Supporting information for:

Isolation of chloride- and hydride-bridged tri-iron and -zinc clusters in a tris(β-oxo-δ-diimine) cyclophane ligand

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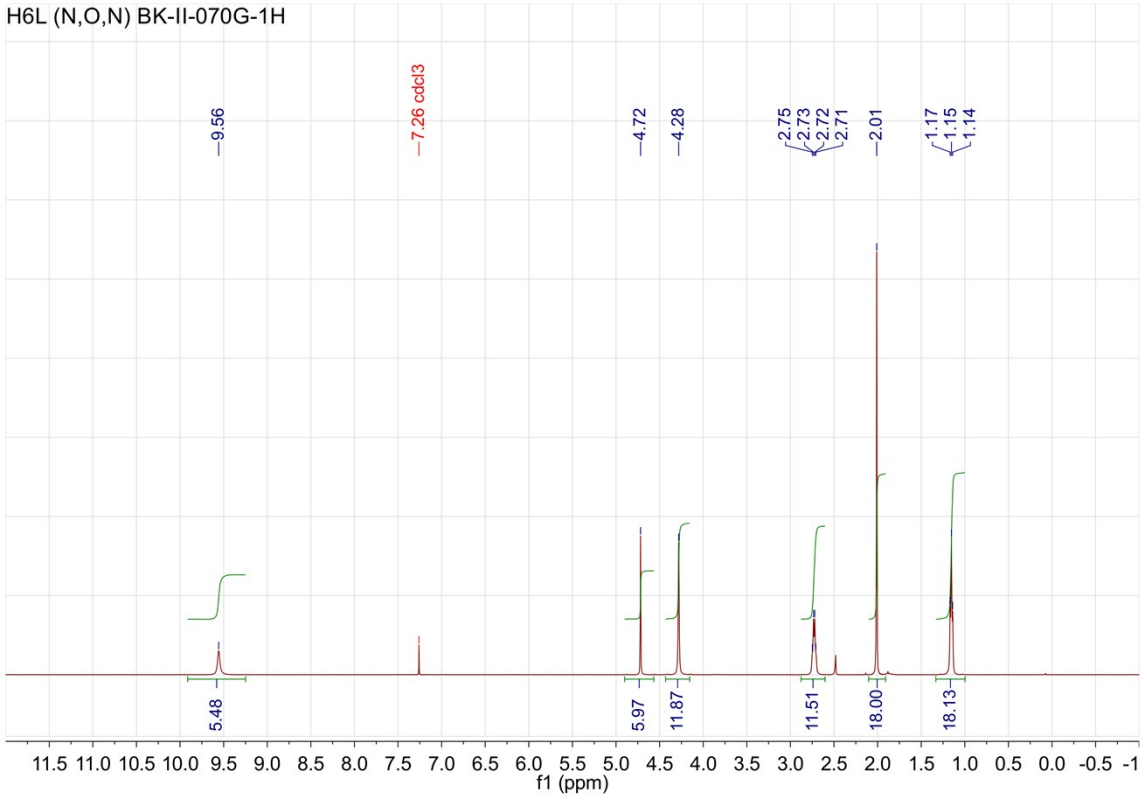

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of H_6**L**

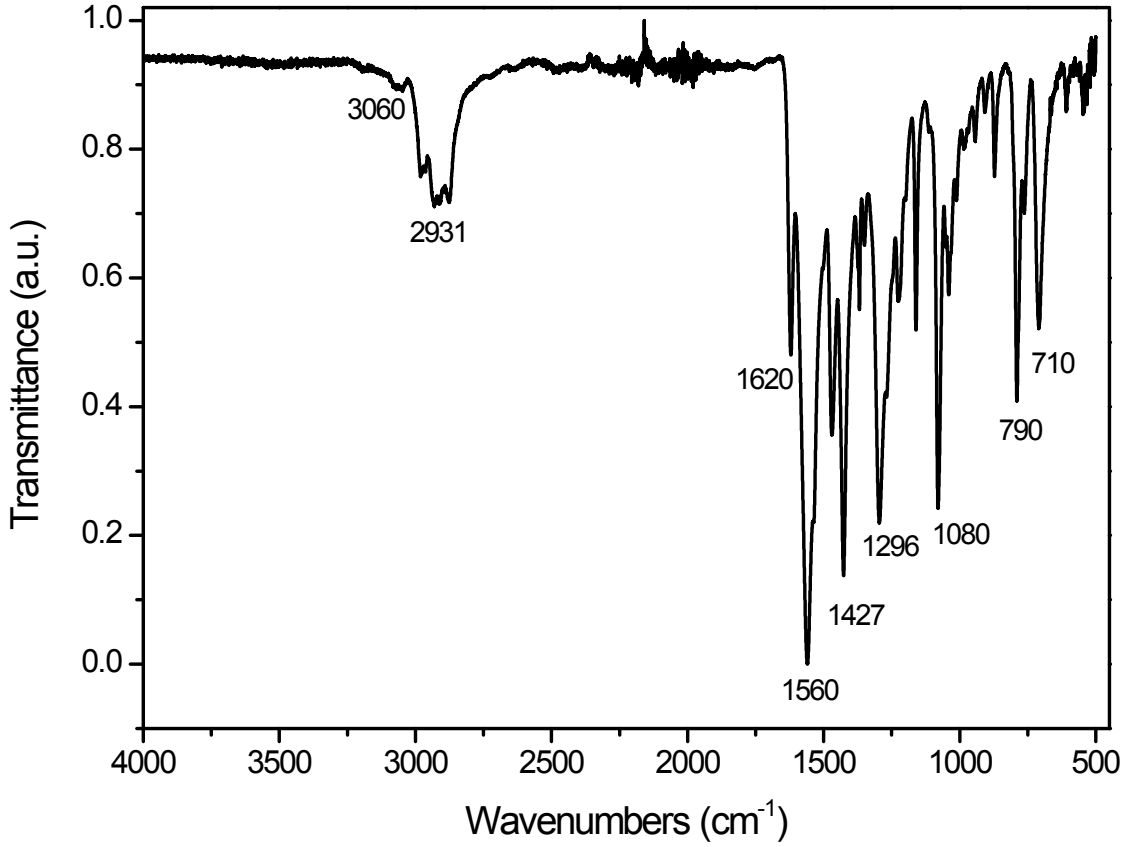

Figure S2. Infrared spectrum of H_6**L**

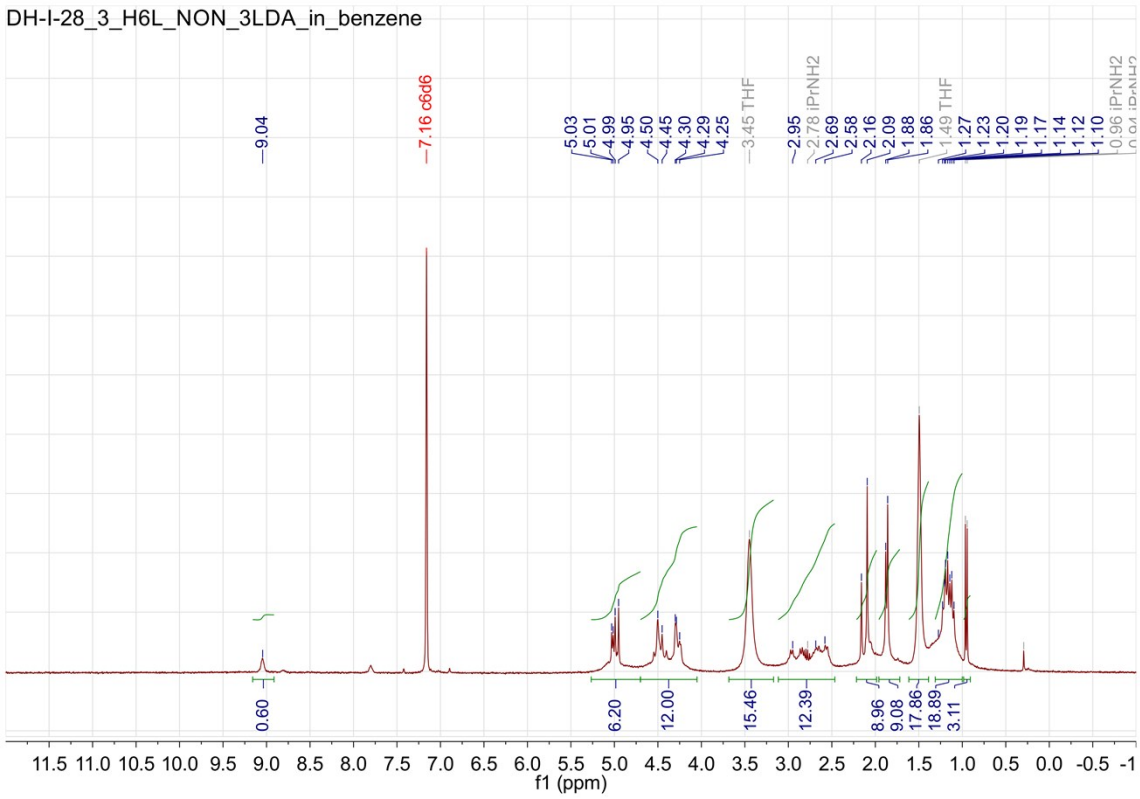

Figure S3. ^{1}H NMR spectrum (C_6D_6, 300 MHz) of H_6**L**+3LDA

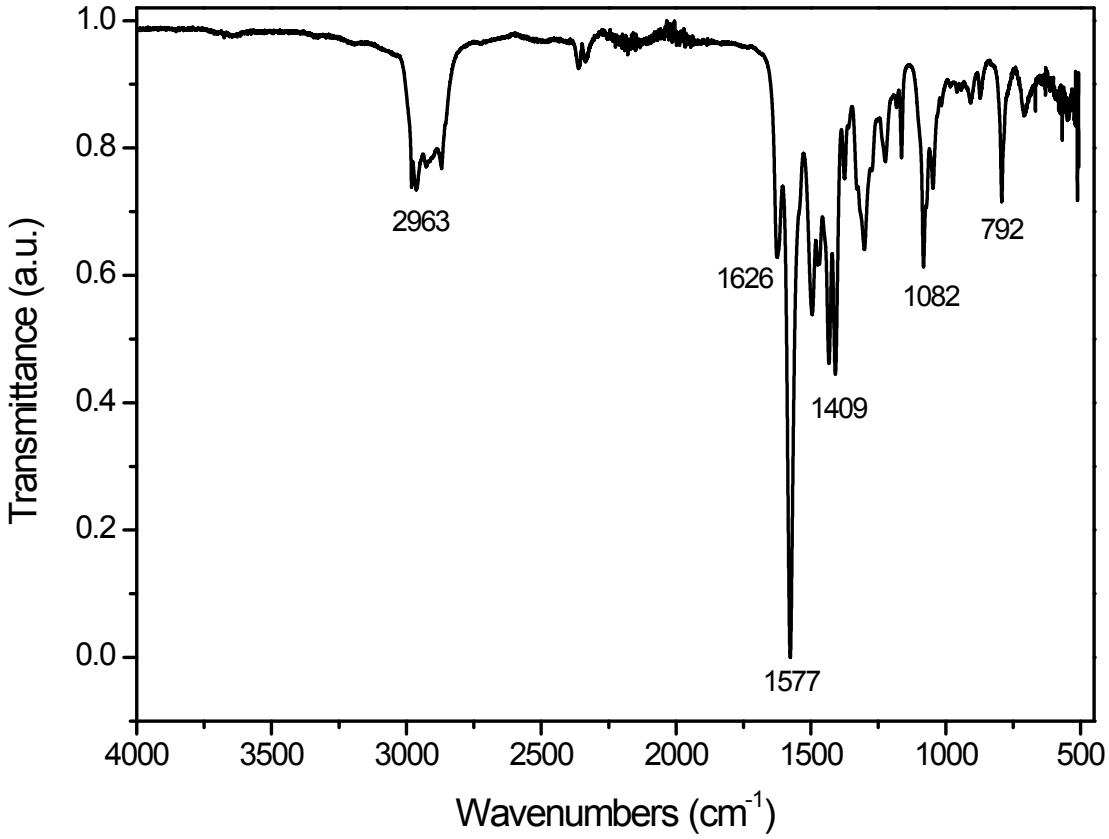

Figure S4. Infrared spectrum of H_6**L**+3LDA

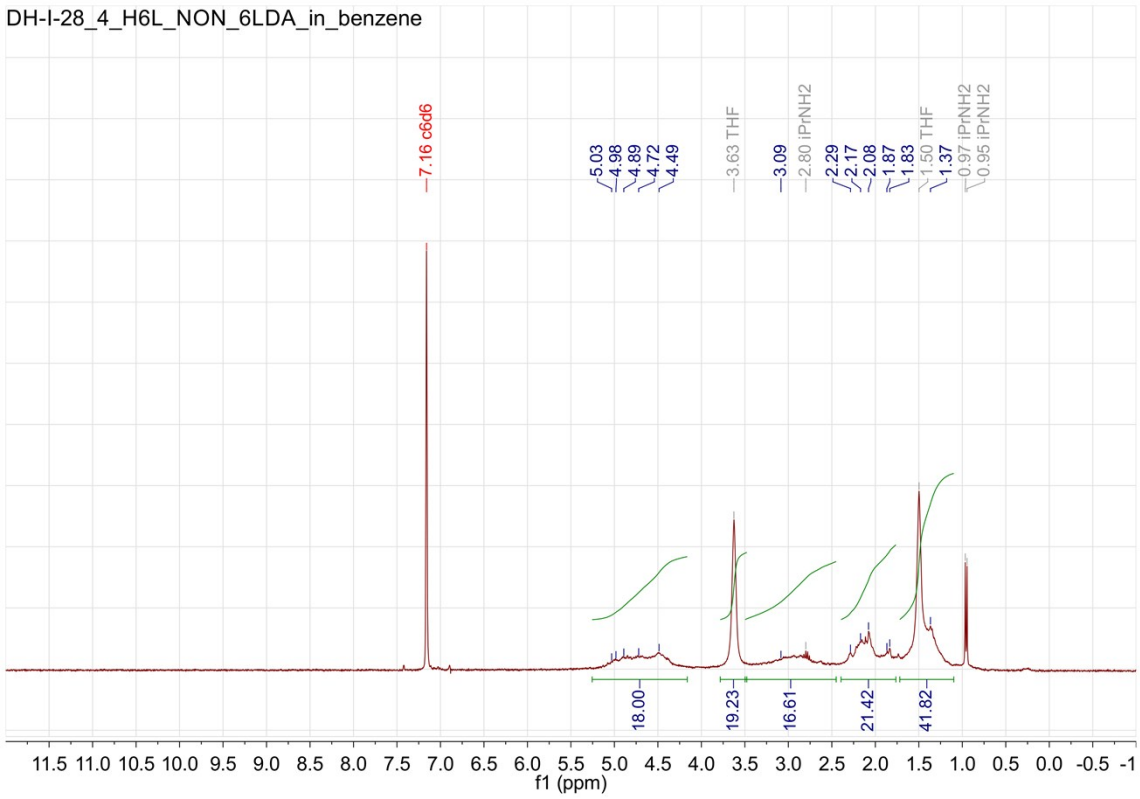

Figure S5. ^{1}H NMR spectrum (C_6D_6, 300 MHz) of H_6**L**+6LDA

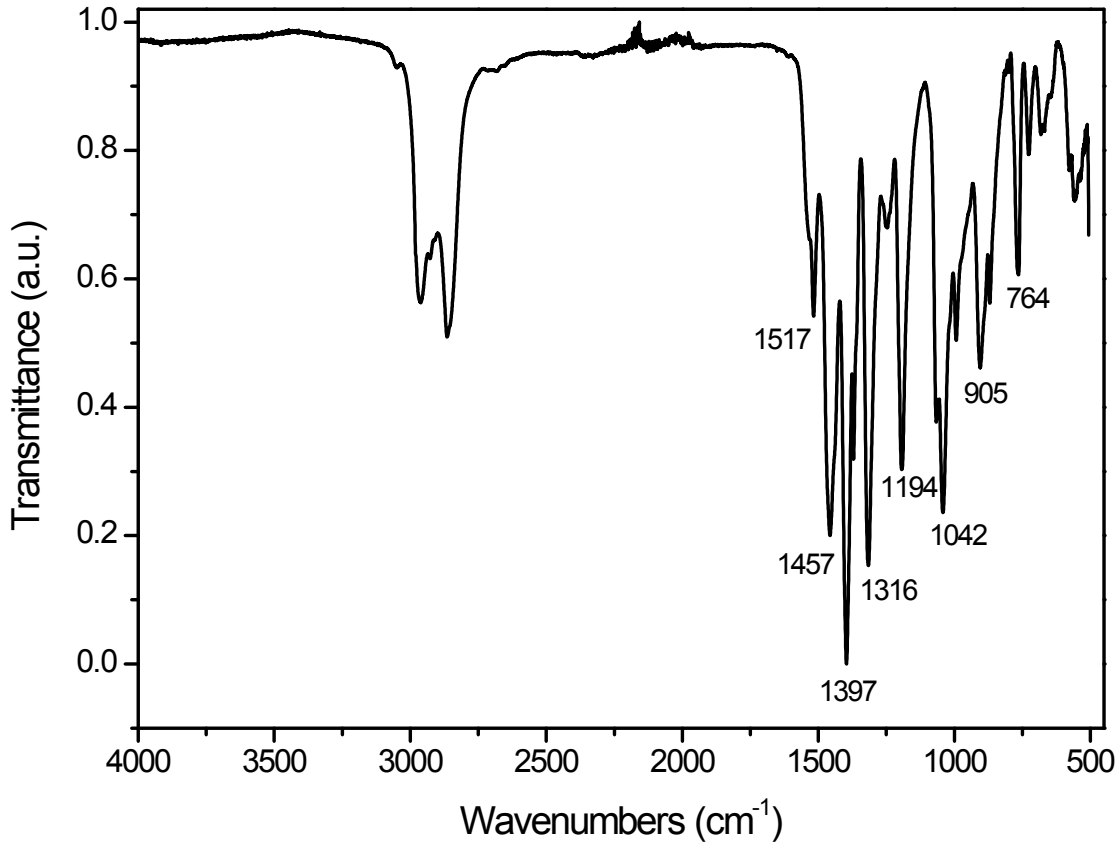

Figure S6. Infrared spectrum of H_6**L**+6LDA

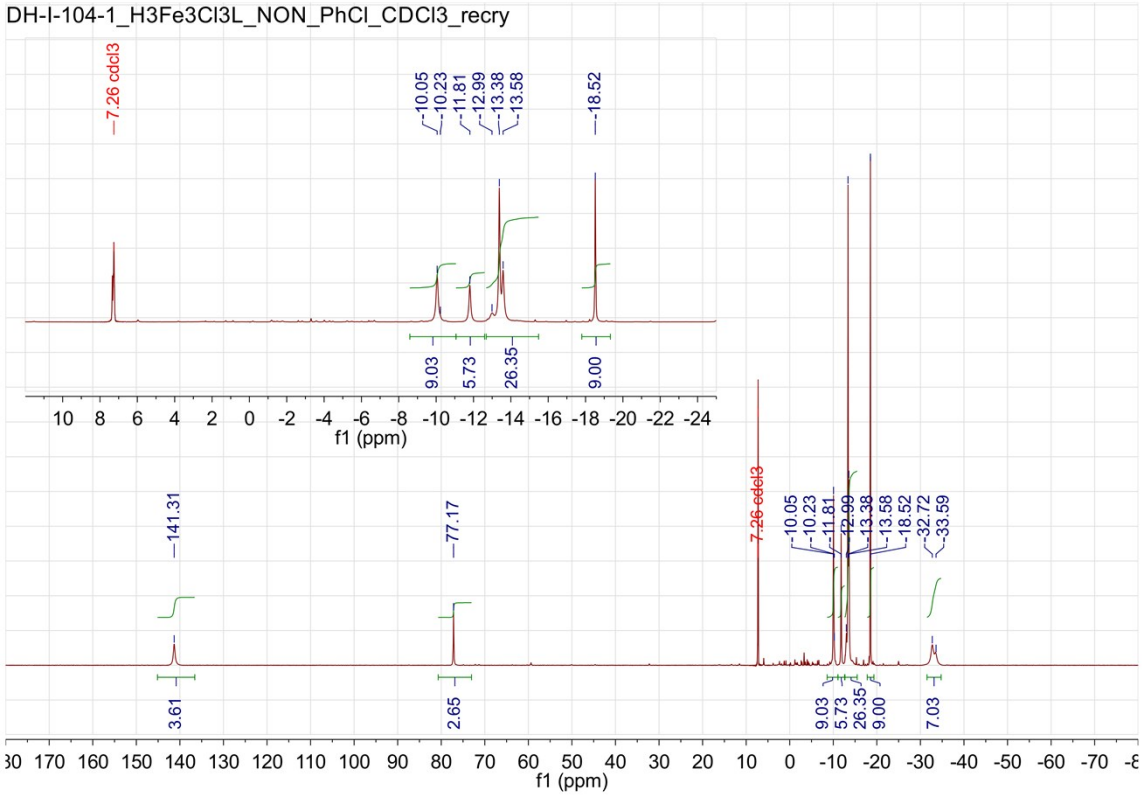

Figure S7. Paramagnetic ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **1**

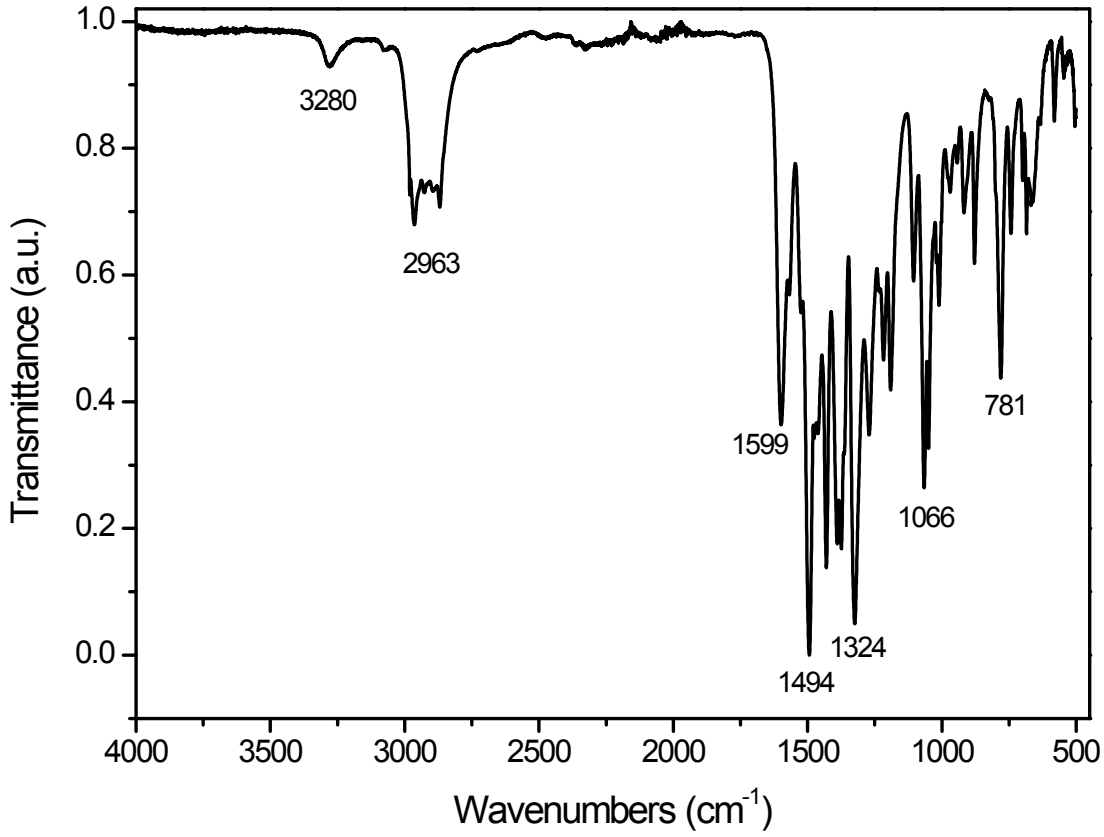

Figure S8. Infrared spectrum of **1**

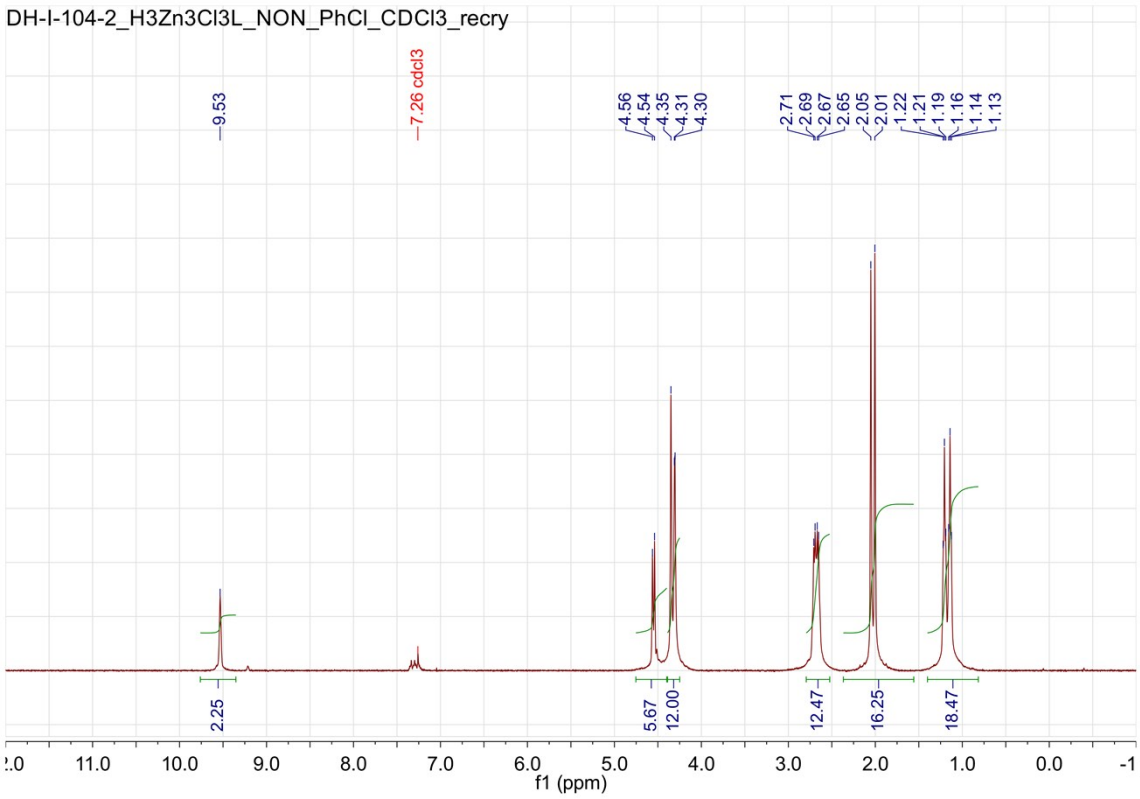

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **2**

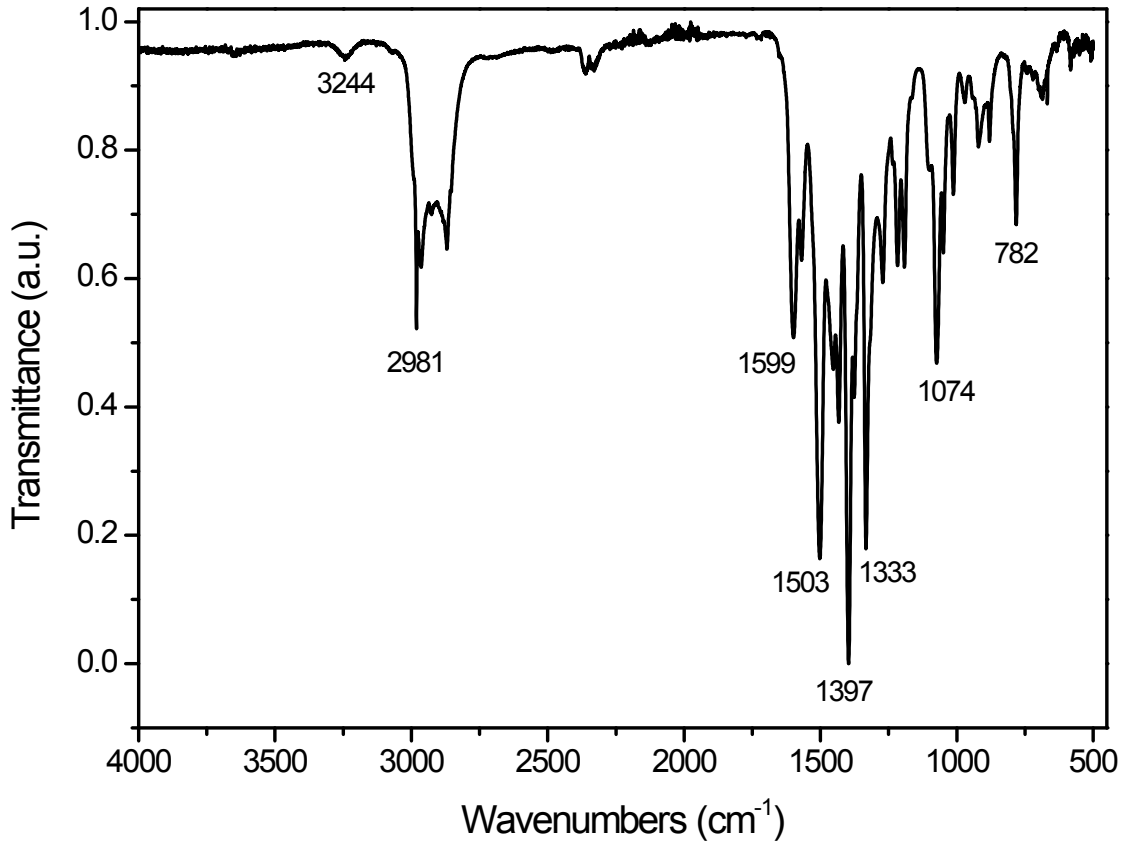

Figure S10. Infrared spectrum of **2**

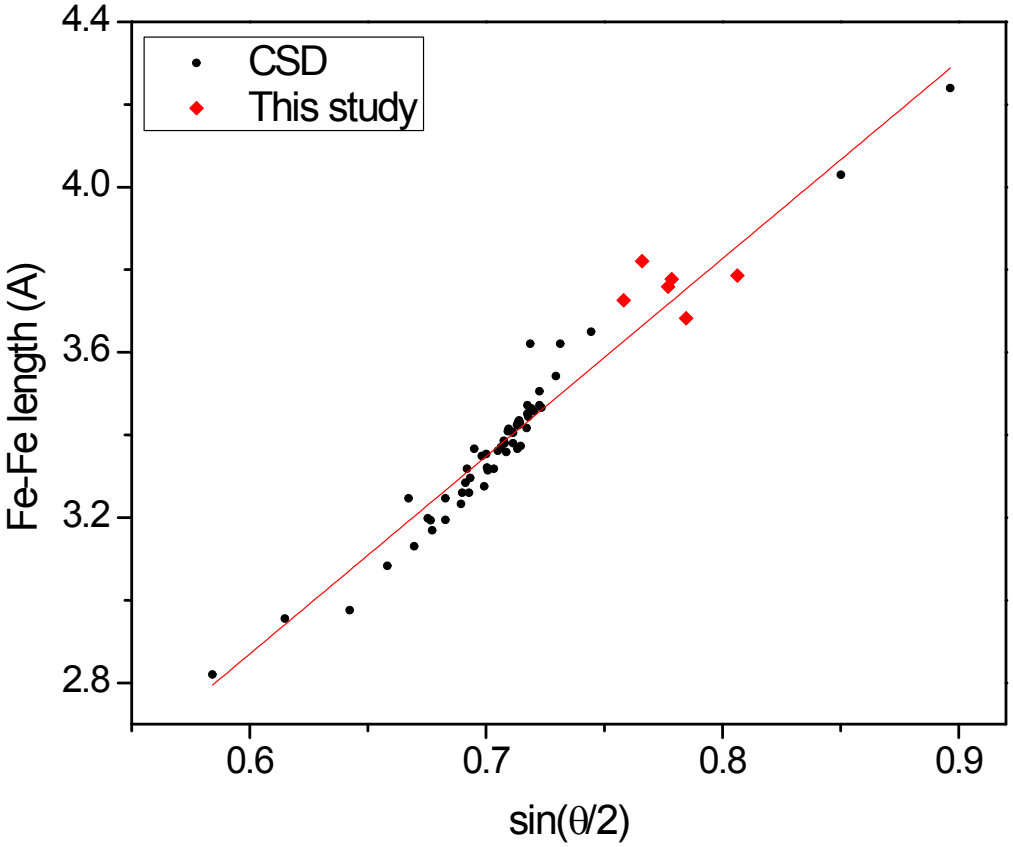

Figure S11. Fe–Fe bond length plotted versus sin(θ/2), where θ is the angle of Fe–Cl–Fe. The straight line calculated from $d_{Fe-Fe} = 4.783\ sin(\theta/2)$ Å with R^2=0.99976. The slope represents twice the bond length of Fe–(μ-Cl).

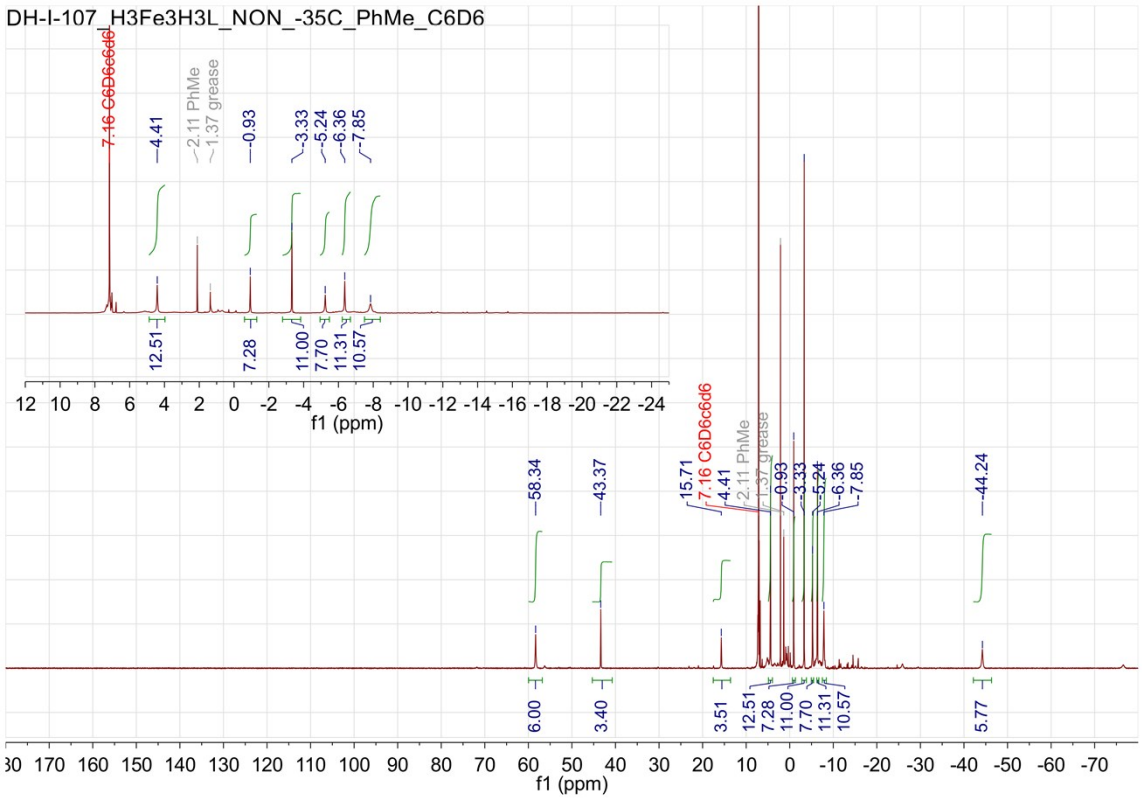

Figure S12. Paramagnetic ^{1}H NMR spectrum (C_6D_6, 500 MHz) of **3**

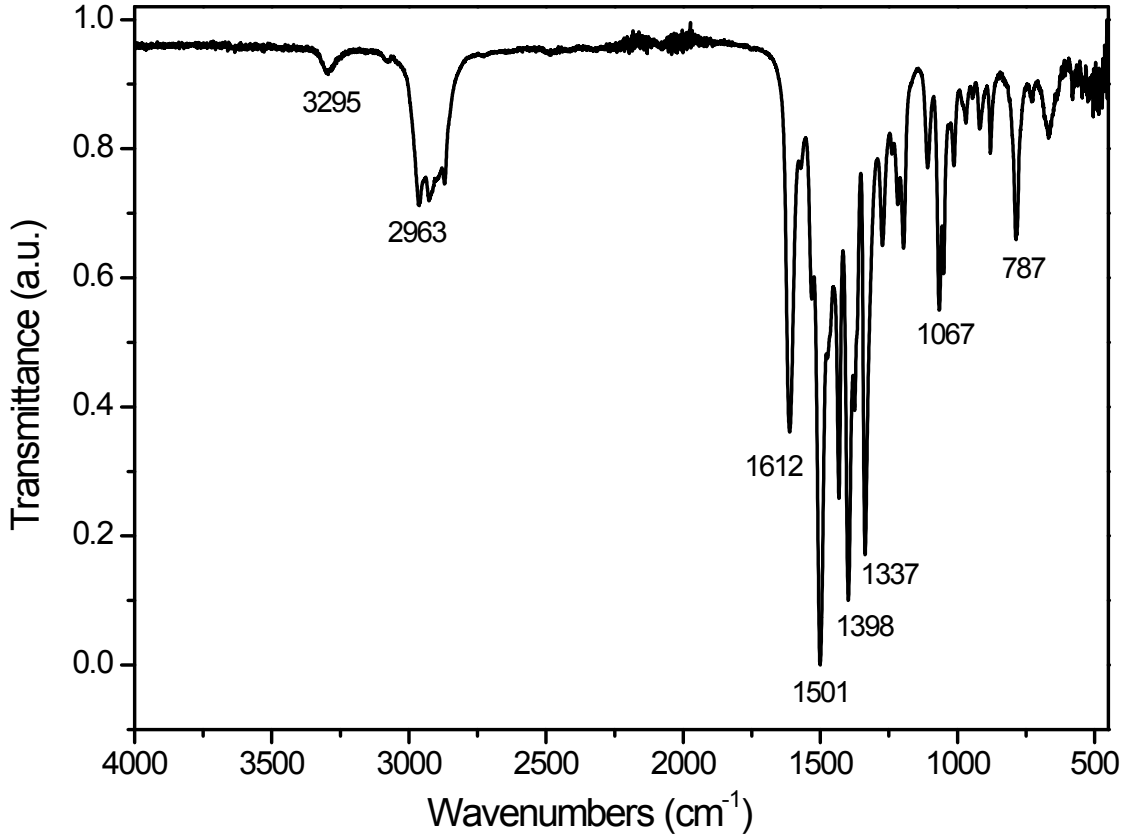

Figure S13. Infrared spectrum of **3**

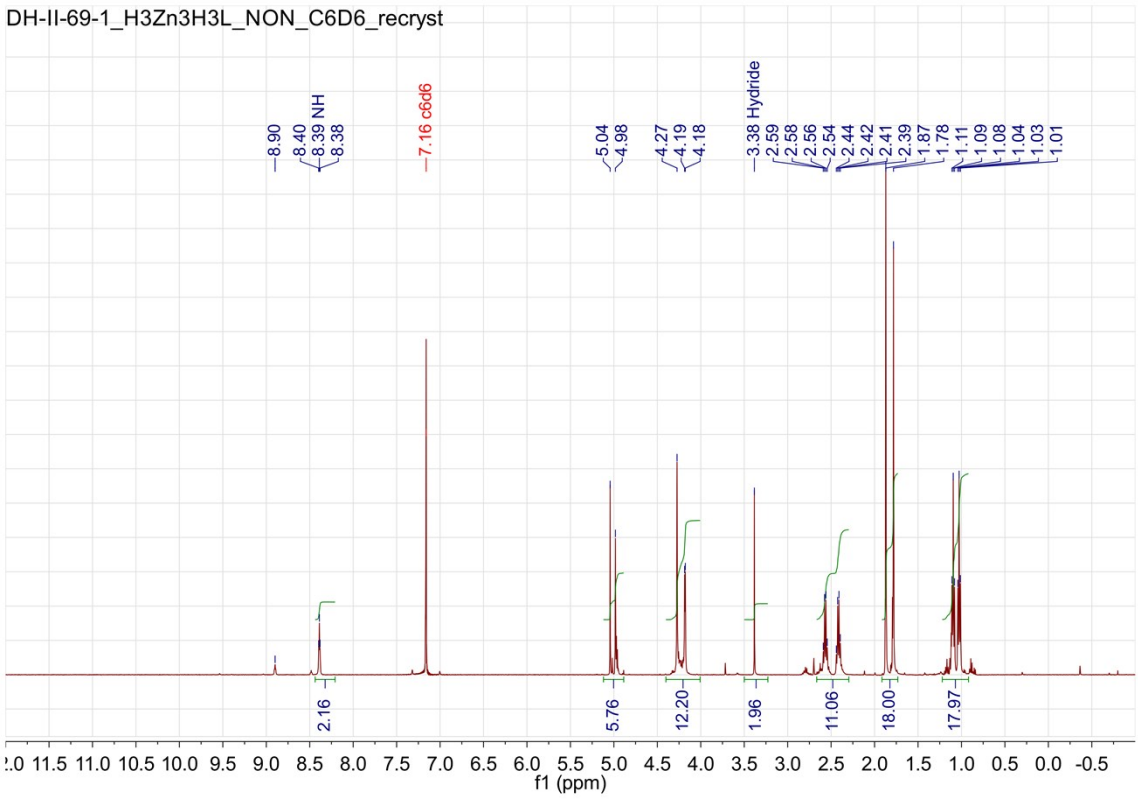

Figure S14. ^{1}H NMR spectrum (C_6D_6, 500 MHz) of **4**

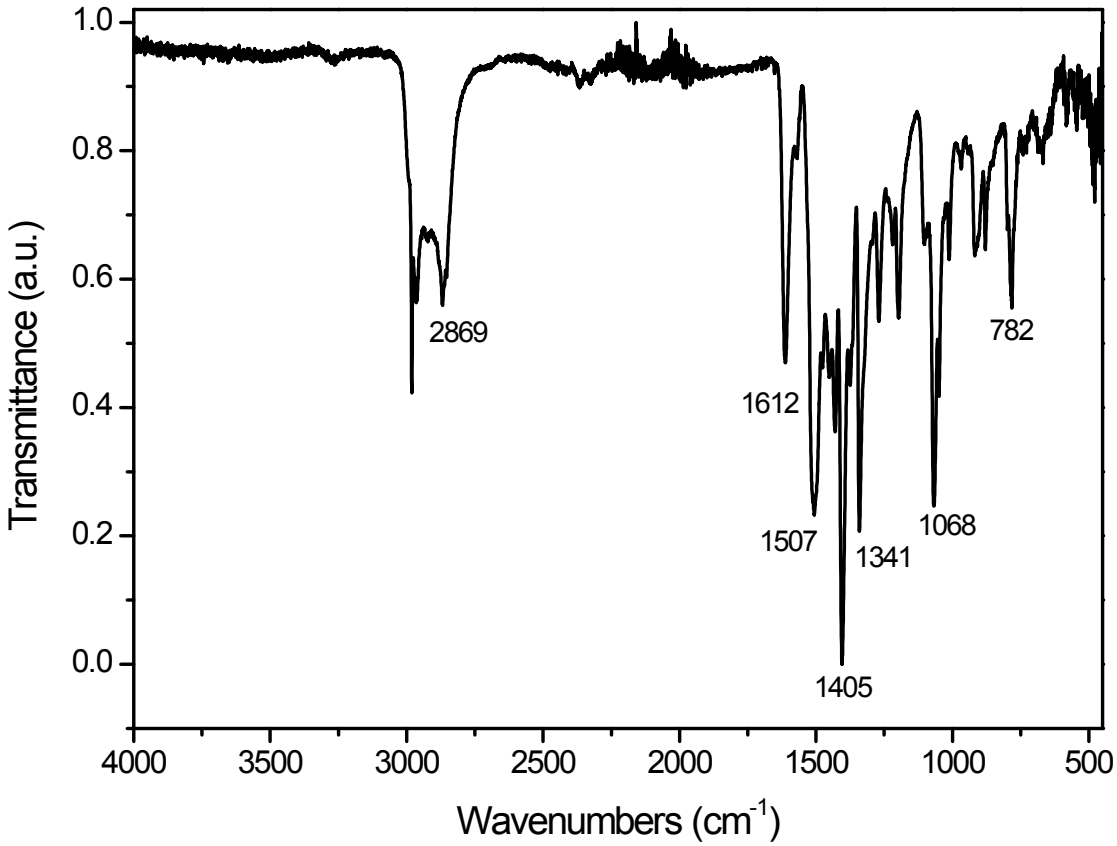

Figure S15. Infrared spectrum of **4**

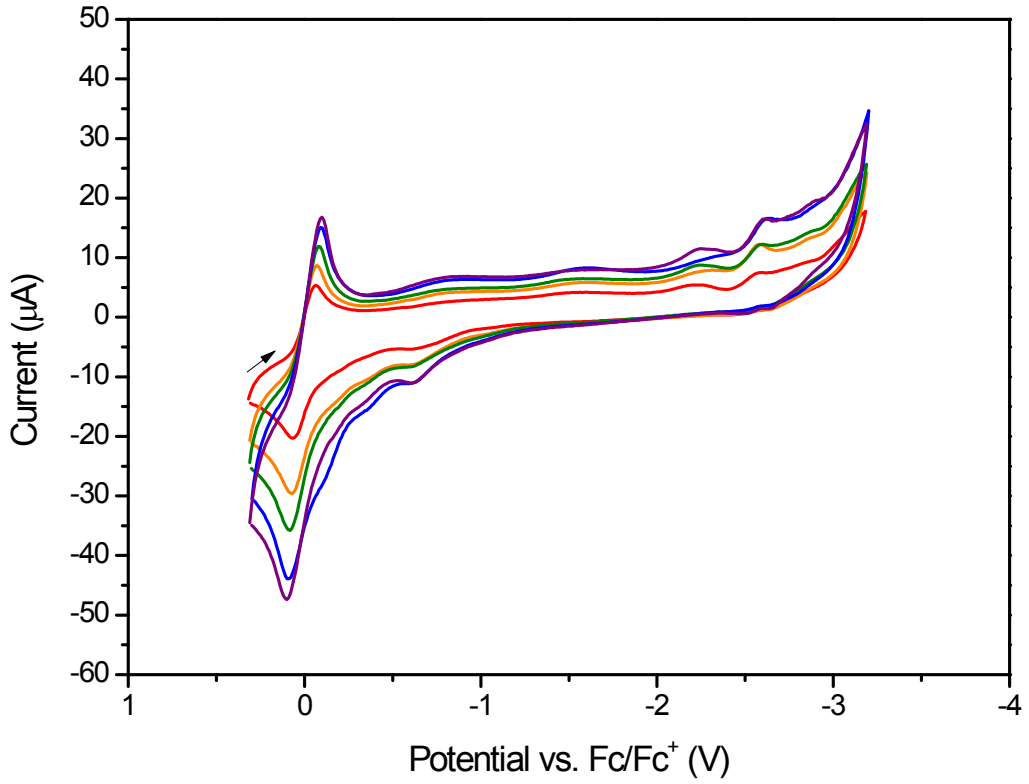

Figure S16. Cyclic voltammograms of **1** (0.87 mM) in THF using 0.30 M $[Bu_4N]PF_6$ as a supporting electrolyte. Ferrocene (1.1mM) was used as internal standard. Electrodes printed on a chip was used. Working electrode: Pt; reference electrode: Ag/AgCl; counter electrode: Pt; scan rate: 100–500 mV/s.

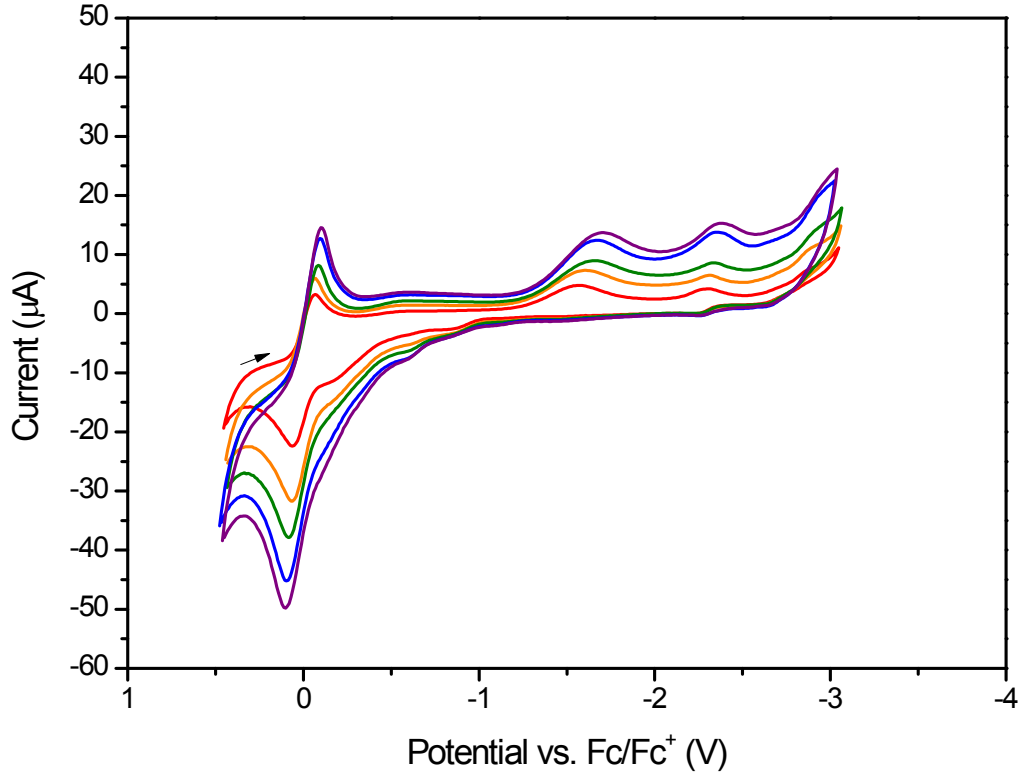

Figure S17. Cyclic voltammograms of **3** (0.87 mM) in THF using 0.30 M $[Bu_4N]PF_6$ as a supporting electrolyte. Ferrocene (1.1mM) was used as internal standard. Electrodes printed on a chip was used. Working electrode: Pt; reference electrode: Ag/AgCl; counter electrode: Pt; scan rate: 100–500 mV/s.

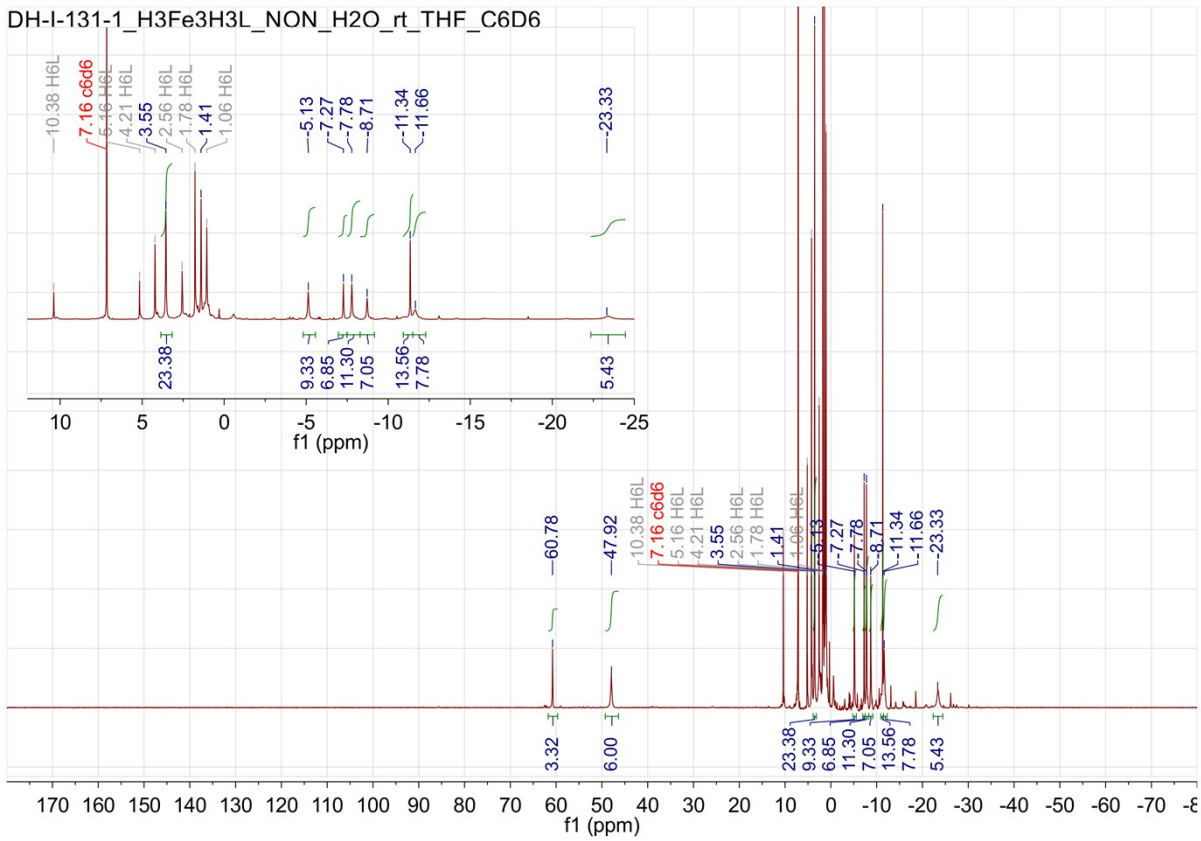

Figure S18. ^{1}H NMR spectrum (C_6D_6, 500 MHz) of **3**+H_2O

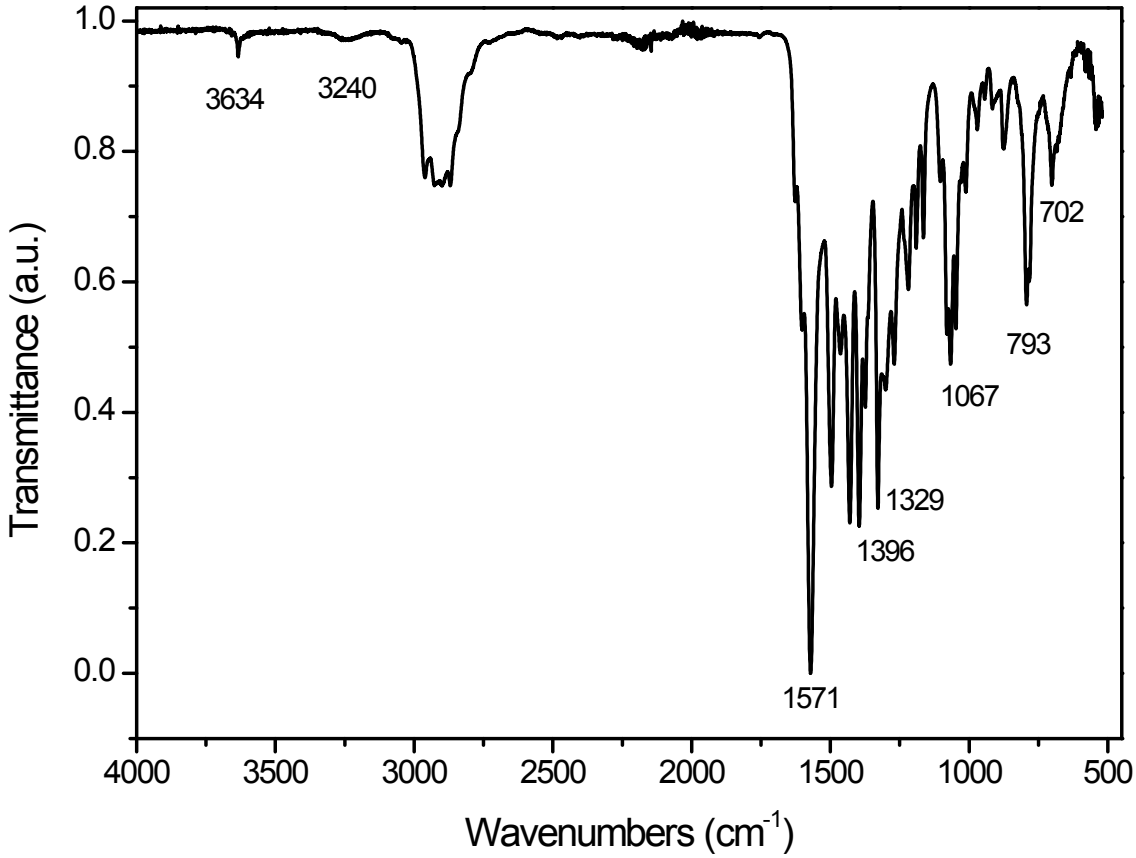

Figure S19. Infrared spectrum of **3**+H_2O

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C72 H90 Cl3 Fe3 N6 O3	
Formula weight	1361.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.9148(13) Å	α= 90°.
	b = 22.857(2) Å	β= 98.891(2)°.
	c = 23.150(2) Å	γ = 90°.
Volume	6751.9(12) $Å^3$	
Z	4	
Density (calculated)	1.339 Mg/m^3	
Absorption coefficient	0.806 mm^{-1}	
F(000)	2868	
Crystal size	0.469 x 0.036 x 0.024 mm^3	
Theta range for data collection	1.259 to 24.999°.	
Index ranges	-15<=h<=15, -27<=k<=27, -27<=l<=27	
Reflections collected	66004	
Independent reflections	11889 [R(int) = 0.1954]	
Completeness to theta = 24.999°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11889 / 0 / 827	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0829, wR2 = 0.1434	
R indices (all data)	R1 = 0.1764, wR2 = 0.1646	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.469 and -0.580 $e.Å^{-3}$	

2. References

(1) Guillet, G. L.; Sloane, F. T.; Ermert, D. M.; Calkins, M. W.; Peprah, M. K.; Knowles, E. S.; Čižmár, E.; Abboud, K. A.; Meisel, M. W.; Murray, L. J. Preorganized Assembly of Three Iron(Ii) or Manganese(Ii) β-Diketiminate Complexes Using a Cyclophane Ligand. *Chem. Commun.* **2013**, *49* (59), 6635 DOI: 10.1039/c3cc43395a.

(2) Lee, Y.; Jeon, I.-R.; Abboud, K. A.; García-Serres, R.; Shearer, J.; Murray, L. J. A [3Fe–3S] $^{3+}$ Cluster with Exclusively μ-Sulfide Donors. *Chem. Commun.* **2016**, *52* (6), 1174–1177 DOI: 10.1039/C5CC07813J.