

Supplementary Information

A recyclable Mn-porphyrin catalyst for enantioselective epoxidation of unfunctionalized olefins using molecular dioxygen

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Content

Fig. S1 FT-IR spectra of H₂TCPP and Mn(TCPP)Cl.

Fig. S2 X-ray powder diffractions of Fe₃O₄/tart/Mn(TCPP)Cl.

Fig. S3 Aerobic asymmetric oxidation of 1-decene and 1-octene against time.

Fig. S4 ¹H-NMR spectrum in CDCl₃ of the oxidation of 1-decene

Fig. S5 ¹³C-NMR spectrum in CDCl₃ of the crude oxidation of 1-decene

Fig. S6 ¹H-NMR spectrum of 1-decene in CDCl₃ as reference.

Fig. S7 ¹³C-NMR spectrum of 1-decene in CDCl₃ as reference.

Fig. S8 ¹H-NMR spectrum of the oxidation of *cis*-stilbene

Fig. S9 ¹³C-NMR spectrum of the oxidation of *cis*-stilbene

Fig. S10 Spectra of the filtrates after each recycle of Fe₃O₄/tart/Mn(TCPP)Cl.

Fig. S11 Particle size distribution of (a) Fe₃O₄/tart and (b) Fe₃O₄/tart/Mn(TCPP)Cl

Table S1 Asymmetric oxidation of styrene by various Mn-porphyrins

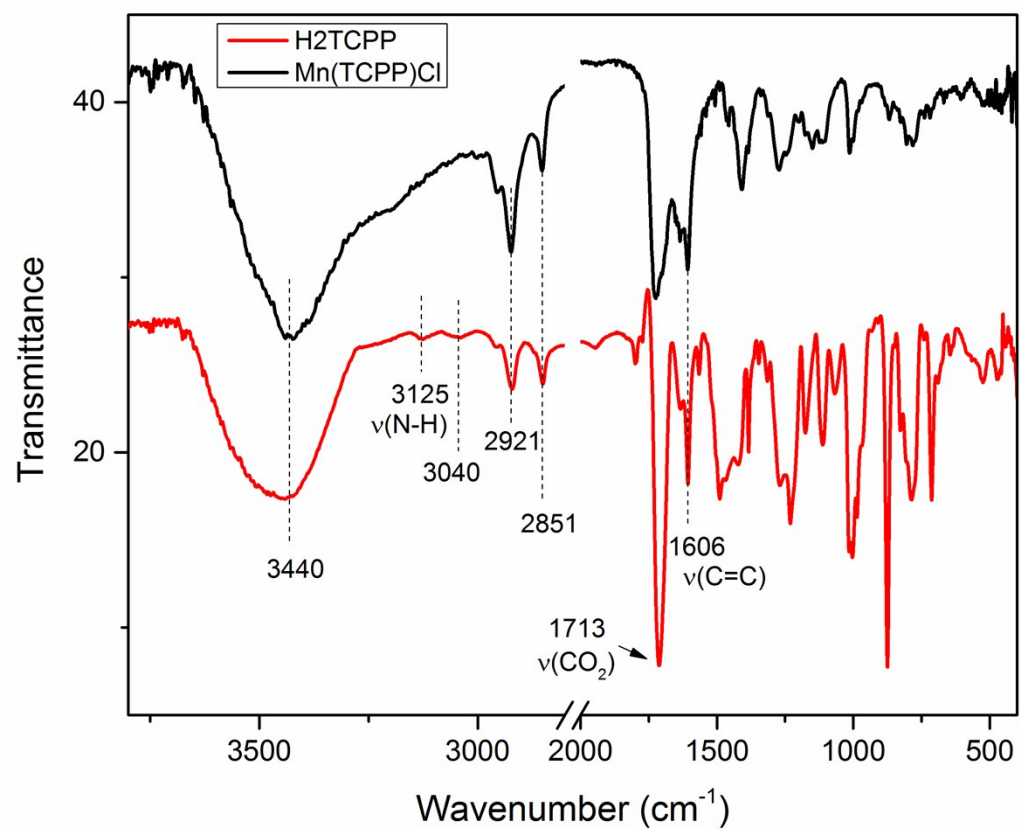


Fig. S1 FT-IR spectra of H₂TCPP and Mn(TCPP)Cl.

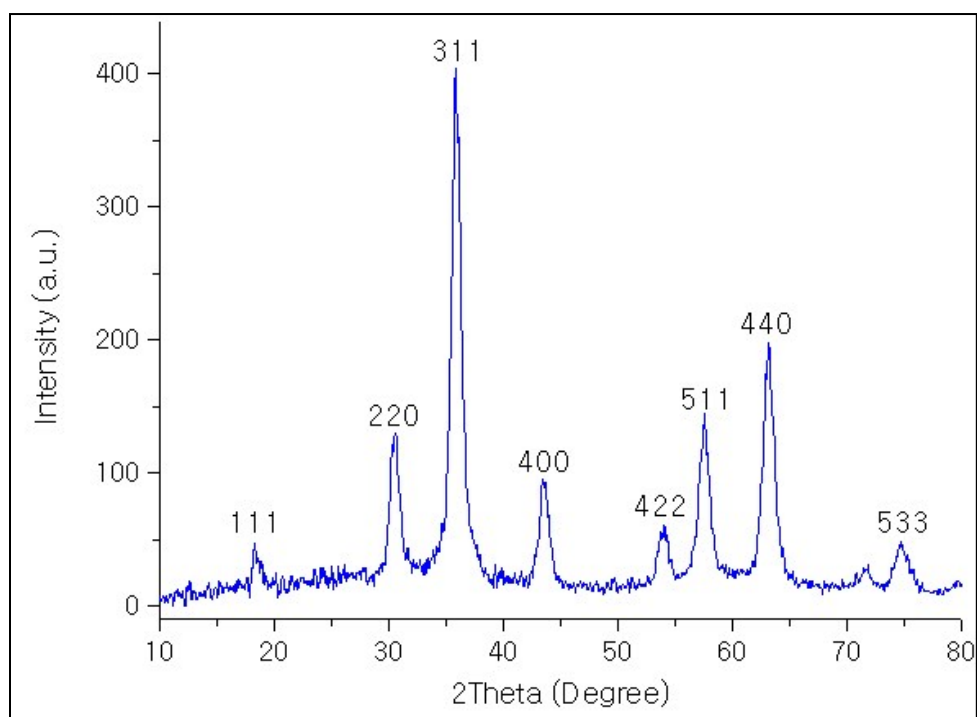


Fig. S2 X-ray powder diffractions of $\text{Fe}_3\text{O}_4/\text{tart}/\text{Mn}(\text{TCPP})\text{Cl}$.

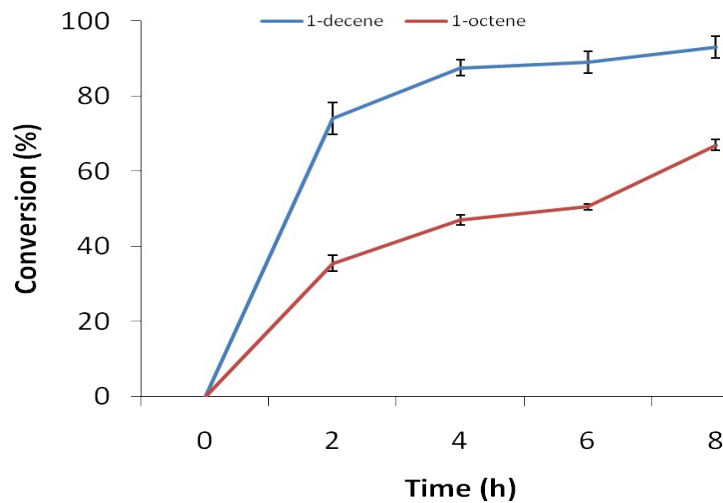


Fig. S3 Aerobic asymmetric oxidation of 1-decene and 1-octene against time. Reaction conditions: catalyst $\text{Fe}_3\text{O}_4/\text{tart}/\text{Mn}(\text{TCPP})\text{Cl}$ 1.0 mg (0.17 μmol Mn-porphyrin), substrate 2 mmol, chlorobenzene 0.1 g, isobutyraldehyde 5 mmol, CH_3CN 5 mL, O_2 balloon, reaction temperature 25 $^\circ\text{C}$, reaction time 8 h.

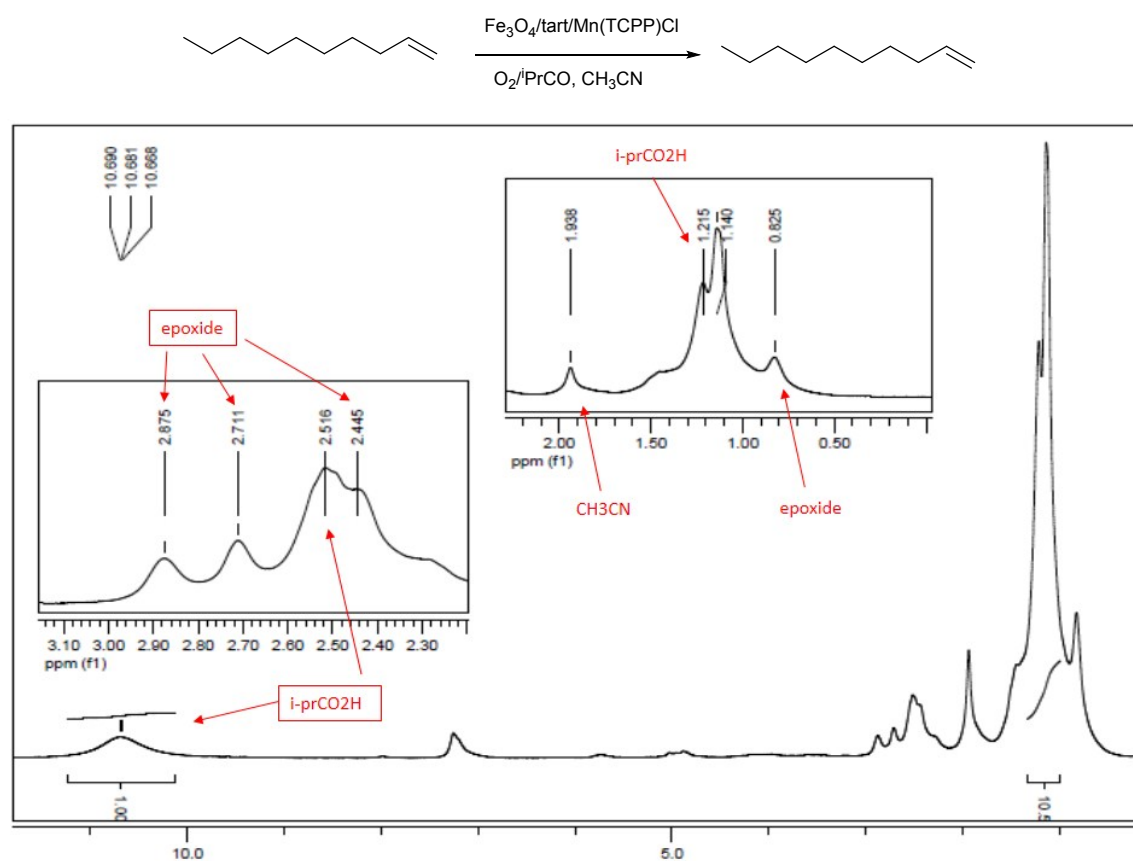


Fig. S4 ¹H-NMR spectrum in CDCl₃ of the crude product obtained upon oxidation of 1-decene provided 95% conversion with epoxide 98%.

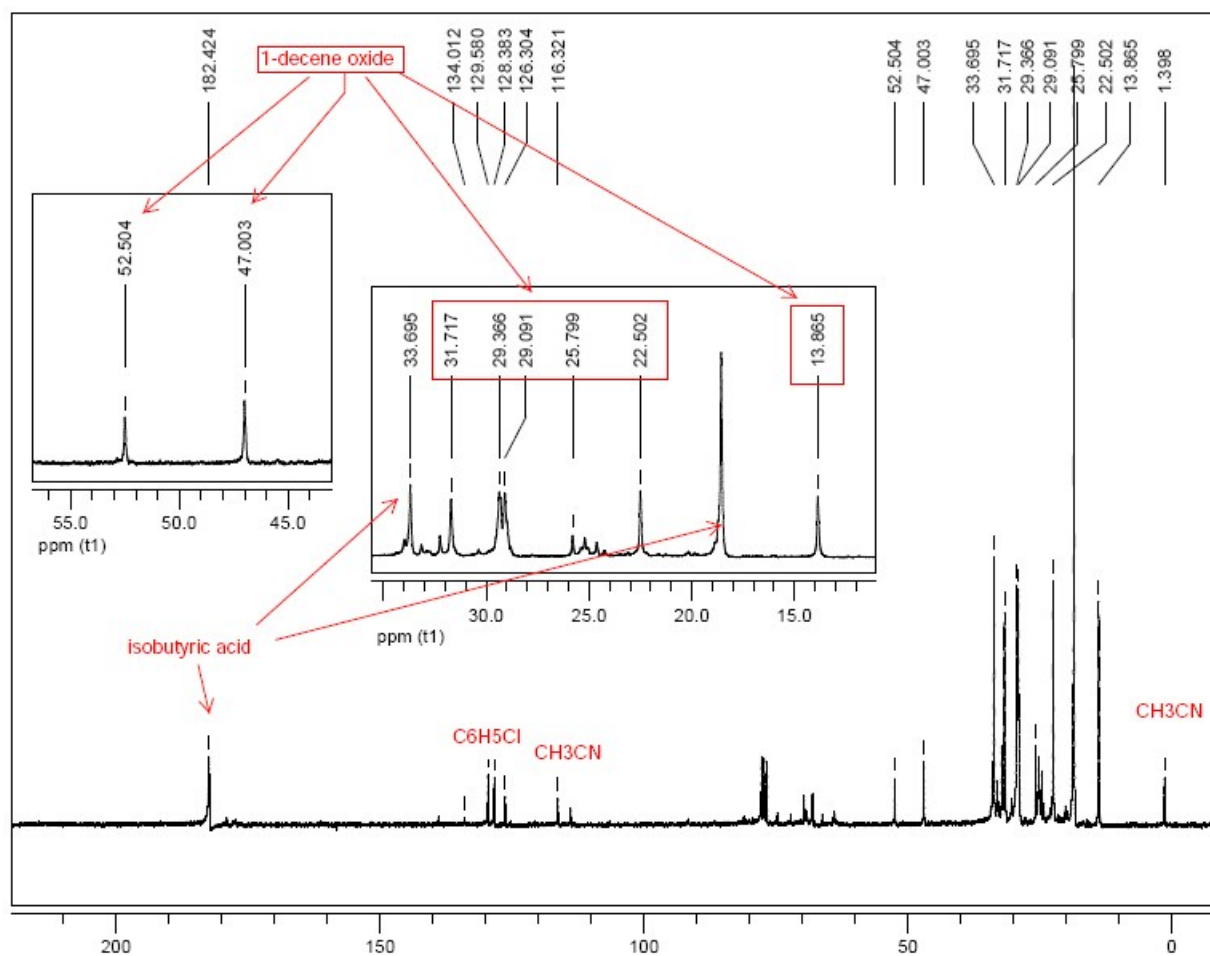


Fig. S5 ^{13}C -NMR spectrum in CDCl_3 of the crude product obtained upon oxidation of 1-decene provided 95% conversion with epoxide 98%.

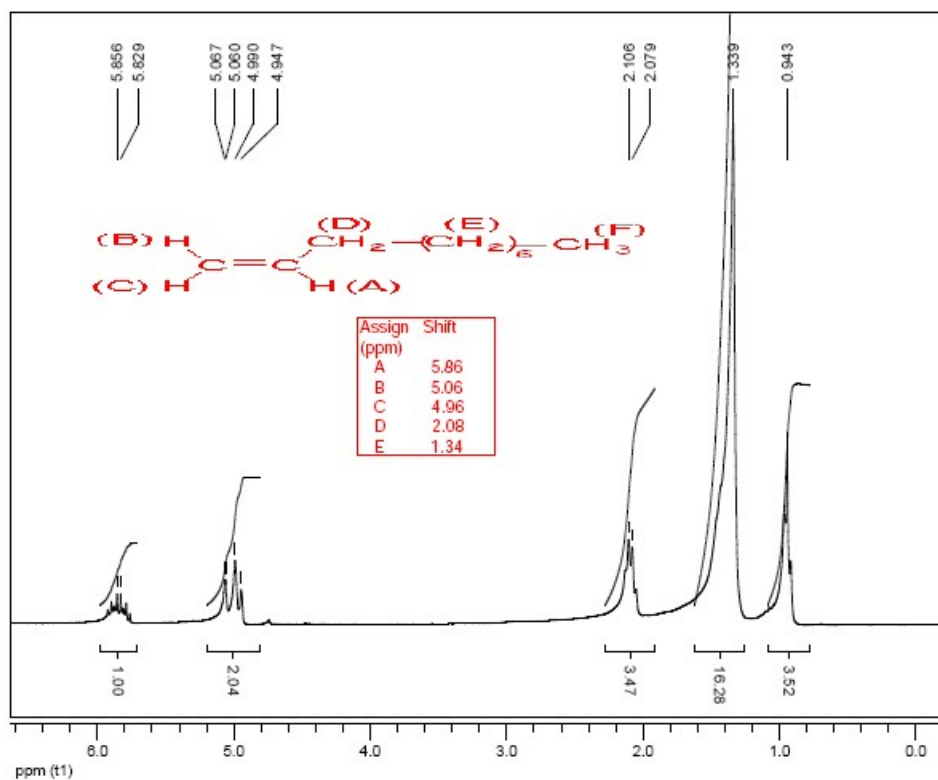


Fig. S6 ^1H -NMR spectrum of 1-decene in CDCl_3 as reference.

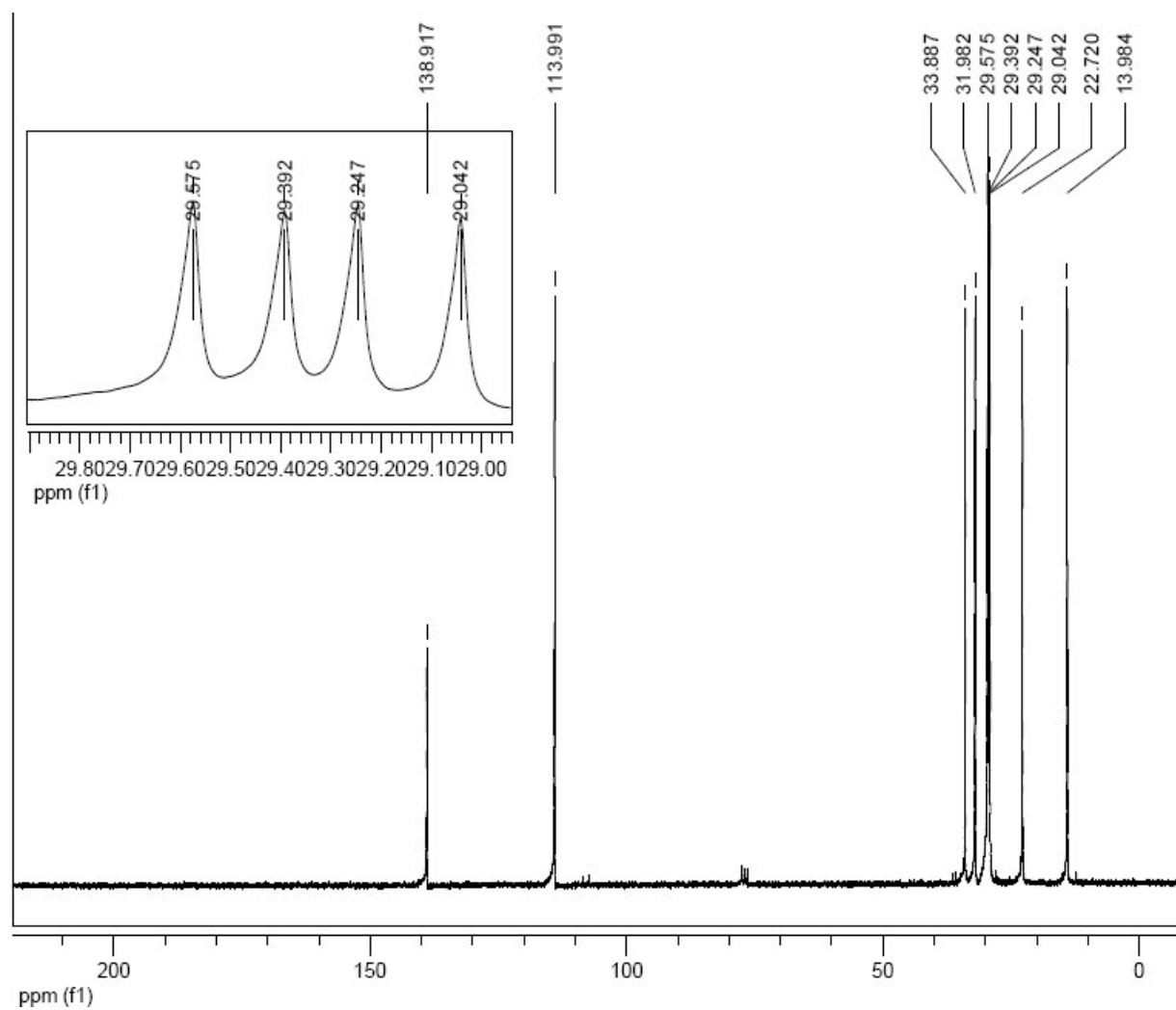


Fig. S7 ^{13}C -NMR spectrum of 1-decene in CDCl_3 as reference.

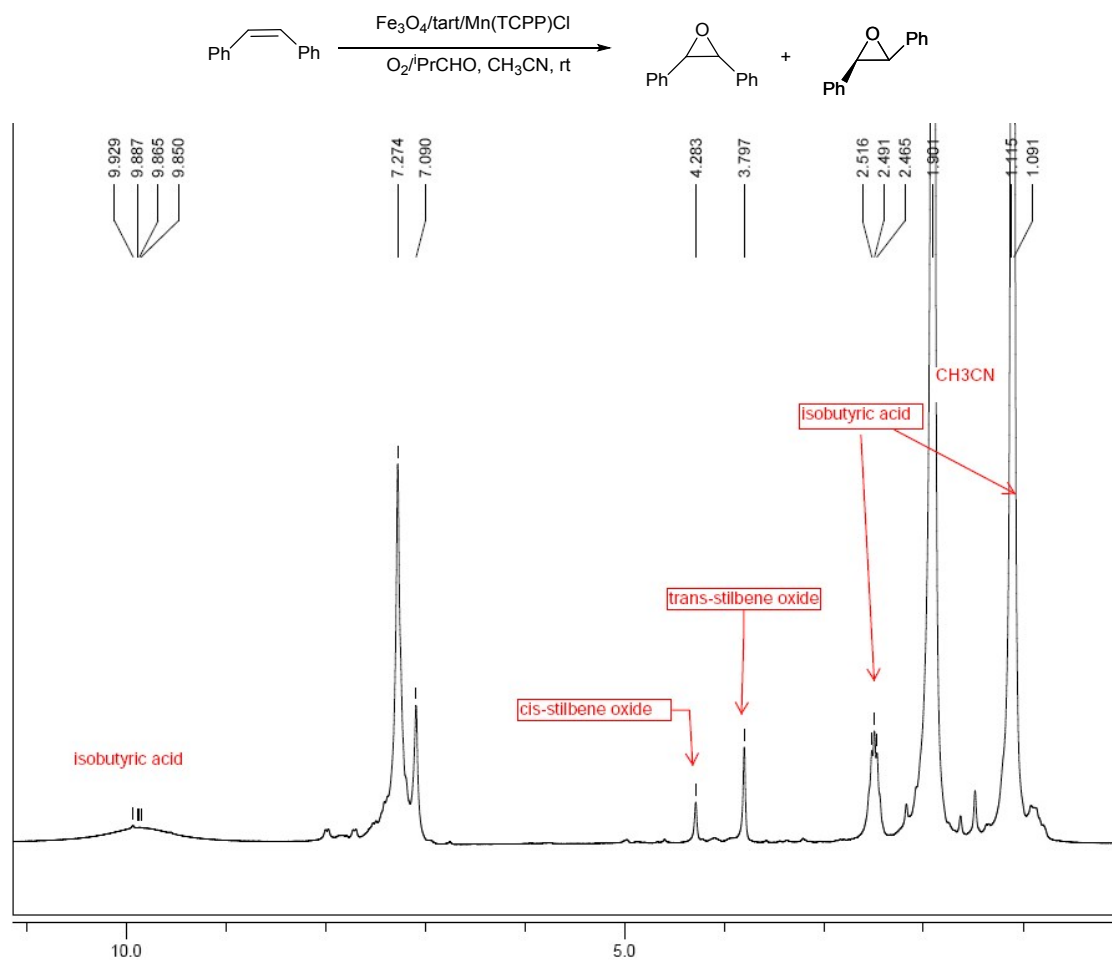


Fig. S8 ^1H -NMR spectrum in CDCl_3 of the crude product obtained upon oxidation of *cis*-stilbene provided 100% conversion with 39% *cis*-epoxide, 5% *trans*-epoxide(R) and 56% *trans*-epoxide (S).

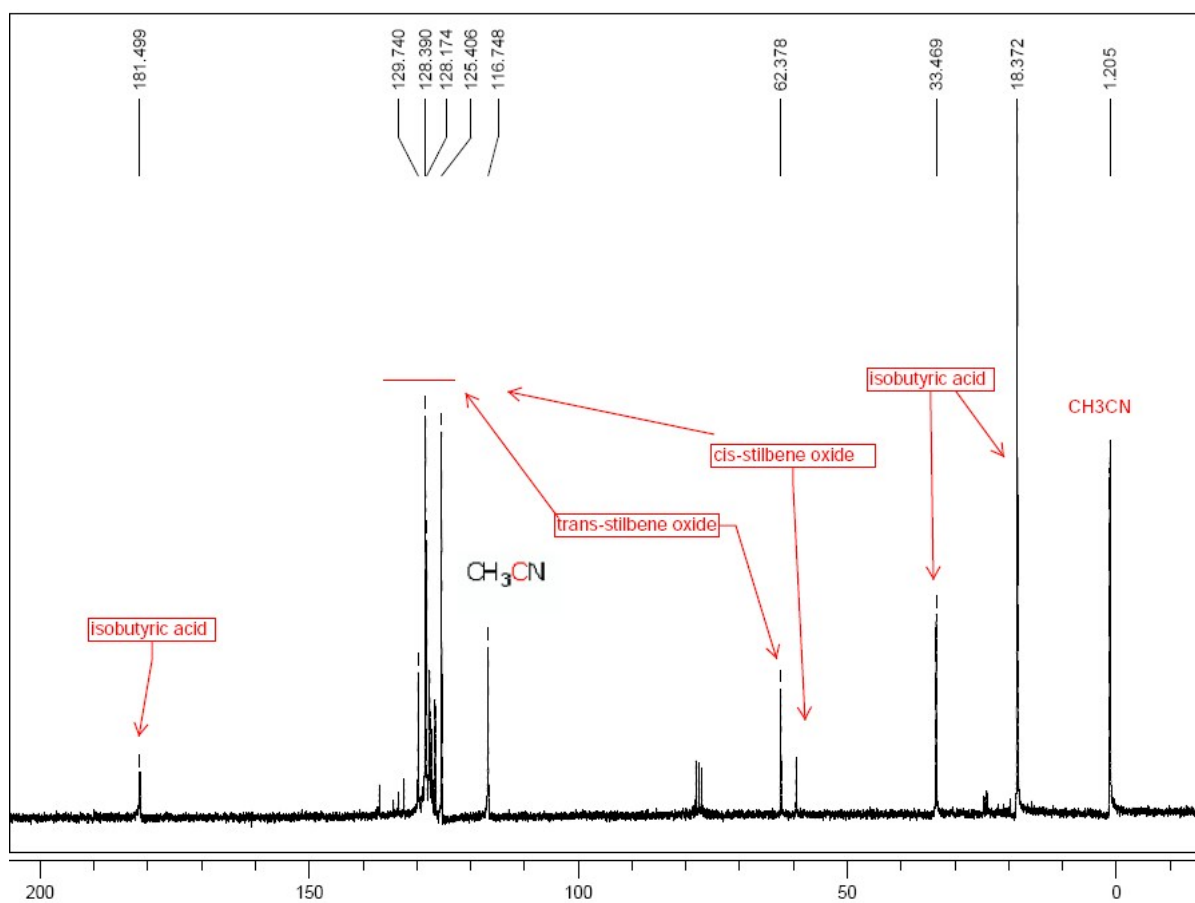


Fig. S9 ^{13}C -NMR spectrum in CDCl_3 of the crude product obtained upon oxidation of *cis*-stilbene provided 100% conversion.

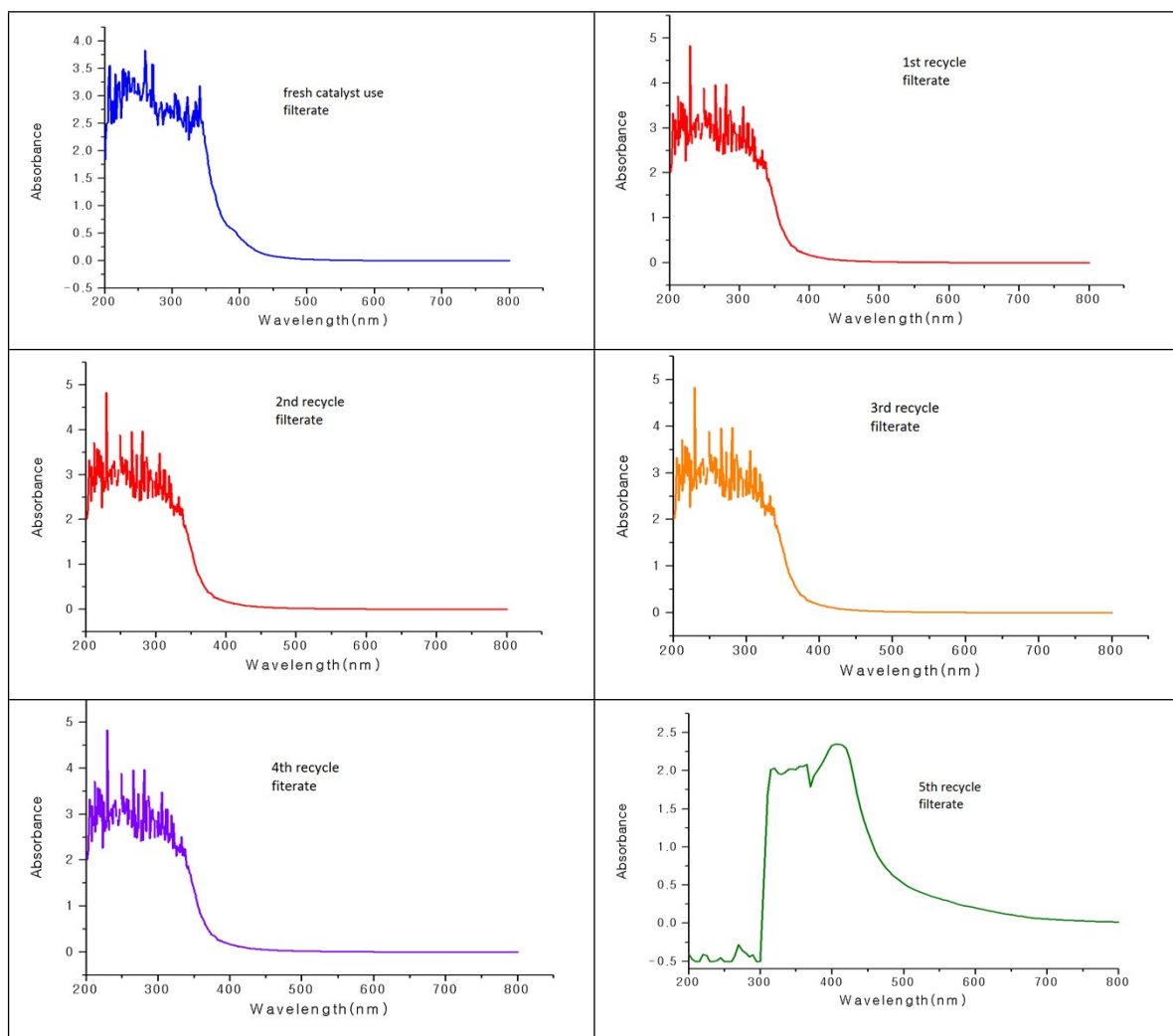


Fig. S10 Spectra of the filtrates after each recycle of $\text{Fe}_3\text{O}_4/\text{tart}/\text{Mn}(\text{TCPP})\text{Cl}$.

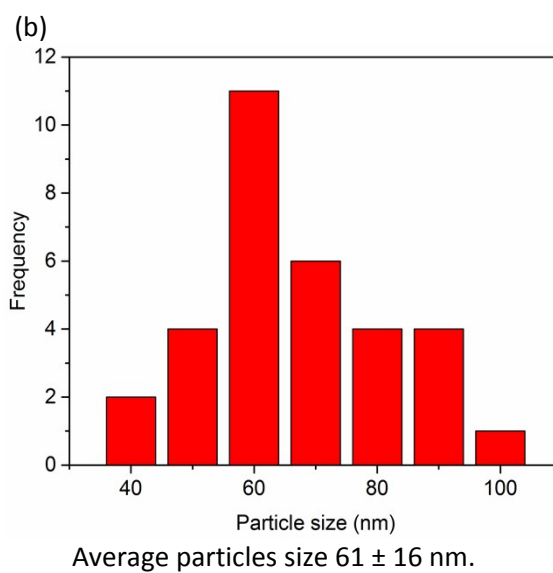
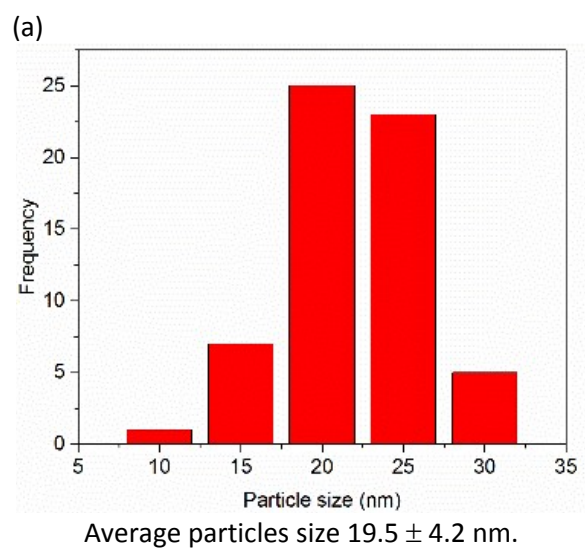
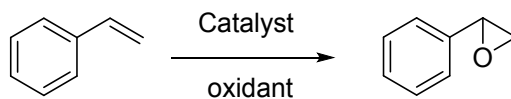
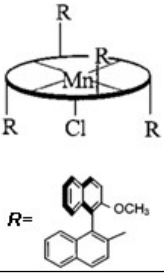
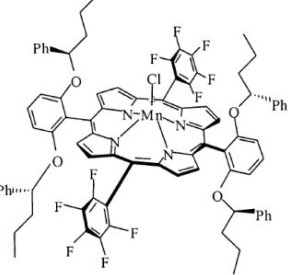
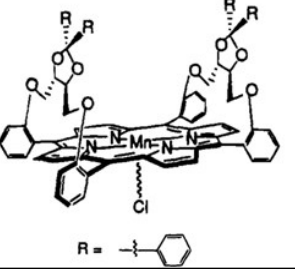
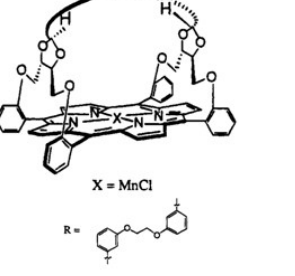


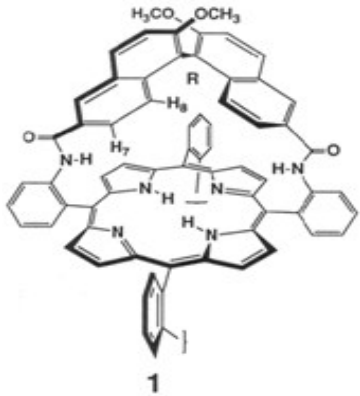
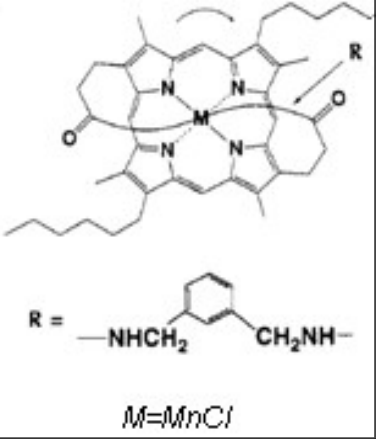
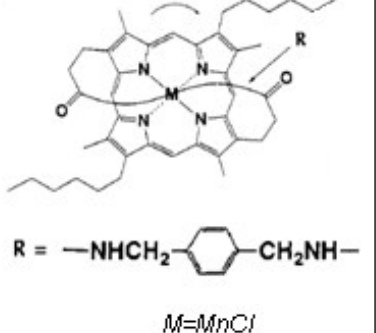
Fig. S11 Particle size distribution of (a) $\text{Fe}_3\text{O}_4/\text{tart}$ and (b) $\text{Fe}_3\text{O}_4/\text{tart}/\text{Mn}(\text{TCPP})\text{Cl}$

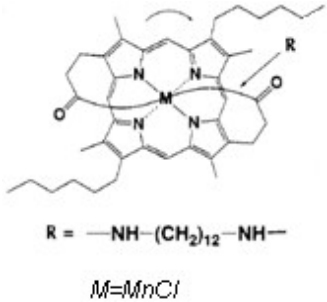
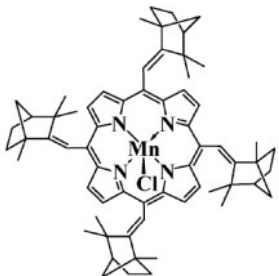
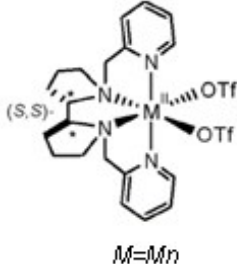
Table S1 Asymmetric oxidation of styrene by various Mn-porphyrins



No.	Catalyst	Oxidant	Time (h)	Epoxide Yield (%)	Ee % (Conf.)	Ref.
1	Fe ₃ O ₄ /tart/Mn(TCPP)Cl	O ₂ / ⁱ PrCHO	8	67	67 (S)	This work
2	 Cl^- =R	NaOCl	3	65	25 (R)	1
3	 $X=\text{MnCl}$	NaOCl	1	90	52 (S)	2
4	 $\text{R} = \text{camphanyl}$ $[\text{MnCP Cl}]$	PhIO	12	51	20	3

No.	Catalyst	Oxidant	Time (h)	Epoxide Yield (%)	Ee % (Conf.)	Ref.
5		PhIO	3	37	8	4
6		PhIO	1.5	87	7.3	5
7		PhIO	1	64	39 (R)	6
8		PhIO	1	86	69 (R)	34

No.	Catalyst	Oxidant	Time (h)	Epoxide Yield (%)	Ee % (Conf.)	Ref.
9	 1 1-Mn^{III}Cl	PhIO	2	21	36 (R)	7
10	 $R = \text{---NHCH}_2\text{---}\langle\text{benzene ring}\rangle\text{---CH}_2\text{NH---}$ $M=\text{MnCl}$	PhIO	3	27	30 (R)	36
11	 $R = \text{---NHCH}_2\text{---}\langle\text{benzene ring}\rangle\text{---CH}_2\text{NH---}$ $M=\text{MnCl}$	PhIO	3	68	50 (R)	8

No.	Catalyst	Oxidant	Time (h)	Epoxide Yield (%)	Ee % (Conf.)	Ref.
12	 $R = -NH-(CH_2)_{12}-NH-$ $M=MnCl$	PhIO	3	33	17 (R)	36
13		NaOCl	80	78	10	9
14	 $M=Mn$	H ₂ O ₂	2.5	92	56 (R)	10

1. S.Banfi, A. Manfredi, F. Montanari, G. Pozzi and S. Quici, *J. Mol. Catal. A: Chem.*, 1996, **113**, 77-86.
2. R.L. Halterman, S. T. Jan, H. L. Nimmons, D. J. Standlee and M.A. Khan, *Tetrahedron*, 1997, **53**, 11257-11276.
3. S. Licoccia, M. Paci, P. Tagliatesta, R. Paolesse, S. Antonaroli and T. Boschi, *Magn. Reson. Chem.*, 1991, **29**, 1084-1091.
4. G. Reginato, L. D. Bari, P. Salvadori and R. Guillard, *Eur. J. Org. Chem.*, 2000, 1165-1171.
5. J. R. L. Smith and G. Reginato, *Org. Biomol. Chem.*, 2003, **1**, 2543-2549.
6. J. P. Collman, V. J. Lee, C. J. Kellen-Yuen, X. Zhang, J. A. Ibers and J. I. Braman, *J. Am.*

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- Chem. Soc.*,1995, **117**, 692-703.
7. J. T. Groves and P. Viski, *J. Org. Chem.*,1990, **55**, 3628-3634.
 8. K. Konishi, K. Oda, K. Nishida, T. Aida and S. Inoue, *J. Am. Chem. Soc.*,1992, **114**, 1313-1317.
 9. Q. H. Xia, H. Q. Ge, C. P. Ye, Z. M. Liu and K. X. Su, *Chem. Rev.*,2005, **105**, 1603-1662.
 10. O. Y. Lyakin, R. V. Ottenbacher, K. P. Bryliakov and E. P. Talsi, *ACS Catal.*,2012, **2**, 1196–1202.