

Electronic Supplementary Information

**A putative heme manganese(V)-oxo species in the C-H activation  
and epoxidation reactions in an aqueous medium**

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### ***Preparation of Iodosobenzene (PhIO)<sup>1</sup>***

Iodosobenzene diacetate (16.1 g., 0.050 mole) powder was taken in a beaker (250 mL). To this 3 M NaOH is added with vigorous stirring over a 5-minute duration. The solid lumps formed in the beaker were triturated for 15 minutes using a stirring rod, and the reaction mixture was kept aside for additional 45 minutes to complete the reaction. To this mixture, 100 mL of distilled water was added and stirred vigorously. The crude solid of iodosobenzene was filtered on a Büchner funnel and the precipitate was transferred to another beaker and triturated in water (200 mL). The solid was isolated by filtration using Büchner funnel, washed with distilled water (200 mL) and dried under vacuum. The dried solid was purified by triturating in chloroform (75 mL). The iodosobenzene (PhIO) was separated by filtration followed by drying in air. Yield: 9.5 g (m.p. 210°C). PhIO was found to be 99 % pure by iodometric titration.

### ***Purification of *m*-Chloroperbenzoic acid (*m*-CPBA)<sup>2</sup>***

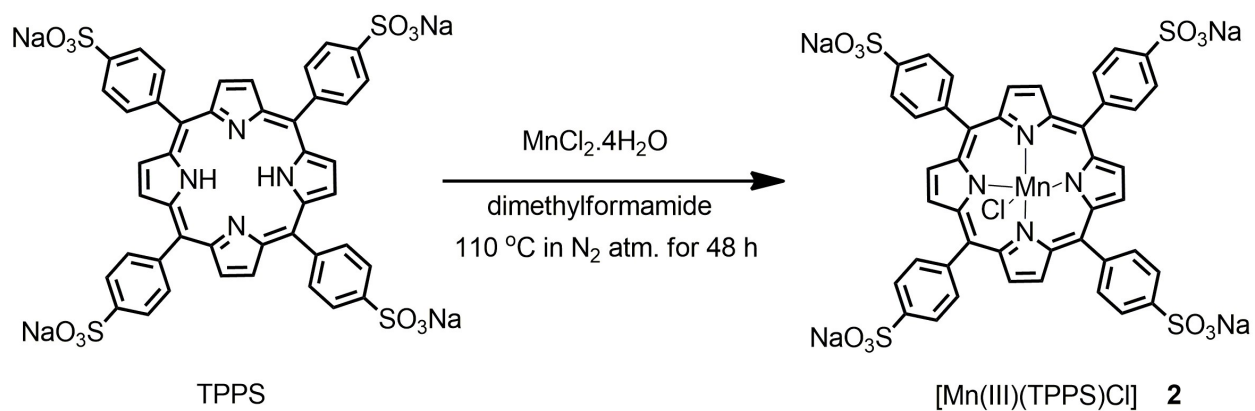
*m*-CPBA (5.0 g, 77 %) was dissolved in 35 mL of diethylether and washed three times with 40 mL of phosphate buffer (pH = 7.5). The ether layer was dried over anhydrous sodium sulphate and carefully evaporated to give *m*-CPBA (yield: 2.5 g). The acid was analysed iodometrically to obtain 99% purity.

### ***Preparation of xanthene-*d*<sub>2</sub><sup>3</sup>***

Xanthene-*d*<sub>2</sub>, was prepared by taking xanthene (0.16 g, 0.87 mmol) in DMSO-*d*<sub>6</sub> (5.0 mL) along with NaH (0.10 g, 4.2 mmol) under an inert atmosphere. The reaction mixture was stirred for ~ 8 hours and then quenched with D<sub>2</sub>O (5.0 mL). The crude product was filtered and washed thoroughly with distilled H<sub>2</sub>O. <sup>1</sup>H NMR of the product confirmed the formation of xanthene-*d*<sub>2</sub> (99%).

### **References**

1. H. Saltzman and J. G. Sharefkin, *Organic Synth.*, 1963, **43**, 60.
2. a) V. K. Aggarwal, Z. Gültekin, R. S. Grainger, H. Adams and P. L. Spargo, *J. Chem. Soc. Perkin Trans.*, 1998, **1**, 2771; b) W.L.F Armarego and D.D Perrin, *Purification of Laboratory Chemicals*, 4th Edn, Butterworth-Heinemann, 2000.
3. C. R. Goldsmith, R. T. Jonas and T. D. P. Stack, *J. Am. Chem. Soc.*, 2002, **124**, 83.



Scheme S1. Synthetic route used for the preparation of [Mn(III)(TPPS)Cl] 2.

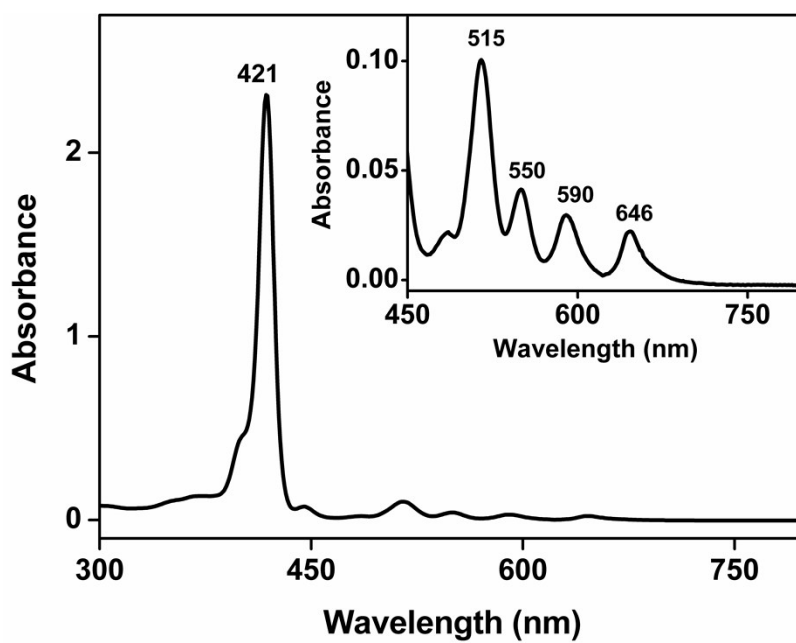


Fig. S1. UV-vis spectrum of TPPH in  $\text{CHCl}_3$ .

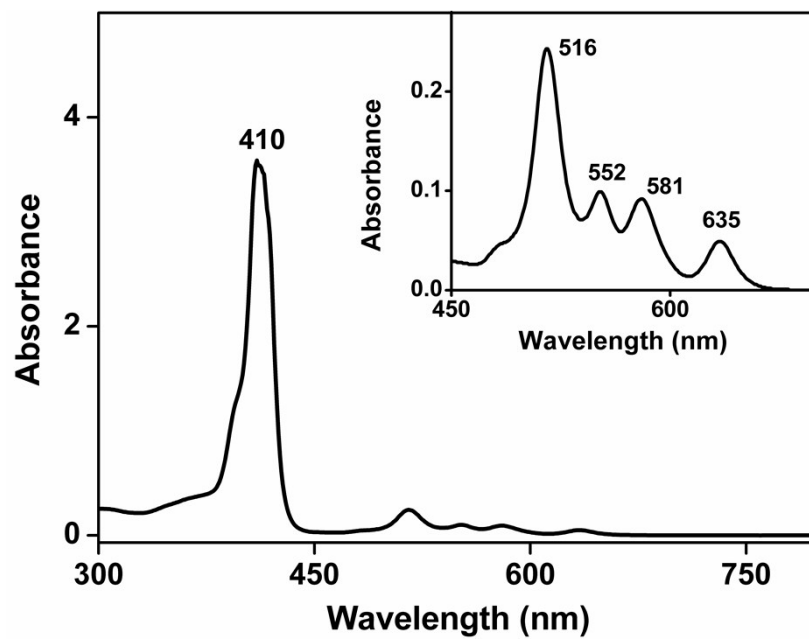


Fig. S2. UV-vis spectrum of TPPS in water.

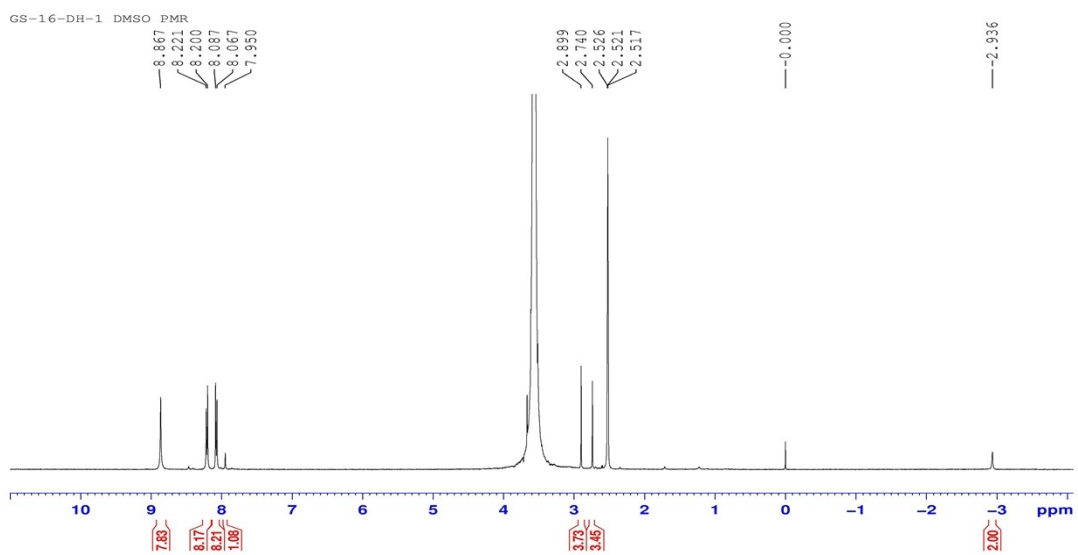


Fig. S3. <sup>1</sup>H-NMR spectrum of TPPS in DMSO-*d*<sub>6</sub>.

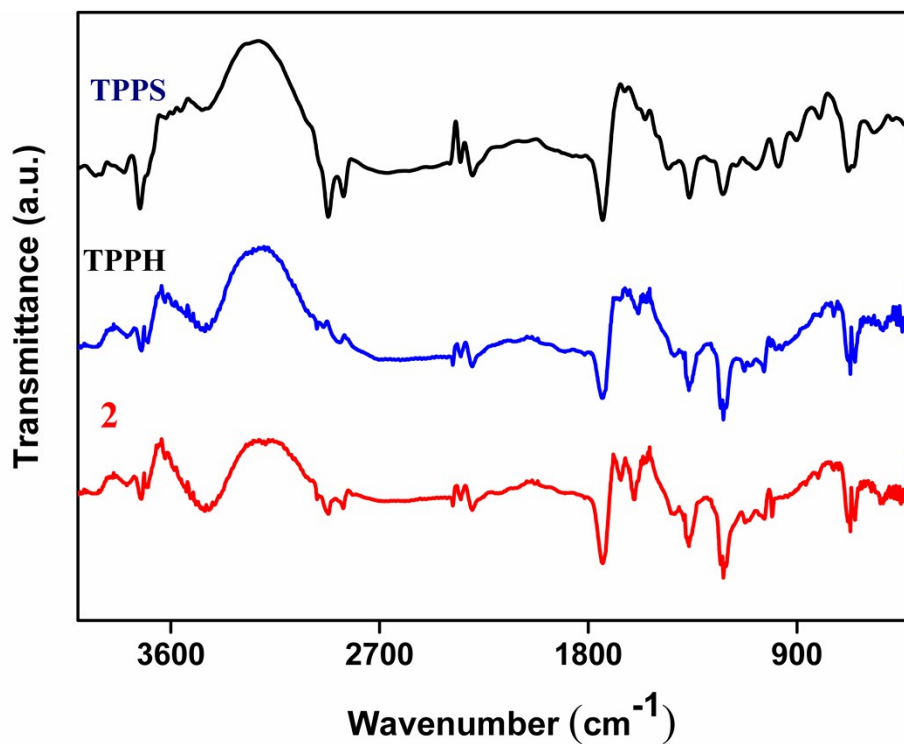


Fig. S4. IR spectra of the TPPH, TPPS and [Mn(III)(TPPS)Cl] **2**.

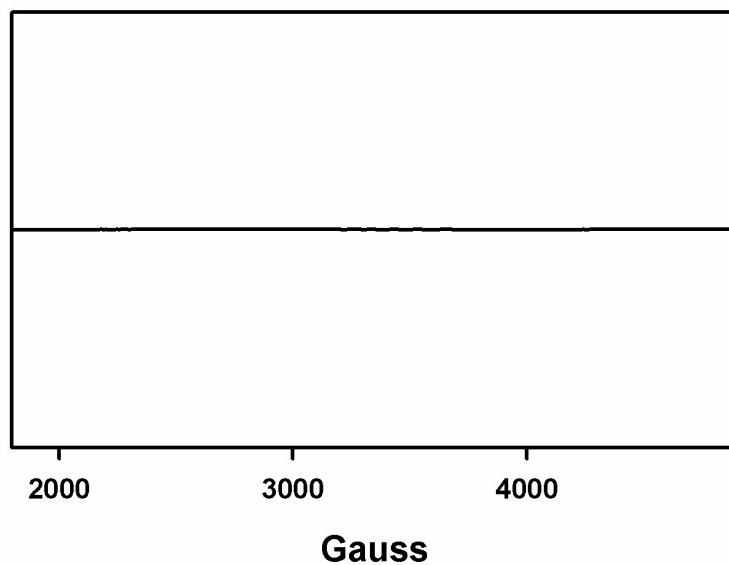


Fig. S5. X-band EPR spectrum of the complete reaction solution obtained in the reaction of [Mn(III)(TPPS)(Cl)] **2** (0.5 mM) with PhIO (0.50 mM) in aqueous buffer (pH = 10.4):CH<sub>3</sub>CN solution (2:1) at 298 K. EPR spectrum was recorded at 77 K.

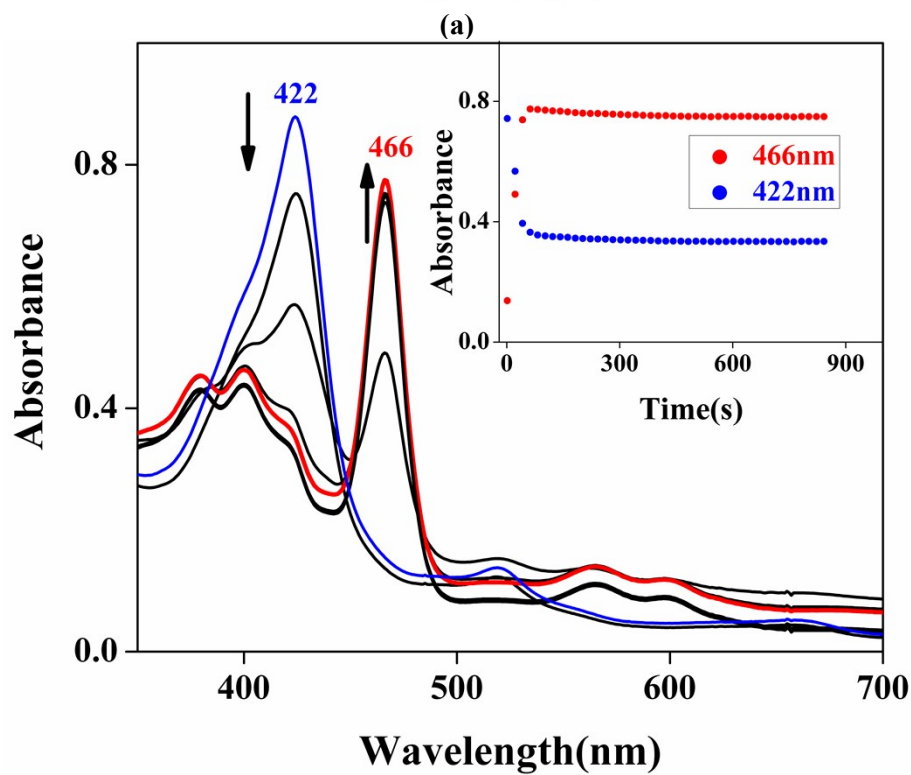
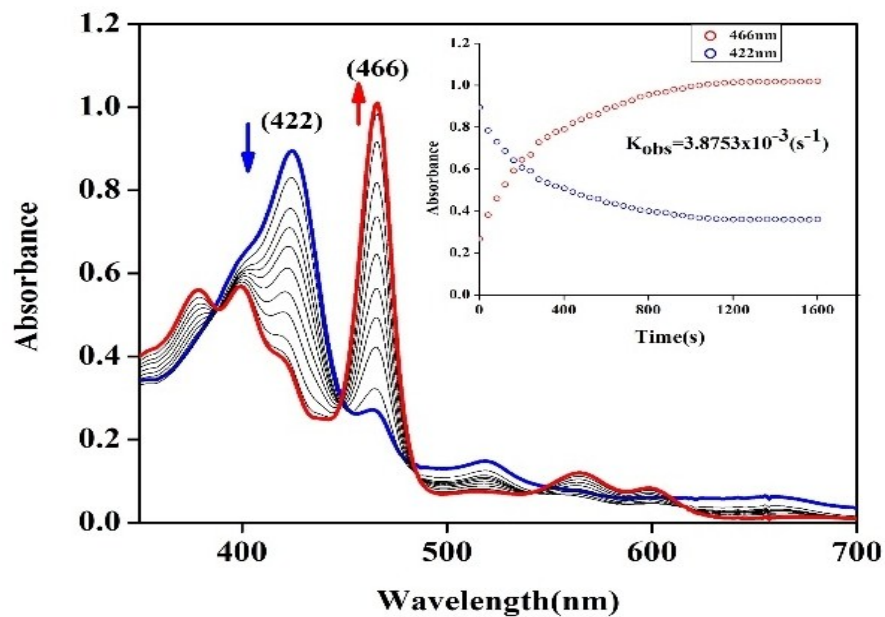


Fig. S6. UV-Vis spectral changes upon addition of a) 25 equiv. of thioanisole (top) and b) 10 equiv. of triphenylphosphine to the solution of intermediate species 1 (0.1 mM) in 2 mL 2:1 aqueous buffer:  $\text{CH}_3\text{CN}$  solution at 298 K. Inset shows a time trace for the decay of the peak at 422 nm of 1 and the formation of 466 nm peak of regenerated compound 2.

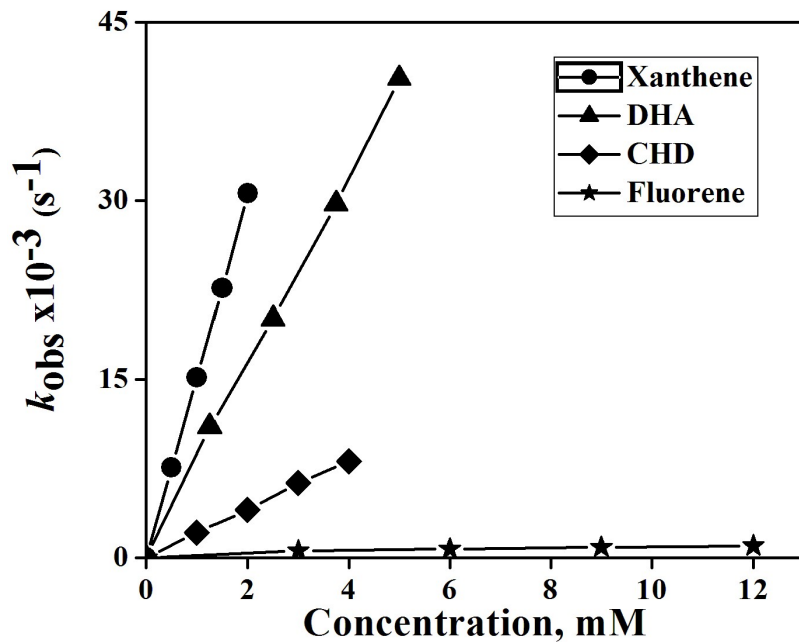


Fig. S7. Plot of pseudo-first order rate constants vs increasing concentrations of the substrates xanthene, DHA, CHD and fluorene to obtain the second order rate constants ( $k_2$ ). The reactions were carried out using **1** (0.1 mM) in 2 mL 2:1 aqueous buffer: CH<sub>3</sub>CN solution at 298 K.

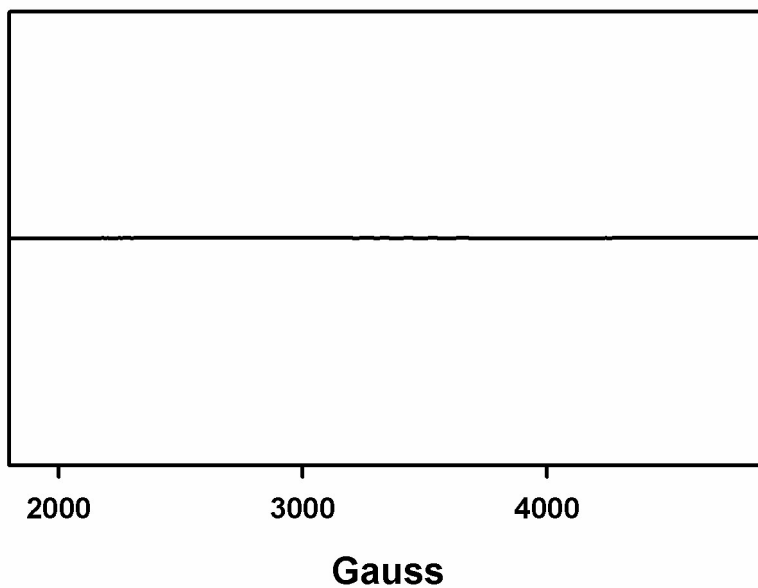
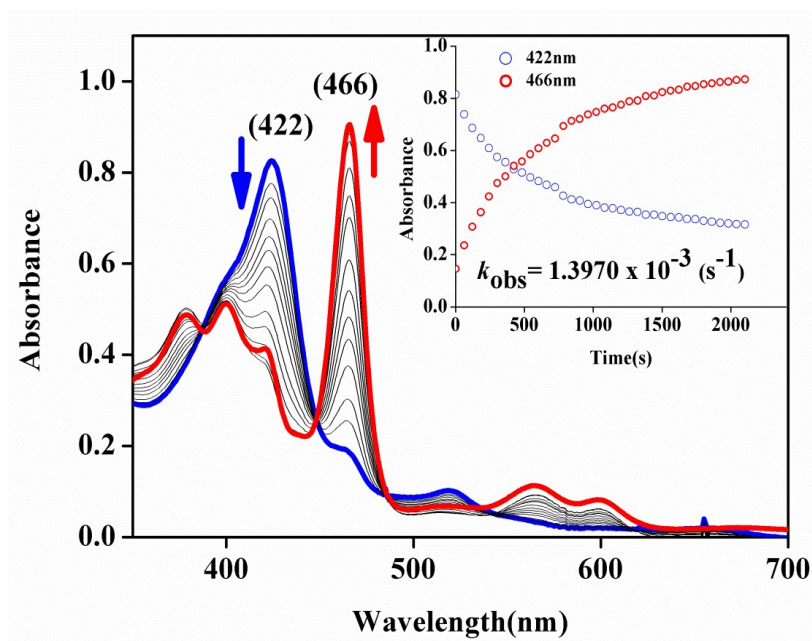
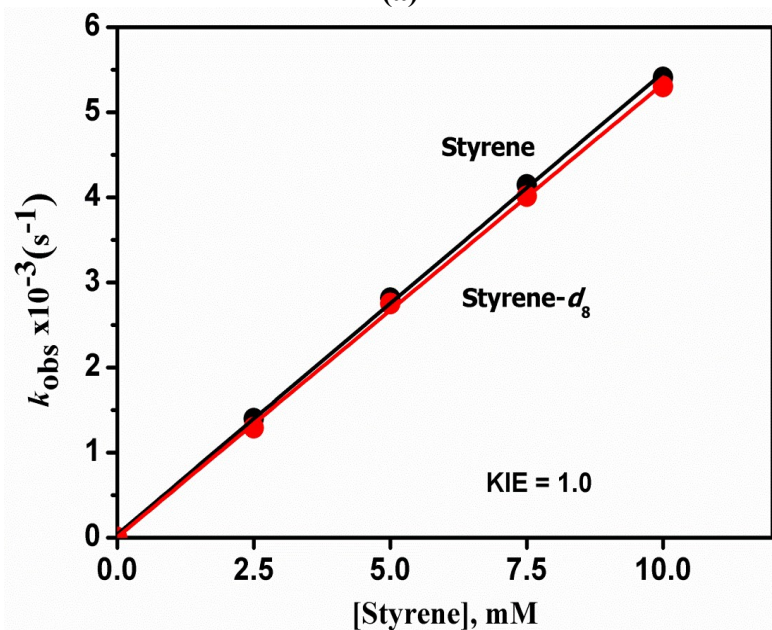


Fig. S8. X-band EPR spectrum of the complete reaction solution obtained in the reaction of [Mn(V)(O)TPPS<sub>4</sub>(Cl)] **1** (0.5 mM) with CHD (5.0 mM) in aqueous buffer (pH = 10.4) : CH<sub>3</sub>CN solution at 298 K. EPR spectrum was recorded at 77 K.



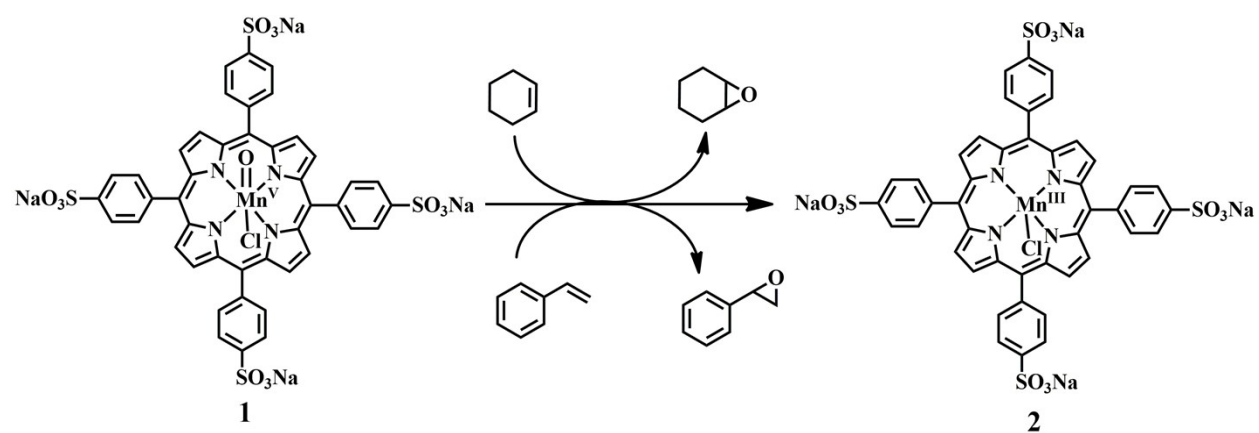
(a)



(b)

Fig. S9. (a) UV-Vis spectral changes observed in the reaction of **1** (0.1 mM, red line) and styrene (2.5 mM) in 1:2 CH<sub>3</sub>CN / buffer, pH = 10.4) at 298 K. The inset shows the time course of the reaction monitored at 422 and 466 nm. (b) Plots of pseudo-first-order rate constants  $k_{\text{obs}}$  (M s<sup>-1</sup>) against the concentrations of styrene (black circles) and styrene- $d_8$  (red circles) to determine the second-order rate constants  $k_2$  and the KIE value in 1:2 CH<sub>3</sub>CN / buffer (pH = 10.4) at 298 K.





Scheme S2. Oxygen atom transfer reaction of **1** with cyclohexene and styrene to yield cyclohexene oxide and styrene oxide respectively and the Mn(III) species **2**.