Supporting Information

for

Synthesis, reactivity and coordination behaviour of a ferrocene phosphinostibine and intramolecular interactions in its P(V) and Sb(V) derivatives

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Content

Experimental

Materials and methods

If not stated otherwise, the syntheses were performed under a nitrogen atmosphere using standard Schlenk techniques. Chlordiphenylstibine,[1] **4**,[2] and [AuCl(tht)][3] (tht = tetrahydrothiophene) were prepared by following the procedures reported in the literature. Other chemicals were purchased from Sigma–Aldrich and TCI and were used without additional purification. Dry and deoxygenated dichloromethane and tetrahydrofuran were obtained from an in-house PureSolv MD5 solvent purification system (Innovative Technology, USA). Toluene was dried over sodium metal and distilled under nitrogen. Solvents used for workup and crystallisation (analytical grade) were purchased from Lach-Ner (Czech Republic) and used as received.

NMR spectra were acquired at 25 °C on a Varian UNITY Inova 400 spectrometer. Chemical shifts (δ/ppm) are expressed relative to internal tetramethylsilane (^{1}H and ^{13}C NMR) and external 85% aqueous H_3PO_4 (^{31}P NMR). FTIR spectra were measured on a Thermo Scientific IS50 instrument over the 400-4000 cm^{-1} range. Electrospray ionisation mass spectra (ESI MS) were recorded with a Compact QTOF-MS spectrometer (Bruker Daltonics) for 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 applicable) was verified by NMR analysis.

Syntheses

Preparation of $Cy_2PfcSbPh_2$ (3). A two-necked, oven-dried flask (50 mL), equipped with a stirring bar and a nitrogen inlet, was charged with **4** (1.61 g, 3.5 mmol), thoroughly purged with nitrogen, and sealed with a rubber septum. Anhydrous tetrahydrofuran (14 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 (1.5 mL of 2.5 M, 3.7 mmol) was slowly introduced and the resulting mixture was stirred for 30 min. Then, a precooled solution of chlorodiphenylstibine (1.41 g, 4.5 mmol) in tetrahydrofuran (7 mL) was added slowly *via* a cannula. The reaction mixture was stirred at −78 °C for 30 min and then at room temperature overnight. On the following day, the cloudy orange mixture was diluted with ethyl acetate (20 mL) and saturated aqueous $NaHCO_3$ (10 mL), and transferred to a separatory funnel. The organic phase was washed with brine (20 mL), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The crude product was taken up with dichloromethane, preadsorbed on silica gel by evaporation, and purified by column chromatography over silica gel, using cyclohexane-ethyl acetate (3:1) as the eluent. The single orange band was collected and evaporated, leaving an orange oil, which was recrystallized by adding boiling heptane (20 mL) and slow cooling to −18 °C. The solid product was decanted, washed with cold pentane (2× 5 mL), and dried under reduced pressure. Yield of **3**: 1.31 g (57 %), pale yellow solid.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.92-1.39 (m, 10 H, Cy), 1.59-1.98 (m, 12 H, Cy), 4.01 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.07 (vq, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.17 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.32 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 7.26-7.35 (m, 6 H, Ph), 7.43-7.52 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 26.43 (CH_2 of Cy), 27.30 (d, J_{CP} = 5 Hz, CH_2 of Cy), 27.40 (d, J_{CP} = 7 Hz, CH_2 of Cy), 30.24 (d, J_{CP} = 9 Hz, CH_2 of Cy), 30.36 (d, J_{CP} = 7 Hz, CH_2 of Cy), 33.51 (d, $^1J_{CP}$ = 12 Hz, CH of Cy), 69.13 (C^{ipso} of C_5H_4Sb), 70.06 (d, J_{CP} = 3 Hz, CH of C_5H_4P), 71.95 (d, J_{CP} = 11 Hz, CH of C_5H_4P), 73.09 (CH of C_5H_4Sb), 75.30 (CH of C_5H_4Sb), 77.03 (d, $^1J_{CP}$ = 17 Hz, C^{ipso} of C_5H_4P), 128.41 (CH of Ph), 128.58 (CH of Ph), 136.16 (CH of Ph), 138.58 (C^{ipso} of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ −7.5 (s, PCy_2). ESI+ MS: *m/z* 657.1 (M^+). Anal. Calc. for $C_{34}H_{40}FePSb$ (657.3): C 62.13, H 6.13%. Found: C 62.20, H 6.04%.

Synthesis of $Cy_2PfcSbPh_2$·BH_3 (3·BH_3). A solution of BH_3·Me_2S in tetrahydrofuran (0.45 mL of 2.5 M solution, 0.9 mmol, 1.5 eq.) was added to **3** dissolved in dichloromethane (394.3 mg, 0.60 mmol in 12 mL). After stirring for 1.5 h, the orange reaction mixture was diluted with methanol (0.25 mL) to destroy the excess borane. After gas evolution subsided (approximately 5 min), the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography over silica gel, eluting with dichloromethane-hexane (3:2). The major orange band was collected, and evaporated under reduced pressure, leaving an orange residue, which was crystallised by dissolving in dichloromethane (2 mL) and adding boiling heptane (13.5 mL). The mixture was boiled briefly to remove the most dichloromethane and slowly cooled down to −18 °C. The crystalline solid was decanted, washed with pentane (3× 3 mL), and dried under reduced pressure. Yield: 365.9 mg (91%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.10-1.04 (br m, 3 H, BH_3), 1.07-1.40 (m, 10 H, Cy), 1.61-1.97 (m, 12 H, Cy), 4.11 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.22 (vq, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.23-4.26 (m, 2 H, CH of fc), 4.54 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 7.28-7.35 (m, 6 H, Ph), 7.44-7.51 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 25.94 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.87 (CH_2 of Cy), 26.97 (CH_2 of Cy; Note: the signal overlaps with the resonance at δ_C 26.99), 26.99 (CH_2 of Cy), 27.23 (d, J_{CP} = 2 Hz, CH_2 of Cy), 32.55 (d, $^1J_{CP}$ = 34 Hz, CH of Cy), 68.94 (d, $^1J_{CP}$ = 56 Hz, C^{ipso} of C_5H_4P), 70.30 (C^{ipso} of C_5H_4Sb), 71.25 (d, J_{CP} = 7 Hz, CH of C_5H_4P), 72.30 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 73.73 (CH of C_5H_4Sb), 75.96 (CH of C_5H_4Sb), 128.55 (CH of Ph), 128.66 (CH of Ph), 136.16 (CH of Ph), 138.41 (C^{ipso} of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ 24.3 (br d, $P(BH_3)Cy_2$). ESI+ MS: *m/z* 669.3 ($[M - H]^+$). Anal. Calc. for $C_{34}H_{43}BFePSb$ (671.1): C 60.85, H 6.46%. Found: C 60.93, H 6.45%.

Synthesis of $Cy_2P(O)fcBr$ (4O). In the air, a flask was charged with **4** (533 mg, 1.2 mmol), and acetone (60 mL) was introduced. The yellow solution was cooled to 0 °C. Then, hydrogen peroxide (0.5 mL of 30% solution, ≈4.9 mmol) was added dropwise under stirring. The mixture was stirred at 0 °C for 10 min and then at ambient temperature for 20 min. The reaction mixture was quenched by adding saturated aqueous sodium thiosulfate (2 mL) and then concentrated under reduced pressure. The orange residue was taken up with dichloromethane (20 mL) and transferred to a separatory funnel. The organic phase was washed successively with water and brine (20 mL each), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The solid residue was redissolved in boiling heptane (20 mL). The solution was treated with charcoal and filtered. The filtrate was slowly cooled to −18 °C to produce a crystalline solid, which was decanted, washed with cold pentane (3× 2 mL), and dried under reduced pressure. Yield: 358 mg (65%), yellow needles.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.13-1.52 (m, 10 H, Cy), 1.64-2.19 (m, 12 H, Cy), 4.33 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.42 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.45 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.53 (vt, J' = 1.9 Hz, 2 H, CH of fc). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.76 (d, J_{CP} = 3 Hz, CH_2 of Cy), 25.98 (CH_2 of Cy), 26.35 (d, J_{CP} = 3 Hz, CH_2 of Cy), 26.60 (d, J_{CP} = 4 Hz, CH_2 of Cy), 26.72 (d, J_{CP} = 4 Hz, CH_2 of Cy), 37.24 (d, $^1J_{CP}$ = 70 Hz, CH of Cy), 69.15 (CH of C_5H_4Br), 71.55 (CH of C_5H_4Br), 73.45 (d, J_{CP} = 10 Hz, CH of C_5H_4P), 74.03 (d, $^1J_{CP}$ = 94 Hz, C^{ipso} of C_5H_4P), 74.19 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 78.15 (C^{ipso} of C_5H_4Br). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 45.6 (s, $P(O)Cy_2$). ESI+MS: m/z 398.1 ($[M - Br + H]^+$), 477.0 ($[M + H]^+$), 499.0 ($[M + Na]^+$). Anal. Calc. for $C_{22}H_{30}BrFeOP$ (477.2): C 55.37, H 6.34%. Found: C 55.67, H 6.17%.

Synthesis of $Cy_2P(O)fcSbPh_2$ (3O). A two-necked, oven-dried flask equipped with a magnetic stirring bar, a septum, and a nitrogen inlet was charged with **4O** (358 mg, 0.75 mmol) and thoroughly purged with nitrogen. Dry tetrahydrofuran (10 mL) was introduced to dissolve the solid educt, and the solution was cooled to −78 °C in a dry ice/ethanol bath. A solution of *n*-BuLi in hexanes (0.33 mL of 2.5 M solution, 0.83 mmol) was introduced dropwise, causing the colour of the mixture to turn red. After stirring at −78 °C for 30 min, a pre-cooled solution of chlorodiphenylstibine (304 mg, 0.98 mmol) in tetrahydrofuran (10 mL) was added slowly to the reaction mixture, which was kept stirring at −78 °C for another 1 h and then at room temperature overnight. The reaction mixture was quenched by adding saturated aqueous $NaHCO_3$ (20 mL), transferred into a separatory funnel, and extracted with ethyl acetate (20 mL). The organic phase was washed with brine (15 mL), dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The orange-brown oily residue was purified by column chromatography over silica gel using ethyl acetate-methanol (100:1 → 50:1) as the eluent. The yellow band was collected (avoiding collecting the tail) and evaporated under reduced pressure. The residue was evaporated several times from pentane to give an orange gum, which was stored for a prolonged time in a vacuum desiccator to yield the product. Yield: 230 mg (45%), orange powdery solid.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.10-1.48 (m, 10 H, Cy), 1.61-2.04 (m, 12 H, Cy), 4.13 (vt, J' = 1.7 Hz, 2 H, CH of fc), 4.25 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.28 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.63 (vt, J' = 1.7 Hz, 2 H, CH of fc), 7.28-7.35 (m, 6 H, Ph), 7.45-7.51 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.63 (d, J_{CP} = 3 Hz, CH_2 of Cy), 25.97 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.29 (d, J_{CP} = 3 Hz, CH_2 of Cy), 26.62 (d, J_{CP} = 4 Hz, CH_2 of Cy), 26.74 (d, J_{CP} = 4 Hz, CH_2 of Cy), 37.26 (d, $^1J_{CP}$ = 69 Hz, CH of Cy), 70.34 (C^{ipso} of C_5H_4Sb), 71.26 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 71.76 (d, J_{CP} = 10 Hz, CH of C_5H_4P), 72.86 (d, $^1J_{CP}$ = 95 Hz, C^{ipso} of C_5H_4P; Note: partial overlap with signal at 73.33 ppm), 73.33 (CH of C_5H_4Sb), 75.84 (CH of C_5H_4Sb), 128.56 (CH of Ph), 128.67 (CH of Ph), 136.15 (CH of Ph), 138.34 (C^{ipso} of Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 45.9 (s, P(O)Cy_2). ESI+ HRMS: m/z 673.1280 ([M + H]$^+$), calc. 673.1283; 695.1101 ([M + Na]$^+$), calc. 695.1102. Anal. Calc. for $C_{34}H_{40}FeOPSb$ (673.3): C 60.66, H 5.99%. Found: C 60.95, H 6.11%.

Synthesis of $Cy_2P(S)fcSbPh_2$ (3S). A reaction flask was charged with **3** (328.6 mg, 0.50 mmol), elemental sulfur (16.0 mg, 0.50 mmol), and dry toluene (15 mL), and the resulting mixture was heated at reflux for 2.5 h, whereupon the colour of the mixture changed from orange to orange-brown. After cooling, the mixture was evaporated under reduced pressure and the oily residue was purified by column chromatography over silica gel, using dichloromethane-methanol (20:1) as the eluent. The first major orange band was collected and evaporated under reduced pressure. The product was further recrystallised from dichloromethane (3 mL) by adding hot heptane (10 mL) and brief boiling to remove the most of dichloromethane and slow cooling to −18 °C. The separated crystalline solid was decanted, washed with pentane (3× 3 mL), and dried under reduced pressure. Yield: 250.6 mg (73%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.07-1.46 (m, 10 H, Cy), 1.62-2.03 (m, 12 H, Cy), 4.14 (vt, J' = 1.7 Hz, 2 H, CH of fc), 4.25 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.29 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.60 (vt, J' = 1.7 Hz, 2 H, CH of fc), 7.28-7.36 (m, 6 H, Ph), 7.44-7.51 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.75 (d, J_{CP} = 3 Hz, CH_2 of Cy), 25.82 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.52 (d, J_{CP} = 3 Hz, CH_2 of Cy), 26.65 (d, J_{CP} = 3 Hz, CH_2 of Cy), 26.77 (d, J_{CP} = 3 Hz, CH_2 of Cy), 37.89 (d, $^1J_{CP}$ = 52 Hz, CH of Cy), 70.51 (C^{ipso} of C_5H_4Sb), 71.12 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 72.18 (d, J_{CP} = 10 Hz, CH of C_5H_4P), 74.09 (CH of C_5H_4Sb), 74.40 (d, $^1J_{CP}$ = 79 Hz, C^{ipso} of C_5H_4P), 76.24 (CH of C_5H_4Sb), 128.53 (CH of Ph), 128.66 (CH of Ph), 136.18 (CH of Ph), 138.52 (C^{ipso} of Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 57.5 (s, P(S)Cy_2). ESI+ MS: m/z 711.1 ([M + Na]$^+$). Anal. Calc. for $C_{34}H_{40}FePSSb$ (689.3): C 59.24, H 5.85%. Found: C 59.00, H 5.56%.

Preparation of [AuCl(1-κ*P*)] (5). A reaction flask was charged successively with **3** (131.5 mg, 0.20 mmol), [AuCl(tht)] (64.1 mg, 0.20 mmol), and dichloromethane (10 mL), and the mixture was stirred in the dark for 70 minutes. The resulting yellow solution was evaporated under reduced pressure and the solid residue was redissolved in dichloromethane (2.0 mL) and precipitated by adding cold pentane (≈15 mL). The turbid mixture was stored in the fridge (4 °C) overnight before the solid product was decanted, washed with cold pentane (3× 2 mL), and dried under reduced pressure. Yield: 166.7 mg (94%), yellow powder.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.09-1.50 (m, 10 H, Cy), 1.64-1.74 (m, 2 H, Cy), 1.75-1.91 (m, 4 H, Cy), 1.92-2.09 (m, 6 H, Cy), 4.15 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.22 (vq, *J*′ = 2.0 Hz, 2 H, CH of fc), 4.28-4.32 (m, 2 H, CH of fc), 4.56 (vt, *J*′ = 1.7 Hz, 2 H, CH of fc), 7.29-7.36 (m, 6 H, Ph), 7.44-7.51 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 25.68 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.57 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.70 (CH_2 of Cy), 29.79 (d, J_{CP} = 2 Hz, CH_2 of Cy), 29.99 (CH_2 of Cy), 34.97 (d, $^{1}J_{CP}$ = 36 Hz, CH of Cy), 68.40 (d, $^{1}J_{CP}$ = 60 Hz, C^{ipso} of C_5H_4P), 70.69 (C^{ipso} of C_5H_4Sb), 71.85 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 72.80 (d, J_{CP} = 11 Hz, CH of C_5H_4P), 74.27 (CH of C_5H_4Sb), 76.42 (CH of C_5H_4Sb), 128.68 (CH of Ph), 128.75 (CH of Ph), 136.17 (CH of Ph), 138.20 (C^{ipso} of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ 42.3 (s, PCy_2). ESI+ MS: *m*/*z* 853.1 ([M – Cl]$^{+}$). Anal. Calc. for $C_{34}H_{40}AuClFePSb$ (889.7): C 45.90, H 4.53%. Found: C 45.88, H 4.38%.

Attempted oxidation of 3 with $SOCl_2$ and SO_2Cl_2. A solution of thionyl chloride (11 μL, 0.15 mmol) or sulfuryl chloride (12 μL, 0.15 mmol) in dichloromethane (2 mL) was added to **3** (65.7 mg, 0.10 mmol) dissolved in the same solvent (5 mL), and the resulting mixture was stirred for 90 min and then evaporated. The orange residue was analysed using ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. In the case of thionyl chloride, the dominant product was **6S** (approximately 56%, based on integration of the ^{31}P{^{1}H} NMR spectra). Additonal signals due to unidentified products were observed at δ_P 66.5 (br s, 40%), 40.0 and 128.4 (together 4%). When sulfuryl chloride was used as the oxidant, two unknown compounds were present in the reaction mixture in an 84:16 ratio: δ_P 67.6 (br s) and 71.4 (br s).

Preparation of $Cy_2PfcSbCl_2Ph_2{\cdot}BH_3$ (6·BH_3). A solution of thionyl chloride (44 μL, 0.60 mmol) in dichloromethane (5 mL) was added to **3**·BH_3 (268.4 mg, 0.40 mmol) dissolved in the same solvent (20 mL). The reaction mixture was stirred for 1.5 h during which time it slightly darkened. The solution was evaporated under reduced pressure and the solid residue was purified by crystallisation from dichloromethane (4 mL) and pentane (25 mL) by cooling to −18 °C. The crystalline product was decanted, washed with pentane, and dried under reduced pressure. The mother liquor was evaporated and recrystallised once again to obtain another batch of the product. The combined yield of **6**·BH_3·0.25CH_2Cl_2 was 205.5 mg (70%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.13-1.04 (br m, 3 H, BH_3), 1.04-1.42 (m, 10 H, Cy), 1.60-2.01 (m, 12 H, Cy), 4.29-4.34 (m, 2 H, CH of fc), 4.39 (vq, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.83 (vt, *J*′ = 1.9 Hz, 2 H, CH of fc), 5.16 (vt, *J*′ = 1.9 Hz, 2 H, CH of fc), 7.51-7.60 (m, 6 H, Ph), 8.22-8.31 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 25.88 (br s, CH_2 of Cy), 26.79 (br s, CH_2 of Cy), 26.90 (d, J_{CP} = 3 Hz, CH_2 of Cy; Note: the signal partly ovelaps with the signal at δ_C 26.93), 26.93 (CH_2 of Cy), 27.22

(d, J_{CP} = 2 Hz, CH_2 of Cy), 32.44 (d, $^1J_{CP}$ = 34 Hz, CH of Cy), 70.99 (d, $^1J_{CP}$ = 54 Hz, C^{ipso} of C_5H_4P), 72.90 (d, J_{CP} = 6 Hz, CH of C_5H_4P), 73.25 (d, J_{CP} = 7 Hz, CH of C_5H_4P), 75.08 (CH of C_5H_4Sb), 76.12 (CH of C_5H_4Sb), 79.76 (C^{ipso} of C_5H_4Sb), 129.45 (CH of Ph), 131.68 (CH of Ph), 133.96 (CH of Ph), 140.93 (C^{ipso} of Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 24.5 (br d, $P(BH_3)Cy_2$). ESI+ MS: *m/z* 687.2 ([M – BH_3 – 2Cl + OCH_3]$^+$). Anal. Calc. for $C_{34}H_{43}BCl_2FePSb{\cdot}0.25CH_2Cl_2$ (763.2): C 53.90, H 5.74%. Found: C 53.82, H 5.78%.

Oxidation of 3·BH_3 with SO_2Cl_2. A solution of sulfuryl chloride (12 μL, 0.15 mmol) in dichloromethane (2 mL) was introduced to a solution of **3**·BH_3 (67.1 mg, 0.10 mmol) in the same solvent (5 mL). The reaction mixture was stirred for 90 min and then evaporated. The orange solid residue was analysed by ^1H and $^{31}P\{^1H\}$ NMR, which revealed the presence of **6**·BH_3 and **6**·BH_2Cl in approximately 75:25 ratio (δ_P 24.5 and 8.4, respectively).

Preparation of $Cy_2P(S)fcSbCl_2Ph_2$ (6S). A solution of sulfuryl chloride (12 μL, 0.15 mmol) in dichloromethane (1 mL) was added to a solution of **3S** (68.9 mg, 0.10 mmol) in the same solvent (3 mL) and the resulting mixture was stirred for 1.5 hours, whereupon it slightly darkened. Next, the mixture was evaporated under reduced pressure and the solid residue was dissolved in dichloromethane (0.7 mL) and crystallized by layering with pentane (7 mL). The crystals, which were deposited after storing the mixture at 4 °C for one week, were decanted, washed with hexane, and dried under reduced pressure. Yield of **6S**·$0.2CH_2Cl_2$: 33.0 mg (43%), orange crystals.

^1H NMR ($CDCl_3$, 399.95 MHz): δ 1.07-1.47 (m, 10 H, Cy), 1.61-2.09 (m, 12 H, Cy), 4.29 (vq, *J*′ = 1.6 Hz, 2 H, CH of fc), 4.47 (vq, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.92 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 5.17 (vq, *J*′ = 1.8 Hz, 2 H, CH of fc), 7.49-7.63 (m, 6 H, Ph), 8.20-8.33 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.69 (d, J_{CP} = 3 Hz, CH_2 of Cy), 25.77 (d, J_{CP} = 1 Hz, CH_2 of Cy), 26.45 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.58 (d, J_{CP} = 1 Hz, CH_2 of Cy), 26.76 (d, J_{CP} = 3 Hz, CH_2 of Cy), 37.80 (d, $^1J_{CP}$ = 52 Hz, CH of Cy), 72.78 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 73.05 (d, J_{CP} = 10 Hz, CH of C_5H_4P), 75.65 (CH of C_5H_4Sb), 76.27 (CH of C_5H_4Sb), 79.84 (C^{ipso} of C_5H_4Sb), 129.44 (CH of Ph), 161.67 (CH of Ph), 133.94 (CH of Ph), 140.95 (C^{ipso} of Ph). The signal due to C^{ipso} of C_5H_4P was obscured by the solvent resonance. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 57.1 (s, $P(S)Cy_2$). ESI+ MS: *m/z* 719.2 ([M – 2Cl + OCH_3]$^+$), 773.1 ([M – 2Cl + 2OCH_3 + Na]$^+$). Anal. Calc. for $C_{34}H_{40}Cl_2FePSSb{\cdot}0.20CH_2Cl_2$ (777.2): C 52.85, H 5.24%. Found: C 52.57, H 5.15%.

Preparation of [AuCl($Cy_2PfcSbCl_2Ph_2$-κ*P*)] (7). A solution of thionyl chloride (6 μL, 0.082 mmol) in dichloromethane (1 mL) was added to a solution of **5** (52.5 mg, 0.055 mmol) in the same solvent (3 mL) and the resulting mixture was stirred in the dark for 1 h. The obtained yellow solution was evaporated and the solid residue was crystallised from dichloromethane (0.6 mL) and hexane (6.5 mL; liquid-phase diffusion). The crystalline solid was decanted, washed with hexane (3× 2 mL), and dried under reduced pressure. Yield: 51.5 mg (96%), orange crystals.

^1H NMR ($CDCl_3$, 399.95 MHz): δ 1.06-1.49 (m, 10 H, Cy), 1.63-2.13 (m, 12 H, Cy), 4.38 (s, 2 H, CH of fc), 4.38 (s, 2 H, CH of fc) (Note: two singlets with practically identical chemical shifts.), 4.84 (vt, J' = 1.9 Hz, 2 H, CH of fc), 5.19 (vt, J' = 1.9 Hz, 2 H, CH of fc), 7.50-7.63 (m, 6 H, Ph), 8.31-8.32 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.62 (CH_2 of Cy), 26.48 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.61 (CH_2 of Cy), 29.77 (d, J_{CP} = 2 Hz, CH_2 of Cy), 29.97 (CH_2 of Cy), 34.76 (d, $^1J_{CP}$ = 36 Hz, CH of Cy), 70.53 (d, $^1J_{CP}$ = 58 Hz, C^{ipso} of C_5H_4P), 73.42 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 73.61 (d, J_{CP} = 10 Hz, CH of C_5H_4P), 75.85 (CH of C_5H_4Sb), 76.39 (CH of C_5H_4Sb), 80.04 (C^{ipso} of C_5H_4Sb), 129.52 (CH of Ph), 131.80 (CH of Ph), 133.96 (CH of Ph), 140.67 (C^{ipso} of Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 41.0 (s, PCy_2). ESI+ MS: *m/z* 907.1 ($[M - 2Cl + OH]^+$), 921.1 ($[M - 2Cl + OCH_3]^+$). Anal. Calc. for $C_{34}H_{40}AuCl_3FePSb$ (960.6): C 42.51, H 4.20%. Found: C 42.30, H 4.04%.

Oxidation of 3 with the stoichiometric amount of *o*-chloranil. A solution of *o*-chloranil (24.6 mg, 0.10 mmol) in dichloromethane (1 mL) was added dropwise to a solution of **3** (65.7 mg, 0.10 mmol) in the same solvent (2 mL). After stirring for 1 h, the orange-brown reaction mixture was evaporated under reduced pressure to dryness. According to $^{31}P\{^1H\}$ NMR analysis, the crude product contained **3** (29%), **8** (29%), and **8O** (42%). Unfortunately, the mixture could not be separated by crystallisation or chromatography. When the reaction was performed at 0.20 mmol scale and under rigorous anhydrous conditions (both reactants were finely ground and dried over P_2O_5 for 48 h, dichloromethane was stored over CaH_2), insoluble $Cy_2P(O_2C_6Cl_4)fcSbPh_2(O_2C_6Cl_4)$ (**9**), the product of twofold oxidation, was formed in addition to the aforementioned products. It was isolated by filtration, washed with dichloromethane, and dried under reduced pressure. Yield: 56.4 mg. Its identity was proven by high-resolution ESI+ MS analysis (*m/z* 1148.8535 ($[M + H]^+$), calc. 1148.8597). Besides, an ion at *m/z* 918.9875 was detected, which can be attributed to $[M + H + O - O_2C_6Cl_4]^+$ (calc. *m/z* 918.9924), a species formed by hydrolysis of phosphorane-stiborane into phosphine oxide-stiborane. The approximate composition of the liquid phase (filtrate) was determined using the $^{31}P\{^1H\}$ NMR spectra as follows: **1** (47%), $Cy_2PfcSbPh_2(O_2C_6Cl_4)$ (26%), and $Cy_2P(O)fcSbPh_2(O_2C_6Cl_4)$ (27%).

Hydrolysis of $Cy_2P(O_2C_6Cl_4)fcSbPh_2(O_2C_6Cl_4)$ (9). A dichloromethane solution of **9** (approximately 10 mg in 10 mL of the solvent) was vigorously shaken in a separatory funnel with deionized water (10 mL) for 5 min. Then, the organic layer was separated, dried over anhydrous magnesium sulfate, and filtered through a PTFE syringe filter (0.45 μm porosity). The filtrate was evaporated under reduced pressure, leaving a yellow solid, which was analysed using ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as pure **8O**.

Preparation of $Cy_2PfcSbPh_2(O_2C_6Cl_4)\cdot BH_3$ (8·BH₃). A solution of *o*-chloranil (25.8 mg, 0.11 mmol) in dichloromethane (1 mL) was added to a solution of **3**·BH_3 (67.2 mg, 0.10 mmol) in the same solvent (2 mL) and the mixture was stirred for 1 h. The orange solution was evaporated and the solid residue was redissolved in dichloromethane (1.5 mL) and crystallised by adding boiling heptane (7.5 mL). The mixture was briefly boiled to remove the most of dichloromethane and slowly cooled to room temperature, whereupon a crystalline solid was deposited. The crystallisation was completed at 4 °C overnight before the separated solid product was isolated by decantation, washed with hexane (3× 3 mL), and dried under reduced pressure. Yield: 85.0 mg (93%), orange crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.10-0.97 (br m, 3 H, BH_3), 1.04-1.37 (m, 10 H, Cy), 1.60-1.92 (m, 12 H, Cy), 4.18 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.29-4.33 (m, 2 H, CH of fc), 4.46 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.80 (vt, J' = 1.9 Hz, 2 H, CH of fc), 7.49-7.61 (m, 6 H, Ph), 7.80-7.88 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 25.84 (d, J_{CP} = 1 Hz, CH_2 of Cy), 26.75 (d, J_{CP} = 5 Hz, CH_2 of Cy), 26.75 (CH_2 of Cy), 26.86 (d, J_{CP} = 7 Hz, CH_2 of Cy), 27.04 (d, J_{CP} = 2 Hz, CH_2 of Cy), 32.24 (d, $^1J_{CP}$ = 34 Hz, CH of Cy), 70.76 (d, $^1J_{CP}$ = 54 Hz, C^{ipso} of C_5H_4P), 70.90 (C^{ipso} of C_5H_4Sb), 71.16 (d, J_{CP} = 6 Hz, CH of C_5H_4P), 72.93 (d, J_{CP} = 7 Hz, CH of C_5H_4P), 75.61 (CH of C_5H_4Sb), 76.04 (CH of C_5H_4Sb), 116.41 (CCl), 120.55 (CCl), 129.55 (CH of Ph), 131.93 (CH of Ph), 134.80 (CH of Ph), 136.42 (C^{ipso} of Ph), 144.47 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ 24.3 (br s, $P(BH_3)Cy_2$). ESI+ MS: *m/z* 687.2 ([M–BH_3 – $O_2C_6Cl_4$ + OCH_3]$^+$), 917.0 ([M + H]$^+$), 939.0 ([M + Na]$^+$). Anal. Calc. for $C_{40}H_{43}BCl_4FeO_2PSb$ (917.0): C 52.39, H 4.73%. Found: C 52.07, H 4.43%.

Preparation of $Cy_2PfcSbPh_2(O_2C_6Cl_4)$ (8). A Schlenk tube was charged with **8**·BH_3 (64.4 mg, 0.070 mmol), dabco (31.4 mg, 0.28 mmol) and dry tetrahydrofuran (3 mL), and the mixture was degassed by three freeze-pump-thaw cycles. The reaction mixture was then stirred at 70 °C for 30 h, during which time its colour changed from orange to orange-brown. After cooling, the mixture was evaporated under reduced pressure and the residue was purified by chromatography over a short silica gel column (5 cm), eluting with cyclohexane-ethyl acetate (1:1). A single yellow band was collected and evaporated under reduced pressure, leaving oily crude product, which was further purified by liquid-phase diffusion of hexane (5.4 mL) into a solution of the crude product in ethyl acetate (0.3 mL). The crystallisation was completed in the fridge (4 °C). After two weeks, the crystalline product was decanted, washed with hexane (3×2 mL), and dried under reduced pressure. Yield **8**·0.9C_6H_{14}: 75.1 mg (77%), orange microcrystalline solid.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.94-1.22 (m, 10 H, Cy), 1.52-1.83 (m, 12 H, Cy), 4.30 (vt, J' = 1.8 Hz, 2 H, CH of fc), 4.36 (vq, J' = 1.6 Hz, 2 H, CH of fc), 4.44 (vt, J' = 1.8 Hz, 2 H, CH of fc), 4.72 (vt, J' = 1.8 Hz, 2 H, CH of fc), 7.40-7.50 (m, 6 H, Ph), 7.75-7.86 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 26.22 (CH_2 of Cy), 27.30 (d, J_{CP} = 9 Hz, CH_2 of Cy), 27.63 (d, J_{CP} = 10 Hz, CH_2 of Cy), 29.60 (d, J_{CP} = 7 Hz, 2× CH_2 of Cy), 34.96 (d, $^1J_{CP}$ = 9 Hz, CH of Cy), 70.80 (d, $^3J_{CP}$ = 3 Hz, CH of C_5H_4P), 72.25 (d, $^3J_{CP}$ = 2 Hz, CH of C_5H_4Sb), 73.25 (d, $^2J_{CP}$ = 8 Hz, CH of C_5H_4P), 74.01 (d, $^1J_{CP}$ = 3 Hz, C^{ipso} of C_5H_4P), 75.85 (CH of C_5H_4Sb), 84.85 (d, $^2J_{CP}$ = 22 Hz, C^{ipso} of C_5H_4Sb), 116.38 (d, $^4J_{CP}$ = 2 Hz, CCl), 119.88 (CCl), 129.18 (CH of Ph), 130.85 (CH of Ph), 134.19 (CH of Ph), 140.67 (d, $^2J_{CP}$ = 13 Hz, C^{ipso} of Ph), 145.18 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ 2.2 (s, PCy_2). ESI+MS: *m/z* = 687.2 ([M –

$O_2C_6Cl_4$ + $OCH_3]^+$), 903.0 ([M + H]$^+$). Anal. Calc. for $C_{40}H_{40}Cl_4FeO_2PSb·0.90C_6H_{14}$ (980.7): C 55.60, H 5.41%. Found: C 55.43, H 5.19%.

Preparation of $Cy_2P(O)fcSbPh_2(O_2C_6Cl_4)$ (8O). A solution of *o*-chloranil (49.2 mg, 0.20 mmol) in dichloromethane (1.5 mL) was added to **3** (65.7 mg, 0.10 mmol) dissolved in wet dichloromethane (4 mL + 4 drops of deionized water). After stirring for 2 h, the orange-brown reaction mixture was dried with anhydrous magnesium sulfate, filtered through a PTFE syringe filter (0.45 μm pore size), and the filtrate was evaporated under reduced pressure. Tetrachloropyrocatechol was removed by layering the solution of the crude product in chloroform (1.5 mL) with hexane (10 mL) in a test tube. After 4 days, the yellow solution was removed, leaving tetrachloropyrocatechol as a brown glassy residue deposited on the walls of the test tube. The solution was evaporated to dryness and crystallised by liquid phase diffusion of hexane (5 mL) into a solution of the crude product in chloroform (0.5 mL) over several days. The solid was decanted, washed with pentane (2× 2 mL), and dried under reduced pressure. Yield of **8O**·$0.35CHCl_3$: 81.2 mg (85%), yellow microcrystalline solid.

^1H NMR (CD_2Cl_2, 399.95 MHz): δ 0.69-1.41 (m, 10 H, Cy), 1.48-1.97 (m, 12 H, Cy), 4.54 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 4.64 (br s, 2 H, CH of fc), 4.75 (very br s, 2 H, CH of fc), 4.88 (very br s, 2 H, CH of fc), 7.28-7.46 (br m, 6 H, Ph), 7.71 (br s, 4 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.58 MHz): δ 26.18 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.77 (br d, J_{CP} = 13 Hz, 3×CH_2 of Cy; Note: an overlap of three signals), 27.14 (d, J_{CP} = 14 Hz, CH_2 of Cy), 38.33 (d, $^1J_{CP}$ = 69 Hz, CH of Cy), 68.06 (d, $^1J_{CP}$ = 92 Hz, C^{ipso} of C_5H_4P), 72.17 (CH of C_5H_4Sb), 73.17 (br s, CH of C_5H_4P), 74.37 (d, J_{CP} = 11 Hz, CH of C_5H_4P), 76.14 (CH of C_5H_4Sb), 86.18 (C^{ipso} of C_5H_4Sb), 116.37 (CCl), 118.94 (CCl), 128.61 (CH of Ph), 129.71 (CH of Ph), 134.25 (br s, CH of Ph), 146.35 (br s, C^{ipso} of Ph), 147.04 (CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 161.90 MHz): δ 53.8 (s, $P(O)Cy_2$). ESI+ MS: *m/z* 689.1 ([M – $O_2C_6Cl_4$ + OH]$^+$), 919.0 ([M + H]$^+$). Anal. Calc. for $C_{40}H_{40}Cl_4FeO_3PSb·0.35CHCl_3$ (960.9): C 50.44, H 4.23%. Found: C 50.56, H 4.04%.

Preparation of $Cy_2P(S)fcSbPh_2(O_2C_6Cl_4)$ (8S). A solution of *o*-chloranil (22.3 mg, 0.091 mmol) in dichloromethane (1 mL) was introduced to **3S** (62.6 mg, 0.091 mmol) dissolved in the same solvent (3 mL). The resulting mixture was stirred for 1 h and evaporated under reduced pressure. The solid residue was dissolved in dichloromethane (1.5 mL) and recrystallised by adding boiling heptane (7.5 mL). The mixture was briefly boiled to remove the most of dichloromethane and slowly cooled to room temperature, whereupon it deposited a crystalline solid. The crystallisation was completed at 4 °C overnight and the separated product was isolated by decantation, washed with pentane (3× 2 mL), and dried under reduced pressure. Yield: 70.8 mg (83%), orange crystals.

^1H NMR ($CDCl_3$, 399.95 MHz): δ 1.02-1.40 (m, 10 H, Cy), 1.59-2.00 (m, 12 H, Cy), 4.29 (vq, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.33 (vq, *J*′ = 1.7 Hz, 2 H, CH of fc), 4.50 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 4.85 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 7.47-7.58 (m, 6 H, Ph), 7.79-7.87 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.57 (d, J_{CP} = 3 Hz, CH_2 of Cy), 25.71 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.40 (CH_2 of Cy), 26.53 (CH_2 of Cy), 26.66 (d, J_{CP} = 3 Hz, CH_2 of Cy), 37.67 (d, $^1J_{CP}$ = 52 Hz, CH of Cy), 71.05 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 72.84 (C^{ipso} of C_5H_4Sb), 72.94 (d, J_{CP} = 10 Hz, CH of C_5H_4P), 75.79 (d, $^1J_{CP}$ = 76 Hz, C^{ipso} of C_5H_4P), 75.96 (CH of C_5H_4Sb), 76.00 (CH of C_5H_4Sb), 116.40 (CCl), 120.40 (CCl), 129.45 (CH of Ph), 131.71 (CH of Ph), 134.73 (CH of Ph), 137.18 (C^{ipso} of Ph), 144.56 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 57.0 (s, P(S)Cy_2). ESI+ MS: *m/z* 719.1 ([M – $O_2C_6Cl_4$ + OCH_3]$^+$), 957.0 ([M + Na]$^+$). Anal. Calc. for $C_{40}H_{40}Cl_4FeO_2PSSb$ (935.2): C 51.37, H 4.31%. Found: C 51.22, H 4.17%.

Preparation of [AuCl(Cy_2PfcSbPh_2($O_2C_6Cl_4$)-κ*P*)] (10). A solution of *o*-chloranil (12.4 mg, 0.05 mmol) in dichloromethane (1 mL) was added to a solution of complex **5** (44.7 mg, 0.05 mmol) in the same solvent (2 mL) and the resulting mixture was stirred for 1 h. The orange solution was evaporated under reduced pressure and the solid residue was redissolved in dichloromethane (0.5 mL), filtered through a PTFE syringe filter (0.45 μm pore size), and the filtrate was added dropwise into hexane (10 mL). The separated solid was filtered off, washed with hexane (3× 2 mL), and dried under reduced pressure. Yield: 38.0 mg (67%), yellow solid.

^1H NMR ($CDCl_3$, 399.95 MHz): δ 1.05-1.44 (m, 10 H, Cy), 1.63-2.09 (m, 12 H, Cy), 4.17 (vq, *J*′ = 2.0 Hz, 2 H, CH of fc), 4.36-4.40 (m, 2 H, CH of fc), 4.51 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 4.79 (vt, *J*′ = 1.9 Hz, 2 H, CH of fc), 7.52-7.62 (m, 6 H, Ph), 7.79-7.87 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.58 (CH_2 of Cy), 26.45 (d, J_{CP} = 3 Hz, CH_2 of Cy), 26.45 (d, J_{CP} = 4 Hz, CH_2 of Cy), 29.67 (br s, 2×CH_2 of Cy; Note: an overlap of two signals), 34.60 (d, $^1J_{CP}$ = 36 Hz, CH of Cy), 70.23 (d, $^1J_{CP}$ = 58 Hz, C^{ipso} of C_5H_4P), 71.45 (C^{ipso} of C_5H_4Sb), 71.78 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 73.19 (d, J_{CP} = 11 Hz, CH of C_5H_4P), 75.82 (CH of C_5H_4Sb), 76.87 (CH of C_5H_4Sb), 116.44 (CCl), 120.66 (CCl), 129.69 (CH of Ph), 132.10 (CH of Ph), 134.80 (CH of Ph), 136.13 (C^{ipso} of Ph), 144.39 (CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 41.1 (s, PCy_2). Anal. Calc. for $C_{40}H_{40}AuCl_5FeO_2PSb$ (1135.6): C 42.31, H 3.55%. Found: C 42.32, H 3.45%.

Preparation of [{(μ-P,*Sb*)-3}$(AuCl)_2$] (11). In air, solid [AuCl(tht)] (64.0 mg, 0.20 mmol) was added to **3** (65.6 mg, 0.10 mmol) dissolved in dichloromethane (20 mL). After stirring in the dark for 40 minutes, the yellow solution was evaporated under reduced pressure. The solid residue was redissolved in dichloromethane (3 mL) and the product was precipitated by adding hexane (≈15 mL). After the mixture was stored at 4 °C overnight, the separated solid was decanted, washed with hexane (3× 2 mL), and dried under reduced pressure. Yield: 102.0 mg (92%), yellow powder.

^1H NMR ($CDCl_3$, 399.95 MHz): δ 1.08-1.51 (m, 10 H, Cy), 1.64-1.74 (m, 2 H, Cy), 1.76-1.93 (m, 4 H, Cy), 1.94-2.11 (m, 6 H, Cy), 4.39 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 4.44 (vq, *J*′ = 1.9 Hz, 2 H, CH of fc), 4.46-4.49 (m, 2 H, CH of fc), 4.68 (vt, *J*′ = 1.8 Hz, 2 H, CH of fc), 7.45-7.55 (m, 6 H, Ph), 7.60-7.67 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.58 MHz): δ 25.63 (d, J_{CP} = 1 Hz, CH_2 of Cy), 26.53 (CH_2 of Cy), 26.66 (CH_2 of Cy), 29.43 (CH_2 of Cy), 29.85 (CH_2 of Cy), 35.06 (d, $^1J_{CP}$ = 35 Hz, CH of Cy), 72.20 (d, J_{CP} = 7 Hz, CH of C_5H_4P), 73.84 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 74.88 (CH of C_5H_4Sb), 76.09 (CH of C_5H_4Sb), 129.86 (CH of Ph), 131.39 (br s, CH of Ph), 133.99 (C^{ipso} of Ph), 135.57 (CH of Ph). The signals due to C^{ipso} of C_5H_4P and C_5H_4Sb were not observed. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.90 MHz): δ 40.7 (s, PCy_2). ESI+ MS: *m/z* 853.2 ([M − AuCl − Cl]$^+$), 1511.2 ([Au(**3**)$_2$]$^+$). Anal. Calc. for $C_{34}H_{40}Au_2Cl_2FePSb$ (1122.1): C 36.39, H 3.59%. Found: C 36.63, H 3.53%.

Preparation of [RuCl(η^6-*p*-cymene)(3-κ^2*P,Sb*)][PF$_6$] (12). In air, solid [RuCl(μ-Cl)(η^6-*p*-cymene)]$_2$ (30.6 mg, 0.050 mmol) was added to a solution of **3** (65.7 mg, 0.10 mmol) in dichloromethane (5 mL). After dissolution, solid Na[PF$_6$] (84 mg, 0.5 mmol) was introduced, followed by acetone (3 mL). The resulting mixture was stirred in the dark for 1 d to give a turbid orange solution, which was evaporated under reduced pressure. The solid residue was extracted with dichloromethane (3× 2 mL) and the solution was filtered through a PTFE syringe filter (0.45 μm porosity). The filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography over silica gel using dichloromethane-methanol (50:1) as the eluent. A single red band was collected and evaporated under reduced pressure. The solid residue was redissolved in chloroform (12 mL) and the solution was concentrated under reduced pressure to approximately 5 mL and layered with diethyl ether (10 mL) in a test tube. The crystalline solid, which separated over several days, was decanted, washed with diethyl ether (3× 3 mL), and dried under reduced pressure. Yield of **12**·0.9$CHCl_3$: 66.0 mg (56%), dark red crystals.

^1H NMR (CD_2Cl_2, 399.95 MHz): δ 0.99-1.77 (m, 13 H, Cy), 1.29 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.34 (d, 3 H, $^3J_{HH}$ = 7.0 Hz, CH*Me*$_2$), 1.80-1.95 (m, 3 H, Cy), 1.89 (s, 3 H, Me), 1.96-2.09 (m, 2 H, Cy), 2.16-2.45 (m, 3 H, Cy), 2.48-2.61 (m, 1 H, Cy), 2.76 (sept, 1 H, $^3J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 4.29 (dvt, *J*´ = 2.4, 1.2 Hz, 1 H, CH of fc), 4.33-4.36 (m, 1 H, CH of fc), 4.36-4.39 (m, 2 H, CH of fc), 4.42 (vtd, *J*´ = 2.5, 1.2 Hz, 1 H, CH of fc), 4.48 (dvt, *J*´ = 2.4, 1.1 Hz, 1 H, CH of fc), 4.50 (tvt, *J*´ = 2.6, 1.3 Hz, 1 H, CH of fc), 5.06 (dvt, *J*´ = 2.7, 1.3 Hz, 1 H, CH of fc), 5.73 (dd, *J*´ = 6.4, 1.4 Hz, 1 H, C_6H_4), 5.90 (br d, *J*´ = 6.0 Hz, 1 H, C_6H_4), 6.18 (ddd, *J*´ = 4.8, 3.6, 1.2 Hz, 1 H, C_6H_4), 6.33 (br d, *J*´ = 6.2 Hz, 1 H, C_6H_4), 7.37-7.60 (m, 8 H, Ph), 7.61-7.67 (m, 2 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.58 MHz): δ 18.72 (Me), 21.73 (CH*Me*$_2$), 22.14 (CH*Me*$_2$), 26.17 (d, J_{CP} = 13 Hz, CH_2 of Cy), 26.29 (br s, CH_2 of Cy), 26.50 (br s, CH_2 of Cy), 26.93 (d, J_{CP} = 8 Hz, CH_2 of Cy), 27.63 (d, J_{CP} = 7 Hz, CH_2 of Cy), 27.48 (d, J_{CP} = 9 Hz, CH_2 of Cy), 27.97 (CH_2 of Cy), 28.42 (d, J_{CP} = 8 Hz, CH_2 of Cy), 29.33 (CH_2 of Cy), 31.62 (*C*HMe$_2$), 33.97 (d, J_{CP} = 3 Hz, CH_2 of Cy), 38.51 (d, $^1J_{CP}$ = 28 Hz, CH of Cy), 43.25 (d, $^1J_{CP}$ = 23 Hz, CH of Cy), 70.02 (d, J_{CP} = 5 Hz, CH of C_5H_4P), 71.19 (CH of C_5H_4Sb), 71.47 (C^{ipso} of C_5H_4Sb), 72.69 (CH of C_5H_4Sb), 73.39 (d, J_{CP} = 2 Hz, CH of C_5H_4P), 73.81 (d, J_{CP} = 6 Hz, CH of C_5H_4P), 75.03 (CH of C_5H_4Sb), 77.04 (d, J_{CP} = 42 Hz, C^{ipso} of C_5H_4P), 79.64 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 79.66 (CH of C_5H_4Sb), 85.22 (CH of C_6H_4), 85.67 (d, J_{CP} = 9 Hz, CH of C_6H_4), 88.73 (CH of C_6H_4), 91.74 (d, J_{CP} = 4 Hz, CH of C_6H_4), 95.02 (C^{ipso} of C_6H_4), 125.87 (C^{ipso} of C_6H_4), 129.50 (CH of Ph), 129.97 (CH of Ph), 130.98 (CH of Ph), 131.41 (CH of Ph), 132.59 (C^{ipso} of Ph), 134.60 (C^{ipso} of Ph), 135.96 (CH of Ph), 136.15 (CH of Ph). $^{31}P\{^1H\}$ NMR

(CD_2Cl_2, 161.90 MHz): δ –141.7 (sept, $^1J_{PF}$ = 710 Hz, PF_6), 40.8 (s, PCy_2). ESI+ MS: *m/z* 929.1 ([M – PF_6]$^+$); ESI– MS: *m/z* 145.0 ([PF_6]$^-$). Anal. Calc. for [$C_{44}H_{54}$ClFeRuSbP][PF_6]·0.90$CHCl_3$ (1180.4): C 45.69, H 4.69%. Found: C 45.55, H 4.43%.

Preparation of [RhCl(η^5-C_5Me_5)(3-κ^2*P,Sb*)]Cl (13a). In air, a solution of [RhCl(μ-Cl)(η^5-C_5Me_5)]$_2$ (15.5 mg, 0.025 mmol) in dichloromethane (2.0 mL) was added to a solution of **3** (32.9 mg, 0.050 mmol) in the same solvent (1.0 mL). After stirring in the dark for 2 h, the red reaction mixture was evaporated under reduced pressure. The solid residue was dissolved in chloroform (1 mL) and layered with hexane (9 mL). Crystallisation by liquid-phase diffusion over several days afforded orange-red crystals, which were decanted, washed with hexane (3× 2 mL) and dried under reduced pressure. Yield of **13a**·2.7$CHCl_3$: 57.2 mg (89%), orange-red crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.14-2.34 (m, 22 H, Cy), 1.81 (d, 15 H, $^4J_{HP}$ = 2.9 Hz, C_5Me_5), 4.05 (dvt, *J*′ = 2.4, 1.2 Hz, 1 H, CH of fc), 4.15-4.20 (br m, 1 H, CH of fc), 4.30-4.36 (br m, 2 H, CH of fc), 4.46 (vtd, *J*′ = 2.5, 1.0 Hz, 1 H, CH of fc), 4.53-4.58 (br m, 1 H, CH of fc), 4.84 (dvt, *J*′ = 2.4, 1.1 Hz, 1 H, CH of fc), 5.25-5.30 (br m, 1 H, CH of fc), 7.30-7.45 (m, 3 H, Ph), 7.52-7.65 (m, 7 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 11.47 (C_5*Me*$_5$), 25.44 (d, J_{CP} = 13 Hz, CH_2 of Cy), 25.81 (d, J_{CP} = 6 Hz, 2× CH_2 of Cy; Note: an overlap of two signals), 26.59 (d, J_{CP} = 11 Hz, CH_2 of Cy), 26.61 (CH_2 of Cy), 26.69 (d, J_{CP} = 8 Hz, CH_2 of Cy), 27.27 (d, J_{CP} = 13 Hz, CH_2 of Cy), 27.50 (d, J_{CP} = 8 Hz, CH_2 of Cy), 28.76 (CH_2 of Cy), 34.55 (d, J_{CP} = 4 Hz, CH_2 of Cy), 35.89 (d, $^1J_{CP}$ = 20 Hz, CH of Cy), 35.89 (d, $^1J_{CP}$ = 25 Hz, CH of Cy), 69.95 (d, J_{CP} = 5 Hz, CH of C_5H_4P), 70.56 (CH of C_5H_4Sb), 72.41 (br s, C^{ipso} of C_5H_4Sb), 72.77 (d, J_{CP} = 2 Hz, CH of C_5H_4P), 72.82 (CH of C_5H_4Sb), 73.25 (d, J_{CP} = 6 Hz, CH of C_5H_4P), 75.78 (CH of C_5H_4Sb), 77.80 (CH of C_5H_4Sb), 78.03 (d, $^1J_{CP}$ = 43 Hz, C^{ipso} of C_5H_4P; Note: the signal partly overlaps with the signal at $δ_C$ 77.80), 78.35 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 103.82 (dd, $^1J_{CRh}$ = 6 Hz, $^2J_{CP}$ = 2 Hz, *C*$_5$Me$_5$), 129.01 (CH of Ph), 129.64 (d, $^2J_{CRh}$ = 4 Hz, C^{ipso} of Ph; Note: the signals partly overlaps with the signal at $δ_C$ 129.69), 129.69 (CH of Ph), 130.80 (CH of Ph), 131.40 (CH of Ph), 133.04 (br s, C^{ipso} of Ph), 136.08 (CH of Ph), 137.24 (CH of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ 40.5 (d, $^1J_{PRh}$ = 136 Hz, PCy_2). ESI+ MS: *m/z* 931.1 ([M – Cl]$^+$). Anal. Calc. for [$C_{44}H_{55}$ClFePRh-Sb]Cl·2.7$CHCl_3$ (1288.6): C 43.53, H 4.51%. Found: C 43.47, H 4.37%.

Preparation of [RhCl(η^5-C_5Me_5)(1-κ^2*P,Sb*)][PF_6] (13b). In air, a reaction flask was charged with [RhCl(μ-Cl)0*(η^5-C_5Me_5)]$_2$ (30.9 mg, 0.050 mmol) and **3** (65.7 mg, 0.10 mmol), and the solid educts were dissolved in a mixture of dichloromethane (7.5 mL) and acetone (5.0 mL). After dissolution, solid Na[PF_6] (84 mg, 0.5 mmol) was added and the reaction mixture was stirred in the dark for 1 d. The turbid orange solution was evaporated under reduced pressure and the residue was taken up with dichloromethane (≈5 mL). The suspension was filtered through a PTFE syringe filter (0.45 μm porosity) and the filtrate was evaporated under reduced pressure. The solid residue was dissolved in chloroform (3 mL), and crystallised by liquid-phase diffusion of diethyl ether (7 mL) over several days. The crystalline product was decanted, washed with diethyl ether, and dried under vacuum. Yield of **13b**·1.1$CHCl_3$: 97.2 mg (81%), orange-red crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.13-2.35 (m, 22 H, Cy), 1.72 (d, 15 H, $^4J_{HP}$ = 2.9 Hz, C_5Me_5), 4.04 (dvt, *J′* = 2.4, 1.1 Hz, 1 H, CH of fc), 4.15-4.20 (br m, 1 H, CH of fc), 4.29-4.35 (br m, 2 H, CH of fc), 4.45 (vtd, *J′* = 2.5, 1.0 Hz, 1 H, CH of fc), 4.52-4.58 (m, 1 H, CH of fc), 4.84 (dvt, *J′* = 2.4, 1.1 Hz, 1 H, CH of fc), 5.26-5.30 (br m, 1 H, CH of fc), 7.30-7.44 (m, 3 H, Ph), 7.53-7.64 (m, 7 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 10.94 ($C_5\mathit{Me}_5$), 25.43 (d, J_{CP} = 13 Hz, CH_2 of Cy), 25.81 (d, J_{CP} = 11 Hz, 2× CH_2 of Cy; Note: an overlap of two signals), 26.52 (d, J_{CP} = 11 Hz, CH_2 of Cy), 26.56 (CH_2 of Cy), 26.64 (d, J_{CP} = 8 Hz, CH_2 of Cy), 27.24 (d, J_{CP} = 14 Hz, CH_2 of Cy), 27.48 (d, J_{CP} = 8 Hz, CH_2 of Cy), 28.76 (d, J_{CP} = 2 Hz, CH_2 of Cy), 34.53 (d, J_{CP} = 4 Hz, CH_2 of Cy), 35.87 (d, $^1J_{CP}$ = 20 Hz, CH of Cy), 36.80 (d, $^1J_{CP}$ = 25 Hz, CH of Cy), 69.59 (d, J_{CP} = 5 Hz, CH of C_5H_4P), 70.50 (CH of C_5H_4Sb), 72.47 (br s, C^{ipso} of C_5H_4Sb), 72.72 (d, J_{CP} = 3 Hz, CH of C_5H_4P; Note: the signal partly overlaps with the signal at δ_C 72.74), 72.74 (CH of C_5H_4Sb), 73.17 (d, J_{CP} = 6 Hz, CH of C_5H_4P), 75.75 (CH of C_5H_4Sb), 77.79 (CH of C_5H_4Sb), 78.11 (d, $^1J_{CP}$ = 43 Hz, C^{ipso} of C_5H_4P; Note: the signal partly overlaps with the signal at δ_C 78.36), 78.36 (d, J_{CP} = 9 Hz, CH of C_5H_4P), 103.89 (dd, $^1J_{CRh}$ = 6 Hz, $^2J_{CP}$ = 2 Hz, C_5Me_5), 128.96 (CH of Ph), 129.63 (CH of Ph), 129.76 (d, $^2J_{CRh}$ = 4 Hz, C^{ipso} of Ph), 130.74 (CH of Ph), 131.35 (CH of Ph), 133.11 (br s, C^{ipso} of Ph), 136.09 (CH of Ph), 137.24 (CH of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ –143.9 (sept, $^1J_{PF}$ = 712 Hz, PF_6), 40.2 (d, $^1J_{PRh}$ = 136 Hz, PCy_2). ESI+ MS: *m/z* 931.1 ([M – PF_6]$^+$); ESI–MS: *m/z* 145.0 ([PF_6]$^-$). Anal. Calc. for [$C_{44}H_{55}ClFeRhSbP$][PF_6]·1.1$CHCl_3$ (1207.1): C 44.87, H 4.68%. Found: C 44.68, H 4.41%.

Preparation of [$PdCl_2$(1-κ^2*P*,*Sb*)] (14). In air, a solution of **3** (65.7 mg, 0.1 mmol) in dichloromethane (4.0 mL) was added to solid [$PdCl_2$(cod)] (28.6 mg, 0.1 mmol). The resulting red mixture was stirred for 1 h in the dark and subsequently evaporated under reduced pressure. The solid residue was redissolved in dichloromethane (3.0 mL), filtered through a PTFE syringe filter (0.45 μm porosity), and the filtrate was layered with diethyl ether (≈10 mL). The crystals, which developed during several days, were decanted, washed with diethyl ether (3× 2 mL), and dried under reduced pressure. Yield of **14**·1.1CH_2Cl_2: 60.8 mg (66%), red crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 1.02-1.19 (m, 4 H, Cy), 1.21-1.43 (m, 4 H, Cy), 1.54-1.75 (m, 6 H, Cy), 1.80-1.97 (m, 4 H, Cy), 2.25-2.38 (m, 2 H, Cy), 2.51-2.64 (m, 2 H, Cy), 4.14 (vt, *J′* = 1.8 Hz, 2 H, CH of fc), 4.47 (vt, *J′* = 1.8 Hz, 2 H, CH of fc), 4.49 (vq, *J′* = 1.8 Hz, 2 H, CH of fc), 4.51-4.54 (br m, 2 H, CH of fc), 7.35-7.48 (m, 6 H, Ph), 7.92-8.01 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 25.82 (d, J_{CP} = 2 Hz, CH_2 of Cy), 26.61 (d, J_{CP} = 12 Hz, CH_2 of Cy), 26.68 (d, J_{CP} = 14 Hz, CH_2 of Cy), 28.68 (CH_2 of Cy), 30.34 (d, J_{CP} = 2 Hz, CH_2 of Cy), 35.13 (d, $^1J_{CP}$ = 29 Hz, CH of Cy), 65.48 (d, $^3J_{CP}$ = 6 Hz, C^{ipso} of C_5H_4Sb), 73.02 (d, J_{CP} = 7 Hz, CH of C_5H_4P), 72.63 (CH of C_5H_4Sb), 73.72 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 77.18 (CH of C_5H_4Sb), 78.49 (d, $^1J_{CP}$ = 45 Hz, C^{ipso} of C_5H_4P), 129.14 (CH of Ph), 130.67 (CH of Ph), 131.66 (C^{ipso} of Ph), 135.99 (CH of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ

55.4 (s, PCy_2). ESI+ MS: m/z 799.0 ($[M - Cl]^+$), 857.0 ($[M + Na]^+$). Anal. Calc. for $C_{34}H_{40}Cl_2FeP$-$PdSb \cdot 1.1CH_2Cl_2$ (928.0): C 45.43, H 4.58%. Found: C 45.51, H 4.33%.

Preparation of [PtCl$_2$(1-κ^2*P,Sb*)] (15). In air, a solution of **3** (98.6 mg, 0.15 mmol) in dichloromethane (6.0 mL) was introduced to solid [$PtCl_2$(cod)] (56.2 mg, 0.15 mmol), whereupon the orange mixture changed colour to yellow. The mixture was stirred in the dark for 1 h and evaporated under reduced pressure. The solid residue was taken up with dichloromethane (3.5 mL) and the solution was layered with diethyl ether (≈10 mL). The yellow crystalline product, which deposited over several days, was decanted, washed with diethyl ether (3× 2 mL), and dried under reduced pressure. Yield of **15**·0.1CH_2Cl_2: 99.5 mg (71%), yellow crystals.

^{1}H NMR ($CDCl_3$, 399.95 MHz): δ 0.99-1.17 (m, 4 H, Cy), 1.21-1.42 (m, 4 H, Cy), 1.52-1.68 (m, 6 H, Cy), 1.76-1.95 (m, 4 H, Cy), 2.21-2.35 (m, 2 H, Cy), 2.45-2.64 (m, 2 H, Cy), 4.09 (vt, J' = 1.8 Hz, 2 H, CH of fc), 4.41-4.46 (m, 4 H, CH of fc), 4.46-4.50 (br m, 2 H, CH of fc), 7.37-7.49 (m, 6 H, Ph), 7.92-7.99 (m, 4 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.58 MHz): δ 25.95 (d, J_{CP} = 1 Hz, CH_2 of Cy), 26.44 (CH_2 of Cy), 26.57 (d, J_{CP} = 3 Hz, CH_2 of Cy), 28.20 (CH_2 of Cy), 29.71 (d, J_{CP} = 3 Hz, CH_2 of Cy), 33.19 (d, $^1J_{CP}$ = 38 Hz, CH of Cy), 60.72 (C^{ipso} of C_5H_4Sb), 71.90 (d, J_{CP} = 7 Hz, CH of C_5H_4P), 72.86 (CH of C_5H_4Sb; Note: the signal partially overlaps with the signal at δ_C 72.91 ppm), 72.91 (d, J_{CP} = 8 Hz, CH of C_5H_4P), 76.35 (d, $^1J_{CP}$ = 56 Hz, C^{ipso} of C_5H_4P), 76.86 (CH of C_5H_4Sb), 129.03 (CH of Ph), 129.65 (C^{ipso} of Ph), 130.71 (CH of Ph), 135.90 (CH of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.90 MHz): δ 21.6 (s with ^{195}Pt satellites, $^1J_{PPt}$ = 3608 Hz, PCy_2). ESI+ MS: m/z 887.1 ($[M - Cl]^+$), 945.0 ($[M + Na]^+$). Anal. Calc. for $C_{34}H_{40}Cl_2FePPdSb \cdot 0.1CH_2Cl_2$ (931.8): C 43.96, H 4.35%. Found: C 44.04, H 4.34%.

X-ray crystallography

The diffraction data ($\pm h\pm k\pm l$, $2\theta_{max}$ = 55°) were collected with a a Nonius KappaCCD diffractometer equipped with a Bruker ApexII detector (**8S**) or a Bruker D8 VENTURE Kappa Duo diffractometer (all other compounds), both equipped with a Cryostream Cooler (Oxford Cryosystems). Mo Kα radiation (λ = 0.71073 Å) was used in all cases. The structures were solved using direct methods (SHELXT-2014 or 2018[4]) and subsequently refined by a least-squares routine based on F^2 (SHELXL-2014 or 2017[5]). The nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their theoretical positions and refined as riding atoms using the standard parameters implemented in SHELXL.

Dichlorostiborane **6S** crystallised with one of the Sb-bound phenyl rings disordered. A similar disorder was observed for both phenyl substituents in one of the two crystallographically independent molecules in the structure of **7** and for one cyclohexyl ring in the structure of **8O**, which also crystallised with two independent molecules in the unit cell. These rings were refined over two positions with constrained displacement parameters.

The solvent molecules in the structures of **12**·$C_2H_4Cl_2$ were extensively disordered and could not be unambiguously included in the structure model. Their contribution to the overall scattering was numerically removed using PLATON SQUEEZE.[6] In total, 184 electrons were eliminated *per* the unit cell, which corresponds with the 200 electrons expected for four molecules of the solvent (space group $P2_1/c$, Z = 4). A partial solvent disorder was observed also for **13b**·$C_2H_4Cl_2$, **14**·1.5CH_2Cl_2, and **15**·CH_2Cl_2. For **13b**·$C_2H_4Cl_2$, the solvent molecule was refined with two orientations for the ethylene linker (CH_2CH_2) between the pivotal chlorine atoms (refined contributions: 57:43). One dichloromethane molecule in the structure of **14**·1.5CH_2Cl_2 was located on the crystallographic inversion centre and was refined with one independent Cl atom and a half of the CH_2 group. Finally, the dichloromethane molecule in the structure of **15**·CH_2Cl_2 was refined with one chlorine atom split over two positions (≈85:15). Lastly, compound **8**·C_6H_{14} crystallised with two stiborane and two solvent molecules in the asymmetric unit. Of the two independent solvent molecules, one was disordered and had to be modelled over two overlapping positions with nearly equal occupancies (refined: 451:49) and constrained displacement parameters. The disorder, affecting the overall diffraction patterns, resulted in a relatively large residual electron density (2.8 e Å^{-3}) in proximity of the Sb atom (0.73 Å from the Sb atom).

Relevant crystallographic data and structure refinement parameters are presented in Table S1. All geometric data and structural diagrams were obtained using the PLATON program.[7] The numerical values were rounded to one decimal place with respect to their estimated standard deviations (ESDs).

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

Compound	**3**	**3**·BH_3	**3O**
Formula	$C_{34}H_{40}FePSb$	$C_{34}H_{43}BFePSb$	$C_{34}H_{40}FeOPSb$
M	657.23	671.06	673.23
Crystal system	monoclinic	triclinic	triclinic
Space group	*Cc* (no. 9)	*P*–1 (no. 2)	*P*–1 (no. 2)
T [K]	120(2)	120(2)	120(2)
a [Å]	7.6981(3)	7.5644(3)	9.9527(3)
b [Å]	57.583(2)	13.3295(5)	11.5385(3)
c [Å]	6.6814(2)	15.4143(6)	14.5599(4)
α [°]	90	100.986(1)	76.936(1)
β [°]	91.615(1)	90.313(1)	73.609(1)
γ [°]	90	92.652(1)	68.547(1)
V [Å]^3	2960.6(2)	1523.9(1)	1478.8(7)
Z	4	2	2
F(000)	1344	688	688
μ(Mo Kα) [mm^{-1}]	1.478	1.436	1.483
Diffrns collected	23922	28960	34828
Independent diffrns	5771	7001	6740
Observed[a] diffrns	5547	5684	6531
R_{int}[b] [%]	3.09	4.36	2.35
No. of parameters	334	343	343
R[b] obsd diffrns [%]	1.88	3.10	1.80
R, wR[b] all data [%]	2.06, 3.87	4.44, 7.46	1.88, 4.43
Δρ [e Å^{-3}]	0.53, −0.37	0.78, −0.75	0.88, −0.45
CCDC ref. no.	2320741	2320742	2320743

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

Table S1 continued

Compound	**3S**	**6**·BH_3	**6S**
Formula	$C_{34}H_{40}FePSSb$	$C_{34}H_{43}BCl_2FePSb$	$C_{34}H_{40}Cl_2FePSSb$
M	689.29	741.96	760.19
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	*P*–1 (no. 2)	*P*–1 (no. 2)
T [K]	120(2)	120(2)	120(2)
a [Å]	14.2751(6)	11.7235(4)	11.8075(5)
b [Å]	12.0458(5)	12.4171(4)	12.1508(5)
c [Å]	17.7478(8)	12.5216(4)	12.4622(5)
α [°]	90	85.495(1)	85.141(2)
β [°]	96.424(1)	67.566(1)	67.956(1)
γ [°]	90	78.088(1)	77.234(1)
V $[Å]^3$	3032.7(2)	1648.6(9)	1616.3(1)
Z	4	2	2
F(000)	1408	756	772
μ(Mo Kα) [mm^{-1}]	1.513	1.492	1.587
Diffrns collected	119121	32669	42500
Independent diffrns	6941	7499	7415
Observed[a] diffrns	6835	7329	7210
R_{int}[b] [%]	2.24	1.83	1.80
No. of parameters	343	361	417
R[b] obsd diffrns [%]	1.76	1.74	1.93
R, *wR*[b] all data [%]	1.79, 4.41	1.79, 4.44	1.99, 5.14
Δρ [e $Å^{-3}$]	0.80, −0.50	0.70, −0.41	0.71, −0.61
CCDC ref. no.	2320744	2320745	2320746

Table S1 continued

Compound	**7**	**8**·C_6H_{14}	**8**·BH_3
Formula	$C_{34}H_{40}AuCl_3FePSb$	$C_{46}H_{54}Cl_4FeO_2PSb$	$C_{40}H_{43}BCl_4FeO_2PSb$
M	960.54	989.26	916.92
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*–1 (no. 2)	P2$_1$/*c* (no. 14)	*P*–1 (no. 2)
T [K]	120(2)	120(2)	150(2)
a [Å]	9.1763(4)	26.584(1)	9.7600(5)
b [Å]	14.8320(6)	9.6286(3)	14.2166(7)
c [Å]	24.839(1)	33.667(1)	15.6102(8)
α [°]	97.404(2)	90	106.166(2)
β [°]	93.523(2)	93.956(1)	91.615(2)
γ [°]	90.020(2)	90	109.122(2)
V [Å]^3	3346.0(2)	8596.9(5)	1948.5(2)
Z	4	8	2
F(000)	1864	4048	928
μ(Mo Kα) [mm^{-1}]	5.914	1.290	1.416
Diffrns collected	64551	103870	45043
Independent diffrns	15313	19730	8920
Observed[a] diffrns	14085	17806	8553
R_{int}^b [%]	3.31	2.71	2.41
No. of parameters	729	1040	451
R^b obsd diffrns [%]	3.92	4.48	1.86
R, wR^b all data [%]	4.37, 7.60	4.99, 10.57	1.97, 4.86
Δρ [e Å^{-3}]	1.94, -2.05	2.79, -1.09	0.44, -0.40
CCDC ref. no.	2320747	2320748	2320749

Table S1 continued

Compound	**8O**	**8S**	**11**
Formula	$C_{40}H_{40}Cl_4FeO_3PSb$	$C_{40}H_{40}Cl_4FeO_2PSSb$	$C_{34}H_{40}Au_2Cl_2FePSb$
M	919.09	935.15	1122.06
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]	15.7678(4)	9.6737(3)	13.8052(3)
b [Å]	12.6028(3)	14.1012(4)	14.1907(3)
c [Å]	36.990(1)	15.5761(5)	18.1418(4)
α [°]	90	106.502(1)	90
β [°]	90.132(1)	91.723(1)	102.830(1)
γ [°]	90	108.829(1)	90
V [Å]^3	7350.5(3)	1910.8(1)	3465.3(1)
Z	8	2	4
F(000)	3712	944	2112
μ(Mo Kα) [mm^{-1}]	1.504	1.498	9.845
Diffrns collected	94459	50835	55243
Independent diffrns	16861	8815	7925
Observed[a] diffrns	15190	7668	7645
R_{int}[b] [%]	3.96	3.07	2.32
No. of parameters	947	451	370
R[b] obsd diffrns [%]	3.26	2.20	1.26
R, wR[b] all data [%]	3.86, 6.99	2.95, 5.10	1.35, 2.71
Δρ [e Å^{-3}]	1.37, −0.82	0.56, −0.29	0.43, −0.63
CCDC ref. no.	2320750	2320751	2320752

Table S1 continued

Compound	**12**·$C_2H_4Cl_2$	**13a**·$4CHCl_3$	**13b**·$C_2H_4Cl_2$
Formula	$C_{46}H_{58}Cl_3F_6FeP_2RuSb$	$C_{48}H_{59}Cl_{14}FePRhSb$	$C_{46}H_{59}Cl_3F_6FeP_2RhSb$
M	1171.88	1443.73	1174.73
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
T [K]	150(2)	120(2)	120(2)
a [Å]	11.315(4)	11.6734(5)	11.8312(5)
b [Å]	15.3071(7)	18.3247(7)	12.9337(5)
c [Å]	28.361(1)	27.430(1)	30.525(1)
α [°]	90	90	90
β [°]	97.502(2)	100.167(1)	97.824(1)
γ [°]	90	90	90
V $[Å]^3$	4870.1(3)	5775.5(4)	4627.5(3)
Z	4	4	4
F(000)	2360	2888	2368
μ(Mo Kα) $[mm^{-1}]$	1.436	1.703	1.541
Diffrns collected	64011	119070	61952
Independent diffrns	11139	13232	10596
Observed[a] diffrns	9962	12803	10397
R_{int}^b [%]	2.99	2.14	1.58
No. of parameters	508	600	553
R^b obsd diffrns [%]	2.88	2.78	2.06
R, wR^b all data [%]	3.42, 6.76	2.88, 6.21	2.10, 4.74
Δρ [e $Å^{-3}$]	0.91, −0.97	1.36, −1.38	0.77, −0.78
CCDC ref. no.	2320753	2320754	2320755

Table S1 continued

Compound	**14**·1.5CH_2Cl_2	**15**·CH_2Cl_2
Formula	$C_{35.5}H_{43}Cl_5FePPdSb$	$C_{35}H_{42}Cl_4FePPtSb$
M	961.92	1008.14
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
T [K]	120(2)	120(2)
a [Å]	10.1237(3)	11.1232(5)
b [Å]	17.2579(6)	20.3402(9)
c [Å]	21.6499(8)	15.3930(6)
α [°]	90	90
β [°]	102.645(1)	93.547(1)
γ [°]	90	90
V [Å]^3	3690.8(2)	3476.0(3)
Z	4	4
F(000)	1916	1960
μ(Mo Kα) [mm^{-1}]	2.027	5.577
Diffrns collected	41643	55657
Independent diffrns	8366	7954
Observed[a] diffrns	7823	7751
R_{int}[b] [%]	2.10	2.35
No. of parameters	401	392
R[b] obsd diffrns [%]	2.10	1.23
R, wR[b] all data [%]	2.35, 4.57	1.30, 2.87
Δρ [e Å^{-3}]	2.19, −1.52	0.43, −0.47
CCDC ref. no.	2320756	2320757

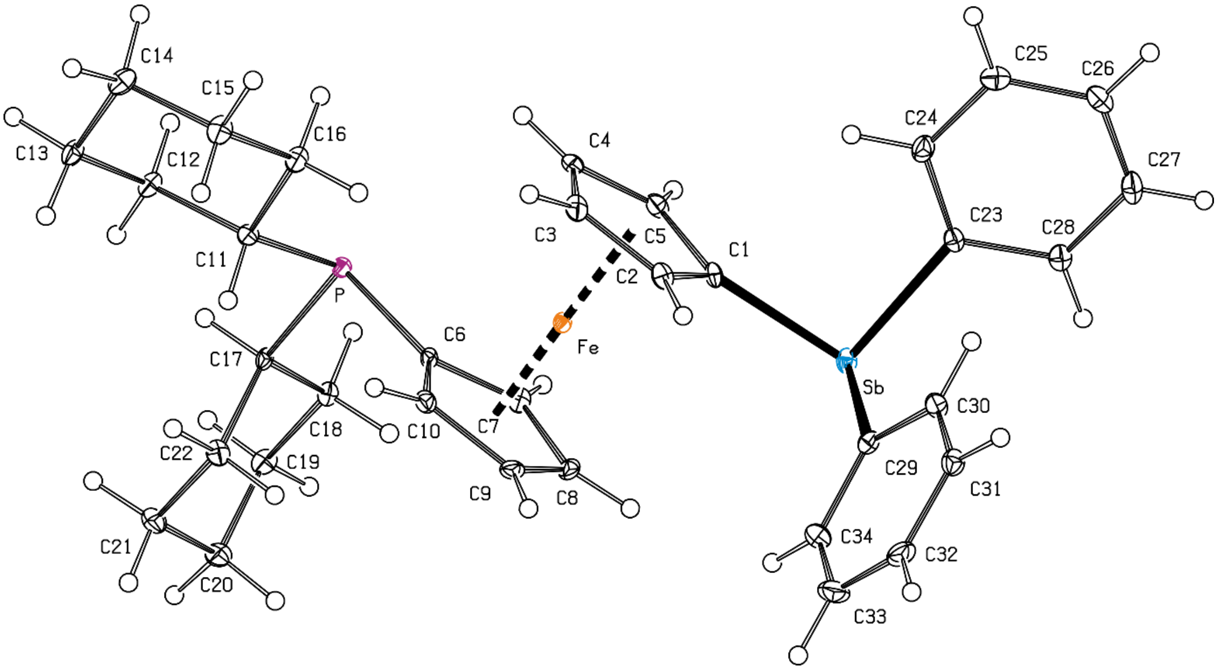


Figure S1 PLATON plot of the molecular structure of **3** (30% probability ellipsoids)

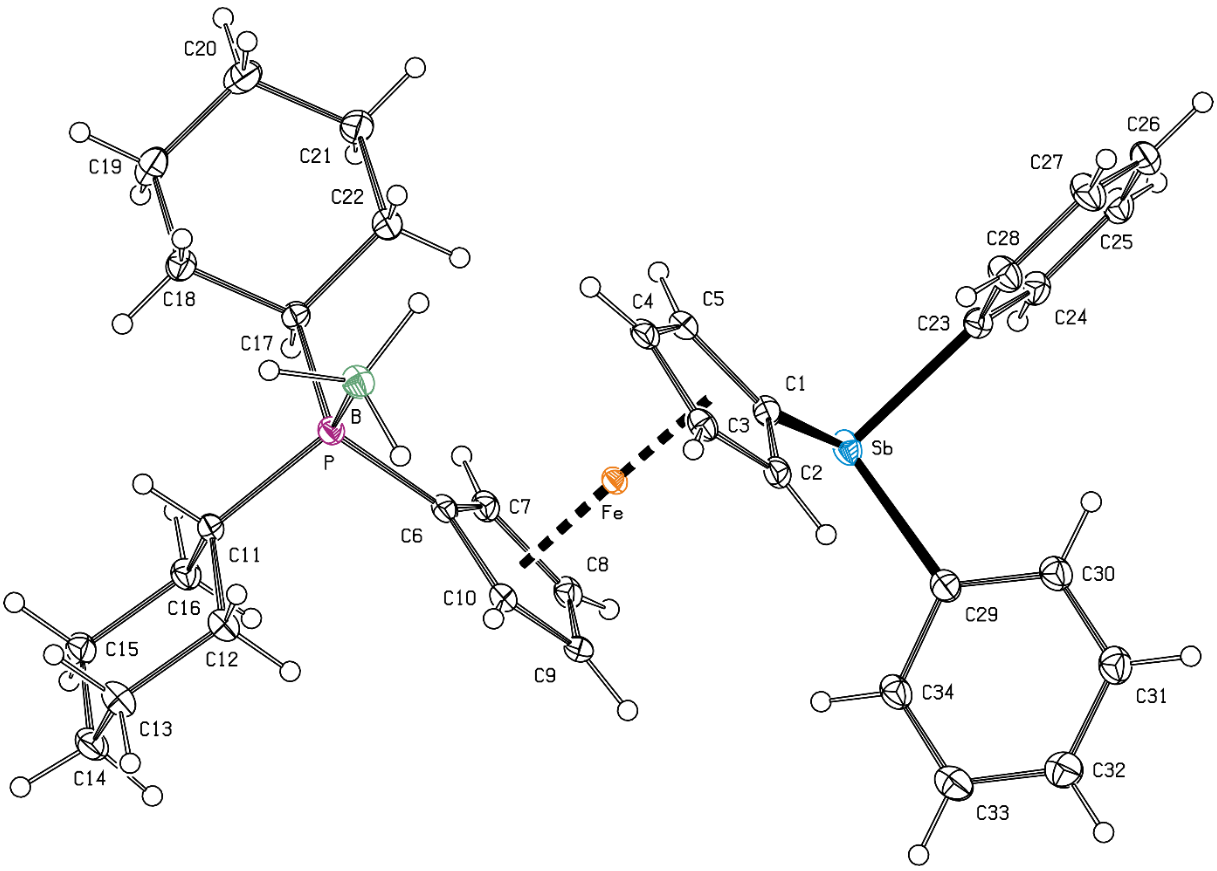


Figure S2 PLATON plot of the molecular structure of **3**·BH_3 (30% probability ellipsoids)

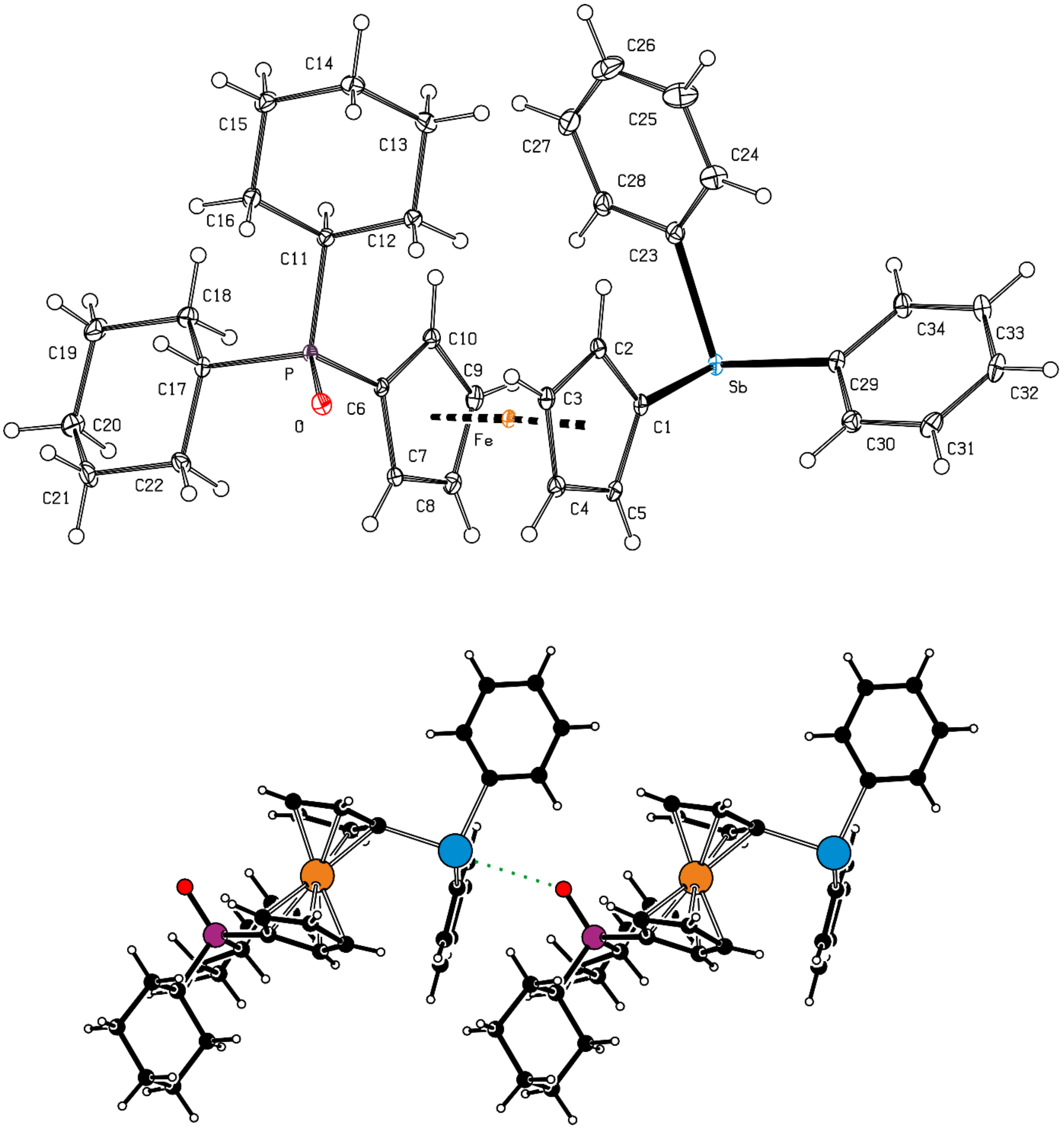


Figure S3 (top) PLATON plot of the molecular structure of **3O** (30% probability ellipsoids) and (bottom) Sb⋯O contacts in the crystal structure of this compound (the two molecules are related by elemental translation along the crystallographic *a* axis)

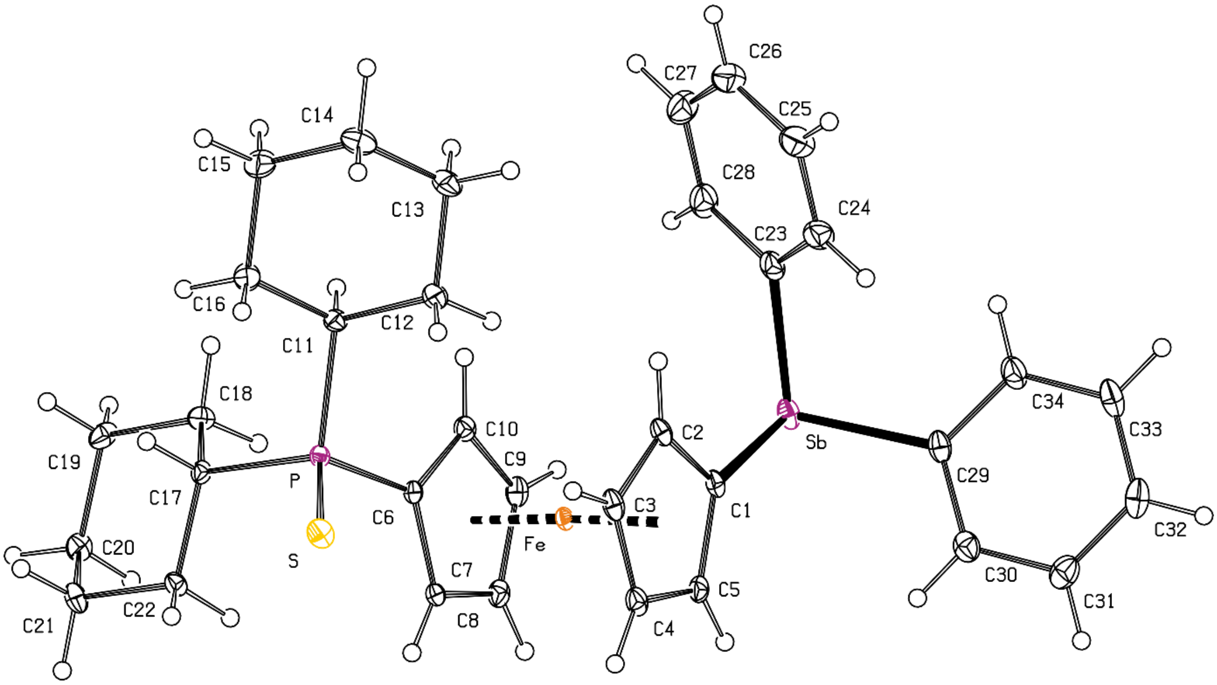


Figure S4 PLATON plot of the molecular structure of **3S** (30% probability ellipsoids)

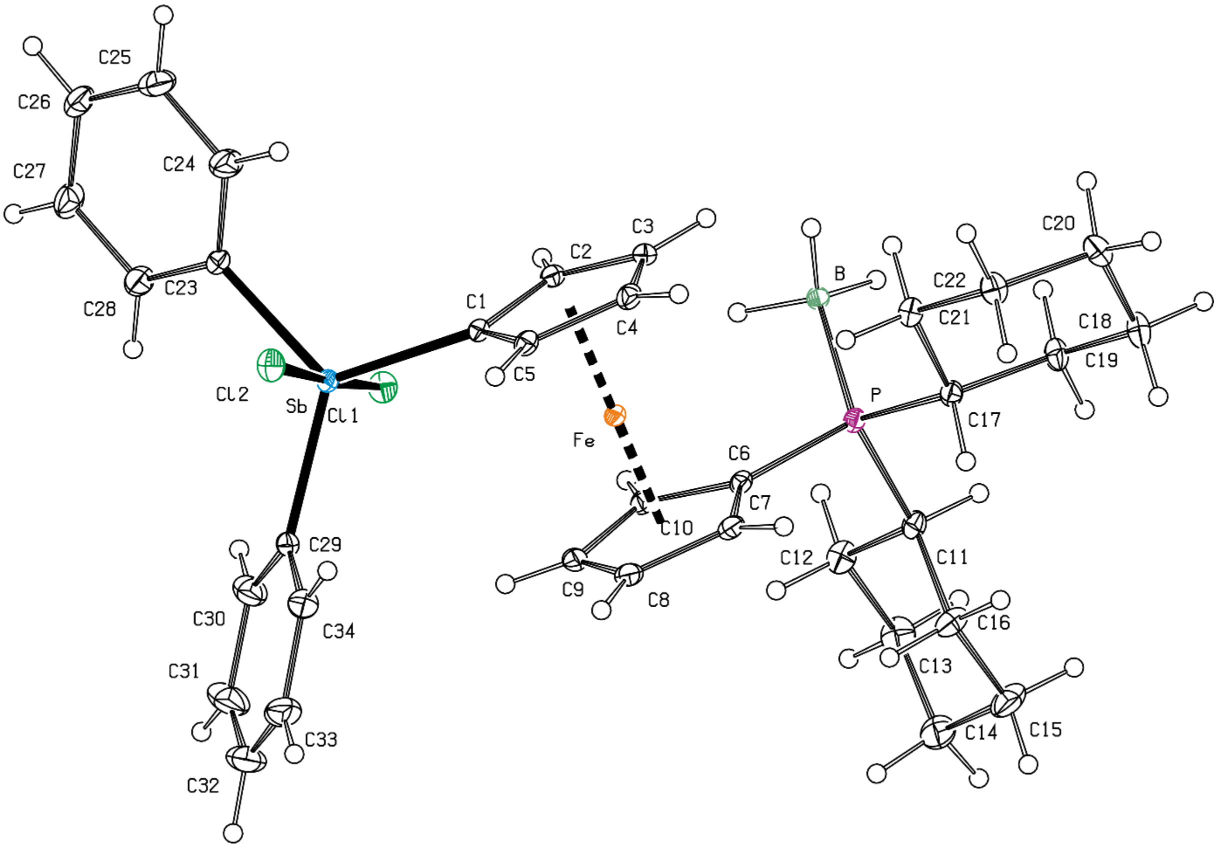


Figure S5 PLATON plot of the molecular structure of **6**·BH_3 (30% probability ellipsoids)

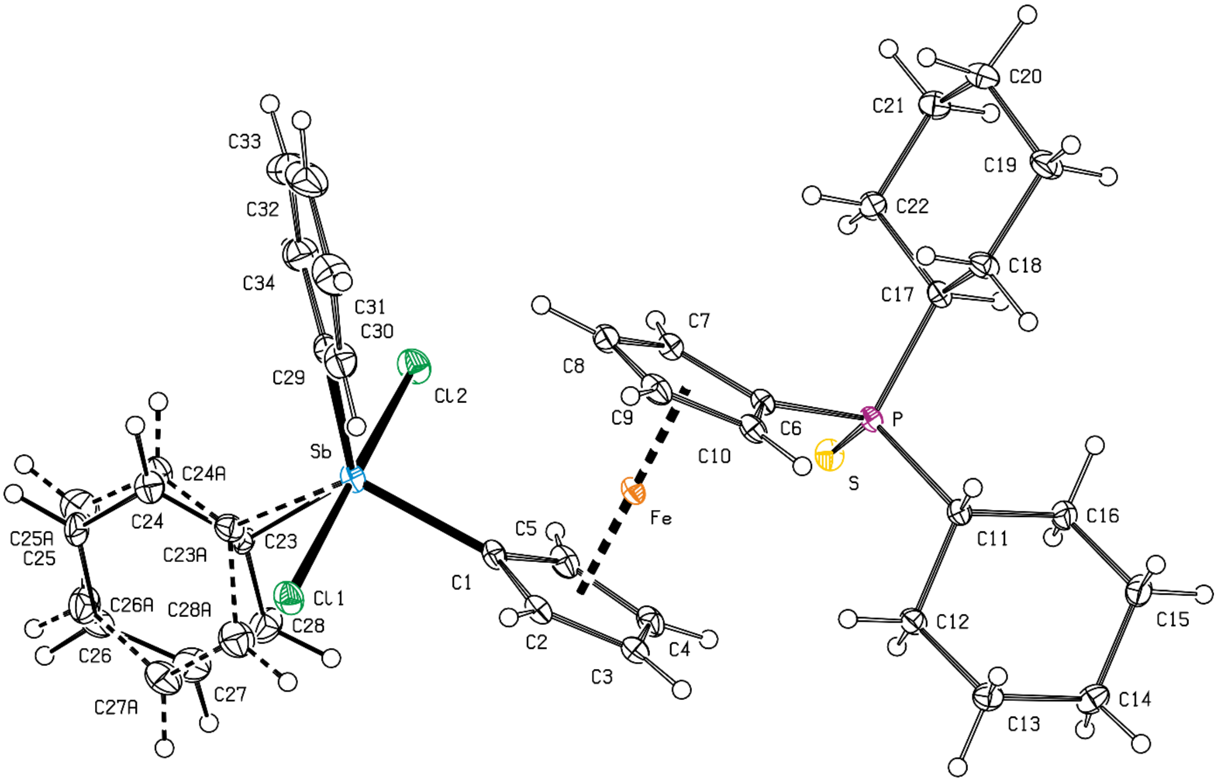


Figure S6 PLATON plot of the molecular structure of **6S** showing both orientations of the disordered phenyl ring C(23-28) (30% probability ellipsoids)

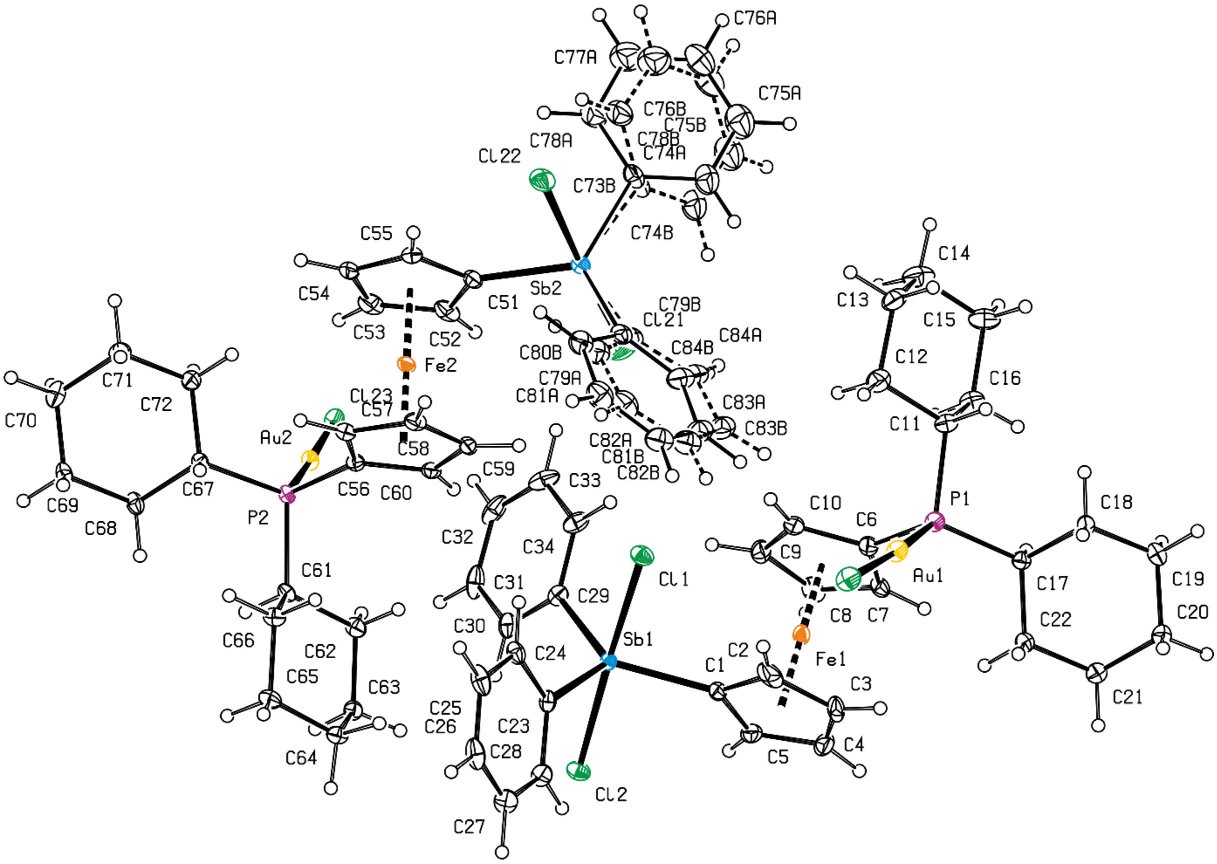


Figure S7 Full PLATON plot of the structure of **7** (30% probability ellipsoids)

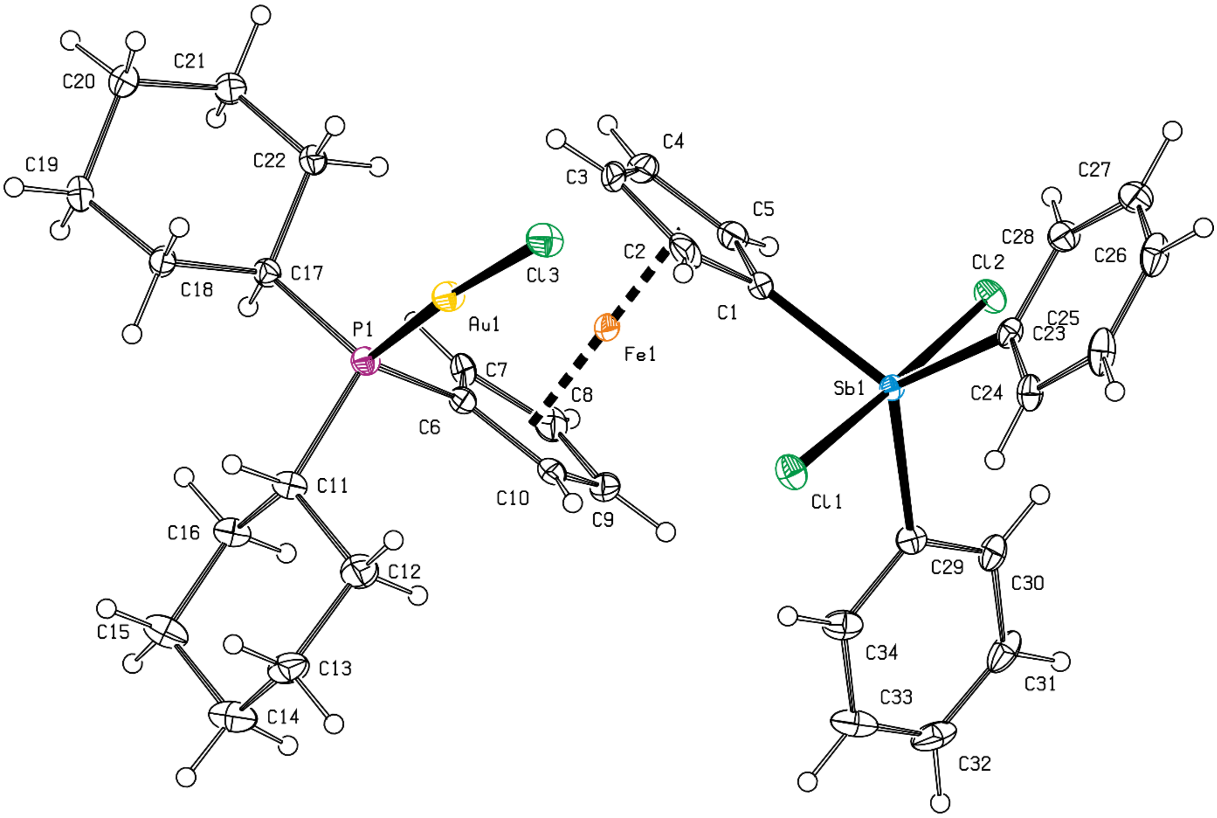


Figure S8 PLATON plot of molecule 1 in the structure of **7** (30% probability ellipsoids)

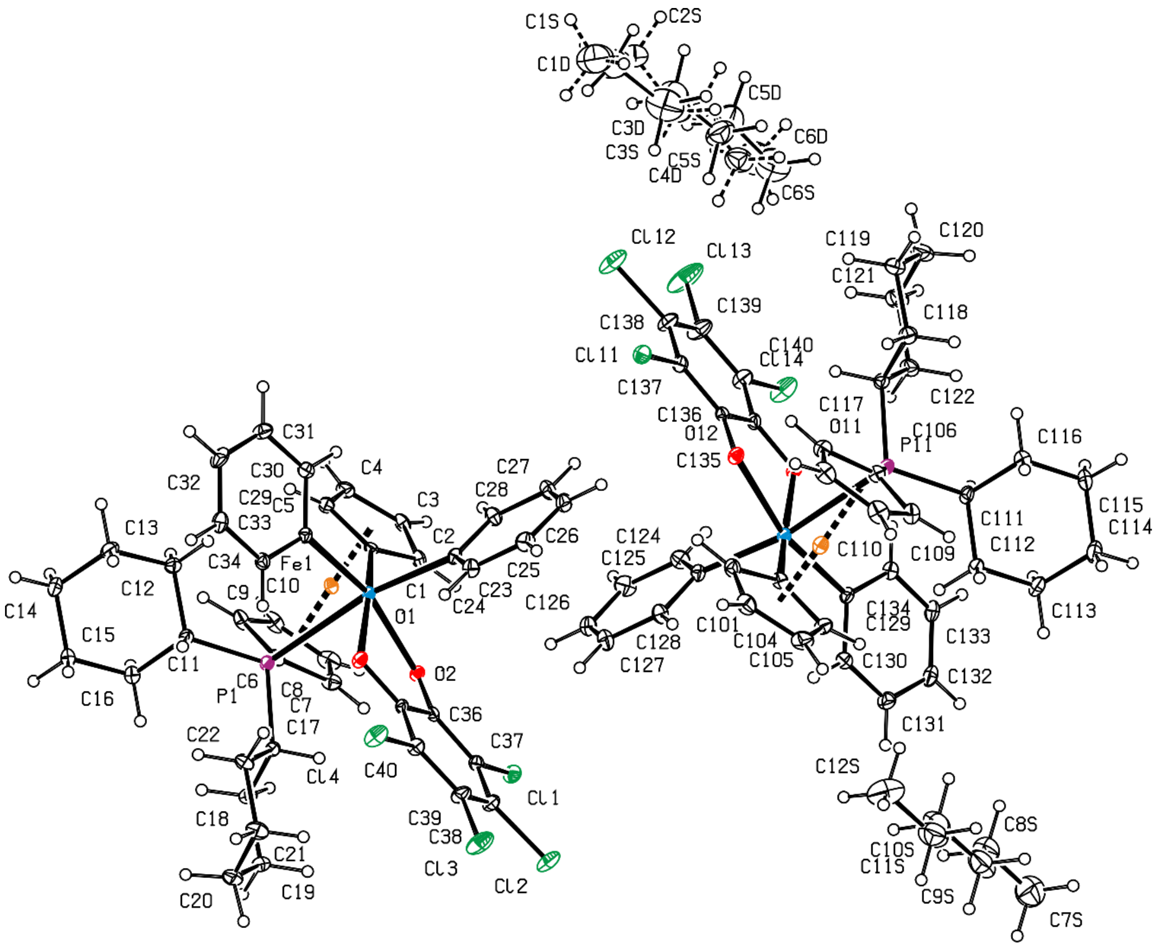


Figure S9 Full PLATON plot of the structure of **8**·C_6H_{14} (30% probability ellipsoids)

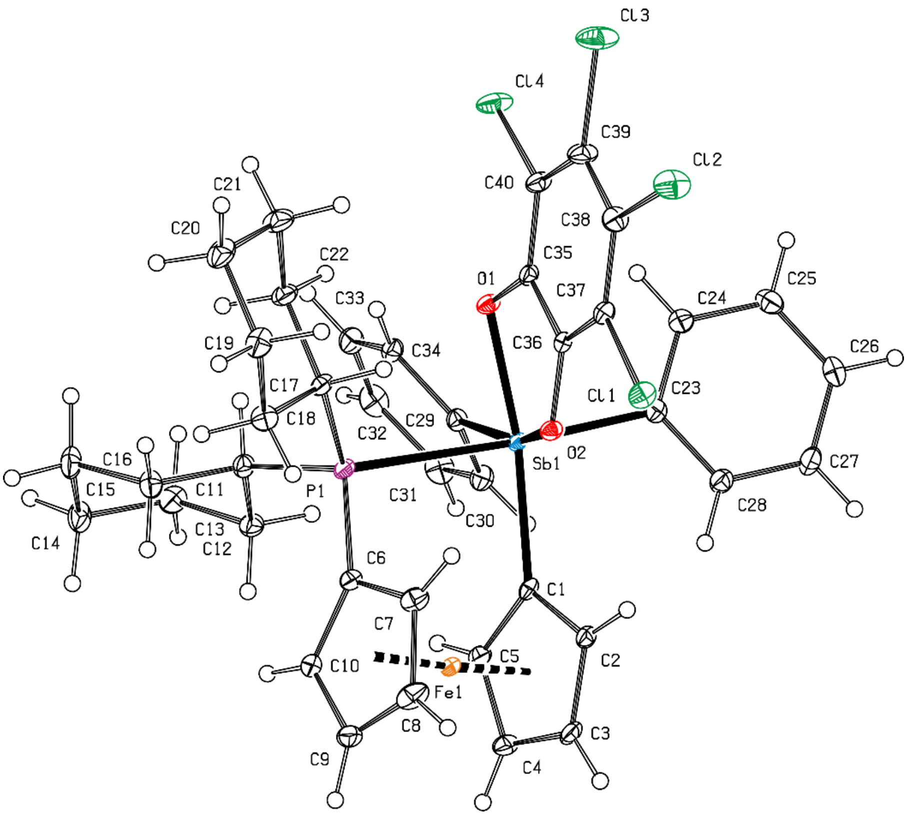


Figure S10 PLATON plot of molecule 1 in the structure of **8**·C_6H_{14} (30% probability ellipsoids)

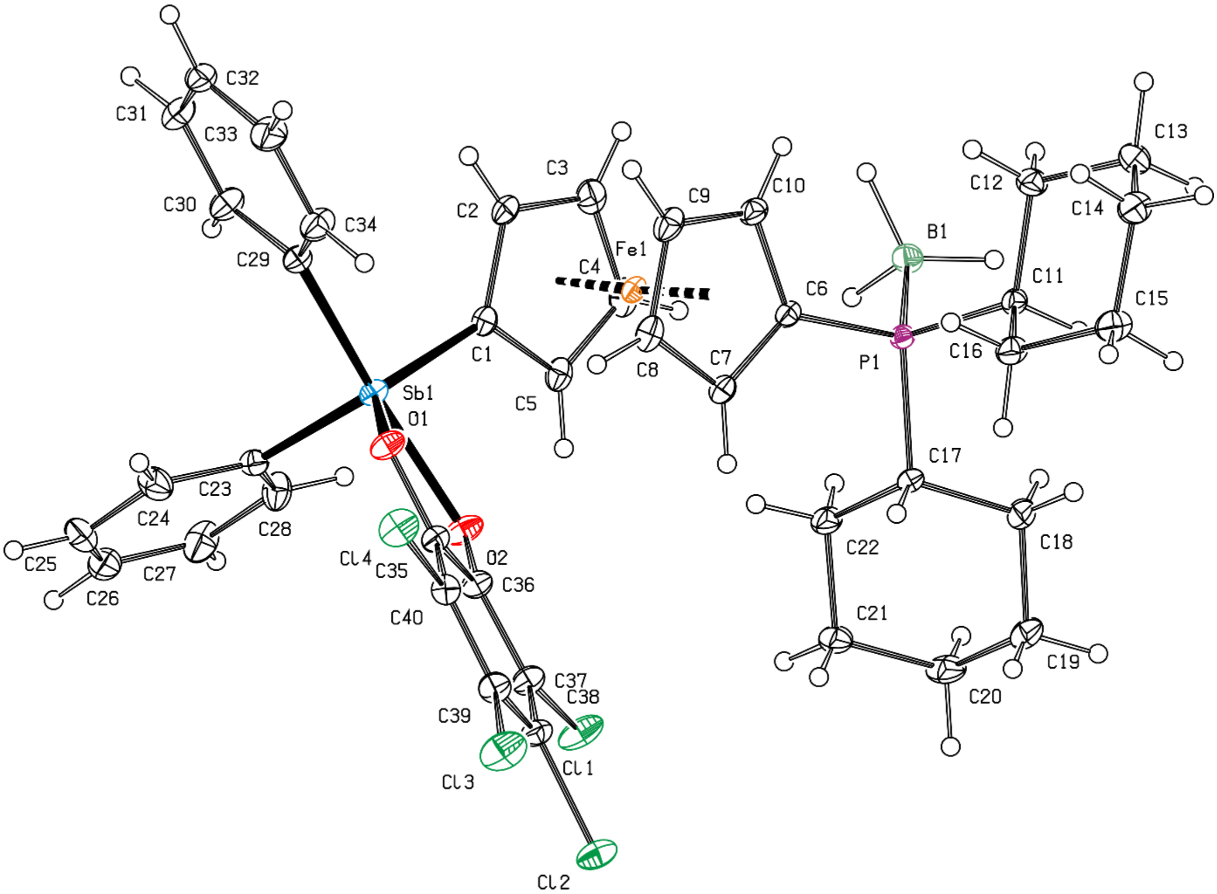


Figure S11 PLATON plot of the molecular structure of **8**·BH_3 (30% probability ellipsoids)

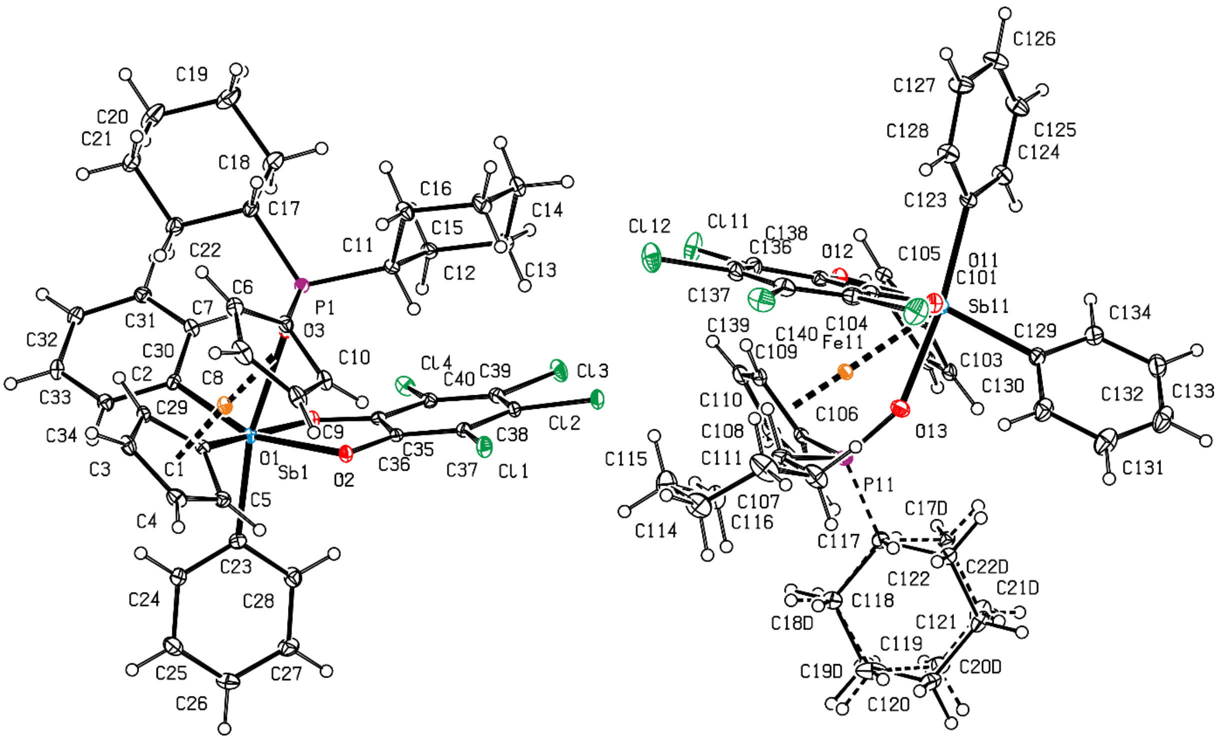


Figure S12 Full PLATON plot of the molecular structure of **8O** (30% probability ellipsoids)

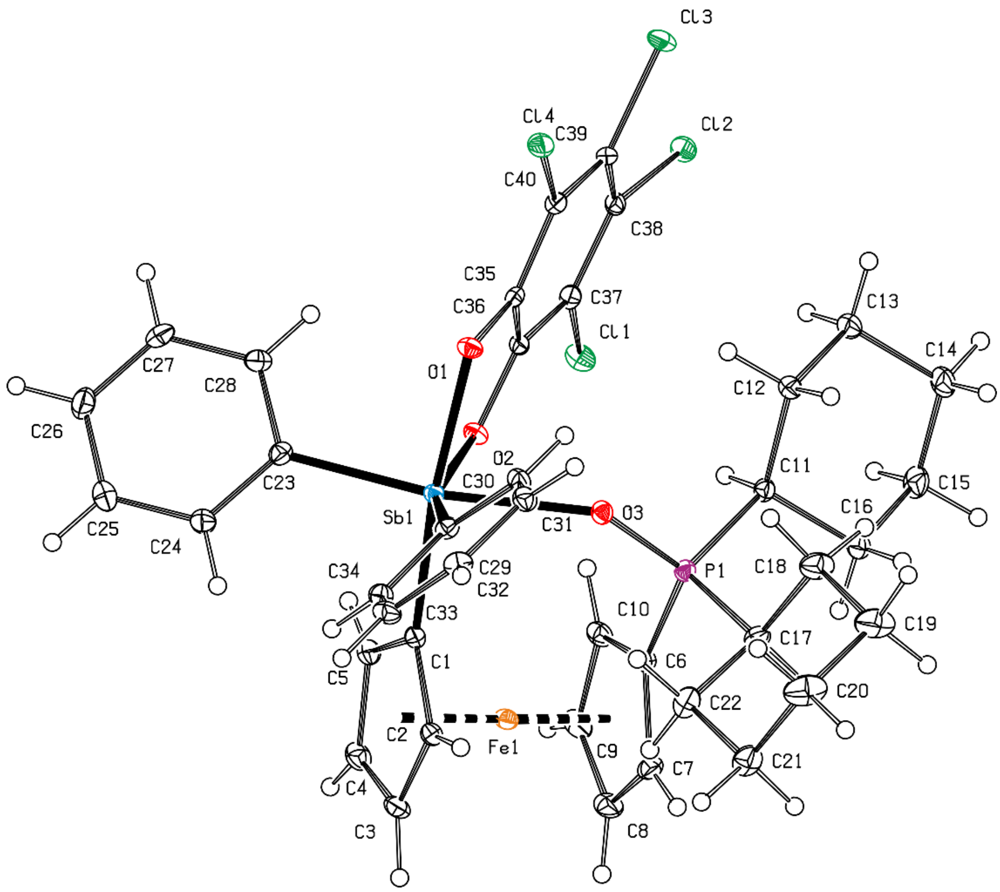


Figure S13 PLATON plot of molecule **1** in the structure of **8O** (30% probability ellipsoids)

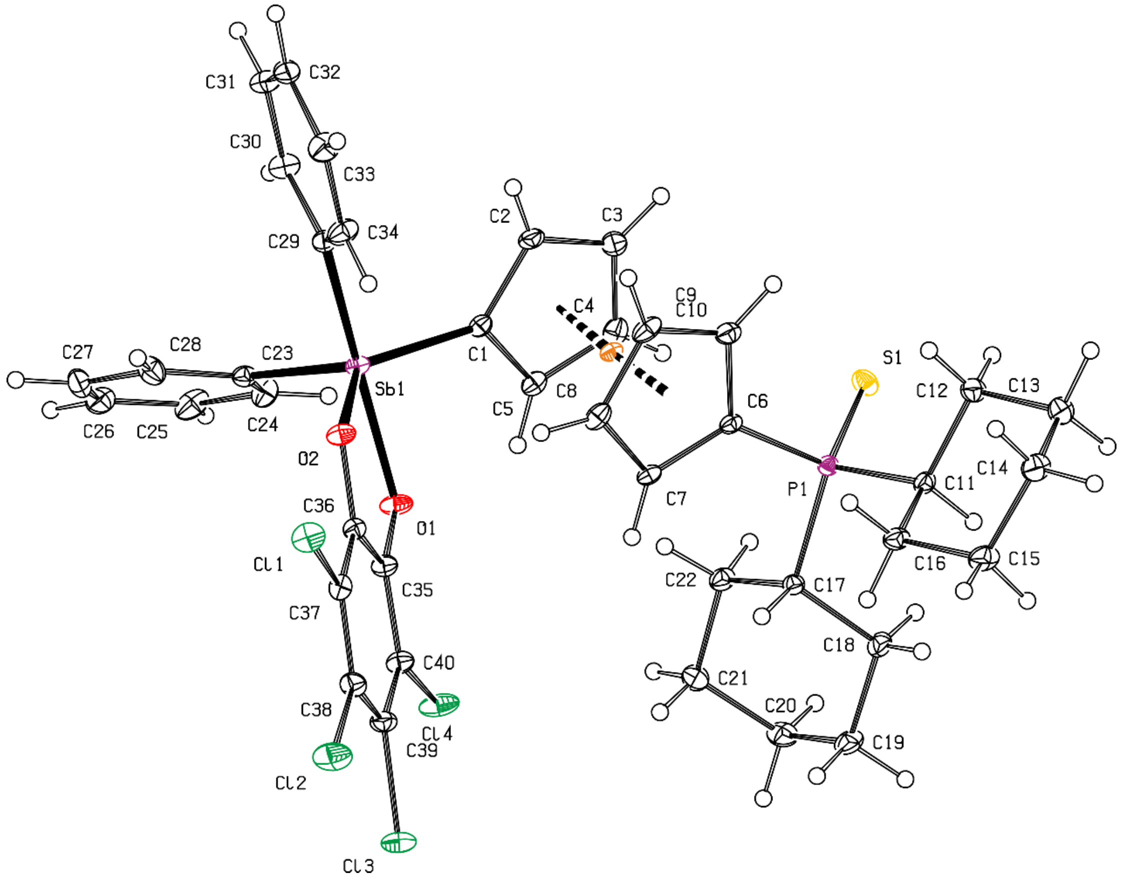


Figure S14 PLATON plot of the molecular structure of **8S** (30% probability ellipsoids)

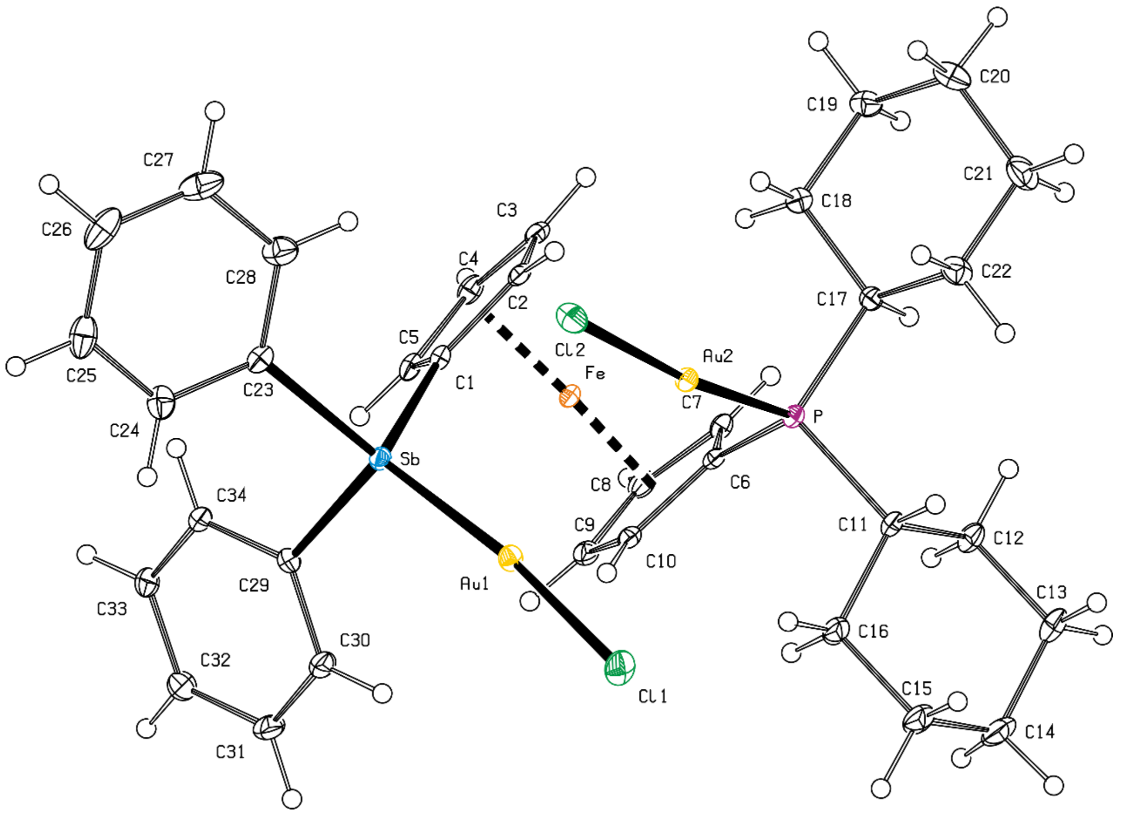


Figure S15 PLATON plot of the molecular structure of **11** (30% probability ellipsoids)

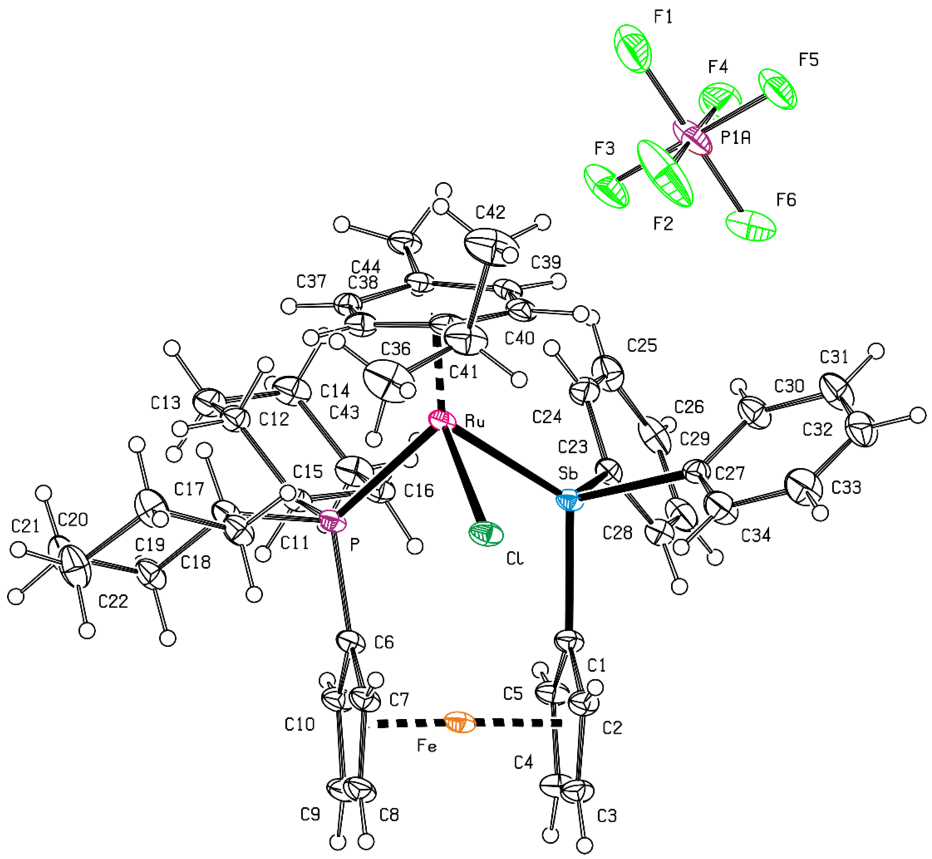


Figure S16 PLATON plot of the molecular structure of **12**·$C_2H_4Cl_2$ (30% probability ellipsoids). The solvent molecule has been eliminated by PLATON/SQUEEZE (*vide supra*).

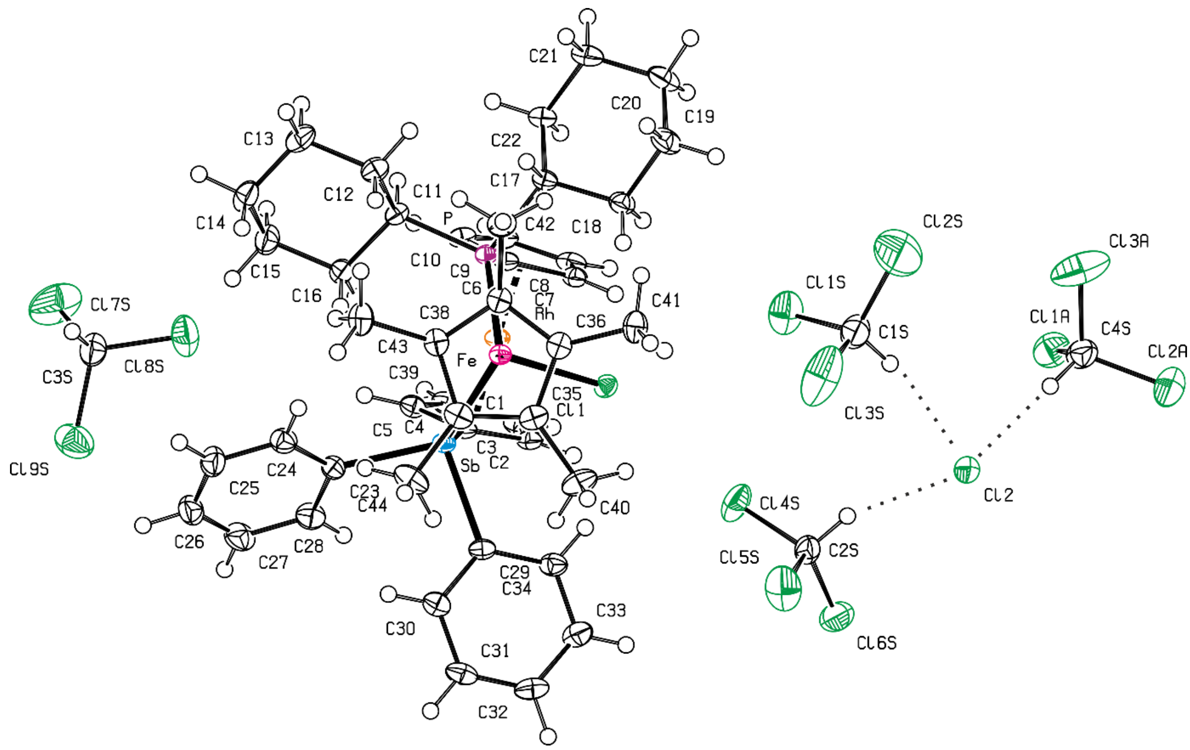


Figure S17 Full PLATON plot of the molecular structure of **13a**·$4CHCl_3$ (50% probability ellipsoids). The C–H···Cl hydrogen bonds are indicated by dotted lines (C1S···Cl2 = 3.408(3) Å, C2S··· Cl2 = 3.366(2) Å, and C4S···Cl2 = 3.362(3) Å).

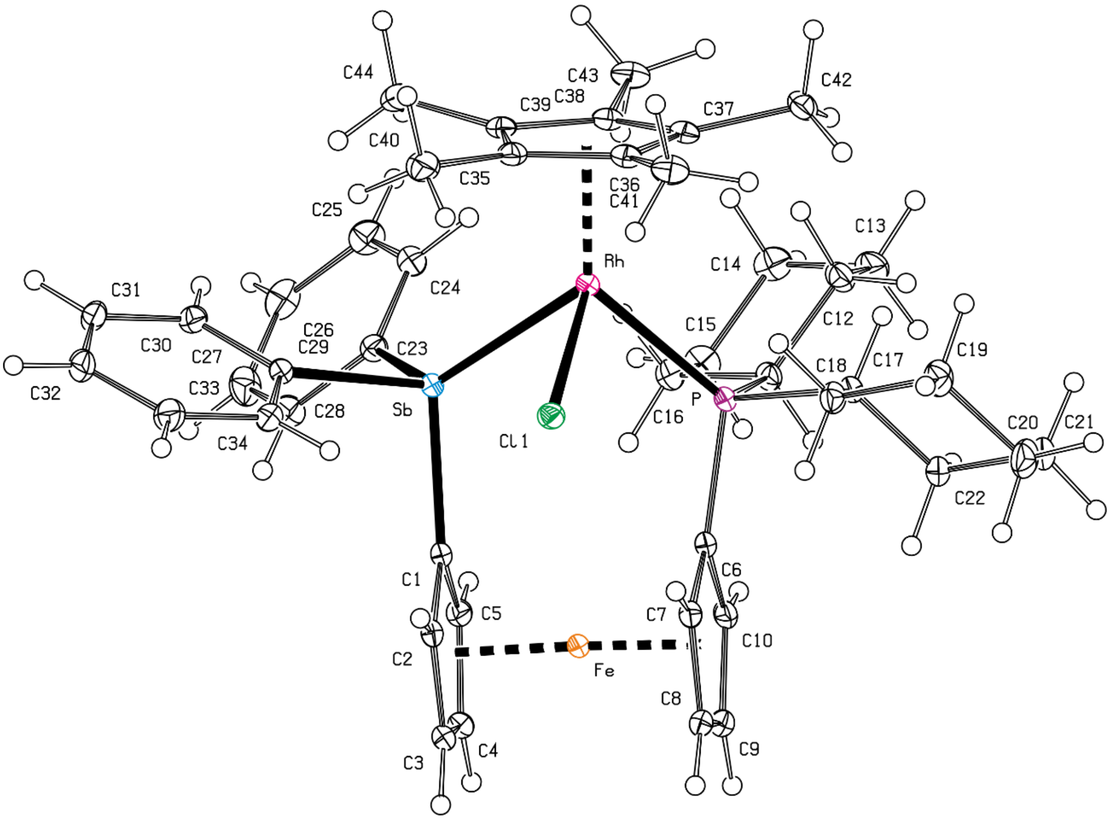


Figure S18 PLATON plot of the complex cation in the structure of **13a**·4$CHCl_3$ (30% probability ellipsoids)

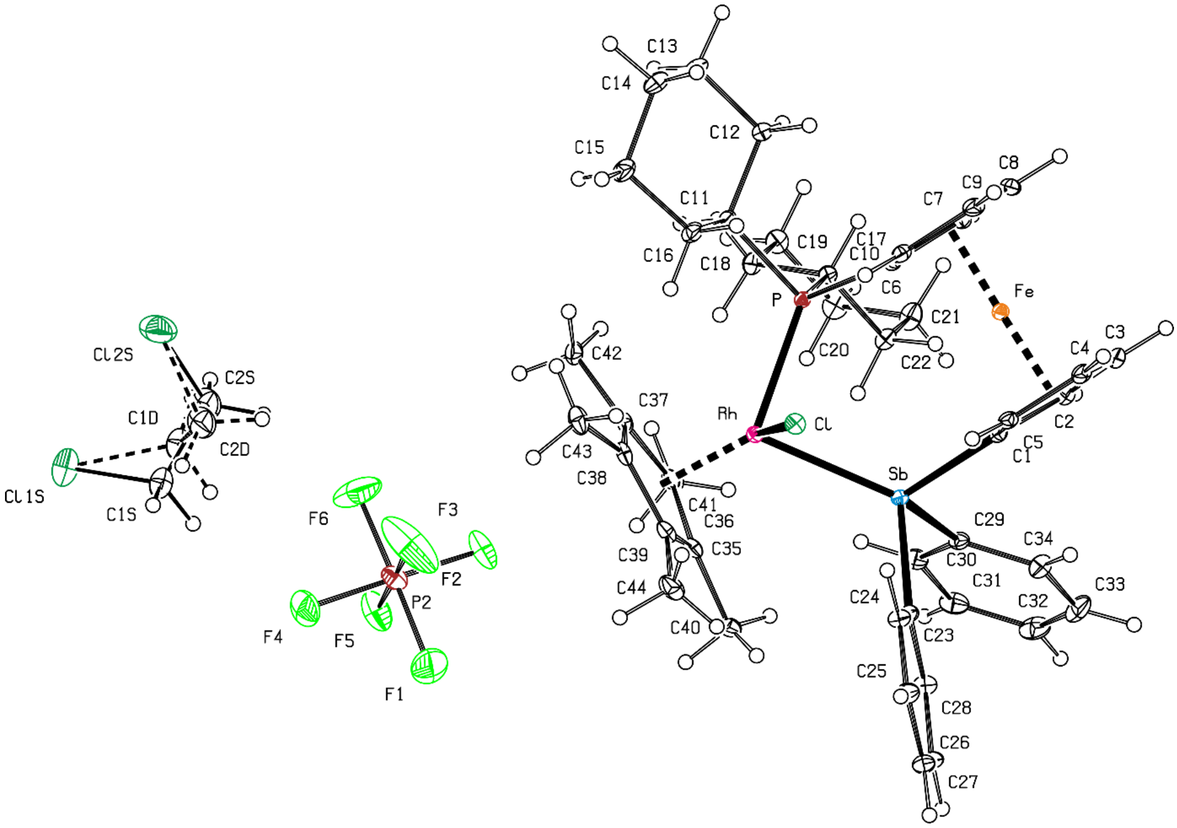


Figure S19 Full Full PLATON plot of the molecular structure of **13b**·$C_2H_4Cl_2$ (30% probability ellipsoids)

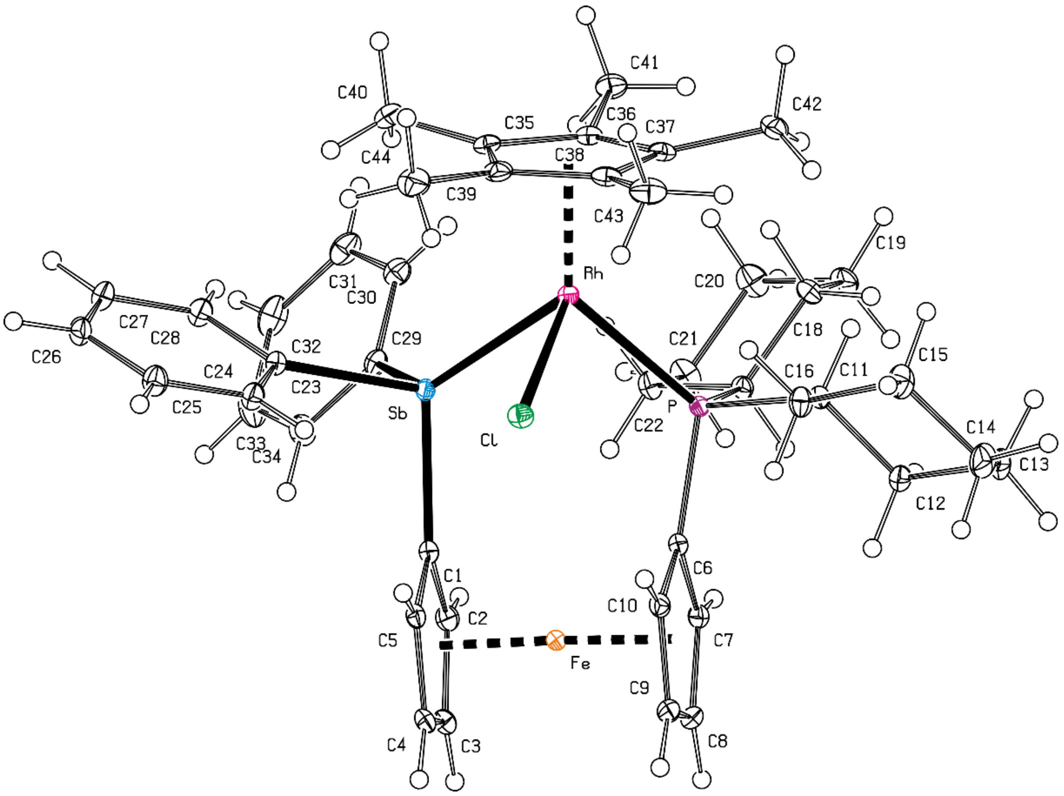


Figure S20 PLATON plot of the complex cation in the structure of **13b**·$C_2H_4Cl_2$ (30% probability ellipsoids)

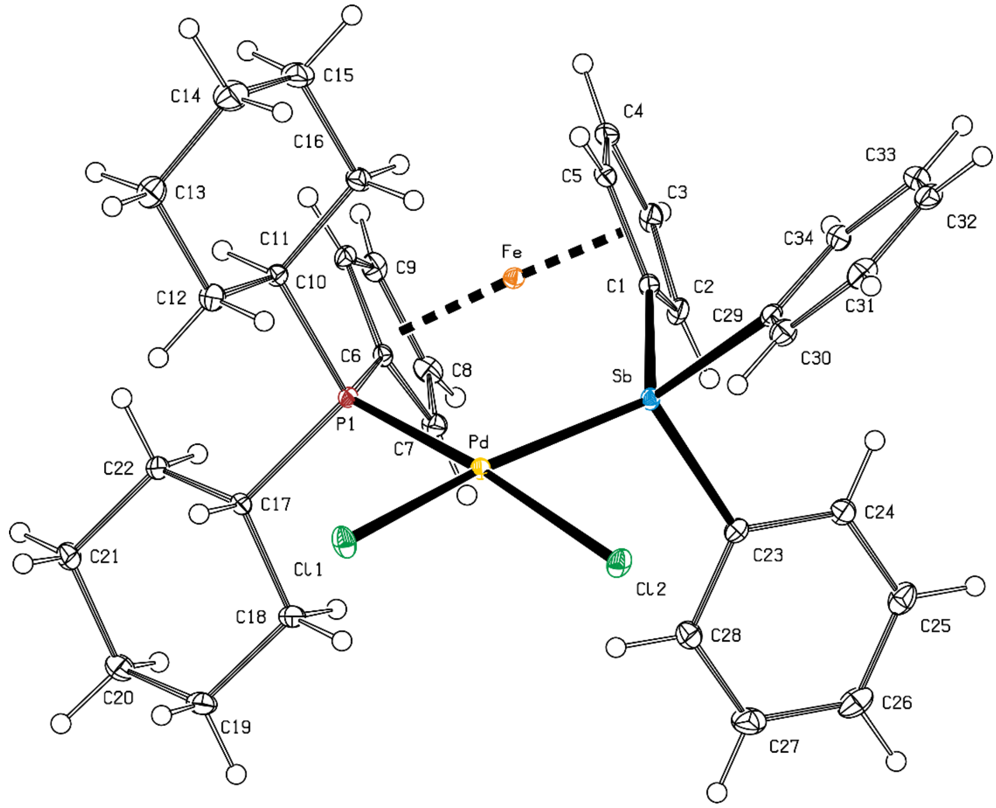


Figure S21 PLATON plot of the molecular structure of **14**·1.5CH_2Cl_2 (30% probability ellipsoids). The solvent molecules were omitted for clarity.

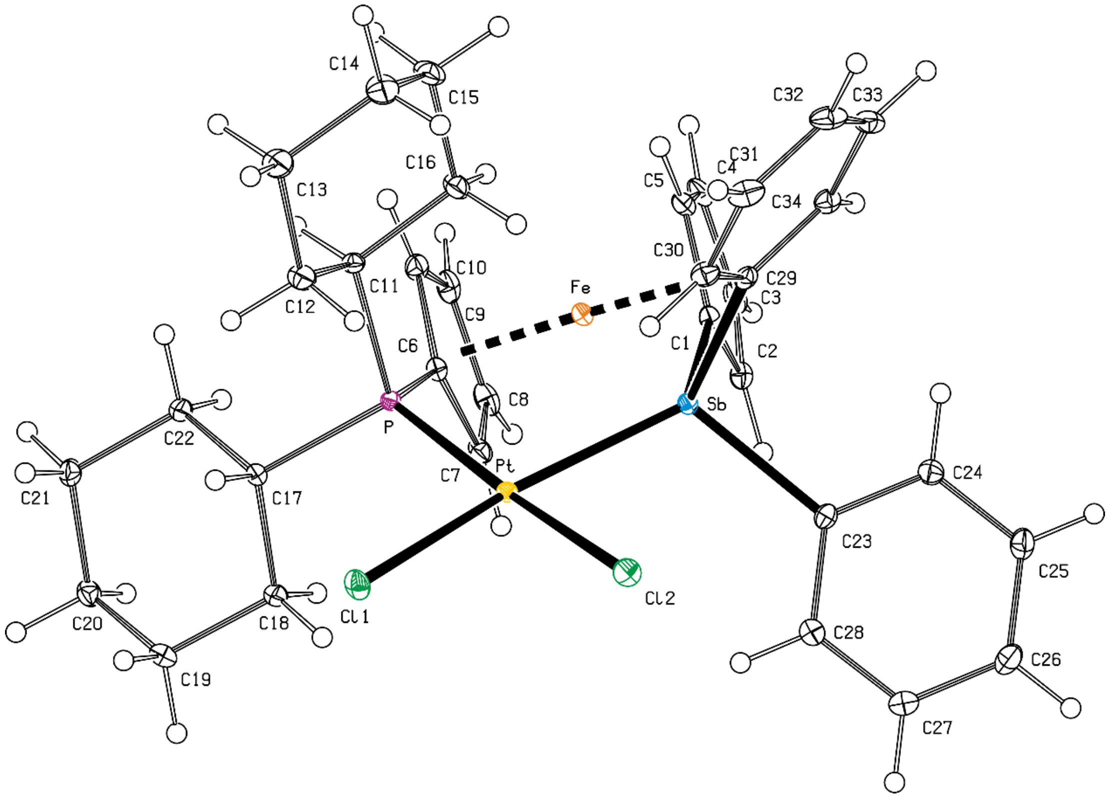


Figure S22 PLATON plot of the molecular structure of **15**·CH_2Cl_2 (30% probability ellipsoids). The solvent molecule was omitted for clarity.

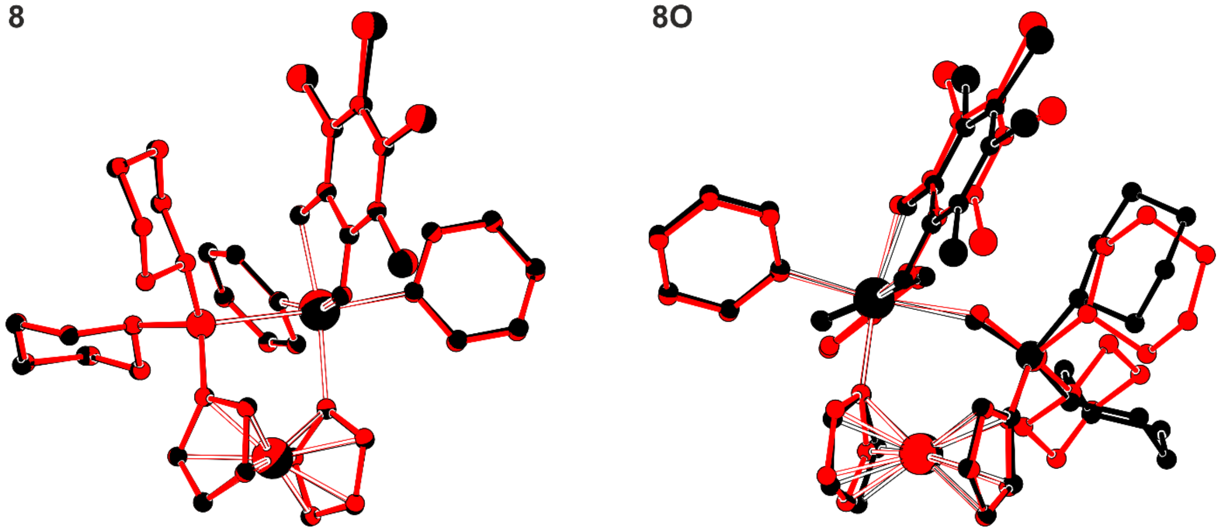


Figure S23 Overlaps of the two independent molecules in the structure of **8**·C_6H_{14} and **8O**.

DFT calculations

Theoretical calculations were performed using the Gaussian 16 program package.[8] If available, the geometry optimizations were started from atomic coordinates determined by X-ray diffraction analysis, using PBE0[9] density functional combined with the Stuttgart effective core potential[10] for metal atoms (Fe, Sb) and the def2-TZVP[11] basis set for all remaining elements (C, H, O, P, S, and Cl) with added Grimme's D3 dispersion correction.[12] Solvent effects (chloroform) were approximated using PCM model.[13] Orbital composition analysis based on the Natural Atomic Orbitals (NAO)[14] (at the PBE0(d3)/def2-TZVP level of theory), as well as the analysis of calculated electron densities by the Atoms in Molecules approach (AIM), were performed using the Multiwfn software package (version 3.8).[15] Molecular orbitals were visualized using the Avogadro programme.[16] Intrinsic bond orbital (IBO) analysis and visualization of the obtained orbitals were performed using the IboView software.[17] The methyl cation affinities (MCA) were calculated according to the literature procedure.[18]

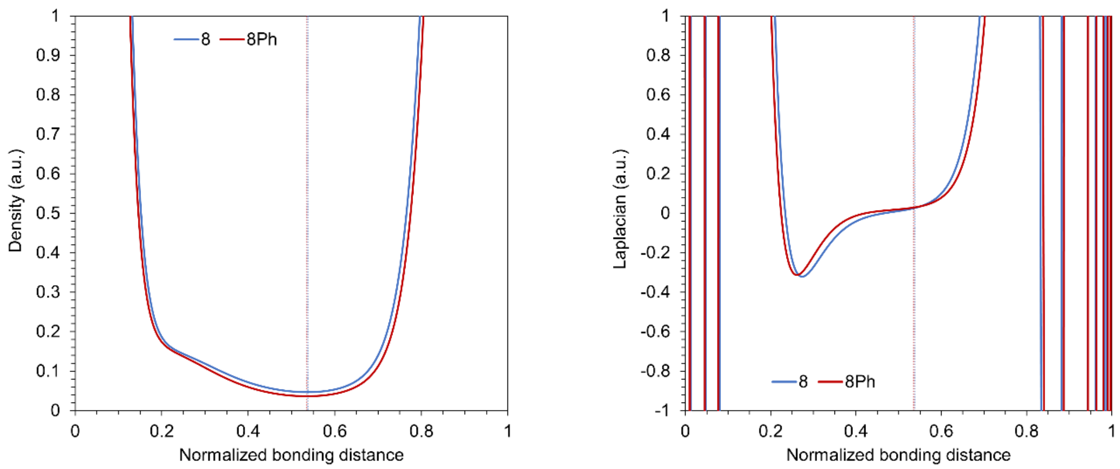
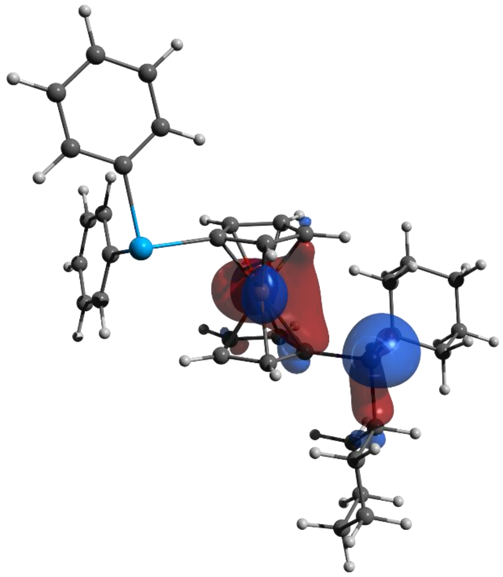
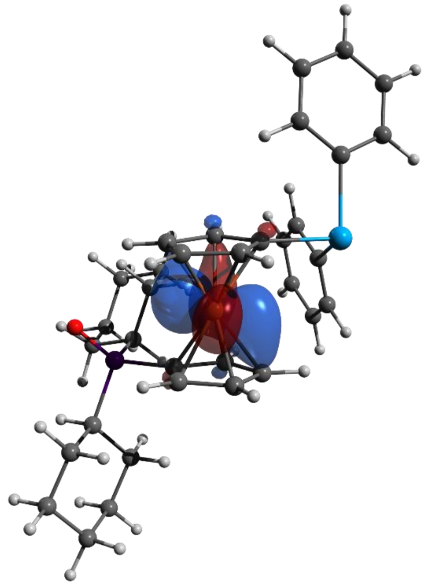


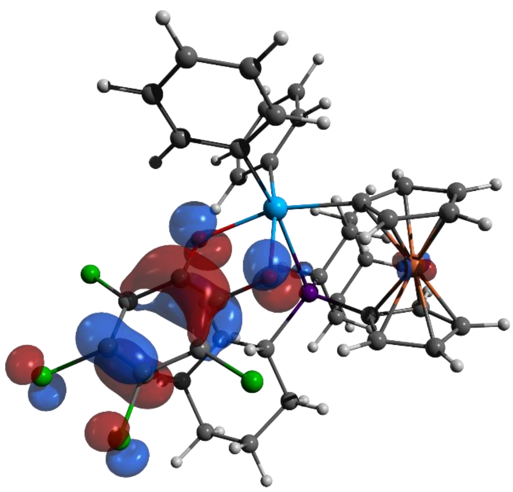
Figure S24 Plots of electron density (ρ; left) and electron density Laplacian ($\nabla^2\rho$; right) along the normalized bond length of the P–Sb bond in phosphinostiborane **8** (blue line) and its phenyl analogue $Ph_2PfcSbPh_2(O_2C_6Cl_4)$ (**8Ph**; red line). Dashed vertical lines represent the position of the bond critical points.



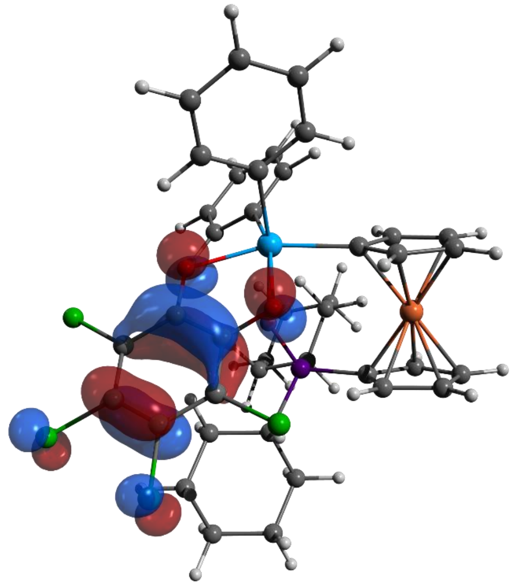
3



3O

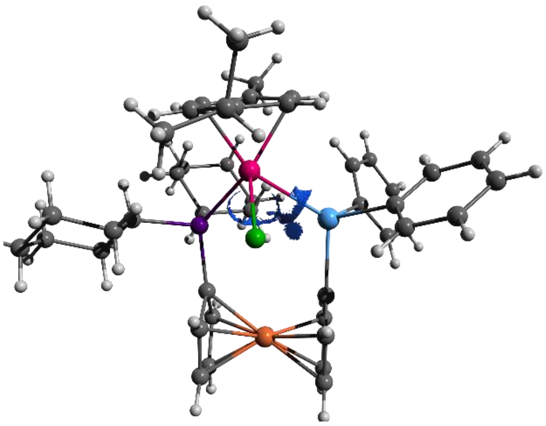


8

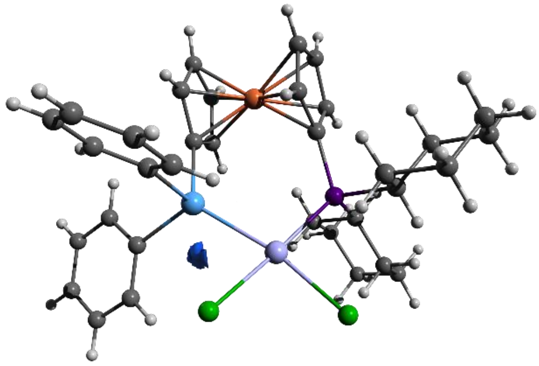


8O

Figure S25 HOMO orbitals of **3**, **3O**, **8** and **8O** (contour maps with isosurfaces at ±0.05 a.u.) at the PBE0(d3)/def2TZVPP:sdd(Fe,Sb) level of theory.



12



14

Figure S26 Non-covalent interactions (NCI) plots for the complex cation of **12** and compound **14** (RDG isosurfaces with $S(r)$ = 0.5; for clarity, the RDG isosurfaces were set to show only the regions with negative sign(λ_2)ρ values in the range −0.05 to −0.02 corresponding to strongly attractive noncovalent interactions. Wavefunctions for the NCI analysis were obtained by single-point calculations at the PBE0(d3)/def2TZVPP:sdd(Fe,Sb) theory level using geometries from X-ray diffraction analysis)

Electrochemistry

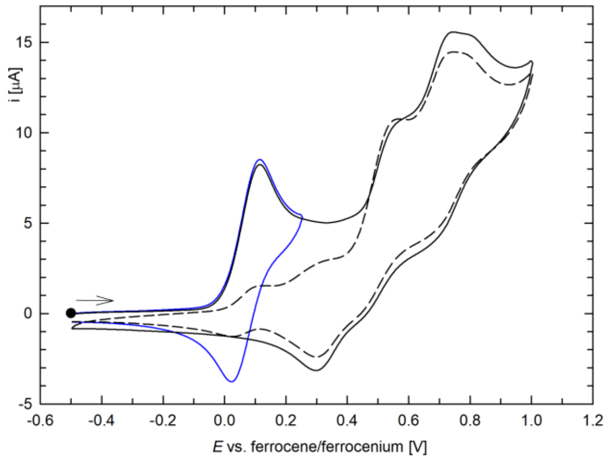


Figure S27 Cyclic voltammograms of **3** recorded over different potential ranges (scan rate: 100 mV s⁻¹, glassy carbon electrode, 0.1 M $Bu_4N[PF_6]$ in dichloromethane)

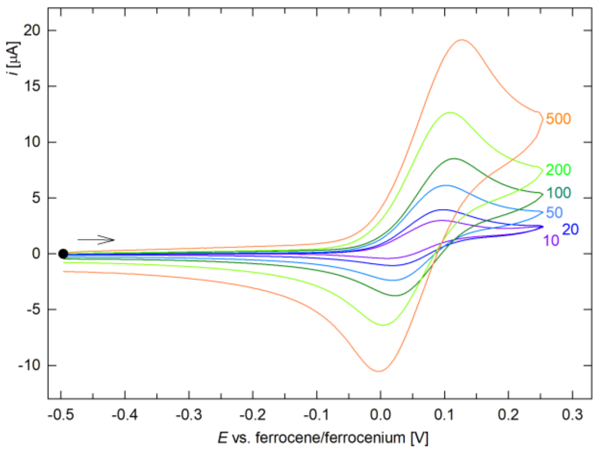


Figure S28 Cyclic voltammograms of **3** recorded at different scan rates (scan rate given in $mV\ s^{-1}$ in the Figure; glassy carbon electrode, 0.1 M $Bu_4N[PF_6]$ in dichloromethane)

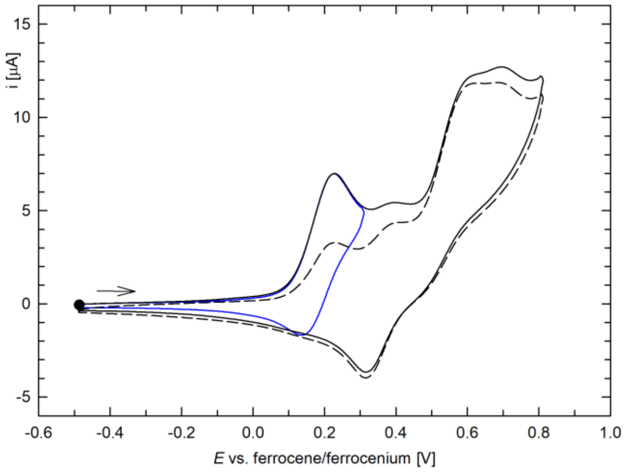


Figure S29 Cyclic voltammograms of **8** recorded over different potential ranges (scan rate: 100 mV s^{-1}, glassy carbon electrode, 0.1 M $Bu_4N[PF_6]$ in dichloromethane)

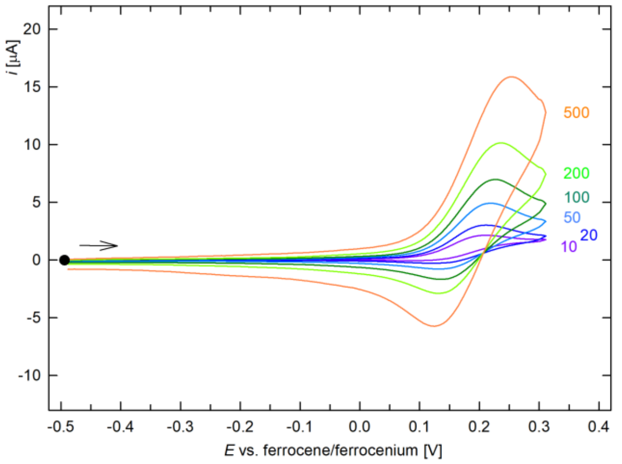


Figure S30 Cyclic voltammograms of **8** recorded at different scan rates (scan rate given in mV s^{-1} in the Figure; glassy carbon electrode, 0.1 M $Bu_4N[PF_6]$ in dichloromethane)

Copies of the NMR spectra

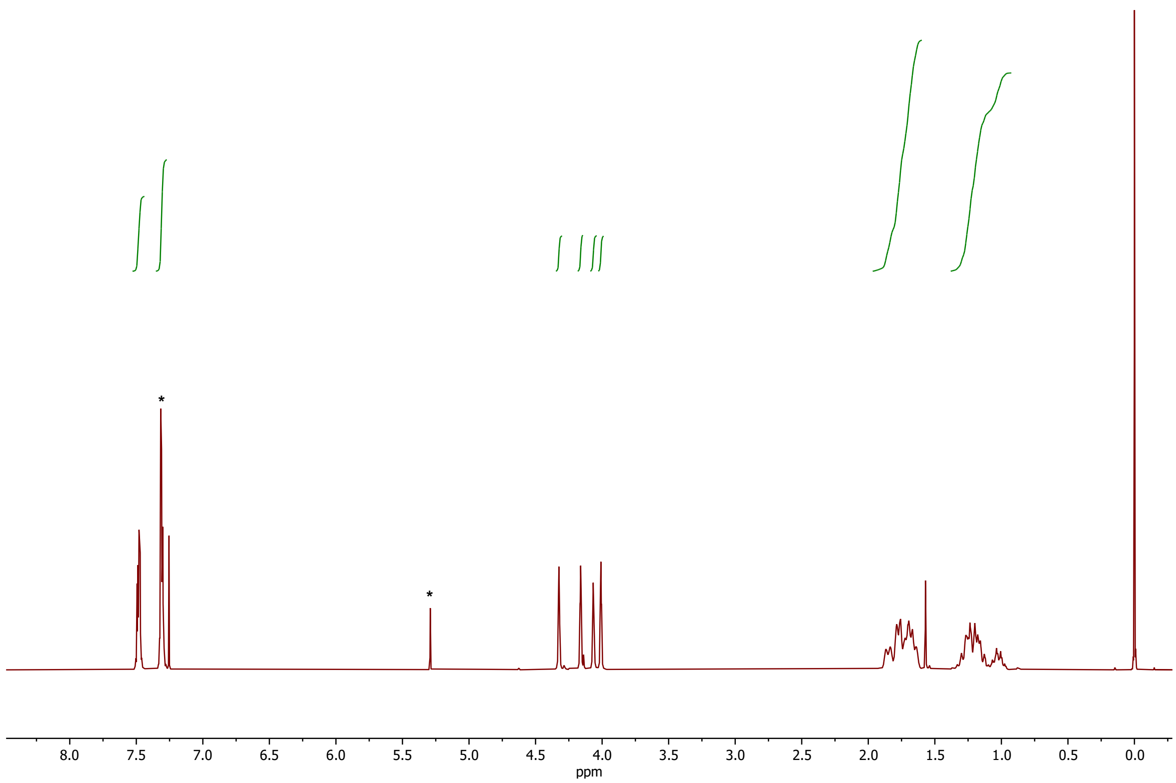


Figure S31 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**

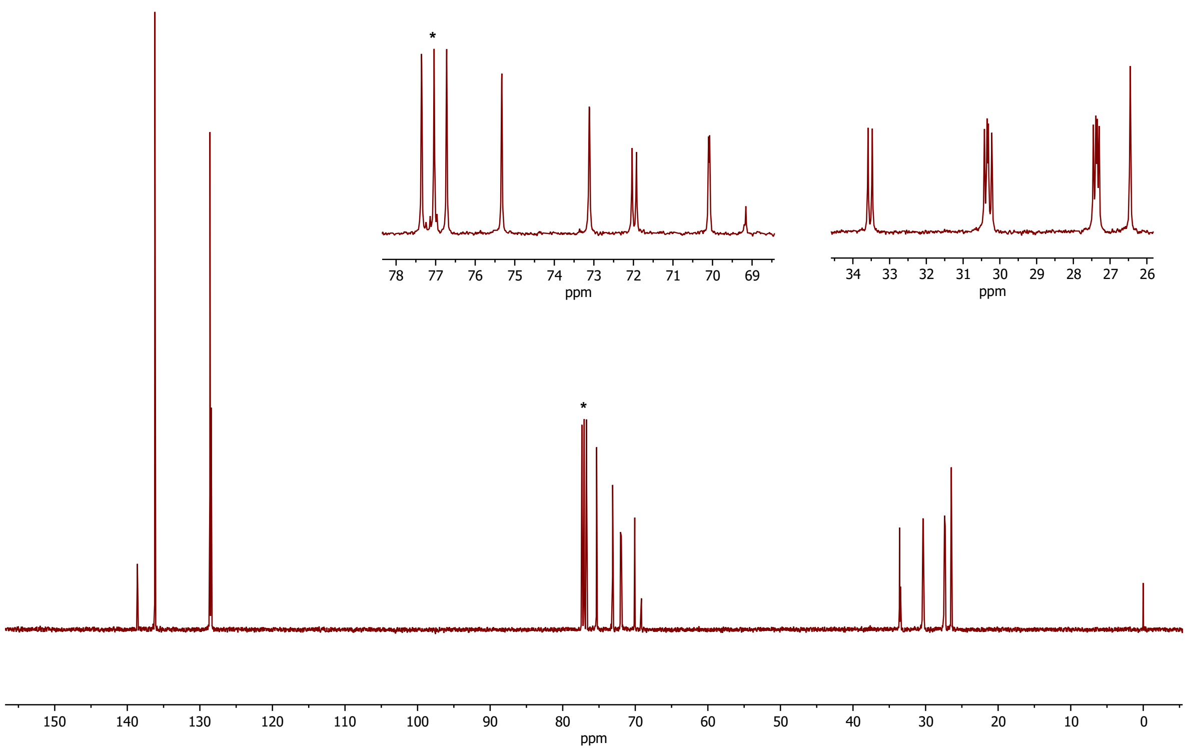


Figure S32 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3**

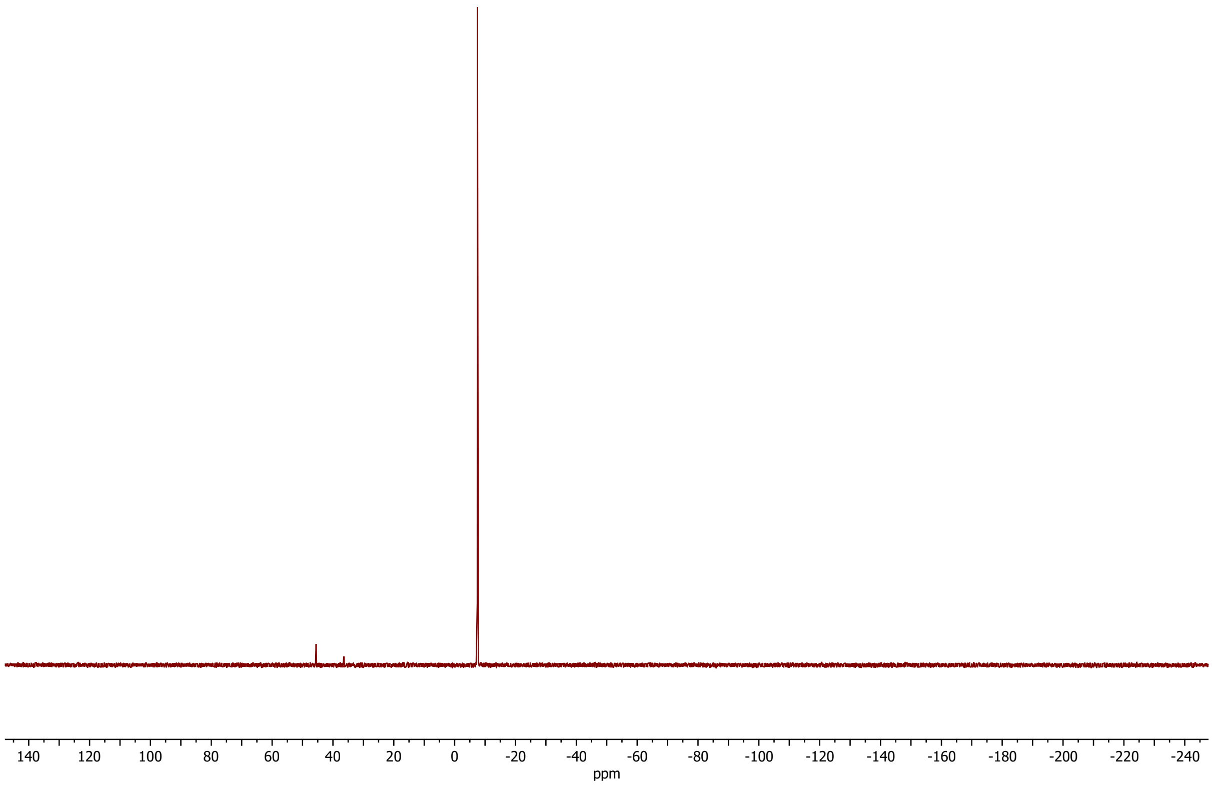


Figure S33 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3**

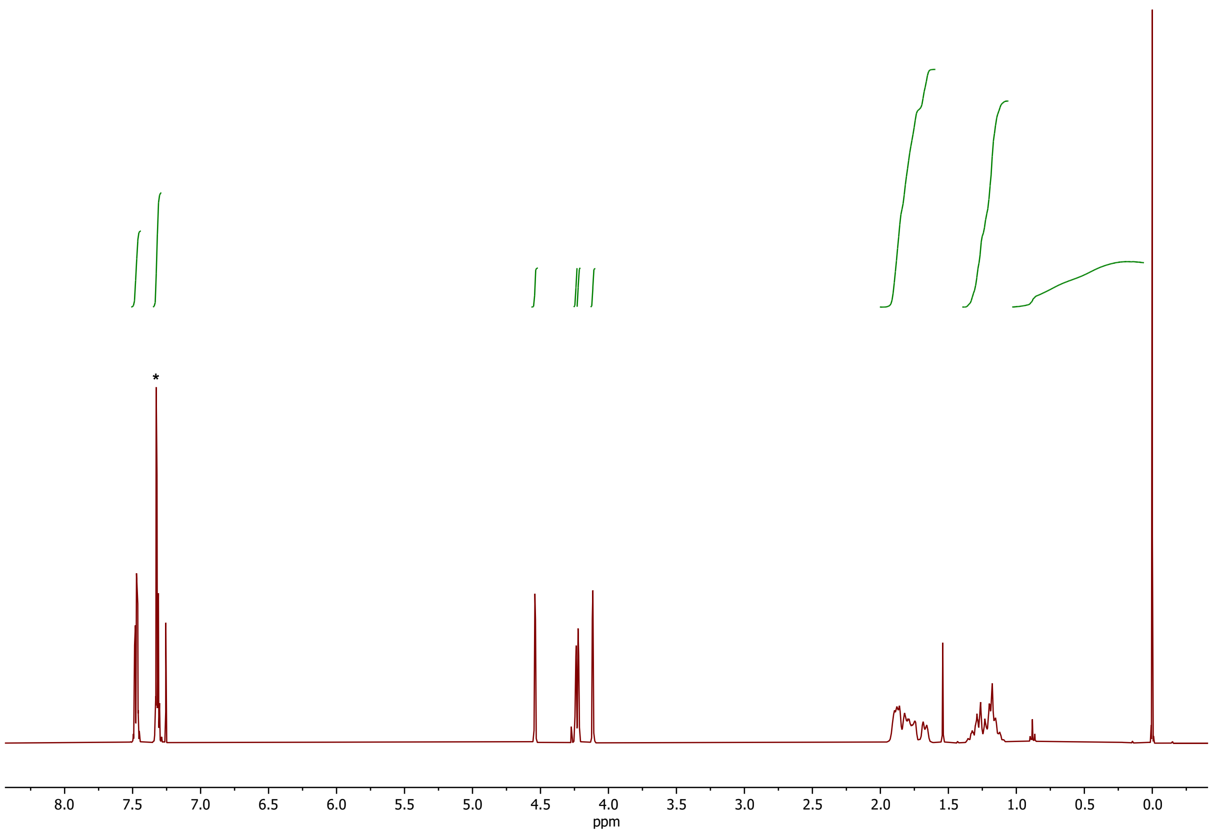


Figure S34 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**·BH_3

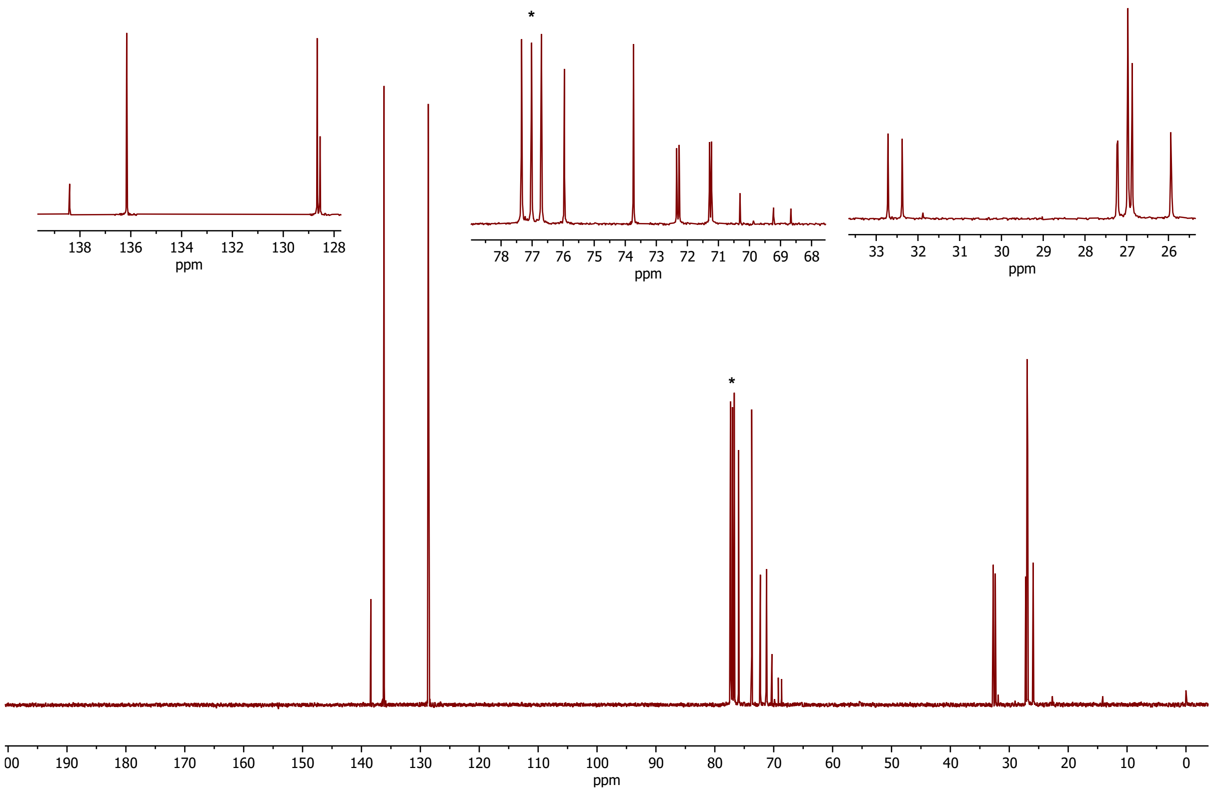


Figure S35 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3**·BH_3

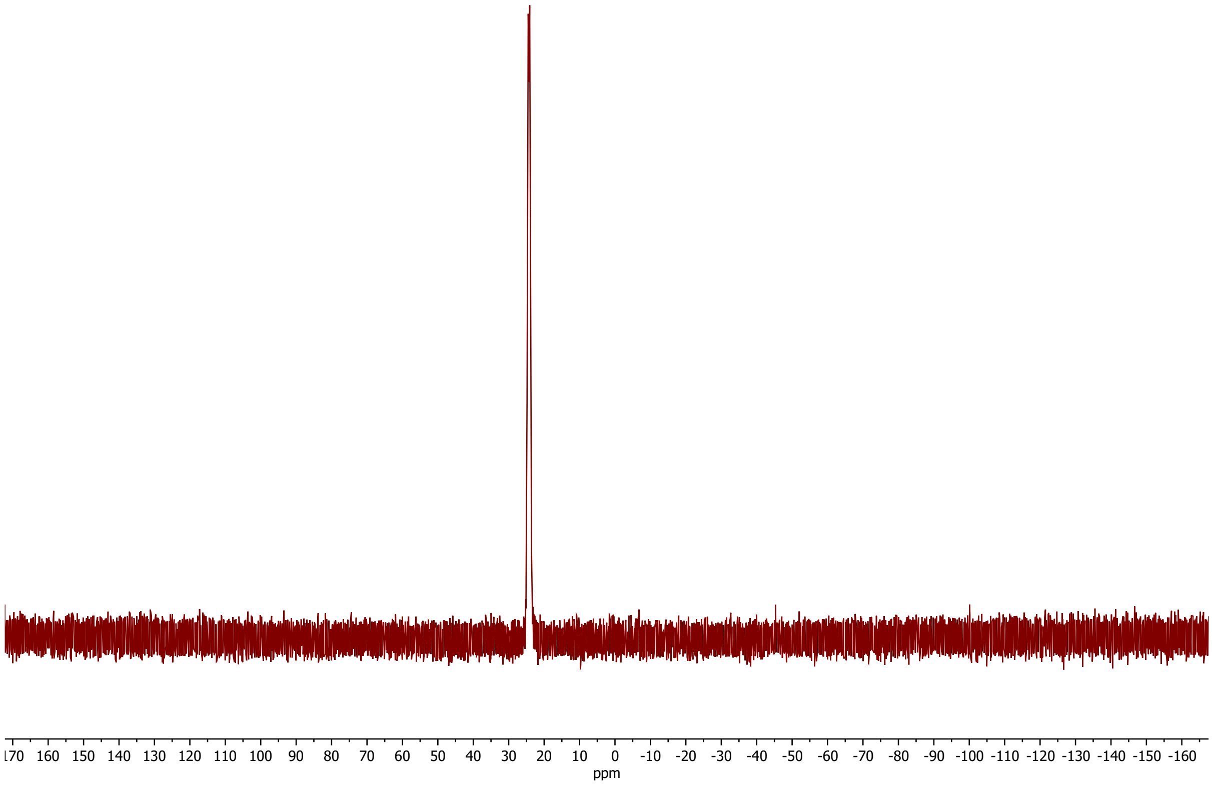


Figure S36 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3**·BH_3

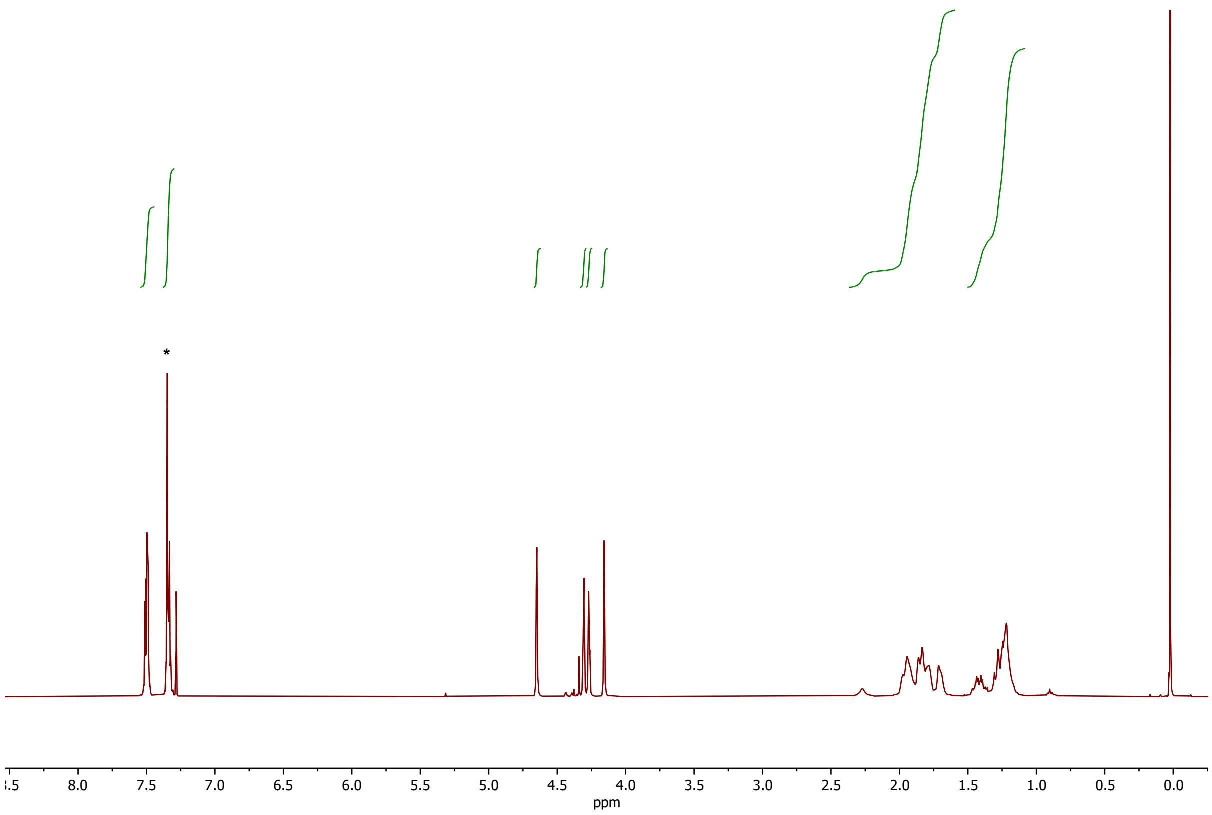


Figure S37 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3O**

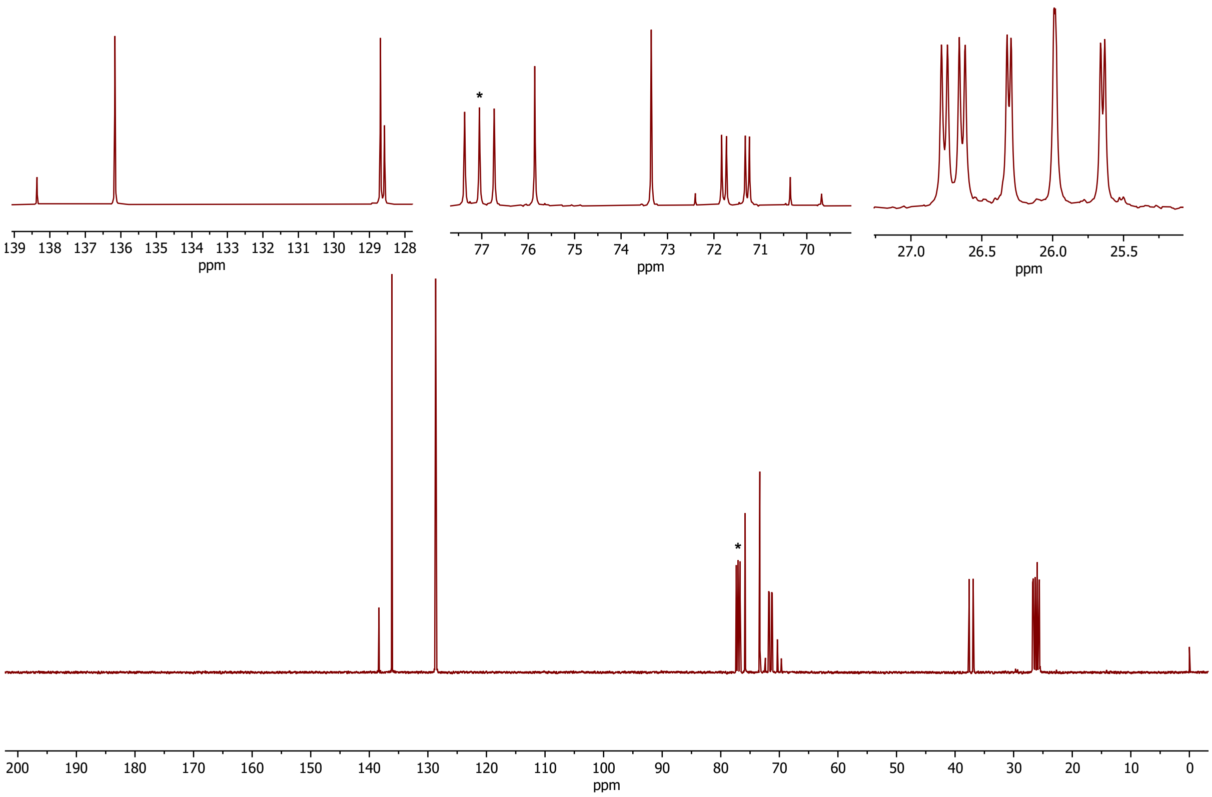


Figure S38 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3O**

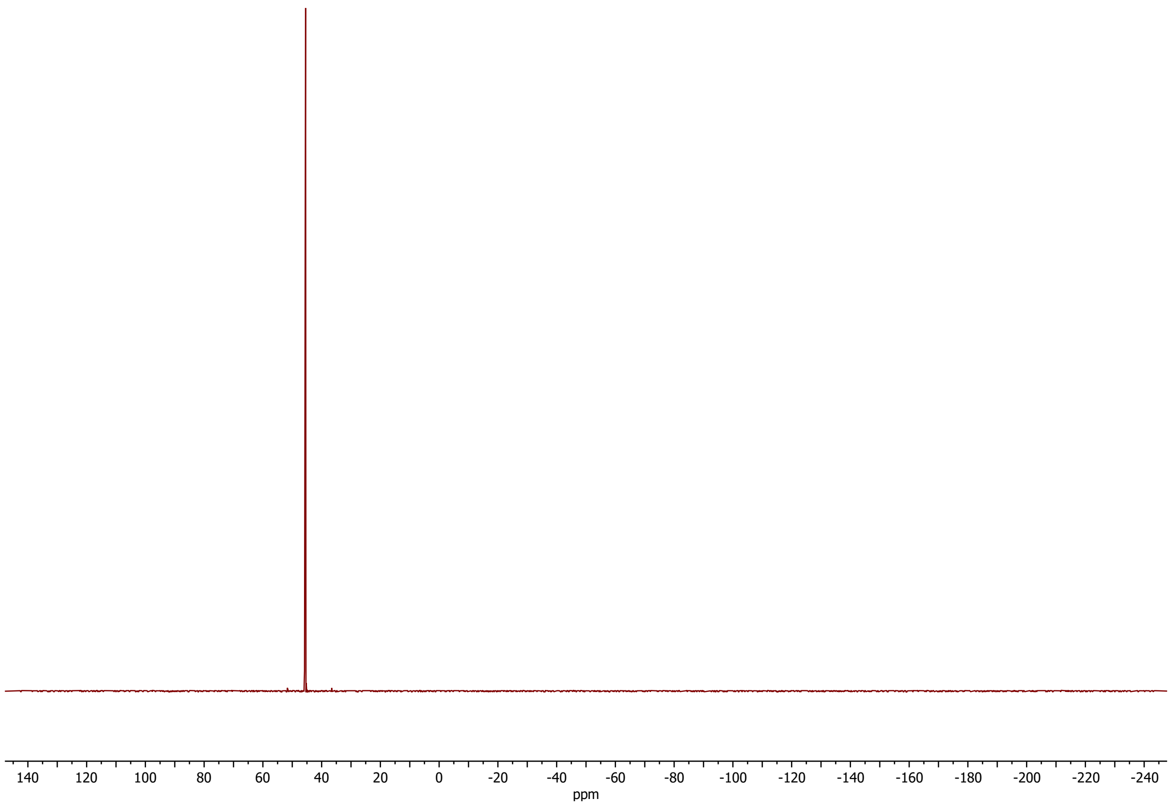


Figure S39 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3O**

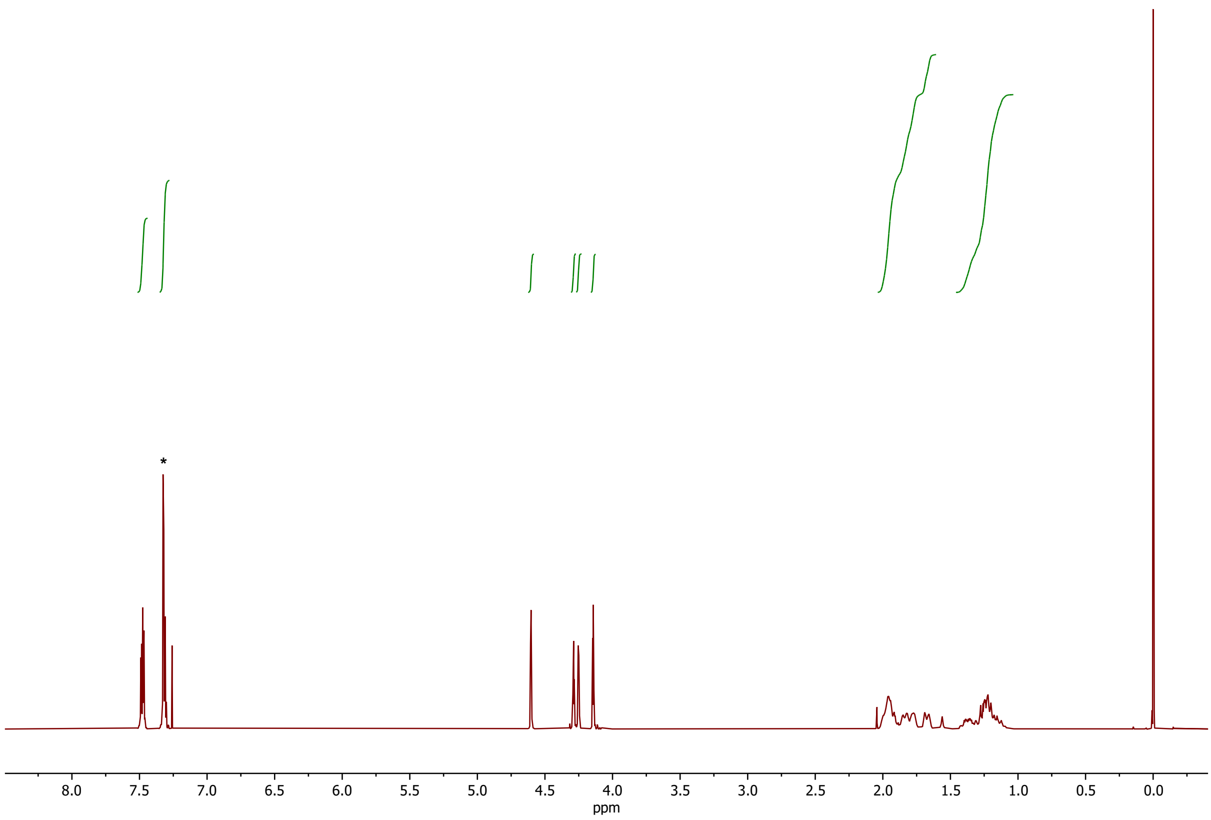


Figure S40 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3S**

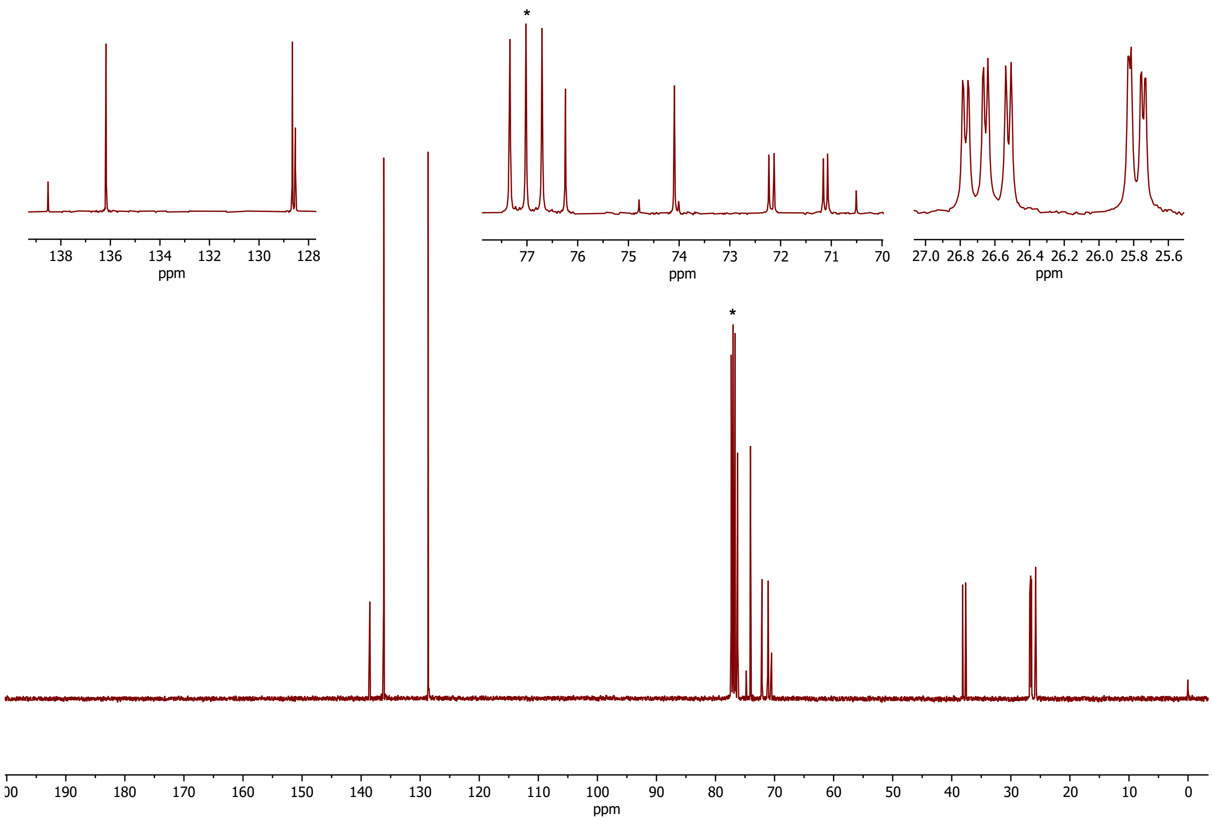


Figure S41 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3S**

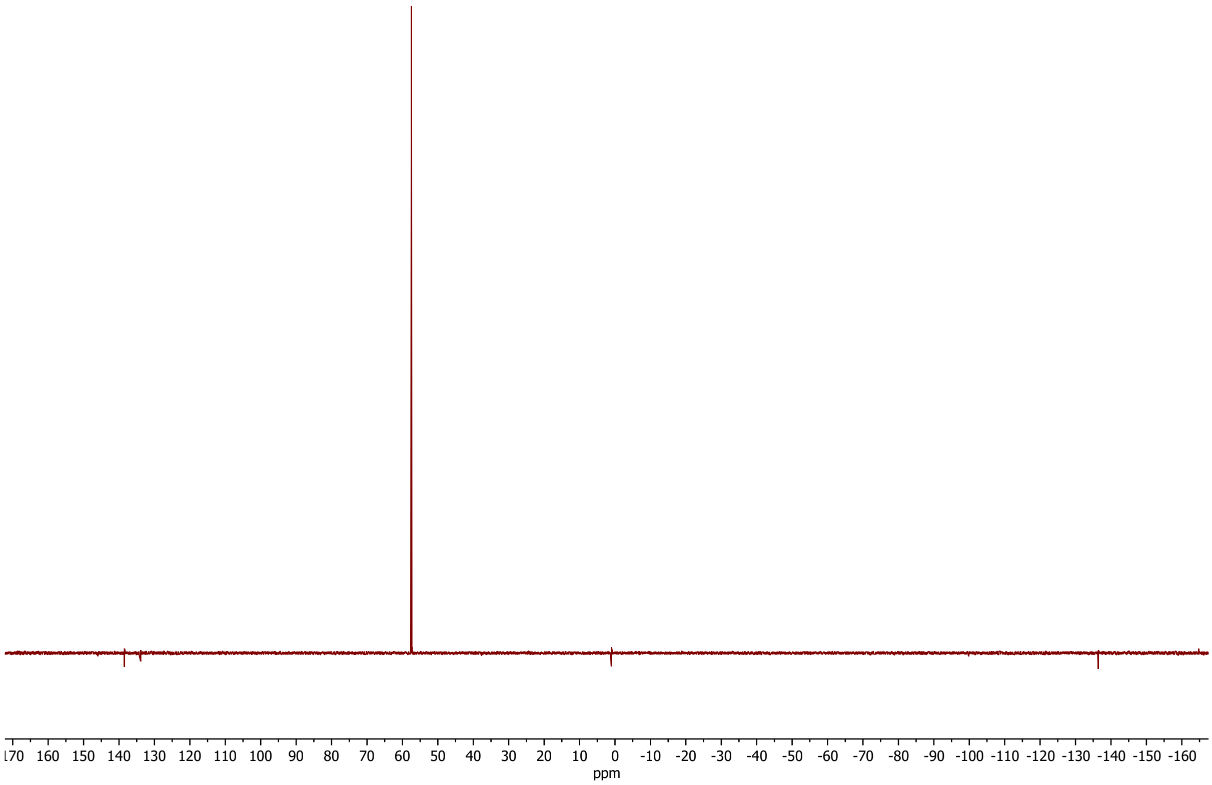


Figure S42 $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3S**

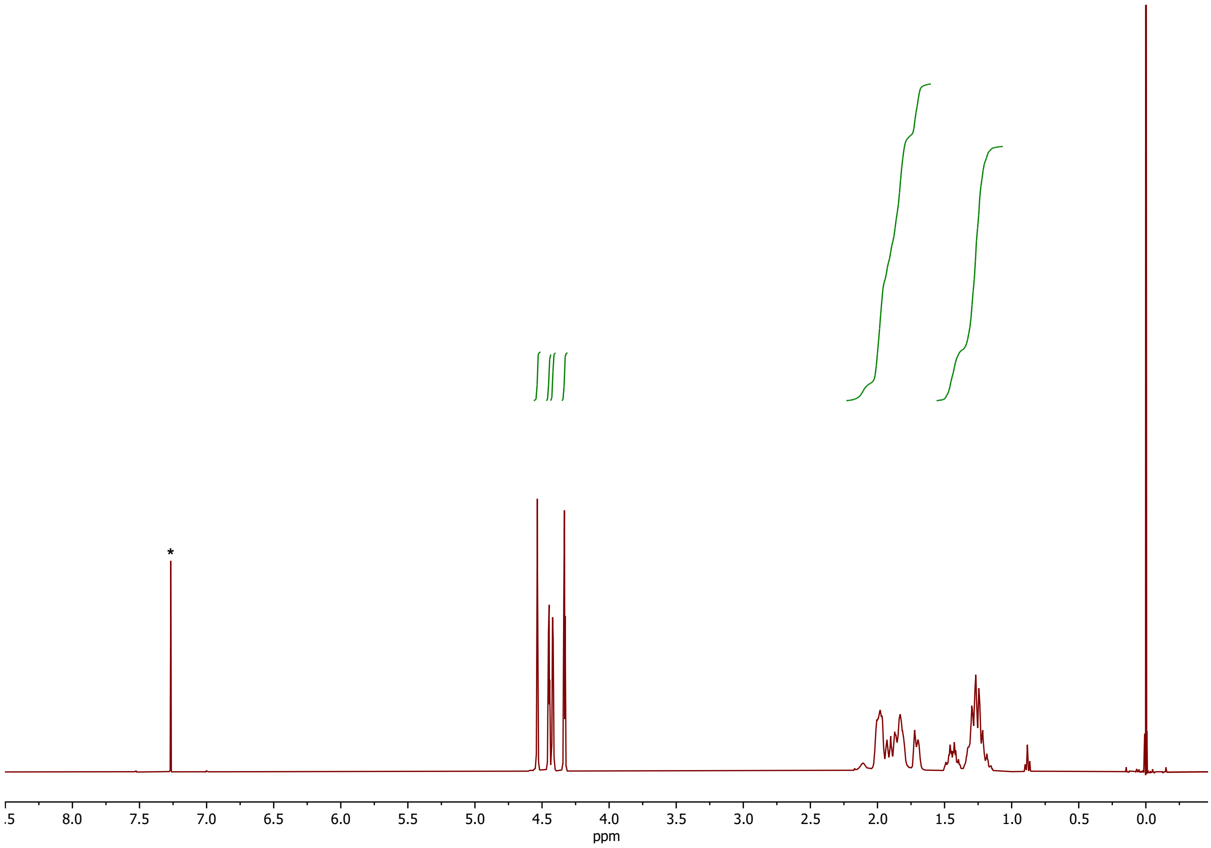


Figure S43 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4O**

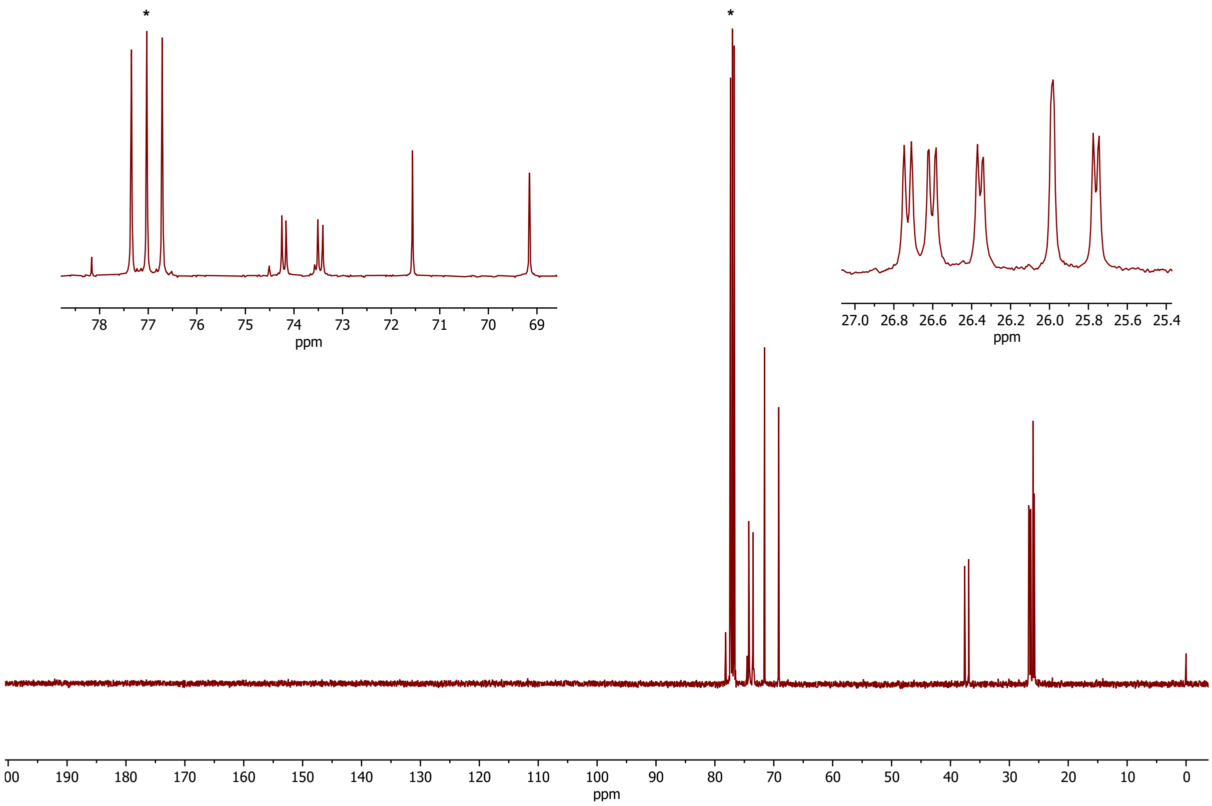


Figure S44 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4O**

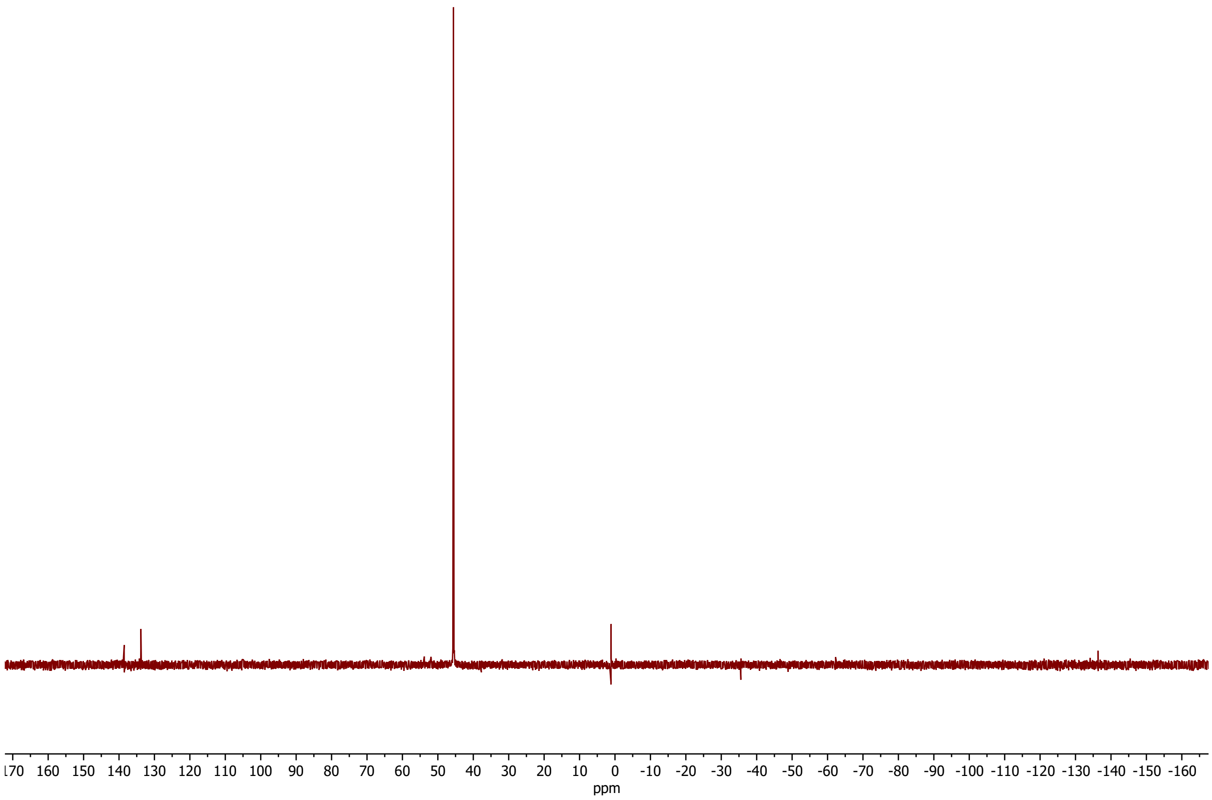


Figure S45 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **4O**

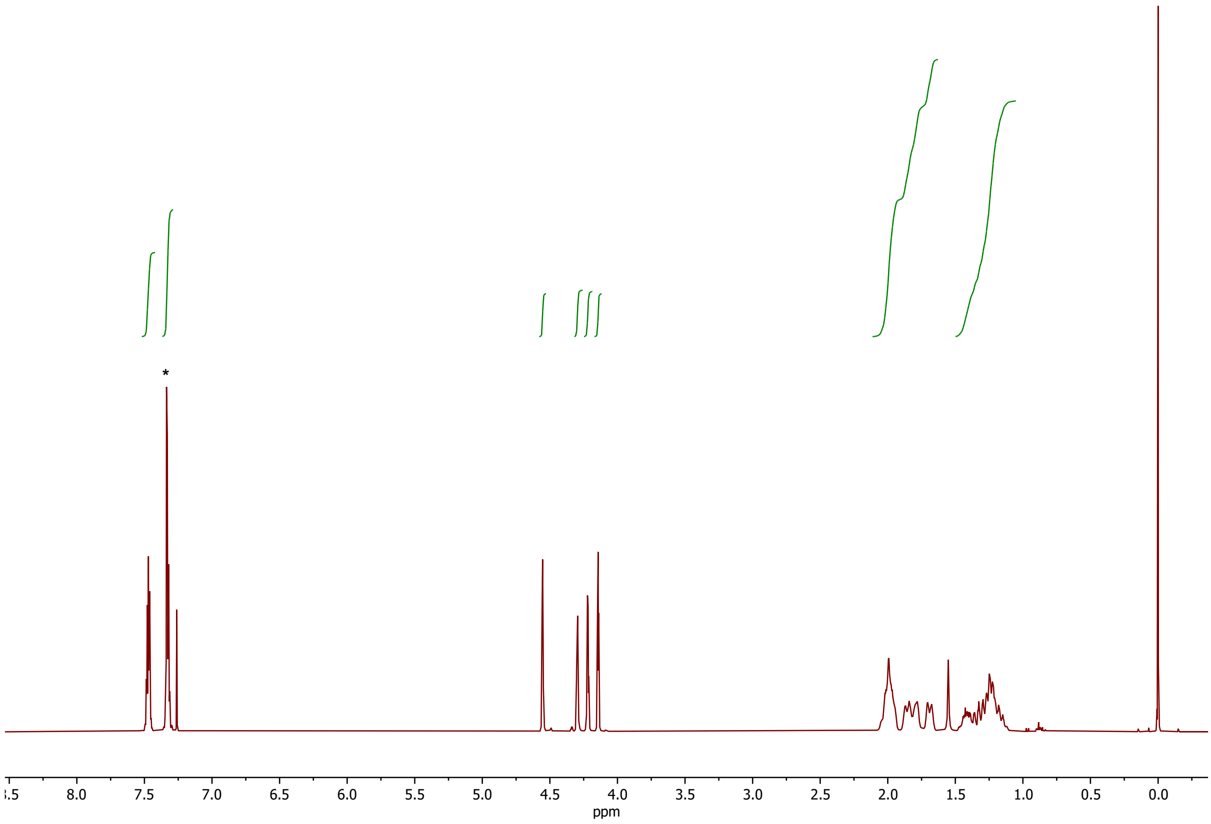


Figure S46 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**

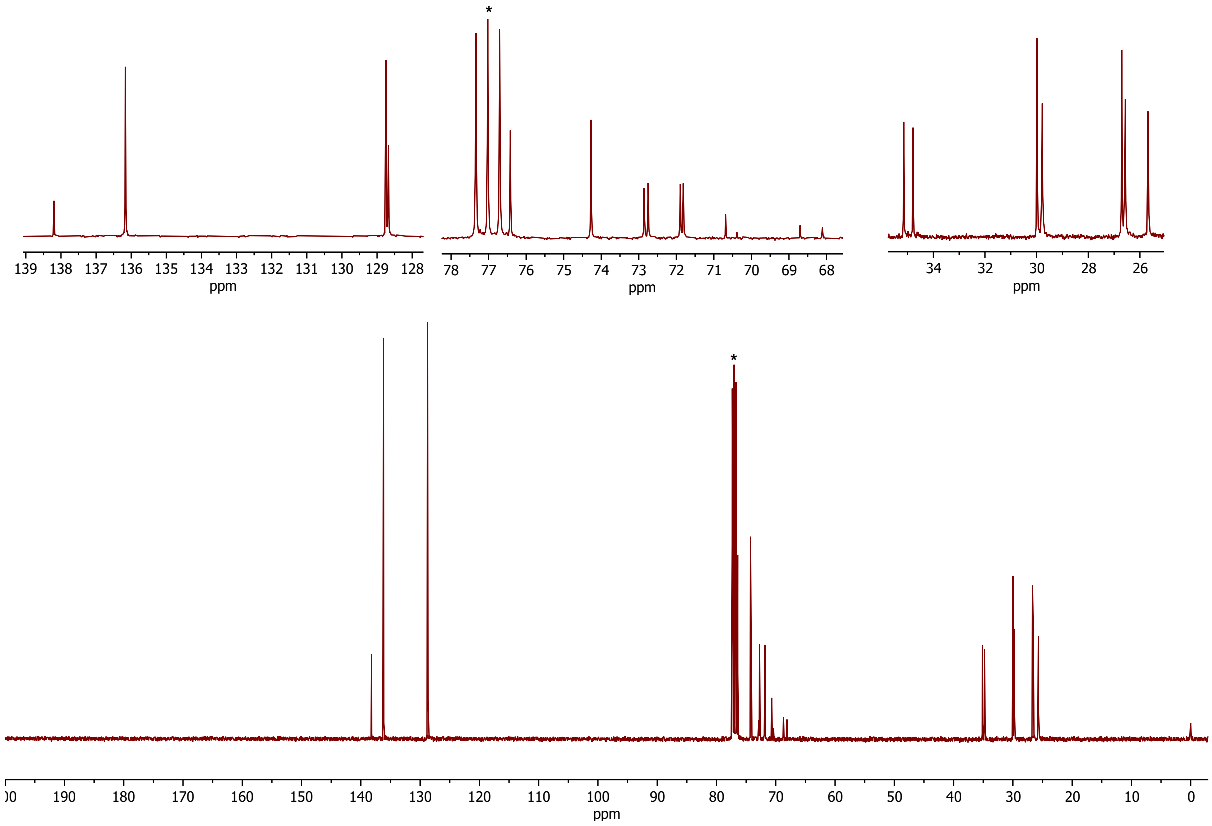


Figure S47 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5**

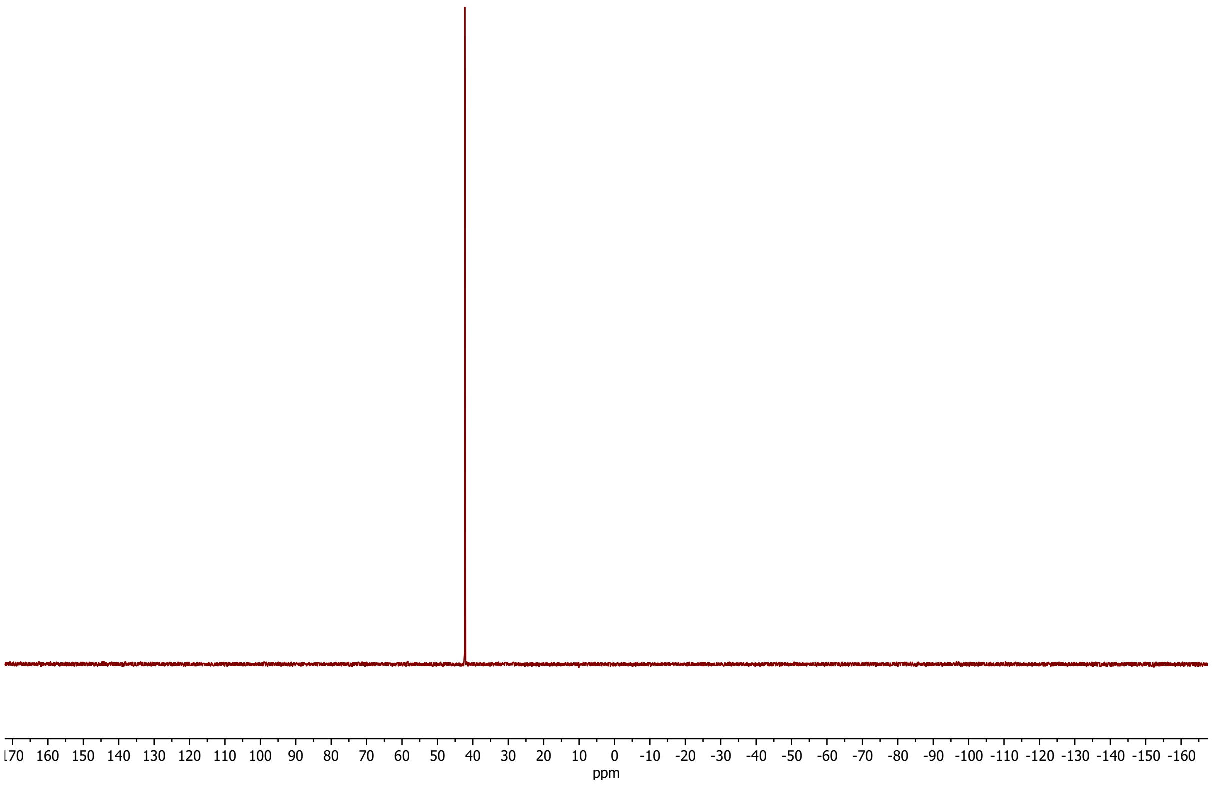


Figure S48 $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5**

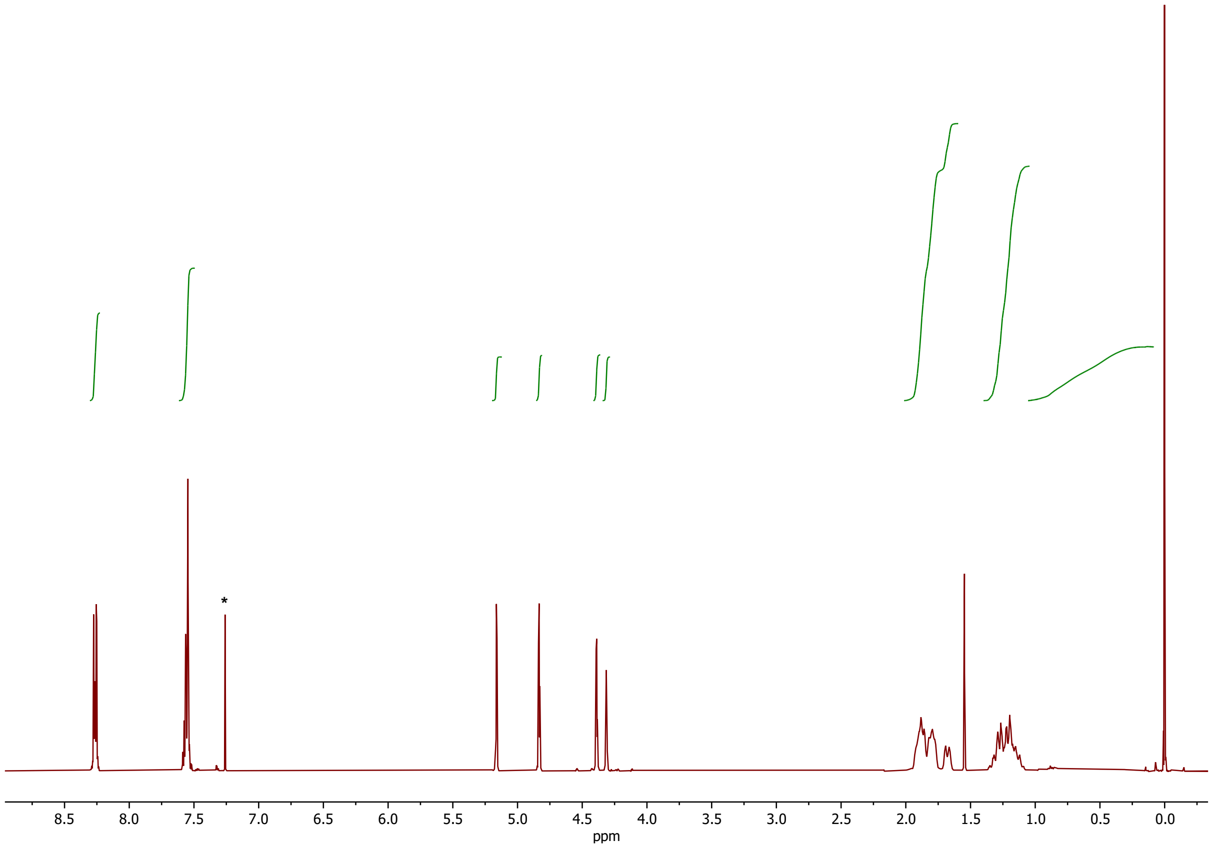


Figure S49 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**·BH_3

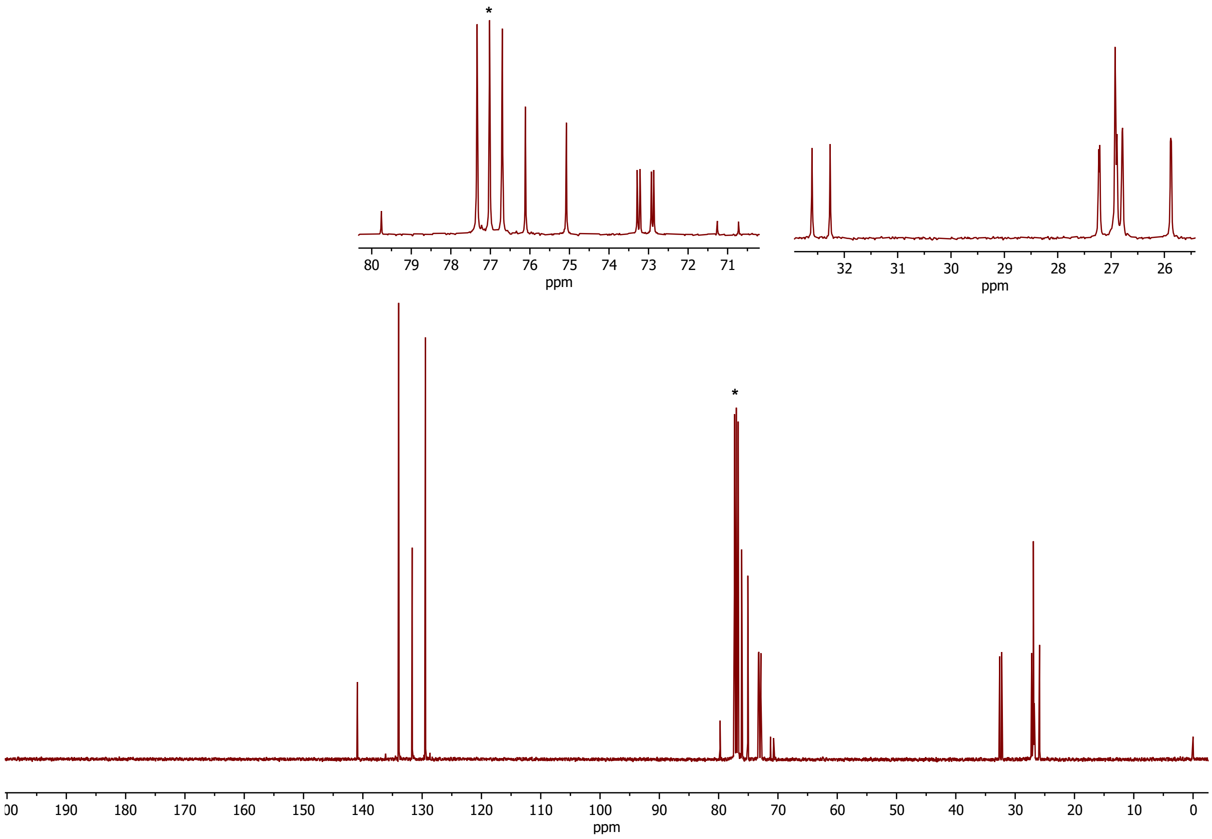


Figure S50 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6**·BH_3

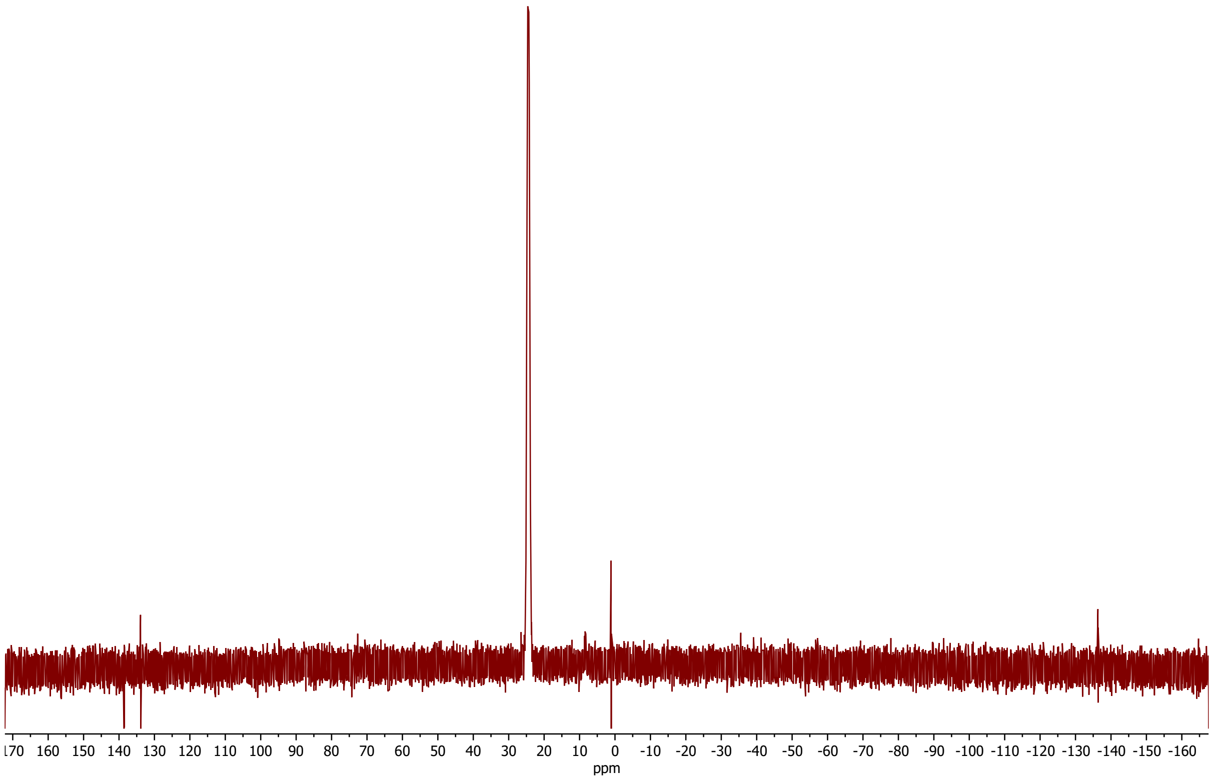


Figure S51 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6**·BH_3

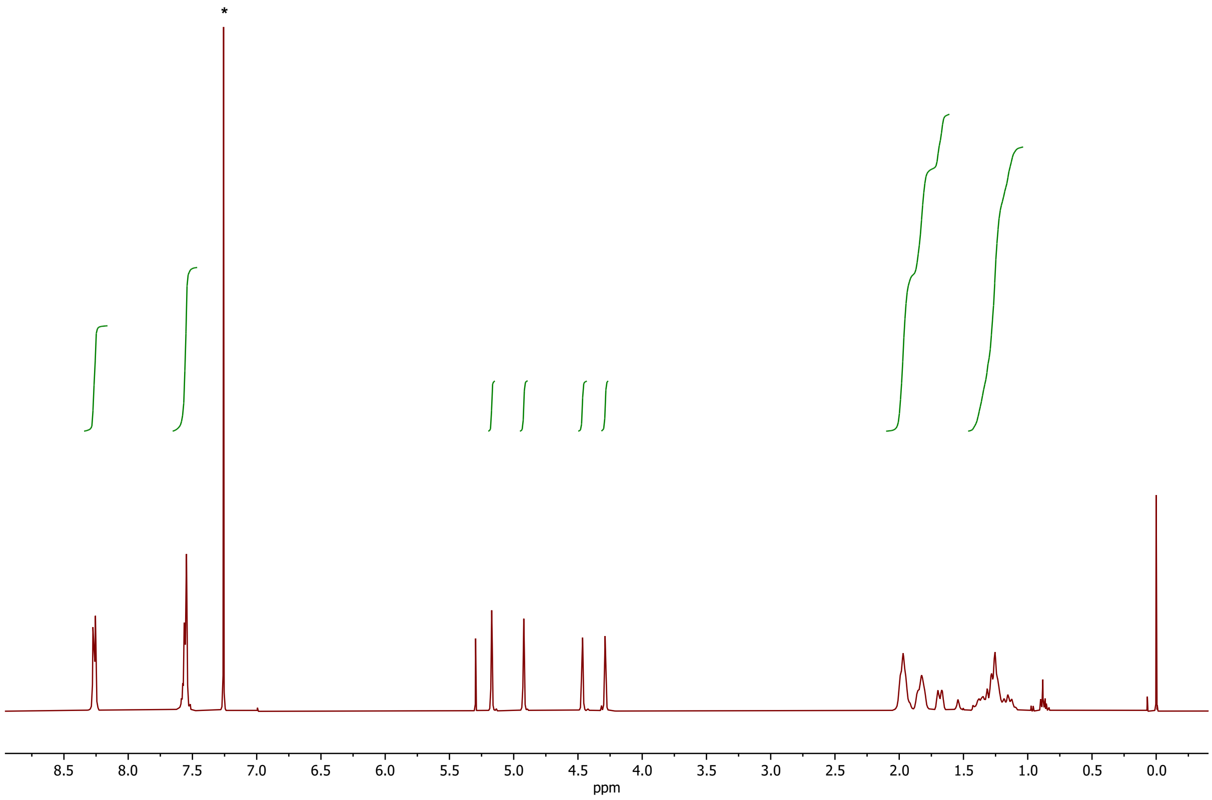


Figure S52 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6S**

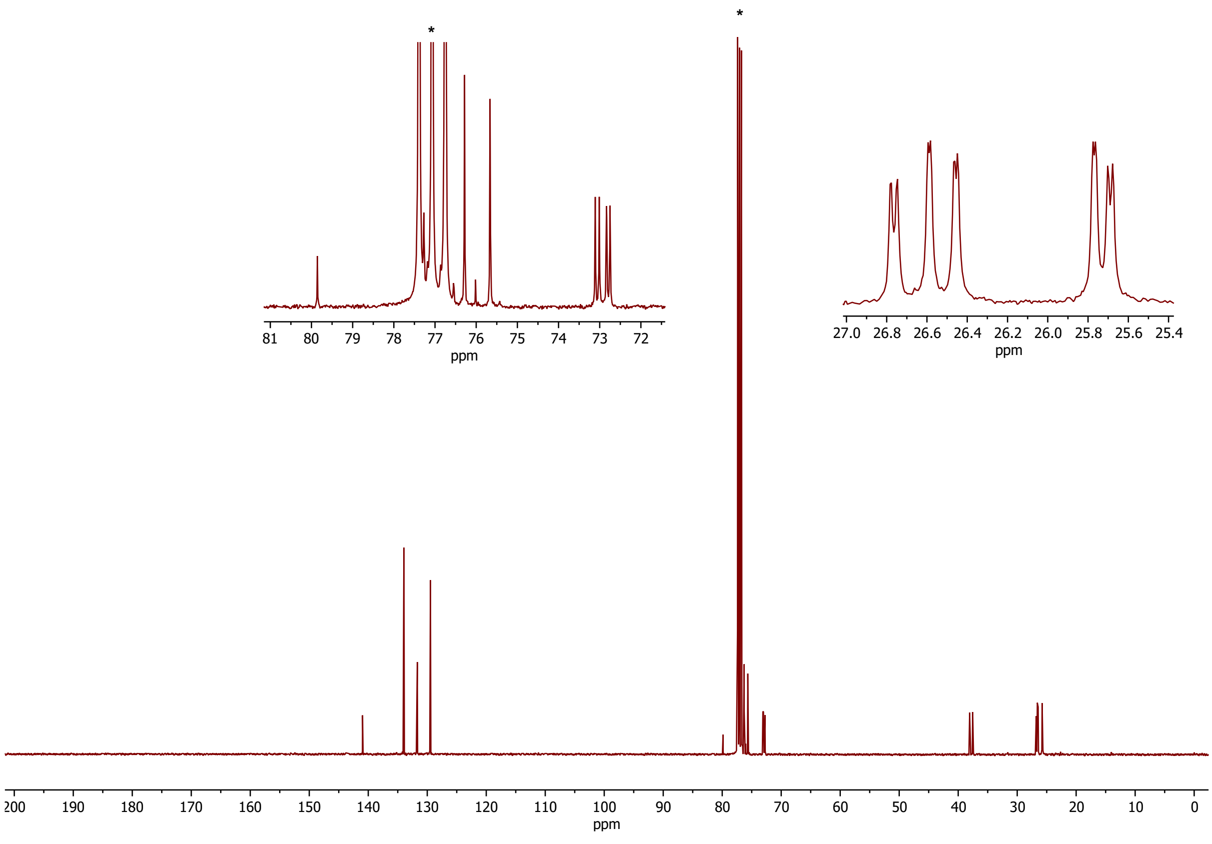


Figure S53 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6S**

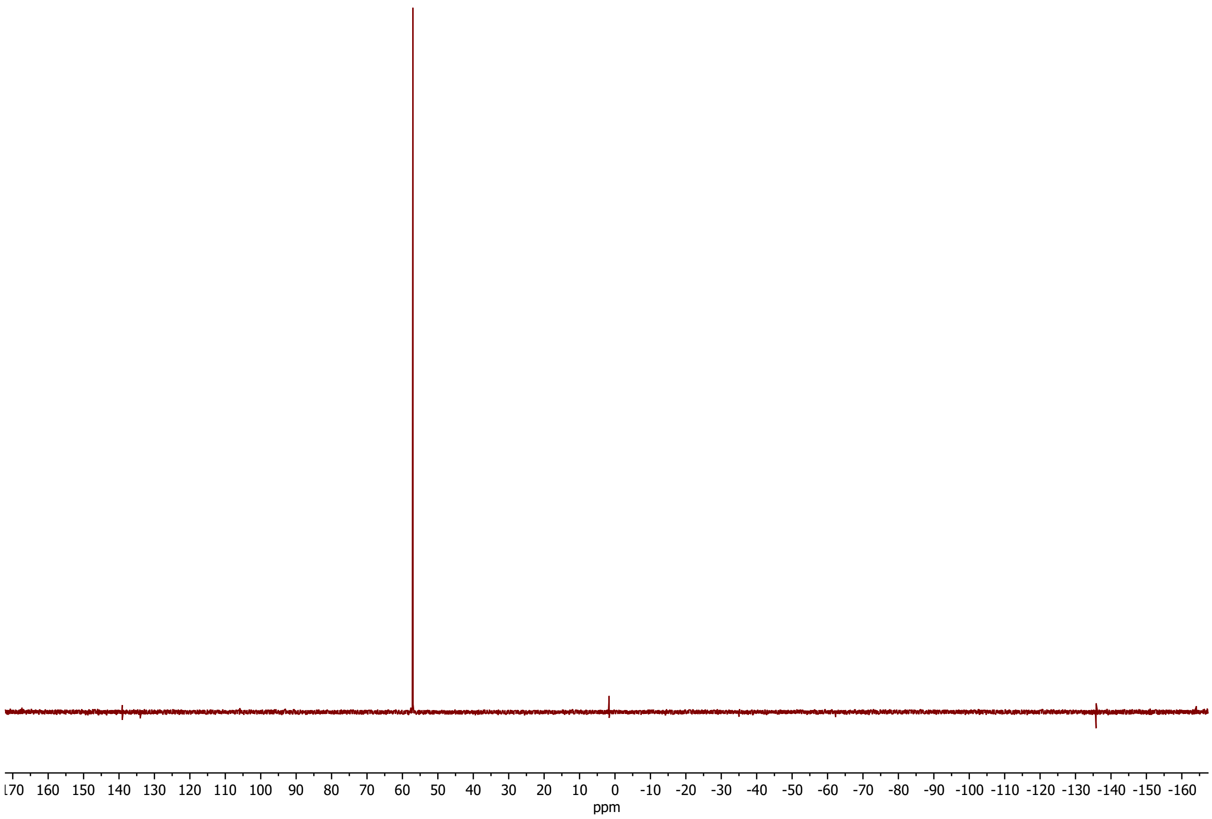


Figure S54 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6S**

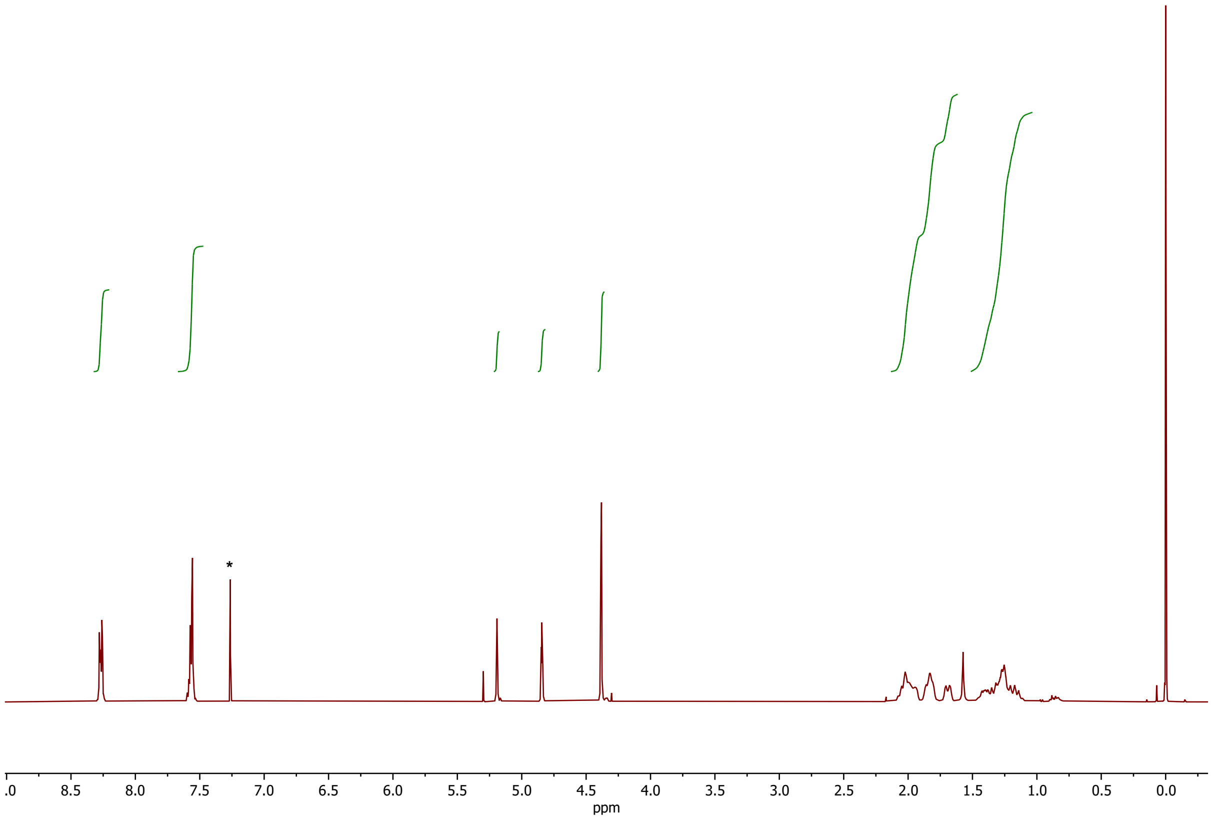


Figure S55 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7**

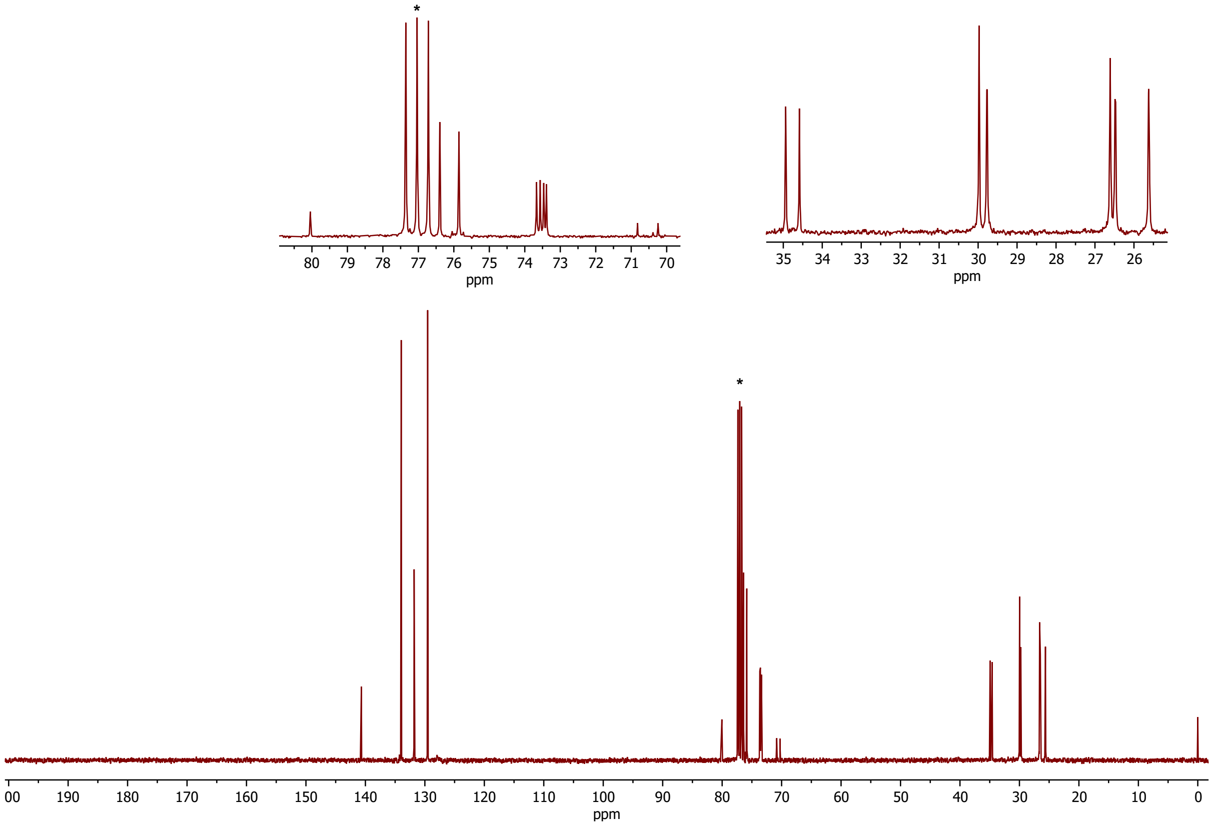


Figure S56 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **7**

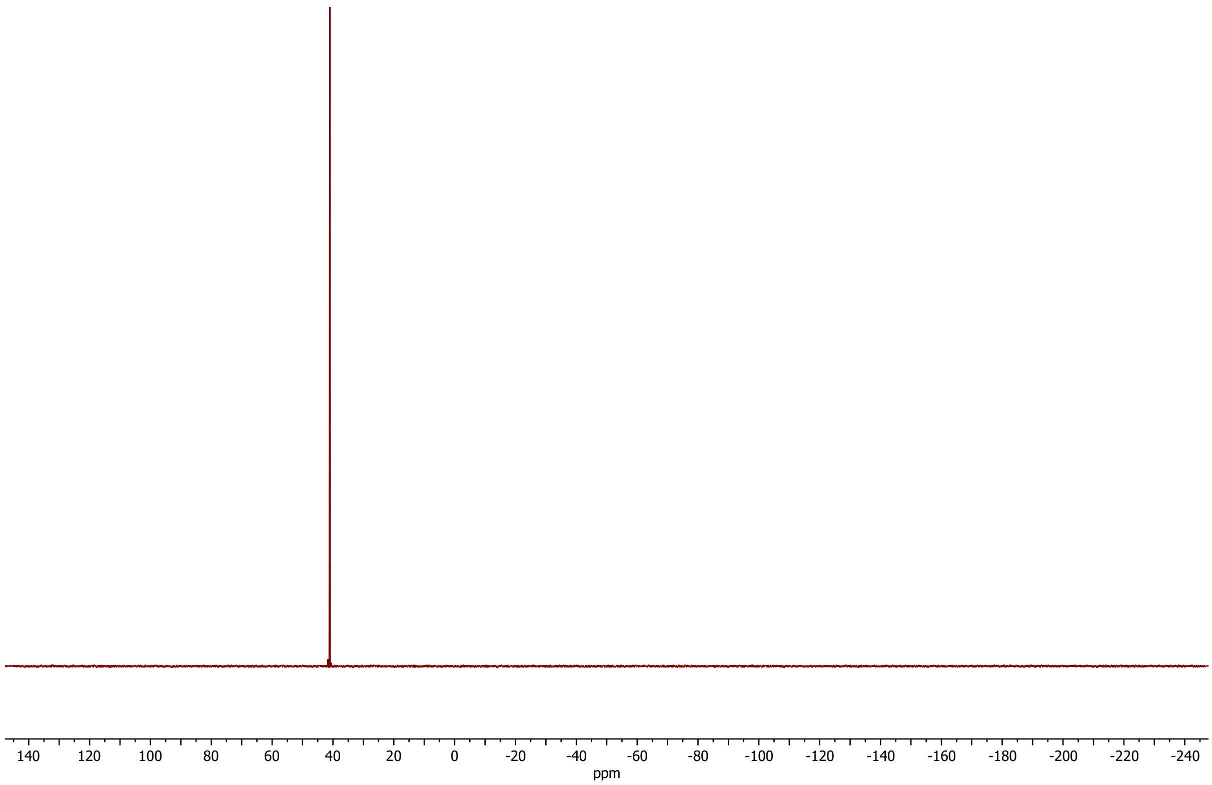


Figure S57 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **7**

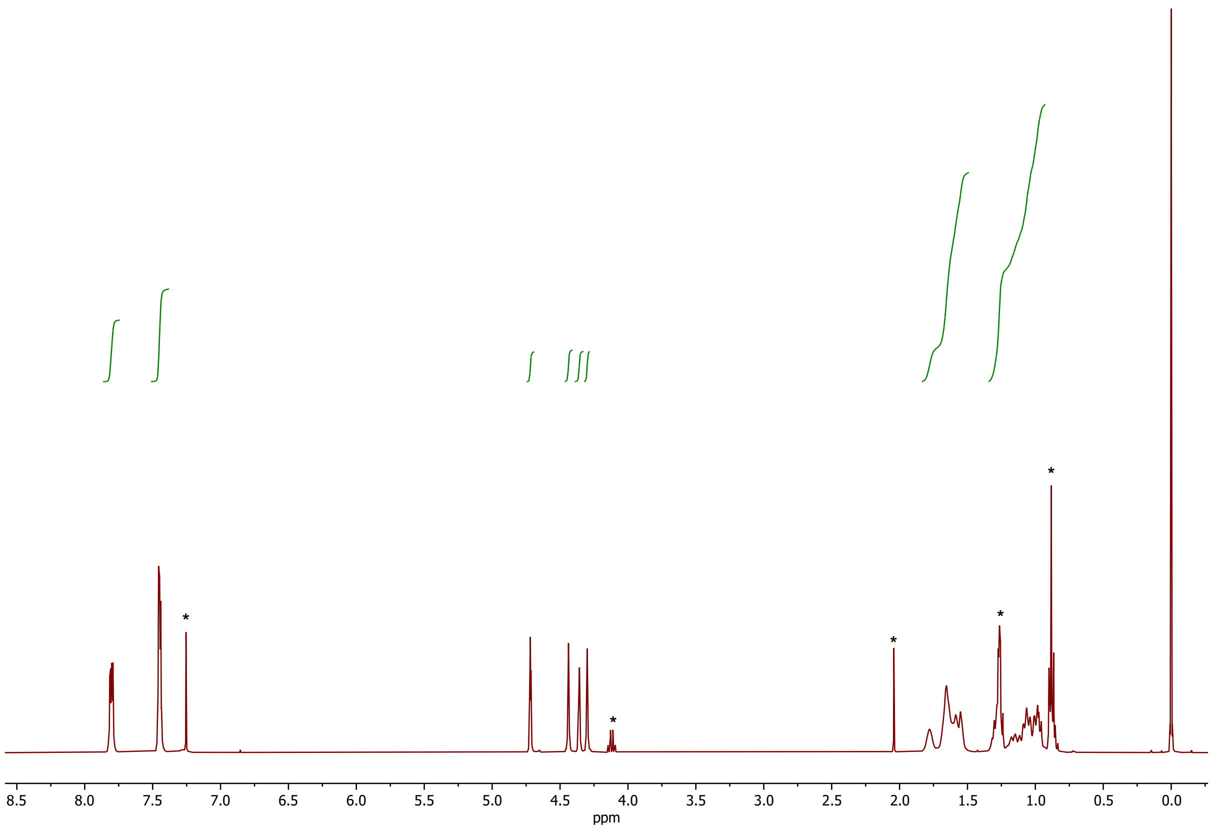


Figure S58 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8**

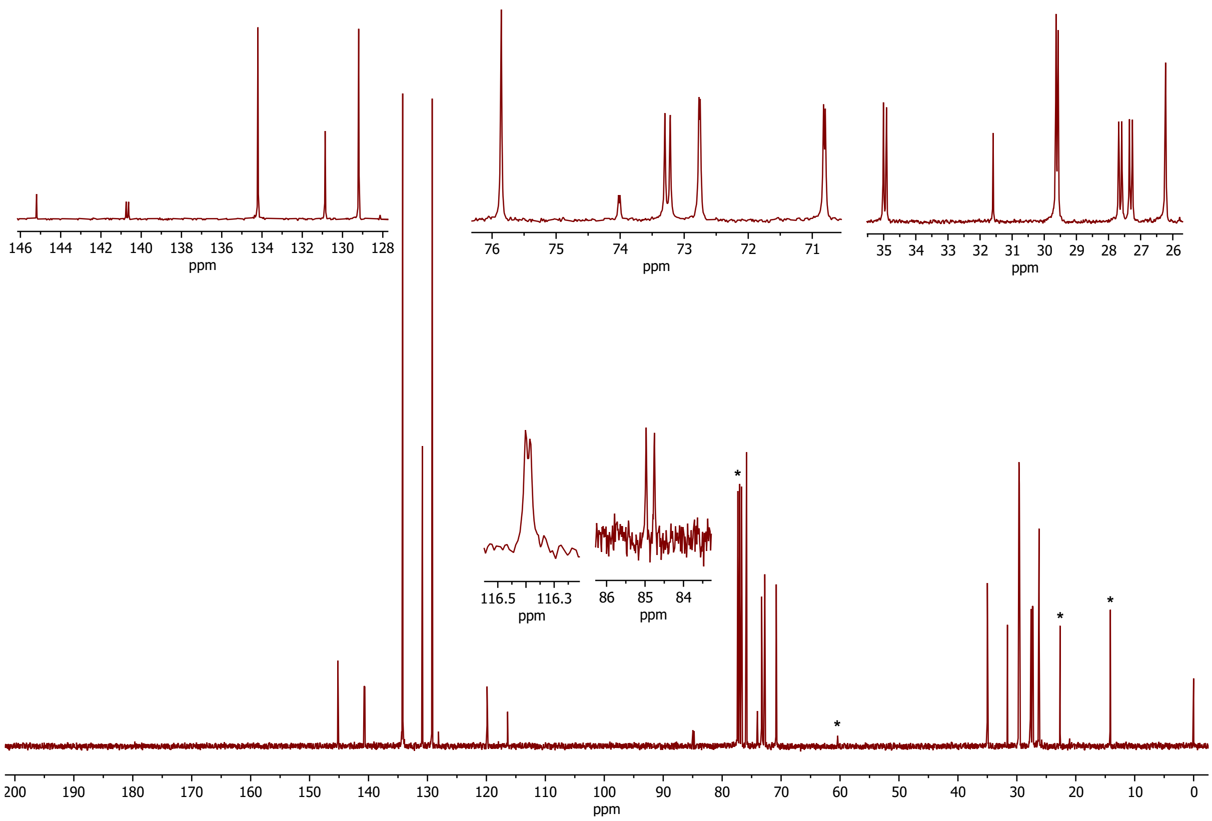


Figure S59 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8**

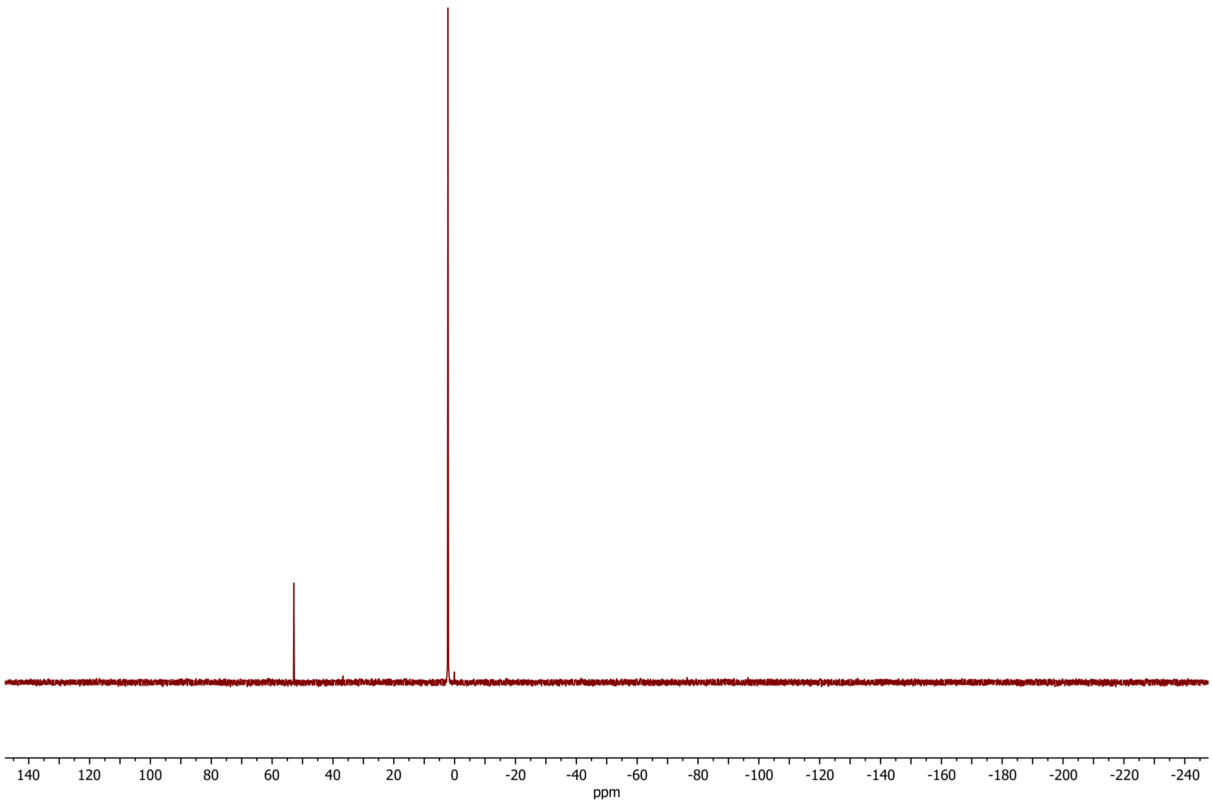


Figure S60 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **8**

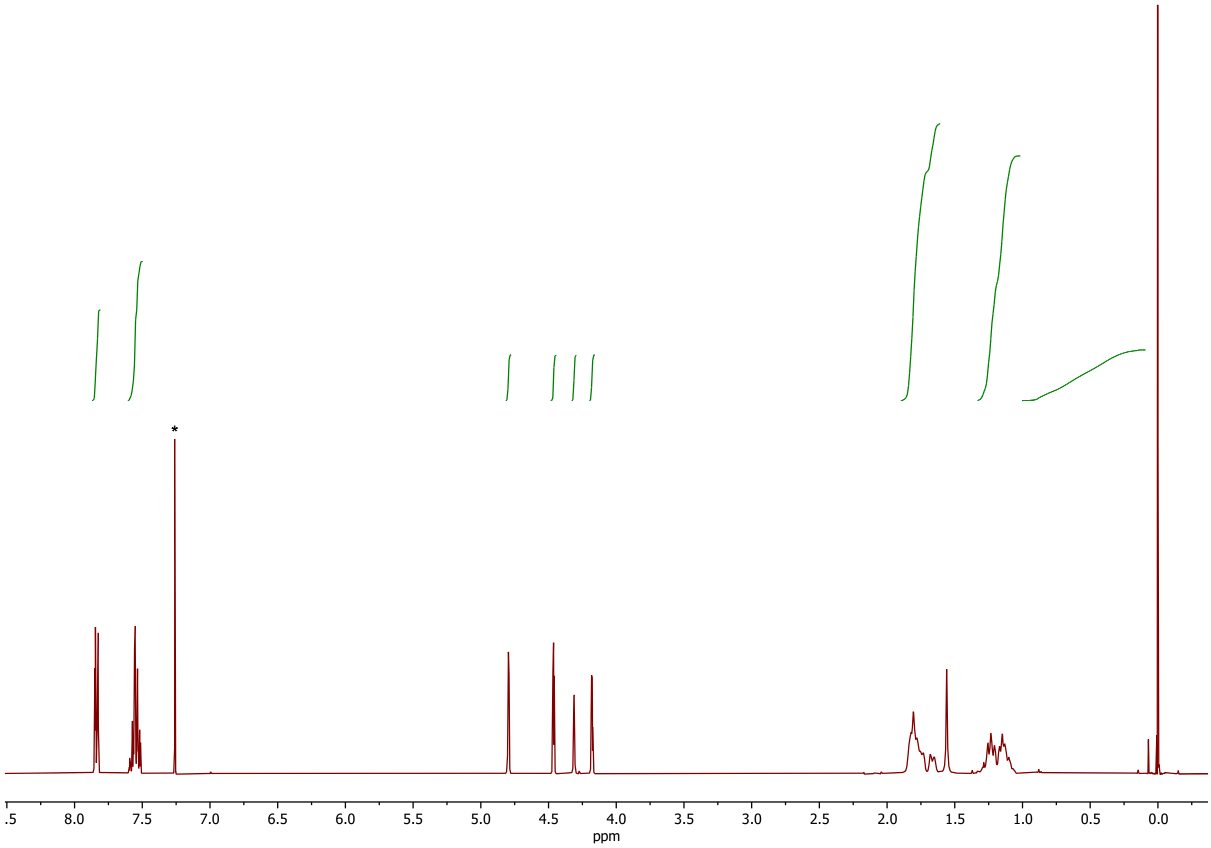


Figure S61 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8**·BH_3

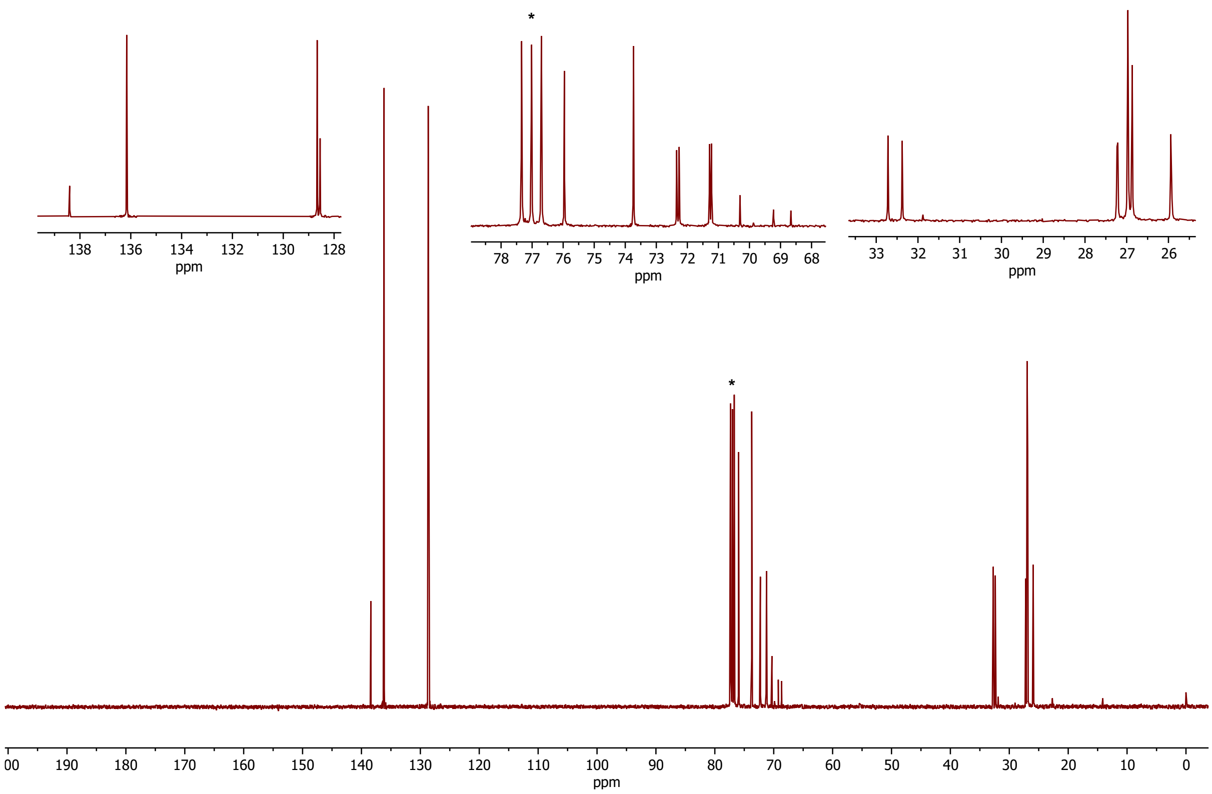


Figure S62 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8**·BH_3

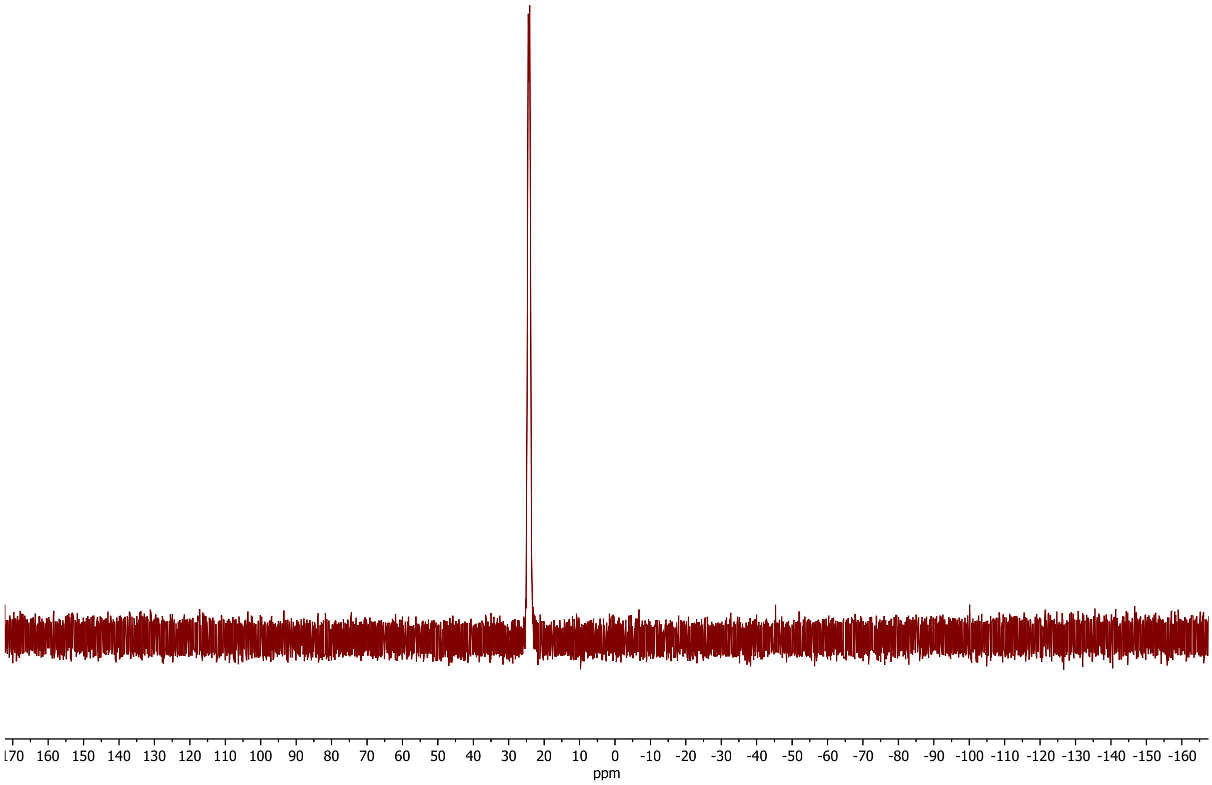


Figure S63 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **8**·BH_3

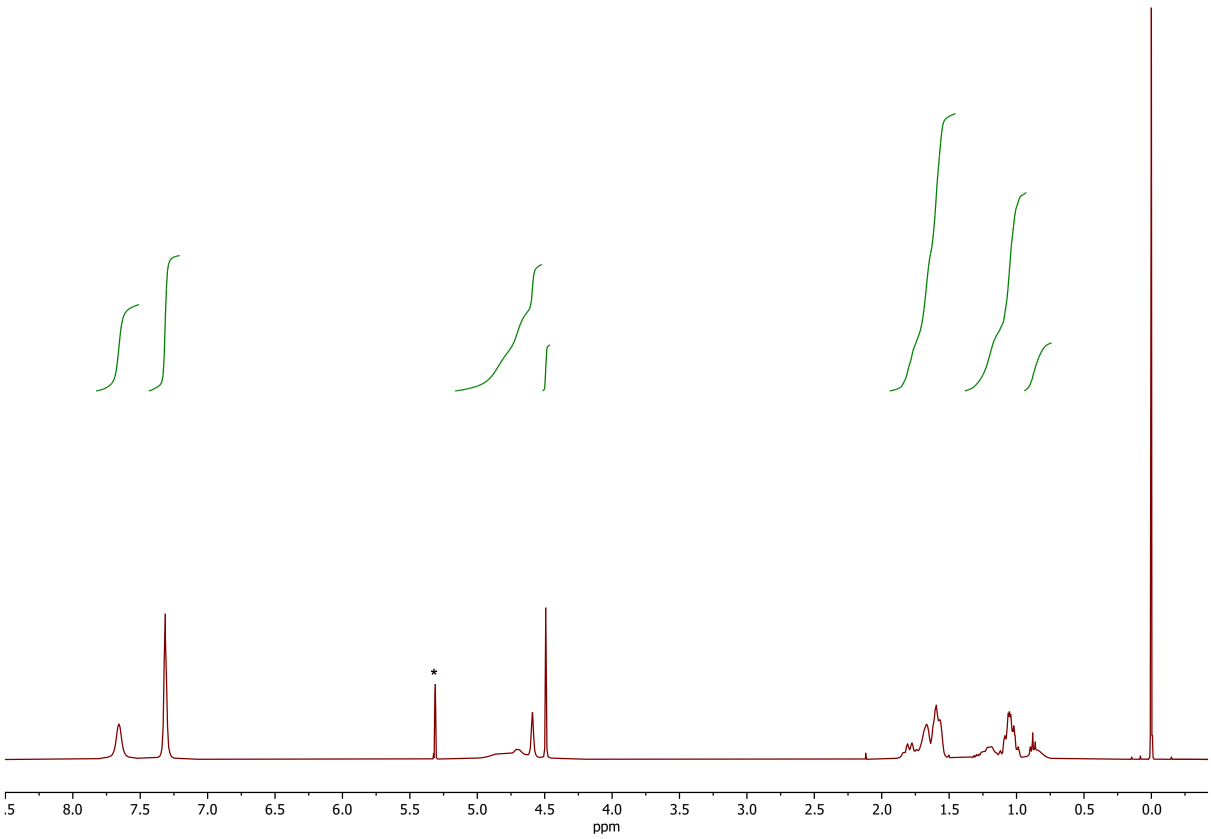


Figure S64 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **8O**

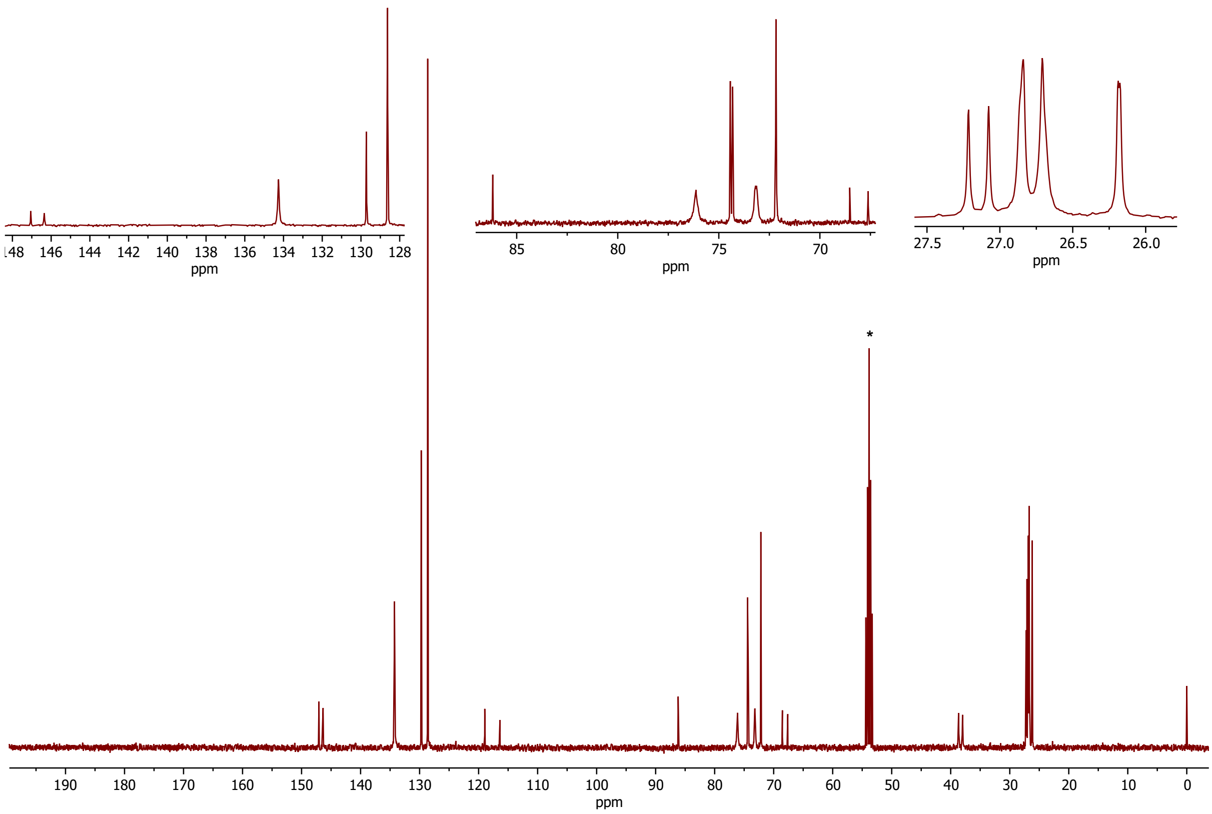


Figure S65 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **8O**

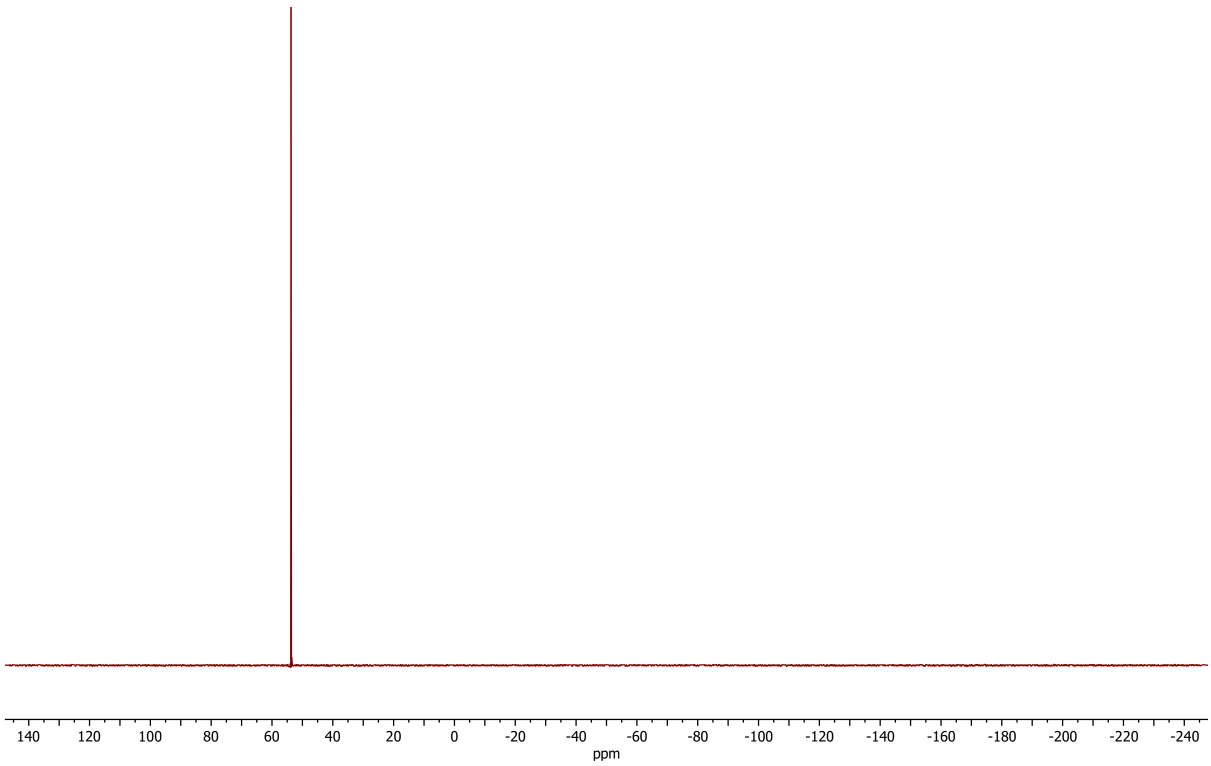


Figure S66 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **8O**

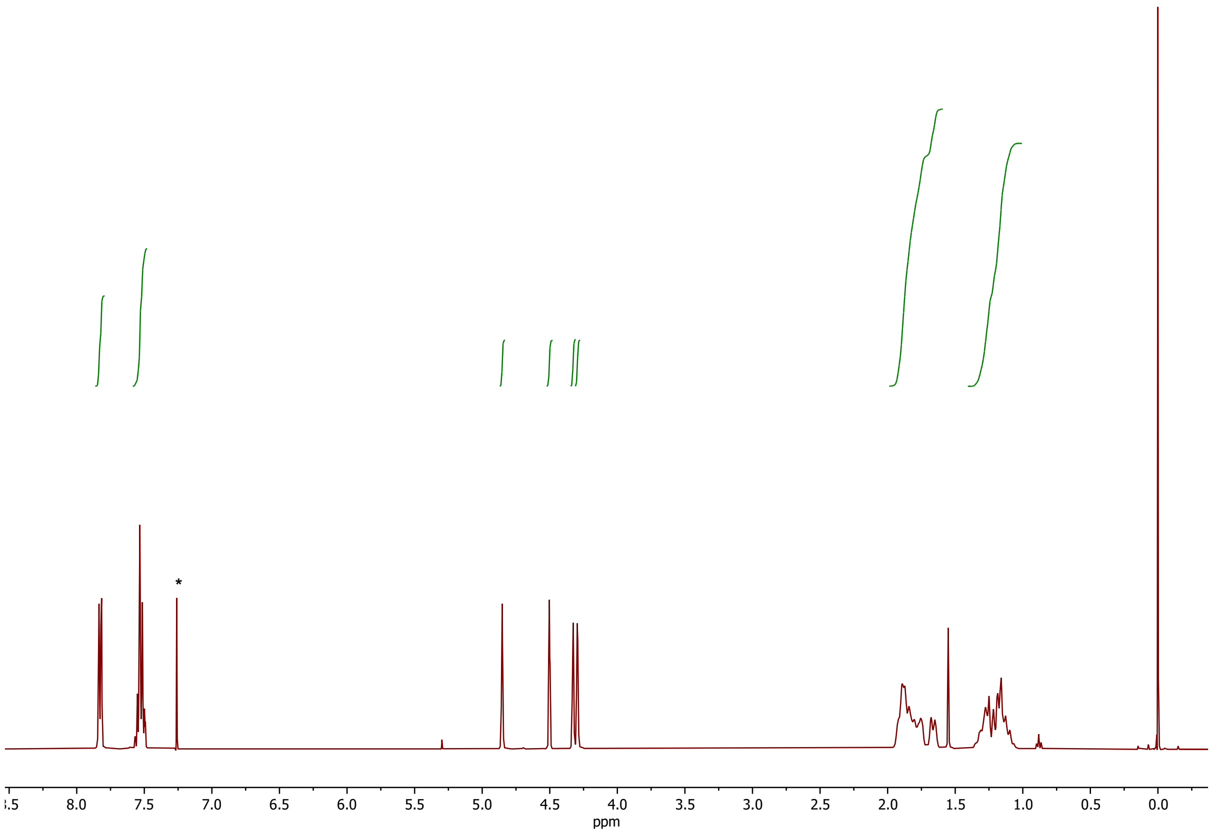


Figure S67 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8S**

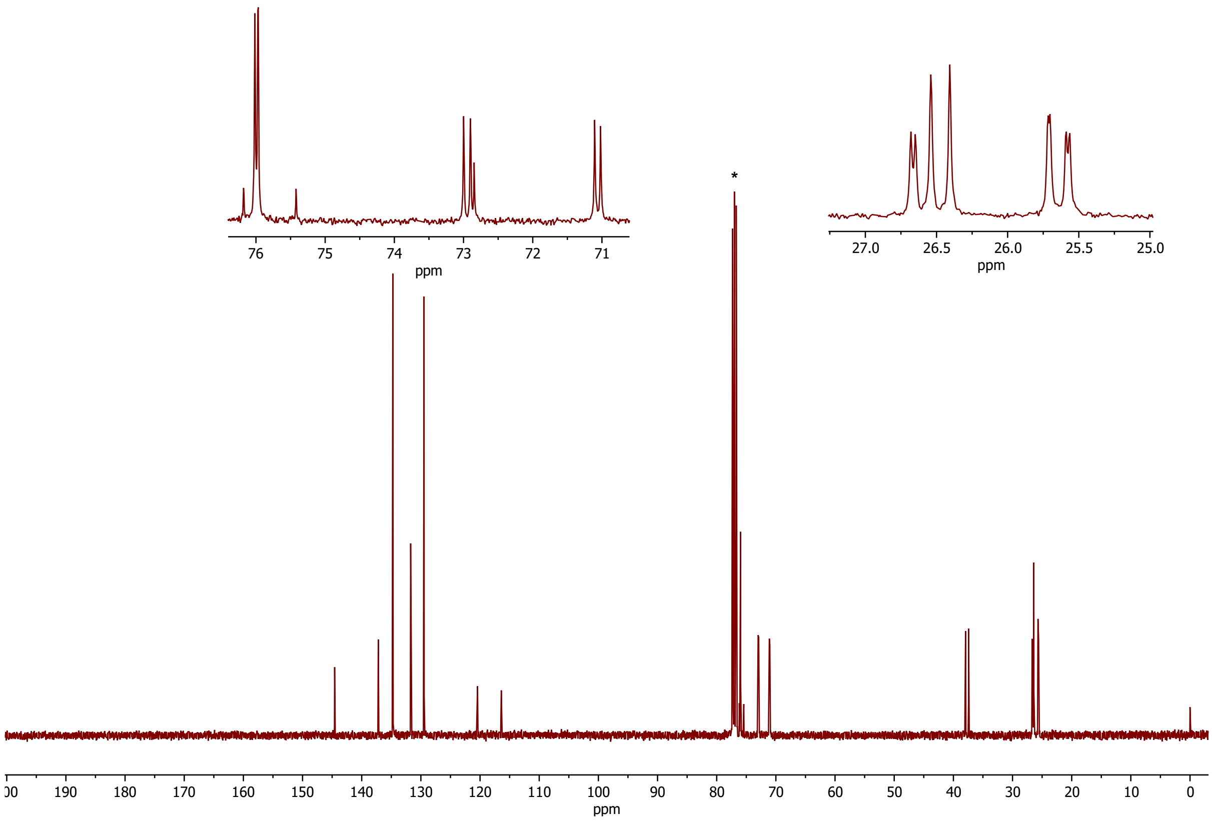


Figure S68 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8S**

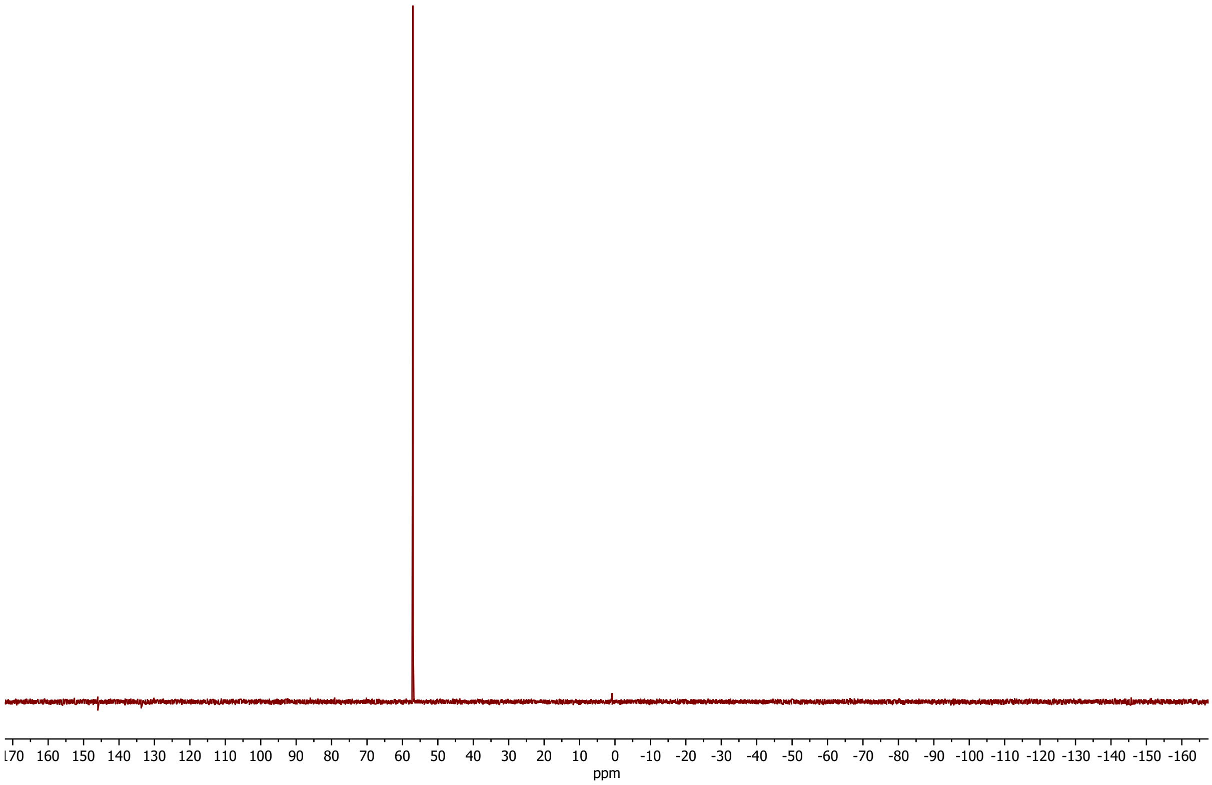


Figure S69 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **8S**

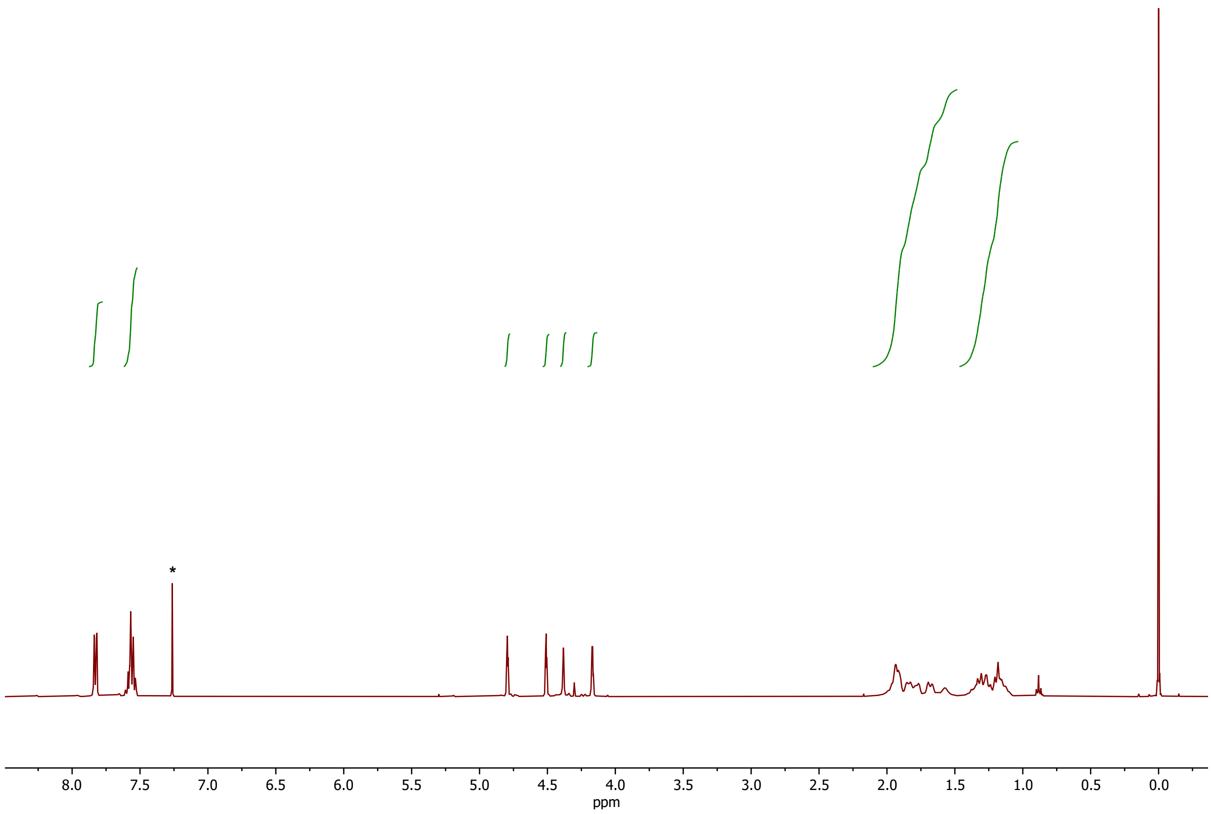


Figure S70 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **10**

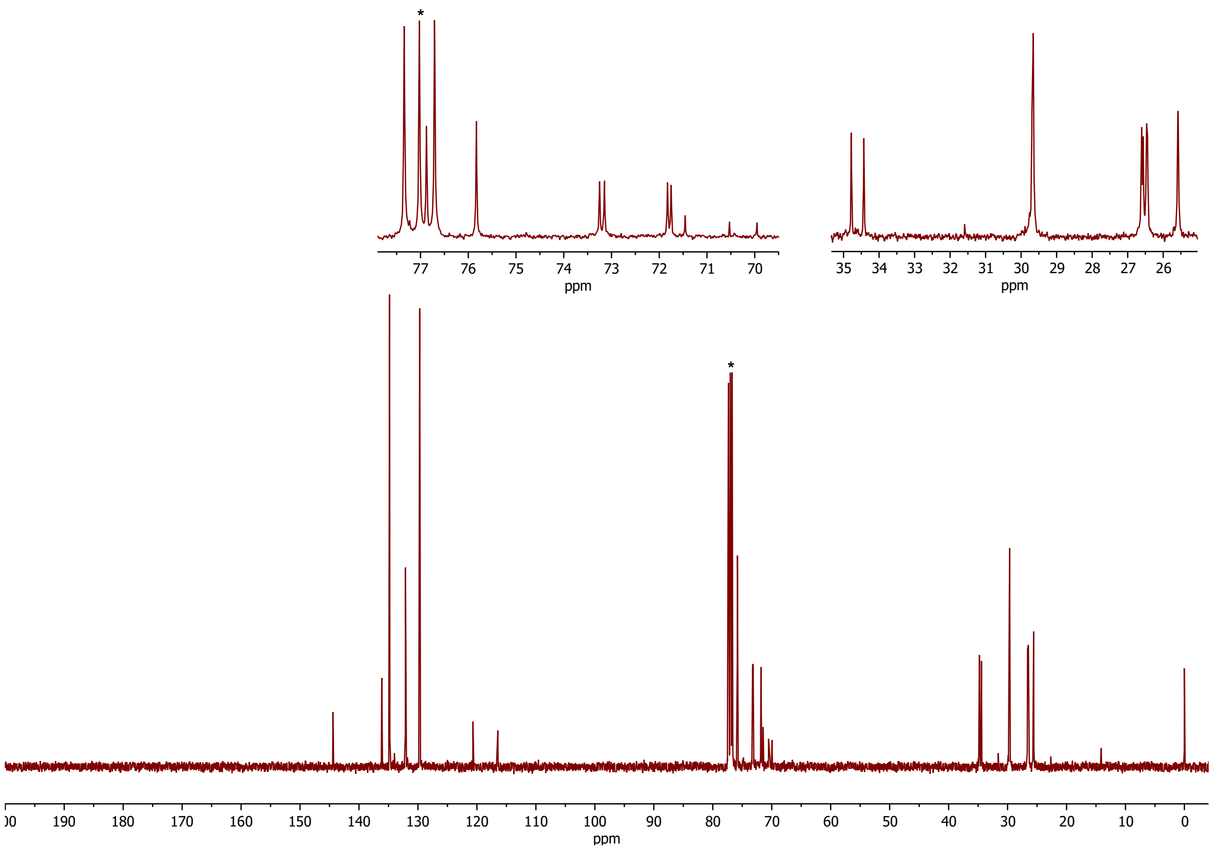


Figure S71 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **10**

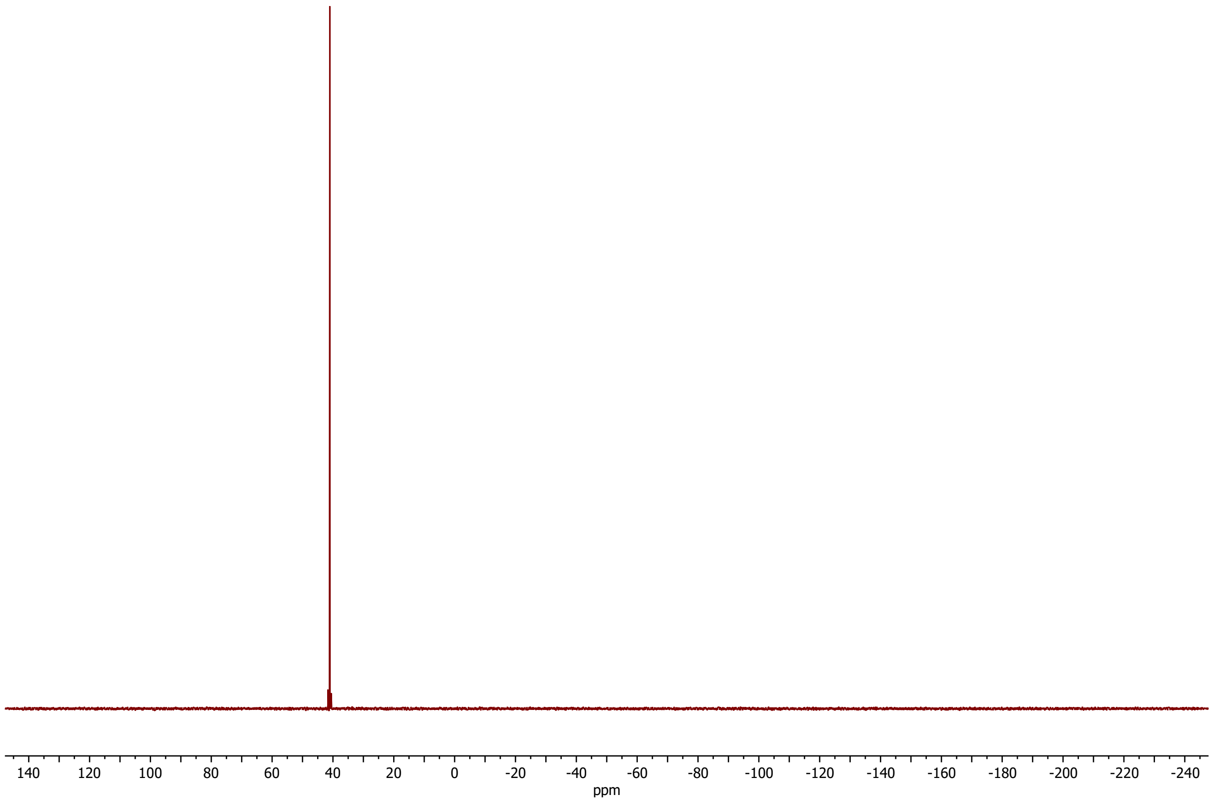


Figure S72 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **10**

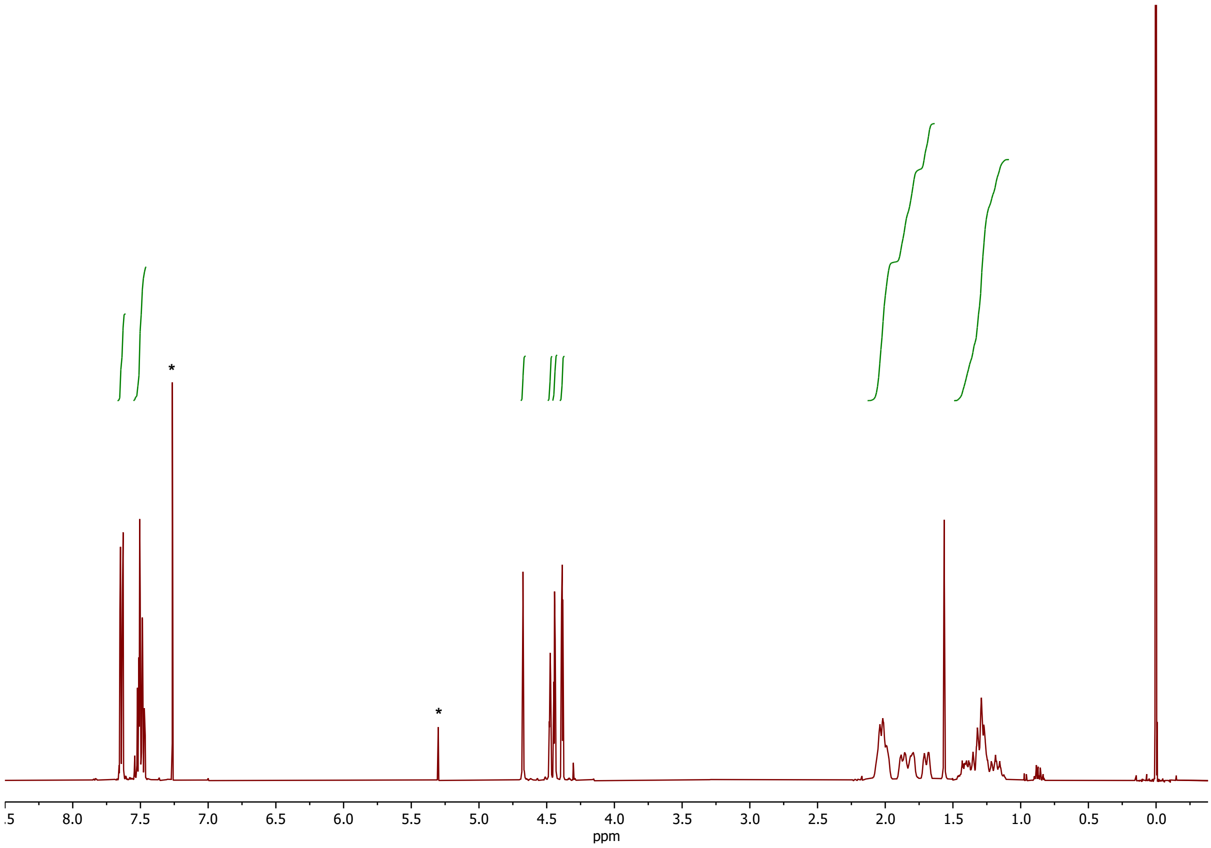


Figure S73 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11**

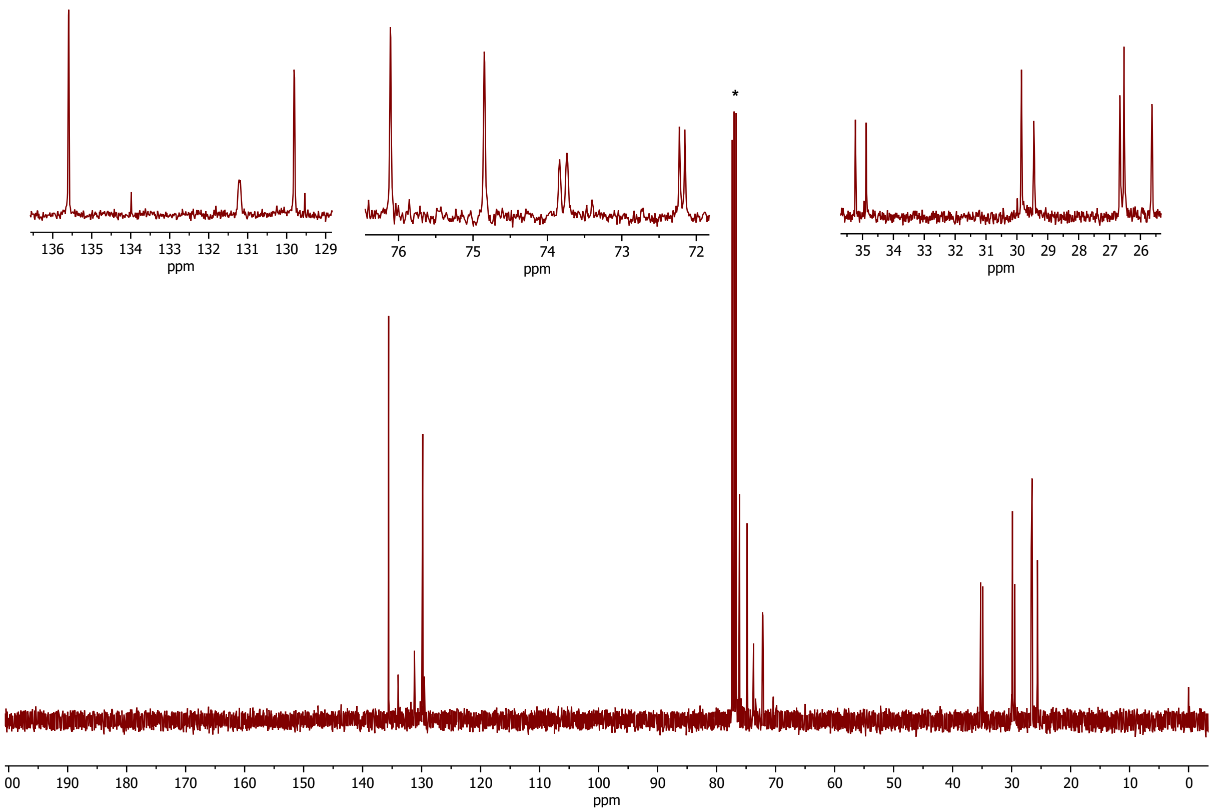


Figure S74 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **11**

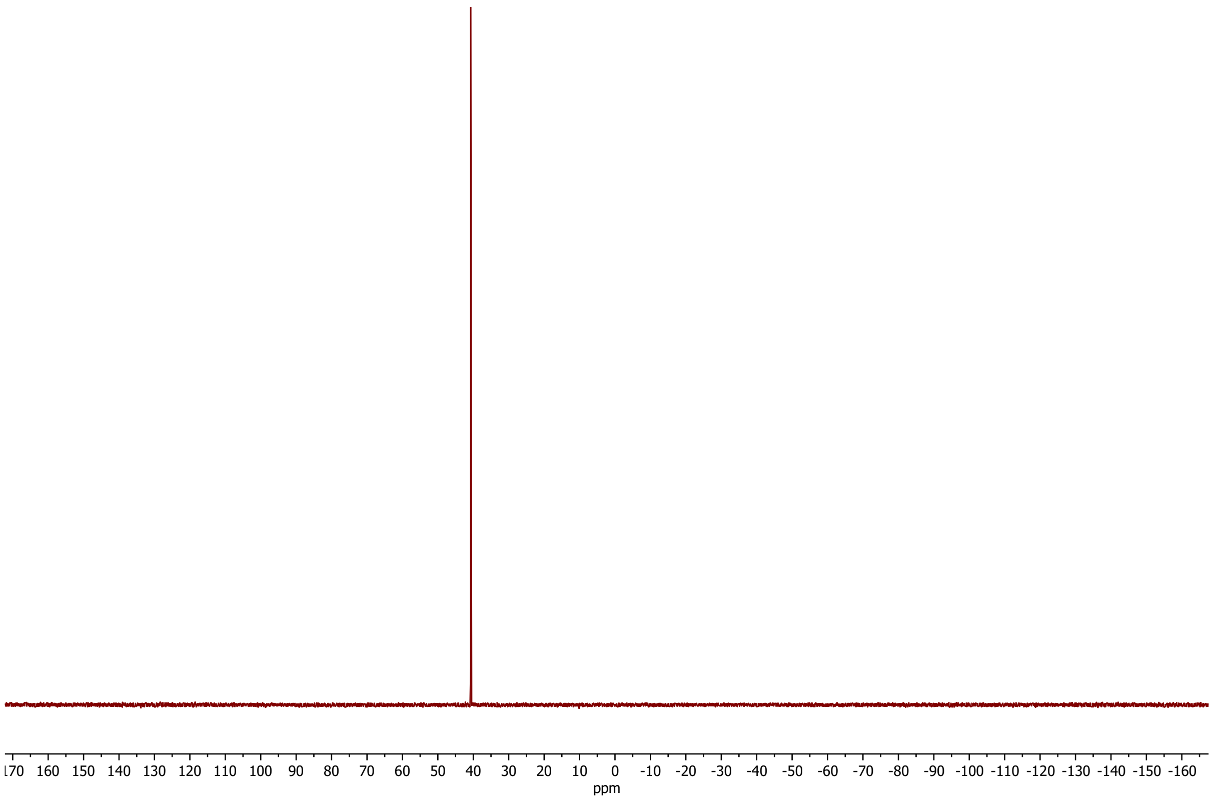


Figure S75 $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **11**

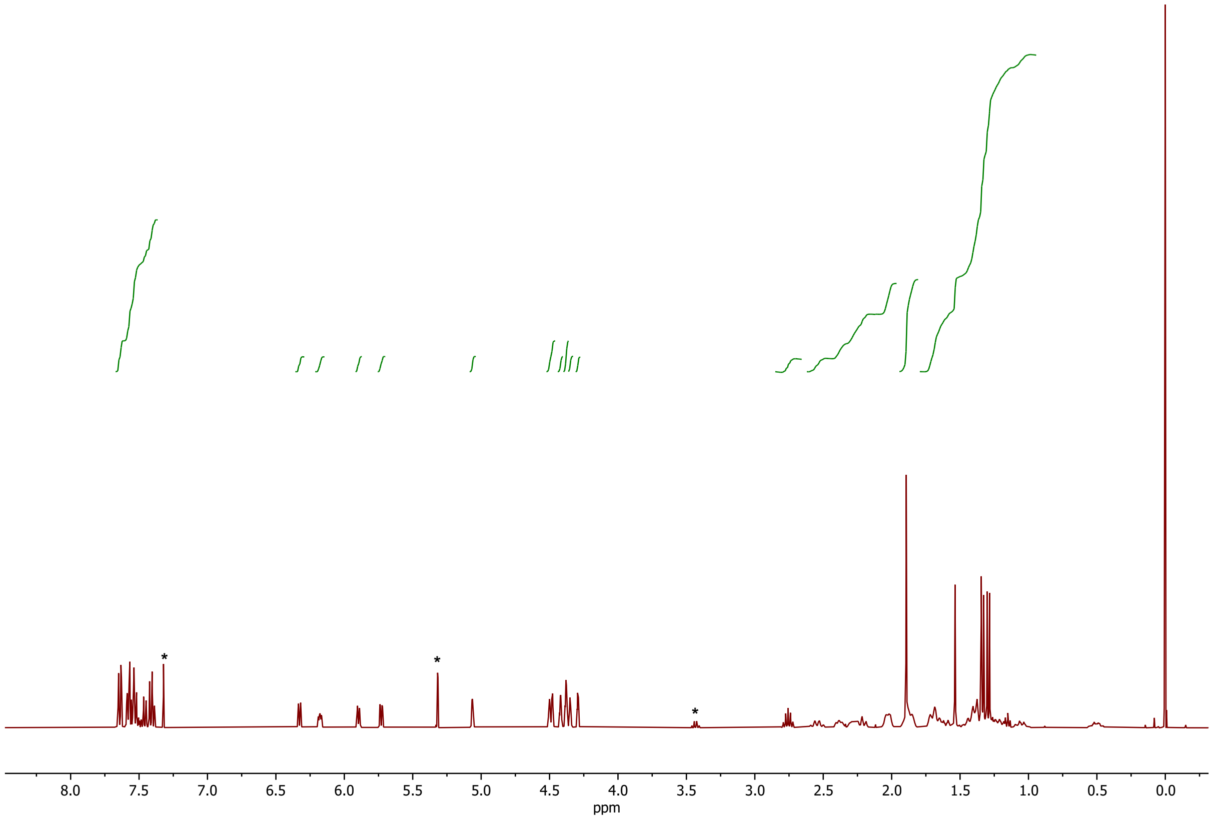


Figure S76 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **12**

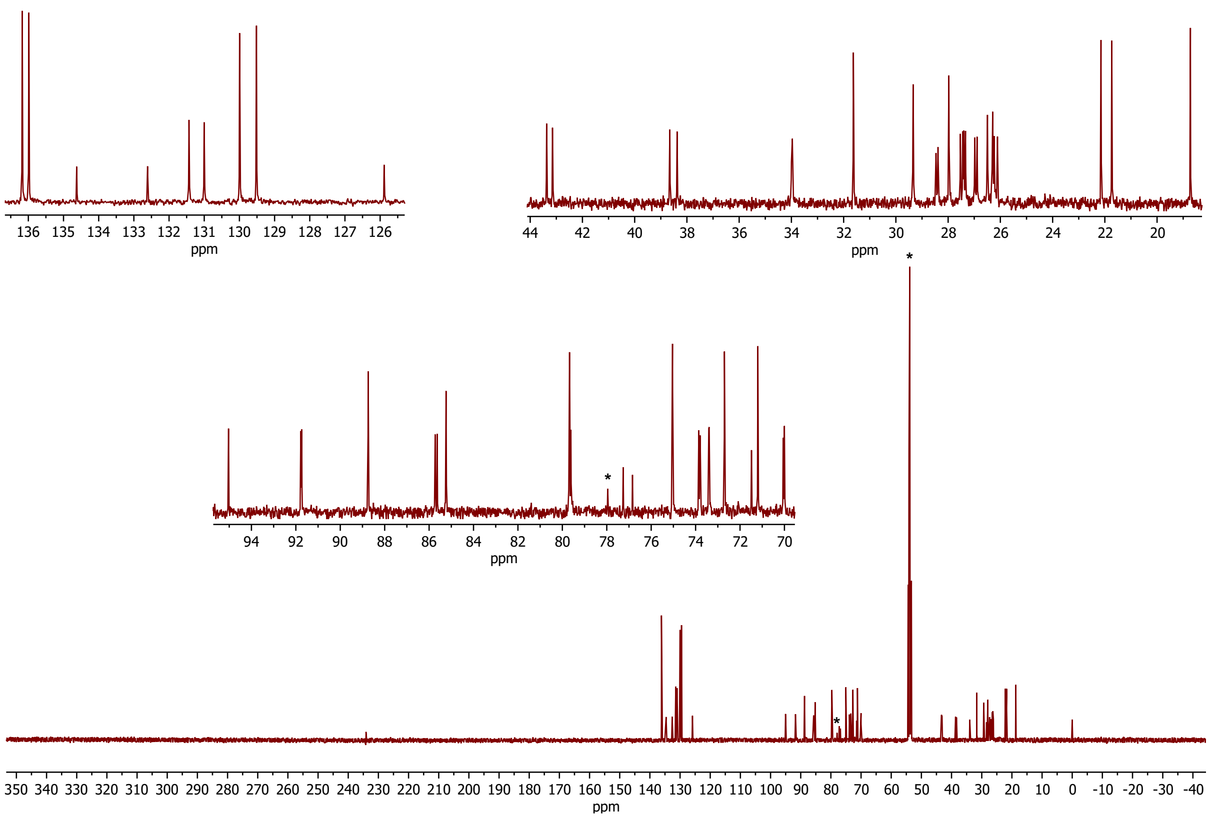


Figure S77 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **12**

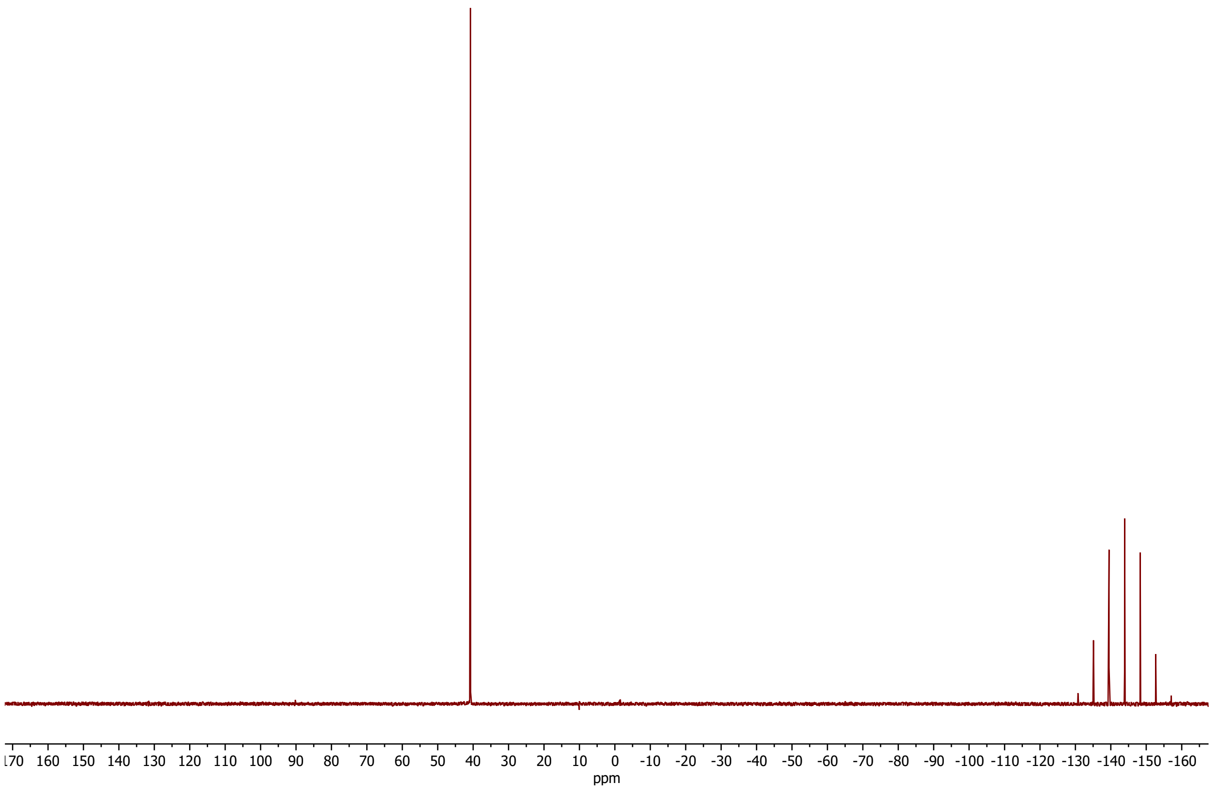


Figure S78 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **12**

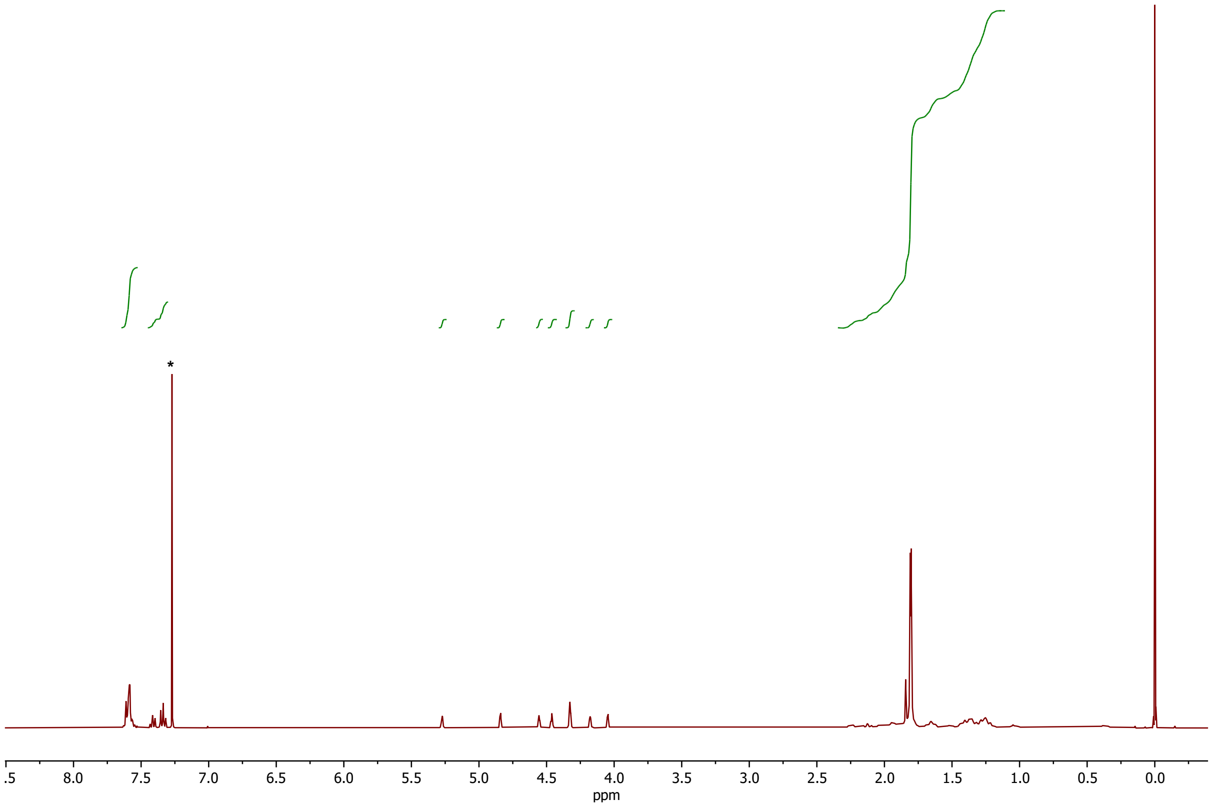


Figure S79 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13a**

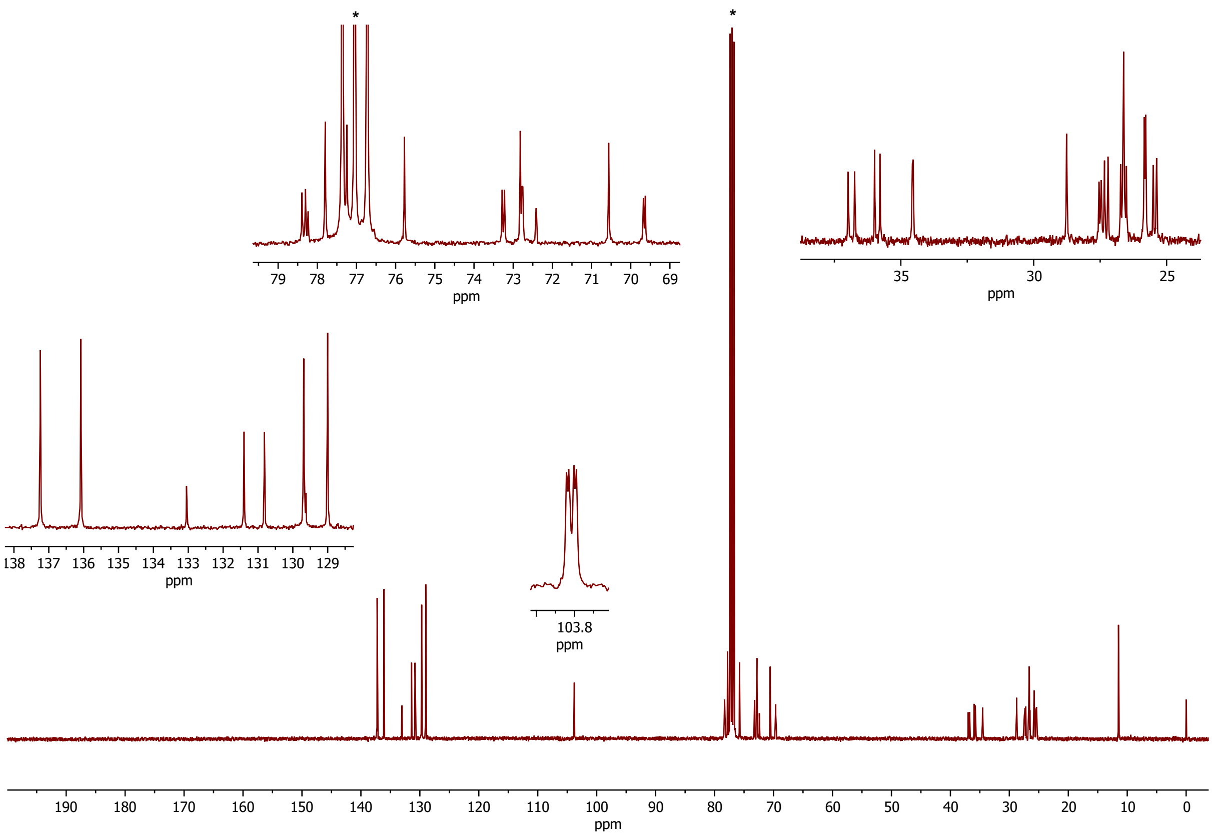


Figure S80^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **13a**

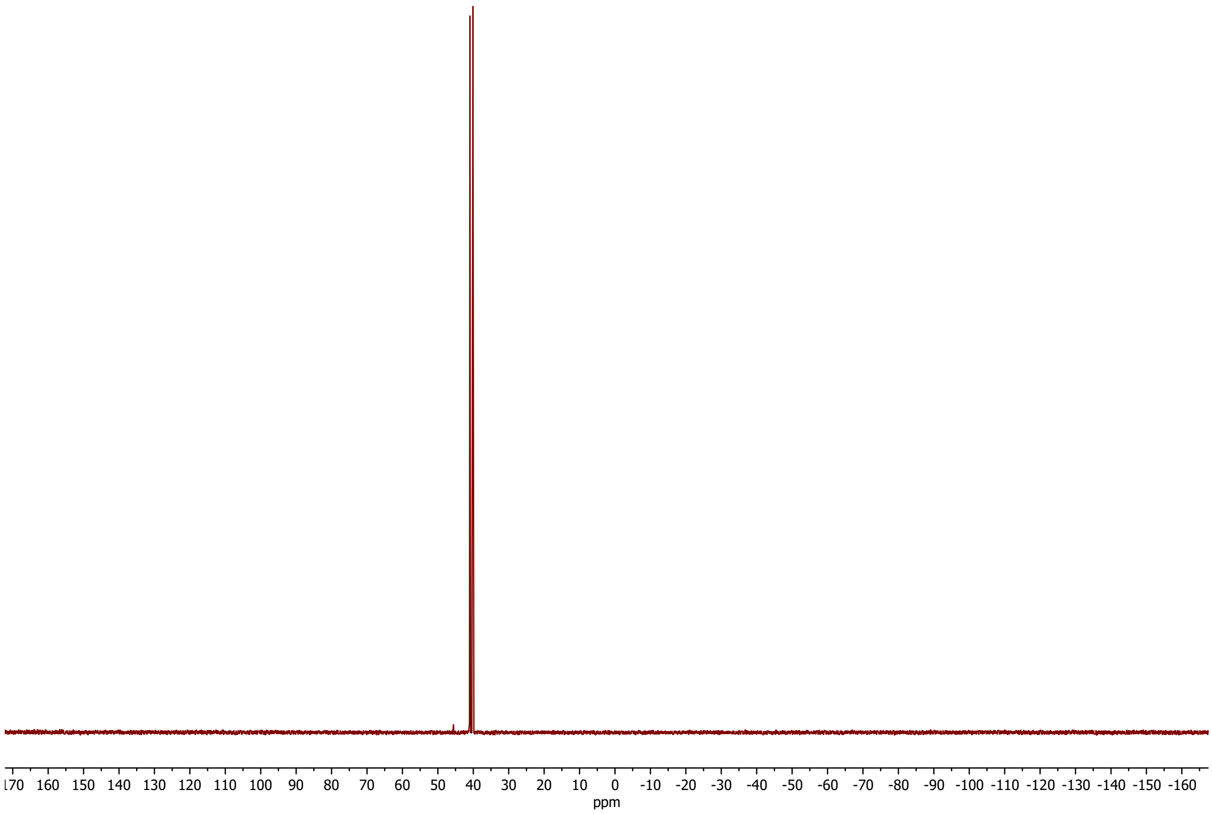


Figure S81 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **13a**

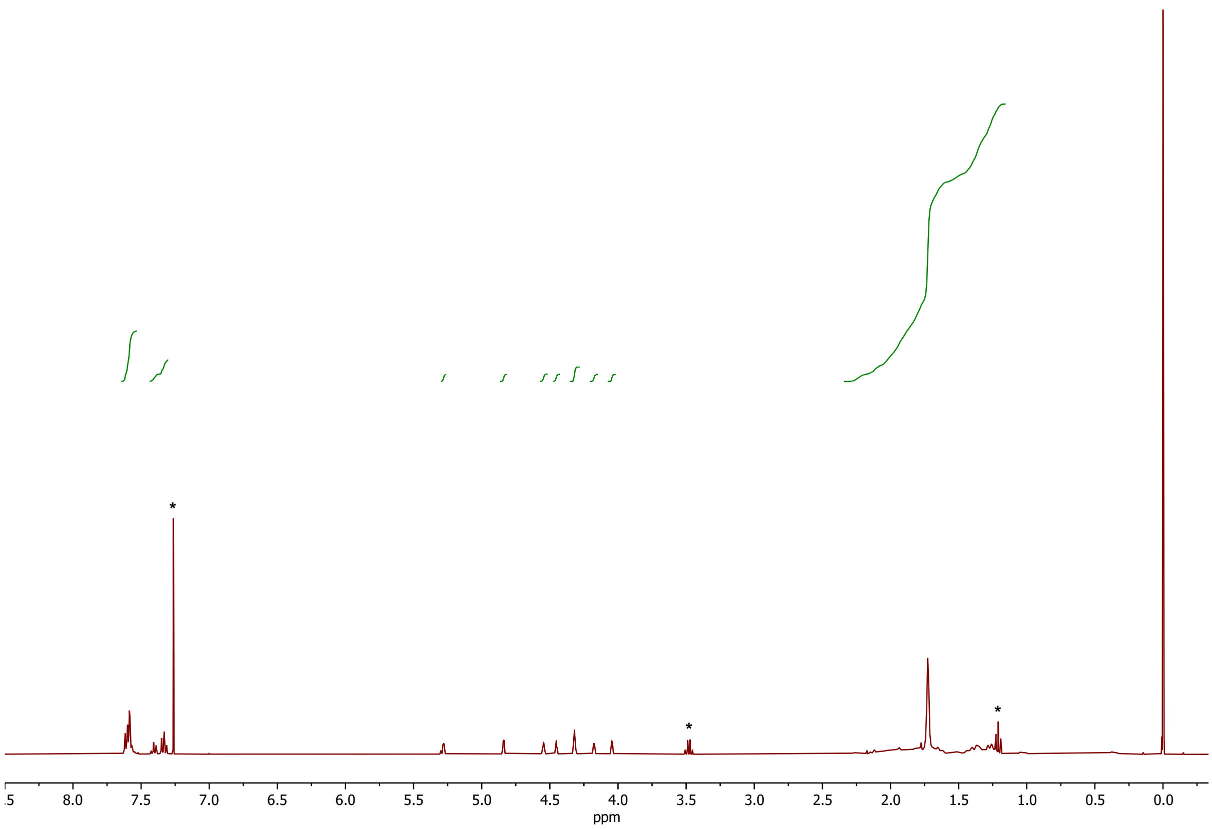


Figure S82 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **13b**

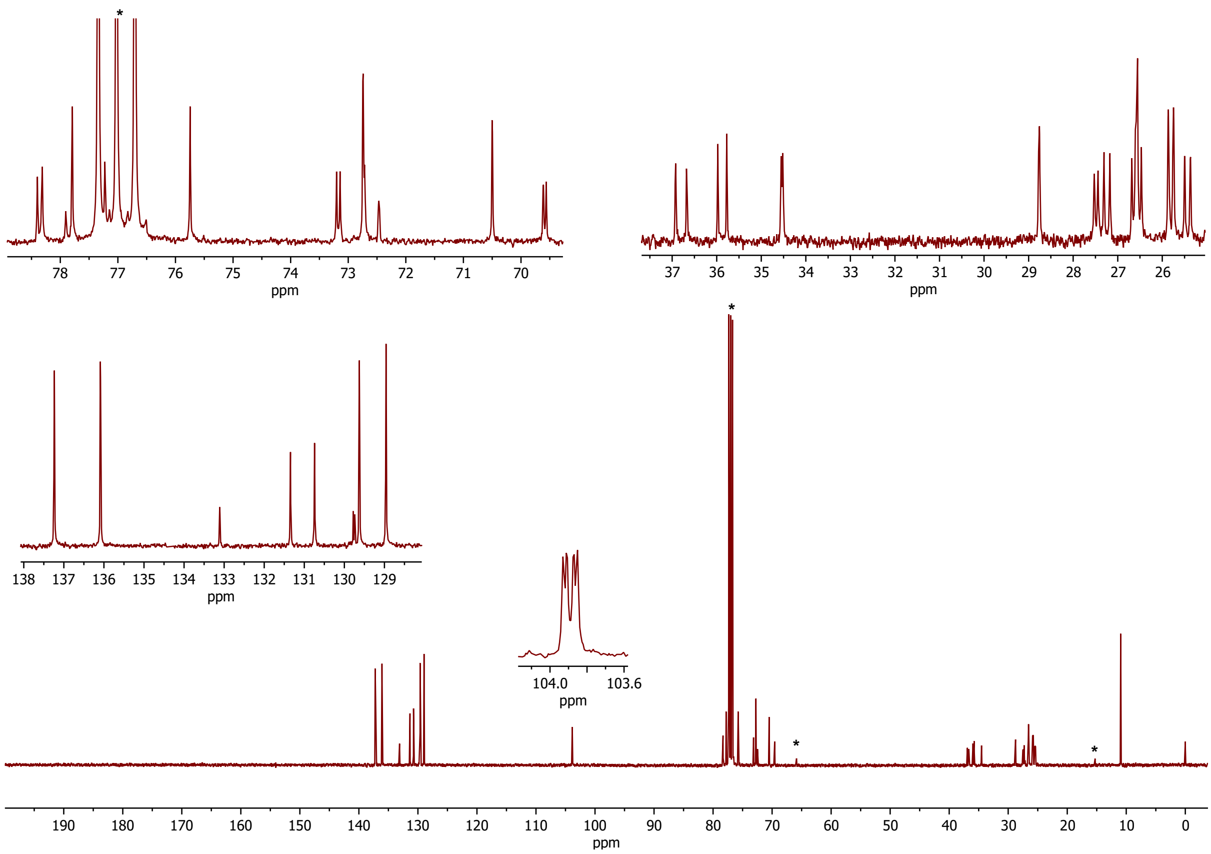


Figure S83 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **13b**

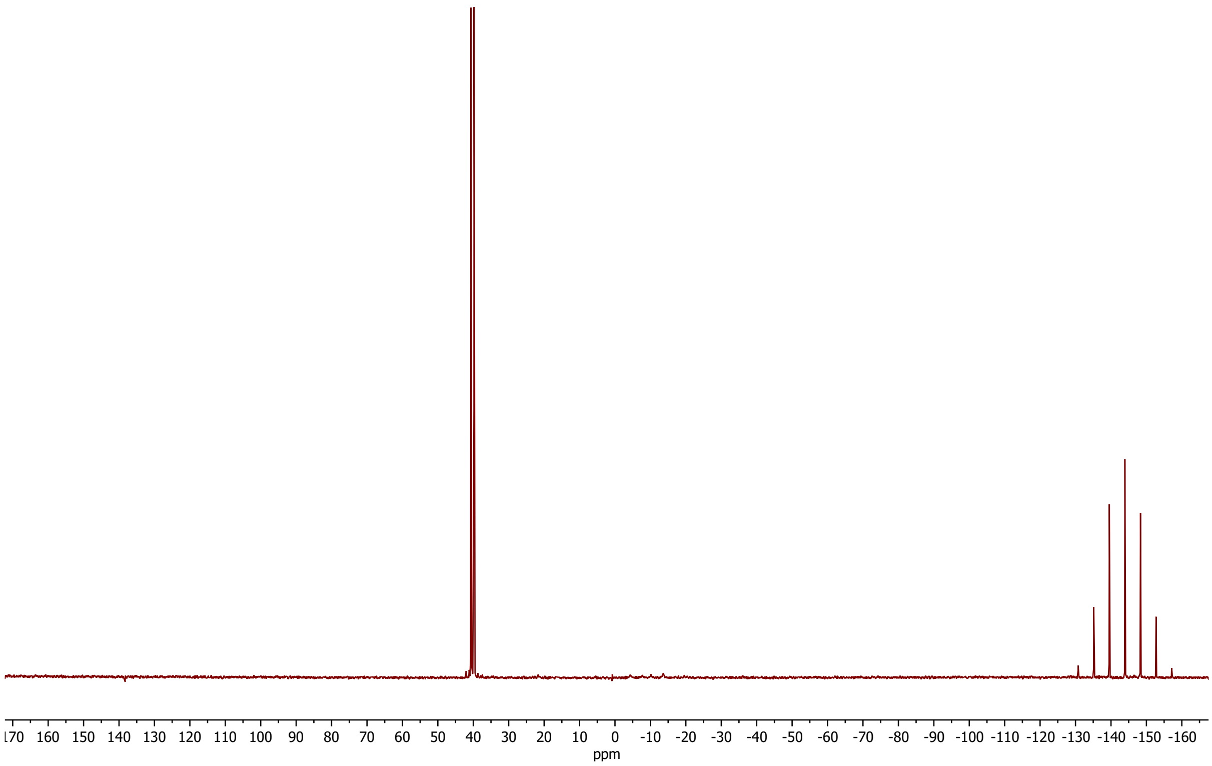


Figure S84 $^{31}P\{^1H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **13b**

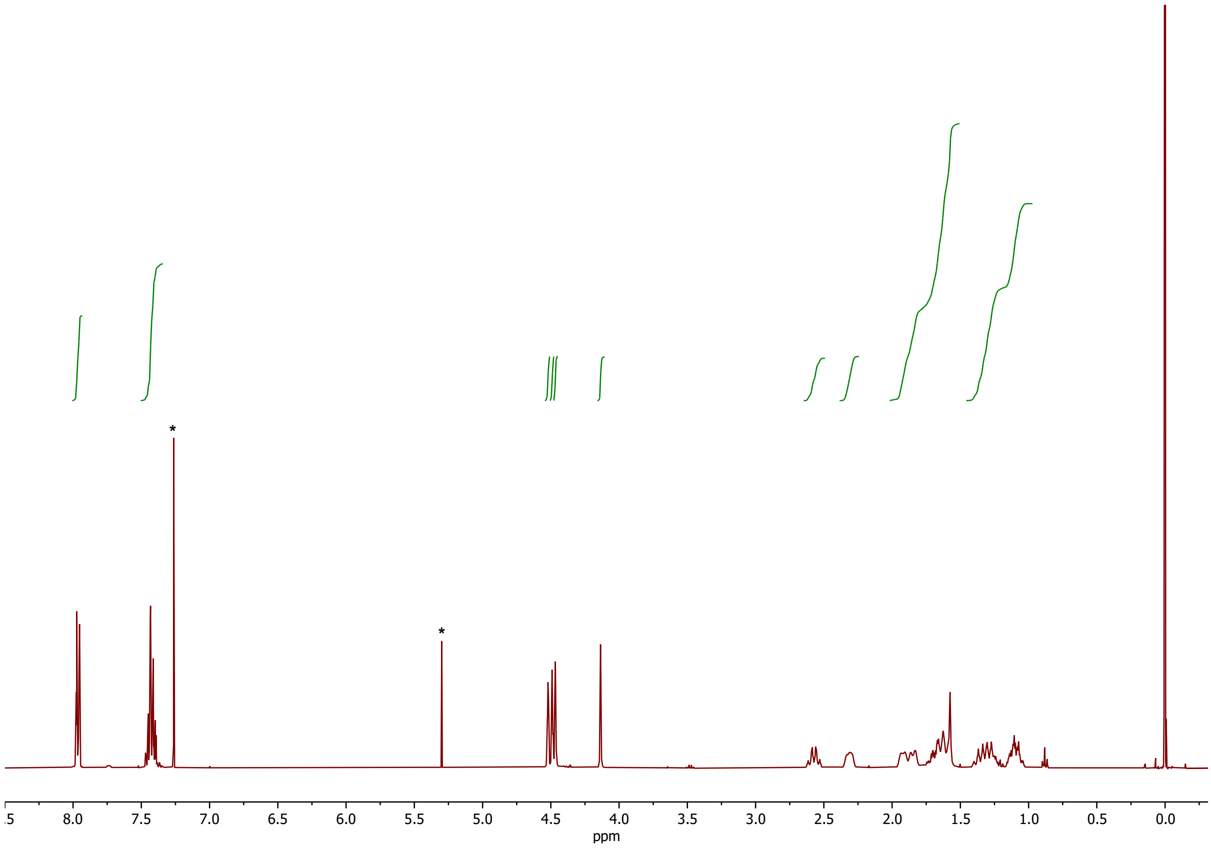


Figure S85 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14**

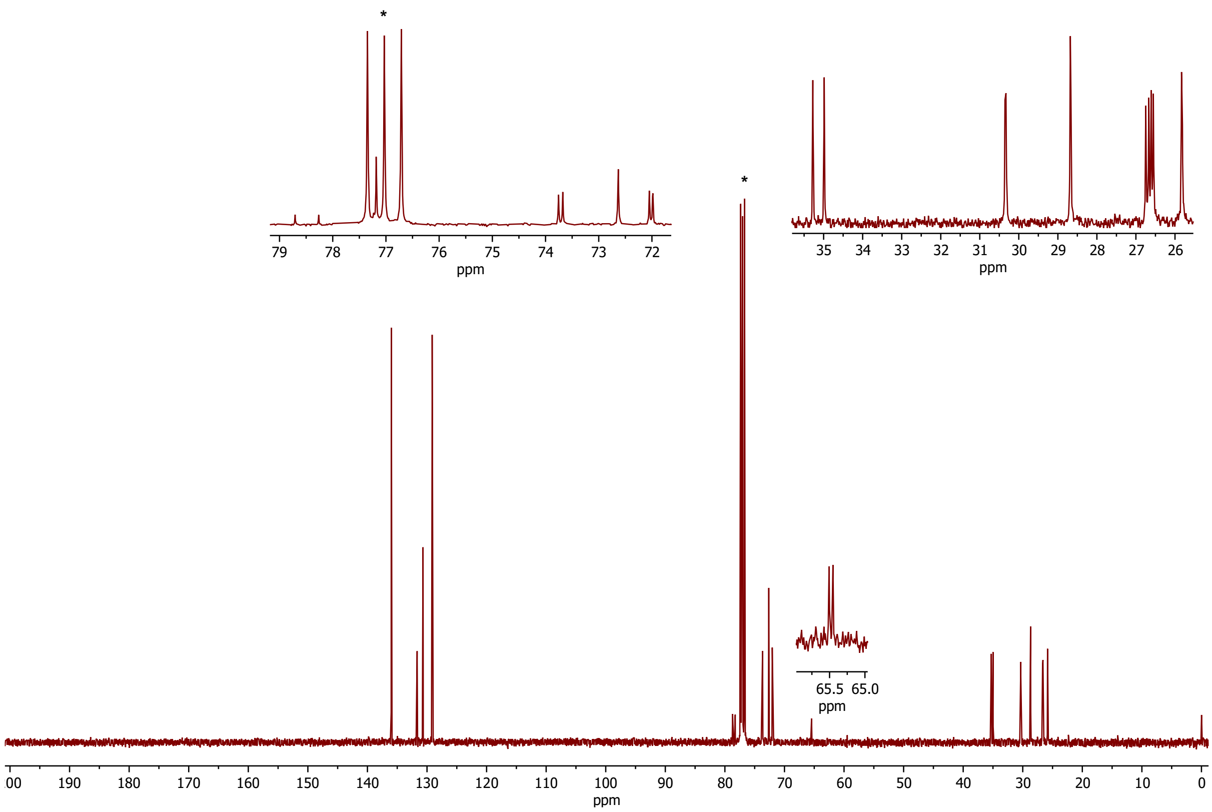


Figure S86 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **14**

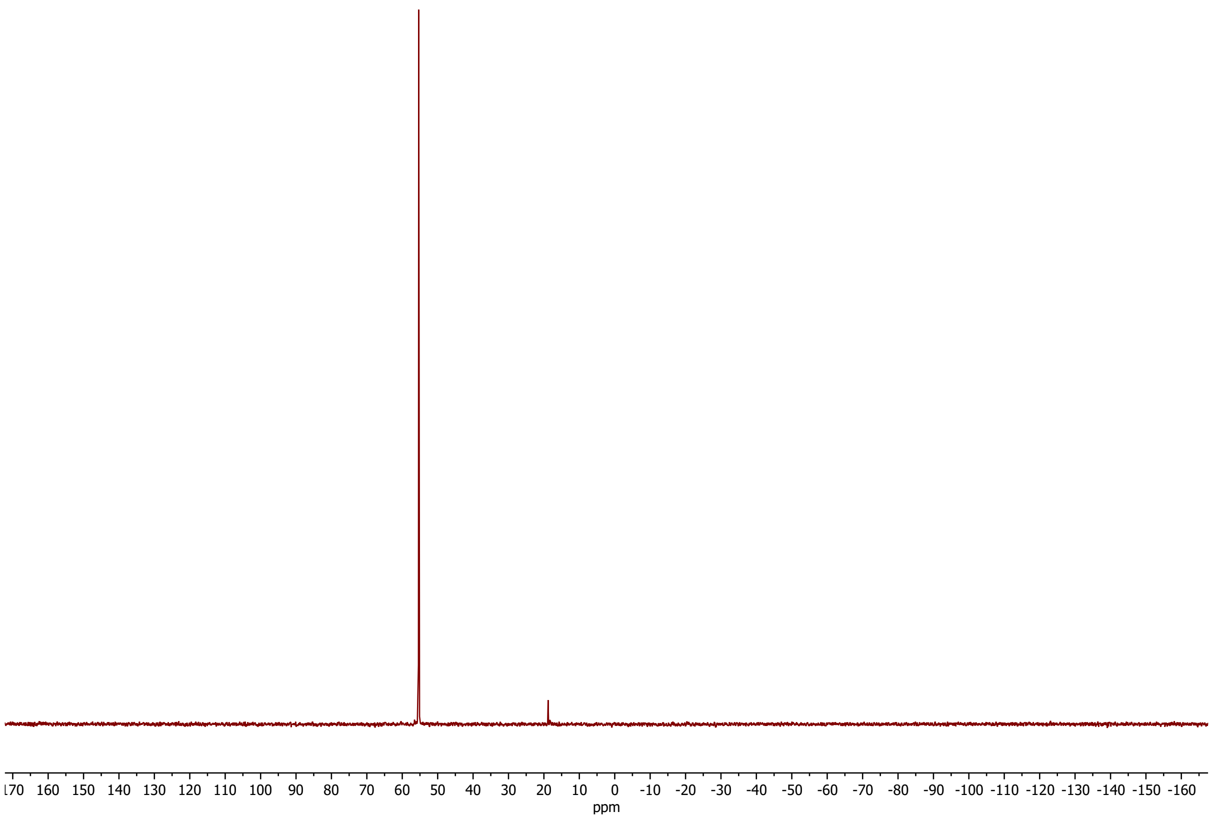


Figure S87 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **14**

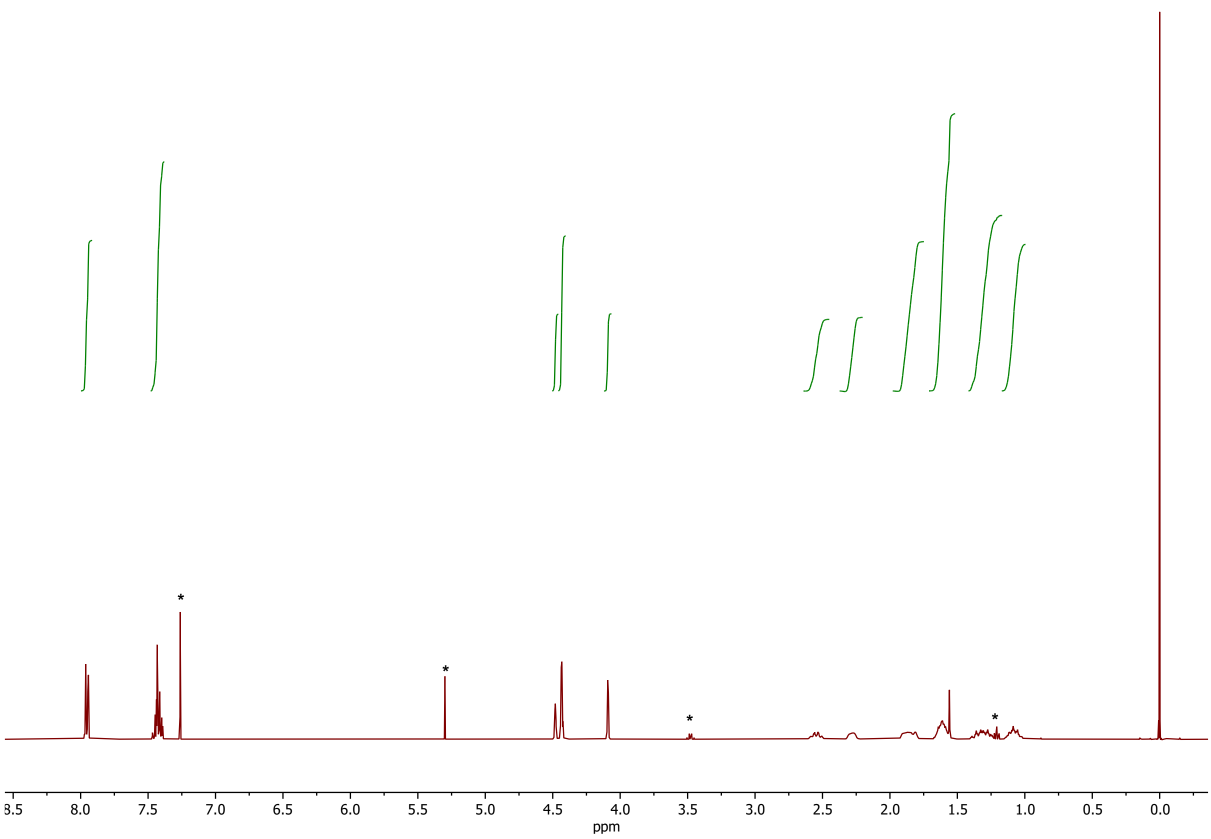


Figure S88 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **15**

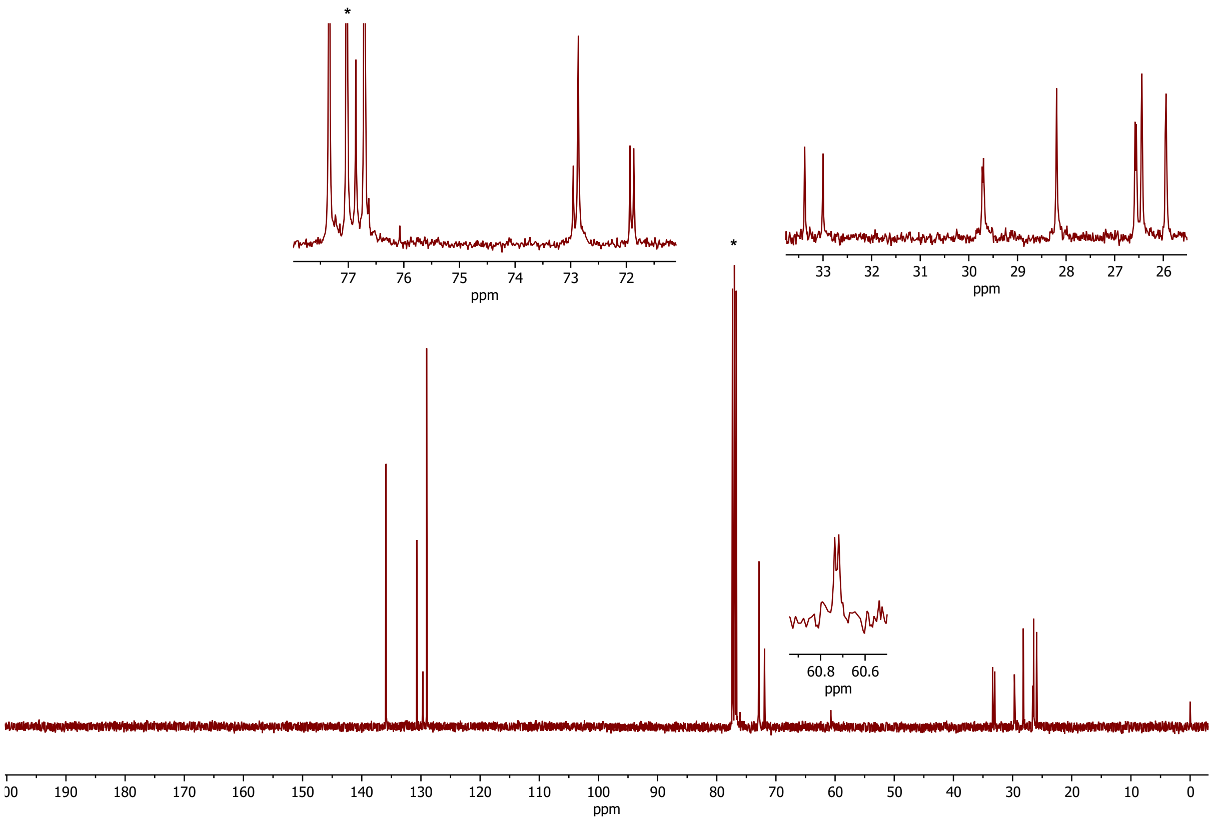


Figure S89 $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **15**

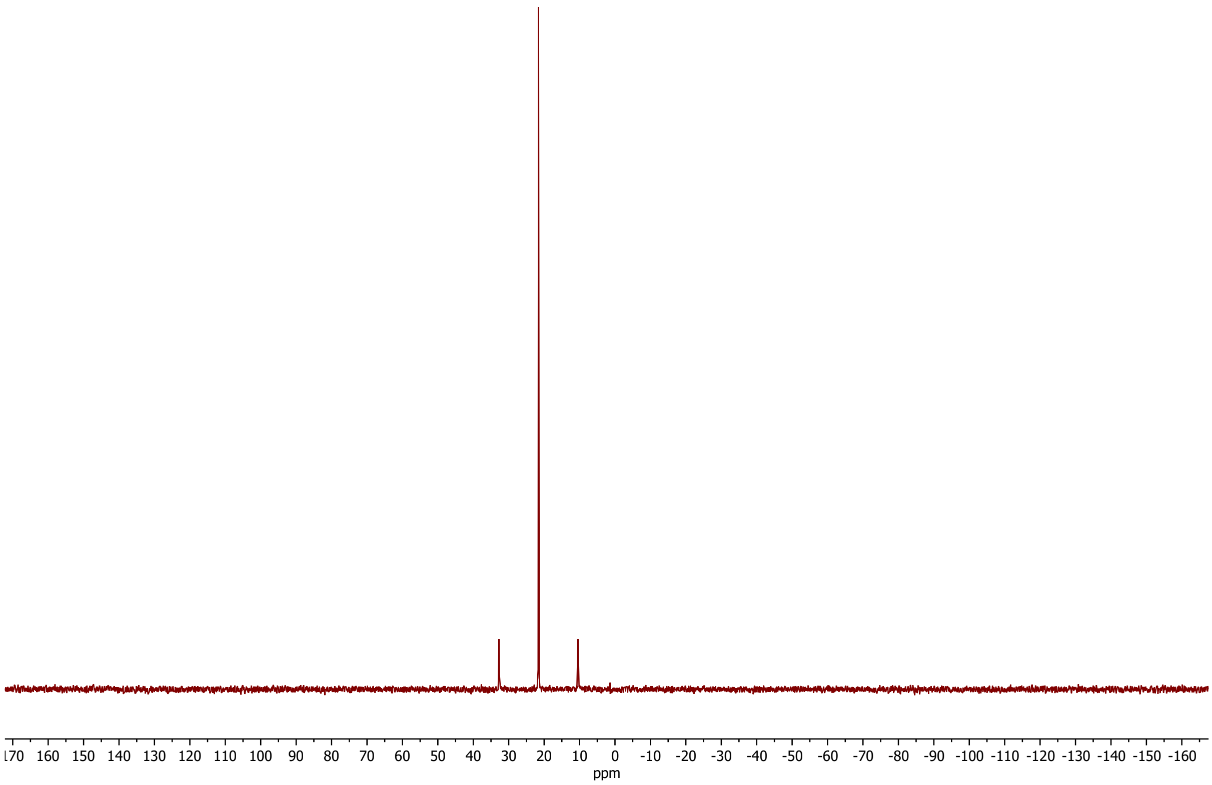


Figure S90 $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **15**

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