# SYNTHESIS AND CATALYTIC APPLICATIONS OF METALLOPORPHYRINS

**A DISSERTATION**

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*requirements for the award of the degree*
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*in*
ADVANCED CHEMICAL ANALYSIS

*By*

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## CANDITATE'S DECLARATION

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I hereby certify that the progress report presented in the dissertation in the entitled "**Synthesis and catalytic applications of metalloporphyrins**" for the award of the degree of Master of technology submitted to the Indian institute of technology roorkee is an authentic record of my won work carried out by me during the period from July 2011 to June 2012 under the supervision of Dr. M Sankar, Assistant Professor, Department of chemistry, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other digree of this or any other institute.

Richa yadav

Place: Roorkee **(RICHA YADAV)**

Date:15th June 2012

This is to certify that the above statement made by the candidate is correct to the best our knowledge.

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# ABSTRACT

Porphyrins are having wide applications such as in catalysis, molecular sensors, photodynamic therapy and dye-sensitized solar cells (DSSC). Due to above-metioned applications, the porphyrin syntheses and their functionalization are quite important. Herein we have synthesized *meso*-tetraphenylporphyrinato oxovanadium [VO(IV)TPP] and *meso*-tetraphenylporphyrinato manganese(III) chloride [Mn(III)TPPCl]. Also we have utilised these porphyrins as catalyst for the oxidation of cyclohexene. We have done a systematic studies by varying reaction parameters (*e.g.*amount of oxidant, catalyst and solvent of the reaction mixture). We observed that cyclohexene requires least amount of vanadyl porphyrin catalyst for the reaction. Furhter we noticed that the increasing amount of $H_2O_2$ favoured the oxidation of cyclohexene. On the other hand, Mn(III)Cl porphyrin was found to be less effective for same reaction. These results suggest that vanadyl porphyrin as an efficient robust catalyst than that of Mn(III)Cl porphyrin for the oxidation of cyclohexene.

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Date: 15th June 2012

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# CHAPTER 1
# INTRODUCTION

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# INTRODUCTION

## 1. A. TETRAPYRROLE PIGMENTS IN NATURE:

Porphyrinoids are the class of tetrapyrrole pigments widely occur in nature. They are highly π-conjugated and in some cases, conjugation is broken at one or more positions resulting in interesting structures with varying degree of nonplanarity of the macrocycle. The four-pyrrole groups are joined together by four methine carbons to give cyclic tetrapyrrole ring system.

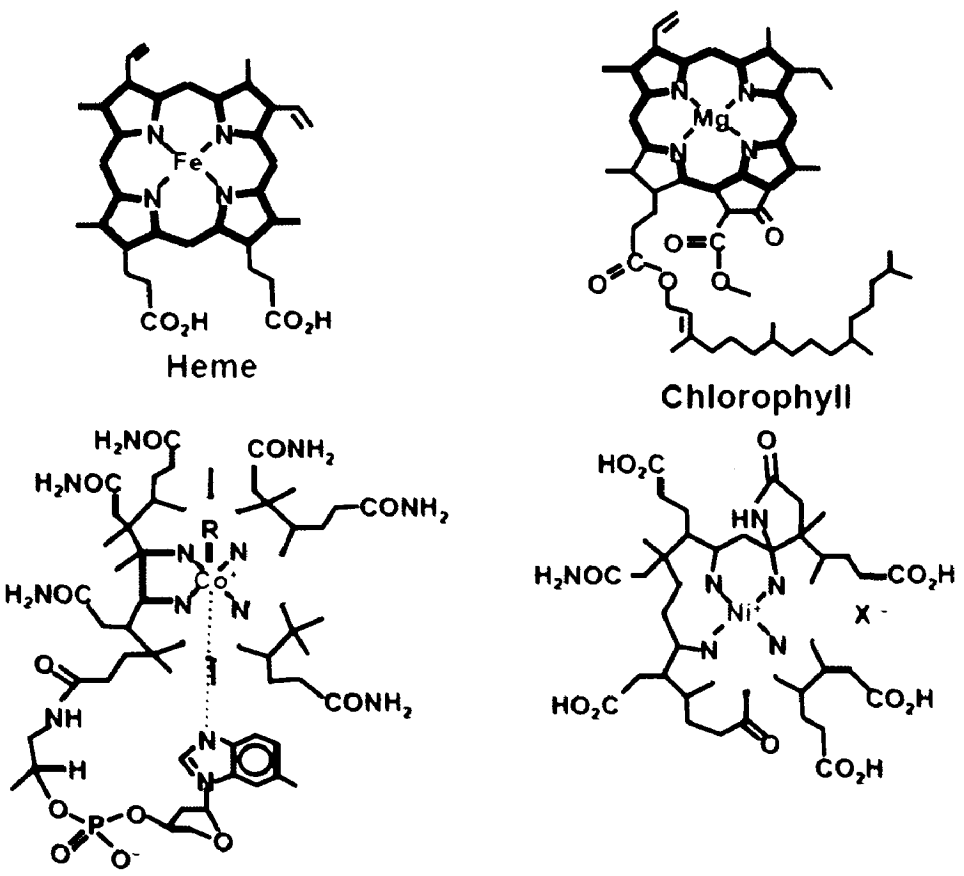


Fig. 1. Chemical structures of various tetrapyrrole pigments found in nature. Heavy lines denote π-bonds/cojucated π-bonds.

The interior pyrrole nitrogens are positioned at the four corners of the square and are ideal for coordination to metal ions. A few macrocycles (porphyrin, chlorin, corrin, methanocorphin) found in biological system are shown in figure 1. In nature, porphyrinoids with appropriate metal ion and suitable protein matrix brings about variety of biological processes.

Among the various porphyrinoids available in biological systems, the highly conjugated porphyrinoid macrocycle known as protoporphyrin IX, in association with iron is found in various functional proteins (for example: hemoglobin, myoglobin, cytochromes etc.).[1] Chlorin in chlorophyll has one reduced β-pyrrole double bond and a fused cyclopentanone ring appended to the adjacent pyrrole group with core magnesium ion. In photosynthesis, chlorophylls play a vital role in the conversion of light energy into chemical energy.[2] In case of corrin ring of vitamin $B_{12}$, the conjugation is further broken and it has a missing *meso*-carbon. The cobalt metal ion in association with the corrin brings about various redox reactions.[3] Further, the highly reduced ring system of methanocorphin with nickel is found in coenzyme $F_{430}$ and it involves in the production of methane in methanogenic bacteria.[4] The specific choice of the metal ion, tetrapyrrole and the protein backbone often dictates selective functions in nature.

## 1. B. SYNTHETIC ANALOGUES AND THEIR APPLICATIONS

In biosynthesis, the modification of the tetrapyrrole pigments and metal insertion proceeds through enzymatic process with high degree of perfection. Generally, the naturally occurring pigments bear substituents at the pyrrole positions and the *meso*-positions are devoid of any substitution. The diverse functions of tetrapyrrole pigments in nature prompted the laboratory synthesis of diverse porphyrins.[5] The synthetic porphyrins such as 2,3,7,8,12,13,17,18-octaethylporphyrin, $H_2OEP$, tetrabenzoporphyrin, $H_2TBP$ and 5,10,15,20-tetraphenylporphyrin, $H_2TPP$ have been employed as model compounds of biological functions of porphyrinoids. Of the known synthetic analogues, 5,10,15,20-tetraphenylporphyrin and its derivatives have been studied extensively owing to their ease of synthesis and versatile functionalisation (Figure 2).

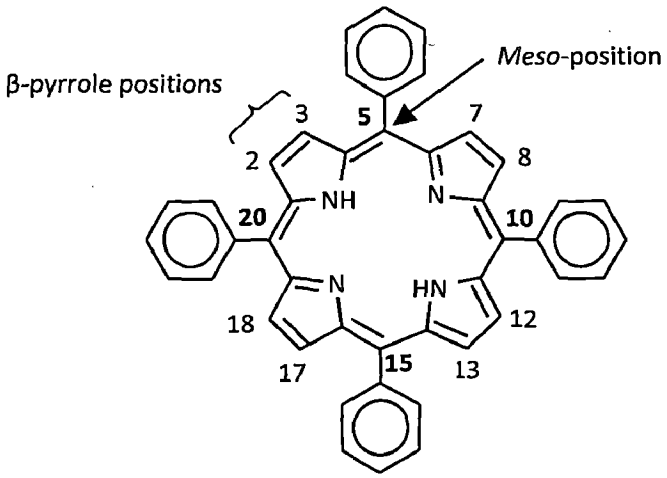


Fig. 2 Molecular Structure and Numbering Scheme for $H_2TPP$.

Rothemund reported the first synthesis of $H_2TPP$ by direct condensation of pyrrole with benzaldehyde in pyridine medium in a sealed tube at 422 K.[6] The yield of the porphyrin was very low (2-5%) and it was associated with chlorin impurities. Adler and coworkers discovered an elegant method for the synthesis of simple *meso*-tetraphenylporphyrins.[7] Dolphin has edited a series of volumes entitled "The Porphyrins" on the synthesis, mechanism and properties of porphyrins and metalloporphyrins. In these volumes, the individual aspects of tetrapyrrole pigments are described in detail.

Synthetic porphyrins are useful biomimetic model compounds and also they exhibit interesting physical and chemical properties. The synthetic utility and availability of many positions of TPP have been exploited for their use in molecular recognition,[8] catalysis,[9] non-linear optics,[10] supramolecular network solids and others.[11] Synthetic porphyrin analogues are potentially attractive because of their interesting physico-chemical properties and are modulated by appending appropriate substituents at the peripheral positions. Kadish and coworkers have edited a series of volumes entitled "The Porphyrin Handbook", wherein they have updated literature[12] on various properties of synthetic analogues.

## 1. C. PORPHYRINS AS BIOMIMETIC MODEL COMPOUNDS

The introduction of bulky substituents at the *o*-phenyl positions of TPP were used as model compounds of biological significance. Interestingly, the

presence of mono bulky substituent at one of the *o*-phenyl positions of the TPP can form atropisomers by orientation of the groups either above or below the faces of the porphyrin plane. Collman and coworkers were able to develop the first *o*-substituted TPP known as 'picket-fence porphyrin' wherein pivalamido groups were used to sterically protect one face of the porphyrin.[13] Several other sterically protected systems, such as capped, basket handle, strapped, pocket, pocket-tailed porphyrins and others have been reported by various groups. Their Fe(II) complexes have been employed as models for hemoglobin or myoglobin. The strategy is to protect the open face of the porphyrin by using an axial ligand and the sterically protected pocket is exploited for binding dioxygen molecule to iron centre. Appending bulky organic groups at both the *o*-phenyl positions of the TPP can protect open faces sterically as in bispocket porphyrin, double picket fence porphyrin, dendrimer porphyrins and silyloxyalkyl porphyrins.

## 1. D. METALLOPORPHYRINS AS CATALYSTS

The active center of the cytochromes is the *heme* group. It consists of porphyrin ring chelated to the iron atom. Cyctochrome P-450 enzyme catalyses the oxidation of harmful organic substrates into water-soluble products. These water-soluble products will be excreted through urine. Superoxide dismutase, catalyase and peroxidase are enzymes those are involved in $H_2O_2$ metabolism. They are also involved in detoxification of

harmful reactive species into water-soluble products. By inspiring from the nature, researchers have synthesised several metalloporphyrin derivatives as efficient catalyst for oxidation reactions.[14-15] Ultimately these porphyrins have shown very high turn over numbers (TON) with excellent yields.[9] It is proven that these metalloporphyrins will form high valent metaloxo species which will be the active intermediate those will react with organic substrates and transfers oxygen to substrates. Also the sterically hindered electron deficient porphyrins are found to be highly efficient catalysts.[14]

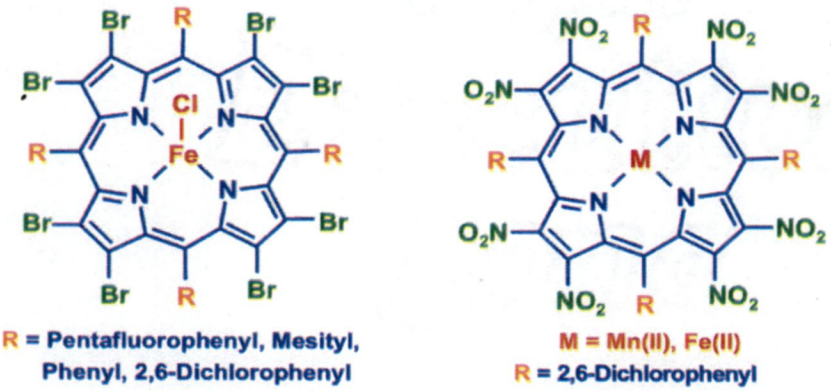


Figure 3. Highly efficient sterically hindered metalloporphyin catalysts.

## 1.E. Aim and Scope of the present work

In nature, heme enzymes (*e.g.* peroxidase, catalase and cytochrome-450) play a crucial role in detoxification processes. In humans, cytochrome-450 involved in hydroxylation of drugs, steriods, pectisides and other foregin organic substances. The hydroxylated compounds are more water-soluble favouring excretion in urine. Researchers have synthesised various metalloporphyrins as catalysts for the oxidation of organic substrates.[14,15] They found that high-valent metal oxo species are the active intermediates in the catalytic cycle. The catalytic studies using Fe(III)Cl and Mn(III)Cl-porphyrin derivatives are widely known[14] whereas the studies on vanadyl porphyrin catalyst is scarely reported due to their synthetic difficulties.[16,17] So we made an effort to synthesise tetraphenylporphyrinato oxovanadium(IV) (VOTPP) and to use as a catalyst for the oxidation of organic substrates and have the compared the catalytic activities with Mn(III)Cl-porphyrin.

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# CHAPTER 2

# SYNTHESIS AND CHARACTERIZATION OF METALLOPORPHYRINS

# CHAPTER 2

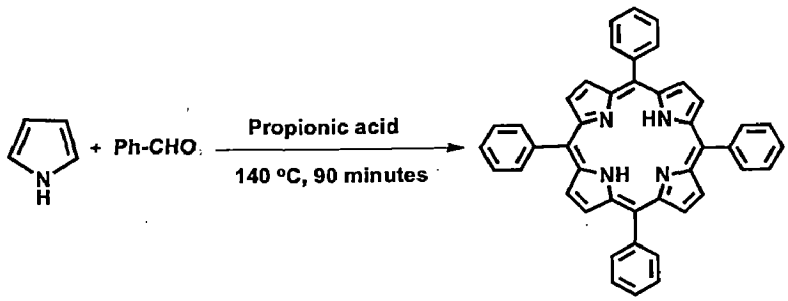
## SYNTHESIS AND CHARACTERISATION OF METALLOPORPHYRINS

### 2. A. Chemicals and Instruments used:

Column Chromatography was performed on silica gel (Rankem laboratory, 100-200 mesh). TLC was performed on aluminium-baked silica plates (contain-13% $CaSO_4 \bullet ½ H_2O$, Silicagel-G/UV-254), which were visualized by nacked eye. UV-Visilbe spectra were recorded using Shimadzu UV-visible spectrometer (UV-3600). Mass spectra were recored using ESI-mass spectrometer (Bruker Daltanics-micro TOF). Gas chromatogram was obtained using Perkin Elmer Instruments unit (Horiba-Jobin).

All chemicals such as pyrrole, benzalehyde, methanol, chloroform, hexane, con. HCl, maganese acetate, vanadyl sulphate, sodium sulphate, cyclohexene, $H_2O_2$, $CH_3CN$ and *n*-Heptane were purchased from Aldrich, Rankem, SRL and Hi-media laborataries.

### 2. B. Synthesis of 5,10,15,20-Tetraphenylporphyrin:



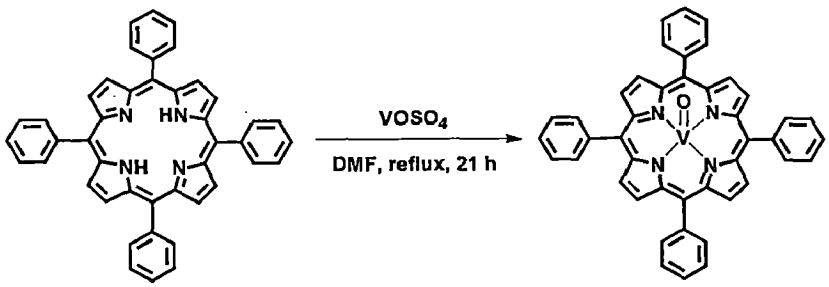

*Meso*-Tetraphenylporphyrin
(*meso*-TPP)

Scheme 1. Synthetic Scheme for free base 5,10,15,20-Tetraphenylporphyrin.

Propanoic acid (300 mL) was taken in round bottom flask (500 mL). It was heated to 100 °C . To this, benzaldehyde (7.32 mL) followed by pyrrole (5 mL) were added. The reaction mixture was refluxed for 90 min then cooled to room temperature and filtered. The residue thus obtained was washed with methanol (4 x15 mL) to remove polypyrrole impurities. Then the crude porphyrin was chromatographed on silica column using $CHCl_3$ as eluent. The first fraction was collected and chloroform was removed using rotary evaporator resulted purple powder. It was recrystallised from $CHCl_3$ and methanol mixture (1:5, v/v) resulted pure 5,10,15,20 tetraphenylporphyrin (Yield: 2.2 g (20%)).

UV-visible data ($CHCl_3$): $\lambda_{max}$ in nm = 417, 515, 550, 591, 647. $^1$H NMR ($CDCl_3$): $\delta$ 8.80 (s, 8H, $\beta$-pyrrolic), 8.2 (d, 8H, J = 8 Hz, *o-Hs* of *meso*-Ph), 7.60-7.80 (m, 12H, *m* and *p-Hs* of *meso*-Ph, -2.80 (s, 2H, imino).

**2. C. Synthesis of 5,10,15,20-Tetraphenylporphyrinato vanadyl (IV):**

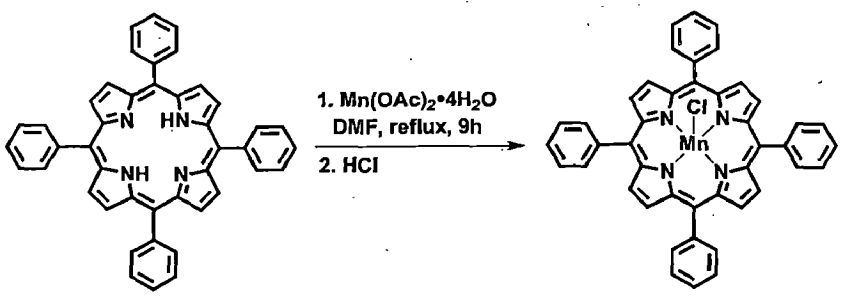



Tetraphenylporphyrin (0.10 g, 0.162 mmol) was dissolved in DMF (50 mL). To this vanadyl sulphate (1 g, 3.95 mmol) was added and the resulting solution was refluxed for 21 h. The reaction mixture was then cooled to

room temperature. To this distilled water (150 mL) was added. Purple coloured precipitate was obtained and filtered using suction. The residue thus obtained was washed with distilled water to remove any soluble impurities. Then the crude product was chromatographed on silica column using chloroform as eluent. The yield of product was found to be (0.08 g, 72 %). It has shown a single spot on TLC using 3:1 ($CHCl_3$/hexanes, v/v) mixture.

UV-visible data ($CHCl_3$): $\lambda_{max}$ in nm] = 424, 547, 581 (sh). MS (ESI): *m/z* = 1381.32 (Calcd. for $(C_{44}H_{28}N_4VO)_2$•Na $[2M•Na]^+$: 1381.33), 2061.5 (Calcd. for $(C_{44}H_{28}N_4VO)_3$•Na $[3M•Na]^+$: 2061.50), 2741.65 (Calcd. for $(C_{44}H_{28}N_4VO)_4$•Na $[4M•Na]^+$: 2741.68).

**2. D. Synthesis of 5,10,15,20-Tetraphenylporphyrinato Mn(III)Cl:**




Tetraphenylporphyrin (0.20 g, 0.325 mmol) was dissolved in 50ml of DMF. To this, magnese acetate (0.798 g, 3.25mmol) and $CH_3COONa$ (0.267 g, 3.25 mmol) were added. The resulting solution was refluxed for 9 h. The reaction mixture was then cooled to room temperature. To this, distilled water (150 mL) was added. The greenish black coloured precipitate was obtained. Then the precipitate was filtered and washed with distilled water

to remove any soluble impurities. Then 4N HCl was added, filtered and washed with 4N HCl. The crude porphyrin was recrystallised from $CHCl_3$/hexanes (1:5, v/v). The green product was dried under vacuum for few hours. The yield of product was found to be (0.15 g, 63 %).

**Characterization data:** UV-vis ($CHCl_3$): $\lambda_{max}$ in nm = 345, 376, 402, 479, 530, 582, 618. MS (ESI): *m/z* = 1369.30 (Calcd. for $(C_{44}H_{28}N_4Mn)_2Cl$ $[2M\text{-}Cl]^+$:1369.31), 2073.43 (Calcd. for $(C_{44}H_{28}N_4Mn)_3Cl_2$ $[3M\text{-}Cl]^+$: 2073.45).



## 2. E. RESULTS AND DISCUSSION:

We have synthesied and characterised *meso*-tetraphenylporphyrin ($H_2TPP$) according to the literature method.[1]

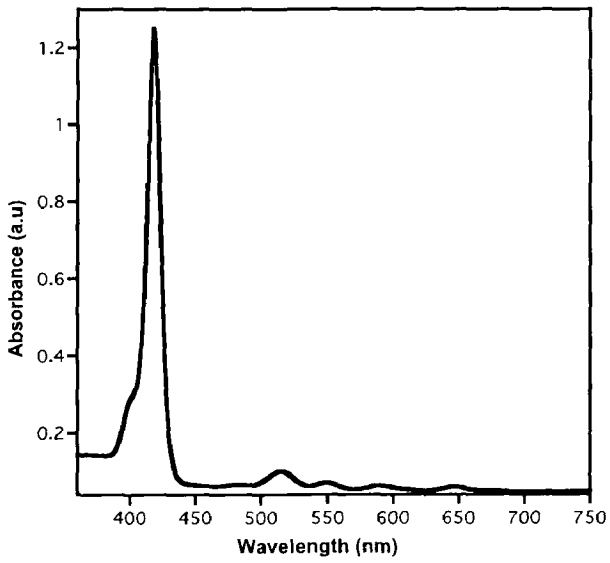



Fig. 1. UV-visible spectrum of 5, 10, 15, 20-tetraphenylporphyrin.

Herein we have developed a simplified method for vanadyl porphyrin synthesis. $H_2TPP$ was metallated using $VOSO_4$ by refluxing in DMF.

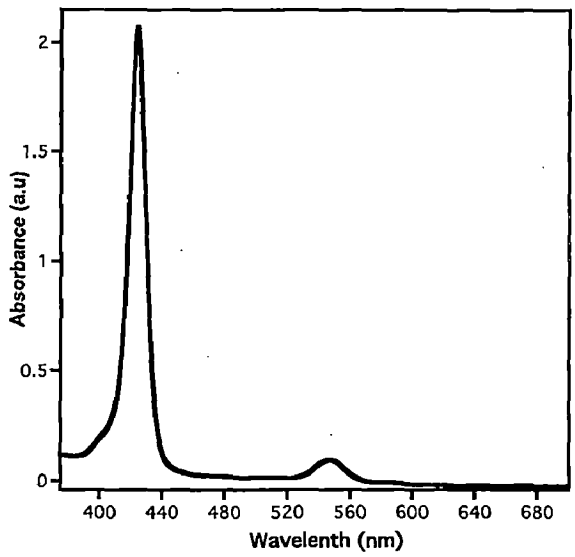



Fig. 2. UV-visible spectrum of *meso*-tetraphenylporphyrinato vanadyl(IV).

The crude product was purified on silica column chromatography using $CHCl_3$ as an eluent. Further it was charaterised by UV-visible and mass spectroscopic techniques.

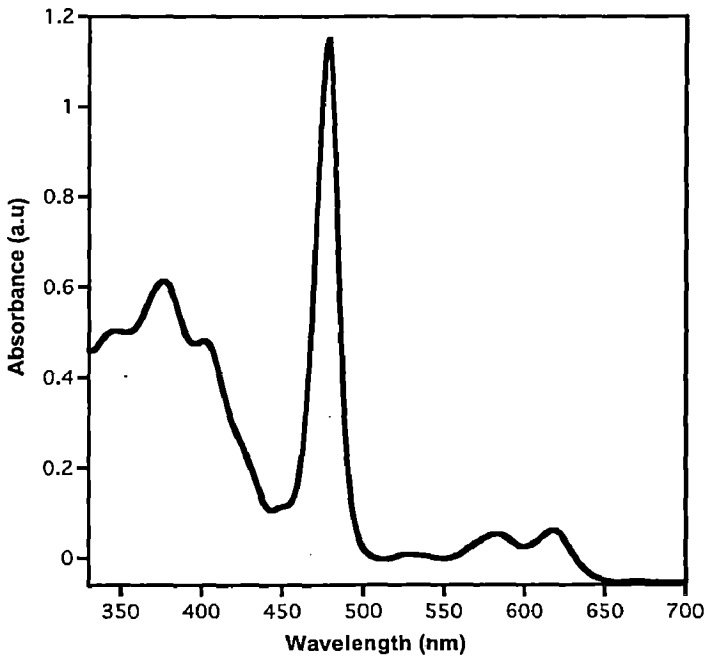


Fig. 3. UV-visible spectrum of *meso*-tetraphenylporphyrinato Mn(III)Cl

Free base tetraphenylporphyrin was metallated using maganese(II) acetate by refluxing in DMF with sodium acetate for 9 hrs.[2] Then the addition of excess distilled water leads to the precipitation of the porphyrin. The ppt was filltered and dried. The counter ion exchange from acetate to chloride was done using HCl. The crude porphyrin was recrystallised from $CHCl_3$/hexanes mixture. Mn(III)Cl porphyrin was characterized by UV-visible and mass spectroscopic methods.

Vanadyl porphyrin has shown typical metalloporphyrin UV-vis spectrum. While Mn(III)Cl porphyrin showed enormous red-shft in comparison to vanadyl porphyrin. This is due to the alteration of electonic energy levels (HOMO and LUMO) of metalloporphyrins. The higher oxidation states of metal were stabilised by electron-rich anionic porphyrin ligands.

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# CHAPTER 3

# CATALYTIC APPLICATIONS USING METALLOPORPHYRINS

# CHAPTER 3

## CATALYTIC APPLICATIONS USING METALLOPORPHYRINS

### 3. A. Introduction:

In Nature, many enzymes are present which are capable of catalyzing oxidation reactions.[1] In a number of these reactions manganese or iron containing enzymes are involved. These enzymes are frequently studied by using model complexes which provide information on the nature and reactivity of the active site and about possible reaction mechanisms.[1] Based on these manganese or iron containing enzymes and on the related model complexes various oxidation catalysts have been evaluated.[2]

The role of vanadate in biological systems is to convert a compound into a form that is recognized by the enzyme so that chemical reactions can occur. Manganese can frequently be found in the catalytic redox centre of several enzymes like superoxide dismutase (SOD), catalase and the oxygen evolving complex photosystem II. By inspiring from the nature, we have synthesized oxovanadium(IV) and Mn(III)Cl porphyrin complexes as catalyst for the oxidation of organic substrates.

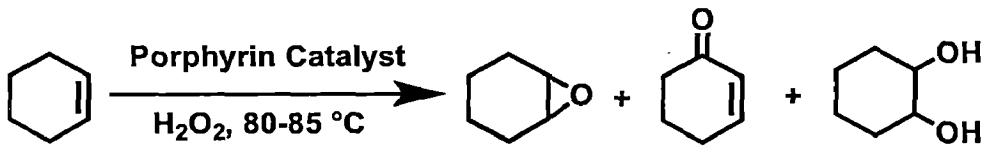
The oxidation of organic compounds with high selectivity is of the extreme importance in synthetic chemistry. Important oxidation reactions include the trasformations of alcohols to either the corresponding carbonyl compounds or carboxylic acids, the oxidation of sulfides to sulfoxides and **alkenes to epoxides and diols**.

**3. B. General procedure for catalytic reaction using metalloporphyrins:**

Cyclohexene and $H_2O_2$ were taken in 50 mL two-necked RB flask. To this, solvent ($CH_3CN$ or heptane) and metalloporphyrin were added. The reaction mixture was heated to 80-85 °C with stirring for 6 h on oil bath. We have monitored the reaction progress for every 2 h. At the end, the reaction mixture was filtered by using Whatmann filter paper or celite. The organic layer was seperated and injected into GC column and monitored the product formation.

**3. C. Oxidation of Cyclohexene using metalloporphyrin catalyst:**

The oxidation of cyclohexene was studied using porphyrin catalyst. The reaction gave mainly four different products, *i.e.* cyclohexane epoxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-ol, cyclohexane-1,2-diol as shown in scheme 1. The formation of allylic oxidation products 2-cyclohexen-1-one and 2-cyclohexen-1-ol reflects the preferential attack of the activated C-H bond over the C=C bond.




Scheme 1. Reaction scheme for catalysis

The different parameters (*e.g.*amount of oxidant, catalyst and solvent of the reaction mixture) were optimized for the maximum oxidation of cyclohexene. We will discuss one by one as follows.

## Vanadyl porphyrin as a catalyst

### 3. D. Catalyst amount variation:

Herein we kept the constant amount of cyclohexene, $H_2O_2$ and solvent and varied the amount of catalyst (*e.g.* 2 mg, 5 mg and 7 mg).

Table 1. The variation in amounts of VOTPP

| S. No. | Catalyst (g) | Time (hrs) | Conv. (%) | Product Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1,2-diol | Ketone | Epoxide | Others |
| 1 | 0.002 | 2 | 54.0 | 44.8 | 30.0 | 18.9 | 6.2 |
| 2 | 0.002 | 4 | 83.0 | 50.5 | 40.1 | 6.6 | 2.3 |
| 3 | 0.002 | 6 | 90.8 | 50.1 | 40.0 | 7.4 | 2.6 |
| 4 | 0.005 | 2 | 60.0 | 46.8 | 37.0 | 10.1 | 6.1 |
| 5 | 0.005 | 4 | 81.7 | 51.3 | 38.5 | 6.6 | 3.6 |
| 6 | 0.005 | 6 | 94.3 | 55.6 | 35.9 | 4.8 | 3.7 |
| 7 | 0.007 | 2 | 67.2 | 36.7 | 36.6 | 16.6 | 9.8 |
| 8 | 0.007 | 6 | 95.0 | 43.1 | 41.0 | 9.2 | 6.6 |

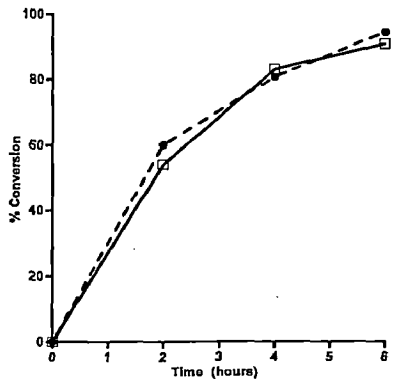



Figure 1. The percentage conversion of cyclohexene with catalyst amount variation (2 mg and 5 mg are shown in solid and dotted lines respectively).

It is found that least amount of catalyst (2 mg) is more efficient for the oxidation of cyclohexane.

**3. E. Solvent amount variation:**

We have kept catalyst amount, cyclohexane/ $H_2O_2$ ratio constant and varied the solvent volume (5-10 mL).

Table 2. Percent conversion of cyclohexene with solvent volume variation

| S. No. | $CH_3CN$ (ml) | Time (hrs) | Conv. (%) | Product Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1,2-diol | Ketone | Epoxide | Others |
| 1 | 5 | 2 | 54.0 | 44.8 | 30.0 | 18.9 | 6.2 |
| 2 | 5 | 4 | 83.0 | 50.5 | 40.5 | 6.6 | 2.3 |
| 3 | 5 | 6 | 90.8 | 50.1 | 40.0 | 7.4 | 2.6 |
| 4 | 7 | 2 | 48.8 | 50.1 | 28.6 | 11.1 | 9.2 |
| 5 | 7 | 4 | 71.5 | 63.5 | 25.3 | 6.2 | 4.8 |
| 6 | 7 | 6 | 98.7 | 63.2 | 24.3 | 24.3 | 5.6 |
| 7 | 10 | 2 | 46.5 | 47.8 | 22.4 | 15.6 | 14.0 |
| 8 | 10 | 4 | 92.8 | 61.7 | 24.4 | 7.6 | 6.1 |
| 9 | 10 | 6 | 89.7 | 57.2 | 25.3 | 9.1 | 8.8 |

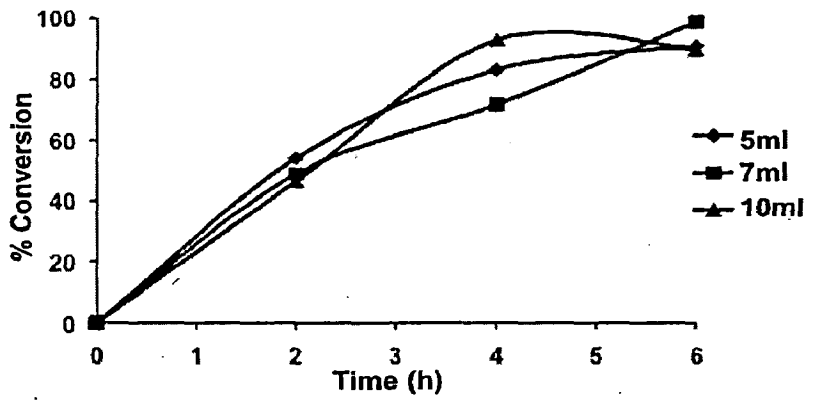



Figure 2. % conversion of cyclohexene with variation of solvent volume.

The optimum condition of solvent volume is 7 mL.

**3. F. Variation of cyclohexene/$H_2O_2$ ratio:** We kept constant the catalyst and solvent amount and **varied the ratio of cyclohexene and $H_2O_2$.**

Table 3. Variation in cyclohexene and $H_2O_2$ ratio.

| S. No. | Cyclohex/ $H_2O_2$ | Time (hrs) | Conv. (%) | Product Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1,2-diol | Ketone | Epoxide | Others |
| 1 | 1:1 | 2 | 5.0 | 41.6 | 27.0 | 19.8 | 12.1 |
| 2 | 1:1 | 4 | 12.5 | 43.7 | 40.0 | 11.7 | 4.4 |
| 3 | 1:1 | 6 | 43.7 | 46.0 | 37.0 | 9.1 | 7.9 |
| 4 | 1:2 | 2 | 41.4 | 43.8 | 34.5 | 15.1 | 6.4 |
| 5 | 1:2 | 4 | 70.3 | 44.9 | 41.7 | 8.2 | 5.1 |
| 6 | 1:2 | 6 | 52.4 | 48.3 | 40.8 | 6.8 | 3.9 |
| 7 | 1:3 | 2 | 54.0 | 44.8 | 30.0 | 18.9 | 6.2 |
| 8 | 1:3 | 4 | 83.0 | 51.0 | 40.5 | 6.6 | 2.3 |
| 9 | 1:3 | 6 | 90.8 | 50.1 | 39.9 | 7.4 | 2.5 |

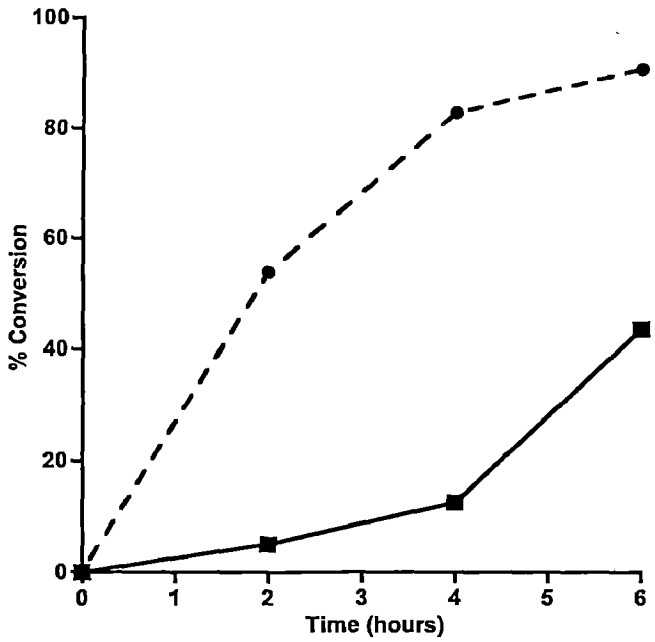



Figure 3. Percent conversion of cyclohexene with variation of cyclohexene/ $H_2O_2$ ratio (1:1 (solid line) and 1:3 (dotted line)).

The optimized condition is 1:3 cyclohexene/$H_2O_2$ ratio.

## Manganese porphyrin as a catalyst

### 3. G. Catalyst amount variation:

Herein we kept the constant amount of cyclohexene, $H_2O_2$ and heptane and varied the amount of catalyst (*e.g.* 2 mg, 5 mg and 7 mg)

| S. No. | Catalyst (g) | Time (hrs) | Conv. (%) | Product Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1,2-diol | Ketone | Epoxide | Others |
| 1 | 0.002 | 6 | 10.0 | 29.7 | 26.7 | 24.5 | 19.3 |
| 2 | 0.005 | 6 | 13.0 | 56.5 | 29.1 | 8.7 | 5.6 |
| 3 | 0.007 | 6 | 7.0 | 39.2 | 29.1 | 22.8 | 8.8 |

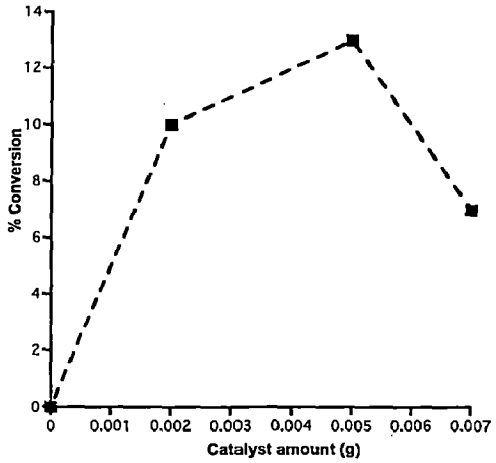



Figure 4. % conversion of cyclohexene with catalyst amount variation.

### 3. H. Solvent amount variation:

| S. No. | $CH_3CN$ (ml) | Time (hrs) | Conv. (%) | Product Selectivity (%) | | | |
|---|---|---|---|---|---|---|---|
| | | | | 1,2-diol | Ketone | Epoxide | Others |
| 1 | 5 | 6 | 10.0 | 29.7 | 26.5 | 24.5 | 19.2 |
| 2 | 7 | 6 | 56.0 | 31.4 | 28.8 | 22.2 | 17.5 |
| 3 | 10 | 6 | 29.0 | 40.2 | 30.5 | 20.2 | 9.1 |

### 3. I. Variation of cyclohexene/$H_2O_2$ ratio:

| S. No. | Cyclohexene (g) | $H_2O_2$ (g) | $C_7H_{14}$ (ml) | Catalyst (g) | % conversion 6h |
|---|---|---|---|---|---|
| 1 | **0.829** | **0.829** | 5 | 0.002 | NA |
| 2 | **0.829** | **1.658** | 5 | 0.002 | 2.3 |
| 3 | **0.829** | **2.487** | 5 | 0.002 | 10 |

We have performed the catalytic reactions varying with different parameters (*e.g.* amount of oxidant, catalyst and solvent of the reaction mixture) are optimized.

**Vanadyl Porphyrins:** We found that the increment of catalyst amount has no effect on the percentage conversion of cyclohexene. The best-optimized condition was with 2 mg of catalyst for 0.83 g of cyclohexene. When we increase the ratio of cyclohexene:$H_2O_2$ (1:1 to 1:3), the yield is dramatically improved. So the enhancement $H_2O_2$ concentration may help for effective oxidation of cyclohexene. The optimum condition of solvent volume is 7 mL for 0.83 g of cyclohexene with 2 mg of the catalyst. M. E. K. Mansour *et al* have reported[1] the photochemical oxidation of cyclohexene using vanadylporphyrin as a catalyst and $H_2O_2$ as an oxygen donor in benzene by irradiating for 180 h. We have done the same reaction by refluxing in acetonitrile for 6 h. The total yield of oxidized products is almost quantitative. Hence our conditions are milder than photocatalytic oxidation.[1] We have developed a simplest method with highest possible yield for the oxidation of cyclohexene in comparison to reported methods.[3,4] Recently S. Fukuzumi *et al* have reported[2] the synthesis of vanadyl porphyrin by mixing $VCl_3$ and tetramethoxyporphyrin in ethanol and then autoclaved the mixture at 453 K for 4 days with the yield of 20%. But we have used an elegant method by reacting $H_2TPP$ and $VOSO_4$ in refluxing DMF with 72% yield.

**Mn(III)Cl Porphyrin:** We found that the increment of catalyst amount has an effect on the percent conversion of cyclohexene. Initially increases till 5 mg of catalyst then decreases for 7 mg (figure 4). With solvent variation the same trend was observed as mentioned above. While increasing the amount $H_2O_2$ the percentage yield was increasing as mentioned for vanadyl porphyrin.[4]

Among two porphyrins, vanadyl porphyrin found to an efficient catalyst than that of Mn(III)Cl porphyrin for the oxidation of cyclohexene. Vanadyl porphyrin found to the robust in nature[2] than manganese(III)Cl porphyrin. The Mn(III)Cl porphyrin might undergo axial ligand exchange with $H_2O_2$ could alter the electronics of the porphyrin that might lead to degradation of the catalyst in presence of $H_2O_2$ during the catalytic cycle.[5]

## References:


1. E. M. K. Mansour, P. Maillard, P. Krauz, S. Gaspard, and C. Giannotti, *J. Mol. Catalysis*, 1987, *41*, 361-366.
2. A. K. Rahiman, K. S. Bharathi, S. Sreedaran, K. Rajesh, and V. Narayanan, *Inorg. Chimica Acta*, 2009, *362*, 1810-1818.
3. W. Chen, T. Suenobu, and S. Fukuzumi, *Chem. Asian J.*, 2011, *6*, 1416-1422.
4. M. R. Maurya, P. Saini, A. Kumar, and J. C. Pessoa, *Eur. J. Inorg. Chem.*, 2011, 4846-4861.
5. S. Zakavi, and L. Ebrahimi, *Polyhedron*, 2011, *30*, 1732-1738.

# CHAPTER 4

## CONCLUSIONS

Porphyrins are having applications ranging from materials chemistry to medicinal chemistry. We have sucessfully synthesised and characterized two different metalloporphyrins namely 5, 10, 15, 20-tetraphenylporphyrinato oxovanadium(IV) and 5, 10, 15, 20-tetraphenylcporphyrinato Mn(III)Cl.

Further we have utilised these porphyrins as a catalyst for the oxidation of cyclohexene using $H_2O_2$ as an oxidant. We observed that cyclohexene requires least amount of vanadyl porphyrin. Furhter we noticed that on increasing amount of $H_2O_2$ favoured the oxidation of cyclohexene. On the other hand, Mn(III)Cl porphyrin was found to be less effective for this reaction. This porphyrin might undergo axial ligand exchange with $H_2O_2$ could alter the electronics of the porphyrin that might lead to degradation of the catalyst in presence of $H_2O_2$ during the catalytic cycle. The yield may be improved up on providing axially ligating base. Based on our results, vanadyl porphyrin found to an efficient catalyst than that of Mn(III)Cl porphyrin for the oxidation of cyclohexene.

| S. No. | Title Name | Page No |
|---|---|---|
| Figure 1 | $^1H$ NMR spectrum of $H_2TPP$ in $CDCl_3$ | 31 |
| Figure 2 | ESI-Mass spectrum of VOTPP in $CHCl_3$ | 32 |
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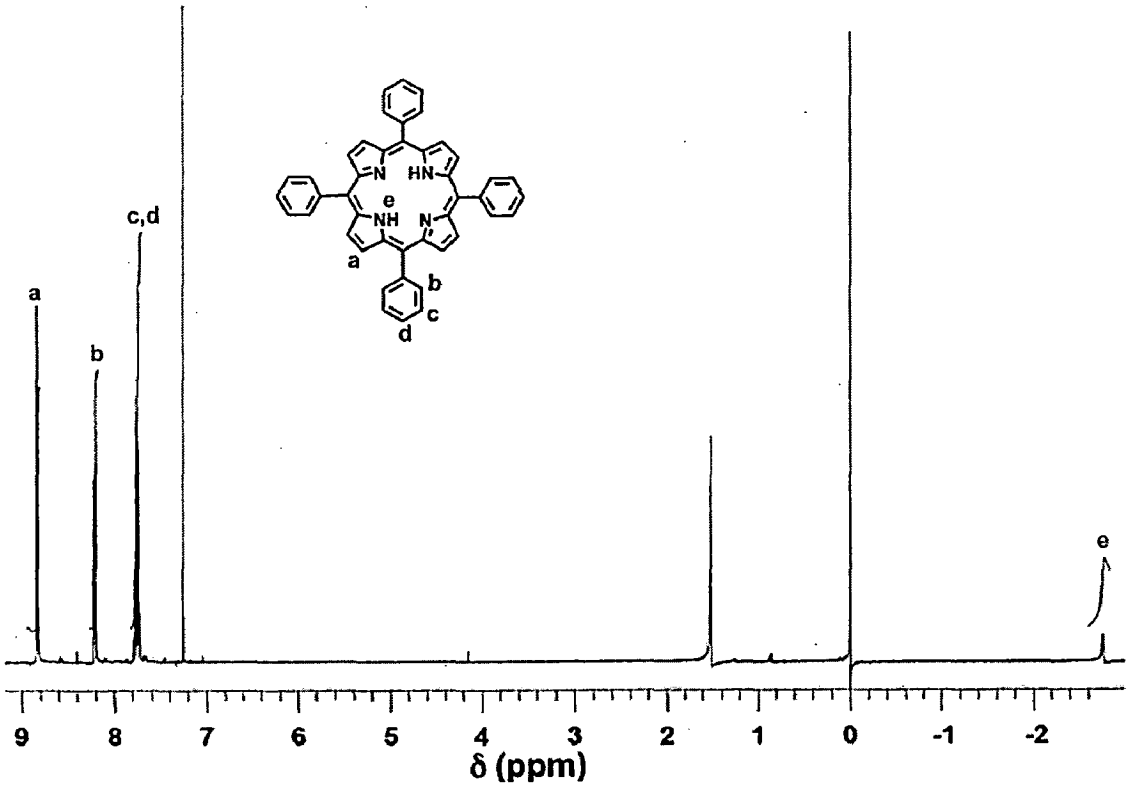


Figure 1. $^1$H NMR spectrum of $H_2TPP$ in $CDCl_3$

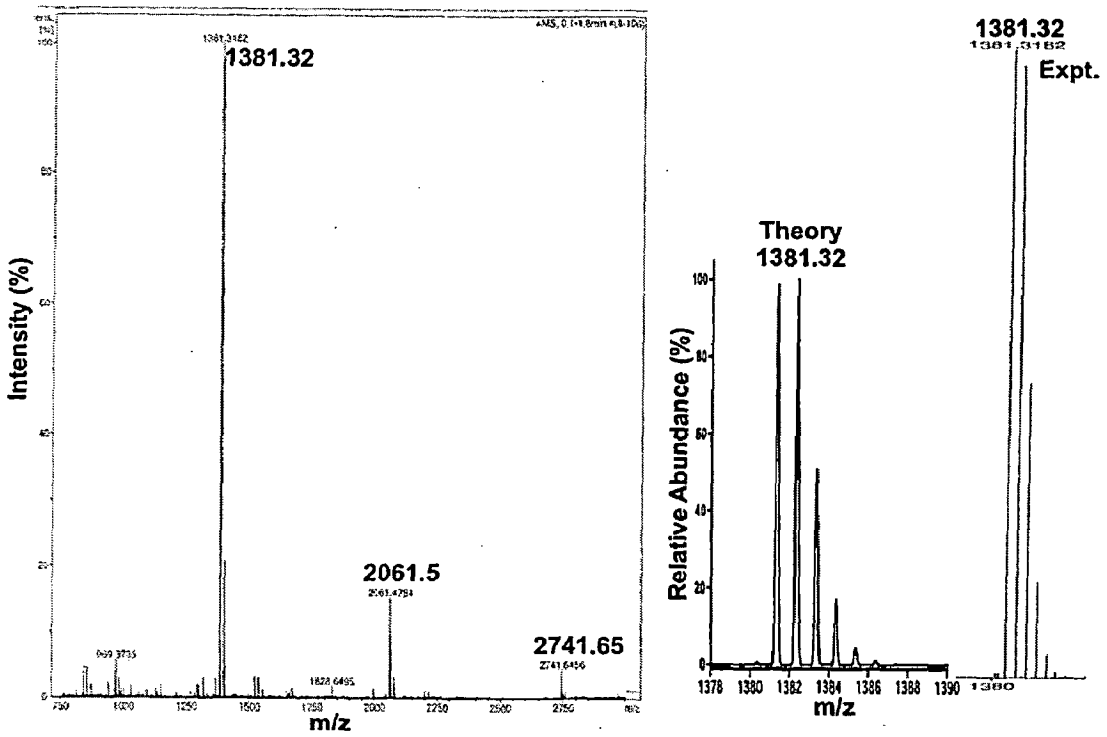


Figure 2. ESI-Mass spectrum of VOTPP in $CHCl_3$

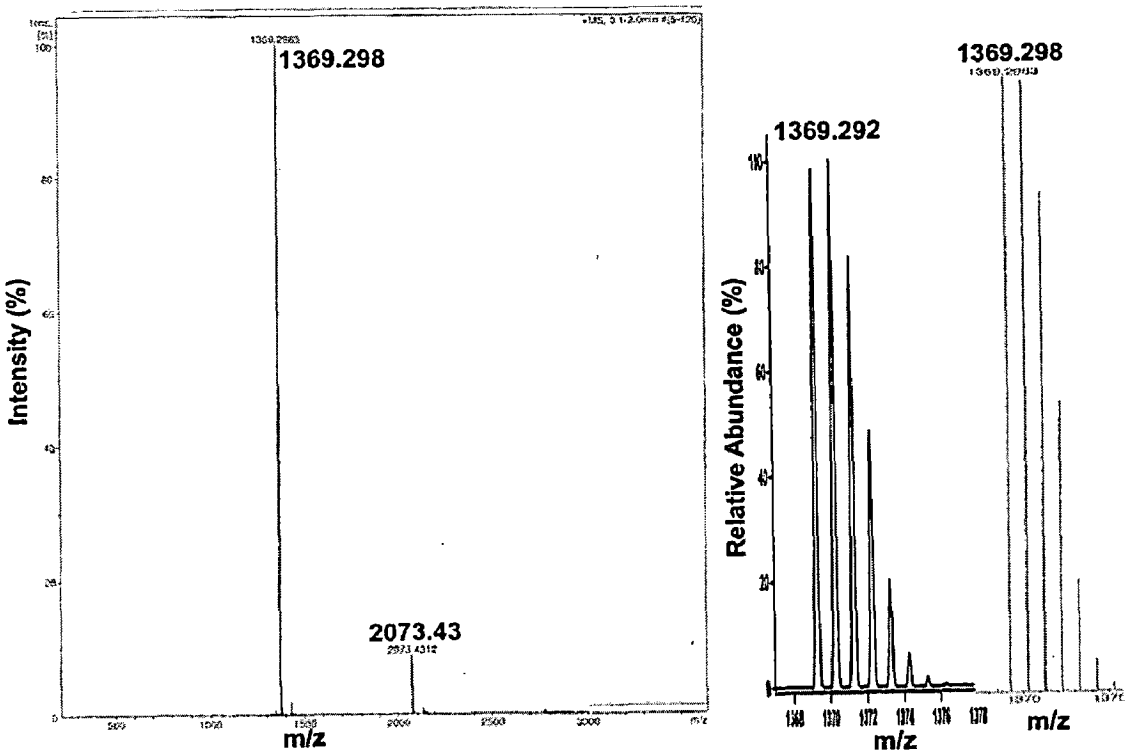


Figure 3. ESI-Mass spectrum of MnClTPP in $CH_3CN$

Sample Information

| | |
|---|---|
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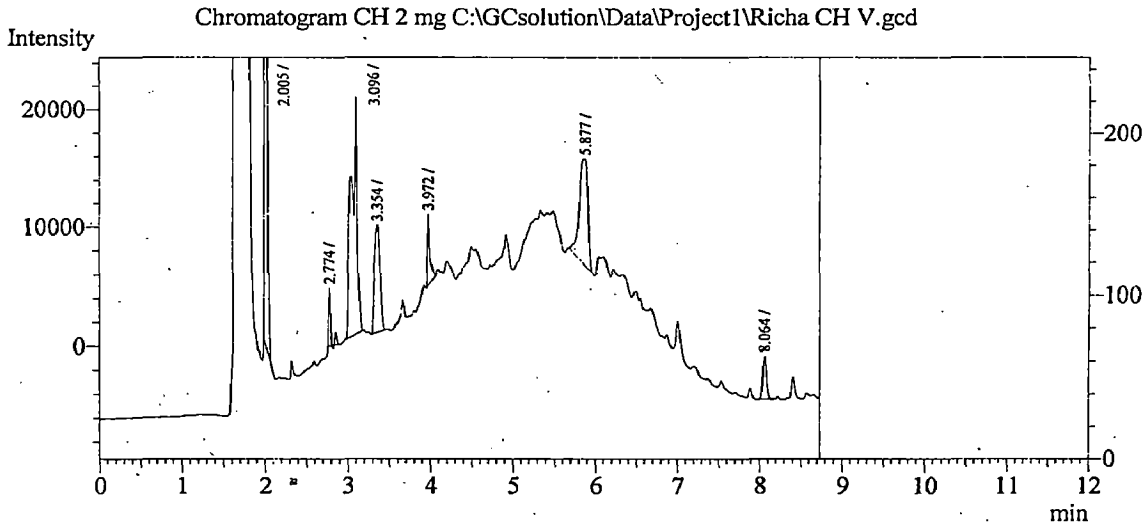
| Vial# | : 1 |
| Sample Name | : CH 2 mg |
| Sample ID | : ch ox V |




Peak Table - Channel 1

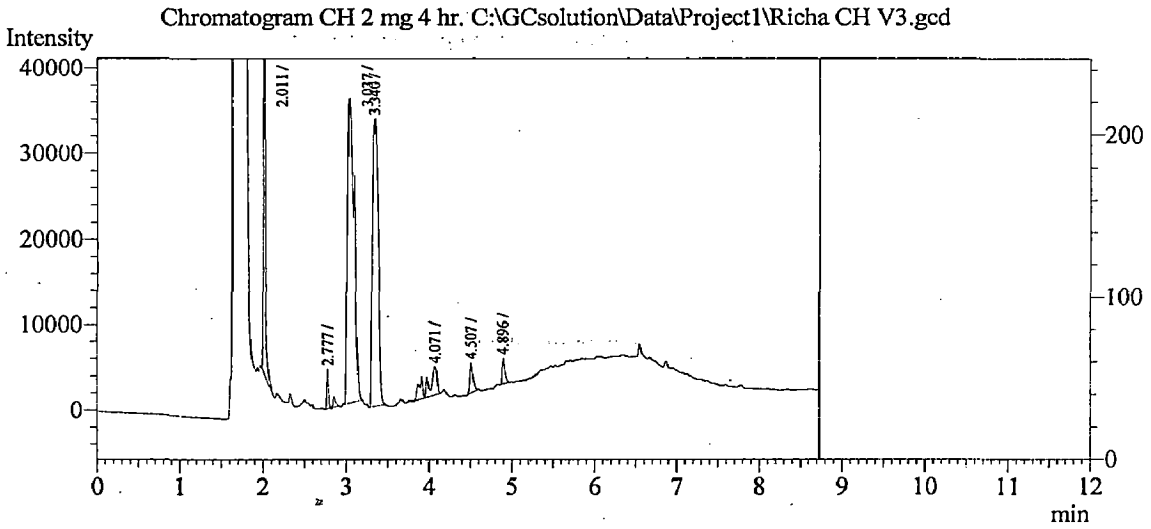
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.005 | 200992 | 133811 | 46.0716 |
| 2 | 2.774 | 8197 | 4806 | 1.8789 |
| 3 | 3.096 | 96681 | 19921 | 22.1613 |
| 4 | 3.354 | 40854 | 8993 | 9.3647 |
| 5 | 3.972 | 13377 | 5882 | 3.0664 |
| 6 | 5.877 | 64834 | 9025 | 14.8614 |
| 7 | 8.064 | 11324 | 3573 | 2.5958 |
| Total | | 436259 | 186011 | 100.0000 |

Figure 4a. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **2 mg, Time: 2h,** 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/23/2012 6:51:23 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 2 mg 4 hr. |
| Sample ID | : ch ox V |




Peak Table - Channel 1

| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.011 | 84687 | 58507 | 16.9976 |
| 2 | 2.777 | 9286 | 4428 | 1.8637 |
| 3 | 3.037 | 200973 | 35580 | 40.3374 |
| 4 | 3.340 | 160941 | 33575 | 32.3026 |
| 5 | 4.071 | 26336 | 3281 | 5.2859 |
| 6 | 4.507 | 8957 | 3506 | 1.7977 |
| 7 | 4.896 | 7050 | 2913 | 1.4151 |
| Total | | 498230 | 141790 | 100.0000 |

Figure 4b. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **2 mg**, **Time: 4h**, 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

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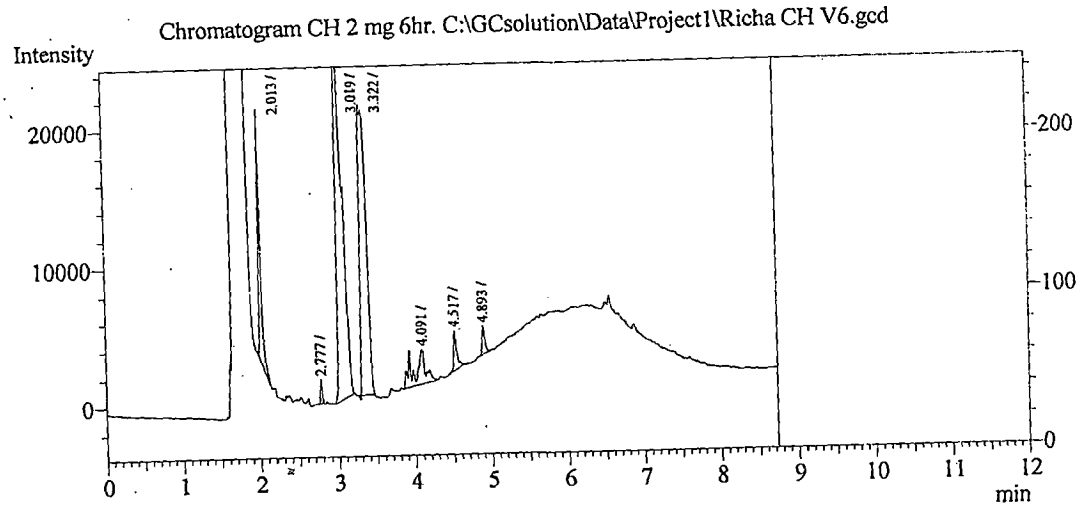
Vial# : 1
Sample Name : CH 2 mg 6hr.
Sample ID : ch ox V




Peak Table - Channel 1

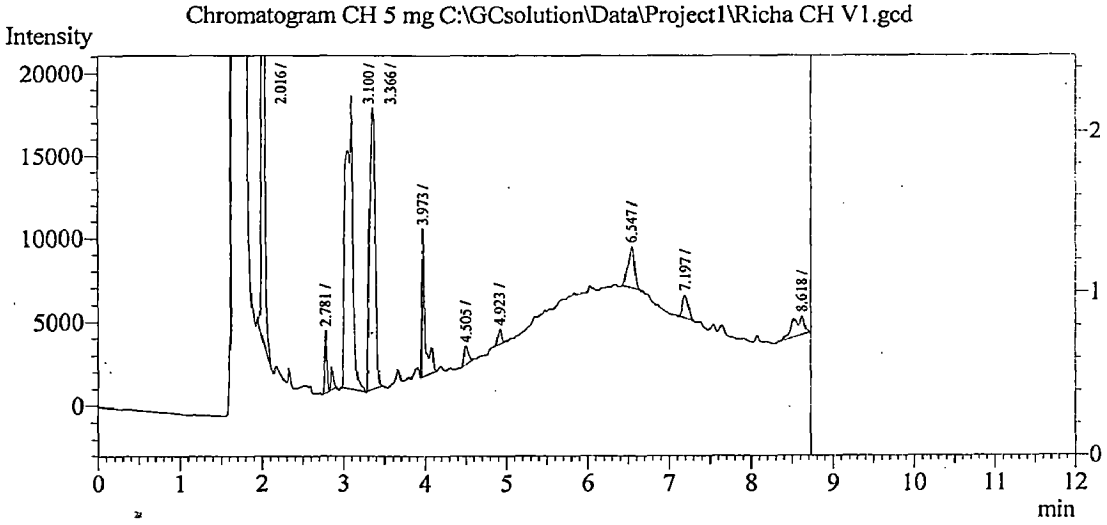
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.013 | 32992 | 17855 | 9.2253 |
| 2 | 2.777 | 2647 | 1690 | 0.7401 |
| 3 | 3.019 | 158717 | 31231 | 44.3806 |
| 4 | 3.322 | 126655 | 20988 | 35.4153 |
| 5 | 4.091 | 23367 | 2446 | 6.5338 |
| 6 | 4.517 | 8178 | 2838 | 2.2869 |
| 7 | 4.893 | 5071 | 2060 | 1.4179 |
| Total | | 357627 | 79108 | 100.0000 |

Figure 4c. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **2 mg, Time 6h,** 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

Analysis Date & Time : 4/23/2012 6:26:29 PM
User Name : Admin
Vial# : 1
Sample Name : CH 5 mg
Sample ID : ch ox V




Peak Table - Channel 1

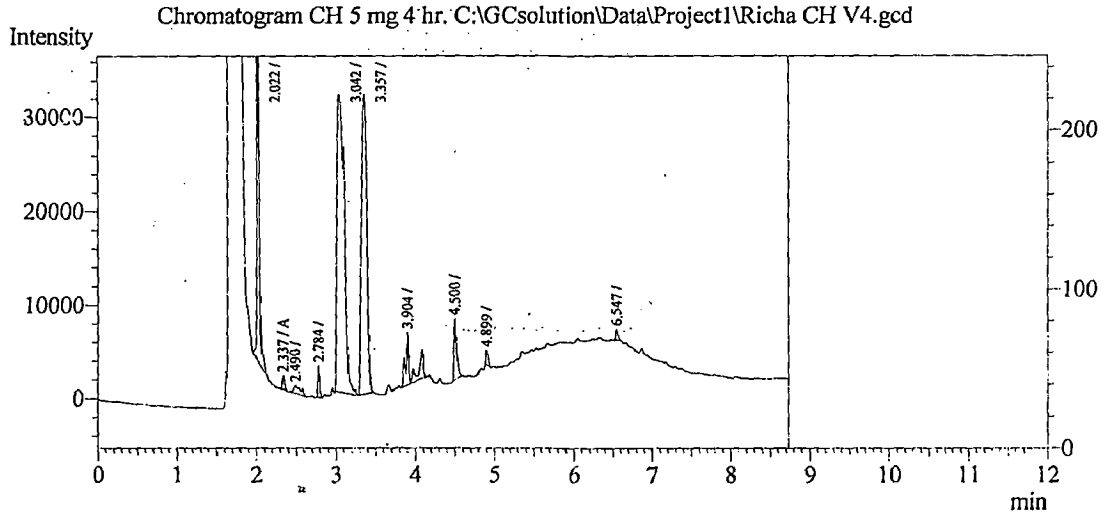
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.016 | 175796 | 112252 | 40.3221 |
| 2 | 2.781 | 9152 | 3690 | 2.0992 |
| 3 | 3.100 | 105911 | 17457 | 24.2926 |
| 4 | 3.366 | 83811 | 16909 | 19.2236 |
| 5 | 3.973 | 22930 | 8671 | 5.2594 |
| 6 | 4.505 | 4047 | 1102 | 0.9282 |
| 7 | 4.923 | 2851 | 891 | 0.6538 |
| 8 | 6.547 | 13751 | 2489 | 3.1540 |
| 9 | 7.197 | 6742 | 1378 | 1.5464 |
| 10 | 8.618 | 10990 | 1086 | 2.5207 |
| Total | | 435981 | 165925 | 100.0000 |

Figure 4d. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **5 mg, Time 2h**, 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/23/2012 7:03:04 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 5 mg 4 hr. |
| Sample ID | : ch ox V |




Peak Table - Channel 1

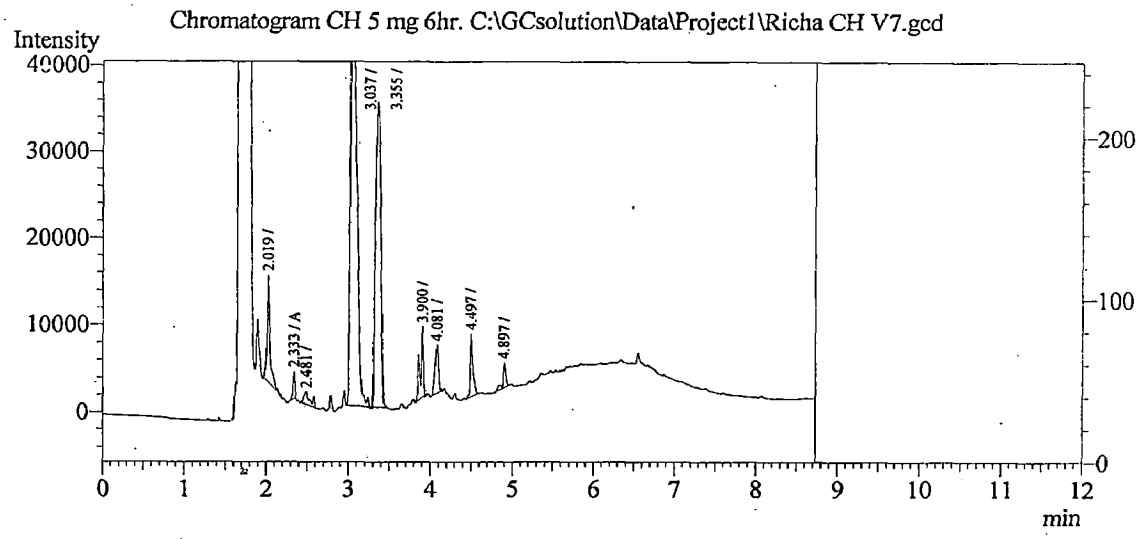
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.022 | 94509 | 61391 | 18.3162 |
| 2 | 2.337 | 2528 | 1413 | 0.4900 |
| 3 | 2.490 | 4900 | 784 | 0.9496 |
| 4 | 2.784 | 5346 | 3350 | 1.0360 |
| 5 | 3.042 | 206875 | 31720 | 40.0931 |
| 6 | 3.357 | 155287 | 31959 | 30.0951 |
| 7 | 3.904 | 26499 | 5565 | 5.1356 |
| 8 | 4.500 | 14687 | 6490 | 2.8464 |
| 9 | 4.899 | 3052 | 1515 | 0.5915 |
| 10 | 6.547 | 2304 | 1111 | 0.4466 |
| Total | | 515987 | 145298 | 100.0000 |

Figure 4e. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **5 mg, Time 4h,** 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/23/2012 7:38:14 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 5 mg 6hr. |
| Sample ID | : ch ox V |




Peak Table - Channel 1

| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.019 | 29180 | 12171 | 5.6142 |
| 2 | 2.333 | 5207 | 3119 | 1.0018 |
| 3 | 2.481 | 7310 | 1418 | 1.4064 |
| 4 | 3.037 | 252890 | 44787 | 48.6560 |
| 5 | 3.355 | 163176 | 35102 | 31.3950 |
| 6 | 3.900 | 21817 | 8065 | 4.1976 |
| 7 | 4.081 | 15884 | 5496 | 3.0560 |
| 8 | 4.497 | 16970 | 7200 | 3.2650 |
| 9 | 4.897 | 7318 | 2785 | 1.4080 |
| Total | | 519752 | 120143 | 100.0000 |

Figure 4f. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **5 mg, Time 6h,** 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

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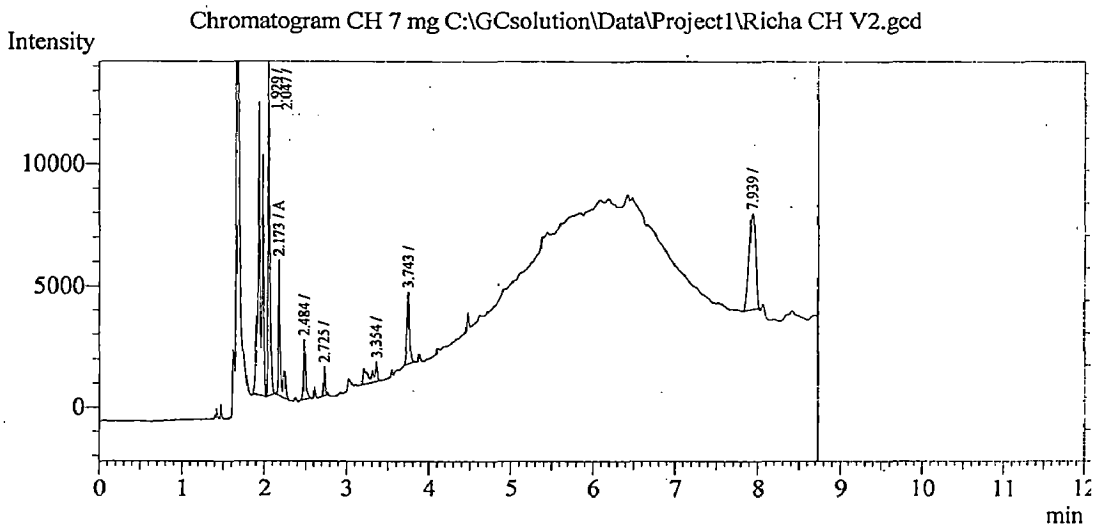
Sample Name : CH 7 mg
Sample ID : ch ox V




Peak Table - Channel 1

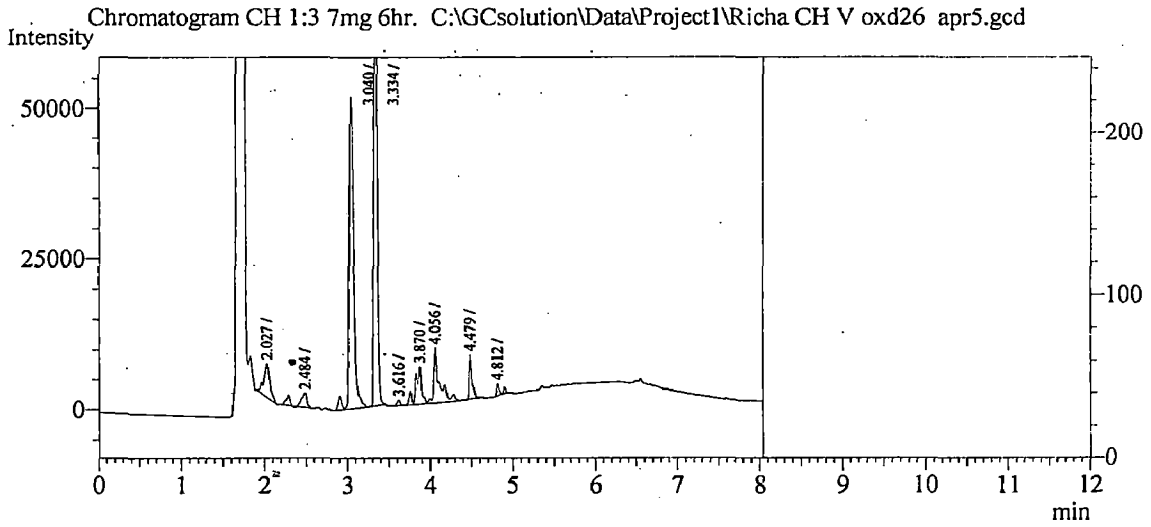
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 1.929 | 34359 | 11714 | 32.7948 |
| 2 | 2.047 | 22226 | 14351 | 21.2142 |
| 3 | 2.173 | 9982 | 5487 | 9.5277 |
| 4 | 2.484 | 4140 | 2413 | 3.9518 |
| 5 | 2.725 | 1641 | 1184 | 1.5659 |
| 6 | 3.354 | 4513 | 804 | 4.3074 |
| 7 | 3.743 | 5918 | 2904 | 5.6484 |
| 8 | 7.939 | 21991 | 3934 | 20.9898 |
| Total | | 104770 | 42791 | 100.0000 |

Figure 4g. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **7 mg, Time 2h,** 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

Analysis Date & Time : 4/26/2012 8:40:32 PM
User Name : Admin
Vial# : 1
Sample Name : CH 1:3 7mg 6hr.
Sample ID : ch ox V




Peak Table - Channel 1

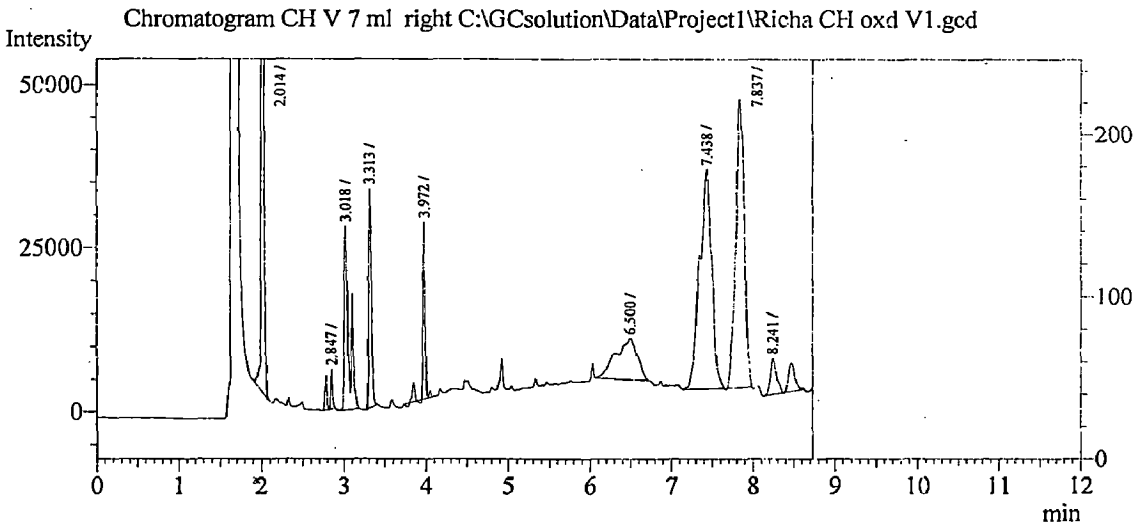
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.027 | 28224 | 5605 | 5.0728 |
| 2 | 2.484 | 15369 | 2342 | 2.7625 |
| 3 | 3.040 | 200301 | 51638 | 36.0018 |
| 4 | 3.334 | 210675 | 72636 | 37.8664 |
| 5 | 3.616 | 2540 | 939 | 0.4566 |
| 6 | 3.870 | 32102 | 6145 | 5.7700 |
| 7 | 4.056 | 45405 | 9033 | 8.1611 |
| 8 | 4.479 | 16051 | 7194 | 2.8849 |
| 9 | 4.812 | 5697 | 1866 | 1.0240 |
| Total | | 556364 | 157398 | 100.0000 |

Figure 4h. Gas Chromatogram of catalyst amount variation. The reaction conditions are given below.

Catalyst Wt.: **7 mg**, **Time 6h**, 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/30/2012 7:38:34 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH V 7 ml right |
| Sample ID | : Richa CH V |




Peak Table - Channel 1

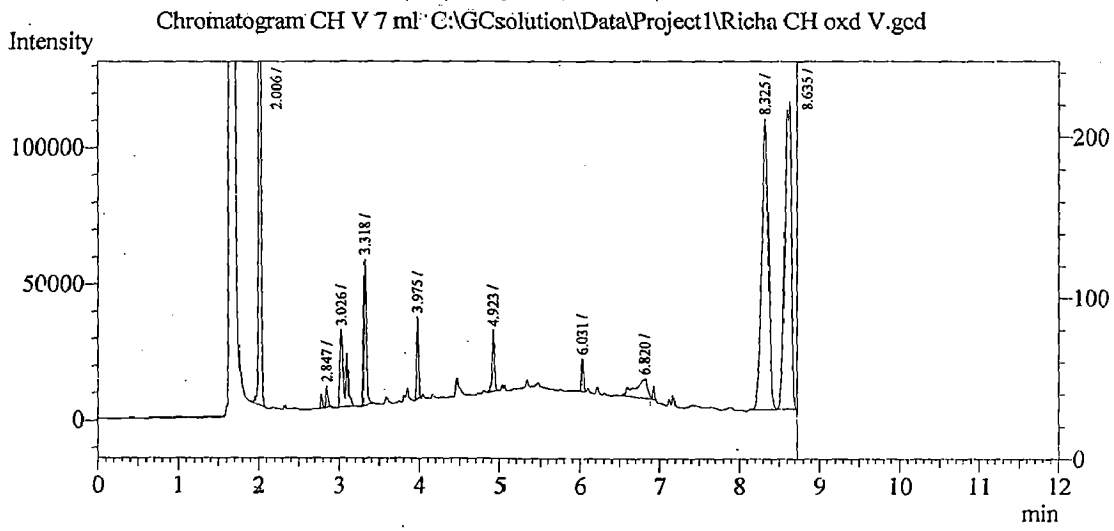
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.014 | 407167 | 240500 | 26.9662 |
| 2 | 2.847 | 18666 | 5988 | 1.2362 |
| 3 | 3.018 | 112953 | 28037 | 7.4808 |
| 4 | 3.313 | 79812 | 33244 | 5.2858 |
| 5 | 3.972 | 52762 | 26433 | 3.4943 |
| 6 | 6.500 | 117436 | 6312 | 7.7776 |
| 7 | 7.438 | 342324 | 33307 | 22.6717 |
| 8 | 7.837 | 325771 | 44057 | 21.5755 |
| 9 | 8.241 | 53024 | 5511 | 3.5117 |
| Total | | 1509915 | 423389 | 100.0000 |

Figure 5b. Gas Chromatogram of solvent volume variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, Time 6h, 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: 7 mL

Sample Information

Analysis Date & Time : 4/30/2012 7:26:04 PM
User Name : Admin
Vial# : 1
Sample Name : CH V 7 ml 10 mL
Sample ID : Richa CH V




Peak Table - Channel 1

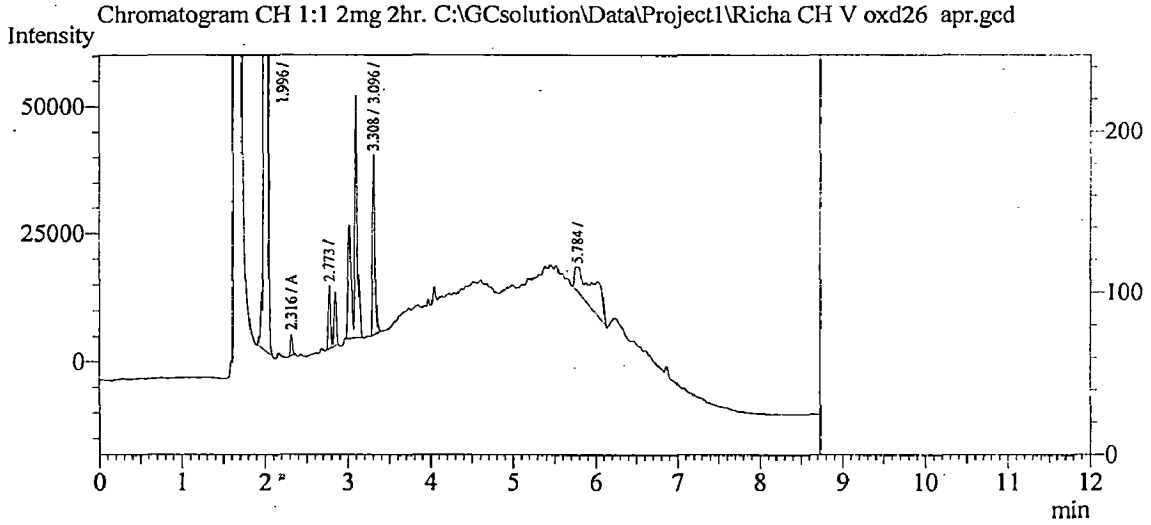
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.006 | 782290 | 498272 | 31.2948 |
| 2 | 2.847 | 21898 | 7721 | 0.8760 |
| 3 | 3.026 | 117138 | 28537 | 4.6860 |
| 4 | 3.318 | 114102 | 52920 | 4.5645 |
| 5 | 3.975 | 51743 | 30129 | 2.0699 |
| 6 | 4.923 | 46056 | 22201 | 1.8424 |
| 7 | 6.031 | 19490 | 11826 | 0.7797 |
| 8 | 6.820 | 81756 | 7161 | 3.2706 |
| 9 | 8.325 | 614495 | 106404 | 24.5823 |
| 10 | 8.635 | 650779 | 112573 | 26.0338 |
| Total | | 2499747 | 877744 | 100.0000 |

Figure 5c. Gas Chromatogram of solvent volume variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, Time 6h, 1:3 $C_6H_{12}/H_2O_2$, $CH_3CN$ Volume: **10 mL**

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/26/2012 7:30:16 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 1:1 2mg 2hr. |
| Sample ID | : ch ox V |




Peak Table - Channel 1

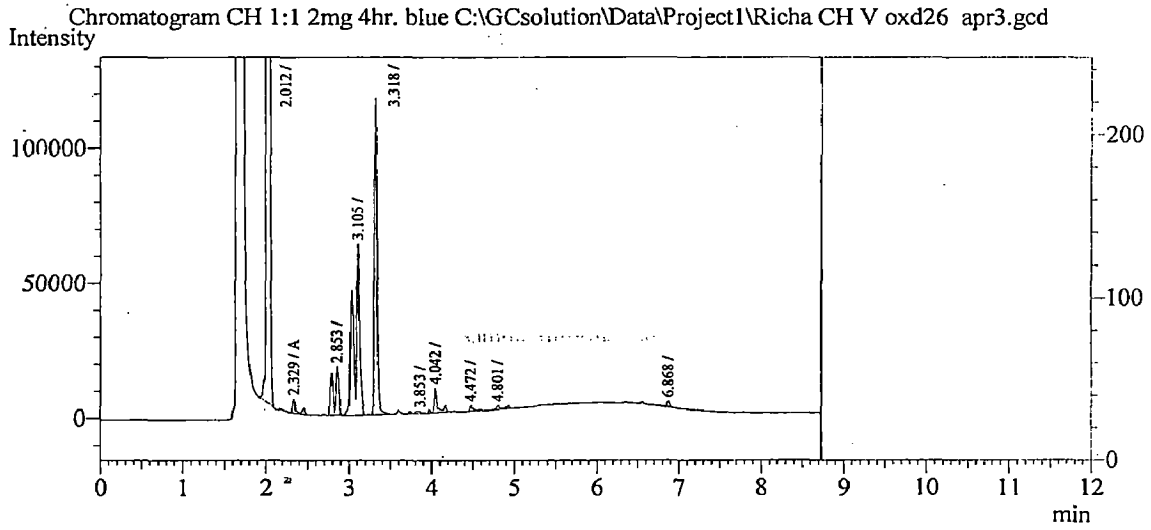
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 1.996 | 8231954 | 5317306 | 95.5049 |
| 2 | 2.316 | 7390 | 4089 | 0.0857 |
| 3 | 2.773 | 45848 | 12069 | 0.5319 |
| 4 | 3.096 | 158226 | 47033 | 1.8357 |
| 5 | 3.308 | 75220 | 35077 | 0.8727 |
| 6 | 5.784 | 100767 | 4821 | 1.1691 |
| Total | | 8619405 | 5420395 | 100.0000 |

Figure 6a. Gas Chromatogram of Cyclohexene/$H_2O_2$ variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, **Time 2h, 1:1 $C_6H_{12}/H_2O_2$,** $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/26/2012 8:16:21 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 1:1 2mg 4hr. blue |
| Sample ID | : ch ox V |




Peak Table - Channel 1

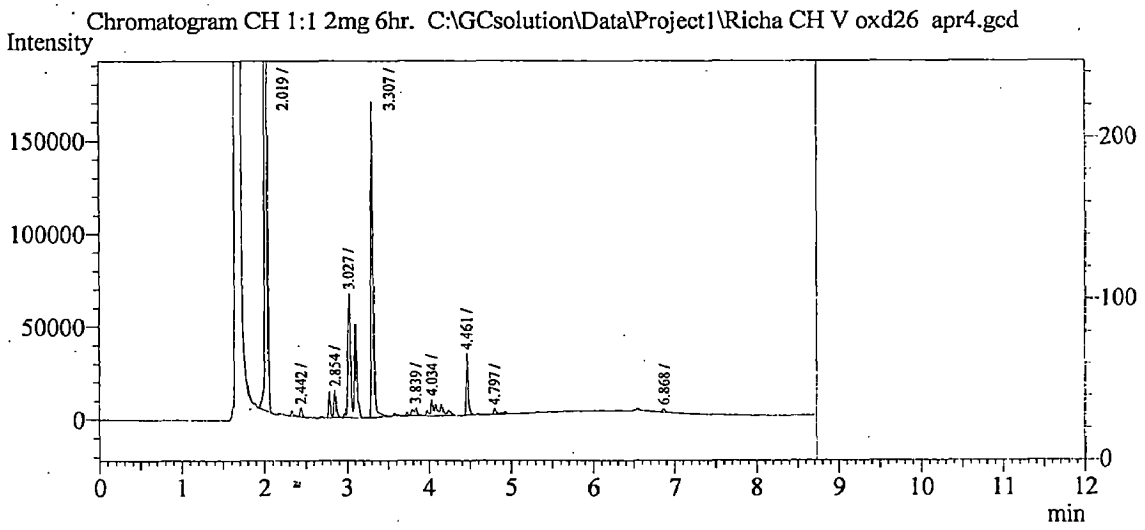
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.012 | 4776278 | 3100861 | 87.5944 |
| 2 | 2.329 | 16198 | 5090 | 0.2971 |
| 3 | 2.853 | 75002 | 17629 | 1.3755 |
| 4 | 3.105 | 279467 | 62884 | 5.1253 |
| 5 | 3.318 | 256270 | 115205 | 4.6998 |
| 6 | 3.853 | 4642 | 811 | 0.0851 |
| 7 | 4.042 | 28388 | 8986 | 0.5206 |
| 8 | 4.472 | 5234 | 2038 | 0.0960 |
| 9 | 4.801 | 7071 | 1498 | 0.1297 |
| 10 | 6.868 | 4171 | 2098 | 0.0765 |
| Total | | 5452721 | 3317100 | 100.0000 |

Figure 6b. Gas Chromatogram of Cyclohexene/$H_2O_2$ variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, **Time 4h, 1:1 $C_6H_{12}/H_2O_2$,** $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/26/2012 8:28:17 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 1:1 2mg 6hr. |
| Sample ID | : ch ox V |




Peak Table - Channel 1

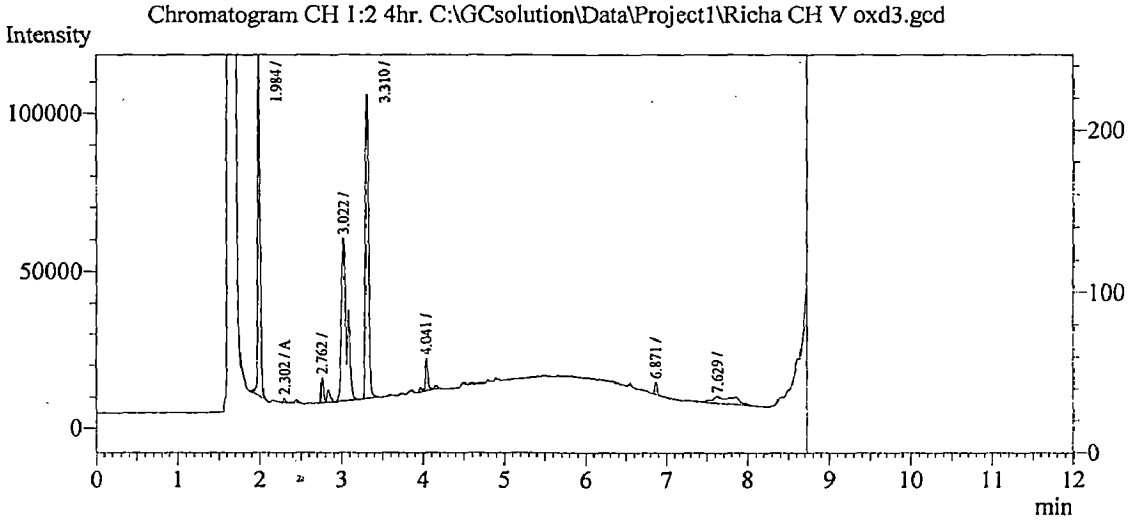
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.019 | 1014642 | 657475 | 56.2934 |
| 2 | 2.442 | 15212 | 5043 | 0.8440 |
| 3 | 2.854 | 47946 | 14467 | 2.6601 |
| 4 | 3.027 | 255585 | 66827 | 14.1801 |
| 5 | 3.307 | 317702 | 168950 | 17.6264 |
| 6 | 3.839 | 18510 | 4415 | 1.0270 |
| 7 | 4.034 | 62856 | 8821 | 3.4873 |
| 8 | 4.461 | 54846 | 32616 | 3.0429 |
| 9 | 4.797 | 10882 | 3143 | 0.6037 |
| 10 | 6.868 | 4235 | 1900 | 0.2350 |
| Total | | 1802416 | 963657 | 100.0000 |

Figure 6c. Gas Chromatogram of Cyclohexene/$H_2O_2$ variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, **Time 6h, 1:1 $C_6H_{12}/H_2O_2$,** $CH_3CN$ Volume: 5 mL

Sample Information

Analysis Date & Time : 4/25/2012 8:00:08 PM
User Name : Admin
Vial# : 1
Sample Name : CH 1:2 4hr.
Sample ID : ch ox V




Peak Table - Channel 1

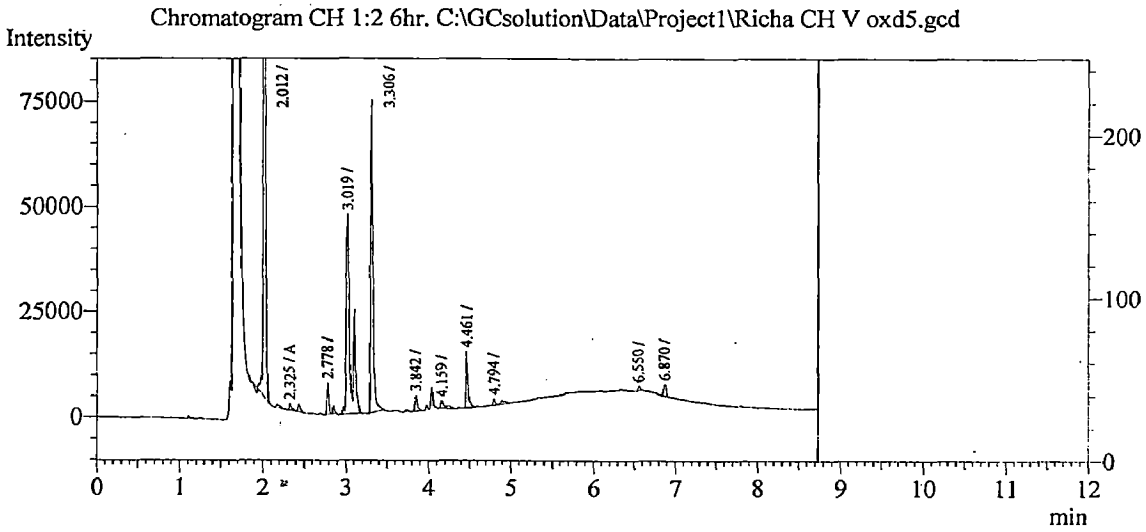
| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 1.984 | 252770 | 134560 | 29.6806 |
| 2 | 2.302 | 4174 | 1332 | 0.4901 |
| 3 | 2.762 | 27489 | 7888 | 3.2278 |
| 4 | 3.022 | 233436 | 51676 | 27.4105 |
| 5 | 3.310 | 250672 | 96216 | 29.4343 |
| 6 | 4.041 | 28536 | 10272 | 3.3507 |
| 7 | 6.871 | 8424 | 3763 | 0.9892 |
| 8 | 7.629 | 46130 | 2213 | 5.4167 |
| Total | | 851631 | 307920 | 100.0000 |

Figure 6e. Gas Chromatogram of Cyclohexene/$H_2O_2$ variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, **Time 4h, 1:2 $C_6H_{12}/H_2O_2$**, $CH_3CN$ Volume: 5 mL

Sample Information

| | |
|---|---|
| Analysis Date & Time | : 4/25/2012 8:36:53 PM |
| User Name | : Admin |
| Vial# | : 1 |
| Sample Name | : CH 1:2 6hr. |
| Sample ID | : ch ox V |




Peak Table - Channel 1

| Peak# | Ret.Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 2.012 | 356789 | 219131 | 47.5431 |
| 2 | 2.325 | 8697 | 1503 | 1.1589 |
| 3 | 2.778 | 14329 | 7372 | 1.9093 |
| 4 | 3.019 | 173399 | 47274 | 23.1059 |
| 5 | 3.306 | 146353 | 73434 | 19.5019 |
| 6 | 3.842 | 7155 | 3636 | 0.9534 |
| 7 | 4.159 | 6365 | 1745 | 0.8482 |
| 8 | 4.461 | 24386 | 13056 | 3.2494 |
| 9 | 4.794 | 5158 | 1473 | 0.6873 |
| 10 | 6.550 | 1992 | 943 | 0.2655 |
| 11 | 6.870 | 5831 | 2733 | 0.7771 |
| Total | | 750454 | 372300 | 100.0000 |

Figure 6f. Gas Chromatogram of Cyclohexene/$H_2O_2$ variation. The reaction conditions are given below.

Catalyst Wt.: 2 mg, **Time 6h, 1:2 $C_6H_{12}/H_2O_2$,** $CH_3CN$ Volume: 5 mL