

Supporting Information for

Ferrous Carbonyl Dithiolates as Precursors to FeFe-, FeCo-, and FeMn-Dithiolates

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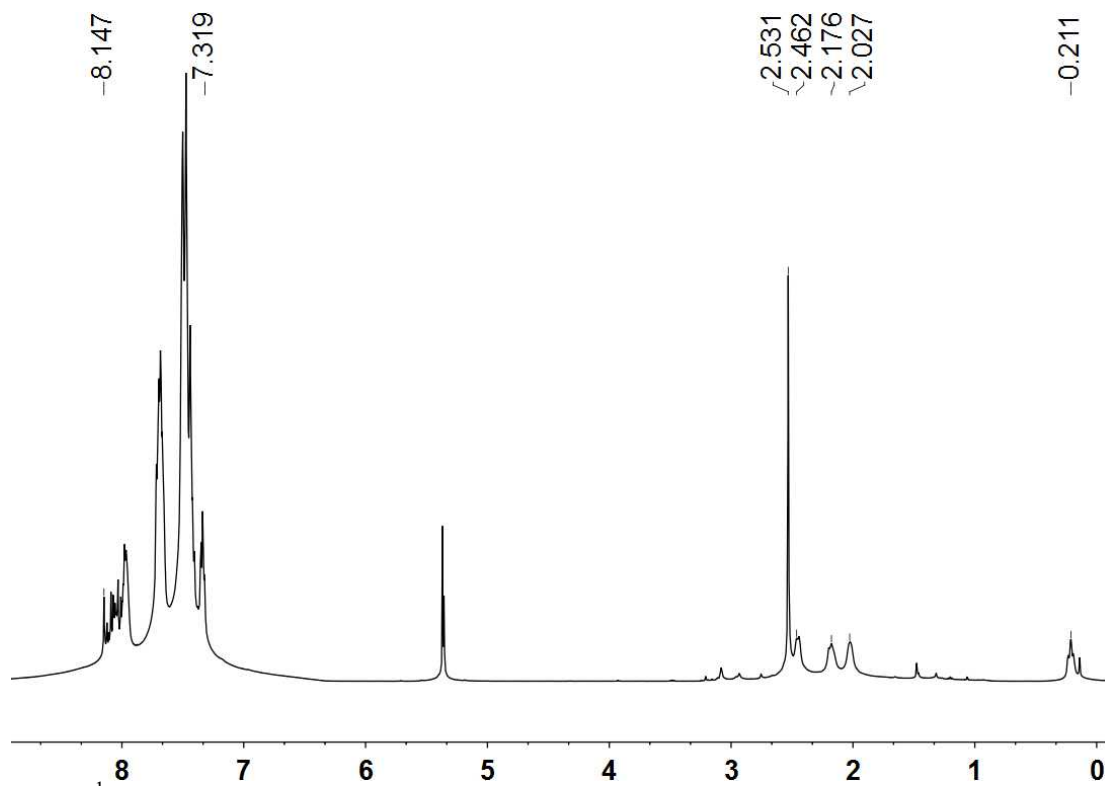


Figure S1. ¹H NMR spectrum (500 MHz) of Fe(edt)(CO)₂(dppv) (**1a**) in CD₂Cl₂ solution.

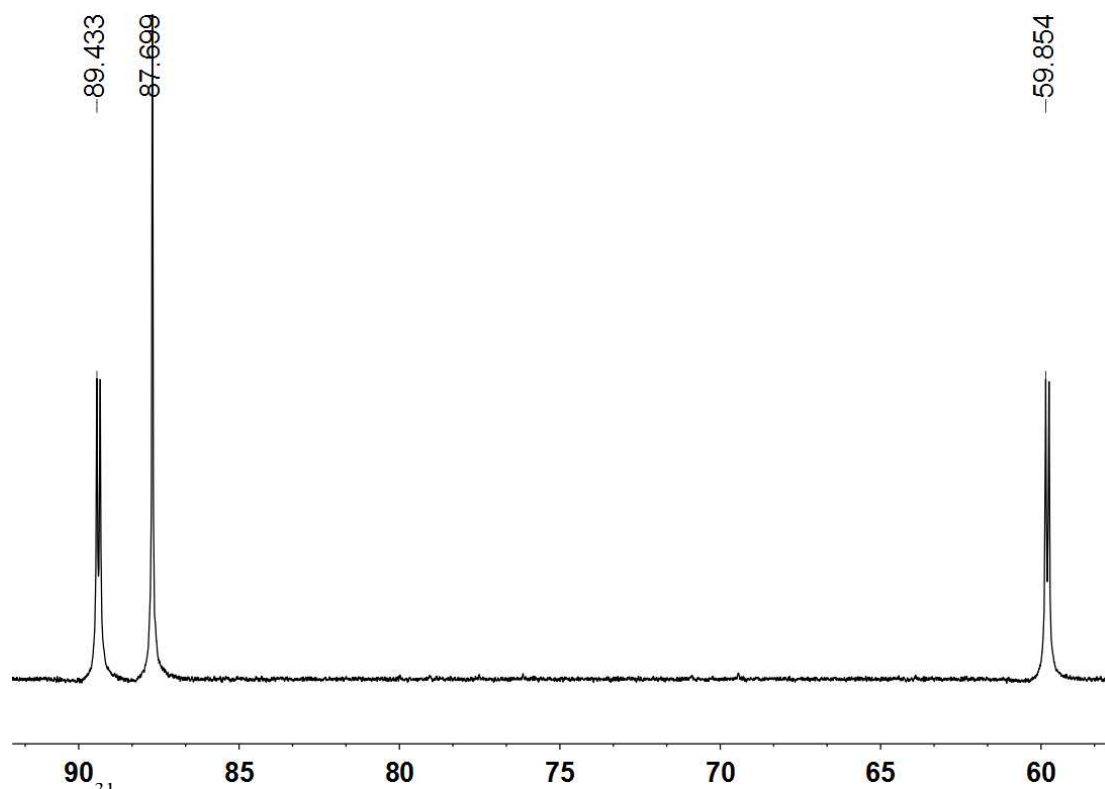


Figure S2. ³¹P NMR spectrum (202 MHz) of Fe(edt)(CO)₂(dppv) (**1a**) in CD₂Cl₂ solution.

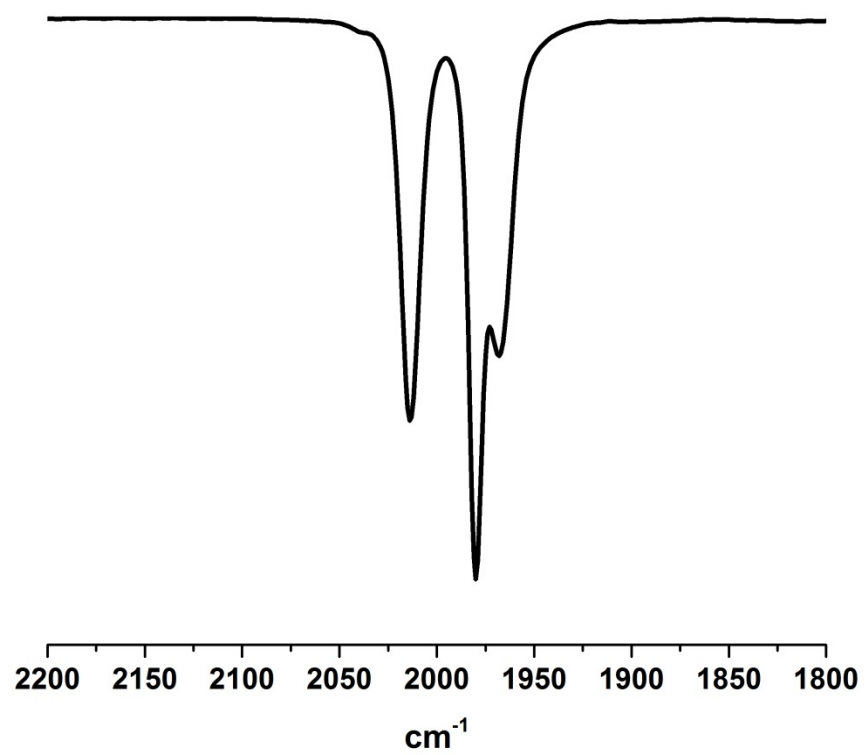


Figure S3. IR spectrum of $\text{Fe}(\text{edt})(\text{CO})_2(\text{dppv})$ (**1a**) in THF solution.

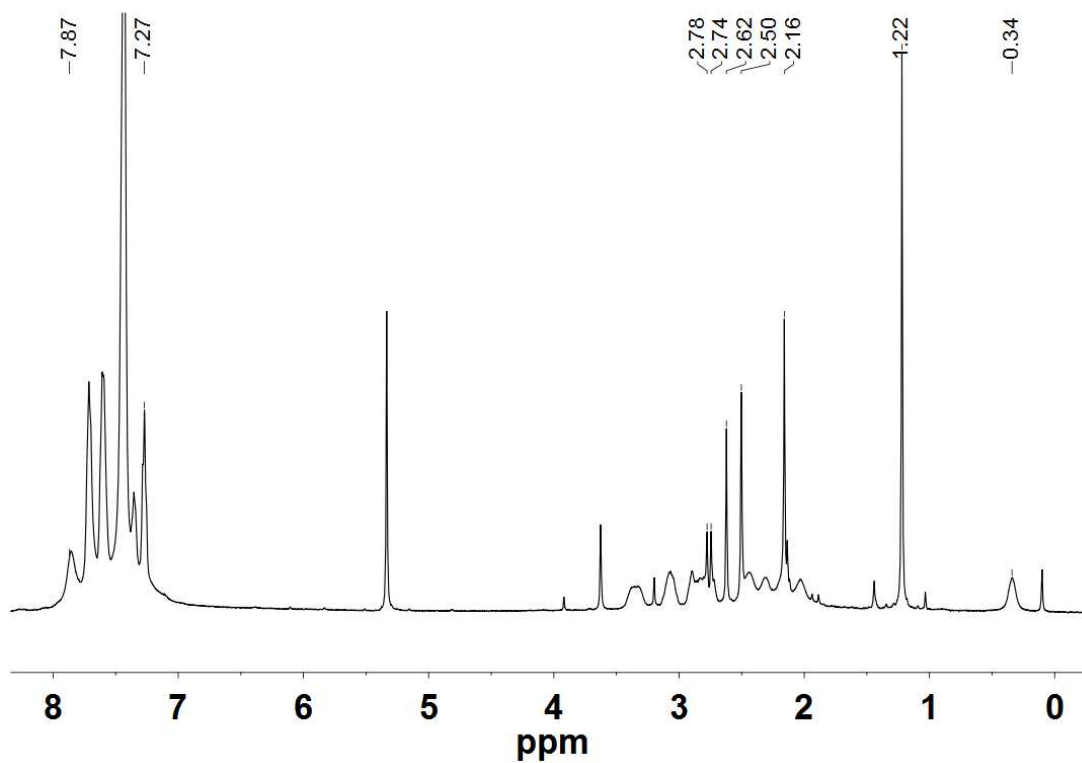


Figure S4. ^1H NMR spectrum (500 MHz) of $\text{Fe}(\text{edt})(\text{CO})_2(\text{dppe})$ (**1b**) in CD_2Cl_2 solution.

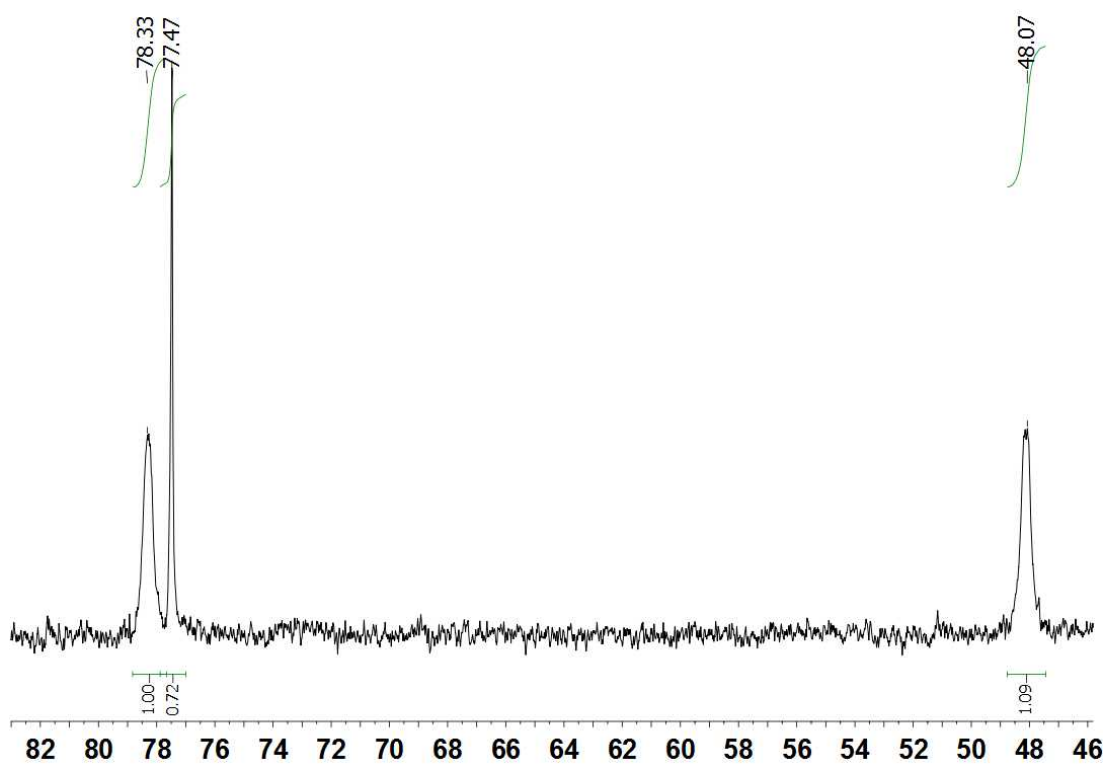


Figure S5. ^{31}P NMR spectrum (202 MHz) of $\text{Fe}(\text{edt})(\text{CO})_2(\text{dppe})$ (**1b**) in CD_2Cl_2 solution.

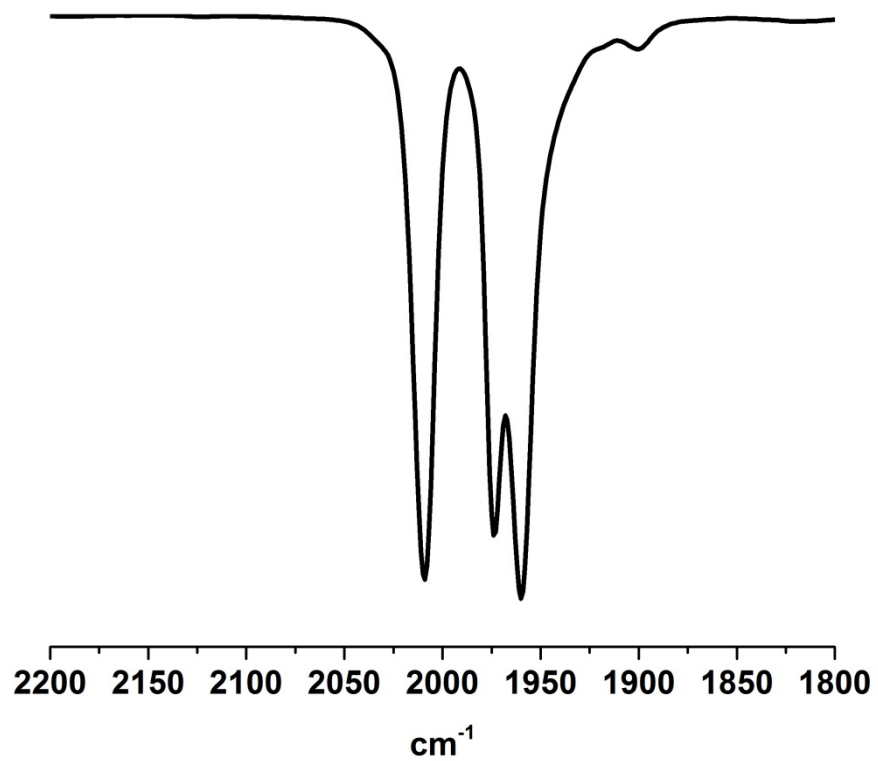


Figure S6. IR spectrum of Fe(edt)(CO)₂(dppe) (**1b**) in THF solution.

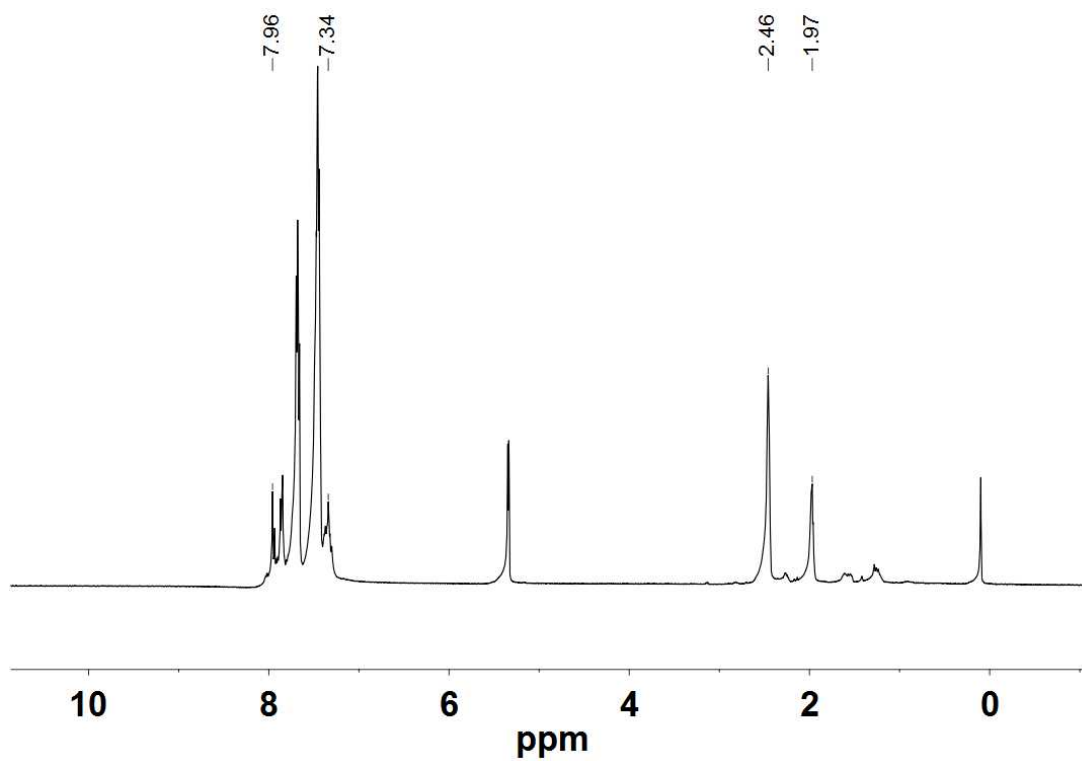


Figure S7. ^1H NMR spectrum (500 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ (**1c**) in CD_2Cl_2 solution.

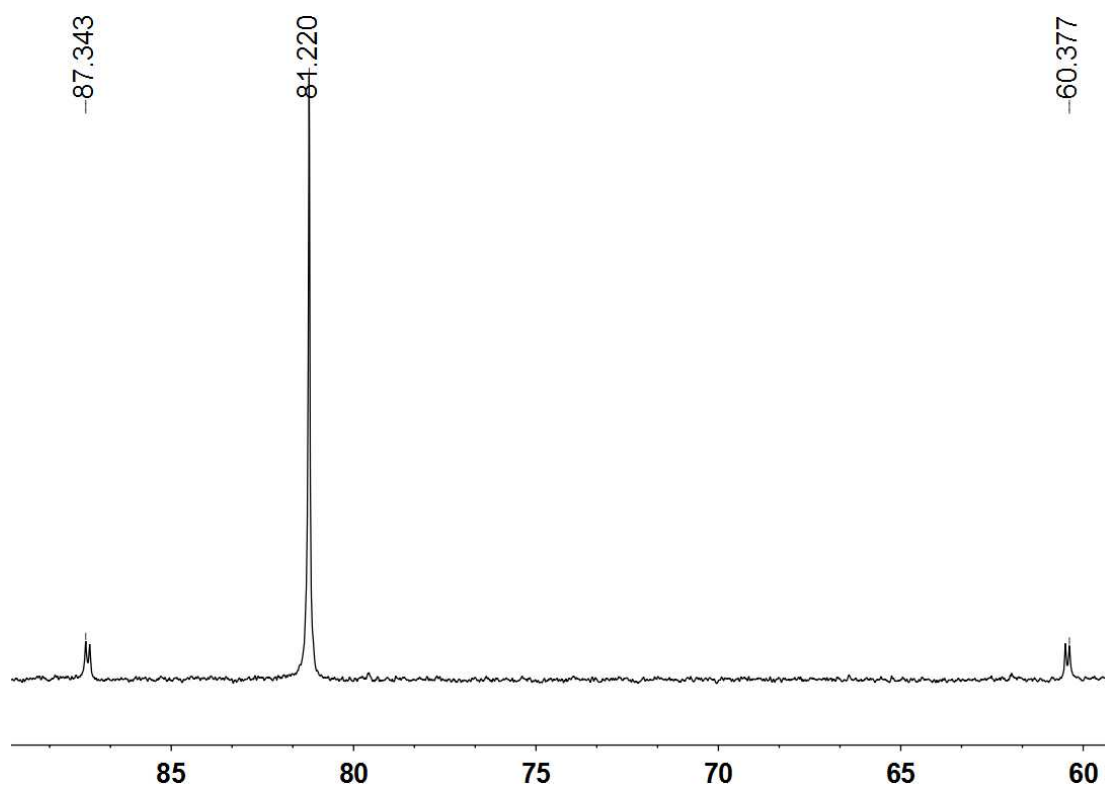


Figure S8. ^{31}P NMR spectrum (202 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ (**1c**) in CD_2Cl_2 solution.

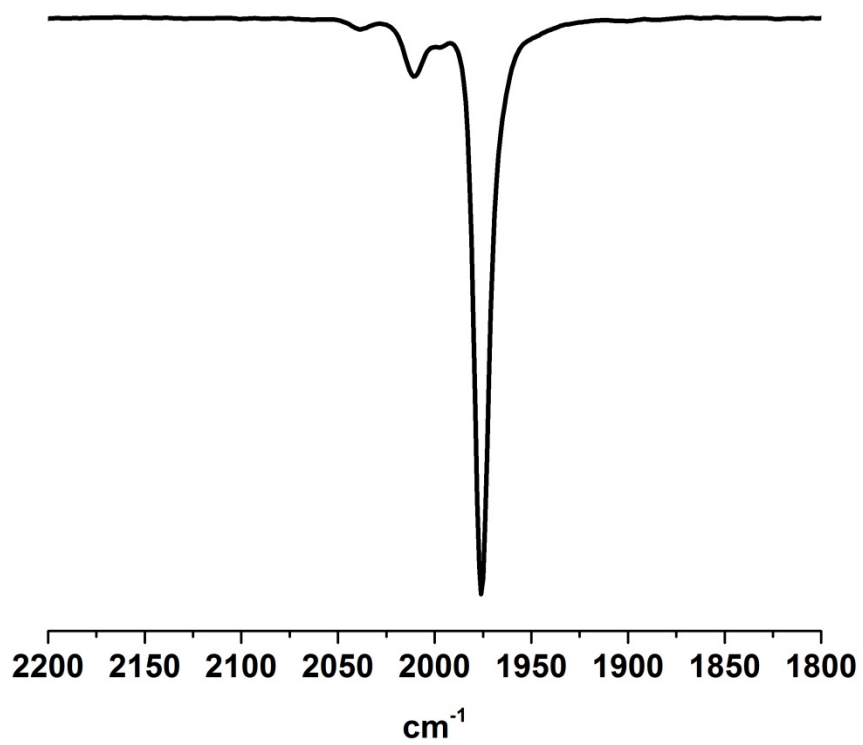


Figure S9. IR spectrum of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ (**1c**) in THF solution.

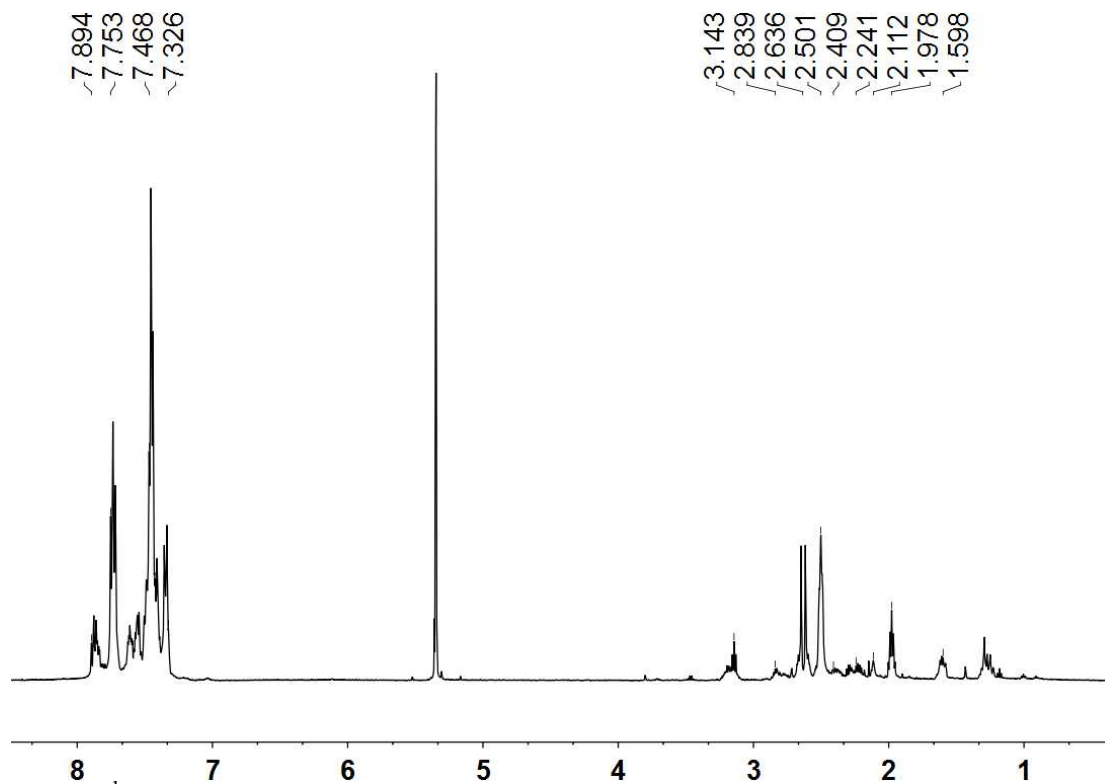


Figure S10. ^1H NMR spectrum (500 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (**1d**) in CD_2Cl_2 solution.

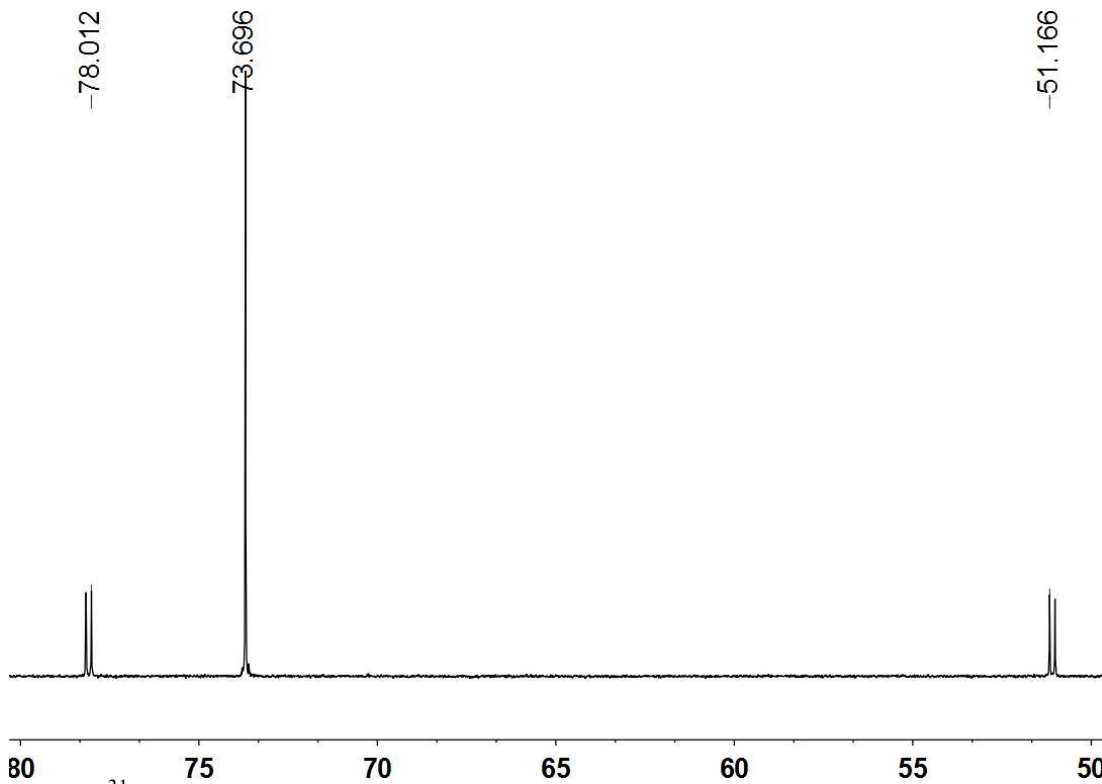


Figure S11. ^{31}P NMR spectrum (202 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (**1d**) in CD_2Cl_2 solution.

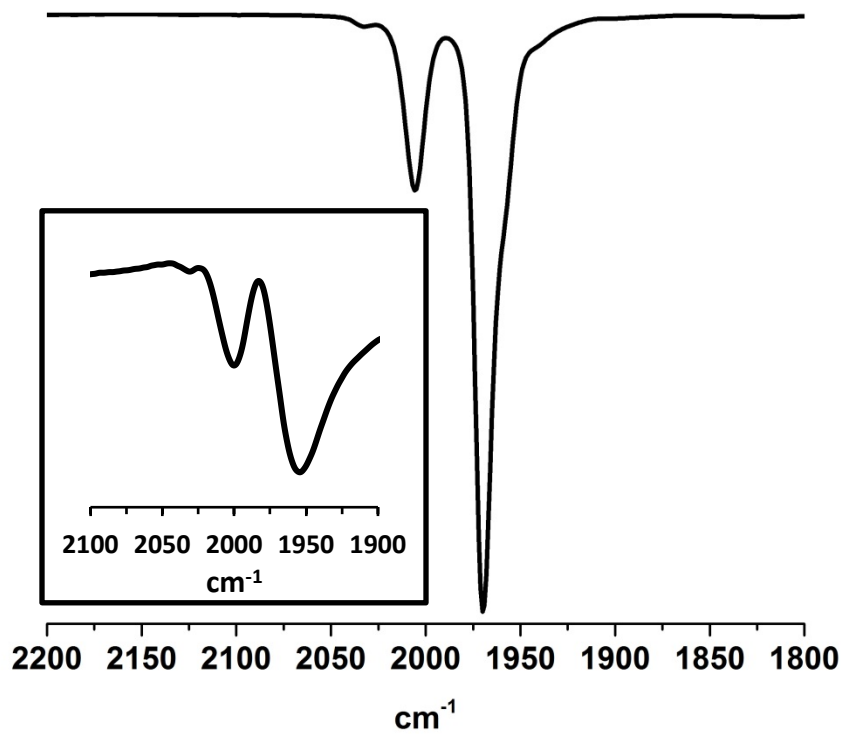


Figure S12. IR spectrum of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (**1d**) in THF solution and as a solid (inset).

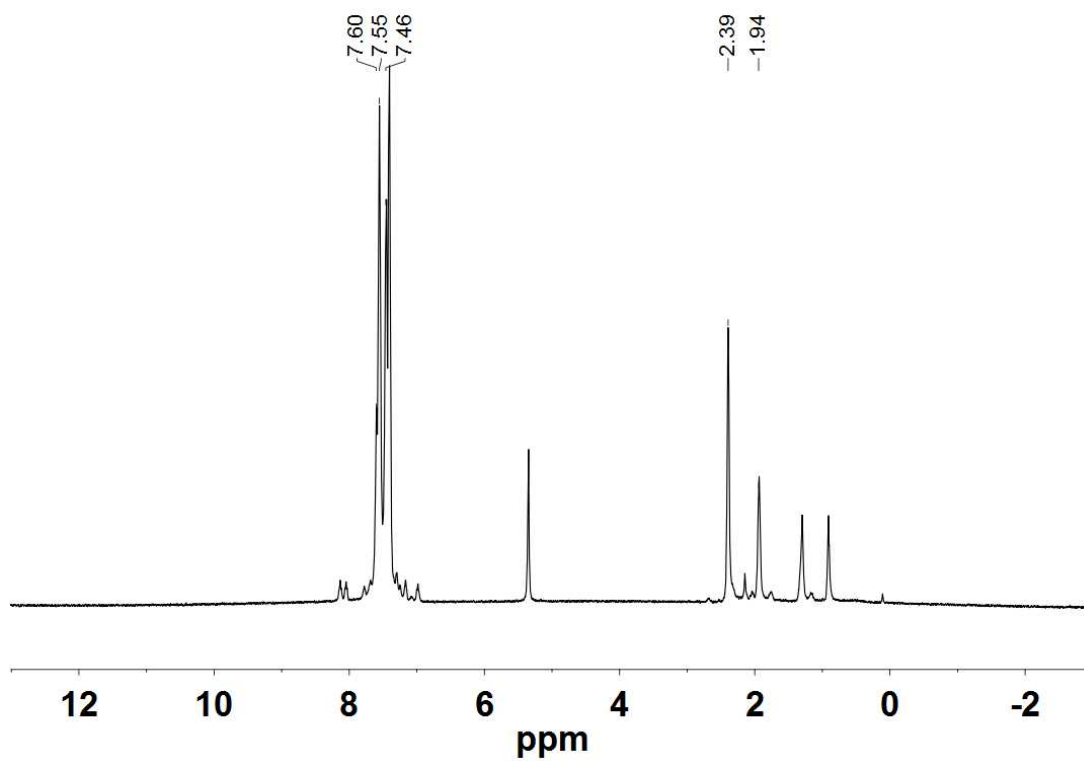


Figure S13. ^1H NMR spectrum (500 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ (**1e**) in CD_2Cl_2 solution.

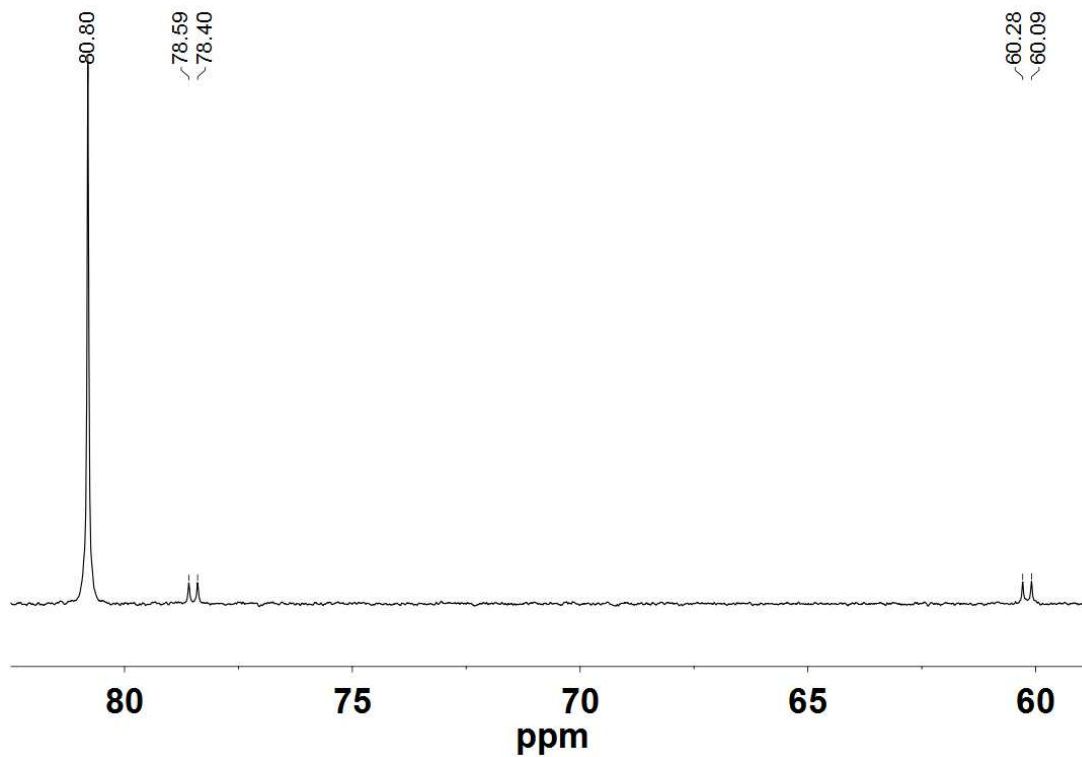


Figure S14. ^{31}P NMR spectrum (202 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ (**1e**) in CD_2Cl_2 solution.

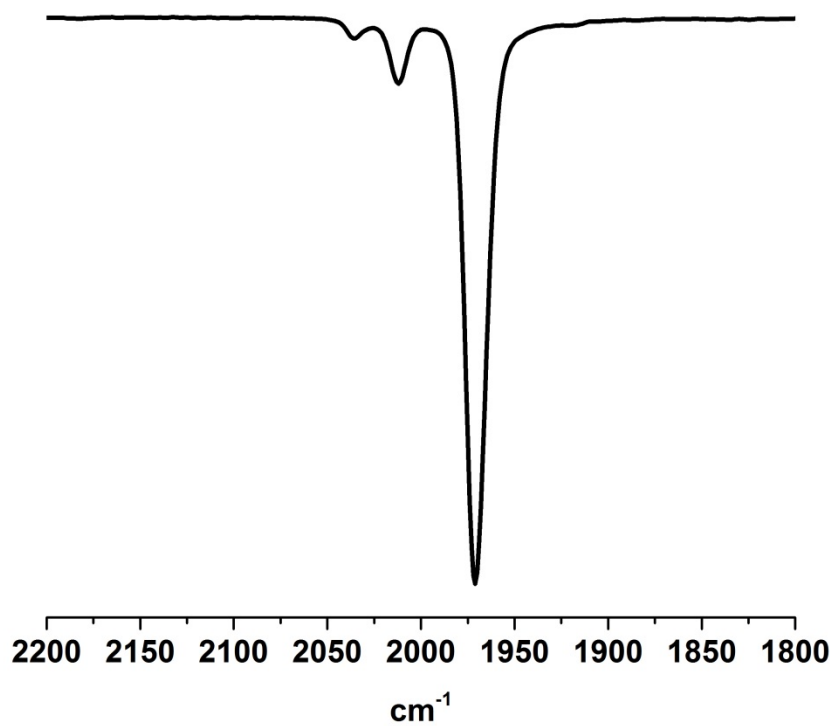


Figure S15. IR spectrum of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ (**1e**) in THF solution.

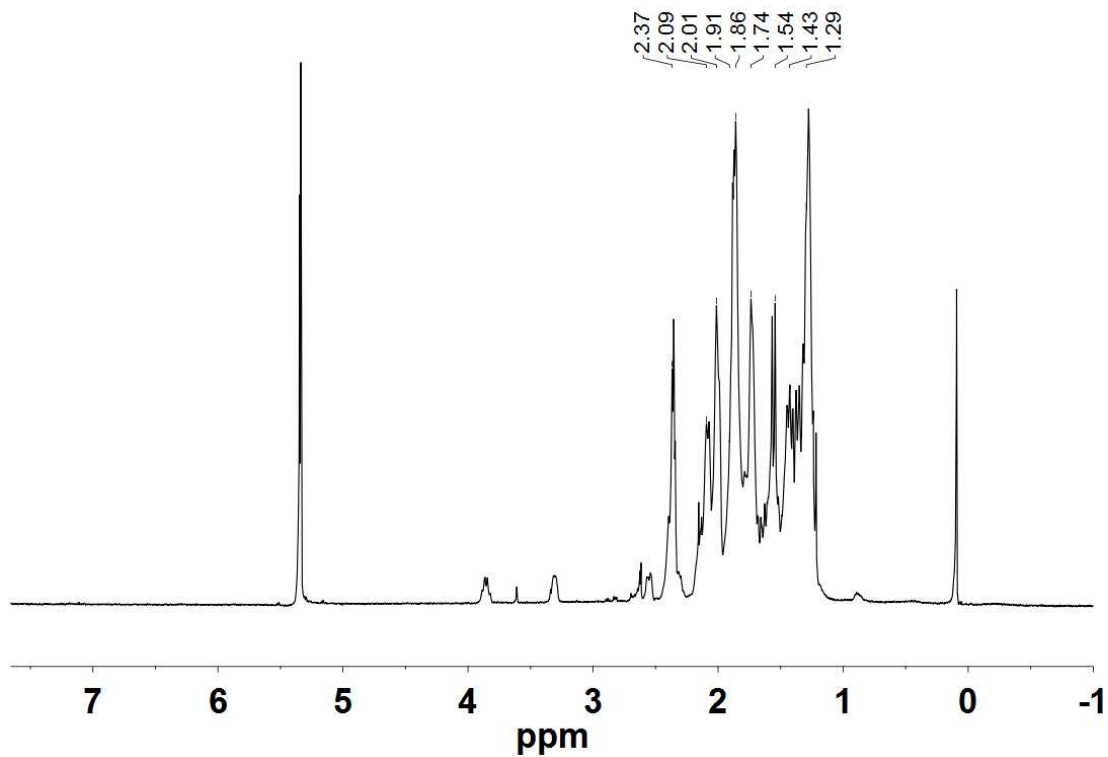


Figure S16. ^1H NMR spectrum (500 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dcpe})$ (**1f**) in CD_2Cl_2 solution.

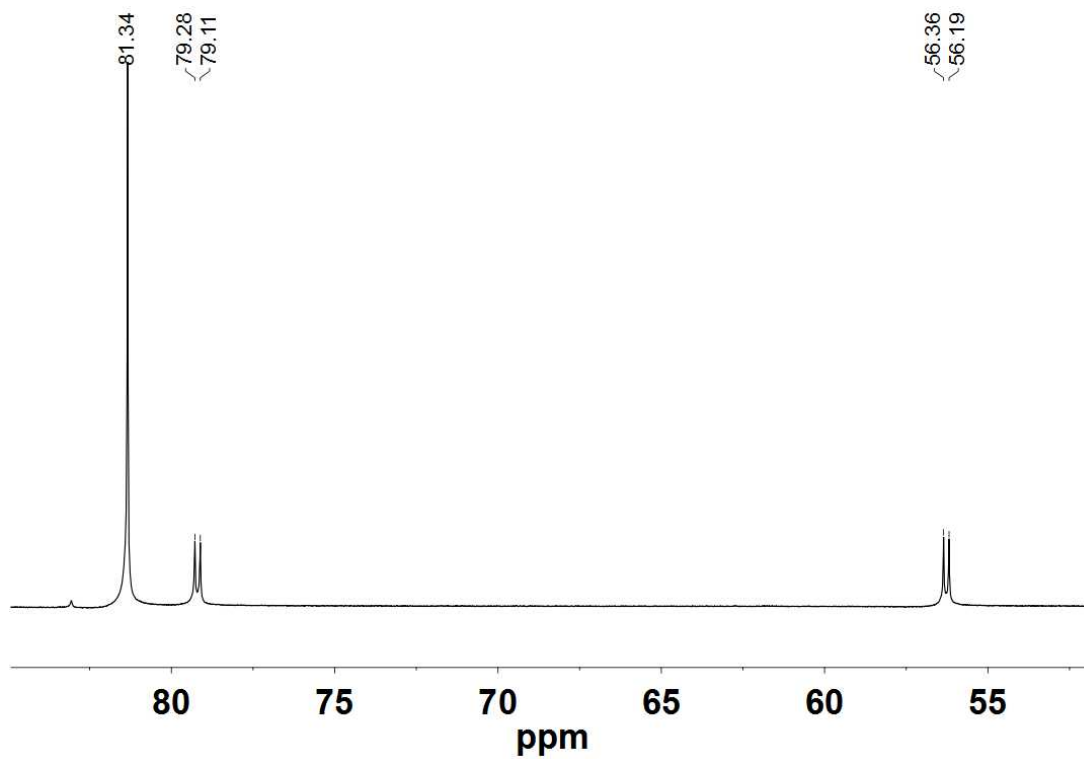


Figure S17. ^{31}P NMR spectrum (202 MHz) of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dcpe})$ (**1f**) in CD_2Cl_2 solution.

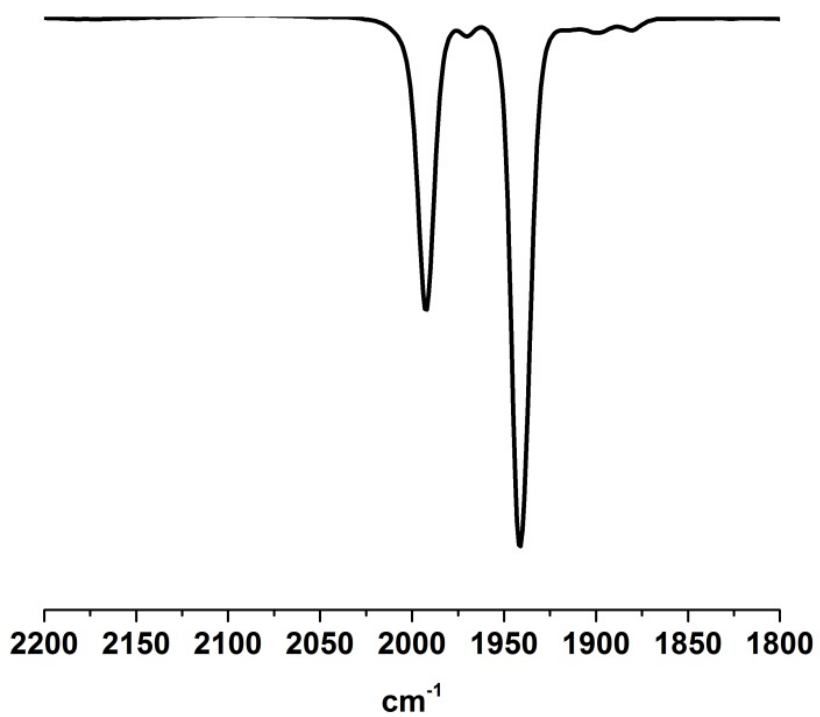


Figure S18. IR spectrum of Fe(pdt)(CO)₂(dcpe) (**1f**) in THF solution.

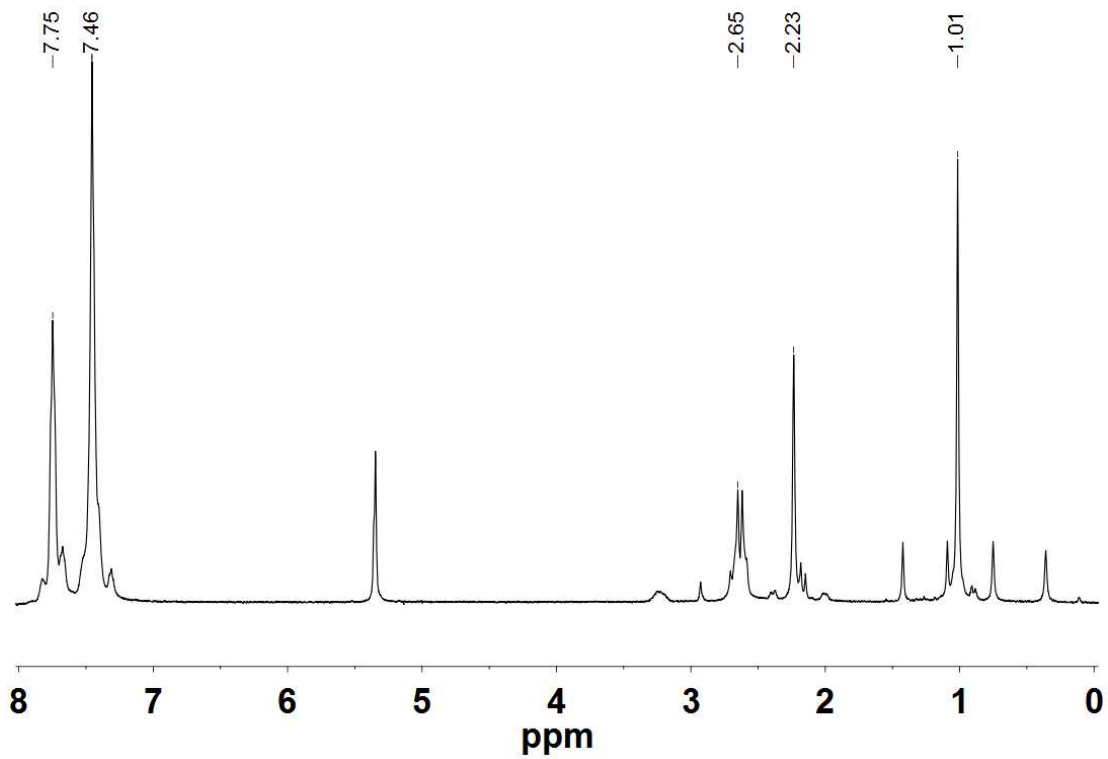


Figure S19. ^1H NMR spectrum (500 MHz) of $\text{Fe}(\text{Me}_2\text{pdt})(\text{CO})_2(\text{dppe})$ (**1g**) in CD_2Cl_2 solution.

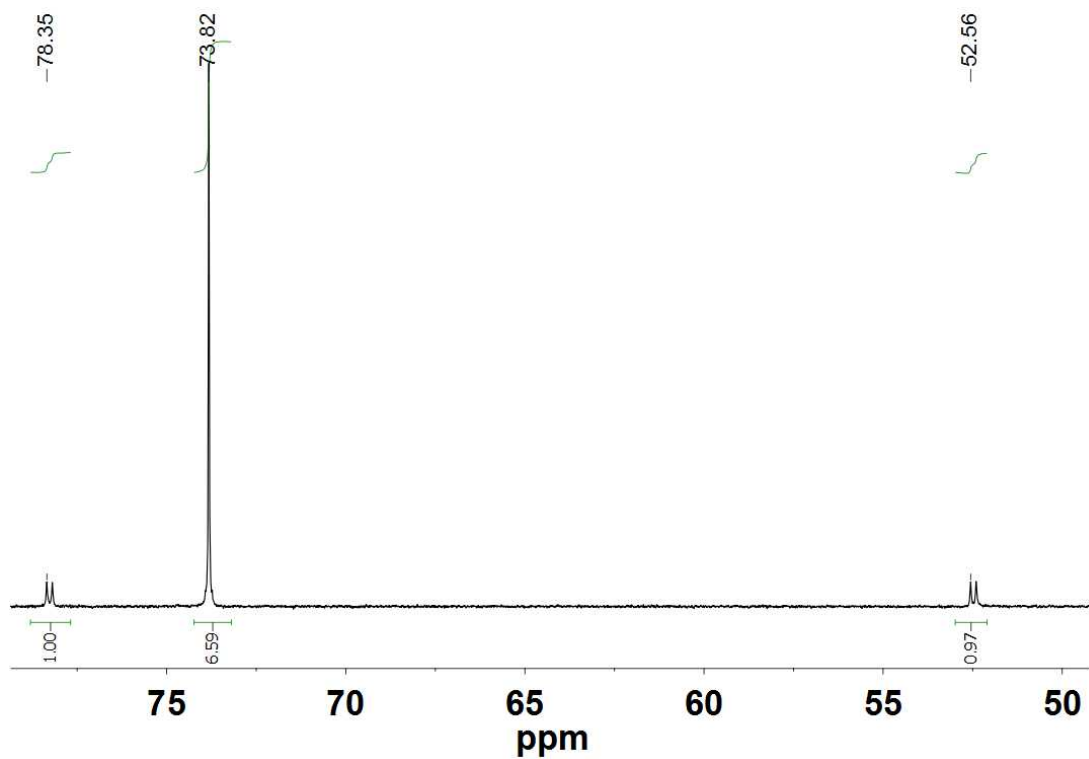


Figure S20. ^{31}P NMR spectrum (202 MHz) of $\text{Fe}(\text{Me}_2\text{pdt})(\text{CO})_2(\text{dppe})$ (**1g**) in CD_2Cl_2 solution.

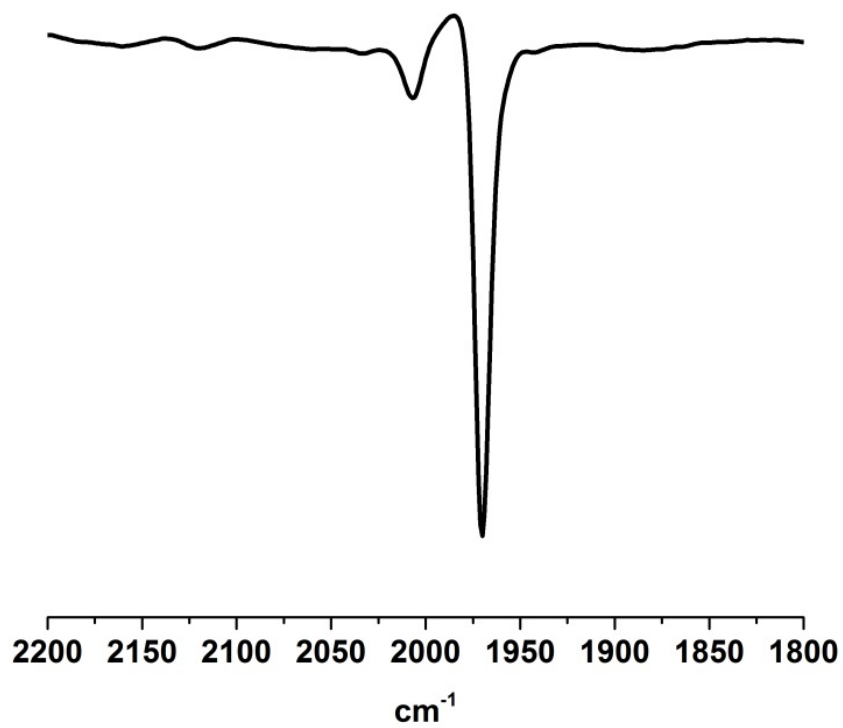


Figure S21. IR spectrum of Fe(Me₂pdt)(CO)₂(dppe) (**1g**) in THF solution.

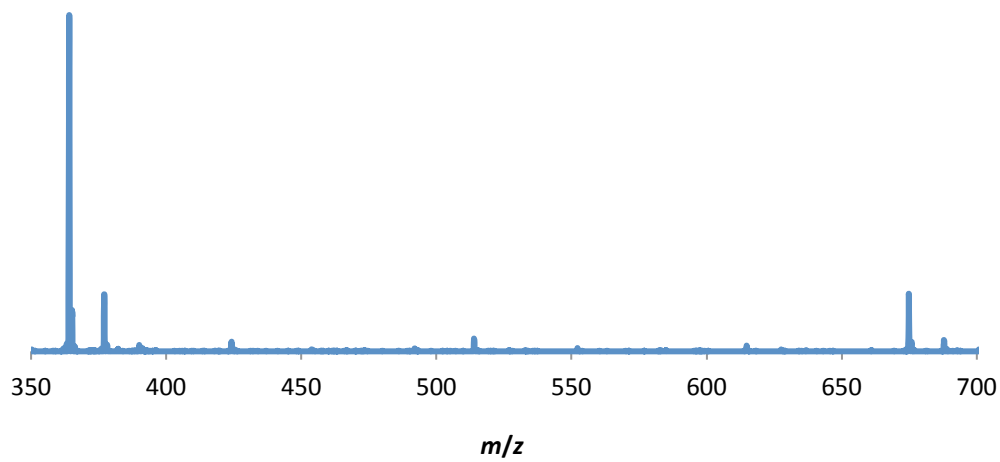


Figure S22. Positive ion ESI mass spectrum of ⁵⁷Fe₂I₄(ⁱPrOH)₄.

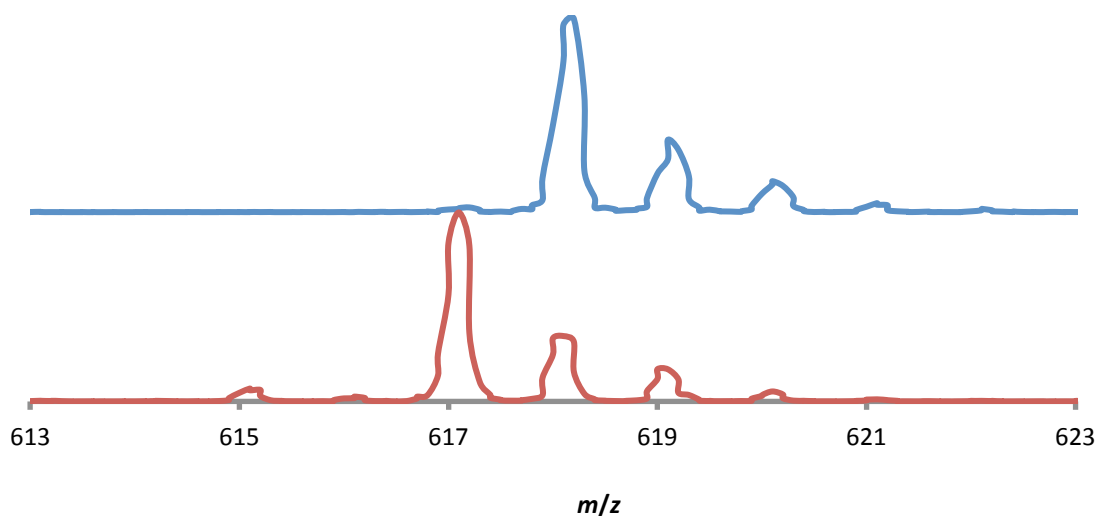


Figure S23. Positive ion ESI mass spectrum of *cis/trans*-[⁵⁷Fe(pdt)(CO)₂(dppe)] (⁵⁷**1d**, top) and *cis/trans*-[Fe(pdt)(CO)₂(dppe)] (**1d**, bottom) prepared using the same method.

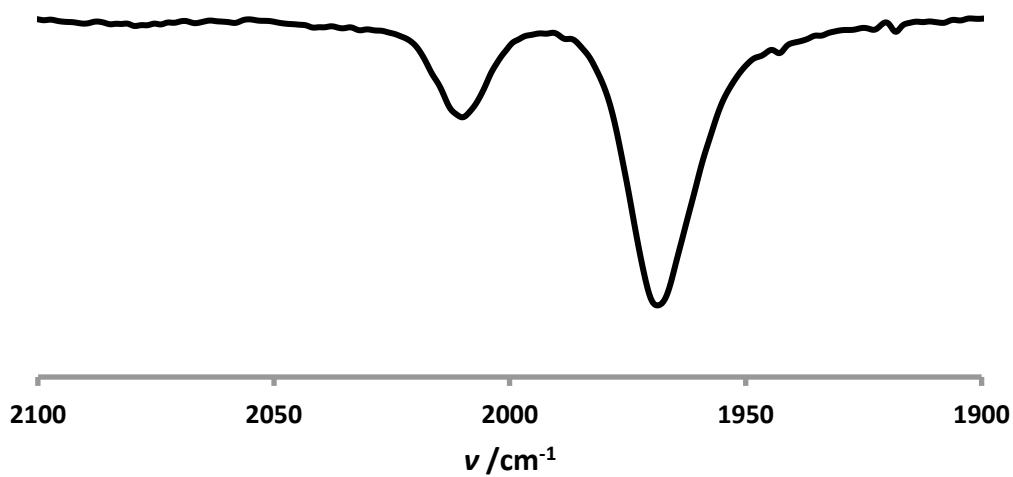


Figure S24. IR spectrum of *cis/trans*-[⁵⁷Fe(pdt)(CO)₂(dppe)] (⁵⁷**1d**) in CH₂Cl₂ solution.

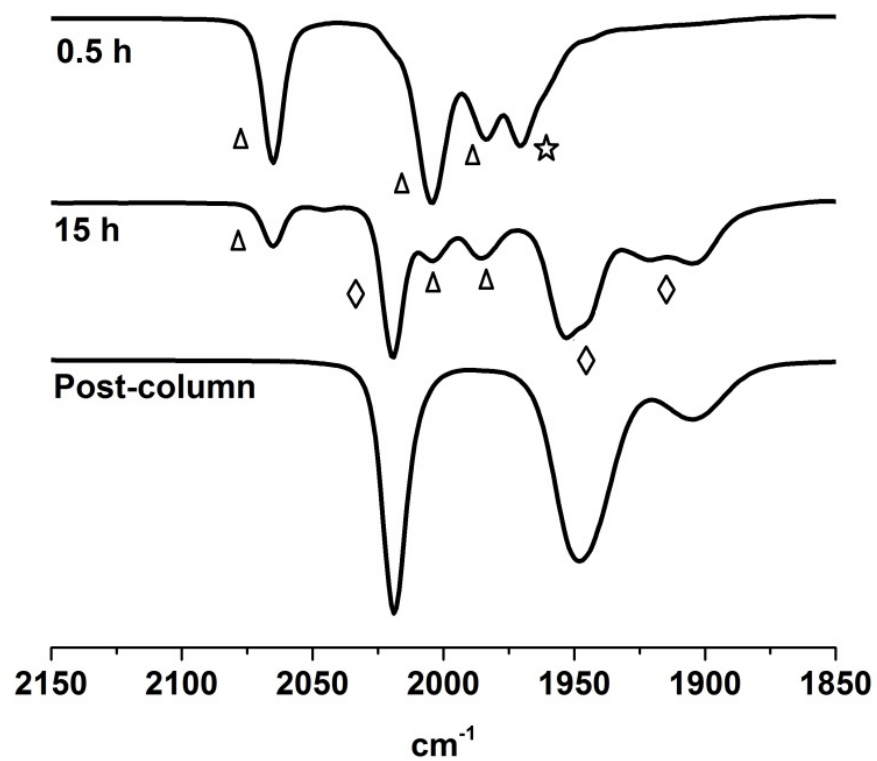


Figure S25. IR spectra of two stages in the reaction $(bda)Fe(CO)_3$ (triangle) + $Fe(pdt)(CO)_2(dppe)$ (**1d**) (star), and the purified $Fe_2(pdt)(CO)_4(dppe)$ (**2d**) (diamond).

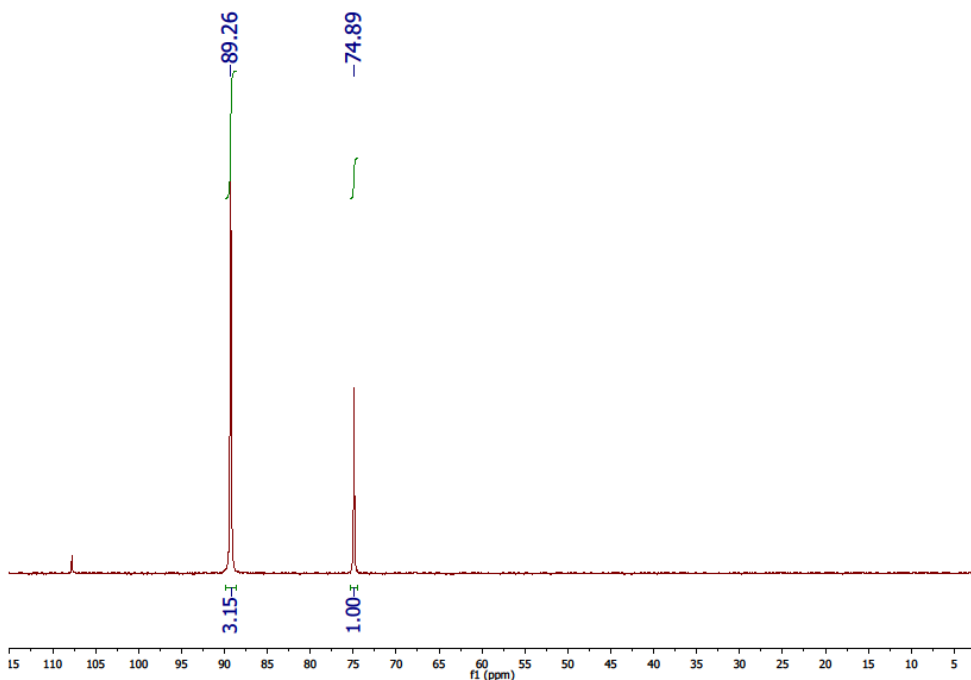


Figure S26. ³¹P NMR spectrum of $Fe_2(pdt)(dcpe)(CO)_4$ (**2f**) in CD_2Cl_2 . Signal at 107 is impurity present as less than 2%.

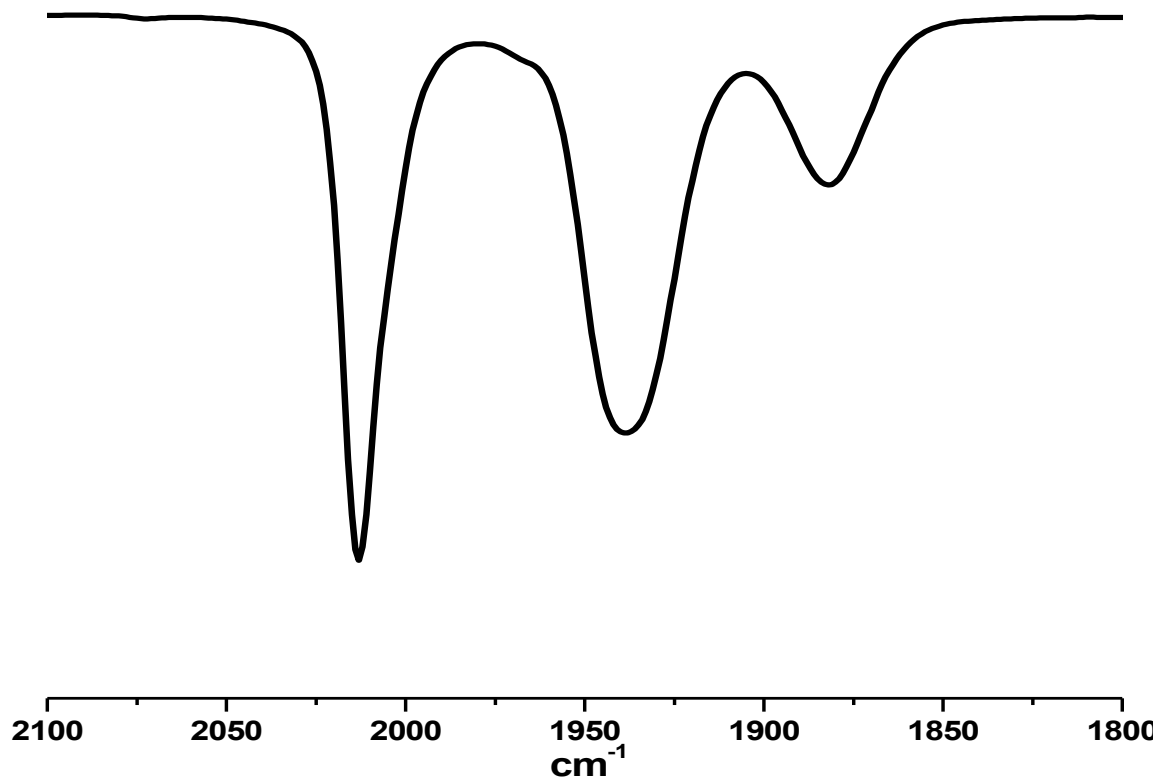


Figure S27. IR spectra of purified $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dcpe})$ (**2f**) in CH_2Cl_2 .

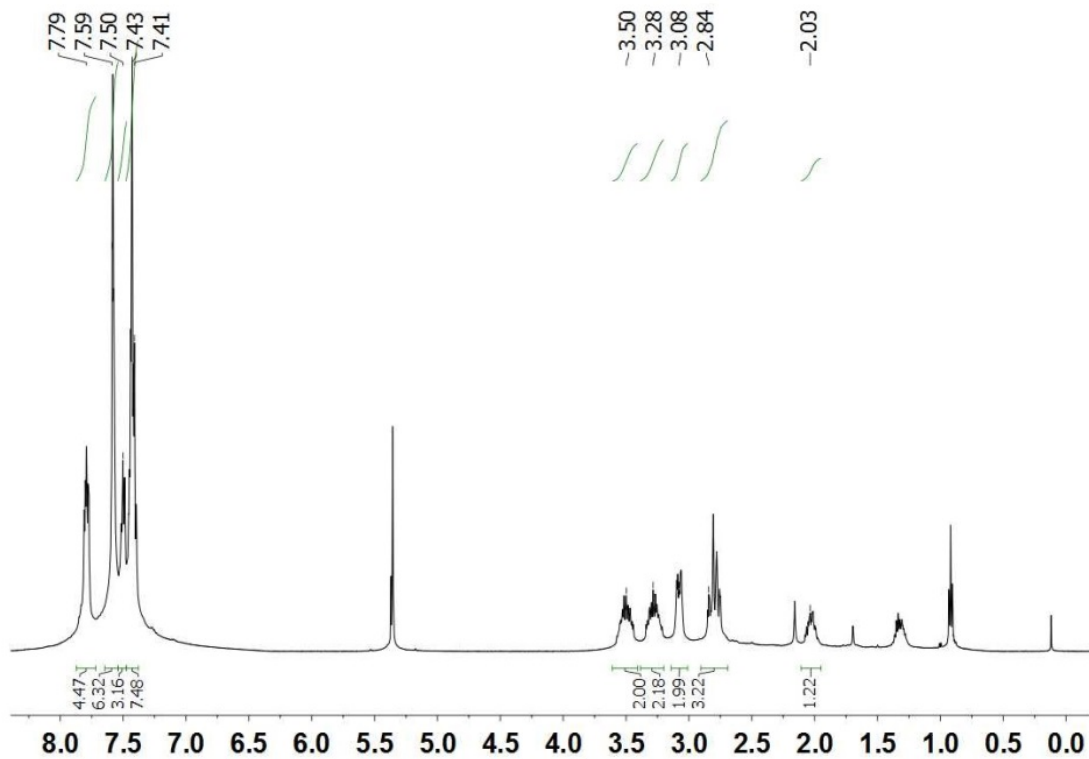


Figure S28. ^1H NMR spectrum of $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ ($[\mathbf{3d}(\text{CO})]\text{BF}_4$) in CD_2Cl_2 .

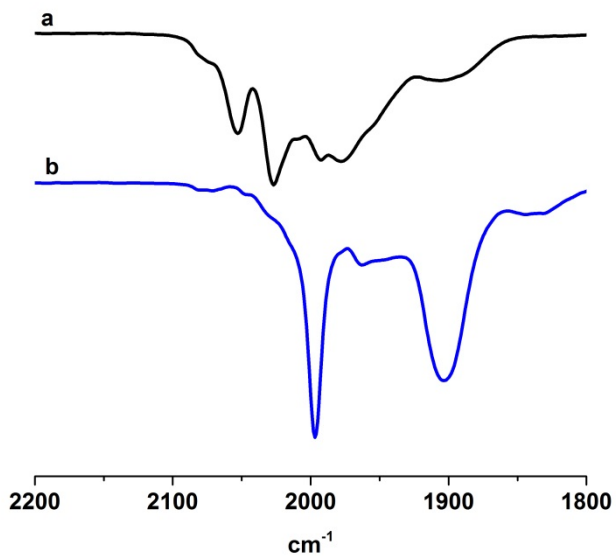


Figure S29. IR spectrum of (a) $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ ($[\mathbf{3d}(\text{CO})]\text{BF}_4$) at 25°C and (b) $(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ ($\mathbf{3d}$) at -78°C in CH_2Cl_2 .

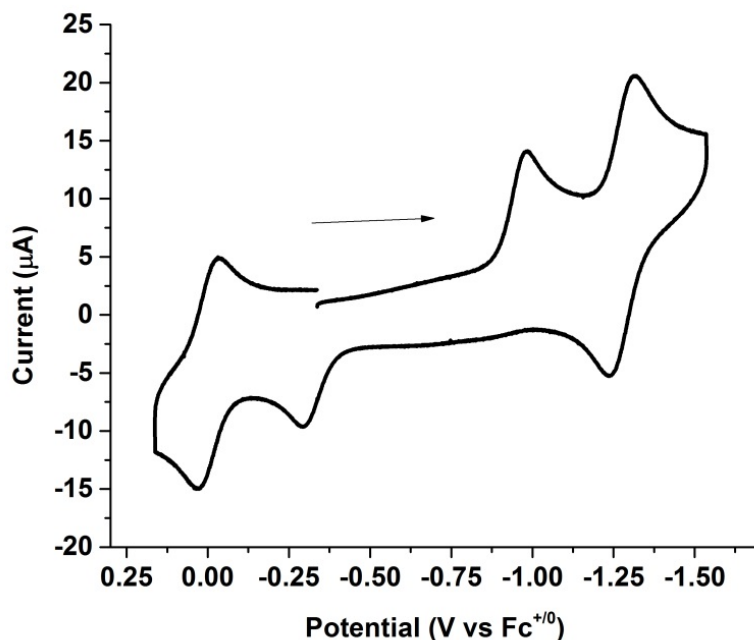


Figure S30. Cyclic voltammogram of 1.0 mM $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ ($[\mathbf{3d}(\text{CO})]\text{BF}_4$) in CH_2Cl_2 at 25 °C. Conditions are described in the caption for Figure S42 but in this experiment, the scan rate was 1.0 V/s.

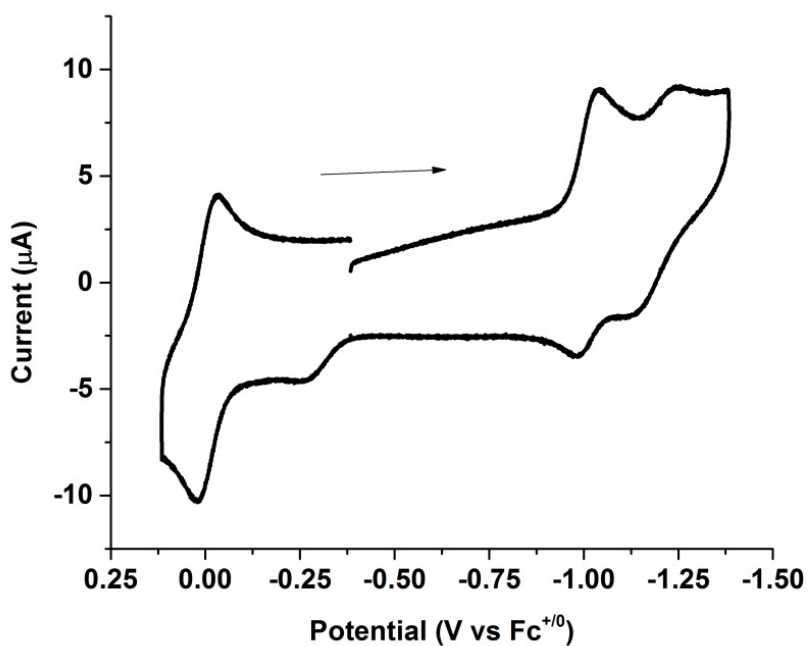


Figure S31. Cyclic voltammogram of 1.0 mM $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ ($[\mathbf{3d}(\text{CO})]\text{BF}_4$) in CH_2Cl_2 at -78 °C. Conditions are described in the caption for Figure S42.

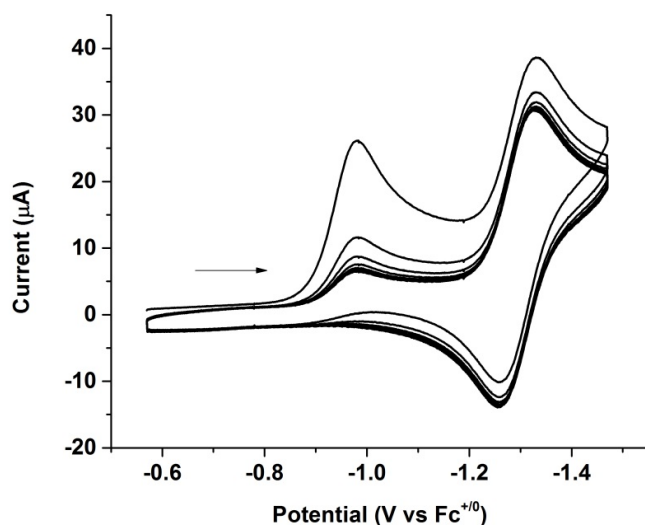


Figure S32. Cyclic voltammogram of $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ in CH_2Cl_2 , scanning 20 segments without disturbing the solution or polishing the working electrode. Conditions are described in the caption for Figure S42 but in this experiment, the scan rate was 1.0 V/s.

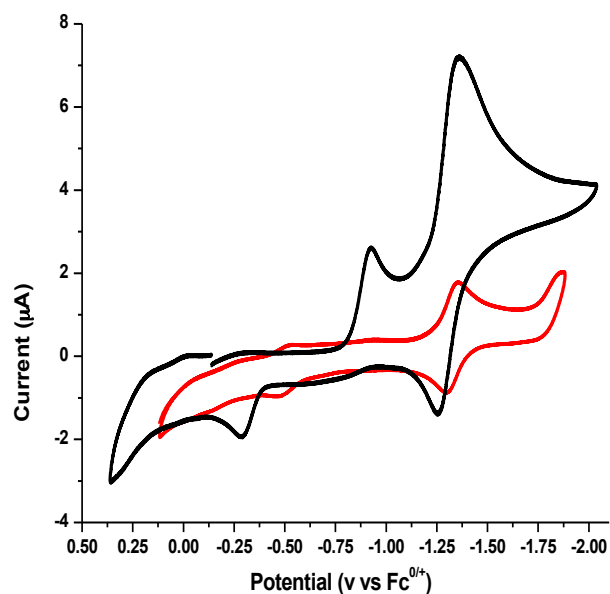


Figure S33. Black trace: Cyclic voltammogram of 1.0 mM $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ ($[\mathbf{3d}(\text{CO})]\text{BF}_4$) in THF at 25 °C. Red Trace: Cyclic voltammogram of 1.0 mM $(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ under identical conditions. Conditions: see Figure S42.

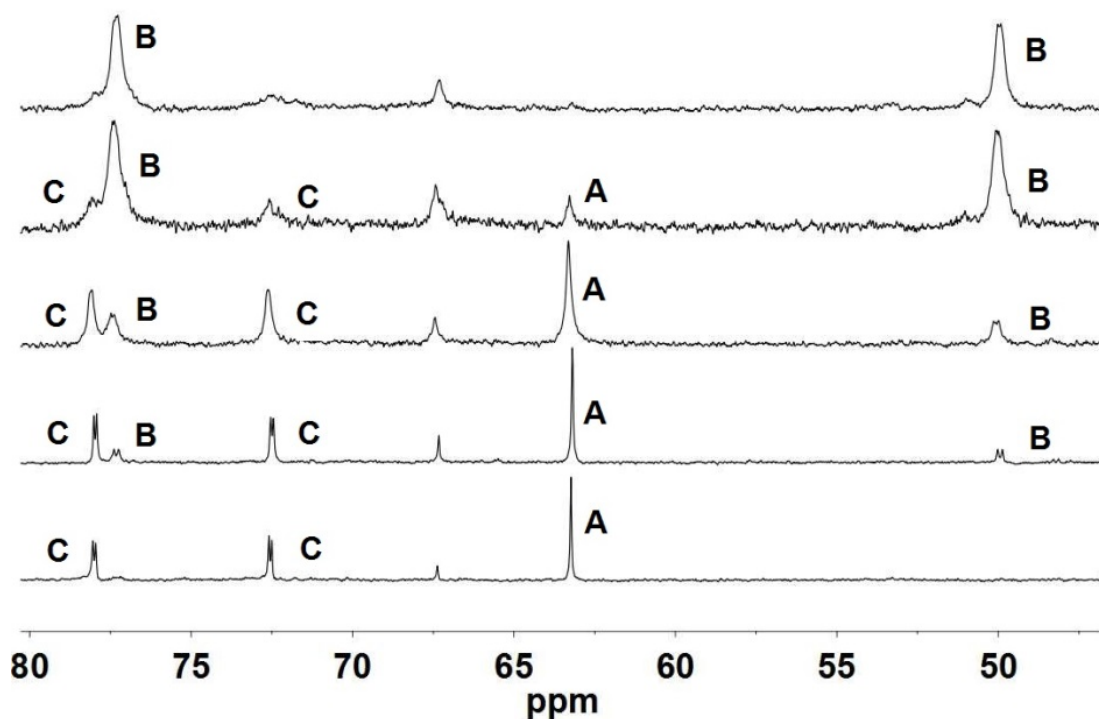
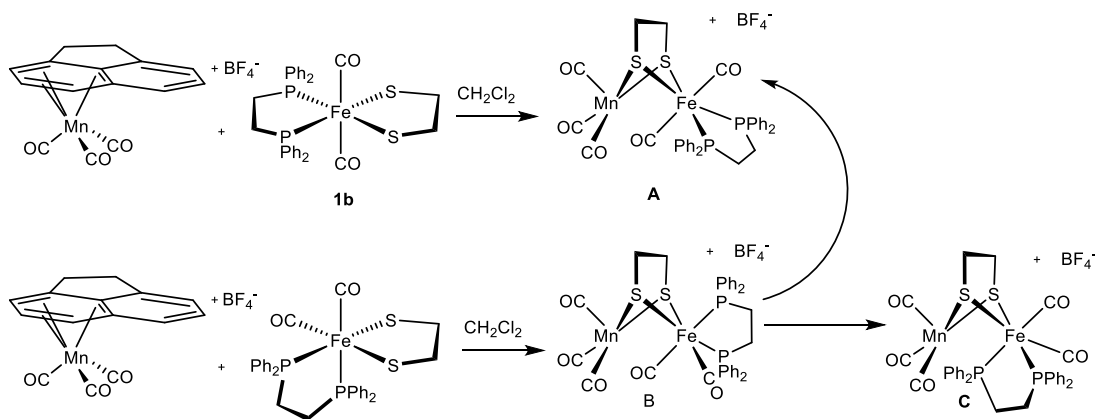


Figure S34. ^{31}P NMR spectra for stages in the reaction of a 1:1 mixture of $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$ with $\text{Fe}(\text{edt})(\text{CO})_2(\text{dppe})$ (**1b**) in CD_2Cl_2 solution at 20°C . From top to bottom reaction time = 15 min, 3.5 h, 30 h, 48 h, 3 weeks). Proposed reaction pathway and isomer assignments are shown below.



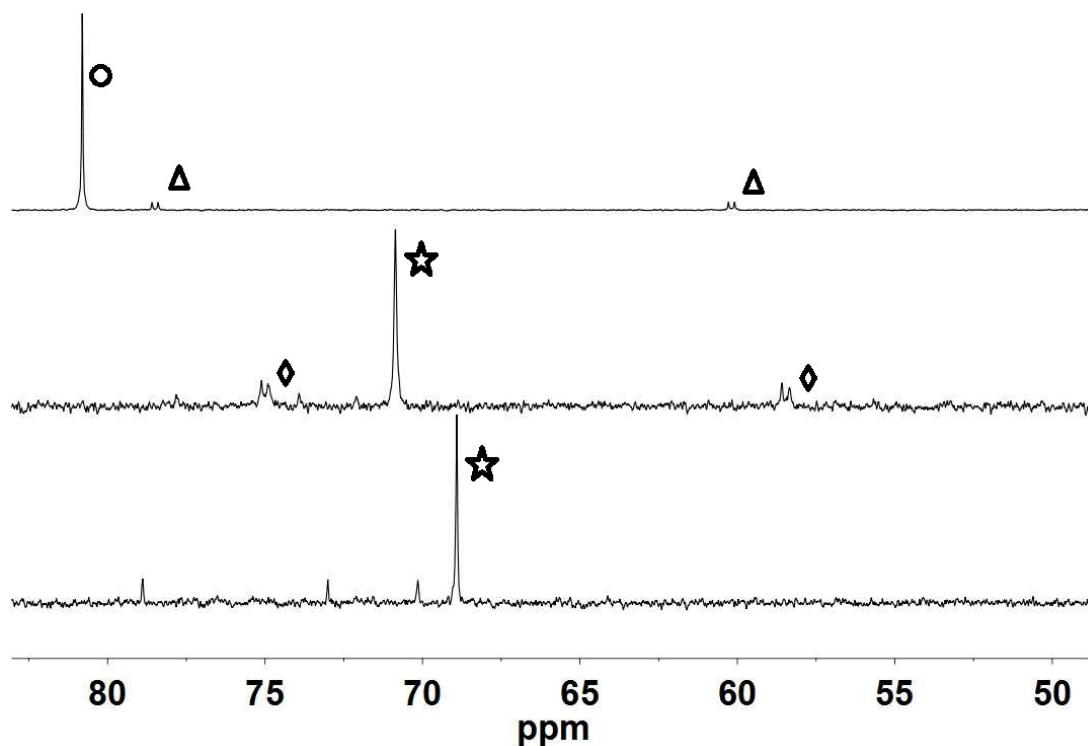


Figure S35. ^{31}P NMR spectra related to the reaction of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ (**1e**) and $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$ to give $[(\text{CO})_4\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dppbz})]\text{BF}_4$ (CD_2Cl_2 solutions):

Top: *unsym-1e* (triangle) and *sym-1e* (circle).

Middle: **1e** + $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$ after 3 h (diamond = *unsym-[(CO)₄Mn(pdt)Fe(CO)(dppbz)]⁺*, star = *sym-[(CO)₄Mn(pdt)Fe(CO)(dppbz)]⁺*)

Bottom: Same mixture was allowed to stand 12 h, evaporated and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexanes}$ (signals at δ 73.1 and 70.2 are unknown impurities).

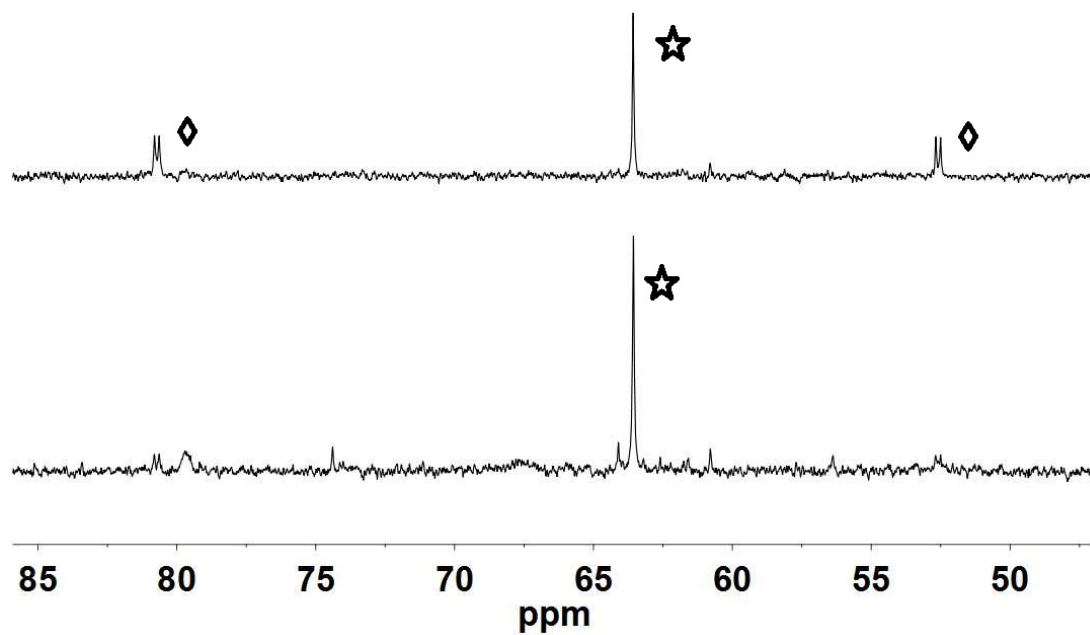


Figure S36. ^{31}P NMR spectra related to the reaction of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dcpe})$ (**1f**) and $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$ to give $[(\text{CO})_4\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dcpe})]\text{BF}_4$ (CD_2Cl_2 solutions):
Top: unsym-1f (diamonds) and *sym-1f* (stars).
Bottom: 1f + [(acenaphthene)Mn(CO)₃]BF₄ after 16 h.

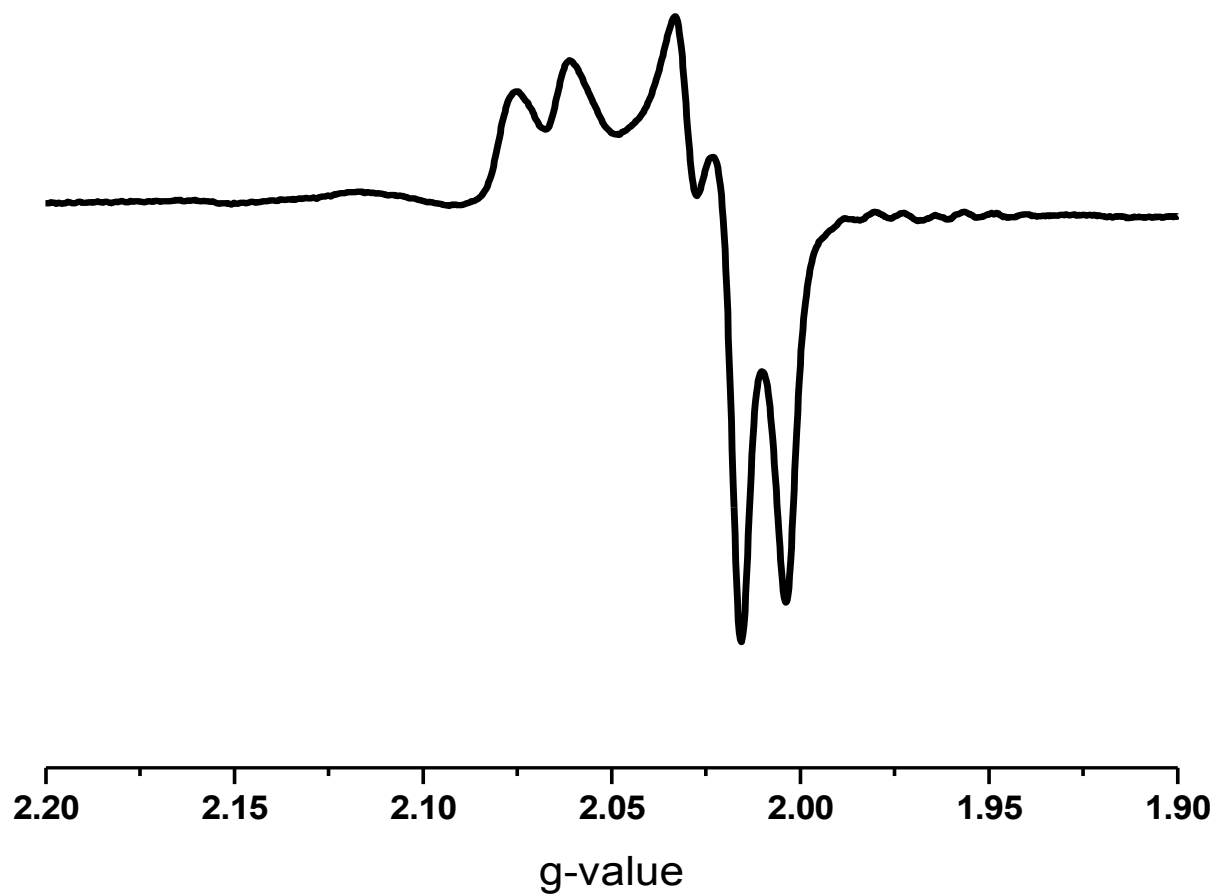


Figure S37. X-band EPR spectra of a mixture of $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ ($[\mathbf{3d}(\text{CO})]\text{BF}_4$) and Cp_2Co in 4:1 mixture of THF and toluene frozen at 77 K.

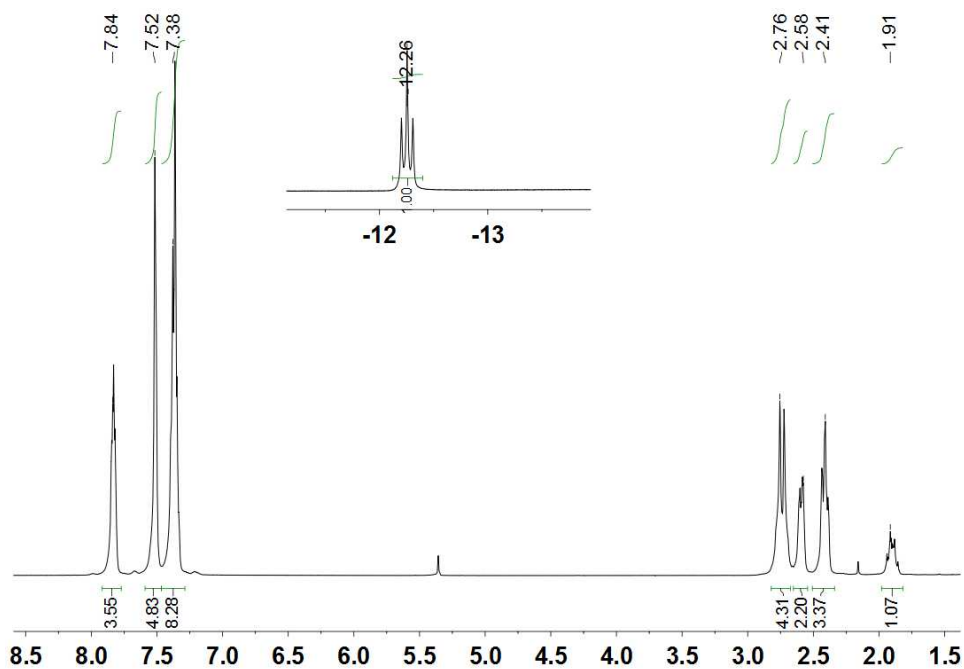


Figure S38. ^1H NMR spectrum of $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (**H3d**) in CD_2Cl_2 solution (*Inset*: High field region of spectrum, showing signal for the hydride ligand).

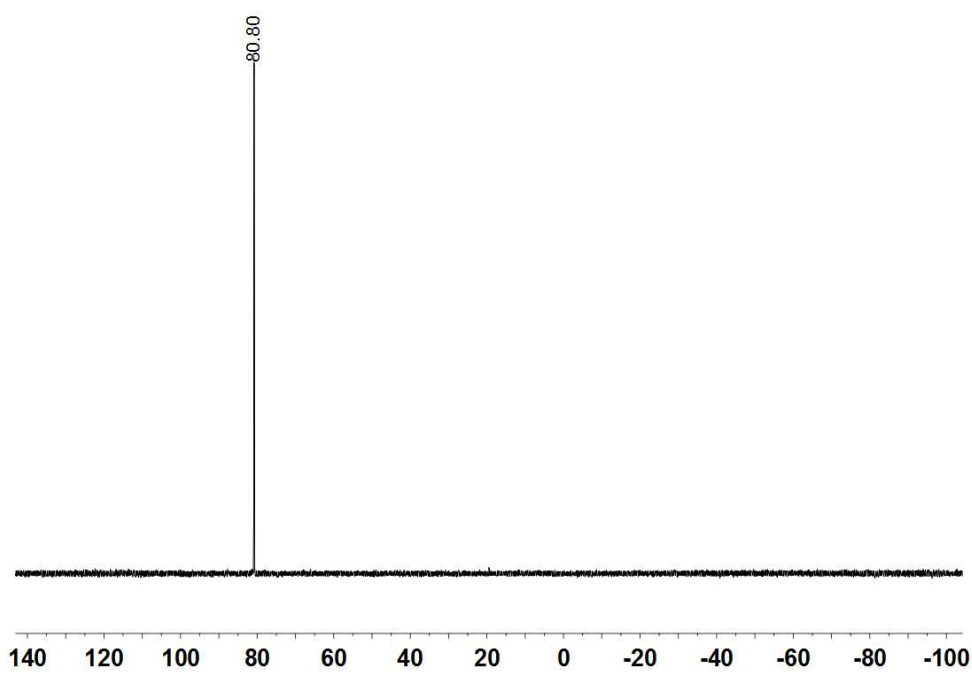


Figure S39. ^{31}P NMR spectrum of $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (**H3d**) in CD_2Cl_2 solution.

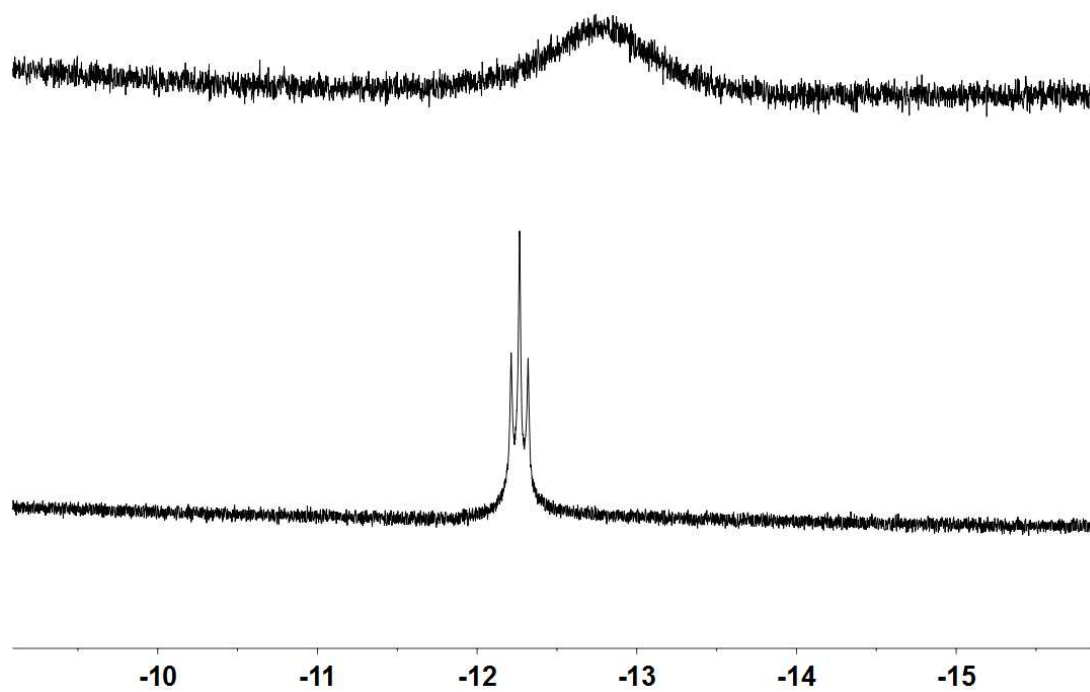


Figure S40. High field region of the ¹H NMR spectra of H3d (bottom) and a 1:1 mixture of H3 and [H(Et₂O)₂]BAR^F₂₄ (top) in CH₂Cl₂ solution.

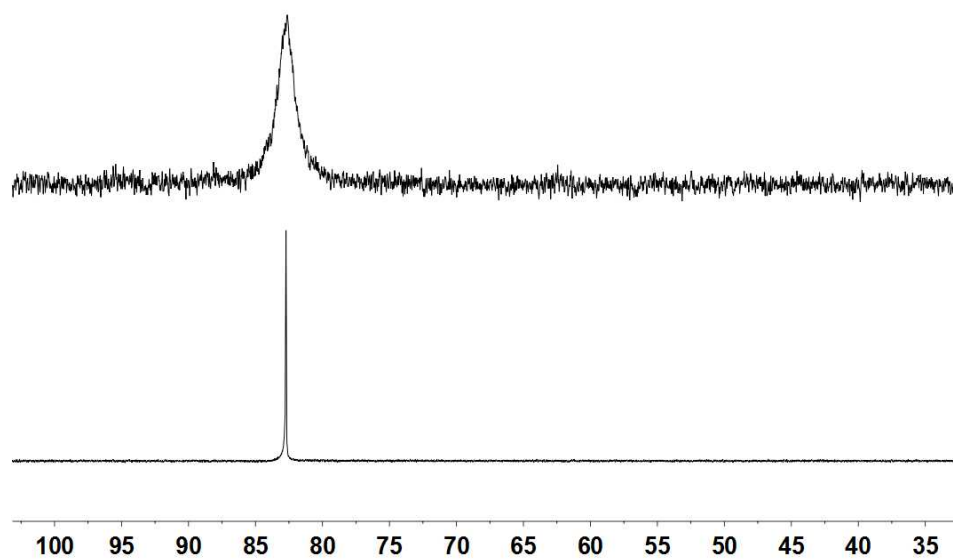


Figure S41. ^{31}P NMR spectra of H3d (bottom) and of a 1:1 mixture of H3d and $[\text{H}(\text{Et}_2\text{O})_2]\text{BAr}^{\text{F}}_{24}$ (top) in CH_2Cl_2 solution.

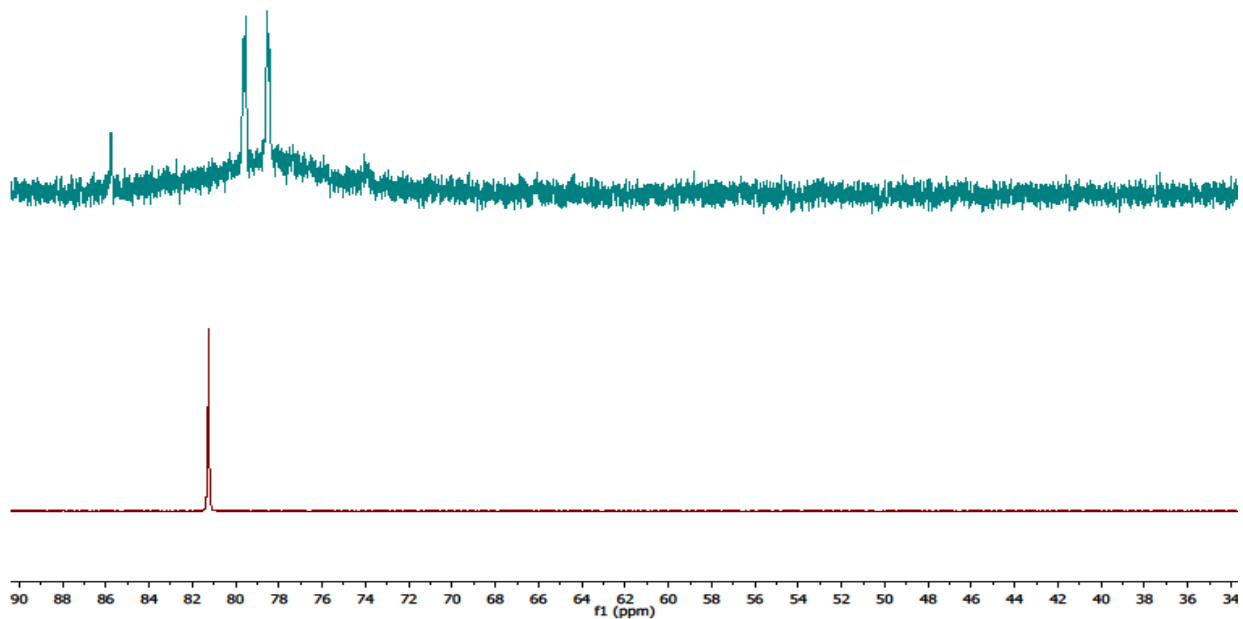


Figure S42. ^{31}P NMR spectra of **H3** (bottom) and of a 1:2 mixture of **H3d** and $[\text{H}(\text{Et}_2\text{O})_2]\text{BAr}^{\text{F}}_{24}$ (top). For the top spectrum, $J_{\text{P-P}}$ is 21.5 Hz. The signal at $\delta 86$ is an unidentified impurity. *Note:* When the protonation was conducted under an atmosphere of CO, however, the IR spectrum of the reaction mixture did not indicate formation of $[\mathbf{3}(\text{CO})]^+$.

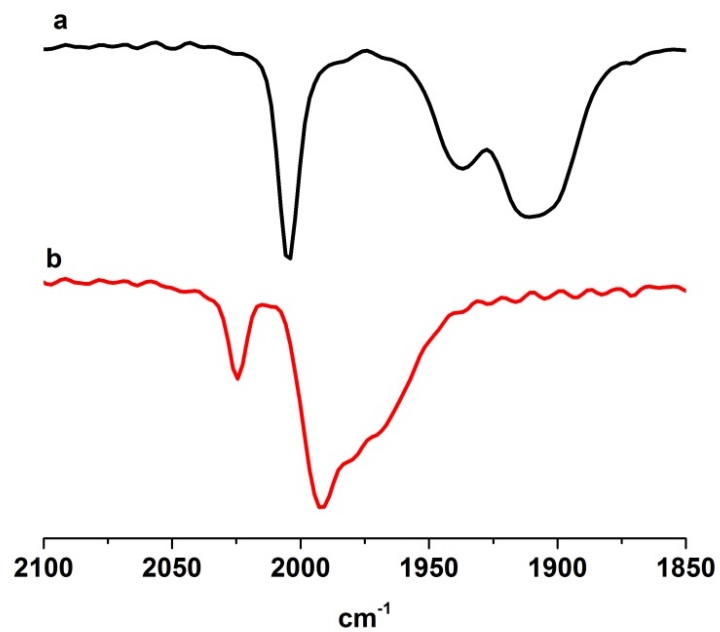


Figure S43. IR spectra of CH₂Cl₂ solutions of (a) (CO)₃Mn(pdt)(μ -H)Fe(CO)(dppe) (H3d) before and after treatment with FcBF₄.

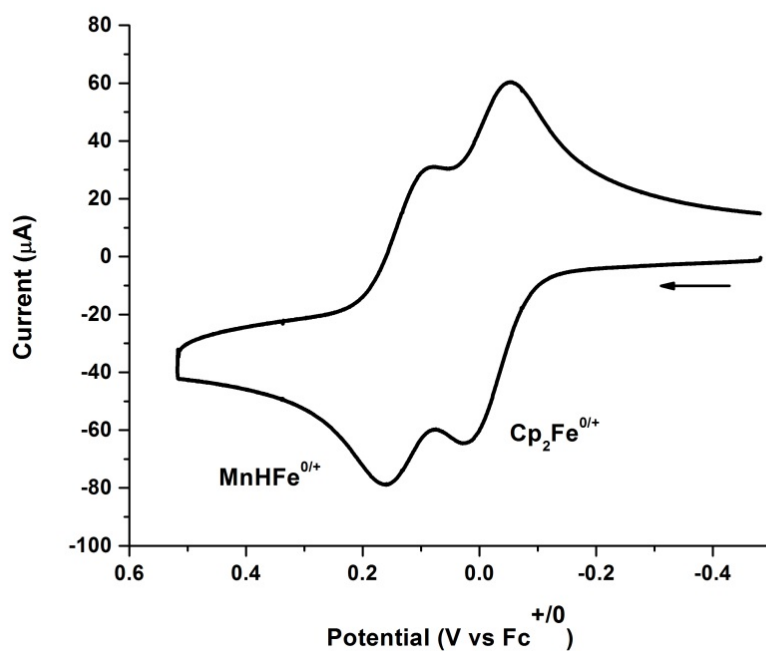


Figure S44. Cyclic voltammogram of $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (**H3d**) in CH_2Cl_2 solution. *Conditions:*

1.0 mM $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$

0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$

working electrode: glassy carbon

counter electrode: Pt

pseudoreference electrode: Ag

scan rate = 0.5 V/s

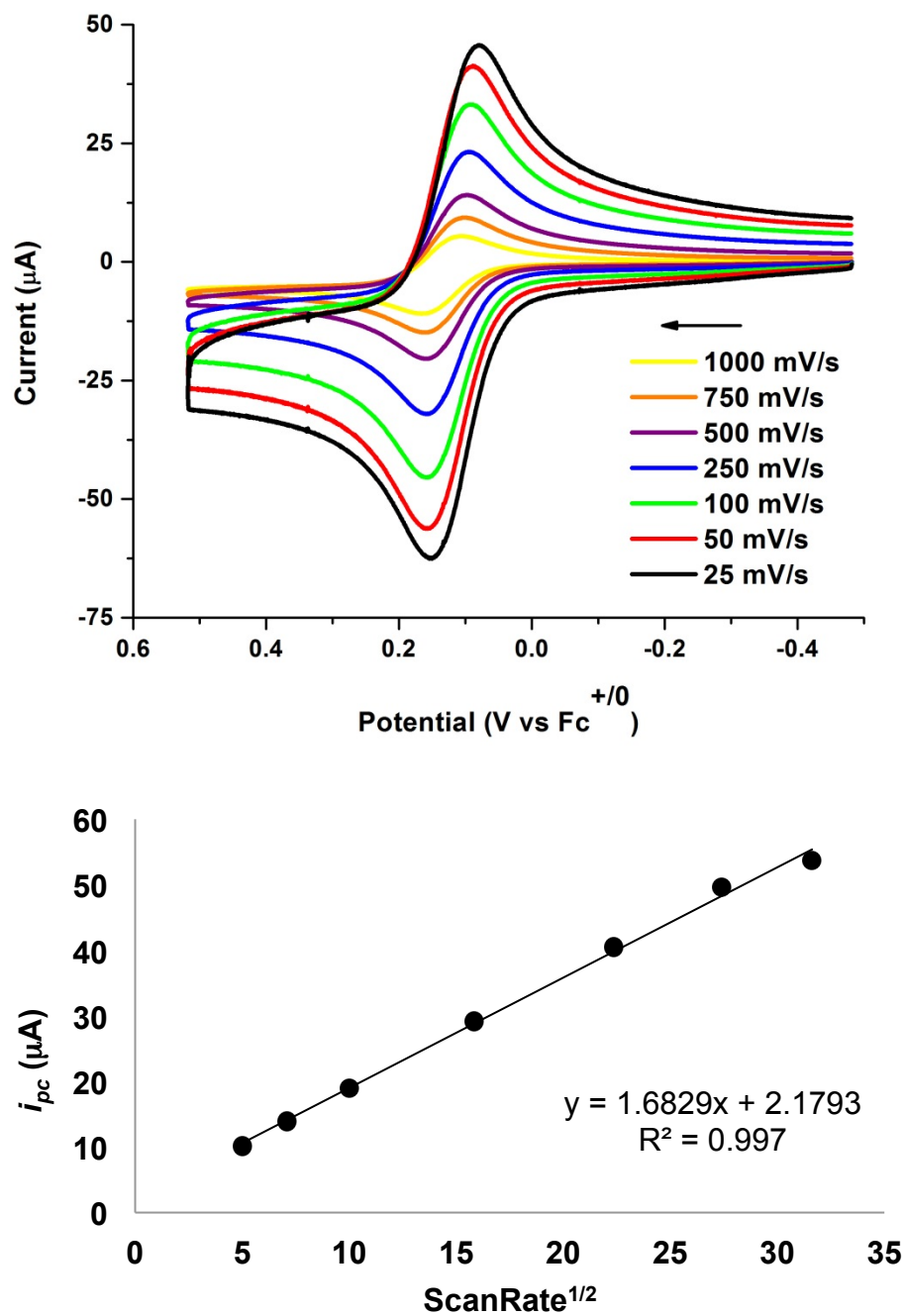


Figure S45. Cyclic voltammograms of $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (**H3d**) at various scan rates (top) and plot of $i_{pc}/(\text{scan rate})^{1/2}$ (bottom).
Conditions: See Figure S42.

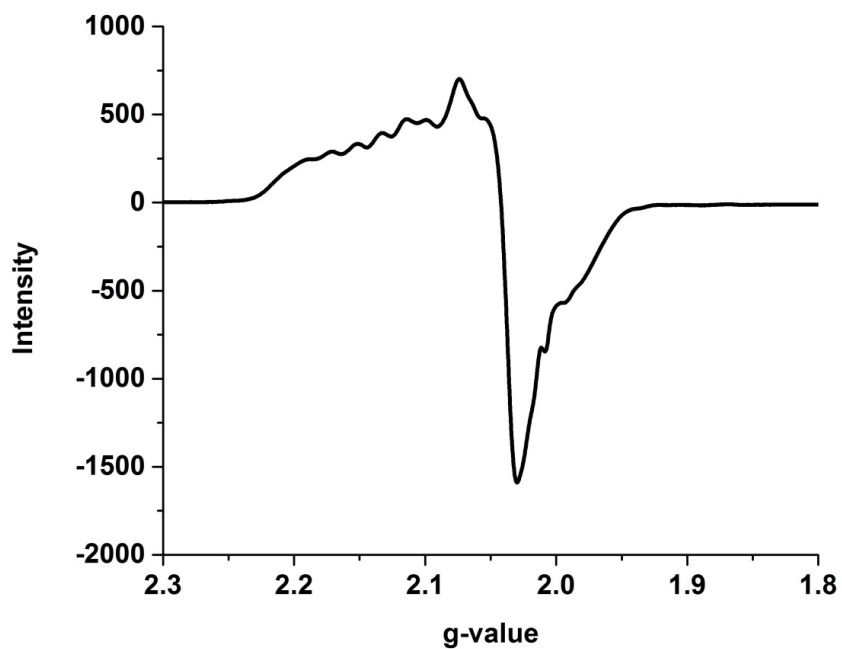


Figure S46. X-band EPR spectrum of a frozen (110 K) mixture of $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (H3) and $[\text{acetylFc}]\text{BAr}^{\text{F}}_{24}$ in 3:1 toluene: CH_2Cl_2 solution.

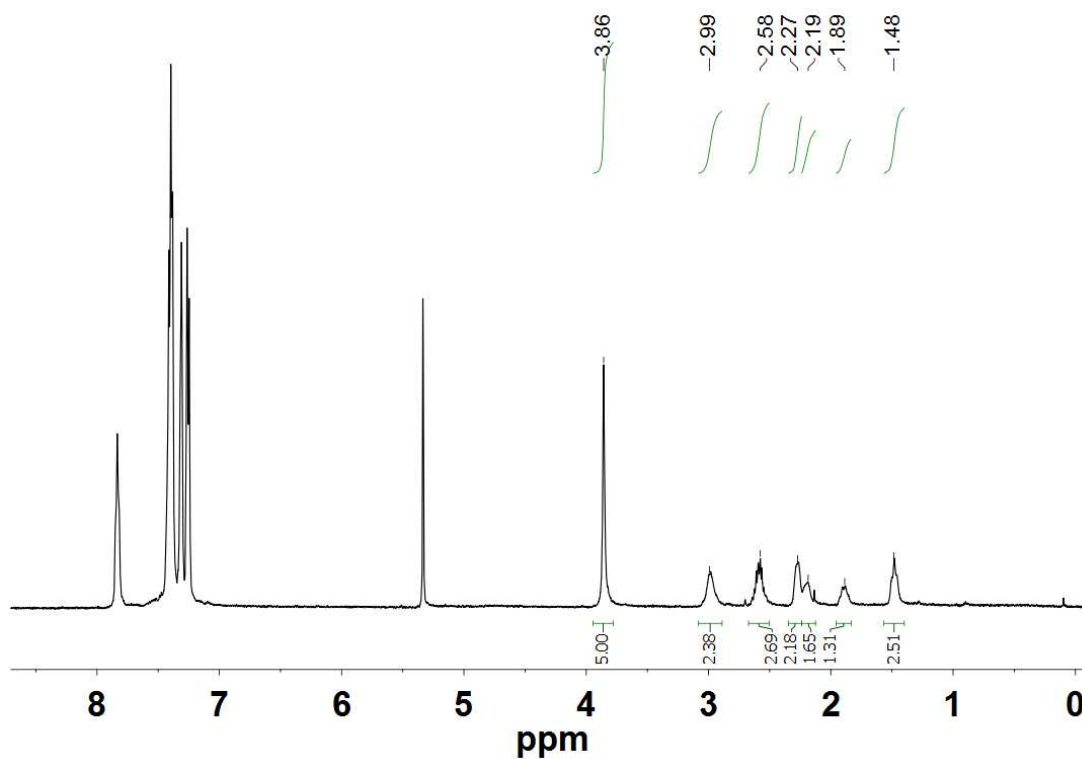


Figure S47. ^1H NMR spectrum of $\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ (**4d**) in CD_2Cl_2 solution.

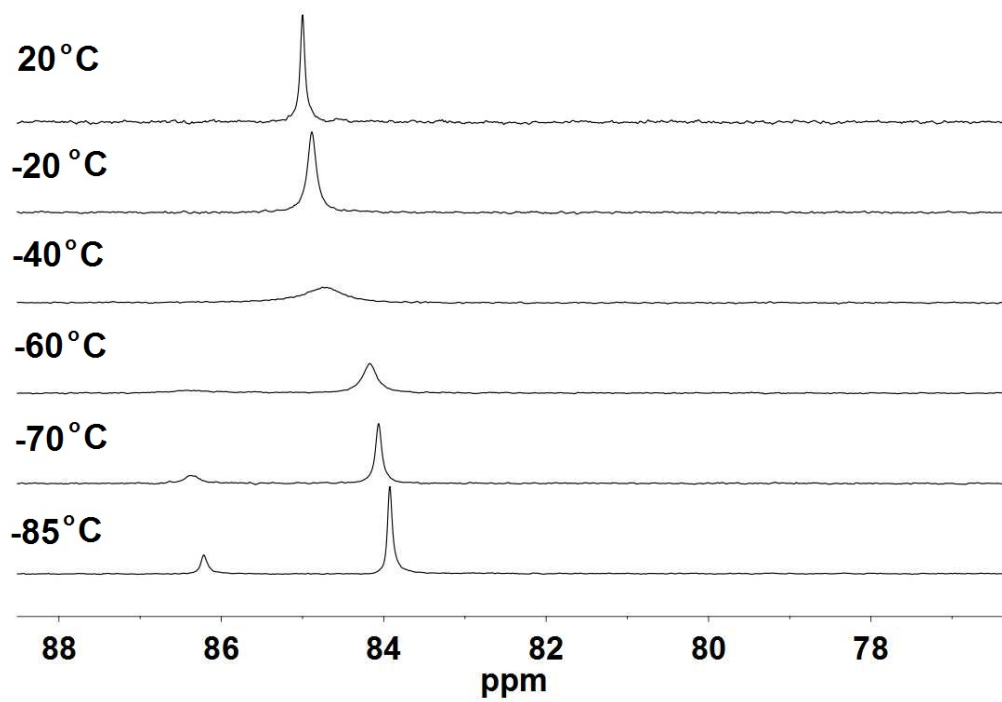


Figure S48. ^{31}P NMR spectrum of $\text{CpCo(pdt)Fe(CO)(dppe)}$ (**4d**) in CD_2Cl_2 solution at various temperatures.

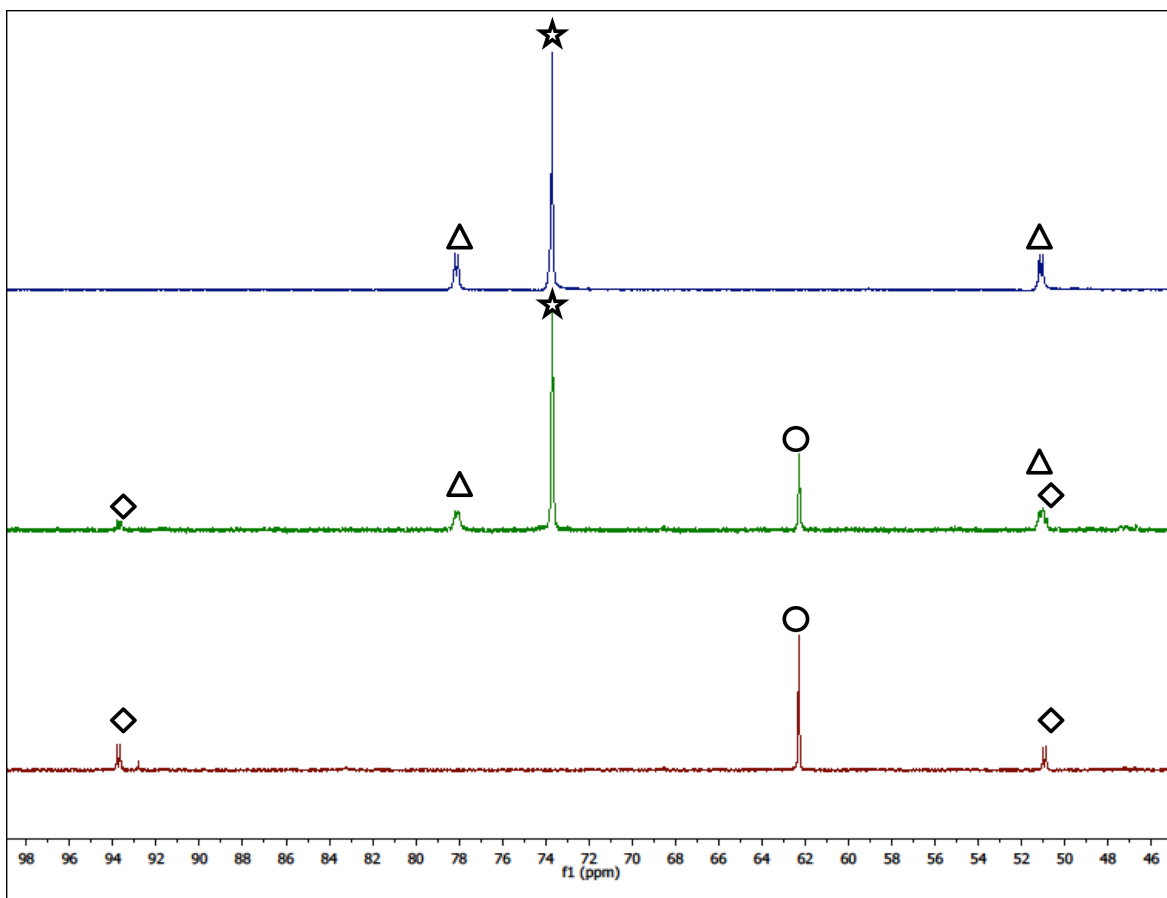


Figure S49. ^{31}P NMR spectra related to the reaction of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (**1d**) and $\text{CpCo}(\text{CO})\text{I}_2$ to give $[\text{CpCoI}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})]\text{I}$ (CD_2Cl_2 solutions):

Top: *unsym-1d* (triangle) and *sym-1d* (star).

Middle: **1d** + $\text{CpCo}(\text{CO})\text{I}_2$ after 30 min. (diamond = *unsym*- $[\text{CpCoI}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})]^+$, circle = *sym*- $[\text{CpCoI}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})]^+$).

Bottom: Same mixture as in middle spectrum, but recorded after a total of 100 min.

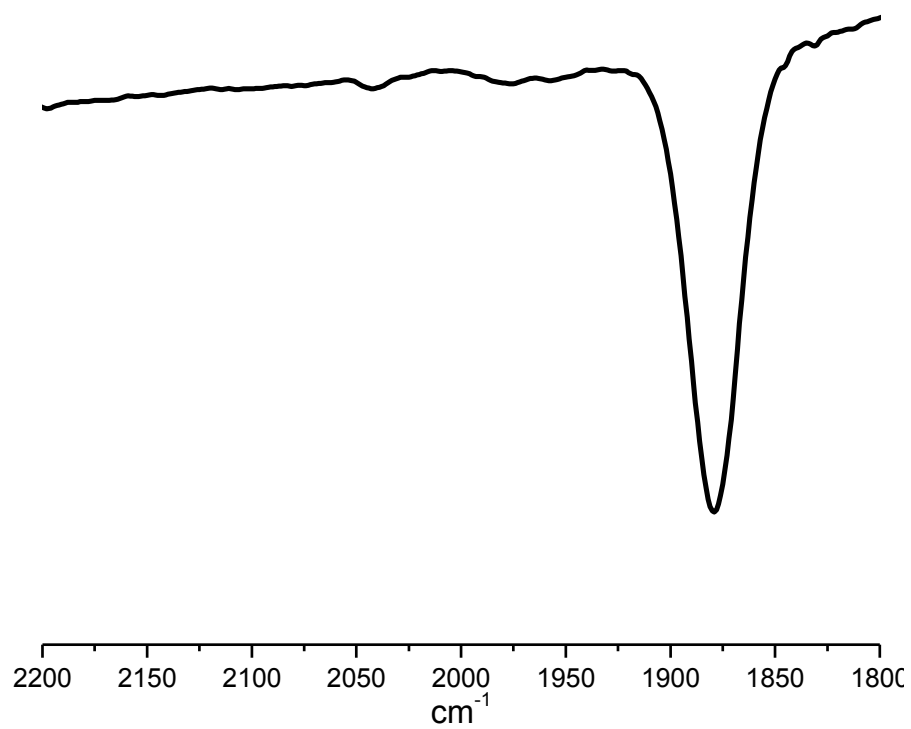


Figure S50. IR spectrum of $\text{CpCo(pdt)Fe(CO)(dppe)}$ (**4d**) in CH_2Cl_2 .

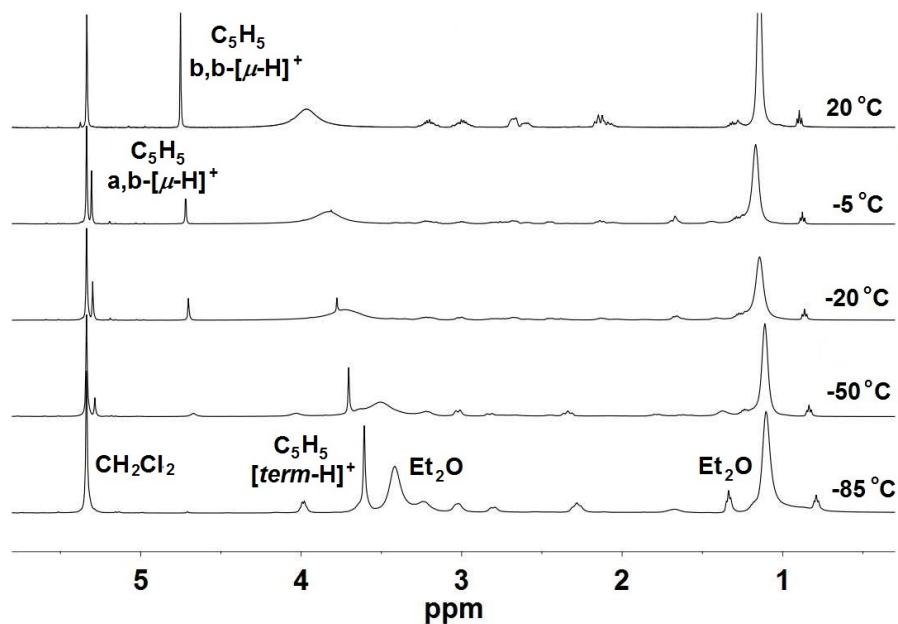


Figure S51. Low field portion of ^1H NMR spectra for the low-temperature ($-85\text{ }^\circ\text{C}$) protonation of $\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ (**4d**) with one equiv $[\text{H}(\text{OEt}_2)_2]\text{BAR}^{\text{F}_4}$ in CD_2Cl_2 followed by warming to the indicated temperatures. For the high field portion of the same spectra, see Figure 9 in the paper.

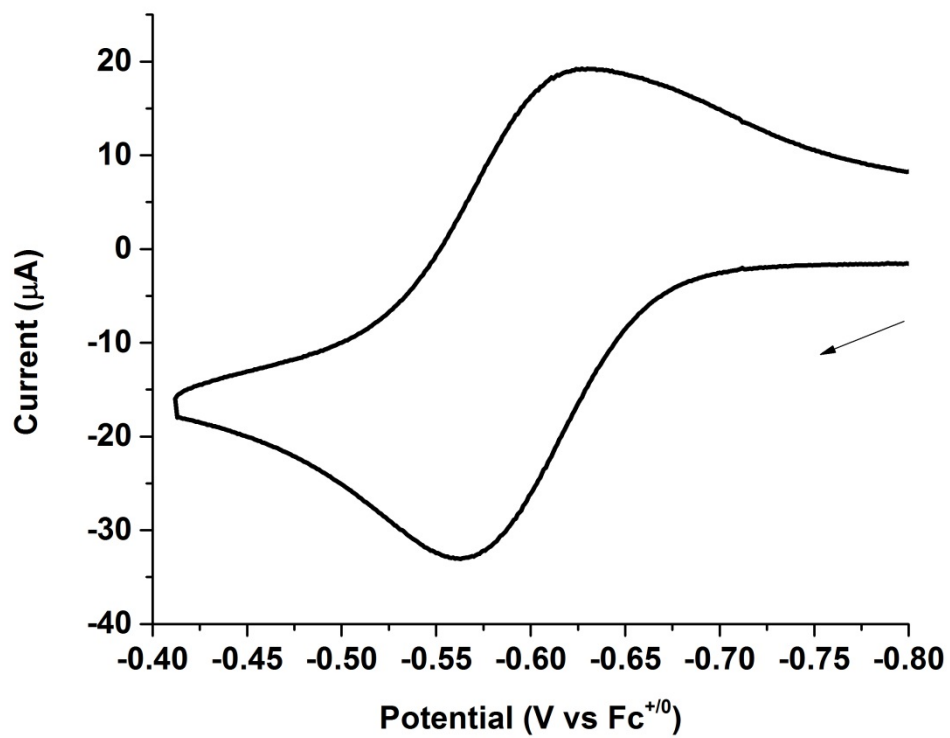


Figure S52. Cyclic voltammogram of CpCo(pdt)Fe(CO)₂(dppe) (**4d**) in CH₂Cl₂.
Conditions: See Figure S42.

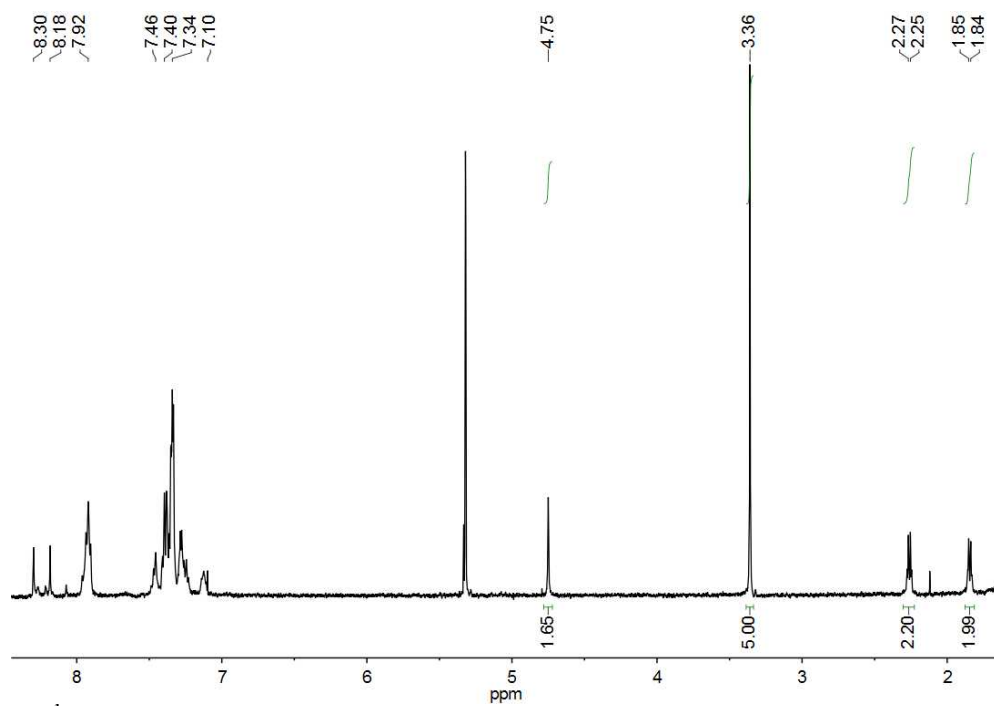


Figure S53. ^1H NMR spectrum of $\text{CpCo}(\text{edt})\text{Fe}(\text{CO})(\text{dppv})$ (**4a**) in CD_2Cl_2 .

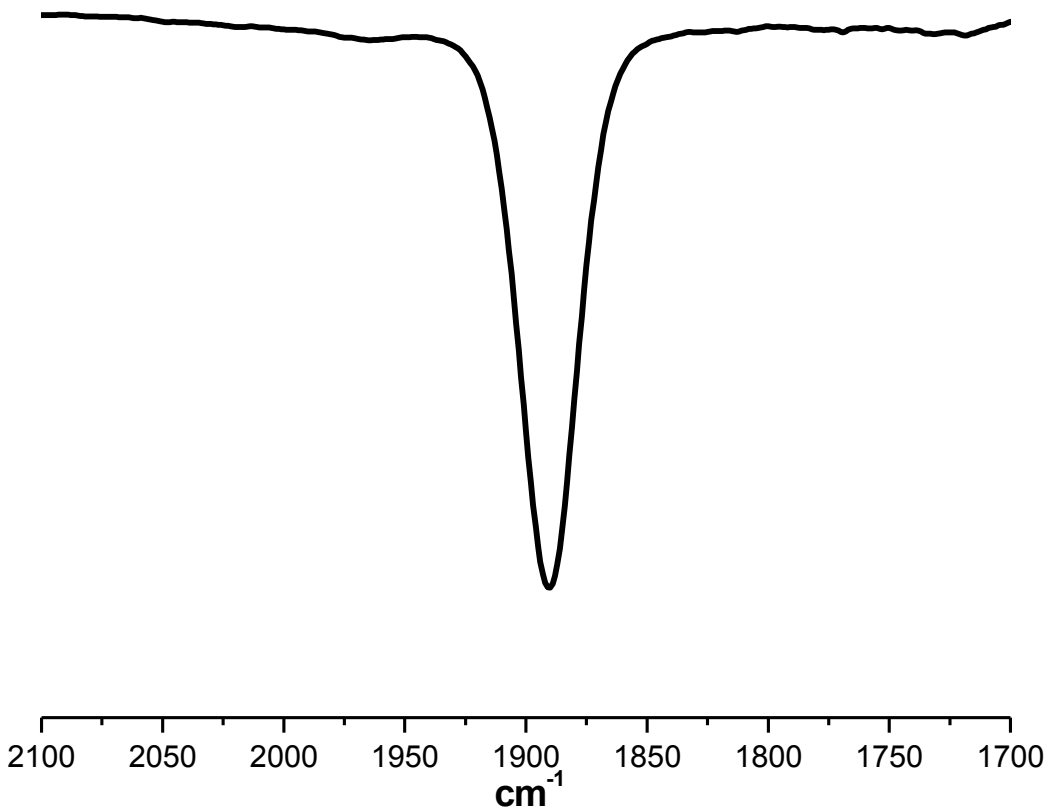


Figure S54. IR spectrum of $\text{CpCo}(\text{edt})\text{Fe}(\text{CO})(\text{dppv})$ (**4a**) in CH_2Cl_2 .