Supporting Information

Trimanganese Complexes Bearing Bidentate Nitrogen Ligands as a Highly Efficient Catalyst Precursor in the Epoxidation of Alkenes

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General. $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, 32% peracetic acid, and olefins were purchased, and used without further purification unless otherwise noted. Dichloromethane and acetonitrile were distilled from calcium hydride. Gas chromatography analyses were performed with a flame ionization detector using two different columns: 30 m x 0.25 mm x 0.25 μm and 30 m x 0.25 mm x 0.25 μm capillary column. All epoxides were identified by their ^1H and ^{13}C NMR spectral signals which were confirmed from literature values. Chemical shift are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane, or in ppm relative to the singlet at 7.26 ppm of CDCl_3 . ^{13}C NMR spectra are reported in ppm relative to the center line of a triplet at 77.0 ppm of CDCl_3 . Splitting patterns are designated as follows: s; singlet, d; doublet, t; triplet, q; quartet, m; multiplet, dd; doublet of doublet.

X-ray Crystal Structure Analysis of $[\text{Mn}_3(\text{ppei})_2(\text{OAc})_6]$ (1) and $[\text{Mn}_3(\text{phen})_2(\text{OAc})_6]$ (3). Reflection data were collected on a Bruker 1K SMART CCD-based diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The hemisphere of reflection data was collected as ω scan frames with a width of $0.3^\circ/\text{frame}$ and exposed time of 5s/frame. Cell parameters were determined and refined by SMART program.^{1a} Data reductions were performed using SAINT software,^{1b} that corrects for Lorentz polarization effects, but any corrections for crystal decay were not required. Empirical absorption corrections were applied with SADABS program.^{1c} Structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. The detailed crystallographic data for **1** and **3** are listed in table (Table S1 and S2).

FIGURE S1. Molecular structure of $[\text{Mn}_3(\text{ppei})_2(\text{OAc})_6]$ (**1**).

TABLE S1. Crystallographic Data of 1

empirical formula	C ₄₀ H ₄₆ Mn ₃ N ₄ O ₁₂
Formula weight	939.63
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2
Unit cell dimensions	a = 25.460(8) Å alpha = 90 deg. b = 10.292(6) Å beta = 98.503(11) deg. c = 16.264(6) Å gamma = 90 deg.
Volume	4215(3) Å ³
Z, Calculated density	4, 1.481 Mg/m ³
Absorption coefficient	0.951 mm ⁻¹
F(000)	1940
Theta range for data collection	1.27 to 28.16 deg.
Limiting indices	-31 ≤ h ≤ 33 -13 ≤ k ≤ 13 -21 ≤ l ≤ 20
Reflections collected / unique	12649 / 7841 [R(int) = 0.0336]
Completeness to theta = 28.01	91.8 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7841 / 1 / 680
Goodness-of-fit on F ²	1.025
Final R indices [I > 2sigma(I)]	R1 = 0.0414, wR2 = 0.0964
R indices (all data)	R1 = 0.0553, wR2 = 0.1041
Largest diff. peak and hole	0.249 and -0.418 e.Å ⁻³

FIGURE S2. Molecular structure of $[\text{Mn}_3(1,10\text{-phenanthroline})_2(\text{OAc})_6]$ (**3**).

Table S2. Crystallographic Data of 3

Empirical formula	$\text{C}_{36}\text{H}_{34}\text{Mn}_3\text{N}_4\text{O}_{12}$
Formula weight	879.49
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $C2/c$
Unit cell dimensions	$a = 11.4098(14)$ Å $\alpha = 90^\circ$ $b = 12.4332(14)$ Å $\beta = 98.624(3)^\circ$ $c = 26.421(3)$ Å $\gamma = 90^\circ$
Volume	$3705.7(8)$ Å ³
Z, Calculated density	4, 1.576 Mg/m^3
Absorption coefficient	1.075 mm^{-1}
$F(000)$	1796
Theta range for data collection	1.56 to 28.01°

Limiting indices	-14≤h≤14 -15≤k≤15 -34≤l≤33
Reflections collected / unique	20497 / 4250 [R(int) = 0.1372]
Completeness to theta = 28.01	94.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4250 / 0 / 253
Goodness-of-fit on F ²	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0785, wR2 = 0.2114
R indices (all data)	R1 = 0.1039, wR2 = 0.2310
Largest diff. peak and hole	1.158 and -1.147 e.Å ⁻³

General Procedure for the Competition Experiments.² A 10 mL round bottom flask was charged with styrene (52.6 mg, 0.5 mmol), *p*-substituted styrene (0.5 mmol), dodecane (0.5 mmol, internal standard), **1** (9.4 mg, 0.01 mmol, 2.0 mol %), and acetonitrile (2.0 mL). To the mixture was added 32% peracetic acid (0.10 mL, 0.5 mmol) dropwise via syringe over 3 min and the reaction mixture was stirred for 15 min at room temperature. Aliquots were taken from the reaction mixture and passed through a pad of silica gel washing with diethyl ether. Conversion of each olefin was determined by GC analysis using an internal standard method. Relative reaction rates of each olefin were calculated from eq 1, where $[S_X]_0$ and $[S_X]$ are the initial and final concentration of *p*-substituted styrenes, and $[S_H]_0$ and $[S_H]$ are the initial and final concentration of styrene.

$$k_X/k_H = \ln([S_X]/[S_X]_0)/\ln([S_H]/[S_H]_0) \quad (1)$$

TABLE S3. Relative reactivity of the epoxidation in *p*-substituted styrene catalyzed by **1^a**

R	α_X/α_H^b	k_{rel}	$\log k_{rel}$	σ_p^+
OMe	3.52	6.3541	0.8031	-0.78
Me	1.83	2.2745	0.3569	-0.31
H	1	1	0	0
F	1.08	1.1775	0.0709	-0.07
Cl	0.92	0.8715	-0.0597	0.11
CF ₃	0.63	0.4261	-0.3705	0.61

^a Reaction conditions: styrene (0.5 mmol), *p*-substituted styrene (0.5 mmol), **1** (2.0 mol %), and 32% CH₃CO₃H (0.5 mmol) in CH₃CN (2.0 mL), 25 °C, 18 min. Conversion was determined by GC using an internal standard. ^b The ratio of conversion between *p*-substituted styrene and styrene in each competition experiment.

Representative Procedure for the Radical Inhibition Experiments with 2,6-Di-*tert*-butyl-*p*-cresol (BHT). To a solution of 4-chlorostyrene (71.4 mg, 0.5 mmol) and dodecane (85.1 mg, 0.5 mmol) in acetonitrile (1.0 mL) was added 2,6-di-*tert*-butyl-*p*-cresol (BHT, 55.1 mg, 0.25 mmol) followed by **1** (5.6 mg, 1.2 mol %). Peracetic acid (32% solution, 0.13 mL, 1.2 equiv to olefin) was added dropwise via

syringe over 3 min and the reaction mixture was stirred for 15 min at room temperature. The mixture was diluted with diethyl ether and small aliquots were taken from the reaction mixture to analyze the conversion and yield using GC. The results show that change of the reaction rate was negligible with aliphatic olefin. However, a significant inhibition was observed with styrene derivatives.

Epoxidation of Alkenes with $\text{Mn}_3(\text{ppe})_2(\text{OAc})_6$ (1).

1-Octene (Table 2, entry 2, condition A).³ In GC, the oven condition was 40 °C for 2 min, 5 °C/min to 80 °C holding for 2 min, and then 25 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of 1,2-epoxyoctane was 10.89 min. The reaction proceeded with >98% conversion and 96% GC yield on the basis of an average of 3 runs. In two trials of gram scale epoxidation process, the desired epoxide was obtained in average 86% yield: ¹H NMR (400 MHz, CDCl_3) δ 2.88 (m, 1H), 2.72 (dd, 1H, J = 5.0, 3.9 Hz), 2.43 (dd, 1H, J = 5.0, 2.7 Hz), 1.24-1.53 (m, 10H), 0.86 (t, 3H, J = 7.0 Hz); ¹³C NMR (100 MHz, CDCl_3) δ 52.4, 47.1, 32.4, 31.7, 29.1, 25.9, 22.5, 14.0.

Trans-2-octene (Table 2, entry 3, condition A).⁴ The oven condition was 40 °C for 2 min, 5 °C/min to 80 °C holding for 2 min, and 25 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of *trans*-2,3-epoxyoctane was 9.22 min. The reaction proceeded with >98% conversion and 94% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation process, *trans*-epoxide product was obtained in average 87% yield: ¹H NMR (400 MHz, CDCl_3) δ 2.72 (m, 1H), 2.60 (m, 1H), 1.28-1.50 (m, 8H), 1.26 (d, 3H, J = 5.3 Hz), 0.86 (t, 3H, J = 6.8 Hz); ¹³C NMR (100 MHz, CDCl_3) δ 59.8, 54.5, 31.9, 31.6, 25.6, 22.5, 17.6, 13.9.

Cis-2-octene (Table 2, entry 4, condition A).⁴ The oven condition was 40 °C for 2 min, 5 °C/min to 80 °C holding for 2 min, and 25 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of *cis*-2,3-epoxyoctane was 10.03 min. The reaction took place with >98% conversion and 97% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 91% yield: ¹H NMR (400 MHz, CDCl_3) δ 3.01 (m, 1H), 2.86 (m, 1H), 1.30-1.53 (m, 8H), 1.23 (d, 3H, J = 5.5 Hz), 0.87 (t, 3H, J = 6.9 Hz); ¹³C NMR (100 MHz, CDCl_3) δ 57.1, 52.6, 31.6, 27.4, 26.1, 22.5, 13.9, 13.1.

2-Methyl-1-heptene (Table 2, entry 5, condition A).⁵ The oven condition was 50 °C for 3 min, 5 °C/min to 90 °C holding for 1 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of 1,2-epoxy-2-methylheptane was 8.01 min. The reaction proceeded with >98% conversion and

97% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 90% yield: ^1H NMR (400 MHz, CDCl_3) δ 2.57 (d, 1H, $J = 4.9$ Hz), 2.54 (d, 1H, $J = 5.0$ Hz), 1.23-1.46 (m, 8H), 1.27 (s, 3H), 0.85 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 57.0, 53.9, 36.6, 31.8, 24.9, 22.5, 20.8, 13.9.

2-Methyl-2-hexene (Table 2, entry 6, condition A). The oven condition was 40 °C for 5 min, 5 °C/min to 70 °C holding for 1 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of 2,3-epoxy-2-methylhexane was 5.93 min. The reaction gave >98% conversion and 92% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 83% yield: ^1H NMR (400 MHz, CDCl_3) δ 2.66 (t, 1H, $J = 6.2$ Hz), 1.37-1.49 (m, 4H), 1.26 (s, 3H), 1.21 (s, 3H), 0.92 (t, 3H, $J = 7.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 64.3, 58.0, 30.7, 24.8, 19.7, 18.6, 13.8.

Cyclohexene (Table 2, entry 7, condition A).⁶ The oven condition was 40 °C for 5 min, 5 °C/min to 70 °C holding for 1 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of cyclohexene oxide was 7.65 min. The reaction provided >98% conversion and 95% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 79% yield: ^1H NMR (400 MHz, CDCl_3) δ 3.09 (s, 2H), 1.76-1.93 (m, 4H), 1.15-1.41 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 52.1, 24.4, 19.4.

Cyclooctene (Table 2, entry 8, condition A).⁵ The oven condition was 50 °C for 3 min, 5 °C/min to 90 °C holding for 3 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of cyclooctene oxide was 13.02 min. The reaction gave >98% conversion and 90% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 81% yield: ^1H NMR (400 MHz, CDCl_3) δ 2.87 (m, 2H), 2.11 (m, 2H), 1.40-1.63 (m, 8H), 1.24 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 26.5, 26.2, 25.5.

Allyl acetate (Table 2, entry 9, condition B).⁷ The oven condition was 40 °C for 5 min, 5 °C/min to 70 °C holding for 1 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of 1,2-epoxypropyl acetate was 9.59 min. The reaction afforded >98% conversion and 97% GC yield based on an average of 3 runs: ^1H NMR (400 MHz, CDCl_3) δ 4.33 (dd, 1H, $J = 12.2, 3.0$ Hz), 3.83 (dd, 1H, $J = 12.3, 6.4$ Hz), 3.14 (m, 1H), 2.77 (t, 1H, $J = 4.3$ Hz), 2.57 (dd, 1H, $J = 4.9, 2.6$ Hz), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 64.9, 49.2, 44.5, 20.6.

9-Decen-1-ol (Table 2, entry 10, condition A). The oven condition was 120 °C for 3 min, 20 °C/min to 150 °C holding for 1 min, and 5 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of 8,9-epoxydecan-1-ol was 7.73 min. The reaction gave 95% conversion and 89% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 82% yield: ¹H NMR (400 MHz, CDCl₃) δ 3.62 (t, 2H, *J* = 8.8 Hz), 2.90 (m, 1H), 2.74 (t, 1H, *J* = 6.4 Hz), 2.46 (dd, 1H, *J* = 6.6, 3.6 Hz), 1.82 (br, 1H), 1.25-1.56 (m, 14H); ¹³C NMR (100 MHz, CDCl₃) δ 62.8, 52.3, 47.0, 32.6, 32.3, 29.39, 29.26, 29.22, 25.8, 25.6.

2-Cyclohexen-1-one (Table 2, entry 11, condition B).⁸ The oven condition was 60 °C for 2 min, 5 °C/min to 110 °C holding for 1 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of 2,3-epoxycyclohexane-1-one was 7.85 min. The reaction resulted in >98% conversion and 95% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 85% yield: ¹H NMR (400 MHz, CDCl₃) δ 3.56 (m, 1H), 3.19 (d, 1H, *J* = 3.9 Hz), 2.48-2.55 (m, 1H), 2.21-2.27 (m, 1H), 1.85-2.07 (m, 3H), 1.62-1.70 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 206.0, 55.9, 55.1, 36.3, 22.8, 16.9.

Norbornene (Table 2, entry 12, condition B).⁶ The oven condition was 40 °C for 5 min, 5 °C/min to 70 °C holding for 1 min, and 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of *exo*-2,3-epoxynorbornane was 10.98 min. The reaction proceeded with >98% conversion and 72% GC yield based on an average of 3 runs: ¹H NMR (400 MHz, CDCl₃) δ 3.01 (s, 2H), 2.39 (br s, 2H), 1.42-1.46 (m, 2H), 1.25-1.30 (m, 1H), 1.15-1.18 (m, 2H), 0.64 (d, 1H, *J* = 9.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 51.3, 36.5, 26.1, 25.0.

***R*-(-)-Carvone** (Table 2, entry 13, condition A).⁹ The oven condition was 105 °C for 3 min, 5 °C/min to 180 °C holding for 1 min on HP-5MS column. Retention times of carvone-8,9-oxide diastereomers and carvone-1,2-oxide diastereomers were 10.68, 10.76, 11.31, and 11.59 min, respectively. The reaction took place with >98% conversion and 93% GC yield based on an average of 3 runs. Diastereomers of carvone-8,9-oxide (1.2:1 mixture of 8,9-oxide and 1,2-oxide): ¹H NMR (400 MHz, CDCl₃) δ 6.70 (m, 2H), 2.67 (d, 1H, *J* = 4.4 Hz), 2.64 (d, 1H, *J* = 4.4 Hz), 2.01-2.57 (m, 12H), 1.74 (br s, 6H), 1.29 (s, 3H), 1.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.7, 144.0, 143.8, 135.6, 135.5, 57.9, 57.8, 52.9, 52.3, 41.3, 40.6, 40.3, 39.9, 27.8, 27.6, 18.9, 18.3, 15.6.

Styrene (Table 3, entry 1, condition A).⁶ The oven condition was 60 °C for 3 min, 15 °C/min to 200 °C holding for 1 min on a HP-5MS column. Retention time of styrene oxide was 7.14 min. The reaction was carried out in >98% conversion and 93% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 84% yield: ¹H NMR (400 MHz, CDCl₃) δ 7.30 (m, 5H), 3.84 (dd, 1H, *J* = 4.0, 2.6 Hz), 3.13 (dd, 1H, *J* = 5.5, 4.1 Hz), 2.79 (dd, 1H, *J* = 5.5, 2.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 137.5, 128.4, 128.1, 125.4, 52.3, 51.1.

4-Chlorostyrene (Table 3, entry 2, condition A).¹⁰ The oven condition was 100 °C for 3 min, 5 °C/min to 140 °C holding for 1 min on a HP-5MS column. Retention time of 4-chlorostyrene oxide was 7.84 min. The reaction proceeded with >98% conversion and 94% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 88% yield: ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, 2H, *J* = 8.4 Hz), 7.19 (d, 2H, *J* = 8.5 Hz), 3.81 (dd, 1H, *J* = 3.9, 2.6 Hz), 3.12 (dd, 1H, *J* = 5.4, 4.0 Hz), 2.73 (dd, 1H, *J* = 5.5, 2.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 136.1, 133.9, 128.6, 126.8, 51.7, 51.2.

4-Acetoxystyrene (Table 3, entry 3, condition A). Yield was measured by the integration of protons for 4-acetoxystyrene oxide in comparison with peak integration of tetrachloroethane (internal standard) from the crude reaction mixture. The reaction proceeded with >98% conversion (analyzed by GC) and 90% NMR yield based on an average of 3 runs: ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, 2H, *J* = 8.6 Hz), 7.05 (d, 2H, *J* = 8.6 Hz), 3.84 (dd, 1H, *J* = 3.9, 2.6 Hz), 3.11 (dd, 1H, *J* = 5.4, 4.0 Hz), 2.74 (dd, 1H, *J* = 5.4, 2.5 Hz), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 150.5, 135.2, 126.5, 121.6, 51.8, 51.1, 21.0.

Trans-β-methylstyrene (Table 3, entry 4, condition A).⁶ The oven condition was 65 °C for 2 min, 5 °C/min to 100 °C holding for 2 min, 30 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of *trans*-β-methylstyrene oxide was 9.64 min. The reaction showed >98% conversion and 91% GC yield based on an average of 3 runs: ¹H NMR (400 MHz, CDCl₃) δ 7.27 (m, 5H), 3.55 (d, 1H, *J* = 2.5 Hz), 3.12 (dq, 1H, *J* = 6.8, 2.6 Hz), 1.43 (d, 3H, *J* = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 137.7, 128.3, 127.9, 125.4, 59.4, 58.9, 17.8.

Trans-stilbene (Table 3, entry 5, condition A).¹⁰ The reaction was performed using a cosolvent system of CH₂Cl₂/CH₃CN (1:1, v/v) due to poor solubility of *trans*-stilbene in CH₃CN alone. The oven condition was 110 °C for 3 min, 15 °C/min to 180 °C holding for 1 min, 5 °C/min to 210 °C holding for 1 min on HP-5MS column. Retention time of *trans*-stilbene oxide was 6.95 min. The reaction took place with

>98% conversion and 94% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 91% yield using condition B (2.0 mol % **1** and 2.0 equiv of peracetic acid): ¹H NMR (400 MHz, CDCl₃) δ 7.35 (m, 10H), 3.86 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 137.1, 128.5, 128.2, 125.5, 62.7.

Cis-β-methylstyrene (Table 3, entry 6, condition A).¹¹ The oven condition was 60 °C for 3 min, 5 °C/min to 100 °C holding for 1 min, 25 °C/min to 200 °C holding for 1 min on HP-1MS column. Retention times of *cis*- and *trans*-β-methylstyrene oxide were 9.95 and 10.27 min, respectively. The reaction proceeded with 97% conversion and 80% GC yield (*cis/trans*, 4.1:1) based on an average of 3 runs. *Cis*-β-methylstyrene oxide: ¹H NMR (400 MHz, CDCl₃) δ 7.29 (m, 5H), 4.05 (d, 1H, *J* = 5.6 Hz), 3.33 (dq, 1H, *J* = 7.1, 5.8 Hz), 1.08 (d, 3H, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 127.9, 127.4, 126.5, 57.5, 55.0, 12.5.

Ethyl-*trans*-cinnamate (Table 3, entry 8, condition B).⁶ The oven condition was 120 °C for 3 min, 20 °C/min to 150 °C holding for 1 min, 5 °C/min to 200 °C holding for 1 min on HP-5MS column. Retention time of ethyl-*trans*-cinnamate oxide was 6.21 min. The reaction was carried out in >98% conversion and 94% GC yield based on an average of 3 runs. In two trials of gram scale epoxidation, product was obtained in average 92% yield using 3.6 mol % **1** and 2.4 equiv peracetic acid under condition B: ¹H NMR (400 MHz, CDCl₃) δ 7.31 (m, 5H), 4.28 (m, 2H), 4.08 (d, 1H, *J* = 1.9 Hz), 3.50 (d, 1H, *J* = 1.9 Hz), 1.32 (t, 3H, *J* = 9.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 134.9, 128.8, 128.5, 125.7, 61.6, 57.8, 56.6, 14.0.

General Procedure for the Kinetic Studies.

Kinetics on the Catalyst. A series of epoxidations were carried out at several concentrations of catalyst **1** (0.0034, 0.0045, 0.0056, 0.0068 M). As an example, determination of the initial rate on 0.0034 M of catalyst **1** was carried out as follows. To a solution of styrene (105.2 mg, 1.0 mmol) in acetonitrile (2.2 mL) was added biphenyl (77.9 mg, 0.5 mmol, internal standard) followed by **1** (7.04 mg, 0.75 mol %, 0.0034 M). 32% peracetic acid (0.25 mL, 1.2 mmol) was added to the reaction mixture at one time at room temperature, aliquots were taken and quenched with saturated NaHCO₃ solution at the indicated

interval (180, 195, 210, 225, 240, 255 sec). After this solution was filtered through a pad of silica gel washing with diethyl ether, yield of styrene oxide was then monitored by GC using an internal standard.

Kinetics on the Olefin. As the same way of catalyst **1**, reactions were performed at several concentrations of styrene (0.22, 0.45, 0.68, 0.91 M). As an example, determination of the initial rate on 0.22 M of styrene was carried out as follows. To a solution of styrene (52.6 mg, 0.5 mmol) in acetonitrile (2.2 mL) was added biphenyl (77.9 mg, 0.5 mmol, internal standard) followed by **1** (9.4 mg, 0.01 mmol). 32% peracetic acid (0.25 mL, 1.2 mmol) was added to the reaction mixture at one time at room temperature and aliquots were withdrawn after 105, 120, 135, 150, 165, 180, and 195 sec. After quenching the aliquots with saturated NaHCO₃ solution, this solution was filtered through a pad of silica gel washing with diethyl ether, and yield of styrene oxide was then monitored by GC using an internal standard.

Kinetics on the Oxidant. Reactions were performed at several concentrations of peracetic acid (0.27, 0.34, 0.41, 0.55 M). As an example, determination of the initial rate on 0.27 M of peracetic acid was carried out as follows. To a solution of styrene (105.2 mg, 1.0 mmol) in acetonitrile (2.2 mL) was added biphenyl (77.9 mg, 0.5 mmol, internal standard) followed by **1** (18.8 mg, 0.02 mmol). 32% peracetic acid (126 μ L, 0.6 mmol) was added to the reaction mixture at one time at room temperature and aliquots were withdrawn after 180, 195, 210, 225, and 240 sec. After quenching the aliquots with saturated NaHCO₃ solution, this solution was filtered through a pad of silica gel washing with diethyl ether, and yield of styrene oxide was then monitored by GC using an internal standard.

Kinetic Data on the Catalyst 1.

$$[\text{cat}] = 3.41 \times 10^{-3} \text{ M}$$

time(sec)	0 to 165	180	195	210	225	240	255
yield(%)	0	6.1	10.4	13.2	16.5	18.9	24.3

$$[\text{cat}] = 4.54 \times 10^{-3} \text{ M}$$

time(sec)	0 to 105	120	135	150	165	180	195
yield(%)	0	6.8	10.9	15.2	19.7	24.8	29.2

$$[\text{cat}] = 5.68 \times 10^{-3} \text{ M}$$

time(sec)	0 to 105	120	135	150	165	180	195
yield(%)	0	3.6	8.4	14.3	19.5	26.0	33.0

$$[\text{cat}] = 6.81 \times 10^{-3} \text{ M}$$

time(sec)	0 to 105	120	135	150	165
yield(%)	0	4.5	11.2	18.3	26.9

[cat] (M)	Initial Rate (M/s)	R ²
3.41×10^{-3}	1.04×10^{-3}	0.9938
4.54×10^{-3}	1.40×10^{-3}	0.9995
5.68×10^{-3}	1.77×10^{-3}	0.9979
6.81×10^{-3}	2.25×10^{-3}	0.9981

Kinetic Data on Olefin (Styrene).

[styrene] = 0.22 M

time(sec)	0 to 90	105	120	135	150	165
yield(%)	0	6.9	14.9	25.1	32.8	41.0

[styrene] = 0.45 M

time(sec)	0 to 105	120	135	150	165	180	195
yield(%)	0	6.8	10.9	15.2	19.7	24.8	29.2

[styrene] = 0.68 M

time(sec)	0 to 165	180	195	210	225	240	255
yield(%)	0	4.7	8.8	11.8	16.0	17.8	20.7

[styrene] = 0.91 M

time(sec)	0 to 165	180	210	240	270	300
yield(%)	0	7.3	11.9	17.2	20.9	26.3

[styrene] (M)	Initial rate (M/s)	R ²
0.22	1.30×10^{-3}	0.9989
0.45	1.40×10^{-3}	0.9995
0.68	1.44×10^{-3}	0.9940
0.91	1.42×10^{-3}	0.9987

Kinetic Data on Oxidant (Peracetic acid).

[peracetic acid] = 0.27 M

time(sec)	0 to 180	195	210	225	240
yield(%)	0	5.4	12.9	24.3	32.9

[peracetic acid] = 0.34 M

time(sec)	0 to 120	150	165	180	195
yield(%)	0	4.7	12.2	25.7	39.8

[peracetic acid] = 0.41 M

time(sec)	0 to 45	60	75	90
yield(%)	0	4.5	26.0	37.6

[peracetic acid] = 0.55 M

time(sec)	0 to 20	35	50	65
yield(%)	0	4.8	23.4	48.0

[peracetic acid] (M)	Initial rate (M/s)	R ²
0.27	0.0028	0.9943
0.34	0.0036	0.9828
0.41	0.0050	0.9710
0.55	0.0065	0.9936

FIGURE S3. Log plots of initial reaction rates vs concentration of **1**, styrene, and oxidant.

Experimental Procedure for the Observation of Induction Period in the Epoxidation with Catalyst

1. To a solution of 4-chlorostyrene (142.8 mg, 1.0 mmol) in acetonitrile (2.0 mL) was added tetrachloroethane (167.8 mg, 1.0 mmol, internal standard) followed by **1** (18.8 mg, 0.02 mmol). Peracetic acid (32%, 0.23 mL, 1.1 mmol) was then added to the reaction mixture at one portion at 0 °C and the reaction mixture was stirred at the same temperature. Aliquots were then withdrawn after 30, 60, 90, 120, 150, 210, 270, 390, and 450 sec. After dilution of the aliquots with chloroform-*d* in NMR tube, conversion of 4-chlorostyrene was then monitored by ¹H NMR using an internal standard method. As can be seen in the below data, the reaction starts only after 90 sec. Likewise, in the reaction of styrene, the epoxide started to produce after 30 sec at 0.55 M of peracetic acid and 180 sec at 0.27 M.

time(sec)	30	60	90	120	150	210	270	390	450
conv.(%)	0	0	0	65	88	89	94	98	>99

Experimental Procedure for the Synthesis of Polymer Supported Mn (4).

Merrifield resin (2.00 g, 3.4 mmol/g, 200-400 mesh) was swollen in anhydrous DMF (30 mL) for 4 h at 60 °C. After cooling to room temperature, 5-hydroxy-2-methylpyridine (2.96 g, 27.2 mmol), cesium carbonate (8.86 g, 27.2 mmol), and sodium iodide (4.08 g, 27.2 mmol) were added under stirring. The mixture was heated at 80 °C for 12 h. The resin was collected by filtration and washed with DMF (3 x 25 mL), MeOH (3 x 25 mL), H₂O (3 x 40 mL), MeOH (3 x 25 mL), CH₂Cl₂ (3 x 25 mL), and finally MeOH (3 x 25 mL). The resin was then dried overnight in vacuum to give **5** (2.3 g). The elemental analysis of **5** afforded a nitrogen content of 2.14 mmol/g (found: C, 80.72; H, 7.37; N, 2.99).

Resin **5** (2.10 g, 4.49 mmol) was swollen in anhydrous CHCl₃ (40 mL) for 6 h at room temperature. To this suspension of resin **3**, *m*-chloroperoxybenzoic acid (77% max, 4.02 g, 17.9 mmol) was added and the resulting mixture was stirred for 24 h at room temperature. The resin was collected by filtration and washed with CHCl₃ (3 x 25 mL), CH₂Cl₂ (3 x 30 mL), MeOH (3 x 25 mL), CH₂Cl₂ (3 x 30 mL), CHCl₃ (3 x 25 mL), and MeOH (3 x 25 mL). The obtained resin was then dried overnight in vacuum to give **6** (2.12 g). IR (KBr) 2919, 1509, 1297, 1173 cm⁻¹. Elemental analysis revealed the nitrogen content of 2.71 wt%.

Resin **6** (1.81 g) was swollen in anhydrous CH₂Cl₂ (30 mL) for 6 h at room temperature. Trifluoroacetic anhydride (2.47 mL, 17.5 mmol) was added dropwise at 0 °C to the above suspension of resin **6**. After being stirred for 30 min at 0 °C, the reaction mixture was allowed to warm to room temperature. The mixture was stirred for 24 h and then MeOH (30 mL) was added. After stirring the reaction mixture for additional 12 h at room temperature, the resin was collected by filtration and washed with CH₂Cl₂ (3 x 30 mL), MeOH (3 x 25 mL), CH₂Cl₂ (3 x 30 mL), and MeOH (3 x 25 mL). The resin was dried overnight in

vacuum to give **7** (1.72 g). IR (KBr) 3392, 2920, 1511, 1451, 1174 cm^{-1} . Elemental analysis revealed the nitrogen content of 2.64 wt%.

Resin **7** (1.60 g) was swollen in anhydrous 1,4-dioxane (30 mL) for 4 h at 60 $^{\circ}\text{C}$. Selenium dioxide (1.99 g, 18.0 mmol) was added to a suspension of resin **7** at room temperature. After being stirred for 20 h at 90 $^{\circ}\text{C}$, the resin was collected by filtration and washed with MeOH (3 x 25 mL), H_2O (3 x 25 mL), MeOH (3 x 25 mL), CH_2Cl_2 (3 x 25 mL), and MeOH (3 x 25 mL). The resin was dried overnight in vacuum to give **8** (1.49 g). IR (KBr) 3445, 2849, 1698, 1270, 1213 cm^{-1} . Elemental analysis revealed the nitrogen content of 2.38 wt%.

Resin **8** (1.35 g) was swollen in anhydrous EtOH (25 mL) for 4 h at 60 $^{\circ}\text{C}$. α -Methylbenzylamine (1.67 g, 13.8 mmol) was added to a suspension of resin **8** at room temperature. After being stirred for 12 h at 80 $^{\circ}\text{C}$, the resin was collected by filtration and washed with CHCl_3 (3 x 20 mL), MeOH (3 x 20 mL), CHCl_3 (3 x 20 mL), MeOH (3 x 20 mL), and CHCl_3 (3 x 20 mL). The resin was dried overnight in vacuum to give **9** (1.38 g). IR (KBr) 2920, 1671, 1601, 1571, 1492, 1374 cm^{-1} . Elemental analysis revealed the nitrogen content of 2.90 wt%.

Resin **9** (1.20 g) was swollen in anhydrous EtOH (40 mL) for 4 h at 60 $^{\circ}\text{C}$. $\text{Mn(OAc)}_2 \cdot \text{H}_2\text{O}$ (1.52 g, 6.2 mmol) was added in one portion to a suspension of resin **9** at 80 $^{\circ}\text{C}$. After being stirred for 12 h at 80 $^{\circ}\text{C}$, the resin was collected by filtration and washed with MeOH (5 x 30 mL) and CHCl_3 (5 x 30 mL) until the filtrate remained colorless. The resin was dried overnight in vacuum to give **4** (1.16 g). IR (KBr) 3030, 1695, 1655, 1530, 1402 cm^{-1} . ICP and EA analysis of **4** afforded a manganese content of 0.329 mmol/g (1.81 wt %) and a nitrogen content of 1.77 mmol/g (found: N, 2.48), respectively.

General Procedure of Epoxidation Using Polymer Supported Manganese Complex (4). A suspension of the polymer supported manganese complex **4** (30.4 mg, 2.0 mol %, 0.329 mmol/g of Mn based on ICP analysis) containing *trans*- β -methylstyrene (59.6 mg, 0.5 mmol) and dodecane (85.1 mg, internal standard) in acetonitrile (1.0 mL) was stirred for 2 h at room temperature to swell the polymer. Peracetic acid (32%, 0.13 mL, 0.6 mmol) was added dropwise via syringe over 3 min to the resulting suspension. After 15 min, the reaction mixture was diluted with diethyl ether and filtered through glass frit washing with diethyl ether. Aliquots were taken from the filtrate, quenched with saturated NaHCO₃, and passed through a pad of silica gel. Samples were analyzed by GC to determine the extent of conversion and yield. *Trans*- β -methylstyrene oxide was produced in 94% selectivity based on 47% conversion as an average of two runs. The separated resin was washed with MeOH (3 x 10 mL) and CHCl₃ (3 x 10 mL), and dried under vacuum before using for the next run. Identical experiments were performed by the recovered resin under the same conditions. In the second run of epoxidation using the recovered polymer supported manganese complex, GC analysis indicated that *trans*- β -methylstyrene oxide was formed with 90% selectivity based on 29% conversion.

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