Supporting Information

Reductive Elimination of C_6F_5-C_6F_5 from Pd(II) Complexes: Influence of α-Dicationic Chelating Phosphines

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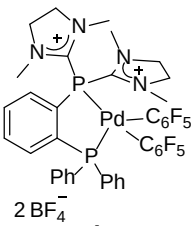
Table of Contents

Experimental procedures:

General: All reactions were carried out in flame-dried glassware under Ar. All solvents were purified by distillation over the appropiate drying agents and were transferred under Ar. IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESIMS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker AV 600, AV 400 or DPX 300; ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. Solvent signals were used as references and the chemical shifts converted to the TMS scale. Column chromatographies were performed on Merck 60 silica gel (40-63 µm), and for thin-layer chromatography (TLC) analyses Merck silica gel 60 F254 TLC plates were used. All commercially available compounds (ABCR, Acros, Aldrich, Fischer) were used as received. Ligands **1**, **2**,[1] 2-(diphenylphosphino)phenylphosphine[2], 2-Chloro-1,3-dimethylimidazolidinium tetrafluoroborate,[3] $[Pd(C_6F_5)_2(cod)]$ **3**,[4] $[Pd(C_6F_5)_2(2,2'\text{-bipyridine})]$ **11**[4], 2-(phenyl)phenylphosphine,[5] and $(C_6F_5)_2PCl$[6] were prepared according to literature procedures.

Compound **4**

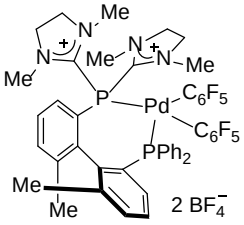


4

Pd complex **3** (100.0 mg, 0.182 mmol) was added to a CH_2Cl_2 (4 ml) solution of **1** (120.3 mg, 0.182 mmol) and the mixture obtained stirred overnight. After removal of the solvent *in vacuo* the solid residue washed with CH_2Cl_2 and dried, affording **4** as a white solid (168.8 mg, 84%). Colorless crystals suitable for X−ray crystallography were obtained by slow diffusion of Et_2O into CH_3CN/CH_2Cl_2 solutions of **4**.

^{1}H NMR (CD_3CN, 400 MHz): δ = 8.25 – 8.20 (m, 1H), 8.16 – 8.11(m, 1H), 8.10 – 8.05 (m, 2H), 7.68 – 7.65 (m, 2H), 7.53 – 7.50 (m, 8H), 4.14 – 4.10 (m, 8H), 3.03 ppm (s, 12H); ^{13}C NMR (CD_3CN, 125 MHz): δ = 157.2 (dd, *J* = 26.2 Hz; 1.1 Hz), 147.6 (dm, *J* = 194.2 Hz), 146.0 (dm, *J* = 191.3 Hz), 144.2 (dd, *J* = 52.0 Hz; 44.5 Hz), 140.6 (br), 138.8 (dd, *J* = 5.6 Hz; 2.3 Hz), 138.3 (d, *J* = 20.2 Hz), 137.8 (dm, *J* = 256.1 Hz), 137.5 (d, *J* = 13.4 Hz), 137.2 (dd, *J* = 7.2 Hz; 1.7 Hz), 134.4 (d, *J* = 12.5 Hz), 134.1 (d, *J* = 2.8 Hz), 130.6 (d, *J* = 11.4 Hz), 127.9 (d, *J* = 53.4 Hz), 126.3 (dd, *J* = 50.3 Hz, *J* = 33.7 Hz), 54.3 (d, *J* = 2.1 Hz), 38.3 ppm (d, *J* = 3.4 Hz); ^{31}P NMR (CD_3CN, 121 MHz): δ = 49.0 (m), 11.9 ppm (m); ^{11}B NMR (CD_3CN, 96 MHz): δ = – 1.1 ppm; ^{19}F NMR (CD_3CN, 282 MHz): δ = -116.8 (m), -117.6 (m), -157.9 (t, *J* = 19.7 Hz), -159.9 (t, *J* = 19.2 Hz), -161.8 (dt, *J* = 19.7; 8.7 Hz), -163.6 ppm (dt, *J* = 20.3; 8.3 Hz); HRMS *calcd.* for $C_{40}H_{34}N_4BF_{14}P_2Pd^+$: 1015.119220; *found* 1015.115674; IR $\tilde{\nu}$ = 465, 499, 518, 536, 643, 691, 735, 775, 1300, 1363, 1440, 1458, 1501, 1589, 1600 cm^{-1}.

Compound **5**

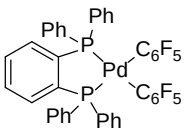


Acetone (3 ml) was added to a mixture of **3** (50.0 mg, 0.065 mmol) and **2** (35.8 mg, 0.065 mmol), and the mixture stirred for 48 h. After removal of the solvent *in vacuo*, the solid residue washed with CH_2Cl_2 and dried, affording **5** as a light yellow solid (57.5 mg, 73%).

^{1}H NMR (CD_3COCD_3, 400 MHz): δ = 8.08 – 8.04 (m, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.93 – 7.78 (m, 3H), 7.71 – 7.62 (m, 2H), 7.56 – 7.44 (m, 3H), 7.43 – 4.40 (m, 1H), 7.36 – 7.29 (m, 3H), 7.20 – 7.12 (m, 2H), 4.49 – 4.31 (m, 4H), 3.84 –

3.74 (m, 8H), 3.59 – 3.54 (m, 2H), 3.25 (s, 3H), 3.23 (s, 3H), 1.89 (s, 3H), 1.50 ppm (s, 3H); ^{13}C NMR (CD_3COCD_3, 100 MHz): δ = 158.3 (dd, *J* = 24.4 Hz; 3.6 Hz), 156.6 (d, *J* = 14.3 Hz), 144.3 (d, *J* = 8.3 Hz), 144.0 (d, *J* = 10.8 Hz), 142.3 (dd, *J* = 23.3 Hz; 3.0 Hz), 138.1 (d, *J* = 2.0 Hz), 137.7(dd, *J* = 13.5 Hz, *J* = 5.5 Hz), 136.8 (dd, *J* = 12.5 Hz; 2.8 Hz), 136.4 (d, *J* = 2.2 Hz), 134.7 (d, *J* = 10.0 Hz), 134.2 (d, *J* = 4.5 Hz), 133.9 (d, *J* = 2.4 Hz), 132.1 (d, *J* = 7.3 Hz), 131.9 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 41.8 Hz), 131.3 (d, *J* = 8.7 Hz), 130.5 (d, *J* = 8.6 Hz), 130.4 (d, *J* = 11.3 Hz), 129.2 (d, *J* = 10.7 Hz), 128.6 (t, *J* = 24.6 Hz), 126.5 (dd, *J* = 51.8 Hz; 1.8 Hz), 125.3 (d, *J* = 48.6 Hz), 56.1 (d, *J* = 1.5 Hz), 54.1 (d, *J* = 2.2 Hz), 53.6 (d, *J* = 2.2 Hz), 53.4, 42.5 (dd, *J* = 6.2 Hz; 5.1 Hz), 39.7 (t, *J* = 9.4 Hz), 37.6, 37.3 (d, *J* = 6.3 Hz), 20.9 (d, *J* = 2.5 Hz), 19.9 ppm (d, *J* = 1.6 Hz); ^{31}P NMR (CD_3COCD_3, 121 MHz): δ = 15.3 (m), 12.6 ppm (m); ^{11}B NMR (CD_3COCD_3, 96 MHz): δ = – 1.0 ppm; ^{19}F NMR (CD_3COCD_3, 282 MHz): δ = -110.8 (m), -111.0 (m), –113.7 (m), -114.2 (m), -156.7 (t, *J* = 19.9 Hz), -160.7 (m), -161.6 (t, *J* = 19.9 Hz), -163.4 (m), -163.9 ppm (m); HRMS *calcd.* for $C_{48}H_{42}N_4BF_{14}P_2Pd^+$: 1119.178050; *found* 1119.178274; IR $\tilde{\nu}$ = 420, 458, 468, 501, 521, 544, 696, 747, 766, 783, 924, 956, 1056, 1298, 1442, 1504, 1580 cm^{-1}.

Compound **6**

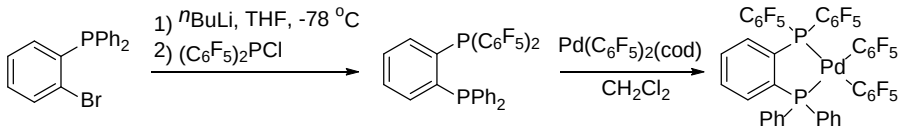


6

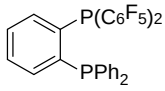
CH_2Cl_2 (2 ml) was added to a mixture of **3** (50.0 mg, 0.091 mmol) and 1,2-bis(diphenylphosphino)benzene (40.4 mg, 0.091 mmol) and the mixture stirred overnight. After removal of the solvent *in vacuo*, the solid residue was washed with pentane and dried, affording the desired product as a white solid (76.8 mg, 95%). Colorless crystals suitable for X−ray crystallography were obtained from CH_2Cl_2.

^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 7.75 – 7.72 (m, 2H), 7.61 – 7.60 (m, 2H), 7.51 – 7.49 (m, 4H), 7.47 – 7.44 (m, 8H), 7.39 – 7.37 ppm (m, 8H); ^{13}C NMR (CD_2Cl_2, 150 MHz): δ = 146.3 (dm, *J* = 230.4), 142.5 (t, *J* = 43.0 Hz), 137.5 (dm, *J* = 241.9 Hz), 136.5 (dm, *J* = 237.4 Hz), 133.9 (t, *J* = 8.6 Hz), 133.7 (t, *J* = 8.6 Hz), 133.1, 131.8, 130.6 (d, *J* = 47.9 Hz), 129.2 ppm (t, *J* = 4.5 Hz); ^{31}P NMR (CD_2Cl_2, 121 MHz): δ = 52.3 ppm; ^{19}F NMR (CD_2Cl_2, 282 MHz): δ = -113.7 (m), -161.2 (t, *J* = 20.7 Hz), -163.1 (tm, *J* = 20.7 Hz) ppm; MS-EI *calcd.* for $C_{42}H_{24}F_{10}P_2Pd$: 886.02; *found* 886.90; IR $\tilde{\nu}$ = 411, 422, 445, 498, 544, 602, 617, 668, 687, 741, 760, 774, 950, 1000, 1027, 1055, 1098, 1159, 1186, 1254, 1281, 1308, 1346, 1432, 1496, 1608, 1633, 3062 cm^{-1}.

Synthesis of **7**



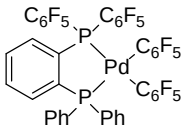
7



(2-Bromophenyl)diphenylphosphine (200.0 mg, 0.586 mmol) was dissolved in THF (5 ml) and *n*BuLi (1.6 M in hexanes, 0.340 ml, 0.590 mmol) was added at -78 °C dropwise. The reaction mixture was stirred for 1 h at -78 °C, and then $(C_6F_5)_2PCl$ (238.0 mg, 0.590 mmol) in THF (2 ml) was added dropwise. Finally the reaction was slowly warmed to

r.t. overnight. Removal of all volatiles *in vacuo* afforded a crude that was purified by column chromatography (SiO_2, hexane : toluene = 5 : 1) to afford the desired diphosphine (103.5 mg, 28%) as a white solid.

^{1}H NMR (C_6D_6, 400 MHz): δ = 7.32 – 7.30 (m, 1H), 7.18 – 7.13 (m, 1H), 7.05 – 7.02 (m, 5H), 6.95 – 6.88 ppm (m, 7H); ^{13}C NMR (C_6D_6, 100 MHz): δ = 149.5 (bs), 146.9 (bs), 142.6 (dm, $J_{C\text{-}F}$ = 258.5 Hz), 138.3 (dd, J = 34.0 Hz; 11.4 Hz), 138.2 (d, J = 34.3 Hz; 11.4 Hz), 137.7 (dm, $J_{C\text{-}F}$ = 252.8 Hz), 135.9 (q, J = 5.0 Hz), 133.6 (d, 19.2 Hz), 132.7 (d, J = 8.9 Hz), 130.4, 129.8, 129.0, 128.8 ppm (d, J = 7.0 Hz); ^{31}P NMR (C_6D_6, 121 MHz): δ = -16.6 (dt, $J_{P\text{-}F}$ = 184.5 Hz; 5.1 Hz), -56.4 ppm (dq, $J_{P\text{-}F}$ = 184.5 Hz; 30.2 Hz); ^{19}F NMR (C_6D_6, 282 MHz): δ = -129.2 (m), -149.8 (m), -160.5 ppm (m); HRMS *calcd.* for $C_{30}H_{14}F_{10}P_2$: 626.040937; *found* 626.041114; IR $\tilde{\nu}$ = 407, 439, 478, 494, 511, 521, 586, 631, 675, 745, 800, 840, 972, 1026, 1082, 1260, 1284, 1306, 1378, 1434, 1440, 1514, 1585, 1641, 2859, 2963, 3055 cm^{-1}.

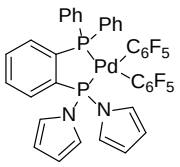


7

A solution of the free diphosphine already prepared above (50.0 mg, 0.080 mmol) in CH_2Cl_2 (2 ml) was added to **3** (43.8 mg, 0.080 mmol) and stirred overnight. After removal of the solvent *in vacuo*, the solid residue was washed with pentane and dried, affording **7** as a white solid (81.7 mg, 96%).

^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 8.07 – 7.96 (m, 1H), 7.84 – 7.82 (m, 1H), 7.76 – 7.65 (m, 2H), 7.63 – 7.54 (m, 2H), 7.36 – 7.52 ppm (m, 8H); ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 148.5 (m), 147.3 (dm, J = 21.0 Hz), 147.2 (dm, 22.4 Hz), 145.9 (m), 145.7 (m), 144.9 (dm, J = 29.2 Hz), 143.1 (m), 141.4 (dd, J = 50.8 Hz; 44.5 Hz), 139.7 (m), 139.2 (m), 138.9, 138.0 (m), 137.2 (m), 135.5 (m), 134.7 (dd, J = 19.9 Hz, J = 1.1 Hz), 134.5 (dd, J = 5.5 Hz, J = 2.0 Hz), 134.3 (dd, J = 6.3 Hz; 1.8 Hz), 133.7 (d, J = 12.5 Hz), 133.3 (dm, J = 15.7 Hz), 132.3 (d, J = 2.6 Hz), 129.8, 129.4 ppm (d, J = 11.1 Hz); ^{31}P NMR (CD_2Cl_2, 121 MHz): δ = 51.0 (m), 16.9 ppm (m); ^{19}F NMR (CD_2Cl_2, 282 MHz): δ = -115.0 (m), -118.1 (m), -127.1 (m), -145.7 (m), -159.0 (m), -160.7 (t, J = 19.7 Hz), -161.4 (t, J = 19.7 Hz), -163.5 (td, J = 20.1 Hz, J = 9.4 Hz), -164.0 ppm (td, J = 20.1 Hz, J = 10.4 Hz); HRMS *calcd.* for $C_{42}H_{14}F_{20}P_2Pd_1Na_1^+$: 1088.917860; *found* 1088.917765; IR $\tilde{\nu}$ = 458, 483, 519, 536, 631, 670, 692, 745, 797, 954, 977, 1017, 1091, 1260, 1297, 1360, 1455, 1475, 1499, 1519, 1642, 2963 cm^{-1}.

Synthesis of **8**

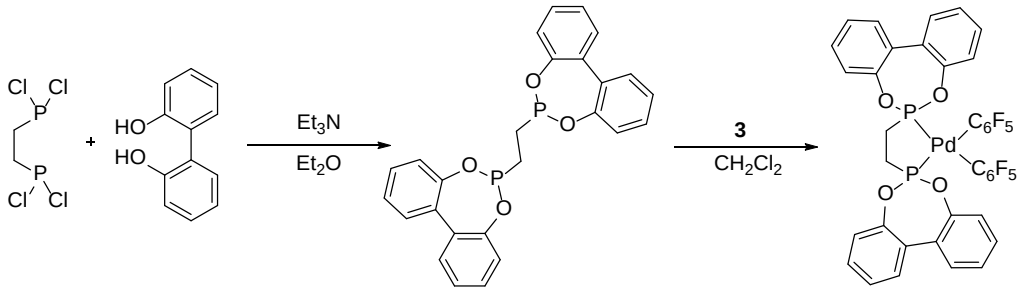


8

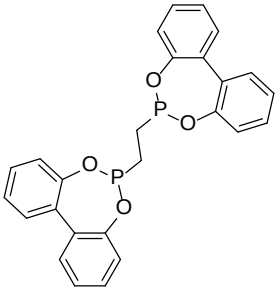
(Dipyrrolylphosphino)–2–diphenylphosphine (38.7 mg, 0.091 mmol) and **3** (50.0 mg, 0.091 mmol) were dissolved in CH_2Cl_2 (1 ml) and stirred overnight. Then, the solvent was evaporated *in vacuo* and washed with Et_2O to afford the desired compound as a white solid (73.3 mg, 93%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.50 – 7.91 (m, 1H), 7.85 – 7.81 (m, 1H), 7.80 – 7.75 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.33 (m, 8H), 6.86 – 6.84 (m, 5H), 6.40 – 6.38 ppm (m, 4H). ^{13}C NMR (CD_2Cl_2, 125 Mz): δ = 147.2 (dm, $J_{C\text{–}F}$ = 68.6 Hz), 145.3 (dm, $J_{C\text{–}F}$ = 72.8 Hz), 141.8 (dd, $J_{C\text{–}P}$ = 49.6, $J_{C\text{–}P}$ = 37.0 Hz), 140.8 (dd, $J_{C\text{–}P}$ = 52.1, $J_{C\text{–}P}$ = 43.2 Hz), 138.1 (dm, $J_{C\text{–}F}$ = 241.6 Hz), 136.8 (d, $J_{C\text{–}F}$ = 250.6 Hz), 135.62 (d, $J_{C\text{–}P}$ = 6.0 Hz), 134.23 (d, $J_{C\text{–}P}$ = 19.3 Hz), 133.59 (d, $J_{C\text{–}P}$ = 12.6 Hz), 133.3 (dd, $J_{C\text{–}P}$ = 5.9 Hz, $J_{C\text{–}P}$ = 1.6 Hz), 132.2 (d, $J_{C\text{–}P}$ = 2.5 Hz), 132.1 (dd, $J_{C\text{–}P}$ =15.8, $J_{C\text{–}P}$ = 2.4 Hz), 129.4 (d, $J_{C\text{–}P}$ = 10.9 Hz), 128.9 (d, $J_{C\text{–}P}$ =49.7 Hz), 124.1 (d, $J_{C\text{–}P}$ =8.2 Hz), 114.8 ppm (d, $J_{C\text{–}P}$ =Hz). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ = 109.1 (br), 47.9 ppm (br). ^{19}F

NMR (CD_2Cl_2, 282 MHz): – 115.02 (m), – 161.59 (m), – 163.57 (dm, J_{F-P} = 139.0 Hz). HRMS *calcd.* for $C_{38}H_{22}N_2F_{10}P_2PdNa^+$: 887.002710, *found* 887.002477. IR ũ = 421, 450, 478, 511, 537, 566, 608, 627, 672, 702, 725, 776, 953, 1001, 1055, 1100, 1115, 1237, 1350, 1360, 1436, 1498, 1531, 3060 cm^{-1}.

Synthesis of **9**:

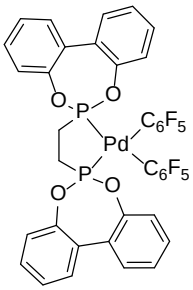


9



1,2-bis(dichlorophosphino)ethane (0.50 ml, 3.30 mmol) was added dropwise to a solution of 2,2'-biphenol (1.2 g, 6.60 mmol) and Et_3N (1.840 ml, 13.20 mmol) in Et_2O (30 ml) at -78 ^oC, and the mixture was allowed to warm to r.t. overnight. The reaction was then filtered and the filtrate evaporated *in vacuo* to give a white solid, which was washed with a small amount of CH_2Cl_2 and dried, affording the desired ligand as a white solid (983.1 mg, 65%).

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.47 (dd, *J* = 7.5 Hz, *J* = 1.8 Hz, 4H), 7.37 (dt, *J* = 7.5 Hz; 1.8 Hz, 4H), 7.30 (dt, *J* = 7.5 Hz; 1.3 Hz, 4H), 7.12 (d, *J* = 7.9 Hz, 4H), 1.95 ppm (t, *J* = 6.7 Hz, 4H); ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 151.4 (t, *J* = 3.1 Hz), 132.2, 130.6, 129.7, 125.6, 122.2, 26.1 ppm (dd, *J* = 42.1 Hz; 19.5 Hz); ^{31}P NMR (CD_2Cl_2, 121 MHz): δ = 207.2 ppm; HRMS *calcd.* for $C_{26}H_{20}$ O_4P_2: 458.083314; *found* 458.083689; IR $\tilde{\nu}$ = 416, 429, 480, 516, 591, 669, 703, 762, 883, 939, 978, 1036, 1060, 1094, 1202, 1245, 1268, 1400, 1435, 1474, 1496, 1595, 1713, 2404, 2943, 3023, 3070, 3185 cm^{-1}.



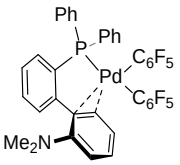
9

Palladium compound **3** (53.8 mg, 0.098 mmol) was added to a solution of the phosphonite already described (45.0 mg, 0.098 mmol) in CH_2Cl_2 (2 ml) and the resulting mixture stirred overnight. After removal of the solvent *in vacuo*, the solid residue was washed with pentane and dried to afford **9** as a white solid (82.1 mg, 93%).

^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.48 – 7.45 (m, 4H), 7.36 – 7.34 (m, 8H), 7.15 – 7.13 (m, 4H), 2.41 ppm (d, *J* = 23.0 Hz, 4H); ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 148.2 (m), 146.1 (dm, *J* = 226.3 Hz), 137.4 (dm, *J* = 245.2 Hz), 136.1 (dm, *J* = 252 Hz), 130.5, 129.6, 129.2, 126.6, 121.0, 26.8 ppm (t, *J* = 23.2 Hz); ^{31}P NMR (CD_2Cl_2, 121 MHz): δ = 202.2 ppm (m); ^{19}F NMR (CD_2Cl_2, 282 MHz): δ = -114.5 (m), -161.9 (t, *J* = 19.9 Hz), -163.1 (td, *J* = 19.9 Hz, *J* = 9.1 Hz) ppm; HRMS *calcd.* for $C_{38}H_{20}O_4F_{10}P_2PdNa^+$: 920.960310; *found* 920.960340; IR

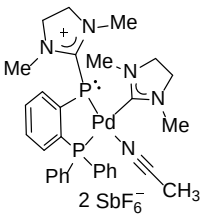
$\tilde{\nu}$ = 493, 523, 536, 595, 654, 716, 755, 772, 823, 871, 912, 954, 1012, 1045, 1094, 1191, 1248, 1274, 1361, 1403, 1456, 1498, 1532, 1606, 1633, 2916, 3067 cm^{-1}.

Synthesis of **10**



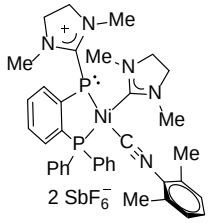
2–Diphenylphosphino–2'–(N,N–dimethylamino)biphenyl (30.0 mg, 0.055 mmol) and **3** (20.8 mg, 0.055 mmol) were stirred in CH_2Cl_2 (2 ml) for 2 d. After that the solvent was evaporated *in vacuo* and washed with Et_2O to afford **10** as a pale yellow solid (41.4 mg, 92%). Yellow crystals suitable for X–ray analysis were obtained from saturated CH_2Cl_2/pentane solution. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 8.05 – 7.99 (m, 2H), 7.70 – 7.65 (m, 1H), 7.55 – 7.46 (m, 4H), 7.42 – 7.32 (m, 2H), 7.23 – 7.16 (m, 3H), 6.98 – 6.75 (m, 5H), 6.59 – 6.56 (m, 1H), 3.04 ppm (s, 6H). ^{13}C NMR (CD_2Cl_2, 125 Mz): δ = 155.33 (m), 150.5 (d, $J_{C–P}$ = 22.0 Hz), 147.2 (m), 145.8 (m), 144.6 (m), 138.2 (m), 135.5 (d, $J_{C–P}$ = 13.3 Hz), 133.7, 132.5 (m), 131.9, 131.6, 131.4 (d, $J_{C–P}$ = 11.4 Hz), 130.5, 129.4 (d, $J_{C–P}$ = 10.6 Hz), 128.4 (d, $J_{C–P}$ = 10.2 Hz), 128.2 (d, $J_{C–P}$ = 5.6 Hz), 122.4 (br), 116.6 (br), 47.3 ppm (m). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ = 23.2 ppm (m). ^{19}F NMR (CD_2Cl_2, 282 MHz): δ = – 112.92 (m), – 114.28 (m), – 115.26 (m), – 117.93 (m), – 162.35 (t, $J_{F–F}$ = 19.8 Hz), – 162.95 (t, $J_{F–F}$ = 19.8 Hz), – 163.64 (m), – 163.88, – 164.43 (m), – 164.94 ppm (m). HRMS *calcd.* for $C_{38}H_{24}NF_{10}PPdNa^+$: 844.041910, *found* 884.041289. IR ũ = 433, 450, 494, 538, 692, 760, 788, 852, 949, 1041, 1058, 1099, 1213, 1274, 1344, 1362, 1435, 1493, 1577, 2965, 3067 cm^{-1}.

Synthesis of **13**



Compound **1** (20.0 mg, 0.021 mmol) and $Pd(dba)_2$ (12.0 mg, 0.021 mmol) were stirred in CH_2Cl_2 (2 ml) at r.t. for 2 h, and then the solvent was evaporated *in vacuo*. The resulting solid was extracted with CH_3CN and recrystallized from CH_3CN, CH_2Cl_2 and Et_2O to afford the desired compound **13** as a yellow solid (4.9 mg, 21%). The colorless crystals suitable for X–ray analysis were obtained from $CH_3CN/CH_2Cl_2/Et_2O$. ^{1}H NMR (CD_3CN, 600 MHz): δ = 7.69 – 7.55 (m, 13H), 7.55 – 7.50 (m, 1H), 3.90 – 3.84 (m, 2H), 3.83 – 3.76 (m, 2H), 3.75 – 3.66 (m, 4H), 3.35 (s, 3H), 3.04 (s, 3H), 2.94 ppm (s, 6H). ^{13}C NMR (CD_3CN, 125 Mz): δ = 196.5 (dd, $J_{C–P}$ = 126.7 Hz, , $J_{C–P}$ = 16.4 Hz), 176.6 (dd, $J_{C–P}$ = 80.7 Hz, $J_{C–P}$ = 1.7 Hz), 146.2 (dd, $J_{C–P}$ = 40.9 Hz, $J_{C–P}$ = 20.9 Hz), 135.4 (dd, $J_{C–P}$ = 56.0Hz, , $J_{C–P}$ = 15.8 Hz), 135.1 (d, $J_{C–P}$ = 2.4 Hz), 134.6 (dd, $J_{C–P}$ = 4.4 Hz, $J_{C–P}$ = 1.8 Hz), 134.21, 134.20 (d, $J_{C–P}$ = 9.3 Hz), 134.1 (d, $J_{C–P}$ = 11.3 Hz), 134.0 (d, $J_{C–P}$ = 21.8 Hz), 133.4 (d, $J_{C–P}$ = 2.6 Hz), 130.8 (dd, $J_{C–P}$ = 11.0 Hz, $J_{C–P}$ = 2.4 Hz), 130.7 (d, $J_{C–P}$ = 1.7 Hz), 130.4 (d, $J_{C–P}$ = 47.5 Hz), 129.7 (d, $J_{C–P}$ = 96.8 Hz), 128.6 (d, $J_{C–P}$ = 48.2 Hz), 52.8 (d, $J_{C–P}$ = 5.2 Hz), 52.5 (d, $J_{C–P}$ = 4.6 Hz), 52.4 (d, $J_{C–P}$ = 1.0 Hz), 37.7, 37.6, 37.4, 37.3, 37.2 ppm (m). ^{31}P NMR (CD_3CN, 162 MHz): δ = 49.4, 15.9 ppm. ^{19}F NMR (CD_3CN, 282 MHz): δ = – 124.0 ppm (sextet, $J_{F–Sb(I=5/2)}$ = 1933 Hz, octet, $J_{F–Sb(I=7/2)}$ = 1049 Hz). HRMS *calcd.* for $C_{28}H_{34}N_4F_6P_2SbPd^+$: 829.022380, *found* 829.022889. IR ũ = 426, 495, 507, 534, 591, 652, 699, 752, 774, 920, 940, 1103, 1203, 1291, 1333, 1407, 1438, 1546, 1567, 2301, 2929 cm^{-1}.

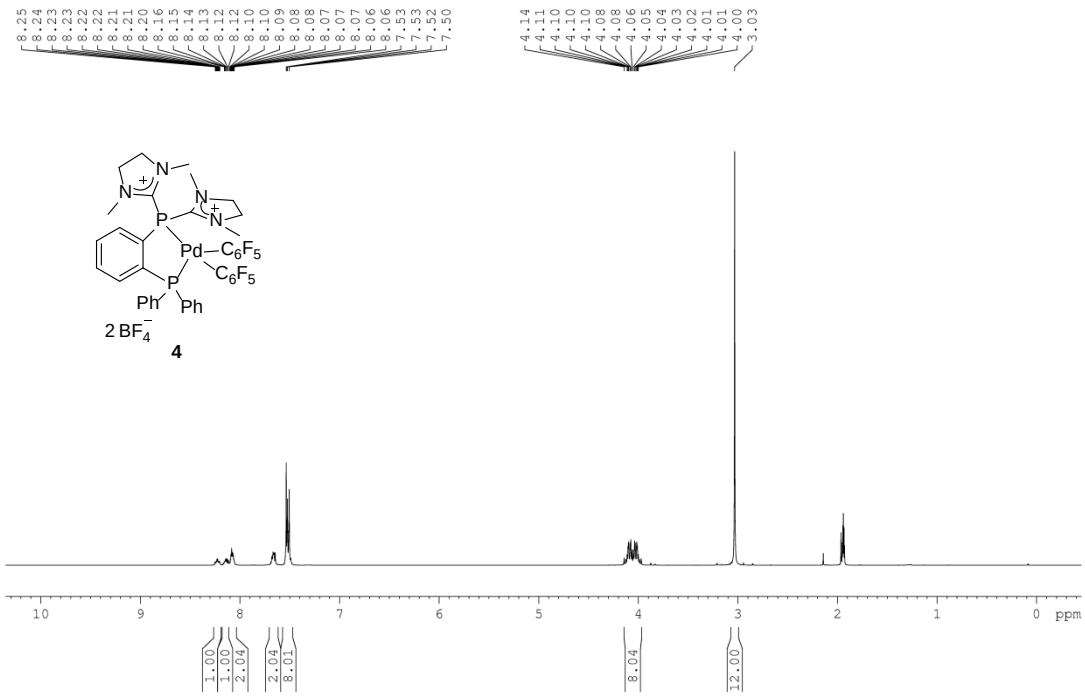
Synthesis of **14**



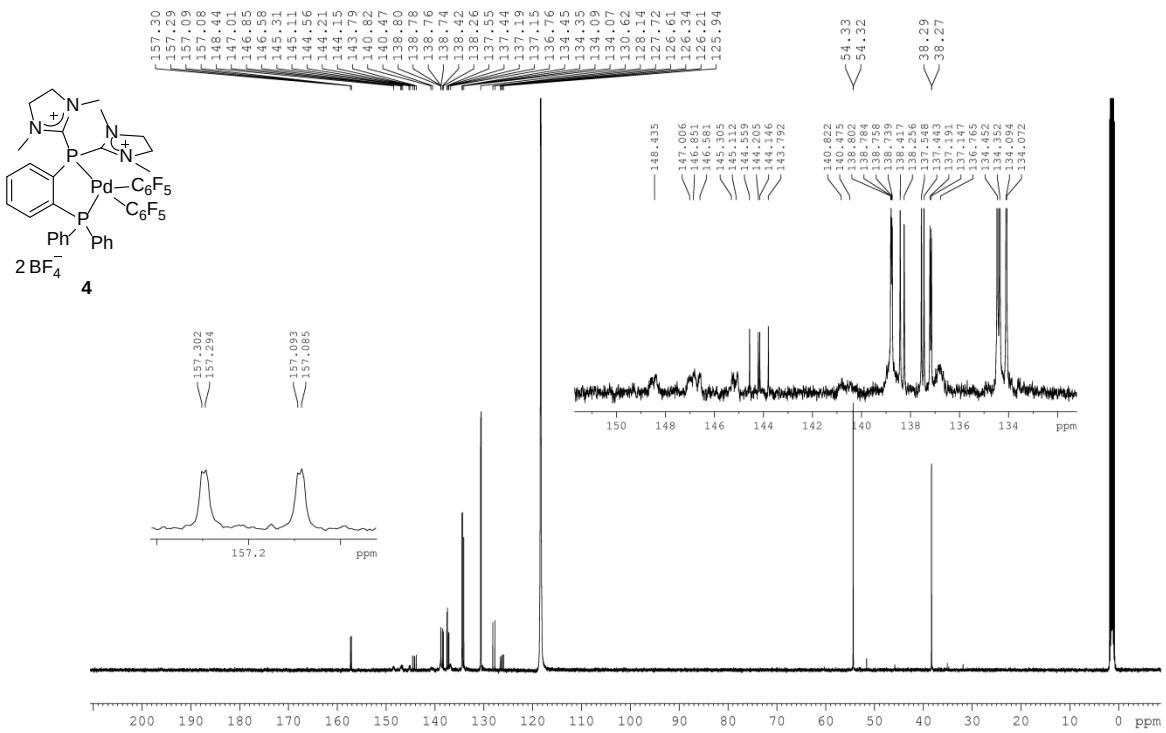
Compound **1** (50.0 mg, 0.052 mmol) and $Ni(cod)_2$ (14.3 mg, 0.052 mmol) were stirred overnight in CH_2Cl_2 (2 ml). A yellow precipitate was separated from the solution. 2,6–dimethylphenyl isocyanide (16.7 mg, 0.128 mmol) was added in CH_2Cl_2 (2 ml) and the mixture stirred overnight. After evaporation of the solvent, the solid was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O to afford the desired compound **14** as a yellow solid (22.1 mg, 37%). The yellow crystal suitable for X–ray analysis was obtained from a saturated solution of the title compound in CH_2Cl_2/Et_2O. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 7.74 – 7.48 (m, 13H), 7.37 (t, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 2H), 3.98 (s, *J* = 4H), 3.88 – 3.71 (m, 4H), 3.33 (s, 6H), 3.01 (s, 6H), 1.98 (s, 6H). ^{13}C NMR (CD_2Cl_2, 125 Mz): δ = 199.2 (dd, $J_{C–P}$ = 71.0 Hz, , $J_{C–P}$ = 22.3 Hz), 176.7 (dd, $J_{C–P}$ = 76.9 Hz, $J_{C–P}$ = 3.7 Hz), 146.2 (m), 144.7 (dd, $J_{C–P}$ = 39.7 Hz, , $J_{C–P}$ = 15.4 Hz), 136.2, 135.4 (dd, $J_{C–P}$ = 59.0 Hz, $J_{C–P}$ = 20.0 Hz), 135.0, 134.1, 133.5, 133.3, 133.2, 132.8 (dd, $J_{C–P}$ = 35.4 Hz, , $J_{C–P}$ = 17.5 Hz), 131.7, 130.7 (d, $J_{C–P}$ = 11.4 Hz), 130.4 (d, $J_{C–P}$ = 8.3 Hz), 129.0, 125.6, 52.7, 51.7, 37.43, 37.41, 37.34, 37.28, 18.3 ppm (m). ^{31}P NMR (CD_2Cl_2, 162 MHz): δ = 56.9 (d, $J_{P–P}$ = 4.3 Hz), 23.7 ppm (d, $J_{P–P}$ = 4.3 Hz). ^{19}F NMR (CD_2Cl_2, 282 MHz): δ = – 124.0 ppm (sextet, $J_{F–Sb(I=5/2)}$ = 1933 Hz, octet, $J_{F–Sb(I=7/2)}$ = 1049 Hz). HRMS *calcd.* for $C_{37}H_{43}N_5F_6P_2Sb^+$: 912.128170, *found* 912.128332. IR ũ = 442, 487, 515, 530, 651, 693, 713, 752, 773, 791, 939, 957, 1097, 1205, 1287, 1438, 1536, 1566, 2164 cm^{-1}.

Selected NMR Spectra:

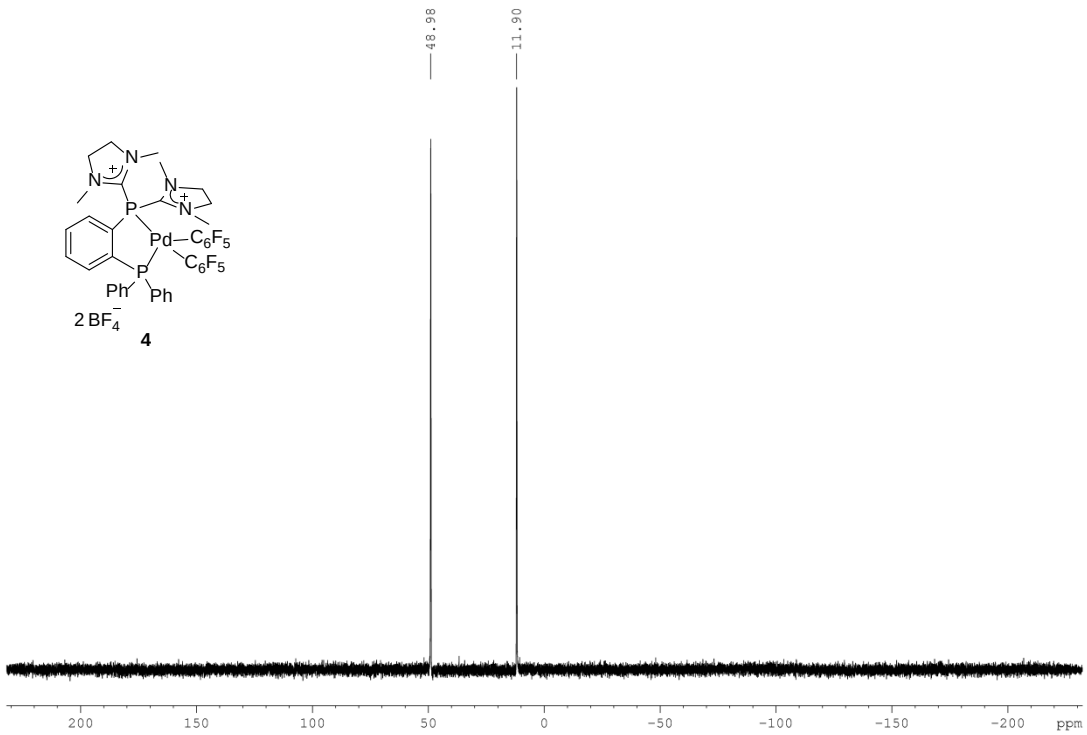
^{1}H NMR (CD_3CN, 400 MHz):



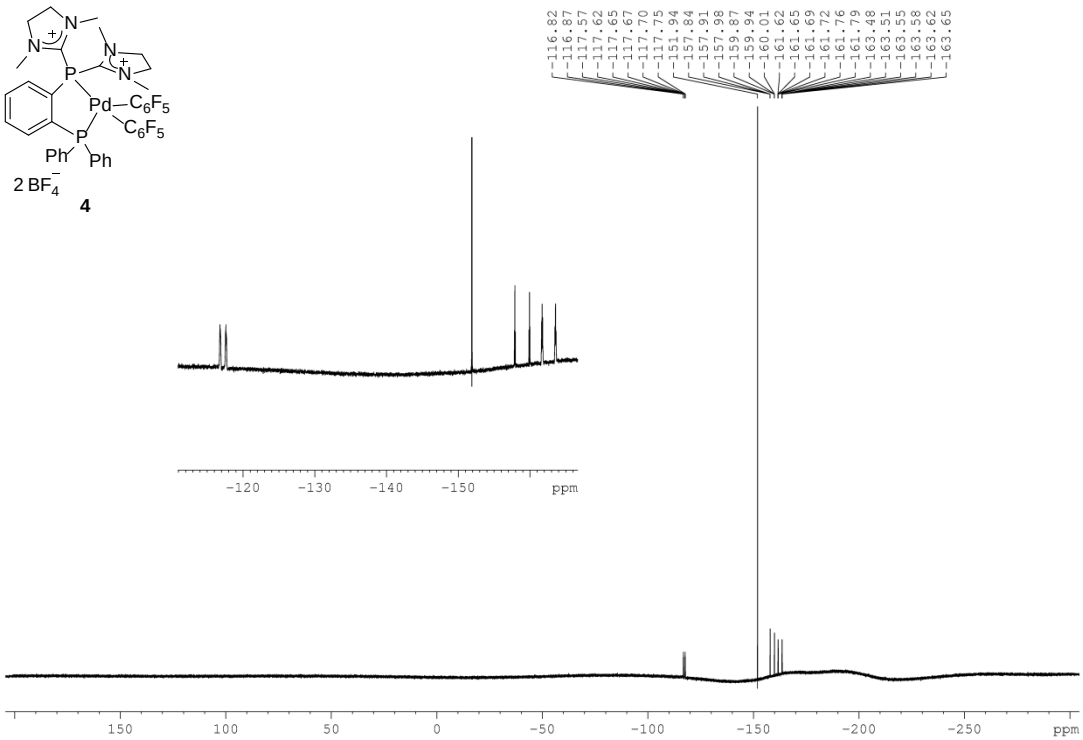
^{13}C NMR (CD_3CN, 100 MHz):



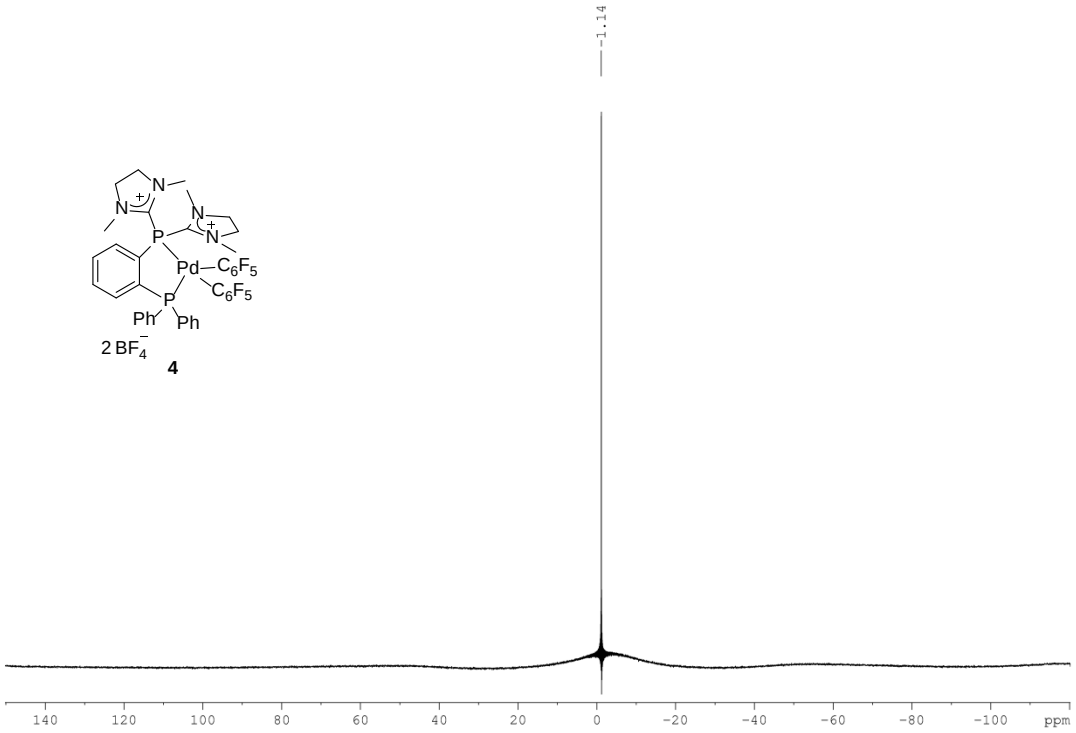
^{31}P NMR (CD_3CN, 121 MHz):



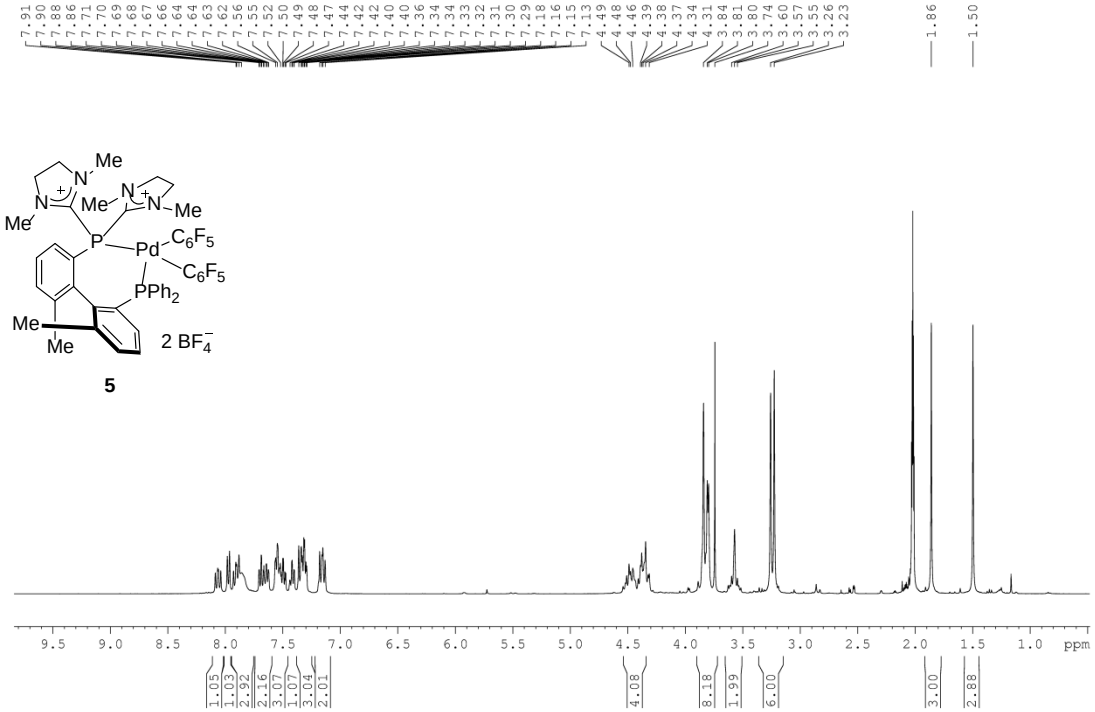
^{19}F NMR (CD_3CN, 282 MHz):



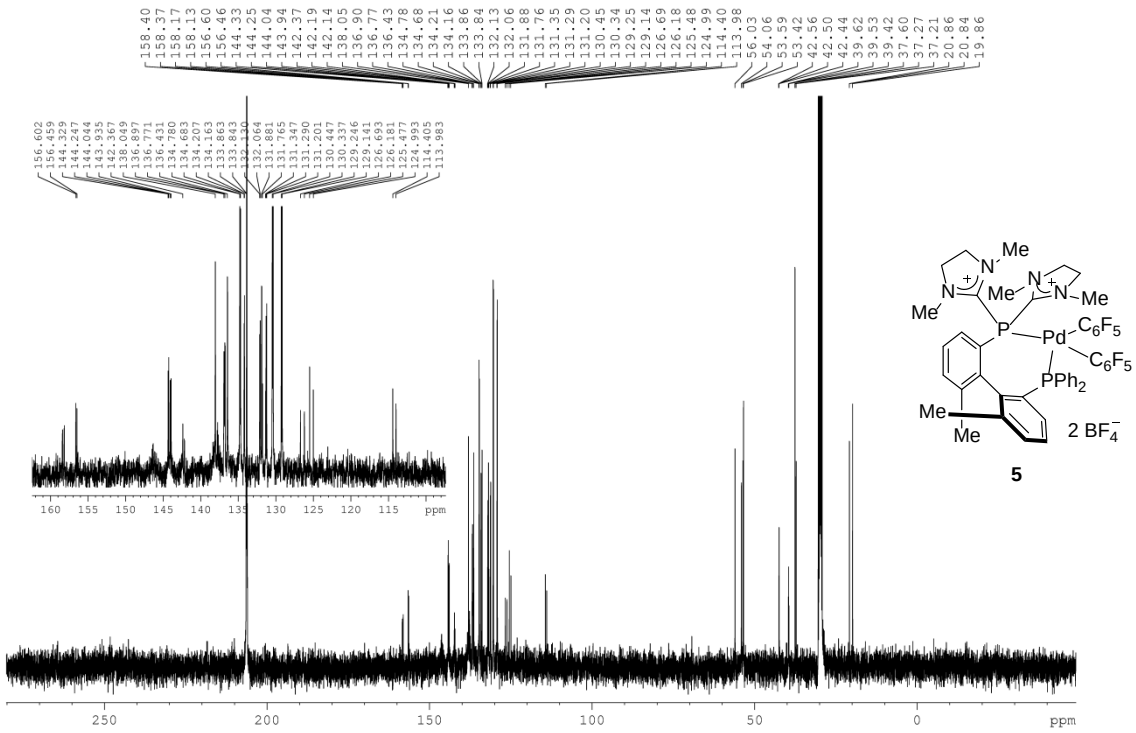
^{11}B NMR (CD_3CN, 96 MHz)



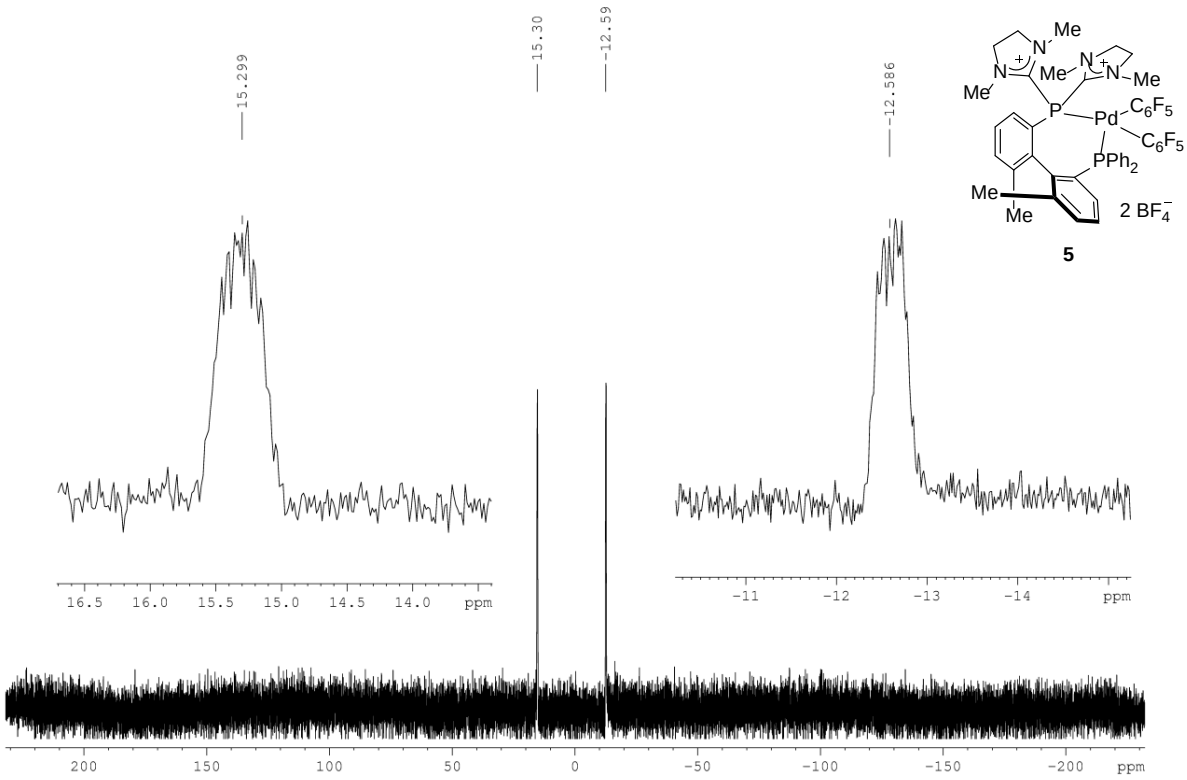
^{1}H NMR (CD_3COCD_3, 400 MHz):



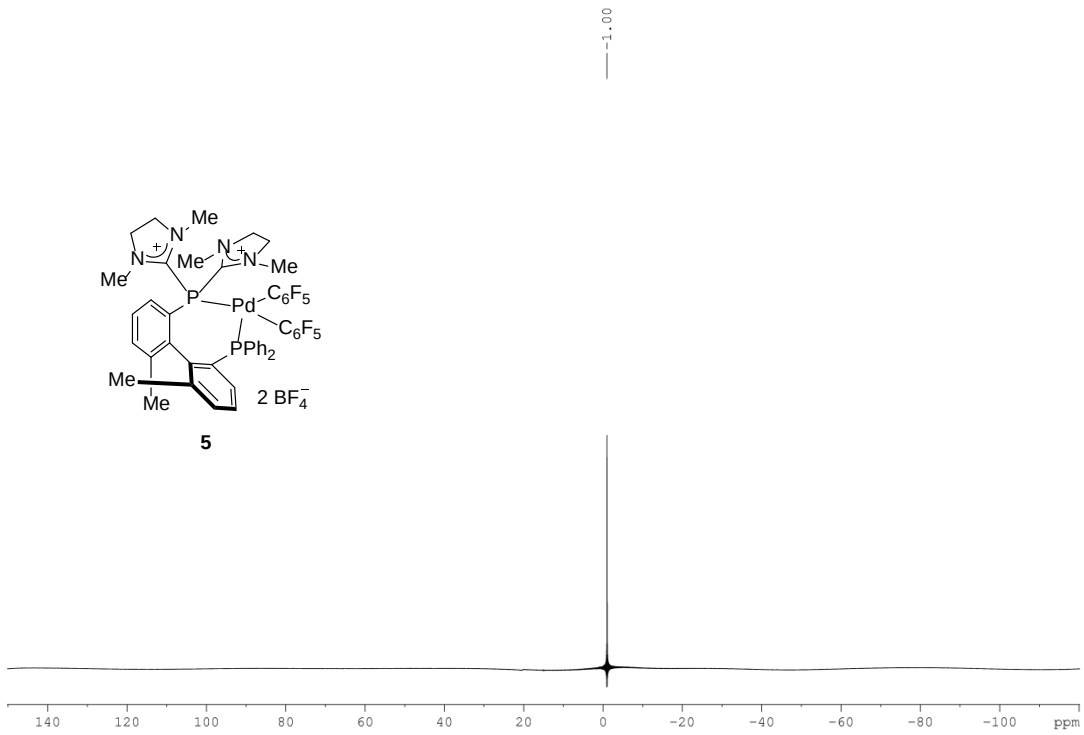
^{13}C NMR (CD_3COCD_3, 100 MHz):



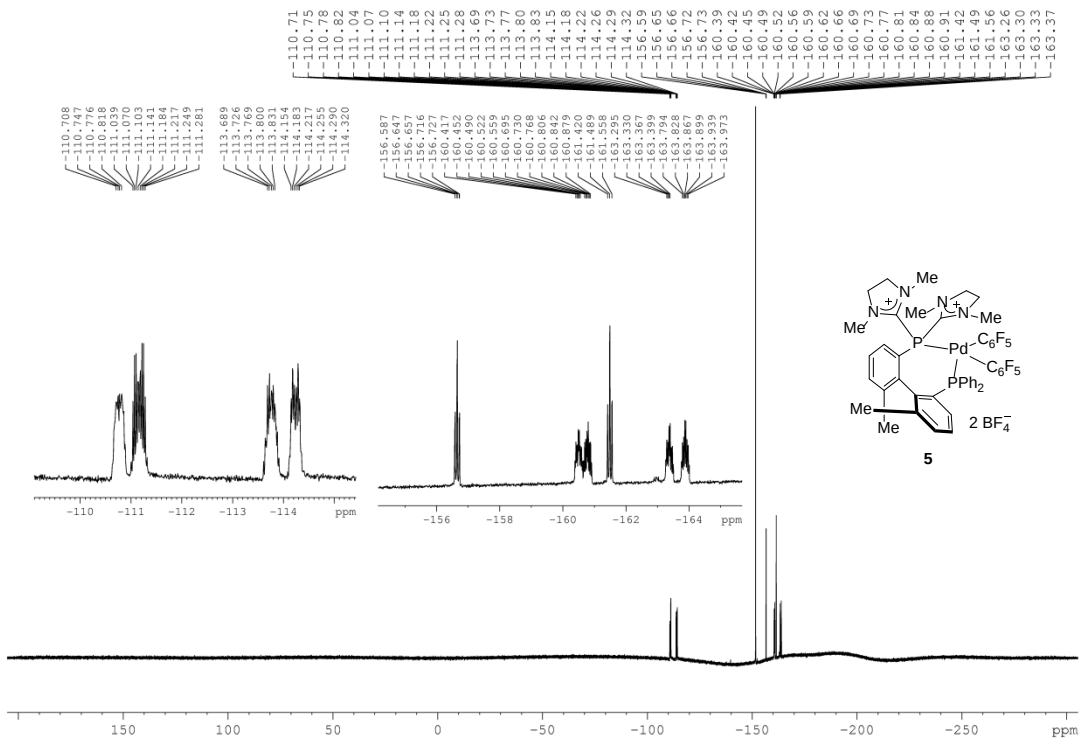
^{31}P NMR (CD_3COCD_3, 121 MHz):



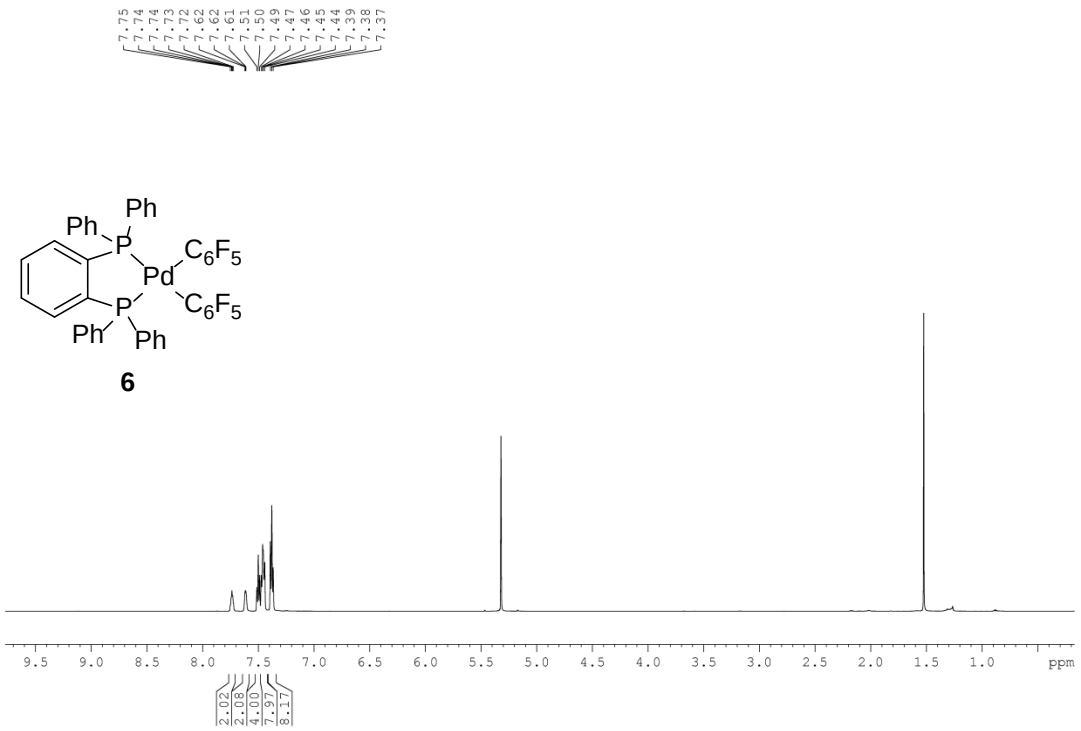
^{11}B NMR (CD_3COCD_3, 96 MHz):



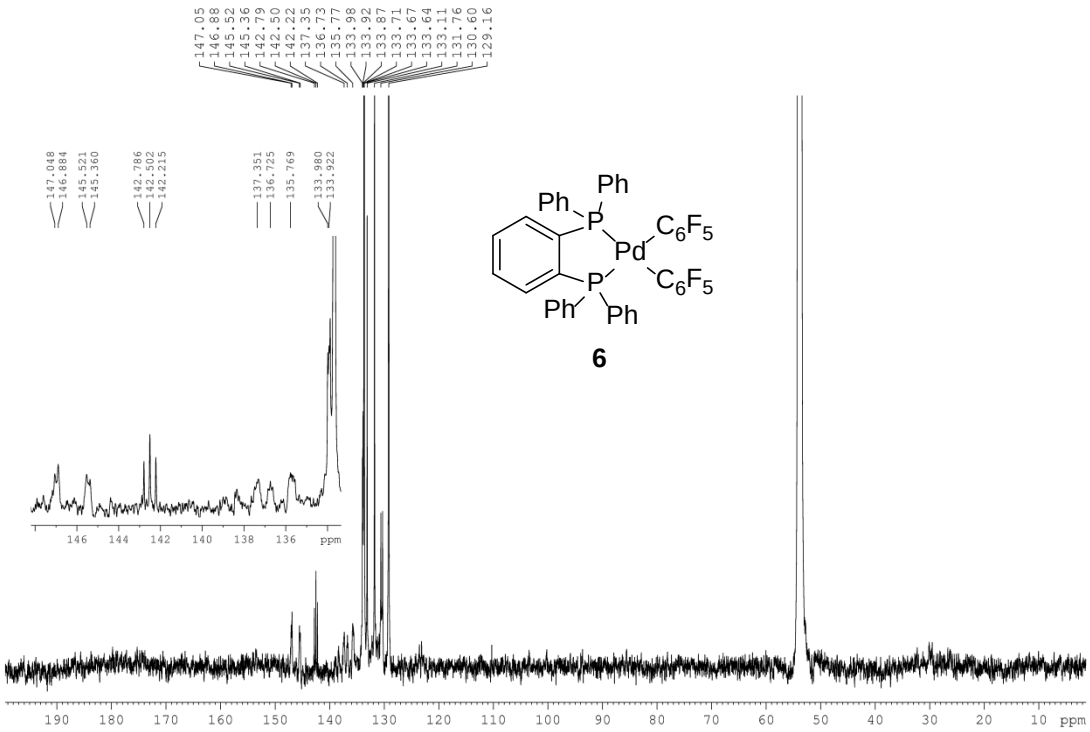
^{19}F NMR (CD_3COCD_3, 282 MHz):



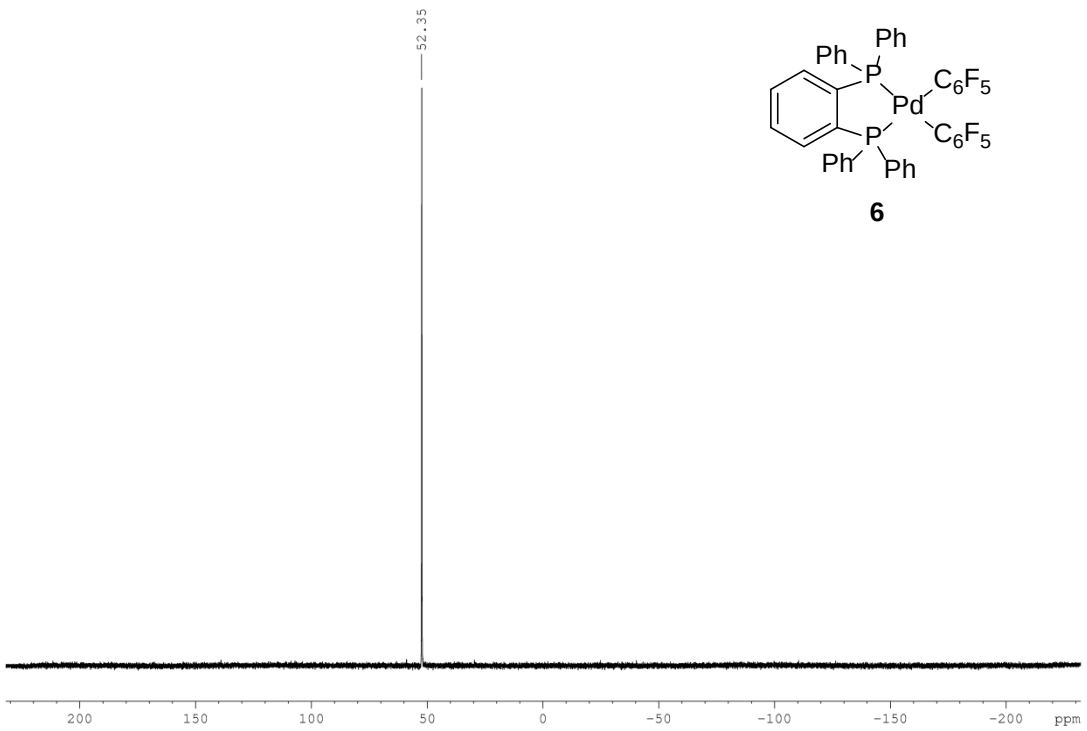
^{1}H NMR (CD_2Cl_2, 400 MHz):



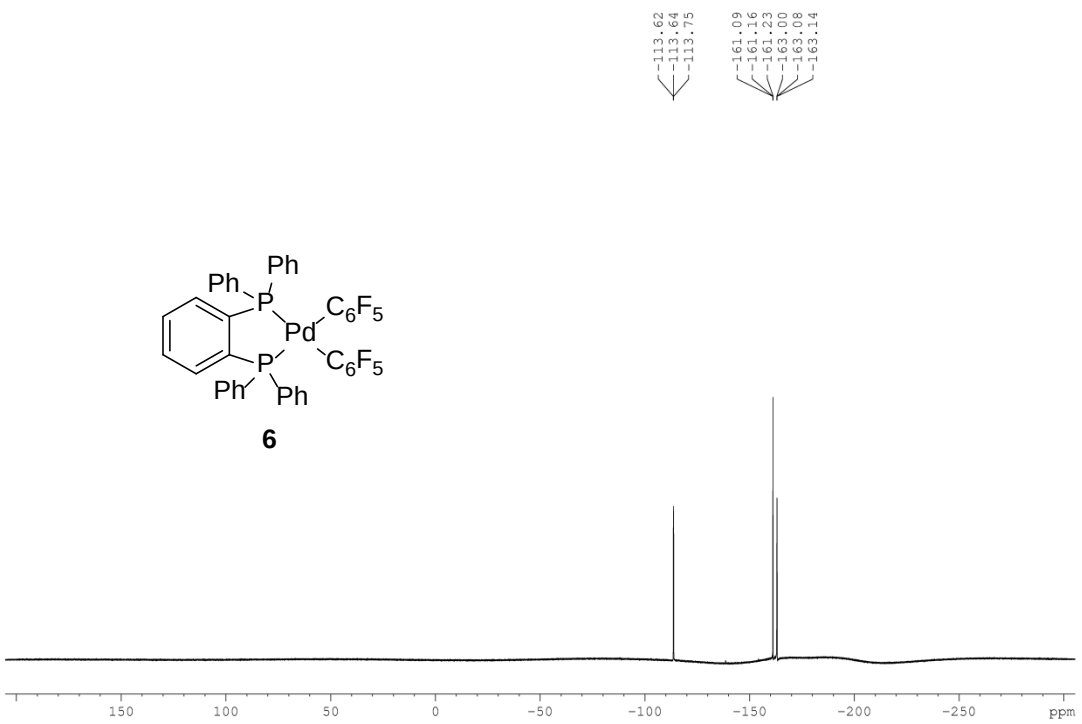
^{13}C NMR (CD_2Cl_2, 150 MHz):



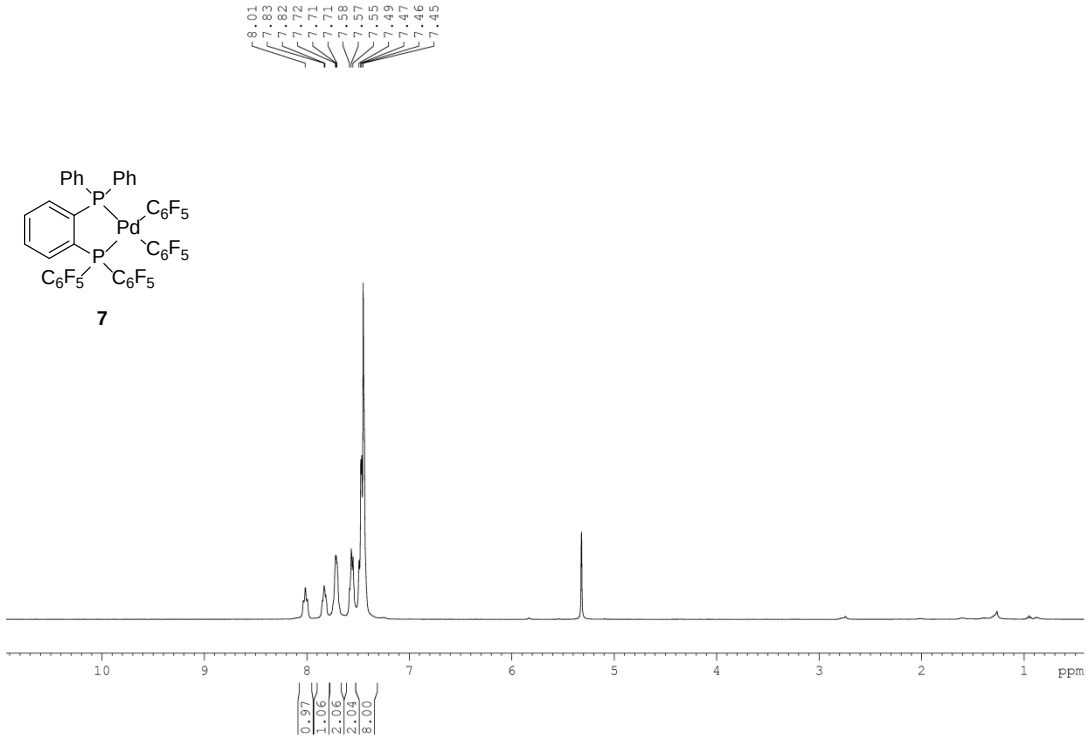
^{31}P NMR (CD_2Cl_2, 121 MHz):



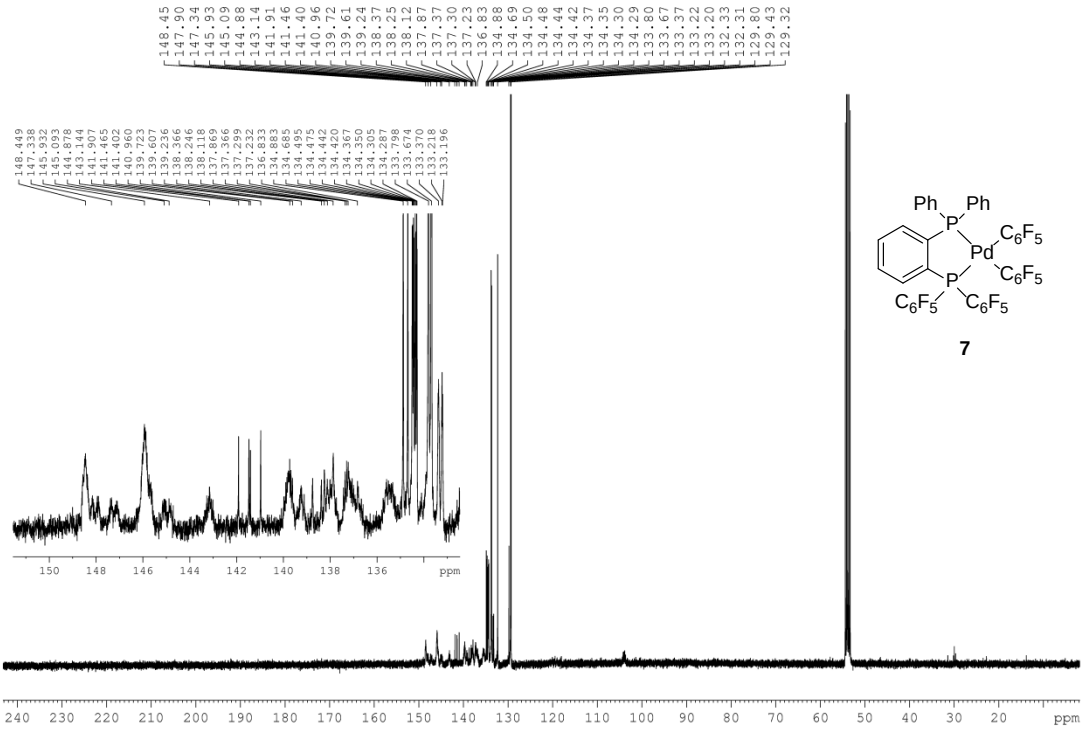
^{19}F NMR (CD_2Cl_2, 282 MHz):



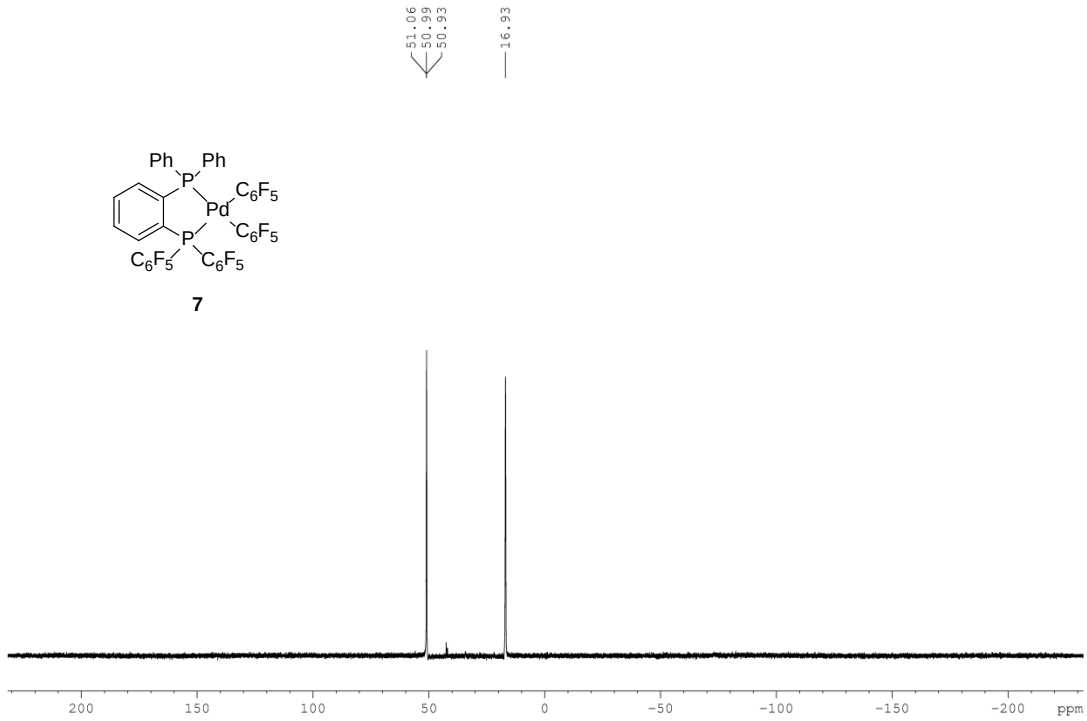
^{1}H NMR (CD_2Cl_2, 400 MHz):



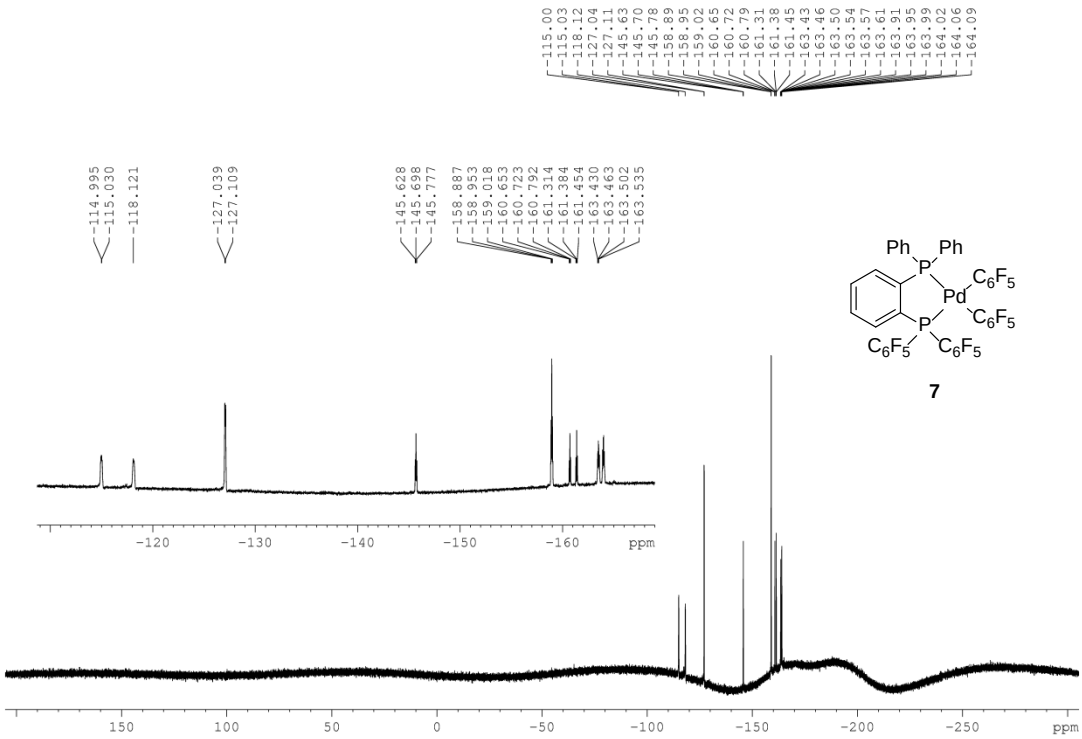
^{13}C NMR (CD_2Cl_2, 100 MHz):



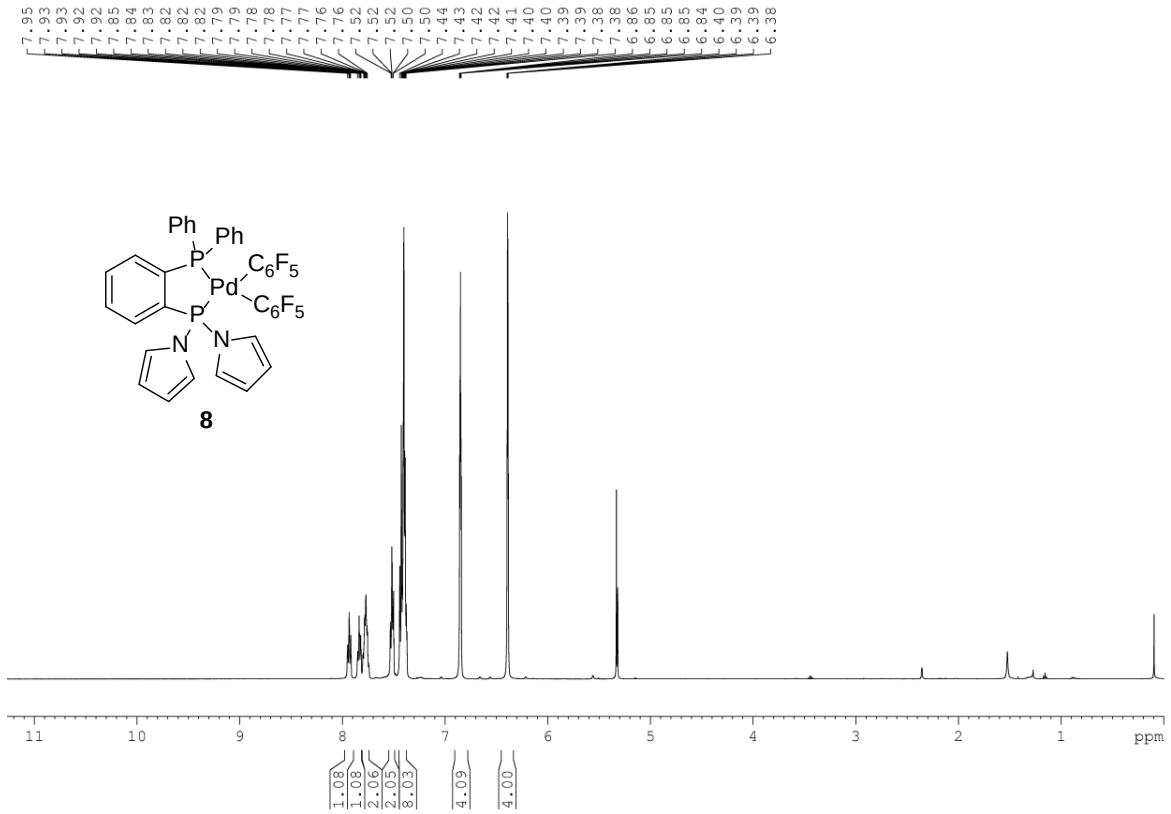
^{31}P NMR (CD_2Cl_2, 121 MHz):



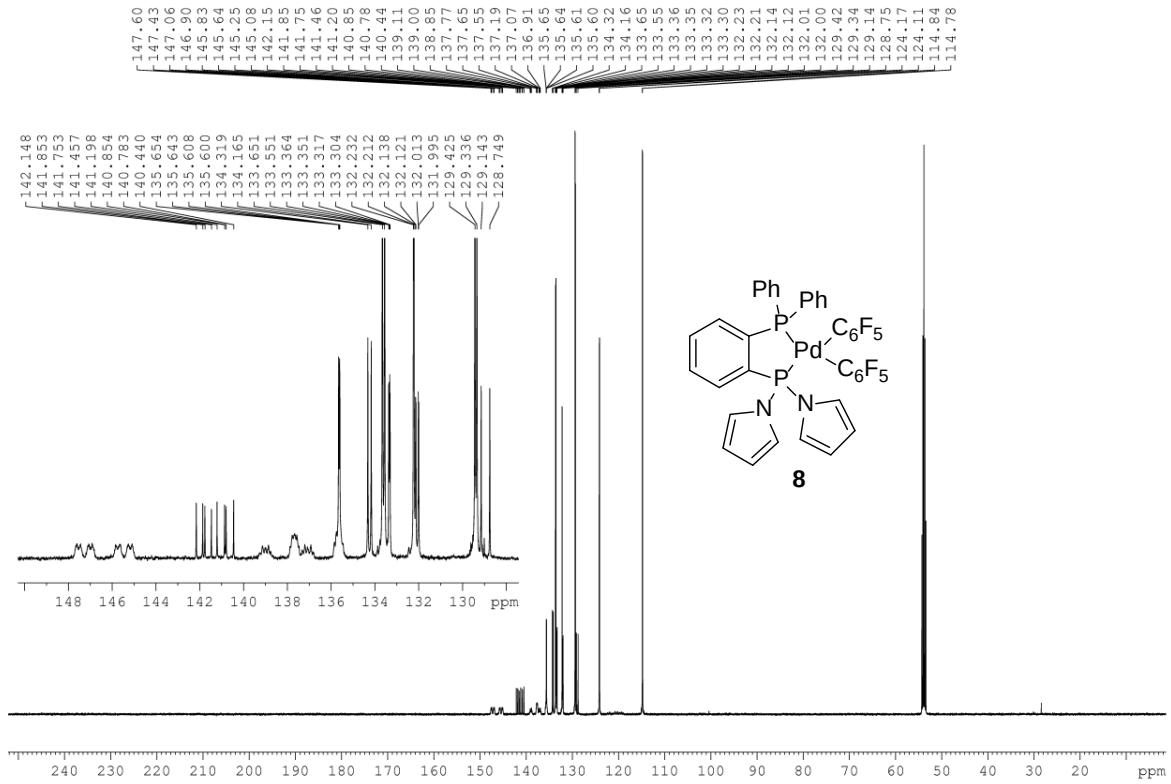
^{19}F NMR (CD_2Cl_2, 282 MHz):



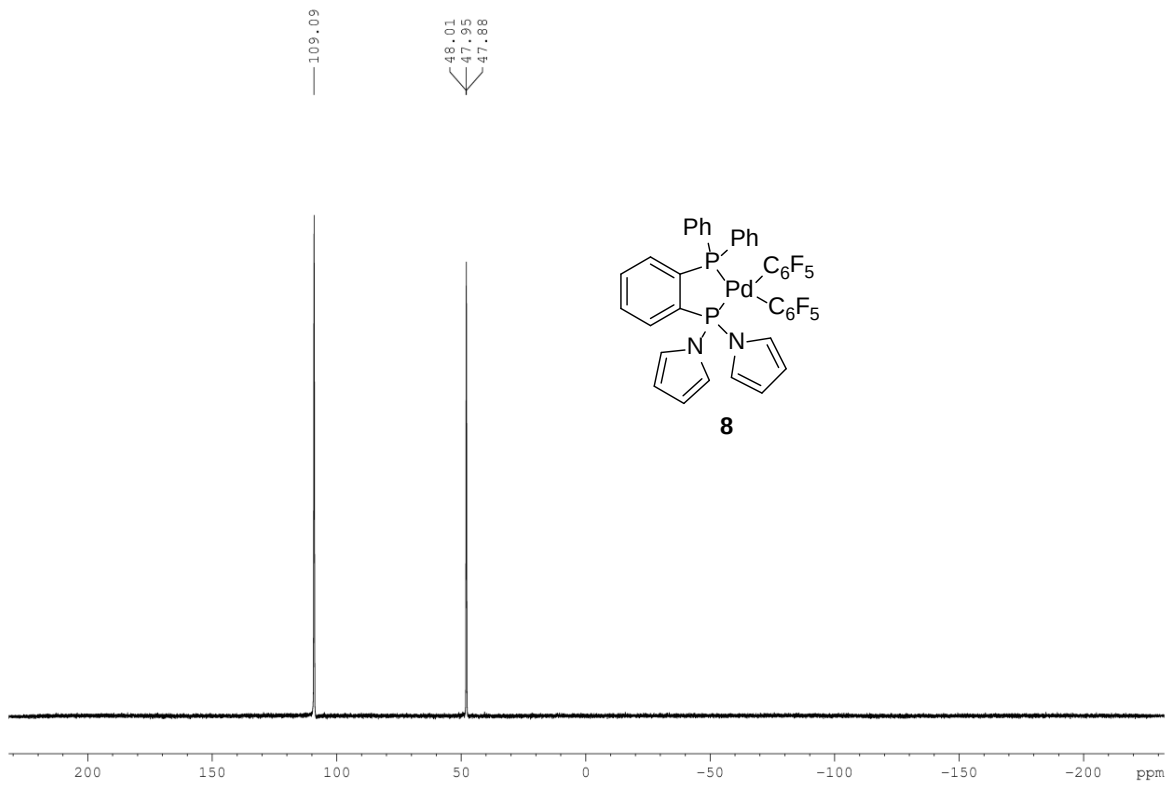
^{1}H NMR (CD_2Cl_2, 500 MHz)**:**



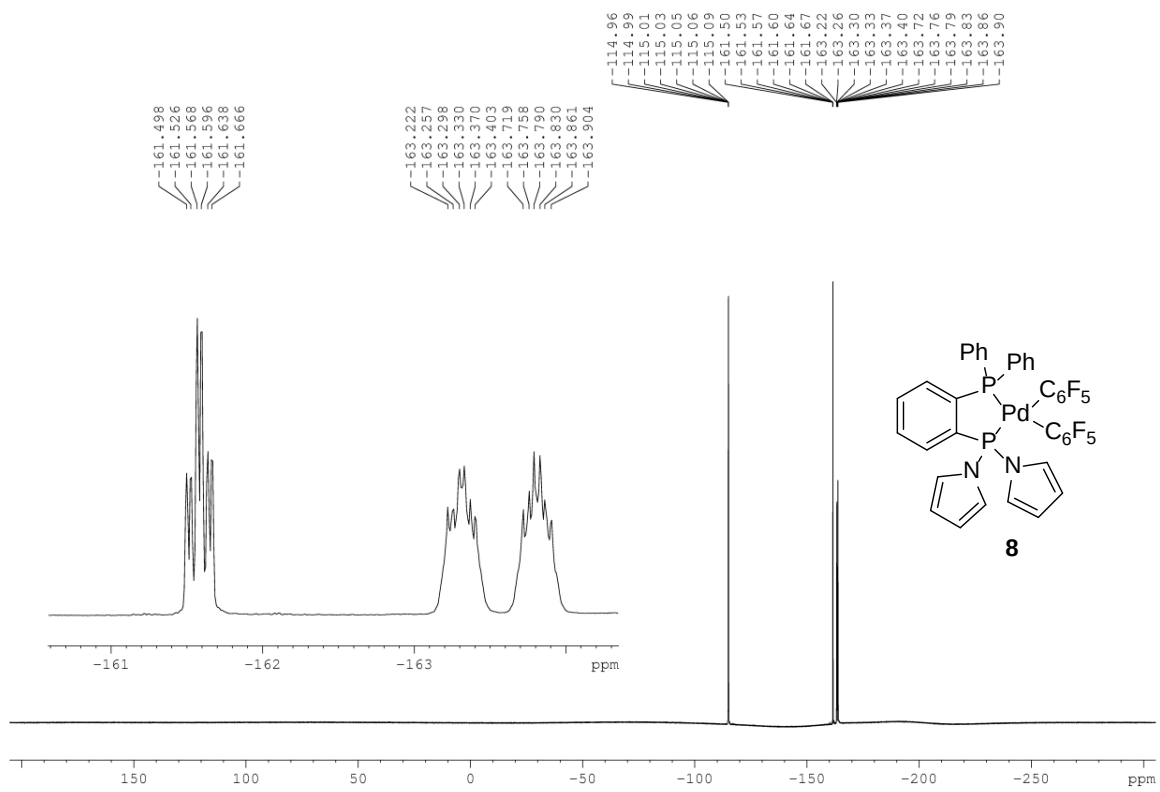
^{13}C NMR (CD_2Cl_2, 125 Mz)



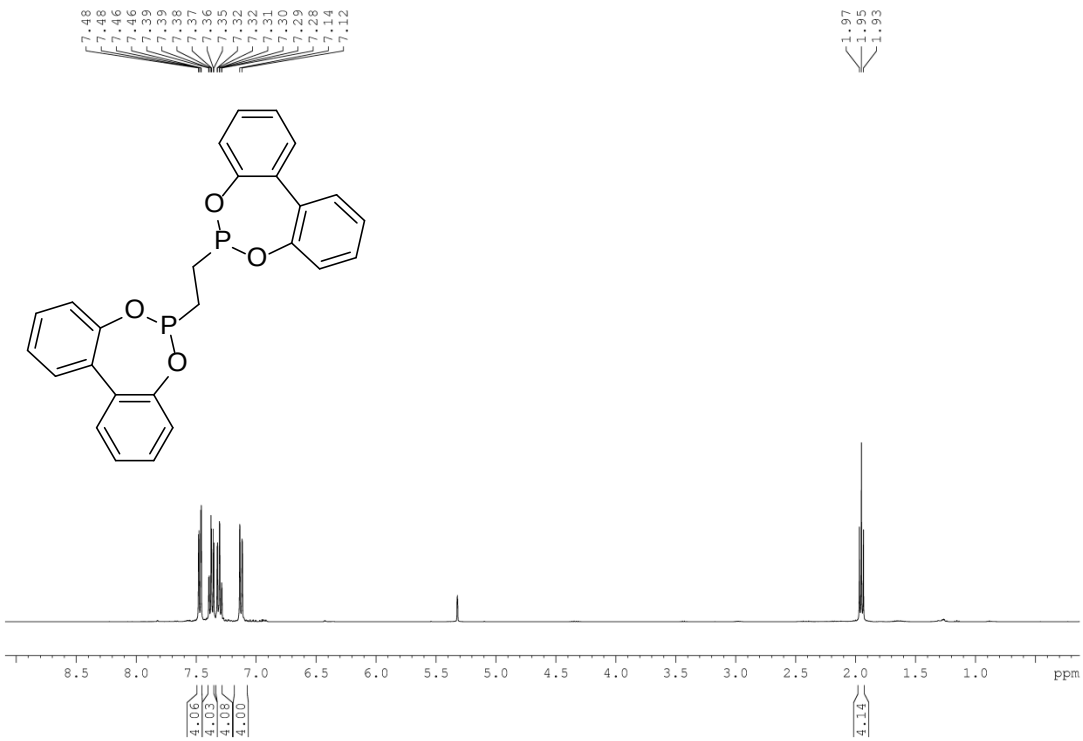
^{31}P NMR (CD_2Cl_2, 162 MHz)



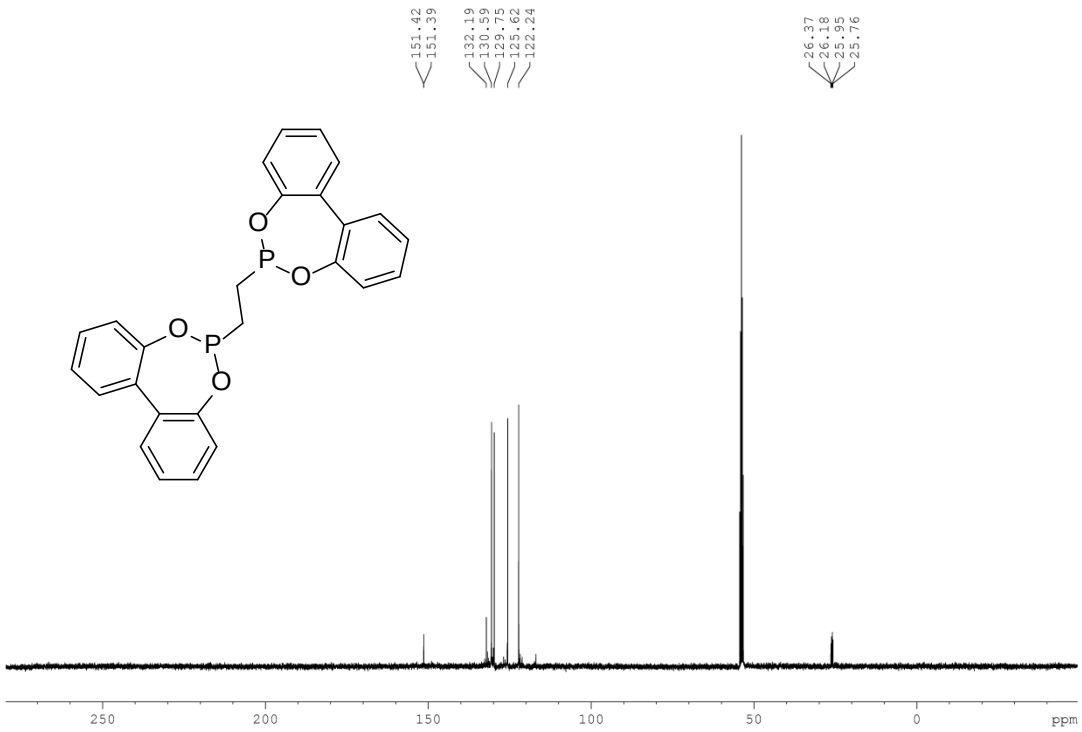
^{19}F NMR (CD_2Cl_2, 282 MHz)



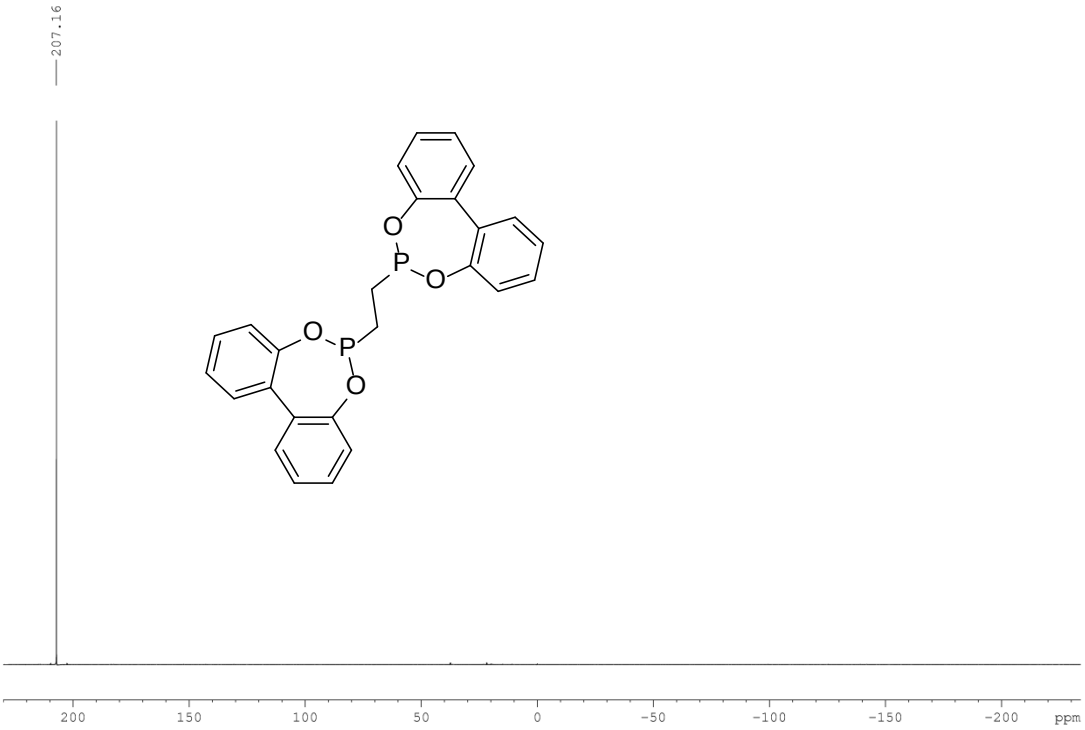
^{1}H NMR (CD_2Cl_2, 400 MHz):



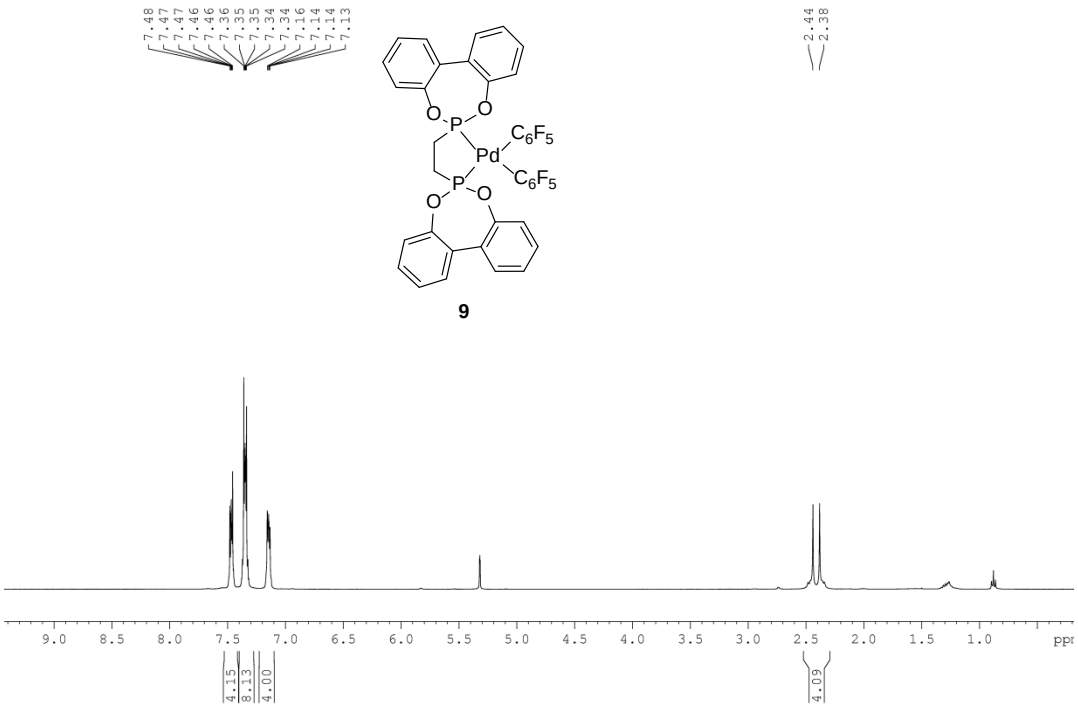
^{13}C NMR (CD_2Cl_2, 100 MHz):



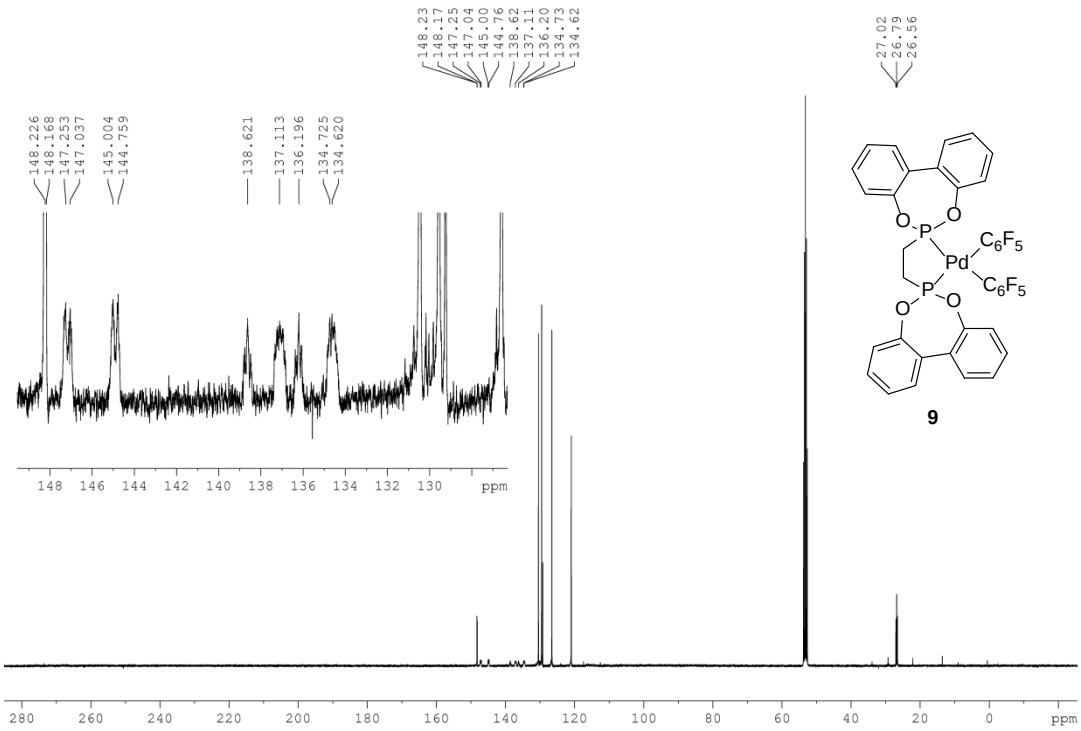
^{31}P NMR (CD_2Cl_2, 121 MHz):



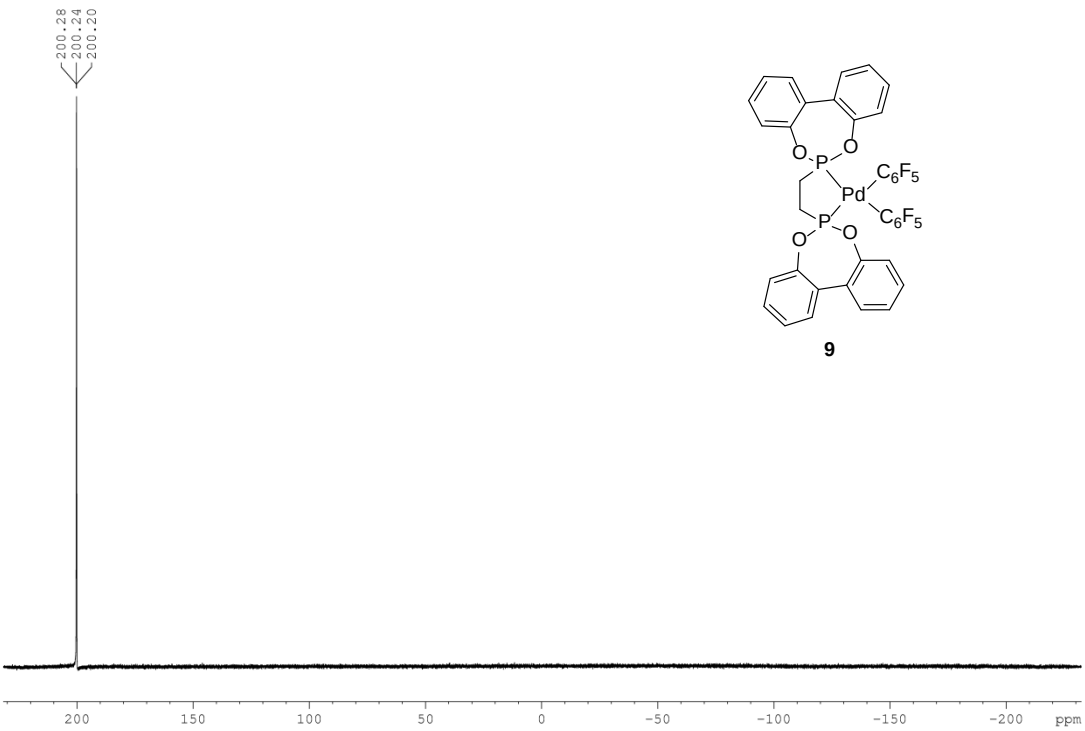
^{1}H NMR (CD_2Cl_2, 400 MHz):



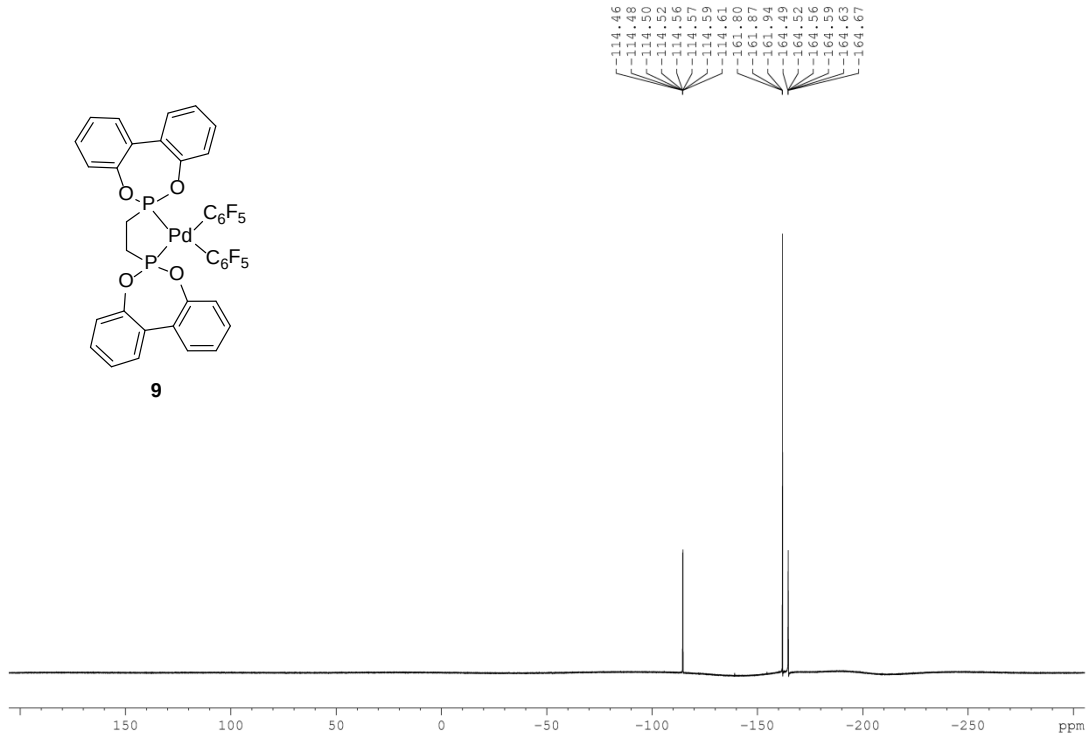
^{13}C NMR (CD_2Cl_2, 100 MHz):



^{31}P NMR (CD_2Cl_2, 121 MHz):

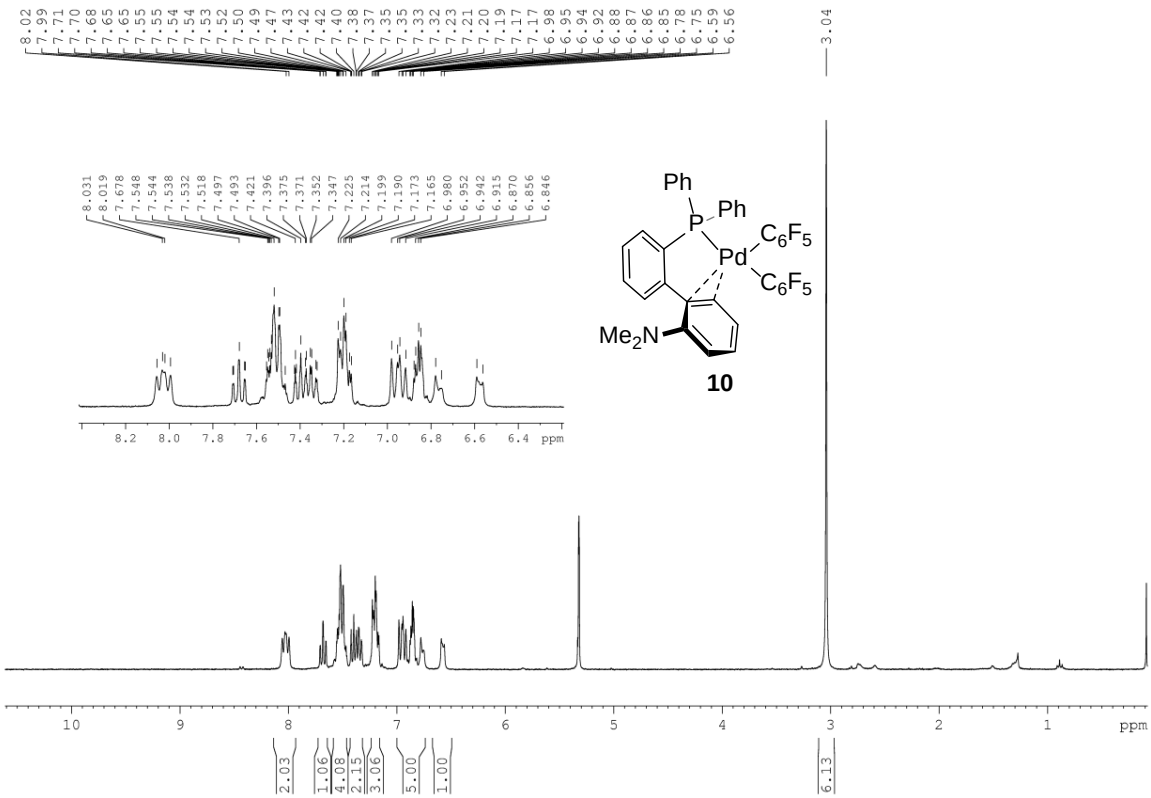


^{19}F NMR (CD_2Cl_2, 282 MHz):

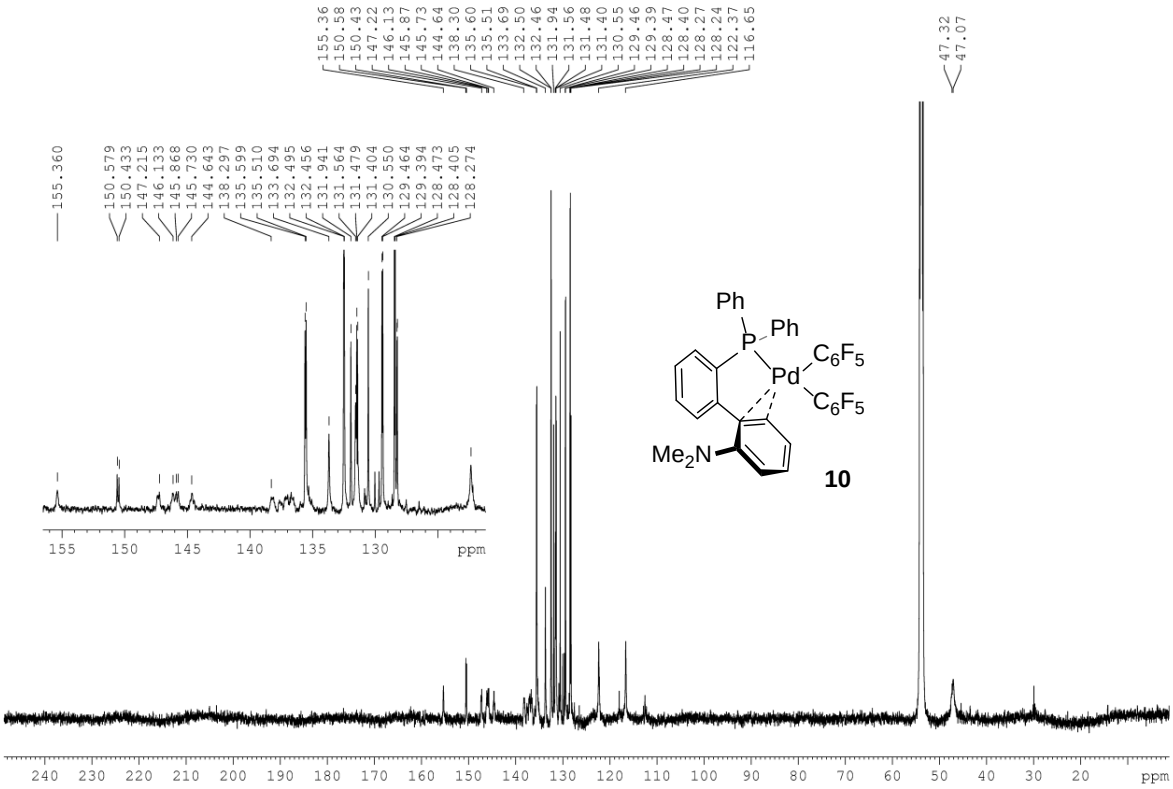


9

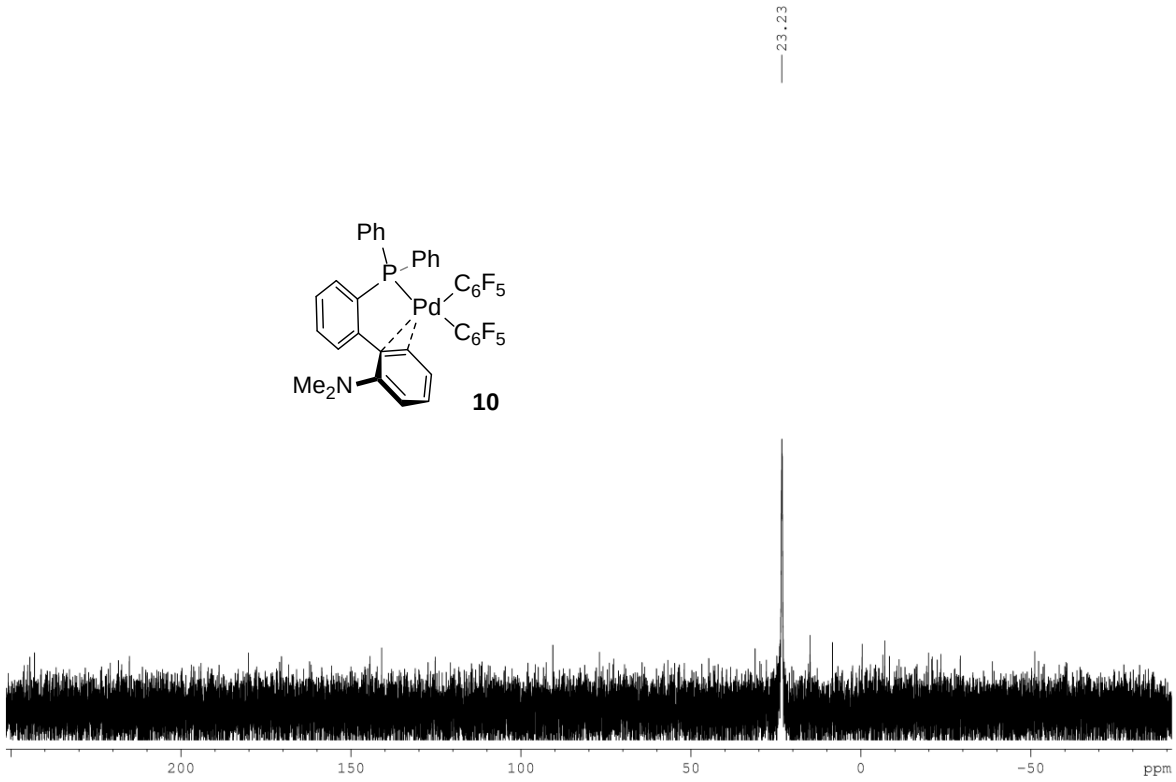
^{1}H NMR (CD_2Cl_2, 300 MHz)



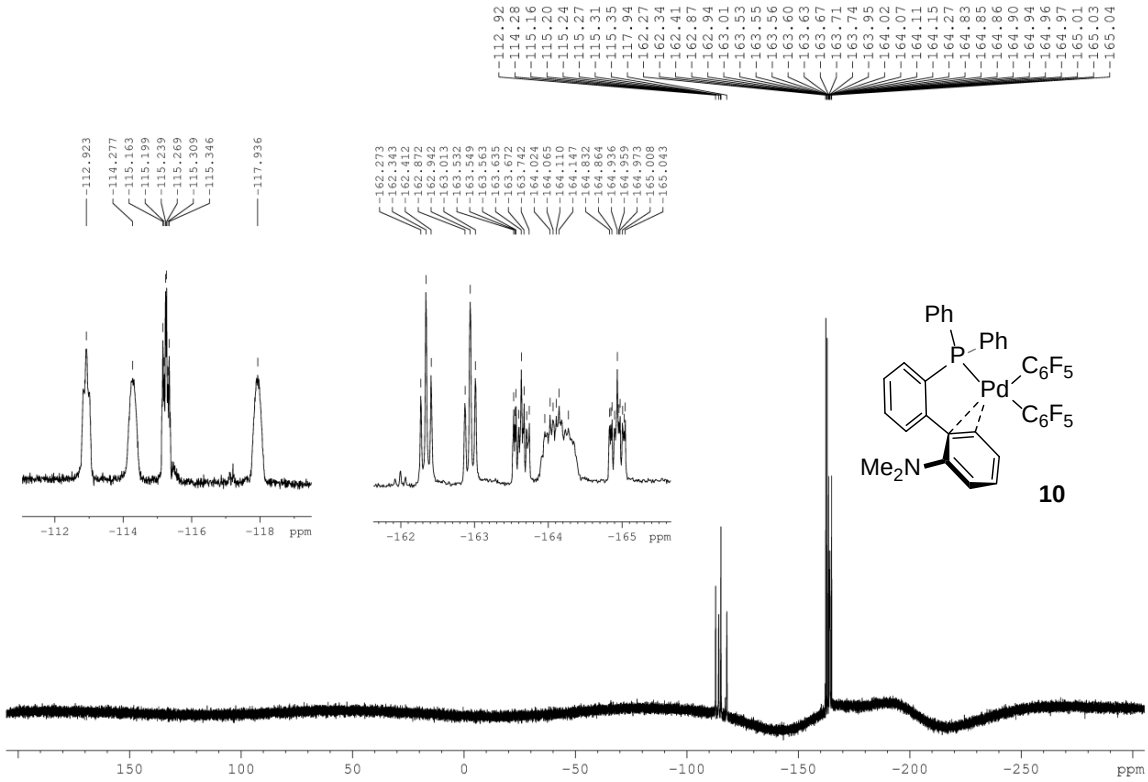
^{13}C NMR (CD_2Cl_2, 125 Mz)



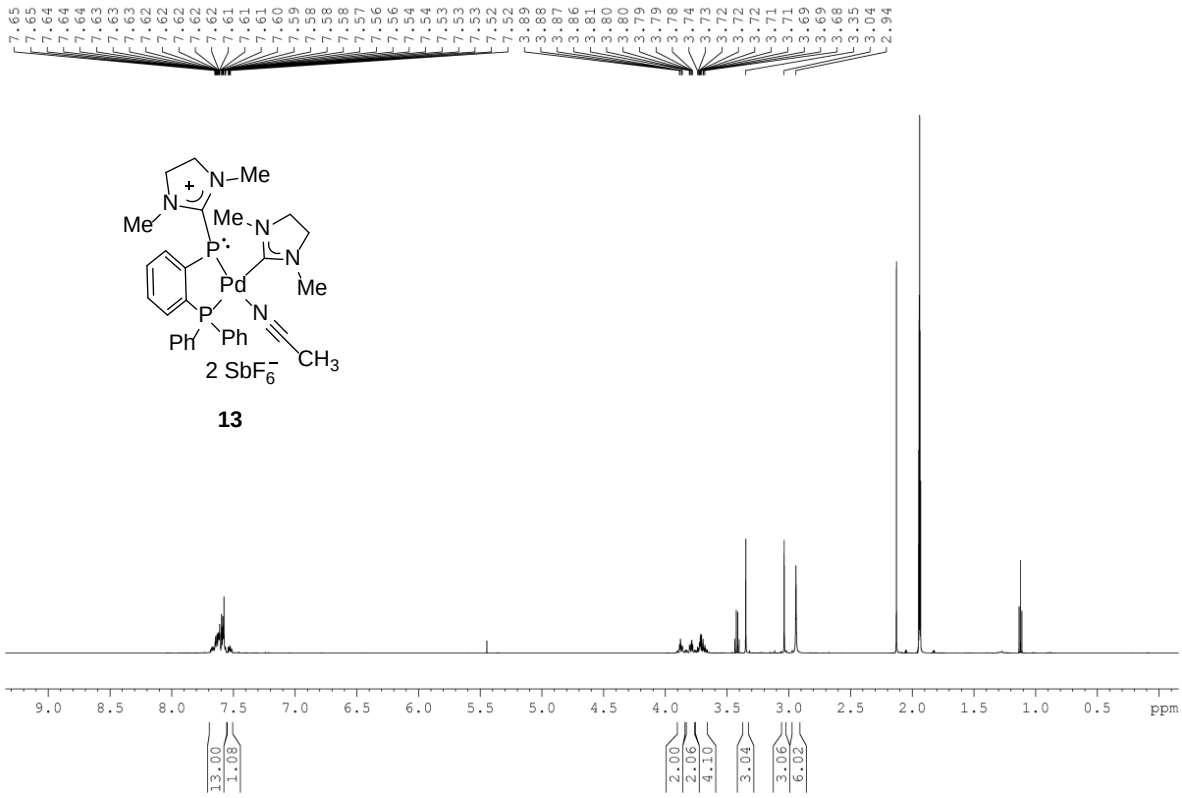
^{31}P NMR (CD_2Cl_2, 162 MHz)



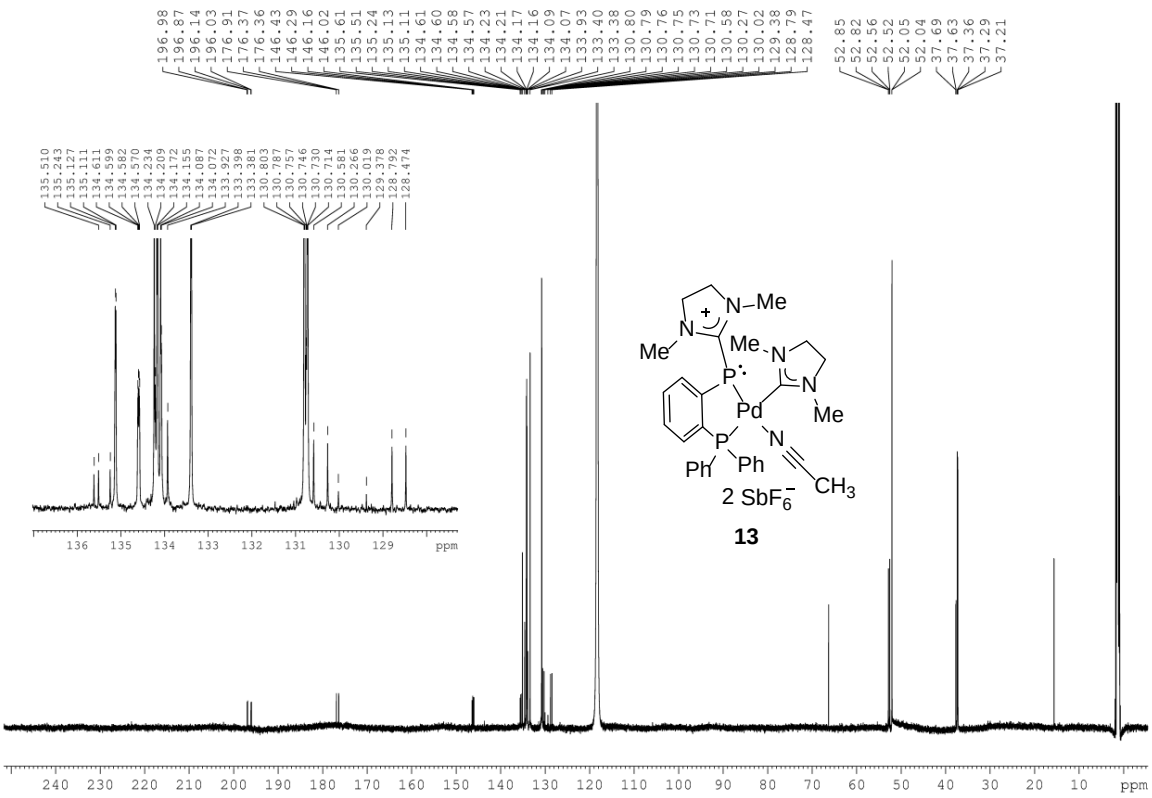
^{19}F NMR (CD_2Cl_2, 282 MHz)



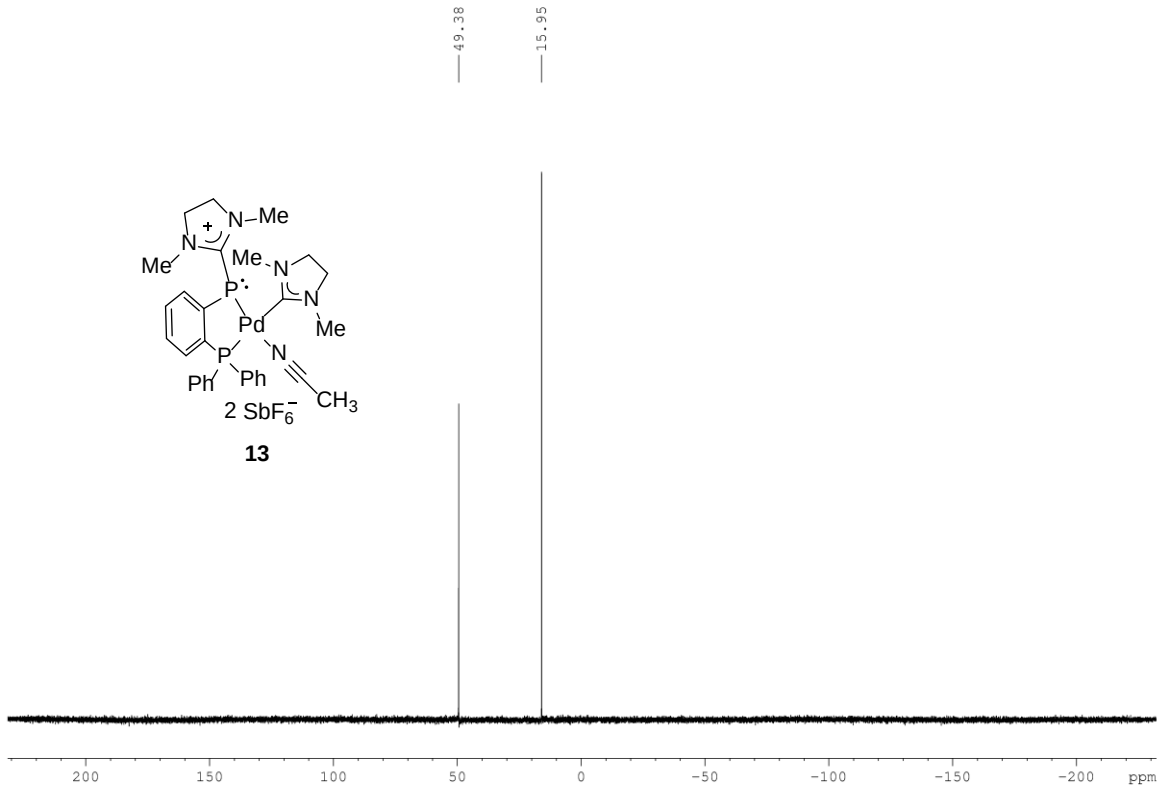
^{1}H NMR (CD_3CN, 600 MHz)



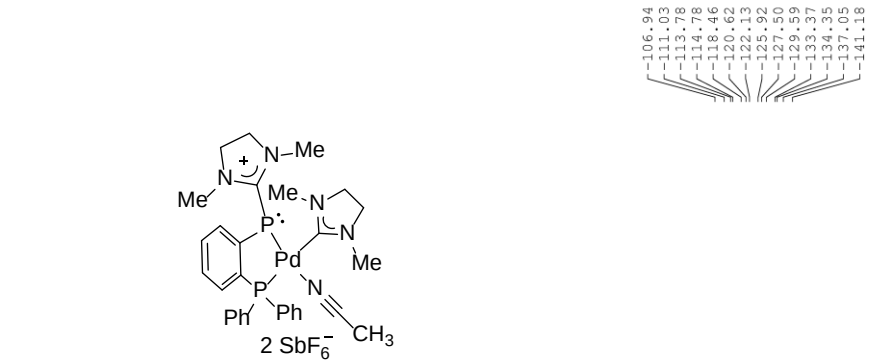
^{13}C NMR (CD_3CN, 125 Mz)



^{31}P NMR (CD_3CN, 162 MHz)

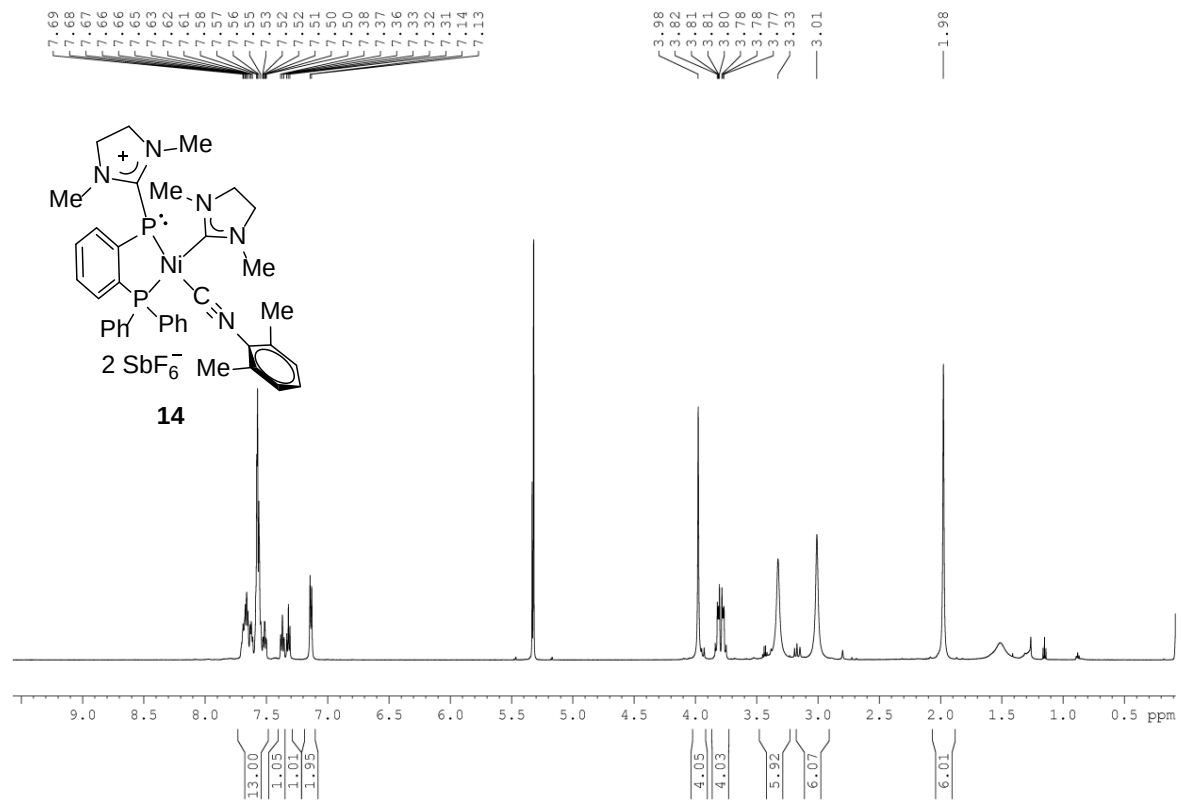


^{19}F NMR (CD_3CN, 282 MHz)

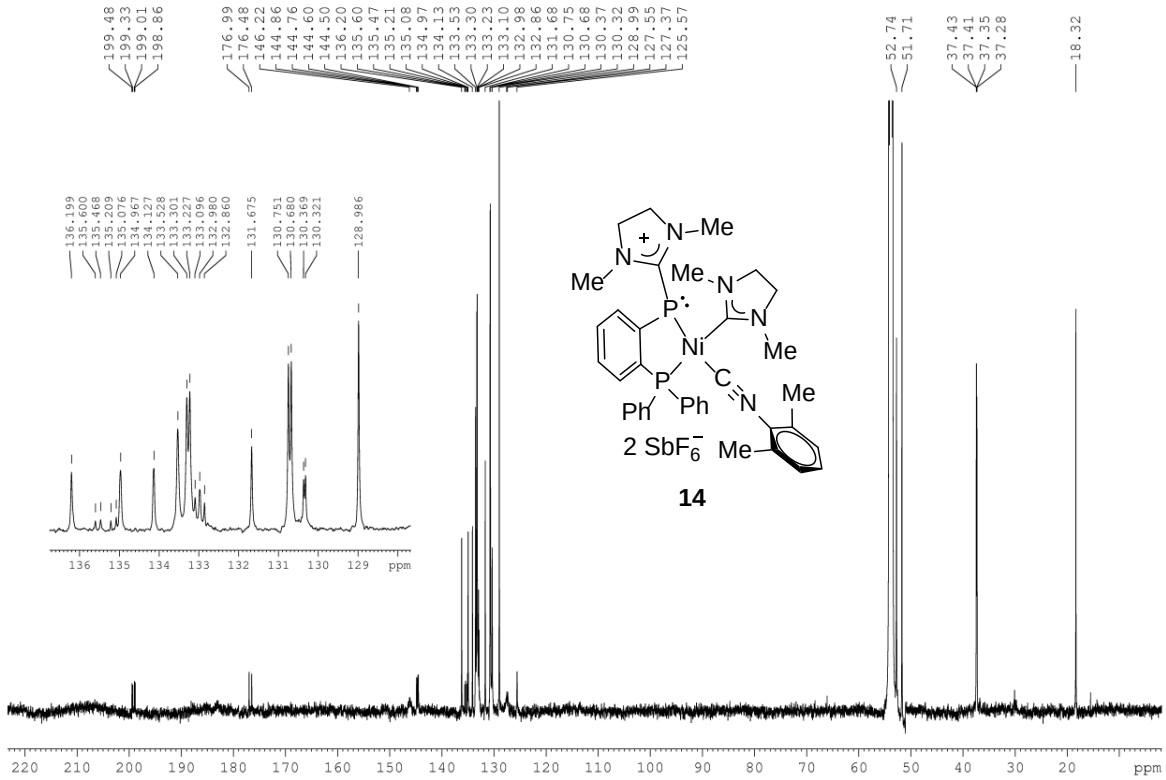


13

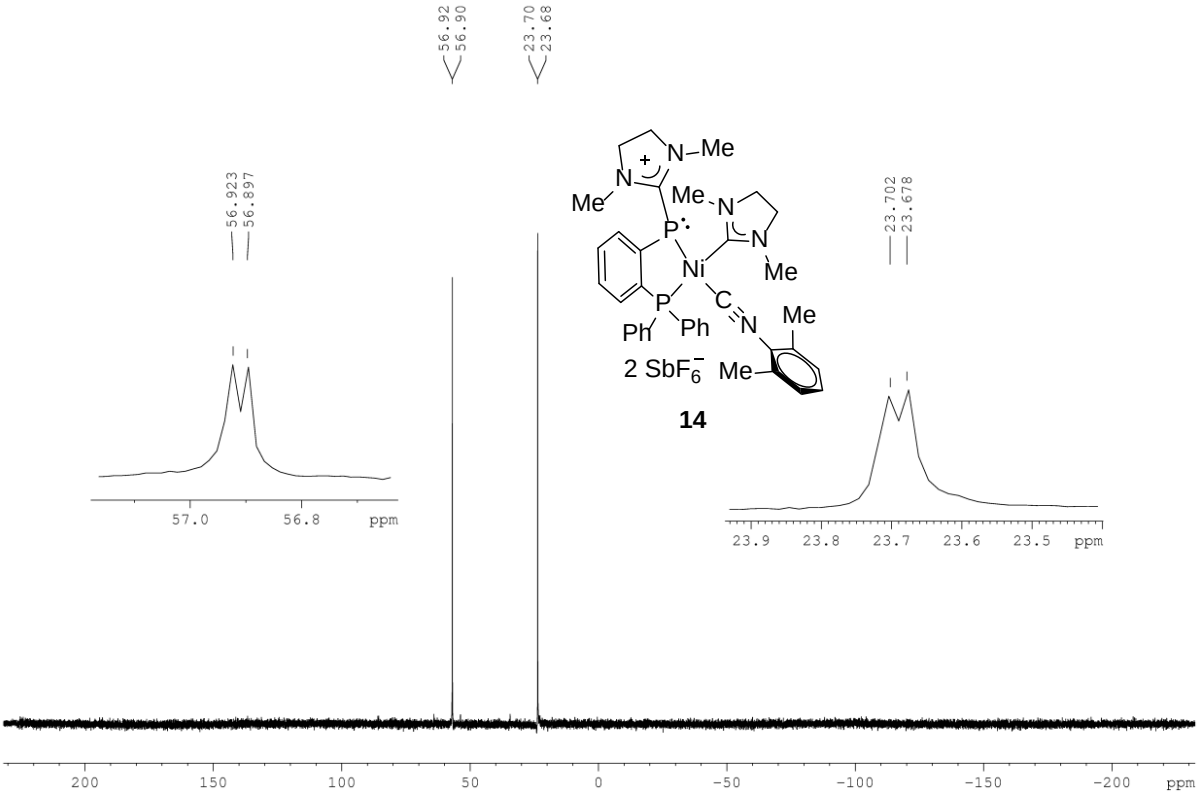
^{1}H NMR (CD_2Cl_2, 600 MHz)



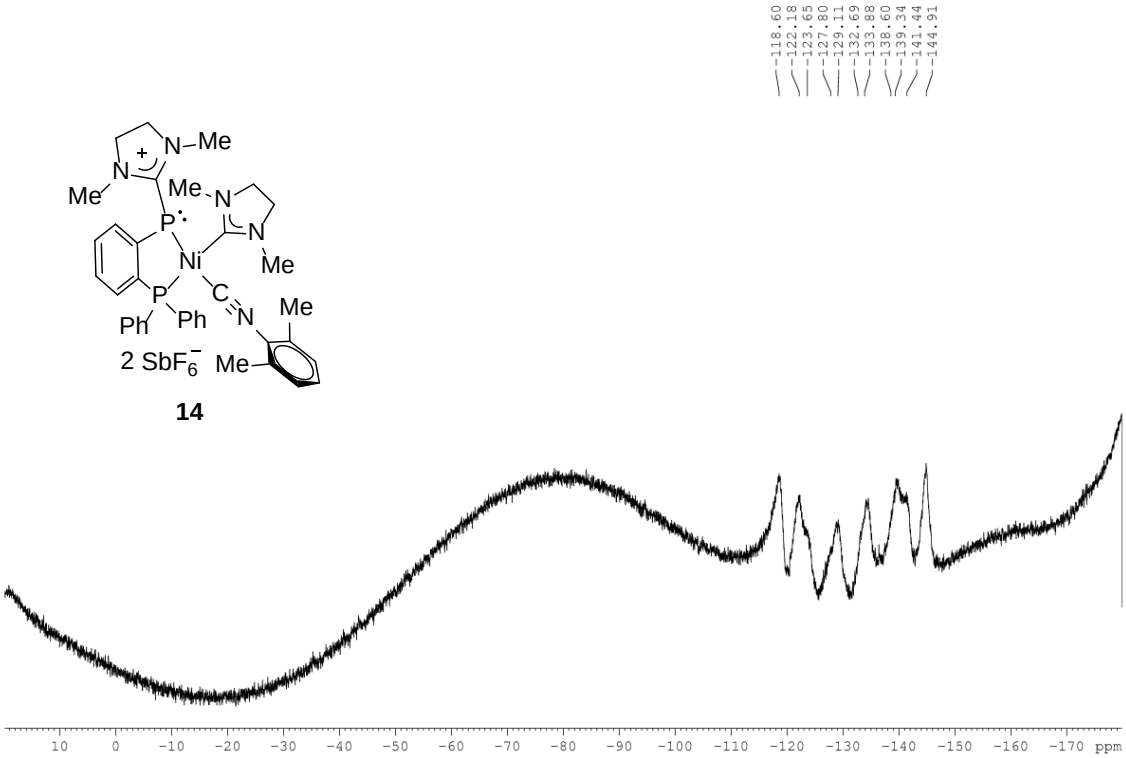
^{13}C NMR (CD_2Cl_2, 125 Mz)



^{31}P NMR (CD_2Cl_2, 162 MHz)



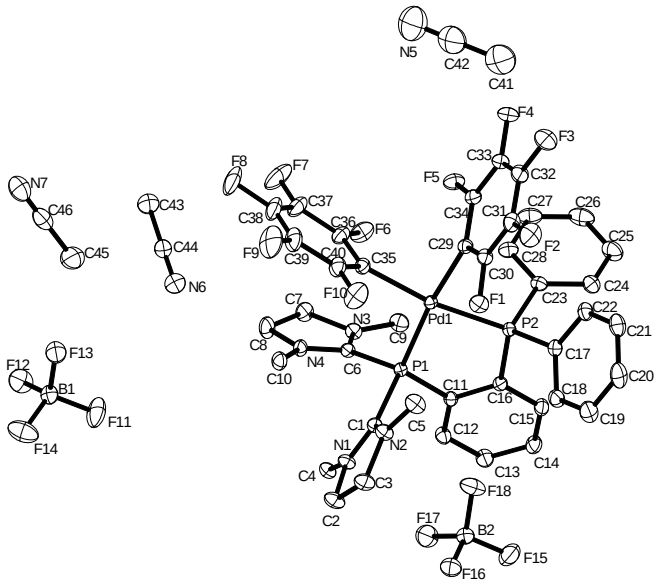
^{19}F NMR (CD_2Cl_2, 282 MHz)



14

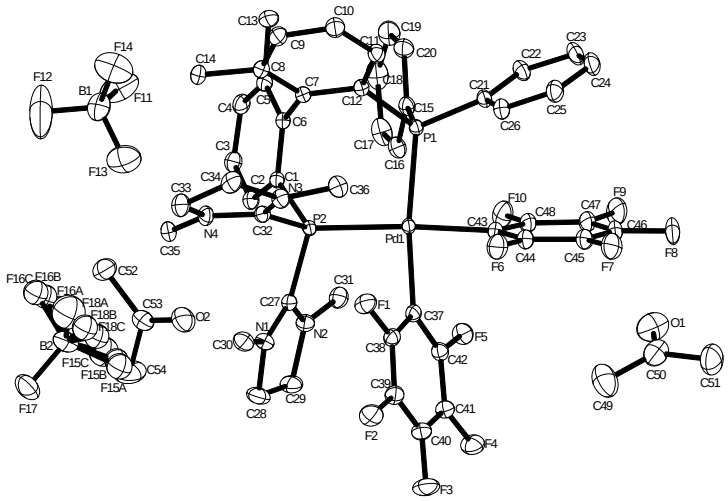
X-ray Structures

Compound **4**



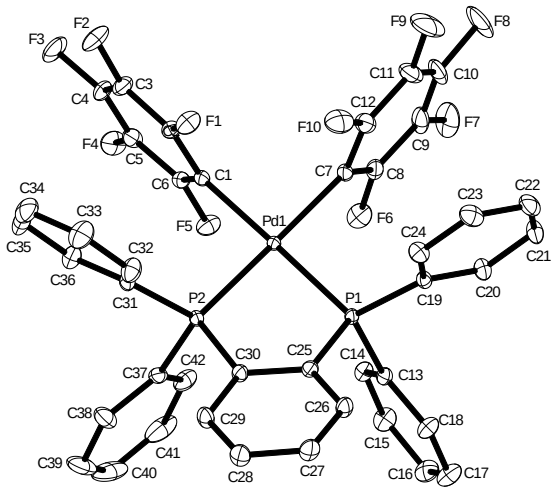
Empirical formula	$C_{46}H_{43}B_2F_{18}N_7P_2Pd$	
Color	colourless	
Formula weight	1225.83 $g \cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 18.3894(13) Å	α= 90°.
	b = 14.7845(14) Å	β= 114.994(4)°.
	c = 20.6566(7) Å	γ = 90°.
Volume	5090.2(7) $Å^3$	
Z	4	
Density (calculated)	1.600 $Mg \cdot m^{-3}$	
Absorption coefficient	0.535 mm^{-1}	
F(000)	2464 e	
Crystal size	0.15 x 0.09 x 0.04 mm^3	
θ range for data collection	2.609 to 35.008°.	
Index ranges	$-29 \le h \le 29$, $-23 \le k \le 23$, $-32 \le l \le 33$	
Reflections collected	124759	
Independent reflections	22373 [R_{int} = 0.0428]	
Reflections with $I>2\sigma(I)$	18998	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98046 and 0.93073	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22373 / 0 / 692	
Goodness-of-fit on F^2	1.048	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0361	wR^2 = 0.0924
R indices (all data)	R_1 = 0.0465	wR^2 = 0.0988
Extinction coefficient	0	
Largest diff. peak and hole	2.507 and -1.787 $e \cdot Å^{-3}$	

Compound **5**



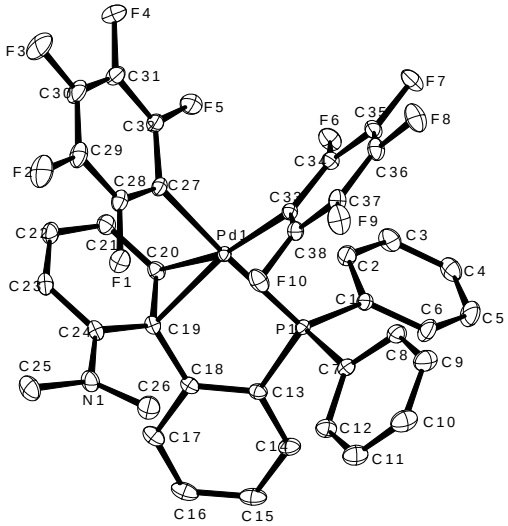
Empirical formula	C54 H54 B2 F18 N4 O2 P2 Pd	
Color	yellow	
Formula weight	1322.97 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	p -1, (no. 2)	
Unit cell dimensions	a = 12.5325(6) Å	α = 93.239(6)°.
	b = 13.8883(13) Å	β = 103.518(7)°.
	c = 18.2445(18) Å	γ = 115.502(6)°.
Volume	2741.7(4) Å3	
Z	2	
Density (calculated)	1.603 mg·m-3	
Absorption coefficient	0.505 mm-1	
F(000)	1340 e	
Crystal size	0.14 x 0.14 x 0.09 mm3	
θ range for data collection	2.607 to 35.056°.	
Index ranges	$-20 \leq h \leq 20$, $-22 \leq k \leq 22$, $-29 \leq l \leq 29$	
Reflections collected	78461	
Independent reflections	24146 [Rint = 0.0279]	
Reflections with I>2σ(I)	21322	
Completeness to θ = 25.242°	99.60%	
Absorption correction	Gaussian	
Max. and min. transmission	0.96402 and 0.92959	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	24146 / 0 / 767	
Goodness-of-fit on F2	1.047	
Final R indices [I>2σ(I)]	R1 = 0.0352	wR2 = 0.0900
R indices (all data)	R1 = 0.0425	wR2 = 0.0946
Extinction coefficient	0	
Largest diff. peak and hole	1.251 and -1.121 e·Å-3	

Compound **6**



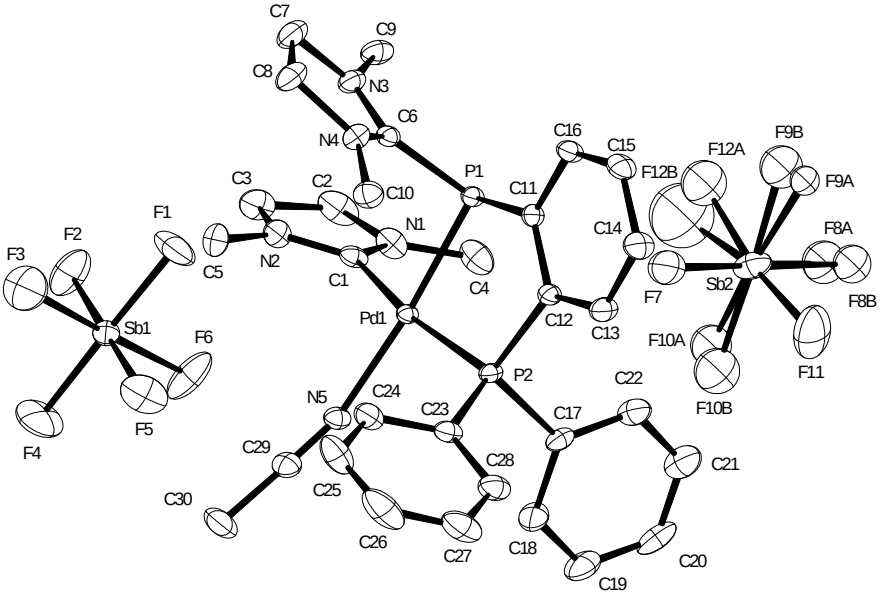
Empirical formula	$C_{42}H_{24}F_{10}P_2Pd$	
Color	colourless	
Formula weight	886.95 $g\cdot mol^{-1}$	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 2_1/n, (no. 14)	
Unit cell dimensions	a = 15.061(3) Å	α= 90°.
	b = 14.768(3) Å	β= 102.298(4)°.
	c = 16.339(4) Å	γ = 90°.
Volume	3550.9(13) $Å^3$	
Z	4	
Density (calculated)	1.659 $Mg\cdot m^{-3}$	
Absorption coefficient	0.698 mm^{-1}	
F(000)	1768 e	
Crystal size	0.07 x 0.06 x 0.04 mm^3	
θ range for data collection	3.039 to 33.647°.	
Index ranges	$-23 \le h \le 23$, $-22 \le k \le 22$, $-25 \le l \le 25$	
Reflections collected	117912	
Independent reflections	14026 [R_{int} = 0.0724]	
Reflections with I>2σ(I)	11056	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.97433 and 0.95301	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14026 / 0 / 496	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2σ(I)]	R_1 = 0.0303	wR^2 = 0.0651
R indices (all data)	R_1 = 0.0483	wR^2 = 0.0706
Extinction coefficient	0	
Largest diff. peak and hole	0.839 and -0.716 $e\cdot Å^{-3}$	

Compound **10**



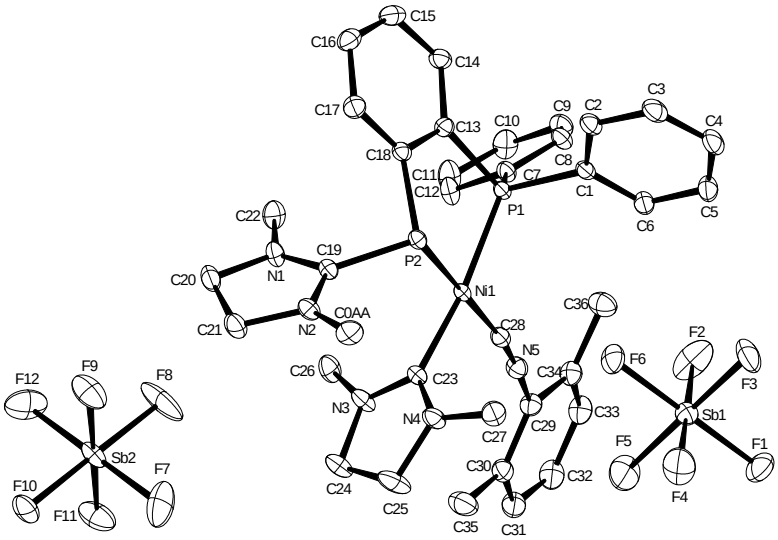
Empirical formula	$C_{38}H_{24}F_{10}NPPd$	
Color	yellow	
Formula weight	821.95 g·mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/c, (no. 14)	
Unit cell dimensions	a = 11.0106(11) Å	α = 90°.
	b = 14.0190(14) Å	β = 96.5422(19)°.
	c = 21.167(2) Å	γ = 90°.
Volume	3246.0(6) Å3	
Z	4	
Density (calculated)	1.682 mg·m-3	
Absorption coefficient	0.709 mm-1	
F(000)	1640 e	
Crystal size	0.22 x 0.21 x 0.19 mm3	
θ range for data collection	2.421 to 37.341°.	
Index ranges	-18 ≤ h ≤ 18, -23 ≤ k ≤ 23, -35 ≤ l ≤ 35	
Reflections collected	127102	
Independent reflections	16348 [Rint = 0.0252]	
Reflections with I>2σ(I)	14984	
Completeness to θ = 25.242°	99.90%	
Absorption correction	Gaussian	
Max. and min. transmission	0.90265 and 0.82904	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	16348 / 0 / 462	
Goodness-of-fit on F2	1.058	
Final R indices [I>2σ(I)]	R1 = 0.0214	wR2 = 0.0575
R indices (all data)	R1 = 0.0250	wR2 = 0.0596
Extinction coefficient	n/a	
Largest diff. peak and hole	0.687 and -0.528 e·Å-3	

Compound **13**



Empirical formula	$C_{30} H_{37} F_{12} N_5 P_2 Pd Sb_2$	
Color	yellow	
Formula weight	1107.48 g · mol-1	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	TRICLINIC	
Space group	**$P^{\bar{}}1$, (no. 2)**	
Unit cell dimensions	a = 10.3416(10) Å	α = 77.0009(18)°.
	b = 13.4178(13) Å	β = 79.6302(17)°.
	c = 15.5829(15) Å	γ = 80.8707(17)°.
Volume	2056.7(3) Å3	
Z	2	
Density (calculated)	1.788 mg · m-3	
Absorption coefficient	1.897 mm-1	
F(000)	1076 e	
Crystal size	0.19 x 0.05 x 0.04 mm3	
q range for data collection	1.570 to 31.543°.	
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22	
Reflections collected	61748	
Independent reflections	13489 [Rint = 0.0329]	
Reflections with I>2σ(I)	11188	
Completeness to q = 25.242°	99.90%	
Absorption correction	Gaussian	
Max. and min. transmission	0.93 and 0.78	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	13489 / 0 / 470	
Goodness-of-fit on F2	1.079	
Final R indices [I>2σ(I)]	R1 = 0.0359	wR2 = 0.0837
R indices (all data)	R1 = 0.0457	wR2 = 0.0873
Largest diff. peak and hole	4.0 and -3.1 e · Å-3	

Compound **14**



Empirical formula	$C_{37} H_{43} F_{12} N_5 Ni P_2 Sb_2$	
Color	yellow	
Formula weight	1149.91 g·mol-1	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	p 21/n, (no. 14)	
Unit cell dimensions	a = 11.903(2) Å	α = 90°.
	b = 12.036(2) Å	β = 97.511(13)°.
	c = 33.183(4) Å	γ = 90°.
Volume	4713.2(14) Å3	
Z	4	
Density (calculated)	1.621 mg·m-3	
Absorption coefficient	1.680 mm-1	
F(000)	2272 e	
Crystal size	0.26 x 0.22 x 0.08 mm3	
θ range for data collection	2.696 to 33.092°.	
Index ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-50 \leq l \leq 50$	
Reflections collected	64200	
Independent reflections	16882 [Rint = 0.0373]	
Reflections with I>2σ(I)	14536	
Completeness to θ = 25.242°	97.50%	
Absorption correction	Gaussian	
Max. and min. transmission	0.87772 and 0.69551	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	16882 / 0 / 538	
Goodness-of-fit on F2	1.123	
Final R indices [I>2σ(I)]	R1 = 0.0338	wR2 = 0.0963
R indices (all data)	R1 = 0.0427	wR2 = 0.1028
Extinction coefficient	n/a	
Largest diff. peak and hole	0.846 and -2.010 e·Å-3	

Kinetic studies

The rate constants for the first-order reductive elimination of decafluorobiphenyl were determined from plots of the decreasing concentration of the different Pd complexes *vs.* time obtained from ^{19}F-NMR data. Reactions were carried out at 70°C and the starting concentration of [Pd] was always 0.015 M.

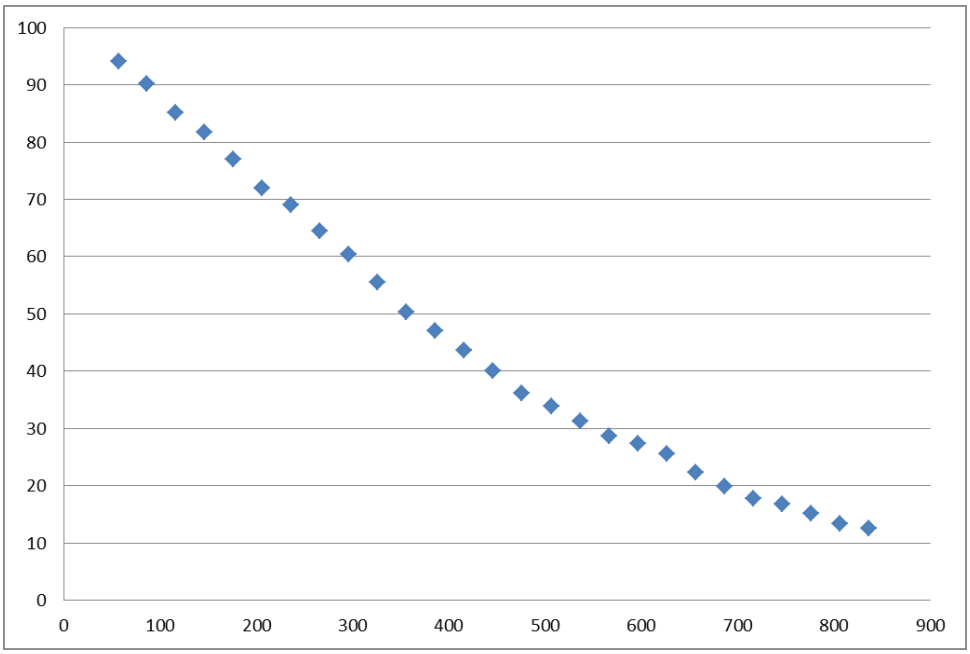


Figure S1: Relative concentration of **4**/ Time in Minutes

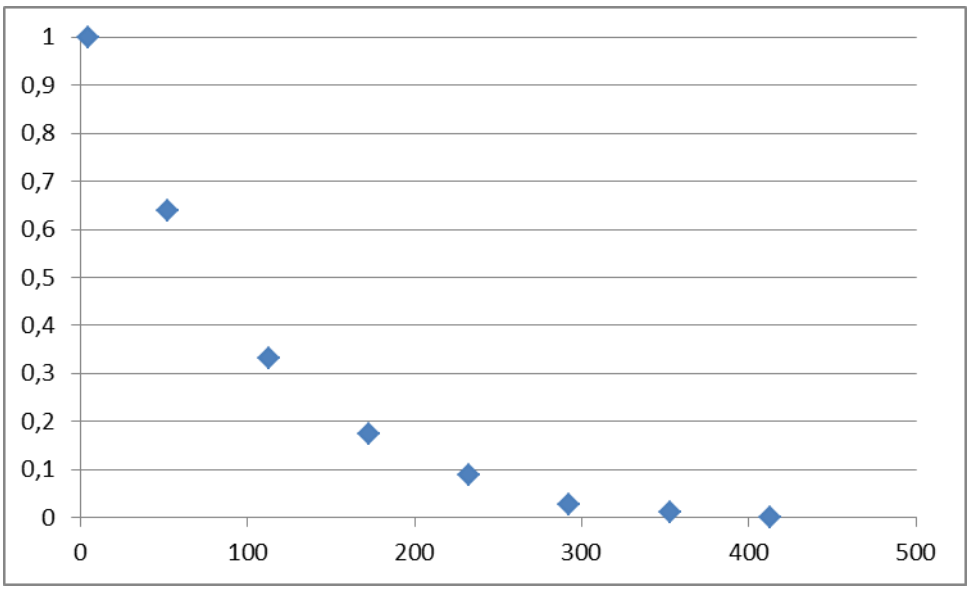


Figure S2: Relative concentration of **5**/ Time in Minutes.

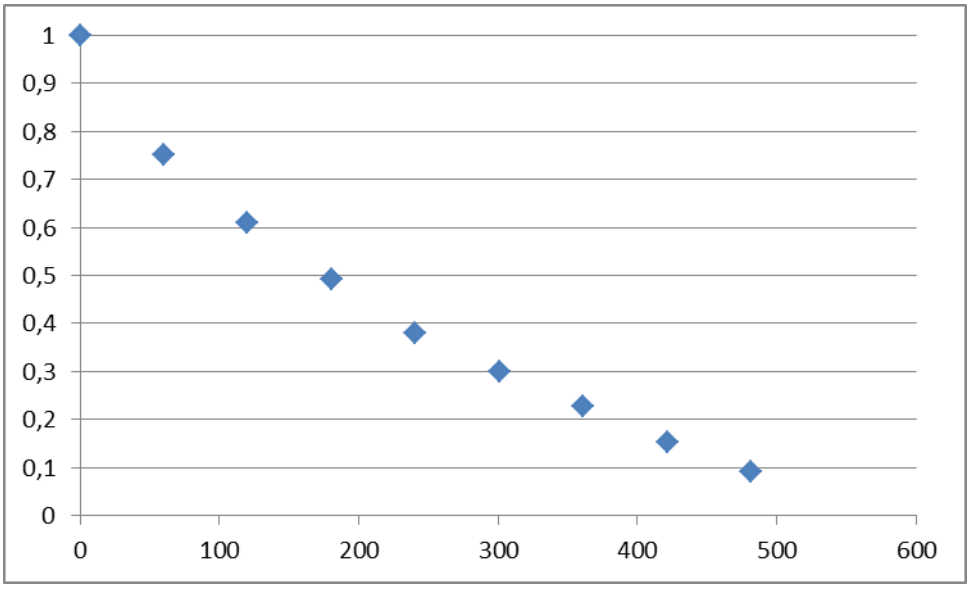


Figure S3: Relative concentration of **10**/ Time in Minutes.

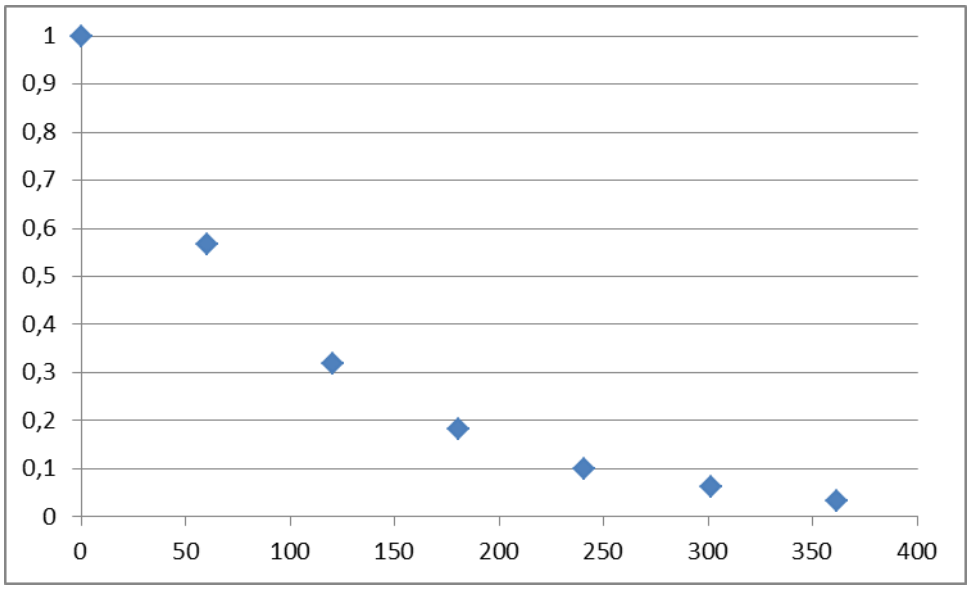


Figure S4: Relative concentration of **12**/ Time in Minutes.

Computational Methods

All geometry optimizations were performed using the BP86[7] and M06L[8] functionals with BP86 being augmented by the D3 dispersion correction with BJ-damping (BP86-D3).[9] The def2-SVP[10] basis set was used for all atoms. The 28 inner-shell core electrons of the palladium atom were described by the corresponding def2 effective core potential[11] accounting for scalar relativistic effects (def2-ecp). For the purpose of computational efficiency, the resolution-of-identity (RI) approximation[12] was applied using auxiliary basis sets to approximate Coulomb potentials in conjunction with the multipole-accelerated resolution of the identity approximation (MA-RI) method for geometry optimizations using the BP86-D3 method.[13]

Stationary points were characterized by evaluating the harmonic vibrational frequencies at the optimized geometries. Zero-point vibrational energies (ZPVE) were computed from the corresponding harmonic vibrational frequencies without scaling. Relative free energies (ΔG) were determined at standard pressure (1 bar) and at an elevated temperature (343 K). The thermal and entropic contributions were evaluated within the rigid-rotor harmonic-oscillator approximation.[14] Solvation contributions were included for acetonitrile on the optimized gas-phase geometries employing the SMD solvation model[15] using the same functional and the def2-TZVP basis set. Geometry optimizations at the BP86-D3 level were performed with TURBOMOLE (version-6.4)[16] and single-point SMD solvation calculations were performed using Gaussian09.[17]

The energy decomposition was performed on BP86-D3/TZVP optimized geometries using the ADF2016[18] program package at the BP86-D3 level in conjunction with a triple-ζ-quality basis set of uncontracted Slater-type orbitals (STOs)[19] augmented with two sets of polarization functions for all atoms; all electrons were included (i.e., inner core electrons were not described by a frozen core). Scalar relativistic effects were accounted for using the zeroth-order regular approximation (ZORA).[20]

Energy table.

Table S1. Listed are the SCF energy, zero-point vibrational energy (*ZPVE*), enthalpy correction (H_{corr}), and Gibbs free energy correction (G_{corr}) determined on the gas-phase geometries for all stationary points calculated. The single imaginary frequency (υ_i cm^{-1}) is also listed for all transition states. Single-point solvent (acetonitrile (CH_3CN)) corrected SCF energies on the gas phase geometries are also tabulated. All energies are in atomic units.

	SCF_{gas}	SCF_{CH3CN}	*ZPVE*	H_{corr}	G_{corr}	υ_i (cm^{-1})
4	-3573.953759	-3573.271121	0.654352	0.728200	0.536938	
4-monoP	-3573.885312	-3573.225157	0.653590	0.727938	0.532893	
TS-4	-3573.923135	-3573.232649	0.654352	0.726144	0.535026	*i*300
Prod-4	-2117.577952	-2117.243047	0.557227	0.605542	0.468859	
$(C_6F_5)_2$	-1456.345288	-1456.012892	0.096553	0.121158	0.038941	
6	-3425.597606	-3424.748896	0.531327	0.596309	0.422575	
TS-6	-3425.549988	-3424.695001	0.529804	0.595106	0.419977	*i*131
Prod-6	-1969.186598	-1968.691104	0.434965	0.474797	0.356721	
5	-3883.818411	-3883.026324	0.788421	0.871777	0.664148	
TS-5	-3883.789083	-3882.993794	0.785755	0.867035	0.666109	*i*279
Prod-5	-2427.437549	-2426.999530	0.690154	0.867035	0.666109	

Energy Decomposition.

Table S2. Listed are the results from the energy decomposition analysis. The first two columns are the strained fragment energies for the $PdAr_2$ and Ligand (L) fragments respectively. All energies are in kcal/mol.

	SCF_$PdAr_2$	SCF-L	ΔE_{Pauli}	ΔE_{elstat}	ΔE_{orb}	ΔE_{disp}	ΔE_{int}	ΔE_{dist}
4	-9295.69	-3359.85	281.27	-205.73	-134.93	-42.5	-101.89	20.08
TS-4	-9298.9	-3345.8	258.32	-201.43	-112.05	-37.56	-92.72	30.92
6	-8424.33	-3358.48	280.29	-227.15	-135.15	-38.37	-120.38	19.49
TS-6	-8433.37	-3348.48	242.1	-210.17	-93.42	-29.51	-91.0	20.45

Energy Profiles.

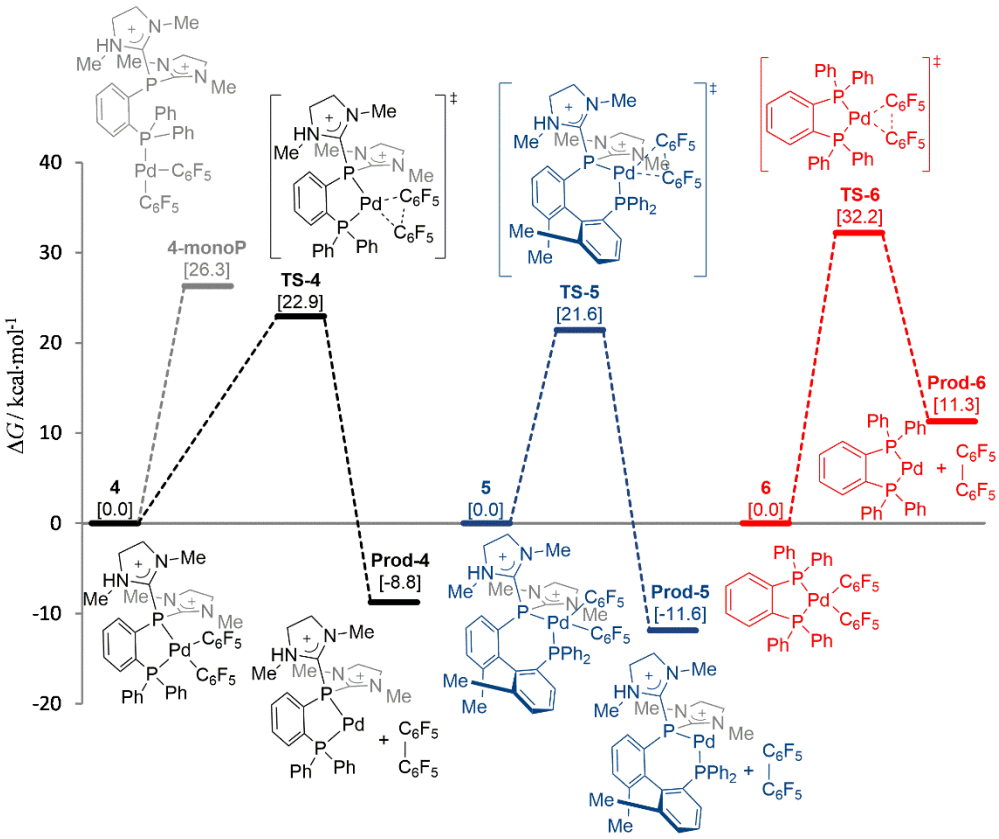


Figure S1. Gibbs free energy profile for the reductive elimination of decafluorobiphenyl from **4** (black), **6** (red), and **5** (blue) calculated at the M06-L(SMD_{CH3CN})/def2-TZVP//BP86-D3/def2-TZVP level of DFT.

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