Supporting Information

for

Synthesis and characterisation of palladium(II) complexes with hybrid phosphinoferrocene ligands bearing additional O-donor substituents

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Contents

Synthesis and characterisation data

Materials and methods. All manipulations were performed under argon atmosphere using standard Schlenk techniques and oven-dried glassware. Compounds **1**,[1] **4**,[2] and $[(L^{NC})Pd(\mu\text{-}Cl)]_2$[3] were prepared according to the literature. Acetyl chloride was freshly distilled under argon. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar) and used as received. Acetone was distilled from anhydrous K_2CO_3. Dry and deoxygenated tetrahydrofuran and dichloromethane were obtained from a PureSolv MD5 solvent purification system (Innovative Technology). Solvents utilized during column chromatography and for crystallizations were used without additional purification (analytical grade, Lach-Ner, Czech Republic).

NMR spectra were measured with a Varian UNITY Inova 400 spectrometer at 25°C. Chemical shifts (δ in ppm) are expressed relative to internal $SiMe_4$ (^1H and ^{13}C), to external 85% aqueous H_3PO_4 (^{31}P), and to external neat $CFCl_3$ (^{19}F), all set to 0 ppm. In addition to the standard notation of the signal multiplicity (s = singlet, d = doublet, t = triplet, etc.),[4] vt and vq are used to label virtual triplet and quartets arising from the AA′BB′ and AA′BB′X spin systems (A, B = ^1H, X = ^{31}P) formed by the protons at the C- and PPh_2-substituted cyclopentadienyl rings, respectively. IR spectra were recorded on a Thermo Nicolet 6700 instrument over the range 400-4000 cm^{-1}. UV-vis spectra were recorded on a Unicam UV 300 spectrometer. Electrospray ionisation (ESI) mass spectra were measured with a Bruker Esquire 3000 instrument using samples dissolved in HPLC-quality methanol. Elemental analyses were performed in a PE 2400 Series II CHNS/O Elemental Analyzer (Perkin Elmer). The amount of residual solvent (if present) was verified by NMR analysis.

Synthesis of 2 from acetyl chloride. Bromide **4** (0.449 g, 1.0 mmol) was dissolved in anhydrous THF (15 mL), and the solution was cooled to −78°C with an ethanol/dry ice bath under continuous stirring. *n*-Butyllithium (0.44 mL 2.5 M, 1.1 mmol) was introduced, and the resulting mixture was stirred at −78°C for 15 min (the colour of the reaction mixture turned into a deep orange-brown hue during this time). Then, acetyl chloride (90 μL, 1.3 mmol) dissolved in THF (3 mL) was introduced and the stirring was continued at −78°C for 15 min and at room temperature for another 30 min. The reaction was terminated by adding saturated aqueous $NaHCO_3$. The organic phase was

separated, and the aqueous residue was back-extracted with diethyl ether (3× 15 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure, leaving an orange oil, which was taken up with hexane-ethyl acetate (3:1, 15 mL) and purified by chromatography over a silica gel column. Elution with the same solvent mixture led to the development of two major bands. The first yellow band predominantly contained (diphenylphosphino)ferrocene (0.144 g, 40%). The following orange band afforded acylphosphine **2** as an orange microcrystalline solid after evaporation (0.050 g, 12%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 2.31 (s, 3H, COMe), 4.12 (vq, *J*' = 1.8 Hz, 2 H, fc), 4.37 (vt, *J*' = 2.0 Hz, 2 H, fc), 4.40 (vt, *J*' = 1.8 Hz, 2 H, fc), 4.67 (vt, *J*' = 2.0 Hz, 2 H, fc), 7.31-7.38 (m, 10 H, PPh_2) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 27.49 (d, J_{PC} = 1 Hz, 1 C, CO*Me*), 70.54 (s, 2 C, CH fc), 72.96 (d, J_{PC} = 4 Hz, 2 C, CH fc), 73.64 (d, J_{PC} = 1 Hz, 2 C, CH fc), 74.18 (d, J_{PC} = 14 Hz, 2 C, CH fc), 78.23 (d, $^1J_{PC}$ = 9 Hz, 1 C, C–P fc), 79.79 (s, 1 C, *C*-CO fc), 128.28 (d, $^3J_{PC}$ = 7 Hz, 4 C, CH^{meta} PPh_2), 128.75 (s, 2 C, CH^{para} PPh_2), 133.44 (d, $^2J_{PC}$ = 20 Hz, 4 C, CH^{ortho} PPh_2), 138.33 (d, $^1J_{PC}$ = 10 Hz, 2 C, C^{ipso} PPh_2), 201.94 (s, 1 C, *C*OMe) ppm. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = −17.6 (s) ppm. The NMR data are in agreement with the literature.[5] IR (Nujol): ν_{max} = 3307 w, 3102 w, 3052 w, 3024 w, 1663 s, 1584 w, 1568 w, 1277 s, 1196 m, 1167 m, 1109 m, 1092 m, 1067 w, 1027 m, 968 w, 888 m, 850 m, 837 m, 826 m, 755 m, 748 s, 703 s, 635 w, 613 w, 598 w, 588 w, 534 w, 514 m, 493 m, 469 m, 450 m, 424 m cm^{-1}. ESI+ MS: *m/z* = 413 $[M + H]^+$, 435 $[M + Na]^+$, 451 $[M + K]^+$. Anal. Calc. for $C_{24}H_{21}FeOP$ (412.24): C 69.92, H 5.13%. Found: C 69.99, H 5.16%.

Synthesis of 2 from a Weinreb amide. Bromide **4** (0.90 g, 2.0 mmol) was dissolved in dry THF (25 mL), and the solution was cooled in an ethanol/dry ice bath under continuous stirring. *n*-Butyllithium (1.0 mL 2.5 M, 2.5 mmol) was added, and the mixture was stirred at −78°C for another 30 min. Then, a THF solution of *N*-methoxy-*N*-methylacetamide (0.43 mL, 4.0 mmol in 5 mL) was introduced, changing the reaction mixture from orange-brown to yellow. The mixture was stirred at −78°C for 30 min and at room temperature for another 2 h before cooling on ice and quenching with saturated aqueous NH_4Cl (5 mL). The resulting heterogeneous mixture was extracted with diethyl ether (20 mL). The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The resulting red oil was purified by

chromatography, as described in the previous section, yielding (diphenylphosphino)ferrocene (0.31 g, 42%) and the desired acylphosphine **2** (0.45 g, 55%).

Synthesis of alcohol 3. A solution of bromide **4** (3.60 g, 8.0 mmol) in anhydrous THF (50 mL) was lithiated with *n*-butyllithium (3.2 mL of 2.5 M, 8.0 mmol) at −78°C for 30 min as described above before neat acetone (1.2 mL, approx. 16 mmol) was added. The reaction mixture was stirred at room temperature overnight and then quenched by adding saturated aqueous NH_4Cl (ca. 25 mL) and stirring for 15 min. Then, the reaction mixture was extracted with CH_2Cl_2 (20 mL), and the organic layer was separated, washed with brine (20 mL) and dried over $MgSO_4$. The crude product resulting from solvent removal was purified by column chromatography over silica gel using hexane-ethyl acetate (30:1) as the mobile phase. The first orange band containing (diphenylphosphino)ferrocene was discarded, and the second major orange band was evaporated to afford alcohol **3** as an orange glassy solid. Yield: 1.44 g (42%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 1.43 (s, 6 H, CMe_2), 4.00 (vt, *J*' = 1.9 Hz, 2 H, fc), 4.10 (vt, *J*' = 1.9 Hz, 2 H, fc), 4.13 (vq, *J*' = 1.9 Hz, 2 H, fc), 4.39 (vt, *J*' = 1.8 Hz, 2 H, fc), 7.28-7.39 (m, 10 H, Ph) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 31.05 (s, 2 C, C*Me*$_2$), 66.37 (d, J_{PC} = 1 Hz, 2 C, CH fc), 68.91 (s, 1 C, *C*Me_2), 68.95 (d, J_{PC} = 1 Hz, 2 C, CH fc), 70.97 (d, J_{PC} = 4 Hz, 2 C, CH fc), 73.13 (d, J_{PC} = 14 Hz, 2 C, CH fc), 76.29 (d, $^1J_{PC}$ = 6 Hz, 1 C, C-P fc), 100.80 (s, 1 C, *C*-CMe_2 fc), 128.18 (d, $^2J_{PC}$ = 7 Hz, 4 C, CH^{ortho} PPh_2), 128.61 (s, 2 C, CH^{para} PPh_2), 133.47 (d, $^3J_{PC}$ = 20 Hz, 4 C, CH^{meta} PPh_2), 138.68 (d, $^1J_{PC}$ = 9 Hz, 2 C, C^{ipso} PPh_2) ppm. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = −16.5 (s) ppm. IR (neat): ν_{max} = 3926 w, 3568 m, 3447 br m, 3069 m, 3052 m, 2975 m, 2929 m, 2867 w, 1956 w, 1891 w, 1814 w, 1736 m, 1664 w, 1585 m, 1570 w, 1478 m, 1456 w, 1434 s, 1377 m, 1361 m, 1322 m, 1262 m, 1194 w, 1162 s, 1139 m, 1111 m, 1095 w, 1069 w, 1027 m, 998 w, 947 m, 912 m, 889 w, 830 m, 742 s, 697 s, 632 w, 605 w, 504 s, 454 m cm^{-1}. ESI+ MS: *m/z* = 429 [M + H]$^+$, 451 [M + Na]$^+$, 467 [M + K]$^+$. Anal. Calc. for $C_{25}H_{25}FeOP$ (428.28): C 70.11, H 5.88%. Found: C 70.29, H 6.01%.

Preparation of trans-[$PdCl_2$(1-κ*P*)$_2$] (5a). A solution of aldehyde **1** (20.0 mg, 50 μmol) in dichloromethane (1 mL) was added to a suspension of [$PdCl_2$(cod)] (7.2 mg, 25 μmol) in the same solvent (0.5 mL). The mixture was stirred for 1 h (the product partly precipitated during this time) and then evaporated under vacuum. The solid residue was dissolved in dichloromethane (3 mL), and the red solution was layered with methyl *tert*-butyl ketone. Slow crystallisation by liquid phase diffusion over several days afforded solvated complex **5a** as a red crystalline solid, which was isolated by suction, washed with pentane and dried under vacuum (with a partial loss of the clathrated solvent). Yield of **5a**·0.25CH_2Cl_2: 15 mg (61%), red-brown crystalline solid. Crystal selected directly from the reaction batch for X-ray diffraction analysis was characterised as the stoichiometric solvate **5a**·2CH_2Cl_2.

^{1}H NMR (399.95 MHz, CD_2Cl_2): δ = 4.57 (m, 4 H, CH fc), 4.64 (m, 4 H, CH fc), 4.90 (vt, *J'* = 1.9 Hz, 4 H, CH fc), 4.93 (vt, *J'* = 1.8 Hz, 4 H, CH fc), 7.41-7.53 (m, 12 H, PPh_2), 7.61-7.68 (m, 8 H, PPh_2), 9.86 (s, 2 H, CHO) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2): δ = 71.53 (s, 4 C, CH fc), 73.42 (apparent t, *J'*= 4 Hz, 4 C, CH fc), 74.15 (apparent t, *J'* = 27 Hz, 2 C, C-P fc), 76.17 (s, 4 C, CH fc), 77.00 (apparent t, *J'* = 6 Hz, 4 C, CH fc), 80.83 (s, 2 C, *C*-CHO fc), 128.36 (apparent t, *J'* = 5 Hz, 8 C, CH^{meta} PPh_2), 131.06 (s, 4 C, CH^{para} PPh_2), 131.11 (apparent t, *J'* = 25 Hz, 4 C, C^{ipso} PPh_2), 134.55 (apparent t, *J'* = 6 Hz, 8 C, CH^{ortho} PPh_2), 193.61 (s, 2 C, CHO) ppm. ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ = 15.2 (s) ppm. IR (Nujol): ν_{max} 1687 s, 1666 m, 1586 w, 1337 w, 1303 w, 1242 m, 1210 w, 1196 w, 1168 m, 1095 m, 1059 w, 1049 w, 1038 w, 1027 m, 1000 w, 918 w, 895 w, 876 w, 843 m, 833 m, 817 w, 750 m, 740 m, 710 w, 692 s, 624 m, 541 m, 512 s, 496 m, 488 m, 476 m, 454 m, 425 w cm^{-1}. ESI+ MS: *m/z* = 995 $[M + Na]^+$. Anal. Calc. for $C_{46}H_{38}Cl_2Fe_2O_2P_2Pd$·0.25$CH_2Cl_2$ (994.99): C 55.83, H 3.90%. Found: C 55.79, H 3.91%.

Preparation of trans-[$PdCl_2$(2-κ*P*)$_2$] (5b). A solution of [$PdCl_2$(cod)] (6.9 mg, 24 μmol) in chloroform (1.5 mL) was added dropwise to ligand **2** dissolved in the same solvent (20.0 mg, 49 μmol in 0.5 mL). The resulting red solution was stirred for 1 h and then evaporated. The crude product was dissolved in a minimum amount of hot chloroform (approximately 1 mL), and the solution was diluted with hot ethyl acetate (5 mL). Red crystals that separated during slow cooling (in a Dewar flask filled with hot water) were isolated by suction, washed with pentane and dried under vacuum. Yield of **5b**: 21.1 mg (87%), deep red crystalline solid.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 2.32 (s, 6 H, COMe), 4.41 (m, 4 H, fc), 4.63 (m, 4 H, fc), 4.86 (vt, *J'* = 2.0 Hz, 4 H, fc), 4.90 (vt, *J'* = 2.0 Hz, 4 H, fc), 7.36-7.66 (m, 20 H, PPh_2) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 27.66 (s, 2 C, CO*Me*), 71.08 (s, 4 C, CH fc), 73.26 (apparent t, *J'* = 27 Hz, 2 C, C–P fc), 73.95 (apparent t, *J'* = 4 Hz, 4 C, CH fc), 75.68 (s, 4 C, CH fc), 80.11 (s, 2 C, *C*-COMe fc), 127.94 (apparent t, *J'* = 5 Hz, 8 C, CH PPh_2), 130.59 (s, 4 C, CH^{para} PPh_2), 130.65 (apparent t, *J'* = 25 Hz, 4 C, C^{ipso} PPh_2), 134.10 (apparent t, *J'* = 6 Hz, 8 C, CH PPh_2), 201.76 (s, 2 C, *C*OMe) ppm. One signal due to ferrocene CH is obscured by the solvent resonance. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = 14.8 (s) ppm. IR (Nujol): ν_{max} = 3322 w, 3119 w, 3108 m, 3071 m, 3056 m, 3042 m, 1898 w, 1830 w, 1671 vs, 1583 w, 1570 w, 1300 m, 1273 s, 1183 m, 1166 s, 1113 m, 1096 s, 1070 w, 1057 m, 1041 m, 1030 m, 998 w, 958 w, 893 w, 847 m, 828 m, 759 s, 746 m, 694 s, 629 m, 621 m, 594 w, 547 w, 527 s, 516 s, 503 s, 492 m, 472 m, 448 m, 435 w cm^{-1}. ESI+ MS: *m/z* = 553 ([PdCl(**2**)]$^{+}$). Anal. Calc. for $C_{48}H_{42}Cl_2Fe_2O_2P_2Pd{\cdot}0.1CHCl_3$ (1013.74): C 56.99, H 4.19 %. Found: C 57.08 %, H 4.04 %.

Preparation of trans-[$PdCl_2$(3-κ*P*)$_2$] (5c). A solution of alcohol **3** (20.0 mg, 47 μmol) in chloroform (1 mL) was added to a suspension of [$PdCl_2$(cod)] (6.7 mg, 23 μmol) in the same solvent (0.5 mL). The clear reaction mixture was stirred for 1 h and then evaporated under reduced pressure. The red residue was dissolved in a little chloroform (≈1 mL), and the solution was layered with hexane and set aside for crystallization. Red crystals, which formed during several days, were isolated by suction, washed with pentane and dried under vacuum. Yield of **5c**: 10.5 mg (41%), dark red crystalline solid.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 1.46 (s, 12 H, CMe_2), 4.41 (vt, *J'* = 1.8 Hz, 4 H, CH fc), 4.44 (vt, *J'* = 1.9 Hz, 4 H, CH fc), 4.56 (vt, *J'* = 1.9 Hz, 4 H, CH fc), 4.60 (vt, *J'* = 1,8 Hz, 4 H, CH fc), 7.34-7.45 (m, 12 H, PPh_2), 7.58-7.65 (m, 8 H, PPh_2) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 31.36 (s, 4 C, C*Me*$_2$), 67.06 (s, 4 C, CH fc), 68.84 (s, 2 C, *C*(OH)Me_2), 70.83 (s, 4 C, CH fc), 71.77 (apparent t, *J'* = 4 Hz, 4 C, CH fc), 72.17 (apparent t, *J'* = 27 Hz, 2 C, C–P fc), 75.85 (apparent t, *J'* = 5 Hz, 4 C, CH fc), 101.75 (s, 2 C, *C*-CMe_2 fc), 127.72 (apparent t, *J'* = 5 Hz, 8 C, CH^{meta} PPh_2), 130.27 (s, 4 C, CH^{para} PPh_2), 131.14 (apparent t, *J'* = 25 Hz, 4 C, C^{ipso} PPh_2), 134.20 (apparent t, *J'* = 6 Hz, 8 C, CH^{ortho} PPh_2) ppm. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = 15.5 (s) ppm. IR (Nujol): ν_{max} = 3486 s, 3127 m, 3090 m, 3043 m, 1571 w, 1321 m, 1301 m, 1264 m, 1223 w, 1167 s, 1135 m, 1110 m, 1097 m, 1056 w, 1033 m, 997 w, 957 m, 915 w, 868 w, 851 w, 838 w, 812 m, 744 m, 707 w, 696 s, 622 m, 548 m,

523 m, 509 m, 498 m, 483 m, 465 m, 438 w cm^{-1}. ESI+ MS: *m/z* = 569 [Pd(**3**)Cl]$^+$. Anal. Calc. for $C_{50}H_{50}Cl_2Fe_2O_2P_2Pd \cdot 0.1\ CHCl_3$ (1045.83): C 57.54, H 4.83%. Found: C 57.51, H 4.63%.

Synthesis of [Pd(μ-Cl)Cl(1-κ*P*)]$_2$ (6a). A solution of compound **1** (20.0 mg, 50 μmol) in chloroform (1 mL) was added to a suspension of [$PdCl_2$(cod)] (14.0 mg, 50 μmol) in the same solvent (0.5 mL), giving a deep red solution, which was stirred for 1 h. The crude product, obtained by evaporation under reduced pressure, was dissolved in a minimum amount of chloroform, and the solution was layered with hexane. Crystallisation by liquid-phase diffusion afforded solvated complex **6a** as a burgundy red solid. Yield of **6a**·2$CHCl_3$: 31.4 mg (90%). Crystals used for structure determination were obtained by recrystallisation from chloroform-heptane.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 4.64 (m, 4 H, CH fc), 4.68 (vq, *J*'= 1.9 Hz, 4 H, CH fc), 5.18 (vt, *J*' = 1.9 Hz, 4 H, CH fc), 5.24 (br s, 4 H, CH fc), 7.37-7.62 (m, 20 H, PPh_2), 10.10 (s, 2 H, CHO) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 71.29 (d, $^1J_{PC}$ = 67 Hz, 2 C, C-P fc), 71.89 (s, 4 C, CH fc), 73.73 (d, J_{PC} = 9 Hz, 4 C, CH fc), 76.62 (s, 4 C, CH fc), 80.45 (s, 2 C, *C*-CHO fc), 128.10 (d, $^1J_{PC}$ = 61 Hz, 4 C, C^{ipso} PPh_2), 128.37 (d, J_{PC} = 13 Hz, 8 C, CH PPh_2), 131.88 (d, $^4J_{PC}$ = 2 Hz, 4 C, CH^{para} PPh_2), 133.70 (d, J_{PC} = 11 Hz, 8 C, CH PPh_2), 193.59 (s, 2 C, CHO) ppm. One signal due to ferrocene CH is obscured by the solvent resonance. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = 30.4 (s) ppm. IR (Nujol): ν_{max} = 1686 s, 1335 w, 1303 w, 1244 w, 1218 w, 1169 m, 1102 m, 1095 m, 1060 w, 1044 w, 1031 m, 998 w, 974 w, 860 w, 839 m, 828 w, 753 s, 746 s, 713 w, 691 m, 668 w, 620 w, 544 m, 520 m, 496 m, 481 m, 445 m cm^{-1}. ESI+ MS: *m/z* = 539 [Pd(**1**)Cl]$^+$, 597 [Pd(**1**)Cl_2 + Na]$^+$. Anal. Calc. for $C_{46}H_{38}Cl_4Fe_2O_2P_2Pd_2 \cdot 2CHCl_3$ (1389.84): C 41.48, H 2.90%. Found: C 41.52, H 2.90%.

Synthesis of [Pd(μ-Cl)Cl(2-κ*P*)]$_2$ (6b). A solution of acylphosphine **2** (20.0 mg, 49 μmol) in chloroform (1 mL) was added to a chloroform suspension of [$PdCl_2$(cod)] (14.0 mg, 49 μmol in 1 mL). The resulting deep red solution was stirred for 1 h and then precipitated with pentane. The separated product was filtered, washed with pentane and dried under vacuum. Yield of **6b**: 19.6 mg (69%), burgundy red solid. Crystals for X-ray diffraction analysis were grown from chloroform-hexane.

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 2.44 (s, 6 H, COMe), 4.53 (vq, *J'* = 2.0 Hz, 4 H, fc), 4.65 (vq, *J'* = 1.8 Hz, 4 H, fc), 5.12 (vt, *J'* = 2.0 Hz, 4 H, fc), 5.25 (br s, 4 H, fc), 7.37-7.66 (m, 20 H, PPh_2) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 27.95 (s, 2 C, CO*Me*), 70.76 (d, $^{1}J_{PC}$ = 67 Hz, 2 C, C-P fc), 71.71 (s, 4 C, CH fc), 74.70 (d, J_{PC} = 9 Hz, 4 C, CH fc), 76.37 (s, 4 C, CH fc), 80.54 (s, 2 C, *C*–COMe fc), 128.17 (d, $^{1}J_{PC}$ = 62 Hz, 4 C, C^{ipso} PPh_2), 128.32 (d, J_{PC} = 13 Hz, 8 C, CH PPh_2), 131.83 (s, CH^{para} PPh_2), 133.69 (d, J_{PC} = 11 Hz, 8 C, CH PPh_2), 201.68 (s, 2 C, *C*OMe) ppm. One resonance due to ferrocene CH overlaps with the solvent signal. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = 30.6 (s) ppm. IR (Nujol): ν_{max} = 1671 s, 1305 w, 1275 s, 1196 w, 1167 m, 1115 w, 1100 m, 1060 w, 1036 m, 999 w, 963 w, 895 w, 841 m, 747 m, 692 m, 621 w, 547 m, 519 m, 498 m, 480 m cm^{-1}. ESI+ MS: *m/z* = 553 [PdCl(**2**)]$^{+}$, 1199 [M + Na]$^{+}$. Anal. Calc. for $C_{48}H_{42}Cl_4Fe_2O_2P_2Pd_2 \cdot 0.5CHCl_3$ (1238.82): C 47.02, H 3.46%. Found: C 47.10, H 3.51 %.

Synthesis of [Pd(μ-Cl)Cl(3-κ*P*)]$_2$ (6c) and isolation of 6d. Alcohol **3** (21.4 mg, 50 μmol) and [$PdCl_2$(cod)] (14.6 mg, 50 μmol) were dissolved in $CHCl_3$ (4 mL), which was freshly dried and neutralised by passing through an alumina column. After stirring for 15 min, the burgundy red reaction mixture was added dropwise to pentane (50 mL). The precipitated solid was isolated by suction, washed with pentane and dried under vacuum. Yield of **6c**: 23 mg (76%), khaki solid. NMR data were obtained on an *in situ* prepared sample. Prolonged standing in a $CHCl_3$ solution or the use of an untreated halogenated solvent results in the formation of **6d** or, typically, mixtures containing both compounds.

To prepare compound **6d**, a solution of alcohol **3** (20.0 mg, 47 μmol) in chloroform (1 mL) was added to a suspension of [$PdCl_2$(cod)] (13.4 mg, 47 μmol) in the same solvent (0.5 mL). The deep red violet mixture was stirred for 1 h and then evaporated under vacuum. The solid residue was dissolved in acetone and layered with hexane. Subsequent crystallisation over several days afforded burgundy red crystals of complex **6d**, which were isolated by suction and dried under vacuum. Yield: 13 mg (48%).

Analytical data for **6c.** ^{1}H NMR (*in situ*, 399.95 MHz, $CDCl_3$): δ = 1.52 (s, 12 H, Me), 4.57 (dd, *J* = 1.8, 1.2 Hz, 4 H, CH fc), 4.60-4.62 (m, 8 H, CH fc), 4.91 (vt, *J'* = 1.9 Hz, 4 H, CH fc), 7.34-7.62 (m, 20 H, PPh_2) ppm. ^{13}C{^{1}H} NMR (*in situ*, 100.58 MHz, $CDCl_3$): δ = 31.47 (s, 4 C, C*Me*$_2$), 67.70 (s, 4 C, CH fc), 68.98 (s, 2 C, *C*(OH)Me$_2$), 69.26 (d, $^{2}J_{PC}$ = 68 Hz, 2 C, *C*–

P fc), 71.71 (s, 4 C, CH fc), 72.86 (d, *J* = 9 Hz, 4 C, CH fc), 76.07 (d, *J* = 11 Hz, 4 C, CH fc), 102.15 (s, 2 C, *C*-CMe_2(OH) fc), 128.14 (d, *J* = 13 Hz, 8 C, CH PPh_2), 128.61 (d, $^1J_{PC}$ = 61 Hz, 4 C, *C*–P PPh_2), 131.56 (s, 4 C, CH^{para} PPh_2), 133.73 (d, *J* = 11 Hz, 8 C, CH PPh_2) ppm. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ = 31.5 (s) ppm. Also observed were the signals due to liberated cycloocta-1,5-diene: ^1H NMR (399.95 MHz, $CDCl_3$): δ = 2.36 (m, 8 H, CH_2), 5.59 (m, 4 H, =CH) ppm. $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ = 28.03 (s, 4 C, *C*H_2), 128.67 (s, 4 C, =*C*H) ppm. IR (isolated material, Nujol): ν_{max} = 3482 m, 1263 w, 1225 w, 1167 s, 1138 w, 1100 s, 1031 m, 999 m, 954 w, 914 w, 890 w, 867 w, 834 m, 785 w, 748 m, 692 s, 619 w, 549 m, 521 m, 487 m, 472 w, 420 w cm^{-1}. ESI– MS: *m/z* = 641 $[PdCl_3(\mathbf{3})]^-$. Anal. Calc. for $C_{50}H_{50}Cl_4Fe_2O_2P_2Pd_2$ (1211.22): C 49.58, H 4.16%; Found: C 49.66, H 4.18%.

Analytical data for **6d**. ^1H NMR (399.95 MHz, $CDCl_3$): δ = 2.07 (dd, *J* = 1.3, 0.7 Hz, 6 H, Me), 4.41 (vq, *J´* = 1.6 Hz, 4 H, CH fc), 4.57 (br d, *J´* = 1.8 Hz, 4 H, CH fc), 4.81 (vt, *J´* = 1.9 Hz, 4 H, CH fc), 4.98-5.02 (m, 4 H, CH fc, 2 H, $=CH_2$), 5.31 (s, 2 H, $=CH_2$), 7.33-7.40 (m, 8 H, PPh_2), 7.44-7.50 (m, 4 H, PPh_2), 7.56-7.64 (m, 8 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ = 21.66 (s, 4 C, Me), 68.18 (s, 4 C, CH fc), 68.50 (d, $^1J_{PC}$ = 64 Hz, 2 C, C–P fc), 72.77 (s, 4 C, CH fc), 74.83 (d, J_{PC} = 9 Hz, 4 C, CH fc), 76.25 (d, J_{PC} = 11 Hz, 4 C, CH fc), 88.72 (s, 2 C, *C*–C(Me)CH_2 fc), 110.75 (s, 2 C, $=CH_2$), 128.08 (d, J_{PC} = 13 Hz, 8 C, CH PPh_2), 128.65 (d, $^1J_{PC}$ = 61 Hz, 4 C, C^{ipso} PPh_2), 131.48 (s, 4 C, CH^{para} PPh_2), 133.73 (d, J_{PC} = 11 Hz, 8 C, CH^{meta} PPh_2), 139.92 (s, 2 C, *C*=CH_2) ppm. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ = 31.9 (s) ppm. IR (Nujol): ν_{max} 1687 m, 1653 w, 1307 m, 1169 m, 1094 m, 1074 w, 1024 m, 1000 w, 918 m, 848 w, 838 m, 830 m, 746 s, 689 s, 669 w, 618 w, 555 m, 545 w, 524 s, 509 m, 494 m, 473 w, 460 w, 446 m cm^{-1}. ESI+ MS: *m/z* = 641 $[PdCl_3(\mathbf{3})]^-$, 655 $[PdCl_3(\mathbf{3}) - H_2O + MeOH]^-$. Anal. Calc. for $C_{50}H_{46}Cl_4Fe_2P_2Pd_2$ (1175.19): C 51.10, H 3.95%; Found: C 50.97, H 4.07%.

Synthesis of [(L^{NC})PdCl(1-κ*P*)] (7a). A chloroform solution of $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ (14.2 mg, 25 μmol in 1.5 mL of the solvent) was added to a solution of ligand **1** (20.0 mg, 50 μmol) in the same solvent (1 mL). The resulting red solution was stirred for 1 h and then evaporated under reduced pressure to afford analytically pure **7a** as a red-brown solid in essentially quantitative yield (34 mg). The amorphous product showed a strong tendency to retain residual solvent.

^1H NMR (399.95 MHz, $CDCl_3$): δ = 2.87 (d, $^4J_{PH}$ = 2.7 Hz, 6 H, NMe_2), 4.15 (d, $^4J_{PH}$ = 2.4 Hz, 2 H, NCH_2), 4.48 (m, 2 H, fc), 4.53 (vq, *J'* = 2.0 Hz, 2 H, fc), 4.98 (vt, *J'* = 1.9 Hz, 2 H,

fc), 5.11 (vt, *J'* = 2,0 Hz, 2 H, fc), 6.24 (ddd, *J* = 7.7, 6.5, 1.1 Hz, 1 H, C_6H_4), 6.39 (td, *J* = 7.6, 1.5 Hz, 1 H, C_6H_4), 6.84 (td, *J* = 7.3, 1.1 Hz, 1 H, C_6H_4), 7.03 (dd, *J* = 7.4, 1.5 Hz, 1 H, C_6H_4), 7.31-7.59 (m, 10 H, PPh_2), 9.94 (s, 1 H, CHO) ppm. $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ = 50.17 (d, $^3J_{PC}$ = 3 Hz, 2 C, NMe_2), 71.14 (s, 2 C, CH fc), 72.86 (d, *J* = 7 Hz, 2 C, CH fc), 73.70 (d, $^3J_{PC}$ = 3 Hz, 2 C, NCH_2), 76.28 (d, $^1J_{PC}$ = 58 Hz, 1 C, C-P fc), 76.43 (s, 2 C, CH fc), 76.80 (d, J_{PC} = 9 Hz, 2 C, CH fc), 80.07 (s, 1 C, *C*-CHO fc), 122.53 (s, 1 C, CH C_6H_4), 123.85 (s, 1 C, CH C_6H_4), 124.96 (d, *J* = 6 Hz, 1 C, CH C_6H_4), 128.10 (d, J_{PC} = 11 Hz, 4 C, CH PPh_2), 130.78 (d, $^4J_{PC}$ = 2 Hz, 2 C, CH^{para} PPh_2), 131.05 (d, $^1J_{PC}$ = 50 Hz, 2 C, C^{ipso} PPh_2), 134.36 (d, $^2J_{PC}$ = 12 Hz, 4 C, CH^{ortho} PPh_2), 138.37 (d, J_{PC} = 11 Hz, 1 C, CH C_6H_4), 148.09 (d, *J* = 2 Hz, 1 C, C^{ipso} C_6H_4), 152.15 (d, *J* = 1 Hz, 1 C, C^{ipso} C_6H_4), 193.55 (s, 1 C, CHO) ppm. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ = 32.4 (s) ppm. IR (Nujol): ν_{max} = 3048 w, 1683 s, 1666 s, 1612 w, 1579 m, 1305 w, 1245 m, 1165 m, 1099 m, 1061 w, 1029 m, 996 m, 972 w, 933 w, 865 w, 845 m, 743 s, 696 s, 655 w, 629 w, 618 w, 543 m, 519 m, 503 m, 478 m, 438 w cm^{-1}. ESI+ MS: *m/z* = 610 $[M - CO - Cl]^+$, 638 $[M - Cl]^+$. Anal. Calc. for $C_{32}H_{31}ClFeNOPPd \cdot 0.4\ CHCl_3$ (722.04): C 53.90, H 4.38, N 1.94%. Found: C 53.81, H 4.71, N 1.98%.

Synthesis of [(L^{NC})PdCl(2-κ*P*)] (7b). Complex **7b** was prepared similarly to **7a**, starting from ligand **2** (41.2 mg, 0.10 mmol) and $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ (27.6 mg, 50 μmol) in 1.5 mL of chloroform. Following evaporation, the complex was isolated as an orange-red amorphous solid, which tenaciously holds the reaction solvent (69 mg, quant.).

^1H NMR (399.95 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, COMe), 2.86 (d, $^4J_{PH}$ = 2.7 Hz, 6 H, NMe_2), 4.14 (d, $^4J_{PH}$ = 2.3 Hz, 2 H, NCH_2), 4.36 (td, *J* = 2.0, 1.0 Hz, 2 H, fc), 4.48 (vq, *J'*= 2.0 Hz, 2 H, fc), 4.92 (vt, *J'* = 2.0 Hz, 2 H, fc), 5.04 (vt, *J'* = 2.0 Hz, 2 H, fc), 6.25 (ddd, *J* = 7.9, 6.5, 1.1 Hz, 1 H, C_6H_4), 6.39 (td, *J* = 7.6, 1.2 Hz, 1 H, C_6H_4), 6.83 (td, *J* = 7.3, 0.9 Hz, 1 H, C_6H_4), 7.02 (dd, *J* = 7.3, 1.5 Hz, 1 H, C_6H_4), 7.30–7.60 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ = 27.63 (s, 1 C, CO*Me*), 50.15 (d, $^3J_{PC}$ = 2 Hz, 2 C, NMe_2), 70.97 (s, 2 C, CH fc), 73.67 (d, $^3J_{PC}$ = 3 Hz, 1 C, NCH_2), 73.74 (d, $^3J_{PC}$ = 7 Hz, 2 C, CH fc), 75.75 (d, $^1J_{PC}$ = 58 Hz, 1 C, C–P fc), 75.98 (s, 2 C, CH fc), 76.68 (d, J_{PC} = 9 Hz, 2 C, CH fc), 80.08 (s, 1 C, *C*–COMe), 122.51 (s, 1 C, CH C_6H_4), 123.81 (s, 1 C, CH C_6H_4), 124.93 (d, J_{PC} = 5 Hz, 1 C, CH C_6H_4), 128.04 (d, $^3J_{PC}$ = 10 Hz, 4 C, CH^{meta} PPh_2), 130.71 (d, $^4J_{PC}$ = 2 Hz, 2 C, CH^{para} PPh_2), 131.15 (d, $^1J_{PC}$ = 50 Hz, 2 C, C^{ipso} PPh_2), 134.34 (d, $^2J_{PC}$ = 12 Hz, 4 C, CH^{ortho} PPh_2), 138.35 (d, J_{PC} = 10 Hz, 1 C, CH C_6H_4), 148.09 (d, J_{PC} = 2 Hz, 1 C, C^{ipso} C_6H_4), 152.16 (d, J_{PC} = 1 Hz, 1 C, C^{ipso} C_6H_4), 201.76 (s, 1 C, *C*OMe) ppm. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ = 32.4 (s) ppm. IR

(Nujol): ν_{max} = 3047 m, 1671 s, 1578 m, 1560 w, 1305 w, 1276 s, 1246 w, 1215 w, 1165 m, 1114 m, 1099 m, 1059 w, 1028 m, 994 m, 972 w, 933 w, 894 w, 864 w, 844 m, 746 s, 695 s, 665 w, 628 w, 619 w, 543 m, 520 m, 502 m, 476 m, 438 w cm^{-1}. ESI+ MS: *m/z* = 652 $[M - Cl]^+$. Anal. Calc. for $C_{33}H_{33}ClFeNOPPd \cdot 0.33CHCl_3$ (727.71): C 55.01, H 4.62, N 1.92%. Found: C 55.03, H 4.64, N 1.93%.

Synthesis of [(L^{NC})PdCl(3-κ*P*)] (7c). Ligand **3** (20.0 mg, 47 μmol) and $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ (12.8 mg, 23 μmol) were reacted in 1.5 mL of chloroform and then worked up as described above to afford **7c** as an amorphous orange solid in quantitative yield (36 mg).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 1.46 (s, 6 H, CMe_2), 2.84 (d, $^4J_{PH}$ = 2.8 Hz, 6 H, NMe_2), 4.14 (d, $^4J_{PH}$ = 2.3 Hz, 2 H, NCH_2), 4.39 (m, 2 H, fc), 4.40 (vt, *J'* = 1.9 Hz, 2 H, fc), 4.47 (vt, *J'* = 2.0 Hz, 2 H, fc), 4.49 (vq, *J'* = 1,9 Hz, 2 H, fc), 6.25 (ddd, *J* = 7.6, 6.3, 1.2 Hz, 1 H, C_6H_4), 6.37 (td, *J* = 7.5, 1.4 Hz, 1 H, C_6H_4), 6.82 (td, *J* = 7.3, 1.2 Hz, 1 H, C_6H_4), 7.01 (dd, *J* = 7.3, 1.5 Hz, 1 H, C_6H_4), 7.29-7.57 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ = 31.61 (s, 2 C, C*Me*$_2$), 50.15 (d, $^3J_{PC}$ = 3 Hz, 2 C, NMe_2), 67.00 (s, 2 C, CH fc), 68.66 (s, 1 C, *C*(OH)Me_2), 70.41 (s, 2 C, CH fc), 71.73 (d, J_{PC} = 7 Hz, 2 C, CH fc), 73.47 (d, $^3J_{PC}$ = 3 Hz, 1 C, NCH_2), 74.25 (d, $^1J_{PC}$ = 60 Hz, 1 C, C-P fc), 75.78 (d, $^2J_{PC}$ = 9 Hz, 2 C, CH fc), 102.11 (s, 1 C, *C*-CMe_2 fc), 122.41 (s, 1 C, CH C_6H_4), 123.65 (s, 1 C, CH C_6H_4), 124.77 (d, J_{PC} = 6 Hz, 1 C, CH C_6H_4), 127.86 (d, J_{PC} = 11 Hz, 4 C, CH PPh_2), 130.49 (d, $^4J_{PC}$ = 2 Hz, 2 C, CH^{para} PPh_2), 131.70 (d, $^1J_{PC}$ = 49 Hz, 2 C, C^{ipso} PPh_2), 134.41 (d, J_{PC} = 12 Hz, 4 C, CH PPh_2), 138.52 (d, J_{PC} = 11 Hz, 1 C, CH C_6H_4), 148.25 (d, J_{PC} = 2 Hz, 1 C, C^{ipso} C_6H_4), 152.35 (s, 1 C, C^{ipso} C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ = 33.0 (s) ppm. IR (Nujol): ν_{max} = 3378 br s, 3173 m, 3050 s, 1739 m, 1667 vs, 1629 m, 1618 m, 1590 w, 1579 w, 1562 w, 1538 m, 1511 w, 1408 w, 1350 m, 1305 m, 1263 w, 1229 w, 1208 w, 1164 m, 1072 w, 1058 w, 1027 m, 994 m, 957 w, 917 w, 864 w, 844 m, 832 m, 773 w, 743 s, 695 s, 626 m, 546 m, 517 m, 486 m, 433 m cm^{-1}. ESI+ MS: *m/z* = 650 $[M - Cl - H_2O]^+$, 668 $[M - Cl]^+$. Anal. Calc. for $C_{34}H_{37}ClFeNOPPd \cdot 0.7CHCl_3$ (787.92): C 52.90, H 4.82, N 1.78%. Found: C 52.87, H 4.99, N 1.73%.

Synthesis of [(L^{NC})Pd(1-κ^2*O*,*P*)][PF_6] (8a). A solution of ligand **1** (20 mg, 50 μmol) in chloroform (1 mL was added to complex $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ (14.2 mg, 25 μmol) dissolved in the same solvent (0.5 mL). The reaction mixture was stirred for 30 min before it was added to solid $Tl[PF_6]$ (17.5 mg, 50 μmol). After stirring for another 30 min, Celite was

added (≈20 mg), and the reaction mixture was filtered through a PTFE syringe filter (0.45 μm pore size). The filtrate was evaporated to afford a crude product, which was immediately dissolved in a little dichloromethane and crystallised by hexane addition as a top layer. Red crystals of the product, formed after several days, were filtered, washed with pentane and dried under vacuum. Yield: 22.0 mg (56%), red crystalline solid. The crystal used for structure determination was selected from the reaction batch.

^{1}H NMR (399.95 MHz, CD_2Cl_2): δ = 2.76 (d, $^{4}J_{PH}$ = 2.8 Hz, NMe_2), 4.08 (vq, *J'* = 1.9 Hz, 2 H, fc), 4.19 (d, $^{4}J_{PH}$ = 2.0 Hz, 2 H, NCH_2), 4.65 (m, 2 H, fc), 5.16 (vt, *J'* = 2.0 Hz, 2 H, fc), 5.70 (br s, 2 H, fc), 6.23 (ddd, *J* = 7.8, 6.6, 1.1 Hz, 1 H, C_6H_4), 6.36 (tdd, *J* = 7.9, 1.6, 0.6 Hz, 1 H, C_6H_4), 6.87 (td, *J* = 7.3, 1.1 Hz, 1 H, C_6H_4), 7.04 (dd, *J* = 7.5, 1.7 Hz, 1 H, C_6H_4), 7.44-7.58 (m, 6 H, PPh_2), 7.77-7.84 (m, 4 H, PPh_2), 9.97 (s, 1 H, CHO) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, CD_2Cl_2): δ = 49.97 (d, $^{3}J_{PC}$ = 3 Hz, 2 C, NMe_2), 71.81 (d, $^{3}J_{PC}$ = 3 Hz, 1 C, NCH_2), 74.24 (d, $^{1}J_{PC}$ = 55 Hz, 1 C, C-P fc), 74.90 (s, 1 C, *C*-CHO fc), 75.58 (d, *J* = 6 Hz, 2 C, CH fc), 76.20 (d, *J* = 2 Hz, 2 C, CH fc), 78.64 (d, J_{PC} = 9 Hz, 2 C, CH fc), 79.60 (s, 2 C, CH fc), 123.76 (s, 1 C, CH C_6H_4), 125.63 (s, 1 C, CH C_6H_4), 126.13 (d, J_{PC} = 6 Hz, 1 C, CH C_6H_4), 128.68 (d, $^{1}J_{PC}$ = 51 Hz, 2 C, CH^{ipso} PPh_2), 129.45 (d, J_{PC} = 11 Hz, 4 C, CH PPh_2), 132.45 (d, $^{4}J_{PC}$ = 3 Hz, 2 C, CH^{para} PPh_2), 135.18 (d, J_{PC} = 13 Hz, 4 C, CH PPh_2), 138.90 (d, J_{PC} = 13 Hz, 1 C, CH C_6H_4), 142.54 (d, *J* = 4 Hz, 1 C, C^{ipso} C_6H_4), 148.22 (d, *J* = 2 Hz, 1 C, C^{ipso} C_6H_4), 198.10 (s, 1 C, CHO) ppm. ^{31}P{^{1}H} NMR (161.90 MHz, CD_2Cl_2): δ = 28.6 (s, PPh_2), –143.9 (septet, $^{1}J_{PF}$ = 711 Hz, PF_6^-) ppm. IR (Nujol): ν_{max} = 1600 s, 1581 m, 1562 w, 1304 w, 1253 m, 1198 w, 1183 w, 1166 m, 1098 m, 1040 w, 1027 w, 995 w, 866 m, 834 vs, 743 m, 711 w, 693 m, 656 w, 631 w, 558 m, 527 w, 519 m, 510 m, 487 m, 468 m, 453 w cm^{-1}. ESI+ MS: *m/z* = 638 $[M - PF_6]^+$. Anal. Calc. for $C_{32}H_{31}F_6FeNOP_2Pd$ (783.80): C 49.04, H 3.99, N 1.79%. Found: C 48.88, H 4.01, N 1.78%.

Synthesis of [(L^{NC})Pd(2-κ^2*O,P*)][SbF_6] (8b). A solution of [(L^{NC})Pd(μ-Cl)]$_2$ (67.0 mg, 0.12 mmol) in chloroform (2.5 mL) was added to a solution of ligand **2** (100 mg, 0.24 mmol) in the same solvent (6 mL), and the resulting red solution was stirred for 30 min. Solid Ag[SbF_6] (85 mg, 0.24 mmol) was added using little THF to transfer the silver(I) salt to the reaction mixture completely (an off-white precipitate (AgCl) formed after the addition. The mixture was stirred for 30 min and then filtered through a Celite pad. The filtrate was evaporated under reduced pressure, the crude product was taken up with a little chloroform (≈2 mL), and the solution was layered with diethyl ether. Red crystals

of **8b**, which formed for several days, were filtered, washed with pentane and dried under vacuum. Yield: 194 mg (91%).

^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, COMe), 2.76 (d, $^{4}J_{PH}$ = 2.7 Hz, 6 H, NMe_2), 3.82 (vq, *J'* = 2.0 Hz, 2 H fc), 4.21 (d, $^{4}J_{PH}$ = 2.3 Hz, 2 H, NCH_2), 4.64 (d of vt, *J* = 0.9, 3.8 Hz, 2 H, fc), 4.96 (vt, *J'*= 2.0 Hz, 2 H, fc), 5.70 (br s, 2 H, fc), 6.22 (m, 1 H, C_6H_4), 6.35 (m, 1 H, C_6H_4), 6.85 (m, 1 H, C_6H_4), 7.00 (m, 1 H, C_6H_4), 7.41-7.81 (m, 10 H, PPh_2) ppm. ^{13}C{^{1}H} NMR (100.58 MHz, $CDCl_3$): δ = 28.84 (s, 1 C, CO*Me*), 49.76 (d, $^{3}J_{PC}$ = 2 Hz, 2 C NMe_2), 71.39 (d, $^{3}J_{PC}$ = 4 Hz, 1 C, NCH_2), 73.30 (d, $^{1}J_{PC}$ = 56 Hz, 1 C, C-P fc), 74.49 (d, J_{PC} = 6 Hz, 2 C, CH fc), 75.00 (s, 1 C, *C*-COMe fc), 75.22 (s, 1 C, CH fc), 77.85 (d, J_{PC} = 10 Hz, 2 C, CH fc), 123.40 (s, 1 C, CH C_6H_4), 125.24 (s, 1 C, CH C_6H_4), 125.73 (d, J_{PC} = 6 Hz, 1 C, CH C_6H_4), 128.47 (s, 1 C, CH C_6H_4), 129.01 (d, J_{PC} = 12 Hz, 4 C, CH PPh_2), 131.90 (d, J_{PC} = 2 Hz, 2 H, CH^{para} PPh_2), 134.65 (d, J_{PC} = 13 Hz, 4 C, CH PPh_2), 138.40 (d, $^{1}J_{PC}$ = 13 Hz, 2 C, C^{ipso} PPh_2), 141.92 (d, J_{PC} = 4 Hz, 1 C, C^{ipso} C_6H_4), 147.63 (d, J_{PC} = 2 Hz, 1 C, C^{ipso} C_6H_4), 212.90 (s, 1 C, *C*OMe) ppm. One signal due to ferrocene CH is most likely obscured by solvent resonance. ^{31}P{^{1}H} NMR (161.90 MHz, $CDCl_3$): δ = 29.4 (s) ppm. IR (Nujol): ν_{max} = 3053 m, 2359 w, 1910 w, 1731 w, 1598 s, 1582 s, 1561 m, 1307 s, 1293 s, 1216 m, 1197 m, 1180 m, 1168 s, 1117 m, 1100 s, 1073 w, 1048 m, 1024 s, 994 m, 977 m, 936 w, 895 m, 863 m, 856 m, 843 s, 745 s, 698 s, 660 s, 570 w, 537 s, 518 s, 506 s, 484 s, 476 s, 437 m cm^{-1}. ESI+ MS: *m/z* = 652 $[M - SbF_6]^+$; ESI– MS: *m/z* 235 $[SbF_6]^-$. Anal. Calc. for $C_{33}H_{33}F_6FeNOPPdSb{\cdot}0.25CHCl_3$ (918.45): C 43.48, H 3.65, N 1.53%; Found: C 43.45, H 3.59, N 1.36%.

Synthesis of 8c and isolation of complex 9. A solution of alcohol **3** (20.0 mg, 47 μmol) in dichloromethane (1 mL) was added to solid $[(L^{NC})Pd(\mu\text{-}Cl)]_2$ (12.9 mg, 23 μmol). After stirring the resulting orange solution for 1 h, a suspension of $Tl[PF_6]$ (17.0 mg, 47 μmol) in dichloromethane (1 mL) was added, continuously stirring for another 1 h. Celite was added, and the mixture was filtered through a PTFE syringe filter. Evaporation of the filtrate afforded compound **8c** as an amorphous brown solid in a virtually quantitative yield (29 mg).

Analytical data for **8c**. ^{1}H NMR (399.95 MHz, $CDCl_3$): δ = 1.58 (s, 6 H, CMe_2), 2.83 (d, $^{4}J_{PH}$ = 2.7 Hz, 6 H, NMe_2), 4.12 (d, $^{4}J_{PH}$ = 2.1 Hz, 2 H, NCH_2), 4.18 (br s, 2 H, CH fc), 4.29 (br s, 2 H, CH fc), 4.33 (vt, *J'* = 1.9 Hz, 2 H, CH fc), 4.53 (br s, 2 H, CH fc), 6.19 (ddd, *J* = 7.6, 6.5, 0.9 Hz, 1 H, C_6H_4), 6.35 (td, *J* = 7.5, 1.2 Hz, 1 H, C_6H_4), 6.83 (td, *J* = 7.3, 1.0 Hz, 1 H,

C_6H_4), 6.97 (dd, J = 7.4, 1.6 Hz, 1 H, C_6H_4), 7.36-7.63 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (100.58 MHz, $CDCl_3$): δ = 32.16 (s, 2 C, CMe_2), 49.97 (d, $^3J_{PC}$ = 2 Hz, 2 C, NMe_2), 67.15 (s, 2 C, CH fc), 69.30 (s, 2 C, CH fc), 71.79 (br s, 1 C, NCH_2), 72.58 (d, J_{PC} = 8 Hz, 2 C, CH fc), 72.83 (d, J_{PC} = 13 Hz, 1 C, C(OH)Me_2) 74.77 (d, J_{PC} = 11 Hz, 2 C, CH fc), 99.59 (s, 1 C, C-CMe_2 fc), 123.22 (s, 1 C, CH C_6H_4), 124.93 (s, 1 C, CH C_6H_4), 125.55 (d, J_{PC} = 5 Hz, 1 C, CH C_6H_4), 128.65 (d, J_{PC} = 11 Hz, 4 C, CH PPh_2), 130.29 (d, $^1J_{PC}$ = 52 Hz, 2 C, C^{ipso} PPh_2), 131.36 (d, $^4J_{PC}$ = 2 Hz, 2 C, CH^{para} PPh_2), 134.21 (d, J_{PC} = 13 Hz, 4 C, CH PPh_2), 137.92 (d, J_{PC} = 10 Hz, 1 C, CH C_6H_4), 142.84 (br s, 1 C, C^{ipso} C_6H_4), 147.48 (s, 1 C, C^{ipso} C_6H_4) ppm. The resonance due to ferrocene C-P overlaps was not found, probably due to overlaps. $^{31}P\{^1H\}$ NMR (161.90 MHz, $CDCl_3$): δ = 31.8 (s, PPh_2), −143.6 (septet, $^1J_{PF}$ = 714 Hz, PF_6) ppm. ^{19}F NMR (376.29 MHz, $CDCl_3$): δ = −71.9 (d, $^1J_{PF}$ = 714 Hz, PF_6) ppm. IR (Nujol): ν_{max} = 3524 s, 1586 w, 1331 w, 1314 w, 1263 w, 1228 w, 1194 w, 1161 m, 1140 w, 1126 w, 1097 m, 1063 w, 1035 m, 997 w, 976 w, 943 w, 850 vs, 754 m, 742 m, 710 w, 695 m, 658 w, 620 w, 558 s, 546 m, 517 m, 488 m, 441 w, 431 w cm^{-1}. ESI+ MS: m/z = 668 $[M - PF_6]^+$. Anal. Calc. for $C_{34}H_{37}F_6FeNOP_2Pd{\cdot}0.2CH_2Cl_2$ (830.85): C 49.44, H 4.54, N 1.69%. Found: C 49.39, H 4.78, N 1.70%.

Crystallisation of the reaction product from ethyl acetate-hexane produced several crystals of solvent complex **9**, which was characterised only by IR and MS spectra. IR (Nujol): ν_{max} = 3558 m, 1652 s, 1580 m, 1560 w, 1314 s, 1265 w, 1199 w, 1168 m, 1138 w, 1117 w, 1101 m, 1074 w, 1041 m, 1024 m, 993 w, 973 w, 947 w, 914 w, 899 w, 875 m, 845 vs, 753 s, 698 m, 655 w, 646 w, 623 w, 602 w, 558 s, 544 m, 520 m, 510 m, 490 m, 482 m, 453 m, 438 m, 405 m cm^{-1}. ESI+ MS: m/z = 668 $[M - AcOEt - PF_6]^+$; ESI− MS: m/z = 145 $[PF_6]^-$.

Reaction of complexes 8 with ($PhCH_2NEt_3$)Cl. Complex **8** (20 μmol; **8b**: 18 mg; **8c**: 16 mg) was dissolved in $CDCl_3$ (0.7 mL), and the solution was analysed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Then, the solution was added onto solid benzyl-trimethylammonium chloride (4.9 mg, 21 μmol). Insoluble $(PhCH_2NEt_3)[SbF_6]$/$(PhCH_2NEt_3)[PF_6]$ was removed by filtration, and the filtrate was analysed again. The NMR spectra confirmed the clean recovery of the respective complex **7**. ^{31}P NMR resonance of the PF_6^- anion was not observed, but the ^1H NMR spectra showed signals assigned to the ammonium cation. In the case of **8a**, the reaction was performed on a smaller scale [using 2.5 mg, 3 μmol of **8a** and 0.9 mg, 4 μmol of $(PhCH_2NEt_3)Cl$] in CD_2Cl_2 (0.7 mL) for consistency reasons. The

reaction mixture was evaporated, and the residue was taken up with $CDCl_3$ (0.7 mL). Insoluble $(PhCH_2NEt_3)[PF_6]$ was removed by filtration, and the filtrate was analysed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The spectra again indicated clean formation of **7a**.

X-ray crystallography

Diffraction data were collected at 150(2) K using a Nonius KappaCCD diffractometer with a Bruker Apex-II image plate detector or with a Bruker D8 VENTURE Duo instrument with a PHOTON100 detector and an IμS microfocus X-ray tube (only compounds **5c** and **6d**), both equipped with a Cryostream Cooler (Oxford Cryosystems). Mo Kα radiation (λ = 0.71073 Å) was used in all cases.

The structures were solved by direct methods (SHELXS-97[6]) and then refined by full-matrix least squares based on F^2 (SHELXL-2014[7]). All nonhydrogen atoms were refined with anisotropic displacement parameters. The OH hydrogens were identified on difference electron density maps and refined as "riding" atoms with U_{iso}(H) set to $1.2U_{eq}$(O). Hydrogen atoms in the CH_n groups were included in their calculated positions and refined similarly. Further details on structure refinement are provided below.

The hexafluorophosphate anion in the structure of **8a** was disordered and required modelling over two positions for all fluorine atoms. Furthermore, the solvent molecules in the structure of **8b**·1/4$CHCl_3$ were disordered (one molecule of chloroform per the unit cell located near the inversion centre), resulting in diffuse electron density, which was modelled by PLATON SQUEEZE.[8]

Relevant crystallographic data, data collection and structure refinement parameters (Table S1) and conventional displacement ellipsoid plots are presented here in Supporting Information. Geometric calculations were performed with a recent version of the PLATON program,[9] which was also used to prepare all structural diagrams.

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

Compound	**2**	**5a**·2CH_2Cl_2	**5b**	**5c**
Formula	$C_{24}H_{21}FeOP$	$C_{48}H_{42}Cl_6Fe_2O_2P_2Pd$	$C_{48}H_{42}Cl_2Fe_2O_2P_2Pd$	$C_{50}H_{50}Cl_2Fe_2O_2P_2Pd$
M	412.23	1143.55	1001.75	1033.84
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
T/K	150(2)	150(2)	150(2)	150(2)
a/Å	8.2802(3)	9.1991(3)	9.0970(3)	22.4994(12)
b/Å	16.2564(6)	11.0936(3)	11.4967(4)	12.4875(7)
c/Å	14.4338(5)	12.7081(4)	11.5044(4)	17.1165(9)
α/°		105.0080(10)	69.7720(10)	
β/°	95.3880(10)	101.0690(10)	68.2780(10)	111.986(2)
γ/°		108.0470(10)	84.5750(10)	
V/Å^3	1934.30(12)	1137.49(6)	1048.05(6)	4459.3(4)
Z	4	1	1	4
μ(Mo Kα)/mm^{-1}	0.873	1.483	1.351	1.273
Diffrns collected	15957	20022	12712	26325
Independent diffrns	4437	5253	4795	5139
Observed[a] diffrns	3982	4874	4036	4798
R_{int}[b]/%	1.97	1.82	2.58	2.20
No. of parameters	245	277	260	288
R[b] obsd diffrns/%	2.62	1.98	2.64	2.66
R, wR[b] all data/%	3.05, 6.71	2.24, 4.82	3.59, 5.43	2.92, 6.76
Δρ/e Å^{-3}	0.40, –0.24	0.75, –0.59	0.42, –0.36	0.48, –1.24
CCDC entry	1882120	1882121	1882122	1882123

[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	**6a**·2$CHCl_3$	**6b**·$CHCl_3$	**6d**
Formula	$C_{48}H_{40}Cl_{10}Fe_2O_2P_2Pd_2$	$C_{49}H_{43}Cl_7Fe_2O_2P_2Pd_2$	$C_{50}H_{46}Cl_4Fe_2P_2Pd_2$
M	1389.74	1298.42	1175.11
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
T/K	150(2)	150(2)	150(2)
a/Å	14.6498(3)	9.3431(3)	10.9962(4)
b/Å	9.3791(2)	13.4139(4)	15.7529(6)
c/Å	18.8830(3)	20.0647(6)	13.3059(5)
α/°		73.5577(11)	
β/°	92.3280(10)	88.5641(12)	98.934(2)
γ/°		88.4939(12)	
V/Å^3	2592.42(9)	2410.58(13)	2276.91(15)
Z	2	2	2
μ(Mo Kα)/mm^{-1}	1.847	1.819	1.742
Diffrns collected	23369	25841	23370
Independent diffrns	5950	11049	4349
Observed[a] diffrns	5472	9696	3567
R_{int}[b]/%	1.76	2.14	4.08
No. of parameters	298	579	272
R[b] obsd diffrns/%	1.87	3.49	2.97
R, wR[b] all data/%	2.15, 4.52	4.14, 8.77	4.29, 7.75
Δρ/e Å^{-3}	0.51, –0.53	2.82, –1.56	0.93, –0.48
CCDC entry	1882124	1882125	1882126

Table S1 continued

Compound	**8a**	**8b**·1/4$CHCl_3$	**9**
Formula	$C_{32}H_{31}F_6FeNOP_2Pd$	$C_{33.25}H_{33.25}Cl_{0.75}F_6FeNOPPdSb$	$C_{38}H_{45}F_6FeNO_3P_2Pd$
M	783.77	918.41	901.94
Crystal system	orthorhombic	triclinic	triclinic
Space group	*Pna*2_1 (no. 33)	*P*–1 (no. 2)	*P*–1 (no. 2)
T/K	150(2)	150(2)	150 (2)
a/Å	15.9560(5)	10.5038(3)	9.6869(2)
b/Å	13.0167(3)	16.8039(6)	11.1888(3)
c/Å	15.0075(4)	22.1244(6)	18.9142(4)
α/°		68.4133(14)	100.4880(10)
β/°		79.3192(10)	96.4760(10)
γ/°		71.8420(11)	106.4900(10)
V/Å^3	3116.97(15)	3439.28(19)	1903.22(8)
Z	4	4	2
μ(Mo Kα)/mm^{-1}	1.209	1.879	1.005
Diffrns collected	23439	37515	25340
Independent diffrns	6976	13481	8760
Observed[a] diffrns	5719	10136	7777
R_{int}[b]/%	4.44	4.32	1.90
No. of parameters	412	817	475
R[b] obsd diffrns/%	3.62	4.27	2.63
R, *wR*[b] all data/%	5.21, 7.95	6.54, 7.53	3.08, 6.80
Δρ/e Å^{-3}	1.03, –0.54	1.51, –1.10	0.95, –0.62
CCDC entry	1882127	1882128	1882129

Additional structural diagrams

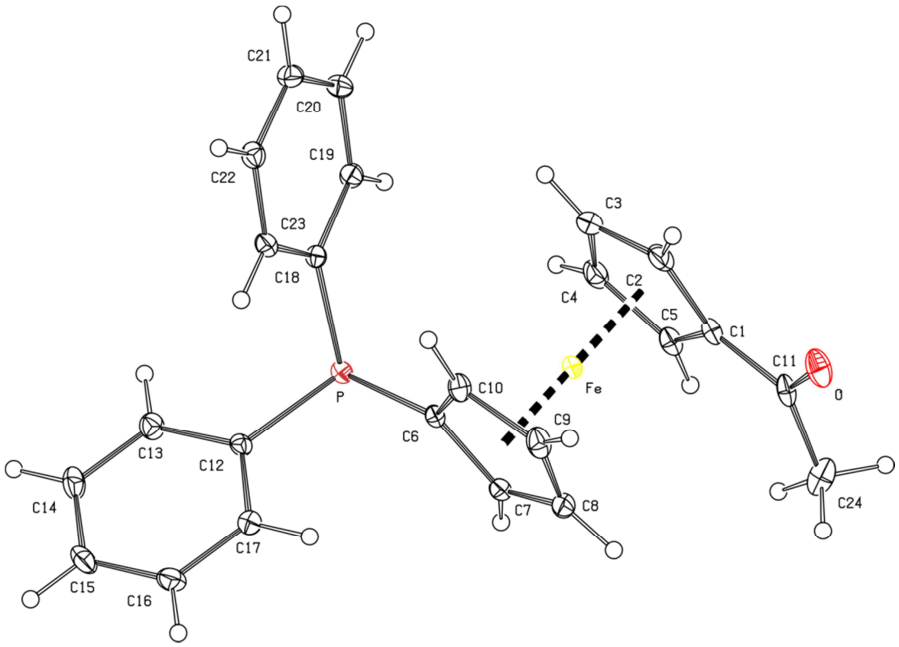

Figure S1. PLATON plot of the molecular structure of **2** showing displacement ellipsoids at the 30% probability level

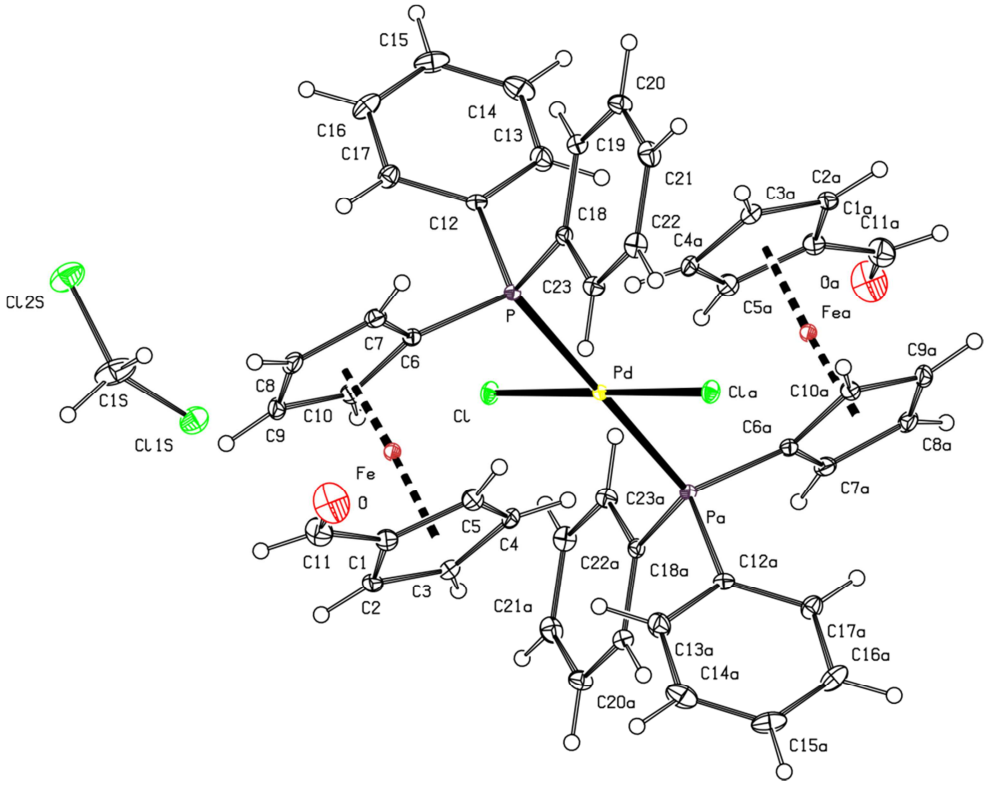

Figure S2. PLATON plot of the structure of **5a**·2CH_2Cl_2 with 30% probability displacement ellipsoids (Note: only the structurally independent solvent molecule is shown for clarity)

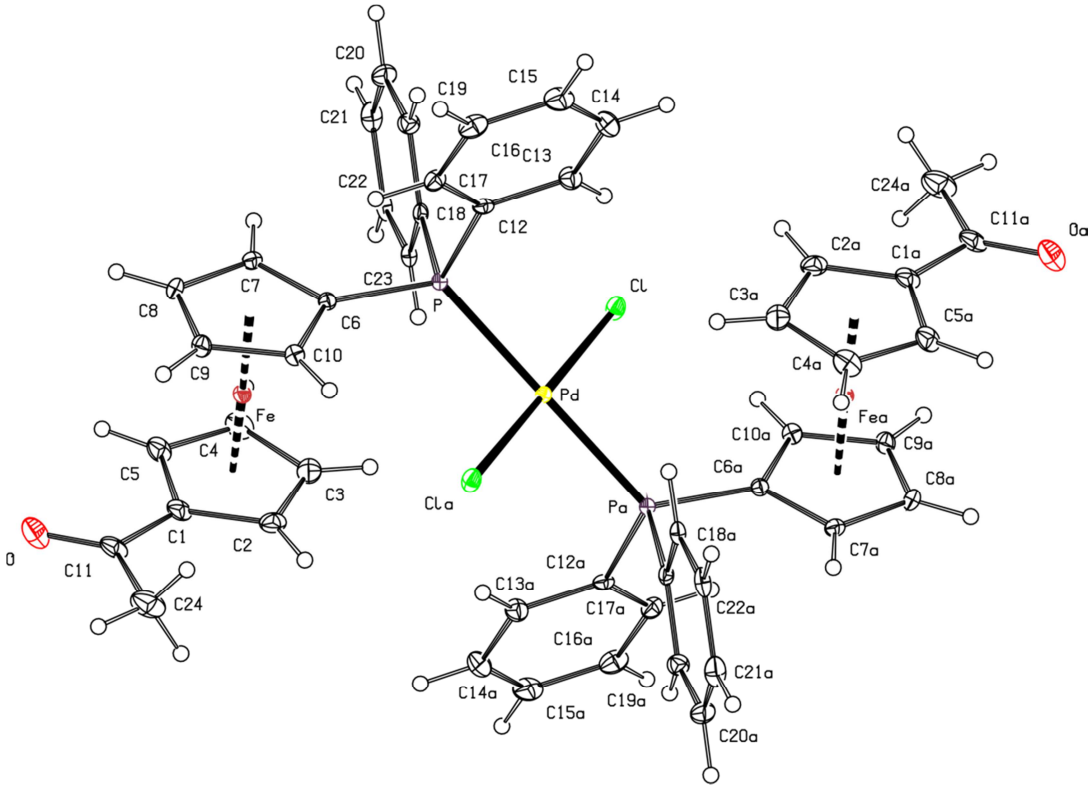

Figure S3. PLATON plot of the structure of **5b** showing displacement ellipsoids at the 30% probability level

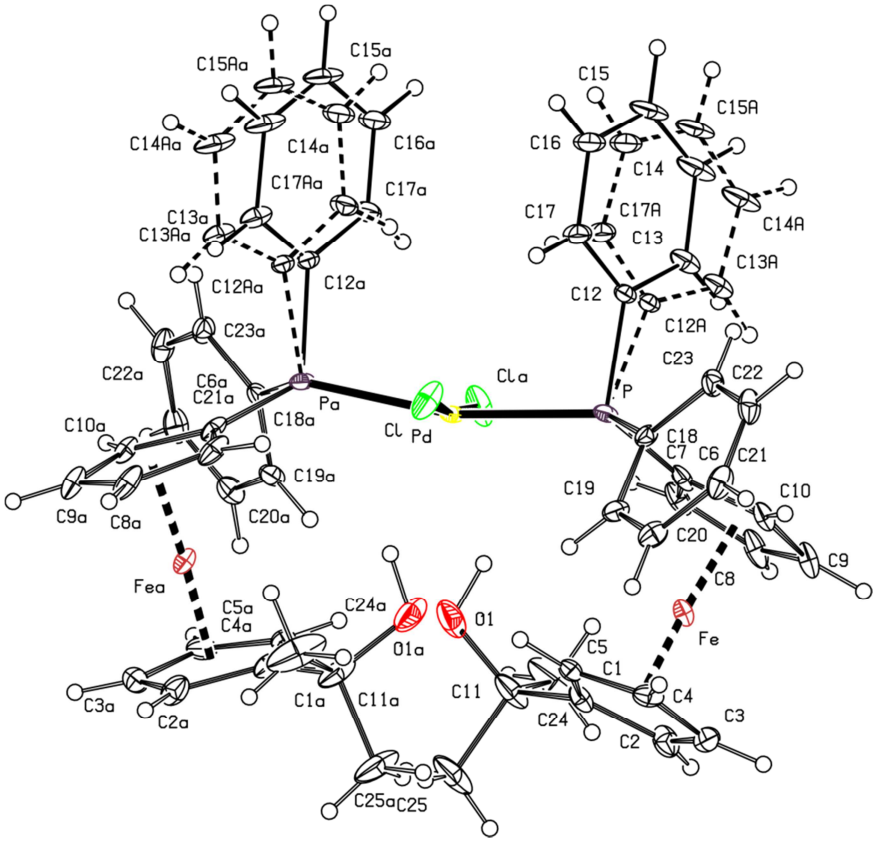

Figure S4. PLATON plot of the structure of **5c** with displacement ellipsoids at the 30% probability level, showing both orientations of the disordered phenyl ring C(12-17)

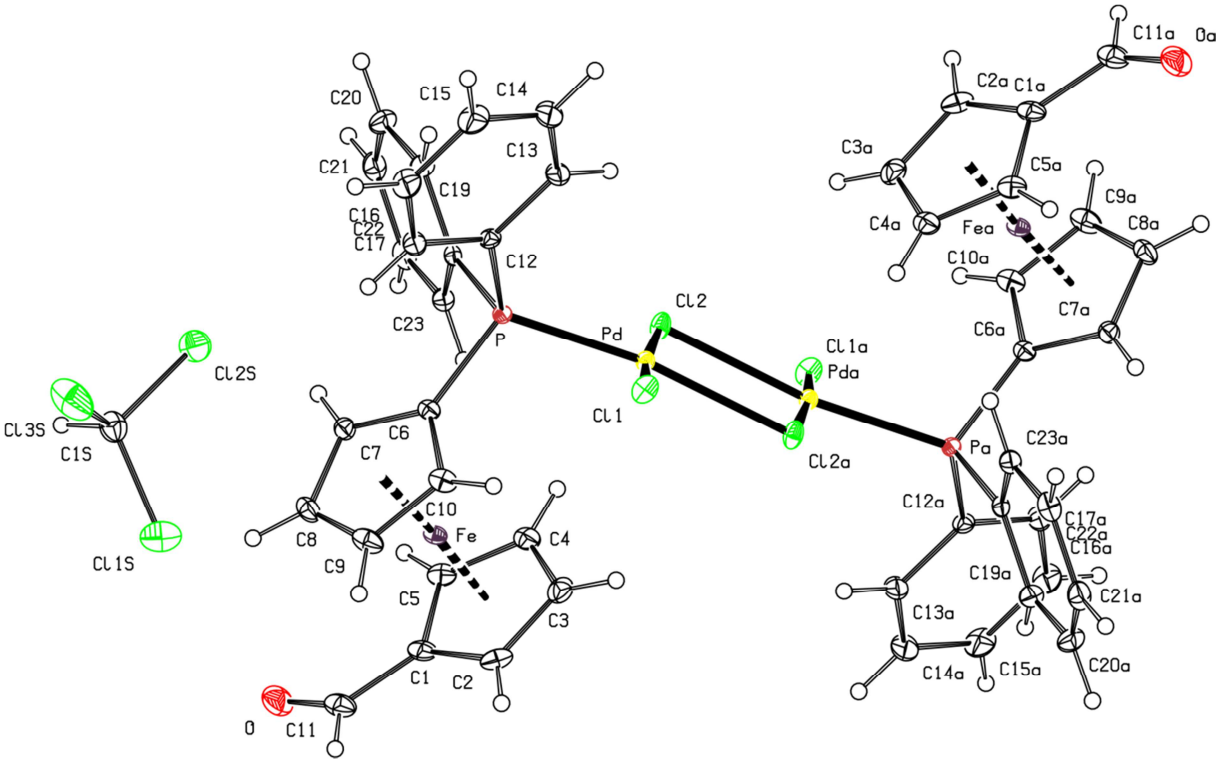

Figure S5. PLATON plot of the structure of **6a**·2CHCl$_3$ with 30% displacement ellipsoids (Note: only the structurally independent solvent molecule is shown for clarity)

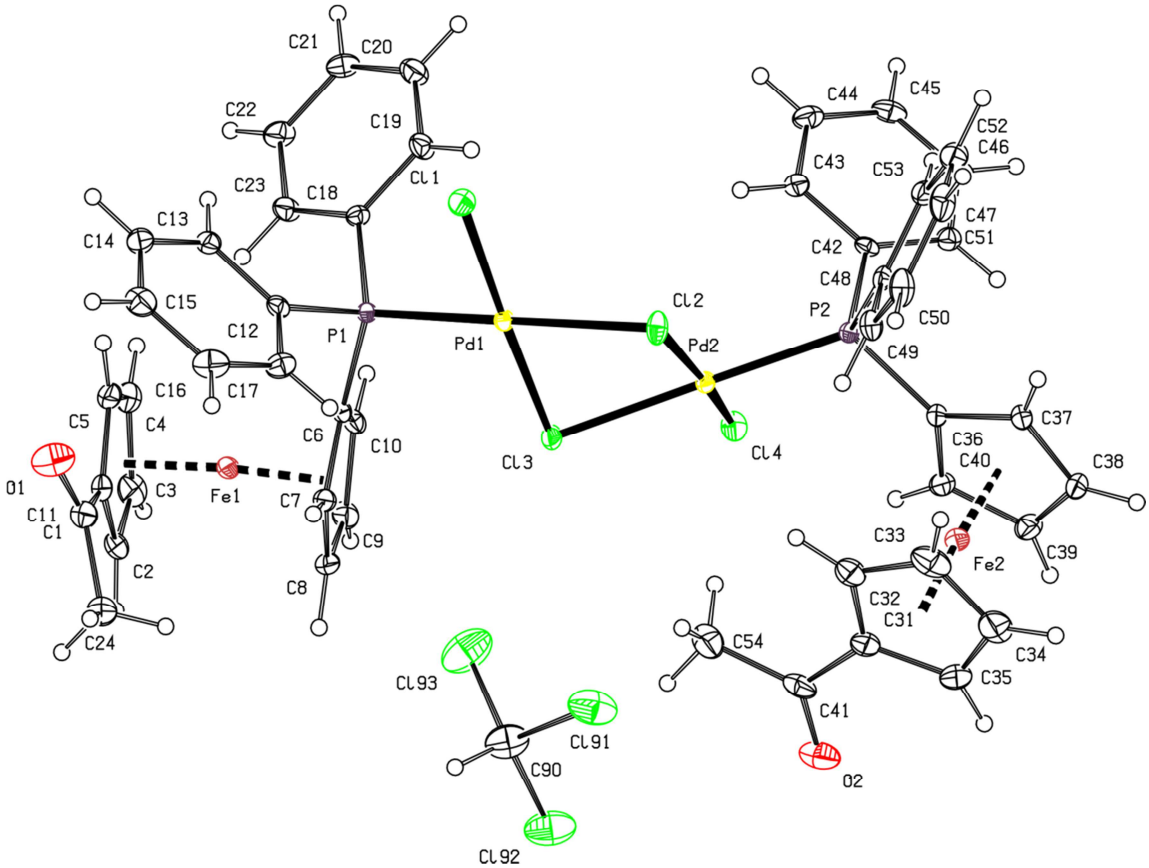

Figure S6. PLATON plot of the structure of **6b**·CHCl$_3$ showing displacement ellipsoids at the 30% probability level

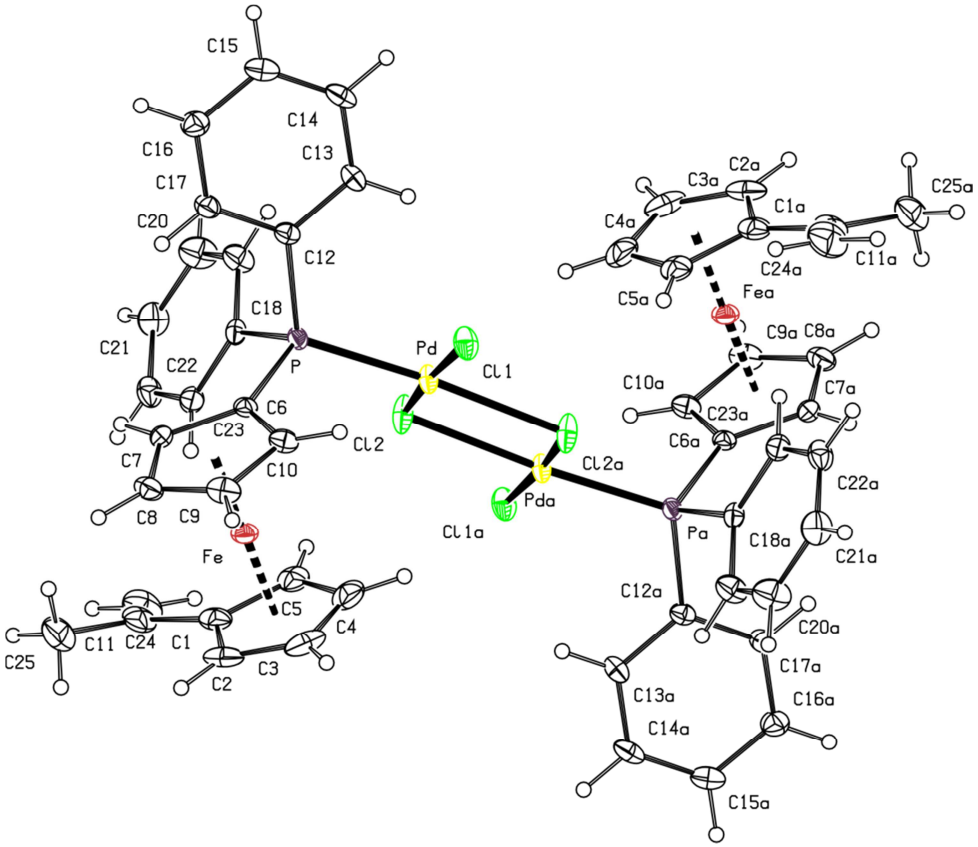

Figure S7. PLATON plot of the structure of **6d** showing displacement ellipsoids at the 30% probability level

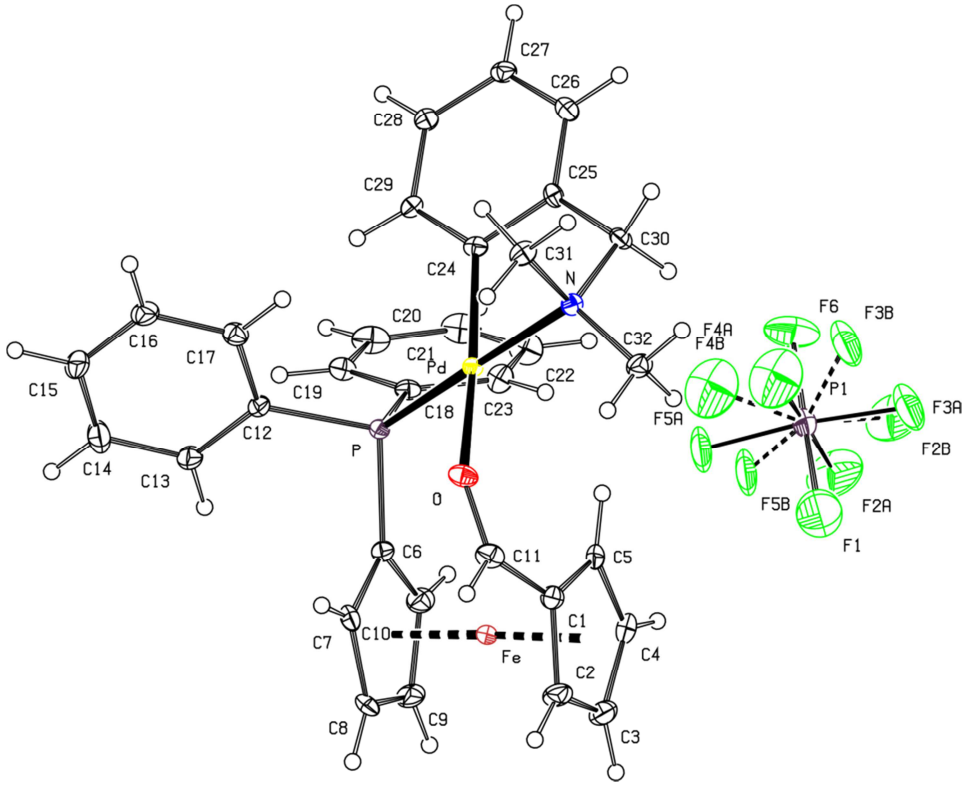

Figure S8 PLATON plot of the structure of **8a** showing displacement ellipsoids at the 30% probability level

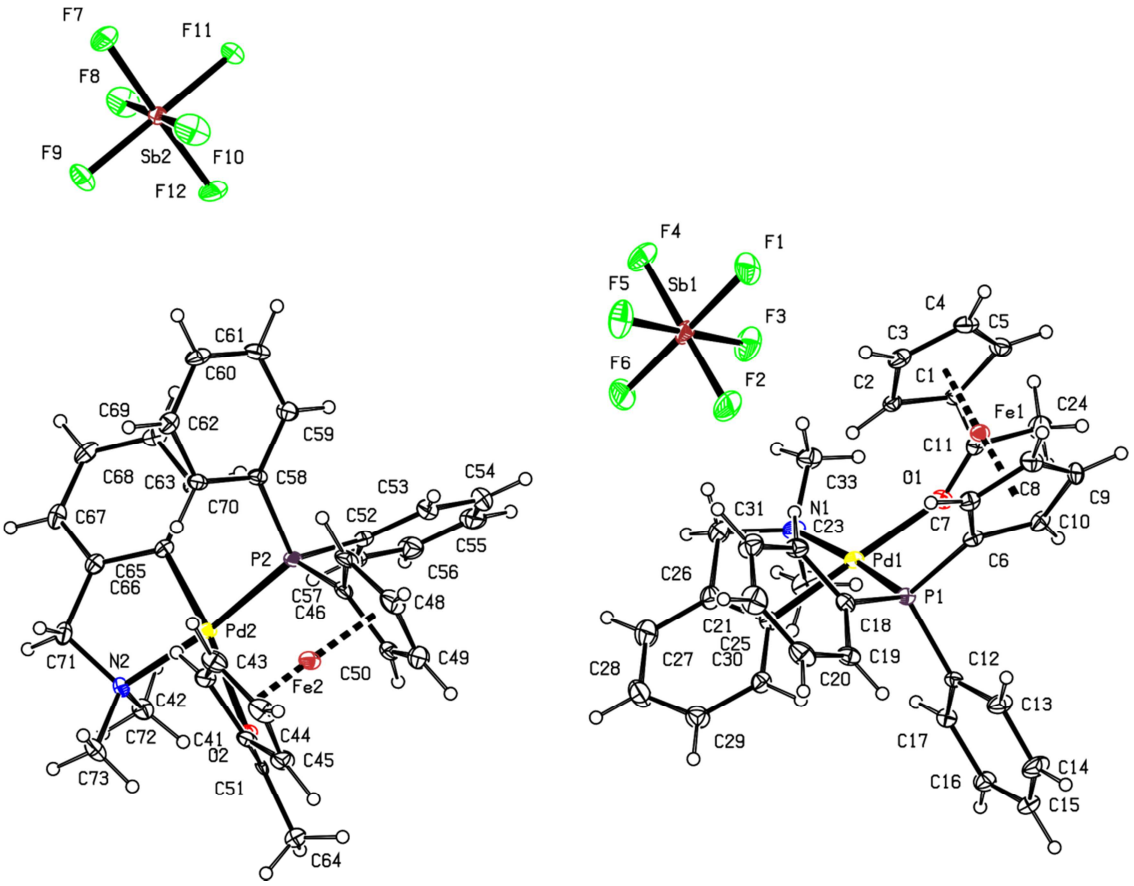

Figure S9. PLATON plot of the structure of **8b**·1/4$CHCl_3$ showing displacement ellipsoids at the 30% probability level

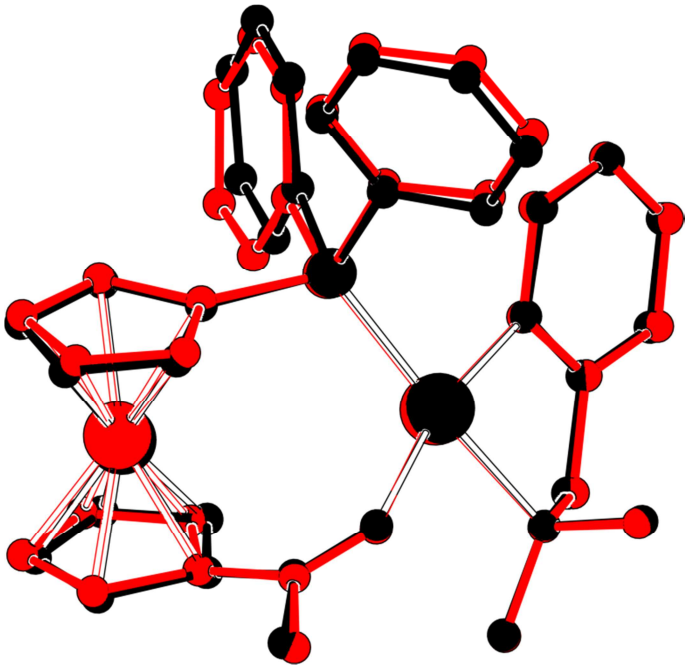

Figure S10. Least-squares overlap of the two independent cations in the structure of **8b**·1/4$CHCl_3$ (cation 1 in black, cation 2 in red)

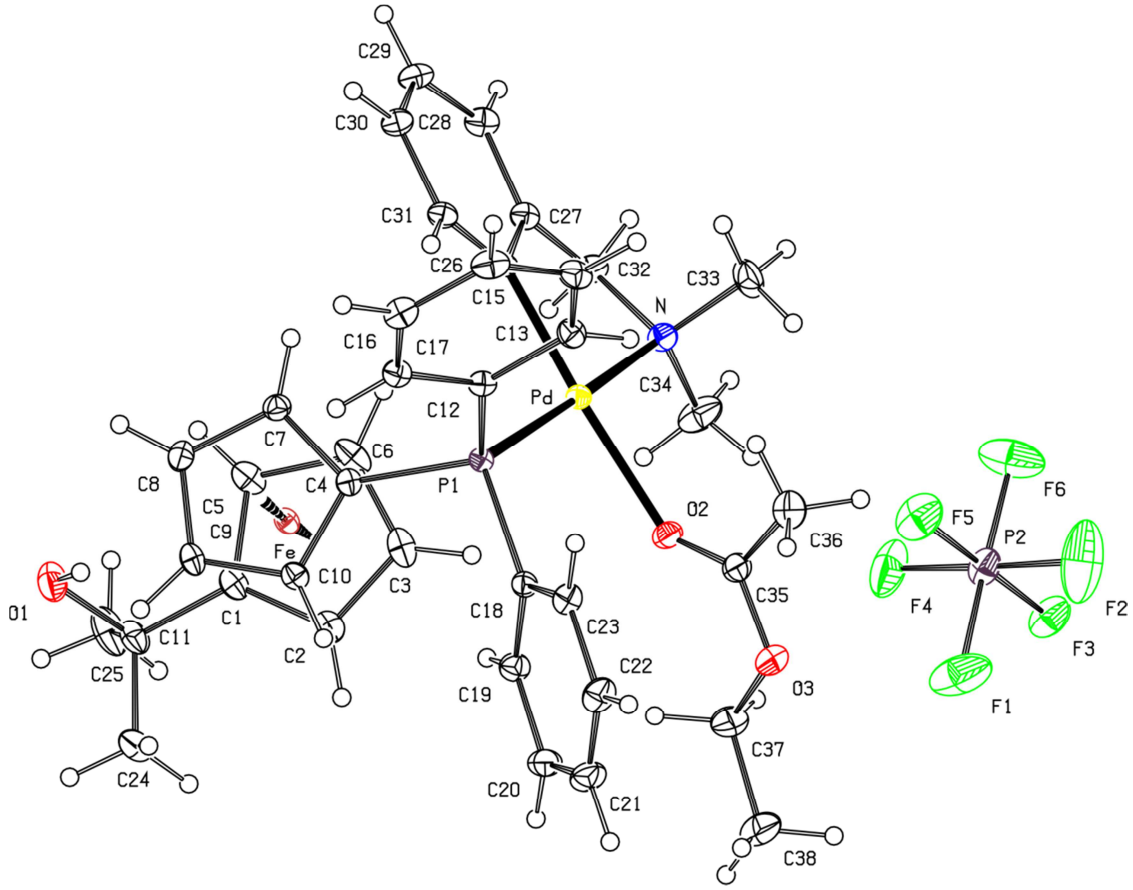

Figure S11. PLATON plot of the structure of **9** showing displacement ellipsoids at the 30% probability level

DFT computations

DFT calculations have been performed using the M06 density functional[10] and SDD[11] (Fe, Pd) and def2-TZVP[12] (C, H, N, O, and P) basis sets together with Grimme's D3 dispersion correction.[13] The solvent effects (chloroform) have been approximated by the polarised continuum model (PCM)[14] as implemented in the Gaussian 09 program package.[15] Geometry optimisations were started from the geometries determined by X-ray crystallographic analysis where possible (complexes **8a**, **8b** and **9**). Generally, the computed geometries correspond very well with the experimental ones. The reported energies refer to the Gibbs free energies at 298 K.

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Copies of the NMR spectra

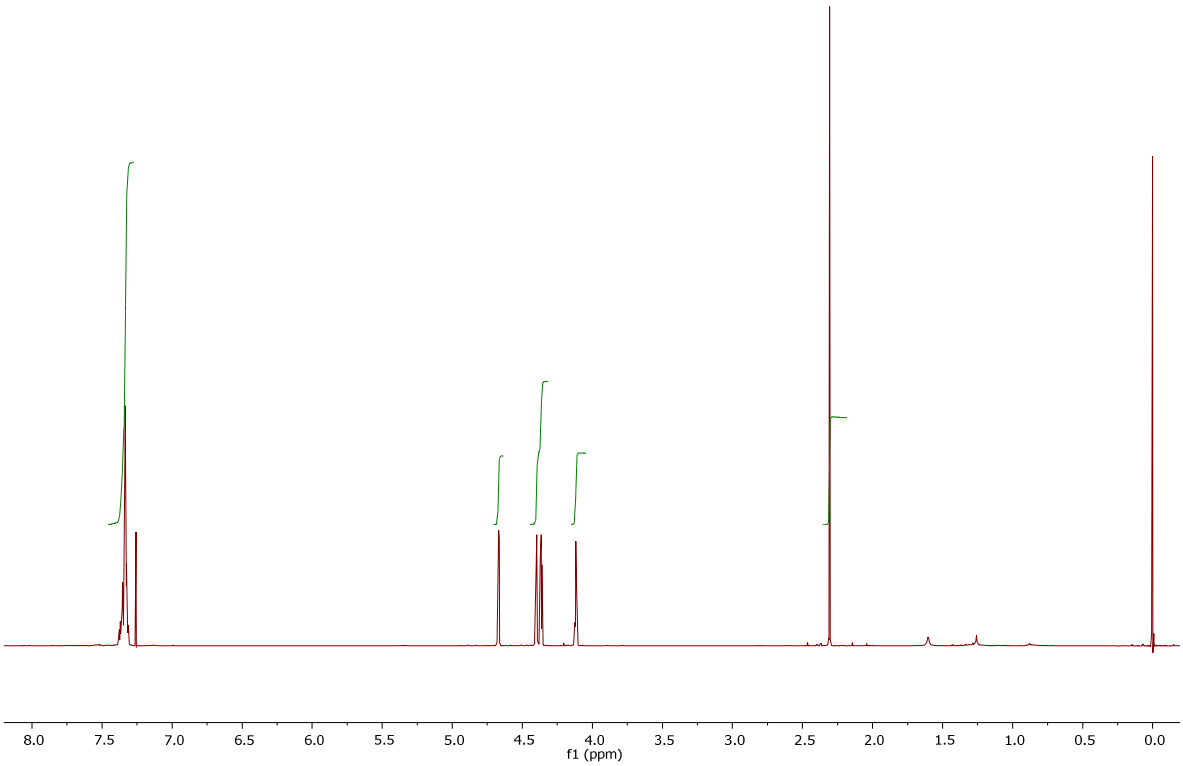

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**.

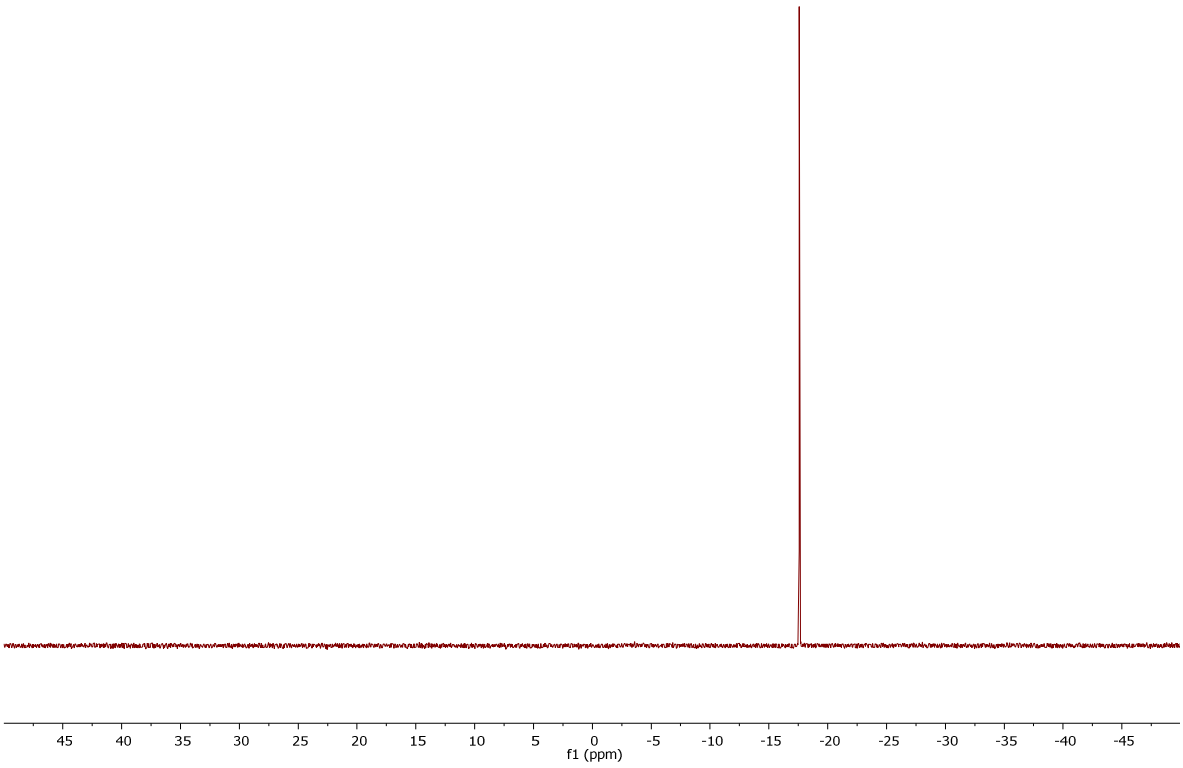

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **2**.

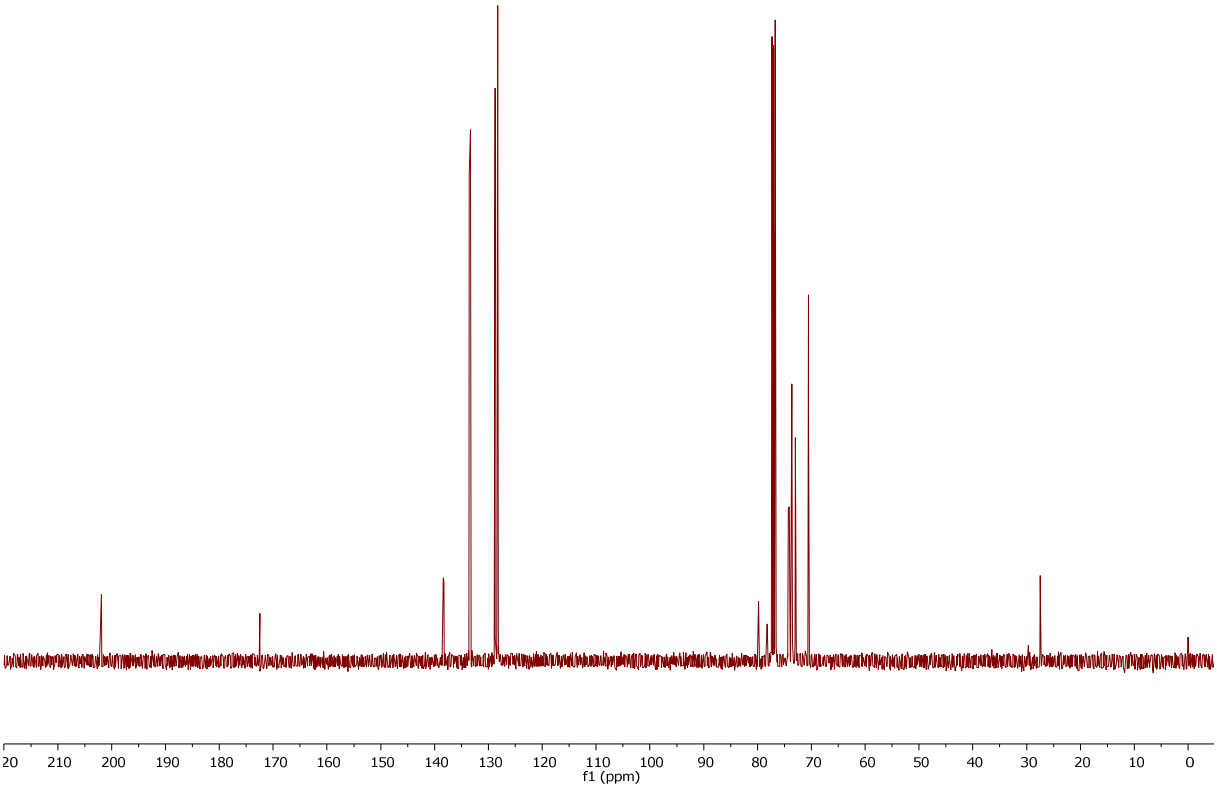

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2**.

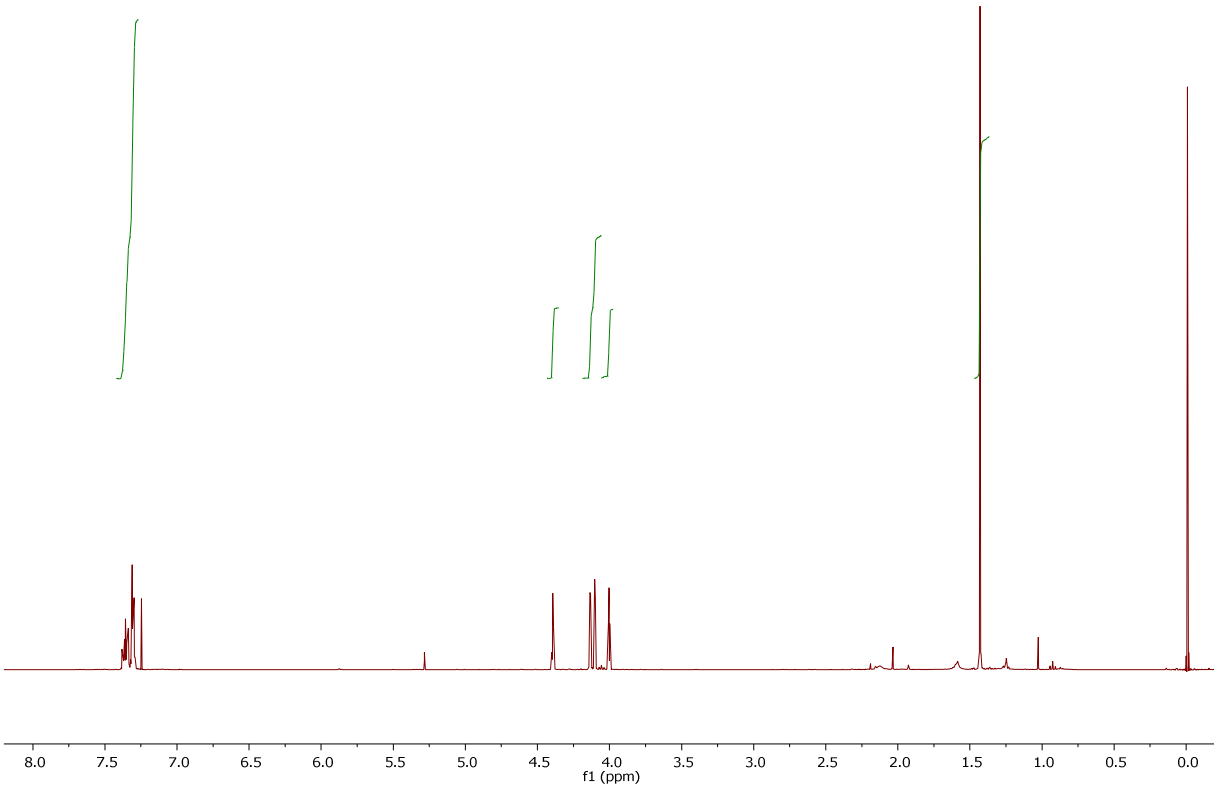

Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**.

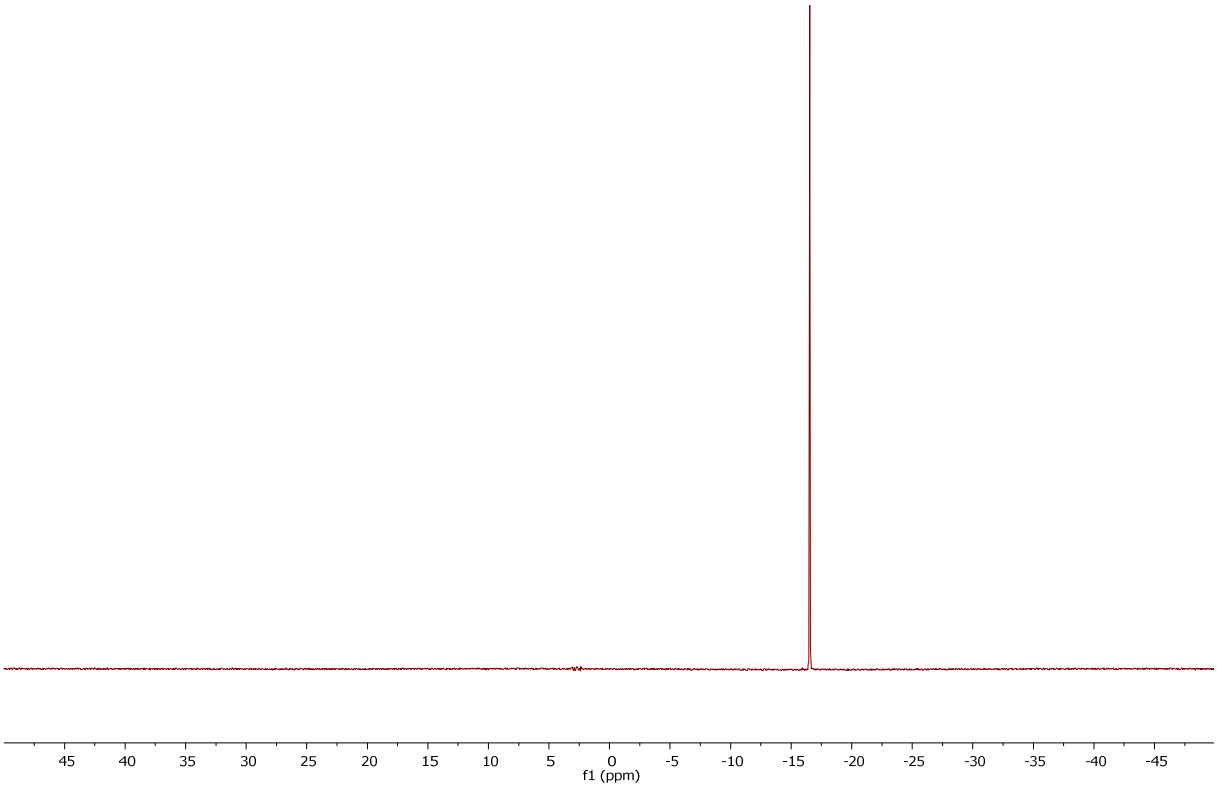

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **3**.

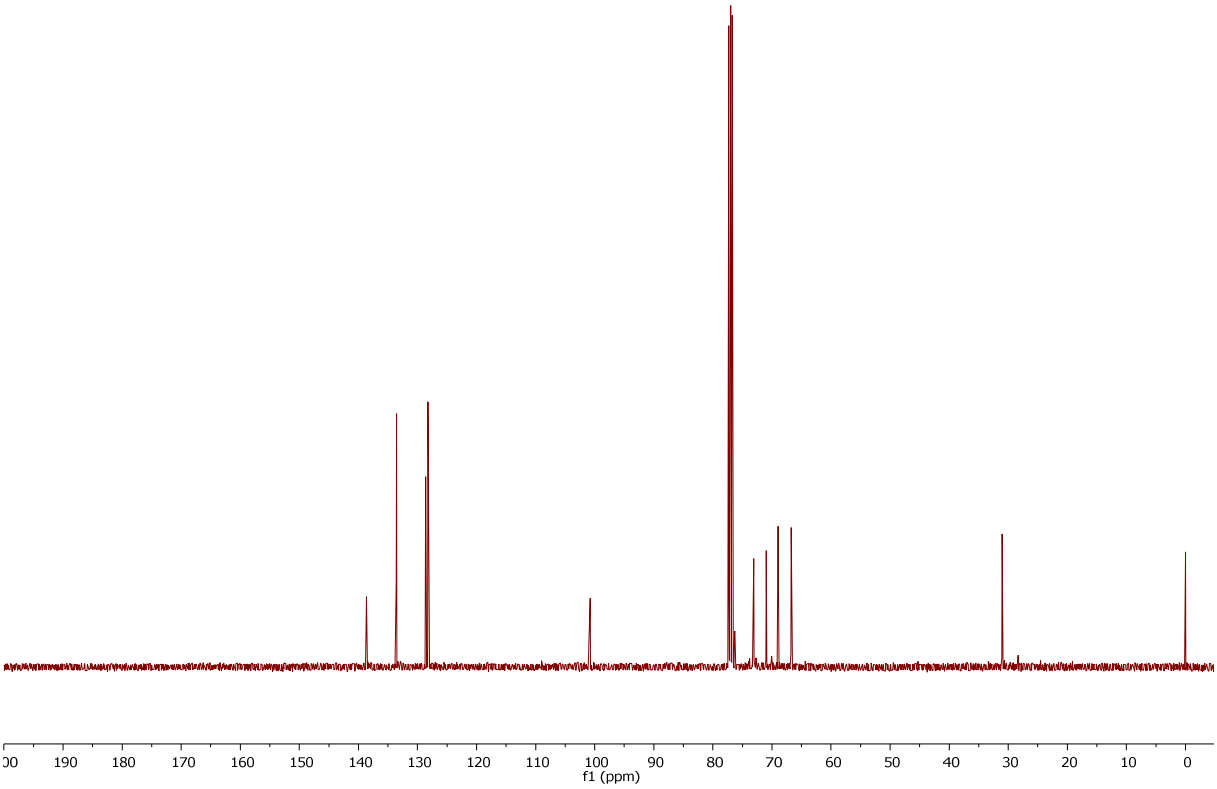

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3**.

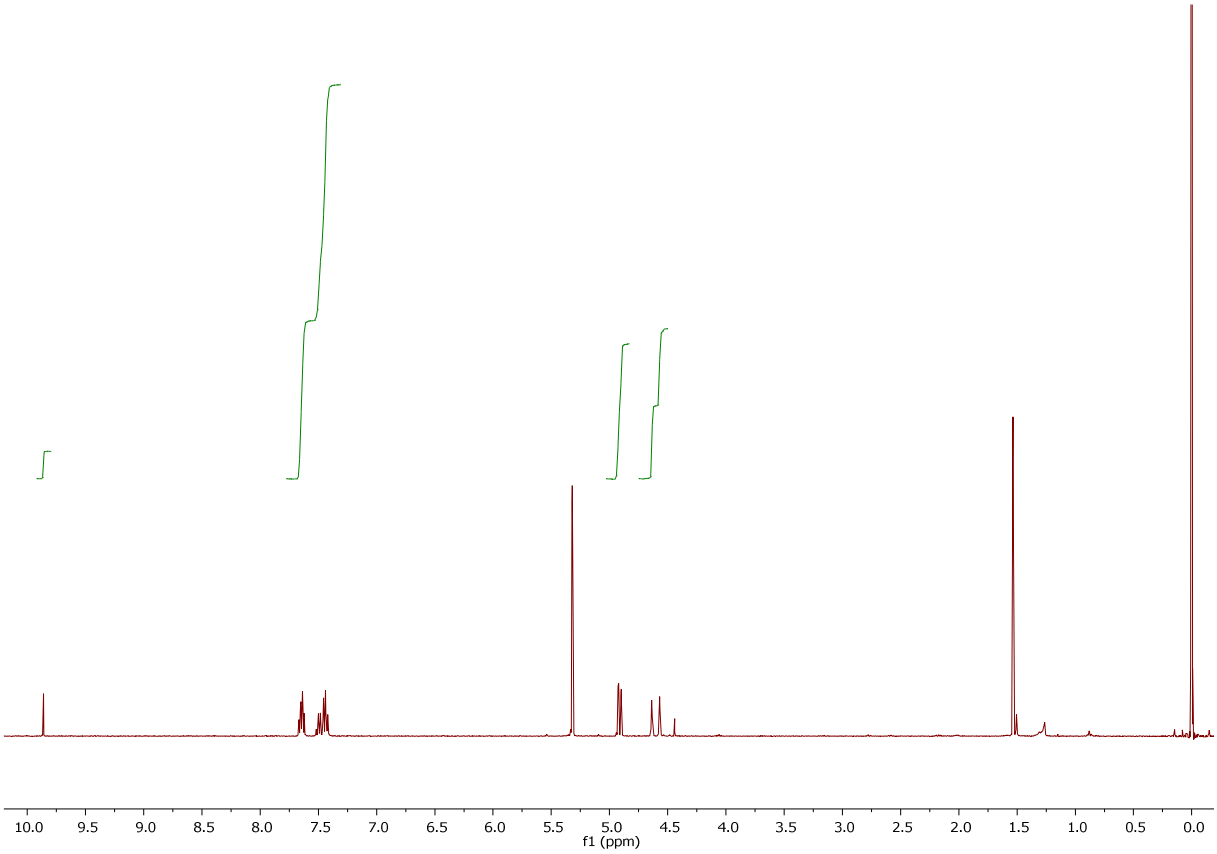

Figure S18. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5a**.

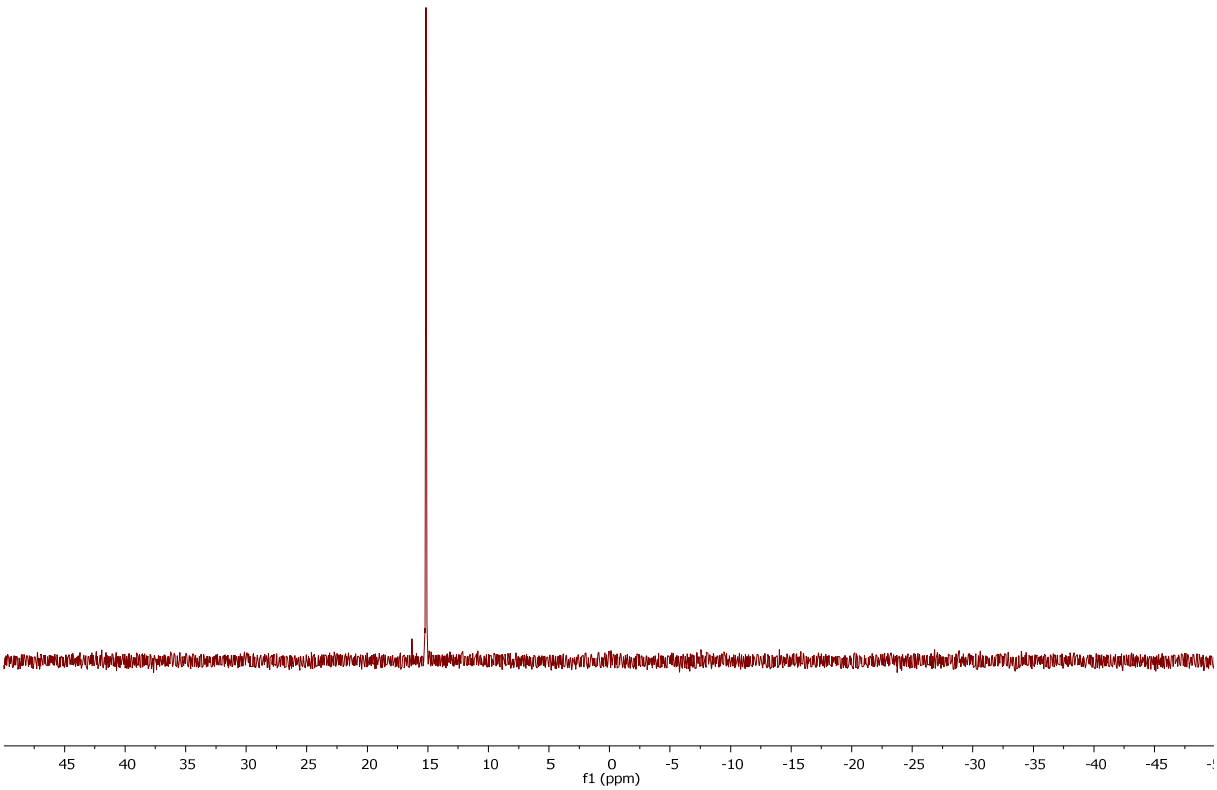

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **5a**.

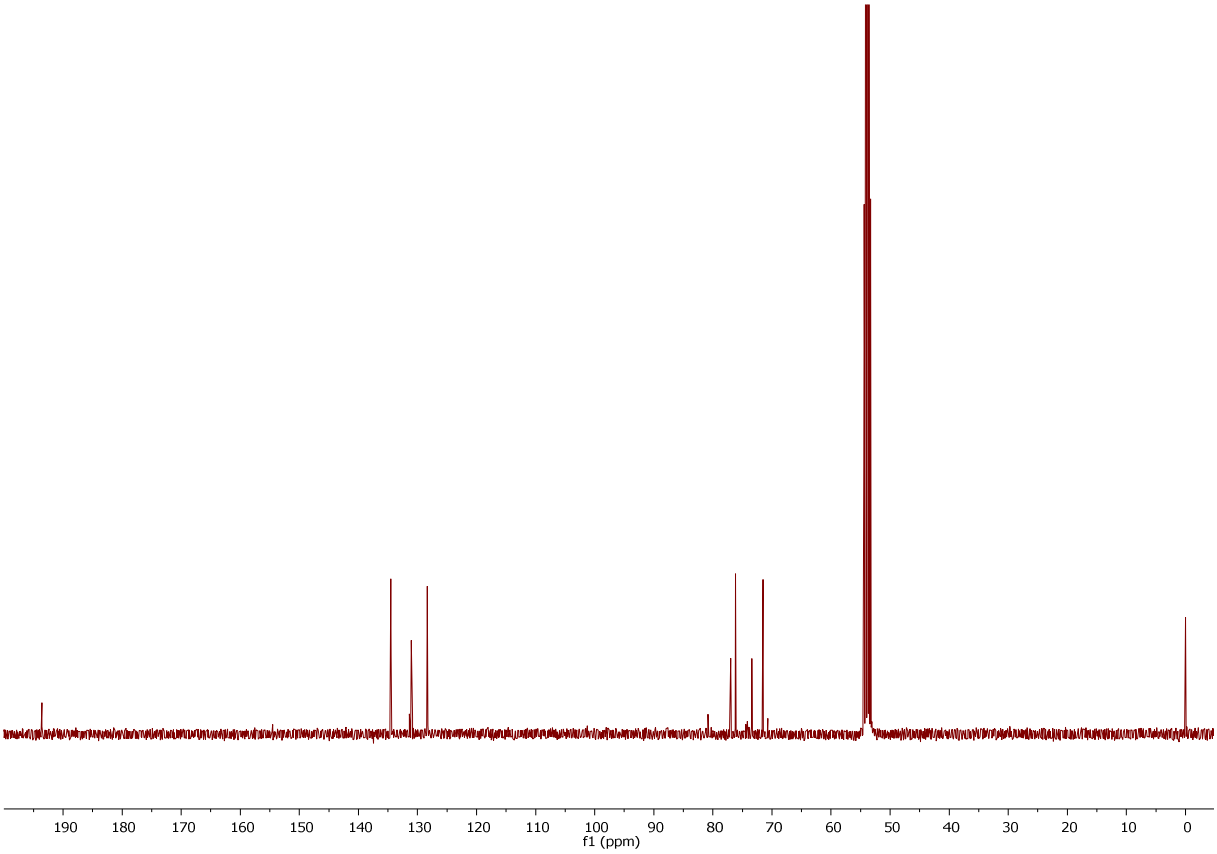

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **5a**.

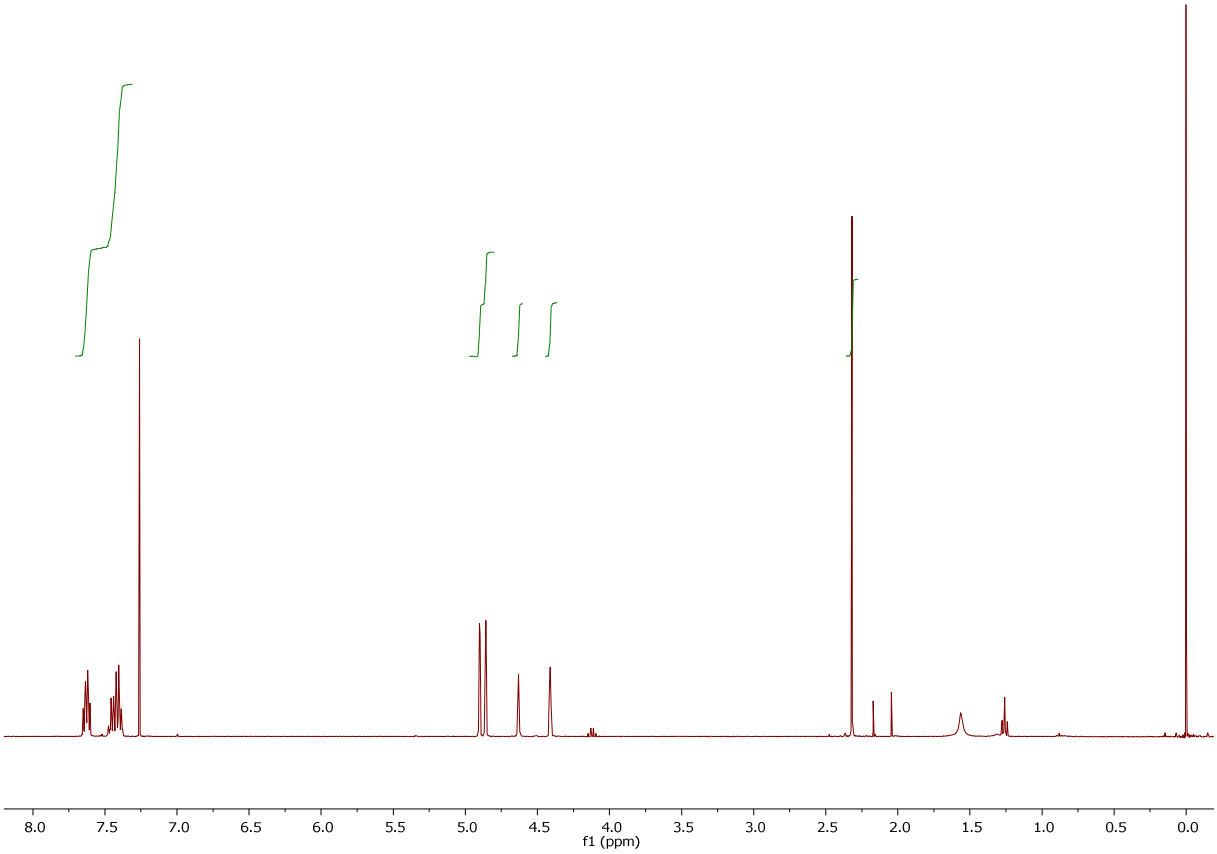

Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**.

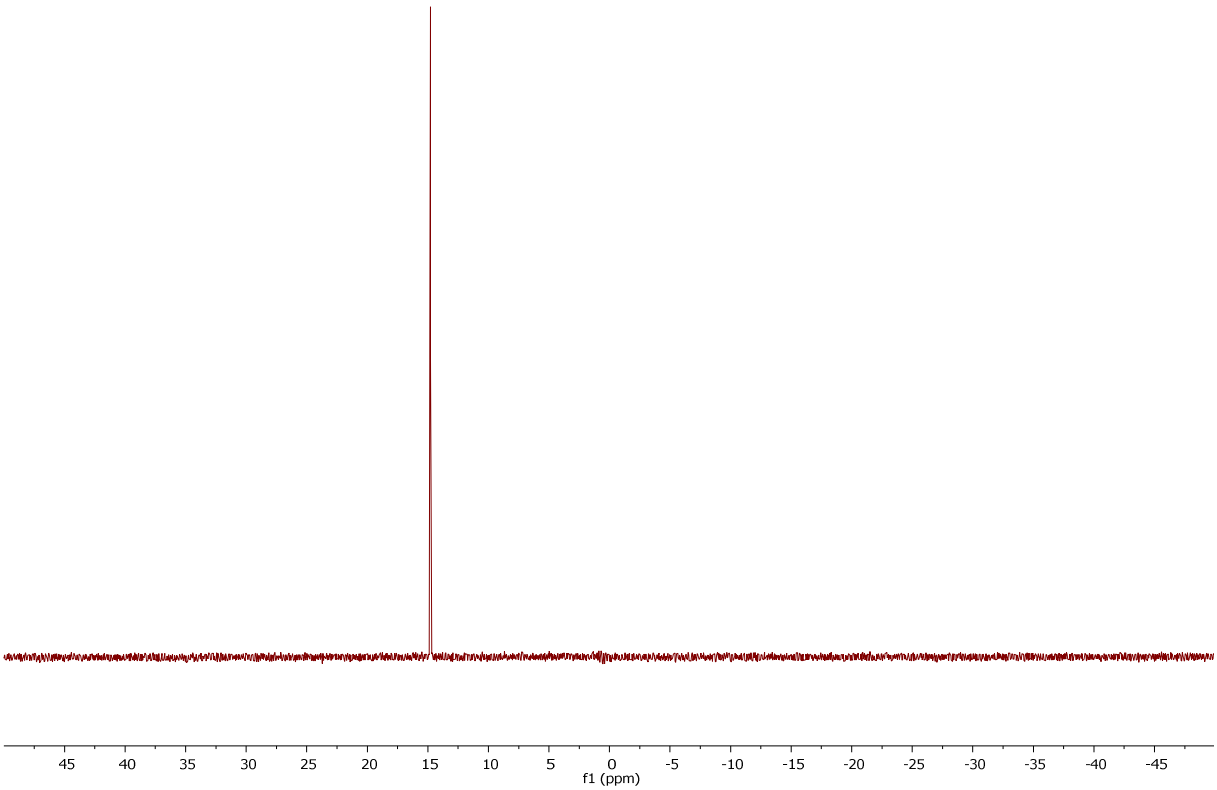

Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5b**.

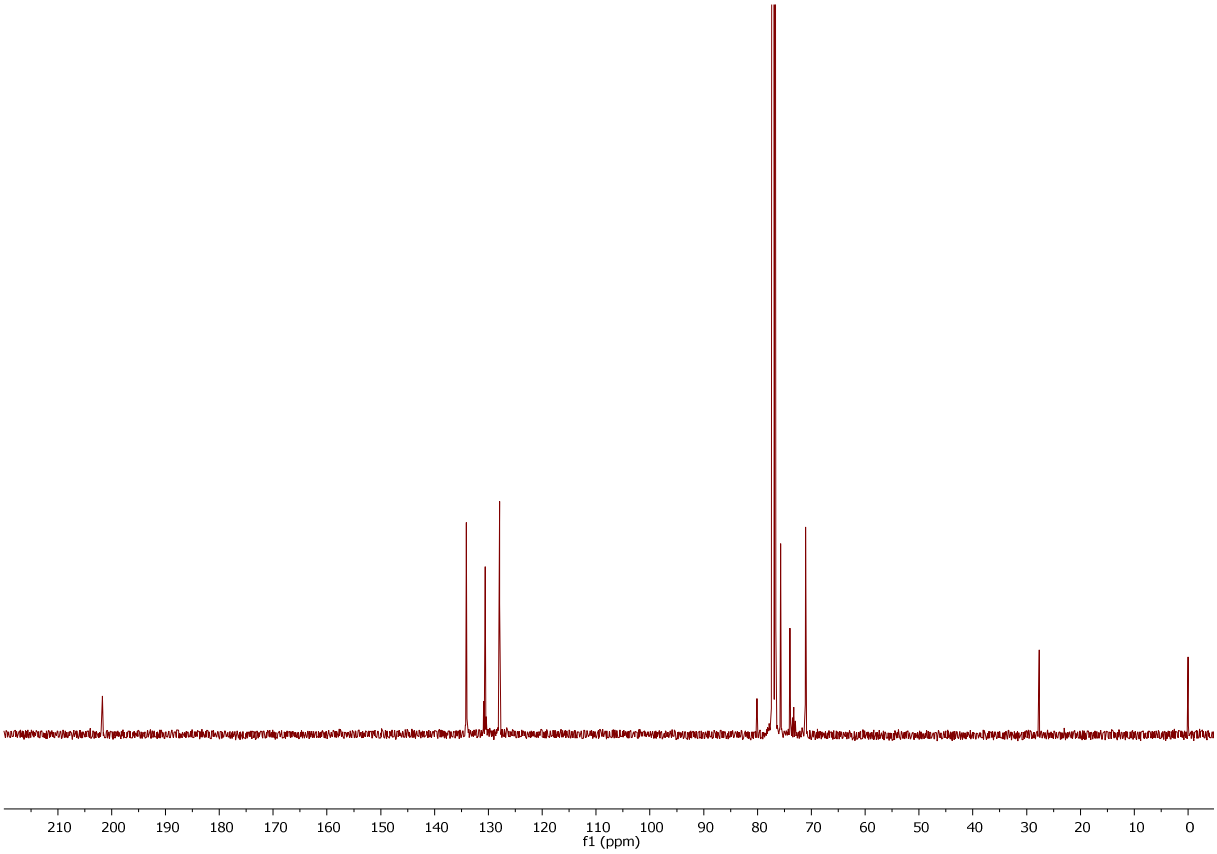

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5b**.

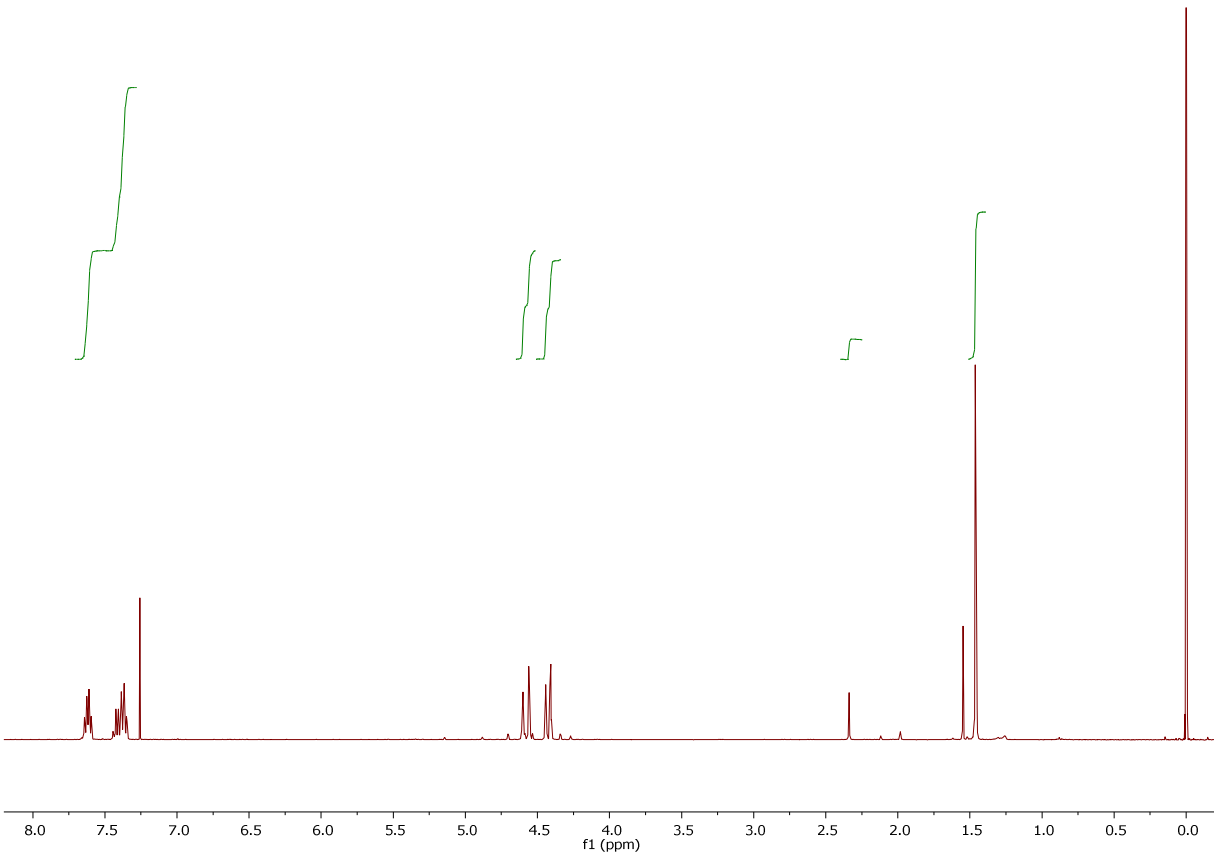

Figure S24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5c**.

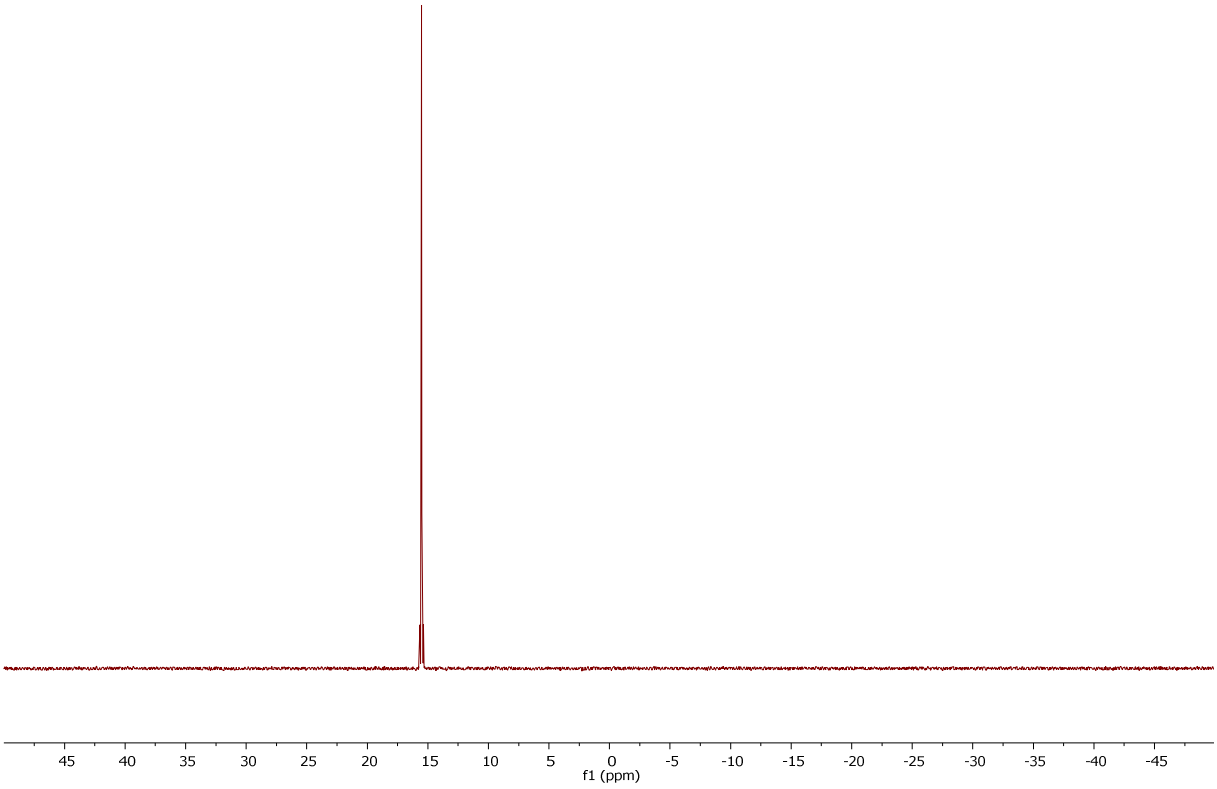

Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **5c**.

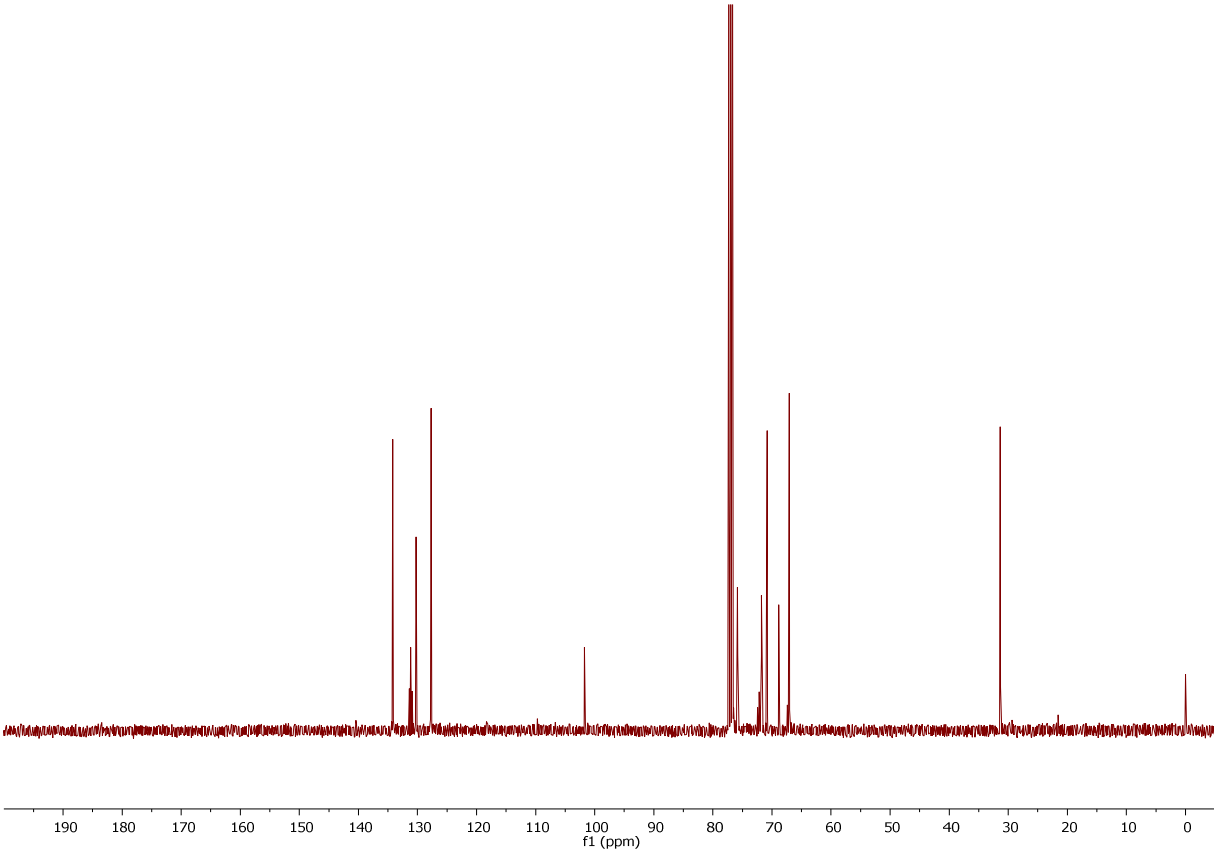

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **5c**.

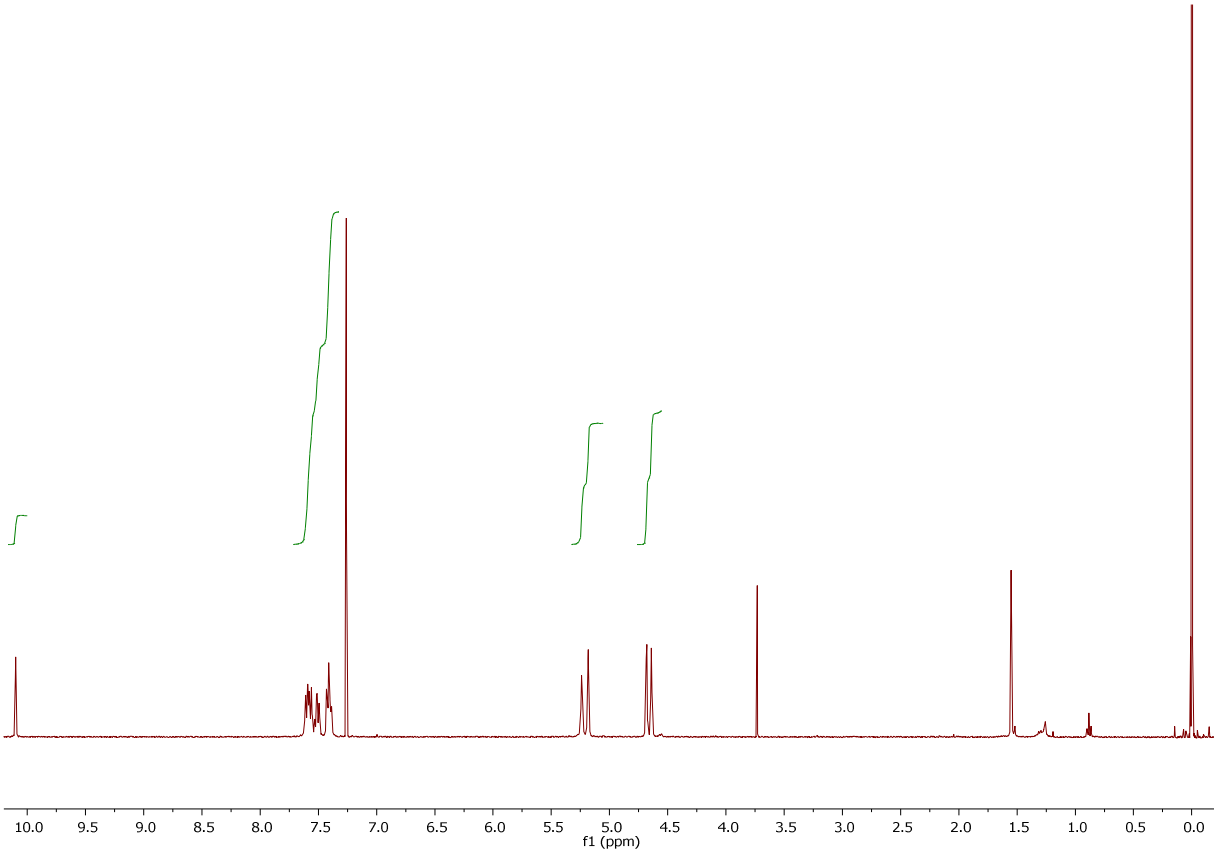

Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6a**.

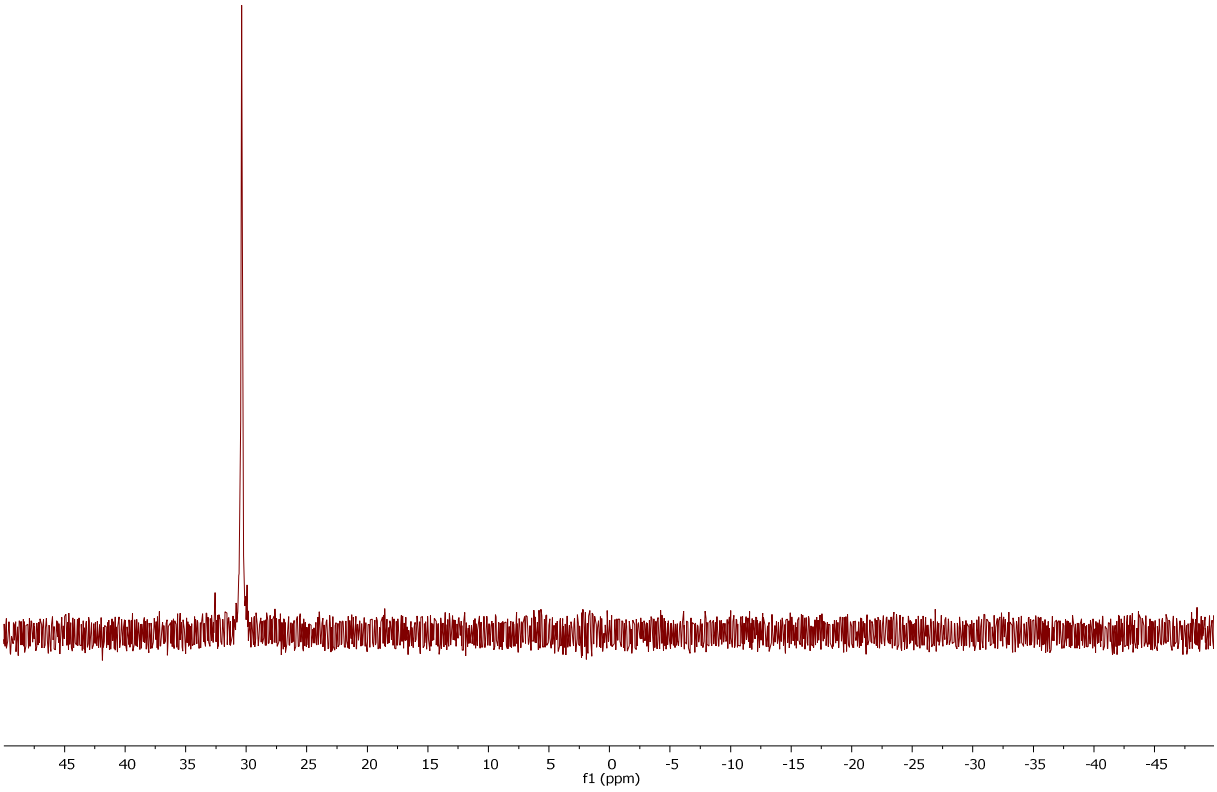

Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6a**.

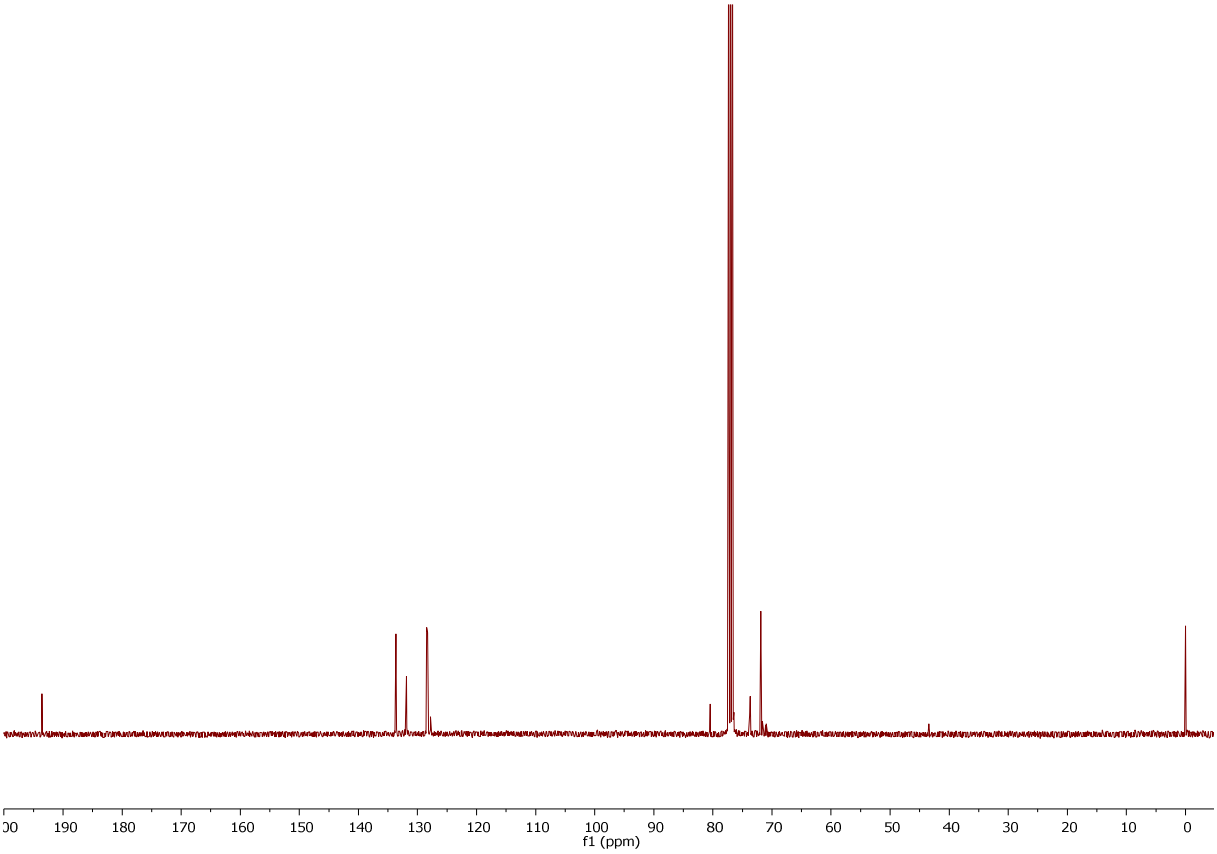

Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6a**.

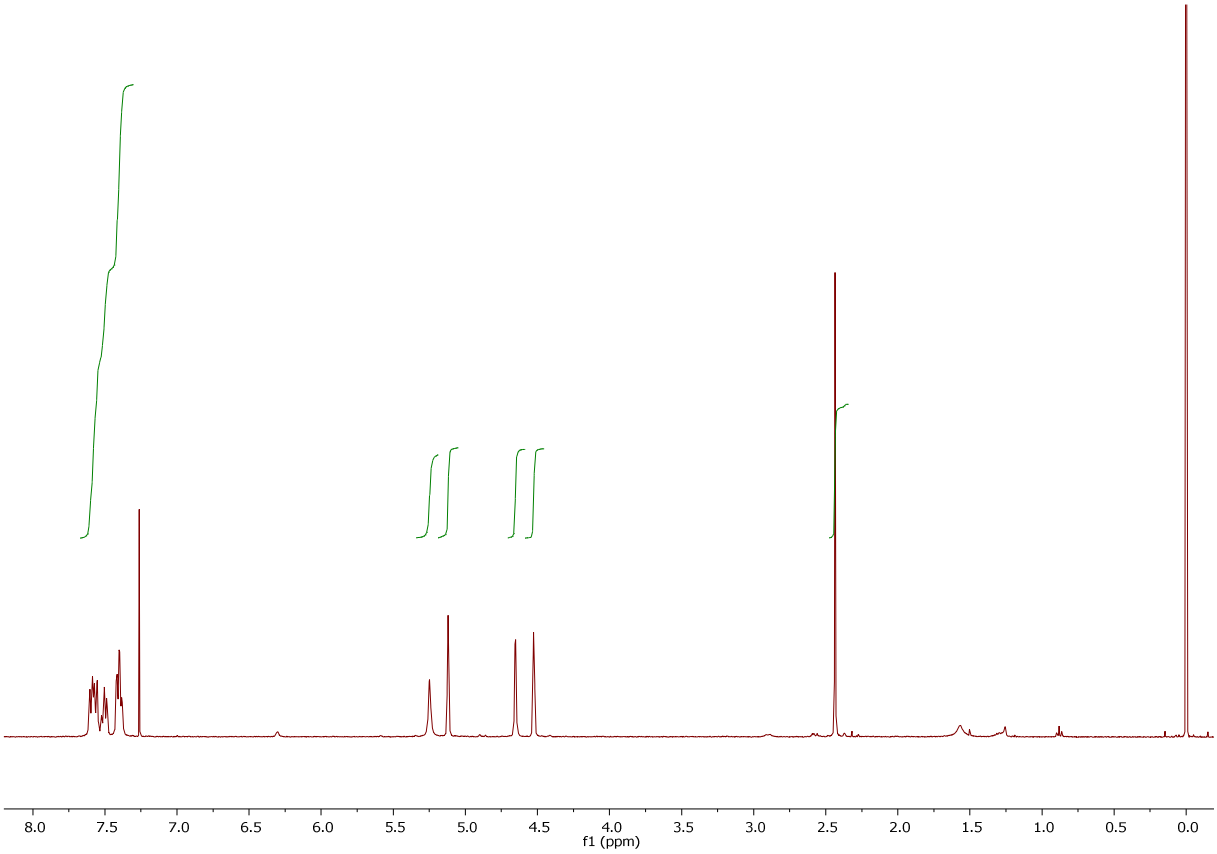

Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6b**.

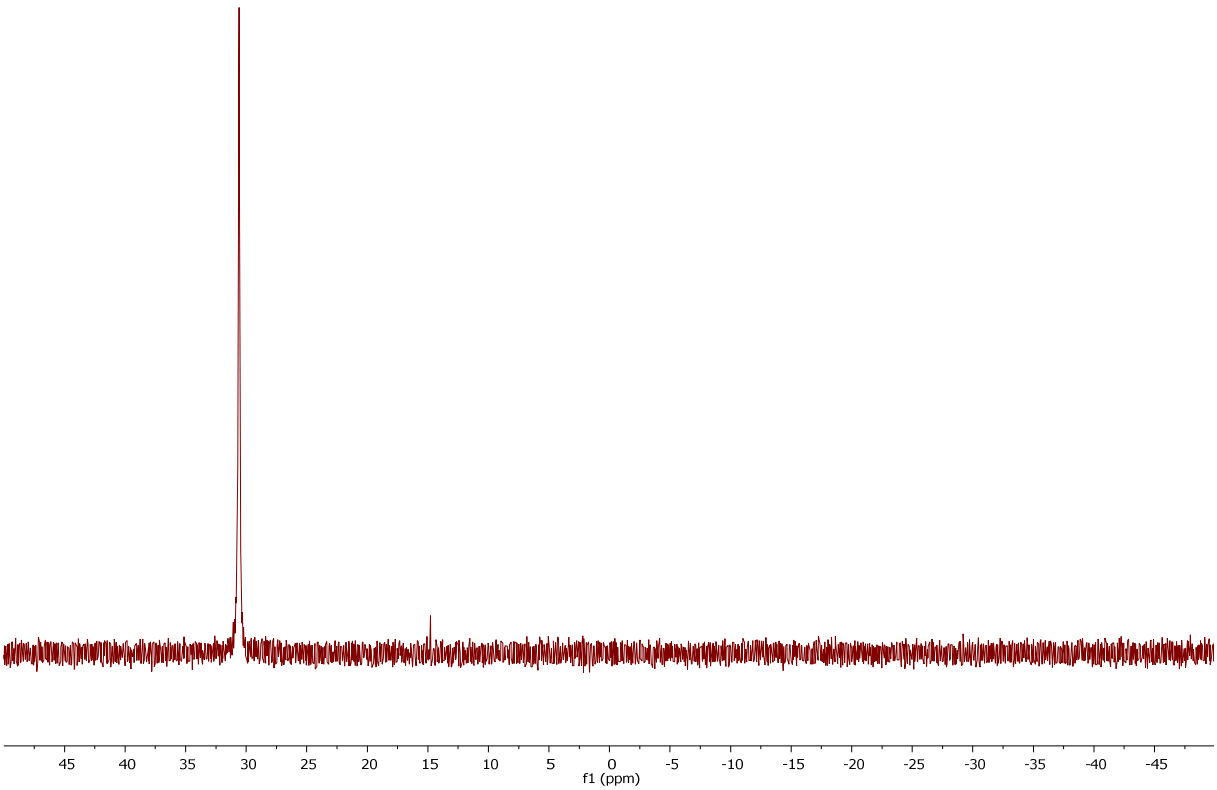

Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6b**.

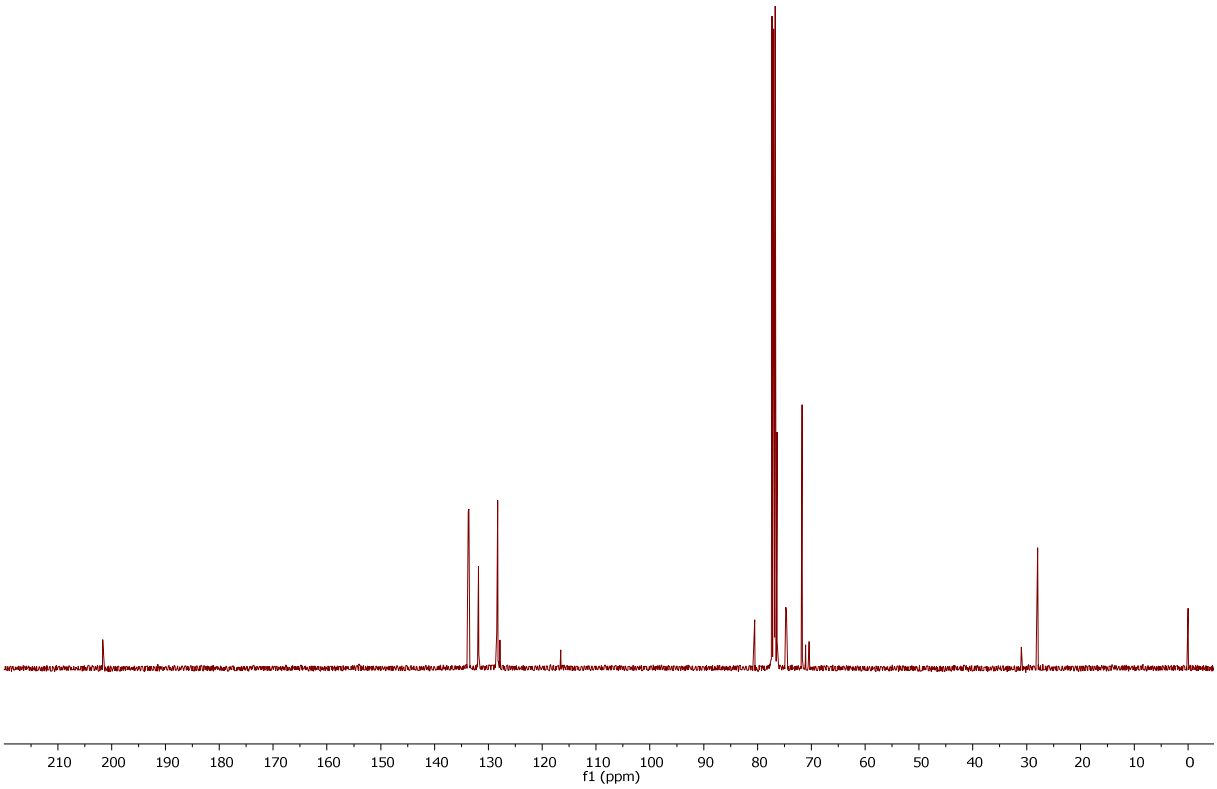

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6b**.

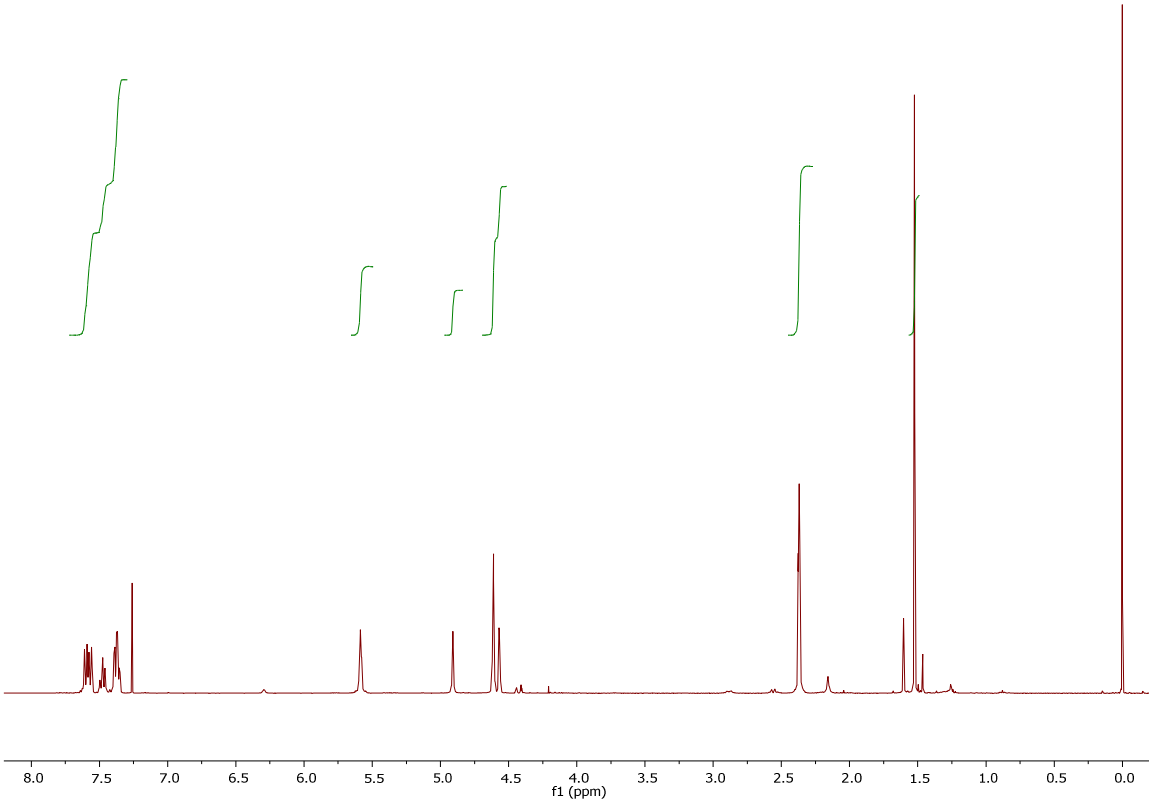

Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6c** generated *in situ* from **3** and $[PdCl_2(cod)]$ (molar ratio Pd:**3** = 1:1).

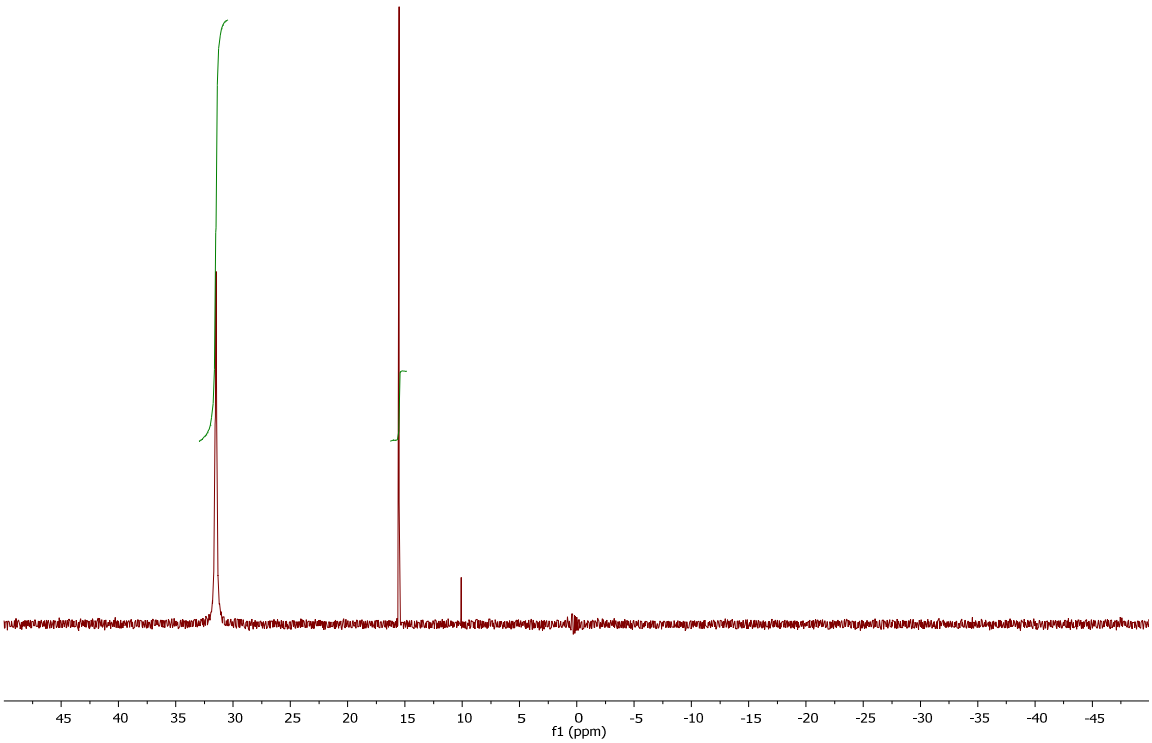

Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6c** generated *in situ* from **3** and $[PdCl_2(cod)]$ (molar ratio Pd:**3** = 1:1). The signal at δ_P 15.5 belongs to **5c**.

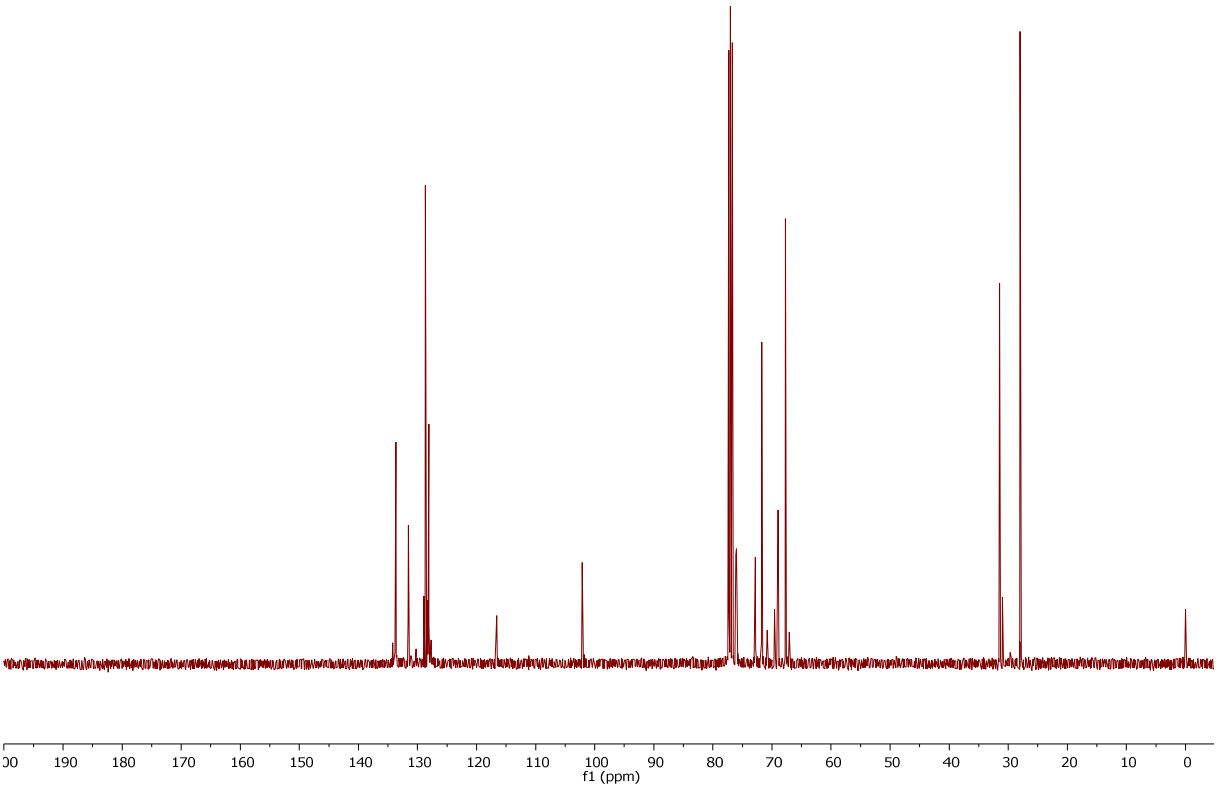

Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6c** generated *in situ* from **3** and $[PdCl_2(cod)]$ (molar ratio Pd:**3** = 1:1).

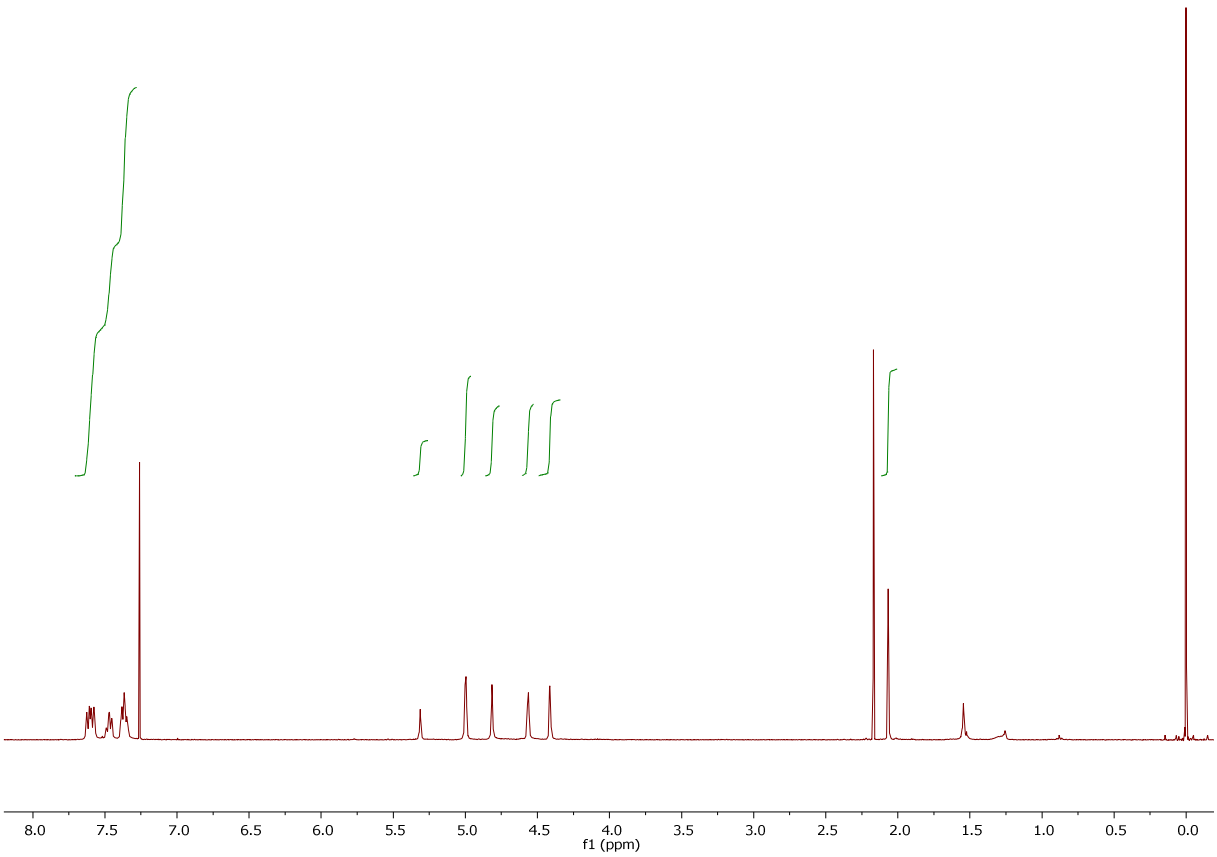

Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6d**.

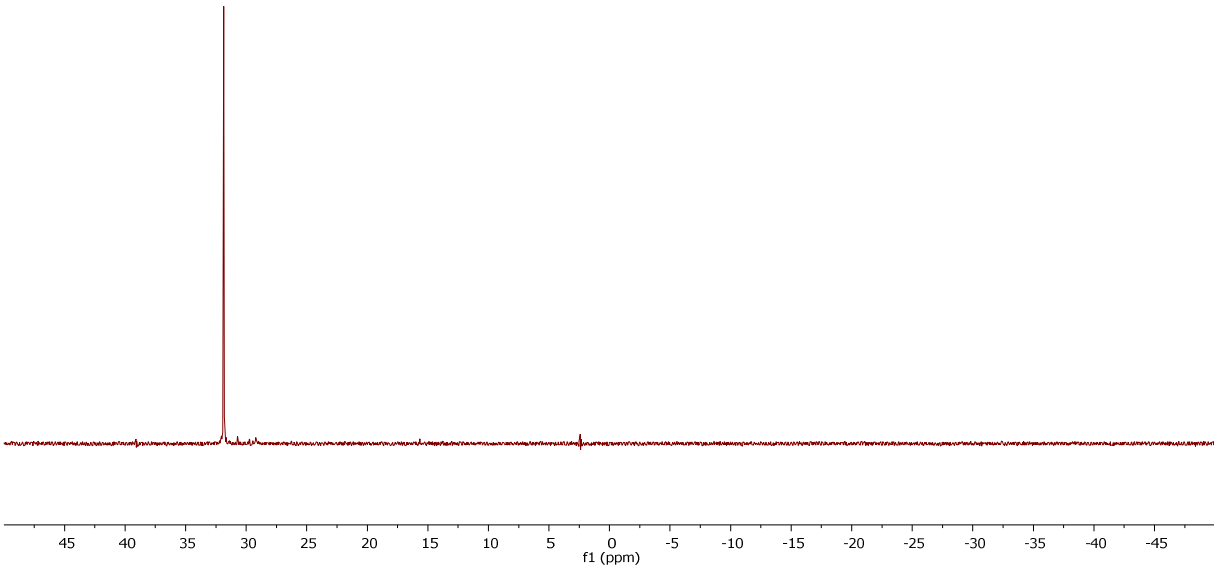

Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **6d**.

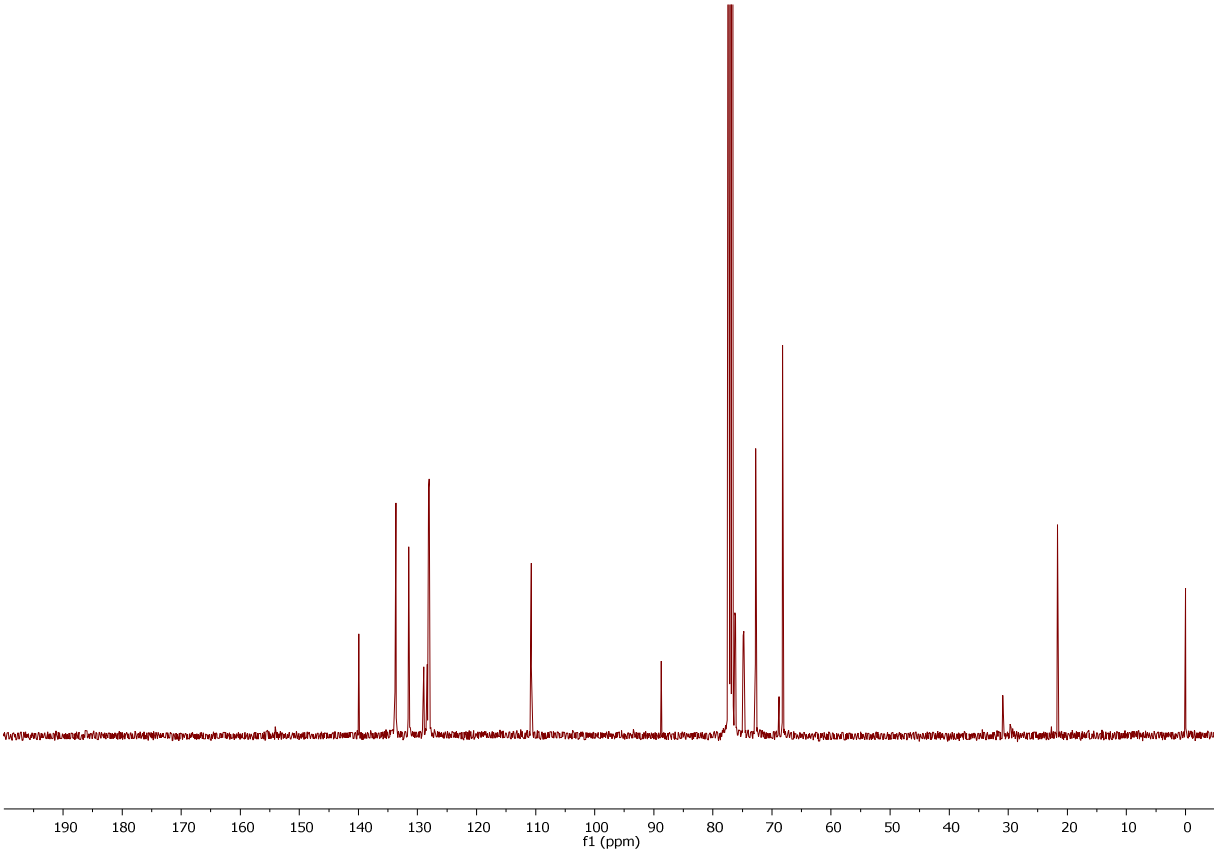

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **6d**.

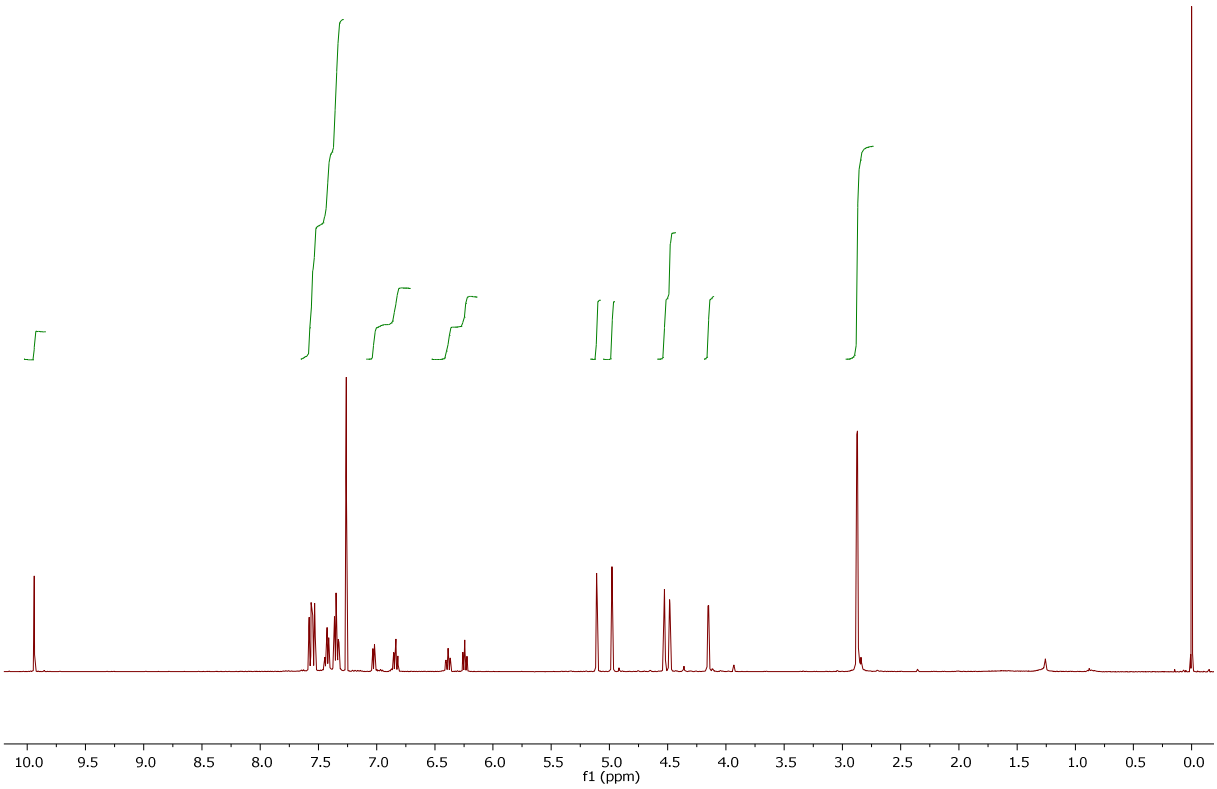

Figure S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a**.

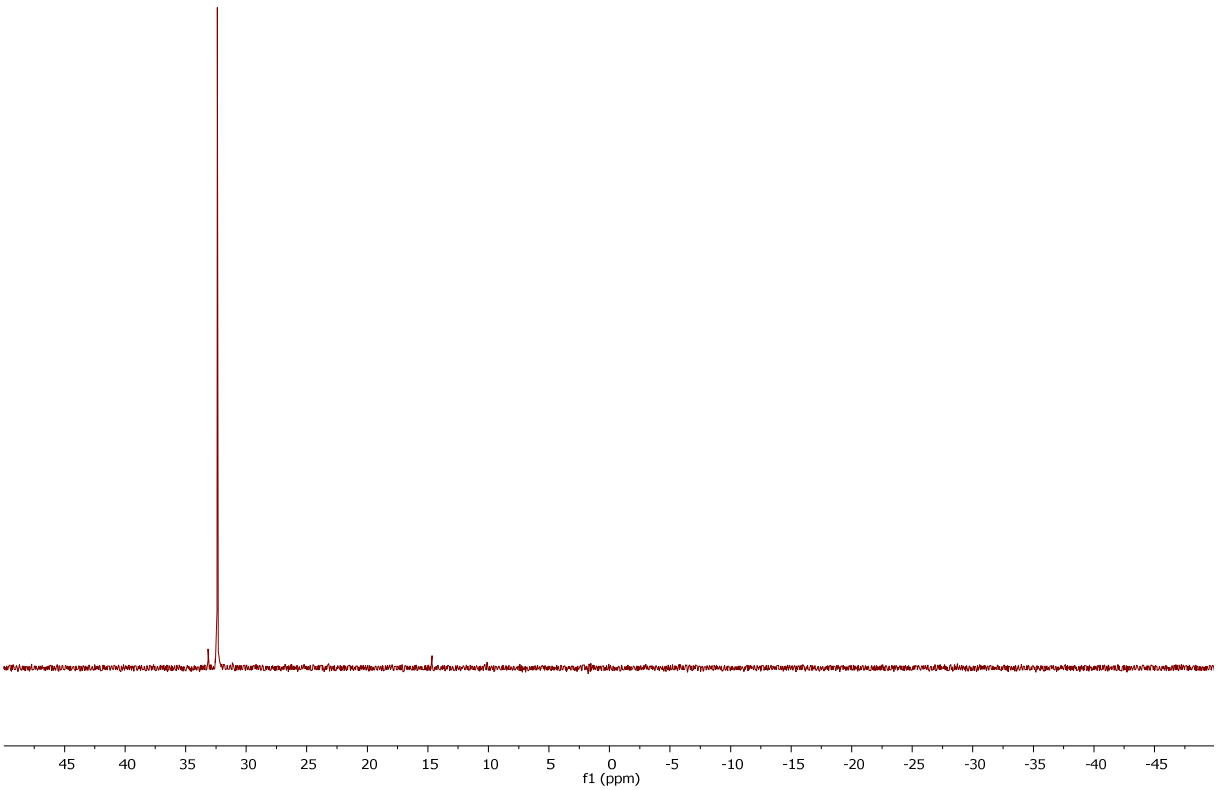

Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **7a**.

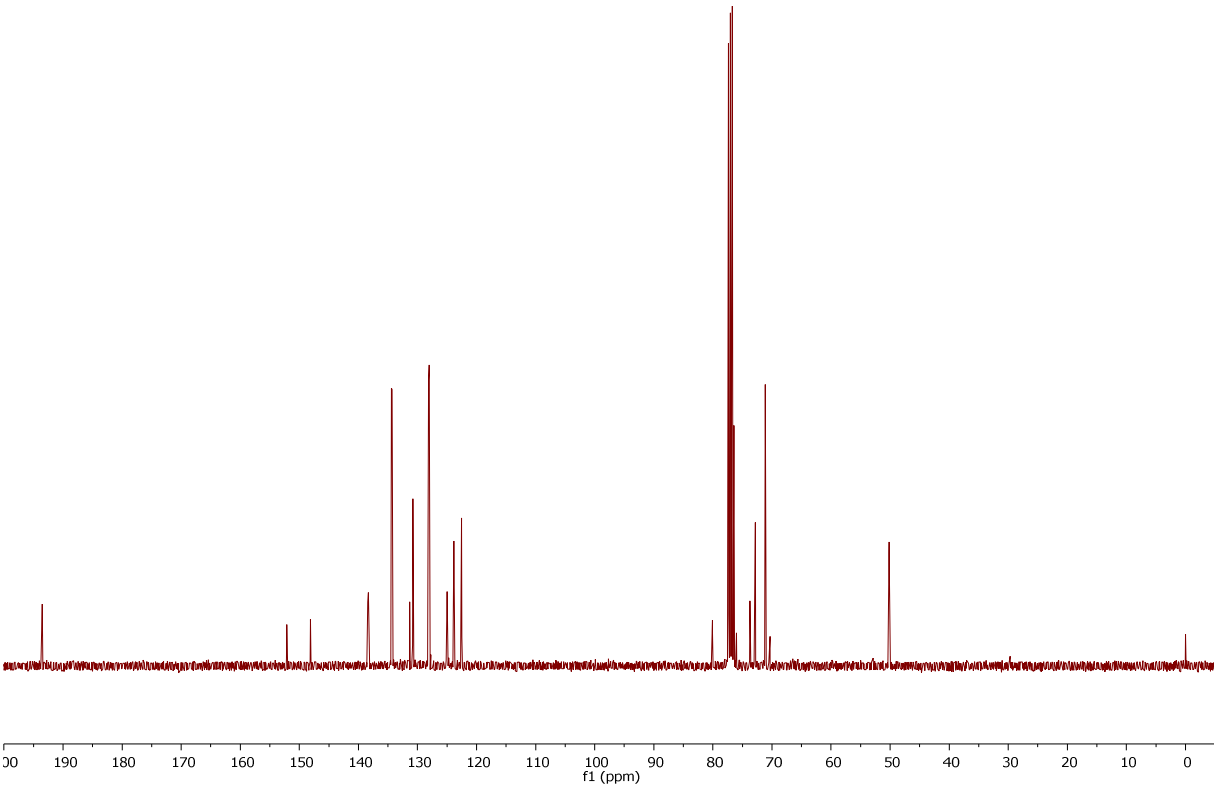

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **7a**.

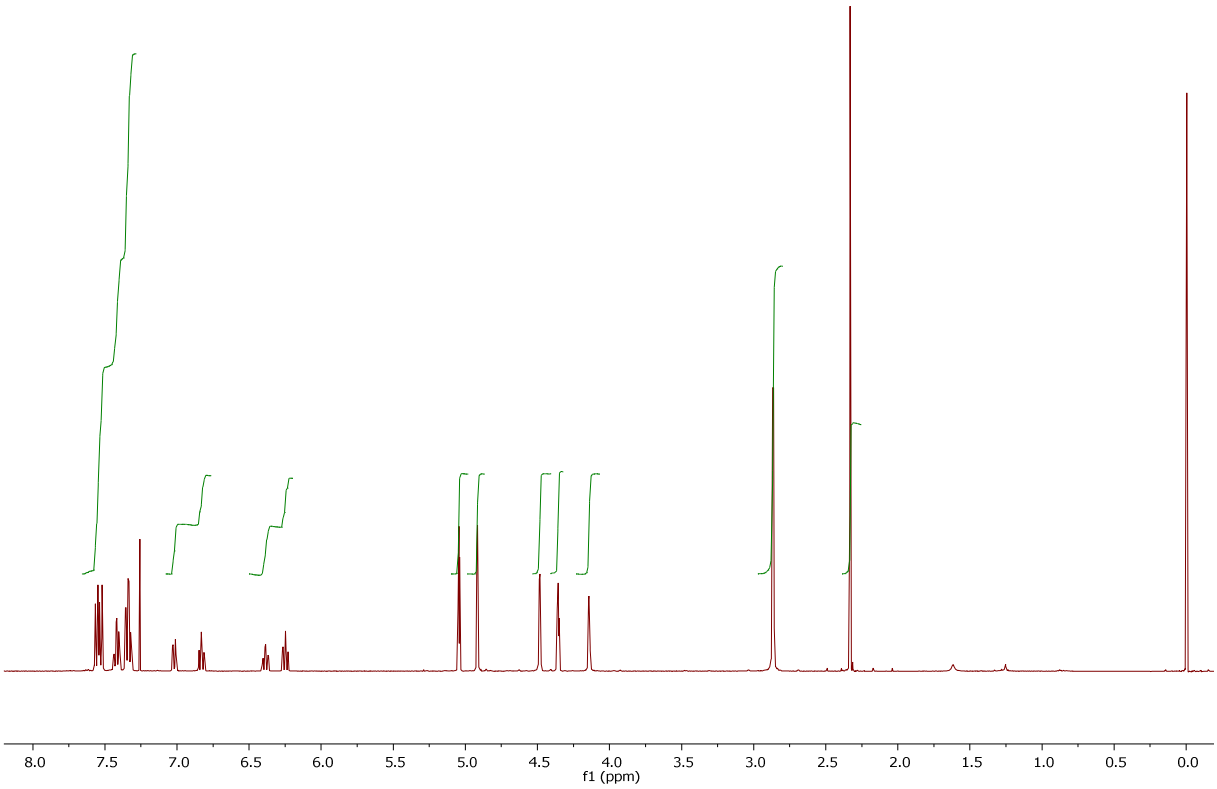

Figure S42. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7b**.

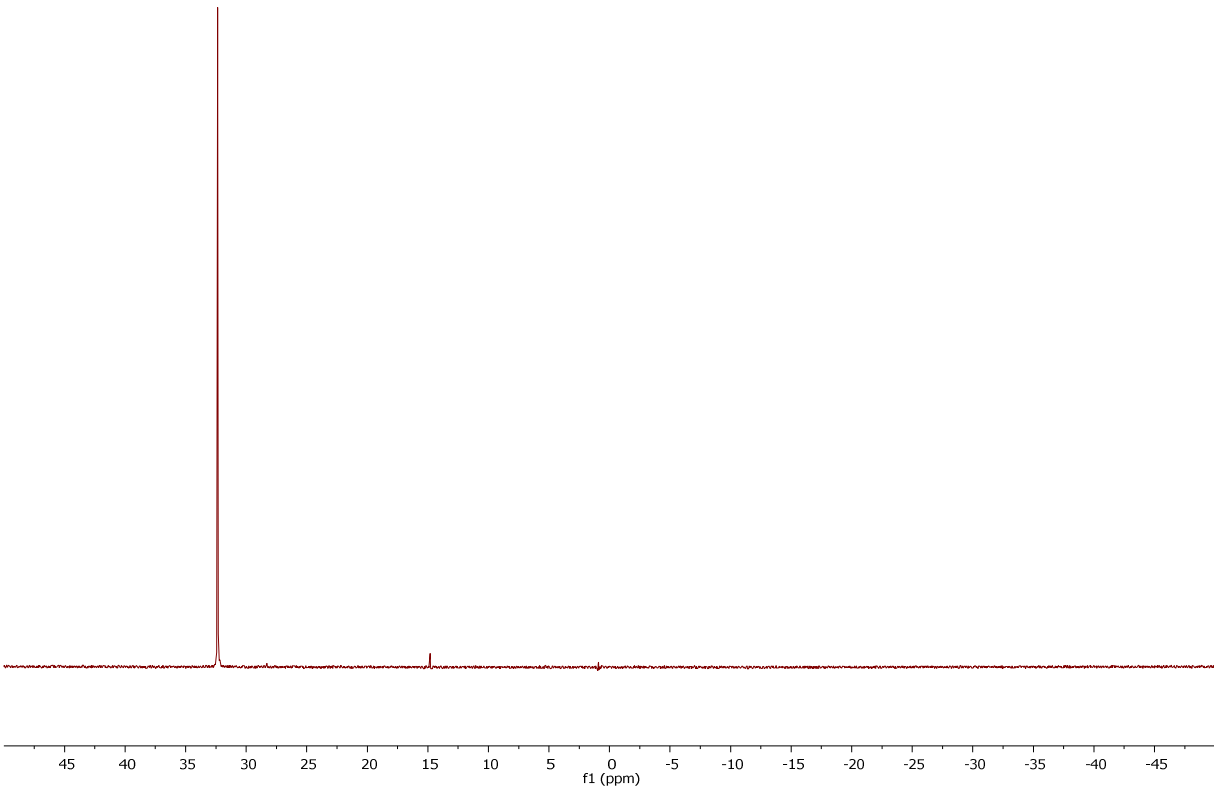

Figure S43. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **7b**.

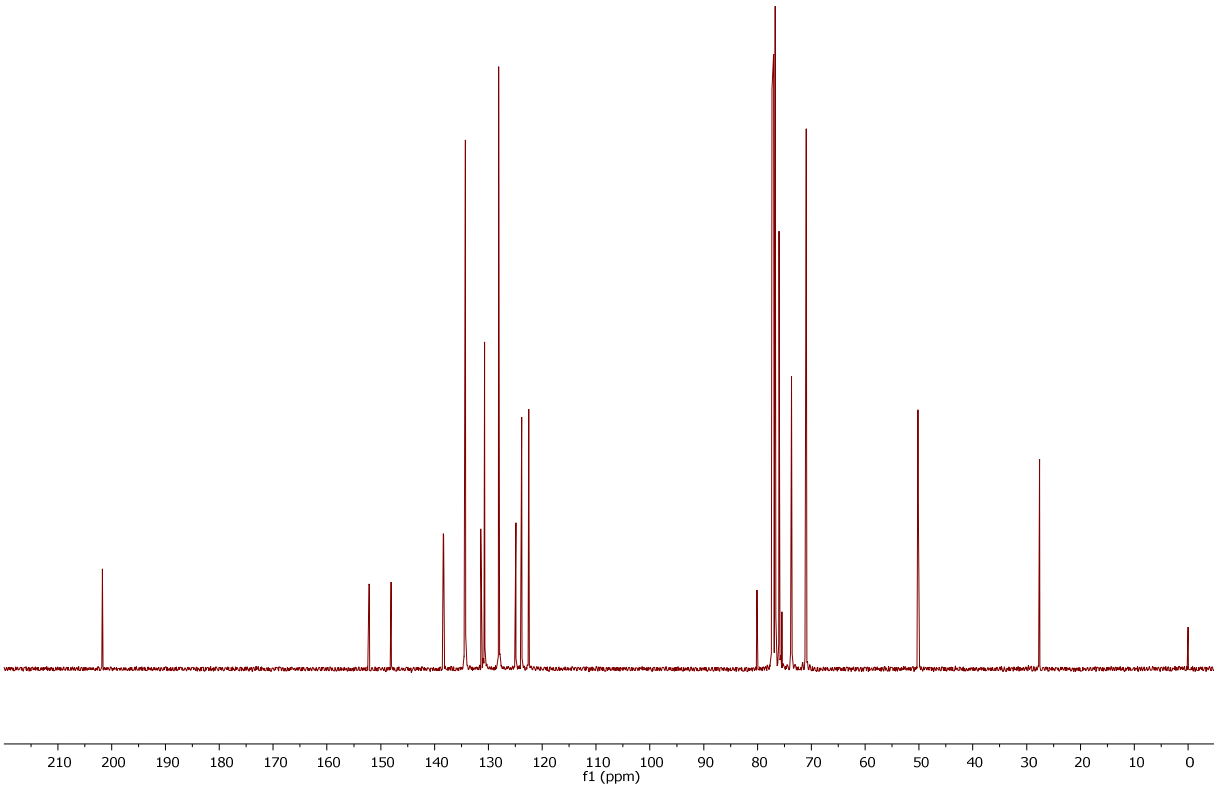

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **7b**.

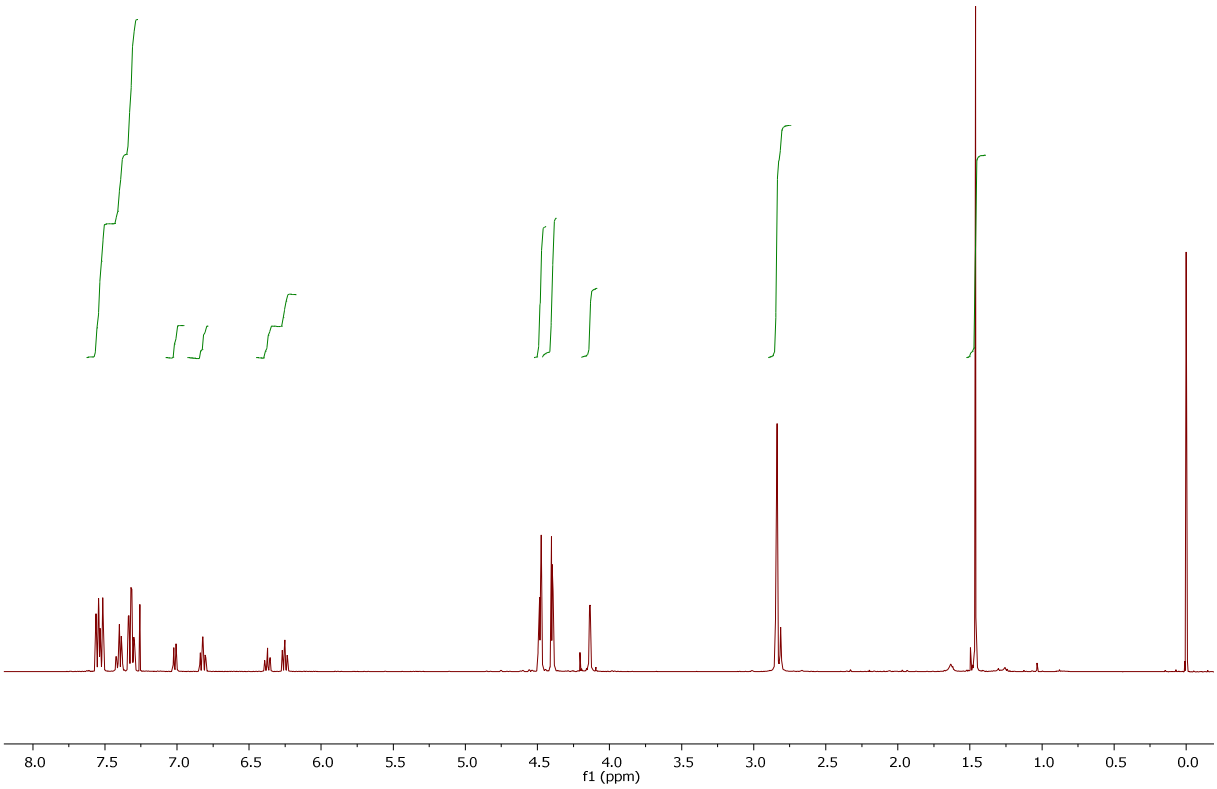

Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7c**.

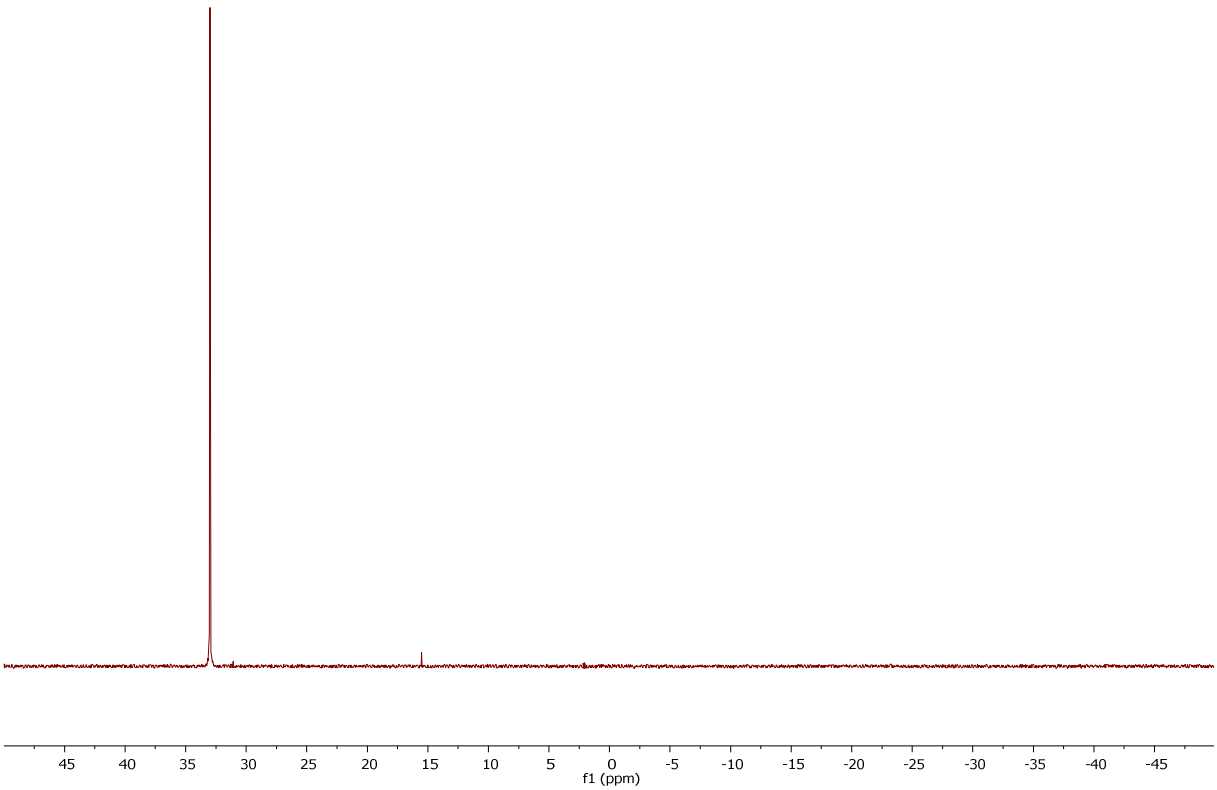

Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **7c**.

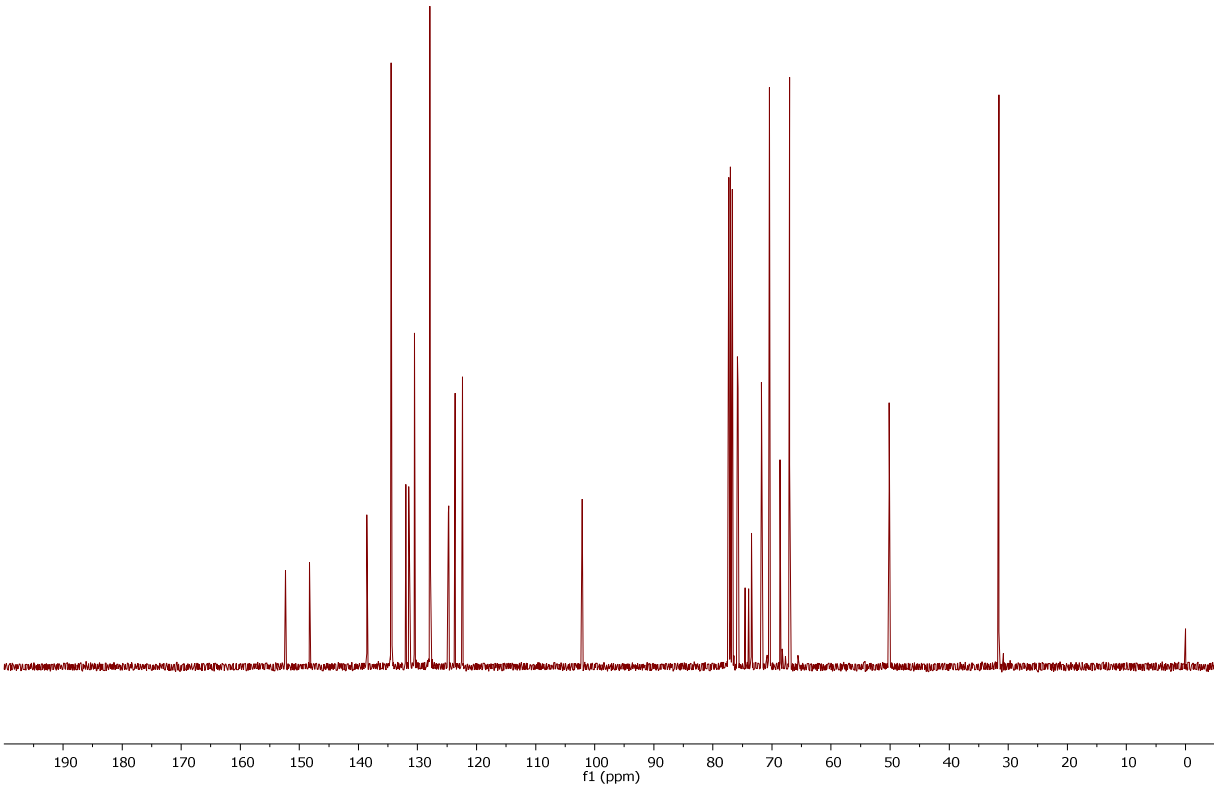

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **7c**.

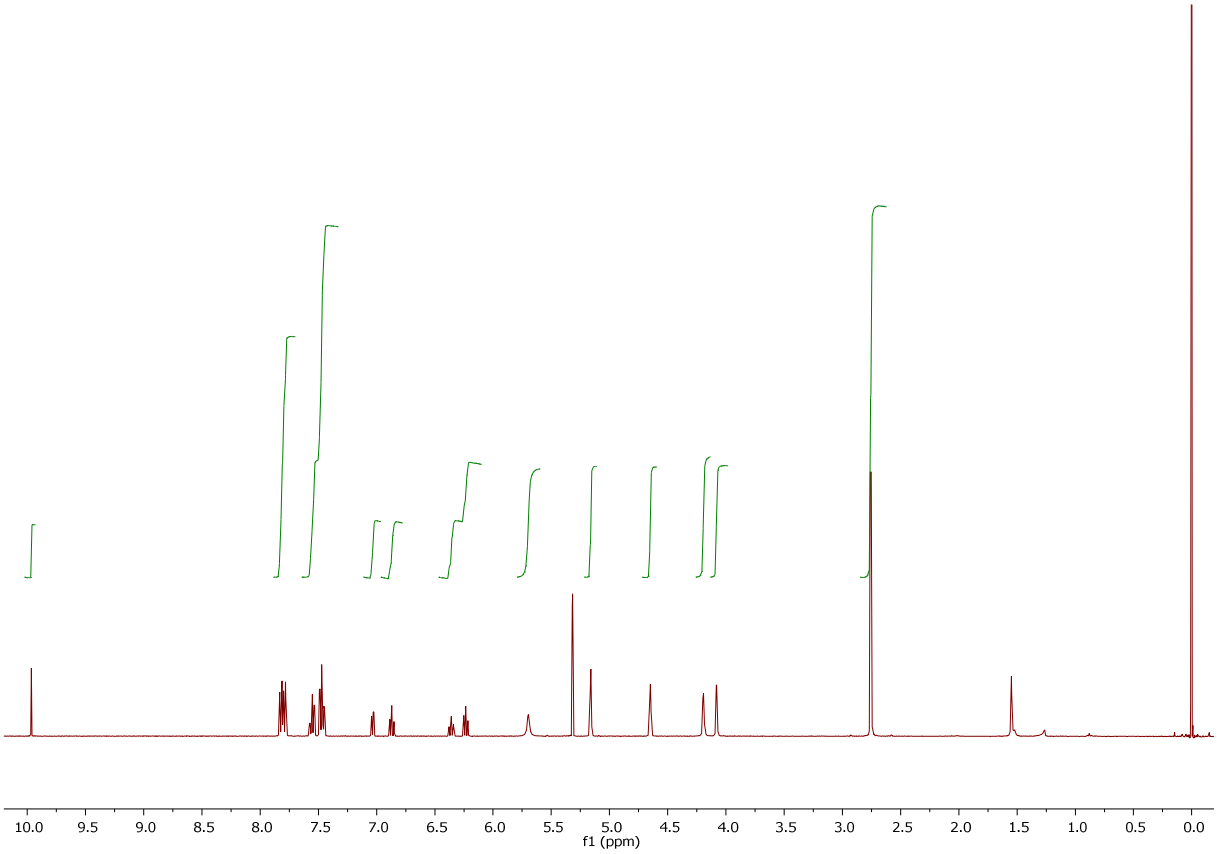

Figure S48. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **8a**.

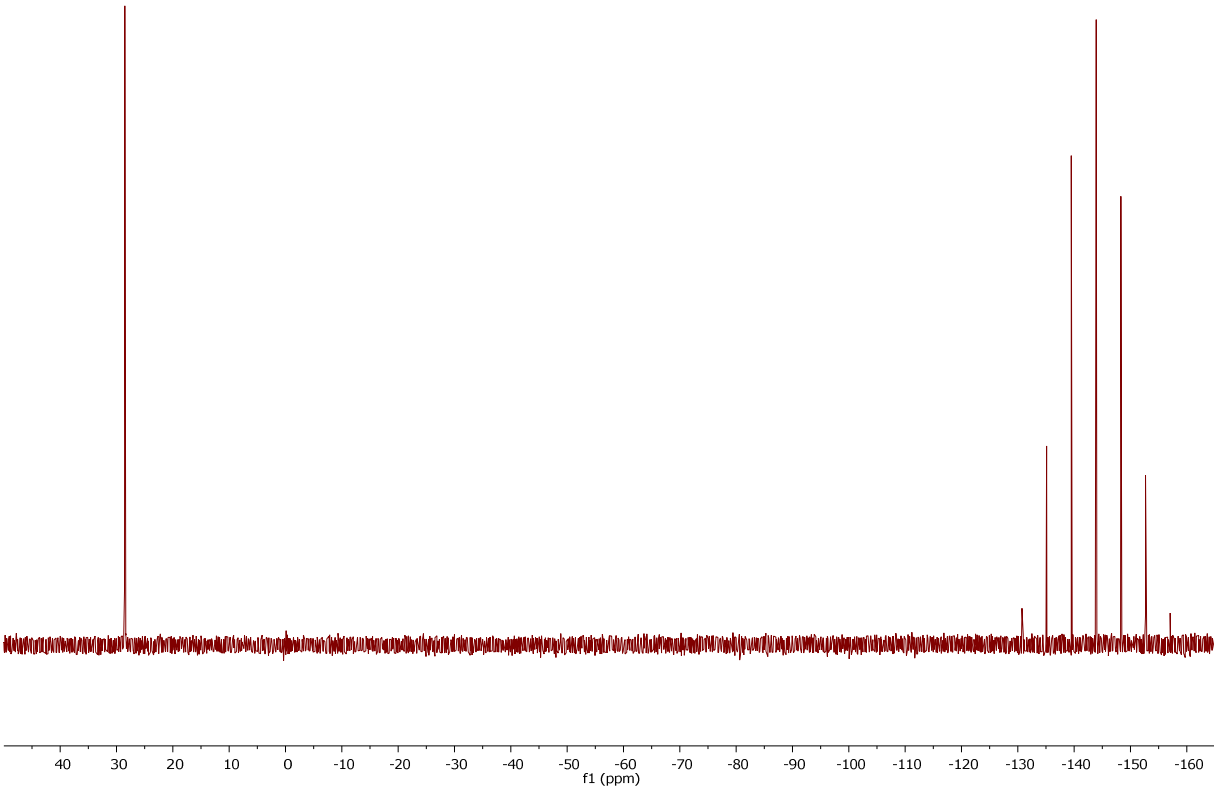

Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **8a**.

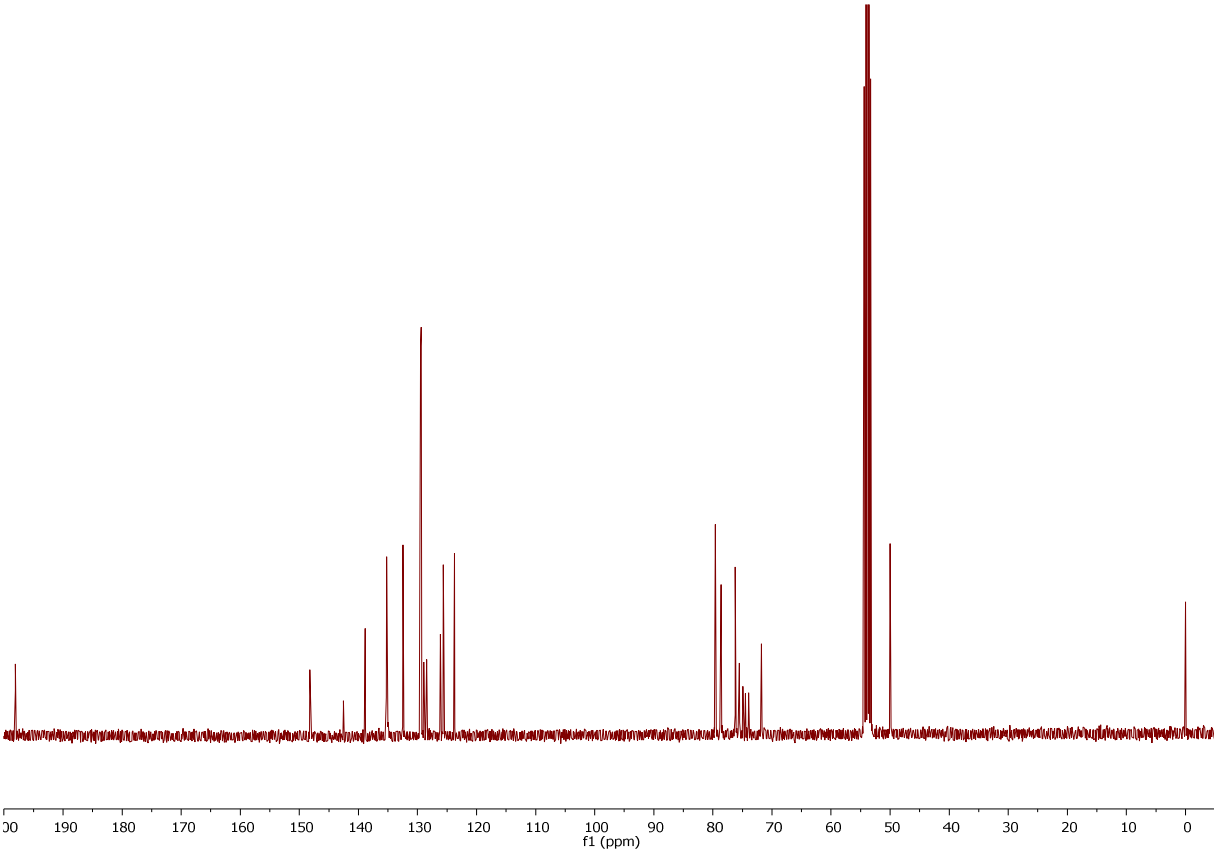

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **8a**.

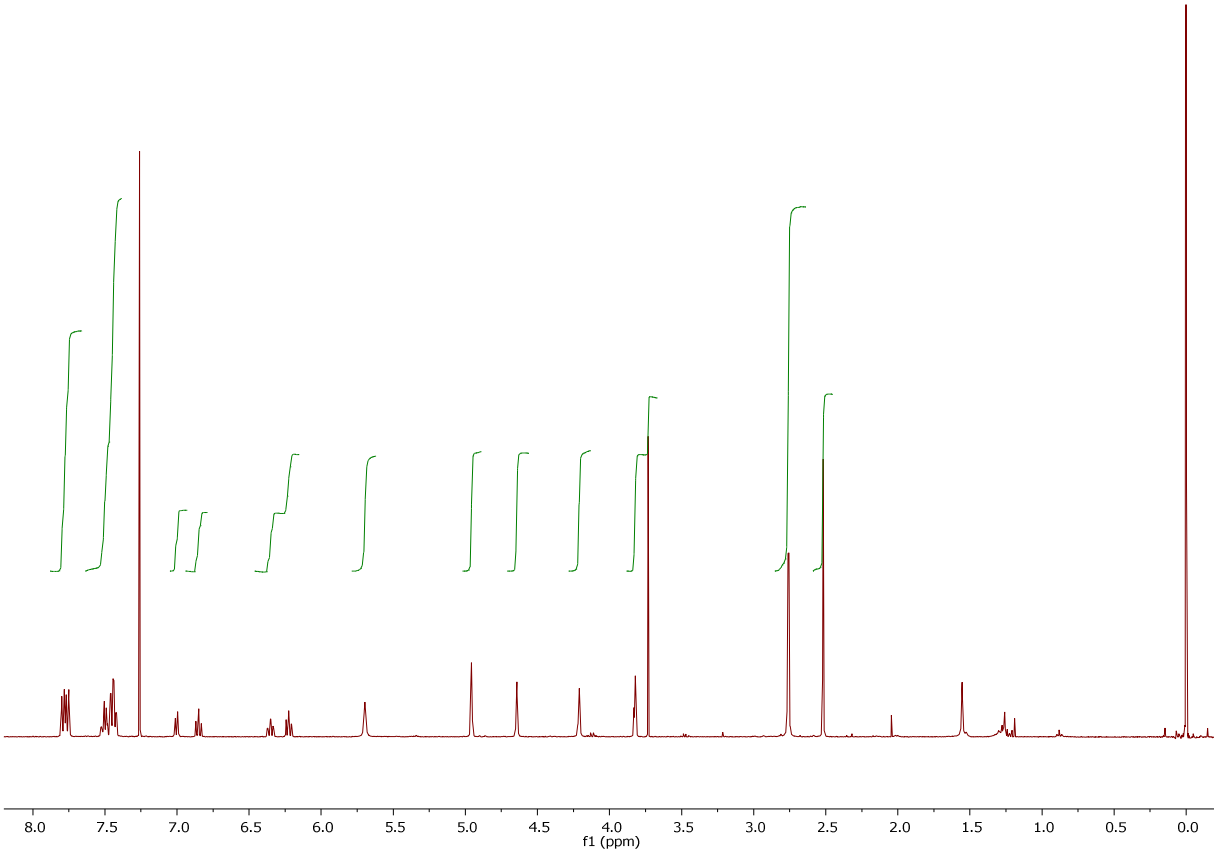

Figure S51. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8b**.

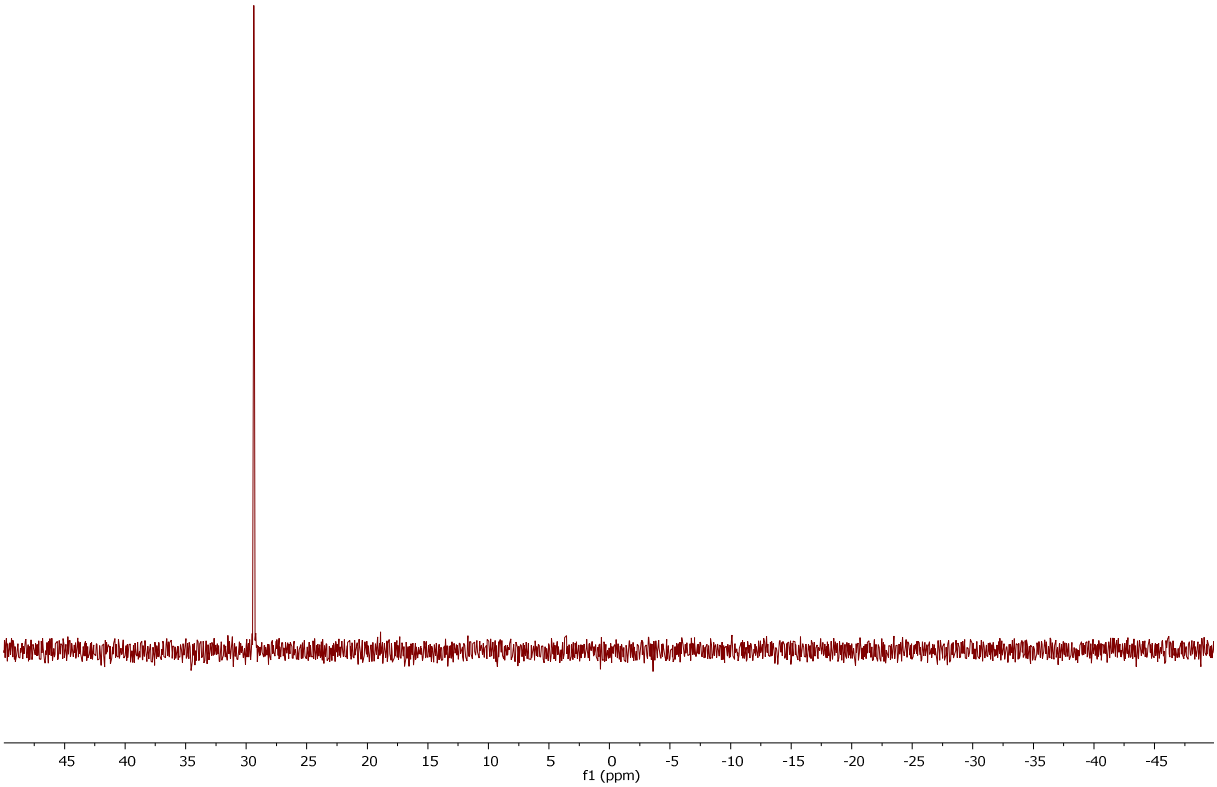

Figure 52. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **8b**.

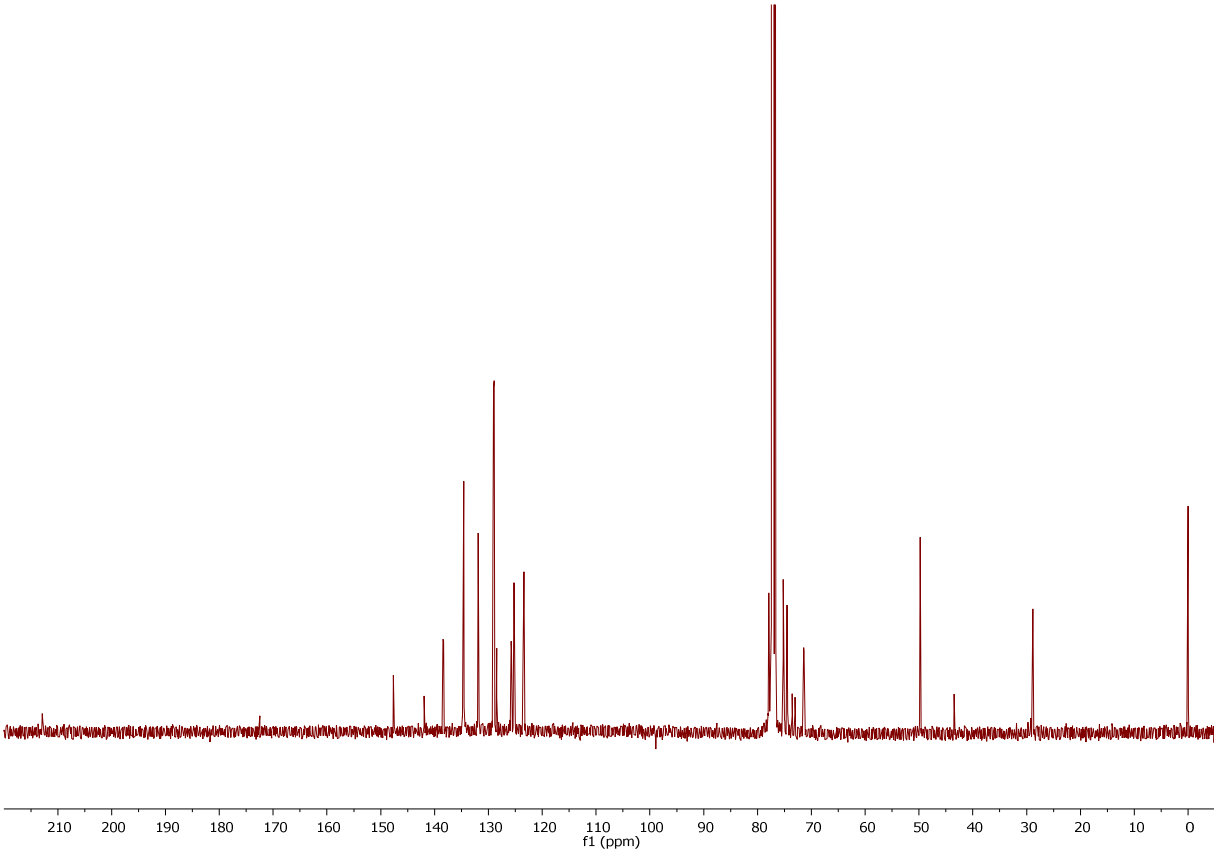

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8b**.

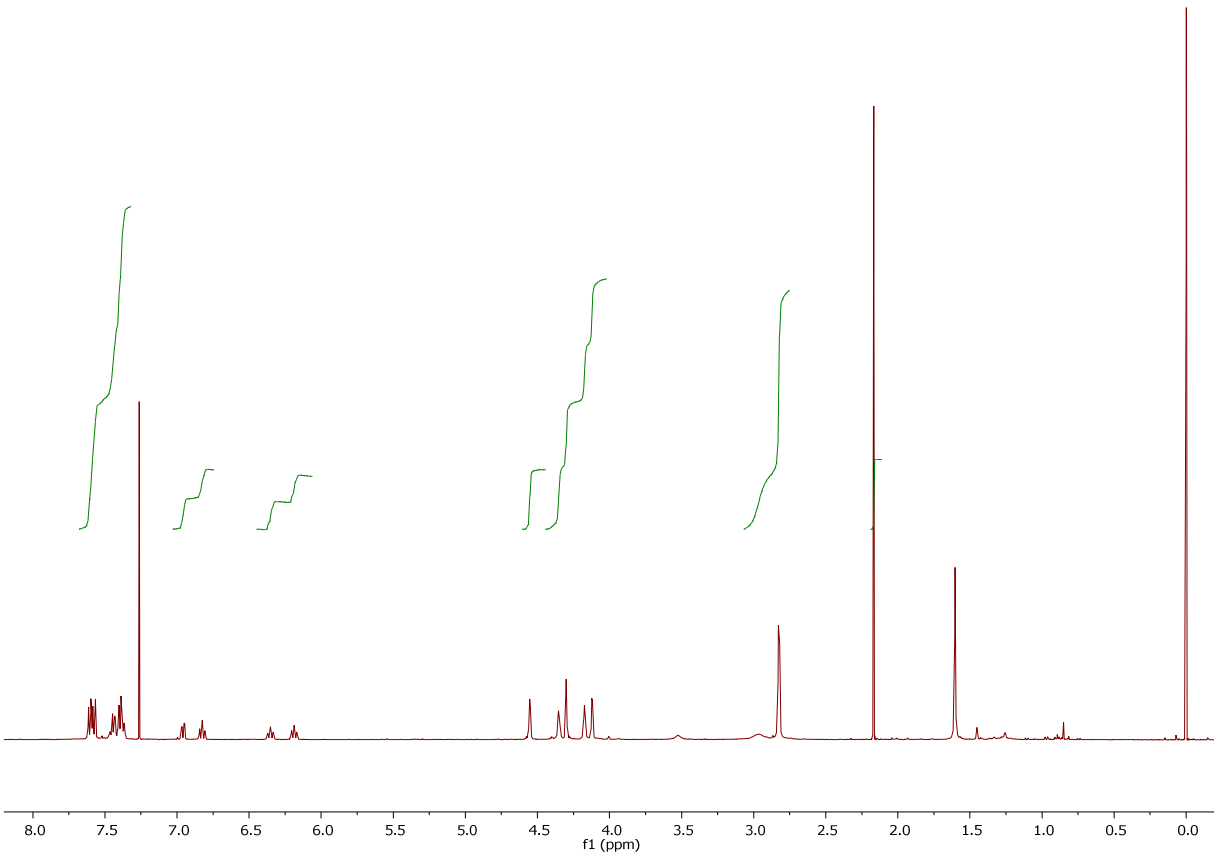

Figure S54. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **8c**.

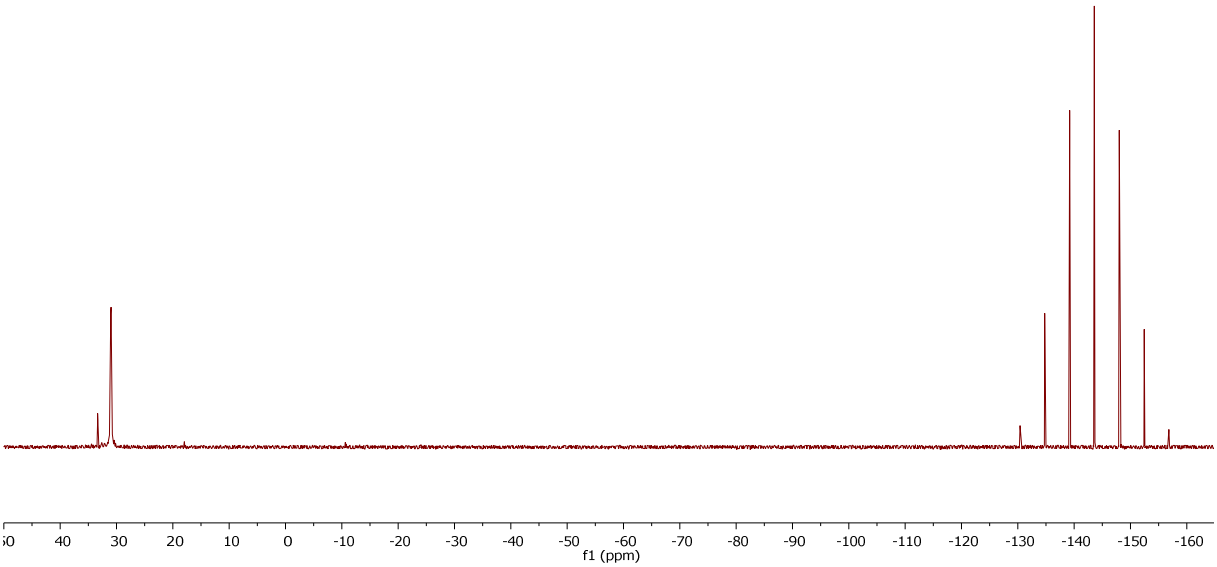

Figure S55. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **8c**.

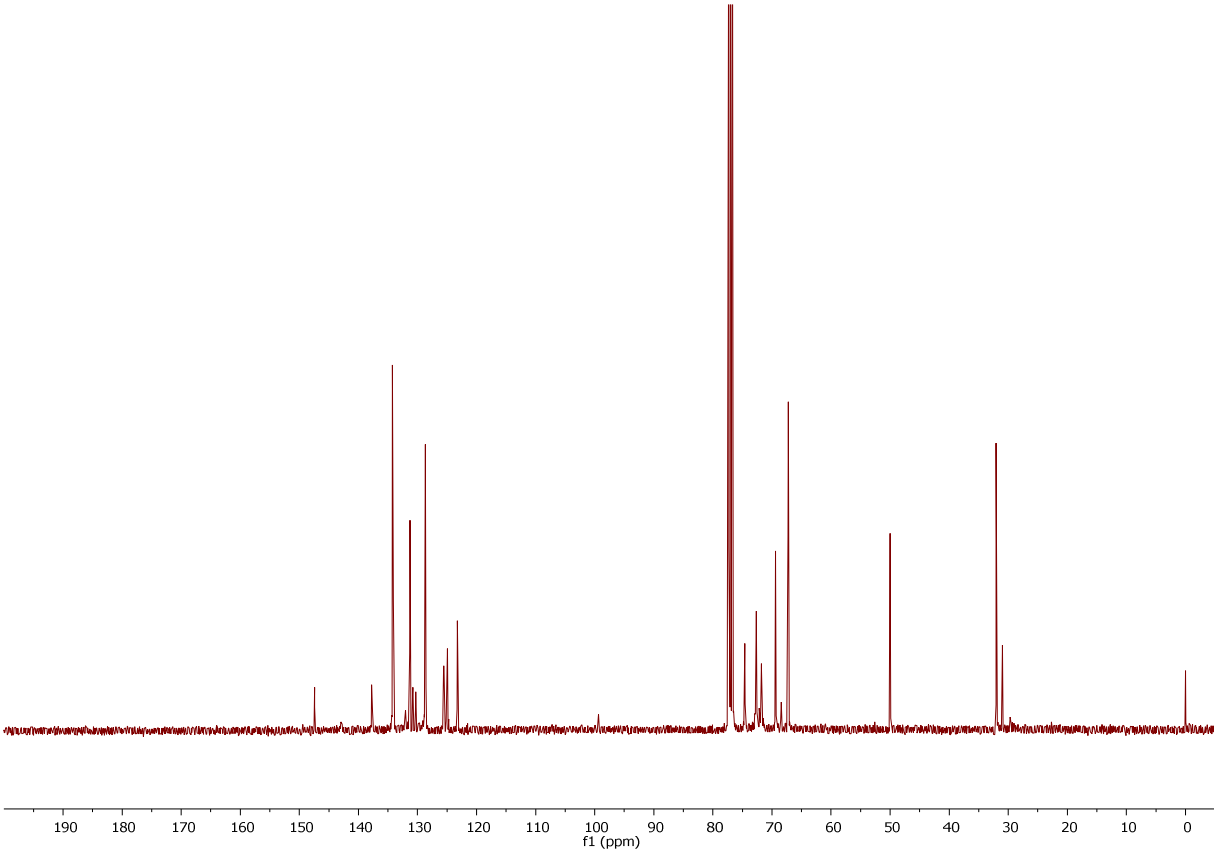

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **8c**.