Supporting information for "Diiron Azamonothiolates via Scission of Dithiadiazacyclooctanes by Iron Carbonyls"

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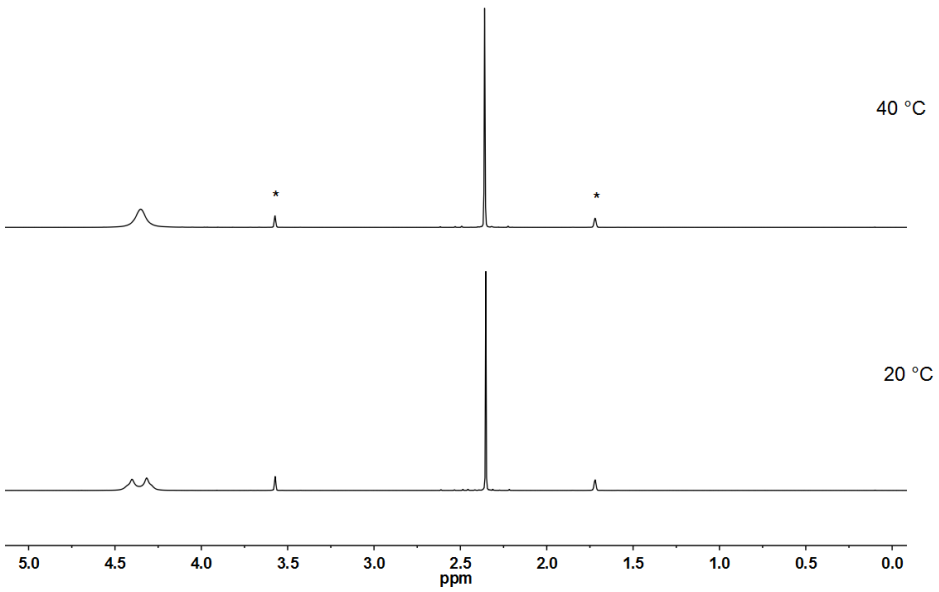

Figure S1: ^{1}H NMR spectra (500 MHz, d_8-THF) of $S_2N^{Me}{}_2$ at two temperatures. * Residual solvent. δ 2.44 (s, 6H, NCH_3), 4.24 (d, 4H, NCH_2S), 4.52 (d, 4H, NCH_2S).

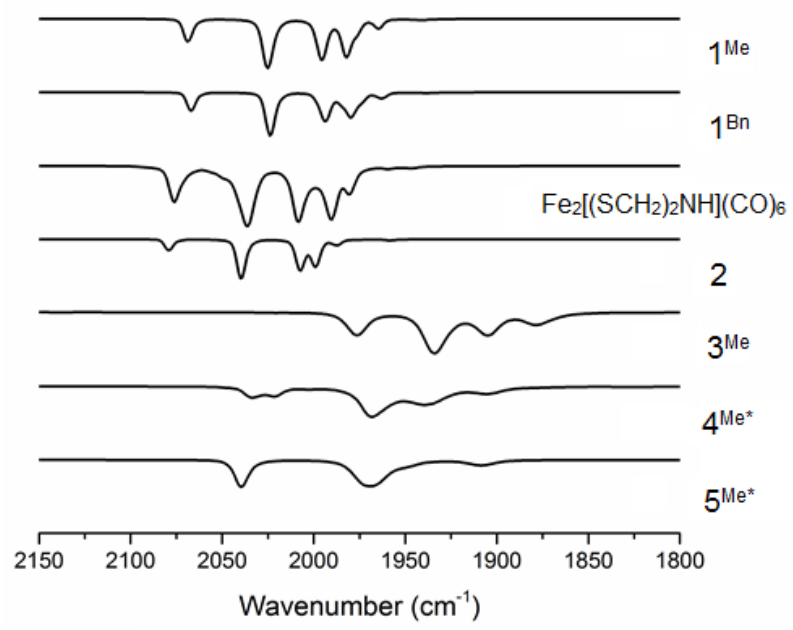

Figure S2. IR spectra of compounds discussed in this report recorded in hexanes.* Recorded on CH_2Cl_2 solutions.

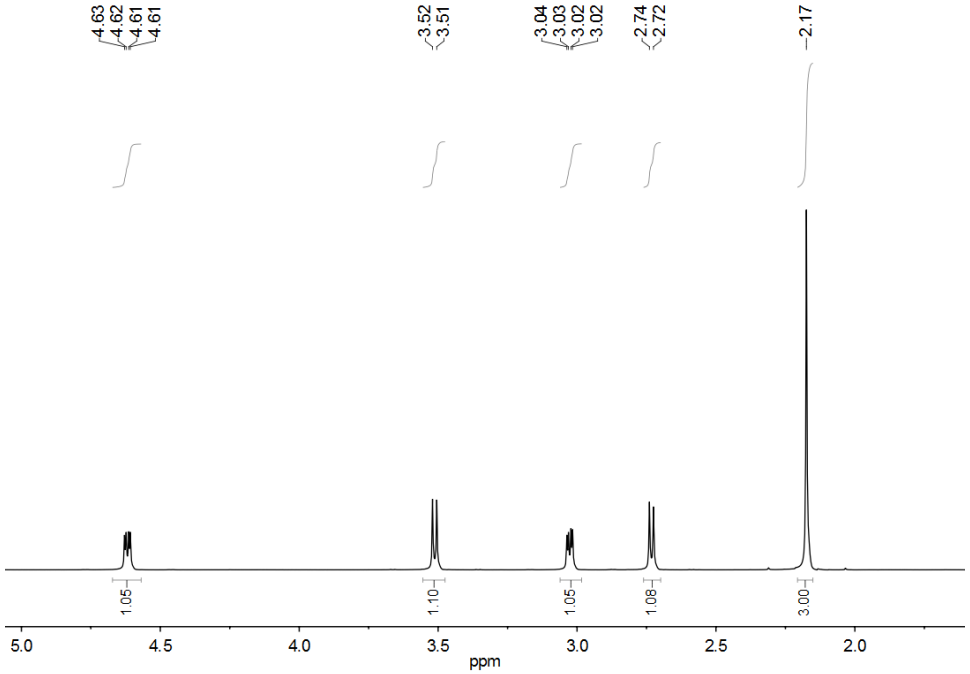

Figure S3. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2 solution) of $\mathbf{1^{Me}}$.
Assignments: δ 2.17 (s, 3H, NC*H*$_3$), 2.73 (d, 1H, NC*H*$_2$Fe), 3.03 (dd, 1H, NC*H*$_2$Fe), 3.52 (d, 1H, NC*H*$_2$S), 4.63 (dd, 1H, NC*H*$_2$S).

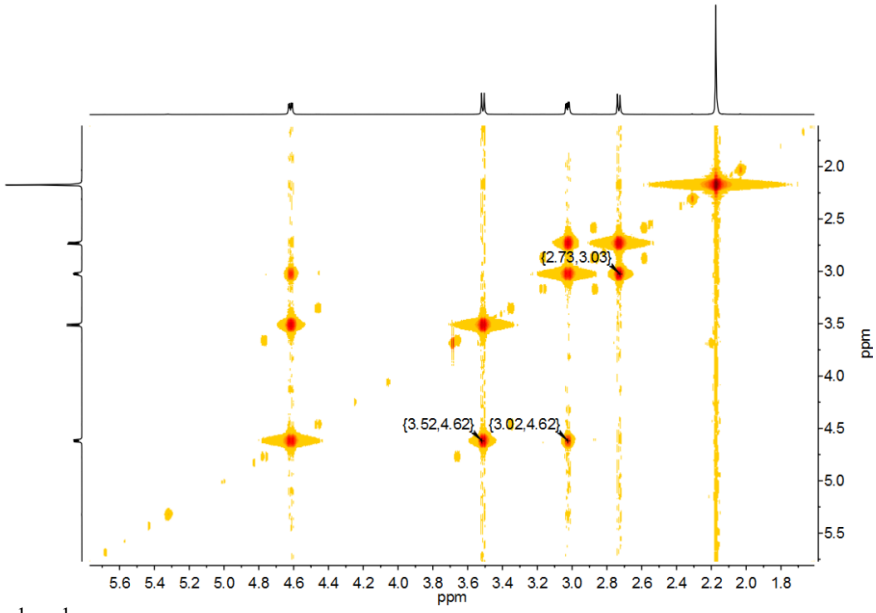

Figure S4. ^{1}H-^{1}H correlation (COSY) NMR spectrum (500 MHz, CD_2Cl_2 solution) of $\mathbf{1^{Me}}$.

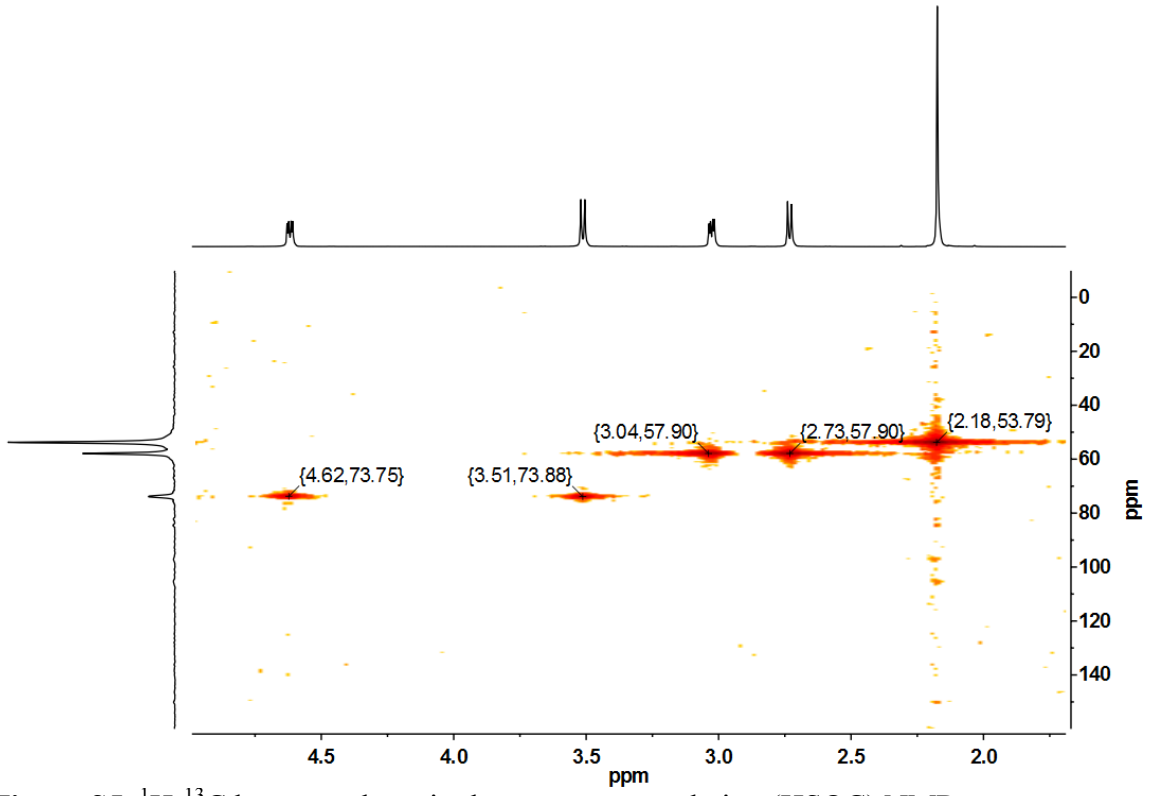

Figure S5. ^{1}H-^{13}C heteronuclear single-quantum correlation (HSQC) NMR spectrum (500 MHz, CD_2Cl_2 solution) of $\mathbf{1^{Me}}$.

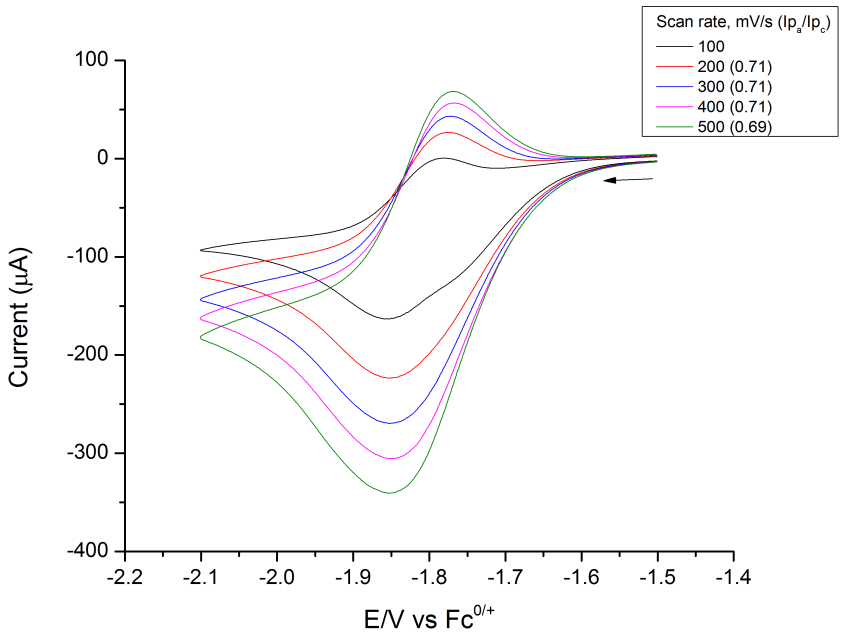

Figure S6. Cyclic Voltammogram of $\mathbf{1^{Me}}$ at various scan rates. *Conditions:* 3mM solution in CH_2Cl_2, 0.1M NBu_4PF_6 electrolyte; glassy carbon working electrode, Ag/AgCl reference electrode, and Pt wire counter electrode.

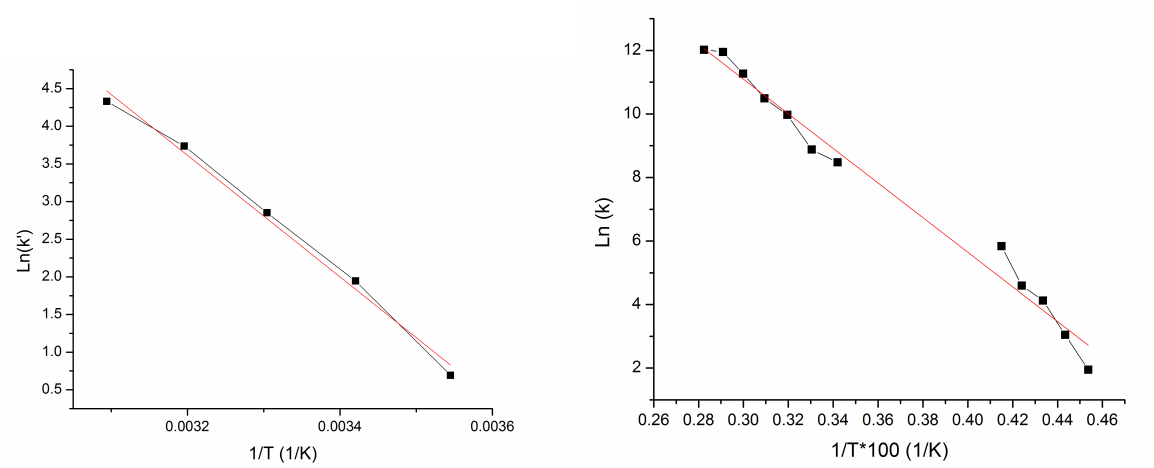

Figure S7. Arrhenius plots for the dynamic processes of **1**^{Me} described by k_{rigid} (left), and $k_{non\text{-}rigid}$ (right).

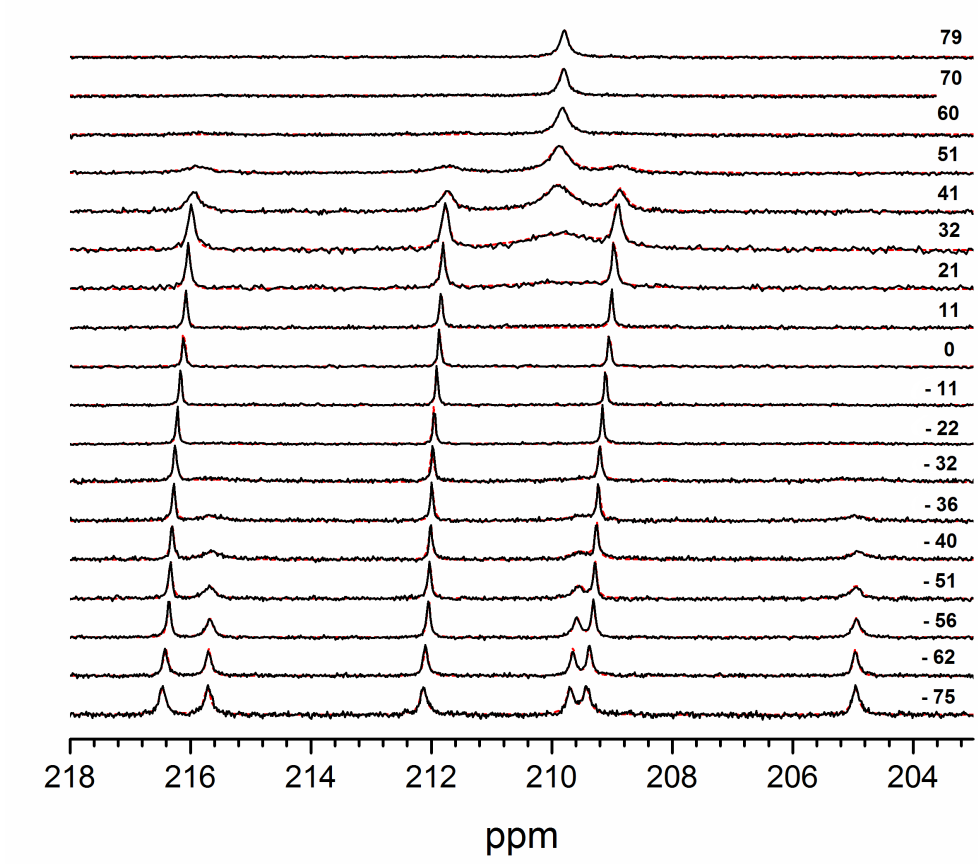

Figure S8: ^{13}C NMR spectra (125.7 MHz, d_8-toluene solution) of compound **1**^{Me} at various temperatures (black), and NMR simulations (red) at various temperatures (°C). Simulations were generated using WIND-NMR software provided by Hans J. Reich, University of Wisconsin.

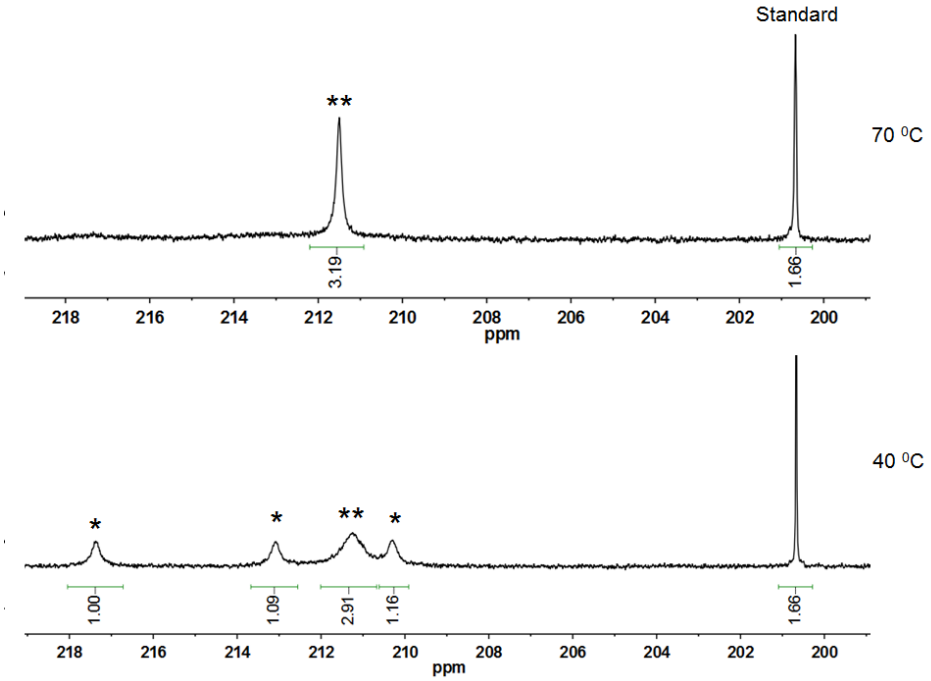

Figure S9. ^{13}C NMR spectra (125.7 MHz, d_8-toluene solution) of **1^{Me}** at two temperatures with ethylacetoacetate as an internal standard. *Rigid, ** Non-rigid.

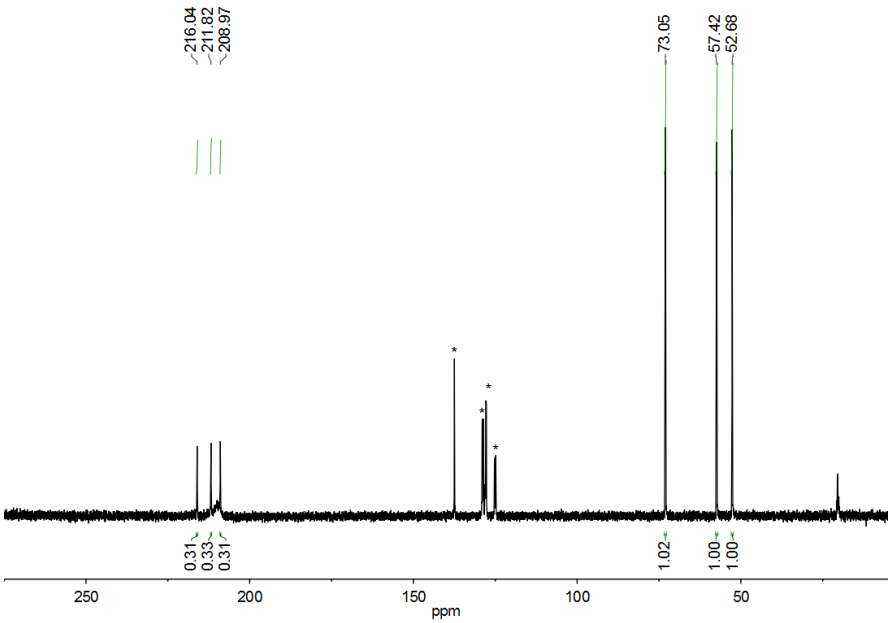

Figure S10. ^{13}C{^{1}H} NMR spectrum (125.7 MHz, d_8-toluene solution) of **1^{Me}** at 20 ºC. * Residual solvent. *Assignments:* δ 52.7 (s, 1C, N*C*H$_3$), 57.4 (s, 1C, N*C*H$_2$Fe), 73.1 (s, 1C, N*C*H$_2$S).

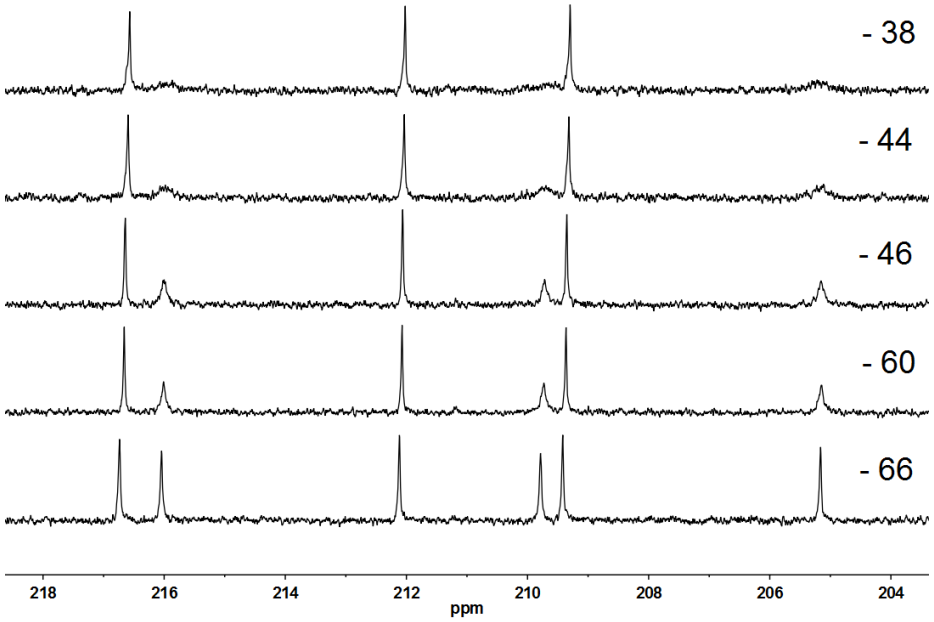

Figure S11. $^{13}C\{^{1}H\}$ NMR spectra (126 MHz, CD_2Cl_2 solution) of **1**^{Me} recorded at various temperatures.

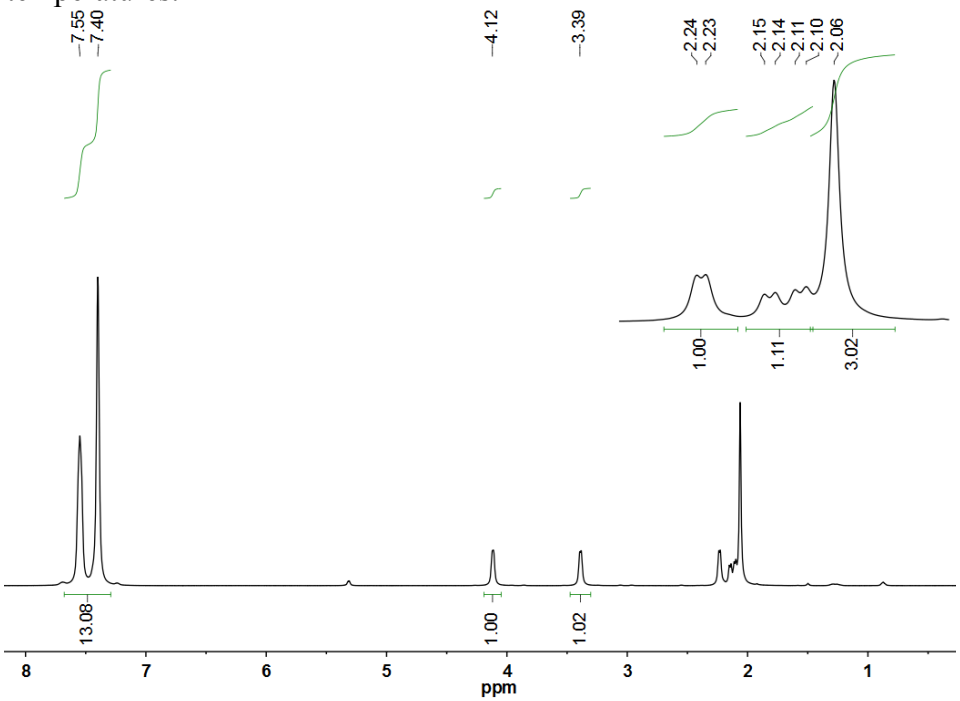

Figure S12. ^{1}H NMR spectrum of crystals of **3**^{Me} (500 MHz, CD_2Cl_2 solution). *Assignments:* δ 2.06 (s, 3H, NCH_3), 2.12 (d, 1H, NCH_2Fe), 2.23 (dd, 1H, NCH_2Fe), 3.39 (d, 1H, NCH_2S), 4.12 (dd, 1H, NCH_2S), 7.40-7.55 (2s, 15H, P(C_6H_5)$_3$.

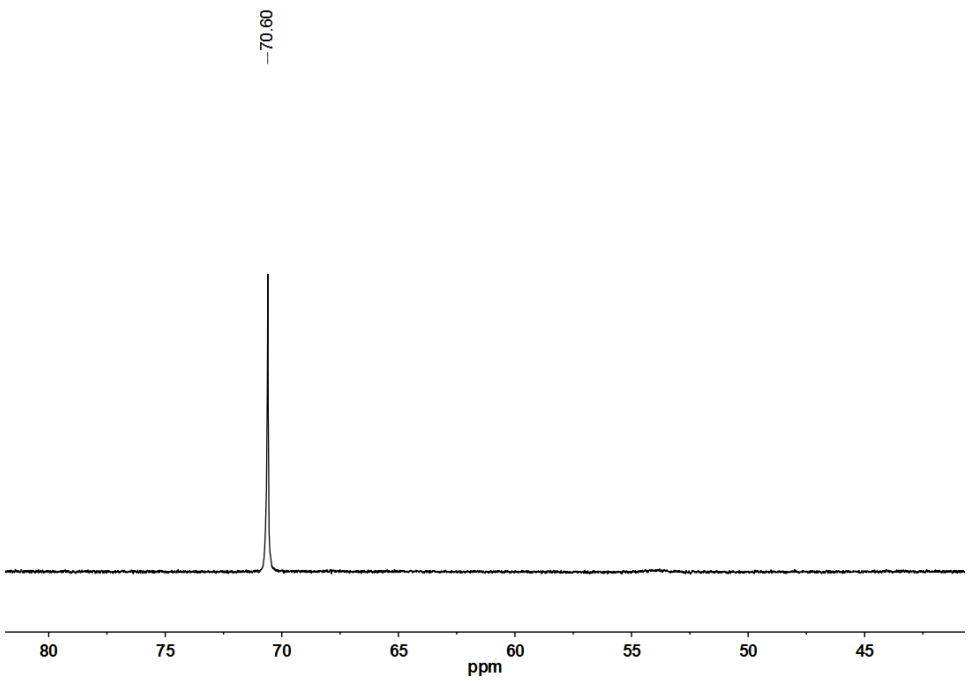

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of crystals of **3^{Me}** (202 MHz, CD_2Cl_2 solution). *Assignments:* δ 70.60 (PPh_3).

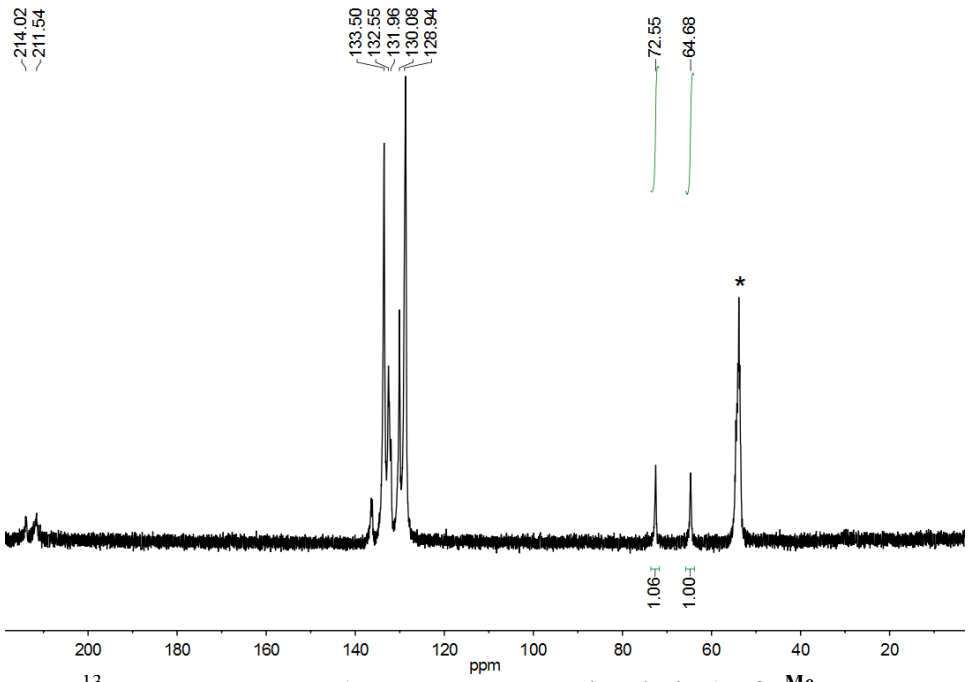

Figure S14. ^{13}C NMR spectrum (125.7 MHz, CD_2Cl_2 solution) of **3^{Me}** at 20 ºC. Inset: * Residual solvent. *Assignments:* δ 64.7 (s, 1C, N*C*H_2Fe), 72.6 (s, 1C, N*C*H_2S), 129-134 (P(C_6H_5)$_3$).

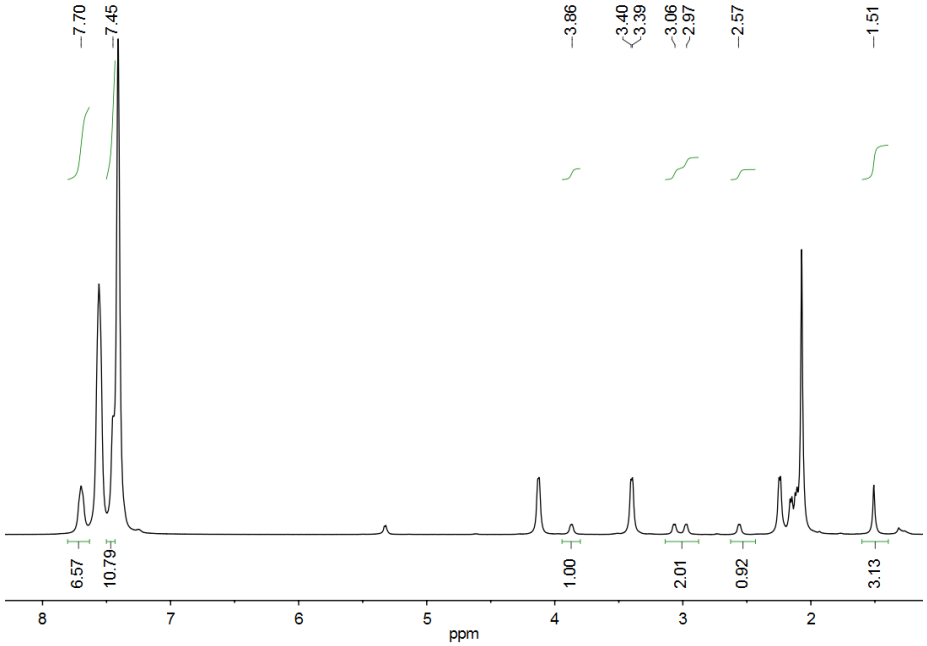

Figure S15. ^{1}H NMR spectrum of crystals of **3^{Me}** (500 MHz, CD_2Cl_2 solution) highlighting minor isomer that forms after 24 h. *Assignments:* δ 1.51 (s, 3H, NCH_3), 2.57 (d, 1H, NCH_2Fe), 2.97 (d, 1H, NCH_2Fe), 3.06 (d, 1H, NCH_2S), 3.86 (d, 1H, NCH_2S), 7.45-7.70 (2s, 15H, P(C_6H_5)$_3$.

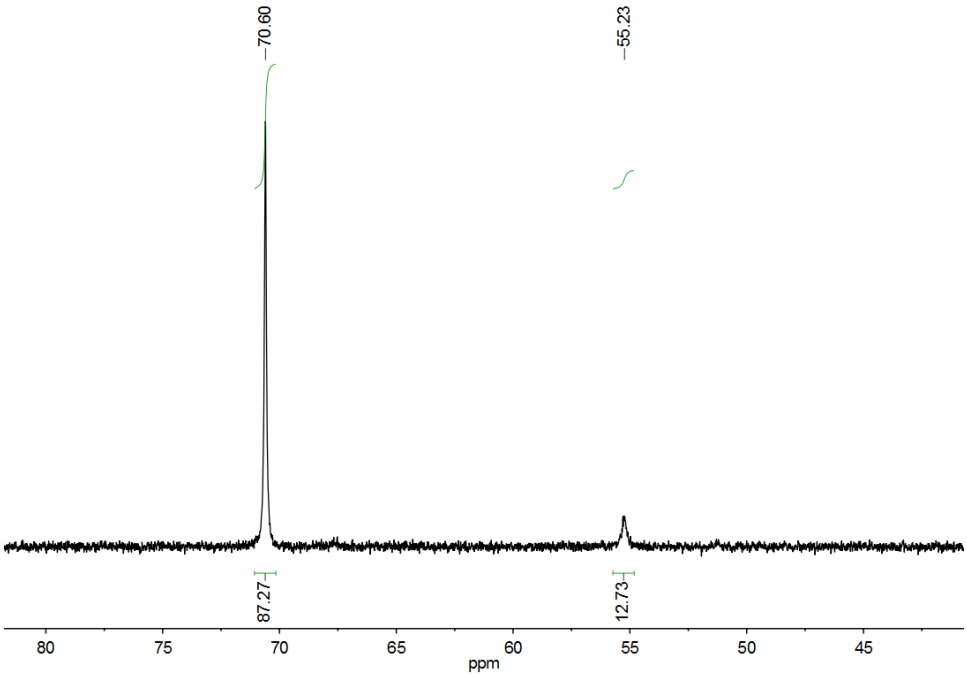

Figure S16. ^{31}P{^{1}H} NMR spectrum of crystals of **3^{Me}** (202.3 MHz, CD_2Cl_2 solution) after 24 h.

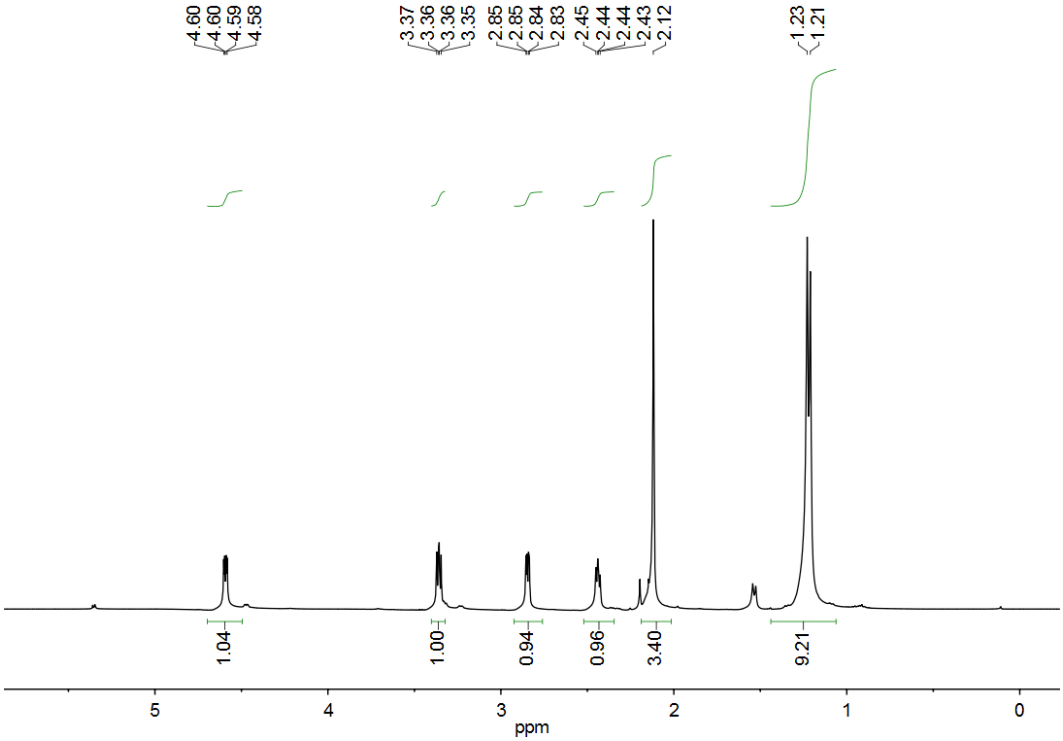

Figure S17. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2 solution) of **4^{Me}**.
Assignments: δ1.21 (d, 9H, P(C*H*$_3$)$_3$), 2.12 (2, 3H, NC*H*$_3$), 2.44 (d, 1H, NC*H*$_2$Fe), 2.85 (dd, 1H, NC*H*$_2$Fe), 3.36 (d, 1H, NC*H*$_2$S), 4.59 (dd, 1H, NC*H*$_2$S).

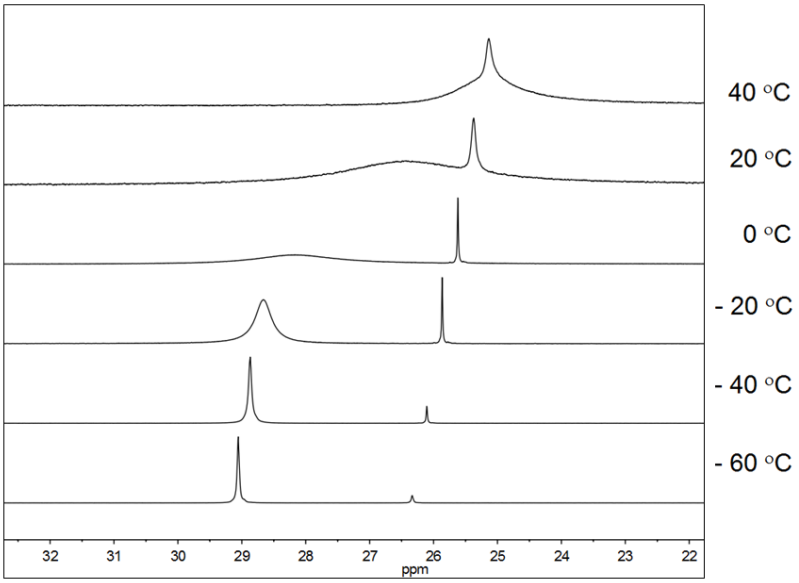

Figure S18. ^{31}P{^{1}H} NMR spectrum (202.3 MHz, d_8-toluene solution) of **4^{Me}** at various temperatures.

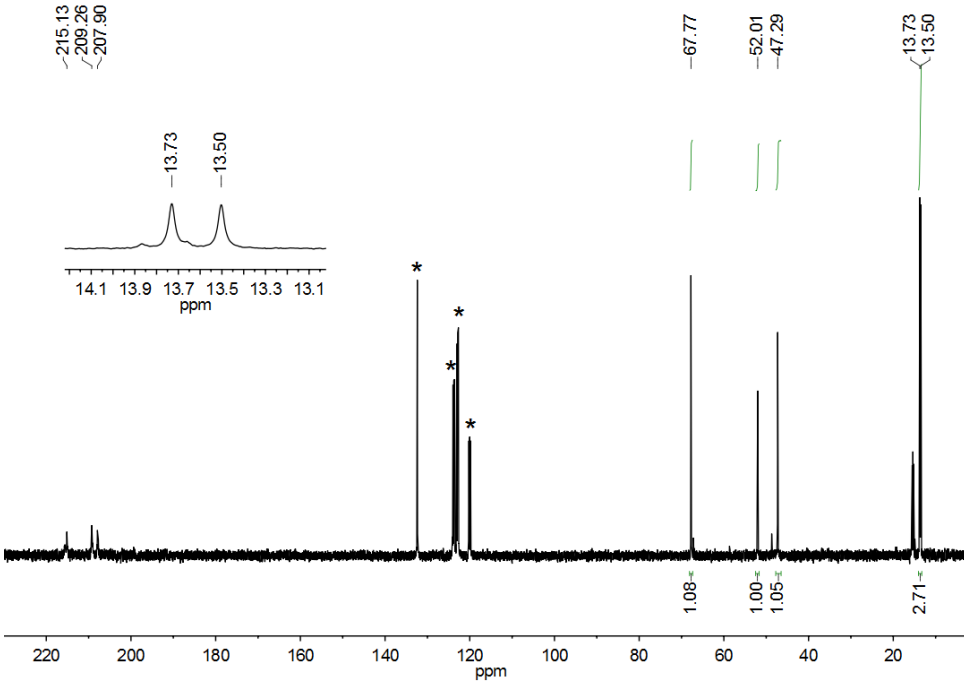

Figure S19. ^{13}C NMR spectrum (125.7 MHz, d_8-toluene solution) of **4^{Me}** at 20 ºC. * Residual solvent. *Assignments:* δ 13.5 (d, 1C, P(CH$_3$)$_3$, J_{PC} = 28.9 Hz), 47.3 (s, 1C, NCH$_3$), 52.0, (s, 1C, NCH$_2$Fe), 67.8 (s, 1C, NCH$_2$S), 208-215 (3s, 3 C, Fe(CO)$_3$).

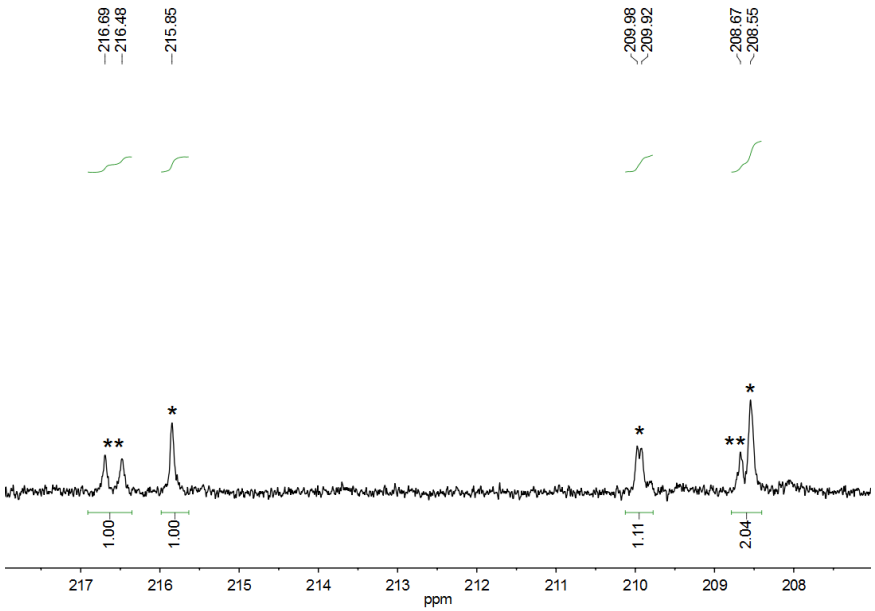

Figure S20. ^{13}C NMR spectrum (125.7 MHz, d_8-toluene solution) of **4^{Me}** at -60 ºC. * Rigid iron center (3C, Fe^{CH2}(CO)$_3$)** non-rigid iron center (2C, Fe^{NMe}(CO)$_2$PMe$_3$).

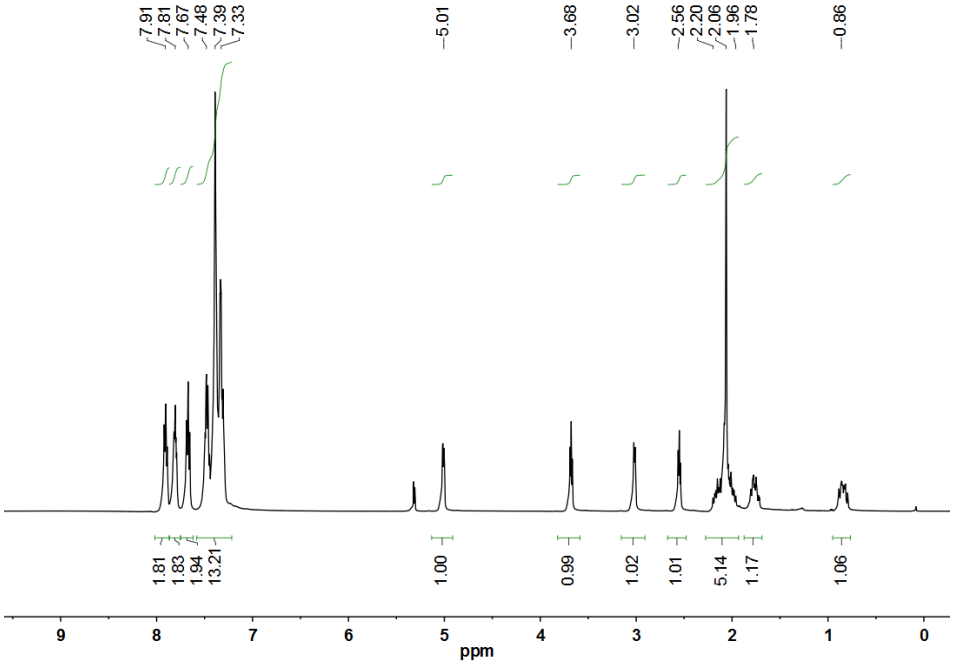

Figure S21. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2 solution) of **5^{Me}**.
Assignments: δ2.06 (s, 3H, NCH_3), 2.56 (dd, 1H, NCH_2Fe), 3.02 (d, 1H, NCH_2Fe), 3.68 (dd, 1H, NCH_2S), 5.01 (d, 1H, NCH_2S), 0.9-2.10 (m, 10H, PCH_2CH_2P), 7.37-7.95 (m, 20H, P(C_6H_5)$_2$).

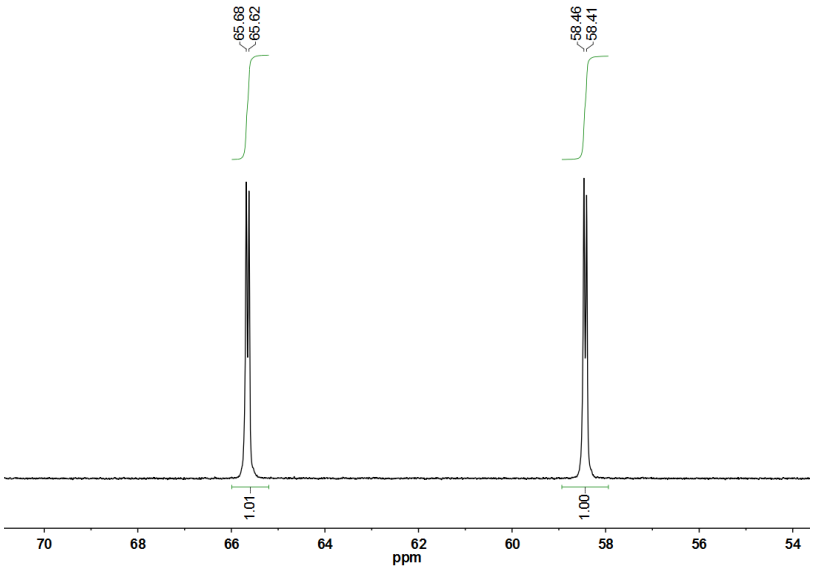

Figure S22. ^{31}P{^{1}H} NMR spectrum (202.3 MHz, CD_2Cl_2 solution) of **5^{Me}**. J_{PP} = 11.8 Hz.

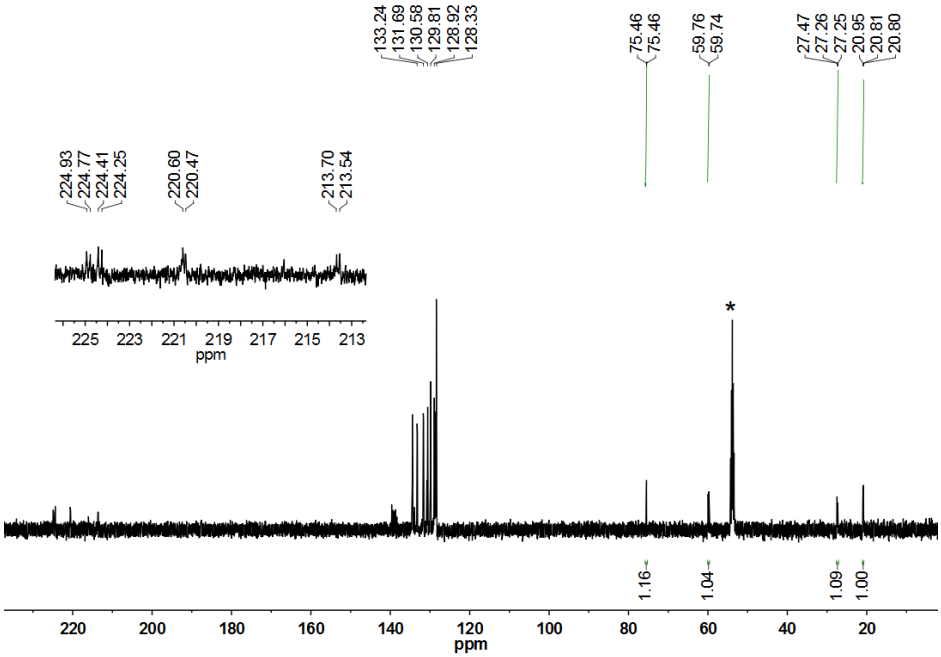

Figure 3. ^{13}C NMR spectrum (125.7 MHz, CD_2Cl_2 solution) of **5^{Me}** at 20 ºC. *Residual solvent. *Assignments:* δ20.8 (t, 1C, P*C*H$_2$*C*H$_2$P), 27.3 (t, 1C, P*C*H$_2$*C*H$_2$P), 560 (d, 1C, N*C*H$_2$Fe), 75.5 (d, 1C, N*C*H$_2$S), 128.33-133.24 (m, 24 C, P(*C*$_6$H$_5$)$_2$), 214-225 (4d, 4C, Fe(*C*O)$_2$).