

# Bioinspired Non-heme Diiron Catalysts for Olefin Epoxidation with Hydrogen Peroxide in the Presence of Acetic Acid

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**Abstract:** Mild epoxidation of olefins catalyzed by non-heme oxo-bridged diiron(III) complexes with tetradentate *N,N'*-bis(2-pyridylmethyl)-diamine ligand moiety and exchangeable water molecule in each iron center,  $[\text{Fe}_2\text{O}(\text{L}^n)(\text{H}_2\text{O})_2](\text{ClO}_4)_4$  ( $n = 1$  and  $2$ ), have been explored at room temperature with environmental-friendly hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) as oxygen source. A series of substrates such as cyclooctene, cyclohexene, 1-octene, norbornene and 1,2-dihydronaphthalene have been chosen as a representative set of olefins. The epoxide yield and product selectivity has been greatly enhanced upon the addition of acetic acid to the reaction mixture. The catalytic results suggest the involvement of metal-based intermediate in the epoxidation reaction.

**Keywords:** Catalysis, Diiron complex, Epoxidation, Hydrogen peroxide, Non-Heme, Olefins.

## 1. Introduction

Oxidation reactions are among the most elementary steps of all organic transformations and popular routes to prepare epoxides, which are valuable building blocks in synthetic organic chemistry and materials science [1, 2]. The wide use of epoxides stimulated the development of oxidation technologies for olefin epoxidation using various oxygen-donors. Moreover, the discovery of catalytic systems those are efficient, selective, and inexpensive using environmentally friendly conditions is an exciting and challenging scientific goal [3]. Nature has evolved several iron-based enzymes to accomplish oxygenation reactions of a variety of substrates, including the stereospecific oxidation of C=C bonds under physiological conditions [4-9]. These iron enzymes have proved useful in the development of model catalytic systems for olefin epoxidation. Among model systems,  $\mu$ -oxo diferric complexes have received much attention as they represent structural mimics of the active center of methane monooxygenase and related enzymes [10, 11]. These enzymes are very attractive as they catalyze oxygenation reactions of a variety of substrates selectively and under very mild conditions [12, 13]. Inspired by these enzymes, much effort has been invested to design new families of non-heme diiron complexes as structural models [14-18]. Furthermore, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is among the most important oxygen-donor compared with other conventional epoxidation reagents with respect to environmental and economic considerations, because it is a cheaper and more environmentally green as it generates only water as a side product and contains the largest amount of active oxygen species among the known oxidants [19, 20]. Therefore, the combination of iron-based catalysts and green  $\text{H}_2\text{O}_2$  as oxidant is an attractive approach for developing epoxidation methods under eco-friendly reaction conditions. It has also been found that the addition of acetic acid (AcOH) to some non-heme iron-catalyzed oxidation of alkenes by  $\text{H}_2\text{O}_2$  resulted in an increase in both catalytic activity and selectivity towards epoxidation [21]. This effect was originally observed by Jacobsen and co-workers for  $[\text{Fe}(\text{bpmen})(\text{CH}_3\text{CN})_2]^{2+}$  and later extension to

$[\text{Fe}(\text{tpa})(\text{CH}_3\text{CN})_2]^{2+}$ , where the preference for epoxidation was greatly enhanced upon addition of AcOH in presence of  $\text{H}_2\text{O}_2$  [22, 23]. In addition, Stack and co-workers also reported  $[\text{((phen)}_2(\text{H}_2\text{O})\text{Fe})_2(\mu\text{-O})](\text{ClO}_4)_4$  as an efficient epoxidation with in situ generation of peracetic acid from AcOH and  $\text{H}_2\text{O}_2$  as the oxidant [24]. This prompted us to investigate the effect of AcOH on iron-catalyzed olefin epoxidation with  $\text{H}_2\text{O}_2$ .

In this paper, we wish to report the environment-friendly epoxidation of olefins catalyzed by synthesized non-heme oxo-bridged diiron(III) complexes containing  $\text{N}_4$ -donor ligands with green  $\text{H}_2\text{O}_2$  as oxidant at room temperature under mild conditions. The role of AcOH as additive on the catalytic activity and selectivity towards olefin epoxidation has also been investigated in this study.

## 2. Experimental Section

### Materials and Methods

All chemicals were purchased from Sigma Aldrich and were used as received unless otherwise noted. Acetonitrile used for the catalytic epoxidation reactions was distilled over  $\text{CaH}_2$  before use [25]. Cyclohexene was distilled under argon to remove the inhibitor and passed through a silica gel column prior to reaction. The exact active oxygen content of  $\text{H}_2\text{O}_2$  (as ~30% solution in water) was determined iodometrically.

Infrared spectra were recorded in KBr plate with JASCO 5300 FT-IR spectrophotometer. Electronic spectra of samples in acetonitrile were performed on a JASCO V-530 spectrophotometer. The  $^1\text{H}$  NMR spectra were collected on a Bruker 400 MHz NMR spectrometer. Elemental analyses for C, H and N were carried out with a Heraeus Carlo Erba 1108 elemental analyzer. Catalytic epoxidation reactions were monitored with a Perkin Elmer Clarus-500 Gas Chromatograph with FID (Elite-I, Polysiloxane, 15-meter column).

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### Synthesis of Ligands

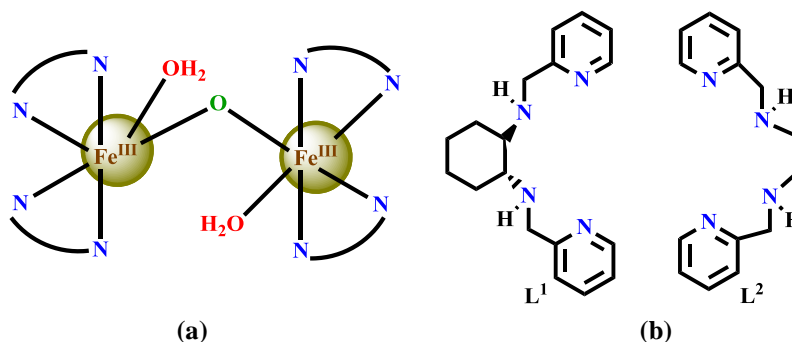
The tetradentate N-donor ligands N, N'-bis(2-pyridylmethyl)-1,2-cyclohexanediamine (**L**<sup>1</sup>) and N,N'-bis(2-pyridylmethyl) ethane-1,2-diamine (**L**<sup>2</sup>) were prepared according to the published procedure [26].

### Synthesis of Diiron(III) Complexes

Oxo-bridged non-heme diiron(III) complexes with ligands **L**<sup>1</sup> and **L**<sup>2</sup> was prepared by adding a solution of Fe(ClO<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O (0.540 g, 1 mmol) in methanol (5 mL) with stirring to a methanolic solution (5 mL) of equivalent amount of the ligand (0.296 g for **L**<sup>1</sup> and 0.242 g for **L**<sup>2</sup>, 1 mmol) at room temperature. The solution was stirred well for 1 h and the resultant brown precipitate was isolated by filtration, washed twice with small quantities of diethyl ether and then dried under vacuum. The brown mass obtained was purified by recrystallization from acetonitrile.

[Fe<sub>2</sub>O(**L**<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (**1**): Yield: 0.51 g (44%). Anal. Calcd. for C<sub>36</sub>H<sub>52</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>8</sub>O<sub>19</sub>: C, 37.44; H, 4.51; N, 9.71. Found: C, 37.15; H, 4.32; N, 9.62%. IR (KBr pellet): selected peaks  $\nu$  (cm<sup>-1</sup>): 798 for Fe-O-Fe<sub>asym</sub>, 1096 for ClO<sub>4</sub><sup>-</sup> ion. Uv-vis (in CH<sub>3</sub>CN)  $\lambda_{max}/nm$  ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 254 (24150), 327 (9630), 489 (850).

[Fe<sub>2</sub>O(**L**<sup>2</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (**2**): Yield: 0.50 g (48%). Anal. Calcd. for C<sub>28</sub>H<sub>40</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>8</sub>O<sub>19</sub>: C, 32.15; H, 3.85; N, 10.71. Found: C, 32.41; H, 3.72; N, 10.58%. IR (KBr pellet): selected peaks  $\nu$  (cm<sup>-1</sup>): 802 for Fe-O-Fe<sub>asym</sub>, 1093 for ClO<sub>4</sub><sup>-</sup> ion. Uv-vis (in CH<sub>3</sub>CN)  $\lambda_{max}/nm$  ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 254 (36500), 324 (18600), 489 (1500).



**Scheme 1:** (a) Proposed Structure of Diiron(III) Complexes; (b) Structure of the Ligands

### Catalytic Olefin Epoxidation

Catalytic epoxidation of olefins using environmentally friendly conditions and inexpensive terminal oxidant is of great significance, because epoxides play a significant role as useful intermediates in various organic syntheses and are also used in the production of drugs, paints, epoxy resins, pesticides and food additives. Thus, the olefin epoxidation ability of the diiron(III) complexes as catalysts with green H<sub>2</sub>O<sub>2</sub> as oxidant has been examined with a wide range of substrate scope at room temperature both in the absence and presence of acetic acid. The epoxidation reaction is carried out in acetonitrile under anaerobic (N<sub>2</sub> atmosphere) conditions with catalyst: oxidant: substrate ratio equal to 1:10:1000.

### Epoxidation of Cis-cyclooctene

The epoxidation of *cis*-cyclooctene was first investigated by the present catalytic system. *Cis*-cyclooctene as a substrate afforded a single-product on reaction with H<sub>2</sub>O<sub>2</sub> catalyzed

### General Catalytic Epoxidation Procedure

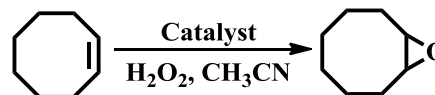
Catalytic epoxidation reactions were carried out under anaerobic conditions in small screw capped vials fitted with PTFE septa. In a typical run, 0.7 mM of catalyst and 700 mM of olefin substrate were dissolved in 2 mL of argon-saturated acetonitrile. The epoxidation reaction was initiated by the addition of 7 mM of H<sub>2</sub>O<sub>2</sub> as oxidant. The mixture was magnetically stirred for 3 h at room temperature (1 h when the epoxidation reaction was carried out in the presence of 50  $\mu$ M of AcOH). The product analysis was done by GC with pentafluoroiodobenzene (PFIB) as internal standard. The products were identified and quantified by a comparison of the GC retention times of the authentic sample and the reaction sample.

## 3. Results and Discussion

### Synthesis and Characterization

Non-heme  $\mu$ -oxo bridged diiron(III) complexes containing exchangeable water molecule in each iron center were synthesized by the reaction of Fe(ClO<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O with equivalent amount of tetradentate N,N'-bis(2-pyridylmethyl)-diamine ligand in methanol at room temperature. The elemental analytical and spectral data are in good agreement with the structure proposed in Scheme 1. Both of them formulated as [Fe<sub>2</sub>O(L<sup>n</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (L<sup>1</sup> for complex **1** and L<sup>2</sup> for complex **2**) on the basis of characterization data.

by diiron (III) complexes resulting only in *cis*-cyclooctene epoxide (Scheme 2). Complex **1** catalyzes the oxidation of cyclooctene to epoxide with 18% conversion of the substrate based on H<sub>2</sub>O<sub>2</sub>. Under the same conditions, substrate conversion decreased to 15% when complex **2** was used as catalyst.



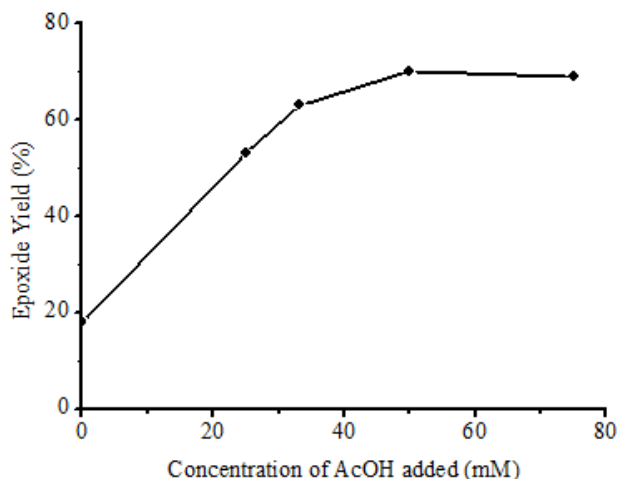
**Scheme 2:** Epoxidation of Cyclooctene by Diiron(III) Complexes

To investigate the effect of acetic acid on cyclooctene epoxidation, preliminary experiments were carried out using complex **1** as catalyst by varying the acetic acid concentration under the similar reaction conditions (Table 1, Fig. 1).

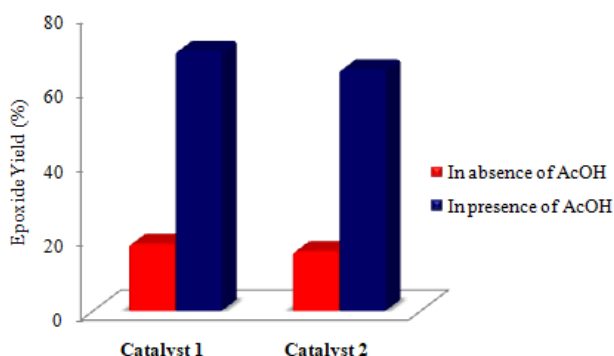
**Table 1:** Effect of Acetic Acid Concentration on Cyclooctene Epoxidation<sup>a</sup>

Entry	AcOH added (mM)	Epoxide Yield (%) <sup>b</sup>
1	0	18
2	25	53
3	35	63
4	50	70
5	75	69

<sup>a</sup>Reaction conditions: Cyclooctene (700 mM), catalyst (0.7 mM), H<sub>2</sub>O<sub>2</sub> (7 mM), CH<sub>3</sub>CN (2 mL), RT; <sup>b</sup>Yields based on oxidant.

**Figure 1:** Variation of Epoxide Yield with Acetic Acid Concentration

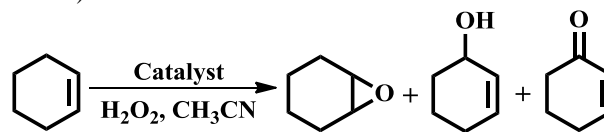
Entry 4 (Table 1) shows that complex **1** catalyzes the oxygenation of cyclooctene with H<sub>2</sub>O<sub>2</sub> to afford maximum epoxide yield of 70% with 50 mM of acetic acid. On the other hand, complex **2** as catalyst promoted 65% cyclooctene epoxidation based on oxidant with H<sub>2</sub>O<sub>2</sub>/AcOH. The results clearly suggested that amount of epoxide obtained was over four-fold higher than that obtained in the absence of acetic acid by catalyst/H<sub>2</sub>O<sub>2</sub> system (Fig. 2). Moreover, addition of AcOH also resulted in an increase in the oxidation rate; the reaction time reduced to 1 h as compared to 3 h in the absence of AcOH.

**Figure 2:** Effect of AcOH on Epoxidation of Cyclooctene

### Epoxidation of Cyclohexene

The epoxidation of relatively reactive alkene, cyclohexene was studied next. Cyclohexene undergoes mainly allylic oxidation forming 2-cyclohexene-1-ol and 2-cyclohexene-1-one as major products, together with a small amount of epoxide product, cyclohexene oxide (Scheme 3). At room

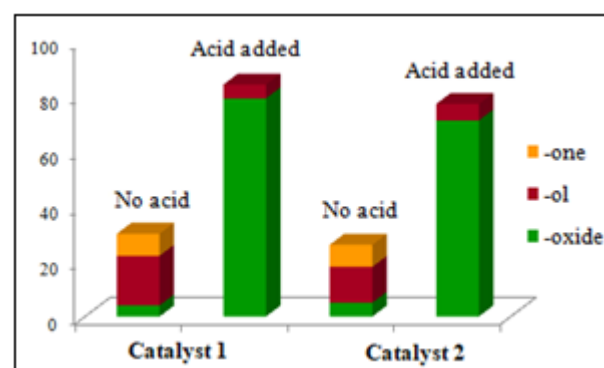
temperature, cyclohexene oxidation catalyzed by diiron complexes with H<sub>2</sub>O<sub>2</sub> provided oxidation products with a combined yield of 30% by **1** and 26% by **2** in acetonitrile with a selectivity of 81-87% for allylic oxidation products (Table 2).

**Scheme 3:** Catalytic Oxidation of Cyclohexene**Table 2:** Catalytic Oxidation of Cyclohexene with H<sub>2</sub>O<sub>2</sub><sup>a</sup>

Catalyst	In absence of acid			In presence of acid				
	Total Yield <sup>b</sup>	Product Selectivity (%) <sup>c</sup>			Total Yield <sup>b</sup>	Product Selectivity (%) <sup>c</sup>		
		-oxide	-ol	-one		-oxide	-ol	-one
1	30	13	60	27	84	94	6	---
2	26	19	50	31	77	92	8	---

<sup>a</sup>Reaction conditions: Cyclohexene (700 mM), catalyst (0.7 mM), H<sub>2</sub>O<sub>2</sub> (7 mM), CH<sub>3</sub>CN (2 mL), RT; <sup>b</sup>Yields based on oxidant; <sup>c</sup>Selectivity is percentage expressed with respect to total yield.

In the presence of acetic acid, epoxidation is favoured over allylic oxidation forming epoxide as the major product. Diiron(III) complex **1** catalyzes the oxygenation of cyclohexene to 79% of epoxide based on H<sub>2</sub>O<sub>2</sub> with the selectivity of 94%. A little amount of allylic oxidation product, 2-cyclohexene-1-ol (5%) was also detected with very low selectivity of 6% and not even a trace amount of subsequent oxidation product cyclohexene-1-one was formed. Total yield of the oxidation products was 84% based on H<sub>2</sub>O<sub>2</sub> (Table 2). Under the same conditions, cyclohexene conversion decreased to 77% when complex **2** was used as catalyst. However, the product profile did not change significantly as that obtained when complex **1** was used as catalyst (Fig. 3). Thus, the formation of cyclohexene oxide without serious competition from the production of 2-cyclohexene-1-ol and 2-cyclohexene-1-one is noteworthy in the presence of AcOH as it is known that cyclohexene is prone to allylic oxidation.

**Figure 3:** Effect of AcOH on Relative Yield of Different Products for Cyclohexene Oxidation

It has been found that both cyclooctene and cyclohexene were not oxidized at all in the absence of catalyst under the similar reaction conditions and very little of products were observed only for cyclohexene oxidation in the presence of Fe(ClO<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O, indicating that diiron(III) complexes have a

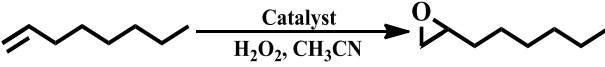
key role as catalyst in the epoxidation reaction in presence of  $H_2O_2$ .

### Epoxidation of Other Olefins

The catalytic results obtained in the epoxidation of cyclooctene and cyclohexene in presence of  $H_2O_2$ /AcOH encouraged us to extend our study on oxidation of other olefins. Hence, the scope of the present catalytic system has also been tested in the epoxidation of 1-octene, norbornene and dihydronaphthalene under the similar reaction conditions.

In metal catalyzed epoxidations, terminal alkenes are known to be least reactive among the olefins [27], yet 1-octene is readily oxidized by  $H_2O_2$  by the diiron(III) catalysts (Table 3). Epoxidation of 1-octene afforded 1,2-epoxyoctane with 14% yield based on  $H_2O_2$  by catalyst **1** whereas the conversion slightly decreases to 12% when complex **2** was used as catalyst. The AcOH enhanced epoxidation by diiron(III) catalysts has also been achieved. Addition of 50 mM of acetic acid to the reaction mixture drastically enhanced the epoxide yield to 68% and 64% by the systems **1**/ $H_2O_2$  and **2**/ $H_2O_2$ , respectively.

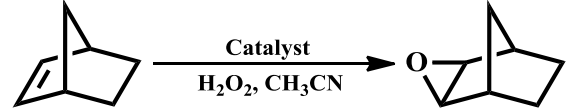
**Table 3:** Catalytic Epoxidation of 1-octene with  $H_2O_2$ <sup>a</sup>

		
Catalyst	Product Yield (%) <sup>b</sup>	
	In absence of AcOH	In presence of AcOH
1	14	68
2	12	64

<sup>a</sup>Reaction conditions: 1-octene (700 mM), catalyst (0.7 mM),  $H_2O_2$  (7 mM),  $CH_3CN$  (2 mL), RT; <sup>b</sup>Yields based on oxidant.

The efficacy of the catalysts was further investigated with norbornene as a substrate. The present oxidizing system selectively oxidizes norbornene to *exo*-epoxynorbornane (Table 4). Norbornene oxidation catalyzed by **1**/ $H_2O_2$  in the presence of acetic acid afforded oxygenates with 42% conversion based on oxidant. However, complex **2** as catalyst provided slightly lower yield of epoxynorborane with 38% conversion. On the other hand, under our standard reaction conditions, the substrate conversion decreased to 14-15% in the diiron complex-catalyzed oxidation of norbornene in absence of AcOH.

**Table 4:** Catalytic Epoxidation of Norbornene with  $H_2O_2$ <sup>a</sup>

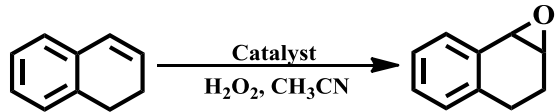
		
Catalyst	Product Yield (%) <sup>b</sup>	
	In absence of AcOH	In presence of AcOH
1	15	42
2	14	38

<sup>a</sup>Reaction conditions: Norbornene (700 mM), catalyst (0.7 mM),  $H_2O_2$  (7 mM),  $CH_3CN$  (2 mL), RT; <sup>b</sup>Yields based on oxidant.

Catalytic epoxidation of dihydronaphthalene was also attempted to cover the wide range of substrate choice (Table 5). Dihydronaphthalene is converted to corresponding epoxide with  $H_2O_2$  with 20% and 15% yields in systems **1**

and **2**, respectively. The presence of 50 mM of acetic acid to the catalytic reaction mixture resulted in a dramatically improvement of the product yield. By using complex **1**, a total conversion of 55% based on oxidant has been achieved whereas the product yield decreased to 50% when complex **2** was used as catalyst by  $H_2O_2$ /AcOH.

**Table 5:** Catalytic Epoxidation of Dihydronaphthalene with  $H_2O_2$ <sup>a</sup>

		
Catalyst	Product Yield (%) <sup>b</sup>	
	In absence of AcOH	In presence of AcOH
1	20	55
2	15	50

<sup>a</sup>Reaction conditions: Dihydronaphthalene (700 mM), catalyst (0.7 mM),  $H_2O_2$  (7 mM),  $CH_3CN$  (2 mL), RT; <sup>b</sup>Yields based on oxidant

The catalytic results presented in Tables 1-5 strongly reflect the role of AcOH on the epoxide yield and selectivity in the oxidation of olefins. Efficient and predominant epoxidation of olefins with an excellent selectivity by the diiron(III) complexes has been achieved with  $H_2O_2$  in the presence of AcOH.

### Mechanistic Considerations

The observation that formation of allylic oxidation products over epoxide in the oxidation of cyclohexene and low epoxide yield in the oxidation of other olefins indicate the involvement of radical-based pathway in the catalytic epoxidation reaction by  $H_2O_2$  in the absence of AcOH [28]. The changes in outcome affected by the addition of AcOH on **1**- and **2**-catalyzed olefin oxidations suggest a potential change in the mechanism to carry out the epoxidation reaction. In the presence of AcOH, both epoxide yield and selectivity has been dramatically enhanced by the present catalytic system with  $H_2O_2$  as oxidant. Moreover, with cyclohexene as substrate, selectivity towards epoxidation has been amplified up to 94%. These results indicated that non-radical species, probably a metal-based intermediate is involved in the epoxidation of olefins [29]. This mechanistic consideration is in agreement with the published results for non-heme iron-complexes that are able to catalyze the stereospecific epoxidation of olefins by  $H_2O_2$  as oxidant [17, 22].

### 4. Conclusion

Oxo-bridged diiron (III) complexes containing  $N_4$ -donor unit in the ligand framework have been readily synthesized from inexpensive and commercially available compounds and characterized by elemental analytical and spectral data. At room temperature epoxidation of a series of olefins has been achieved by the present oxidation system comprising synthesized diiron(III) complexes as catalysts and green  $H_2O_2$  as terminal oxidant under eco-friendly reaction conditions. In all cases, the pronounced effect of addition of AcOH toward catalytic activity of the diiron(III) complexes has been observed with  $H_2O_2$ . The use of AcOH as an additive resulted in an enhancement of both product yield

and selectivity towards epoxidation using H<sub>2</sub>O<sub>2</sub> as compared with the reactivity in the absence of AcOH. The catalytic experimental results suggest that the epoxidation of olefins occurs via a mechanism involving metal-based oxidants by H<sub>2</sub>O<sub>2</sub>/AcOH. The present work thus demonstrates that oxo-bridged non-heme diiron(III) complexes together with environmentally benign H<sub>2</sub>O<sub>2</sub> as oxidant is an efficient, safe, selective and low-cost system for the efficient epoxidation of a wide range of olefins in the presence of acetic acid as additive under eco-friendly reaction condition.

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