Supplementary Materials: Synthesis and Characterisation of Linear and Towards Cyclic Diferrocenes with Alkynyl Spacers

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1. NMR Spectroscopy

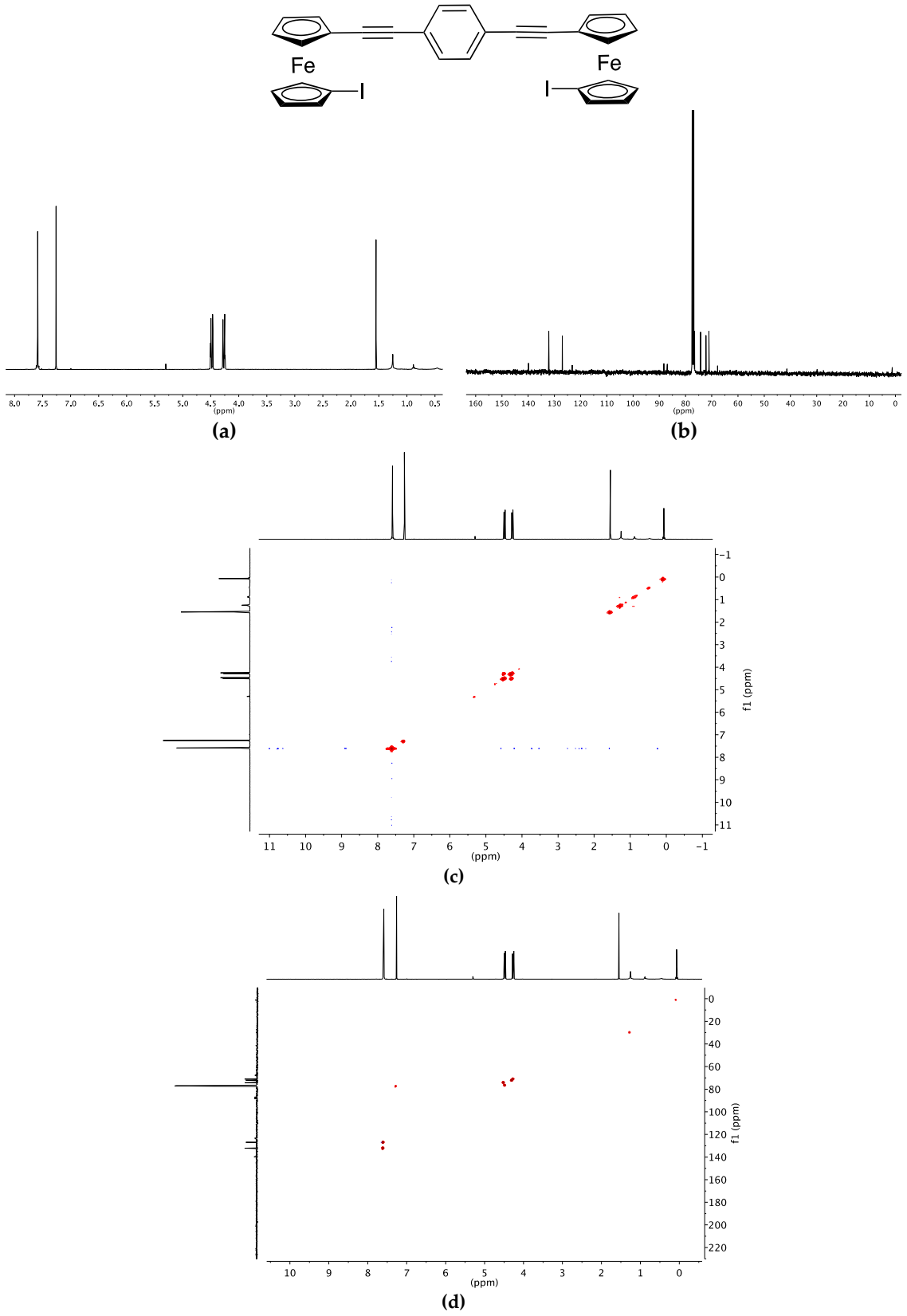


Figure S1. Compound **1:** (**a**) ^{1}H NMR, (**b**) ^{13}C{^{1}H} NMR, (**c**) COSY and (**d**) HSQC in $CDCl_3$.

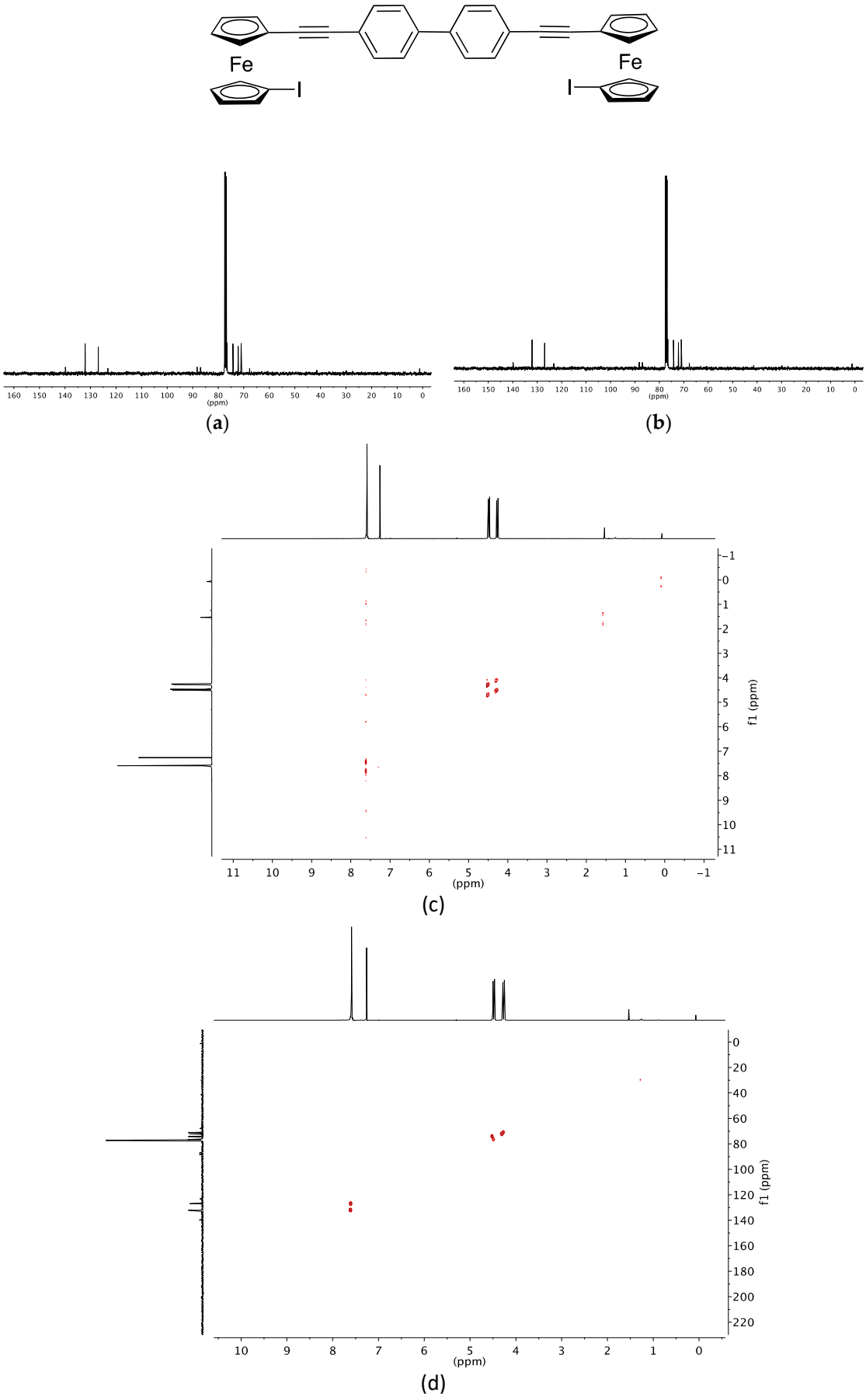


Figure S2. Compound **2:** (**a**) ^{1}H NMR, (**b**) ^{13}C{^{1}H} NMR, (**c**) COSY and (**d**) HSQC in $CDCl_3$.

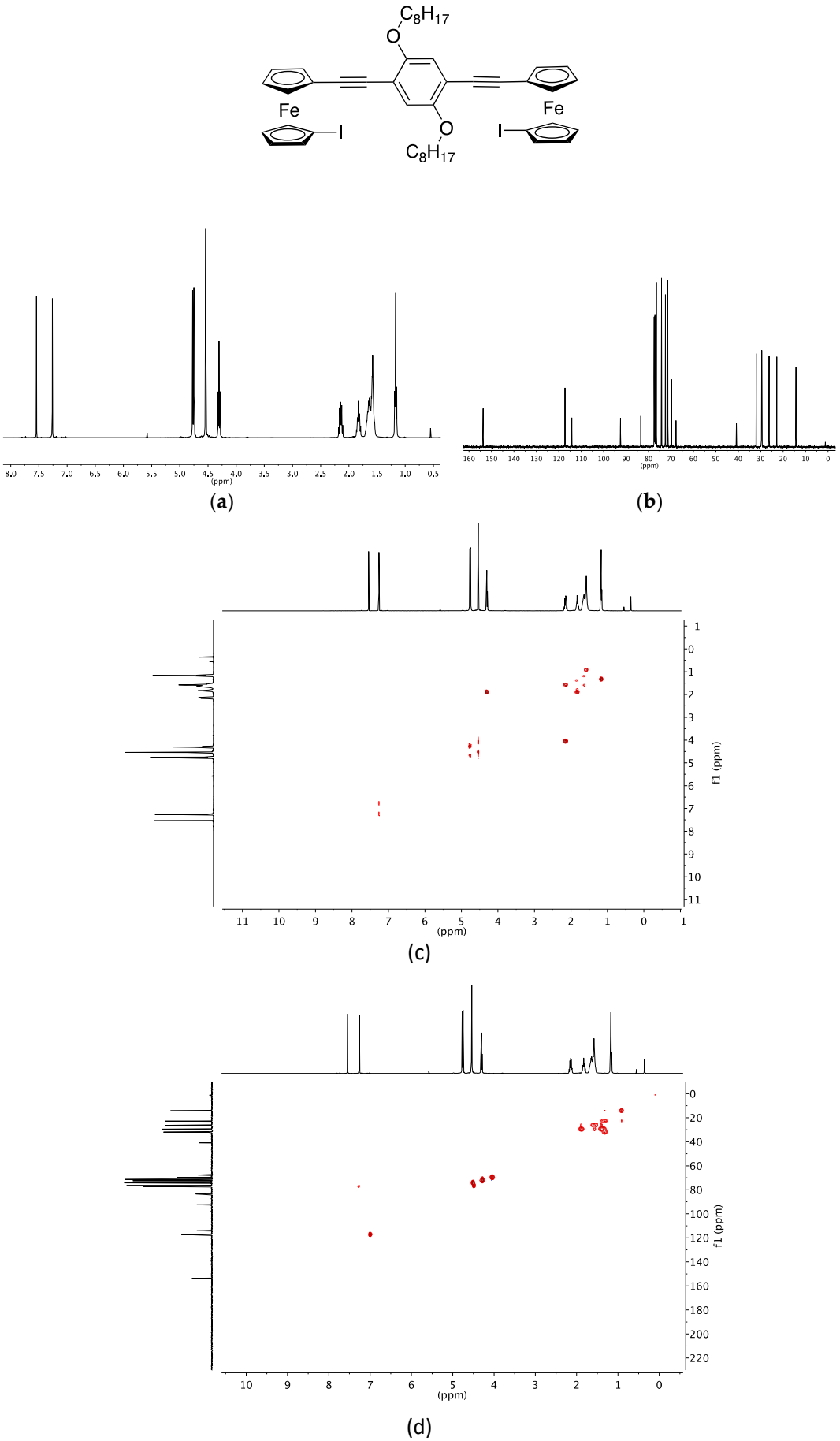


Figure S3. Compound **3:** (**a**)^{1}H NMR, (**b**) ^{13}C{^{1}H} NMR, (**c**) COSY and (**d**) HSQC in $CDCl_3$.

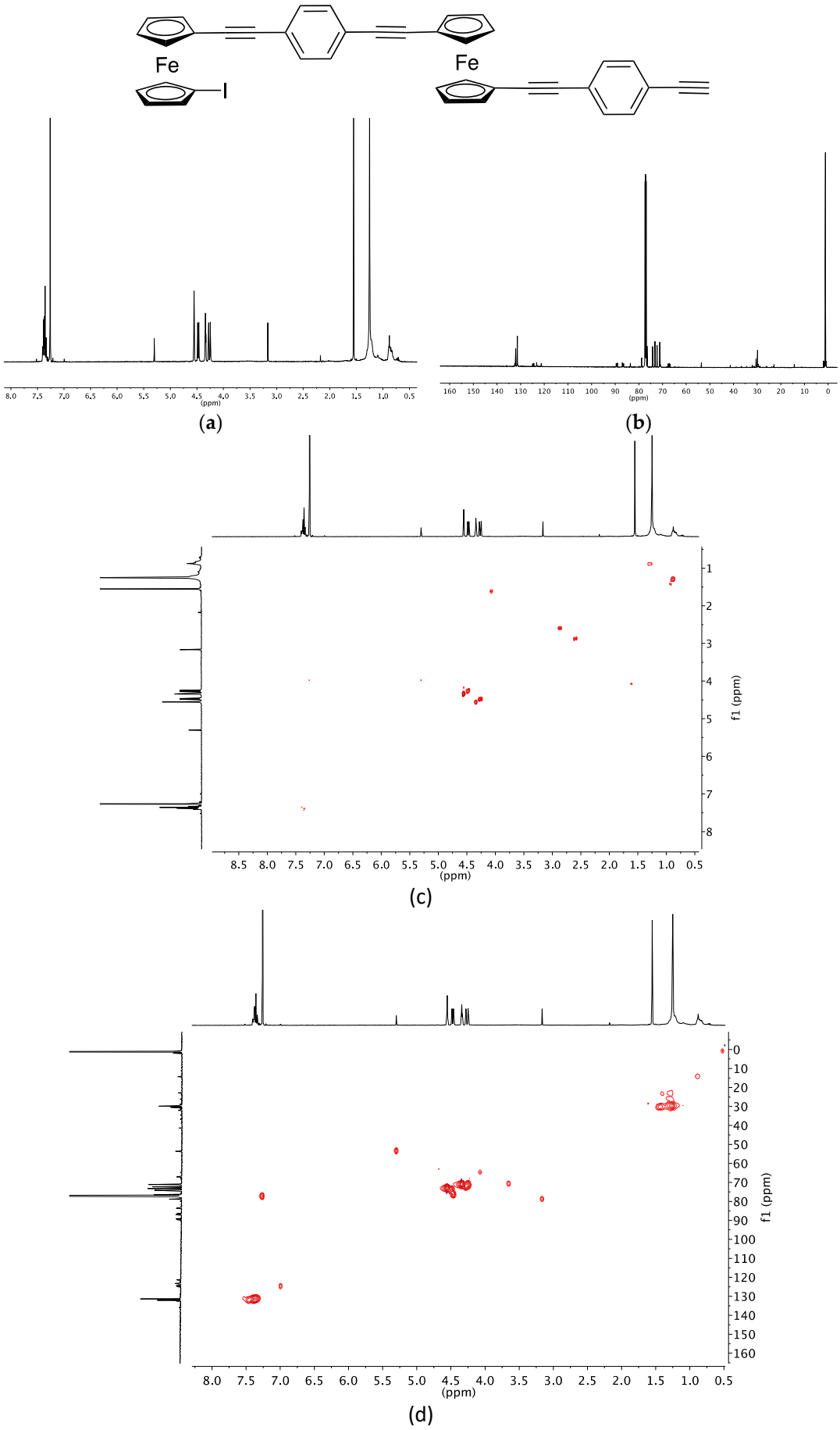


Figure S4. Compound **4:** (**a**) ^{1}H NMR, (**b**) ^{13}C{^{1}H} NMR, (**c**) COSY and (**d**) HSQC in $CDCl_3$.

2. Electrochemistry

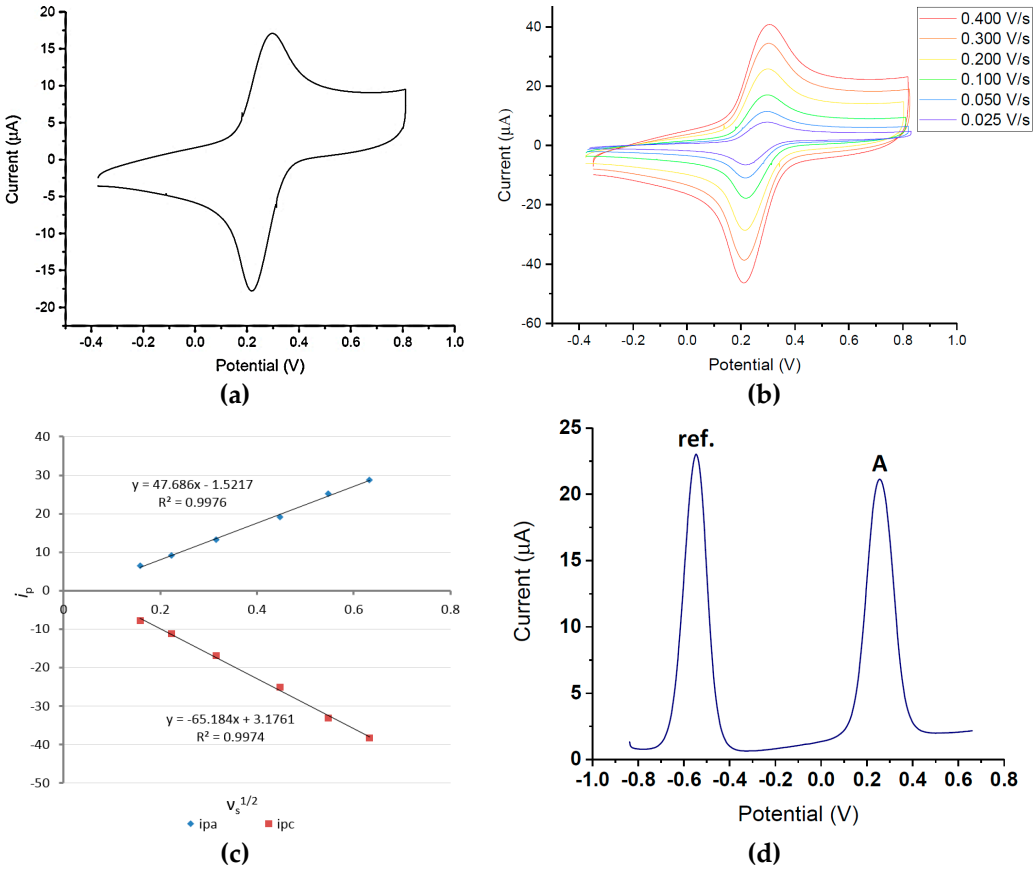
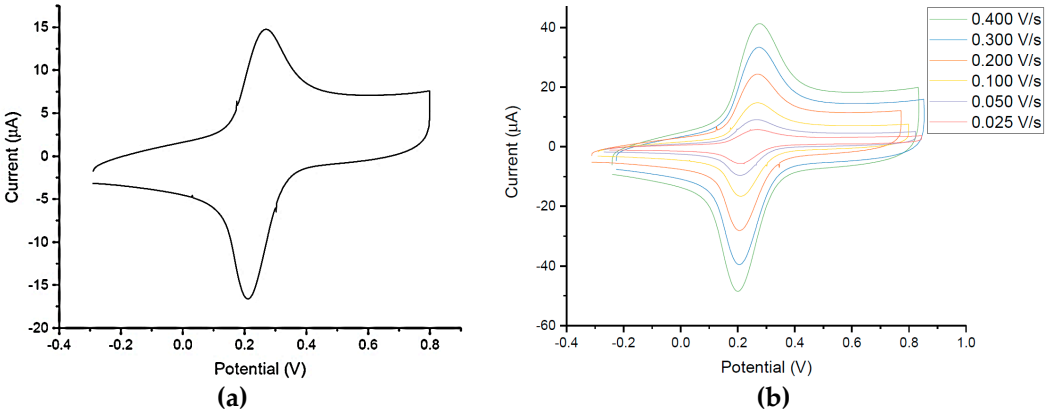


Figure S5. Compound **1** in 0.1M [(^{n}Bu)$_4$N]PF$_6$/CH$_2$Cl$_2$ (E vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$), (**a**): CV at 100 mVs^{-1} . (**b**): Varying scan rates (25 mV–400 mV). (**c**): i_{pa}/i_{pc} vs. $V_s^{1/2}$ plot. (**d**): DPV of oxidation with a decamethylferrocene reference.



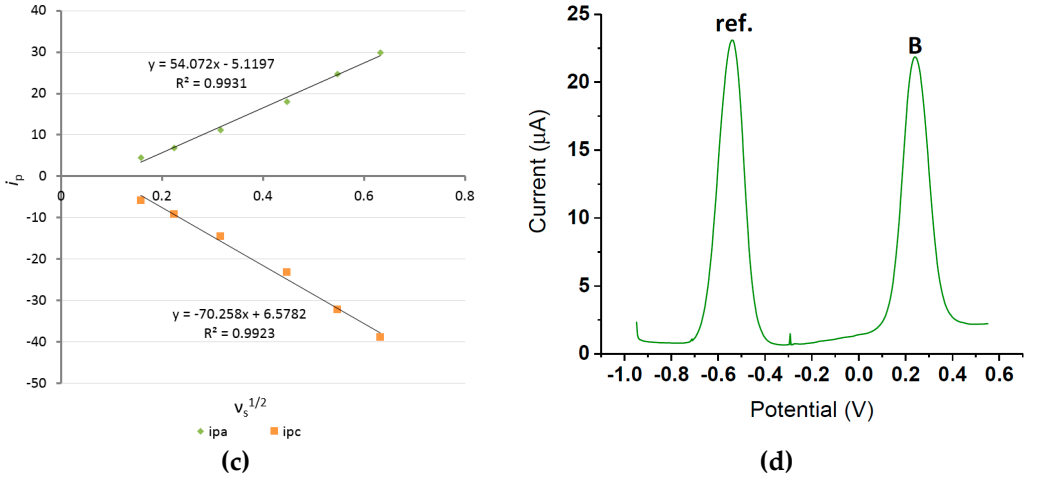


Figure S6. Compound **2** in 0.1M [(^{n}Bu)$_4$N]PF$_6$/CH$_2$Cl$_2$ (E vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$), (**a**): CV at 100 mVs^{-1}. (**b**): Varying scan rates (25 mV–400 mV). (**c**): i_{pa}/i_{pc} vs. $V_s^{1/2}$ plot. (**d**): DPV of oxidation with a decamethylferrocene reference.

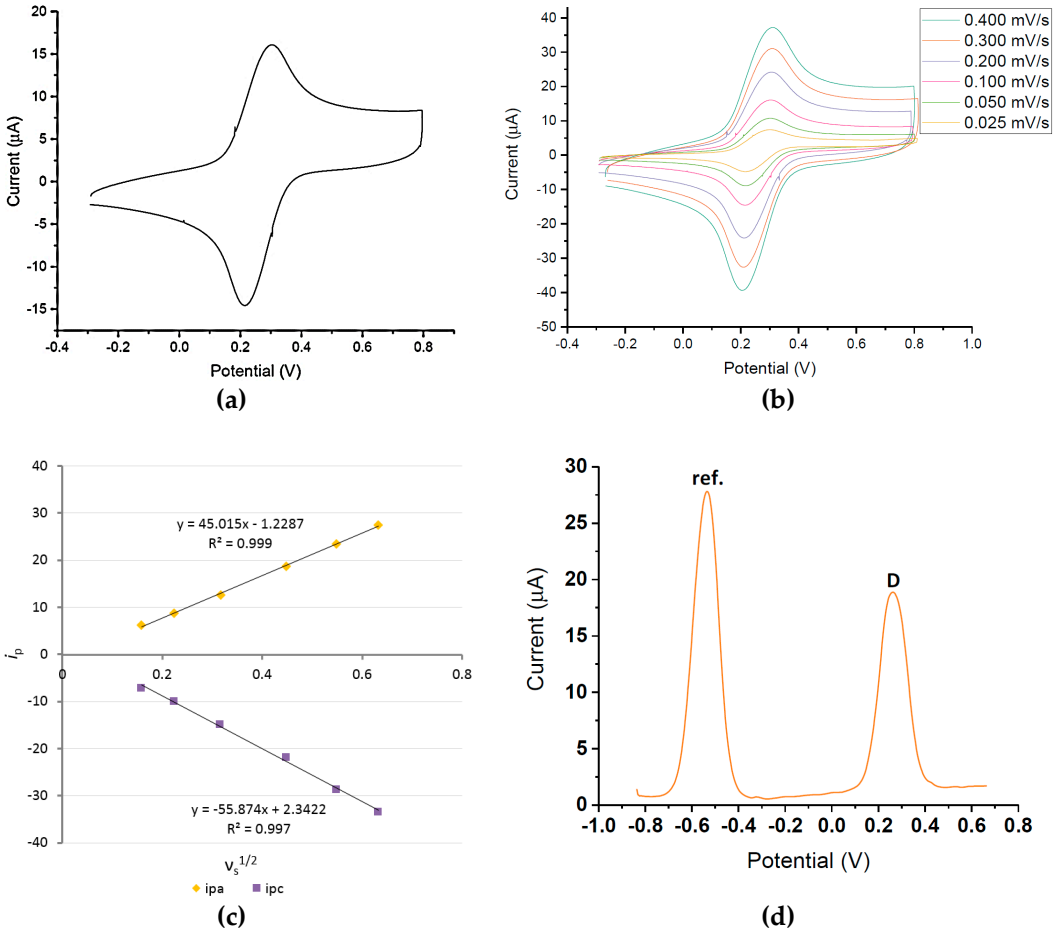


Figure S7. Compound **3** in 0.1M [(^{n}Bu)$_4$N]PF$_6$/CH$_2$Cl$_2$ (E vs. [Cp$_2$Fe]/[Cp$_2$Fe]$^+$), (**a**): CV at 100 mVs^{-1} . (**b**): Varying scan rates (25 mV–400 mV). (**c**): i_{pa}/i_{pc} vs. $V_s^{1/2}$ plot. (**d**): DPV of oxidation with a decamethylferrocene reference.

3. X-ray Crystallography

Crystal data for **1**: $C_{30}H_{20}Fe_2I_2$, M = 745.96, monoclinic, $P2_1/c$ (no. 14), a = 7.6679(4), b = 15.1621(6), c = 11.0464(6) Å, β = 107.689(6)°, V = 1223.54(11) Å^3, Z = 2 [C_i symmetry], D_c = 2.025 g cm^{-3}, μ(Mo-Kα) = 3.726 mm^{-1}, T = 173 K, orange shards, Agilent Xcalibur 3 E diffractometer; 2433 independent measured reflections (R_{int} = 0.0208), F^2 refinement [21,22], R_1(obs) = 0.0304, wR_2(all) = 0.0814, 2095 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(25.2°) = 98.6%), 154 parameters. CCDC 1861394.

The structure of **1** was found to sit across a centre of symmetry at the middle of the C_6H_4 ring.