Communication

A Mild Catalytic Oxidation System: FePcOTf/H₂O₂ Applied for Cyclohexene Dihydroxylation

Baocheng Zhou [1,2] and Wenxing Chen [2,*]

[1] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China;
E-Mail: zhoubc1982@163.com
[2] Key Laboratory of Advanced Textile Materials and Manufacturing Technology,
Ministry of Education of China, Zhejiang Sci-Tech University, Hangzhou 310018, China

* Author to whom correspondence should be addressed; E-Mail: wxchen@zstu.edu.cn;
Tel.: +86-571-86843611.

Academic Editor: Giuseppe Mele

Abstract: Iron (III) phthalocyanine complexes were employed for the first time as a mild and efficient Lewis acid catalyst in the selective oxidation of cyclohexene to cyclohexane-1,2-diol. It was found that the catalyst FePcOTf shown excellent conversion and moderate selectivity relative to other iron (III) phthalocyanine complexes. The optimum conditions of the oxidation reaction catalyzed by FePcOTf/H₂O₂ have been researched in this paper. Iron (III) phthalocyanine triflate (1 mol %) as catalyst, hydrogen peroxide as oxidant, methanol as solvent, and a mole ratio of substrate and oxidant (H₂O₂) of 1:1 were used for achieving moderate yields of 1,2-diols under reflux conditions after eight hours.

Keywords: iron (III) phthalocyanine; cyclohexene; triflate; cyclohexane-1,2-diols

1. Introduction

In 1988, Sharpless and Jacobsen developed the OsO₄/*N*-methylmorpholine *N*-oxide (NMO) oxidation system using cinchona alkaloid derivatives as chiral ligands for the asymmetric dihydroxylation of alkenes to obtain 1,2-diols [1]. 1,2-Diols are useful building blocks in the design of pharmaceuticals [2] and natural product synthesis [3]. These compounds can be synthesized from alkenes through alkene dihydroxylation [4]. As many alkenes can be obtained directly from

petrochemicals, the conversion of alkene to 1,2-diols by oxidation is of great interest in both academia and industry. Although OsO_4 is the most commonly used catalyst, several group VIII transition metal oxides, such as Fe [5–7], Ru [8–10], have been employed to catalyst these dihydroxylations too. The industrial use of OsO_4 is restricted on account of its expensive price and toxic properties. Therefore, several catalysts such as polyoxometalates [11,12], sodium tungstate [13], $Mg_xFe_{3-x}O_4$ complex oxide [14], peroxovanadium [15] and oxorhenium [16] have been developed. However, most of them have limitations such as the usage of stoichiometric oxidants as well as toxic solvents and they suffer from low selectivity, harsh reaction conditions, and cumbersome work-up procedures and thus are not suitable for modern industrial practice. Therefore, it would still be highly desirable to develop new efficient methods for the dihydroxylation reaction, and clean dihydroxylations using hydrogen peroxide under mild conditions continue to be a challenge in catalysis. The selective dihydroxylation of olefins with high efficiency in terms of the amount of H_2O_2 is particularly difficult to achieve.

Metalloporphyrins in oxidation of substrates with various single-oxygen atom donors have played a major role in the understanding of the biologically related reactions of cytochrome P-450 [17], where oxo-metalloporphyrins are the accepted reactive intermediates. There is a stark contrast between the state of the art in porphyrin and phthalocyanine oxidation chemistry. Although phthalocyanine complexes with a similar planar structure to the porphyrins have been actively investigated as oxidation catalysts, their catalytic chemistry is practically undeveloped in terms of mechanisms and identification of the active species involved in these catalytic oxidations [18,19]. Phthalocyanines have demonstrated a wide range of applications in catalytic oxidation reactions, including alkene cyclopropanation [20], C-S bond formation [21], saturated C-H bond amination [22,23], and alkene epoxidation [24]. Our research group has been involved in the development of the catalytic chemistry of metal phthalocyanine complexes [25–28]. As for the phthalocyanine core, two methods were employed to modify the phthalocyanine. The first approach was to modify the parent phthalocyanine ring [22,29,30]. Another possible approach was to modify the parent ring system of the axial ligands, thus obtaining new complexes.

The anionic axial ligands effects of iron (III) porphyrin complexes were researched by Nam [31] and Bell [32–35]. They found that the electronegativity of anionic axial ligands affected the heterolysis or homolysis of oxoiron (IV) porphyrin intermediates, and thus decided the oxidation products. Recently Che and co-workers found that iron (III) porphyrins with triflate ($CF_3SO_3^-$) as a counter anion show higher efficiency in the selective oxidation of terminal aryl and aliphatic alkenes to aldehydes than other counter anions, such as Cl^-, ClO_4^-, and SbF_6^- [36]. As for phthalocyanines, only a few cases have focused on the catalysis of iron (III) phthalocyanines [18,23]. Sorokin [37–39] and McGaff [40,41] reported recently that iron (III) "helmet" phthalocyanines generated by reacting iron (II) phthalocyanines with 14,28-[1, 3-diiminoisoindolinato] species can efficiently epoxidize of olefins using H_2O_2. It was found that the "helmet" plays an important role in the catalytic efficiency of these iron (III) phthalocyanines. White and co-workers recently developed iron (III) phthalocyanines with hexafluoroantimonate as a counter anion [$FePc \cdot SbF_6$] as catalysts showing highly selectivity in C-H amination reactions [23]. As far as we know, there is no report about the selective oxidation of cyclohexenes to 1,2-diols catalyzed by iron (III) phthalocyanines with triflate as a counter anion and using H_2O_2 as an oxidant.

2. Results and Discussion

At the outset, we examined the oxidation of cyclohexene with H_2O_2 using FePcX [23] (generated *in situ* by reacting commercially available FePcCl with AgX; Pc = phthalocyanine; X = NO_3, CF_3SO_3, BF_4, SbF_6) as the catalyst. Treatment of cyclohexene with H_2O_2 (1.0 equiv.) in the presence of a catalytic amount of FePcX (1 mol %) in the DMF at 80 °C (Scheme 1, Table 1) did not produced detectable amounts of 1,2-diol when FePc was employed as a catalyst under these conditions (Table 1, entry 1).
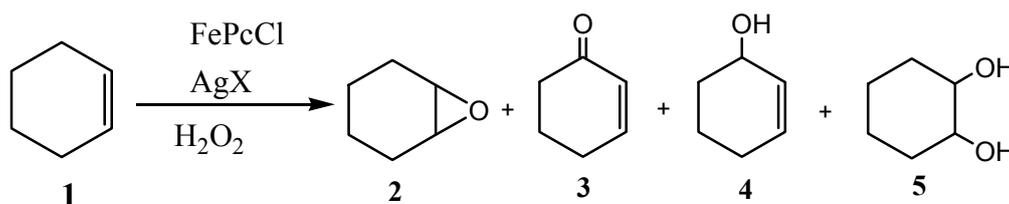
Scheme 1. The iron (III) phthalocyanine catalyzed the oxidation of cyclohexene with H_2O_2.

Table 1. The selective oxidation of cyclohexene to 1,2-diols catalyzed by iron (III) phthalocyanines with different counter anions by using H_2O_2 as an oxidant.

Entry [a]	Catalyst	Conversion (%)	Selectivity (%)			
			Cyclohexene oxide (2)	2-Cyclohexen-1-ol (3)	2-Cyclohexen-1-one (4)	Cyclohexane-1,2-diol (5)
1	FePc	94.0	13.7	32.4	53.9	/
2	FePcCl	85.0	59.1	16.5	21.4	3.0
3	FePcNO₃	92.3	69.6	14.7	13.8	1.9
4	FePcOTf	97.1	20.2	18.6	15.3	45.9
5	FePcBF₄	96.4	32.8	23.1	14.9	29.2
6	FePcSbF₆	94.9	33.1	45.1	21.8	/
7 [b]	AgCl	trace	ND [c]	ND	ND	ND

[a] Conditions: the amount of catalyst was 1 mol %; the mole ratio of substrate and oxidant (H_2O_2) was 1:1; reaction time was 8 h; temperature was 80 °C; solvent was DMF; [b] AgCl was employed in the oxidation reaction under the same conditions; [c] ND means not detected.

As an iron (III) porphyin with a weakly coordinating anion as the axial ligand would have the strong Lewis acidity that is needed for promoting the isomerization of epoxides to aldehydes [42], we tested the activity of five iron (III) phthalocyanines with different coordinating anions is this oxidation reaction. The conversion of cyclohexene was good to excellent in this system. Interestingly, 1,2-diol was detected in this system for the first time, which was totally different from other reports [29,30]. Replacing Cl^- by other anions such as NO_3^-, $CF_3SO_3^-$, BF_4^-, SbF_6^- afforded similar results (Table 1, entries 2–6). According to [42], the Lewis acidity of the metallporphyrins in the solvents used seems to affect the reactivity and selectivity of the oxidation reactions. Phthalocyanines are structurally related to porphyrins, but have a distinct framework from that of porphyrins in that all the *meso* positions of its tetrapyrrolic macrocycle system are substituted with nitrogen atoms [43]. Owing to the electron-withdrawing nature of its *meso* nitrogen atoms, the iron (III) phthalocyanine with the weaker

electron donors (NO_3^-, OTf^-, BF_4^-, SbF_6^-) would be a stronger Lewis acid catalyst than iron (III) phthalocyanine with the stronger electron donors (Cl^-), and thus would be expected to exhibit enhanced reactivity and selectivity toward the oxidation reaction. Indeed, as expected, the amount of 1,2-diol increased obviously when the weaker electron donors were employed (Table 1, entries 2–6). Surprisingly, FePcOTf displayed excellent selectively to obtain 1,2-diol although NO_3^- was the weakest electron donor. To explore the universality of the FePcOTf catalyst, several oxidants were tested as stoichiometric oxidants. Besides H_2O_2, *tert*-butylhydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and O_2 were also tested (Table 2). It was found that the conversion of cyclohexene was good to excellent, however the 1,2-diol was not produced using other oxidants (Table 2, entries 1,2,4). We have also optimized the reaction temperature (Table 3). As for the conversion aspect, the optimum temperature was 50 °C, but the 1,2-diol selectively rose from 17.4% to 45.9% when the reaction temperature was increased to 80 °C (Table 3, entry 3).

Table 2. The selective oxidation of cyclohexene to 1,2-diols catalyzed by iron (III) phthalocyanines with triflate as a counter anion and different oxidants.

Entry [a]	Oxidant	Conversion (%)	Selectivity (%)			
			Cyclohexene oxide (2)	2-Cyclohexen-1-ol (3)	2-Cyclohexene-1-one (4)	Cyclohexane-1,2-diol (5)
1	TBHP	86.0	/	70.7	29.3	/
2	*m*-CPBA	84.0	30.0	42.1	27.9	/
3	30% H_2O_2	97.1	20.2	18.6	15.3	45.9
4 [b]	O_2	46.0	13.7	32.4	53.9	/

[a] Conditions: the amount of catalyst was 1 mol %; the mole ratio of substrate and oxidant was 1:1; reaction time was 8 h; temperature was 80 °C; solvent was DMF; [b] The reaction was carried out in an autoclave under 1.5 MPa pressure.

Table 3. The selective oxidation of cyclohexene to 1,2-diols catalyzed by iron (III) phthalocyanines with triflate as a counter anion by using H_2O_2 as an oxidant at different temperatures.

Entry [a]	Reaction temperature (°C)	Conversion (%)	Selectivity (%)			
			Cyclohexene oxide (2)	2-Cyclohexen-1-ol (3)	2-Cyclohexene-1-one (4)	Cyclohexane-1,2-diol (5)
1	25	91.0	58.2	14.4	13.4	14.0
2	50	97.0	45.3	20.3	18.0	17.4
3	80	97.1	20.2	18.6	15.3	45.9

[a] Condition: the amount of catalyst was 1 mol %; the mole ratio of substrate and oxidant (H_2O_2) was 1:1; reaction time was 8 h; solvent was DMF.

In order to achieve optimum conditions, three different cyclohexene to aqueous 30% H_2O_2 molar ratios, *viz.* 1:1, 1:2, 1:5 were considered for a fixed amount of cyclohexene (10 mmol) and catalyst (1 mol %) in the DMF at 80 °C (Table 4). A maximum of 45.9% selectivity for the 1,2-diol was obtained for a cyclohexene to H_2O_2 molar ratio of 1:1 in 8 h of reaction time. The conversion was 98.0% when the ratio was 1:2 and decreased slightly at 1:5. However, cyclohexene oxide was absent when the ratio to 1:5 (Table 4, entry 3).

Table 4. The selective oxidation of cyclohexene to 1,2-diols catalyzed by iron (III) phthalocyanines with triflate as a counter anion using H_2O_2 as an oxidant at different condition.

Entry [a]	Substrate: oxidant	Conversion (%)	Selectivity (%)			
			Cyclohexene oxide (2)	2-Cyclohexen-1-ol (3)	2-Cyclohexene-1-one (4)	Cyclohexane-1,2-diol (5)
1	1:1	97.1	20.2	18.6	15.3	45.9
2	1:2	98.0	18	30.3	12.5	39.2
3	1:5	97.2	/	30.5	37.5	32.0

[a] Conditions: the amount of catalyst was 1 mol %; reaction time was 8 h; temperature was 80 °C; solvent was DMF.

Under the operating conditions as fixed above, the effect of catalyst considering three different amount viz. 0.1 mol %, 0.2 mol %, 1 mol %, 2 mol % as a function of time was studied and results are listed in Table 5. It is clear that 1 mol % catalyst was the best one to obtain a maximum of 97.1% conversion of cyclohexene and highest selectively for 1,2-diol (Table 5, entry 3).

Table 5. The selective oxidation of cyclohexene to 1,2-diols catalyzed by iron (III) phthalocyanines with triflate as a counter anion by using H_2O_2 as an oxidant at different condition.

Entry [a]	Amount of catalyst (mol %)	Conversion (%)	Selectivity (%)			
			Cyclohexene oxide (2)	2-Cyclohexen-1-ol (3)	2-Cyclohexene-1-one (4)	Cyclohexane-1,2-diol (5)
1	0.1	94.2	20.0	27.4	52.6	/
2	0.5	95.0	15.2	23.1	23.2	37.5
3	1	97.1	20.2	18.6	15.3	45.9
4	2	95.5	20.0	23.2	19.4	37.4

[a] Conditions: the mole ratio of substrate and oxidant (H_2O_2) was 1:1; reaction time was 8 h; temperature was 80 °C; solvent was DMF.

The conversion of cyclohexene and selectivity of the different reaction products under the optimized reaction conditions have been analyzed as a function of time and are presented in Figure 1. The time that the injection of H_2O_2 was finished was defined as the zero time (see the procedure in the Experimental Section). It was clear from the plot that with a conversion of 68% of cyclohexene at the zero time, no 1,2-diol was been detected. After 4 h, 8.4% selectivity of 1,2-diol has been obtained, while the conversion of cyclohexene was 89%. The selectivity of cyclohexene oxide, 2-cyclohexene-1-one, and 2-cyclohexene-1-ol obviously decreased as time goes on. After 8 h, the selectivity for 1,2-diol was the highest and reached 45.9%. At the end of 10 h, a small decrease was detected both in the conversion of cyclohexene and the selectivity of 1,2-diol.
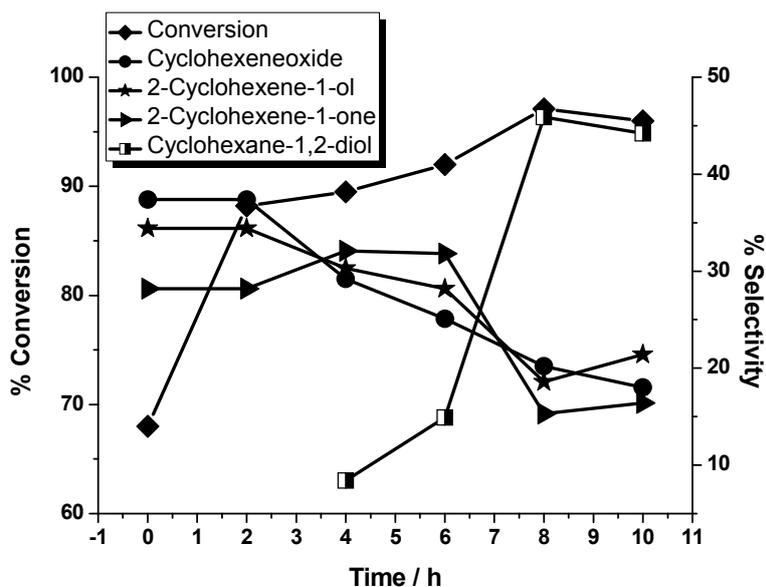
Figure 1. Plots showing percentage selectivity of cyclohexene oxide, 2-cyclohexene-1-one, 2-cyclohexene-1-ol and cyclohexane-1,2-diol formation and percentage conversion of cyclohexene as a function of time. Conditions: the amount of catalyst was 1 mol %; the mole ratio of substrate and oxidant (H_2O_2) was 1:1; temperature was 80 °C; solvent was DMF.

Finally, the influence of solvent (DMF, acetonitrile, methanol) was also been researched (Table 6). 5.0% cyclohexene oxide and 52.0% 1,2-diol have been obtained when using CH_3OH as a solvent, and the conversion of cyclohexene was a little higher than with other solvents. CH_3OH was found to be most suitable solvent in which the iron (III) phthalocyanine complexes showed a lesser protonation tendency and sufficient stability of the formed oxo species [39].

Table 6. The selective oxidation of cyclohexene to 1,2-diols catalyzed by iron (III) phthalocyanines with triflate as a counter anion using H_2O_2 as an oxidant in different solvents.

Entry [a]	Solvent	Conversion (%)	Selectivity (%)			
			Cyclohexene oxide (2)	2-Cyclohexen-1-ol (3)	2-Cyclohexene-1-one (4)	Cyclohexane-1,2-diol (5)
1	CH₃OH	97.5	5.0	24.5	18.5	52.0
2	CH₃CN	97.2	18.2	26.4	14.0	41.2
3	DMF	97.1	20.2	18.6	15.3	45.9

[a] Conditions: the mole ratio of substrate and oxidant (H_2O_2) was 1:1; reaction time was 8 h; the reaction was researched under reflux condition ; the amount of solvent was 3 mL.

High-valent iron oxocomplexes are well-documented and characterized by Sorokin and co-workers. High-valent iron oxocomplexes were considered be the intermediates or active species in the oxidation of olefins [39]. According to the reports, a possible mechanism for the formation of this species is proposed in Scheme 2. It should be noted that all iron (III) phthalocyanine complexes exhibit excellent conversions. However, the iron (III) phthalocyanine complexes with weaker electron donors (*i.e.*, $CF_3SO_3^-$, NO_3^-, BF_4^- and SbF_6^-) as axial ligands gave high selectivity for 1,2-diol in the H_2O_2 reaction, whereas the iron (III) phthalocyanine complexes with the axial ligands of stronger electron

donors (*i.e.*, Cl⁻) gave no 1,2-diol in the H_2O_2 reaction [31]. Although we propose at this time that the electron-donating ability of the anionic axial ligands is an important factor in controlling the catalytic activity of the iron (III) phthalocyanine complexes in the H_2O_2 reactions, more detailed studies are in progress to gain a better understanding of the exact roles of the anionic axial ligands by density functional theory (DFT), low temperature UV-Vis and electrospray ionization mass spectrometry (ESI-MS) [37–39].

X: Cl, OTf, NO_3, BF_4, SbF_6
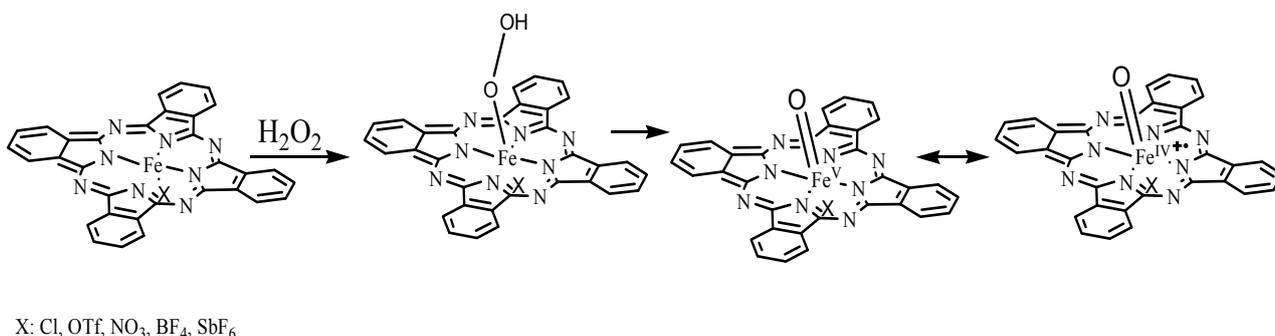
Scheme 2. Proposed mechanism for the formation of high-valent iron oxo-phthalocyanine species.

In summary, a mild oxidation system has been developed to convert cyclohexene into 1,2-diol, with excellent conversion. To the best of our knowledge, this is the first efficient method to prepare 1,2-diols catalyzed by the $FePcOTf/H_2O_2$ system. Such an interesting reactivity and selectivity of $FePcOTf/H_2O_2$ may provide a new strategy for preparing 1,2-diols, even regio- and stereoselective 1,2-diols. Besides, the results provide a rationale for the application of the accessible iron phthalocyanine complexes in catalytic oxidation.

3. Experimental Section

3.1. Materials

Iron (III) phthalocyanine chloride (FePcCl), $AgNO_3$, AgOTf, $AgBF_4$, $AgSbF_6$ cyclohexene, cyclohexene oxide, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, and cyclohexane-1,2-diol were purchased from Aldrich (Sigma-Aldrich Co., Ltd., Shanghai, China) and used as received. Dimethylformamide (DMF), acetonitrile, dichloromethane and methanol of gas chromatography (GC) grade were purchased from Hangzhou Jiachen Chemical Co., Ltd. (Hangzhou, China), as were *tert*-butylhydroperoxide (TBHP, 70% in water), and *m*-chloroperoxybenzoic acid (*m*-CPBA), H_2O_2 (9.7 M) were purchased from Hangzhou Jiachen Chemical Co., Ltd. which were used without further purification. O_2 was provided by Hangzhou Minxing Gas Co., Ltd. (Hangzhou, China).

3.2. Physical Measurements

The GC traces were recorder with a GC-2014C Gas Chromatograph (Shimadzu, Suzhou, China) fitted with an FID detector, using a "Crossbond" 5% diphenyl/95% dimethylpolysiloxane capillary column (30 m length, 0.25 mm ID, 0.25 μm df) . The parameters for analysis were: injector temperature = 250 °C, detector temperature = 260 °C. Temperature program: initial temperature = 40 °C with a 2 min hold,

then warmed up to 105 °C at 5 °C·min^{-1} and held for 0 min, before finally heating up to 230 °C at 20 °C·min^{-1}. Mass spectra were recorded with a 6890N/5973I GC-MS system (Agilent Technologies Co., Ltd., Shanghai, China) coupled with an Agilent Technologies column of 30 m length, 0.25 mm internal diameter and 0.25 μm df.

3.3. General Procedure for the Preparation of 1,2-Diols

FePcCl (60.3 mg, 0.1 mmol) and AgX (0.12 mmol) were added to a two-necked 25 mL round-bottomed flask equipped with a condenser. DMF (3 mL) and cyclohexene (10 mmol) were added. The mixture was refluxed, then H_2O_2 (10 mmol) was added slowly within 30 min. The reaction mixture was allowed to cool to room temperature. The solution was diluted with CH_2Cl_2, and the reaction monitored over time using gas chromatography (GC). The oxidation products were identified by spiking using standards and by measurements of GC retention times in. The identity of products was also determined by a gas chromatograph connected to a mass spectrometer (GC-MS).

4. Conclusions

Several iron (III) phthalocyanines with different counter anions have been researched in the selective oxidation of cyclohexene using H_2O_2 as an oxidant. It was found iron (III) phthalocyanines with triflate as a counter anion was the best catalyst, and cyclohexane-1,2-diol was first detected in this system. A proposed mechanism for the formation of high-valent iron oxo-phthalocyanine species has been given. Besides, many effects were studied to find optimum reaction conditions. Such an amazing reactivity and selectivity of $FePcOTf/H_2O_2$ system may further develop the applied of metal phthalocyanines in catalytic oxidized organic compounds.

Author Contributions

Wenxing Chen has made important contribution to the design and write of the paper. Baocheng Zhou was contribution to the experiment research.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Jacobsen, E.N.; Marko, I.; Mungall, W.S.; Schroeder, G.; Sharpless, K.B. Asymmetric dihydroxylation via ligand-accelerated catalysis. *J. Am. Chem. Soc.* **1988**, *110*, 1968–1970.

2. Jung, J.-K.; Johnson, B.R.; Duong, T.; Decaire, M.; Uy, J.; Gharbaoui, T.P.; Boatman, D.; Sage, C.R.; Chen, R.P.; Richman, J.G.; *et al*. Analogues of acifran: Agonists of the high and low affinity niacin receptors, GPR109a and GPR109b. *J. Med. Chem.* **2007**, *50*, 1445–1448.

3. Padwa, A.; Zhang, H. Synthesis of some members of the hydroxylated phenanthridone subclass of the amaryllidaceae alkaloid family. *J. Org. Chem.* **2007**, *72*, 2570–2582.

4. Gancitano, P.; Cirimina, R.; Testa, M.L.; Fidalgo, A.; Ilharco, L.M.; Pagliaro, M. Enhancing selectivity in oxidation catalysis with sol-gel nanocomposites. *Org. Biomol. Chem.* **2005**, *3*, 2389–2392.

5. Oldenburg, P.D.; Shteinman, A.A.; Lawrence, Q.J. Iron-catalyzed olefin *cis*-dihydroxylation using a bio-inspired *N,N,O*-ligand. *J. Am. Chem. Soc.* **2005**, *127*, 15672–15673.

6. Aciro, C.; Davies, S.G.; Kurosawa, W.; Roberts, P.M.; Russel, A.J.; Thomson, J.E. Highly diastereoselective anti-dihydroxylation of 3-*N,N*-dibenzylaminocyclohex-1-ene N-oxide. *Org. Lett.* **2009**, *11*, 1333–1336.

7. Emmanuvel, L.; Shaikh, T.M.A.; Sudalai, A. NaIO$_4$/LiBr-mediated diastereoselective dihydroxylation of olefins: A catalytic approach to the Prevost—Woodward reaction. *Org. Lett.* **2005**, *7*, 5071–5074.

8. Carl, D.; Robert, R.E. Oxidations with ruthenium tetroxide. *J. Am. Chem. Soc.* **1953**, *75*, 3838–3840.

9. Tony, K.M.S.; Eric, K.W.T.; Vincent, W.F.T.; Ivan, H.F.C.; Qin, J. Ruthenium-catalyzed cis-dihydroxylation of alkenes: scope and limitations. *Chem. Eur. J.* **1996**, *2*, 50–57.

10. Plietker, B.; Niggemann, M. An improved protocol for the RuO$_4$-catalyzed dihydroxylation of olefins. *Org. Lett.* **2003**, *5*, 3353–3356.

11. Venturello, C.; Alneri, E; Ricci, M. A new effective catalytic system for epoxidation of olefins by hydrogen peroxide under phase transfer conditions. *J. Org. Chem.* **1983**, *8*, 3831–3833.

12. Choudhary, V.R.; Patil, N.S.; Chaudhari, N.K.; Bhargava, S.K. Biphasic selective epoxidation of styrene by *t*-butyl hydroperoxide to styrene oxide using potassium chromate or dichromate catalyst in aqueous medium. *Catal. Commun.* **2004**, *5*, 205–208.

13. Sato, K.; Aoki, M.; Takagi, J.; Noyori, R. Organic solvent- and halide-free oxidation of alcohols with aqueous hydrogen peroxide. *J. Am. Chem. Soc.* **1997**, *119*, 12386–12387.

14. Ma, N.; Yue, Y.H.; Hua, W.M.; Gao, Z. Selective oxidation of styrene over nanosized spinel-type Mg$_x$Fe$_{3-x}$O$_4$ complex oxide catalysts. *Appl. Catal. A* **2003**, *251*, 39–47.

15. Choudary, B.M.; Reddy, P.N. A new peroxo vanadium catalyst for selective oxidation of aralkenes to benzaldehydes. *J. Mol. Catal. A: Chem.* **1995**, *103*, L1–L3.

16. Herrmann, W.A.; Weskam, P.T.; Zoller, J.P.; Fishcher, R.W. Methyltrioxorhenium: Oxidative cleavage of CC-double bonds and its application in a highly efficient synthesis of vanillin from biological waste. *J. Mol. Catal. A: Chem.* **2000**, *153*, 49–52.

17. Safari, N.; Bahadoran, F. Cytochrome P-450 model reactions: a kinetic study of epoxidation of alkenes by iron phthalocyanine. *J. Mol. Catal. A: Chem.* **2001**, *171*, 115–151.

18. Mirela, F.L.; Litvić, M.; Vinković, V. A highly efficient biomimetic aromatization of Hantzsch-1, 4-dihydropyridines with t-butylhydroperoxide, catalysed by iron (III) phthalocyanine chloride. *Bioorg. Med. Chem.* **2008**, *16*, 9276–9282.

19. Sorokin, A.B. Phthalocyanine metal complexes in catalysis. *Chem. Rev.* **2013**, *113*, 8152–8191.

20. Mackintosh, H.J.; Budd, P.M.; McKeown, N.B. Catalysis by microporous phthalocyanine and porphyrin network polymers. *J. Mater. Chem.* **2008**, *18*, 573–578.

21. Taniguchi, T.; Idota, A.; Ishibashi, H. Iron-catalyzed sulfonyl radical formations from sulfonylhydrazides and oxidative addition to alkenes. *Org. Biomol. Chem.* **2011**, *9*, 3151–3153.

22. Murahashi, S.; Zhou, X.G.; Komiya, N. Chlorinated phthalocyanine iron (II) complex catalyzed oxidation of alkanes and alkenes with molecular oxygen in the presence of acetaldehyde. *Synlett* **2003**, *3*, 321–324.

23. Paradine, S.M., White, M.C. Iron-catalyzed intramolecular allylic C-H amination. *J. Am. Chem. Soc.* **2012**, *134*, 2036–2039.

24. Seelan, S.; Agashe, M.S.; Srinivas, D.; Sivasanker, S. Effect of peripheral substitution on spectral and catalytic properties of copper phthalocyanine complexes. *J. Mol. Catal. A: Chem.* **2001**, *168*, 61–68.

25. Chen, W.; Lv, W.; Yao, Y.; Xu, M. Highly efficient decomposition of organic dyes by aqueous-fiber phase transfer and in situ catalytic oxidation using fiber-supported cobalt phthalocyanine. *Environ. Sci. Technol.* **2007**, *41*, 6240–6245.

26. Lv, W.; Chen, W.; Li, N.; Xu, M.; Yao, Y. Oxidative removal of 4-nitrophenol using activated carbon fiber and hydrogen peroxide to enhance reactivity of metallophthalocyanine. *Appl. Catal. B Environ.* **2009**, *87*, 146–151.

27. Lv, W.; Li, N.; Chen, W.; Yao, Y. The role of multiwalled carbon nanotubes in enhancing the catalytic activity of cobalt tetraaminophthalocyanine for oxidation of conjugated dyes. *Carbon* **2009**, *47*, 3337–3345.

28. Zhou, B.C.; Chen, W. Preparation and catalytic activity of carbon nanofibers anchored metallophthalocyanine in decomposing acid orange 7. *Materials* **2014**, *7*, 1370–1383.

29. Kasuga, K.; Tsuboi, K.; Handa, M.; Sugimori, T.; Sogabe, K. Oxygen-oxygenation of cyclohexene catalyzed by manganese (III), iron (III) and cobalt (III) complexes of tetra-tert-butylphthalocyanine in the presence of iso-butyraldehyde. *Inorg. Chem. Commun.* **1999**, *2*, 507–509.

30. Sehlotho, N.; Nyokong, T. Catalytic activity of iron and cobalt phthalocyanine complexes towards the oxidation of cyclohexene using tert-butylhydroperoxide and chlorperoxybenzoic acid. *J. Mol. Catal. A: Chem.* **2004**, *209*, 51–57.

31. Nam, W.; Lim, M.H.; Oh, S.Y.; Lee, J.H.; Lee, H.J.; Woo, S.K.; Kim, C.; Shin, W. Remarkable anionic axial ligand effects of iron (III) porphyrin complexes on the catalytic oxygenations of hydrocarbons by H_2O_2 and the formation of oxoiron (IV) porphyrin intermediates by m-chloroperoxybenzoic acid. *Angew. Chem. Int. Ed.* **2000**, *39*, 3646–3649.

32. Stephenson, N.A.; Bell, A.T. A study of the mechanism and kinetics of cyclooctene epoxidation catalyzed by iron (III) tetrakispentafluorophenyl porphyrin. *J. Am. Chem. Soc.* **2005**, *127*, 8635–8643.

33. Stephenson, N.A.; Bell, A.T. The influence of substrate composition on the kinetics of olefin epoxidation by hydrogen peroxide catalyzed by iron (III) [tetrakis(pentafluorophenyl)] porphyrin. *J. Mol. Catal. A: Chem.* **2006**, *258*, 213–235.

34. Stephenson, N.A.; Bell, A.T. Mechanistic study of iron (III) porphyrin triflate (F_{20}TPP)Fe(OTf) catalyzed cyclooctene epoxidation by hydrogen peroxide. *Inorg. Chem.* **2007**, *46*, 2278–2285.

35. Stephenson, N.A.; Bell, A.T. Effects of porphyrin composition on the activity and selectivity of the iron (III) porphyrin catalysts for the epoxidation of cyclooctene by hydrogen peroxide. *J. Mol. Catal. A: Chem.* **2007**, *272*, 108–117.

36. Chen, G.Q.; Xu, Z.J.; Zhou, C.Y.; Che, C.M. Selective oxidation of terminal aryl and aliphatic alkenes to aldehydes catalyzed by iron (III) porphyrines with triflate as a counter anion. *Chem. Commun.* **2011**, *47*, 10963–10965.

37. Afanasiev, P.; Kudrik, E.V.; Millet, J.M.; Bouchu, D.; Sorokin, A.B. High-valent diiron species generated from N-bridged diiron phthalocyanine and H_2O_2. *Dalton Trans.* **2011**, *40*, 701–710.

38. Afanasiev, P.; Kudrik, E.V.; Albrieux, F.; Briois, V.; Koifman, O.I.; Sorokin, A.B. Generation and characterization of high-valent iron oxo phthalocyanines. *Chem. Commun.* **2012**, *48*, 6088–6090.

39. Skobelev, I.Y.; Kudrik, E.V.; Zalomaeva, O.V.; Albrieux, F.; Afanasiev, P.; Kholdeeva, O.A.; Sorokin, A.B. Efficient epoxidation of olefins by H_2O_2 catalyzed by iron "helmet" phthalocyanines. *Chem. Commun.* **2013**, *49*, 5577–5579.

40. Kieler, H.M.; Bierman, M.J.; Guzei, I.A.; Liska, P.J.; MaGaff, R.W. Racemic iron (III) and cobalt (III) complexes containing a new pentadentate "helmet" phthalocyaniate ligand. *Chem. Commun.* **2006**, *31*, 3326–3328.

41. Brown, E.S.; Robinson, J.R.; McCoy, A.M.; McGaff, R.W. Efficient catalytic cycloalkane oxidation employing a "helmet" phthalocyaninato iron (III) complex. *Dalton Trans.* **2011**, *40*, 5921–5925.

42. Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. High-valent metalloporphyrin, Fe(tpp)OTf, catalyzed rearrangement of α,β-epoxy ketones into 1, 2-diketones. *Chem. Commun.* **2002**, 2570–2571.

43. Suda, K.; Nakajima, S.; Satoh, Y.; Takanami, T. Metallophthalocyanine complex, Cr(TBPC)OTf: an efficient, recyclable Lewis acid catalyst in the regio- and stereoselective rearrangement of epoxides to aldehydes. *Chem. Commun.* **2009**, 1255–1257.