

Supporting Information

Dioxygen Activation by a Non-heme Iron(II) Complex: Formation of an Iron(IV)-Oxo Complex via C-H Activation by a Putative Iron(III)-Superoxo Species

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Experimental Section

Materials and Instrumentation. Commercially available chemicals were used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use.¹ Cyclohexene, cycloheptene, and cyclooctene were purchased from Aldrich Chemical Co. Cyclohexene-*d*₁₀ was purchased from CDN Isotopes Inc. Olefins were refluxed and distilled under Ar, and filtered through a column of silica gel 60 and then filtered again through a column of active alumina prior to use.¹ ¹⁸O₂ (80% ¹⁸O-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA). TMC ligand was purchased from Aldrich Chemical Co. Iron(II) complex, [Fe^{II}(TMC)(CH₃CN)₂](CF₃SO₃)₂, was prepared by literature methods.²

UV/Vis spectra were recorded on a Hewlett Packard Agilent 8453 UV-visible spectrophotometer equipped with a circulating water bath or an UNISOKU cryostat system (USP-203; UNISOKU, Japan). Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source at 20 μL/min using a syringe pump. The spray voltage was set at 4.7 kV and the capillary temperature at 100 °C. An ESI-MS sample of [(TMC)Fe^{IV}(O)]²⁺ intermediate was generated in the reaction of [Fe^{II}(TMC)](CF₃SO₃)₂ (5.0 × 10⁻⁴ M) with cyclohexene (2.5 × 10⁻² M) under air atmosphere in CH₃CN at 25 °C. CW-EPR spectra were taken at 5 K using a X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperatures were achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. The experimental parameters for EPR spectra were as follows: Microwave frequency = 9.646 GHz, microwave power = 1 mW, modulation amplitude = 10 G, gain = 1 × 10⁴, modulation frequency = 100 kHz, time constant = 40.96 ms and conversion time = 85.00 ms. Product analysis was performed with an Agilent Technologies 6890N gas chromatograph (GC) and Thermo Finnigan (Austin, Texas, USA) FOCUS DSQ (dual stage quadrupole) mass spectrometer interfaced with Finnigan FOCUS gas chromatograph (GC-MS). ¹H NMR spectra were measured with Bruker model digital AVANCE III 400 FT-NMR spectrometer. Quantitative analyses were made on the basis of comparison of NMR peak integration between products and authentic samples.

Kinetic Studies and Product Analysis. All reactions were followed by monitoring UV-vis spectral changes of reaction solutions with a Hewlett Packard 8453 spectrophotometer. Dioxygen activation by a nonheme iron(II) complex, $[\text{Fe}^{\text{II}}(\text{TMC})]^{2+}$ (**1**) (5.0×10^{-4} M), was examined with appropriate amounts of olefins ($1.5 \times 10^{-2} \sim 1.0 \times 10^{-1}$ M), by monitoring spectral changes in air-saturated CH_3CN at the given temperatures. Pseudo-first-order fitting of the kinetic data allowed us to determine k_{obs} values for the formation of **2**. Reactions were run at least in triplicate, and the data reported represent the average of these reactions.

Products formed in the reaction of **1** and O_2 in the presence of olefins under air were analyzed by ^1H NMR spectroscopy. Quantitative analysis was done by comparing ^1H NMR peak areas of products with those of authentic samples. Four products, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, 1,3-cyclohexadiene and benzene, were formed with the yields of 26(3)%, 21(2)%, 9(2)% and 5(2)%, respectively, in the reaction of cyclohexene (see Figure S4 for ^1H NMR spectrum). Products were also analyzed by GC and GC-MS. Products were identified by comparing with authentic samples, and product yields were determined by comparison against standard curves prepared with authentic samples and using decane as an internal standard. The ^{18}O -labeled experiment was performed with $^{18}\text{O}_2$ in a manner similar to that described above. The ^{16}O and ^{18}O compositions in allylic oxidation products were analyzed by GC-MS, by comparing the relative abundances of $m/z = 83$ and 98 for unlabeled 2-cyclohexen-1-ol and $m/z = 85$ and 100 for ^{18}O -labeled 2-cyclohexen-1-ol and $m/z = 68$ and 96 for unlabeled 2-cyclohexen-1-one and $m/z = 68$ and 96 for ^{18}O -labeled 2-cyclohexen-1-one (see Figure S5 for GC-MS spectra).

References

- [1] Purification of Laboratory Chemicals; Armarego, W. L. F.; Perrin, D. D. Eds., Pergamon Press, Oxford, 1997.
- [2] Rohde, J.-U.; In, J.-H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Münck, E.; Nam, W.; Que, L., Jr. *Science* **2003**, 299, 1037-1039.

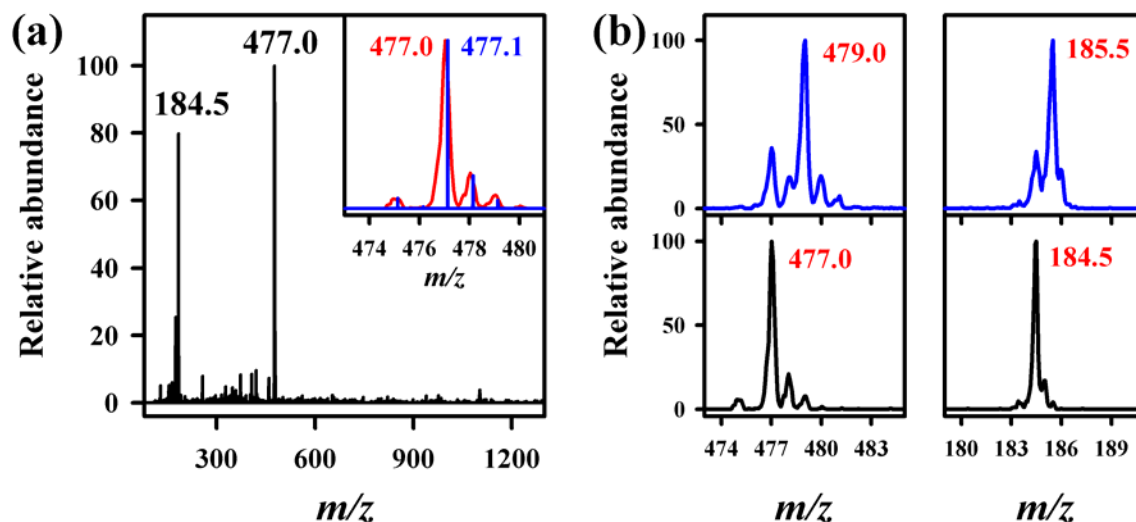


Figure S1. (a) ESI-MS spectrum of $[(\text{TMC})\text{Fe}^{\text{IV}}(\text{O})]^{2+}$ (**2**). Peaks at m/z of 184.5 and 477.0 correspond to $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{CH}_3\text{CN})]^{2+}$ and $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{CF}_3\text{SO}_3)]^+$, respectively. Inset shows the observed (red) and calculated (blue) isotope distribution patterns of the peak at m/z of 477.0 (calculated $m/z = 477.1$). An ESI-MS sample of **2**- ^{16}O was generated in a reaction solution containing $[\text{Fe}^{\text{II}}(\text{TMC})](\text{CF}_3\text{SO}_3)_2$ (5.0×10^{-4} M) and cyclohexene (2.5×10^{-2} M) under air in CH_3CN at 25°C . (b) ESI-MS spectra of **2**- ^{18}O (upper panel) and **2**- ^{16}O (lower panel). An ESI-MS sample of **2**- ^{18}O was generated in a reaction solution containing $[\text{Fe}^{\text{II}}(\text{TMC})](\text{CF}_3\text{SO}_3)_2$ (5.0×10^{-4} M) and cyclohexene (2.5×10^{-2} M) under $^{18}\text{O}_2$ gas (80% ^{18}O -enriched) in CH_3CN at 25°C . The percentages of **2**- ^{18}O and **2**- ^{16}O in the upper panel were calculated to be 76% and 24%, respectively.

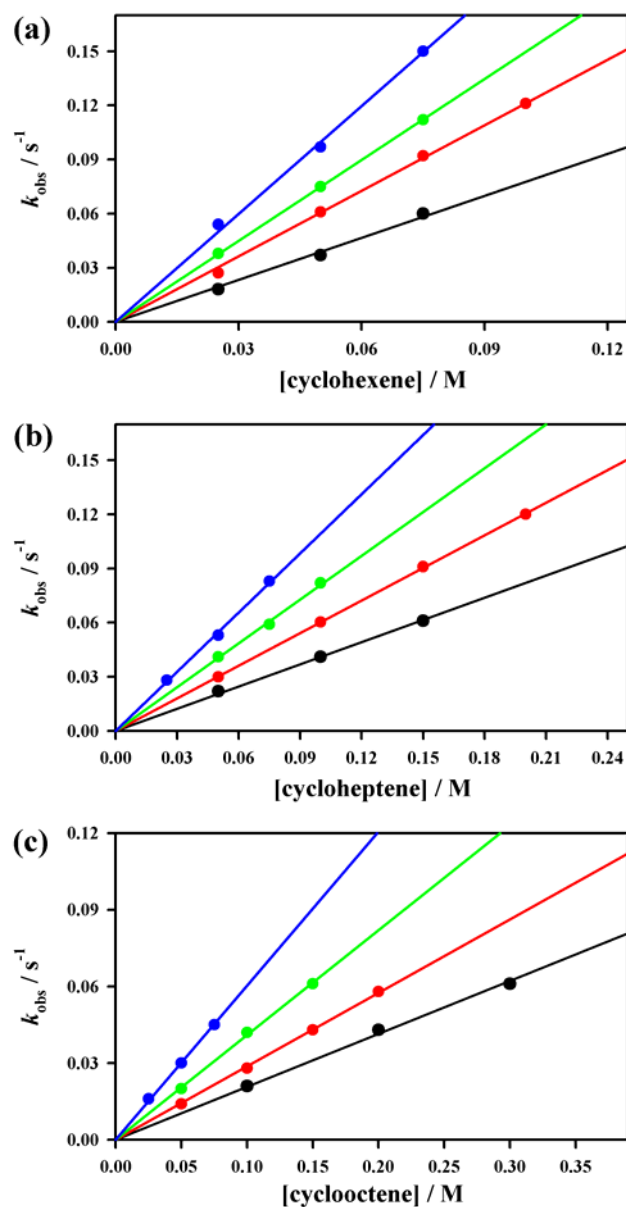


Figure S2. Plots of k_{obs} against olefin concentration to determine second-order rate constants in the reaction of **1** (5.0×10^{-4} M) and O_2 in the presence of (a) cyclohexene, (b) cycloheptene and (c) cyclooctene in CH_3CN at 20 °C (black), 25 °C (red), 30 °C (green) and 35 °C (blue).

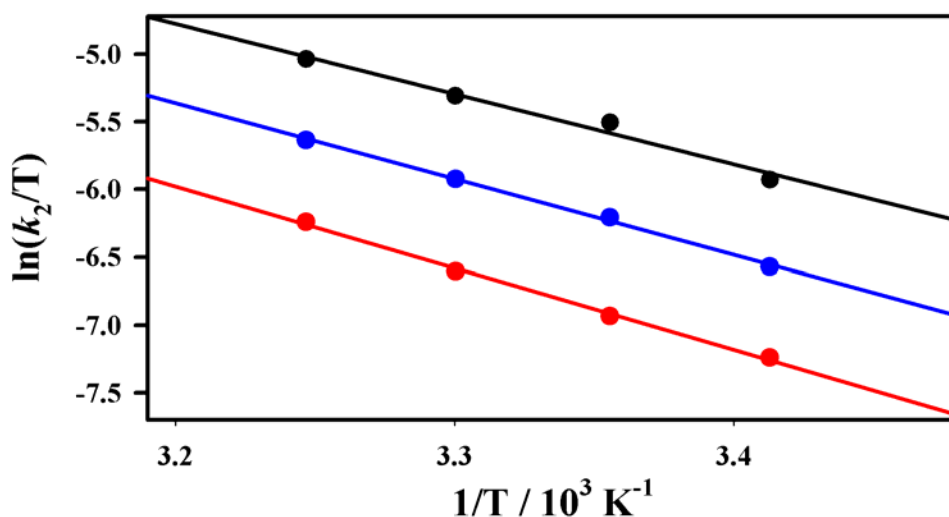


Figure S3. Eyring plots to determine activation parameters for the formation of **2** in the reaction of **1** (5.0×10^{-4} M) and O₂ in the presence of cyclohexene (black), cycloheptene (blue) and cyclooctene (red) in CH₃CN. The activation parameters calculated from the plots are as follows: $\Delta H^\ddagger = 43$ kJ mol⁻¹ and $\Delta S^\ddagger = -99$ J mol⁻¹ K⁻¹ for cyclohexene, $\Delta H^\ddagger = 47$ kJ mol⁻¹ and $\Delta S^\ddagger = -94$ J mol⁻¹ K⁻¹ for cycloheptene, and $\Delta H^\ddagger = 50$ kJ mol⁻¹ and $\Delta S^\ddagger = -88$ J mol⁻¹ K⁻¹ for cyclooctene.

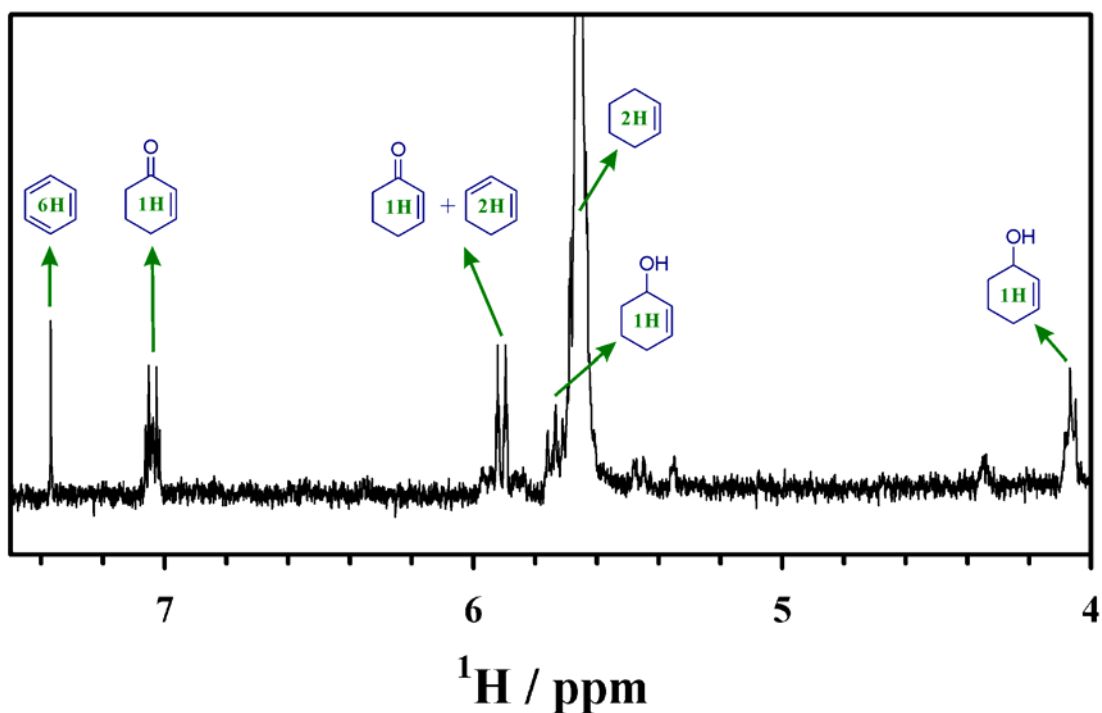


Figure S4. ^1H NMR spectrum of products formed in the reaction of **1** (2 mM) and O_2 in the presence of cyclohexene (20 mM, 10 equiv to **1**) in CD_3CN at 25 $^\circ\text{C}$. Reaction time was 10 min. Quantitative analyses were made on the basis of comparison of NMR peak integration between products and authentic samples. In this reaction, four products, 2-cyclohexen-1-ol, 2-cyclohexen-1-one, 1,3-cyclohexadiene and benzene, were obtained with the yields of 26(3)%, 21(2)%, 9(2)% and 5(2)%, respectively.

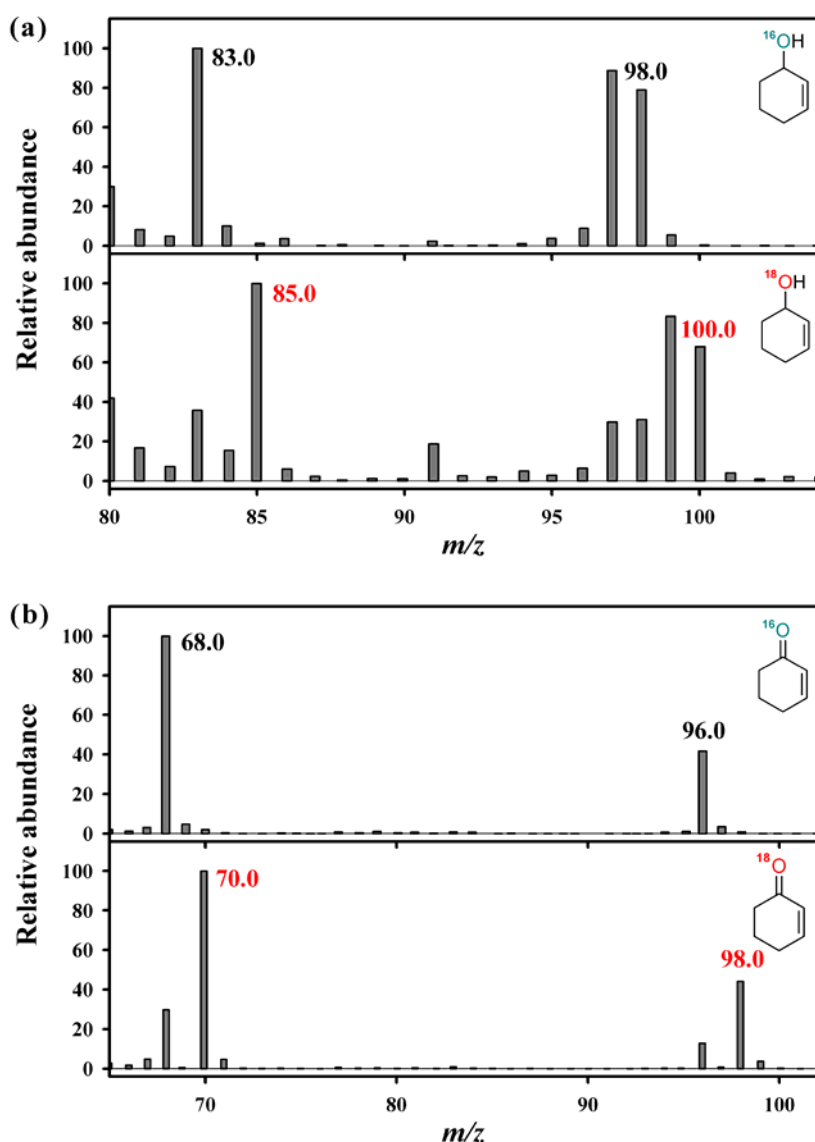


Figure S5. GC-MS spectra of allylic oxidation products, 2-cyclohexen-1-ol (a) and 2-cyclohexene-1-one (b), formed in a reaction solution containing $[\text{Fe}^{\text{II}}(\text{TMC})](\text{CF}_3\text{SO}_3)_2$ (5.0×10^{-4} M) and cyclohexene (2.5×10^{-2} M) under $^{16}\text{O}_2$ (upper panels) and $^{18}\text{O}_2$ (80% ^{18}O -enriched) (lower panels) in CH_3CN at 25°C .

The ^{16}O and ^{18}O compositions in 2-cyclohexen-1-ol and 2-cyclohexene-1-one formed under $^{18}\text{O}_2$ (80% ^{18}O -enriched) atmosphere were determined by the relative abundances of (a) $m/z = 83.0$ and 98.0 for unlabeled cyclohexen-1-ol and $m/z = 85.0$ and 100.0 for ^{18}O -labeled cyclohexen-1-ol and (b) $m/z = 68.0$ and 96.0 for unlabeled cyclohexen-1-one and $m/z = 70.0$ and 98.0 for ^{18}O -labeled cyclohexen-1-one. The ^{18}O percentages found in the cyclohexen-1-ol and cyclohexen-1-one products were 78%.

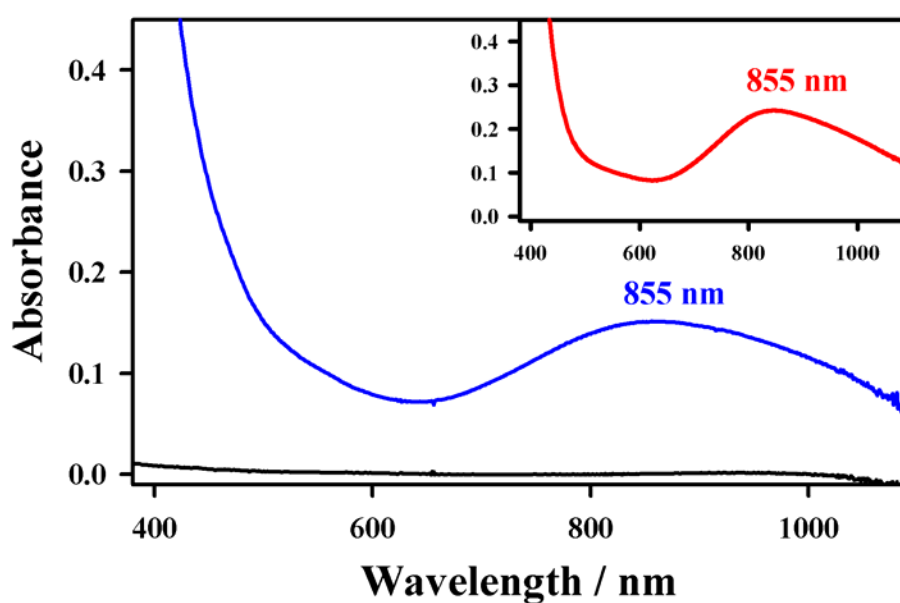


Figure S6. UV-vis spectra of **1** (black line) and $[(\text{TMC})\text{Fe}^{\text{III}}(\text{O}_2)]^+$ (**5**) species (blue line) generated in the reaction of **1** (1.0 mM) and O₂ in the presence of triethylamine (TEA, 5.0 mM) and cyclohexene (50 mM) in CH₃CN at 25 °C. Inset shows UV/Vis spectrum of **5** (red line) prepared by reacting **1** (1.0 mM) with H₂O₂ (10 mM) in the presence of TEA (5.0 mM) in CH₃CN at 25 °C. Although we were able to obtain the UV-vis spectrum of **5** with the yield of > 60% in the reaction of **1** and O₂ in the presence of TEA and olefins, we were not able to follow the second-order kinetics due to the instability of **5** in CH₃CN. **5** decayed fast and disappeared within 5 min in CH₃CN at 25 °C. However, initial rate of the formation of **5** was similar to that of the formation of **2**, indicating that the intermediate **4** is generated in the reaction as a precursor to **2**. In addition, although we were not able to follow the complete kinetics, we were able to observe the formation of **5** with the order of xanthene > cyclohexene > cyclohexene-*d*₁₀.

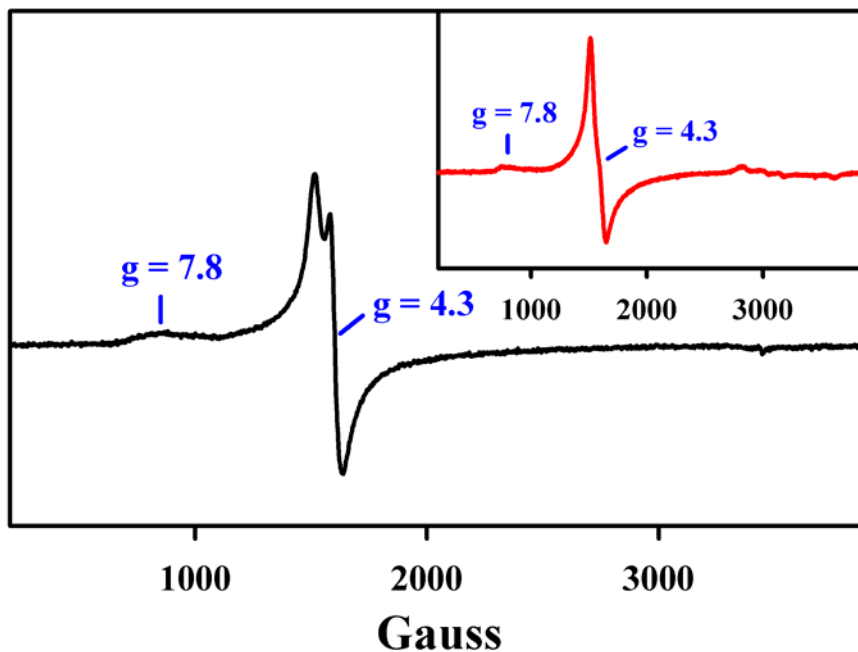


Figure S7. CW-EPR spectrum of **5** (black line) generated in the reaction of **1** (1.0 mM) and O_2 in the presence of triethylamine (TEA, 5.0 mM) and cyclohexene (50 mM) in CH_3CN at 25 °C. Inset shows CW-EPR spectrum of **5** (red line) formed in the reaction of **1** (1.0 mM) and H_2O_2 (10 mM) in the presence of TEA (5.0 mM) in CH_3CN at 25 °C. The experimental parameters for EPR spectra are as follows: Microwave frequency = 9.646 GHz, microwave power = 1 mW, modulation amplitude = 10 G, gain = 1×10^4 , modulation frequency = 100 kHz, time constant = 40.96 ms, conversion time = 85.00 ms and measuring temperature = 7 K.