

Supporting Information for:

**Determining the Fate of a Non-heme Iron Oxidation Catalyst Under Illumination, Oxygen, and Acid**

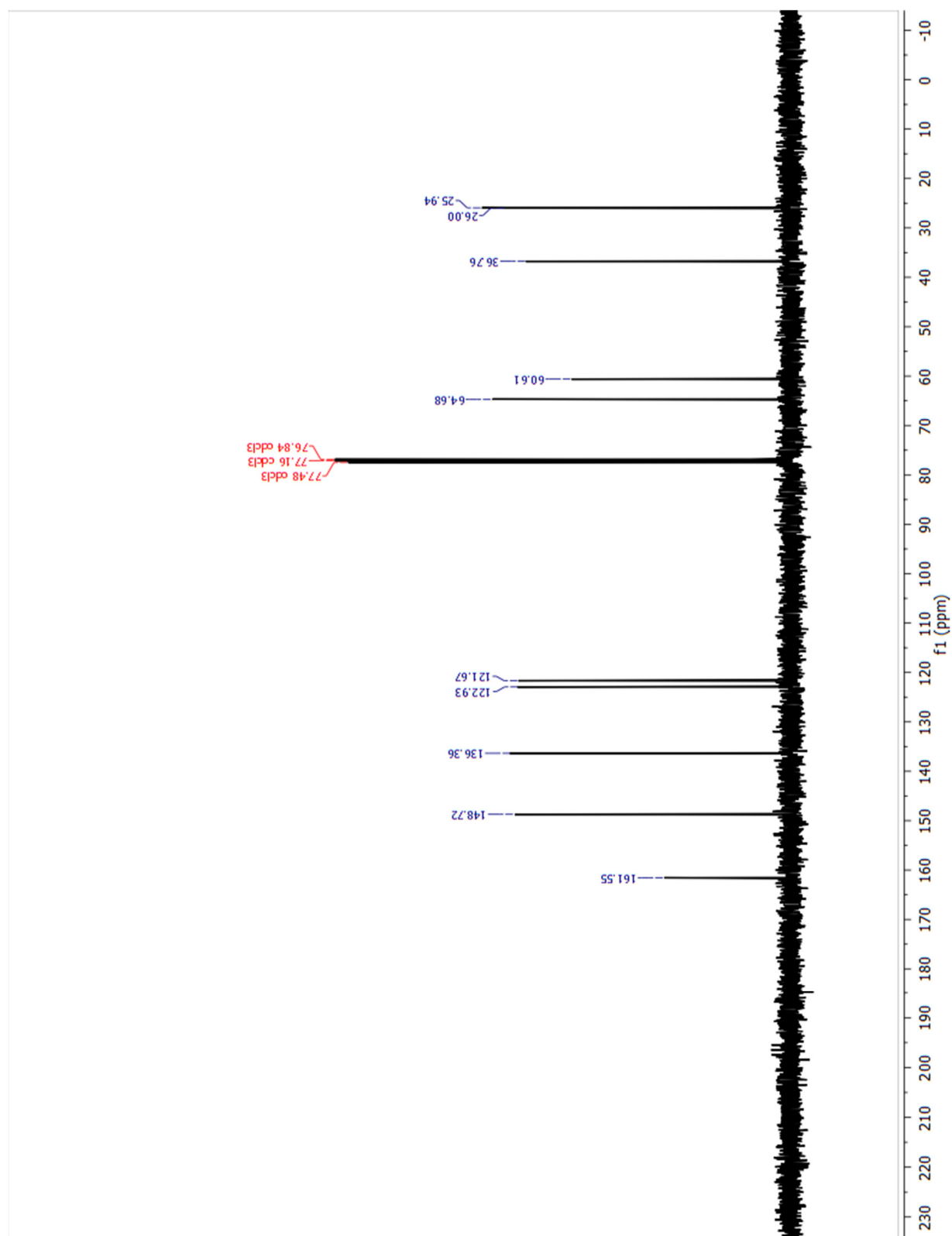
*Samuel L. Esarey, Joel C. Holland, and Bart M. Bartlett\**

Department of Chemistry, University of Michigan, 930 North University Avenue, Ann Arbor, MI 48109, United States

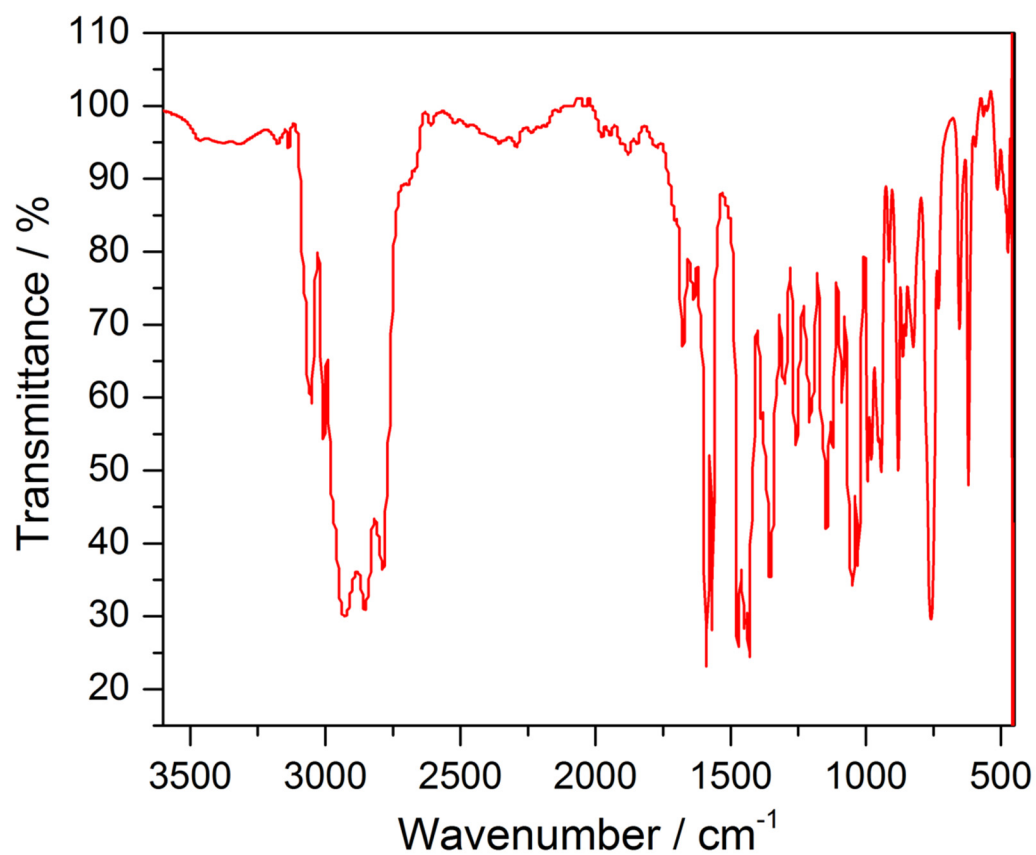
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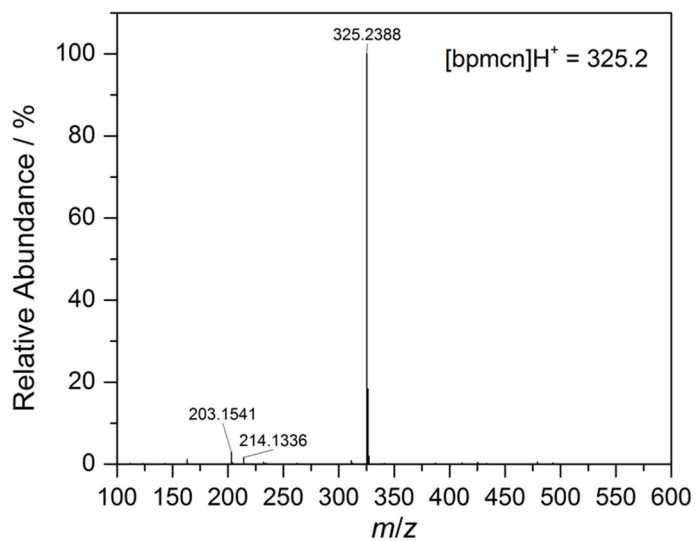
**Figure S1.** <sup>1</sup>H NMR spectrum of bpmcn ligand in CDCl<sub>3</sub>



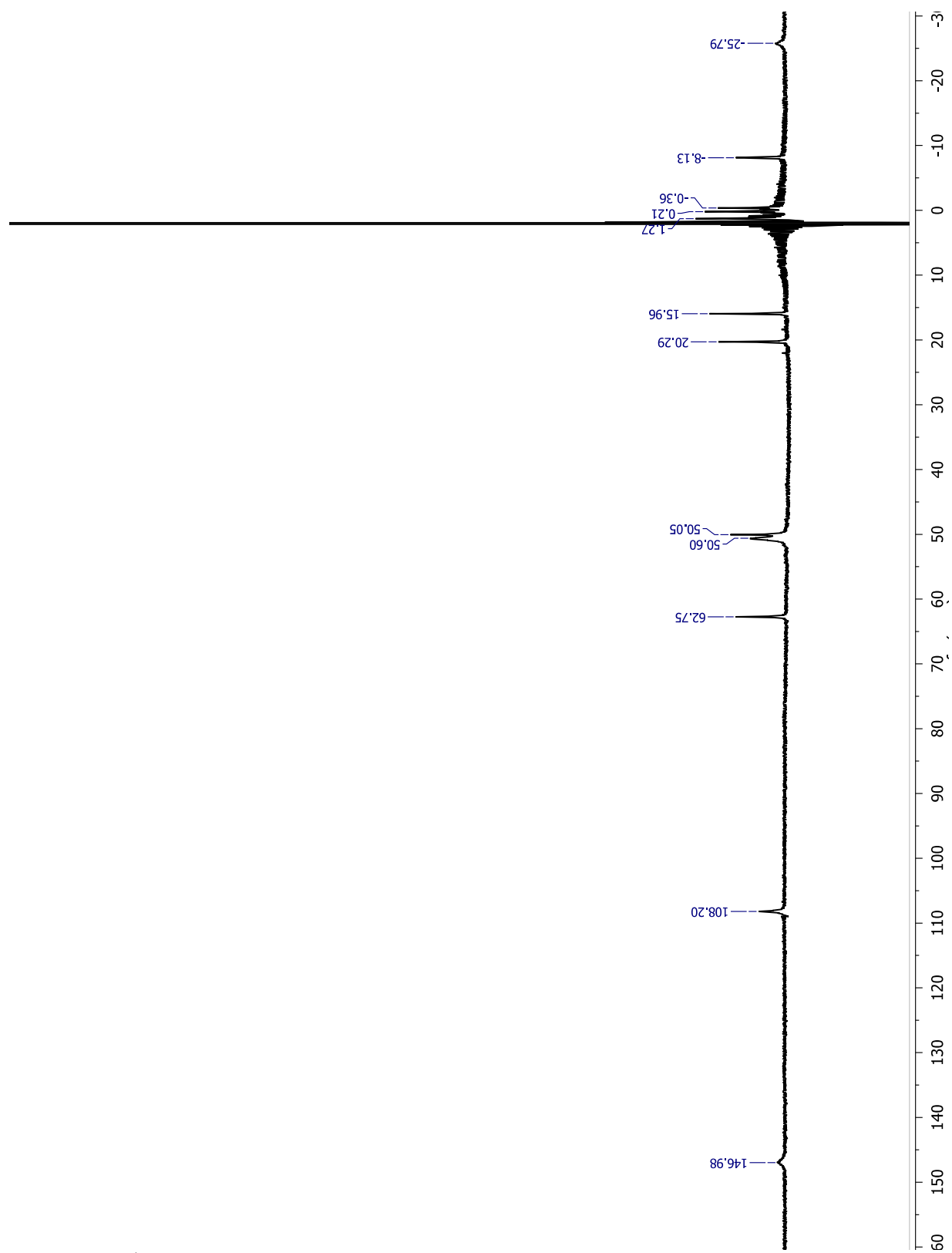
**Figure S2.** <sup>13</sup>C NMR spectrum of bpmcn ligand in CDCl<sub>3</sub>



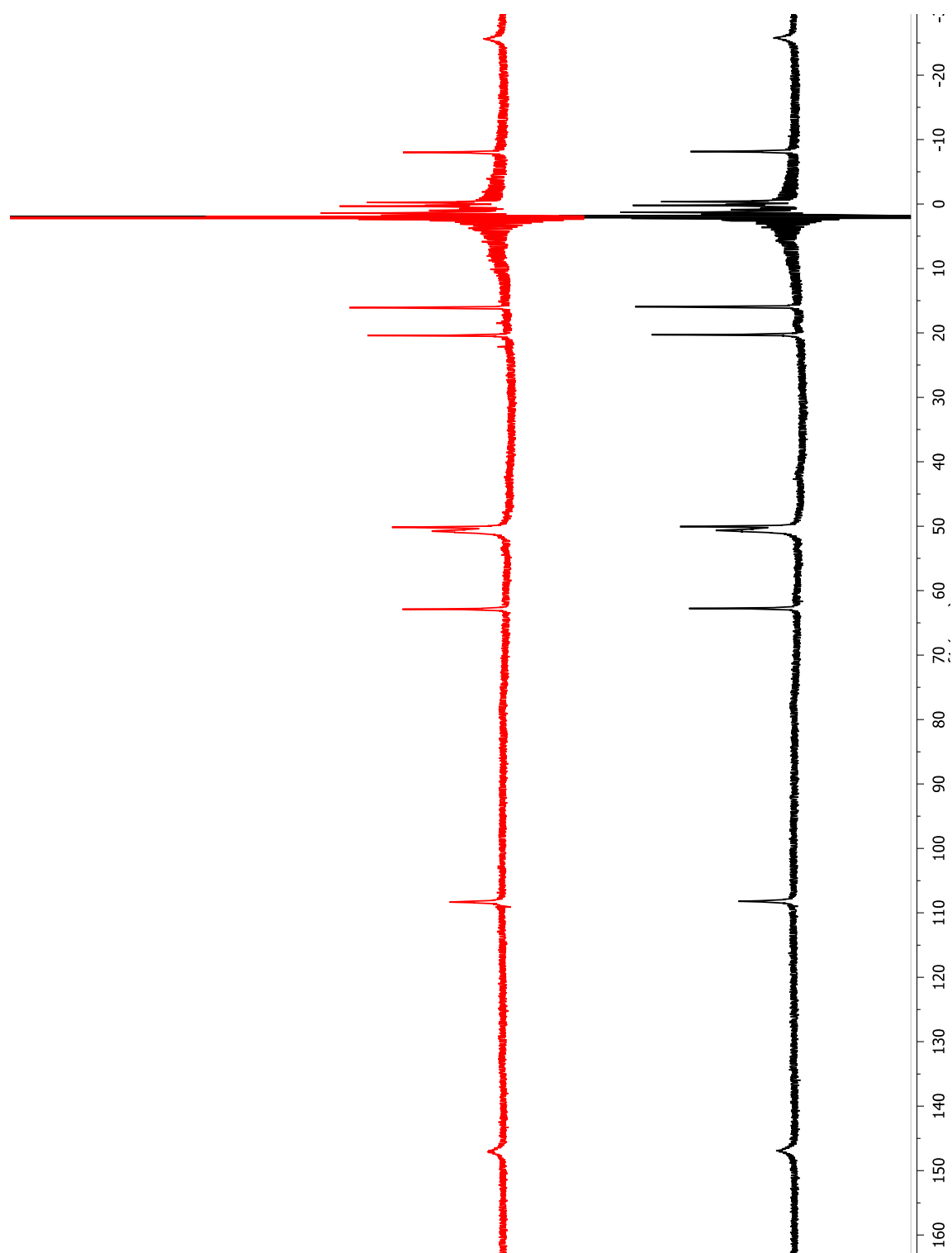
**Figure S3.** FTIR spectrum of the bpmcn ligand



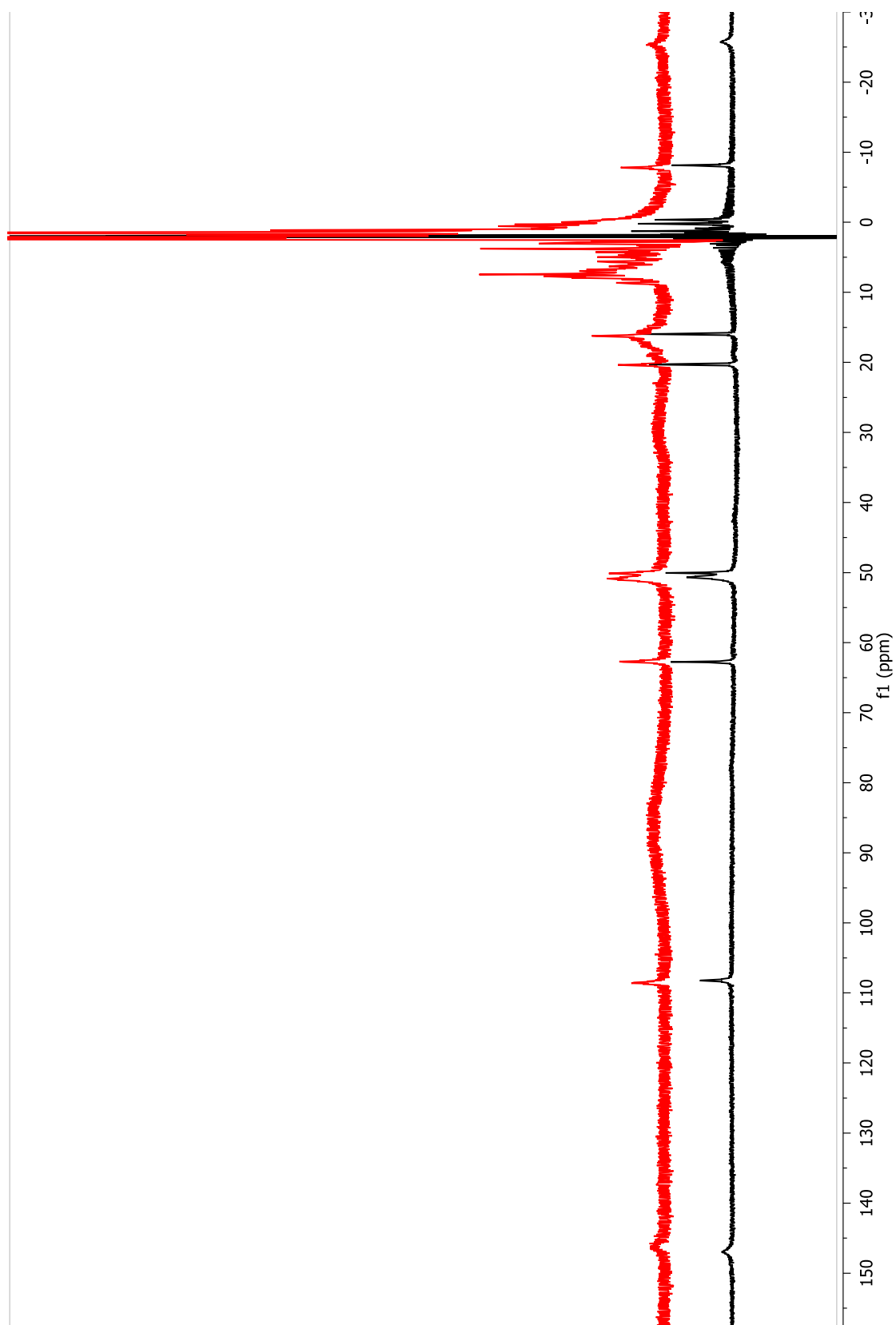
**Figure S4.** ESI-MS(+) spectrum of purified bpmcn ligand



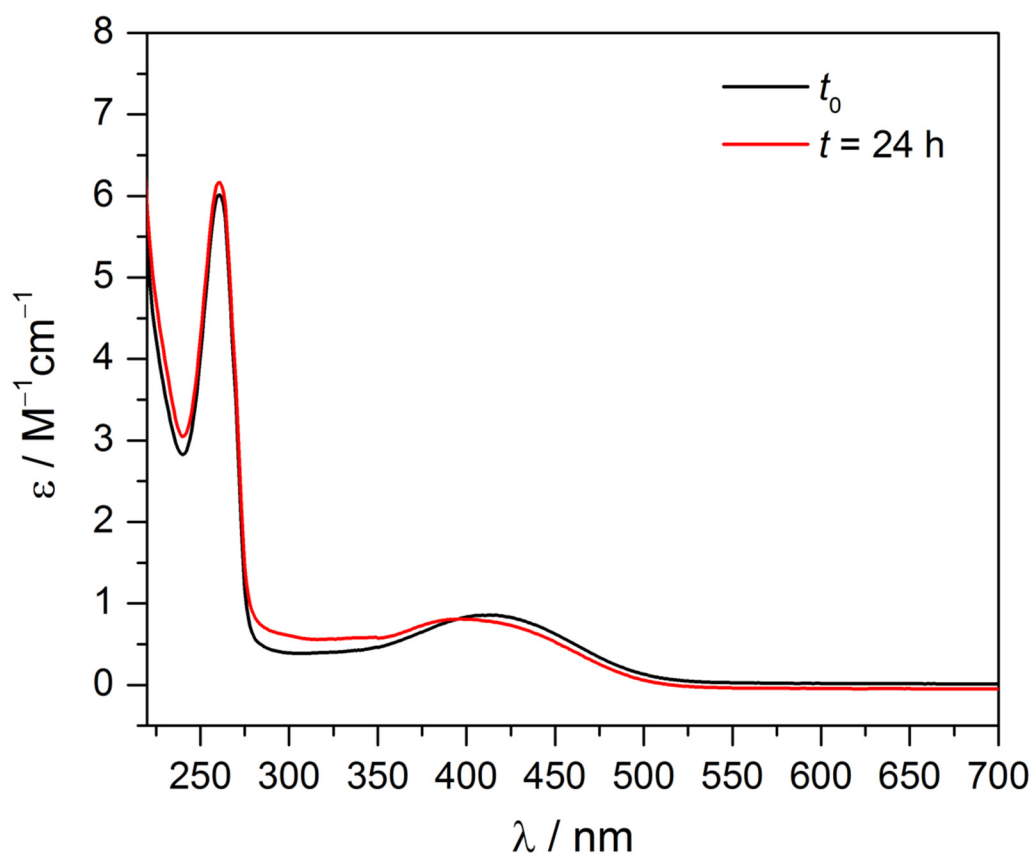
**Figure S5.**  $^1\text{H}$  NMR spectrum of  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  in  $\text{CD}_3\text{CN}$



**Figure S6.**  $^1\text{H}$  NMR spectra of a solution of  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  in dry  $d_3\text{-CD}_3\text{CN}$  under  $\text{N}_2$  (black) in the dark and (red) under 1 sun of illumination for  $t = 24$  hours.

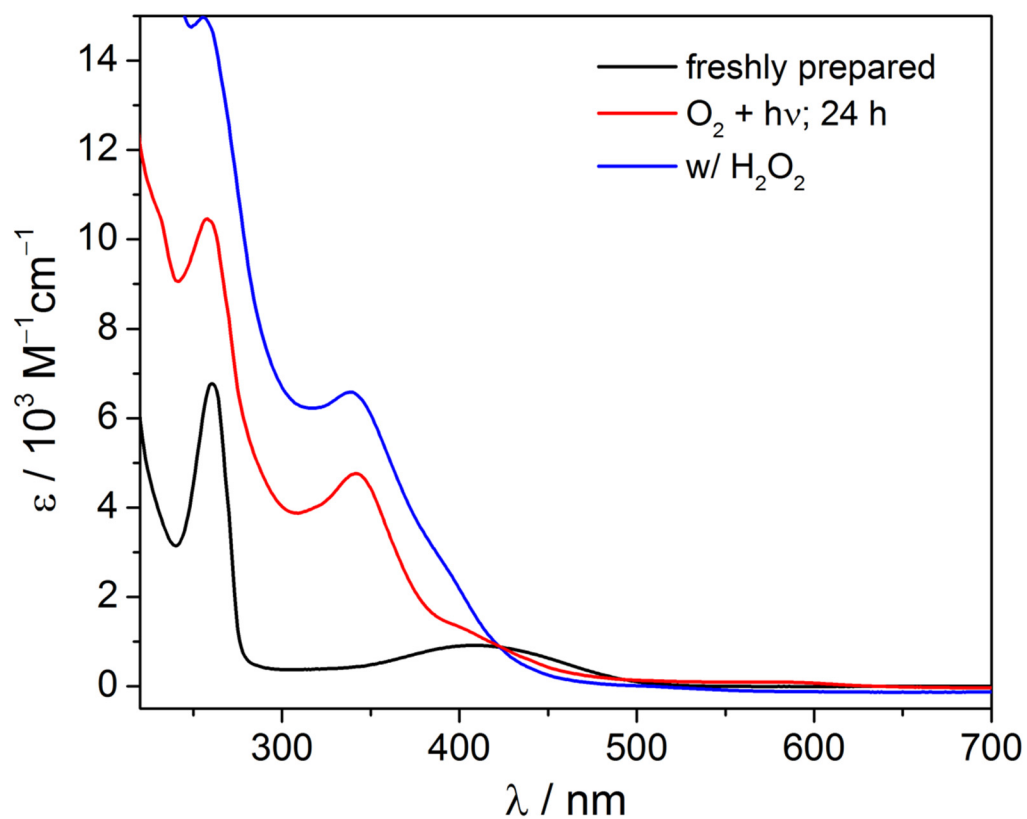


**Figure S7.**  $^1\text{H}$  NMR spectra of  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  (black) in the dark and (red) after exposure of 1 sun illumination under  $\text{O}_2$  for 24 hours in dry acetonitrile.

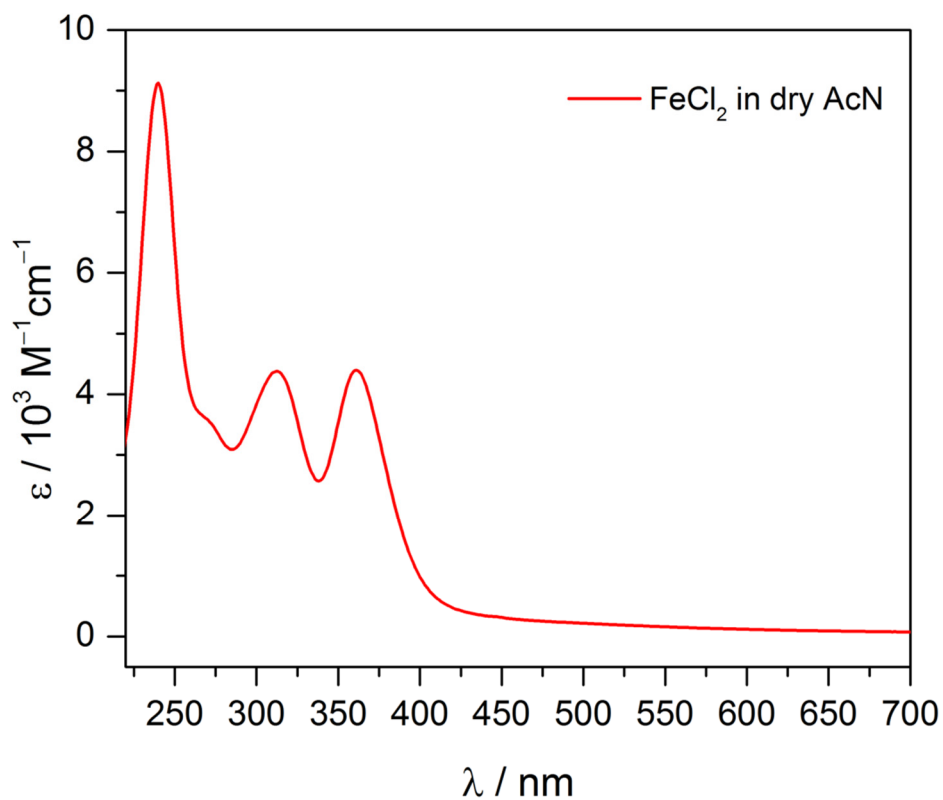


**Figure S8.** UV-Vis spectra of Fe(bpmcn)Cl<sub>2</sub> under O<sub>2</sub> (black) in the dark and (red) under illumination at 1.5 W with a Xe lamp and 550 nm cutoff filter equipped.

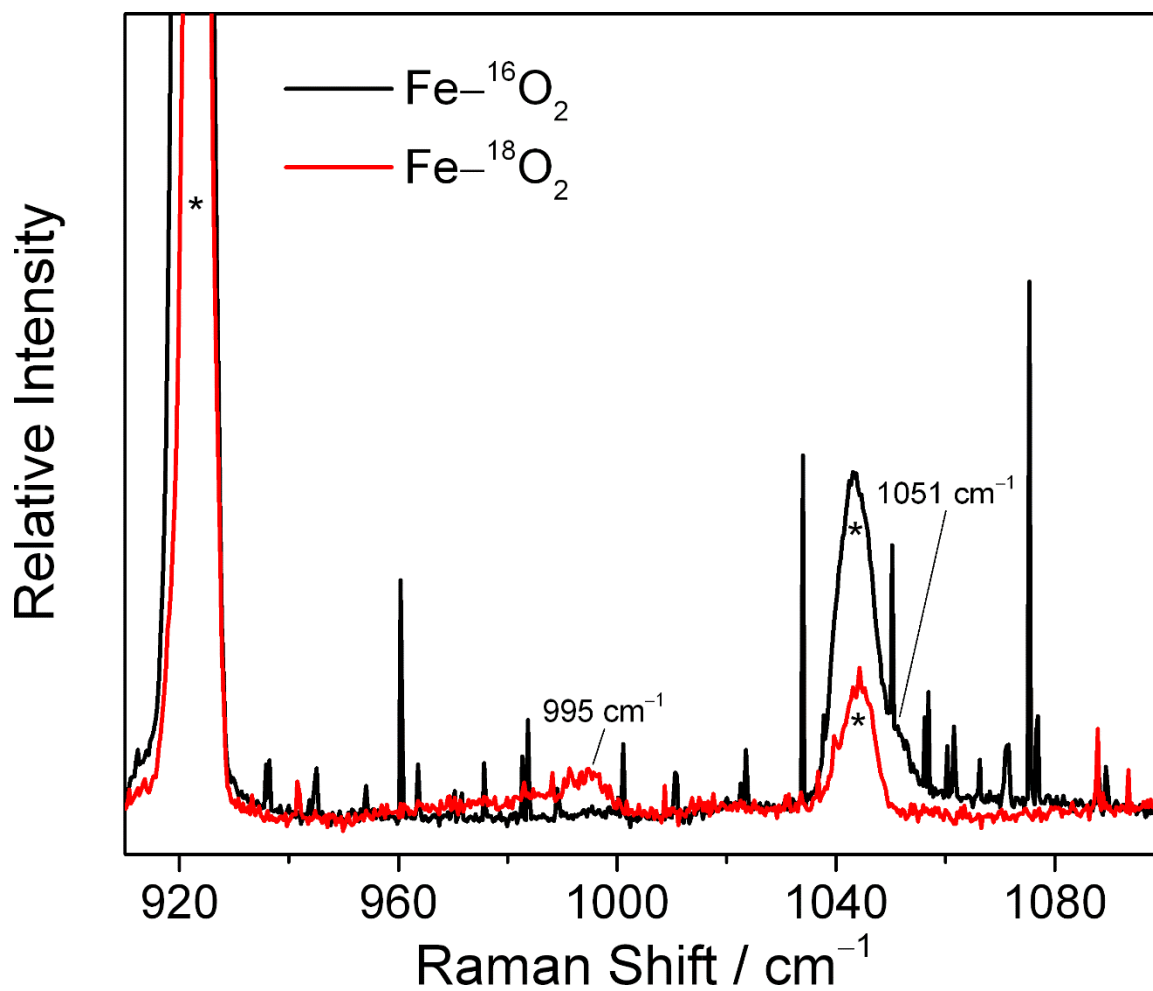




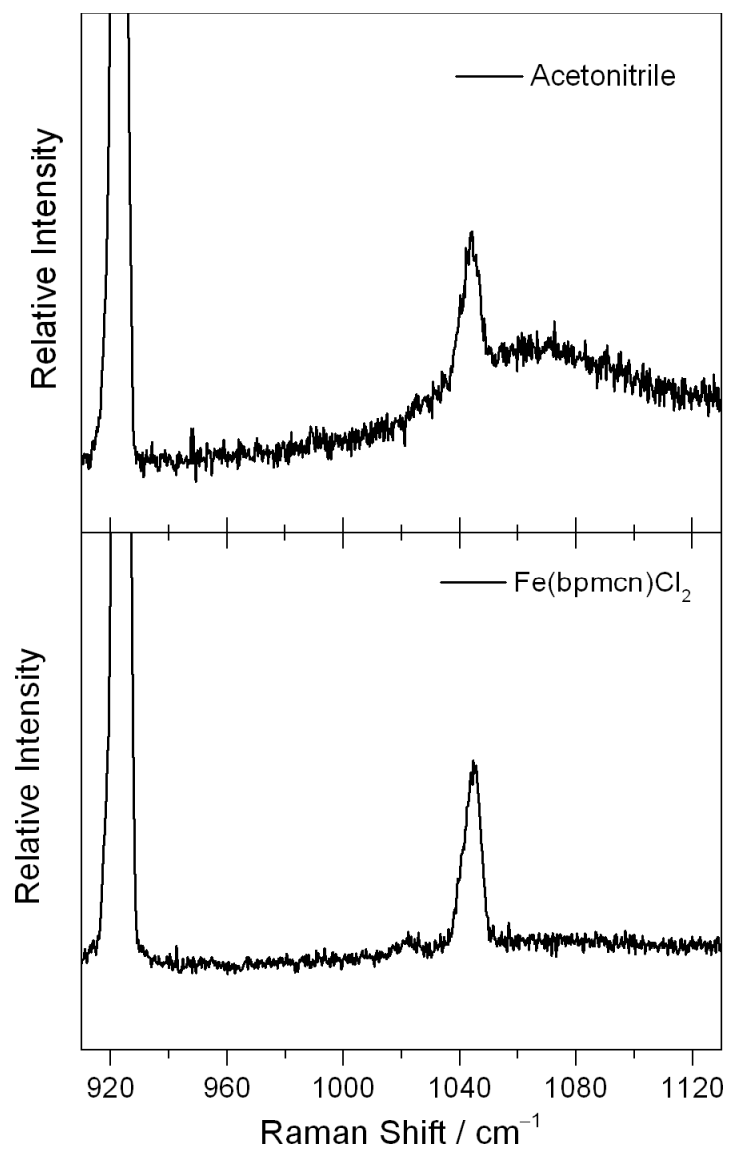
**Figure S9.** UV-Vis spectrum of 0.2mM Fe(bpmcn)Cl<sub>2</sub> (black) prior to and (red) after adding 5  $\mu$ L of 30 wt-wt% H<sub>2</sub>O<sub>2</sub> (added to a 10 mL solution of the iron complex), compared to (blue) 0.2 mM Fe(bpmcn)Cl<sub>2</sub> under 1 sun illumination for 24 hours.



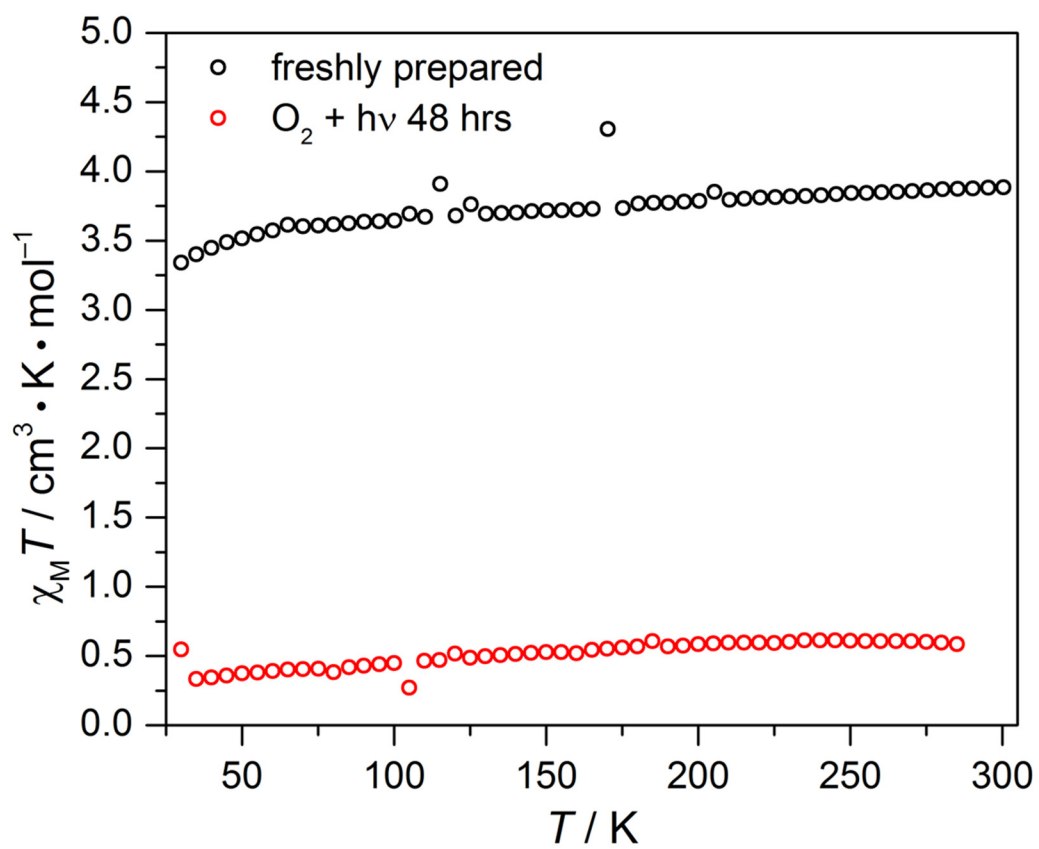
**Figure S10.** UV-Vis spectrum of FeCl<sub>2</sub> in dry acetonitrile under N<sub>2</sub>. In dry acetonitrile, absorption bands appear for FeCl<sub>2</sub> at  $\lambda_{\text{max}} = 240 \text{ nm}$ ,  $\lambda_{\text{max}} = 312 \text{ nm}$ , and  $\lambda_{\text{max}} = 361 \text{ nm}$



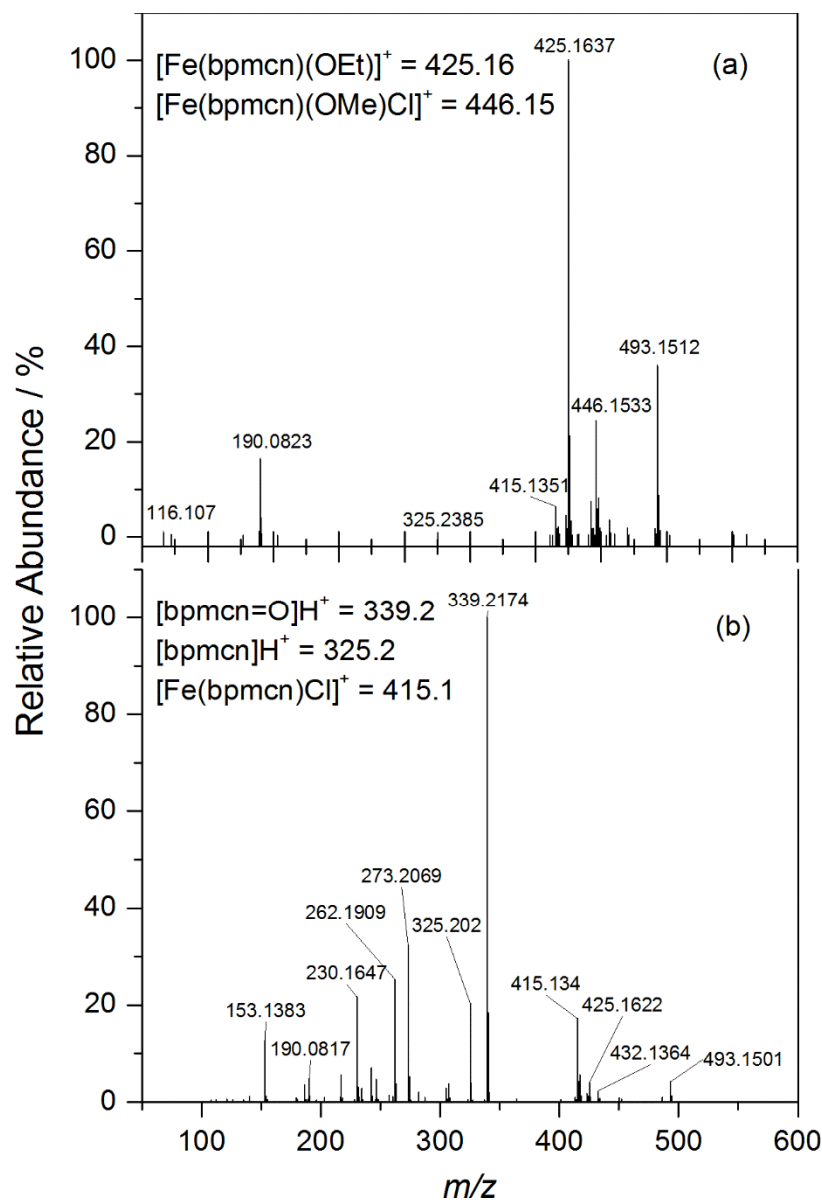
**Figure S11.** Raw resonance Raman spectra of  $\text{Fe-}^{32}\text{O}_2$  (black) and  $\text{Fe-}^{36}\text{O}_2$  (red) in dry acetonitrile, including cosmic rays detected by the detector. Solvent peaks are denoted with an asterisk.



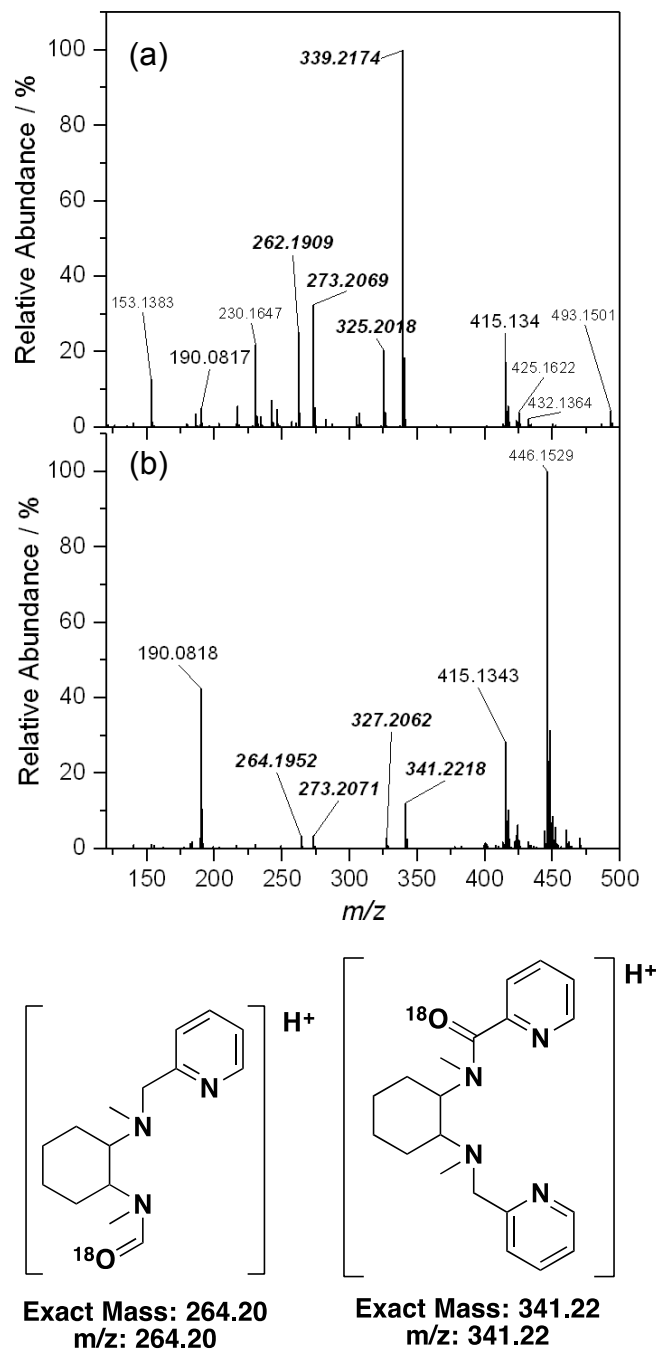
**Figure S12.** Resonance Raman spectra of (a) dry acetonitrile, and (b) Fe(bpmcn)Cl<sub>2</sub> in dry acetonitrile recorded at 77 K with 413 nm laser.



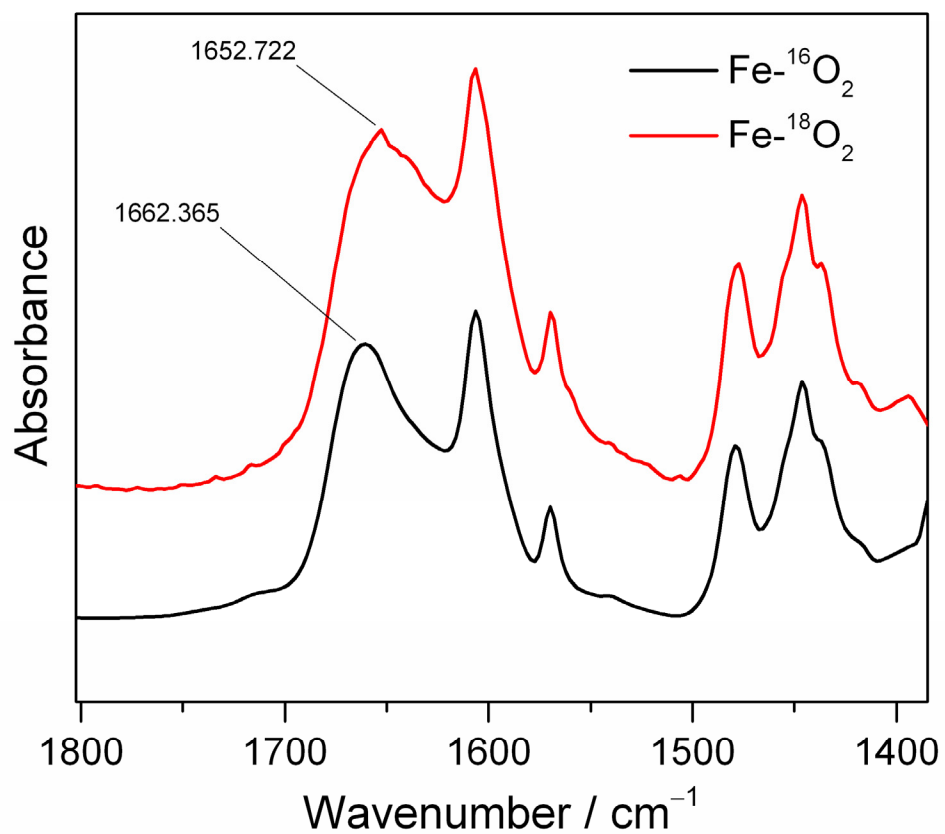
**Figure S13.** Variable-temperature magnetic susceptibility of Fe(bpmcn)Cl<sub>2</sub> (black) pre- and (red) post-exposure to O<sub>2</sub> under 1.5 W of illumination through an AM 1.5G filter.



**Figure S14.** ESI-MS<sup>+</sup> spectra of Fe(bpmcn)Cl<sub>2</sub> (a) prior to and (b) after exposure to 1.5 W illumination with AM 1.5G filter for 48 hours under O<sub>2</sub>.

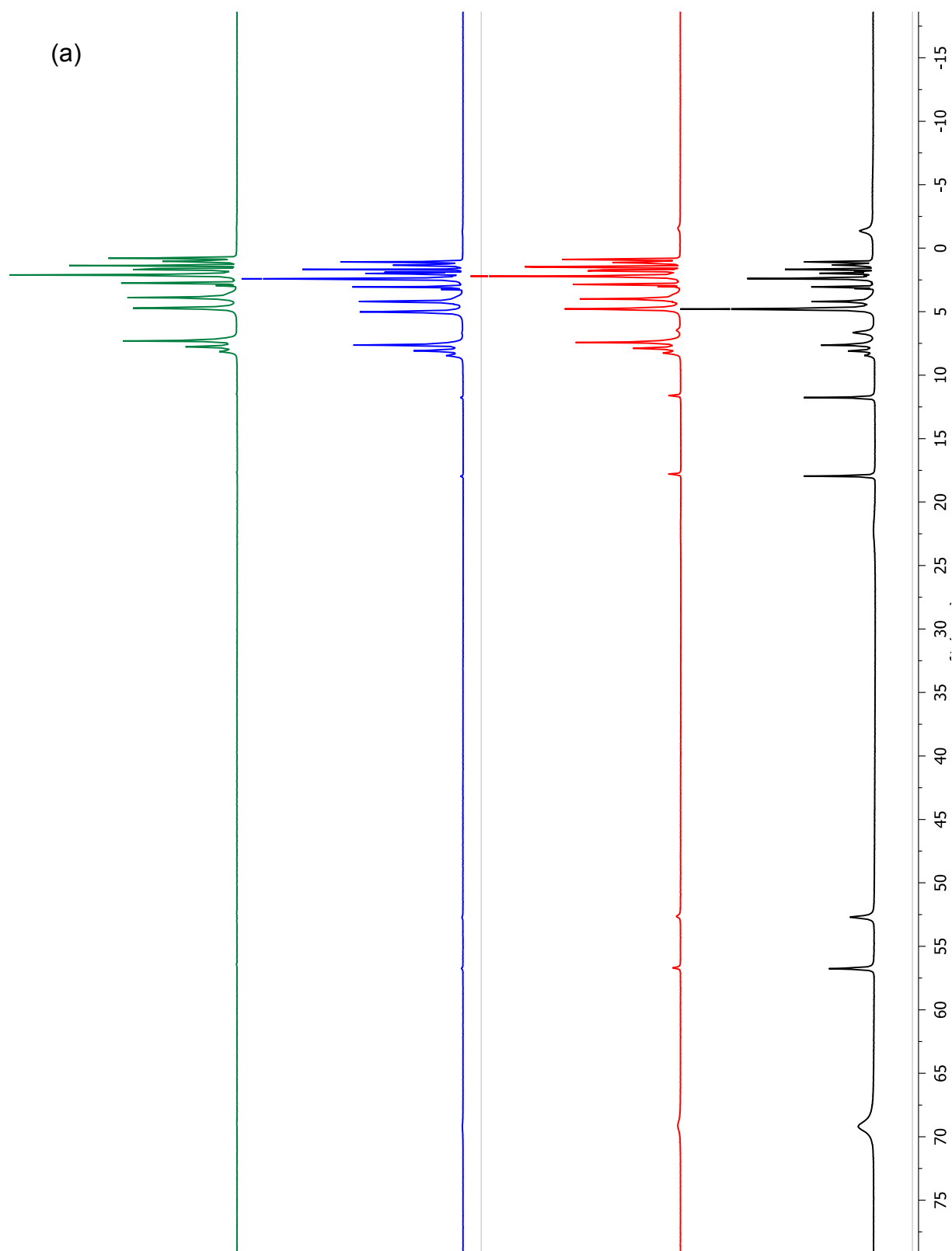


**Figure S15.** ESI-MS<sup>+</sup> spectra of Fe(bpmcn)Cl<sub>2</sub> exposed to 1.5 W illumination with AM 1.5G filter for 48 hours under (a) <sup>32</sup>O<sub>2</sub> or (b) <sup>36</sup>O<sub>2</sub>



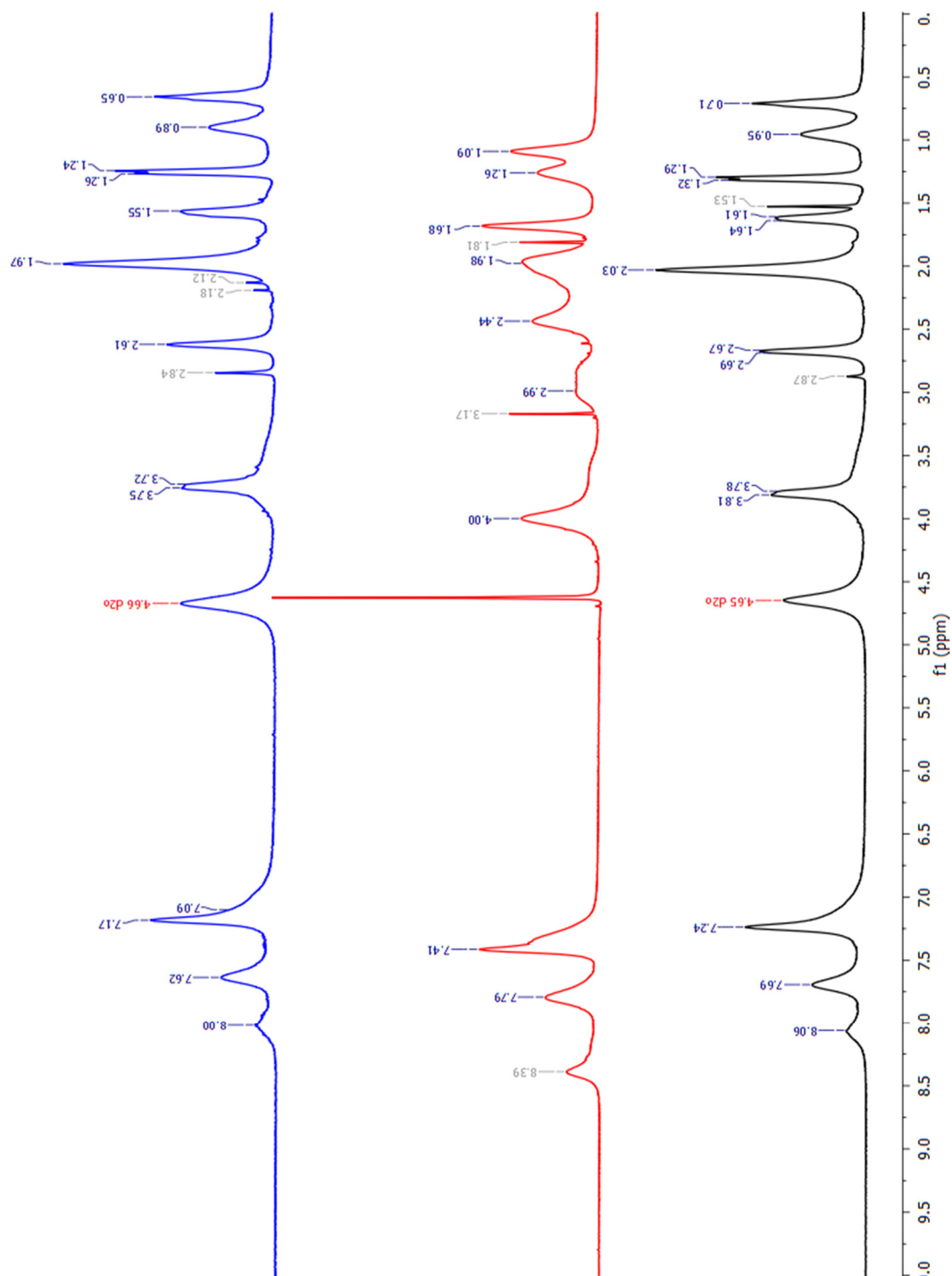
**Figure S16.** FTIR spectra of Fe(bpmcn)Cl<sub>2</sub> after illumination with 1.5W through an AM 1.5G filter in acetonitrile under (black) <sup>32</sup>O<sub>2</sub> and (red) <sup>36</sup>O<sub>2</sub>. Note the region between 1600 – 1700 cm<sup>-1</sup> where an amide bond typically appears in the IR spectrum.



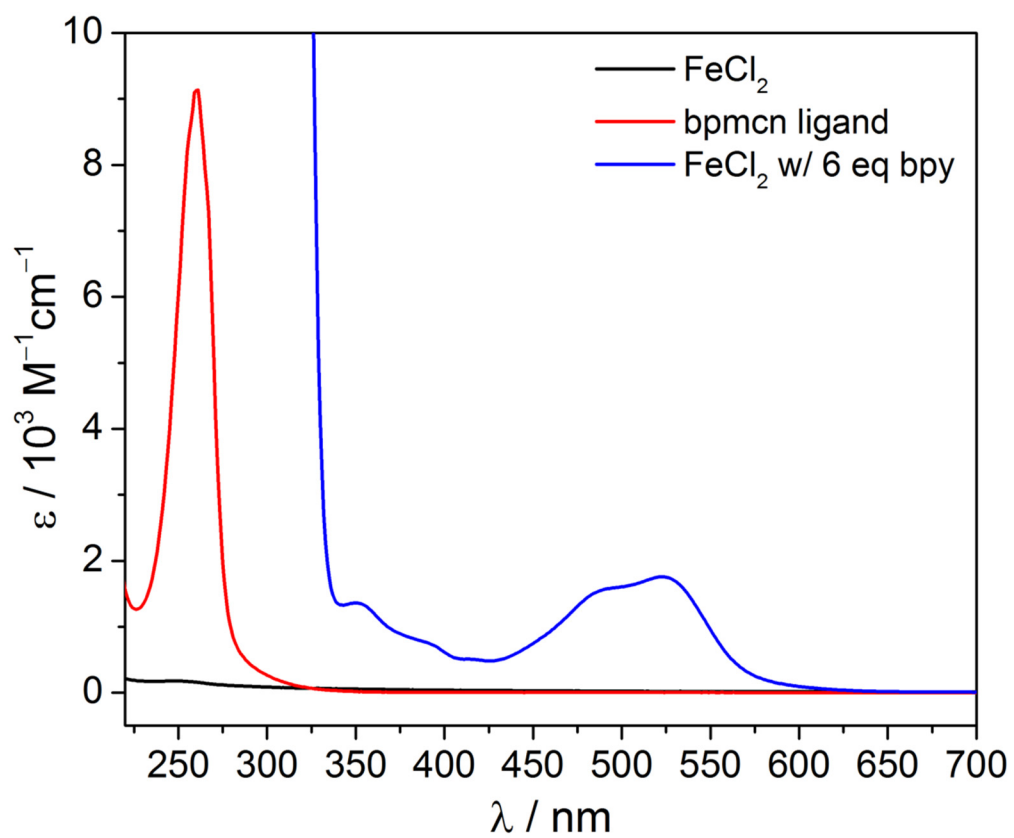


**Figure S17.**  $^1\text{H}$  NMR spectra of a solution of  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  in degassed  $\text{D}_2\text{O}$  with 0.1 M  $d$ -TFA (pH = 1) in the dark for  $t=0$  minutes (black), 2 hours (red), 4 hours (blue), and 8 hours (green).

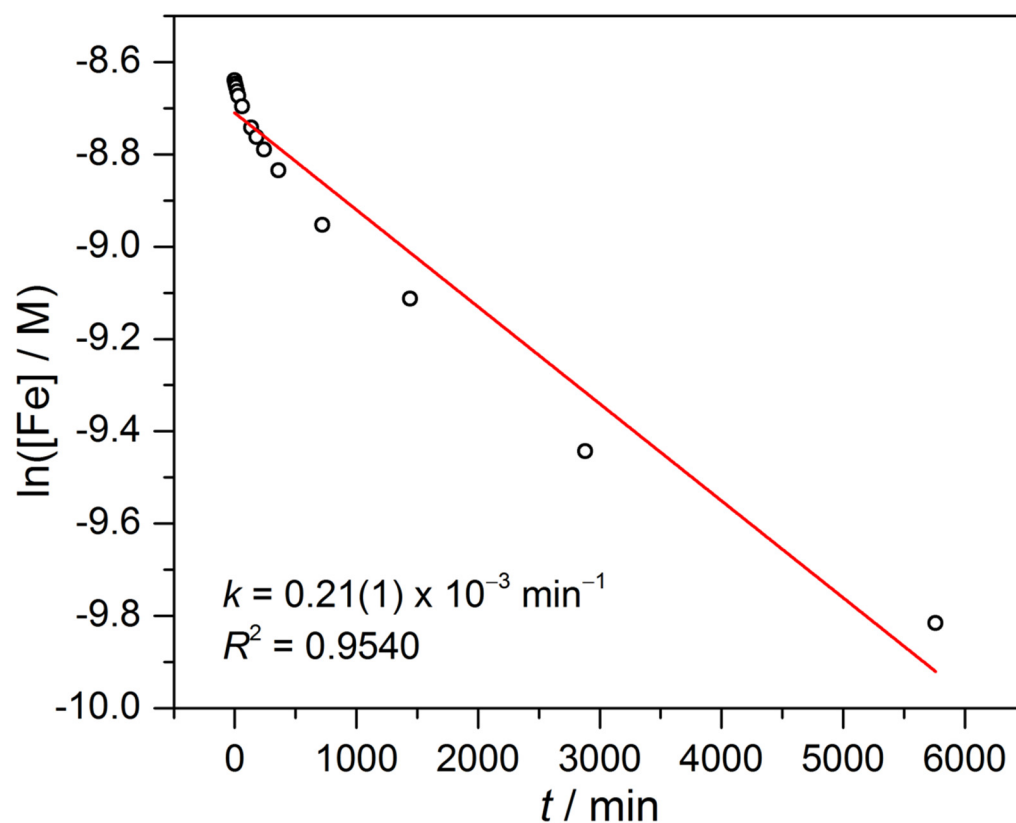
(b)



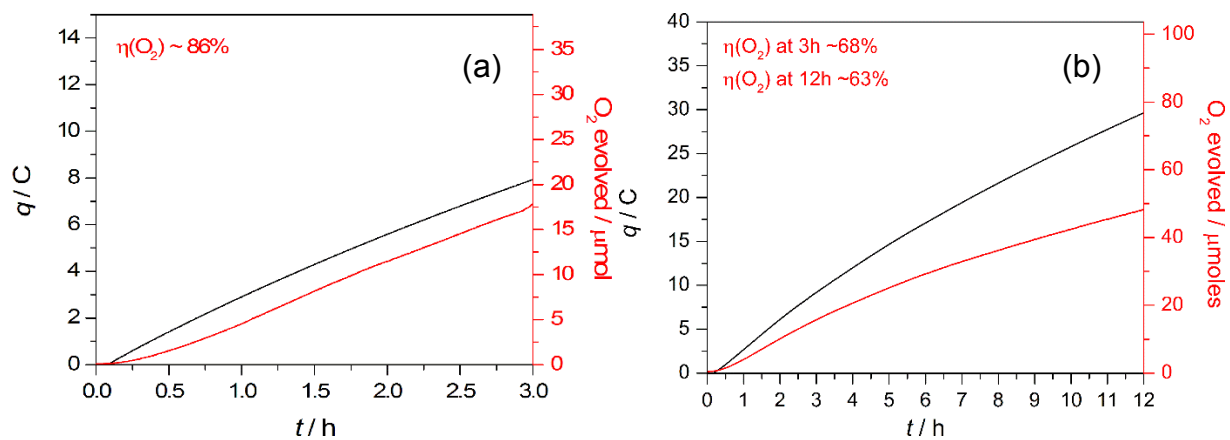
**Figure S18**  $^1\text{H}$  NMR spectra of (black)  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  in 0.1 M  $d\text{-TFA}$  for 8 hours, (red) free bpmcn in 0.1M  $d\text{-TFA}$ , and (blue)  $\text{FeCl}_2 + \text{bpmcn}$  in 0.1M  $d\text{-TFA}$ .



**Figure S19.** UV-Vis spectrum of (black)  $\text{FeCl}_2(\text{aq})$ , (red) bpmcn ligand, and (blue)  $\text{FeCl}_2$  with 6 equivalents of 2,2' bpy in TfOH at pH 1 under  $\text{N}_2$ .



**Figure S20.**  $\ln([\text{Fe}])$  vs time of the  $\lambda_{\text{max}} = 364 \text{ nm}$  absorption of  $\text{Fe}(\text{bpmcn})\text{Cl}_2$  ( $\text{Fe}$ ) in pH 3 TfOH under  $\text{N}_2$  over 4 days. Linear fitting:  $\ln([\text{Fe}]) = -0.00021t - 8.709$ ;  $R^2 = 0.9540$ . The data deviate significantly from first-order kinetics after 1 h.



**Figure S21.** OER data collected of an Fe|WO<sub>3</sub> electrode in 100 mM NaSO<sub>4</sub> pH 3 during bulk electrolysis held at 1.23 V vs RHE, SCE RE, Pt CE for 12 hours with charged passed (black) and oxygen evolved (red). Reproduced with permission from ref. 19. Copyright 2014 American Chemical Society.