Supporting Information

for

The protonation state governs the coordination of phosphinoferrocene guanidines

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Contents

EXPERIMENTAL

Materials and methods

All syntheses were performed under an atmosphere of an inert gas (argon or nitrogen) using standard Schlenk techniques and dry, deoxygenated solvents. Chloroform and acetonitrile (analytical grade) were dried over calcium hydride and distilled under an argon atmosphere. Dichloromethane and tetrahydrofuran (HPLC grade) were purified using a Pure Solv MD-5 (Inovative Technology, USA) solvent purification system. All solvents required for work-up and crystallisation were used without additional purification (analytical grade solvents from Lach-Ner, Czech Republic). Commercially available starting materials were purchased from Merck, Alfa-Aesar and TCI and used as received. Compounds **1**^{iPr},[1] *cis*-[$PdCl_2${**1**^{iPr}-κ^2*P,N*}] (**2**),[1] and $[Pd_2(\mu\text{-}Br)_2(C_6H_4CN\text{-}4)_2\{P(o\text{-tolyl})_3\}_2]$[2] were prepared according to literature procedures.

NMR spectra were recorded at 25°C on a Varian INOVA 400 spectrometer, operating at 399.95 MHz (^{1}H), 100.58 MHz (^{13}C) and 161.90 MHz (^{31}P), or on a Bruker Avance III 400 spectrometer, at operating frequencies of 400.13 (^{1}H), 100.62 (^{13}C) and 161.97 MHz (^{31}P). Chemical shifts (δ in ppm) are given relative to tetramethylsilane as an internal reference (^{1}H and ^{13}C), and to 85% aqueous H_3PO_4 as an external reference (^{31}P). Standard signal notation is used. In addition, vt and vq are used to distinguish second-order multiplets, virtual triplets and quartets, arising from the AA'BB' and AA'BB'X spin systems (A, B = H, X = P) of the substituted cyclopentadienyl rings in ^{1}H NMR spectra. FTIR spectra of samples diluted with KBr were recorded in diffuse reflectance mode (DRIFTS) over the range of 400-4000 cm^{-1} on a Thermo Nicolet 6700 FTIR spectrometer. ESI mass spectra were obtained on a Compact QTOF-MS spectrometer (Bruker Daltonics) from samples dissolved in HPLC-grade solvents (methanol, acetonitrile, or acetone). Elemental analyses were performed on a Perkin–Elmer 2400 Series II CHNS/O analyser. The presence of residual solvent (if applicable) was confirmed by NMR analysis. The following abbreviations are used in the following text: fc = ferrocene-1,1′-diyl, *i*Pr = *iso*-propyl, $BAr^F{}_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, dmap = 4-(dimethylamino)-pyridine, PhPy = 2-phenylpyridine.

Syntheses

Preparation of cis-[$PtCl_2${Ph_2PfcN=C(NHiPr)$_2$-κ^2P,N}] (4)

Ligand **1**^{iPr} (256 mg, 0.50 mmol) and *cis*-dichlorobis(dimethylsulfoxide)platinum(II) (211 mg, 0.50 mmol) were dissolved in dry chloroform (20 mL), and the mixture was stirred at room temperature for 2 h. The resulting orange solution was filtered through a PTFE syringe filter

(0.45 μm pore size), and the filtrate was layered with diethyl ether. After several days, tiny yellow crystals formed, which were isolated by suction. To remove residual solvents, the crystals were ground in an agate mortar, and the resulting yellow powder was dried under vacuum. Yield of **4**: 331 mg (85%), yellow powder. Crystals used for structure determination were obtained by liquid-phase diffusion of diethyl ether into a chloroform solution of the complex.

^{1}H NMR (CD_2Cl_2): δ 0.90-1.50 (br m, 12 H, CH*Me*$_2$), 3.40-4.00 (br m, 2 H, C*H*Me$_2$), 3.96 (m, 1 H, CH of fc), 4.22 (m, 1 H, CH of fc), 4.29 (m, 2 H, CH of fc), 4.34 (m, 1 H, CH of fc), 4.69 (m, 1 H, CH of fc), 5.12 (m, 1 H, CH of fc), 5.43 (m, 1 H, CH of fc), 6.33 (br s, 1 H, NH), 7.28-7.48 (m, 7 H, PPh_2), 7.52-7.58 (m, 1 H, PPh_2), 7.82-7.90 (m, 2 H, PPh_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.30 (br s, CH*Me*$_2$), 24.22 (br s, CH*Me*$_2$), 47.30 (br s, *C*HMe$_2$), 65.98 (s, CH of fc), 68.22 (s, CH of fc), 68.49 (s, CH of fc), 69.08 (s, CH of fc), 71.27 (d, J_{CP} = 70 Hz, C^{ipso}–P of fc), 71.73 (d, J_{CP} = 7 Hz, CH of fc), 73.97 (d, J_{CP} = 10 Hz, CH of fc), 75.20 (d, J_{CP} = 6 Hz, CH of fc), 77.92 (d, J_{CP} = 18 Hz, CH of fc), 110.85 (d, J_{CP} = 2 Hz, C^{ipso}–N of fc), 127.76 (d, J_{CP} = 11 Hz, CH of PPh_2), 128.73 (d, J_{CP} = 11 Hz, CH of PPh_2), 129.50 (d, J_{CP} = 62 Hz, C^{ipso}–P of PPh_2), 130.40 (d, J_{CP} = 3 Hz, CH of PPh_2), 131.20 (d, J_{CP} = 66 Hz, C^{ipso}–P of PPh_2), 131.68 (d, J_{CP} = 3 Hz, CH of PPh_2), 133.05 (d, J_{CP} = 10 Hz, CH of PPh_2), 134.42 (d, J_{CP} = 11 Hz, CH of PPh_2), 159.76 (s, C^{ipso} of guanidine). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 2.2 (s with ^{195}Pt satellites, $^{1}J_{PPt}$ = 4125 Hz). ESI+ MS: *m*/*z* 742 ([M – Cl]$^{+}$). IR (DRIFTS): ν_{max} 3298 s, 3093 w, 3059 w, 3046 w, 2975 m, 2928 w, 2867 w, 1582 s, 1559 s, 1482 w, 1463 m, 1435 s, 1404 w, 1387 m, 1365 w, 1323 m, 1309 m, 1258 w, 1211 w, 1196 m, 1171 m, 1130 w, 1102 m, 1093 m, 1054 w, 1030 w, 1201 m 999 w, 936 w, 868 w, 846 w, 832 w, 817 m, 801 w, 750 m, 709 w, 697 s, 636 w, 623 w, 547 m, 531 s, 516 m, 508 m, 482 s, 452 w, 432 w. Anal. Calc. for $C_{29}H_{34}Cl_2FeN_3PPt$ (777.4): C 44.80, H 4.41, N 5.41%. Found: C 45.06, H 4.38, N 5.51%.

Preparation of [Pt(μ-Cl){Ph$_2$PfcN=C(NHiPr)$_2$-κ^{2}P,N}]$_2$[BAr$^F_4$]$_2$ (5)

A mixture of **4** (155 mg, 0.20 mmol) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (177 mg, 0.20 mmol) in dry chloroform (10 mL) was stirred at room temperature for 2 h. During this period, the suspension slowly changed from orange to orange-red. The separated sodium chloride was filtered off, and the clear filtrate was evaporated. The orange-red waxy residue was dissolved in chloroform (approximately 5 mL) to give a saturated solution. Crystallisation at 8 °C for several days produced orange-red crystals (also used for structure determination), which were separated by suction. To remove residual solvents, the crystals were pulverised, drying the orange-red powder under vacuum. Yield of **5**: 273 mg (85%), orange-red solid. *Note: Although only one of the possible stereoisomers was identified by X-ray diffraction analysis, signals attributable to four distinct species were observed in the NMR spectra (see below). Two major and two minor isomers detected after dissolving the crystalline material transformed to a ca. 1:1:1:1 mixture over time, suggesting an equilibrium between the stereoisomers in solution.*

^{1}H NMR (CD_2Cl_2): δ 0.50-1.60 (br m, 48 H, CH*Me*$_2$), 2.90-4.10 (br m, 8 H, C*H*Me$_2$), 4.09 (m, 1 H, CH of fc), 4.12 (m, 2 H, CH of fc), 4.20 (m, 1 H, CH of fc), 4.27 (m, 1 H, CH of fc), 4.32 (m, 2 H, CH of fc), 4.36 (m, 1 H, CH of fc), 4.39 (m, 2 H, CH of fc), 4.41 (m, 2 H, CH of fc), 4.45 (m, 2 H, CH of fc), 4.49 (m, 1 H, CH of fc), 4.53 (m, 2 H, CH of fc), 4.61 (m, 2 H, CH of fc), 4.69 (m, 1 H, CH of fc), 4.86 (m, 2 H, CH of fc), 4.92 (m, 1 H, CH of fc), 4.99 (m, 3 H, CH of fc), 5.12 (m, 1 H, CH of fc), 5.27 (m, 1 H, CH of fc), 5.44 (m, 1 H, CH of fc), 5.51 (m, 1 H, CH of fc), 5.57 (m, 1 H, CH of fc), 5.61 (m, 1 H, CH of fc), 7.14-7.26 (m, 4 H, aromatic CH), 7.30-7.46 (m, 8 H, aromatic CH), 7.48-7.59 (m, 12 H, aromatic CH), 7.60-7.78 (m, 28 H, aromatic CH). Signals due to guanidine NH were not observed. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 2.3, 3.0, 5.0, 5.4 (4× s with ^{195}Pt satellites). The $^{1}J_{PPt}$ interaction constants were not resolved. ESI+ MS: *m*/*z* 705 ([Pt(**1**^{iPr} – H)]$^{+}$), 741 ([PtCl(**1**^{iPr})]$^{+}$). IR (DRIFTS): ν_{max} 3402 w, 3339 w, 2976 w, 1609 m, 1586 s, 1511 m, 1488 w, 1466 w, 1440 m, 1393 w, 1375 w, 1356 s, 1304 w, 1282 s, 1161 s, 1128 s, 1101 s, 1053 w, 1043 w, 1030 w, 1001 w, 932 w, 897 m, 887 m, 840 m, 824 w, 774 m, 712 m, 701 w, 692 m, 682 m, 672 m, 637 m, 578 w, 546 w, 527 w, 514 w, 508 m, 500 w, 450 w. Anal. Calc. for $C_{122}H_{92}B_2Cl_2F_{48}Fe_2N_6P_2Pt_2$ (3210.4): C 45.64, H 2.89, N 2.62%. Found: C 45.27, H 2.93, N 2.80%.

Preparation of [PdBr(p-C$_4$H$_4$CN){Ph$_2$PfcN=C(NHiPr)$_2$-κ^{2}P,N}] (6)

Ligand **1**^{iPr} (103 mg, 0.20 mmol) and [Pd(μ-Br)(*p*-C_4H_4CN){P(*o*-tolyl)$_3$}]$_2$ (119 mg, 0.10 mmol) were dissolved in dry dichloromethane (10 mL) and the resulting solution was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure. The yellow residue was triturated with diethyl ether to remove P(*o*-tolyl)$_3$, and the resulting yellow solid was isolated by suction. The crude product was further crystallised by liquid phase diffusion of methyl *tert*-butyl ether into a chloroform solution (single-crystals suitable for X-ray determination were obtained using the same method). Yield of **6**·$CHCl_3$: 153 mg (83%), orange-yellow crystalline solid. *Note: As a chloroform solvate, the product slowly releases the clathrated solvent.*

^{1}H NMR (CD_2Cl_2): δ 0.84-1.22 (broad d, 6 H, CH*Me*$_2$), 1.47 (s, 6 H, CH*Me*$_2$), 3.50 (broad s, 1 H, CH of fc), 3.85-4.10 (broad m, 3 H, CH of fc + C*H*Me$_2$), 4.18 (broad s, 1 H, CH of fc), 4.32 (broad s, 1 H, CH of fc), 4.73 (broad s, 1 H, CH of fc), 4.94 (broad s, 1 H, CH of fc), 5.64 (broad s, 1 H, CH of fc), 5.89 (broad s, 1 H, CH of fc), 6.72-6.83 (broad m, 4 H, aromatics), 6.92 (broad s, 2 H, aromatics), 7.11 (broad s, 1 H, aromatics), 7.24 (broad s, 2 H, aromatics), 7.43 (broad s, 2 H, aromatics), 7.54 (broad s, 1 H, aromatics), 7.82 (broad s, 2 H, aromatics). Signals due to NH hydrogens were not found. ^{13}C NMR spectra could not be obtained due to extensive broadening. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 21.7 (s). ESI+ MS: *m*/*z* 696 ([PdBr(**1**^{iPr})]$^{+}$), 719 ([Pd(C_6H_4CN)(**1**^{iPr})]$^{+}$). IR (DRIFTS): ν_{max} 3404 w, 3321 s, 3096 w, 3085 w, 3058 w, 3014 w, 2969 m, 2930 w, 2869 w, 2216 s, 1570 s, 1484 m, 1472 m, 1466 m, 1451 s, 1439 m, 1425 m, 1385 m, 1373 w, 1365 m, 1341 w,

1308 m, 1247 w, 1195 w, 1171 s, 1128 m, 1101 m, 1095 m, 1054 m, 1027 m, 1012 w, 999 w, 944 w, 903 w, 867 w, 850 w, 829 w, 809 s, 752 s, 707 m, 693 s, 667 w, 632 w, 607 w, 563 w, 550 m, 536 m, 517 s, 502 s, 478 m, 465 w, 426 w. Anal. Calc. for $C_{36}H_{38}BrFeN_4PPd \cdot \frac{1}{2}CHCl_3$ (859.6): C 51.00, H 4.51, N 6.52%. Found: C 51.06, H 4.48, N 6.16%.

Preparation of [Pd(μ-p-C_4H_4CN-κ²C,N){Ph_2PfcN=C(NHiPr)$_2$-κ²P,N}]$_n$[SbF_6]$_n$ (7)

Complex **6** (80 mg, 0.10 mmol) and silver(I) hexafluoroantimonate(V) (35 mg, 0.10 mmol) were mixed in dry dichloromethane (15 mL), and the suspension was stirred at room temperature in the dark for 1 h. The precipitated silver(I) bromide was removed by filtration through a Celite pad, and the filtrate was precipitated by adding pentane. The solid yellow product was collected on a frit, washed with pentane, and dried under vacuum. Yield of **7**: 68 mg (71%), yellow powder. Crystals suitable for X-ray structure determination were obtained by liquid-phase diffusion of methyl *tert*-butyl ether into fluorobenzene solution of the complex.

ESI+ MS: *m*/*z* 528 ([**1**^{iPr} + O]$^+$), 616 ([Pd(**1**^{iPr} – H)]$^+$), 719 ([Pd(C_4H_4CN)(**1**^{iPr})]$^+$). IR (DRIFTS): ν_{max} 3650 w, 3400 w, 2976 m, 2934 w, 2258 m, 1652 m, 1584 s, 1569 s, 1474 m, 1437 m, 1389 m, 1372 w, 1310 w, 1250 w, 1169 m, 1129 w, 1100 m, 1056 w, 1029 w, 1012 w, 816 m, 748 m, 696 m, 660 s, 643 m, 536 m, 524 m, 503 m, 482 m. Anal. Calc. for $C_{36}H_{38}F_6FeN_4PPdSb$ (955.7, monomeric unit): C 45.24, H 4.01, N 5.86%. Found: C 44.67, H 4.00, N 5.42%.

Preparation of [Ph_2PfcNHC(NHiPr)$_2$]Cl ((**1**^{iPr}**H**)Cl)

A hydrogen chloride solution (1.6 mL, 1.25 M in methanol, 2.00 mmol) was added to a solution of **1**^{iPr} (1.02 g, 2.00 mmol) in dry dichloromethane (15 mL), and the resulting orange solution was stirred at room temperature for 10 minutes and evaporated under vacuum. (*Note: longer reaction times resulted in partial oxidation of the phosphine*). Crystallization of the crude product from ethyl acetate/hexane mixture produced (**1**^{iPr}**H**)Cl as an orange microcrystalline solid. Yield: 0.96 g (88%). Crystals used for structure determination were grown by liquid-phase diffusion of hexane into the ethyl acetate solution of the compound.

^{1}H NMR ($CDCl_3$): δ 1.24 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, CH*Me*$_2$), 3.89 (sept, $^3J_{HH}$ = 6.4 Hz, 2 H, C*H*Me$_2$), 4.05 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.18 (m, 4 H, CH of fc), 4.60 (vt, J' = 1.7 Hz, 2 H, CH of fc), 7.30-7.40 (m, 10 H, PPh_2). Signals due to NH of guanidinium were not observed. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.02 (s, CH*Me*$_2$), 45.03 (s, *C*HMe$_2$), 64.82 (broad s, CH of fc), 67.47 (s, CH of fc), 72.72 (d, J_{CP} = 3 Hz, CH of fc), 73.67 (d, J_{CP} = 14 Hz, CH of fc), 76.25 (d, J_{CP} = 4 Hz, C^{ipso}–P of fc), 128.31 (d, J_{CP} = 7 Hz, CH of PPh_2), 128.79 (s, CH of PPh_2), 133.43 (d, J_{CP} = 20 Hz, CH of PPh_2), 138.01 (d, J_{CP} = 9 Hz, C^{ipso} of PPh_2), 153.39 (s, C^{ipso} of guanidinium). The signal due to C^{ipso}–N of fc was not found. ^{31}P{^{1}H} NMR ($CDCl_3$): δ –18.2 (s). ESI+ MS: *m*/*z* 512 ([**1**^{iPr}**H**]$^+$). IR (DRIFTS): ν_{max} 3289 s, 3240 w, 3173 m, 3119 m, 3095 m, 3056 s, 2979 s, 2874 m, 2800 s, 2737 m, 1636 s, 1605 s, 1569 m, 1529

w, 1478 s, 1459 m, 1444 m, 1432 m, 1406 m, 1386 m, 1370 m, 1358 w, 1339 m, 1313 w, 1260 m, 1215 w, 1201 w, 1158 m, 1127 m, 1091 m, 1068 w, 1057 w, 1043 w, 1027 m, 1020 w, 999 w, 947 m, 928 w, 911 w, 890 w, 868 w, 828 m, 818 w, 811 w, 780 w, 742 s, 717 m, 696 s, 683 m, 639 w, 630 w, 588 w, 566 w, 533 w, 519 w, 502 m, 487 s, 456 w, 437 w. Anal. Calc. for $C_{29}H_{35}ClFeN_3P$ (547.9): C 63.57, H 6.44, N 7.67%. Found: C 63.04, H 6.29, N 7.49%.

Preparation of [Ph$_2$PfcNHC(NHiPr)$_2$][SbF$_6$]·CH$_2$Cl$_2$ ((1^{iPr}H)[SbF$_6$]·CH$_2$Cl$_2$)

Compound **1^{iPr}** (274 mg, 0.50 mmol) and potassium hexafluoroantimonate(V) (165 mg, 0.60 mmol) were mixed in dry dichloromethane (10 mL), and the heterogenous mixture was stirred at room temperature overnight. On the following day, the precipitated potassium chloride was filtered off, and the clear orange filtrate was concentrated under reduced pressure to ca. 5 mL and layered with hexane. Crystallisation by liquid-phase diffusion over several days at 8 °C afforded orange prismatic crystals, which were isolated by suction, washed with pentane, and dried under vacuum. Yield of (**1^{iPr}H**)[SbF$_6$]·CH$_2$Cl$_2$: 263 mg (63%), orange crystalline solid. Crystals used for structure determination were obtained using the same procedure.

^{1}H NMR (CDCl$_3$): δ 1.32 (d, $^3J_{HH}$ = 6.2 Hz, 12 H, CH*Me*$_2$), 3.96 (d of sept, $J \approx {}^3J_{HH} \approx$ 6.2 Hz, 2 H, C*H*Me$_2$), 4.16 (vq, J' = 1.8 Hz, 2 H, CH of fc), 4.24 (vt, J' = 2.0 Hz, 2 H, CH of fc), 4.35 (vt, J' = 2.0 Hz, 2 H, CH of fc), 4.52 (vt, J' = 1.8 Hz, 2 H, CH of fc), 5.30 (s, 2 H, CH$_2$Cl$_2$), 5.44 (s, 2 H, NH), 7.33-7.41 (m, 10 H, PPh$_2$), 7.71 (s, 1 H, NH). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 22.40 (s, CH*Me*$_2$), 45.17 (d, J = 2 Hz, *C*HMe$_2$), 53.43 (s, CH$_2$Cl$_2$), 67.32 (s, CH of fc), 68.98 (s, CH of fc), 72.63 (d, J_{CP} = 3 Hz, CH of fc), 73.67 (d, J_{CP} = 12 Hz, CH of fc), 76.22 (s, C^{ipso}–P of fc), 87.68 (s, C^{ipso}–N of fc), 128.73 (d, J_{CP} = 8 Hz, CH of PPh$_2$), 129.54 (s, CH of PPh$_2$), 133.44 (d, J_{CP} = 19 Hz, CH of PPh$_2$), 135.80 (d, J_{CP} = 4 Hz, C^{ipso}–P of PPh$_2$), 152.95 (C^{ipso} of guanidinium). ^{31}P{^{1}H} NMR (CDCl$_3$): δ –21.8 (s). ESI+ MS: *m*/*z* 512 ([**1^{iPr}H**]$^+$). IR (DRIFTS): ν_{max} 3389 m, 3225 m, 3109 w, 3055 w, 2981 m, 2941 w, 2882 w, 1634 s, 1614 s, 1471 m, 1435 s, 1394 m, 1375 m, 1326 m, 1265 w, 1214 w, 1195 w, 1162 m, 1132 w, 1093 w, 1071 w, 1052 w, 1029 m, 999 w, 946 w, 875 w, 842 w, 821 m, 748 s, 698 s, 662 s, 565 w, 518 w, 488 m, 463 w. Anal. Calc. for $C_{29}H_{35}F_6FeN_3PSb{\cdot}CH_2Cl_2$ (833.1): C 43.25, H 4.48, N 5.04%. Found: C 43.16, H 4.15, N 4.92%.

Preparation of [PdCl$_3${Ph$_2$PfcNHC(NHiPr)$_2$-κP}] (8)

A solution of hydrogen chloride (0.4 mL, 0.5 M in methanol, 0.2 mmol) was added to a solution of complex **2** (138 mg, 0.20 mmol) in dry dichloromethane (10 mL), and the resulting red mixture was stirred at room temperature for 30 minutes. Subsequent evaporation under vacuum left a red residue, which was dissolved in chloroform (2 mL). Crystallization at –18°C produced a red crystalline solid, which was isolated by suction, washed with pentane, and dried under vacuum. Yield of **8**·2.5CHCl$_3$: 165 mg (81%), red microcrystalline powder. *Note: The product was obtained*

as a chloroform solvate, which slowly released the clathrated solvent, as indicated by elemental analysis. Crystals used for structure determination were obtained by slowly cooling a saturated solution of the compound in chloroform.

^{1}H NMR (CD_2Cl_2/CD_3OD): δ 1.27 (d, $^{3}J_{HH}$ = 6.1 Hz, 12 H, CH*Me*$_2$), 4.03 (sept, $^{3}J_{HH}$ = 6.1 Hz, 2 H, C*H*Me$_2$), 4.44 (m, 2 H, CH of fc), 4.60 (m, 2 H, CH of fc), 4.76 (m, 2 H, CH of fc), 5.19 (m, 2 H, CH of fc), 6.13 (s, 1 H, NH), 7.36 (s, 2 H, $CHCl_3$), 7.36-7.43 (m, 4 H, PPh_2), 7.47-7.52 (m, 2 H, PPh_2), 7.53-7.60 (m, 4 H, PPh_2). The remaining NH signals were not observed, presumably due to H-D exchange. ^{13}C{^{1}H} NMR (CD_2Cl_2/CD_3OD): δ 22.88 (s, CH*Me*$_2$), 45.93 (s, *C*HMe$_2$), 68.15 (s, CH of fc), 68.92 (s, CH of fc), 73.02 (d, J_{CP} = 7 Hz, CH of fc), 73.37 (d, J_{CP} = 63 Hz, C^{ipso}–P of fc), 77.87 (d, J_{CP} = 9 Hz, CH of fc), 78.05 (s, $CHCl_3$), 93.58 (s, C^{ipso}–N of fc), 128.09 (d, J_{CP} = 11 Hz, CH of PPh_2), 130.74 (d, J_{CP} = 57 Hz, C^{ipso}–P of PPh_2), 131.30 (d, J_{CP} = 3 Hz, CH of PPh_2), 134.34 (d, J_{CP} = 10 Hz, CH of PPh_2), 154.23 (s, C^{ipso} of guanidinium). ^{31}P{^{1}H} NMR (CD_2Cl_2/CD_3OD): δ 23.9 (s). ESI+ MS: *m*/*z* 652 ([M – Cl – HCl]$^+$). IR (DRIFTS): ν_{max} 3408 w, 3239 m, 3201 m, 3111 m, 3077 m, 2975 m, 2933 w, 1633 s, 1601 s, 1508 w, 1482 m, 1470 m, 1454 m, 1436 s, 1391 m, 1373 m, 1320 m, 1260 w, 1211 w, 1165 s, 1130 m, 1100 m, 1063 w, 1033 m, 998 w, 942 w, 910 w, 840 w, 825 w, 747 s, 711 m, 694 s, 664 w, 625 m, 545 m, 525 s, 505 s, 476 s, 452 w, 428 w, 418 w. Anal. Calc. for $C_{29}H_{35}Cl_3FeN_3PPd$·1.5 $CHCl_3$ (904.3): C 40.51, H 4.07, N 4.65%. Found: C 40.75, H 4.34, N 4.63%.

Reaction of (1^{iPr}H)Cl with [PdCl$_2$(MeCN)$_2$]

In a microscale experiment, a mixture of [$PdCl_2(MeCN)_2$] (5.2 mg, 0.020 mmol) and (**1^{iPr}H**)Cl (22.0 mg, 0.040 mmol) were dissolved in $CDCl_3$ (0.6 mL). The resulting red solution was stirred at room temperature for 1 hour, filtered through a PTFE syringe filter (0.45 μm porosity) and analysed by NMR spectroscopy.

^{31}P{^{1}H} NMR ($CDCl_3$): δ 18.2 (s, major - approx. 65%, **9**-Cl), 26.7 (s, minor - approx. 20%, **2**), 33.3 (s, minor - approx. 15%, presumably [Pd(**1^{iPr}**)$_2$]Cl_2).

Preparation of trans-[PdCl$_2${Ph$_2$PfcNHC(NHiPr)$_2$-κP}$_2$][SbF$_6$]$_2$ (9-SbF$_6$)

A mixture of (**1^{iPr}H**)[SbF_6]·CH_2Cl_2 (75 mg, 0.10 mmol) and bis(acetonitrile)dichloropalladium(II) (26 mg, 0.05 mmol) in dry dichloromethane (2 mL) was stirred at room temperature for 2 h. The separated orange-red solid was collected on a frit, washed with diethyl ether and dried under vacuum. Yield of **9**-SbF_6: 77 mg (92%), orange-red powder. Crystals used for structure determination were obtained by liquid-phase diffusion of diethyl ether into a methanolic solution of the complex.

^{1}H NMR (CD_2Cl_2/CD_3OD): δ 1.13 (d, $^{3}J_{HH}$ = 6.4 Hz, 12 H, CH*Me*$_2$), 3.60 (sept, $^{3}J_{HH}$ = 6.4 Hz, 2 H, C*H*Me$_2$), 4.38 (vt, J' = 2.0 Hz, 2 H, CH of fc), 4.43 (m, 2 H, CH of fc), 4.60 (m, 2 H, CH of fc), 4.63 (vt, J' = 2.0 Hz, 2 H, CH of fc), 7.39-7.46 (m, 4 H, PPh_2), 7.47-7.54 (m, 2 H, PPh_2), 7.58-7.65 (m, 4 H,

PPh_2). Signals due to NH hydrogens were not observed, presumably due to H-D exchange. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD): δ 22.49 (s, CH*Me*$_2$), 45.49 (s, *C*HMe$_2$), 67.05 (s, CH of fc), 69.10 (s, CH of fc), 73.61 (apparent t, J' = 4 Hz, CH of fc), 74.24 (apparent t, J' = 28 Hz, C^{ipso}–P of fc), 78.34 (apparent t, J' = 5 Hz, CH of fc), 92.91 (s, C^{ipso}–N of fc), 128.77 (apparent t, J' = 5 Hz, CH of PPh_2), 130.89 (apparent t, J' = 25 Hz, C^{ipso}–P of PPh_2), 131.60 (s, CH of PPh_2), 134.48 (apparent t, J' = 6 Hz, CH of PPh_2), 153.07 (s, C^{ipso} of guanidinium). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD): δ 16.9 (s). ESI+ MS: *m*/*z* 616 ([Pd(**1**^{iPr} – H)]$^+$), 652 ([PdCl(**1**^{iPr})]$^+$), 1435 ([PdCl$_2$(**1**^{iPr}**H**)$_2$][SbF_6]$^+$). IR (DRIFTS): ν_{max} 3389 m, 3315 m, 3095 m, 2982 m, 2933 w, 2876 w, 1651 s, 1613 s, 1478 m, 1435 m, 1403 w, 1392 m, 1374 m, 1352 w, 1338 w, 1306 w, 1199 w, 1168 m, 1132 w, 1099 m, 1063 w, 1037 w, 1028 m, 859 w, 848 m, 831 w, 745 m, 711 w, 691 m, 659 s, 642 m, 622 w, 565 w, 540 w, 520 m, 490 s, 476 m, 458 w. Anal. Calc. for $C_{58}H_{70}Cl_2F_{12}Fe_2N_6P_2PdSb_2$ (1673.7): C 41.62, H 4.22, N 5.02%. Found: C 41.40, H 4.11, N 5.25%.

Preparation of [PdCl(μ-Cl){Ph$_2$PfcNHC(NHiPr)$_2$-κP}]$_2$[SbF$_6$]$_2$ (10)

A mixture of (**1**^{iPr}**H**)[SbF_6]·CH_2Cl_2 (75 mg, 0.10 mmol) and bis(acetonitrile)dichloropalladium(II) (26 mg, 0.10 mmol) in dry dichloromethane (5 mL) was stirred at room temperature for 1 h, producing a purple-red solution, which was filtered through a PTFE syringe filter (0.45 μm pore size), concentrated under reduced pressure to ≈2 mL, and layered with diethyl ether. Crystallization by liquid-phase diffusion over several days produced dark red crystals (also used for structure determination), which were isolated by suction, washed with diethyl ether, and dried under vacuum. During the isolation, the crystals disintegrated into a dark red powder, presumably due to loss of clathrated solvent. Yield of **10**: 82 mg (89%), dark red powder.

^1H NMR (CD_2Cl_2/CD_3OD): δ 1.24 (d, $^3J_{HH}$ = 6.3 Hz, 12 H, CH*Me*$_2$), 3.89 (d of sept, $J \approx {}^3J_{HH}$ = 6.3 Hz, 2 H, C*H*Me$_2$), 4.58 (vt, J' = 1.8 Hz, 2 H, CH of fc), 4.65 (vq, J' = 1.8 Hz, 2 H, CH of fc), 4.74 (vq, J' = 1.7 Hz, 2 H, CH of fc), 4.96 (vt, J' = 1.8 Hz, 2 H, CH of fc), 6.18 (s, 2 H, NH), 7.39-7.48 (m, 4 H, PPh_2), 7.52-7.63 (m, 6 H, PPh_2). Signals due to NH hydrogens were not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD): δ 22.63 (s, CH*Me*$_2$), 45.59 (s, *C*HMe$_2$), 68.72 (s, CH of fc), 69.42 (s, CH of fc), 71.70 (d, J_{CP} = 67 Hz, C^{ipso}–P of fc), 74.39 (d, J_{CP} = 9 Hz, CH of fc), 76.69 (d, J_{CP} = 10 Hz, CH of fc), 92.95 (s, C^{ipso}–N of fc), 128.76 (d, J_{CP} = 12 Hz, CH of PPh_2), 132.46 (s, CH of PPh_2), 134.12 (d, J_{CP} = 10 Hz, CH of PPh_2), 153.40 (s, C^{ipso} of guanidinium). The signal due to C^{ipso}–P of Ph was not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD): δ 31.2 (s). ESI+ MS: *m*/*z* 652 ([PdCl(**1**^{iPr})]$^+$). IR (DRIFTS): ν_{max} 3357 m, 3260 m, 3115 w, 2982 m, 2939 w, 1634 s, 1609 s, 1482 m, 1471 m, 1437 s, 1394 m, 1375 m, 1331 m, 1213 w, 1193 w, 1169 s, 1132 m, 1103 m, 1063 w, 1032 m, 999 w, 945 w, 871 w, 848 w, 836 m, 751 m, 714 m, 692 s, 665 s, 640 s, 623 w, 571 w, 548 m, 526 s, 503 s, 495 s, 482 s, 447 w. Anal. Calc. for $C_{58}H_{70}Cl_4F_{12}Fe_2N_6P_2Pd_2Sb_2$ (1851.0): C 37.64, H 3.81, N 4.54%. Found: C 37.52, H 3.58, N 4.37%.

Preparation of [PdCl{Ph_2PfcN=C(NHiPr)(NiPr)-κ^3P,N,N'}]·Et_2O (11·Et_2O)

A suspension of **2** (0.69 g, 1.0 mmol) in dry tetrahydrofuran (20 mL), cooled to 0 °C in an ice bath, was treated with a solution of potassium bis(trimethylsilyl)amide (1.0 mL of 1M solution in THF, 1.0 mmol). The resulting mixture was stirred for 15 minutes whilst cooling and then for another 45 minutes at room temperature. During this period, the solid starting material completely dissolved, giving a dark red solution, which was subsequently filtered through a PTFE syringe filter (0.45 μm pore size) and evaporated. The dark red residue was extracted with warm diethyl ether to prepare a saturated solution, which was left standing at –18 °C. After several days, dark red crystals formed, which were collected on a frit, washed with pentane, and dried under vacuum. Yield of **11**·Et_2O: 0.59 g (81%), dark red crystalline solid. Crystals suitable for X-ray diffraction analysis were obtained using the procedure that was followed to prepare the bulk material.

^{1}H NMR (C_6D_6): δ 0.67 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CHMe_2), 1.12 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, OCH$_2$CH_3), 1.57 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CHMe_2), 3.10 (d of sept, $^3J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 6.3 Hz, 1 H, CHMe$_2$), 3.20 (d, $^3J_{HH}$ = 9.7 Hz, 1 H, NH), 3.26 (q, $^3J_{HH}$ = 7.0 Hz, 4 H, OCH_2CH$_3$), 3.31 (d of sept, J_{HP} = 14.9 Hz, $^3J_{HH}$ = 6.3 Hz, 1 H, CHMe$_2$), 3.53 (vt, J' = 1.8 Hz, 2 H, CH of fc), 3.96 (m, 2 H, CH of fc), 4.49 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.77 (m, 2 H, CH of fc), 6.99-7.08 (m, 6 H, PPh$_2$), 7.94-8.05 (m, 4 H, PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 15.57 (s, OCH$_2$CH_3), 23.21 (s, CHMe_2), 24.36 (s, CHMe_2), 43.99 (s, CHMe$_2$), 47.52 (d, J_{CP} = 5 Hz, CHMe$_2$), 65.41 (s, CH of fc), 65.88 (s, OCH$_2$CH$_3$), 67.67 (s, CH of fc), 71.21 (d, J_{CP} = 8 Hz, CH of fc), 77.66 (d, J_{CP} = 12 Hz, CH of fc), 81.66 (d, J_{CP} = 55 Hz, C^{ipso}–P of fc), 116.92 (s, C^{ipso}–N of fc), 127.95 (d, J_{CP} = 12 Hz, CH of PPh$_2$), 130.57 (d, J_{CP} = 2 Hz, CH of PPh$_2$), 131.88 (d, J_{CP} = 50 Hz, C^{ipso}–P of PPh$_2$), 135.18 (d, J_{CP} = 11 Hz, CH of PPh$_2$), 168.73 (d, J_{CP} = 5 Hz, C^{ipso} of guanidinate). ^{31}P{^{1}H} NMR (C_6D_6): δ 35.3 (s). ESI+ MS: *m*/*z* 616 ([Pd(**1**^{iPr} – H)]$^+$), 648 ([Pd(OMe)(**1**^{iPr})]$^+$). IR (DRIFTS): ν_{max} 3323 m, 3074 w, 3054 m, 3022 w, 2975 s, 2961 m, 2932 m, 2870 m, 2810 w, 1596 s, 1586 s, 1483 m, 1450 s, 1436 s, 1399 s, 1381 s, 1364 m, 1348 m, 1324 m, 1253 m, 1205 w, 1194 w, 1169 m, 1149 m, 1126 w, 1100 s, 1074 m, 1045 w, 1026 m, 999 w, 986 m 933 m, 896 w, 867 w, 854 w, 841 w, 816 m, 748 m, 708 m, 694 s, 673 w, 635 m, 591 w, 542 m, 522 m, 508 m, 497 m, 483 m, 455 w, 444 w. Anal. Calc. for $C_{29}H_{33}ClFeN_3PPd$·Et_2O (726.4): C 54.56, H 5.97, N 5.78%. Found: C 54.08, H 6.02, N 5.63%.

Reaction of 11 with HCl

In a microscale experiment, complex **11**·Et_2O (18.2 mg, 0.025 mmol) was dissolved in $CDCl_3$ (0.6 mL) to give a red solution. Then, a solution of HCl in methanol (46 μL of 0.5M, 0.025 mmol) was added and the solution was stirred at room temperature for 30 minutes, and the mixture was analysed by NMR spectroscopy. The ^{1}H and ^{31}P{^{1}H} NMR spectra confirmed quantitative formation of complex **2**.

Preparation of [Pd{Ph_2PfcN=C(NHiPr)(NiPr)-κ^{3}P,N,N'}(MeCN)][SbF_6] (12)

A suspension of **11**·Et_2O (363 mg, 0.50 mmol) and silver(I) hexafluoroantimonate(V) (172 mg, 0.50 mmol) in dry acetonitrile (10 mL) was stirred at room temperature, protected from direct daylight, for 1 h. Subsequently, the suspension was filtered through a short Celite pad, and the clear, dark red filtrate was evaporated under reduced pressure. The oily residue was dried in several freeze-pump cycles, leaving a dark red solid. Yield of **12**: 412 mg (92%), red powder. *Note: The product was contaminated with acetonitrile and prone to decomposition. Therefore, no reliable microanalytical data could be collected, but the product was sufficiently pure for use in further syntheses.*

^{1}H NMR (CD_2Cl_2): δ 0.91 (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH*Me*$_2$), 1.69 (s, 3 H, MeCN–Pd), 2.94 (d of sept, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 6.4 Hz, 1 H, C*H*Me$_2$), 3.38 (sept, $^3J_{HH}$ = 6.4 Hz, 1 H, C*H*Me$_2$), 3.78 (d, $^3J_{HH}$ = 9.2 Hz, 1 H, NH), 3.91 (vt, J' = 1.9 Hz, 2 H, CH of fc), 4.49 (m, 2 H, CH of fc), 4.56 (vt, J' = 1.9 Hz, 2 H, CH of fc), 5.10 (vq, J' = 2.1 Hz, 2 H, CH of fc), 7.51-7.58 (m, 4 H, PPh_2), 7.59-7.66 (m, 2 H, PPh_2), 7.77-7.86 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 2.51 (s, *Me*CN–Pd), 23.13 (s, CH*Me*$_2$), 24.33 (s, CH*Me*$_2$), 44.43 (s, *C*HMe$_2$), 46.31 (d, J_{CP} = 4 Hz, *C*HMe$_2$), 66.56 (s, CH of fc), 68.46 (s, CH of fc), 72.95 (d, J_{CP} = 8 Hz, CH of fc), 77.10 (d, J_{CP} = 60 Hz, C^{ipso}–P of fc), 78.74 (d, J_{CP} = 13 Hz, CH of fc), 116.31 (s, C^{ipso}–N of fc), 123.84 (s, Me*C*N–Pd), 129.26 (d, J_{CP} = 11 Hz, CH of PPh_2), 129.97 (d, J_{CP} = 51 Hz, C^{ipso}–P of PPh_2), 132.22 (d, J_{CP} = 3 Hz, CH of PPh_2), 134.15 (d, J_{CP} = 12 Hz, CH of PPh_2), 171.07 (d, J_{CP} = 5 Hz, C^{ipso} of guanidinate). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 36.1 (s). ESI+ MS: *m*/*z* 616 ([Pd(**1^{iPr}** – H)]$^+$), 706 ([Pd(**1^{iPr}** – H)(MeOH)(Me_2CO)]$^+$). IR (DRIFTS): ν_{max} 3384 m, 3056 w, 2974 m, 2935 m, 2873 w, 2326 m, 1584 s, 1483 1452 m, 1437 s, 1405 s, 1369 m, 1327 m, 1262 w, 1170 m, 1126 w, 1101 m, 1073 w, 1030 m, 999 w, 987 w, 933 w, 897 w, 820 m, 750 m, 712 w, 698 m, 660 s, 568 w, 542 m, 524 m, 494 m, 483 m, 445 w.

Reaction of 12 with HCl

A solution of hydrogen chloride (0.4 mL, 0.5 M in methanol, 0.2 mmol) was introduced to a solution of **12** (179 mg, 0.20 mmol) in dry dichloromethane (5 mL), and the resulting red mixture was stirred at room temperature for 1 h, filtered through a PTFE syringe filter (pore size 0.45 μm), and evaporated. The dark red residue was analysed by NMR spectroscopy, which confirmed the selective formation of [PdCl{Ph_2PfcN=C(NH*i*Pr)$_2$-κ^3*P,N,Fe*}][SbF_6] (**3**).[1] The crude product was crystallised from dichloromethane/methyl *tert*-butyl ether, producing **3** as a red crystalline solid. Yield: 135 mg (76%). The analytical data (NMR) matched those in the literature.[1]

Preparation of [Pd{Ph_2PfcN=C(NHiPr)(NiPr)-κ^{3}P,N,N'}(dmap)][SbF_6] (13)

Method A: A mixture of crude **12** (179 mg, 0.20 mmol) and 4-(dimethylamino)pyridine (24 mg, 0.20 mmol) in dry dichloromethane (5 mL) was stirred at room temperature for 1 h. The resulting dark red solution was filtered through a PTFE syringe filter (0.45 μm pore size) and layered with methyl *tert*-butyl ether. Crystallisation over several days afforded dark red crystals, which were isolated by suction, washed with pentane, and dried under vacuum. Yield of **13**: 142 mg (73%), dark red crystalline solid.

Method B: A dark red suspension of **11**·Et_2O (145 mg, 0.20 mmol) and silver(I) hexafluoroantimonate(V) (69 mg, 0.20 mmol) in dry acetonitrile (10 mL) was stirred at room temperature, protected from daylight, for 1 h. The precipitated silver(I) chloride was filtered off using PTFE syringe filter (0.45 μm pore size), and the dark red filtrate was treated with a solution of 4-(dimethylamino)pyridine (24 mg, 0.20 mmol) in dry dichloromethane (2 mL). The mixture was stirred at room temperature for another 30 minutes before evaporating the volatiles under reduced pressure. The dark red solid residue was redissolved in dichloromethane (3 mL), and the solution was layered with methyl *tert*-butyl ether. Crystallisation over several days afforded dark red crystals, which were isolated by suction, washed with pentane, and dried under vacuum. Yield of **13**: 160 mg (82%), dark red crystalline solid. Crystals used for structure determination were obtained using the same procedure.

^{1}H NMR (CD_2Cl_2): δ 0.82 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CH*Me*$_2$), 0.94 (d, $^3J_{HH}$ = 6.4 Hz, 6 H, CH*Me*$_2$), 2.90 (s, 6 H, NMe_2), 3.01 (d of sept, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 6.4 Hz, 1 H, C*H*Me_2), 3.35 (sept, $^3J_{HH}$ = 6.3 Hz, 1 H, C*H*Me_2), 3.69 (d, $^3J_{HH}$ = 9.4 Hz, 1 H, NH), 3.90 (vt, J' = 2.1 Hz, 2 H, CH of fc), 4.49 (vq, J' = 1.6 Hz, 2 H, CH of fc), 4.99 (vq, J' = 2.1 Hz, 2 H, CH of fc), 5.32 (vt, J' = 1.1 Hz, 2 H, CH of fc), 6.12 (m, 2 H, CH of dmap), 7.31-7.37 (m, 4 H, PPh_2), 7.43-7.49 (m, 2 H, PPh_2), 7.58-7.66 (m, 4 H, PPh_2), 7.71 (m, 2 H, CH of dmap). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 23.24 (s, CH*Me*$_2$), 24.17 (s, CH*Me*$_2$), 39.40 (s, NMe_2), 44.42 (s, *C*HMe_2), 46.36 (d, J_{CP} = 4 Hz, *C*HMe_2), 66.33 (s, CH of fc), 67.90 (s, CH of fc), 72.64 (d, J_{CP} = 8 Hz, CH of fc), 77.77 (d, J_{CP} = 59 Hz, C^{ipso}–P of fc), 78.15 (d, J_{CP} = 13 Hz, CH of fc), 108.50 (s, CH of dmap), 115.65 (d, J_{CP} = 1 Hz, C^{ipso}–N of fc), 128.96 (d, J_{CP} = 11 Hz, CH of PPh_2), 129.74 (d, J_{CP} = 50 Hz, C^{ipso}–P of PPh_2), 131.55 (d, J_{CP} = 3 Hz, CH of PPh_2), 134.04 (d, J_{CP} = 12 Hz, CH of PPh_2), 150.67 (d, J_{CP} = 1 Hz, CH of dmap), 154.81 (s, C^{ipso}–N of dmap), 170.45 (d, J_{CP} = 4 Hz, C^{ipso} of guanidinate). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 35.9 (s). ESI+ MS: *m*/*z* 616 ([Pd(**1**^{iPr} – H)]$^+$), 738 ([Pd(**1**^{iPr} – H)(dmap)]$^+$). IR (DRIFTS): ν_{max} 3387 m, 3091 w, 3054 w, 2971 m, 2930 m, 2870 w, 1617 s, 1578 s, 1537 s, 1482 m, 1437 m, 1399 s, 1389 s, 1365 m, 1326 m, 1310 w, 1252 m, 1225 s, 1174 m, 1123 w, 1102 m, 1073 m, 1026 m, 999 w, 983 w, 948 w, 931 w, 896 w, 867 w, 856 w, 834 w, 816 m, 750 m, 711 w, 700 m, 657 s, 635 w, 541 m, 522 m, 510 m, 495 m, 484 m, 445 w. Anal. Calc. for $C_{36}H_{43}F_6FeN_5PPdSb$ (974.7): C 44.36, H 4.45, N 7.18%. Found: C 44.36, H 4.12, N 7.11%.

Preparation of [Pd{Ph_2PfcN=C(NHiPr)(NiPr)-κ^{3}P,N,N'}(PhPy-κN)][SbF_6] (14)

A solution of crude **12** (179 mg, 0.20 mmol) and 2-phenylpyridine (34 mg, 0.20 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 1 h. The resulting mixture was filtered through a PTFE syringe filter (pore size 0.45 μm), and the dark red filtrate was concentrated under reduced pressure to approximately 3 mL and layered with hexane. Dark red crystals, formed during several days (and used for X-ray structure determination as well), were collected on a frit suction, washed with pentane, and dried under vacuum. Yield of **14**: 142 mg (70%), dark red crystalline solid.

^{1}H NMR (CD_2Cl_2): δ 0.85 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, CH*Me*$_2$), 0.91 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, CH*Me*$_2$), 1.02 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH*Me*$_2$), 1.09 (d, $^3J_{HH}$ = 6.3 Hz, 3 H, CH*Me*$_2$), 3.03 (d of sept, J = 9.0 Hz, $^3J_{HH}$ = 6.5 Hz, 1 H, C*H*Me$_2$), 3.55 (d of sept, J_{HP} = 10.4 Hz, $^3J_{HH}$ = 6.3 Hz, 1 H, C*H*Me$_2$), 3.74 (m, 1 H, CH of fc), 3.79 (d, $^3J_{HH}$ = 9.3 Hz, 1 H, NH), 3.82 (m, 1 H, CH of fc), 3.89 (m, 1 H, CH of fc), 4.02 (m, 1 H, CH of fc), 4.20 (broad s, 1 H, CH of fc), 4.31 (m, 1 H, CH of fc), 4.44 (m, 1 H, CH of fc), 4.62 (m, 1 H, CH of fc), 6.63 (m, 2 H, PPh_2), 7.05 (m, 2 H, PPh_2), 7.20 (m, 1 H, Phpy), 7.26-7.33 (m, 2 H, Phpy + PPh_2), 7.55 (m, 2 H PPh_2), 7.62-7.74 (m, 2 H, Phpy + PPh_2), 7.79-7.89 (m, 3 H, Phpy), 8.06-8.15 (m, 4 H, Phpy + PPh_2), 8.99 (m, 1 H, Phpy). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 22.72 (s, CH*Me*$_2$), 23.75 (s, CH*Me*$_2$), 23.92 (s, CH*Me*$_2$), 24.71 (s, CH*Me*$_2$), 44.30 (s, *C*HMe$_2$), 47.23 (d, J_{CP} = 5 Hz, *C*HMe$_2$), 66.00 (s, CH of fc), 66.82 (s, CH of fc), 68.05 (s, CH of fc), 68.38 (s, CH of fc), 70.19 (d, J_{CP} = 7 Hz, CH of fc), 74.15 (d, J_{CP} = 10 Hz, CH of fc), 75.72 (d, J_{CP} = 19 Hz, CH of fc), 77.57 (d, J_{CP} = 61 Hz, C^{ipso}–P of fc), 78.59 (d, J_{CP} = 6 Hz, CH of fc), 116.27 (d, J_{CP} = 2 Hz, C^{ipso}–N of fc), 124.40 (s, CH of PhPy), 127.43 (s, CH of PhPy), 128.50 (d, J_{CP} = 10 Hz, CH of PPh_2), 128.88 (d, J_{CP} = 54 Hz, C^{ipso}–P of PPh_2), 129.15 (d, J_{CP} = 11 Hz, CH of PPh_2), 129.49 (s, CH of PhPy), 129.55 (s, CH of PhPy), 130.94 (d, J_{CP} = 3 Hz, CH of PPh_2), 131.54 (s, CH of PhPy), 131.80 (d, J_{CP} = 11 Hz, CH of PPh_2), 132.64 (d, J_{CP} = 3 Hz, PPh_2), 135.96 (d, J_{CP} = 13 Hz, CH of PPh_2), 138.52 (s, C^{ipso} of Phpy), 139.77 (s, CH of PhPy), 152.95 (s, CH of PhPy), 161.02 (s, C^{ipso} of PhPy), 170.77 (d, J_{CP} = 4 Hz, C^{ipso} of guanidinate). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 35.5 (s). ESI+ MS: *m*/*z* 616 ([Pd(**1**^{iPr} – H)]$^+$), 771 ([Pd(**1**^{iPr} – H)(PhPy)]$^+$). IR (DRIFTS): ν_{max} 3392 m, 3093 w, 3078 w, 3060 w, 2970 m, 2933 w, 2873 w, 1603 m, 1563 s, 1473 s, 1453 m, 1437 s, 1407 s, 1388 m, 1377 m, 1368 m, 1361 m, 1317 m, 1267 m, 1228 w, 1202 w, 1180 m, 1163 m, 1131 w, 1124 w, 1101 m, 1079 w, 1033 m, 1000 w, 985 w, 929 w, 866 w, 827 w, 813 m, 794 w, 761 s, 753 m, 744 m, 701 s, 660 s, 644 m, 545 m, 524 m, 504 m, 484 m, 441 w, 430 w. Anal. Calc. for $C_{40}H_{42}F_6FeN_4PPdSb$ (1007.8): C 47.67, H 4.20, N 5.56%. Found: C 47.47, H 4.18, N 5.40%.

Preparation of [Pd(μ-OH){Ph_2PfcN=C(NHiPr)$_2$-κ^{2}P,N}]$_2$[SbF_6]$_2$ (15)

Crude complex **12** (179 mg, 0.20 mmol) was dissolved in "wet" dichloromethane (10 mL, shaken with water prior to use) to produce a dark red solution, which was filtered through a PTFE

syringe filter (0.45 μm pore size) and layered with diethyl ether. Crystallisation at –18°C, over several days, provided a microcrystalline solid, which was isolated by suction, washed with pentane, and dried under vacuum. Yield of **15**·2CH_2Cl_2: 160 mg (84%), red-orange powder. *Note: The product was obtained as a dichloromethane solvate, which gradually released the solvent as indicated by elemental analysis.* The crystals used for structure determination were obtained by liquid phase diffusion of diethyl ether into a dichloromethane solution of the complex at –18°C.

^{1}H NMR (CD_3NO_2): δ –4.29 (s, OH), –3.11 (s, OH), –2.61 (s, OH). Signals due to *iso*-propyl (0.7-1.6 ppm), ferrocene (3.7-5.8 ppm) and PPh_2 protons (7.3-8.1 ppm) were severely broadened and overlapped due to molecular dynamics and to the presence of several stereoisomers. Hence, they could not be interpreted individually. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 29.0, 29.9, 30.5 (3× s). ESI+ MS: *m*/*z* 528 ([**1**^{iPr}**H** + O]$^+$), 616 ([Pd(**1**^{iPr} – H)]$^+$), 648 ([Pd(MeO)(**1**^{iPr})]$^+$). IR (DRIFTS): ν_{max} 3674 w, 3566 m, 3372 m, 3290 w, 3058 w, 2978 m, 2933 w, 2874 w, 1601 s, 1587 s, 1485 m, 1463 m, 1438 s, 1389 m, 1372 m, 1357 w, 1337 w, 1312 m, 1249 w, 1196 w, 1170 m, 1131 m, 1103 m, 1028 m, 1000 w, 930 w, 824 m, 756 m, 747 m, 704 m, 695 m, 661 s, 543 m, 534 m, 518 m, 497 s, 485 s, 454 m. Anal. Calc. for $C_{58}H_{70}F_{12}Fe_2N_6O_2P_2Pd_2Sb_2$·½$CH_2Cl_2$ (1783.7): C 39.39, H 4.01, N 4.71%. Found: C 39.14, H 4.06, N 5.03%.

Preparation of [Pd(acac-κ^{2}O,O′){Ph$_2$PfcN=C(NHiPr)$_2$-κ^{2}P,N}][SbF$_6$] (16)

A mixture of crude **12** (179 mg, 0.20 mmol) and acetylacetone (20 mg, 0.20 mmol) in dry dichloromethane (10 mL) was stirred at room temperature for 1 h. The resulting red solution was filtered through a PTFE syringe filter (pore size 0.45 μm), and all volatiles evaporated under reduced pressure. The crude product was dissolved in dichloromethane and layered with hexane. Red crystals (of sufficient quality for X-ray structure elucidation), which formed during several days, were isolated by suction, washed with pentane, and dried under vacuum. Yield of **16**: 144 mg (76%), red crystalline solid.

^{1}H NMR (CD_2Cl_2): δ1.13 (d, $^3J_{HH}$ = 6.4 Hz, 12 H, CH*Me*$_2$), 1.61 (s, 3 H, CO*Me*), 2.03 (s, 3 H, CO*Me*), 3.75 (broad s, 2 H, C*H*Me$_2$), 4.06 (broad s, 1 H, CH of fc), 4.37 (broad s, 1 H, CH of fc), 4.46 (broad s, 2 H, CH of fc), 4.69 (broad m, 4 H, CH of fc + NH), 5.09 (broad s, 1 H, CH of fc), 5.24 (broad s, 1 H, CH of fc), 5.49 (s, 1 H, COC*H*CO), 7.34-7.93 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.14 (broad s, CH*Me*$_2$), 23.69 (broad s, CH*Me*$_2$), 26.02 (d, J_{CP} = 2 Hz, CO*Me*), 26.82 (d, J_{CP} = 8 Hz, CO*Me*), 46.82 (s, *C*HMe), 66.69 (broad s, CH of fc), 67.74 (broad s, CH of fc), 69.32 (broad s, CH of fc), 70.18 (d, J_{CP} = 65 Hz, C^{ipso}–P of fc), 70.89 (broad s, CH of fc), 72.28 (broad s, CH of fc), 74.57 (broad s, CH of fc), 76.47 (broad s, CH of fc), 76.87 (broad s, CH of fc), 101.08 (s, CO*C*HCO), 112.15 (d, J_{CP} = 2 Hz, C^{ipso}–N of fc), 128.53 (broad d, J_{CP} = 11 Hz, CH of PPh_2), 129.77 (broad d, J_{CP} = 8 Hz, CH of PPh_2), 131.76 (broad s, CH of PPh_2), 132.83 (broad s, CH of PPh_2), 133.54 (broad s, CH of PPh_2), 133.85 (broad s, CH of PPh_2), 160.14 (s, C^{ipso} of guanidine), 186.14 (s, *C*OMe), 188.08

(d, J_{CP} = 3 Hz, *C*OMe). Signals due to C^{ipso}–P of PPh_2 were not found, presumably due to overlaps. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.3 (s). ESI+ MS: *m*/*z* 616 ([Pd(**1**^{iPr} – H)]$^+$), 716 ([Pd(acac)(**1**^{iPr})]$^+$). IR (DRIFTS): ν_{max} 3405 m, 3078 w, 2988 m, 2937 w, 2875 w, 1577 s, 1519 s, 1483 w, 1465 m, 1447 m, 1437 m, 1386 s, 1375 s, 1369 s, 1338 w, 1308 m, 1272 w, 1251 w, 1199 w, 1170 m, 1130 w, 1105 m, 1095 w, 1061 w, 1025 m, 1001 w, 936 w, 875 w, 858 w, 821 m, 801 w, 752 m, 747 m, 714 w, 698 m, 660 s, 643 m, 628 w, 569 w, 543 w, 520 s, 505 m, 483 m, 450 m, 427 w. Anal. Calc. for $C_{34}H_{41}F_6FeN_3O_2PPdSb$ (952.7): C 42.86, H 4.34, N 4.41%. Found: C 42.58, H 4.18, N 4.24%.

Reaction of 12 and 13 with alkynes

Experiment A. In a microscale experiment, a mixture of **12** (22.3 mg, 0.025 mmol) and 1-ethynyl-4-nitrobenzene (3.7 mg, 0.025 mmol) was dissolved in CD_2Cl_2 (0.6 mL) and the red solution was stirred at room temperature for 3 h. Then, it was filtered through a PTFE syringe filter (0.45 μm porosity) and analysed by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −2.6 (s, major component).

Experiment B. Solid **13** (4.9 mg, 5 μmol) was loaded into a Schlenk tube and an argon atmosphere was established. 4-Ethynyltoluene (0.13 mL, 1.0 mmol) was added *via* a syringe followed by dry toluene (2 mL). The resulting mixture was stirred at 80°C for 24 hours, during which time the yellow suspension turned into a red solution. The resulting solution was filtered through a PTFE filter (0.45 μm porosity) and the volatiles were evaporated at reduced pressure. The red liquid residue was analysed by NMR spectroscopy.

X-Ray crystallography

Full-set diffraction data (±*h*±*k*±*l*) were collected on a Bruker D8 VENTURE Kappa Duo diffractometer with a PHOTON detector equipped with a Cryostream Cooler (Oxford Cryosystems). The diffraction data for complex **4**, which crystallised in the form of small needle-like crystals, were collected using CuKα radiation. The compound was isostructural to its previously reported Pd(II) analogue **2**.[1] In all other cases, Mo Kα radiation was used.

The structures were solved using direct methods (SHELXT-2014[3]) and refined with a full-matrix least squares routine based on F^2 (SHELXL-2017[4]). The non-hydrogen atoms were refined with anisotropic displacement parameters. The guanidine hydrogen atoms (NH) were identified on difference density maps and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(N)$. Hydrogens residing on the carbon atoms were placed in their theoretical positions and refined similarly. Relevant crystallographic data and structure refinement parameters are outlined in Table S1.

The partly disordered solvent molecules in the structure of **6**·$CHCl_3$, (**1**^{iPr}**H**)[SbF_6]·CH_2Cl_2 and **15**·$2CH_2Cl_2$ were modelled with two positions for one chlorine atom (in the latter, one

isopropyl group was also refined with positions for the methyl substituents). Conversely, the solvent molecules in the structure of **7**·C_6H_5F·$C_5H_{12}O$ were extensively disordered within large structural voids (2636 Å^3). Hence, their contribution to the overall scattering was removed by PLATON/SQUEEZE.[5] In total, 838 electrons were eliminated per unit cell, which corresponds to the expected value (800 electrons). In addition, one isopropyl moiety was disordered and required refinement over two positions. Even so, one of the solvent molecules in the structure of **8**·2.5$CHCl_3$ was severely disordered and thus treated similarly (one $CHCl_3$ molecule in the unit cell; 55 electrons removed, 58 electrons expected). The remaining two chloroform molecules in the asymmetric unit were refined, and some of their chlorine atoms were split over two positions. In the structure of **13**, one of the isopropyl groups also exerted a positional disorder and was refined with two positions for its methyl groups. A similar refinement was applied for **16**, whose hexafluoroantimonate ions also required refinement over two positions.

All geometric calculations were performed and the structural diagrams constructed using a recent version of the PLATON program.[6] The corresponding 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	(**1**^{iPr}**H**)Cl	(**1**^{iPr}**H**)[SbF_6]·CH_2Cl_2	**4**
Formula	$C_{29}H_{35}ClFeN_3P$	$C_{30}H_{37}Cl_2F_6FeN_3PSb$	$C_{29}H_{34}Cl_2FeN_3PPt$
M	547.87	833.09	777.40
m	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a [Å]	13.9859(6)	9.5123(5)	13.1436(4)
b [Å]	9.5728(4)	9.6515(6)	13.0775(4)
c [Å]	20.6633(9)	20.813(1)	16.9749(4)
α [°]	90	95.262(2)	90
β [°]	99.693(2)	98.024(2)	98.675(2)
γ [°]	90	114.946(2)	90
V [Å]^3	2727.0(2)	1691.3(2)	2884.4(1)
Z	4	2	4
μ(Mo Kα) [mm^{-1}]	0.732	1.491	15.381
Diffrns collected	42321	48922	25775
Independent diffrns	6268	7771	4754
Observed[a] diffrns	5720	7285	3749
R_{int}[b] [%]	2.15	2.07	8.20
No. of parameters	323	426	338
R[b] obsd diffrns [%]	2.61	3.79	3.54
R, *wR*[b] all data [%]	2.98, 6.63	4.03, 9.83	5.73, 7.01
Δρ [e Å^{-3}]	0.49, –0.37	1.85, –1.38	0.87, –0.88
CCDC deposition no.	2105424	2105425	2105420

[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	**5**·2$CHCl_3$	**6**·$CHCl_3$	**7**·C_6H_5F·MTBE
Formula	$C_{124}H_{94}B_2Cl_8F_{48}Fe_2N_6P_2Pt_2$	$C_{37}H_{39}BrCl_3FeN_4PPd$	$C_{47}H_{55}F_7FeN_4OPPdSb$
M	3449.09	919.20	1139.92
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*–1 (no. 2)	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
a [Å]	14.1749(4)	11.4217(5)	19.1783(7)
b [Å]	14.2935(4)	12.2753(5)	23.3714(8)
c [Å]	17.5227(4)	13.5820(6)	21.2267(6)
α [°]	70.720(1)	88.887(1)	90
β [°]	89.867(1)	84.124(2)	92.220(1)
γ [°]	83.515(1)	86.811(1)	90
V [Å]^3	3327.4(2)	1891.1(1)	9507.2(5)
Z	1	2	8
μ(Mo Kα) [mm^{-1}]	2.612	2.202	1.340
Diffrns collected	44765	41596	123433
Independent diffrns	13077	8639	21853
Observed[a] diffrns	12097	8344	15776
R_{int}[b] [%]	2.78	1.91	6.88
No. of parameters	878	441	934
R[b] obsd diffrns [%]	2.81	2.49	4.79
R, wR[b] all data [%]	3.18, 6.95	2.59, 7.14	7.25, 13.92
Δρ [e Å^{-3}]	3.09, –1.08	0.63, –1.13	2.95, –2.26
CCDC deposition no.	2105421	2105422	2105423

Table S1 continued

Compound	**8**·2.5$CHCl_3$	**9**-SbF_6	**10**·2CH_2Cl_2
Formula	$C_{31.5}H_{37.5}Cl_{10.5}FeN_3PPd$	$C_{58}H_{70}Cl_2F_{12}Fe_2N_6P_2PdSb_2$	$C_{60}H_{74}Cl_8F_{12}Fe_2N_6P_2Pd_2Sb_2$
M	1023.59	1673.64	2020.79
Crystal system	triclinic	triclinic	triclinic
Space group	*P*–1 (no. 2)	*P*–1 (no. 2)	*P*–1 (no. 2)
a [Å]	12.5962(5)	9.830(2)	13.7155(9)
b [Å]	13.5142(6)	10.785 (2)	15.400(1)
c [Å]	14.1211(6)	16.810(2)	19.757(1)
α [°]	114.103(1)	90.376(8)	88.358(2)
β [°]	93.921(1)	104.974(6)	85.451(2)
γ [°]	108.668(1)	112.399(5)	65.734(2)
V [Å]^3	2022.9(2)	1580.6(4)	3792.3(5)
Z	2	1	2
μ(Mo Kα) [mm^{-1}]	1.564	1.784	1.933
Diffrns collected	40304	32266	55268
Independent diffrns	9326	7260	14923
Observed[a] diffrns	8566	6401	11850
R_{int}[b] [%]	1.74	3.40	3.19
No. of parameters	433	389	855
R[b] obsd diffrns [%]	2.83	3.64	4.93
R, wR[b] all data [%]	3.20, 6.73	4.38, 7.85	6.60, 13.77
Δρ [e Å^{-3}]	1.62, –1.04	0.99, –0.96	2.53, –1.54
CCDC deposition no.	2105426	2105427	2105428

Table S1 continued

Compound	**11**·Et_2O	**13**	**14**
Formula	$C_{33}H_{43}ClFeN_3OPPd$	$C_{36}H_{43}F_6FeN_5PPdSb$	$C_{40}H_{42}F_6FeN_4PPdSb$
M	726.37	974.72	1007.74
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$ (no. 14)	*Pbca* (no. 61)	*Cc* (no. 9)
a [Å]	13.2618(6)	17.1620(9)	10.8193(5)
b [Å]	11.2018(5)	20.788(1)	26.314(1)
c [Å]	21.993(1)	21.742(1)	14.9826(6)
α [°]	90	90	90
β [°]	101.127(1)	90	108.307(1)
γ [°]	90	90	90
V [Å]^3	3205.8(3)	7756.9(7)	4049.6(3)
Z	4	8	4
μ(Mo Kα) [mm^{-1}]	1.177	1.622	1.556
Diffrns collected	48171	93777	75080
Independent diffrns	7383	8927	9237
Observed[a] diffrns	6938	8331	9196
R_{int}[b] [%]	2.02	2.13	1.89
No. of parameters	376	488	491
R[b] obsd diffrns [%]	2.00	2.07	1.38
R, wR[b] all data [%]	2.22, 5.13	2.32, 4.97	1.40, 3.55
Δρ [e Å^{-3}]	0.40, –0.77	0.80, –0.67	0.42, –0.50
CCDC deposition no.	2105429	2105430	2105431

Table S1 continued

Compound	**15**·2CH_2Cl_2	**16**	**1^{iPr}O**
Formula	$C_{60}H_{74}Cl_4F_{12}Fe_2N_6O_2P_2Pd_2Sb_2$	$C_{34}H_{41}F_6FeN_3O_2PPdSb$	$C_{29}H_{34}FeN_3OP$
M	1910.99	952.67	527.41
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	12.9629(5)	19.7508(6)	11.2137(6)
b [Å]	15.5152(7)	16.9406(6)	18.859(1)
c [Å]	17.6064(8)	21.6364(8)	13.3837(7)
α [°]	90	90	90
β [°]	95.763(2)	94.266(1)	113.500(2)
γ [°]	90	90	90
V [Å]^3	3523.1(3)	7219.3(4)	2595.6(2)
Z	2	8	4
μ(Mo Kα) [mm^{-1}]	1.931	1.743	0.670
Diffrns collected	43206	130083	27508
Independent diffrns	8047	16550	5953
Observed[a] diffrns	7602	15058	5332
R_{int}[b] [%]	2.09	3.11	2.53
No. of parameters	423	1030	320
R[b] obsd diffrns [%]	2.42	2.37	2.84
R, wR[b] all data [%]	2.58, 5.80	2.75, 6.05	3.41, 6.95
Δρ [e Å^{-3}]	0.71, –0.92	0.94, –0.62	O.37, –0.36
CCDC deposition no.	2105432	2105433	2105434

ADDITIONAL STRUCTURAL DIAGRAMS

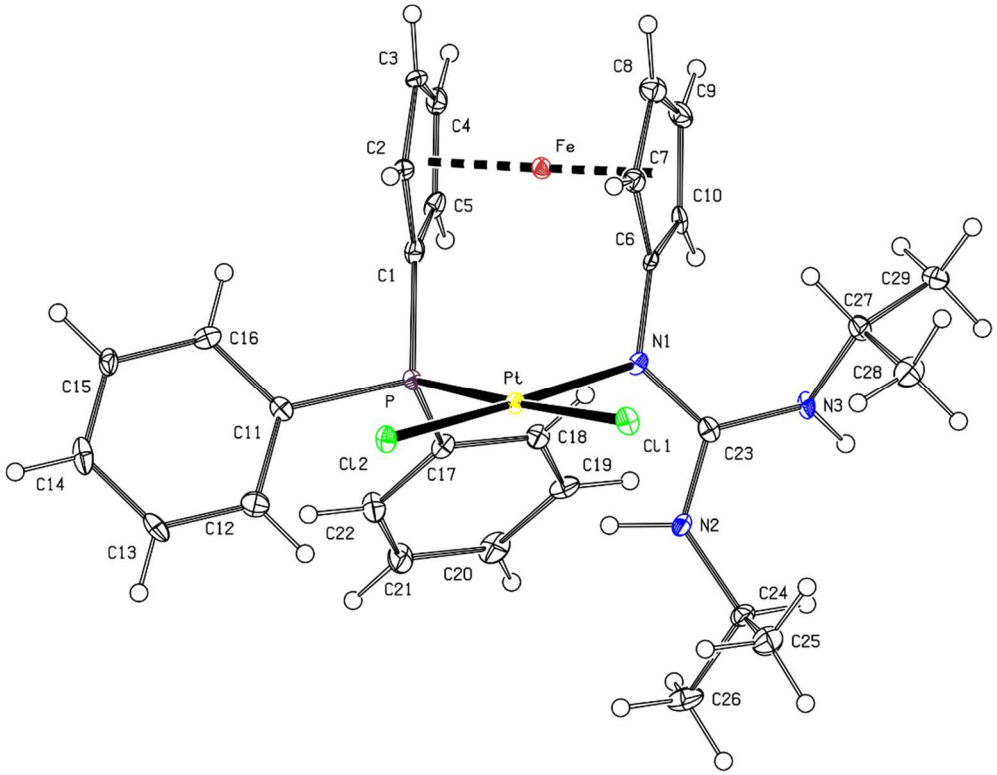

Figure S1. PLATON plot (30% probability) of molecular structure of **4**

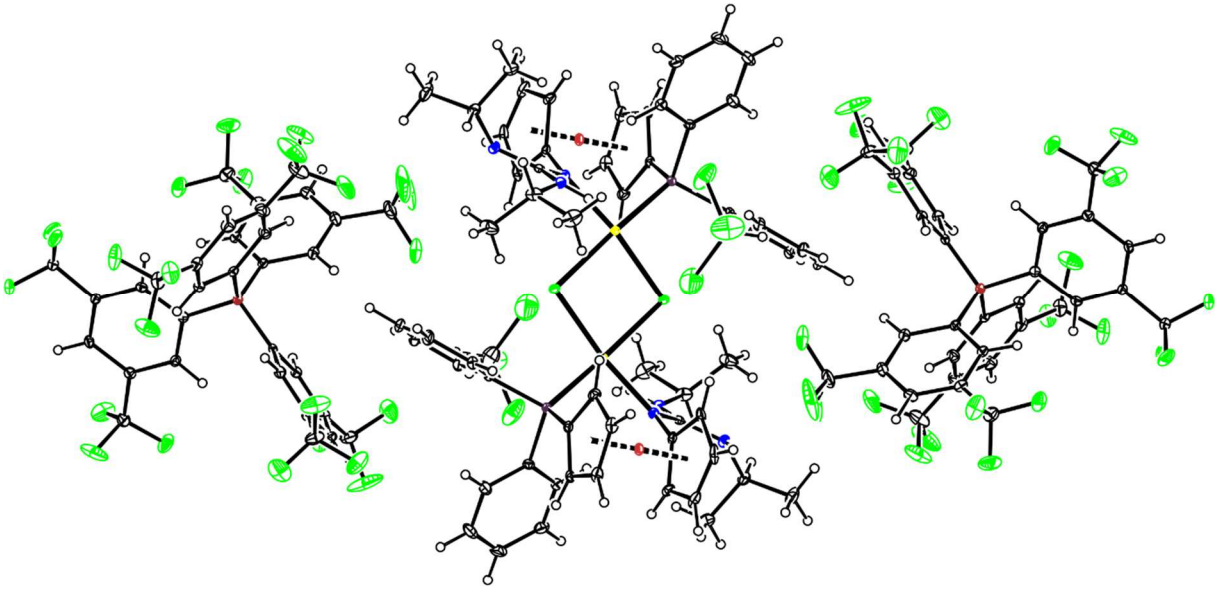

Figure S2. Complete PLATON plot (30% probability) for **5**·2$CHCl_3$

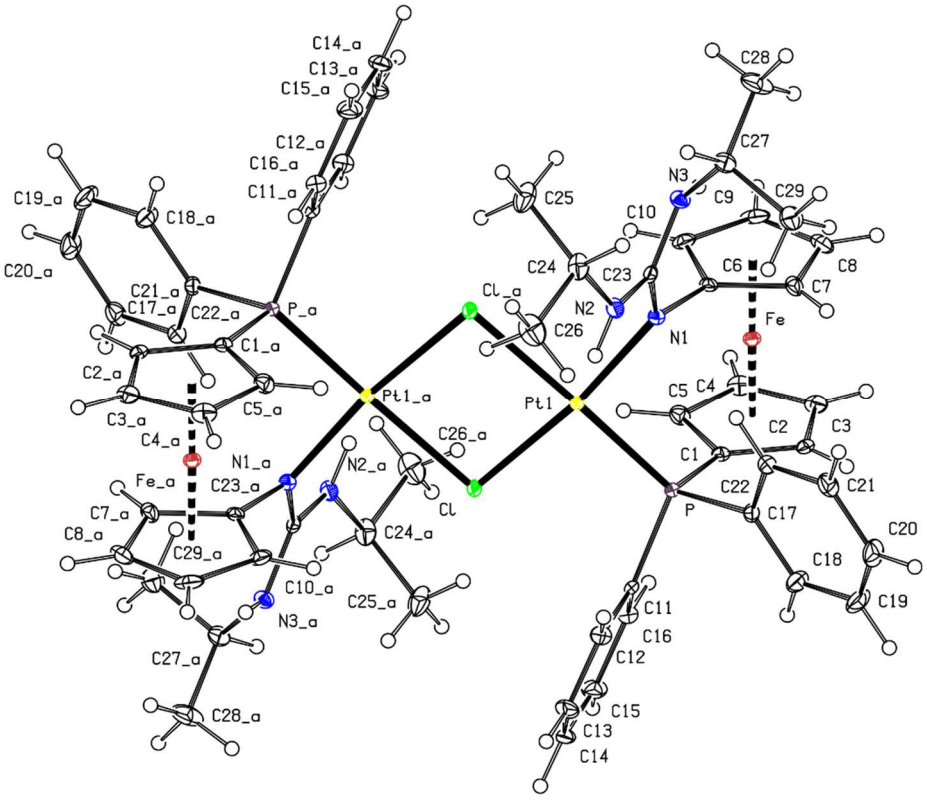

Figure S3. PLATON plot (30% probability) of the complex cation in the structure of **5**·2$CHCl_3$ (the cation resides on the crystallographic inversion centre)

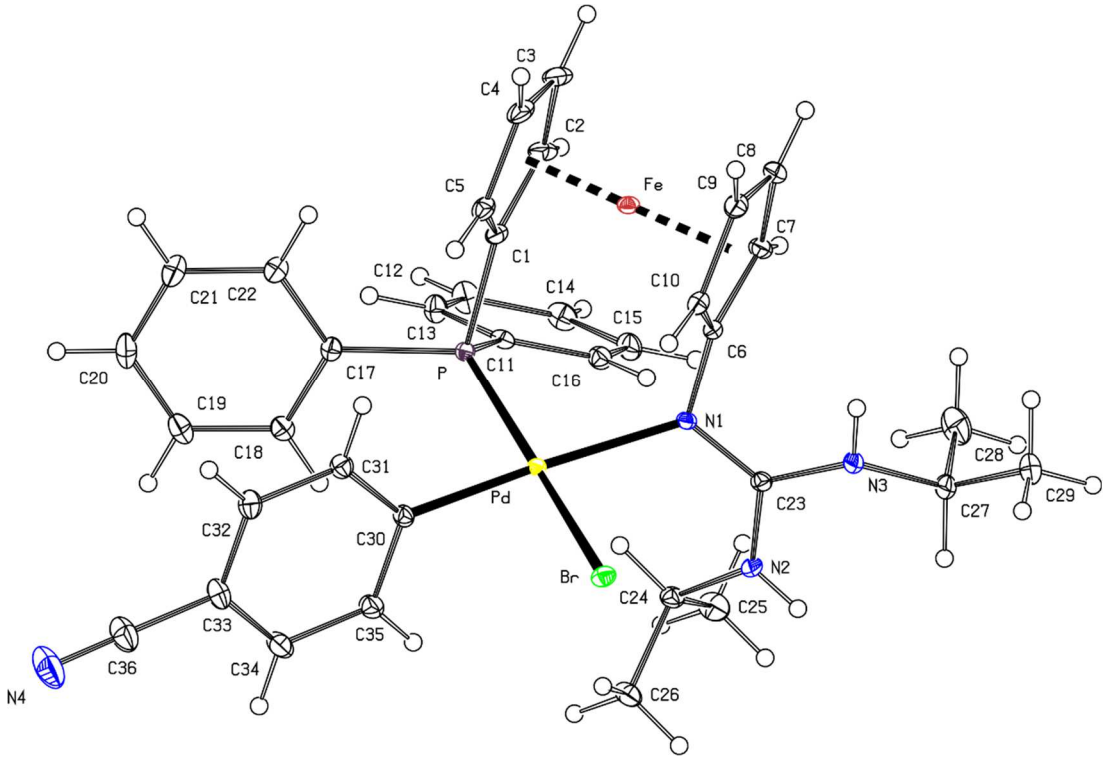

Figure S4. PLATON plot (30% probability) of the complex molecule in the structure of **6**·$CHCl_3$

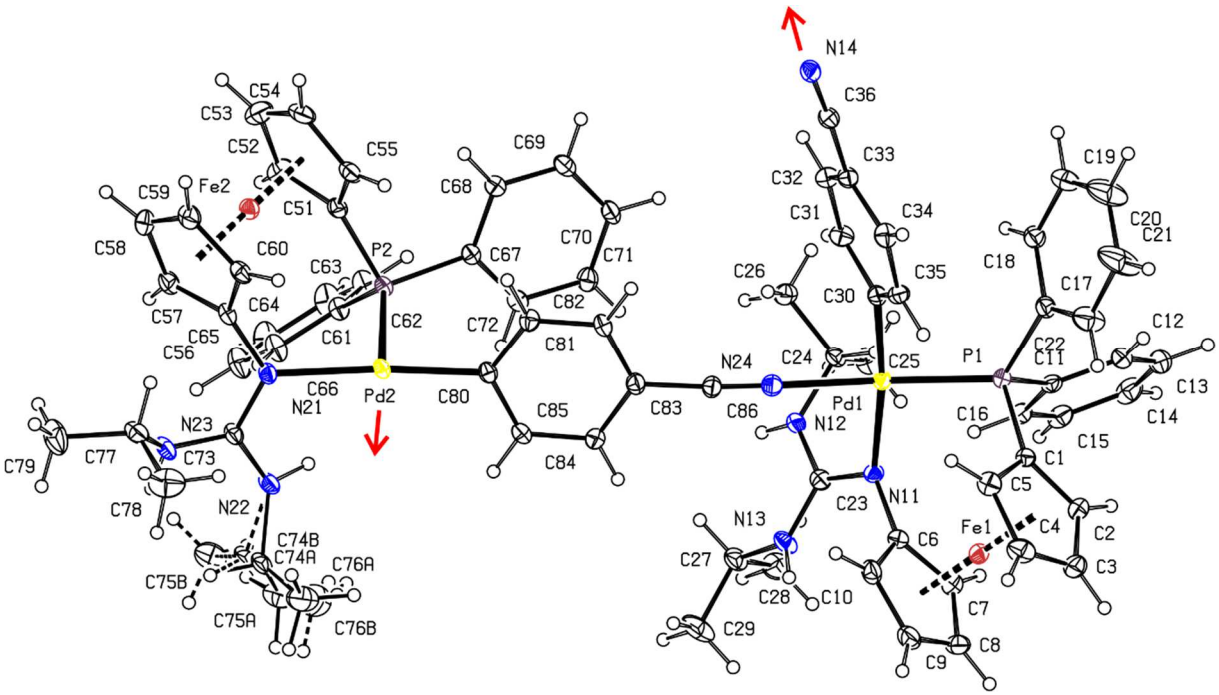

Figure S5. PLATON plot (30% probability) of the repeating unit in the crystal structure of **7**·C_6H_5F·$C_5H_{12}O$ (Note: the hexafluoroantimonate anions are omitted for clarity, and the arrows indicate the propagation of the polymeric chain).

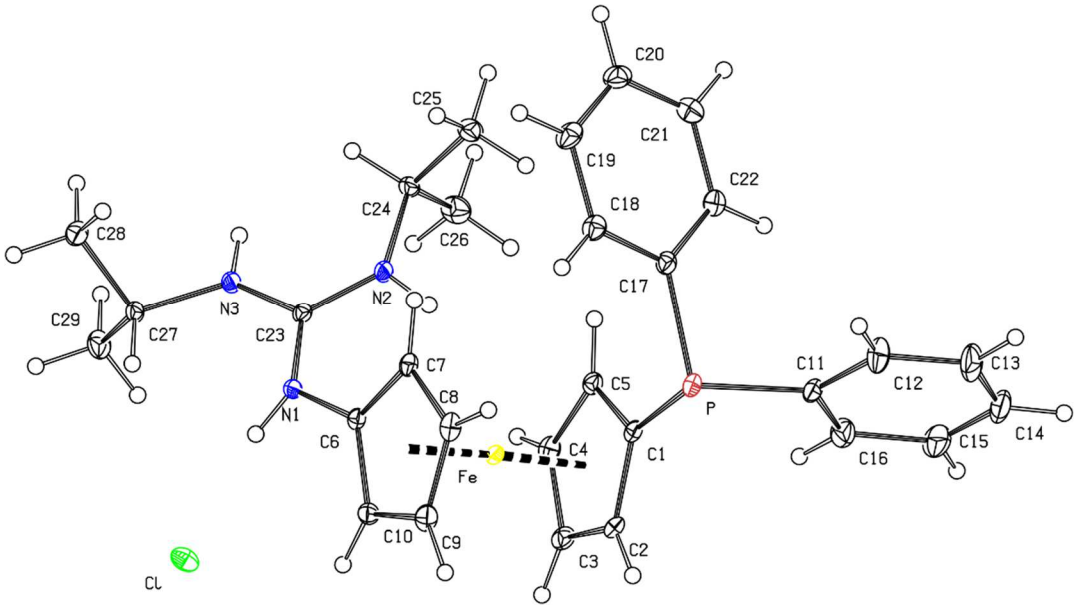

Figure S6. PLATON plot (30% probability) of the structure of (**1**^{iPr}**H**)Cl

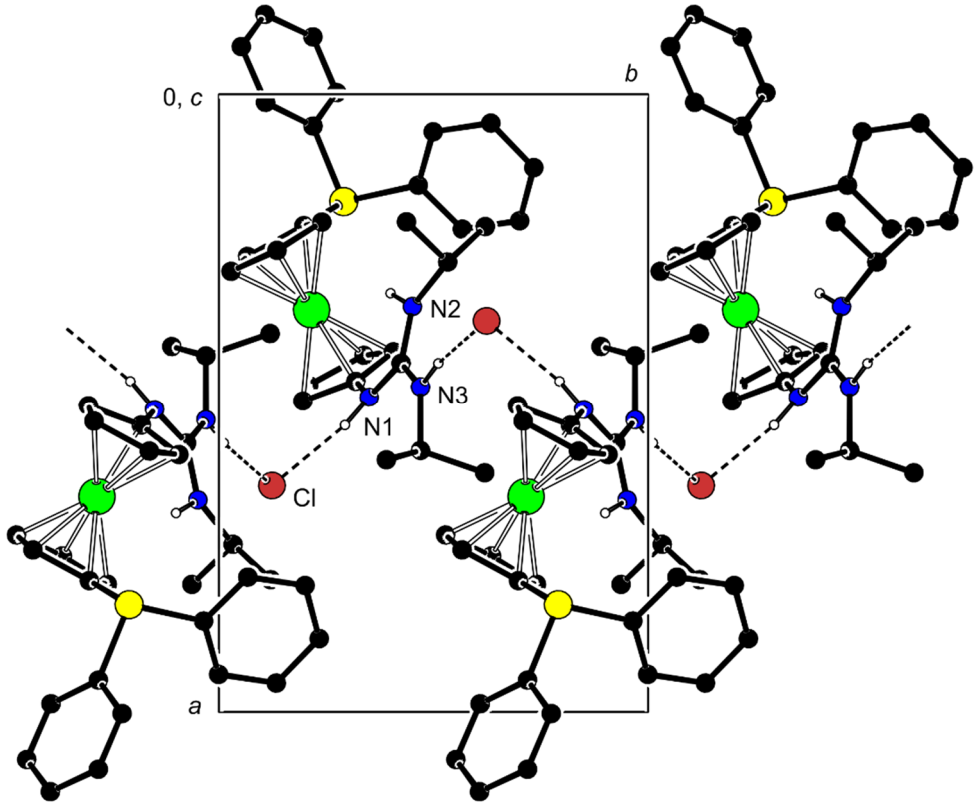

Figure S7. Section of the hydrogen-bonded chains in the structure of (**1**^{iPr}**H**)Cl (N1···Cl = 3.076(1) Å, N3···Cl = 3.195(1) Å; only NH hydrogens are shown for clarity).

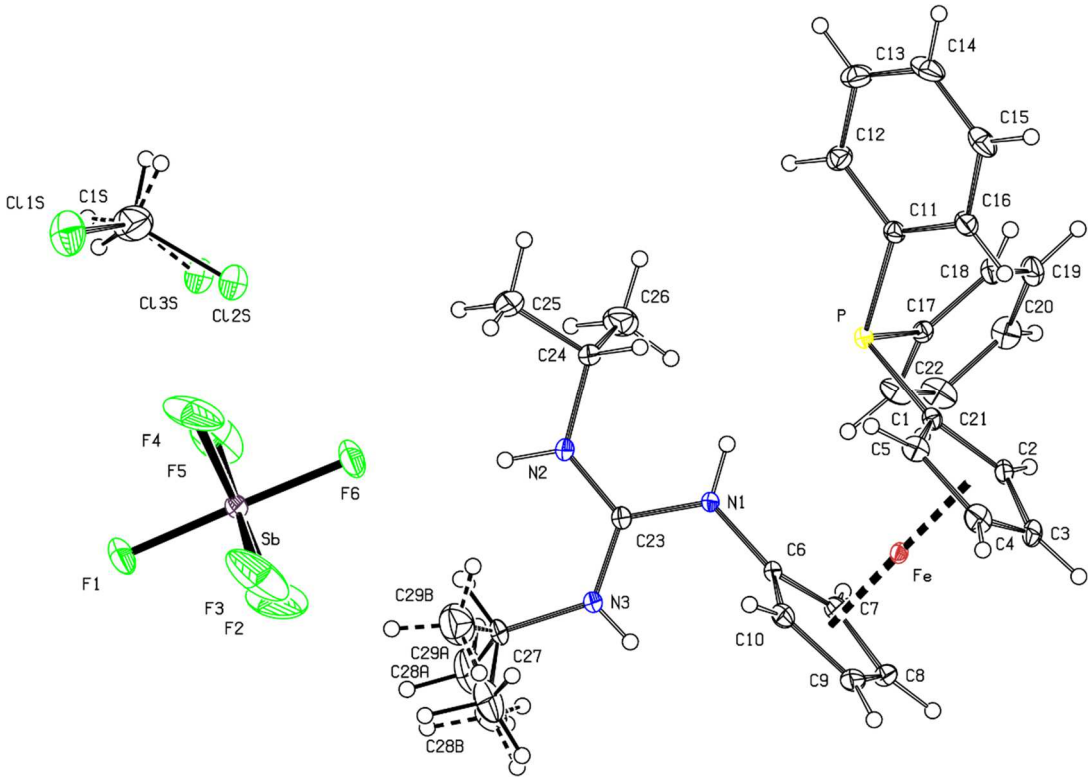

Figure S8. PLATON plot (30% probability) of the structure of (**1**^{iPr}**H**)[SbF_6]·CH_2Cl_2

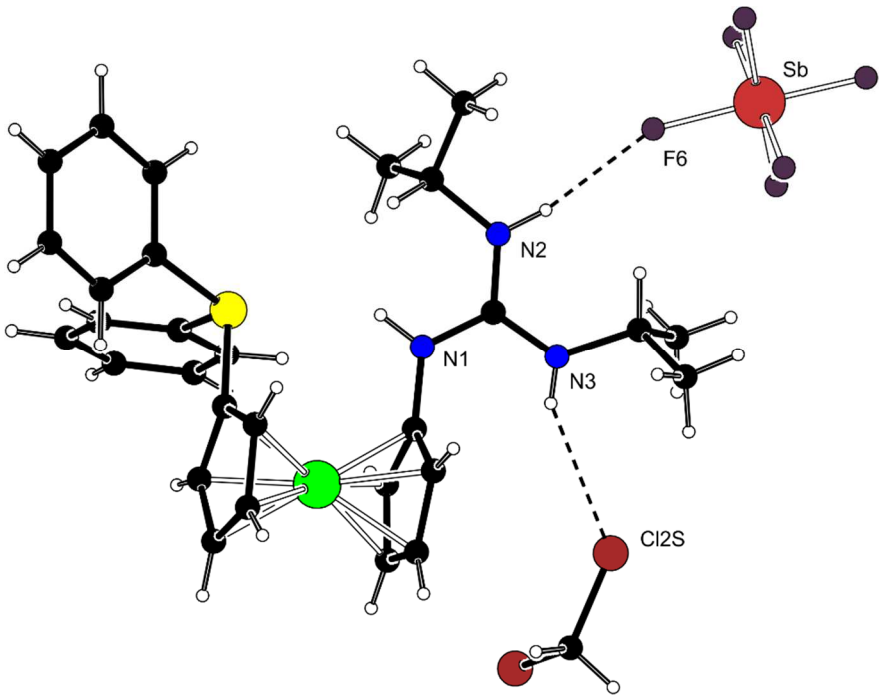

Figure S9. Hydrogen bond interactions in the structure of (**1**^{iPr}**H**)[SbF_6]·CH_2Cl_2 (N2···F6 = 3.194(3) Å, N3···Cl2S = 3.558(4) Å; only one position of the disordered atoms and the NH hydrogens are shown for clarity).

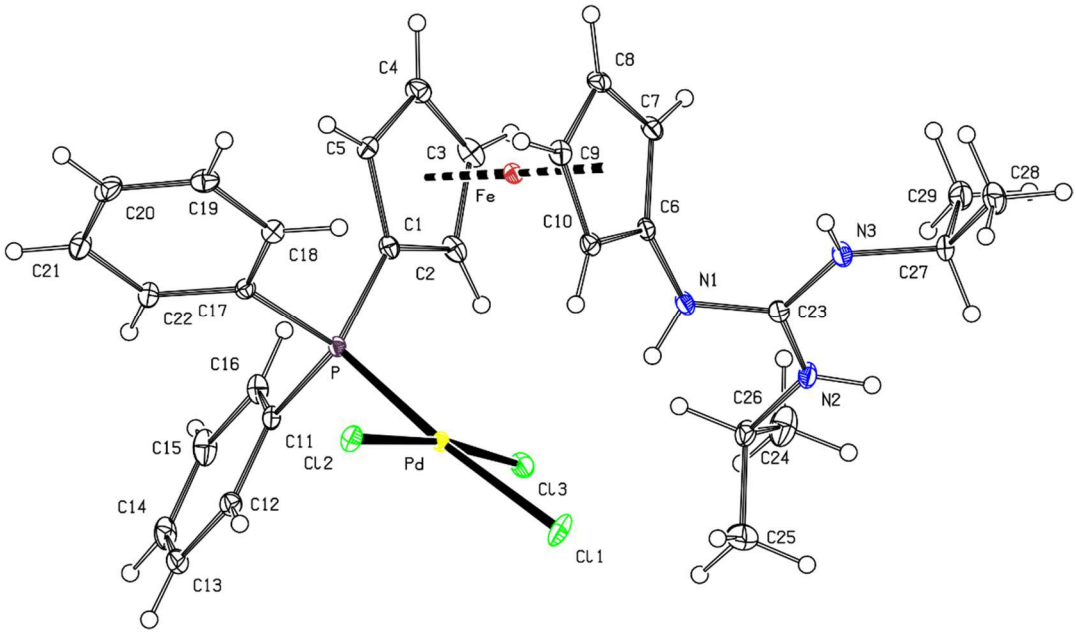

Figure S10. PLATON plot (30% probability level) of the complex molecule in the structure of **8**·2.5$CHCl_3$

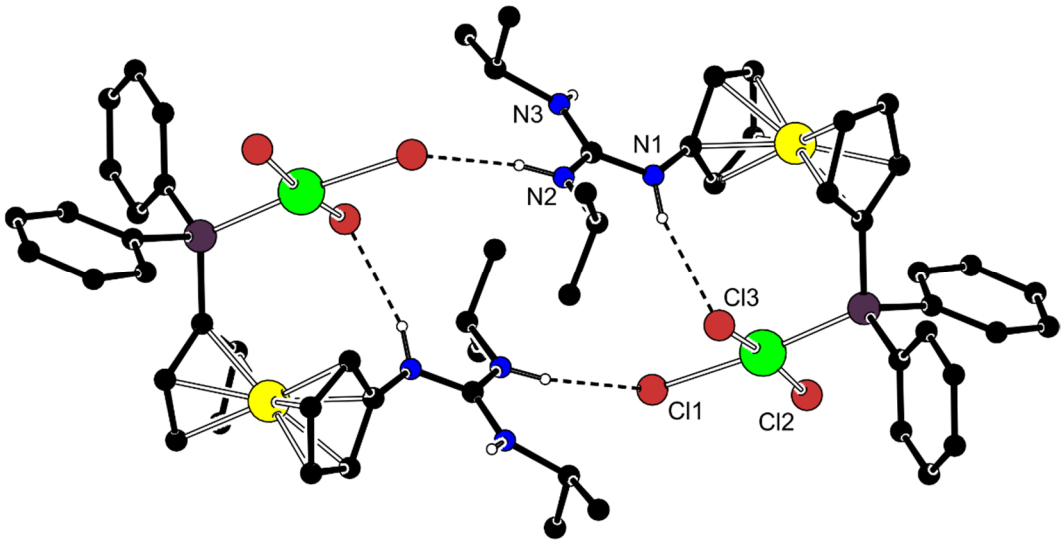

Figure S11. Hydrogen bonding in the structure of **8**·2.5$CHCl_3$ (N1···Cl3 = 3.205(2) Å, N2···Cl1 = 3.253(2) Å; the two molecules are related by crystallographic inversion; only the NH hydrogens are shown for clarity).

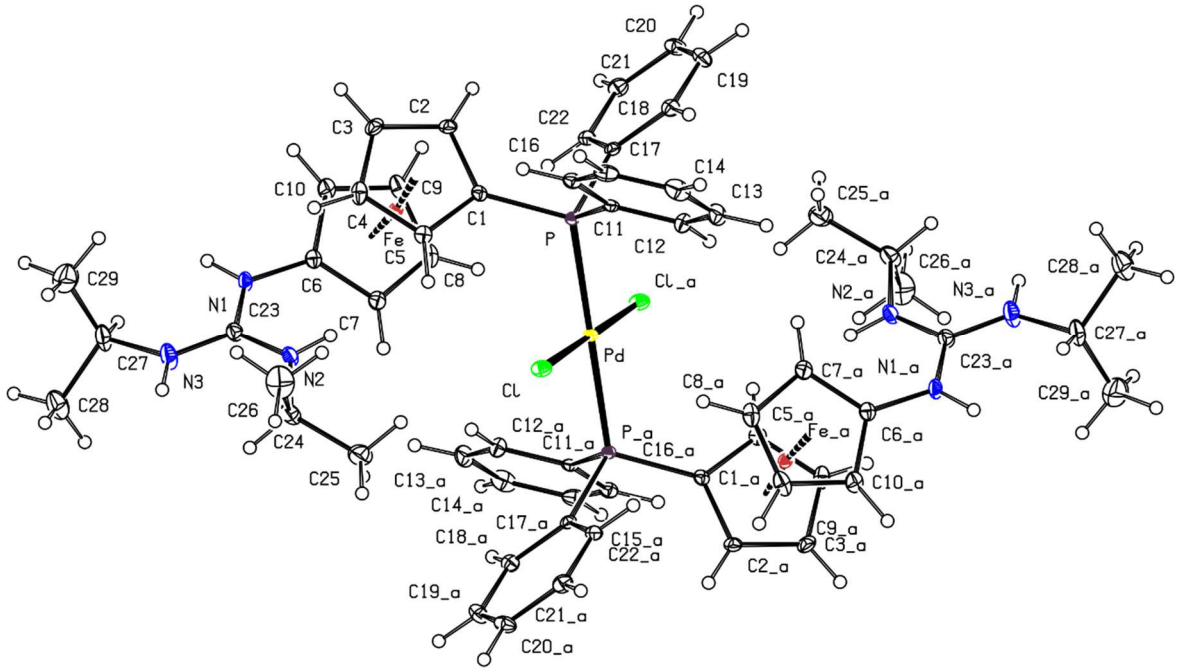

Figure S12. PLATON plot (30% probability) of the complex cation in the structure of **9**-SbF_6. The half of the cation is generated by crystallographic inversion.

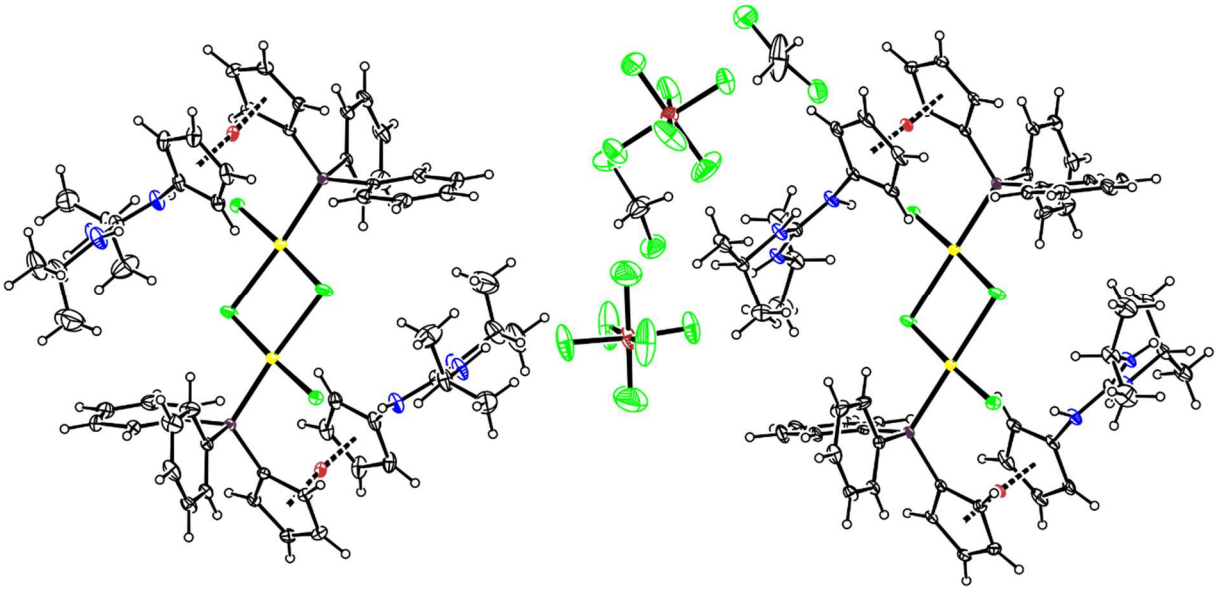

Figure S13. Complete PLATON plot (30% probability) of the crystal structure of **10**·$2CH_2Cl_2$

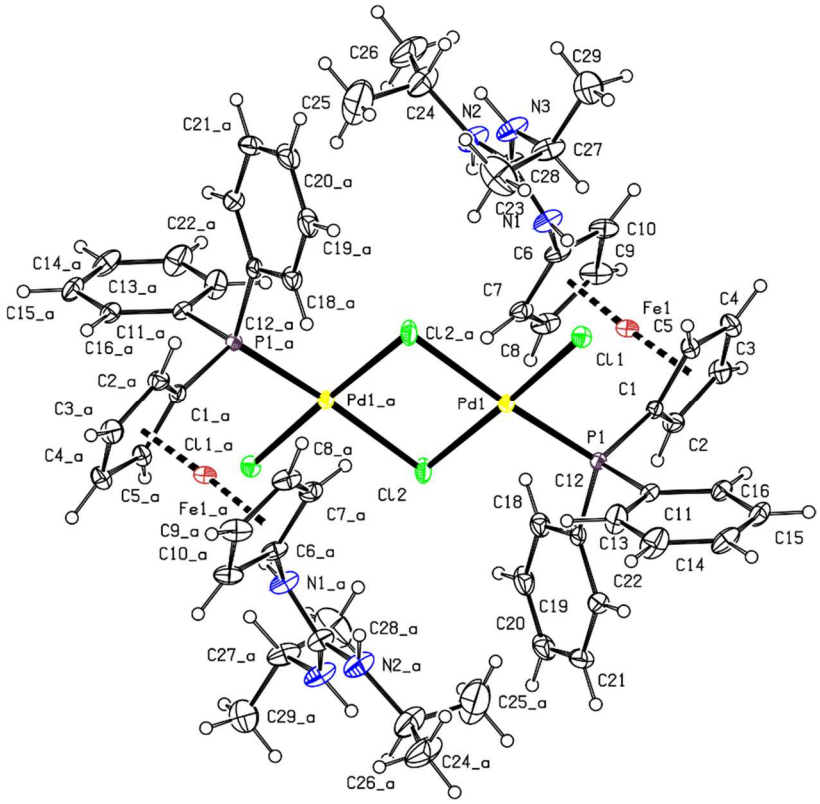

Figure S14. PLATON plot (30% probability) of complex cation 1 in the structure of **10**·2CH_2Cl_2. The half of the cation is generated by crystallographic inversion.

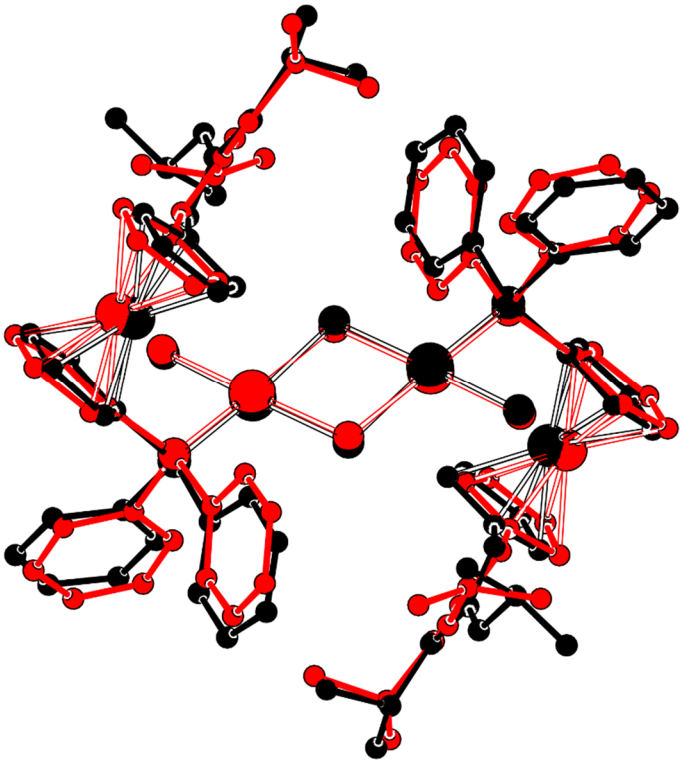

Figure S15. Least squares overlap of the two structurally independent complex cations in the structure of **10**·2CH_2Cl_2 (hydrogen atoms were omitted for clarity).

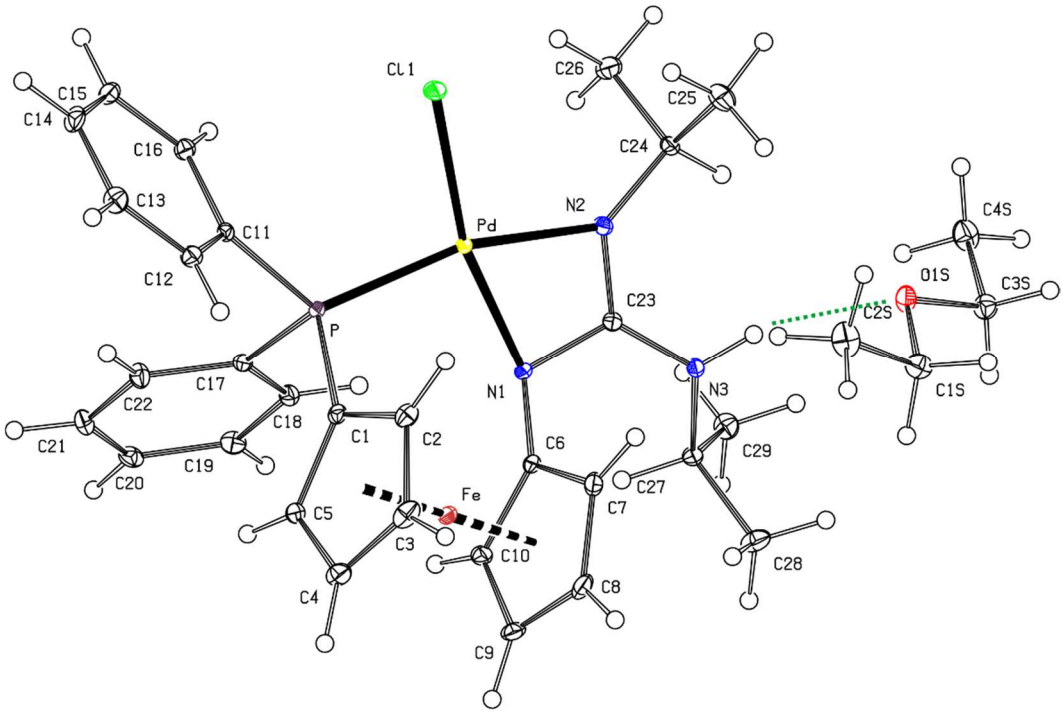

Figure S16. PLATON plot (30% probability) of the molecular structure of **11**·Et_2O (the N-H···O hydrogen bond is indicated by a dashed line; N3···O1S = 3.058(2) Å).

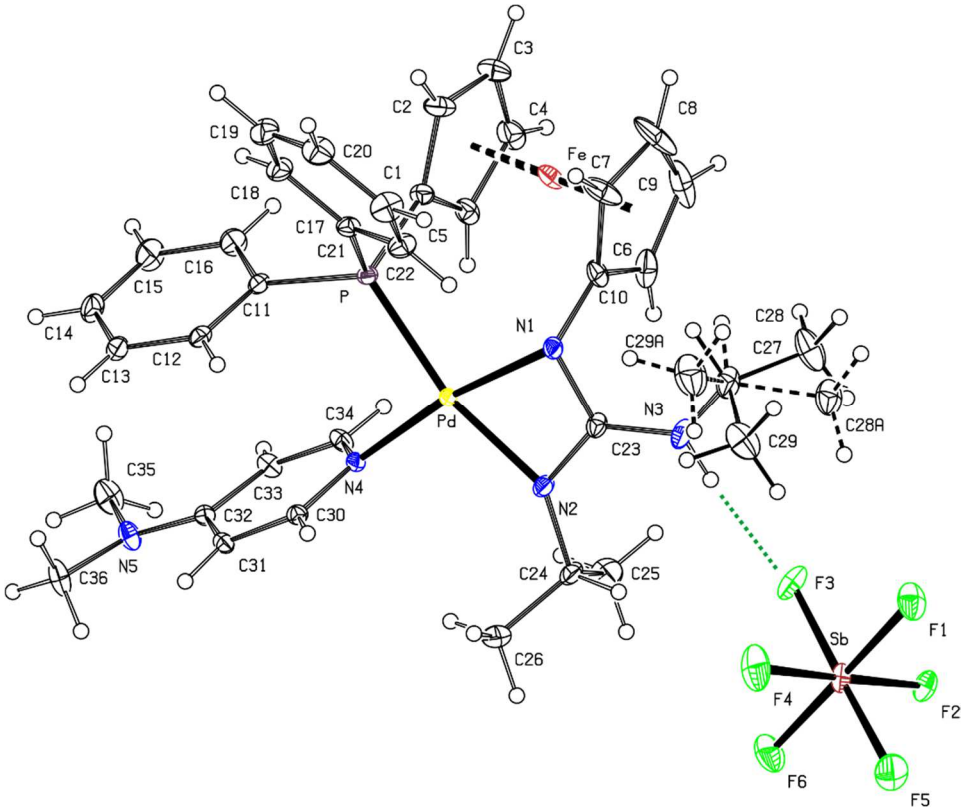

Figure S17. PLATON plot (30% probability) of the molecular structure of complex **13** (the N-H···F hydrogen bond is indicated by a dashed line; N3···F3 = 2.982(2) Å).

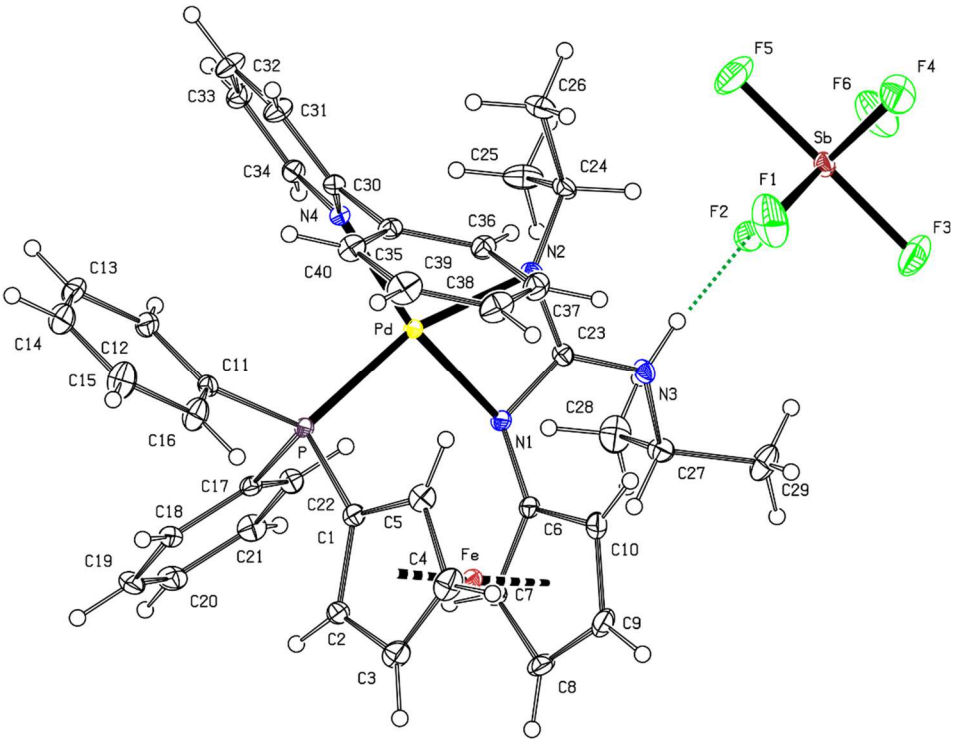

Figure S18. PLATON plot (30% probability) of the molecular structure of **14** (the N-H···F hydrogen bond is indicated by a dashed line; N3···F1 = 3.103(3) Å).

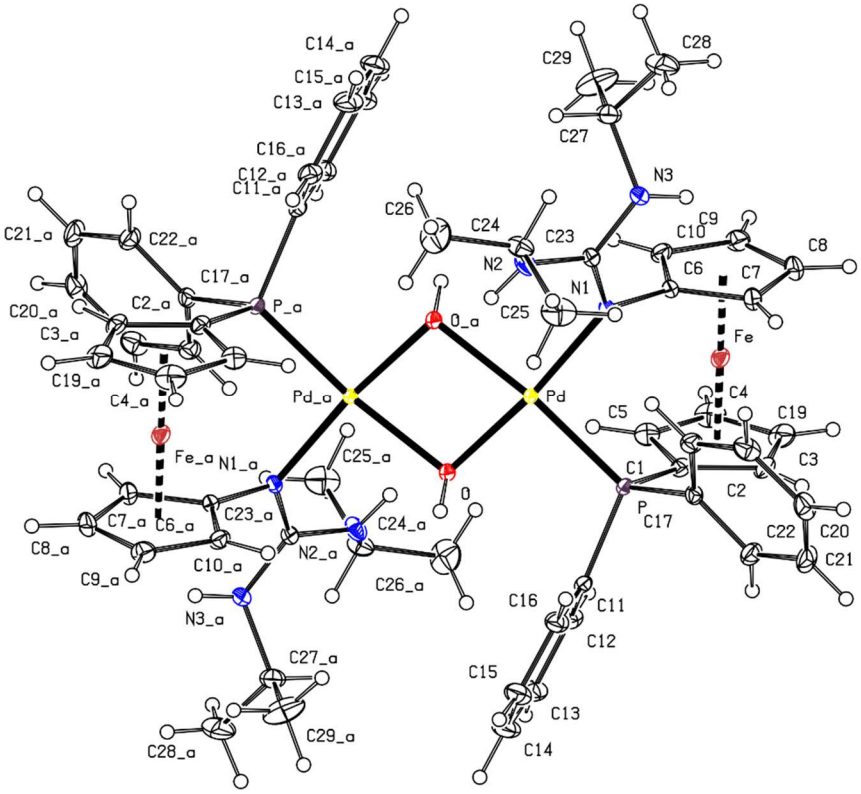

Figure S19. PLATON plot (30% probability) of the complex cation in the structure of **15**·2CH_2Cl_2. The cation is located on the crystallographic inversion centre.

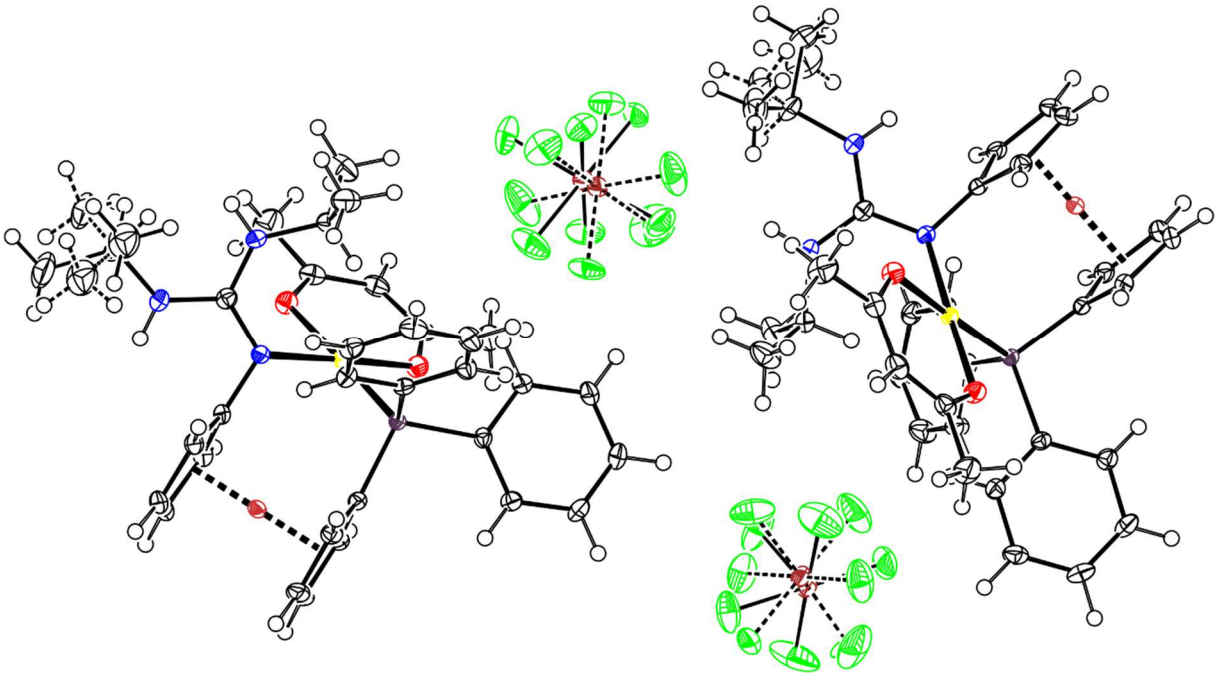

Figure S20. Full PLATON plot (30% probability) of the crystal structure of **16**

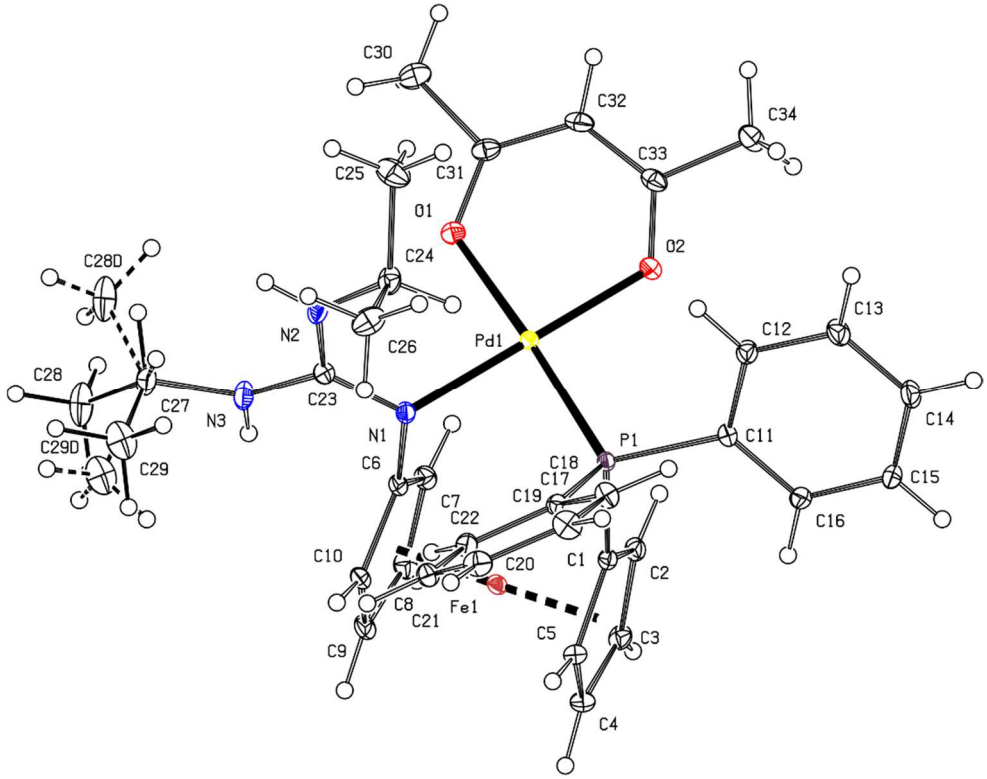

Figure S21. PLATON plot (30% probability) of complex cation 1 in the structure of **16**

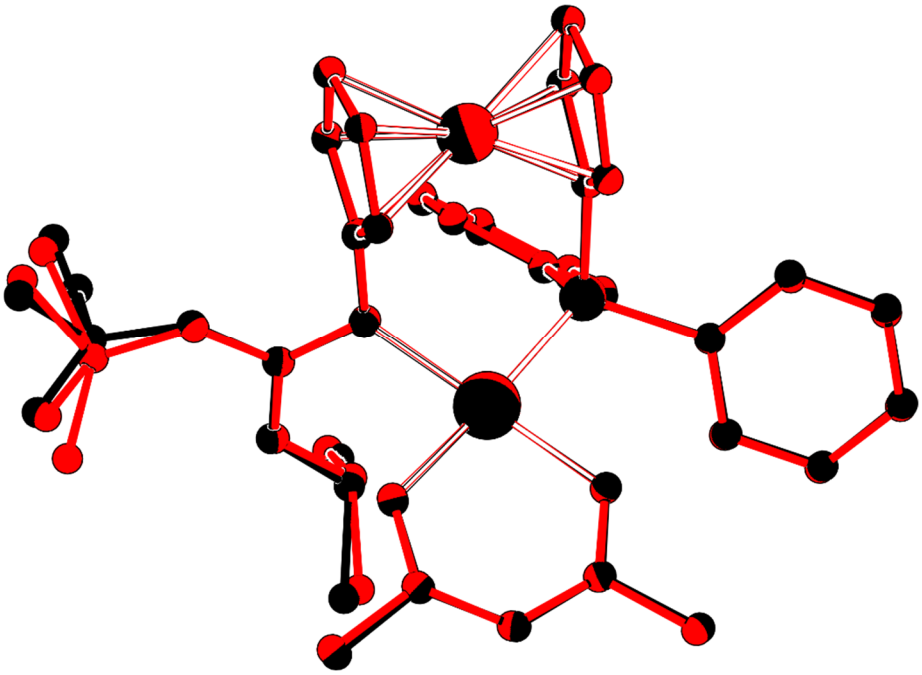

Figure S22. Least squares overlap of the two structurally independent cations in the structure of **16** (all hydrogen atoms were omitted for clarity).

The crystal structure of $\mathbf{1^{iPr}O}$

Crystals of phosphine oxide $\mathbf{1^{iPr}O}$ were isolated serendipitously when crystallising the reaction mixture after synthesizing $\mathbf{1^{iPr}}$ from tetrahydrofuran/hexane. The compound crystallises with the symmetry of the monoclinic space group $P2_1/n$ and with one molecule per asymmetric unit.

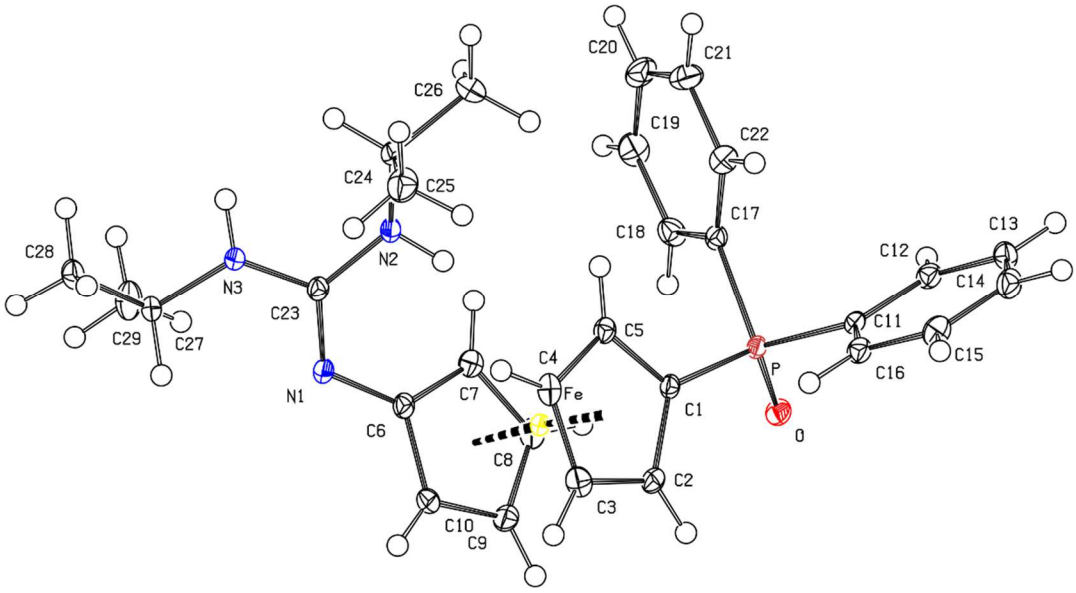

Figure S23. PLATON plot (50% probability) of molecular structure of $\mathbf{1^{iPr}O}$

The cyclopentadienyl rings in the structure of $\mathbf{1^{iPr}O}$ (Figure S23) are tilted by 6.60(9)° and adopt an intermediate conformation near a 1,3' arrangement with a τ = –132.8(1)°. The guanidine moiety (CN_3) is planar and rotated by 41.11(9)° with respect to the parent cyclopentadienyl ring C(6-10). The hydrogen atoms reside on the nitrogens bearing the electron-donating and non-conjugated isopropyl groups. Due to the localized nature of the guanidine moiety, the C23-N1 bond (1.305(2) Å) is significantly shorter that the C(iPr)-NH distances (1.373(2) and 1.367(2) Å). Variation is observed even for the N-C23-N angles, among which the N1-C23-N2 angle is the widest (124.8(1)°; *cf.* N1-C23-N3 = 118.3(1)° and N2-C23-N3 = 116.9(1)°). The geometry of the phosphoryl substituent in $\mathbf{1^{iPr}O}$ (P=O = 1.493(1) Å) is unexceptional in view of the parameters reported for $dppfO_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene).[7] In the crystal, the individual molecules of the phosphine oxide assemble into chains through P=O···H-N hydrogen bonds with an O···N distance of 3.027(2) Å (Figure S24).

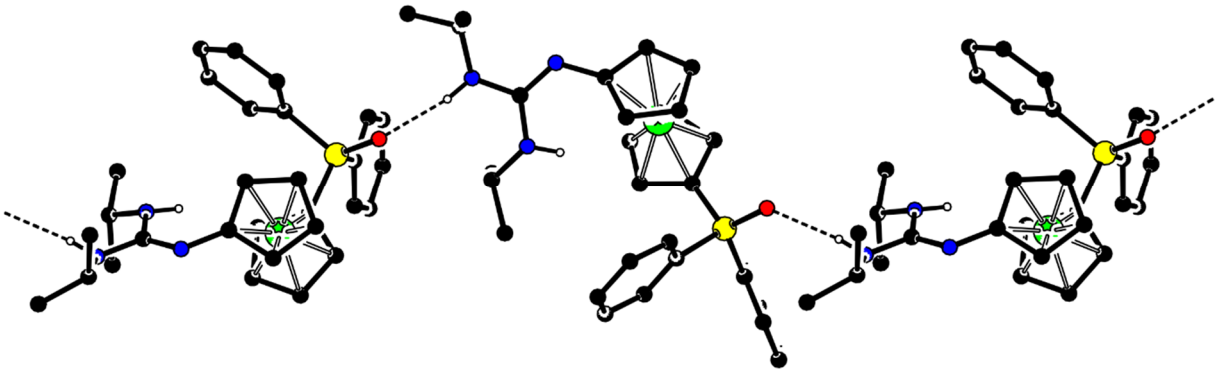

Figure S24. Section of the hydrogen-bonded chains in the structure of **1^{iPr}O** (only NH hydrogens are shown for clarity).

COPIES OF THE NMR SPECTRA

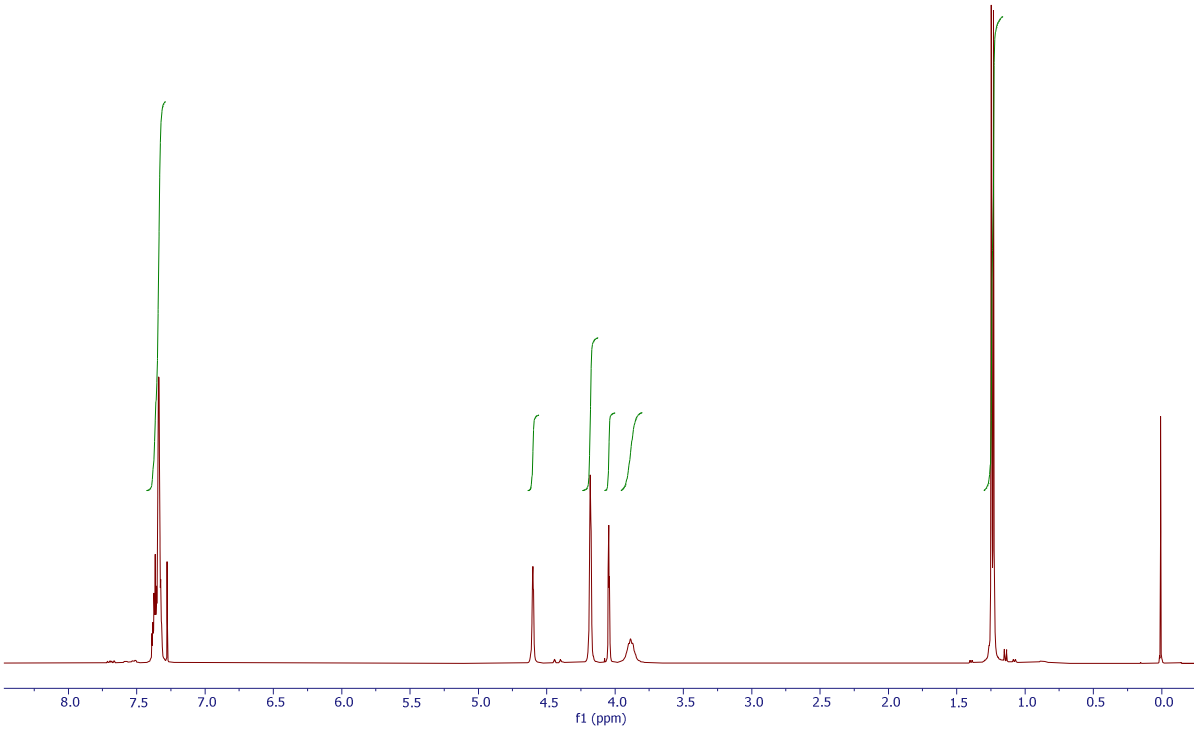

Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (**1^{iPr}H**)Cl

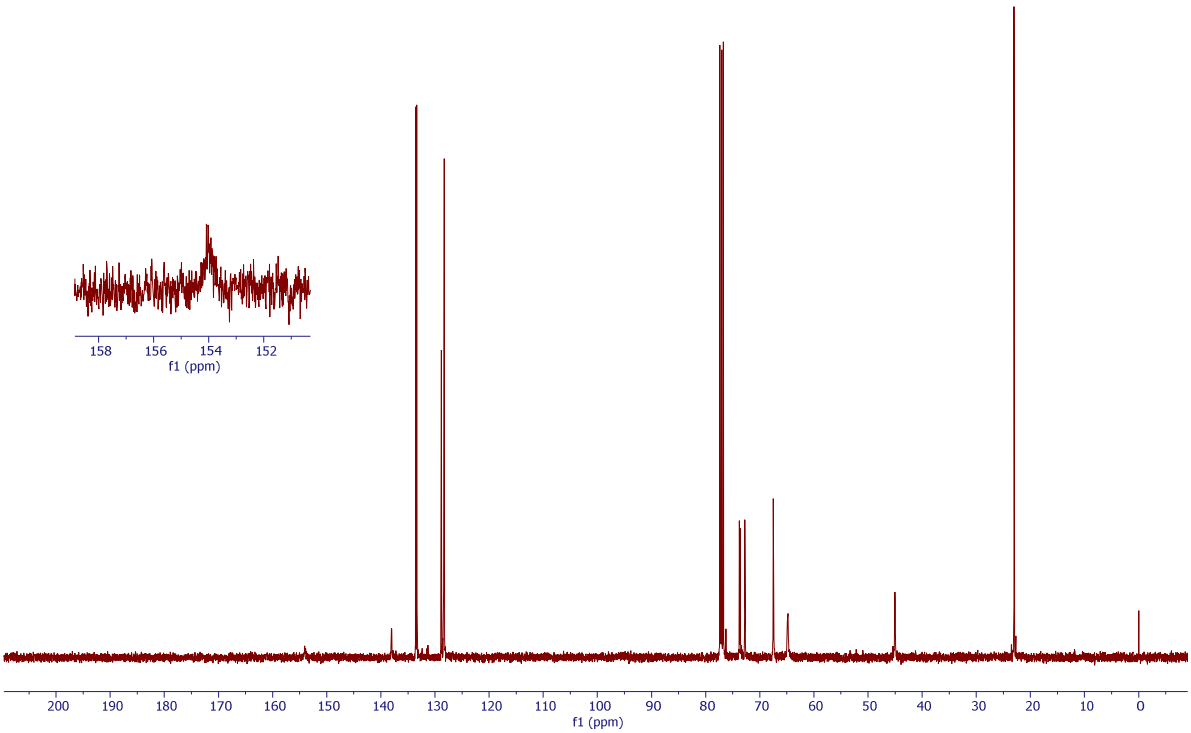

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of (**1^{iPr}H**)Cl

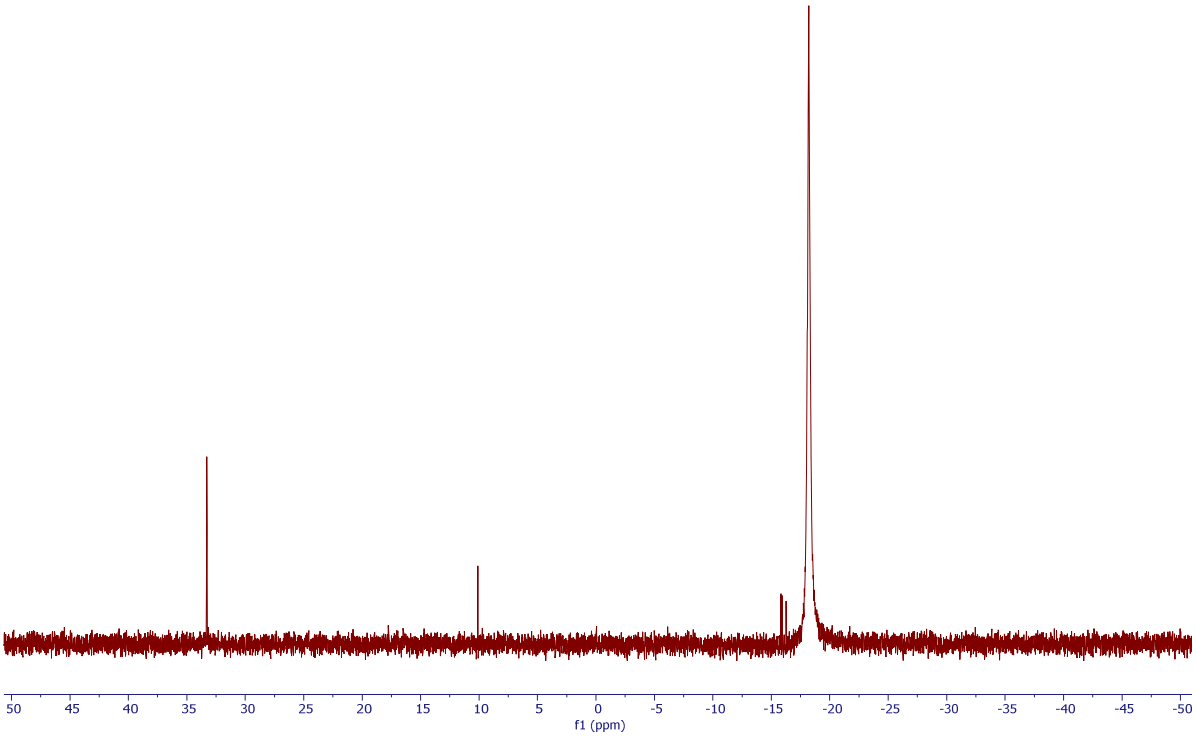

Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of (**1^{iPr}H**)Cl

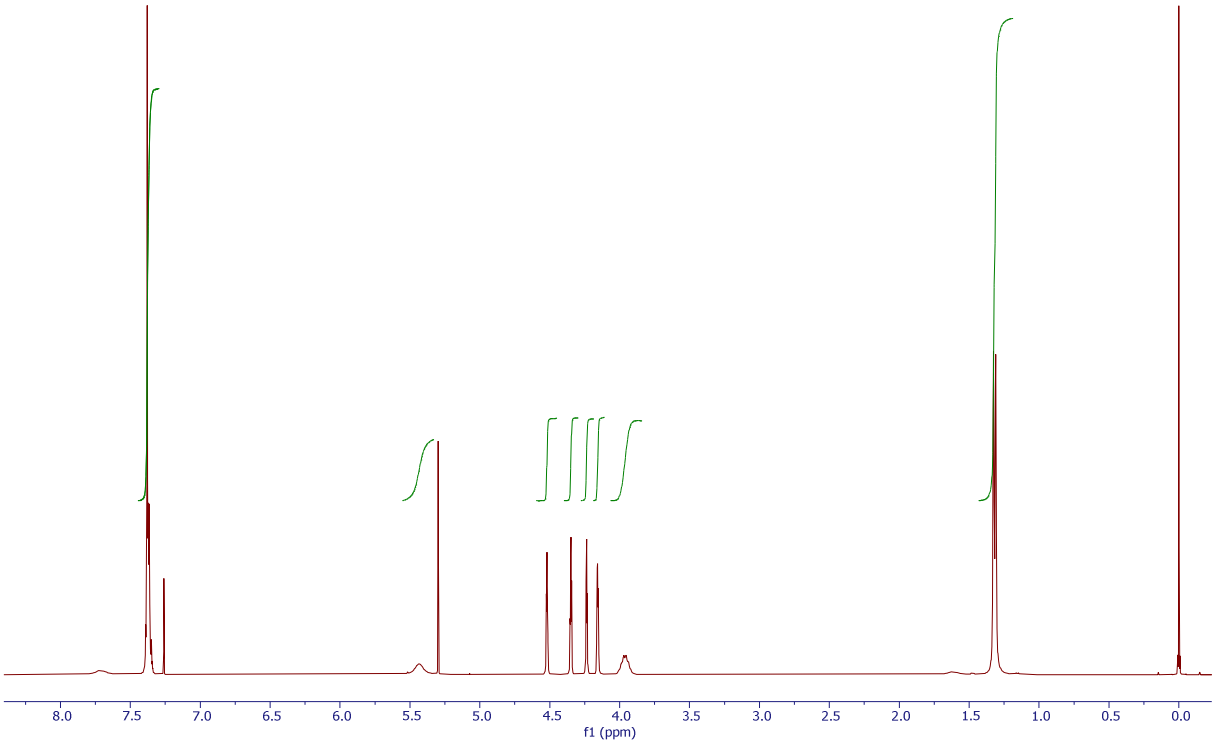

Figure S28 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (**1^{iPr}H**)[SbF_6]

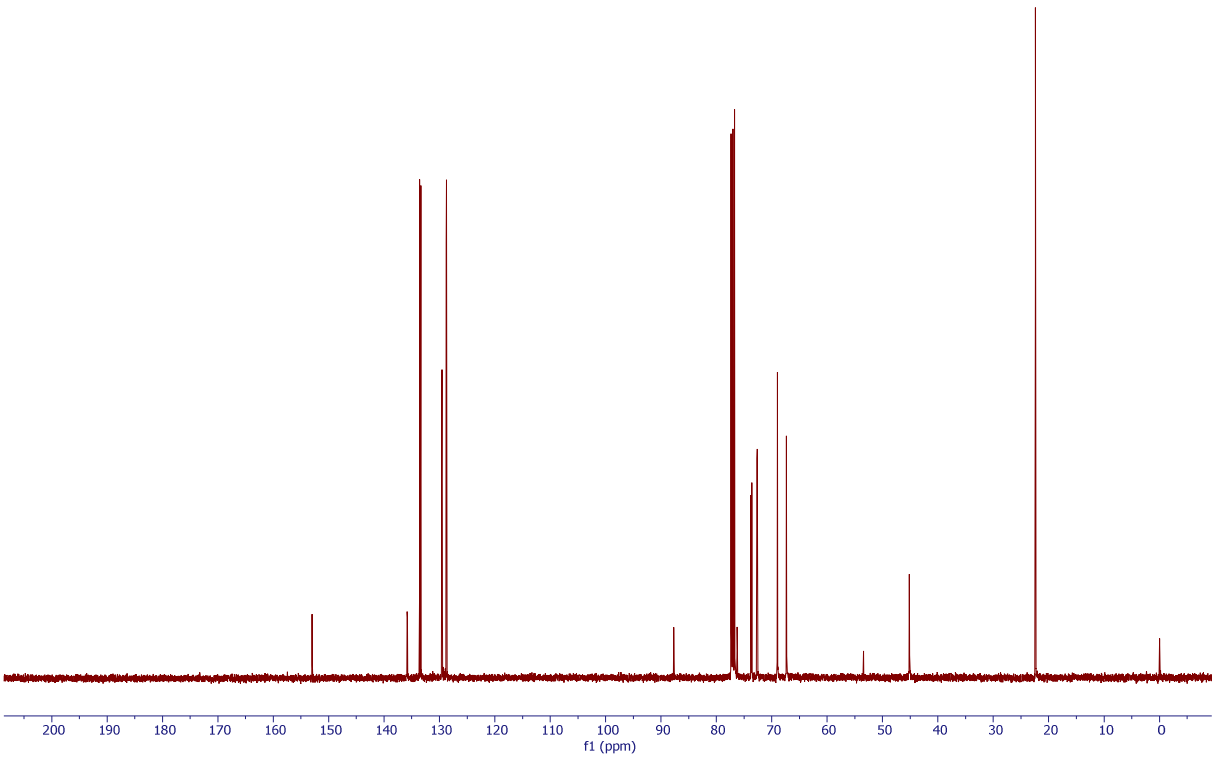

Figure S29. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of (**1^{iPr}H**)[SbF_6]

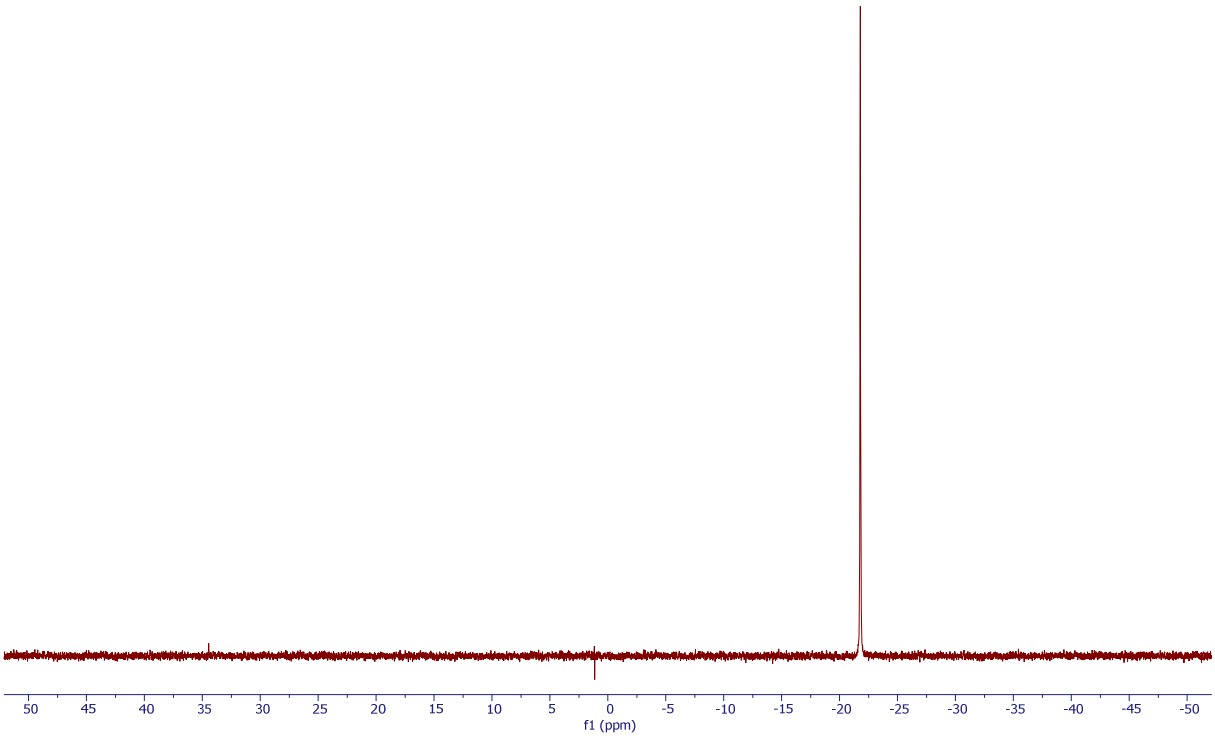

Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of (**1^{iPr}H**)[SbF_6]

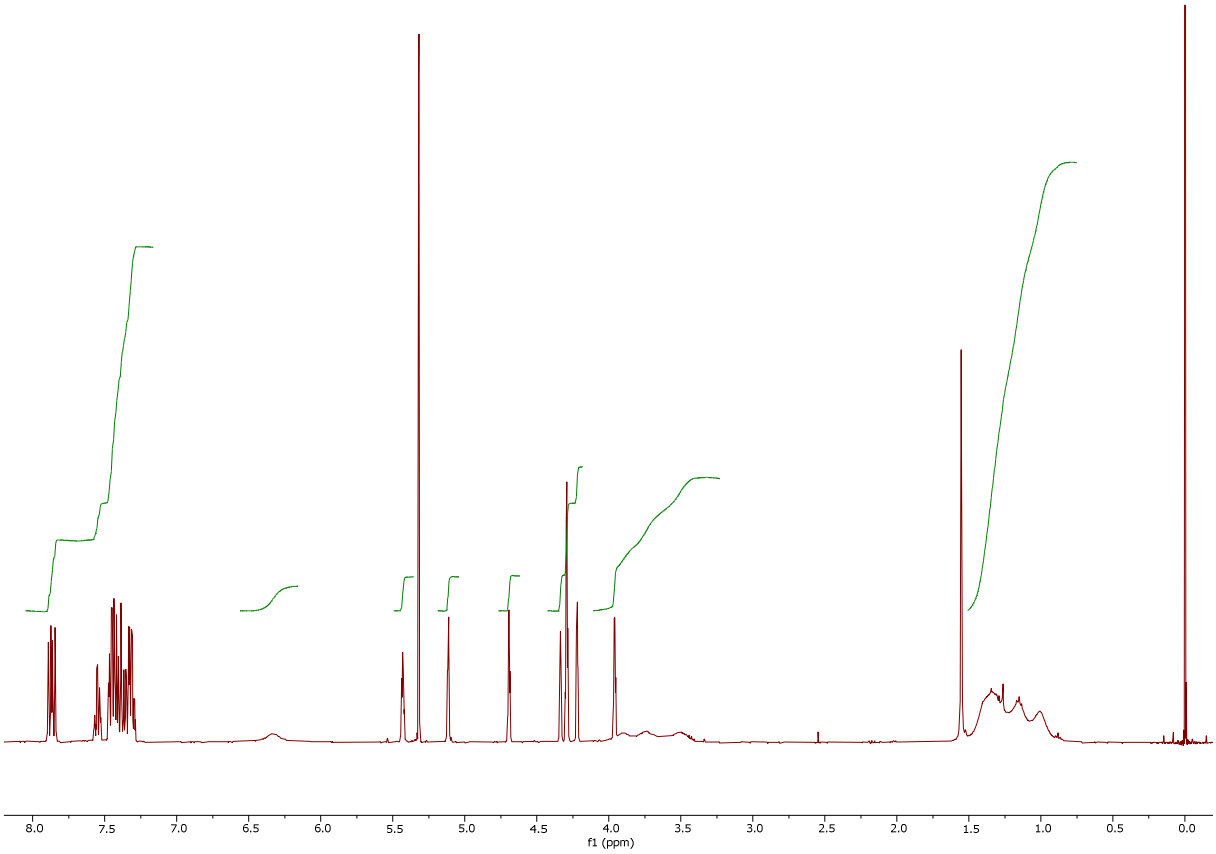

Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**.

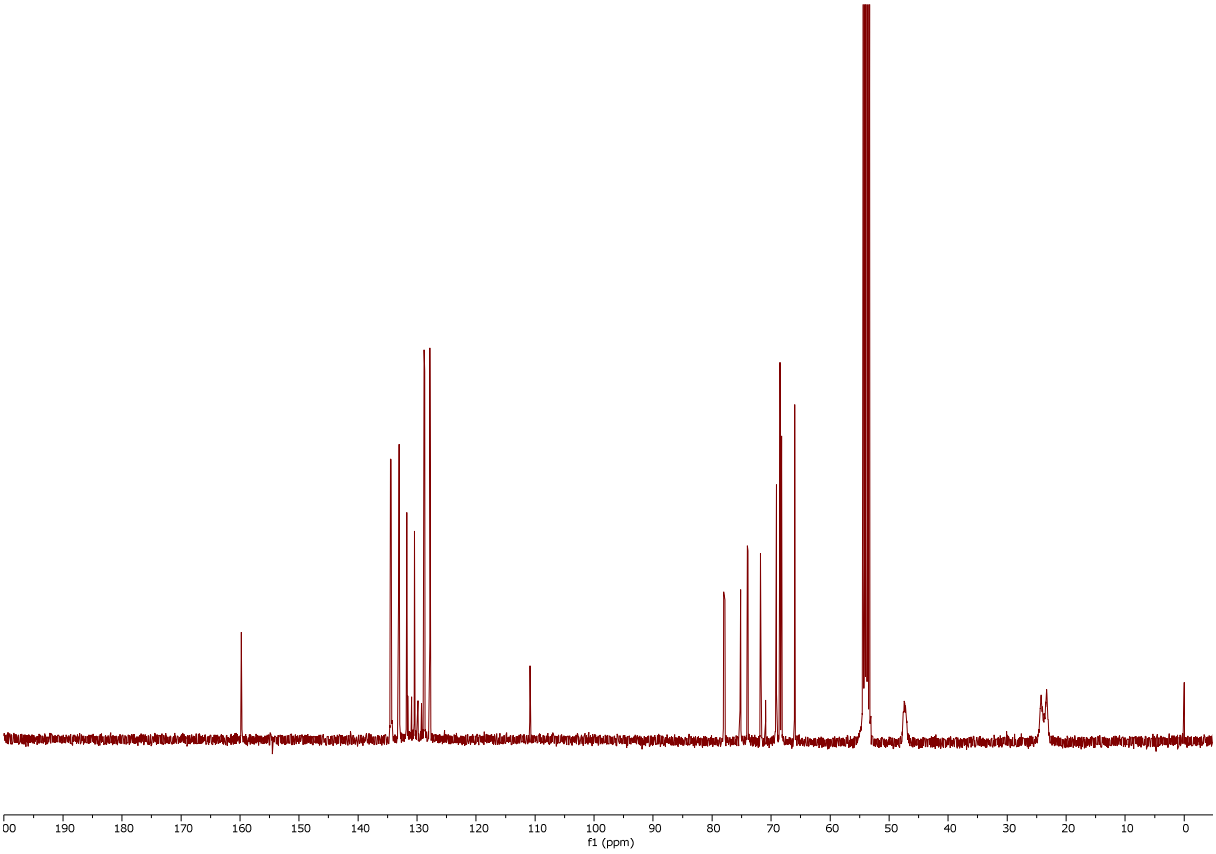

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **4**

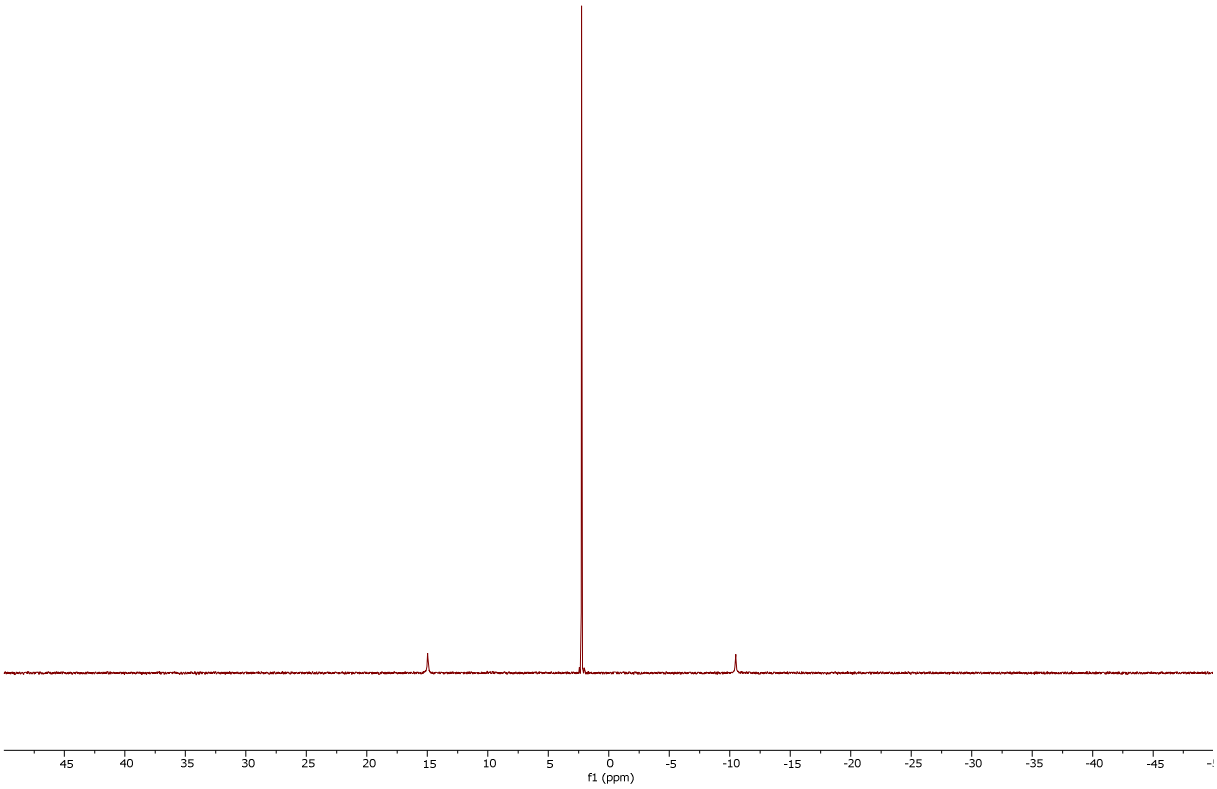

Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of **4**

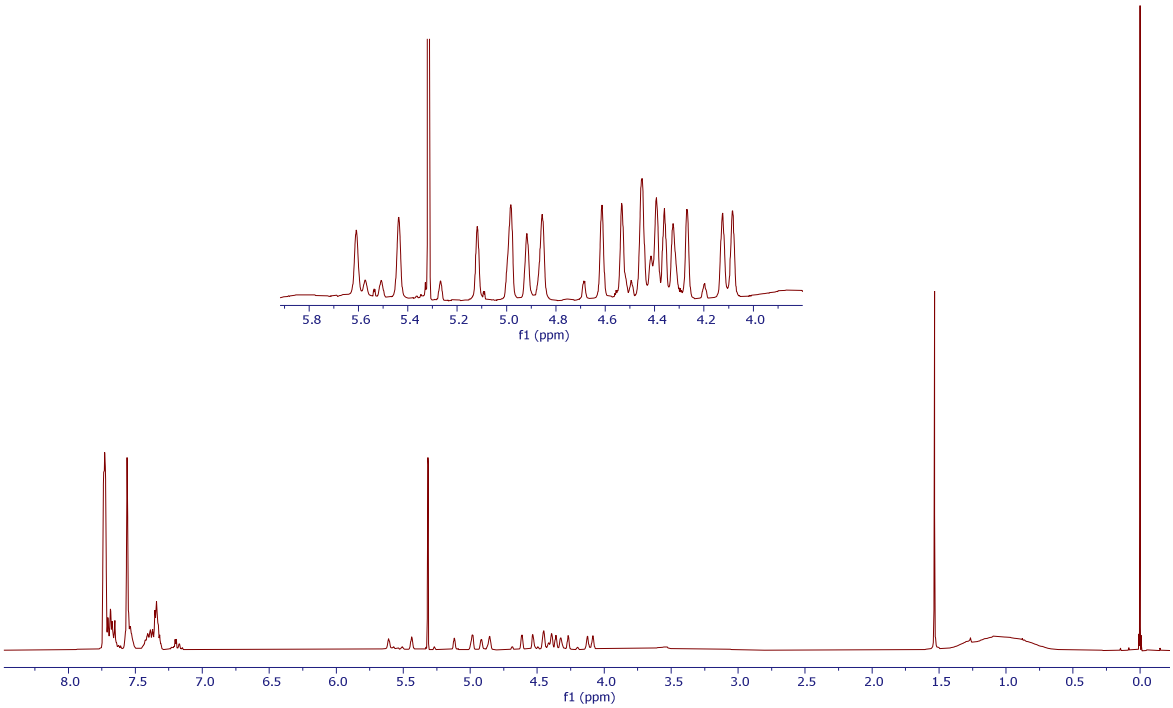

Figure S34. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5**. The spectrum was recorded immediately after dissolving a crystalline sample.

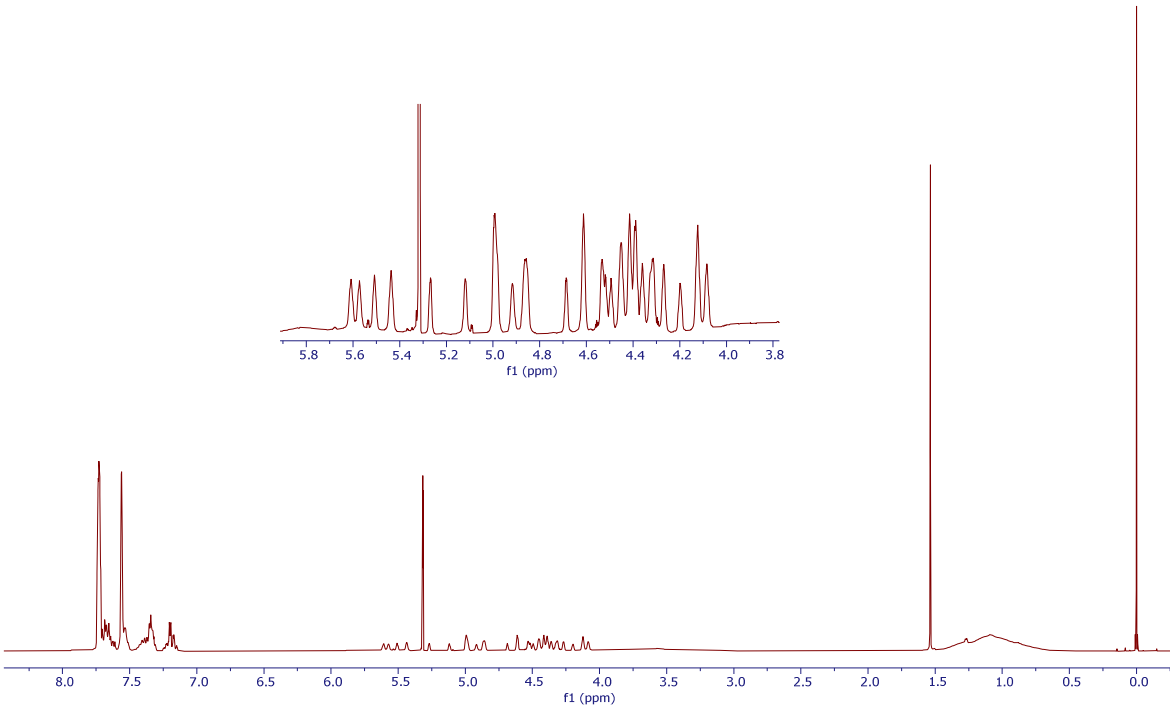

Figure S35. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **5** recorded after standing for 24 h

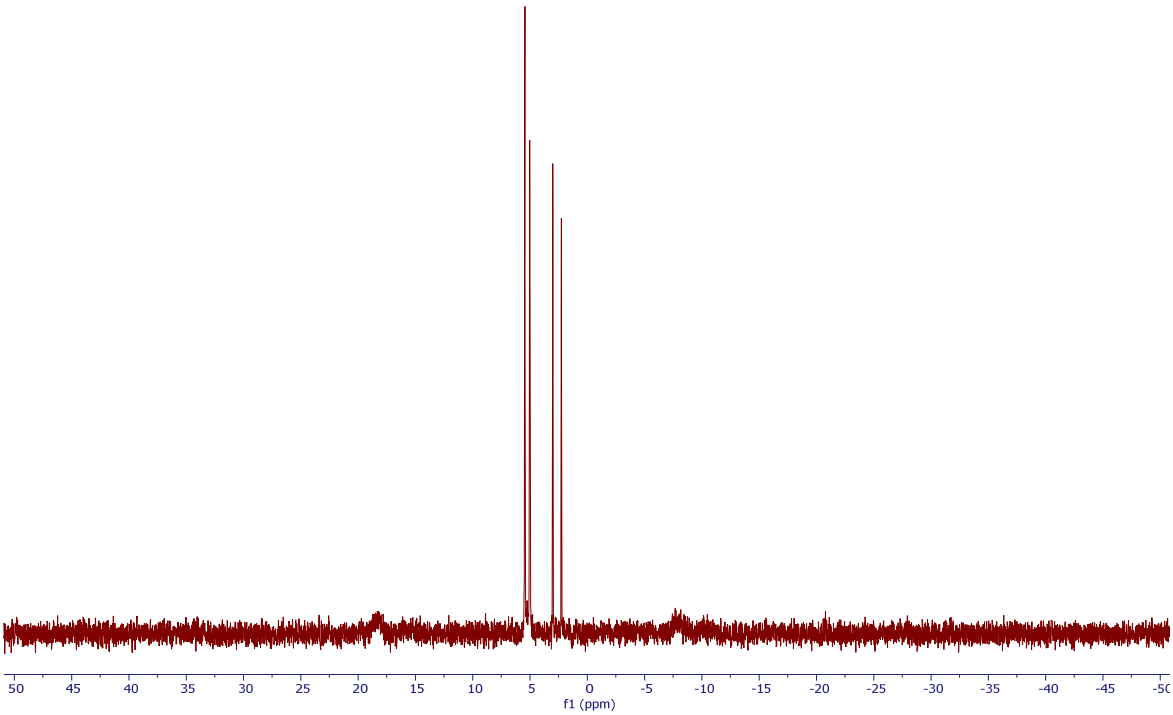

Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **5**. The spectrum was recorded immediately after dissolving a crystalline sample.

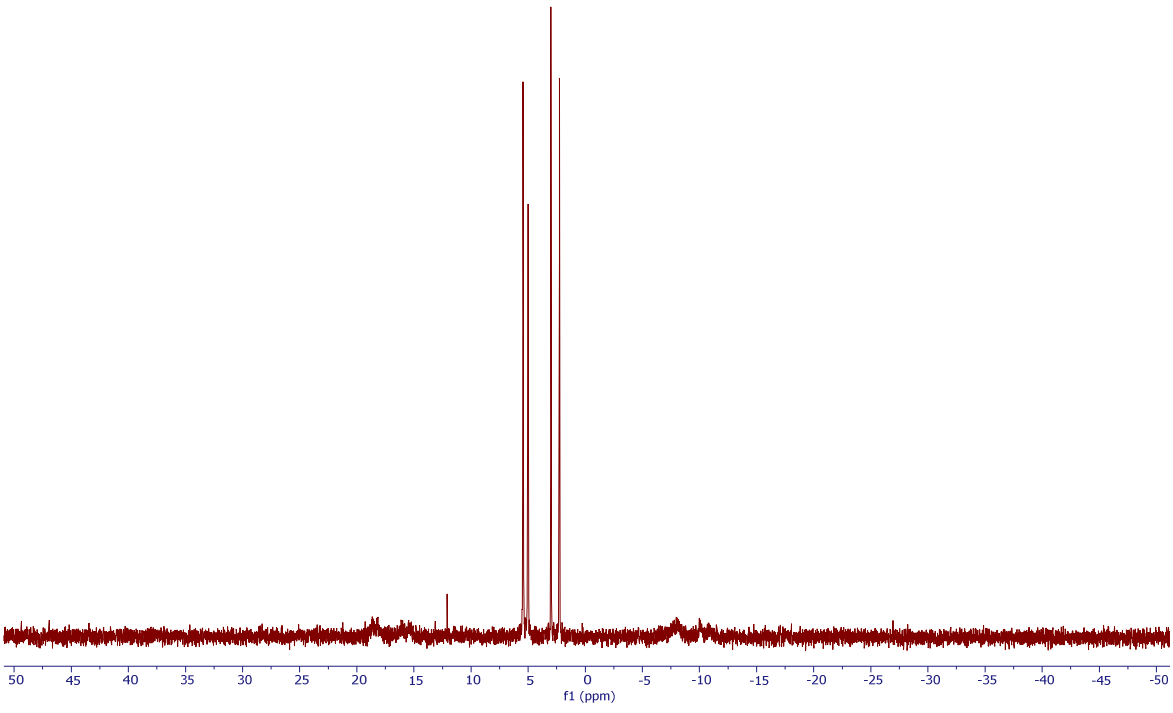

Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **5** recorded after standing for24 h

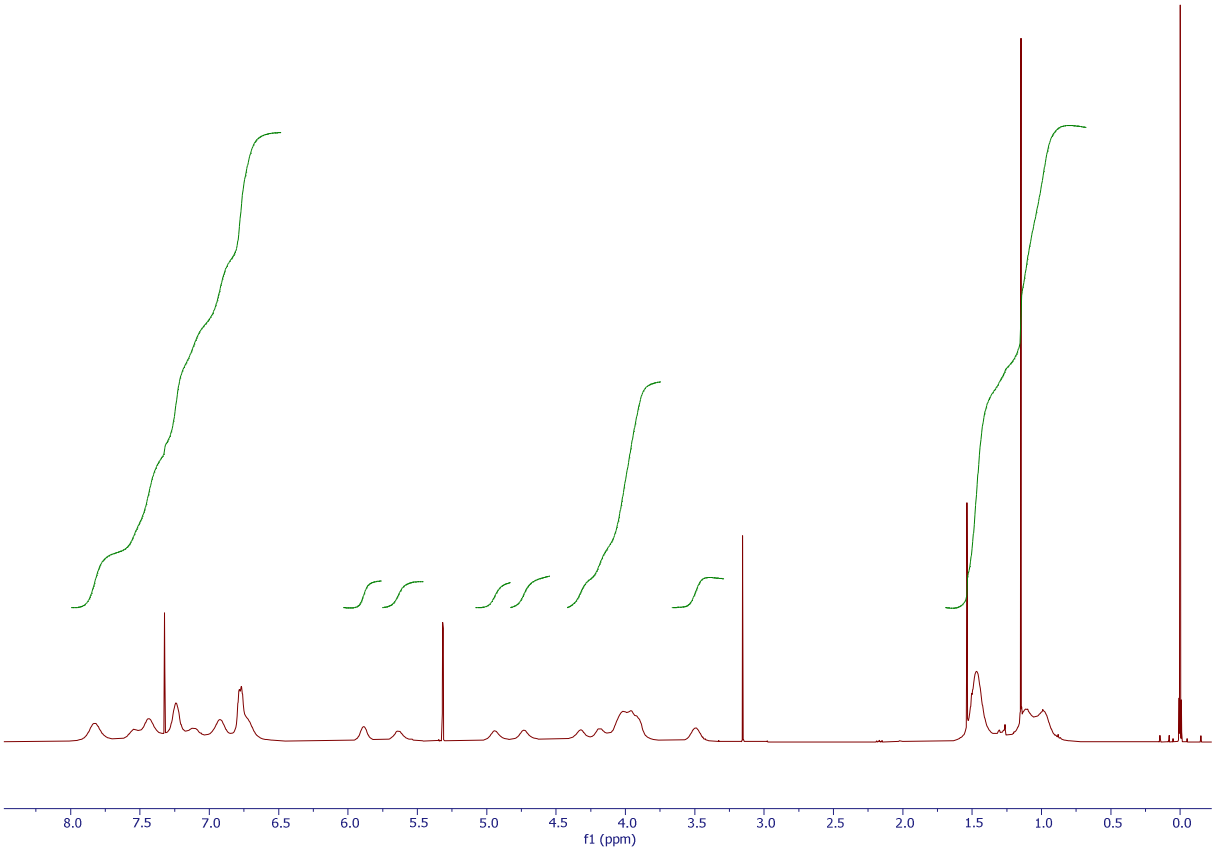

Figure S38. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **6**

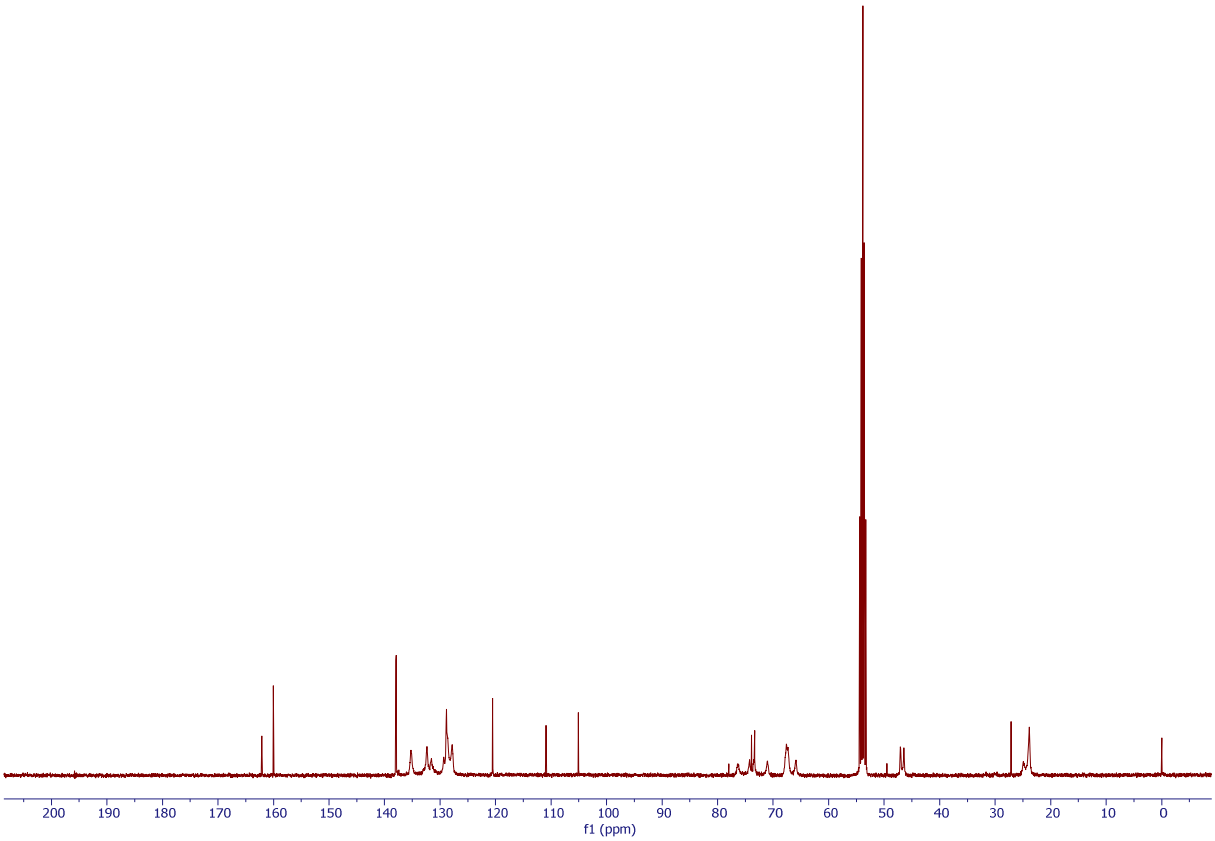

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **6**

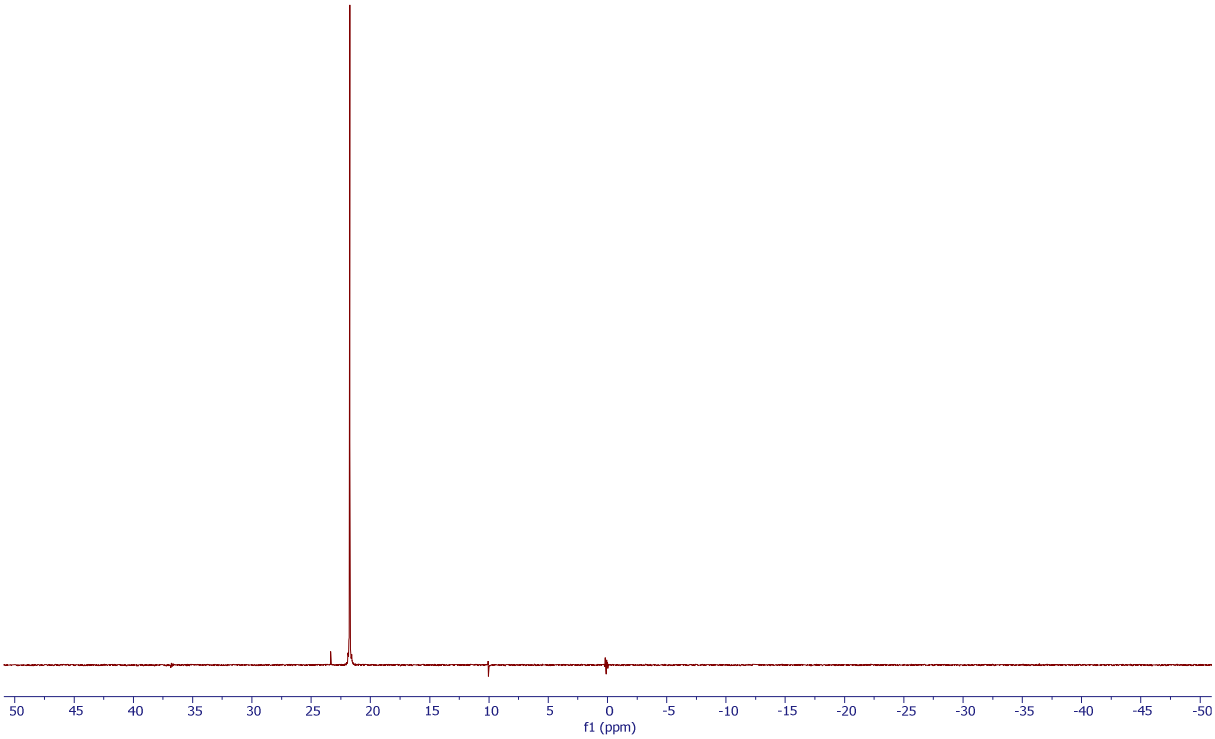

Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **6**

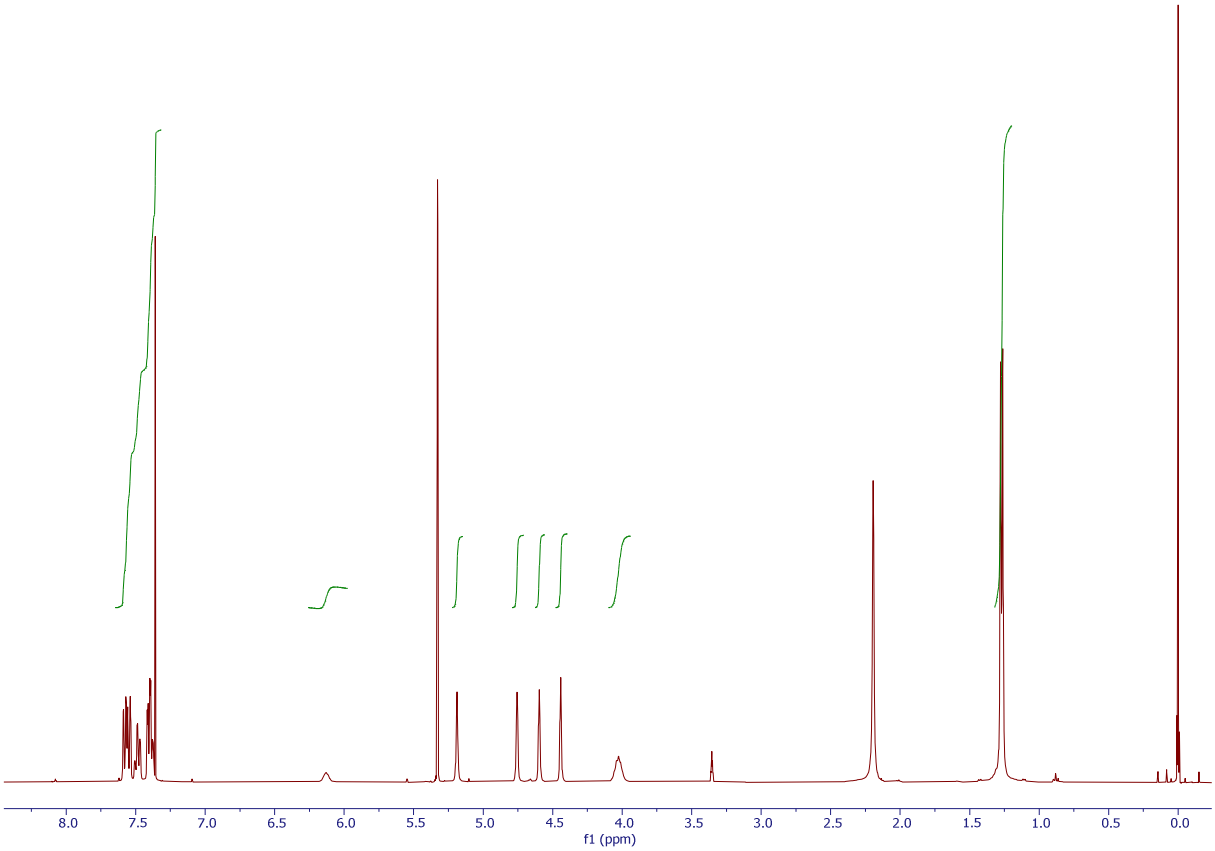

Figure 41. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2/CD_3OD) of **8**

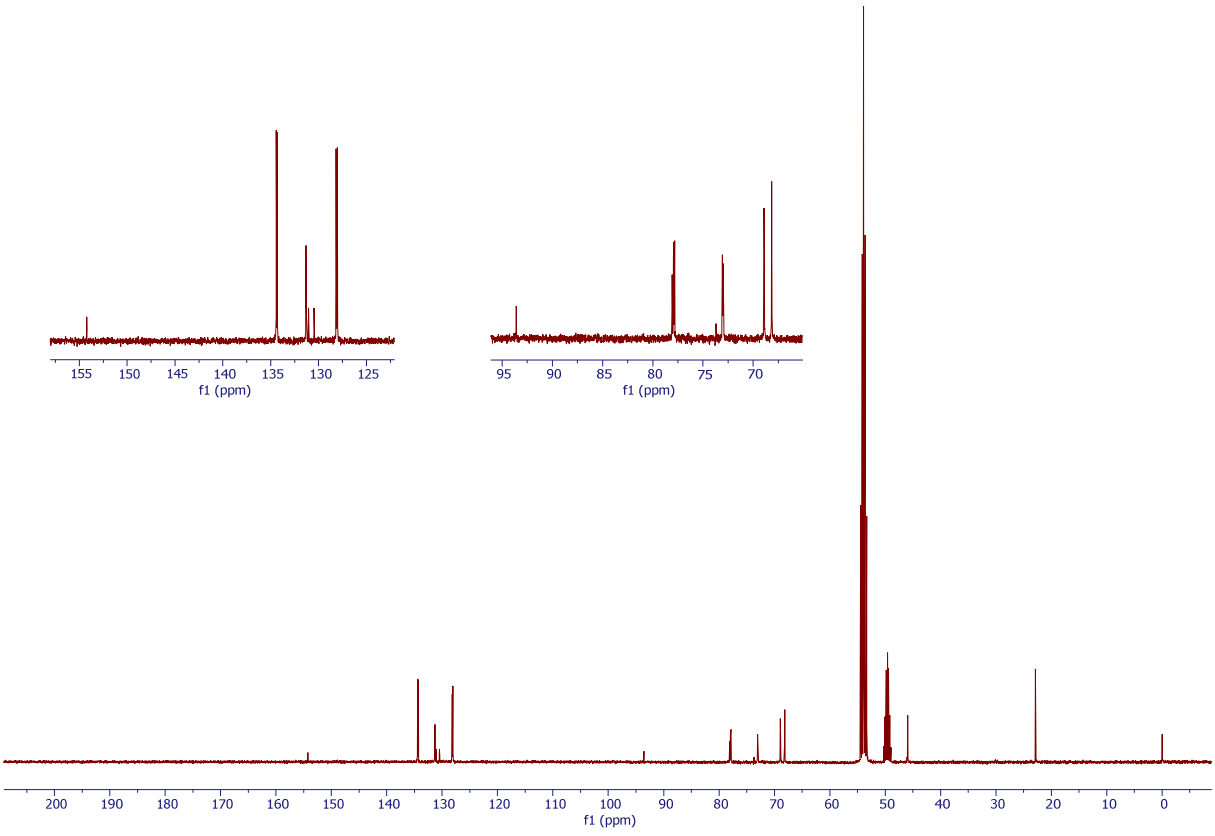

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2/CD_3OD) of **8**

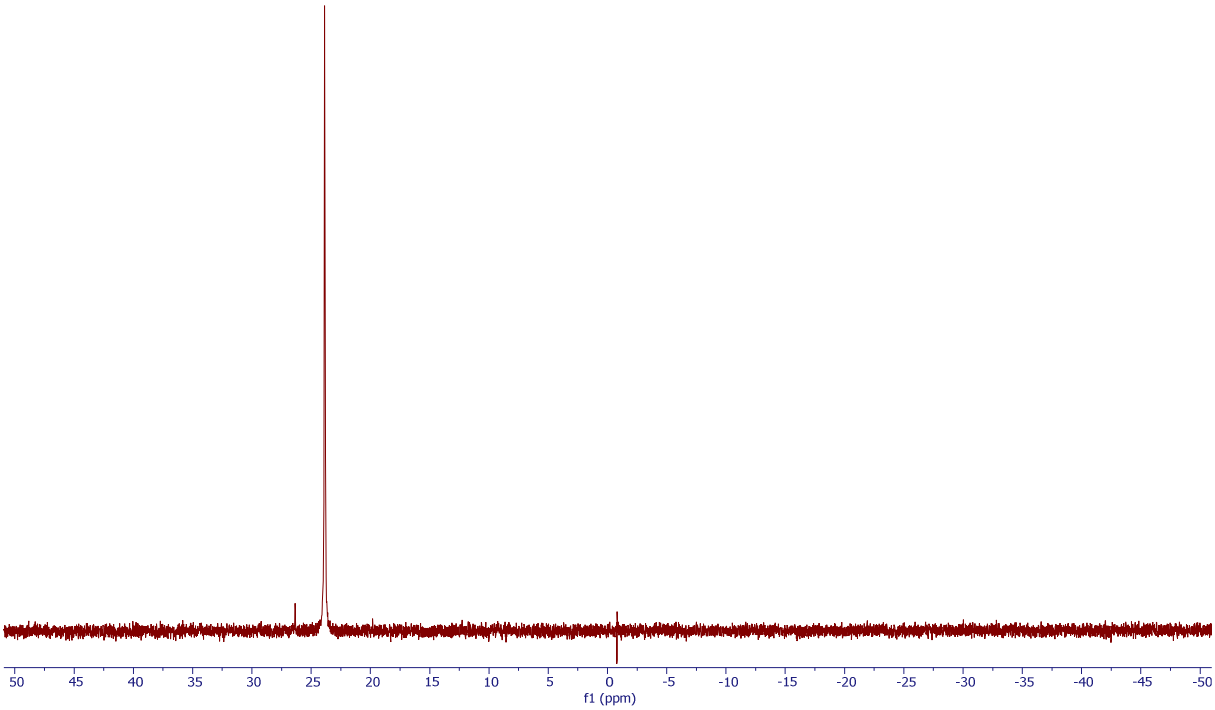

Figure S43. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2/CD_3OD) of **8**

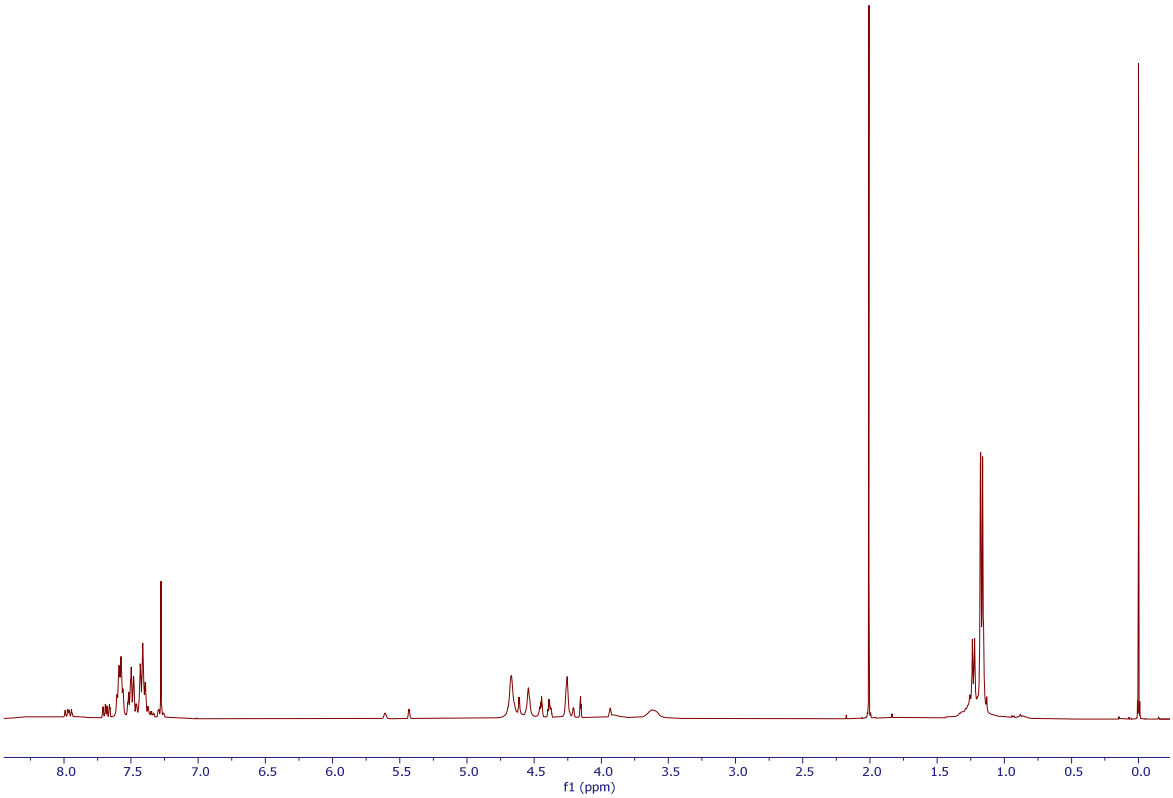

Figure S44. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the reaction mixture obtained by mixing (**1**^{iPr}**H**)Cl (2 equiv.) and $[PdCl_2(MeCN)_2]$ (1 equiv.). The major product is **9**-Cl.

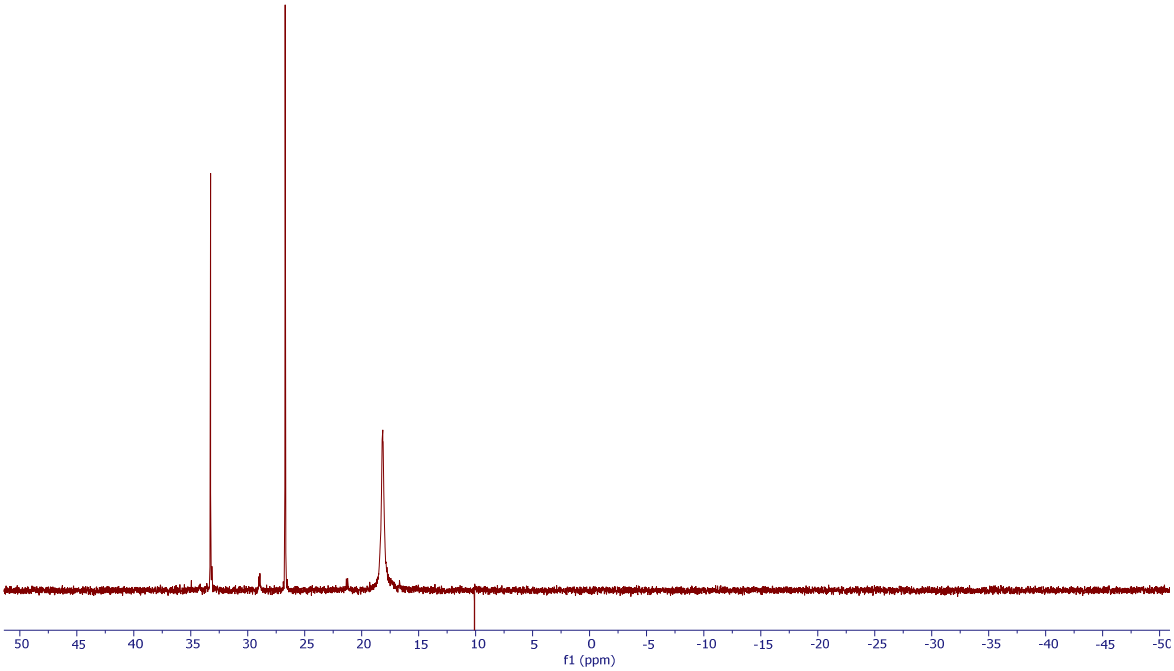

Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, $CDCl_3$) of the reaction mixture obtained by mixing (**1**^{iPr}**H**)Cl (2 equiv.) and $[PdCl_2(MeCN)_2]$ (1 equiv.). The major product is **9**-Cl.

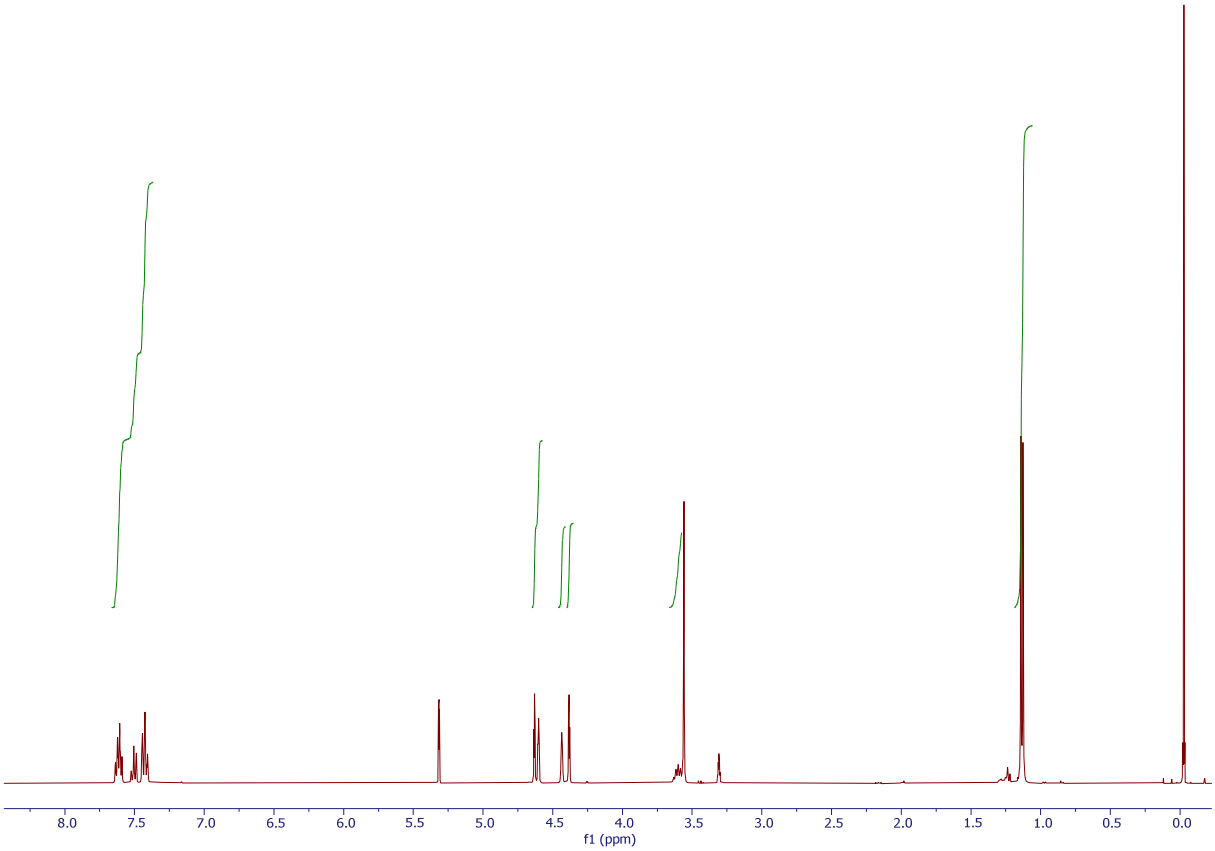

Figure S46. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2/CD_3OD) of **9**-SbF_6

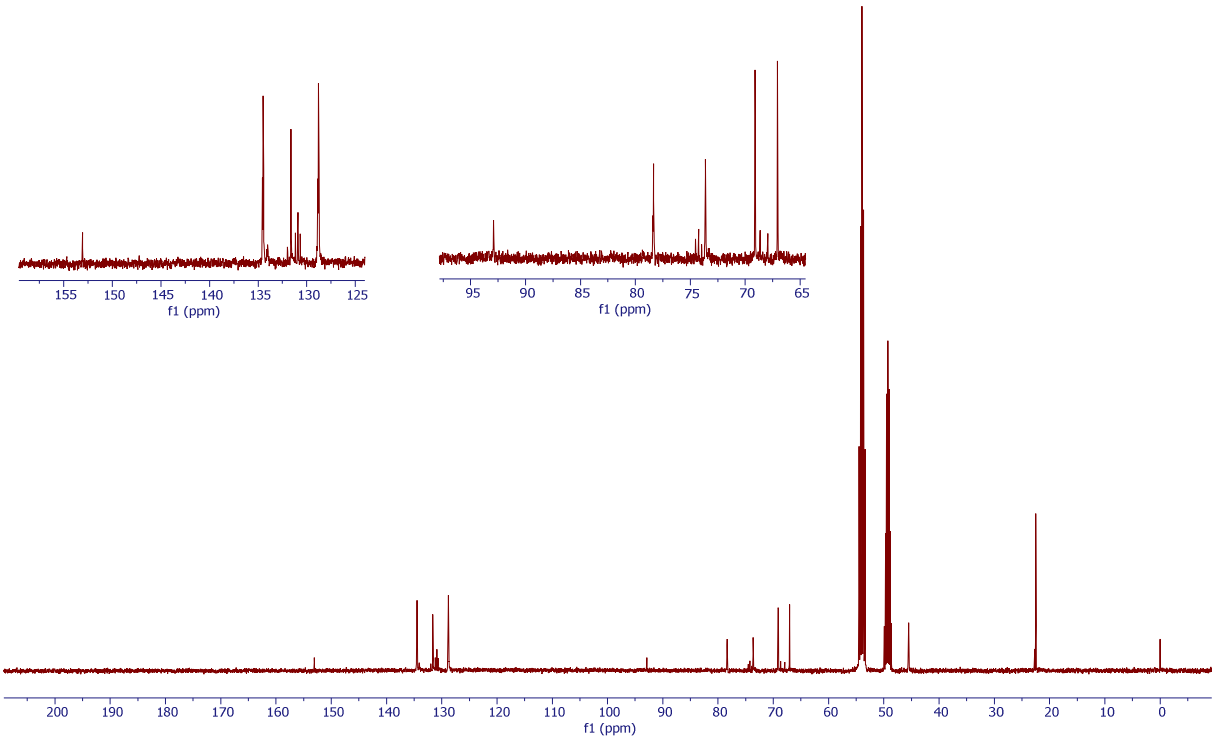

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2/CD_3OD) of **9**-SbF_6

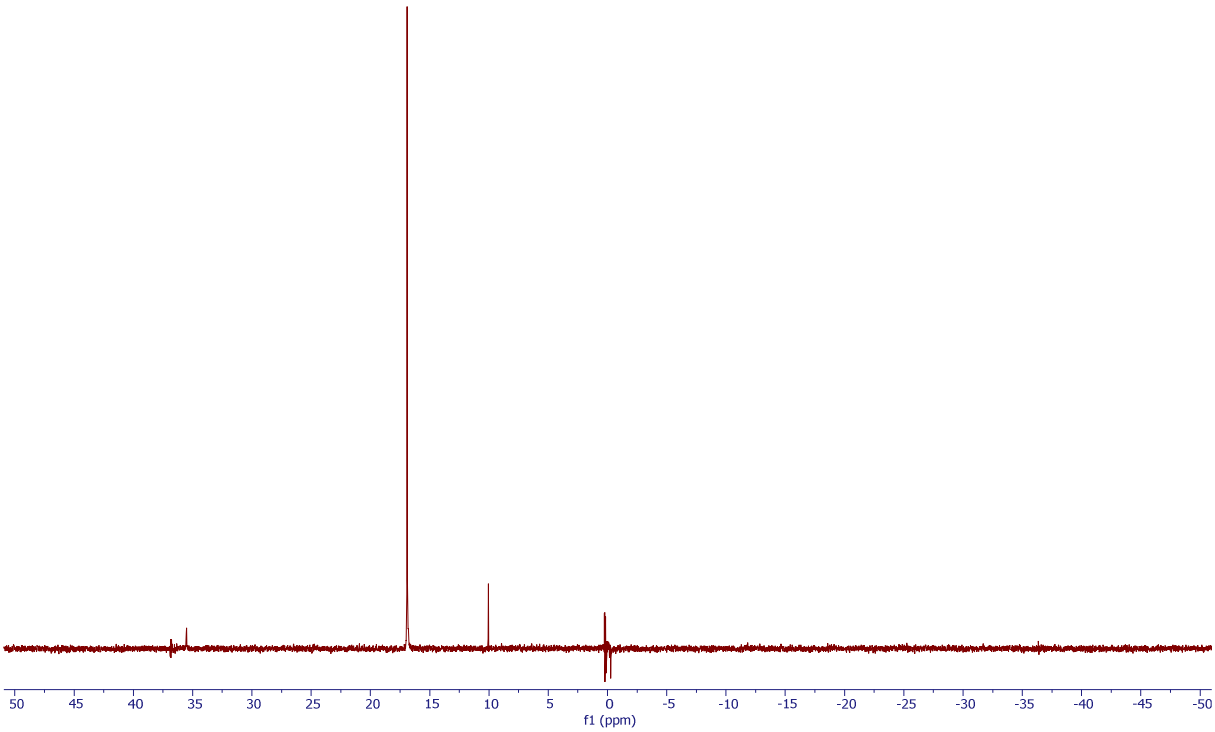

Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2/CD_3OD) of **9**-SbF_6

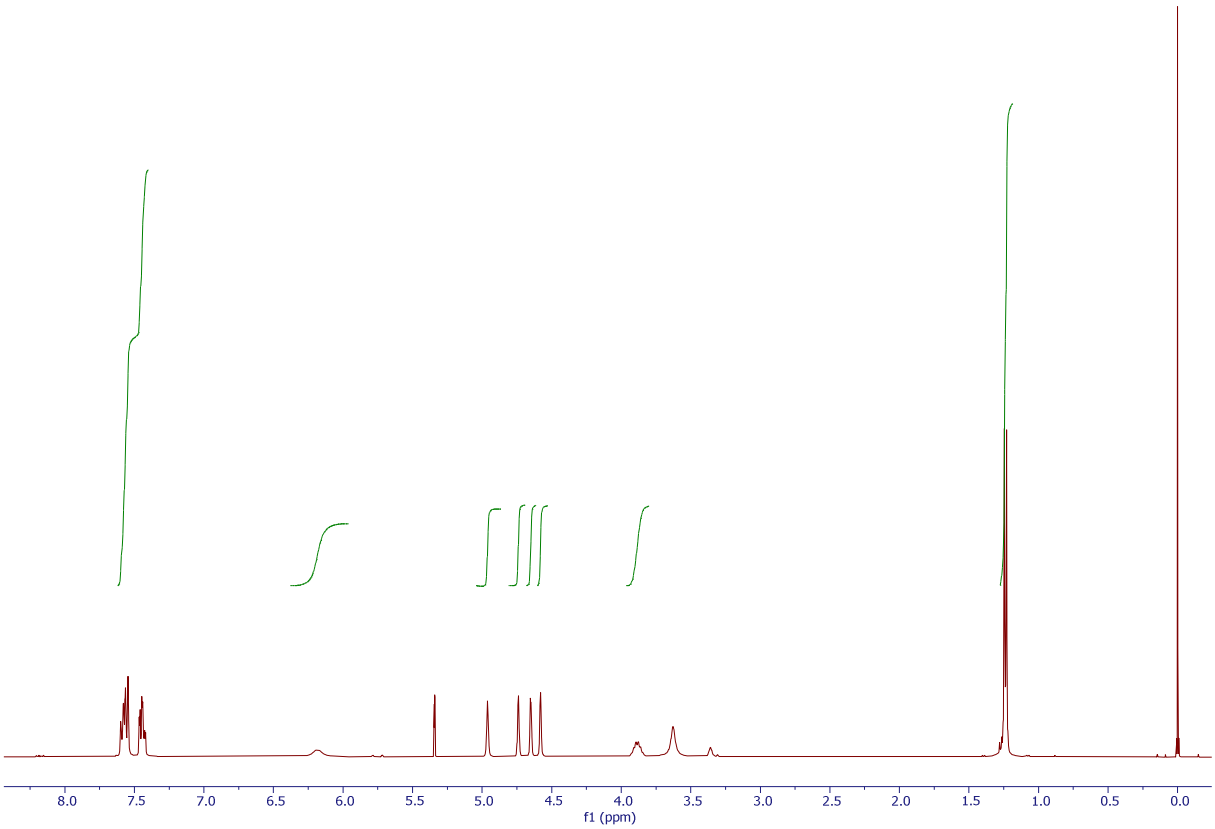

Figure S49. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2/CD_3OD) of **10**

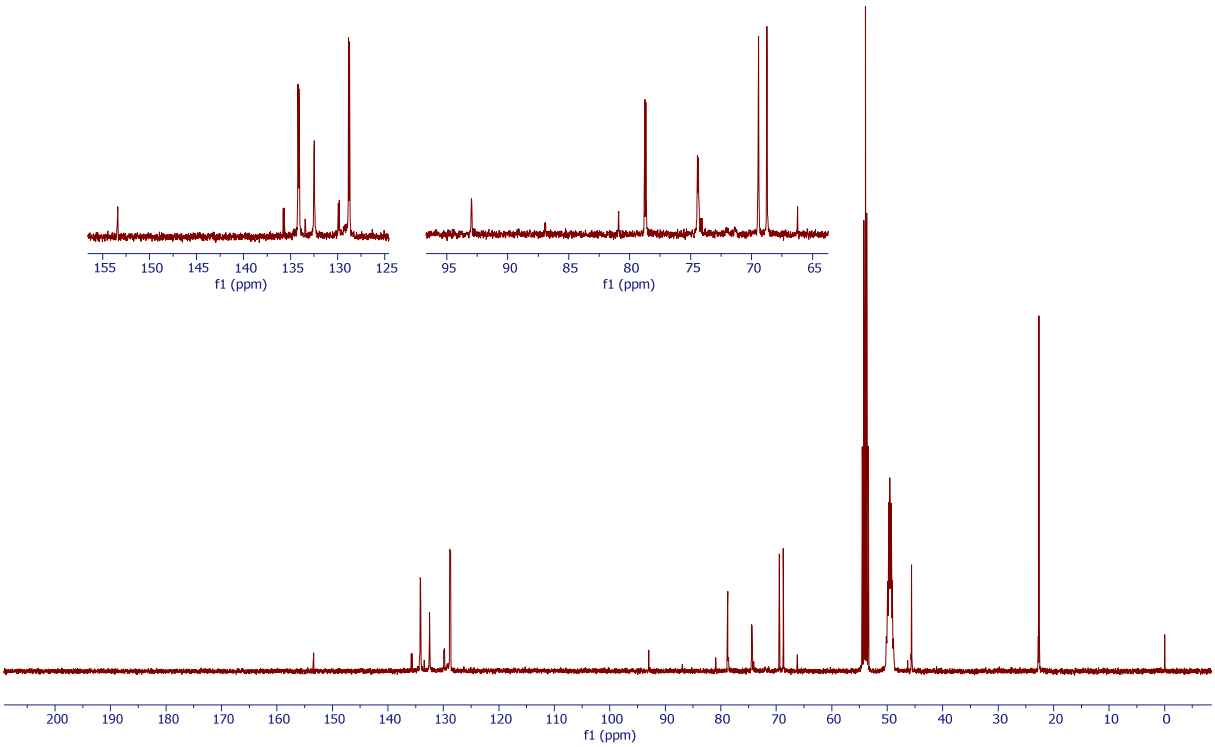

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2/CD_3OD) of **10**

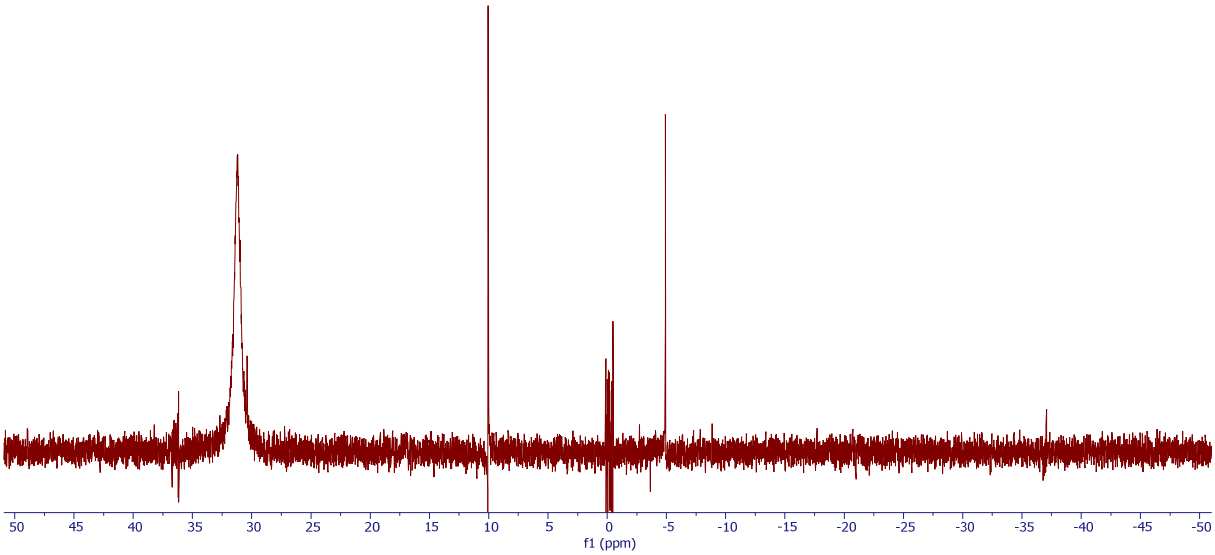

Figure S51. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2/CD_3OD) of **10**. The sharp signals at 10 ppm and near 0 ppm are spikes (electronic artefacts).

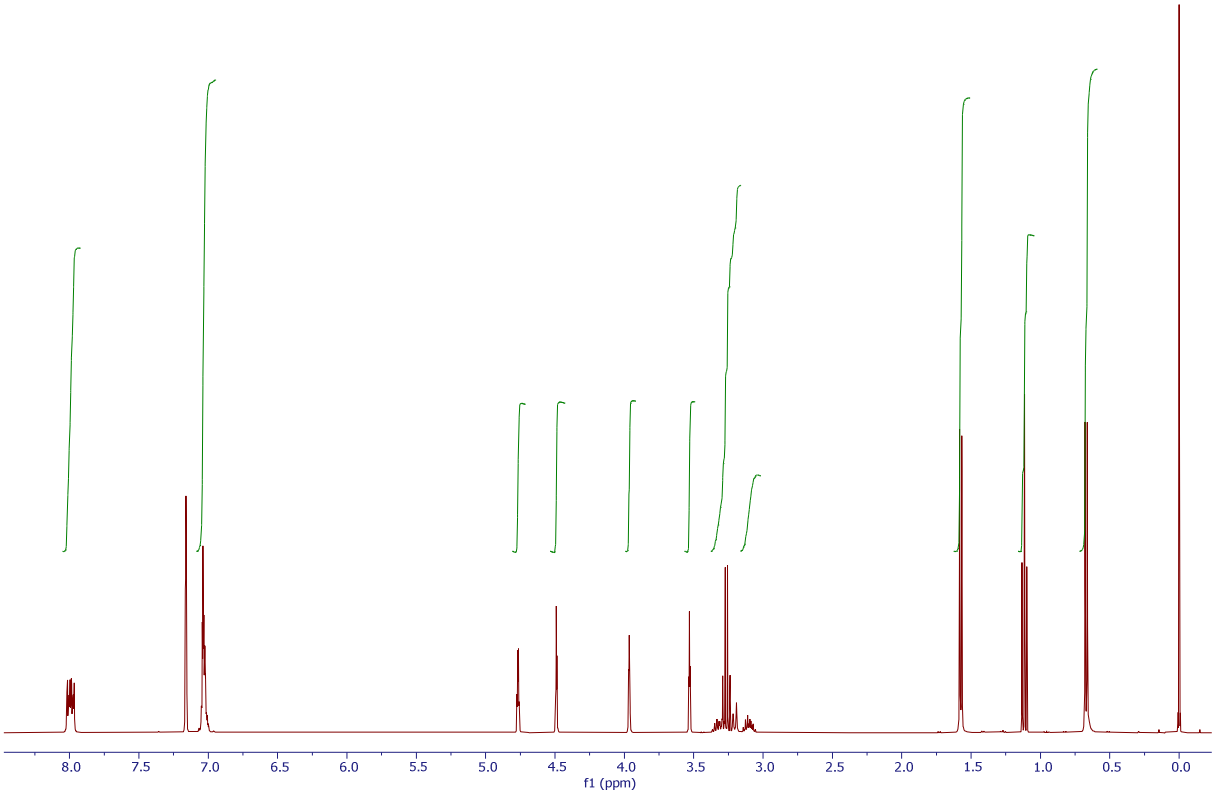

Figure S52. ^{1}H NMR spectrum (400 MHz, C_6D_6) of **11**

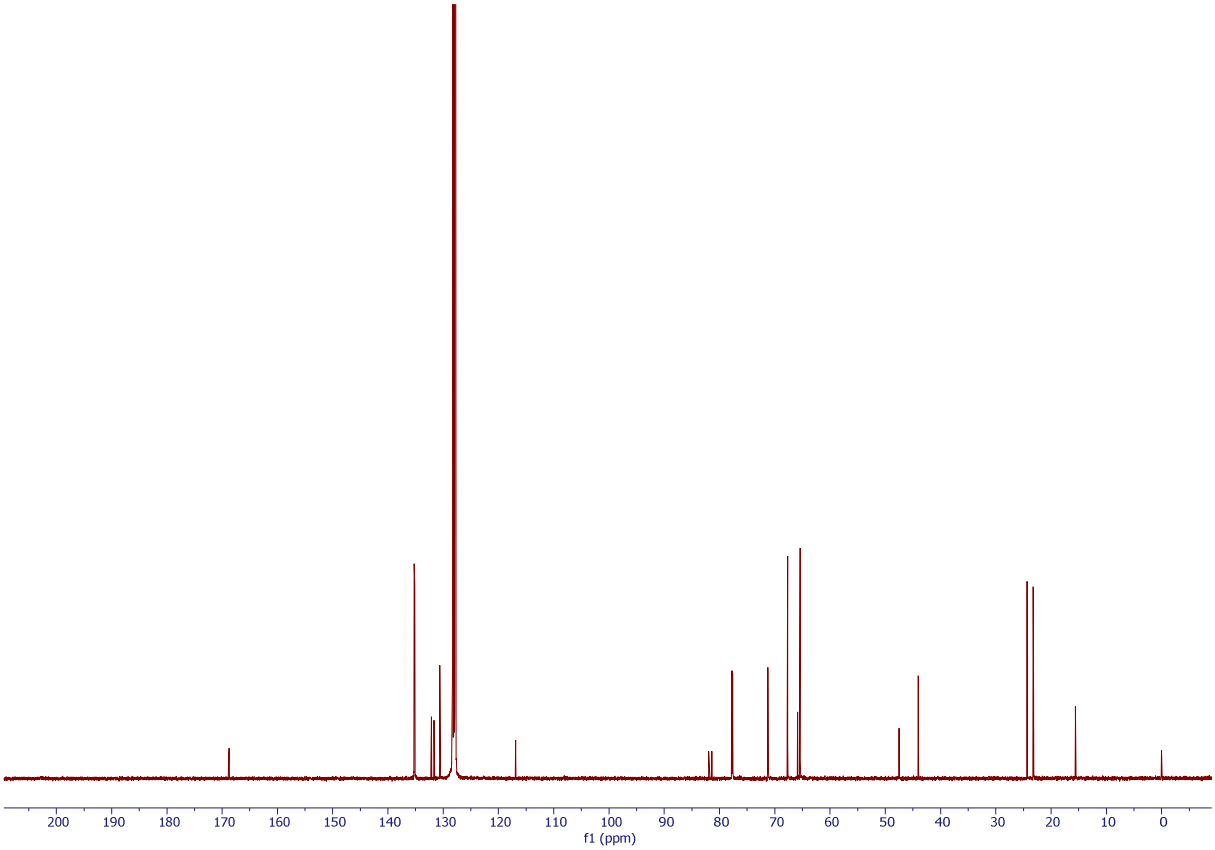

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of **11**

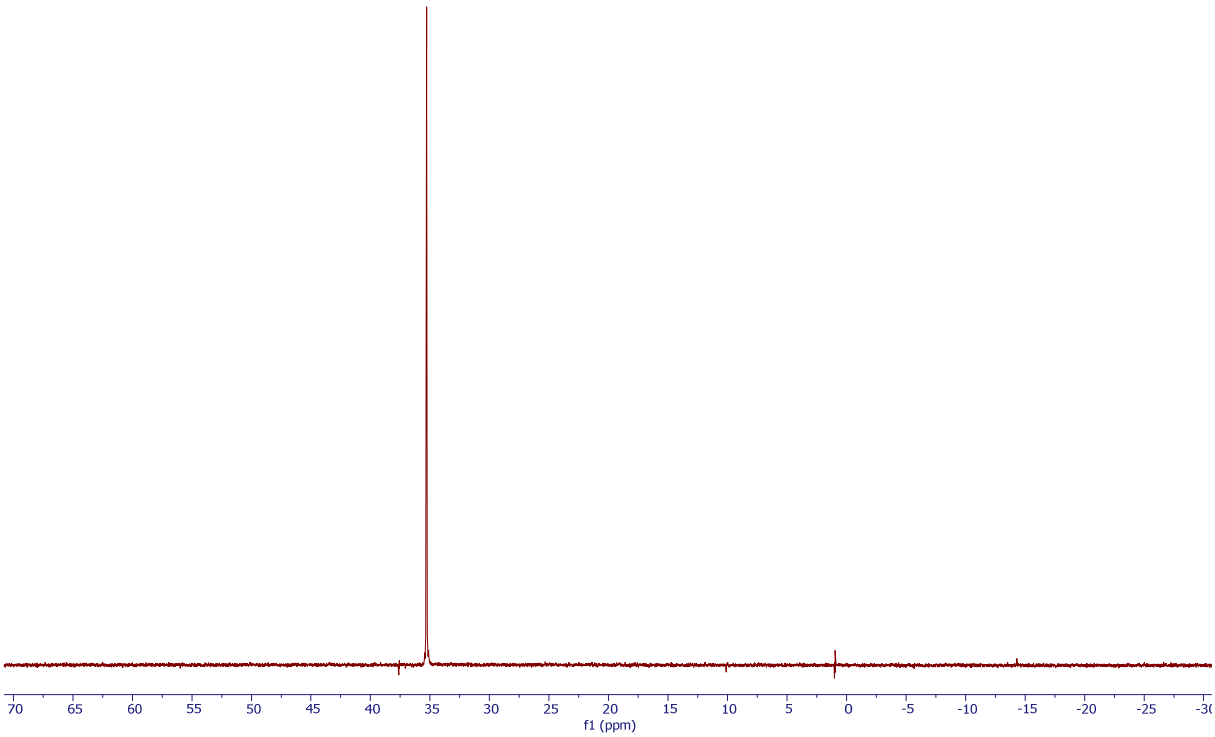

Figure S54. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, C_6D_6) of **11**

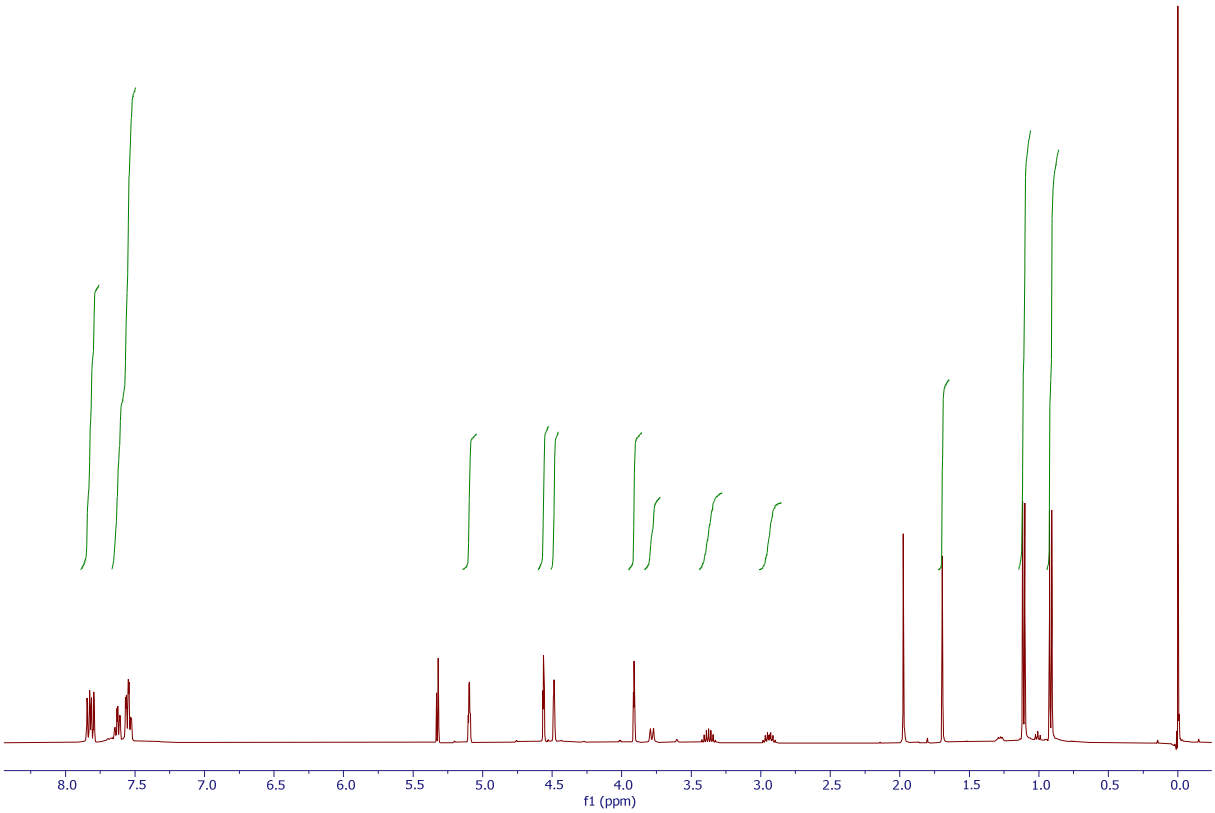

Figure 55. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **12**

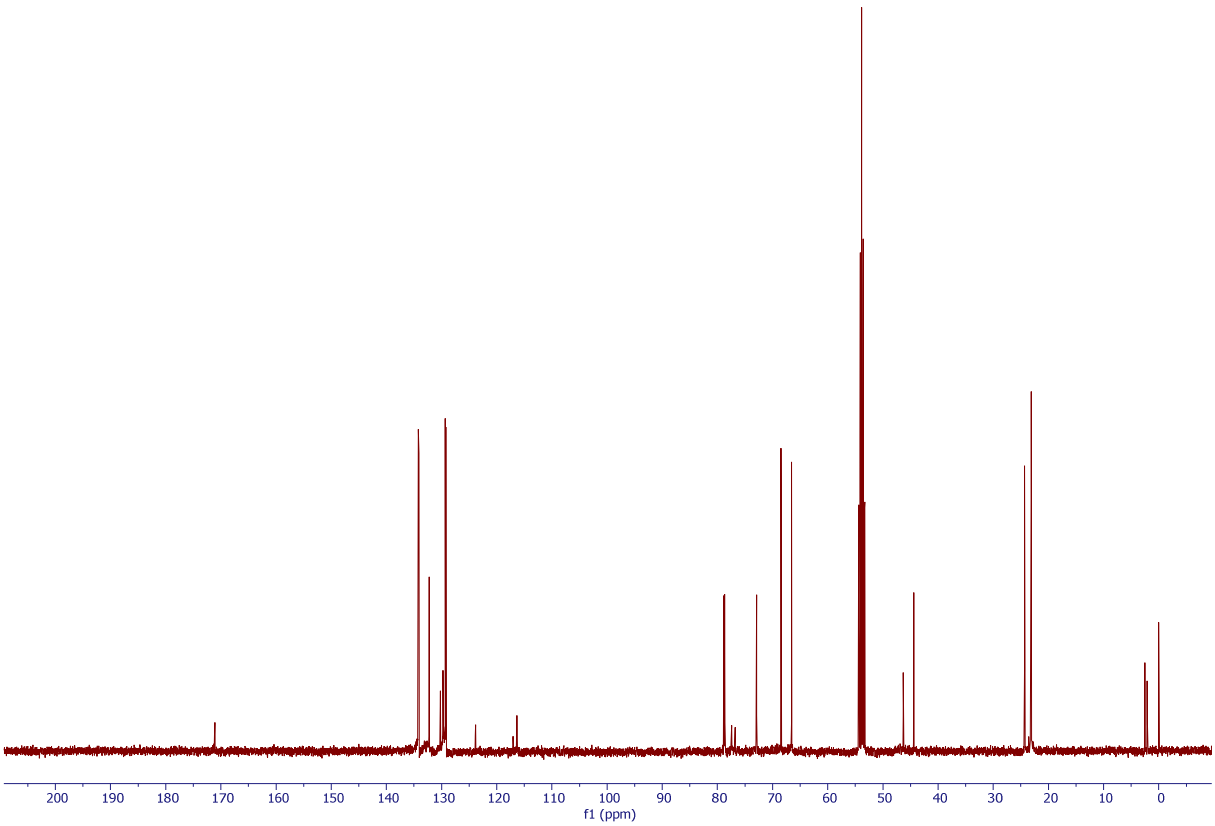

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **12**

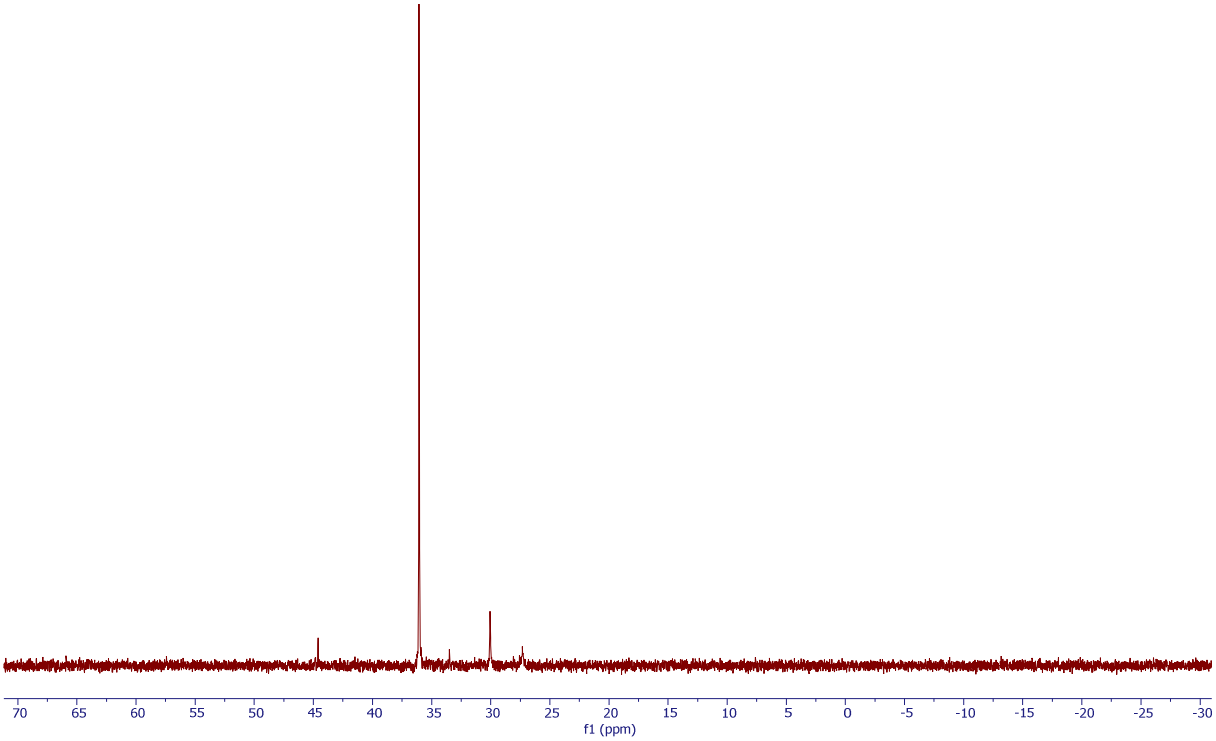

Figure S57. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **12**

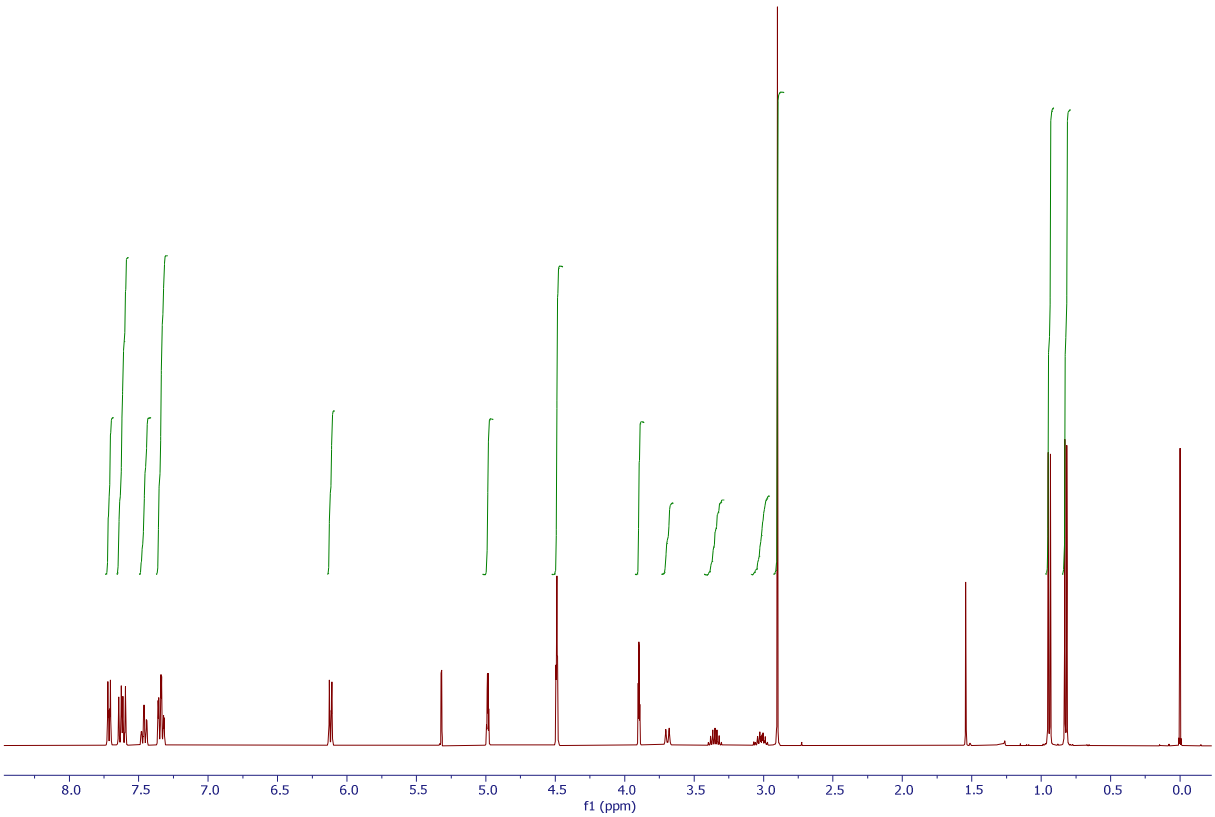

Figure S58. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **13**

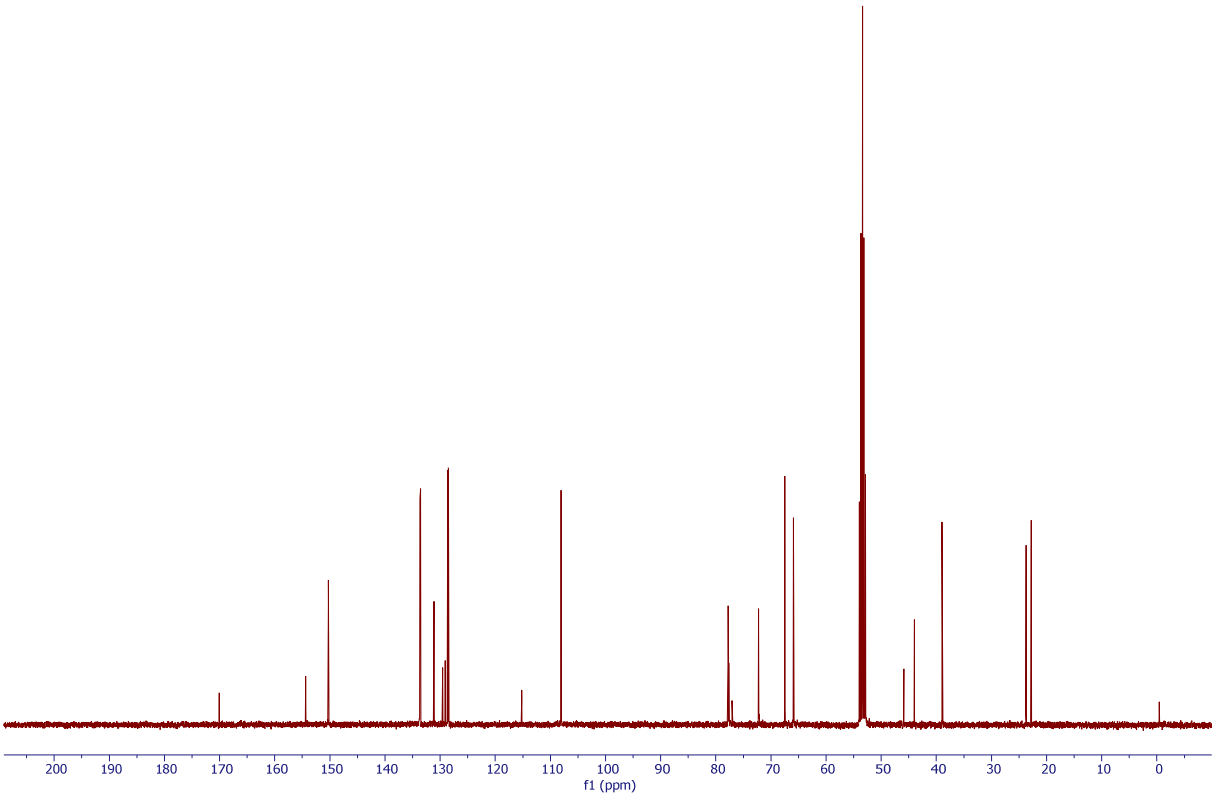

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **13**

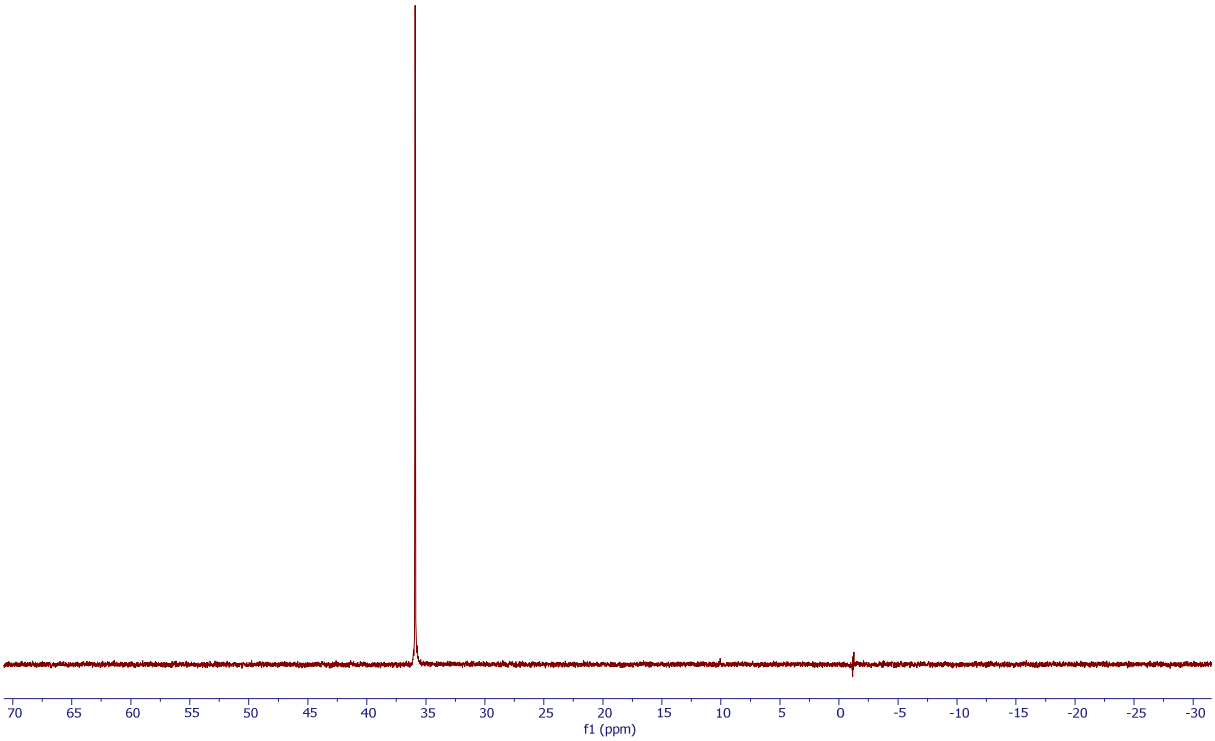

Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **13**

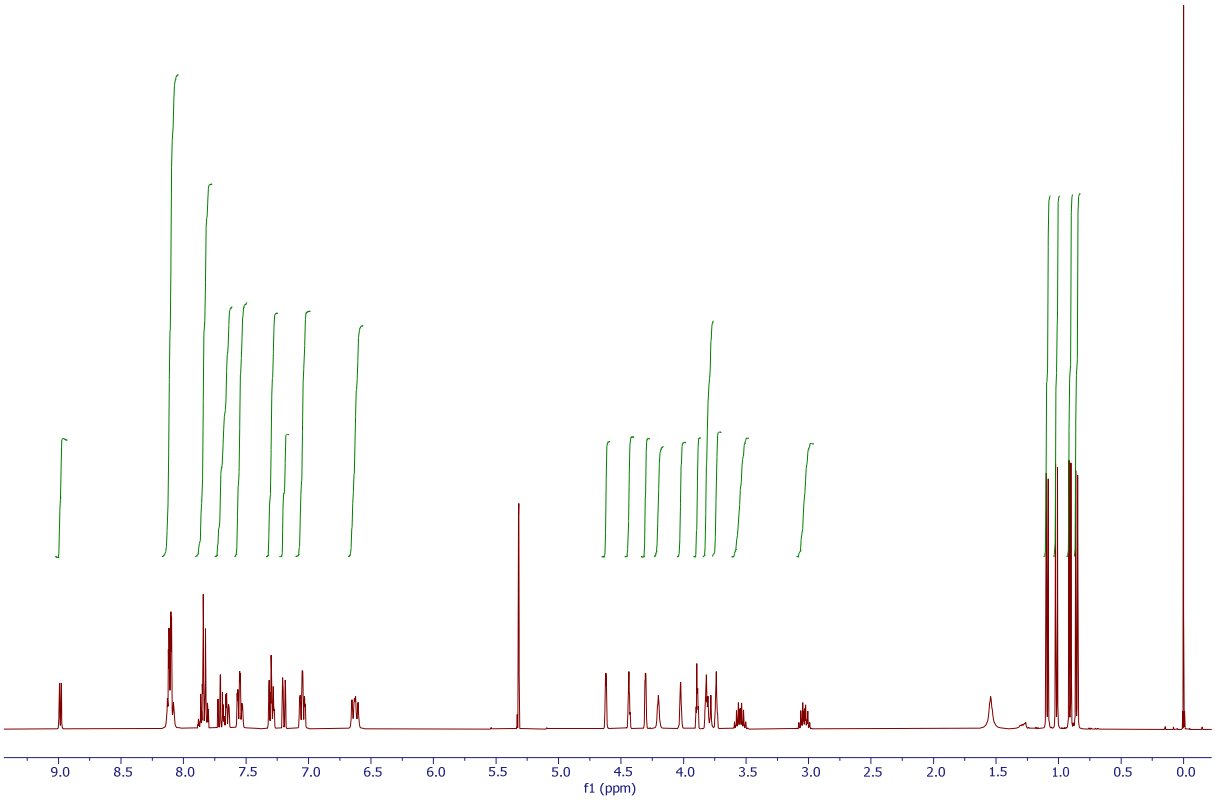

Figure S61. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **14**

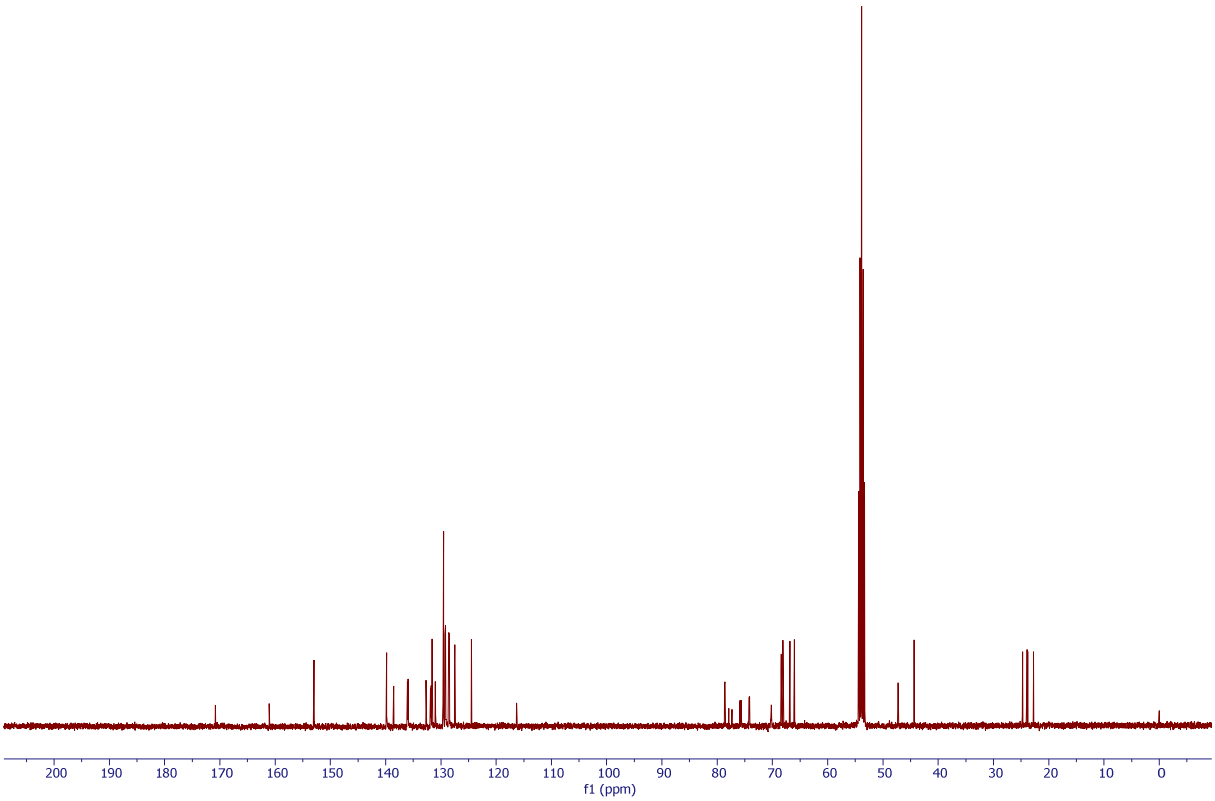

Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **14**

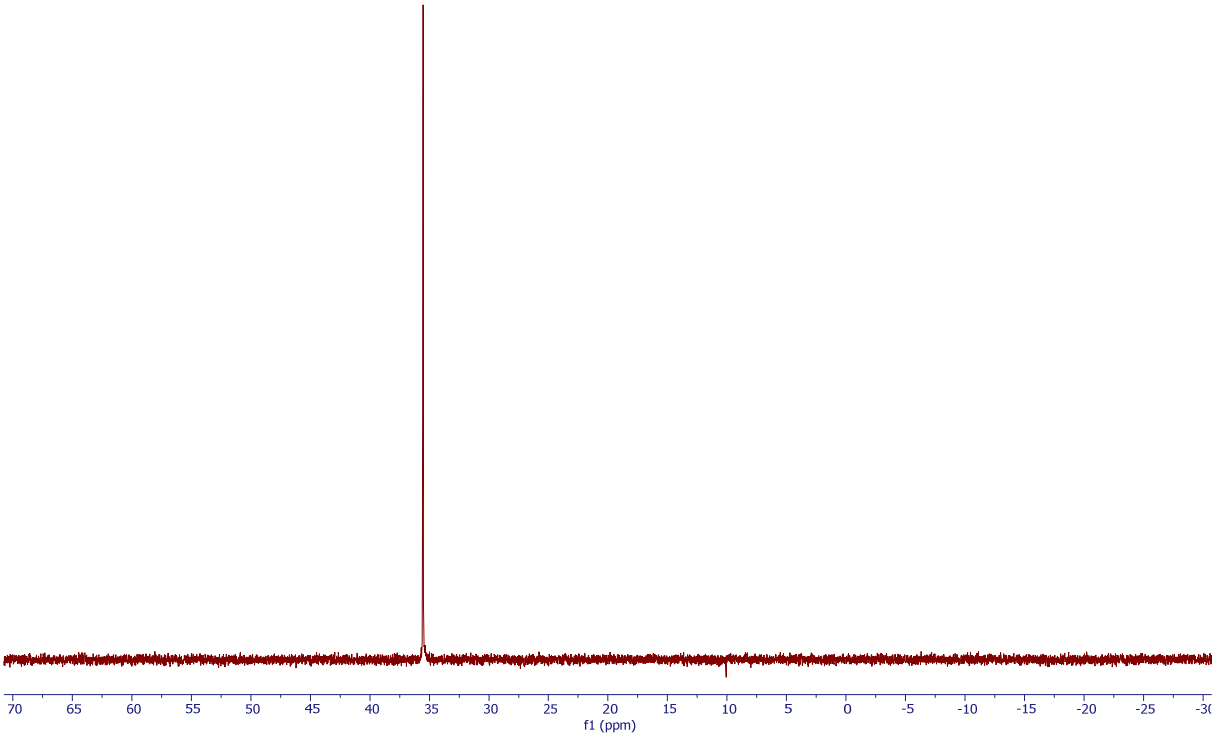

Figure S63. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **14**

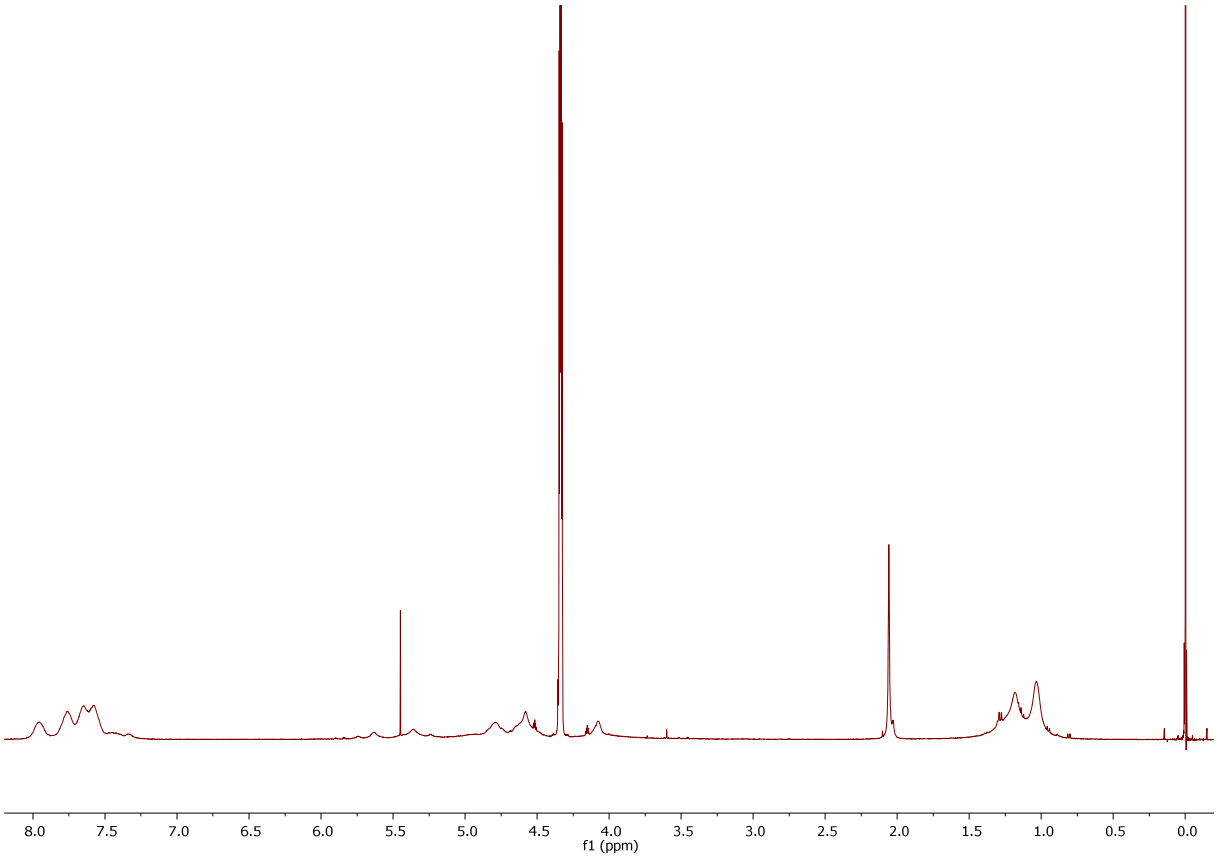

Figure S64. ^{1}H NMR spectrum (400 MHz, CD_3NO_2) of **15**

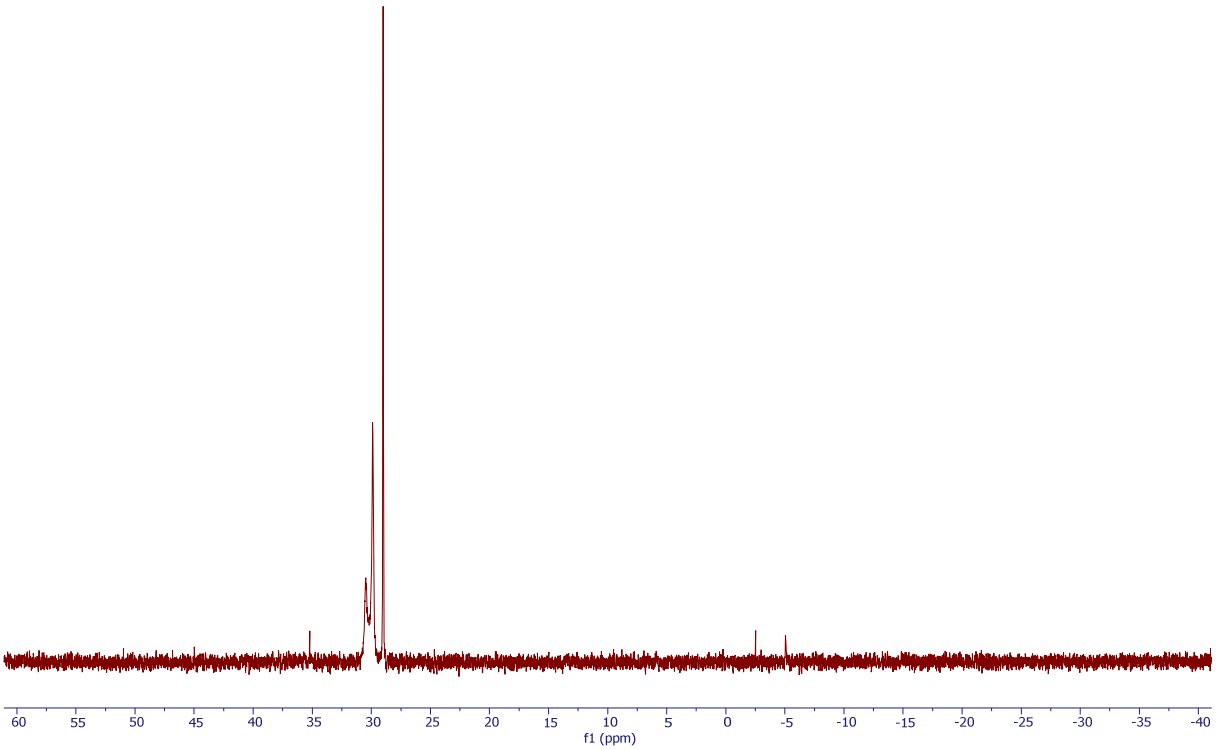

Figure S65. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_3NO_2) of **15**

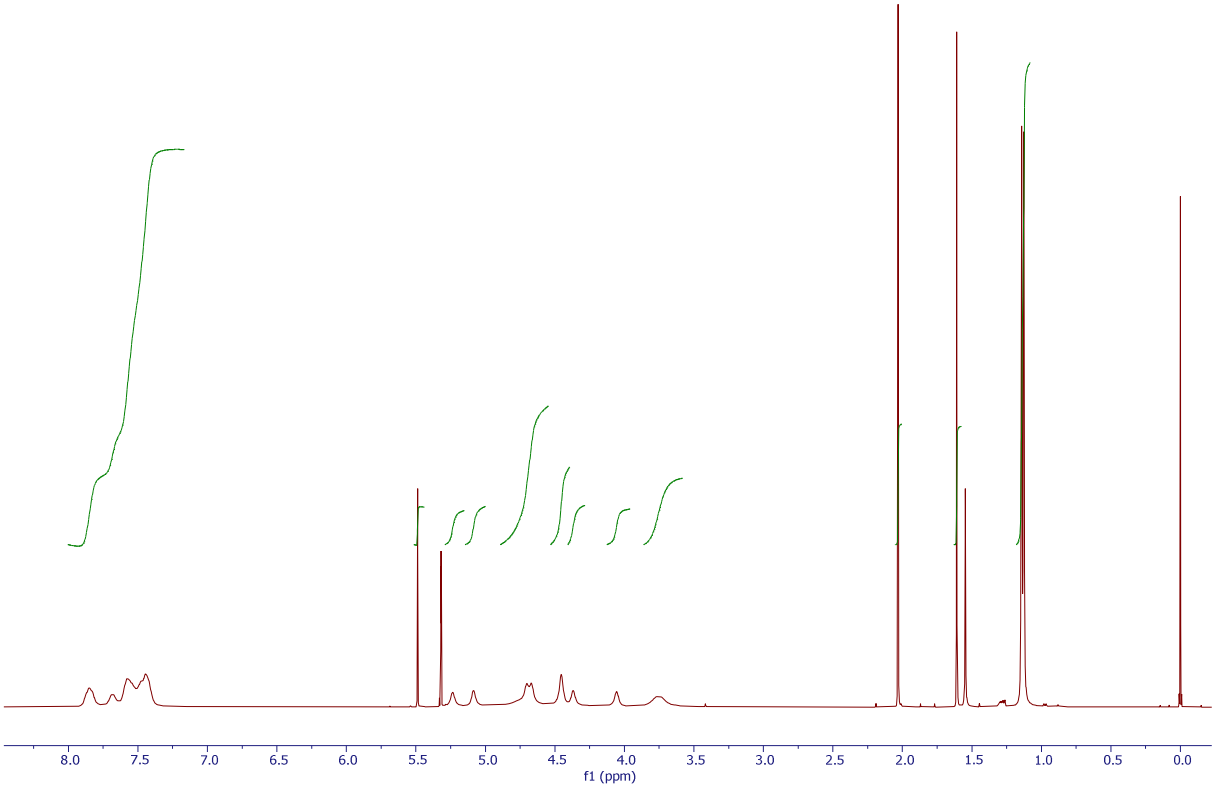

Figure S66. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of **16**

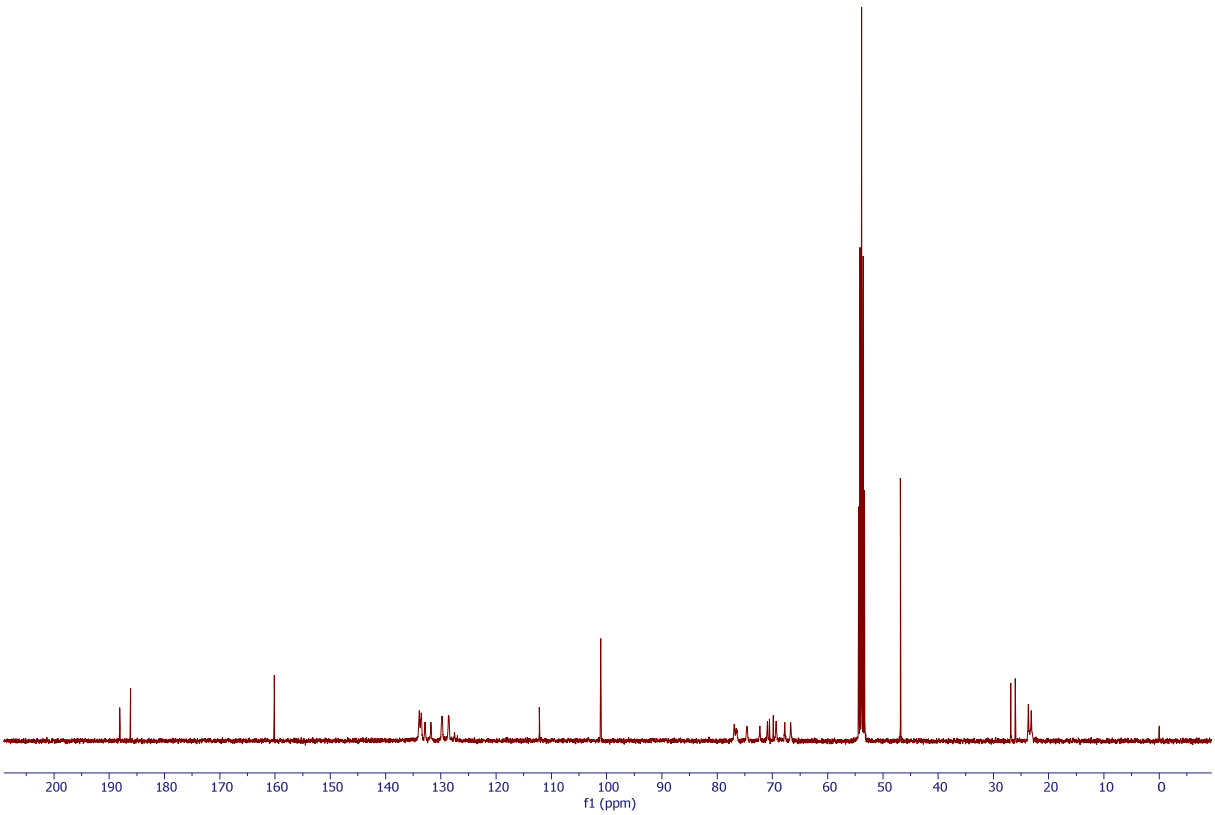

Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **16**

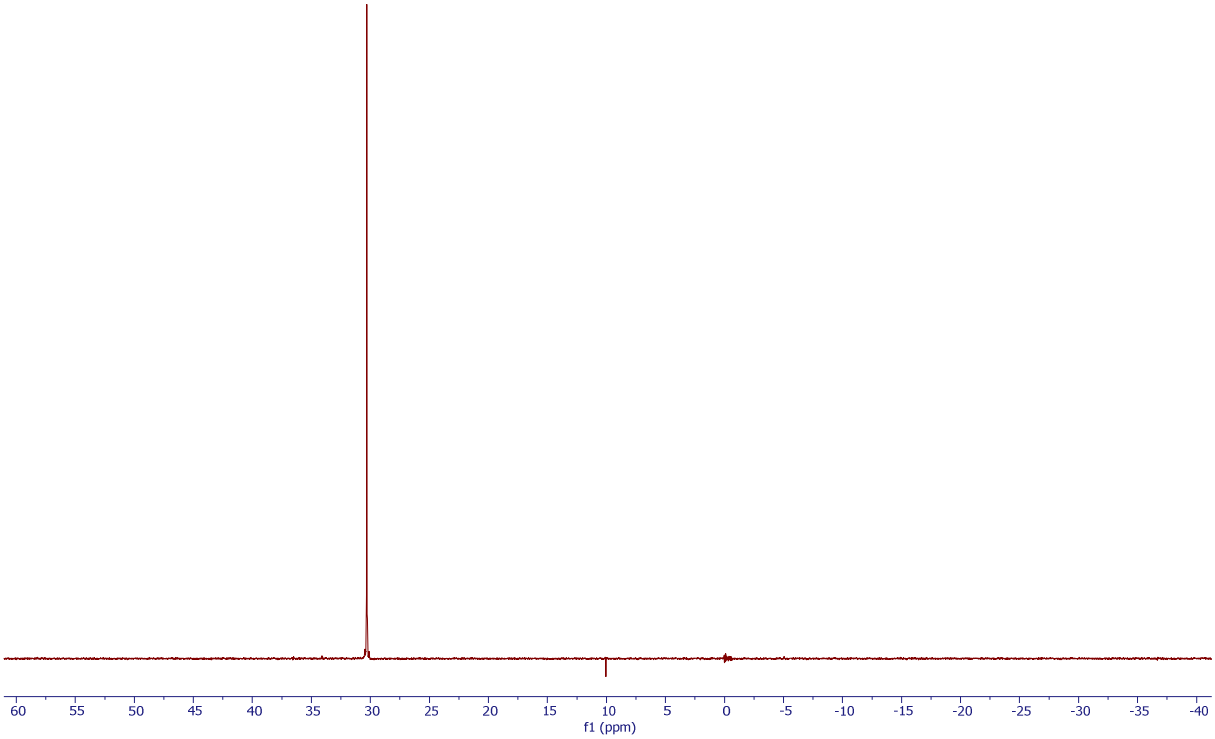

Figure S68. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, CD_2Cl_2) of **16**

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