Supporting Information

for

Pd-catalysed C–H bond functionalisation route to 1,2-dihydroferroceno[c]isoquinoline and its annellated derivatives and the reactivity of these compounds

Věra Varmužová,[a] Ivana Císařová,[a] Jiří Schulz,[a] Květa Kalíková[b] and Petr Štěpnička*[a]

[a] Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic; E-mail: stepnic@natur.cuni.cz; [b] Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 00 Prague, Czech Republic

Contents

Syntheses

General comments

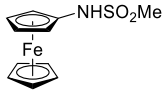
All syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. Aminoferrocene was prepared according to the literature procedure.[1] Other chemicals were purchased from commercial suppliers (Sigma–Aldrich, TCI, and ABCR) and used as received. Anhydrous tetrahydrofuran (THF), dichloromethane and methanol were obtained from a PureSolv MD5 solvent purification system (Innovative Technology, Inc.). Acetonitrile was dried over CaH_2 and distilled under nitrogen. 1,4-Dioxane and toluene were dried over sodium metal and freshly distilled under nitrogen. Dry pyridine and 1,2-dichloroethane were obtained from Sigma–Aldrich. Compounds **1**, **2c** and **11** were purified by chromatography on a Reveleris PREP Purification System (Büchi) using HPLC grade solvents (Fisher Chemical) and UV. Details are given below. Solvents employed during conventional column chromatography and for crystallisations were used as received (reagent grade from Lach-Ner, Czech Republic).

The NMR spectra were recorded on a Varian Unity Inova 400, a Bruker Avance III 400 or a Bruker Avance NEO 400 spectrometer at 25 °C. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C NMR) and 85% aqueous H_3PO_4 (^{31}P NMR). FTIR spectra were measured in diffuse reflectance mode (DRIFTS) using samples diluted with spectroscopic grade KBr using a Nicolet iS50 instrument (Thermo Fisher Scientific) in the 400–4000 cm^{-1} range and with 4 cm^{-1} resolution. UV-VIS absorption spectra were recorded on a Unicam UV 300 instrument in the 300–800 nm range using quartz cells (optical path: 1 cm). The samples were dissolved in acetonitrile (for HPLC, Fischer Chemical). Electrospray ionisation mass spectra (ESI MS) were recorded on a Bruker QTOF Micro spectrometer using samples dissolved in HPLC-grade methanol. Elemental analyses were performed on a PE 2400 Series II CHNS/O Elemental Analyser (Perkin Elmer). The amount of residual solvent (if present) was checked by NMR spectroscopy.

Electrochemical measurements were performed with a μAUTOLAB III instrument (Eco Chemie) at room temperature using a Metrohm three-electrode cell equipped with a glassy carbon disc working electrode (2 mm diameter), a platinum sheet auxiliary electrode, and an Ag/AgCl (3 M KCl) reference electrode. The samples were dissolved in dry dichloromethane to give a solution containing 1 mM analyte and 0.1 M $Bu_4N[PF_6]$ (TCI) as the supporting electrolyte. The solutions were deaerated with argon before the measurements and then maintained under an argon flow. Decamethylferrocene (Alfa-Aesar) was used as an internal standard during the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[2]

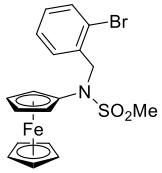
Details on structure determination, chromatographic separations and DFT calculations are provided below.

Syntheses



Synthesis of [(methylsulfonyl)amino]ferrocene (1). An oven-dried flask equipped with a stirring bar was charged with aminoferrocene (1.743 g, 8.7 mmol), flushed with nitrogen, and sealed with a rubber septum. The solid amine was dissolved in dry THF (150 mL), pyridine (1.1 mL, 13 mmol) was added and the mixture was cooled to 0 °C in an ice bath before neat methanesulfonyl chloride (0.74 mL, 9.6 mmol) was slowly introduced with continuous stirring. After the addition was complete, the cooling bath was removed and the stirring was continued at ambient temperature for 3 h. During this time, the colour of the reaction mixture changed from the initial orange to brown. The mixture was filtered through a short silica gel column, eluting with dichloromethane-2-propanol mixture (50:1) and the yellow eluate was evaporated with chromatographic silica gel. The crude, preadsorbed product was transferred into a solid loader and purified on a silica gel column (Interchim puriFlash, 30 μm, 40 g) using Buchi Reveleris X2 automatic chromatograph and dichloromethane-2-propanol (50:1) as the eluent (flow rate 25 ml min^{-1}). The first orange band was collected and evaporated, leaving amide **1** as a golden-yellow solid. Yield: 2.009 g (83%).

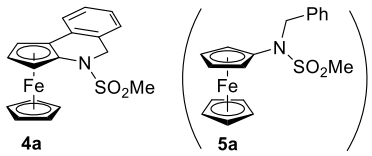
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91 (s, 3 H, CH_3), 4.10 (vt, *J′* = 1.9 Hz, 2 H, C_5H_4), 4.23 (s, 5 H, C_5H_5), 4.38 (vt, *J′* = 1.9 Hz, 2 H, C_5H_4), 6.02 (br s, 1 H, NH). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 38.69 (s, CH_3), 65.13 (s, CH of C_5H_4), 66.33 (s, CH of C_5H_4), 69.56 (s, C_5H_5), 92.51 (s, C^{ipso} of C_5H_4). HRMS (ESI) *m/z* calc. for $C_{11}H_{13}FeNO_2S$ (M^+): 279.0017, found: 279.0010. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 3245 s, 3013 w, 1459 m, 1435 w, 1416 w, 1386 m, 1341 m, 1323 m, 1307 s, 1161 m, 1148 s, 1104 w, 1032 w, 1023 w, 986 w, 967 m, 933 w, 835 w, 815 w, 791 w, 758 w, 645 w, 606 w, 527 w, 493 w, 427 w. Anal. calc. for $C_{11}H_{13}FeNO_2S$ (279.1): C 47.33, H 4.69, N 5.02%, found: C 47.34, H 4.66, N 4.76%.



Synthesis of *N*-(2-bromobenzyl)-*N*-(methylsulfonyl)aminoferrocene (3a). An oven-dried reaction flask equipped with a stirring bar was charged successively with compound **1** (837 mg, 3.0 mmol), 2-bromobenzyl bromide (750 mg, 3.0 mmol), and caesium carbonate (1.173 g, 3.6 mmol). Anhydrous acetonitrile (50 mL) was introduced and the reaction flask was equipped with a reflux condenser, flushed with nitrogen, and transferred to an oil bath maintained at 70 °C. The

heterogeneous mixture was heated at gentle reflux and stirred for 3 h before it was cooled to room temperature and concentrated under vacuum. The solid residue was taken up with ethyl acetate (30 mL) and the solution was washed with brine (25 mL). The aqueous layer was back-extracted with ethyl acetate (2× 20 mL) and the combined organic layers were dried over anhydrous magnesium sulfate and evaporated with chromatographic silica gel. The preadsorbed product was transferred onto the top of a chromatographic column. Elution with dichloromethane produced a single orange band, which was evaporated under vacuum to give compound **3a** as an orange powdery solid. Yield: 1.260 g (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 (s, 3 H, CH_3), 4.03 (s, 5 H, C_5H_5), 4.09 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.31 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.91 (s, 2 H, CH_2), 7.16-7.21 (m, 1 H, C_6H_4Br), 7.40 (ddd, *J* = 7.9, 7.4, 1.2 Hz, 1 H, C_6H_4Br), 7.59 (dd, *J* = 7.9, 1.2 Hz, 1 H, C_6H_4Br), 7.65-7.70 (m, 1 H, C_6H_4Br). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 36.73 (s, CH_3), 55.75 (s, CH_2), 62.78 (s, CH of C_5H_4), 65.61 (s, CH of C_5H_4), 69.22 (s, C_5H_5), 100.50 (s, C^{ipso} of C_5H_4), 121.66 (s, C^{ipso} of C_6H_4Br), 127.85 (s, CH of C_6H_4Br), 128.45 (s, CH of C_6H_4Br), 128.93 (s, CH of C_6H_4Br), 132.64 (s, CH of C_6H_4Br), 136.65 (s, C^{ipso} of C_6H_4Br). HRMS (ESI) *m/z* calc. for $C_{18}H_{18}{}^{79}BrFeNO_2S$ (M^+): 446.9593, found: 446.9593. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 1472 w, 1337 m, 1323 w, 1162 s, 1154 m, 1101 w, 1025 w, 958 w, 912 w, 835 m, 760 w, 746 w, 538 w, 518 m, 495 m, 485 w. Anal. calc. for $C_{18}H_{18}BrFeNO_2S$ (448.2): C 48.24, H 4.05, N 3.13%, found: C 48.57, H 3.82, N 2.91%.



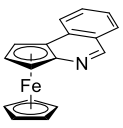
4a **5a**

Synthesis of 1,2-dihydro-2-(methylsulfonyl)ferroceno[*c*]isoquinoline (4a). A dry, 15-mL pressure tube equipped with a stirring bar was charged with amide **3a** (44.8 mg, 0.10 mmol), tricyclohexylphosphonium tetrafluoroborate ($Cy_3PH[BF_4]$) (1.5 mg, 4 μmol), potassium carbonate (20.7 mg, 0.15 mmol) and di-μ-methanesulfonyl-bis[2-(amino-κ*N*)[1,1′-biphenyl]-2-yl-κ*C*^{2}]-dipalladium (0.7 mg, 1 μmol), weighed on a small piece of broken thin glass. The tube was flushed with nitrogen, dry toluene (1.5 mL) was introduced and the tube was sealed. Then, the reaction vessel was transferred to an oil bath maintained at 140 °C and stirred at this temperature for 24 h, whereupon a black solid was deposited. The reaction mixture was cooled and partitioned between ethyl acetate and brine (15 ml each). The aqueous phase was extracted with ethyl acetate (3× 10 mL) and the combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was dissolved in dichloromethane (20 mL) and evaporated with chromatographic silica gel. The preadsorbed product was transferred onto the top of a chromatographic column. Elution with dichloromethane developed a single orange band, which was collected and evaporated,

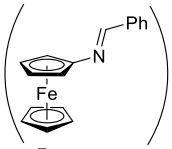
leaving 32.3 mg of the mixture of **4a** and **5a** in a 97:3 molar ratio according to the NMR analysis. Analytically pure **4a** was obtained by recrystallisation from THF-hexane.

Analytical data for **4a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3 H, CH_3), 4.18 (s, 5 H, C_5H_5), 4.30 (t, *J* = 2.6 Hz, 1 H, C_5H_3), 4. 63 (dd, *J* = 2.6, 1.2 Hz, 1 H, C_5H_3), 4.87 (d, *J* = 16.0 Hz, 1 H, CH_2), 4.97 (dd, *J* = 2.6 Hz, 1.2 Hz, 1 H, C_5H_3), 5.07 (d, *J* = 16.0 Hz, 1 H, CH_2), 7.20-7.29 (m, 3 H, C_6H_4, the signal is partly obscured by the solvent resonance), 7.35-7.38 (m, 1 H, C_6H_4). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 36.60 (s, CH_3), 50.94 (s, CH_2), 59.57 (s, CH of C_5H_3), 65.42 (s, CH of C_5H_3), 67.42 (s, CH of C_5H_3), 70.23 (s, C_5H_5), 71.02 (s, C^{ipso} of C_5H_3), 96.38 (s, C^{ipso} of C_5H_3), 123.32 (s, CH of C_6H_4), 126.17 (s, CH of C_6H_4), 126.37 (s, CH of C_6H_4), 128.33 (s, CH of C_6H_4), 130.16 (s, C^{ipso} of C_6H_4), 133.09 (s, C^{ipso} of C_6H_4). HRMS (ESI) *m/z* calc. for $C_{18}H_{17}FeNO_2S$ (M^+): 367.0330, found: 367.0325. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 1439 w, 1342 m, 1323 w, 1158 s, 1032 w, 1006 w, 969 m, 956 w, 846 w, 833 w, 819 w, 801 w, 767 m, 630 w, 610 w, 544 w, 529 w, 504 m. Anal. calc. for $C_{18}H_{17}FeNO_2S$ (367.2): C 58.87, H 4.67, N 3.81%, found: C 59.03, H 4.92, N 3.80%.

Analytical data for **5a**. ^{1}H NMR (400 MHz, $CDCl_3$): selected resonances – δ 2.89 (s, CH_3, $NHSO_2$*Me*), 4.06 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.07 (s, 5 H, C_5H_5), 4.34 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.88 (s, 2 H, CH_2).



6a



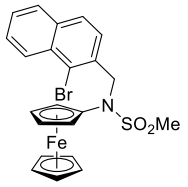
7a

Synthesis of ferroceno[*c*]isoquinoline (6a). The mixture of **4a** and **5a** (97:3 molar ratio, 32.3 mg) from the previous step and potassium *tert*-butoxide (49.3 mg, 0.44 mmol) were mixed in dry toluene (5 mL) in a 25-mL flask equipped with a stirring bar and a reflux condenser. The flask was flushed with nitrogen and heated at 100 °C in an oil bath for 2 h. The colour of the reaction mixture changed from orange to deep red during this time. Then, the reaction mixture was cooled to ambient temperature and partitioned between ethyl acetate and brine (15 mL each). The aqueous layer was washed with ethyl acetate (2× 10 mL) and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated under vacuum. The residue was dissolved in dichloromethane (approximately 5 mL) and evaporated with silica gel. The preadsorbed product was purified by chromatography over a silica gel column, eluting with dichloromethane-methanol (20:1). A pinkish band containing impure **7a** eluted first, followed by the major red band due to **6a**. Evaporation of the second band produced **6a** as a red solid. Yield: 20.5 mg (71% with respect to **3a**; *i.e.*, over the two steps).

Analytical data for **6a**. ^{1}H NMR (400 MHz, acetone-d_6): δ 3.75 (s, 5 H, C_5H_5), 4.29 (t, *J* = 2.6 Hz, 1 H, C_5H_3), 5.12 (dd, *J* = 2.6, 1.2 Hz, 1 H, C_5H_3), 5.33 (dd, *J* = 2.6, 1.2 Hz, 1 H, C_5H_3), 7.57

(ddd, *J* = 7.8, 7.3, 1.3 Hz, 1 H, C_6H_4), 7.75 (ddd, *J* = 7.8, 7.3, 1.3 Hz, 1 H, C_6H_4), 7.94 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1 H, C_6H_4), 8.09-8.14 (m, 1 H, C_6H_4), 8.89 (s, 1 H, CH=N). $^{13}C\{^1H\}$ NMR (100.6 MHz, acetone-d_6): δ 59.82 (s, CH of C_5H_3), 65.73 (s, CH of C_5H_3), 69.27 (s, CH of C_5H_3), 70.17 (s, C_5H_5), 76.59 (s, C^{ipso} of C_5H_3), 105.01 (s, C^{ipso} of C_5H_3), 123.61 (s, CH of C_6H_4), 126.79 (s, CH of C_6H_4), 127.13 (s, C^{ipso} of C_6H_4), 130.37 (s, CH of C_6H_4), 132.01 (s, CH of C_6H_4), 139.27 (s, C^{ipso} of C_6H_4), 156.69 (s, CH=N). HRMS (ESI) *m/z* calc. for $C_{17}H_{14}FeN$ ($[M + H]^+$): 288.0476; found: 288.0470. Anal. calc. for $C_{17}H_{13}FeN$ (287.1): C 71.11, H 4.56, N 4.88%, found: C 70.91, H 4.60, N 4.62%.

Analytical data for **7a**. ^1H NMR (400 MHz, $CDCl_3$): δ 4.19 (s, 5 H, C_5H_5), 4.26 (vt, *J′* = 1.9 Hz, 2 H, C_5H_4), 4.60 (vt, *J′* = 1.9 Hz, 2 H, C_5H_4), 7.41-7.47 (m, 3 H, C_6H_4), 7.79-7.86 (m, 2 H, C_6H_4), 8.63 (s, 1 H, CH=N).[3] HRMS (ESI) *m/z* calc. for $C_{17}H_{16}FeN$ ($[M + H]^+$): 290.0632, found: 290.0621.

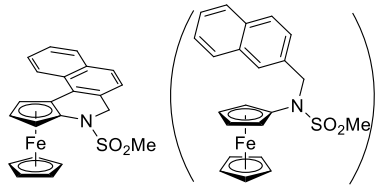


3b

Synthesis of *N*-(2-bromonaphthyl)-*N*-(methylsulfonyl)aminoferrocene (3b). A dry reaction flask equipped with a reflux condenser and a stirring bar was charged successively with compound **1** (837 mg, 3.0 mmol), 1-bromo-2-(bromomethyl)naphthalene (900 mg, 3.0 mmol), and caesium carbonate (1.173 g, 3.6 mmol) and flushed with nitrogen. Acetonitrile (70 mL) was introduced and the flask was transferred to an oil bath maintained at 70 °C. After stirring at this temperature for 3 h, the reaction mixture was evaporated under vacuum. The residue was extracted with hot chloroform (150 mL) and the extract was filtered and evaporated. The residue was redissolved in chloroform and evaporated with chromatographic silica gel. The crude preadsorbed product was purified by chromatography over a silica gel column, using dichloromethane as the eluent. A single yellow-orange band was collected and evaporated, leaving compound **3b** as a yellow solid. Yield: 1.424 g (95%).

^1H NMR (400 MHz, $CDCl_3$): δ 3.02 (s, 3 H, CH_3), 4.03 (s, 5 H, C_5H_5), 4.08 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.34 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 5.16 (s, 2 H, CH_2), 7.53 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1 H, $C_{10}H_6Br$), 7.62 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1 H, $C_{10}H_6Br$), 7.80 (d, *J* = 8.5 Hz, 1 H, $C_{10}H_6Br$), 7.85 (dt, *J* = 8.1, 0.7 Hz, 1 H, $C_{10}H_6Br$), 7.90 (d, *J* = 8.5 Hz, 1 H, $C_{10}H_6Br$), 8.31–8.36 (m, 1 H, $C_{10}H_6Br$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 36.84 (s, CH_3), 56.62 (s, CH_2), 62.56 (s, CH of C_5H_4), 65.58 (s, CH of C_5H_4), 69.22 (s, C_5H_5), 100.75 (s, C^{ipso} of C_5H_4), 121.48 (s, C^{ipso} of $C_{10}H_6Br$), 125.29 (s, CH of $C_{10}H_6Br$), 126.55 (s, CH of $C_{10}H_6Br$), 126.65 (s, CH of $C_{10}H_6Br$), 127.62 (s, CH of $C_{10}H_6Br$), 128.12 (s, CH of $C_{10}H_6Br$), 128.31 (s, CH of $C_{10}H_6Br$), 132.23 (s, C^{ipso} of $C_{10}H_6Br$), 134.07 (s, C^{ipso} of $C_{10}H_6Br$), 134.97 (s, C^{ipso} of $C_{10}H_6Br$). HRMS (ESI) *m/z* calc. for $C_{22}H_{20}{}^{79}BrFeNO_2S$ (M^+): 496.9749, found: 496.9746. IR

(DRIFTS, KBr, cm^{-1}): ν_{max} 1470 w, 1339 m, 1323 w, 1157 s, 1102 m, 961 m, 910 w, 837 w, 818 w, 809 w, 754 w, 745 w, 554 w, 514 m, 502 m, 495 m, 482 m. Anal. calc. for $C_{22}H_{20}BrFeNO_2S$ (498.2): C 53.04, H 4.05, N 2.81%, found: C 52.80, H 3.87, N 2.66%.

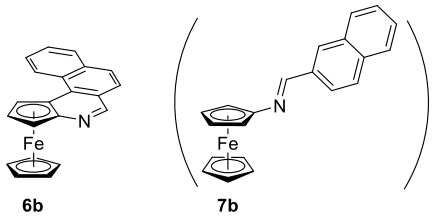


4b **5b**

Synthesis of 1,2-dihydro-2-(methylsulfonyl)benzo[*f*]ferroceno[*c*]isoquinoline (8). Using the procedure for the preparation of **4a**, amide **3b** (49.8 mg, 0.10 mmol) was converted to a mixture of compounds **4b** and **5b** in an 89:11 ratio (combined yield: 36.5 mg), which was isolated as a deep orange solid. Pure **4b** was obtained by recrystallisation from acetone-hexane. Crystallisation from hot heptane produced two types of crystals (due to **4b** and **5b**), which were manually separated to give a sample of pure compound **5b**.

Analytical data for **4b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3 H, CH_3), 4.17 (s, 5 H, C_5H_5), 4.48 (t, *J* = 2.6 Hz, 1 H, C_5H_3), 5.07 (dd, *J* = 2.6, 1.2 Hz, 1 H, C_5H_3), 5.14 (br s, 2 H, CH_2), 5.18 (ddd, *J* = 2.8, 1.2, 0.4 Hz, 1 H, C_5H_3), 7.35 (d, *J* = 8.3 Hz, 1 H, $C_{10}H_6$), 7.51 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1 H, $C_{10}H_6$), 7.58 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1 H, $C_{10}H_6$), 7.74 (d, *J* = 8.2 Hz, 1 H, $C_{10}H_6$), 7.86-7.90 (m, 1 H, $C_{10}H_6$), 8.51 (d, *J* = 8.6 Hz, 1 H, $C_{10}H_6$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 36.66 (s, CH_3), 52.31 (s, CH_2), 63.82 (s, CH of C_5H_3), 66.00 (s, CH of C_5H_3), 67.54 (s, CH of C_5H_3), 70.63 (s, C_5H_5), 71.77 (s, C^{ipso} of C_5H_3), 97.72 (s, C^{ipso} of C_5H_3), 124.44 (s, CH of $C_{10}H_6$), 124.66 (s, CH of $C_{10}H_6$), 125.85 (s, CH of $C_{10}H_6$), 126.60 (s, CH of $C_{10}H_6$), 126.86 (s, CH of $C_{10}H_6$), 129.02 (s, CH of $C_{10}H_6$), 129.72 (s, C^{ipso} of $C_{10}H_6$), 129.85 (s, C^{ipso} of $C_{10}H_6$), 130.23 (s, C^{ipso} of $C_{10}H_6$), 134.00 (s, C^{ipso} of $C_{10}H_6$). HRMS (ESI) *m/z* calc. for $C_{22}H_{19}FeNO_2S$ (M^+): 417.0486, found: 417.0483. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 1464 w, 1377 w, 1345 s, 1319 w, 1164 s, 1154 s, 1106 w, 1069 w, 1044 w, 1007 w, 965 m, 862 w, 847 w, 832 w, 815 w, 807 w, 760 m, 587 w, 565 w, 542 w, 517 m, 499 m, 477 w, 461 m. Anal. calc. for $C_{22}H_{19}FeNO_2S$ (417.3): C 63.32, H 4.59, N 3.36%, found: C 63.14, H 4.38, N 3.10%.

Analytical data for **5b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.93 (s, 3 H, CH_3), 4.06 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.07 (s, 5 H, C_5H_5), 4.37 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 5.04 (s, 2 H, CH_2), 7.44-7.54 (m, 2 H, $C_{10}H_7$), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1 H, $C_{10}H_7$), 7.83-7.94 (m, 4 H, $C_{10}H_7$). HRMS (ESI) *m/z* calc. for $C_{22}H_{21}FeNNaO_2S$ ($[M + Na]^+$): 442.0540, found: 442.0533.

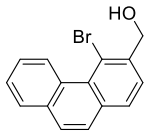


6b **7b**

Synthesis of benzo[*f*]ferroceno[*c*]isoquinoline (6b). Compound **6b** was obtained similarly to **6a**, starting from the 89:11 mixture of **4b** and **5b** (36.5 mg), and was isolated as a deep violet solid. Yield: 22.3 mg (66% from compound **3b**; *i.e.*, over two steps).

Analytical data for **6b**. ^{1}H NMR (400 MHz, acetone-d_6): δ 3.76 (s, 5 H, C_5H_5), 4.45 (t, *J* = 2.7 Hz, 1 H, C_5H_3), 5.37 (dd, *J* = 2.7, 1.2 Hz, 1 H, C_5H_3), 5.83 (ddd, *J* = 2.9, 1.2, 0.3 Hz, 1 H, C_5H_3), 7.81 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1 H, $C_{10}H_6$), 7.92 (ddd, *J* = 8.4, 6.7, 1.4 Hz, 1 H, $C_{10}H_6$), 7.97 (d, *J* = 8.4 Hz, 1 H, $C_{10}H_6$), 8.06 (d, *J* = 8.4 Hz, 1 H, $C_{10}H_6$), 8.13-8.18 (m, 1 H, $C_{10}H_6$), 9.07 (s, 1 H, CH=N), 9.17-9.22 (m, 1 H, $C_{10}H_6$). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6): δ 63.76 (s, CH of C_5H_3), 65.92 (s, CH of C_5H_3), 69.73 (s, C_5H_5), 71.15 (s, CH of C_5H_3), 75.91 (s, C^{ipso} of C_5H_3), 107.88 (s, C^{ipso} of C_5H_3), 125.12 (s, C^{ipso} of $C_{10}H_6$), 127.43 (s, CH of $C_{10}H_6$), 127.54 (s, CH of $C_{10}H_6$), 127.68 (s, CH of $C_{10}H_6$), 127.93 (s, CH of $C_{10}H_6$), 128.69 (s, CH of $C_{10}H_6$), 129.85 (s, CH of $C_{10}H_6$), 130.63 (s, C^{ipso} of $C_{10}H_6$), 135.79 (s, C^{ipso} of $C_{10}H_6$), 138.38 (s, C^{ipso} of $C_{10}H_6$), 156.97 (s, CH=N). HRMS (ESI) *m/z* calc. for $C_{21}H_{16}FeN$ ([M + H]$^+$): 338.0632, found: 338.0628. Anal. calc. for $C_{21}H_{15}FeN$ (337.2): C 74.80, H 4.48, N 4.15%, found: C 74.18, H 4.41, N 3.83%. Note: the compound readily decomposes, which affected the microanalytical results obtained in an external laboratory.

Analytical data for **7b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (s, 5 H, C_5H_5), 4.29 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 4.65 (vt, *J′* = 2.0 Hz, 2 H, C_5H_4), 7.49-7.57 (m, 2 H, $C_{10}H_7$), 7.83-7.94 (m, 3 H, $C_{10}H_7$), 8.10 (dd, *J* = 8.5, 1.7 Hz, 1 H, $C_{10}H_7$), 8.12-8.14 (m, 1 H, $C_{10}H_7$), 8.79 (s, 1 H, CH=N). HRMS (ESI) *m/z* calc. for $C_{21}H_{18}FeN$ ([M + H]$^+$): 340.0789, found: 340.0779.

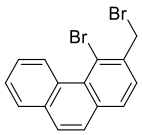


11

Synthesis of (4-bromophenanthren-3-yl)methanol (11). In a dry Schlenk tube, 4-bromophenanthrene-3-carbaldehyde (**10**; 1.141 g, 4 mmol) was dissolved in a mixture of anhydrous THF and methanol (25 mL each). Solid sodium tetrahydridoborate (167 mg, 4.4 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. Next, the reaction mixture was cooled on ice and quenched by adding saturated aqueous ammonium chloride (20 mL). The organic solvents were removed under vacuum and the aqueous residue was extracted with ethyl acetate (30 mL). The aqueous layer was separated and extracted with ethyl acetate (3× 15 mL). The combined organic layers were washed with brine, dried over anhydrous magnesium

sulfate, and evaporated. The off-white solid residue was taken up with ethyl acetate (60 mL) and evaporated with chromatographic silica gel. The crude, preadsorbed product was transferred to a solid loader and purified on a silica gel column (Interchim puriFlash, 30 μm, 40 g) using a Buchi Reveleris X2 chromatograph and hexane-ethyl acetate (88:12) as the eluent (flow rate 25 ml min^{-1}). The first colourless band was collected and evaporated to give **11** as a white solid. Yield: 1.023 g (89%). The product contains approximately 6 mol.% of a structurally similar impurity which could not be removed by chromatography or crystallisation. This impurity does not impede the subsequent synthetic step.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.03 (d, *J* = 6.1 Hz, 2 H, CH_2), 7.58-7.66 (m, 3 H, $C_{14}H_8Br$), 7.68-7.75 (m, 2 H, $C_{14}H_8Br$), 7.83 (d, *J* = 8.0 Hz, 1 H, $C_{14}H_8Br$), 7.87-7.93 (m, 1 H, $C_{14}H_8Br$), 9.85-9.93 (m, 1 H, $C_{14}H_8Br$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 66.91 (s, CH_2), 119.94 (s, C^{ipso} of $C_{14}H_8Br$), 125.01 (s, CH of $C_{14}H_8Br$), 126.43 (s, CH of $C_{14}H_8Br$), 126.71 (s, CH of $C_{14}H_8Br$), 127.05 (s, CH of $C_{14}H_8Br$), 127.36 (s, CH of $C_{14}H_8Br$), 128.11 (s, CH of $C_{14}H_8Br$), 128.44 (s, CH of $C_{14}H_8Br$), 128.52 (s, CH of $C_{14}H_8Br$), 129.21 (s, C^{ipso} of $C_{14}H_8Br$), 129.91 (s, C^{ipso} of $C_{14}H_8Br$), 133.74 (s, C^{ipso} of $C_{14}H_8Br$), 134.40 (s, C^{ipso} of $C_{14}H_8Br$), 140.44 (s, C^{ipso} of $C_{14}H_8Br$). HRMS (ESI+): *m/z* calc. for $C_{15}H_{11}{}^{79}BrNaO$ ($[M + Na]^+$): 308.9891, found: 308.9885.

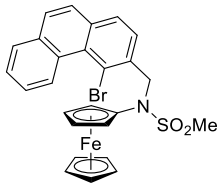


2c

Synthesis of 4-bromo-3-(bromomethyl)phenanthrene (2c). Compound **11** (574 mg, 2.0 mmol) was dissolved in anhydrous dichloromethane (30 mL) under nitrogen. The solution was cooled on ice and treated dropwise with neat phosphorus tribromide (0.1 ml, 1 mmol). The resulting mixture was stirred for 1 h before quenching with solid $NaHCO_3$ (0.5 g) and ethyl acetate (10 mL). After stirring for 10 min, the mixture was filtered and the filtrate was evaporated under vacuum. The residue was dissolved in dichloromethane (40 mL) and evaporated with chromatographic silica gel. The preadsorbed product was transferred into a solid loader and purified on a silica gel column (Interchim puriFlash, 30 μm, 40 g) using a Buchi Reveleris X2 chromatograph and hexane-ethyl acetate (99:1) as the eluent (flow rate 25 ml min^{-1}). Evaporation of the first colourless band afforded dibromide **2c** as a white solid. Yield: 438 mg (63%). The product contains approximately 6 mol.% of a chemically similar impurity which could not be removed by chromatography or crystallisation. This impurity does not interfere with the following alkylation reaction and is easily removed after it.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.93 (s, 2 H, CH_2), 7.53-7.67 (m, 4 H, $C_{14}H_8Br$), 7.71 (d, *J* = 8.8 Hz, 1 H, $C_{14}H_8Br$), 7.75 (d, *J* = 8.1 Hz, 1 H, $C_{14}H_8Br$), 7.83-7.89 (m, 1 H, $C_{14}H_8Br$), 9.82-9.95 (m, 1 H, $C_{14}H_8Br$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ 36.68 (s, CH_2), 122.23 (s, C^{ipso} of $C_{14}H_8Br$), 125.18 (s,

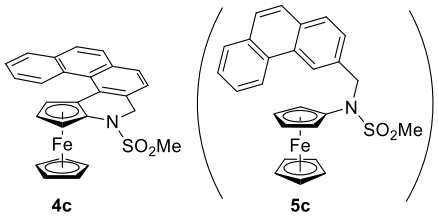
CH of $C_{14}H_8Br$), 126.42 (s, CH of $C_{14}H_8Br$), 127.25 (s, CH of $C_{14}H_8Br$), 127.46 (s, CH of $C_{14}H_8Br$), 128.43 (s, CH of $C_{14}H_8Br$), 128.55 (s, CH of $C_{14}H_8Br$), 128.71 (s, CH of $C_{14}H_8Br$), 128.95 (s, CH of $C_{14}H_8Br$), 129.87 (s, C^{ipso} of $C_{14}H_8Br$), 129.98 (s, C^{ipso} of $C_{14}H_8Br$), 133.70 (s, C^{ipso} of $C_{14}H_8Br$), 134.80 (s, C^{ipso} of $C_{14}H_8Br$), 137.40 (s, C^{ipso} of $C_{14}H_8Br$). HRMS (APPI+): *m/z* calc. for $C_{15}H_{10}{}^{79}Br^{81}Br$ (M^+): 349.9129, found: 349.9119.



3c

Synthesis of *N*-((4-bromophenanthren-3-yl)methyl)-*N*-(methylsulfonyl)aminoferrocene (3c). A 100-mL, round bottom flask equipped with a stirring bar was charged with **1** (349 mg, 1.25 mmol), 4-bromo-3-(bromomethyl)phenanthrene (**2c**; 437 mg, 1.25 mmol) and caesium carbonate (489 mg, 1.5 mmol), equipped with a reflux condenser and flushed with nitrogen. Anhydrous acetonitrile (40 mL) was introduced and the resulting mixture was heated at 70 °C in an oil bath for 3 h with continuous stirring. Then, the mixture was cooled and concentrated under vacuum. The residue was extracted with hot chloroform (70 mL) and filtered. The filtrate was evaporated, redissolved in chloroform, and evaporated with chromatographic silica gel. The product was isolated by column chromatography over silica gel, eluting with dichloromethane. Evaporation of a single yellow-orange band produced compound **3c** as a yellow solid, Yield: 629 mg (92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.04 (s, 3 H, CH_3), 4.04 (s, 5 H, C_5H_5), 4.11 (vt, *J´* = 2.0 Hz, 2 H, C_5H_4), 4.37 (vt, *J´* = 2.0 Hz, 2 H, C_5H_4), 5.22 (s, 2 H, CH_2), 7.61-7.76 (m, 4 H, $C_{14}H_8Br$), 7.88-7.92 (m, 1 H, $C_{14}H_8Br$), 7.93 (s, 2 H, $C_{14}H_8Br$), 9.91-9.97 (m, 1 H, $C_{14}H_8Br$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ 36.83 (s, CH_3), 58.08 (s, CH_2), 62.99 (s, CH of C_5H_4), 65.71 (s, CH of C_5H_4), 69.26 (s, C_5H_5), 100.73 (s, C^{ipso} of C_5H_4), 119.10 (s, C^{ipso} of $C_{14}H_8Br$), 125.01 (s, CH of $C_{14}H_8Br$), 125.95 (s, CH of $C_{14}H_8Br$), 126.83 (s, CH of $C_{14}H_8Br$), 127.08 (s, CH of $C_{14}H_8Br$), 127.30 (s, CH of $C_{14}H_8Br$), 128.11 (s, CH of $C_{14}H_8Br$), 128.51 (s, CH of $C_{14}H_8Br$), 128.63 (s, CH of $C_{14}H_8Br$), 129.33 (s, C^{ipso} of $C_{14}H_8Br$), 129.81 (s, C^{ipso} of $C_{14}H_8Br$), 133.85 (s, C^{ipso} of $C_{14}H_8Br$), 134.42 (s, C^{ipso} of $C_{14}H_8Br$), 137.37 (s, C^{ipso} of $C_{14}H_8Br$). HRMS (ESI+): *m/z* calc. for $C_{26}H_{22}{}^{79}BrFeNO_2S$ (M^+): 546.9906; found: 546.9904. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 1468 w, 1452 w, 1411 w, 1395 w, 1378 w, 1340 m, 1323 w, 1312 w, 1289 w, 1249 w, 1157 s, 1106 m, 1056 w, 1013 w, 963 m, 911 m, 881 w, 865 w, 845 m, 837 m, 814 w, 788 w, 755 w, 743 m, 706 w, 622 w, 556 w, 534 w, 517 s, 500 m, 482 m. Anal. calc. for $C_{26}H_{22}BrFeNO_2S$ (548.3): C 56.96, H 4.04, N 2.55%. Found: C 56.98, H 3.85, N 2.74%.

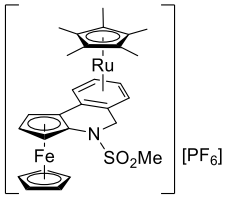


Cyclisation of 3c. A 15-mL pressure tube was charged successively with compound **3c** (54.8 mg, 0.10 mmol), tricyclohexylphosphonium tetrafluoroborate (1.5 mg, 4 μmol), potassium carbonate (20.7 mg, 0.15 mmol) and di-μ-methanesulfonyl-bis[2-(amino-κ*N*)[1,1′-biphenyl]-2-yl-κ*C*^{2}]-dipalladium (0.7 mg, 1 μmol) weighed on a small piece of broken glass. The reaction vessel was flushed with nitrogen, and anhydrous 1,4-dioxane (1.5 mL) was introduced. The sealed tube was heated at 140 °C in an oil bath with stirring for 24 h, during which time the initially orange-yellow mixture turned deep orange. After cooling, the reaction mixture was partitioned between ethyl acetate and brine (15 mL each). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3× 10 mL). The combined organic layers were dried over magnesium sulfate and evaporated. The residue was taken up with dichloromethane (20 mL) and evaporated with chromatographic silica gel. The preadsorbed product was purified by chromatography over silica gel using dichloromethane-hexane (2:1) as the eluent. A minor pink band was discarded and the following major band was collected and evaporated to afford a mixture of **4c** and **5c** in an 80:20 molar ratio. Yield: 43.5 mg, orange solid. Pure samples were obtained by crystallisation from dichloromethane-hexane and manual separation of the two types of crystals formed. Compound **5c** was also isolated from an experiment, in which improperly dried and deoxygenated dioxane was used. In this case, **5c** was obtained exclusively.

Analytical data for **4c**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64 (s, 3 H, CH_3), 3.98 (s, 5 H, C_5H_5), 4.25 (t, *J* = 2.6 Hz, 1 H, C_5H_3), 4.74 (dd, *J* = 2.8, 1.2 Hz, 1 H, C_5H_3), 5.16 (dd, *J* = 2.6, 1.2 Hz, 1 H, C_5H_3), 5.22 (d, *J* = 17.0 Hz, 1 H, CH_2), 5.30 (d, *J* = 17.0 Hz, 1 H, CH_2), 7.27-7.41 (m, 2 H, $C_{14}H_8$), 7.53 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1 H, $C_{14}H_8$), 7.61-7.67 (m, 2 H, $C_{14}H_8$), 7.70 (d, *J* = 8.7 Hz, 1 H, $C_{14}H_8$), 7.85 (dd, *J* = 8.0, 1.4 Hz, 1 H, $C_{14}H_8$), 8.69 (d, *J* = 8.4 Hz, 1 H, $C_{14}H_8$). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 36.81 (s, CH_3), 52.99 (s, CH_2), 64.33 (s, CH of C_5H_3), 66.09 (s, CH of C_5H_3), 68.40 (s, CH of C_5H_3), 70.73 (s, C_5H_5), 77.22 (s, C^{ipso} of C_5H_3), 97.70 (s, C^{ipso} of C_5H_3), 123.65 (s, CH of $C_{14}H_8$), 123.72 (s, CH of $C_{14}H_8$), 126.41 (s, CH of $C_{14}H_8$), 126.75 (s, CH of $C_{14}H_8$), 126.81 (s, CH of $C_{14}H_8$), 127.29 (s, CH of $C_{14}H_8$), 127.89 (s, CH of $C_{14}H_8$), 128.41 (s, CH of $C_{14}H_8$), 128.59 (s, C^{ipso} of $C_{14}H_8$), 129.47 (s, C^{ipso} of $C_{14}H_8$), 129.86 (s, C^{ipso} of $C_{14}H_8$), 133.33 (s, C^{ipso} of $C_{14}H_8$), 133.36 (s, C^{ipso} of $C_{14}H_8$), 134.25 (s, C^{ipso} of $C_{14}H_8$). HRMS (ESI+): *m/z* calc. for $C_{26}H_{21}FeNNaO_2S$ ([M + Na]$^+$): 490.0540, found: 490.0534. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 1464 m, 1445 w, 1346 s, 1317 w, 1164 s, 1107 w, 1093 w, 1070 w, 1028 w, 958 m, 914 w, 845 m, 815 m, 791 w, 756 m, 727 w, 659 w, 601 w, 571 m, 553 w, 540 w, 527 w, 509 s, 488

m, 477 m, 448 w, 436 w, 424 w, 403 w. Anal. calc. for $C_{26.15}H_{21.3}Cl_{0.3}FeNO_2S$ (**4c**·015CH_2Cl_2; 480.1): C 65.42, H 4.47, N 2.92%. Found: C 65.88, H 4.26, N 3.22%.

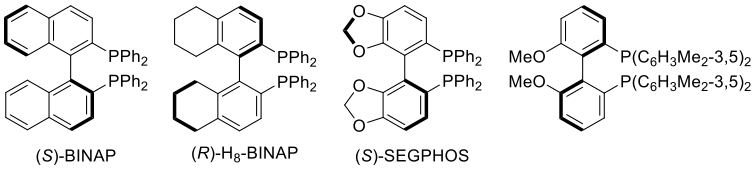
Analytical data for **5c**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (s, 3 H, CH_3), 4.06 (s, 5 H, C_5H_5), 4.07 (vt, *J*´ = 2.0 Hz, 2 H, C_5H_4), 4.41 (vt, *J*´ = 2.0 Hz, 2 H, C_5H_4), 5.15 (s, 2 H, CH_2), 7.62 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1 H, $C_{14}H_9$), 7.66-7.71 (m, 1 H, $C_{14}H_9$), 7.71-7.77 (m, 3 H, $C_{14}H_9$), 7.88-7.92 (m, 1 H, $C_{14}H_9$), 7.94 (d, *J* = 8.2 Hz, 1 H, $C_{14}H_9$), 8.74 (dd, *J* = 8.3, 1.1 Hz, 1 H, $C_{14}H_9$), 8.79 (br s, 1 H, $C_{14}H_9$). HRMS (ESI+): *m/z* calc. for $C_{26}H_{23}FeNNaO_2S$ ([M + Na]$^+$): 492.0697, found: 492.0696. The compound is poorly soluble, which made it impossible to record good-quality ^{13}C NMR spectra.



12

Synthesis of complex 12. An oven-dried, 25-mL flask equipped with a stirring bar and a reflux condenser was charged with [(η^5-C_5Me_5)Ru(MeCN)$_3$][PF_6] (50.4 mg, 0.10 mmol) and flushed with nitrogen. A solution of **4a** (47.7 mg, 0.13 mmol) in 1,2-dichloroethane (7 mL) was introduced and the stirred mixture was heated at 40 °C for 3 h. After cooling to room temperature, the reaction mixture was filtered through a PTFE syringe filter (0.45 μm porosity), and the filtrate was evaporated with chromatographic alumina (neutral, Brockmann I). The crude preadsorbed product was transferred onto the top of an alumina column packed in dichloromethane-methanol (50:1). Elution with the same solvent mixture initially developed a minor orange band, which was discarded. The following orange band due to the product was collected and evaporated, leaving **12** as a light orange powdery solid. Yield of **12**: 56.3 mg (75%).

^{1}H NMR (400 MHz, acetone-d_6, ppm): δ 1.83 (s, 15 H, C_5Me_5), 3.46 (s, 3 H, SO_2Me), 4.41 (s, 5 H, C_5H_5), 4.54 (t, *J* = 2.7 Hz, 1 H, C_5H_3), 4.74 (s, 2 H, CH_2), 4.87 (dd, *J* = 2.7, 1.2 Hz, 1 H, C_5H_3), 4.91 (dd, *J* = 2.7, 1.2 Hz, 1 H, C_5H_3), 6.06 (td, *J* = 5.8, 0.7 Hz, 1 H, C_6H_4), 6.12 (td, *J* = 5.8, 0.7 Hz, 1 H, C_6H_4), 6.21 (d, *J* = 5.8 Hz, 1 H, C_6H_4), 6.31 (d, *J* = 5.8 Hz, 1 H, C_6H_4). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6): δ –138.2 (septet, $^1J_{PF}$ = 708 Hz). ^{13}C{^{1}H} NMR (101 MHz, acetone-d_6): δ 10.30 (s, $C_5\mathit{Me}_5$), 36.58 (s, SO_2Me), 47.81 (s, CH_2), 60.50 (s, CH of C_5H_3), 63.60 (s, CH of C_5H_3), 64.11 (s, C^{ipso} of C_5H_3), 66.91 (s, CH of C_5H_3), 71.03 (s, C_5H_5), 82.88 (s, CH of C_6H_4), 85.90 (s, CH of C_6H_4), 86.51 (s, CH of C_6H_4), 88.08 (s, CH of C_6H_4), 97.05 (s, C^{ipso} of C_6H_4), 97.55 (s, C_5Me_5), 97.96 (s, C^{ipso} of C_6H_4), 99.56 (s, C^{ipso} of C_5H_3). HRMS (ESI) *m/z* calc. for $C_{28}H_{32}FeNO_2{}^{102}RuS$ ([M – PF_6]$^+$): 604.0556, found: 604.0549. IR (DRIFTS, KBr, cm^{-1}): ν_{max} 1411 w, 1350 m, 1165 m, 1040 w, 1008 w, 949 w, 894 w, 845 s, 810 w, 755 w, 599 w, 557 m, 515 m, 488 w, 453 m, 443 m. Anal. calc. for $C_{28}H_{32}F_6FeNO_2PRuS$·2$CH_2Cl_2$ (918.4): C 39.23, H 3.95, N 1.53%, found: C 39.38, H 3.63, N 1.62% (crystallised sample).



Scheme S1. Compounds tested as chiral auxiliary ligands for asymmetric synthesis of **4a**.

X-ray crystallography

Data collection was performed on a Bruker D8 VENTURE Kappa Duo diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) at 120 or 125 K using either Cu Kα (λ = 1.54178 Å; compound **4b** for which only tiny crystals could be obtained) or Mo Kα radiation (λ = 0.71073 Å; all other compounds). The structures were solved by direct methods (SHELXT-2014 or 2018[4]) and refined using a weighted full-matrix least-squares routine against F^2 (SHELXL-2014 or 2017[5]).

The NH hydrogen in the structure of **1** was identified on a difference electron density map and refined as a "riding atom" with U_{iso}(H) = 1.2U_{eq}(N). Hydrogen atoms bonding to carbon atoms were included in their theoretical positions and treated as riding atoms using the standard parameters implemented in SHELXL and U_{iso}(H) set to 1.2 or 1.5U_{eq}(C). The bromine atom in the structure of **3c** was disordered. It was modelled over two positions with refined relative occupancies ≈65:35. Compound **4a** crystallised as a tetrahydrofuran solvate, **4a**·1/4C_4H_8O, with the solvent molecules severely disordered in structural voids around the crystallographic inversion centres. The entire solvent molecule was included in the structure model as a rigid moiety from the DSR library.[6]

Selected crystallographic data and structure refinement parameters are presented in Table S1. All geometric data and structural diagrams were obtained using a recent version of the PLATON program.[7] The numerical values were rounded with respect to their standard deviations. Note: the relatively larger uncertainty of geometric parameters determined for **4b** reflects the poor quality of the available crystals.

Table S1. Selected crystallographic data and structure refinement parameters[a]

Compound	**1**	**3a**	**4a**·0.25C_4H_8O
Formula	$C_{11}H_{13}FeNO_2S$	$C_{18}H_{18}BrFeNO_2S$	$C_{19}H_{19}FeNO_{2.25}S$
M [g mol^{-1}]	279.13	448.15	385.26
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
T [K]	125(2)	120(2)	120(2)
a [Å]	13.7051(5)	23.846(1)	15.7505(3)
b [Å]	7.6440(2)	11.9269(5)	12.2238(2)
c [Å]	10.7512(4)	12.1075(5)	17.1904(3)
α [°]	90	90	90
β [°]	98.175(1)	94.159(2)	100.605(1)
γ [°]	90	90	90
V [Å]^3	1114.87(7)	3434.4(2)	3253.2(1)
Z	4	8	8
F(000)	576	1808	1600
μ(Mo Kα) [mm^{-1}]	1.522	3.337	1.069
Diffrns collected	16058	54665	49254
Independent diffrns	2524	7848	7452
Observed diffrns[a]	2462	7445	7196
R_{int}[b] [%]	1.96	2.30	1.82
No. of parameters	147	435	450
R[b] obsd diffrns [%]	1.90	1.83	2.67
R, wR[b] all data [%]	1.95, 4.98	1.99, 4.62	2.76, 6.87
Δρ [e Å^{-3}]	0.354, –0.371	0.380, –0.328	1.025, –0.555
CCDC deposition no.	2389173	2389174	2389175

[a] Diffractions with $I > 2\sigma(I)$. [b] Definitions: $R_{int} = \Sigma \left| F_o^2 - F_o^2(\text{mean}) \right| / \Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry-equivalent diffractions. $R = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$.

Table S1 continued

Compound	**3b**	**4b**	**3c**
Formula	$C_{22}H_{20}BrFeNO_2S$	$C_{22}H_{19}FeNO_2S$	$C_{26}H_{22}BrFeNO_2S$
M [g mol^{-1}]	498.21	417.29	548.26
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	P–1 (no. 2)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)	120(2)
a [Å]	11.9274(2)	8.3913(8)	12.6893(5)
b [Å]	15.8153(3)	14.559(1)	16.3022(6)
c [Å]	11.2907(2)	16.359(2)	11.2724(5)
α [°]	90	67.187(7)	90
β [°]	114.259(1)	88.963(7)	112.868(1)
γ [°]	90	73.568(7)	90
V [Å]^3	1941.76(6)	1757.5(3)	2148.6(2)
Z	4	4	4
F(000)	1008	864	1112
μ(Mo Kα) [mm^{-1}]	2.961	8.135	2.684
Diffrns collected	27579	14868	155310
Independent diffrns	4451	5971	6250
Observed diffrns[a]	4272	2946	5848
R_{int}[b] [%]	2.04	12.64	3.25
No. of parameters	254	489	300
R[b] obsd diffrns [%]	1.73	7.41	3.04
R, wR[b] all data [%]	1.83, 4.26	16.85, 19.19	3.26, 9.41
Δρ [e Å^{-3}]	0.356, –0.329	0.982, –0.470	0.600, –0.661
CCDC deposition no.	2389176	2389177	2389178

Table S1 contiuned

Compound	**4c**	**12**·2CH_2Cl_2
Formula	$C_{26}H_{21}FeNO_2S$	$C_{30}H_{36}Cl_4F_6FeNO_2PRuS$
M [g mol^{-1}]	467.35	918.35
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
T [K]	120(2)	120(2)
a [Å]	10.8319(3)	9.3915(4)
b [Å]	9.5698(3)	10.6510(5)
c [Å]	20.1927(6)	18.0749(9)
α [°]	90	105.218(2)
β [°]	100.296(1)	97.607(2)
γ [°]	90	94.929(2)
V [Å]^3	2059.5(1)	1715.4(1)
Z	4	2
F(000)	968	924
μ(Mo Kα) [mm^{-1}]	0.858	1.346
Diffrns collected	36071	43822
Independent diffrns	4701	7831
Observed diffrns[a]	4586	7502
R_{int}[b] [%]	1.87	2.02
No. of parameters	281	430
R[b] obsd diffrns [%]	2.43	1.83
R, wR[b] all data [%]	2.49, 6.29	1.92, 4.70
Δρ [e Å^{-3}]	0.375, –0.419	0.618, –0.458
CCDC deposition no.	2389179	2389180

Amide **1** crystallised with the symmetry of the monoclinic space group $P2_1/c$ and one molecule in the asymmetric unit (Figure S1). Its molecule comprises an undistorted ferrocene unit with parallel cyclopentadienyl rings (Fe-C (range): 2.020(1)-2.052(1) Å, tilt angle: 1.76(8)°) in a practically eclipsed conformation. The geometry of the sulfonyl group, directed above the ferrocene unit, is very similar to that reported in $PhNHSO_2Me$.[8] Individual molecules of **1** in the crystal are interlinked *via* N-H···O1 hydrogen bonds into infinite chains oriented along the crystallographic axis *b* (Figure S1). Additionally, the O2 oxygen atom is involved in H-bond interactions with a proximal C-H group. Notably, the different role of the sulfonate oxygen atoms in the crystal assembly is reflected in a relatively minor but statistically significant difference in the S-O bond lengths (S-O1 > S-O2).

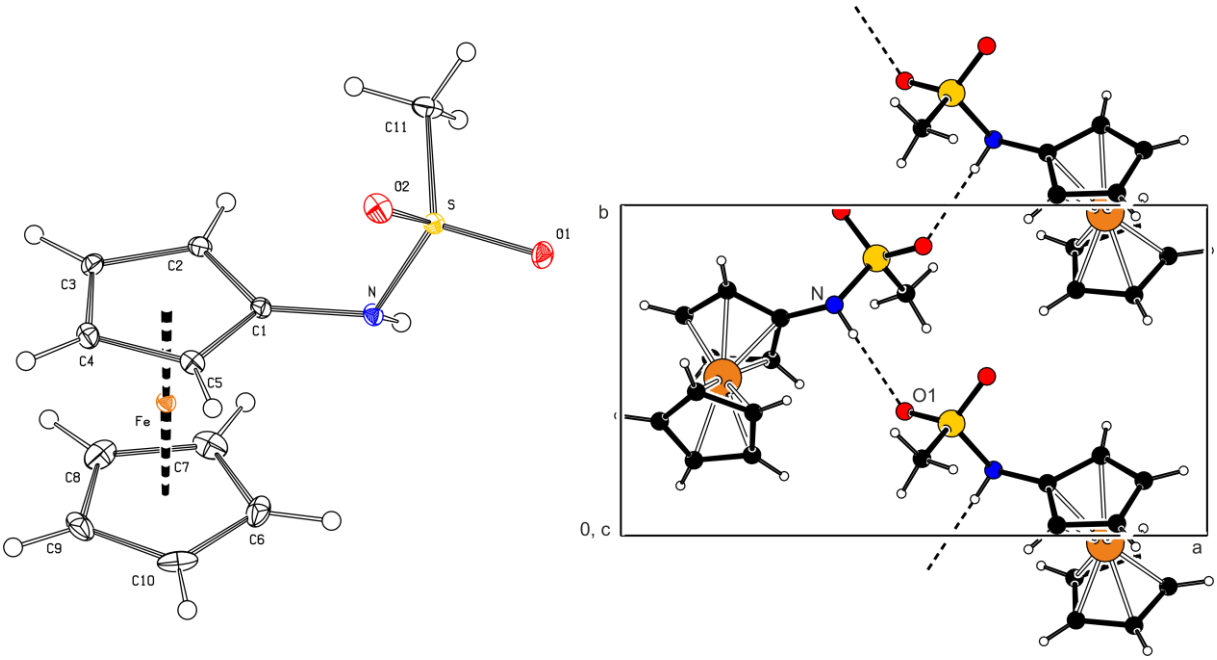


Figure S1 (left) PLATON plot of the molecular structure of **1** (30% probability ellipsoids). Selected distances and angles (in Å and deg): S-N 1.638(1), S-O1 1.442(1), S-O2 1.433(2), S-C11 1.757(1), C1-N-S 116.69(8), N-S-O1 106.29(5), N-S-O2 107.80(5), O1-S-O2 118.50(6), N-S-C11 107.14(6). (right) Hydrogen bond interactions between the individual molecules of **1**. Hydrogen bond parameters are as follows: N···O1^{i} = 2.956(1), N-H···O1^{i} angle = 161°, i. (1−*x*, *y*−1/2, 3/2−*z*).

Compounds **3a**-**c** crystallised all with the symmetry of the space group $P2_1/c$ (monoclinic) but with either one (**3b** and **3c**) or two structurally independent molecules (**3a**) in the asymmetric unit (**3c**). Views of the molecular structures are presented in Figures S2-4. Selected geometric parameters are outlined in Table S2.

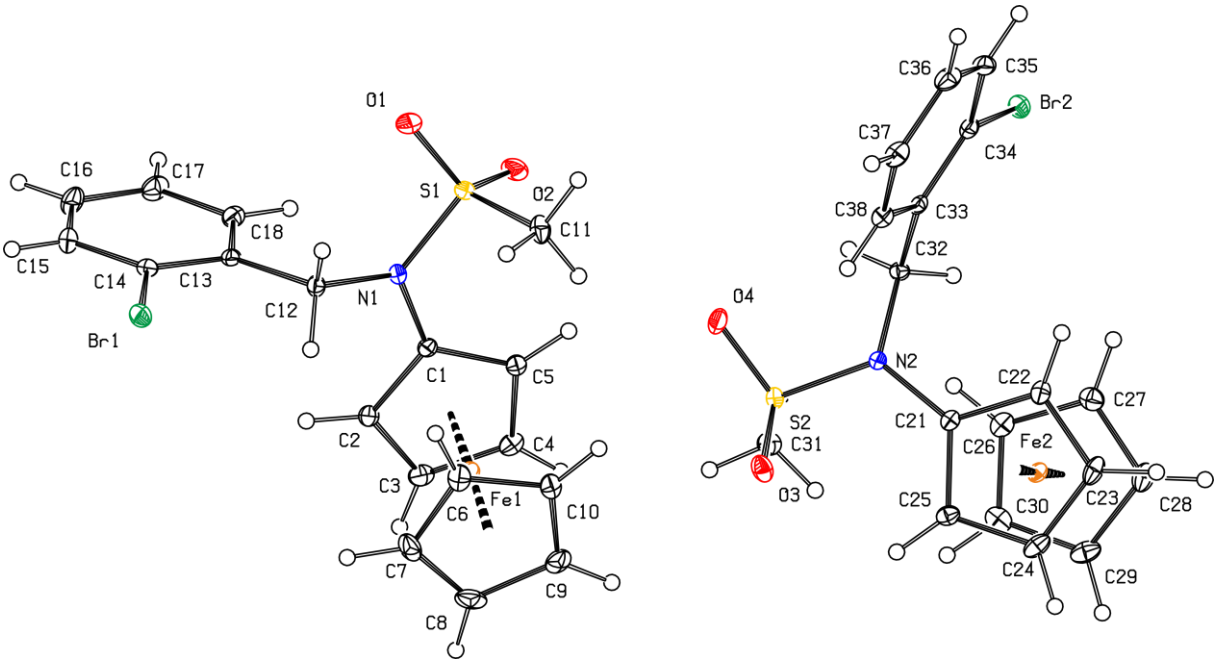


Figure S2 PLATON plot of the two independent molecules of **3a** (30% probability level)

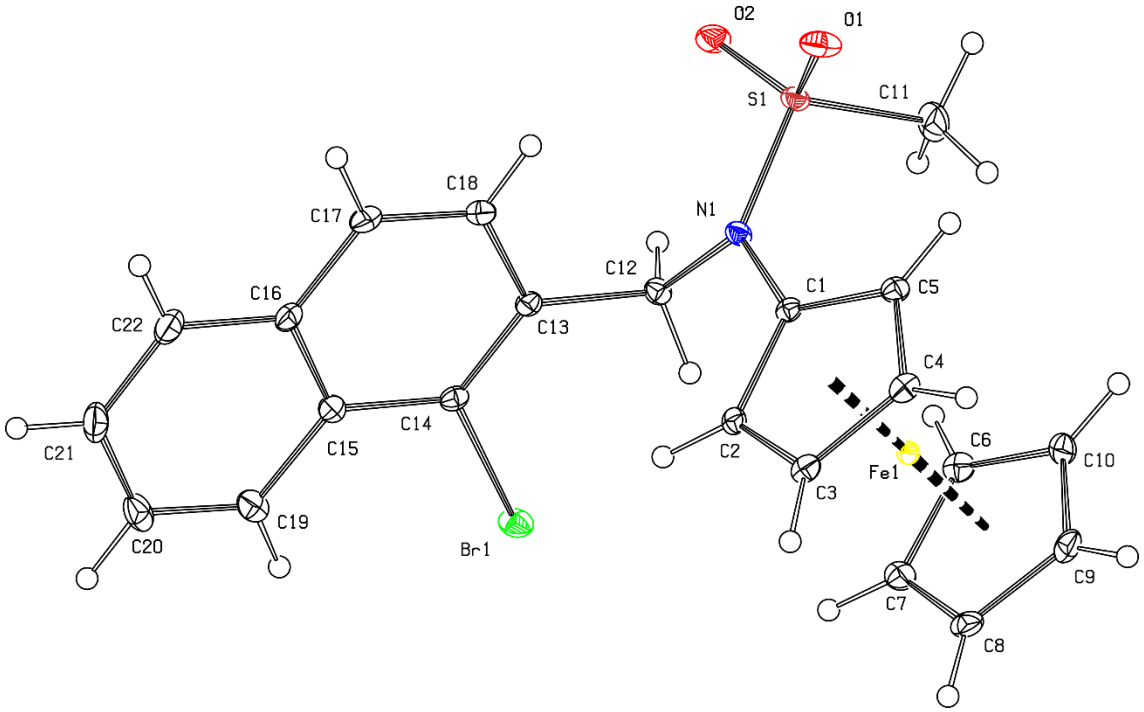


Figure S3 PLATON plot of the molecular structure of **3b** (30% probability level)

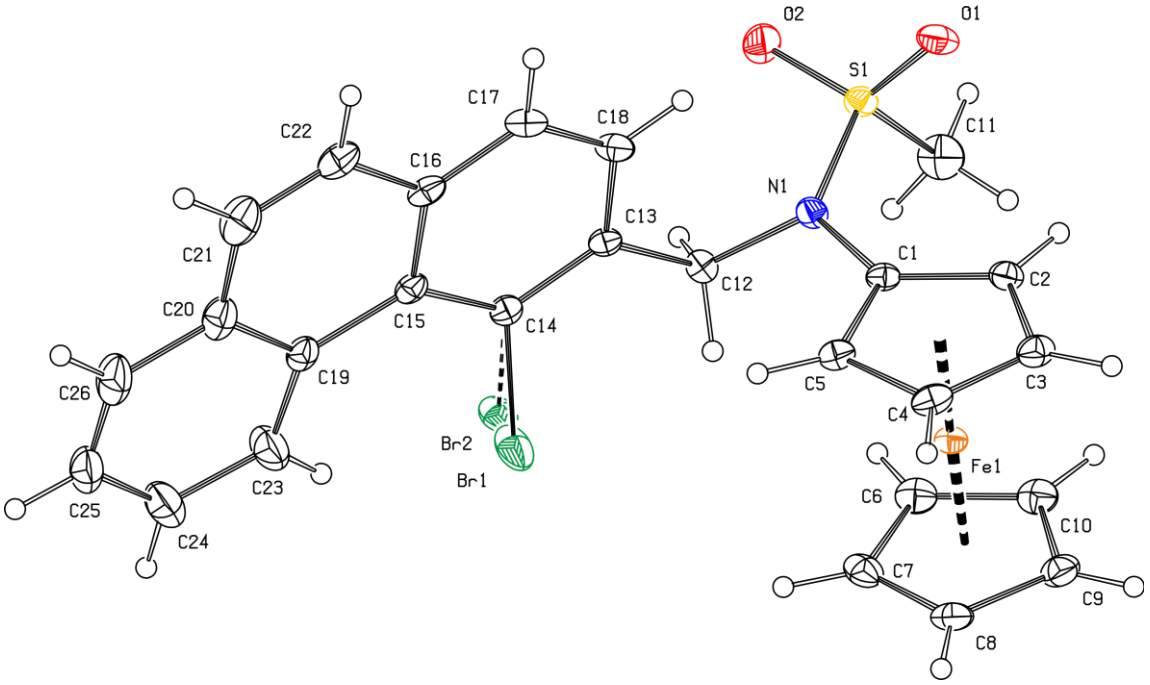


Figure S4 PLATON plot of the molecular structure of **3c** (30% probability level), showing both positions of the disordered bromine atom

Table S2 Selected geometric parameters for **3a-c** (in Å and deg)

Parameter	**3a** (molecule 1)	**3a** (molecule 2)[b]	**3b**	**3c**
N1-S1	1.641(1)	1.643(1)	1.636(1)	1.635(1)
N1-S1-C11	106.24(7)	106.70(7)	106.64(7)	106.45(9)
N1-C1	1.423(2)	1.419(2)	1.426(2)	1.422(2)
N1-C12	1.469(2)	1.471(2)	1.471(2)	1.470(2)
C1-N1-C12	117.8(1)	117.3(1)	117.0(1)	116.6(1)
S1-O1	1.434(1)	1.434(1)	1.432(1)	1.428(1)
S1-O2	1.432(1)	1.430(1)	1.435(1)	1.434(2)
O1-S1-O2	119.29(6)	119.72(6)	118.89(7)	119.41(9)
S1-C11	1.758(2)	1.756(2)	1.762(2)	1.753(3)
C14-Br1	1.903(1)	1.905(1)	1.906(1)	disorder
Fe1-C(1-10)	2.036(2)-2.059(2)	2.036(2)-2.068(1)	2.033(1)-2.058(1)	2.032(2)-2.058(2)
tilt[a]	2.75(9)	3.12(8)	1.99(8)	2.1(1)
Cp1 *vs.* arene[a]	82.95(8)	84.50(8)	86.15(6)	86.67(8)

[a] Tilt is the dihedral angle of the cyclopentadienyl least-square planes and Cp1 *vs.* arene stands for the dihedral angle between the cyclopentadienyl plane C(1-5) and the entire aromatic substituent (*i.e.*, C(13-18) for **3a**, C(13-22) for **3b**, and C(13-26) for **3b**). [b] The labelling of atoms in molecule 2 is strictly analogous to that of molecule 1.

The two independent molecules of **3a** are similar, differing only by the positioning of the bromophenyl substituent (Figure S5). Both molecules contain unperturbed ferrocene units showing similar Fe-C distances and tilt angles of approximately 3°. Presumably for steric reasons, the nitrogen atoms are displaced above the planes of their parent cyclopentadienyl rings C(1-5)/ C(21-25) by 0.061(1) and 0.040(1) Å in molecules 1 and 2, respectively, and the {N1, C12, S1}/{N2, C32, S2} planes are twisted by 20.9(1) and 22.3(1)° (the oxygen atoms are directed above the ferrocene unit). The terminal 2-bromophenyl substituents are practically perpendicular to the substituted cyclopentadienyl planes and their bromine atoms point towards the ferrocene moiety.

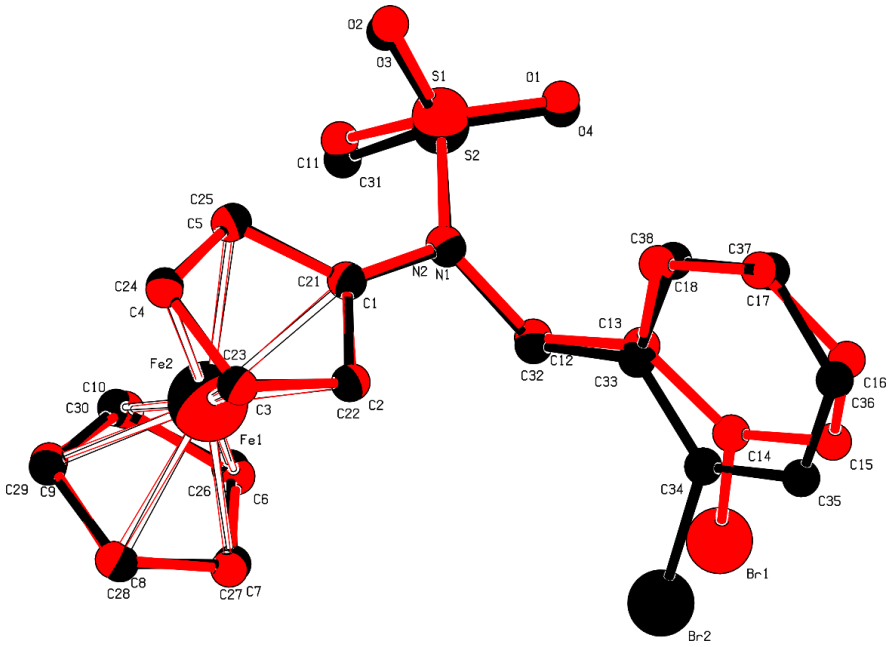


Figure S5 An overlap of the independent molecules of **3a** (red – molecule 1, black – molecule31 2)

Geometric parameters describing the molecule of **3b** do not depart significantly from those observed for **3a** and the two compounds even have a similar spatial arrangement. Thus, the nitrogen atom in **3b** is displaced by 0.069(1) above the ring C(1-5) and the {N1, C12, S1} moiety is twisted by 19.4(1)° with respect to the cyclopentadienyl ring. The disubstituted naphthalene ring is essentially planar (within 0.03 Å) and is oriented nearly perpendicularly to the ferrocene unit (dihedral angle of the C(1-5) and C(13-22) planes is 86.15(6)°) with the bromine atom directed to the ferrocene unit. A similar can be said about the geometry of **3c**, where the departure of the nitrogen atom from the C(1-5) plane is 0.058(1) Å and the {N1, C12, S1} fragment is twisted by 25.3(2)°. Even in **3c**, the entire aromatic substituent is planar (within 0.04 Å for the 15 ring carbon atoms) and nearly perpendicular to the ferrocene unit (86.67(8)°).

The bond distances in the N-SO_2CH_3 fragment do not differ across the series of **3a-c** and are similar to those in **1**. The N-S-CH_3 angles are consistently narrower than the O-S-O angles, likely due to the repulsion of the polarised O atoms that are directed away from the ferrocene unit.

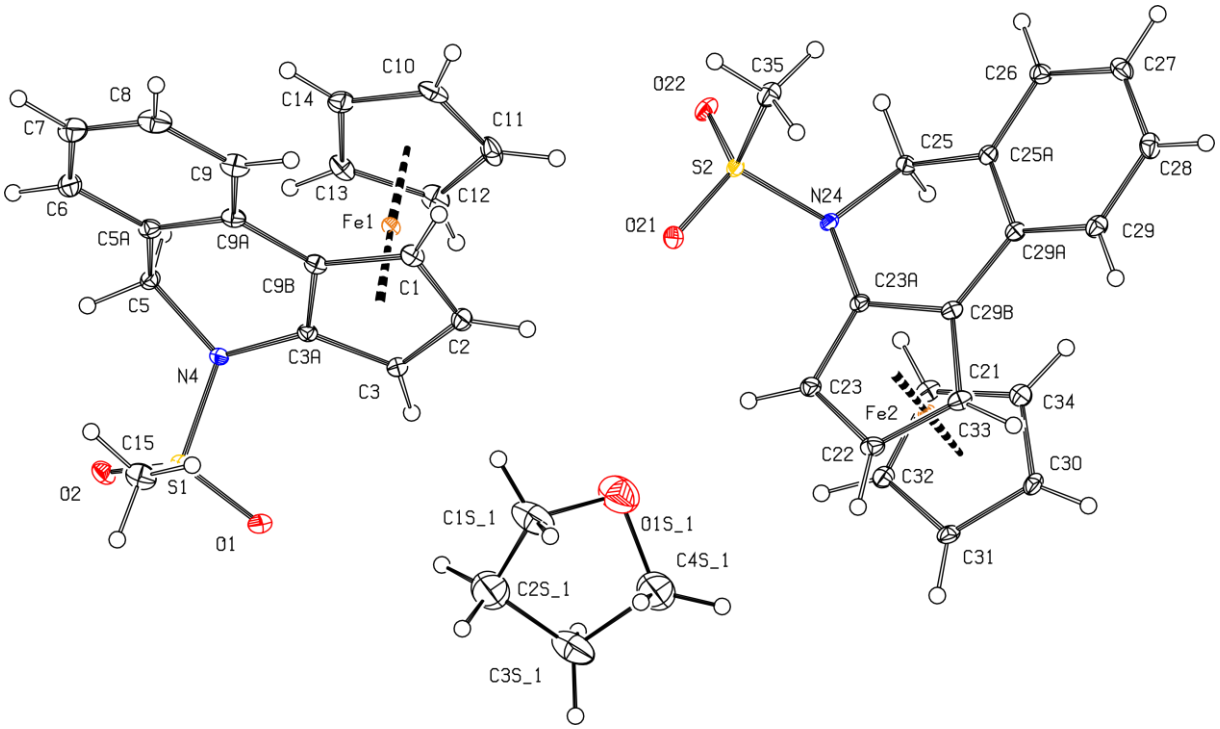


Figure S6 PLATON plot of the molecular structure of **4a**·0.25THF (20% probability level)

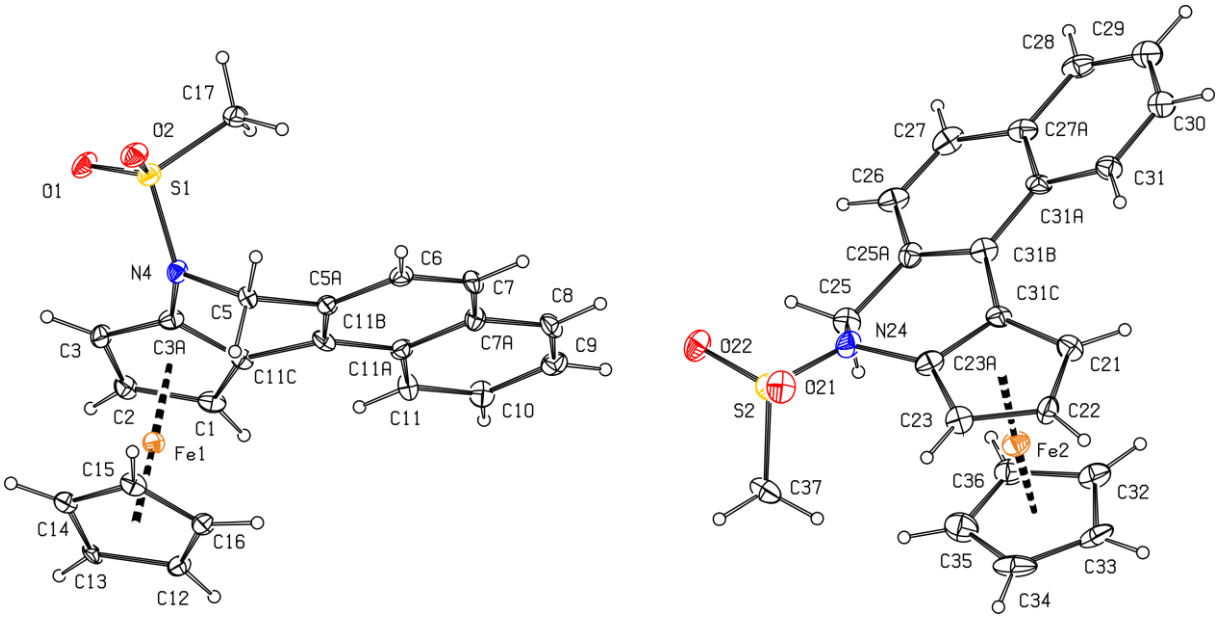


Figure S7 PLATON plot of the molecular structure of **4b** (30% probability level)

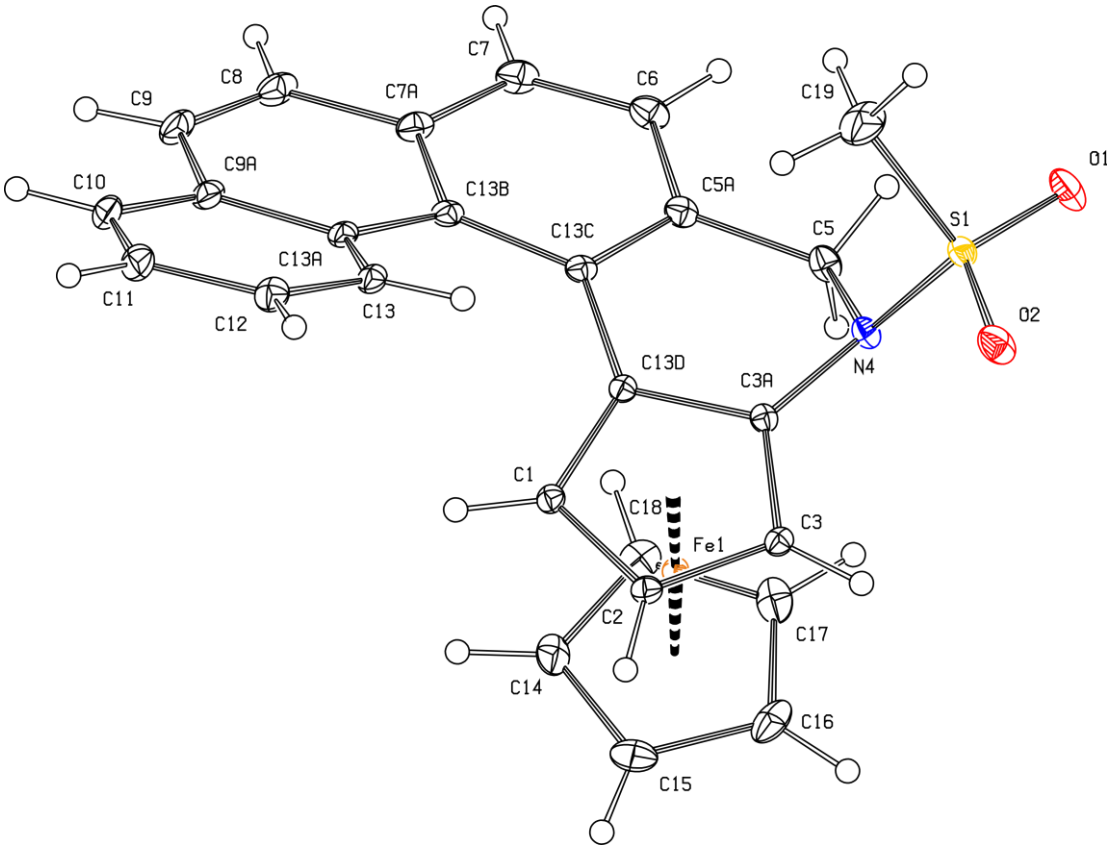


Figure S8 PLATON plot of the molecular structure of **4c** (30% probability level)

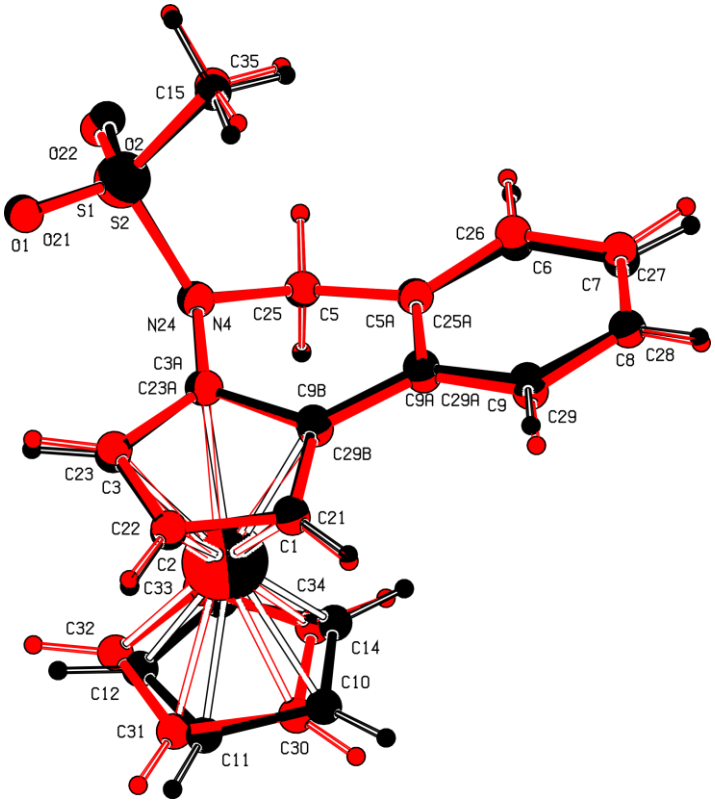


Figure S9 An overlap of the two symmetrically independent molecules in the structure of **4a** (molecule 1 in red, molecule 2 in black)

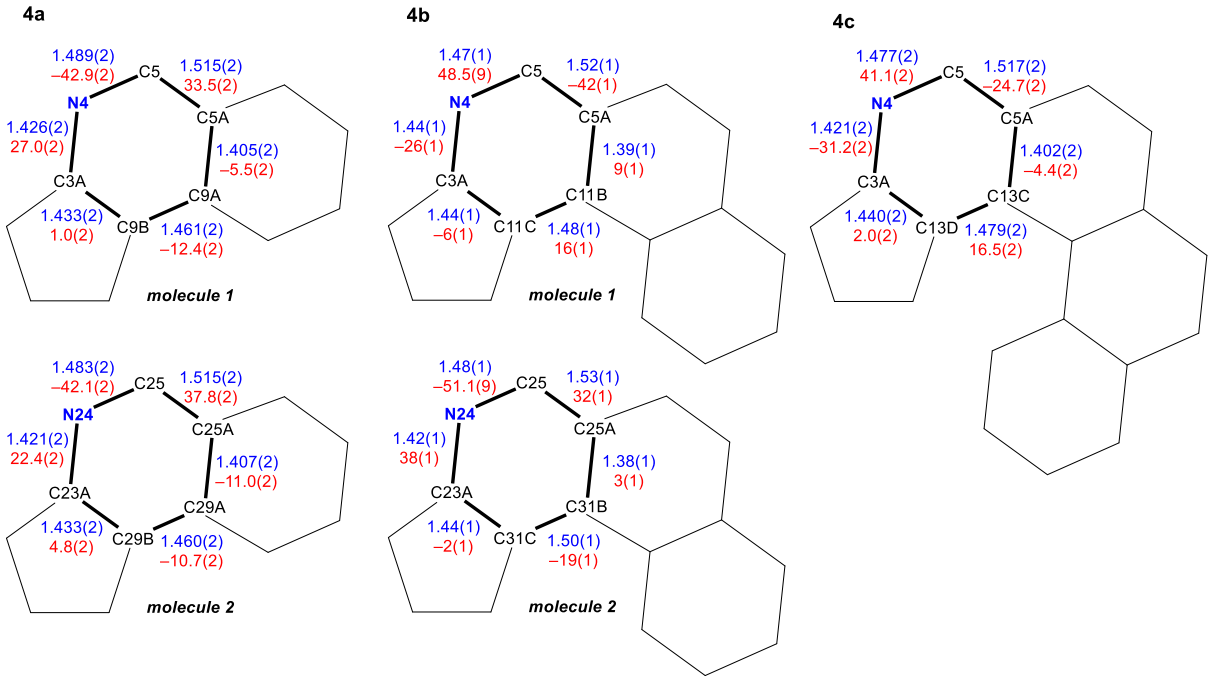


Figure S10 Bond lengths (in Å; blue) and torsion angles (in degrees; red) in the non-planar dihydropyridine rings of **4a**-**4c**. The signs of the torsion angles depend on the choice of the refined molecule (enantiomer in the centrosymmetric structure). Hence, only their absolute values and mutual relationship are important because the signs are reversed for the respective enantiomer.

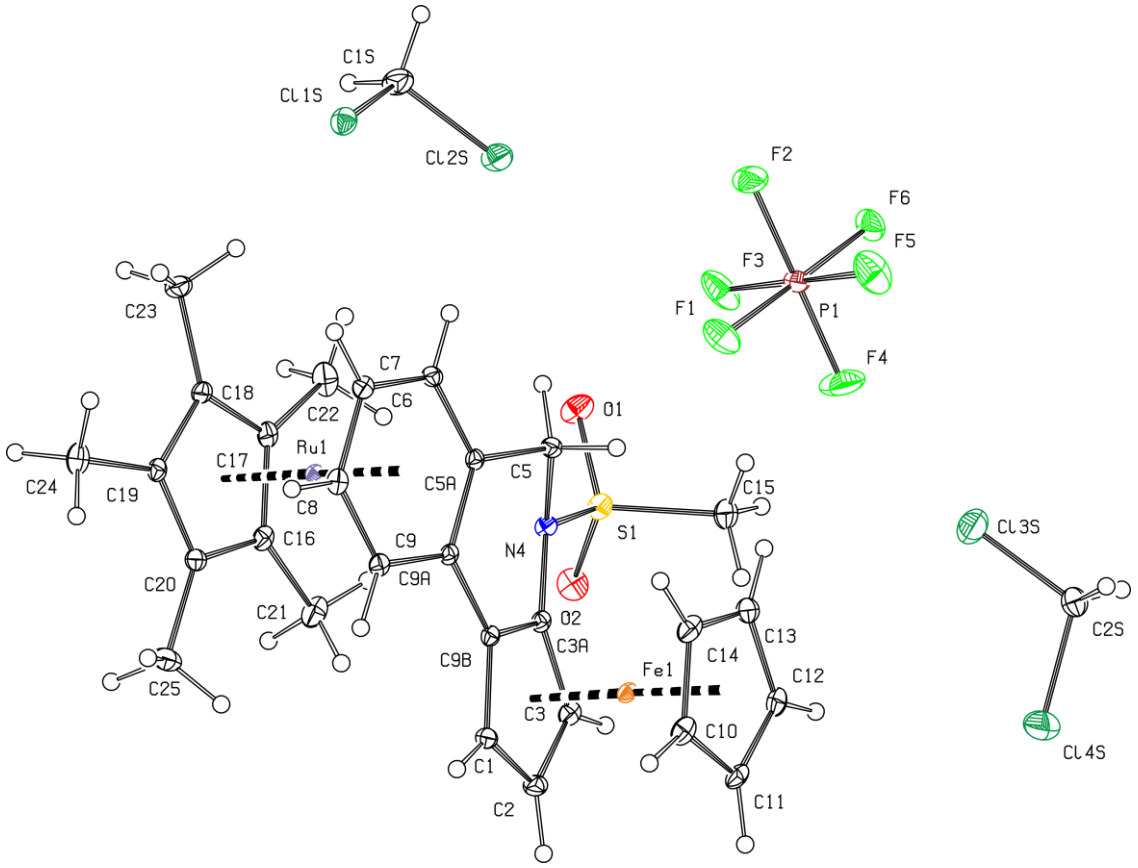


Figure S11 PLATON plot of the molecular structure of **12**·2CH_2Cl_2 (30% probability level)

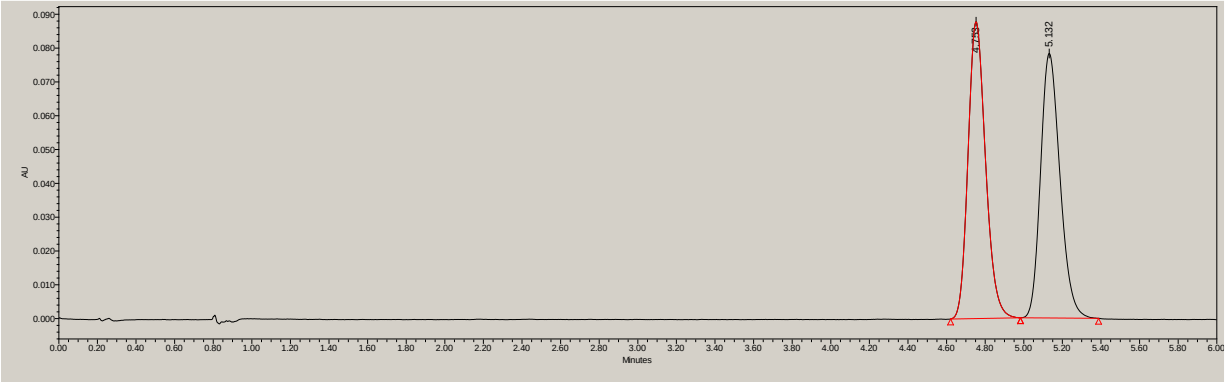
Chromatographic separations

Sub/supercritical fluid chromatography (SFC) analyses were performed on a Waters Acquity Ultra Performance Convergence Chromatography (UPC²) system. This instrument includes a binary solvent delivery pump with mobile phase flow rates up to 4 mL min^{-1} and pressures up to 6000 psi, an autosampler with a partial loop volume injection system, a back-pressure regulator, a column oven, and a photodiode array detector (Waters Corporation). The Empower 3 software was used for system control and data acquisition. The mobile phase consisted of CO_2 and methanol in various volume ratios. Column temperature of 40 °C, back pressure of 2000 psi, UV detection at 254 nm and flow rate of 2.0 mL min^{-1} were applied in all cases. Stock solutions of individual analytes at a concentration of 0.5 mg mL^{-1} were prepared by dissolving samples in MeOH and were filtered using a 0.2 μm PTFE syringe filter. The injected volume was 2 μL and the sample temperature was 10 °C.

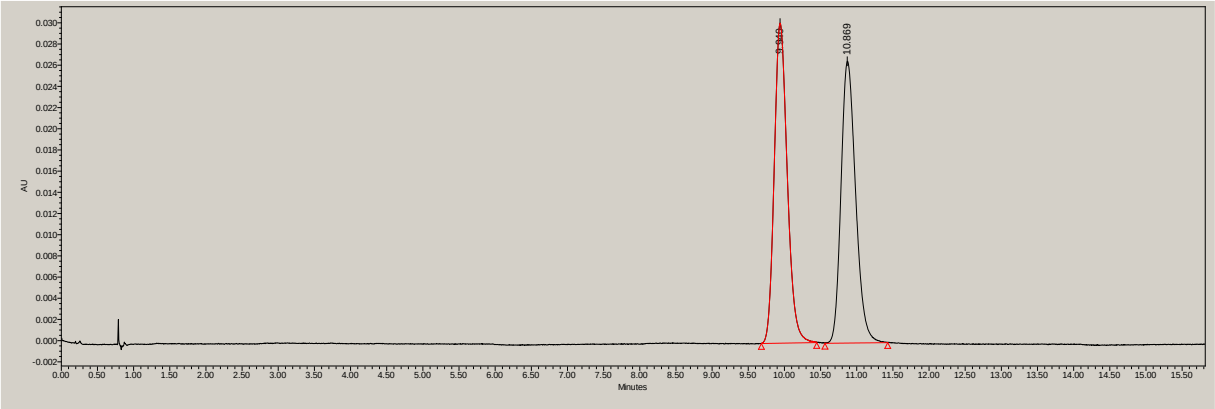
HPLC experiments were carried out using a Waters system equipped with an autosampler 717 plus, a 2487 dual λ absorbance detector, a binary pump 1515, and a column heater (Waters Corporation). Data evaluations were processed by the Empower 3 software. Analyses were performed at 25 °C with a flow rate of 1.0 mL min^{-1} and an injection volume of 10 μL. UV detection wavelength was set at 254 nm. *n*-Heptane/2-propanol 80/20 (v/v) was used as the mobile phase. A stock solution of **4a** (2 mg mL^{-1}) was prepared by dissolving the sample in THF.

Polysaccharide-based column Lux® i-Amylose-3, 150 × 4.6 mm, particle size 3 μm (Phenomenex, Torrance, CA, USA) with amylose tris(3-chloro-5-methylphenylcarbamate) as a chiral selector was used for both SFC and HPLC analyses.

CO_2:methanol = 70:30



CO_2:methanol = 80:20



CO_2:methanol = 90:10

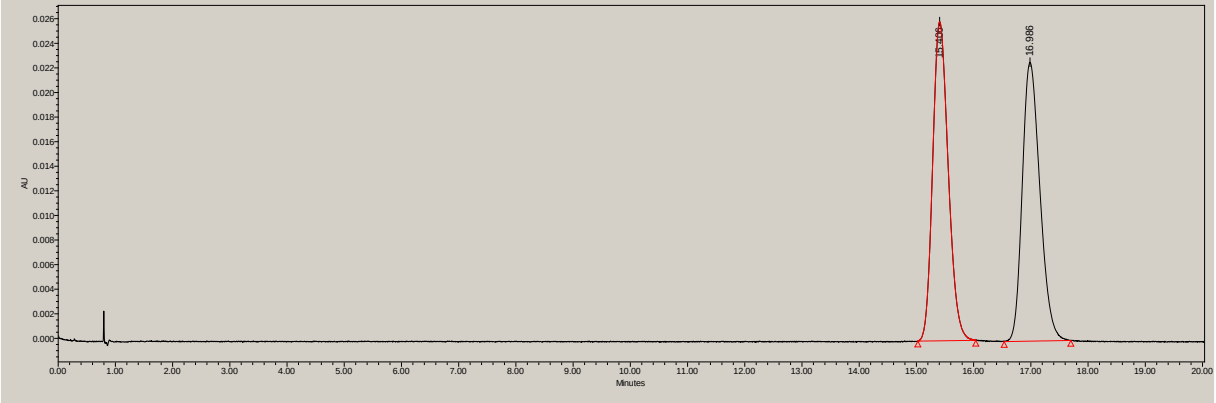
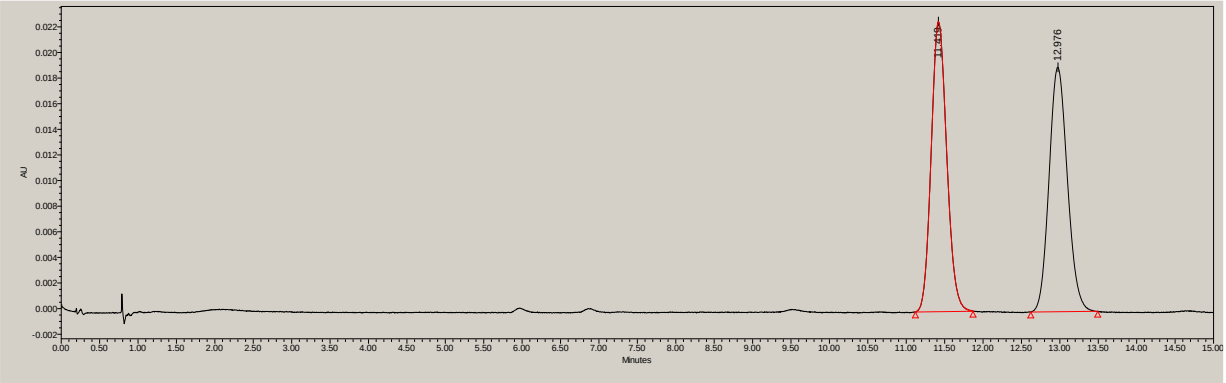


Figure S12 SFC chromatograms of **4a** recorded at varying CO_2/methanol ratios (for detailed conditions, see previous page)

4b



4c

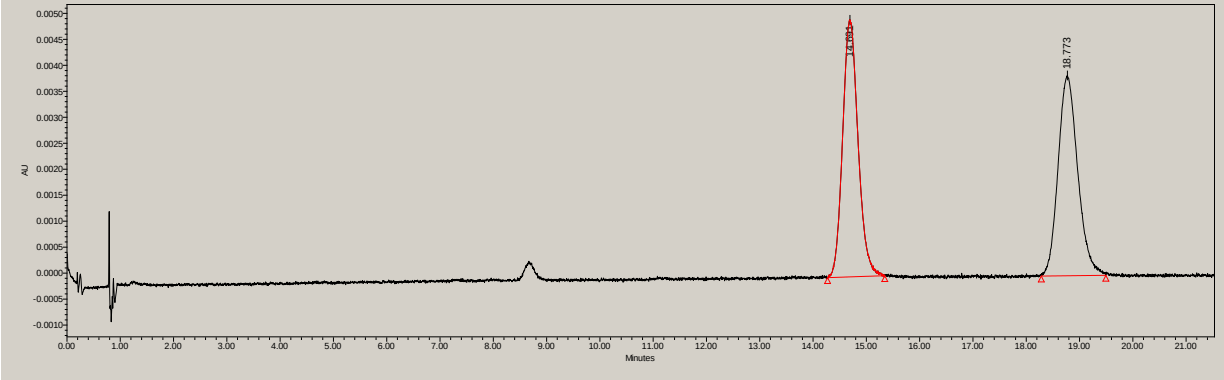


Figure S13 SFC chromatograms of **4b** and **4c** as recorded at an 80:20 CO_2/methanol ratio (for detailed conditions, see p. S-25)

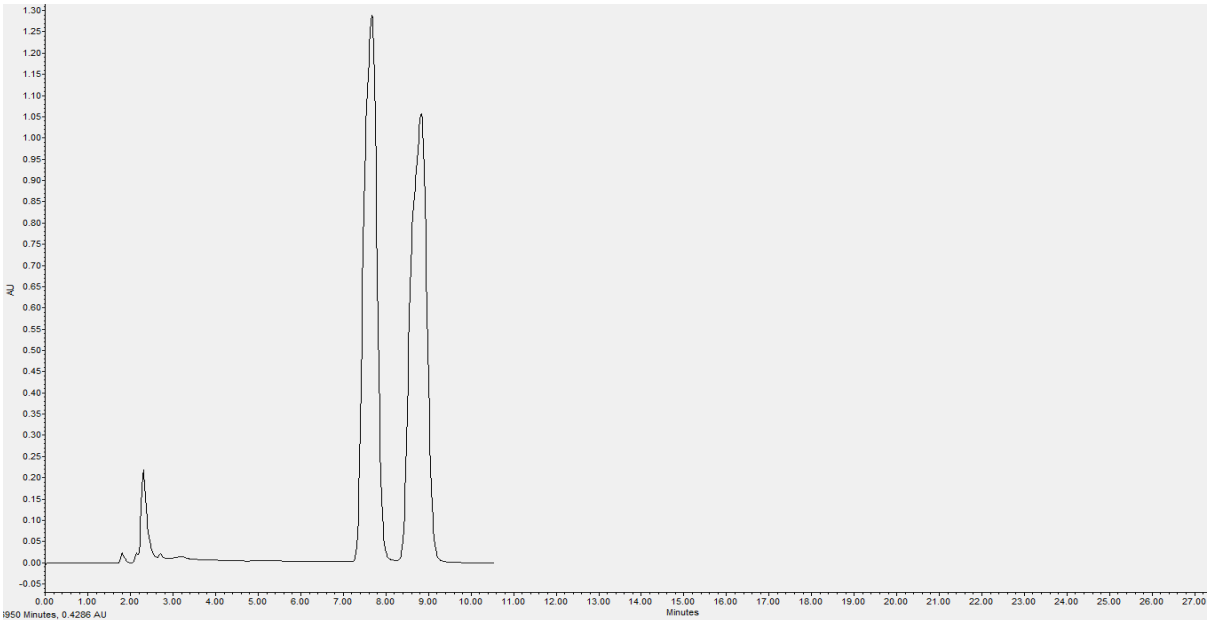


Figure S14 HPLC chromatogram for **4a** (for conditions, see p. S-25)

Electrochemistry

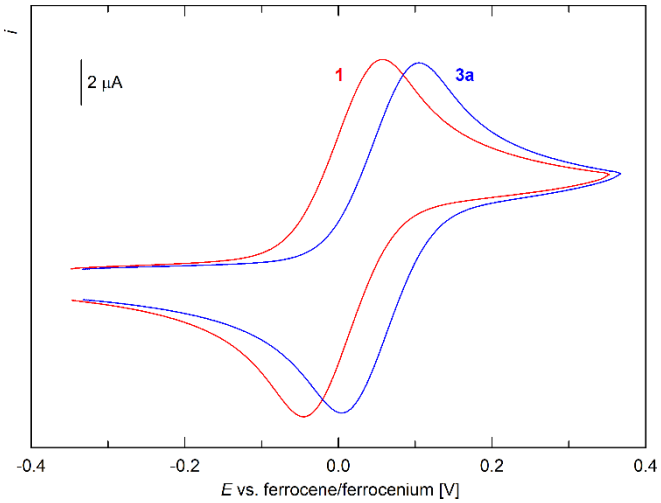


Figure S15 Cyclic voltammograms of **1** and **3a** as recorded on a glassy carbon disc electrode in CH_2Cl_2 (0.1 M $Bu_4N[PF_6]$, scan rate 100 mV s^{-1})

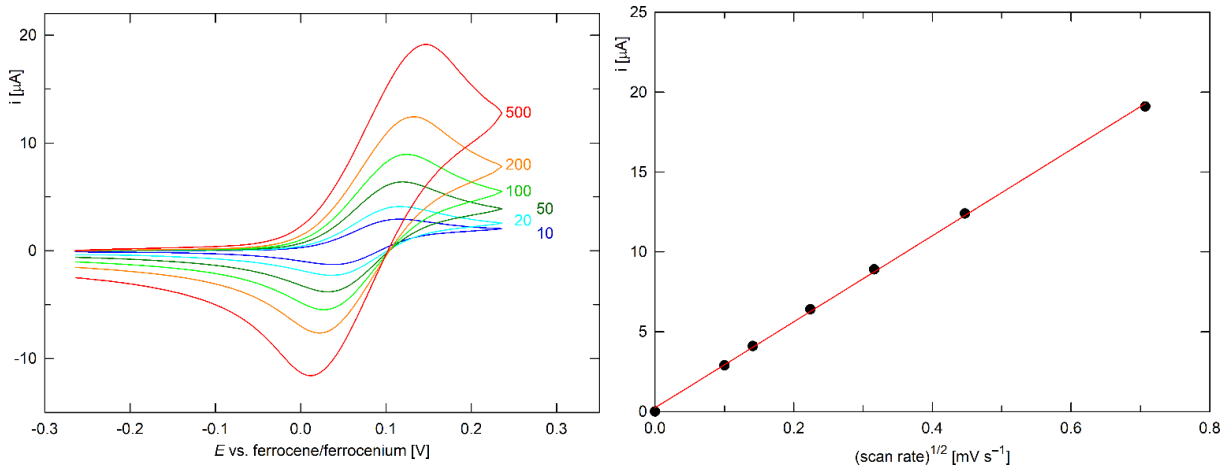


Figure S16 (left) Cyclic voltammograms of **4a** recorded on a glassy carbon disc electrode in CH_2Cl_2 (0.1 M $Bu_4N[PF_6]$) at varying scan rates (indicated in mV s^{-1} in the figure). (right) Dependence of the anodic peak potential (i_{pa}) on the square root of the scan rate for the first oxidation of **4a**. A linear fit is shown by a red line (i_{pa} [µA] = 0.2(1) + 26.9(3) × $\nu^{½}$ [$mV^{½}$ $s^{-½}$], r^2 = 0.9994).

DFT calculations

Theoretical calculations were performed using the Gaussian 16 program package.[9] The geometry optimisations were started from atomic coordinates determined by X-ray diffraction analysis and performed using PBE0[10] density functional combined with the def2-TZVPP[11] basis set with added Grimme's D3 dispersion correction.[12] The selected basis set uses Stuttgart effective core potential[13] to describe ruthenium core electrons. Orbital composition analysis based on the Natural Atomic Orbitals (NAO)[14] was performed using the Multiwfn software package (version 3.8).[15] Molecular orbitals were visualised using the Avogadro programme.[16]

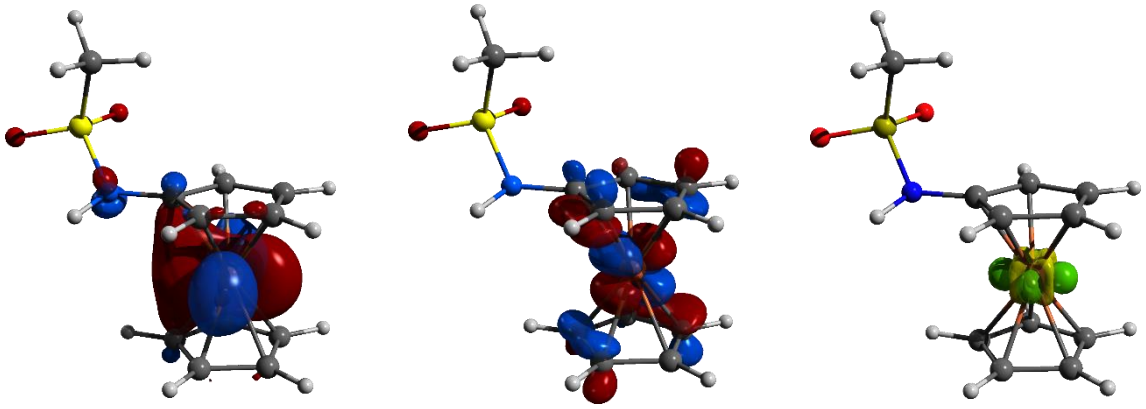
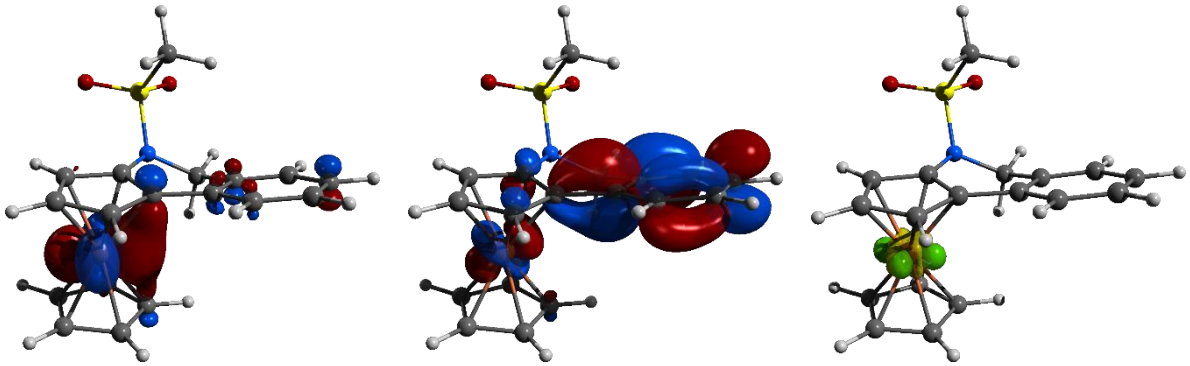
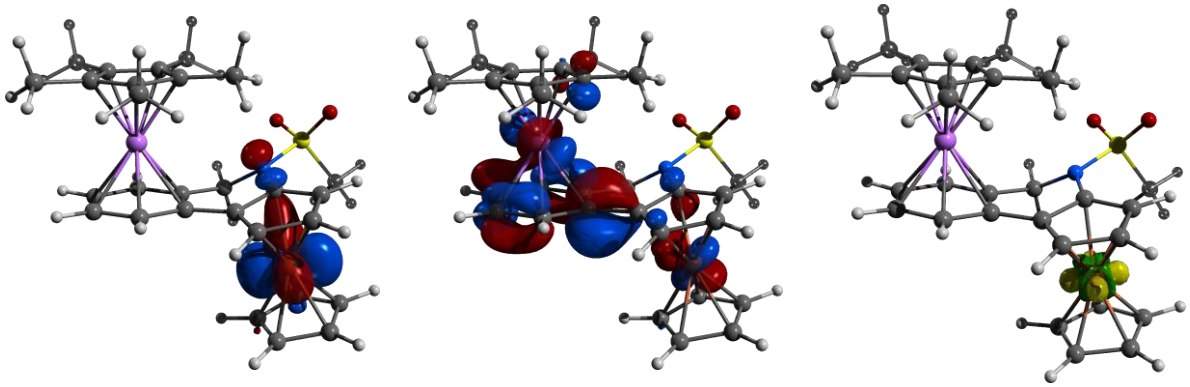


Figure S17 Frontier molecular orbitals (contours at ±0.05 a.u.) and electron density difference upon electron removal mapped at the geometry of the parent species, ρ(M+) – ρ(M) (contours at ±0.02 a.u.) for compound **1**



HOMO LUMO $\rho(M^+) - \rho(M)$

Figures S18 Frontier molecular orbitals (contours at ±0.05a.u.) and electron density difference upon electron removal mapped at the geometry of the parent species, $\rho(\mathbf{4a}^+) - \rho(\mathbf{4a})$ (contours at ±0.02 a.u.) for compound **3a**



HOMO LUMO $\rho(M^+) - \rho(M)$

Figures S19 Frontier molecular orbitals (contours at ±0.05 a.u.) and electron density difference upon electron removal mapped at the geometry of the parent species, $\rho(\mathbf{12}^+) - \rho(\mathbf{12})$ (contours at ±0.02 a.u.) for the cation of compound **12**

Copies of the NMR spectra

(solvent signals are marked with an asterisk)

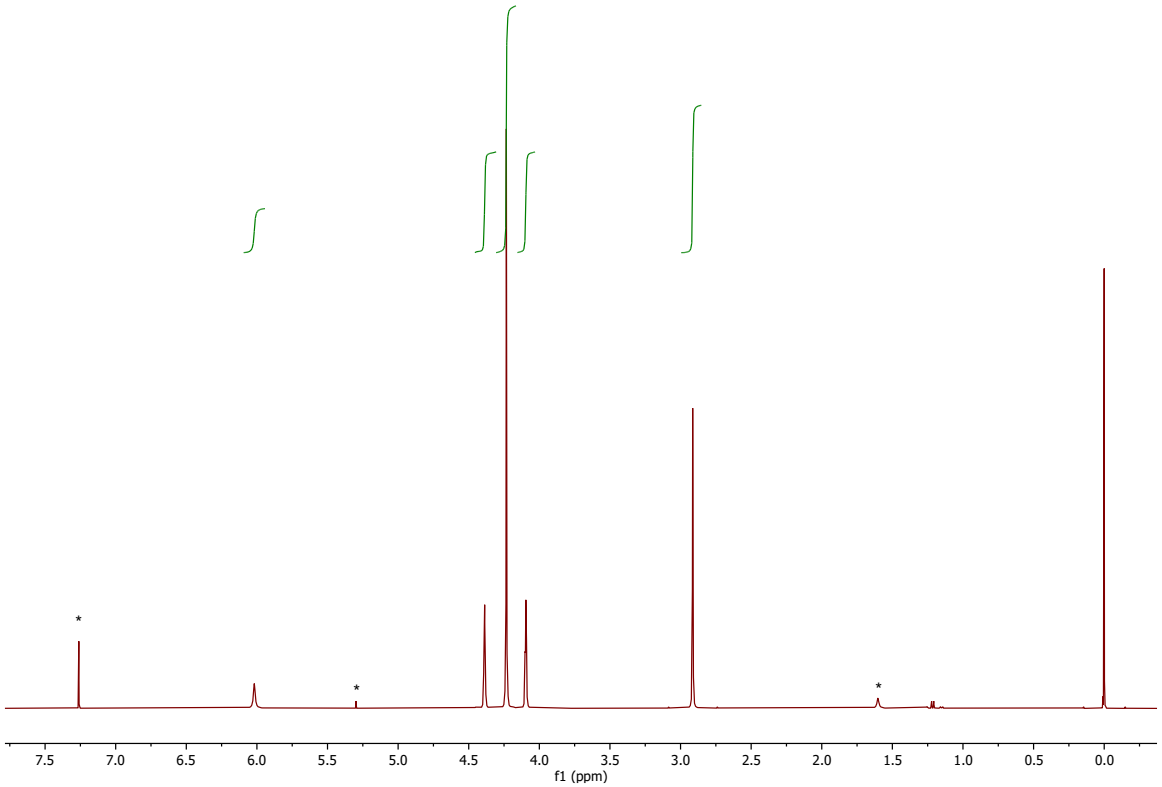


Figure S20 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**

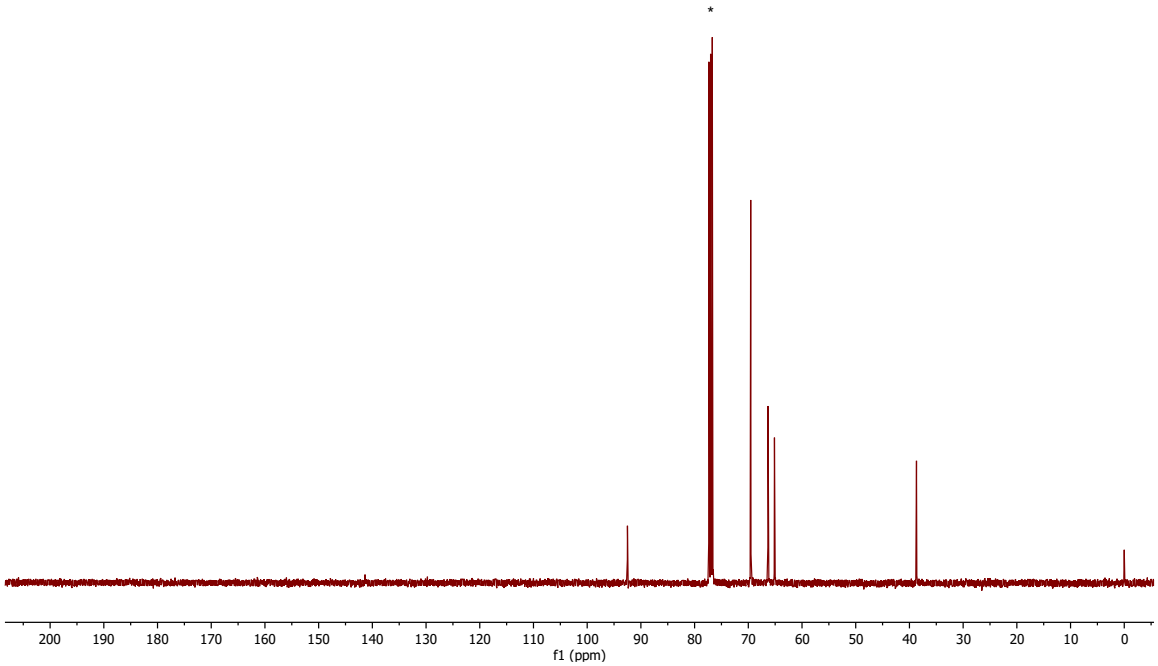


Figure S21 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1**

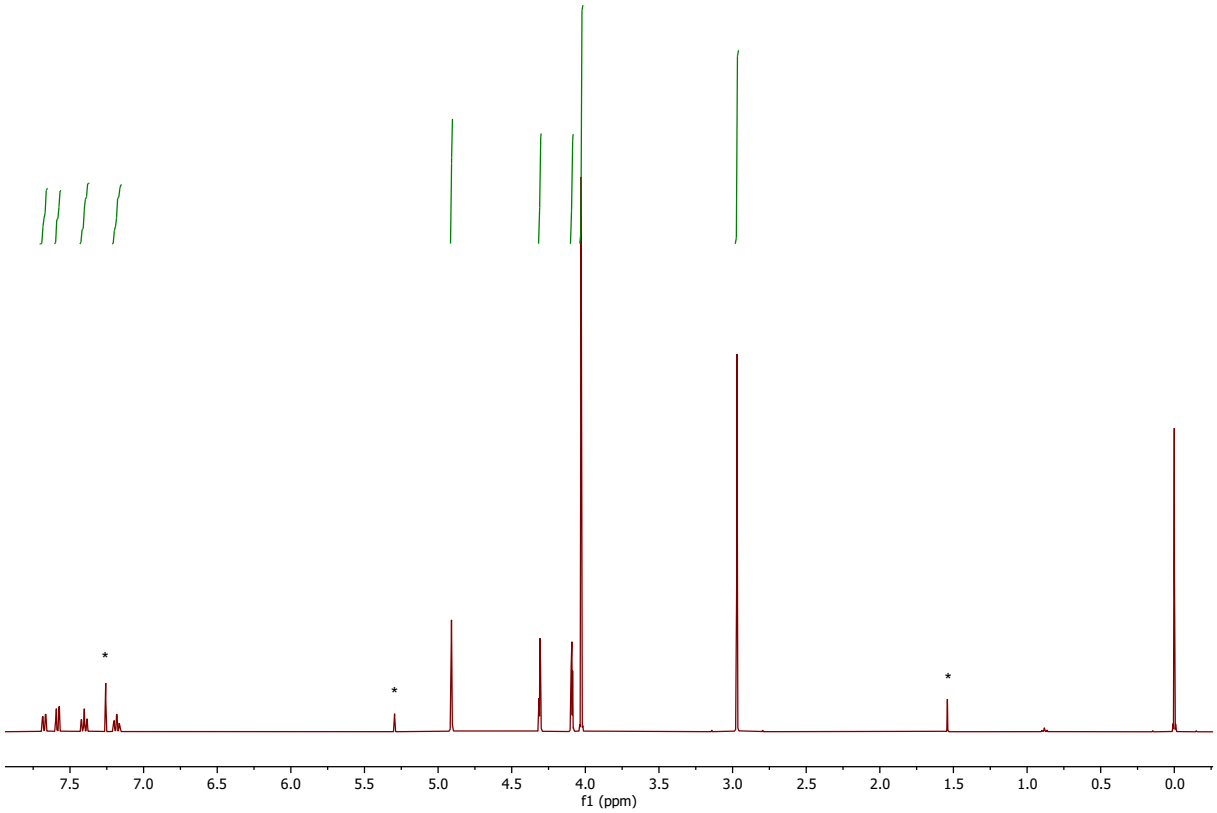


Figure S22 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**

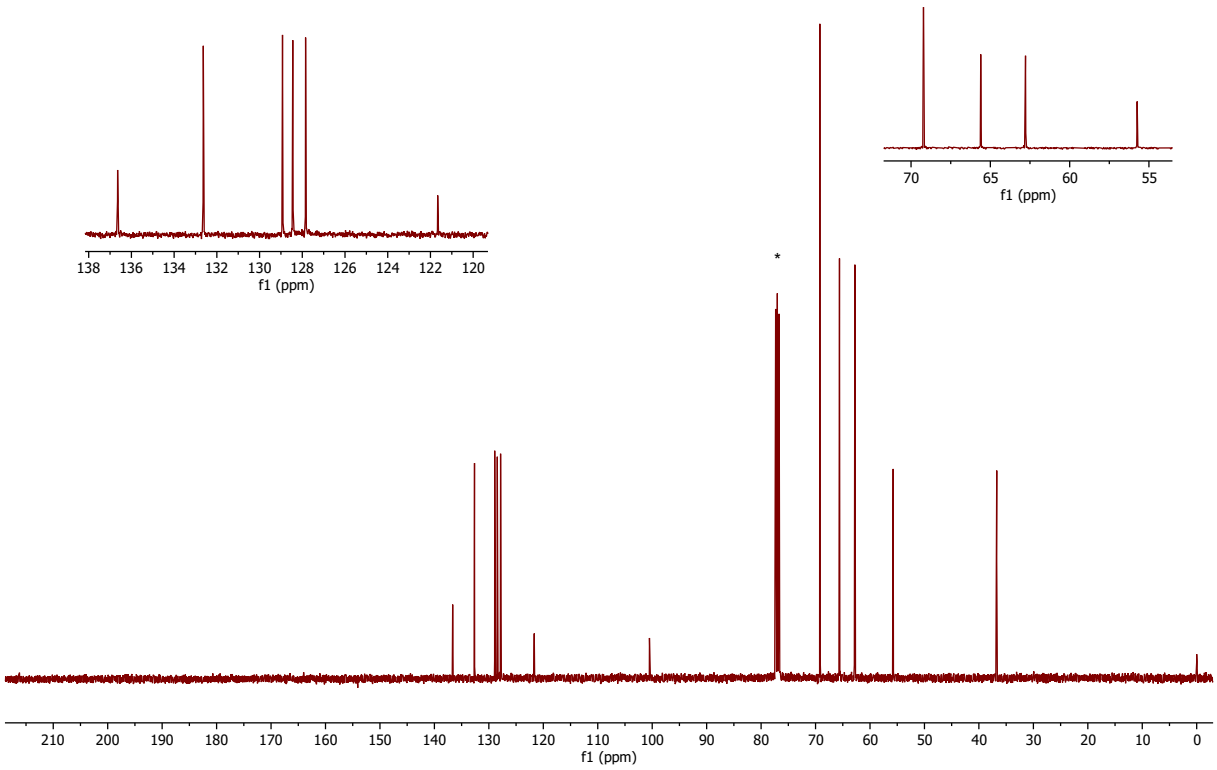


Figure S23 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3a**

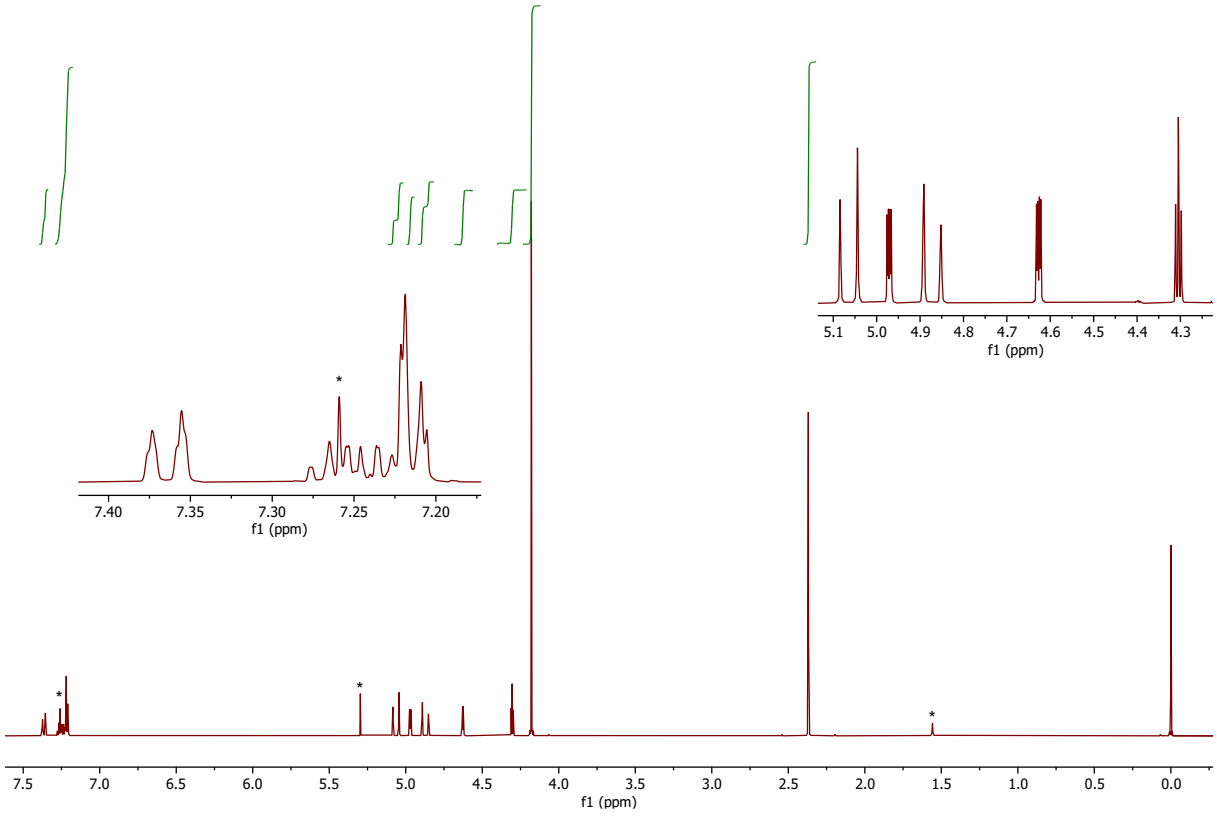


Figure S24 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**

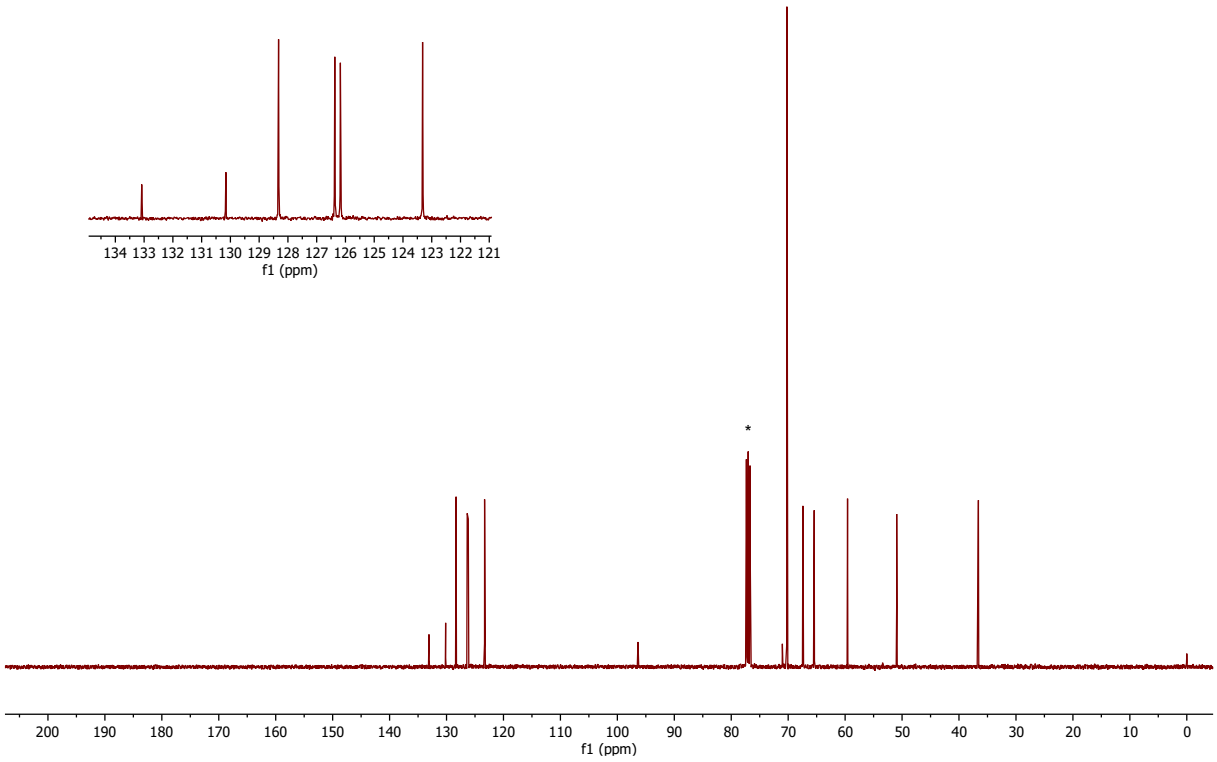


Figure S25 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4a**

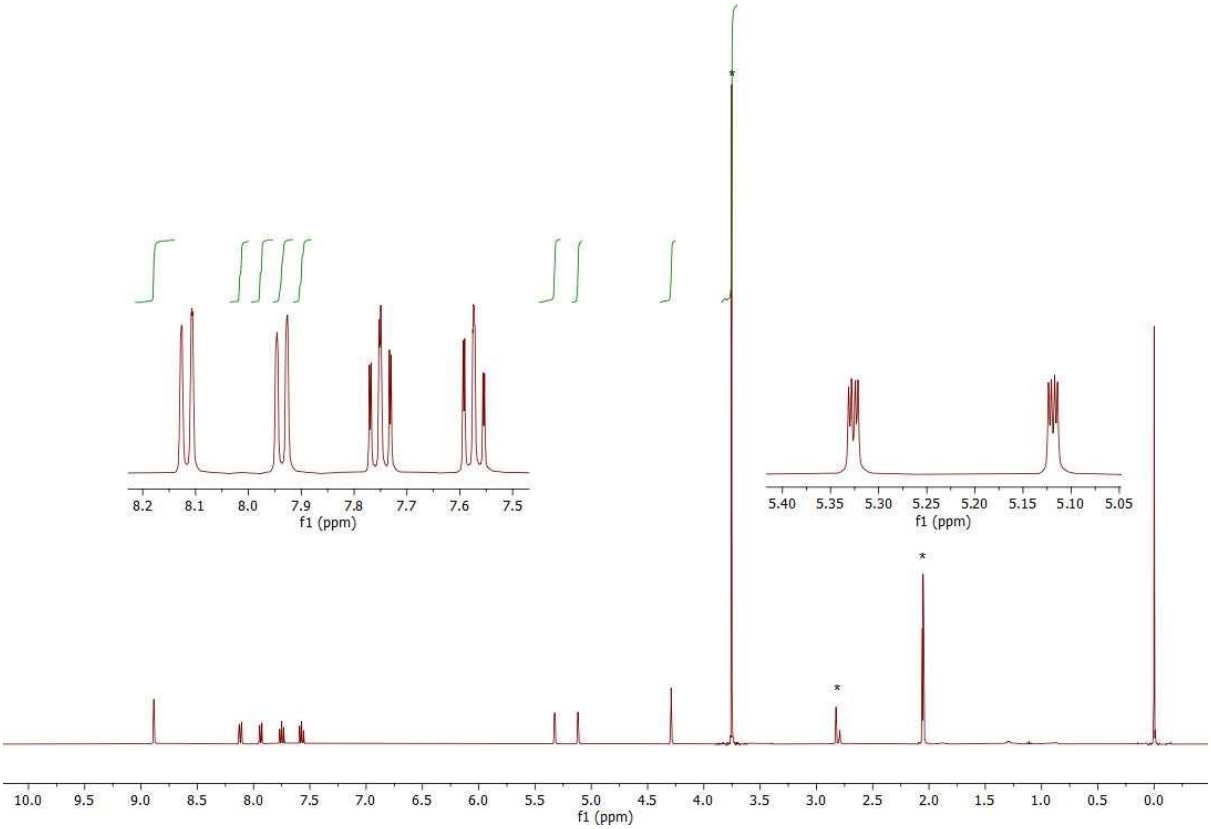


Figure S26 ^{1}H NMR spectrum (400 MHz, acetone-d_6) of **6a**

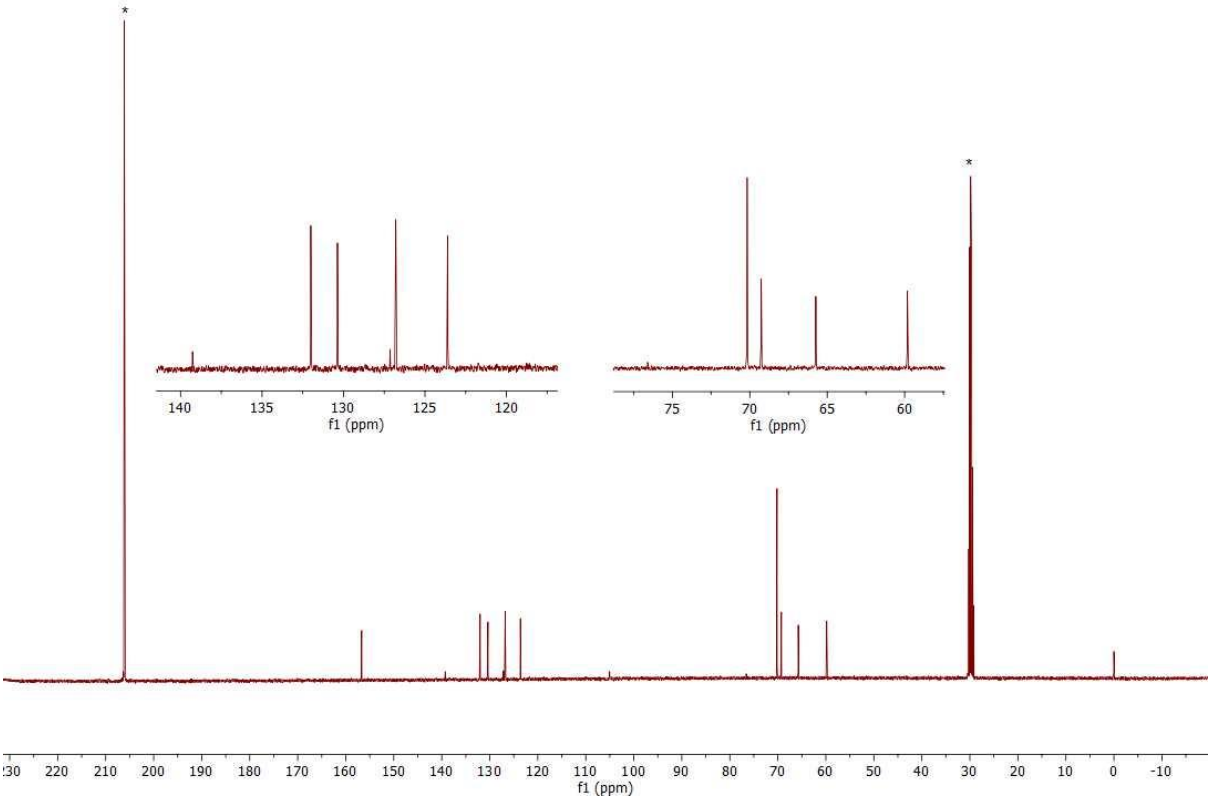


Figure S27 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, acetone-d_6) of **6a**

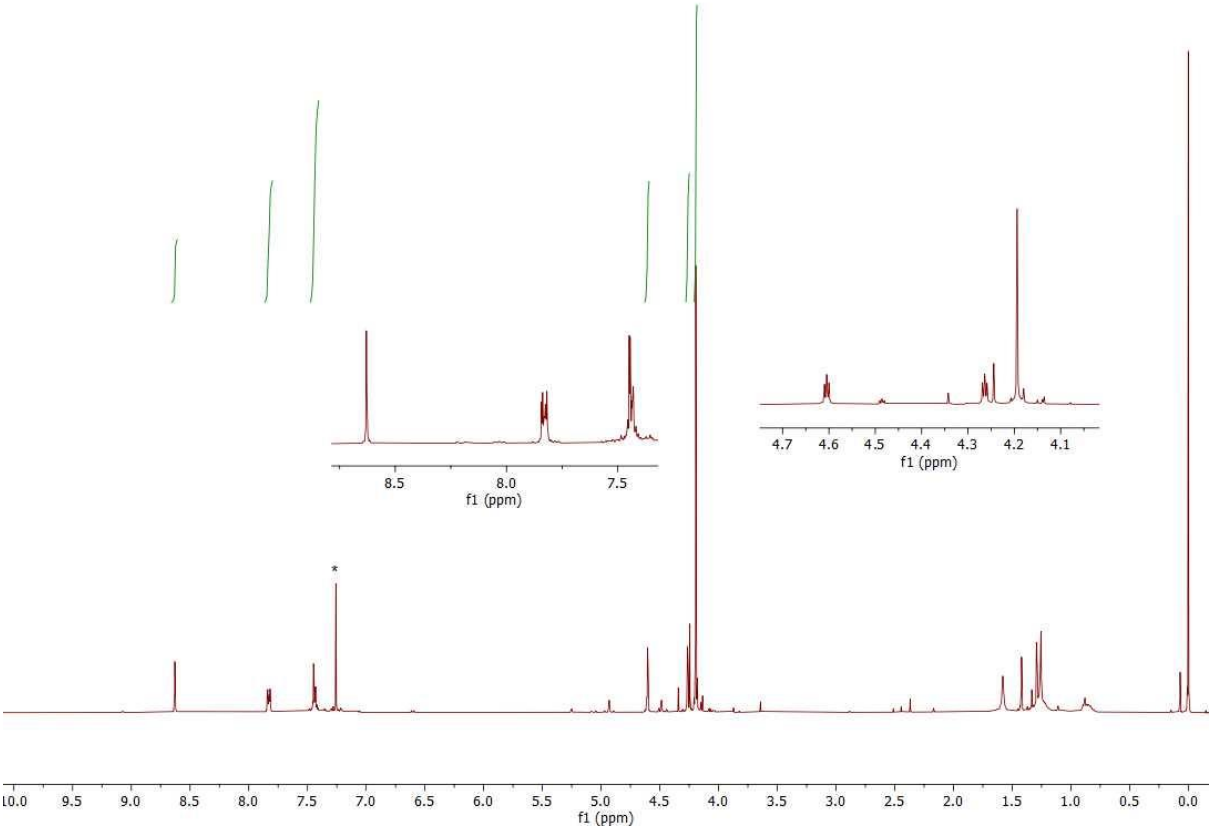


Figure S28 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a**

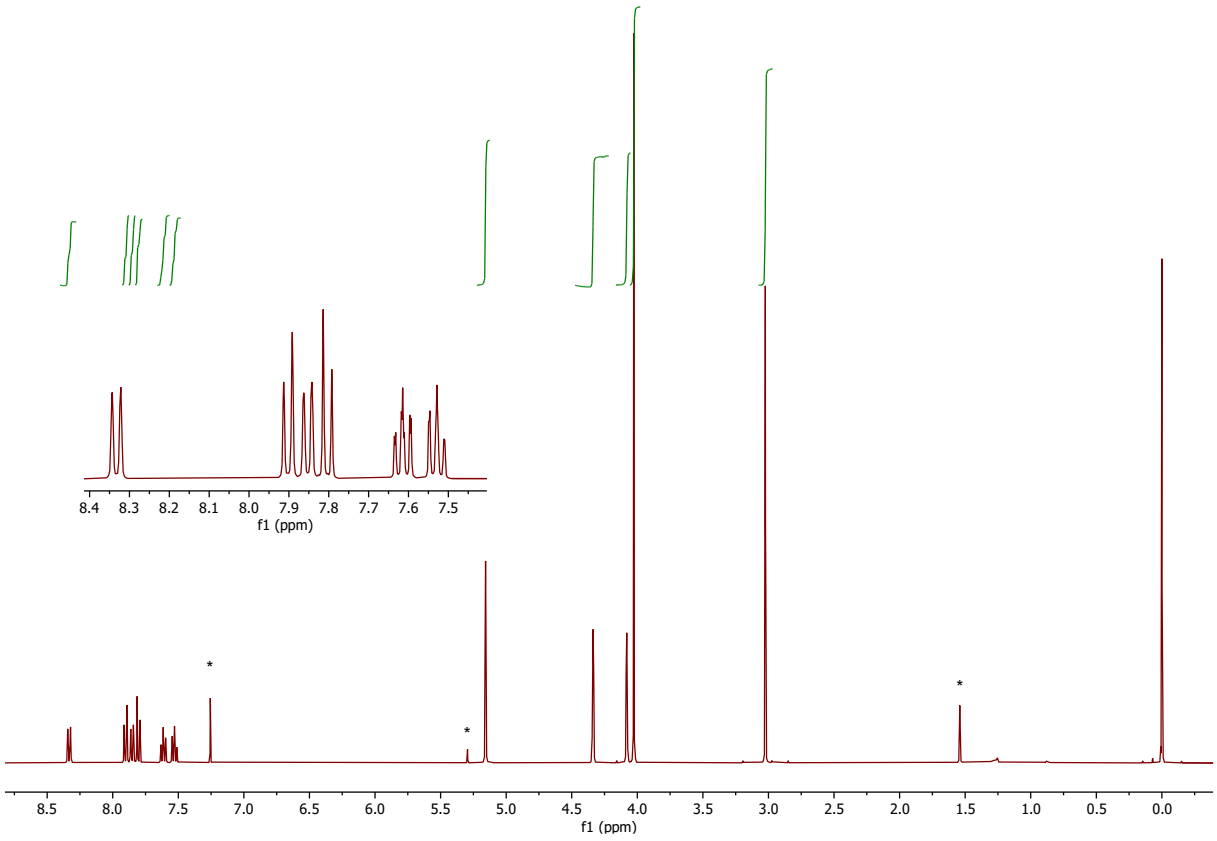


Figure S29 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**

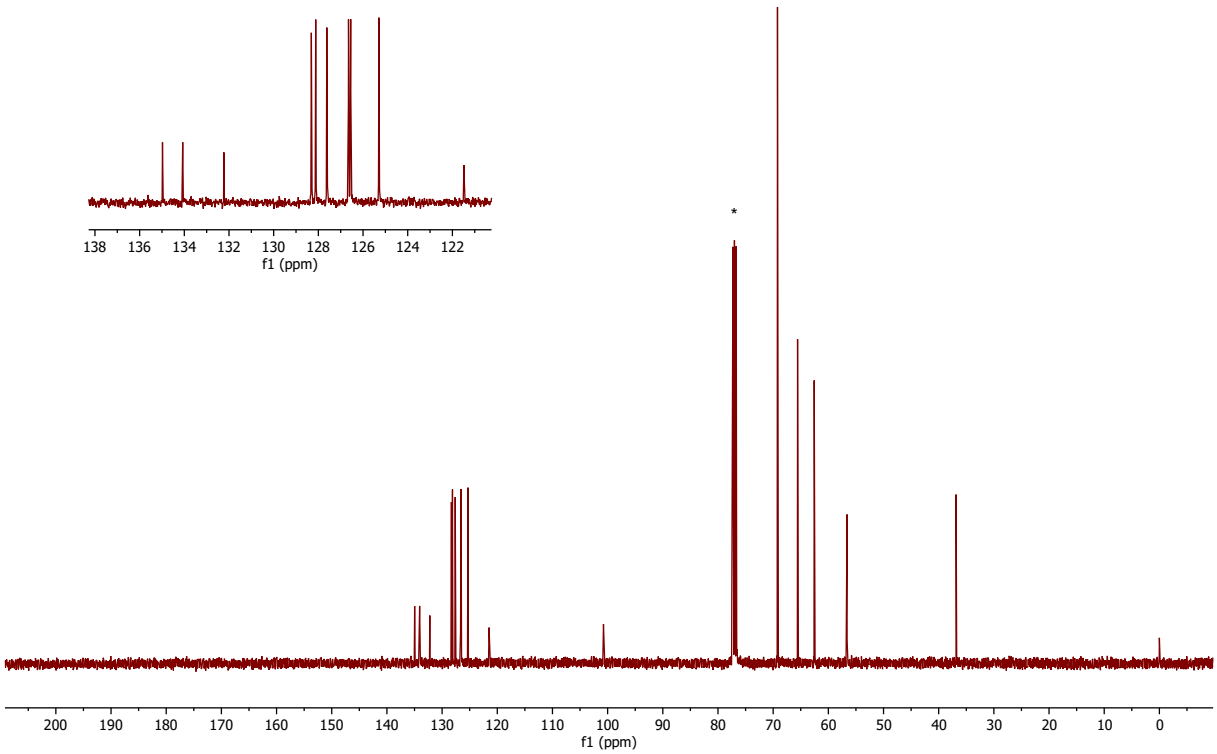


Figure S30 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3b**

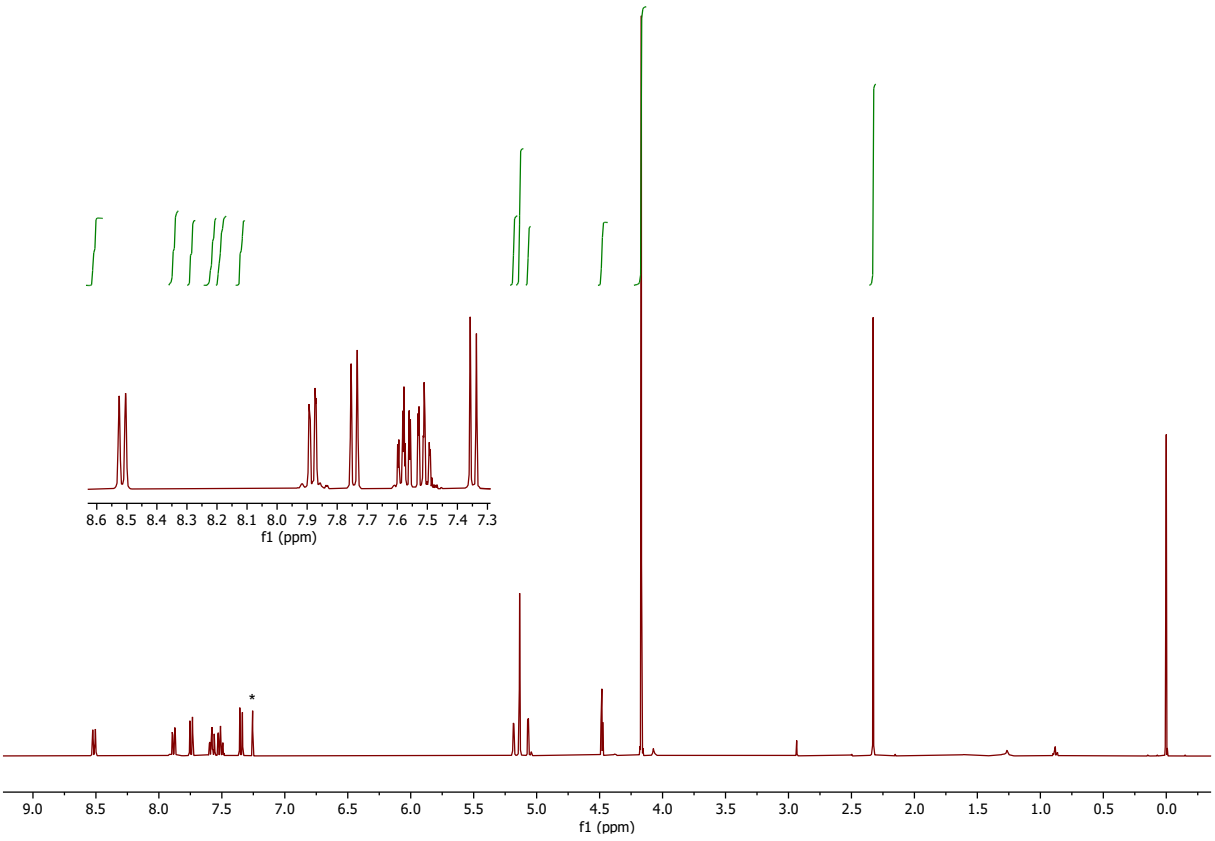


Figure S31 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4b**

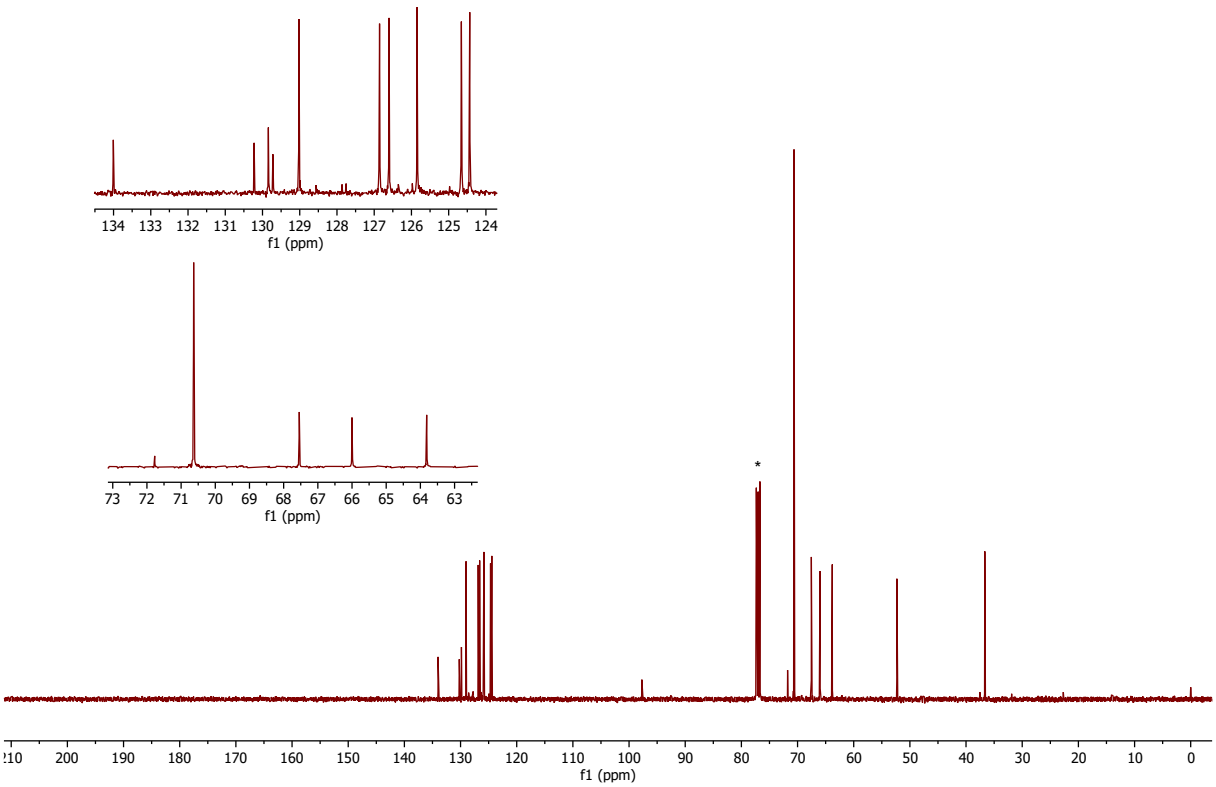


Figure S32 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4b**

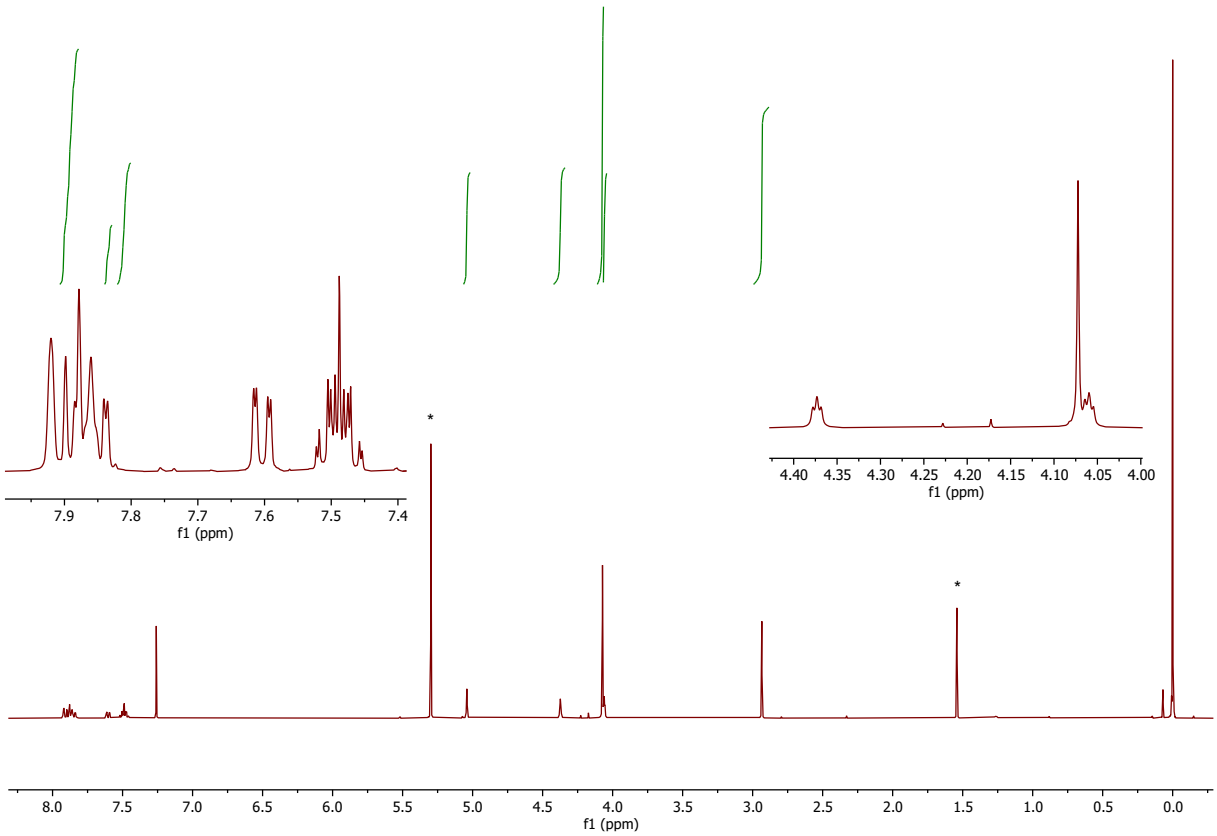


Figure S33 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**

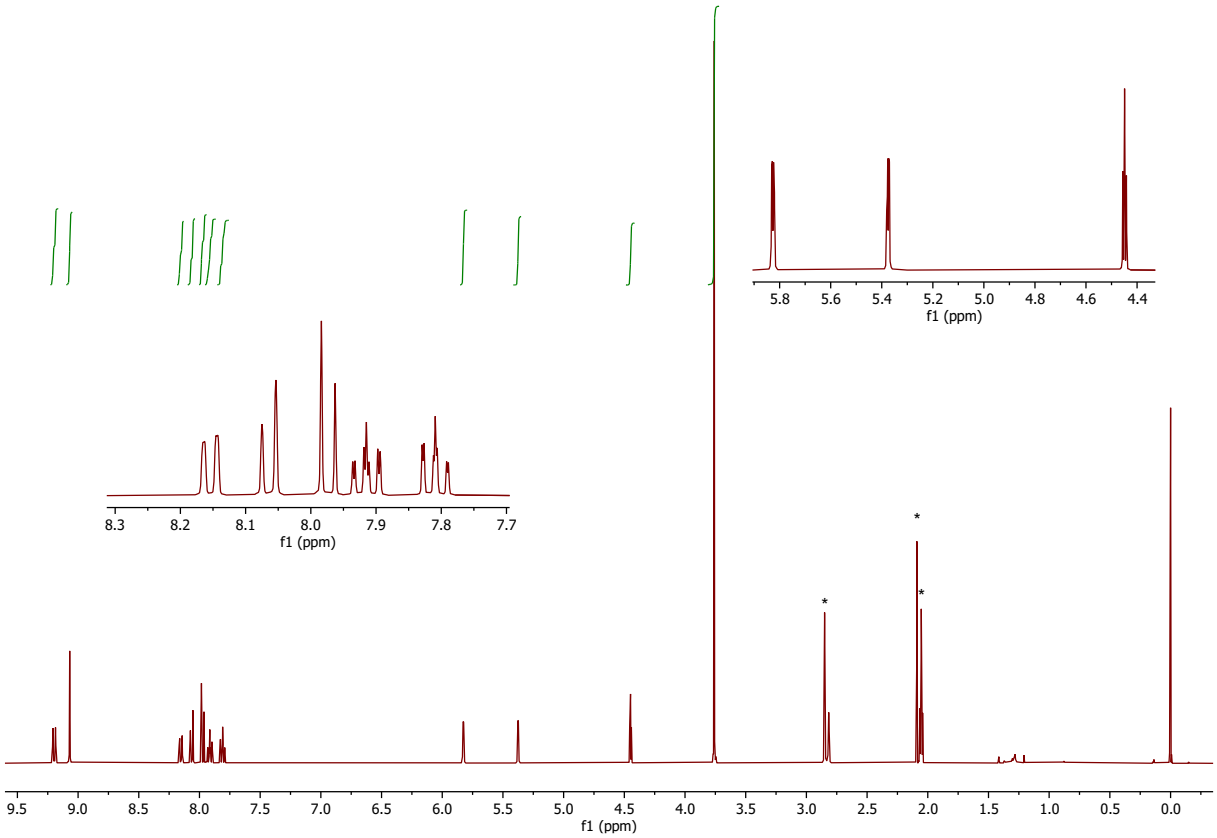


Figure S34 ^{1}H NMR spectrum (400 MHz, Me_2CO-d_6) of **6b**

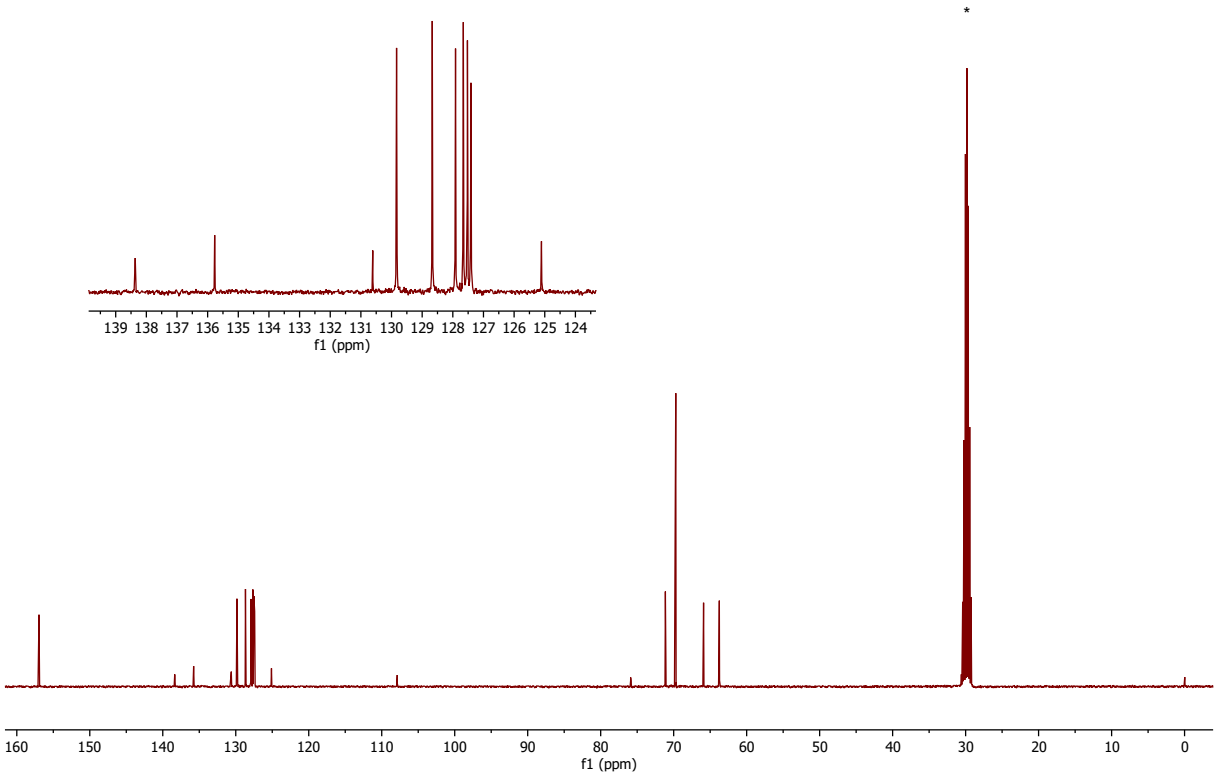


Figure S35 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Me_2CO-d_6) of **6b**

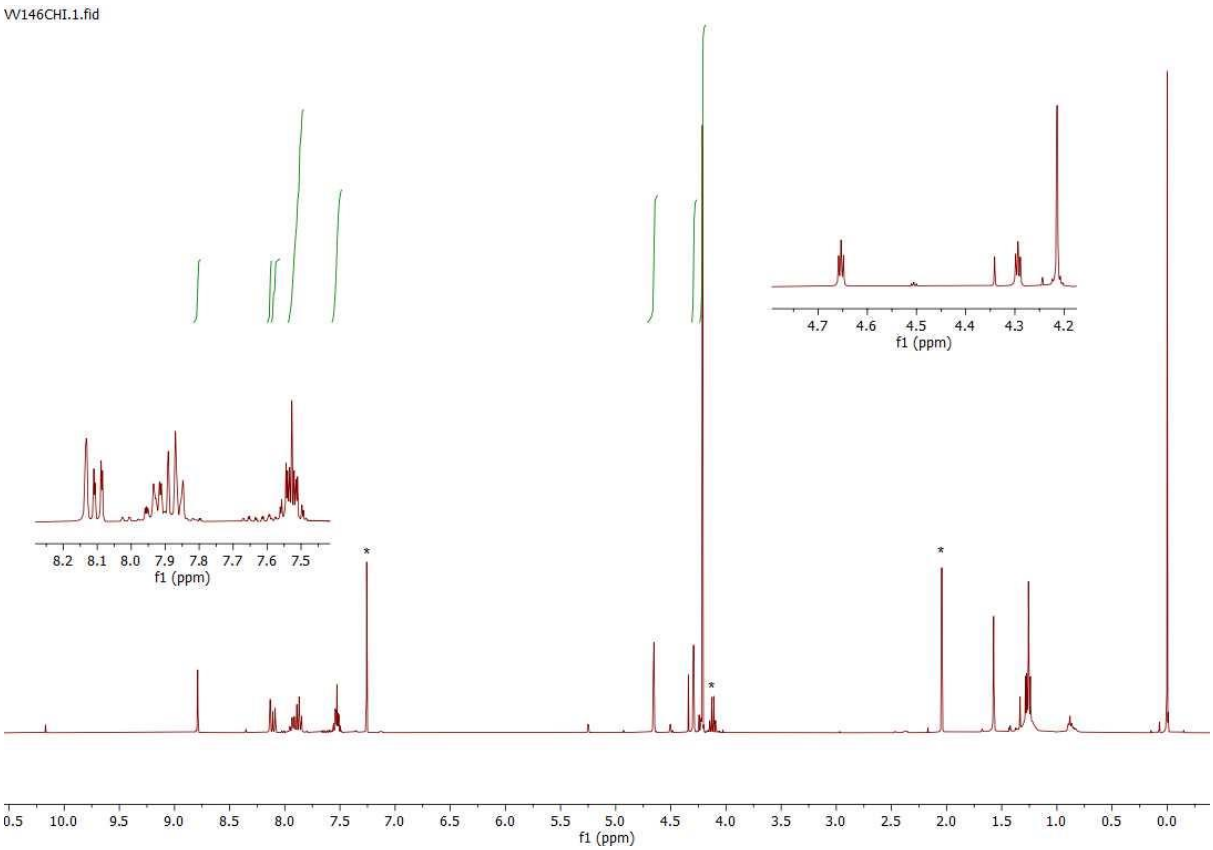


Figure S36 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7b**

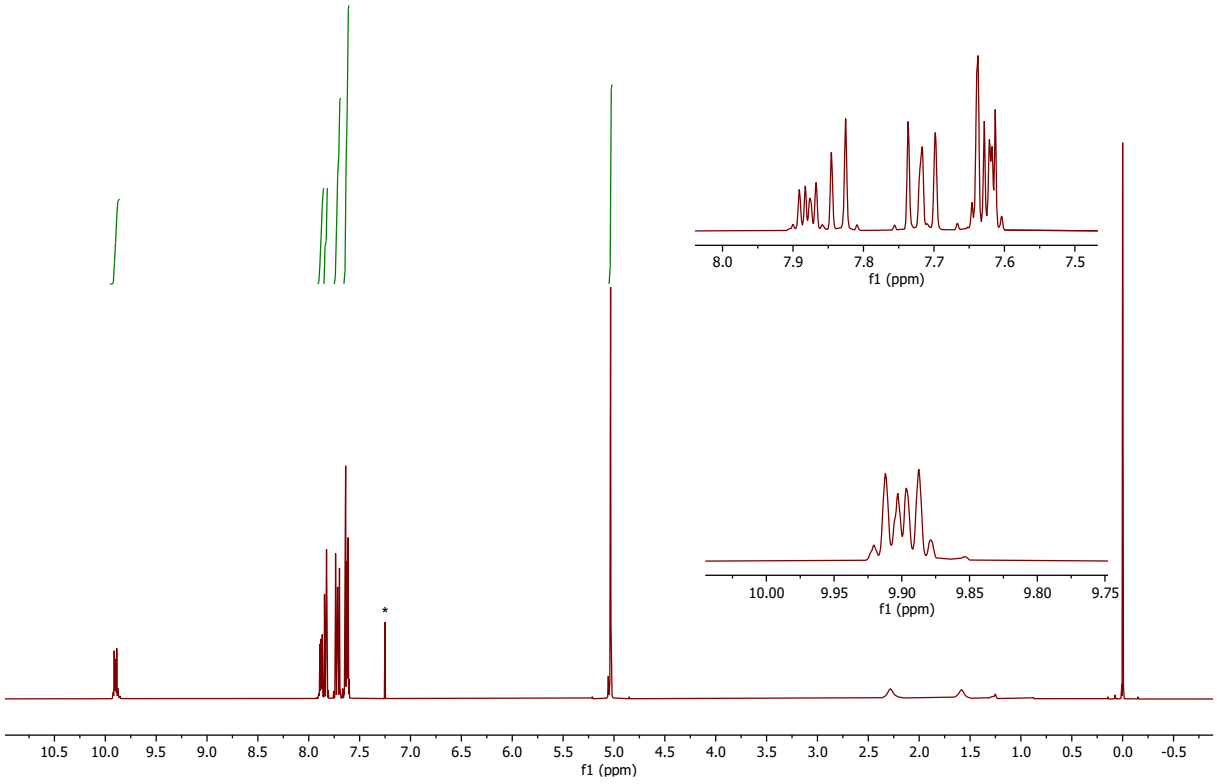


Figure S37 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11**

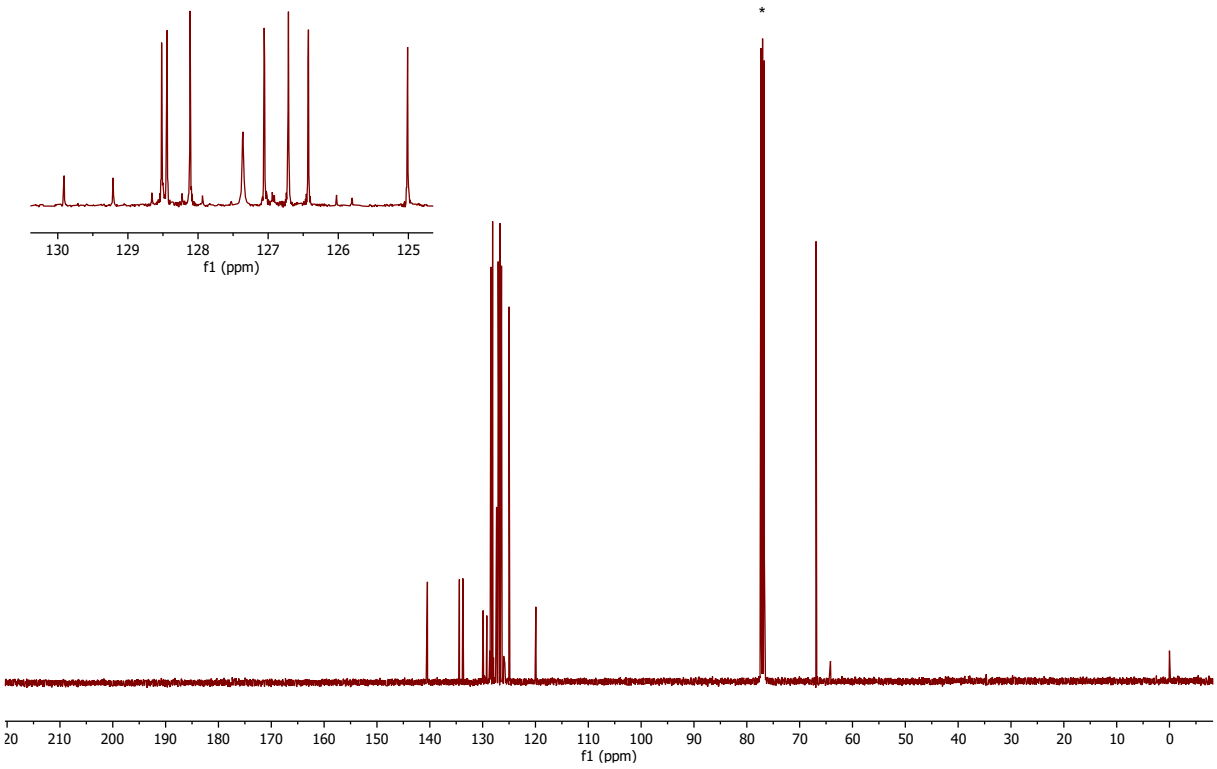


Figure S38 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **11**

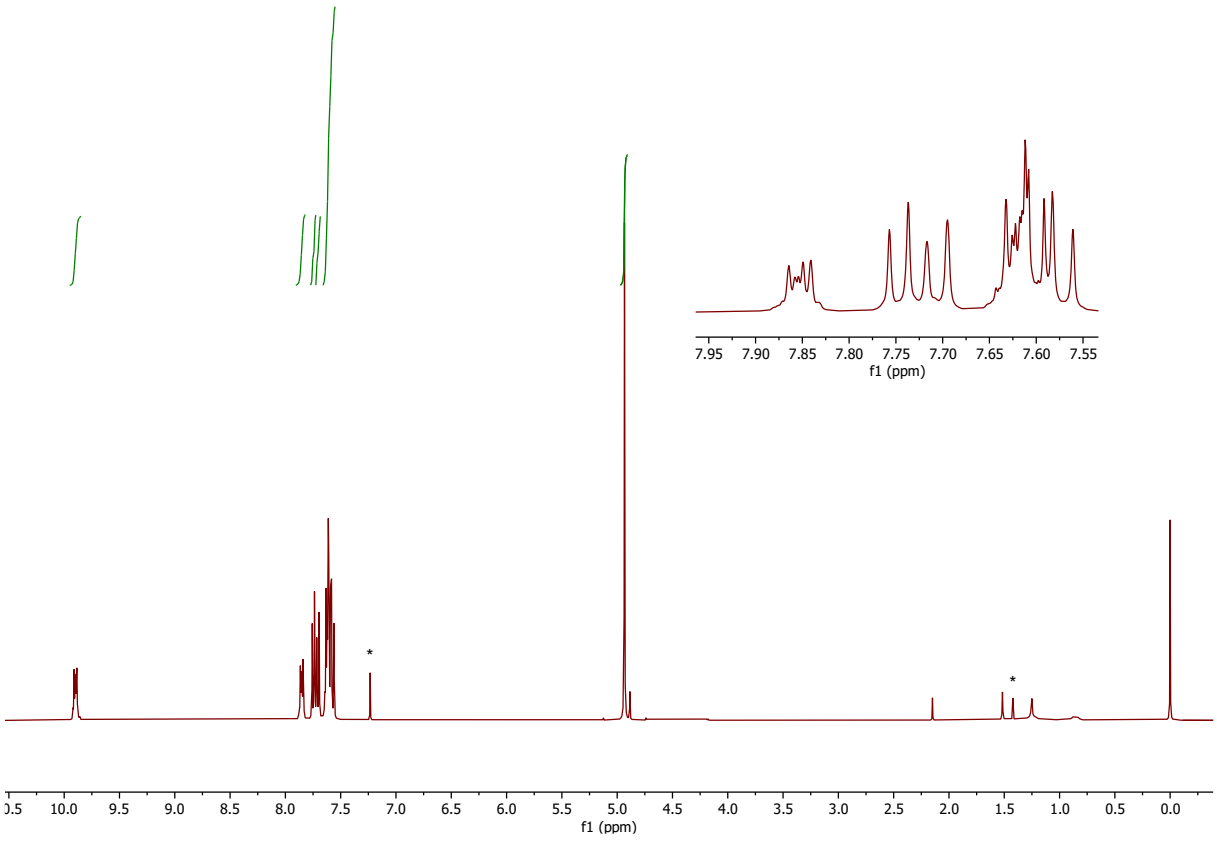


Figure S39 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**

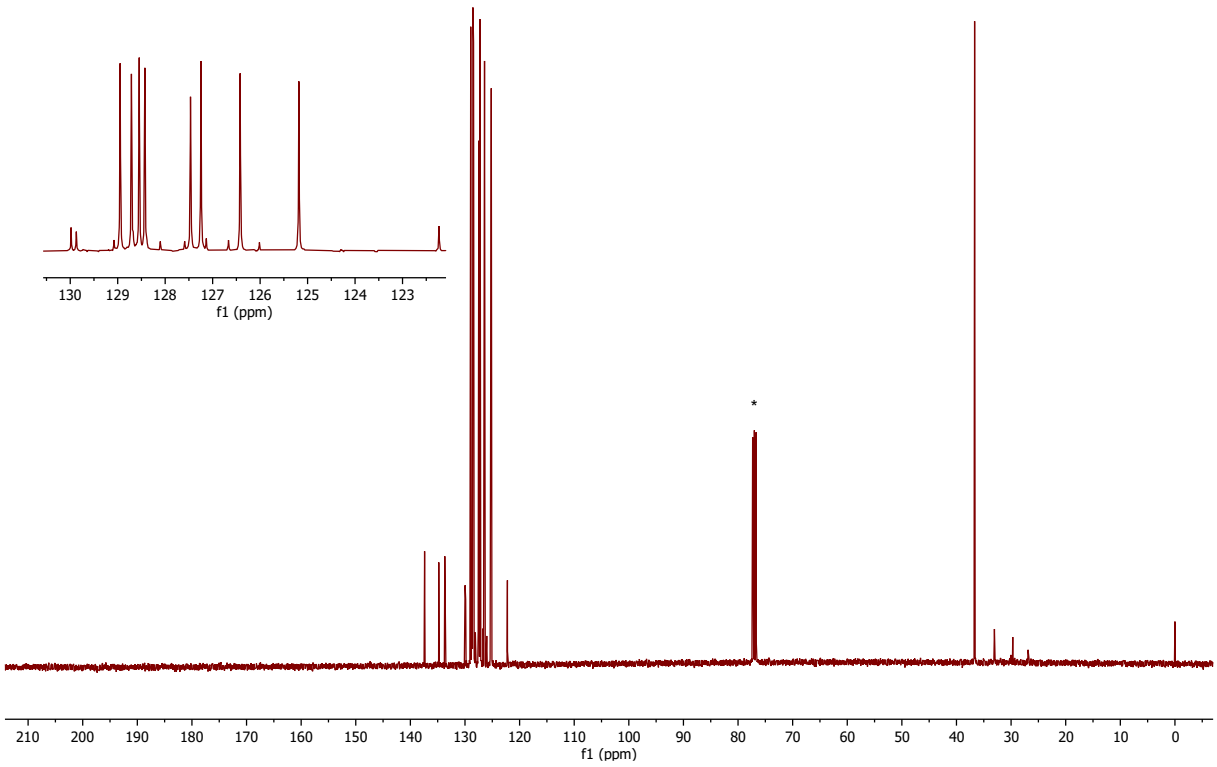


Figure S40 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2c**

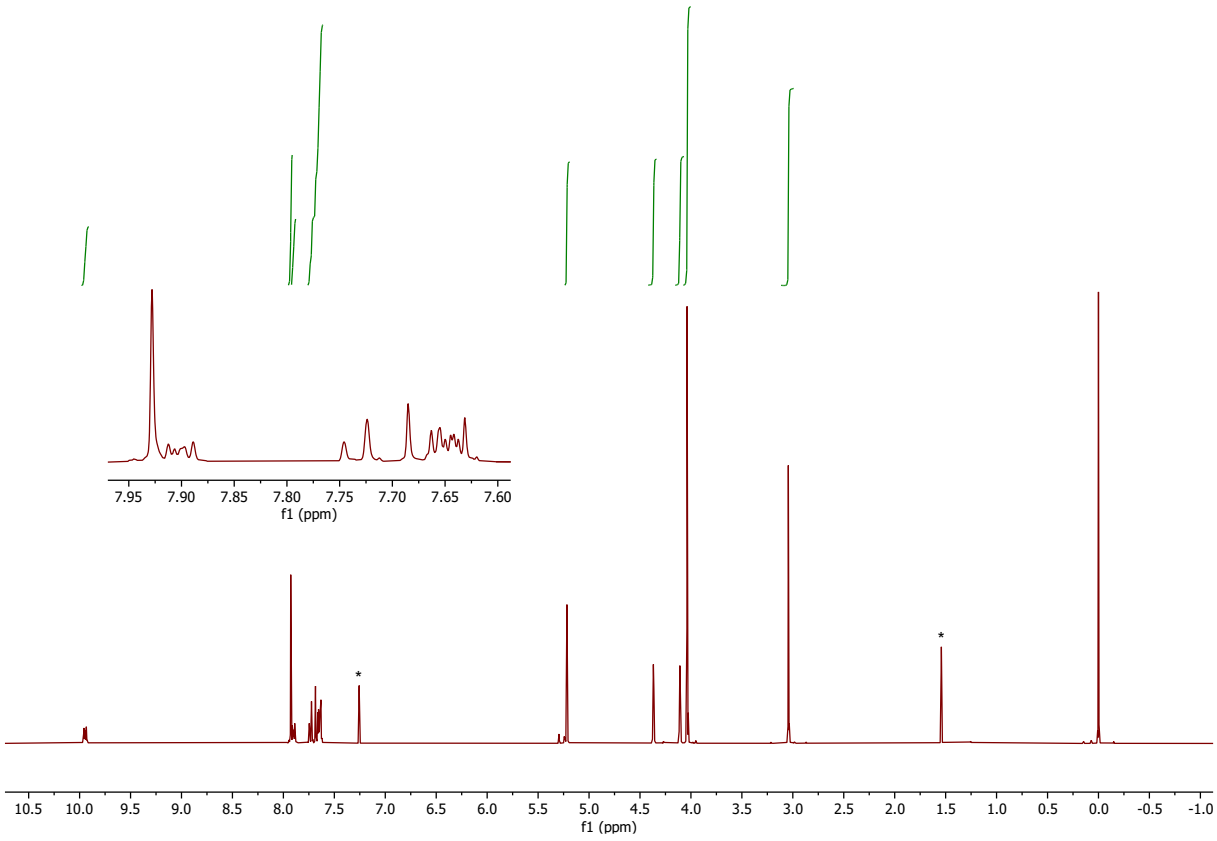


Figure S41 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**

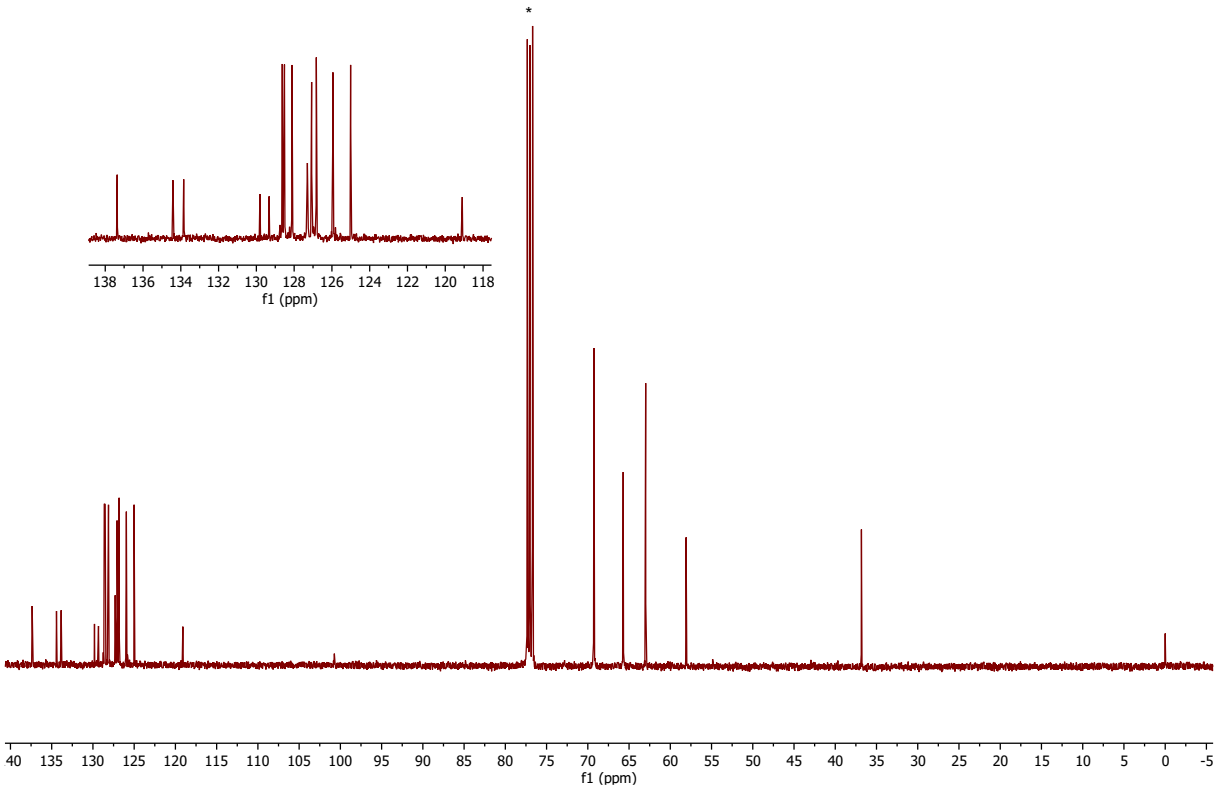


Figure S42 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3c**

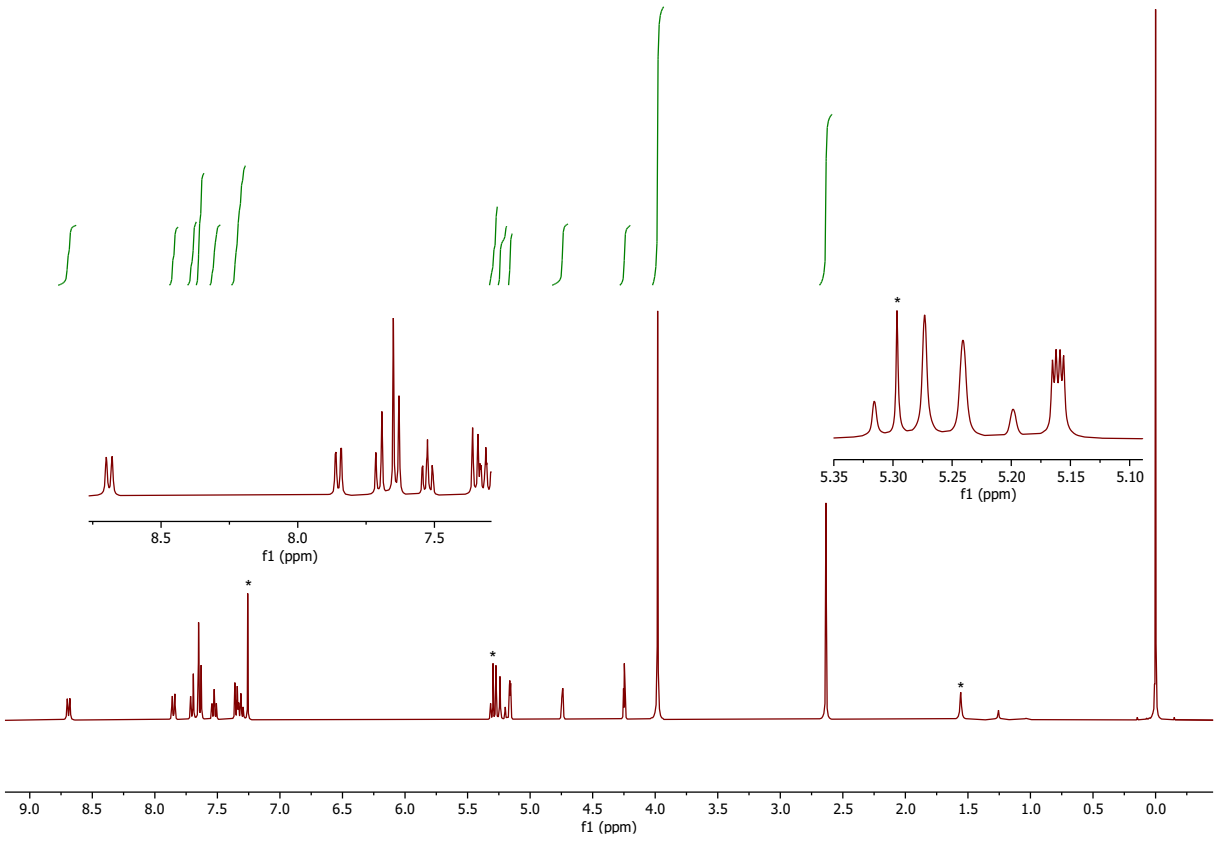


Figure S43 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4c**

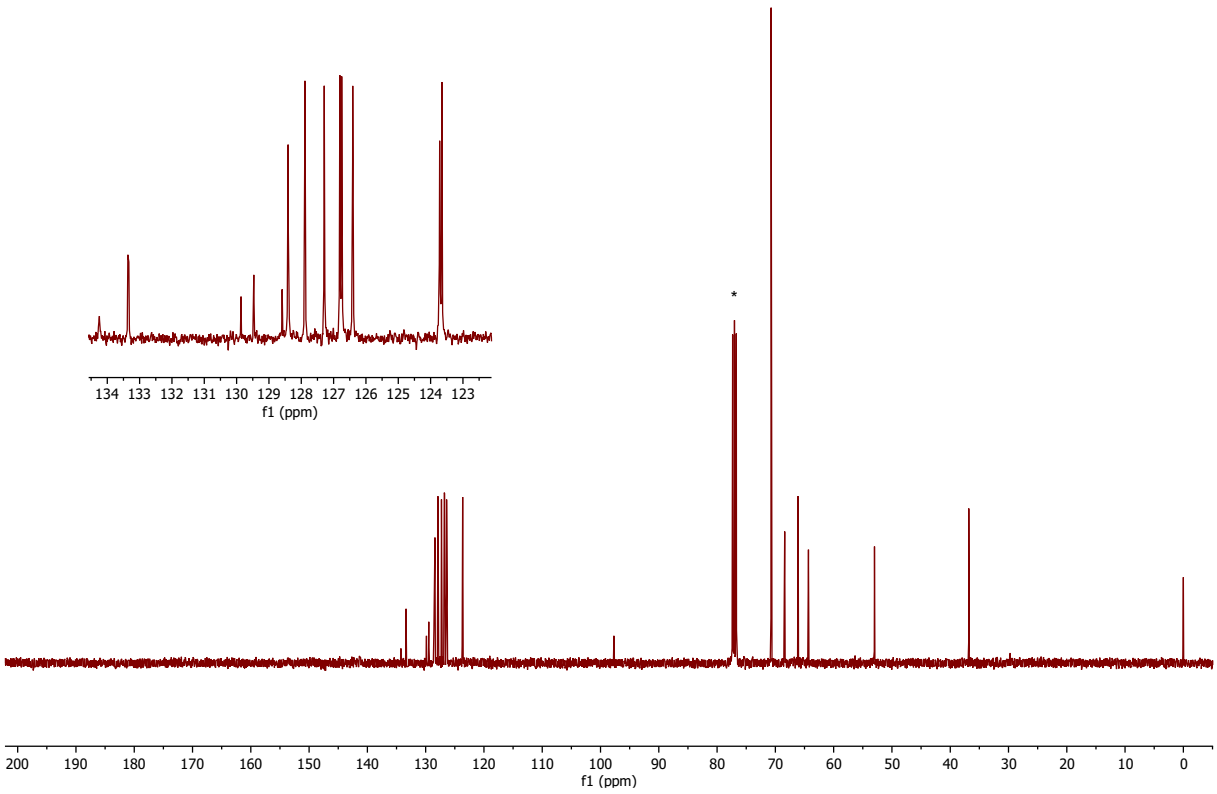


Figure S44 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4c**

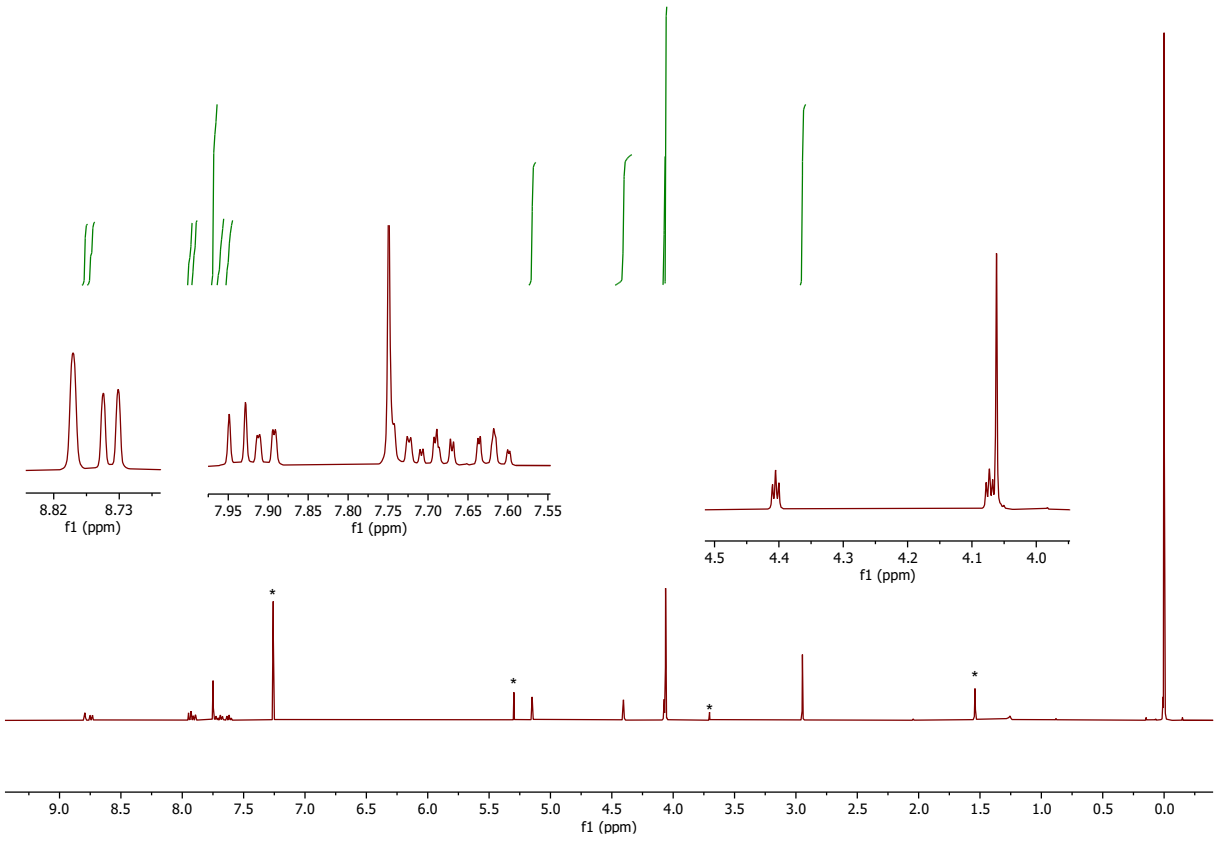


Figure S45 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c**

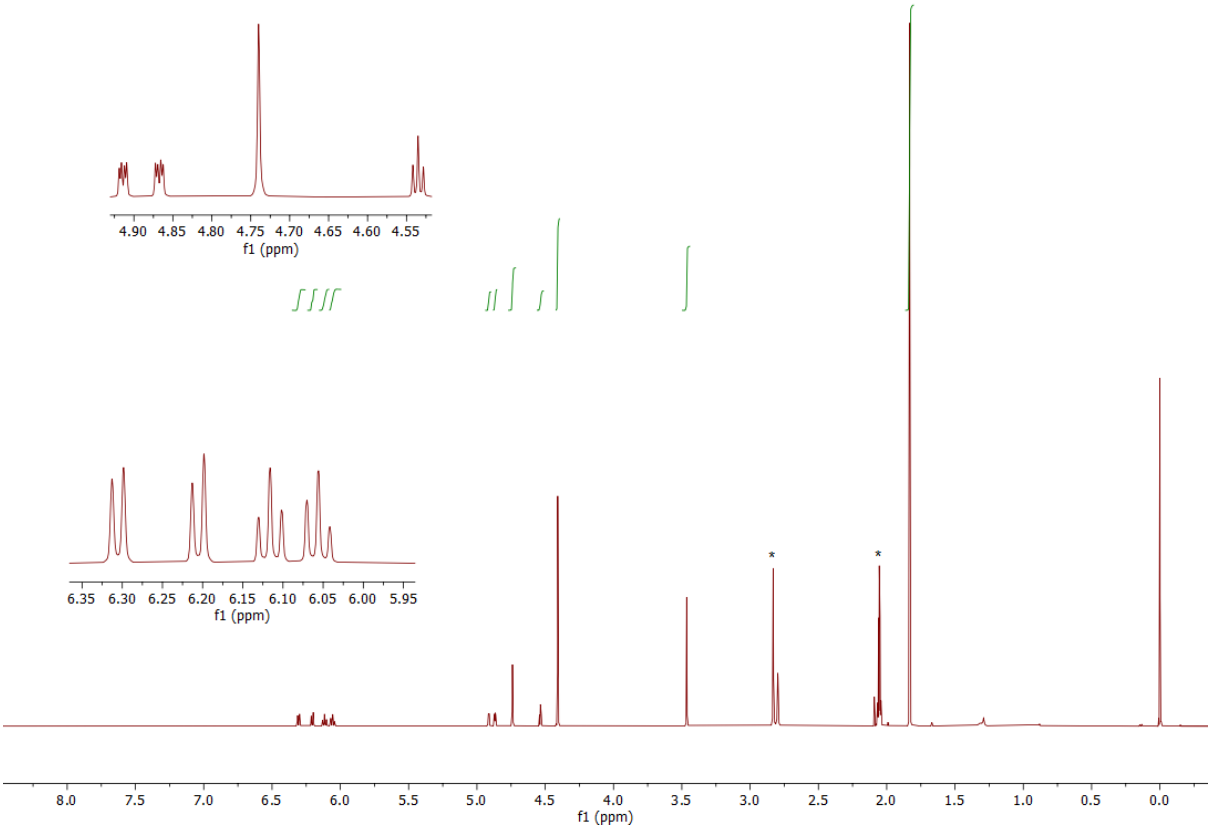


Figure S46 ^{1}H NMR spectrum (400 MHz, Me_2CO-d_6) of **12**

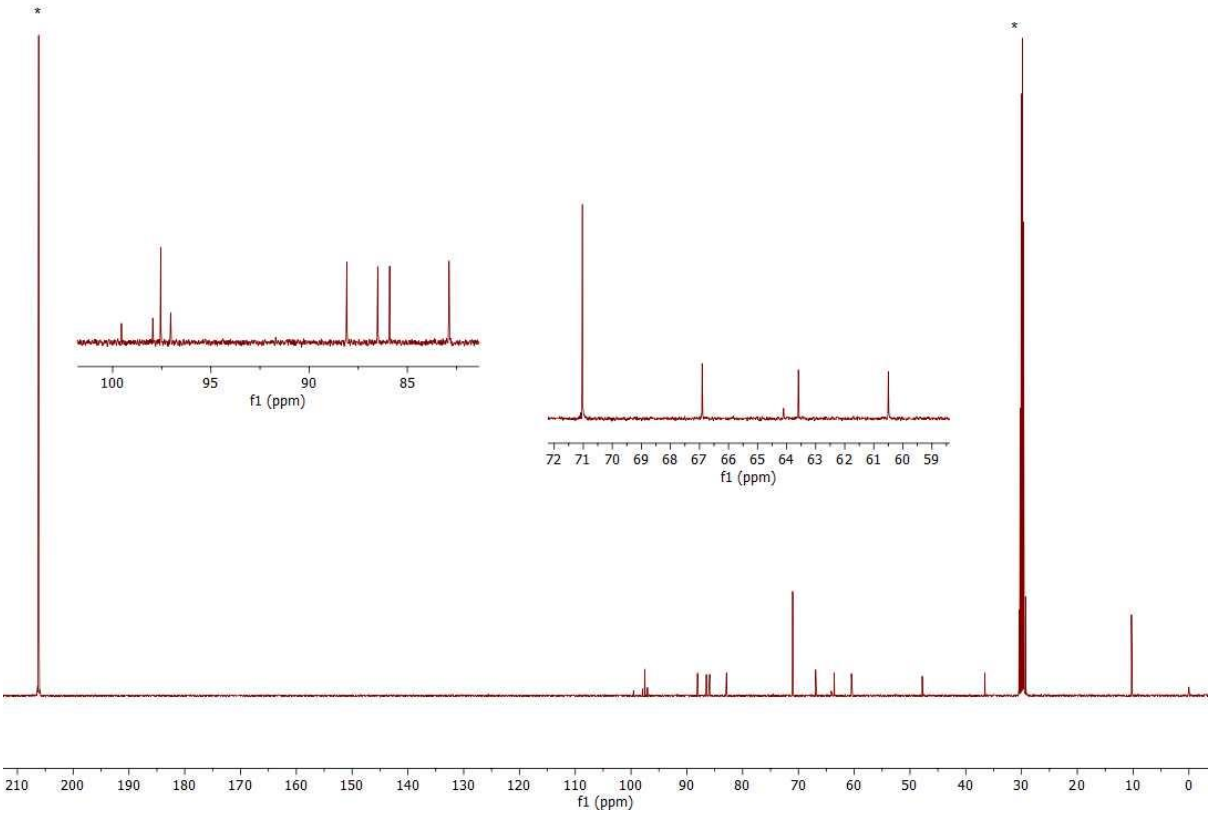


Figure S47 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, Me_2CO-d_6) of **12**

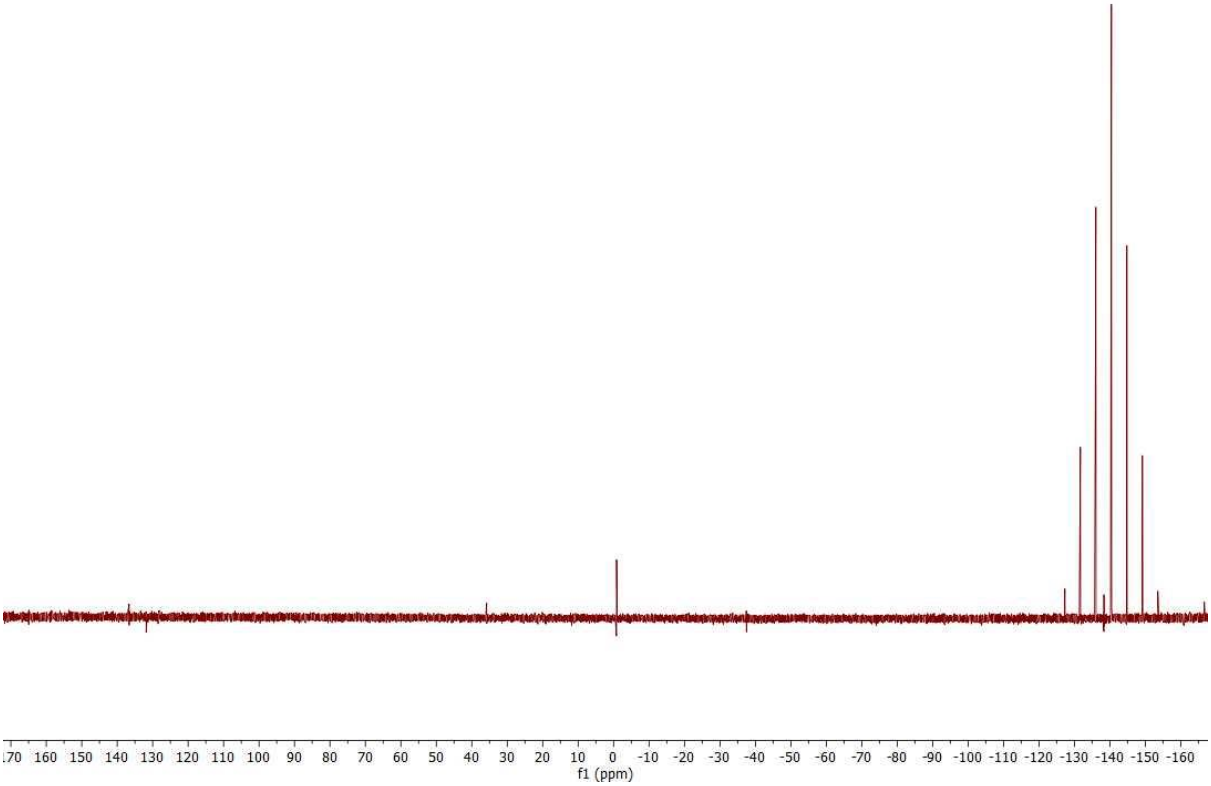


Figure S48 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, Me_2CO-d_6) of **12** (the peak at ≈0 ppm is a spike)

References

1 A. Leonidova, T. Joshi, D. Nipkow, A. Frei, J.-E. Penner, S. Konatschnig, M. Patra and G. Gasser, *Organometallics*, 2013, **32**, 2037.

2 F. Barrière and W. E. Geiger, *J. Am. Chem. Soc*., 2006, **128**, 3980.

3 M. Konhefr, K. Lacina, M. Skrutová Langmajerová, Z. Glatz, P. Skládal and C. Mazal, *ChemistrySelect*, 2018, **3**, 9641.

4 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.

5 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, **71**, 3.

6 a) D. Kratzert, J. J. Holstein and I. Krossing, *J. Appl. Crystallogr*., 2015, **48**, 933; b) D. Kratzert and I. Krossing, *J. Appl. Crystallogr*., 2018, **51**, 928.

7 a) A. L. Spek, *J. Appl. Crystallogr*., 2003, **36**, 7; b) A. L. Spek, *Acta Crystallogr. D, Biol. Crystallogr*., 2009, **65**, 148.

8 H. P. Klug, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1968, **24**, 792.

9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M.; Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, K.; J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J.; Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B: Foresman and D. J. Fox, Gaussian 16, Revision C.01; Gaussian, Inc., Wallingford CT, 2016.

10 a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865; b) J. P. Perdew, M. Ernzerhof and K. Burke, *J. Chem. Phys.,* 1996, **105**, 9982; c) M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.,* 1999, **110**, 5029; d) C. Adamo and V. Barone, *J. Chem. Phys.,* 1999, **110**, 6158.

11 a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.,* 2005, **7**, 3297; b) F. Weigend, *Phys. Chem. Chem. Phys.,* 2006, **8**, 1057.

12 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.,* 2010, **132**, 154104.

13 a) M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.,* 1987, **86**, 866; b) A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuss, *Mol. Phys.,* 1993, **80**, 1431; c) G. Igel-Mann, H. Stoll and H. Preuss, *Mol. Phys.,* 1988, **6**, 1321.

14 T. Lu and F. Chen, *Acta Chim. Sin.,* 2011, **69**, 2393.

15 T. Lu and F. Chen, *J. Comput. Chem.,* 2012, **33**, 580.

16 a) Avogadro: An Open-Source Molecular Builder and Visualization Tool, version 1.2.0, http://avogadro.openmolecules.net/; b) M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *J. Cheminf.,* 2012, **4**, 17.