

**Supporting Information** 

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Supporting Information

# Practical Iron–Catalyzed Hydrogen Peroxide Epoxidation of Aromatic Olefins Using a Combination of Two Kinds of Simple Picolinate Ligands under Halide–Free Reaction Conditions

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### 1. Instrumentation and Chemicals

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on JEOL 400 MHz NMR spectrometers. All spectra were recorded at  $25 \pm 1$  °C. Chemical shifts ( $\delta$ ) are in parts per million relative to tetramethylsilane at 0.00 ppm for <sup>1</sup>H and relative to residual CHCl<sub>3</sub> at 77.0 ppm for <sup>13</sup>C unless otherwise noted. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 using an INERT CAP column (0.25 mm x 30 m, GL Sciences Inc.). All samples were analyzed and quantified by using biphenyl as an internal standard. Electron spray mass spectra were measured on a Waters micromass ZQ mass spectrometer. Characteristic fragments with their relative intensities in percentages are shown. Melting points were measured with a Mettler FP90 microscope on an object slide. Elemental analyses, data were collected on a Bruker APEX-II CCD diffractometer using graphite-monochromated Mo<sub>Kα</sub> radiation. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares techniques on *F*<sup>2</sup> (SHELXL-97).

2-Picolinic acid (picH), 6-methyl-2-picolinic acid (Me-picH), styrene, 4-methylstyrene,  $\alpha$ -methylstyrene, *cis*- $\beta$ -methylstyrene, *trans*- $\beta$ -methylstyrene, styrene oxide, *trans*-stilbene, trans-stilbene oxide, 1-octene, cyclooctene, epoxycyclooctane, 4-methoxystyrene, 4-nitrostyrene, 1,2-epoxycyclohexane,  $\alpha$ -Pinene,  $\alpha$ -Pinene oxide and biphenyl were purchased from Tokyo Kasei Inc., iron(II) acetate, 4-fluorostyrene, 4-chlorostyrene, 4-bromostyrene, 4-(trifluoromethyl)styrene, from 4-phenylstyrene, *N-tert*-butyl- $\alpha$ -phenylnitrone, and 4-chlorostyrene oxide were Shigma-Aldrich, iron(III) nitrate nonahydrate, iron(III) chloride, 1,2-epoxyoctane, duroquinone, N,N'-dimethylacetamide, cyclohexene, toluene, THF, pyridine, tBuOH, Et<sub>3</sub>N, CDCl<sub>3</sub>, and MeCN were from Wako Pure Chemical Industries, Ltd., 35% hydrogen peroxide aqueous solution was from Kanto Chemical Co., Inc., and iron(III) acetate hydroxide was form Kishida Inc., respectively. All chemicals were used as received. 4-Bromostyrene oxide, 4-fluorostyrene oxide, 4-(trifluoromethyl)styrene oxide, 4-methylstyrene oxide, 4-phenylstyrene oxide,  $\alpha$ -methylstyrene oxide, cis-\beta-methylstyrene oxide, and trans-\beta-methylstyrene oxide were prepared according to literature.<sup>[1]</sup> Oxidation reactions of styrenes in small scale were performed using ChemiStation (Tokyo Rika Inc.) equipped with thermostated apparatus.

### 2. Experimental procedures for Epoxidation of styrene derivatives

### Preparation of catalyst solution.

Iron(II) acetate (43.5 mg, 0.25 mmol), picH (30.8 mg, 0.25 mmol), and Me-picH (34.3 mg, 0.25 mmol) were suspended in CH<sub>3</sub>CN (20 mL). The mixture was warmed to 40 °C with gentle stirring until almost all of iron acetate was dissolved (ca. 15 min), then the solution was filtered with membrane filter (pour size: 0.20  $\mu$ m). The filtrate was diluted with CH<sub>3</sub>CN, to adjust the total volume to 25 mL (the concentration of iron: 0.01 mol·L<sup>-1</sup>). The catalyst solutions with the different ligand ratio were also prepared in the same manner using the appropriate amount of picH and Me-picH. This procedure was also applied for preparation of catalyst solution with other iron salts such as iron(III) nitrate.

### Typical procedure for the epoxidation reaction.

Olefin (1.0 mmol) was dissolved in 2 mL of the catalyst solution. 35% aqueous H<sub>2</sub>O<sub>2</sub> (112.8 µL, 1.25 mmol) was added dropwise to the solution via a syringe pump for 10 min at 25 °C, and the reaction solution was further stirred for 5 min at 25 °C. To the resulting mixutre was then added 10mL of CH<sub>3</sub>CN and measured amount of biphenyl (as an internal standard for GC analysis). The conversion of substrate and the yield of styrene oxide were determined by GC analysis. Products were identified by comparison to the GC retention time of authentic samples. The same reaction was performed three times for each substrate, confirming the errors of less than 5% in conversion and yield for each runs.

#### Epoxidation of styrene (100-g scale).

Styrene (100 g, 0.96 mol) was dissolved in 1.92 L of the catalyst solution prepared above. To the solution was added 35% aqueous H<sub>2</sub>O<sub>2</sub> (106 mL, 1.2 mol) dropwise via a dropping funnel for 30 min at 25 °C, and the reaction solution was further stirred for 5 min at 25 °C. Saturated sodium thiosulfate solution (25 mL) was added to the resulting solution, and the mixture was stirred for another 5 min at 25 °C. The organic layer was separated, and CH<sub>3</sub>CN was removed by rotary evaporator. The residual crude product was purified by distillation under reduced pressure (62 – 65 °C at 4.0 mmHg), to give 92.7 g of styrene oxide (80% yield). The structure was characterized by <sup>1</sup>H and <sup>13</sup>CNMR analyses. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.77$  (dd, J = 5.5, 2.5 Hz, 1H), 3.11 (dd, J = 5.5, 4.0 Hz, 1H), 3.83 (dd, J = 4.0, 2.5 Hz, 1H), 7.21 – 7.35 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 51.1$ , 52.2, 125.4, 128.1, 128.4, 137.5.

## Synthesis of Fe<sup>III</sup>(pic)(Me-pic)<sub>2</sub>.

Fe<sup>II</sup>(OAc)<sub>2</sub> (174 mg, 1.00 mmol), picH (123.2 mg, 1.00 mmol) and Me-picH (274.4 mg, 2.00 mmol)

were suspended in MeCN (80 mL). The mixture was warmed to 40 °C with gentle stirring until almost all of the iron acetate was dissolved (ca. 15 min). The solution was then filtered. Recrystallization from MeCN afforded pure  $Fe^{III}(pic)(Me-pic)_2$  1 (207.8 mg, 0.462 mmol, 46% yield) as pale yellow crystals. M.p. 227 °C (decomp.); MS (ESI+) m/z (%): 465 (7) [Fe (Me-pic)<sub>3</sub> + H]<sup>+</sup>, 451 (16) [Fe(pic)(Me-pic)<sub>2</sub> + H]<sup>+</sup>, 437 (5) [Fe(pic)<sub>2</sub>(Me-pic) + H]<sup>+</sup>, 138 (100) [Me-picH + H]<sup>+</sup>; Anal. Calcd for C<sub>20</sub>H<sub>16</sub>FeN<sub>3</sub>O<sub>6</sub>: C 53.36; H 3.58; N 9.33. Found: C 53.35; H 3.42; N 9.29.

#### 3. NMR spectroscopy / Evans method

In a typical experiment, catalyst solution prepared in CD<sub>3</sub>CN (concentration of iron: 10mM) was placed in the sample tube. The coaxial insert as internal reference was filled with CD<sub>3</sub>CN, placed inside the sample tube and then sealed with the suitable cap. <sup>1</sup>H NMR was obtained and referenced as usual, with the paramagnetically–shifted solvent peak occuring downfield of the reference solvent peak.

The equation  $\mu_{\text{eff}} / \mu_{\text{B}} = 2.828 (\chi_{\text{M}}T)^{1/2}$  was used for the calculation of the magnetic moment, where *T* is the temperature of the measurement (298 K) and  $\chi_{M}$  is determined by the following equation (Eq. S1).<sup>[2]</sup>

$$\chi_M^p = \left( \begin{array}{cc} \frac{3\Delta f}{4\pi fm} + \chi_0 + \frac{\chi_0(d_0 - d_S)}{m} \end{array} \right) \cdot M^p - \chi_M^{\text{dia}}$$
(S1)

where,

 $\chi_M^P$  = Molar paramagnetic susceptibility (cm<sup>3</sup>·mol<sup>-1</sup>)  $\Delta f$  = Frequency difference between the two peaks of the inner and outer tube (Hz) f = Frequency of the NMR instrument (Hz) m = Mass of the substance in 1 cm3 of solution (g·cm<sup>-3</sup>)  $\chi_0$  = Mass susceptibility of the solvent (cm<sup>3</sup>·mol<sup>-1</sup>)  $d_0$  = Density of the solvent (g·cm<sup>-3</sup>)  $d_s$  = Density of the solution (g·cm<sup>-3</sup>)  $M^P$  = Molecular weight of the substance (g·mol<sup>-1</sup>)  $d_0$ 

 $\chi_M^{\text{dia}}$  = Diamagnetic correction to the magnetic susceptibility (cm<sup>3</sup>·mol<sup>-1</sup>)

The densities of the solutions were found almost equal to that of solvent because of the relatively low concentration, and so the  $(d_0-d_s)/m$  term was neglected. Diamagnetic corrections were calculated form Pascal's constants to be found insignificant, and were not applied.  $M^P$  values of  $[Fe(pic)(Me-pic)_2] = 450.21$ , based on the expected formulae from ESI-MS observation, was tentatively used for the calculation. The effective magnetic moments were determined by average of three independent runs, to be  $\mu_{eff} = 5.1 \mu_B$ . This result indicate that the iron ion is high-spin Fe<sup>III</sup> in the catalyst solutions.

### 4. Epoxidation using Fe(pic)(Me-pic)<sub>2</sub> catalyst (1)

Styrene (114.6  $\mu$ L, 1.0 mmol), **1** (9.0 mg, 0.02 mmol), and MeCN (2 mL) were added into test tube. 35% aqueous H<sub>2</sub>O<sub>2</sub> (112.8  $\mu$ L, 1.25 mmol) was added to the solution dropwise via a syringe pump for 10 min at 25 °C, and the reaction solution was further stirred for 5 min at 25 °C. To the resulting mixutre was then added 10mL of CH<sub>3</sub>CN and measured amount of biphenyl (as an internal standard for GC analysis). The conversion of substrate and the yield of styrene oxide were determined by GC analysis. The addition of 0.02 eq. of picH to the same reaction diminished the yield of styrene oxide (15% yield).

Table S1. Epoxidation of styrene with 35% H<sub>2</sub>O<sub>2</sub> using 1 in the presence of various solvents<sup>[a]</sup>



Entry	Solvent [mL]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>	Sel. [%] <sup>[c]</sup>
1	none	0	0	0
2	MeCN [2]	98	93	95
3	Toluene [2]	0	0	0
4	THF [2]	19	13	68
5	<i>t</i> BuOH [2]	81	59	73
6	Pyridine [2]	33	3	9

[a] Reaction was run using styrene (1.0 mmol), 35% H<sub>2</sub>O<sub>2</sub>, and **1** in a 100:125: 2 molar ratio at 25 °C for 15 min in the presence of various solvent (2 mL). [b] Determined by GC analysis. [c] 100 x yield / conversion.

Table S2. Epoxidation of styrene with 35% H<sub>2</sub>O<sub>2</sub> using Iron catalysts <sup>[a]</sup>

	1.25 eq. 35% 0.02 eq. iron MeCh 25 °C, 15	% H <sub>2</sub> O <sub>2</sub> aq. <u>n catalyst</u> N 5 min		)
Entry	Iron catalyst (with additive) [eq.]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>	Sel. [%] <sup>[c]</sup>
1	1 [0.02]	98	93	95
2	<b>1</b> [0.02] + picH [0.02]	18	15	83
3	1 [0.02] + Me-picH [0.02]	78	66	85

[a] Reaction was run using styrene (1.0 mmol), 35% H<sub>2</sub>O<sub>2</sub>, and iron catalyst (with additive) in a 100:125: 2 molar ratio at 25 °C for 15 min in MeCN (2 mL) solution. [b] Determined by GC analysis. [c] 100 x yield / conversion.

Table S3. Epoxidation of styrene with 35%  $H_2O_2$  using 1 in the presence of various radical trapping agents<sup>[a]</sup>

	$\frac{1.25 \text{ eq. } 35\%}{0.02 \text{ eq. } 1}$	$H_2O_2$ aq.		
	25 °C, 1 Radical trap	15 min ping agents		
Entry	Radical trapping agent [eq.]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>	Sel. [%] <sup>[c]</sup>
1	none	98	93	95
2	BPN [0.02] <sup>[d]</sup>	97	90	93
3	BPN [1]	34	21	62
4	Duroquinone[0.02]	95	88	93
5	Duroquinone[1]	92	83	90

[a] Reaction was run using styrene (1.0 mmol), 35% H<sub>2</sub>O<sub>2</sub>, and Fe(Pic)(Me-Pic)<sub>2</sub> in a 100:125: 2 molar ratio at 25 °C for 15 min in the presence of various radical trapping agents. [b] Determined by GC analysis. [c] 100 x yield / conversion. [d] BPN = N-tert-Butyl- $\alpha$ -phenylnitrone.

## 5. Hammett plots for epoxidation of *p*-styrene derivatives

A test tube equipped with a magnetic stirring bar and a reflux condenser was charged with 1.0 mmol of *p*-substituted styrene, 1.0 mmol of styrene, and 4.5 mg (0.01 mmol) of **1**. After the mixture was vigorously stirred at 25 °C for 1 min, 0.02 ml (0.20 mmol) of aqueous 35% H<sub>2</sub>O<sub>2</sub> was added dropwise over the course of 3 min, and **1** was then separated by filtration. The disappearance of the substrates was monitored by GC analysis with 0.2 mmol of internal standard, typically biphenyl. Initial relative rates (log( $k_X/k_H$ )) thus determined were 1.06 (*p*-OMe), 0.50 (*p*-Me), 0.00 (*p*-H), -0.14 (*p*-Cl), and -0.64 (*p*-NO<sub>2</sub>), respectively.

Entry	p-substituents(X)	Conv. of <i>p</i> -X[%] <sup>[b]</sup>	Conv. of <i>p</i> -H [%] <sup>[b]</sup>
1	Me	7.7	2.5
2	Cl	2.5	3.5
3	OMe	11.4	1.0
4	NO <sub>2</sub>	1.6	7.2

Table S4. Competitive oxidation of *p*-substituted styrenes<sup>[a]</sup>

[a] Reaction was run using a 1:1 mixture of styrene and *p*-substituted styrenes (2.0 mmol), 35%  $H_2O_2$ , and 1 in a 100:10:0.5 molar ratio at 25 °C for 3 min. [b] Determined by GC analysis.



Figure S1. Hammett Plot

#### 6. Epoxidation of styrene using various iron metal precursors

Preparation of catalyst solution with other iron metal salts and epoxidation reaction of styrene were performed according to procedures described above. The results were summarized in Table S5. Iron(III) acetate-hydroxide showed similar reactivity with that prepared from iron(II) acetate (Entries 1 and 2). Iron(III) nitrate could also be used (Entry 3), however, 0.06 equiv of base, such as triethylamine, was required for the reaction (Entry 4). In this case, larger amount of base also inhibited the reaction (Entry 5). On the other hand, iron(III) chloride was ineffective (Entries 6 and 7), presumably because of inactivation of the catalyst by the coordination of chloride toward iron ion, or catalytic degradation of  $H_2O_2$  by chloride anion.<sup>[3]</sup>

	1.4 eq. 35% H 0.02 eq. iron 0.02 eq. picH 0.02 eq. Me-p 25 °C, 15	I <sub>2</sub> O <sub>2</sub> aq. <u>bicH</u> →	∕_°
Entry	Iron precursor	Conversion, % <sup>[b]</sup>	Yield, % <sup>[b]</sup>
1	Fe <sup>II</sup> (OAc) <sub>2</sub>	99	95
2	Fe <sup>III</sup> (OAc) <sub>2</sub> (OH)	99	84
3	$Fe^{III}(NO_3)_3 \cdot 9H_2O + 0.06$ equiv Et <sub>3</sub> N	99	83
4	$Fe^{III}(NO_3)_3 \cdot 9H_2O$	0	0
5	$Fe^{III}(NO_3)_3 \cdot 9H_2O + 0.08$ equiv Et <sub>3</sub> N	0	0
6	Fe <sup>III</sup> Cl <sub>3</sub>	25	18
7	$Fe^{III}Cl_3 + 0.06$ equiv $Et_3N$	0	0

Table S5. Epoxidation of styrene with 35% H<sub>2</sub>O<sub>2</sub> using various iron metal precursors<sup>[a]</sup>

[a] Reaction conditions:  $H_2O_2$ : styrene : Fe : picH : Me-picH = 140 : 100 : 2 : 2 : 2 molar ratio in CH<sub>3</sub>CN with substrate concentration of 500 mM, 25 °C, dropwise addition of  $H_2O_2$  for 10 min and further stirring for 5 min. [b] Determined by GC using biphenyl as an internal standard. Average of three runs.

## 7. ESI-MS spectra of 1

ESI-MS measurements were preformed with a Waters micromass ZQ mass spectrometer in the positive ion mode. Direct introduction of a sample (complex 1 in MeCN) into the mass spectrometer was carried out by using syringe-pump. Data were collected at a capillary voltage of 3500 V, a sample cone voltage of 30 V, a desolvation temperature of 150 °C, and a source temperature of 80 °C. Each data was identified by using isotopic pattern.



Figure S2. ESI-MS spectrum



Exact Mass: 437.03

+H ő

Exact Mass: 451.05



 $Chemical \ Formula: \ C_{19}H_{15}FeN_3O_6^+ \quad Chemical \ Formula: \ C_{20}H_{17}FeN_3O_6^+ \quad Chemical \ Formula: \ C_{21}H_{19}FeN_3O_6^+ \quad Chemical \ Formula: \ C_{21}H_{21}FeN_3O_6^+ \quad Chemical \ Formula: \ Chemical \ Formula: \ Chemical \ Formula: \ Chem$ Exact Mass: 465.06





=0

Chemical Formula: C<sub>32</sub>H<sub>24</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>10</sub> Exact Mass: 750.02

Chemical Formula: C<sub>33</sub>H<sub>26</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>10</sub> Exact Mass: 764.04

Figure S3. Estimated structures from ESI data

-S11-



Chemical Formula: C<sub>34</sub>H<sub>28</sub>Fe<sub>2</sub>N<sub>5</sub>O<sub>10</sub> Exact Mass: 778.05

#### 8. Plausible Reaction Mechanism

At the reaction mechanism, we have no rationale or experimental data for iron(III) active species and many great previous reports suggested that an iron(V) oxo species effectively work for epoxidation supported by spectroscopic and theoretical studies as mentioned by reviewer. We revised active species from  $Fe^{III}(pic)(Me-pic)OOH$  to  $Fe^{V}(O)(pic)(Me-pic)(OOCC_5H_3N-Me)$  as an iron(V) oxo active species derived from dehydration of  $Fe^{III}(pic)(Me-pic)(Me-pic)$  (Me-picH) OOH as shown below.



Figure S4. Plausible Mechanism

In this mechanism, an iron atom at iron(V) oxo species do not receive efficient electron donation from picolinate ligands different from the case of previously reported iron complexes coordinated by donar N-ligands, therefore it is reasonable that the system shown in this paper did not show high reactivities for less reactive terminal olefins. However it showed moderate reactivities with high selectivities for styrene epoxidation by the optimization of ligands in iron complex.

## 9. Single-crystal X-ray analyses of 1 and (Me-pic)<sub>2</sub>FeOFe(Me-pic)<sub>2</sub>

9-1. X–ray analysis of 1

Table S6.         Crystal data and structure refinement	t	
Empirical formula	C <sub>20</sub> H <sub>16</sub> Fe N <sub>3</sub> O <sub>6</sub>	
Formula weight	450.21	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 29.653(12) Å	α= 90°
	b = 8.330(4)  Å	β= 90.896(4)°
	c = 15.191(6)  Å	$\gamma = 90^{\circ}$
Volume	3752(3) Å <sup>3</sup>	
Ζ	8	
Density (calculated)	1.594 g/m <sup>3</sup>	
Absorption coefficient	0.849 mm <sup>-1</sup>	
F(000)	1848	
Crystal size	0.20 x 0.08 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.37 to 25.58°	
Index ranges	-35<=h<=35, -10<=k<=10, -1	18<=1<=18
Reflections collected	16293	
Independent reflections	3490 [R(int) = 0.0302]	
Completeness to theta = $25.58^{\circ}$	99.1 %	
Absorption correction	Semi-empirical from equivale	ents
Max. and min. transmission	0.9586 and 0.8480	
Refinement method	Full-matrix least-squares on I	<u>-</u> 2
Data / restraints / parameters	3490 / 0 / 273	
Goodness-of-fit on F <sup>2</sup>	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.1103	
R indices (all data)	R1 = 0.0499, wR2 = 0.1158	
Largest diff. peak and hole	0.925 and -0.370 eÅ <sup>-3</sup>	



Figure S5. ORTEP drawings of 1 with atom labeling scheme. Hydrogen atoms are omitted for clarity.



Figure S6. Views of Crystal Packing of 1.



**Figure S7.** Views of Crystal Packing of **1**. (a) along the a axis. (b) along the b axis. (c) along the c axis.

## 9-2. X-ray analysis of (Me-pic)<sub>2</sub>FeOFe(Me-pic)<sub>2</sub> (including one MeCN)

Table STU. Crystal data and structure refinement	
Empirical formula	C <sub>30</sub> H <sub>27</sub> Fe <sub>2</sub> N <sub>5</sub> O <sub>9</sub>
Formula weight	713.27
Temperature	183(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	P 4/ncc
Unit cell dimensions	$a = 14.3498(11) \text{ Å}$ $\alpha = 90^{\circ}$
	$b = 14.3498(11) \text{ Å} \qquad \beta = 90^{\circ}$
	$c = 15.6138(16) \text{ Å} \qquad \gamma = 90^{\circ}$
Volume	3215.1(5) Å <sup>3</sup>
Ζ	4
Density (calculated)	1.474 Mg/m <sup>3</sup>
Absorption coefficient	0.962 mm <sup>-1</sup>
F(000)	1464
Crystal size	0.25 x 0.20 x 0.07 mm <sup>3</sup>
Theta range for data collection	2.01 to 28.61°
Index ranges	-19<=h<=16, -19<=k<=19, -19<=l<=20
Reflections collected	19650
Independent reflections	1979 [R(int) = 0.0225]
Completeness to theta = $27.0^{\circ}$	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9497 and 0.8357
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1979 / 2 / 110
Goodness-of-fit on F <sup>2</sup>	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0929
R indices (all data)	R1 = 0.0401, $wR2 = 0.1014$
Largest diff. peak and hole	0.642 and -0.473 eÅ <sup>-3</sup>

 Table S10.
 Crystal data and structure refinement for (Me-pic)<sub>2</sub>FeOFe(Me-pic)<sub>2</sub>(MeCN).



**Figure S8.** ORTEP drawings of (Me-pic)<sub>2</sub>FeOFe(Me-pic)<sub>2</sub>(MeCN) with atom labeling scheme. Hydrogen atoms are omitted for clarity.



Figure S9. Views of Crystal Packing of (Me-pic)<sub>2</sub>FeOFe(Me-pic)<sub>2</sub>(MeCN).



**Figure S10.** Views of Crystal Packing of (Me-pic)<sub>2</sub>FeOFe(Me-pic)<sub>2</sub>(MeCN). (a) along the a axis. (b) along the b axis. (c) along the c axis.

### 10. Characterization Data for Compounds

## styrene oxide<sup>[4]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.77 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.11 (dd, *J* = 5.5, 4.0 Hz, 1H), 3.83 (dd, *J* = 4.0, 2.5 Hz, 1H), 7.21 – 7.35 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 51.1, 52.2, 125.4, 128.1, 128.4, 137.5.

### **4-fluorostyrene oxide**<sup>[5]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.75 (dd, *J* = 5.6, 2.6 Hz, 1H), 3.12 (dd, *J* = 5.6, 4.0 Hz, 1H), 3.84 (dd, *J* = 4.0, 2.6 Hz, 1H), 6.95 - 7.10 (m, 2 H), 7.16 - 7.32 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 51.1, 51.8, 115.4 (d, *J* = 20 Hz), 127.1 (d, *J* = 7 Hz), 133.3 (d, *J* = 2 Hz), 162.6 (d, *J* = 24 Hz).

## 4-chlorostyrene oxide<sup>[4]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.74 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.13 (dd, *J* = 5.5, 4.0 Hz, 1H), 3.82 (dd, *J* = 4.0, 2.5 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 51.2, 51.7, 126.8, 128.6, 133.8, 136.1.

### 4-bromostyrene oxide<sup>[6]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.74 (dd, *J* = 5.5, 2.5 Hz, 1H), 3.13 (dd, *J* = 5.5, 4.1 Hz, 1H), 3.81 (dd, *J* = 4.1, 2.5 Hz, 1H), 7.08-7.20 (m, 2H), 7.40-7.52 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 51.2, 51.8, 121.9, 127.1, 131.6, 136.7.

### 4-(trifluoromethyl)styrene oxide<sup>[7]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.77 (dd, *J* = 5.6, 2.6 Hz, 1H), 3.18 (dd, *J* = 5.6, 4.0 Hz, 1H), 3.91 (dd, *J* = 4.0, 2.6 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 51.4, 51.7, 125.4 (q, *J* = 3.8 Hz), 125.7, 141.8.

### 4-Methylstyrene oxide<sup>[5]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.33 (s, 3H), 2.78 (dd, *J* = 5.5, 2.6 Hz, 1H), 3.11 (dd, *J* = 5.5, 4.1 Hz, 1H), 3.82 (dd, *J* = 4.1, 2.6 Hz, 1H), 7.10-7.20 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.1, 51.0, 52.3, 125.4, 129.1, 134.5, 137.9.

### 4-phenylstyrene oxide<sup>[9]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.83 (dd, *J* = 2.7, 5.5 Hz, 1H), 3.16 (dd, *J* = 4.1, 5.5 Hz, 1H), 3.89 (dd, *J* = 2.7, 4.1 Hz, 1H), 7.27-7.37 (m, 3H), 7.39-7.46 (m, 2H), 7.51-7.62 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 51.2, 52.2, 125.9, 127.0, 127.2, 127.3, 128.7, 136.6, 140.6, 141.1.

## α-methylstyrene oxide<sup>[10]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.71 (s, 3H), 2.79 (d, *J* = 5.4 Hz, 1H), 2.96 (d, *J* = 5.4 Hz, 1H), 7.21 – 7.42 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.8, 56.7, 57.0, 125.2, 127.4, 128.3, 141.1. *trans*-β-methylstyrene oxide<sup>[11]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.44 (d, *J* = 6.8 Hz, 3H), 3.03 (dq, *J* = 6.8, 2.6 Hz, 1H), 3.56 (d, *J* = 2.6 Hz, 1H), 7.22 - 7.36 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.9, 59.0, 59.5, 125.5, 127.9, 128.4, 137.7.

## *cis*-β-methylstyrene oxide<sup>[11]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.08 (d, *J* = 7.1 Hz, 3H), 3.33 (dq, *J* = 7.1, 5.8 Hz, 1H), 4.05 (d, *J* = 5.8 Hz, 1H), 7.23 – 7.40 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 12.5, 55.1, 57.5, 126.5, 127.4, 127.9, 135.5.

## *trans*-stilbene oxide<sup>[10]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.86 (s, 2H), 7.25-7.46 (m, 10H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 62.8, 125.5, 128.3, 128.5, 137.1.

## **1,2-epoxyoctane**<sup>[11]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.89 (t, *J* = 7.0 Hz, 3H), 1.20 - 1.64 (m, 10H), 2.46 (dd, *J* = 2.7, 5.0 Hz, 1H), 2.74 (dd, *J* = 3.9, 5.0 Hz, 1H), 2.88 - 2.93 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.0, 22.5, 25.9, 29.1, 31.7, 32.5, 47.0, 52.3.

## 1,2-epoxycyclooctane<sup>[8]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.16 - 1.36 (m, 2H), 1.36 - 1.72 (m, 8H) , 2.05 - 2.25 (m, 2H) , 2.82 - 3.00 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 25.6, 26.3, 26.5, 55.6.

## 1,2-epoxycyclohexane<sup>[11]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.15-1.49 (m, 4H), 1.74-2.01 (m, 4H) , 3.12 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 19.4, 24.4, 52.1.

## **α-Pinene oxide**<sup>[12]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.94$  (s, 3H), 1.29 (s, 3H), 1.34 (s, 3H), 1.62 (d, J = 9.6 Hz, 1H), 1.70-1.75 (br m, 1H), 1.87-2.03 (m, 4H), 3.07 (dd, J = 4.1, 1.4 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 20.2$ , 22.4, 25.9, 26.7, 27.6, 39.7, 40.5, 45.1, 56.9, 60.3.

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## 12. <sup>1</sup>H and <sup>13</sup>C NMR Spectra:

Styrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



Styrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)





## 4-Fluorostyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



4-Fluorostyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## 4-Chlorostyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



4-Chlorostyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## 4-Bromostyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



4-Bromostyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## 4-(Trifluoromethyl)styrene oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



4-(Trifluoromethyl)styrene oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## 4-Methylstyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



4-Methylstyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## 4-phenylstyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



4-phenylstyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## α-Methylstyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



α-Methylstyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## *trans*-β-Methylstyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



*trans*-β-Methylstyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



## *cis*-β-Methylstyrene Oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



# *cis*-β-Methylstyrene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



trans-Stilbene oxide <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



trans-Stilbene oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)



1,2-epoxyoctane <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)

**1,2-epoxyoctane** <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)









1,2-epoxycyclooctane <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)







# 1,2-epoxycyclohexane <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)

**α-Pinene Oxide** <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



α-Pinene Oxide <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)

