Supporting Information for

Hydrogen Production Catalyzed by Bidirectional, Biomimetic Models of the [FeFe]-Hydrogenase Active Site

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Contents:

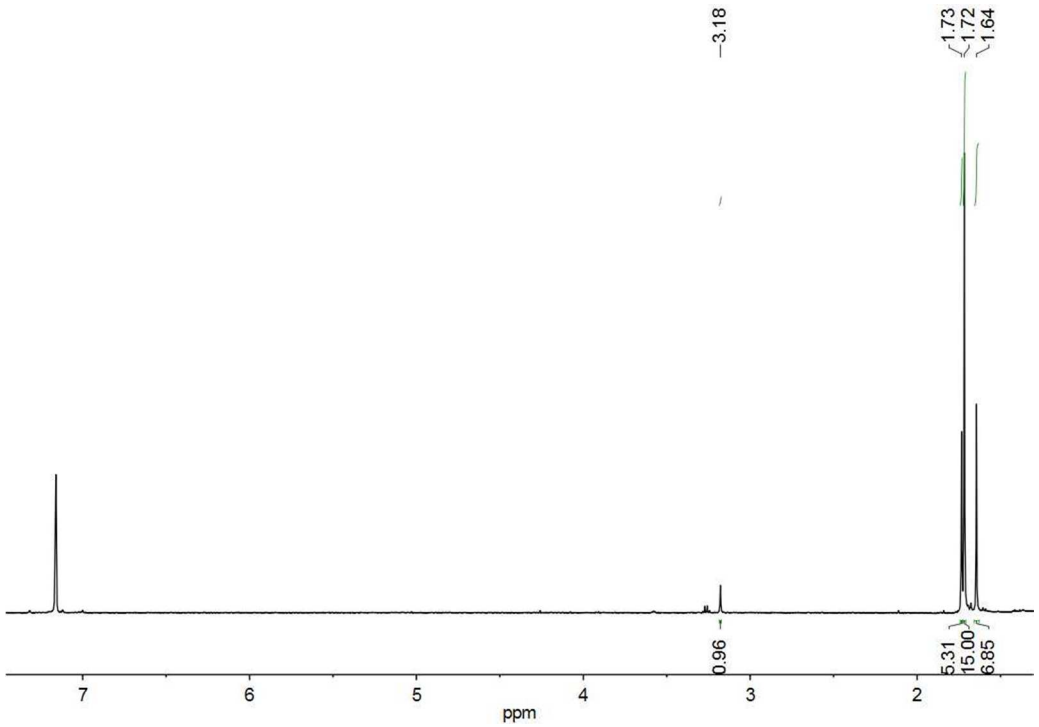

Figure S1. ^{1}H NMR spectrum of $FcMe_9$ in C_6D_6 solution.

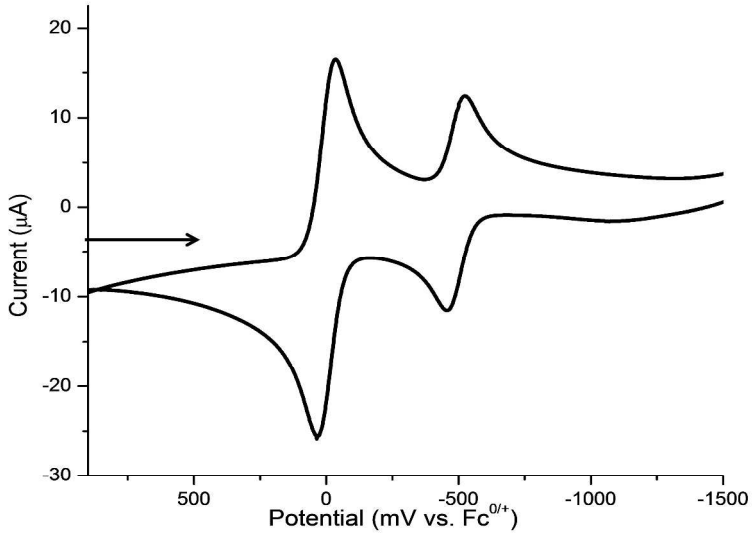

Figure S2. Cyclic voltammogram of 1.0 mM $FcMe_9$ in CH_2Cl_2 solution at 25 °C at 0.05 V/s. $E_{1/2}$ = -490 mV (i_{pa}/i_{pc} = 0.88). *Conditions:* 0.1 M $[Bu_4N]PF_6$ supporting electrolyte, Pt working and counter electrodes, Ag wire pseudoreference electrode. $FeCp_2$ is present as an internal standard.

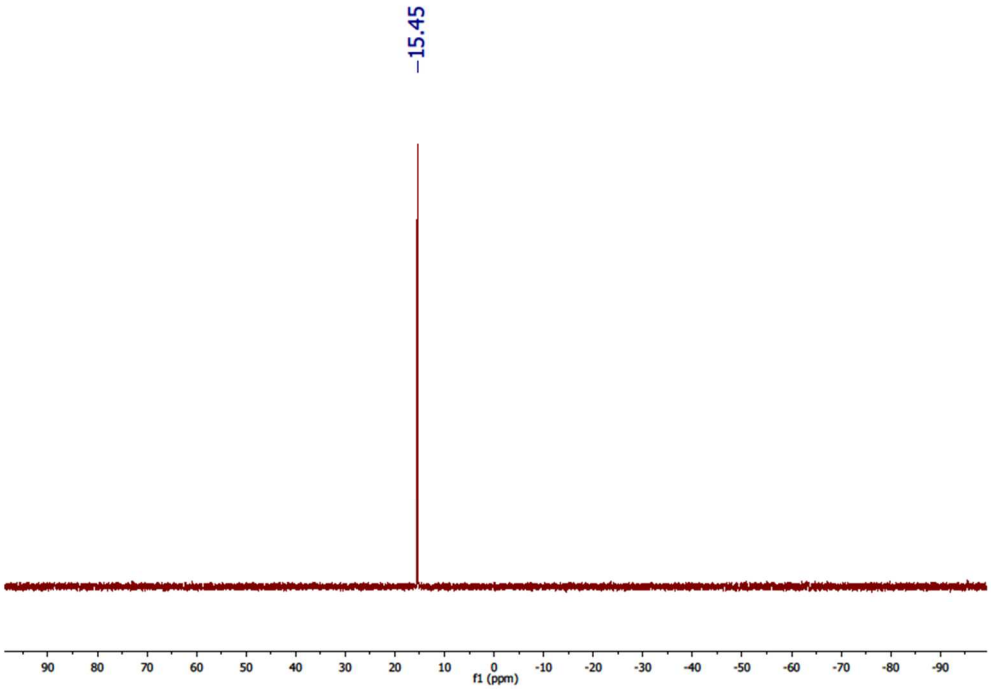

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of $[Fe(C_5Me_5)(C_5Me_4CH_2PEt_2H)]^+$ in CD_2Cl_2 solution.

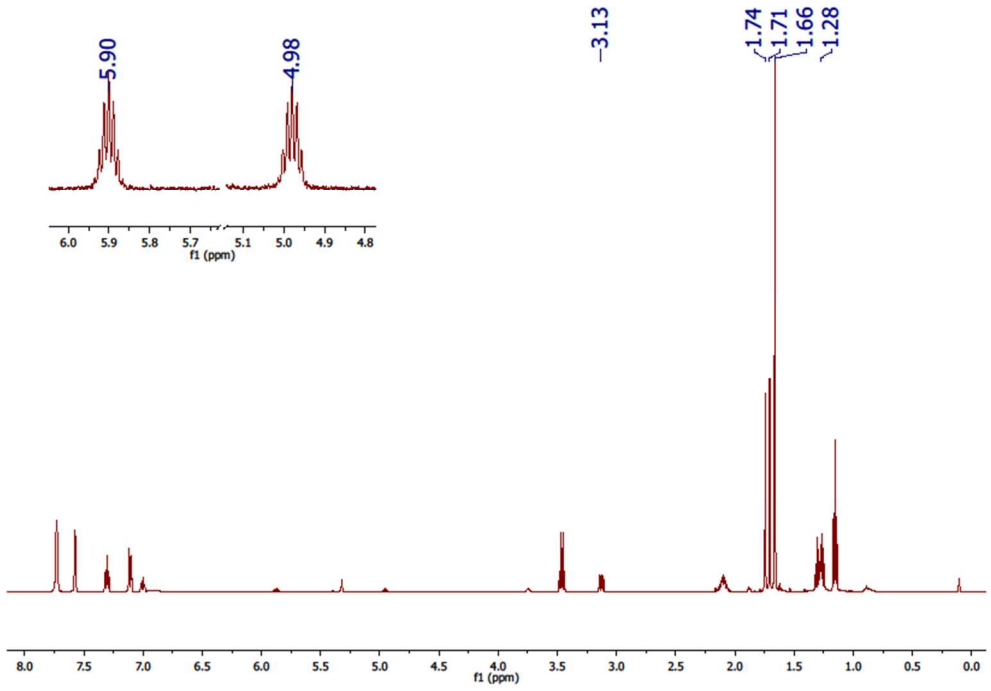

Figure S4. ^{1}H NMR spectrum of $[Fe(C_5Me_5)(C_5Me_4CH_2PEt_2H)]^+$ in CD_2Cl_2 solution. Region for the P*H* proton is enhanced.

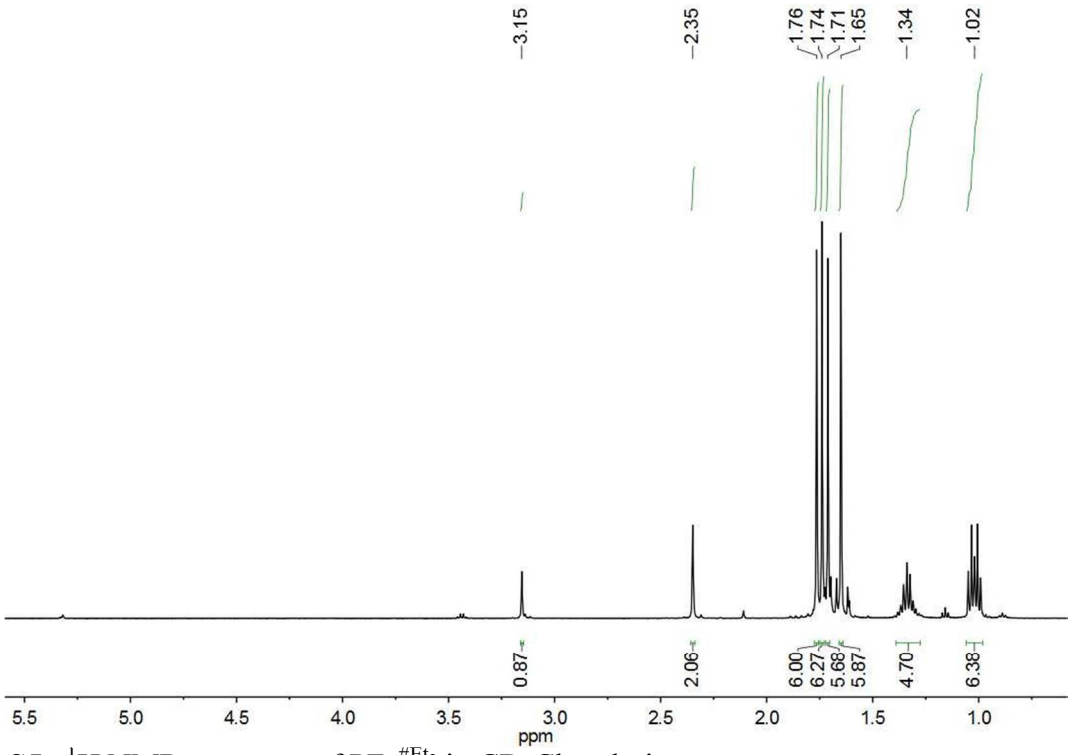

Figure S5. ^{1}H NMR spectrum of $PFc^{\#Et_2}$ in CD_2Cl_2 solution.

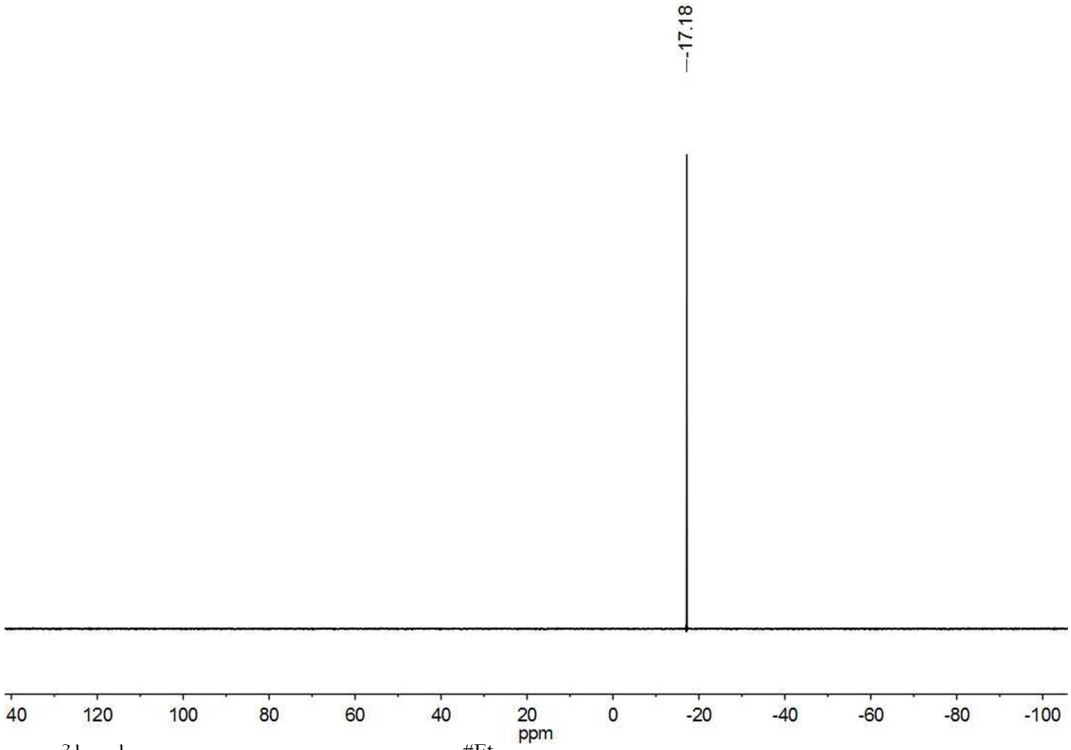

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of $PFc^{\#Et_2}$ in CD_2Cl_2 solution.

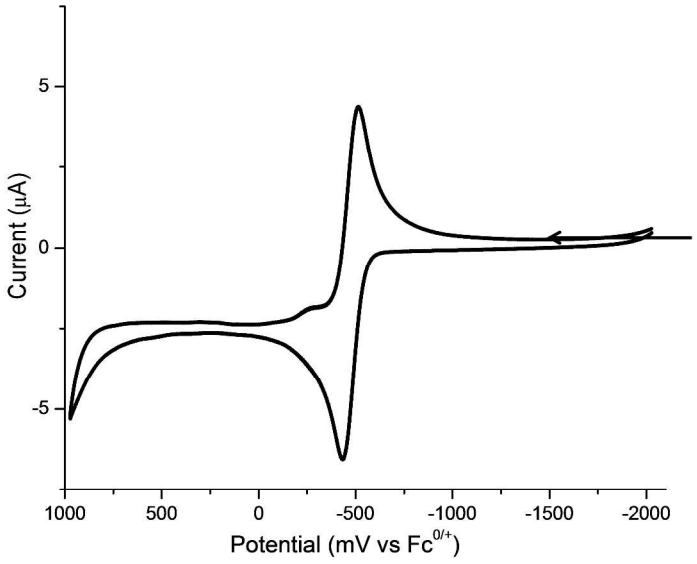

Figure S7. Cyclic voltammogram of 1.0 mM $PFc^{\#Et_2}$ in CH_2Cl_2 at 25 °C at 0.1 V/s. $E_{1/2}$ = -475 mV (i_{pa}/i_{pc} = 1.0). *Conditions:* 0.1 M $[Bu_4N]PF_6$ supporting electrolyte, Pt working and counter electrodes, Ag wire pseudoreference electrode. Ferrocene (Fc) was added at a later scan as an internal standard.

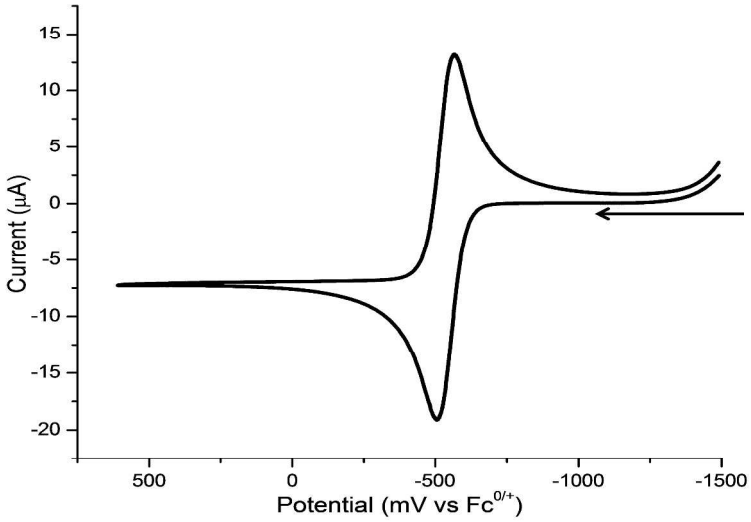

Figure S8. Cyclic voltammogram of 1.0 mM $PFc^{\#Et_2}$ in CH_2Cl_2 at 25 °C at 0.1 V/s. $E_{1/2}$ = -536 mV (i_{pa}/i_{pc} = 0.98). *Conditions:* 0.025 M $[Bu_4N]BAr^F{}_4$ supporting electrolyte, Pt working and counter electrodes, Ag wire pseudoreference electrode. Fc was added at a later scan as an internal standard.

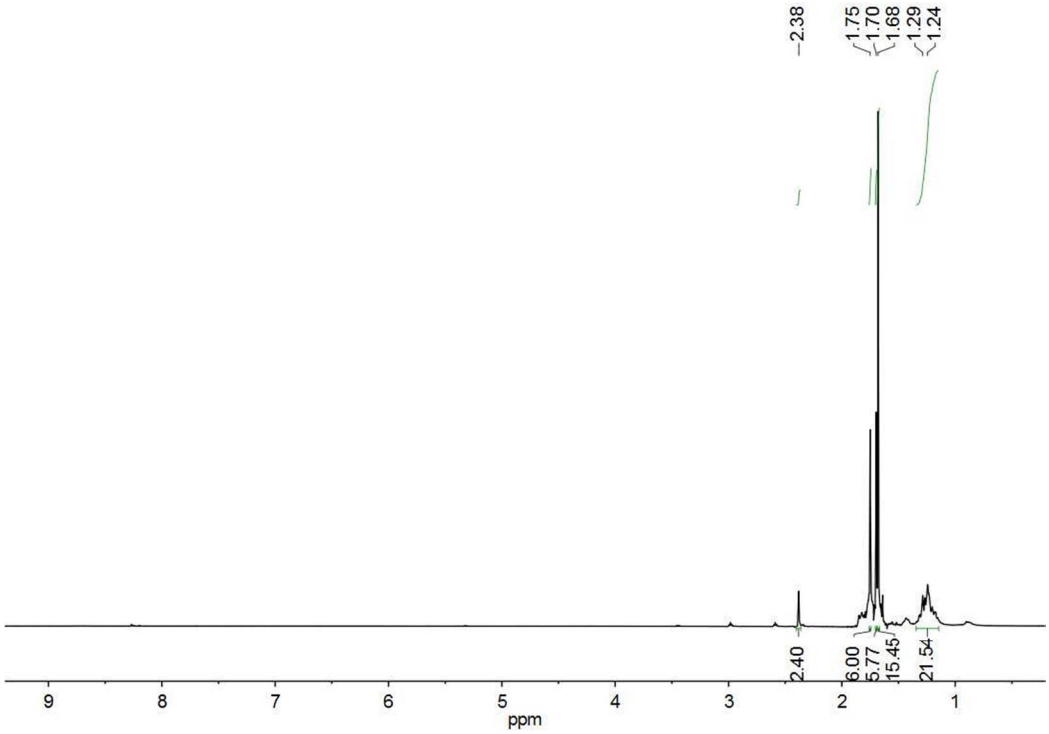

Figure S9. ^{1}H NMR spectrum of PFc*^{Cy_2} in CD_2Cl_2 solution.

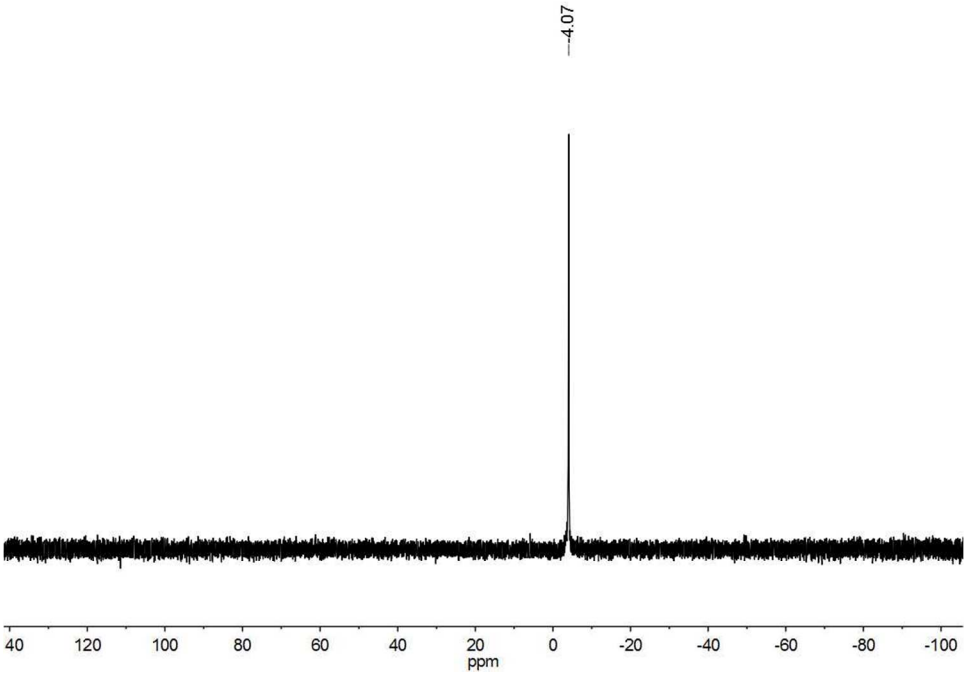

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of PFc*^{Cy_2} in CD_2Cl_2 solution.

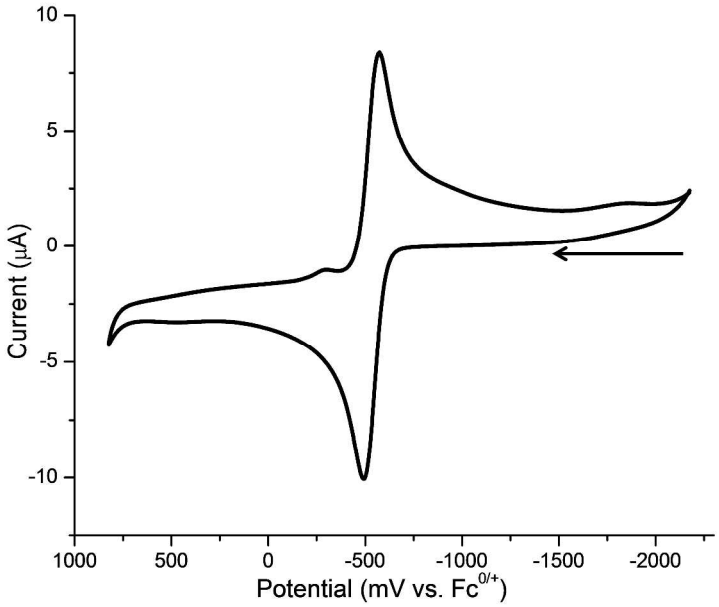

Figure S11. Cyclic voltammogram of 1.0 mM PFc*^{Cy_2} in CH_2Cl_2 at 25 °C at 0.1 V/s in $[Bu_4N]PF_6$. $E_{1/2}$ = -539 mV (i_{pa}/i_{pc} = 0.96). *Conditions:* see Figure S7.

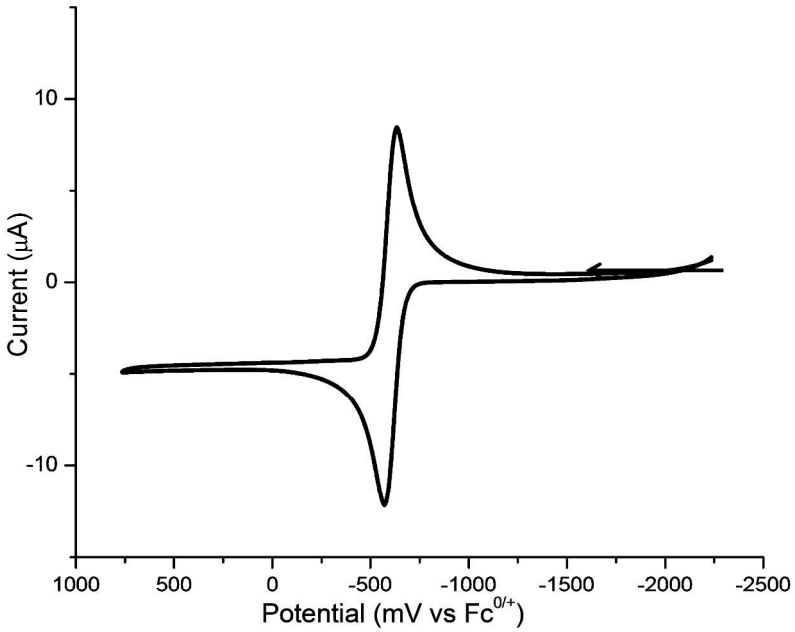

Figure S12. Cyclic voltammogram of 1.0 mM PFc*^{Cy_2} in CH_2Cl_2 solution at 25 °C at 0.1 V/s in $[Bu_4N]BAr^F{}_4$. $E_{1/2}$ = -602 mV (i_{pa}/i_{pc} = 0.96). *Conditions:* see Figure S8.

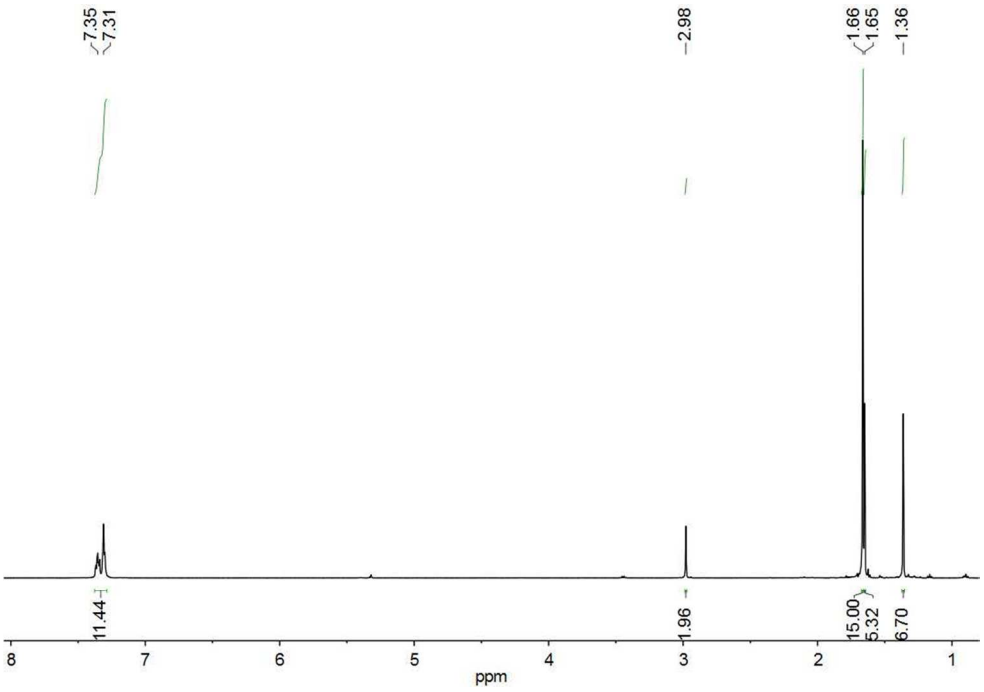

Figure S13. ^{1}H NMR spectrum of PFc*^{Ph_2} in CD_2Cl_2 solution.

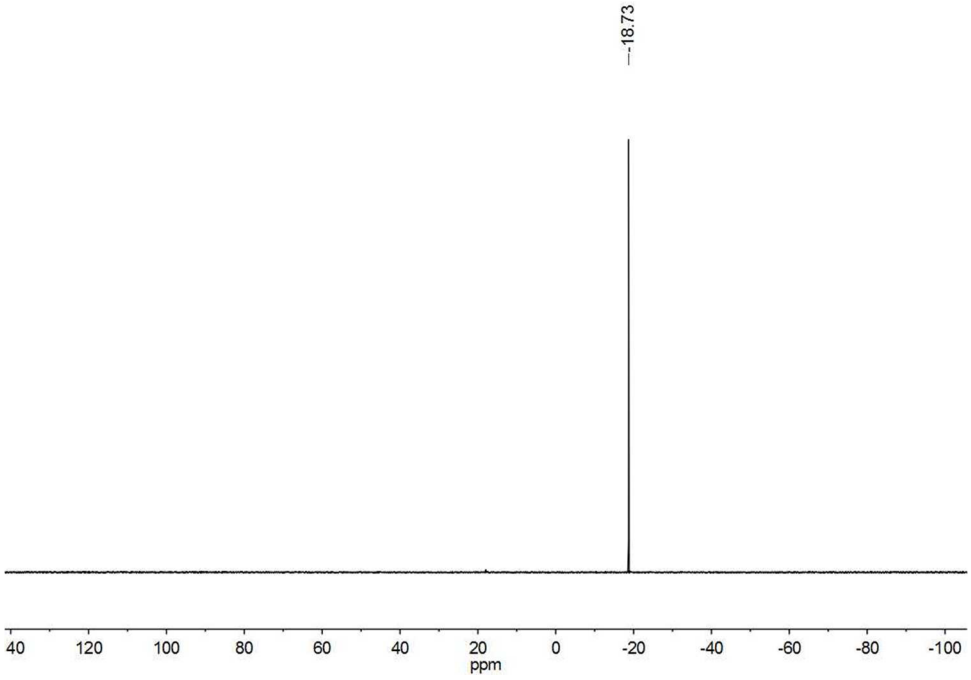

Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum of PFc*^{Ph_2} in CD_2Cl_2 solution.

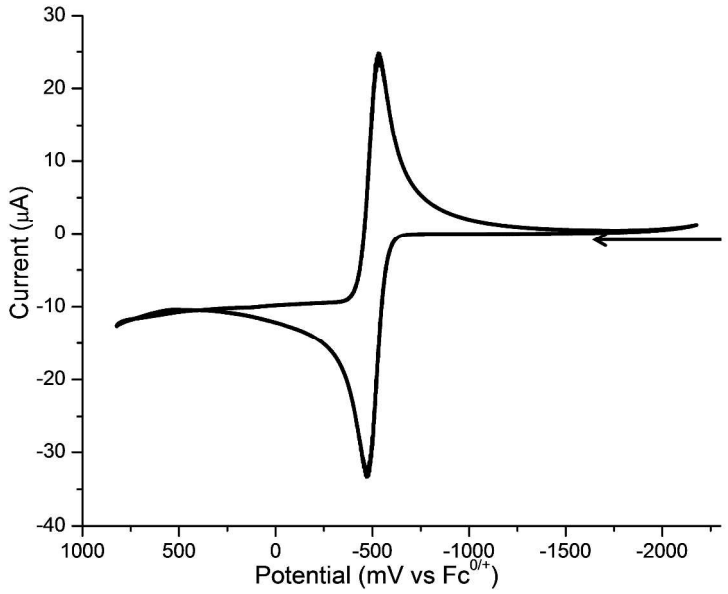

Figure S15. Cyclic voltammogram of 1.0 mM PFc*^{Ph_2} in CH_2Cl_2 at 25 °C at 0.1 V/s in $[Bu_4N]PF_6$. $E_{1/2}$ = -501 mV (i_{pa}/i_{pc} = 0.98). *Conditions:* see Figure S7.

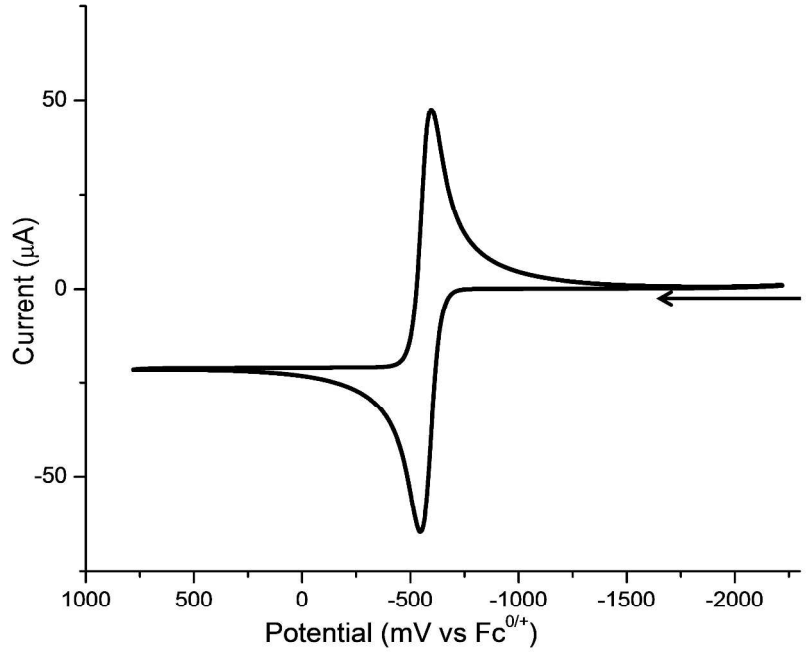

Figure S16. Cyclic voltammogram of 1.0 mM PFc*^{Ph_2} in CH_2Cl_2 solution at 25 °C at 0.1 V/s in $[Bu_4N]BAr^F{}_4$. $E_{1/2}$ = -572 mV (i_{pa}/i_{pc} = 0.95). *Conditions:* see Figure S8.

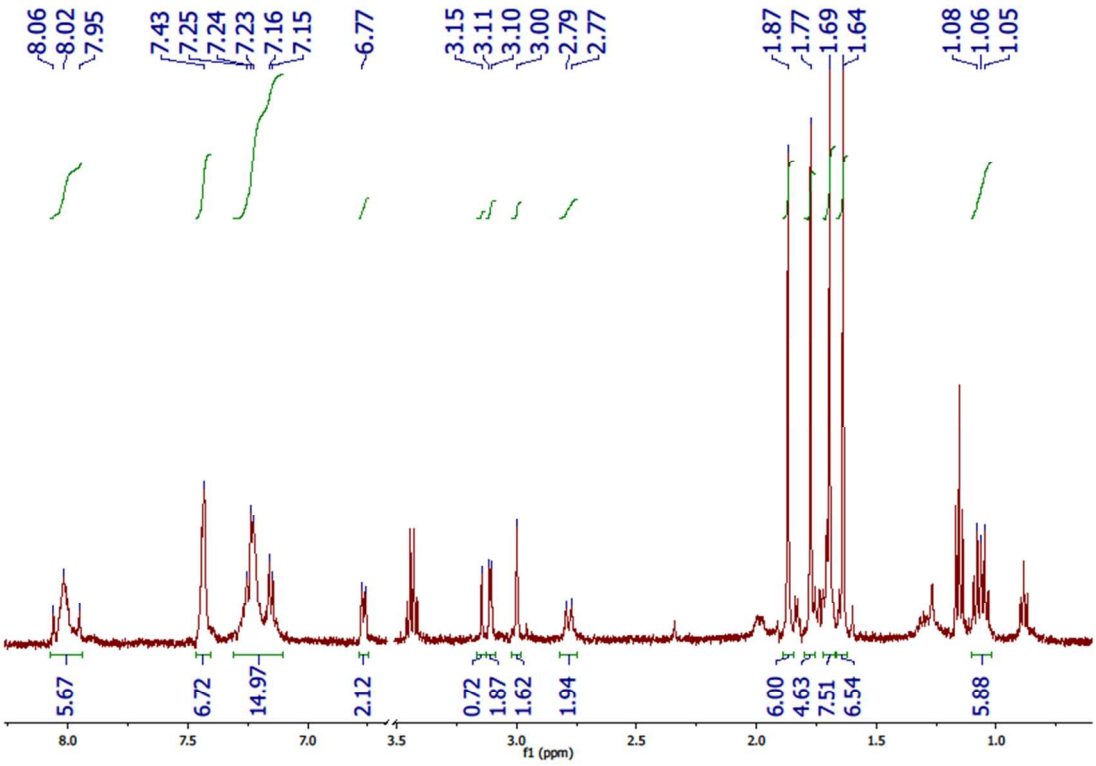

Figure S17. ^{1}H NMR spectrum of $Fe_2(adt^{Bn})(CO)_3(dppv)(PFc^{\#Et_2})$ in CD_2Cl_2 solution.

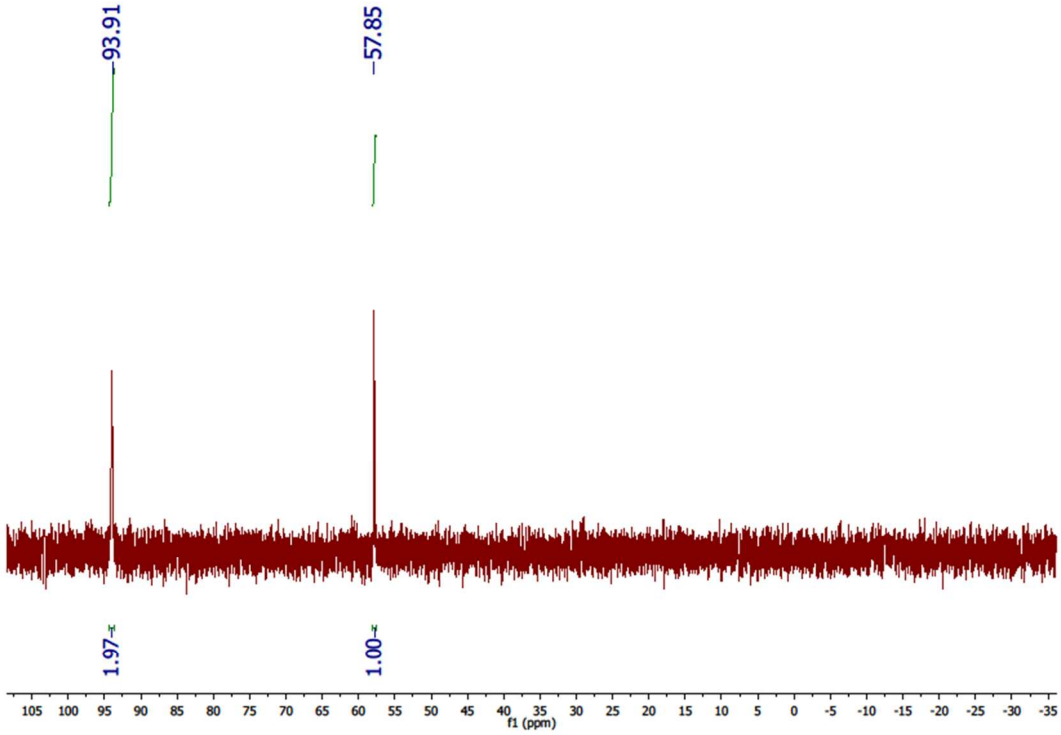

Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of $Fe_2(adt^{Bn})(CO)_3(dppv)(PFc^{\#Et_2})$ in CD_2Cl_2 solution.

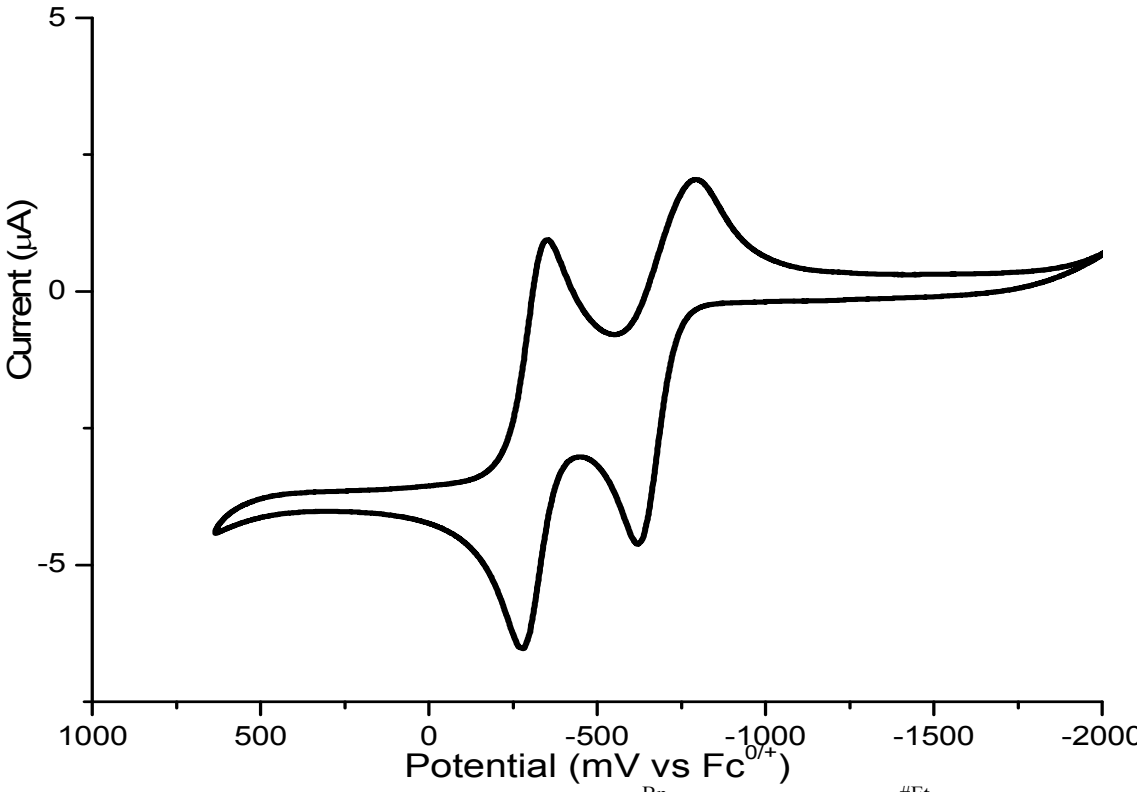

Figure S19. Cyclic voltammogram of 1.0 mM $Fe_2(adt^{Bn})(CO)_3(dppv)(PFc^{\#Et_2})$ in CH_2Cl_2 solution at 25 °C at 0.1 V/s in $[Bu_4N]BAr^F_4$. $E_{1/2}$ = -713 mV (i_{pa}/i_{pc} = 0.77), -315 mV (i_{pa}/i_{pc} = 0.86). *Conditions:* see Figure S8.

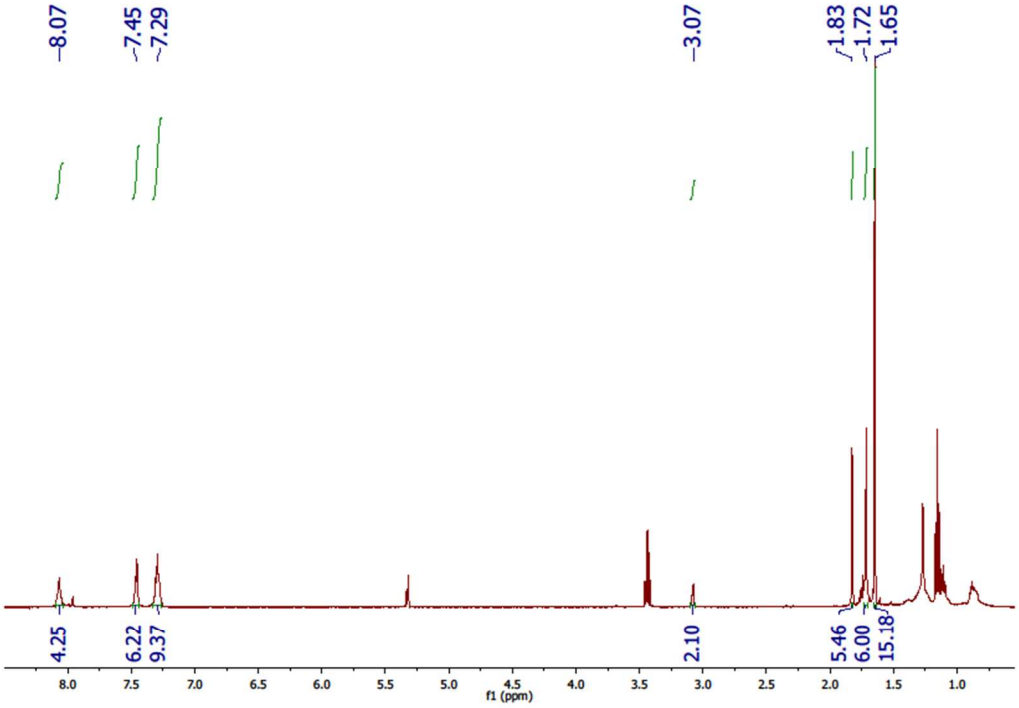

Figure S20. ^1H NMR spectrum of $Fe_2(pdt)(CO)_3(dppv)(PFc^{*Et_2})$ in CD_2Cl_2 solution.

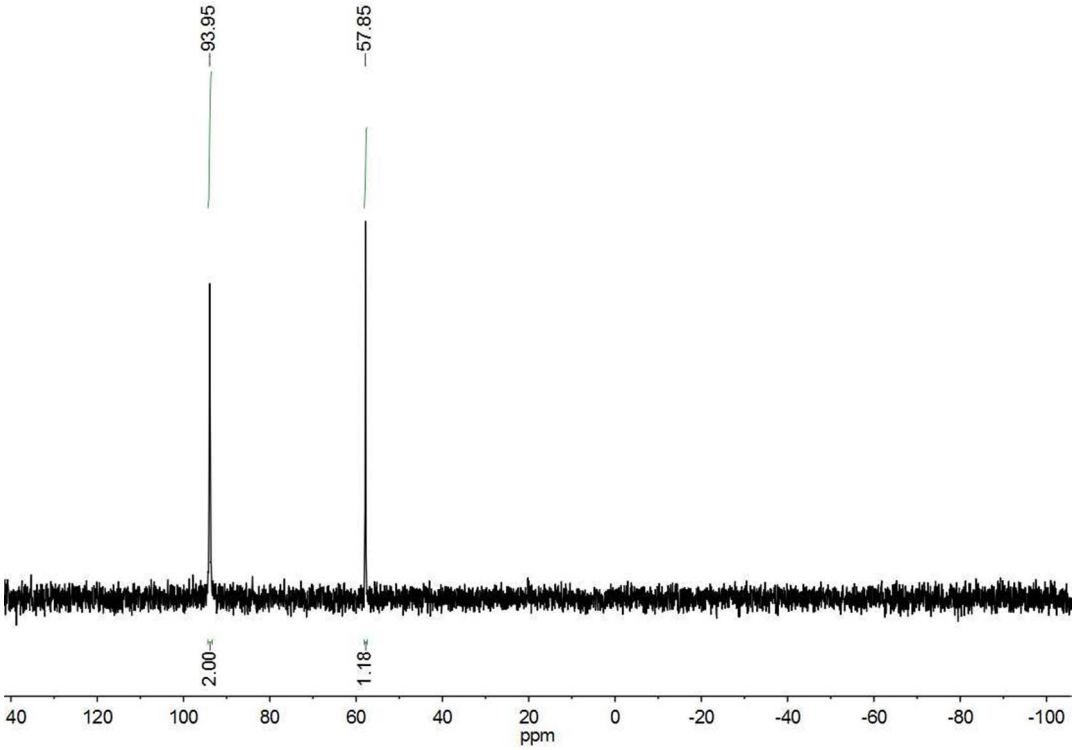

Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of $Fe_2(pdt)(CO)_3(dppv)(PFc^{*Et_2})$ in CD_2Cl_2 solution.

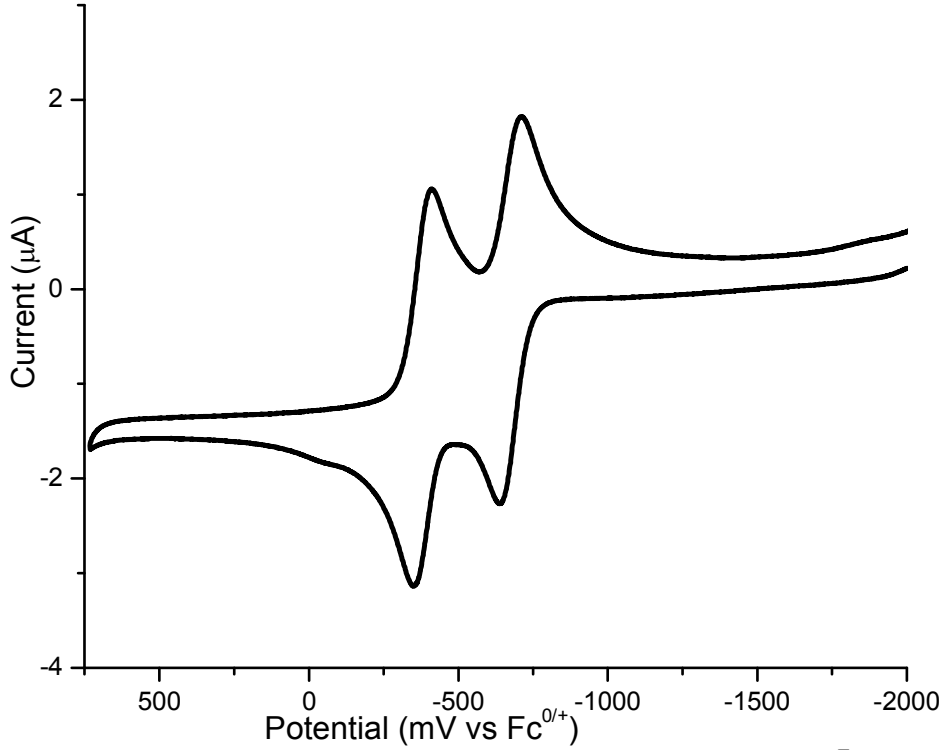

Figure S22. Cyclic voltammogram of 1.0 mM of $Fe_2(pdt)(CO)_3(dppv)(PFc^{*Et_2})$ in CH_2Cl_2 solution at 25 °C at 0.1 V/s in $[Bu_4N]BAr^F{}_4$. $E_{1/2}$ = -675 mV (i_{pa}/i_{pc} = 0.73), -382 mV (i_{pa}/i_{pc} = 0.97). *Conditions:* see Figure S8.

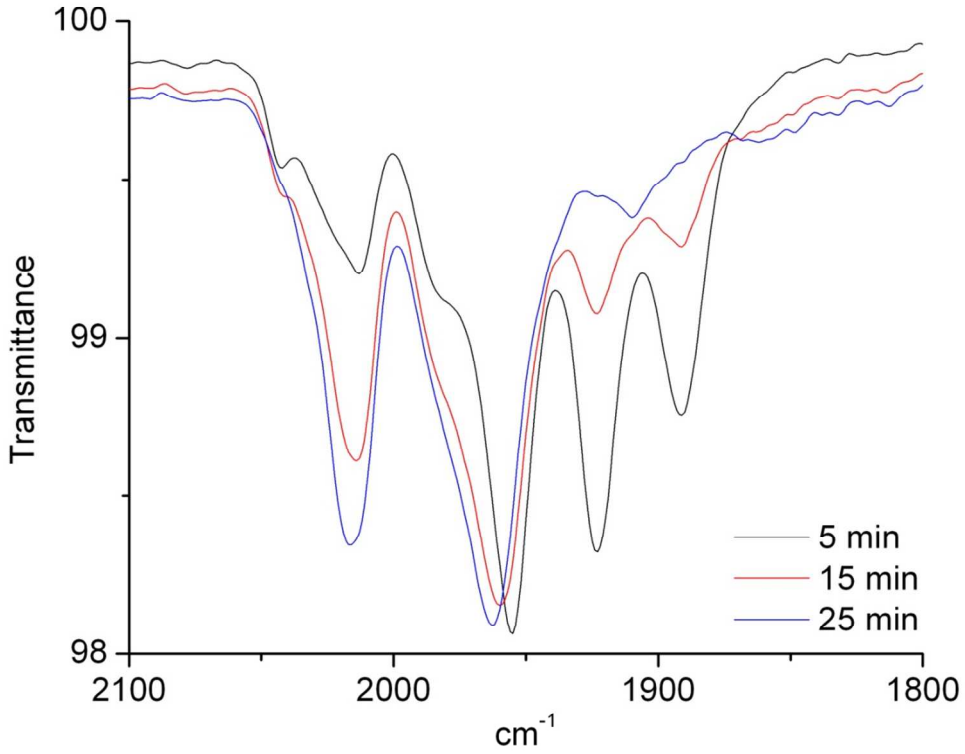

Figure S23. Tautomerization of N-protonated [**1**H]$^+$ to the hydride [H**1**]$^+$ monitored by solution IR spectroscopy (CH_2Cl_2, 28 °C).

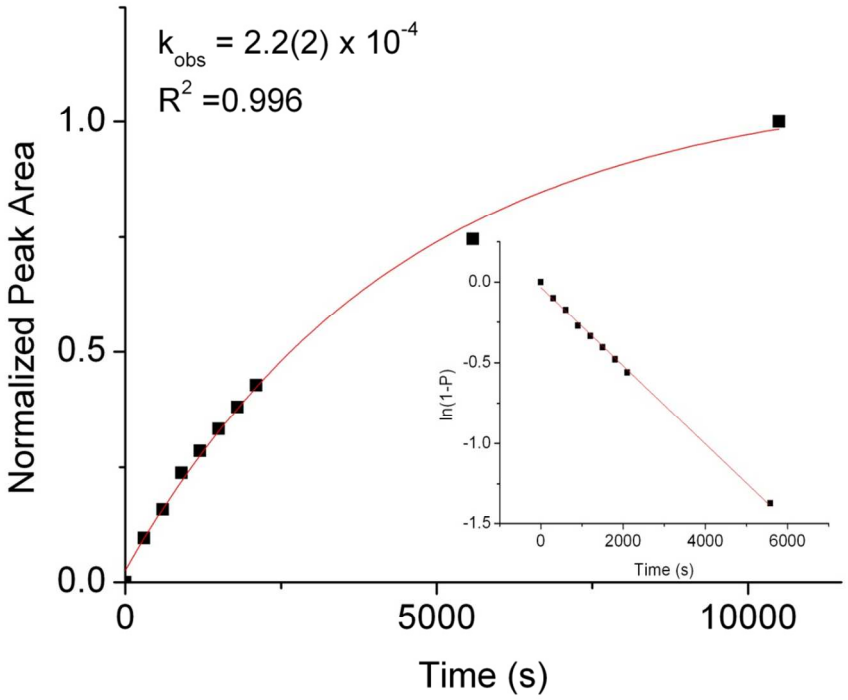

Figure S24. Kinetic plot of the tautomerization of N-protonated [**1**H]$^+$ to the hydride [μ-H**1**]$^+$, as monitored by ^{1}H NMR spectroscopy and fit to a first order exponential. *Inset:* linearized first plot.

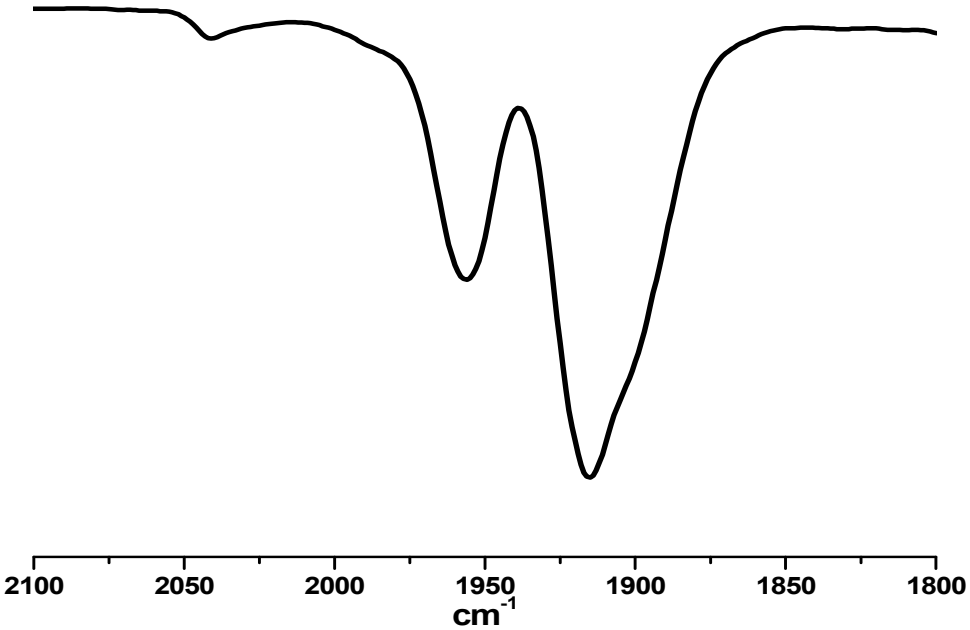

Figure S25. IR spectra (CH_2Cl_2 solution) of a solution prepared by treating [**1**]^0 at -15 °C with >2 equiv of $[H(OEt_2)_2]BAr^F{}_4$.

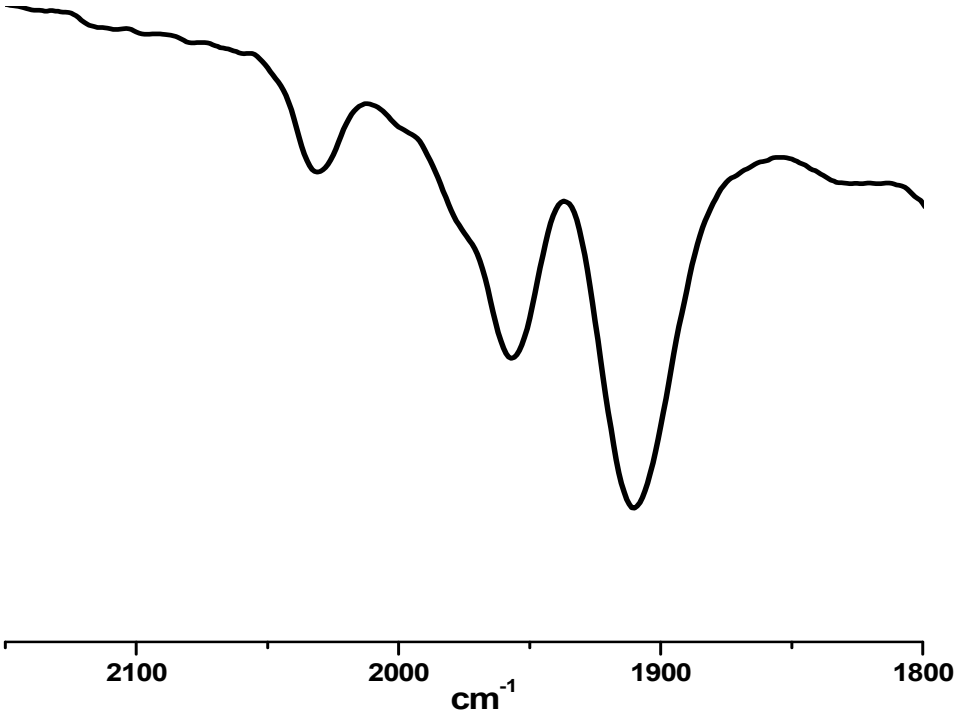

Figure S26. IR spectrum 2.5 h after the addition of 5 equiv Fc* and 10 equiv of $[H(OEt_2)_2]BAr^F{}_4$ to $[\mathbf{2}]^0$.
Assignments:
$[\mathbf{2}H]^{2+}$: 1957 and 1910 cm^{-1}
$[\mu\text{-}H\mathbf{2}]^{+}$: 2031 cm^{-1}

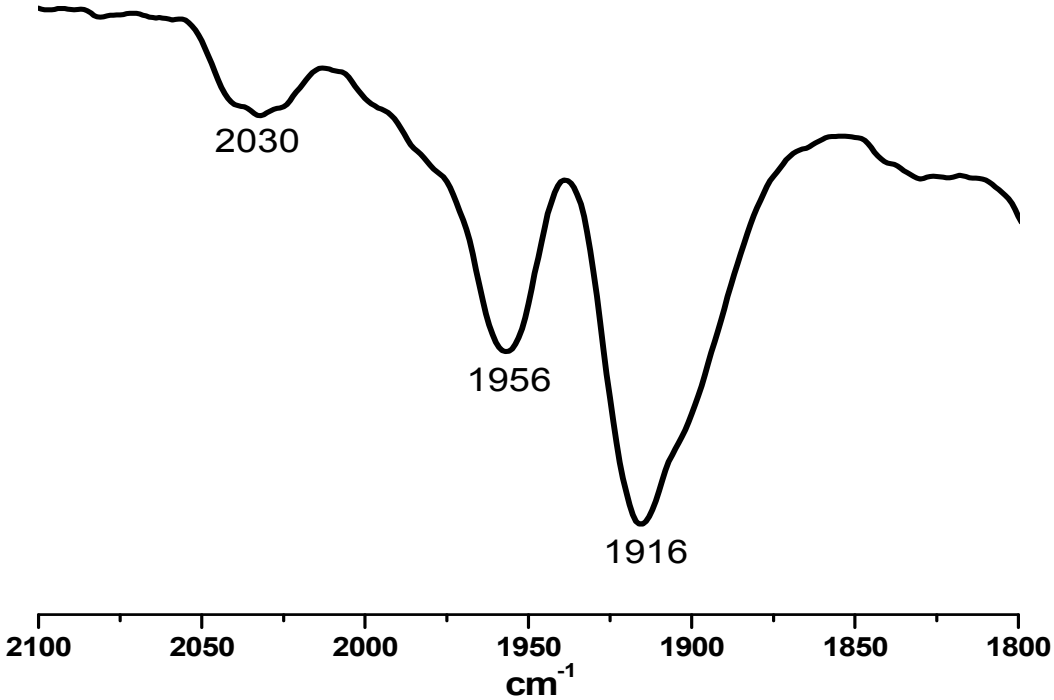

Figure S27. IR spectrum of reaction solution at the 2nd time point in Figure 8. Predominant species in solution identified as the ammonium-ferrocenium dication $[\mathbf{1}H]^{2+}$.

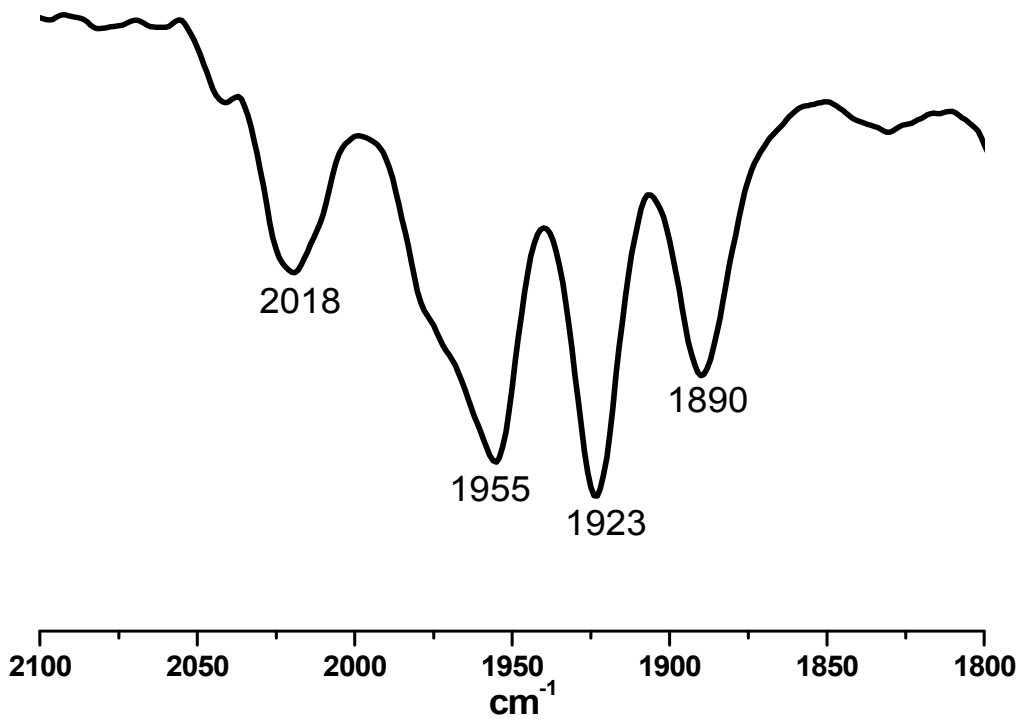

Figure S28. IR spectrum of reaction solution at the 3rd time point in Figure 8.
Assignments:
$[H\mathbf{1}]^+$: 1955, 1923, 1890 cm^{-1}
$[\mu\text{-}H\mathbf{1}]^+$: 2018, shoulder near 1970 cm^{-1}

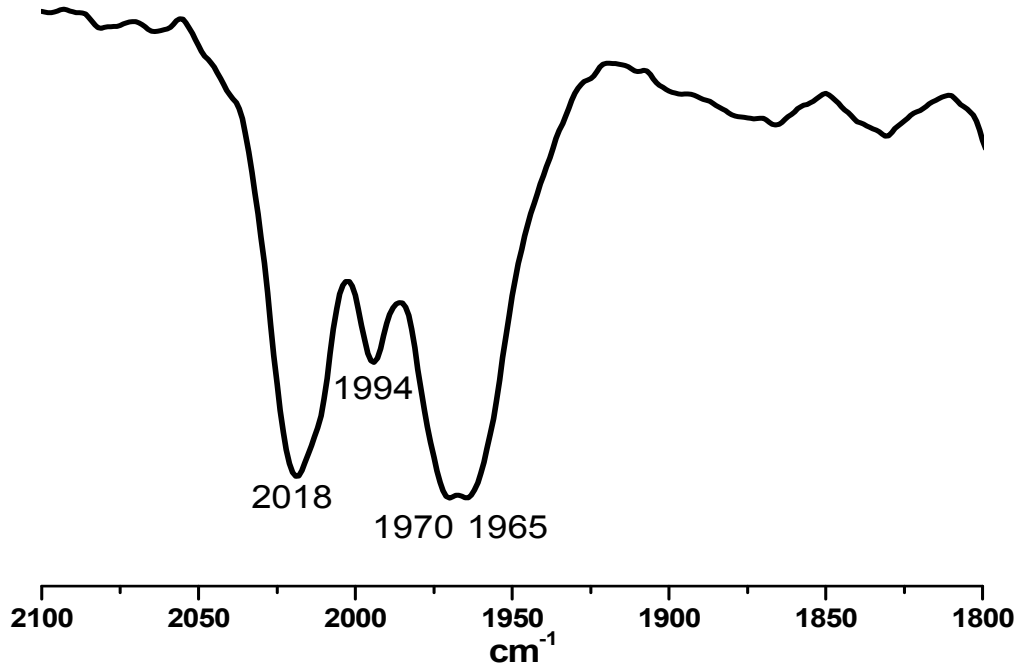

Figure S29. IR spectrum of reaction solution at the 4th time point in Figure 8.
Assignment:
$[\mu\text{-}H\mathbf{1}]^+$:2018, 1970 cm^{-1}.

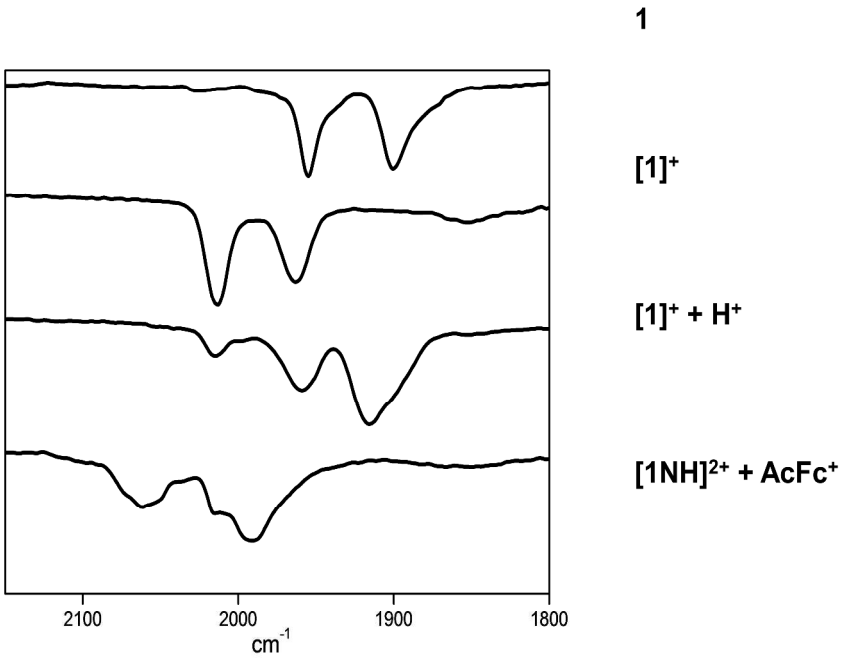

Figure S30. IR spectra (CH_2Cl_2 solutions) for $Fe_2(adt^{Bn})(CO)_3(dppv)(PFc*^{Et_2})$ ($[\mathbf{1}]^0$) (top), the resulting solution after 1.0 equiv of $FcBAr^F{}_4$ (middle top), further reaction of $[\mathbf{1}]^+$ with an equiv of $[H(OEt_2)_2]BAr^F{}_4$ (middle bottom) and the result of addition of 1 equiv of acetylferrocenium to that solution.

Reference:

$[\mathbf{1}]^0$: 1955, 1900 cm^{-1}

$[\mathbf{1}]^+$: 2013, 1963 cm^{-1}

$[\mathbf{1}H]^{2+}$: 1960, 1916 cm^{-1}

$[\mathbf{1}H]^{3+}$: 2062, 1991 cm^{-1}

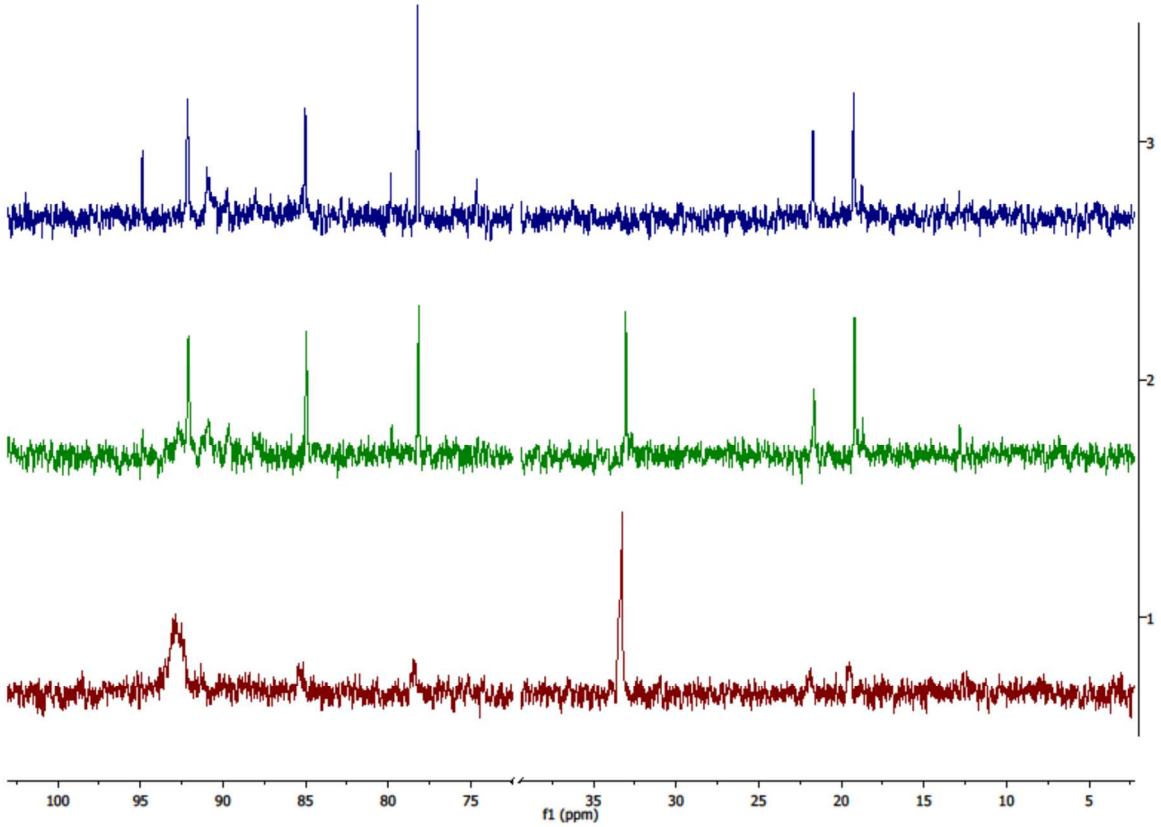

Figure S31. $^{31}P\{^{1}H\}$ NMR spectra of various stages in the reaction of $Fe_2(adt^{Bn})(CO)_3(dppv)(PMe_3)$ and 5 equiv of $[H(OEt_2)_2]BAr^F{}_4$: 50 min (bottom, red) and 260 min (middle, green) and 18.25 h (top, blue). The solution was maintained at 0 °C for the first 3 h before being allowed to warm to room temperature overnight.
Assignments:
$Fe_2(adt^{Bn})(CO)_3(dppv)(PMe_3)$: δ 92.6, 19.7
$[(\mu\text{-}H)Fe_2(adt^{Bn})(CO)_3(dppv)(PMe_3)]^+$: δ 93 and 24.[1]

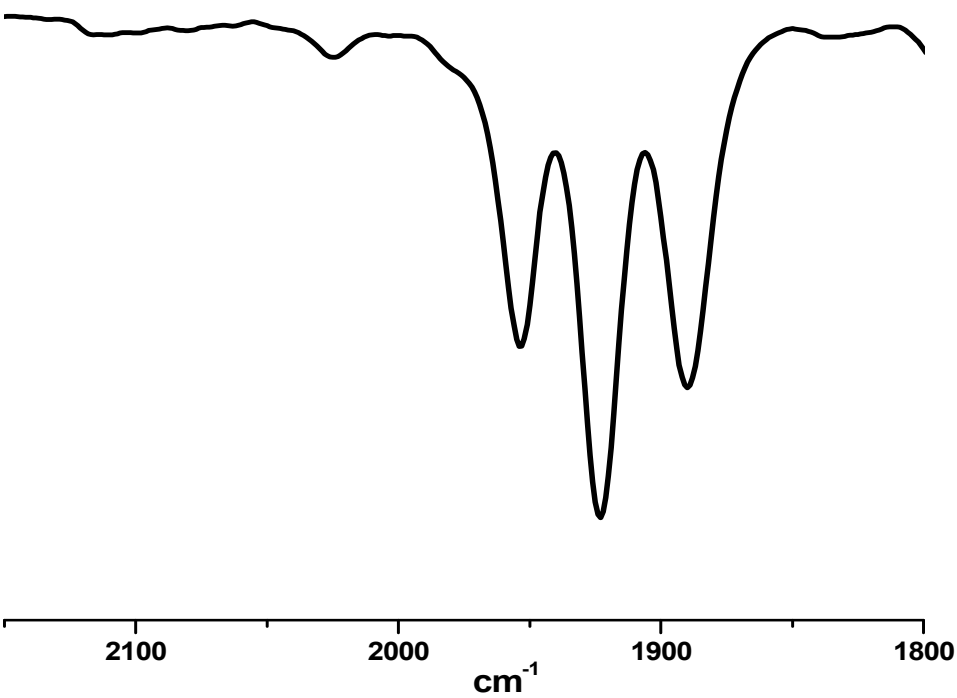

Figure S32. IR spectrum resulting from treating [**1**]^0 with 5 equiv of Fc* and 10 equiv of $[NPh_2H_2]BAr^F{}_4$. By gas chomatographic analysis, ~ 0.30 equiv H_2 was produced. IR was recorded 4.25 hours after acid was added to [**1**]^0.

(1) Olsen, M. T.; Barton, B. E.; Rauchfuss, T. B. *Inorg. Chem.* 2009, *48*, 7507.