Electronic Supplementary Information

Redox-inactive Metal Ions Promoted Catalytic Reactivity of Non-heme Manganese Complex towards Oxygen Atom Transfer

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1) Influence of the $Al(OTf)_3$ concentration on the catalytic oxidation of cyclooctene.
2) Influence of proton acids and water on the catalytic oxidation of cyclooctene.
3) GC-MS graph of catalytic epoxidation of cyclooctene.
4) Catalytic epoxidation of *cis*-stilbene by $Mn(TPA)Cl_2$ alone.
5) EPR spectra of $Mn(TPA)Cl_2$ plus various Lewis acids.
6) Influence of water concentration on the epoxidation of *cis*- and *trans*-stilbene by $Mn(TPA)Cl_2$ Catalyst and $Al(OTf)_3$.
7) UV-Vis spectra of the manganese complex, $PhI(OAc)_2$ and redox-inactive metal trifluoromethanesulfonates.
8) GC-MS graph of $H_2{}^{18}O$ labelled experiment catalytic *cis*-stilbene epoxidation by $Mn(TPA)Cl_2$ plus $Al(OTf)_3$ with $PhI(OAc)_2$.
9) Catalytic oxidation of cyclooctene by $Mn(TPA)Cl_2$ and $Al(OTf)_3$ with PhIO as oxidant.
10) Kinetics of catalytic epoxidation of 1-hexene by $Mn(TPA)Cl_2$ plus $Al(OTf)_3$ with $PhI(OAc)_2$.
11) ^{1}H-NMR spectra of $Al(OTf)_3$ and $PhI(OAc)_2$.

Table S1. Influence of the $Al(OTf)_3$ concentration on the catalytic oxidation of cyclooctene

Entry	$Mn(TPA)Cl_2$ (mM)	$Al(OTf)_3$ (mM)	Conv. (%)	Yield (%)
1	0	0	2.4(0.1)	1.5(0.1)
2	0	2	3.7(0.2)	1.7(0.1)
3	1	0	9.9(0.2)	4.1(0.1)
4	1	0.5	38.3(1.6)	21.9(1.3)
5	1	1	85.0(0.7)	77.2(0.2)
6	1	2	97.8(1.0)	91.4(0.3)
7	1	4	98.7(0.2)	51.8(3.2)

Conditions: solvent: acetonitrile/CH_2Cl_2 (4:1,v/v) 5 mL, cyclooctene 0.05 M, $PhI(OAc)_2$ 0.1 M, 273 K, 3.5 h. Data in parentheses represent the deviations.

Table S2. Influence of proton acids and water on catalytic oxidation of cyclooctene by $Mn(TPA)Cl_2$ with $PhI(OAc)_2$ as oxidant.

Entry	Additives	Mn(II)+proton acid		Only proton acid	
		Conv. (%)	Yield (%)	Conv. (%)	Yield (%)
1	Acetic acid (2 mM)	23.7(1.3)	5.9(0.3)	3.2(0.1)	1.8(0.3)
2	Hydrochloric acid (2 mM)	28.1(1.5)	10.5(1.4)	3.0(0.2)	1.1(0.5)
3	Al^{3+} (2 mM) + H_2O (0.01 mL)	87.0(2.6)	76.1(1.0)	—	—
4	Al^{3+} (2 mM) + H_2O (0.02 mL)	53.9(1.2)	44.6(1.6)	—	—
5	Al^{3+} (2 mM) + H_2O (0.04 mL)	29.6(1.3)	18.0(0.7)	—	—

Conditions: solvent: acetonitrile/CH_2Cl_2 (4:1,v/v) 5 mL, cyclooctene 0.05 M, $Mn(TPA)Cl_2$ 1 mM, $PhI(OAc)_2$ 0.1 M, 273 K, 3.5 h. Data in parentheses represent the deviations.

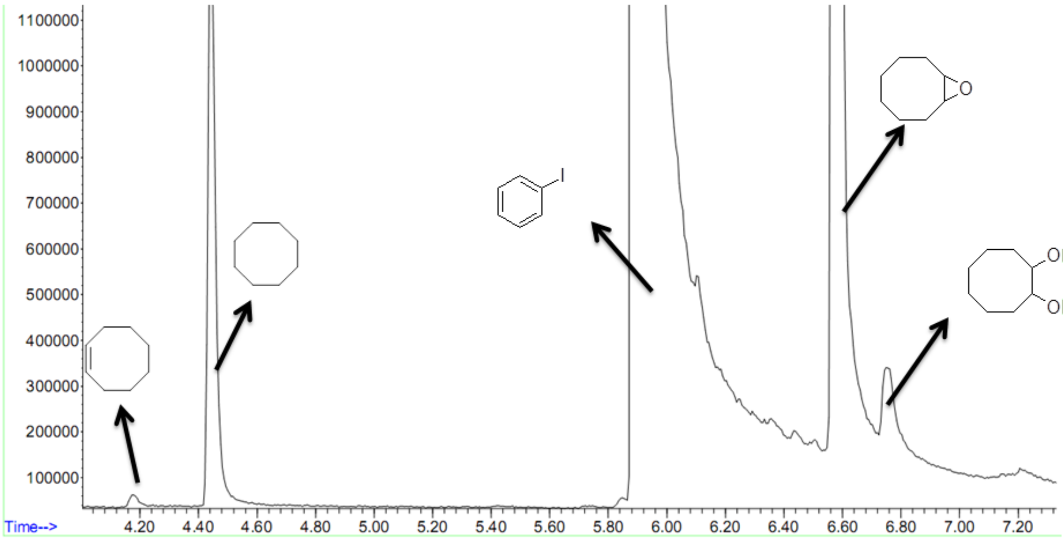

Figure S1. Enlarged GC-MS graph of catalytic epoxidation of cyclooctene by the Mn(TPA)Cl_2 catalyst and Al(OTf)$_3$ to illustrate trace 1,2-cyclooctanediol product. Conditions: solvent: acetonitrile/CH_2Cl_2 (4:1,v/v) 5 mL, cyclooctene 0.05 M, Mn(TPA)Cl_2 1 mM, Al(OTf)$_3$ 2 mM, PhI(OAc)$_2$ 0.1 M, 273 K, 3.5 h.

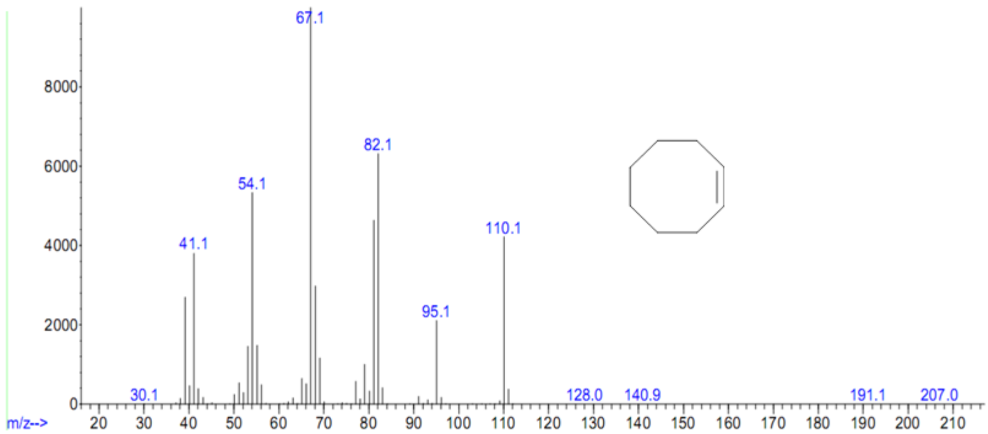

Figure S1-1. MS graph of cyclooctene from catalytic epoxidation of cyclooctene by Mn(TPA)Cl_2 catalyst and Al(OTf)$_3$.

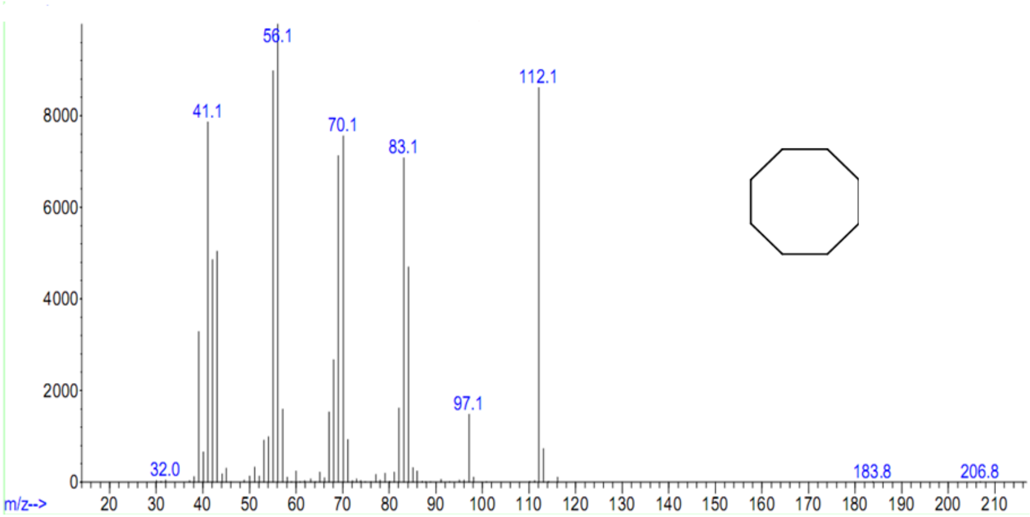

Figure S1-2. MS graph of cyclooctane from catalytic epoxidation of cyclooctene by $Mn(TPA)Cl_2$ catalyst and $Al(OTf)_3$.

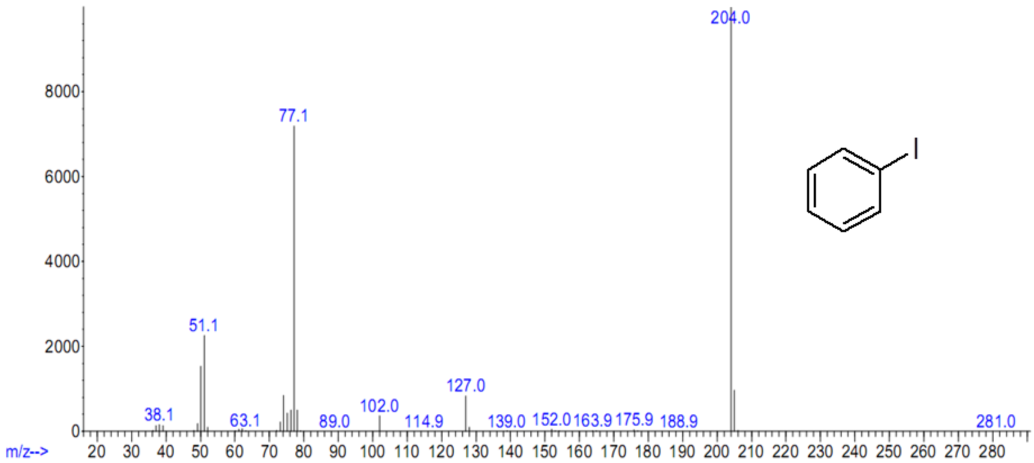

Figure S1-3. MS graph of iodobenzene from catalytic epoxidation of cyclooctene by $Mn(TPA)Cl_2$ catalyst and $Al(OTf)_3$.

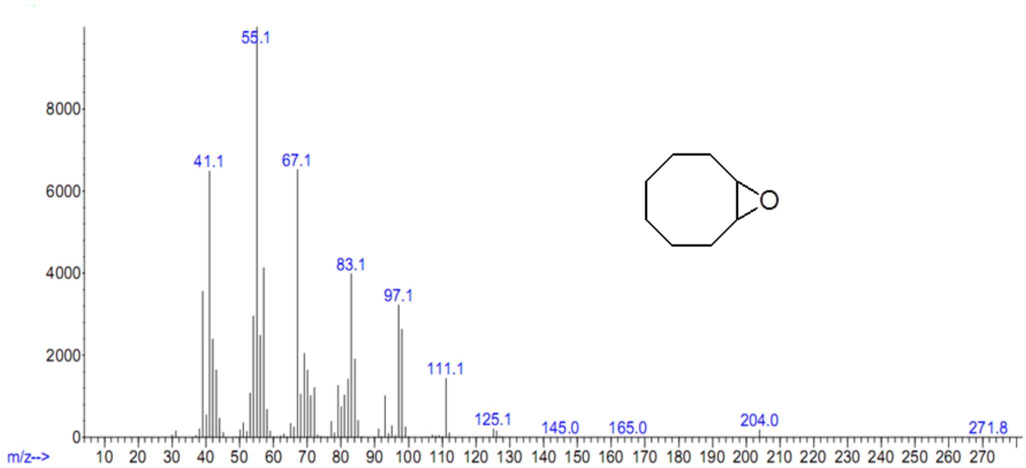

Figure S1-4. MS graph of cyclooctene oxide from catalytic epoxidation of cyclooctene by $Mn(TPA)Cl_2$ catalyst and $Al(OTf)_3$.

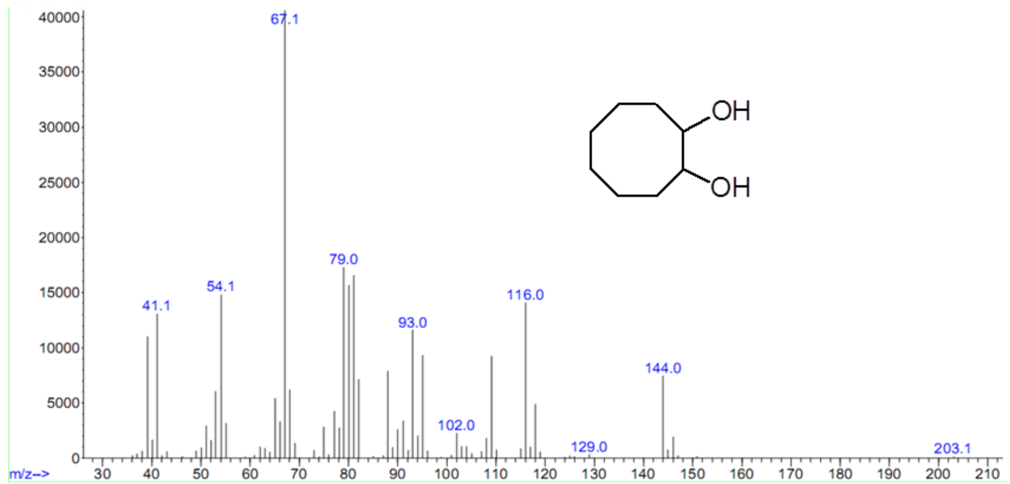

Figure S1-5. MS graph of 1,2-cyclooctanediol from catalytic epoxidation of cyclooctene by $Mn(TPA)Cl_2$ catalyst and $Al(OTf)_3$.

Table S3. Catalytic epoxidation of *cis*-stilbene by Mn(TPA)Cl_2 alone

Substrate : catalyst.	Conv. (%)	Yield *cis*-epoxide (%)	Yield *trans*-epoxide (%)	Yield benzaldehyde (%)
100:1	7.5(0.4)	1.6(0.1)	1.3(0.1)	1.4(0.2)
50:1	25.1(0.3)	5.9(0.1)	3.5(0.3)	3.3(0.2)
25:1	37.9(0.7)	6.7(0.3)	5.3(0.2)	5.3(0.4)

Conditions: solvent: acetonitrile/CH_2Cl_2 (4:1,v/v) 5 mL, *cis*-stilbene 0.1 M, Mn(TPA)Cl_2 1 mM in the case of substrate : catalyst = 100:1, PhI$(OAc)_2$ 0.2 M, 273 K, 8 h. Data in parentheses represent the deviations.

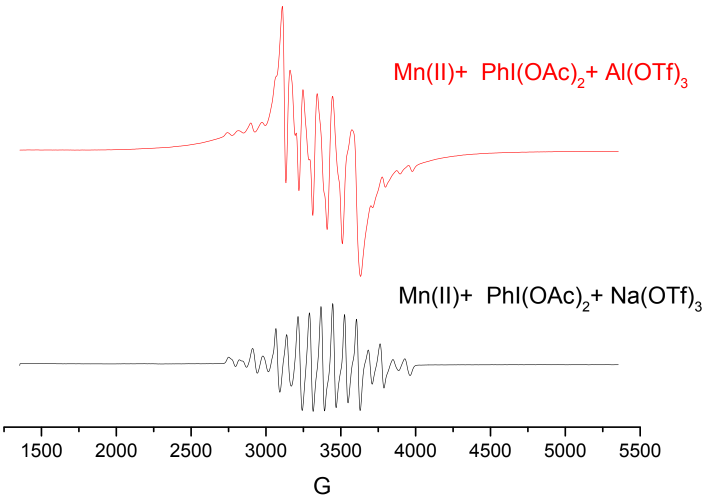

Figure S2. EPR spectra of $Mn(TPA)Cl_2$ plus various Lewis acids at 130 K. Conditions: $Mn(TPA)Cl_2$ 5 mM, 5 equiv. of $PhI(OAc)_2$, one equiv. of $Al(OTf)_3$ or 3 equiv. of NaOTf.

Table S4. Influence of water concentration on the epoxidation of *cis*- and *trans*-stilbene by $Mn(TPA)Cl_2$ catalyst and $Al(OTf)_3$

Substrate	Water (mL)	Conv. (%)	Yield *cis*-epoxide (%)	Yield *trans*-epoxide (%)	Yield benzaldehyde (%)
cis-Stilbene	0	83.8(1.8)	50.7(0.2)	5.8(0.4)	6.1(0.6)
	0.01	72.2(0.3)	27.3(1.2)	7.1(0.7)	8.3(0.2)
	0.02	65.1(0.3)	25.4(0.5)	2.4(0.2)	4.1(0.3)
	0.05	46.4(0.3)	20.4(0.7)	3.8(0.2)	7.4(0.3)
trans-Stilbene	0	73.7(0.7)	-	64.7(1.9)	2.8(0.4)
	0.01	54.4(1.8)	-	36.1(0.8)	11.2(0.3)
	0.02	45.8(0.3)	-	31.5(0.8)	11.1(0.7)
	0.05	36.9(0.5)	-	22.1(0.2)	3.8(0.3)

Conditions: solvent: acetonitrile/CH_2Cl_2 (4:1,v/v) 0.5 mL, olefin 0.1 M, $Mn(TPA)Cl_2$ 2 mM, $PhI(OAc)_2$ 0.2 M, 273 K, 8 h. Data in parentheses represent the deviations.

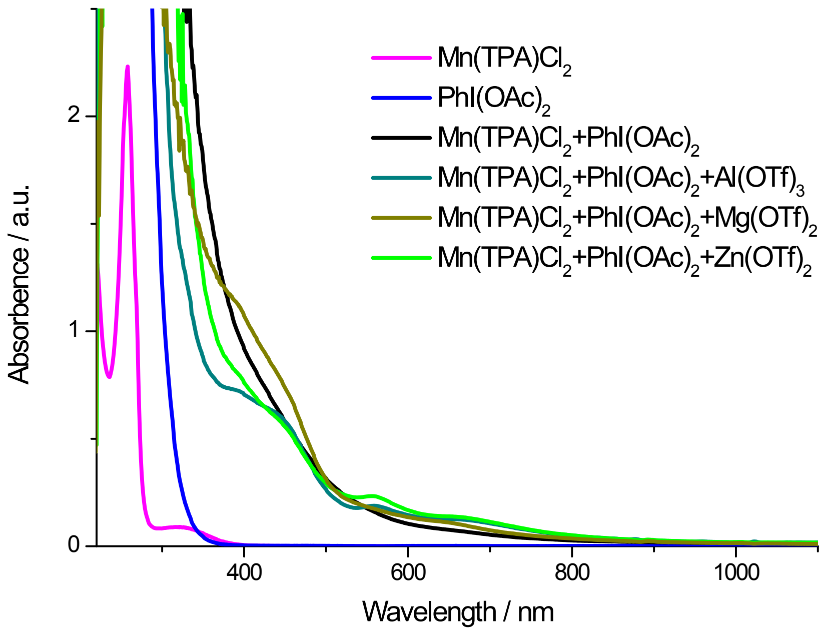

Figure S3. UV-Vis spectra of manganese complex, PhI(OAc)$_2$ and redox-inactive metal trifluoromethanesulfonates. Conditions: 1 mM Mn(TPA)Cl$_2$ in acetonitrile/CH_2Cl_2 (4:1, v/v), 5 equiv. of PhI(OAc)$_2$, 2 equiv. of redox-inactive metal trifluoromethanesulfonates.

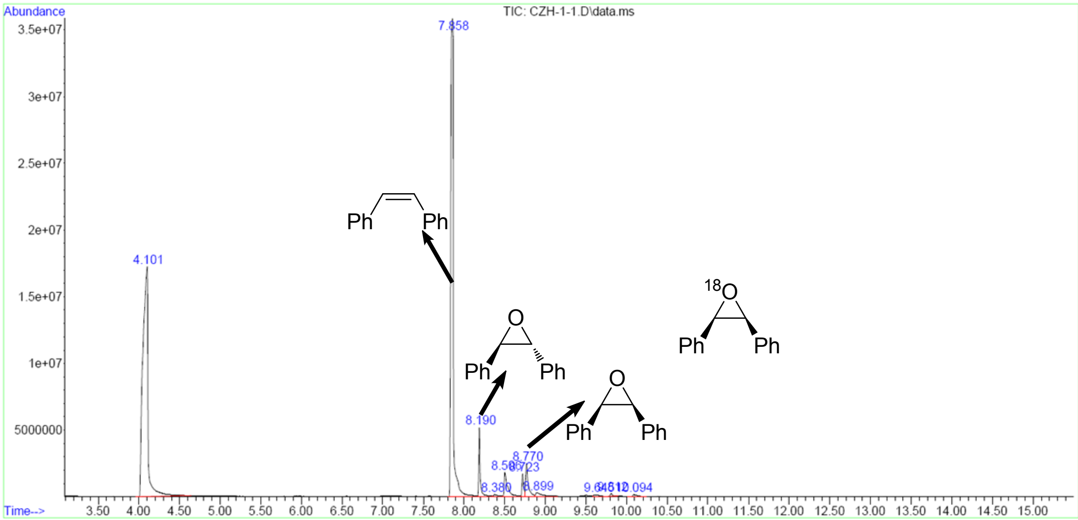

Figure S4-1. GC-MS graph of $H_2{}^{18}O$ labelled catalytic *cis*-stilbene epoxidation by $Mn(TPA)Cl_2$ plus $Al(OTf)_3$ with $PhI(OAc)_2$. Conditions: solvent $H_2{}^{18}O$ 0.1 mL acetonitrile 0.4 mL CH_2Cl_2 0.1 mL, olefin 0.05 M, manganese(II) catalyst 1 mM, Lewis acid 2 mM, $PhI(OAc)_2$ 0.05 mmol, 273 K, 8 h.

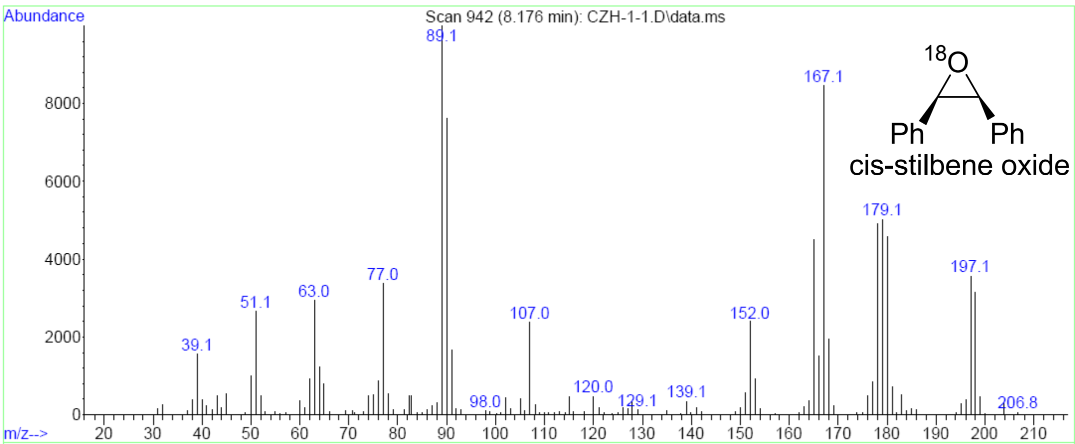

Figure S4-2. MS graph of ^{18}O labeled *cis*-stilbene oxide from catalytic epoxidation of *cis*-stilbene by $Mn(TPA)Cl_2$ plus $Al(OTf)_3$ with $PhI(OAc)_2$.

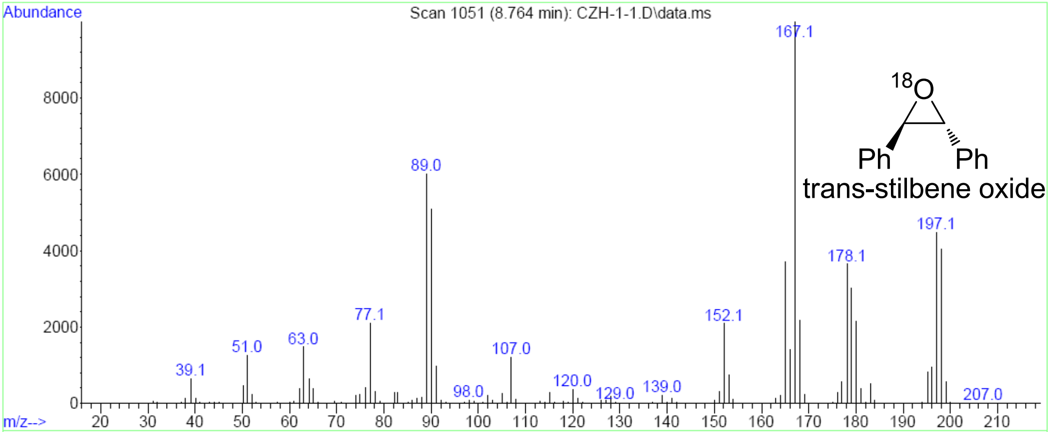

Figure S4-3. MS graph of ^{18}O labeled *trans*-stilbene oxide from catalytic epoxidation of *cis*-stilbene by $Mn(TPA)Cl_2$ complexes plus $Al(OTf)_3$ with $PhI(OAc)_2$.

Table S5. Catalytic oxidation of cyclooctene by $Mn(TPA)Cl_2$ and $Al(OTf)_3$ with PhIO as oxidant

Entry	$Mn(TPA)Cl_2$ (mM)	$Al(OTf)_3$ (mM)	Conv. (%)	Yield (%)
1	0	0	2.4(0.2)	0.9(0.1)
2	0	2	5(0.3)	2.7(0.2)
3	1	0	14.8(0.4)	10.8(0.1)
4	1	2	27.1(0.6)	23.3(1.0)

Conditions: solvent: acetonitrile/CH_2Cl_2 (4:1,v/v) 5 mL, cyclooctene 0.05 M, PhIO 0.1 M, 273 K, 3.5 h . Data in parentheses represent the deviations.

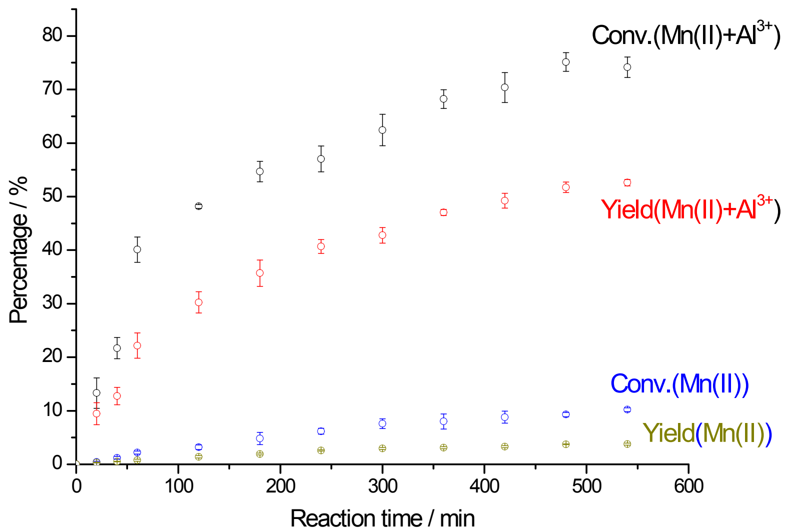

Figure S5-1. Kinetics of 1-hexene epoxidation by $Mn(TPA)Cl_2$ catalyst. Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 5 mL, 1-hexene 0.05 M, $Mn(TPA)Cl_2$ 1 mM, $Al(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.1 M, 273 K.

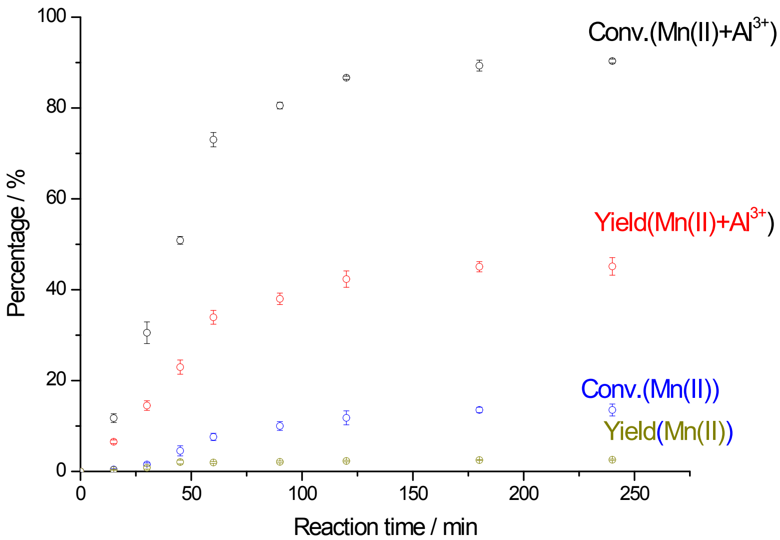

Figure S5-2. Kinetics of 1-dodecene epoxidation by $Mn(TPA)Cl_2$ catalyst. Conditions: acetonitrile/CH_2Cl_2 (4:1, v/v) 5 mL, 1-dodecene 0.05 M, $Mn(TPA)Cl_2$ 1 mM, $Al(OTf)_3$ 2 mM, $PhI(OAc)_2$ 0.1 M, 273 K.

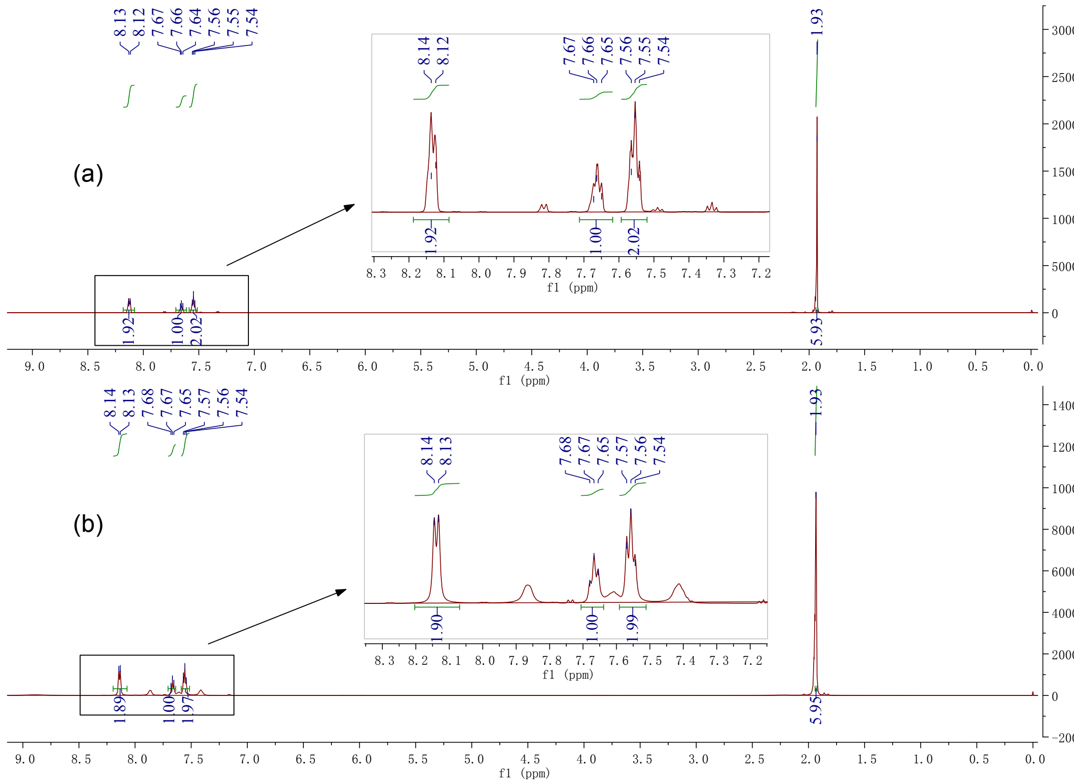

Figure S6. ^{1}H-NMR spectra of (a) $PhI(OAc)_2$ and (b) $Al(OTf)_3$ plus $PhI(OAc)_2$ in CD_3CN/CD_3Cl solution (4:1, v/v). The NMR data indicate that there is no direct reaction between Al(III) and $PhI(OAc)_2$.