Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Beyond phosphorus: synthesis, reactivity, coordination behaviour and catalytic properties of 1,1'-bis(diphenylstibino)ferrocene

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EXPERIMENTAL

Materials and Methods

Unless stated otherwise, the syntheses were performed by standard Schlenk techniques under nitrogen or argon atmosphere and in dry solvents. Anhydrous tetrahydrofuran, dichloromethane and diethyl ether were obtained from a PureSolv MD5 Solvent Purification System (Innovative Technology, USA). Solvents utilised for workup, chromatography and crystallisations were of reagent grade and were used without additional purification (Lach-Ner, Czech Republic).

Chlorodiphenylstibine,[1] $[(\mu\text{-Cl})_3\{Ru(\eta^6\text{-cym})\}_2][PF_6]$,[2] (*N,N*'-di-*t*-butyl-ethanedialdimine-κ^2*N*,*N*')(η^2-2,5-furandione)palladium(0) (referred to as [Pd(η^2-ma)(N^N)]),[3] [AuCl(tht)],[4] $[Au(tht)_2][SbF_6]$[5] (tht = tetrahydrothiophene), $[PdCl_2(dppf\text{-}\kappa^2P,P')]$[6] and [Pd($\eta^2$-ma)(dppf-$\kappa^2P,P'$)][7] were prepared according to literature procedures. Other chemicals were purchased from commercial suppliers and were used without additional purification (Sigma-Aldrich, TCI and Alfa-Aesar). Abbreviations: cod = cycloocta-1,5-diene, cym = *p*-cymene, ma = maleic anhydride, tht = tetrahydrothiophene.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95 MHz; ^{13}C{^{1}H}, 100.58 MHz) at 25°C. Chemical shifts (δ/ppm) are expressed relative to internal tetramethylsilane. Standard notation of the NMR signal multiplicity is used.[8] In addition, vt is used to distinguish virtual triplets due to AA'BB' spin systems of the ferrocene protons (C_5H_4). ESI mass spectra were recorded using a Bruker Esquire 3000 spectrometer using samples dissolved in HPLC-grade methanol. The identity of the observed ionic species was confirmed by comparison of the theoretical and experimentally determined isotopic patterns. Elemental analyses were performed using a Perkin-Elmer PE 2400 CHN analyser. The amount of residual solvent was verified by NMR analysis.

Electrochemical measurements were performed with a μAUTOLAB III instrument (Eco Chemie, Netherlands) at ambient temperature. A standard Metrohm three-electrode cell equipped with a glassy carbon disc (2 mm diameter) working electrode, a platinum sheet auxiliary electrode and an Ag/AgCl (3 M KCl) reference electrode were used. The samples were dissolved in anhydrous dichloromethane to give a 1 mM solution of the analyte and 0.1 M $Bu_4N[PF_6]$ (Fluka, puriss. for electrochemistry) as the supporting electrolyte. The solutions were deaerated with argon before the measurements and then maintained under an argon blanket. Decamethylferrocene (Alfa-Aesar) was added as an internal standard for the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[9]

Syntheses

Preparation of 1,1'-(diphenylstibino)ferrocene (1). 1,1'-Dibromoferrocene (1.72 g, 5.0 mmol) was introduced into a flame-dried, three-necked flask (250 mL) equipped with a magnetic stirring bar and an argon inlet. The flask was sealed with a rubber septum and thoroughly purged with argon. Anhydrous tetrahydrofuran (40 mL) was added and the resulting solution was cooled to −78 °C in a dry ice/ethanol bath. A solution of *n*-BuLi in hexanes (5.2 mL of 2.5 M solution, 13 mmol) was added dropwise and the resulting mixture was stirred at −78°C for 1 h. Then, a pre-cooled solution of chlorodiphenylstibine (3.43 g, 11 mmol) in THF (20 mL) was slowly added and the reaction mixture was stirred at −78 °C for 1 h and then at room temperature overnight. The reaction was terminated by adding saturated aqueous sodium bicarbonate (50 mL) and ethyl acetate (50 mL), and the obtained biphasic mixture was transferred to a separatory funnel. The aqueous layer was separated, and the organic layer was washed with brine (50 mL), dried over magnesium sulfate and evaporated under vacuum. The crude product was purified by flash column chromatography over silica gel using ethyl acetate-hexane (1:3) as the eluent. The first yellow band was collected and evaporated, leaving a yellow solid, which was crystallised from boiling heptane (approximately 50 mL) by cooling slowly to −18°C. The separated crystalline material was filtered off, washed with cold pentane, and dried under vacuum. The mother liquor was evaporated and crystallised once again to produce a second batch of the product. Combined yield of **1**: 2.64 g (72%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 3.99 (vt, *J*' = 1.7 Hz, 4 H, CH of fc), 4.21 (vt, *J*' = 1.7 Hz, 4 H, CH of fc), 7.26-7.32 (m, 12 H, $SbPh_2$), 7.42-7.47 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 69.29 (C^{ipso} of fc), 71.80 (CH of fc), 74.92 (CH of fc), 128.43 (CH^{para} of $SbPh_2$), 128.61 (CH of $SbPh_2$), 136.16 (CH of $SbPh_2$), 138.59 (C^{ipso} of $SbPh_2$) ppm. ESI+ MS: *m/z* 759 ($[M + Na]^+$). Anal. Calc. for $C_{34}H_{28}FeSb_2$ (735.95): C 55.49, H 3.84%. Found: C 55.44, H 3.82%.

Preparation of fc($SbCl_2Ph_2$)$_2$ (2). Distibine **1** (368.0 mg, 0.50 mmol) was dissolved in anhydrous dichloromethane (20 mL) and the solution was cooled on ice. Thionyl chloride (0.11 mL, 1.5 mmol) diluted with dichloromethane (20 mL) was slowly introduced, and the resulting mixture was stirred at room temperature for 2 h and subsequently concentrated under reduced pressure. The solid residue was dissolved in chloroform (ca. 5 mL) and the solution was added to cold pentane (200 mL). The mixture was stored at 4°C overnight to complete crystallisation and the separated crystalline solid was filtered off, washed with pentane and dried under vacuum. Yield of **2**: 388.8 mg (89%); orange, needle-shaped crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.45 (vt, 4 H, *J*' = 2.0 Hz, CH of fc), 5.18 (vt, 4 H, *J*' = 2.0 Hz, CH of fc), 7.50-7.63 (m, 12 H, $SbPh_2$), 8.23-8.31 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): 74.61 (CH of fc), 76.30 (CH of fc), 80.29 (C^{ipso} of fc), 129.50 (CH of $SbPh_2$), 131.73 (CH^{para} of

$SbPh_2$), 133.92 (CH of $SbPh_2$), 140.73 (C^{ipso} of $SbPh_2$) ppm. ESI+ MS: *m/z* 783 ([M – 4Cl + O + CH_3O]$^+$). Anal. Calc. for $C_{34}H_{28}Sb_2FeCl_4$ (877.8): C 46.52, H 3.22%. Found: C 46.58, H 3.15%.

Synthesis of fc(SbClPh$_2$)$_2$O (3). A solution of sodium hydroxide in methanol (213 μL of 0.481 M solution, 0.103 mmol) was added to a solution of **2** (43.9 mg, 0.050 mmol) in a mixture of reagent-grade acetone (5 mL) and methanol (3 mL). The reaction mixture was stirred for 90 min and evaporated under reduced pressure. The solid residue was taken up with dichloromethane and filtered through a PTFE syringe filter (0.45 μm porosity) to produce a yellow solution. The filtrate was evaporated under reduced pressure and the solid residue was crystallised by liquid-phase diffusion of hexane (8 mL) into a dichloromethane solution (1 mL) of the crude product. The crystalline product was filtered off, washed with hexane and dried under vacuum. Yield of **3**: 31.6 mg (77%), yellow crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.43 (vt, *J′* = 1.8 Hz, 4 H, CH of fc), 4.48 (vt, *J′* = 1.8 Hz, 4 H, CH of fc), 7.39-7.46 (m, 8 H, $SbPh_2$), 7.48-7.55 (m, 4 H, $SbPh_2$), 8.06-8.12 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 72.84 (CH of fc), 74.34 (CH of fc), 80.38 (C^{ipso} of fc), 129.31 (CH of $SbPh_2$), 131.28 (CH^{para} of $SbPh_2$), 134.19 (CH of $SbPh_2$), 140.57 (C^{ipso} of $SbPh_2$) ppm. ESI+ MS: *m/z* 783 ([M – 2 Cl + CH_3O]$^+$). Anal. Calc. for $C_{34}H_{28}Cl_2FeOSb_2$ (822.9): C 49.63, H 3.43%. Found: C 49.51, H 3.12%.

Preparation of fc(SbPh$_2$(NO$_3$))$_2$O (4a). From fc(SbCl$_2$Ph$_2$)$_2$ (2). A solution of silver(I) nitrate (67.8 mg, 0.40 mmol) in methanol (6 mL) was added to a solution of **2** (87.8 mg, 0.10 mmol) in reagent-grade acetone (3 mL). The reaction mixture was stirred in the dark for 45 min and then filtered through a PTFE syringe filter to give a clear yellow solution. The filtrate was evaporated under reduced pressure and the brown solid residue was dissolved in chloroform (3 mL) and filtered through a PTFE syringe filter, adding Celite. The brown filtrate was evaporated under reduced pressure and the solid residue was crystallised *twice* by liquid-phase diffusion of pentane (8 mL) into a chloroform solution (2 mL) of the crude product. The crystalline product was isolated by decantation, washed with pentane and dried under vacuum. Yield of **4a**·$CHCl_3$: 59.7 mg (60%), yellow crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.34 (vt, 4 H, *J′*= 1.8 Hz, CH of fc), 4.56 (vt, 4 H, *J′*= 1.8 Hz, CH of fc), 7.44-7.50 (m, 8 H, $SbPh_2$), 7.54-7.60 (m, 4 H, $SbPh_2$), 7.82-7.87 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 72.51 (C^{ipso} of fc), 73.51 (CH of fc), 73.83 (CH of fc), 129.98 (CH of $SbPh_2$), 132.04 (CH^{para} of $SbPh_2$), 133.33 (CH of $SbPh_2$), 137.02 (C^{ipso} of $SbPh_2$) ppm. ESI+ MS: *m/z* 783 ([M – 2NO_3 + CH_3O]$^+$). Anal. Calc. for $C_{34}H_{28}FeN_2O_7Sb_2$·$CHCl_3$ (995.4): C 42.23, H 2.93, N 2.81%. Found C 42.44. H 2.88, N 2.59%.

From fc(SbClPh$_2$)$_2$O (3). A solution of silver(I) nitrate (8.5 mg, 0.050 mmol) in methanol (1.5 mL) was added to a solution of **3** (20.6 mg, 0.025 mmol) in acetone (5.5 mL; both solvents were of reagent grade). The resulting mixture was stirred in the dark for 75 min and filtered

through a PTFE syringe filter, adding Celite. The yellow filtrate was evaporated under reduced pressure, leaving a yellow solid residue, which was crystallised by liquid-phase diffusion of pentane (5.5 mL) into chloroform solution (1.5 mL) of the crude product. The crystalline solid, which formed over several days, was isolated by decantation, washed with pentane and dried under vacuum. Yield of **4a**: 24.1 mg (97%), yellow crystals.

Conversion of fc(SbPh$_2$(NO$_3$))$_2$O (4a) to fc(SbClPh$_2$)$_2$O (3). Solid benzyl triethylammonium chloride (11.4 mg, 0.050 mmol) was added to a solution of **4a**·$CHCl_3$ (24.9 mg, 0.025 mmol) in dichloromethane (3.5 mL). The reaction mixture was stirred for 1 h and evaporated under reduced pressure. The solid residue was crystallised by liquid-phase diffusion of pentane (≈4 mL) into a dichloromethane solution (2.5 mL) of the crude product. The separated crystalline solid was isolated by decantation, washed with methanol (to remove a yellow oil) and pentane and dried under vacuum. Yield of **3**: 19.0 mg (92%).

Preparation of fc(SbPh$_2$(ClO$_4$))$_2$O (4b). A solution of silver(I) perchlorate (41.5 mg, 0.20 mmol) in methanol (4 mL) was added to **3** (44.0 mg, 0.050 mmol) dissolved in acetone (5 mL; reagent grade solvents were used). The reaction mixture was stirred in the dark for 80 min and filtered through a PTFE filter, adding Celite. The yellow filtrate was evaporated under reduced pressure and the solid residue was crystallised by liquid-phase diffusion of hexane (7 mL) into a dichloromethane (3 mL) solution of the crude product. The crystalline solid was filtered off, washed with hexane and dried under vacuum. Yield of **4b**: 30.6 mg (64%), yellow crystals.

^{1}H NMR (CD_2Cl_2, 399.95 MHz): δ 4.66 (vt, 4 H, *J*′ = 1.9 Hz, CH of fc), 4.85 (vt, 4 H, *J*′ = 1.9 Hz, CH of fc), 7.55-7.61 (m, 8 H, $SbPh_2$), 7.66-7.72 (m, 4 H, $SbPh_2$), 7.82-7.88 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.58 MHz): δ 71.94 (C^{ipso} of fc), 74.61 (CH of fc), 75.12 (CH of fc), 130.86 (CH of $SbPh_2$), 133.67 (C^{ipso} of $SbPh_2$), 133.76 (CH^{para} of $SbPh_2$), 134.29 (CH of $SbPh_2$). ESI+ MS: *m/z* 783 ([M – 2ClO_4 + CH_3O]$^+$). Anal. Calc. for $C_{34}H_{28}Cl_2FeO_9Sb_2$ (950.9): C 42.95, H 2.97%. Found: C 42.46, H 3.40%. Note: although analytically pure, the compound notoriously gives erratic microanalytical results (higher C and H content). The presented values are the best from five independent measurements.

Conversion of fc(SbPh$_2$(ClO$_4$))$_2$O (4b) to fc(SbClPh$_2$)$_2$O (3). Solid benzyl triethylammonium chloride (8.9 mg, 0.040 mmol) was added to a solution of **4b** (18.6 mg, 0.020 mmol) in dichloromethane (7 mL). The mixture was stirred for 2 h and evaporated under reduced pressure. The yellow residue was dissolved in dichloromethane and the solution was layered with pentane. The crystalline solid, which formed over several days, was isolated by decantation, washed with pentane, dried under vacuum and mechanically separated from the colourless crystals of benzyl-triethylammonium perchlorate. Yield of **3**: 11.9 mg (74%).

Oxidation of 1 with NO[BF_4]. Isolation of $Ph_2SbfcSbF_2Ph_2$ (5). A reaction flask was charged successively with nitrosonium tetrafluoroborate (9.5 mg, 0.081 mmol), distibine **1** (56.9 mg, 0.077 mmol) and dichloromethane (4.5 mL). The resulting mixture was stirred at room temperature for 2 h, whereupon its colour changed from the initial orange to green. The mixture was slowly added into pentane (25 mL) and the resulting turbid mixture was stored at 4°C for 2 h, providing a clear yellow solution, which was subsequently evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate-cyclohexane (1:8) as the eluent. The second, major yellow band was collected and evaporated. The solid residue was recrystallised from chloroform/pentane at –18°C. The crystalline product was isolated by decantation, washed with pentane and dried under vacuum. Yield of **6**: 14.9 mg (25%), orange crystals. Note: a similar reaction employing 2.1 equiv. of NO[BF_4] produced a mixture of **1**, **5** and **6** in approximately 1:2.8:1.2 molar ratio.

Analytical data for **5**. ^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 3.92 (vt, 2 H, J' = 1.7 Hz, CH of fc), 4.16 (vt, 2 H, J' = 1.7 Hz, CH of fc), 4.34 (t of vt, 2 H, J' = 2.1, 1.1 Hz, CH of fc), 4.69 (vt, 2 H, J' = 1.9 Hz, CH of fc), 7.25-7.37 (m, 6 H, $SbPh_2$), 7.38-7.46 (m, 4 H, $SbPh_2$), 7.48-7.57 (m, 6 H, $SbPh_2F_2$), 8.11-8.17 (m, 4 H, $SbPh_2F_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 69.73 (t, $^2J_{HF}$ = 22 Hz, C^{ipso} of fc), 70.60 (C^{ipso} of fc), 72.44 (CH of fc), 72.58 (t, $^4J_{CF}$ = 2 Hz, CH of fc), 73.86 (t, $^3J_{CF}$ = 4 Hz, CH of fc), 75.54 (CH of fc), 128.55 (CH^{para} of $SbPh_2$), 128.68 (CH of $SbPh_2$), 129.50 (t, $^4J_{CF}$ = 2 Hz, CH^{meta} of $SbPh_2F_2$), 132.07 (CH^{para} of $SbPh_2F_2$), 135.03 (t, $^3J_{CF}$ = 5 Hz, CH^{orto} of $SbPh_2F_2$), 136.15 (CH of $SbPh_2$), 138.33 (C^{ipso} of $SbPh_2$). The signal due to C^{ipso} of $SbPh_2F_2$ was not observed, presumably due to overlaps. ^{19}F NMR ($CDCl_3$, 376.29 MHz): δ –149.03 (s, $SbPh_2F_2$). ESI+ MS: *m/z* 753 ([M – F]$^+$), 767 ([M –2F + OCH_3]$^+$). Anal. Calc. for $C_{34}H_{28}F_2FeSb_2$ (772.0): C 52.76, H 3.65 %. Found: C 52.61, H 3.55 %.

Synthesis of $fc(SbF_2Ph_2)_2$ (6). A solution of potassium fluoride (13.6 mg, 0.234 mmol) in methanol (1.5 mL was added to a solution of stiborane **2** (26.8 mg, 0.031 mmol) in a mixture of acetone (2 mL) and methanol (1 mL). The resulting turbid mixture was stirred at ambient temperature for 4 h and evaporated under reduced pressure. The solid residue was dissolved in chloroform and filtered through a PTFE syringe filter to give a clear yellow solution. The filtrate was evaporated under reduced pressure and the solid residue was crystallised from the chloroform/pentane (0.3/3 mL) mixture by cooling to –18°C. The crystalline product was isolated by decantation, washed with pentane and dried under vacuum. Yield of **6**: 24.6 mg (99%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.25 (t of vt, 4 H, J' = 2.0, 1.1 Hz, CH of fc), 4.66 (vt, 4 H, J' = 1.9 Hz, CH of fc), 7.49-7.61 (m, 12 H, $SbPh_2F_2$), 8.12-8.22 (m, 8 H, $SbPh_2F_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 70.96 (t, $^2J_{CF}$ = 23 Hz, C^{ipso} of fc), 73.25 (CH of fc), 74.48 (t, $^3J_{CF}$ = 4 Hz, CH of fc), 129.61 (CH^{meta} of SbF_2Ph_2), 132.24 (CH^{para} of SbF_2Ph_2), 134.68 (t, $^2J_{CF}$ = 14 Hz, C^{ipso} of SbF_2Ph_2),

135.04 (t, $^{3}J_{CF}$ = 5 Hz, CH^{orto} of SbF_2Ph_2). ^{19}F NMR ($CDCl_3$, 376.29 MHz): δ –149.02 (s, SbF_2Ph_2). ESI+ MS: *m/z* 812 (M^+), 835 ($[M + Na]^+$); the sample was dissolved in acetonitrile. Anal. Calc. for $C_{34}H_{28}F_4FeSb_2$ (812.0): C 47.54, H 3.29 %. Found: C 47.55, H 3.17 %.

Synthesis of fc(SbFPh$_2$)$_2$O (7). From fc(SbF$_2$Ph$_2$)$_2$ (6). A solution of sodium hydroxide in methanol (204.5 μL of 0.501 M solution, 0.103 mmol) was added to a solution of **6** (40.6 mg, 0.050 mmol) in a mixture of acetone (3.0 ml) and methanol (1.8 ml; reagent grade solvents were used). The reaction mixture was stirred for 90 min and evaporated under reduced pressure. The solid residue was taken up with dichloromethane and filtered through a PTFE syringe filter (0.45 μm porosity) to produce a yellow solution. The filtrate was evaporated under reduced pressure and the solid residue was crystallised by liquid-phase diffusion of hexane (9 mL) into a dichloromethane solution (1 mL) of the crude product. The crystalline product was isolated by decantation, washed with pentane and dried under vacuum. Yield of **7**: 30.7 mg (78%), yellow crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.39 (vt, 4 H, *J´* = 1.8 Hz, CH of fc), 4.41 (vt, 4 H, *J´* = 1.8 Hz, CH of fc), 7.41-7.47 (m, 8 H, $SbPh_2$), 7.48-7.54 (m, 4 H, $SbPh_2$), 8.17-8.23 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 72.63 (CH of fc), 74.05 (d, $^{3}J_{CF}$ = 2 Hz, CH of fc), 75.86 (d, $^{2}J_{CF}$ = 47 Hz, C^{ipso} of fc), 129.26 (d, $^{4}J_{CF}$ = 1 Hz, CH^{meta} of $SbPh_2$), 131.40 (CH^{para} of $SbPh_2$), 135.38 (d, $^{3}J_{CF}$ = 5 Hz, CH^{orto} of $SbPh_2$), 137.96 (d, $^{2}J_{CF}$ = 20 Hz, C^{ipso} of $SbPh_2$). ^{19}F NMR ($CDCl_3$, 376.29 MHz): δ –104.61 (s, $SbFPh_2$). ESI+ MS: *m/z* 771 ($[M – F]^+$). Anal. Calc. for $C_{34}H_{28}F_2FeOSb_2$ (790.0): C 51.70, H 3.57%. Found: C 51.41, H 3.40%.

From fc(SbCl$_2$Ph$_2$)$_2$ (3). A solution of potassium fluoride (11.0 mg, 0.189 mmol) in methanol (1.5 ml) was added to a solution of **3** (30.5 mg, 0.037 mmol) in acetone (7.0 ml; both solvents were of reagent grade). The turbid mixture was stirred for 2 h and then evaporated under reduced pressure. The solid residue was taken up with dichloromethane and filtered through a PTFE syringe filter (0.45 μm porosity) to produce a yellow solution. The filtrate was evaporated under reduced pressure and the solid residue was crystallised by liquid-phase diffusion of hexane into a dichloromethane solution of the crude product. The crystalline product was isolated by decantation, washed with pentane and dried under vacuum. Yield of **7**: 24.6 mg (84%), yellow crystals.

Preparation of [(μ-ClO$_4$){Ag(1-κ^2*Sb*,*Sb*')}]$_2$ (8). A solution of silver(I) perchlorate (5.1 mg, 0.025 mmol) in benzene (1 mL) was added to a solution of **1** (18.1 mg, 0.025 mmol) in the same solvent (1 mL) and the resulting mixture was stirred in the dark for 35 min. The separated solid was filtered off, washed successively with benzene and pentane, and dried under vacuum to give complex **8**. Yield: 19.7 mg (85%), orange powder.

^{1}H NMR (acetone-d_6, 399.95 MHz): δ 4.40 (br s, 4 H, CH of fc), 4.51 (br s, 4 H, CH of fc), 7.39-7.52 (m, 12 H, $SbPh_2$), 7.58-7.71 (m, 8 H, $SbPh_2$). ESI+ MS: *m/z* 759 ([**1** + Na]$^+$). Anal. Calc. for $C_{68}H_{56}Ag_2Cl_2Fe_2O_8Sb_4$ (1886.6): C 43.29, H 2.99%. Found: C 43.31, H 2.89%.

Synthesis of [Ag(1-κ^2*Sb*,*Sb*')$_2$]ClO_4 (9a). A solution of silver(I) perchlorate (3.0 mg, 0.015 mmol) in THF (0.5 mL) was added to a solution of **1** (21.3 mg, 0.029 mmol) in the same solvent (1 mL). The resulting yellow solution was stirred at room temperature for 5 hours and evaporated under reduced pressure. The solid yellow residue was dissolved in chloroform-d and analysed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.14 (br s, 4 H, CH of fc), 4.46 (br s, 4 H, CH of fc), 7.20-7.27 (m, 8 H, $SbPh_2$), 7.34-7.42 (m, 12 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 65.27 (C^{ipso} of fc), 72.96 (CH of fc), 75.00 (CH of fc), 129.75 (CH of $SbPh_2$), 130.48 (CH^{para} of $SbPh_2$), 131.95 (C^{ipso} of $SbPh_2$), 135.32 (CH of $SbPh_2$). HR MS calc. for $[C_{68}H_{56}Fe_2AgSb_4]^+$ (= [Ag(**1**)$_2$]$^+$) 1578.8305, found 1578.8320.

Synthesis of [Ag(1-κ^2*Sb*,*Sb*')$_2$][SbF_6] (9b). A solution of silver(I) hexafluoroantimonate (8.8 mg, 0.026 mmol) in THF (1 mL) was added to a solution of **1** (37.7 mg, 0.051 mmol) in the same solvent (1 ml). The resulting yellow solution was stirred at room temperature for 4.5 hours and then filtered through a PTFE syringe filter. The filtrate was evaporated under reduced pressure, leaving a solid residue, which was dissolved in chloroform (2 mL) and crystallised by liquid-phase diffusion of diethyl ether (8 mL) over several days. The crystalline product was isolated by decantation, washed with diethyl ether and pentane, and dried under vacuum. Yield of **9b**·0.4$CHCl_3$: 35.5 mg (73%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.13 (vt, 4 H, *J*´ = 1.8 Hz, CH of fc), 4.47 (vt, 4 H, *J*´ = 1.7 Hz, CH of fc), 7.20-7.26 (m, 8 H, $SbPh_2$), 7.32-7.42 (m, 12 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 65.13 (C^{ipso} of fc), 73.01 (CH of fc), 74.98 (CH of fc), 129.80 (CH of $SbPh_2$), 130.55 (CH^{para} of $SbPh_2$), 131.78 (C^{ipso} of $SbPh_2$), 135.24 (CH of $SbPh_2$). ESI+ MS: *m/z* 1579 ([M – SbF_6]$^+$); ESI– MS: *m/z* 235 ([SbF_6]$^-$). Anal. Calc. for $C_{68}H_{56}AgF_6Fe_2Sb_5$·0.4$CHCl_3$ (1863.3): C 44.09, H 3.05%. Found: C 44.01, H 2.79%.

Preparation of [(μ-1){$RuCl_2$(η^6-cym)}$_2$] (10). A solution of [$RuCl_2$(η^6-cym)]$_2$ (61.2 mg, 0.10 mmol) in dichloromethane (6 mL) was added to a solution of **1** (73.6 mg, 0.10 mmol) in the same solvent (6 mL). An additional 3 mL of dichloromethane were used to completely transfer [$RuCl_2$(cym)]$_2$ into the reaction mixture. After stirring in dark for 2 h, all volatiles were removed under reduced pressure. The solid residue was dissolved in dichloromethane (ca. 3 mL) and the solution was layered with diethyl ether. The crystalline product, which separated during several days, was filtered off, washed with diethyl ether and dried under vacuum. Yield of **10**·1.3CH_2Cl_2: 121.9 mg (88%), red crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.08 (d, $^{3}J_{HH}$ = 6.9 Hz, 12 H, CH*Me*$_2$), 1.93 (s, 6 H, Me), 2.69 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2 H, C*H*Me$_2$), 4.09 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 4.18 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 5.30 (s, 1.3 H, CH_2Cl_2), 5.31 (br d, *J* = 5.9 Hz, 4 H, C_6H_4), 5.42 (br d, *J* = 5.9 Hz, 4 H, C_6H_4), 7.28-7.41 (m, 12 H, $SbPh_2$), 7.61-7.67 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 18.39 (Me), 22.06 (CH*Me*$_2$), 30.48 (*C*HMe$_2$), 68.34 (C^{ipso} of fc), 73.61 (CH of fc), 74.92 (CH of fc), 83.28 (CH of C_6H_4), 83.84 (CH of C_6H_4), 96.65 (C^{ipso} of C_6H_4), 106.77 (C^{ipso} of C_6H_4), 128.66 (CH of $SbPh_2$), 129.93 (CH^{para} of $SbPh_2$), 132.73 (C^{ipso} of $SbPh_2$), 136.15 (CH of $SbPh_2$) ppm. ESI+ MS: *m/*z 1007 ([M – $RuCl_2$(cym) – Cl]$^+$). Anal. Calc. for $C_{54}H_{54}Cl_4FeRu_2Sb_2$·1.3$CH_2Cl_2$ (1458.8): C 45.53, H 4.05%. Found: C 45.60, H 3.85%.

Preparation of [(μ-1){$RhCl_2$(η^5-C_5Me_5)}$_2$] (11). A solution of [$RhCl_2$(η^5-C_5Me_5)]$_2$ (61.9 mg, 0.10 mmol) in dichloromethane (6 mL) was added to **1** (73.7 mg, 0.10 mmol) dissolved in the same solvent (6 mL). An additional 3 mL of dichloromethane were used to completely transfer the rhodium precursor into the reaction flask. After stirring in the dark for 2 h, the solvent was removed under reduced pressure, and the solid residue was dissolved in dichloromethane (4 mL) and filtered through a PTFE syringe filter and Celite pad. The filtrate was layered with diethyl ether and the mixture was set aside for crystallisation. The separated solid was filtered off, washed with diethyl ether and dried under vacuum. Yield of **11**: 107.7 mg (79%), red crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.53 (s, 30 H, C_5Me_5), 4.02 (br s, 4 H, CH of fc), 4.24 (vt, *J*' = 1.7 Hz, 4 H, CH of fc), 7.28-7.40 (m, 12 H, $SbPh_2$), 7.65-7.69 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 9.33 (C_5*Me*$_5$), 67.70 (d, $^{2}J_{CRh}$ = 3 Hz, C^{ipso} of C_5H_4), 73.85 (CH of fc), 74.81 (CH of fc), 96.94 (d, $^{1}J_{CRh}$ = 7 Hz, *C*$_5$Me$_5$), 128.55 (CH of $SbPh_2$), 129.92 (CH^{para} of $SbPh_2$), 132.23 (d, $^{2}J_{CRh}$ = 2 Hz, C^{ipso} of $SbPh_2$), 136.38 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 1009 ([M – $RhCl_2$(C_5Me_5) – Cl]$^+$). Anal. Calc. for $C_{54}H_{58}Cl_4FeRh_2Sb_2$ (1354.0): C 47.90, H 4.32%. Found: C 47.91, H 4.26%.

Preparation of [RuCl(η^6-cym)(1-κ^2*Sb*,*Sb*')][PF_6] (12). A solution of [(μ-Cl)$_3${Ru(η^6-cym)}$_2$][PF_6] (36.1 mg, 0.050 mmol) in dichloromethane (3 mL) was added to **1** (73.6 mg, 0.10 mmol) dissolved in the same solvent (3 mL). An additional 1.5 mL of dichloromethane were used to completely transfer the ruthenium precursor into the reaction flask. Solid Na[PF_6] (84 mg, 0.50 mmol) was added, followed by acetone (5 mL), and the resulting mixture was stirred in the dark for 1.5 d. The resulting mixture was evaporated and the solid residue was taken up with dichloromethane (ca. 3 mL). The mixture was filtered through a PTFE syringe filter and Celite and the filtrate was layered with diethyl ether. Crystallisation by liquid-phase diffusion produced a crystalline solid, which was filtered off, washed with diethyl ether and dried under vacuum. Yield of **12**: 78.3 mg (67%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.91 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH*Me*$_2$), 1.57 (br s, 3 H, Me), 2.37 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1 H, C*H*Me$_2$), 4.14 (d of vt, *J*' = 1.2 Hz, 2 H, CH of fc), 4.33 (td, *J*' = 1.2 Hz, 2

H, CH of fc), 4.46 (td, *J*' = 1.2 Hz, 2 H, CH of fc), 4.62 (d of vt, *J*' = 1.2 Hz, 2 H, CH of fc), 5.86 (br d, *J* = 5.8 Hz, 2 H, C_6H_4), 5.91 (br d, *J* = 5.8 Hz, 2 H, C_6H_4), 7.46-7.69 (m, 20 H, $SbPh_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 18.11 (Me), 21.35 (CH*Me*$_2$), 30.63 (*C*HMe$_2$), 69.38 (C^{ipso} of fc), 70.82 (CH of fc), 73.03 (CH of fc), 73.77 (CH of fc), 86.51 (CH of C_6H_4), 87.00 (CH of C_6H_4), 98.00 (C^{ipso} of C_6H_4), 117.54 (C^{ipso} of C_6H_4), 129.68 (CH of $SbPh_2$), 129.92 (C^{ipso} of $SbPh_2$), 130.03 (CH of $SbPh_2$), 131.04 (CH^{para} of $SbPh_2$), 131.71 (CH^{para} of $SbPh_2$), 131.81 (C^{ipso} of $SbPh_2$), 135.11 (CH of $SbPh_2$), 135.70 (CH of $SbPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ –143.78 (sept, $^1J_{FP}$ = 713 Hz, PF_6). ESI+ MS: *m/z* 1007 ($[M - PF_6]^+$); ESI– MS: *m/z* 145 ($[PF_6]^-$). Anal. Calc. for $C_{44}H_{42}ClF_6FePRuSb_2$ (1151.7): C 45.89, H 3.68%. Found: C 45.69, H 3.61%.

Preparation of [RhCl(η^5-C$_5$Me$_5$)(1-κ^2*Sb*,*Sb*')][PF$_6$] (13). A solution of $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ (61.7 mg, 0.10 mmol) in dichloromethane (6 mL) was added to a solution of **1** (147.2 mg, 0.20 mmol) in the same solvent (6 mL), followed by solid $Na[PF_6]$ (168 mg, 1.0 mmol) and acetone (10 mL). After stirring in the dark for 1 d, the solvents were evaporated and the solid residue was extracted with dichloromethane (4 mL). The mixture was filtered through a PTFE syringe filter and Celite and the filtrate was layered with diethyl ether. Crystallisation by liquid-phase diffusion over several days produced a crystalline solid, which was isolated by filtered off, washed with diethyl ether and dried under vacuum. Yield of **13**: 163.4 mg (70%), orange crystalline solid.

^1H NMR ($CDCl_3$, 399.95 MHz): δ 1.52 (s, 15 H, C_5Me_5), 4.13 (d of vt, *J*' = 1.2 Hz, 2 H, CH of fc), 4.28 (td, *J*' = 1.2 Hz, 2 H, CH of fc), 4.43 (td, *J*' = 1.2 Hz, 2 H, CH of fc), 4.71 (d of vt, *J*' = 1.2 Hz, 2 H, CH of fc), 7.44-7.72 (m, 20 H, $SbPh_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 9.75 (C_5Me_5), 70.67 (CH of fc), 71.48 (d, $^2J_{CRh}$ = 2 Hz, C^{ipso} of fc), 72.91 (CH of fc), 73.30 (CH of fc), 76.64 (CH of fc), 102.79 (d, $^1J_{CRh}$ = 6 Hz, *C*$_5$Me$_5$), 127.95 (d, $^2J_{CRh}$ = 3 Hz, C^{ipso} of $SbPh_2$), 129.03 (s, C^{ipso} of $SbPh_2$), 129.59 (CH of $SbPh_2$), 130.14 (CH of $SbPh_2$), 131.24 (CH^{para} of $SbPh_2$), 131.96 (CH^{para} of $SbPh_2$), 135.81 (CH of $SbPh_2$), 136.16 (CH of $SbPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ –144.06 (sept, $^1J_{FP}$ = 712 Hz, PF_6) ppm. ESI+ MS: *m/z* 1009 ($[M - PF_6]^+$); ESI– MS: *m/z* 145 ($[PF_6]^-$) . Anal. Calc. for $C_{44}H_{43}ClF_6FePRhSb_2$ (1154.9): C 45.78, H 3.75%. Found: C 45.76, H 3.68%.

Preparation of [RuCl(η^5-C$_5$Me$_5$)(1-κ^2*Sb*,*Sb*')] (14). A flame-dried Schlenk flask was charged with **1** (73.6 mg, 0.10 mmol), $[RuCl(\eta^5\text{-}C_5Me_5)(cod)]$ (38.0 mg, 0.1 mmol) and a magnetic stirring bar. The reaction vessel was sealed with a rubber septum and purged with argon. The reactants were dissolved by adding anhydrous dichloromethane (5 mL) and the resulting cloudy brown reaction mixture was stirred for 1 hour and filtered through a PTFE syringe filter to give a clear orange solution. The filtrate was evaporated under reduced pressure and the solid residue was dissolved in chloroform and crystallised by liquid-phase diffusion of hexane. The crystalline product, which separated within several days, was isolated by

decantation, washed with cold pentane, and dried under vacuum. Yield of **14**: 58 mg (56%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.46 (s, 15 H, C_5Me_5), 3.96 (d of vt, J_{HH} = 2.4, 1.2 Hz, 2 H, CH of fc), 4.07 (d of vt, J_{HH} = 2.4, 1.2 Hz, 2 H, CH of fc), 4.20 (d of vt, J_{HH} = 2.4, 1.1 Hz, 2 H, CH of fc), 4.67 (d of vt, J_{HH} = 2.4, 1.2 Hz, 2 H, CH of fc), 7.33-7.38 (m, 6 H, $SbPh_2$), 7.43-7.51 (m, 6 H, $SbPh_2$), 7.70-7.75 (m, 4 H, $SbPh_2$), 7.51-7.81 (m, 4 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 10.58 ($C_5\mathit{Me}_5$), 69.49 (CH of fc), 71.20 (CH of fc), 72.50 (CH of fc), 73.90 (C^{ipso} of fc), 76.53 (CH of fc), 83.65 (C_5Me_5), 128.36 (CH of $SbPh_2$), 128.54 (CH of $SbPh_2$), 128.95 (CH^{para} of $SbPh_2$), 129.41 (CH^{para} of $SbPh_2$), 134.44 (C^{ipso} of $SbPh_2$), 135.12 (C^{ipso} of $SbPh_2$), 136.49 (CH of $SbPh_2$), 136.55 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 973 ([M – Cl]$^+$). Anal. Calc. for $C_{44}H_{43}ClFeSb_2Ru{\cdot}0.2CHCl_3$ (1031.6): C 51.46, H 4.22%. Found: C 51.54, H 4.04%.

Preparation of [$PdCl_2$(1-κ^2*Sb*,*Sb*')] (15). A solution of distibine **1** (73.6 mg, 0.10 mmol) in dichloromethane (10 mL) was added to solid [$PdCl_2$(cod)] (28.5 mg, 0.10 mmol) and the deep red reaction mixture was stirred for 30 min. The resulting solution was filtered through a PTFE syringe filter and the filtrate was evaporated under vacuum. The solid residue was dissolved in chloroform and crystallised by liquid-phase diffusion of diethyl ether. Well-developed crystals, which separated over several days, were filtered off by decantation, washed with diethyl ether, and dried under vacuum. Yield of **15**·0.3CH_2Cl_2: 67 mg (71%), brown crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.13 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 4.47 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 7.38-7.51 (m, 12 H, $SbPh_2$), 7.79-7.73 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 66.51 (C^{ipso} of fc), 73.01 (CH of fc), 74.89 (CH of fc), 129.38 (CH of $SbPh_2$), 130.17 (C^{ipso} of $SbPh_2$), 131.03 (CH^{para} of $SbPh_2$), 136.18 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 935 ([M + Na]$^+$), 953 ([M + K]$^+$). Anal. Calc. for $C_{34}H_{28}Cl_2FePdSb_2{\cdot}0.3CHCl_3$ (949.1): C 43.31, H 3.01%. Found: C 43.26, H 2.92%.

Preparation of [$PtCl_2$(1-κ^2*Sb*,*Sb*')] (16). A solution of distibine **1** (73.6 mg, 0.10 mmol) in dichloromethane (10 mL) was added to solid [$PtCl_2$(cod)] (37.4 mg, 0.10 mmol) and the orange reaction mixture was stirred until the platinum precursor completely dissolved (1 h). Then, it was filtered through a PTFE syringe filter and evaporated under vacuum. The solid residue was dissolved in dichloromethane (2 mL), and the solution was slowly mixed with diethyl ether (4 mL) and allowed to crystallise at room temperature overnight and then at 4 °C. The separated orange crystals were isolated by decantation, washed with diethyl ether, and dried under vacuum. Yield of **16**: 84 mg (84%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.11 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 4.43 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 7.37-7.50 (m, 12 H, $SbPh_2$), 7.78-7.82 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 63.71 (C^{ipso} of fc), 73.13 (CH of fc), 74.59 (CH of fc), 128.31 (C^{ipso} of $SbPh_2$), 129.24 (CH of $SbPh_2$), 130.99 (CH^{para} of $SbPh_2$), 136.10 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 1025 ([M + Na]$^+$),

1041 ([M + K]$^+$). Anal. Calc. for $C_{34}H_{28}Cl_2FePtSb_2 \cdot 1.5CHCl_3$ (1181.0): C 36.10, H 2.52%. Found: C 36.27, H 2.33% (a crystallised sample was used for the analysis).

Preparation of [Pd(1-κ²*Sb*,*Sb*')₂][BF₄]₂ (17a). A reaction flask was charged with **1** (20.9 mg, 0.028 mmol) and $[Pd(CH_3CN)_4][BF_4]_2$ (6.3 mg, 0.014 mmol), dichloromethane (2 mL) was introduced and the resulting mixture was stirred at room temperature for 1 h. The palladium precursor slowly dissolved and the colour of the solution changed to green. The reaction mixture was filtered through a PTFE syringe filter and the filtrate was added dropwise into hexane (10 mL). The separated solid was filtered off, washed with hexane and dried under vacuum. Yield of **17a**: 21.5 mg (86%), green powdery solid.

Alternatively, a glass vial was charged with **1** (14.9 mg, 0.020 mmol), $[Pd(CH_3CN)_4][BF_4]_2$ (4.5 mg, 0.010 mmol) and dichloromethane-d_2 (0.75 ml) in air. The resulting mixture was stirred at room temperature for 1 h. During this time, the palladium precursor slowly dissolved and the colour of the mixture turned green. The mixture was filtered through a PTFE syringe filter (0.45 μm porosity) and the dark green filtrate was analysed by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

^{1}H NMR (CD_2Cl_2, 399.95 MHz): δ 1.97 (s, CH_3CN), 4.14 (vt, 4 H, *J′* = 1.8 Hz, CH of fc), 4.53 (vt, 4 H, *J′* = 1.8 Hz, CH of fc), 7.18-7.25 (m, 8 H, $SbPh_2$), 7.28-7.34 (m, 8 H, $SbPh_2$), 7.39-7.44 (m, 4 H, $SbPh_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.58 MHz): δ 2.09 (*C*H_3CN), 65.93 (C^{ipso} of fc), 74.76 (CH of fc), 76.31 (CH of fc), 130.20 (C^{ipso} of $SbPh_2$), 130.64 (CH of $SbPh_2$), 132.19 (CH^{para} of $SbPh_2$), 136.36 (CH of $SbPh_2$). The signal due to CH_3*C*N was not observed. ESI+ MS: *m/z* 1578 ([Pd(**1**)$_2$]$^+$). HR MS calc. for $[C_{68}H_{56}Fe_2PdSb_4]^+$ (= [Pd(**1**)$_2$]$^+$) 1577.8297, found 1577.8271. Anal. Calc. for $C_{68}H_{56}B_2F_8Fe_2PdSb_4$ (1752.0): C 46.62, H 3.22%. Found: C 46.38, H 3.09%.

Preparation of [Pd(1-κ²*Sb*,*Sb*')₂][SbF₆]₂ (17b). A solution of silver(I) hexafluoroantimonate (13.7 mg, 0.040 mmol) in acetonitrile (1 ml) was added to a solution of $[PdCl_2(CH_3CN)_2]$ (5.2 mg, 0.020 mmol) in the same solvent (1.5 ml). The resulting mixture was stirred in the dark for 1 h and then filtered through a PTFE syringe filter, adding Celite. The filtrate was evaporated under reduced pressure to give cream coloured solid. This solid was redissolved in acetonitrile (2 ml) and treated with a solution of **1** (29.4 mg, 0.040 mmol) in dichloromethane (2.5 ml), whereupon the colour of the reaction mixture changed to olive green. The mixture was stirred at room temperature for 30 min and filtered through a PTFE syringe filter (0.45 μm porosity). The filtrate was evaporated under reduced pressure to produce an emerald green solid (41.8 mg, quantitative).

The compound is very poorly soluble. To obtain NMR data, the synthesis was repeated on a smaller scale (half molar amounts) in deuterated solvents and the reaction mixture was analysed by NMR spectroscopy. ^{1}H NMR (CD_2Cl_2/CD_3CN = 1/1, 399.95 MHz): δ 1.97 (s, CH_3CN), 4.17 (br s, 4 H, CH of fc), 4.47 (br s, 4 H, CH of fc), 7.29-7.59 (m, 20 H, $SbPh_2$). ESI+ MS: *m/z* 1578 ([Pd(**1**)$_2$]$^+$, calc. 1578); ESI– MS: *m/z* 235 ([SbF_6]$^-$).

Single crystals used for structure determination were obtained by dissolving a small amount of the crude product in acetone and layering the solution with diethyl ether in an NMR tube. Due to its poor solubility and instability in solution, the crude product could not be purified by crystallisation.

Preparation of [Pd(η²-ma)(1-κ²*Sb*,*Sb*')] (18). A solution of (*N*,*N*'-di-*t*-butyl-ethanedialdimine-κ²*N*,*N*')(η²-2,5-furandione)palladium(0) ([Pd(η²-ma)(N^N)]; 37.0 mg, 0.10 mmol) in dichloromethane (5 mL) was mixed with a solution of **1** (73.6 mg, 0.10 mmol) in the same solvent (2 mL). The reaction mixture was stirred for 1 h and evaporated to dryness. The solid residue was purified by column chromatography (silica gel, CH_2Cl_2/MeOH 50:1). The first, minor yellow band was discarded, and the second orange band was collected. The volatiles were removed under vacuum and the crude product was crystallised from dichloromethane/diethyl ether (1:2, 6 mL) at 4 °C. The obtained crystalline product was isolated by decantation, washed with diethyl ether and dried under vacuum. Yield of **18**: 79 mg (84%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.14 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 4.39 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 4.91 (br s, 2 H, CH of ma), 7.35-7.44 (m, 12 H, $SbPh_2$), 7.57-7.62 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 53.36 (CH of ma), 67.53 (C^{ipso} of fc), 72.19 (CH of fc), 74.64 (CH of fc), 129.29 (CH of $SbPh_2$), 130.00 (CH^{para} of $SbPh_2$), 133.40 (C^{ipso} of $SbPh_2$), 135.76 (CH of $SbPh_2$), 170.22 (C=O) ppm. ESI+ MS: *m/z* 963 ($[M + Na]^+$). Anal. Calc. for $C_{38}H_{30}Fe_2O_3PdSb_2$ (940.4): C 48.53, H 3.22%. Found: C 48.34, H 3.13%.

Preparation of [(μ-1)(AuCl)₂] (19). A solution of **1** (73.6 mg, 0.10 mmol) in dichloromethane (10 mL) was added to solid [AuCl(tht)] (64.1 mg, 0.20 mmol). The resulting solution was stirred for 30 min, concentrated to approximately 1 mL under reduced pressure and precipitated by diethyl ether addition (10 mL). The obtained yellow precipitate was filtered off and washed successively with diethyl ether (10 mL) and pentane (10 mL). The crude product was redissolved in dichloromethane (3 mL) and crystallised by adding diethyl ether (1 mL) and storing it at room temperature overnight. The resulting orange crystals were isolated by filtration, washed with diethyl ether, and dried under vacuum. Yield of **19**: 58 mg (48%), orange crystals. Note: the complex gradually darkens when stored at ambient temperature.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.37 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 4.45 (vt, *J*' = 1.8 Hz, 4 H, CH of fc), 7.44-7.53 (m, 12 H, $SbPh_2$), 7.62-7.66 (m, 8 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 64.38 (C^{ipso} of fc), 73.02 (CH of fc), 75.85 (CH of fc), 129.42 (C^{ipso} of $SbPh_2$), 129.89 (CH of $SbPh_2$), 131.41 (CH^{para} of $SbPh_2$), 135.54 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 1223 ($[M + Na]^+$), 1165 ($[M - Cl]^+$). Anal. Calc. for $C_{34}H_{28}Au_2Cl_2FeSb_2 \cdot CH_2Cl_2$ (1285.7): C 32.70, H 2.35%. Found: C 32.33, H 2.13%.

Preparation of [Au(1-κ²*Sb*,*Sb*')₂][AuCl₂] (20a). A solution of **1** (73.6 mg, 0.10 mmol) in dichloromethane (10 mL) was added to solid [AuCl(tht)] (32.0 mg, 0.10 mmol), and the resulting

solution was stirred for 30 min and then evaporated to dryness. The solid residue was taken up with dichloromethane (1 mL) and crystallised by slowly adding diethyl ether (1 mL). The first crystals were observed already within minutes. The crystallisation was completed at 4°C overnight. The orange crystals were filtered off, washed with diethyl ether, and dried under vacuum. Yield of **20a**·CH_2Cl_2: 84 mg (83%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.18 (br s, 8 H, CH of fc), 4.47 (vt, *J*' = 1.7 Hz, 8 H, CH of fc), 7.22-7.30 (m, 16 H, $SbPh_2$), 7.36-7.45 (m, 24 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 66.46 (C^{ipso} of fc), 72.95 (CH of fc), 74.94 (CH of fc), 129.68 (CH of $SbPh_2$), 130.78 (CH^{para} of $SbPh_2$), 131.64 (br s, C^{ipso} of $SbPh_2$), 135.01 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 1669 ([M – $AuCl_2$]$^+$); ESI– MS: *m/z* 267 ([$AuCl_2$]$^-$). Anal. Calc. for $C_{68}H_{56}Au_2Cl_2Fe_2Sb_4$·$CH_2Cl_2$ (2021.7): C 40.99, H 2.89%. Found: C 41.16, H 2.67%.

Preparation of [Au(1-κ^2*Sb*,*Sb*')$_2$][SbF_6] (20b). A solution of **1** (73.6 mg, 0.10 mmol) in dichloromethane (5 mL) was added to solid [Au(tht)$_2$][SbF_6] (30.4 mg, 0.050 mmol). The reaction mixture was stirred for 1 hour and then evaporated to dryness. The solid residue was dissolved in dichloromethane (2 mL) and the solution was filtered through a PTFE syringe filter. Diethyl ether (2 mL) was added dropwise to the filtrate to induce rapid crystallisation, which was completed at room temperature overnight. The separated crystalline solid was filtered off, washed with dichloromethane-diethyl ether (1:1 v/v; 5 mL) and diethyl ether, and dried under vacuum. Yield of **20b**: 87 mg (92%), orange crystals. Note: the identical product was obtained when the reaction was performed using equimolar amounts of the reactants.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 4.13 (vt, *J*' = 1.8 Hz, 8 H, CH of fc), 4.48 (vt, *J*' = 1.8 Hz, 8 H, CH of fc), 7.15-7.21 (m, 16 H, $SbPh_2$), 7.30-7.38 (m, 24 H, $SbPh_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 67.04 (C^{ipso} of fc), 72.94 (CH of fc), 74.65 (CH of fc), 129.65 (CH of $SbPh_2$), 130.64 (CH^{para} of $SbPh_2$), 132.11 (C^{ipso} of $SbPh_2$), 134.77 (CH of $SbPh_2$) ppm. ESI+ MS: *m/z* 1669 ([M – SbF_6]$^+$); ESI– MS: *m/z* 235 ([SbF_6]$^-$). Anal. Calc. for $C_{68}H_{56}AuF_6Fe_2Sb_5$ (1904.6): C 42.88, H 2.96%. Found: C 42.67, H 2.84%.

Catalytic experiments. A Schlenk test tube was charged with arylboronic acid (0.50 mmol), 4-bromotoluene (85.5 mg, 0.50 mmol), potassium carbonate (138.2 mg, 2.0 mmol) and the respective palladium complex (0.005 mmol, 1 mol.%). The reaction flask was deoxygenated using three vacuum-nitrogen cycles and stoppered with a rubber septum. Benzene-d_6 (1.5 ml) and degassed water (1.5 ml) were introduced, the septum was replaced with a glass stopper and the reaction flask was transferred into a preheated oil bath (50 °C) and stirred for 1 h. Then, the reaction vessel was cooled in cold water, and anisole (54.3 μL, 0.50 mmol; internal standard) was added. The organic layer was removed with a Pasteur pipette, dried over $MgSO_4$ and filtered through a PTFE syringe filter (0.45 μm porosity). The product yield was determined using ^{1}H NMR spectroscopy.

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Full-sphere diffraction data (±*h*±*k*±*l*) were collected with a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTON detector and a Cryostream Cooler (Oxford Cryosystems) using Mo Kα radiation (λ = 0.71073 Å). The structures were solved using direct methods (SHELXT-2014 or 2018[10]) and refined by a full-matrix least-squares routine based on F^2 (SHELXL-2017[11]). All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their theoretical positions and refined as riding atoms using the standard routines implemented in SHELXL.

The solvent molecules in the structures of **4b**·CH_2Cl_2, **6**·$CHCl_3$ and **11**·$2CH_2Cl_2$ were partly disordered and were refined with one or more atoms split into two positions. In the case of **8**·$4CH_2Cl_2$ (only one of the two crystallographically independent dichloromethane molecules) and **12**·½CH_2Cl_2·½Et_2O, the solvent molecules were disordered to such an extent that they could not be unambiguously included in the structure model. Therefore, their contribution to the overall scattering was numerically removed using PLATON SQUEEZE.[12] In the latter compound, the methyl groups at the cymene isopropyl substituent also had to be refined over two positions. The counterions (PF_6^- and SbF_6^-) in the structure of **9**, **13**, and **20b** were partly disordered and were refined with some fluorine atoms over two positions (typically, they were disordered in a "spinning top" fashion and, consequently, refined with four F "equatorial" atoms in two positions). Lastly, one of the $[AuCl_2]^-$ anions (50% occupancy) and the solvent molecule in the structure of **20a**·½$C_2H_4Cl_2$ resided over crystallographic inversion centres. The other $[AuCl_2]^-$ anion (50% occupancy) was disordered over two positions mutually related by crystallographic inversion.

Crystallographic data and structure refinement parameters are outlined in Table S1. The geometric data and structural diagrams were obtained using a recent version of the PLATON program.[13] All numerical values were rounded to one decimal place with respect to the respective estimated standard deviations (ESDs).

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

Compound	**1**	**2**	**3**
Formula	$C_{34}H_{28}FeSb_2$	$C_{34}H_{28}Cl_4FeSb_2$	$C_{34}H_{28}Cl_2FeOSb_2$
M	735.91	877.71	822.81
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
T [K]	150(2)	120(2)	120(2)
a [Å]	14.1459(4)	9.2571(5)	8.8290(3)
b [Å]	13.0300(5)	15.2508(9)	29.3646(12)
c [Å]	15.2921(5)	23.3178(13)	12.1854(5)
α [°]	90	99.319(2)	90
β [°]	90.576(1)	101.128(2)	105.7320(10)
γ [°]	90	91.338(2)	90
V [Å]^3	2818.6(2)	3182.4(3)	3040.8(2)
Z	4	4	4
μ(Mo Kα) [mm^{-1}]	2.432	2.495	2.437
Diffrns collected	32862	65654	36589
Independent diffrns	6495	14547	6967
Observed[a] diffrns	5514	13700	6710
R_{int}[b] [%]	2.65	2.04	2.43
No. of parameters	334	739	361
R[b] obsd diffrns [%]	2.70	1.83	3.49
R, *wR*[b] all data [%]	3.44, 6.84	2.03, 4.35	3.63, 8.34
Δρ [e Å^{-3}]	1.72, –0.42	0.925, –0.688	0.764, –0.745
CCDC no.	2219074	2219055	2219053

[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	**4a**·$CHCl_3$	**4b**·CH_2Cl_2	**5**
Formula	$C_{34}H_{28}FeN_2O_7Sb_2 \cdot CHCl_3$	$C_{34}H_{28}Cl_2FeO_9Sb_2 \cdot CH_2Cl_2$	$C_{34}H_{28}F_2FeSb_2$
M	995.30	1035.74	773.91
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*–1 (no. 2)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)	120(2)
a [Å]	9.7288(4)	19.6555(6)	17.0025(8)
b [Å]	12.4015(6)	10.0924(3)	9.1706(5)
c [Å]	15.6280(8)	19.8006(5)	19.5817(10)
α [°]	76.729(2)	90	90
β [°]	89.536(2)	111.8640(10)	105.473(2)
γ [°]	80.201(2)	90	90
V [Å]^3	1807.48(15)	3645.34(18)	2942.6(3)
Z	2	4	4
μ(Mo Kα) [mm^{-1}]	2.152	2.212	2.344
Diffrns collected	31997	53290	176557
Independent diffrns	8245	8366	8589
Observed[a] diffrns	7863	7666	8124
R_{int}[b] [%]	2.23	3.02	2.77
No. of parameters	451	464	352
R[b] obsd diffrns [%]	2.18	2.08	1.83
R, wR[b] all data [%]	2.30, 5.76	2.43, 4.68	1.99, 4.67
Δρ [e Å^{-3}]	1.081, –0.934	0.834, –1.242	1.804, –0.495
CCDC no.	2219058	2219059	2219057

Table S1 continued

Compound	**6**·$CHCl_3$	**7**	**8**·$4CH_2Cl_2$
Formula	$C_{34}H_{28}F_4FeSb_2$·$CHCl_3$	$C_{34}H_{28}F_2FeOSb_2$	$C_{68}H_{56}Ag_2Cl_2Fe_2O_8Sb_4$·$4CH_2Cl_2$
M	931.28	789.91	2226.17
Crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)	*P*–1 (no. 2)
T [K]	120(2)	120(2)	120(2)
a [Å]	24.4241(11)	12.0562(3)	12.2579(5)
b [Å]	8.5633(3)	28.0108(8)	12.7402(5)
c [Å]	16.9344(7)	18.0496(5)	13.6247(6)
α [°]	90	90	87.6850(10)
β [°]	105.9820(10)	106.0870(10)	69.5700(10)
γ [°]	90	90	73.4420(10)
V [Å]^3	3404.9(2)	5856.7(3)	1907.08(14)
Z	4	8	1
μ(Mo Kα) [mm^{-1}]	2.278	2.360	2.668
Diffrns collected	36442	123245	38508
Independent diffrns	3898	17099	8722
Observed[a] diffrns	3771	15994	8458
R_{int}[b] [%]	2.42	2.56	2.03
No. of parameters	223	721	415
R[b] obsd diffrns [%]	2.16	1.95	1.63
R, *wR*[b] all data [%]	2.23, 5.89	2.18, 4.33	1.70, 3.94
Δρ [e Å^{-3}]	1.040, –0.807	1.032, –1.135	0.974, –0.763
CCDC no.	2219054	2219056	2219073

Table S1 continued

Compound	**9b**	**10**·CH_2Cl_2	**11**·$2CH_2Cl_2$
Formula	$C_{68}H_{56}AgFe_2Sb_4SbF_6$	$C_{54}H_{56}Cl_4FeRu_2Sb_2{\cdot}CH_2Cl_2$	$C_{54}H_{58}Cl_4FeRh_2Sb_2{\cdot}2CH_2Cl_2$
M	1815.44	1433.20	1523.82
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	*P*–1 (no. 2)	*P*–1 (no.)
T [K]	120(2)	120(2)	120(2)
a [Å]	19.4717(8)	9.2480(5)	12.6197(5)
b [Å]	14.6121(5)	12.3490(7)	15.2205(6)
c [Å]	23.3149(9)	12.7685(7)	17.2276(7)
α [°]	90	104.707(2)	95.650(2)
β [°]	109.2700(10)	92.922(2)	107.2080(10)
γ [°]	90	108.949(2)	109.8750(10)
V [Å]^3	6262.0(4)	1319.73(13)	2898.8(2)
Z	4	1	2
μ(Mo Kα) [mm^{-1}]	2.936	2.178	2.126
Diffrns collected	489694	25843	58547
Independent diffrns	14391	6008	13359
Observed[a] diffrns	13699	5772	11620
R_{int}[b] [%]	3.13	1.77	2.94
No. of parameters	756	312	636
R[b] obsd diffrns [%]	2.03	1.60	2.96
R, *wR*[b] all data [%]	2.20, 5.33	1.70, 3.87	3.83, 6.63
Δρ [e Å^{-3}]	1.749, –0.787	0.492, –0.521	1.150, –1.613
CCDC no.	2219068	2219060	2219071

Table S1 continued

Compound	**12**·½CH_2Cl_2·½Et_2O	**13**	**14**
Formula	$C_{44}H_{42}ClFeRuSb_2PF_6$ ·½CH_2Cl_2·½$C_4H_{10}O$	$C_{44}H_{43}ClFeRhSb_2PF_6$	$C_{44}H_{43}ClFeRuSb_2$
M	1231.14	1154.46	1007.65
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)	150(2)
a [Å]	11.7079(6)	15.2124(7)	11.6926(6)
b [Å]	29.3735(15)	16.7760(7)	30.723(2)
c [Å]	13.4240(6)	16.1922(7)	11.8129(6)
α [°]	90	90	90
β [°]	100.153(2)	92.786(2)	118.336(2)
γ [°]	90	90	90
V [Å]^3	4544.2(4)	4127.4(3)	3735.0(3)
Z	4	4	4
μ(Mo Kα) [mm^{-1}]	2.027	92.786(2)	2.311
Diffrns collected	106826	71747	116841
Independent diffrns	10468	9502	8630
Observed[a] diffrns	9548	8854	7965
R_{int}[b] [%]	2.62	2.04	3.00
No. of parameters	530	547	447
R[b] obsd diffrns [%]	2.18	2.55	1.98
R, *wR*[b] all data [%]	2.61, 5.01	2.82, 6.30	2.36, 4.10
Δρ [e Å^{-3}]	0.682, –0.706	1.222, –0.854	4.66, –5.85
CCDC no.	2219064	2219063	2219069

Table S1 continued

Compound	**15**·$CHCl_3$	**16**·$CHCl_3$	**17b**·Me_2CO
Formula	$C_{35}H_{29}Cl_5FePdSb_2$	$C_{35}H_{29}Cl_5FePtSb_2$	$C_{68}H_{56}Fe_2PdSb_4Sb_2F_{12}·C_3H_6O$
M	1032.58	1121.27	2107.80
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)
T [K]	150(2)	150(2)	120(2)
a [Å]	12.5589(5)	12.5657(4)	21.2838(7)
b [Å]	16.8733(7)	16.8584(5)	13.1838(5)
c [Å]	17.0801(7)	17.1074(5)	24.6950(9)
α [°]	90	90	90
β [°]	94.915(2)	94.940(1)	101.9740(10)
γ [°]	90	90	90
V [Å]^3	3606.1(3)	3610.5(2)	6778.7(4)
Z	4	4	4
μ(Mo Kα) [mm^{-1}]	2.762	6.131	3.102
Diffrns collected	62345	29789	34669
Independent diffrns	8295	8321	7777
Observed[a] diffrns	7550	7560	7433
R_{int}[b] [%]	2.12	2.05	2.54
No. of parameters	397	397	423
R[b] obsd diffrns [%]	2.11	2.03	2.06
R, wR[b] all data [%]	2.42, 4.84	2.40, 4.50	2.19, 4.82
Δρ [e Å^{-3}]	1.01, –0.87	1.12, –0.97	1.237, –1.565
CCDC no.	2219067	2219065	2219062

Table S1 continued

Compound	**18**	**19**·2$CHCl_3$
Formula	$C_{38}H_{30}FeO_3PdSb_2$	$C_{36}H_{30}Au_2Cl_8FeSb_2$
M	940.37	1439.48
Crystal system	triclinic	monoclinic
Space group	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)
a [Å]	10.2112(5)	12.720(1)
b [Å]	12.0289(6)	12.1154(9)
c [Å]	14.7499(7)	26.462(2)
α [°]	92.786(2)	90
β [°]	100.603(1)	98.133(3)
γ [°]	113.284(1)	90
V [Å]^3	1620.9(1)	4037.0(5)
Z	2	4
μ(Mo Kα) [mm^{-1}]	2.670	9.471
Diffrns collected	41150	83700
Independent diffrns	7391	9265
Observed[a] diffrns	7248	9077
R_{int}[b] [%]	1.77	2.50
No. of parameters	406	442
R[b] obsd diffrns [%]	1.32	1.50
R, *wR*[b] all data [%]	1.36, 3.20	1.55, 3.51
Δρ [e $Å^{-3}$]	3.87, –4.46	1.14, –0.88
CCDC no.	2219061	2219072

Table S1 continued

Compound	**20a**·½$C_2H_4Cl_2$	**20b**
Formula	$C_{69}H_{58}Au_2Cl_3Fe_2Sb_4$	$C_{68}H_{56}AuF_6Fe_2Sb_5$
M	1986.13	1904.54
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)
a [Å]	13.1245(3)	19.399(2)
b [Å]	21.5627(5)	14.486(1)
c [Å]	22.3494(5)	23.340(2)
α [°]	90	90
β [°]	92.235(1)	108.845(3)
γ [°]	90	90
V [Å]^3	6320.1(2)	6203.5(9)
Z	4	4
μ(Mo Kα) [mm^{-1}]	6.919	5.010
Diffrns collected	115573	102710
Independent diffrns	14434	14188
Observed[a] diffrns	13742	13984
R_{int}[b] [%]	3.03	2.31
No. of parameters	737	776
R[b] obsd diffrns [%]	1.90	1.29
R, *wR*[b] all data [%]	2.06, 4.60	1.32, 2.96
Δρ [e Å^{-3}]	1.42, –1.87	0.95, –0.74
CCDC no.	2219066	2219070

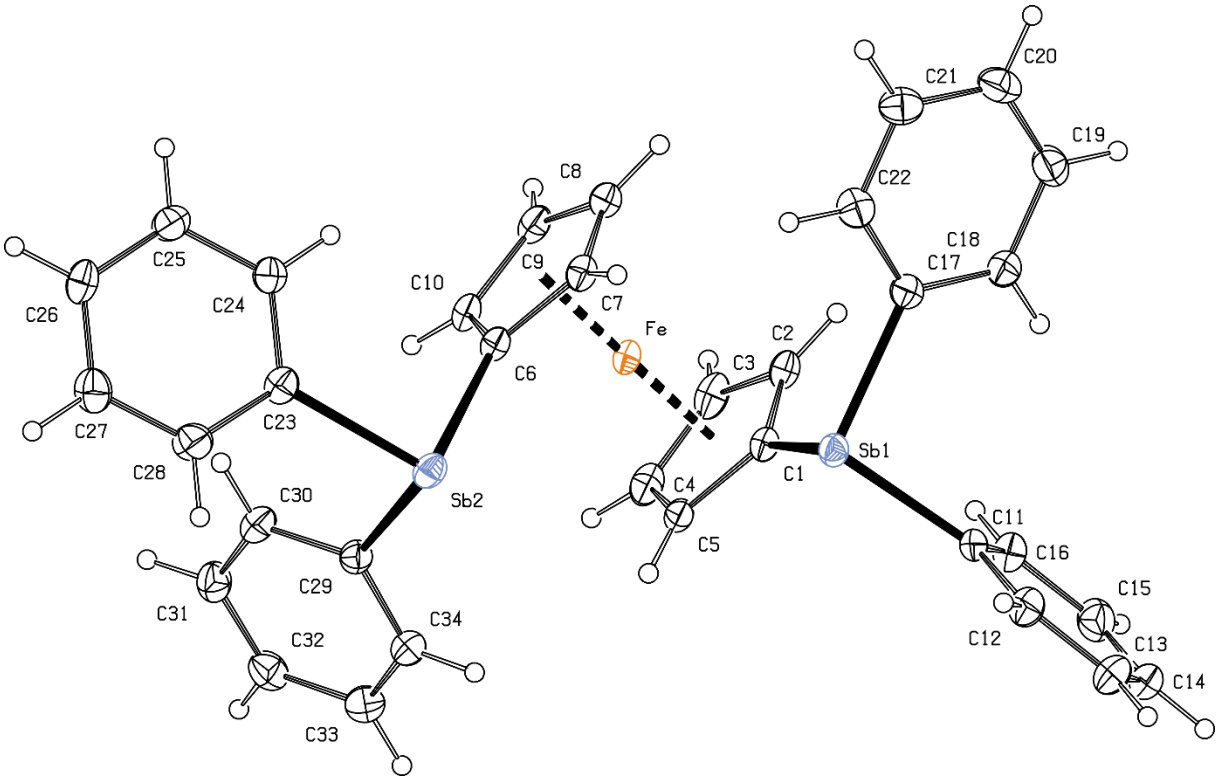

Figure S1 PLATON plot of the molecular structure of **1** showing 30% probability ellipsoids

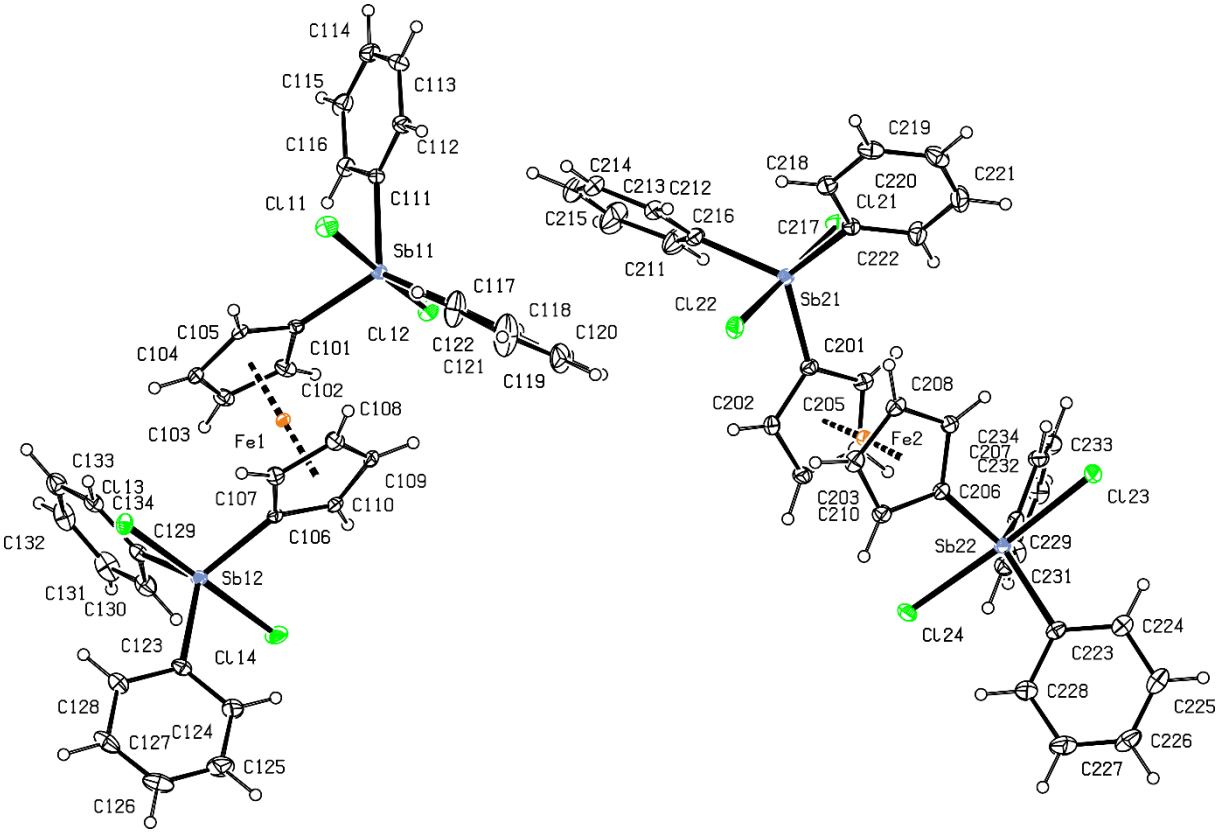

Figure S2 PLATON plot of the molecular structure of **2** showing 30% probability ellipsoids

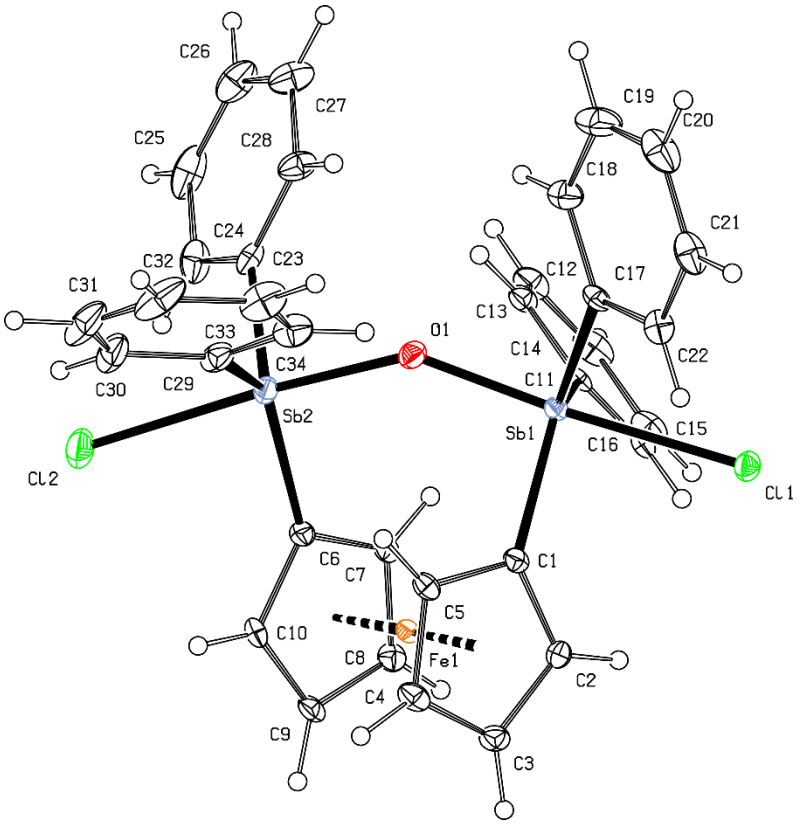

Figure S3 PLATON plot of the molecular structure of **3** showing 30% probability ellipsoids

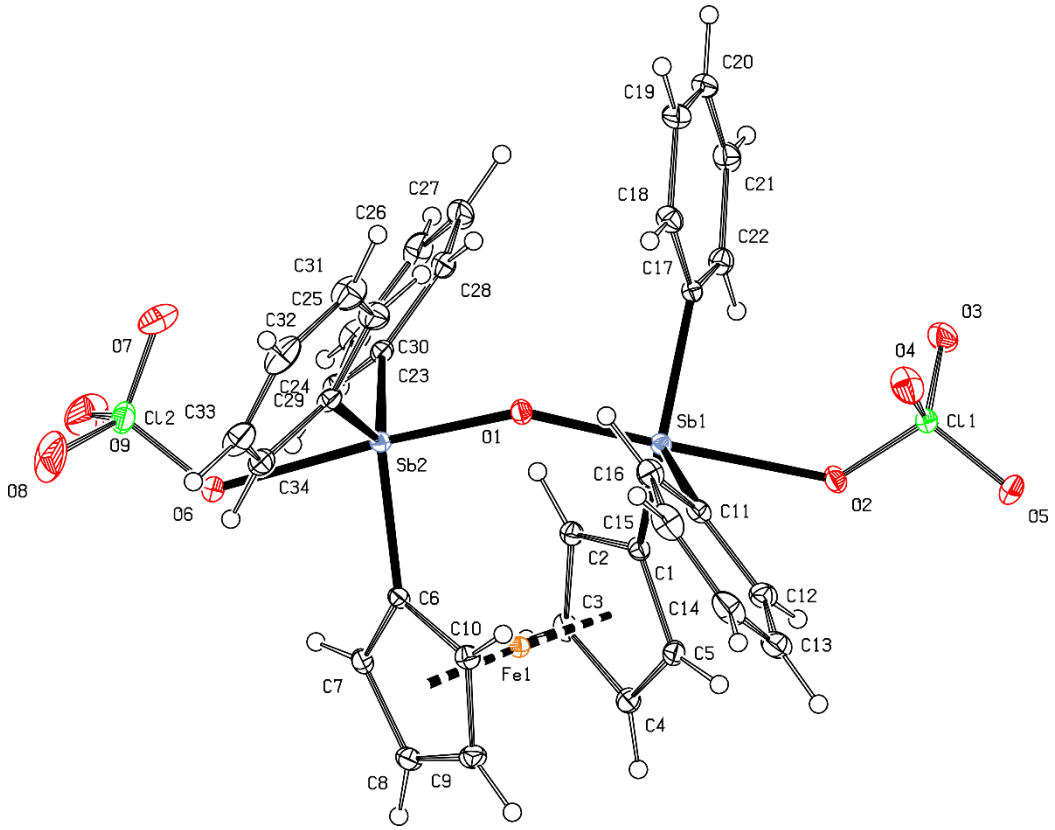

Figure S4 PLATON plot of the molecular structure of **4a**·$CHCl_3$ showing 30% probability ellipsoids (the solvent molecule was omitted for clarity)

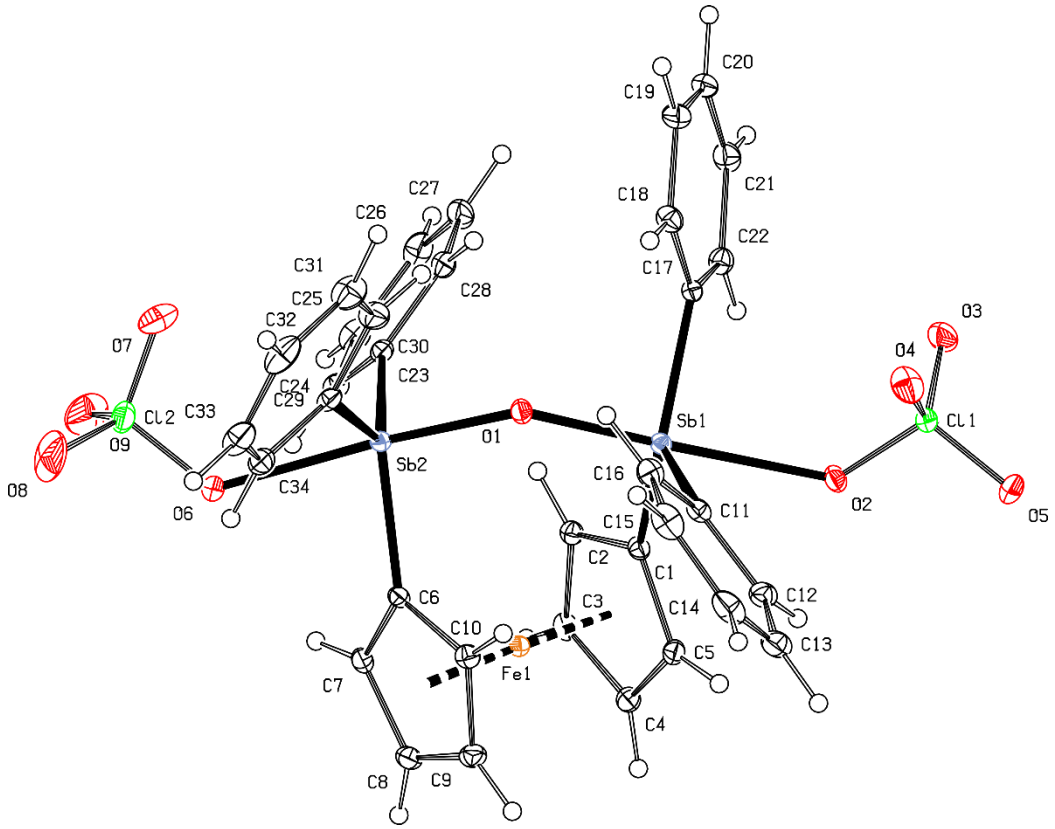

Figure S5 PLATON plot of the molecular structure of **4b**·CH_2Cl_2 showing 30% probability ellipsoids (the solvent molecule was omitted for clarity)

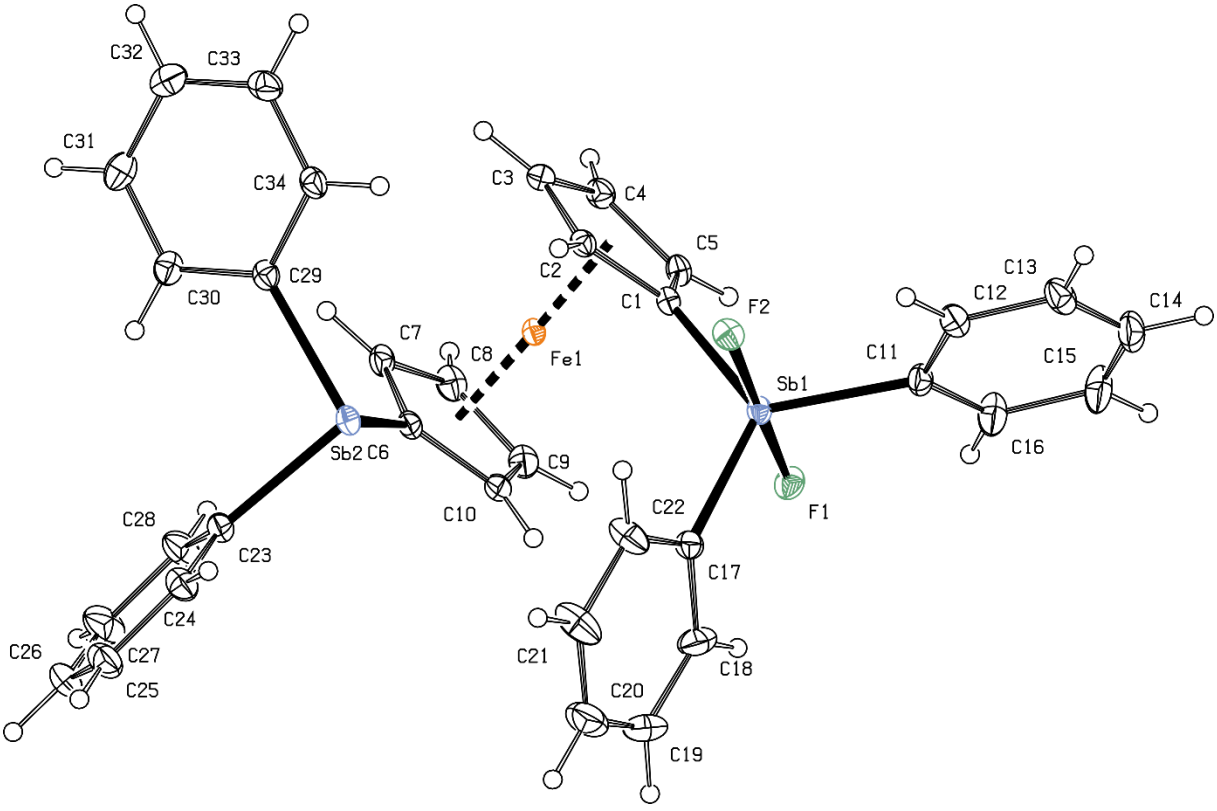

Figure S6 PLATON plot of the molecular structure of **5** showing 30% probability ellipsoids

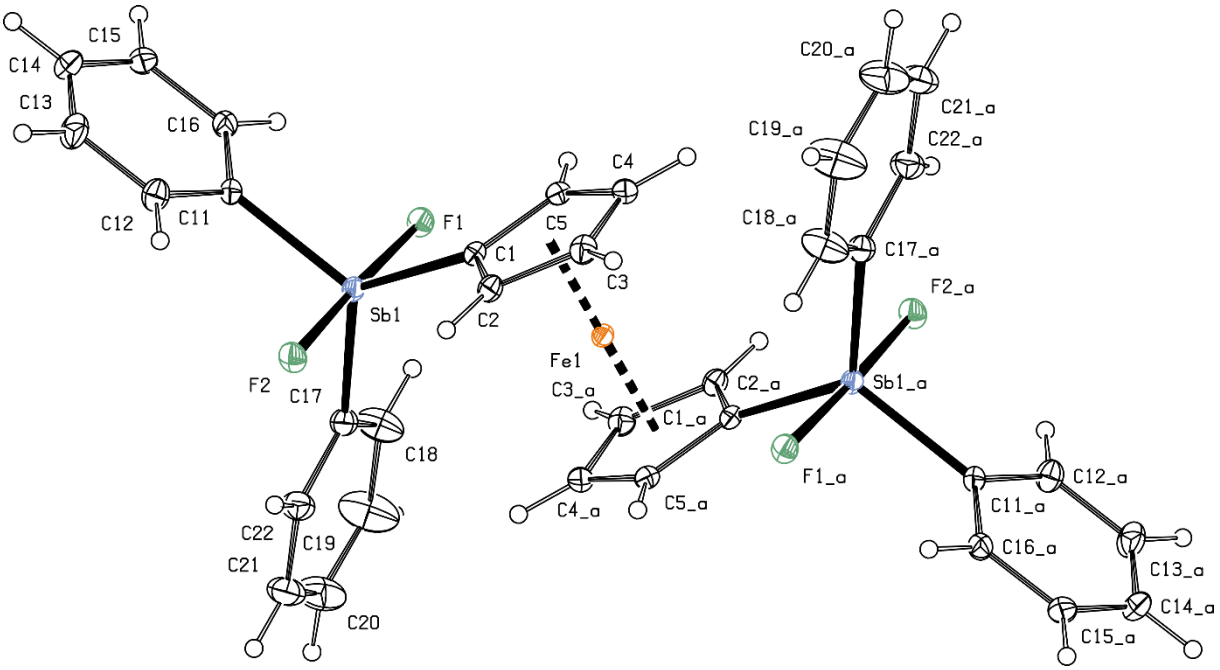

Figure S7 PLATON plot of the molecular structure of **6**·$CHCl_3$ showing 30% probability ellipsoids (the solvent molecule was omitted for clarity)

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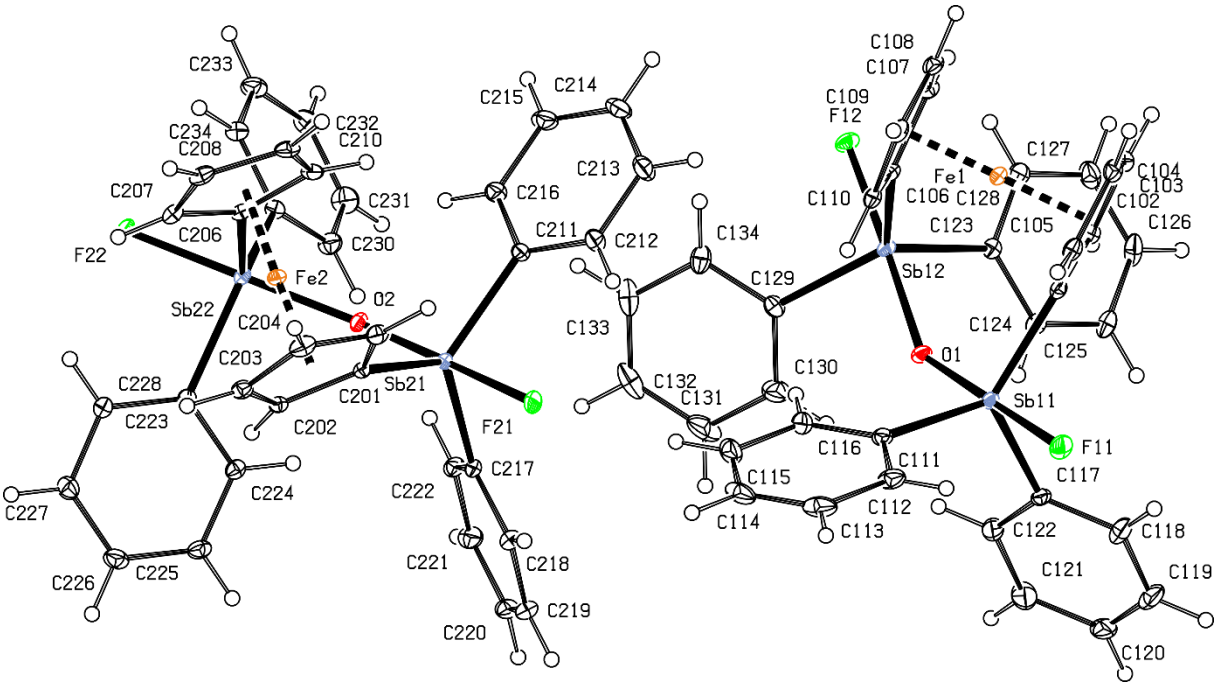

Figure S8 PLATON plot of the molecular structure of **7** showing 30% probability

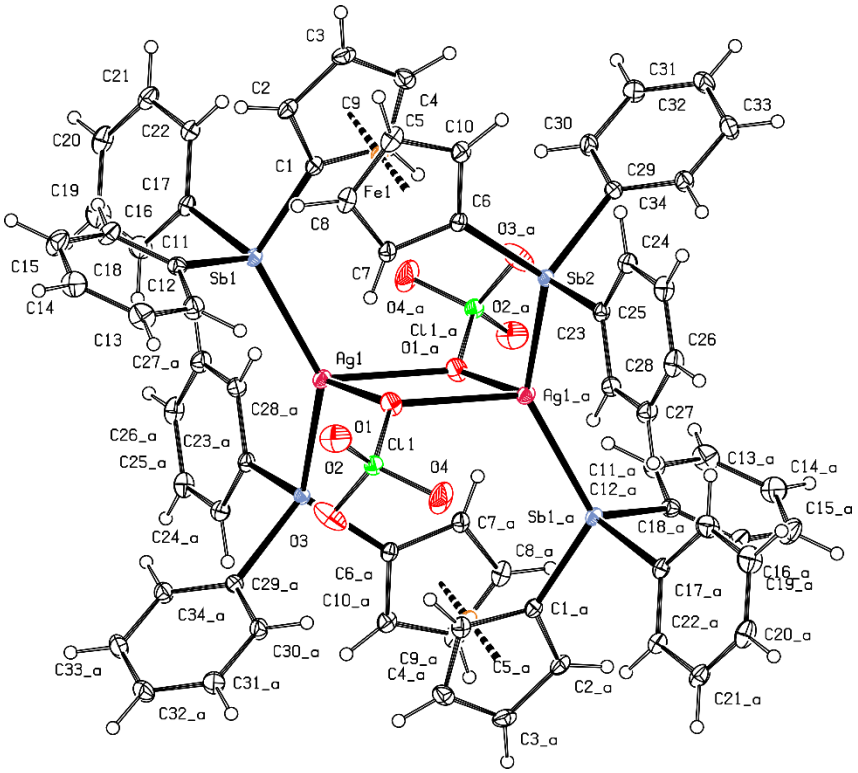

Figure S9 PLATON plot of the molecular structure of **8**·4CH_2Cl_2 showing 30% probability ellipsoids (the solvent molecules were omitted for clarity). The prime-labelled atoms are generated by the crystallographic inversion operation.

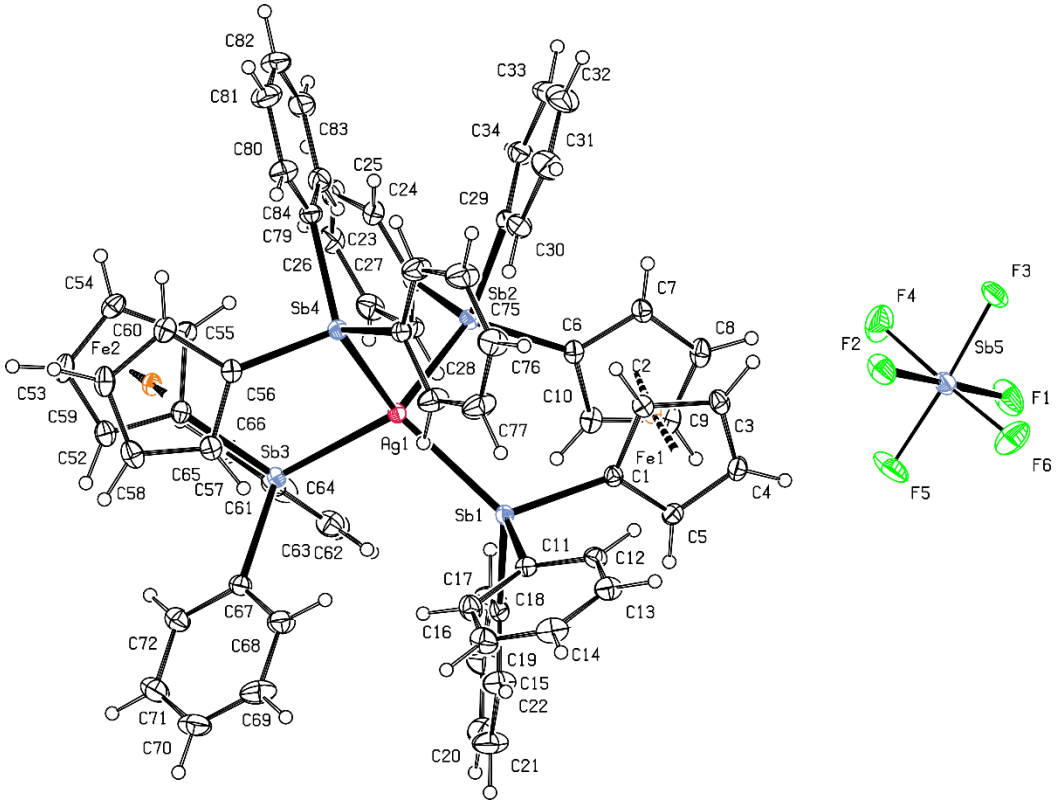

Figure S10 PLATON plot of the molecular structure of **9** showing 30% probability ellipsoids (only one position of the disordered fluorine atoms F3-F6 is shown)

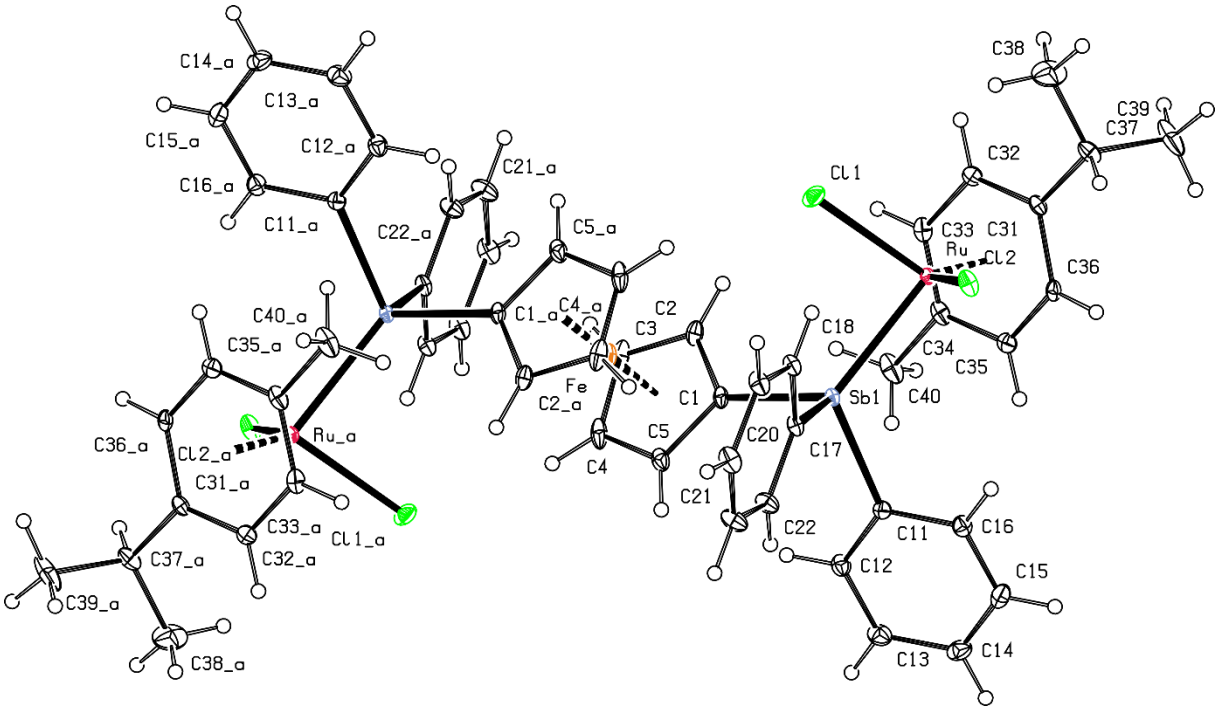

Figure S11 PLATON plot of the molecular structure of **10**·CH_2Cl_2 showing 30% probability ellipsoids (the solvent molecule was omitted). The molecule resides on an inversion centre.

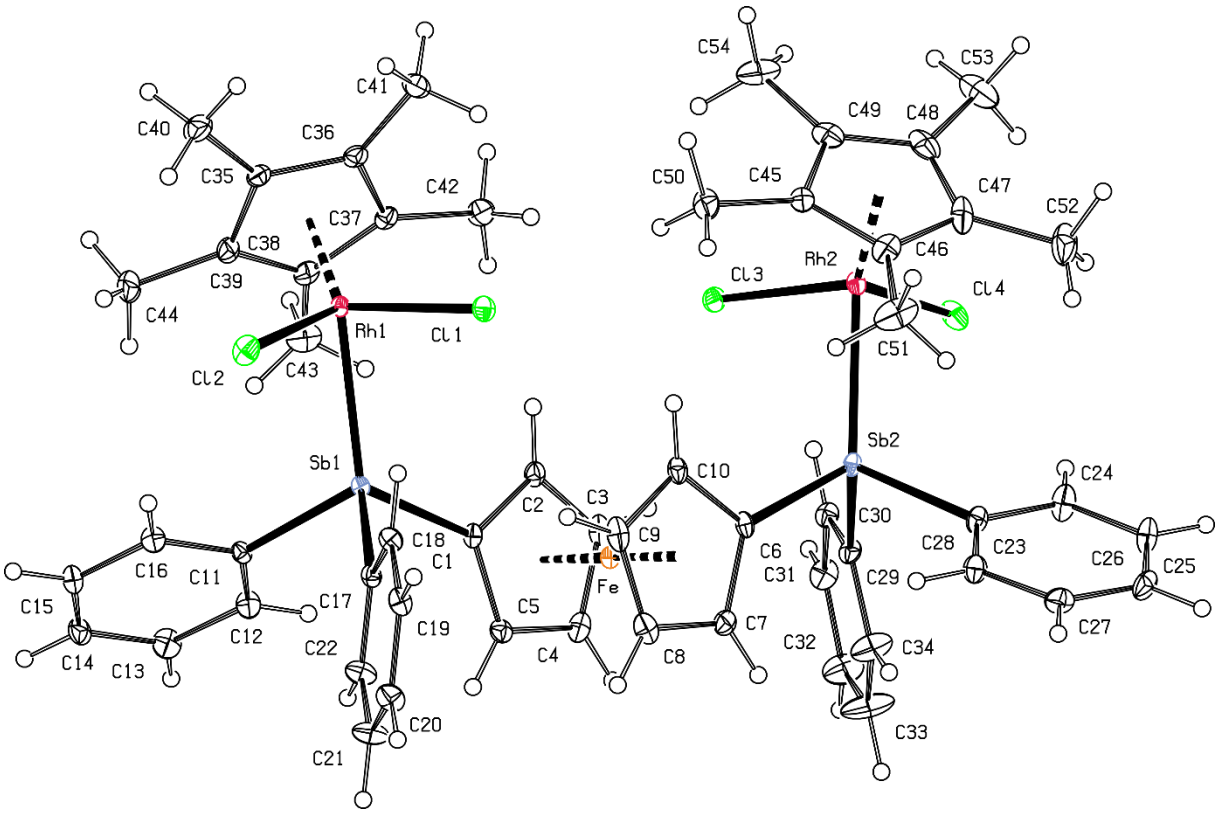

Figure S12 PLATON plot of the molecular structure of **11**·2CH_2Cl_2 showing 30% probability ellipsoids (the solvent molecules were omitted for clarity)

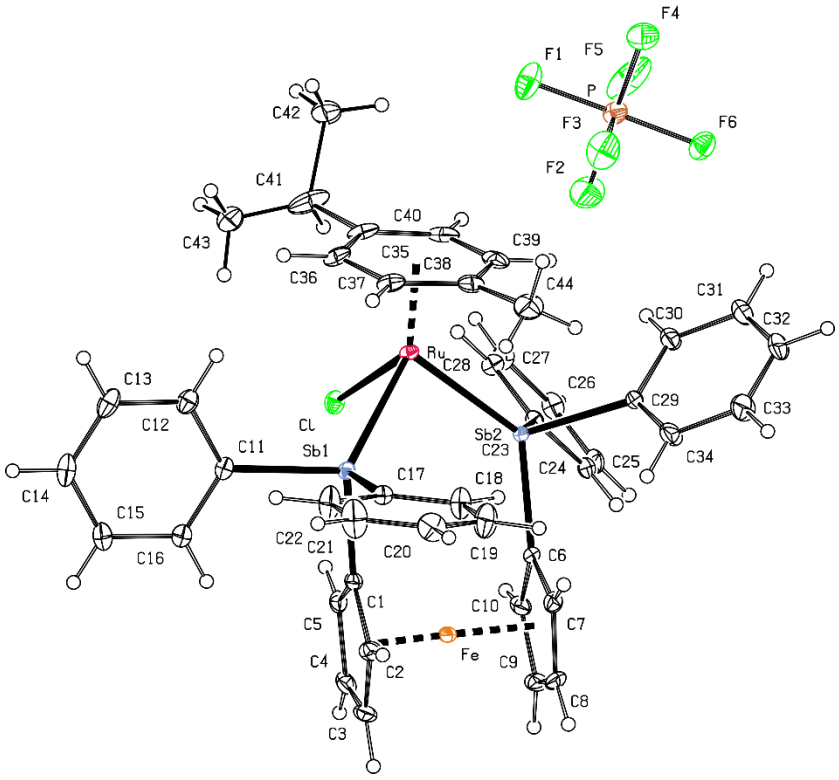

Figure S13 PLATON plot of the molecular structure of **12**·½CH_2Cl_2·½Et_2O showing 30% probability ellipsoids (the solvent molecules and the second position of the disordered isopropyl substituent are not shown; see page S-15)

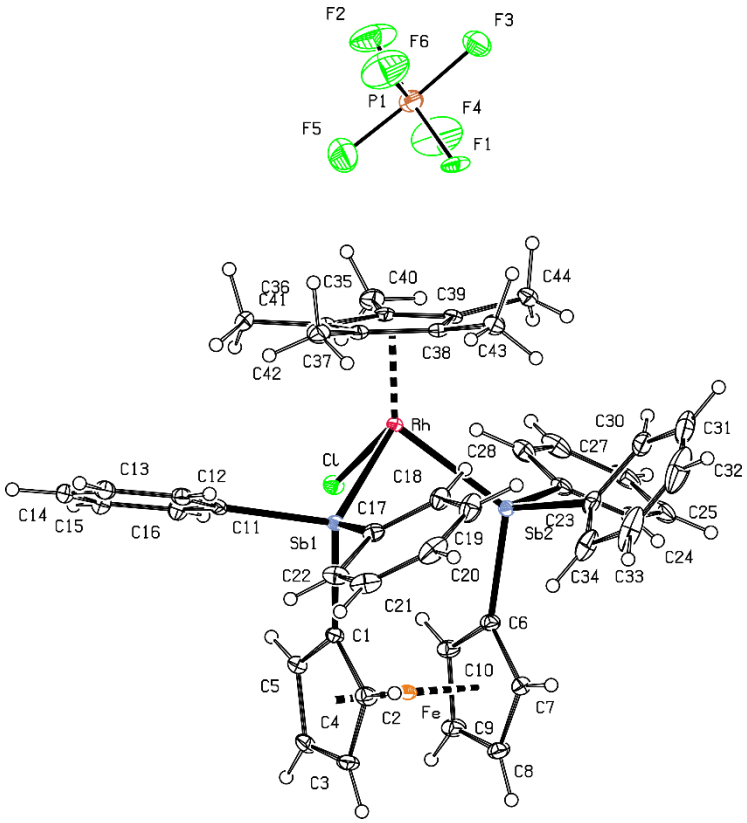

Figure S14 PLATON plot of the molecular structure of **13** showing 30% probability ellipsoids (only one position for the disordered fluorine atoms is shown for clarity)

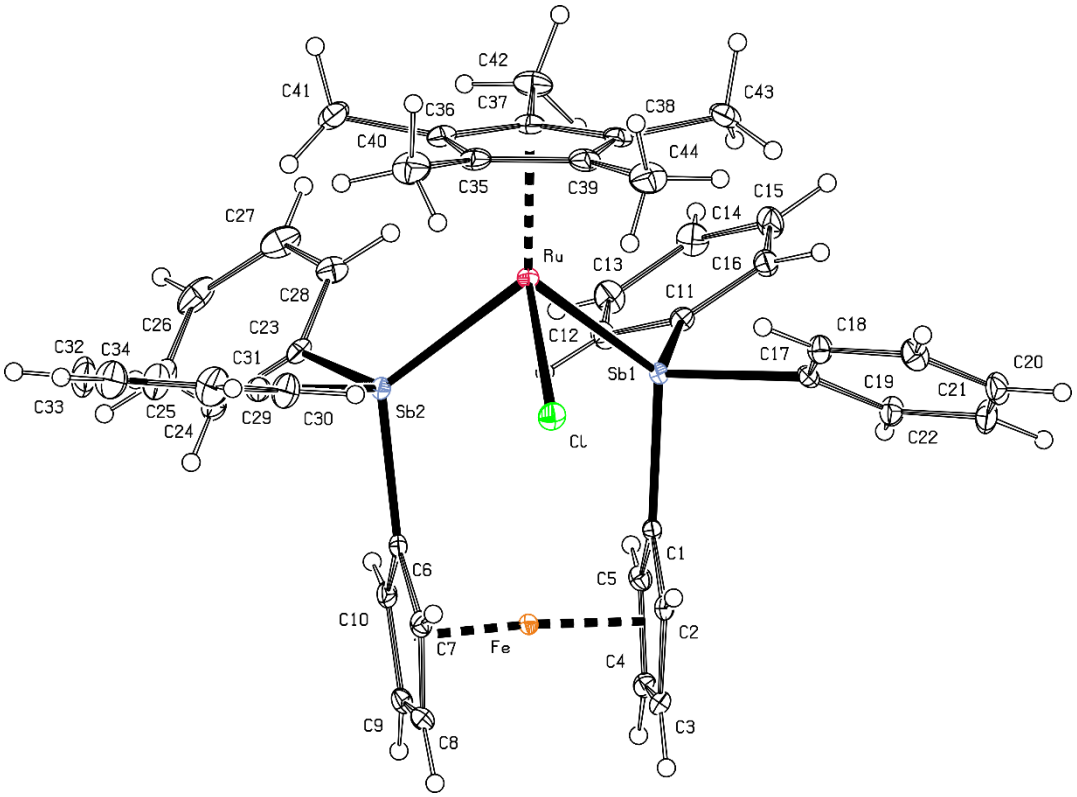

Figure S15 PLATON plot of the molecular structure of **14** showing 30% probability ellipsoids

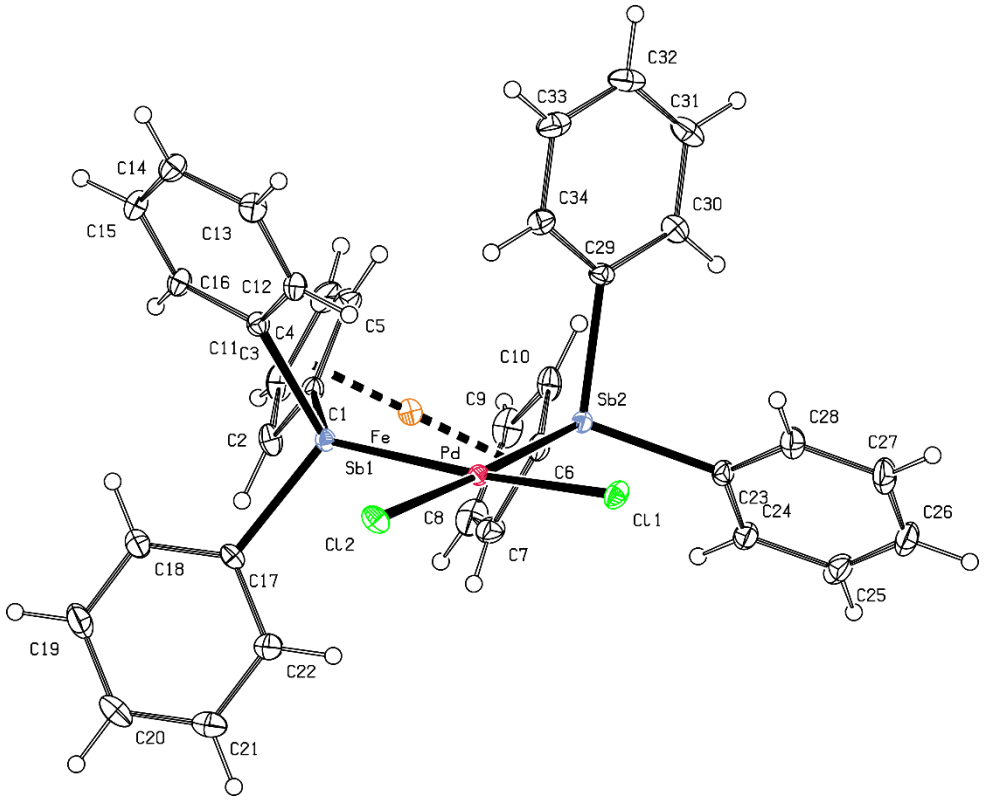

Figure S16 PLATON plot of the molecular structure of **15**·$CHCl_3$ showing 30% probability ellipsoids (the solvent molecule was omitted for clarity)

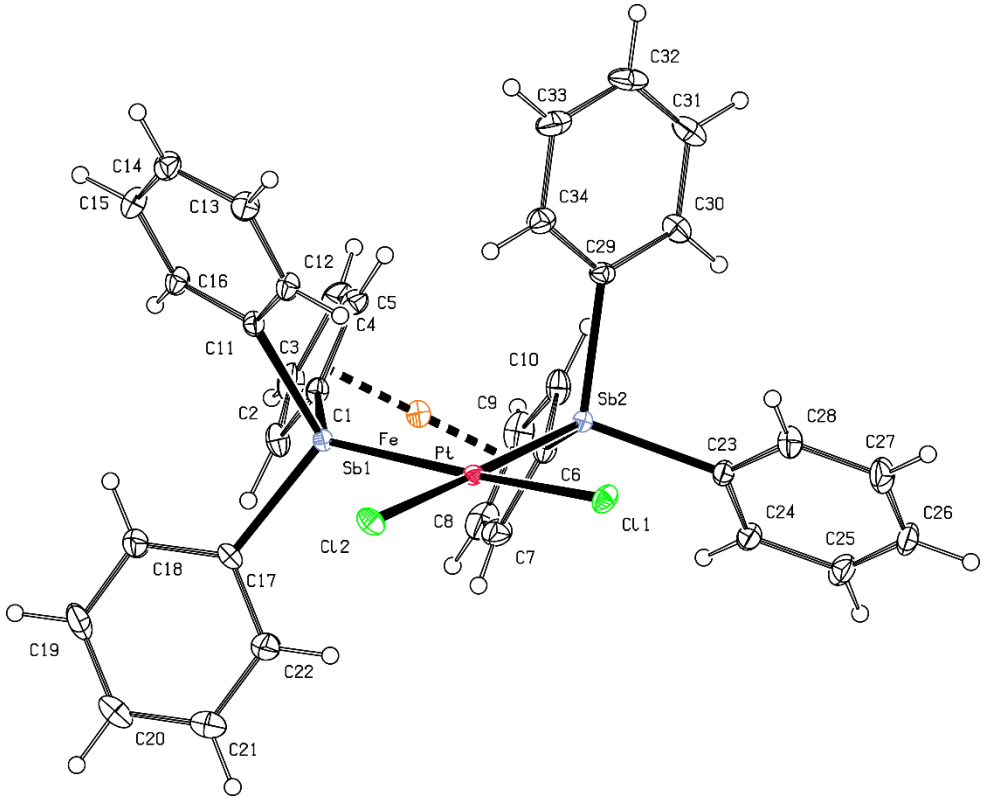

Figure S17 PLATON plot of the molecular structure of **16**·$CHCl_3$ showing 30% probability ellipsoids (the solvent molecule was omitted for clarity)

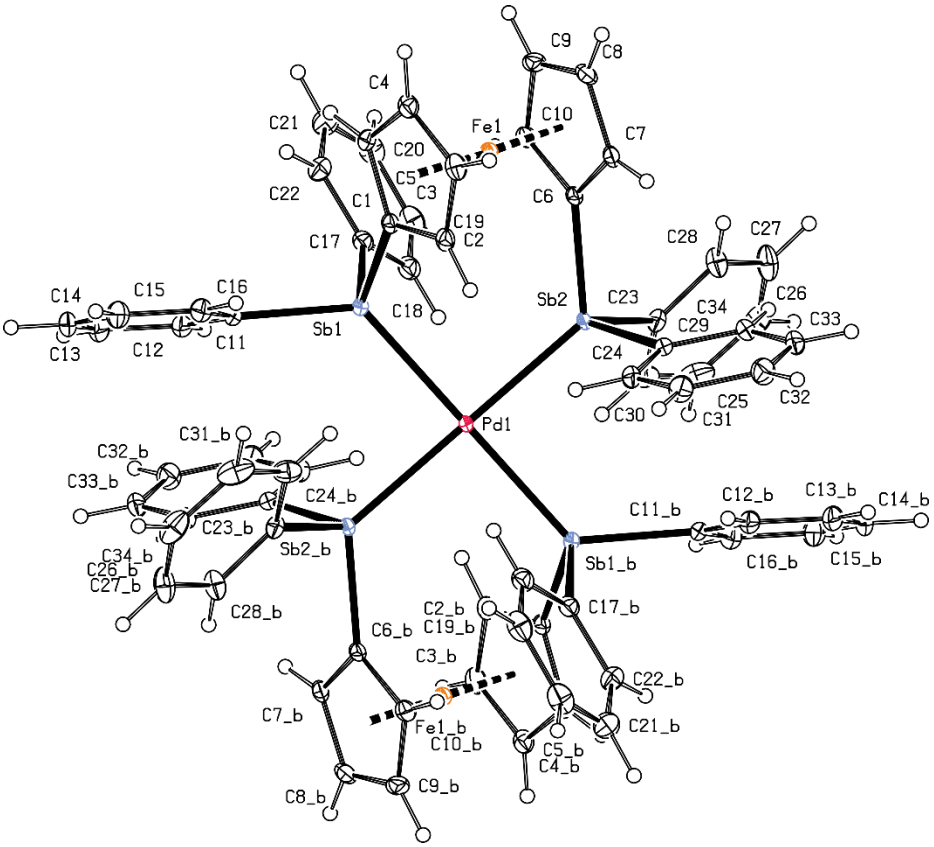

Figure S18 PLATON plot of the molecular structure of **17b**·Me_2CO showing 30% probability ellipsoids (the solvent molecule and the counter ion were omitted for clarity)

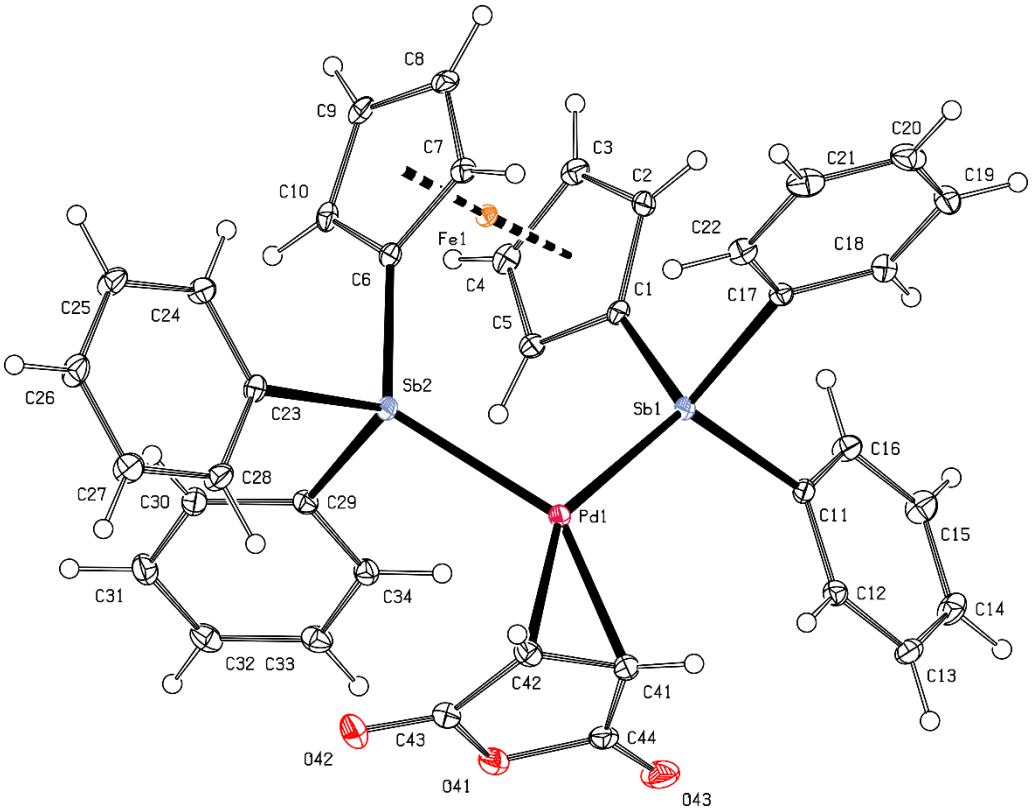

Figure S19 PLATON plot of the molecular structure of **18** showing 30% probability ellipsoids

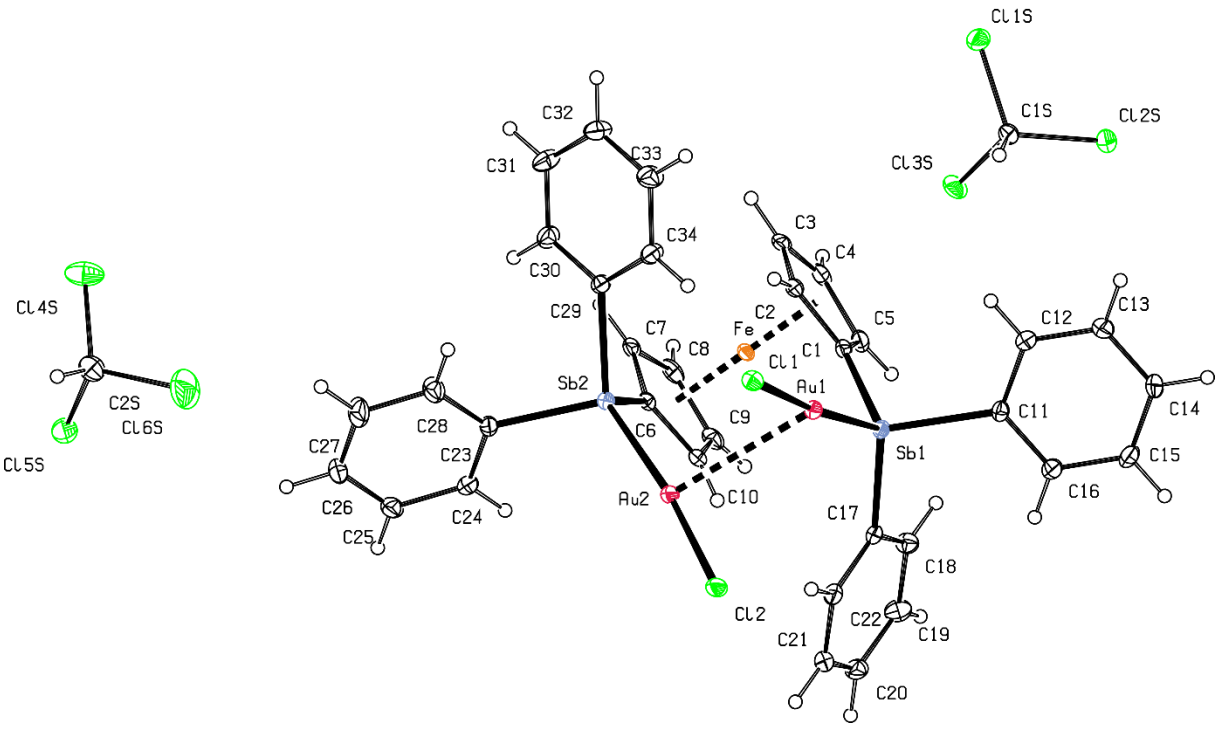

Figure S20 PLATON plot of the molecular structure of **19**·2$CHCl_3$ showing 30% probability ellipsoids. The Au1···Au2 interaction is indicated by a dotted line.

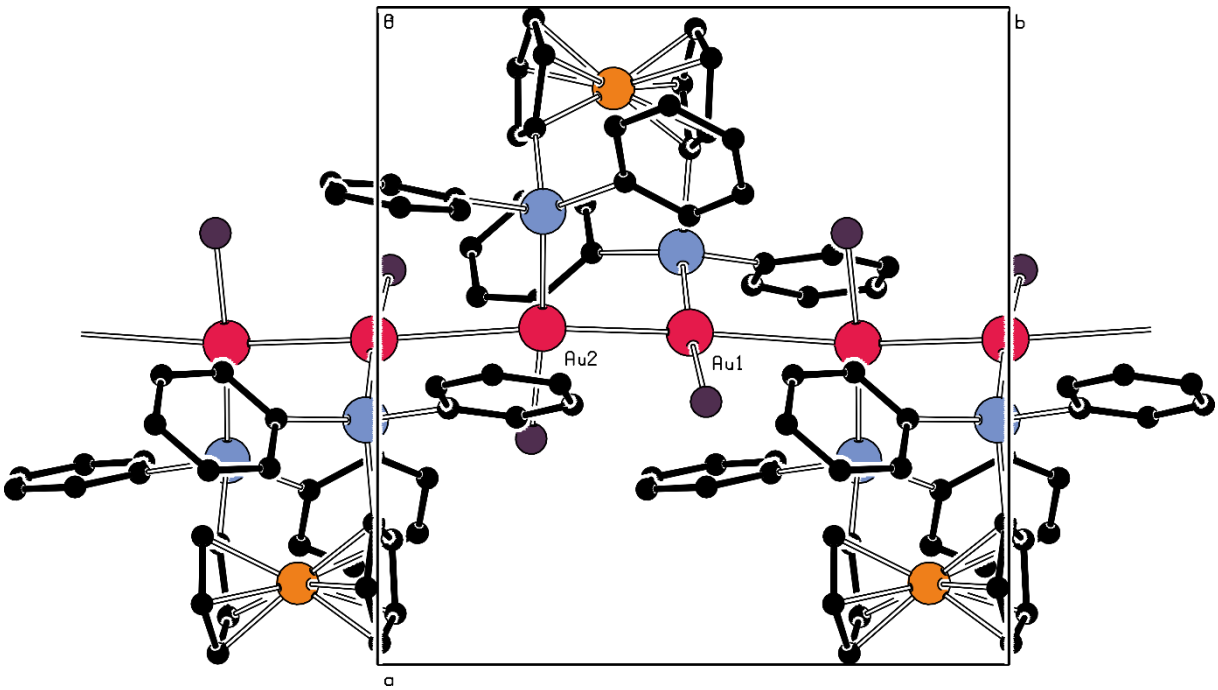

Figure S21 Simplified packing diagram showing the chains linked by aurophilic interactions in the structure of **19**·2$CHCl_3$. The hydrogen atoms and solvent molecules are omitted.

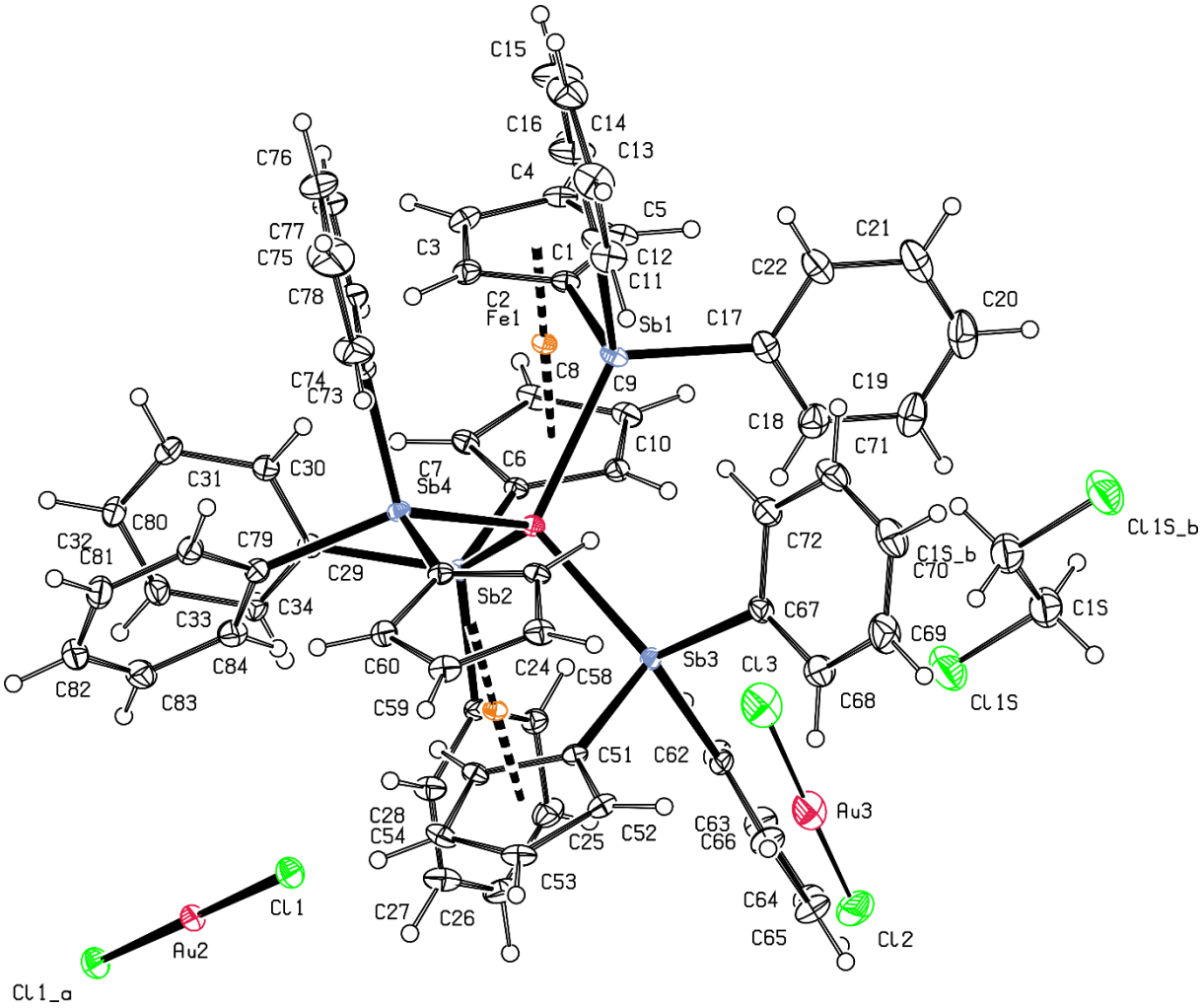

Figure S22 PLATON plot of the molecular structure of **20a**·½$C_2H_4Cl_2$ showing 30% probability ellipsoids

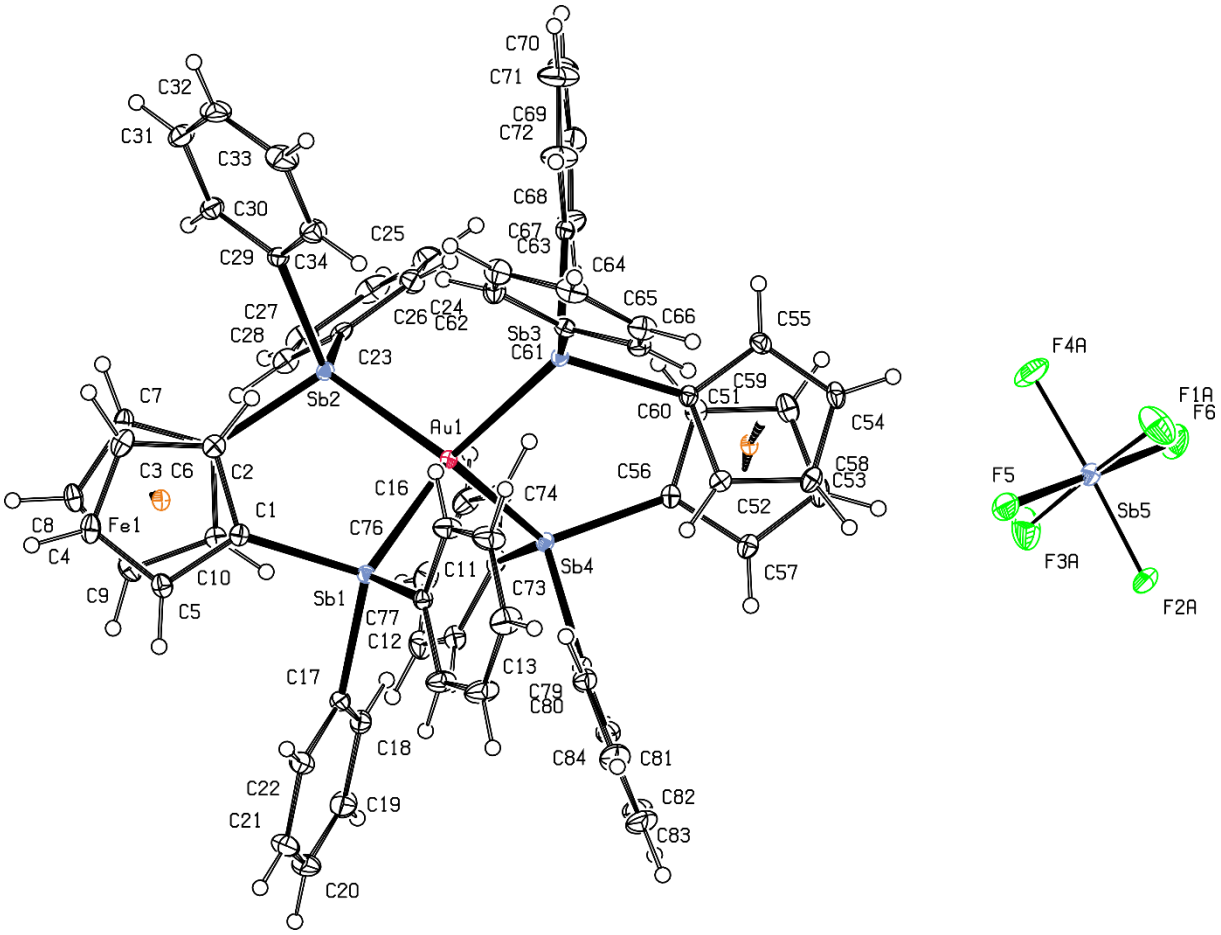

Figure S23 PLATON plot of the molecular structure of **20b** showing 30% probability ellipsoids (only position of the disordered fluorine atoms F1-4 is shown for clarity)

COPIES OF THE NMR AND MS SPECTRA

(Note: solvent signals in the NMR spectra are marked by an asterisk.)

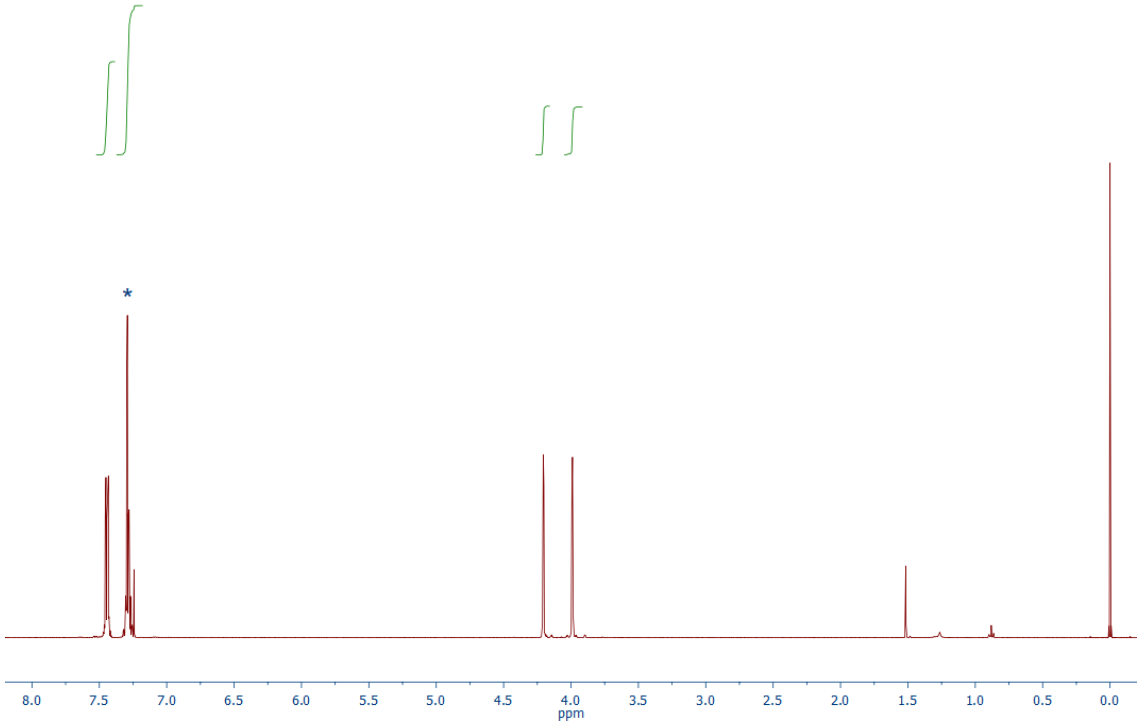

Figure S24 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**

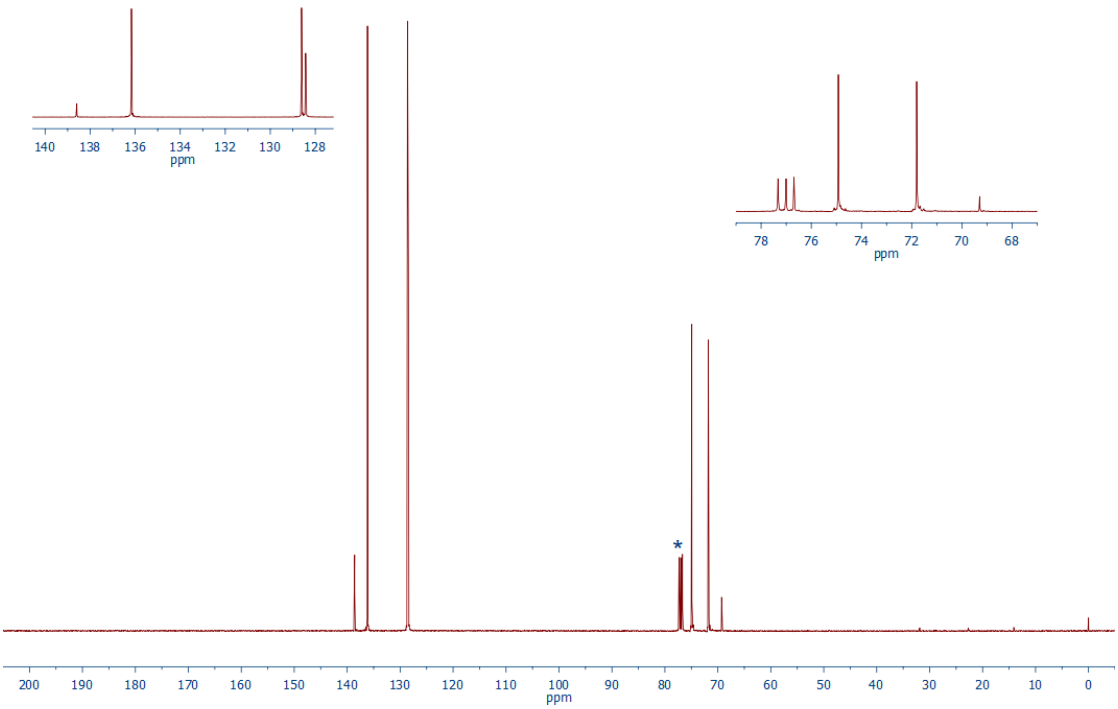

Figure S25 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **1**

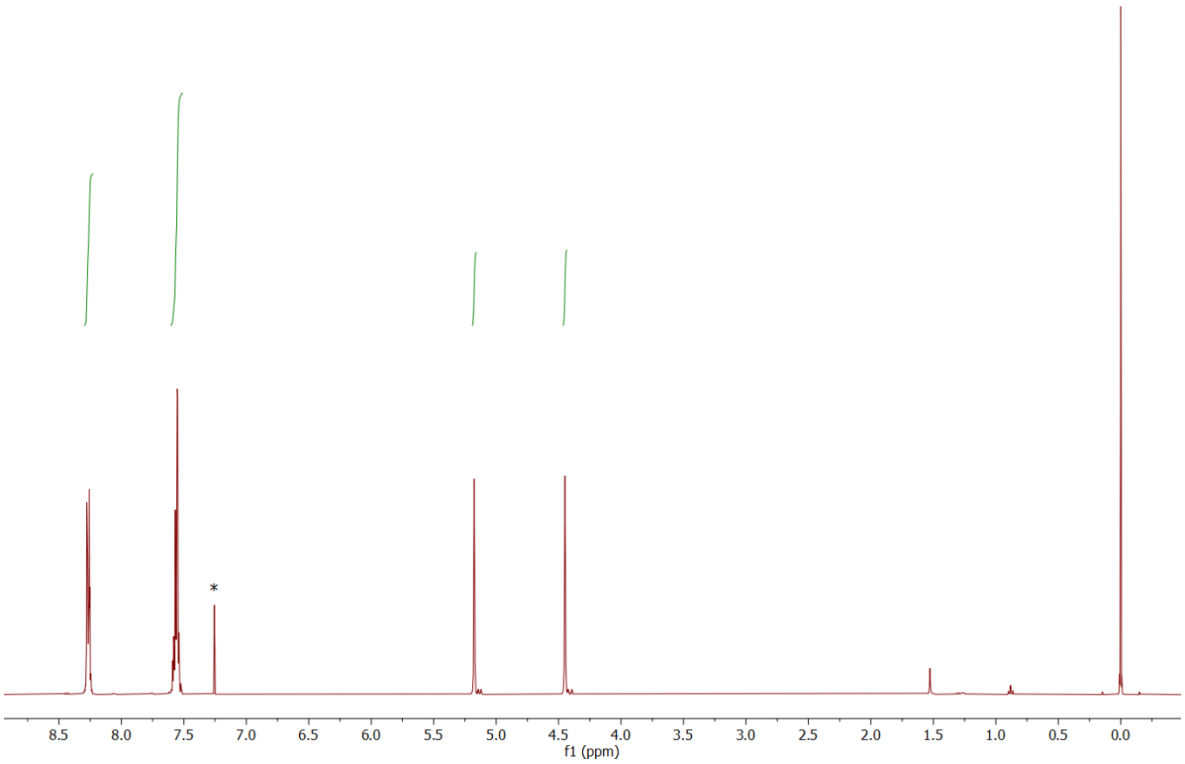

Figure S26 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**

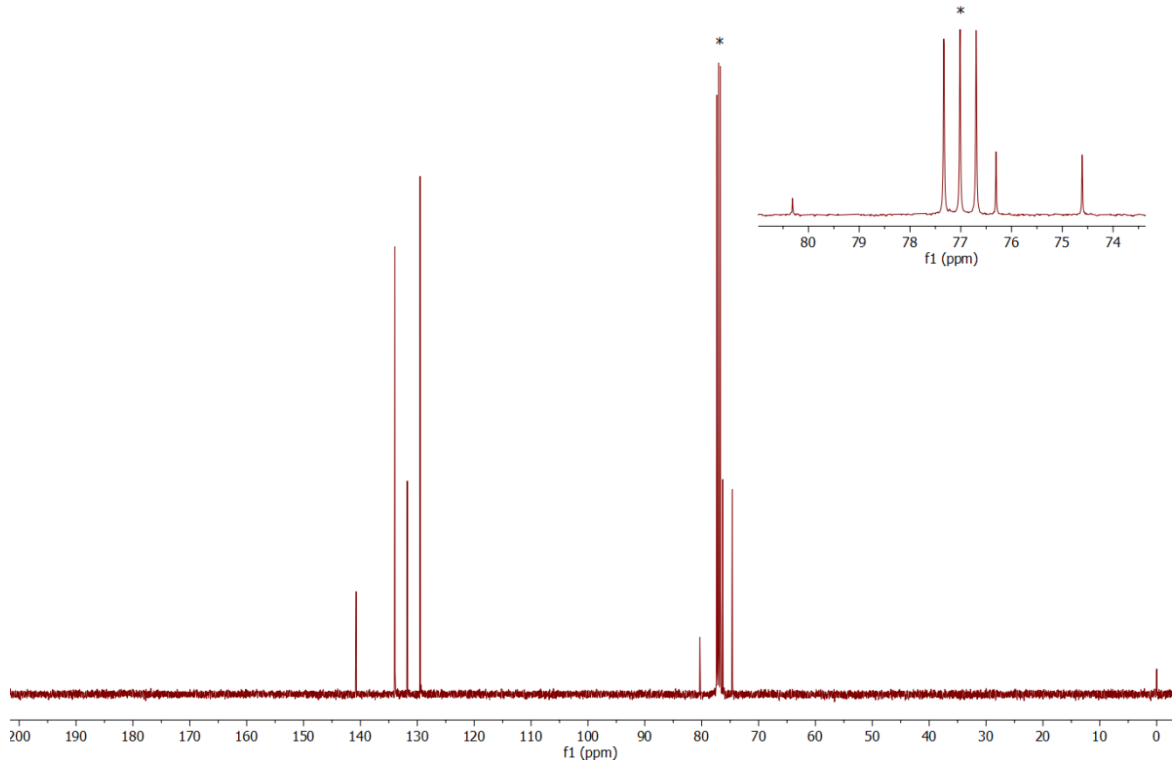

Figure S27 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2**

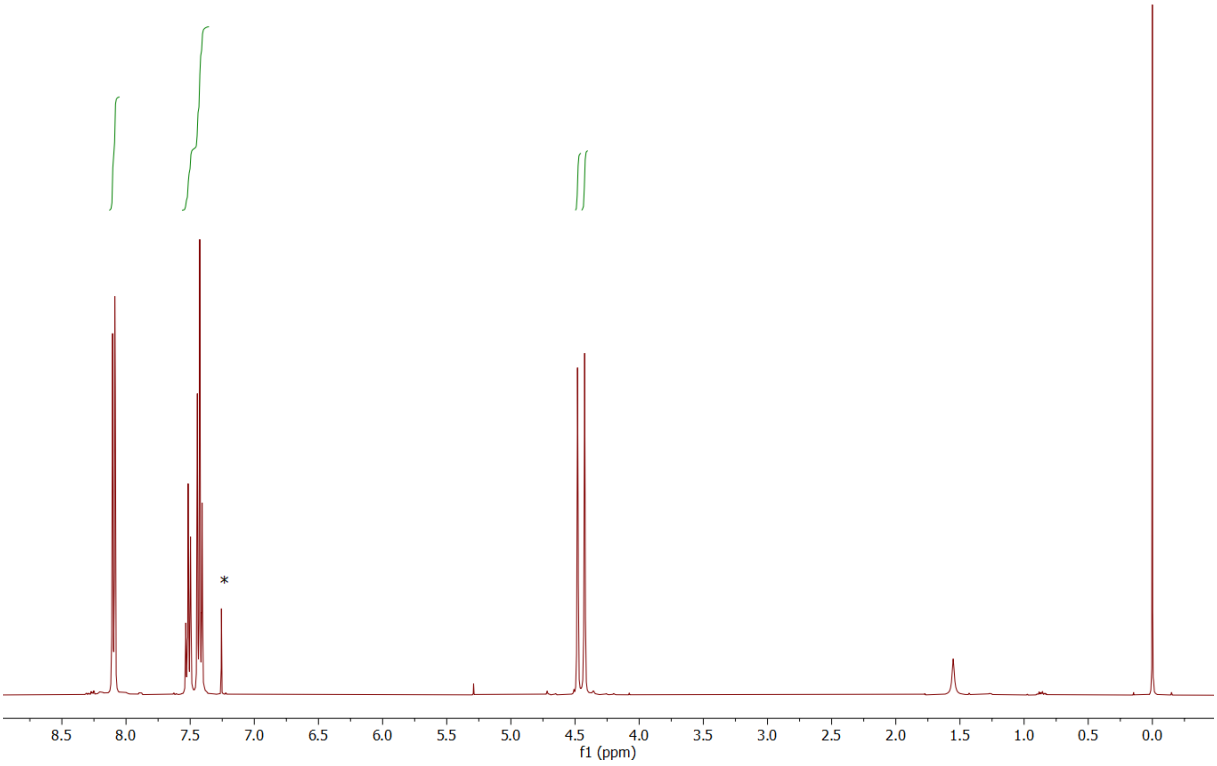

Figure S28 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**

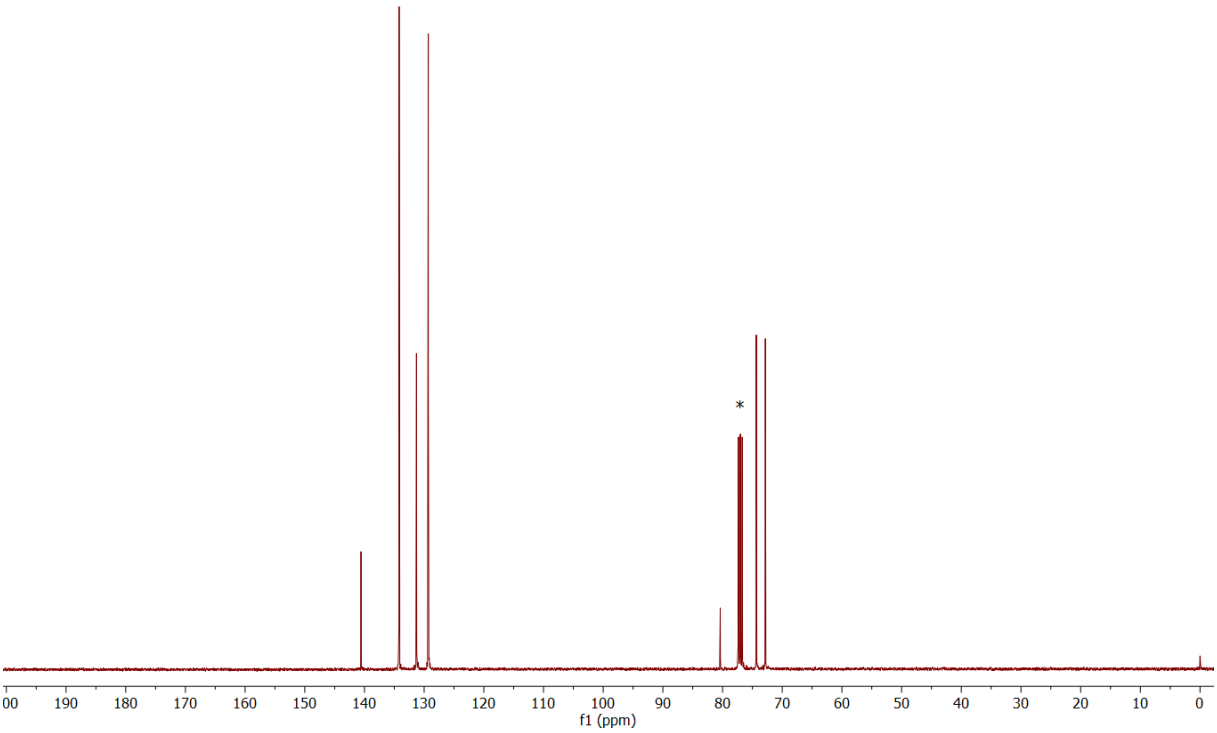

Figure S29 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3**

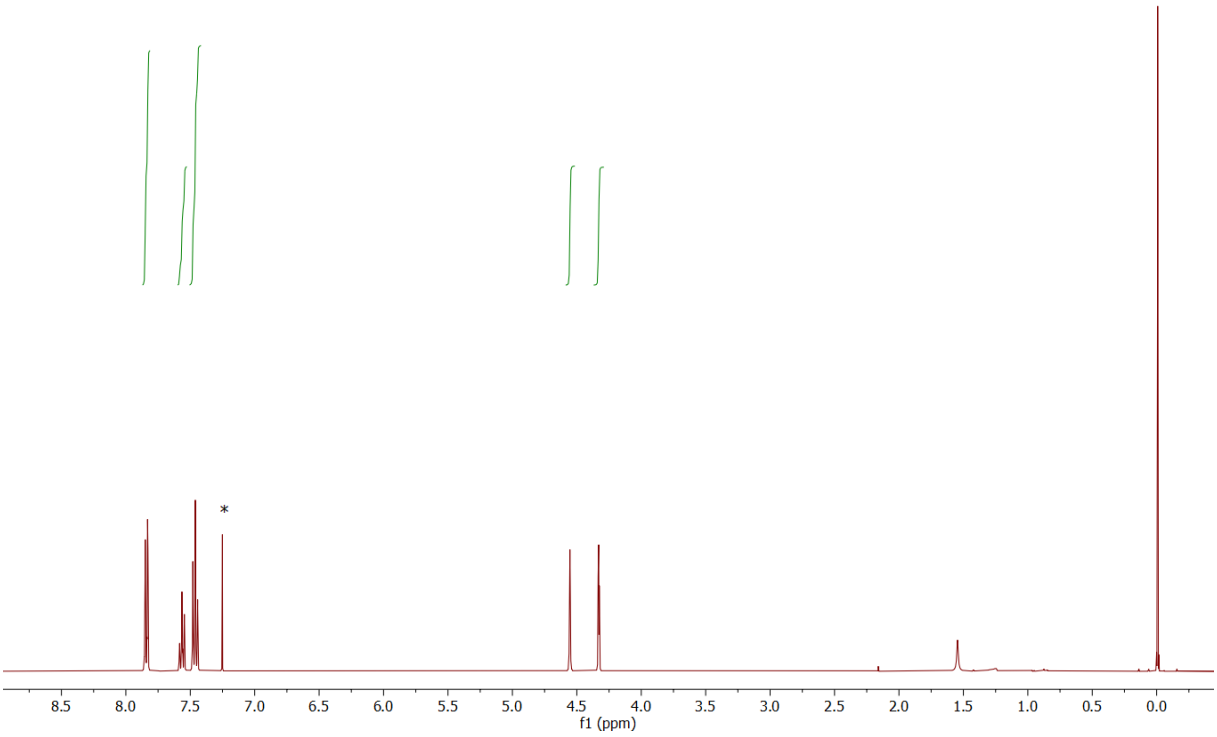

Figure S30 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4a**

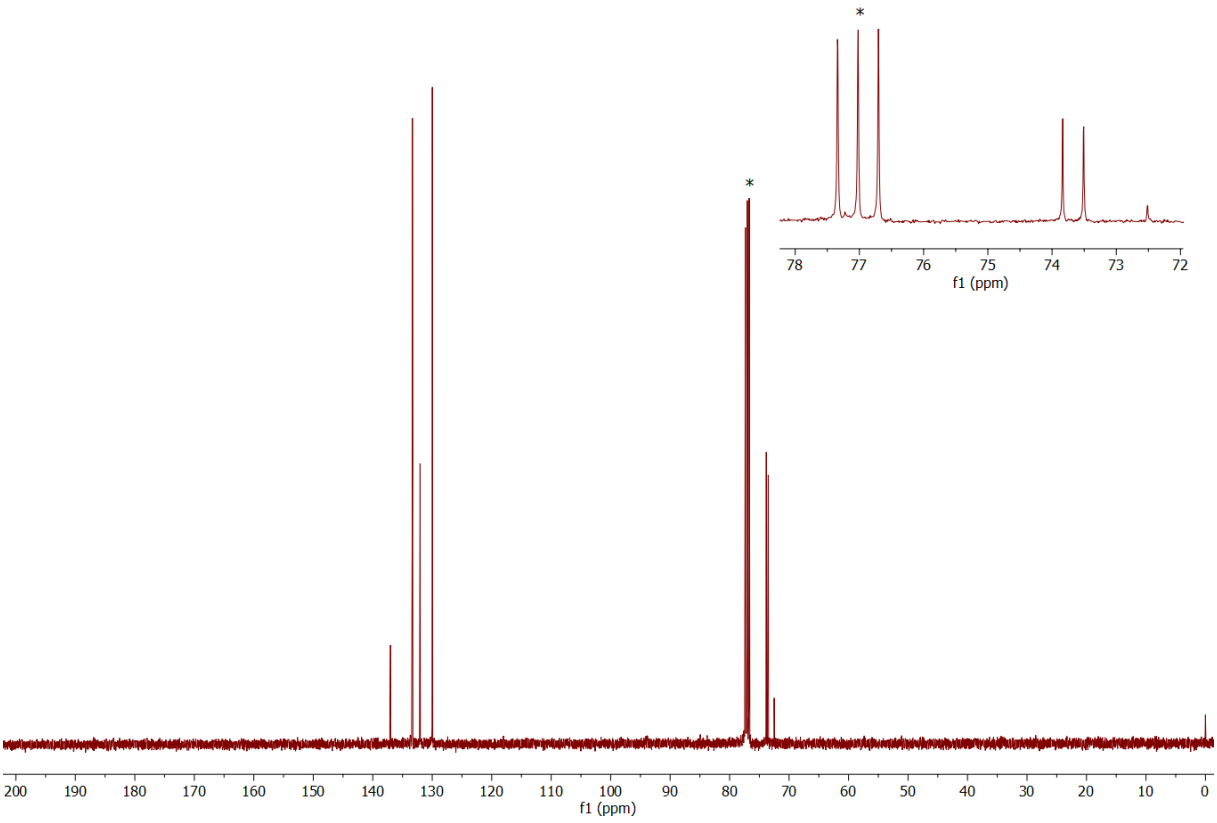

Figure S31 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4a**

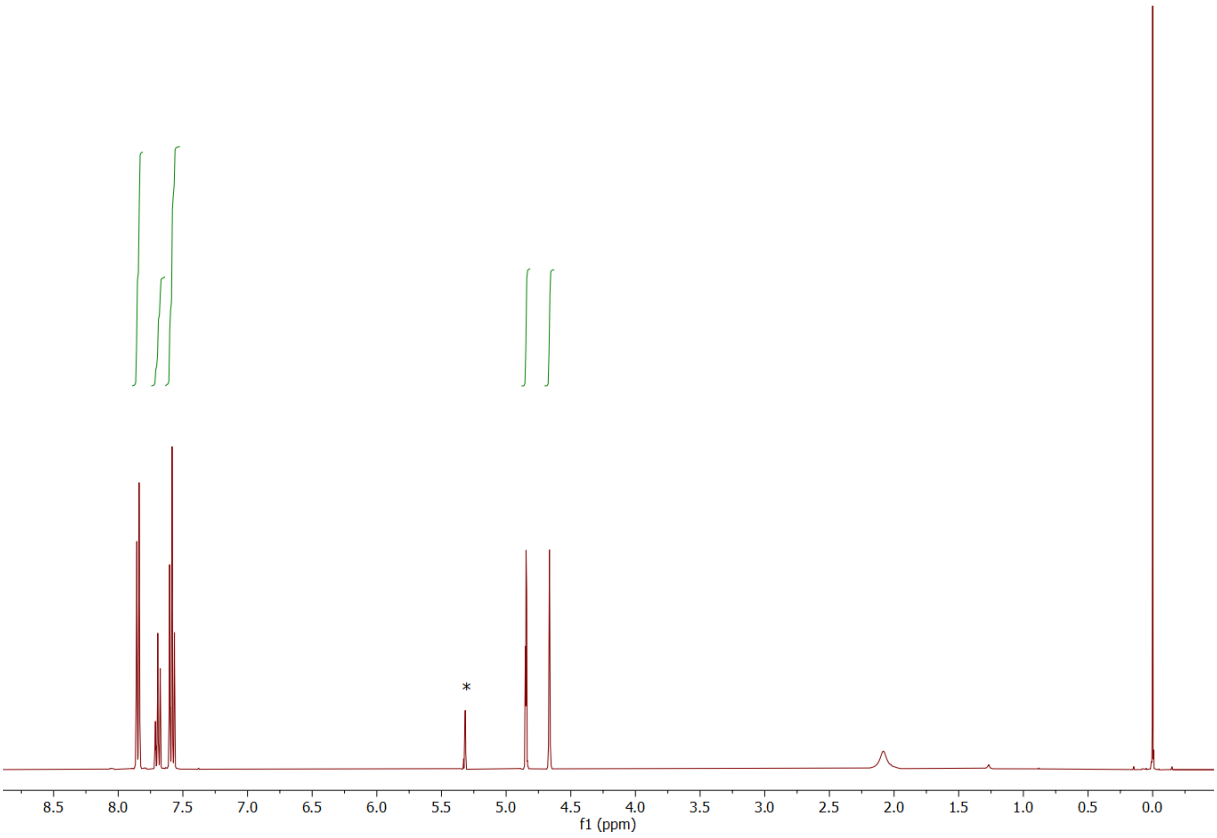

Figure S32 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **4b**

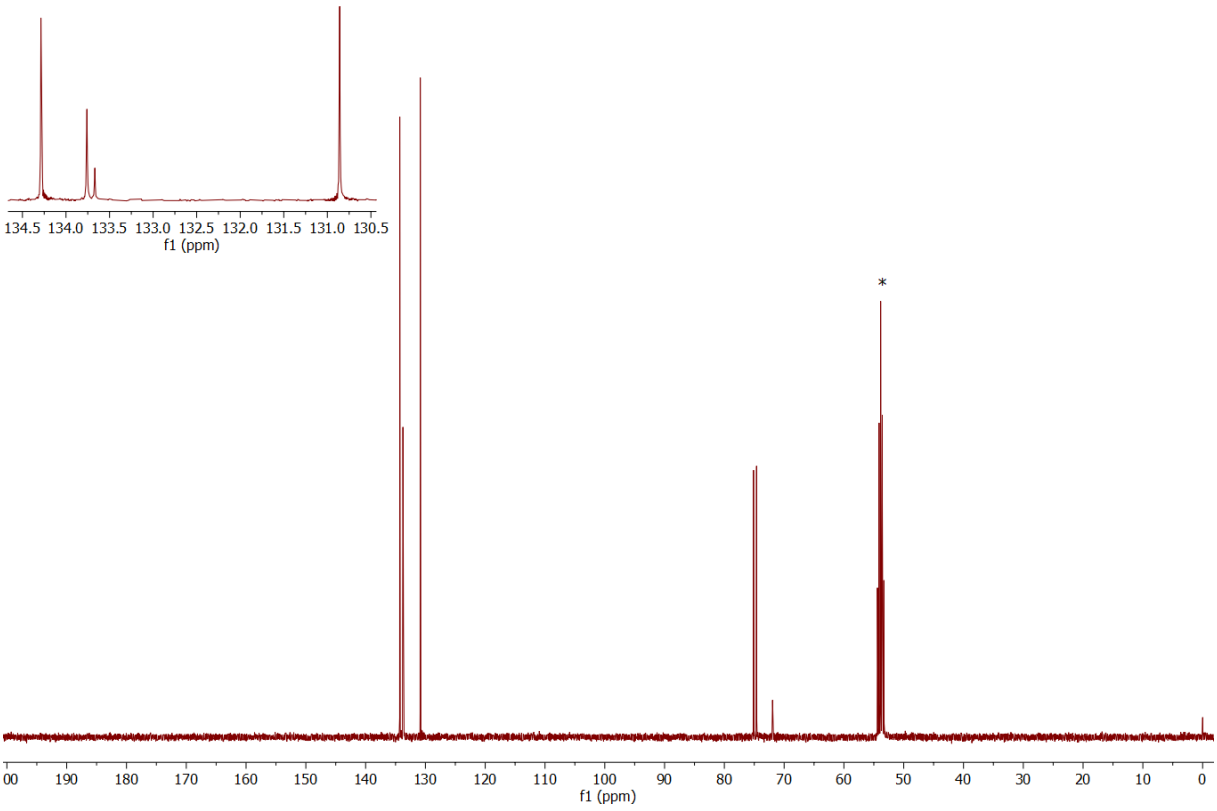

Figure S33 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **4b**

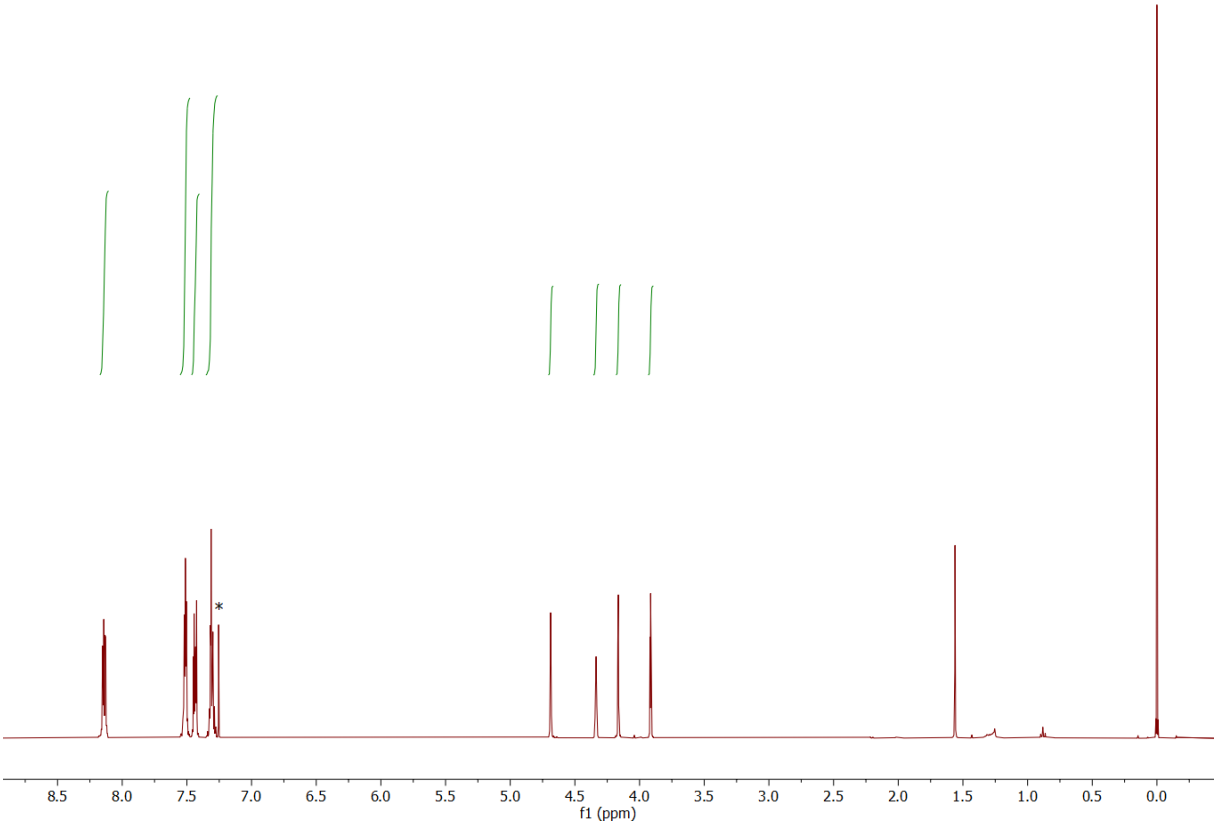

Figure S34 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**

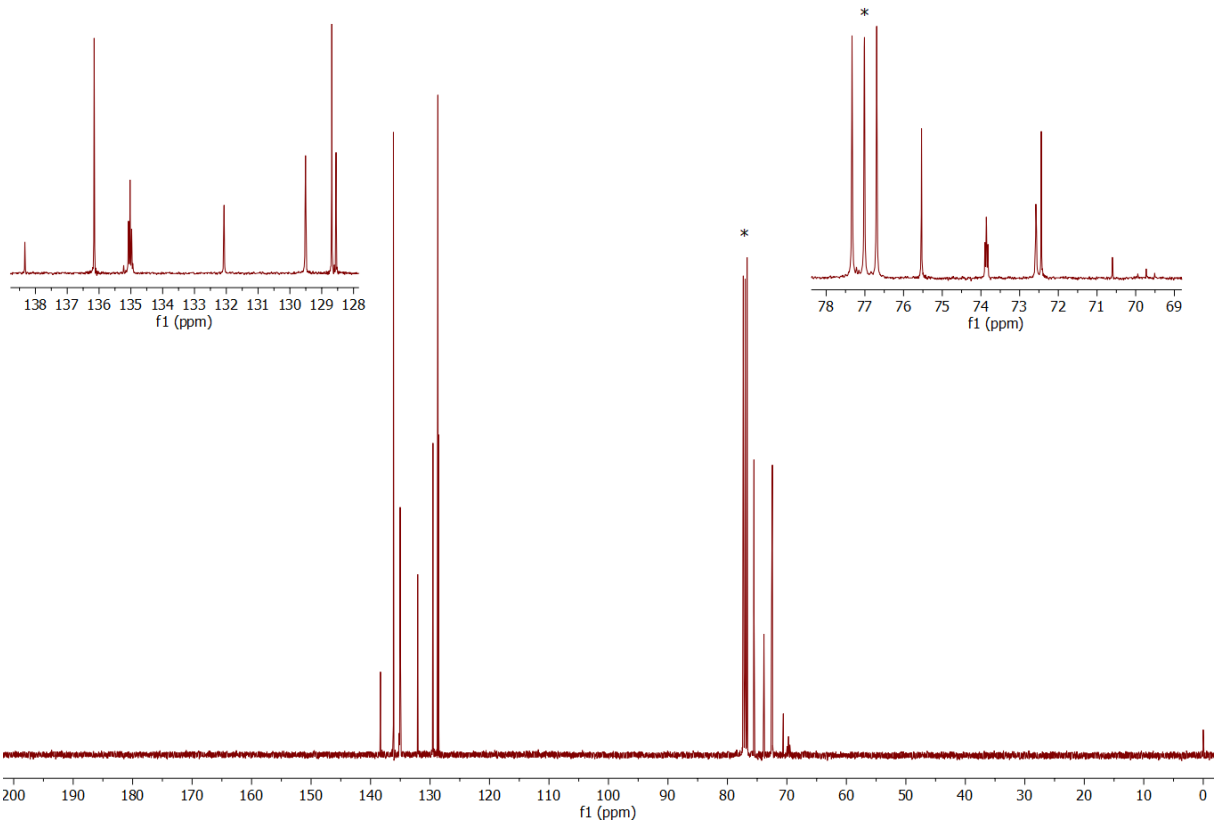

Figure S35 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5**

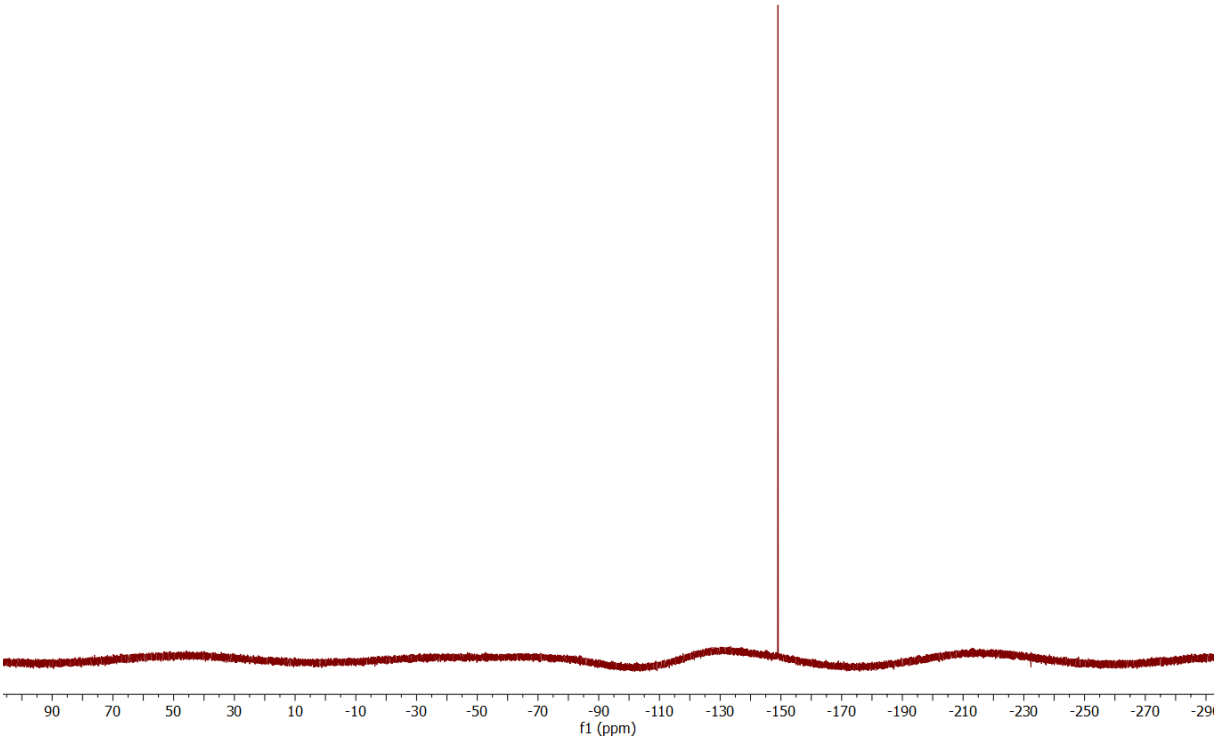

Figure S36 ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **5**

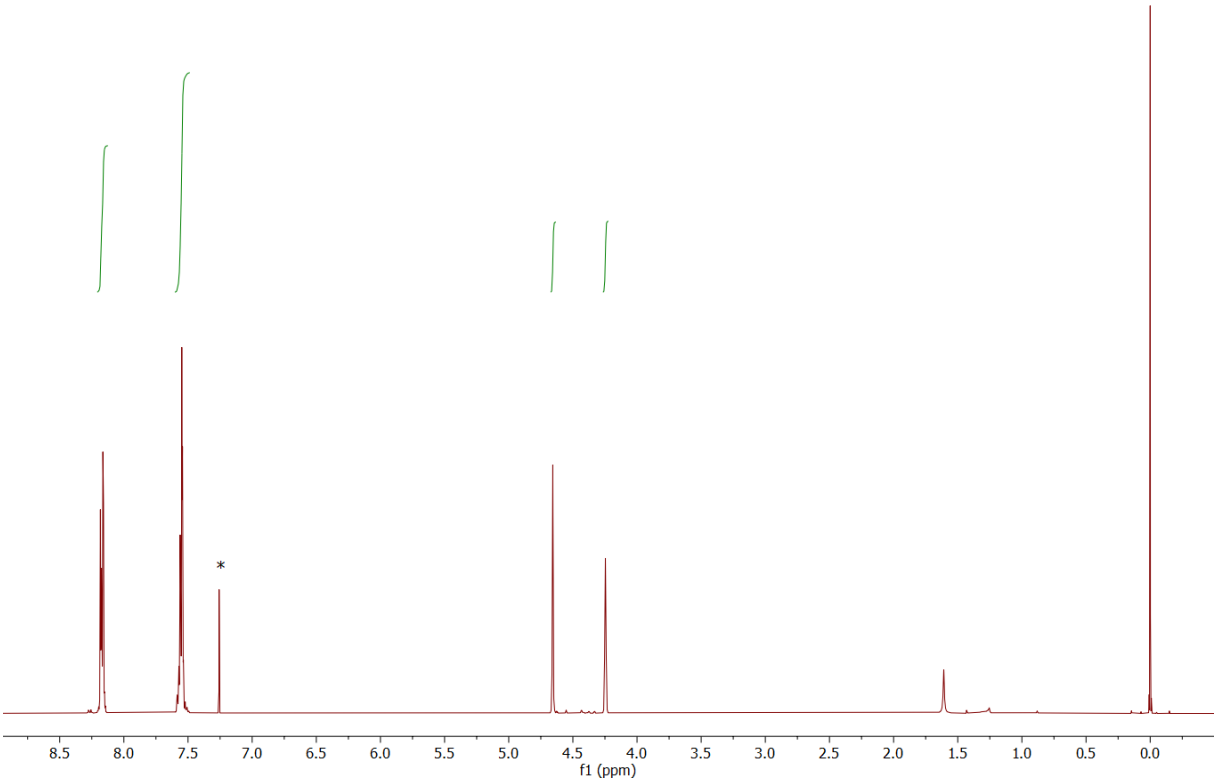

Figure S37 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**

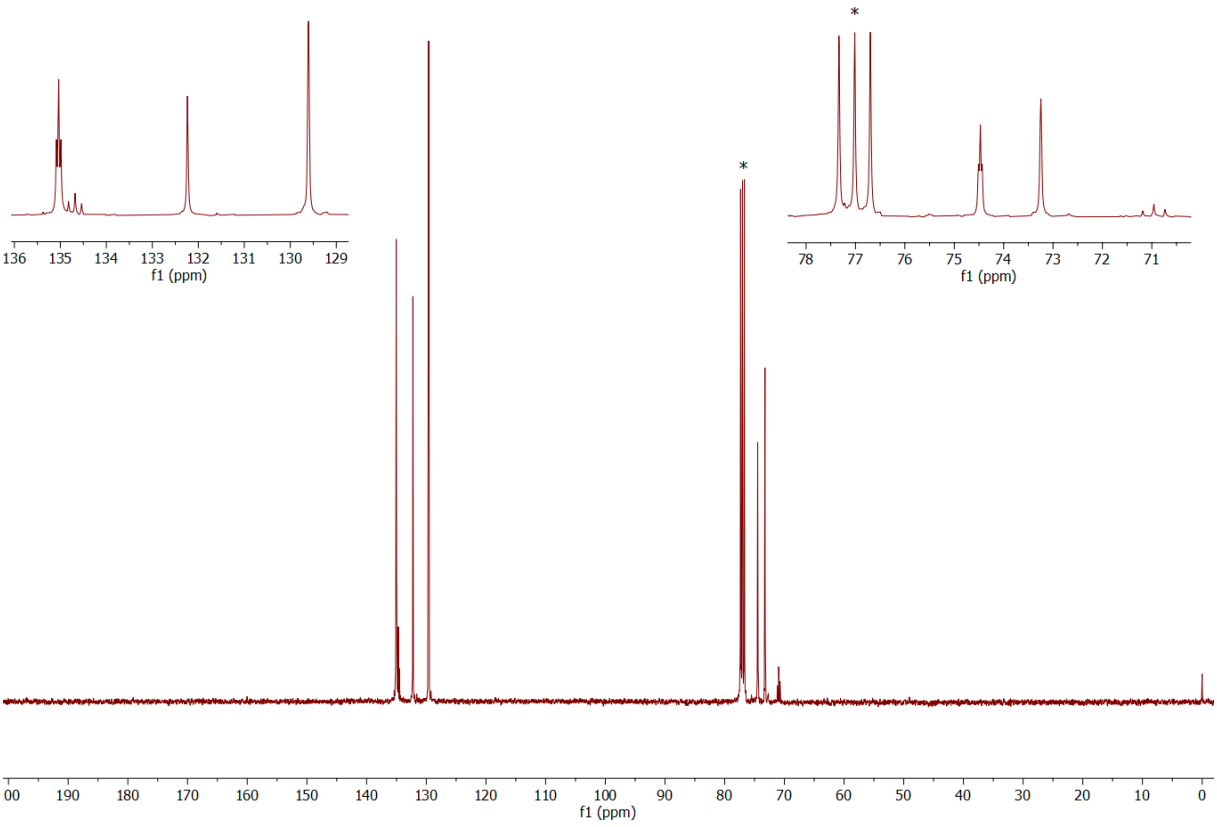

Figure S38 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6**

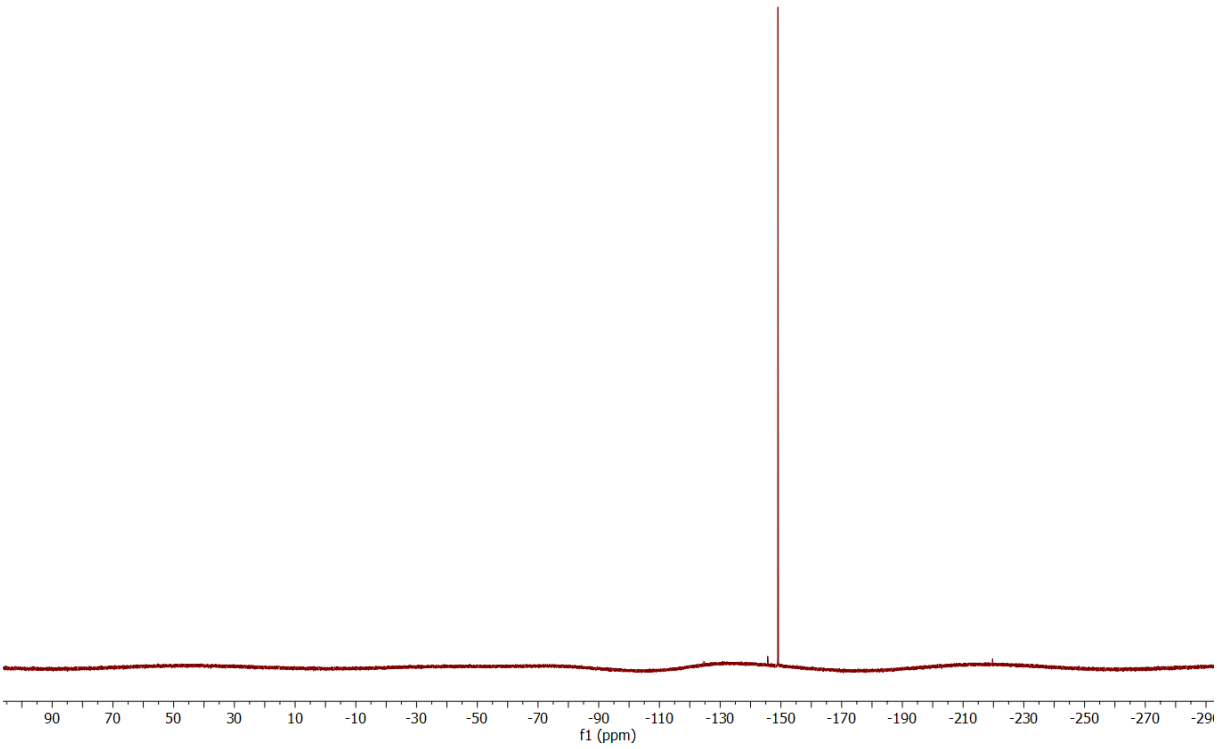

Figure S39 ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **6**

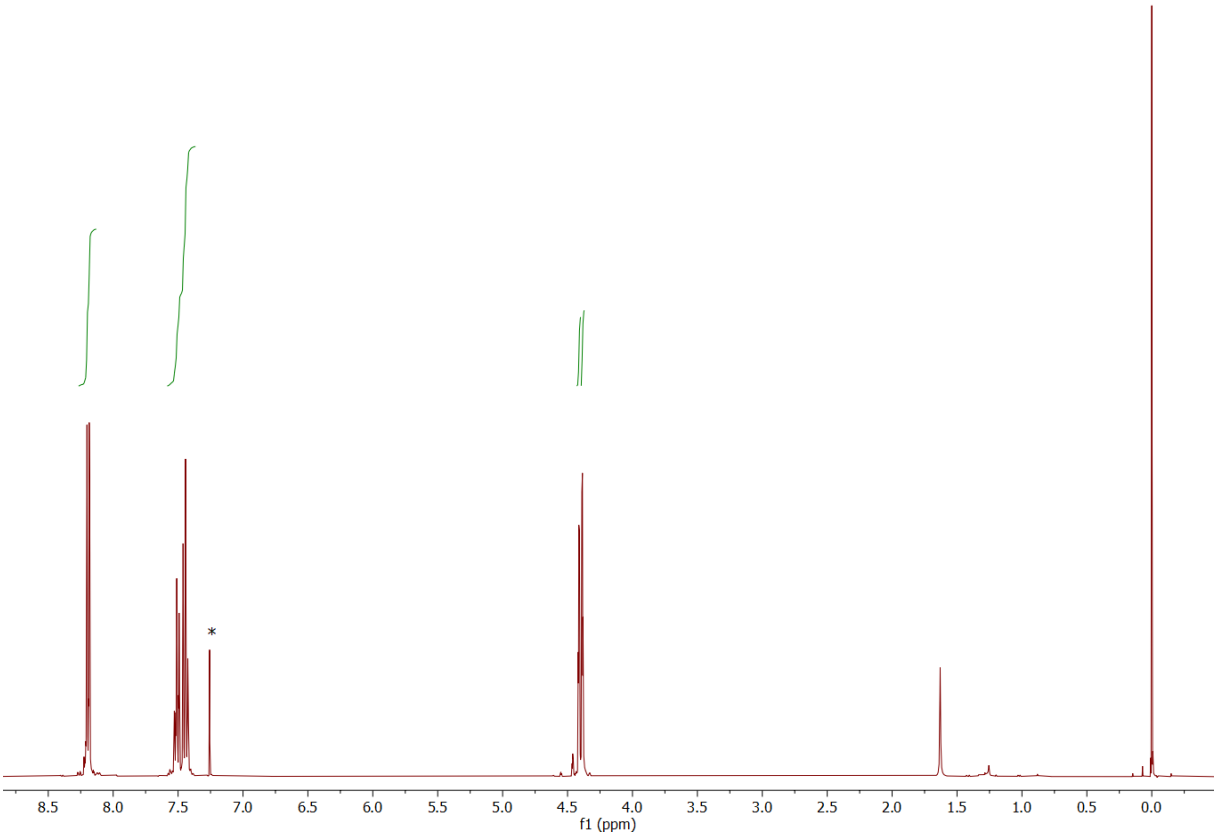

Figure S40 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7**

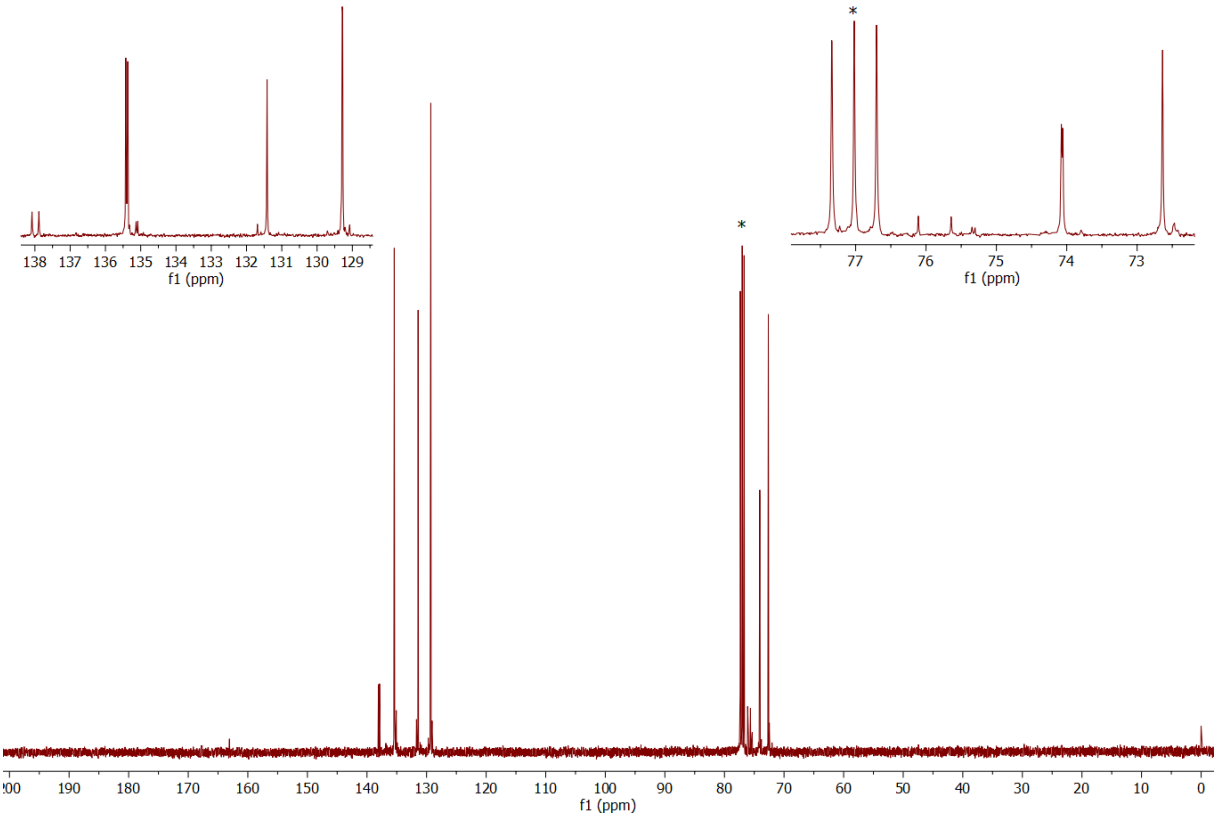

Figure S41 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **7**

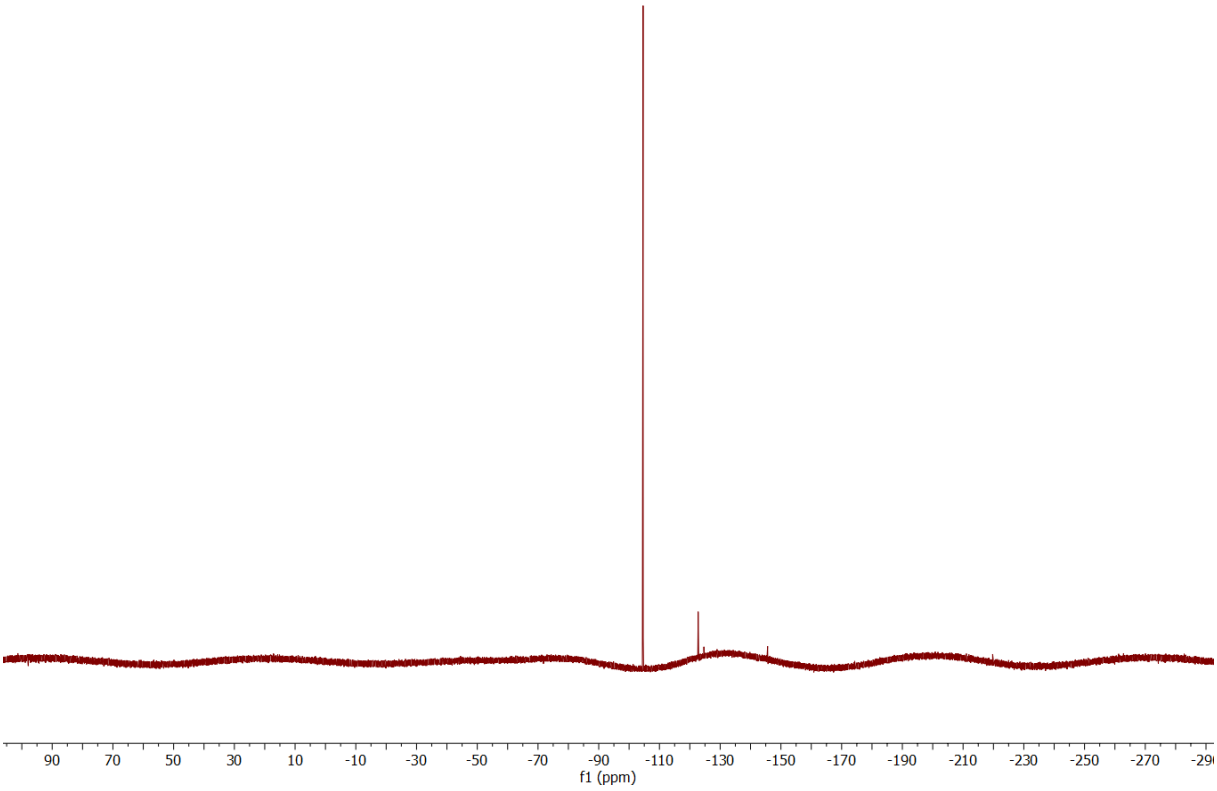

Figure S42 ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of **7**

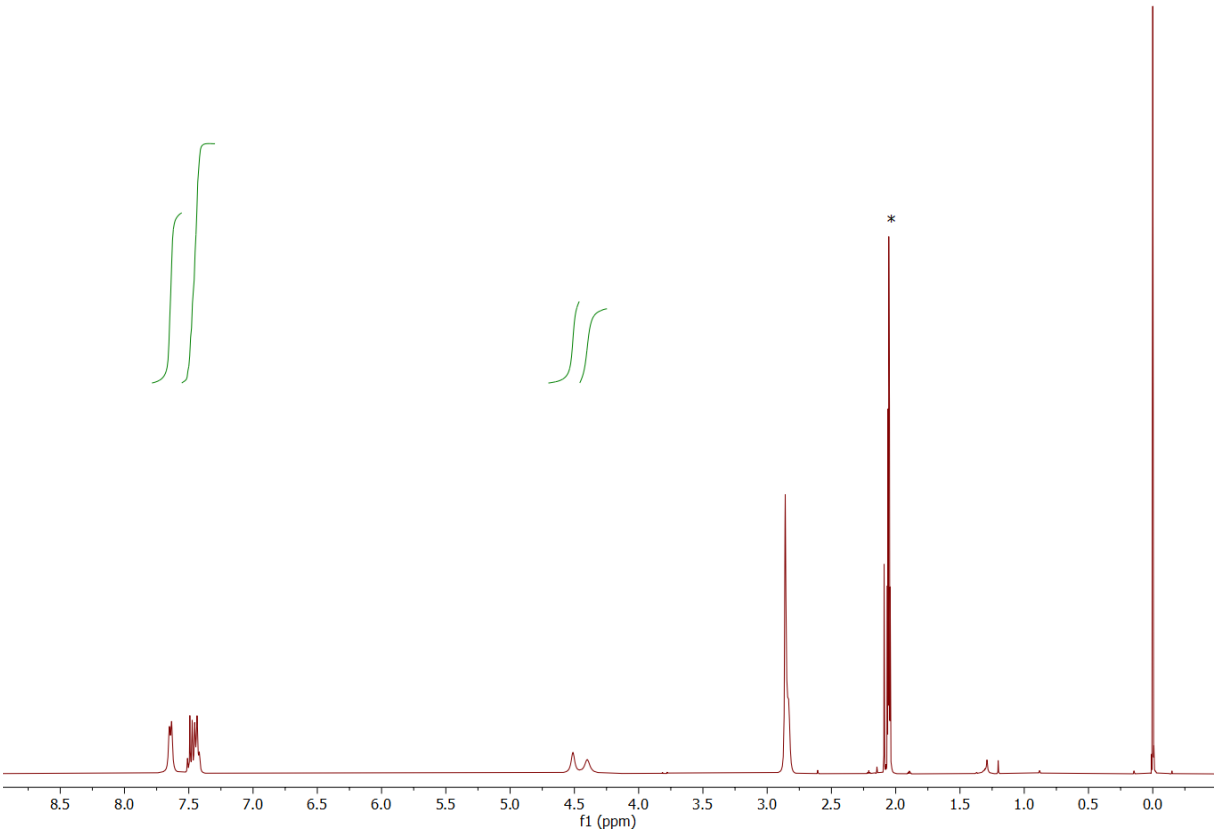

Figure S43 ^{1}H NMR spectrum (400 MHz, acetone-d_6) of **8**

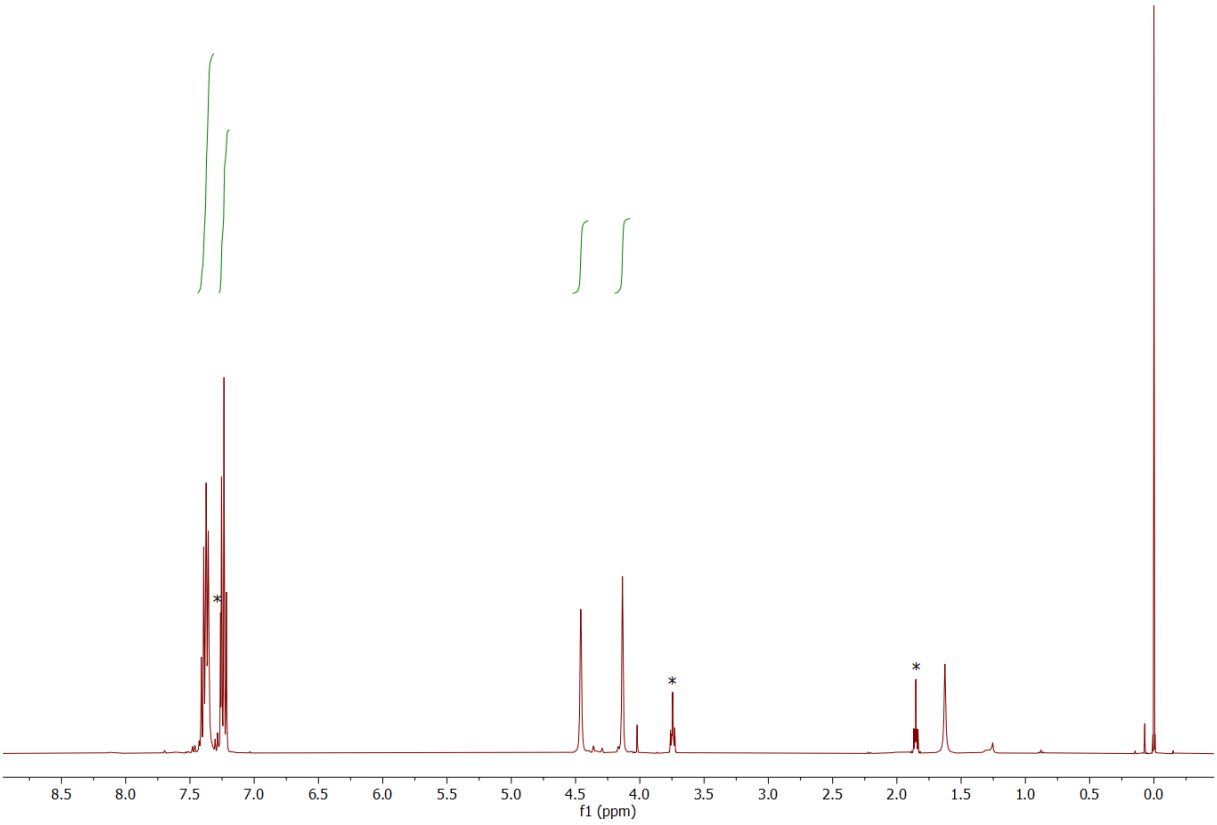

Figure S44 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9a**

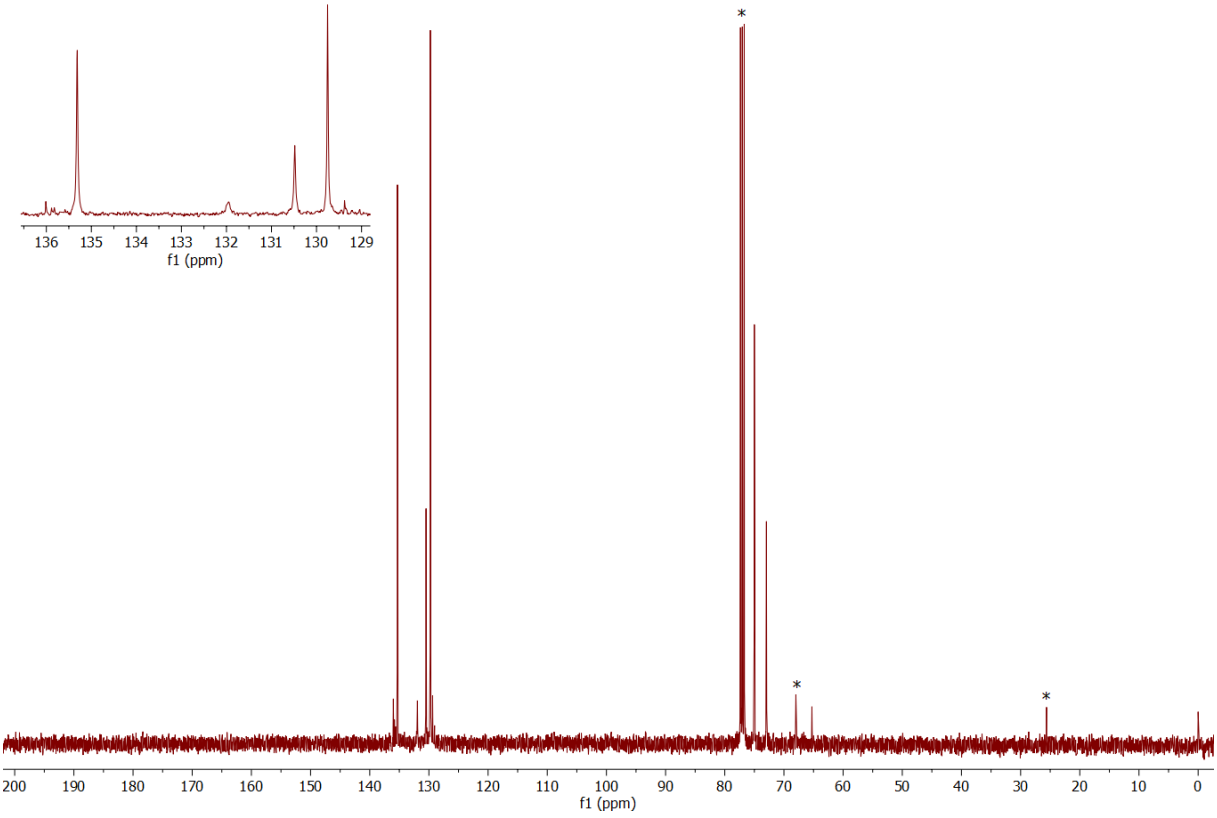

Figure S45 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **9a**

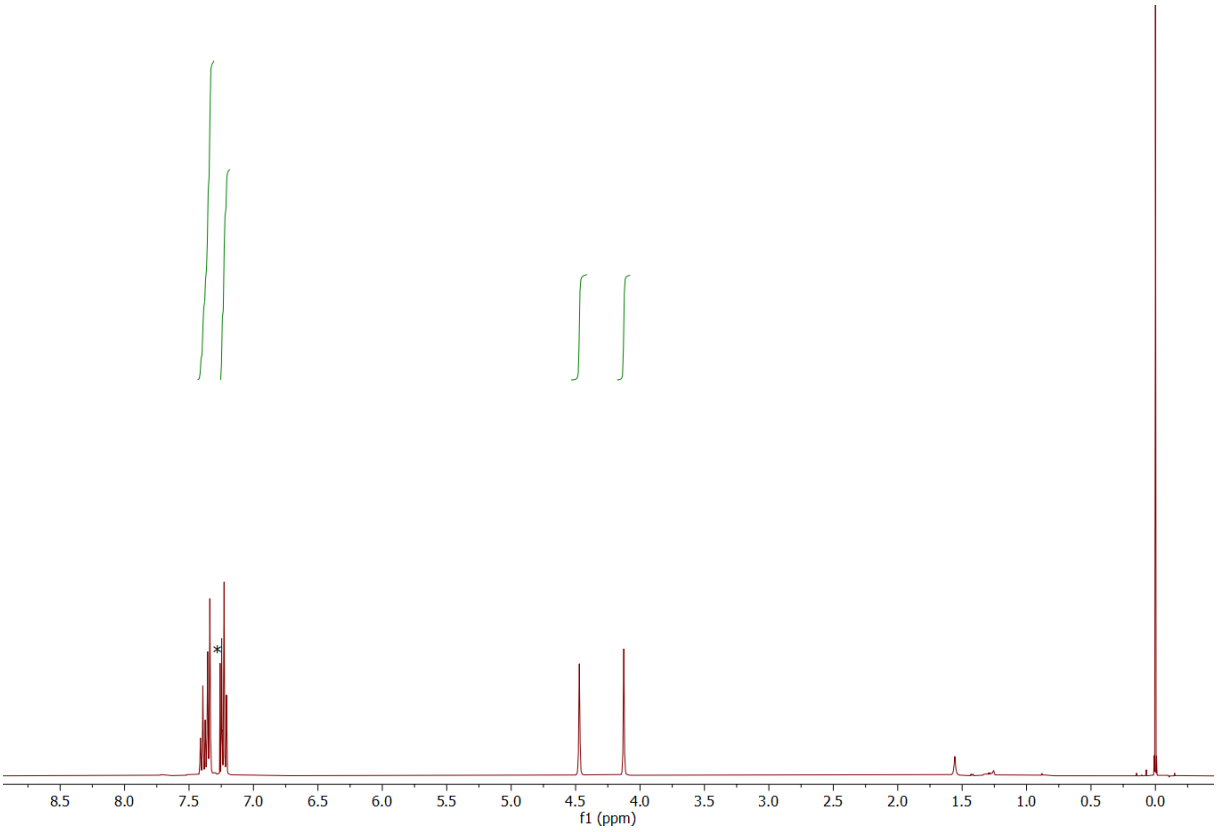

Figure S46 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9b**

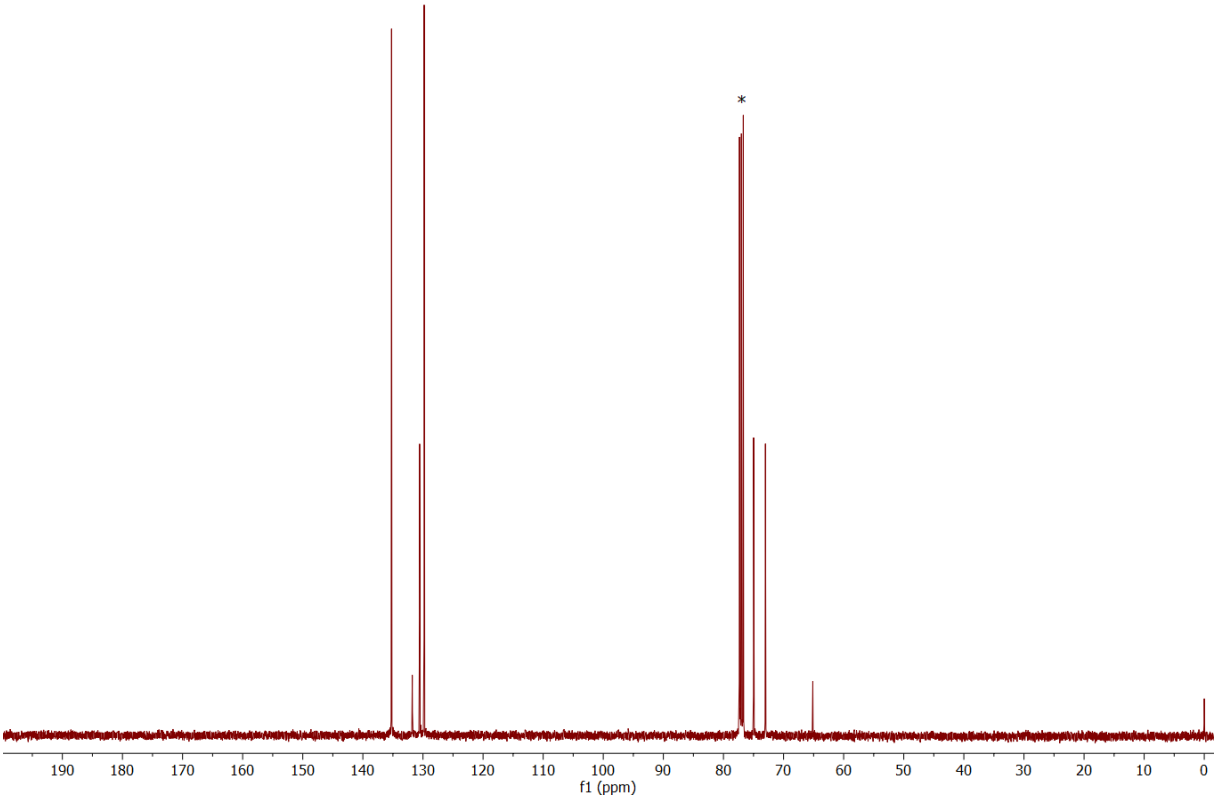

Figure S47 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **9b**

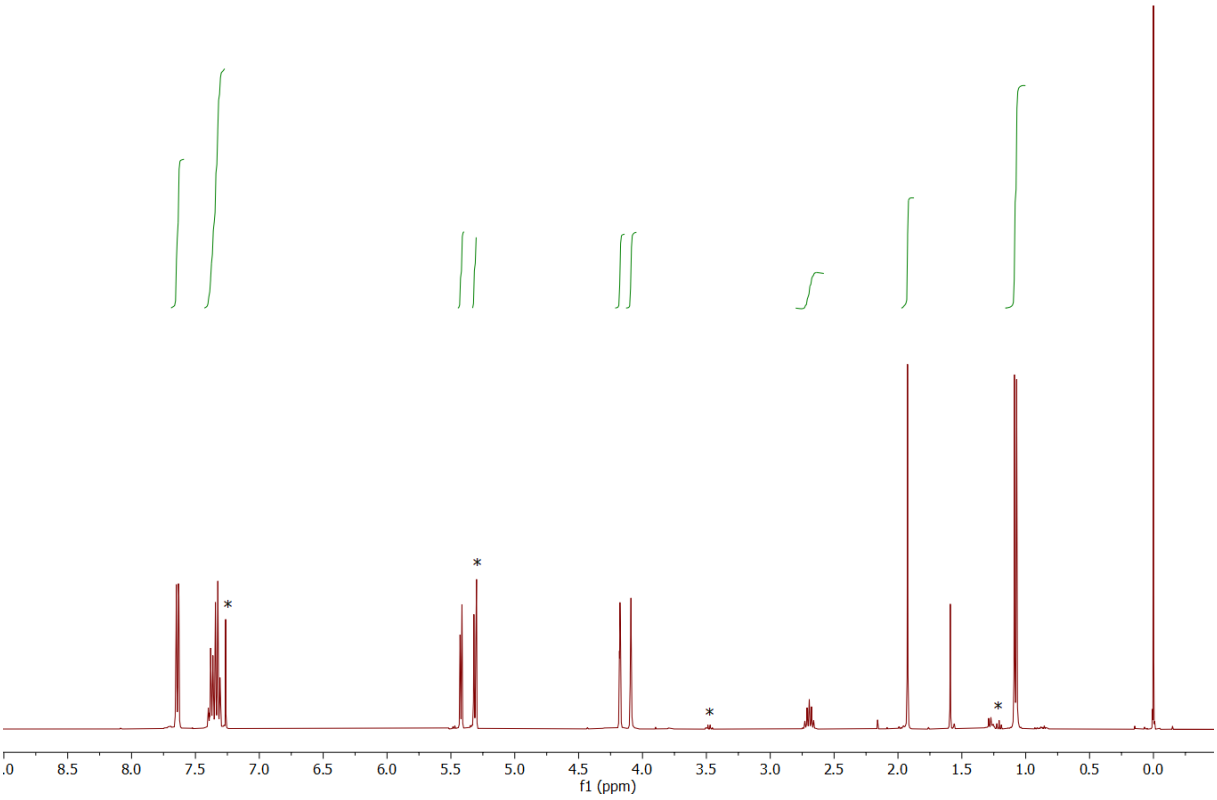

Figure S48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **10**

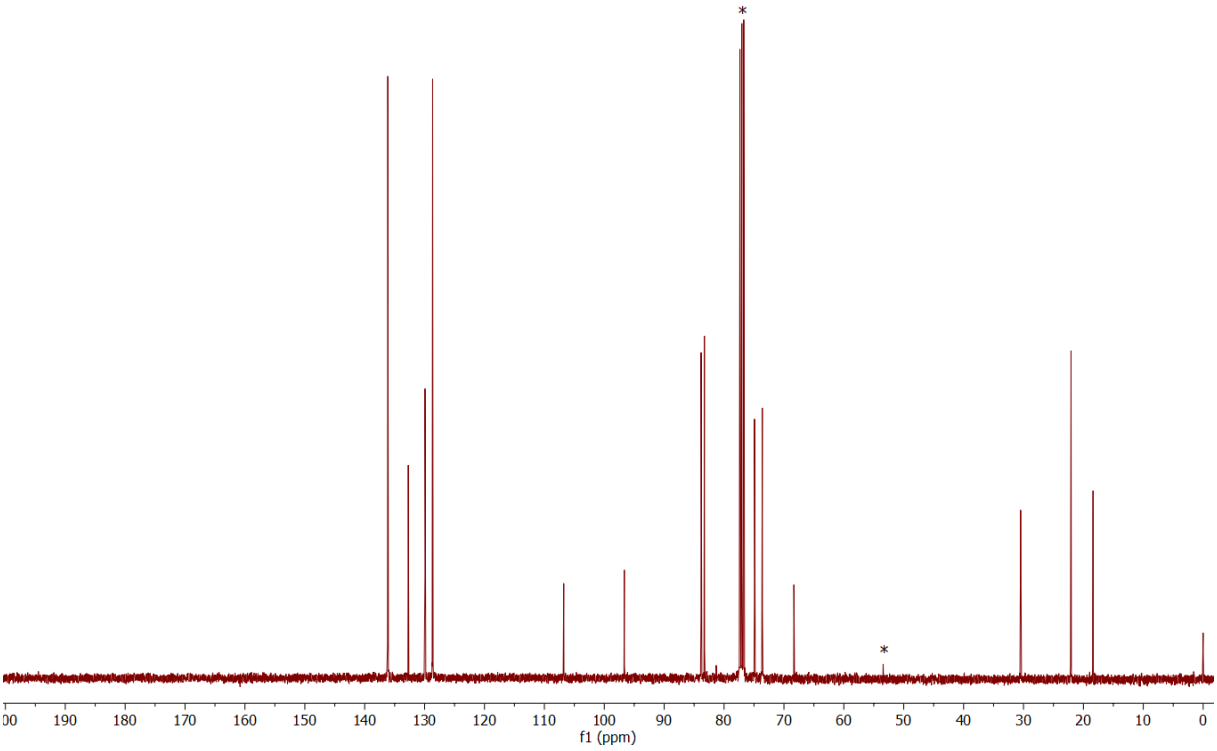

Figure S49 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **10**

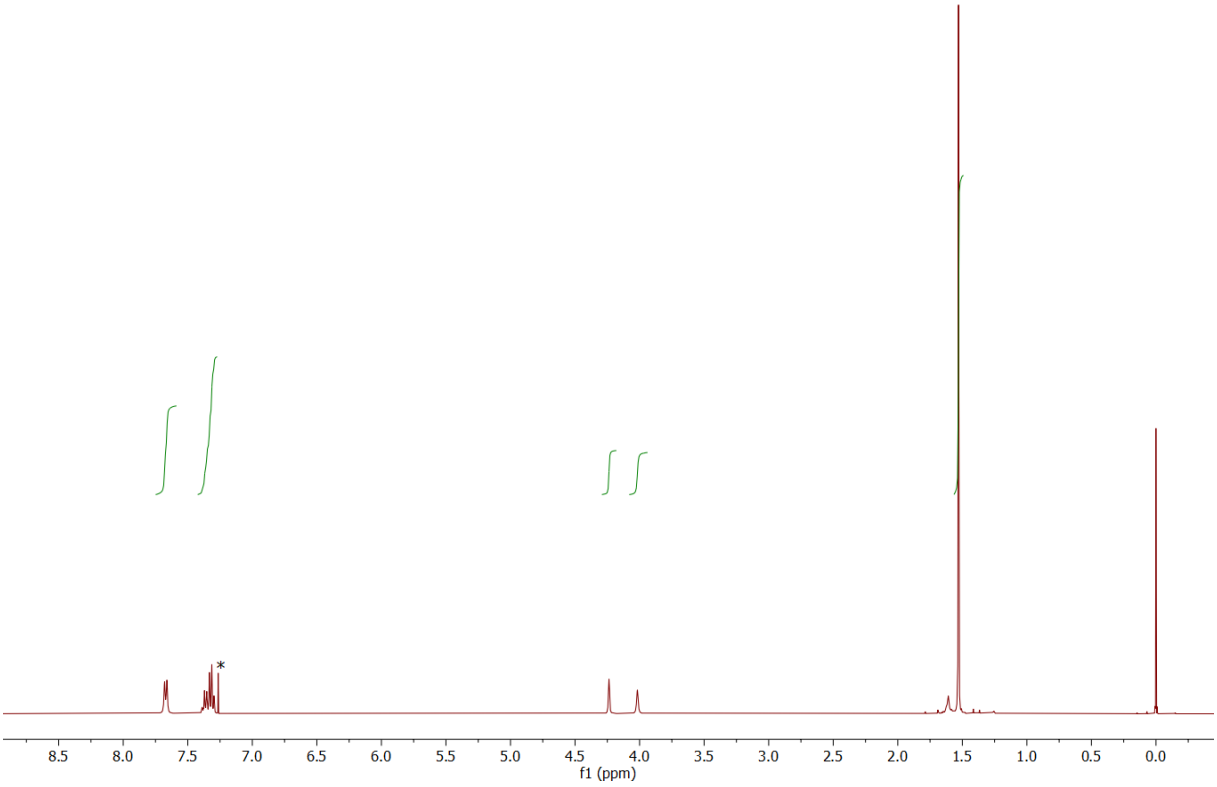

Figure S50 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11**

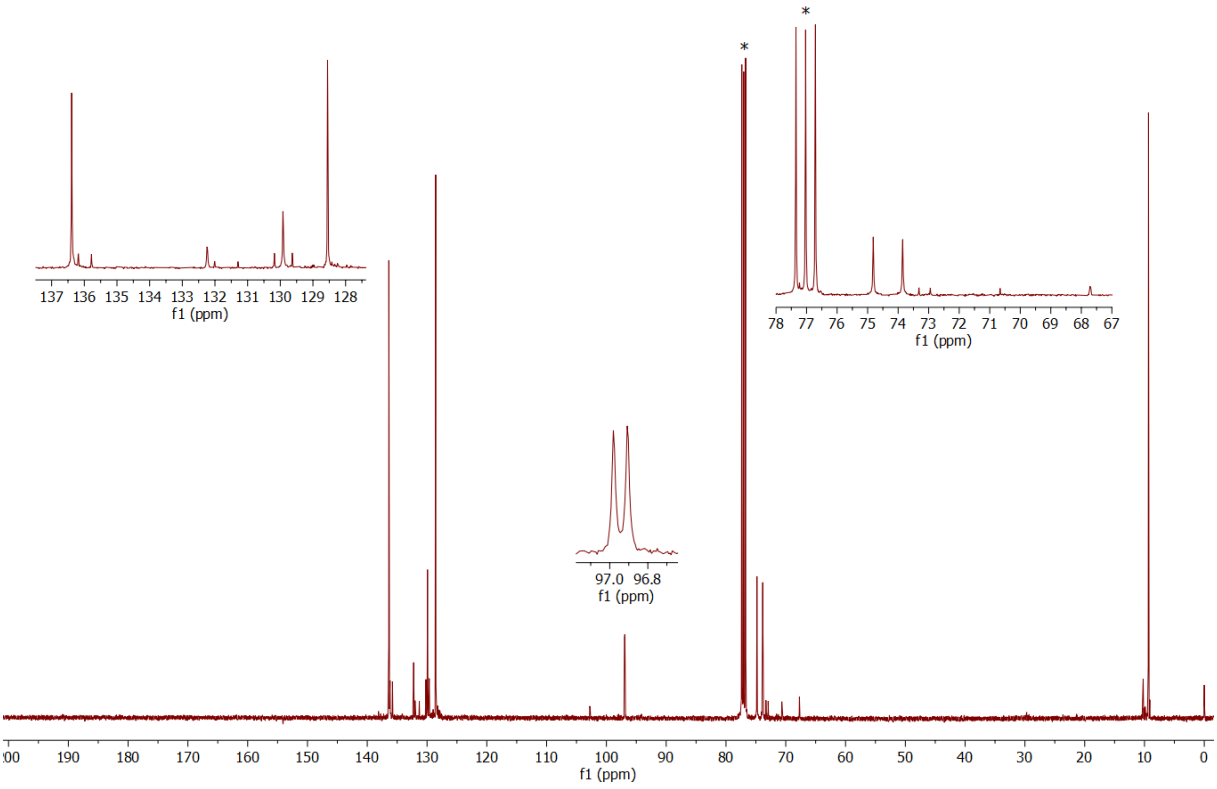

Figure S51 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **11**

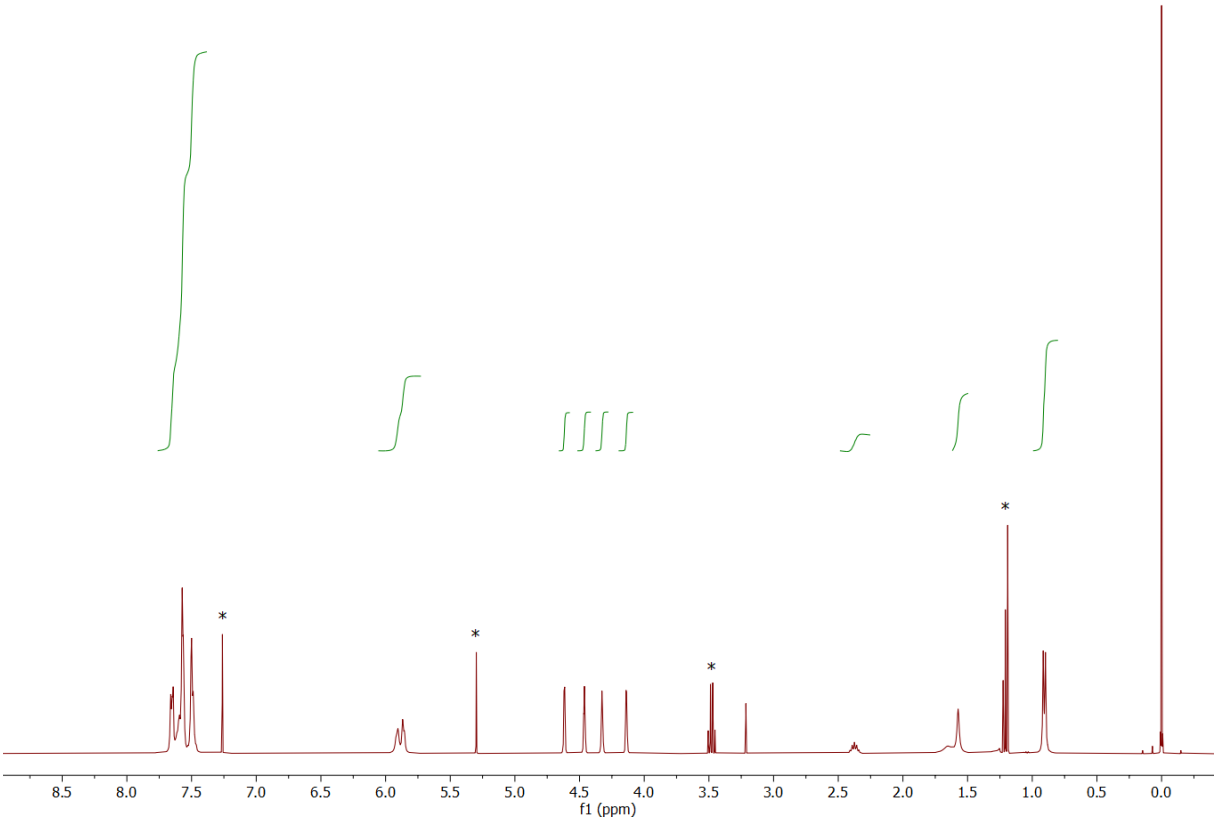

Figure S52 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **12**

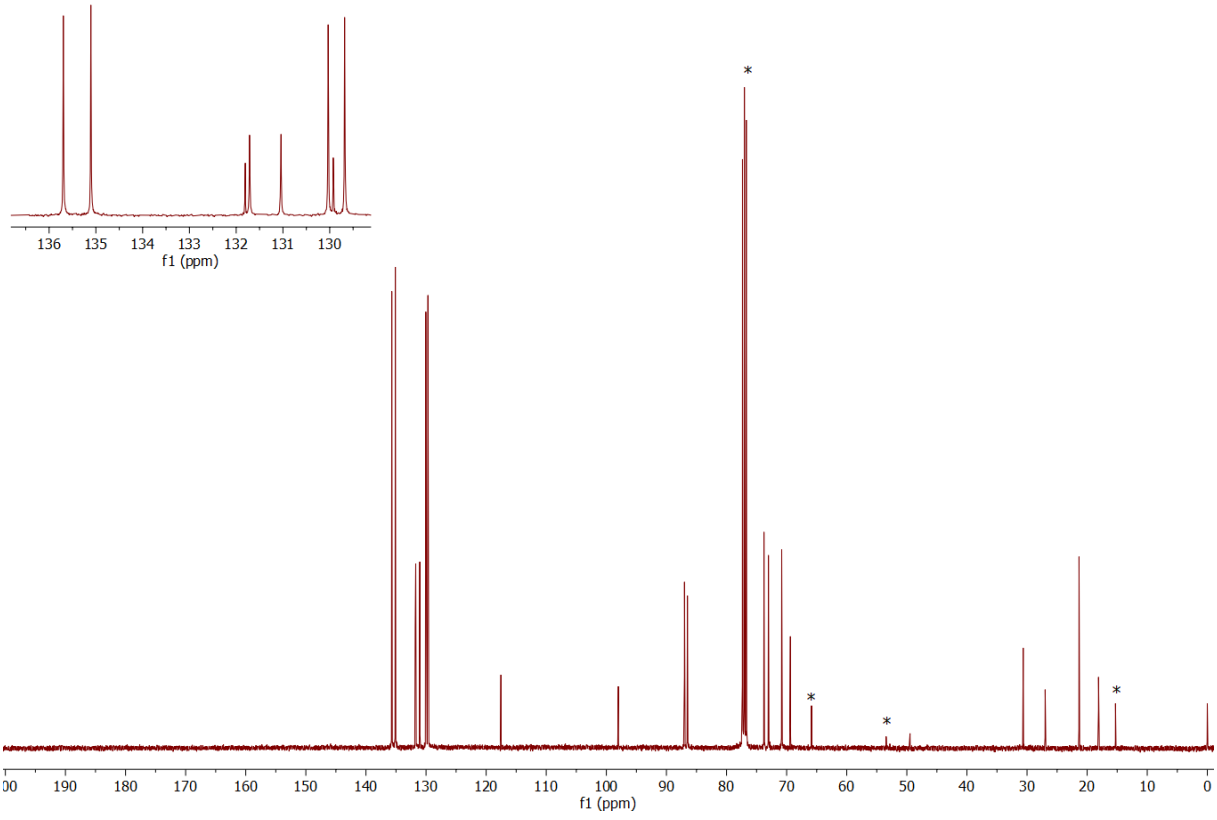

Figure S53 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **12**

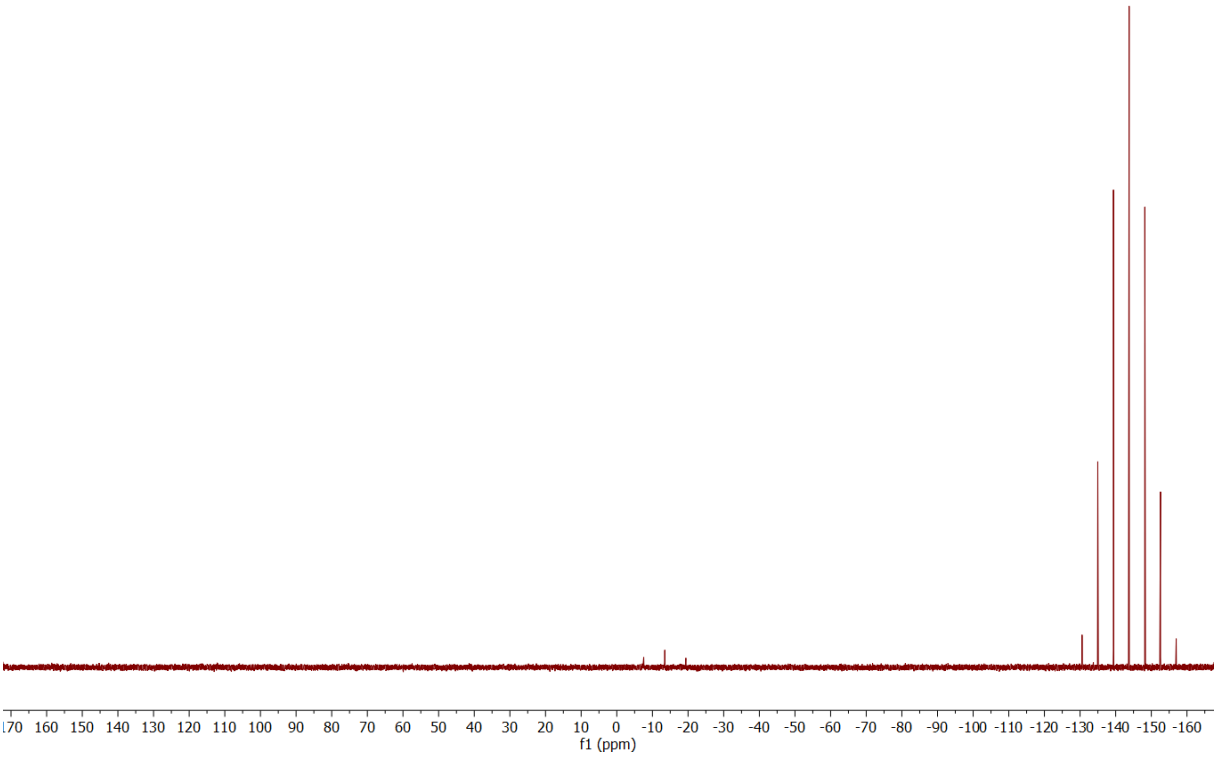

Figure S54 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **12**

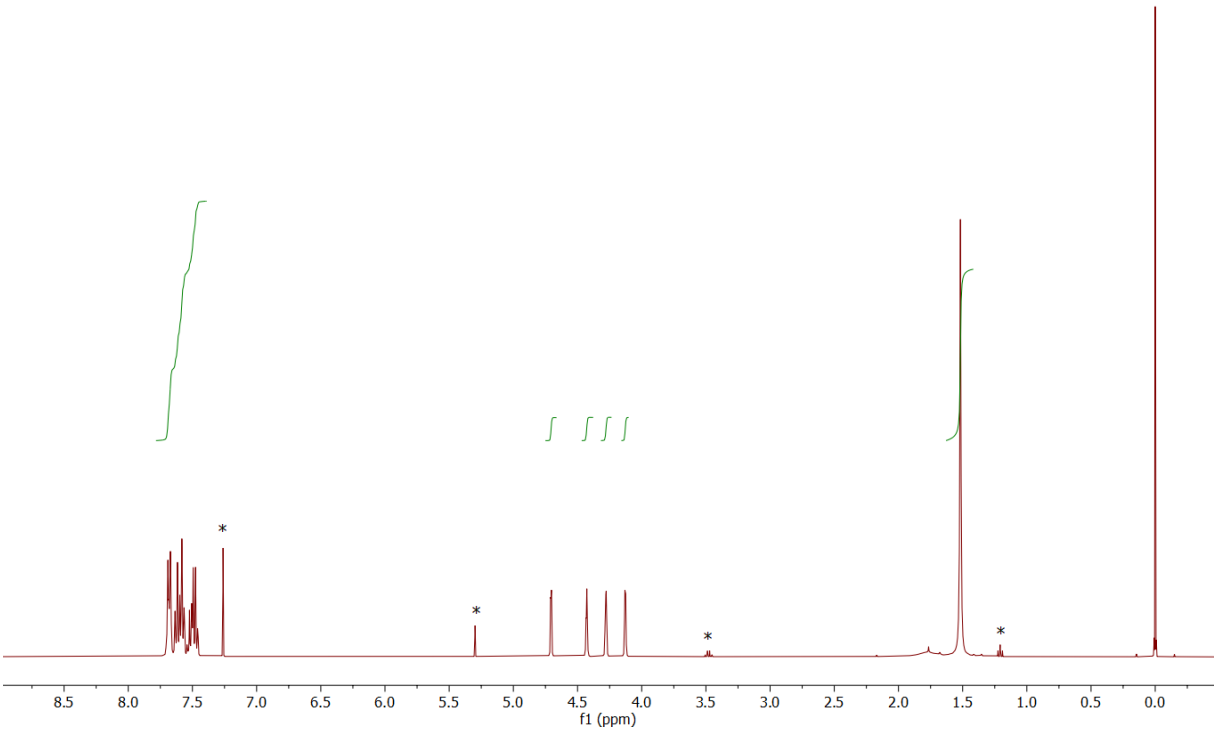

Figure S55 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13**

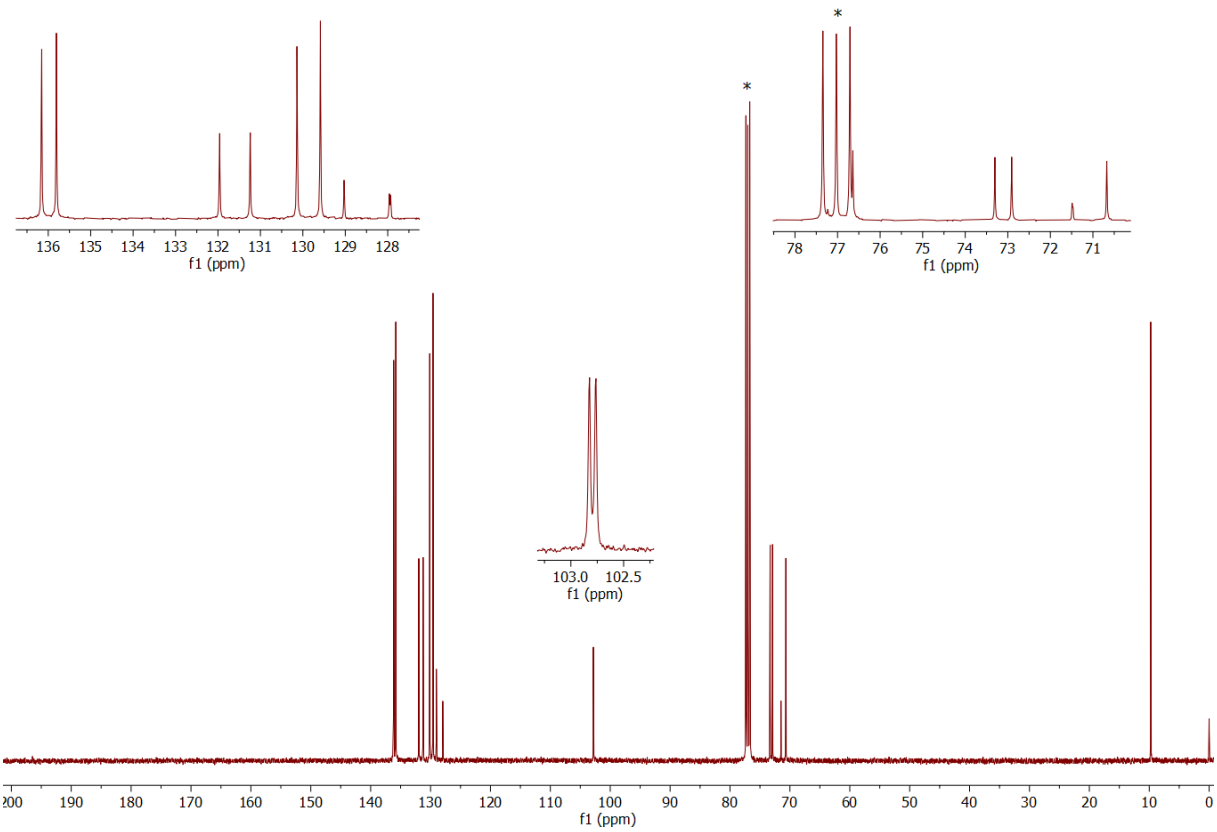

Figure S56 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **13**

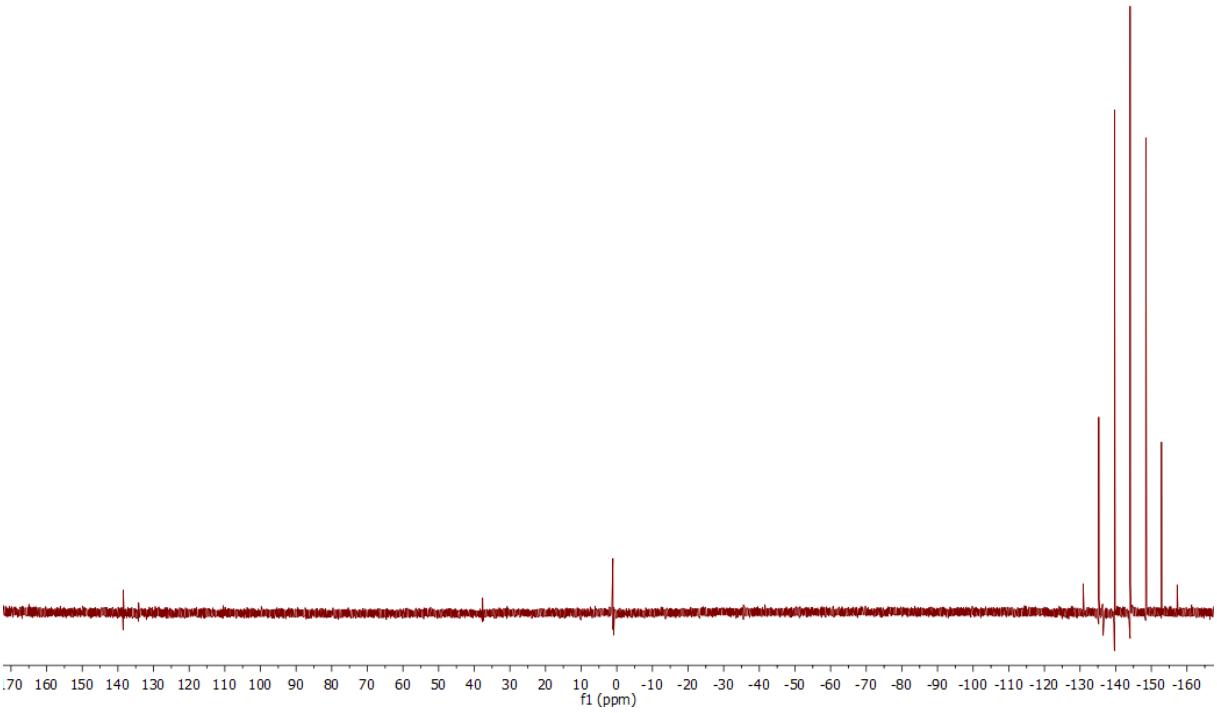

Figure S57 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **13**

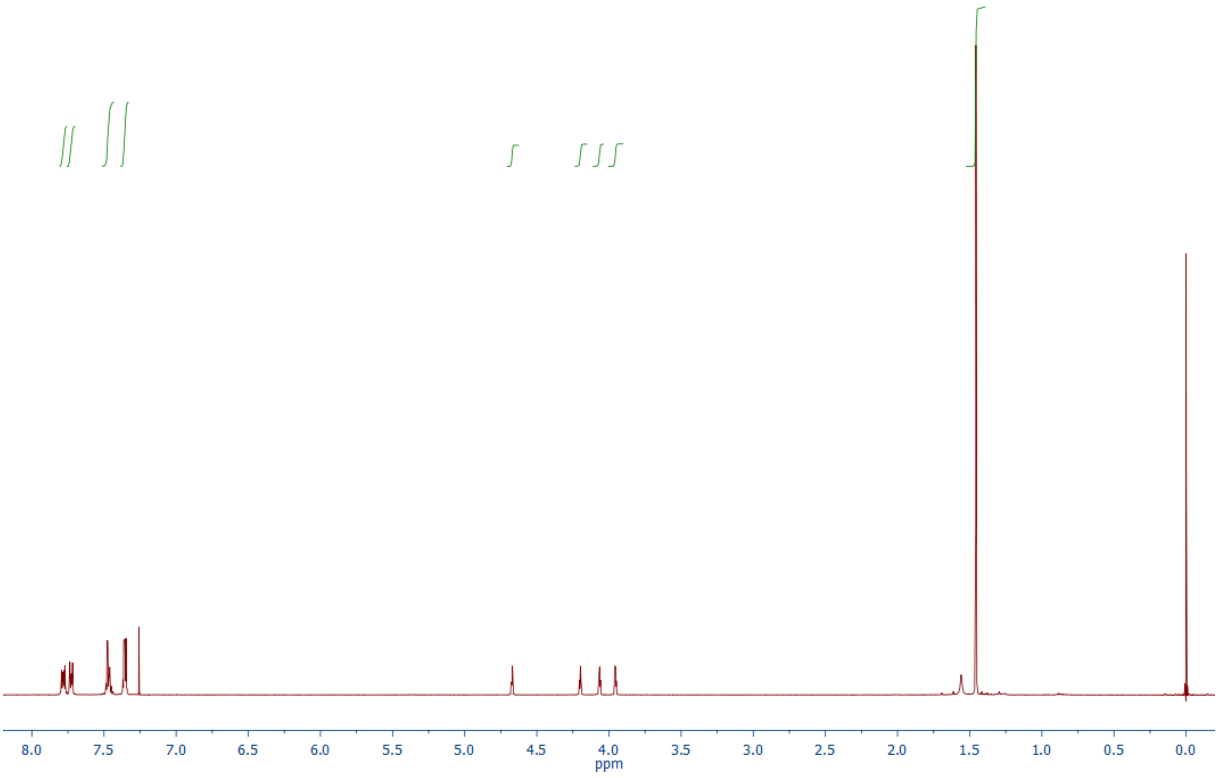

Figure S58 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14**

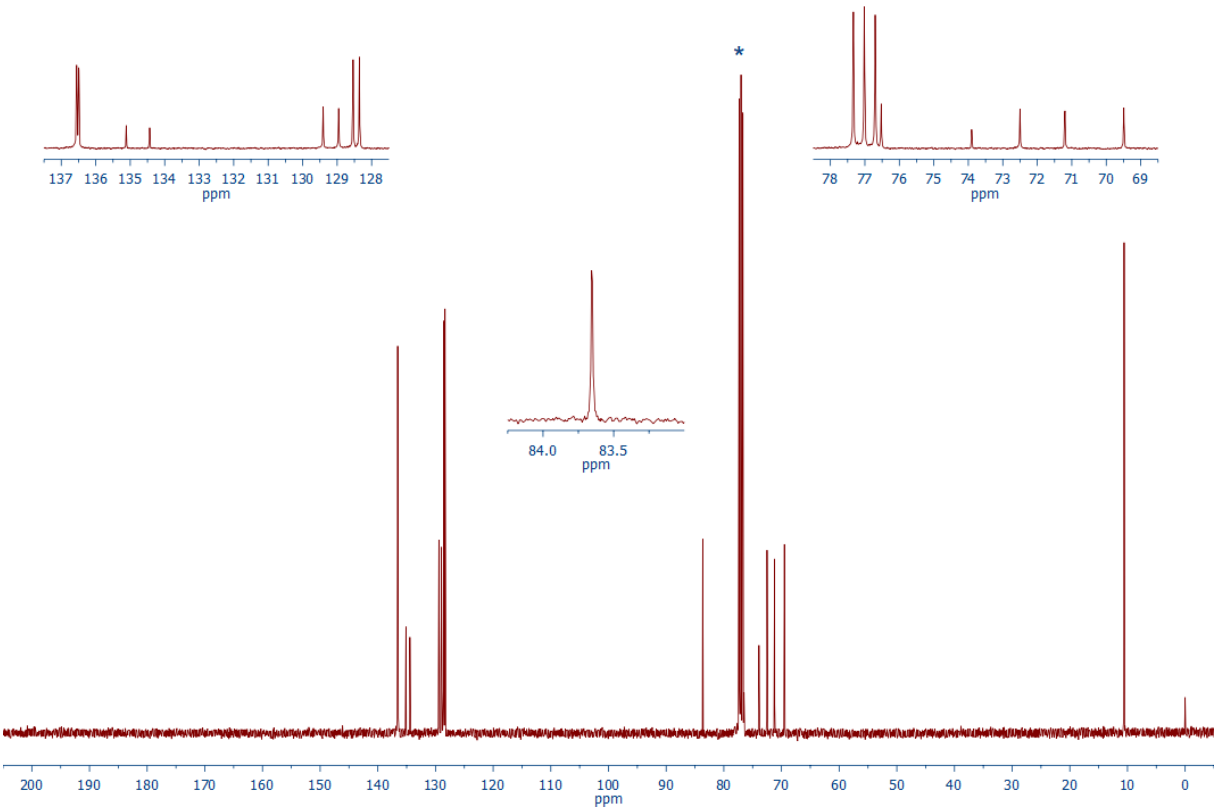

Figure S59 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **14**

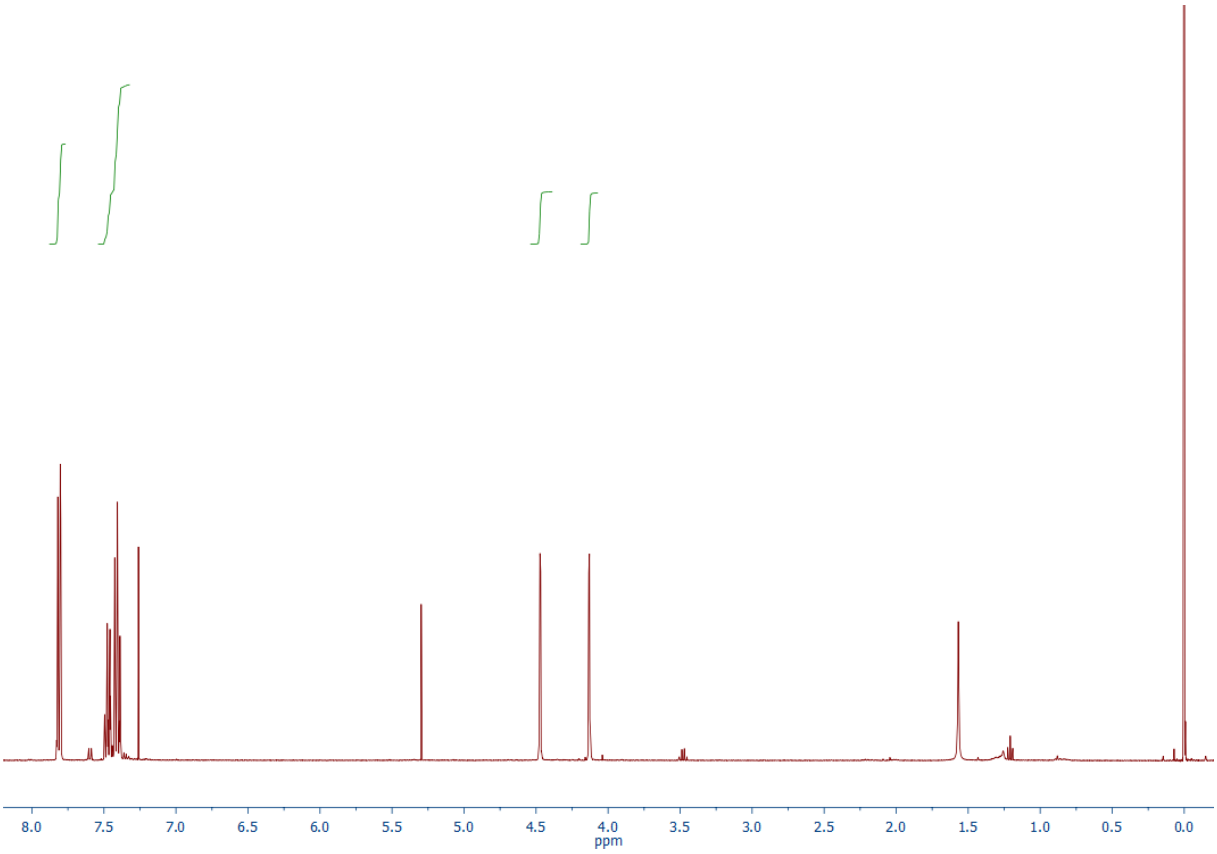

Figure S60 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **15**

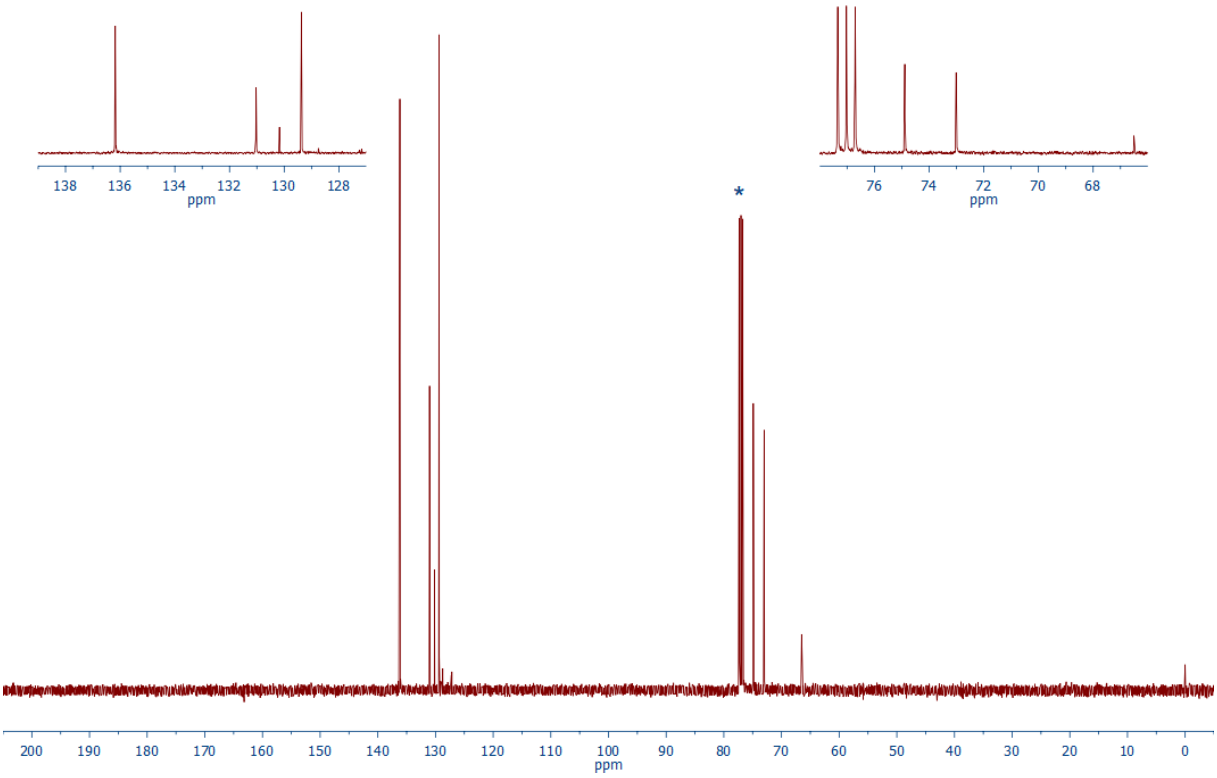

Figure S61 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **15**

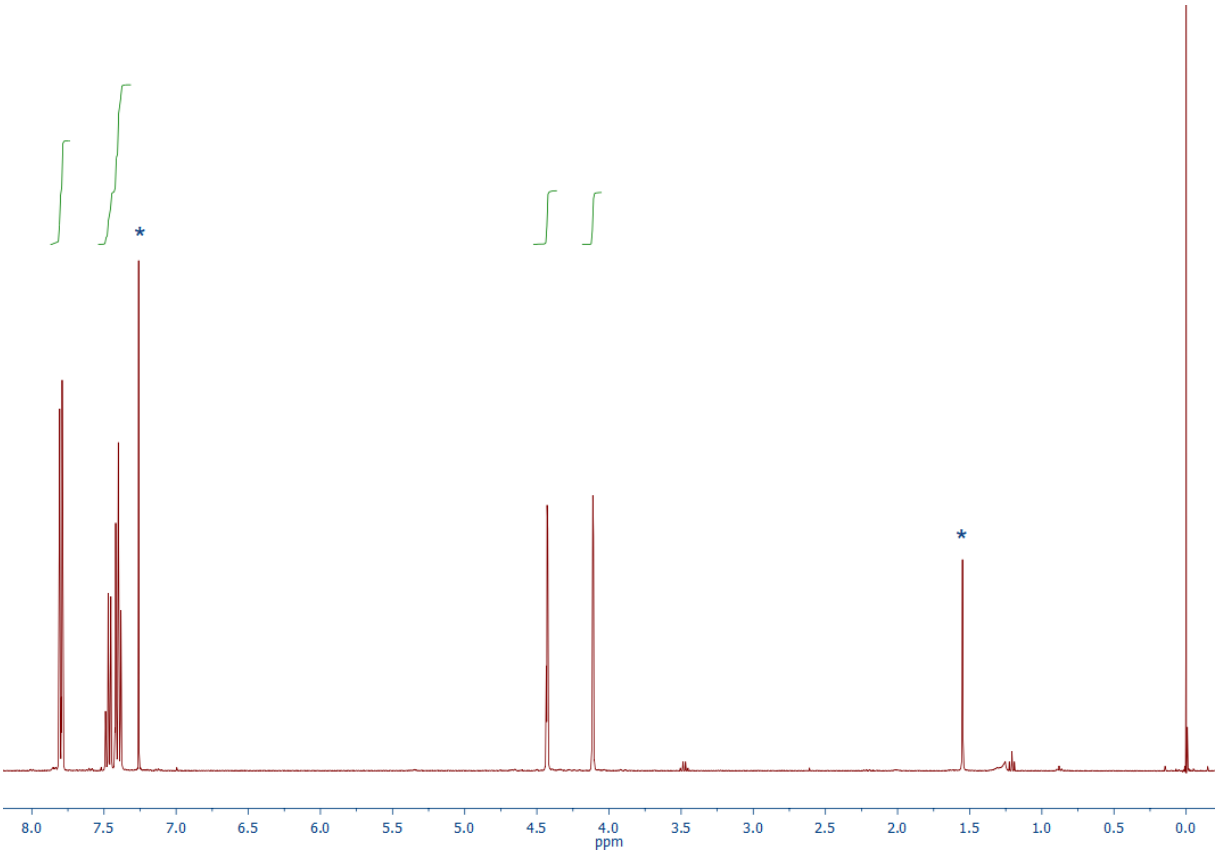

Figure S62 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **16**

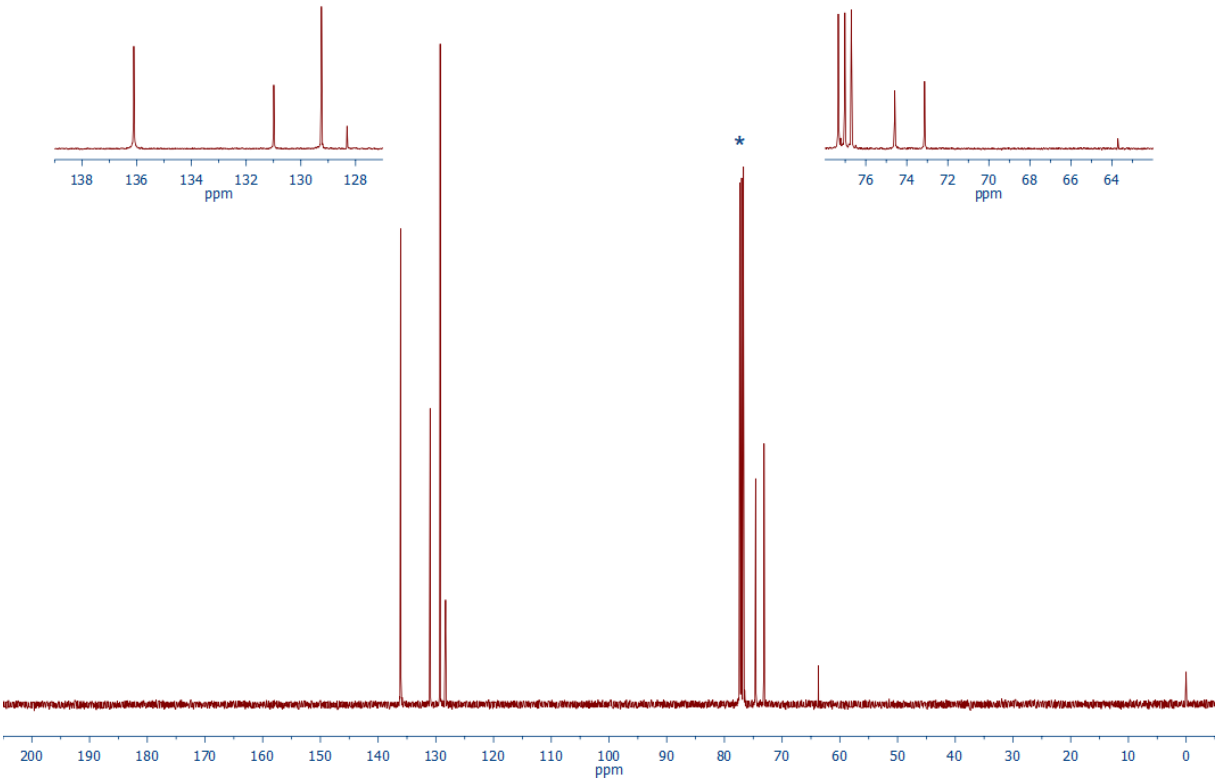

Figure S63 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **16**

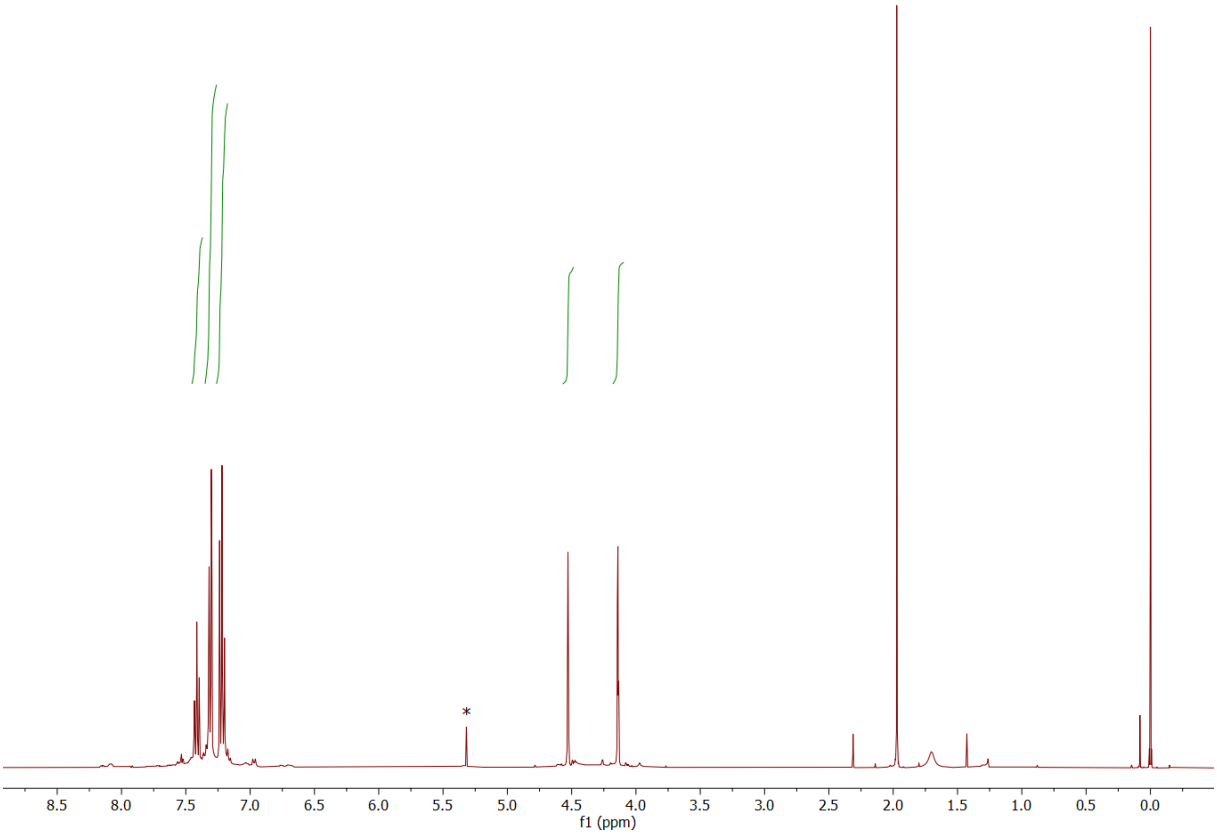

Figure S64 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **17a**

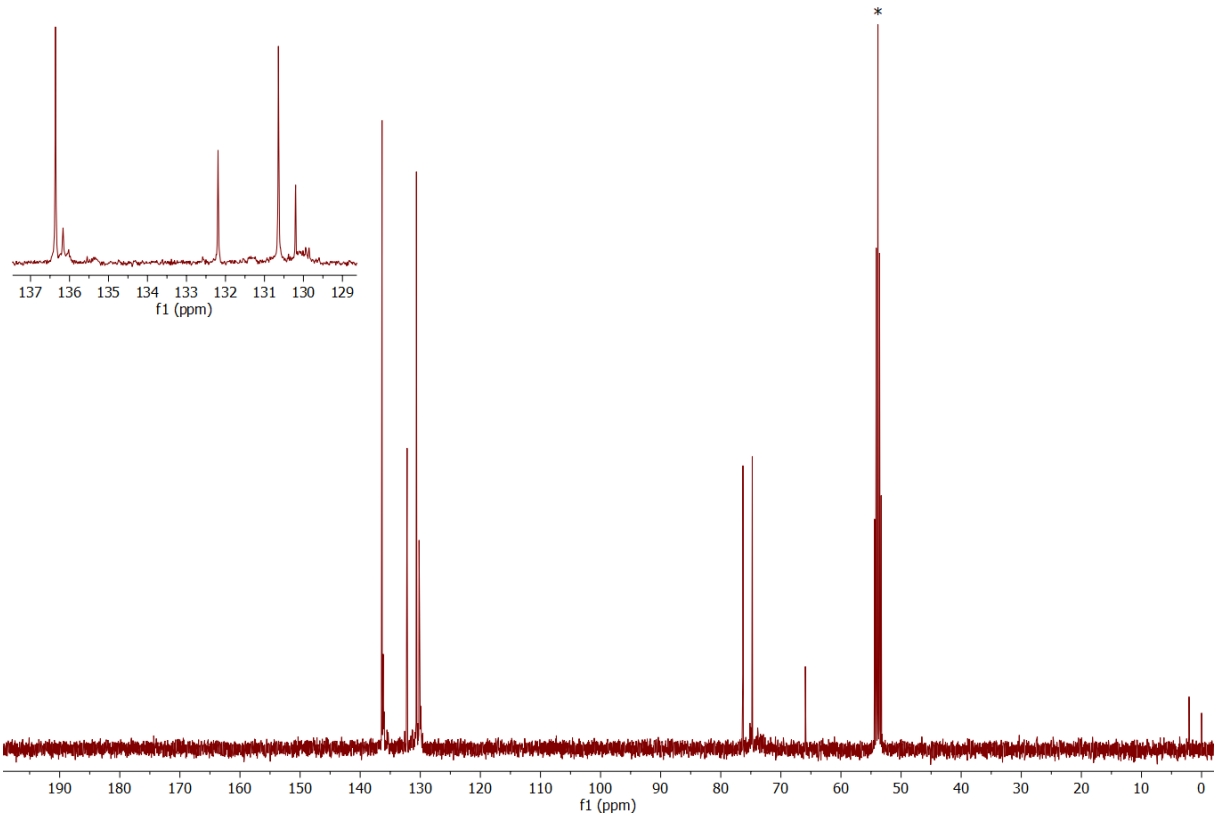

Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **17a**

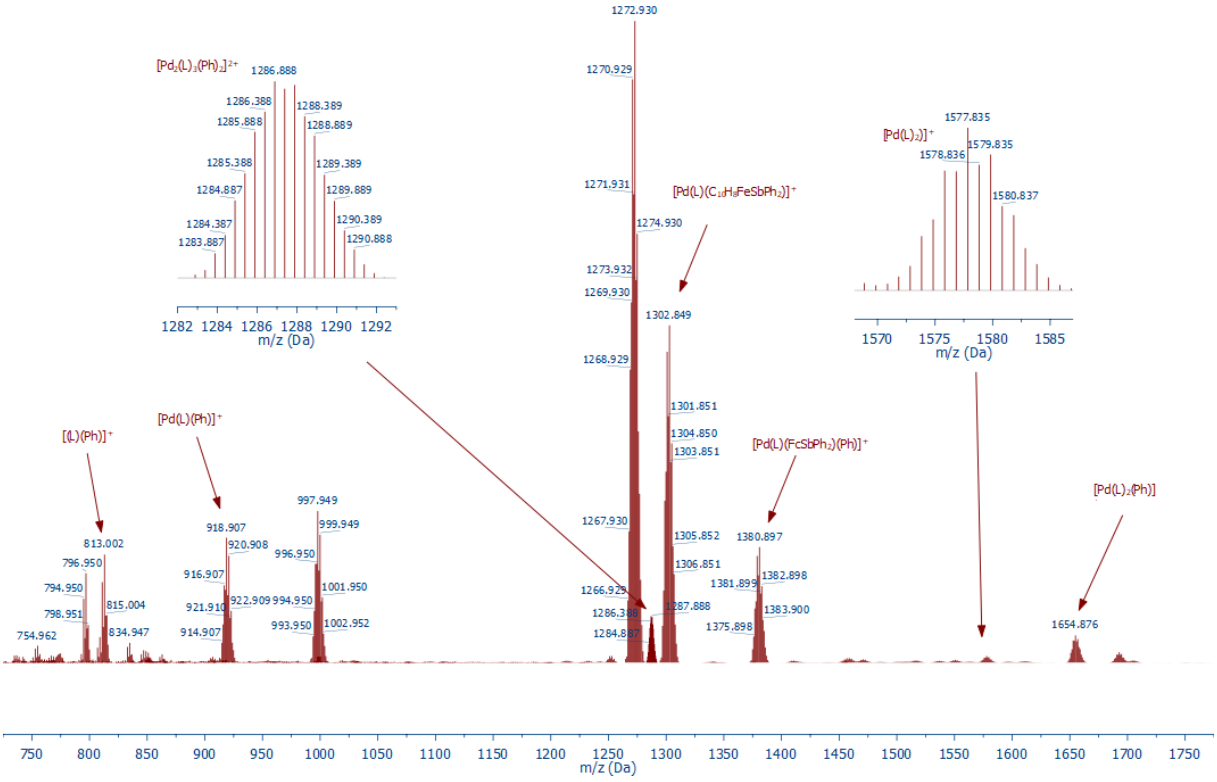

Figure S66 ESI+ HRMS spectrum of **17a**

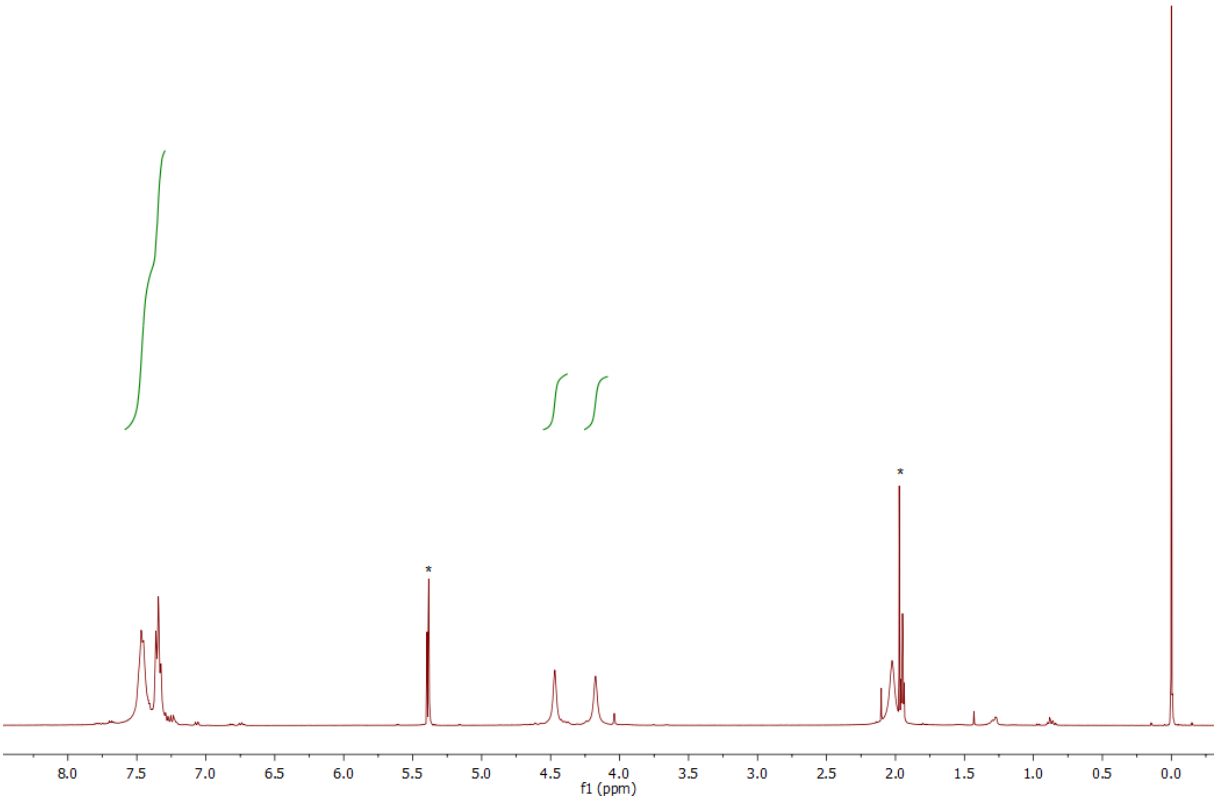

Figure S67. *In situ* ^{1}H NMR spectrum (399.95 MHz, CD_2Cl_2/CD_3CN = 1/1) of **17b**

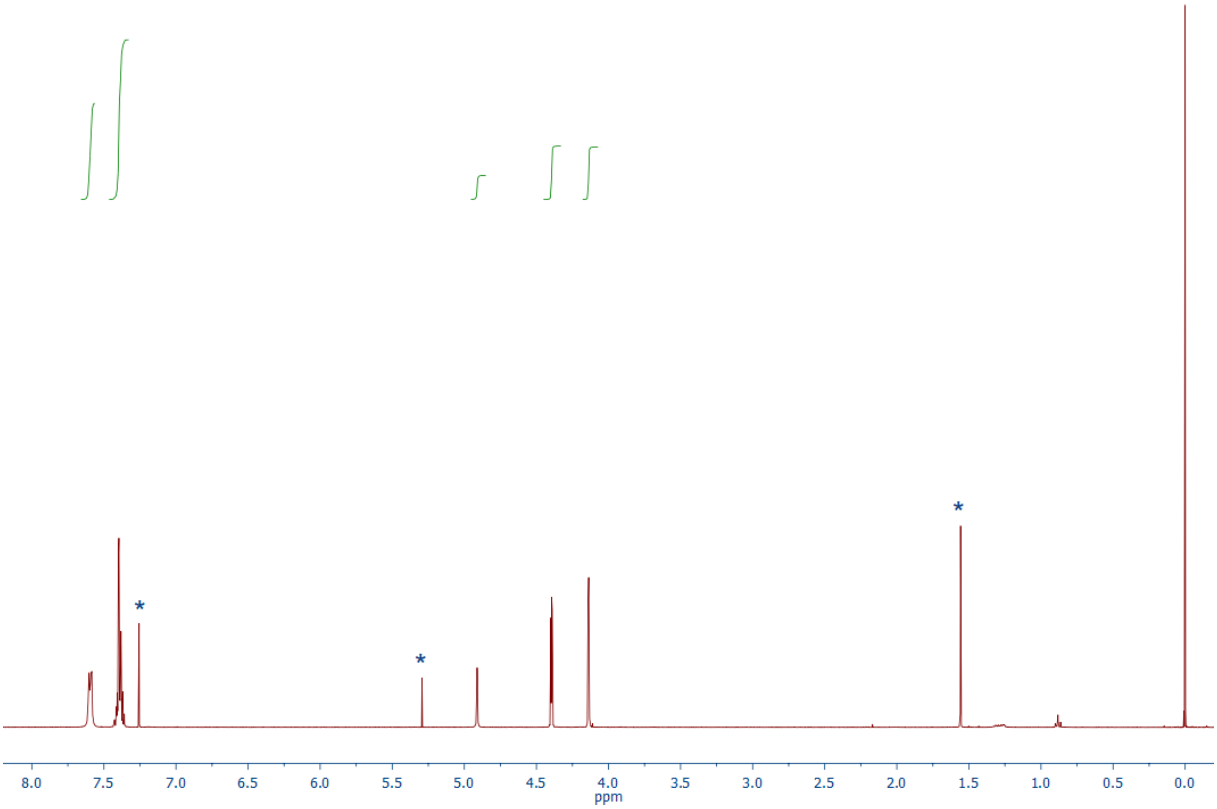

Figure S68 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **18**

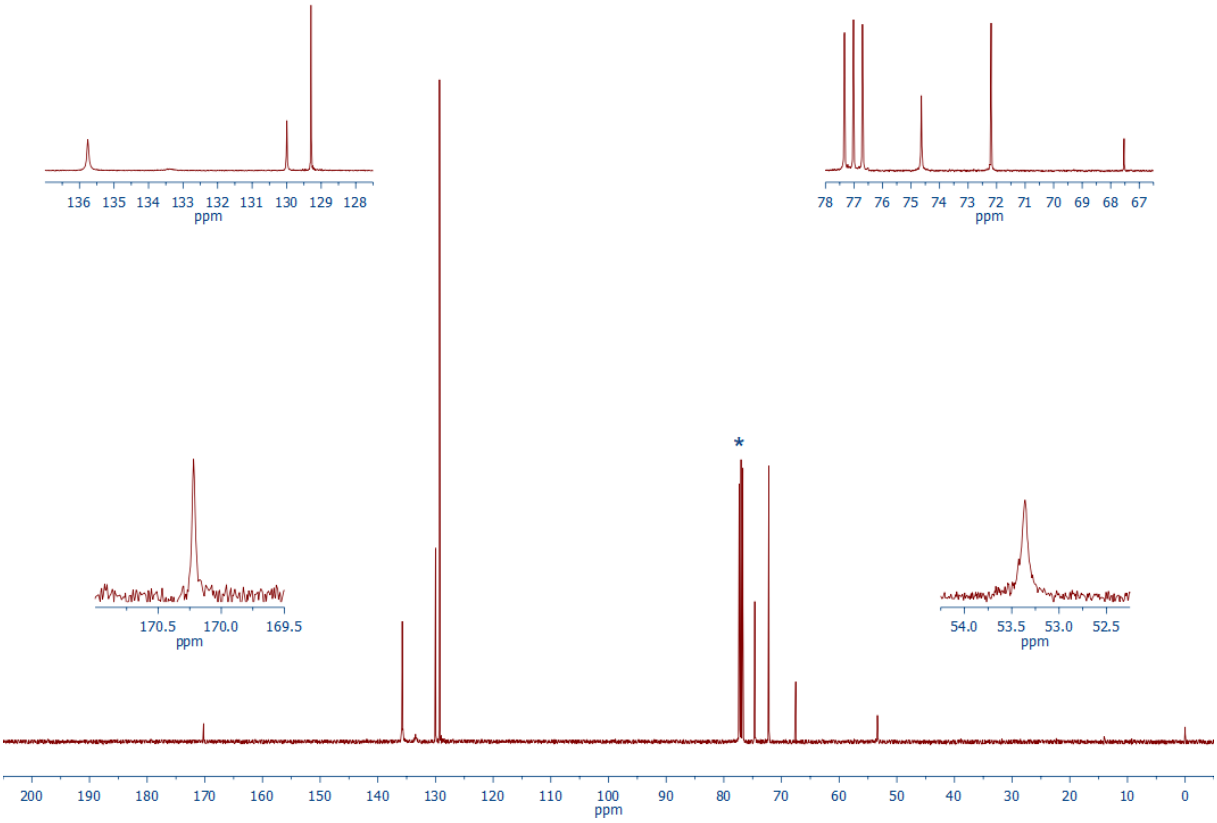

Figure S69 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **18**

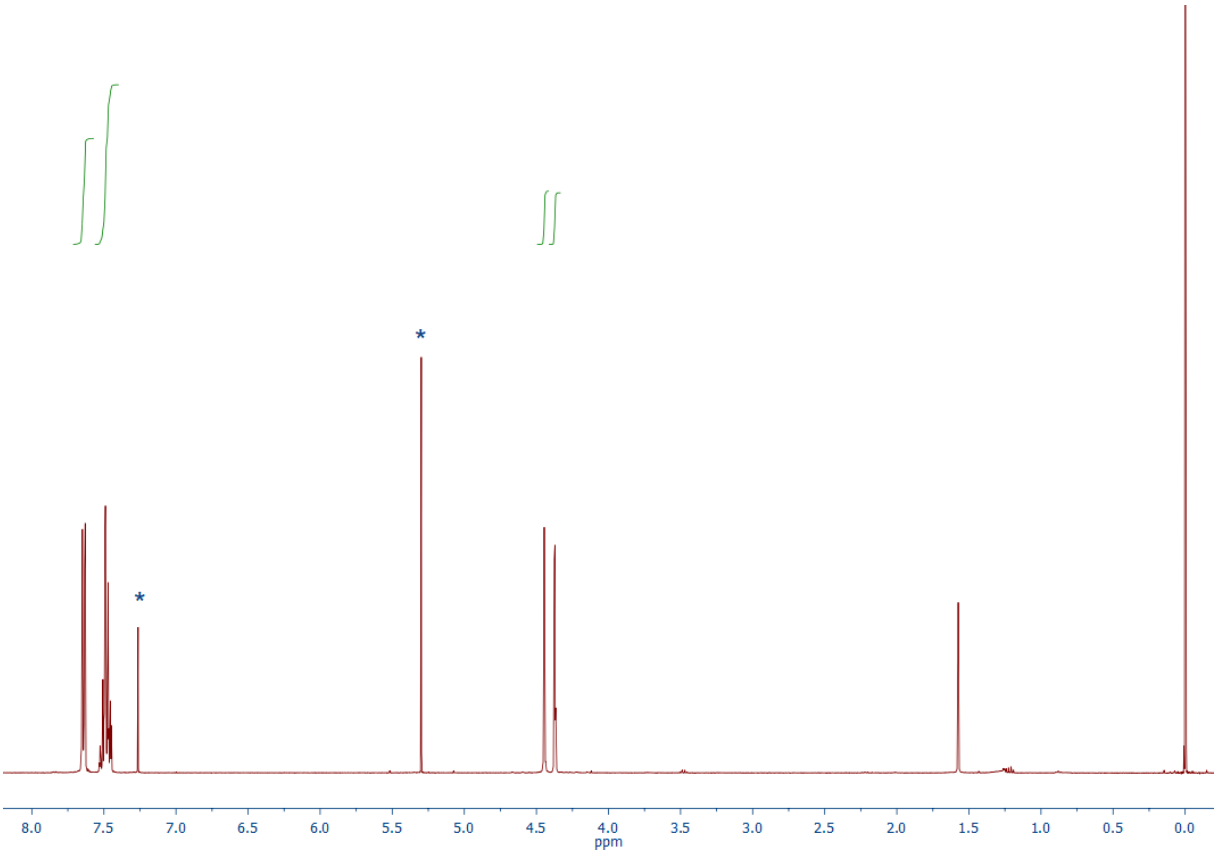

Figure S70 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **19**

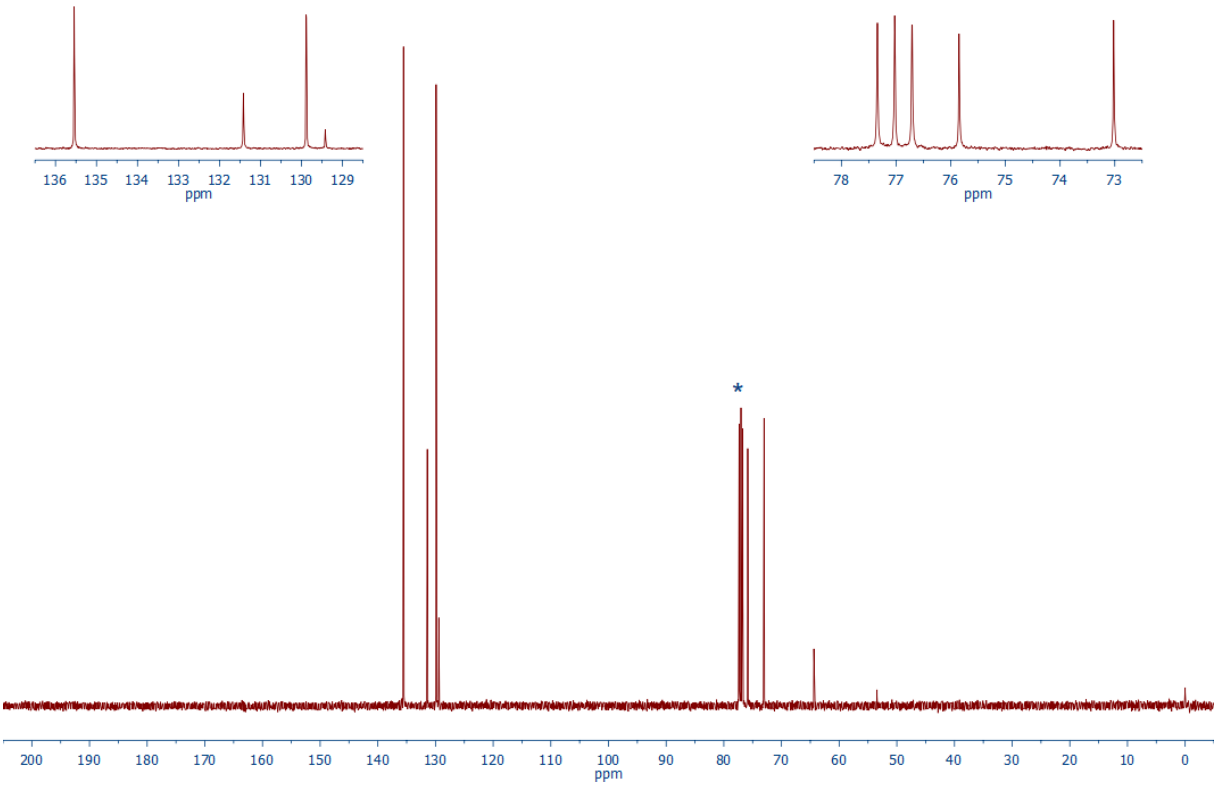

Figure S71 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **19**

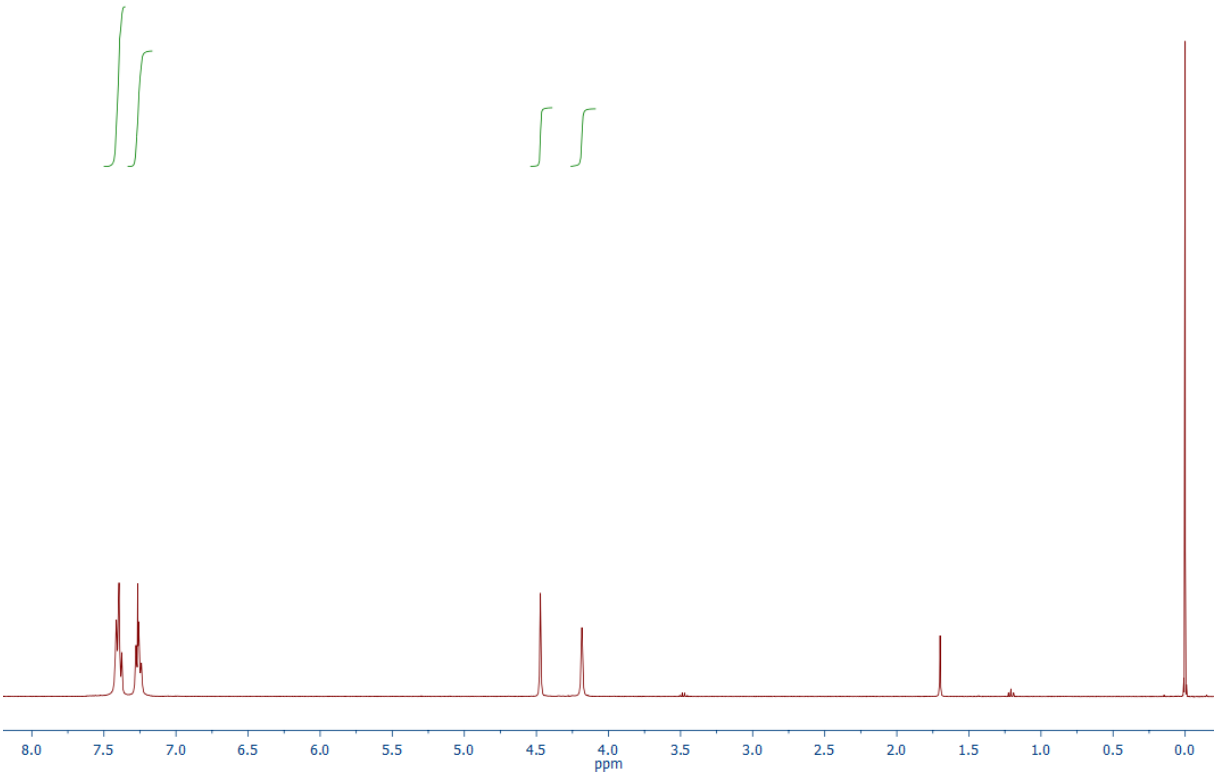

Figure S72 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **20a**

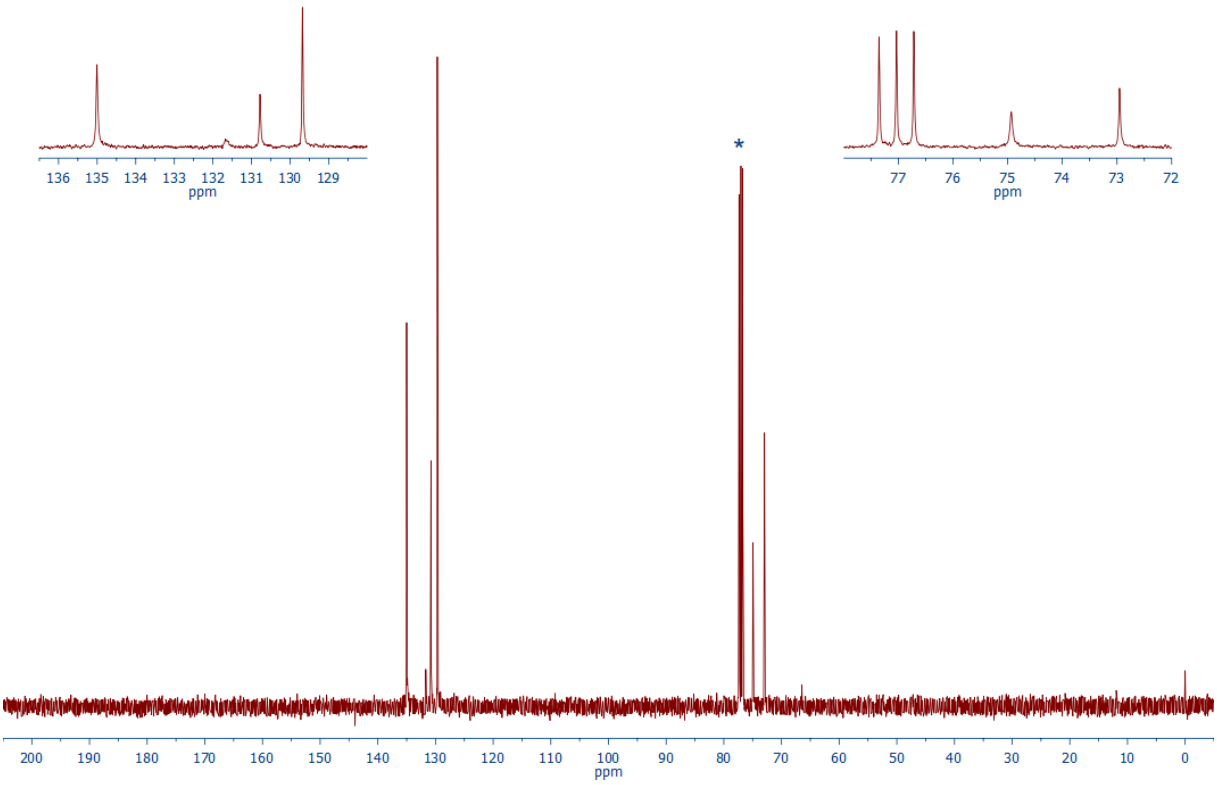

Figure S73 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **20a**

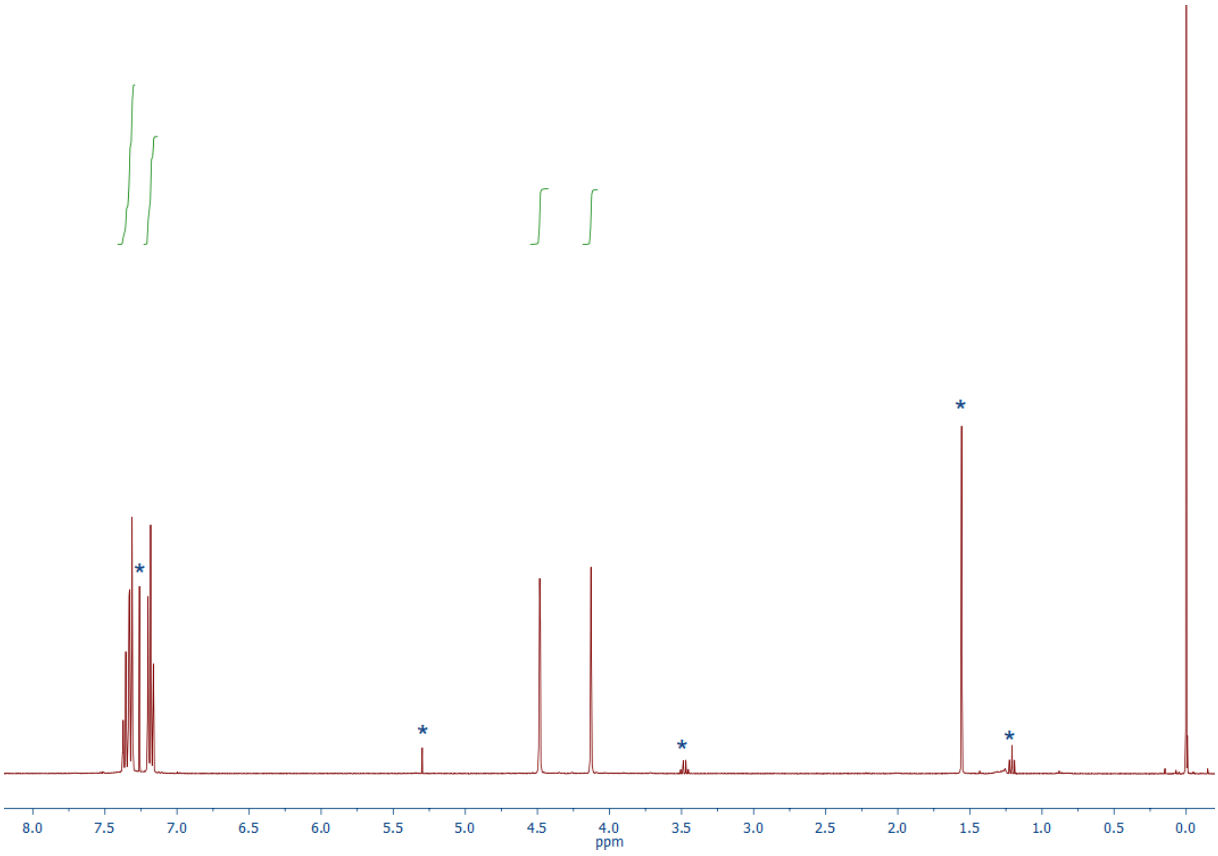

Figure S74 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **20b**

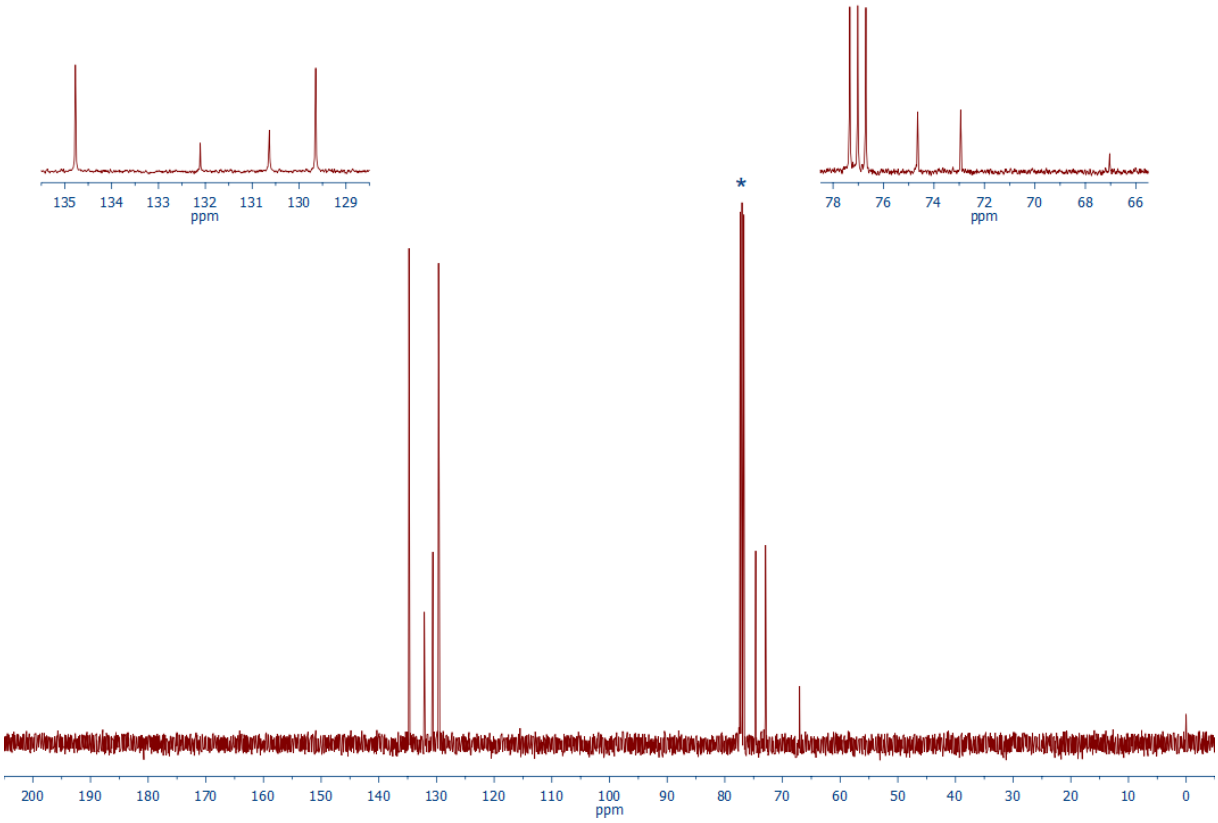

Figure S75 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **20b**

DFT CALCULATIONS

DFT calculations were performed using the Gaussian 16 program package.[14] The geometry optimizations were started from atomic coordinates determined by X-ray diffraction analysis using PBE0[15] density functional in conjunction with the Stuttgart effective core potential[16] used for metal atoms (Fe, Sb) and the def2-TZVP[17] basis set for the remaining elements (C, H) with added Grimme's D3 dispersion correction.[18] Orbital composition analysis based on natural atomic orbitals (NAO)[19] was performed using the Multiwfn software package (version 3.7).[20] Molecular orbitals were visualized using the Avogadro programme.[21]

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