Supporting Information

Efficient Catalytic Epoxidation in Water by Axial N-Ligand-Free Mn-Porphyrins within a Micellar Capsule

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Contents

Materials and methods

NMR: Bruker AVANCE-400 (400 MHz), MALDI-TOF MS: Shimadzu AXIMA-CFR Plus, ESI-TOF MS: Bruker micrOTOF II, Particle Size Analysis (DLS): Wyatt Technology DynaPro Nanostar, FT-IR: JASCO FT/IR-4200, UV-vis: JASCO V-670DS, Gas Chromatograph: Shimadzu GC-2014AFsc.

Solvents and reagents: TCI Co., Ltd., Wako Pure Chemical Industries Ltd., Kanto Chemical Co., Inc., Sigma-Aldrich Co., and Cambridge Isotope Laboratories, Inc.

Compounds: **1**, **2**, and metallo-porphyrins $\mathbf{3}_{\mathbf{M}}$ and $\mathbf{4}_{\mathbf{Mn\text{-}Cl}}$ were synthesized according to previously published procedures.[1,2]

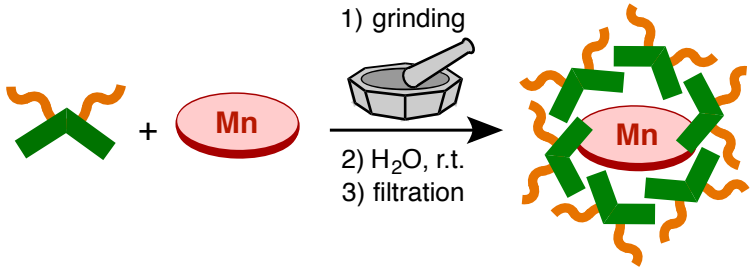
References

[1] Kondo, K.; Suzuki, A.; Akita, M.; Yoshizawa, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 2308–2312.

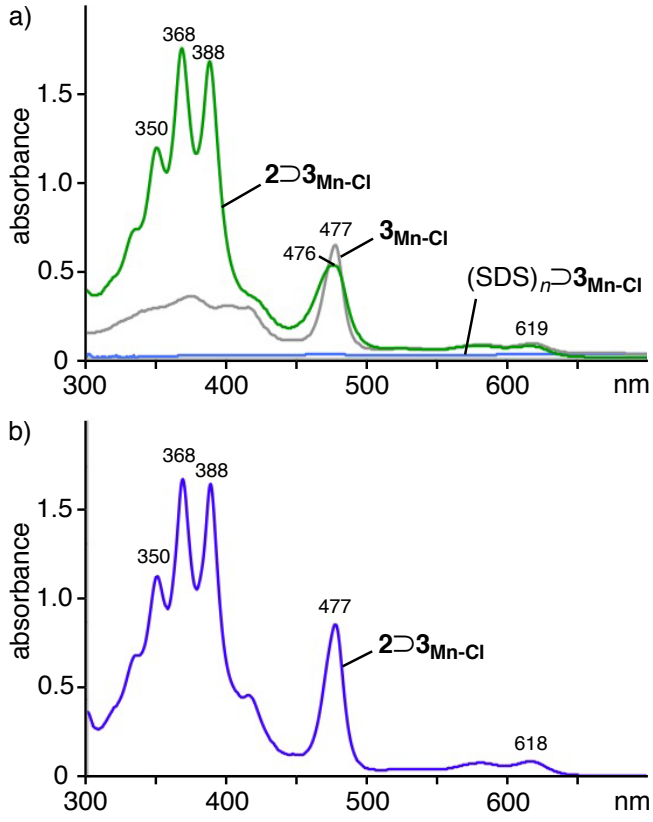
[2] Alder, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2445.

[3] Guo, C. C.; Li, H. P.; Xu, J. B. *J. Catal.* **1999**, *185*, 345–351.

Synthesis of $2\supset 3_{M}$ and $2\supset 4_{Mn\text{-}Cl}$



A mixture of amphiphilic compound **1** (1.5 mg, 2.0 μmol) and tetraphenylporphine manganese(III) chloride ($\mathbf{3}_{Mn\text{-}Cl}$; 0.7 mg, 1.0 μmol) was ground for 5 min by using an agate mortar and pestle followed by the addition of H_2O (1.0 mL) at r.t. After an excess $\mathbf{3}_{Mn\text{-}Cl}$ was removed by centrifugation and filtration, a clear green solution of **2** containing $\mathbf{3}_{Mn\text{-}Cl}$ (63%) was obtained. The formation of $\mathbf{2}\supset\mathbf{3}_{Mn\text{-}Cl}$ composite was confirmed by ^{1}H NMR, UV-visible, and DLS analyses. By using zinc(II) tetraphenylporphine $\mathbf{3}_{Zn}$, nickel(II) tetraphenylporphine $\mathbf{3}_{Ni}$, cobalt(II) tetraphenylporphine $\mathbf{3}_{Co}$, and fluorinated tetraphenylporphyrin manganese(III) chloride $\mathbf{4}_{Mn\text{-}Cl}$, host-guest composites $\mathbf{2}\supset\mathbf{3}_{Zn}$, $\mathbf{2}\supset\mathbf{3}_{Ni}$, $\mathbf{2}\supset\mathbf{3}_{Co}$, and $\mathbf{2}\supset\mathbf{4}_{Mn\text{-}Cl}$ were also prepared by the same procedure. The host-guest ratios were estimated by UV-visible analysis in CH_2Cl_2 after freeze-drying of the aqueous solutions.



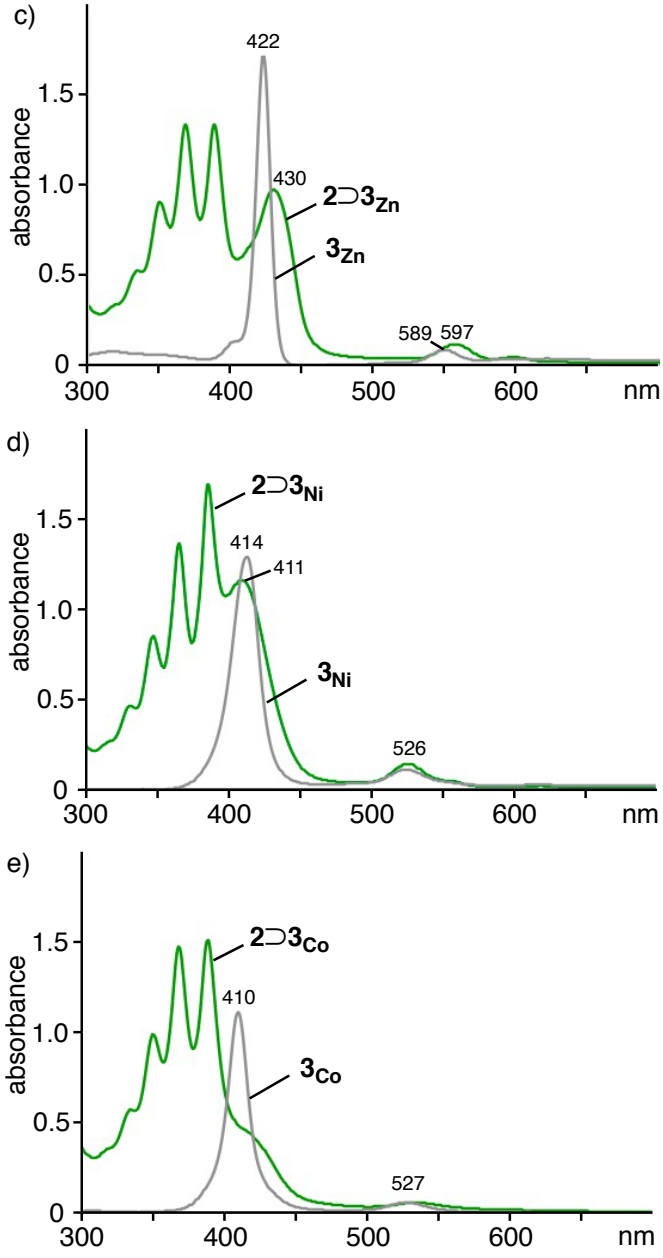


Figure S1. UV-visible spectra (r.t.) of $\mathbf{3_M}$ in CH_2Cl_2 (0.05 mM) and $\mathbf{2}\supset\mathbf{3_M}$ in H_2O (1.0 mM based on **1**). M = a) Mn-Cl, c) Zn, d) Ni, and e) Co. b) UV-visible spectrum (r.t.) of $\mathbf{2}\supset\mathbf{3_{Mn\text{-}Cl}}$ in CH_2Cl_2 after freeze-drying of the aqueous $\mathbf{2}\supset\mathbf{3_{Mn\text{-}Cl}}$ solution.

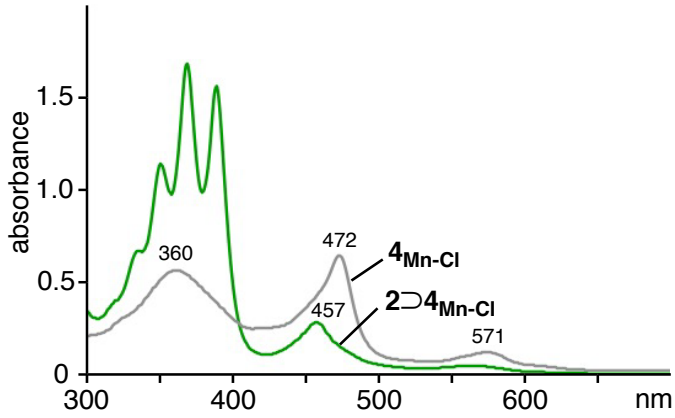


Figure S2. UV-visible spectra (r.t.) of $\mathbf{4}_{\mathbf{Mn\text{-}Cl}}$ in CH_2Cl_2 (0.05 mM) and $\mathbf{2}\supset\mathbf{4}_{\mathbf{Mn\text{-}Cl}}$ in H_2O (1.0 mM based on **1**).

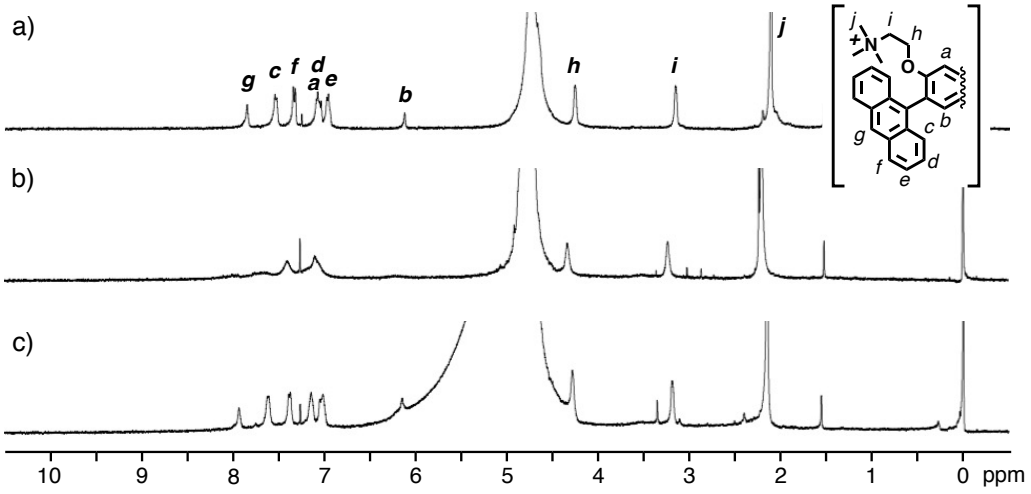


Figure S3a. ^{1}H NMR spectra (400 MHz, D_2O, r.t.) of a) **2**, b) $\mathbf{2}\supset\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$, and c) $\mathbf{2}\supset\mathbf{3}_{\mathbf{Zn}}$.

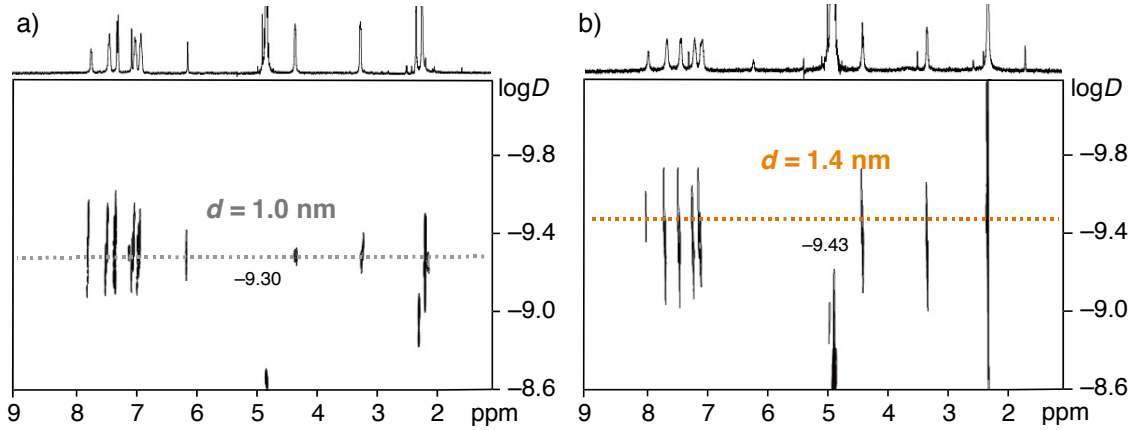


Figure S3b. DOSY NMR spectra (400 MHz, D_2O, r.t.) of a) **2** and b) $\mathbf{2}\supset\mathbf{3}_{\mathbf{Zn}}$.

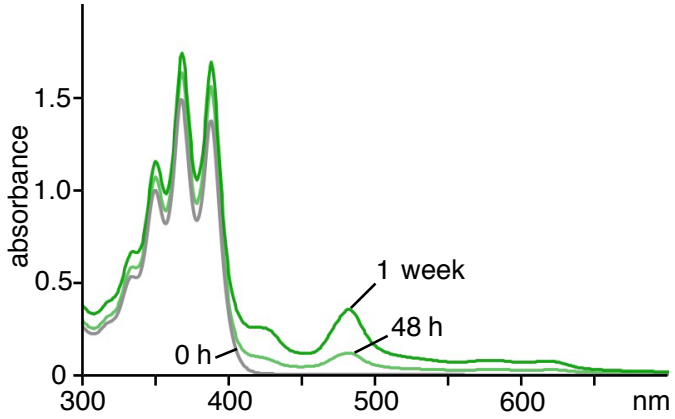


Figure S4. UV-visible spectra (H_2O, r.t., 1.0 mM based on **1**) of **2⊃3**$_{Mn\text{-}Cl}$ by the preparation through stirring a mixture of capsule **2** and **3**$_{Mn\text{-}Cl}$ in H_2O at r.t. without grinding.

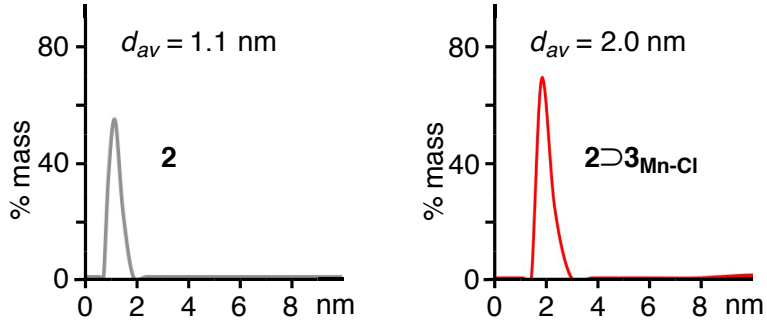


Figure S5. Size distribution of **2** and **2⊃3**$_{Mn\text{-}Cl}$ in H_2O (1.0 mM based on **1**) by DLS measurement at r.t.

General procedure for the catalytic epoxidation of styrenes by 2⊃3$_{Mn\text{-}Cl}$

A H_2O solution (1.0 mL) of **2⊃3**$_{Mn\text{-}Cl}$ (0.2 μmol based on **3**$_{Mn\text{-}Cl}$), imidazole (0.7 mg, 10 μmol), and iodosylbenzene (44.0 mg, 200 μmol) were added to a microtube containing 4-chlorostyrene (13.9 mg, 100 μmol). The reaction mixture was vigorously stirred (600 rpm) for 4 h at r.t. under air. NaCl (~10 mg) was added to the resultant solution and then the products were extracted with $CDCl_3$ (2 × 0.25 mL). The organic layer was separated after centrifuging for 1 min at 13000 rpm. The obtained products

were analyzed by ^{1}H NMR after adding tetraethylsilane (7.2 mg, 50 μmol) as an internal standard to the organic solution. After the addition of naphthalene (12.8 mg, 100 μmol) as an internal standard, the products were further analyzed by GC.

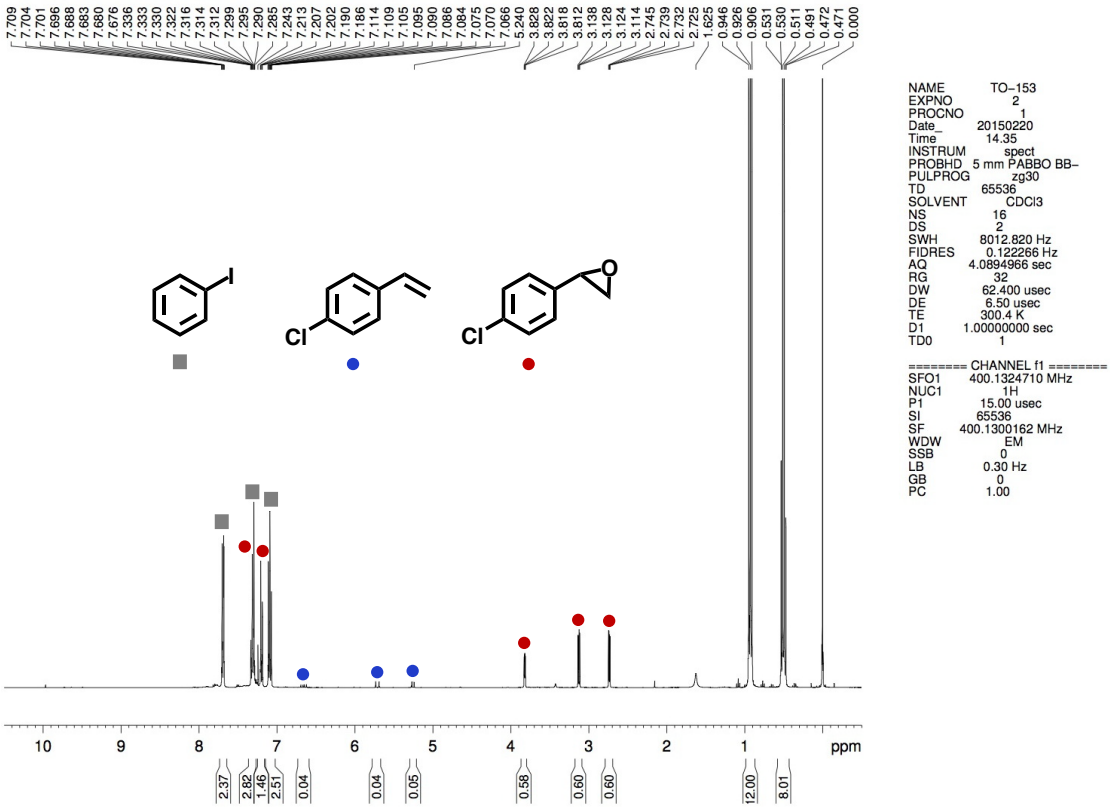
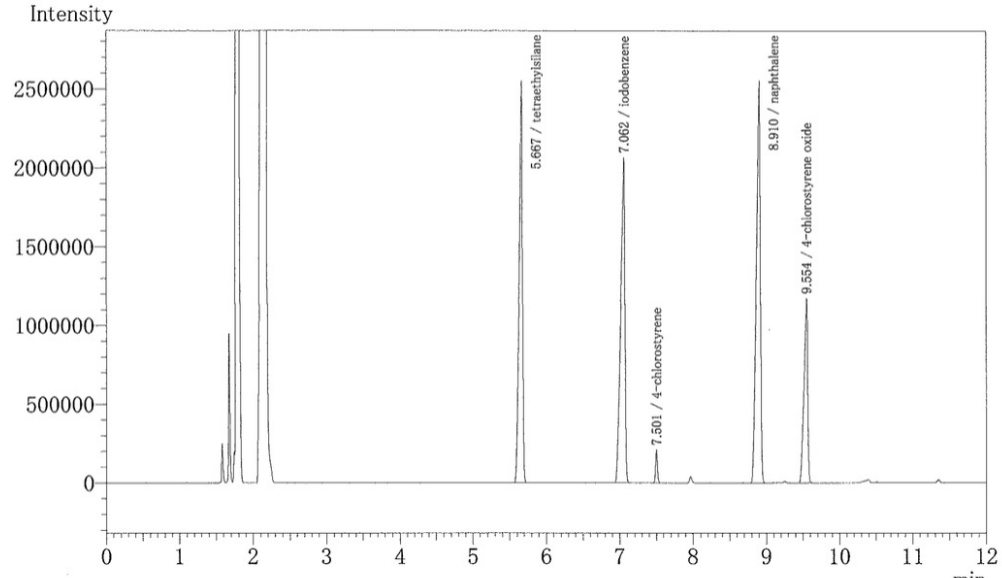
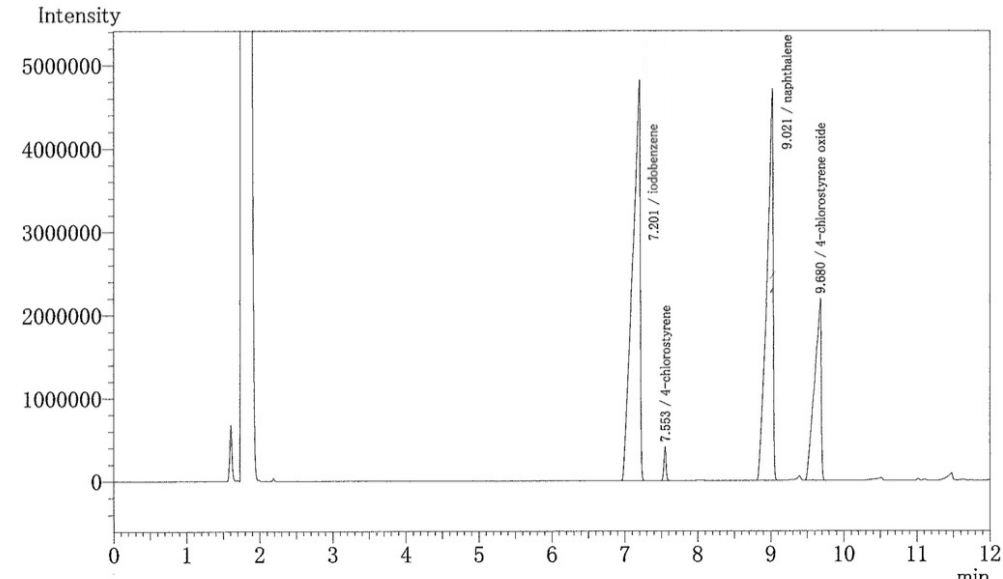


Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, r.t.) of crude products after the catalytic epoxidation of **5** by $\mathbf{2}\supset\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$ (Table 1, entry 1).



Peak No	Time [min]	Area	Intensity		Compounds
1	5.667	7838746	2497814	0.000 ppm	7 tetraethylsilane
2	7.062	7974391	2025149	0.000 ppm	3 iodobenzene
3	7.501	367154	205147	0.000 ppm	2 4-chlorostyrene
4	8.910	9278990	2528395	0.000 ppm	1 naphthalene
5	9.554	3968163	1152333	0.000 ppm	4 4-chlorostyrene oxi
Totals		29427444	8408838		

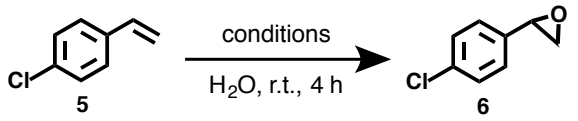
Figure S7a. GC chart of crude products after the catalytic epoxidation of **5** by **2**⊃**3**$_{\mathbf{Mn\text{-}Cl}}$.



Peak No	Time [min]	Area	Intensity		Compounds
1	7.201	34826540	4775617	0.000 ppm	3 iodobenzene
2	7.553	814736	410621	0.000 ppm	2 4-chlorostyrene
3	9.021	27365525	4646479	0.000 ppm	1 naphthalene
4	9.680	13885797	2190638	0.000 ppm	4 4-chlorostyrene oxi
Totals		76892598	12023355		

Figure S7b. GC chart of crude products after the catalytic epoxidation of **5** by **2**⊃**4**$_{\mathbf{Mn\text{-}Cl}}$.

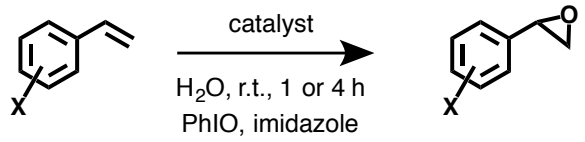
Table S1. Control experiments of the catalytic epoxidation of **5**.



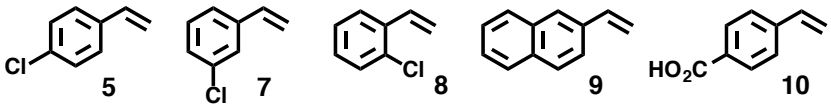
entry	catalyst [μmol]	imidazole [μmol]	PhIO [μmol]	yield [%]	TON
1	**2**⊃**3**$_{Mn\text{-}Cl}$ (0.2)	10	200	69	345
2	-	10	200	0	0
3	**2**⊃**3**$_{Mn\text{-}Cl}$ (0.2)	0	200	56	280
4	**2**⊃**3**$_{Mn\text{-}Cl}$ (0.2)	10	0	0	0
5	**2**	10	200	0	0

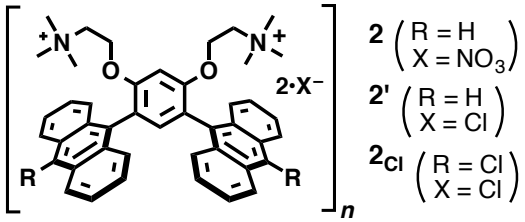
Conditions: catalyst (0.2 or 0 μmol), **5** (100 μmol), imidazole (10 or 0 μmol), PhIO (200 or 0 μmol) in H_2O at r.t. for 4 h.

Table S2. The catalytic epoxidation of various styrenes.



entry	catalyst [μmol]	substrate	time [h]	imidazole [μmol]	yield [%]	TON
1	**2'**⊃**3**$_{Mn\text{-}Cl}$ (0.2)	**5**	4	10	58	290
2	**2**$_{Cl}$⊃**3**$_{Mn\text{-}Cl}$ (0.1)	**5**	4	10	55	550
3	(SDS)$_n$⊃**3**$_{Mn\text{-}Cl}$ (0.01)	**5**	4	10	2	200
4	**2**⊃**3**$_{Mn\text{-}Cl}$ (0.2)	**9**	4	0	29	145
5	**2**⊃**4**$_{Mn\text{-}Cl}$ (0.06)	**7**	1	0	78	1300
6	**2**⊃**4**$_{Mn\text{-}Cl}$ (0.06)	**8**	1	0	81	1350
7	**2**⊃**4**$_{Mn\text{-}Cl}$ (0.06)	**10**	1	0	34	567





2 (R = H, X = NO_3)
2' (R = H, X = Cl)
2$_{Cl}$ (R = Cl, X = Cl)

Conditions: catalyst (0.01-0.2 μmol), styrenes (100 μmol), imidazole (10 or 0 μmol), PhIO (200 μmol) in H_2O at r.t. for 1 or 4 h.

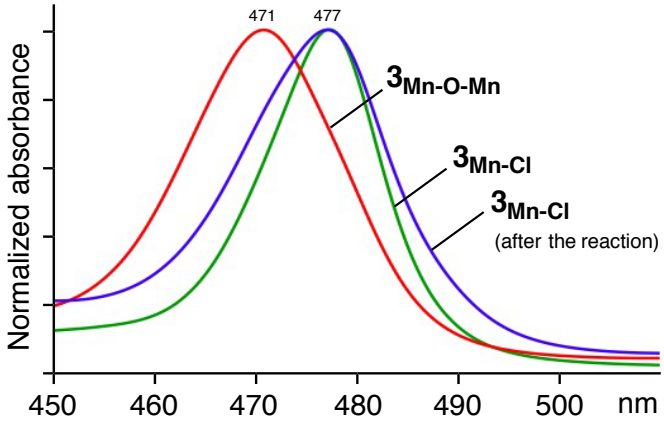


Figure S8. UV-visible spectra (CH_2Cl_2, r.t.) of $\mathbf{3}_{\mathbf{Mn\text{-}O\text{-}Mn}}$[3] and $\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$ before/after the catalytic reaction within capsule **2**.

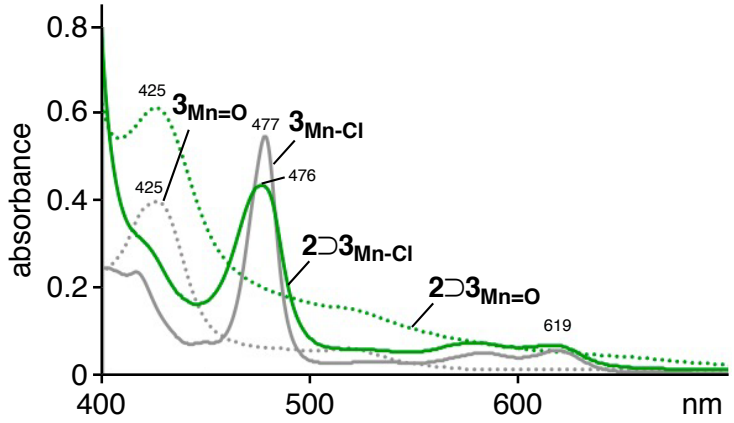


Figure S9. UV-visible spectra (r.t.) of $\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$ and $\mathbf{3}_{\mathbf{Mn=O}}$ in CH_2Cl_2 (0.05 mM) and $\mathbf{2}\supset\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$ and $\mathbf{2}\supset\mathbf{3}_{\mathbf{Mn=O}}$ (1.0 mM based on **1**) in H_2O.

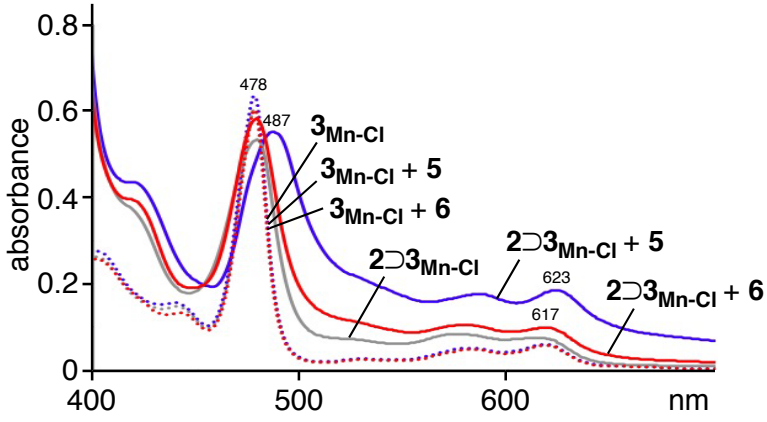


Figure S10. UV-visible spectra of $\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$ before and after the addition of **5** or **6** (50 equiv. each) in CH_2Cl_2 (dot lines) and $\mathbf{2}\supset\mathbf{3}_{\mathbf{Mn\text{-}Cl}}$ before and after the addition of **5** or **6** (50 equiv. each) in H_2O (solid lines).

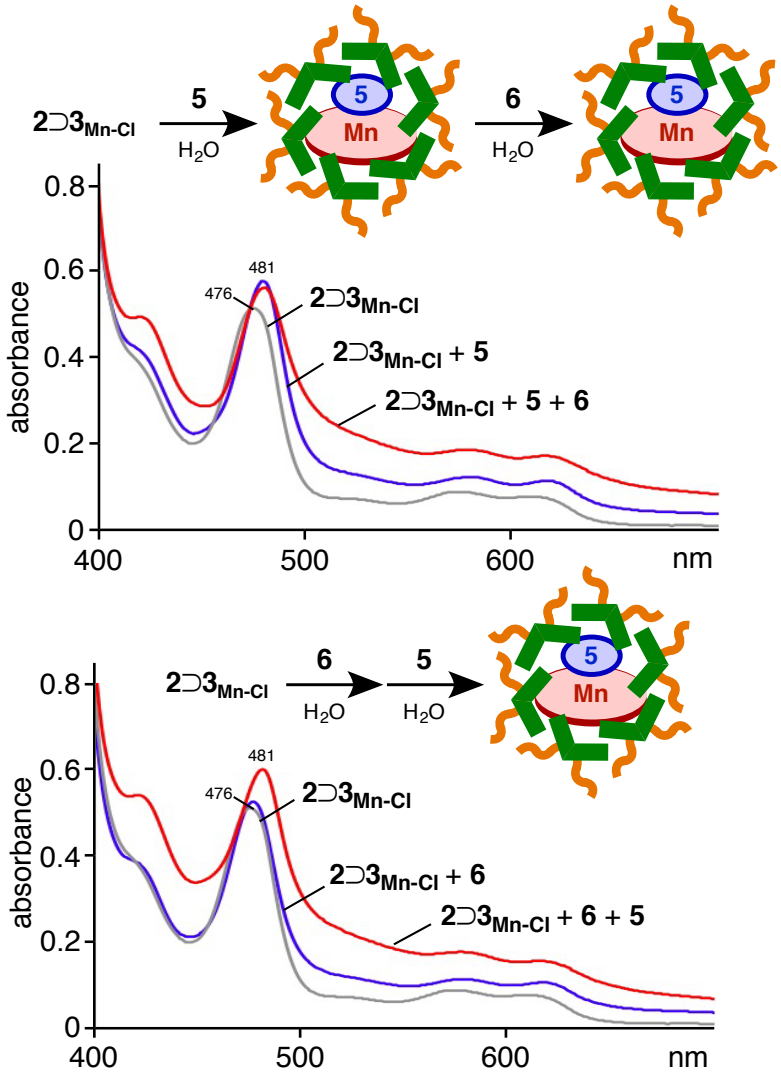


Figure S11. UV-visible spectra of **2⊃3**$_{\text{Mn-Cl}}$ after the addition of **5** and/or **6** (25 equiv. each) in H_2O.

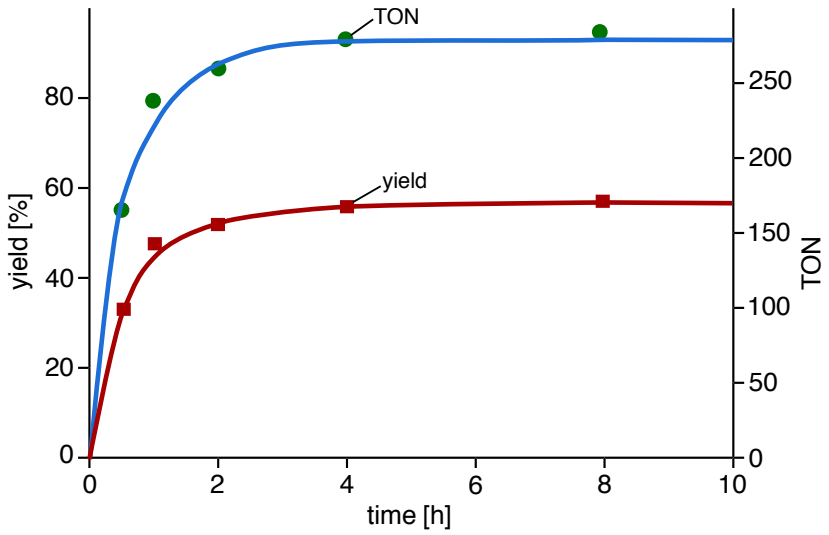


Figure S12. Time course of the epoxidation of **5** by **2⊃3**$_{\text{Mn-Cl}}$ without imidazole in H_2O.