Supporting Information for

Non-redox Metal Ions Promoted Oxygen Transfer by a Non-heme Manganese Catalyst

Zhuqi Chen, Ling Yang, Cholho Choe, Zhanao Lv, Guochuan Yin*

School of Chemistry and Chemical Engineering, Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, Huazhong University of Science and Technology, Wuhan 430074, PR China.

Email: gyin@hust.edu.cn

Experimental Section

Iodobenzene diacetate ($PhI(OAc)_2$), sodium trifluoromethanesulfonate (NaOTf), magnesium trifluoromethanesulfonate ($Mg(OTf)_2$), and scandium trifluoromethanesulfonate ($Sc(OTf)_3$) came from Aldrich. Other trifluoromethanesulfonates including $Ca(OTf)_2$, $Al(OTf)_3$, $Y(OTf)_3$ and $Yb(OTf)_3$ came from local chemical companies. Cyclooctane and other olefins as well as 1,2-epoxycyclooctane and other epoxides were purchased from either Aldrich or Alfa Aesar. $H_2{}^{18}O$ (90% ^{18}O atom) came from Acros. The manganese(II) complex, $Mn(BPMEN)Cl_2$, was synthesized according to the literature, and the crystals of the manganese(II) complex were collected and employed as the catalyst in olefin epoxidation.[1] To confirm the correct synthesis of this complex, we also collected its X-ray structure data as shown in Scheme S1.

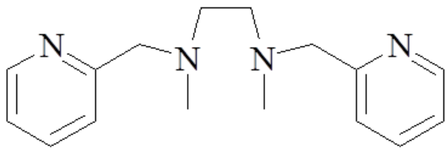
UV-Vis spectra were collected on Analytik jena, specord 205. GC-MS analysis was performed on Agilent7890A/5975C. FTIR spectra were collected on Bruker VERTEX70. Electrochemical studies were performed on a CS Corrtest electrochemical workstation equipped with glassy carbon as both working and counter electrodes and saturated calomel as reference electrode, and the redox potentials were measured under argon in dry acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. EPR experiments were conducted on Bruker A200 at 130 K, with center field of 3352.488 G, frequency of 9.395 GHz, power of 19.44 mW, modulation amplitude of 2.00 G and receiver gain of 1.00×10^3.

General procedure for the Lewis acid promoted catalytic epoxidation by the manganese(II) complex: 0.1 M olefin, 1 mM manganese(II) complex and 2 mM Lewis acid were dissolved in 4 mL of acetone and 1 mL of CH_2Cl_2, then 1 mmol of $PhI(OAc)_2$ was added into this solution. The reaction solution was stirred in an ice-water bath at 273 K for 2 h. Yield of epoxide and conversion of olefin were quantitatively analyzed by GC using the internal standard method. Control experiments with the manganese(II) complex or Lewis acid alone as catalyst were carried out in parallel. Reactions were performed at least in duplicate, and average data were used in discussion.

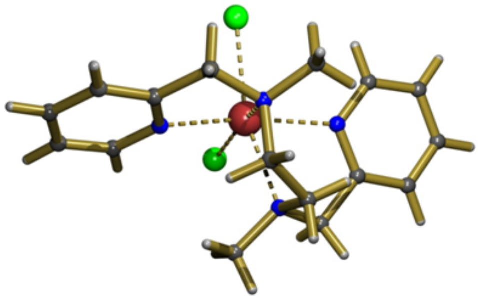
General procedure for Lewis acid promoted catalytic epoxidation of *cis* and *trans*-stilbene by the manganese(II) complex: 0.1 M olefin, 1 mM manganese(II) complex and 2 mM $Sc(OTf)_3$ were dissolved in 4 mL of acetone and 1 mL of CH_2Cl_2, then 1 mmol of $PhI(OAc)_2$ was added into this solution. The reaction solution was stirred in an ice-water bath at 273 K for 4 h. Yield of epoxide and conversion of olefin were quantitatively analyzed by HPLC using the internal standard method. Control experiments with the manganese(II) complex or Lewis acid alone as catalyst were carried out in parallel. Reactions were performed at least in duplicate, and average data were used in the discussion.

General procedure for Lewis acid promoted catalytic epoxidation by the manganese(II) complex with water: 0.05 M olefin, 1 mM manganese(II) complex and 2 mM $Sc(OTf)_3$ were dissolved in 0.4 mL of acetone, 0.1 mL of CH_2Cl_2 and a certain amount of water. Then 0.05 mmol of $PhI(OAc)_2$ were added into this solution. The reaction solution was stirred in an ice-water bath at 273 K for 8 h. Product analysis was performed by HPLC using the internal standard method. Control experiments with the manganese(II) complex or Lewis acid alone as catalyst were carried out in parallel. Reactions were performed at least in duplicate, and average data were used in the discussion.

Isotope-labelled epoxidation with $H_2{}^{18}O$: 0.05 M olefin, 1 mM manganese(II) complex and 2 mM $Sc(OTf)_3$ were dissolved in 0.4 mL of acetone and 0.1 mL of CH_2Cl_2, then 0.1 mL $H_2{}^{18}O$ (90% ^{18}O enrichment as received) and 0.05 mmol of $PhI(OAc)_2$ were added. The reaction mixture was stirred in an ice-water bath at 273 K for 8 hours. The ^{18}O enrichments are calculated based on the peak abundances of ^{16}O- and ^{18}O-epoxide in GC-MS graphs



BPMEN



Mn(BPMEN)Cl_2

Scheme S1 Chemical structure of BPMEN and X-ray structure of Mn(BPMEN)Cl_2.[1]

Reference:

[1] C. Hureau, G. Blondin, M. F. Charlot, C. Philouze, M. Nierlich, M. Cesario, E. Anxolabehere-Mallart, *Inorg. Chem*. **2005**, *44*, 3669

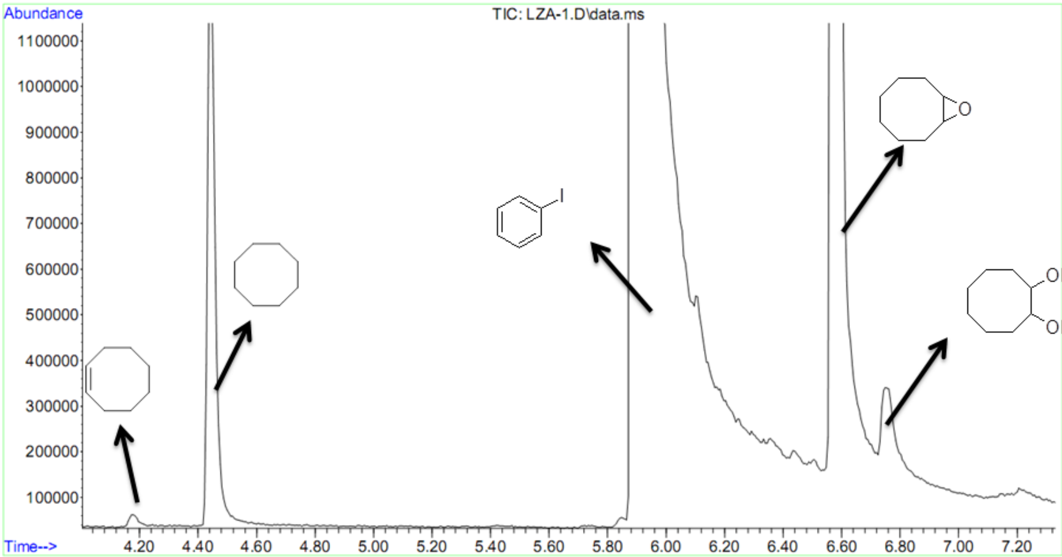


Figure S1 Enlarged GC-MS graph of catalytic epoxidation of cyclooctene by the manganese(II) complex and Al(OTf)$_3$ to illustrate trace 1,2-cyclooctanediol product. Conditions: acetone 4 mL, CH_2Cl_2 1 mL, olefin 0.1 M, manganese(II) complex 1 mM, Al(OTf)$_3$ 2 mM, PhI(OAc)$_2$ 0.2 M, 273 K, 2 h.

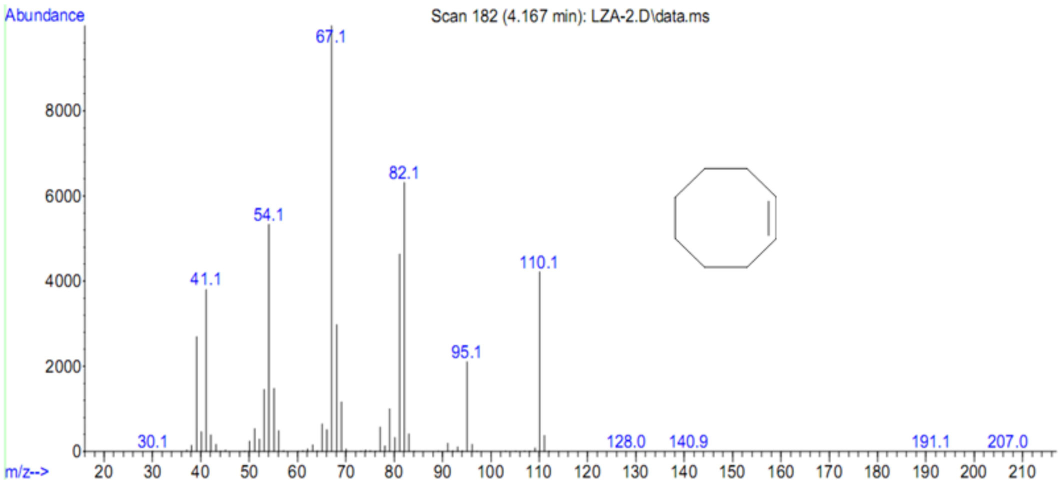


Figure S1-1 MS graph of cyclooctene from catalytic epoxidation of cyclooctene by the manganese(II) complex and Al(OTf)$_3$.

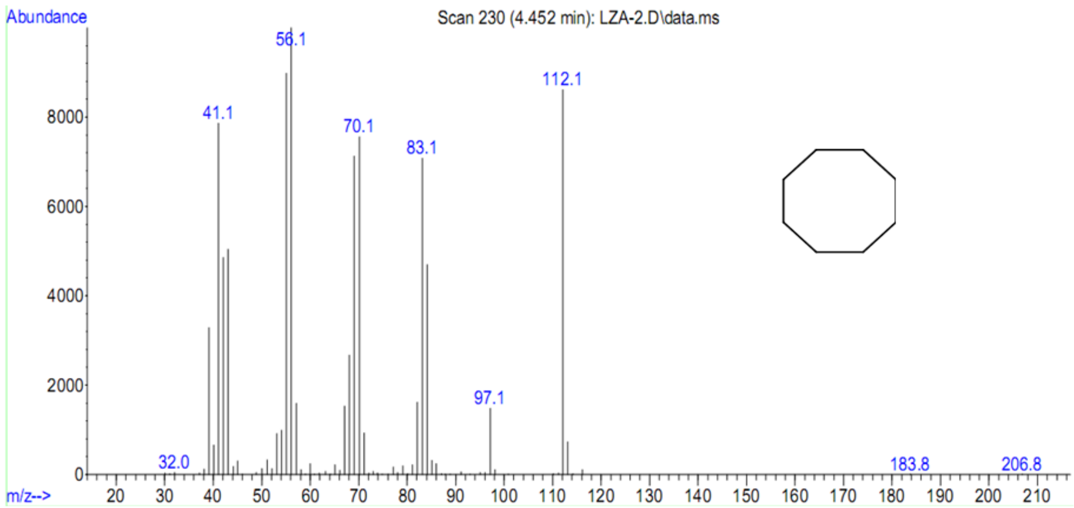


Figure S1-2 MS graph of cyclooctane from catalytic epoxidation of cyclooctene by the manganese(II) complex and $Al(OTf)_3$.

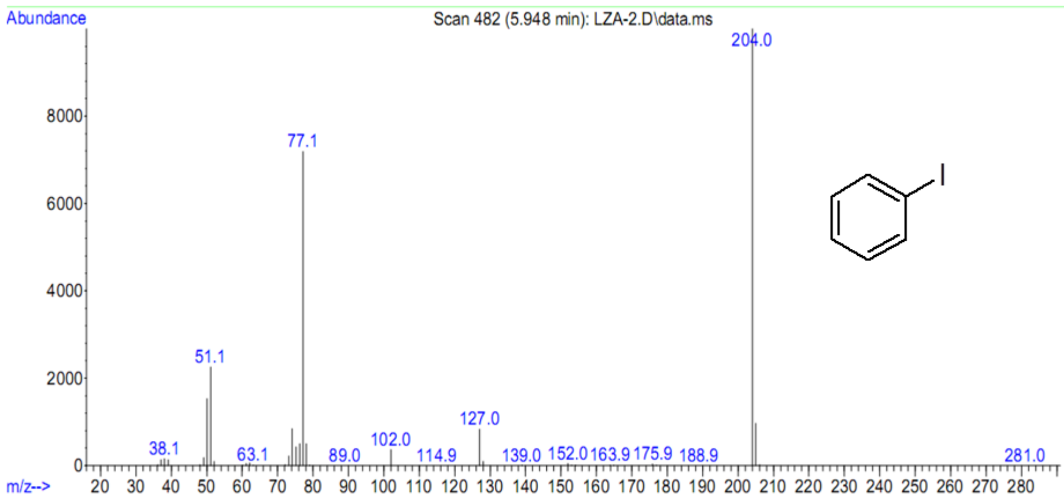


Figure S1-3 MS graph of iodobenzene from catalytic epoxidation of cyclooctene by the manganese(II) complex and $Al(OTf)_3$.

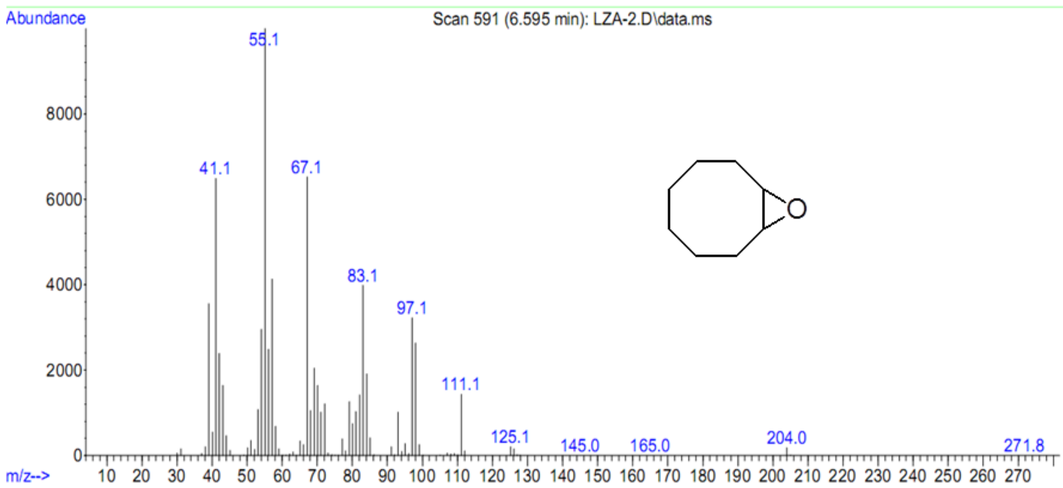


Figure S1-4 MS graph of cyclooctene oxide from catalytic epoxidation of cyclooctene by the manganese(II) complex and $Al(OTf)_3$.

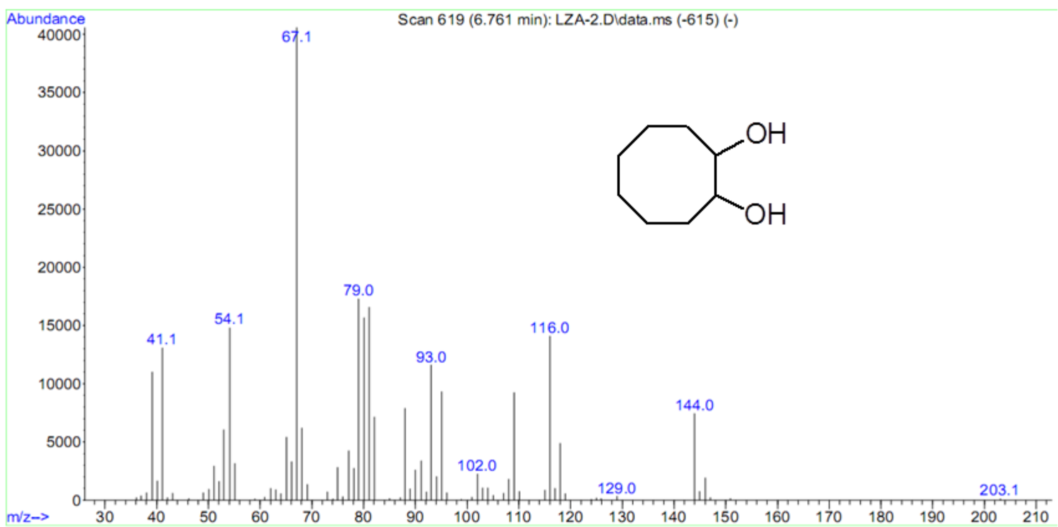


Figure S1-5 MS graph of 1,2-cyclooctanediol from catalytic epoxidation of cyclooctene by the manganese(II) complex and $Al(OTf)_3$.

Table S1 Influence of the Lewis acid concentration on the catalytic oxidation of cyclooctene to 1,2-epoxyoctane

$Mn(BPMEN)Cl_2$	$Sc(OTf)_3$	Conversion (%)	Yield (%)
0	0	4.8	1.8
1	0	7.6	6.4
0	2	4.6	2.9
1	0.5	39.3	27.4
1	1	96.4	77.7
1	2	100	94.4
1	4	100	77.6

Conditions: solvent 5 mL acetone/CH_2Cl_2 (4:1, v/v), cyclooctene 0.1 M, manganese(II) complex 1 mM, $Sc(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.2 M, 273 K, 2 h.

Table S2 Catalytic epoxidation of *cis*-stilbene by the manganese(II) complex alone

Sub.:Cat.	Conv. (%)	Yield-*cis* (%)	Yield-*trans* (%)	Yield-benzaldehyde (%)
100:1	7.9	1.7	1.4	3.7
50:1	15.8	3.6	3.2	5.3
25:1	23.1	5.4	5.9	6.0

Conditions: solvent 5 mL acetone/CH_2Cl_2 (4:1, v/v), cyclooctene 0.1 M, manganese(II) complex 1 mM, $PhI(OAc)_2$ 0.2 M, 273 K, 8 h.

Table S3 $Sc(OTf)_3$ promoted catalytic olefin epoxidations by the manganese(II) complex

Substrate	Product	Conversion (%)			Yield (%)		
		Mn^{2+}	Sc^{3+}	Mn^{2+} plus Sc^{3+}	Mn^{2+}	Sc^{3+}	Mn^{2+} plus Sc^{3+}
cyclooctene	1,2-epoxyclclooctene	7.6	4.6	100	6.4	2.9	94.4
cyclohexene	1,2-epoxycyclohexane	14.9	16.3	98.2	6.5	2.6	74.9
norborylene	2,3-epoxynorbornene	10.7	5.1	93.8	10.1	3.0	81.5
1-hexene	1,2-epoxyhexane	19.9	0.9	85.3	3.6	0.3	69.5
1-dodecene	1,2-epoxydecane	13.0	9.3	76.2	2.2	3.2	70.8
trans-stilbene	*cis*-epoxide	17.5	9.9	97.5	0	0	0
	trans-epoxide				10.8	0	41.4
	benzaldehyde				6.4	5.2	18.6
cis-stilbene	*cis*-epoxide	7.9	5.0	90.1	1.7	0	52.1
	trans-epoxide				1.4	0	2.7
	benzaldehyde				3.7	3.0	18.7

Conditions: solvent 5 mL acetone/CH_2Cl_2 (4:1, v/v), olefin 0.1 M, manganese(II) complex 1 mM, $Sc(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.2 M, 273 K.

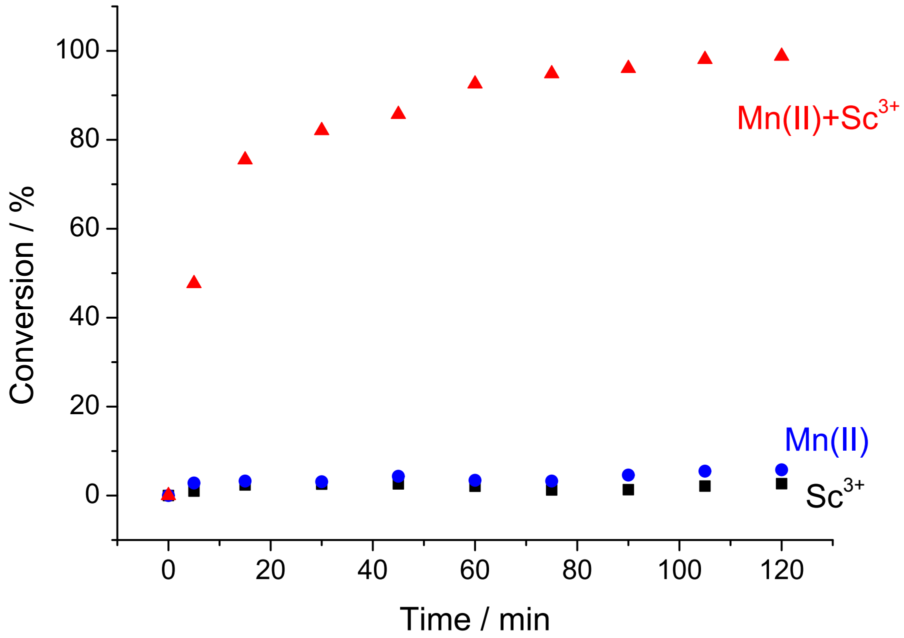


Figure S2 Lewis acid accelerated epoxidation kinetics by the manganese(II) complex. Conditions: solvent 5 mL acetone/CH_2Cl_2 (4:1, v/v), cyclooctene 0.1 M, manganese(II) complex 1 mM, $Sc(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.2 M,, 273 K.

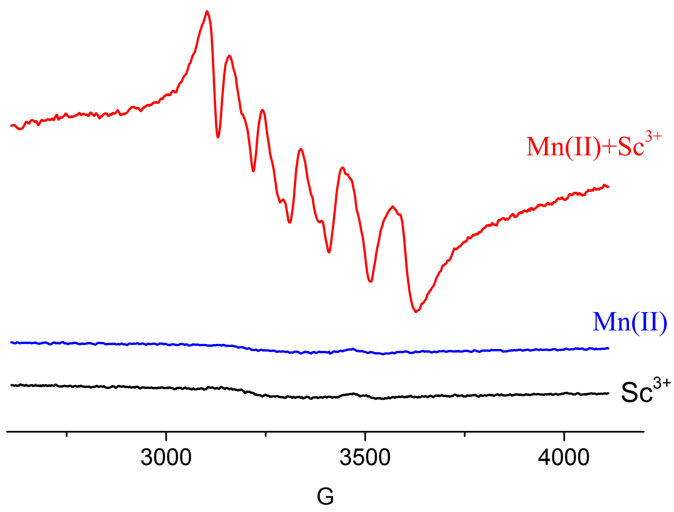


Figure S3 EPR spectra of the manganese(II) complex in acetone/CH_2Cl_2 mixture (4:1, v/v) at 130 K. Conditions: manganese(II) complex 5 mM, one equiv. of $Sc(OTf)_3$.

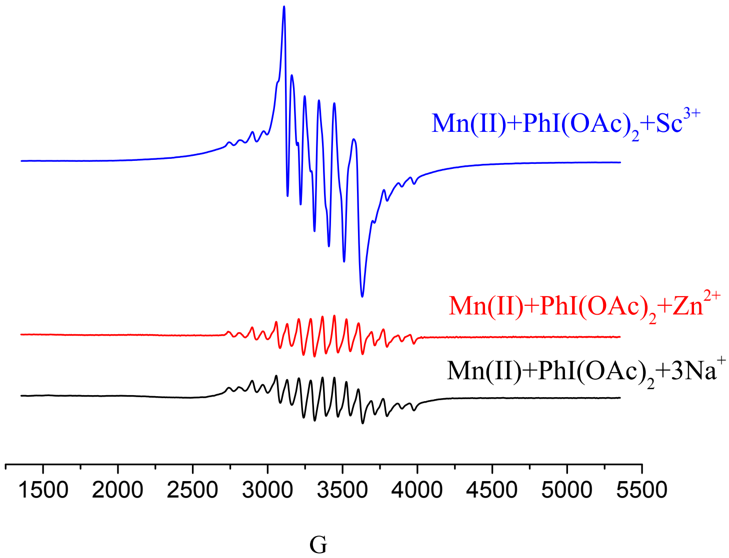


Figure S4 EPR spectra of the manganese(II) complex in acetone/CH_2Cl_2 mixture (4:1, v/v) at 130 K. Conditions: manganese(II) complex 5 mM, 5 equiv. of $PhI(OAc)_2$, one equiv. of $Sc(OTf)_3$, one equiv. of $Zn(OTf)_2$, or 3 equiv. of Na(OTf).

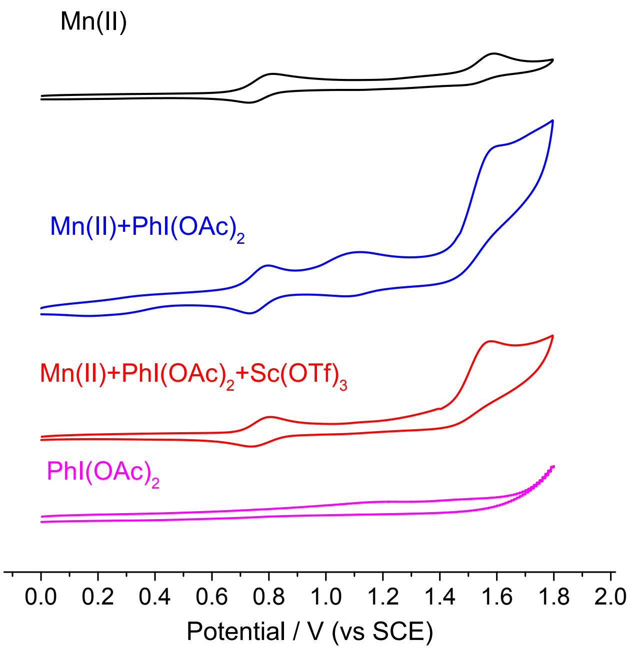


Figure S5 Cyclic voltammograms of $Mn(BPMEN)Cl_2$ in the presence/absence of $PhI(OAc)_2$ and $Sc(OTf)_3$ in acetone/CH_2Cl_2 mixture (4:1, v/v). Conditions: $Mn(BPMEN)Cl_2$ 5 mM, one equiv. of $Sc(OTf)_3$, 5 equiv. of $PhI(OAc)_2$, 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

Table S5 Reduction potential of the manganese(II) complex with $PhI(OAc)_2$ in the presence/absence of $Sc(OTf)_3$. [a]

	Mn(II)/Mn(III)	Mn(III)/Mn(IV)	Mn_2(III,IV)/ Mn_2(IV,IV)
$Mn(BPMEN)Cl_2$	0.76	1.56	
$Mn(BPMEN)Cl_2$+$PhI(OAc)_2$	0.76	1.52	1.10
$Mn(BPMEN)Cl_2$+$PhI(OAc)_2$+$Sc(OTf)_3$	0.76	1.53	
$Mn^{III}(\mu\text{-}O)_2Mn^{IV}(BPMEN)_2(ClO_4)_3$[b]			1.12
$Mn(BPMEN)Cl_2$[b]	0.74	1.46	

[a] Potentials are given in volts vs SCE. Conditions: manganese(II) complex 5 mM in acetone/CH_2Cl_2 mixture (4:1, v/v) at 130 K, 5 equiv. of $PhI(OAc)_2$, 2 equiv. of $Sc(OTf)_3$. [b] the data from ref. 2.

Reference:

[2] C. Hureau, G. Blondin, M. F. Charlot, C. Philouze, M. Nierlich, M. Cesario, E. Anxolabehere-Mallart, *Inorg. Chem.* **2005**, *44*, 3669.

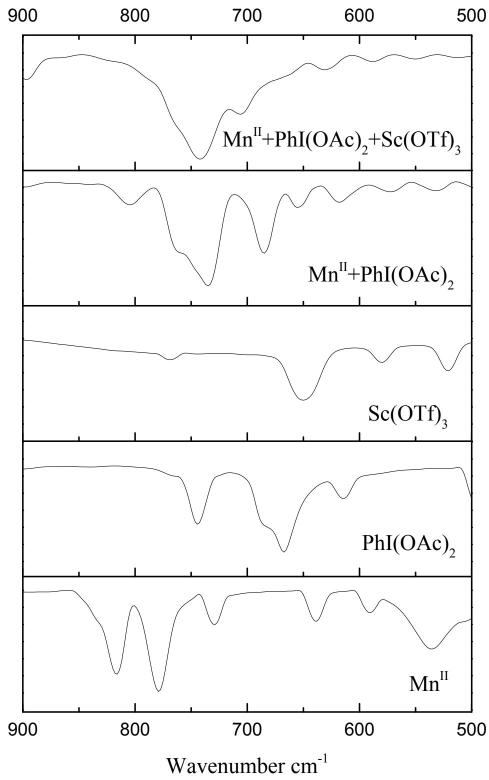


Figure S6 FTIR spectra of the manganese(II) complex in the presence/absence of $Sc(OTf)_3$ and $PhI(OAc)_2$ in acetone/CH_2Cl_2 mixture (4:1, v/v). Conditions: manganese(II) complex 5 mM, one equiv. of $Sc(OTf)_3$, 5 equiv. of $PhI(OAc)_2$.

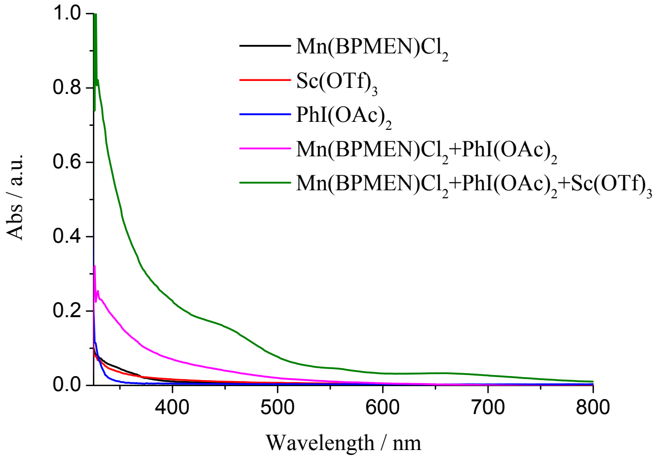


Figure S7 UV-Vis spectra of the manganese(II) complex in the presence/absence of $Sc(OTf)_3$ and $PhI(OAc)_2$ in acetone/CH_2Cl_2 mixture (4:1, v/v). Conditions: manganese(II) complex 0.25 mM, one equiv. of $Sc(OTf)_3$, 5 equiv. of $PhI(OAc)_2$.

Table S6 Influence of water concentration on the epoxidation of *cis* and *trans*-stilbene by the manganese(II) complex and Lewis acid

Substrate	Water (mL)	Conversion (%)	Yield *cis*-epoxide(%)	Yield *trans*-epoxide(%)	Yield benzaldehyde(%)
cis-stilbene	0	90.1	52.1	2.7	18.7
	0.01	86.3	41.4	5.3	9
	0.02	76.8	14	2.6	9.3
	0.05	63.4	11.8	2.2	11.3
	0.1	70.7	11.8	4	8.7
trans-stilbene	0	97.5	0	41.4	18.6
	0.01	54.1	0	35.4	13.6
	0.02	38.7	0	32.3	6.4
	0.05	27.5	0	22.6	3.6
	0.1	27.6	0	20.7	3.1

Conditions: solvent 0.5 mL acetone/CH_2Cl_2 (4:1, v/v), olefin 0.05 M, manganese(II) complex 1 mM, $Sc(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.1 M, 273 K, 8 h.

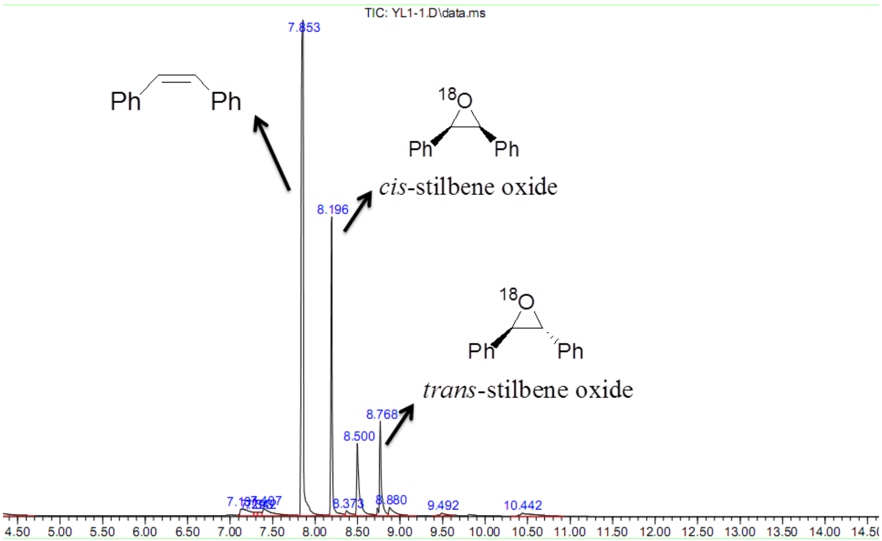


Figure S8 GC-MS graph of $H_2{}^{18}O$ labeled catalytic *cis*-stilbene epoxidation by the manganese(II) complex and $Sc(OTf)_3$. Conditions: $H_2{}^{18}O$ 0.1 mL, acetone 0.4 mL, CH_2Cl_2 0.1 mL, olefin 0.1 M, manganese(II) complex 1 mM, $Sc(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.2 M, 273 K, 8 h.

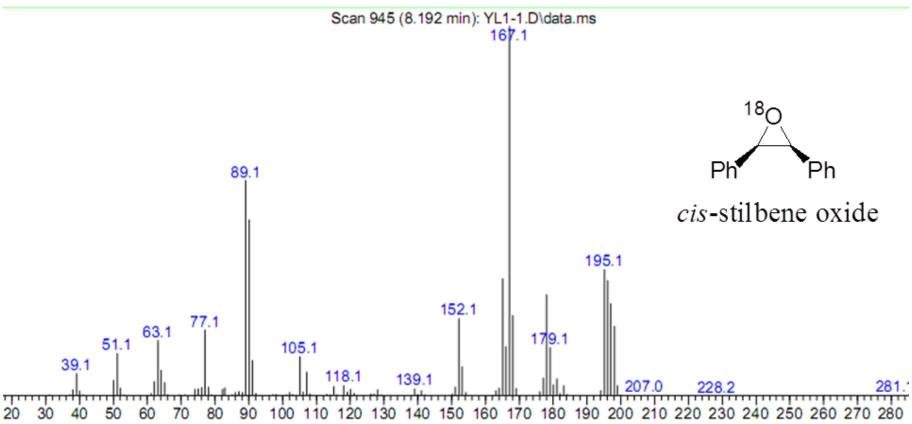


Figure S8-1 MS graph of ^{18}O labeled *cis*-stilbene oxide from catalytic epoxidation of *cis*-stilbene by the manganese(II) complex and $Sc(OTf)_3$.

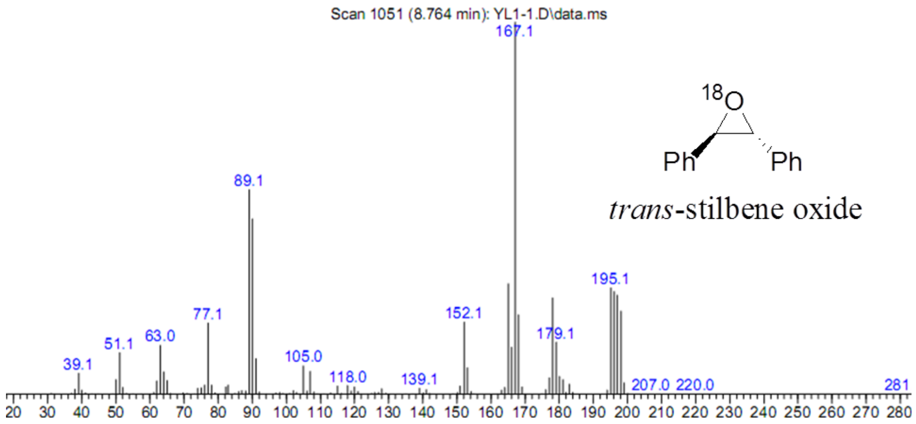


Figure S8-2 MS graph of ^{18}O labeled *trans*-stilbene oxide from catalytic epoxidation of *cis*-stilbene by the manganese(II) complex and $Sc(OTf)_3$.