Supporting Information for:

Selective Synthesis of Site-Differentiated Fe_4S_4 and Fe_6S_6 Clusters

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NMR Spectra

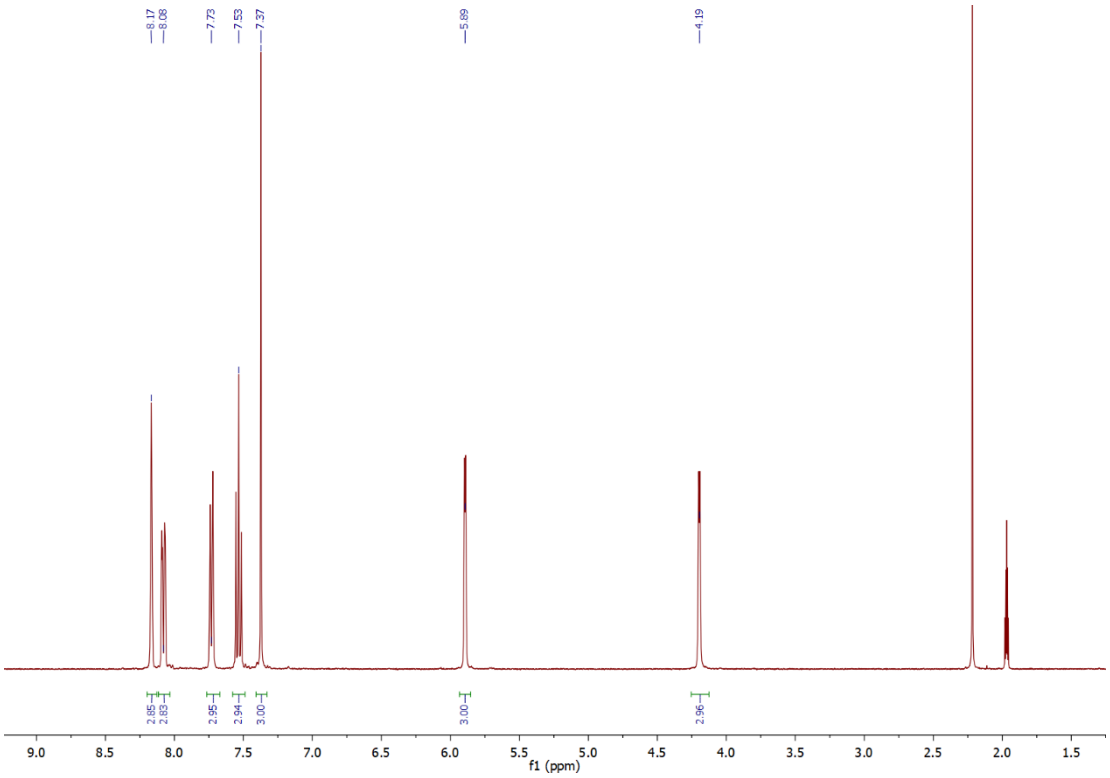

Figure S1. ^{1}H NMR spectrum of **3** recorded in CD_3CN at 400 MHz.

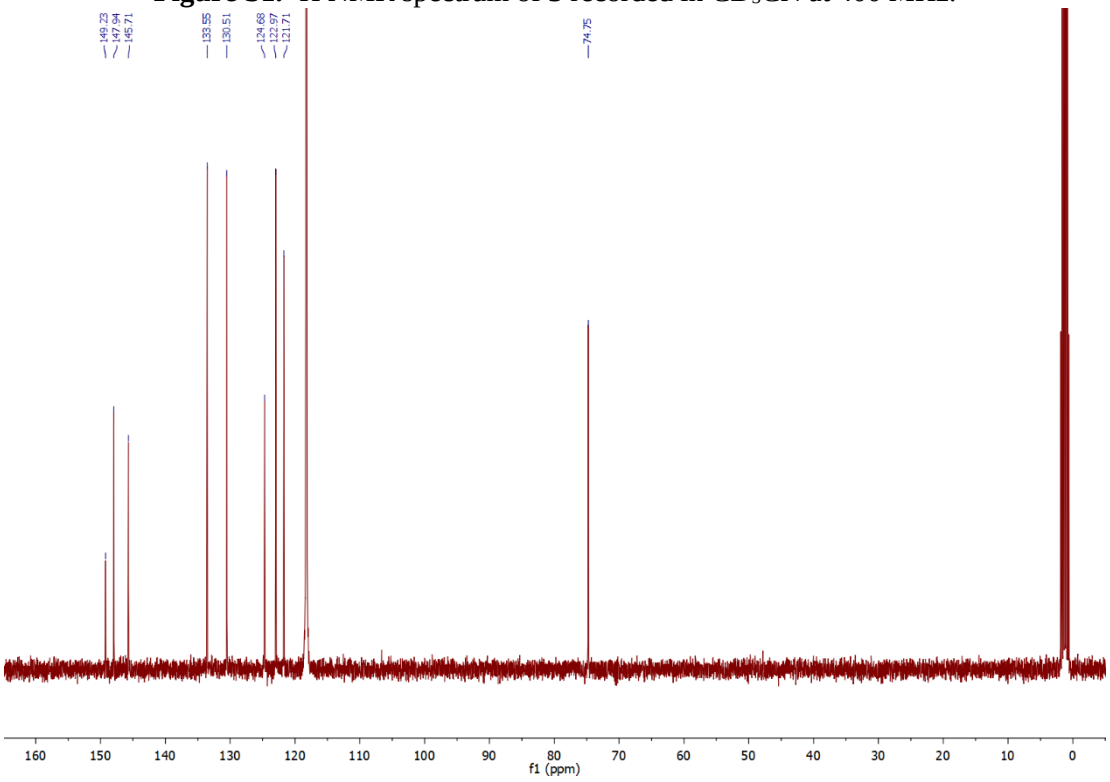

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3** recorded in CD_3CN at 100.5 MHz.

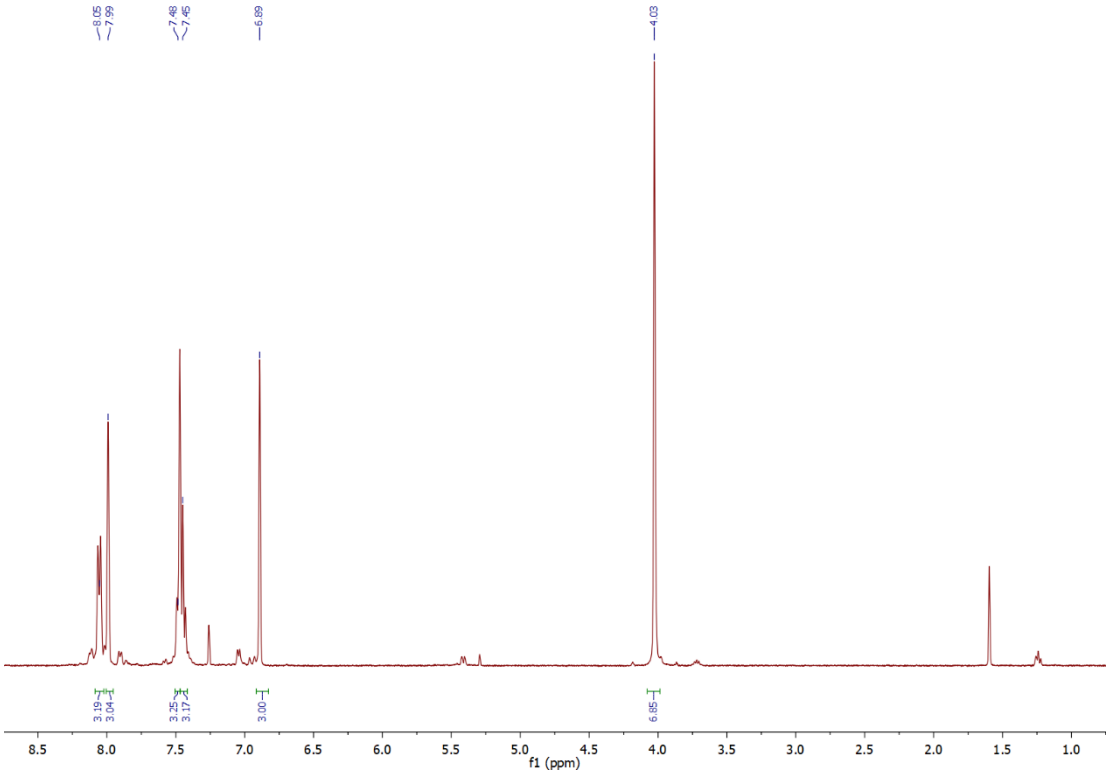

Figure S3. ^{1}H NMR spectrum of **4** recorded in $CDCl_3$ at 400 MHz.

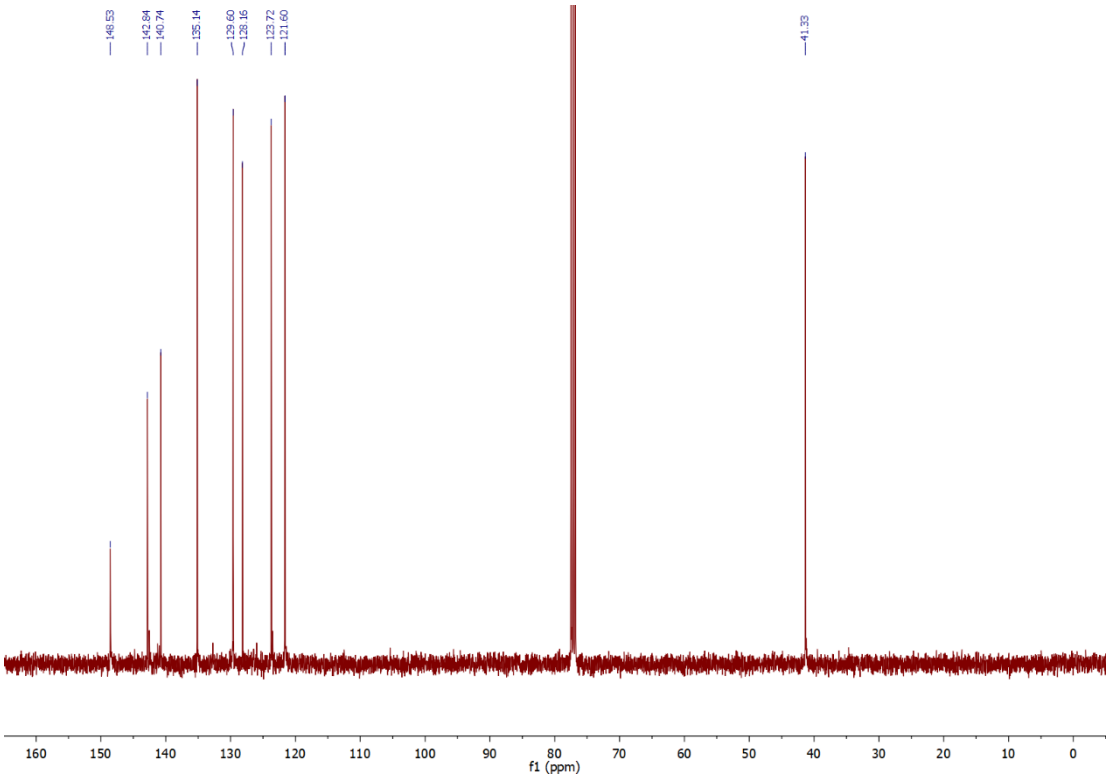

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **4** recorded in $CDCl_3$ at 100.5 MHz.

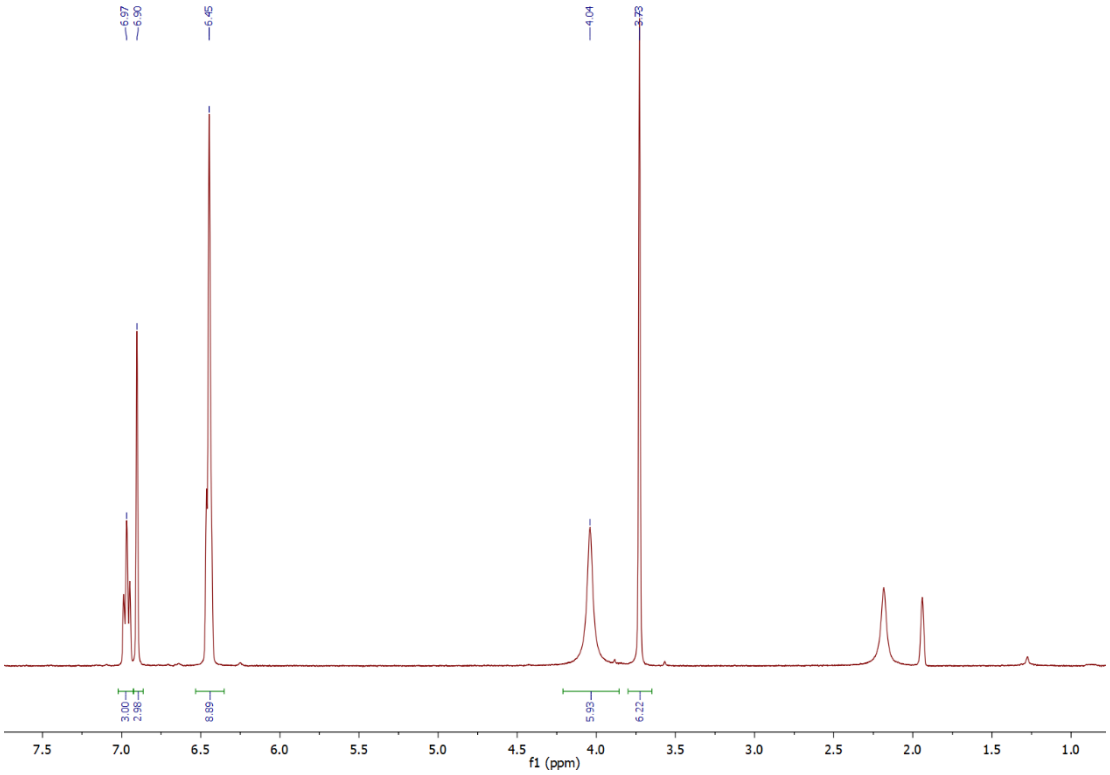

Figure S5. ^{1}H NMR spectrum of **5** recorded in CD_3CN at 400 MHz.

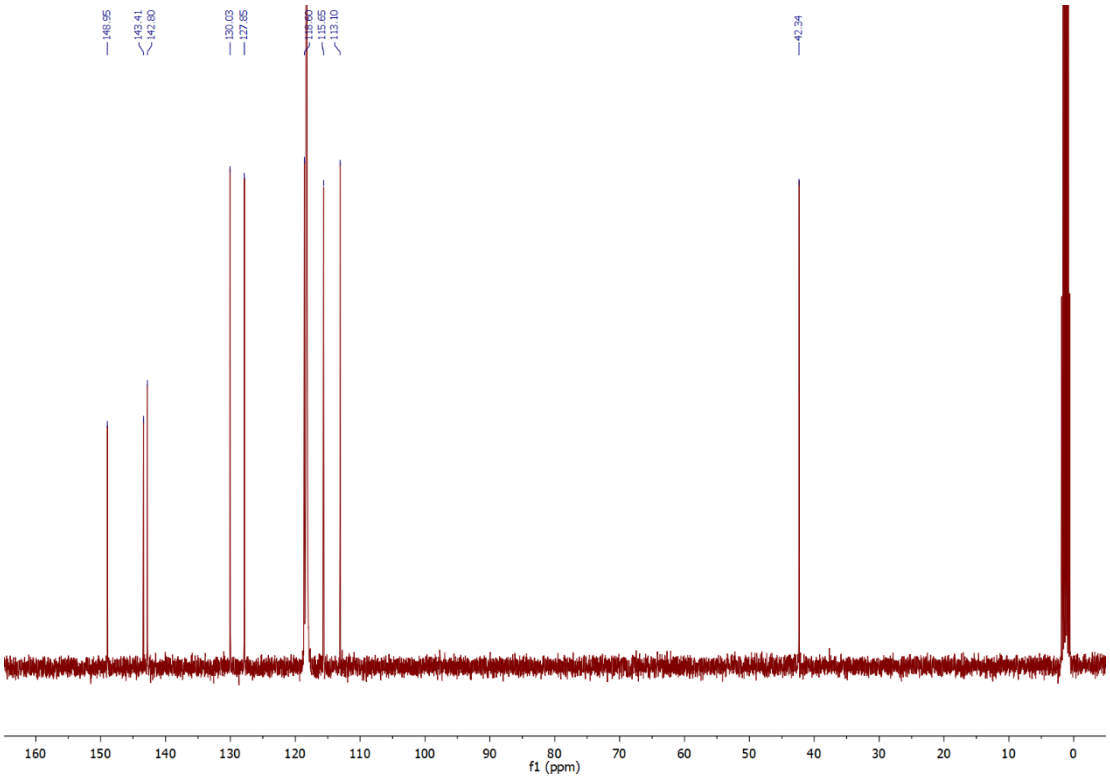

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **5** recorded in CD_3CN at 100.5 MHz.

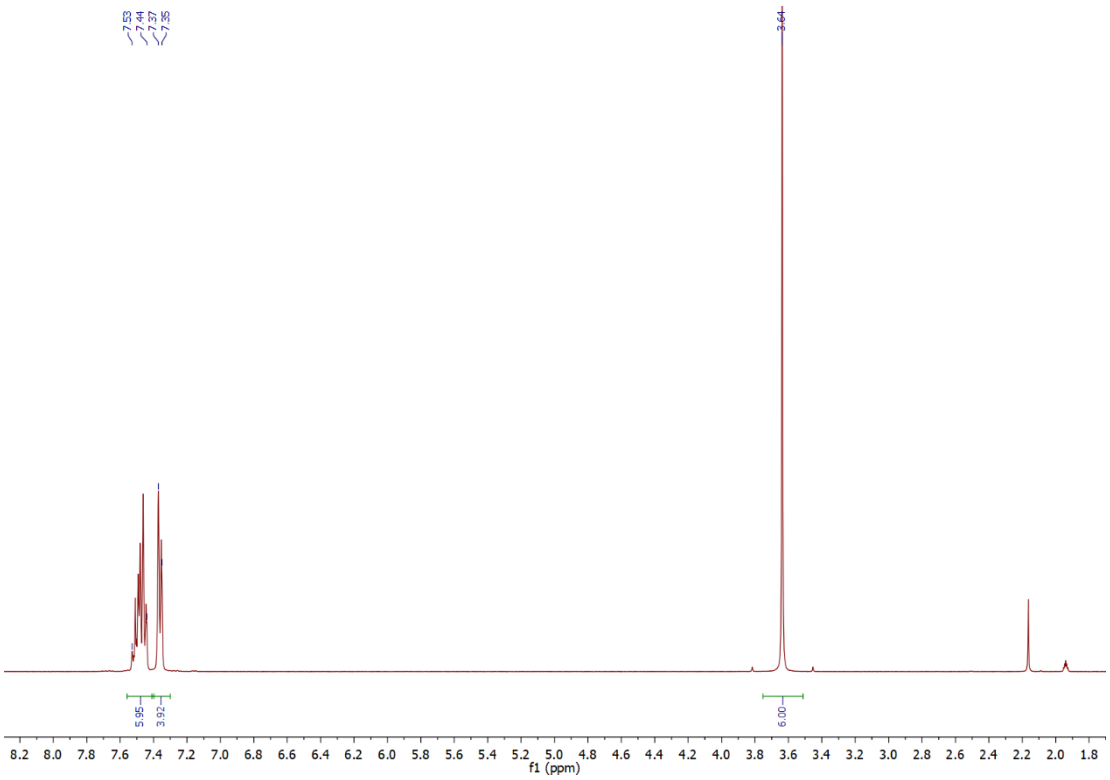

Figure S7. ^{1}H NMR spectrum of **6** recorded in CD_3CN at 400 MHz.

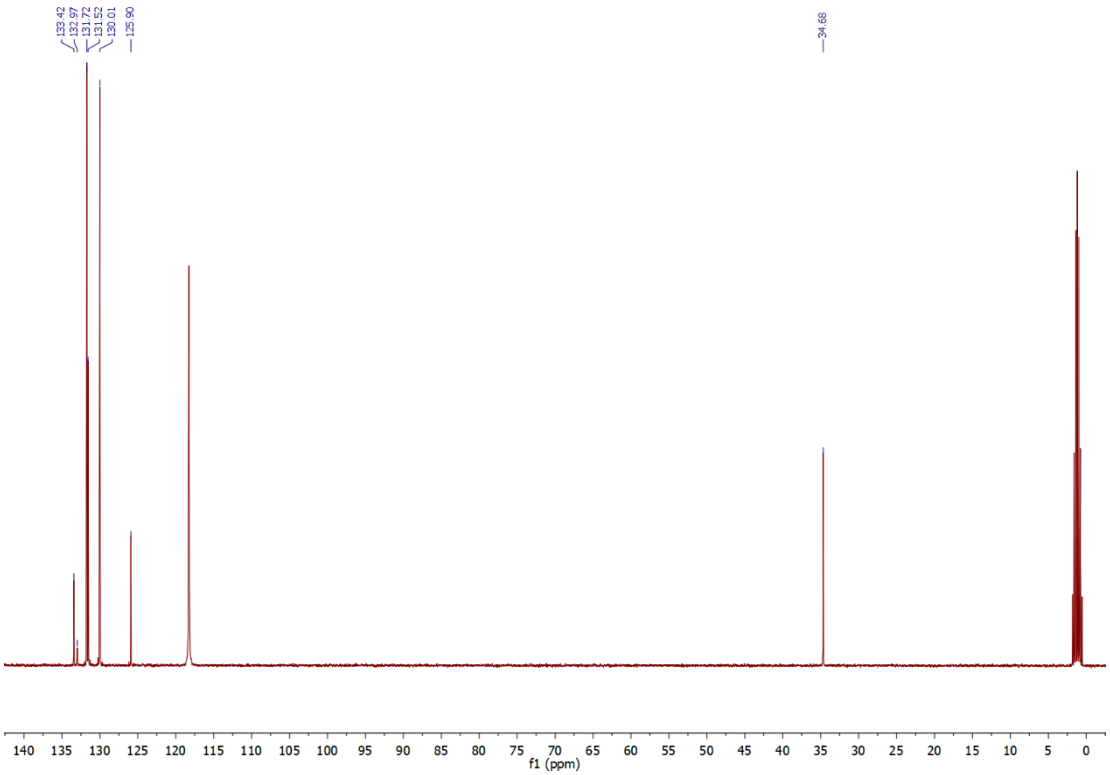

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **6** recorded in CD_3CN at 100.5 MHz.

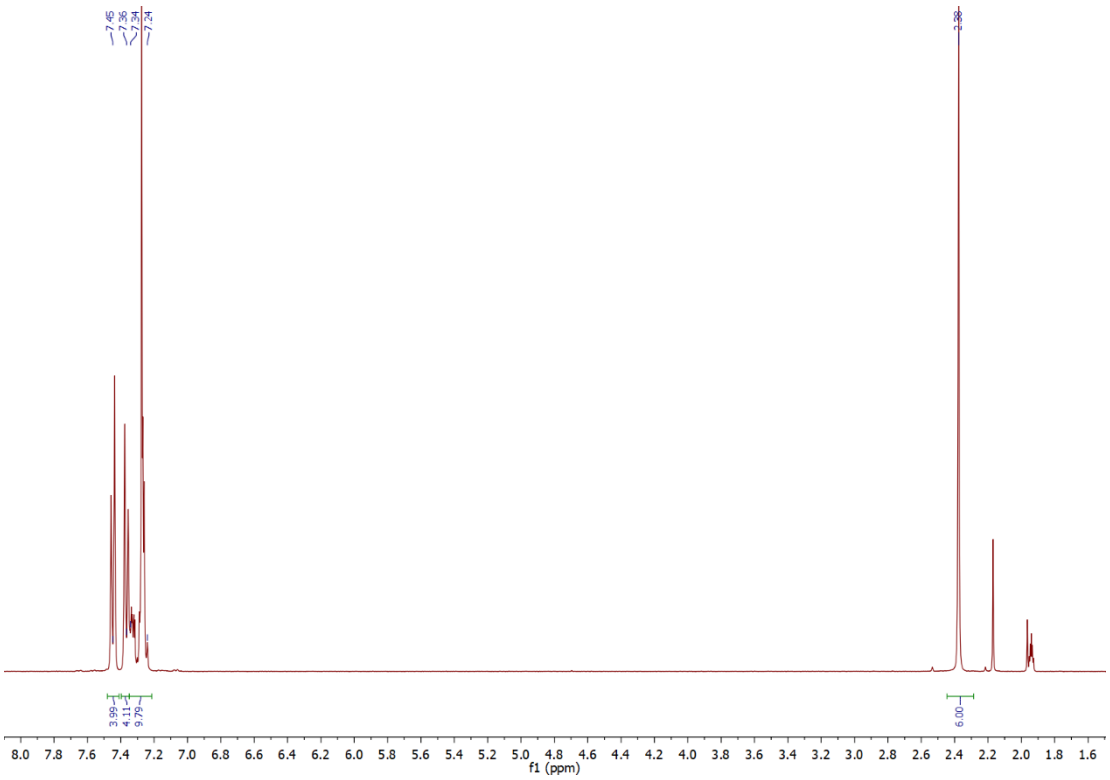

Figure S9. ^{1}H NMR spectrum of **7** recorded in CD_3CN at 400 MHz.

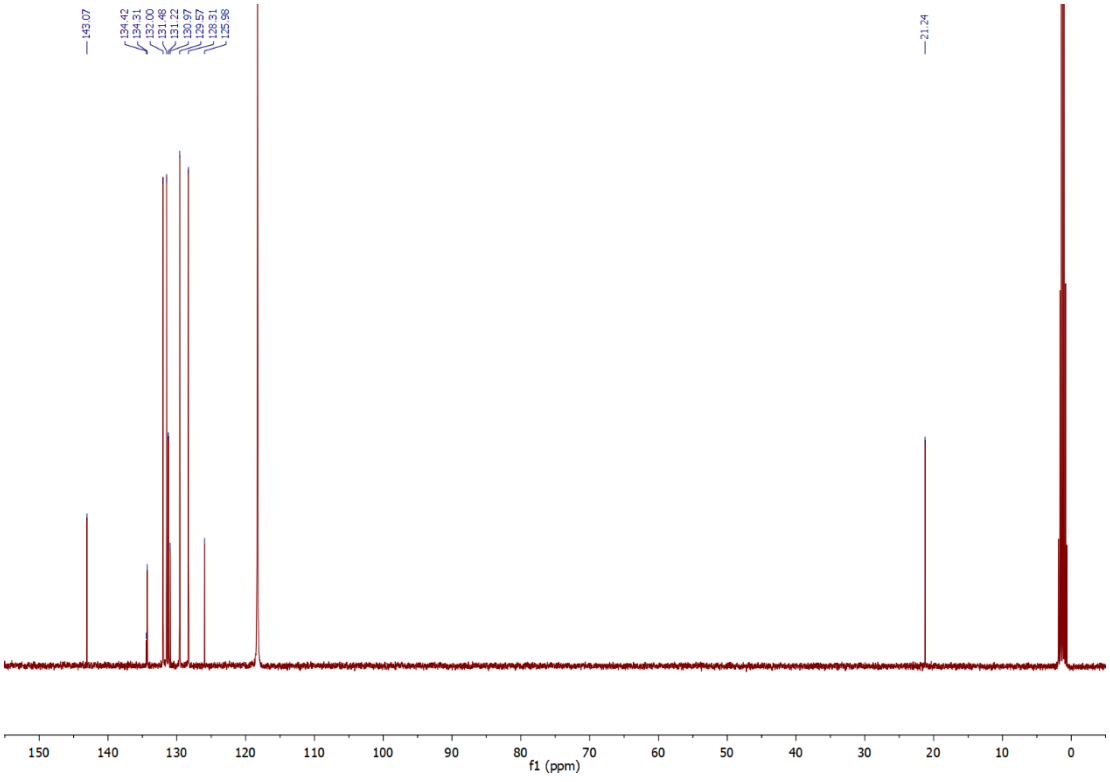

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **7** recorded in CD_3CN at 100.5 MHz.

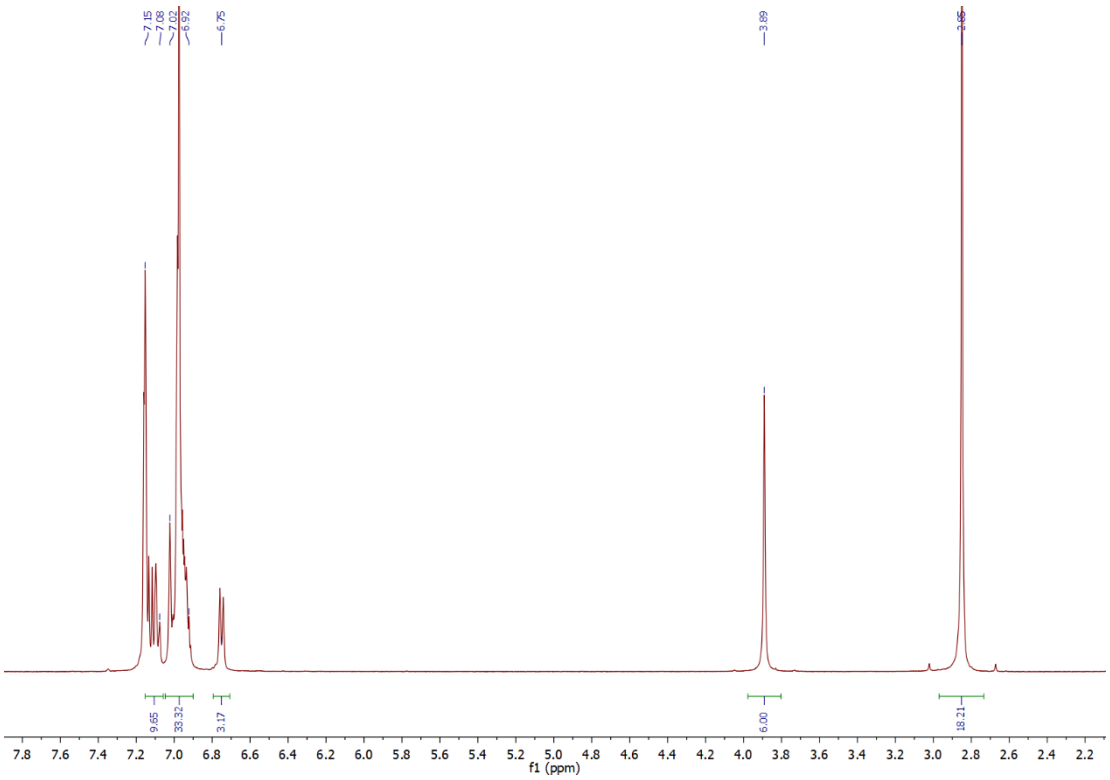

Figure S11. ^{1}H NMR spectrum of L(NIm^{Me})$_3$ (**8**) recorded in C_6D_6 at 400 MHz.

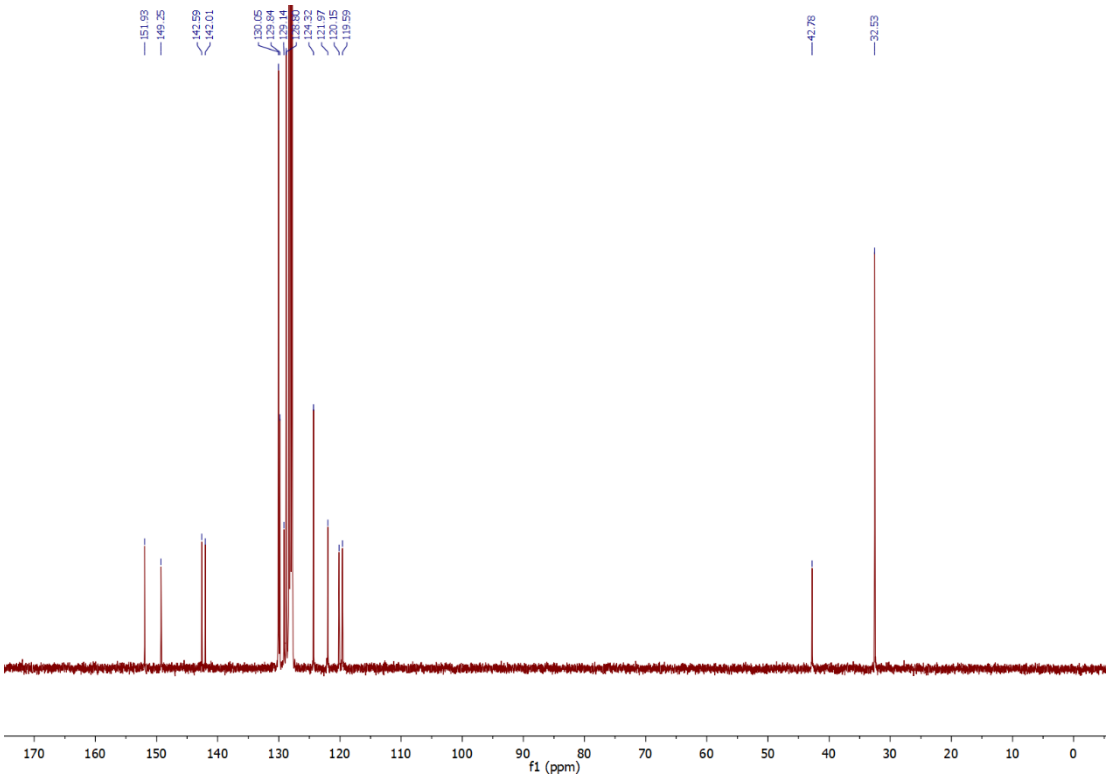

Figure S12. ^{13}C{^{1}H} NMR spectrum of L(NIm^{Me})$_3$ (**8**) recorded in C_6D_6 at 100.5 MHz.

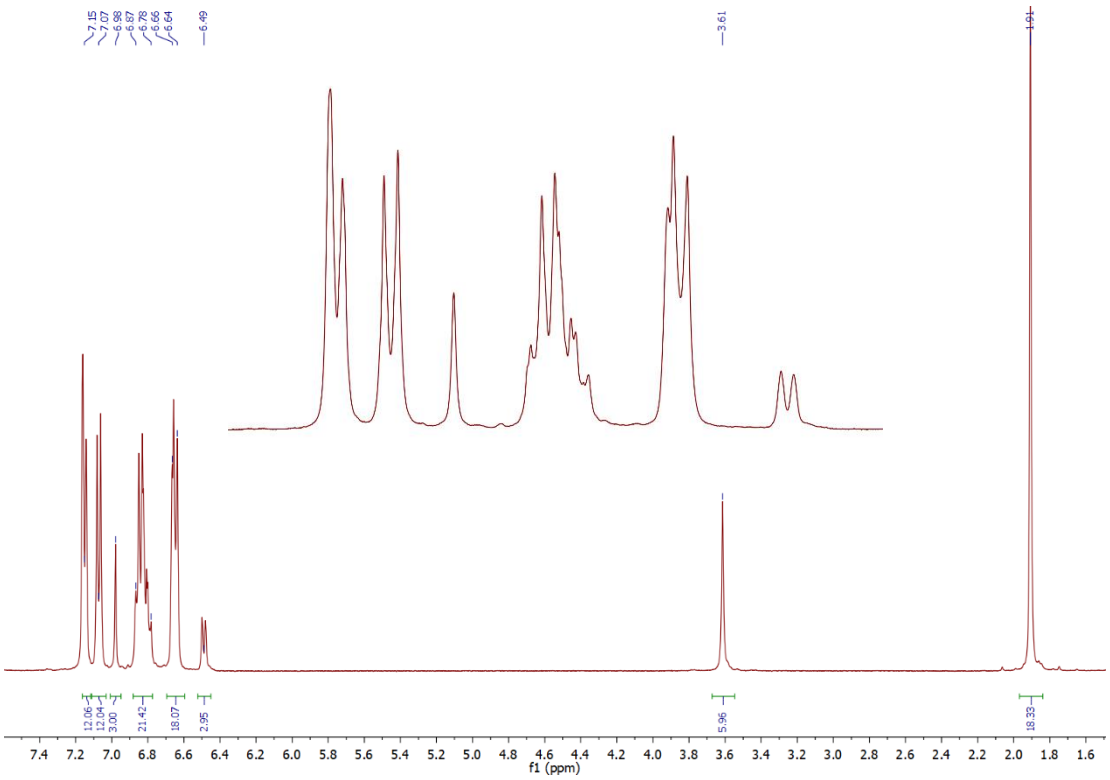

Figure S13. ^{1}H NMR spectrum of L(NIm^{Tol})$_3$ (**9**) recorded in C_6D_6 at 400 MHz (aromatic region inset).

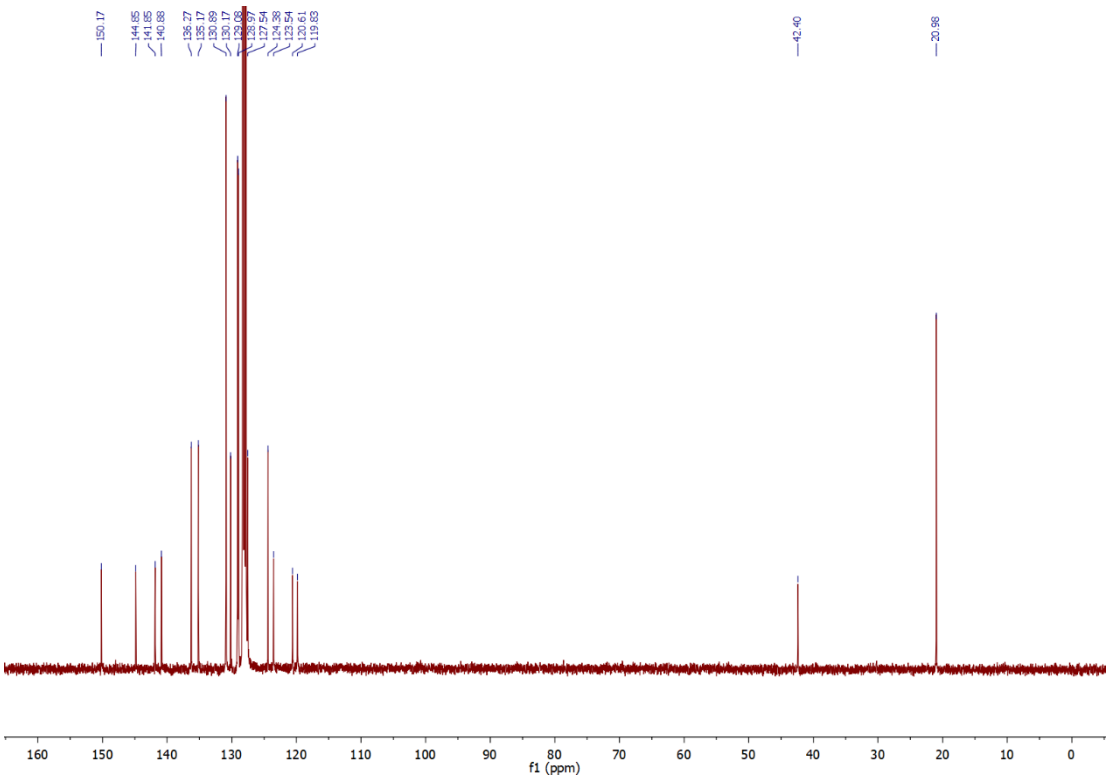

Figure S14. ^{13}C{^{1}H} NMR spectrum of L(NIm^{Tol})$_3$ (**9**) recorded in C_6D_6 at 100.5 MHz.

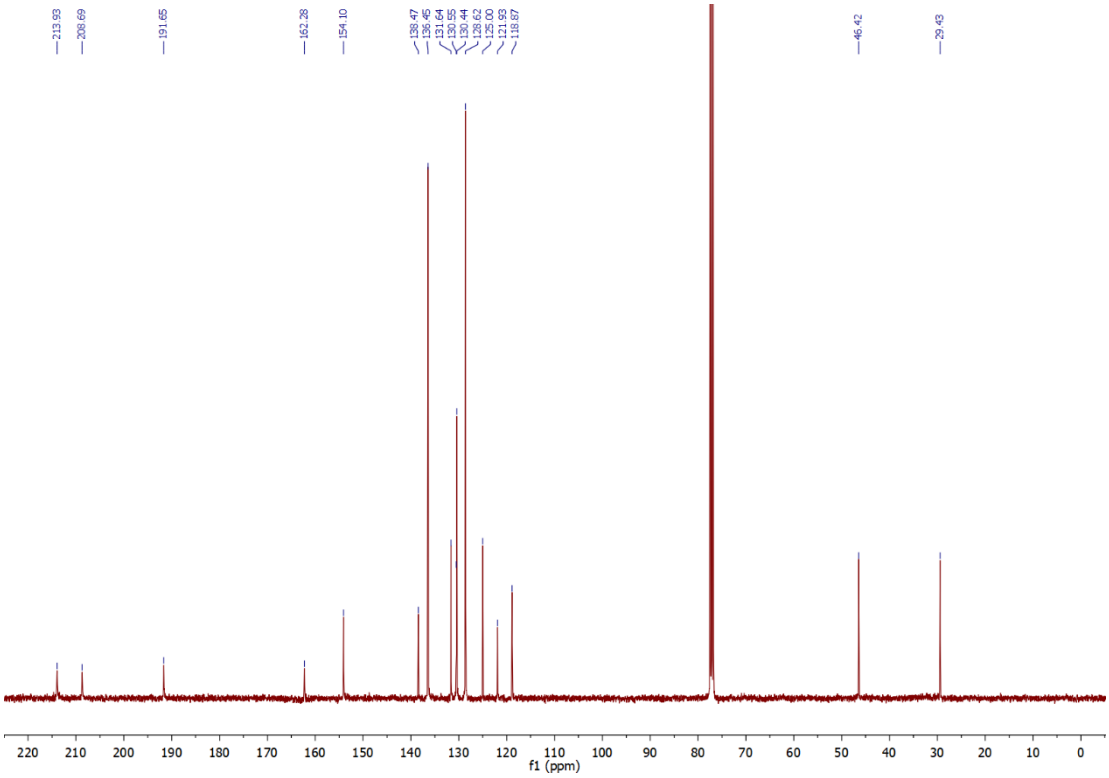

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of $L(NIm^{Me})_3Fe_6S_6Cl_3$ (**11**) recorded in $CDCl_3$ at 100.5 MHz.

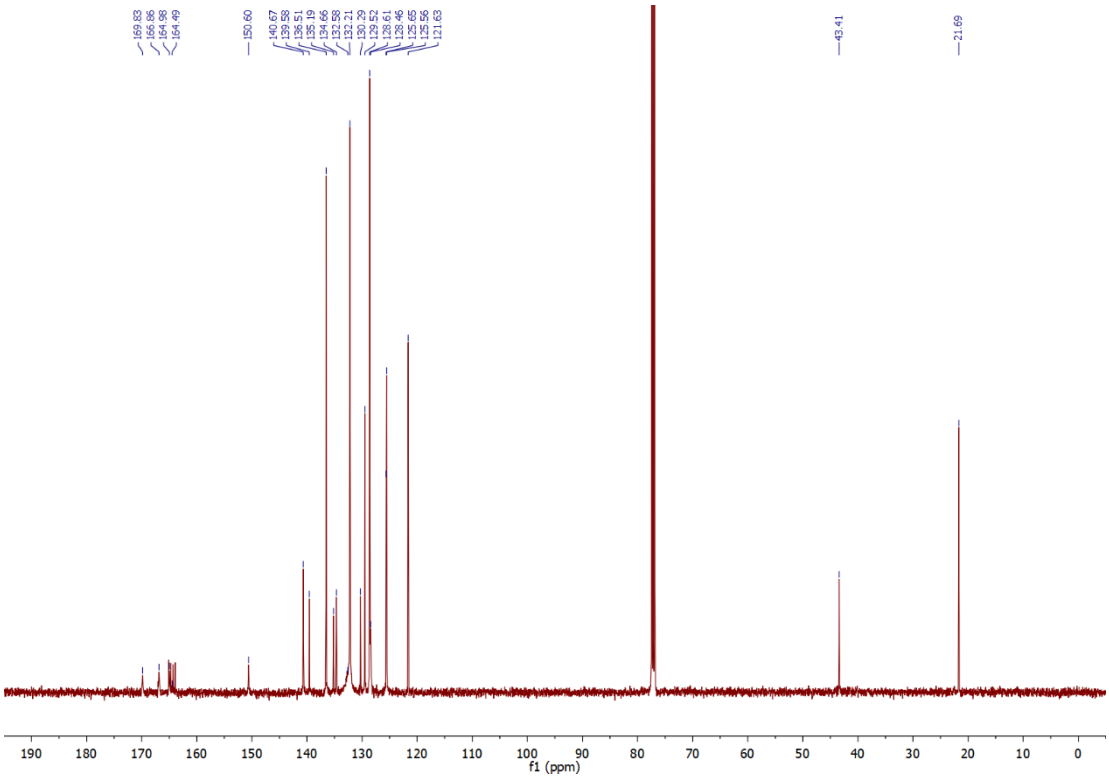

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of $[(L(NIm^{Tol})_3)Fe_4S_4Cl][BPh_4]$ (**12**) recorded in $CDCl_3$ at 100.5 MHz.

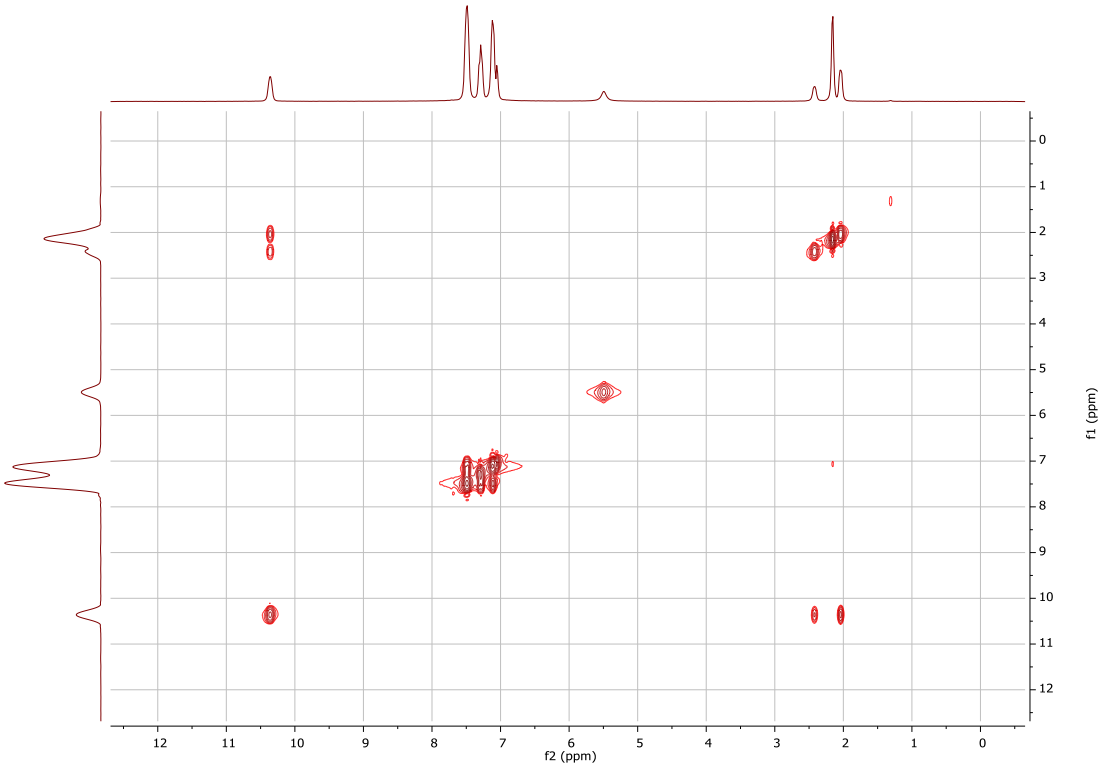

Figure S17. ^{1}H-^{1}H COSY spectrum of $(L(NIm^{Me})_3)Fe_6S_6Cl_3$ (**11**).

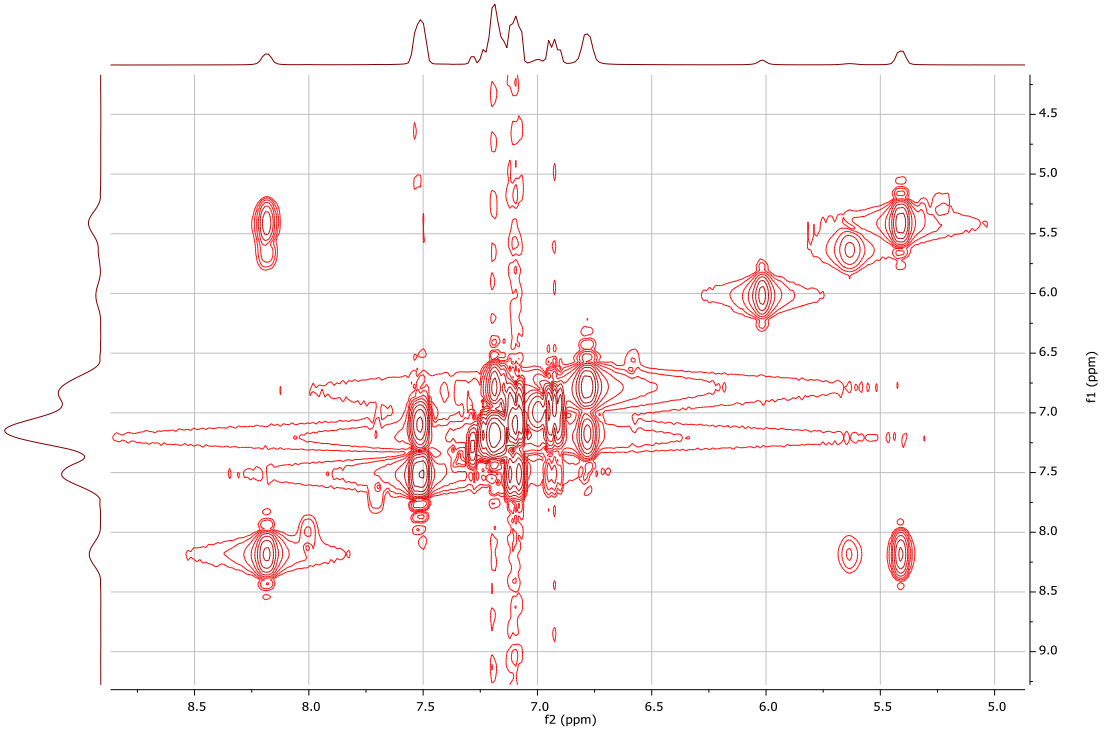

Figure S18. ^{1}H-^{1}H COSY spectrum of $[(L(NIm^{Tol})_3)Fe_4S_4Cl][BPh_4]$ (**12**) in the aromatic region.

FTIR Spectra

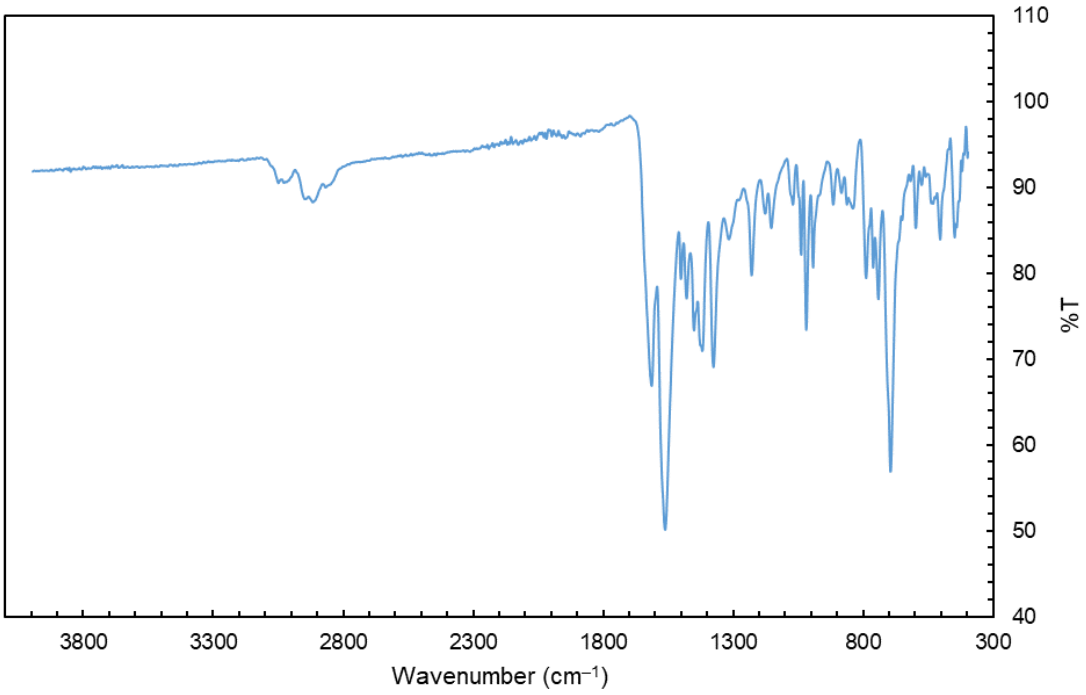

Figure S19. FTIR spectrum of L(NIm^{Me})$_3$ (**8**).

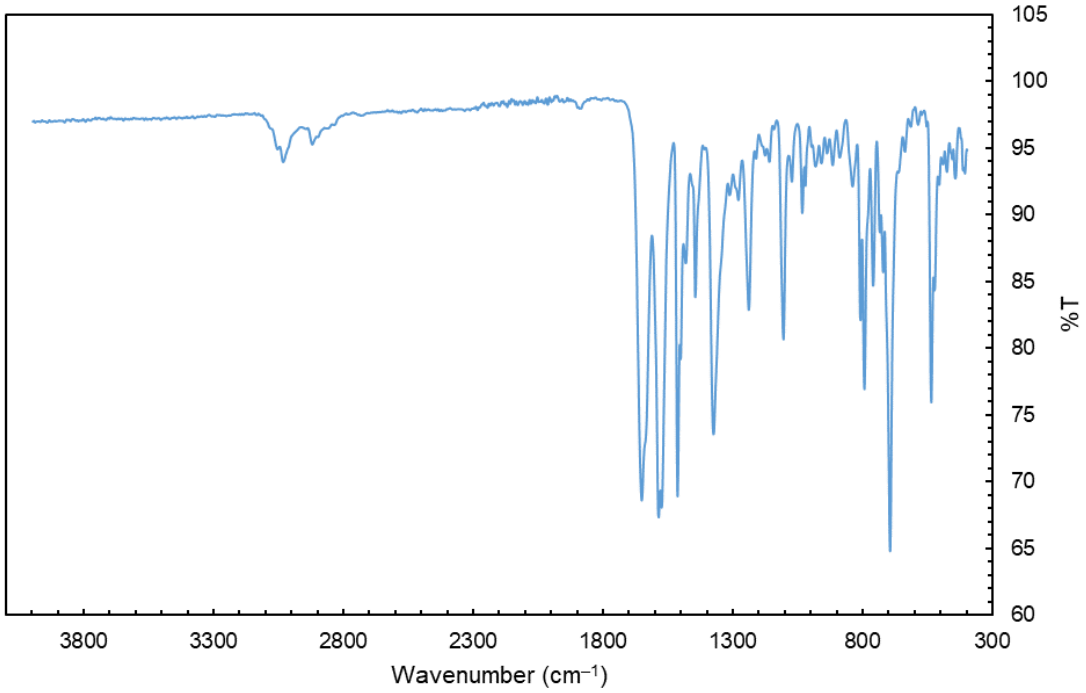

Figure S20. FTIR spectrum of L(NIm^{Tol})$_3$ (**9**).

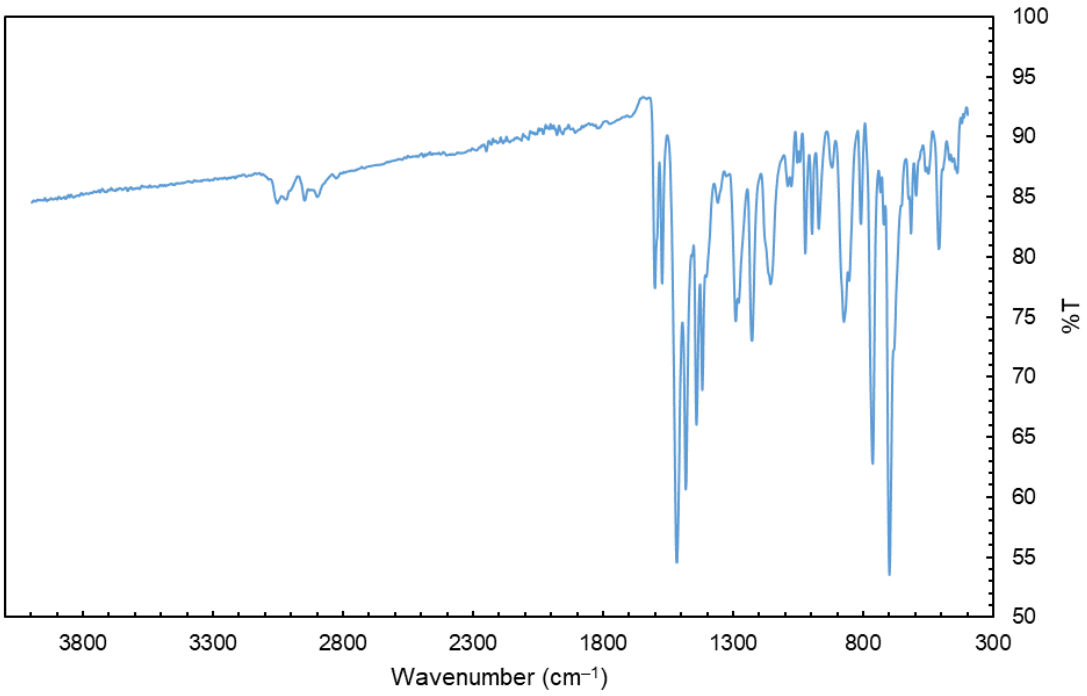

Figure S21. FTIR spectrum of $L(NIm^{Me})_3Fe_6S_6Cl_3$ (**11**).

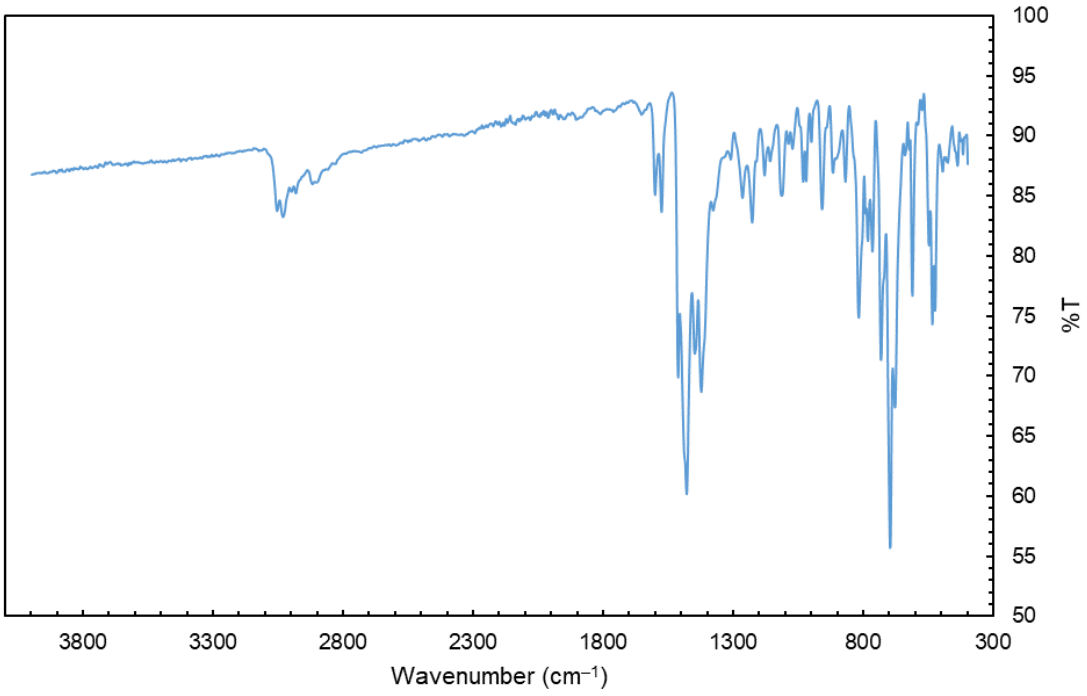

Figure S22. FTIR spectrum of $[(L(NIm^{Tol})_3)Fe_4S_4Cl][BPh_4]$ (**12**).

Additional Spectroscopy

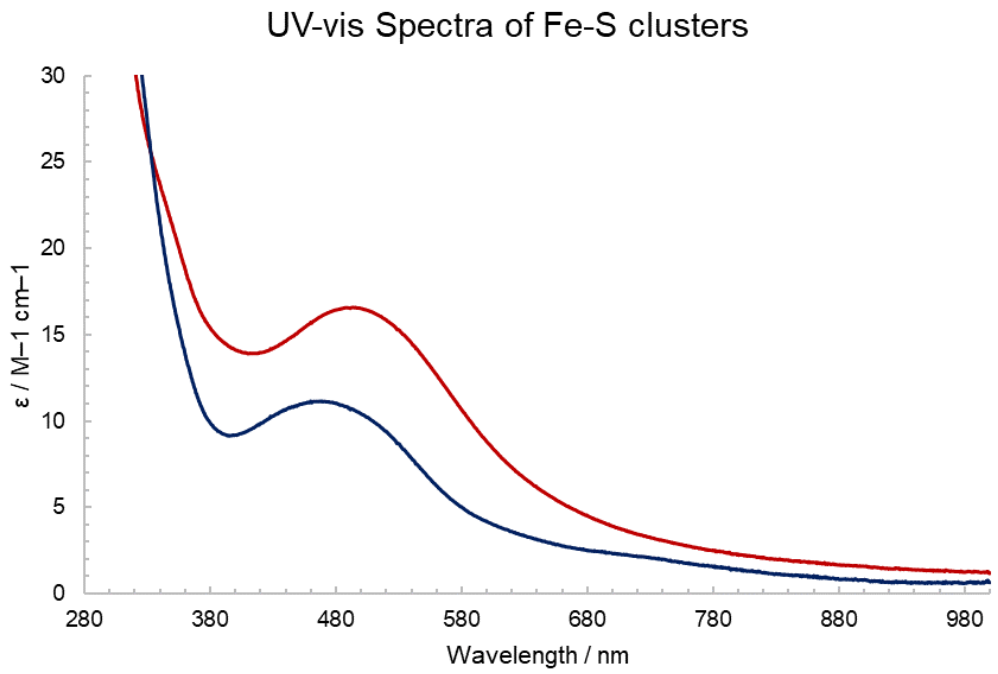

Figure S23. UV-Vis spectra of $(L(NIm^{Me})_3)Fe_6S_6Cl_3$ (**11**; **red trace**) and $[(L(NIm^{Me})_3)Fe_4S_4Cl_4][BPh_4]$ (**12**; **blue trace**) (*ca.* 1mM in THF).

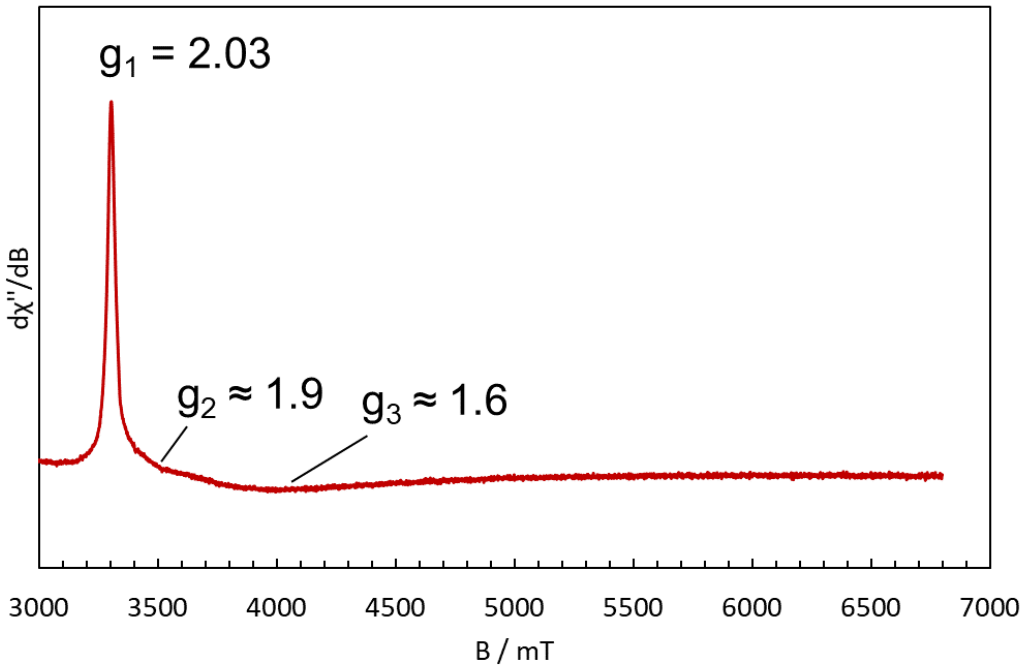

Figure S24. X-band EPR spectrum of $(L(NIm^{Me})_3)Fe_6S_6Cl_3$ (**11**) in a 2-MeTHF glass at 8 K. MW frequency = 9.374 MHz.

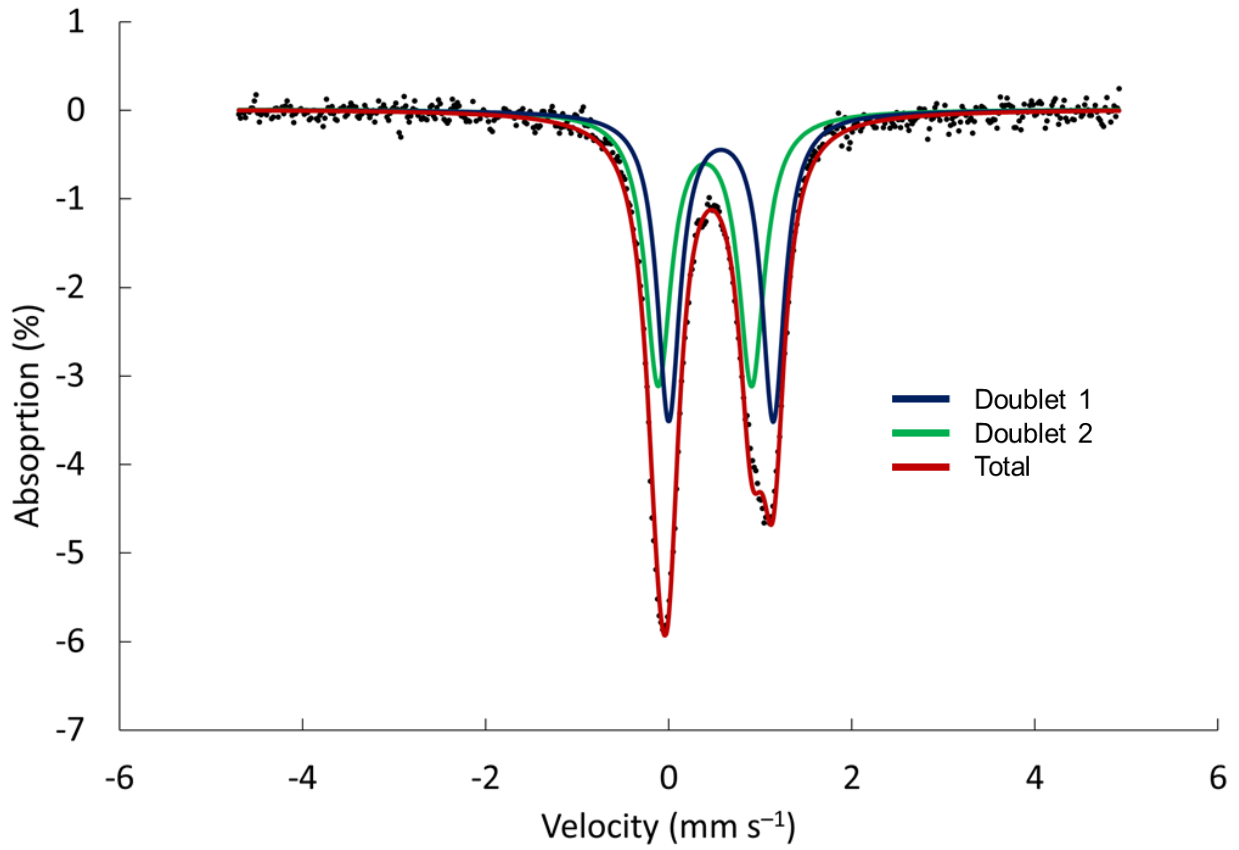

Figure S25. Zero-field ^{57}Fe Mössbauer spectrum of solid (L(NIm^{Me})$_3$)Fe$_6$S$_6$Cl$_3$ (**11**) at 90 K with alternative simulations. Black circles represent experimental data, solid lines are simulations. Simulation parameters: Doublet 1: δ = 0.57 mm s^{-1}, ΔE_Q = 1.14 mm s^{-1}, Γ = 0.30 mm s^{-1}, relative area = 0.5; Doublet 2: δ = 0.39 mm s^{-1}, ΔE_Q = 1.02 mm s^{-1}, Γ = 0.34 mm s^{-1}, relative area = 0.5. We disfavor this simulation as the isomer shift values differ significantly from those reported for $[Fe_6S_6X_6]^{3-}$ (X = halide, RS$^-$, RO$^-$) clusters.[1]

^{1}H NMR Spectra of Reaction Mixtures

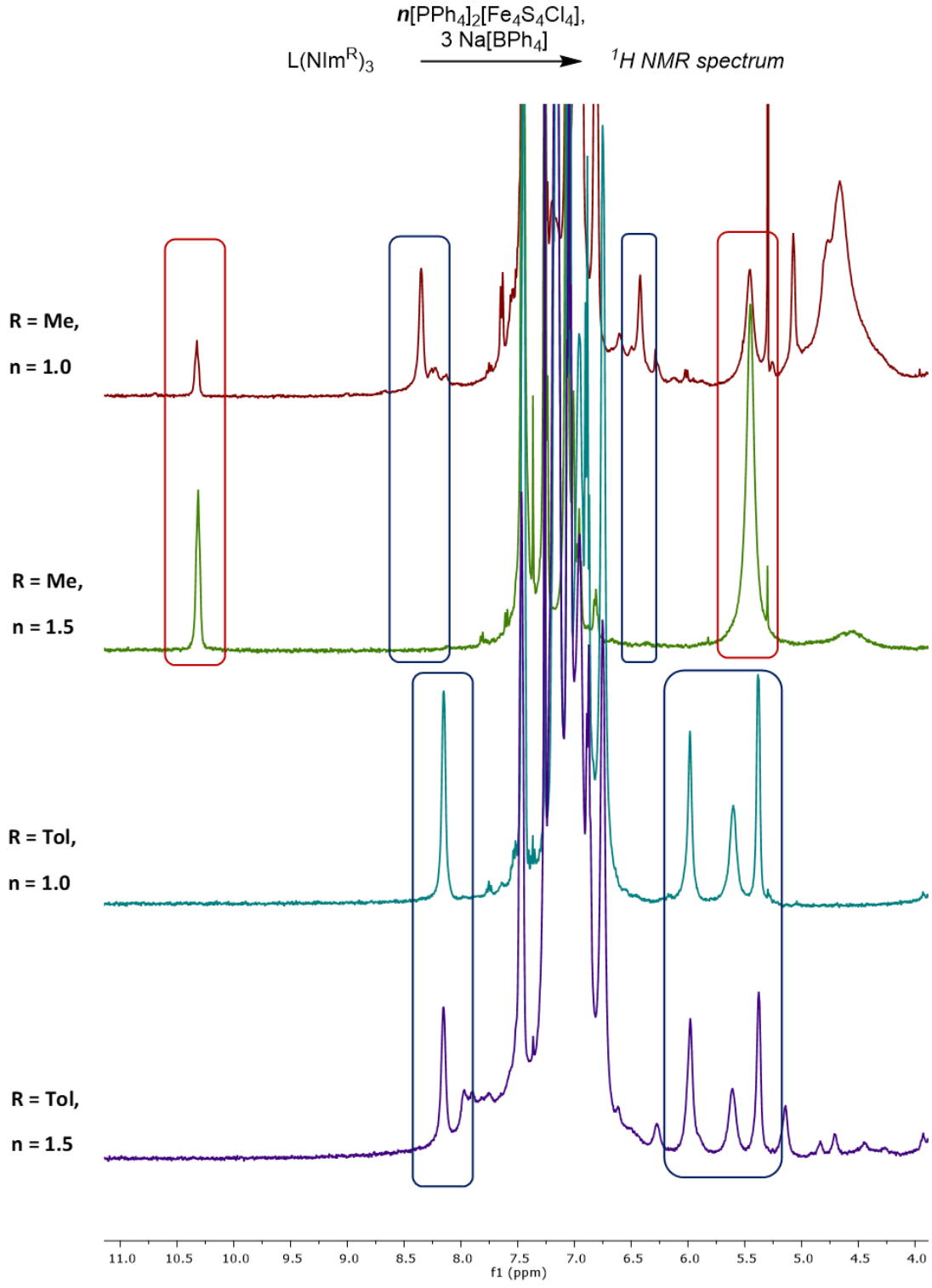

Figure S26. ^{1}H NMR spectra in $CDCl_3$ of the crude mixtures from the reactions between $L(NIm^R)_3$ and different stoichiometries of $[PPh_4]_2[Fe_4S_4Cl_4]$ and $Na[BPh_4]$. **Blue boxes** indicate peaks assigned to $[(L(NIm^R)_3)Fe_4S_4Cl_4]^+$ clusters; **red boxes** peaks assigned to $(L(NIm^R)_3)Fe_6S_6Cl_3$ clusters.

References

1. Kanatzidis, M. G.; Hagen, W. R.; Dunham, W. R.; Lester, R. K.; Coucouvanis, D. Metastable Fe/S Clusters. The Synthesis, Electronic Structure, and Transformations of the $[Fe_6S_6Cl_6]^{3-}$, $[Fe_6S_6Br_6]^{3-}$, $[Fe_6S_6I_6]^{3-}$, $[Fe_6S_6(RS)_6]^{3-}$, $[Fe_6S_6(RO)_6]^{3-}$ Clusters and the Structure of $[(C_2H_5)_4N]_3[Fe_6S_6Cl_6]$. *J Am Chem Soc* **1985,** *107* (4), 953-961.