Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Cleavage of Cluster Iron-Sulfide Bonds in Cyclophane-Coordinated Fe_nS_m Complexes

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Experimental Section

General Considerations. All manipulations were carried out inside a N_2-filled Innovative Technologies glovebox unless otherwise stated. Tetrahydrofuran (THF), benzene, toluene, *n*-hexane, and *n*-decane were purchased from Sigma-Aldrich, then purified through drying columns from Innovative Technologies solvent purification system and stored over activated 3 Å molecular sieves. Applicable solvents were tested for water content using standard Karl-Fischer titration methods and all showed water content < 1.0 ppm. C_6D_6 was purchased from Cambridge Isotope Laboratories, dried over CaH_2 under reflux, then distilled and degassed and stored over 3 Å molecular sieves. $Fe_3S_3\mathbf{L}$, $Fe_3Br_3\mathbf{L}$, $Fe_3Br_2S\mathbf{L}$, and $Fe_3H_3\mathbf{L}$ were synthesized as reported previously. $NaSCPh_3$ was prepared according to published procedures. All other reagents were purchased from Sigma-Aldrich and used without further purification.

^1H Nuclear Magnetic Resonance (^1H NMR) spectra were recorded on a Varian Inova 500 MHz spectrometer or a Mercury operating at 300 MHz equipped with a three-channel 5 mm indirect detection probe with z-axis gradients. Chemical shifts were reported in δ (ppm) and were referenced to solvent resonance $\delta_H = 7.16$ ppm for benzene-d_6. FT-IR spectra were collected on drop-casted samples using a ThermoFisher Scientific Nicolet iS5 spectrometer equipped with an iD7 ATR stage and using the OMNIC software package at 1.0 cm^{-1} resolution and 32 scans per sample. Mass spectrometry data were collected using an Agilent 6220 ESI-TOF on samples prepared in THF at analyte concentrations of 16.0 μM. Solution samples were prepared in anhydrous THF and loaded into Hamilton Gastight Sample Lock syringes in an N_2-filled glove box. Samples were introduced into the MS by direct infusion concurrent with a continuous flow of the anhydrous THF.

X-Ray Crystallography. Single crystal X-ray diffraction was performed on a Bruker SMART Apex II CCD instrument at 100 K using graphite-monchromated Mo Kα radiation. The crystals were covered in Paratone oil and mounted on glass fibers. Lorentz and polarization effects were corrected using SAINT, and the absorption corrections were applied using SADABS. The structures were solved using direct methods or Patterson syntheses using SHELXS and SHELXL.

Mössbauer Spectroscopy. All samples were ground, placed in Delrin sample containers, and sealed with screw caps in an N2-filled glovebox. Mössbauer spectra were measured either on a lowfield Mössbauer spectrometer equipped with a closed-cycle SHI-850-5 cryostat from 57 Janis and SHI or an Oxford Instruments Spectromag 4000 cryostat containing an 8T split-pair superconducting magnet. Both spectrometers were operated in constant acceleration mode in transmission geometry. The isomer shifts are referenced against a room temperature metallic iron foil. Analysis of the data was performed using the program WMOSS (WEB Research).

Scrambling 1 and 2. To a 20 mL scintillation vial was added a solid mixture of $Fe_3Br_3\mathbf{L}^{\mathbf{Et/Me}}$ (13.1 mg, 0.0120 mmol) and $Fe_3S_3\mathbf{L}^{\mathbf{Et/Me}}$ (11.4 mg, 0.0120 mmol) that was dissolved in THF (5 mL) resulting in immediate formation of a dark green solution. The reaction was stirred overnight, which was proceeded by filtration through a THF-rinsed celite plug separating a black, insoluble byproduct from the dark green filtrate. The filtrate was left under vacuum to remove all volatiles to afford a dark green-grey powder (~5 mg). The powder was dissolved in C_6D_6 for characterization by ^{1}H-NMR spectroscopy. Variations of this experiment were conducted using an analogous procedure. Variations include: stoichiometric ratios, temperature, solvent, and reaction time.

Demetallation of 2. To a solid mixture of $Fe_3Br_3\mathbf{L}^{\mathbf{Et/Me}}$ (73.1 mg, 0.0667 mmol) and S_8 (4.3 mg, 0.0168 mmol) was added THF (14 mL), resulting in immediate formation of a dark green mixture which was stirred for 8 h. Upon completion, the mixture was filtered through a THF-rinsed celite plug, and the resulting dark green filtrate was left under vacuum to remove all volatiles affording a dark green solid. C_6H_6 (8 mL) was added to the solid, partially dissolving the produced material. The benzene solution was decanted then frozen and lyophilized, and a sample of the resulting green powder (13.4 mg, yield 20.1%) was taken up in C_6D_6 for characterization by ^{1}H-NMR spectroscopy. ^{1}H-NMR (benzene-d$_6$, 500 MHz) δ: 65.30 (2H, s, br), 52.15 (2H, s, br), 11.75 (1H, s, br), -0.27 (3H, s, br), -1.63 (2H, s, br), -2.56 (7H, s, br), -3.26 (7H, s, br), -12.49 (2H, s, br), -15.39 (2H, s, br), -17.67 (1H, s, br), -66.73 (5H, s, br). HRMS(ESI+) m/z calcd for $(M+H^+)$ $[C_{45}H_{65}Br_2Fe_2N_6S]$: 993.2036; found: 993.1979. FTIR (cm^{-1}): 3522, 2922, 1616, 1518, 1430, 1325, 1016, 730.

Synthesis of 5. $Fe_3H_3\mathbf{L}^{\mathbf{Et/Me}}$ (52.4 mg, 0.061 mmol) was dissolved in 10 mL of THF and a solution of S_8 (31.3 mg, 0.122 mmol) in THF (5 mL) was added dropwise at room temperature. After 12 h, the dark green mixture was filtered over THF-rinsed Celite. All volatiles were removed from the filtrate resulting in a dark green solid. The solid was dissolved in C_6H_6 (10 mL) and filtered on a C_6H_6-rinsed Celite plug to afford a dark green solution. C_6H_6 was lyophilized to yield a dark green fine powder that was dried under reduced pressure at 60 °C (38.8 mg, yield 73%). Crystals were obtained by hexane diffusion to a saturated solution of the compound in THF. ^{1}H-NMR (benzene-*d$_6$*, 500 MHz) δ: 23.07 (8 H), 5.07 (4 H), 4.67 (1 H), 3.57 (2 H), 3.01 (8 H), 1.85 (6 H), 1.57 (12 H), 1.42 (2 H), 1.05 (6 H), -0.26 (12 H), -8.11 (2 H). Mössbauer (80 K, mm/s): $\delta = 0.30$, $|\Delta E_Q| = 0.80$. ESI(+)-HRMS ($[M+H^+]^+$) m/z calcd. for $C_{45}H_{65}Fe_2N_6S_2$: 865.3411. Found: 865.3310.

Scrambling 2 and 5. To a 20 mL scintillation vial was added a solid mixture of $Fe_3Br_3\mathbf{L}^{\mathbf{Et/Me}}$ (14.6 mg, 0.0133 mmol) and $Fe_2S_2\mathbf{HL}^{\mathbf{Et/Me}}$ (10.8 mg, 0.0125 mmol) that was dissolved in THF (5 mL) resulting in immediate formation of a dark green solution. The reaction was stirred overnight, which was proceeded by filtration through a THF-rinsed celite plug separating a black, insoluble byproduct from the dark green filtrate. The filtrate was left under vacuum to remove all volatiles to afford a dark green-grey powder (~8 mg). The powder was dissolved in C_6D_6 for characterization by ^{1}H-NMR spectroscopy. Additionally, a similar procedure was used utilizing toluene as solvent.

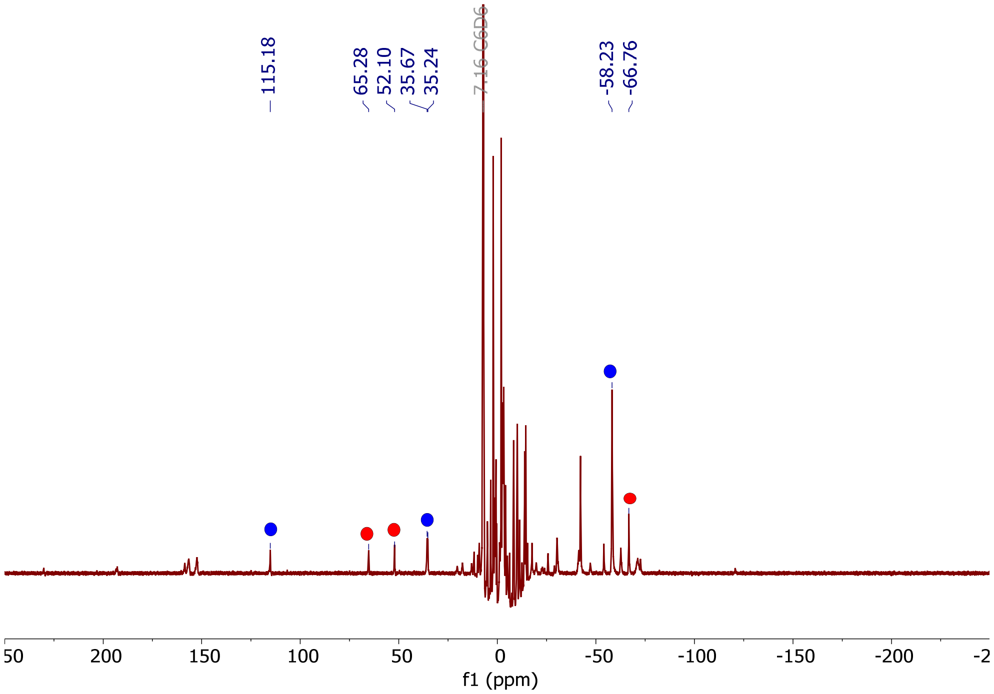


Figure S1. ^{1}H-NMR spectrum of the scrambling between **1** and **2** reaction performed in toluene at room temperature for ~18 h. The spectrum was taken in C_6D_6 at room temperature. Blue and red circles correspond to **3** and **4**, respectively. For clarity, only diagnostic resonances are labelled for the two major species.

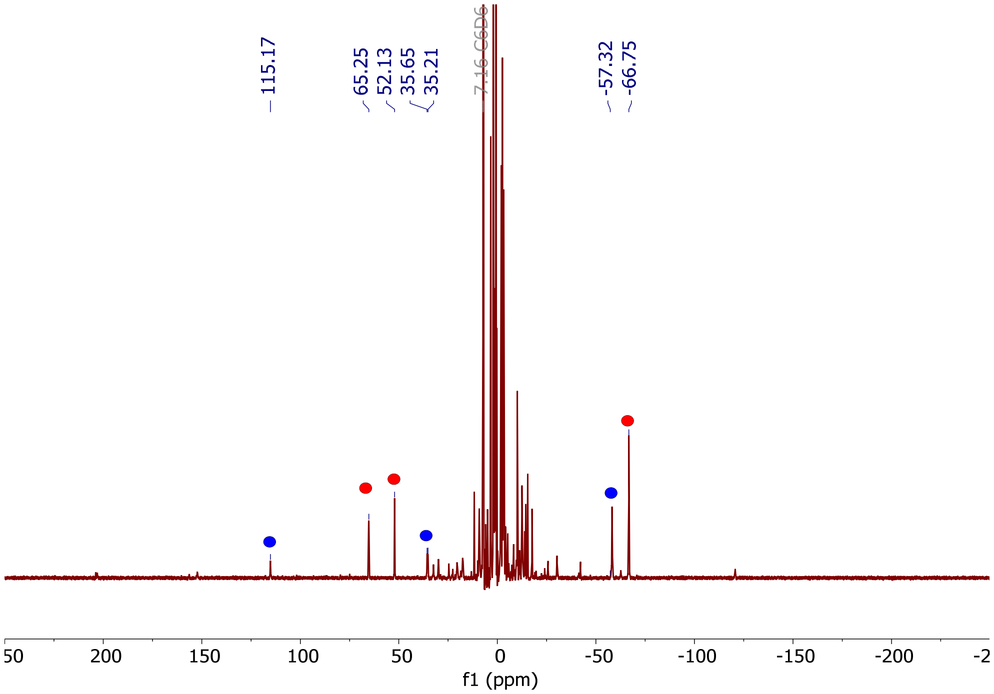


Figure S2. ^{1}H-NMR spectrum of the scrambling reaction between **1** and **2** performed in toluene at 90 °C for ~18 h. The spectrum was taken in C_6D_6 at room temperature. Blue and red circles correspond to **3** and **4**, respectively. For clarity, only diagnostic resonances are labelled for the two major species.

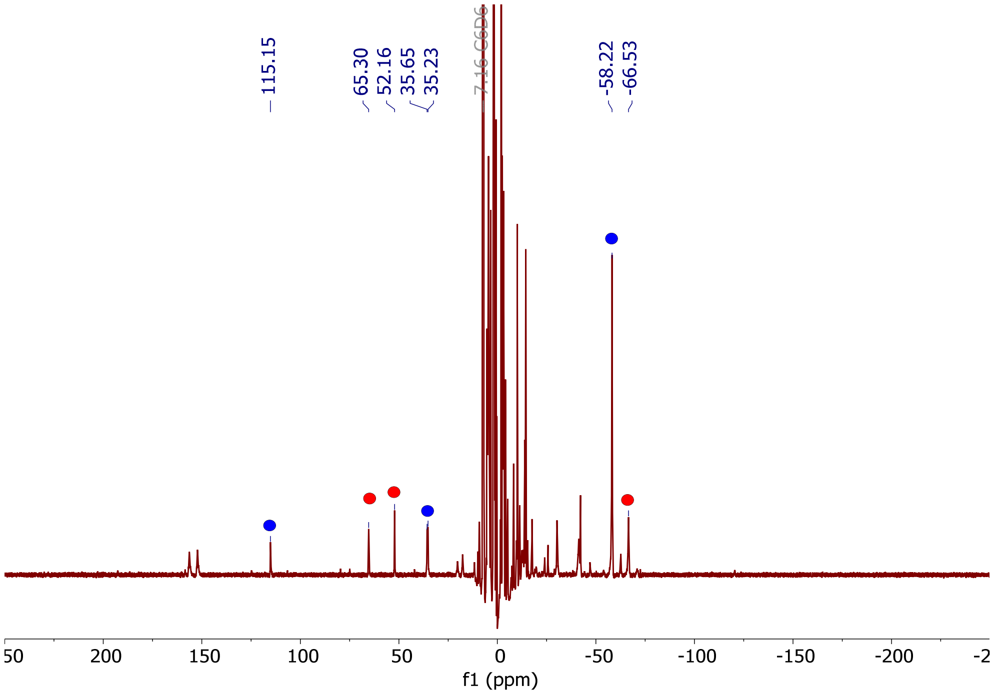


Figure S3. ^{1}H-NMR spectrum of the scrambling between **1** and **2** reaction performed in THF at room temperature for ~18 h using 2 equiv. of **2**. The spectrum was taken in C_6D_6 at room temperature. Blue and red circles correspond to **3** and **4**, respectively. For clarity, only diagnostic resonances are labelled for the two major species.

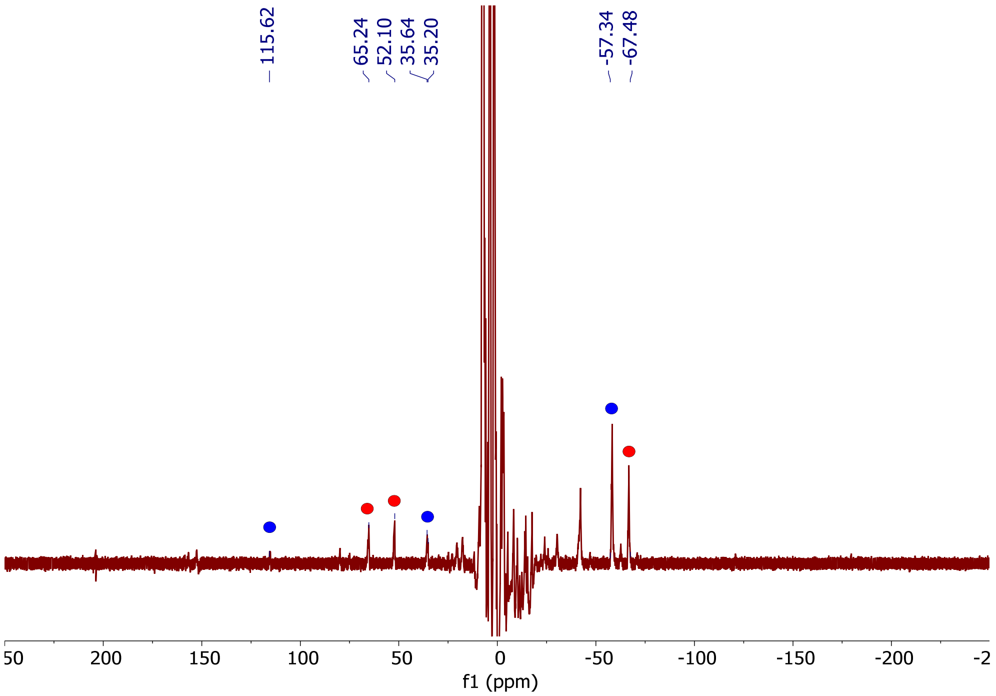


Figure S4. ^{1}H-NMR spectrum of the scrambling between **1** and **2** reaction performed in THF at room temperature for ~18 h using 2 equiv. of **1**. The spectrum was taken in C_6D_6 at room temperature. Blue and red circles correspond to **3** and **4**, respectively. For clarity, only diagnostic resonances are labelled for the two major species.

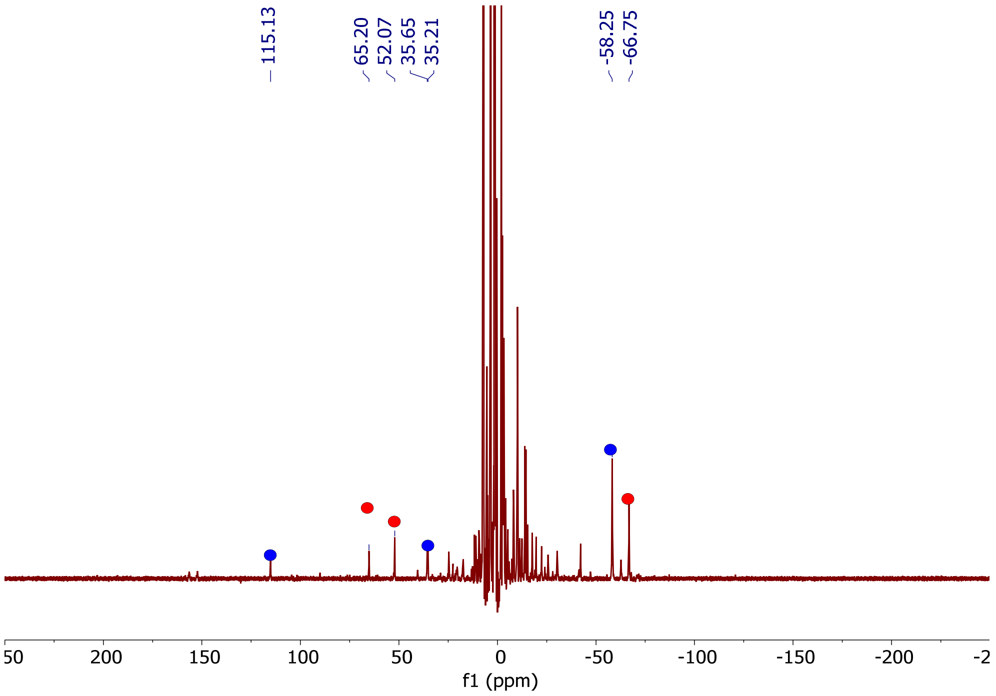


Figure S5. ^{1}H-NMR spectrum of the scrambling between **1** and **2** reaction performed in THF at room temperature for ~48 h. The spectrum was taken in C_6D_6 at room temperature. Blue and red circles correspond to **3** and **4**, respectively. For clarity, only diagnostic resonances are labelled for the two major species.

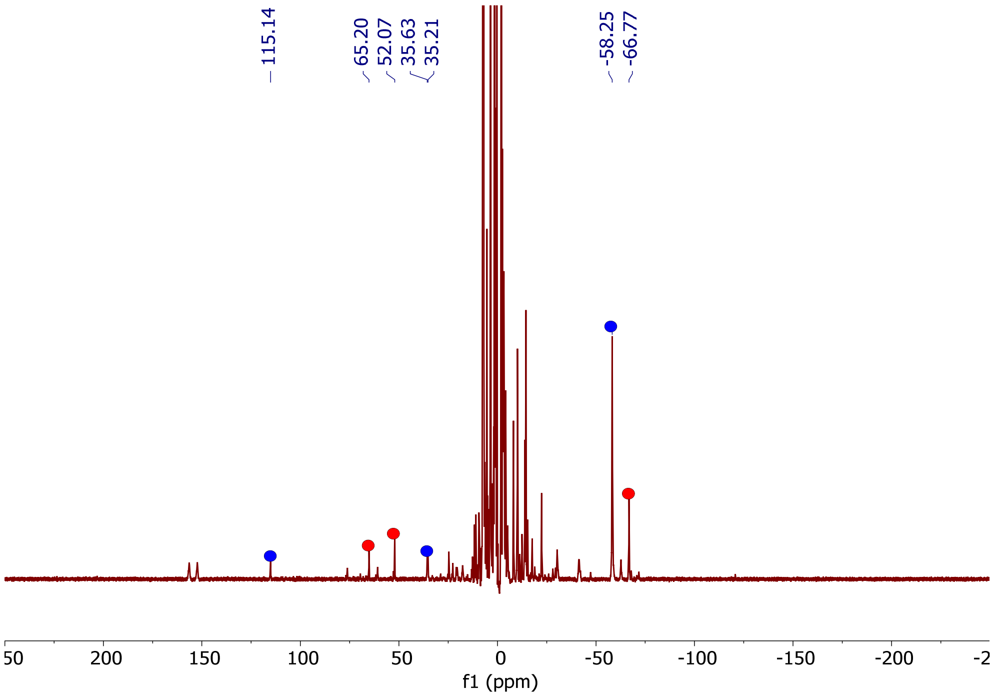


Figure S6. ^{1}H-NMR spectrum of the scrambling between **1** and **2** reaction performed in PhMe at room temperature for ~5 min. The spectrum was taken in C_6D_6 at room temperature. Blue and red circles correspond to **3** and **4**, respectively. For clarity, only diagnostic resonances are labelled for the two major species.

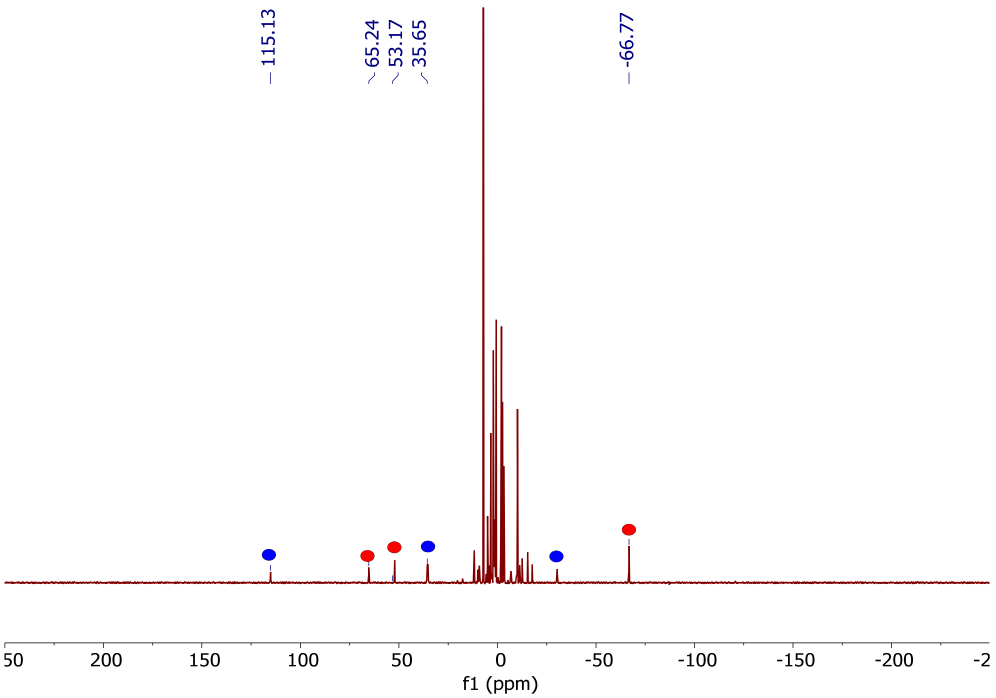


Figure S7. ^{1}H-NMR spectrum of product mixture from the scrambling reaction between **1** and **2** in THF at -40 °C.

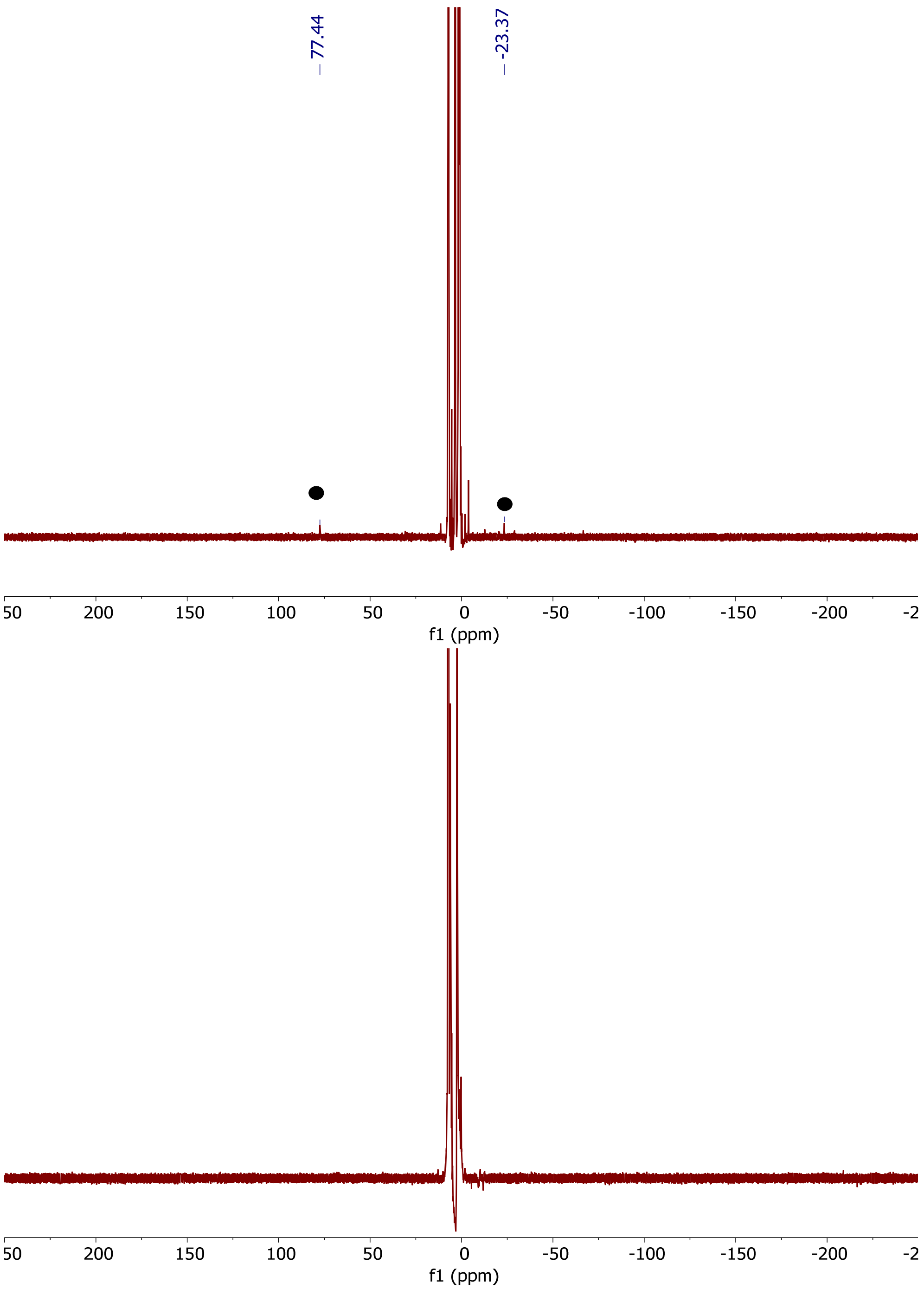


Figure S8. ^{1}H-NMR spectra of **1** with TBABr (top) and FeBr2 (bottom).

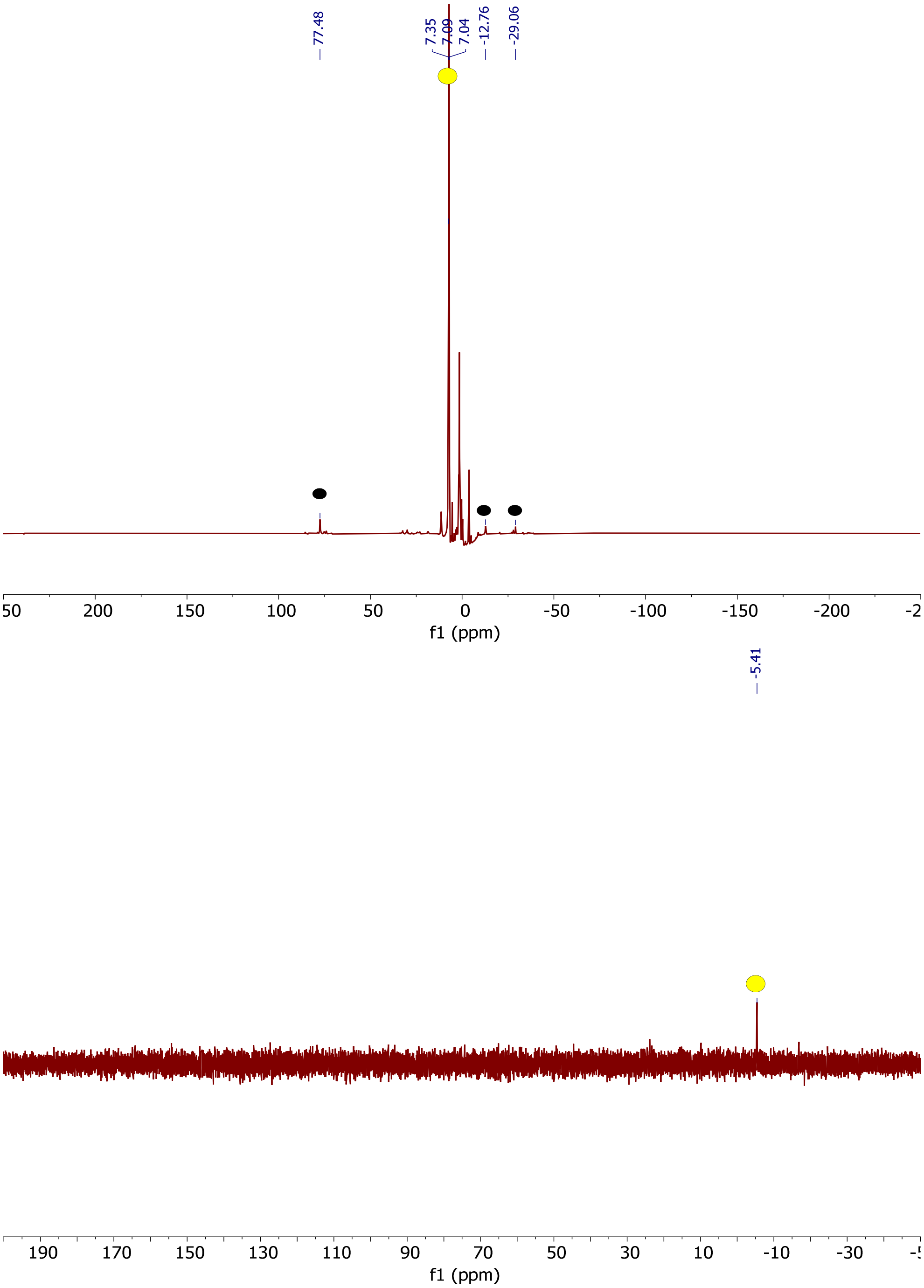


Figure S9. ^{1}H- (top) and ^{31}P-NMR (bottom) spectra of PPh_3 (yellow) with **1** (black).

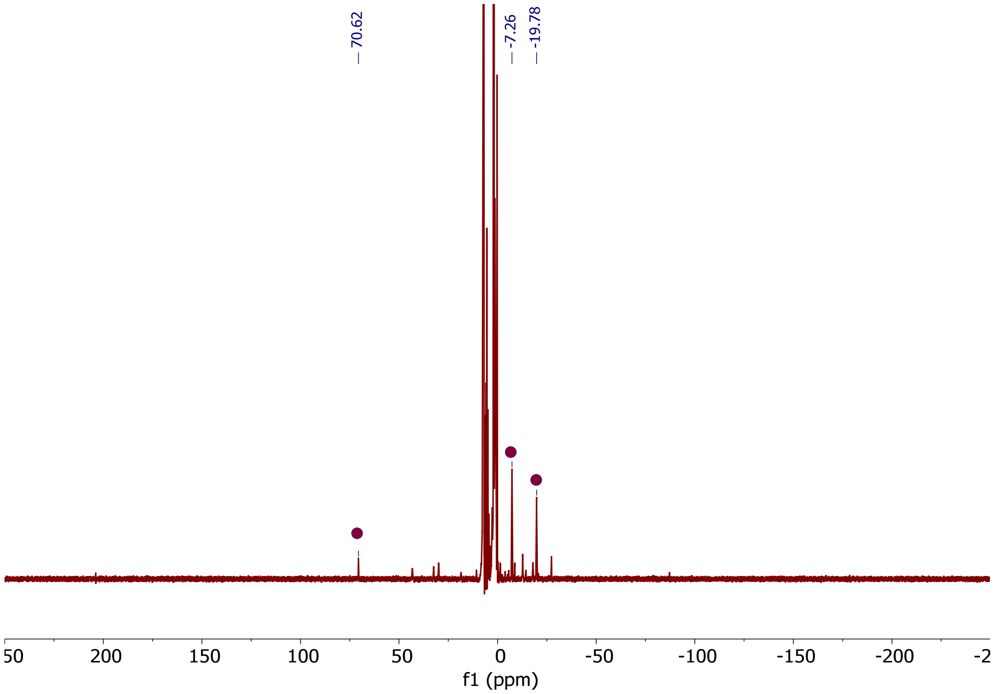


Figure S10. ^{1}H-NMR spectrum of product mixture from scrambling between **1** and $Fe_3(NH_2)_3$**L**$^{\mathbf{Et/Me}}$ (purple) after 18 h.

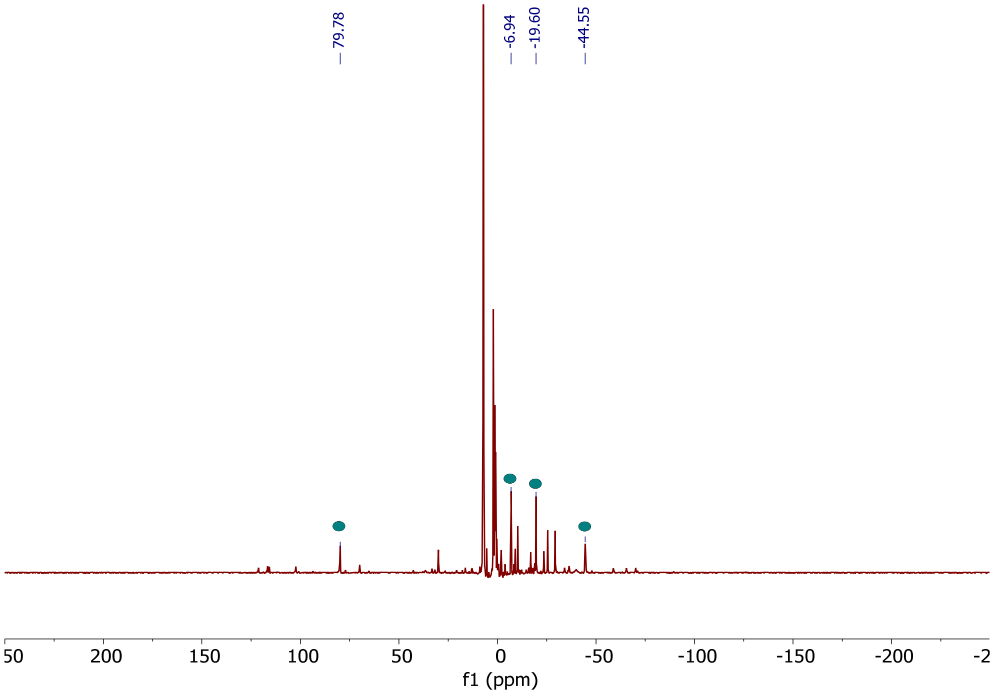


Figure S11. ^{1}H-NMR spectrum of product mixture from scrambling between **1** and Fe$_3$H$_3$**L**$^{\mathbf{Et/Me}}$ (teal).

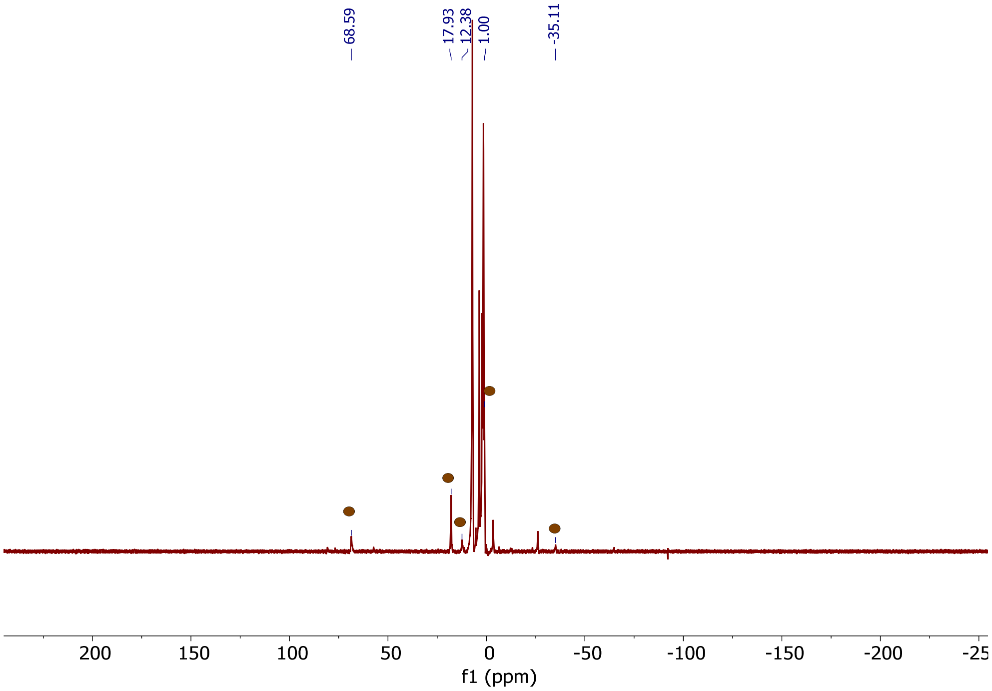


Figure S12. ^{1}H-NMR spectrum of product mixture from scrambling between **1** and Fe$_3$(OMe)$_3$**L**$^{\mathbf{Et/Me}}$ (brown).

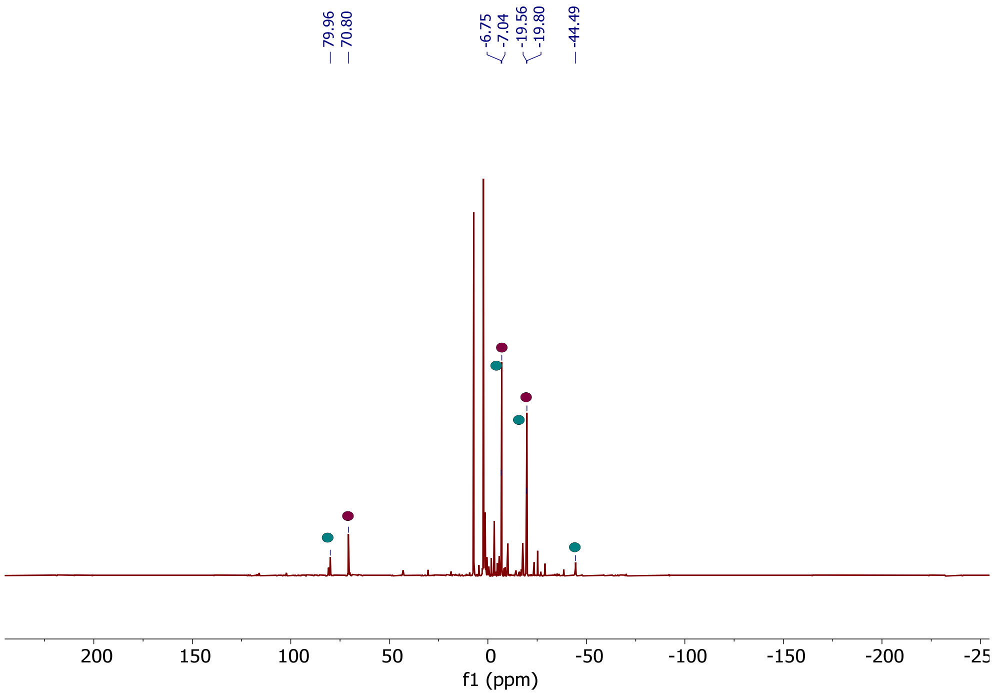


Figure S13. ^{1}H-NMR spectrum of product mixture from scrambling between $Fe_3H_3\mathbf{L}^{\mathbf{Et/Me}}$ (teal) and $Fe_3(NH_2)_3\mathbf{L}^{\mathbf{Et/Me}}$ (purple).

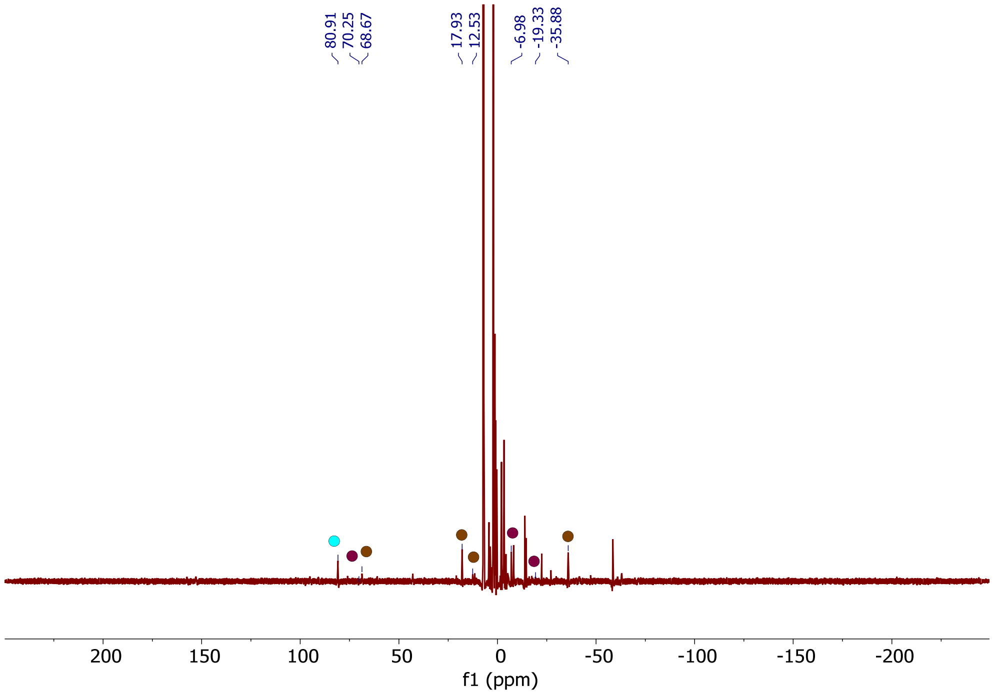


Figure S14. ^{1}H-NMR spectrum of product mixture from scrambling between $Fe_3(OMe)_3$**L**$^{\mathbf{Et/Me}}$ and $Fe_3(NH_2)_3$**L**$^{\mathbf{Et/Me}}$. Spectrum taken in toluene-d_8. Light blue circle indicates moisture-derived impurity.

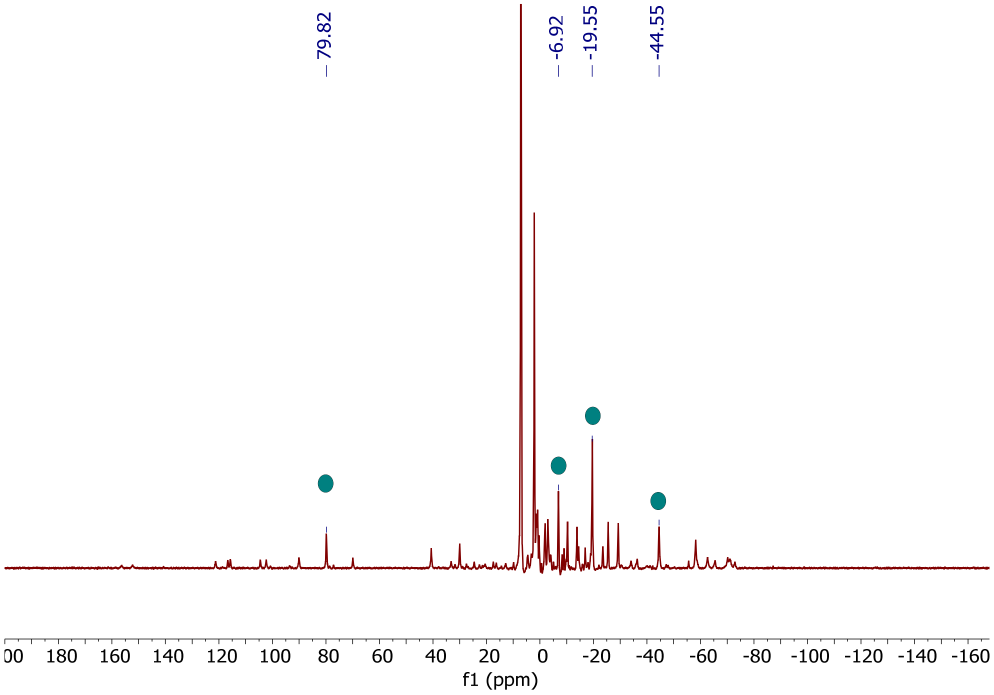


Figure S15. ^{1}H-NMR spectrum of product mixture from scrambling between **2** and Fe$_3$H$_3$**L**$^{\mathbf{Et/Me}}$. The spectrum was taken in benzene-*d*$_6$. Teal circles correspond to the Fe$_3$H$_3$**L**$^{\mathbf{Et/Me}}$ starting material.

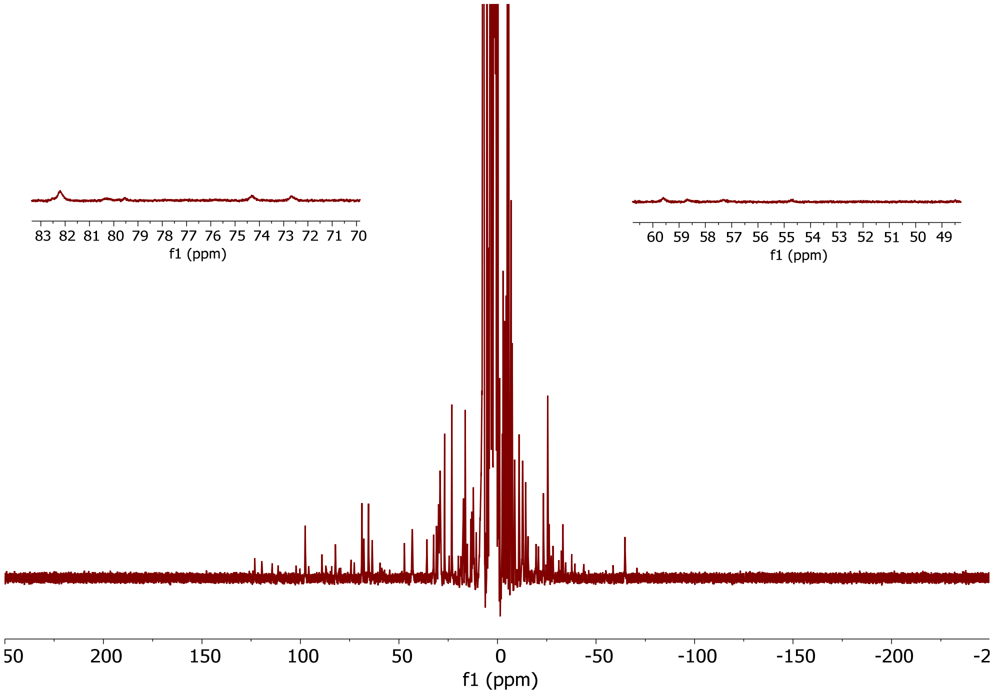


Figure S16. ^{1}H-NMR spectrum of product mixture from scrambling between **1** and Fe$_3$N**L**$^{\mathbf{Et/Me}}$. Left-side inset displays diagnostic range for **1**, right-side displays diagnostic range for Fe$_3$N**L**$^{\mathbf{Et/Me}}$.

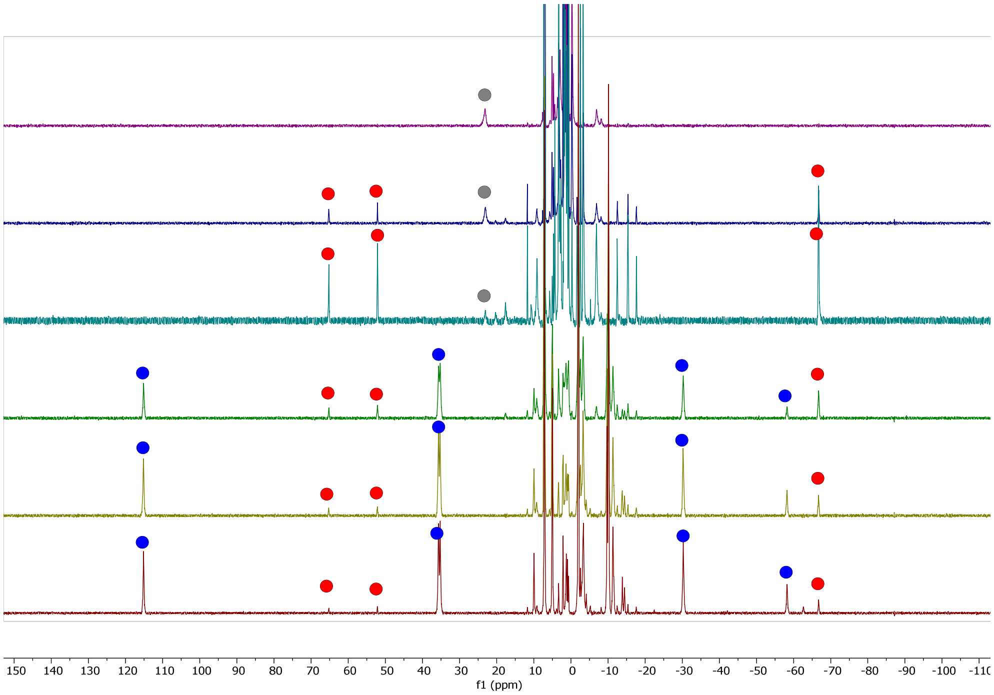


Figure S17. ^{1}H-NMR spectra of **3** with 1/8 equiv. of S_8. Chronology from bottom to top: 5 min, 1 h, 12 h, 48 h, 6 d, 9 d. Diagnostic resonances for **3**, **4**, and **5** are marked by blue, red, and grey circles, respectively.

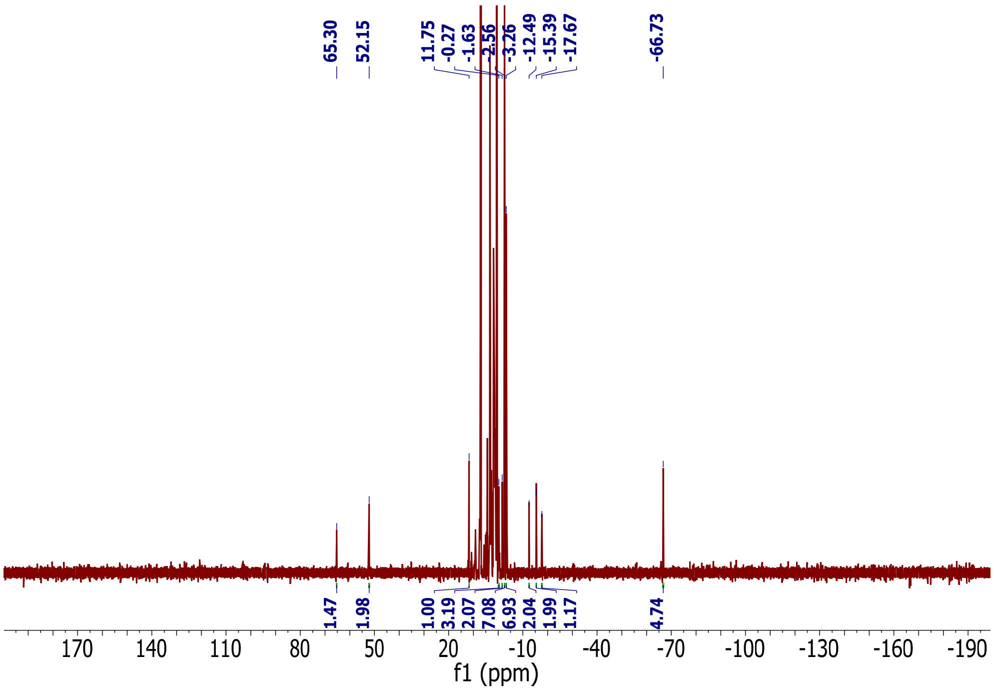


Figure S18. ^{1}H-NMR spectrum of demetallation of **2** using S_8 to yield **4** as the major species.

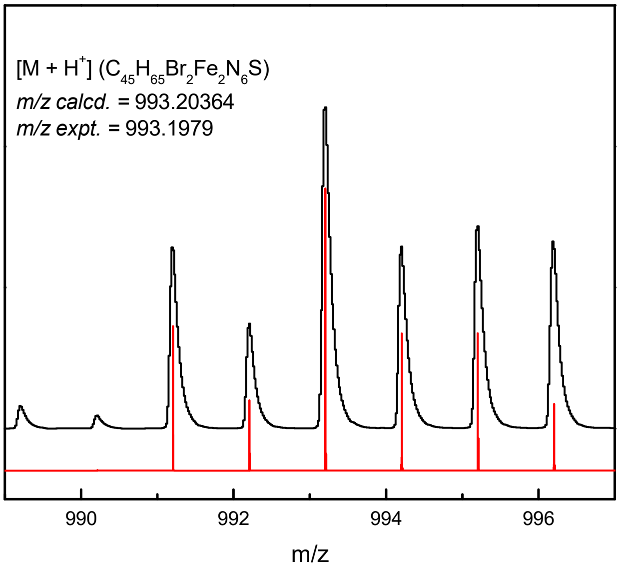


Figure S19. ESI-MS(+) data for demetallation product mixture in THF. Peaks corresponding to **4** match well with the simulated data. Capillary voltage: 4000 V. Fragmentation voltage: 175 V. Desolvation temperature: 350 °C.

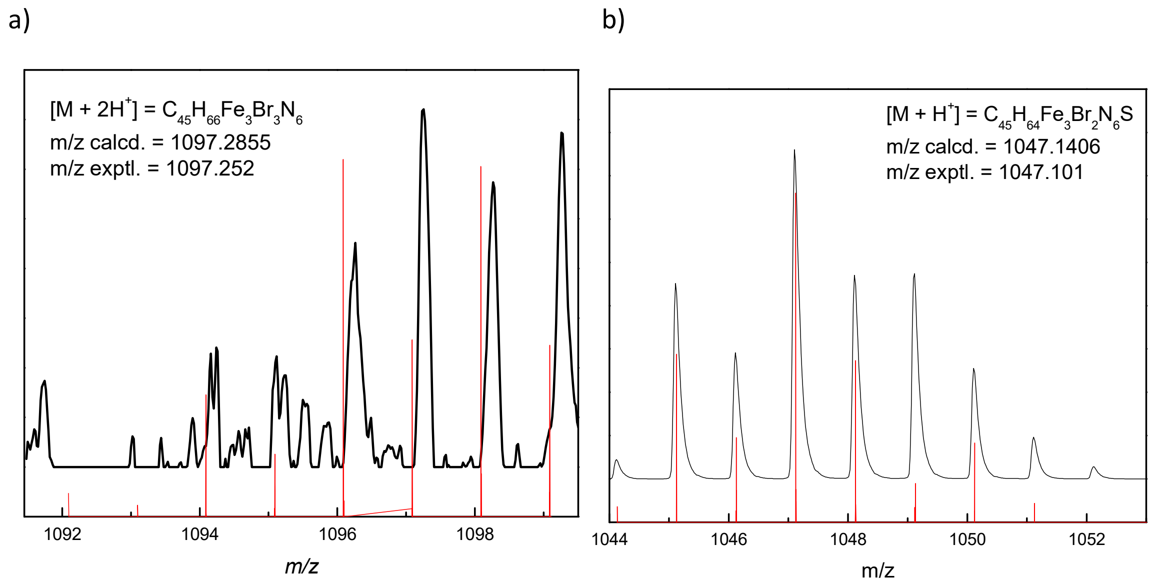


Figure S20. ESI-MS(+) data for demetallation product mixture in THF. Peaks corresponding to **2** (a) and **3** (b) are also present in the spectrum.

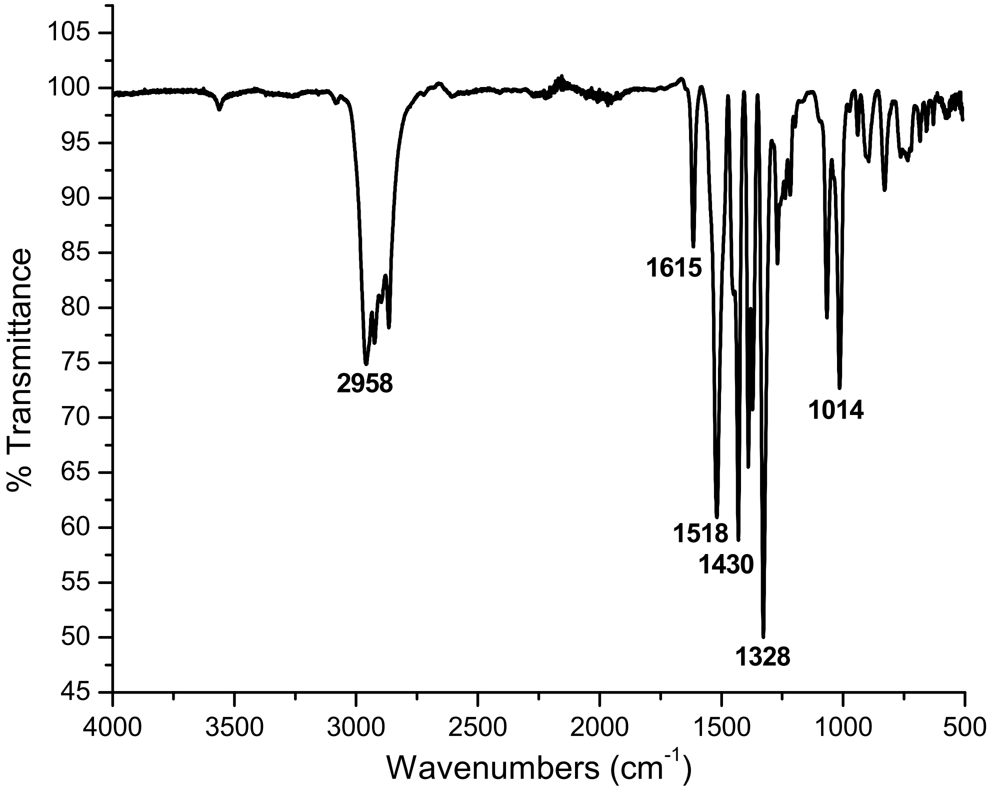


Figure S21. FTIR spectrum of demetallation product mixture.

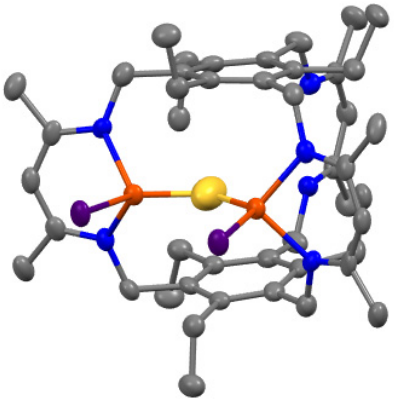


Figure S22. Preliminary structure assignment for **4** (50 % probability). H atoms and guest solvent molecules have been omitted for clarity. Fe, S, N, and Br atoms are depicted as orange, yellow, blue, and purple ellipsoids, respectively.

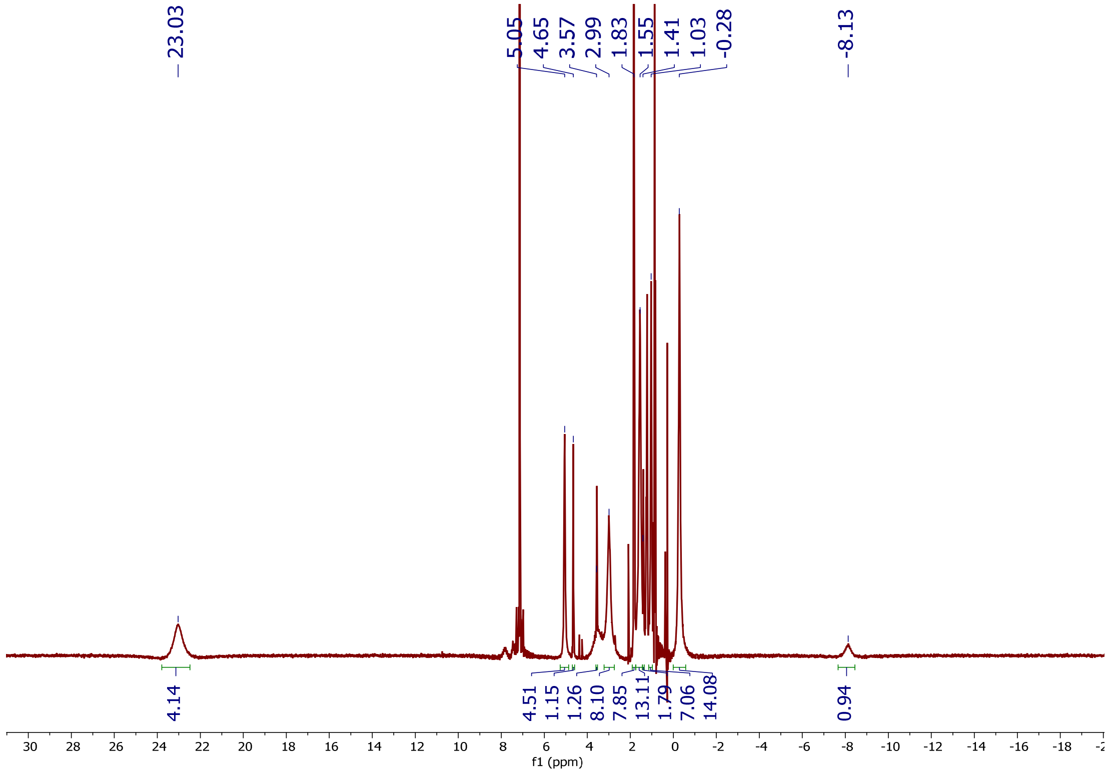


Figure S23. ^{1}H-NMR spectrum of Fe_2S_2**HL**$^{\mathbf{Et/Me}}$ (**5**) in C_6D_6 at room temperature.

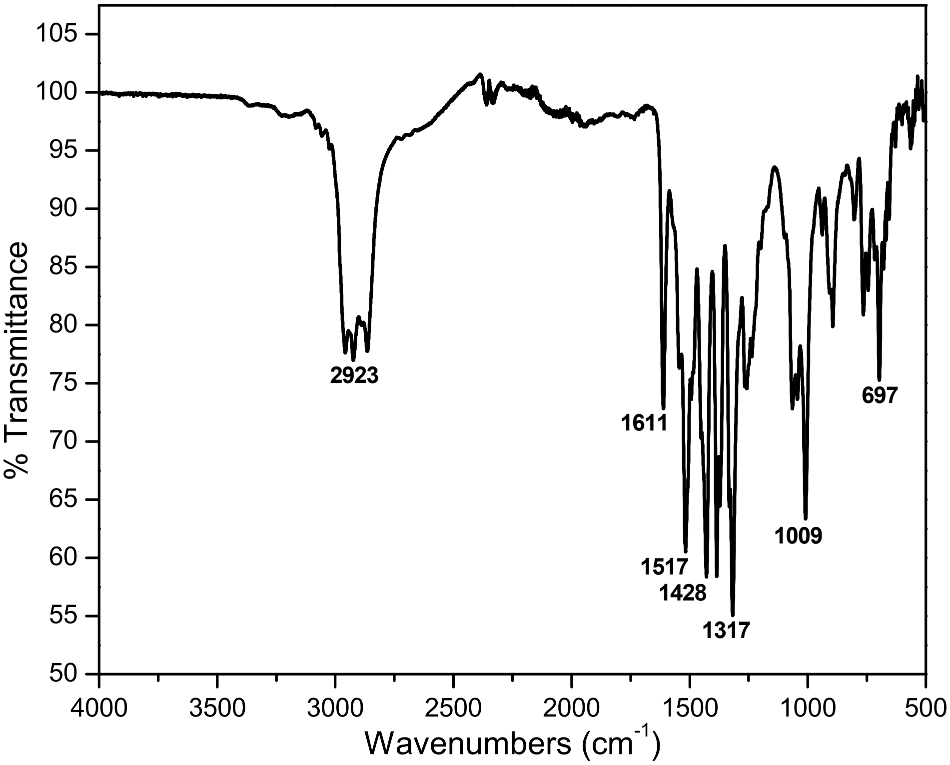
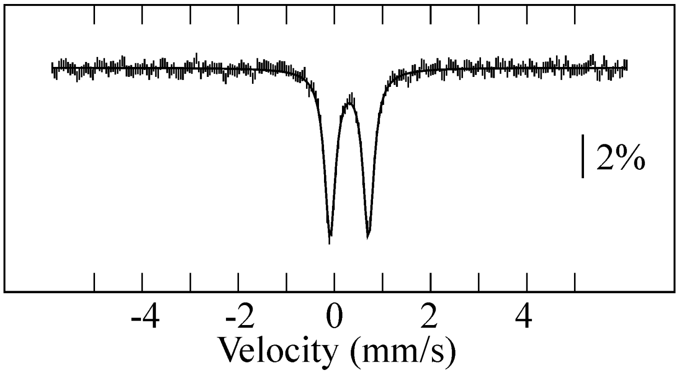


Figure S24. Infrared spectrum of Fe_2S_2**HL**$^{\mathbf{Et/Me}}$ (**5**).



δ = 0.31 mm/s, ΔE_Q = 0.80 mm/s, Γ = 0.28 mm/s

Figure S25. Mössbauer spectrum of Fe_2S_2**HL**$^{Et/Me}$ (**5**). Spectrum recorded at 80 K in zero field.

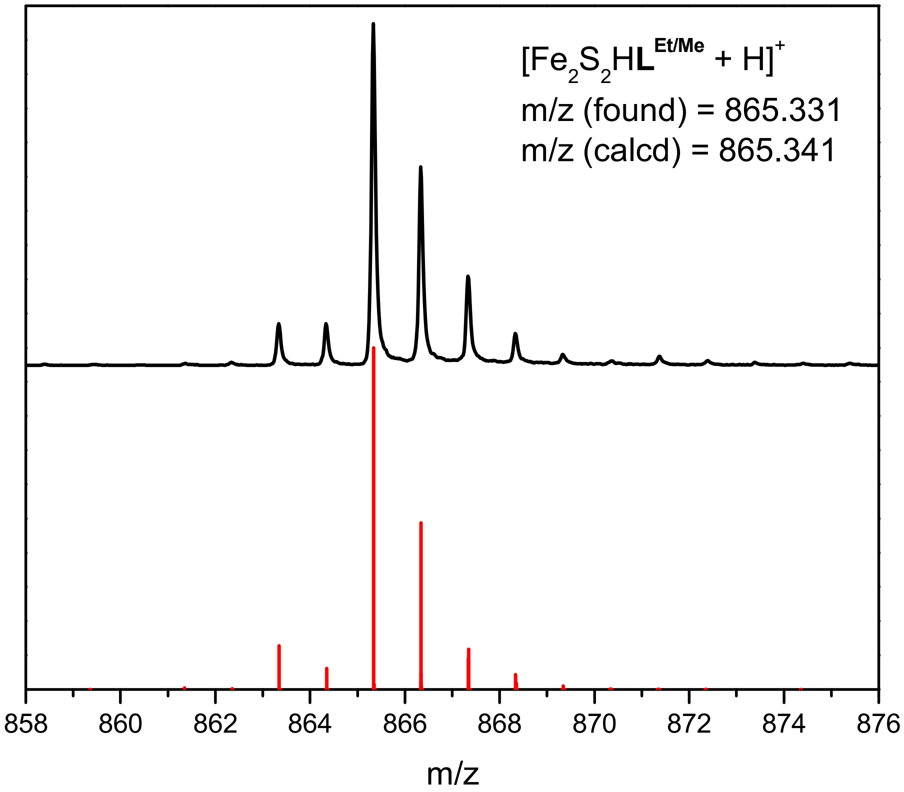


Figure S26. ESI-MS(+) data for Fe$_2$S$_2$**HL**$^{Et/Me}$ (**5**) in THF. Capillary voltage: 4000 V. Fragmentation voltage: 175 V. Desolvation temperature: 350 °C.

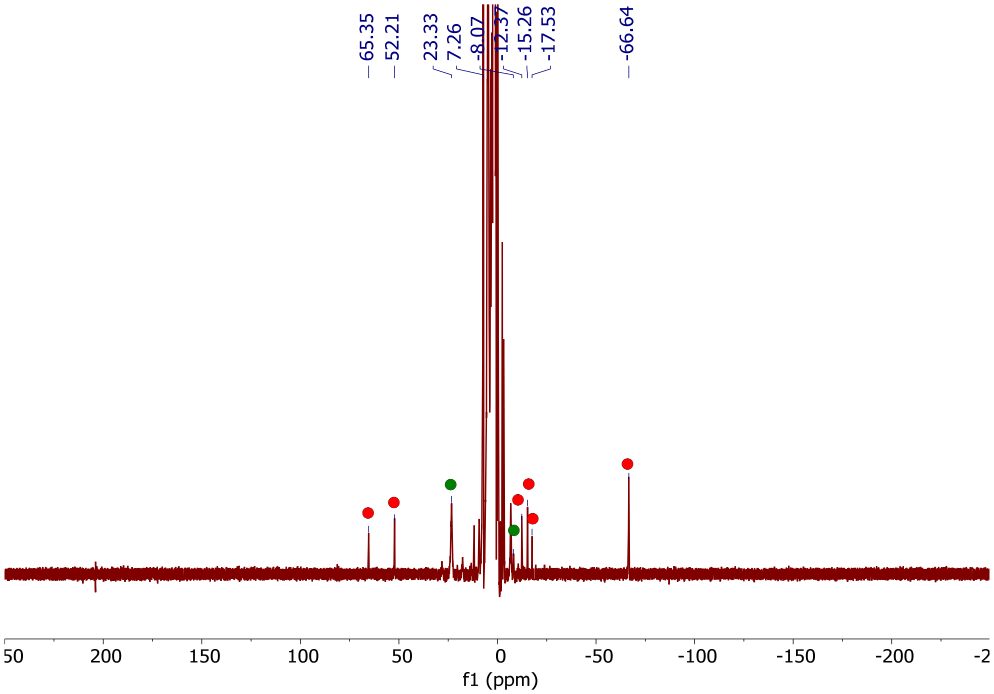


Figure S27. ^{1}H-NMR spectrum of the product mixture from the scrambling between **2** and **5** in C_6D_6 at room temperature. Red circles highlight **4** as the lone product, while the green circles indicate unreacted **5**.

Table S1. Crystal data and structure refinement for Fe$_2$S$_2$**HL**$^{\mathbf{Et/Me}}$ (**5**).

Item	Value	
Identification Code	rf881_0m	
Empirical Formula	C51 H78 Fe2 N6 S2	
Formula Weight	951.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal System	Triclinic	
Space Group	P-1	
Unit Cell Dimensions	a = 12.5051(3) Å	α = 89.9530(10)°
	b = 12.9415(4) Å	β = 87.6360(10)°
	c = 15.0445(4) Å	γ = 80.6400(10)°
Volume	2400.22(11) Å^3	
Z	2	
Density (calculated)	1.316 Mg/m^3	
Absorption Coefficient	0.733 mm^{-1}	
F(000)	1020	
Crystal Size	0.353 x 0.210 x 0.173 mm^3	
Theta Range for Data Collection	1.355 to 30.998°	
Index Ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-21 \leq l \leq 21$	
Reflections Collected	63442	
Independent Reflections	15258 [R(int) = 0.0447]	
Completeness to Theta	99.9 %	
Absorption Correction	None	
Refinement Method	Full-Matrix Least Squares on F^2	
Data / Restraints / Parameters	15258 / 0 / 564	
Goodness-of-Fit on F^2	1.069	
Final R Indices [l > 2sigma(l)]	R1 = 0.0361, wR2 = 0.1056	
R Indices (all data)	R1 = 0.0485, wR2 = 0.1093	
Extinction Coefficient	n/a	
Largest Diff. Peak and Hole	1.430 and -0.431 e.Å^{-3}	

$$R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

$w = 1/[\sigma^2(F_o^2) + (m*p)^2 + n*p]$, $p = [\max(F_o^2, 0) + 2* F_c^2]/3$, m & n are constants.