

Supplementary Information

Photochemical generation and reactivity of a new phthalocyanine- manganese-oxo intermediate

Tristan Skipworth,^a Seth Klaine,^a and Rui Zhang^a

^a Department of Chemistry, Western Kentucky University, 1906 College Heights
Blvd., Bowling Green, Kentucky, USA. Fax: 1-270-7455631; Tel: +1-270-7453803;
E-mail: rui.zhang@wku.edu

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Experimental:

Chemicals and Instrumentation

All commercial reagents were of the best available purity and were used as supplied unless otherwise specified. Acetonitrile was obtained from Sigma Aldrich (HPLC grade) and passed through a dry alumina column prior to use. All organic substrates for kinetic studies were also purified by passing through a flash chromatography column of active alumina (Grade I) before use. H₂¹⁸O (97% ¹⁸O-enriched) and Mn^{III}(^tBu₄-Pc)Cl (**1**) were directly obtained from Sigma-Aldrich and used as such. UV-vis spectra were performed on an Agilent 8454 diode array spectrometer using standard 1.0-cm quartz cuvettes. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on an Agilent GC7820A/MS5977B, coupled with an auto sample injector using Agilent HB-5 capillary columns. Electrospray ionization-mass spectroscopy (ESI-MS) data were collected using an Agilent 500 LC-MS Ion Trap System. Visible light was produced from a SOLA SE II light engine (Lumencor) configured with a liquid light guide (60-120 W).

Photochemical generation of manganese-oxo species **3**

Treatment of compound **1** (typically 2×10^{-5} M) with a 2-fold excess of Ag(ClO₃) or Ag(NO₂) in anaerobic CH₃CN quickly formed the corresponding complexes **2**, as evidenced by UV-vis spectroscopy. When the solution of **2** was irradiated with visible light from a Solar engine (60 or 120 W) at ambient temperature, the formation of **3** was complete in *ca.* 1-2 min, which was monitored by UV-visible. The photochemical reactions became very slow or inert at higher concentrations of the precursor ($>10^{-4}$ M), apparently due to light blocking.

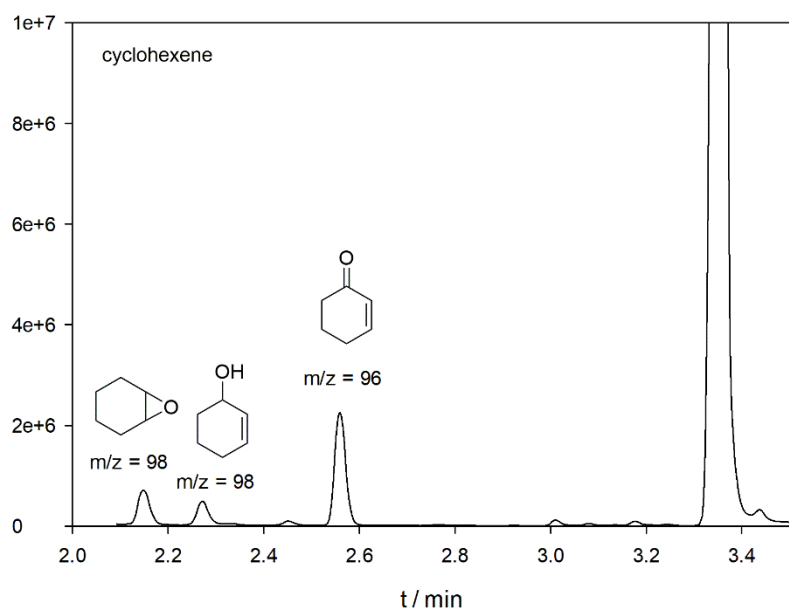
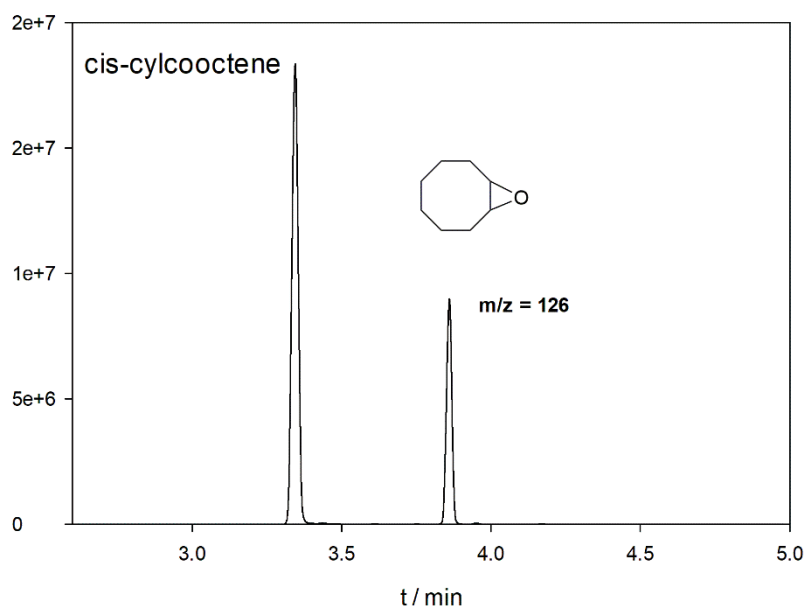
Kinetic studies

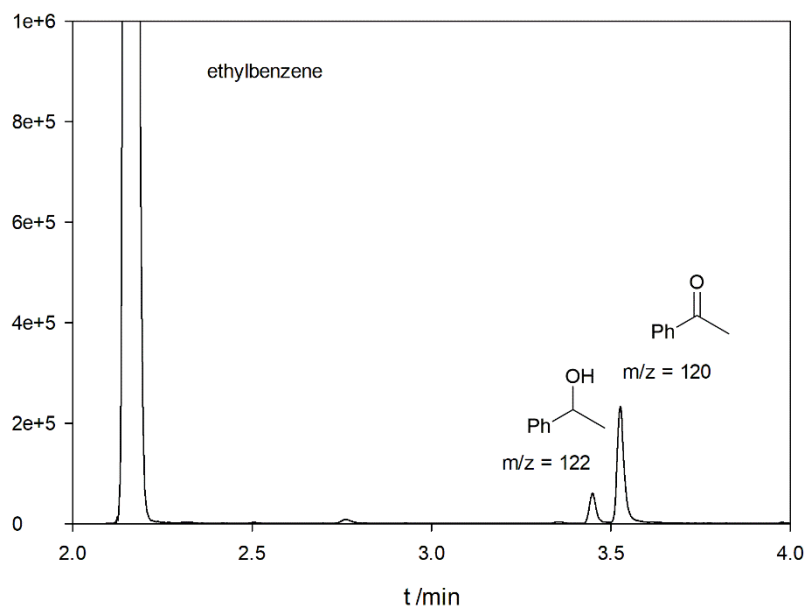
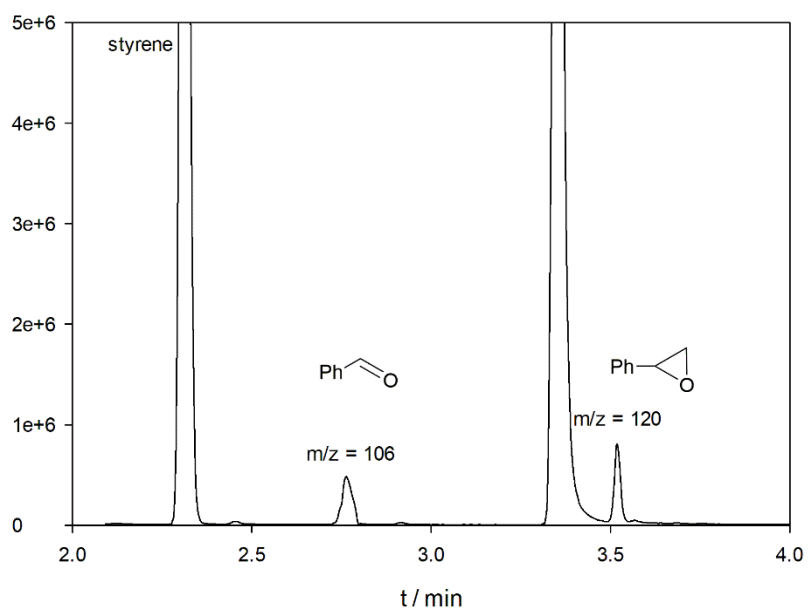
Reactions of oxo-species **3** with an excess of organic substrates (>10,00 equiv.) were conducted in an acetonitrile solution at 23 ± 2 °C. The rates of the oxo group transfer reactions from **3** to substrates were monitored by the decay of the Q-band absorption band of the oxo-species **3**. The kinetic traces at $\lambda_{\text{max}} = 620$ nm displayed good pseudo-first-order behavior for at least four half-lives, and the data gave pseudo-first-order observed rate constants, k_{obs} . Plots of these values against the concentration of substrate (final concentration) were linear and the slope gave the second-order rate constant, which is an average of 2-3 determinations consisting of **3** independent kinetic measurements. The standard deviations in Table 1 are 2σ .

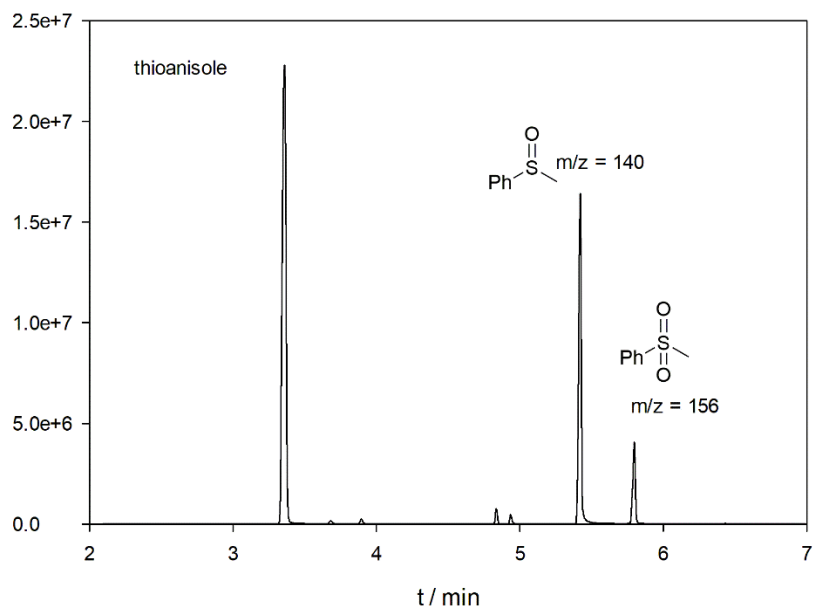
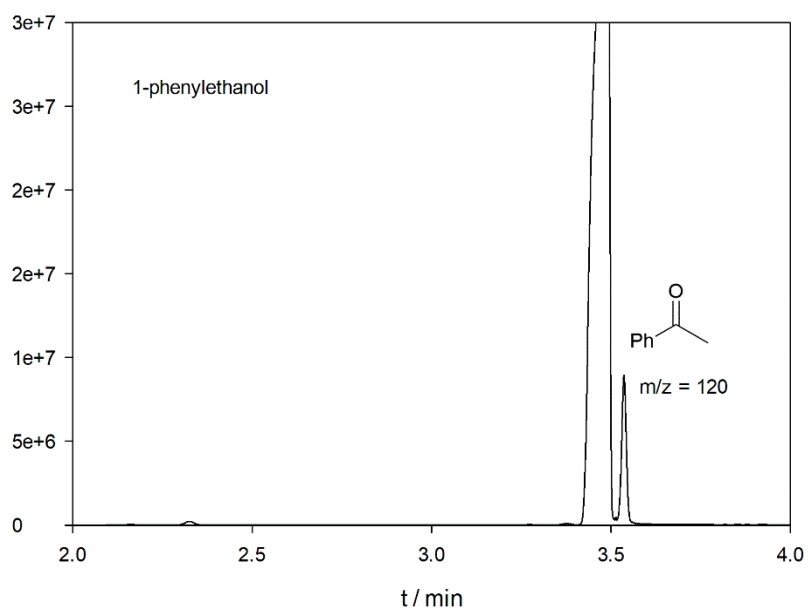
General procedure for preparative reactions

Reactions for product analysis were carried out in CH₃CN at a higher amount of **3** (*ca.* 10 μmol) and a large excess of organic substrates (same molar ratio range as kinetic studies) in 20 mL vial and monitored by UV-vis spectroscopy for completion of the reaction.

Oxidized products were well known and identified by GC-MS with Mass Spectral libraries for the MSD ChemStation (Agilent). Yields were calculated based on precursor **2a** used for generation of **3** (> 95%) by GC analysis of the spent reaction solutions with internal standard (1,2,4-trichlorobenzene or iodobenzene). The corresponding GC traces for oxidized products in Table 1 are listed below:







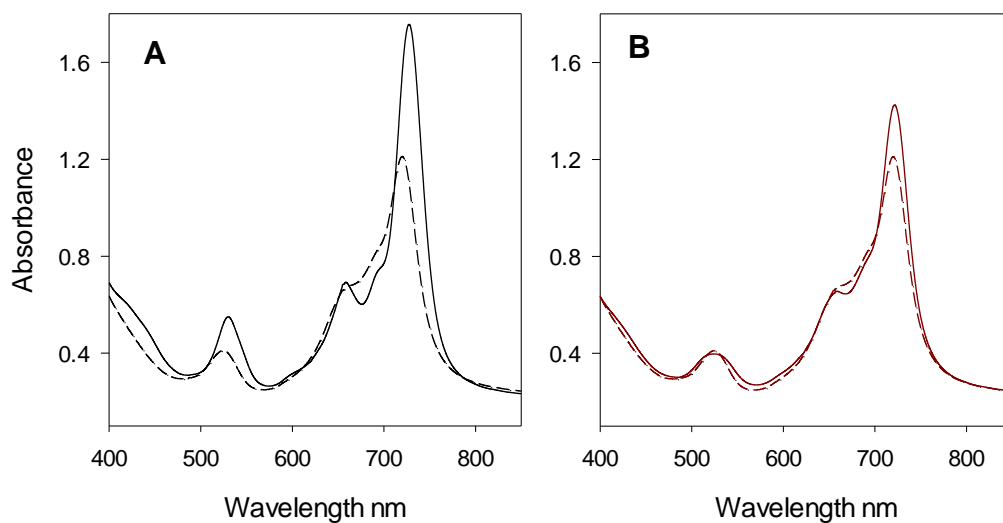


Fig. S1. UV-vis spectra of $[\text{Mn}^{\text{III}}(\text{tBu}_4\text{Pc})]\text{Cl}$ (**1**) (2×10^{-5} M, dashed line) and (A) $[\text{Mn}^{\text{III}}(\text{tBu}_4\text{Pc})](\text{ClO}_3)$ (**2a**, solid), and (B) $[\text{Mn}^{\text{III}}(\text{tBu}_4\text{Pc})](\text{NO}_2)$ (**2b**, solid) in CH_3CN solution at room temperature.

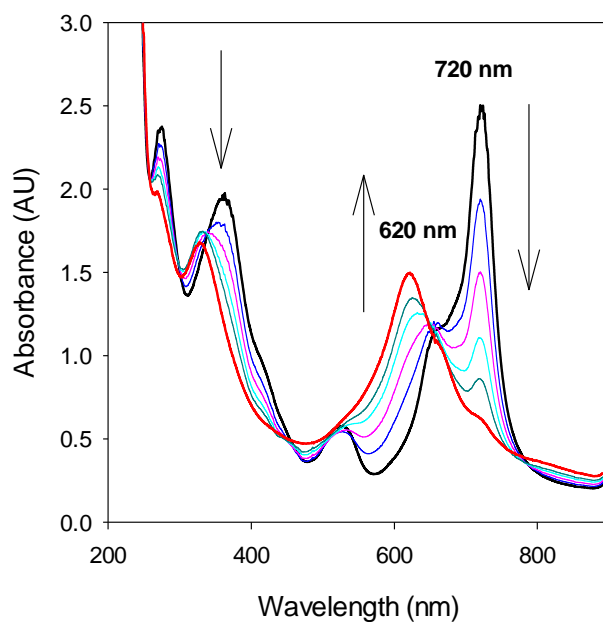


Fig. S2. Time-resolved spectra for generating $[\text{Mn}^{\text{IV}}(\text{tBu}_4\text{Pc})(\text{O})]$ (**3**) by photolysis of **2b** (2.0×10^{-5} M) over 100 s with visible light (120 W) in CH_3CN at 22°C .

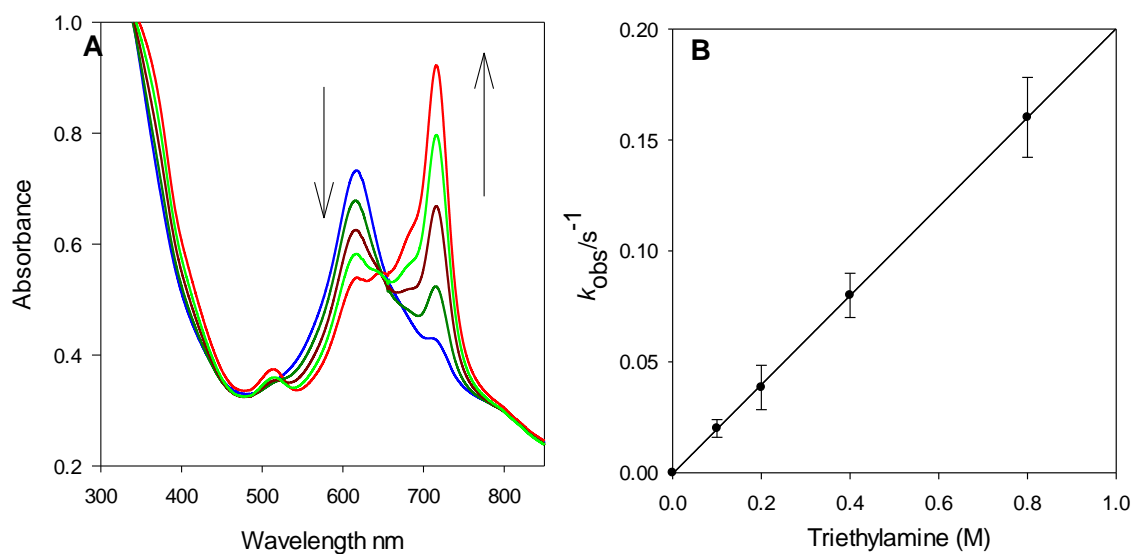


Fig. S3. (A) Time-resolved spectra of the one-electron reduction of $[\text{Mn}^{\text{IV}}(\text{'Bu}_4\text{Pc})(\text{O})]$ (**3**) with triethylamine (0.1 M) in CH_3CN over 150 s. (B) Kinetic plot of observed rate constant versus the concentrations of trimethylamine with $k_{\text{ox}} = (0.21 \pm 0.02) \text{ M}^{-1}\text{s}^{-1}$.