

A Convenient Synthesis of Ferrocene(Ethynylphenyl)Thioacetates

Troy L. R. Bennett^a and Nicholas J. Long^{a,*}

^aDepartment of Chemistry, Imperial College London, MSRH, White City, London, W12 0BZ, UK.

Contents

1. Experimental	2
1.1 Materials and Methods	2
1.2 Instrumentation	2
1.3 Synthesis	2
2. Cyclic Voltammetry	33
2.1 Experimental	33
3. Ultraviolet-Visible Spectroscopy	3856
4. Infrared Spectroscopy	68
5. High-Resolution Mass Spectrometry	81
6. References	96

1. Experimental

1.1 Materials and Methods

1,1'-Diiodoferrocene (Fcl₂)¹, 1,1''-diiodobiferrocene¹, 4-(cyanoethylthio)ethynylbenzene², 3-ethynylpyridine³, 6-ethynyl-2,2'-bipyridine⁴, 4-(ethynylphenyl)-2-phenyldiazene⁵ and 1,3,5-triethynylbenzene⁶ were synthesised according to previously published literature procedures. All other reagents were obtained from commercial sources and used as received. Diisopropylamine was distilled, sparged with nitrogen and stored in an inert atmosphere over activated molecular sieves prior to use. All other reaction solvents were obtained from a Grubbs-type solvent purification system and were sparged with nitrogen prior to use. All reactions were performed under an inert atmosphere using standard Schlenk line techniques and workups were performed under air. Within this report, 'deactivated' silica was prepared by forming a slurry of silica, suspended in a solvent of choice, usually hexane, that contained 1% trimethylamine (v/v%).

1.2 Instrumentation

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 or 500 MHz spectrometer and referenced to the residual solvent peaks of CDCl₃ at 7.26 and 77.2 ppm respectively. ¹³C{¹H} spectra were fully assigned where possible using 2D correlation spectroscopy. Coupling constants are measured in Hz. Mass spectrometry analyses were conducted by Lisa Haigh of the Mass Spectrometry Service, Imperial College London. UV/Vis spectra were recorded on an Agilent Cary60 spectrometer and are reported in Section 3. Infrared spectra were recorded on a PerkinElmer Spectrum FT-IR spectrometer and are reported in Section 4.

1.3 Synthesis

General procedure for the coupling of terminal alkynes to iodoferrocenes (Procedure A);

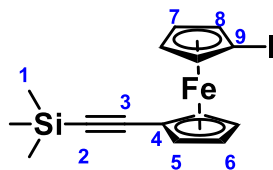
- specific details regarding molar equivalents and column conditions are reported below.

This synthetic procedure is adapted from a published method.³ 1,1'-diiodoferrocene, terminal alkyne, CuI (5 mol%) and Pd(P^tBu₃)₂ (5 mol%) were dissolved in a 1:3 mixture of DIPA and THF. The mixture was stirred at 50 °C overnight (>16 hours). The solvent was then removed *in vacuo* to give a dark-brown crude material which was purified by flash-chromatography.

General procedure for the conversion of cyanoethylthio to thioacetates (Procedure B);

- specific details regarding molar equivalents and column conditions are reported below.

This synthetic procedure is adapted from a published method.² A cyanoethylthio-substituted ferrocene was dissolved in THF. NaOMe (25% in MeOH) was added, causing the solution to turn from red to brown, and the solution was stirred at room temperature for 30 minutes. Ac₂O was then added, causing the solution to turn from brown to red, and the solution was stirred for 30 minutes. The solution was diluted with ethyl acetate, washed with water (3 x 50 mL) and brine (50 mL), dried over MgSO₄ and filtered. The solvent was removed *in vacuo* to give an orange crude material which was purified by flash-chromatography. In some cases, a precipitation was also required to achieve acceptable purity (>95%), specific details reported below.

1-(Trimethylsilyl)ethynyl-1'-iodoferrocene (**1a**)⁷

FeI_2 (0.50 g, 1.14 mmol), TMSA (0.09 g, 0.95 mmol) and CuI (0.01 g, 0.01 mmol) were dissolved in DIPA (10 mL). $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (0.01 g, 0.01 mmol) was added, and the solution was left to stir overnight to form a dark brown solution. The solvent was removed *in vacuo* to yield a brown solid which was purified by chromatography on a silica column, eluted with n-hexane/DCM (1:0 \rightarrow 9:1 v/v) to give the product as a dark red oil (0.08 g, 0.20 mmol, 21%).

$^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): $\delta_{\text{H}} = 4.40$ (t, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.39 (t, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.19 (t, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.18 (t, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 0.23 (s, 9H, H1) ppm; **MS ES+**: calcd. for $\text{C}_{15}\text{H}_{17}\text{SiFeI}[\text{M}]^+$ 407.9494; found 407.9490.

This data is in accordance with a previously reported synthesis of this molecule.⁷

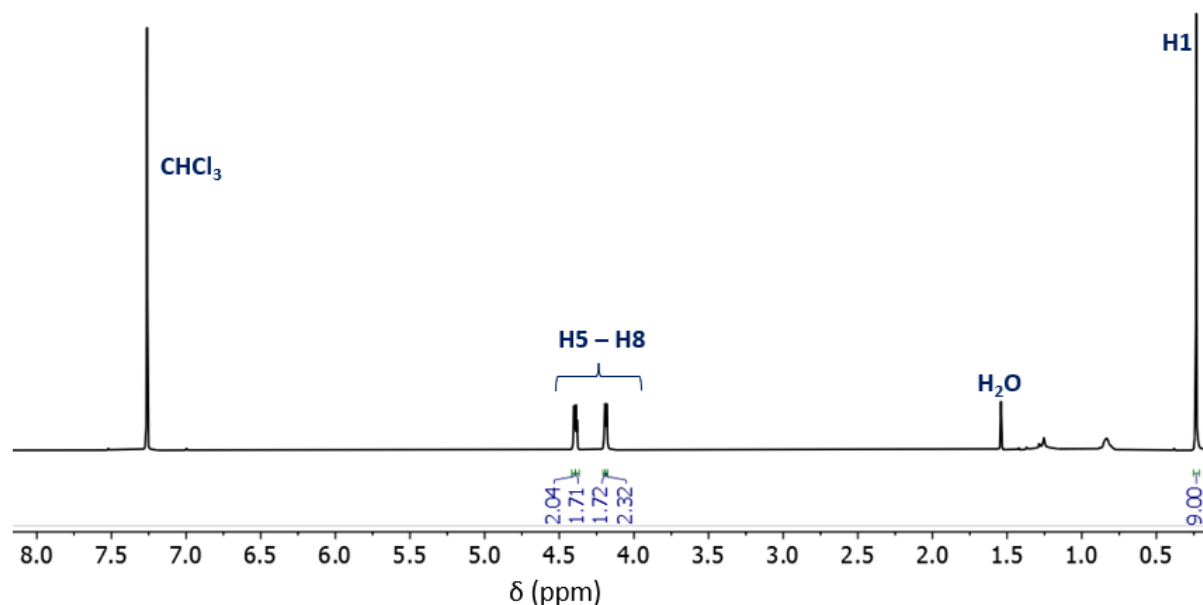
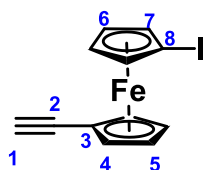


Figure S1: The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of **1a**.

1-Ethynyl-1'-iodoferrocene (1)⁸

(**1a**) (0.25 g, 1.10 mmol) was dissolved in a 1:1 mixture of THF:MeOH (30 mL). An aqueous solution of NaOH (1.0 M, 20 mL) was added and the solution was stirred overnight. A saturated aqueous solution of NaHCO₃ (30 mL) was added and the solvent was concentrated *in vacuo*. The product was extracted into DCM (100 mL), washed with water (3 x 100 mL) and brine (100 mL) before being dried over MgSO₄. The solvent was removed *in vacuo* to give the product as a dark red oil (0.32 g, 0.94 mmol, 86%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 4.43 (t, ³J_{H-H} = 2.0 Hz, 2H, Fc-H), 4.42 (t, ³J_{H-H} = 2.0 Hz, 2H, Fc-H), 4.23 - 4.20 (m, 4H, Fc-H), 2.78 (s, 1H, H1) ppm; **MS ES+**: calcd. for C₁₂H₁₀IFe [M+H]⁺ 336.9177; found 336.9167.

This data is in accordance with a previously reported synthesis of this molecule.⁸

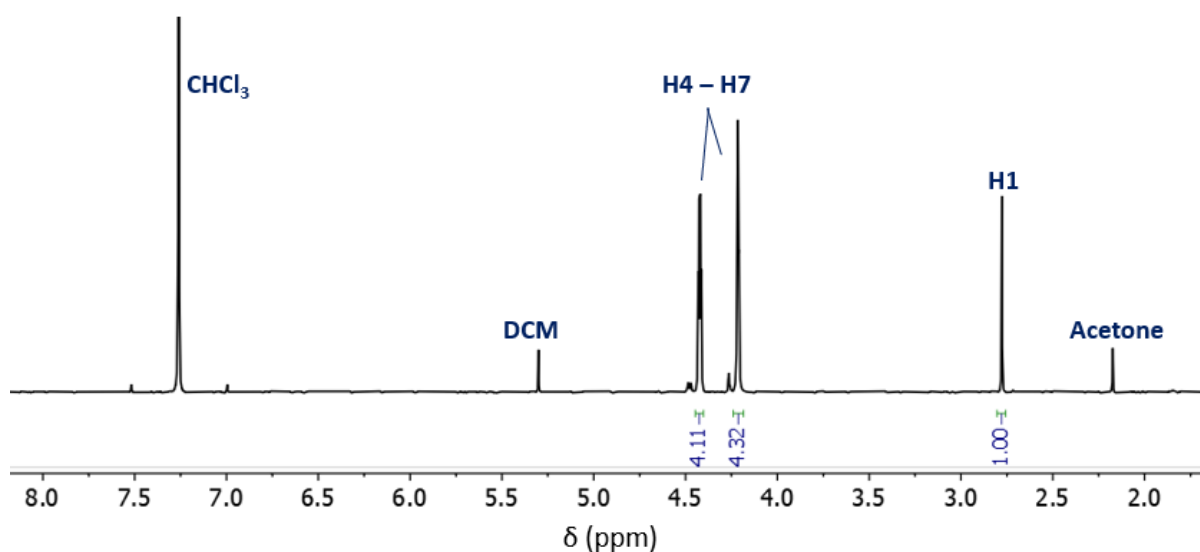
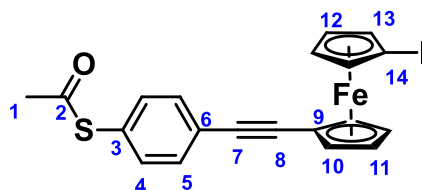


Figure S2: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **1**.

1-Iodo-1'-(4-(ethynylphenyl)thioacetate)ferrocene (2)

Synthesis from (1): 4-Iodo-phenylthioacetate (1.24 g, 4.47 mmol), (1) (0.50 g, 1.49 mmol), CuI (0.01 g, 0.08 mmol) and PdCl₂(PPh₃)₂ (0.10 g, 0.08 mmol) were dissolved in DIPA (30 mL) and stirred overnight to give an orange precipitate. The solvent was removed *in vacuo* and the crude product was purified by chromatography on a silica column, eluting with n-hexane/DCM (1:0 → 0:1) to give the product as a red solid (0.49 g, 1.01 mmol, 67 %).

Synthesis from (2a): Following general procedure B, (2a) (0.06 g, 0.12 mmol), NaOMe (0.5 M in MeOH, 0.04 mL, 0.20 mmol) and Ac₂O (0.04 mL, 0.40 mmol) gave a red oil which was purified by chromatography on a 'deactivated' silica column, eluting with n-hexane/DCM (1:0 → 4:1) gave the product as a bright red oil which slowly solidified when left to stand (0.04 g, 0.08 mmol, 67 %)

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 7.54 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H5), 7.37 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H4), 4.48 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11), 4.45 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H12), 4.28 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10), 4.23 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H13), 2.43 (s, 3H, H1); **¹³C {¹H} NMR** (CDCl₃, 298 K, 100 MHz): δ_C = 193.8 (C2), 134.4 (C4), 132.2 (C5), 127.5 (C6), 125.3 (C3), 89.2 (C8), 86.4 (C7), 76.5 (C12), 74.3 (C11), 72.3 (C10), 71.1 (C13), 67.2 (C9), 41.3 (C14), 30.4 (C1) ppm; **MS ES+**: calcd. for C₂₀H₁₅OSFe [M]⁺ 485.9238; found. 485.9262.

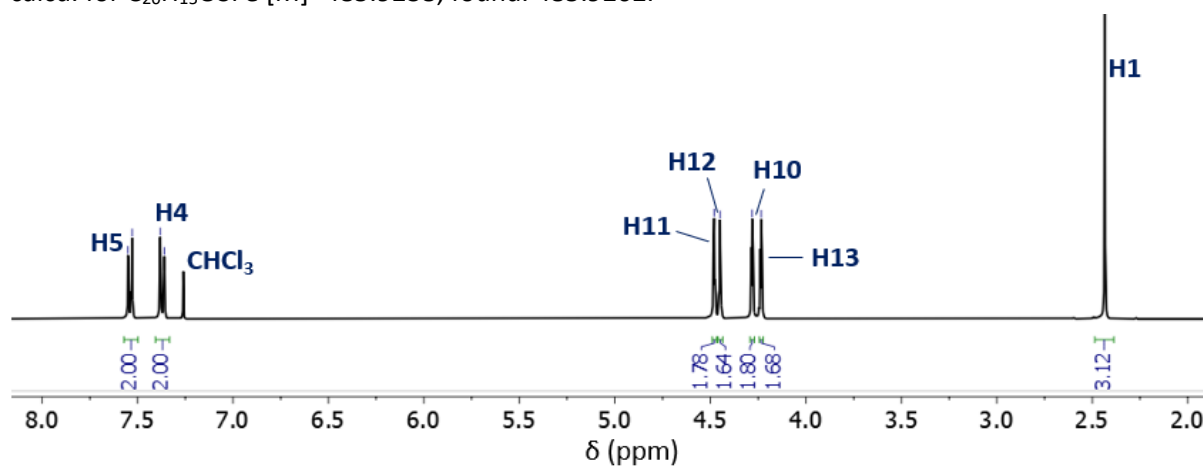


Figure S3: The ¹H NMR (CDCl₃, 400 MHz) spectrum of 2.

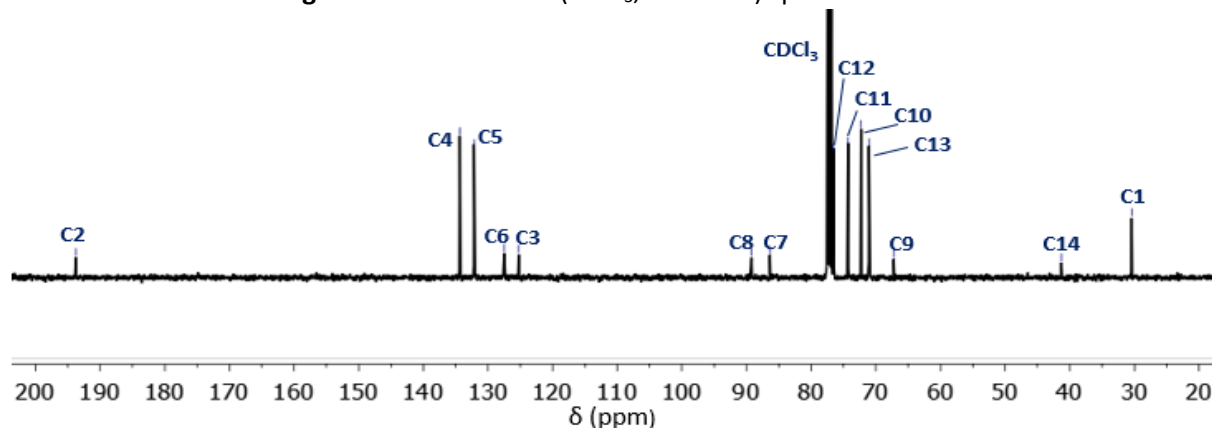
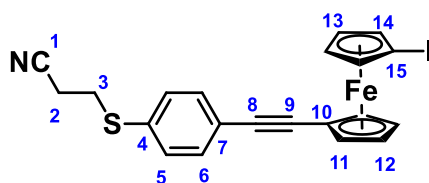


Figure S4: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of 2.

1-Iodo-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (2a)

Following general procedure **A**, 4-(2-cyanoethylthio)ethynylbenzene (0.50 g, 1.93 mmol), FeCl_2 (3.37 g, 7.71 mmol), CuI (0.04 g, 0.19 mmol) and $\text{Pd}(\text{P}^t\text{-Bu}_3)_2$ (0.10 g, 0.19 mmol) gave a dark brown oil, which was purified by chromatography on a silica column, eluting with n-hexane/DCM (1:0 \rightarrow 2:3) to give the product as an orange solid (0.62 g, 1.25 mmol, 65%).

$^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): $\delta_{\text{H}} = 7.47$ (dt, $^3J_{\text{HH}} = 8.4$, $^4J_{\text{HH}} = 2.0$ Hz, 2H, H5), 7.35 (dt, $^3J_{\text{HH}} = 8.8$, $^4J_{\text{HH}} = 2.0$ Hz, 2H, H6), 4.47 (*pseudo-t*, $^3J_{\text{HH}} = 2.0$ Hz, 2H, H12), 4.45 (*pseudo-t*, $^3J_{\text{HH}} = 2.0$ Hz, 2H, H13), 4.28 (*pseudo-t*, $^3J_{\text{HH}} = 2.0$ Hz, 2H, H11), 4.23 (*pseudo-t*, $^3J_{\text{HH}} = 2.0$ Hz, 2H, H14), 3.15 (t, $^3J_{\text{HH}} = 6.0$ Hz, 2H, H2), 2.61 (t, $^3J_{\text{HH}} = 6.0$ Hz, 2H, H3) ppm; $^{13}\text{C NMR}$ (CDCl_3 , 298 K, 100 MHz) $\delta_{\text{C}} = 133.2$ (C7), 132.4 (C6), 130.8 (C5), 123.3 (C4), 118.0 (C1), 88.8 (C9), 86.3 (C8), 76.5 (C13), 74.3 (C14), 72.2 (C12), 71.0 (C11), 67.4 (C10), 41.4 (C15), 30.1 (C3), 18.4 (C2) ppm; **MS ES+**: calcd. for $\text{C}_{21}\text{H}_{16}\text{NSiFe} [\text{M}]^+$ 496.9392; found. 496.9395.

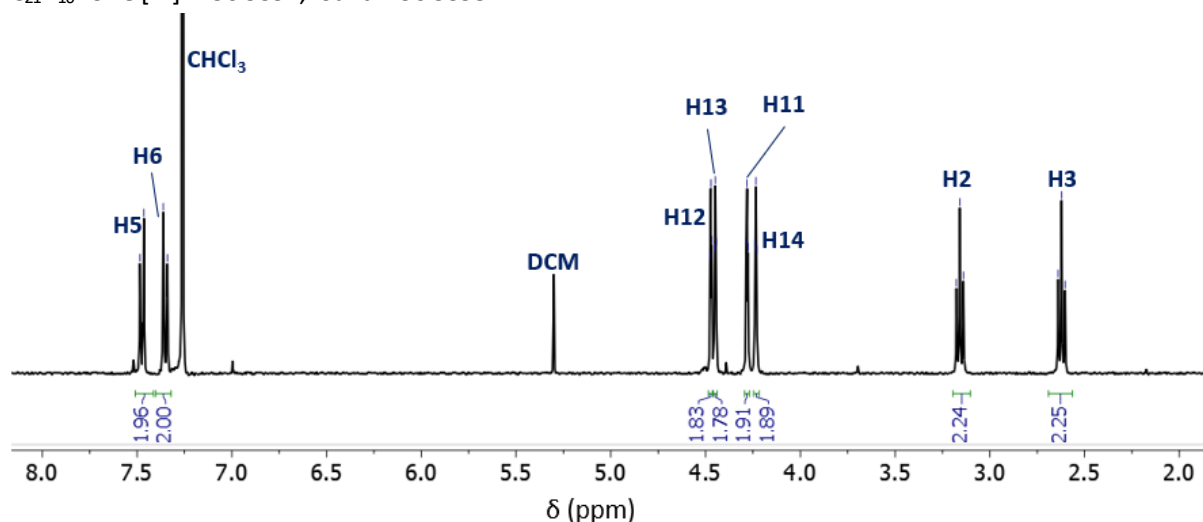


Figure S5: The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of **2a**.

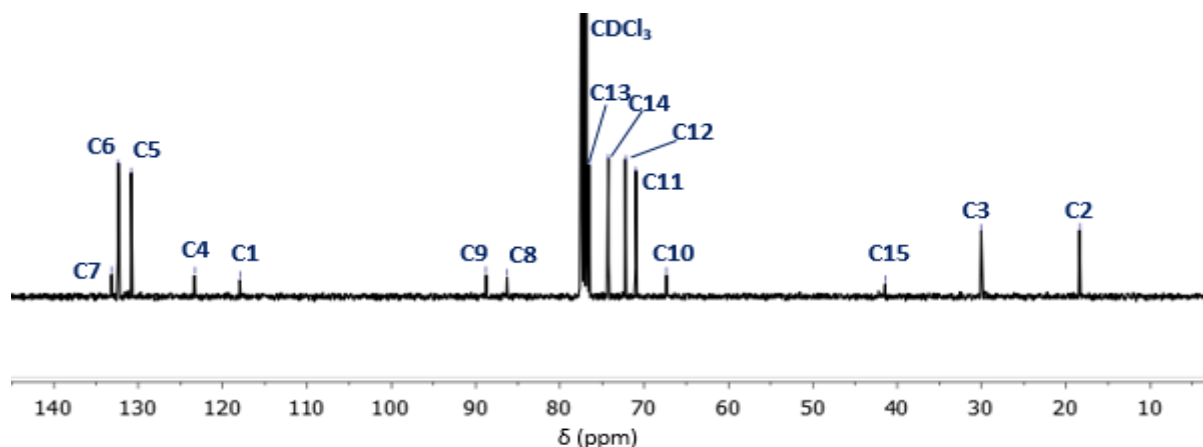
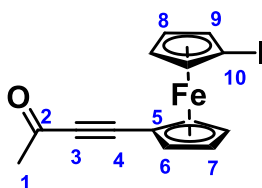


Figure S6: The $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2a**.

1-Iodo-1'-(but-3-yn-2-one)ferrocene (2b)

Formed as an impurity in the synthesis of **2**. Eluted from a silica column in n-hexane/DCM (1:0 → 0:1) to give a red solid (0.02 g, 0.05 mmol, 3%).

$^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): $\delta_{\text{H}} = 4.55$ (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 4H, H7), 4.47 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 4H, H8), 4.39 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 4H, H6), 4.25 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 4H, H9), 2.42 (s, 3H, H1) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K, 100 MHz): $\delta_{\text{C}} = 184.6$ (C2), 92.1 (C4), 87.6 (C3), 76.8 (C8), 75.7 (C7), 74.0 (C6), 71.5 (C9), 62.4 (C5), 40.7 (C10), 32.8 (C1) ppm; **MS ES+**: calcd. for $\text{C}_{14}\text{H}_{12}\text{OFeI}$ [$\text{M}+\text{H}$] $^+$ 378.9282; found. 378.9293.

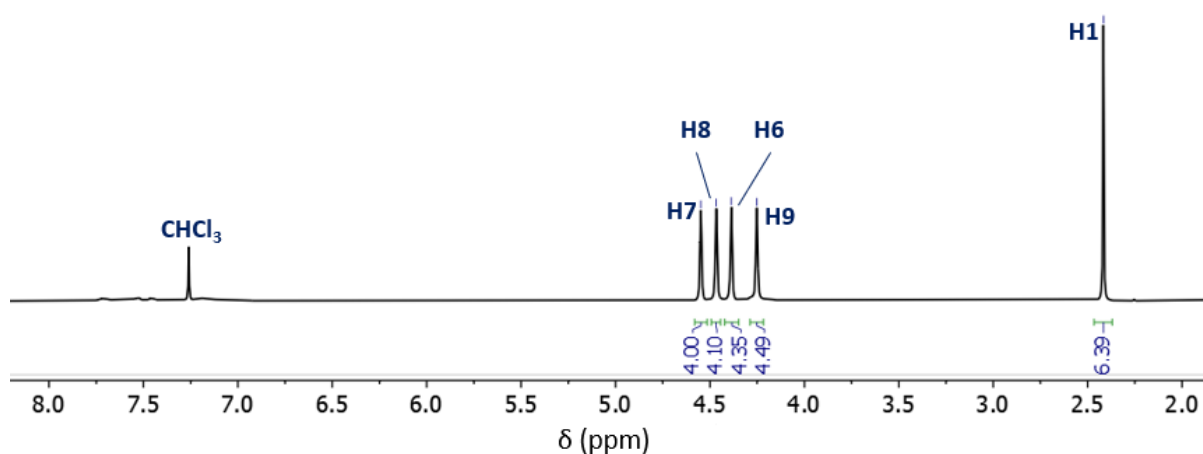


Figure S7: The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of **2b**.

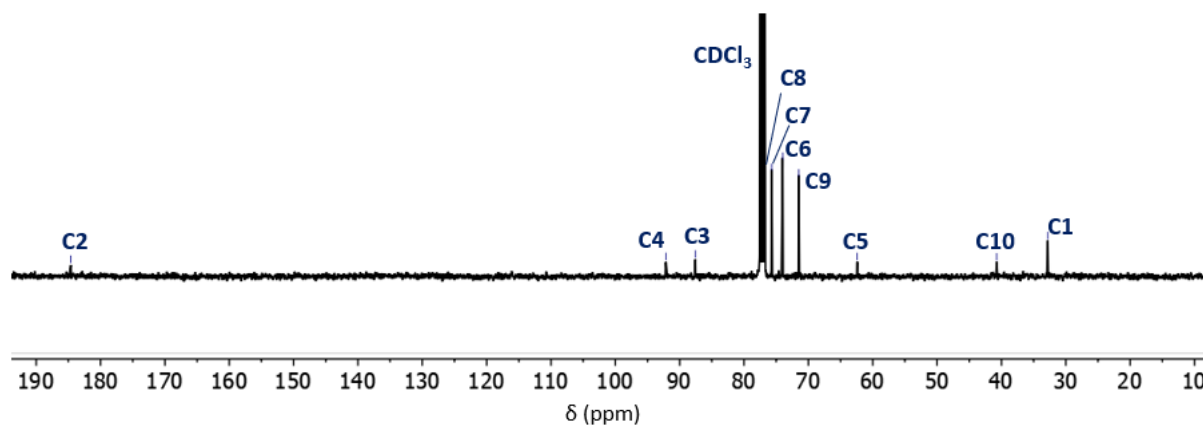
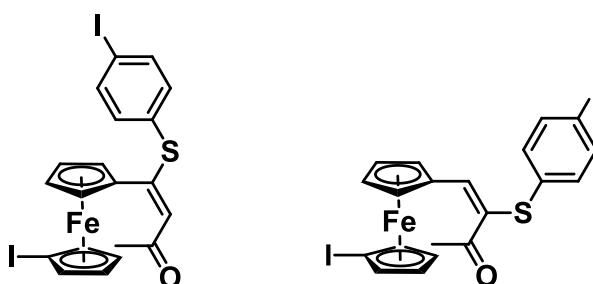


Figure S8: The $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2b**.

Mixture of isomers (**2c**)

Formed as an impurity in the synthesis of **2**. Eluted from a silica column in n-hexane/DCM (1:0 → 0:1) to give a red solid (0.05 g, 0.07 mmol, 5%), consisting of two molecules formed in a ~ 1:2.4 ratio.

Isomer 1: $^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): $\delta_{\text{H}} = 7.46$ (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, Ar-H), 7.05 (s, 1H, -C=C-H), 6.87 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, Ar-H), 4.30 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.27 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.23 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.13 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 2.34 (s, 3H, CO-CH₃) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K, 100 MHz): $\delta_{\text{C}} = 196.1$ (-C=O), 152.0 (Ar-C-C), 137.8 (Ar-C-H), 135.2 (Ar-C-C), 133.0 (Ar-C-H), 126.1 (-C=C-H), 92.7 (-C=C-C), 86.0 (Fc-C-C), 77.1 (Fc-C-H), 73.3 (Fc-C-H), 72.9 (Fc-C-H), 71.3 (Fc-C-H), 41.0 (Fc-C-I), 31.0 (CO-CH₃) ppm.

Isomer 2: $^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): $\delta_{\text{H}} = 7.76$ (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, Ar-H), 7.28 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 2H, Ar-H), 5.60 (s, 1H, -C=C-H), 4.60 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.50 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.43 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 4.32 (*pseudo-t*, $^3J_{\text{H-H}} = 2.0$ Hz, 2H, Fc-H), 1.95 (s, 3H, -CH₃) ppm. A carbon-nmr could not be acquired for this species due to limited amounts of sample.

MS ES+ (of the mixture): calcd. for $\text{C}_{20}\text{H}_{17}\text{OSFeI}_2$ [M+H]⁺ 614.8439; found. 614.8446.

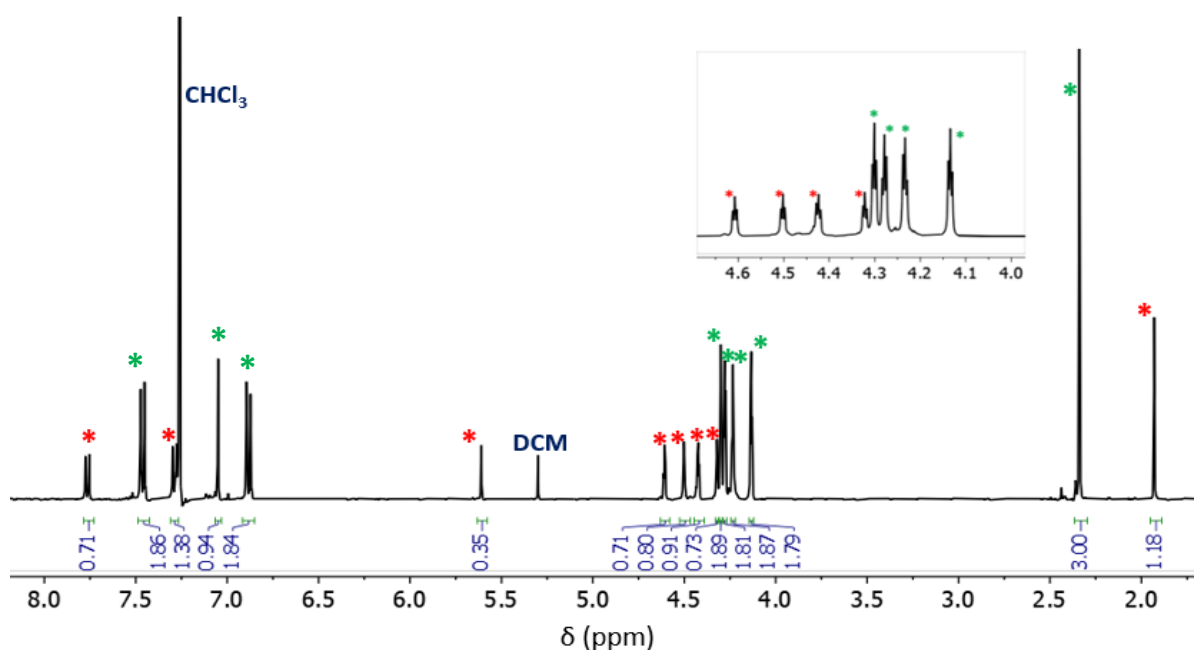


Figure S9: The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of **2c**. Distinct isomers are labelled with * and * respectively.

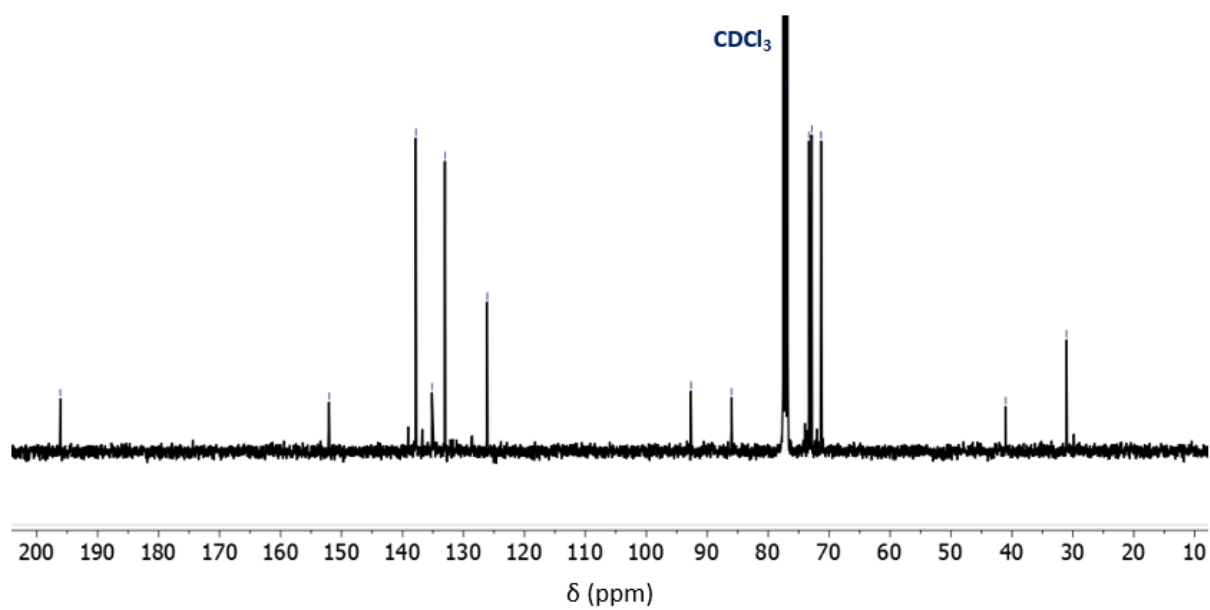
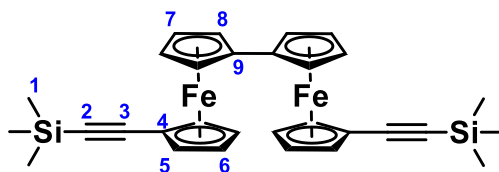


Figure S10: The $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **2c**. Only a single isomer could be identified here, due to limitations relating to sample quantities.

1,1'''-Bis(trimethylsilyl)ethynylbiferrocene (3a)⁷

1,1'-Diiodobiferrocene (0.50 g, 0.80 mmol), TMSA (0.07 g, 0.67 mmol) and CuI (0.01 g, 0.03 mmol) were dissolved in DIPA (10 mL). Pd(P-^tBu₃)₂ (0.02 g, 0.03 mmol) was added, and the solution was left to stir overnight to form a dark brown solution. The solvent was removed *in vacuo* to yield a brown solid which was purified by chromatography on a silica column, eluted with n-hexane/DCM (1:0 → 4:1 v/v) to give the product as an orange solid (0.07 g, 0.12 mmol, 36%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 4.37 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 4.23 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 4.20 (t, ³J_{H-H} = 2.0 Hz, 4, Fc-H), 4.02 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 0.23 (s, 18H, H1) ppm; MS ES⁺: calcd. for C₃₀H₃₄Si₂Fe₂ [M]⁺ 562.0898; found 562.0893.

This data is in accordance with a previously reported synthesis of this molecule.⁹

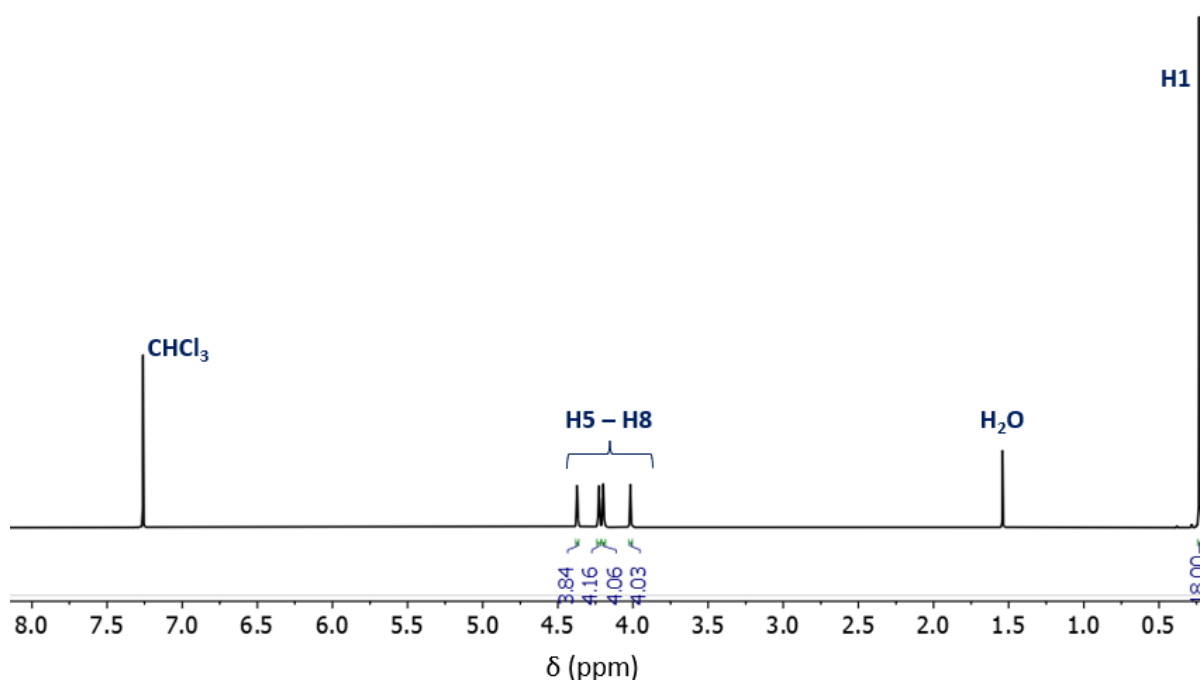
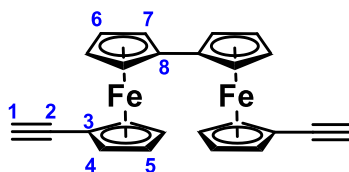


Figure S11: The ¹H NMR (CDCl₃, 400 MHz) spectrum of 3a.

1,1'''-Bisethynylbiferrocene (3)⁷

(3a) (0.25 g, 0.53 mmol) was dissolved in a 1:1 mixture of THF:MeOH (45 mL). An aqueous solution of NaOH (1.0 M, 10 mL) was added and the solution was stirred overnight to form a dark red solution. A saturated aqueous solution of NaHCO₃ (aq. 30 mL) was added and the solvent was concentrated *in vacuo*. The solution was then extracted into DCM (100 mL) before being washed with water (3 x 100 mL) and brine (100 mL). The solution was then dried over MgSO₄ and the solvent was removed *in vacuo* to give the product as a dark red solid (0.13 g, 0.31 mmol, 72%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 4.40 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 4.25 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 4.23 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 4.02 (t, ³J_{H-H} = 2.0 Hz, 4H, Fc-H), 2.66 (s, 2H, H1) ppm; **MS ES+**: calcd. for C₂₄H₁₈Fe₂ [M]⁺ 418.0107; found. 418.0103.

This data is in accordance with a previously reported synthesis of this molecule.⁹

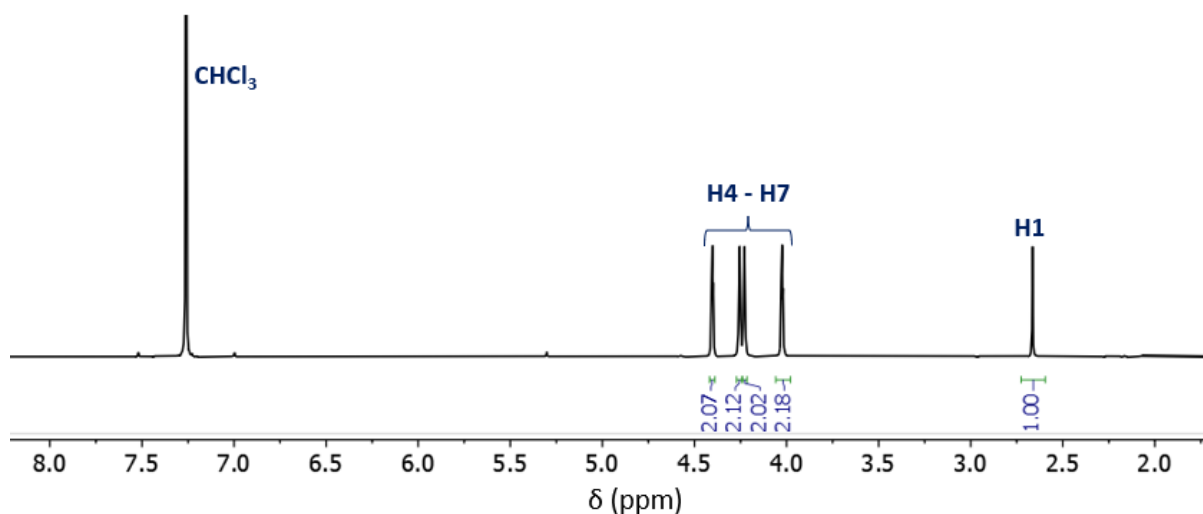
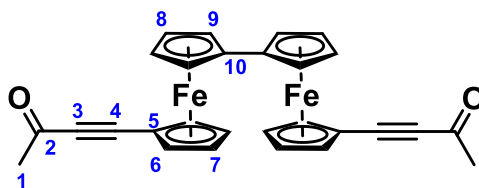


Figure S12: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **3**.

1,1'''-Bis(but-3-yn-2-one)biferrocene (4)

(**3**) (0.10 g, 0.24 mmol), 4-iodophenylthioacetate (0.27 g, 0.96 mmol) and CuI (0.01 g, 0.02 mmol) were dissolved in DIPA (20 mL) to give a red solution. This solution was degassed for 15 minutes, Pd(P-^tBu₃)₂ (0.01 g, 0.02 mmol) was added, and the solution was stirred overnight, forming a dark black precipitate. The solvent was removed *in vacuo* and the dark black solid was purified by chromatography on a silica column, eluting with chloroform to give the product as a dark red solid (0.10 g, 0.15 mmol, 61%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 4.47 (t, ³J_{H-H} = 2.0 Hz, 4H, H9), 4.40 (t, ³J_{H-H} = 2.0 Hz, 4H, H7), 4.31 (t, ³J_{H-H} = 2.0 Hz, 4H, H6), 4.24 (t, ³J_{H-H} = 2.0 Hz, 4H, H8), 2.32 (s, 6H, H1) ppm; ¹³C{¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 184.4 (C2), 93.4 (C5), 87.5 (C3), 84.5 (C4), 74.3 (C7), 71.9 (C8), 70.2 (C6), 68.2 (C9), 61.3 (C10), 32.6 (C1) ppm; MS ES⁺: calcd. for C₂₈H₂₃O₂Fe₂ [M+H]⁺ 503.0397; found. 503.0406.

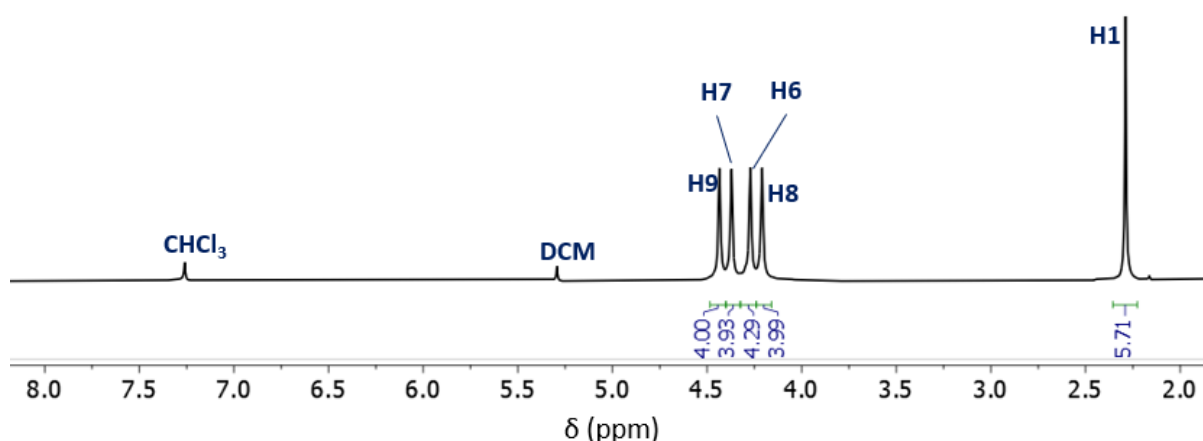


Figure S13: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **4**.

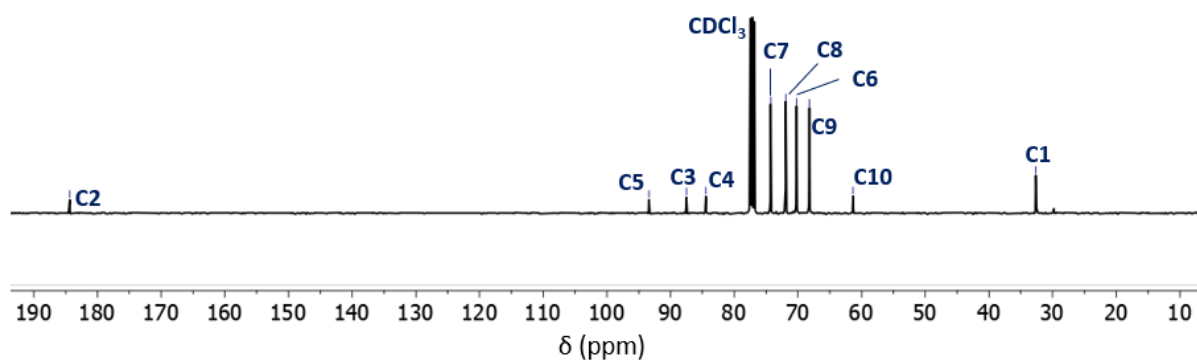
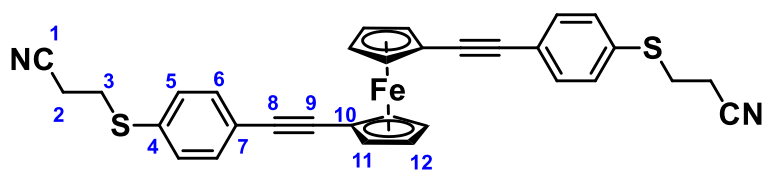


Figure S14: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **4**.

1,1'-Di(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (5a)

Following general procedure **A**, 4-(2-cyanoethylthio)ethynylbenzene (0.24 g, 0.91 mmol), FeCl_2 (0.23 g, 0.23 mmol), CuI (0.01 g, 0.02 mmol) and $\text{Pd}(\text{P}^t\text{-Bu}_3)_2$ (0.01 g, 0.02 mmol) gave a dark-brown oil which was purified by chromatography on an alumina column, eluting with *n*-hexane/DCM (1:0 \rightarrow 0:1) to give the product as a dark red solid (0.12 g, 0.21 mmol, 93%).

$^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): $\delta_{\text{H}} = 7.37$ (dt, $^3J_{\text{HH}} = 8.4$, $^4J_{\text{HH}} = 2.0$ Hz, 4H, H6), 7.27 (dt, $^3J_{\text{HH}} = 8.8$, $^4J_{\text{HH}} = 2.0$ Hz, 4H, H5), 4.57 (*pseudo-t*, $^3J_{\text{HH}} = 2.0$ Hz, 4H, H12), 4.36 (*pseudo-t*, $^3J_{\text{HH}} = 2.0$ Hz, 4H, H11), 3.18 (t, $^3J_{\text{HH}} = 6.0$ Hz, 4H, H2), 2.65 (t, $^3J_{\text{HH}} = 6.0$ Hz, 4H, H3) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K, 100 MHz): $\delta_{\text{C}} = 133.4$ (C7), 132.2 (C6), 130.5 (C5), 129.9 (C4), 118.0 (C1), 88.7 (C9), 86.2 (C8), 73.1 (C12), 71.0 (C11), 67.1 (C10), 30.0 (C2), 18.4 (C3) ppm; **MS ES+**: calcd. for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{S}_2\text{Fe}$ [M] $^+$ 556.0730; found. 556.0727.

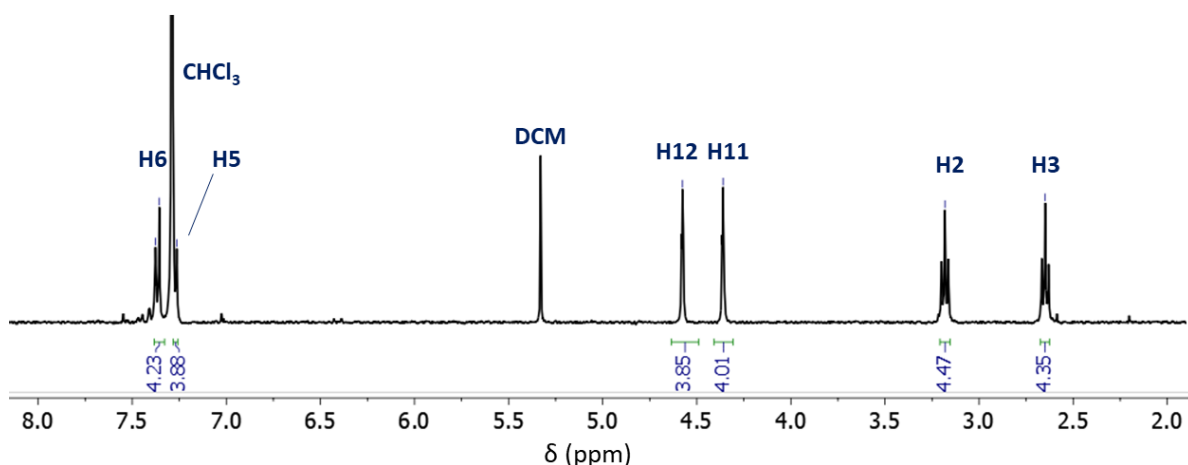


Figure S15: The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of **5a**.

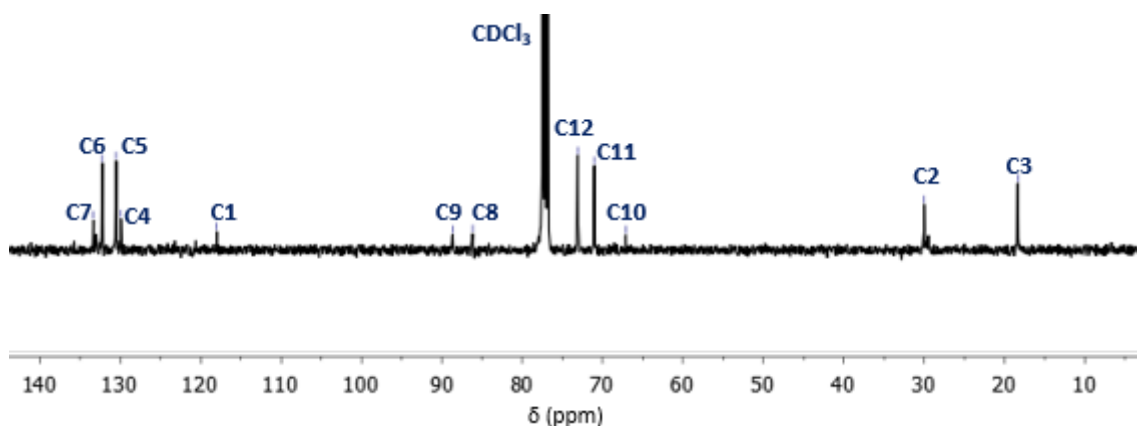
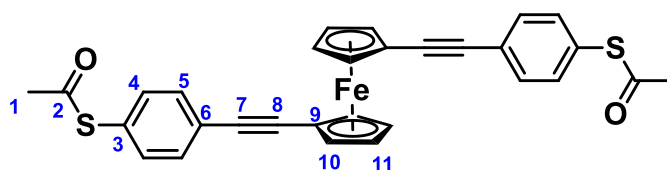


Figure S16: The $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **5a**.

1,1'-Di(4-(ethynylphenyl)thioacetate)ferrocene (5)⁹

Following general procedure B, (5a) (0.06 g, 0.11 mmol), NaOMe (25% in MeOH, 0.25 mL) and Ac₂O (0.50 mL) gave a light-orange powder which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, to give the product as an orange solid (0.04 g, 0.08 mmol, 70%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 7.41 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 4H, H5), 7.28 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 4H, H4), 4.55 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H11), 4.34 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H10), 2.43 (s, 6H, H1) ppm; ¹³C{¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 193.7 (C2), 134.2 (C5), 132.0 (C4), 127.3 (C6), 125.2 (C3), 89.2 (C8), 86.3 (C7), 73.2 (C11), 71.1 (C10), 66.9 (C9), 30.4 (C1) ppm; MS ES⁺: calcd. for C₃₀H₂₂O₂S₂Fe [M]⁺ 534.0405; found. 534.0412.

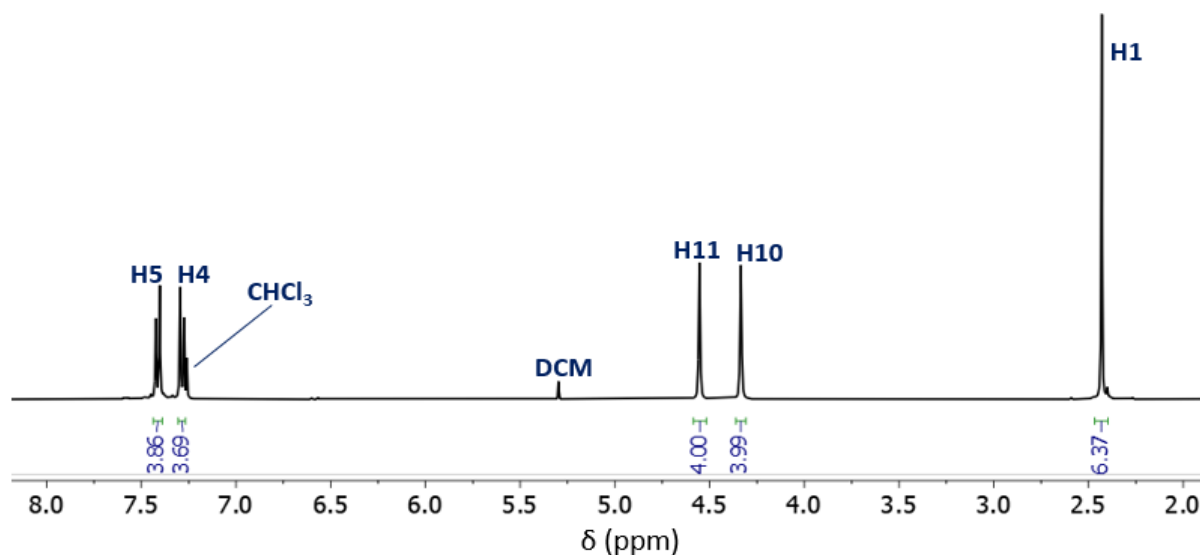


Figure S17: The ¹H NMR (CDCl₃, 400 MHz) spectrum of 5.

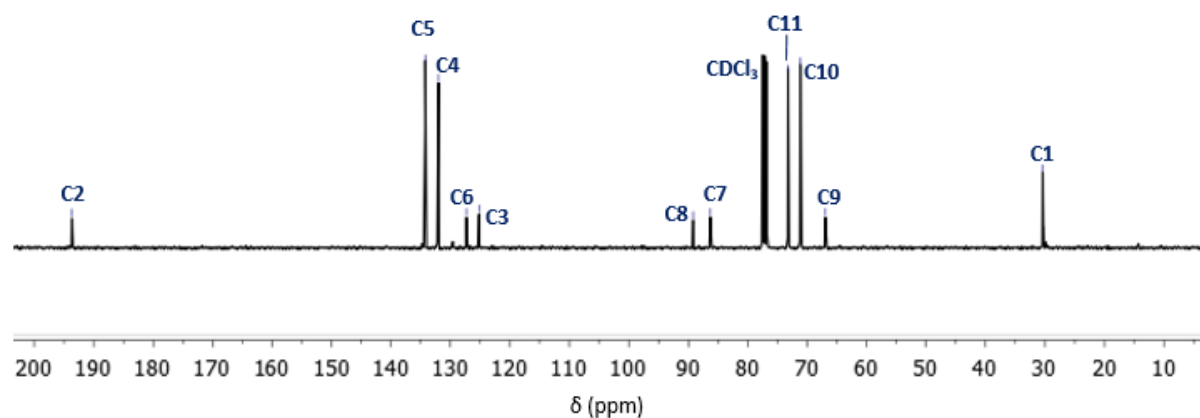
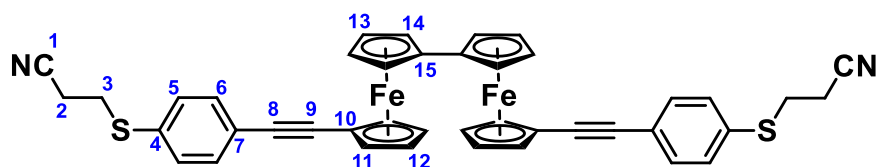


Figure S18: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of 5.

1,1'''-Di(4-(2-cyanoethylthio)ethynylbenzene)biferrocene (6a)

Following general procedure **A**, 1,1'''-diiodobiferrocene (0.20 g, 0.32 mmol), 4-(2-cyanoethylthio)ethynylbenzene (0.12 g, 0.68 mmol), CuI (0.01 g, 0.03 mmol) and Pd(P-^tBu)₃ (0.02 g, 0.03 mmol) gave a dark-brown oil. This was purified by chromatography on a silica column, eluting with DCM to give the product as a red solid (0.16 g, 0.21 mmol, 65%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 7.37 (dd, ³J_{H-H} = 6.4, ⁴J_{H-H} = 2.0 Hz, 4H, H6), 7.32 (dd, ³J_{H-H} = 6.4, ⁴J_{H-H} = 2.0 Hz, 4H, H5), 4.42 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H13), 4.27 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H12), 4.22 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H14), 4.09 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H11), 3.16 (t, ³J_{H-H} = 7.6 Hz, 4H, H2), 2.62 (t, ³J_{H-H} = 7.6 Hz, 4H, H3) ppm; ¹³C {¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 132.7 (C7), 132.2 (C5), 130.8 (C6), 123.6 (C4), 118.0 (C1), 89.9 (C9), 85.3 (C8), 84.4 (C15), 72.8 (C12), 70.3 (C11/C14), 69.9 (C11/C14), 68.4 (C13), 65.7 (C10), 30.1 (C3), 18.4 (C2) ppm. MS ES⁺: calcd. for C₄₂H₃₂N₂S₂Fe₂ [M]⁺ 740.0700; found.740.0712.

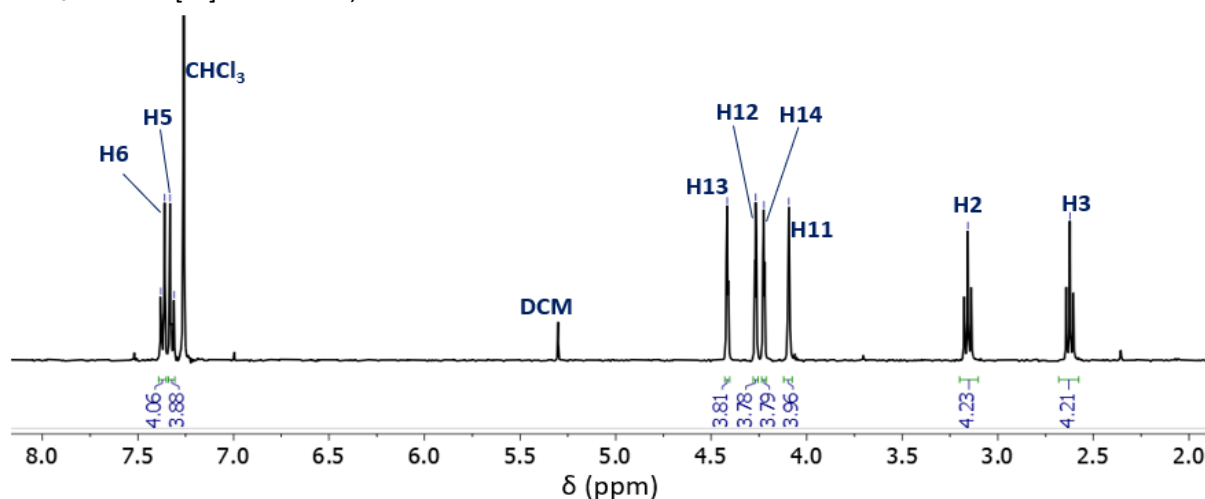


Figure S19: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **6a**.

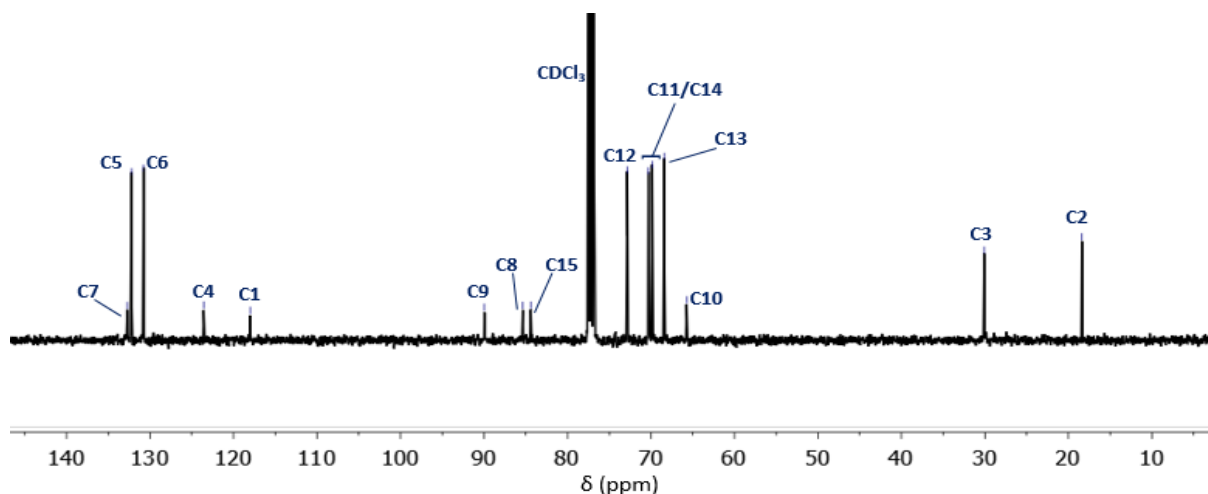
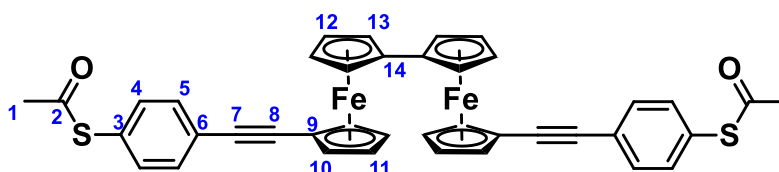


Figure S20: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **6a**.

1,1'''-Di(4-(ethynylphenyl)thioacetate)biferrocene (6)⁹

Following general procedure **B**, (**6a**) (0.06 g, 0.08 mmol), NaOMe (25% in MeOH, 0.25 mL) and Ac₂O (0.50 mL) gave a red-solid which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, to give the product as a bright red solid (0.04 g, 0.06 mmol, 76%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 7.46 (d, ³J_{H-H} = 8.4 Hz, 4H, H5), 7.37 (d, ³J_{H-H} = 8.4 Hz, 4H, H4), 4.44 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H11), 4.30 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H12), 4.25 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H10), 4.12 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H13), 2.47 (s, 6H, H1) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_C = 193.9 (C2), 134.3 (C5), 132.0 (C4), 127.0 (C6), 125.6 (C3), 90.5 (C8), 85.5 (C7), 84.4 (C14), 72.9 (C12), 70.3 (C13), 69.9 (C10), 68.4 (C11), 65.7 (C9), 30.4 (C1) ppm. **MS ES+**: calcd. for C₄₀H₃₀O₂S₂Fe₂ [M]⁺ 718.0386; found. 718.0390.

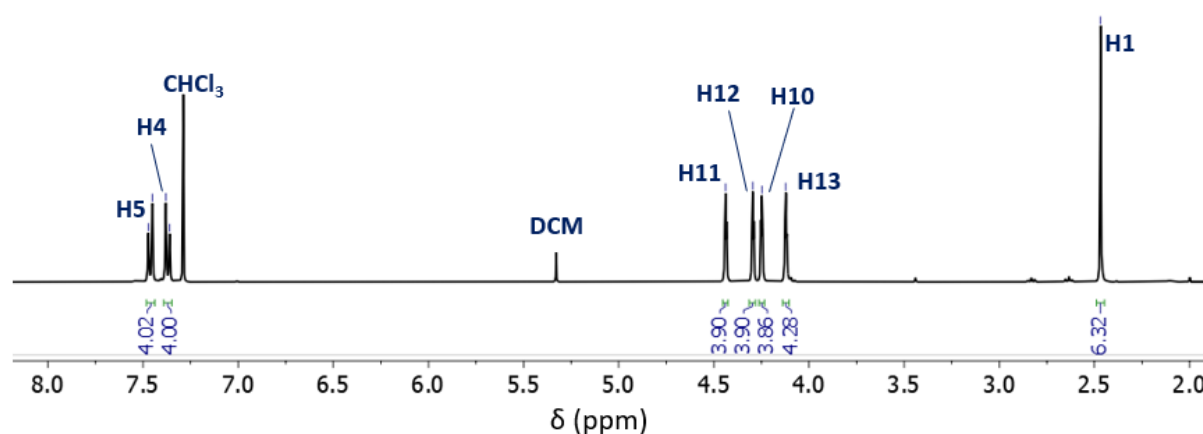


Figure S21: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **6**.

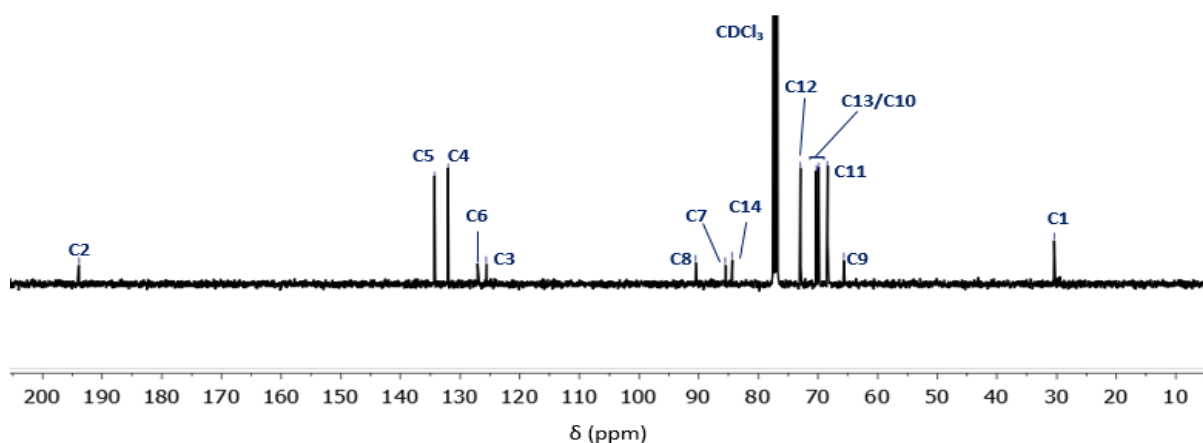
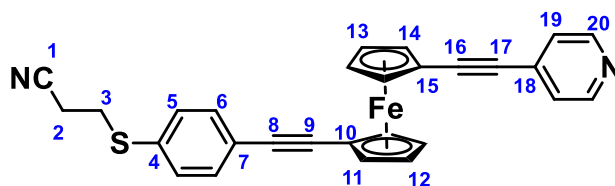


Figure S22: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **6**.

1-(4-Ethynylpyridine)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (**7a**)

Following general procedure **A**, (**2a**) (0.20 g, 0.40 mmol), 4-ethynylpyridine hydrochloride (0.17 g, 1.21 mmol), CuI (0.01 g, 0.04 mmol) and Pd(P-^tBu₃)₂ (0.02 g, 0.04 mmol) gave a dark-brown solid, which was purified by chromatography on an alumina column, eluting with DCM to give the product as an orange solid (0.14 g, 0.30 mmol, 75%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 8.45 (br s, 2H, H₂₀), 7.33 (d, ³J_{H-H} = 8.4 Hz, 2H, H₅), 7.26 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H₆), 7.23 (br s, 2H, H₁₉), 4.63 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₃), 4.60 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₂), 4.43 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₄), 4.40 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₁), 3.20 (t, ³J_{H-H} = 6.0 Hz, 2H, H₃), 2.70 (t, ³J_{H-H} = 6.0 Hz, 2H, H₂) ppm; ¹³C {¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_{C} = 149.6 (C₂₀), 133.2 (C₄), 132.1 (C₅), 132.0 (C₁₈), 130.5 (C₆), 125.4 (C₁₉), 123.0 (C₇), 118.0 (C₁), 92.8 (C₁₆), 88.2 (C₉), 86.4 (C₈), 84.6 (C₁₇), 73.3 (C₁₃), 73.1 (C₁₂), 71.4 (C₁₄), 71.0 (C₁₁), 67.5 (C₁₀), 66.0 (C₁₅), 29.9 (C₃), 18.4 (C₂) ppm; **MS ES+**: calcd. for C₂₈H₂₁N₂SFe [M+H]⁺ 473.0769; found. 473.0777.

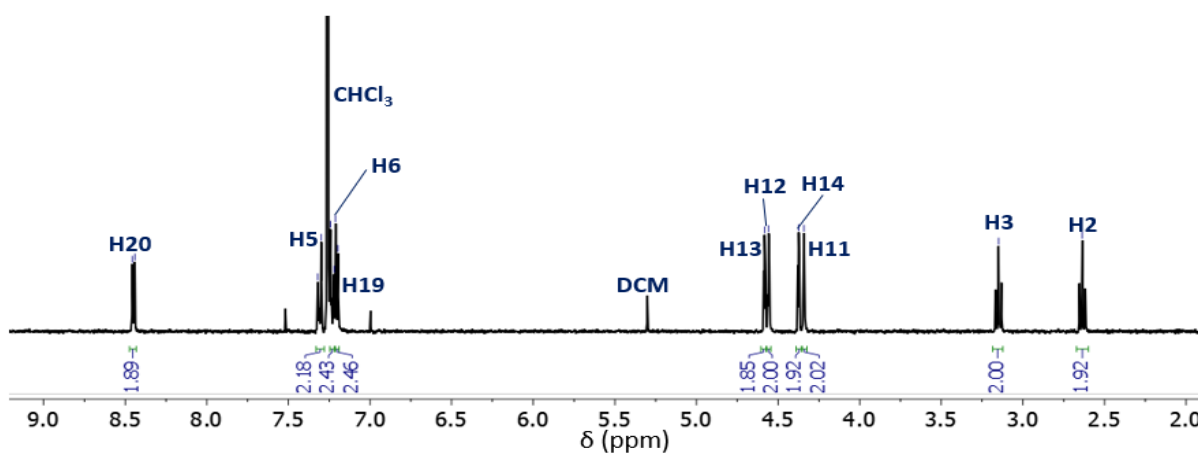


Figure S23: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **7a**.

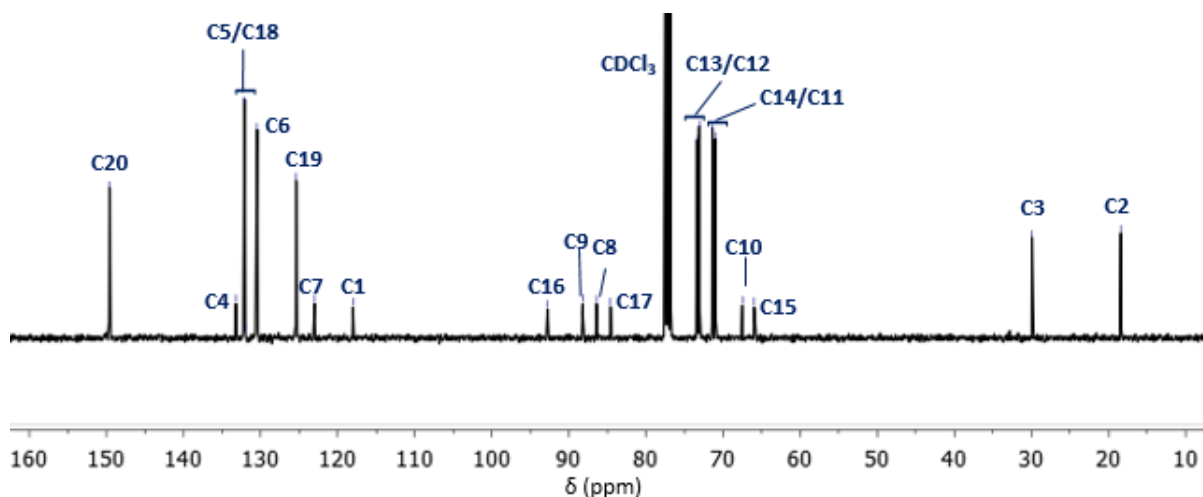
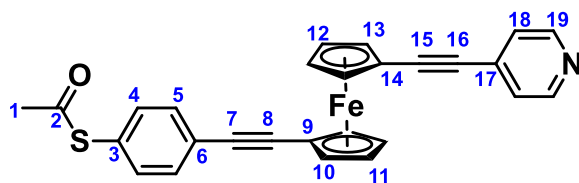


Figure S24: The ¹³C {¹H} NMR (CDCl₃, 100 MHz) spectrum of **7a**.

1-(4-Ethynylpyridine)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (7)

Following general procedure **B**, (**7a**) (0.06 g, 0.13 mmol), NaOMe (25% in MeOH, 0.25 mL) and Ac₂O (0.50 mL) gave an orange solid which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, to give the product as an orange solid (0.04 g, 0.08 mmol, 70%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 8.47 (dd, ³J_{H-H} = 4.4, ⁴J_{H-H} = 1.6 Hz, 2H, H19), 7.39 (d, ³J_{H-H} = 8.4 Hz, 2H, H5), 7.29 (dd, ³J_{H-H} = 4.4, ⁴J_{H-H} = 1.6 Hz, 2H, H18), 7.20 (d, ³J_{H-H} = 8.4 Hz, 2H, H4), 4.58 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H13), 4.56 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10), 4.37 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H12), 4.34 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11), 2.44 (s, 3H, H1) ppm; ¹³C {¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 193.6 (C2), 149.7 (C19), 134.2 (C4), 132.1 (C17), 131.9 (C5), 127.5 (C6), 125.4 (C18), 125.0 (C3), 92.8 (C15), 88.8 (C8), 86.5 (C7), 84.6 (C16), 73.4 (C13), 73.2 (C10), 71.4 (C12), 71.1 (C11), 67.3 (C9), 65.9 (C15), 30.4 (C1) ppm; MS ES⁺: calcd. for C₂₇H₂₀NOSFe [M+H]⁺+462.0610; found. 462.0618.

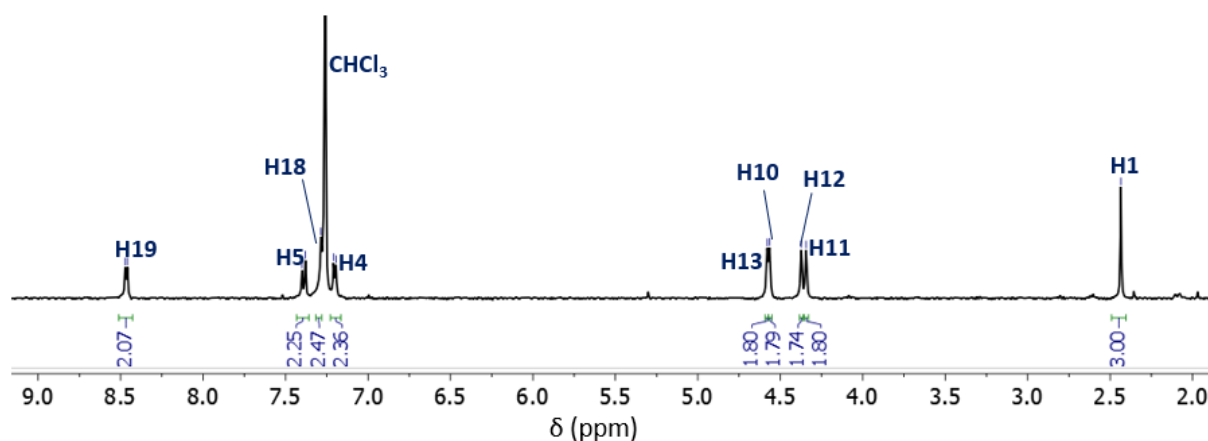


Figure S25: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **7**.

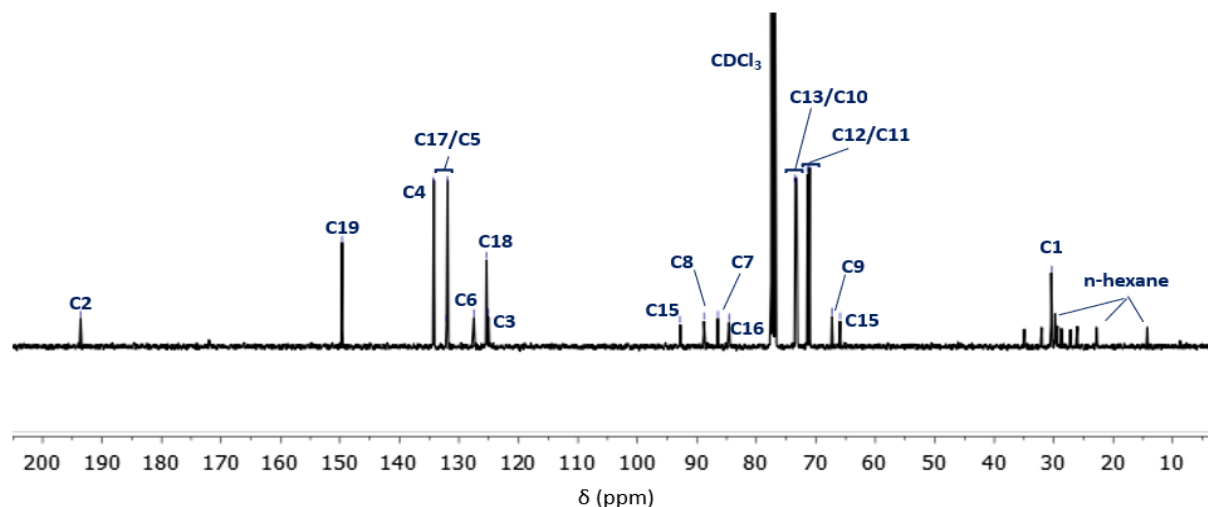
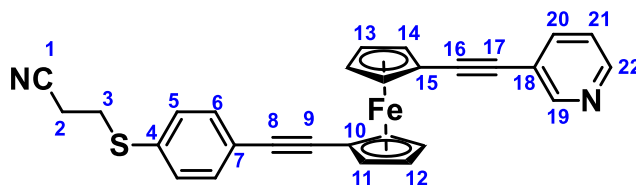


Figure S26: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **7**.

1-(3-Ethynylpyridine)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (**8a**)

Following general procedure **A**, (**2a**) (0.20 g, 0.40 mmol), 3-ethynylpyridine (0.12 g, 1.21 mmol), CuI (0.01 g, 0.04 mmol) and Pd(P-^tBu₃)₂ (0.02 g, 0.04 mmol) gave an orange powder, which was purified by chromatography on an alumina column, eluting with DCM, to give the product as an orange solid (0.17 g, 0.37 mmol, 91%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 8.57 (br m, 2H, H19/H22) 7.63 (d, ³J_{H-H} = 8.4 Hz, 1H, H20), 7.30 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H5), 7.22 (dt, ³J_{H-H} = 8.8, ⁴J_{H-H} = 2.0 Hz, 2H, H6), 7.17 (br s, 1H, H21), 4.56 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H12/13), 4.55 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H12/13), 4.35 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/14), 4.34 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/14), 3.14 (t, ³J_{H-H} = 6.0 Hz, 2H, H2), 2.64 (t, ³J_{H-H} = 6.0 Hz, 2H, H3) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_C = 153.2 (C19), 151.8 (C18), 147.5 (C22), 139.5 (C20), 138.0 (C21), 133.0 (C4), 132.1 (C5), 130.6 (C6), 123.1 (C7), 118.0 (C1), 90.8 (C16), 88.4 (C9), 86.3 (C8), 83.8 (C17), 73.2 (C12/C13), 73.1 (C12/C13), 71.1 (C11/C14), 71.0 (C11/C14), 67.3 (C15), 66.7 (C10), 30.0 (C3), 18.35 (C2) ppm; MS ES⁺: calcd. for C₂₈H₂₁N₂SFe [M+H]⁺ 473.0769; found. 473.0778.

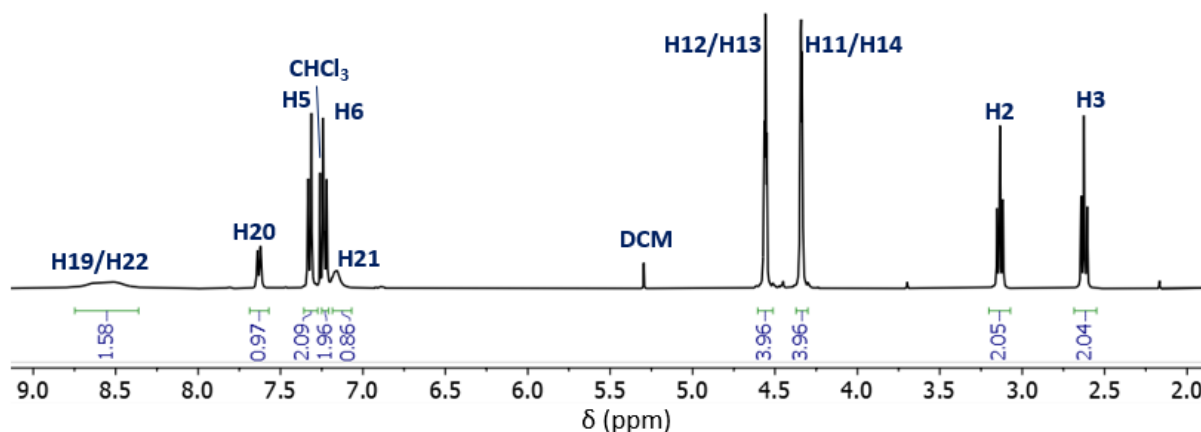


Figure S27: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **8a**.

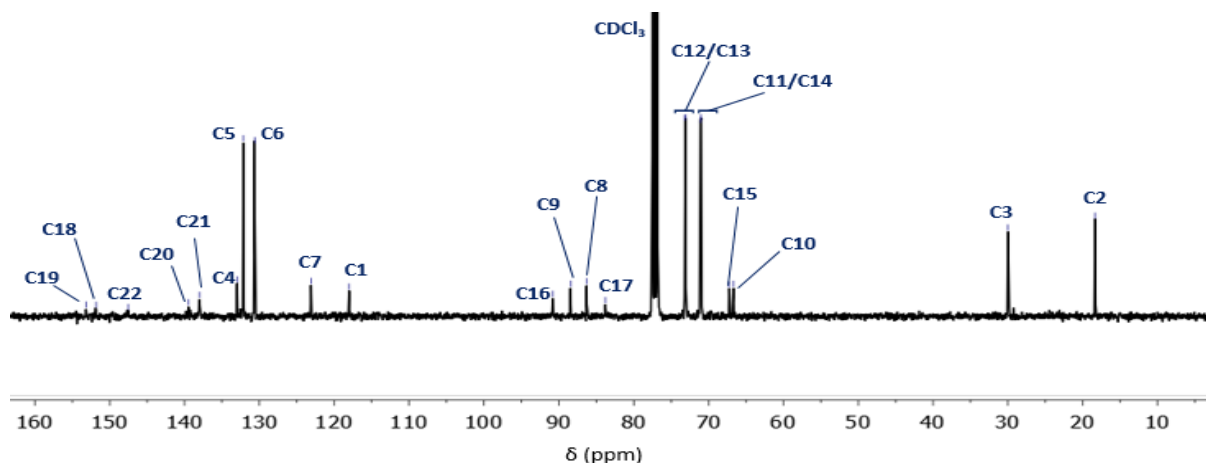
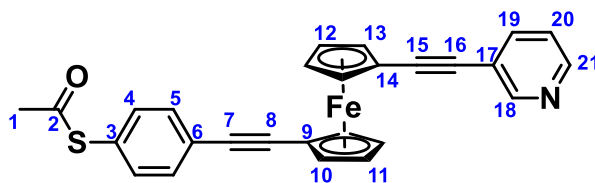


Figure S28: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **8a**.

1-(3-Ethynylpyridine)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (**8**)

Following general procedure B, (**8a**) (0.06 g, 0.13 mmol), NaOMe (25% in MeOH, 0.25 mL) and Ac₂O (0.50 mL) gave an orange solid, which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, to give the product as an orange solid (0.03 g, 0.08 mmol, 61%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 8.66 (d, ⁴J_{H-H} = 1.6 Hz, 1H, H18), 8.47 (dd, ³J_{H-H} = 4.8, ⁴J_{H-H} = 1.6 Hz, 1H, H21), 7.61 (dt, ³J_{H-H} = 7.6, ⁴J_{H-H} = 1.6 Hz, 1H, H19), 7.41 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H5), 7.28 (dt, ³J_{H-H} = 8.8, ⁴J_{H-H} = 2.0 Hz, 2H, H4), 7.17-7.14 (m, 1H, H20), 4.58 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10/13), 4.57 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10/13), 4.36 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/12), 4.36 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/12), 2.44 (s, 3H, H1) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_{C} = 193.6 (C2), 152.1 (C18), 148.0 (C21), 138.2 (C19), 134.3 (C5), 132.0 (C4), 127.4 (C6), 125.1 (C3), 123.1 (C20), 123.0 (C17), 90.8 (C14), 89.0 (C8), 86.4 (C7), 83.7 (C16), 73.2 (C10/13), 71.2 (C11/12), 71.1 (C11/12), 67.1 (C9), 66.6 (C14), 30.4 (C1) ppm; MS ES⁺: calcd. for C₂₇H₂₀NOSFe [M+H]⁺ 462.0610; found. 462.0615.

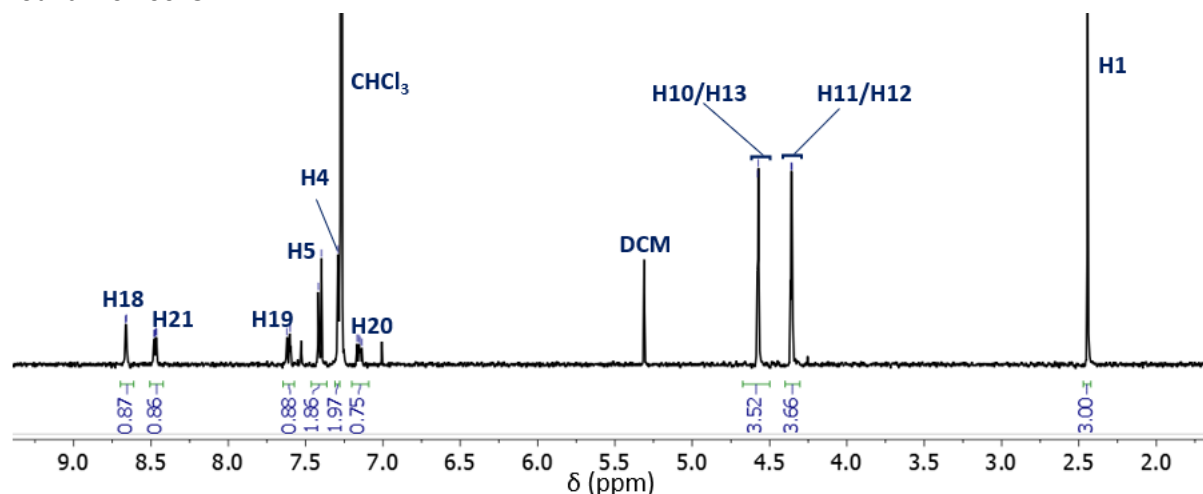


Figure S29: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **8**.

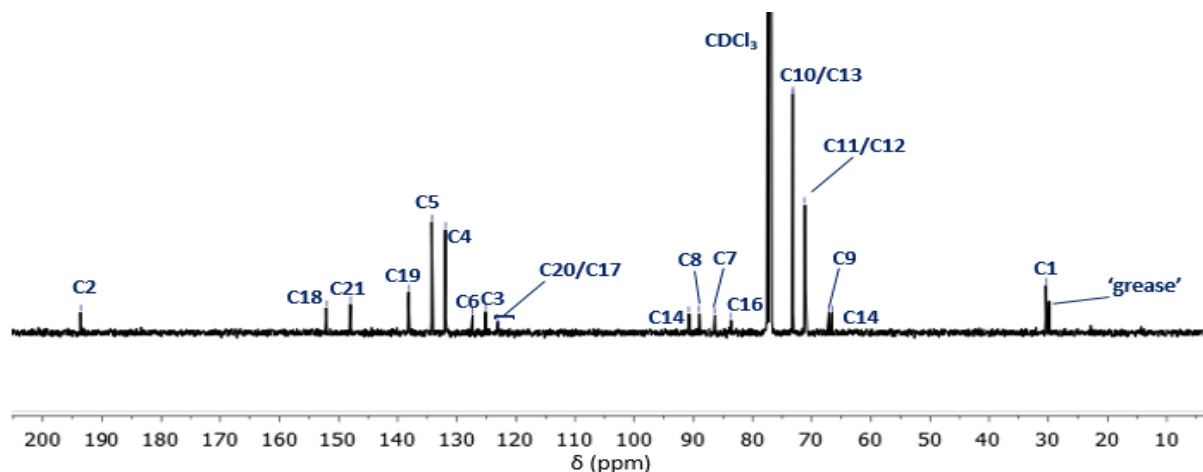
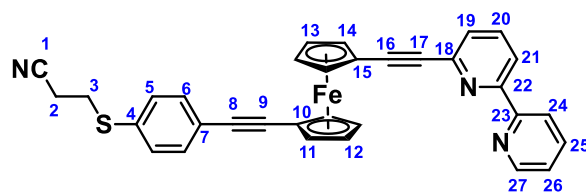


Figure S30: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **8**.

1-(6-Ethynyl-2,2'-bipyridine)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (**9a**)

Following general procedure **A**, (**2a**) (0.20 g, 0.40 mmol), 6-ethynyl-2,2'-bipyridine (0.22 g, 1.20 mmol), CuI (0.01 g, 0.04 mmol) and Pd(P-^tBu₃)₂ (0.02 g, 0.04 mmol) gave a black solid which was purified by chromatography on a silica column, eluting with n-hexane/ethyl acetate (1:0 → 1:1) to give the product as an orange solid (0.10 g, 0.18 mmol, 45%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 8.69 (d, ³J_{H-H} = 4.0 Hz, 1H, H₂₁), 8.42 (d, ³J_{H-H} = 8.0 Hz, 1H, H₂₇), 8.27 (d, ³J_{H-H} = 7.6 Hz, 1H, H₂₄), 7.82 (td, ³J_{H-H} = 7.2, ⁴J_{H-H} = 1.6 Hz, 1H, H₂₆), 7.66 (t, ³J_{H-H} = 7.6 Hz, 1H, H₂₀), 7.38 (d, ³J_{H-H} = 7.6 Hz, 1H, H₂₅), 7.36-7.29 (m, 3H, H₅, H₁₉), 7.14 (d, ³J_{H-H} = 8.0 Hz, 2H, H₆), 4.65 (pseudo-t, 2H, ³J_{H-H} = 2.0 Hz, H₁₁/H₁₄), 4.58 (pseudo-t, 2H, ³J_{H-H} = 2.0 Hz, H₁₁/H₁₄), 4.36 (pseudo-t, 4H, ³J_{H-H} = 2.0 Hz, H₁₂, H₁₃), 3.07 (t, ³J_{H-H} = 7.6 Hz, 2H, H₃), 2.56 (t, ³J_{H-H} = 7.6 Hz, 2H, H₂) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_C = 156.5 (C₂₂), 155.7 (C₂₃), 149.3 (C₂₁), 143.4 (C₁₈), 137.0 (C₂₆), 136.9 (C₂₀), 132.9 (C₄), 132.2 (C₅), 130.3 (C₆), 127.1 (C₂₅), 124.1 (C₁₉), 123.0 (C₇), 121.7 (C₂₇), 119.7 (C₂₄), 118.0 (C₁), 88.4 (C₉/C₁₆), 87.6 (C₉/C₁₆), 86.9 (C₈/C₁₇), 86.4 (C₈/C₁₇), 73.4 (C₁₁/C₁₄), 73.0 (C₁₁/C₁₄), 71.3 (C₁₂/C₁₃), 71.1 (C₁₂/C₁₃), 67.3 (C₁₀/C₁₅), 66.3 (C₁₀/C₁₅), 29.8 (C₃), 18.3 ppm (C₂); MS ES⁺: calcd. for C₃₃H₂₄N₃SFe [M+H]⁺ 550.1040; found. 550.1050.

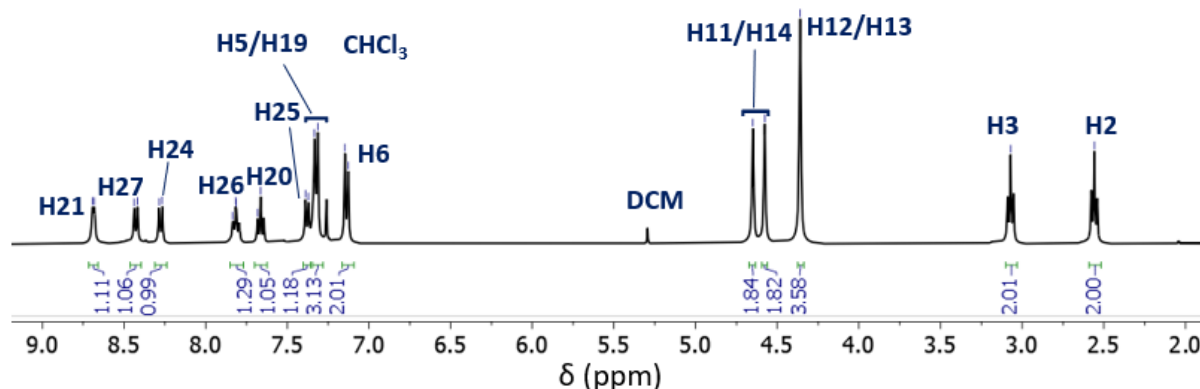


Figure S31: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **9a**.

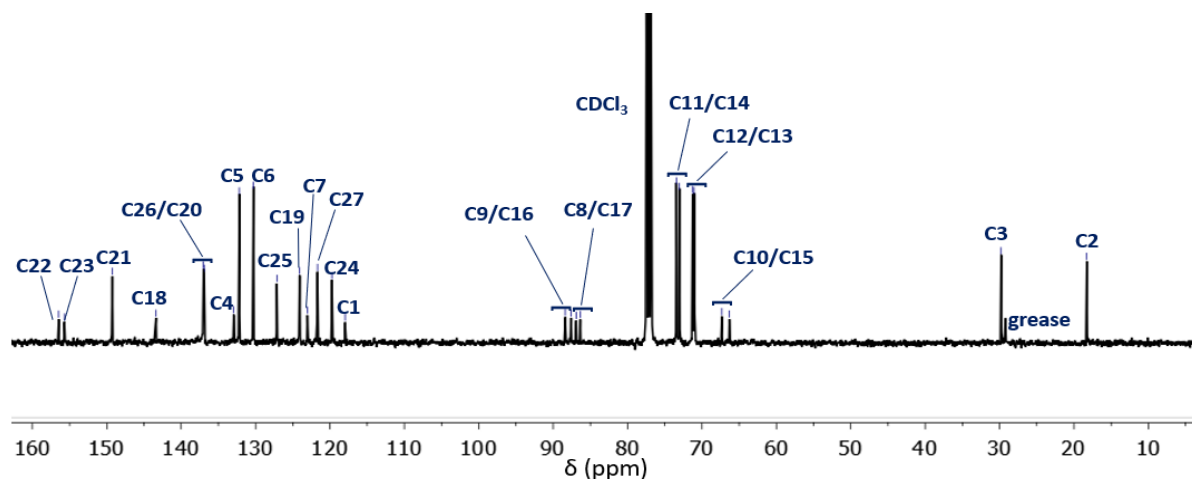
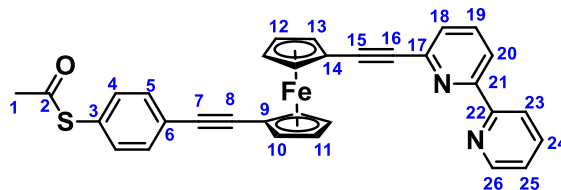


Figure S32: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **9a**.

1-(6-Ethynyl-2,2'-bipyridine)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (**9**)

Following general procedure **B**, (**9a**) (0.03 g, 0.06 mmol), NaOMe (25% in MeOH, 0.01 mL) and Ac₂O (0.02 mL) gave a dark-red powder which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, and subsequently precipitated from a mixture of ethyl acetate/hexane to give the product as a dark-red solid (0.02 g, 0.04 mmol, 63%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 8.68 (ddd, ³J_{H-H} = 4.8, ⁴J_{H-H} = 1.7, ⁵J_{H-H} = 0.9 Hz, 1H, H26), 8.44 (dt, ³J_{H-H} = 8.0, ⁴J_{H-H} = 1.0 Hz, 1H, H23), 8.28 (dd, ³J_{H-H} = 8.0, ⁴J_{H-H} = 1.0 Hz, 1H, H18), 7.81 (td, ³J_{H-H} = 7.6, ⁴J_{H-H} = 1.8 Hz, 1H, H24), 7.68 (t, ³J_{H-H} = 7.8 Hz, 1H, H19), 7.42 (d, ³J_{H-H} = 8.5 Hz, 2H, H5), 7.37 (dd, ³J_{H-H} = 7.7, ⁴J_{H-H} = 1.0 Hz, 1H, H20), 7.32 (ddd, ³J_{H-H} = 7.5, ⁴J_{H-H} = 4.8, ⁴J_{H-H} = 1.2 Hz, 1H, H25), 7.23 (d, ³J_{H-H} = 8.5 Hz, 2H, H4), 4.65 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10/H13), 4.59 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10/H13), 4.37 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/H12), 4.37 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/H12), 2.42 (s, 3H, H1) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_{C} = 193.7 (C2), 156.5 (C21), 155.8 (C22), 149.2 (C26), 143.3 (C17), 137.1 (C25), 137.0 (C20), 134.2 (C5), 132.0 (C3), 127.3 (C4), 127.2 (C24), 125.1 (C6), 124.0 (C25), 121.7 (C23), 119.9 (C18), 89.1 (C8/C15), 87.6 (C8/C15), 86.9 (C7/C16), 86.4 (C7/C16), 73.5 (C10/C13), 73.2 (C10/C13), 71.4 (C11/C12), 71.2 (C11/C12), 67.1 (C9/C14), 66.2 (C9/C14), 29.9 (C1) ppm; MS ES⁺: calcd. for C₃₂H₂₂N₂OSFe [M]⁺ 539.0880; found. 539.0890.

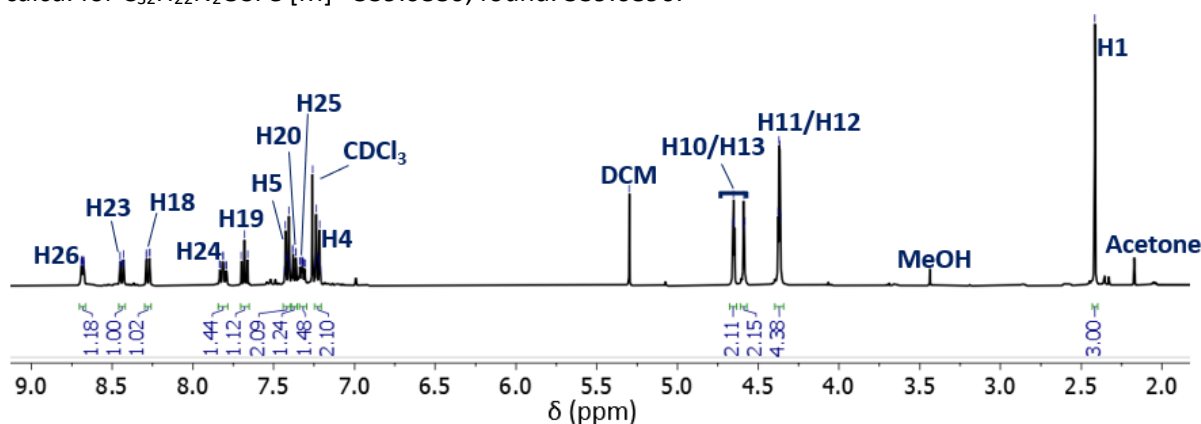


Figure S33: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **9**.

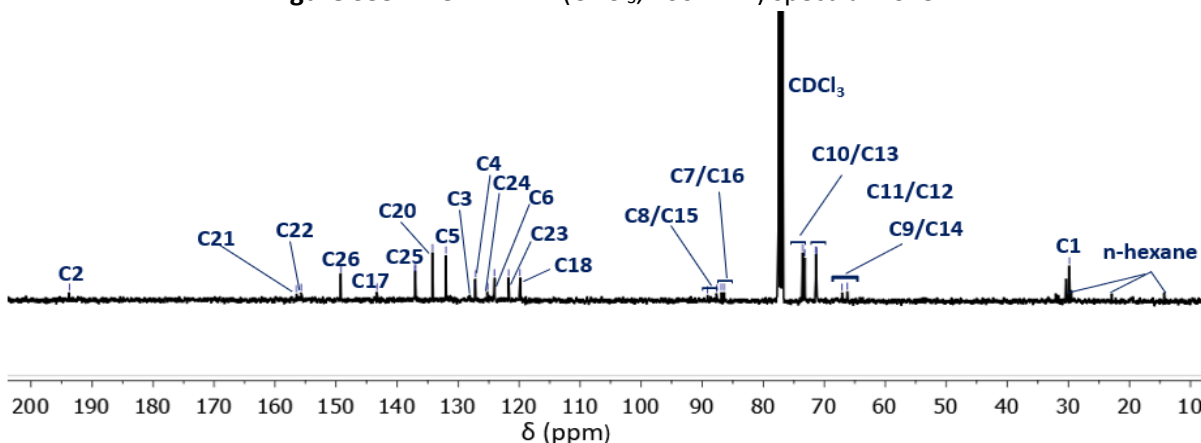
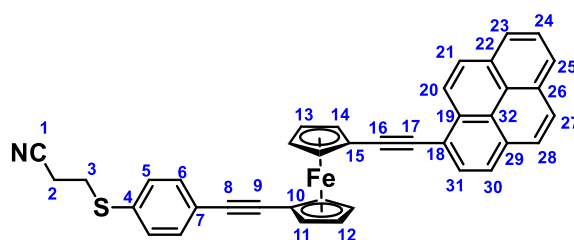


Figure S34: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **9**.

1-(Ethynylpyrene)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (**10a**)

Following general procedure **A**, (**2a**) (0.15 g, 0.30 mmol), 1-ethynylpyrene (0.27 g, 1.20 mmol), CuI (0.01 g, 0.03 mmol) and Pd(^tBu₃)₂ (0.02 g, 0.03 mmol) gave a black solid which was purified by chromatography on a silica column, eluting with n-hexane/DCM (1:0 → 6:4) to give the product as a bright orange solid (0.16 g, 0.27 mmol, 91%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 8.56 (d, ³J_{H-H} = 8.8 Hz, 1H, Ar-H), 8.23-8.16 (m, 2H, Ar-H), 8.11-7.99 (m, 6H, Ar-H), 7.07 (d, ³J_{H-H} = 8.0 Hz, 2H, H₅), 6.76 (d, ³J_{H-H} = 8.0 Hz, 2H, H₆), 4.78 (br s, 2H, H₁₂/H₁₃), 4.68 (br s, 2H, H₁₂/H₁₃), 4.45 (br s, 2H, H₁₁/H₁₄), 4.44 (br s, 2H, H₁₁/H₁₄), 2.81 (t, ³J_{H-H} = 7.6 Hz, 2H, H₃), 2.35 (t, ³J_{H-H} = 7.6 Hz, 2H, H₂) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_C = 132.7 (C₄), 131.9 (C₅), 131.8 (Ar-C-C), 131.4 (Ar-C-C), 131.2 (Ar-C-C), 130.9 (Ar-C-C), 129.7 (C₆), 129.5 (Ar-C-H), 128.2 (Ar-C-H), 128.0 (Ar-C-H), 127.4 (Ar-C-H), 126.3 (Ar-C-H), 125.8 (Ar-C-H), 125.6 (Ar-C-H), 125.6 (Ar-C-H), 124.5 (Ar-C-H), 124.4 (Ar-C-C), 122.7 (C₇), 118.7 (Ar-C-C), 117.9 (C₁), 92.9 (C₉/C₁₆), 88.2 (C₉/C₁₆), 88.6 (C₈/C₁₇), 86.5 (C₈/C₁₇), 73.3 (C₁₂/C₁₃), 73.3 (C₁₂/C₁₃), 71.1 (C₁₁/C₁₄), 71.1 (C₁₁/C₁₄), 68.8 (C₁₀/C₁₅), 68.4 (C₁₀/C₁₅), 29.6 (C₃), 18.1 (C₂) ppm; MS ES⁺: calcd. for C₃₉H₂₆NSFe [M+H]⁺ 596.1135; found. 596.1149.

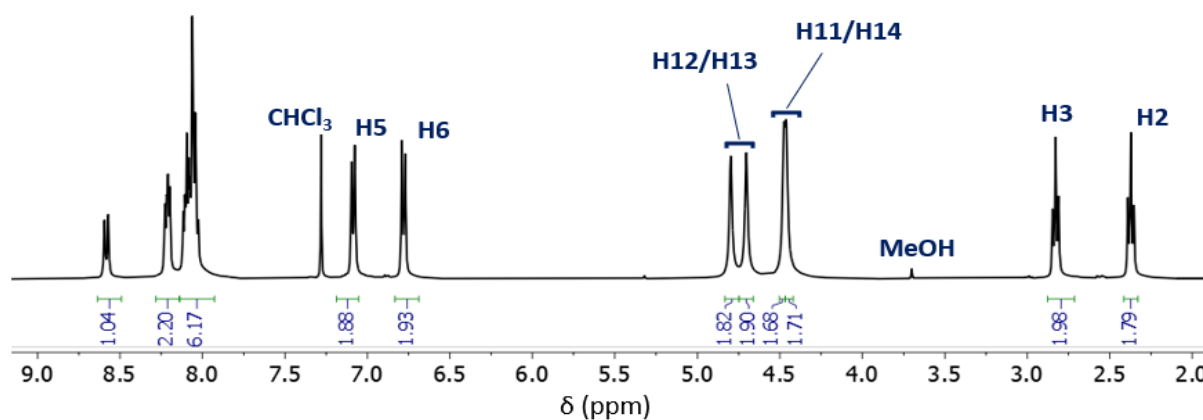


Figure S35: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **10a**. Labels provided for unambiguous peaks.

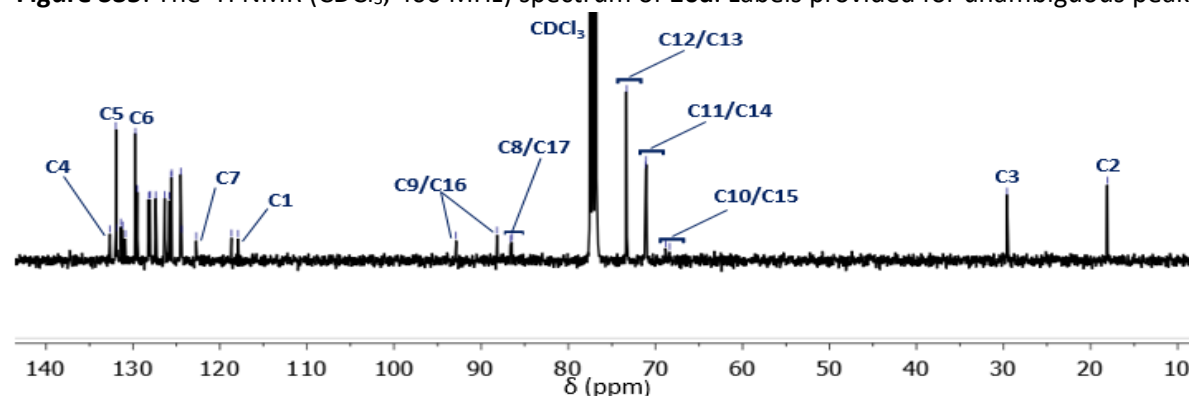
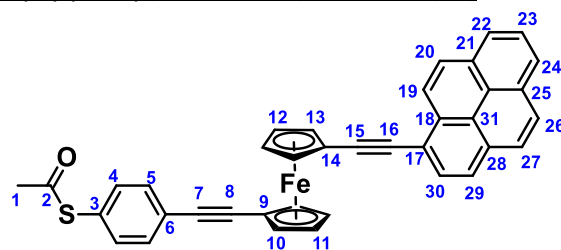


Figure S36: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **10a**. Labels provided for unambiguous peaks.

1-(Ethynylpyrene)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (10)

Following general procedure **B**, (**10a**) (0.06 g, 0.10 mmol), NaOMe (25% in MeOH, 0.02 mL) and Ac₂O (0.04 mL) gave a red solid which was purified by chromatography on a 'deactivated' silica column, eluting with n-hexane/DCM (1:0 → 1:1) to give the product as a bright-red solid (0.02 g, 0.04 mmol, 35%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 8.58 (d, ³J_{H-H} = 9.2 Hz, 1H, Ar-H), 8.20 (dd, ³J_{H-H} = 7.6, ⁴J_{H-H} = 1.6 Hz, 2H, Ar-H), 8.12-7.99 (m, 6H, Ar-H), 7.23 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H5), 6.94 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H4), 4.72 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10/H13), 4.63 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H10/H13), 4.42 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/H12), 4.41 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H11/H12), 2.37 (s, 3H, H1) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_C = 193.8 (C2), 133.8 (C4), 131.8 (C5), 131.8 (Ar-C-C), 131.4 (Ar-C-C), 131.2 (Ar-C-C), 130.9 (Ar-C-C), 129.4 (Ar-C-H), 128.2 (Ar-C-H), 127.9 (Ar-C-H), 127.4 (Ar-C-C), 126.9 (C6), 126.3 (Ar-C-H), 125.8 (Ar-C-H), 125.5 (Ar-C-C), 125.5 (Ar-C-H), 125.0 (C3), 124.6 (Ar-C-H), 124.4 (Ar-C-C), 118.6 (Ar-C-C), 93.0 (C8/C15), 89.1 (C8/C15), 86.5 (C7/C16), 86.2 (C7/C16), 73.3 (C10/C13), 73.3 (C10/C13), 71.0 (C11/C12), 71.0 (C11/C12), 67.8 (C9/C14), 67.3 (C9/C14), 30.3 (C1) ppm; **MS ES+**: calcd. for C₃₈H₂₅OSFe [M+H]⁺ 585.0976; found. 585.0991.

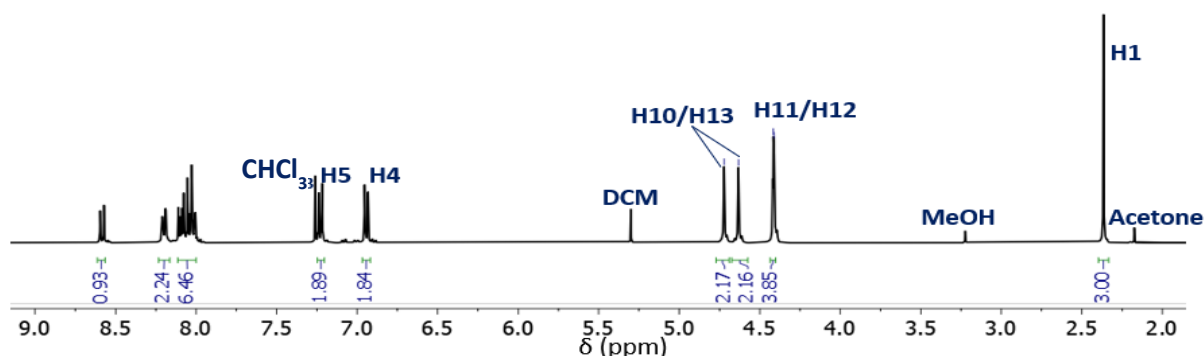


Figure S37: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **10**. Labels provided for unambiguous peaks.

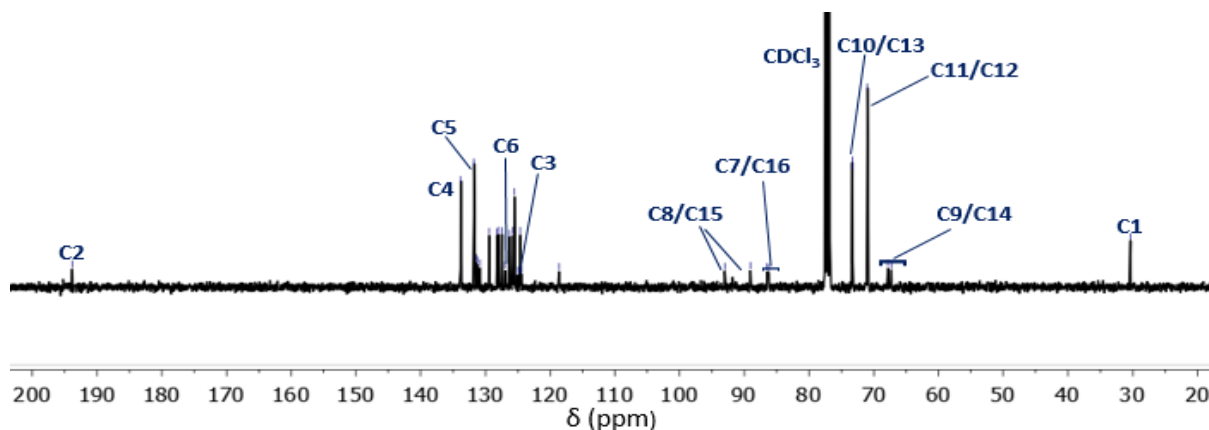
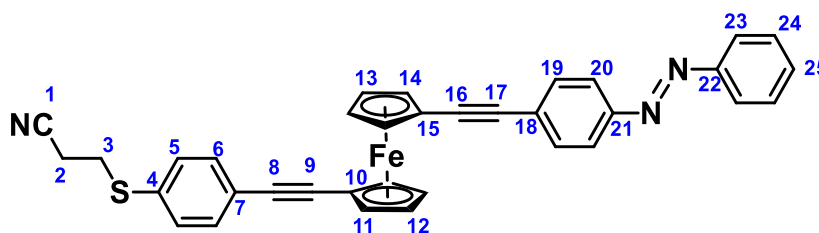


Figure S38: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **10**. Labels provided for unambiguous peaks.

1-(4-(Ethynylphenyl)-2-phenyldiazene)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (11a)

Following general procedure **A**, (**2a**) (0.20 g, 0.40 mmol), 4-(ethynylphenyl)-2-phenyldiazene (0.33 g, 1.61 mmol), CuI (0.01 g, 0.04 mmol) and Pd(P^{-t}Bu₃)₂ (0.02 g, 0.04 mmol) gave a black solid, which was purified by chromatography on a silica column, eluting with n-hexane/DCM (1:0 → 4:6) to give the produce as a deep-red solid (0.20 g, 0.35 mmol, 87%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 7.94 (d, ³J_{H-H} = 7.2 Hz, 2H, H₂₄), 7.79 (d, ³J_{H-H} = 8.4 Hz, 2H, H₂₀), 7.58-7.48 (m, 5H, H₁₉, H₂₃, H₂₅), 7.32 (d, ³J_{H-H} = 8.4 Hz, 2H, H₆), 7.19 (d, ³J_{H-H} = 8.4 Hz, 2H, H₅), 4.59 (*pseudo-t*, 2H, ³J_{H-H} = 2.0 Hz, H₁₁/H₁₄), 4.58 (*pseudo-t*, 2H, ³J_{H-H} = 2.0 Hz, H₁₁/H₁₄), 4.36 (*pseudo-t*, 2H, ³J_{H-H} = 2.0 Hz, H₁₂/H₁₃), 4.35 (*pseudo-t*, 2H, ³J_{H-H} = 2.0 Hz, H₁₂/H₁₃), 3.04 (t, ³J_{H-H} = 7.6 Hz, 2H, H₃), 2.51 (t, ³J_{H-H} = 7.6 Hz, 2H, H₂) ppm; ¹³C NMR (CDCl₃, 298 K, 100 MHz): δ_C = 152.8 (C₂₂), 151.3 (C₂₁), 133.0 (C₄), 132.2 (C₆), 132.2 (C₇), 131.3 (C₂₅), 130.4 (C₅), 129.3 (C₂₃), 126.8 (C₁₈), 123.1 (C₂₄), 123.0 (C₂₀), 122.9 (C₁₉), 118.0 (C₁), 90.2 (C₉/C₁₆), 88.4 (C₉/C₁₆), 87.0 (C₈/C₁₇), 86.4 (C₈/C₁₇), 73.1 (C₁₁/C₁₄), 73.1 (C₁₁/C₁₄), 71.1 (C₁₂/C₁₃), 71.0 (C₁₂/C₁₃), 67.4 (C₁₀/C₁₅), 67.2 (C₁₀/C₁₅), 29.8 (C₃), 18.2 (C₂) ppm; MS ES⁺: calcd. for C₃₅H₂₆N₃SFe [M+H]⁺ 576.1197; found. 576.1204.

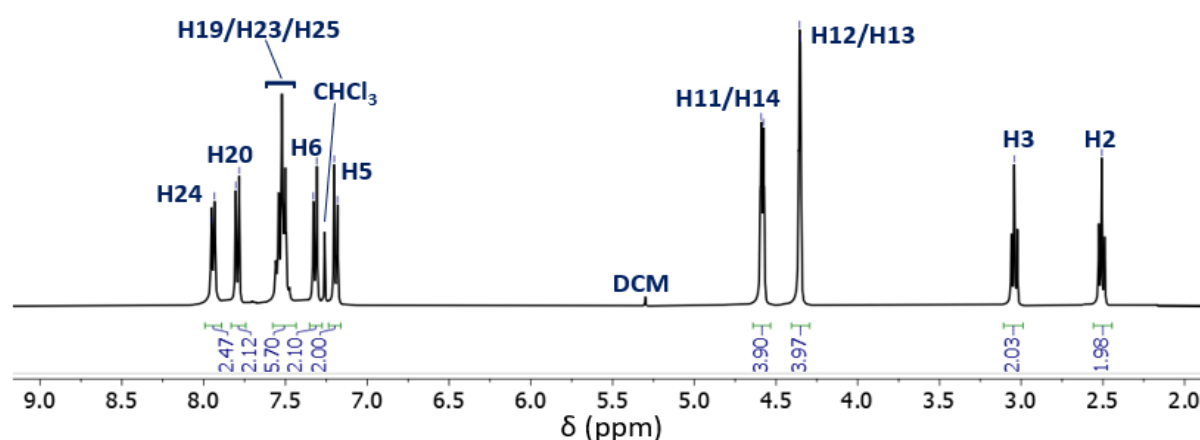


Figure S39: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **11a**.

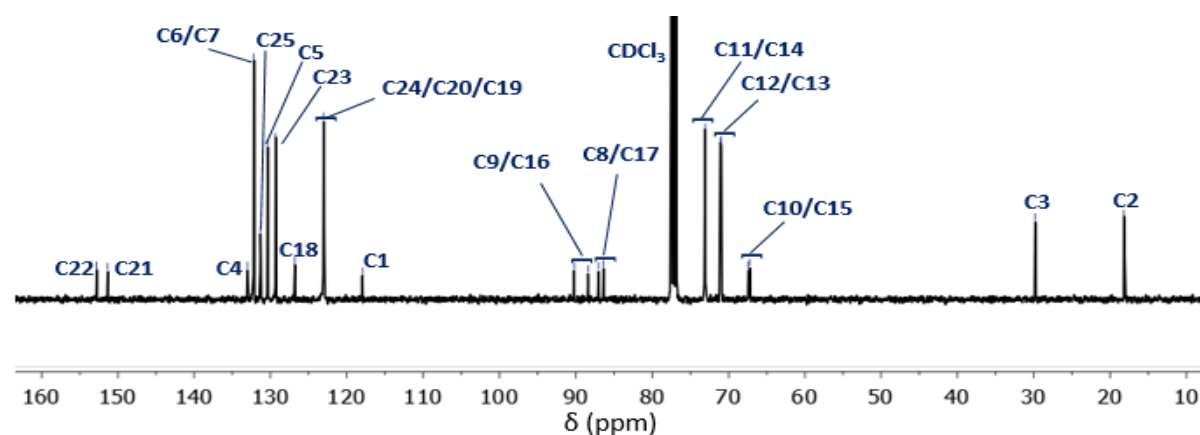
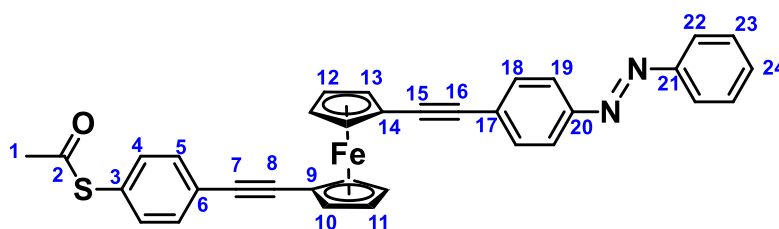


Figure S40: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **11a**.

1-(4-(Ethynephenyl)-2-phenyldiazene)-1'-(4-(ethynephenyl)thioacetate)ferrocene (11)

Following general procedure B, (**11a**) (0.04 g, 0.07 mmol), NaOMe (25% in MeOH, 0.10 mL) and Ac₂O (0.20 mL) gave a red-solid, which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, and then precipitated from an equal parts mixture of DCM/hexane to give the product as a deep-red solid (0.03 g, 0.05 mmol, 74%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 7.94 (dt, ³J_{H-H} = 6.8, ⁴J_{H-H} = 1.6 Hz, 2H, H₂₃), 7.80 (d, ³J_{H-H} = 8.8 Hz, 2H, H₁₉), 7.57-7.46 (m, 5H, H₁₈, H₂₂, H₂₄), 7.41 (d, ³J_{H-H} = 8.8 Hz, 2H, H₅), 7.26 (d, ³J_{H-H} = 8.8 Hz, 2H, H₄), 4.59 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₂), 4.58 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₂), 4.36 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 4H, H₁₀, H₁₃), 2.36 (s, 3H, H₁) ppm; **¹³C NMR** (CDCl₃, 298 K, 100 MHz): δ_C = 193.7 (C₂), 152.9 (C₂₀), 151.4 (C₂₁), 134.2 (C₄), 132.2 (C₅), 132.0 (C₂₃), 131.2 (C₂₄), 129.2 (C₁₈), 127.3 (C₆), 126.7 (C₁₇), 125.1 (C₃), 123.1 (C₂₃), 123.0 (C₁₉), 90.2 (C₈/C₁₅), 89.1 (C₈/C₁₅), 87.0 (C₇/C₁₆), 86.4 (C₇/C₁₆), 73.2 (C₁₀/C₁₃), 73.2 (C₁₀/C₁₃), 71.2 (C₁₁/C₁₂), 71.1 (C₁₁/C₁₂), 67.1 (C₉/C₁₄), 67.1 (C₉/C₁₄), 29.8 (C₁) ppm; **MS ES⁺**: calcd. for C₃₄H₂₅N₂OSFe [M+H]⁺ 565.1037; found. 565.1044.

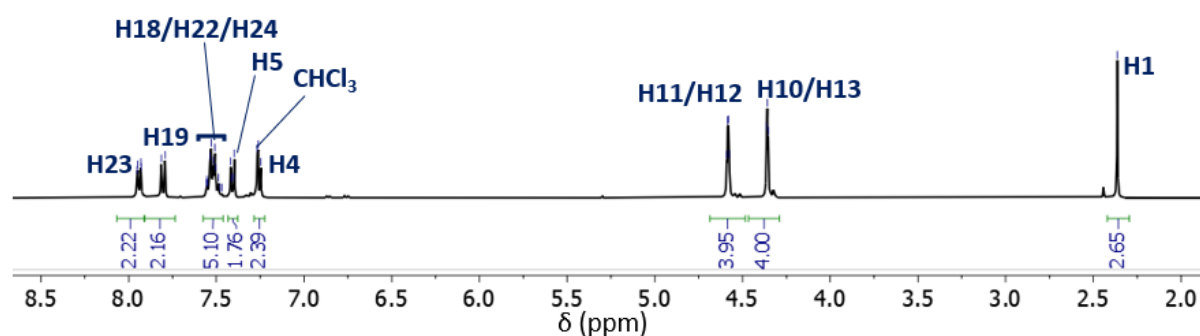


Figure S41: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **11**.

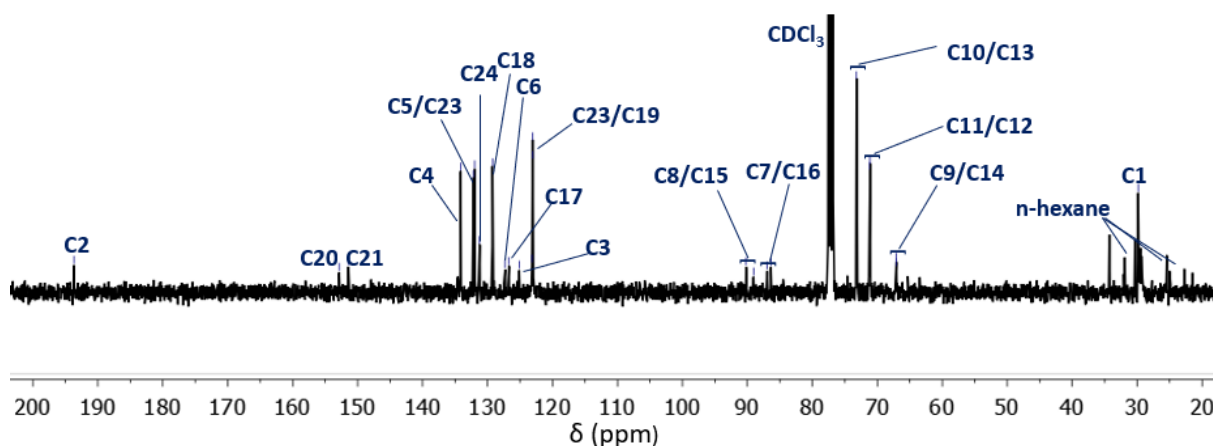
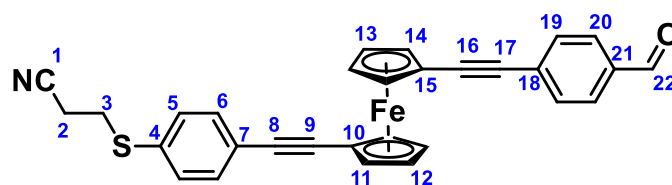


Figure S42: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **11**.

1-(4-Ethynylbenzaldehyde)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (**12a**)

Following general procedure **A**, (**2a**) (0.20 g, 0.40 mmol), 4-ethynylbenzaldehyde (0.13 g, 1.00 mmol), CuI (0.01 g, 0.04 mmol) and Pd(P-^tBu₃)₂ (0.02 g, 0.04 mmol) gave a dark-brown solid, which was purified by chromatography on a silica column, eluting with *n*-hexane/DCM (1:0 → 4:6) to give the product as a red powder (0.17 g, 0.34 mmol, 85%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 9.98 (s, 1H, H₂₂), 7.72 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H₂₀), 7.49 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 1.6 Hz, 2H, H₁₉), 7.30 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H₆), 7.19 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H₅), 4.58 (pseudo-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₂/H₁₃), 4.56 (pseudo-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₂/H₁₃), 4.37 (pseudo-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₄), 4.34 (pseudo-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₄), 3.12 (t, ³J_{H-H} = 7.2 Hz, 2H, H₃), 2.61 (t, ³J_{H-H} = 7.2 Hz, 2H, H₂) ppm; ¹³C {¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 191.6 (C₂₂), 134.9 (C₁₈, C₂₁), 133.1 (C₄), 132.1 (C₆), 131.8 (C₁₉), 130.4 (C₅), 129.6 (C₂₀), 123.0 (C₇), 118.0 (C₁), 92.2 (C₉/C₁₆), 88.3 (C₉/C₁₆), 86.5 (C₈/C₁₇), 86.4 (C₈/C₁₇), 73.3 (C₁₂/C₁₃), 73.1 (C₁₂/C₁₃), 71.3 (C₁₁/C₁₄), 71.0 (C₁₁/C₁₄), 67.5 (C₁₀/C₁₅), 66.6 (C₁₀/C₁₅), 29.9 (C₃), 18.3 (C₂) ppm; **MS ES+**: calcd. for C₃₀H₂₂NOSFe [M+H]⁺ 500.0772; found. 500.0784.

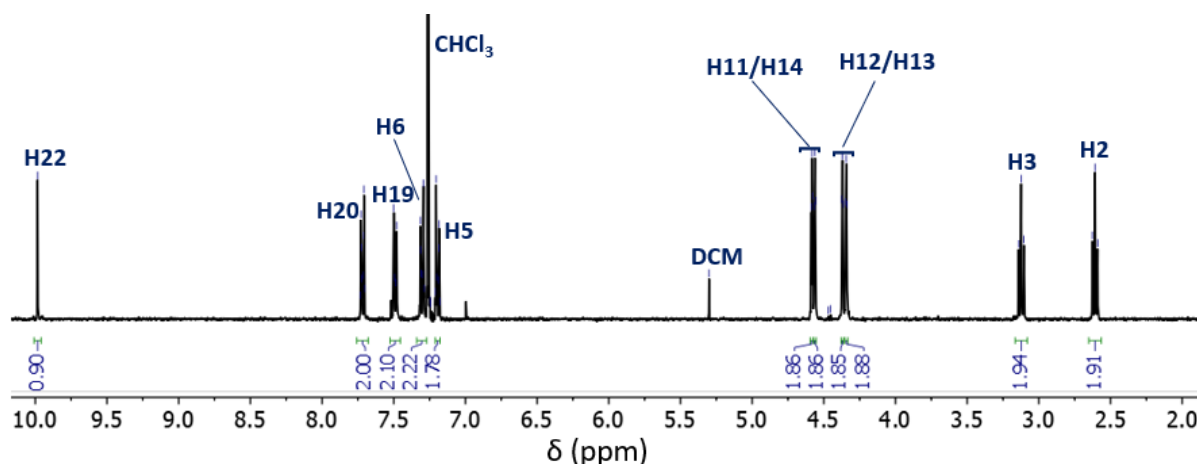


Figure S43: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **12a**.

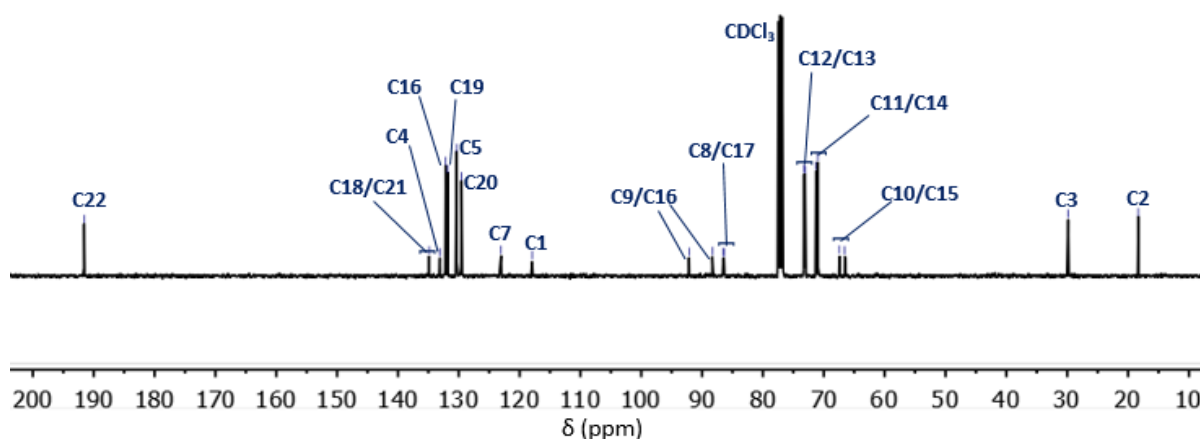
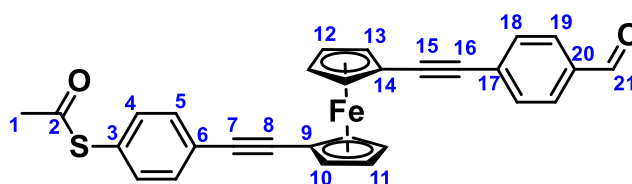


Figure S44: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **12a**.

1-(4-Ethynylbenzaldehyde)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (12)

Following general procedure **B**, (**12a**) (0.10 g, 0.20 mmol), NaOMe (25% in MeOH, 0.03 mL) and Ac₂O (0.05 mL) gave a red-solid, which was purified by chromatography on a 'deactivated' silica column, eluting with n-hexane/DCM (1:0 → 7:3), to give the product as a bright-red solid (0.02 g, 0.04 mmol, 21%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 9.95 (s, 1H, H₂₁), 7.71 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 1.6 Hz, 2H, H₁₈), 7.47 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 1.6 Hz, 2H, H₁₉), 7.35 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H₅), 7.22 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 2H, H₄), 4.58 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₂), 4.57 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₂), 4.37 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₀/H₁₃), 4.34 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 2H, H₁₀/H₁₃), 2.43 (s, 3H, H₁) ppm; ¹³C {¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 193.6 (C₂), 191.8 (C₂₁), 134.9 (C₂₀), 134.1 (C₄), 131.9 (C₅), 131.8 (C₁₉), 130.3 (C₁₇), 129.6 (C₁₈), 127.3 (C₆), 125.1 (C₃), 92.0 (C₈/C₁₅), 91.7 (C₈/C₁₅), 88.8 (C₇/C₁₆), 86.6 (C₇/C₁₆), 73.3 (C₁₁/C₁₂), 73.2 (C₁₁/C₁₂), 71.2 (C₁₀/C₁₃), 70.9 (C₁₀/C₁₃), 67.5 (C₉/C₁₄), 66.7 (C₉/C₁₄), 30.4 (C₁) ppm; **MS ES+**: calcd. for C₂₉H₂₁O₂SFe [M+H]⁺ 489.0612; found. 489.0620.

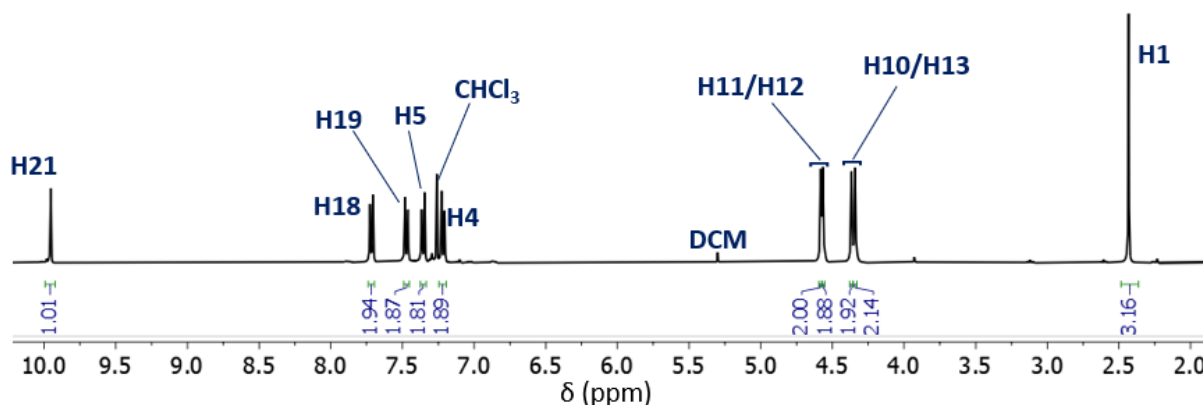


Figure S45: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **12**.

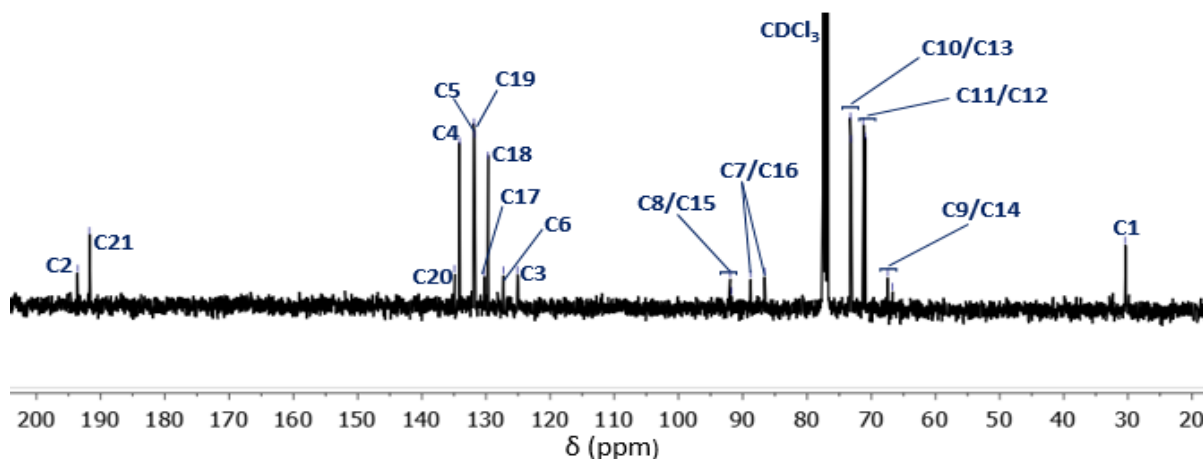
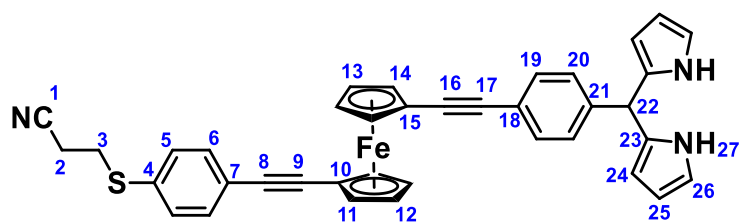


Figure S46: The ¹³C {¹H} NMR (CDCl₃, 100 MHz) spectrum of **12**.

1-(4-(Ethynylphenyl)methylene-bis(1H-pyrrole))-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (13a)



(**12a**) (0.20 g, 0.40 mmol) was dissolved in pyrrole (50 mL). TFA (6.00 μ L, 0.08 mmol) was added and the solution was stirred at room temperature for 4 hours. Triethylamine (11.00 μ L, 0.08 mmol) was added and the solution was stirred for a further 30 minutes. The solvent was removed *in vacuo* and the crude material was purified by chromatography on a silica column, eluting with *n*-hexane/DCM (1:0 \rightarrow 3:7) to give the product as a red solid (0.24 g, 0.39 mmol, 97%).

$^1\text{H NMR}$ (CDCl_3 , 298 K, 400 MHz): δ_{H} = 8.00 (br s, 2H, H27), 7.41-7.36 (m, 4H, H5/H20), 7.26 (d, $^3J_{\text{H-H}}$ = 8.4 Hz, 2H, H6), 7.13 (d, $^3J_{\text{H-H}}$ = 8.4 Hz, 2H, H19), 6.75 (br s, 2H, H26), 6.20 (q, $^3J_{\text{H-H}}$ = 2.8 Hz, 2H, H25), 5.93 (br s, 2H, H24), 5.48 (s, 1H, H22), 4.56 (br s, 4H, H12/H13), 4.35 (*pseudo-t*, $^3J_{\text{H-H}}$ = 2.0 Hz, 2H, H11/H14), 4.34 (*pseudo-t*, $^3J_{\text{H-H}}$ = 2.0 Hz, 2H, H11/H14), 3.13 (t, $^3J_{\text{H-H}}$ = 7.2 Hz, 2H, H3), 2.59 (t, $^3J_{\text{H-H}}$ = 7.2 Hz, 2H, H2) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 298 K, 100 MHz): δ_{C} = 141.9 (C21), 132.8 (C4), 132.3 (C5/C19), 132.2 (C23), 131.8 (C5/C19), 130.7 (C6), 128.4 (C20), 123.3 (C7), 122.5 (C18), 118.0 (C1), 117.5 (C26), 108.6 (C25), 107.5 (C24), 88.9 (C9/C16), 87.3 (C9/C16), 86.7 (C8/C17), 86.0 (C8/C17), 73.2 (C12/C13), 73.2 (C12/C13), 71.1 (C11/C14), 70.9 (C11/C14), 67.4 (C10/C15), 66.9 (C10/C15), 44.0 (C22), 30.0 (C3), 18.3 (C2) ppm; **MS ES+**: calcd. for $\text{C}_{38}\text{H}_{30}\text{N}_3\text{SFe}$ $[\text{M}+\text{H}]^+$ 616.1510; found. 616.1500.

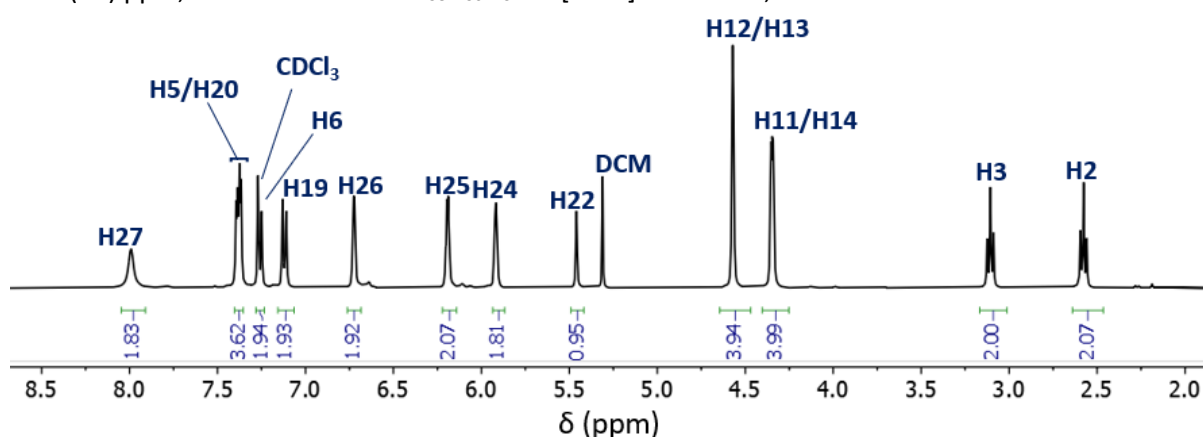


Figure S47: The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of **13a**.

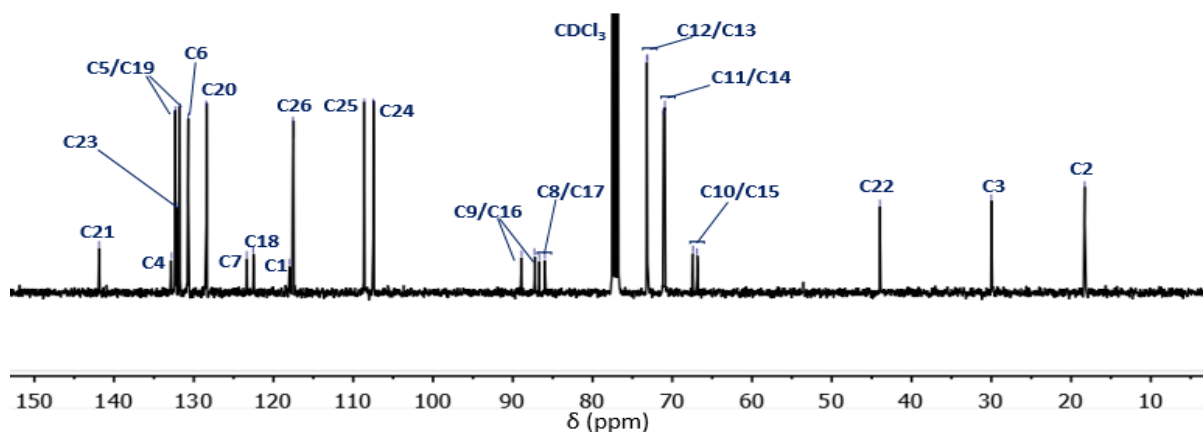
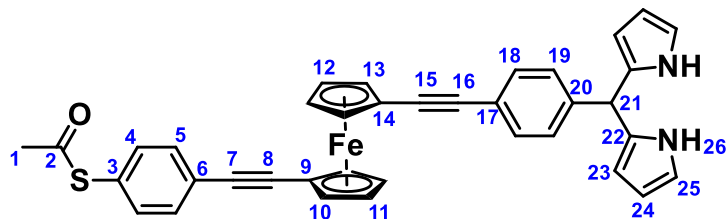


Figure S48: The $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) spectrum of **13a**.

1-(4-(Ethynylphenyl)methylene-bis(1H-pyrrole))-1'-(4-(ethynylphenyl)thioacetate)ferrocene (**13**)

Following general procedure **B**, (**13a**) (0.07 g, 0.11 mmol), NaOMe (25% in MeOH, 0.01 mL) and Ac₂O (0.02 mL) gave a red-oil, which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, to give the product as a deep-red oil (0.05 g, 0.08 mmol, 73%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_H = 8.03 (br s, 2H, H₂₆), 7.44 (d, ³J_{H-H} = 8.4 Hz, 2H, H₅), 7.35 (d, ³J_{H-H} = 8.4 Hz, 2H, H₁₈), 7.28 (d, ³J_{H-H} = 8.4 Hz, 2H, H₄), 7.11 (d, ³J_{H-H} = 8.4 Hz, 2H, H₁₉), 6.71 (*pseudo*-q, ³J_{H-H} = 2.0 Hz, 2H, H₂₅), 6.16 (q, ³J_{H-H} = 3.2 Hz, 2H, H₂₄), 5.91 (br s, 2H, H₂₃), 5.45 (s, 1H, H₂₁), 4.55 (*pseudo*-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₂), 4.55 (*pseudo*-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₁/H₁₂), 4.33 (*pseudo*-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₀/H₁₃), 4.31 (*pseudo*-t, ³J_{H-H} = 2.0 Hz, 2H, H₁₀/H₁₃), 2.42 (s, 3H, H₁) ppm; ¹³C {¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_C = 194.1 (C₂), 141.8 (C₂₀), 134.2 (C₄), 132.2 (C₂₂), 132.1 (C₅), 131.8 (C₁₈), 128.4 (C₁₉), 127.2 (C₆), 125.3 (C₃), 122.5 (C₁₇), 117.5 (C₂₅), 108.6 (C₂₄), 107.4 (C₂₃), 89.4 (C₈/C₁₅), 87.1 (C₈/C₁₅), 86.7 (C₇/C₁₆), 86.2 (C₇/C₁₆), 73.2 (C₁₁/C₁₂), 73.1 (C₁₁/C₁₂), 71.1 (C₁₀/C₁₃), 70.9 (C₁₀/C₁₃), 67.5 (C₉/C₁₄), 66.9 (C₉/C₁₄), 44.0 (C₂₁), 30.4 (C₁) ppm; MS ES⁺: calcd. for C₃₇H₂₉ON₂SFe [M+H]⁺ 605.1350; found. 603.1360.

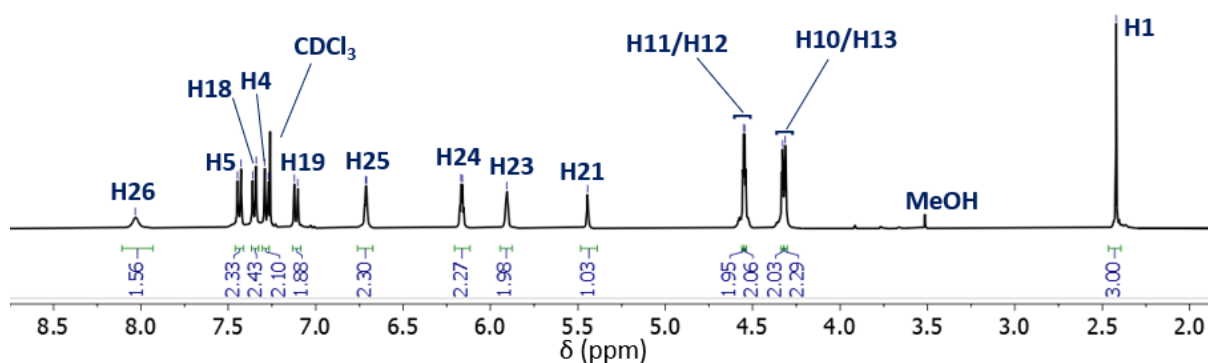


Figure S49: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **13**.

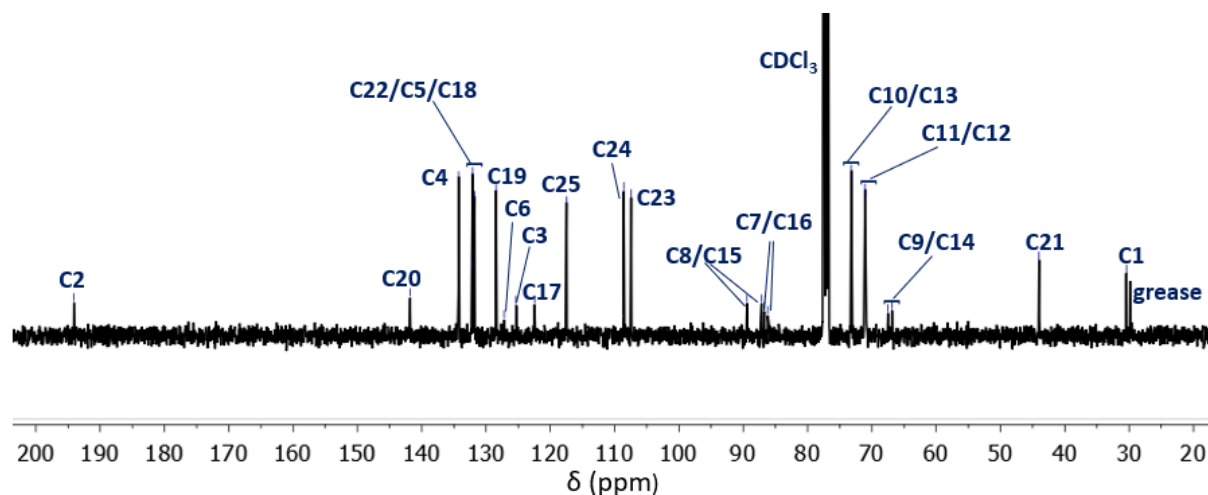
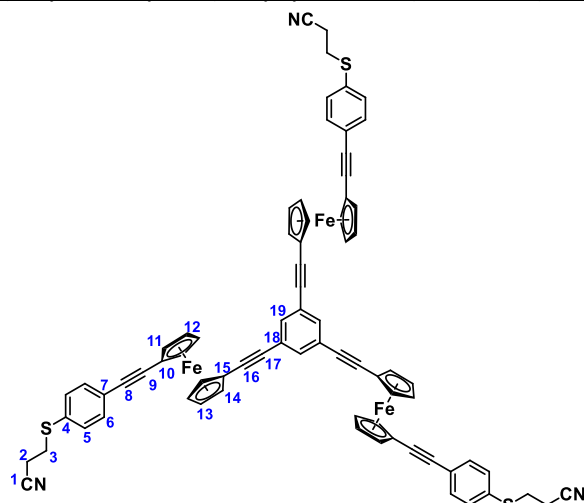


Figure S50: The ¹³C {¹H} NMR (CDCl₃, 100 MHz) spectrum of **13**.

(μ -1,3,5)-(1-Ethynyl-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene)benzene (**14a**)

Following general procedure **A**, freshly prepared 1,3,5-triethynylbenzene (approx. 0.03 g, 0.17 mmol), (**2a**) (0.37 g, 0.75 mmol), CuI (0.01 g, 0.02 mmol), [Pd(CH₃CN)₂Cl₂] (0.01 g, 0.02 mmol) and [PH(^tBu)₃]BF₄ (0.01 g, 0.03 mmol) gave a dark brown solid, which was purified by chromatography on a silica column, eluting with hexane/DCM (1:1), to give the product as a red solid (0.14 g, 0.11 mmol, 67%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 7.39 – 7.35 (m, 9H, H6 and H19), 7.24 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 6H, H6), 4.56 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 12H), 4.36 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 6H), 4.35 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 6H), 3.08 (t, ³J_{H-H} = 6.0 Hz, 6H, H2), 2.56 (t, ³J_{H-H} = 6.0 Hz, 6H, H3); ¹³C{¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_{C} = 133.1 (C4/C19), 133.0 (C4/C19), 132.2 (C5), 130.6 (C6), 124.4 (C18), 123.1 (C7), 118.0 (C1), 88.5 (C9/C16), 88.4 (C9/C16), 86.3 (C8/C17), 85.6 (C8/C17), 73.2 (C12/C13), 73.2 (C12/C13), 71.1 (C11/C14), 71.1 (C11/C14), 67.2 (C10/C15), 66.9 (C10/C15), 30.0 (C3), 18.4 (C2) ppm; MS ES⁺: calcd. for C₇₅H₅₂N₃S₃Fe₃ [M+H]⁺ 1258.1371; found. 1258.1277.

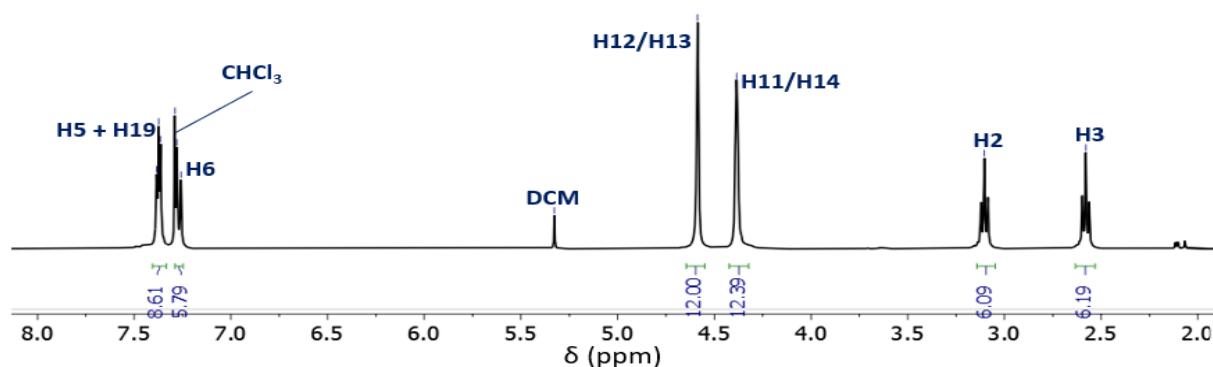


Figure S51: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **14a**.

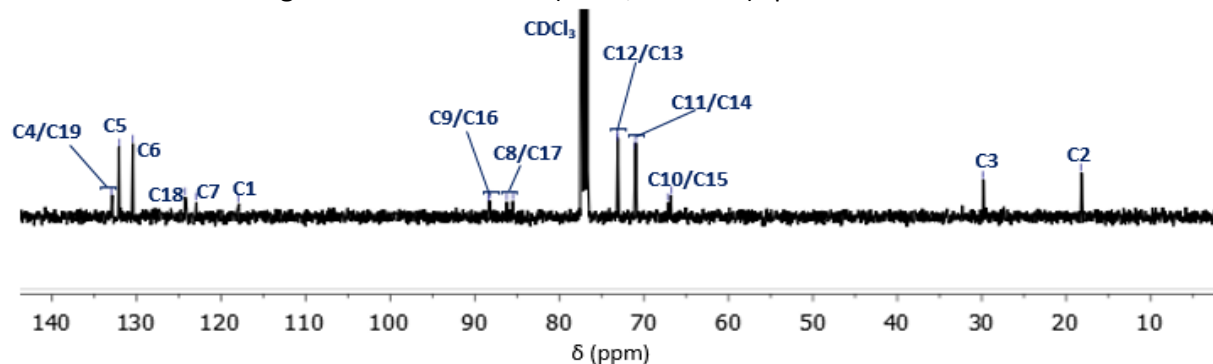
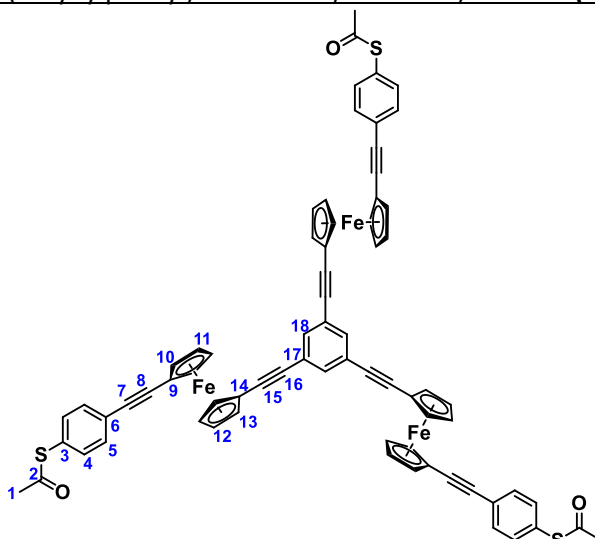


Figure S52: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **14a**.

(μ -1,3,5)-(1-Ethynyl-1'-(4-(ethynylphenyl)thioacetate)ferrocene)benzene (14)

Following general procedure B, (**14a**) (0.07 g, 0.06 mmol), NaOMe (25% in MeOH, 0.25 mL) and Ac₂O (0.50 mL) gave a red solid, which was purified by chromatography on a 'deactivated' silica column, eluting with DCM, give the product as an orange solid (0.06 g, 0.05 mmol, 87%).

¹H NMR (CDCl₃, 298 K, 400 MHz): δ_{H} = 7.46 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 6H, H5), 7.38 (s, 3H, H18), 7.31 (dt, ³J_{H-H} = 8.4, ⁴J_{H-H} = 2.0 Hz, 6H, H4), 4.56 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 6H, H11/H12), 4.55 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 6H, H11/H12), 4.35 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 6H, H10/H13), 4.35 (*pseudo-t*, ³J_{H-H} = 2.0 Hz, 6H, H10/H13), 2.40 (s, 9H, H1); ¹³C{¹H} NMR (CDCl₃, 298 K, 100 MHz): δ_{C} = 193.8 (C2), 134.3 (C4), 133.1 (C18), 132.0 (C5), 127.4 (C6), 125.2 (C3), 124.4 (C17), 89.3 (C8/C15), 88.4 (C8/C15), 86.3 (C7), 85.6 (C16), 73.3 (C11/C12), 71.4 (C10/C13), 71.3 (C10/C13), 66.8 (C9/C14), 30.4 (C1) ppm; MS ES⁺: calcd. for C₇₂H₄₉Fe₃O₃S₃ [M+H]⁺ 1225.0887; found. 1225.0874.

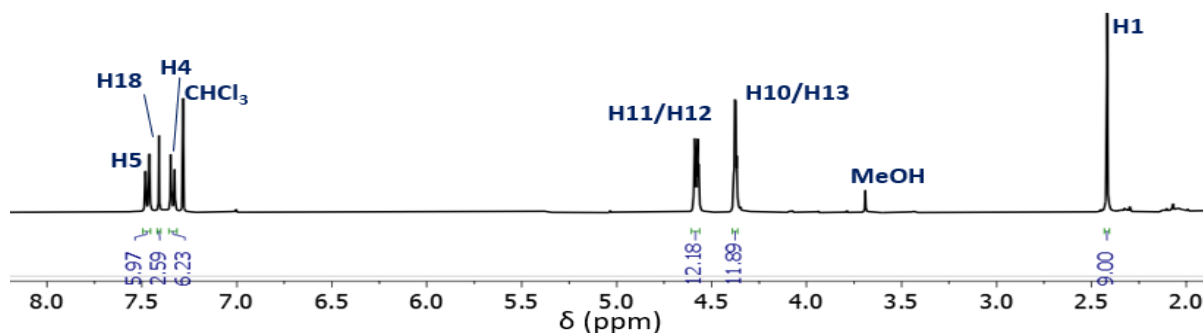


Figure S53: The ¹H NMR (CDCl₃, 400 MHz) spectrum of **14**.

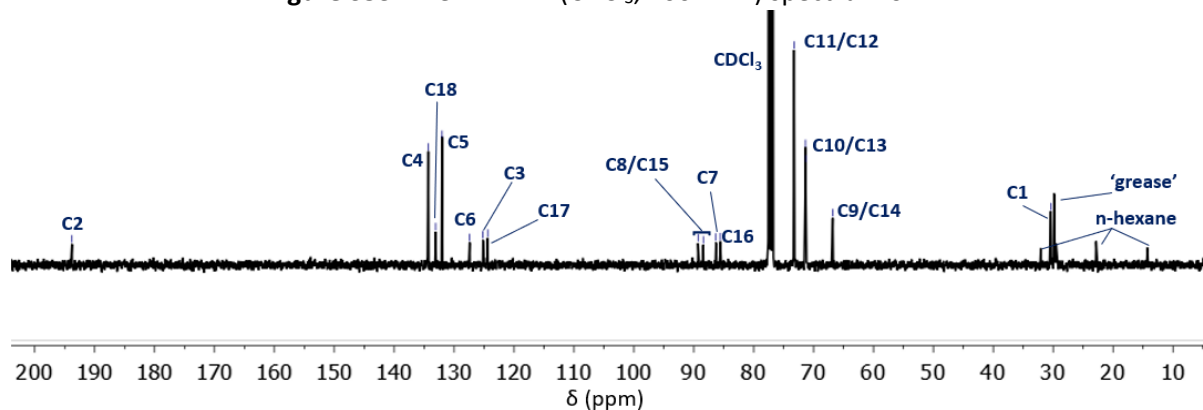


Figure S54: The ¹³C{¹H} NMR (CDCl₃, 100 MHz) spectrum of **14**.

2. Cyclic Voltammetry

2.1 Experimental

Cyclic voltammograms of compounds in solution were recorded under an atmosphere of nitrogen in CH₂Cl₂ / 0.1 M [ⁿBu₄][PF₆] on a Gamry reference 600TM (Gamry Instruments, Warminster, PA, USA) potentiostat with a glassy carbon disc as the working electrode (diameter = 2.5 mm), and Pt-wire as reference and counter electrodes. Analyte solutions were between 0.1-1.0 mM. All potentials (mV) are reported relative to [Cp₂Fe]⁺/[Cp₂Fe] and were measured against either [Cp₂Fe]⁺/[Cp₂Fe] or [Cp*₂Fe]⁺/[Cp*₂Fe] as internal references. All scans have been corrected for iR_s with values obtained from AC impedance measurements.

Table S1: Electrochemical data obtained from cyclic voltammetry of all compounds.

Compound	E _p /mV	E _c /mV	E _{1/2} /mV	ΔE/mV	i _{pa} /i _{pc}
2a	245	178	211	66	1.03
2	252	186	219	66	0.98
5a	194	125	160	69	0.97
5	218	144	181	74	1.04
6a	-11	-79	-45	68	0.99
	338	269	303	69	
6	-2	-60	-31	58	1.01
	350	292	321	58	
7a	234	169	206	75	1.01
7	258	186	221	72	0.91
8a*	223	148	185	75	0.98
8	229	166	197	63	1.00
9a	229	152	190	77	0.97
9	233	163	198	70	0.98
10a	167	101	133	66	0.97
10	176	117	146	59	0.97
11a	199	132	165	67	0.99
11	208	143	175	65	0.96
12a	227	148	187	78	0.98
12	233	160	196	73	0.97
13a	180	117	149	63	0.95
13	196	133	165	64	1.05
14a	207	135	171	72	1.02
14	223	158	190	65	0.92

*This molecule showed significant instability over multiple scans, values reported are taken from a single scan at 100 mV/s.

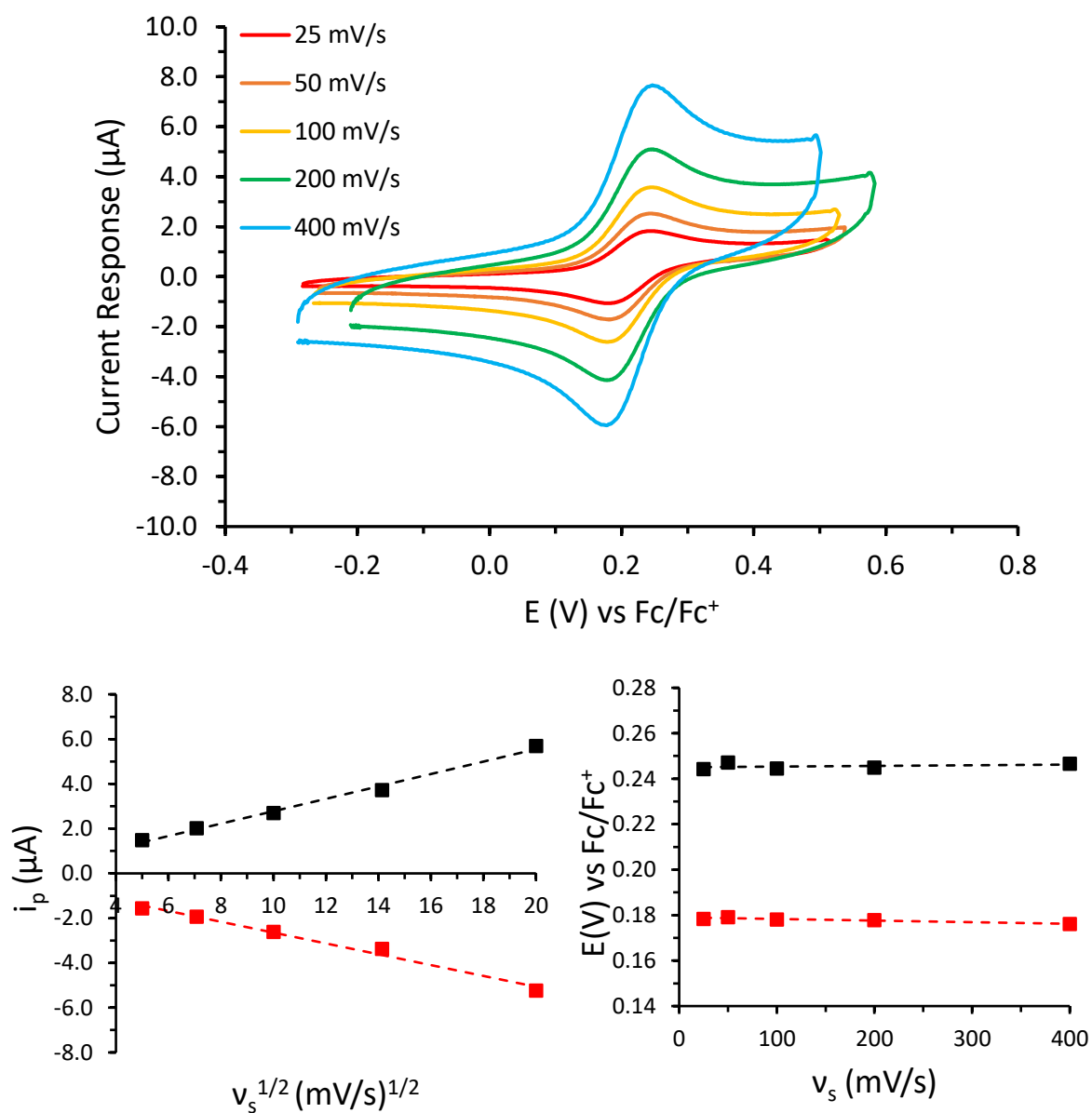
1-Iodo-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (2a)

Fig S55: Scan rate dependent cyclic voltammetry of **2a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

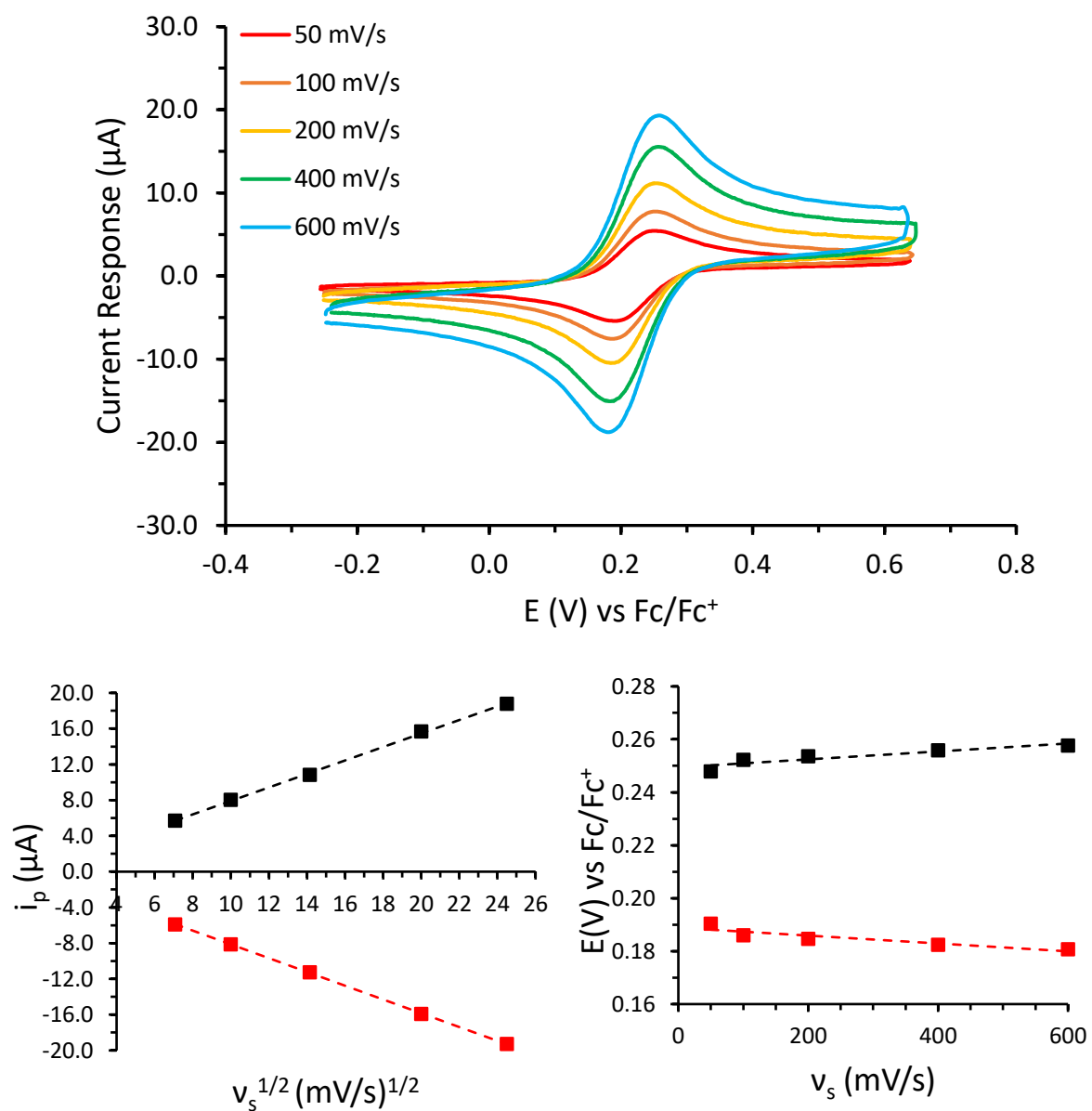
1-Iodo-1'-(4-(ethynylphenyl)thioacetate)ferrocene (2)

Fig S56: Scan rate dependent cyclic voltammetry of **2** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

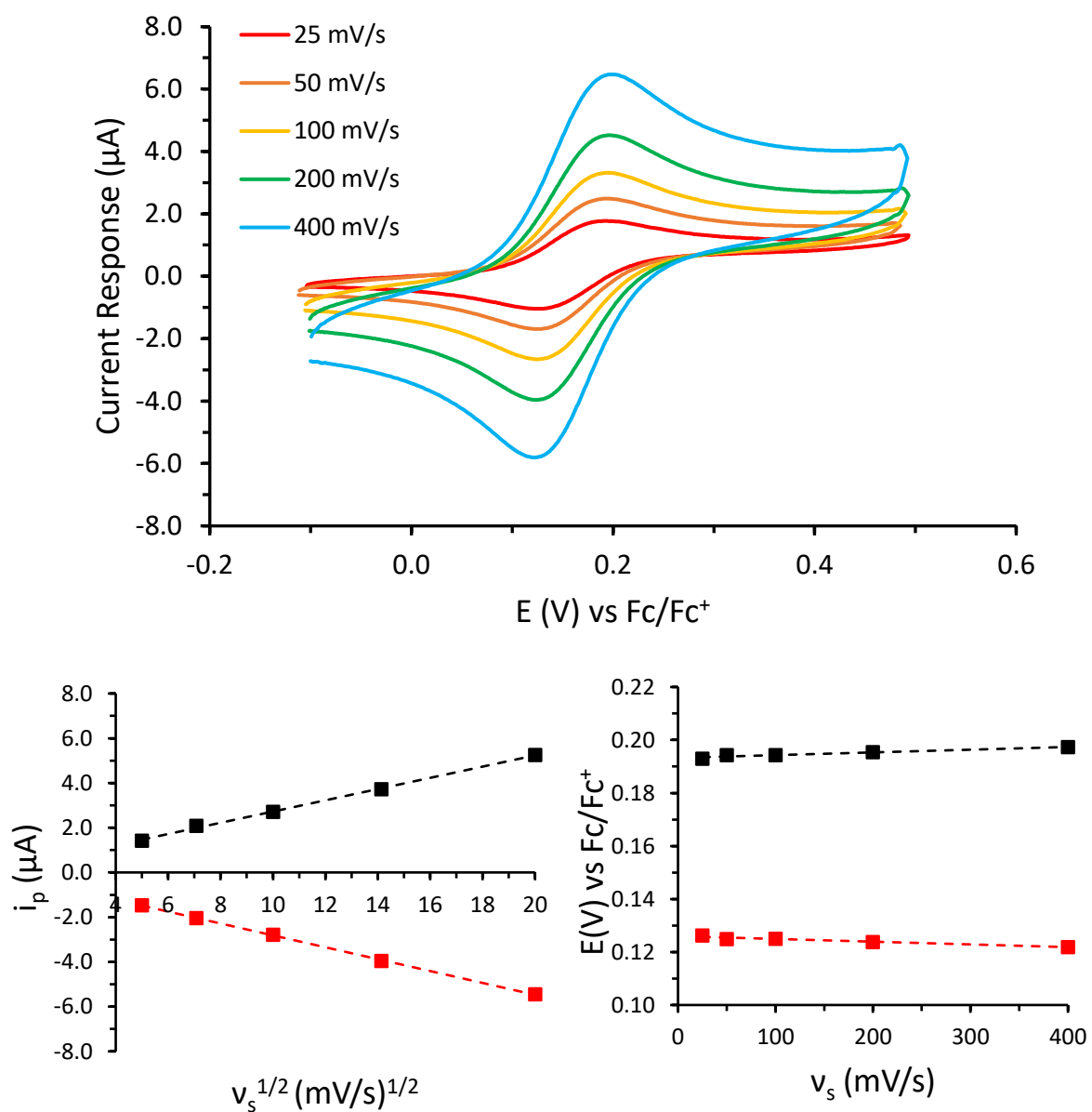
1,1'-Di(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (5a)

Fig S57: Scan rate dependent cyclic voltammetry of **5a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

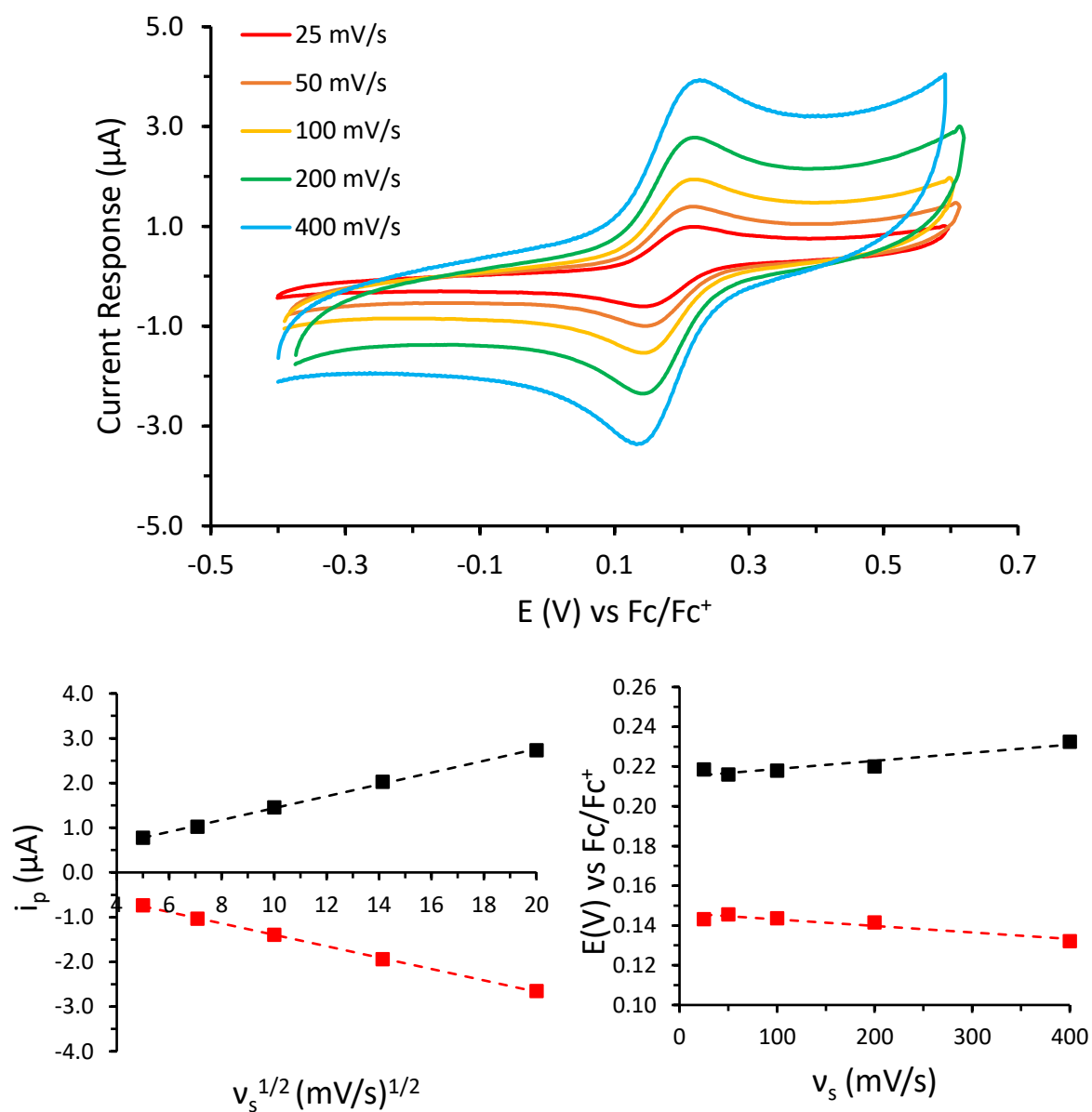
1,1'-Di(4-(ethynylphenyl)thioacetate)ferrocene (5)

Fig S58: Scan rate dependent cyclic voltammetry of **5** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

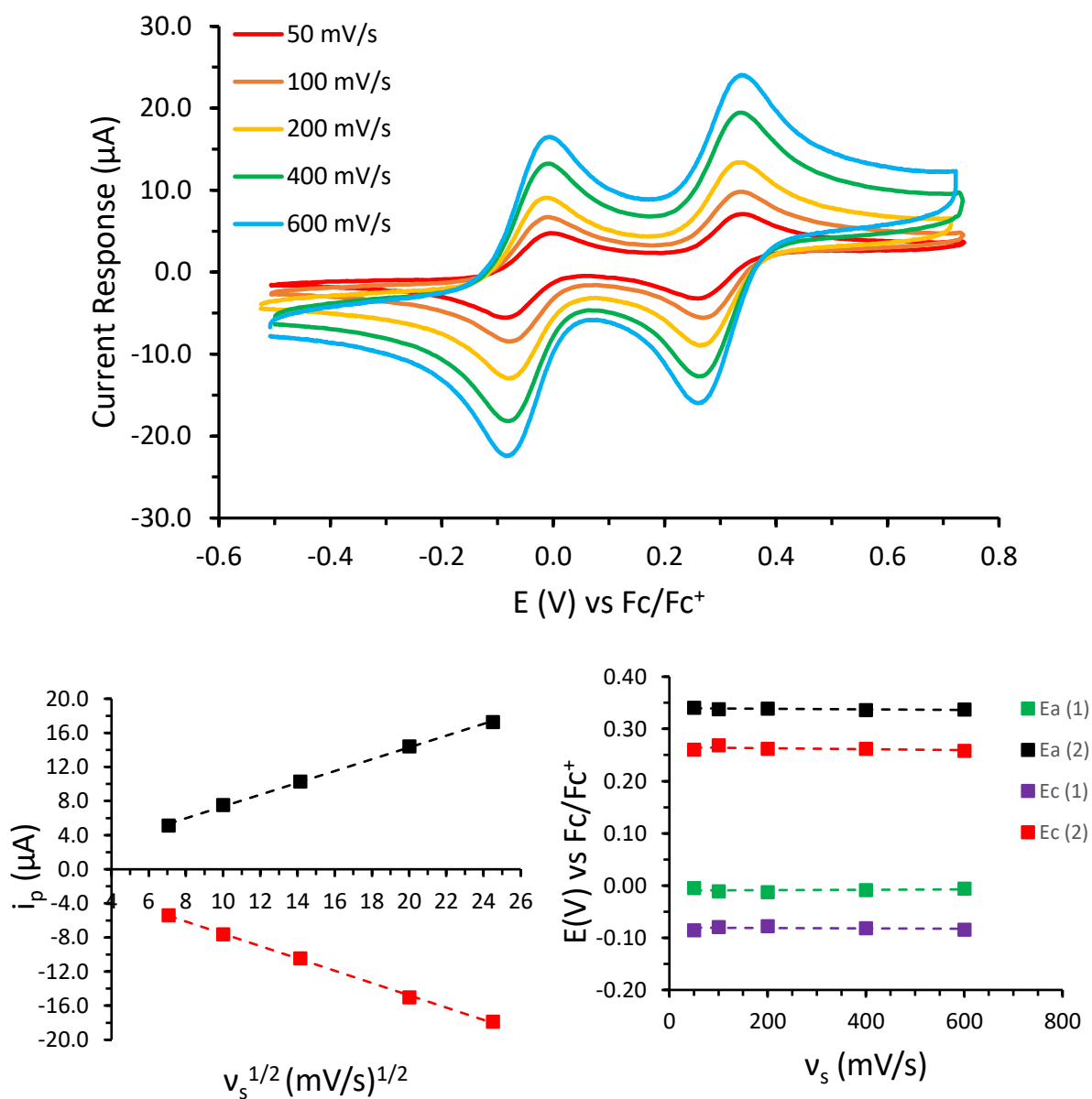
1,1'''-Di(4-(2-cyanoethylthio)ethynylbenzene)biferrocene (6a)

Fig S59: Scan rate dependent cyclic voltammetry of **6a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

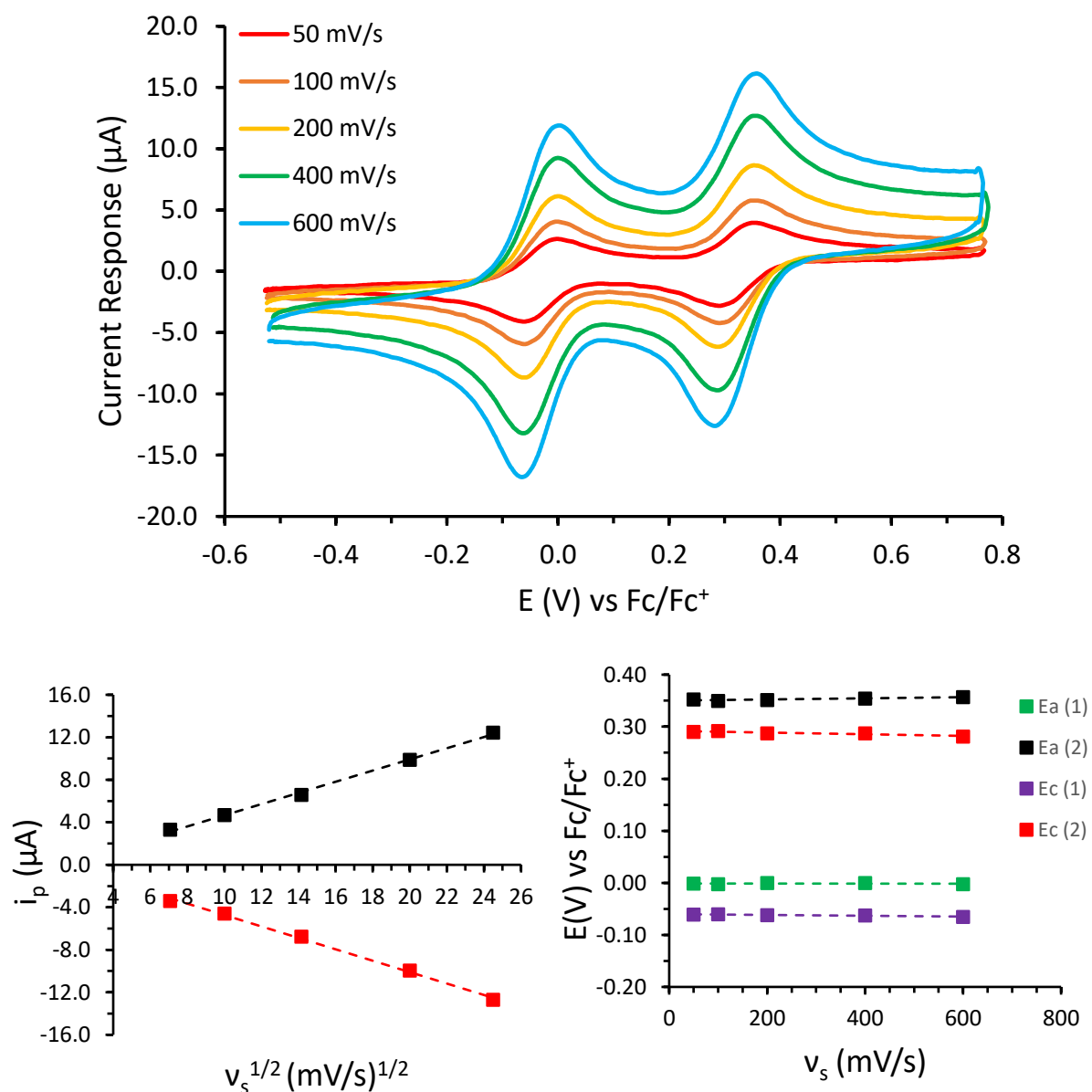
1,1'''-Di(4-(ethynylphenyl)thioacetate)biferrocene (6)

Fig S60: Scan rate dependent cyclic voltammetry of **6** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

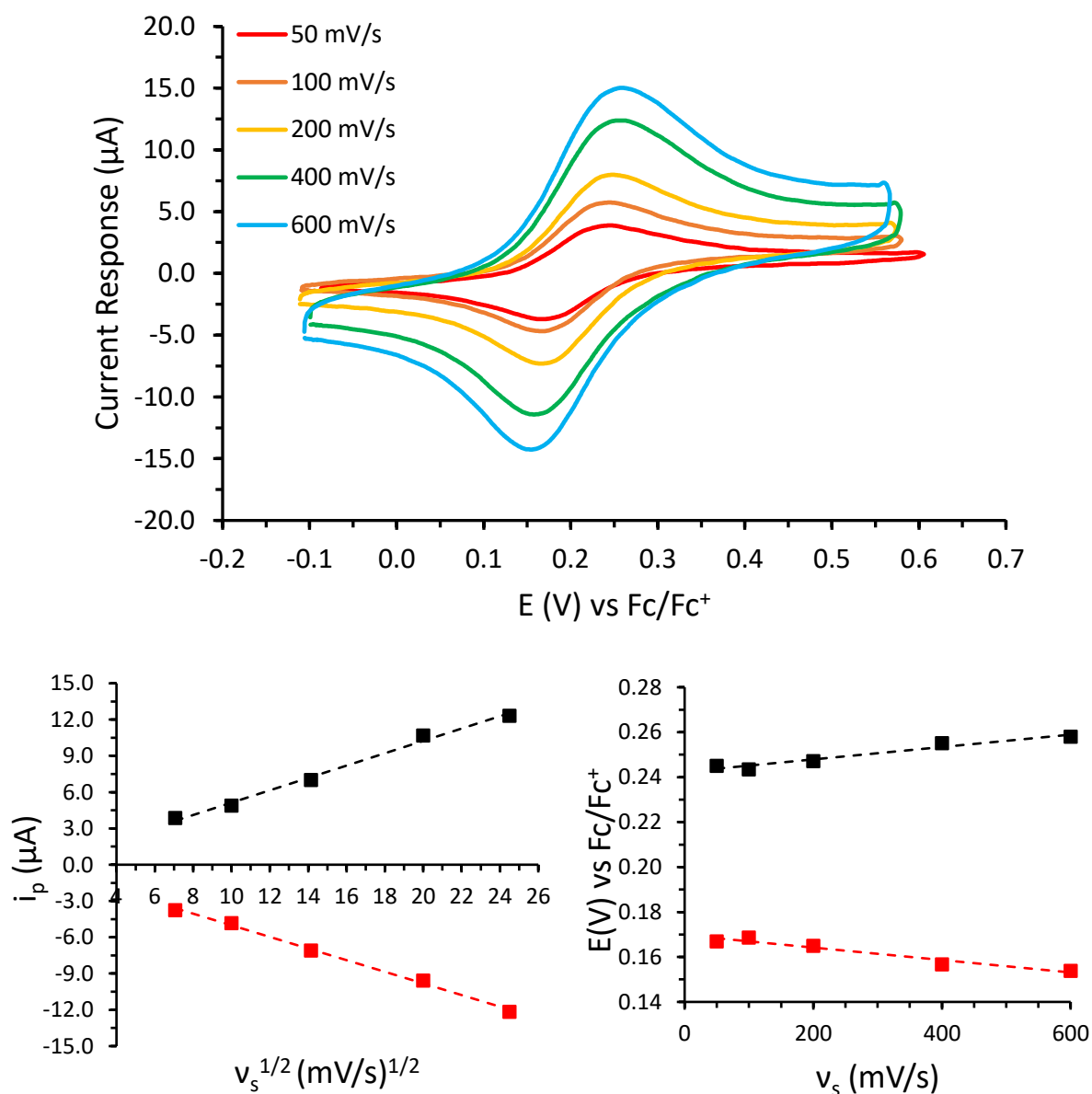
1-(4-Ethynylpyridine)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (7a)

Fig S61: Scan rate dependent cyclic voltammetry of **7a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

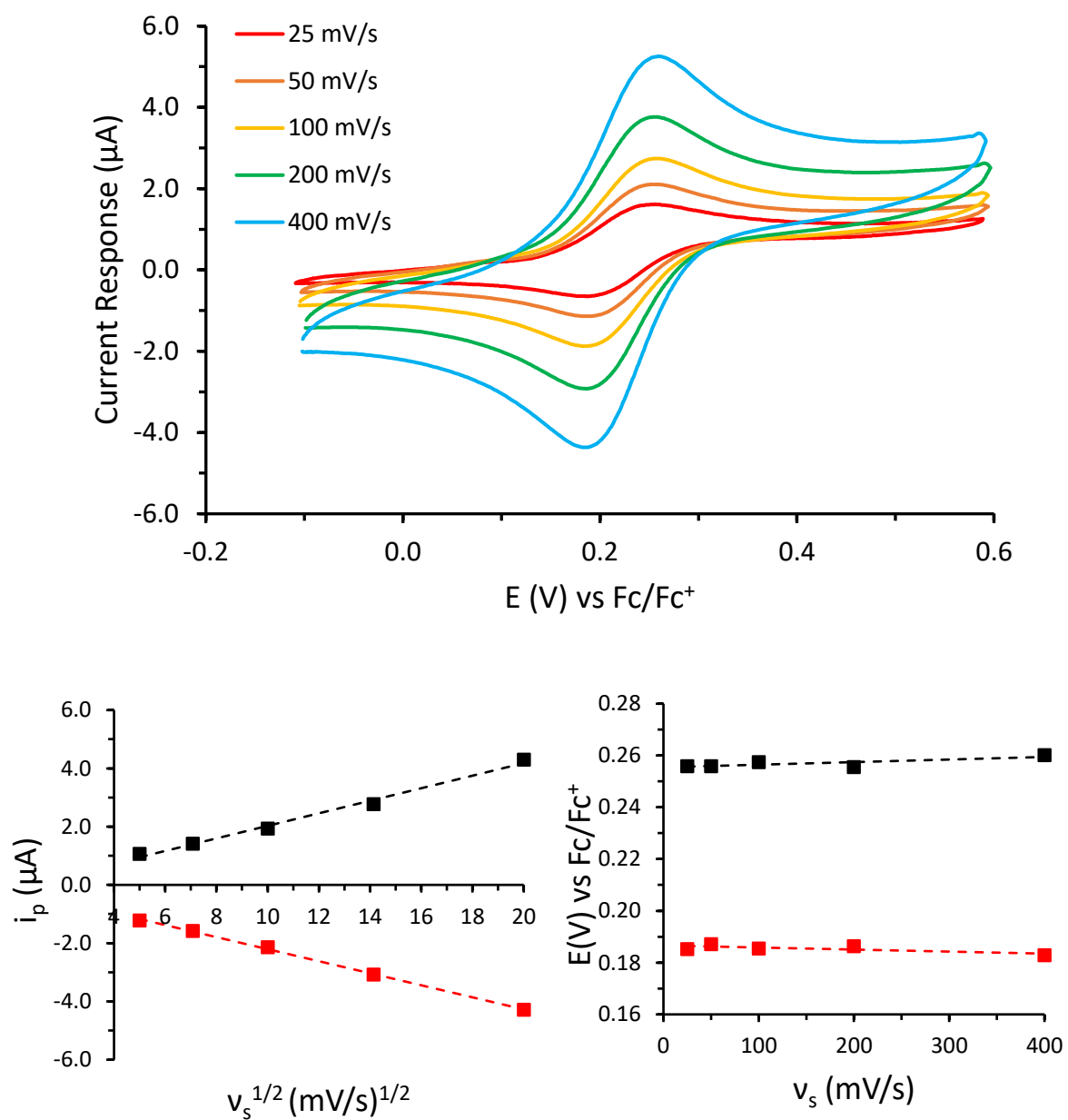
1-(4-Ethynylpyridine)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (7)

Fig S62: Scan rate dependent cyclic voltammetry of **7** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

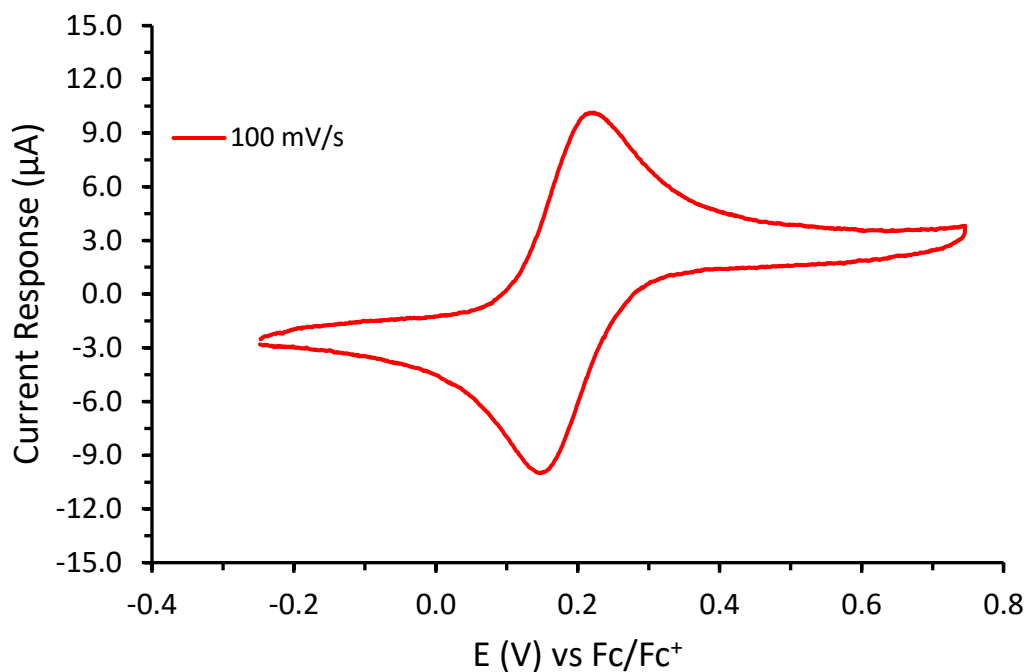
1-(3-Ethynylpyridine)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (8a)

Fig S63: Cyclic voltammetry collected at 100 mV/s for compound **8a**. A full scan rate dependency was not obtained for this system as it showed significant instability under the conditions we used.

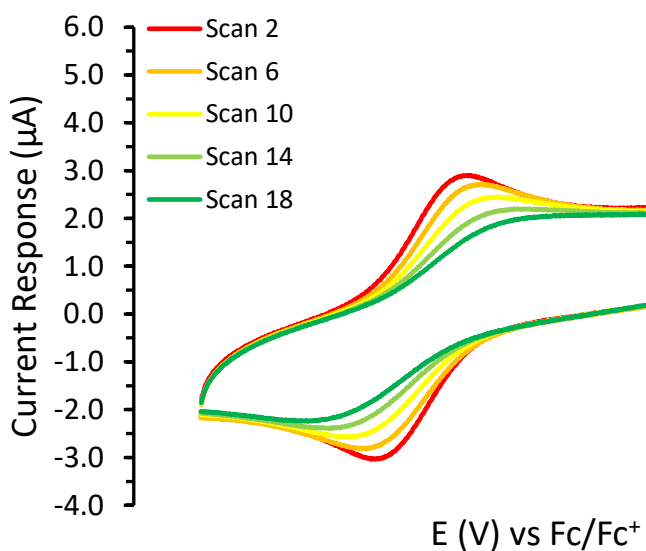


Fig S64: Sequential scans of **8a** at 300 mV/s showing a clear change in the redox profile.

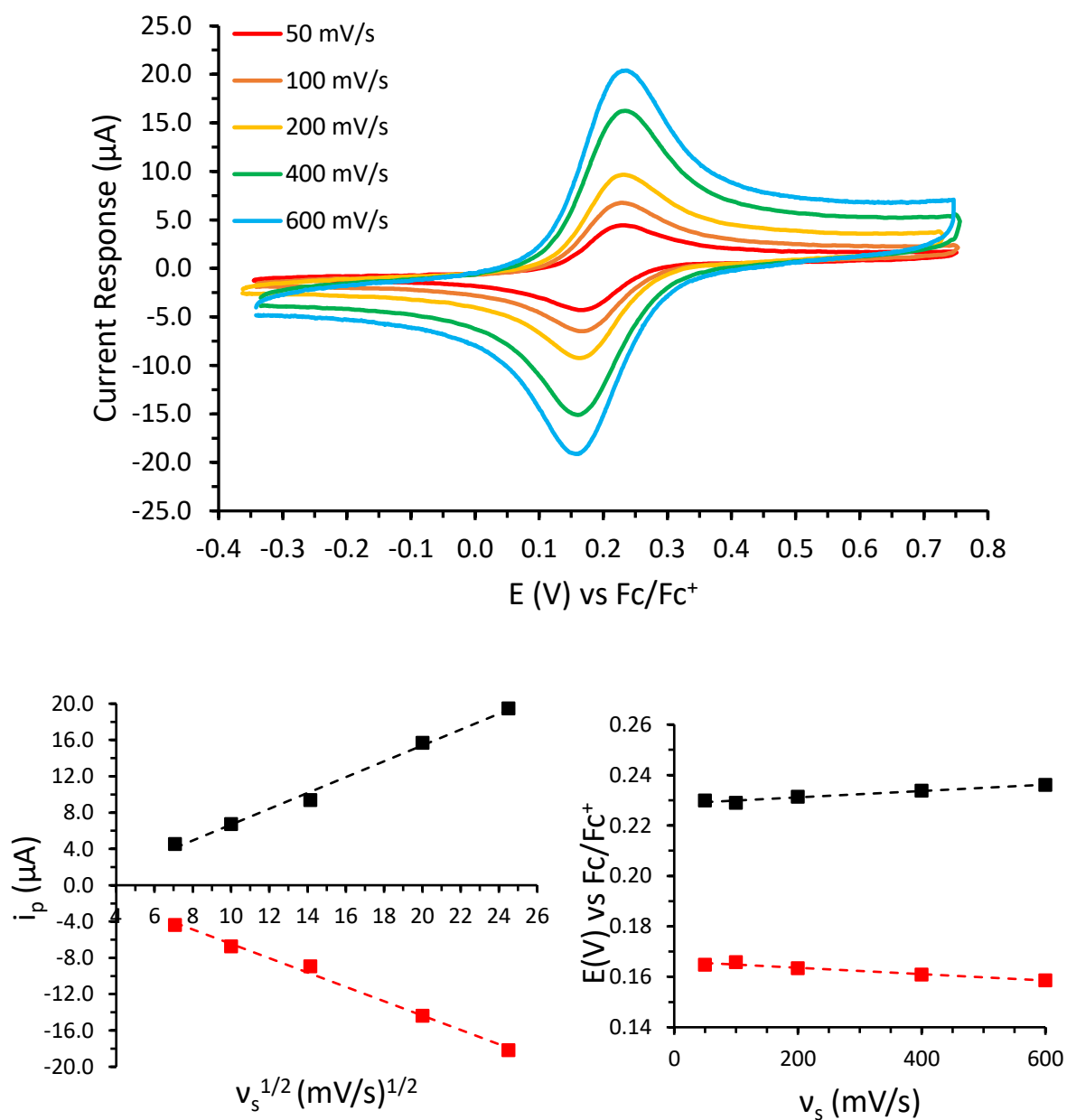
1-(3-Ethynylpyridine)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (8)

Fig S65: Scan rate dependent cyclic voltammetry of **8** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

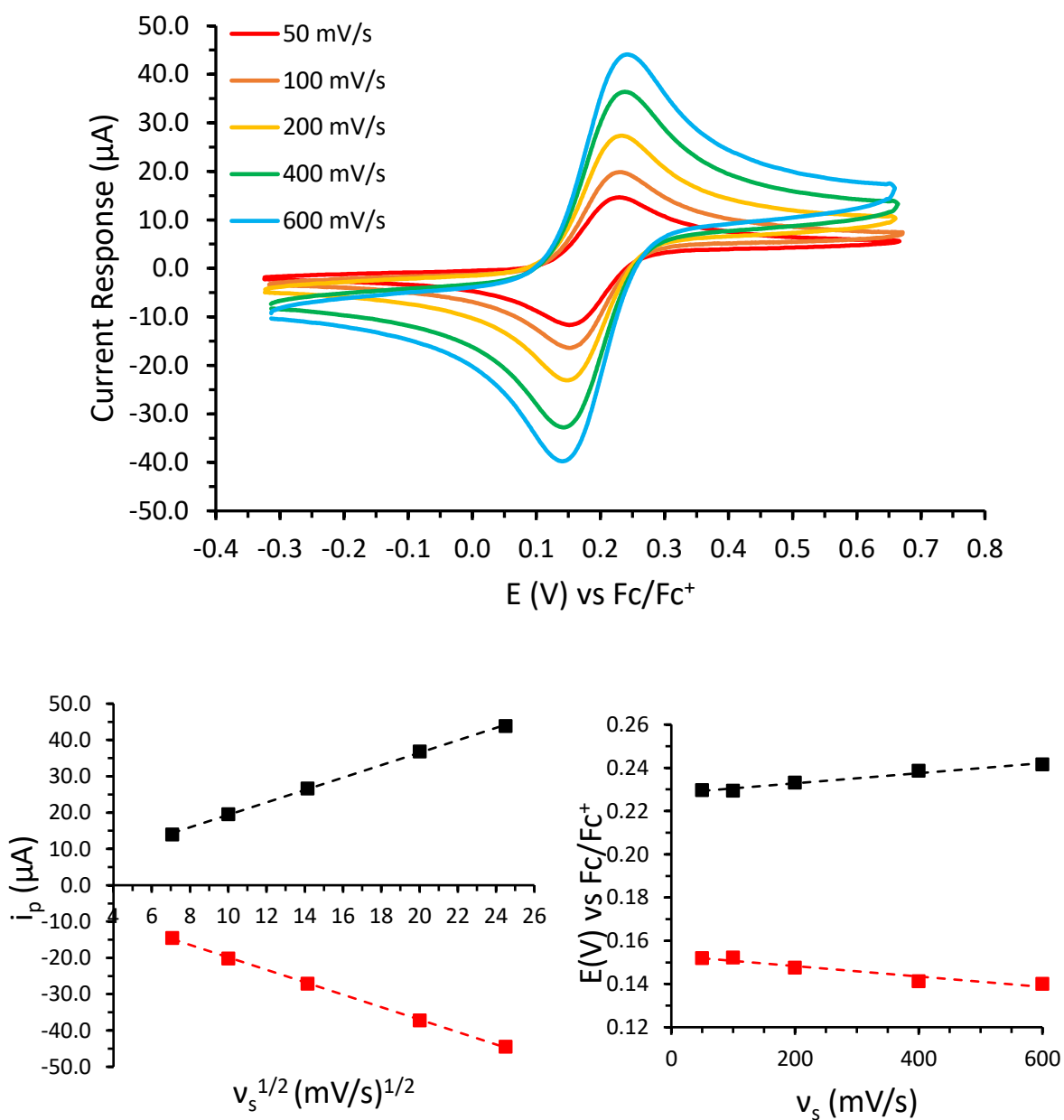
1-(6-Ethynyl-2,2'-bipyridine)-1'-(4-(2-cyanoethylthio)ethynyl)benzene)ferrocene (**9a**)

Fig S66: Scan rate dependent cyclic voltammetry of **9a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

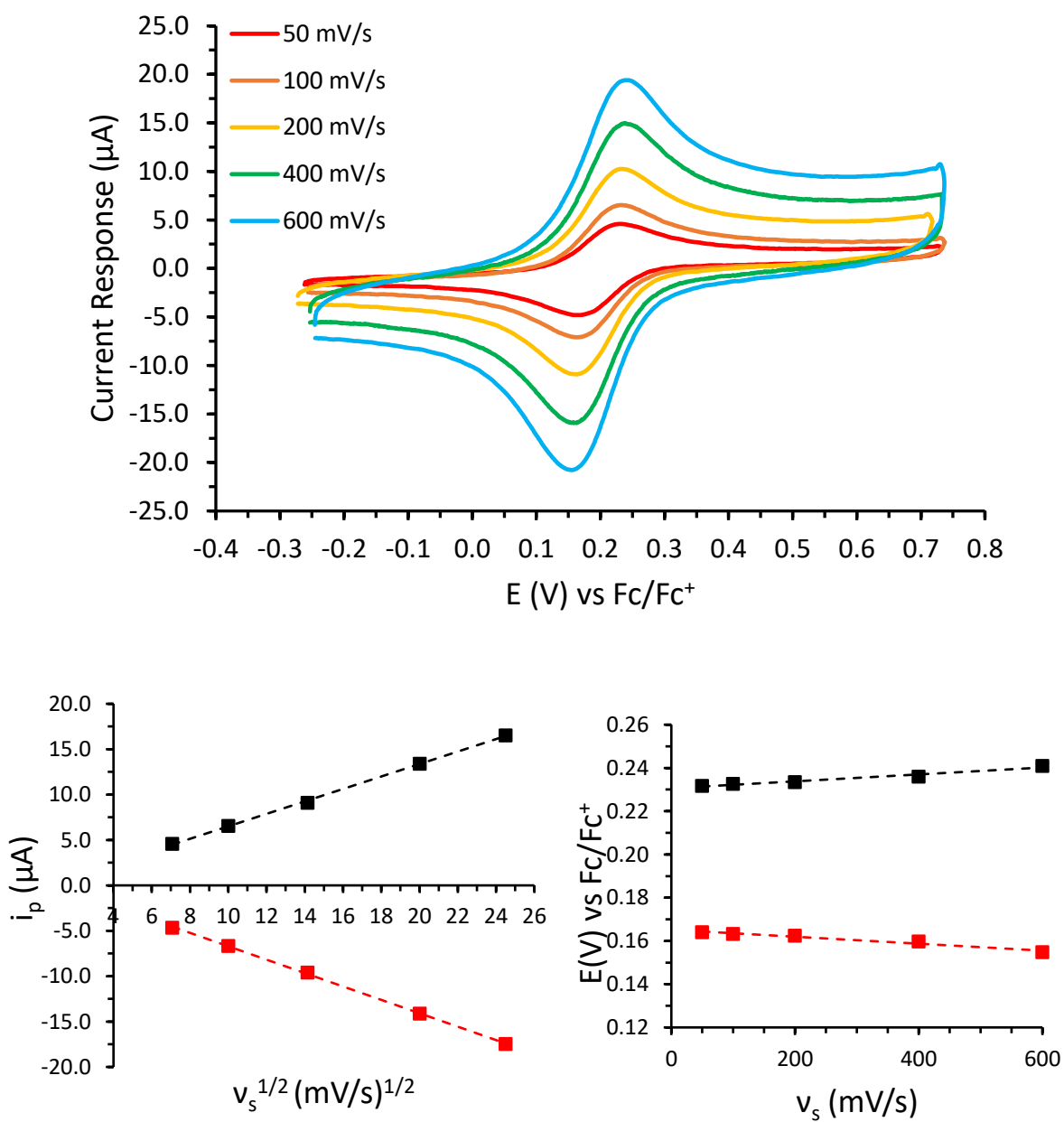
1-(6-Ethynyl-2,2'-bipyridine)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (9)

Fig S67: Scan rate dependent cyclic voltammetry of **9** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

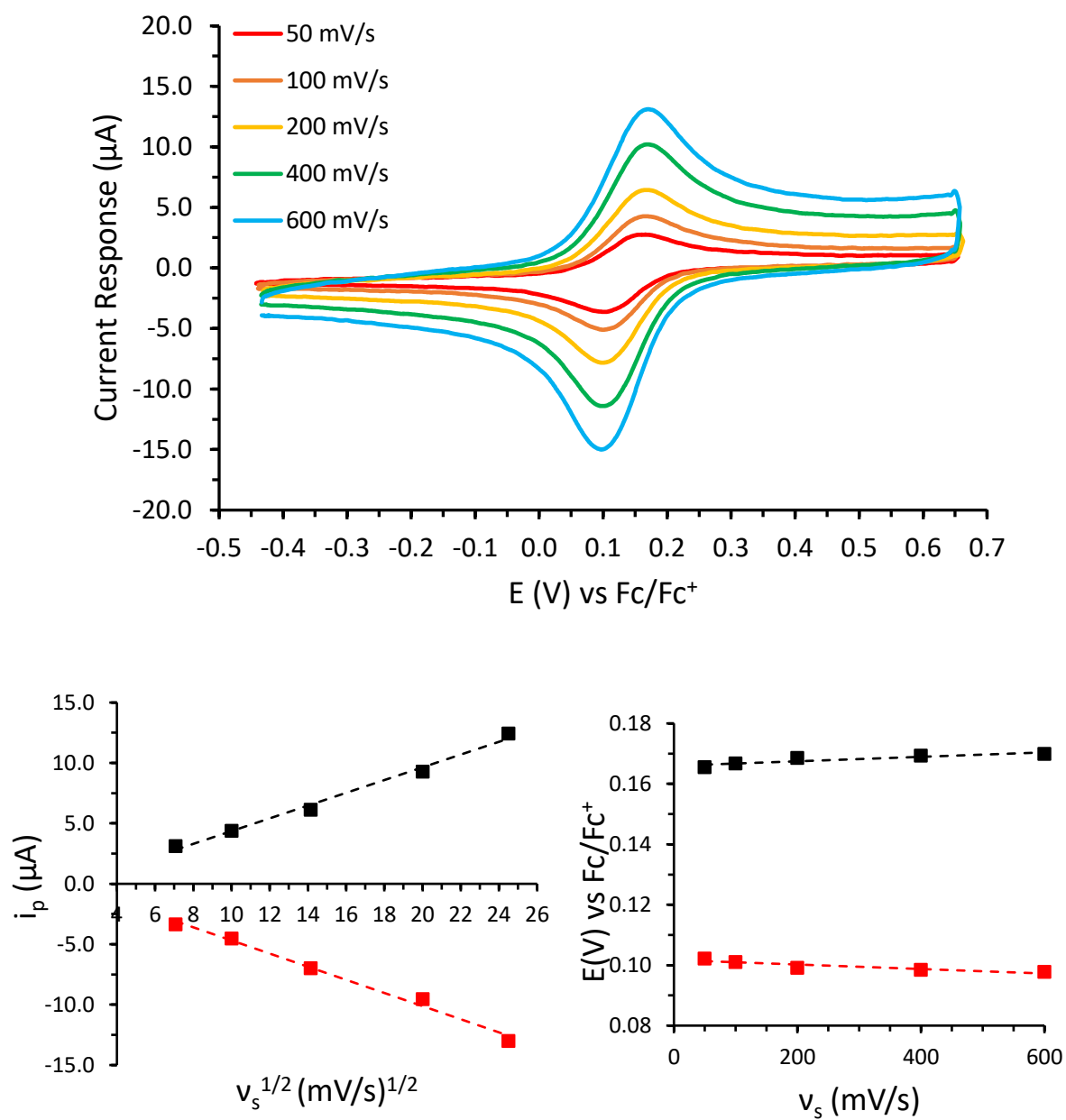
1-(Ethynylpyrene)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (10a)

Fig S68: Scan rate dependent cyclic voltammetry of **10a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

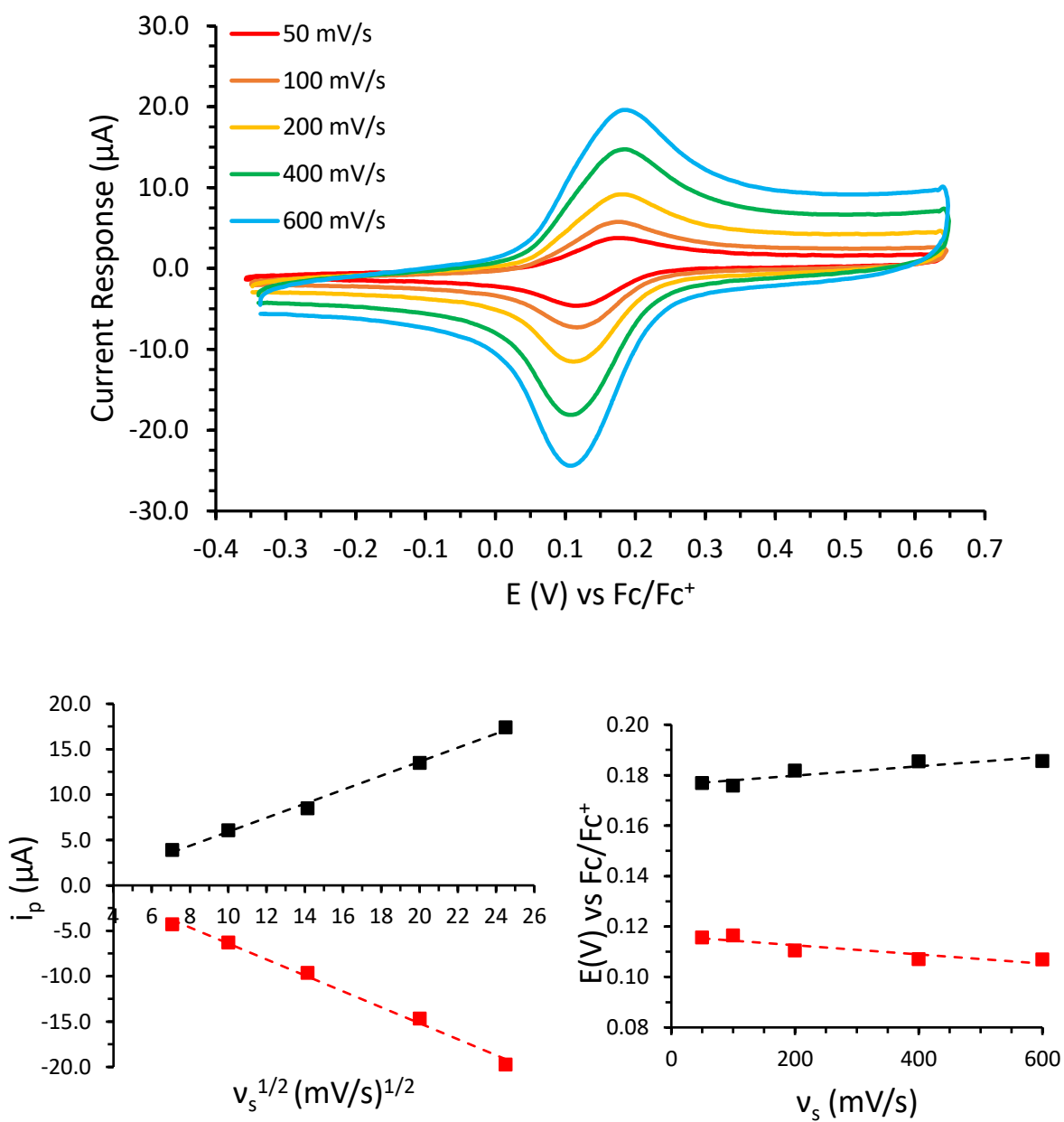
1-(Ethynylpyrene)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (10)

Fig S69: Scan rate dependent cyclic voltammetry of **10** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

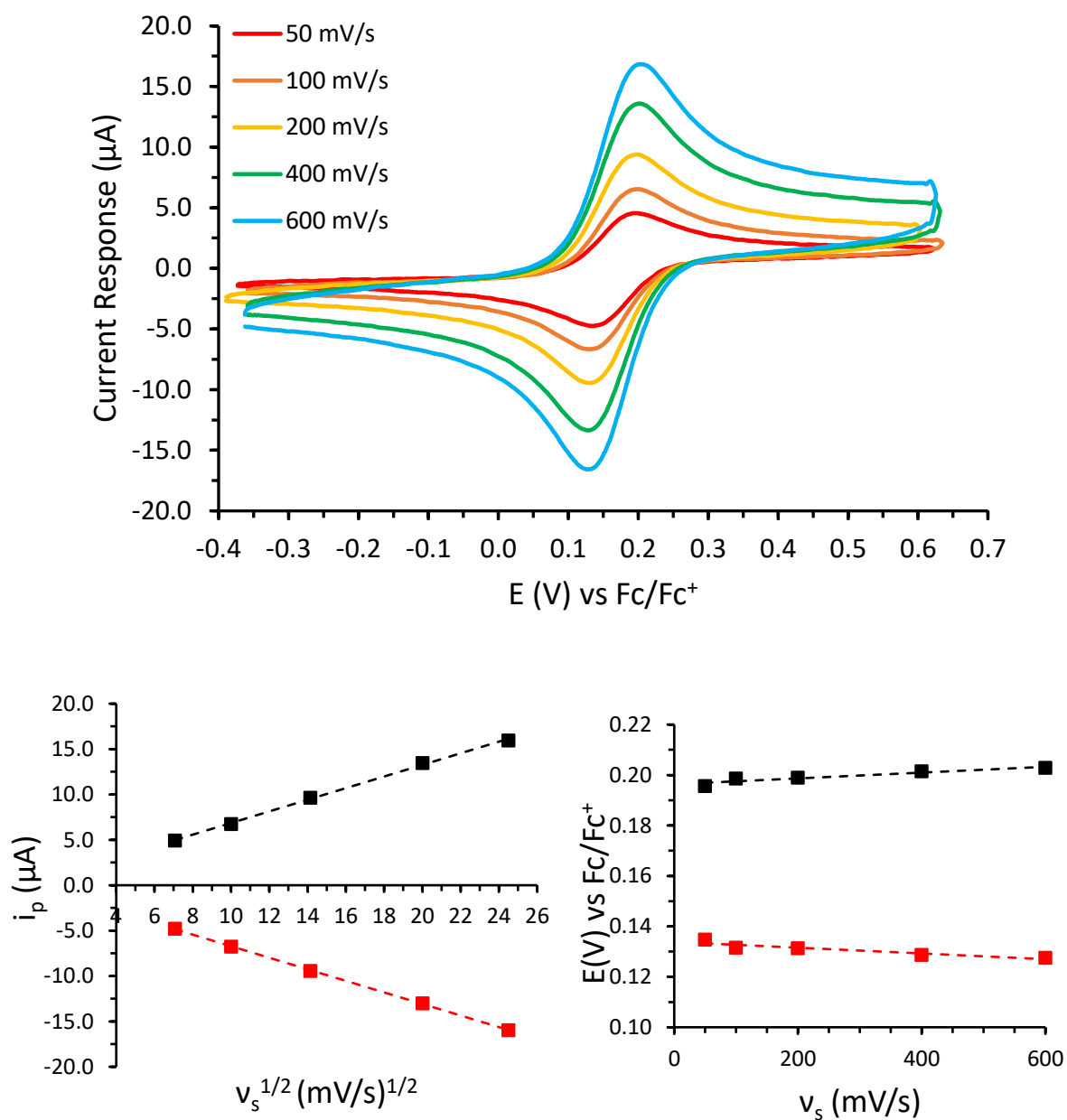
1-(4-(Ethynylphenyl)-2-phenyldiazene)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (**11a**)

Fig S70: Scan rate dependent cyclic voltammetry of **11a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

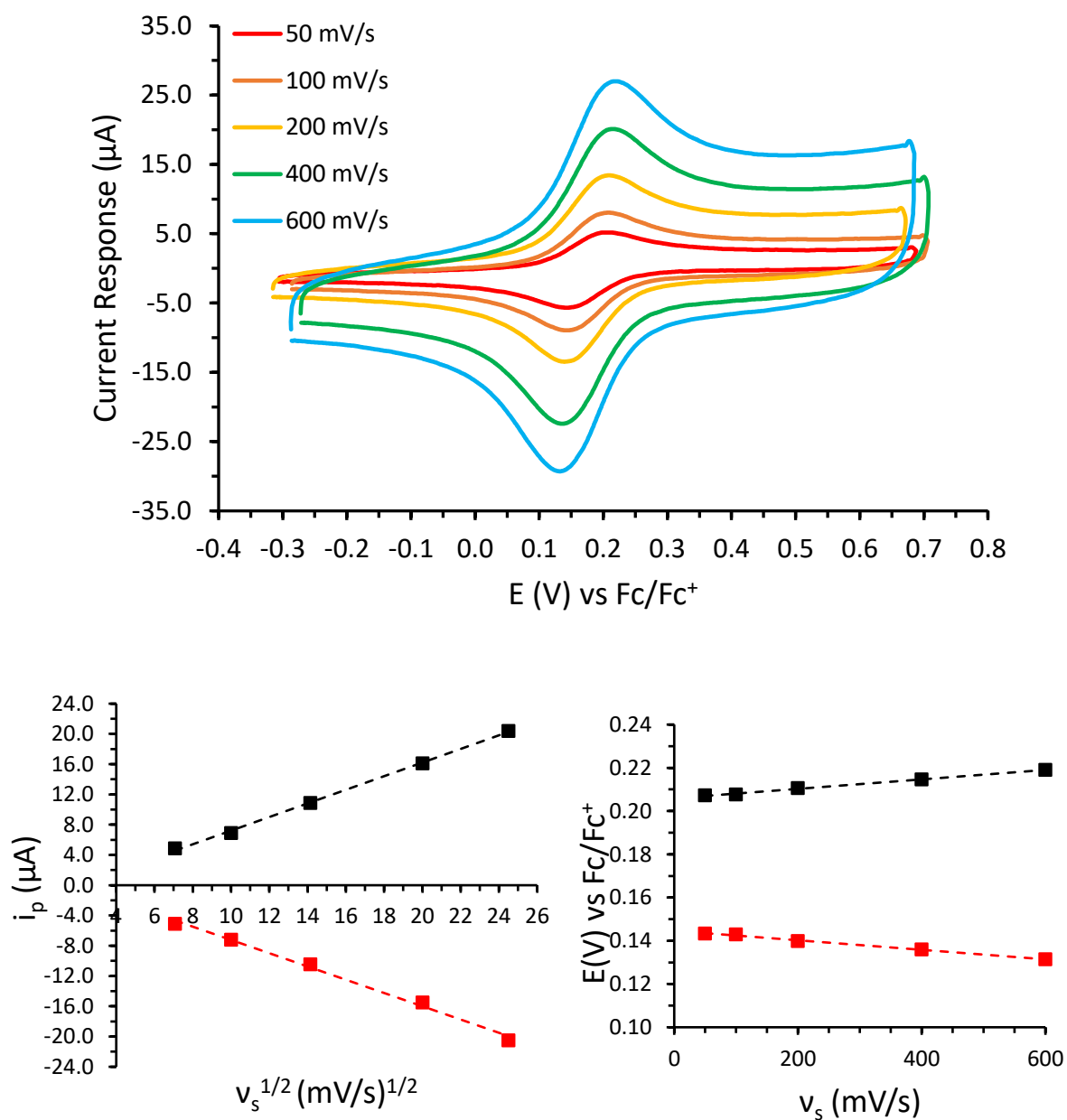
1-(4-(Ethynylphenyl)-2-phenyldiazene)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (**11**)

Fig S71: Scan rate dependent cyclic voltammetry of **11** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

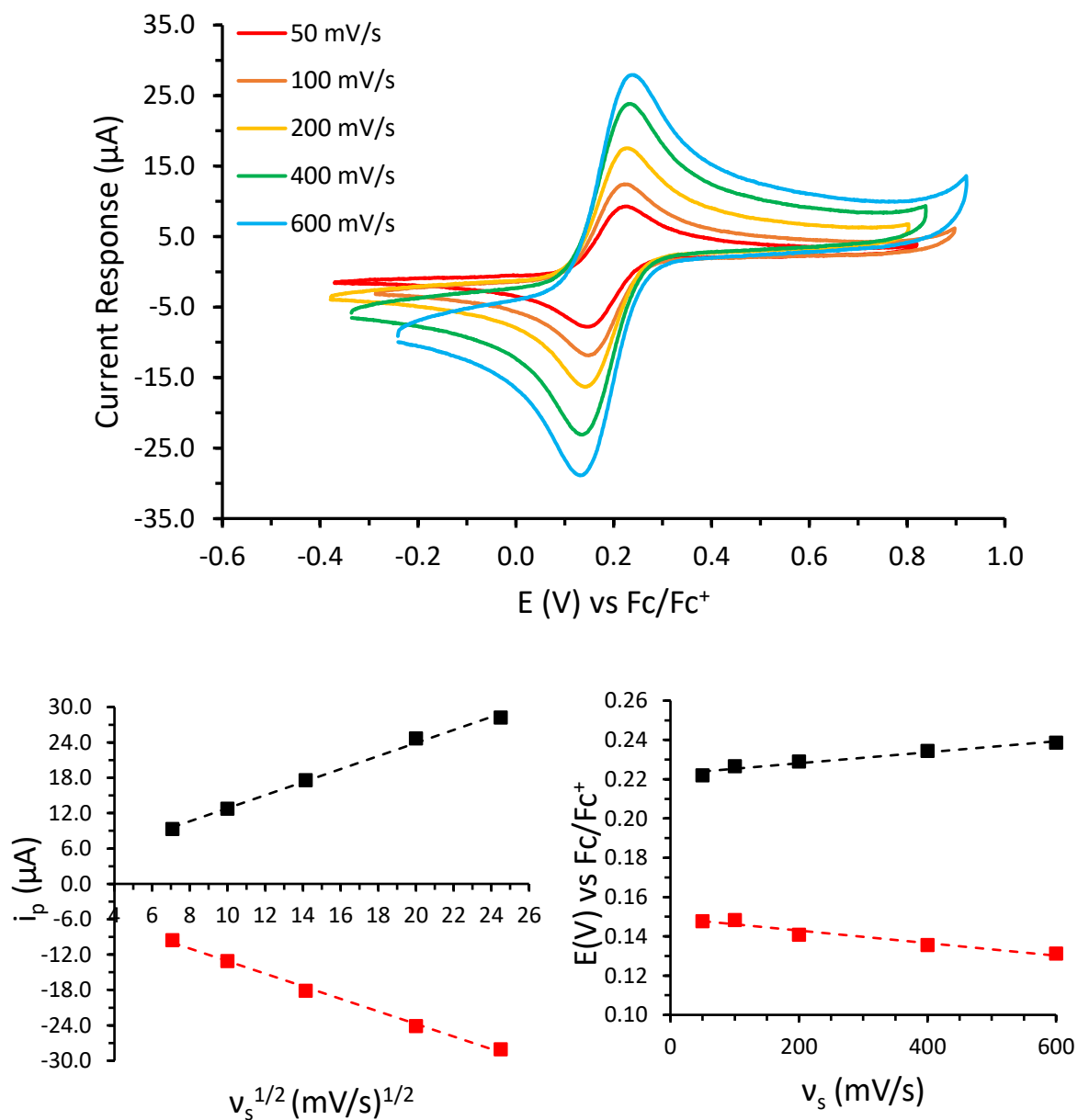
1-(4-Ethynylbenzaldehyde)-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (12a)

Fig S72: Scan rate dependent cyclic voltammetry of **12a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

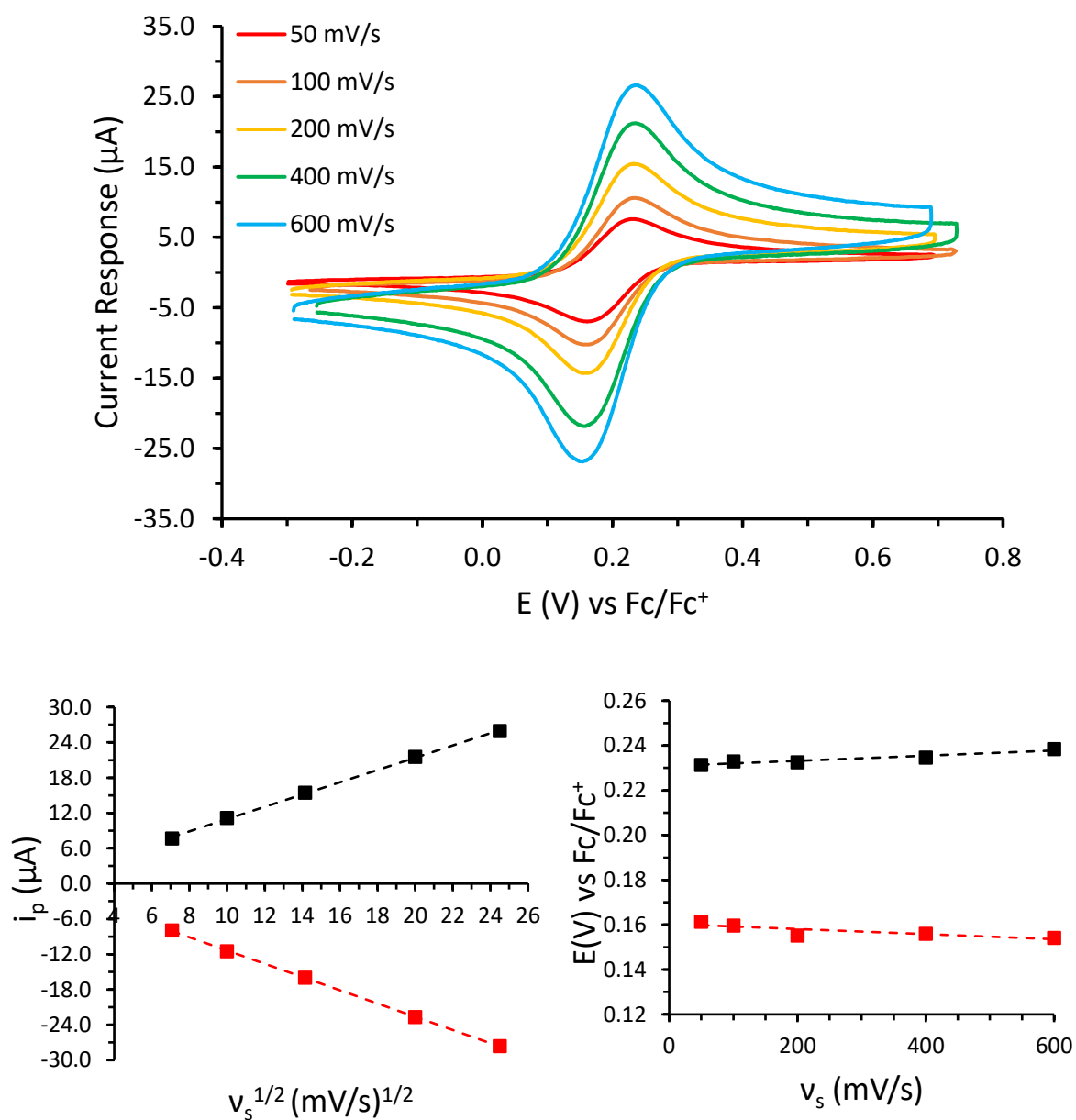
1-(4-Ethynylbenzaldehyde)-1'-(4-(ethynylphenyl)thioacetate)ferrocene (12)

Fig S73: Scan rate dependent cyclic voltammetry of **12** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

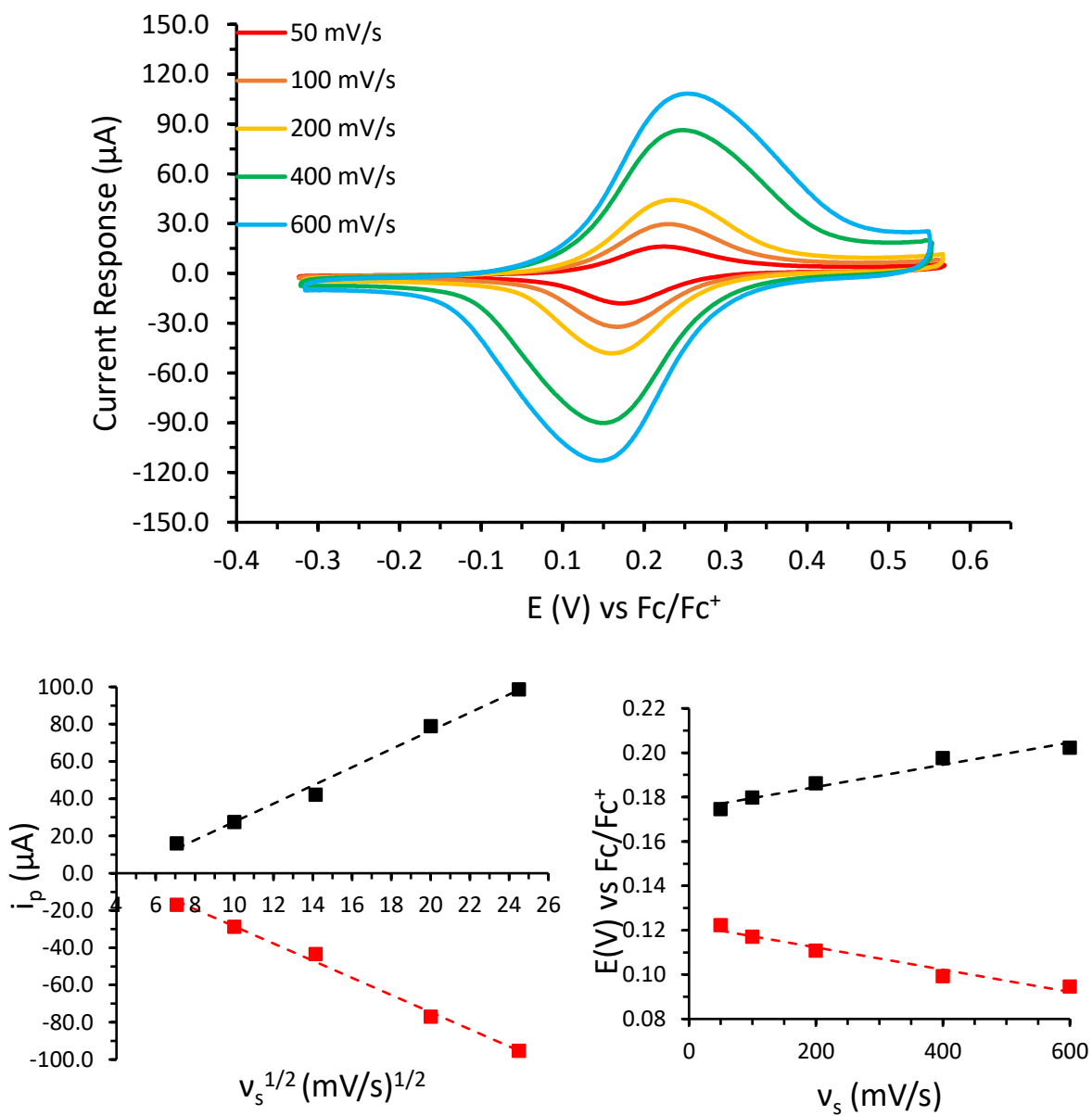
1-(4-(Ethynylphenyl)methylene-bis(1H-pyrrole))-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene (13a)

Fig S74: Scan rate dependent cyclic voltammetry of **13a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

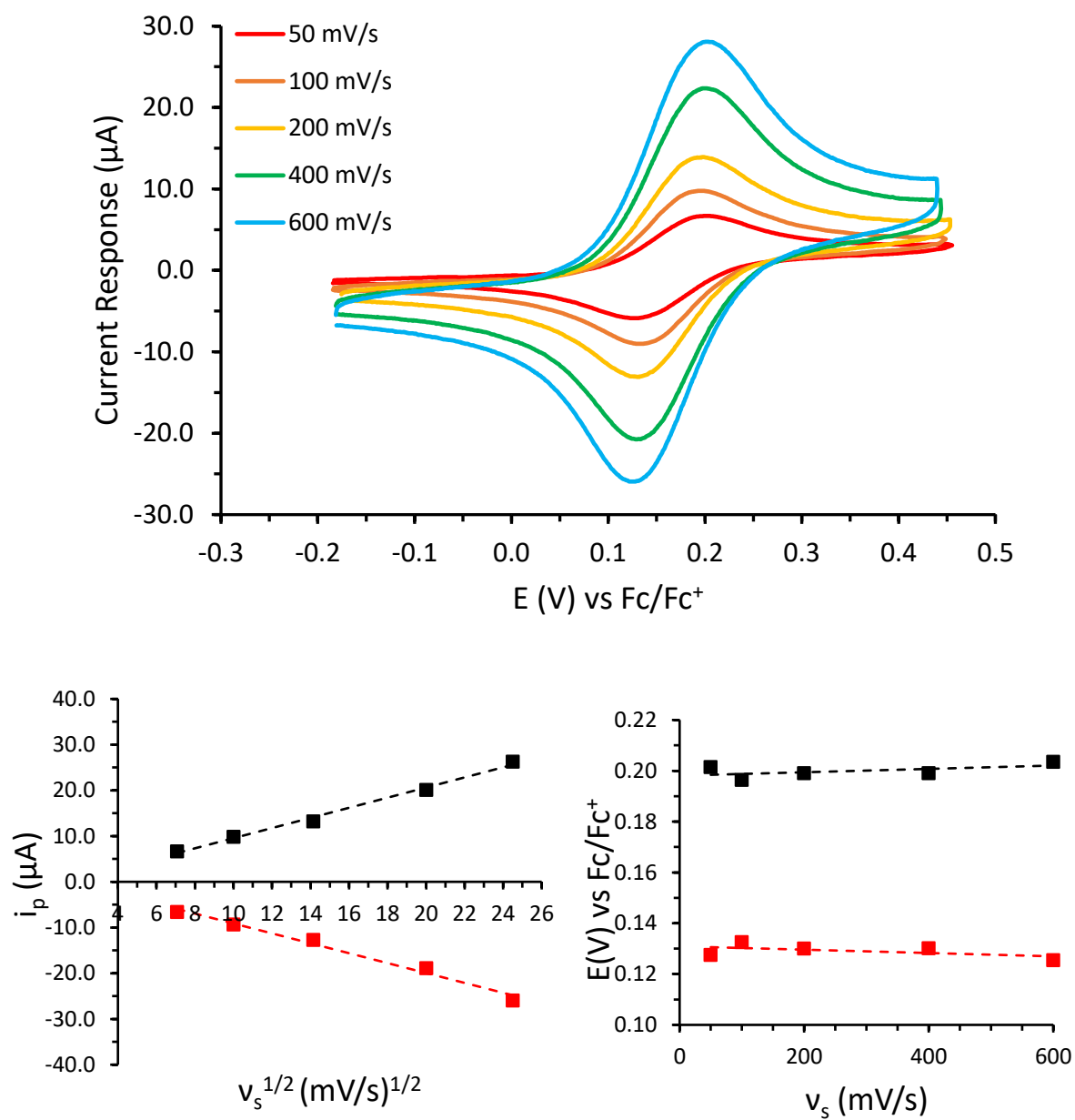
1-(4-(Ethynylphenyl)methylene-bis(1H-pyrrole))-1'-(4-(ethynylphenyl)thioacetate)ferrocene (13)

Fig S75: Scan rate dependent cyclic voltammetry of **13** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

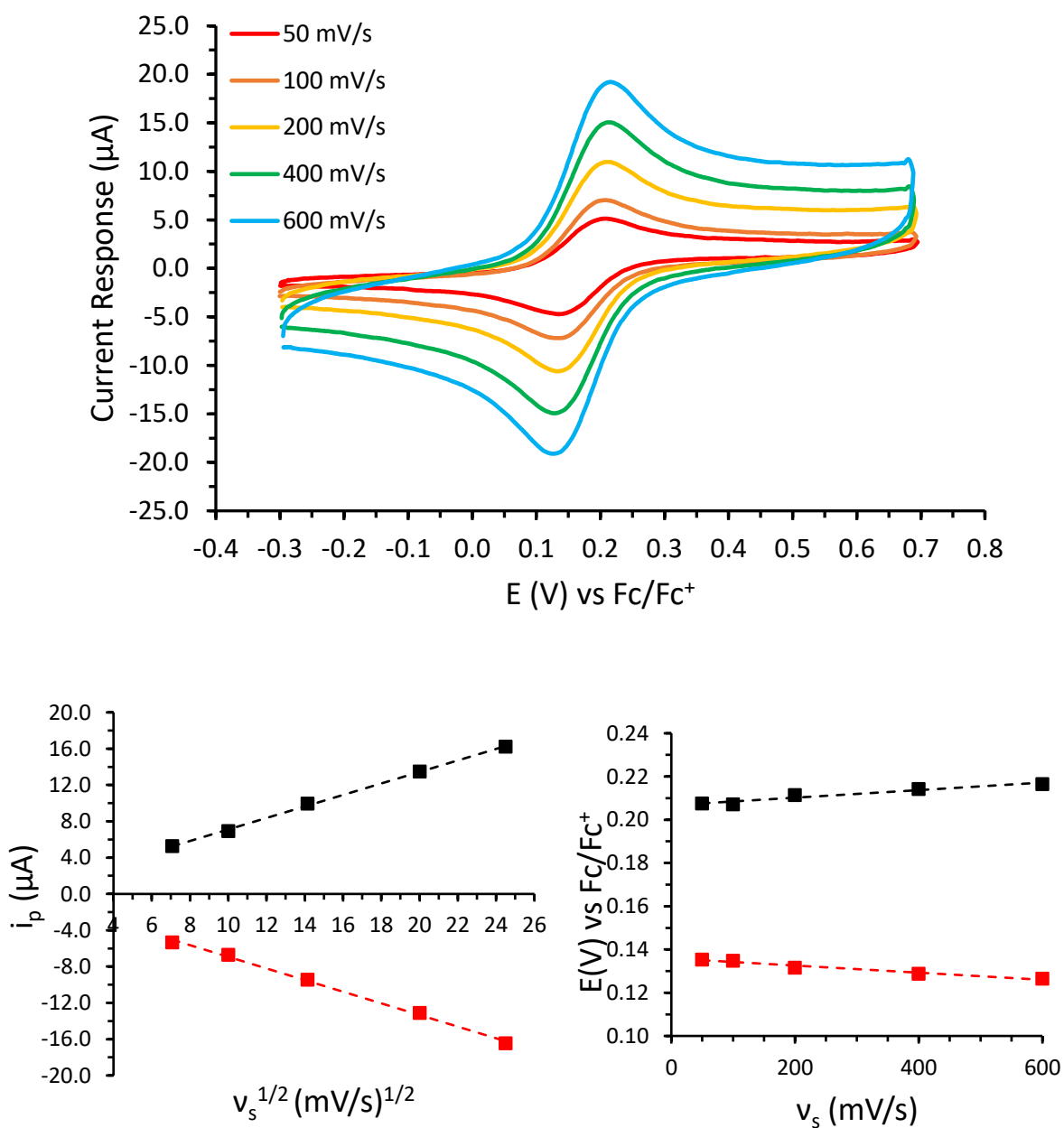
(μ -1,3,5)-(1-Ethynyl-1'-(4-(2-cyanoethylthio)ethynylbenzene)ferrocene)benzene (**14a**)

Fig S76: Scan rate dependent cyclic voltammetry of **14a** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

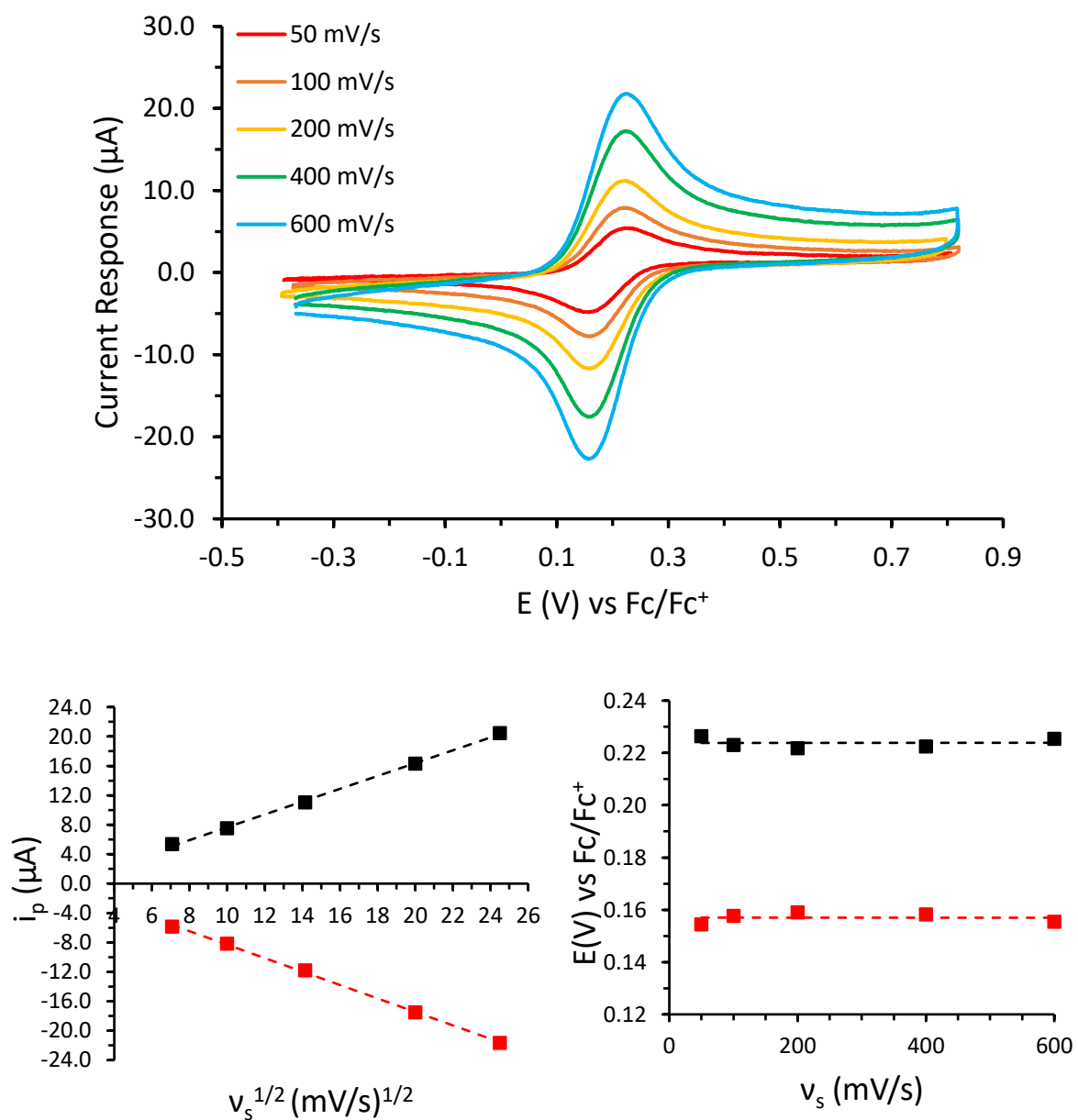
(μ -1,3,5)-(1-Ethynyl-1'-(4-(ethynylphenyl)thioacetate)ferrocene)benzene (**14**)

Fig S77: Scan rate dependent cyclic voltammetry of **14** (top), with linear fits to compare the scan rates to their respective peak currents (bottom left) and peak potentials (bottom right).

3. Ultraviolet-Visible Spectroscopy

Table S2: Peak positions obtained from UV-vis. spectroscopy of all cyanoethyl/thioacetate compounds. All data were recorded at room temperature in CH₂Cl₂ using a quartz cell with a path length of 1 cm. For each compound, the mass of sample and the volume of solvent were both recorded and used to determine extinction coefficients through use of the Beer-Lambert law.⁹ 'sh' denotes a shoulder rather than a well-defined peak.

Compound	λ_{\max}/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)
2a	282 (28239), 313 (31491), 360 sh (3508), 442 (1044)
2	271 (24038), 315 (25132), 357 sh (3485), 446 (958)
5a	280 sh (39657), 299 (43950), 311 (45003), 326 sh (42292), 356 sh (17505), 446 (1377)
5	269 (31516), 294 (26940), 319 (27086), 359 sh (5997), 451 (1037)
6a	286 sh (48272), 315 (51304), 365 sh (9383), 455 (2870)
6	269 (45712), 314 (43836), 364 sh (9605), 455 (2691)
7a	246 (20466), 252 (20772), 257 (21157) 274 (21497), 291 (25287), 305 sh (21770), 318 (20798), 324 (21026), 360 (3403), 451 (1246)
7	267 (17349), 291 (18165), 320 (17324), 362 sh (4898), 461 sh (1292)
8a	253 sh (22272), 291 (27892), 310 (27769), 365 sh (3259), 465 (1146)
8	269 (31225), 291 sh (28075), 312 (27692), 365 (4175), 450 (1303)
9a	288 (36799), 300 (35930), 454 (1174)
9	276 (29840), 316 (26627), 460 (1066)
10a	240 (61122), 286 (61290), 321 (35522), 367 (39941), 386 (38293), 467 (3354)
10	248 sh (59220), 285 (60606), 318 (34120), 367 (42390), 386 (40466), 473 (3072)
11a	287 sh (34436), 320 (46689), 360 (43149), 470 (7364)
11	268 (28113), 322 (36043), 358 (35699), 471 (6096)
12a	285 sh (28080), 301 (31565), 324 sh (26083), 387 sh (4124), 454 sh (1737)
12	277 sh (34723), 300 (39254), 325 sh (31549), 393 sh (4926), 470 (2100)
13a	267 (30050), 299 (32954), 317 (32592), 367 sh (3597), 453 (1383)
13	269 (31782), 296 (27755), 315 (28536), 367 sh (2986), 457 (1030)
14a	272 (89123), 293 (90493), 316 (89180), 368 sh (13130), 451 (3929)
14	268 (71659), 293 (60257), 314 (62245), 364 sh (10877), 457 (2928)

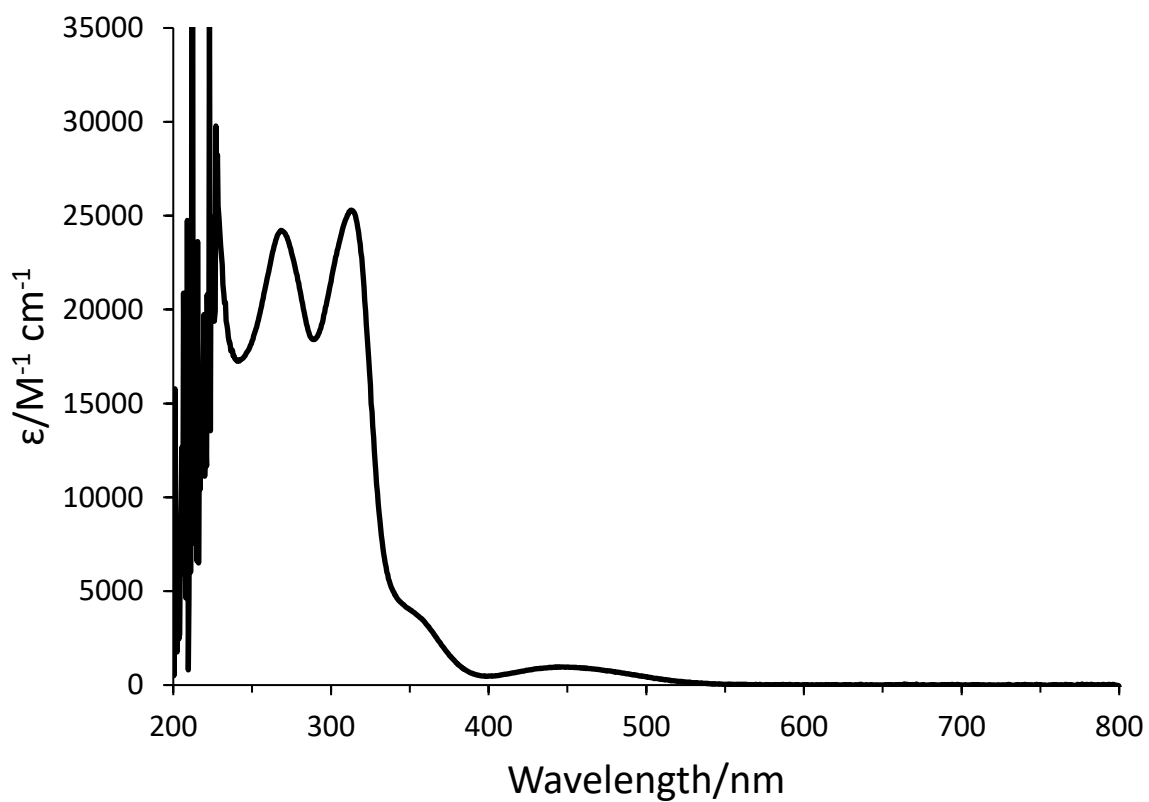


Fig S87. UV-Vis spectrum of compound 2a, measured in CH_2Cl_2 .

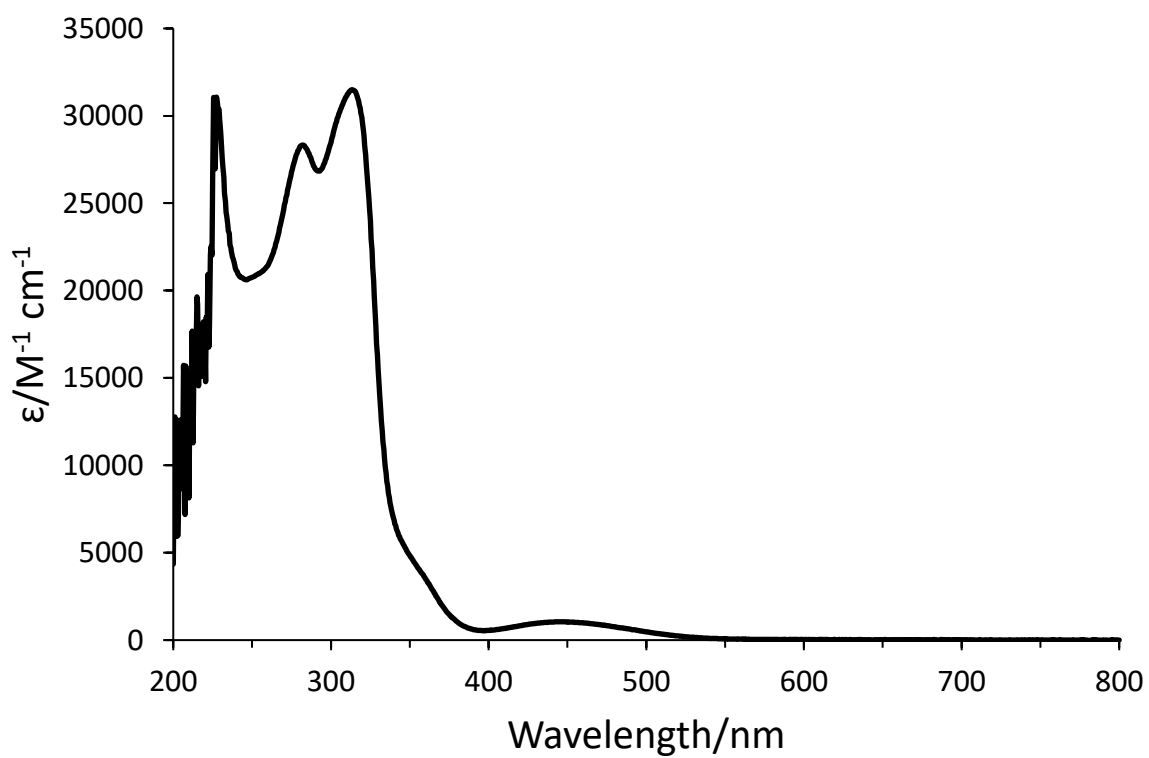


Fig S88. UV-Vis spectrum of compound 2, measured in CH_2Cl_2 .

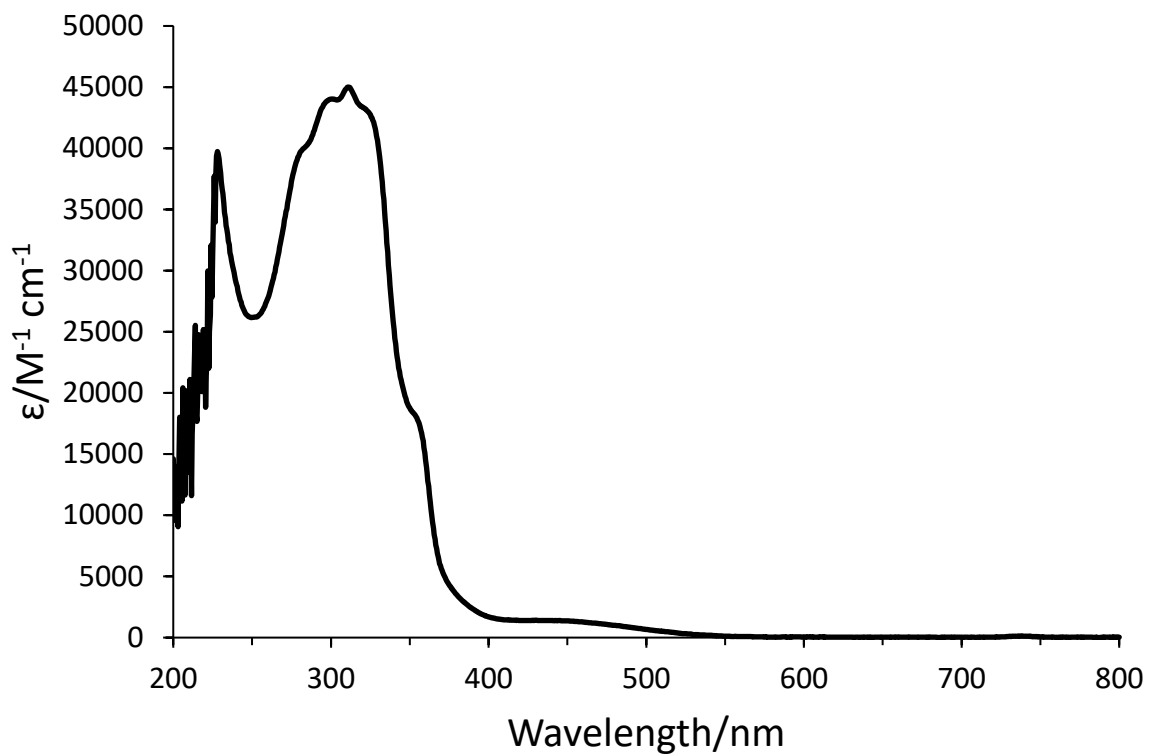


Fig S89. UV-Vis spectrum of compound **5a**, measured in CH_2Cl_2 .

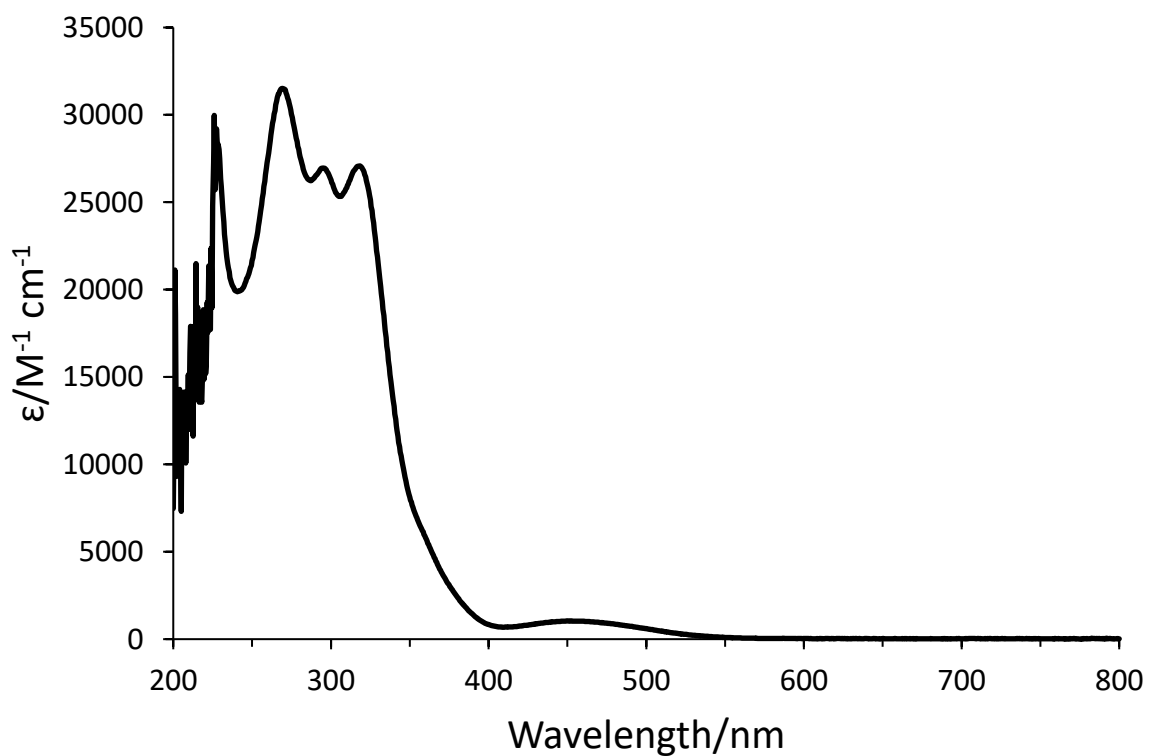


Fig S90. UV-Vis spectrum of compound **5**, measured in CH_2Cl_2 .

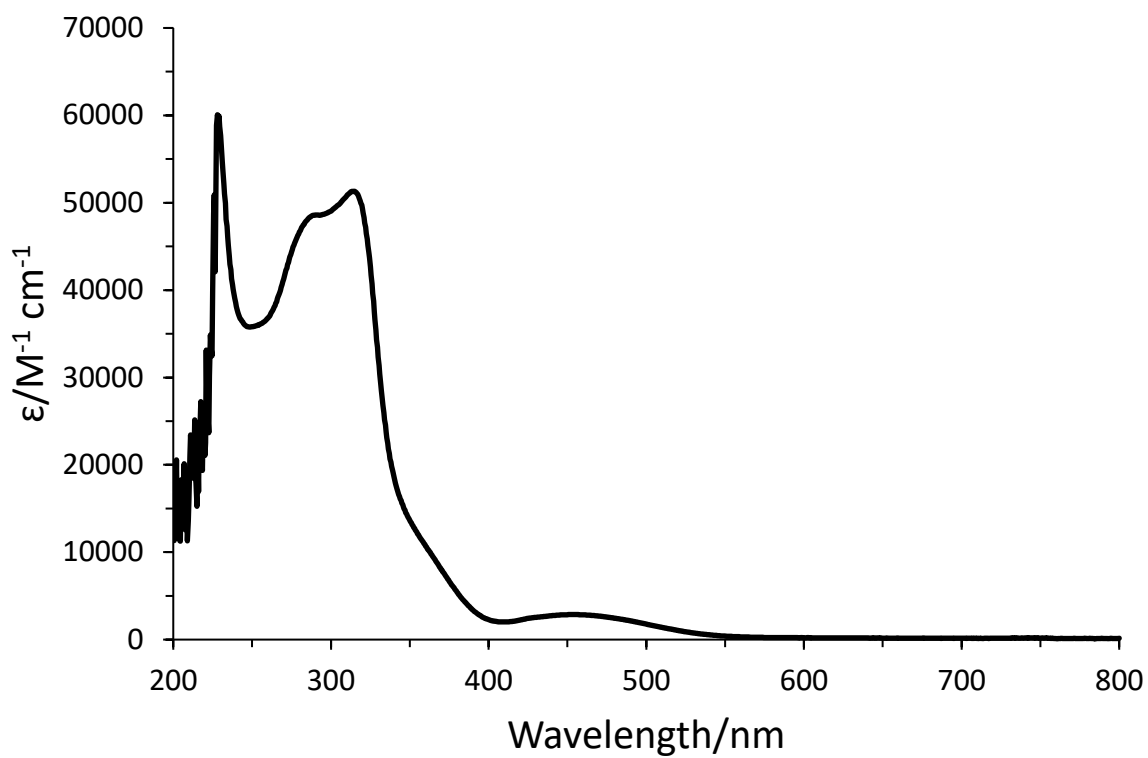


Fig S91. UV-Vis spectrum of compound **6a**, measured in CH₂Cl₂.

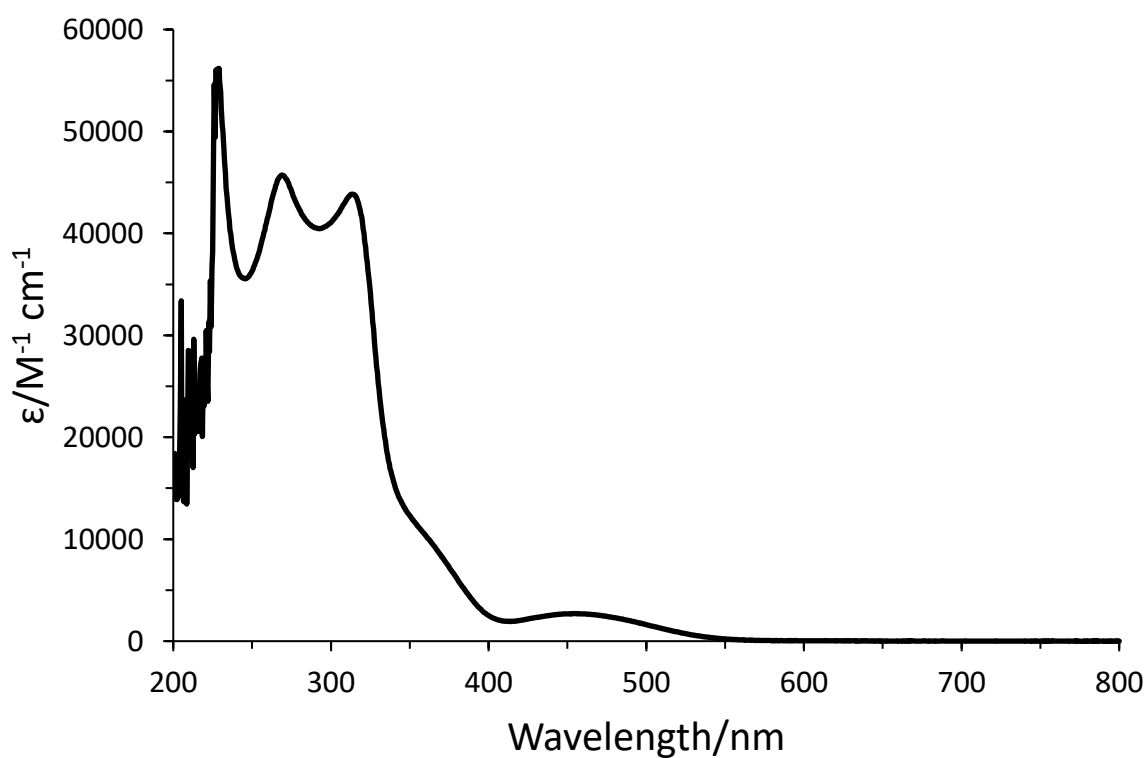


Fig S92. UV-Vis spectrum of compound **6**, measured in CH₂Cl₂.

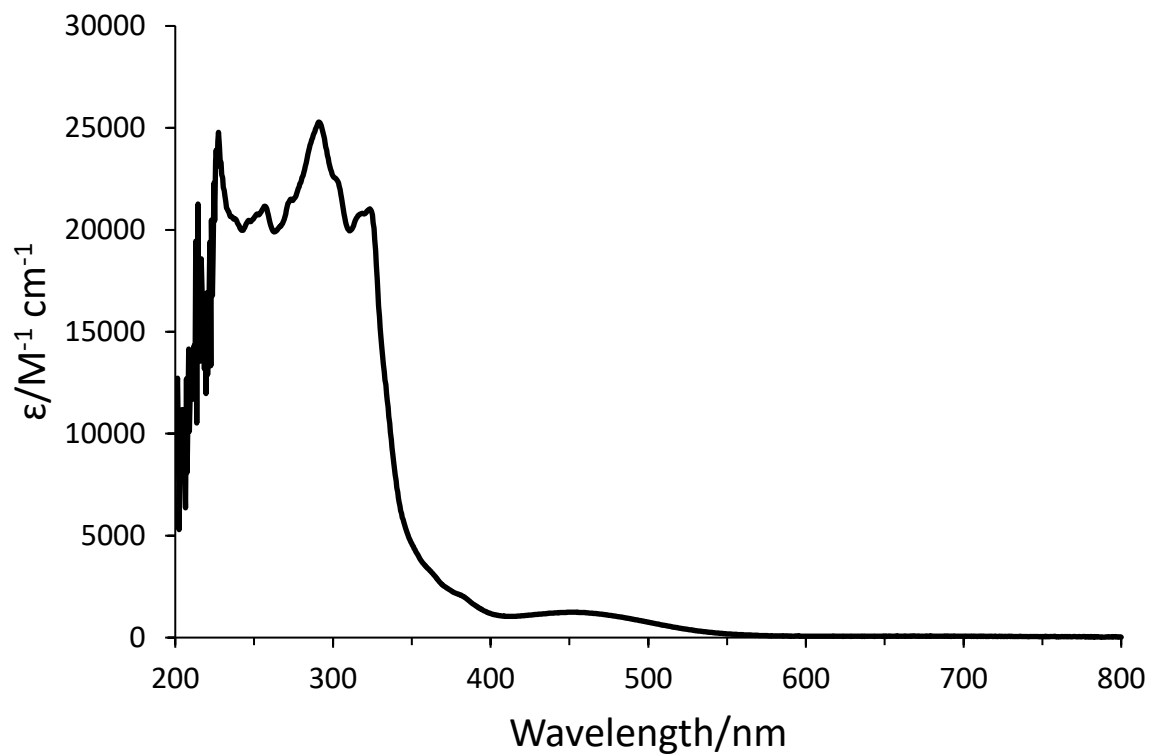


Fig S93. UV-Vis spectrum of compound **7a**, measured in CH_2Cl_2 .

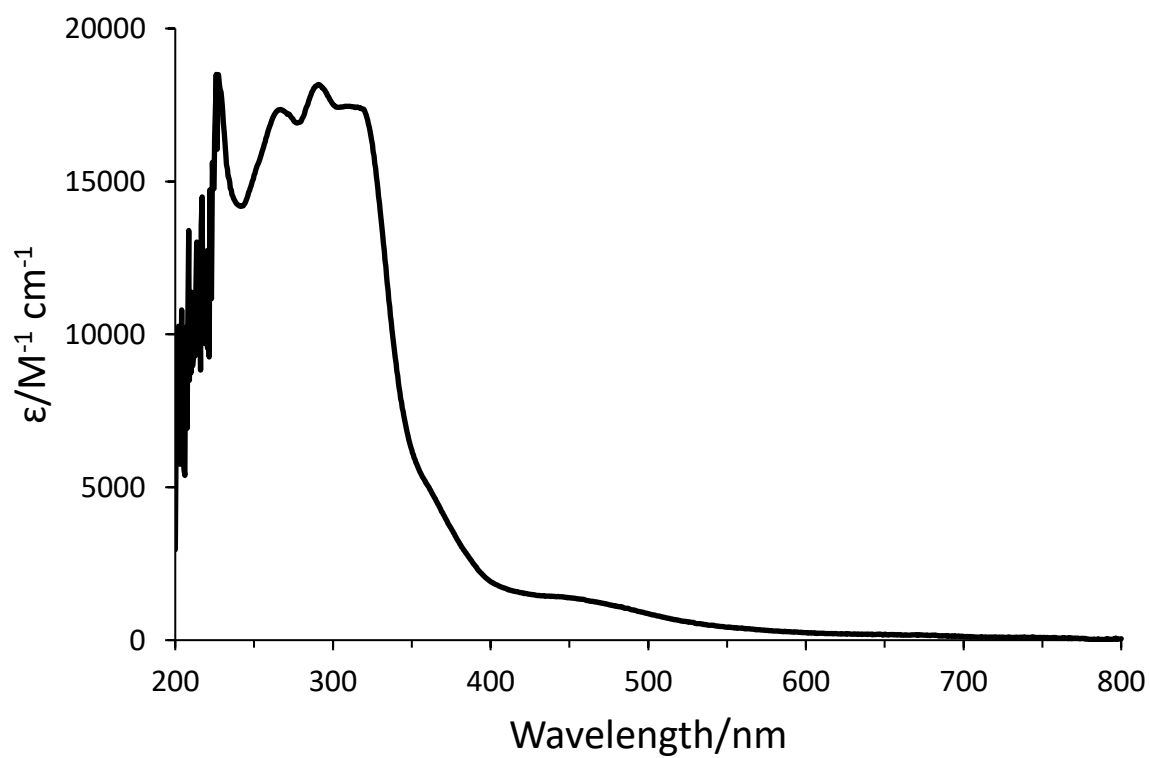


Fig S94. UV-Vis spectrum of compound **7**, measured in CH_2Cl_2 .

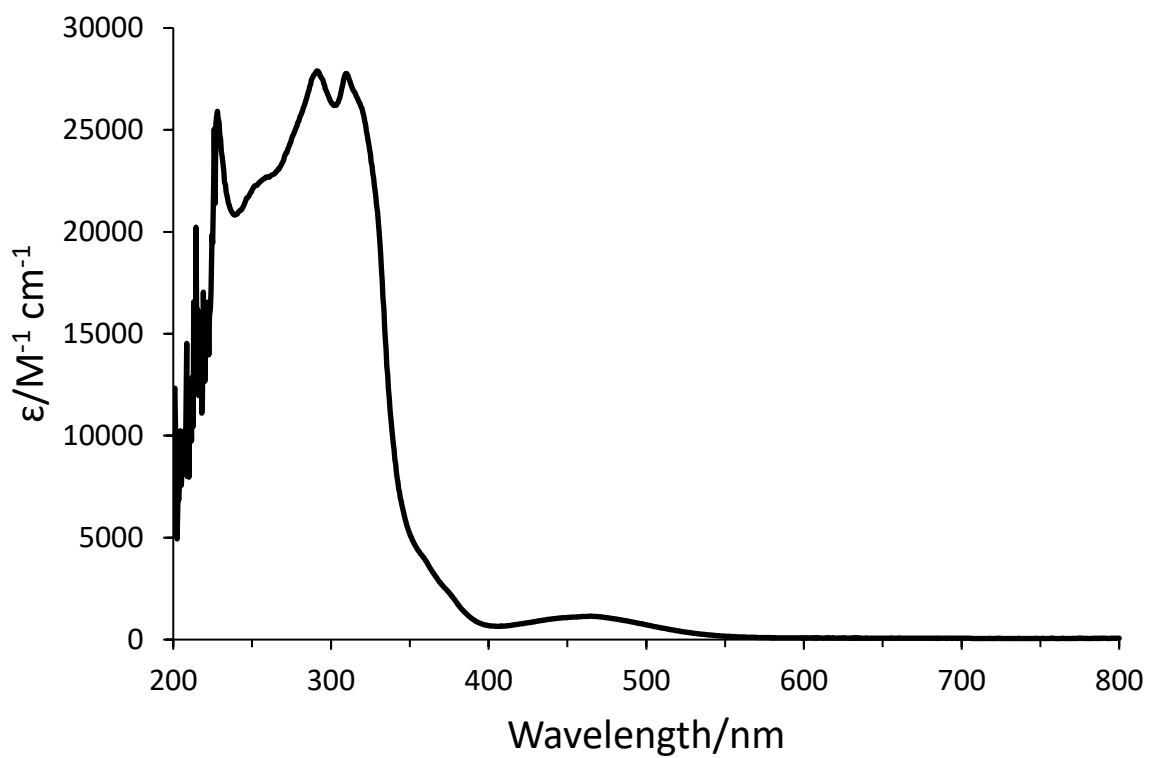


Fig S95. UV-Vis spectrum of compound **8a**, measured in CH₂Cl₂.

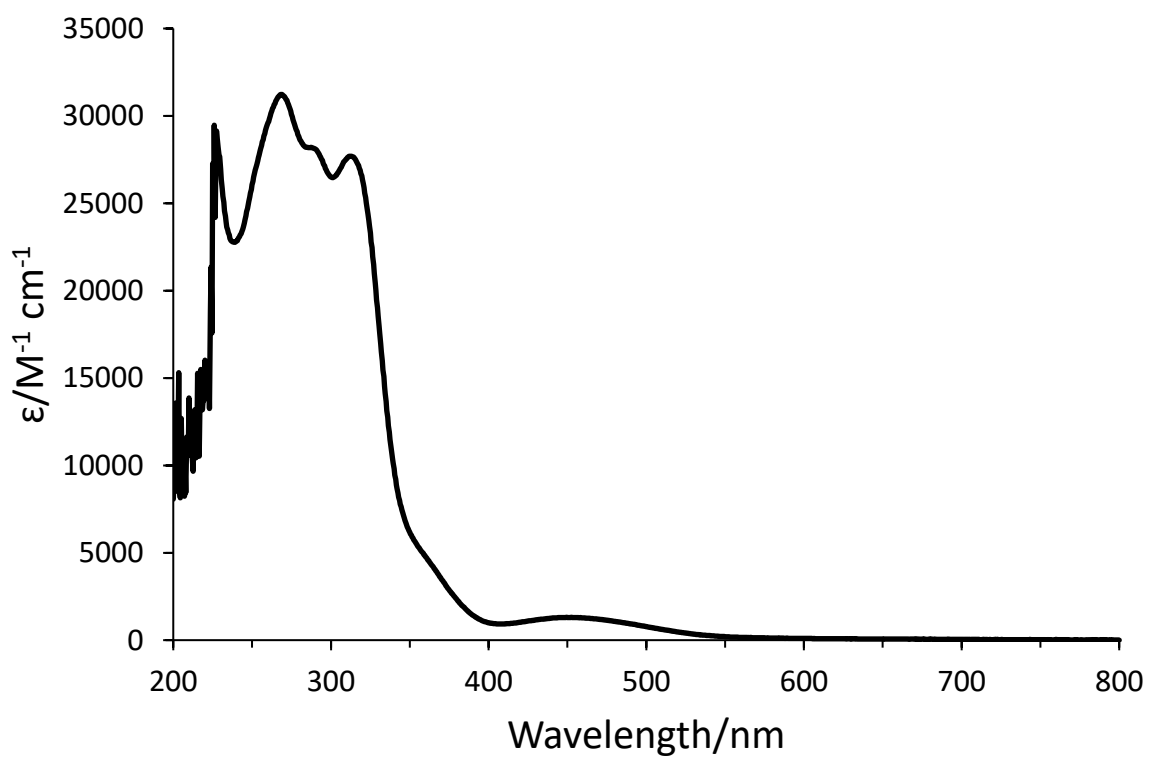


Fig S96. UV-Vis spectrum of compound **8**, measured in CH₂Cl₂.

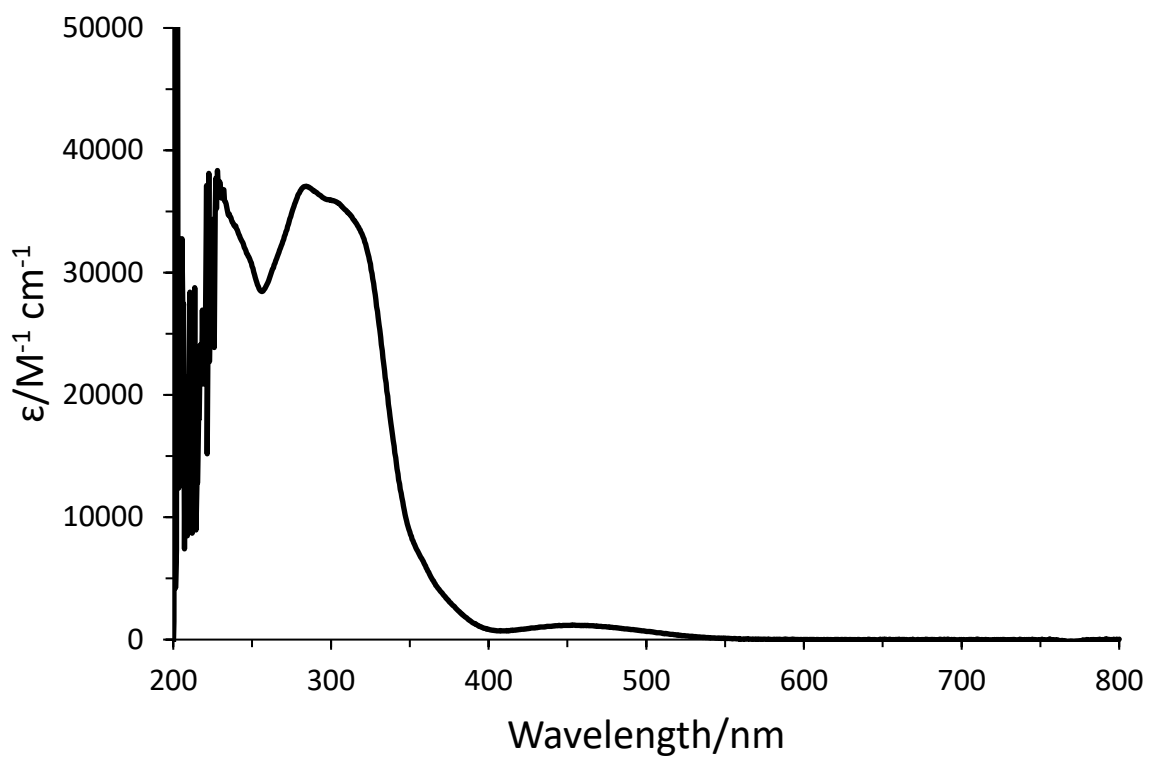


Fig S97. UV-Vis spectrum of compound **9a**, measured in CH_2Cl_2 .

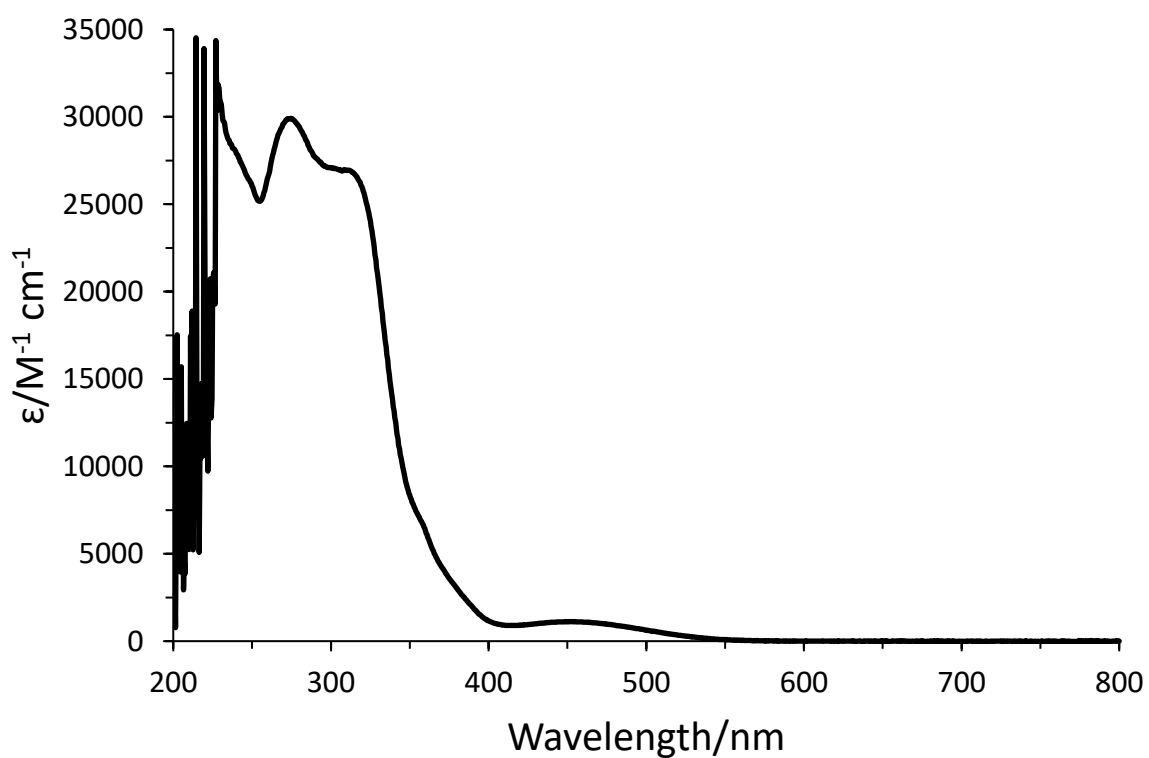


Fig S98. UV-Vis spectrum of compound **9**, measured in CH_2Cl_2 .

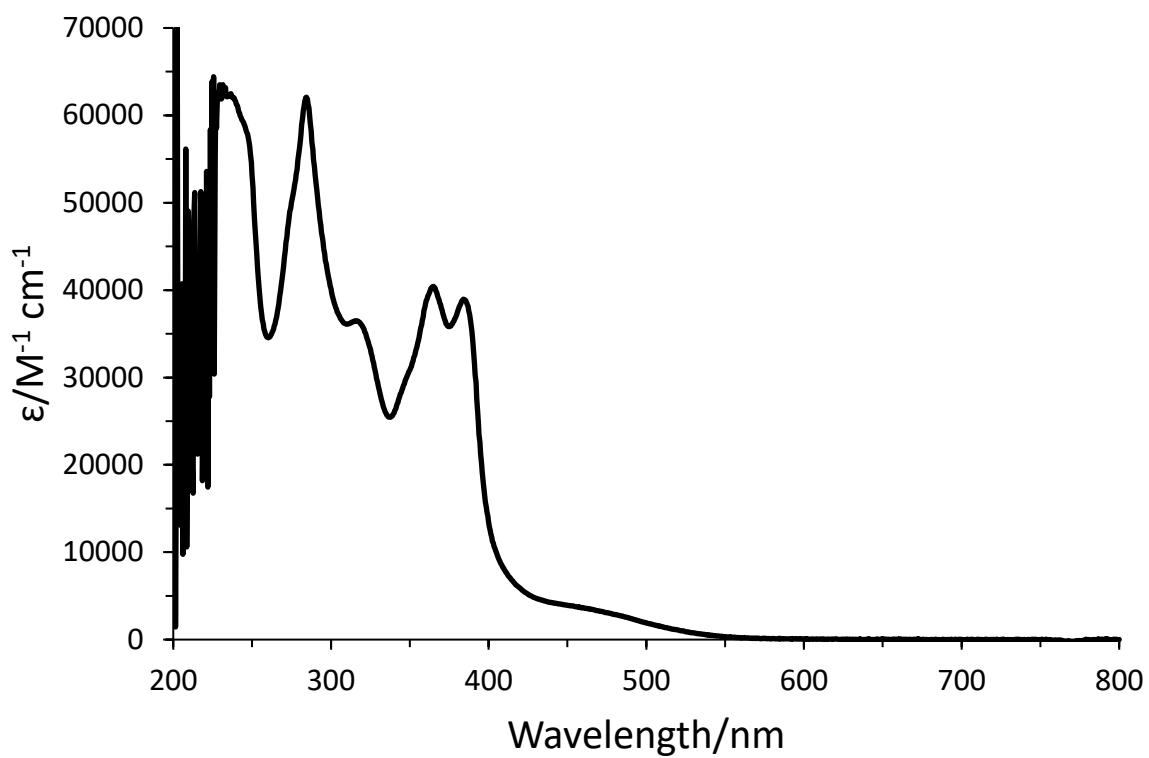


Fig S99. UV-Vis spectrum of compound **10a**, measured in CH₂Cl₂.

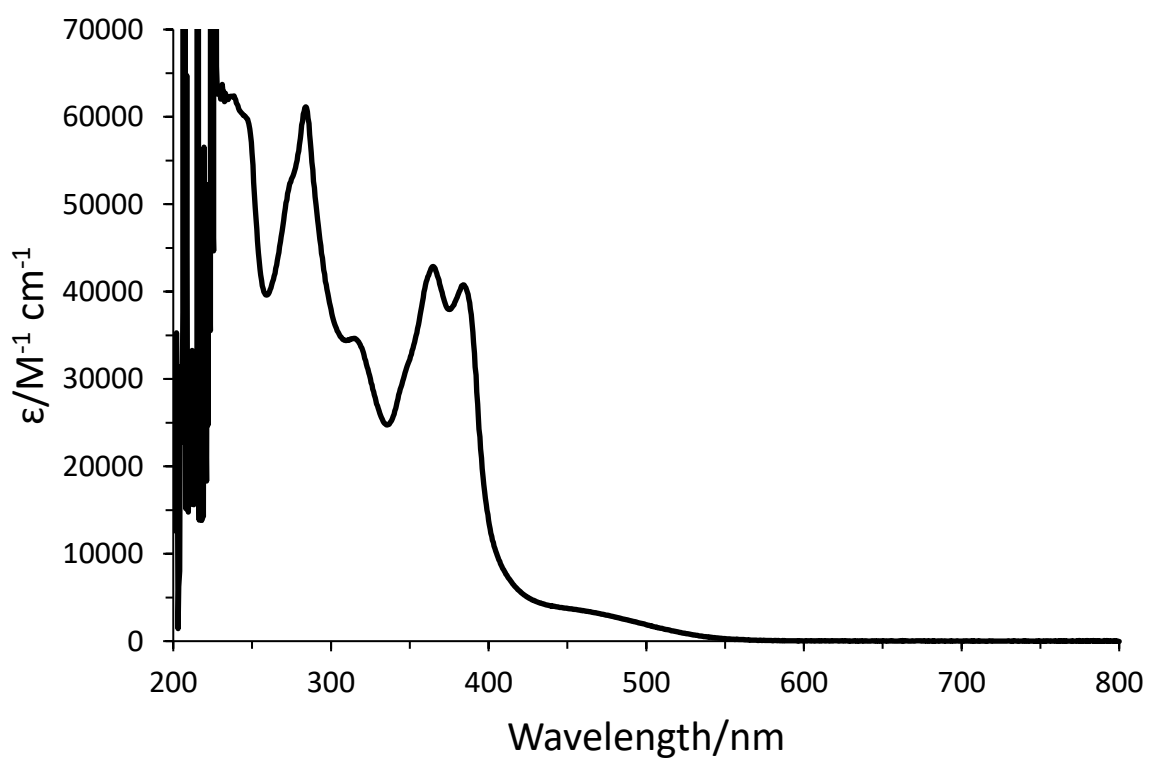


Fig S100. UV-Vis spectrum of compound **10**, measured in CH₂Cl₂.

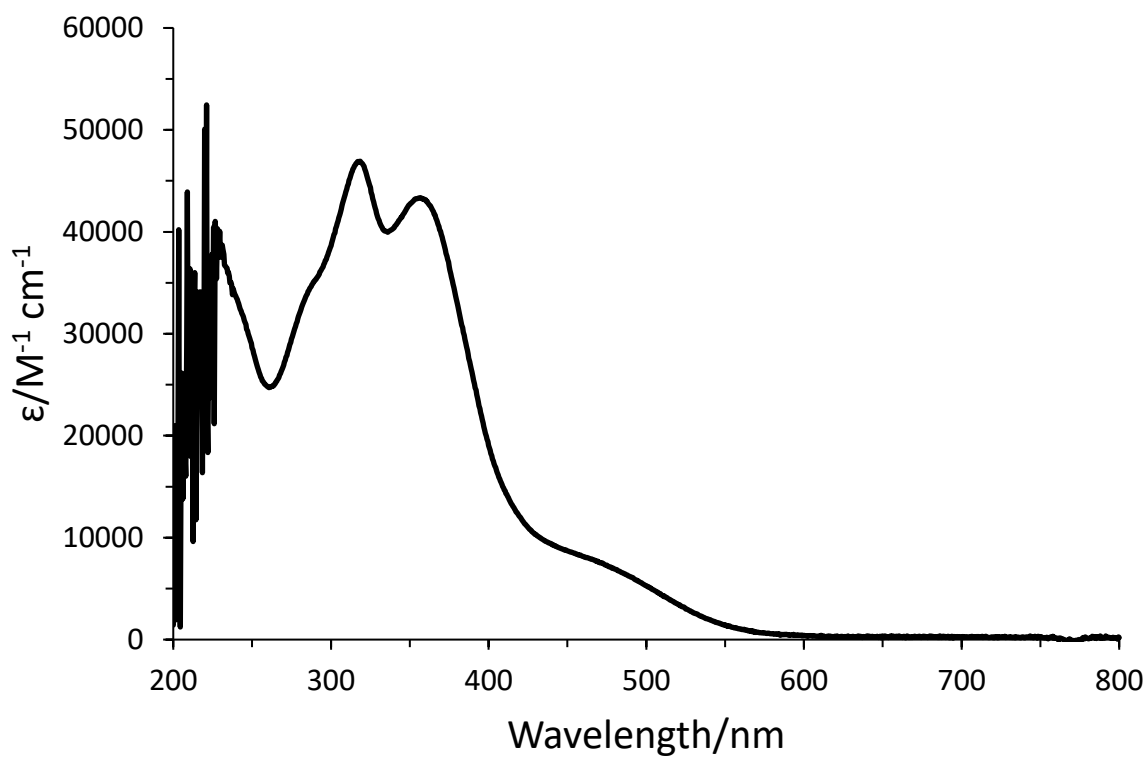


Fig S102. UV-Vis spectrum of compound **11a**, measured in CH_2Cl_2 .

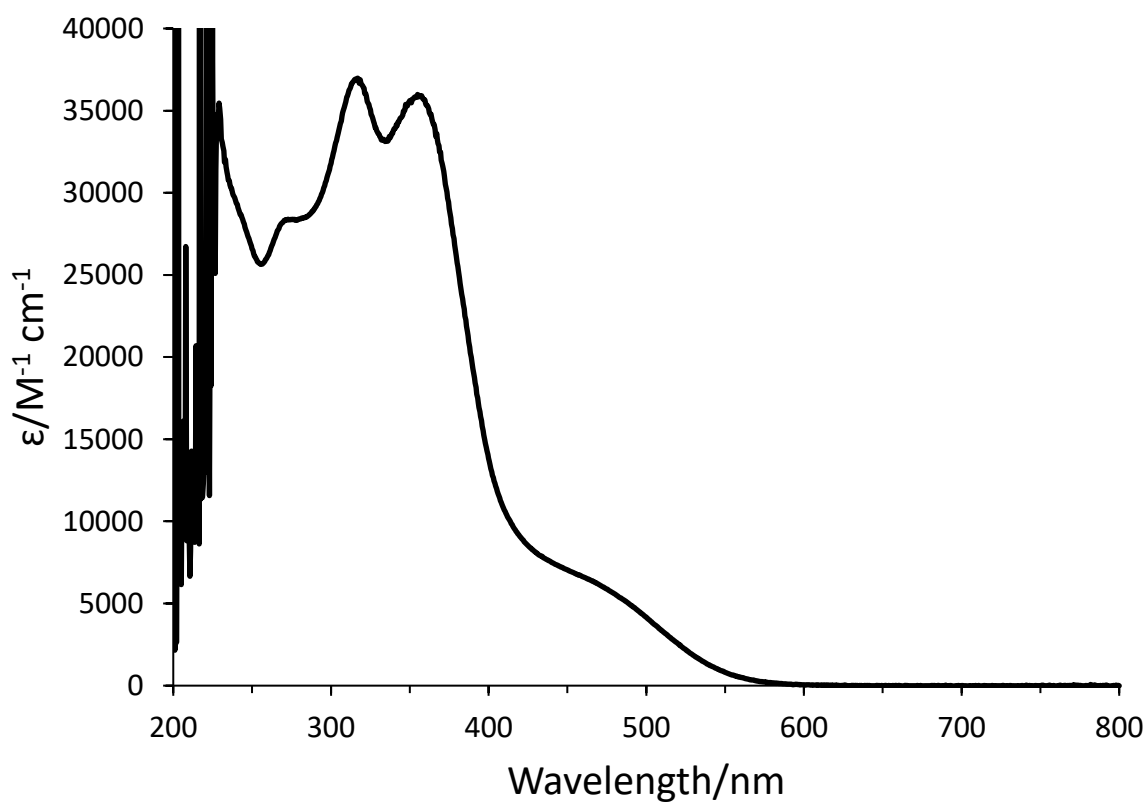


Fig S103. UV-Vis spectrum of compound **11**, measured in CH_2Cl_2 .

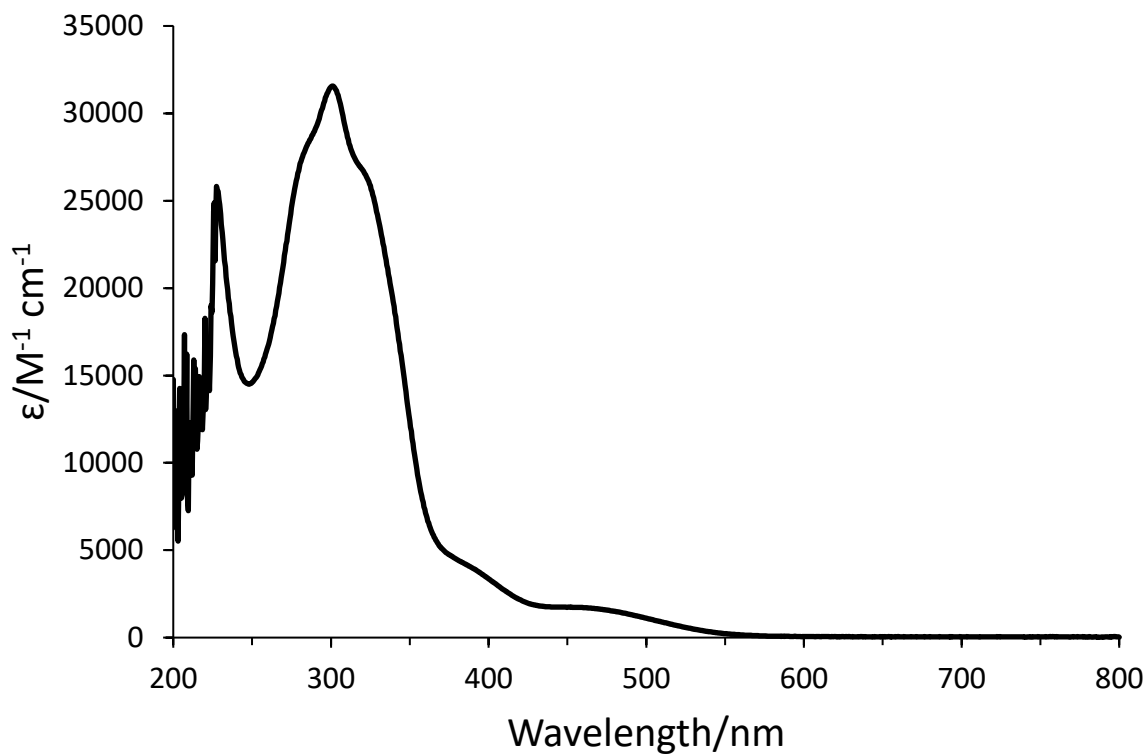


Fig S104. UV-Vis spectrum of compound **12a**, measured in CH_2Cl_2 .

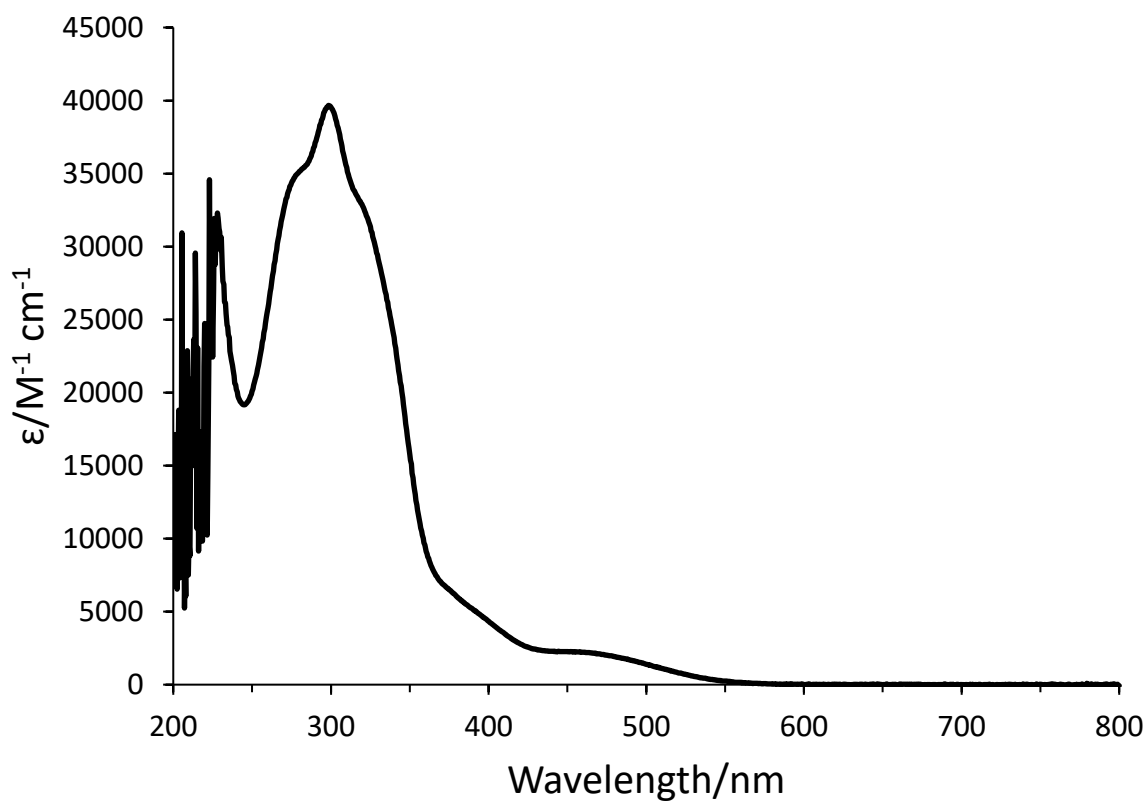


Fig S105. UV-Vis spectrum of compound **12**, measured in CH_2Cl_2 .

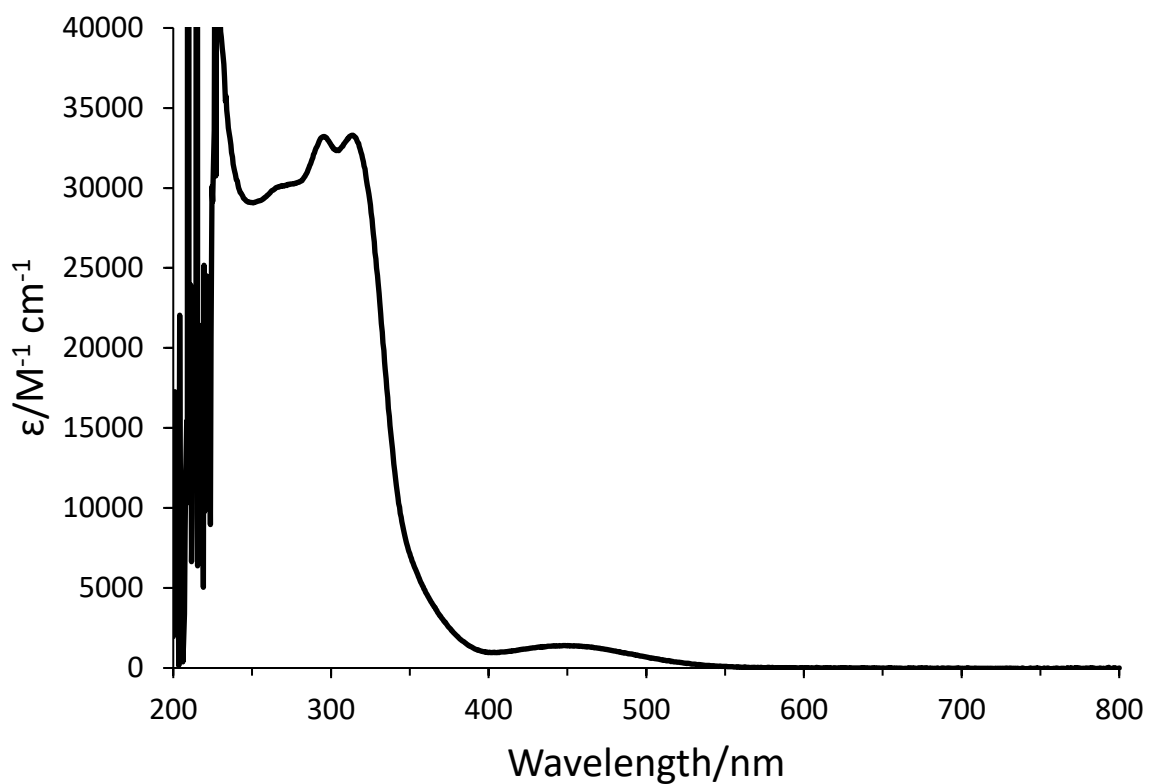


Fig S106. UV-Vis spectrum of compound **13a**, measured in CH_2Cl_2 .

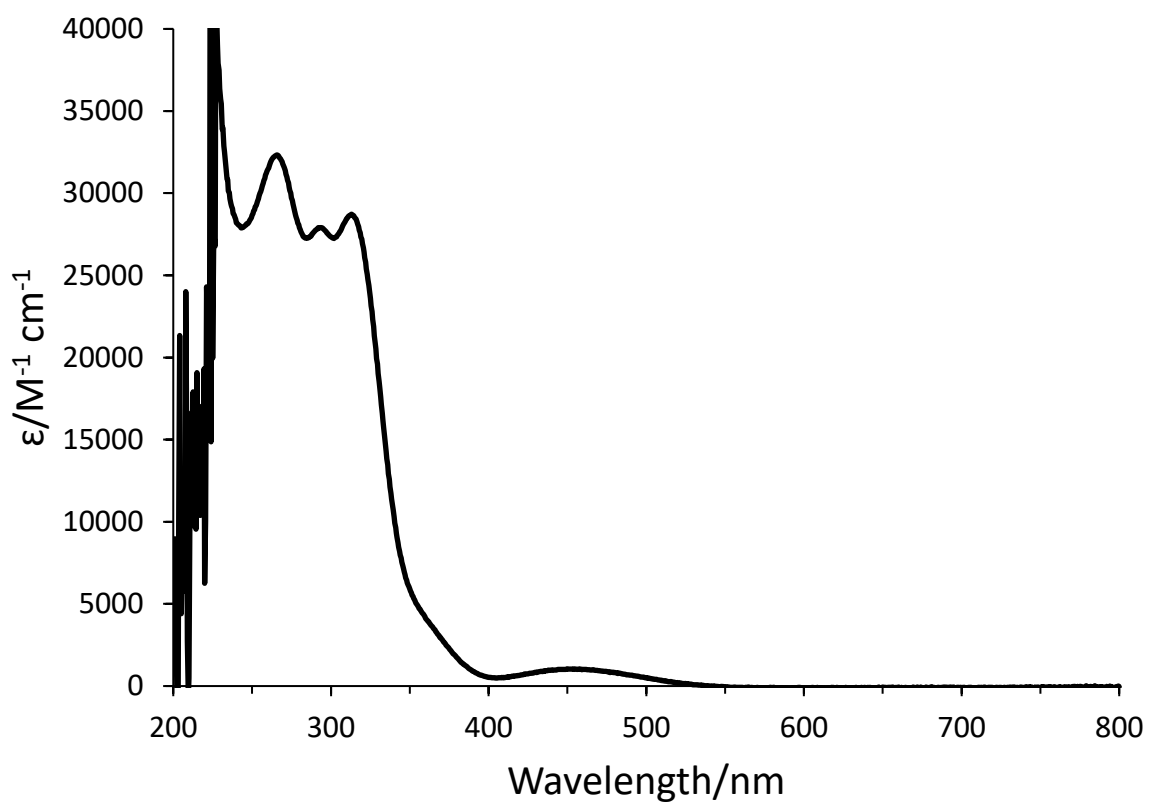


Fig S107. UV-Vis spectrum of compound **13**, measured in CH_2Cl_2 .

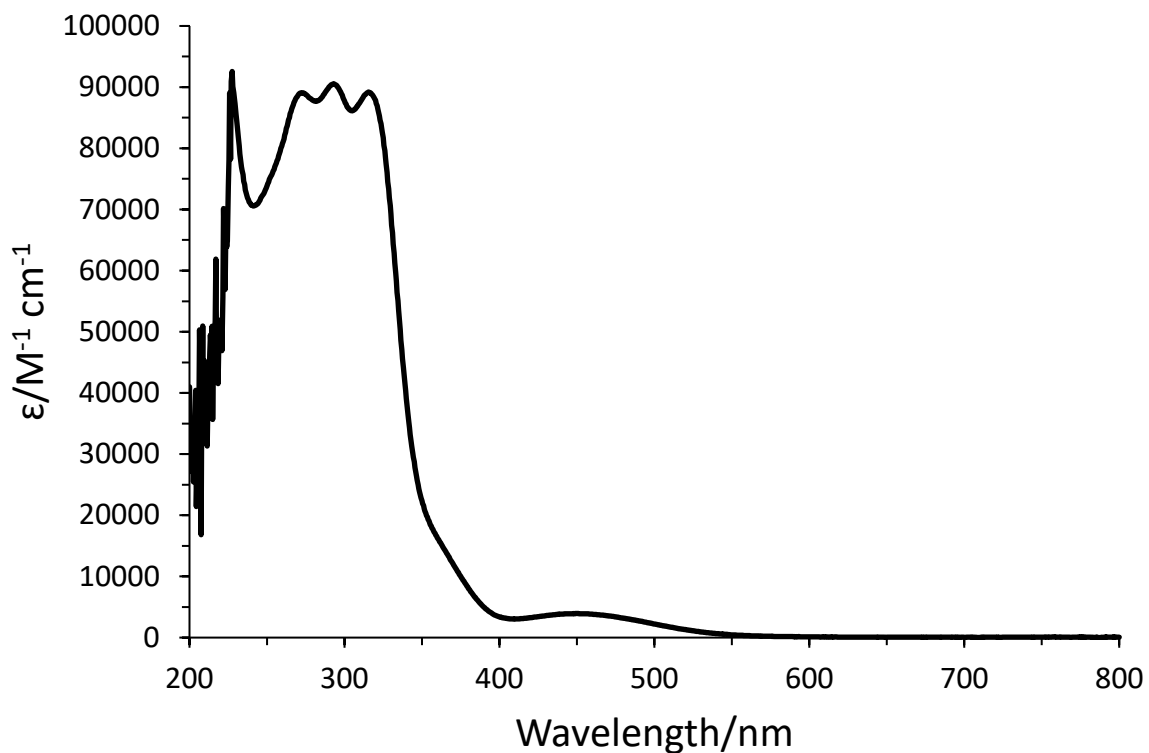


Fig S108. UV-Vis spectrum of compound **14a**, measured in CH₂Cl₂.

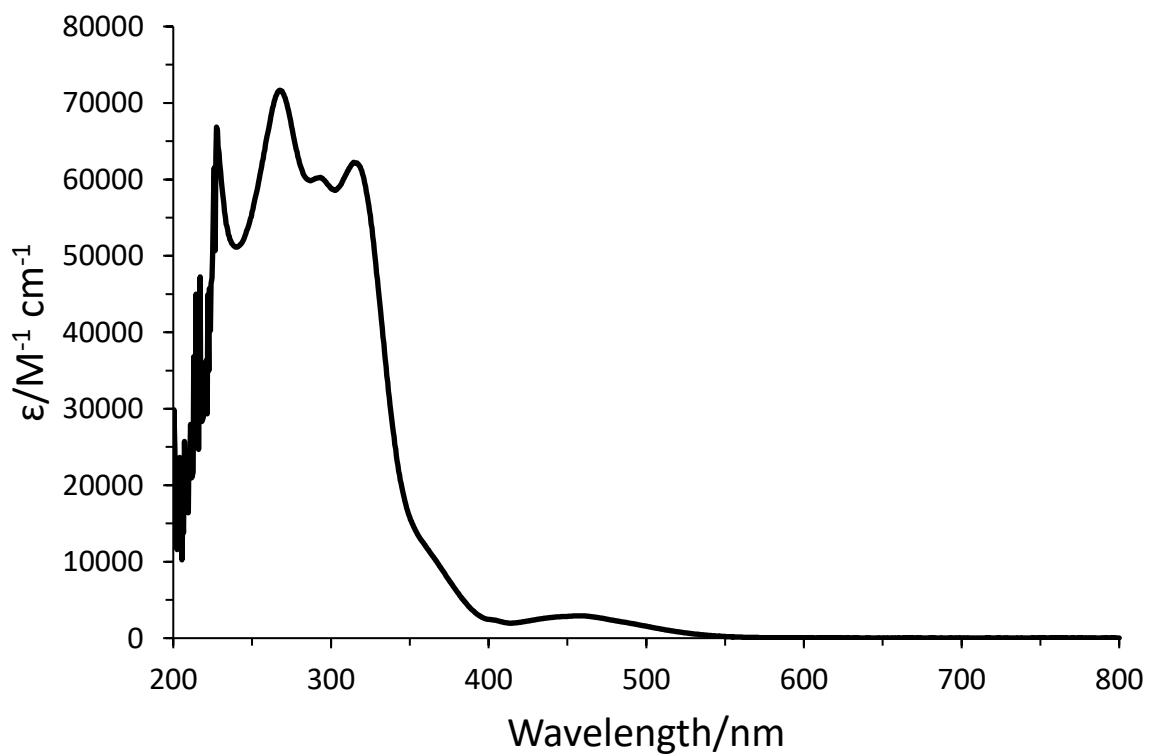


Fig S109. UV-Vis spectrum of compound **14**, measured in CH₂Cl₂.

4. Infrared Spectroscopy

Table S3: Peak positions (4000-1450 cm^{-1}) obtained from infrared-spectroscopy of cyanoethyl/thioacetate compounds. Relative peak intensities are denoted as 'w' (weak), 'm' (medium) or 's' (strong).

Compound	Absorption Frequency (cm^{-1})
2a	3104 (w), 3090 (w), 3056 (w), 3043 (w), 2247 (m), 2227 (w), 2211 (m), 1906 (w), 1653 (w), 1592 (w), 1544 (w), 1496 (s), 1458 (w)
2	3099 (w), 3051 (w), 2921 (w), 2852 (w), 2208 (m), 1906 (w), 1704 (s), 1591 (m), 1546 (w), 1493 (m), 1455 (w)
5a	3089 (w), 2958 (w), 2926 (m), 2852 (w), 2251 (m), 2009 (m), 1588 (s), 1499 (s), 1487 (s)
5	3101 (w), 3059 (w), 2957 (w), 2920 (m), 2851 (w), 2208 (w), 1691 (s), 1593 (w), 1499 (m), 1456 (w)
6a	3112 (w), 3083 (m), 2954 (w), 2926 (m), 2851 (w), 2247 (m), 2205 (m), 1913 (w), 1733 (w), 1653 (w), 1590 (s), 1546 (w), 1497 (s), 1457 (m)
6	3111 (w), 3086 (w), 3084 (w), 2957 (m), 2919 (m), 2851 (m), 2203 (m), 2161 (w), 1736 (m), 1691 (s), 1590 (m), 1547 (w), 1491 (m), 1454 (m)
7a	3027 (w), 2955 (w), 2923 (m), 2853 (w), 2247 (w), 2212 (m), 1715 (w), 1593 (s), 1585 (s), 1538 (w), 1498 (m), 1457 (w)
7	2956 (w), 2919 (w), 2851 (w), 2210 (m), 1737 (m), 1707 (s), 1592 (s), 1537 (w), 1498 (w), 1456 (w)
8a	3083 (w), 2954 (w), 2918 (w), 2850 (w), 2244 (w), 2210 (m), 1656 (w), 1591 (m), 1563 (m), 1497 (s), 1488 (s)
8	3102 (w), 3082 (w), 3023 (w), 2958 (m), 2922 (m), 2852 (m), 2209 (m), 1700 (s), 1592 (m), 1559 (m), 1487 (s)
9a	3099 (w), 3066 (w), 2960 (w), 2926 (w), 2853 (w), 2254 (w), 2222 (m), 1894 (w), 1773 (w), 1735 (w), 1589 (m), 1576 (s), 1558 (s), 1506 (s), 1474 (s)
9	3086 (w), 3055 (w), 2955 (w), 2923 (w), 2853 (w), 2218 (m), 2210 (m), 1703 (s), 1590 (m), 1578 (s), 15558 (s), 1496 (w), 1472 (m)
10a	3089 (w), 3045 (w), 2926 (w), 2852 (w), 2252 (m), 2211 (m), 2197 (m), 1808 (w), 1773 (w), 1735 (w), 1642 (w), 1623 (w), 1598 (s), 1582 (m), 1498 (s), 1487 (s), 1457 (w)
10	3104 (w), 3086 (w), 3037 (w), 3023 (w), 2918 (w), 2209 (m), 1801 (w), 1697 (s), 1600 (m), 1585 (m), 1500 (m), 1489 (m), 1457 (w)
11a	3092 (w), 3060 (w), 2926 (w), 2851 (w), 2250 (w), 2199 (m), 1740 (w), 1655 (w), 1593 (s), 1503 (s), 1482 (m), 1464 (m)
11	3058 (w), 2918 (m), 2851 (m), 2204 (m), 1732 (s), 1700 (s), 1594 (m), 1500 (m), 1484 (w), 1464 (m)
12a	3086 (w), 2929 (w), 2849 (w), 2247 (w), 2204 (m), 1696 (s), 1684 (s), 1598 (s), 1560 (m), 1500 (m), 1457 (w)
12	3086 (w), 3055 (w), 2954 (w), 2920 (m), 2849 (m), 2735 (w), 2203 (m), 1700 (s), 1598 (s), 1560 (m), 1496 (m), 1457 (w)

Compound	Absorption Frequency (cm ⁻¹)
13a	3420 (m), 3376 (m), 3099 (w), 3046 (w), 2976 (w), 2928 (w), 2853 (w), 2252 (w), 2209 (m), 2031 (w), 1948 (w), 1909 (w), 1751 (w), 1707 (m), 1591 (w), 1561 (m), 1512 (s), 1498 (s), 1466 (m), 1457 (m)
13	3411 (m), 3371 (m), 3099 (w), 3030 (w), 2957 (w), 2920 (m), 2852 (w), 2208 (m), 2033 (w), 1951 (w), 1909 (w), 1694 (s), 1591 (m), 1562 (w), 1512 (m), 1498 (m), 1456 (w)
14a	3094 (w), 2959 (w), 2924 (m), 2852 (w), 2251 (w), 2210 (m), 1734 (m), 1577 (m), 1545 (w), 1499 (m), 1456 (w)
14	3099 (w), 2954 (w), 2922 (m), 2852 (w), 2210 (m), 1734 (m), 1698 (s), 1581 (w), 1578 (m), 1500 (w), 1456 (w)

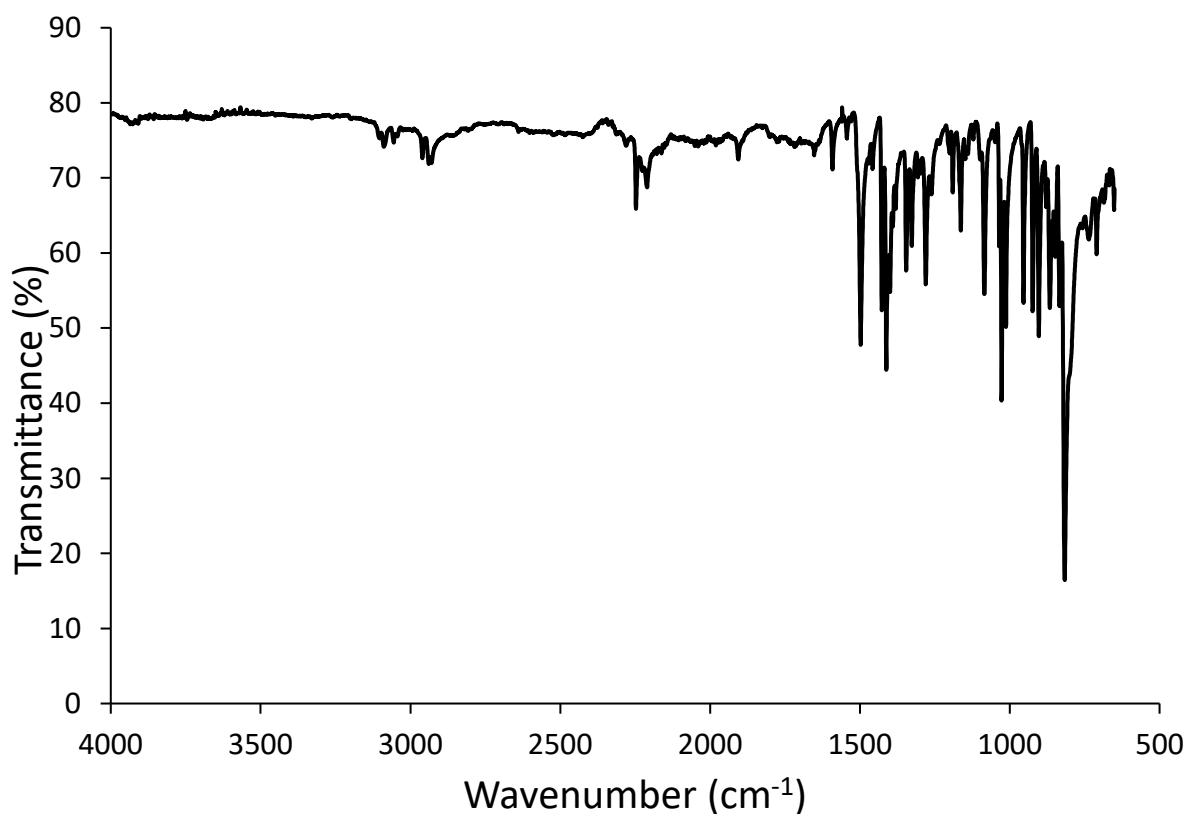


Fig S110. IR spectrum of compound 2a.

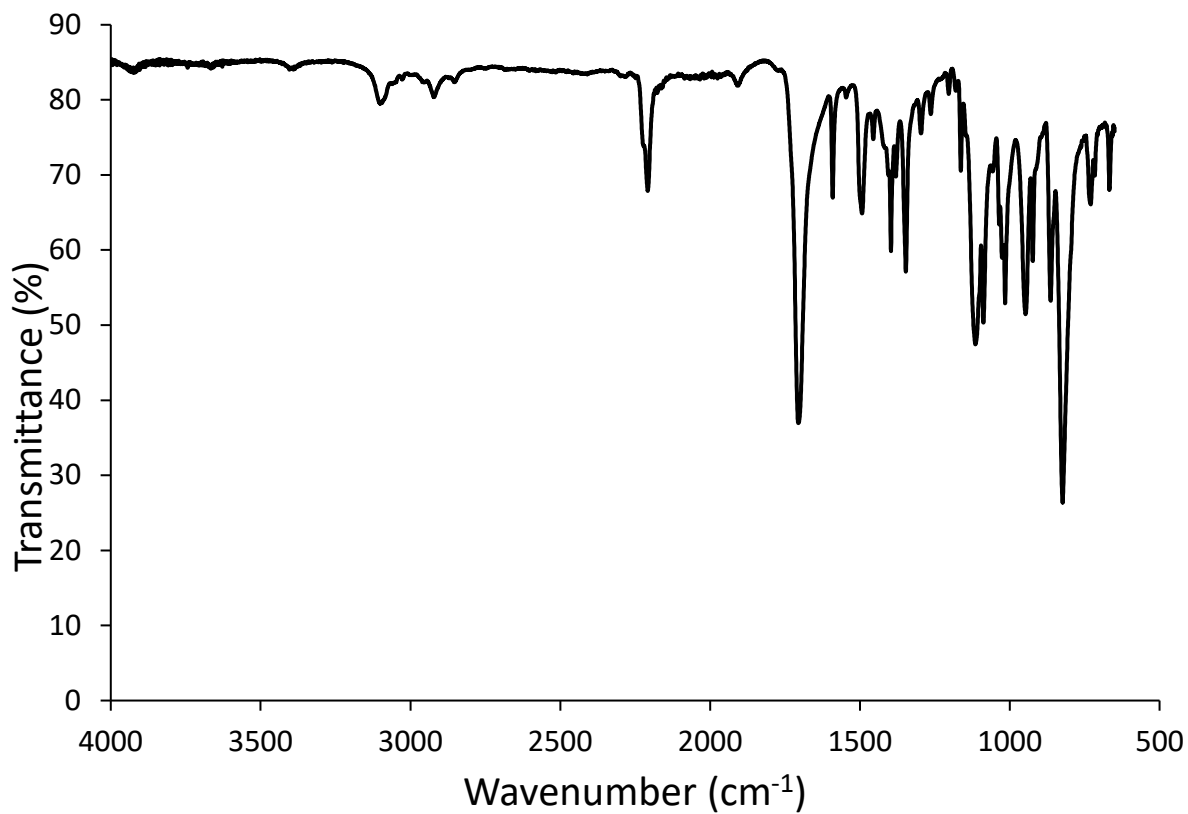


Fig S111. IR spectrum of compound 2.

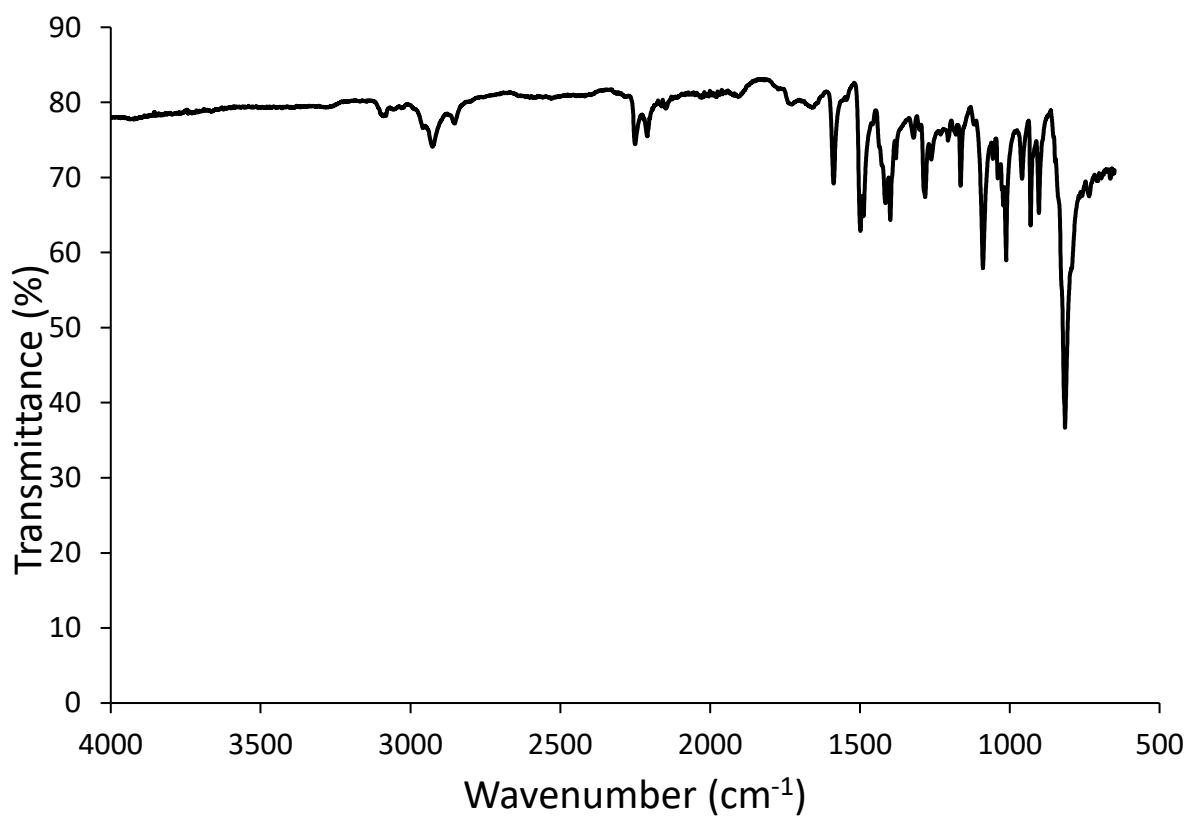


Fig S112. IR spectrum of compound 5a.

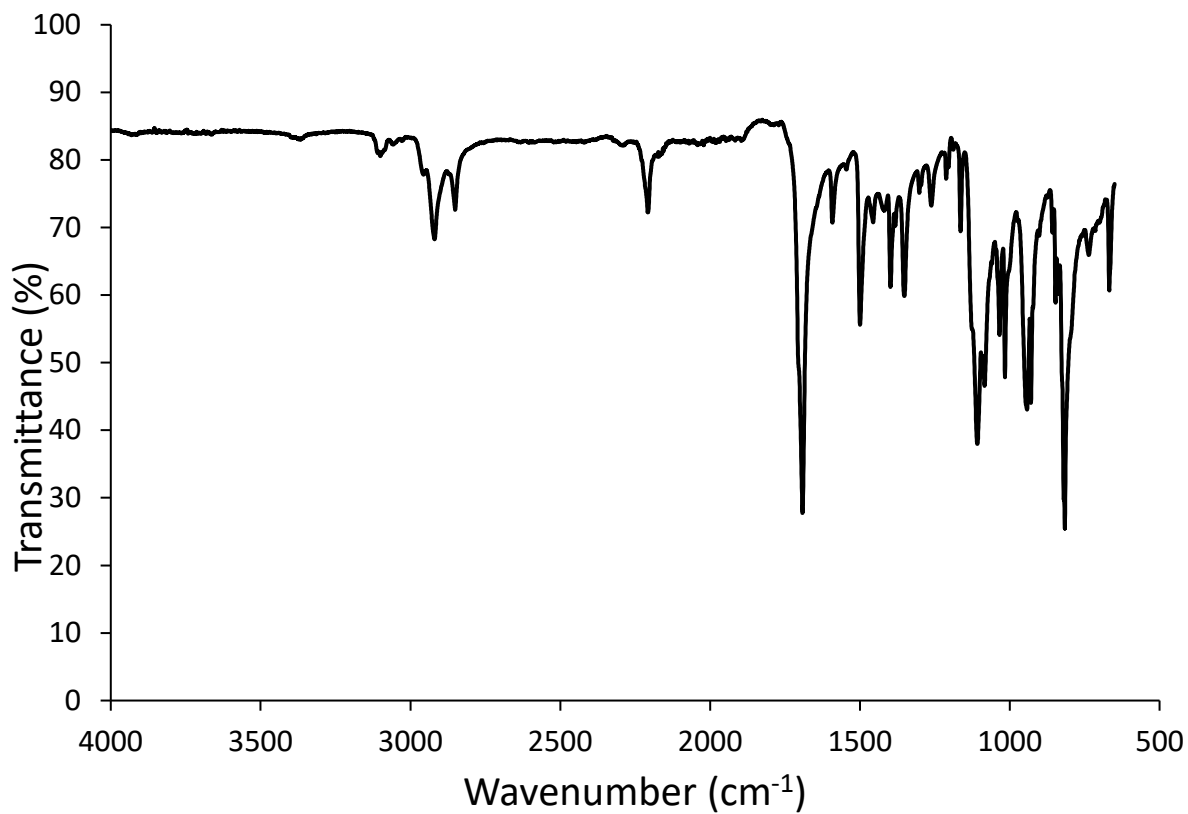


Fig S113. IR spectrum of compound 5.

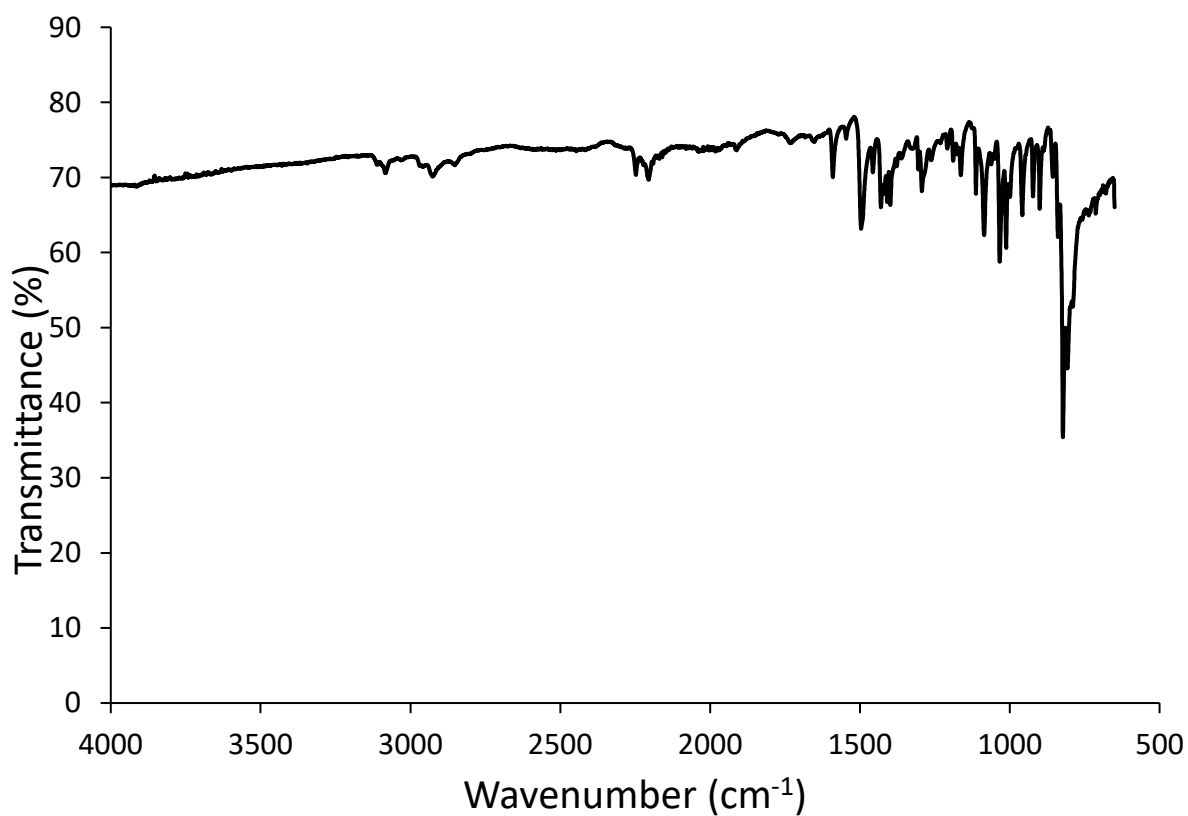


Fig S114. IR spectrum of compound 6a.

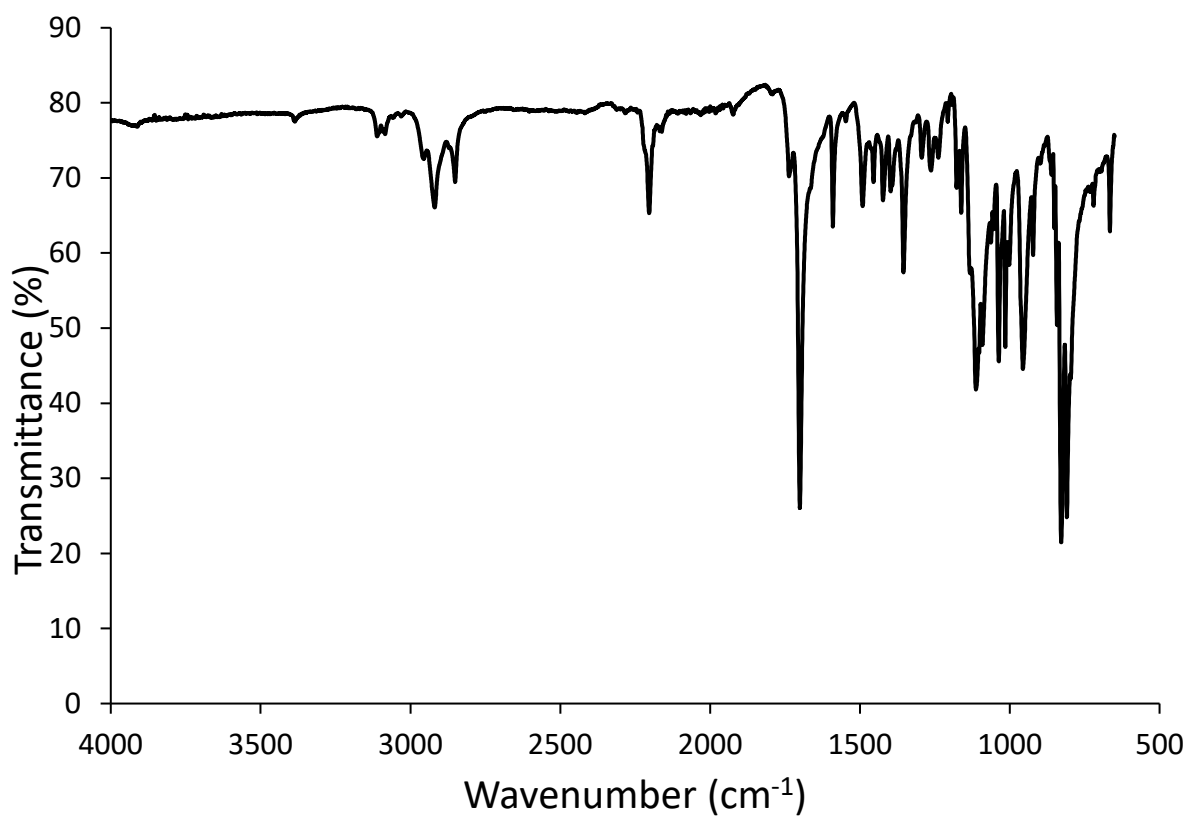


Fig S115. IR spectrum of compound 6.

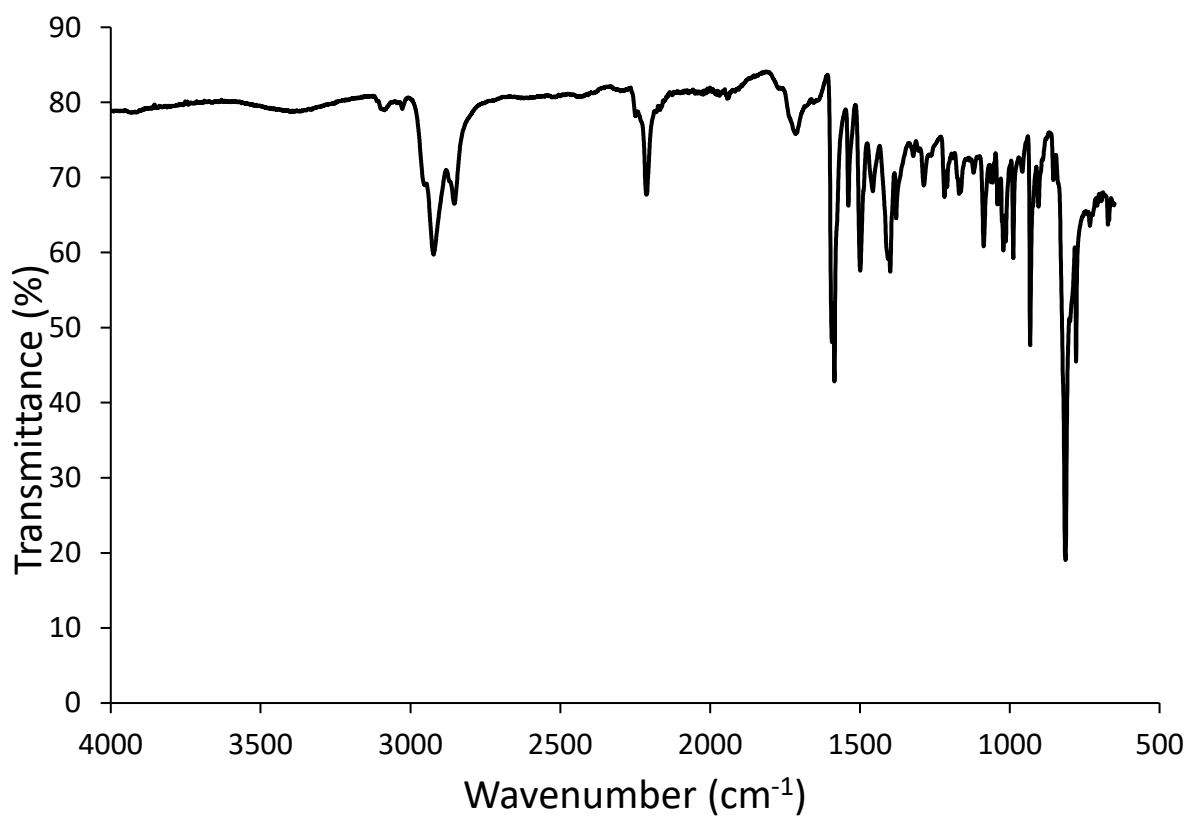


Fig S116. IR spectrum of compound 7a.

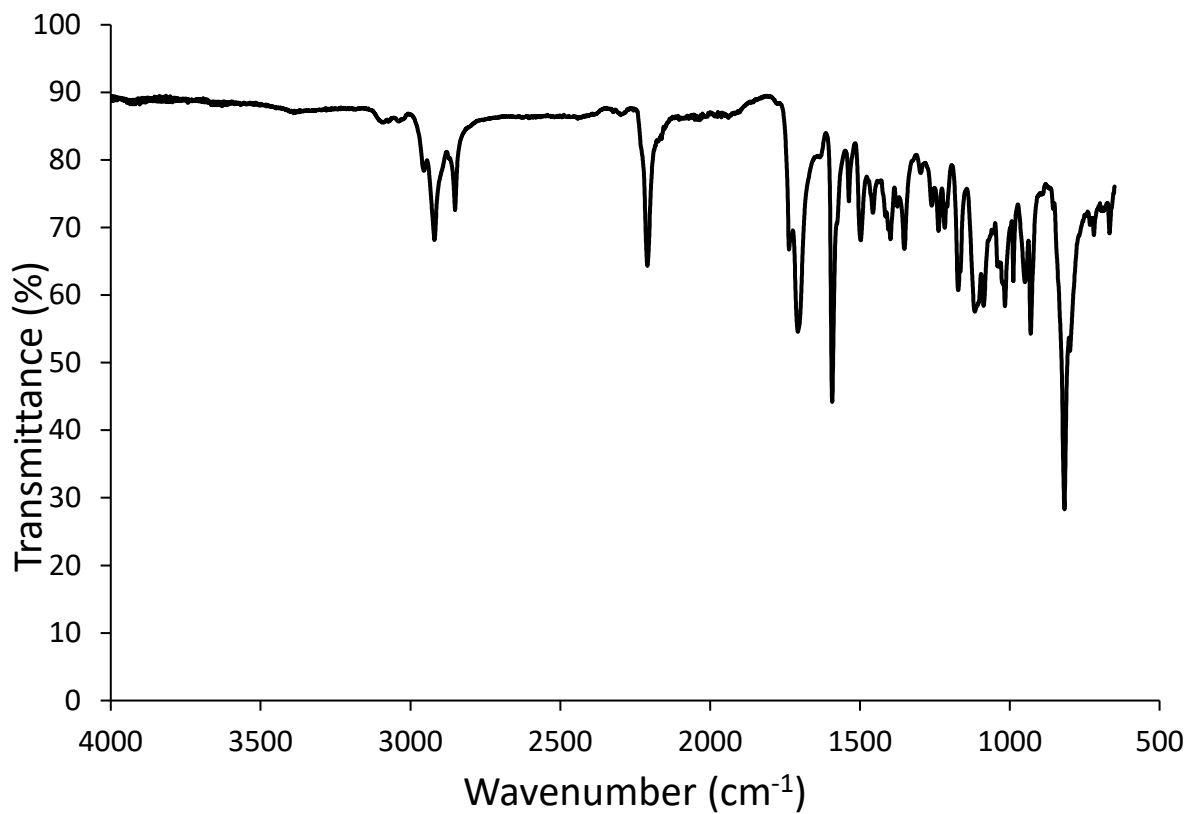


Fig S117. IR spectrum of compound 7.

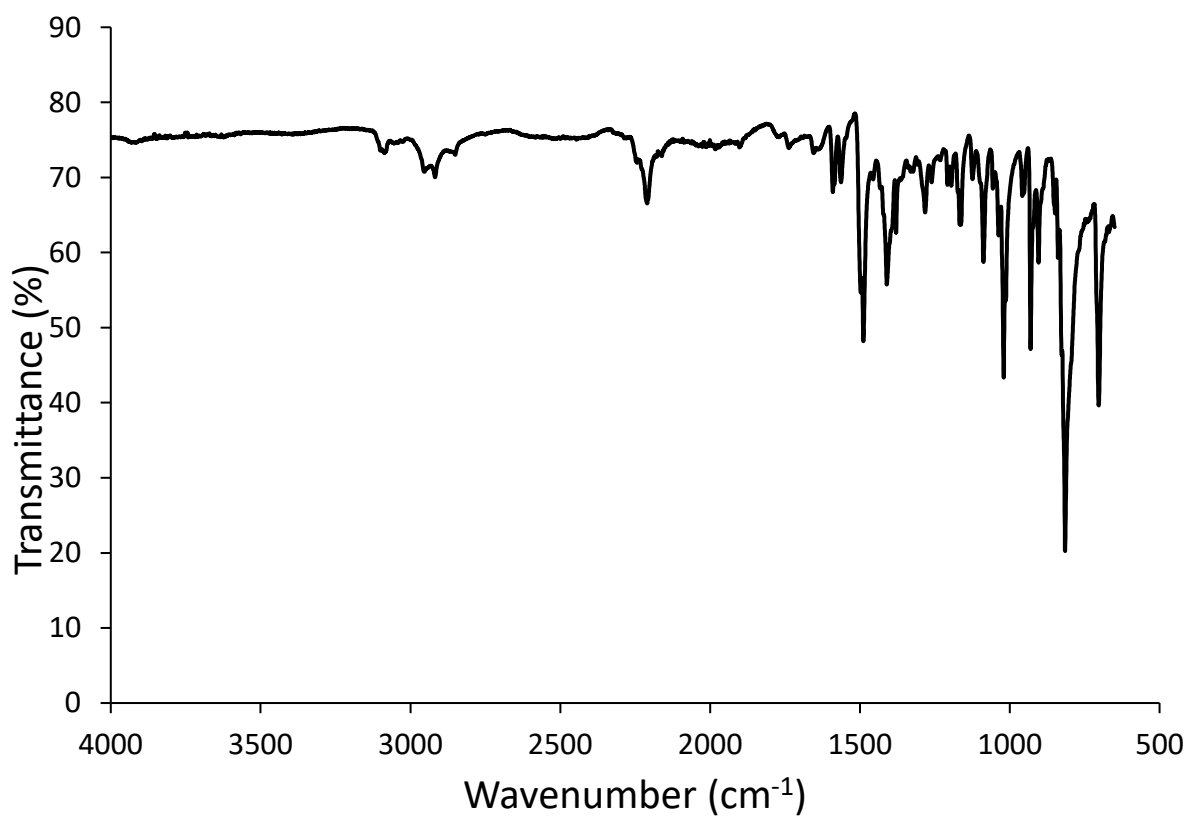


Fig S118. IR spectrum of compound 8a.

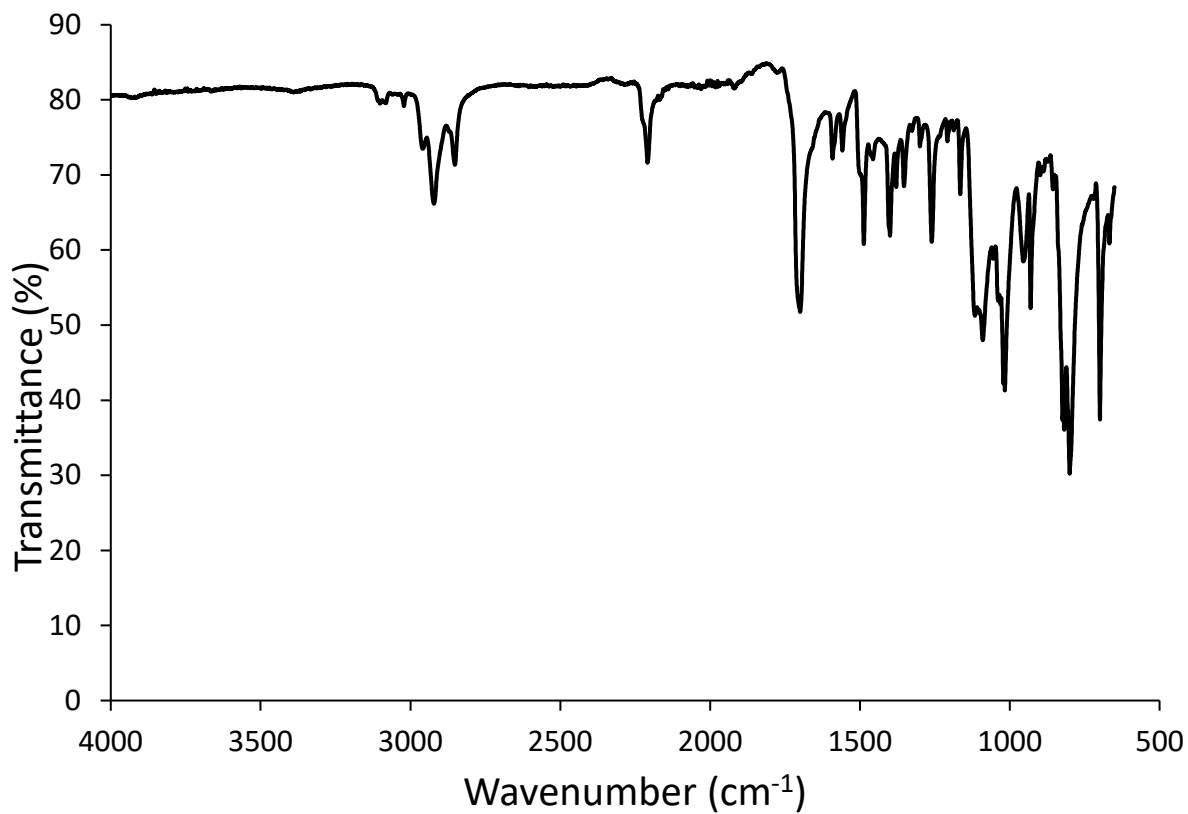


Fig S119. IR spectrum of compound **8**.

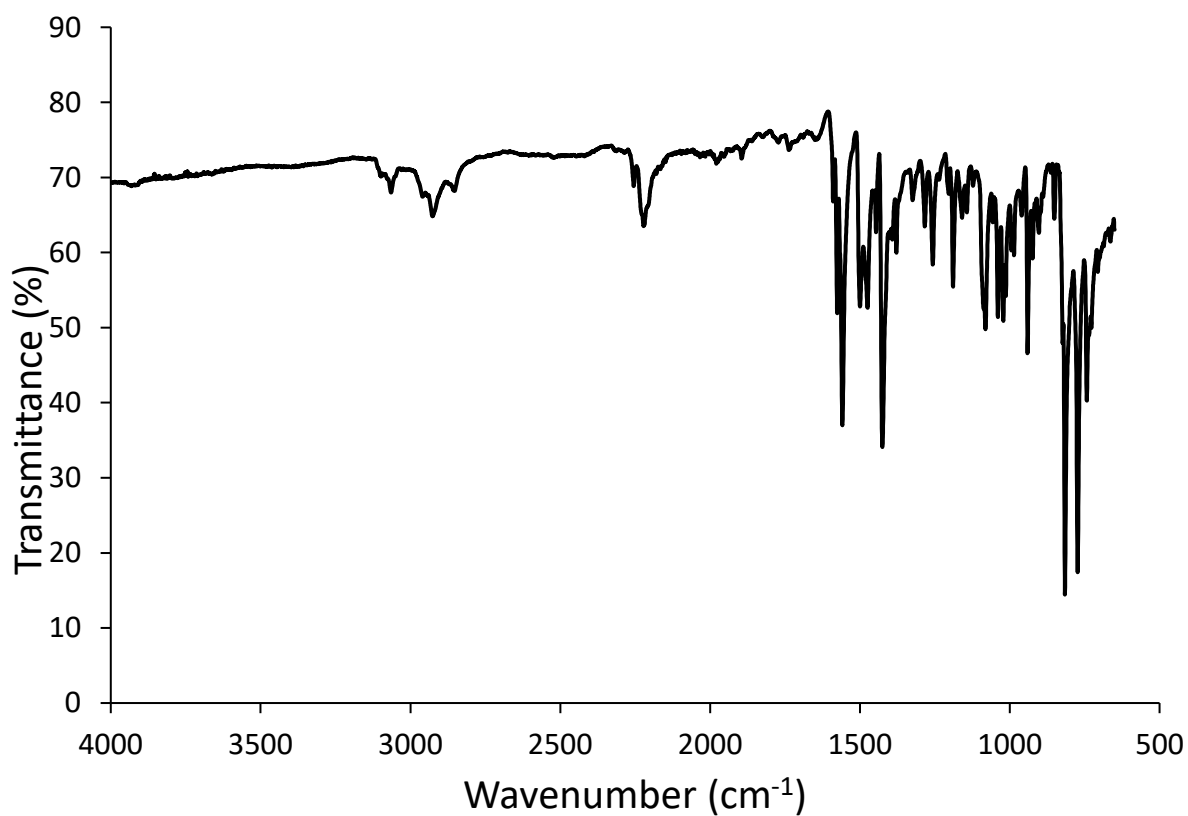


Fig S120. IR spectrum of compound **9a**.

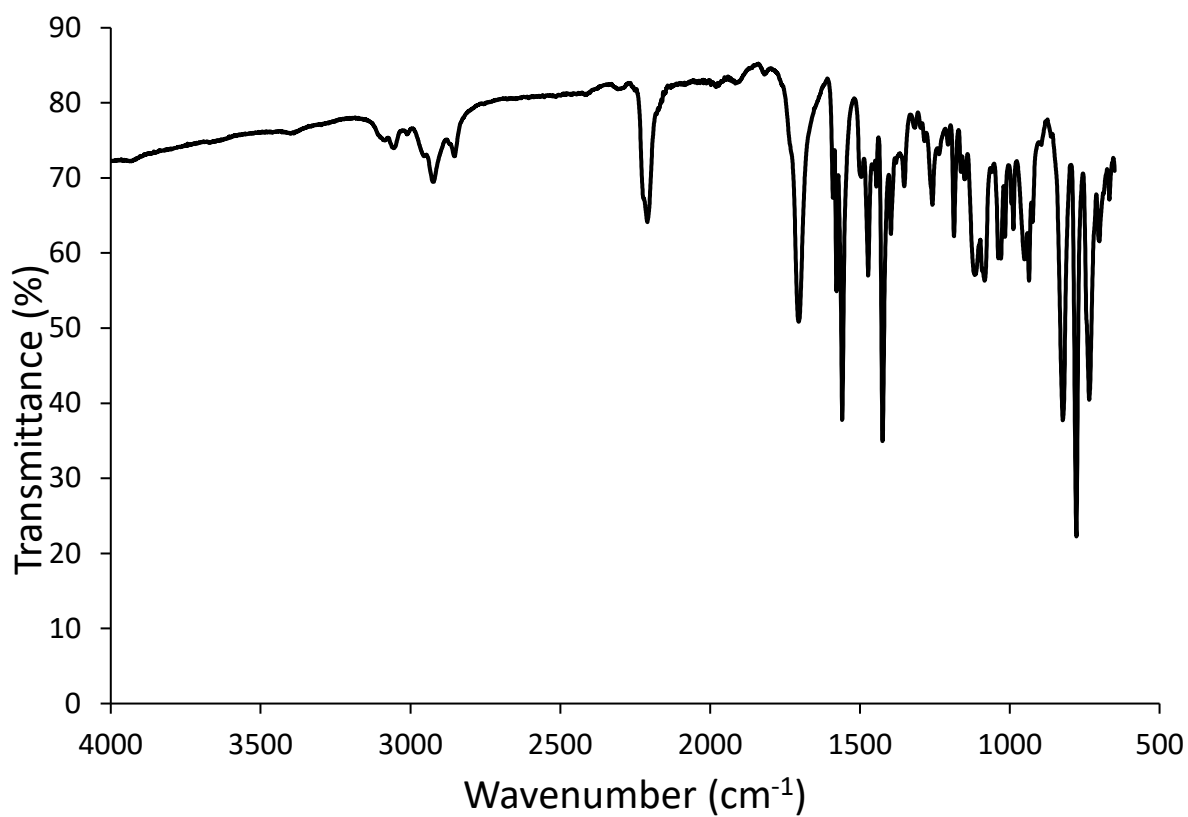


Fig S121. IR spectrum of compound 9.

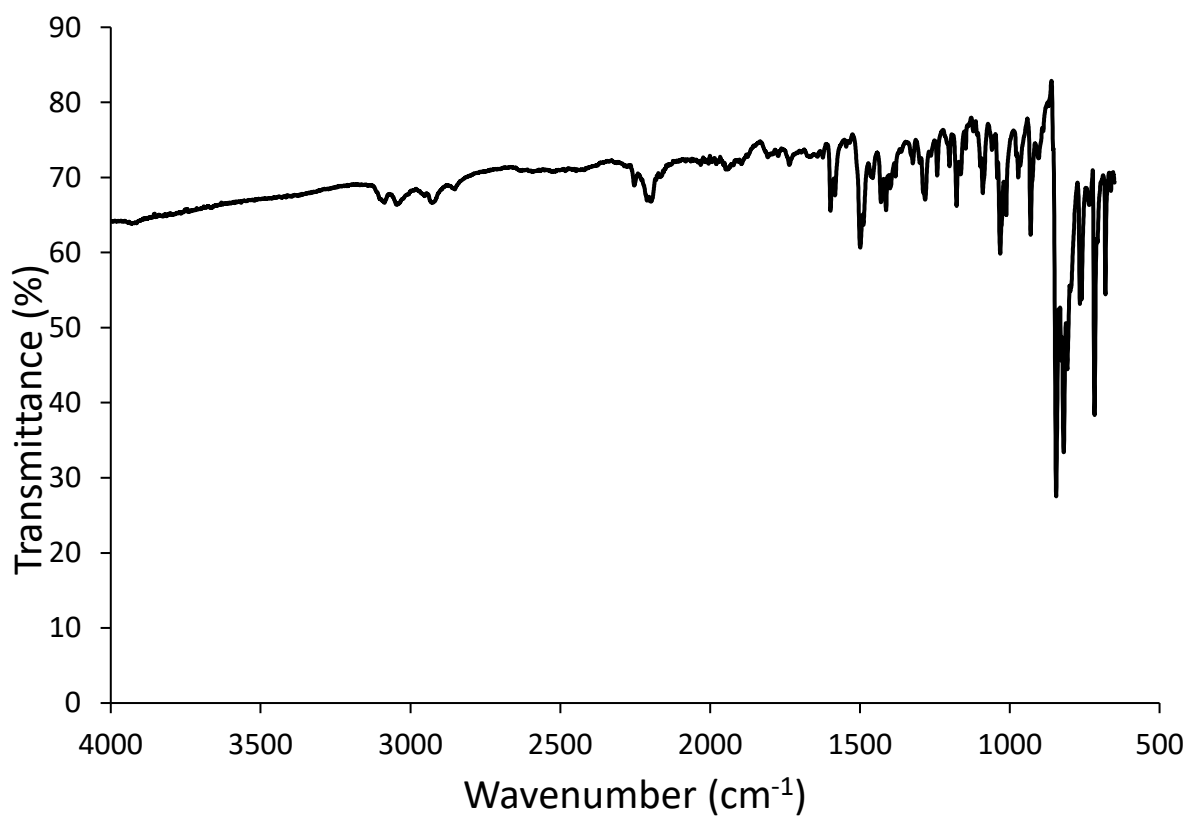


Fig S122. IR spectrum of compound 10a.

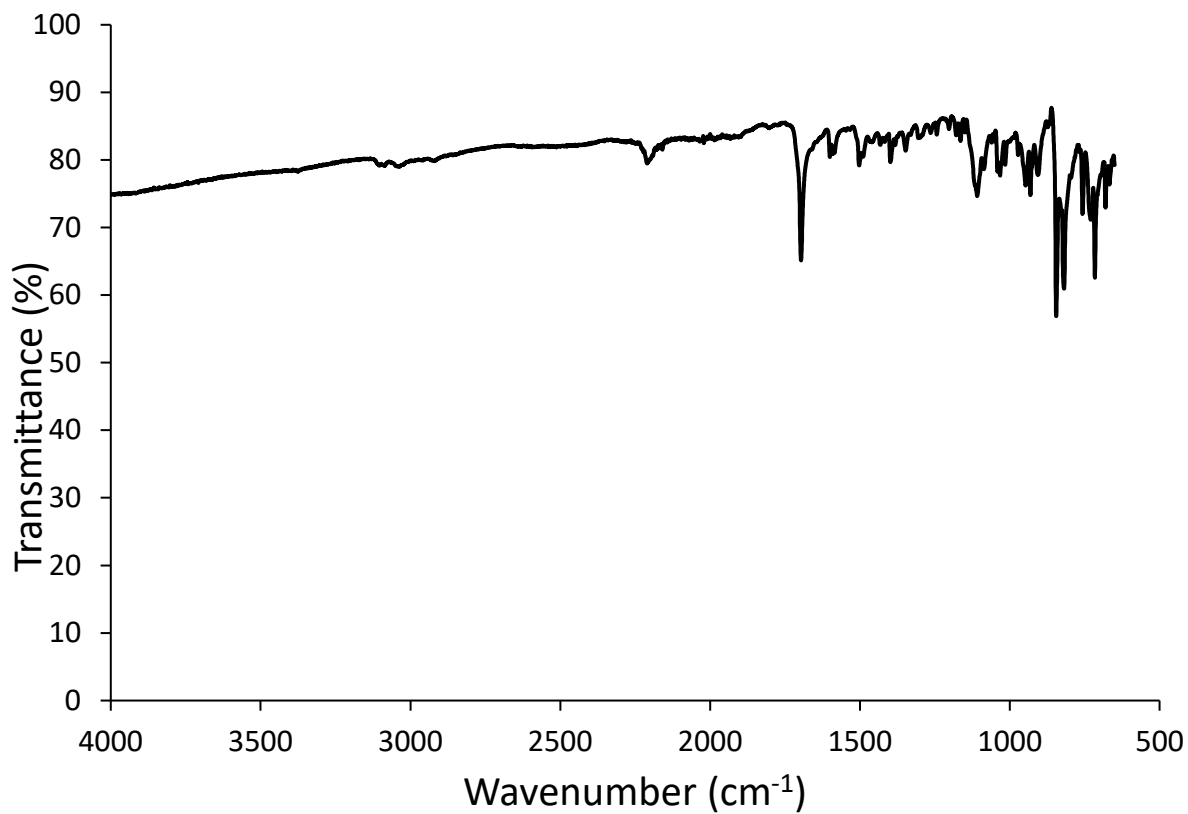


Fig S123. IR spectrum of compound **10**.

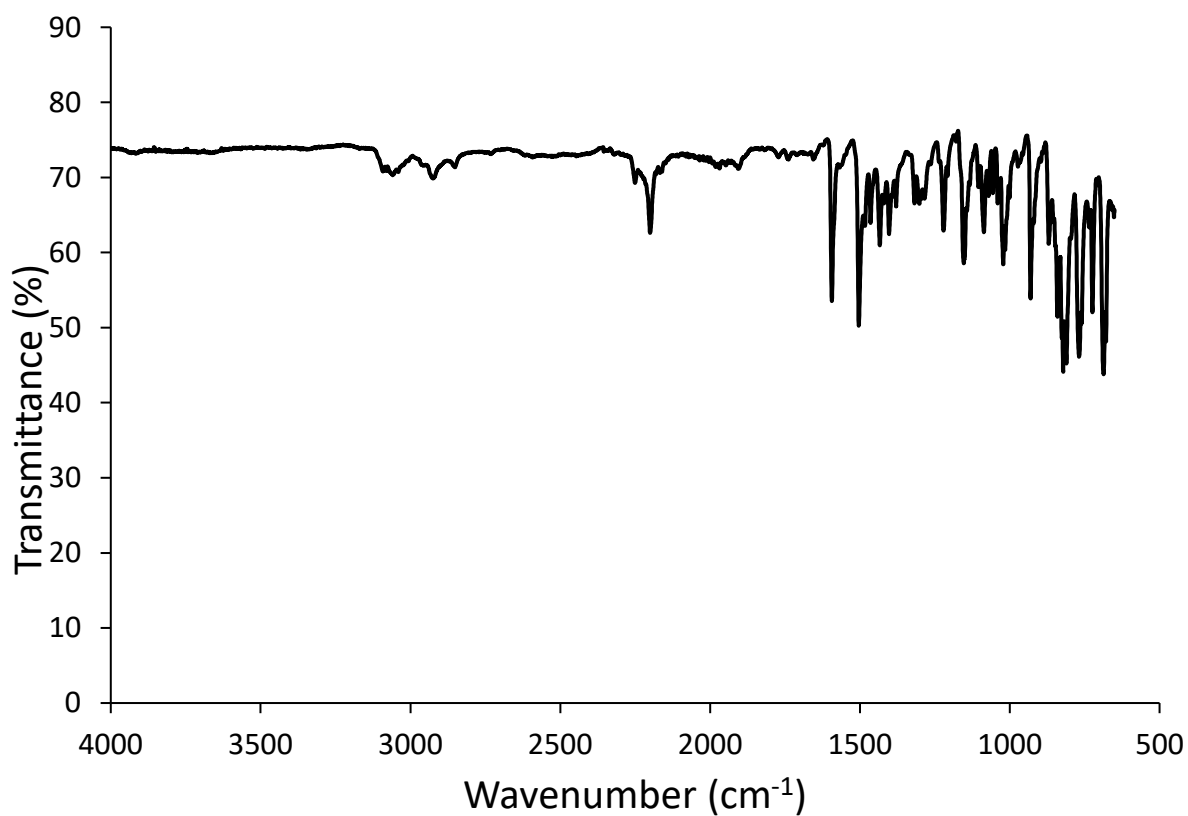


Fig S124. IR spectrum of compound **11a**.

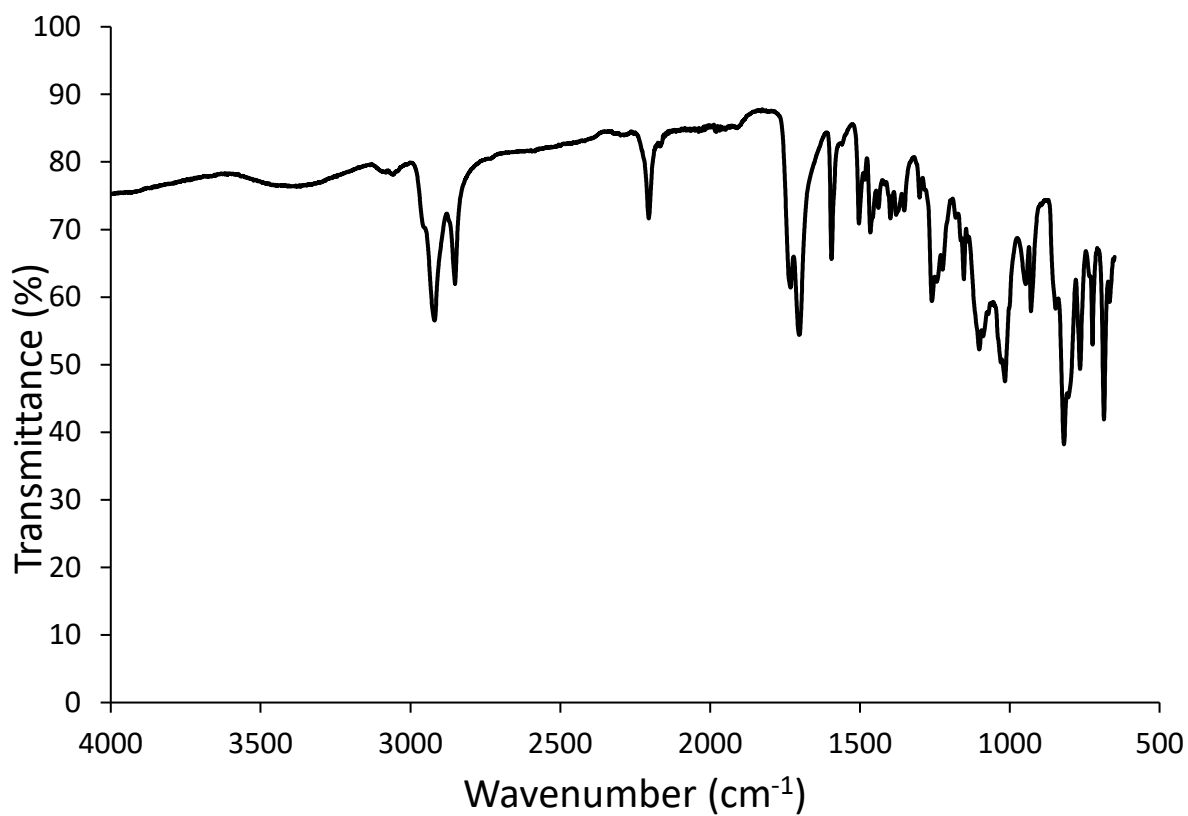


Fig S125. IR spectrum of compound 11.

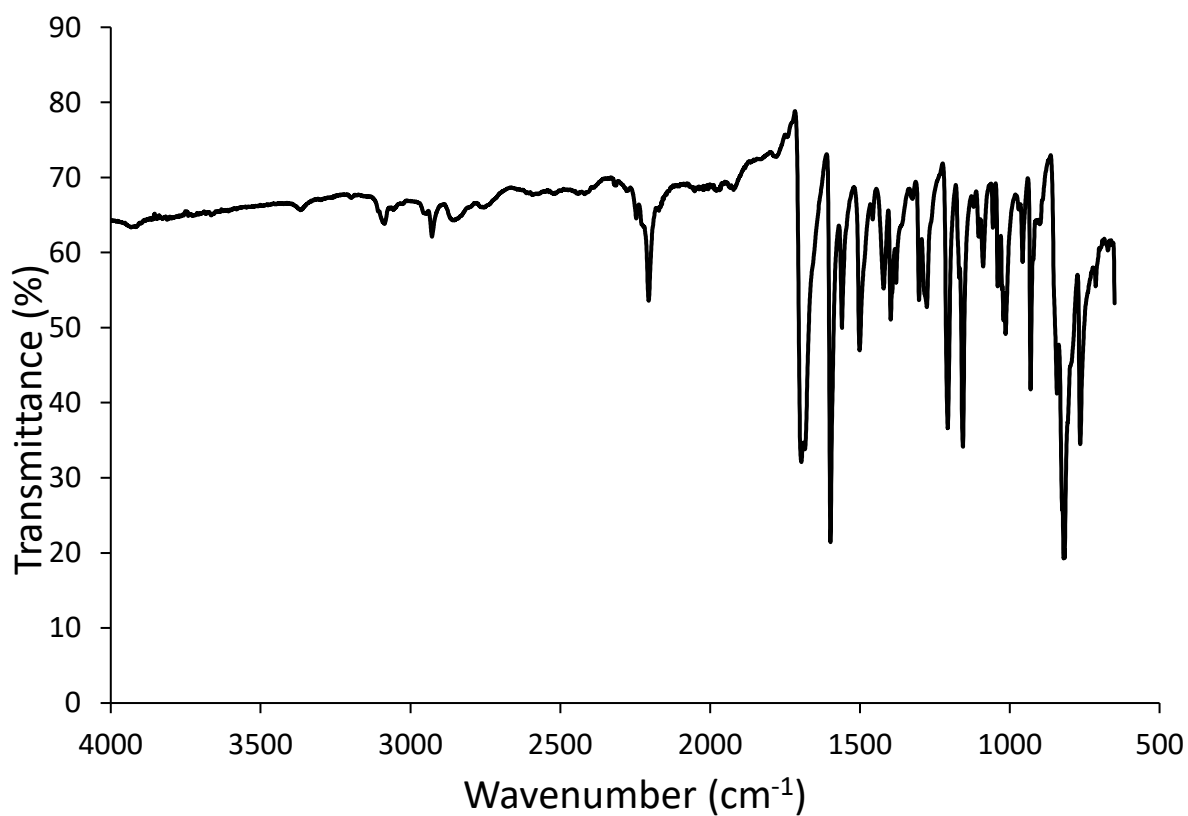


Fig S126. IR spectrum of compound 12a.

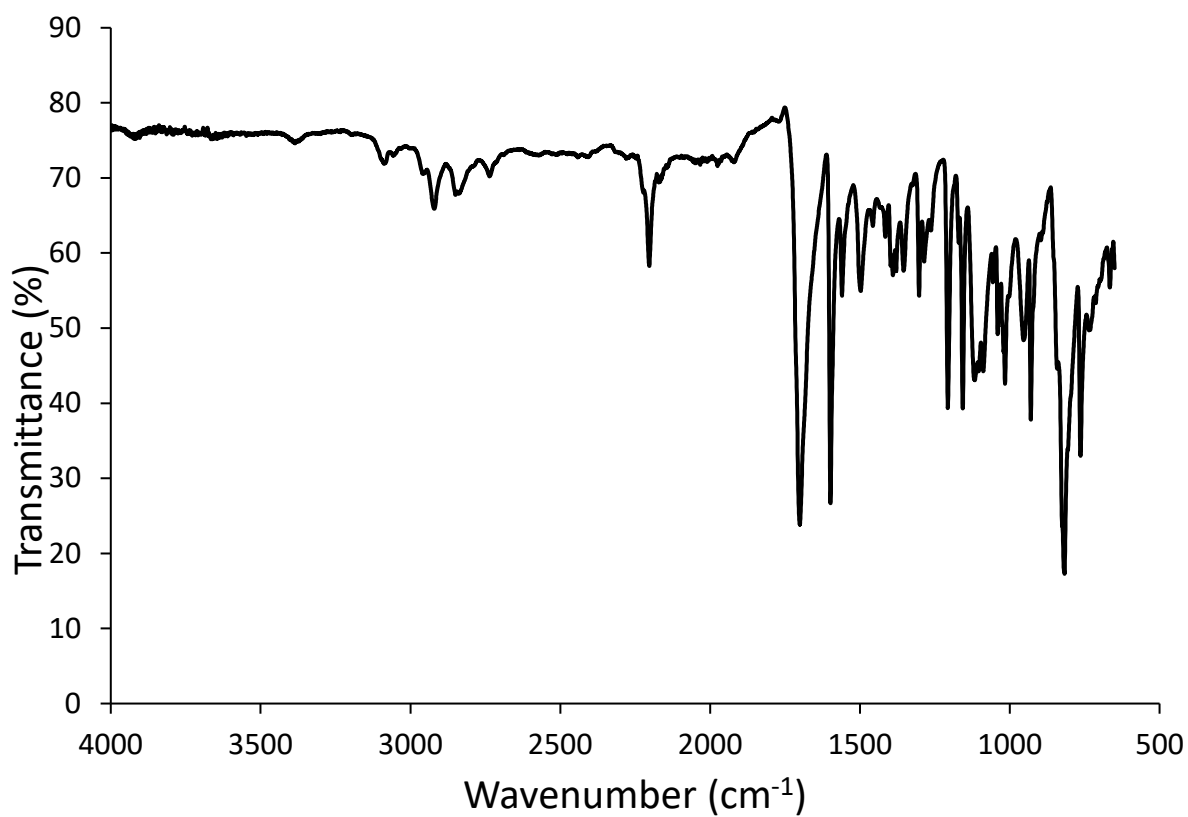


Fig S127. IR spectrum of compound **12**.

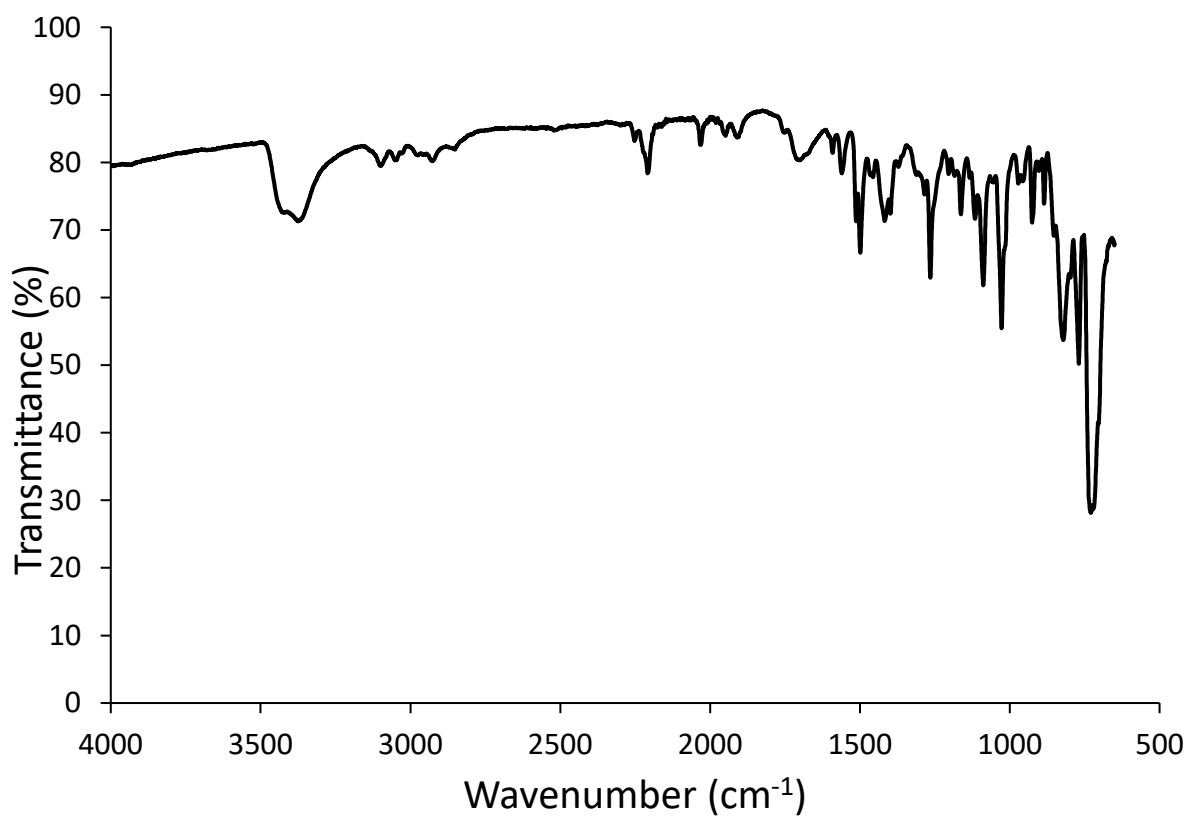


Fig S128. IR spectrum of compound **13a**.

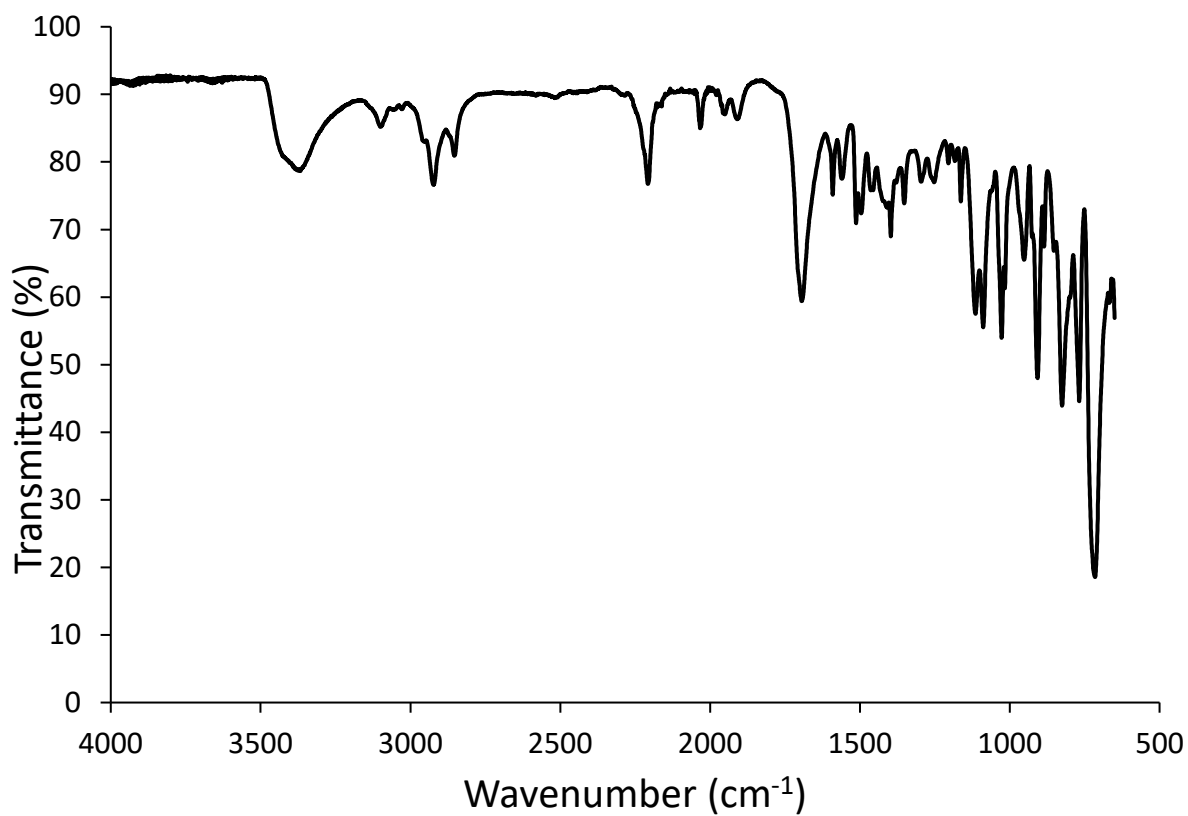


Fig S129. IR spectrum of compound **13**.

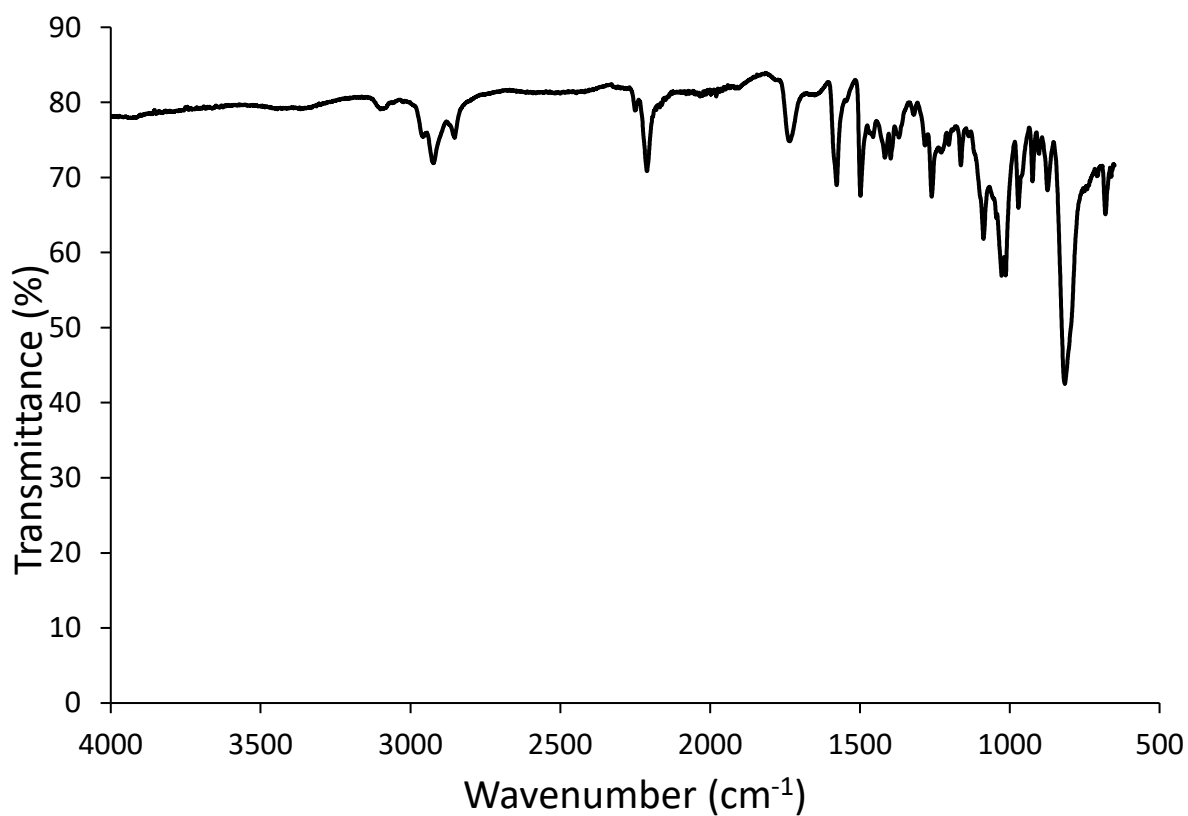


Fig S130. IR spectrum of compound **14a**.

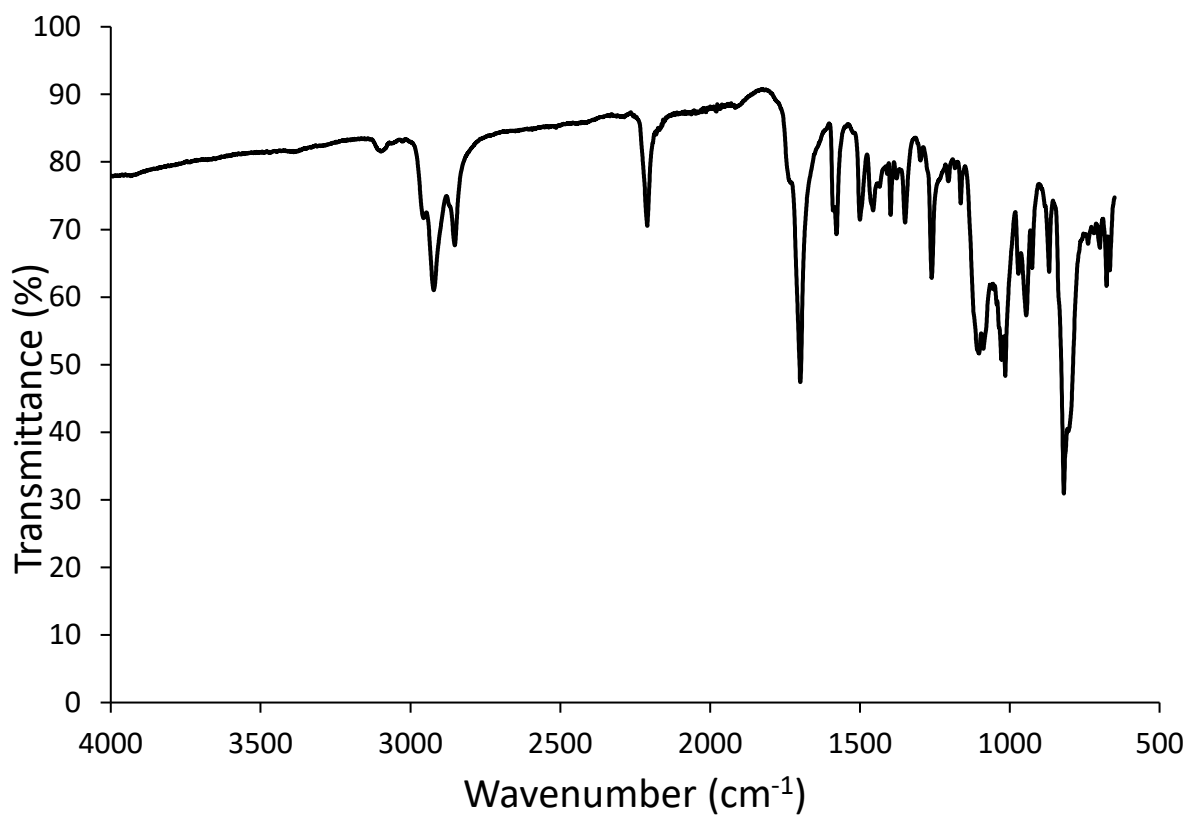


Fig S131. IR spectrum of compound **14**.

5. High-Resolution Mass Spectrometry

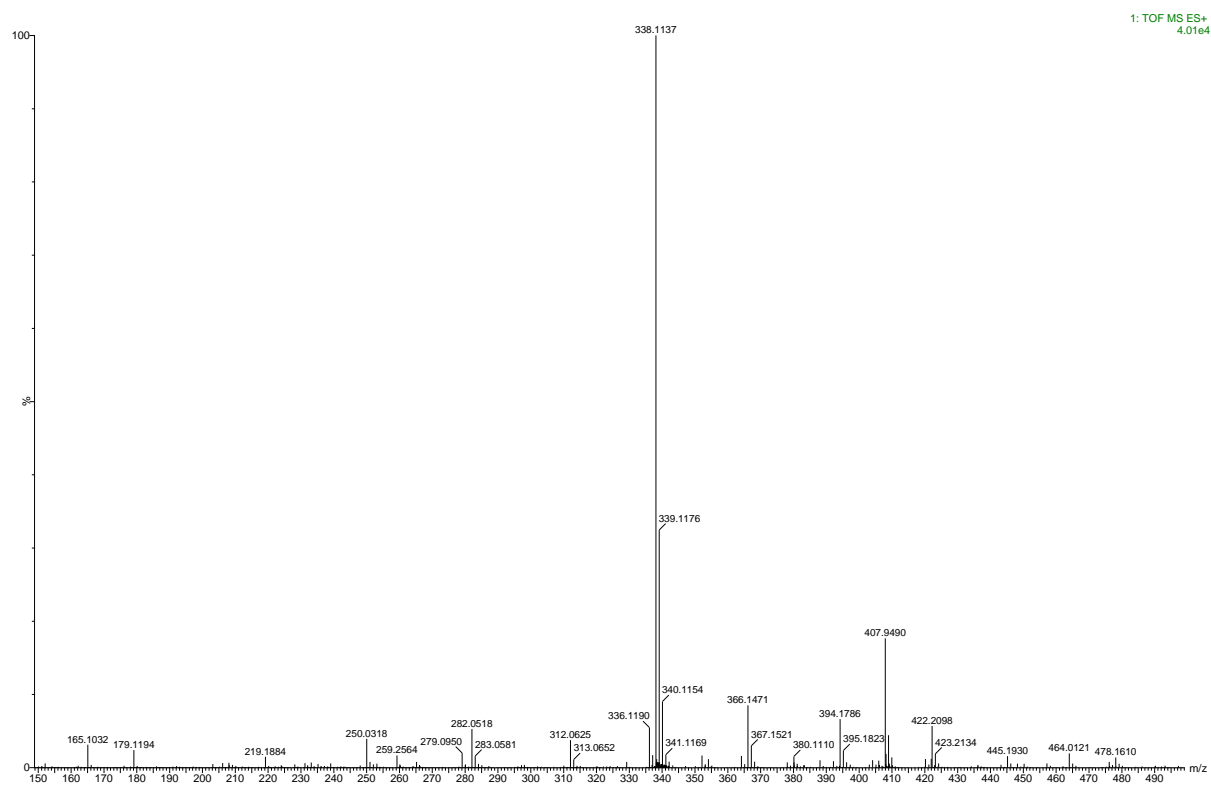


Fig S132. High-resolution mass spectrometry data for compound 1a.

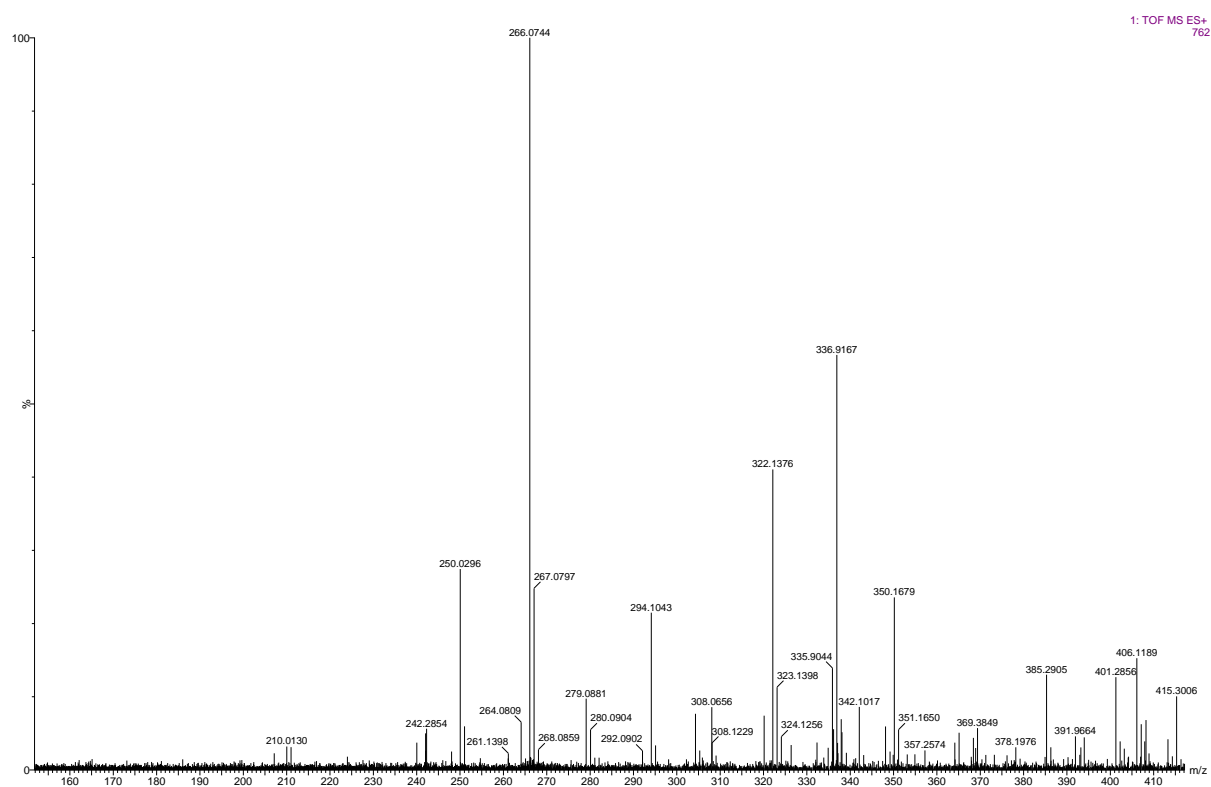


Fig S133. High-resolution mass spectrometry data for compound 1.

Supporting Information

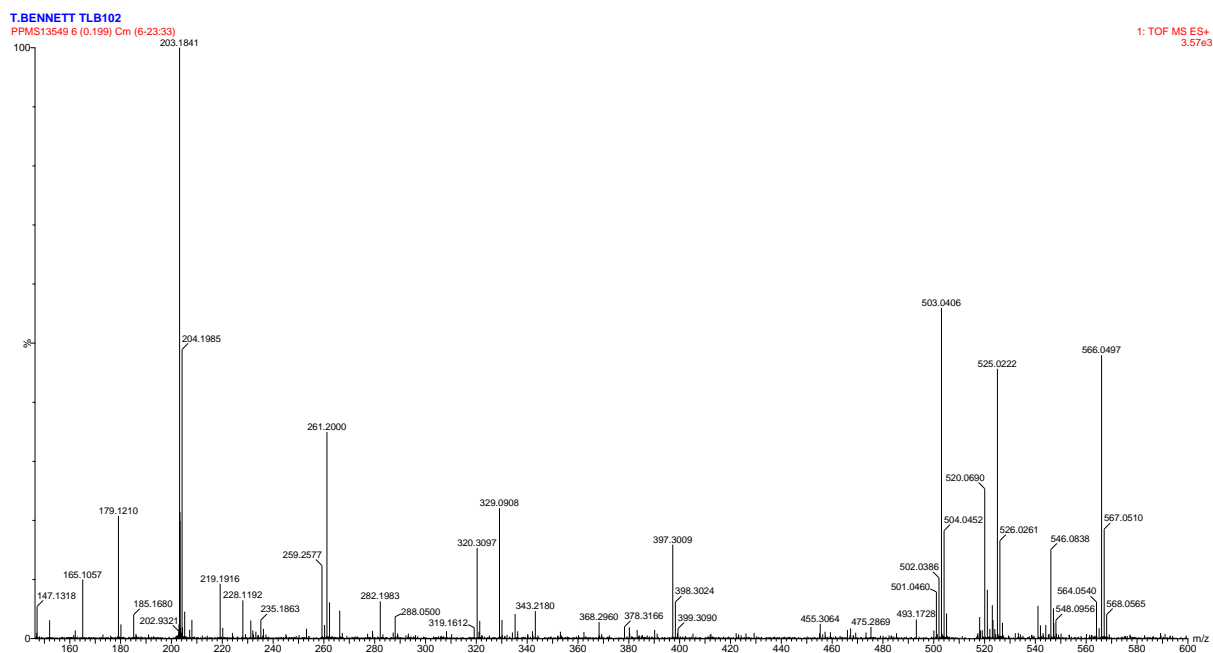


Fig S134. High-resolution mass spectrometry data for compound 2.

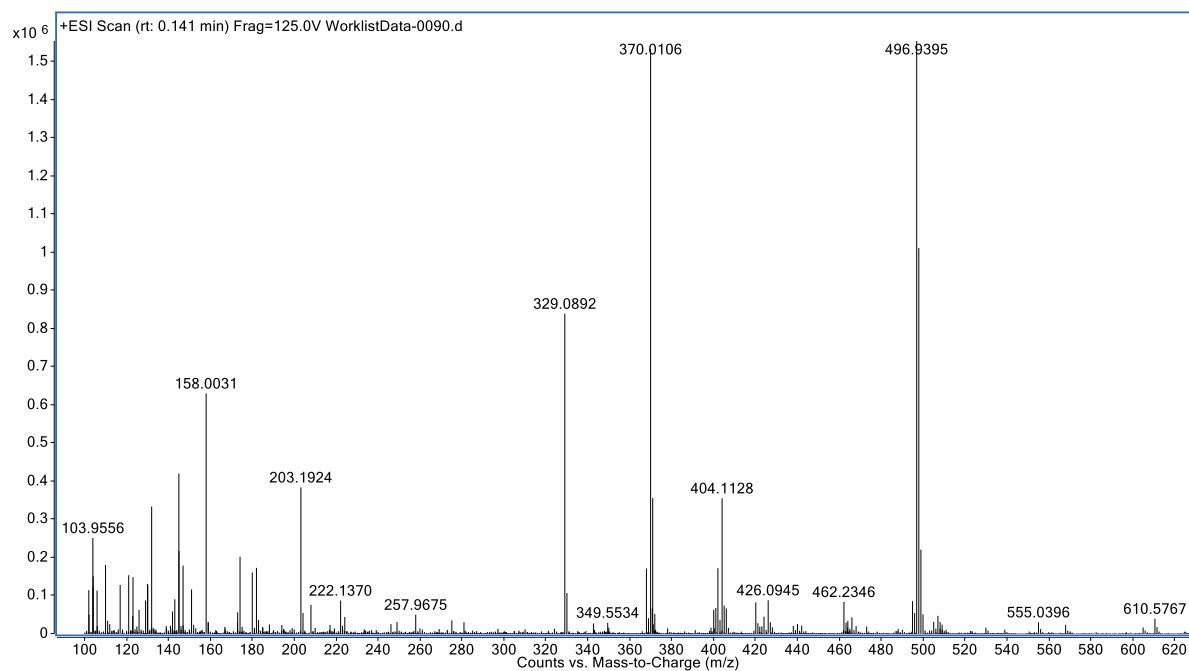


Fig S135. High-resolution mass spectrometry data for compound 2a.

Supporting Information

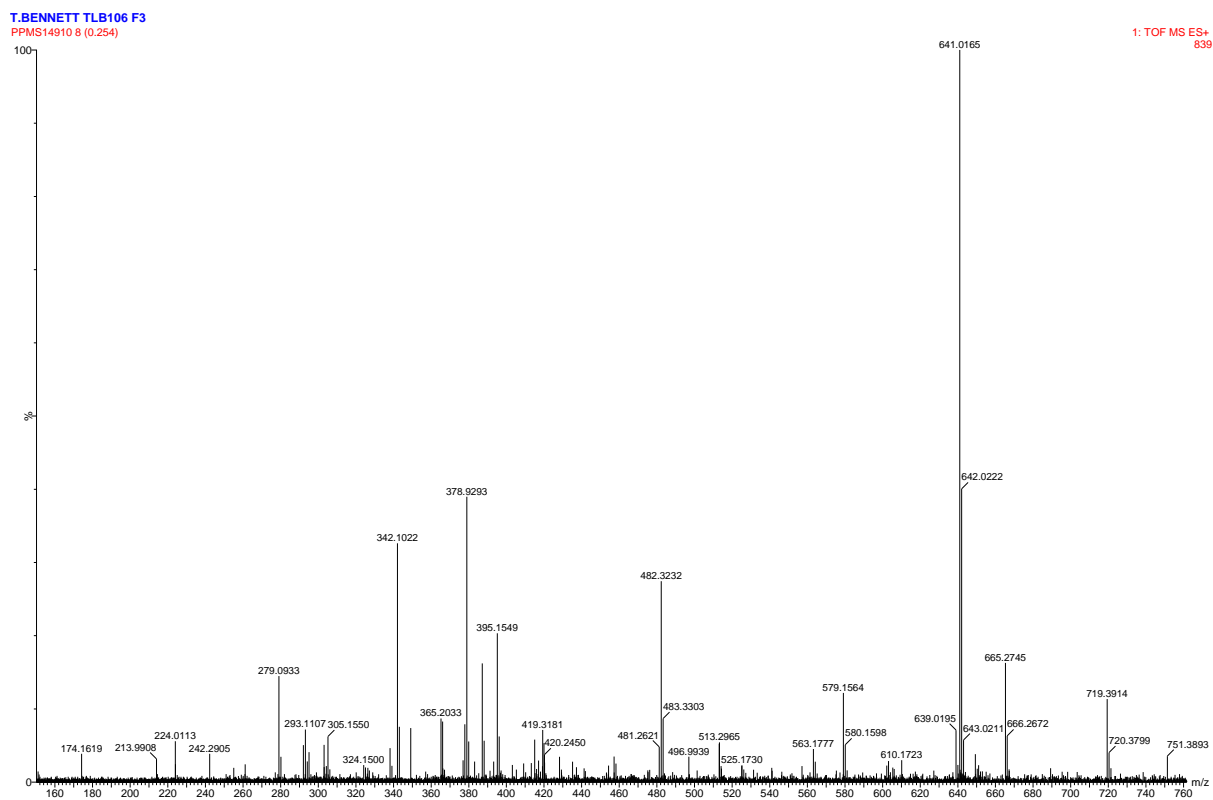


Fig S136. High-resolution mass spectrometry data for compound 2b.

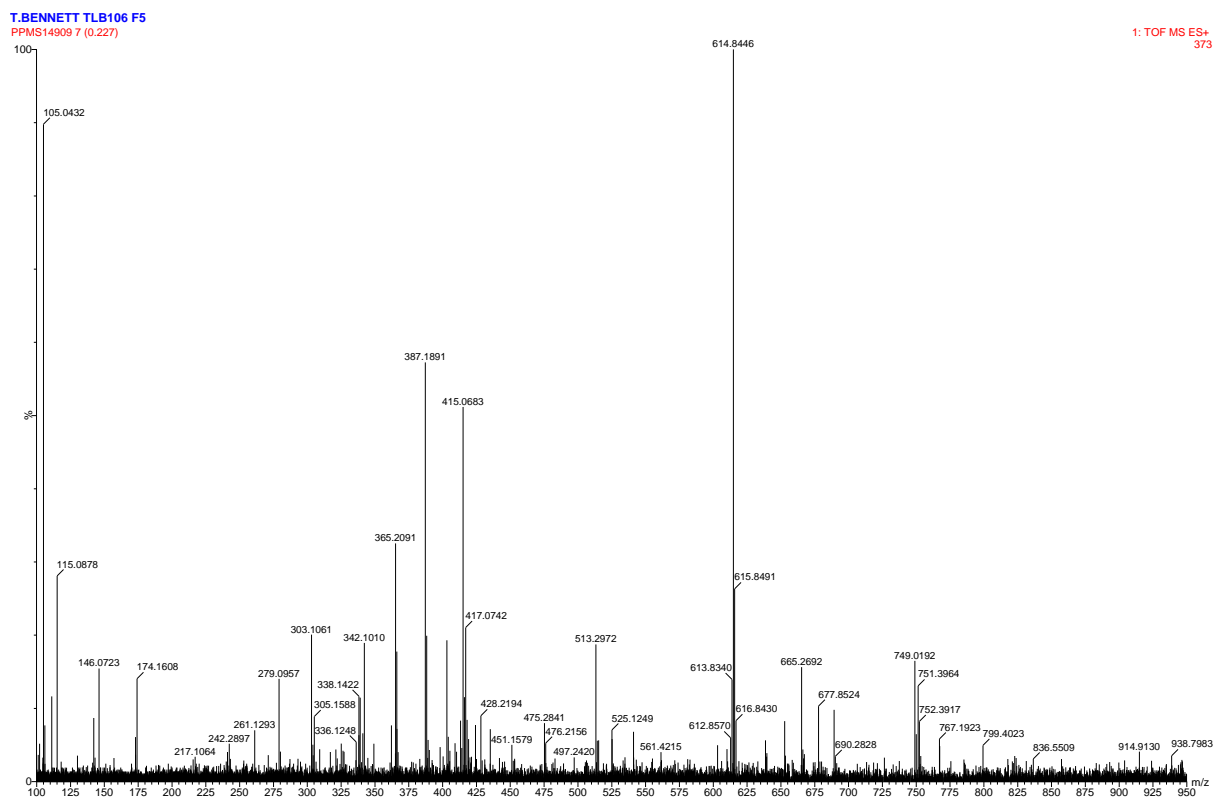


Fig S137. High-resolution mass spectrometry data for compound 2c.

Supporting Information

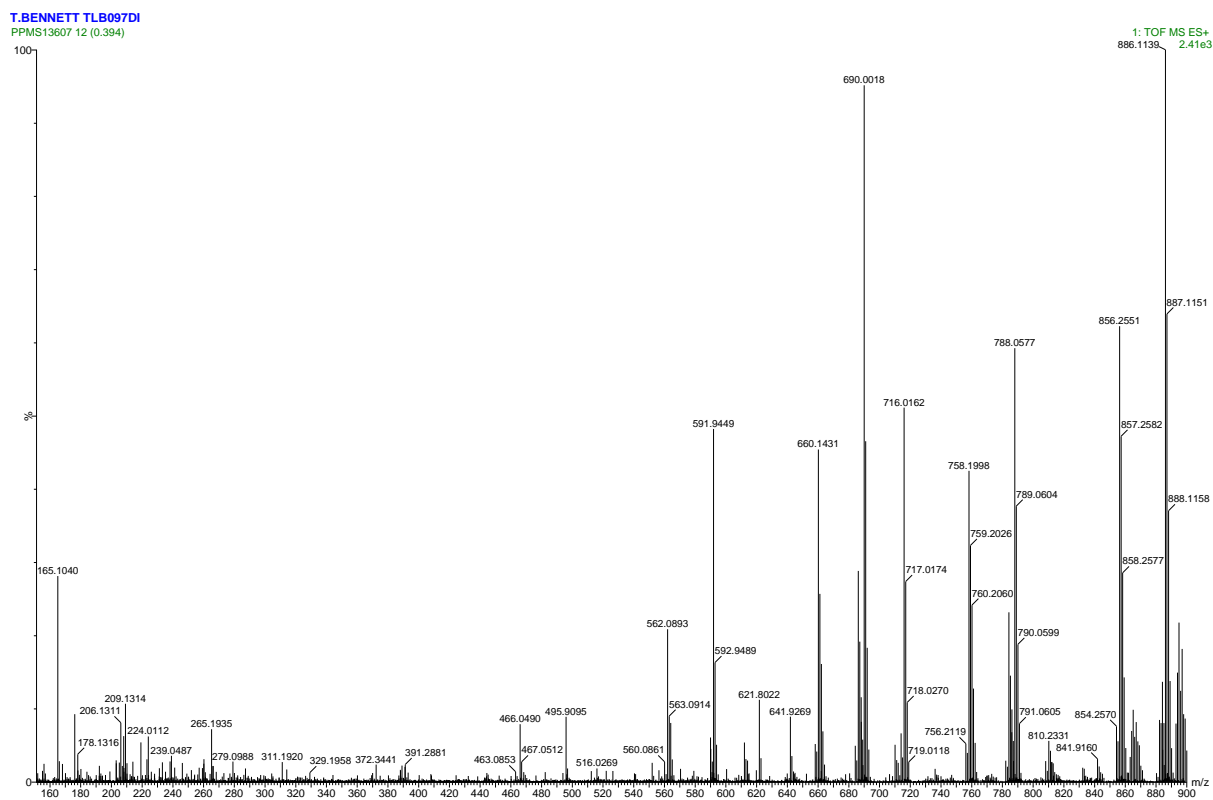


Fig S138. High-resolution mass spectrometry data for compound 3a.

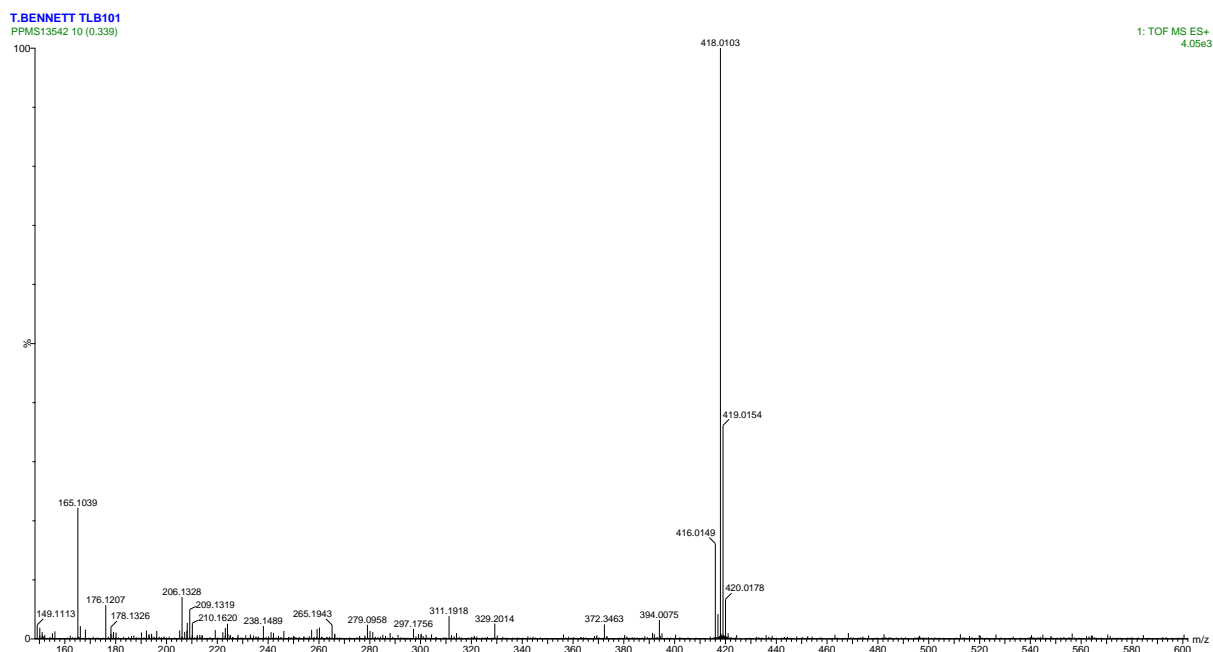


Fig S139. High-resolution mass spectrometry data for compound 3.

Supporting Information

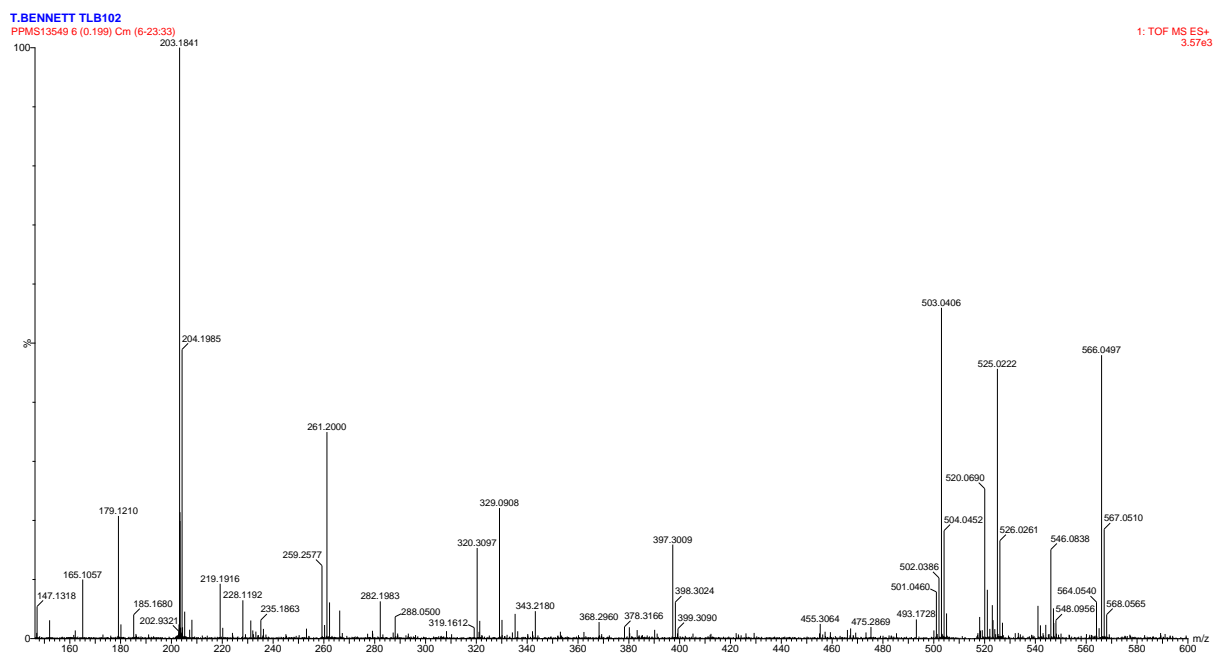


Fig S140. High-resolution mass spectrometry data for compound 4.

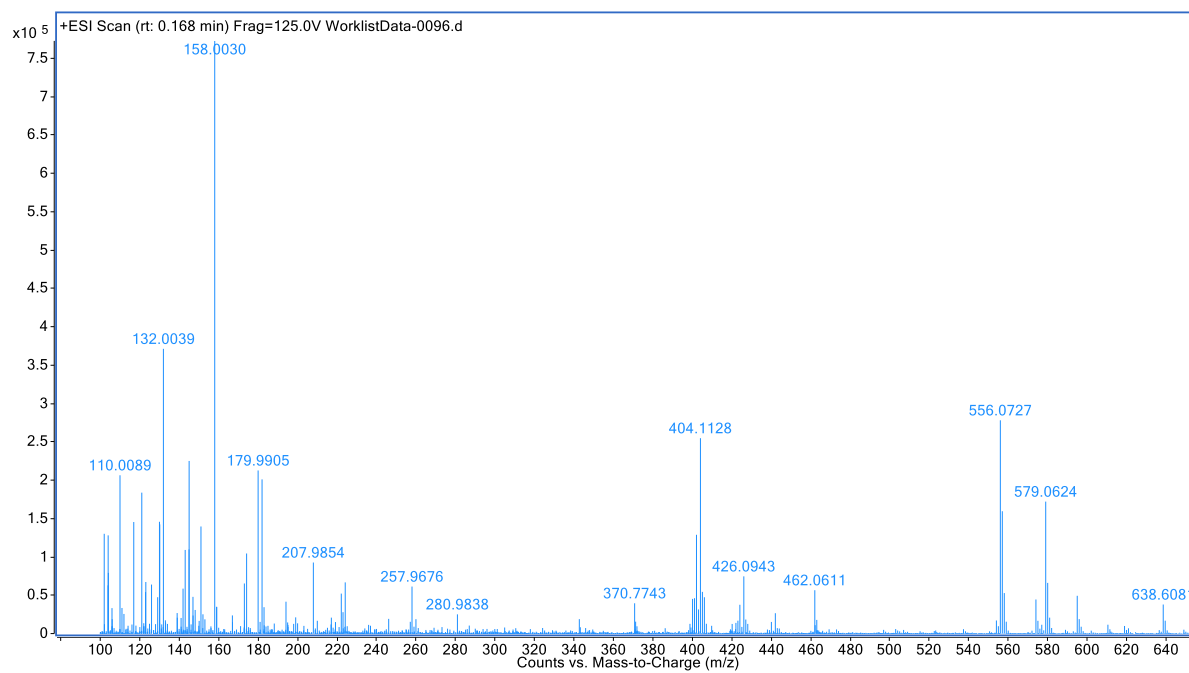


Fig S141. High-resolution mass spectrometry data for compound 5a.

Supporting Information

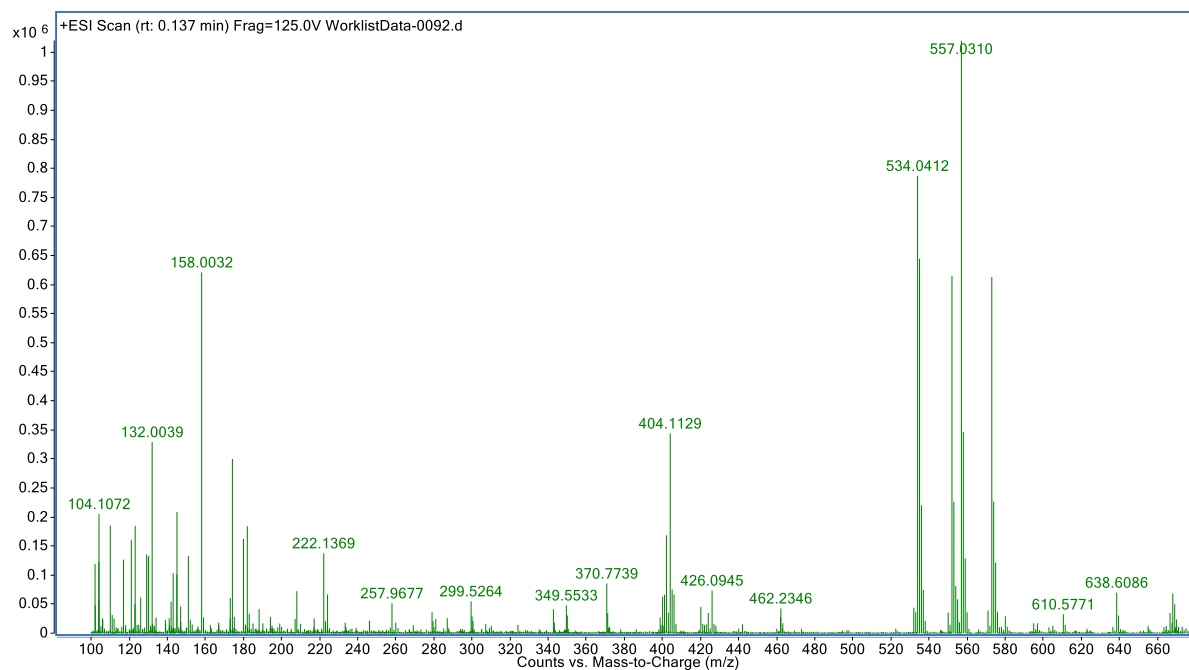


Fig S142. High-resolution mass spectrometry data for compound **5**.

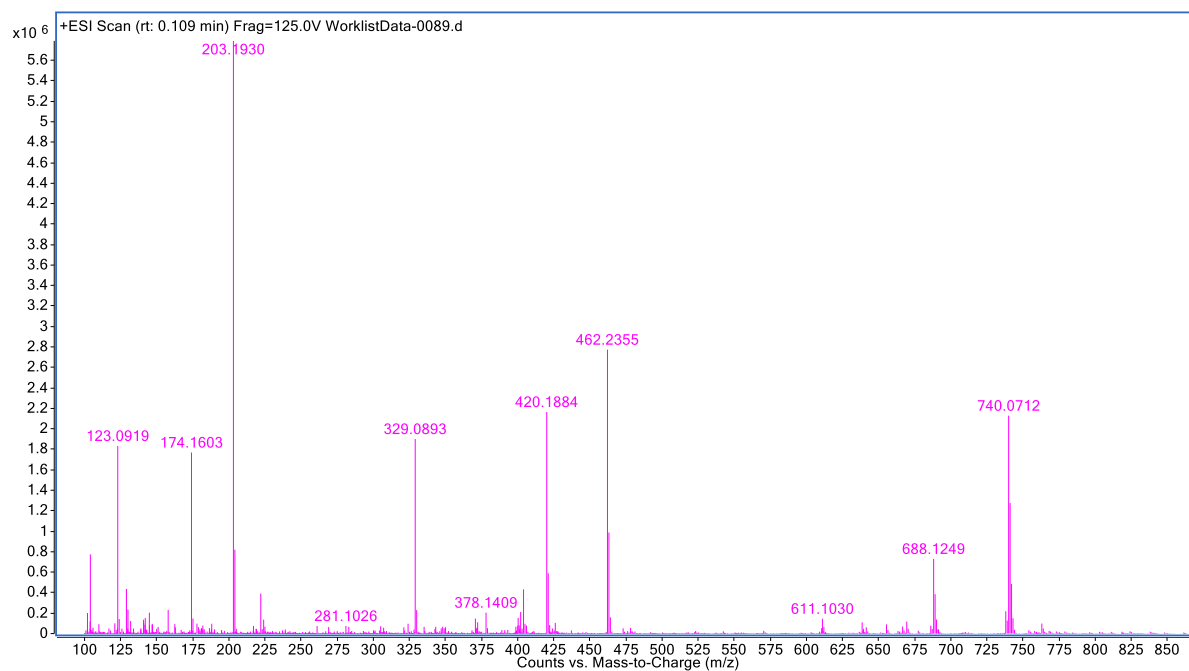


Fig S143. High-resolution mass spectrometry data for compound **6a**.

Supporting Information

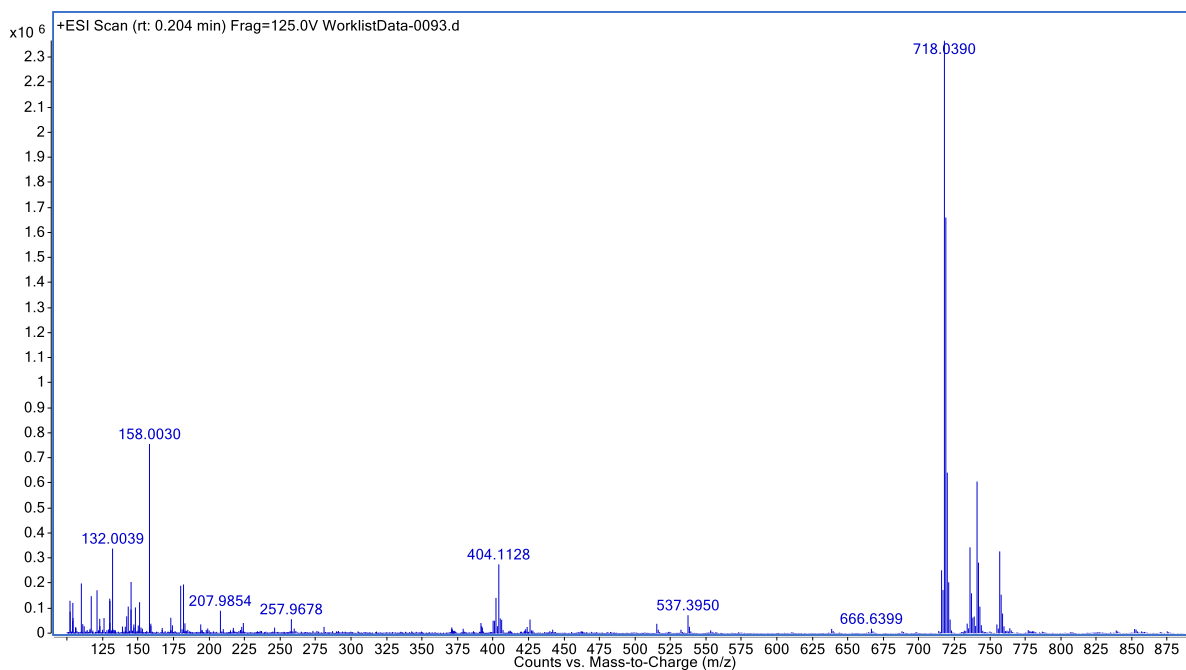


Fig S144. High-resolution mass spectrometry data for compound **6**.

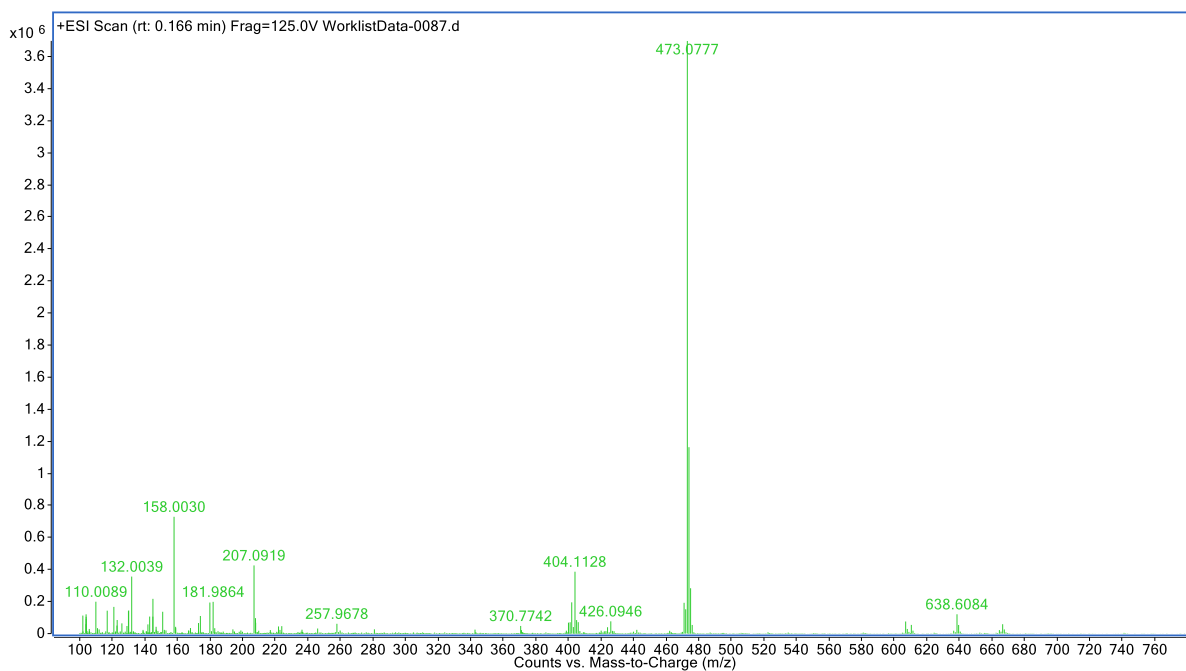


Fig S145. High-resolution mass spectrometry data for compound **7a**.

Supporting Information

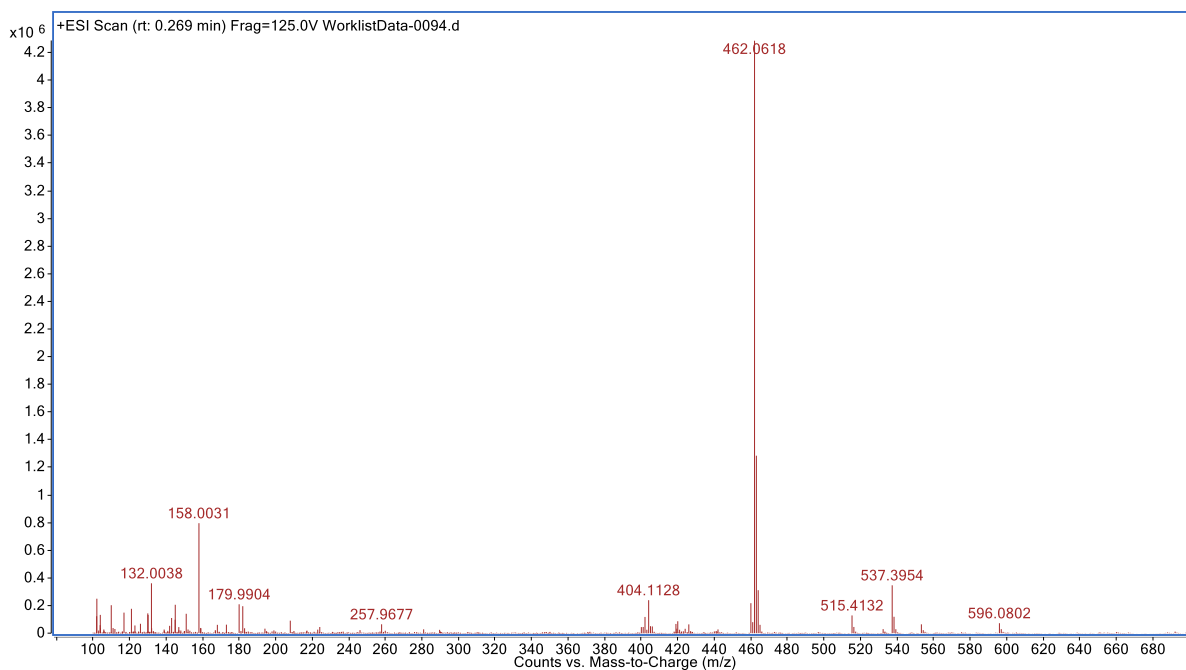


Fig S146. High-resolution mass spectrometry data for compound **7**.

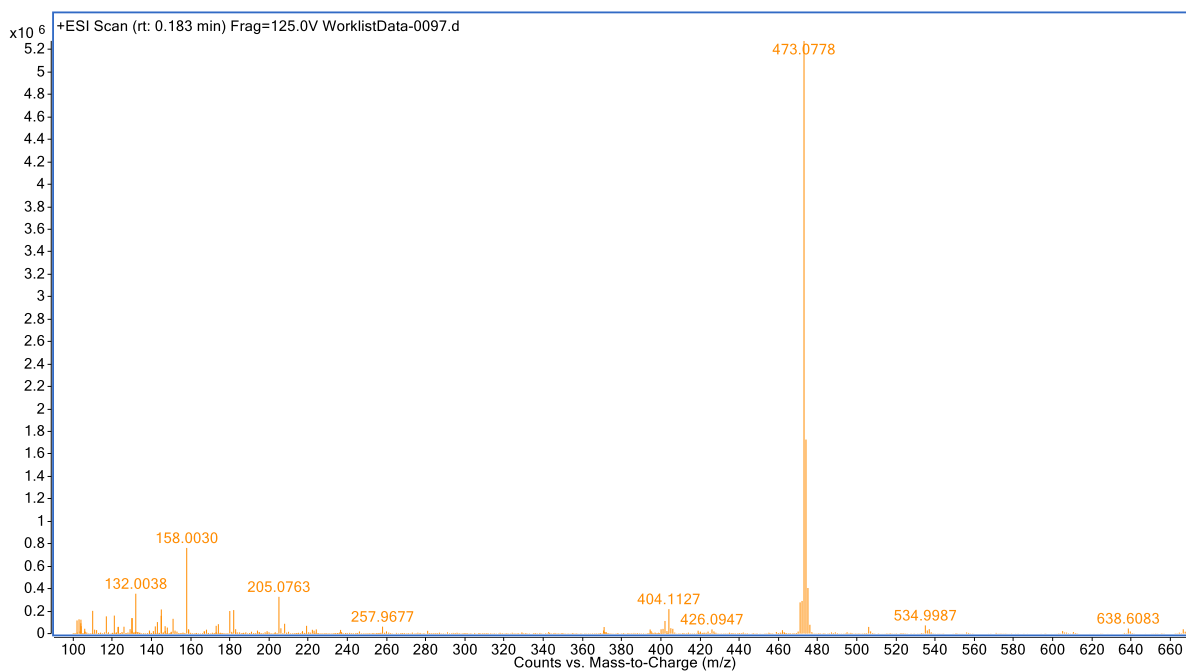


Fig S147. High-resolution mass spectrometry data for compound **8a**.

Supporting Information

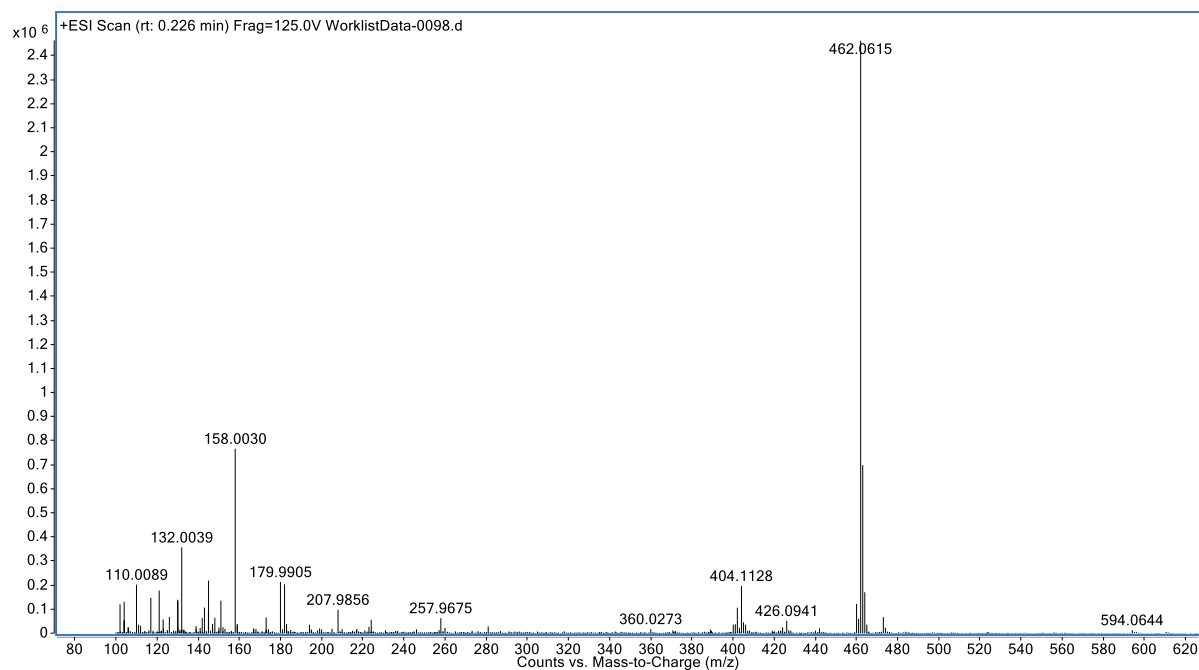


Fig S148. High-resolution mass spectrometry data for compound **8**.

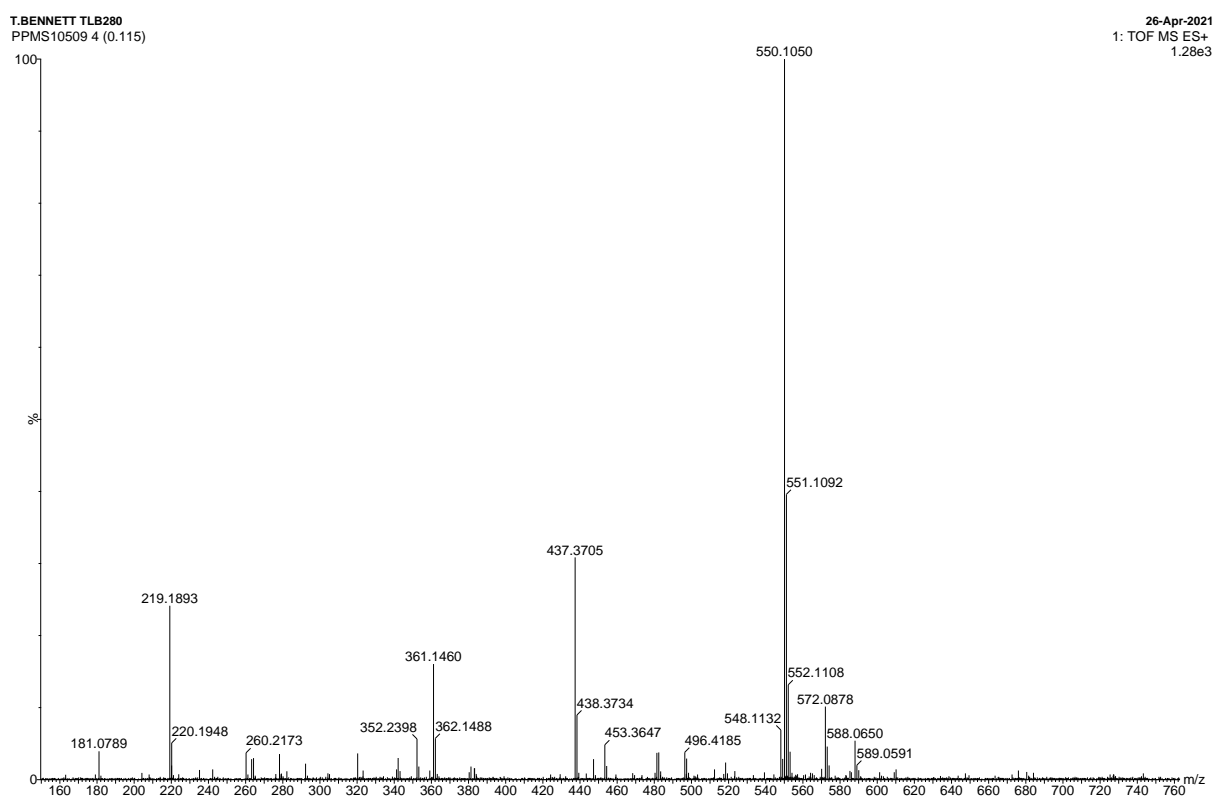


Fig S149. High-resolution mass spectrometry data for compound **9a**.

Supporting Information

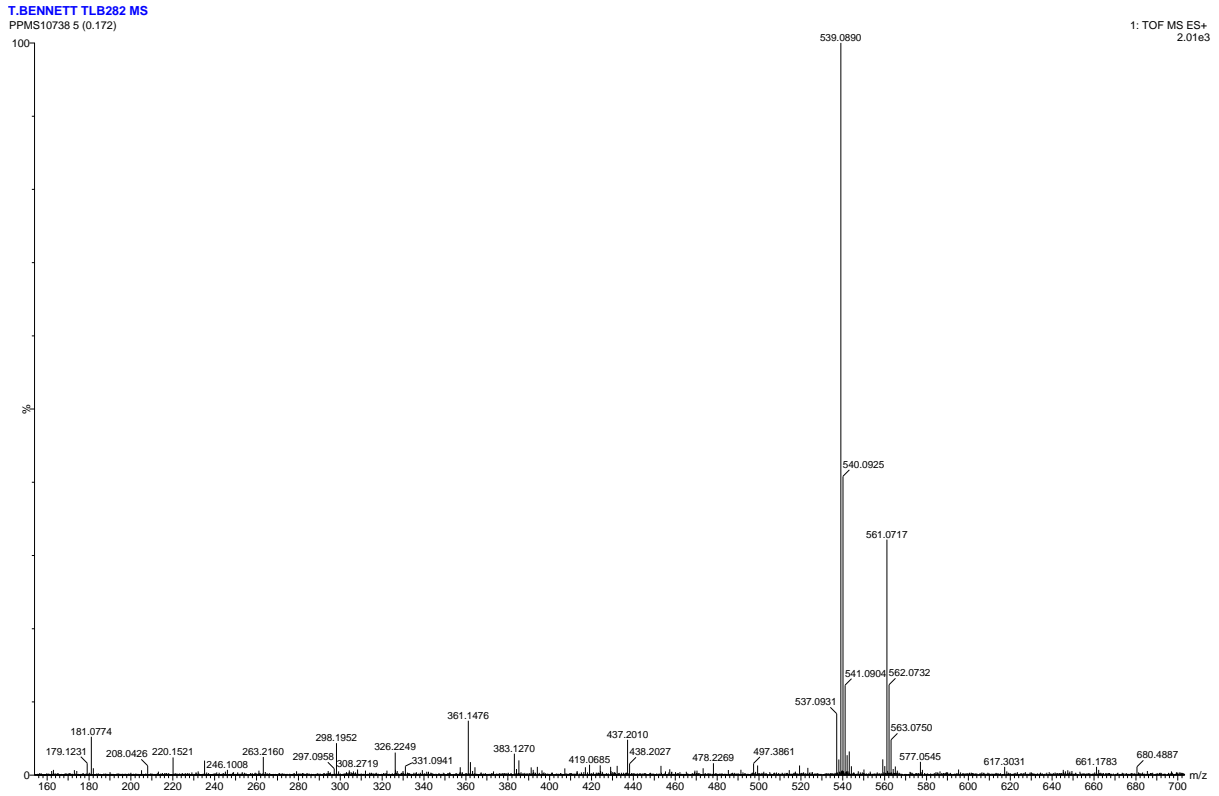


Fig S150. High-resolution mass spectrometry data for compound 9.

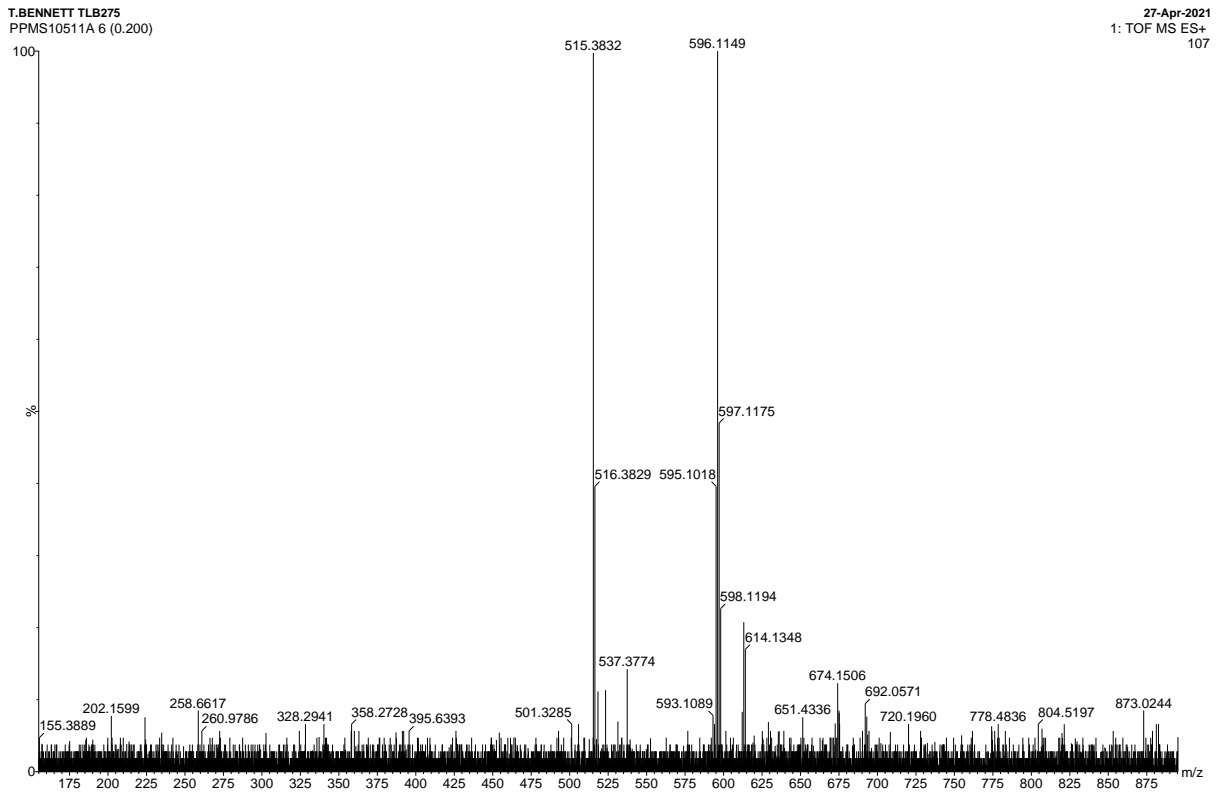


Fig S151. High-resolution mass spectrometry data for compound 10a.

Supporting Information

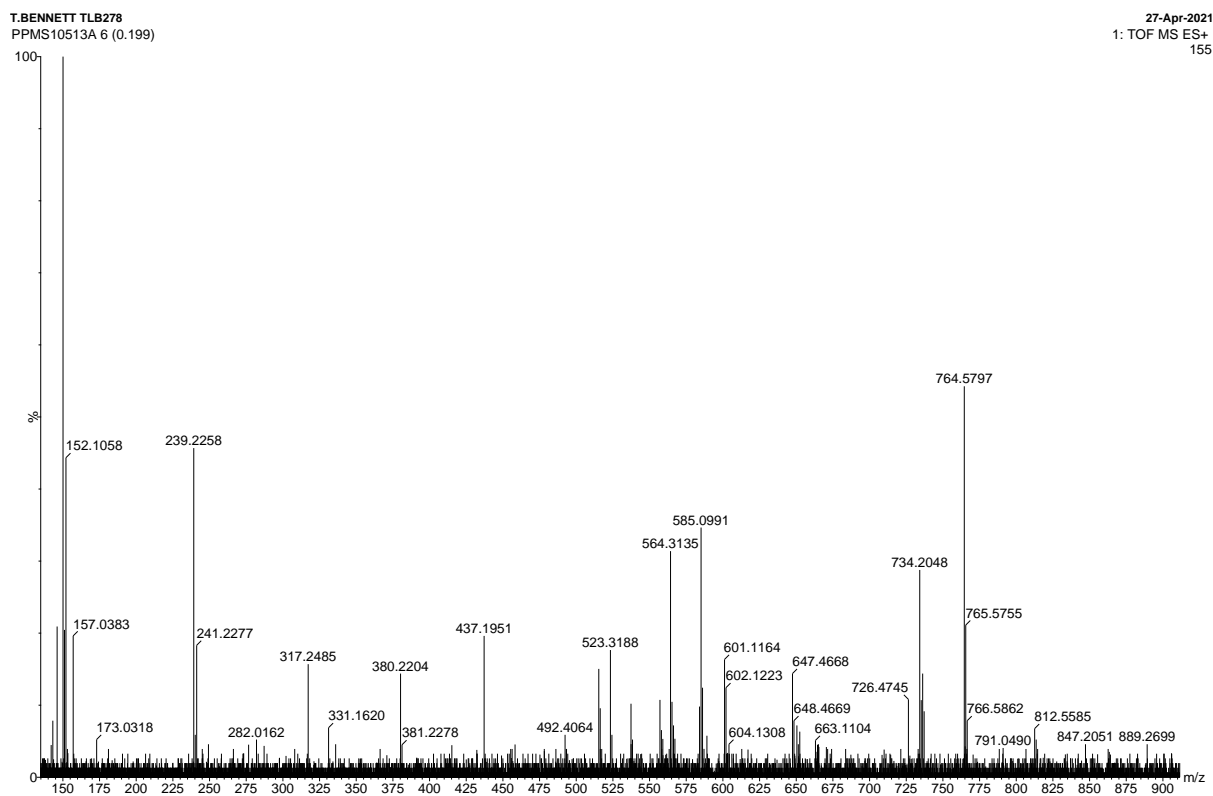


Fig S152. High-resolution mass spectrometry data for compound 10.

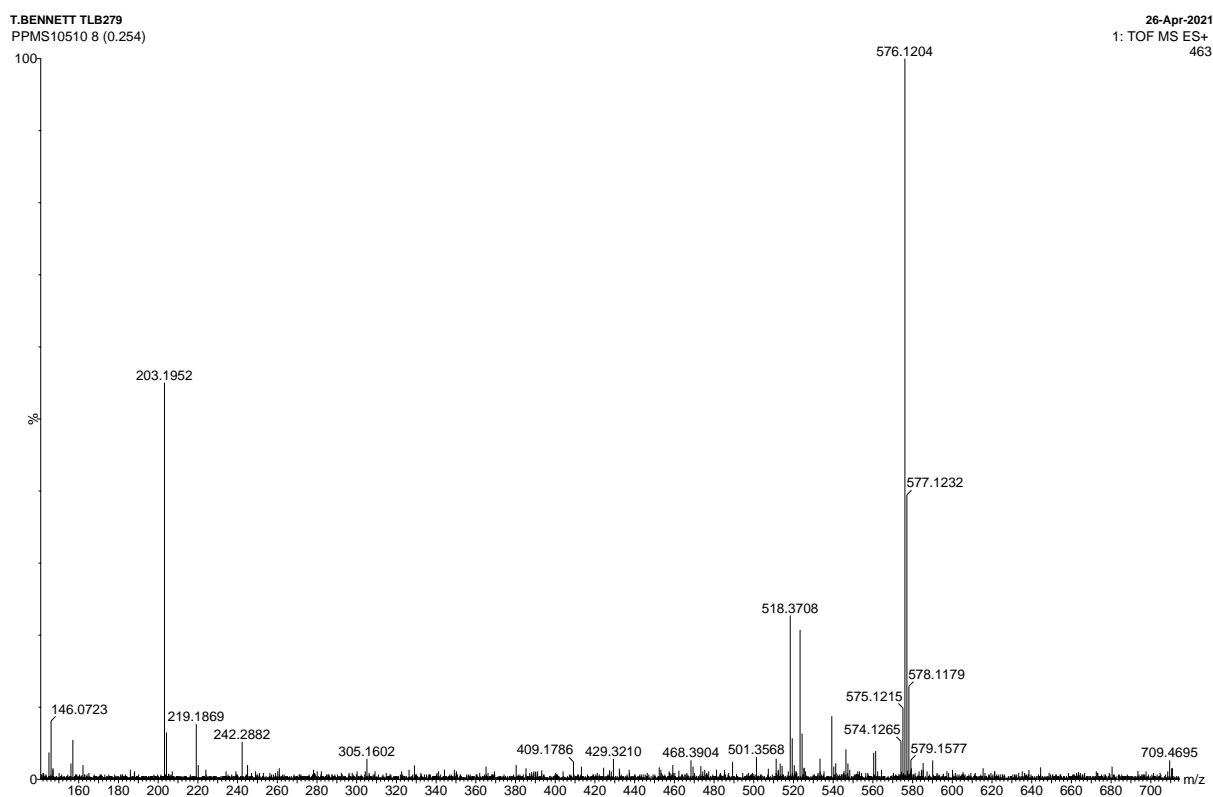


Fig S153. High-resolution mass spectrometry data for compound 11a.

Supporting Information

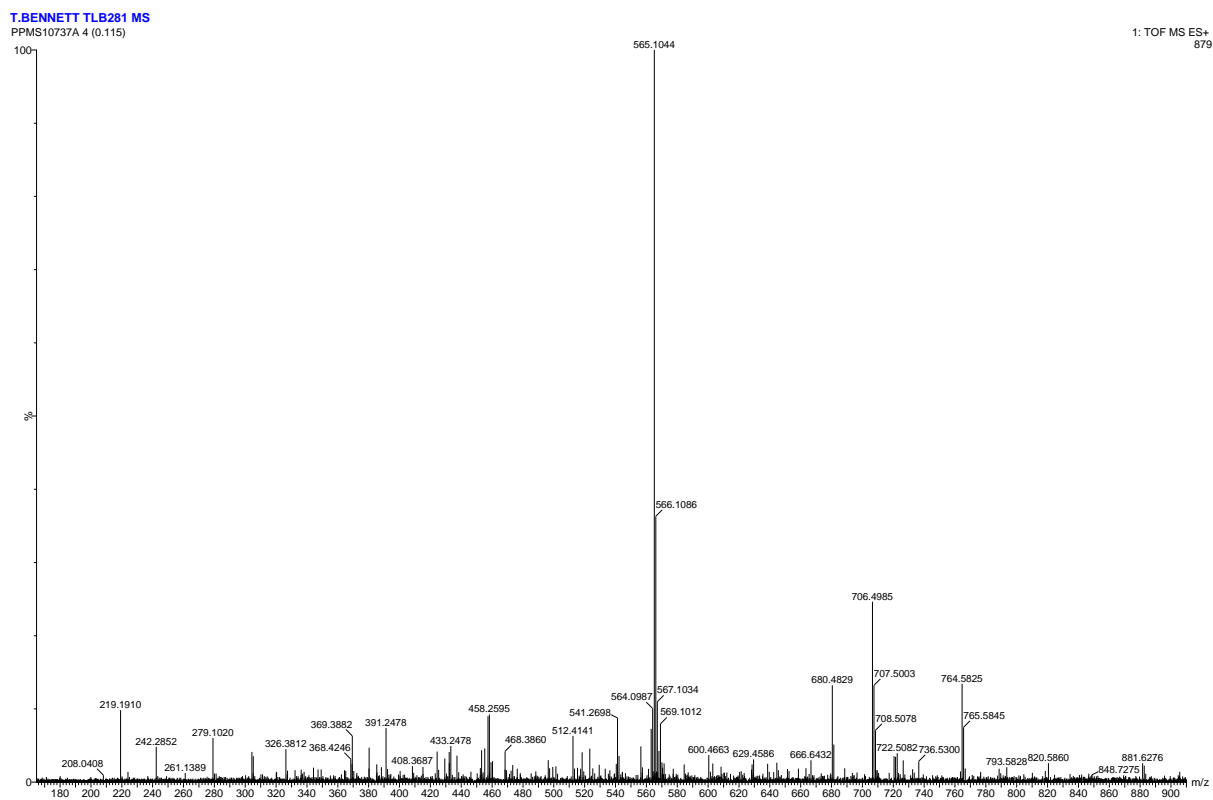


Fig S154. High-resolution mass spectrometry data for compound **11**.

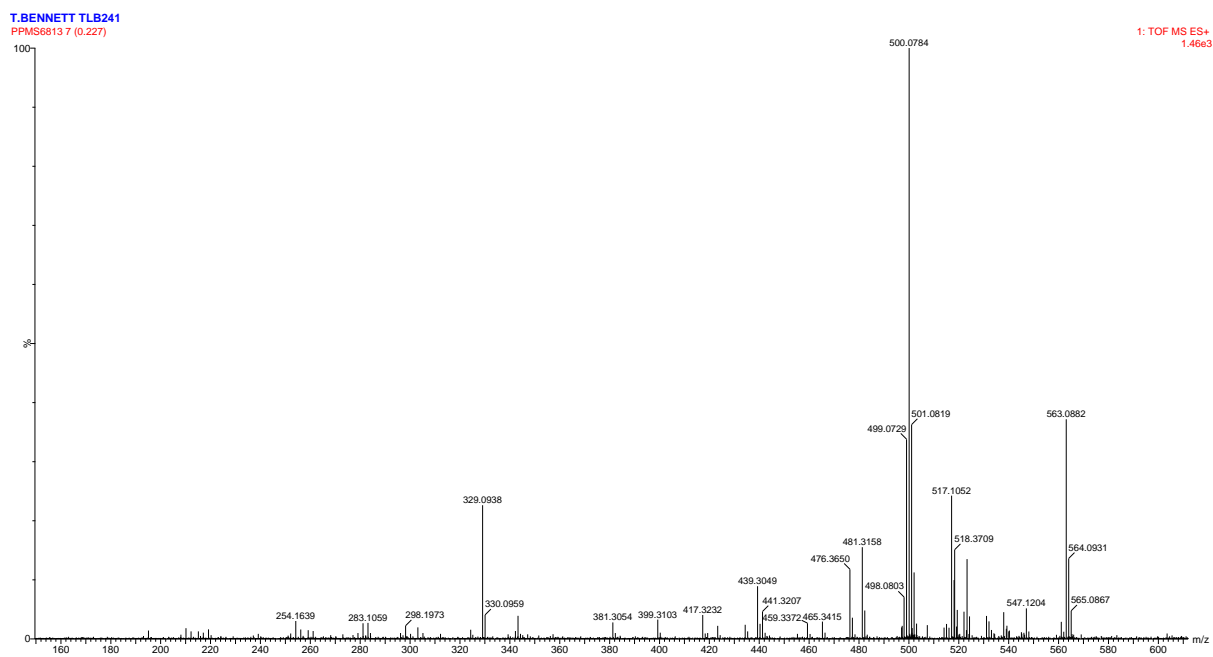


Fig S155. High-resolution mass spectrometry data for compound **12a**.

Supporting Information

T.BENNETT TLB277
PPMS10512A 7 (0.227)

27-Apr-2021
1: TOF MS ES+
149

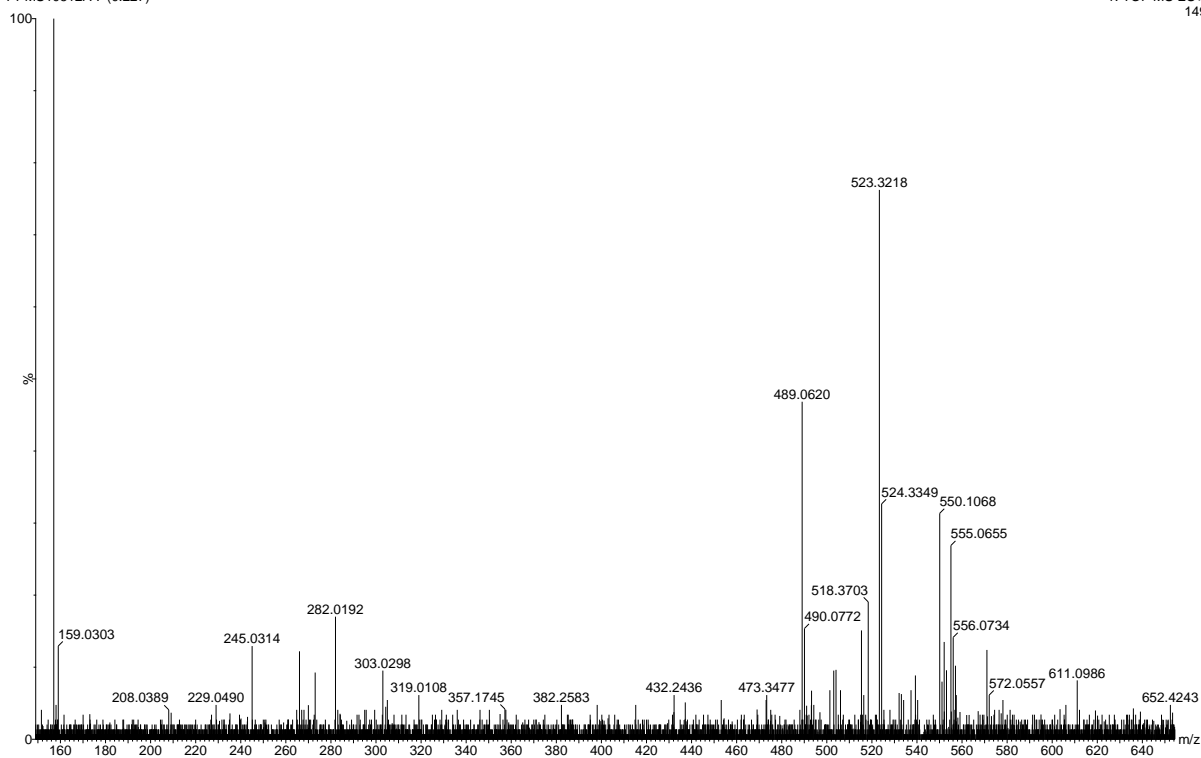


Fig S156. High-resolution mass spectrometry data for compound 12.

T.BENNETT TLB261
PPMS9228 7 (0.227)

1: TOF MS ES+
447

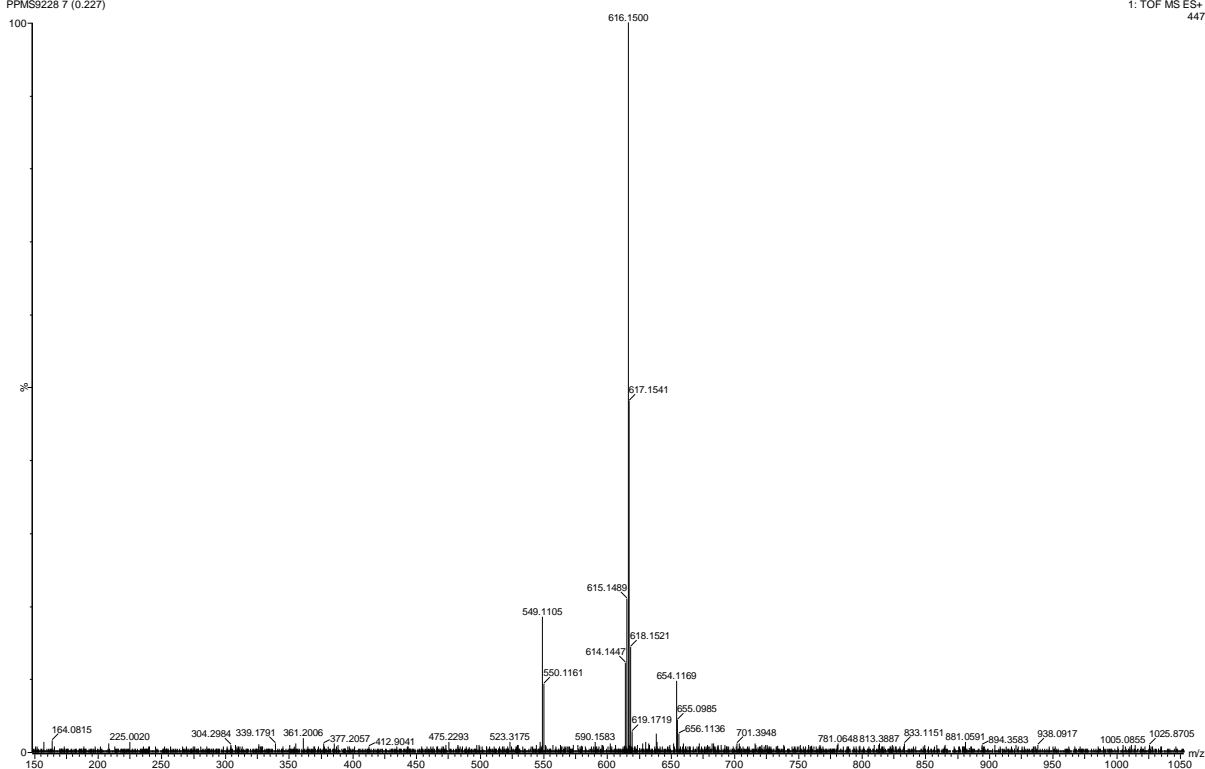


Fig S157. High-resolution mass spectrometry data for compound 13a.

Supporting Information

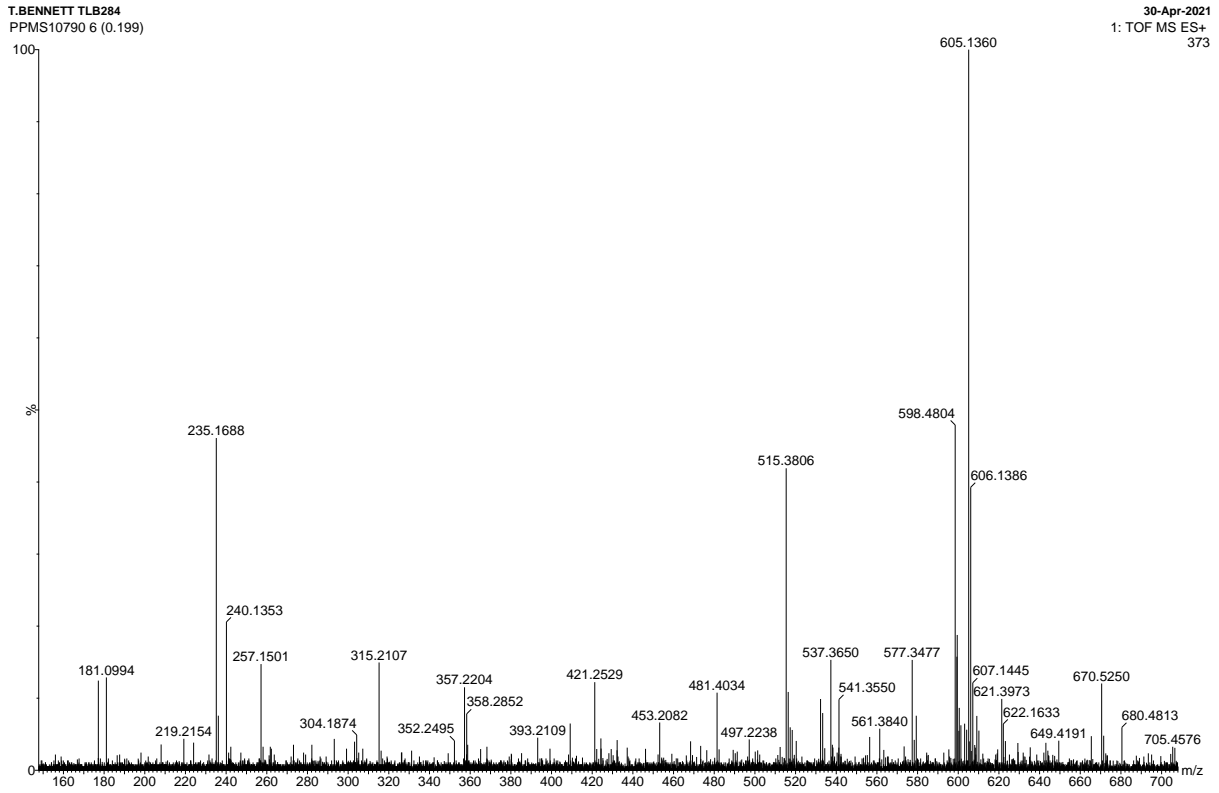


Fig S158. High-resolution mass spectrometry data for compound **13**.

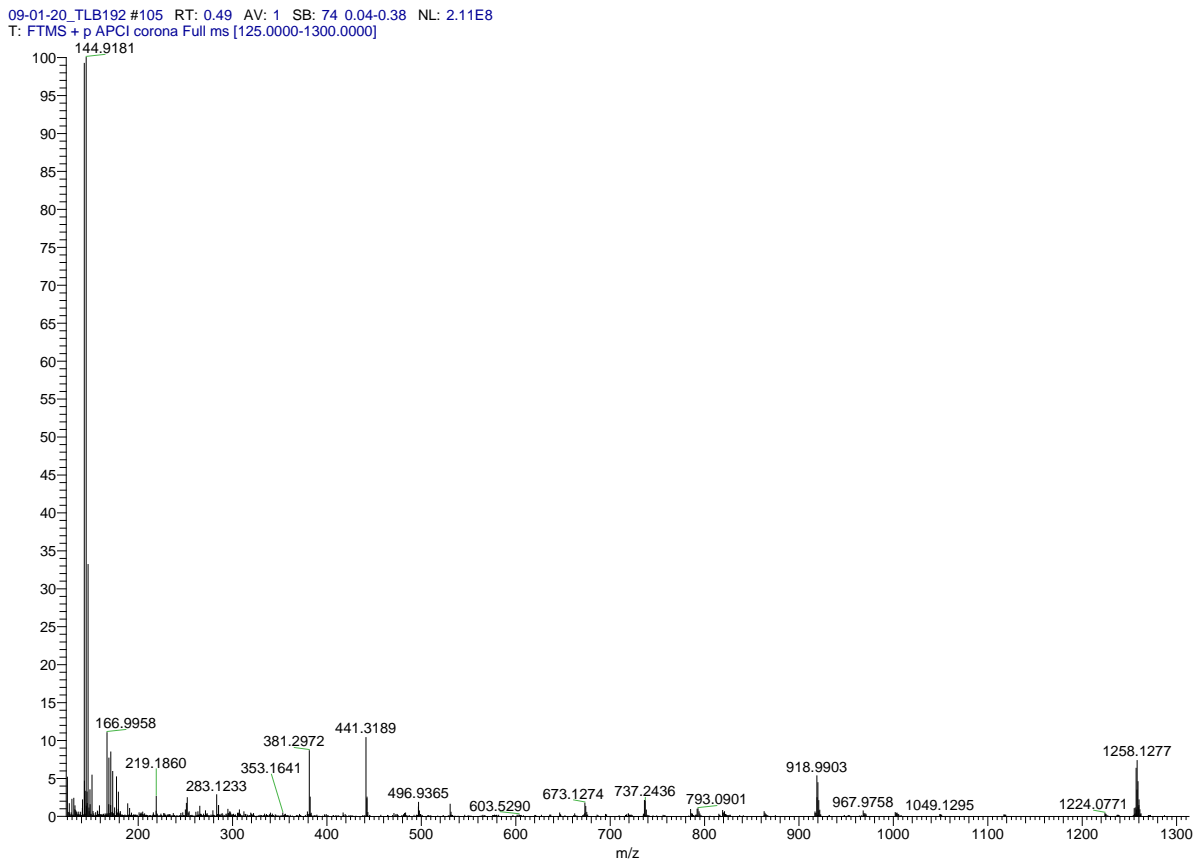


Fig S159. High-resolution mass spectrometry data for compound **14a**.

Supporting Information

09-01-20_TLB194 #160 RT: 0.71 AV: 1 NL: 4.85E7
T: FTMS + p APCI corona Full lock ms [125.0000-1300.0000]

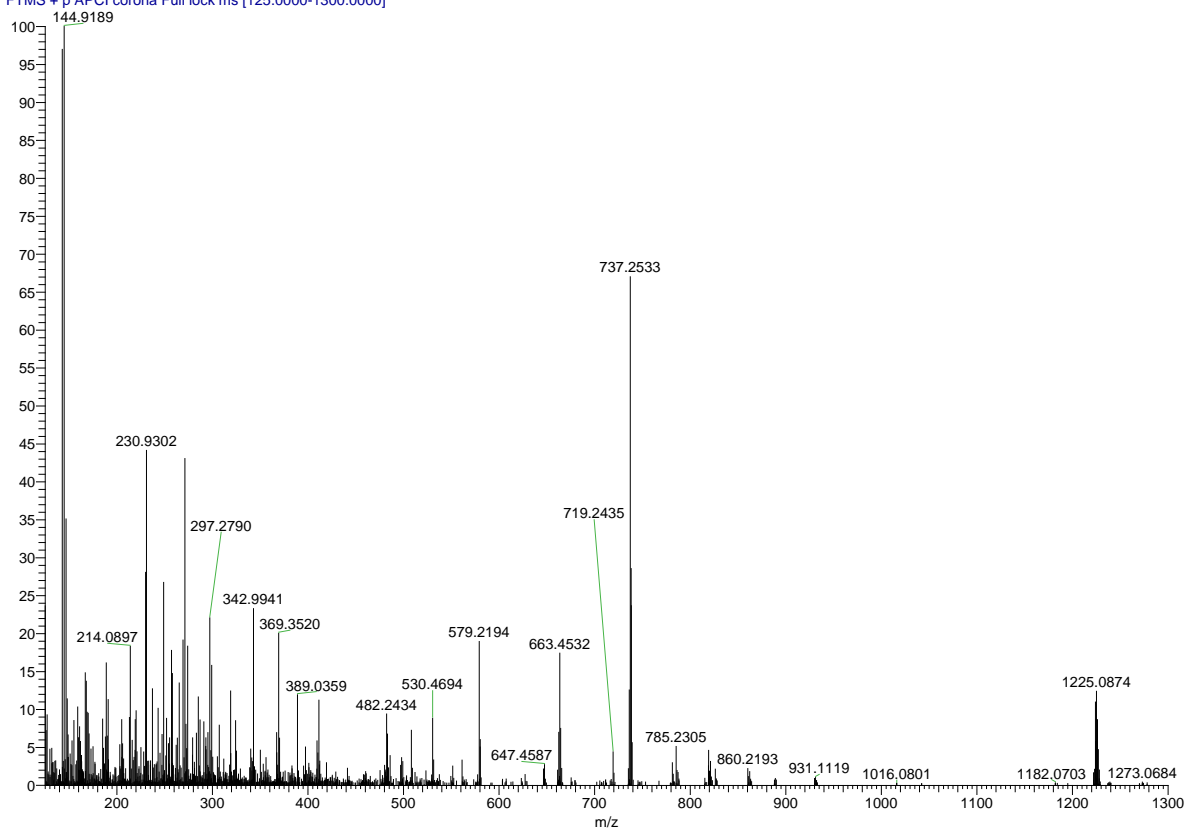


Fig S160. High-resolution mass spectrometry data for compound **14**.

6. References

- (1) Inkpen, M. S.; Du, S.; Driver, M.; Albrecht, T.; Long, N. J. Oxidative Purification of Halogenated Ferrocenes. *Dalton Trans.* **2013**, 42 (8), 2813–2816.
- (2) Wang, C.; Bryce, M. R.; Gigon, J.; Ashwell, G. J.; Grace, I.; Lambert, C. J. Synthesis and Properties of Functionalized 4 Nm Scale Molecular Wires with Thiolated Termini for Self-Assembly onto Metal Surfaces. *J. Org. Chem.* **2008**, 73 (13), 4810–4818.
- (3) Wilson, L. E.; Hassenrück, C.; Winter, R. F.; White, A. J. P.; Albrecht, T.; Long, N. J. Functionalised Biferrocene Systems towards Molecular Electronics. *Eur. J. Inorg. Chem.* **2017**, 2017 (2)(2), 496–504.
- (4) Sinn, S.; Schulze, B.; Friebe, C.; Brown, D. G.; Jäger, M.; Altuntaş, E.; Kübel, J.; Guntner, O.; Berlinguette, C. P.; Dietzek, B.; Schubert, U. S. Physicochemical Analysis of Ruthenium(II) Sensitizers of 1,2,3-Triazole-Derived Mesoionic Carbene and Cyclometalating Ligands. *Inorg. Chem.* **2014**, 53 (4), 2083–2095.
- (5) Möller, N.; Rühling, A.; Lamping, S.; Hellwig, T.; Fallnich, C.; Ravoo, B. J.; Glorius, F. Stabilization of High Oxidation State Upconversion Nanoparticles by N-Heterocyclic Carbenes. *Angew. Chem - Int. Ed.* **2017**, 56 (15), 4356–4360.
- (6) Kobayashi, N.; Kijima, M. 1,3,5-Tris(Functionalised-Phenylethynyl)Benzene-Metal Complexes: Synthetic Survey of Mesoporous Coordination Polymers and Investigation of Their Carbonisation. *J. Mater. Chem.* **2008**, 18 (9), 1037–1045.
- (7) Chen, C. P.; Luo, W. R.; Chen, C. N.; Wu, S. M.; Hsieh, S.; Chiang, C. M.; Dong, T. Y. Redox-Active π -Conjugated Organometallic Monolayers: Pronounced Coulomb Blockade Characteristic at Room Temperature. *Langmuir* **2013**, 29 (9), 3106–3115.
- (8) Dong, T. Y.; Chen, K.; Lin, M. C.; Lee, L. Toward the Development of Molecular Wires: Ruthenium(II) Terpyridine Complexes Containing Polyferrocenyl as a Spacer. *Organometallics* **2005**, 21 (17), 4198–4206.
- (9) Swinehart, D. F. The Beer-Lambert Law. *J. Chem. Educ.* **1962**, 39 (7), 333–335.