Supporting Information

Epoxidation of Cyclooctene Using Water as the Oxygen Atom Source at Manganese Oxide Electro catalysts

Kyoungsuk Jin¹, Joseph H. Maalouf¹, Nikifar Lazouski¹, Nathan Corbin¹, Dengtao Yang¹, and Karthish Manthiram¹,*

¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

*Correspondence: karthish@mit.edu

Contents

A. Materials and Methods ................................................................. 2
A.1. Materials .................................................................................. 2
A.2. Catalysis preparation ................................................................. 2
A.2.1. MnO Nanoparticle synthesis ................................................. 2
A.2.2. Purification ........................................................................... 3
A.2.3. Ligand exchange ................................................................. 3
A.3. XRD, SEM, and TEM analysis .................................................. 4
B. Electrochemical study ................................................................. 5
B.1. Electrode preparation ............................................................... 5
B.2. Electrochemical methods ......................................................... 5
C. Product analysis ........................................................................... 6
D. Supplementary Figures ............................................................... 8
E. Proposed mechanism ................................................................. 21
F. Other olefin substrates .............................................................. 22
F.1. Linear aliphatic olefin substrates .............................................. 22
F.2. Cyclic aliphatic olefin substrates .............................................. 25
F.3. Other substrates ...................................................................... 26
References ....................................................................................... 27
A. Materials and Methods

A.1. Materials

Manganese(III) acetate dihydrate (97%, Sigma Aldrich), octadecene (90%, Sigma Aldrich), decanol (90% Sigma Aldrich), cis-cyclooctene (cyclooctene, 95%, Sigma Aldrich), myristic acid (99%, Sigma Aldrich), cis-cyclooctene oxide (99%, Sigma Aldrich), cyclooctanone (98%, Sigma Aldrich), tertrabutylammonium tetrafluoroborate (TBABF4) (99%, Acros Organics), and nitrosyl tetrafluoroborate (NOBF4, 95%, Sigma Aldrich) were purchased and used without additional treatment. Acetonitrile (ACN, anhydrous, 99.8+%, Alfa Aesar), Deuterated acetonitrile (≥99.8 atom % D, Sigma Aldrich), dichloromethane (DCM, 99.5%, Fisher Scientific), 1,3,5-Trimethoxybenzene (TMB, 99 %, Sigma Aldrich), acetone (99.5%, VWR), toluene (99.5%, VWR), hexane (99.9%, Fisher Scientific), ethanol (Anhydrous, KOPTEC USP), and N,N-Dimethylformamide (DMF, 99.8%, Sigma Aldrich) were purchased and used without additional treatment. Disk shaped carbon paper electrodes with a diameter of 0.5 inches were punched from carbon paper (Toray, TGP-H-060, Fuel Cell Earth LLC).

A.2. Catalyst preparation

A.2.1. MnO nanoparticle synthesis

The manganese oxide nanoparticles (NPs) were synthesized by a hot injection method. A Schlenk line (James Glass), 4-channel temperature controller (J-KEM, QUAD-J-S), heating mantle (capacity: 100 mL), 3-neck flask (capacity: 100 mL, joint size: 14/20), glass condenser, and vacuum adapter, hypodermic needle (Air-Tite, 16G X 5”), glass syringe with metal luer-lock hub (capacity: 10 mL), and injection needle (BD Medical, 18G X 1 ½”) were used for the synthesis (Figure S1A).

Two different mixtures were prepared in two separate 3-neck flasks under air. In the first mixture, 1 mmol of manganese (III) acetate dihydrate and 1 mmol of myristic acid were dissolved in 20 mL of octadecene. In the second flask, 0.457 mL of decanol and 3.072 mL of octadecene were added. The holes of each 3-neck flask were plugged with a rubber septum, thermocouple and condenser (Figure S1A). Next, an argon backfill and vacuum cycle was done at least twice at room temperature to remove the oxygen from both flasks. This consisted of introducing argon gas into the flask first and waiting for 30 seconds, followed by closing the gas valve and then opening the vacuum valve for 30 seconds. This argon and vacuum cycle
was then performed one more time, twice in total. After this, these two separate mixtures were degassed at 110 °C for at least 1 hour with vigorous stirring under vacuum (Figure S1B).

After degassing, both flasks were switched back to an argon atmosphere by flowing argon into each flask. Next, the Mn-myristic acid mixture was heated to 290 °C under argon with ~15-20 °C /min ramp rate, while maintaining the decanol pot at 110 °C under an argon atmosphere. When the Mn-myristic pot reached ~280 °C, a hypodermic needle was put in decanol pot and an injection needle in Mn-myristic pot, respectively. Immediately after the Mn-myristic acid mixture reached 295 °C, the 1.2 mL of decanol mixture was taken by glass syringe and injected rapidly into the Mn-myristic solution (Figure S1C). The reaction temperature was then set to be 285 °C and aged for 1 hour. The MnO solution was naturally cooled to below 100 °C under argon. Then, all the ports are detached carefully and the brownish MnO solution was transferred into glass vials.

**A.2.2. Purification**

Prior to purification, the as-synthesized MnO containing solution was sonicated for 5 minutes to make it homogeneous. A 1:1:2 ratio of the synthesized solution (400 µL), toluene (400 µL), and acetone (800 µL), were mixed and centrifuged (15,500 rpm, 10 min) to obtain MnO precipitates. The supernatant was discarded. Then 400 µL of toluene and 800 µL of acetone were added to the precipitates again. The mixture was sonicated and vortexed for 1 min and centrifuged (15,500 rpm, 5 min). After removing the supernatant carefully, 400 µL of hexane was added and sonicated to re-disperse the MnO NPs.

**A.2.3. Ligand exchange**

To deposit the MnO NPs on hydrophilic carbon paper, a ligand exchange was performed. The MnO NPs obtained from section A.2.2. were initially dispersed in 400 µL of
hexane (Figure S2A). Then, 400 µl of DMF solution of 0.01 M NOBF₄ was mixed with 400 µL of MnO NPs solution in hexanes (Figure S2B). The mixed solution was sonicated and vortexed until a phase transfer occurred (~30 min). It should be observed that MnO NPs in the hydrophobic hexane layer are transferred to the hydrophilic DMF layer (Figure S2C). For purification, centrifugation (15,500 rpm, 5 min) was done with 400 µl of toluene where the resulting supernatant was discarded. Finally, the ligand exchanged MnO NPs were re-dispersed in 400 µL of ethanol with help of sonication (Figure S2D).

**Figure S2. Ligand exchange procedure.** Picture of A. the MnO NPs in Hexane, B. the mixture of Hexane (MnO NPs) and DMF, C. the mixture of Hexane and DMF (MnO NPs), and D. the MnO NPs in ethanol.

**A.3. XRD, SEM, and TEM analysis**

Powder X-ray diffraction (PXRD) was carried out on a D-8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.54056 Å) to check the phase of ligand exchanged MnO NPs. For the analysis, first, 5 mL of precipitated ligand exchanged MnO NPs were dried in 60°C oven and then annealed at 400°C for 5 hours, using a muffle furnace. During the annealing process, MnO NPs were transformed into Mn₃O₄ phase while maintaining the spherical particle morphology (Figure S4 and Figure S5). The morphology of the ligand exchanged Mn₃O₄ NPs on the hydrophilic carbon paper (see section B.1.) was characterized with a high resolution scanning electron microscope (Supra 55VP, Carl Zeiss, Germany). Transmission electron microscopy (TEM) images were obtained using a high-resolution transmission electron microscope (JEM-2100, JEOL, Japan) with an acceleration voltage of 200 kV. For the analysis, a dispersed MnO ethanol solution was dropped on the TEM grid and dried in an oven under 60°C before analysis.
B. Electrochemical study

B.1. Electrode preparation

The punched hydrophobic carbon papers were heated in a muffle furnace at 600°C for 1 hour to make hydrophilic carbon paper. Next, 13µL of BF₄ ligand exchanged MnO NPs (the 400 µL ethanol solution obtained from Section A.2.3) was dropped on the hydrophilic carbon paper in a 60°C oven. The MnO droplet was well spread out over the entire carbon paper. The drop-casting was repeated 4 times; 2 drops on the front side and 2 drops on the back side. The electrode was dried in a 60°C oven for 5 min and transferred to a muffle furnace. Ramp rates for a furnace was set to be 5°C/min from room temperature to 400°C and the electrode was aged for 5 hours at 400°C. The Mn₃O₄ electrode was naturally cooled to room temperature and used for electrochemical experiments.

B.2. Electrochemical methods

Electrochemical experiments were conducted with a one compartment electrochemical cell. Platinum foil and manganese oxide loaded carbon paper were used as the counter and working electrode, respectively (Figure S3). An Ag/AgCl electrode (3.4 M KCl leak-free 2.0 mm diameter Innovative Instruments) was used as the reference electrode and aluminum foil was used as the current collector. Hydrophobic carbon paper was placed behind the Mn₃O₄ NPs loaded carbon paper to prevent leakage of the solvent. To determine the catalytic activity of manganese oxide NPs towards cyclooctene activation, cyclic voltammetry(CV) curves were recorded. Acetonitrile with 0.1M tetrabutylammonium tetrafluoroborate (TBABF₄) was used as the solvent with varying concentrations of cyclooctene and water. Total volume of electrolyte was set to be 4 mL. All the potentials were 85% IR compensated manually, and the resistance value at open circuit potential (OCP) was measured by EIS techniques. The reported potentials were calibrated by measuring 5 mM ferrocene / ferrocenium redox couple.

Prior to each experiment, an ACN solution of 0.1M TBABF₄ was treated with molecular sieves (4 x 8 Mesh Type 3A, Acros Organics) for at least 12 hours to remove residual water in ACN. For each measurement, 4 mL of electrolyte containing a specified composition of cyclooctene, water, and buffered ACN was added into the 1-compartment cell. A micro-magnetic spin bar was placed into the cell for stirring. For the cyclic voltammetry analysis, CV scans were initiated from the open-circuit potential, and two cycles (From OCP to 1.45 V vs Fe/Fe³⁺) were recorded successively at a scan rate of 50 mV/sec. The chronoamperometry
analysis was conducted at 1.8 V vs Ag/AgCl (1.45 V vs Fe/Fe⁺) to obtain electrokinetic data. Prior to each chronoamperometry measurement, CV scans were initiated at the open circuit potential and three cycles were obtained consecutively in quiescent solution to stabilize the current. The electrochemical measurements were conducted with VMP3 Multi-channel potentiostat from BioLogic.

![Image of electrochemical cell](image)

**Figure S3. Picture of electrochemical cell.** A. before, and B. after assembly. (1: Electrochemical cell body, 2: Pt foil, 3: Aluminum current collector, 4: Silicon gasket, 5: Ag/AgCl reference electrode, and 6: Mini magnetic bar)

### C. Product analysis

All the products generated by electrochemical olefin oxidation were analyzed by Gas chromatography–mass spectrometry (GC-MS, 5977B MSD and 7890B GC, Agilent) and NMR spectrometry (Varian 500 MHz). After each electrolysis, we took out 50 µl of electrolyte from the electrochemical cell and diluted it with 950 µl of dichloromethane (DCM). The 20-fold diluted solution was analyzed by GC-MS. External standard curves of cis-cyclooctene oxide and cyclooctanone were obtained to quantify the product, Cepoxide (Figure S9). The epoxide partial current ($i_{\text{epoxide}}$) values were obtained with following equation:

$$i_{\text{epoxide}} = \frac{(\text{Averaged total current}) \times C_{\text{epoxide}} \times n \times F \times V}{\text{Passed charge}} , \text{(where } n = 2, F = 96,500 \text{ C/mol, } V = 4 \text{ mL, and Passed charge } = 20 \text{ C})$$

For the potential dependent and water dependent experiments, 20 coulombs were passed and the product was analyzed by GC-MS right after electrolysis. For the substrate dependent analysis, 5 C were passed for 10, 25, and 50 mM cyclooctene and 20 C were passed for 100, 200, and 500 mM cyclooctene. All the presented quantification data was obtained based on the GC-MS analysis. NMR analysis was conducted as follows. We first took out 630 µl of electrolyte and mixed it with 70 µl of deuterated ACN. An internal standard, 1,3,5-
trimethoxybenzene was added. The NMR spectra were measured on a Varian 500 instrument with solvent suppression at 1.98 ppm.
D. Supplementary Figures

Figure S4. X-ray diffraction spectra of Mn₃O₄ nanoparticles.
Figure S5. SEM images of Mn$_3$O$_4$ nanoparticles on the carbon paper electrode.
Figure S6. Isotopic distribution patterns obtained from epoxidation when using A. H$_2^{16}$O and B. H$_2^{18}$O as oxygen source.
Figure S7. CV curves of Mn₃O₄ NPs under various water concentrations with 5 mM ferrocene. E½ potentials of Fc/Fc⁺ are 0.37 V, 0.35 V, and 0.33 V vs Ag/AgCl for 1 M H₂O, 5 M H₂O, and 10 M H₂O, respectively.
Figure S8. Cyclic voltammetry curves of Mn₃O₄ NPs with 200 mM of cyclooctene and 5 M of H₂O in 0.1M TBABF₄/ACN solvent (Scan rate: 50 mV/sec). The redox features at 0.84 V and 0.52 V (E₁/₂ = 0.68 V) likely correspond to Mn(III)/Mn(IV) redox couple.¹,²
Figure S9. Calibration curves for GC-MS analysis. External standard curves for quantitative analysis were obtained using mixtures of cis-cyclooctene, cis-cyclooctene oxide, and cyclooctanone. Standard solutions (concentration range was from 0.25 mM to 25 mM) were prepared in 0.1 M TBABF₄ of acetonitrile solvent. A. Gas chromatography spectra of the standard solution. The peaks around 5.06, 8.85, and 9.08 min correspond to cis-cyclooctene, cis-cyclooctene oxide, and cyclooctanone, respectively. By integrating area we were able to obtain the standard curve for B. cyclooctanone (Slope: $(9.79 \pm 0.03) \times 10^{-5}$, intercept: $0.13 \pm 0.03$) and C. cis-cyclooctene oxide (Slope: $(9.94 \pm 0.03) \times 10^{-5}$, intercept: $0.12 \pm 0.04$).
Figure S10. Catalytic activity of bare hydrophilic carbon paper electrode. A. CV curve of bare carbon paper obtained in 200 mM cyclooctene and 5 M H₂O with 50 mV/sec scan rate and B. Gas chromatography spectra of electrolyte solution at 1.45 V vs Fc/Fc⁺. FE_{epoxide} was 7.8% and FE_{ketone} was 2.4%. Total amount of product from oxidation was 2.6 mM.
Figure S11. Catalytic activity of Mn$_3$O$_4$ electrode. A. Gas chromatograph and B. NMR spectra of electrolyte solution at 1.45 V vs Fc/Fc$^+$ with 5 M H$_2$O and 200 mM cyclooctene (Total passed charge: 20 C). We were not able to clearly identify ketone or trans-cyclooctene oxide formation by NMR, because peak positions overlapped with water or the TBABF$_4$ electrolyte. C. NMR spectra of reference materials, containing cis-cyclooctene, cis-cyclooctene oxide, and cyclooctanone. 5.65 ppm: cis-cyclooctene (C, yellow), 2.88 ppm: cis-cyclooctene oxide (cis-E, green), 2.40 ppm: cyclooctanone (K, red), 3.12 ppm: TBABF$_4$ (#), 2.52 ppm: water (W, black), and 3.75, 6.12 ppm: internal standard, 1,3,5-trimethoxybenzene (I).
Figure S12. Hydrogen peroxide assay test. Hydrogen peroxide in acetonitrile solution can react with (NH₄)₆Mo₇O₂₄ to form a yellowish complex which has a maximum absorption peak at around 350 nm. A. In order to obtain the standard curve, we first prepared i) assay solution containing the 2.4 mM of (NH₄)₆Mo₇O₂₄ and 0.5 M H₂SO₄ solution and ii) standard solution in 0.1 M TBABF₄ of acetonitrile containing 0 to 1000 µM H₂O₂. UV-Vis spectrum was recorded using mixture of 990 µl of assay solution and 10 µl of the standard solution. B. Standard curve was obtained using the absorption intensity of UV-Vis spectra at 350 nm wavelength. C. In order to confirm the absence of hydrogen peroxide in the electrolyte solution, we conducted two control experiments: Electrolysis at 1.45 V vs Fe/Fe⁺ for one hour with 200 mM cyclooctene and 5 M H₂O (black) and electrolysis only with 5 M H₂O (red). We were not able to see any peak around 350 nm wavelength, which suggests that hydrogen peroxide is not involved in the epoxidation reaction.
Figure S13. Total current density values depending on A. cyclooctene concentration with 5 M H$_2$O and B. water concentration with 200 mM cyclooctene at 1.45 V vs Fe/Fe$^+$. 
Figure S14. Reaction rate dependence on product concentration. Dependence of partial current on A. concentration of cis-cyclooctene oxide and B. concentration of 1,2-epoxyoctane at 1.45 V vs Fc/Fc⁺. C. GC-MS spectra of electrolyte solution at 1.45 V vs Fc/Fc⁺ with 5 M H₂O, 200 mM cyclooctene, and various concentration of 1,2-epoxyoctane. Inset figure shows whole GC-MS spectra. The peak at 3.37 min and 7.82 min are corresponding to 1-octene and 1,2-epoxyoctane, respectively.
Figure S15. H/D Isotope test. A. Chronoamperometry curves and B. GC-MS spectra of 5 M H₂O (black) and 5 M D₂O (red). Total passed charge was 20 C. GC-MS spectra showed that similar FE\textsubscript{epoxide} (~30%) was obtained in D₂O and H₂O, and H/D KIE value was 1.54.
Figure S16. **Long term electrolysis test.** A. GC-MS spectra of product at 25, 50, 75, and 100 °C of passed charge, and B. NMR spectra of the product at 100 °C of passed charge (C: cis-cyclooctene, cis-E: cis-cyclooctene oxide, trans-E: trans-cyclooctene oxide, K: cyclooctanone, and I: internal standard, 1,3,5-trimethoxybenzene).
E. Mechanisms

**Mechanism I. (Proposed in manuscript)**

![Diagram of Mechanism I](image)

Mechanism I presented in the manuscript (Scheme 2) involves a reversible oxygen atom transfer step followed by a rate-limiting one electron transfer; the KIE does not make clear whether or not a proton is involved in the rate determining step. This is consistent with the observed water order dependence, observation of reversibility in epoxidation, cyclooctene order dependence, and Tafel slope.

Based the previous studies on epoxidation reactions, we were able to think of several mechanisms and exclude implausible mechanisms based on the kinetic data. Here, we propose one alternative mechanism (Figure S18):

**Mechanism II. (Alternative mechanism)**

![Diagram of Mechanism II](image)

Figure S17. Proposed mechanism of electrochemical epoxidation reaction by Mn₃O₄ NPs

Figure S18. In this mechanism, Mn(III)-OH species are the resting state. Water is assumed to bind to the active site in a pre-equilibrium step. Then, cyclooctene reacts in the rate limiting step accompanied with one electron transfer to produce protonated cyclooctene oxide.
F. Other olefin substrates

F.1. Linear aliphatic olefin substrates

Figure S19. Reaction scheme of electrochemical linear aliphatic olefin epoxidation.

Figure S20. 1-hexene epoxidation reaction. GC-MS spectra of A. 1-hexene concentration variation, B. Water concentration variation, C. chronopotentiometry at various currents and D. chronoamperometry at various potentials. Major peaks at 3.88, 4.05, 4.93 min are corresponding to 2-hexanone, 1,2-epoxyhexane, and 2-hexanal. Total passed charge was 50 C. For 1-hexene epoxidation, chronoamperometry at 1.3 V with 500 mM of 1-hexene and 10 M H2O was chosen as the optimized condition. Inset figure shows GC-MS spectrum of 1,2-epoxyhexane products from 1-hexene oxidation.
Table S1. Reaction conditions for linear aliphatic olefin substrates (n=6-12). 0.1M TBABF₄ in ACN was used as the solvent. Total volume was set to be 4 mL. Concentration of water and substrates have been adjusted depending on the solubility of substrates in water/acetonitrile mixture.

| Substrates | n  | Water (M) | Substrate (mM) | Passed Charge (C) |
|------------|----|-----------|----------------|-------------------|
| 1-hexene   | 6  | 10        | 500            | 60                |
| 1-heptene  | 7  | 10        | 200            | 90                |
| 1-octene   | 8  | 5         | 200            | 50                |
| 1-nonene   | 9  | 5         | 200            | 50                |
| 1-decene   | 10 | 4         | 200            | 60                |
| 1-undecene | 11 | 2.5       | 200            | 50                |
| 1-dodecene | 12 | 2         | 100            | 50                |

Table S2. Epoxidation of different linear aliphatic olefins (n=6-12) catalyzed by manganese oxide nanoparticles. Chronoamperometry has been conducted at 1.3 V vs Fe/Fc⁺. 100 mM of 1-dodecene (for n = 6-11) and 1-octene (for n=12) were used as internal GC-MS standards for the quantification.

| Substrates   | Selectivity (%) | Conversion (%) | Yield (%) | FE_{\text{epoxide}} (%) |
|--------------|-----------------|----------------|-----------|-------------------------|
| 1-hexene     | 92.6            | 8.35           | 15.3      | 8.2                     |
| 1-heptene    | 70.2            | 30.2           | 18.9      | 9.8                     |
| 1-octene     | 54.1            | 47.3           | 6.43      | 9.4                     |
| 1-nonene     | 51.4            | 20.2           | 10.9      | 6.8                     |
| 1-decene     | 47.2            | 16.9           | 35.9      | 15.6                    |
| 1-undecene   | 32.5            | 7.8            | 15.8      | 3.8                     |
| 1-dodecene   | 25.4            | 4.8            | 17.5      | 1.3                     |

Conversion (%) = \frac{\text{initial substrate (mM)} - \text{final substrate (mM)}}{\text{initial substrate (mM)}} \quad (S1)

Yield_{\text{epoxide}}(\%) = \frac{\text{epoxide (mM)}}{\text{initial substrate (mM)} - \text{final substrate (mM)}} \quad (S2)

Selectivity_{\text{epoxide}}(\%) = \frac{\text{epoxide (mM)}}{\text{total products observed (mM)}} \quad (S3)

Faradaic efficiency_{\text{epoxide}}(\%) = \frac{\text{epoxide (mM)}}{\text{theoretical yield}_{\text{epoxide}} (mM)} \quad (S4)
Figure S21. Side reactions for linear aliphatic olefin substrates.
F.2. Cyclic aliphatic olefin substrates

Figure S22. Reaction scheme of electrochemical cyclic aliphatic olefin epoxidation.

Table S3. Reaction conditions for cyclic aliphatic olefin substrates. 0.1M TBABF₄ in ACN was used as the solvent. Total volume was set to be 4 mL. Concentration of water and substrates have been adjusted depending on the solubility of substrates in water/ACN mixture.

| Substrates   | n  | Water (M) | Substrate (mM) |
|--------------|----|-----------|----------------|
| Cyclopentene | 5  | 10        | 200            |
| Cyclohexene  | 6  | 10        | 200            |
| Cycloheptene | 7  | 5         | 200            |
| Cyclooctene  | 8  | 5         | 200            |
| Cyclodecene  | 10 | 5         | 100            |

Table S4. Epoxidation of different cyclic aliphatic olefins catalyzed by manganese oxide nanoparticles. Chronoamperometry has been conducted at 1.3 V vs Fe/Fe⁺. 100 mM of 1-dodecene (n = 5-8) and 1-octene (n=10) were used as internal GC-MS standards for the quantification.

| Substrates   | Selectivity (%) | Conversion (%) | Yield (%) | FE_{epoxide} (%) |
|--------------|-----------------|----------------|-----------|------------------|
| Cyclopentene | 15.0            | 54.7           | 5.0       | 2.84             |
| Cyclohexene  | 8.0             | 30.2           | 2.8       | 1.67             |
| Cycloheptene | 13.1            | 47.9           | 6.9       | 10.2             |
| Cyclooctene  | 72.1            | 55.1           | 28.3      | 24.1             |
| Cyclodecene  | 67.5            | 25.4           | 27.1      | 10.6             |

Figure S23. Side reaction pathways for cyclic aliphatic olefin substrates
F.3. Other substrates

![Chemical structures of olefin substrates](image)

**Figure S24.** Other olefin substrates.

**Table S5. Reaction conditions for olefin substrates.** 0.1M TBABF₄ in ACN was used as the solvent. Total volume was set to be 4 mL. Concentration of water and substrates have been adjusted depending on the solubility of substrates in water/ACN mixture. Total passed charge was 50 C.

| Substrates          | Water (M) | Substrate (mM) |
|---------------------|-----------|----------------|
| Styrene             | 5         | 200            |
| Norbornene          | 10        | 200            |
| Trans-stilbene      | 5         | 200            |
| Trans-beta-methylstyrene | 10      | 200            |

**Figure S25.** GC-MS spectra of the products from olefin substrates oxidation. A. Styrene, B. trans-stilbene, C. norbornene, and D. trans-beta-methylstyrene. For norbornene substrates, conversion, yield, selectivity, and Faradaic efficiency towards epoxide were 25.7, 11.4, 66.4, and 9.1%, respectively. Chronoamperometry has been conducted at 1.3 V vs Fc/Fc⁺.
References

(s1) Solis, B. H.; Hammes-Schiffer, S. Proton-Coupled Electron Transfer in Molecular Electrocatalysis: Theoretical Methods and Design Principles. *Inorg. Chem.* **2014**, *53* (13), 6427–6443.

(s2) Jin, K.; Seo, H.; Hayashi, T.; Balamurugan, M.; Jeong, D.; Go, Y. K.; Hong, J. S.; Cho, K. H.; Kakizaki, H.; Bonnet-Mercier, N.; et al. Mechanistic Investigation of Water Oxidation Catalyzed by Uniform, Assembled MnO Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139* (6), 2277–2285.