were stirred at *ca.* 80 °C.

[b] Isolated yield.

and cetyl alcohols, required 15 equiv of H_2O_2. The reaction of secondary alcohols required 5 equiv H_2O_2 to give the corresponding ketones in high yields (entries 11-14). Under these conditions, cinnamyl alcohol and benzoin underwent oxidative cleavage to provide the corresponding carboxylic acids in high yields (Scheme 12-13).



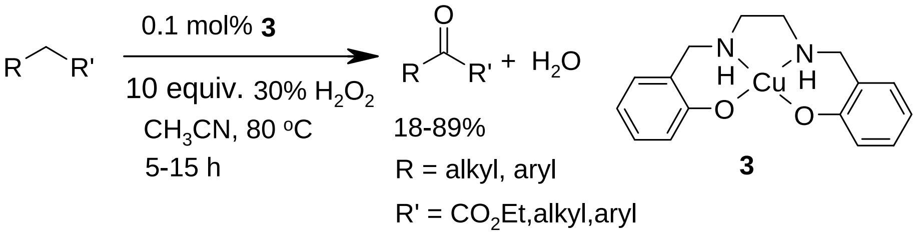
Scheme 12



Scheme 13

Oxidation of Alkylbenzenes and Cyclohexane

Since Cu^{II}salan is readily accessible, soluble in common organic solvents and efficiently catalyzes the oxidation of alcohols with 30% H_2O_2, we wanted to further explore its catalytic activity for the oxidation of other substrates. The oxidation of alkylbenzenes and cyclohexane was next studied (Scheme 14).



Scheme 14

The oxidation of diphenylmethane was first examined as a standard substrate with 30% H_2O_2 in the presence of Cu^{II}salan **3** in CH_3CN under ambient conditions (Table 4). As expected the oxidation took place to afford a 1:1 mixture of diphenylmethanol and benzophenone with 34% yield in the presence of Cu^{II}salan **3** and 10 equiv. of 30% H_2O_2 after 16 h at ambient conditions. When the reaction mixture was allowed to stir at 80 °C for 5 h benzophenone was obtained with 87% yield (entry 2).

Table 4: Copper(II) Catalyzed Oxidation of Diphenylmethane to Benzophenone[a]

Entry	Catalyst (0.1 mol%)	Time(h)	Conversion (%)[b]	Selectivity [b]
1[c,d]	1	16	18	99
2	1	5	87	99
3	None	16	-	-
4	$Cu(OAc)_2$	5	8	99
5[c]	Cu^{II}salen	5	58	99

[a] A solution of the catalyst (0.1 mol%), diphenylmethane (2 mmol) and 30% H_2O_2 (2.26 ml, 20 mmol) in acetonitrile (2 ml) was stirred at ca. 80 °C under atmospheric oxygen.

[b] Determined by GC.

[c] Reaction was performed at ambient temperature.

[d] Diphenylmethanol (16%) obtained.

A control experiment without catalyst **3** showed no oxidation. $Cu(OAc)_2$ and Cu^{II}salen were also examined as catalysts, but they were less effective in comparison to Cu^{II}salan providing benzophenone with moderate yield (entries 4-5).

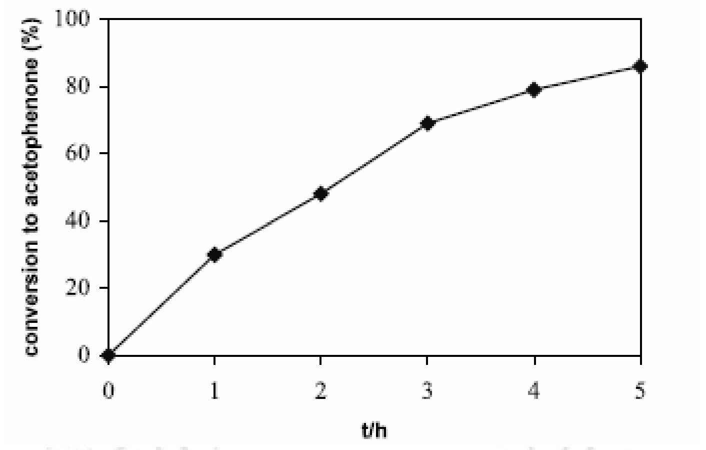
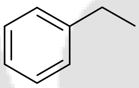
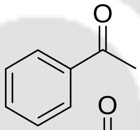
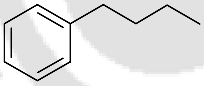
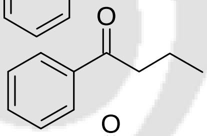
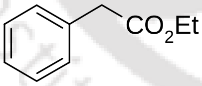
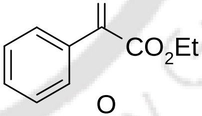
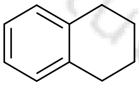
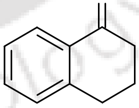
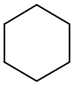
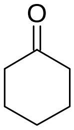


Figure 2: Progress of the Oxidation of Ethylbenzene to Acetophenone.

Table 5: Cu^{II}salan **3** Catalyzed Oxidation of Alkylbenzenes and Cyclohexane with 30% H_2O_2[a]

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1		5		86
2		5		88
3	 CO$_2$Et	5	 CO$_2$Et	82
4		5	 O	89
5[c]		10	 O	18

[a] A solution of the catalyst (0.1 mol%), alkylbenzene (2 mmol) and 30% H_2O_2 (2.26 ml, 20 mmol) in acetonitrile (2 ml) was stirred at *ca.* 80 °C under atmospheric oxygen.

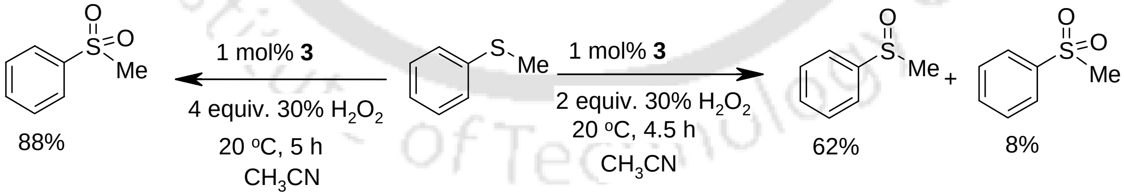
[b] Determined by GC.

[c] 4 mmol of substrate used.

The oxidation of ethylbenzene, butylbenzene, ethyl phenylacetate, tetralin and cyclohexane was further studied (Table 5). The oxidation selectively occurred to give the corresponding ketones in high yields. The substrates with benzylic C-H bonds underwent oxidation with 82-89% yields (Figure 2). The oxidation of cyclohexane was sluggish in comparison to benzylic substrates providing cyclohexanone in 18% yield.

Oxidation of Sulfide to Sulfone

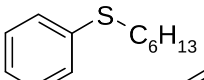
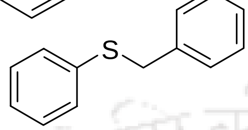
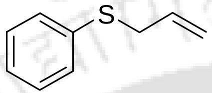
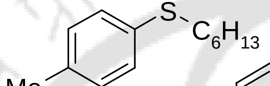
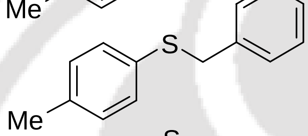
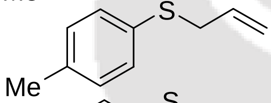
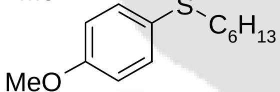
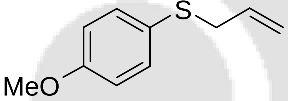
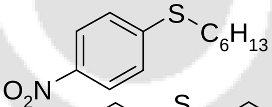
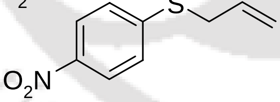
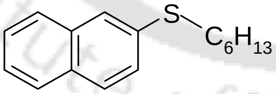
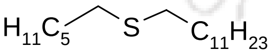
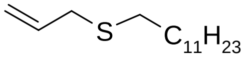
Following the above observation, the oxidation of sulfide to sulfone was investigated. The oxidation of methyl phenyl sulfide was first studied for the standardization. We were pleased to find the oxidation occurred to afford a 8:1 mixture of sulfoxide and sulfone in 70% yield in the presence of 1 mol% of the complex **3** and 2 equiv of 30% H_2O_2 in acetonitrile at ambient temperature. When the amount of H_2O_2 reduced to one equiv, the selectivity was not increased but yield of sulfoxide and sulfone was decreased. However, when the quantity of H_2O_2 increased to 4 equiv, the sulfide was converted sulfone as sole product (Scheme 15).



Scheme 15

Since the selective oxidation of sulfide to sulfone will be useful, the oxidation of other sulfides was further studied (Table 6). Aryl sulfides having electron donating- and

Table 6: Cu^{II}salan **3** Catalyzed Oxidation of Sulfides to Sulfones with 30% H_2O_2

Entry	Substrate	Time (h)	Sulfone (%)
1		22	80
2		26	52
3		18	64
4		23	88
5		28	51
6		24	86
7		21	81
8		18	80
9		27	46
10		25	50
11		30	43
12		31	45
13		26	68

[a]Substrate (5 mmol), complex **3** (1 mol%) and 30% H_2O_2 (20 mmol) were stirred in acetonitrile (10 ml) at 20 °C

withdrawing groups in the aromatic ring were oxidized to the corresponding sulfones in moderate to good yields (entries 4-10). Under these conditions, allylic double bonds did not undergo any oxidation. The reactivity was dependent on the nature of the substituents. Alkyl sufides were less reactive in comparison to aryl and allyl sulfides.

In summary, Cu^{II}salan has been shown to catalyze the oxidation of alcohols to carboxylic acids and ketones in high yields in the presence of aqueous 30% H_2O_2. Under similar conditions alkylbenzenes and cylohexane are oxidized to the corresponding ketones with good yields. These reactions are found to be efficient in the presence of 5-15 equiv of 30% H_2O_2 and 1 mol% of **3** under heating conditions. Sulfides could be transformed to the corresponding sulfones in high yields using **3** in the presence of 4 equiv of 30% H_2O_2 under ambient conditions.

Experimental Section

General. Alkanes, thiols and alkyl or aryl haildes were purchased from Aldrich, Fluka and Lancaster.

Preparation of Ligand 2. Salicylaldehyde (1 mmol, 122 mg) and ethylenediamine (0.5 mmol, 30 mg) were stirred in MeOH (5 ml) at ambient temperature for 2 h to afford Schiff base **1** as yellow powder in 81% (217 mg), which was further reacted with $NaBH_4$ (32 mg) in methanol (5 ml) for 2 h at ambient temperature. Removal of the solvent on a rotary evaporator followed by treatment with water afforded **2** as a colorless powder in 72% (162 mg) yield.

^{1}H NMR ($CDCl_3$, 90 MHz): δ 2.85 (s, 4H), 3.9 (s, 4H), 6.7–7.2 (m, 8H).

IR (KBr): 999, 1260, 1398, 1565, 1608, 2827, 2868, 2909, 3288 cm^{-1}.

Anal Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.42; H, 7.39; N, 10.31.

Preparation of Cu^{II}salan 3. $Cu(OAc)_2 \cdot 1H_2O$ (1 mmol, 200 mg) and **2** (0.55 mmol, 150 mg) were stirred in methanol (10 ml) at 50 °C for 2.5 h under a nitrogen atmosphere. Evaporation of the solvent on a rotary evaporator gave a residue which was purified on silica gel (60–120 mesh) column chromatography using EtOAc and MeOH (15:5) as an eluent to afford Cu^{II}salan **3** as a green powder in 70% yield.

UV/Vis (CH_3CN): λ_{max} 328, 584 nm.

MS (FAB): *m*/*z* 334 (M^+).

General Procedure for Oxidation of Alcohols

A homogeneous solution of the alcohol (2 mmol), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) was stirred at 80 °C for the appropriate time (Table 5). The reaction mixture was then cooled to room temperature and dimethyl sulphide (50 μl) was added. The aqueous solution was removed on a rotary evaporator and the residue was passed through a short pad of silica gel using CH_2Cl_2 and hexane as eluent to afford the analytically pure products.

Benzoic acid. Benzyl alcohol (2 mmol, 206 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the reaction conditions described in the general procedure for 5 h to afford benzoic acid in 92% (225 mg) yield as a colorless solid.

Mp: 123 °C.

^{1}H NMR ($CDCl_3$): δ 7.31-7.8 (m, 5H).

^{13}C NMR ($CDCl_3$): δ 128.4, 129.3, 130.17, 133.7, 172.6.

IR (KBr): 1679 cm^{-1}.

4-Anisic acid. 4-Anisyl alcohol (2 mmol, 276 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the above described reaction conditions for 3 h to provide 4-methoxybenzoic acid in 93% (283 mg) yield as a colorless solid.

Mp: 184 °C.

^{1}H NMR ($CDCl_3$-DMSO-d_6): δ 3.8 (s, 3H), 6.9 (d, *J* = 8.0 Hz, 2H), 7.9 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR ($CDCl_3$-DMSO-d_6): δ 55.2, 113.4, 123.0, 131.3, 162.7, 167.2.

IR (KBr): 1682 cm^{-1}.

Anal Calcd for $C_8H_8O_3$: C, 67.61; H, 5.63. Found: C, 67.58; H, 5.64.

4-Cholorobenzoic acid. 4-Cholorobenzyl alcohol (2 mmol, 286 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the above described reaction conditions for 4.5 h to afford 4-chlorobenzoic acid in 93% (292 mg) yield as a colorless solid.

Mp: 240 °C.

^{1}H NMR ($CDCl_3$-DMSO-d_6): δ 7.5 (d, 2H, *J* = 8.4 Hz), 8.0 (d, 2H, *J* = 8.4 Hz).

^{13}C NMR ($CDCl_3$-DMSO-d_6): 128.4, 129.5, 130.9, 138.1, 166.5.

IR (KBr): 1672 cm^{-1}.

Anal Calcd for $C_7H_5ClO_2$: C, 53.85; H, 3.91. Found: C, 53.88; H, 3.94.

4-Bromobenzoic acid. 4-Bromobenzyl alcohol (2 mmol, 374 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the above described reaction conditions for 4 h to afford 4-bromobenzoic acid in 94% (378 mg) yield as a colorless solid.

Mp: 253 °C.

^{1}H NMR ($CDCl_3$-DMSO-d_6): δ 7.6 (d, 2H, *J* = 8.4 Hz), 8.0 (d, 2H, *J* = 8.4 Hz).

^{13}C NMR ($CDCl_3$-DMSO-d_6): 128.4, 129.5, 131.1, 131.4, 166.6.

IR (KBr): 1673 cm^{-1}.

Anal Calcd for $C_7H_5BrO_2$: C, 42.00; H, 2.50. Found: C, 42.05; H, 2.52.

2-Nitrobenzoic acid. 2-Nitrobenzyl alcohol (2 mmol, 306 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the above described reaction conditions for 8 h to afford 2-nitrobenzoic acid in 83% (277 mg) yield as a yellow solid.

Mp: 147 °C.

^{1}H NMR ($CDCl_3$-DMSO-d_6): δ 7.7-8.0 (m, 4H).

^{13}C NMR ($CDCl_3$-DMSO-d_6): 123.4, 127.5, 129.8, 131.8, 132.6, 148.5, 166.0.

IR (KBr): 1681 cm^{-1}.

Anal Calcd for $C_7H_5NO_4$: C, 49.12; H, 2.92; N, 8.19. Found: C, 49.09; H, 2.94; N, 8.23.

4-Nitrobenzoic acid. 4-Nitrobenzyl alcohol (2 mmol, 306 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the above described reaction conditions for 8 h to provide 4-nitrobenzoic acid in 82% (274 mg) yield as a yellow solid.

Mp: 241 ^{o}C.

^{1}H NMR ($CDCl_3$-DMSO-d_6): δ 8.2-8.4 (m, 4H).

^{13}C NMR ($CDCl_3$+DMSO-d_6): 123.3, 130.6, 136.5, 149.9, 165.7.

IR (KBr): 1684 cm^{-1}.

Anal Calcd for $C_7H_5NO_4$: C, 49.12; H, 2.92; N, 8.19. Found: C, 49.10; H, 2.93; N, 8.22.

3-Nitrobenzoic acid. 3-Nitrobenzyl alcohol (2 mmol, 306 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the reaction conditions described in the general procedure for 7 h to provide 3-nitrobenzoic acid in 79% (279 mg) yield as a yellow solid.

Mp: 141 ^{o}C.

^{1}H NMR ($CDCl_3$+DMSO-d_6): δ 7.8-8.3 (m, 4H).

^{13}C NMR ($CDCl_3$-DMSO-d_6): 123.6, 127.2, 130.4, 132.4, 135.3, 147.8, 165.4.

IR (KBr): 1683 cm^{-1}.

Anal Calcd for $C_7H_5NO_4$: C, 49.12; H, 2.92; N, 8.19. Found: C, 49.09; H, 2.94; N, 8.21.

3,4,5-Trimethoxybenzoic acid. 3,4,5-Trimethoxybenzyl alcohol (2 mmol, 396 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the reaction conditions described in the general procedure for 2 h to afford 3,4,5-trimethoxybenzoic acid in 93% (394 mg) yield as a colorless solid.

Mp: 170 ^oC.

^1H NMR ($CDCl_3$): δ 3.8 (s, 3H), 3.9 (s, 3H), 7.3 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 55.8, 60.16, 106.6, 126.0, 141.4, 152.5, 167.1.

IR (KBr): 1686 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.66. Found: C, 56.58; H, 5.69.

Decanoic acid. Decyl alcohol (2 mmol, 316 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (30 mmol, 3.19 ml) in CH_3CN (2 ml) were subjected to reaction conditions described in the general procedure for 8 h to provide decanoic acid in 93% (320 mg) yield as a colorless solid.

Mp: 33 ^oC.

^1H NMR ($CDCl_3$): δ 0.9 (t, 3H), 1.2-1.4 (m, 13H), 1.6-1.7 (m, 2H), 2.3-2.4 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 24.7, 29.1, 29.3, 29.5, 31.9, 34.2, 180.6.

IR (KBr): 1691 cm^{-1}.

Anal Calcd for $C_{10}H_{20}O_2$: C, 69.77; H, 11.63. Found: C, 69.79; H, 11.66.

Palmitic acid. Cetyl alcohol (2 mmol, 484 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (30 mmol, 3.19 ml) in CH_3CN (2 ml) were subjected to the reaction conditions described in the general procedure for 9 h to provide palmitic acid in 90% (461 mg) yield as a colorless solid.

Mp: 63 °C.

^{1}H NMR (CDCl$_3$): δ 0.9 (t, 3H), 1.2-1.4 (m, 25H), 1.6-1.7 (m, 2H), 2.3-2.4 (m, 2H).

^{13}C NMR (CDCl$_3$): δ 14.1, 22.7, 24.7, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 34.2, 180.5.

IR (KBr): 1690 cm^{-1}.

Anal Calcd for $C_{16}H_{32}O_2$: C, 75.00; H, 12.52. Found: C, 75.03; H, 12.54.

Cyclododecanone. Cyclododecyl alcohol (2 mmol, 368 mg), Cu^{II}salan **3** (1 mol%, 7 mg) and 30% H_2O_2 (10 mmol, 1.2 ml) in CH_3CN (2 ml) were subjected to the reaction conditions described in the general procedure for 4 h to provide cyclododecanone in 81% (295 mg) yield as a colorless solid.

Mp: 58 °C.

^{1}H NMR (CDCl$_3$): δ 1.2-1.7 (m, 14H), 1.7-2.1 (m, 4H), 2.2-2.4 (m, 4H).

^{13}C NMR (CDCl$_3$): δ 23.3, 24.5, 25.8, 25.9, 26.5, 42.0, 212.7.

IR (KBr): 1711 cm^{-1}.

Anal Calcd for $C_{12}H_{22}O$: C, 79.12; H, 12.09. Found: C, 79.15; H, 12.07.

General Procedure for the Oxidation of Alkylbenzenes and Cyclohexane

Substrate (2 mmol), Cu^{II}salan **3** (1 mol%, 0.7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were stirred at 80 °C for the appropriate time (see Table 2). The reaction mixture was then cooled to room temperature and Me_2S (50 µl) was added. The aqueous solution was removed on a rotary evaporator and the residue was treated with diethyl ether (15 ml), and washed with brine. Drying (Na_2SO_4) and evaporation of the solvent on rotary evaporator afforded a residue which was, after GC analysis, passed through a short pad of silica gel using ethyl acetate and hexane as eluent to afford the analytically pure products.

Butyrophenone. Butylbenzene (2 mmol, 268 mg), Cu^{II}salan **3** (0.1 mol%, 0.7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to the above described reaction conditions for 5 h to provide butyrophenone in 88% (260 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 1.0-1.1 (t, 3H), 1.7-1.8 (m, 2H), 1.9-2.0 (t, 2H), 7.4-7.9 (m, 5H).

^{13}C NMR ($CDCl_3$): δ 13.8, 17.8, 40.5, 127.9, 128.5, 132.8, 137.0, 200.2.

IR (neat): 1680 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 81.08; H, 8.11.

Ethyl phenyl mendalate. Ethyl phenyl benzoate (2 mmol, 328 mg), Cu^{II}salan **3** (1 mol%, 0.7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected to reaction conditions described in the general procedure for 5 h to afford ethyl phenyl mendalate in 82% (292 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 1.2 (t, 3H), 4.1-4.3 (q, 2H), 7.3-7.5 (m, 5H).

IR (neat): 1687, 1741 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O_2$: C, 64.08; H, 4.85. Found: C, 64.12; H, 4.83.

α-Tetralone. Tetralin (2 mmol, 264 mg), Cu^{II}salan **3** (1 mol%, 0.7 mg) and 30% H_2O_2 (20 mmol, 2.26 ml) in CH_3CN (2 ml) were subjected the reaction conditions described in the general procedure for 5 h to provide tetralone in 89% (260 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 2.1-2.2 (m, 2H), 2.6 (m, 2H), 2.9-3.0 (m, 2H), 7.3-8.0 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 23.3, 29.7, 39.1, 126.5, 127.1, 128.7, 132.6, 133.3, 144.4, 198.1.

IR (neat): 1683 cm^{-1}.

Anal Calcd for $C_{10}H_{10}O$: C, 82.19; H, 6.85. Found: C, 82.16; H, 6.82.

General Procedure for the Preparation of Sulfides

To a stirred solution of thiol (6 mmol) in ethanol (15 ml), KOH (6 mmol) was added at ambient temperature. Finally alkyl or aryl halide (6 mmol) was added drop wise through the reaction mixture. The progress of the reaction was monitored by TLC. After completion, the ethanol was removed on a rotary evaporator under reduced pressure and the residue was treated with ethyl acetate and water (3:1). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to yield a residue which was passed trough a short pad of silica gel using ethyl acetate and hexane as eluent to provide analytically pure sulfides.

Methyl phenyl sulfide. Benzenethiol (6 mmol, 660 mg), KOH (6mmol, 337 mg) and methyl iodide (6 mmol, 852 mg) in ethanol (15 ml) were subjected to the reaction conditions described in the general procedure for 2 h to provide methyl phenyl sulfide in 89% (662 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3H), 7.51 (s, 5H).

Hexyl phenyl sulfide. Benzenethiol (6 mmol, 660 mg), KOH (6 mmol, 337 mg) and 1-bromohexane (6 mmol, 991 mg) in ethanol (15 ml) were subjected to the reaction conditions described in the general procedure for 4 h to provide hexyl phenyl sulfide in 86% (990 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.84 (t, 3H, J = 6.8 Hz), 2.92-3.01 (m, 10H), 7.0-7.5 (m, 5H).

Benzyl phenyl sulfide. Benzenethiol (6 mmol, 660 mg), KOH (6mmol, 337 mg) and benzyl bromide (6 mmol, 1.03 g) in ethanol (15 ml) were subjected to the reaction conditions described in the general procedure for 2 h to provide benzyl phenyl sulfide in 83% (1.06 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 4.01 (s, 2H), 6.90-7.00 (m, 2H), 7.15-7.19 (m, 4H), 7.34-7.39 (m, 4H).

Allyl phenyl sulfide. Benzenethiol (6 mmol, 660 mg), KOH (6mmol, 337 mg) and allyl bromide (6 mmol, 726 mg) in ethanol (15 ml) were subjected to the reaction conditions described in the general procedure for 2 h to provide allyl phenyl sulfide in 91% (819 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.45-3.50 (m, 2H), 5.17 (d, lH, J = 14 Hz), 5.23 (d, 1H, J = 12 Hz), 5.55-5.59 (m, lH), 7.51-7.55 (m, 5H).

Hexyl 4-methylphenyl sulfide. 4-Methylbenzenethiol (6 mmol, 744 mg), KOH (6mmol, 337 mg) and 1-bromohexane (6 mmol, 991 mg) in ethanol (15 ml) were subjected to the reaction conditions described in the general procedure for 5 h to provide hexyl 4-methylphenyl sulfide in 82% (1.08 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.82 (t, 3H, *J* = 6.8 Hz), 2.59-2.69 (m, 8H), 3.00 (t, 2H), 3.76 (s, 3H), 7.49 (d, 2H, *J* = 8.1 Hz), 7.58 (d, 2H, *J* = 8.1 Hz).

Benzyl 4-methylphenyl sulfide. 4-Methylbenzenethiol (6 mmol, 744 mg), KOH (6mmol, 337 mg) and benzyl bromide (6 mmol, 1.03 g) in ethanol (15 ml) were subjected to the reaction conditions described in the general procedure for 3 h to provide benzyl 4-methylphenyl sulfide in 90% (1.16 g) yield as a colorless solid.

Mp: 44-46 °C.

^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H), 4.14 (s, 2H), 6.97 (d, 2H, *J* = 8.0 Hz), 7.24-7.55 (m, 5H), 7.78 (d, 2H, *J* = 8.0 Hz).

Allyl 4-methylphenyl sulfide. 4-Methylbenzenethiol (6 mmol, 744 mg), KOH (6mmol, 337 mg) and allyl bromide (6 mmol, 726 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 2 h to provide allyl 4-methylphenyl sulfide in 89% (876 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H), 3.85-3.90 (m, 2H), 5.05 (d, 1H, *J* = 15 Hz), 5.22 (d, 1H, *J* = 11 Hz), 5.73-5.80 (m, 1H), 6.97 (d, 2H, *J* = 6.8 Hz), 7.68 (d, 2H, *J* = 7.2 Hz).

Hexyl 4-methoxyphenyl sulfide. 4-Methoxybenzenethiol (6 mmol, 840 mg), KOH (6mmol, 337 mg) and 1-bromohexane (6 mmol, 991 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 4.5 h to provide hexyl 4-methoxyphenyl sulfide in 87% (1.16 g) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 0.87 (t, 3H, *J* = 6.8 Hz), 2.64-2.75 (m, 8H), 3.00-3.13 (m, 2H), 3.77 (s, 3H), 6.90 (d, 2H, *J* = 8.1 Hz), 7.70 (d, 2H, *J* = 8.1Hz).

Allyl 4-methoxyphenyl sulfide. 4-Methoxybenzenethiol (6 mmol, 840 mg), KOH (6mmol, 337 mg) and allyl bromide (6 mmol, 726 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 2.5 h to provide Allyl 4-methoxyphenyl sulfide in 92% (993 mg) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 3.70 (m, 2H), 3.82 (s, 3H), 5.00 (d, 1H, *J* = 15 Hz), 5.17 (d, 1H, *J* = 11 Hz), 5.63-5.70 (m, 1H), 6.83 (d, 2H, *J* = 6.8 Hz), 7.64 (d, 2H, *J* = 7.2 Hz).

Hexyl 4-nitrophenyl sulfide. 4-Nitrobenzenethiol (6 mmol, 1.020 g), KOH (6mmol, 337 mg) and 1-bromohexane (6 mmol, 991mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 8 h to provide hexyl 4-nitrophenyl sulfide in 80% (1.15 g) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 0.83 (t, 3H, *J* = 6.8 Hz), 2.56-2.65 (m, 8H), 3.01 (t, 2H), 7.51 (d, 2H, *J* = 8.1 Hz), 7.69 (d, 2H, *J* = 8.1 Hz).

Allyl 4-nitrophenyl sulfide. 4-Nitrobenzenethiol (6 mmol, 1.02 g), KOH (6mmol, 337 mg) and allyl bromide (6 mmol, 726 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 6 h to provide allyl 4-nitrophenyl sulfide in 90% (1.74 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.74-3.83 (m, 2H), 4.91 (d, 1H, *J* = 15 Hz), 5.24 (d, 1H, *J* = 11 Hz), 5.80 (m, 1H), 7.15 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz).

2-Bromophenyl hexyl sulfide. 2-Bromobenzenethiol (6 mmol, 945 mg), KOH (6mmol, 337 mg) and 1-bromohexane (6 mmol, 991 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 9 h to provide 2-bromophenyl hexyl sulfoxide in 79% (1.30 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, *J* = 6.8 Hz), 2.67-2.74 (m, 8H), 3.02 (t, 2H), 6.90-7.60 (m, 4H).

2-Bromo benzyl phenyl sulfoxide. 2-Bromobenzenethiol (6 mmol, 945 mg), KOH (6mmol, 337 mg) and benzylbromide (6 mmol, 1.03 g) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 6 h to provide 2-bromo benzyl phenyl sulfoxide in 84% (1.40 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 4.0 (s, 2H), 6.82-7.91 (m, 9H).

Allyl 2-bromophenyl sulfide. 2-Bromobenzenethiol (6 mmol, 945 mg), KOH (6mmol, 337 mg) and allyl bromide (6 mmol, 726 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 5.5 h to provide allyl 2-bromo phenyl sulfide in 88% (1.21 g) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 3.85 (d, 2H, *J* = 15 Hz), 5.26 (d, 1H, *J* = 11 Hz), 5.70-5.80 (m, 1H), 6.82-7.94 (m, 5H).

Benzyl dodecyl sulfide. 1-Dodecanethiol (6 mmol, 1.21 g), KOH (6mmol, 337 mg) and benzylbromide (6 mmol, 1.03 g) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 8 h to provide benzyl dodecyl sulfide in 83% (1.46 g) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 0.80-0.84 (m, 3H), 1.21-1.24 (m, 4H), 1.30-1.36 (m, 12H), 1.61-1.66 (m, 6H), 3.94 (s, 2H), 7.1-7.29 (m, 5H).

Hexyl 2-napthyl sulfoxide. 2-Napthalenethiol (6 mmol, 960 mg), KOH (6mmol, 337 mg) and 1-bromohexane (6 mmol, 991 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 8 h to provide hexyl 2-napthyl sulfide in 81% (1.21 g) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 0.85 (t, 3H, *J* = 6.8 Hz), 2.64-2.84 (m, 8H), 3.01 (m, 2H), 7.20-7.97 (m, 7H).

Allyl dodecyl sulfide. 1-Dodecanethiol (6 mmol, 1.21 g), KOH (6mmol, 337 mg) and allyl bromide (6 mmol, 726 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 8 h to provide allyl dodecyl sulfide in 90% (1.31 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.85-0.89 (m, 3H), 1.27-1.29 (m, 4H), 1.31-1.37 (m, 12H), 1.63-1.69 (m, 4H), 3.24 (m, 2H), 3.74 (m, 2H), 5.01 (d, 1H, *J* = 15 Hz), 5.18 (d, 1H, *J* = 11 Hz), 5.64-5.70 (m, 1H).

Dodecyl hexyl sulfoxide. 1-Dodecanethiol (6 mmol, 1.21 g), KOH (6mmol, 337 mg) and 1-bromohexane (6 mmol, 991 mg) in ethanol (15 ml) were subjected in the reaction conditions described in the general procedure for 2 h to provide dodecyl hexyl sulfide in 82% (1.40 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.84-0.87 (m, 6H), 1.23-1.27 (m, 4H), 1.29-1.36 (m, 12H), 1.67-1.76 (m, 12H), 3.32 (m, 4H).

General Procedure for the Oxidation of Sulfides

To a stirred solution of sulfide (5 mmol) and Cu^{II}salan **3** (1 mol%, 17 mg) in acetonitrile (10 ml) at ambient temperature (20 °C), 30% H_2O_2 (20 mmol, 2.27 ml) was added. The progress of the reaction was monitored by TLC. After completion, the aqueous acetonitrile was removed on a rotary evaporator under reduced pressure and the residue was treated with ethyl acetate and water (3:1). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to yield a residue which was passed through a short pad of silica gel using ethyl acetate and hexane as eluent to provide analytically pure sulfone.

Methyl phenyl sulfone. Methyl phenyl sulfide (5 mmol, 720 mg), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 22 h to afford phenyl methyl sulfone in 88% (550 mg) yield as a colorless solid.

Mp: 100 °C.

^{1}H NMR (CDCl$_3$): δ 3.12 (s, 3H), 7.71 (s, 5H).

IR (neat): 1151, 1362 cm^{-1}.

Anal Calcd for $C_7H_8O_2S$: C, 53.85; H, 5.13; S, 20.51. Found: C, 53.82; H, 5.17; S, 20.55.

Hexyl phenyl sulfone. Phenyl hexyl sulfide (5 mmol, 970 mg), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the above reaction conditions afford hexyl phenyl sulfone 80% (906 mg) as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ. 0.96 (t, 3H, *J* = 6.8 Hz), 2.92-3.10 (m, 10H), 7.41-7.90 (m, 5H).

IR (neat): 1162, 1358 cm^{-1}.

Anal Calcd for $C_{12}H_{18}O_2S$: C, 63.71; H, 7.97; S, 14.16. Found: C, 63.67; H, 7.93; S, 14.20.

Benzyl phenyl sulfone. Benzyl phenyl sulfide (5 mmol, 1 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 26 h to afford benzyl phenyl sulfone in 52% (604 mg) yield as a colorless solid.

Mp: 146-148 °C.

^{1}H NMR (CDCl$_3$): δ 4.12 (s, 2H), 7.10-7.16 (m, 2H), 7.30-7.40 (m, 4H), 7.47-7.58 (m, 4H).

IR (KBr): 1155, 1370 cm^{-1}.

Anal Calcd for $C_{13}H_{12}O_2S$: C, 67.24; H, 5.17; S, 13.79. Found: C, 67.28; H, 5.20; S, 13.76.

Allyl phenyl sulfone. Allyl phenyl sulfide (5 mmol, 750 mg), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the above reaction conditions for 18 h to afford allyl phenyl sulfone in 64% (583 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.61-3.69 (m, 2H), 5.35 (d, lH, *J* = 14 Hz), 5.42 (d, 1H, *J* = 12 Hz), 5.74-5.77 (m, lH), 7.60-7.64 (m, 5H).

IR (neat): 1144, 1358 cm^{-1}.

Anal Calcd for $C_9H_{10}O_2S$: C, 59.34; H, 5.50; S, 17.58. Found: C, 59.38; H, 5.53; S, 17.54.

Hexyl 4-methylphenyl sulfone. Hexyl 4-methylphenyl sulfide (5 mmol, 1.17 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 23 h to afford hexyl 4-methylphenyl sulfone 88% (1.06 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 1.0 (t, 3H, *J* = 6.8 Hz), 2.76-2.87 (m, 8H), 3.18 (t, 2H, *J* = 6.8 Hz), 3.91 (s, 3H), 7.65 (d, 2H, *J* = 8.1 Hz), 7.79 (d, 2H, *J* = 8.1 Hz).

IR (KBr): 1145, 1380 cm^{-1}.

Anal Calcd for $C_{13}H_{20}O_2S$: C, 65.00; H, 8.34; S, 13.33. Found: C, 65.04; H, 8.38; S, 13.29.

Benzyl 4-methylphenyl sulfone. Benzyl 4-methylphenyl sulfide (5 mmol, 1.01 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 28 h to afford benzyl 4-methylphenyl sulfone 51% (596 mg) yield as a colorless solid.

Mp: 112-114 ^oC.

^1H NMR ($CDCl_3$): δ 3.90 (s, 3H), 4.24 (s, 2H), 7.04 (d, 2H, J = 8.1 Hz), 7.4-7.6 (m, 5H), 7.85 (d, 2H, J = 8.1 Hz).

IR (KBr): 1150, 1350 cm^{-1}.

Anal Calcd for $C_{13}H_{14}O_2S$: C, 61.20; H, 6.18; S, 16.30. Found: C, 61.24; H, 6.21; S, 16.27.

Allyl 4-methyphenyl sulfone. Allyl 4-methylphenyl sulfide (5 mmol, 820 mg), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 24 h to afford allyl 4-methylphenyl sulfone in 86% (842 mg) as a colorless solid.

Mp: 52-54 ^oC.

^1H NMR ($CDCl_3$): δ 3.90 (s, 3H), 3.92-3.97 (m, 2H), 5.20 (d, 1H, J = 15 Hz), 5.34 (d, 1H, J = 11 Hz), 5.78-5.81 (m, 1H), 7.10 (d, 2H, J = 6.8 Hz), 7.89 (d, 2H, J = 7.2 Hz).

IR (KBr): 1151, 1380 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.12; S, 16.33. Found: C, 61.27; H, 6.15; S 16.37.

Hexyl 4-methoxyphenyl sulfone. Hexyl 4-methoxyphenyl sulfide (5 mmol, 1.12 g), Cu^{II}salan **3** (1 mol%. 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 21 h to afford hexyl 4-methoxyphenyl sulfone in 81% (1.03 g) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 1.1 (t, 3H, *J* = 6.8 Hz), 3.16 (t, 2H, *J* = 6.9 Hz), 2.80-2.91 (m, 8H), 3.90 (s, 3H), 7.07 (d, 2H, *J* = 8.4 Hz), 7.89 (d, 2H, *J* = 8.4 Hz).

IR (neat): 1165, 1381 cm^{-1}.

Anal Calcd for $C_{13}H_{20}O_3S$: C, 60.94; H, 7.81; S, 12.50. Found: C, 60.90; H, 7.84; S, 12.54.

Allyl 4-methoxyphenyl sulfide. Allyl 4-methoxyphenyl sulfide (5 mmol, 820 mg), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 18 h to provide allyl 4-methoxyphenyl sulfone 80% (785 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$) δ 3.85-3.88 (m, 2H), 3.97 (s, 3H), 5.17 (d, 1H, *J* = 15 Hz), 5.32 (d, 1H, *J* = 11 Hz), 5.78-5.82 (m, 1H), 6.99 (d, 2H, *J* = 6.8 Hz), 7.80 (d, 2H, *J* = 7.2 Hz).

IR (neat): 1171, 1369 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O_3S$: C, 61.22; H, 6.12; S, 16.32. Found: C, 61.24; H, 6.15; S, 16.37.

Hexyl 4-nitrophenyl sulfone. Hexyl 4-nitrophenyl sulfide (5 mmol, 1.22 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 27 h to afford hexyl 4-nitrophenyl sulfone 46% (633 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3H, *J* = 6.8 Hz), 2.79-2.86 (m, 8H), 3.10 (t, 2H, *J* = 6.8 Hz), 7.68 (d, 2H, *J* = 8.1 Hz), 7.87 (d, 2H, *J* = 8.1 Hz).

IR (neat): 1165, 1372 cm^{-1}.

Anal Calcd for $C_{12}H_{17}NO_4S$: C, 52.36; H, 6.18; N, 5.091; S, 11.64. Found: C, 52.41; H, 6.15; N, 5.13; S, 11.68.

Allyl 4-nitrophenyl sulfone. Allyl 4-nitrophenyl sulfide (5 mmol, 975 mg), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 25 h to afford allyl 4-nitrophenyl sulfone in 50% (568 mg) yield as a colorless solid.

Mp: 140-142 °C.

^{1}H NMR ($CDCl_3$): δ 3.90-3.93 (m, 2H), 5.01 (d, 1H, *J* = 15 Hz), 5.42 (d, 1H, *J* = 11 Hz), 5.98 (m, 1H), 7.36 (d, 2H, *J* = 8.4 Hz), 7.89 (d, 2H, *J* = 8.4 Hz).

IR (KBr): 1167, 1367 cm^{-1}.

Anal Calcd for $C_9H_9NO_4S$: C, 47.59; H, 3.96; S, 14.10; N, 6.17. Found: C, 47.64; H, 3.92; S, 14.06; N, 6.20.

Hexyl 2-napthyl sulfone. Hexyl 2-napthyl sulfide (5 mmol, 1.22 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 30 h to afford hexyl 2-napthyl sulfone 43% (593 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.91 (t, 3H, J = 6.8 Hz), 2.81-2.99 (m, 8H), 3.20 (t, 2H, J = 6.8 Hz), 7.33-8.36 (m, 7H).

IR (neat): 1166, 1380 cm^{-1}.

Anal Calcd for $C_{16}H_{20}O_2S$: C, 69.57; H, 7.24; S, 11.59. Found: C, 69.61; H, 7.27; S, 11.53.

Dodecyl hexyl sulfone. Dodecyl hexyl sulfide (5 mmol, 1.48 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 31 h to afford dodecyl hexyl sulfone 45% (739 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.90-0.93 (m, 6H), 1.36-1.39 (m, 4H), 1.46-1.57 (m, 12H), 1.81-1.96 (m, 12H), 3.43-3.47 (m, 4H).

IR (neat): 1178, 1370 cm^{-1}.

Anal Calcd for $C_{18}H_{38}O_2S$: C, 68.90; H, 11.59; S, 9.76. Found: C, 68.95; H, 11.56; S, 9.79.

Allyl dodecyl sulfone. Allyl dodecyl sulfide (5 mmol, 1.21 g), Cu^{II}salan **3** (1 mol%, 17 mg) and 30% H_2O_2 (20 mmol, 2.27 ml) in acetonitrile (10 ml) were subjected to the reaction conditions described in the general procedure for 26 h to afford *p*-dodecyl allyl sulfone 68% (932 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.89-0.94 (m, 3H), 1.32-1.35 (m, 4H), 1.39-1.48 (m, 2H), 1.73-1.88 (m, 14H), 3.34 (m, 2H), 3.85 (m, 2H), 5.13 (d, J = 15 Hz, 1H), 5.31 (d, J = 11 Hz, 1H), 5.77-5.83 (m, 1H).

IR (neat): 1175, 1361 cm^{-1}.

Anal Calcd for $C_{15}H_{30}O_2S$: C, 65.69; H, 10.95; S, 11.68. Found: C, 65.64; H, 10.92; S, 11.72.

2.5 References

1. (*a*) Jones, C. W. *Applications of Hydrogen Peroxide and Derivatives*, Royal Society of Chemistry, Cambridge, 1999; (*b*) *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, ed. Strukul, G. Kluwer Academic, Dordrecht, The Netherlands, 1992.
2. (*a*) *Kirk–Othmer Encyclopedia of Chemical Technology*, ed. Kroschwitz, J. I.; Howe-Grant, M. John Wiley & Sons, Inc., New York, 4th edn., 1995, vol. 13, p. 961; (*b*) *Ullmann's Encyclopedia of Industrial Chemistry*, ed. Elvers, B.; Hawkins, S.; Ravenscroft, M.; Schulz, G. VCH, New York, 5th edn., 1989, vol. A13, p. 443.
3. For the International Regulations, see: Regulations Concerning the International Carriage of Dangerous Goods by Rail (RID); European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR); International Maritime Dangerous Goods Code (IMDG Code); International Civil Aviation Organization Technical Instructions for the Safe Transport of Dangerous Goods by Air (ICAOTI); International Air Transport Association Dangerous Goods Regulation (IATA DGR).
4. Berkessel, A.; Sklorz, C. A. *Tetrahedron Lett.* **1999**, *40,* 7965

5. Ligtenbarg, A. G. J.; Oosting, P.; Roelfes, G.; La Crois, R. M.; Hage, R.; Feringa, B. L.; Lutz, M.; Spek, A. L. *Chem. Commun.* **200l**, 385.
6. Martin, S. E.; Garrone, A. *Tetrahedron Lett.* **2002**, *44,* 549.
7. Rothenberg, G.; Barak, G.; Sasson, Y. *Tetrahedron* **1999**, *55,* 6301.
8. Sato, K.; Aoki, M.; Takagi, J.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119,* 12386
9. Sloboda-Rozner, D.; Alsters, P. L..; Neumann, R. *J. Am. Chem. Soc.* **2003**, *125,* 5280.
10. Barton, D. H. R.; Beviere, S. D.; Chavasiri, W.; Csuhai, E.; Doller, D. *Tetrahedron* **1992**, *48,* 2895; (b) Faraj, M.; Hill, C. L. *Chem. Commun.* **1987**, 1487; (c) Murahashi, S.-I.; Oda, Y.; Naota, T.; Komiya, N. *Chem. Commun.* **1993**, 139; (d) Tateiwa, J.-I.; Horiuchi, H.; Uemura, S. *Chem. Commun.* **1994**, 2567; (e) Punniyamurthy, T.; Kalra, S. J. S.; Iqbal, J. *Tetrahedron Lett.* **1995**, *36,* 8497; (f) Dura-Vila, V.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2000**, 1525; (g) Elemans, J. A. A. W.; Bijsterveld, E. J. A.; Rowan, A. E.; Nolte, R. J. M. *Chem. Commun.* **2000**, 2443.
11. Groves, J. T.; Krishnan, S.; Avaria, G. E.; Nemo, T. J. *Adv. Chem. Ser.* **1980**, *191,* 277.
12. Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110,* 8462; (b) Robert, A.; Loock, B.; Momenteau, M.; Meunier, B. *Inorg. Chem.* **1991**, *30,* 706; (c) Bandyopadhyay, R.; Biswas, S.; Guha, S.; Mukherjee, A. K.; Bhattacharyya, R. *Chem. Commun.* **1999**, 1627.
13. Shul'pin, G. B.; Süss-Fink, G.; Shul'pina, G. *J. Mol. Catal. A: Chem.* **2001,** *170,* 17.

14. Nizova, G. V.; Krebs, B.; Suss-Fink, G.; Schindler, S.; Westerheide, L. Gonzalez Cuervo, L.; Shul'pin, G. B. *Tetrahedron.* **2000**, *58,* 9231.
15. Shul'pin, G. B.; Süss-Fink, G.; Shul'pina, G. J. *Chem. Commun.* **2000**, 1131
16. Mckillop, A.; Tarbin, J. A. *Tetrahedron Lett*. **1983**, *24,* 1505
17. Khurana, J. M.; Panda, A. K.; Ray, A.; Gogia, A. *Org. Prep. Proc.* **1996**, *28,* 234.
18. Weber, J. V.; Schneider, M.; Salami, B.; Paquer, D. *Recl. Trav. Chim. Pays-Bas* **1986**, *105,* 99.
19. Barton, D. H. R.; Li, W.; Smith, J. A. *Tetrahedron Lett.* **1998**, *39,* 7055.
20. Kennedy, R. J.; Stock, A. M. *J. Org. Chem*. **1960**, *25,* 1901.
21. Trost, B. M.; Curran, D. P. *Tetrahedron Lett.* **1981**, *22,* 1287.
22. Goheen, D. W.; Bennett, C. F. *J. Org. Chem.* **1961**, *26,* 1331.
23. Ho, T.-L.; Wong, C. M. *Synthesis* **1972**, 561.
24. Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27,* 282.
25. Varma, R. S.; Saini, R. K.; Meshram, H. M. *Tetrahedron Lett.* **1997**, *38,* 6525.
26. Edwards, D.; Stenlake, J. B. *J. Chem. Soc.* **1954**, 3272.
27. Gokel, G. W.; Gerdes, H. M.; Dishong, D. M. *J. Org. Chem.* **1980**, *45,* 3634.
28. Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75,* 3838.
29. Venier, C. G.; Squires, T. G.; Chen, Y.-Y.; Hussmann, G. P.; Shei, J. C.; Smith, B. F. *J. Org. Chem.* **1982**, *47,* 3773.
30. Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50,* 2847.
31. Adam, W.; Hadjiarapoglou, L. *Tetrahedron Lett.* **1992**, *33,* 469.
32. Breton, G. W.; Fields, J. D.; Kropp, P. J. *Tetrahedron Lett.* **1995**, *36,* 3825.
33. Kaldor, S. W.; Hammond, M. *Tetrahedron Lett.* **1991**, 32, 5043.

34. Paquette, L. A.; Carr, R. V. C. *Org. Synth. Coll*. **1990**, *7,* 453.

35. Trost, B. M.; Braslau, R. *J. Org. Chem.* **1988**, *53,* 532.

36. Kagan, H. B.; Rebiere, F. *Synlett* **1990**, 643.

37. Corey, E. J.; Ouannes, C. *Tetrahedron Lett.* **1976**, *47,* 4263.

38. Khanna, V.; Maikap, G. C.; Iqbal, J. *Tetrahedron Lett.* **1996**, *37,* 3367.

39. Dell'Anna, M. M.; Mastrorilli, P.; Nobile, C. F. *J. Mol. Catal***. 1996**, *108,* 57.

40. Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X.Q.; Nayori, R. *Tetrahedron,* **2001**, *57,* 2469.

Chapter 3

Cu^{II}salan and TEMPO Catalyzed Oxidation of Primary Alcohols to Aldehydes and Sulfides to Sufoxides

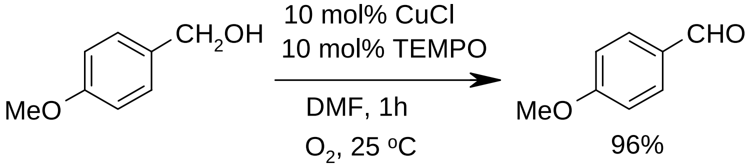
This chapter describes the oxidation of primary alcohols to aldehdyes and sulfides to sulfoxides. These reactions employ a combination of Cu^{II} salan and TEMPO in the presence of molecular oxygen and 30% H_2O_2, respectively.

3.1.1 The Oxidation of Alcohols

The selective oxidation of primary alcohols to aldehydes is crucial for the synthesis of fine chemicals such as fragrances and food additives.[1] So far only few studies have been reported for this purpose with molecular oxygen as terminal oxidant.

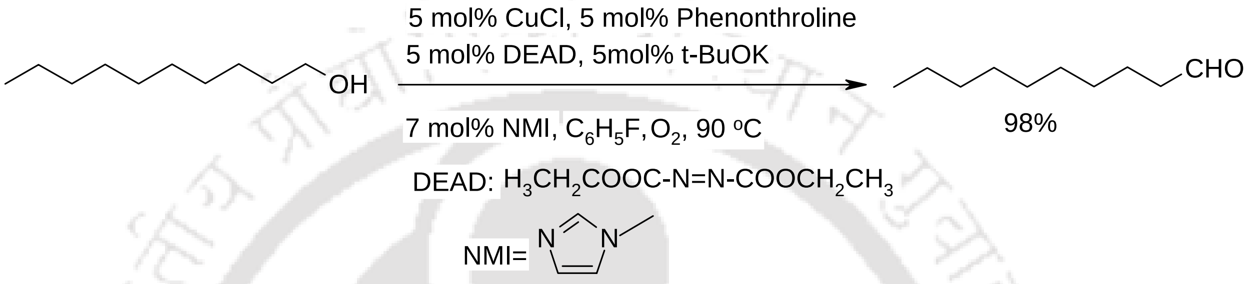
3.1.1.1 Copper Catalysts

In 1984 Semmelhack and co-workers reported the aerobic oxidation of alcohols using CuCl in the presence of TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidinyloxy) (Scheme 1).[2] Under these conditions, the oxidation of primary alcohols is found to superior in comparison to secondary alcohols.



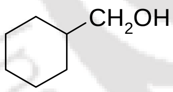
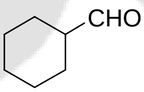
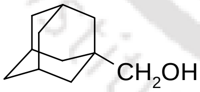
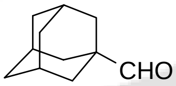
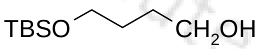
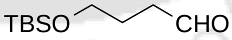
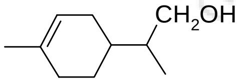
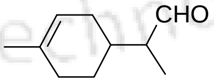
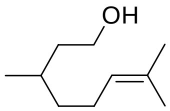
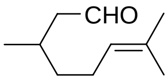
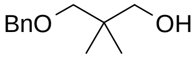
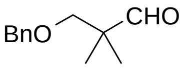
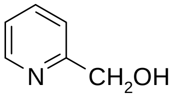
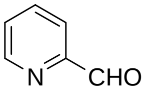
Scheme 1

CuCl-1,10-phenanthroline complex has been subsequently found to catalyze the oxidation of alcohols with atmospheric oxygen (Scheme 2).[3,4] This catalytic system works efficiently in the presence of additive such as DEAD, NMI and DMAP, and base such as K_2CO_3 and *t*-BuOK (Table 1).



Scheme 2

Table 1: CuCl-1,10-phenanthroline Catalyzed Aerobic Oxidation of Alcohols

Entry	Substrate	Product	Yield (%)
1	$C_9H_{19}CH_2OH$	$C_9H_{19}CHO$	95
2			93
3			95
4			94
5			94
6			82
7			97
8			93

Few functional models of galactose oxidase (GO) have been developed by the groups of Stack,[5] Wieghardt[6] and Fukuzumi.[7] These systems operate at ambient conditions in the presence of base such as K_2CO_3 generating H_2O_2 as by-product. For an example, Stack's [Cu(II)BSP], where BSP is a salen-ligand with a binaphthyl backbone, catalyzes the aerobic oxidation of activated alcohols to aldehydes at ambient temperature (Figure 1). The proposed mechanism involves inner sphere one-electron transfer from the alkoxide ligand to Cu(II) followed by hydrogen-transfer to the phenoxyl radical yielding Cu(II), phenol and carbonyl product. Similarly, Wieghardt and co-workers reported a dinuclear Cu(II)-phenoxyl complex which proved to be effective for the aerobic oxidation of non-activated alcohols as well.

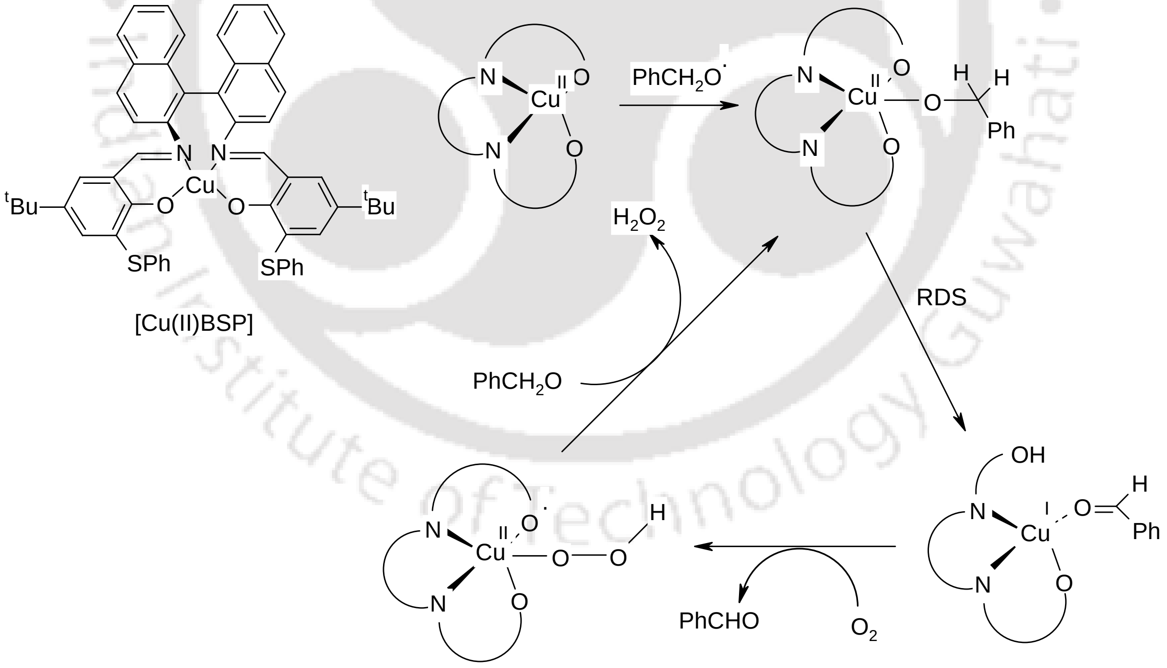
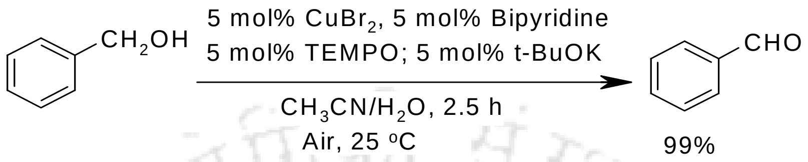


Figure 1. [Cu^{II} BSP]-Catalyzed Aerobic Oxidation of Benzyl Alcohol

Following these studies, $CuBr_2$(Bipy)–TEMPO (Bipy = 2,2-bipyridine) has been reported to catalyze the oxidation of alcohols to aldehydes in the presence of base such as *tert*-BuOK (Scheme 3).[8] The proposed mechanism for this reaction is shown in figure 2.



Scheme 3

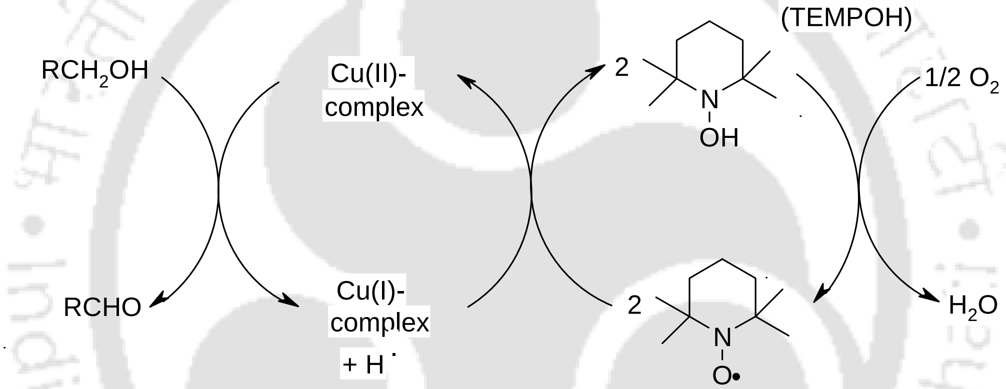
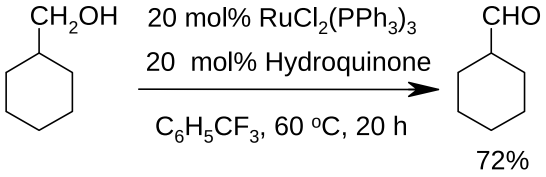


Figure 2: Mechanism for Cu(II)–TEMPO Catalyzed Aerobic Oxidation of Alcohols.

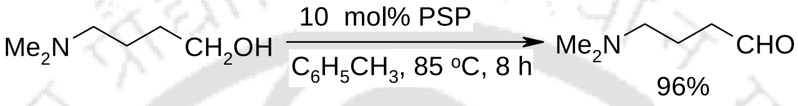
3.1.1.2 Ruthenium Catalysts

Few studies are available on the ruthenium catalyzed oxidation of primary alcohols to aldehydes. $Ru(PPh_3)_3Cl_2$-hydroquinone has been shown to catalyze the oxidation of primary alcohols to aldehydes under atmospheric oxygen (Scheme 4).[9]



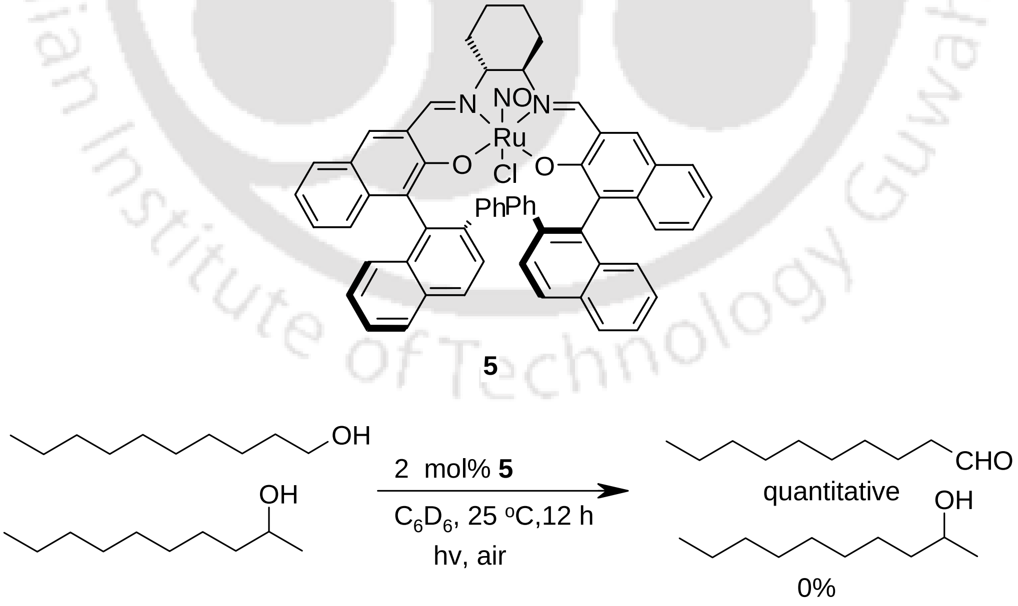
Scheme 4

Polymer supported perruthenate (PSP) has been investigated for the oxidation of primary alcohols to aldehydes in the presence of molecular oxygen (Scheme 5).[10] In this system, molecular oxygen has been bubbled through the reaction mixture of alcohol, PSP (10 mol%) and toluene at 75-85 °C. The reactivity of activated alcohols is found to be greater in comparison to non-activated substrates.



Scheme 5

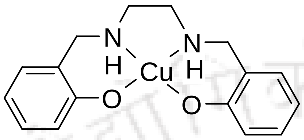
Chiral Ru^{III}salen has been investigated for the oxidation of primary alcohols in the presence of secondary alcoholic groups (Scheme 6).[11] This reaction works efficiently under irradiation at ambient temperature.



Scheme 6

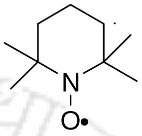
3.1.2 Present Study

Since the selective oxidation of primary alcohols to aldehydes is important and only few studies are available with molecular oxygen, we wanted to further explore Cu^{II}salan for the aerobic oxidation of primary alcohols to aldehydes with suitable additives.



Cu^{II}salan

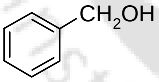
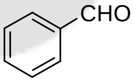
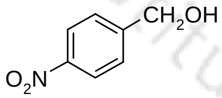
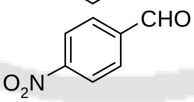
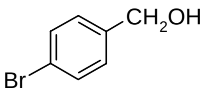
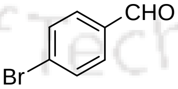
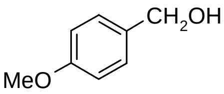
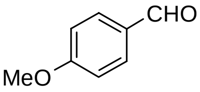
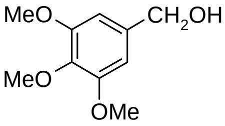
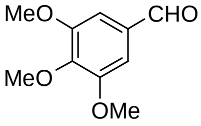
1

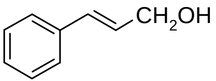
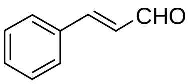
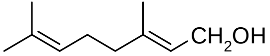
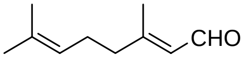
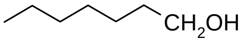
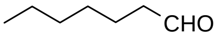
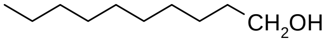
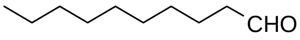
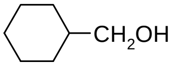
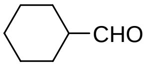
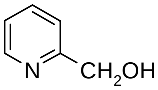
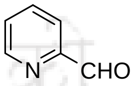
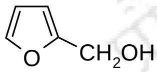
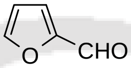
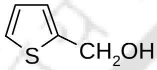
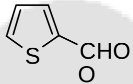
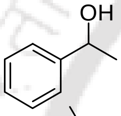
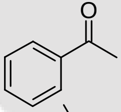
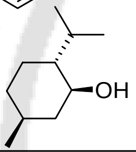
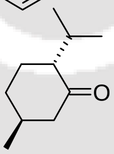


TEMPO

The oxidation of benzyl alcohol was first investigated as a standard substrate. When a combination of Cu^{II}salan and TEMPO was employed, we were pleased to find that the oxidation occurred to provide benzaldehyde in quantitative yield at 100 °C in toluene

Table 2: Cu^{II}salan and TEMPO Catalyzed Chemoselective Oxidation of Primary Alcohols to Aldehydes with Atmospheric Oxygen

Entry	Substrate	Product	Time (h)	Yield (%)^{b}
1			10	99^{c}
2			14	98
3			19	70
4			9	98
5			13	97

6			11	98
7			23	79
8			21	90[d]
9			25	84[d]
10			22	75[d]
11			26	92[d]
12			19	98
13			21	94
14			12	2
15			20	No reaction

[a]Alcohol (5 mmol), Cu^{II}salan (5 mol %) and TEMPO (5 mol %) were stirred in toluene (10 ml) at 100 °C under atmospheric oxygen.

[b]Isolated yield.

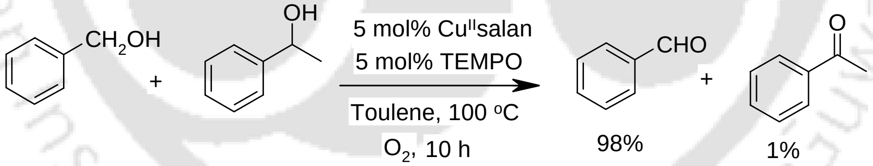
[c]GC yield.

[d]7 mol % of Cu^{II}salan and TEMPO used.

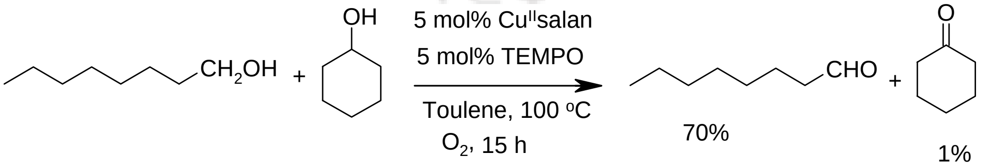
(Table 2, entry 1). No over oxidation to benzoic acid was observed. A control experiment without TEMPO showed no reaction.

To evaluate the scope of this procedure, the oxidation of other alcohols was studied (Table 2, entries 2-15). Aromatic alcohols having both electron withdrawing and donating groups in the benzene ring were oxidized to the corresponding aldehydes in high yields. Allylic alcohols, cinnamyl alcohol and geraniol, underwent oxidation without affecting the carbon-carbon double bonds. The oxidation of aliphatic alcohols, heptanol, decanol and cylcohexylmethanol, required longer reaction time in comparison to activated substrates. Heterocyclic alcohols, pyridine-2-methanol, 2-furfurol and thiophene-2-methanol, could be transformed to the respective aldehydes in high yields. While, secondary alcohols, 1-phenylethanol and (-)-menthol, were less reactive affording the corresponding ketones in <2% yield.

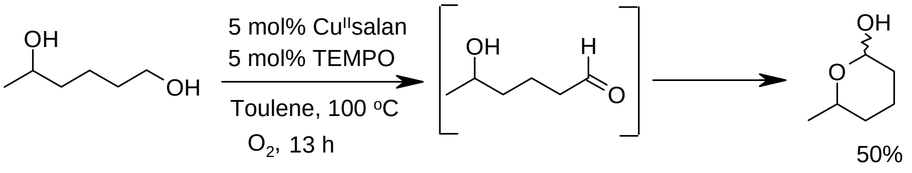
To study the selectivity, the oxidation of a 1:1 mixture of benzyl alcohol and 1-phenylethanol was investigated. As above, the reaction occurred to afford benzaldehyde and acetophenone in 98% and <1% yield, respectively (Scheme 7). A similar result was obtained with a 1:1 mixture of heptanol and cyclohexanol providing heptanal and cyclohexanone in 70% and <1% yield, respectively (Scheme 8). Furthermore, 1,5-hexanediol oxidized to provide 6-methyl-δ-lactol as a mixture of diastereomers with 50% yield (Scheme 9).



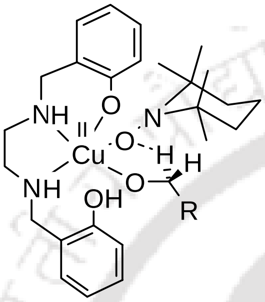
Scheme 7



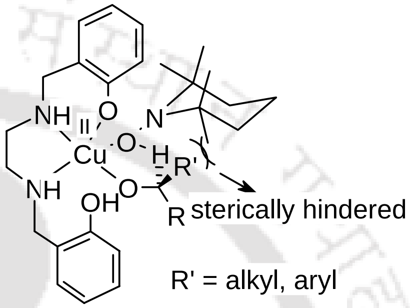
Scheme 8



Scheme 9

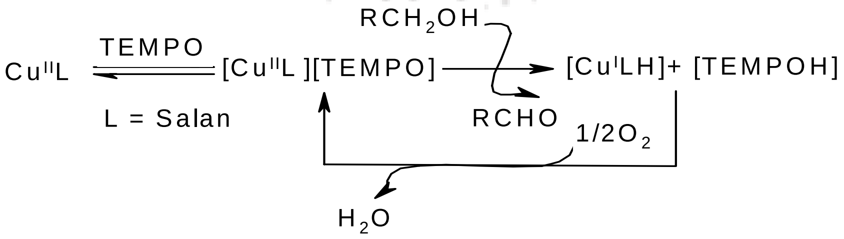


a



b

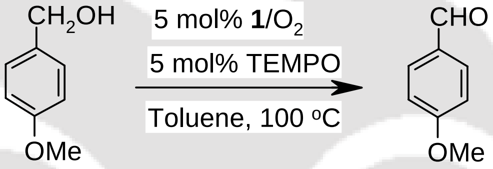
These studies clearly reveal that primary alcohols could be oxidized chemoselectively in the presence of secondary hydroxyl groups. This may be due to less steric hindrance between the methyl groups of TEMPO and β-hydrogen of primary alcohol enhancing the formation of the active species **a** compared to **b** that would arise from secondary alcohol. Intramolecular transfer of β-hydrogen followed by oxidative elimination of **a** would lead to copper(I) complex, TEMPOH and carbonyl compound (Scheme 10). Oxidation of TEMPH to TEMPO by copper(I) complex with molecular oxygen would complete the catalytic cycle.



Scheme 10

Regarding the recyclability of the catalyst **1**, after completion of the oxidation of 4-methoxybenzyl alcohol, the reaction mixture was treated with water (3 ml), and the organic layer, after drying (Na_2SO_4) and GC analysis, was passed through a short pad of silica gel using ethyl acetate and hexane as eluent to afford analytically pure 4-methoxybenzaldehyde in quantitative yield. Evaporation of the aqueous layer afforded a copper complex that was reused for the oxidation of 4-methoxybenzyl alcohol up to three runs in the presence of fresh TEMPO and no loss of activity was observed (Table 3).

Table 3: Recycling of the Cu^{II}salan using *p*-Methoxybenzyl Alcohol



Run	Recovery (%)[a]	Product (%)
1	>99	97
2	>98	96
3	>96	95

[a] Alcohol (1 mmol), TEMPO (5 mol%) and recovered Cu^{II}salan complex **1** were stirred in toluene (3 ml) at 100 °C for 9 h under atmospheric oxygen.

In summary, the oxidation of primary alcohols to aldehydes has been accomplished by the combined use of Cu^{II}salan and TEMPO with atmospheric oxygen. The catalyst is recyclable without loss of activity. Both aliphatic and aromatic alcohols could be oxidized in high yields with excellent selectivity.

Experimental Section

General. 1,5-Hexanediol was purchased from Aldrich.

General Procedure for Oxidation of Alcohols

Alcohol (5 mmol), Cu^{II}salan (5 mol%, 84 mg) and TEMPO (5 mol%, 39 mg) were stirred at *ca.* 100 ^{o}C in toluene (10 ml) under atmospheric oxygen for the appropriate time (Table 2). After completion, the reaction mixture was treated with water (3 ml) and the organic layer, after drying (Na_2SO_4) and GC analysis, was passed through a short pad of silica gel using diethyl ether and hexane as eluent to provide the analytically pure aldehyde or ketone.

4-Nitrobenzaldehyde. 4-Nitrobenzyl alcohol (5 mmol, 765 mg), Cu^{II}salan (5 mol%, 84 mg) and TEMPO (5 mol%, 39 mg) in toluene (10 ml) were subjected to the above described reaction conditions for 14 h to provide the analytically pure 4-nitrobenzaldehyde in 98% (740 mg) yield as a yellow solid.

Mp: 107 ^{o}C.

^{1}H NMR ($CDCl_3$): δ 8.0 (d, 2H, *J* = 8.3 Hz), 8.3 (d, 2H, *J* = 8.3 Hz), 10.3 (s, 1H),

^{13}C NMR ($CDCl_3$): δ 124.3, 130.4, 140.1, 151.1, 190.2.

IR (KBr): 1678 cm^{-1}.

Anal Calcd for $C_7H_5NO_3$: C, 55.63; H, 3.30, N, 9.27, Found: C, 55.65; H, 3.33, N, 9.30.

4-Bromobenzaldehyde. 4-Bromobenzyl alcohol (5 mmol, 935 mg), Cu^{II}salan (5 mol%, 84 mg) and TEMPO (5 mol%, 39 mg) in toluene (10 ml) were subjected to the above described reaction conditions for 19 h to provide the analytically pure 4-bromobenzaldehyde in 70% (648 mg) yield as a colorless solid.

Mp: 57 ^{o}C.

^{1}H NMR (CDCl$_3$): δ 7.6 -7.8 (m, 4H), 10.1 (s, 1H).

^{13}C NMR (CDCl$_3$): δ 129.7, 130.9, 132.4, 135.1, 190.8.

IR (KBr): 1705 cm^{-1}.

Anal Calcd for C_7H_5OBr: C, 45.65; H, 2.72. Found: C, 45.68; H, 2.75.

Cyclohexanecarboxaldehyde. Cyclohexyl methanol (5 mmol, 570 mg), Cu^{II}salan (7 mol%, 118 mg) and TEMPO (7 mol%, 56 mg) in toluene (10 ml) were subjected to the reaction conditions described in the general procedure for 22 h to afford cyclohexane carboxaldehyde in 75% (420 mg) yield as a light yellow liquid.

^{1}H NMR (CDCl$_3$): δ 1.2-1.9 (m, 10H), 2.2-2.3 (m, 1H), 9.6 (s, 1H).

^{13}C NMR (CDCl$_3$): δ 25.0, 25.9, 26.0, 50.0, 204.9.

IR (neat): 1710 cm^{-1}.

Anal Calcd for $C_7H_{12}O$: C, 75.00; H, 10.71. Found: C, 75.03; H, 10.73.

Decanal. Decyl alcohol (5 mmol, 790 mg), Cu^{II}salan (7 mol%, 118 mg), TEMPO (7 mol %, 56 mg) in toluene (10 ml) were subjected to the reaction conditions described in the general procedure for 25 h to provide the analytically pure decanal in 84% (655 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, *J* = 6.0 Hz), 1.2-1.7 (m, 14H), 2.2-2.4 (m, 2H), 9.9 (t, 1H, *J* = 7.3 Hz).

^{13}C NMR ($CDCl_3$): δ 14.5, 22.1, 22.5, 29.3, 29.4, 29.5, 29.6, 31.7, 43.7, 202.5;

IR (neat): 1716 cm^{-1}.

Anal Calcd for $C_{10}H_{20}O$: C, 76.92; H, 12.82. Found: C, 76.94; H, 12.85.

6-Methyl-δ-lactol. 1,5-Hexanediol (5 mmol, 590 mg), Cu^{II}salan (5 mol %, 84 mg) and TEMPO (5 mol %, 39 mg) in toluene (10 ml) were subjected to the reaction conditions described in the general procedure to afford 6-methyl-δ-lactol in 50% (285 mg) as a light yellow liquid.

^{1}H NMR ($CDCl_3$): δ diastereomer A 1.0-1.92 (m, 9H), 3.2 (s, 1H), 4.0-4.1 (m, 1H), 5.2-5.4 (m, 1H); diastereomer B 1.0-1.92 (m, 9H), 3.2 (s, 1H), 3.5-3.6 (m, 1H), 4.6-4.8 (m, 1H).

IR (neat): 1025, 1081, 1255, 1378, 1465, 1593, 2930, 3401 cm^{-1}.

Anal Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41. Found: C, 62.00; H, 10.22.

3.1.3 References

1. (a) Mallat, T.; Baiker, A.; *Catal. Today* **1994**, *19*, 247; (b) Musawir, M.; Davey, P. N.; Kelly, G.; Kozhevnikov, I. V. *Chem. Commun.* **2003**, 1414.
2. Semmelhack, M. F.; Schmid, C. R.; Cortes, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 3374.
3. (a) Wang, Y.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *Science*, **1998**, *279*, 537; (b) Mahadevan, V.; Klein Gebbink, R. J. M.; Stack, T.

D. P. *Current Opinion in Chemical Biology*, **2000**, *4,* 228; (c) Wang, Y.; Stack, T. D. P. *J. Am. Chem. Soc.* **1996,** *118,* 13097; (d) Mahadevan, V.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *J. Am. Chem. Soc.* **1999**, *121*, 5583.

4. Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Brown, S. M.; Urch, C. J. *Science* **1996**, *274*, 2044.
5. Marko, I. E.; Gautier, A.; Dumeunier, R.; Doda, K.; Philippart, F.; Brown, S. M.; Urch, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1588.
6. Chaudhuri, P.; Hess, M.; Flörke, U.; Wieghardt, U. K. *Angew. Chem., Int. Ed.* **1998**, *37,* 2217; (b) Chaudhuri, P.; Hess, M.; Weyhermüller, T.; Wieghardt, K. *Angew. Chem., Int. Ed.* **1999**, *38,* 1095; (c) Chaudhuri, P.; Hess, M.; Muller, J.; Hildenbrand, K.; Bill, E. ; Weyhermuller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1999**, *121,* 9599.
7. Itoh, S.; Taki, M.; Fukuzumi, S. *Coord. Chem. Rev.* **2000**, *198,* 3; (b) Taki, M.; Kumei, H.; Nagatomo, S.; Kitagawa, T.; Itoh, S.; Kukuzumi, S. *Inorg. Chim. Acta*, **2000**, *300,* 622.
8. Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. *Chem. Commun.* **2003**, 2414.
9. Dijksman, A; Marino-Gonzalez, A; Mairata, A; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123,* 6826.
10. Hanyu, A.; Takezawa, E.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **1998**, *39*, 5557.

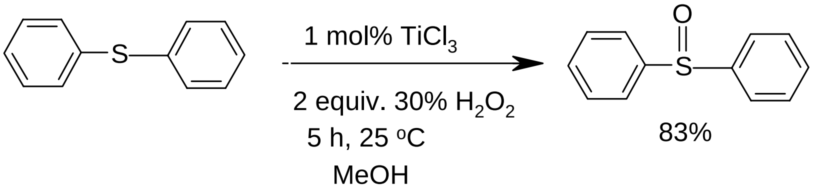
11. (a) Masutani, K.; Uchida, T.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2000**, *41*, 5119; (b) Miyata, A.; Murakami, M.; Irie, R.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7067.

3.2.1 Oxidation of Sulfides to Sulfoxides

The selective oxidation of sulfides to sulfoxides is one of the important synthetic transformations in organic chemistry. Synthetic building blocks containing sulfoxide functional groups are particularly useful for the construction of various important compounds. These derivatives are usually prepared by oxidation of sulfides and several oxidative procedures are applicable for this transformation. Generally, it is important to stop the oxidation at the sulfoxide stage by controlling the electrophilic character of the oxidant, but this requirement is often hard to meet and failure results in over oxidation to sulfones. Thus, there is still considerable interest in the development of selective oxidants for this important transformation with atom efficient oxidant such as H_2O_2.

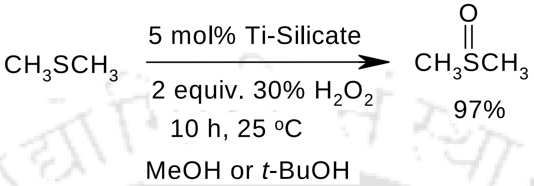
3.2.1.1 Titanium Catalysts

Few studies are focused on the titanium catalyzed oxidation of sulfides with H_2O_2. Titanium trichloride ($TiCl_3$) has been shown to catalyze the oxidation of sulfides to sulfoxides in high yields at ambient conditions (Scheme 1).[1]

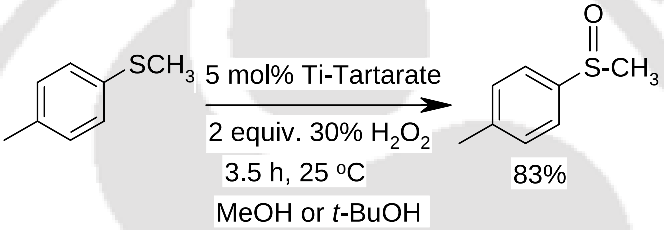


Scheme 1

Titanium containing zeolite has been used for oxidation of dialkyl sulfides in the presence of aqueous H_2O_2 (Scheme 2).[2] Subsequently, $Ti(Oi\text{-}Pr)_4$ supported on silica is found to catalyze the oxidation of sulfides with 13% ee in the presence of *(R)*-DET and 30% aqueous H_2O_2 (Scheme 3).[3]



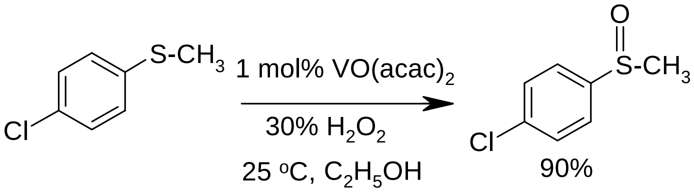
Scheme 2



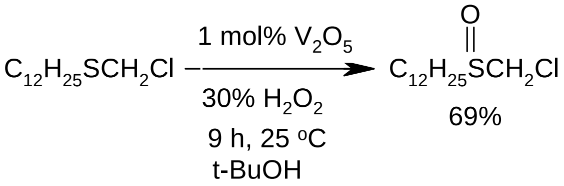
Scheme 3

3.2.1.2 Vanadium Catalysts

Vanadium based catalysts have been considerably studied for the oxidation of sulfides. Ammonium metavanadate (NH_4VO_3),[4] vanadium pentoxide (V_2O_5),[5,6] sodium metavanadate ($NaVO_3$),[7] and vanadium(IV) acetylacetonate $[(CH_3COCH_2COCH_2)_2\text{-}VO]$[8] have been shown to catalyze the oxidation of sulfides with aqueous H_2O_2 (Scheme 4-5). These reactions work efficiently at ambient conditions with high yields.



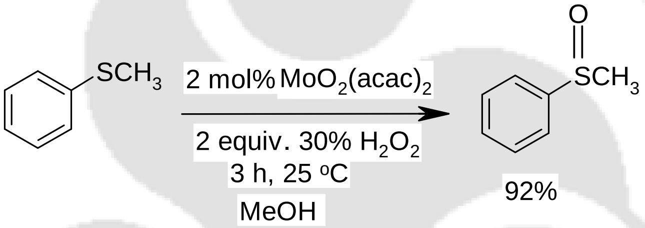
Scheme 4



Scheme 5

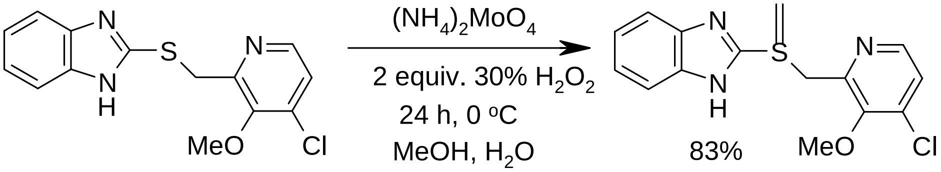
3.2.1.3 Molybdenum Catalysts

Few studies are focused on the oxidation sulfides with molybdenum compounds. Molybdyldiacetylacetonate [$MoO_2(acac)_2$], hexacarbonylmolybdenum [$Mo(CO)_6$] and molybdenum pentoxide [MoO_5] have been shown to catalyze the oxidation of sulfides with aqueous H_2O_2 at ambient conditions (Scheme 6).[9-11]



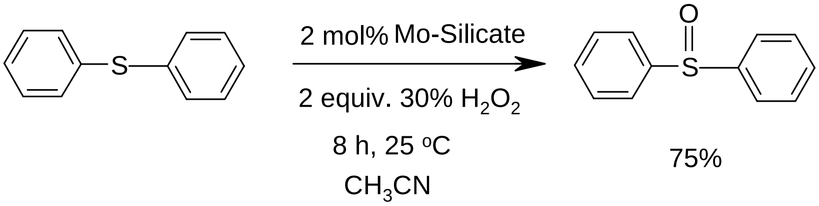
Scheme 6

Ammonium molybdate has been used for the oxidation of [5-(difluoromethoxy)-2-{[(3-methoxy-4-chloro-2-pyridinyl)-methyl]thio}-1H-benzimidazole] to provide the corresponding the anti-ulcer agent pantoprazole (anti-ulcer agent) in the presence of aqueous 30% H_2O_2 (Scheme 7).[12]



Scheme 7

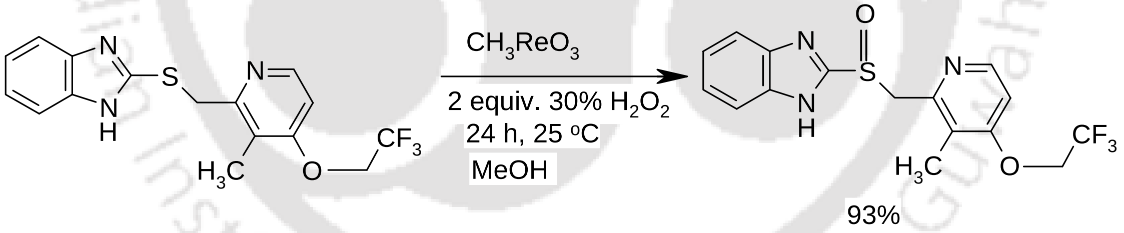
Al-free Mo-silicate-1 (MoS-1) has been shown to catalyze the oxidation of sulfides to sulfoxides with high yields in the presence of 30% H_2O_2 (Scheme 8).[13]



Scheme 8

3.2.1.4 Rhenium Catalyst

Rhenium based catalysts have also been considerably investigated for the oxidation of sulfides.[14-19] For an application, the synthesis of an anti-ulcer drug lansoprazole has been accomplished in 93% yield using methyltrioxorhenium (MTO) in the presence of aqueous H_2O_2 (Scheme 9).[1]



Scheme 9

3.2.1.5 Tungsten Catalysts

Tungsten based catalysts have been found to catalyze the oxidation of sulfides to sufoxides with H_2O_2.[20-29] Nayori and coworkers reported the oxidation of sulfides to sulfoxides by H_2O_2 in the presence of Na_2WO_4, $C_6H_5PO_3H_2$ and a phase-transfer catalyst [PTC= $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$] (Table 1).[30]

Table 1: Tungsten Catalyzed Oxidation of Sulfides to Sulfoxides with 30% H_2O_2

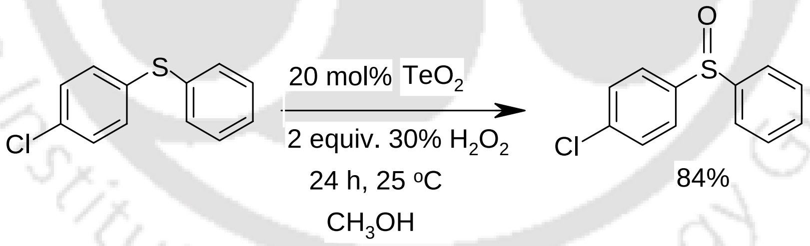
$$RSR' \xrightarrow{1\ mol\%[C_5H_5N(n\text{-}C_{16}H_{33})]_3PO_4[W(O)(O_2)_2]_4} RSOR'$$

entry	R	R'	Na_2WO_4, $C_6H_5PO_3H_2$ PTC, mmol, (S/C)[a]	30% H_2O_2 (equiv)	temp (°C)	time (h)	yield (%)
1	CH_3	C_6H_5	–	1.0	35	18	99
2	CH_3	C_6H_5	–	1.1	0	9	39
3	CH_3	C_6H_5	0.005	1.1	0	9	94
4	n-C_4H_9	n-C_4H_9	–	1.0	35	18	99
5	n-C_4H_9	n-C_4H_9	–	1.1	0	9	31
6	n-C_4H_9	n-C_4H_9	0.005	1.1	0	9	93
7	C_6H_5	C_6H_5	–	2.5	50	12	2
8	C_6H_5	C_6H_5	0.005	1.2	25	3	61

[a] substrate/catalyst ratio

3.2.1.6 Tellurium Catalyst

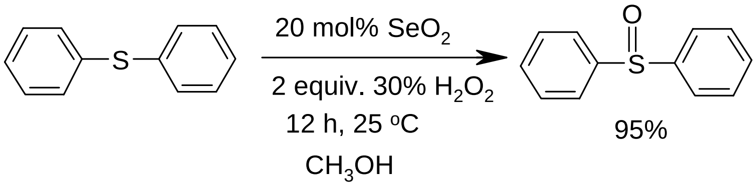
TeO_2 has been shown to catalyze the oxidation of sulfides to sulfoxides with H_2O_2.[31-35] The oxidation of aliphatic sulfides proceeds more smoothly in comparison to the aromatic derivatives (Scheme 10).[31]



Scheme 10

3.2.1.7 Selenium Catalyst

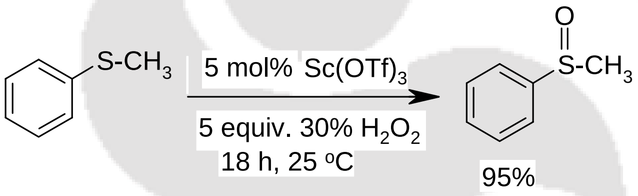
The oxidation of diphenyl sulfide has been accomplished with SeO_2 in the presence of 30% H_2O_2 in high yield (Scheme 11).[36]



Scheme 11

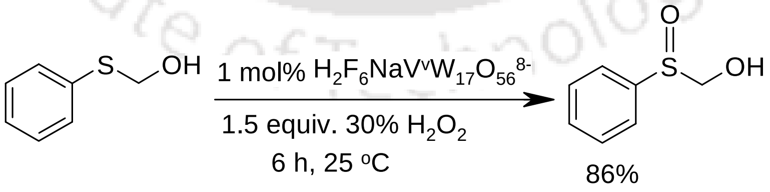
3.2.1.8 Scandium Triflate and Polyoxometalate Catalysts

Bradely and co-workers reported the oxidation of sulfides to sulfoxides with high yield in the presence of 5 mol% $Sc(OTf)_3$ at ambient conditions (Scheme 12).[37]



Scheme 12

Keggin-type polyfluorooxometalate, $[H_2F_6NaV^VW_{17}O_{56}]^{8-}$, has been shown to catalyze the oxidation of sulfides to sulfoxides. The reaction occurred selectively without affecting functional groups such as OH, CN, CHO and double bond (Scheme 13).[38]

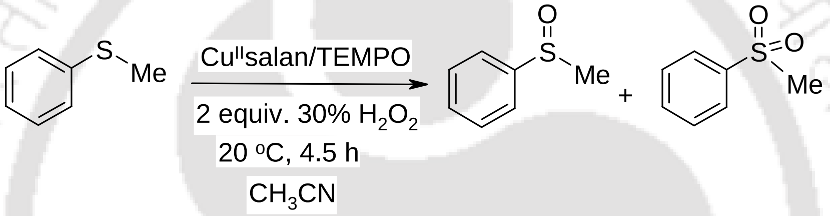


Scheme 13

3.2.2 Present Study

The oxidation of primary alcohols to aldehydes by the combined use of Cu^{II}salan and TEMPO led us to further investigate their application for the oxidation of other organic substrates. The oxidation of sulfide to sufoxide has been accomplished with high selectivity by the combined use of Cu^{II}salan and TEMPO in the presence of 30% H_2O_2.

Table 2: Oxidation of Methyl Phenyl Sulfide[a]



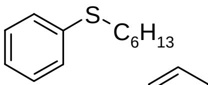
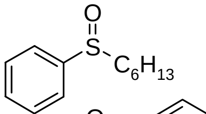
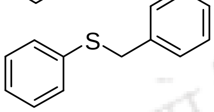
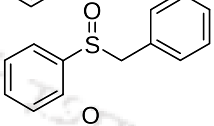
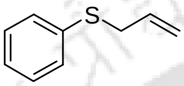
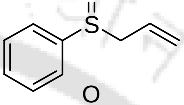
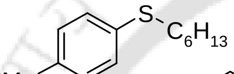
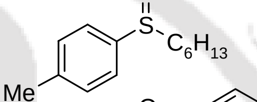
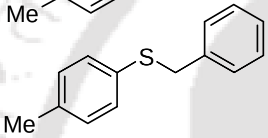
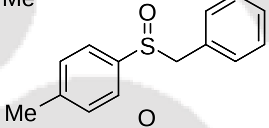
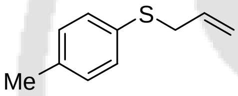
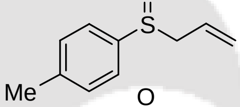
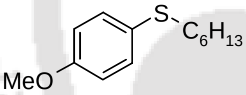
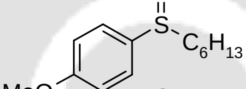
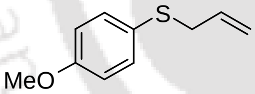
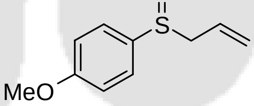
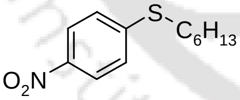
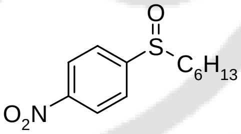
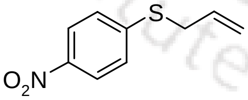
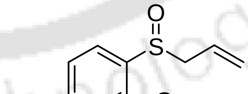
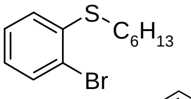
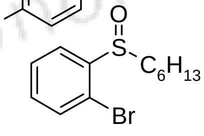
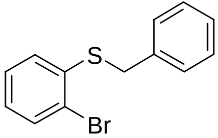
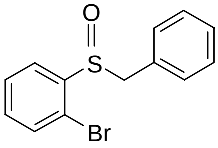
Entry	Cu^{II}salan	TEMPO	Conversion (%)[b]	Sulfoxide (%)[b]	Sulfone (%)[b]
1	none	5 mol%	5	>99	----
2	1 mol%	none	70	89	11
3	1 mol%	3 mol%	90	94	6
4	1 mol%	5 mol%	>99	>99	----
5[c]	recovered	5 mol%	>99	>99	----

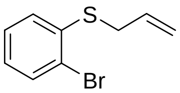
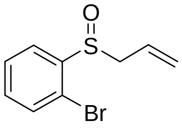
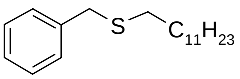
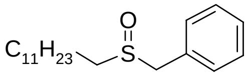
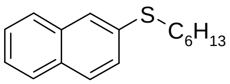
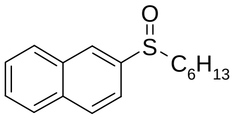
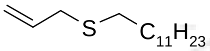
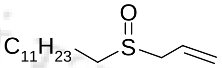
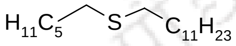
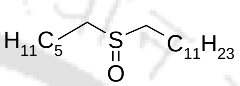
[a] Substrate (5 mmol), Cu^{II}salan complex (1 mol%), TEMPO (5 mol%) and 30% H_2O_2 (10 mmol) were stirred for 4.5 h at 20 °C in CH_3CN (2 ml).

[b] Determined from 400 MHz ^1H NMR of the crude product.

[c] Recovered copper(II) complex was used.

Table 3. Cu^{II}salan and TEMPO Catalyzed Selective Oxidation of Sulfides to Sulfoxides with 30% H_2O_2

Entry	Substrate	Time (h)	Sulfoxide	Yield (%)[b,c]
1		15		83
2		20		52
3		11		92
4		16		89
5		21		57
6		14		96
7		15		87
8		11		94
9		23		51
10		22		71
11		23		51
12		22		48

13		23		69
14		21		54
15		24		40
16		23		62
17		24		48[d]

---

[a] Substrate (5 mmol), Cu^{II}salan (1 mol%), TEMPO (5 mol%) and 30% H_2O_2 (10 mmol) were stirred in acetonitrile (2 ml) at 20 °C.

[b] Isolated yield.

[c] No sulfone was observed.

[d] Accompanied by sulfone <2%.

The oxidation of methyl phenyl sulfide was first studied as a standard substrate by the combined use of Cu^{II}salan and TEMPO in the presence of 30% aqueous H_2O_2 at ambient conditions (Table 2). We were pleased to find the oxidation occurred selectively to provide the corresponding sulfoxide in high yield when the reaction was allowed to stir in the presence of 1 mol% of Cu^{II}salan, 5 mol% of TEMPO and 2 equiv of 30% H_2O_2. A control experiment without Cu^{II}salan provided the sulfoxide with 5% yield and no sulfone was observed (entry 1). The presence of TEMPO enhances the reactivity as well as selectivity of the sulfoxides in comparison to the reaction without TEMPO (entry 2-4).

To study the scope of the procedure, the oxidation of other sulfides was studied (Table 3). Aryl sulfides having both electron donating and withdrawing substituents in the aromatic ring were oxidized to the corresponding sulfoxides in high yields (entries 4-13). A similar result was observed with the allyl sulfides. Alkyl sulfides were less reactive in comparison to aryl and allyl sulfides (entry 17). In the case of allyl sulfides, no oxidation was observed at the carbon-carbon double bond.

To study the recyclability of Cu^{II}salan, after the completion of the oxidation methyl phenyl sulfide, acetonitrile was evaporated under reduced pressure to provide an aqueous residue which was treated with ethyl acetate and water (3:1). The organic layer, after drying (Na_2SO_4) and HPLC analysis (>99% conversion), was evaporated under reduced pressure to provide a residue which was passed through a short pad of silica gel using ethyl acetate and hexane to give analytically pure sulfoxide. Evaporation of the aqueous layer afforded the Cu^{II}salan complex, which was reused for the oxidation of methyl phenyl sulfide in the presence of 5 mol % of fresh TEMPO and 2 equiv of 30% H_2O_2 in acetonitrile (Table 2, entry 5). As above, the oxidation occurred to provide methyl phenyl sulfoxide in high yield suggesting Cu^{II}salan complex could be recycled without loss of activity.

In summary, the oxidation of sulfides to sulfoxides has been carried out by the combined use of Cu^{II}salan and TEMPO in the presence of 30% aqueous H_2O_2 at ambient conditions. The presence of TEMPO not only enhances the progress of the reaction and the selectivity towards sulfoxides has also significantly increased.

Experimental section

General Procedure for the Oxidation of Sulfides to Sulfoxides

To a stirred solution of sulfide (5 mmol), Cu^{II}salan (1 mol%, 17 mg) and TEMPO (5 mol%, 39 mg) in acetonitrile (2 ml) at ambient temperature (20 °C), 30% H_2O_2 (10 mmol, 1.13 ml) was added. The progress of the reaction was monitored by TLC. After completion, the aqueous acetonitrile was removed on a rotary evaporator under reduced pressure and the residue was treated with ethyl acetate and water (3:1). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to yield a residue which was passed through a short pad of silica gel using ethyl acetate and hexane as eluent to provide analytically pure sulfoxide. Evaporation of the aqueous layer provided Cu^{II}salan which could be recycled without loss of activity.

Methyl phenyl sulfoxide. Methyl phenyl sulfide (5 mmol, 720 mg), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 4.5 h to afford methyl phenyl sulfoxide in 99% (712 mg) yield as a colorless solid.

^{1}H NMR ($CDCl_3$): δ 2.73 (s, 3H), 7.66 (s, 5H).

IR (neat): 1041 cm^{-1}.

Anal Calcd for C_7H_8OS: C, 59.84; H, 5.67; S, 22.63. Found: C, 59.94; H, 5.71; S, 22.85.

Hexyl phenyl sulfoxide. Hexyl phenyl sulfide (5 mmol, 970 mg), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the above described reaction conditions for 15 h to provide hexyl phenyl sulfoxide in 83% (871 mg) yield as a colorless solid.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, J = 6.8 Hz), 2.92-3.10 (m, 10H), 7.9-7.4 (m, 5H).

IR (KBr): 1062 cm^{-1}.

Anal Calcd for $C_{12}H_{18}OS$: C, 72.00; H, 9.00; S, 16.00. Found: C, 72.05; H, 9.04; S, 16.04.

Benzyl phenyl sulfoxide. Benzyl phenyl sulfide (5 mmol, 1 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 20 h to afford benzyl phenyl sulfoxide in 52% (572 mg) yield as a colorless solid.

Mp: 125 ^{o}C.

^{1}H NMR ($CDCl_3$): δ 4.08 (s, 2H), 7.01-7.10 (m, 2H), 7.29-7.25 (m, 4H), 7.47-7.38 (m, 4H).

IR (KBr): 1055 cm^{-1}.

Anal Calcd for $C_{13}H_{12}OS$: C, 72.21; H, 5.60; S, 14.79. Found**:** C, 72.28; H, 5.64; S, 14.82.

Allyl phenyl sulfoxide. Allyl phenyl sulfide (5 mmol, 750 mg), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 11 h to afford allyl phenyl sulfoxide in 92% (764 mg) yield as a pale yellow liquid.

^{1}H NMR ($CDCl_3$): δ 3.55-3.60 (m, 2H), 5.25 (d, lH, *J* = 14 Hz), 5.31 (d, 1H, *J* = 12 Hz), 5.65-5.69 (m, lH), 7.51-7.55 (m, 5H).

IR (neat): 1044 cm^{-1}.

Anal Calcd for $C_9H_{10}OS$: C, 65.04; H, 6.06; S, 19.26. Found: C, 65.09; H, 6.02; S, 19.22.

Hexyl 4-methylphenyl sulfoxide. Hexyl 4-methylphenyl sulfide (5 mmol, 1.17 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 16 h to afford hexyl 4-methylphenyl sulfoxide in 89% (996 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, *J* = 6.8 Hz), 2.69-2.79 (m, 8H), 3.06 (t, 2H), 3.81 (s, 3H), 7.54 (d, 2H, *J* = 8.1 Hz), 7.66 (d, 2H, *J* = 8.1 Hz).

IR (KBr): 1045 cm^{-1}.

Anal Calcd for $C_{13}H_{20}OS$: C, 69.61; H, 8.98; S, 14.26. Found: C, 69.66; H, 8.95; S, 14.30.

Benzyl 4-methylphenyl sulfoxide. Benzyl 4-methylphenyl sulfide (5 mmol, 1.01 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 21 h to afford benzyl 4-methylphenyl sulfoxide in 57% (577 mg) yield as a colorless soild.

Mp: 140-142 ^oC.

^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H), 4.2 (s, 2H), 7.01 (d, 2H, *J* = 8.0 Hz), 7.31-7.65 (m, 5H), 7.85 (d, 2H, *J* = 8.0Hz).

IR (KBr): 1045 cm^{-1}.

Anal Calcd for $C_{14}H_{14}OS$: C, 73.02; H, 6.12; S, 13.89, Found: C, 73.06, H, 6.16, S, 13.86.

Allyl 4-methylphenyl sulfoxide. Allyl 4-methylphenyl sulfide (5 mmol, 820 mg), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 14 h to afford allyl 4-methylphenyl sulfoxide in 96% (864 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H), 3.90-3.96 (m, 2H), 5.11 (d, 1H, *J* = 15 Hz), 5.29 (d, 1H, *J* = 11 Hz), 5.73-5.80 (m, 1H), 6.97 (d, 2H, *J* = 6.8 Hz), 7.77 (d, 2H, *J* = 7.2 Hz).

IR (neat): 1051 cm^{-1}.

Anal Calcd for $C_{10}H_{12}OS$: C, 66.65; H, 6.71; S, 17.75. Found: C, 66.69; H, 6.74; S, 17.78.

Hexyl 4-methoxyphenyl sulfoxide. Hexyl 4-methoxyphenyl sulfide (5 mmol, 1.12 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 15 h to afford hexyl 4-methoxyphenyl sulfoxide in 87% (974 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, *J* = 6.8 Hz), 2.70-2.81 (m, 8H), 3.06-3.11 (m, 2H), 3.87 (s, 3H), 7.01 (d, 2H, *J* = 8.1 Hz), 7.85 (d, 2H, *J* = 8.1Hz).

IR (KBr): 1045 cm^{-1}.

Anal Calcd for $C_{13}H_{20}O_2S$: C, 64.97; H, 8.39; S, 13.32. Found: C, 64.93; H, 8.42; S, 13.36.

Allyl 4-methoxyphenyl sulfoxide. Allyl 4-methoxyphenyl sulfide (5 mmol, 820 mg), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the above described reaction conditions for 11 h to provide allyl 4-methoxyphenyl sulfoxide in 94% (846 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.80 (m, 2H), 3.90 (s, 3H), 5.11 (d, 1H, *J* = 15 Hz), 5.29 (d, 1H, *J* = 11 Hz), 5.73-5.80 (m, 1H), 6.97 (d, 2H, *J* = 6.8 Hz), 7.77 (d, 2H, *J* = 7.2 Hz).

IR (neat): 1071 cm^{-1}.

Anal Calcd for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.16; S, 16.31. Found: C, 61.27; H, 6.19; S, 16.34.

Hexyl 4-nitrophenyl sulfoxide. Hexyl 4-nitrophenyl sulfide (5 mmol, 1.22 g), Cu^{II}salan (1 mol%. 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the above described reaction conditions for 23 h to provide hexyl 4-nitrophenyl sulfoxide in 51% (650 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, *J* = 6.8 Hz), 2.69-2.79 (m, 8H), 3.10 (t, 2H), 7.62 (d, 2H, *J* = 8.1 Hz), 7.82 (d, 2H, *J* = 8.1 Hz).

IR (KBr): 1065 cm^{-1}.

Anal Calcd for $C_{12}H_{17}NO_3S$: C, 56.68; H, 6.74; N, 6.28; S, 12.59. Found: C, 56.72; H, 6.77; N, 6.31; S, 12.62.

Allyl 4-nitrophenyl sulfoxide. Allyl 4-nitrophenyl sulfide (5 mmol, 975 mg), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the above described reaction conditions for 22 h to provide 4-nitro phenyl sulfoxide in 71% (749 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 3.84-3.90 (m, 2H), 4.99 (d, 1H, *J* = 15 Hz), 5.31(d, 1H, *J* = 11 Hz), 5.87 (m, 1H), 7.23 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 2H, *J* = 8.4 Hz).

IR (neat): 1067 cm^{-1}.

Anal Calcd for $C_9H_9SO_3N$: C, 51.19; H, 4.30; N, 6.63; S, 15.15. Found: C, 51.23; H, 4.26; N, 6.67; S, 15.18.

2-Bromophenyl hexyl sulfoxide. 2-Bromophenyl hexyl sulfide (5 mmol, 1.37 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 23 h to provide 2-bromophenyl hexyl sulfoxide in 51% (737 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.9 (t, 3H, *J* = 6.8 Hz), 2.71-2.94 (m, 8H), 3.09 (t, 2H), 6.97-7.70 (m, 4H).

IR (KBr): 1052 cm^{-1}.

Anal Calcd for $C_{12}H_{17}OSBr$: C, 49.83; H, 5.92; S, 11.06. Found: C, 49.87; H, 5.95; S, 11.10.

2-Bromophenyl benzyl sulfoxide. 2-Bromophenyl benzyl sulfide (5 mmol, 1.39 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 22 h to afford 2-bromophenyl benzyl sulfoxide in 48% (679 mg) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 4.2 (s, 2H), 6.92-8.01 (m, 9H).

IR (neat): 1067 cm^{-1}.

Anal Calcd for $C_{13}H_{11}OSBr$: C, 53.66; H, 3.74; S, 10.88. Found: C, 53.68; H, 3.77; S, 10.86.

Allyl 2-bromophenyl sulfoxide. Allyl 2-bromophenyl sulfide (5 mmol, 1.15 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 23 h to provide allyl 2-bromophenyl sulfoxide in 69% (845 mg) yield as a colorless liquid.

^{1}H NMR (CDCl$_3$): δ 3.91 (d, 2H, J = 15 Hz), 5.31 (d, 1H, J = 11 Hz), 5.87-5.90 (m, 1H), 6.92-8.01 (m, 5H).

IR (neat): 1067 cm^{-1}.

Anal Calcd for C_9H_9OSBr: C, 44.09; H, 3.70; S, 13.05. Found: C, 44.13; H, 3.73; S, 13.07.

Benzyl dodecyl sulfoxide. Benzyl dodecyl sulfide (5 mmol, 1.46 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 21 h to provide benzyl dodecyl sulfoxide in 54% (831 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.89-0.91 (m, 3H), 1.31-1.33 (m, 4H), 1.39-1.46 (m, 12H), 1.71-1.86 (m, 6H), 4.02 (s, 2H), 7.2-7.4 (m, 5H).

IR (KBr): 1037 cm^{-1}.

Anal Calcd for $C_{19}H_{32}OS$: C, 78.22; H, 8.75; S, 8.69. Found: C, 78.25; H, 8.79; S, 8.73.

Hexyl 2-napthyl sulfoxide. Hexyl 2-napthyl sulfide (5 mmol, 1.22 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 24 h to provide hexyl 2-napthyl sulfoxide in 40% (520 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.87 (t, 3H, *J* = 6.8 Hz), 2.71-2.94 (m, 8H), 3.09 (m, 2H), 8.12-7.23 (m, 7H).

IR (KBr): 1046 cm^{-1}.

Anal Calcd for $C_{16}H_{20}OS$: C, 73.82; H, 7.74; S, 12.29. Found: C, 73.87; H, 7.77; S, 12.32.

Allyl dodecyl sulfoxide. Allyl dodecyl sulfide (5 mmol, 1.21 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 23 h provide allyl dodecyl sulfoxide in 62% (774 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.89-0.91 (m, 3H), 1.31-1.33 (m, 4H), 1.39-1.46 (m, 12H), 1.71-1.86 (m, 4H), 3.32 (m, 2H), 3.81 (m, 2H), 5.11 (d, 1H, *J* = 15 Hz), 5.29 (d, 1H, *J* = 11 Hz), 5.73-5.80 (m, 1H).

IR (KBr): 1007 cm^{-1}.

Anal Calcd for $C_{15}H_{30}OS$: C, 69.72; H, 11.70; S, 12.38. Found: C, 69.76; H, 11.74; S, 12.33.

Dodecyl hexyl sulfoxide. Dodecyl hexyl sulfide (5 mmol, 1.48 g), Cu^{II}salan (1 mol%, 17 mg), TEMPO (5 mol%, 39 mg) and 30% H_2O_2 (10 mmol, 1.13 ml) in acetonitrile (2 ml) were subjected to the reaction conditions described in the general procedure for 24 h to provide dodecyl hexyl sulfoxide in 48% (724 mg) yield as a colorless liquid.

^{1}H NMR ($CDCl_3$): δ 0.89-0.91 (m, 6H), 1.31-1.33 (m, 4H), 1.39-1.46 (m, 12H), 1.71-1.86 (m, 12H), 3.32 (m, 4H).

IR (KBr): 1007 cm^{-1}.

Anal Calcd for $C_{18}H_{38}OS$: C, 71.47; H, 12.66; S, 10.58. Found: C, 71.51; H, 12.70; S, 10.62.

3.2.3 References

1. Watanabe, Y.; Numata, T.; Oae, S. *Synthesis* **1981**, 204.
2. (a) Corma, A.; Iglesias, M.; Sa´nchez, F. *Catal. Lett.* **1996**, *39,* 153; (b) Iwamoto, M.; Tanaka, Y.; Hirosumi, J.; Kita, N.; Triwahyono, S. *Microporous Mesoporous Mater.* **2001**, 48, 271; (c) Paukshtis, E. A.; Tuel, A.; Romannikov, V. N. *J. Mol. Catal. A: Chem.* **2000**, *158,* 417.
3. Fraile, J. M.; Garcia, J. I.; La´zaro, B.; Mayoral, J. A. *Chem. Commun.* **1998**, 1807.
4. Masayasu, K.; Yoshio, T.; Norio, I. EP Patent 0302720B1.

5. Hardy, F. E.; Speakman, P. R. H.; Robson, P. *J. Chem. Soc. (C),* **1969**, 2334.
6. Madesclaire, M. *Tetrahedron* **1986**, *42,* 5459.
7. Anisimov, A. V.; Fedorova, E. V.; Lesnugin, A. Z.; Senyavin, V. M.; Aslanov, L. A.; Rybakov, V. B.; Tarakanova, A. V. *Catal. Today* **2003**, *78*, 319.
8. Slemon, C.; Macel, B. WO Patent 95/12590.
9. Winter, W.; Mark, C.; Schurig, V. *Inorg. Chem.* **1980**, *19*, 2045.
10. Bonchio, M.; Carofiglio, T.; Di Furia, F.; Fornasier, R. *J. Org. Chem.* **1995**, *60*, 5986.
11. Bortolini, O.; Furia, F. D.; Modena, G.; Scardellato, C. *J. Mol. Catal. A: Chem.* **1981**, *11,* 107.
12. Coll, A. B. WO Patent 02/28852 A1.
13. Raghavan, P. S.; Ramaswamy, V.; Upadhya, T. T.; Sudalai, A.; Ramaswamy, A. V.; Sivasanker, S. *J. Mol. Catal. A: Chem.* **1997**, *122*, 75.
14. Byun, Y. S.; Choi, S. J. WO Patent 01/21617A1.
15. Espenson, J. H. *Chem. Commun.* **1999**, 479.
16. Adam, W.; Mitchell, C. M.; Saha-Mo¨ller, Ch. R. *Tetrahedron* **1994**, *50*, 13121.
17. Romao, C. C.; Khun, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197.
18. Herrman, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal. A: Chem.* **1994**, *86*, 243.
19. Bringsma, J.; La Crois, R.; Feringa, B. L.; Donnoli, M. J.; Rosini, C. *Tetrahedron Lett.* **2001**, *42*, 4049.
20. Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Furia, F. D.; Modena, G. *J. Mol. Catal. A: Chem.* **1984**, *24*, 189.

21. Harlen, B. F.; Saul, R. B. US Patent 3006963.

22. Schultz, H. S.; Freyermuth, H. B.; Buc, S. R. *J. Org. Chem.* **1963,** *28*, 1140.

23. Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Furia, F. D.; Modena, G. *J. Mol. Catal*. **1983**, *18*, 177.

24. Palomo Coll, A. ES Patent 2105953.

25. Ishii, Y.; Tanaka, H.; Nisiyama, Y. *Chem. Lett*. **1994**, 1.

26. Stec, Z.; Zawadiak, J.; Skibinski, A.; Pastuch, G. *Pol. J. Chem*. **1996**, *70*, 1121.

27. Neumann, R.; Juwiler, D. *Tetrahedron* **1996**, *52*, 8781.

28. Gresley, N. M.; Griffith, W. P.; Laemmel, A. C.; Nogueira, H. I. S.; Parkin, B. C. *J. Mol. Catal. A: Chem.* **1997**, *117*, 185.

29. Collins, F. M.; Lucy, A. R.; Sharp, C. *J. Mol. Catal. A: Chem.* **1997**, *117*, 397.

30. Sato, K.; Hyodo, M.; Aoki, M.; Zheng, X.-Q.; Noyori, R. *Tetrahedron* **2001**, *57,* 2469.

31. Kim, K. S.; Hwang, H. J.; Cheong, Ch. S.; Hahn, Ch. S. *Tetrahedron Lett.* **1990**, *31,* 2893.

32. Drabowicz, J.; Mikołajczyk, M. *Synthesis* **1978**, 758.

33. Chambers, R. D.; Clark, M. *Tetrahedron Lett.* **1970**, *11,* 2741.

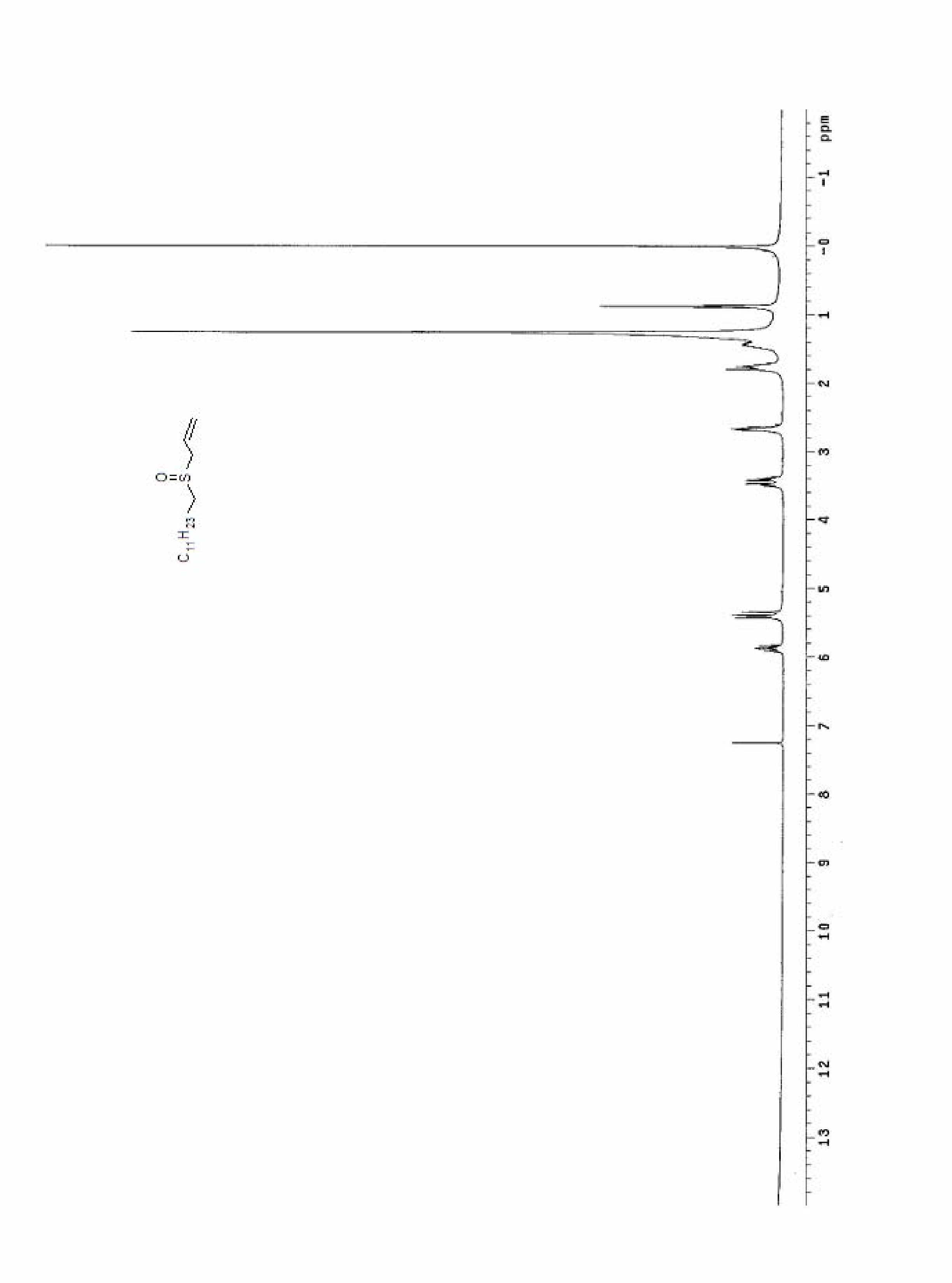
34. Heggs, R. P.; Ganem, B. *J. Am. Chem. Soc.* **1979**, *101,* 2484.

35. Ganem, B.; Heggs, R. P.; Biloski, A. J.; Schwartz, D. R. *Tetrahedron Lett.* **1980**, *21,* 685.

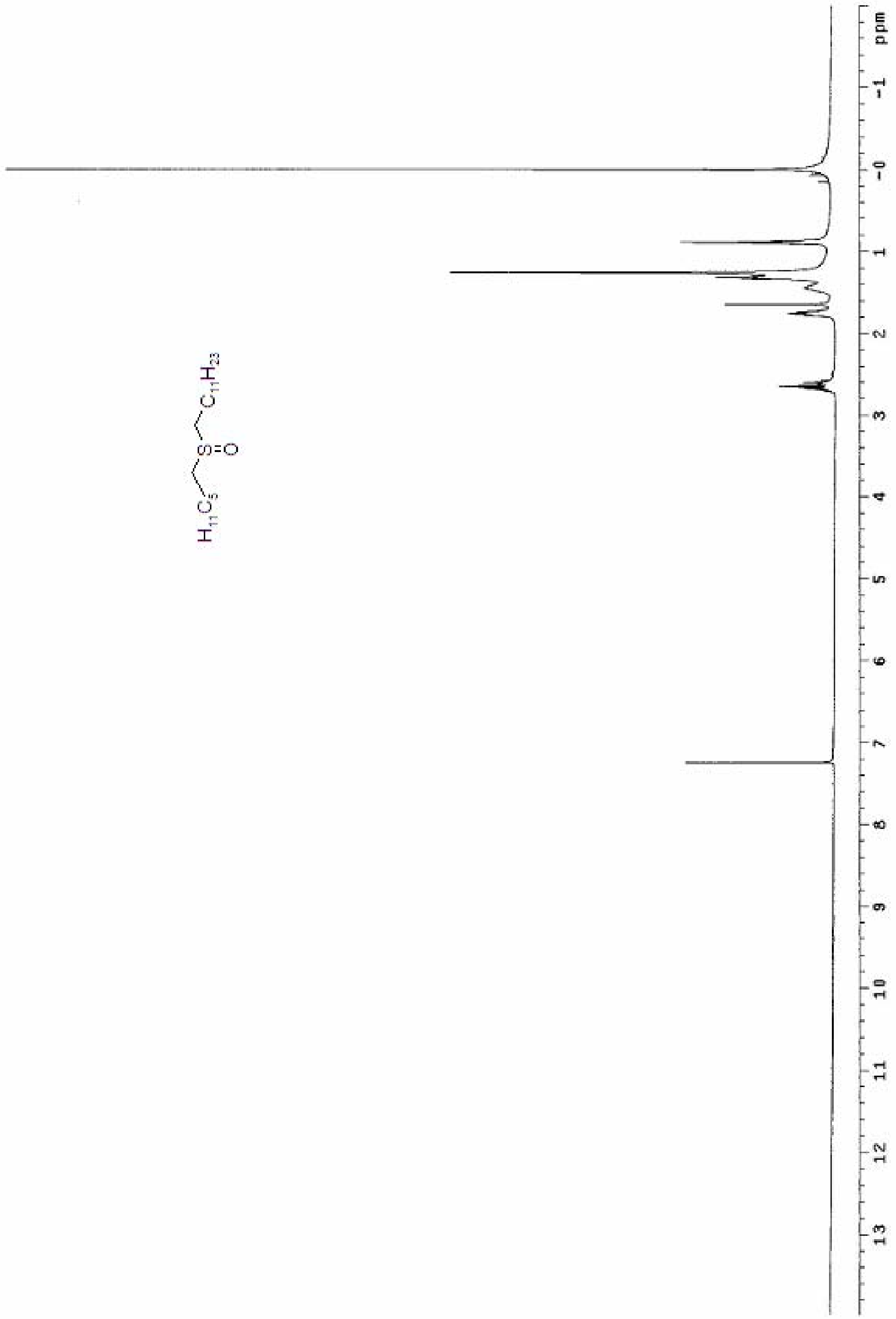
36. Jang, J. M.; Kim, M. H. WO Patent 02074766.

37. Matteucci, M.; Bhalay, G.; Bradley, M. *Org. Lett.* **2003**, *5,* 235.

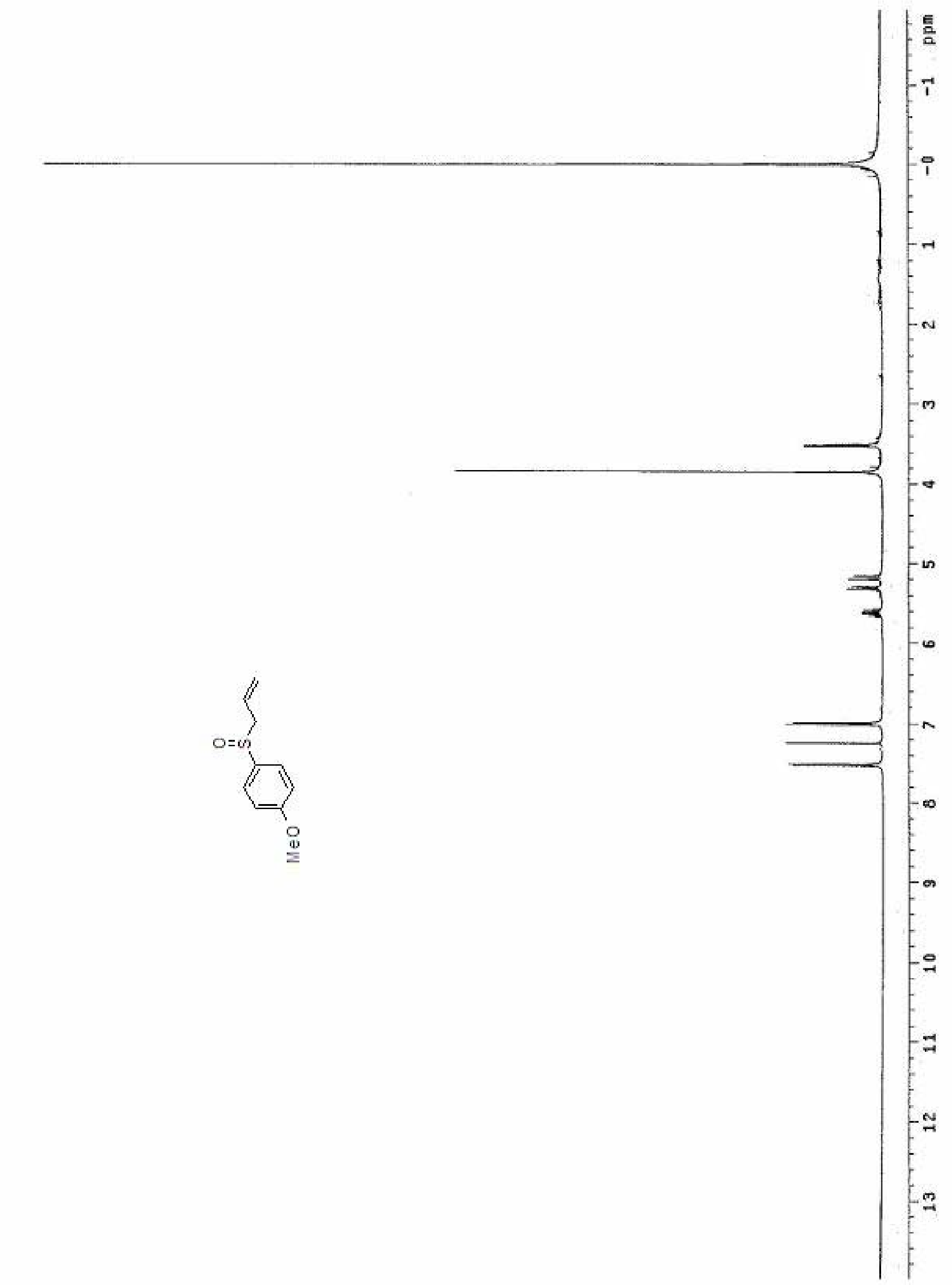
38. Yadollahi. B. *Chem. Lett.* **2003**, *32,* 1066.



$C_{11}H_{23}$
S
O
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13



$H_{11}C_5$–S(=O)–$C_{11}H_{23}$
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13

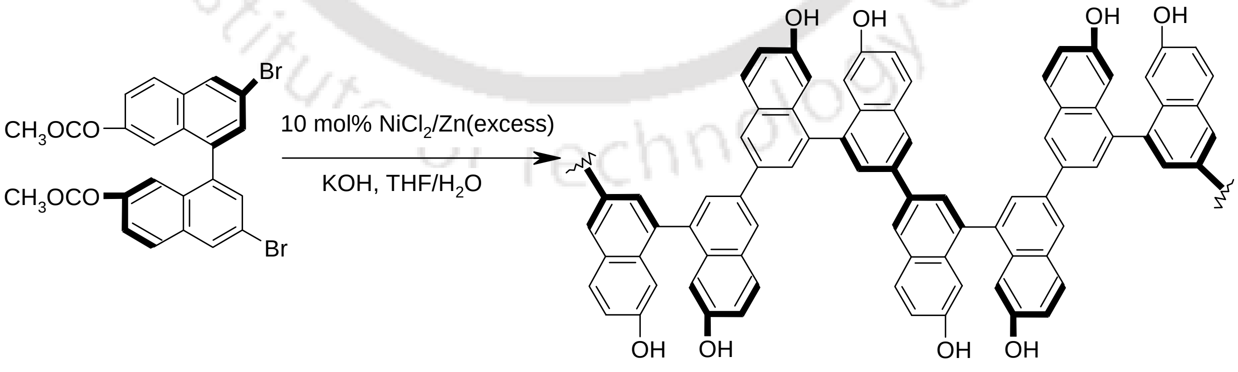

MeO
S
O
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13

Synthesis of Stereoregular Chiral Main Chain Polymer with (1*R*, 2*R*)-Diamidocyclohexane

Owing to their remarkable electronic and photonic properties, which result from the existence of an extended conjugated π-system, conjugated organic polymers are receiving much attention and very diverse applications of these materials have emerged.[1-4] Many efforts are being made to control the bulk properties of these materials by a design strategy based on molecular engineering.[5-9] The tuning of the optical properties of conjugated polymers results from the control and variation of the structure of the chain unit. For example, the use of organometallic coupling reactions allowed a controlled synthesis of various polymers and nano-architectures.[6,7,10] Additionally, the arrangement of the polymeric chain in the solid is also of great importance since interchain interactions and dimensionality also play a determining role in the physical properties of the material[11,12] which are critically dependent on supramolecular features such as molecular packing. High-charge mobility arose from well-defined arrangement of the conjugated segments in supramolecular assemblies.[13] Conversely, solid-state quantum efficiency is related to the degree of long-range order, decreasing with increasing order.[14] The coplanar orientation of conjugated polymer backbones is assumed to lead to the formation of excimer complex which provides a non emissive decay channel for the excited state. A helical polymer, with conformation arises from the main chain chirality[15] may exhibit lower interactions which may help to prevent the polymer chain from packing.[16] Also, chiral conjugated polymers[17] are potentially useful in areas such as photo- or electroluminescence, non-linear optics, enantioselective sensing, molecular recognition or asymmetric catalysis.

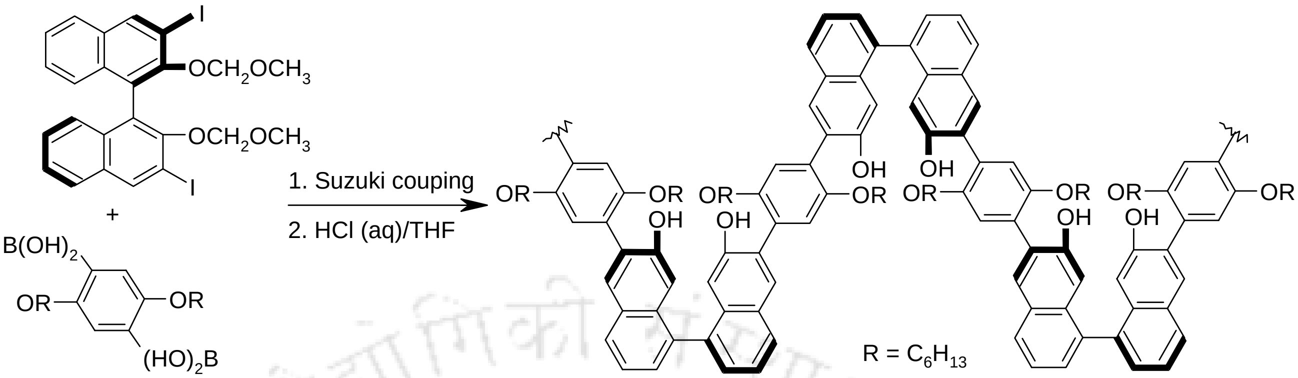
4.1 Binapthyl Based Chiral Main Chain Polymers

A series of chiral main chain polymers with optically active (*R*)-1,1’-binapthyl has been recently reported. The polyhydroxyl groups of these polymers allow the introduction of different Lewis acid metal centres to prepare novel polymeric chiral catalysts (Scheme 1-2).[8] In these polymeric complexes, the catalytic sites are expected to be highly organized along the rigid and sterically regular backbone. This is different from most of the polymer-supported catalysts where flexible and sterically irregular polymers are used. The rigidity and stereoregularity of the chiral conjugated binapthyl polymers makes it possible to systematically adjust the microenvironment of the catalytic sites for the development of enantioselective polymeric catalysts. For an example, up to 92% ee is observed in the reaction of diethylzinc with aldehydes using polymer **2** as a catalyst (Table 1).[18d] The alkoxy chain in the polymer enhances the solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene and THF.



1

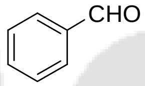
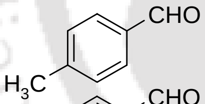
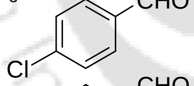
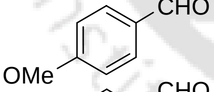
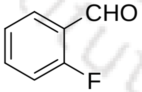
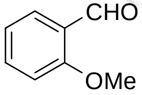
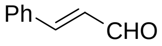
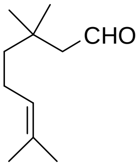
Scheme 1



2

Scheme 2

Table 1: Application of the Polymer **2** in Diethylzinc Addition to Aldehydes

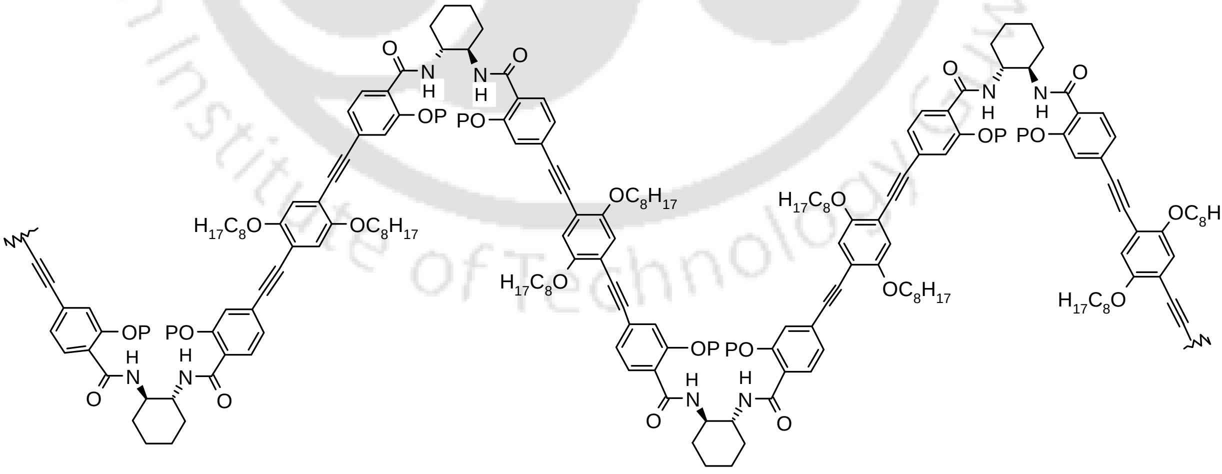
Entry	aldehyde	solvent	isolated yield (%)	ee (%)
1		THF	70	85
2		toluene	89	92
3		toluene	91	92[a]
4		hexane-toluene (2:1)	92	92
5		toluene	90	93[a]
6		toluene	94	93
7		toluene	84	88
8		toluene	86	35
9		toluene	90	59
10		toluene	86	90
11		toluene	67	83

[a] The recycle polymer was used.

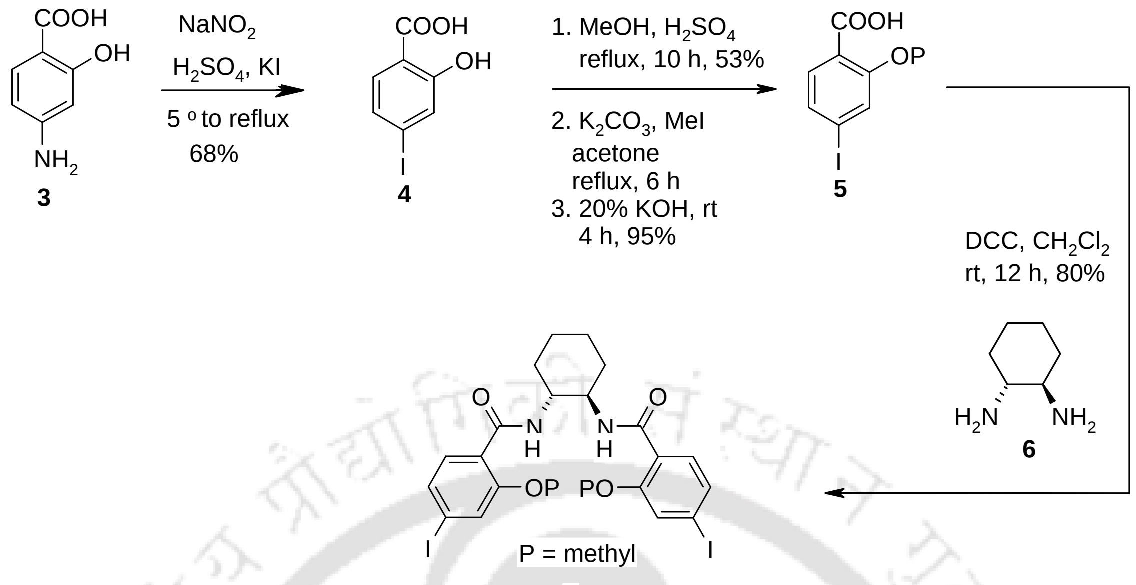
4.2 Present Study

The application of optically active 1,2-diamine derivatives in asymmetric catalysis has attracted very extensive attention. These molecules have demonstrated excellent chiral induction in a number of organic transformations when used either as chiral auxiliary or chiral ligand. Thus, the design and development of stereoregular main chain polymers with optically active 1,2-diamine derivatives will be valuable for enantioseletive catalysis because these materials provide the advantages of simplified product isolation, easy recovery of the chiral catalysts, and potential use for continuous production.

The synthesis of an optically active stereoregular polymer **A** from (1*R*,2*R*)-1,2-diamidocyclohexane **7** and conjugate segment, 1,4-diethynyl-2,5-bis(octyloxy)benzene **12**, in the presence of $Pd(PPh_3)_4$ and CuI has been performed. This polymer has exhibited enhanced enantioselectivity over the corresponding monomer unit when used as chiral ligand for the desymmetrization of cylohexene oxide with 4-methoxybenzyl alcohol.



A

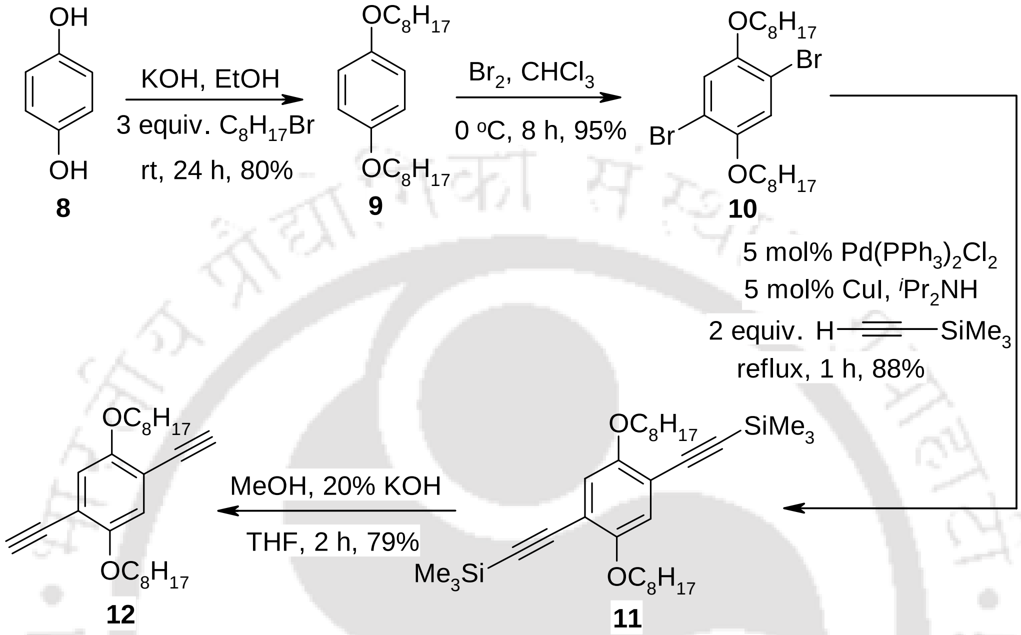


Scheme 3

The synthesis of the chiral unit, (1*R*,2*R*)-1,2-diamido-cyclohexane **7**, was carried out from (1*R*,2*R*)-1,2-diamino-cyclohexane **6** and 4-iodo-2-methoxybenzoic acid **5** in the presence of dicyclohexylcarbodiimide (DCC) in CH_2Cl_2 at ambient temperature (Scheme 3). It is a colorless solid whose specific rotation is $[\alpha]_D^{25}$ -4.0 (c = 0.1, $CHCl_3$). The carboxylic acid **5** could be obtained from 4-amino-2-hydroxybenzoic acid **3** by diazotization using sodium nitrite and potassium iodide followed by protection of the phenolic OH with methyl iodide.

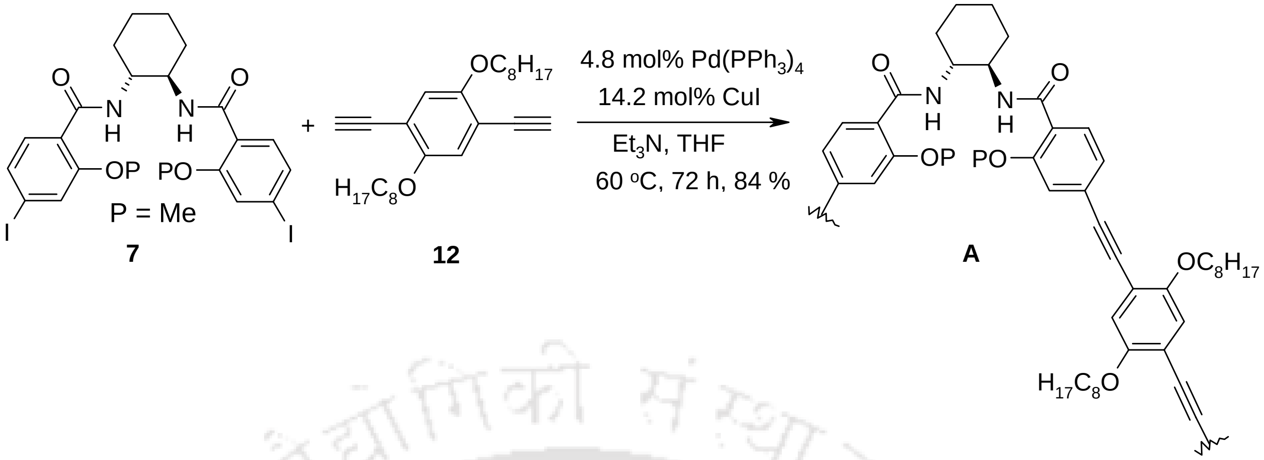
The conjugate segment, 1,4-diethynyl-2,5-bis(octyloxy)-benzene **10**, was prepared from 1,4-hydroquinone **8** (Scheme 2). *o*-Alkylation of **8** with 1-bromooctane in the presence of KOH afforded 1,4-bis(octyloxy)benzene **9** as a colorless solid. It could be transformed to an intermediate **11** *via* bromination using Br_2 followed by coupling with (trimethylsilyl)acetylene in the presence of $Pd(PPh_3)_2Cl_2$ and CuI in diisopropylamine.

Desilylation of the latter with aqueous KOH in methanol yielded **12** as pale yellow needles (Scheme 4).



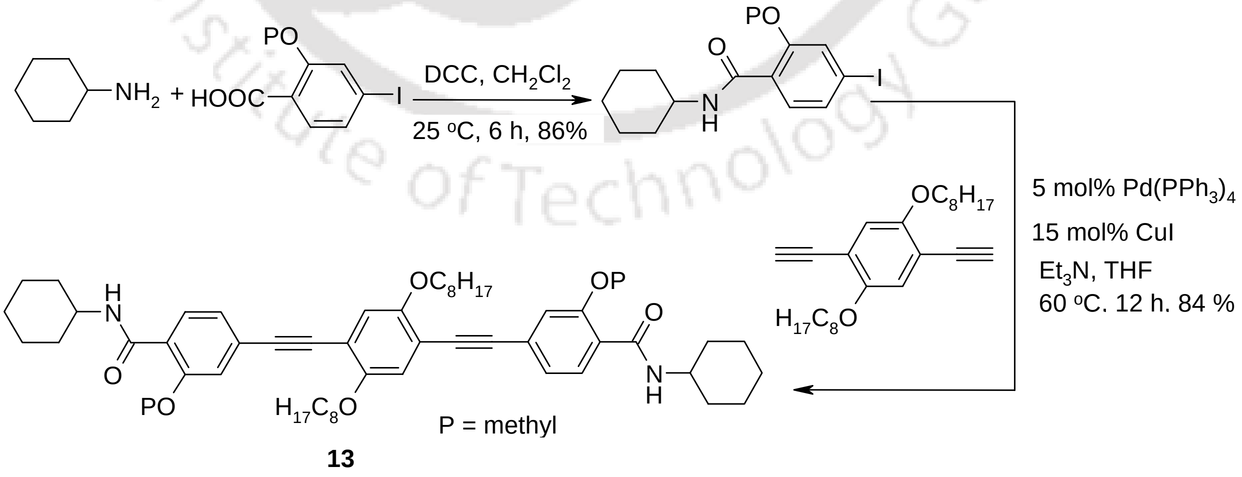
Scheme 4

The synthesis of polymer **A** was carried out using equimolar quantities **7** and **12** in the presence of Pd(PPh$_3$)$_4$ and CuI at 60 ^{o}C in THF and triethylamine mixture (Scheme 5). It was soluble in CH$_2$Cl$_2$, CHCl$_3$, THF, toluene and DMF. The ^{1}H NMR spectrum recorded at 400 MHz and IR data of **A** are consistent with the polymer structure. Its molecular weight is 6977 as measured by MALDI TOF Mass spectrometer, corresponding to an average degree of polymerization of nine. The specific rotation of polymer **A** is $[\alpha]_D^{25}$ -18.0 (c = 0.1, CHCl$_3$) which is higher than the monomer **7**. The purpose of the alkyl chain in the polymer is to enhance its solubility in common organic solvents.



Scheme 5

The stereoregularity of the polymer **A** was revealed by comparing its absorption and emission spectra with the rigid conjugated molecule **13** (Scheme 6). The latter contains the same unsaturated unit as an alternating conjugated substructure separated by the chiral unit which limits the conjugation length by isolating the unsaturated segments. The $CHCl_3$ solution of **A** showed absorption at 317 and 377 nm and emission at 424 and 446 (shoulder) nm. Similarly, the compound **13** in $CHCl_3$ showed absorption at 317 and 380 nm and emission at 423 (shoulder) and 445 nm. These results clearly indicate the similar conjugation properties in **A** and **13**.



Scheme 6

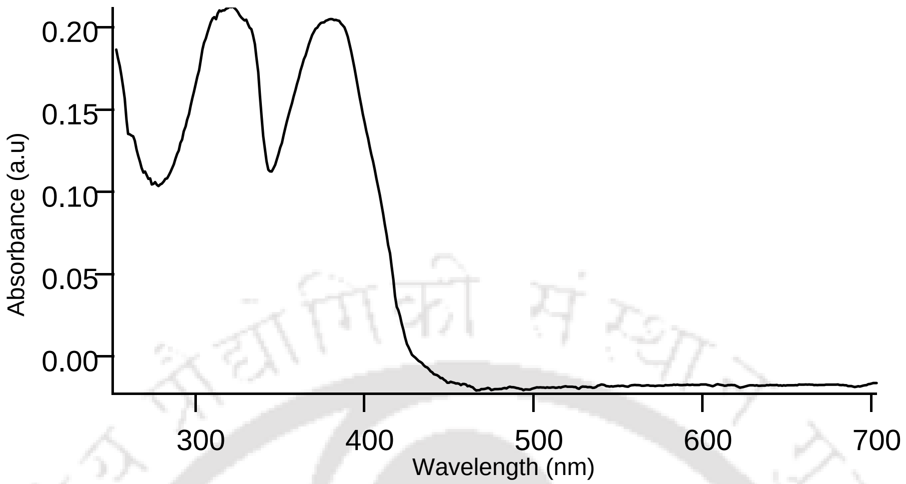


Figure 1: UV/Visible Spectrum of **A**

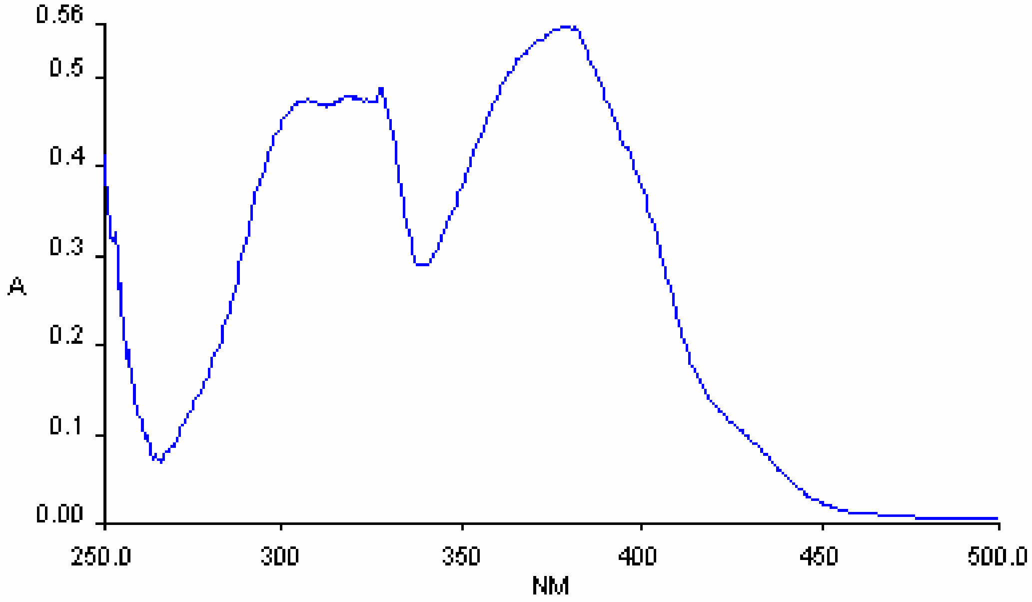


Figure 2: UV-Visible Spectrum of **13**

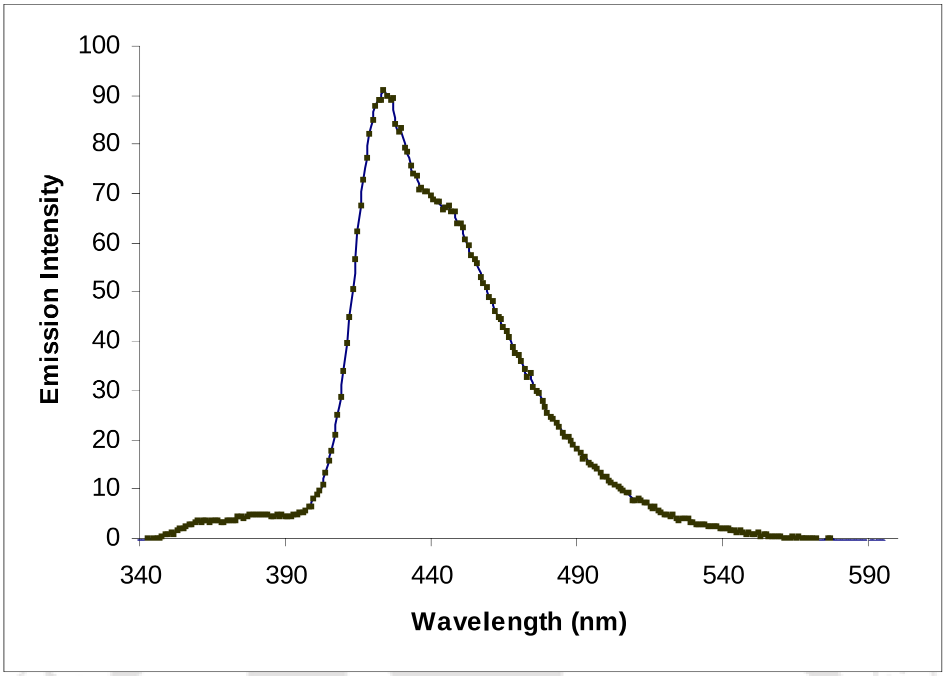


Figure 3: Fluorescence Spectrum of **A**

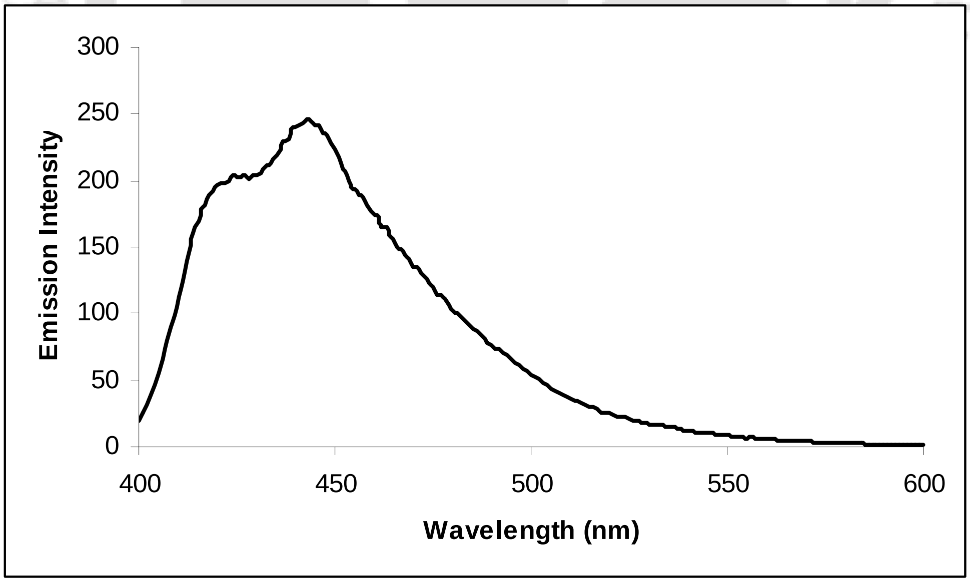
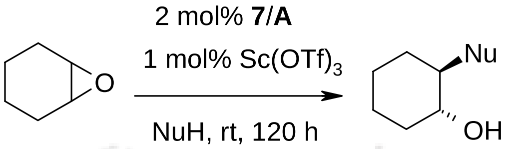
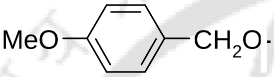
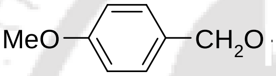
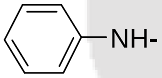


Figure 4: Fluorescence Spectrum of **13**

Table 2: Asymmetric Desymmetrization of Cyclohexene Oxide with Aniline and 4-Methoxybenzyl Alcohol



Ligand	Nu	Yield (%)	ee (%)	Config
7		50	31	R,R
A		34	43	R,R
A		30	20	R,R

The chiral unit **7** and the polymer **A** were then employed as chiral ligands for the asymmetric desymmetrization of cyclohexene oxide with 4-methoxybenzyl alcohol in the presence of Sc(OTf)$_3$ at ambient temperature (Table 2).[10] We were pleased to find that the reactions occurred to provide **14** with 31% and 43% ee, respectively. The enhanced enantioselectivity with the polymer **A** may be due to its main chain chirality. We also investigated the desymmetrization of cyclohexene oxide with aniline affording the corresponding amino alcohol **15** with 20% ee. To study the recyclability of **11**, the reaction mixture of cyclohexene oxide and 4-methoxybenzyl alcohol was treated with methanol and the polymer precipitate was collected by filtration. It was reused, after drying under vacuum, for the desymmetrization of cyclohexene oxide with 4-methoxybenzyl alcohol in the presence of fresh Sc(OTf)$_3$. As above, reaction occurred to provide **14** with same enantioselectivity indicating that the polymer is recyclable without loss of activity.

In summary, chiral main chain polymer **A** with (1*R*,2*R*)-1,2-diamidocyclohexane **7** and conjugate segment **12** has been designed and synthesized. This multifunctional polymer has shown enhanced enantioselectivity in the asymmetric desymmetrization of cyclohexene oxide comparing its monomer unit. It demonstrates that the rigidity and stereoregularity of the polymer can preserve the properties of the monomer. The use of polymer ligand greatly simplifies the recovery of the ligand as well as purification of the product. In addition, the rigid polymer structure prevents possible interference between the monomer catalysts.

4.2.1 Experimental Section

Materials and Methods. All the reactions were performed under nitrogen atmosphere. The solvents were distilled under nitrogen over Na/benzophenone (THF), Na_2CO_3 (acetone) and P_2O_5 (CH_2Cl_2) prior to use. 4-Amino-2-hydroxybenzoic acid, methyl iodide, KI, CuI, DCC, 1-bromooctane, *trans*-(1*R*,2*R*)-1,2-diaminocyclohexane, $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$ were purchased from Aldrich or Fluka. Fluorescence spectra were recorded using Varian Cary Eclipse fluorescence spectrophotometer. FAB-MS spectra obtained from JEOL SX 102/DA-6000 mass spectrometer utilizing *m*-nitrobenzyl alcohol as matrix. MALDI TOF MS was recorded using Micromass TofSpec 2E spectrophotometer using 2,5-dihydroxy benzoic acid as matrix. Melting points were measured using Buchi B-450 apparatus and uncorrected. HPLC analysis was carried out on Waters 2410 instrument with a chiral stationary phase column (Daicel Chiralcel OD column).

2-Hydroxy-4-iodobenzoic acid (4): To a stirred solution of 4-amino-2-hydroxybenzoic acid **3** (81.5 mmol, 12.5 g) in a mixture of water (75 ml) and Conc. H_2SO_4 (15 ml) at 5 ^oC, a cold solution of sodium nitrite (81.5 mmol, 5.6 g) in 15 ml of water was added drop wise. The clear solution was treated with KI (98 mmol, 16.3 g) in 50 ml of 1M H_2SO_4 and heated to reflux for 20 minutes. The resultant solid was filtered and recrystallized in hot water to afford **4** in 68% (14.6 g) yield.

Mp: 228 ^oC.

^1H NMR (DMSO-d_6): δ 3.7 (s, 1H), 7.29 (d, 1H, J = 8.8 Hz), 7.36 (s, 1H), 7.5 (d, 1H, J = 8.4 Hz).

^{13}C NMR (DMSO-d_6): δ 108.46, 118.23, 131.23, 133.67, 136.88, 166.39, 176.76.

IR (KBr): 1250, 1322, 1486, 1534, 1583, 1685, 3268 cm^{-1}.

Anal Calcd for $C_7H_5O_3I$: C, 31.85; H 1.89. Found: C, 31.82; H 1.91.

4-Iodo-2-methoxybenzoic acid (5): 2-Hydroxy-4-iodobenzoic acid **4** (37.88 mmol, 10 g) with a catalytic amount of Conc. H_2SO_4 was stirred under reflux in methanol (100 ml) for 10 h. The solvent was then evaporated under reduced pressure to provide a residue which was dissolved in dichloromethane (100 ml). The solution was successively washed with saturated $NaHCO_3$ (2 x 10 ml), brine (2 x10 ml) and water (2 x10 ml). Drying (Na_2SO_4) and evaporation of the solvent on a rotary evaporator provided a residue which was purified on silica gel column chromatography using ethyl acetate and hexane to give 2-hydroxy-4-iodo-methylbenzoate in 53% (5.58 g) yield.

^{1}H NMR ($CDCl_3$): δ 3.9 (s, 3H), 7.2 (d, 1H, J = 8.4 Hz), 7.4 (s, 1H), 7.5 (d, 1H, J = 8.8 Hz), 10.3 (s, 1H).

The resultant product was further reacted with methyl iodide (24.12 mmol, 4.9 g) and K_2CO_3 (22.1 mmol, 3.5 g) under reflux in acetone (100 ml) for 6 h. The solid was filtered and the filtrate was concentrated on a rotary evaporator to provide a residue which was stirred with aqueous NaOH (30 ml, 20%) for 5 h at ambient temperature. Neutralization with diluted HCl gave **5** as a colorless solid with 95% (4.52 g) yield.

Mp: 181-183 ^{0}C.

^{1}H NMR ($CDCl_3$): δ 1.6 (s, 1H), 4.1 (s, 3H), 7.4 (s, 1H), 7.50 (d, 1H, J = 8.4 Hz), 7.84 (d, 1H, J = 8 Hz).

^{13}C NMR ($CDCl_3$): δ 57.1, 117.3, 121.2, 134.5, 148.0, 157.8, 165.0.

IR (KBr): 1486, 1534, 1583, 1685, 2853, 2935, 2853 cm^{-1}.

Anal Calcd for $C_8H_7O_3I$: C, 34.53; H, 2.50. Found: C, 34.50; H, 2.52.

***trans*-(1*R*,2*R*)-1,2-Bis(4-iodo-2-methoxybenzamido)cyclohexane (7):** To a stirred solution of *trans*-(1*R*,2*R*)-1,2-diaminocyclohexane **6** (2.63 mmol, 301 mg) and DCC (10.5 mmol, 2.16 g) in dichloromethane (60 ml) at ambient temperature, 4-iodo-2-methoxybenzoic acid **3** (5.25 mmol, 1.5 gm) was added. The reaction mixture was allowed to stir for 12 h and the solid was filtered. The filtrate was concentrated under reduced pressure to provide a residue which was passed through a short pad of silica gel using ethyl acetate and hexane as eluent to provide **7** as a colorless solid with 80% (1.33 g) yield.

Mp: 310 ^{0}C.

$[\alpha]^{25}_{D}$ - 4.0 (c = 0.1, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 1.23-2.00 (m, 10H), 3.98 (s, 6H), 7.26 (s, 2H), 7.41 (d, 2H, *J* = 8.0 Hz), 7.61 (s, 2H), 7.86 (d, 2H, *J* = 8.4 Hz).

^{13}C NMR ($CDCl_3$): δ 24.66, 25.71, 32.93, 48.16, 56.31, 98.19, 120.60, 121.63, 130.51, 133.25, 157.03, 163.14.

MS (FAB): m/z 634 (M^+).

IR (KBr): 1445, 1534, 1552, 1629, 2853, 2930, 3068, 3268 cm^{-1}.

Anal Calcd for $C_{22}H_{24}N_2O_4I_2$: C, 41.66; H, 3.81; N, 4.42. Found: C, 41.70; H, 3.79; N, 4.46.

1,4-Bis(octyloxy)benzene (9): 1-Bromooctane (144 mmol, 27.95 g), 1,4-hydroquinone **8** (48.2 mmol, 5.31 g) and KOH (144 mmol, 20 g) were stirred in ethanol (75 ml) for 24 h at ambient temperature. The solvent was then evaporated on a rotary evaporator and the residue was dissolved in ethyl acetate (100 ml). The solution was washed with water (2 x 10 ml), dried (Na_2SO_4) and concentrated on a rotary evaporator to give **9** which was crystallized in ethanol. Yield: 80% (12.9 g).

Mp: 54-55 °C.

^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H, *J* = 3.0 Hz), 1.20-1.57 (m, 20H), 1.70-1.79 (m, 4H), 3.89 (t, 4H, *J* = 3.1 Hz), 6.84 (s, 4H).

^{13}C NMR ($CDCl_3$): δ 11.02, 24.11, 53.03, 112.41, 129.61, 131.25, 140.32, 155.51.

Anal Calcd for $C_{22}H_{38}N_2O_2$: C, 79.46; H, 10.91. Found: C, 79.48; H, 10.88.

1,4-Bis(octyloxy)-2,5-dibromobenzene (10): To a stirred solution of 1,4-bis(octlyoxy)benzene **9** (63 mmol, 21.0 g) in chloroform (400 ml) at 0 °C, chloroform (100 ml) solution of bromine (134 mmol, 10 ml) was added drop wise. After allowing the reaction mixture at ambient temperature for 8 h, cooled to 0 °C and aqueous KOH (1 N) was added until the excess bromine reacted. The organic layer was separated and the aqueous solution was extracted with dichloromethane (2 x 500 ml). The combined organic solution was washed with water (2 x 50 ml), dried (Na_2SO_4) and evaporated in vacuum to provide a residue which was crystallized in ethanol to afford **10** as a colorless solid with 95% (29.1 g) yield.

Mp: 64-65 °C.

^{1}H NMR ($CDCl_3$): δ 0.88 (t, 6H, *J* = 3.0 Hz), 1.20-1.57 (m, 20H), 1.70-1.79 (m, 4H), 3.95 (t, 4H, *J* = 3.1 Hz), 7.08 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 14.12, 22.67, 25.95, 29.13, 29.28, 31.81, 70.31, 111.14, 118.48, 150.09.

Anal Calcd for $C_{22}H_{36}O_2Br_2$: C, 53.67; H, 7.37. Found: C, 53.60; H, 7.26.

1,4-Bis((trimethylsilyl)ethynyl)-2,5-bis(octyloxy)benzene (11): To a stirred solution of 1,4-bis(octyloxy)-2,5-dibromobenzene **10** (13.0 g, 26.4 mmol), $PdCl_2(PPh_3)_2$ (0.925 g, 1.33 mmol) and CuI (0.252 g, 1.32 mmol) in diisopropylamine (50 ml) at ambient temperature, (trimethylsilyl)acetylene (5.5 g, 56.0 mmol) was added. The reaction mixture was then allowed to stir at reflux for 1 h and toluene (50 ml) was added. The resultant solid was filtered and the filtrate was passed through a short pad of silica gel using toluene as eluent. Removal of the solvent on a rotary evaporator gave yellow oil which was crystallized upon standing. Recrystallization from ethanol (twice) yielded **11** as white needles in 88% (12.3 g) yield.

Mp: 65-66 °C.

^{1}H NMR (CDCl$_3$): δ 0.22 (s, 18H), 0.88 (t, 6H, *J* = 3.0 Hz), 1.3-1.82 (m, 24H), 3.93 (t, 4H, *J* = 3.1 Hz), 6.89 (s, 2H).

^{13}C NMR (CDCl$_3$): δ 0.44, 14.50, 23.10, 26.45, 29.71, 29.77, 29.81, 32.26, 69.79, 100.30, 101.32, 124.18, 117.44, 154.14.

Anal Calcd for $C_{32}H_{54}O_2Si_2$: C, 72.94; H, 10.33. Found: C, 72.78; H, 10.32.

1,4-Diethynyl-2,5-bis(octyloxy)benzene (12): Methanol (220 ml) and aqueous KOH (15 mL, 20%) were added to a stirred solution of 1,4-bis((trimethylsilyl)ethynyl)-2,5-bis(octyloxy)-benzene **11** (13.1 g, 24.9 mmol) in THF (440 ml) at ambient temperature. After stirring the reaction mixture for 2 h, the solid was filtered and the filtrate was concentrated on a rotary evaporator to provide a residue which was crystallized from hexane to give **12** as pale yellow crystals with 79% (7.47 g) yield. Mp: 64 °C.

^{1}H NMR (CDCl$_3$): δ 0.91 (t, 6H, *J* = 2.0 Hz) 1.20-1.57 (m, 20H), 1.70-1.79 (m, 4H), 3.3 (s, 2H), 3.97 (t, 4H, *J* = 3.0 Hz), 6.95 (s, 2H).

^{13}C NMR (CDCl$_3$): δ 14.10, 22.66, 25.90, 29.12, 29.22, 31.80, 69.67, 79.78, 82.39, 113.26, 117.75, 153.98.

Anal Calcd for $C_{26}H_{38}O_2$: C, 81.62; H, 10.01. Found: C, 81.78; H, 9.96.

Polymer A: To a stirred solution of **7** (0.78 mmol, 500 mg), Pd(PPh$_3$)$_4$ (0.04 mmol, 42 mg), CuI (0.11 mmol, 21.2 mg) and triethylamine (4 ml) in THF (20ml) at ambient temperature, 1,4-diethynyl-2,5-bis(octlyoxy)benzene **12** (0.78 mmol, 298 mg) was added. The reaction mixture was then heated at 60 °C for 3 days and the solid was filtered. The filtrate was concentrated on a rotary evaporator to provide a residue which was dissolved in chloroform (25 ml). Addition of methanol (10 ml) to the solution provided **A** as a precipitate which was collected by filtration as yellow powder with 84% (0.745 g) yield.

MALDI TOF MS: 6977.

^{1}H NMR ($CDCl_3$): δ 2.01-0.84 (m, 40H), 3.97-4.00 (m, 10H), 7.0 (s, 2H), 7.1 (s, 2H), 7.24 (s, 2H), 7.75 (d, 2H, *J* = 7.6 Hz), 8.16 (d, 2H, *J* = 8.0 Hz).

^{13}C NMR ($CDCl_3$): δ 14.20, 22.74, 24.74, 25.82, 26.15, 29.39, 31.89, 33.05, 48.19, 56.08, 69.61, 87.84, 94.25, 113.75, 114.11, 121.82, 124.53, 127.2, 132.14, 153.55, 156.80, 163.30.

IR (KBr): 1445, 1534, 1552, 1629, 2853, 2930, 3329 cm^{-1}.

UV/Vis ($CHCl_3$): λ_{max} 317, 377 nm.

Anal Calcd for $C_{432}H_{541}N_{18}O_{54}I$: C, 74.37; H, 7.81; N, 3.61. Found: C, 73.92; H, 8.00; N, 3.41.

$[\alpha]^{25}_{D}$ -19.0 (c = 0.1, $CHCl_3$).

Compound (13): To a stirred solution of amide (0.35 mmol, 120 mg), $Pd(PPh_3)_4$ (0.009 mmol, 10 mg), CuI (0.027 mmol, 5 mg) and triethylamine (1 ml) in THF (5 ml), 1,4-bis(octlyoxy)-2,5-di(ethynyl) benzene **12** (0.18 mmol, 67mg) was added. After heating the reaction mixture at 65 °C for 12 h, the solvent was evaporated and the residue was dissolved in chloroform (15 ml). The solution was washed with water (2 x 5 ml), dried (Na_2SO_4) and evaporated on a rotary evaporator to provide a residue which was purified on silica gel column chromatography using ethyl acetate and hexane as eluent to provide **13** with 84% (126 mg) yield.

^{1}H NMR ($CDCl_3$): δ 0.84-2.12 (m, 52H), 3.8-4.1 (m, 10H), 6.90- 8.20 (m, 10H).

IR (KBr): 1445, 1534, 1552, 1631, 2853, 2930, 3068, 3270 cm^{-1}.

UV/Vis ($CHCl_3$): λ_{max} 317, 380.

Anal Calcd for $C_{52}H_{72}O_6N_2$: C, 76.08; H, 8.88; N, 3.41. Found: C, 76.12; H, 8.92; N, 3.44.

(1*R*,2*R*)-2-(4-Methoxybenzyloxy)-cyclohexanol (14): To a stirred solution of $Sc(OTf)_3$ (19.6 mg, 0.04 mmol) and polymer **A** (69.8 mg, 0.01 mmol, based on the polymer repeating unit) in dichloromethane (5 ml) at ambient temperature for 2 h, cyclohexene oxide (98 mg, 1.00 mmol) and 4-methoxybenzyl alcohol (276 mg, 2.00 mmol) were added. After allowing the reaction mixture for 120 h, methanol was added and the precipitate was collected by filtration. The filtrate was concentrated on a rotary evaporator to provide a residue which was purified on silica gel column chromatography using ether-hexane as eluent to give **14** as a colorless liquid in 34% (81 mg) yield.

^{1}H NMR ($CDCl_3$): δ 1.19-1.33 (m, 4H), 1.69-1.77 (m, 2H), 2.01-2.04 (m, 1H), 2.13-2.17 (m, 1H), 2.92 (s, 1H), 3.16-3.22 (m, 1H), 3.48-3.51 (m, 1H), 3.82 (s, 3H), 4.43 (d, 1H, *J* = 11.1 Hz), 4.65 (d, 1H, *J* = 11.1 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 7.25 (d, 2H, *J* = 8.6 Hz).

^{13}C NMR ($CDCl_3$): δ 23.9, 24.2, 29.2, 32.0, 55.2, 70.4, 73.7, 83.1, 113.8, 129.3, 130.7, 159.2.

IR (neat): 1022, 1079, 1299, 1511, 1610, 2861, 2998, 3438 cm^{-1}.

Anal Calcd for $C_{14}H_{20}O_3$: C, 71.21; H, 8.54. Found: C, 71.26; H, 8.50.

$[\alpha]^{25}_{D}$ = -19.9° (c = 1.6, CH_2Cl_2) for 43% ee; chiral GC analysis 15 m (2,6-Me-3-pentyl-γ-CD), 135° (50% in OV 1701).

(1*R*,2*R*)-2-(Phenylamino)-1-cyclohexanol (15): To a stirred solution of $Sc(OTf)_3$ (19.6 mg, 0.04 mmol) and polymer **A** (69.8 mg, 0.01 mmol, based on the polymer repeating unit) in dichloromethane (5 ml) at ambient temperature for 2 h, cyclohexene oxide (98 mg, 1.00 mmol) and aniline (93 mg, 1.00 mmol) were added. After allowing the reaction mixture for 120 h, the product **15** was isolated as described above with 30% (57 mg) yield.

Mp: 57 °C.

^1H NMR ($CDCl_3$): δ 1.07-1.12 (m, 1H), 1.29-1.48 (m, 3H), 1.74-1.85(m, 2H), 2.14-2.17 (m, 2H), 3.13-3.20 (m, 3H), 3.34-3.42 (m, 1H), 6.73-6.83 (m, 3H), 7.19-7.29 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 24.8, 25.4, 32.0, 33.7, 60.5, 74.9, 114.8, 129.9, 148.52.

IR (KBr): 748, 1069, 1450, 1498, 1601, 2856, 2931, 3049, 3390 cm^{-1}.

Anal Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.49; H, 8.83; N, 7.40.

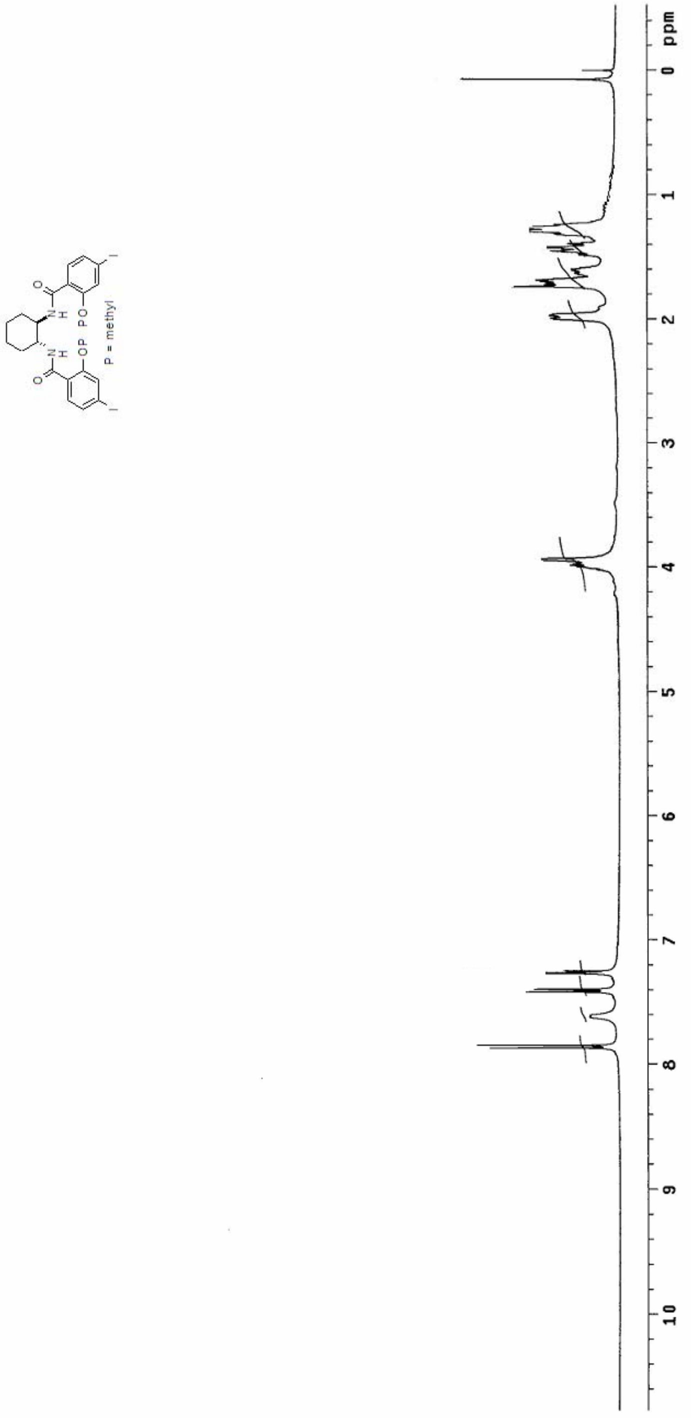
$[\alpha]^{25}_{D}$ = -13.96 (c = 0.53, CH_2Cl_2) for 20% ee; chiralcel OD, (n-hexane: *i*-PrOH = 85:15, 1 mL/min).

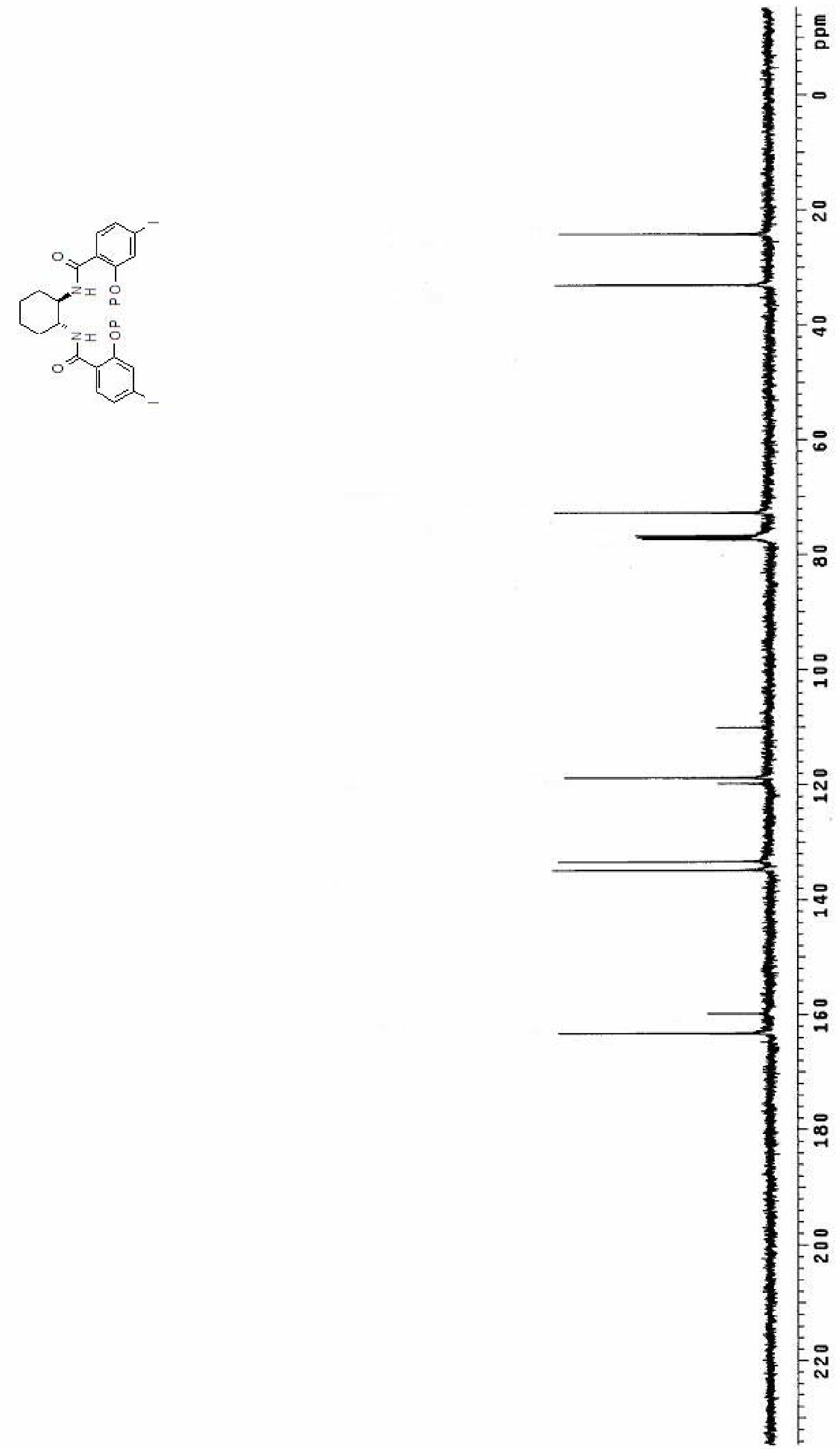
4.3 References

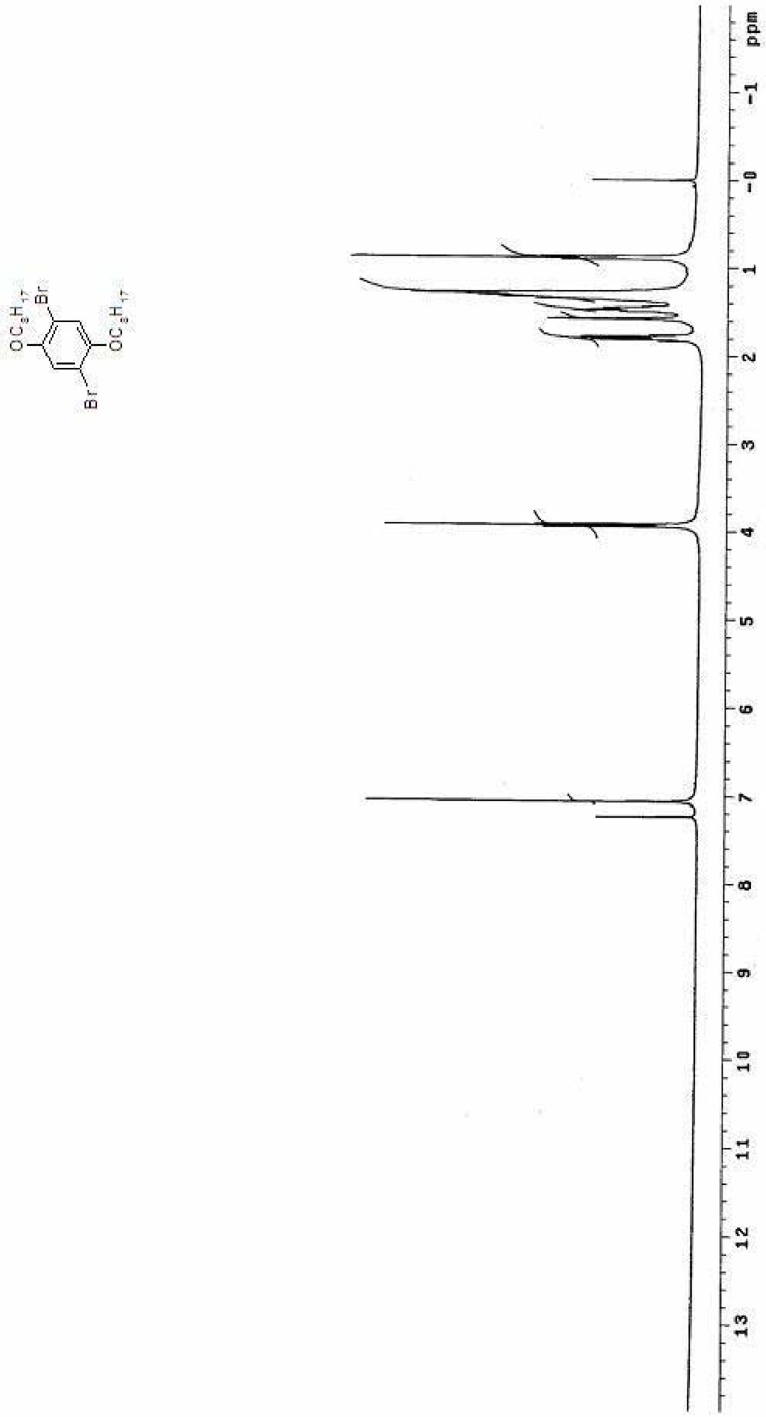
1. Skotheim, T. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.
2. Nalwa, H. S. *Handbook of Organic Conductive Molecules and Polymers*; Wiley & Sons: New York, 1996.

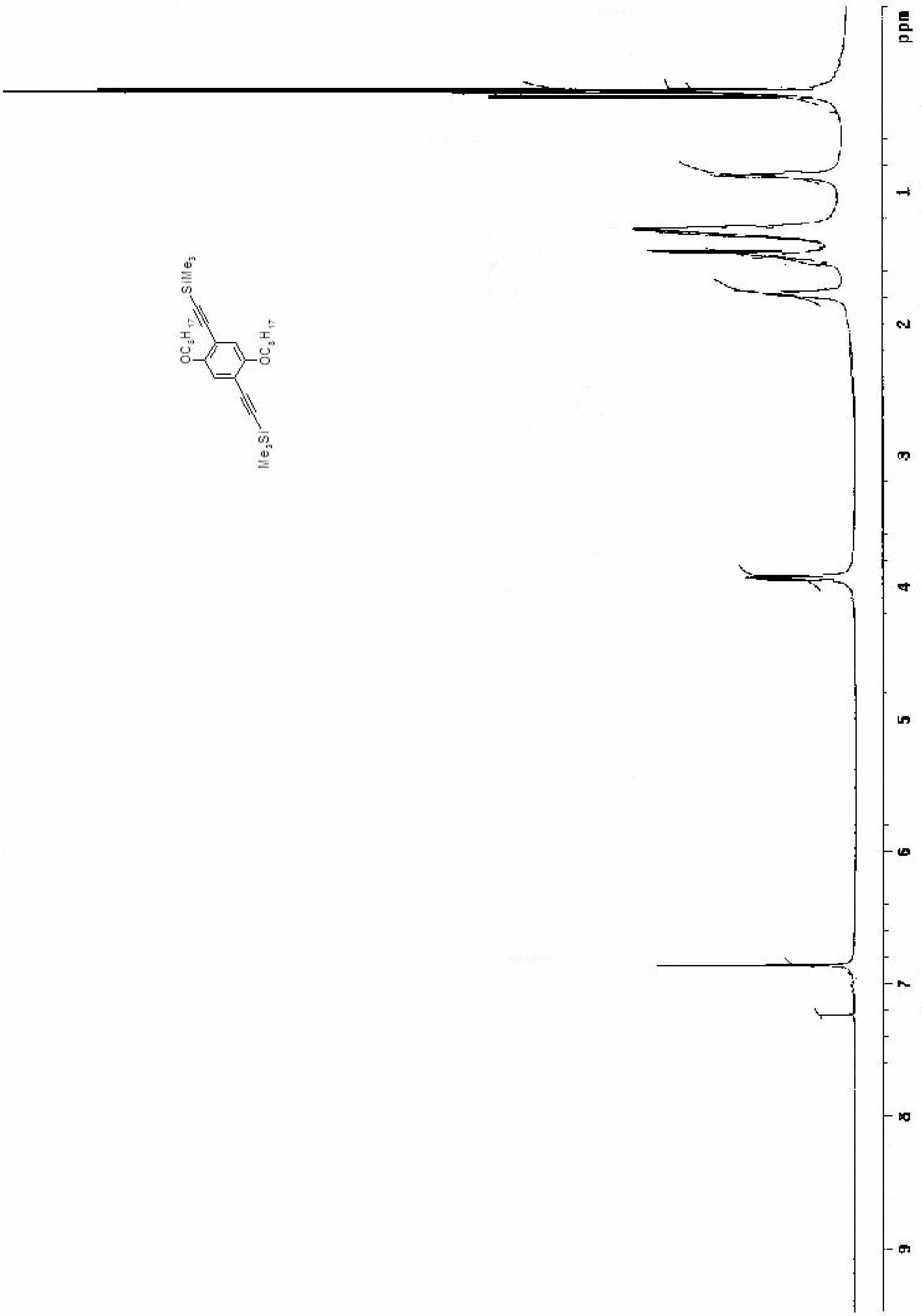
3. Skotheim, T.; Reynolds, J.; Elsenbaumer, R. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1998.
4. Miyata, S.; Nalwa, H. S. In *Organic Electroluminescent Material and Devices*; Gordon and Breach: Amsterdam, 1997.
5. Roncali, J. *Chem. Rev.* **1992**, *92,* 711.
6. Tour, J. M. *Chem. Rev.* **1996**, *96,* 537.
7. McCullough, R. D. *Adv. Mater.* **1998**, *10,* 93.
8. Schopf, G.; Kossmehl, G. A. *Adv. Polym. Sci.* **1997**, *129,* 1.
9. Roncali, J. *Chem. Rev.* **1997**, *97,* 173.
10. Le`re-Porte, J.-P.; Moreau, J. J. E.; Torreilles, C. *Eur. J. Org. Chem.* **2001**, 1249.
11. Lorwer, R. S.; McCullough, R. D. *Chem. Mater.* **2000**, *12,* 3214.
12. Le`re-Porte, J.-P.; Moreau, J. J. E.; Serein-Spirau, F.; Torreilles, C.; Righi, A.; Sauvajol, J.-L.; Brunet, M. *J. Mater. Chem.* **2000**, *10,* 927.
13. Schoonbeek, F. S.; Van Esch, J. H.; Wegewijs, B.; Rep, D. B. A.; De Haas, M. P.; Klapwijk, T. M.; Kellog, R. M.; Feringa, B. L. *Angew. Chem., Int. Ed.* **1999**, *38,* 1393.
14. Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29,* 5157.
15. Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28,* 21.
16. Zheng, L.; Urian, R. C.; Liu, Y.; Jen, A. K.-Y.; Pu, L. *Chem. Mater.* **2000**, *12,* 13.
17. (a) Pu, L. *Acta Polym.* **1997**, *48,* 116; (b) Pu, L. *Chem. Rev.* **1998**, *98,* 2405.
18. (a) Hu, Q.-S.; Zheng, X.-F.; Pu, L. *J. Org. Chem.* **1996**, *61,* 5200; (b) Ma, L.; Hu, Q.-S.; Vitharana, D.; Wu, C.; Kwan, C. M. S.; Pu, L. *Macromolecules* **1997**, *30,* 202; (c) Hu, Q.-S.; Huang, W-S.; Vitharana, D.; Zheng, X.-Fan.; Pu, L. *J. Am.*

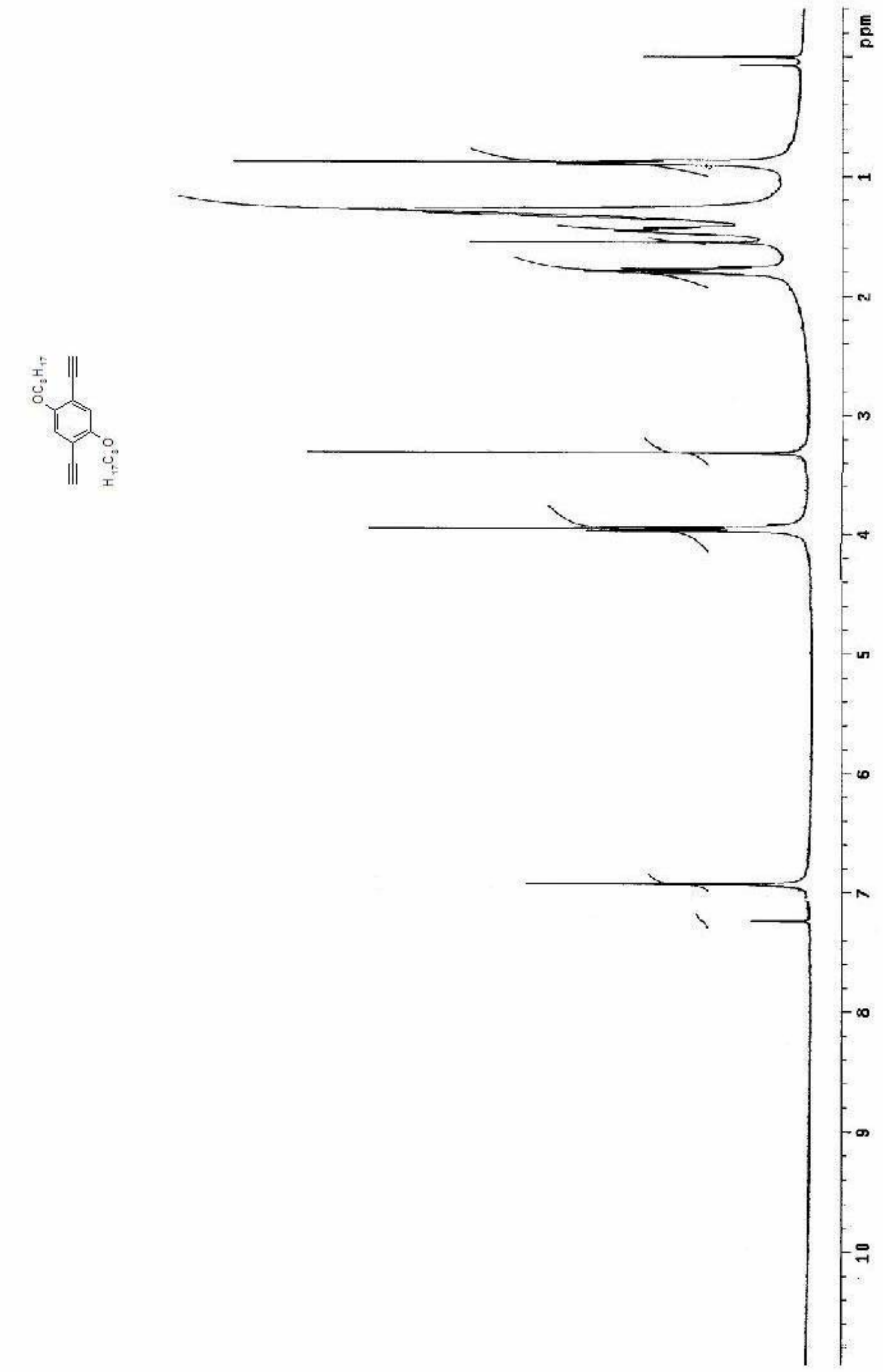
Chem. Soc. **1997**, *119,* 12454; (d) Huang, W-S.; Hu, Q.-S.; Zheng, X.-F.; Anderson, J.; Pu, L. *J. Am. Chem. Soc.* **1997**, *119,* 4313.

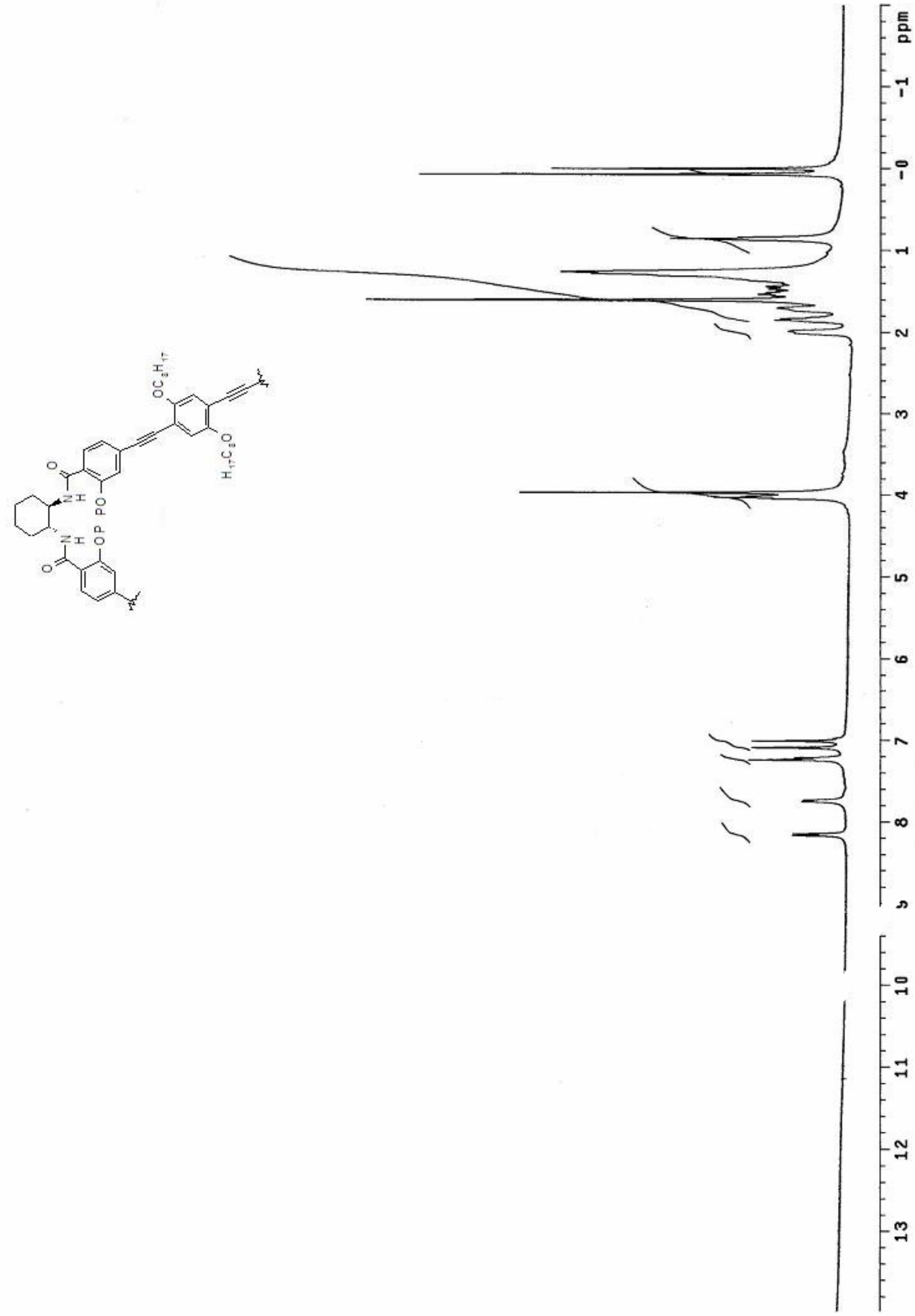

P = methyl
O
N H
OP
PO
I
ppm
0
1
2
3
4
5
6
7
8
9
10

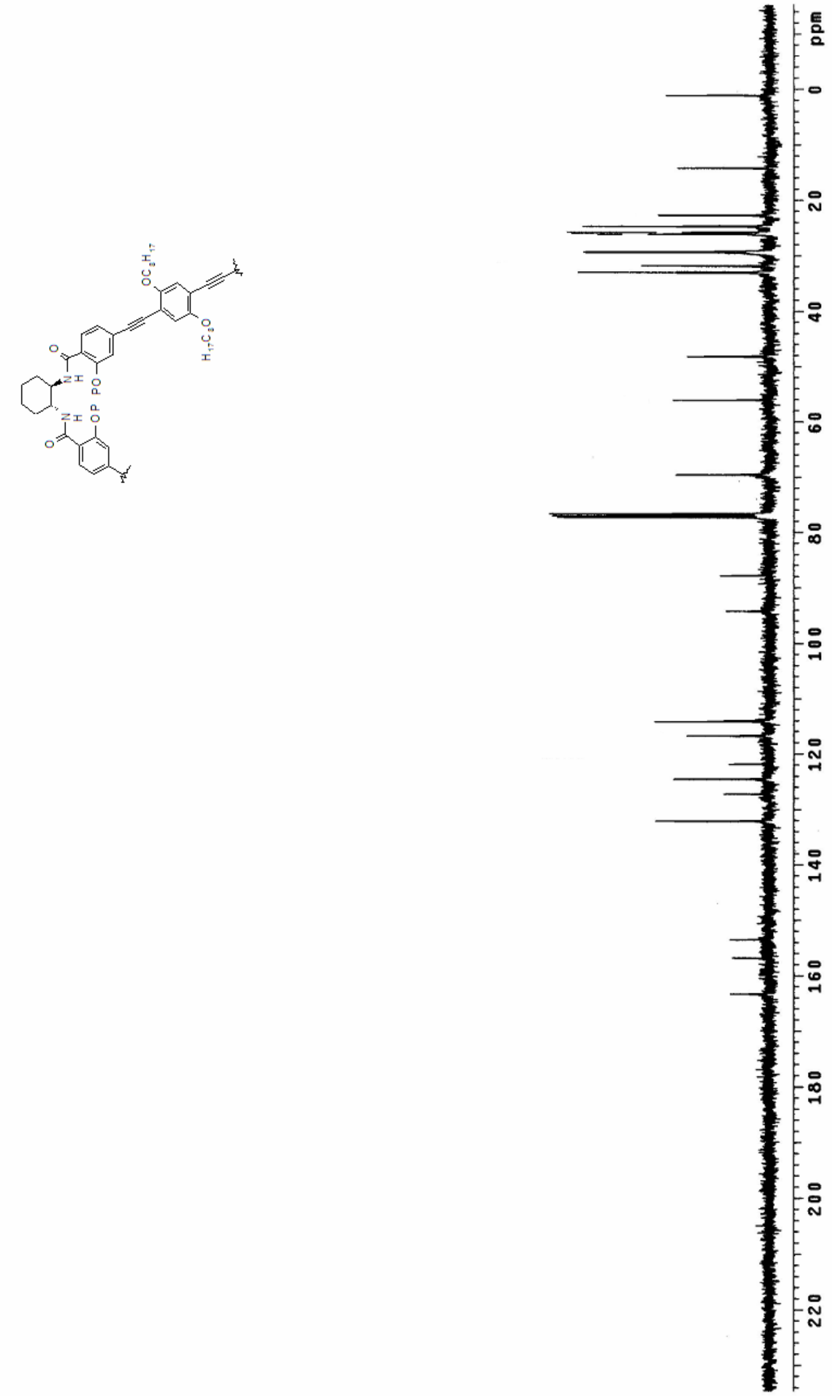

ppm
0
20
40
60
80
100
120
140
160
180
200
220
O
N H
PO
OP
I

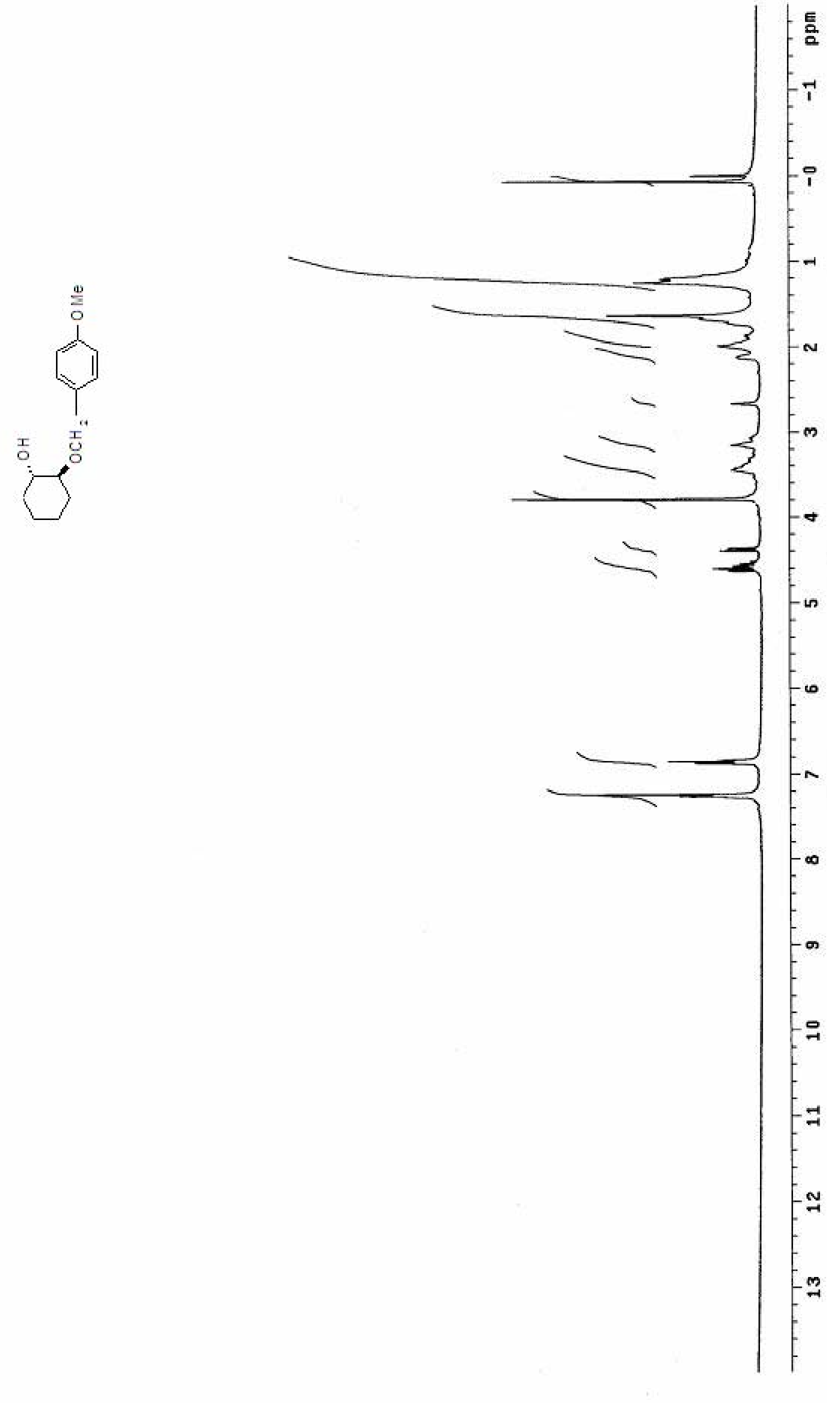

OC8H17
Br
Br
OC8H17
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13

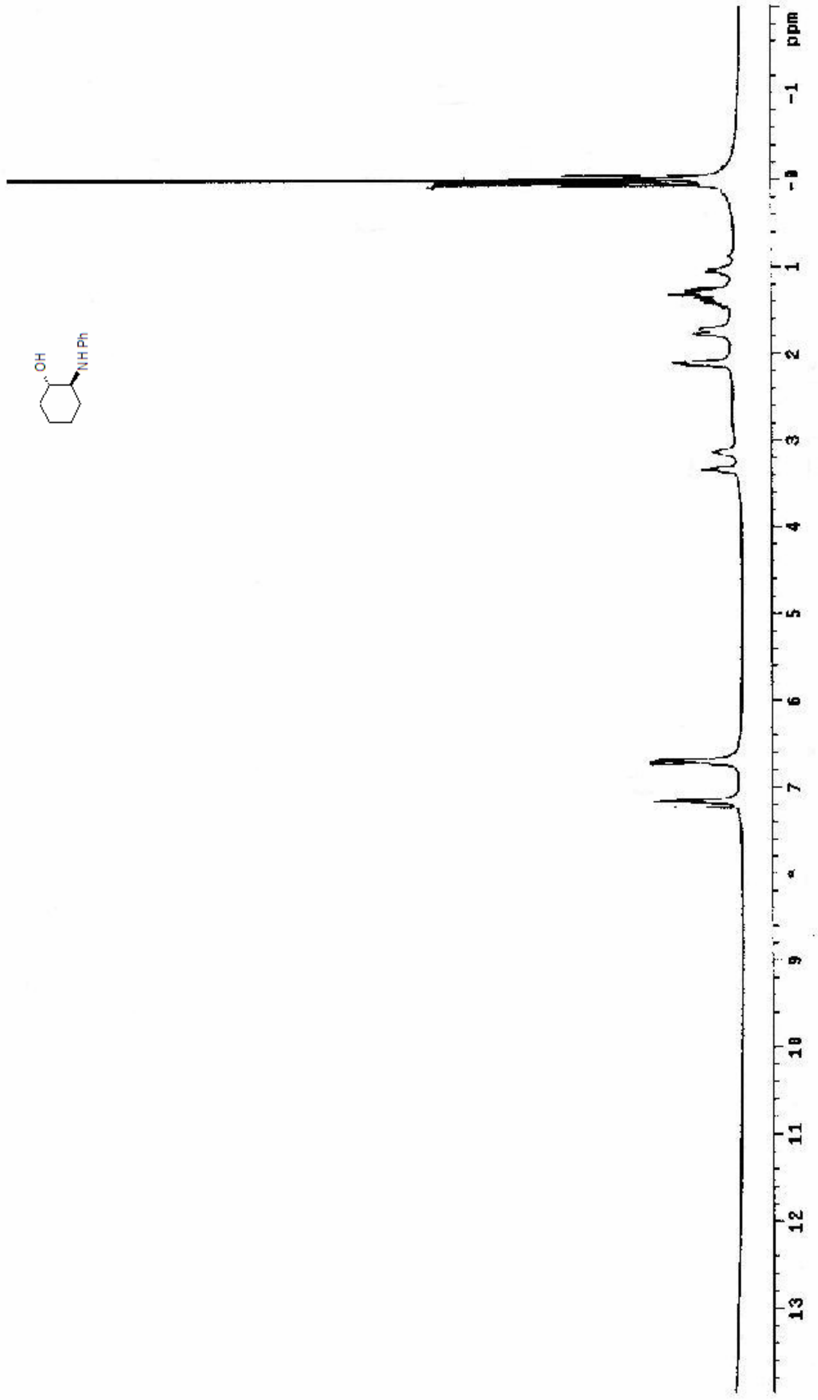

OC8H17
SiMe3
OC8H17
Me3Si
ppm
1
2
3
4
5
6
7
8
9


OC8H17
H17C8O
ppm
1
2
3
4
5
6
7
8
9
10


ppm
-1
-0
1
2
3
4
5
6
7
8
9
10
11
12
13
OC8H17
H17C8O
O
N H
OP
PO


ppm
0
20
40
60
80
100
120
140
160
180
200
220
OC8H17
H17C8O
OP
PO
NH
O


OH
OCH2
OMe
ppm
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13


OH
NH Ph
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

List of Publications

1. Copper(II) Catalyzed Oxidation of Alcohols to Carbonyl compounds with Hydrogen Peroxide.
   Velusamy, S.; Punniyamurthy, T. *Eur. J. Org. Chem.* **2003**, 3913.

2. Copper(II) Catalyzed Oxidation of Alkylbenzenes and Cyclohexane with Hydrogen Peroxide.
   Velusamy, S.; Punniyamurthy, T. *Tetrahedron Lett.* **2003**, *44*, 8955.

3. Cobalt(II) Catalyzed Direct Tosylation of Alcohols with *p*-TsOH.
   Velusamy, S.; Kumar, J. S. K.; Punniyamurthy, T. *Tetrahedron Lett.* **2004**, *44*, 203.

4. Novel Vanadium Catalyzed Oxidation of Alcohols to Aldehydes and Ketones with Atmospheric Oxygen.
   Velusamy, S.; Punniyamurthy, T. *Org. Lett.* **2004**, *6*, 217.

5. Cobalt (II) Catalyzed Chemoselective Synthesis of Acetals from Aldehydes.
   Velusamy, S.; Punniyamurthy, T. *Tetrahedron Lett.* **2004**, *44*, 3561.

6. Novel Polyaniline Supported Molybdenum Catalyzed Aerobic Oxidation of Alcohols to Carbonyl Compounds.
   Velusamy, S.; Ahamed, M.; Punniyamurthy, T. *Org. Lett.* **2004**, *6*, 4821.

7. Copper(II)- TEMPO Catalyzed Selective Oxidation of Sulphides to Sulphoxides with Aqueous Hydrogen Peroxide.
   Velusamy, S.; Kumar, A. V.; Saini, R.; Punniyamurthy, T. *Tetrahedron Lett.* **2005**, *46*, 3819.

8. Cobalt(II) Catalyzed Direct Acetylation of Alcohols with Acetic Acid.

Velusamy, S.; borpuzari, S.; Punniyamurthy, T. *Tetrahedron* **2005**, *61*, 2011.

9. Recent Advances in Transition Metal Catalyzed Oxidation of Organic Substates with Molecular Oxygen (Thematic Issue in Inorganic and Bioinorganic Mechanisms).
   Punniyamurthy, T.; Velusamy, S.; Iqbal, J. *Chem. Rev.* **2005**, *105*, 2329.

10. Copper(II) Catalyzed Selective Oxidation of Primary Alcohols to Aldehydes with Atmospheric Oxygen.
    Velusamy, S.; Srinivasan, A. Punniyamurthy, T. *Tetrahedron Lett.* **2006**, *47,* 923.

11. Silica Supported Vanadium(IV) Catalyzed Tetrahydropyranylation of Alcohols.
    Velusamy, S.; Nath, P.; Punniyamurthy, T. *Synthesis* **2006** (Communicated).

12. Palladium Catalyzed Stereoregular Chiral Co-Polymer with (1 *R*, 2 *R*)- 1,2-Diamidocyclohexane and 1,4-Diethynyl-2,5-dioctyloxybenzene: Application to Asymmetric Desymmetrization of meso-Epoxides.
    Velusamy, S.; Punniyamurthy, T. *Org. Lett.* **2006** (Communicated).