Electronic Supplementary Information (ESI) for

Isolation of a Mn$^{IV}$ acylperoxo complex and its monooxidation ability

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Experimental

Materials and methods. Experiments were carried out under an N₂ atmosphere by using standard Schlenk techniques. NaOCl aqueous solution (available chlorine: >5.0%) was purchased from Wako Pure Chemical Industries, Ltd. and was used as received. CH₂Cl₂ and CH₃CN were distilled over CaH₂ prior to use. Styrene was washed with 5% NaOH aqueous solution, washed with water (3 times), dried with MgSO₄, and distilled under reduced pressure. m-Chloroperoxybenzoic acid (m-CPBA) was purified by washing with a phosphate buffer and recrystallization in CH₂Cl₂ at 0 °C. ¹⁸O-m-CPBA (m-Cl-C₆H₄C(O)¹⁸O¹⁸OH) was prepared by the modified method described in the literature.¹ N,N’-bis-(3,5-di-tert-butylsalicylidene)-1,2-diaminoethane (tBu-salenH₂) was prepared by the method described in the literature.²

Electro-spray ionization mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC AccuTOF. Infrared (IR) spectra of solid compounds in KBr disks were recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument from 650 to 4000 cm⁻¹ using 2 cm⁻¹ standard resolution at 25 °C. Gas chromatography mass spectrometry (GC-MS) data were recorded on a SHIMADZU GCMS-QP 2010. Elemental analysis data were obtained by a PerkinElmer 2400II series CHNS/O analyzer. X-band electron spin resonance (ESR) spectra were measured by using a Bruker EMX plus spectrometer.

[Mn³⁺(tBu-salen)(CH₃C(O)O)(CH₃OH)] (1). Mn³⁺(CH₃C(O)O)₂·4H₂O (0.15 g, 0.61 mmol) and tBu-salenH₂ (0.30 g, 0.61 mmol) were dissolved in CH₃OH (3.5 mL) and the resulting solution was stirred at 60 °C for 2 h. After 2 h, the solution was cooled to 25 °C, to which was added water (4.0 mL) to yield brown powders of 1. The powders were collected by filtration and dried in vacuo (yield: 96% based on Mn³⁺(CH₃C(O)O)₂·4H₂O). ESI-MS (CH₃OH): m/z (% in the range m/z 200–2000): 545.3 (100) [1 – CH₃C(O)O – CH₃OH]⁺; FT-IR (cm⁻¹, KBr disk): 2868–2957 (aliphatic C–H), 1620 (C=N or C=C), 1554 (C=O); elemental analysis cald (%) for C₃₆H₅₇N₂MnO₆ (1·CH₃OH): C 64.65, H 8.59, N 4.19; found: C 64.35, H 8.44, N 4.41.

[Mn⁴⁺(tBu-salen)(CH₃O)₂] (2). CH₃ONa in CH₃OH (5 M, 250 µL) and NaOCl aqueous solution (available chlorine: >5.0%, 2.5 mL) were added to 1 (0.20 g, 0.31 mmol) in CH₃OH (15 mL) at 0 °C and the resulting solution was stirred for 30 min. To the
solution was added water (2.5 mL) to afford dark brown powders of 2, which were collected by filtration and dried in vacuo (yield: 73% based on 1). ESI-MS (CH$_3$OH): m/z (% in the range m/z 200–2000): 545.3 (100) [Mn$^{III}$(tBu-salen)]$^+$. 576.3 (49) [2 – CH$_3$O]$^+$; FT-IR (cm$^{-1}$, KBr disk): 2785–3060 (aliphatc C–H), 1632 (C=N or C=C); elemental analysis cald (%) for C$_{39}$H$_{60}$N$_2$MnO$_6$ (2·CH$_3$OH·H$_2$O): C 63.91, H 8.89, N 4.26; found: C 63.78, H 8.64, N 4.54.

[Mn$^{IV}$(tBu-salen)(m-Cl-C$_6$H$_4$C(O)O)$_2$] (3). [Mn$^{IV}$(tBu-salen)(CH$_3$O)$_2$] (2) (0.148 g, 0.244 mmol) was dissolved in 1,2-dichloroethane (5 mL) at 0 °C, to which was added m-chlorobenzoic acid (m-CBA) (0.153 g, 0.977 mmol). The resulting mixture was stirred for 1 h and the excess m-CBA was removed by filtration. The solvent of the filtrate was evaporated and the residue was recrystallized from 1,2-dichloroethane/pentane to afford dark green crystals of 3 (yield: 72% based on 2). ESI-MS (CH$_3$Cl/CH$_3$OH): m/z (% in the range m/z 200–2000): 576.3 (100) [3 – 2(m-Cl-C$_6$H$_4$C(O)O) + CH$_3$O]$^+$. 700.3 (17) [3 – m-Cl-C$_6$H$_4$C(O)O]$^+$. FT-IR (cm$^{-1}$, KBr disk): 2869–2960 (aliphatc C–H), 1622 (C=N or C=C), 1700, 1569 (C=O); elemental analysis cald (%) for C$_{48}$H$_{59}$N$_2$Cl$_4$MnO$_{6.5}$ (3·CH$_2$ClCH$_2$Cl·0.5H$_2$O): C 59.76, H 6.16, N 2.90; found: C 59.87, H 6.00, N 3.02.

**Procedure for isolation of [Mn$^{IV}$(tBu-salen)(m-Cl-C$_6$H$_4$C(O)OO)-(m-Cl-C$_6$H$_4$C(O)O)] (4).** m-CPBA (0.040 g, 0.23 mmol) was added into a CH$_2$Cl$_2$ solution (500 μL) of [Mn$^{IV}$(tBu-salen)(m-Cl-C$_6$H$_4$C(O)O)$_2$] (3) (0.020 g, 0.023 mmol) at −40 °C and the resulting solution was stirred for 2 h at −40 °C. To the resulting solution was added 2,2,4-trimethylpentane (1.5 mL) at −40 °C to precipitate excess amount of m-CPBA, which was removed by filtration at −40 °C. The solvent of the filtrate was evaporated at −40 °C to afford green powders of 4 (yield: 48% based on 3).

**Resonance Raman spectroscopy.** The resonance Raman spectra were obtained using a SpectraPro-300i spectrometer (Acton Research) with a 3600-grooves grating, a holographic Supernotch filter (Kaiser Optical Systems), 364 nm ultrasteeep long-pass edge filter (Semrock, RazorEdge), and LN-1100PB CCD detector (Princeton Instruments) cooled with liquid N$_2$. The 363.8 nm line was obtained from an Ar ion laser (Spectra physics, Stabilite 2017). The sample was sealed in NMR tubes and kept
in liquid N\textsubscript{2} in a double walled low-temperature quartz dewar. The sample cell was continuously rotated with a motor during data accumulation to reduce photodegradation. Power at the sample was less than 20 mW. Peak frequencies were calibrated relative to toluene (accurate to ± 1 cm\textsuperscript{-1}).

**Reaction of 3 with m-CPBA and reaction of 4 with styrene monitored by ESI-MS.**

To a CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}OH solution (5.0 mL/0.55 mL) of 3 (11.7 µmol), was added a CH\textsubscript{2}Cl\textsubscript{2} solution of 3 equivalents of m-CPBA at –40 °C to form 4. The signal at m/z 716.3 derived from 4 was detected by ESI-MS as shown in Fig. 3 in the manuscript. Addition of styrene (200 equivalents) to the CH\textsubscript{2}Cl\textsubscript{2}/CH\textsubscript{3}OH solution of 4 resulted in disappearance of the signal at m/z 716.3, which was monitored by ESI-MS.

**Quantitative analysis of styrene oxide produced from the catalytic epoxidation of styrene with 3 and m-CPBA by GC-MS.** To a mixture of 3 (10 nmol) and styrene (100 µmol) in CH\textsubscript{2}Cl\textsubscript{2} (400 µL) at –40 °C, was added a CH\textsubscript{2}Cl\textsubscript{2} solution (100 µL) of m-CPBA (10 µmol). The resulting solution was stirred for 3 h at –40 °C and addition of a CH\textsubscript{2}Cl\textsubscript{2} solution (500 µL) of nBu\textsubscript{4}NI (100 µmol) to the reaction mixture quenched the excess m-CPBA. Styrene oxide was quantified by GC-MS using hexamethylbenzene as an internal standard (yield: 773 nmol). Blank experiment except catalyst 3 was performed under the same experimental conditions (yield of styrene oxide: 93 nmol). In consideration of the blank experiment, the turnover number (mol of styrene oxide formed/mol of 3) was determined as 68. The epoxidation reaction was also performed using \textsuperscript{18}O-m-CPBA. The procedure was the same as that of the \textsuperscript{16}O-m-CPBA experiment except for using \textsuperscript{18}O-m-CPBA and \textsuperscript{18}O-styrene oxide as the product was detected by GC-MS.

**Quantitative analysis of styrene oxide produced from the epoxidation of styrene with 4 by GC-MS.** Styrene (5.5 mmol) was added into a CH\textsubscript{2}Cl\textsubscript{2} solution (500 µL) of 4 (0.55 µmol) at –40 °C. The resulting solution was stirred for 3 h at –40 °C, to which was added a CH\textsubscript{2}Cl\textsubscript{2} solution (50 µL) of nBu\textsubscript{4}NI (5.5 µmol) to quench the reaction at –40 °C. Styrene oxide was quantified by GC-MS using hexamethylbenzene as an internal standard (yield: 47% based on 4).
**X-ray crystallographic analysis.** X-ray quality crystals of 1, 2, and 3 were prepared by recrystallization from a CH$_3$OH/diethyl ether solution of 1 at 0 °C, a CH$_3$OH solution of 2 at 0 °C, and a CHCl$_3$/diethyl ether solution of 3 at –30 °C, respectively. Measurements were made on a Rigaku/MSC Saturn CCD diffractometer with confocal monochromated Mo-Kα radiation (λ = 0.7107 Å). Data were collected and processed using the CrystalClear program (Rigaku). Calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97 for 1 and 2 and the teXsan crystallographic software package of Molecular Structure Corporation for 3.
**Fig. S1** ORTEP drawing of [Mn$^{	ext{III}}$(tBu-salen)(CH$_3$C(O)O)(CH$_3$OH)] (1) with ellipsoids at 50% probability. The solvents (methanol) and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Mn1–O1 = 1.8725(19), Mn1–O2 = 1.876(2), Mn1–O3 = 2.142(3), Mn1–O5 = 2.400(3), Mn1–N1 = 1.990(3), Mn1–N2 = 1.980(2).
**Fig. S2** ORTEP drawing of [Mn$^{IV}$($t$Bu-salen)(CH$_3$O)$_2$] (2) with ellipsoids at 50% probability. The solvents (methanol) and hydrogen atoms are omitted for clarity. Selected interatomic distances (\(\text{Å}\)): Mn1–O1 = 1.8783(19), Mn1–O2 = 1.8682(17), Mn1–O3 = 1.849(2), Mn1–O4 = 1.881(2), Mn1–N1 = 1.980(2), Mn1–N2 = 1.981(2).
**Fig. S3** (a) Positive-ion ESI mass spectrum of \([\text{Mn}^{\text{III}}(t\text{Bu-salen})(\text{CH}_3\text{C}(\text{O})\text{O})(\text{CH}_3\text{OH})]\) (1) in CH$_3$OH. (b) The signal at \(m/z\) 545.3 corresponds to \([1 - \text{CH}_3\text{C}(\text{O})\text{O} - \text{CH}_3\text{OH}]^+\). (c) Calculated isotopic distribution for \([1 - \text{CH}_3\text{C}(\text{O})\text{O} - \text{CH}_3\text{OH}]^+\).
**Fig. S4** (a) Positive-ion ESI mass spectrum of $[\text{Mn}^\text{IV}(\text{tBu-salen})(\text{CH}_3\text{O})_2]$ (2) in CH$_3$OH. †: the signal at 545.3 corresponds to $[\text{Mn}^\text{III}(\text{tBu-salen})]^+$. (b) The signal at $m/z$ 576.3 corresponds to [2 – CH$_3$O]$^+$. (c) Calculated isotopic distribution for [2 – CH$_3$O]$^+$. 
Fig. S5 (a) Positive-ion ESI mass spectrum of 3 in CH₂Cl₂/CH₃OH. †: the signal at 1307.6 corresponds to [2(3) – 3(m-Cl-C₆H₄C(O)O) + 2(CH₃O)]⁺. ‡: the signal at 1276.6 to [3 – m-Cl-C₆H₄C(O)O + CH₃O + Mn³⁺(tBu-salen)]⁺. §: the signal at 576.3 to [3 – 2(m-Cl-C₆H₄C(O)O) + CH₃O]⁺. ¶: the signal at 545.3 corresponds to [Mn³⁺(tBu-salen)]⁺. (b) The signal at m/z 700.3 corresponds to [3 – m-Cl-C₆H₄C(O)O]⁺. (c) Calculated isotopic distribution for [3 – m-Cl-C₆H₄C(O)O]⁺.
Fig. S6 IR spectrum of [Mn$^{III}$(tBu-salen)(CH$_3$C(O)O)(CH$_3$OH)] (1) as a KBr disk.
**Fig. S7** IR spectrum of [Mn$^{IV}$($t$Bu-salen)(CH$_3$O)$_2$] (2) as a KBr disk.
**Fig. S8** IR spectrum of \([\text{Mn}^{IV}(\text{tBu-salen})(m-\text{Cl-C}_6\text{H}_4\text{C(0)O}_2)] (3)\) as a KBr disk.
**Fig. S9** ESR spectrum of [Mn<sup>III</sup>(tBu-salen)(CH<sub>3</sub>C(O)O)(CH<sub>3</sub>OH)] (1) in CH<sub>2</sub>Cl<sub>2</sub> at –170 °C.
**Fig. S10** ESR spectrum of \([\text{Mn}^{IV}(t\text{Bu-salen})(\text{CH}_3\text{O})_2]\) (2) in CH$_2$Cl$_2$ at –170 °C.
**Fig. S11** ESR spectrum of [Mn$^{IV}$($t$Bu-salen)(m-Cl-$C_6$H$_4$C(O)O)$_2$] (3) in CH$_2$Cl$_2$ at –170 °C.
**Fig. S12** ESR spectrum of $\text{[Mn}^{IV}(t\text{Bu-salen})(m\text{-Cl-C}_6\text{H}_4\text{C(O)OO})(m\text{-Cl-C}_6\text{H}_4\text{C(O)O})]\}$ (4) in CH$_2$Cl$_2$ at $-170 \, ^\circ\text{C}$. Complex 4 was prepared from the reaction of 3 with 4 equivalents of $m$-CPBA in CH$_2$Cl$_2$ at $-40 \, ^\circ\text{C}$.
References
