

# Supporting Information For:

## Photochemical Organic Oxidations and Dechlorinations with a $\mu$ -Oxo Bridged Heme/Non-Heme Diiron Complex.

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**Figure S1.** UV-visible spectra showing the photoreduction of  $[(^6\text{L})\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}-\text{Cl}]^+$  (**1**)  $\{\lambda_{\text{max}}$  418 (Soret), 575 nm $\}$  to  $[(^6\text{L})\text{Fe}^{\text{II}}\dots\text{Fe}^{\text{II}}-\text{Cl}]^+$  (**2**)  $\{\lambda_{\text{max}}$  415 (Soret), 432 (sh), 532, 550 (sh) nm $\}$  in benzene-triphenylphosphine.

**Figure S2.** UV-visible spectra showing the photoreduction of  $[(^6\text{L})\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}-\text{Cl}]^+$  (**1**)  $\{\lambda_{\text{max}}$  418 (Soret), 575 nm $\}$  to  $[(^6\text{L})\text{Fe}^{\text{II}}\dots\text{Fe}^{\text{II}}-\text{Cl}]^+$  (**2**)  $\{\lambda_{\text{max}}$  415, 430 (sh), 532, 550 (sh) nm $\}$  in toluene.

**Figure S3.** EI-MS spectrum for either biphenyl trichloride product  $\text{C}_{12}\text{H}_7\text{Cl}_3$  at  $m/z$  256, which is derived from the photolysis of  $[(^6\text{L})\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}-\text{Cl}]^+$  (**1**) in 1,2-dichlorobenzene. The calculated isotope pattern for  $\text{C}_{12}\text{H}_7\text{Cl}_3$  is shown at the bottom.

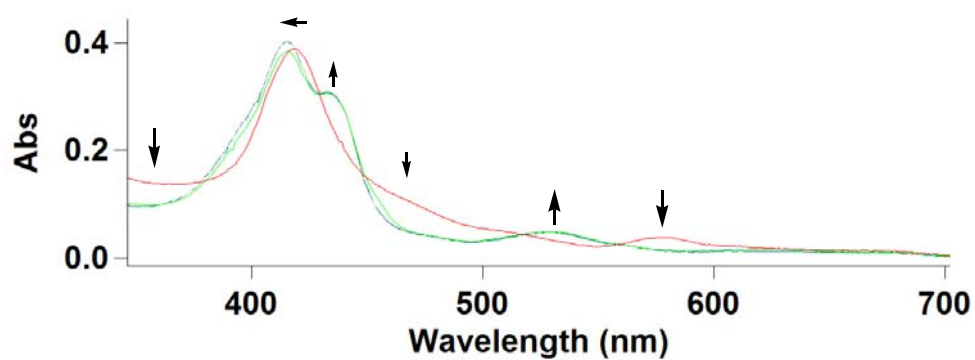
**Figure S4.** EI-MS spectrum for either biphenyl monochloride product  $\text{C}_{12}\text{H}_9\text{Cl}$  at  $m/z$  188, which is derived from the photolysis of  $[(^6\text{L})\text{Fe}^{\text{III}}-\text{O}-\text{Fe}^{\text{III}}-\text{Cl}]^+$  (**1**) in chlorobenzene. The calculated isotope pattern for  $\text{C}_{12}\text{H}_9\text{Cl}$  is shown at the bottom.

**Figure S5.** ESI-MS spectrum (positive ion mode) for  $\{[(^6\text{L})\text{Fe}^{\text{III}}-\text{Cl}\dots\text{Fe}^{\text{III}}-\text{Cl}]_2\text{O}\}^+$  (**3**) in showing the ion peak at  $m/z$  1221 which corresponds to the broken-oxo ion  $[(^6\text{L})\text{Fe}^{\text{III}}-\text{Cl}\dots\text{Fe}^{\text{III}}-\text{Cl}]^+$ . The inset shows the spectrum calculated for  $\text{C}_{63}\text{H}_{40}\text{N}_8\text{OFe}_2\text{Cl}_2\text{F}_6$ .

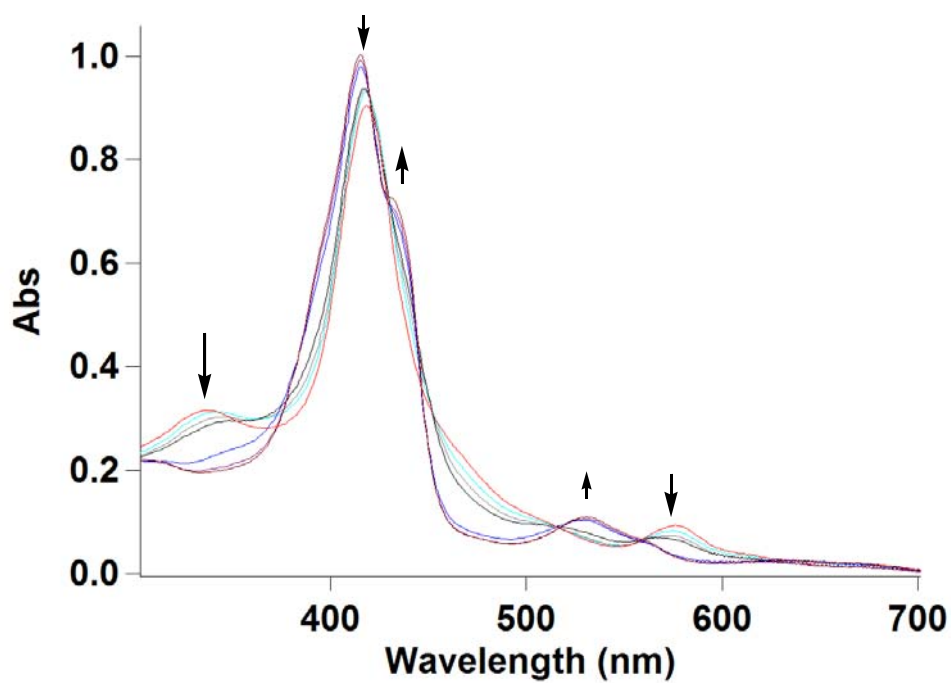
**Figure S6.** Full  $^1\text{H}$ -NMR spectrum for  $\{[(^6\text{L})\text{Fe}^{\text{III}}-\text{Cl}\dots\text{Fe}^{\text{III}}-\text{Cl}]_2\text{O}\}^+$  (**3**) recorded at 296 K in  $\text{CDCl}_3$ .

**Figure S7.** Diamagnetic region  $^1\text{H}$ -NMR spectrum for  $\{[(^6\text{L})\text{Fe}^{\text{III}}-\text{Cl}\dots\text{Fe}^{\text{III}}-\text{Cl}]_2\text{O}\}^{2+}$  (**3**) recorded in  $\text{CDCl}_3$ .

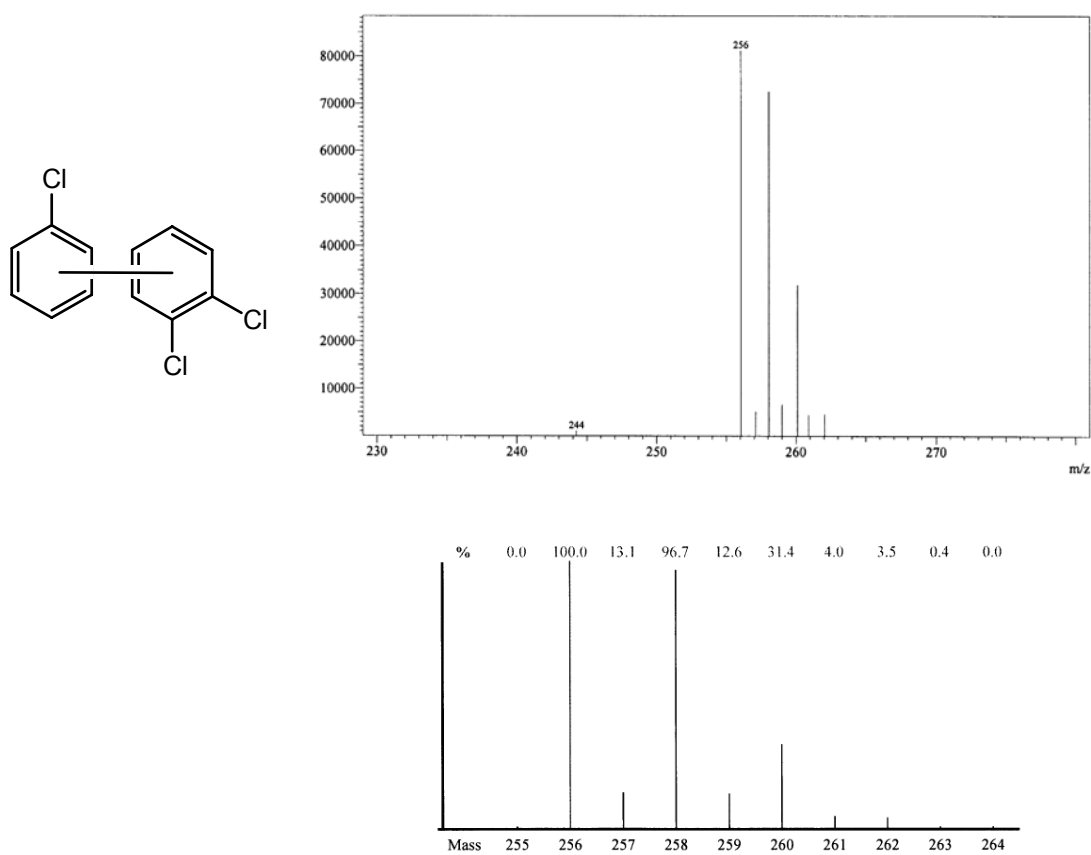
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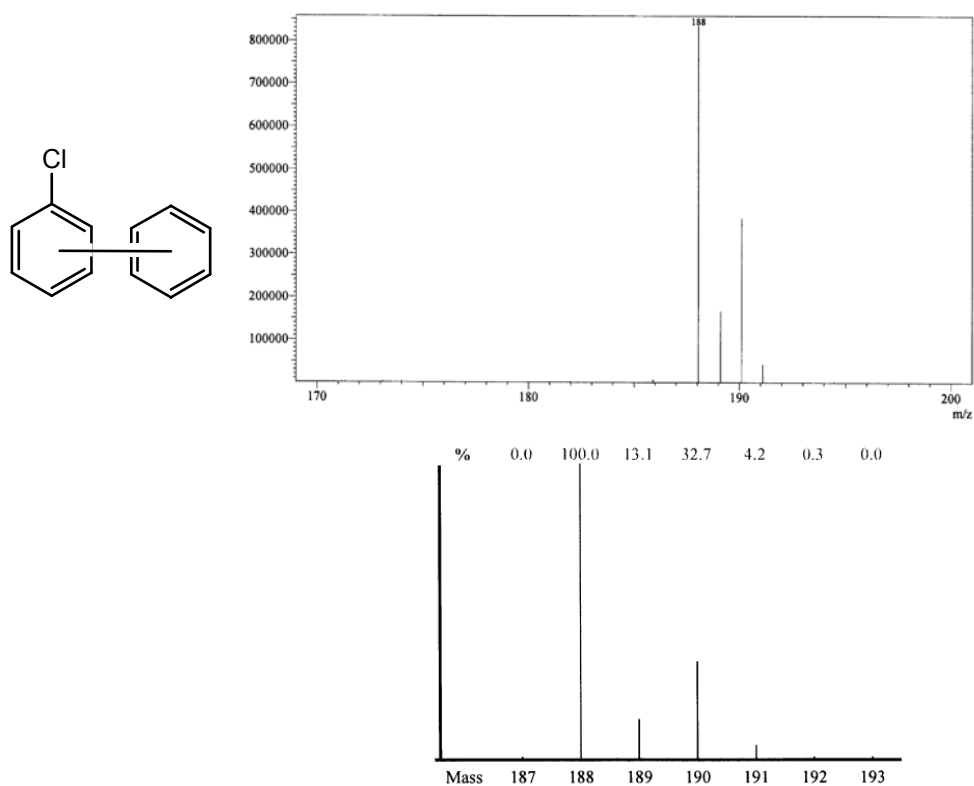
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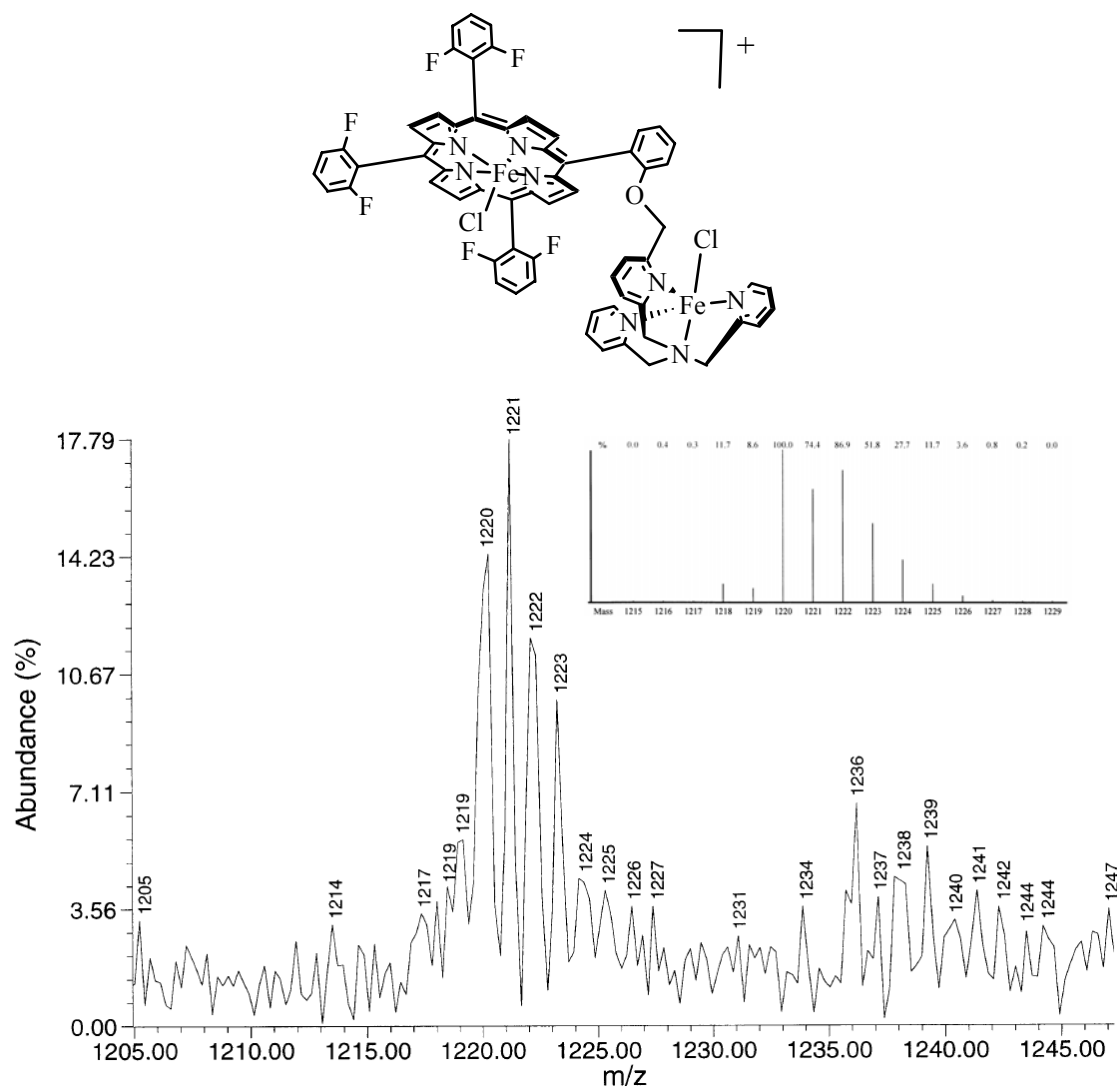
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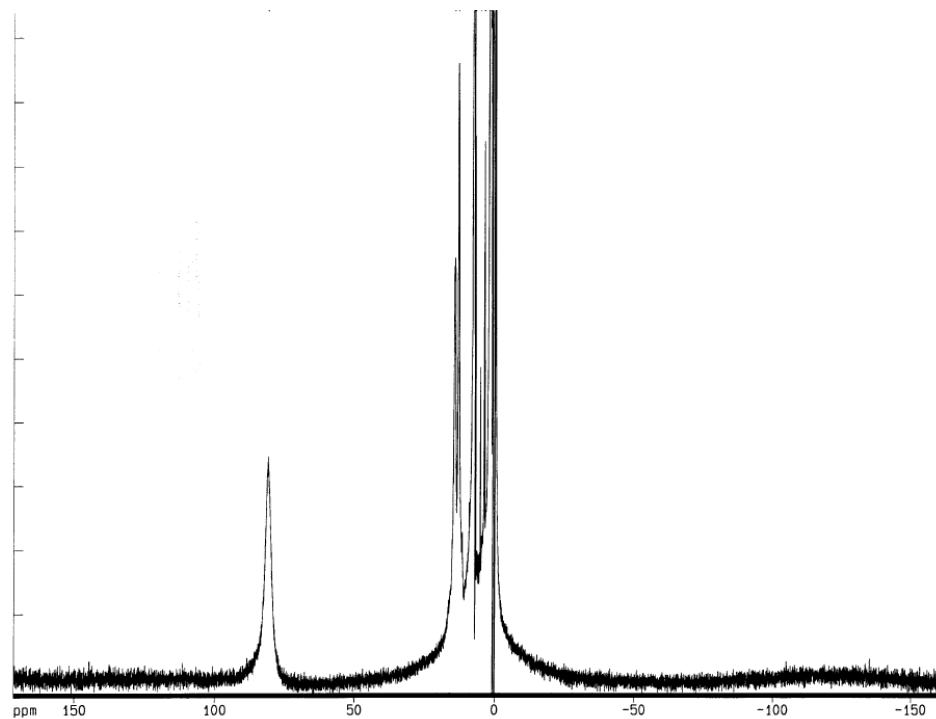
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