Supporting Information

Catalytically active μ-oxodiiron(IV) oxidants from iron(III) and dioxygen

Anindya Ghosh, Filipe Tiago de Oliveira, Toshihiro Yano, Takanori Nishioka, Evan S. Beach, Isamu Kinoshita,* Eckard Münck,* Alexander D. Ryabov, Colin P. Horwitz, Terrence J. Collins*

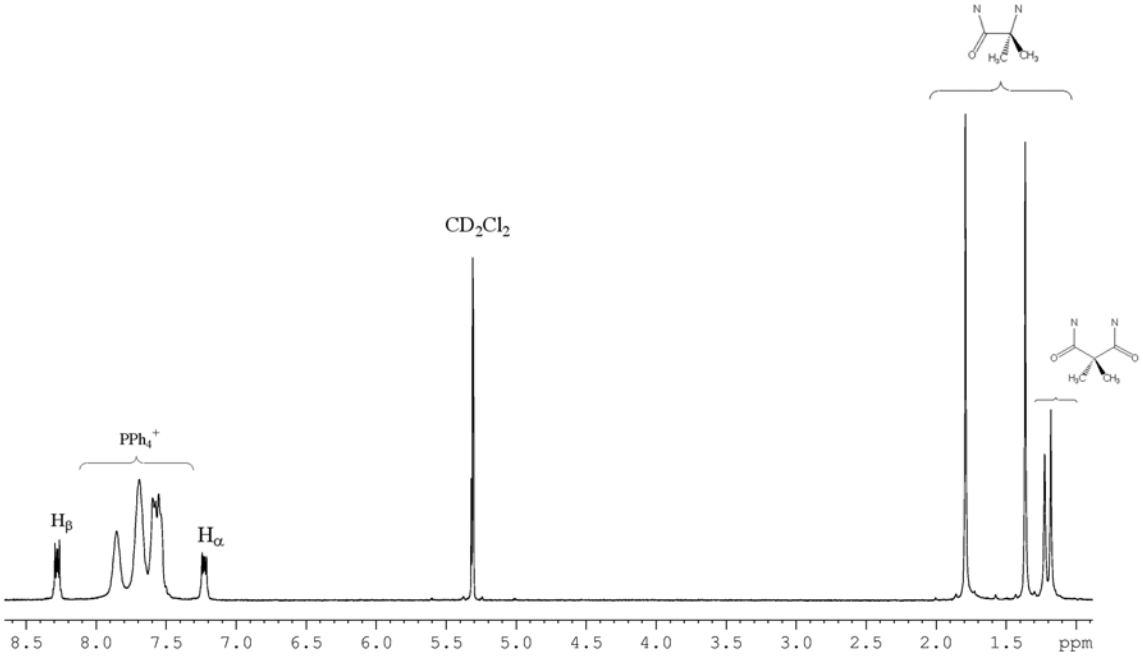

Figure S1. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **2a.** δ = 1.18 (s, 6 H, diastereotopic CH_3 6-membered rings), 1.23 (s, 6 H, diastereotopic CH_3 6-membered rings), 1.36 (s, 12 H, diastereotopic CH_3 5-membered rings), 1.79 (s, 12 H, diastereotopic CH_3 5-membered rings), 7.23 (m, 4 H, macrocyclic ArH), 7.57-7.85 (m, PPh_4^+), 8.27 (m, 4 H, macrocyclic ArH)

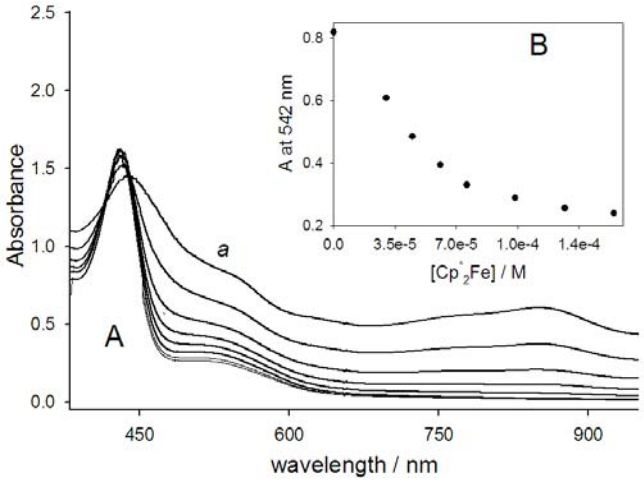

Figure S2**.** (A) Changes in the UV/Vis spectrum upon incremental addition of Cp^*_2Fe to **2a** (0.109 mM) in dichloromethane. Spectrum *a* was obtained at time $t = 0$. (B) Change in absorbance at 542 nm as a function of $[Cp^*_2Fe]$.

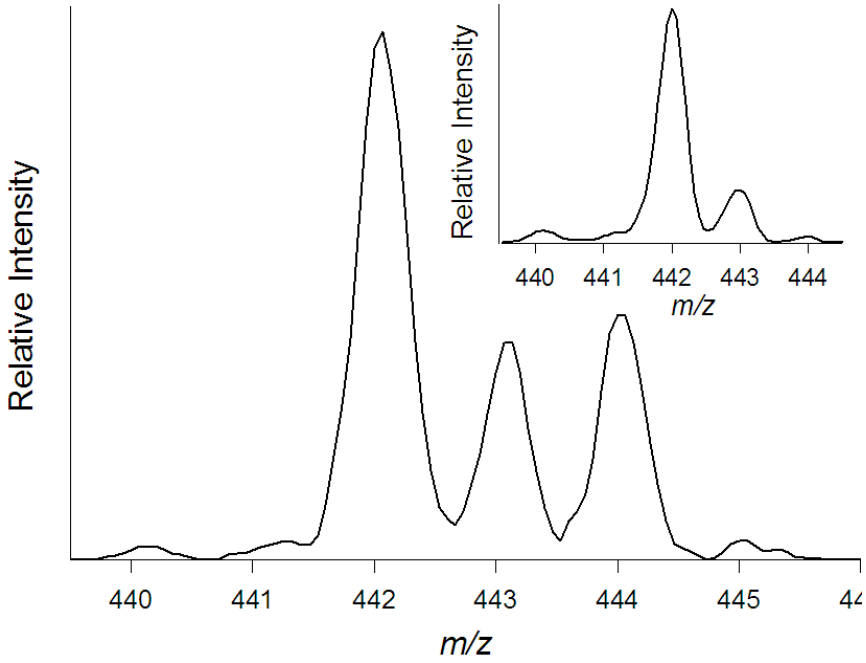

Figure S3. The ESI-MS analysis of a dichloromethane solution of **2a**. Compound **2a** was prepared by reacting [PPh_4]**1a**-H_2O with $^{18}O_2$ giving 31% ^{18}O incorporation. Inset shows the isotope distribution of *m/z* 442 of **2a** prepared from $^{16}O_2$.

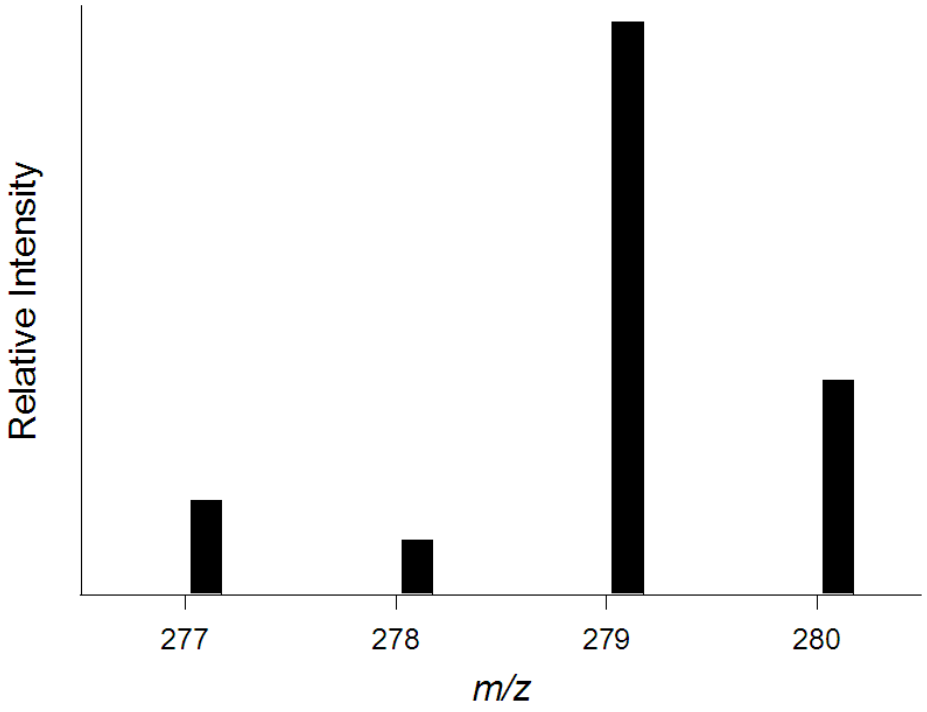

Figure S4. The mass spectrum of 86% ^{18}O enriched $OPPh_3$ {$(M–1)^+$ peak is shown}.

Compound **2a** was generated from $[PPh_4]$**1a**-$H_2{}^{18}O$ and $^{18}O_2$ in CH_2Cl_2.

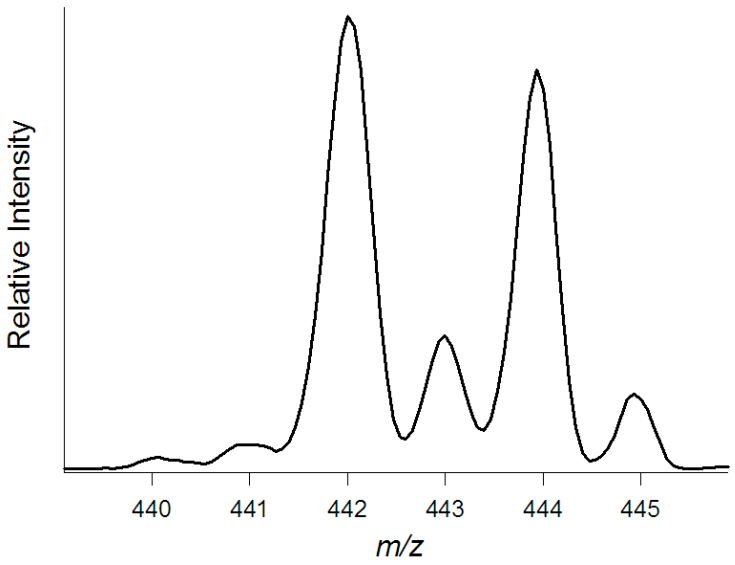

Figure S5. The ESI mass spectrum of compound **2a** that was generated from [PPh_4]**1a**-$H_2{}^{18}O$, dissolved in dichloromethane, and then exposed to $^{16}O_2$. 44% of ^{18}O incorporation was found in **1a**(O); peak at *m/z* = 444.

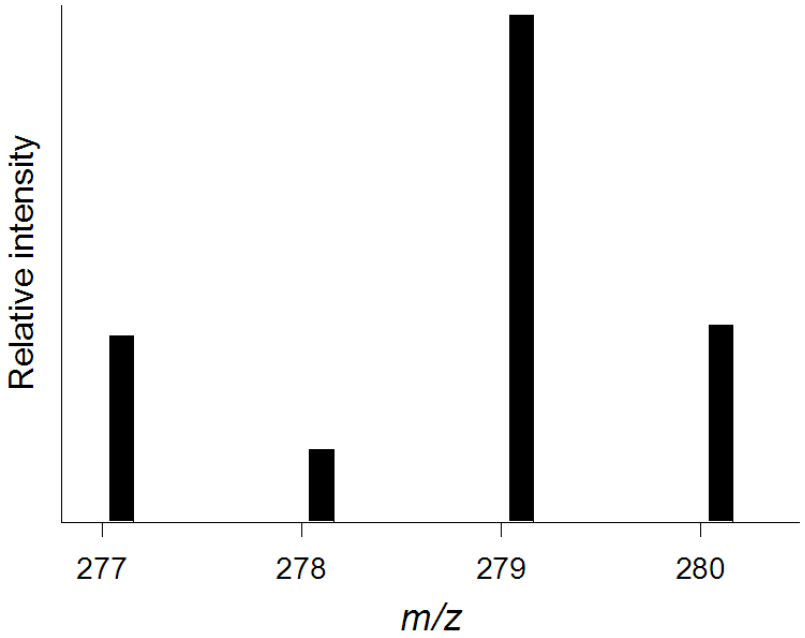

Figure S6. The GC-MS spectrum of the ^{18}O enriched $OPPh_3$ {$(M–1)^+$ peak is shown}. Compound **2a** was stirred with $H_2{}^{18}O$ (95%) for 3 h and then reacted with PPh_3. 73% incorporation of ^{18}O-isotope in $OPPh_3$; peak at *m/z* 279.

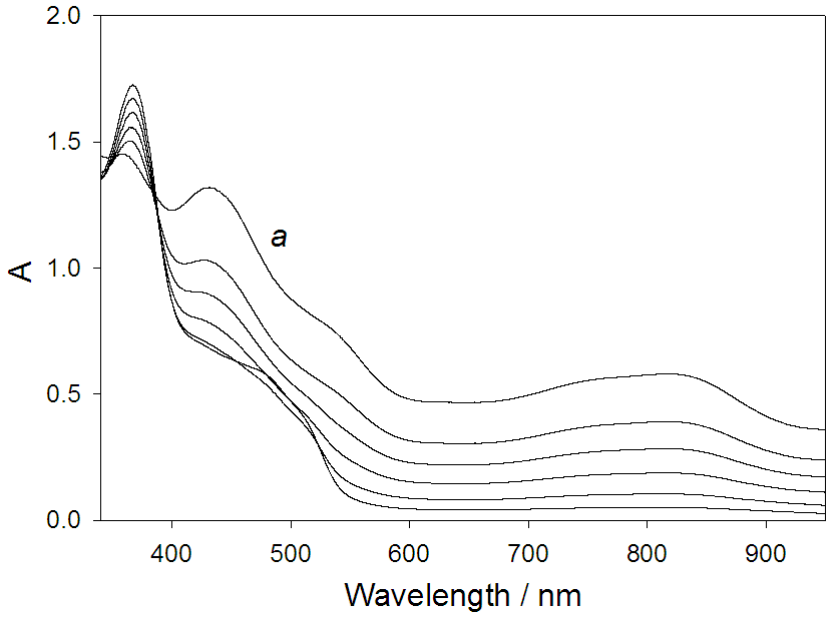

Figure S7. **(A)** Changes in the UV/Vis spectrum upon incremental addition of Orange II to **2a** (1.12×10^{-4} M) dissolved in acetonitrile/water mixture (1:1). Spectrum *a* is of **2a** before dye addition.