Supporting Information

Unified Mechanism of Oxygen Atom Transfer and Hydrogen Atom Transfer Reactions with a Triflic Acid-Bound Nonheme Manganese(IV)–Oxo Complex via Outer-Sphere Electron Transfer

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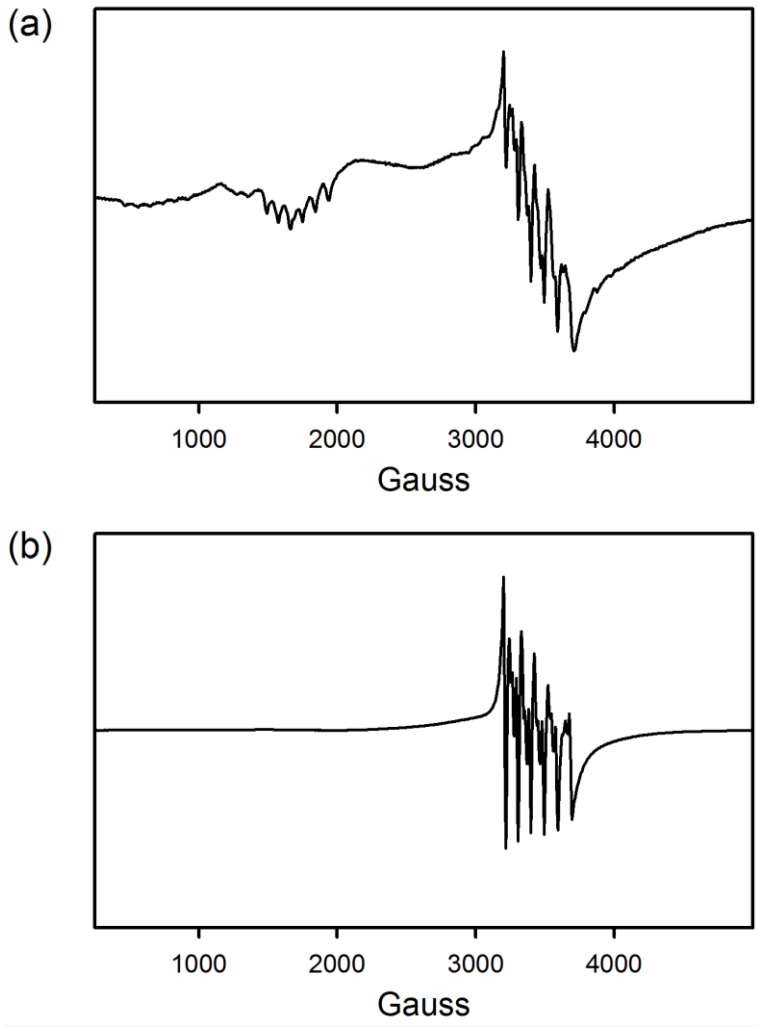

Figure S1. (a) X-band CW-EPR spectrum of the complete reaction solution obtained in the oxidation of *cis*-stilbene (200 mM) by **1** (0.50 mM) in TFE/MeCN (v/v = 1:1) at 273 K. It should be noted that EPR spectra obtained in the oxidation of other styrene derivatives by **1** are virtually identical to that in the oxidation of *cis*-stilbene by **1**. (b) X-band CW-EPR spectrum of the complete reaction solution obtained in the oxidation of *cis*-stilbene (20 mM) by **2** (0.50 mM) in the presence of HOTf (50 mM) in TFE/MeCN (v/v = 1:1) at 273 K. It should be noted that EPR spectra obtained in the oxidation of other styrene derivatives by **2** are virtually identical to that in the oxidation of *cis*-stilbene by **2**. All spectra were recorded at 5 K.

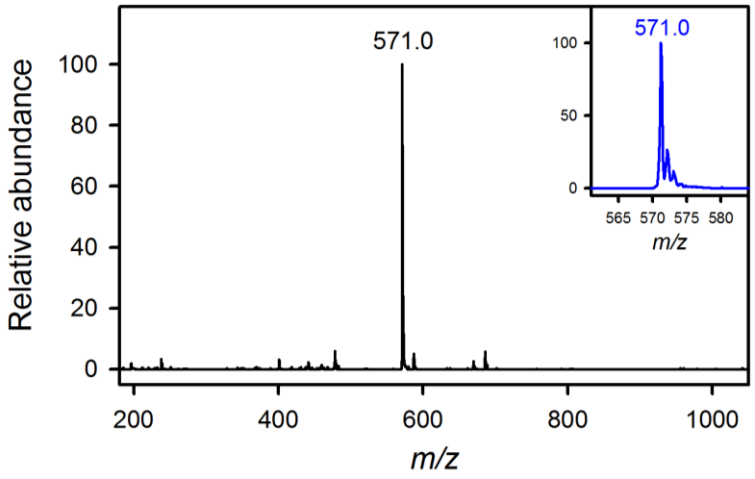

Figure S2. ESI-MS spectrum of the complete reaction solution obtained in the oxidation of *cis*-stilbene (200 mM) by **1** (0.50 mM) in TFE/MeCN (v/v = 1:1) at 273 K. Peak at *m/z* = 571.0 corresponds to $[Mn^{II}(N4Py)(CF_3SO_3)]^+$ (calculated *m/z* = 571.1). It should be noted that ESI-MS spectra obtained in the oxidation of *cis*-stilbene by **2** and in the oxidation of other styrene derivatives by **1** and **2** are virtually identical to that in the oxidation of *cis*-stilbene by **1**.

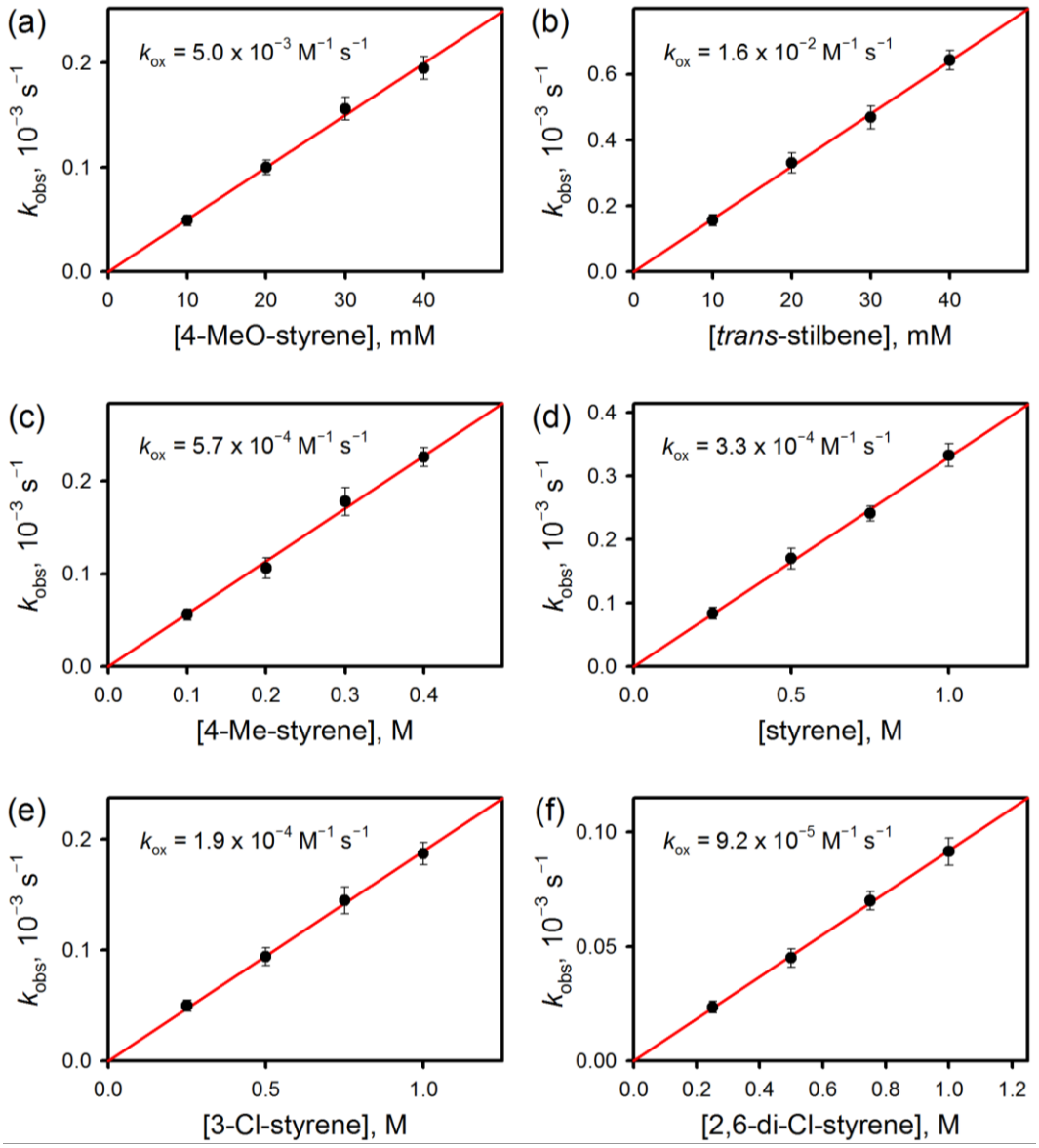

Figure S3. Plots of pseudo-first-order rate constants (k_{obs}) vs concentrations of styrene derivatives to determine second-order rate constants (k_2) of epoxidation of styrene derivatives [(a) 4-MeO-styrene, (b) *trans*-stilbene, (c) 4-Me-styrene, (d) styrene, (e) 3-Cl-styrene and (f) 2,6-di-Cl-styrene] by **1** (0.5 mM) in TFE/MeCN (v/v = 1:1) at 273 K.

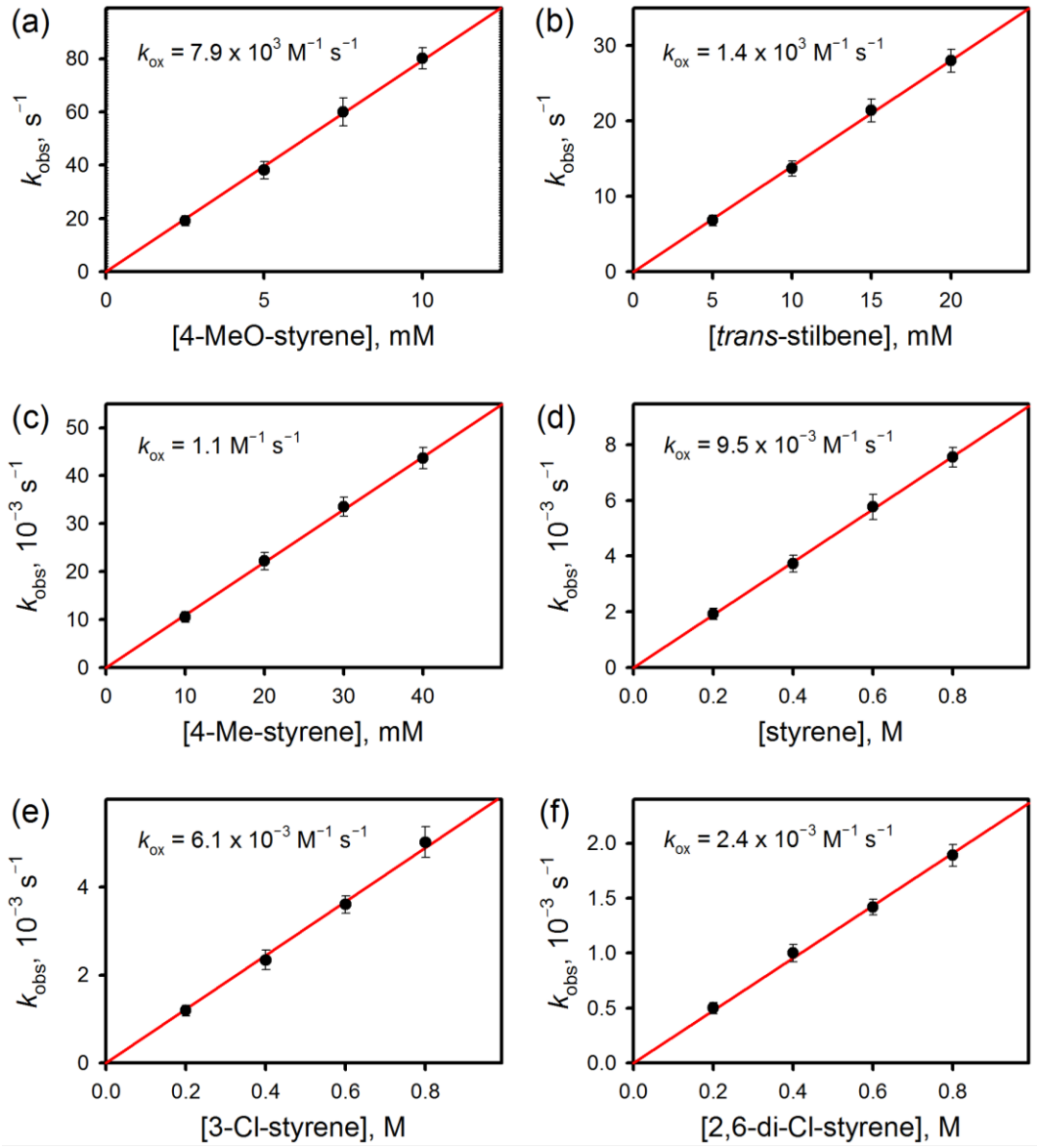

Figure S4. Plots of pseudo-first-order rate constants (k_{obs}) vs concentrations of styrene derivatives to determine second-order rate constants (k_2) of epoxidation of styrene derivatives [(a) 4-MeO-styrene, (b) *trans*-stilbene, (c) 4-Me-styrene, (d) styrene, (e) 3-Cl-styrene and (f) 2,6-di-Cl-styrene] by **2** (0.50 mM) in the presence of HOTf (50 mM) in TFE/MeCN (v/v = 1:1) at 273 K.

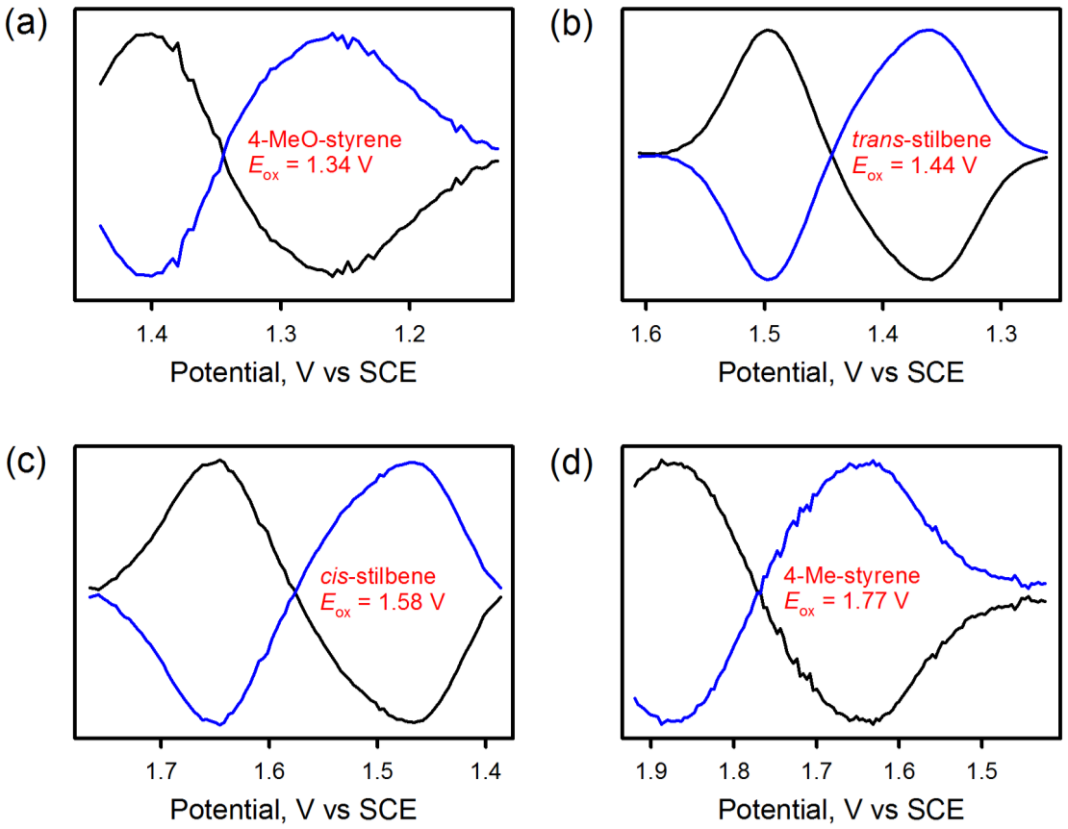

Figure S5. Second-harmonic alternating current voltammograms (SHACVs) of styrene derivatives (10 mM) [(a) 4-MeO-styrene, (b) *trans*-stilbene, (c) *cis*-stilbene and (d) 4-Me-styrene] in TFE/MeCN (v/v = 1:1) at 273 K. Scan rate was 4 mV/s.