Electronic Supplementary Information.

Redox-mediated reactions of vinylferrocene: Toward redox auxiliaries.

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Compound 2.

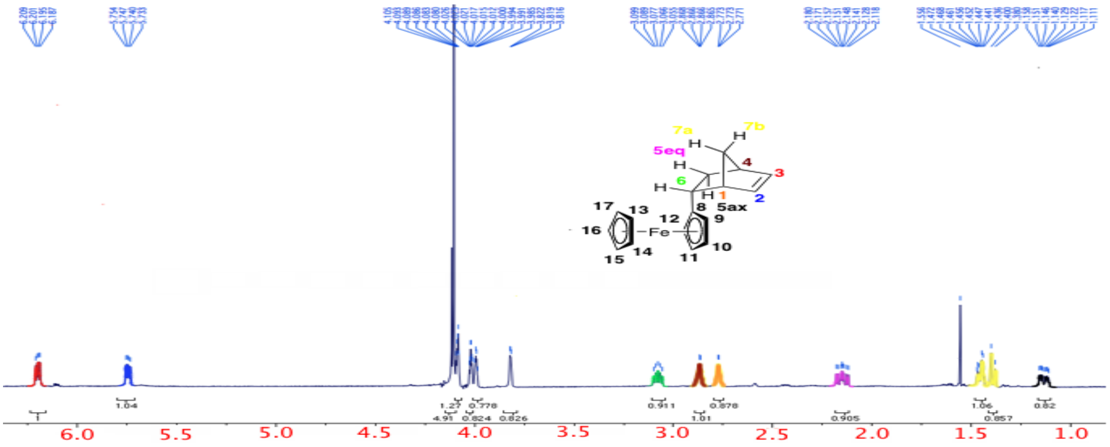


Fig S1. ^{1}H NMR of compound **2**.

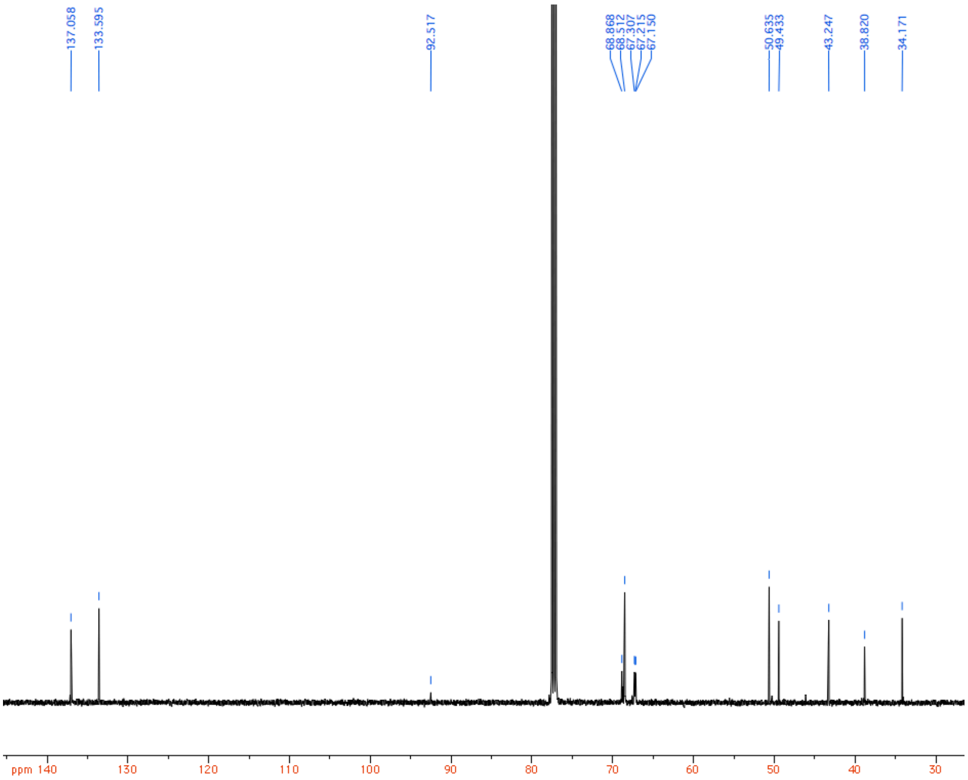


Fig S2. ^{13}C NMR of compound **2**.

Table S1. Selected optimisation conditions for the synthesis of compound **2** by a DA reaction of **1** and CP.

Entry	$FeCl_3$ (eq)	CP (eq)	Solvent	T (°C)	Yield (%)
1	1.5	1.5	1:1Acetone/H_2O [e]	r.t.	40[b]
2	1.5	5	Acetone [e]	r.t.	0 [b]
3	1.05	5	THF [e]	-78	SM [c]
4	1.05	5	THF [e]	reflux	49 [b]
5	1.05	5	Toluene [e]	reflux	20 [d]
5	1.05	5	THF [e]	reflux	59 [d]
6	3	5	THF [f]	reflux	9 [d]
7	1.1	10	THF [f]	reflux	64 [d]
8	1.1	20	THF [f]	reflux	66 [d]
9	1.1	50	THF [f]	reflux	88 [d]

[a] Reactions were run using compound **1** (0.47 mmol) for 24h. [b] $FeCl_3$ was added at room temperature. [c] $FeCl_3$ was added at -78°C. [d] $FeCl_3$ was added at -40°C. [e] Solvent volume 10mL. [f] Solvent volume 5mL. CP = freshly-distilled cyclopentadiene.

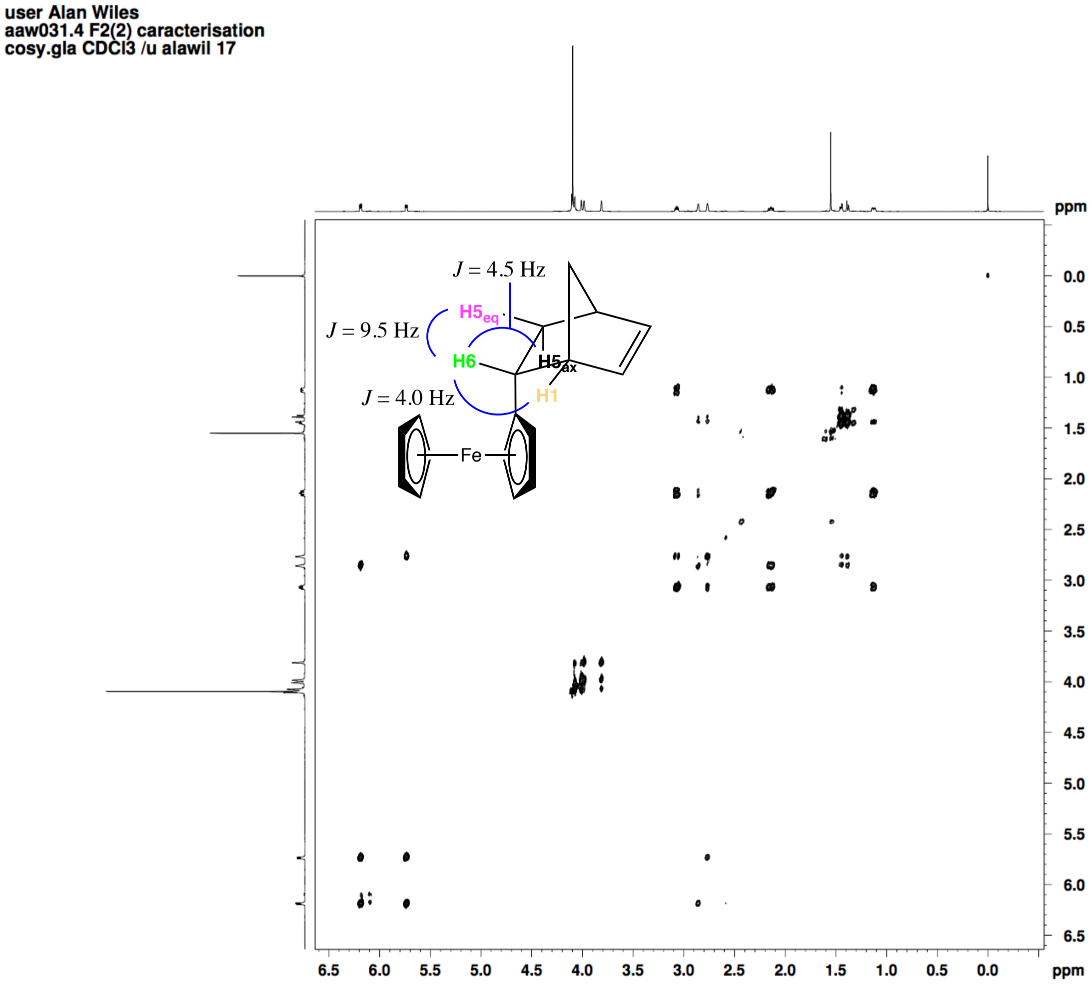


Fig. S3. COSY spectrum of compound **2**. Inset shows selected coupling constants.

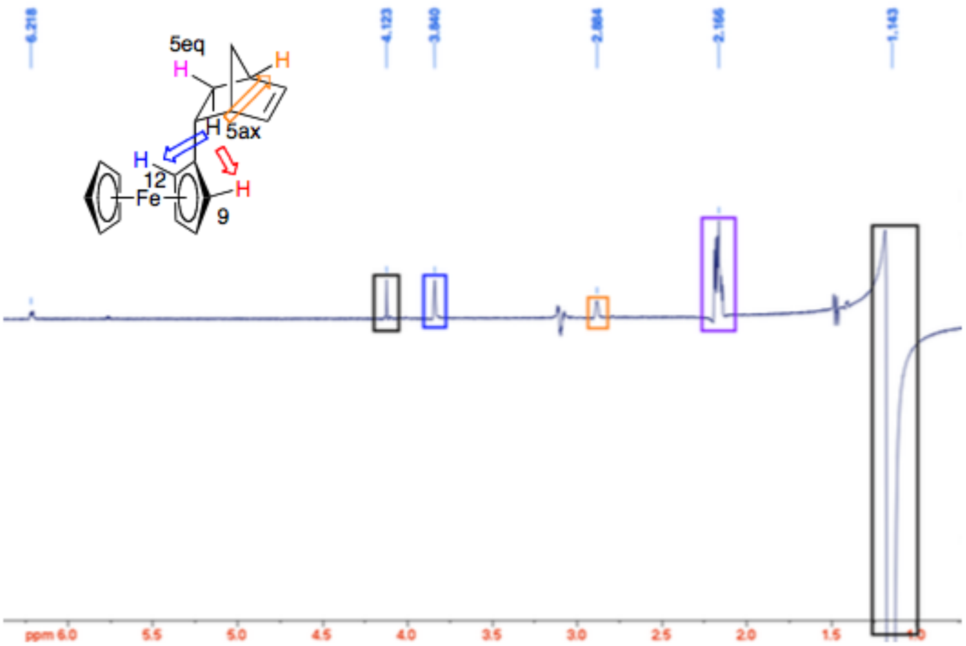


Fig. S4. Selective 1D NOESY spectrum indicating the through-space interactions of H5$_{ax}$ **2**.

We have assigned an *endo* structure for compound **2** based upon solution NMR experiments. The COSY spectrum of compound **2** indicates that H6 is coupled to three other protons (Fig. S2). Notably the coupling between H6 and H1 is in accordance with those typically observed for this proton and those attached to adjacent bridgehead carbons. Furthermore, selective 1D NOESY experiments indicate that through-space interactions are observed for hydrogen H5$_{ax}$ and the two of the ferrocene hydrogen atoms, which further supports the *endo* structure (Fig. S3). The *endo*/*exo* ratio for compound **2** was estimated by integrating the resonances for the *endo* and *exo* signals in the ^{1}H spectrum of the mixture.

Compound 3.

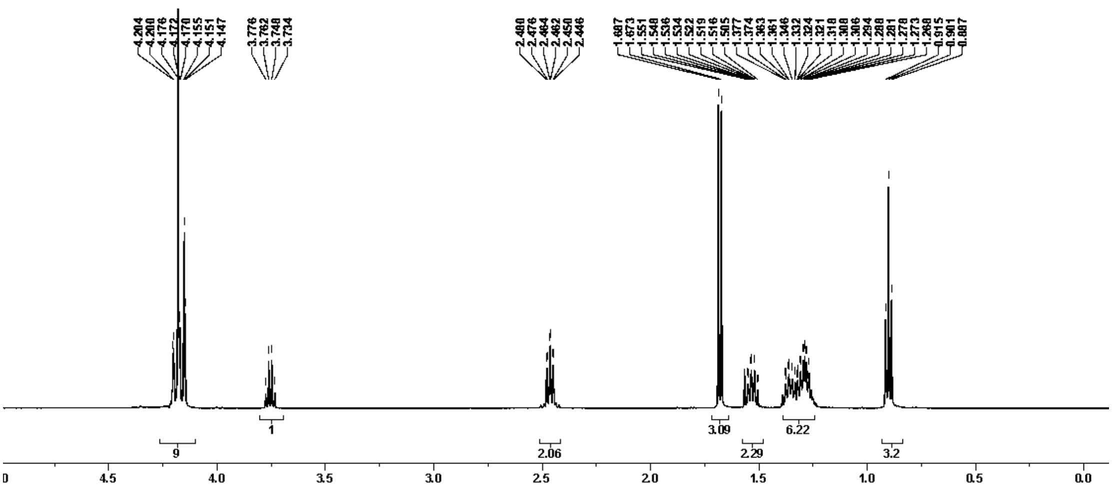


Fig. S5. ^{1}H NMR of compound **3**.

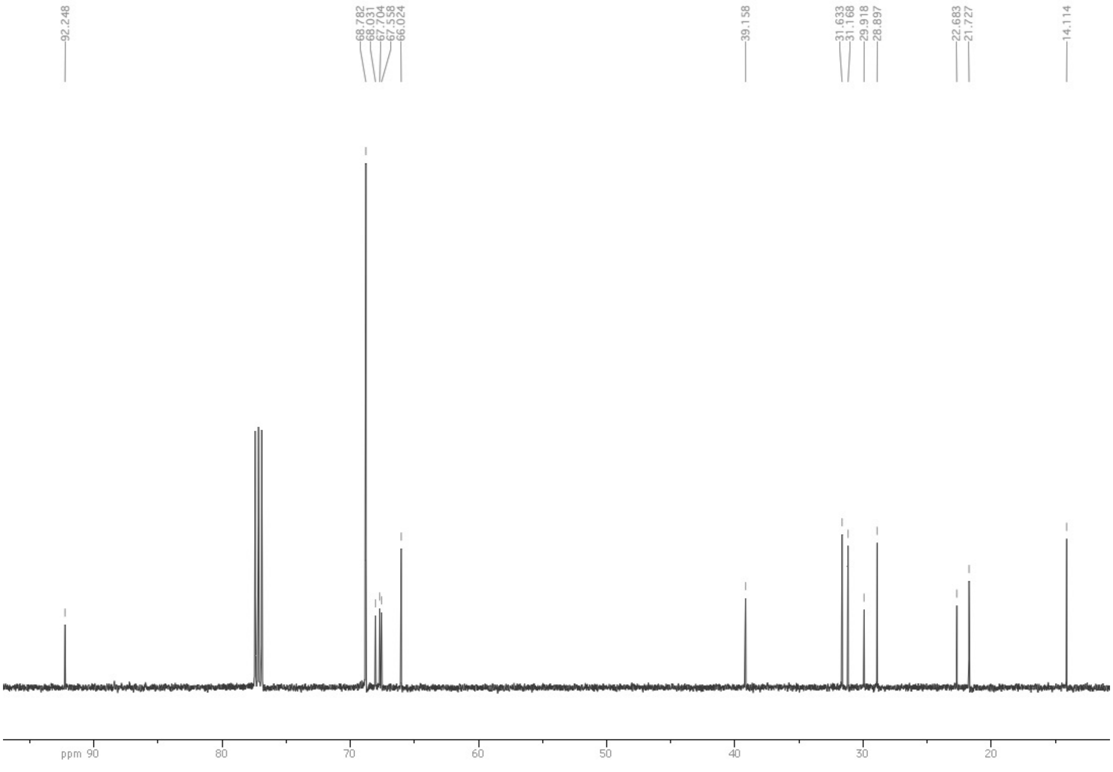


Fig. S6. ^{13}C NMR of compound **3**.

Compound 4.

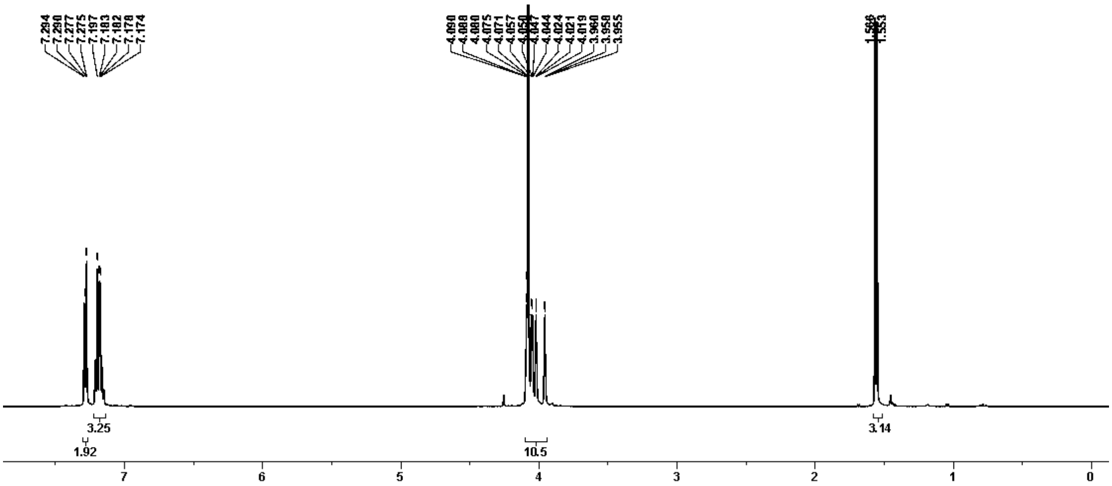


Fig. S7. ^{1}H NMR of compound **4**.

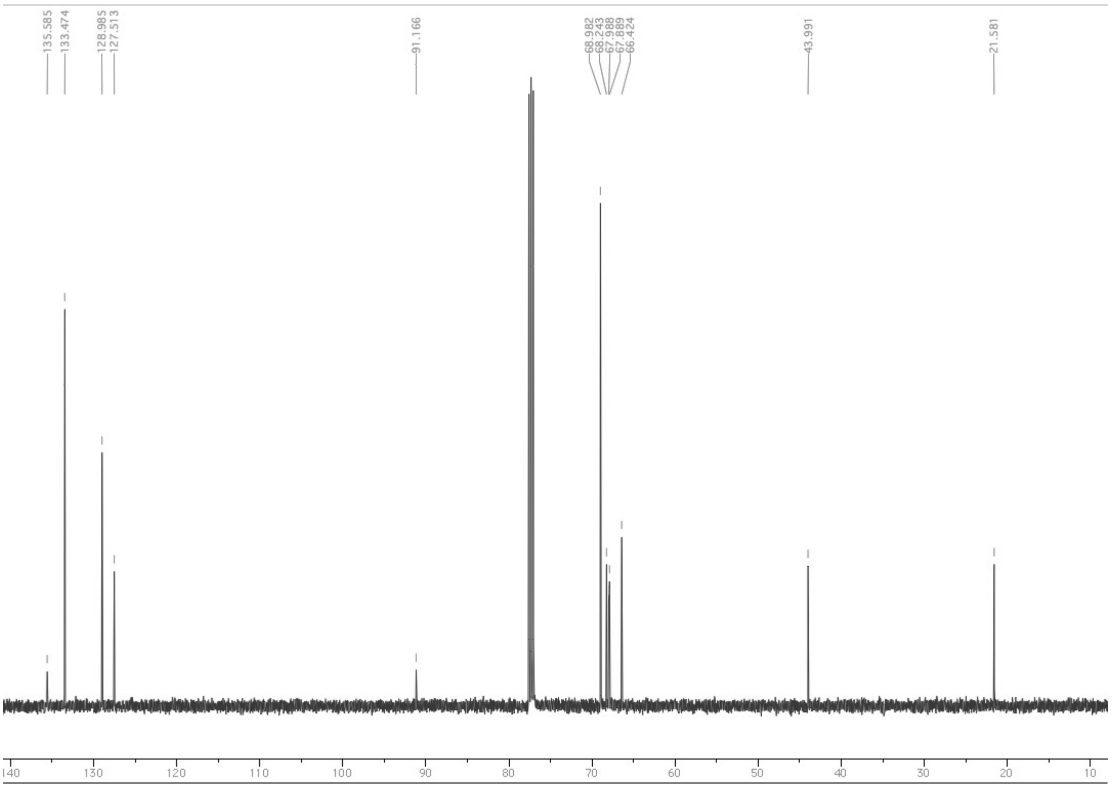


Fig. S8. ^{13}C NMR of compound **4**.

Compound 7.

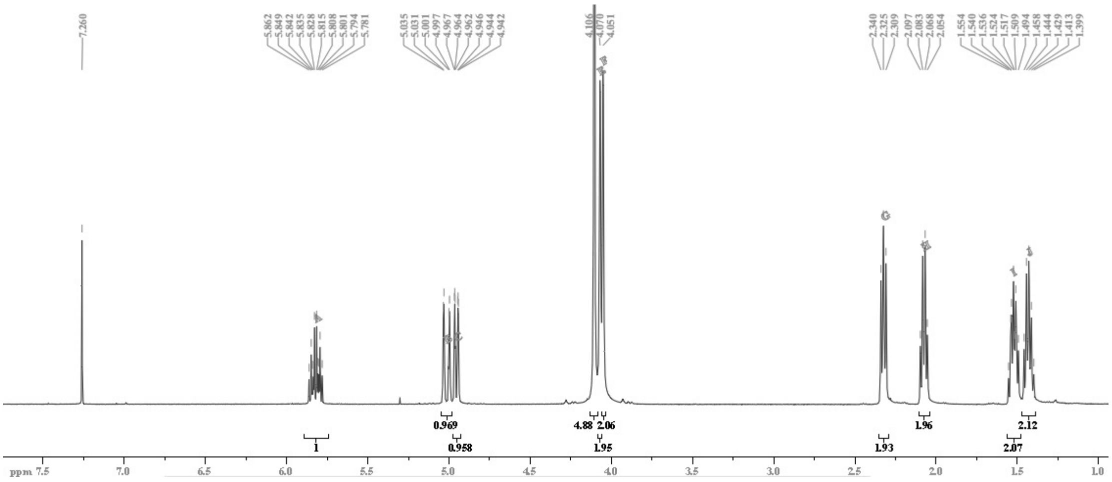
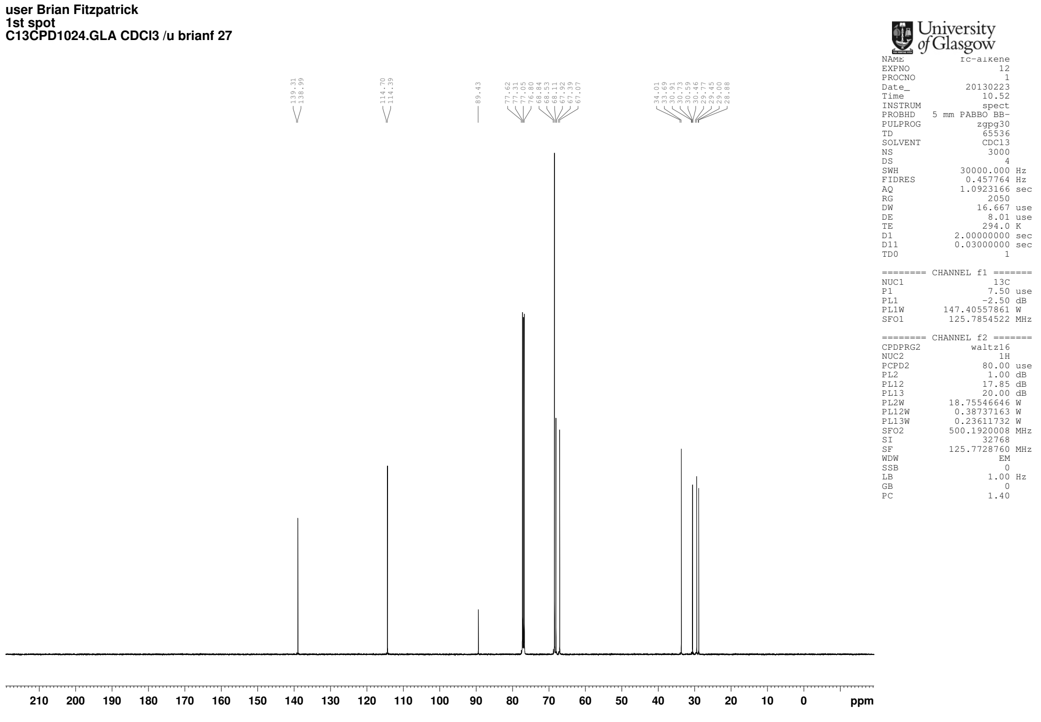


Fig. S9. ^{1}H NMR of compound **7**.



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user Brian Fitzpatrick
1st spot
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Time                10.52
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FIDRES          0.457764 Hz
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RG                  2050
DW                16.667 use
DE                  8.01 use
TE                 294.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

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P1                  7.50 use
PL1                -2.50 dB
PL1W        147.40557861 W
SFO1         125.7854522 MHz

======== CHANNEL f2 =======
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PCPD2              80.00 use
PL2                 1.00 dB
PL12               17.85 dB
PL13               20.00 dB
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PL12W         0.38737163 W
PL13W         0.23611732 W
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PC                  1.40
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Fig. S10. ^{13}C NMR of compound **7**.

Compound 8.

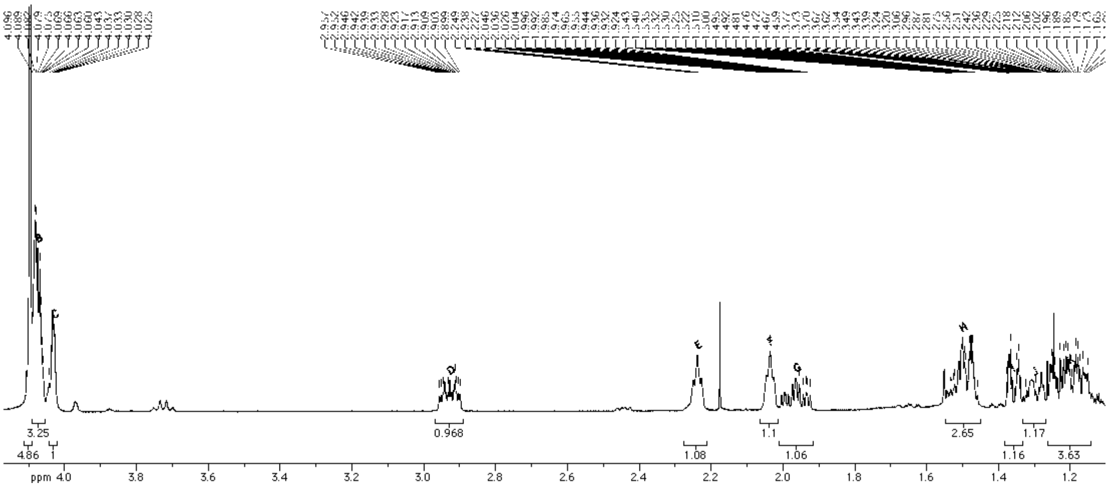


Fig. S11. ^{1}H NMR of compound **8**.

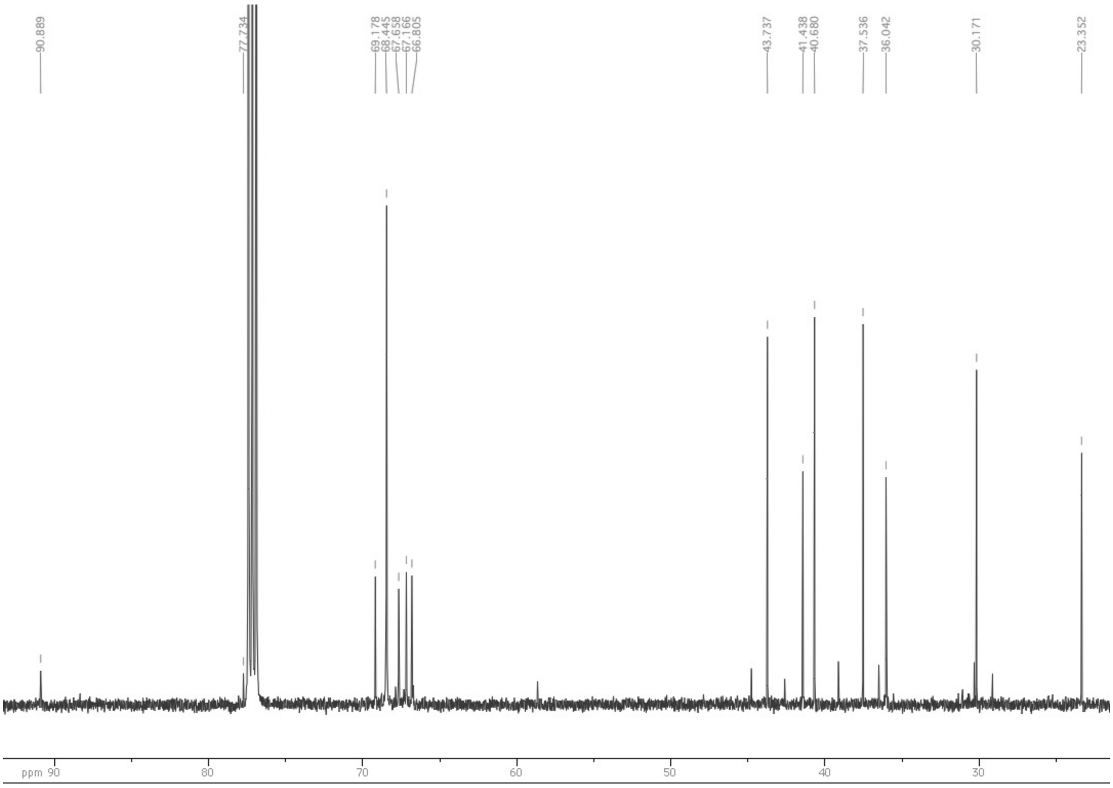
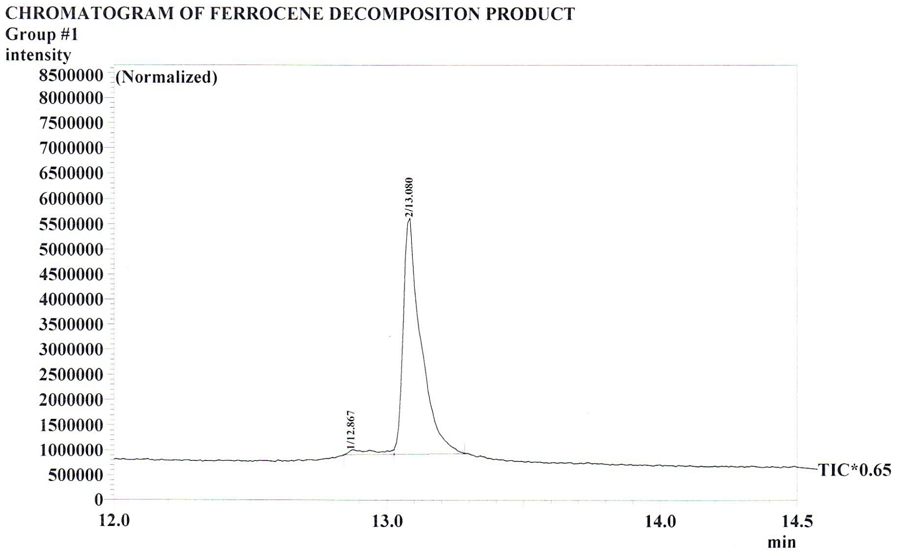


Fig. S12. ^{13}C NMR of compound **8**.

Compound 9.

Compound **9** was analysed using GC-MS. The spectra for the minor peak at 12.9 min and major peak at 13.1 min are shown in Figure S13. The molecular weight of the peak at 13.1 min (m/z = 164.1) is consistent with the proposed structure of compound **9**.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%
1	12.867	12.842	13.025	1097513	3.26	126239	1.72
2	13.080	13.025	13.283	32557855	96.74	7224447	98.28
				33655368	100.00	7350686	100.00

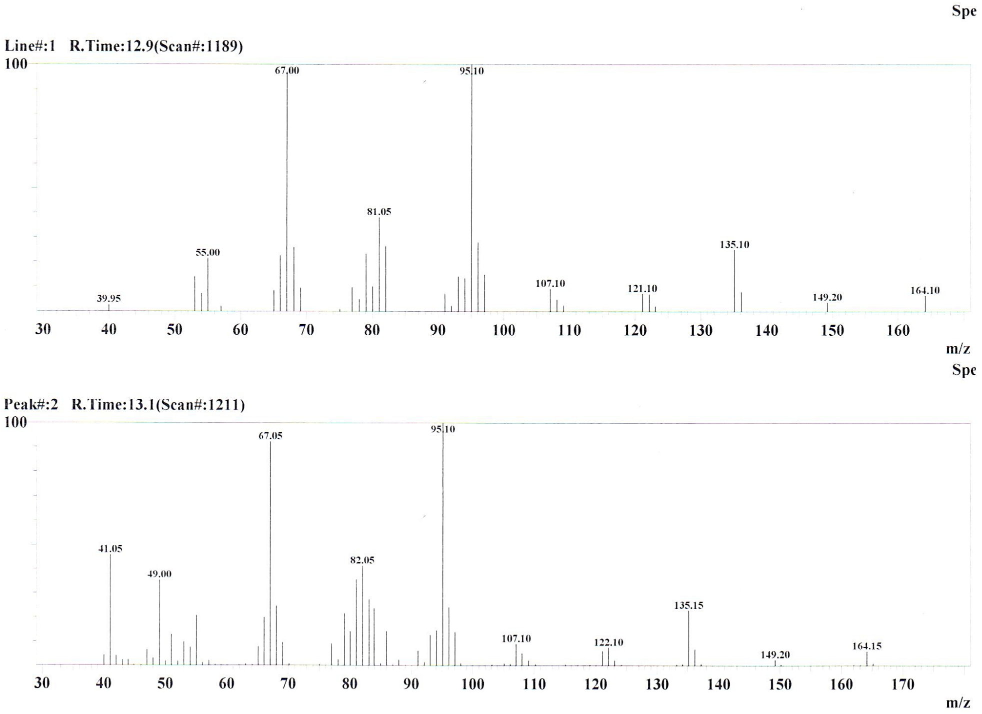


Fig. S13. GC-MS of compound **9**.

(2). Single crystal X-ray structure determination of 4.

Crystal with size 0.30 x 0.28 x 0.04 was scanned on Oxford Diffraction Gemini A Ultra [(λ ($Cu_{K\alpha}$) = 0.71073 Å] at 150(2) K. The diffraction data were collected and processed using the CrysAlisPro software package. Corrections for incident and diffracted beam absorption effects were applied utilising analytical numeric absorption correction with a multifaceted crystal model.[1] Structure solution and refinement were carried out with SHELXS-97[2] and SHELXL-97[2] using WinGX[3] *via* a full matrix least-squares on F^2 method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added and refined using riding models. Crystal data for **4**: $C_{18}H_{18}FeS$, M_r = 322.23, monoclinic system, space group $P2_1/c$, a = 19.1342(5), b = 7.59440(10), c = 10.3523(2) Å, β = 92.834(2), V = 1502.48(5) Å^3. Z = 4, ρ_{calcd} = 1.425 g cm^{-3}; $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, μ = 1.129 mm^{-1}, T = 150 K. 23151 data collected, 2958 unique, R_{int} = 0.0233, θ < 26°; w$R2$ = 0.058, $R1$ = 0.025, S = 1.047 for 182 parameters; Residual electron density extrema were 0.28 and -0.35 e Å^{-3}.

Crystallography References

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(3). DFT calculations.

Computational Details. DFT calculations were run with Gaussian 03 (Revision D.01)[1] and Gaussian 09 (Revision D.01).[2] Fe centres were described with the Stuttgart RECPs and associated basis sets[3] and 6-31G** basis sets were used for C and H atoms.[4] Optimizations were performed with the BP86[5] functional with Gaussian 03, with all stationary points being fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. A correction for the effect of THF (ε = 7.4257) solvent were run with Gaussian 09 and used the polarizable continuum model.[6] Single-point dispersion corrections to the BP86 results employed Grimme's D3 parameter set.[7] Orbital plots were produced with Chemcraft v 1.7 (see www.chemcraftprog.com)

Computational References

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