

Electronic Supplementary Information (ESI)

A Mn(III)-superoxo complex of a zwitterionic calix[4]arene with an unprecedented linear end-on Mn(III)-O₂ arrangement and good catalytic performance for alkene epoxidation

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Experimental Section

General Procedures

5,11,17,23-tetramino-25,26,27,28-tetrahydroxy-calix[4]arene and [5,11,17,23-tetrakis(trimethyl ammonium)-25,26,27,28-tetrahydroxycalix[4]arene](PF₆)₄ (**1**) were prepared according to the literature methods.^{1a,1b} All chemicals and reagents were obtained from commercial sources and distilled prior to use. IR spectra were recorded with a Varian 1000 FT-IR spectrometer as KBr disks (4000-400 cm⁻¹). ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature with a Varian UNITYplus-400 spectrometer. The ¹H NMR chemical shifts are reported relative to TMS in CD₃CN and DMSO-*d*₆. The ¹³C NMR chemical shifts were referenced to the deuterated CD₃CN and DMSO-*d*₆ signal. The elemental analyses for C, H, and N were performed on an EA1110 CHNS elemental analyzer. The Electrospray ion mass spectra (ESI-MS) are performed on an Agilent 1200/6220 mass spectrometer using MeCN as mobile phase. The EPR spectra are obtained on a BRUKER EMX-10/12 spectrometer. The Raman spectra were recorded on a LabRam I confocal micro-Raman system from Dilor (HR800).

Synthesis of [Mn(III)L(O₂)(H₂O)](PF₆)₂·4H₂O (**2**)

To a solution of Mn(OAc)₂·4H₂O (98 mg, 0.4 mmol) in MeOH (2 mL) was added a solution of **1** (123 mg, 0.1 mmol) in MeCN (6 mL) in air. The resulting mixture was stirred for 3h to form a deep purple suspension. After filtration, diethyl ether (40 mL) was allowed to diffuse into the filtrate at ambient temperature for one week to form deep purple prisms of **2**, which were collected by filtration, washed by Et₂O, and dried *in vacuo*. Yield: 85 mg (80%). Anal. Calcd. for C₄₀H₆₂F₁₂MnN₄O₁₁P₂: C, 42.90; H, 5.58; N, 5.00. Found: C, 42.57; H, 5.19; N, 4.83. IR (KBr disc): 3433 (w), 2964 (w), 1668 (w), 1494 (s), 1384 (m), 1294 (w), 1232 (w), 949 (m), 839 (vs), 740 (w), 558 (s) cm⁻¹. ¹H NMR (400 MHz, CD₃CN): δ 7.49 (s, 8H, ArH), 3.64 and 4.43 (br, d, 8H, ArCH₂Ar), 3.43 (s, 36H, CH₃), 3.30 (s, 3H, CH₃). ¹³C NMR [400 MHz, CD₃CN]: δ 157.14, 138.67, 132.11, 120.44, 82.29, 58.11, 33.18.

Synthesis of [Mn(III)L(¹⁸O₂)(H₂O)](PF₆)₂ (**2'**)

A solution of Mn(OAc)₂·4H₂O (98 mg, 0.4 mmol) in MeOH (2 mL) was added to a solution of

2 (123 mg, 0.1 mmol) in MeCN (6 mL). The resulting mixture was bubbled with $^{18}\text{O}_2$ and stirred for 3h to form a deep purple suspension. After filtration, the solution was evaporated in *vacuo* and washed by 8 mL MeOH. Then the resulting purple precipitate of the ^{18}O -labeled complex **2'** was dried in *vacuo*. Yield: 75 mg (67%). IR (KBr disc): 3437 (w), 2964 (w), 1630 (w), 1494 (s), 1384 (m), 1262 (w), 1232 (w), 949 (m), 839 (vs), 740 (m), 558 (s) cm^{-1} .

The spin state determination

The spin state of **2** was determined using the modified ^1H NMR method of Evans and Nam at room temperature.^{2,3} A coaxial insert (sealed capillary) tubes containing the complexes (60 μL , 2.5 mM) dissolved in $\text{DMSO-}d_6$ (with 0.03% TMS) was inserted into the normal NMR tubes containing the blank $\text{DMSO-}d_6$ solvent (with 0.03% TMS) only. The chemical shift of the TMS peak in the presence of the paramagnetic metal complexes was compared to that of the TMS peak in the outer NMR tube. The effective magnetic moment was calculated using the following equation, where f is the oscillator frequency (MHz) of the superconducting spectrometer, T is the

$$\mu = 0.0618(\Delta\nu \cdot T / 2fM)^{1/2}$$

absolute temperature, M is the molar concentration of the metal ion, and $\Delta\nu$ is the difference in frequency (Hz) between the two reference signals.

X-ray crystal structure determination

Single crystals of **2** were obtained directly from the above preparation. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated Mo $K\alpha$ ($\lambda = 0.071073$ nm). Diffraction data were collected at ω mode with a detector distance of 35 mm to the crystal. Cell parameter was refined by using the program *CrystalClear* (Rigaku and MSC, version 1.3, 2001) on all observed reflections between θ of 3.056° and 25.0° . The collected data were reduced by using the program *CrystalClear* (Rigaku and MSC, Ver.1.3, 2001), and the reflection data were also corrected for Lorentz and polarization effects.

The crystal structure of **2** was solved by direct methods⁴ refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. The H atoms of the coordinated and uncoordinated water solvent molecules were located from Fourier maps. All other hydrogen atoms were introduced at the calculated positions and included in the

structure-factor calculations. The final refinement was based on 1199 reflections with $I > 2\sigma(I)$, and 112 variable parameters, and $w = 1/[\sigma^2(F_o^2) + (0.0900P)^2 + 1.9900P]$ (where $P = (F_o^2 + 2F_c^2)/3$). All the calculations were performed on a Dell workstation using the *CrystalStructure* crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). A summary of key crystallographic data for **2** is given in Table S1.

Epoxidation of Alkenes with **2 on GC Scale**

A solution of the cyclic alkene (0.88 mmol), isobutyraldehyde (1.76 mmol) and the catalyst (1.76×10^{-3} mmol) in 2 mL of MeCN was loaded into a flask at 20 °C. The mixture was stirred under an oxygen atmosphere for the time indicated in Table 1. The reaction mixture was then filtered and analyzed by GLC based on the internal standard and using authentic samples for comparison. The epoxide product was identified by a comparison of the GC retention time of an authentic sample and the reaction sample.

Analyses of the oxidation products

The normalized amount of substrate converted and the normalized yields of the oxidation products were estimated by addition of internal standard (*tert*-butylbenzene) before injection in the GC and were calculated from standard calibration curves. The GC analyses were performed on a Varian CP-3800 instrument with a capillary column (25 m \times 0.25 mm \times 0.25 μ m) with a HP-1 stationary phase (see Fig. S7 as an example of GC chromatogram). The instrument was equipped with a flame ionization detector. The identification of the products was verified by co-injection with authentic samples and by GC-MS.

Experimental conditions for isotope labeling studies⁵

Acetonitrile (anhydrous) was purified by distillation over CaH₂ prior to use. ¹⁸O₂ (97% ¹⁸O-enriched) was obtained from Shanghai research institute of chemical industry. The ¹⁶O and ¹⁸O compositions in products were analyzed by the relative abundances of the following mass peaks: $m/z = 97.1$ (¹⁶O) and 99.1 (¹⁸O) for cyclohexene oxide. All isotope labeling experiments were run at least in triplicate, and the data reported were the average of these reactions and calculated based on the ¹⁸O-enrichment of the reagents containing the isotope.

Epoxidation reaction catalyzed by [Mn(III)L(¹⁸O₂)(H₂O)](PF₆)₂ (2'**) under an ¹⁶O₂ atmosphere.** A solution of the cyclic alkene (0.88 mmol), isobutyraldehyde (1.76 mmol) and the catalyst of [Mn(III)L(¹⁸O₂)(H₂O)](PF₆)₂ (**2'**) (1.76×10^{-3} mmol) in 2 mL MeCN was prepared in a flask at 20 °C. The mixture was stirred under an ¹⁶O₂ atmosphere about 6 h. The resulting solution was directly analyzed by GC-MS.

Epoxidation reaction catalyzed by [Mn(III)L(¹⁶O₂)(H₂O)](PF₆)₂ (2**) under an ¹⁸O₂ atmosphere.** A solution of the cyclic alkene (0.88 mmol), isobutyraldehyde (1.76 mmol) and the catalyst of [Mn(III)L(¹⁶O₂)(H₂O)](PF₆)₂ (**2**) (1.76×10^{-3} mmol) in 2 mL MeCN was prepared in a flask at 20 °C. The mixture was stirred under an ¹⁸O₂ atmosphere about 6 h. The resulting solution was directly analyzed by GC-MS.

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1. (a) Y. Morita and T. Agawa, *J. Org. Chem.*, 1992, **57**, 3658; (b) L. L. Liu, Z. G. Ren, L. M. Wan, H. Y. Ding and J. P. Lang, *CrystEngComm.*, 2011, DOI: 10.1039/c1ce05377a.
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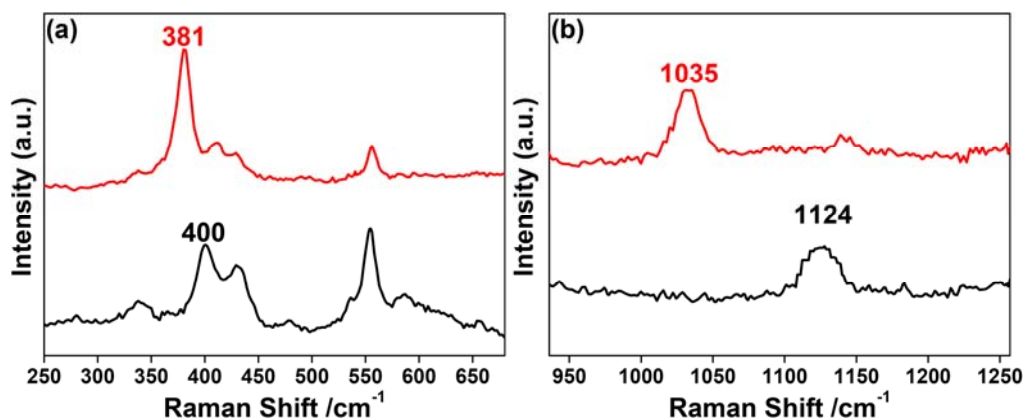


Figure S1. The resonance Raman spectra of **2** (solid, $\lambda_{\text{ex}} = 632.8$ nm) prepared with $^{16}\text{O}_2$ (black line) and $^{18}\text{O}_2$ (red line). (a) Detail of the $\nu_{\text{Mn-O}}$ region. (b) Detail of the $\nu_{\text{O-O}}$ region.

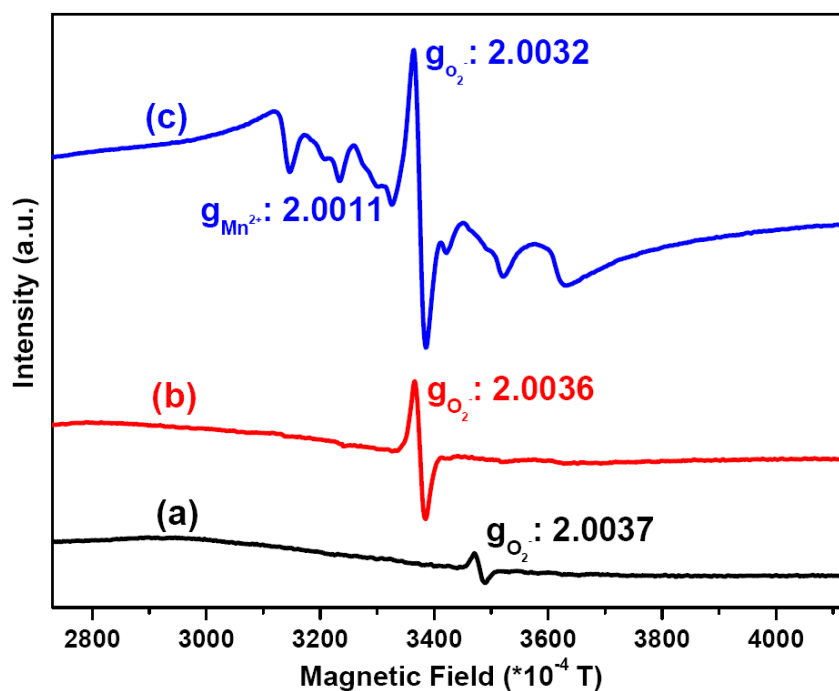


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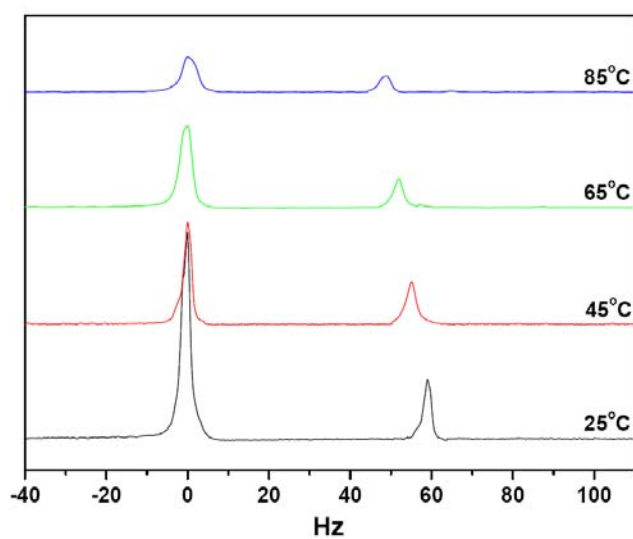


Figure S3. The temperature-dependent ^1H NMR spectra of **2** in $\text{DMSO-}d_6$ from 25 °C to 85 °C. The obtained magnetic moments ($5.795\mu_{\text{B}}$ for 25 °C, $5.782\mu_{\text{B}}$ for 45 °C, $5.793\mu_{\text{B}}$ for 65 °C, $5.788\mu_{\text{B}}$ for 85 °C) remain constant (within experimental error) over the temperature range.

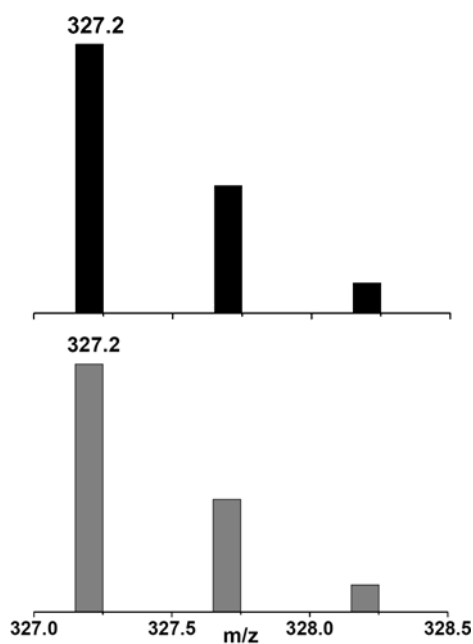


Fig. S4. The positive ion peak at a mass-to-charge ratio (m/z) of 327.2 (black column) whose mass and isotope distribution pattern corresponds to $[\text{H}_2\text{L}]^{2+}$ (calculated m/z 327.2, gray column).

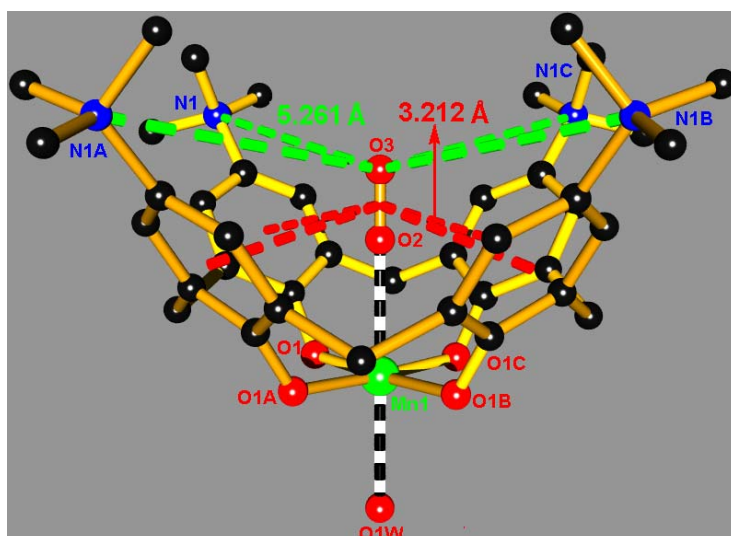


Figure S5. View of the $\pi\cdots\pi$ interactions (3.212(1) Å) among O_2^- and four surrounding phenyl groups and electrostatic interactions ($\text{O}\cdots\text{N} = 5.261(2)$ Å) among the terminal oxygen atom (O3) of O_2^- and four N atoms of NMe_3^+ groups in **2**. Symmetry codes: A, $-x, y, z$; B, y, x, z ; C, $x, -y, z$. All hydrogen atoms are omitted for clarity.

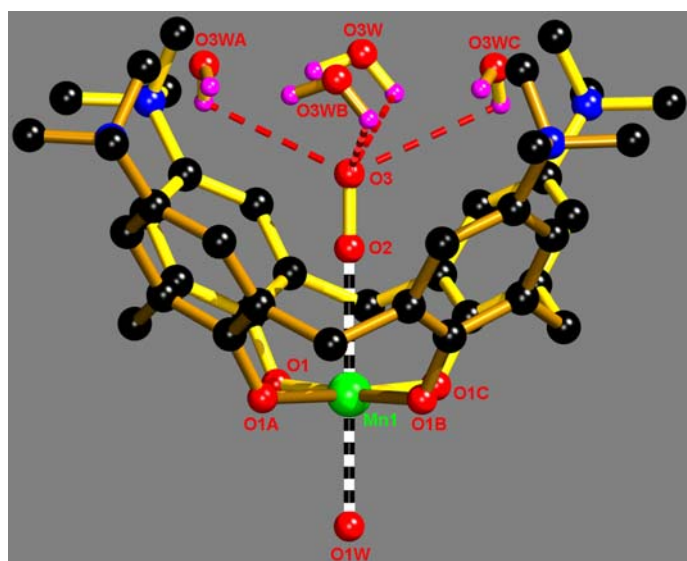


Figure S6. View of the hydrogen-bonding interactions ($\text{O3W}\cdots\text{O3} = 3.023(2)$ Å) among the terminal oxygen atom (O3) of O_2^- and four water molecules (O3W) in **2**. Symmetry codes: A, $-x, y, z$; B, y, x, z ; C, $x, -y, z$. All hydrogen atoms are omitted for clarity.

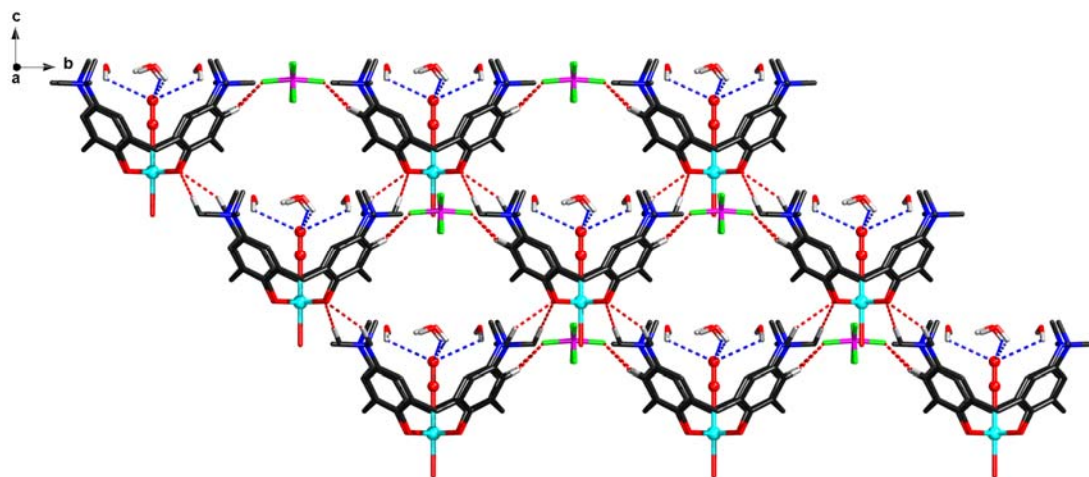


Figure S7. View of a 2D hydrogen-bonded network formed by hydrogen bonding interactions of the F atoms and PF_6^- and the phenyl groups of calix[4]arene and the OH groups of calix[4]arene and the methyl groups of the NMe_3^+ groups in **2**.

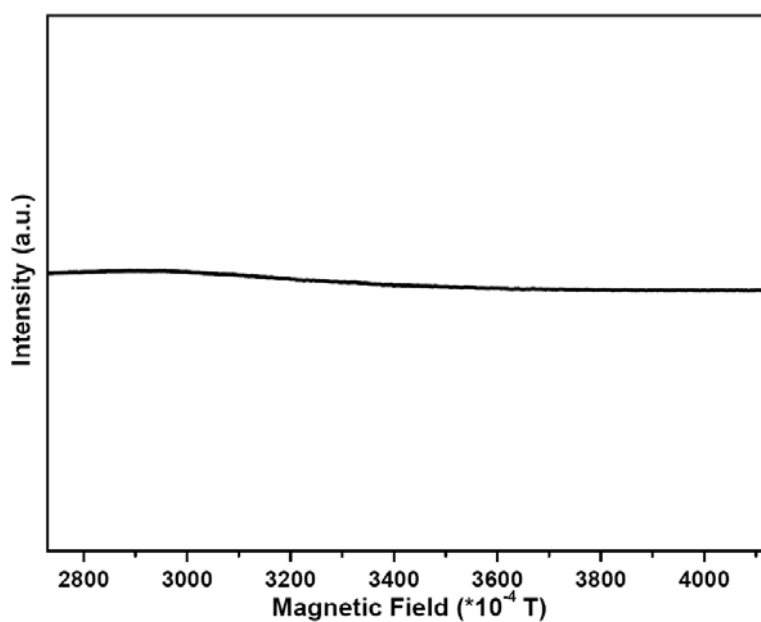


Figure S8. The EPR spectra of solution after epoxidation (3.52 mM). Instrumental parameters: temperature, 110 K; microwaves, 9.4806 GHz at 20 mW; modulation 100 KHz.

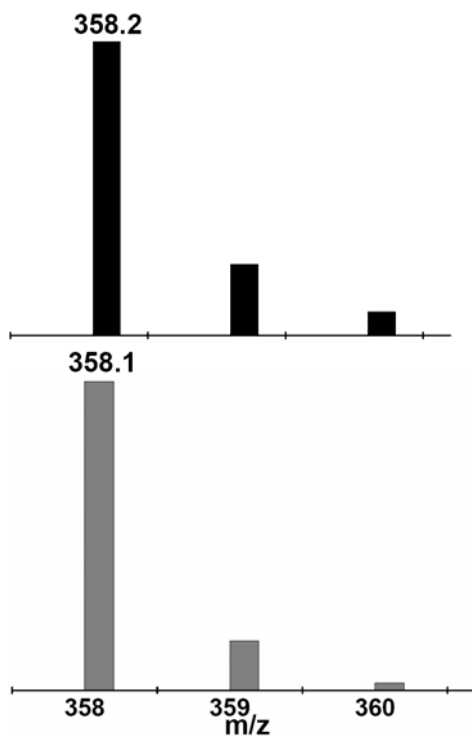


Figure S9. The positive ion peak at a mass-to-charge ratio (m/z) of 358.2 (black column) whose mass and isotope distribution pattern corresponds to $[(\text{Me}_2\text{CHCOO})_3\text{Mn(III)(MeCN)H}]^+$ (calculated m/z 358.1, gray column).

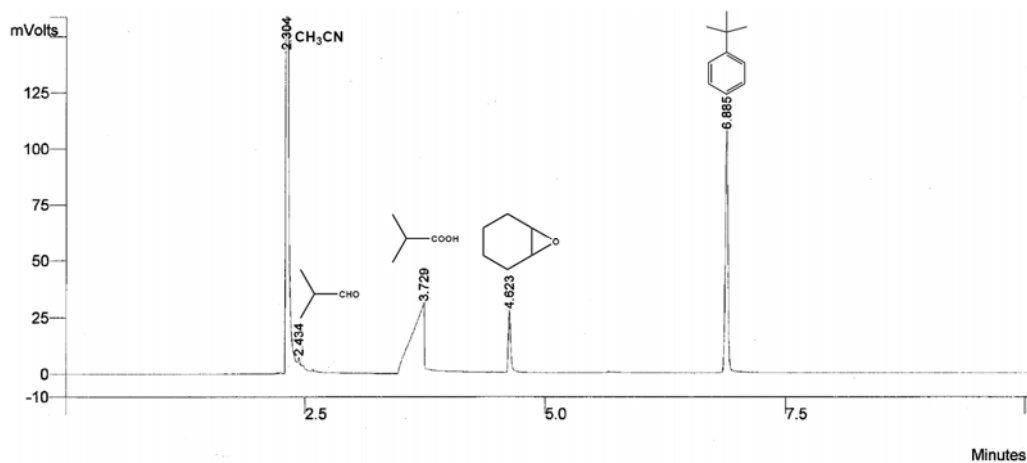
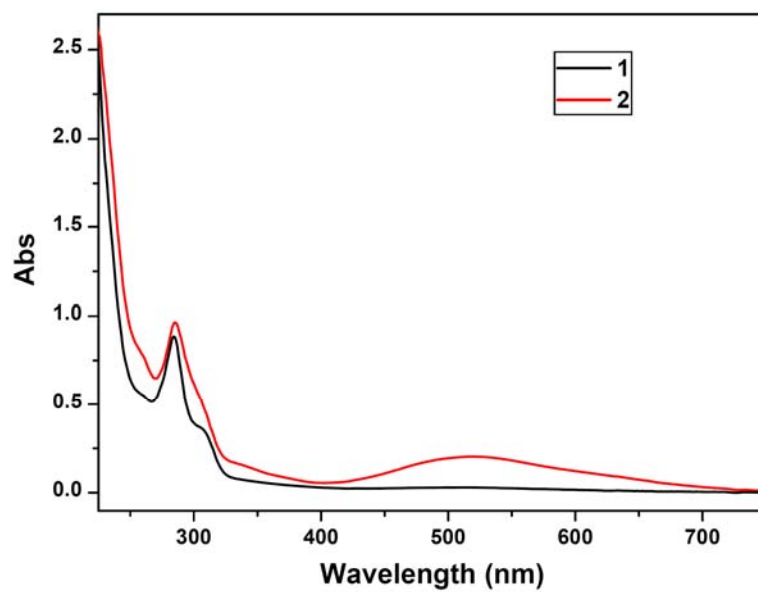


Figure S10. The GC chromatogram of cyclohexene oxidation by O_2 in the presence of isobutyraldehyde as co-substrate in MeCN solvent (Table 1, entry 2). Reaction conditions are: substrate (0.88 mmol), catalyst (1.76×10^{-3} mmol), isobutyraldehyde (0.88 mmol), O_2 (1 atm) in 2 mL MeCN solvent. Retention times (min); 2.304 (MeCN), 2.434, (isobutyraldehyde), 3.729 (isobutyric acid), 4.623 (cyclohexene oxide), 6.885 (*tert*-butylbenzene, internal standard).

(a)



(b)

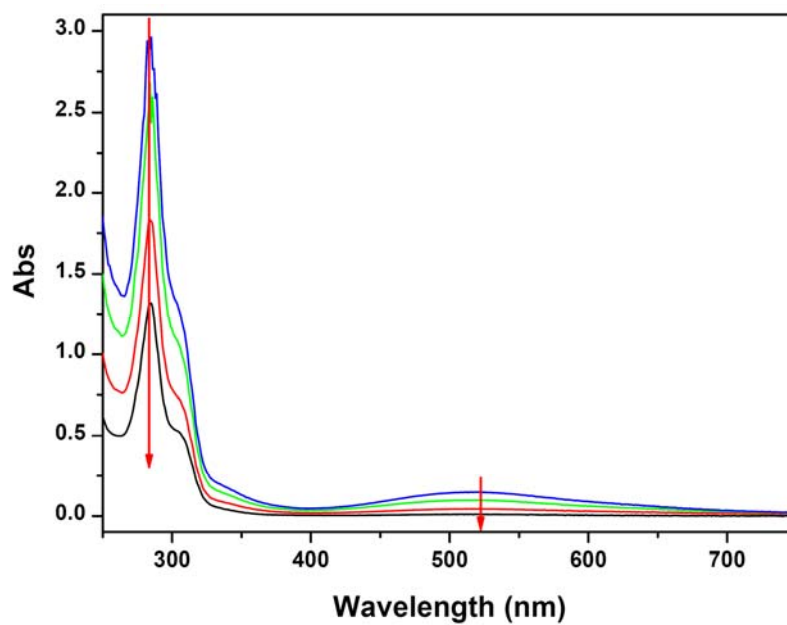


Figure S11. (a) UV-Vis absorption spectra of **1** (black line, 5×10^{-5} M) and **2** (red line, 5×10^{-5} M) in MeCN at room temperature. (b) UV-Vis spectral changes of **2** (5×10^{-4} M) within one day in MeCN at room temperature.

Table S1. Summary of crystallographic data for **2**

Compound	2
Empirical Formula	C ₄₀ H ₆₂ F ₁₂ MnN ₄ O ₁₁ P ₂
Formula Weight	1119.82
Crystal System	tetragonal
Space Group	<i>I4mm</i>
<i>a</i> (Å)	14.6070(10)
<i>c</i> (Å)	13.5758(12)
<i>V</i> (Å ³)	2896.6(4)
<i>Z</i>	2
<i>T</i> (K)	223(2)
ρ_{calc} (g/cm ³)	1.284
F(000)	1162.0
μ (MoK α , mm ⁻¹)	0.372
Total reflections	4756
Unique reflections	1424 ($R_{\text{int}} = 0.0500$)
No. of observations	1199
No. of parameters	112
R_1^a	0.0602
wR_2^b	0.1514
GOF ^c	1.059

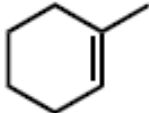
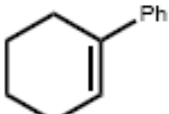

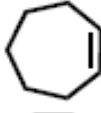
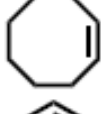
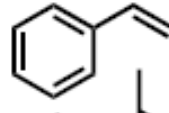
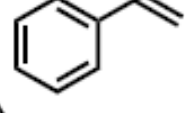
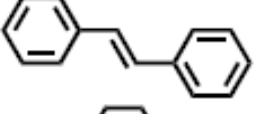
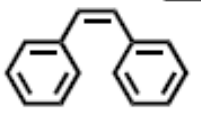
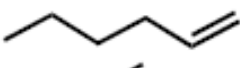
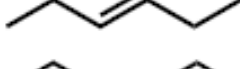
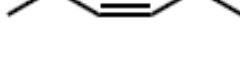
^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$. ^c $GOF = \{ \sum w(F_o^2 - F_c^2)^2 / (n-p) \}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

Table S2. Epoxidation of cyclohexene catalyzed by complex **2**^a

Entry	t (h)/T (°C)	Catalyst (mmol)	Conv. (%)	Selectivity (%)	
				Epoxide ^b	Others
1	3/20	1.76×10^{-3}	91.3	95.8	4.2
2	5/20	1.76×10^{-3}	99.9	99.9	0.1
3	8/20	1.76×10^{-3}	99.9	84.5	15.5 ^c
4	12/20	1.76×10^{-3}	99.9	80.3	19.7 ^c
5	5/0	1.76×10^{-3}	75.3	96.2	3.8
6	5/40	1.76×10^{-3}	99.9	84.4	15.6 ^d
7	5/60	1.76×10^{-3}	99.9	82.4	17.6 ^d
8	5/20	0.88×10^{-3}	65.9	98.3	1.7
9 ^e	5/20	–	16.3	81.8	17.0
10 ^f	5/20	1.76×10^{-3}	32.7	78.3	21.7
11 ^g	5/20	1.76×10^{-3}	13.8	83.1	16.9
12 ^h	5/20	–	14.1	80.2	20.8

^a Reaction condition: substrate (0.88 mmol), catalyst (1.76×10^{-3} mmol), isobutyraldehyde (0.88 mmol), O₂ (1 atm) in 2 mL of MeCN. ^b By gas/liquid chromatography determination based on internal standards and using authentic samples for comparison. ^c The main byproduct was cyclohexanone (from GC-MS analysis). ^d The main byproduct was 2-cyclohexen-1-one (from GC-MS analysis). ^e No catalyst. ^f Catalyst was 1.76×10^{-3} mmol of Mn(OAc)₂·4H₂O. ^g Catalyst was 1.76×10^{-3} mmol of the free ligand **1**. ^h Catalyst was the remaining solution after epoxidation.

Table S3. Epoxidation of alkenes catalyzed by complex **2**^a

Entry	Substrate	t (h)/T (°C)	Conv. (%)	Selectivity (%)	
				Epoxide ^b	Others
1		5/50	99.9	99.9	0.1
2		5/50	99.5	99.1	0.9
3		5/50	99.9	98.8	1.2
4		5/50	99.7	94.2	5.8
5		5/50	99.8	99.3	0.7
6		12/50	99.3	99.4	0.6
7		12/50	99.5	99.2	0.8
8		12/50	99.5	99.0	1.0
9		12/50	99.1	99.6	0.4
10		5/50	99.9	98.8	1.2
11		5/50	99.3	98.6	1.4
12		5/50	99.1	99.1	0.9

^a Reaction conditions: substrate (0.88 mmol), catalyst (1.76×10^{-3} mmol), isobutyraldehyde (0.88 mmol), O₂ (1 atm) in 2 mL of MeCN. ^b By gas/liquid chromatography determination based on internal standards and using authentic samples for comparison.