Supporting information for:

Frustrated Lewis Pair-Like Reactions of Nucleophilic Palladium Carbenes with $B(C_6F_5)_3$

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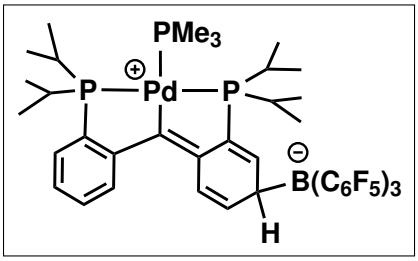
1 Experimental

1.1 General remarks

All experiments are performed under an inert atmosphere of N_2 using standard glovebox techniques. Solvents hexane, pentane, CH_2Cl_2 and diethylether were dried by passing through a column of activated alumina and stored in the glovebox. THF was dried over $LiAlH_4$ followed by vacuum transfer and stored in the glovebox. Deuterated solvents $CDCl_3$ and CD_2Cl_2 were dried over 4 Å molecular sieves under N_2, while C_6D_6 was dried over CaH_2 followed by vacuum transfer, and stored in the glovebox. 2,2'-dibromo-4,4'-di-*tert*-butyldiphenylmethane[1] and $[H(OEt_2)_2][BAr^F_4]$[2] were prepared according to the literature procedure, **1** was synthesized as we previously reported.[3] ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ and $^{11}B\{^1H\}$ NMR spectra were recorded on Bruker DRX 400 or 500 spectrometer. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, to external H_3PO_4, $BF_3{\cdot}OEt_2$ and $CFCl_3$ for ^{31}P, ^{11}B and ^{19}F chemical shifts. CHN analyses were performed on a CE-440 Elemental Analyzer, or by Midwest Microlab, LLC. Gaussian 03 (revision D.02) was used for all reported calculations.[4] The B3LYP (DFT) method was used to carry out the geometry optimizations on model compounds specified in text using the LANL2DZ basis set. The validity of the true minima was checked by the absence of negative frequencies in the energy Hessian.

1.2 Synthesis of $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (4)

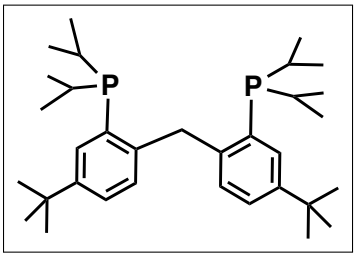


To a solution of $[PC(sp^2)P]^HPd(PMe_3)$ (**1**) (46.4 mg, 0.08 mmol) in 5 mL of THF, a solution of $B(C_6F_5)_3$ (41 mg, 0.08 mmol) in 5 mL of THF was added dropwise. The solution turned yellow within minutes. The volatiles were removed under reduced pressure and the resulting solid residue was triturated with *n*-pentane. Analytically pure **4** (43.6 mg, 0.039 mmol, 49%) was isolated by recrystallization from a concentrated CH_2Cl_2 solution layered with Et_2O.

For 4: ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.45 (t, $^3J_{HH}$ = 7.2 Hz, 1H, Ar*H*), 7.31–7.21 (m, 2H, Ar*H*), 7.07 (t, $^3J_{HH}$ = 6.8 Hz, 1H, Ar*H*), 6.55 (d, $^3J_{HH}$ = 13.6 Hz, 1H, C_6H_4-$B(C_6F_5)_3$), 6.36 (dd, $^3J_{HH}$ = 10.0, $^4J_{HH}$ = 2.8 Hz, 1H, C_6H_4-$B(C_6F_5)_3$), 5.95 (br d, $^3J_{HH}$ = 8.8 Hz, 1H, C_6H_4-$B(C_6F_5)_3$), 4.74 (br d, $^3J_{HH}$ = 12.4 Hz 1H, C_6H_4-$B(C_6F_5)_3$), 2.62–2.51 (m, 1H, C*H*$(CH_3)_2$), 2.50–2.39 (m, 2H, C*H*$(CH_3)_2$), 2.24–2.13 (m, 1H, C*H*$(CH_3)_2$), 1.53 (d, $^2J_{HP}$ = 7.2 Hz, 9H, P(C*H*$_3)_3$), 1.34 (dd, $^3J_{HP}$ = 11.7 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH(C*H*$_3)_2$), 1.29 (dd, $^3J_{HP}$ = 6.8 Hz, $^3J_{HH}$ = 3.6 Hz, 3H, CH(C*H*$_3)_2$), 1.23 (dd, $^3J_{HP}$ = 14.0 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, CH(C*H*$_3)_2$), 1.18 (dd, $^3J_{HP}$ = 12.8 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, CH(C*H*$_3)_2$), 1.13 (dd, $^3J_{HP}$ = 11.6 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, CH(C*H*$_3)_2$), 1.05 (dd, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, CH(C*H*$_3)_2$), 0.86 (dd, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 161.51 (d, $^1J_{CF}$ = 111.2 Hz, Ar*C*), 159.48 (d, *J* = 37.3 Hz, Ar*C*), 149.91 (m, Ar*C*), 149.38 (s, Ar*C*), 149.02 (m, Ar*C*), 148.77 (s, Ar*C*), 147.57 (m, Ar*C*), 141.47 (s, Ar*C*), 139.78 (m, Ar*C*), 138.42 (m, Ar*C*), 137.31 (m, Ar*C*), 135.99 (m, Ar*C*), 132.60 (d, *J* = 32.7 Hz, Ar*C*), 132.12 (s, Ar*C*), 131.35 (d, *J* = 2.6 Hz, Ar*C*), 129.88

(d, J = 8.5 Hz, Ar*C*), 129.51 (d, J = 5.6 Hz, Ar*C*), 129.73 (dd, J = 43.0, 7.6 Hz, Ar*C*), 128.73 (s, Ar*C*), 128.02 (dd, J = 18.3, 5.2 Hz, Ar*C*), 126.00 (d, J = 6.6 Hz, Ar*C*), 122.51 (dd, J = 16.8, 7.8 Hz, Ar*C*), 43.87 (br m, *C*(H)B(C_6F_5)$_3$), 28.11 (dd, $^1J_{CP}$ = 15.3 Hz, J_{CF} = 2.5 Hz, *C*H(CH_3)$_2$), 27.97 (dd, $^1J_{CP}$ = 12.6 Hz, J_{CF}= 2.5 Hz, *C*H(CH_3)$_2$), 27.10 (ddd, $^1J_{CP}$ = 19.6 Hz, J_{CF} = 4.0 Hz, J_{CF} = 2.0 Hz, *C*H(CH_3)$_2$), 26.07 (ddd, $^1J_{CP}$ = 19.9 Hz, J_{CF} = 4.2 Hz, J_{CF} = 2.0 Hz, *C*H(CH_3)$_2$), 21.18 (d, $^2J_{CP}$ = 6.5 Hz, CH(*C*H_3)$_2$), 20.54 (d, $^2J_{CP}$ = 4.0 Hz, CH(*C*H_3)$_2$), 20.08 (d, $^2J_{CP}$ = 4.0 Hz, CH(*C*H_3)$_2$), 20.00 (d, $^2J_{CP}$ = 5.4 Hz, CH(*C*H_3)$_2$), 19.88 (d, $^2J_{CP}$ = 5.3 Hz, CH(*C*H_3)$_2$), 19.69 (d, $^1J_{CP}$ = 23.1 Hz, P(*C*H_3)$_3$), 19.22 (m, CH(*C*H_3)$_2$), 18.78 (dd, $^2J_{CP}$ = 5.8 Hz, J_{CF} = 3.2 Hz, CH(*C*H_3)$_2$), 18.69 (app t, J_{CP} = 5.2 Hz, CH(*C*H_3)$_2$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, −40 °C): δ = −127.66 (d, $^3J_{FF}$ = 24.0 Hz, 1F), −130.70 (dd, $^3J_{FF}$ = 26.3 Hz, J_{FP} = 54.5 Hz, 1F), −131.49 (dd, $^3J_{FF}$ = 24.0 Hz, J_{FP} = 55.9 Hz, 1F), −134.28 (s, 1F), −137.62 (d, $^3J_{FF}$ = 23.8 Hz, 1F), −138.97 (s, 2F), −140.75 (d, $^3J_{FF}$ = 23.0 Hz, 1F), −164.58 (dt, $^3J_{FF}$ = 21.0 Hz, J_{FP} = 78.5 Hz, 1F), −165.14 (br s, 1F), −165.69 (t, $^3J_{FF}$ = 20.9 Hz, 1F), −167.82 (dt, $^3J_{FF}$ = 21.2 Hz, J_{FP} = 76.1 Hz, 1F), −168.17 (dt, $^3J_{FF}$ = 21.5 Hz, J_{FP} = 95.9 Hz, 1F), −168.80 (t, $^3J_{FF}$ = 20.2 Hz, 1F), −169.87 (t, $^3J_{FF}$ = 21.6 Hz, 1F). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ = 74.79 (dd, $^2J_{PP\text{-}trans}$ = 281.4 Hz, $^2J_{PP\text{-}cis}$ = 39.8 Hz, 1P, *P*^{i}Pr$_2$), 64.83 (dd, $^2J_{PP\text{-}trans}$ = 281.4, $^2J_{PP\text{-}cis}$ = 43.4 Hz, 1P, *P*^{i}Pr$_2$), −30.61 (t, $^2J_{PP\text{-}cis}$ = 41.6 Hz, 1P, *P*Me_3). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 25 °C): δ = −11.59 (s). Anal. Calcd for $C_{46}H_{45}BF_{15}P_3Pd{\cdot}CH_2Cl_2$: C, 47.92; H, 4.02. Found: C, 48.02; H, 3.91.

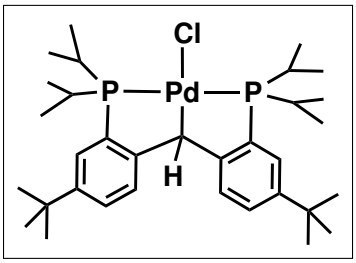
1.3 Synthesis of [PC(sp^3)H_2P]$^{t\mathrm{Bu}}$ (7)



^{n}BuLi (3.53 mL, 1.6 M in hexanes, 5.64 mmol) was added to a solution of bis(2-bromo-4-(tert-butyl)phenyl)methane (1.18 g, 2.686 mmol) in 20 mL of diethylether at −35 °C. The reaction mixture was allowed to stir at room temperature for 2 h. After cooling at −35 °C, ^{i}Pr$_2$PCl (860 mg, 5.64 mmol) in 10 mL of diethylether were added and the reaction mixture was stirred at room temperature overnight. Degassed saturated aqueous NH_4Cl (0.1 mL) was added to quench the reaction. The solution was filtered and the residual solid was washed with diethlyether (3 × 10 mL). The combined organic extract was dried over anhydrous Na_2SO_4, and after the removal of volatiles under reduced pressure the ligand [PC(sp^3)H_2P]$^{t\mathrm{Bu}}$ (**7**) was obtained as a colorless oil. Yield: 1.3 g (94 %).

For 7: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.63 (t, $^3J_{HP}$ = 2.3 Hz, 2H, Ar*H*), 7.19 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HP}$ = 3.8 Hz, 2H, Ar*H*), 7.15 (dd, $^2J_{HH}$ = 8.0 Hz, $^5J_{HP}$ = 2.0 Hz, 2H, Ar*H*), 5.21 (t, $^4J_{HP}$ = 3.3 Hz, 2H, CH_2), 2.13 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH_3)$_2$), 1.29 (s, 18H, C(CH_3)$_3$), 1.18 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 15.0 Hz, 12H, CH(CH_3)$_2$), 1.05 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 11.3 Hz, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): δ = 147.49 (s, Ar*C*), 146.72 (d, $^1J_{CP}$ = 27.6 Hz, Ar*C*), 130.66 (d, $^3J_{CP}$ = 6.8 Hz, Ar*C*), 129.81 (s, Ar*C*), 128.35 (s, Ar*C*), 125.86 (s, Ar*C*), 38.23 (t, $^3J_{CP}$ = 25.3 Hz, *C*H_2), 34.57 (s, *C*(CH_3)$_3$), 31.53 (s, C(*C*H_3)$_3$), 24.48 (d, $^1J_{CP}$ = 14.1 Hz, *C*H(CH_3)$_2$), 20.57 (d, $^2J_{CP}$ = 20.1 Hz, CH(*C*H_3)$_2$), 19.51 (d, $^2J_{CP}$ = 10.3 Hz, CH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 25 °C): δ = −6.15 (s, *P*^{i}Pr$_2$). HRMS (ESI, CH_3CN): Calcd for $C_{33}H_{55}P_2$ (M–H$^+$) 513.3774, found 513.3784.

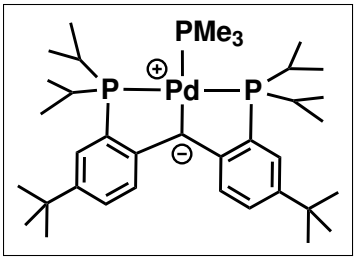
1.4 Synthesis of [PC(sp^3)HP]$^{t\mathrm{Bu}}$PdCl (6)



A solution of **7** (680 mg, 1.326 mmol) in 5 mL benzene was added to a yellow slurry of [(COD)$PdCl_2$] (379 mg, 1.326 mmol) in 5 mL benzene at room temperature. After heating the yellow reaction mixture at 75 °C for 12 h, the solvent was removed under vacuum and the residue was washed with pentane to give the product as yellow solid. Yield: 700 mg (81 %).

For 6: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 7.41–7.38 (m, 4H, Ar*H*), 7.20 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar*H*), 6.21 (s, 1H, C$H_{backbone}$), 2.66 (m, 2H, C*H*$(CH_3)_2$), 2.44 (m, 2H, C*H*$(CH_3)_2$), 1.50 (dt, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 7.0 Hz, 6H, CH(C$H_3)_2$), 1.44 (dt, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 7.0 Hz, 6H, CH(C$H_3)_2$), 1.22 (s, 18H, C(C$H_3)_3$), 1.19 (dt, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 6H, CH(C$H_3)_2$), 1.12 (dt, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 7.6 Hz, 6H, CH(C$H_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 25 °C): δ = 156.08 (t, $^1J_{CP}$ = 15.0 Hz, Ar*C*), 148.24 (t, $^3J_{CP}$ = 2.9 Hz, Ar*C*), 134.00 (t, $^2J_{CP}$ = 16.4 Hz, Ar*C*), 128.65 (s, Ar*C*), 127.49 (s, Ar*C*), 127.05 (t, $^2J_{CP}$ = 9.4 Hz, Ar*C*), 50.59 (t, $^3J_{CP}$ = 2.8 Hz, *C*H$_{backbone}$), 34.45 (s, *C*$(CH_3)_3$), 31.49 (s, C(*C*$H_3)_3$), 25.90 (t, $^1J_{CP}$ = 9.8 Hz, *C*H$(CH_3)_2$), 25.37 (t, $^1J_{CP}$ = 11.8 Hz, *C*H$(CH_3)_2$), 19.44 (t, $^2J_{CP}$ = 2.8 Hz, CH(*C*$H_3)_2$), 18.96 (s, $^2J_{CP}$ = 2.3 Hz, CH(*C*$H_3)_2$), 18.44 (s, CH(*C*$H_3)_2$), 18.38 (s, CH(*C*$H_3)_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 25 °C): δ = 49.36 (s, *P*^{i}Pr$_2$). Anal. Calcd for $C_{33}H_{53}ClP_2Pd$ (653.59 g/mol): C, 60.64; H, 8.17. Found: C, 60.58; H, 8.21.

1.5 Synthesis of [PC(sp^2)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (3)

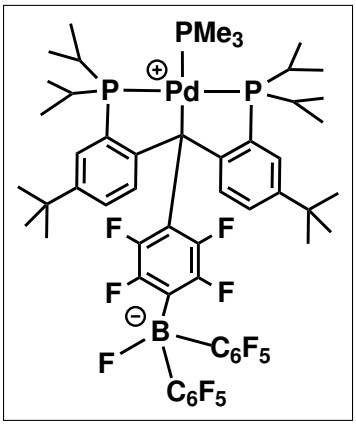


PMe_3 (0.9 mL, 1M in THF, 0.903 mmol) and **6** (281 mg, 0.430 mmol) were mixed in 3 mL of THF at room temperature. After stirring for 5 min, a solution of KN$(SiMe_3)_2$ (94 mg, 0.473 mmol) in 3 mL THF was added. The resulting dark brown reaction mixture was further stirred at room temperature for 90 min. The volatiles were removed under reduced pressure and the dark brown residues were extracted with hexane (8 × 8 mL). The combined extracts were concentrated to about 2 mL and stored at -35 °C to induce crystallization. Analytically pure **3** was isolated as a dark brown crystalline solid. Yield: 214 mg (72 %).

For 3: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.98 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 6.92–6.89 (m, 4H, Ar*H*), 2.18 (m, 4H, C*H*$(CH_3)_2$), 1.40 (s, 18H, C(C$H_3)_3$), 1.28 (dt, $^3J_{HH}$ = 6.5 Hz, $^3J_{HP}$ = 6.8 Hz, 12H, CH(C$H_3)_2$), 1.10 (dt, $^3J_{HH}$ = 9.0 Hz, $^3J_{HP}$ = 7.3 Hz, 12H, CH(C$H_3)_2$), 0.92 (d, $^2J_{HP}$ = 6.0 Hz, 9H, P(C$H_3)_3$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): δ = 162.72 (br s, Ar*C*), 133.09 (br s, Ar*C*), 128.72 (d, $^1J_{CP}$ = 22.3 Hz, Ar*C*), 128.35 (s, Ar*C*), 116.28 (br s, Ar*C*), 34.72 (s, *C*$(CH_3)_3$), 32.06 (s, C(*C*$H_3)_3$), 27.21 (t, $^1J_{CP}$ = 10.7 Hz, *C*H$(CH_3)_2$), 20.96 (t, $^2J_{CP}$ = 3.2 Hz, CH(*C*$H_3)_2$), 19.81 (d, $^1J_{CP}$ = 18.0 Hz, P(*C*$H_3)_3$), 19.08 (s, CH(*C*$H_3)_2$). ^{13}C{^{1}H} NMR (126 MHz, toluene-d8, 25 °C): δ = 162.81 (t, $^1J_{CP}$ = 19.8 Hz, Ar*C*), 136.06 (d, $^2J_{CP-trans}$ = 103.7 Hz, $C_{carbene}$), 133.09 (s, Ar*C*), 128.76 (s, Ar*C*), 128.20 (s, Ar*C*), 116.36 (m, Ar*C*), 115.84 (td, J_{CP} = 22.4 Hz, J_{CP} = 10.9 Hz, Ar*C*), 33.66 (s, *C*$(CH_3)_3$), 31.96 (s, C(*C*$H_3)_3$), 27.21 (t, $^1J_{CP}$ = 10.6 Hz, *C*H$(CH_3)_2$), 20.85 (t, $^2J_{CP}$ = 3.3 Hz, CH(*C*$H_3)_2$), 19.83 (d, $^1J_{CP}$ = 17.6 Hz, P(*C*$H_3)_3$), 18.96 (s, CH(*C*$H_3)_2$).

$^{13}C\{^1H\}$ NMR (126 MHz, toluene-d8, −40 °C): δ = 162.54 (t, $^1J_{CP}$ = 17.8 Hz, Ar*C*), 134.17 (d, $^2J_{CP-trans}$ = 106.7 Hz, $C_{carbene}$), 132.44 (s, Ar*C*), 128.93 (s, Ar*C*), 128.23 (s, Ar*C*), 116.05 (m, Ar*C*), 115.92 (td, J_{CP} = 22.2 Hz, J_{CP} = 10.8 Hz, Ar*C*), 33.59 (s, *C*$(CH_3)_3$), 31.87 (s, C(*C*$H_3)_3$), 26.89 (t, $^1J_{CP}$ = 10.8 Hz, *C*H$(CH_3)_2$), 20.68 (s, CH(*C*$H_3)_2$), 19.11 (d, $^1J_{CP}$ = 18.6 Hz, P(*C*$H_3)_3$), 18.79 (s, CH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 25 °C): δ = 61.86 (d, $^2J_{PP}$ = 44.2 Hz, 2P, *P*^{i}Pr$_2$), −35.52 (t, $^2J_{PP}$ = 44.2 Hz, 1P, *P*Me$_3$). Anal. Calcd for $C_{36}H_{61}P_3Pd$ (693.21 g/mol): C, 62.37; H, 8.87. Found: C, 62.44; H, 8.82.

1.6 Synthesis of $[(C_6F_5)_2BF(C_6F_4)$-PC(*sp*^{3})P]^{tBu}Pd(PMe$_3$) (5)

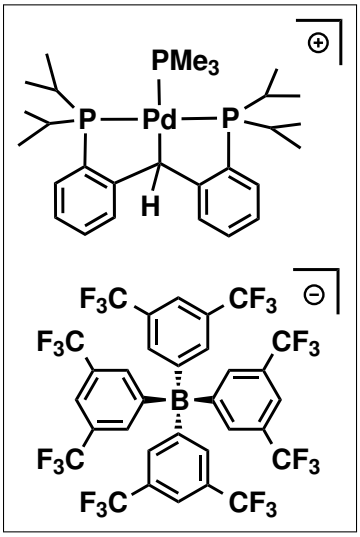


A solution of $B(C_6F_5)_3$ (30 mg, 0.058 mmol) in 3 mL of hexane was added to a drak brown solution of **3** (40 mg, 0.058 mmol) in 4 mL of hexane. A greenish-yellow slurry was formed immediately. After stirring the mixture at room temperature for 20 min, the supernatant was decanted and the residual solids were washed with pentane, and dried under reduced pressure to give the crude product as greenish-yellow solid. Recrystallization from diethylether at −35 °C afforded analytically pure **5** as a greenish-yellow crystalline solid. Yield: 33 mg (47 %).

For 5: ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.48 (d, $^3J_{HH}$ = 7.5 Hz, 3H, Ar*H*), 7.13 (br s, 2H, Ar*H*), 6.42 (br s, 1H, Ar*H*), 2.53 (br s, 4H, C*H*$(CH_3)_2$), 1.58 (d, $^2J_{HP}$ = 8.0 Hz, 9H, P(C*H*$_3)_3$), 1.49 (br s, 6H, CH(C*H*$_3)_2$), 1.31 (br s, 21H, CH(C*H*$_3)_2$and C(C*H*$_3)_3$), 1.09 (br s, 12H, CH(C*H*$_3)_2$), 0.77 (br s, 3H, CH(C*H*$_3)_2$). ^1H NMR (500 MHz, $CDCl_3$, −35 °C): δ = 7.45 (t, $^3J_{HH}$ = 7.3 Hz, 3H, Ar*H*), 7.13 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar*H*), 7.07 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, Ar*H*), 6.43 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, Ar*H*), 2.62–2.47 (m, 4H, C*H*$(CH_3)_2$), 1.57 (d, $^2J_{HP}$ = 8.5 Hz, 9H, P(C*H*$_3)_3$), 1.49 (m, 6H, CH(C*H*$_3)_2$), 1.32 (s, 9H, C(C*H*$_3)_3$), 1.23 (s, 12H, CH(C*H*$_3)_2$ and C(C*H*$_3)_3$), 1.12 (dd, $^3J_{HP}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3)_2$), 0.97 (dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, CH(C*H*$_3)_2$), 0.72 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 55 °C): δ = 150.13 (m, Ar*C*), 149.30 (m, Ar*C*), 148.24 (m, Ar*C*), 147.35 (m, Ar*C*), 144.03 (m, Ar*C*), 142.12 (m, Ar*C*), 139.93 (m, Ar*C*), 137.94 (m, Ar*C*), 135.89 (m, Ar*C*), 131.83 (d, J_{CP} = 39.2 Hz, Ar*C*), 128.83 (br s, Ar*C*), 126.97 (m, Ar*C*), 72.47 (br d, $^2J_{CP}$ = 95.3, $C_{backbone}$), 34.75 (s, *C*$(CH_3)_3$), 31.47 (s, C(*C*$H_3)_3$), 27.03 (br s, *C*H$(CH_3)_2$), 20.18 (d, J_{CF} = 57.3 Hz, CH(*C*$H_3)_2$), 19.63 (d, $^1J_{CP}$ = 22.1 Hz, P(*C*$H_3)_3$), 18.84 (d, J_{CF} = 44.7 Hz, CH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ = 63.11 (d, $^2J_{PP\text{-}trans}$ = 278.6 Hz, 1P, *P*^{i}Pr$_2$), 44.82 (dd, $^2J_{PP\text{-}trans}$ = 281.4 Hz, $^2J_{PP\text{-}cis}$ = 64.8 Hz, 1P, *P*^{i}Pr$_2$), −26.12 (t, $^2J_{PP\text{-}cis}$ = 54.6 Hz, 1P, *P*Me$_3$). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, −35 °C): δ = 62.68 (ddd, $^2J_{PP\text{-}trans}$ = 281.4 Hz, $^2J_{PP\text{-}cis}$ = 44.0 Hz, J_{PF} = 33.1 Hz, 1P, *P*^{i}Pr$_2$), 44.92 (dd, $^2J_{PP\text{-}trans}$ = 281.4 Hz, $^2J_{PP\text{-}cis}$ = 62.4 Hz, 1P, *P*^{i}Pr$_2$), −25.06 (dd, $^2J_{PP\text{-}cis}$ = 62.2, 45.1 Hz, 1P, *P*Me$_3$) ppm; $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$, 25 °C): δ = −137.11 (br s, 1F, B(C$_6F_4$)), −137.98 (br s, B(C$_6F_5)_2$, (*o*-F)) and −138.12 (br m, B(C$_6F_5)_2$, (*o*-F)), −138.55 (br s, 1F, B(C$_6F_4$)), −140.77 (br s, 1F, B(C$_6F_4$)), −146.81 (br s, 1F, B(C$_6F_4$)), −165.28 (t, $^3J_{FF}$ = 20.4 Hz, B(C$_6F_5)_2$, (*p*-F)), −165.34 (t, $^3J_{FF}$ = 19.5 Hz, B(C$_6F_5)_2$, (*p*-F)), −169.56 (td, $^3J_{FF}$ = 23.5 Hz, $^4J_{FF}$ = 5.7 Hz, B(C$_6F_5)_2$, (*m*-F)), −169.67 (td, $^3J_{FF}$ = 23.5 Hz, $^4J_{FF}$ = 6.2 Hz, B(C$_6F_5)_2$, (*m*-F)), −195.46 (br s, 1F, B*F*). $^{19}F\{^1H\}$

NMR NMR (470 MHz, $CDCl_3$, 55 °C): δ = −136.93 (br 1F, $B(C_6F_4)$), −137.95 (s, 3F, $B(C_6F_4)$ and $B(C_6F_5)_2$, (*o*-F)), −140.99 (br 1F, $B(C_6F_4)$), −146.62 (br 1F, $B(C_6F_4)$), −165.67 (t, $^3J_{FF}$ = 20.7 Hz, $B(C_6F_5)_2$, (*p*-F)), −165.72 (t, $^3J_{FF}$ = 20.2 Hz, $B(C_6F_5)_2$, (*p*-F)), −169.86 (td, $^3J_{FF}$ = 19.7 Hz, $^4J_{FF}$ = 5.2 Hz, $B(C_6F_5)_2$, (*m*-F)), −169.98 (td, $^3J_{FF}$ = 21.4 Hz, $^4J_{FF}$ = 6.4 Hz, $B(C_6F_5)_2$, (*m*-F)), −195.24 (br s, 1F, B*F*). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): δ = 0 (br). Anal. Calcd. for $C_{54}H_{61}BF_{15}P_3Pd$ (1205.19 g/mol): C, 53.82; H, 5.10. Found: C, 53.48; H, 5.05.

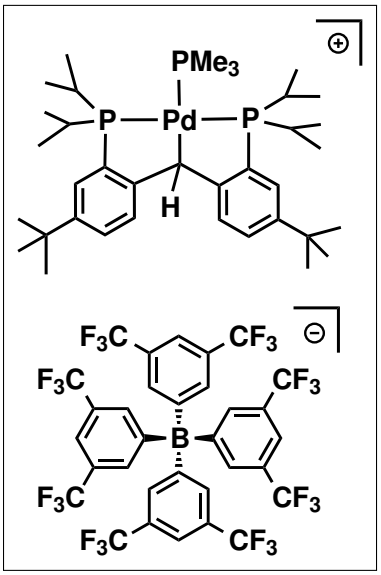
1.7 Synthesis of [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] ([8][BAr$^F_4$])



$[H(OEt_2)_2][BAr^F_4]$ (16.6 mg, 0.016 mmol) in 1 mL of diethyl ether was slowly added to a dark-brown solution of **1** (9.5 mg, 0.016 mmol) in 1 mL of ether at −35°C. The resulted pale yellow solution was then allowed to stir at room temperature for 10 min. After reducing volume of the solution to about 0.5 mL under reduced pressure, *n*-pentane (5 mL) was layered and the mixture was stored at −35 °C to give product **[8][BAr$^F_4$]** as yellow crystalline blocks. Yield: 24 mg (quantitative).

For [8][BAr$^F_4$]: ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.72 (s, 8H, ortho-Ar_FH), 7.53 (s, 4H, para-Ar_FH), 7.55–7.51 (m, 2H, Ar*H*), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 7.25 (t, $^3J_{HH}$ = 7.9 Hz, Ar*H*), 7.13 (d, t, $^3J_{HH}$ = 7.9 Hz, Ar*H*), 6.36 (d, $^3J_{HP}$ = 12.0 Hz, 1H, $CH_{backbone}$), 2.57 (m, 2H, C*H*$(CH_3)_2$), 2.50 (m, 2H, C*H*$(CH_3)_2$), 1.53 (d, $^2J_{HP}$ = 7.6 Hz, 9H, P(C*H*$_3)_3$), 1.40 (td, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 6.8 Hz, 6H, CH(C*H*$_3)_2$), 1.18 (td, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 9.2 Hz, 6H, CH(C*H*$_3)_2$), 1.12 (td, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 8.4 Hz, 6H, CH(C*H*$_3)_2$), 1.09 (td, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 7.4 Hz, 6H, CH(C*H*$_3)_2$). $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$, 25 °C): δ = 161.90 (q, $^1J_{CB}$ = 49.53 Hz, ipso-Ar_FC), 156.06 (td, J_{CP} = 13.5 Hz, J_{CP} = 4.9 Hz, Ar*C*), 134.99 (s, ortho-Ar_FC), 132.20 (s, Ar*C*), 131.86 (s, Ar*C*), 130.70 (td, J_{CP} = 20.0 Hz, J_{CP} = 9.0 Hz, Ar*C*), 129.11 (qq, $^2J_{CF}$ = 31.2 Hz, $^4J_{CF}$ = 2.8 Hz, meta-Ar_FC), 127.85 (td, J_{CP} = 9.5 Hz, J_{CP} = 6.5 Hz, Ar*C*), 126.72 (t, J_{CP} = 3.6 Hz, Ar*C*), 124.74 (q, $^1J_{CF}$ = 273.1 Hz, *C*F_3), 117.63 (m, para-Ar_FC), 63.70 (dt, $^2J_{CP}$ = 85.2 Hz, $^3J_{CP}$ = 5.3 Hz, *C*$H_{backbone}$), 27.47 (t, $^1J_{CP}$ = 10.1 Hz, *C*H$(CH_3)_2$), 27.41 (td, $^1J_{CP}$ = 12.8 Hz, J_{CP} = 2.0 Hz, *C*H$(CH_3)_2$), 20.58 (t, $^2J_{CP}$ = 3.2 Hz, CH(*C*$H_3)_2$), 19.38 (m, CH(*C*$H_3)_2$), 19.03 (d, $^1J_{CP}$ = 20.8 Hz, P(*C*$H_3)_3$), 18.93 (s, CH(*C*$H_3)_2$), 18.15 (s, CH(*C*$H_3)_2$). $^{31}P\{^1H\}$ NMR (162 Hz, $CDCl_3$, 25 °C): δ = 59.99 (d, $^2J_{PP\text{-}cis}$ = 45.5 Hz, *P*^{i}Pr$_2$), −29.93 (t, $^2J_{PP\text{-}cis}$ = 45.8 Hz, *P*Me_3). $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$, 25 °C): δ = −65.46 (s). $^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): δ = −6.58 (s). Anal. Calcd. for $C_{60}H_{58}BF_{24}P_3Pd$ (1445.22 g/mol): C, 49.86; H, 4.05. Found: C, 49.40; H, 3.80.

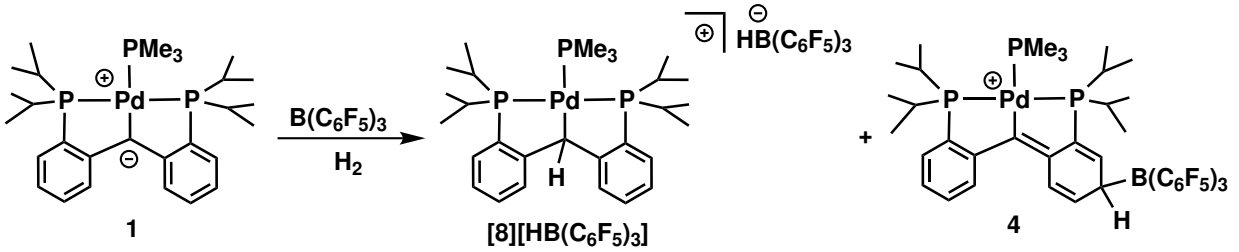
1.8 Synthesis of [{PC(sp^3)HP}$^{t\mathrm{Bu}}$PdPMe$_3$][BAr$^{\mathrm{F}}_4$] ([9][BAr$^{\mathrm{F}}_4$])



[H(OEt$_2$)$_2$][BAr$^{\mathrm{F}}_4$] (44 mg, 0.043 mmol) in 1 mL of diethyl ether was slowly added to a brown solution of **3** (30 mg, 0.043 mmol) in 2 mL of ether at −35 °C. The resulted bright yellow solution was then allowed to stir at room temperature for 10 min. After reducing volume of the solution to about 1 mL under reduced pressure, *n*-pentane (8 mL) was layered and the mixture was stored at −35 °C to give product **[9][BAr$^{\mathrm{F}}_4$]** as yellow blocks. Yield: 67 mg (quantitative).

For [9][BAr$^{\mathrm{F}}_4$]: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.73 (s, 8H, ortho-Ar$_{\mathrm{F}}$*H*), 7.55 (s, 4H, para-Ar$_{\mathrm{F}}$*H*), 7.50 (td, $^3J_{\mathrm{HH}}$ = 9.0 Hz, $^4J_{\mathrm{HH}}$ = 2.0 Hz, 2H, Ar*H*), 7.44 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 2H, Ar*H*), 7.13 (d, $^3J_{\mathrm{HH}}$ = 8.0 Hz, 2H, Ar*H*), 6.28 (d, $^3J_{\mathrm{HP}}$ = 12.0 Hz, 1H, C*H*$_{\mathrm{backbone}}$), 2.57 (m, 2H, C*H*(CH$_3$)$_2$), 2.50(m, 2H, C*H*(CH$_3$)$_2$), 1.53 (d, $^2J_{\mathrm{HP}}$ = 7.5 Hz, 9H, P(C*H*$_3$)$_3$), 1.42 (dt, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^3J_{\mathrm{HP}}$ = 6.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.34 (s, 9H, C(C*H*$_3$)$_3$), 1.17 (dt, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^3J_{\mathrm{HP}}$ = 9.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16–1.09 (m, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ = 161.87 (q, $^1J_{\mathrm{CB}}$ = 49.9 Hz, ipso-Ar$_{\mathrm{F}}$*C*), 153.32 (td, J_{CP} = 13.5 Hz, J_{CP} = 5.0 Hz, Ar*C*), 149.89 (s, Ar*C*), 134.96 (s, ortho-Ar$_{\mathrm{F}}$*C*), 130.30 (td, J_{CP} = 20.0 Hz, J_{CP} = 9.5 Hz, Ar*C*), 129.08 (s, Ar*C*), 129.07 (qq, $^2J_{\mathrm{CF}}$ = 31.8 Hz, $^4J_{\mathrm{CF}}$ = 2.6 Hz, meta-Ar$_{\mathrm{F}}$*C*), 128.64 (s, Ar*C*), 127.33 (td, J_{CP} = 10.2 Hz, J_{CP} = 6.6 Hz, Ar*C*), 124.72 (q, $^1J_{\mathrm{CF}}$ = 273.1 Hz, *C*F$_3$), 117.61 (m, para-Ar$_{\mathrm{F}}$*C*), 62.94 (dt, $^2J_{\mathrm{CP}}$ = 85.9 Hz, $^3J_{\mathrm{CP}}$ = 5.4 Hz, *C*H$_{\mathrm{backbone}}$), 34.71 (s, *C*(CH$_3$)$_3$), 31.36 (s, C(*C*H$_3$)$_3$), 27.43 (t, $^1J_{\mathrm{CP}}$ = 10.2 Hz, *C*H(CH$_3$)$_2$), 27.37 (td, $^1J_{\mathrm{CP}}$ = 10.2 Hz, J_{CP} = 2.2 Hz, *C*H(CH$_3$)$_2$), 20.71 (t, J_{CP} = 3.3 Hz, CH(*C*H$_3$)$_2$), 19.43 (s, CH(*C*H$_3$)$_2$), 19.15 (d, $^1J_{\mathrm{CP}}$ = 22.6 Hz, P(*C*H$_3$)$_3$), 19.02 (s, CH(*C*H$_3$)$_2$), 18.33 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (202 Hz, $CDCl_3$, 25 °C): δ = 59.64 (d, $^2J_{\mathrm{PP\text{-}cis}}$ = 45.3 Hz, *P*^{i}Pr$_2$), −30.43 (t, $^2J_{\mathrm{PP\text{-}cis}}$ = 46.3 Hz, *P*Me$_3$). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$, 25 °C): δ = −65.51 (s). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C): δ = −6.57 (s). Anal. Calcd for $C_{68}H_{74}BF_{24}P_3Pd$ (1557.43 g/mol): C, 52.44; H, 4.79. Found: C, 52.37; H, 4.59.

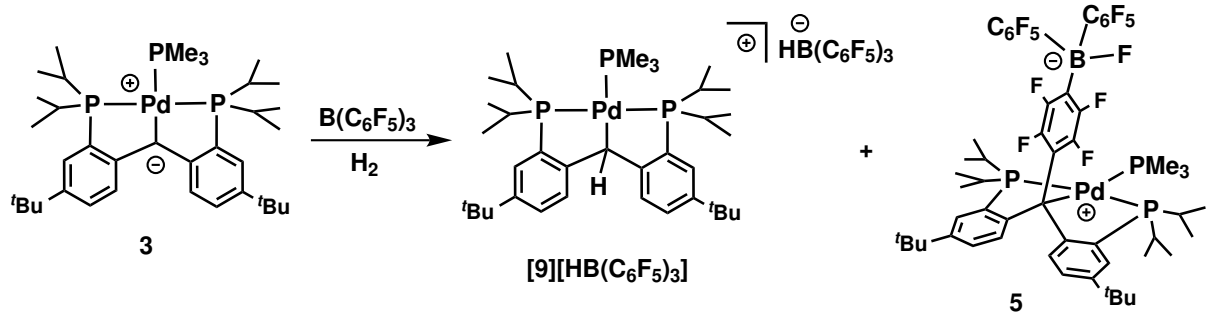
1.9 Reaction of [PC(sp^2)P]$^{\mathrm{H}}$Pd(PMe$_3$) (1) with B(C$_6$F$_5$)$_3$ and H$_2$



In a 100 mL of round-bottom flask purged with H_2 was added B(C$_6$F$_5$)$_3$ (7.4 mg, 0.014 mmol) in 1 mL of Et$_2$O through the septum by syringe. After stirring for about 1 min, [PC(sp^2)P]$^{\mathrm{H}}$Pd(PMe$_3$) (**1**) (10 mg, 0.014 mmol) in 1 mL of Et$_2$O was slowly added by syringe in the same way. The bright yellow slurry was then monitored by NMR spectroscopy in C_6D_6. After 1 h full conversion of the starting material was observed.The final reaction mixture contained **4** and **[8][HB(C$_6$F$_5$)$_3$]**

in a 95:5 ratio. The identity of **[8][HB(C$_6$F$_5$)$_3$]** was confirmed by comparing the NMR spectra with the one obtained for [{PC(*sp*^{3})HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**). Due to the low yield we were not able to isolate a pure sample of **[8][HB(C$_6$F$_5$)$_3$]**. For **[8][HB(C$_6$F$_5$)$_3$]** (selected data): ^{1}H NMR (500 MHz, C$_6$D$_6$/Et$_2$O, 25 °C): δ = 6.13 (d, $^3J_{HP}$ = 12.0 Hz, 1H, CH$_{backbone}$). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$/Et$_2$O, 25 °C): δ = 59.39 (br, *P*^{i}Pr$_2$), −30.54 (t, $^2J_{PP\text{-}cis}$ = 45.5 Hz, *P*Me$_3$). ^{11}B{^{1}H} NMR (160 MHz, C$_6$D$_6$/Et$_2$O, 25 °C): δ = −24.62 (br s).

1.10 Reaction of [PC(*sp*^{2})P]$^{t\text{Bu}}$Pd(PMe$_3$) (3) with B(C$_6$F$_5$)$_3$ and H$_2$



In a 100 mL of round-bottom flask purged with H$_2$ was added B(C$_6$F$_5$)$_3$ (7.4 mg, 0.014 mmol) in 1 mL of hexane through the septum by syringe. After stirring for about 1 min, **3** (10 mg, 0.014 mmol) in 1 mL of hexane was slowly added by syringe in the same way. The greenish yellow slurry was then allowed to stirr under H$_2$ for 1 h. All volatiles were removed under reduced pressure to give a greenish yellow residue. The ^{1}H and ^{31}P{^{1}H} NMR spectra recorded in CDCl$_3$ showed the formation of a mixture of **5** and **[9][HB(C$_6$F$_5$)$_3$]** in a 3:1 ratio. The identity of **[9][HB(C$_6$F$_5$)$_3$]** was confirmed by comparing the NMR spectra with the one obtained for [{PC(*sp*^{3})HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**). Because of the similar solubilities we were not able to separate the two products. For **[9][HB(C$_6$F$_5$)$_3$]** (selected data): ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ = 6.24 (d, $^3J_{HP}$ = 12.0 Hz, 1H, C*H*$_{backbone}$). ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$, 25 °C): δ = 59.62 (d, $^2J_{PP\text{-}cis}$ = 45.7 Hz, *P*^{i}Pr$_2$), -30.19 (t, $^2J_{PP\text{-}cis}$ = 46.2 Hz, *P*Me$_3$). ^{11}B{^{1}H} NMR (160 MHz, CDCl$_3$, 25 °C): δ = −25.40 (br s).

1.11 X-ray data for compounds 3-6, [8][BAr$^F_4$] and [9][BAr$^F_4$]

X-Ray crystal structure of [(C$_6$F$_5$)$_3$B-PC(*sp*^{2})P]^{H}Pd(PMe$_3$) (4). Single crystals were obtained from a concentrated CH$_2$Cl$_2$ solution layered with Et$_2$O at −35 °C. The resulting crystals were bright, light yellow plates. Crystal and refinement data for **4**: C$_{46}$H$_{45}$BF$_{15}$P$_3$Pd; M$_r$ =1092.94; Monoclinic; space group *P*2$_1$/*n*; *a* = 9.7351(4) Å; *b* = 29.7778(12) Å; *c* = 16.3484(6) Å; α = 90°; β = 104.9431(16)°; γ = 90°; V = 4579.0(3) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.605 mm^{-1}; d$_{calc}$ = 1.585 g·cm^{-3}; 88562 reflections collected; 11118 unique (R$_{int}$ = 0.1029); giving R$_1$ = 0.0399, wR$_2$ = 0.0651 for 7584 data with [I>2σ(I)] and R$_1$ = 0.0814, wR$_2$ = 0.0749 for

all 11118 data. Residual electron density ($e^{-}\cdot Å^{-3}$) max/min: 0.486/−0.604. CCDC Deposition: 1002270.

X-Ray crystal structure of [PC(sp^3)HP]$^{t\mathrm{Bu}}$PdCl (6). Single crystals were obtained as pale yellow blocks from a concentrated diethyl ether solution at −35 °C. Crystal and refinement data for **6**: $C_{33}H_{53}ClP_2Pd$; M_r =653.54; Monoclinic; space group $P2_1/c$; a = 12.3466(7) Å; b = 11.6819(7) Å; c = 23.5089(14) Å; α = 90°; β = 91.4208(9)°; γ = 90°; V = 3389.7(3) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.740 mm^{-1}; d_{calc} = 1.281 g·cm^{-3}; 45195 reflections collected; 5975 unique (R_{int} = 0.0509); giving R_1 = 0.0300, wR_2 = 0.0706 for 5310 data with [I>2σ(I)] and R_1 = 0.0356, wR_2 = 0.0731 for all 5975 data. Residual electron density ($e^{-}\cdot Å^{-3}$) max/min: 1.846/−1.555. CCDC Deposition: 1038108.

X-Ray crystal structure of [PC(sp^2)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (3). Single crystals were obtained as dark brown blocks from a concentrated hexane solution at −35 °C. Crystal and refinement data for **3**: $C_{36}H_{61}P_3Pd$; M_r =693.16; Monoclinic; space group $C2/c$; a = 28.976(3) Å; b = 14.6255(14) Å; c = 31.853(4) Å; α = 90°; β = 106.946(2)°; γ = 90°; V = 12913(2) Å^3; Z = 12; T = 120(2) K; λ = 0.71073 Å; μ = 0.561 mm^{-1}; d_{calc} = 1.070 g·cm^{-3}; 103779 reflections collected; 11379 unique (R_{int} = 0.0366); giving R_1 = 0.0347, wR_2 = 0.0835 for 10264 data with [I>2σ(I)] and R_1 = 0.0395, wR_2 = 0.0858 for all 11379 data. Residual electron density ($e^{-}\cdot Å^{-3}$) max/min: 1.525/−0.772. CCDC Deposition: 1038109.

X-Ray crystal structure of [(C$_6$F$_5$)$_2$BF(C$_6$F$_4$)-PC(sp^3)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (5). Single crystals were obtained as greenish-yellow needles from a concentrated solution of fluorobenzene layered with hexane at room temperature. Crystal and refinement data for **5**: $C_{54}H_{61}BF_{15}P_3Pd$; M_r =1205.15; Monoclinic; space group $P2_1/c$; a = 14.7706(10) Å; b = 13.9199(9) Å; c = 28.5994(19) Å; α = 90°; β = 93.208(2)°; γ = 90°; V = 5871.0(7) Å^3; Z = 4; T = 120(2) K; λ = 0.71073 Å; μ = 0.479 mm^{-1}; d_{calc} = 1.363 g·cm^{-3}; 92881 reflections collected; 10345 unique (R_{int} = 0.0419); giving R_1 = 0.0379, wR_2 = 0.0880 for 8827 data with [I>2σ(I)] and R_1 = 0.0481, wR_2 = 0.0917 for all 10345 data. Residual electron density ($e^{-}\cdot Å^{-3}$) max/min: 0.600/−0.364. CCDC Deposition: 1038110.

X−Ray crystal structure of [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] ([8][BAr$^F_4$]). Single crystals were obtained from a concentrated solution of diethyl ether layered with *n*-pentane at −35 °C. Crystal and refinement data for **[8][BAr$^F_4$]**: $C_{60}H_{58}BF_{24}P_3Pd$; M_r =1445.18; Monoclinic; space group $P2_1/n$; a = 13.1862(3) Å; b = 12.7167(3) Å; c = 37.1231(8) Å; α = 90°; β = 94.9670(9)°; γ = 90°; V = 6201.6(2) Å^3; Z = 4; T = 120(2) K; λ = 1.54178 Å; μ = 4.145 mm^{-1}; d_{calc} = 1.548 g·cm^{-3}; 112788 reflections collected; 11345 unique (R_{int} = 0.0404); giving R_1 = 0.0453, wR_2 = 0.1137 for 10917 data with [I>2σ(I)] and R_1 = 0.0465, wR_2 = 0.1146 for all 11345 data. Residual electron density ($e^{-}\cdot Å^{-3}$) max/min: 1.245/−1.122.

X−Ray crystal structure of [{PC(sp^3)HP}$^{t\mathrm{Bu}}$PdPMe$_3$][BAr$^F_4$] ([9][BAr$^F_4$]). Single crystals were obtained as yellow blocks from a concentrated solution of diethyl ether layered with *n*-pentane at −35 °C. Crystal and refinement data for **[9][BAr$^F_4$]**: $C_{68}H_{74}BF_{24}P_3Pd$; M_r =1557.39; Triclinic; space group $P\bar{1}$; a = 13.7002(14) Å; b = 17.7228(18) Å; c = 18.5200(19) Å; α = 65.531(3)°; β = 74.700(3)°; γ = 88.259(3)°; V = 3931.8(7) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 0.390 mm^{-1}; d_{calc} = 1.315 g·cm^{-3}; 71970 reflections collected; 13848 unique (R_{int} = 0.0347); giving R_1 = 0.0492, wR_2 = 0.1270 for 11804 data with [I>2σ(I)] and R_1 = 0.0575, wR_2 = 0.1325 for all 13848 data. Residual electron density ($e^{-}\cdot Å^{-3}$) max/min: 2.142/−1.161.

1.12 References

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2 DFT Results

2.1 $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (4)

Table S1. Optimized coordinates for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**).

atom	x	y	z
C	−2.318511	0.420889	2.256113
C	−2.611130	−0.527832	1.262324
C	−2.172984	−1.825174	1.596426
C	−1.547727	−2.167067	2.799808
C	−1.322218	−1.182859	3.765222
C	−1.715555	0.125904	3.485093
B	−3.237901	−0.158218	−0.217689
C	−4.122083	1.258443	−0.211710
C	−5.184129	1.407157	0.705620
C	−6.042165	2.507626	0.770227
C	−5.872844	3.561120	−0.133571
C	−4.846658	3.474668	−1.073584
C	−4.011509	2.346857	−1.094207
F	−5.414516	0.400421	1.641468
F	−7.050977	2.568739	1.716595
F	−6.704855	4.665309	−0.095038
F	−4.652855	4.507355	−1.979148
F	−3.016535	2.392559	−2.083093
F	−2.357520	−2.880265	0.701996
F	−1.136597	−3.471151	3.036932
F	−0.694924	−1.491702	4.960643
F	−1.466964	1.132614	4.409354
F	−2.598174	1.780469	2.049815
C	−1.875340	−0.076259	−1.256926
C	−0.861662	0.927869	−0.794668
C	0.455609	0.646049	−0.594997
C	1.003675	−0.713352	−0.699529
C	0.057667	−1.705522	−1.239981
C	−1.237400	−1.402112	−1.528104
C	2.317142	−0.993574	−0.331905
C	2.784866	−2.369602	−0.050272
C	4.142709	−2.741175	−0.256180
C	4.572342	−4.072037	−0.098493
C	3.679085	−5.058272	0.356908
C	2.355467	−4.688272	0.674119

atom	x	y	z
C	1.915470	−3.372619	0.475581
P	5.257156	−1.313314	−0.677633
C	6.783969	−1.425292	0.497178
C	7.807044	−2.538577	0.175024
P	1.733075	1.904349	−0.084066
C	1.626005	3.372576	−1.325837
C	2.029297	2.884486	−2.735522
C	−4.344729	−1.271325	−0.773146
C	−4.727864	−1.299862	−2.129465
C	−5.681604	−2.165954	−2.676799
C	−6.337060	−3.074708	−1.843834
C	−6.027081	−3.078584	−0.482477
C	−5.064022	−2.191361	0.018743
F	−4.165240	−0.390665	−3.035756
F	−5.984549	−2.123518	−4.028679
F	−7.282548	−3.944823	−2.355624
F	−6.678688	−3.960322	0.363679
F	−4.863833	−2.269752	1.392862
Pd	3.726179	0.542154	−0.258792
P	5.462182	2.397387	0.034611
C	6.034842	2.462851	1.838158
C	1.162865	2.565266	1.627956
C	1.418111	1.479839	2.696436
C	5.037787	4.217779	−0.270409
C	7.124200	2.343762	−0.873613
C	5.881701	−1.686720	−2.455974
C	6.926425	−0.660698	−2.940492
C	1.832072	3.898785	2.019605
C	0.266093	4.108775	−1.358413
C	4.677672	−1.762186	−3.420221
C	6.295176	−1.518181	1.961836
H	4.745567	4.361751	−1.314874
H	5.914013	4.840826	−0.056369
H	4.215680	4.530421	0.377188
H	6.965129	2.509724	−1.943575
H	7.607243	1.373584	−0.740643
H	7.784103	3.128726	−0.485974
H	6.746686	3.283254	1.987170
H	6.513090	1.517597	2.110574
H	5.171138	2.611922	2.493246
H	0.079621	2.720732	1.530011
H	1.649274	4.698770	1.292154

atom	x	y	z
H	2.916776	3.776695	2.143991
H	1.430436	4.233381	2.984835
H	0.974776	0.518688	2.415932
H	0.980400	1.789698	3.653009
H	2.494982	1.321033	2.841155
H	2.386681	4.076066	−0.965551
H	0.382564	5.049868	−1.913362
H	−0.108317	4.360519	−0.358926
H	−0.498681	3.521468	−1.875093
H	2.032262	3.731046	−3.435351
H	1.314441	2.142328	−3.110603
H	3.026973	2.426809	−2.739913
H	5.026356	−2.043940	−4.422743
H	4.170052	−0.792388	−3.495673
H	3.940816	−2.504728	−3.095577
H	6.347112	−2.681084	−2.395437
H	5.562258	−0.737712	2.201225
H	7.147142	−1.416189	2.647496
H	5.819349	−2.486202	2.154587
H	7.268892	−0.932098	−3.947604
H	7.810208	−0.614605	−2.291379
H	6.485842	0.342244	−2.998286
H	7.286681	−0.457356	0.358859
H	8.138169	−2.524279	−0.869707
H	7.404747	−3.532307	0.397848
H	8.697014	−2.401539	0.804679
H	5.599434	−4.350056	−0.317363
H	4.014049	−6.083479	0.489787
H	1.665305	−5.423783	1.079843
H	0.896890	−3.112754	0.740692
H	−1.230369	1.933576	−0.624848
H	−2.311722	0.293108	−2.193650
H	−1.858459	−2.165455	−1.992225
H	0.435331	−2.694807	−1.476731

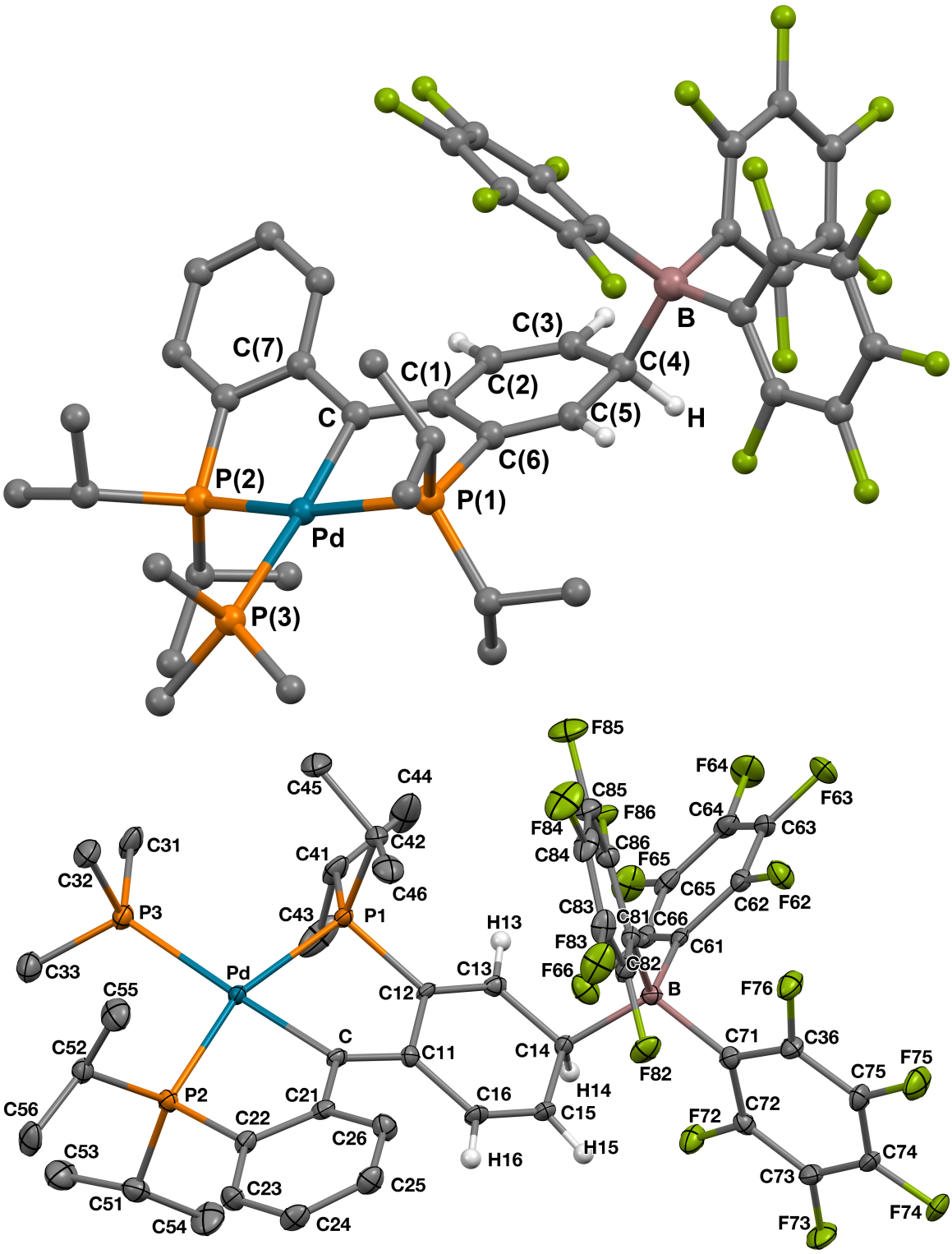


Figure S1. Top: optimized geometry for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**). Bottom: Xray structure of **4**.

Table S2. Selected distances (Å) and angles (°) for the optimized geometry and the crystal structure of $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**).

Bond / Angle*	**Calculated**	**Bond / Angle****	**X-Ray**
B – C(4)	1.716	B – C(14)	1.681(4)
C(4) – C(3)	1.496	C(14) – C(15)	1.484(4)
C(4) – C(5)	1.500	C(14) – C(13)	1.492(4)
C(2) – C(3)	1.361	C(16) – C(15)	1.336(4)
C(2) – C(1)	1.474	C(16) – C(11)	1.462(4)
C(1) – C(6)	1.469	C(11) – C(12)	1.455(4)
C(6) – C(5)	1.362	C(12) – C(13)	1.334(4)
C(1) – C	1.392	C(11) – C	1.362(4)
C – Pd	2.085	C – Pd	2.071(3)
P(3) – Pd – C	175.39	P(3) – Pd – C	175.08(7)
P(1) – Pd – P(2)	163.01	P(1) – Pd – P(2)	160.08(3)
P(2) – Pd – C	81.84	P(2) – Pd – C	81.19(7)
P(1) – Pd – C	81.99	P(1) – Pd – C	79.01(7)

*Optimized structure
**Xray structure

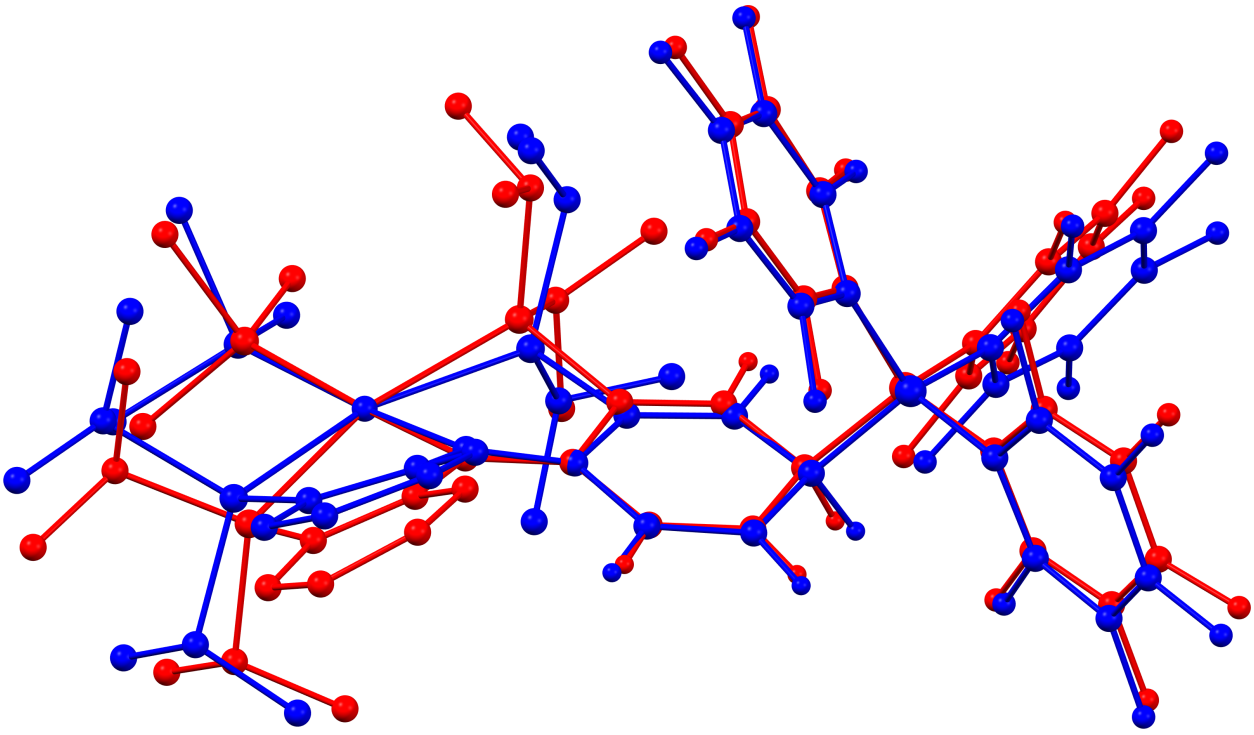


Figure S2. Overlaid structures for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**) (red: Xray, blue: optimized).

2.2 [*o*-$(C_6F_5)_3$B-PC(sp^2)P]^{H}Pd(PMe_3) (*o*-**4**)

Table S3. Optimized coordinates for [*o*-$(C_6F_5)_3$B-PC(sp^2)P]^{H}Pd(PMe_3) (***o*-4**).

atom	x	y	z
Pd	2.816224	−0.433860	−0.244889
C	4.904620	−3.229181	1.391597
H	3.999970	−3.775604	1.669024
H	5.687577	−3.447816	2.127013
H	5.235850	−3.563129	0.404456
P	1.848267	−2.495939	−1.094731
P	4.546935	−1.370562	1.368696
C	4.104268	−1.092276	3.185233
H	3.185477	−1.633171	3.429528
H	3.924373	−0.031904	3.374410
H	4.913465	−1.451254	3.832207
P	3.583045	1.921353	−0.224447
C	6.322283	−0.715466	1.300553
H	6.948230	−1.261360	2.016239
H	6.340988	0.346524	1.556461
H	6.731220	−0.849312	0.293993
C	2.629629	−3.260785	−2.678216
H	1.914050	−4.023947	−3.014363
C	3.983012	−3.940889	−2.379973
H	3.895830	−4.750611	−1.644594
H	4.715837	−3.210737	−2.010192
H	4.387846	−4.376204	−3.303165
C	2.763441	−2.194445	−3.785222
H	1.805083	−1.709490	−3.999469
H	3.121803	−2.667222	−4.709847
H	3.481391	−1.416242	−3.501004
C	1.536104	−4.004440	0.062871
H	2.536689	−4.415765	0.251086
C	0.663536	−5.106028	−0.581484
H	0.604192	−5.960804	0.105927
H	1.072648	−5.475499	−1.529832
H	−0.357933	−4.749452	−0.749515
C	0.915164	−3.532223	1.393223
H	0.820108	−4.381157	2.083055
H	−0.086978	−3.126733	1.223160
H	1.521310	−2.759592	1.881771
C	2.544356	3.665389	1.831561

atom	x	y	z
H	2.731748	4.524966	2.490006
H	2.159767	2.845544	2.441208
H	1.763594	3.950054	1.118693
C	3.858342	3.278105	1.123813
H	4.208956	4.148390	0.551837
C	1.189238	0.374683	−1.284192
C	5.104482	1.054448	−2.483815
H	4.786003	0.039664	−2.216568
H	6.069651	0.992063	−3.005151
H	4.367216	1.466777	−3.183740
C	4.959058	2.883115	2.129357
H	5.124024	3.708514	2.834343
H	5.920168	2.671219	1.642381
H	4.659985	2.007367	2.717807
C	5.241028	1.950204	−1.233452
H	5.967519	1.488001	−0.551564
C	5.760723	3.351928	−1.620062
H	5.928920	4.001881	−0.753351
H	5.072692	3.855322	−2.307971
H	6.723716	3.245104	−2.138506
C	2.308732	2.653283	−1.360423
C	2.355833	3.987742	−1.813698
H	3.090663	4.679012	−1.409091
C	1.465366	4.439425	−2.799440
H	1.504122	5.468409	−3.146473
C	0.550762	3.523265	−3.362611
H	−0.110090	3.837435	−4.166655
C	0.483816	2.207508	−2.892849
H	−0.205881	1.516507	−3.363479
C	1.307879	1.752220	−1.815935
C	0.035065	−0.400807	−1.368728
C	0.191931	−1.838302	−1.610829
C	−0.674675	−2.475906	−2.463447
H	−0.494863	−3.499659	−2.782991
C	−1.806904	−1.761925	−3.036749
H	−2.391084	−2.243058	−3.817350
C	−2.125934	−0.510435	−2.591744
H	−2.971343	0.024197	−3.017494
C	−1.393237	0.146318	−1.453716
H	−1.329360	1.215783	−1.621148
B	−2.482270	0.151518	0.002523
C	−3.740353	−0.889321	−0.281606

atom	x	y	z
C	−3.039326	1.716889	0.202597
C	−1.649370	−0.252205	1.372126
C	−6.102626	−1.434087	−0.838047
C	−5.825700	−2.799083	−0.900319
C	−4.518438	−3.226049	−0.649613
C	−3.537320	−2.281982	−0.351164
C	−5.074651	−0.525667	−0.535340
C	−3.338950	2.266630	1.465255
C	−3.775225	3.579871	1.685034
C	−3.958326	4.437142	0.599776
C	−3.720553	3.943413	−0.684350
C	−3.287980	2.623641	−0.847012
C	−0.483968	0.452300	1.728180
C	−2.021837	−1.211519	2.337279
C	−1.264259	−1.534782	3.470440
C	−0.076985	−0.850240	3.722805
C	0.298623	0.170604	2.851266
F	−5.482418	0.811029	−0.505582
F	−7.390542	−0.982281	−1.077337
F	−6.819919	−3.712402	−1.202464
F	−4.210426	−4.578603	−0.696227
F	−2.270053	−2.804616	−0.077433
F	−3.248801	1.486934	2.623528
F	−4.030455	4.032040	2.969766
F	−4.380570	5.740504	0.789450
F	−3.928829	4.758786	−1.785995
F	−3.172403	2.213813	−2.182634
F	−1.685212	−2.523146	4.345907
F	−3.240634	−1.881763	2.261231
F	0.718587	−1.171080	4.813648
F	1.455159	0.897157	3.124987
F	−0.107693	1.578484	0.989688

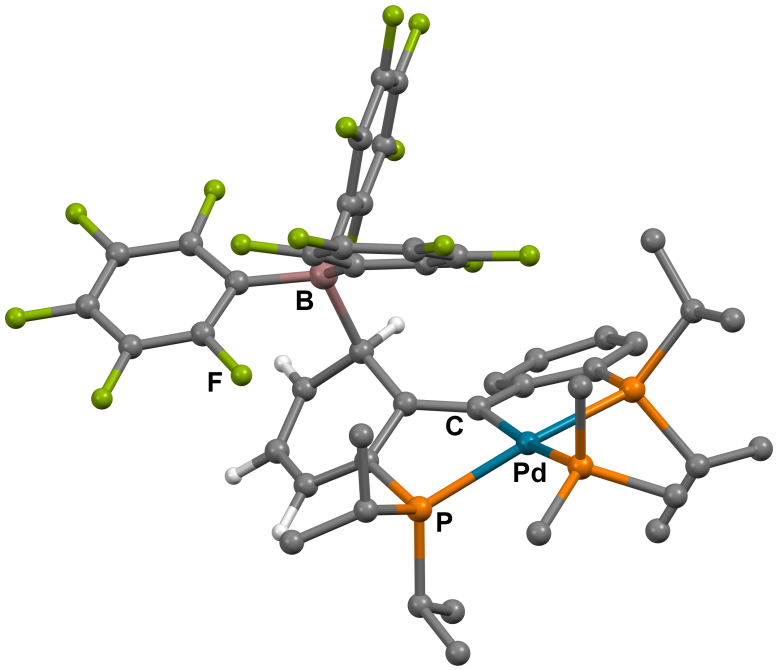


Figure S3. Optimized geometry for [*o*-$(C_6F_5)_3$B-PC(sp^2)P]^{H}Pd(PMe_3) (***o*-4**).

2.3 $(C_6F_5)_3B$

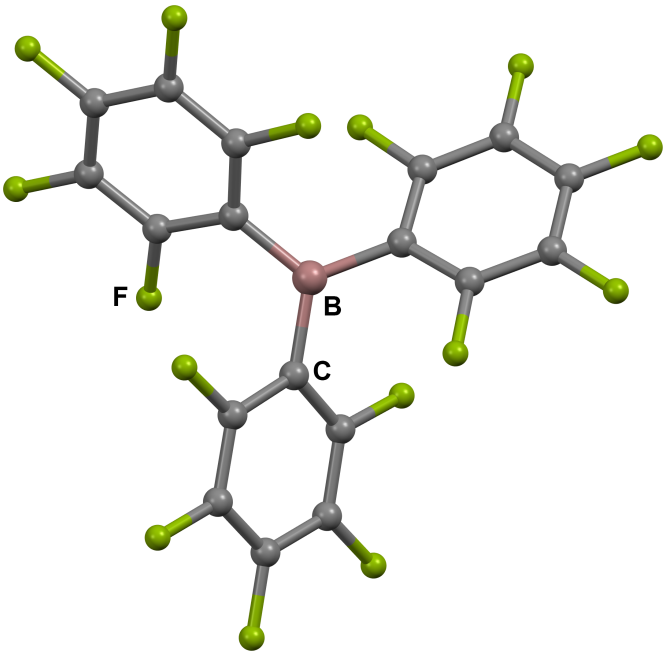
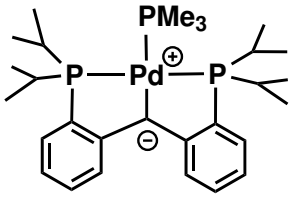
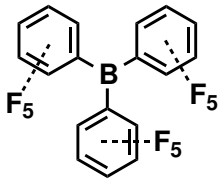
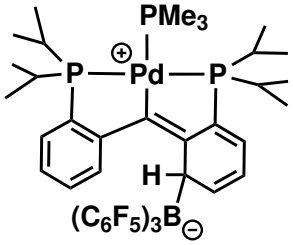
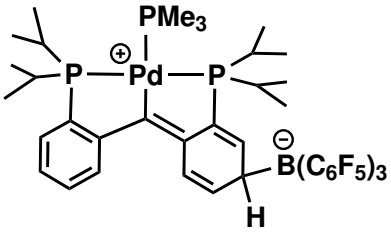
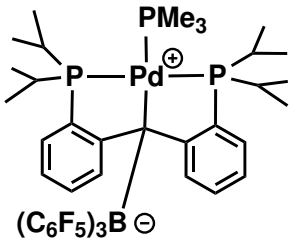
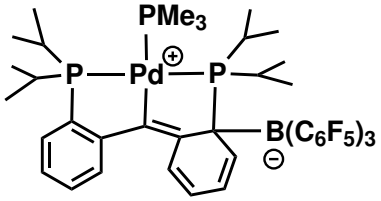


Figure S4. Optimized geometry for $(C_6F_5)_3B$.

Table S4. Optimized coordinates for $(C_6F_5)_3B$.

atom	x	y	z
B	0.618090	0.881920	0.332244
C	0.213315	0.397086	1.767707
C	1.891373	0.289678	−0.366094
C	−0.251205	1.959073	−0.405354
C	1.926586	−0.012415	−1.741861
C	3.046813	−0.550205	−2.381292
C	4.209400	−0.787722	−1.636703
C	4.231322	−0.495262	−0.266881
C	3.082330	0.021795	0.337636
F	0.792544	0.194992	−2.516746
F	3.019511	−0.844517	−3.727170
F	5.325152	−1.305939	−2.248324
F	5.376015	−0.720279	0.466502
F	3.153920	0.307896	1.694998
C	0.319633	2.990740	−1.176571
C	−0.435838	3.965905	−1.833235
C	−1.833366	3.918256	−1.748971
C	−2.452393	2.906547	−1.003424
C	−1.658794	1.963610	−0.344693
F	1.701944	3.083819	−1.278420
F	0.176125	4.964453	−2.559361
F	−2.594844	4.861283	−2.395864
F	−3.827085	2.852177	−0.925419
F	−2.315260	0.971984	0.373440
C	−0.288280	1.276171	2.747896
C	−0.645331	0.867035	4.035564
C	−0.525339	−0.485524	4.379984
C	−0.041451	−1.403766	3.439106
C	0.324569	−0.948893	2.169443
F	−0.412214	2.628364	2.454896
F	−1.112770	1.774119	4.961588
F	−0.880973	−0.910247	5.637228
F	0.070625	−2.736091	3.772409
F	0.787875	−1.896357	1.265407

2.4 Calculated energies for borane adducts

		Energy (hartree)	Energy gain (kcal/mol)
Carbene (**1**)		−1240.157101	—
Borane		−2208.242571	—
Ortho (***o*-4**)		−3448.414260	9.14
Para (**4**)		−3448.444732	28.27
Backbone carbon		could not be optimized	—
Ortho’		could not be optimized	—

2.5 [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (3)

Table S5. Optimized coordinates for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**).

atom	x	y	z
C	1.448526	2.823317	0.634195
C	1.309205	1.449587	0.196266
C	2.567703	0.801649	−0.053384
C	3.799257	1.486853	−0.048748
C	3.899196	2.847986	0.292346
C	2.677247	3.476112	0.673652
C	0.038697	0.776499	0.047686
C	−1.222379	1.465863	−0.119080
C	−2.493643	0.827143	0.112644
C	−3.721078	1.501388	−0.007939
C	−3.808753	2.850707	−0.410646
C	−2.571605	3.476723	−0.720601
C	−1.343071	2.827558	−0.587802
P	−2.318852	−0.971644	0.491281
C	−2.922213	−1.333413	2.293025
C	−1.734208	−1.147742	3.266585
C	−5.179876	3.553647	−0.521032
C	−5.045009	5.024705	−0.990169
P	2.394639	−1.003899	−0.386522
C	3.537584	−1.948123	0.848626
C	5.053874	−1.702922	0.676398
C	5.223091	3.640596	0.300608
C	5.516059	4.169894	1.736718
Pd	0.026480	−1.312723	0.021181
P	−0.087275	−3.870679	−0.054777
C	1.432101	−4.967588	0.241480
C	−3.488619	−1.954807	−0.691940
C	−5.002038	−1.904577	−0.382104
C	3.165902	−1.292494	−2.123019
C	3.260627	−2.787709	−2.489760
C	−0.678760	−4.573802	−1.714594
C	−1.285551	−4.719260	1.148853
C	−6.084782	2.806087	−1.546048
C	−5.886110	3.555039	0.867936
C	5.112121	4.853453	−0.671602
C	6.429537	2.777288	−0.146910
C	−3.200112	−1.517773	−2.147063

atom	x	y	z
C	−4.122080	−0.474001	2.751331
C	2.359915	−0.501023	−3.176258
C	3.085479	−1.631228	2.292221
H	−4.637217	0.958680	0.211138
H	−6.253373	1.763095	−1.248343
H	−5.619068	2.800051	−2.540127
H	−7.066629	3.294781	−1.626534
H	−0.446829	3.355499	−0.893461
H	−2.561827	4.498022	−1.092805
H	−6.872179	4.037950	0.803014
H	−5.283048	4.098425	1.606806
H	−6.034882	2.534657	1.243761
H	−6.038324	5.490520	−1.042990
H	−4.590813	5.091165	−1.987391
H	−4.434103	5.615688	−0.295604
H	4.698190	0.941840	−0.319867
H	2.691311	4.509174	1.020201
H	0.565850	3.355683	0.971136
H	4.927523	4.510773	−1.698205
H	6.039585	5.444476	−0.664560
H	4.286217	5.517456	−0.389123
H	6.586852	1.922942	0.525448
H	7.345831	3.382540	−0.134951
H	6.295182	2.393680	−1.167190
H	−0.775317	−5.665488	−1.667824
H	0.043009	−4.308944	−2.494207
H	−1.644535	−4.135523	−1.981263
H	4.705470	4.812770	2.100916
H	6.445350	4.757619	1.752224
H	5.622508	3.335323	2.442263
H	−2.303754	−4.351143	0.995037
H	−0.985791	−4.490812	2.176818
H	−1.273512	−5.806301	1.003925
H	1.155823	−6.025067	0.150756
H	1.826387	−4.786922	1.246524
H	2.209743	−4.738396	−0.491948
H	−3.164212	−2.998655	−0.568438
H	−3.217689	−2.394288	2.285398
H	−3.745340	−2.163278	−2.850183
H	−2.129259	−1.569814	−2.380489
H	−3.522110	−0.483037	−2.310114
H	−5.536355	−2.551494	−1.092932

atom	x	y	z
H	−5.404183	−0.892301	−0.496392
H	−5.234588	−2.261536	0.627897
H	−5.012724	−0.615377	2.130503
H	−3.862906	0.590405	2.734174
H	−4.386486	−0.741958	3.784296
H	−1.377169	−0.110683	3.248320
H	−0.885199	−1.788856	3.003003
H	−2.050756	−1.384334	4.292457
H	4.179652	−0.869065	−2.069446
H	3.340237	−3.008325	0.643780
H	1.330111	−0.874311	−3.245372
H	2.831895	−0.602831	−4.163702
H	2.311927	0.563865	−2.924076
H	2.259600	−3.237378	−2.537525
H	3.866438	−3.359466	−1.774667
H	3.721490	−2.901936	−3.480500
H	2.021657	−1.854838	2.439362
H	3.235602	−0.569051	2.520387
H	3.670971	−2.223111	3.009997
H	5.608987	−2.384231	1.337278
H	5.324182	−0.679845	0.957229
H	5.399394	−1.883673	−0.349107

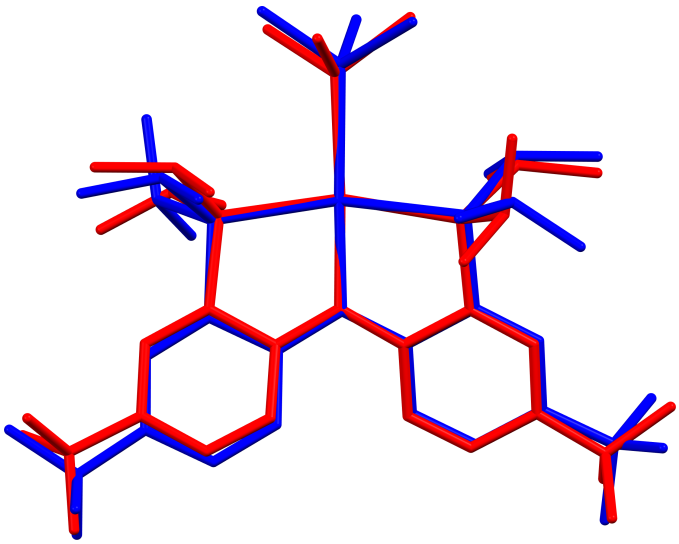


Figure S5. Overlaid structures for [PC(sp^2)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (**3**) (red: Xray, blue: optimized).

Table S6. Selected distances (Å) and angles (°) for the optimized geometry and the crystal structure of [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**).

Bond / Angle*	**Calculated**	**Bond / Angle****	**X-Ray**
Pd – C	2.089	Pd – C	2.076(3)
Pd – P(1)	2.423	Pd – P(1)	2.3120(7)
Pd – P(2)	2.416	Pd – P(2)	2.3099(7)
Pd – P(3)	2.562	Pd – P(3)	2.3701(7)
Pd – C – C(11)	118.17	Pd – C – C(11)	118.51(18)
Pd – C – C(21)	118.03	Pd – C – C(21)	118.79(18)
C(11) – C – C-(21)	123.79	C(11) – C – C-(21)	122.7(2)

*Optimized structure
**Xray structure

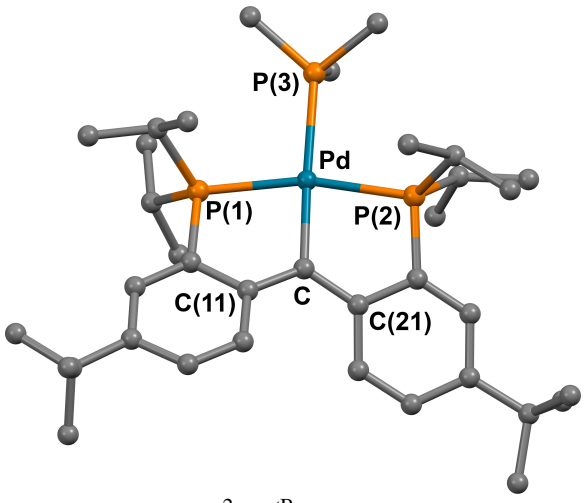


Figure S6. Optimized geometry for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**).

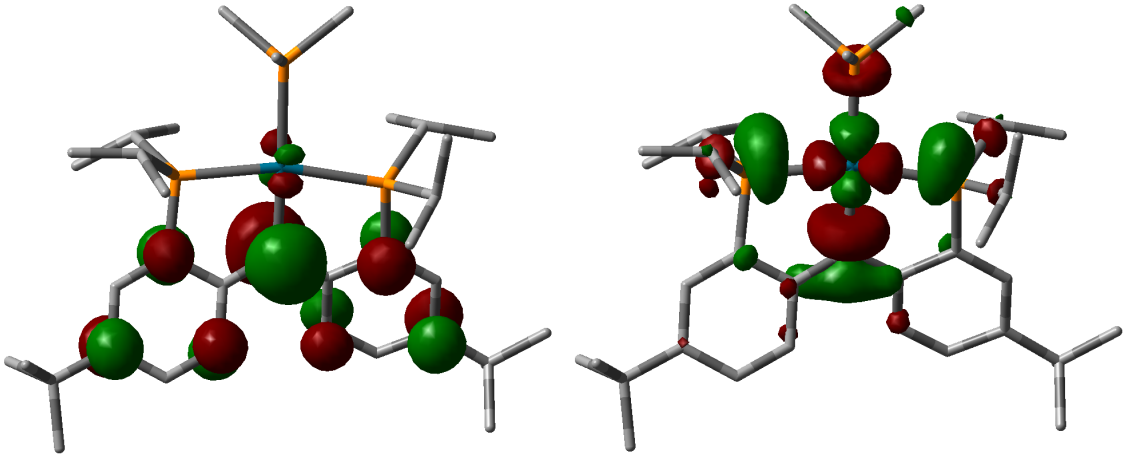


Figure S7. Frontier molecular orbitals for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**). Left: HOMO, right: LUMO.

3 NMR Spectra

3.1 NMR Spectra for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (4)

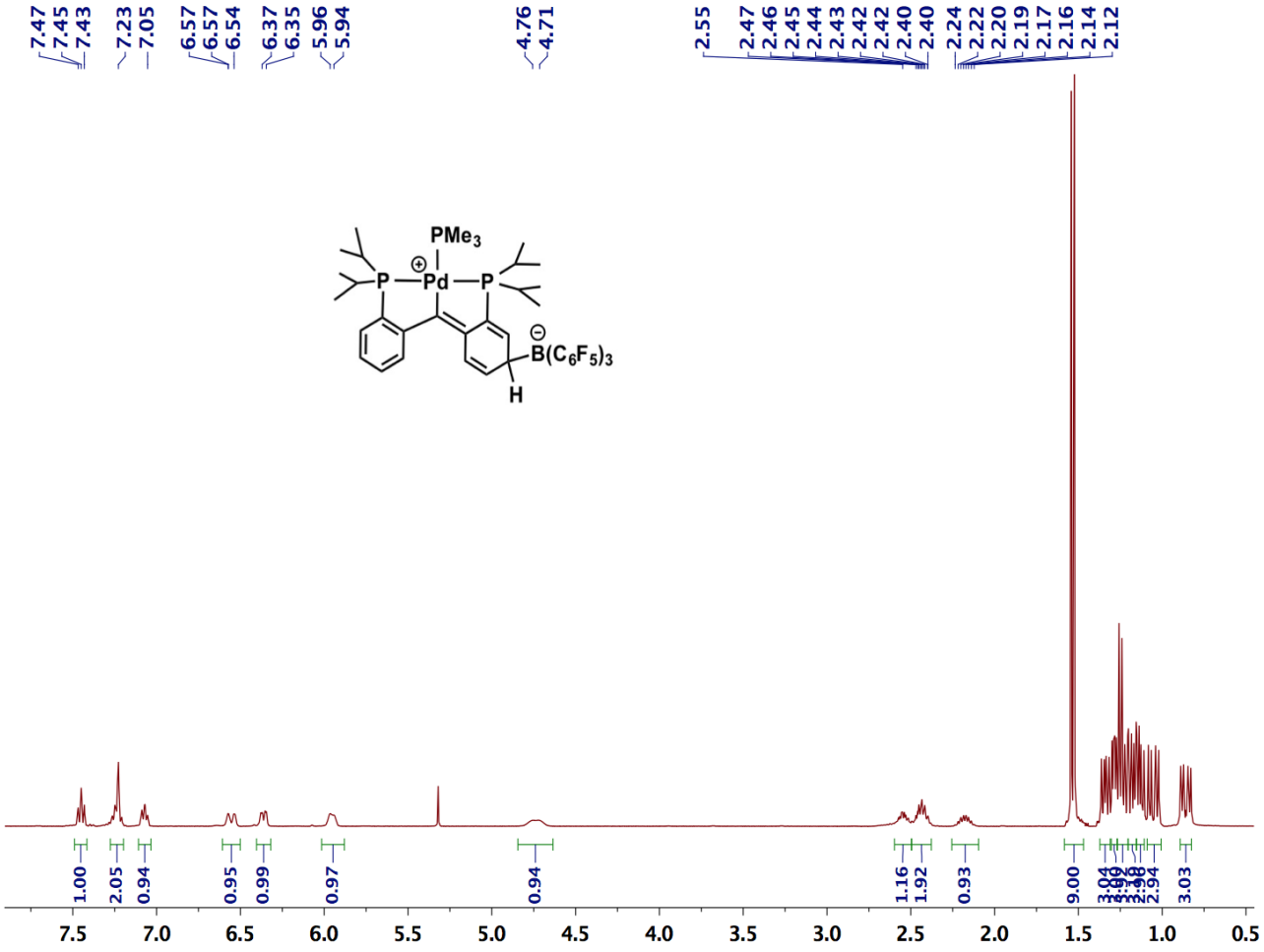


Figure S8. ^{1}H NMR spectrum for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**).

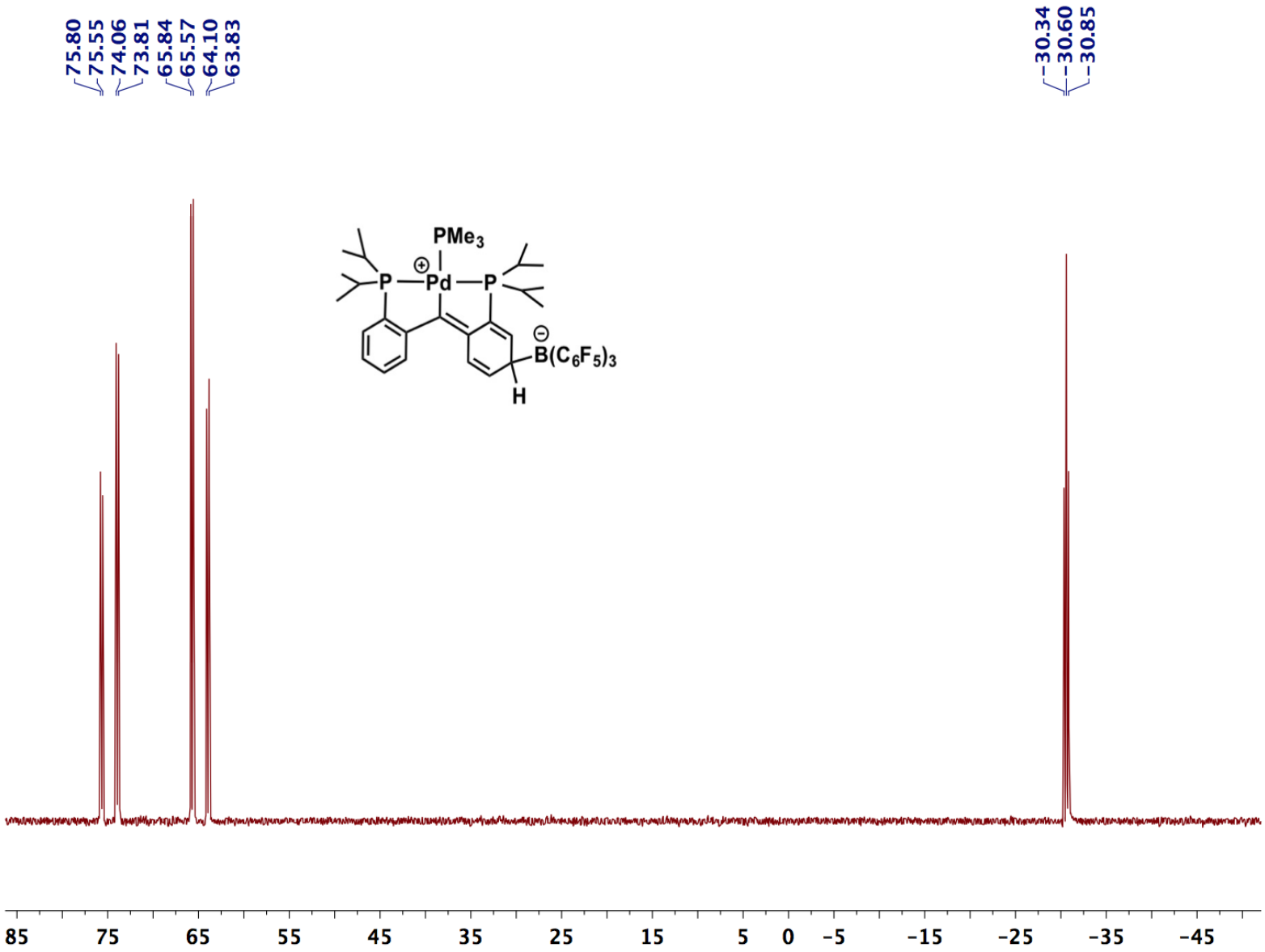


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^{H}Pd(PMe_3)$ (**4**).

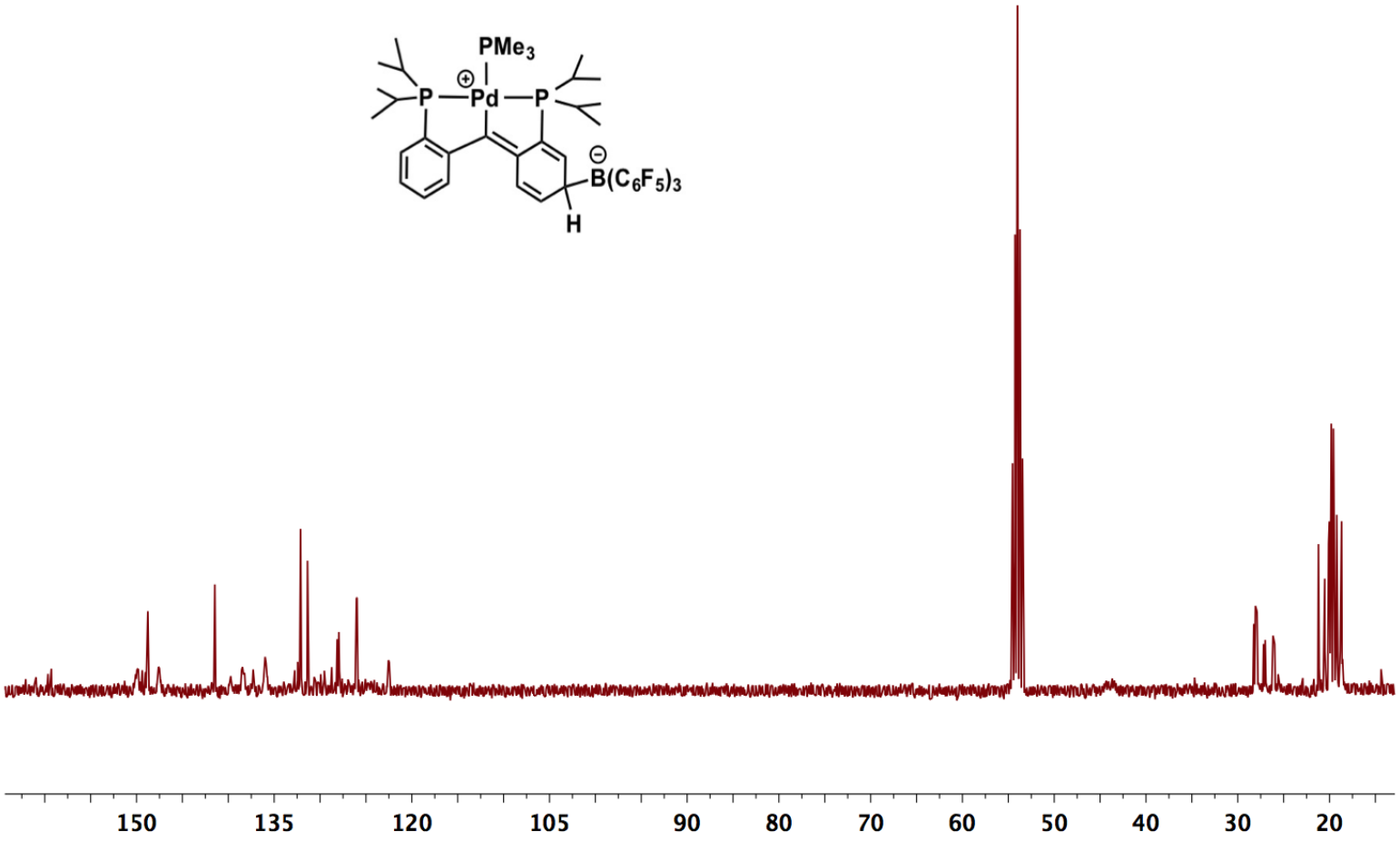


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^{H}Pd(PMe_3)$ (**4**).

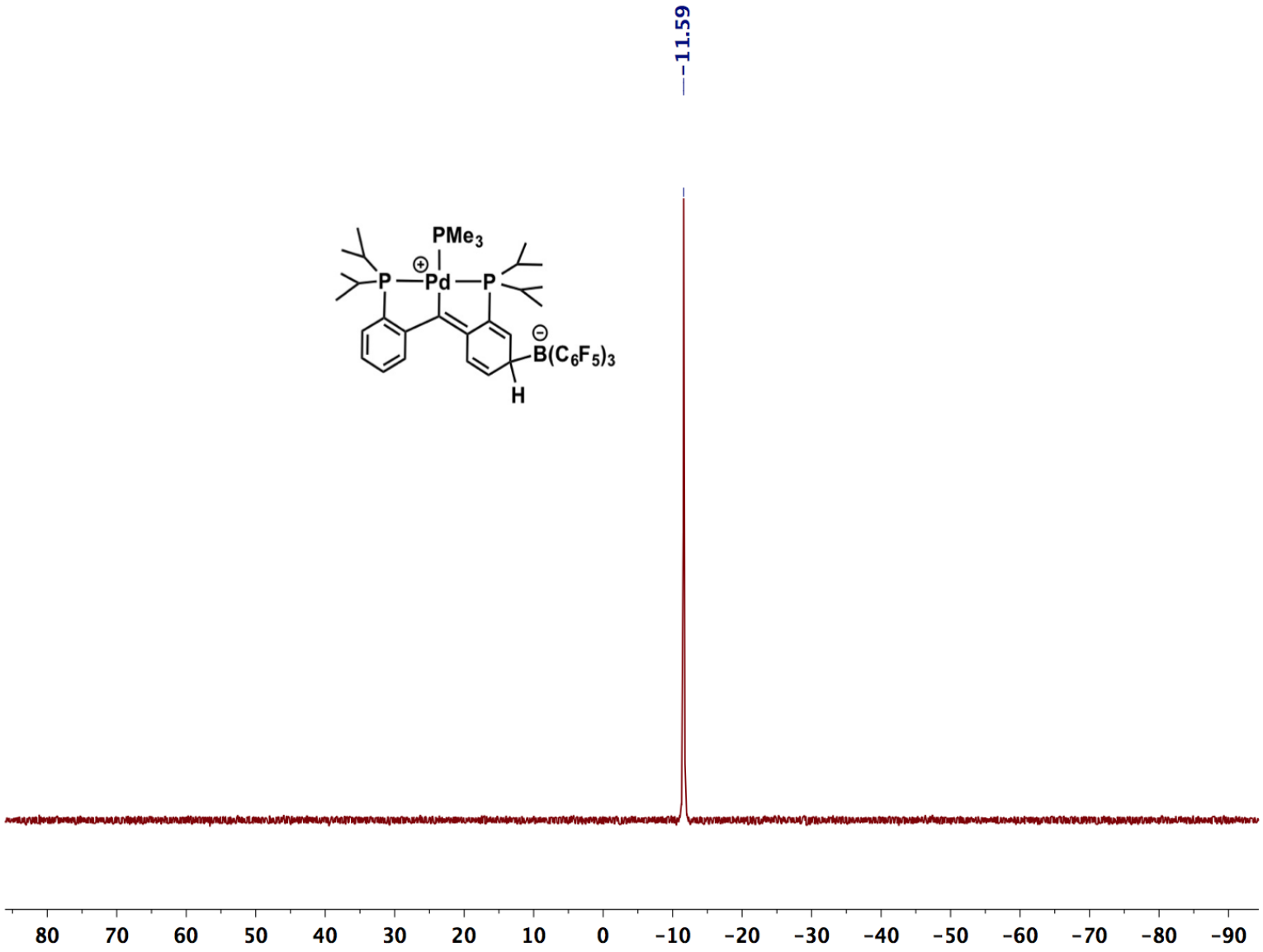


Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^{H}Pd(PMe_3)$ (**4**).

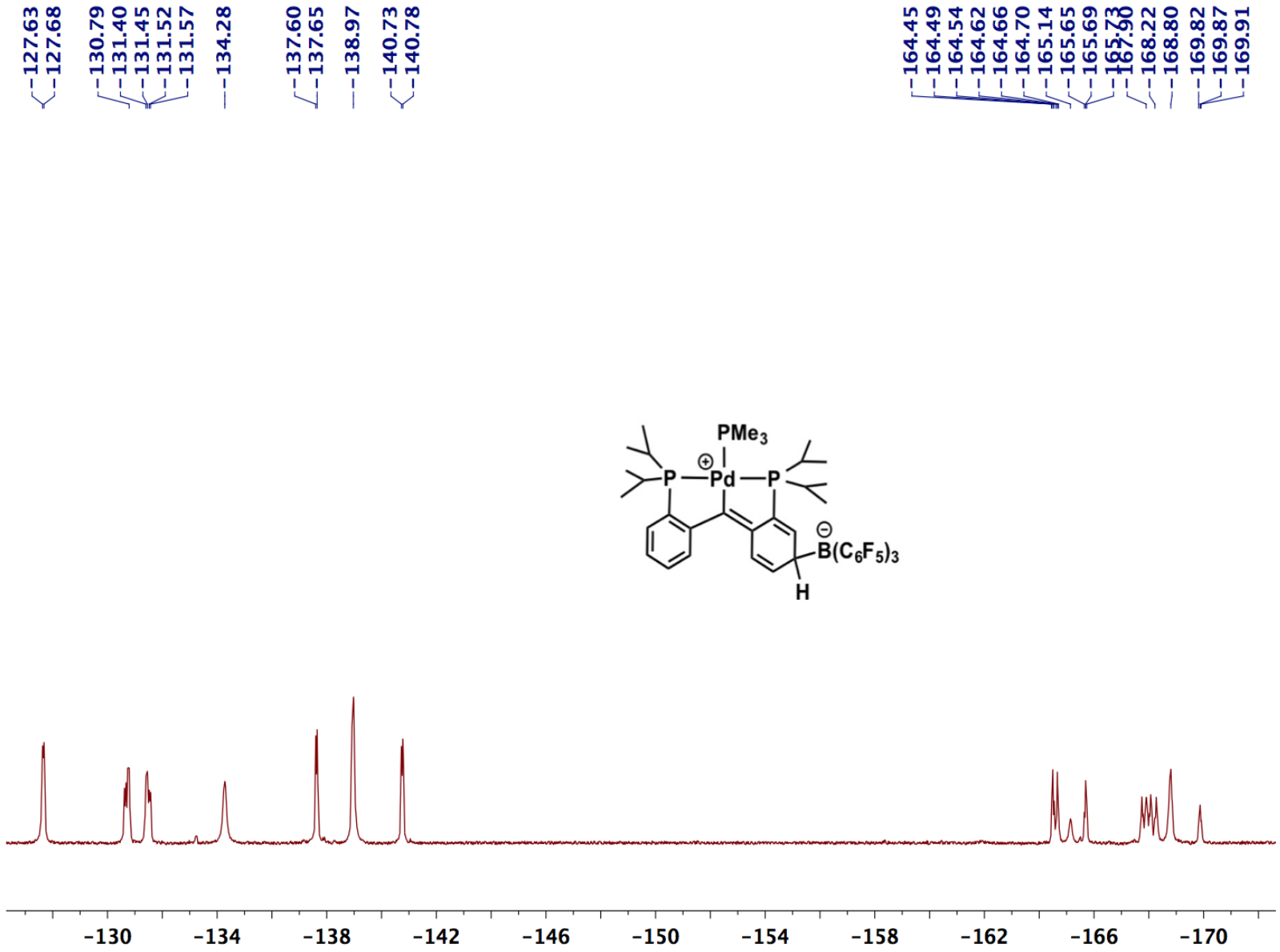


Figure S12. −40 °C $^{19}F\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^{H}Pd(PMe_3)$ (**4**).

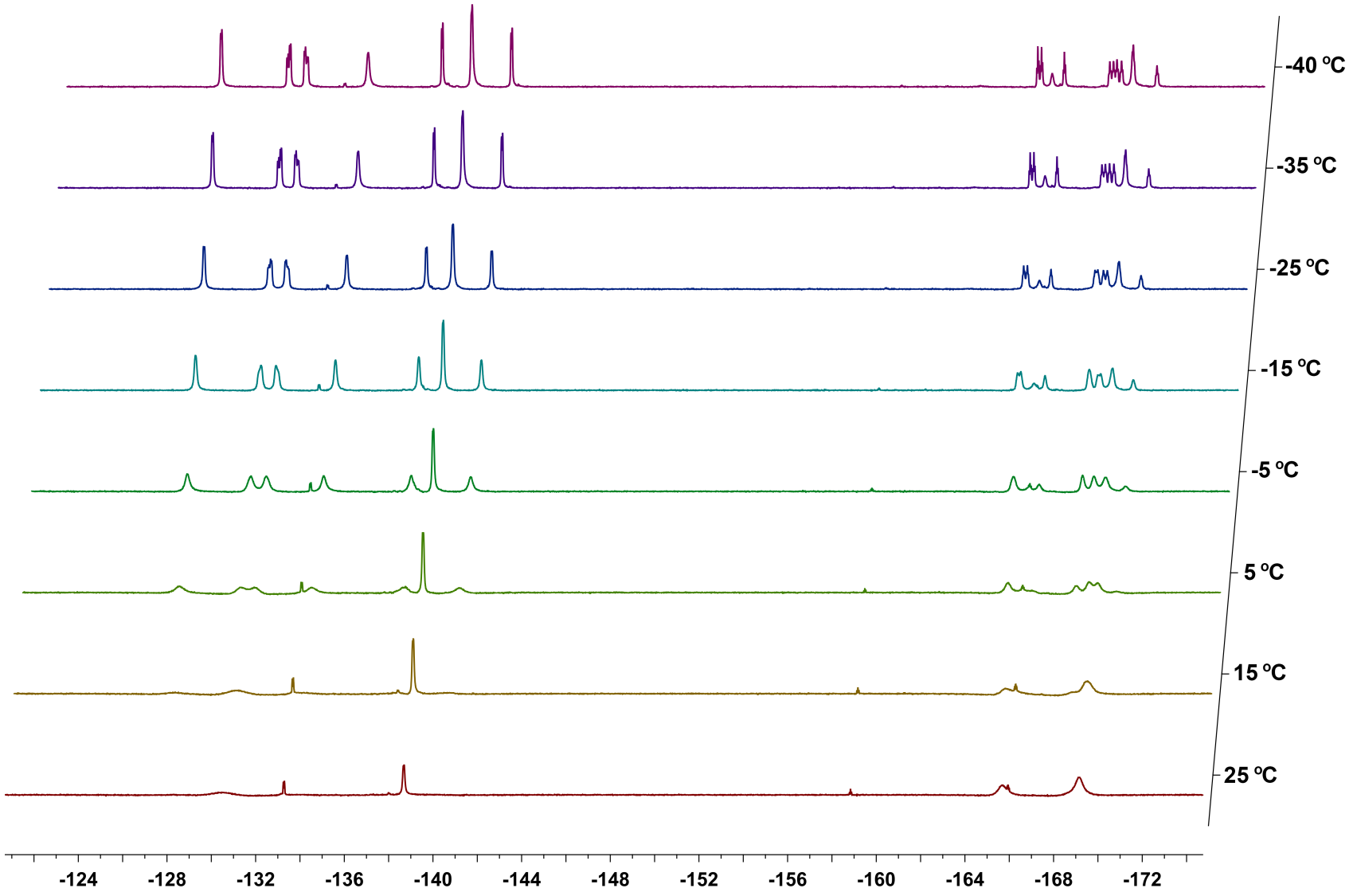


Figure S13. Variable temperature $^{19}F\{^{1}H\}$ NMR spectra for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^{H}Pd(PMe_3)$ (**4**).

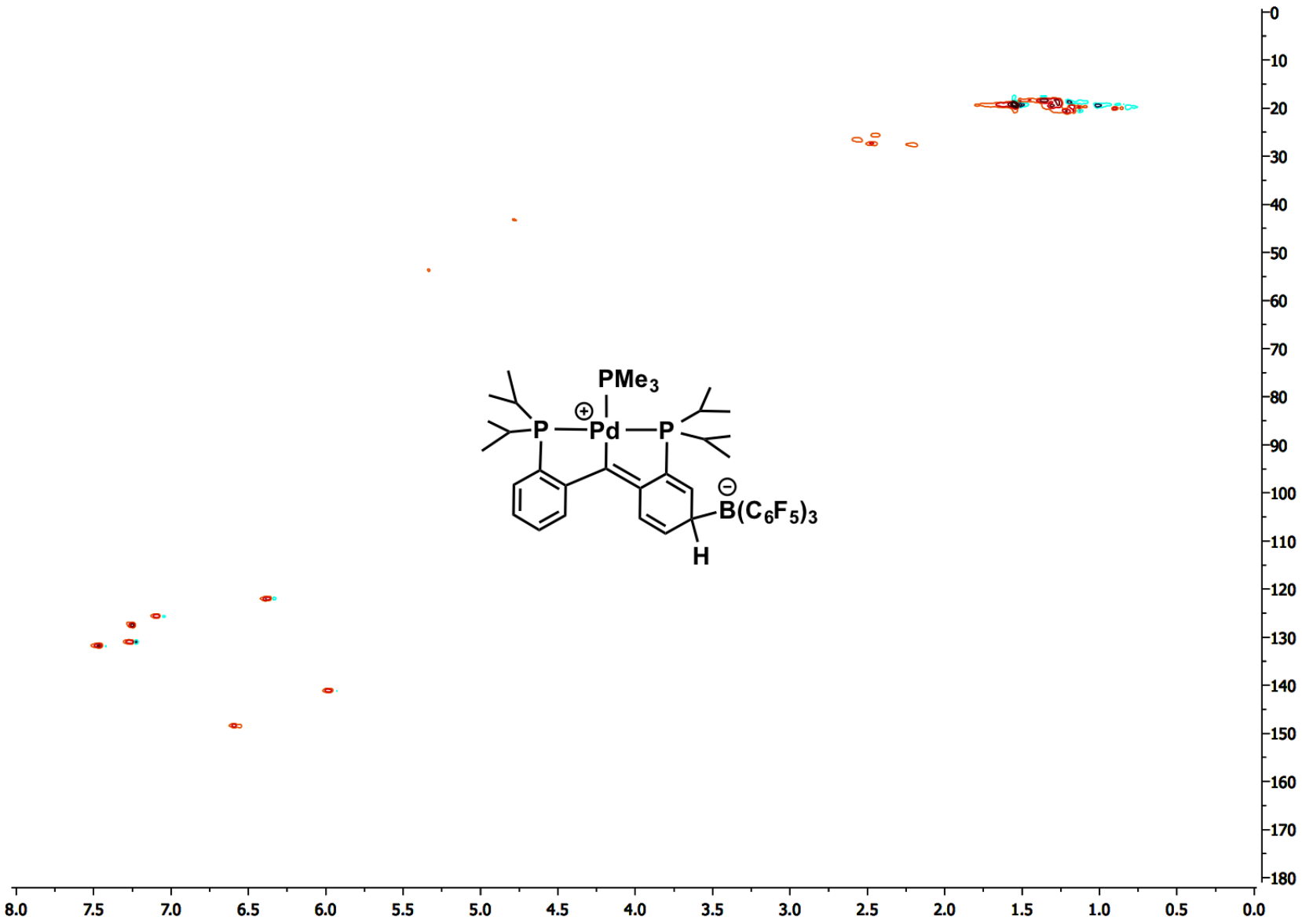


Figure S14. ^{1}H-^{13}C HSQC NMR spectrum for [$(C_6F_5)_3$B-PC(sp^2)P]^{H}Pd(PMe_3) (**4**).

3.2 NMR Spectra for [PC(sp^3)H_2P]^{tBu} (7)

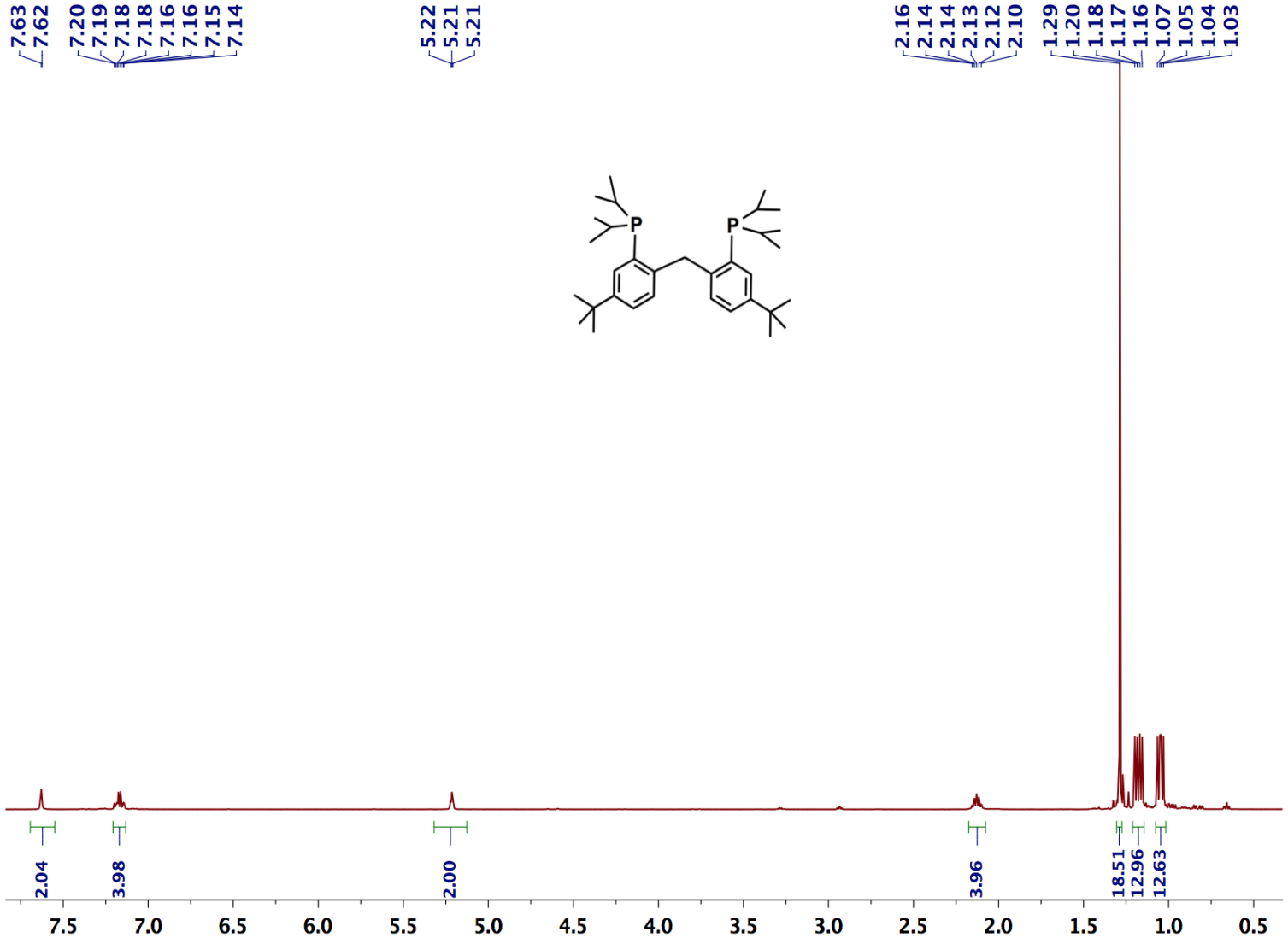


Figure S15. ^{1}H NMR spectrum for [PC(sp^3)H_2P]^{tBu} (**7**).

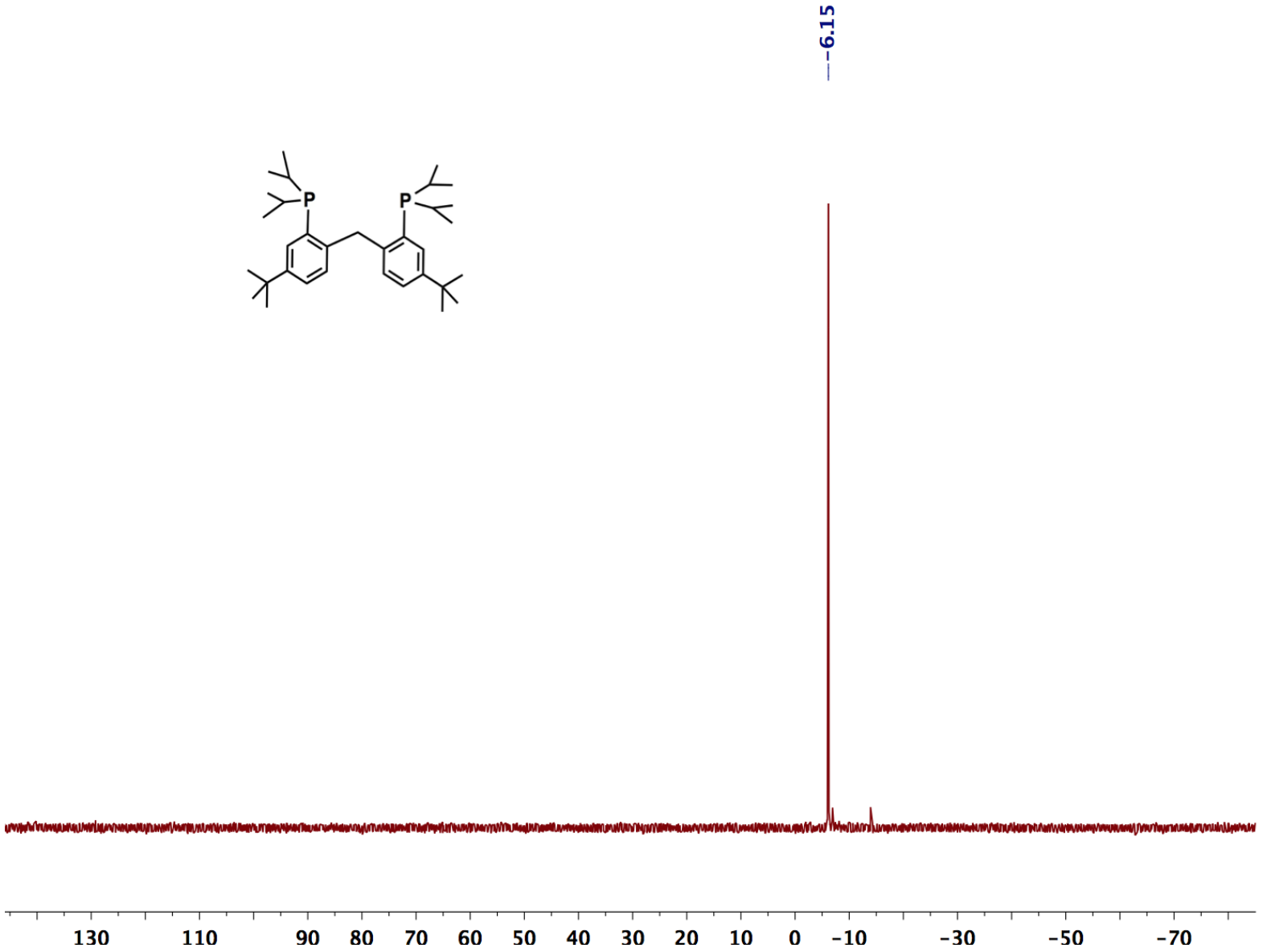


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum for $[PC(sp^3)H_2P]^{t\text{Bu}}$ (**7**).

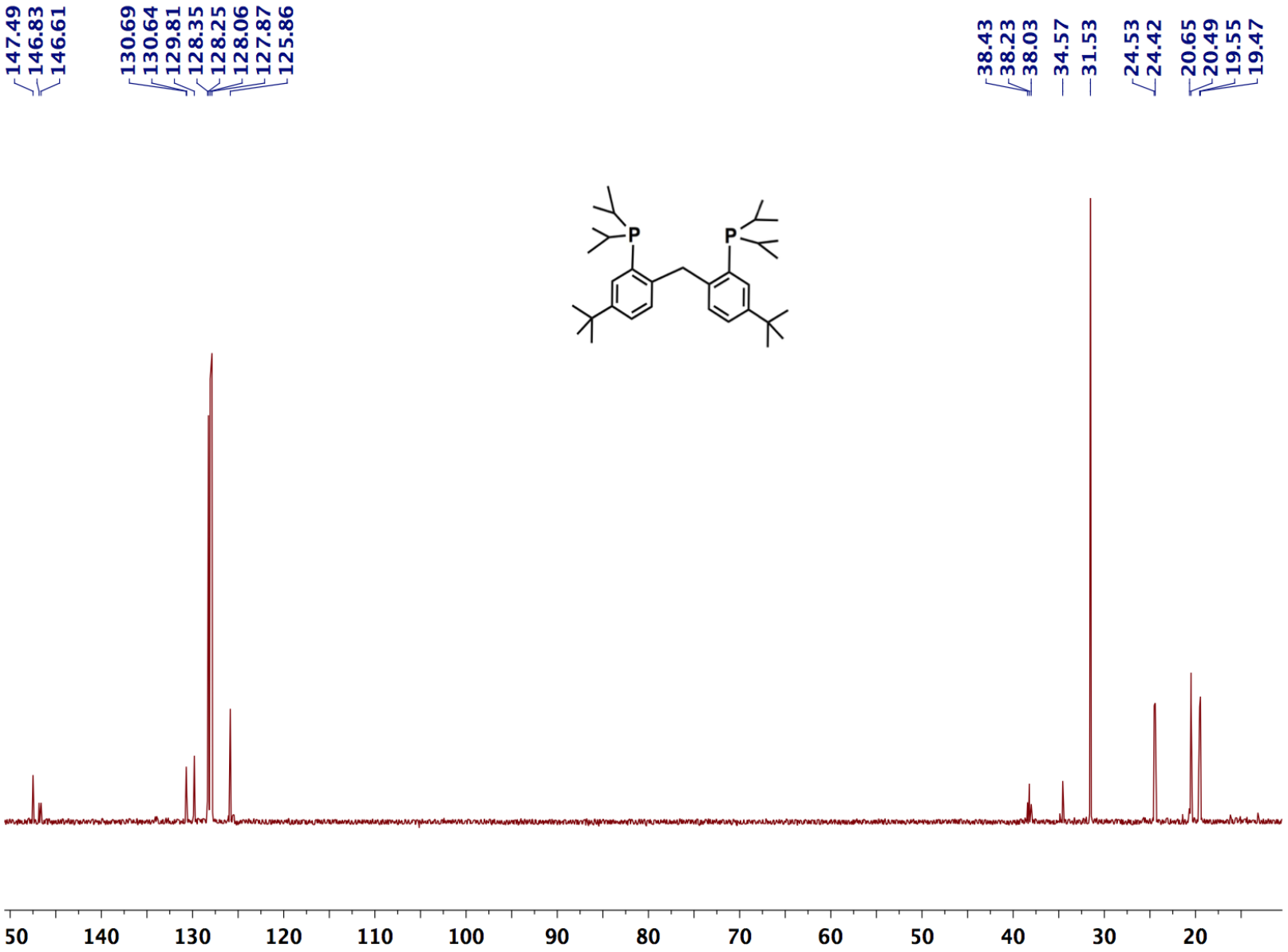


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum for $[PC(sp^3)H_2P]^{tBu}$ (**7**).

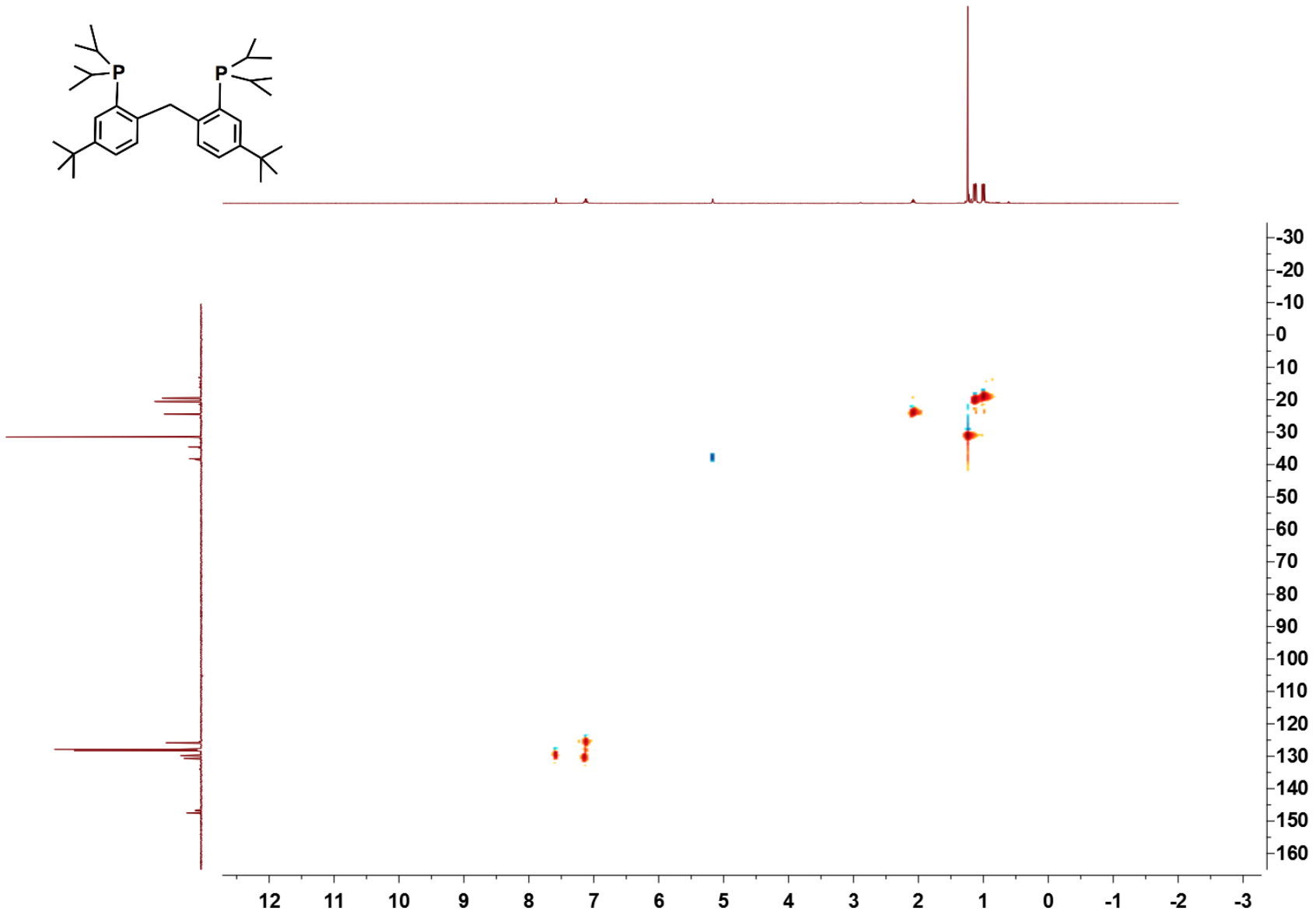


Figure S18. ^{1}H-^{13}C HSQC NMR spectrum for $[PC(sp^3)H_2P]^{tBu}$ (**7**).

3.3 NMR Spectra for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (6)

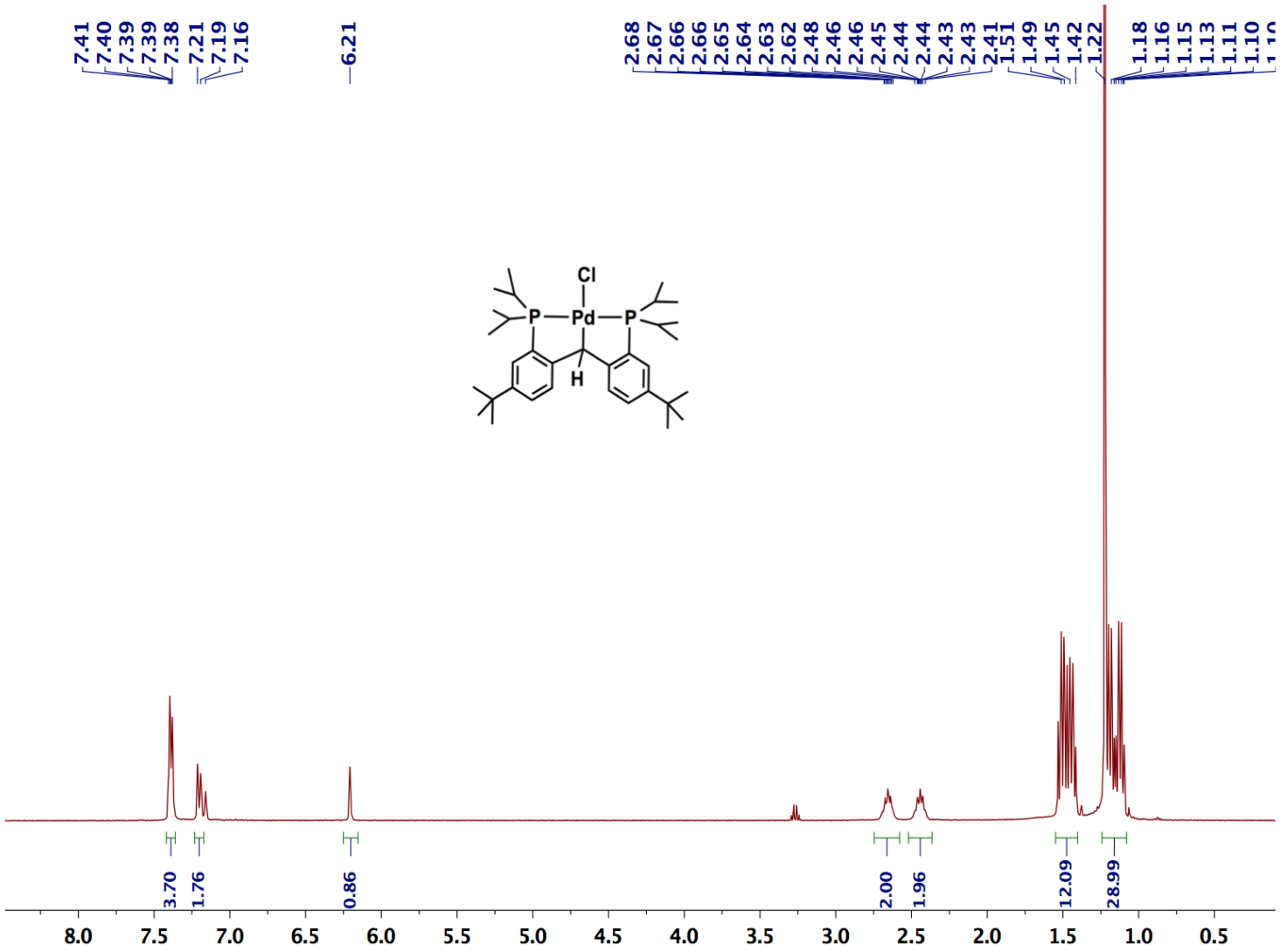


Figure S19. ^{1}H NMR spectrum for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**).

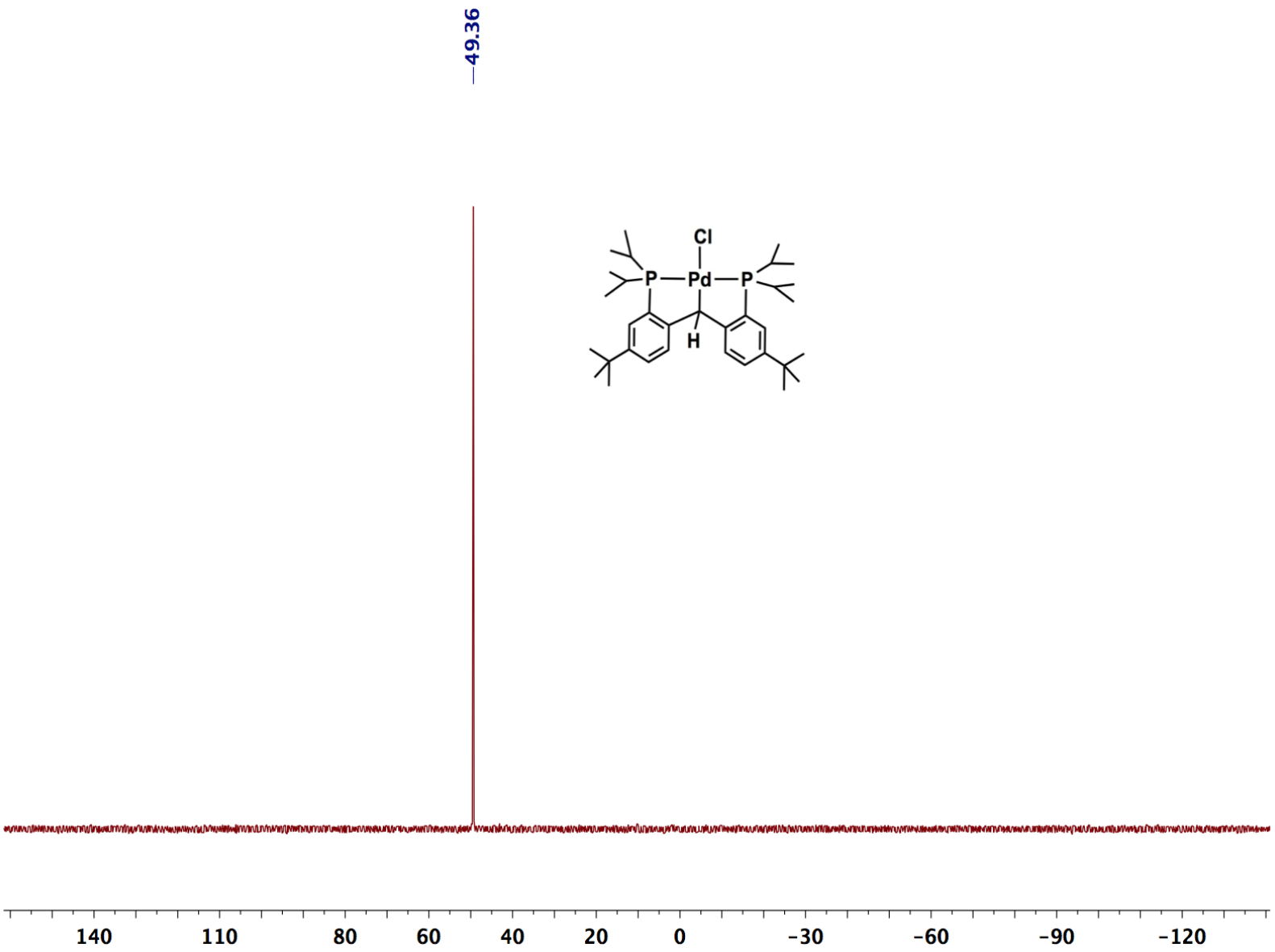


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**).

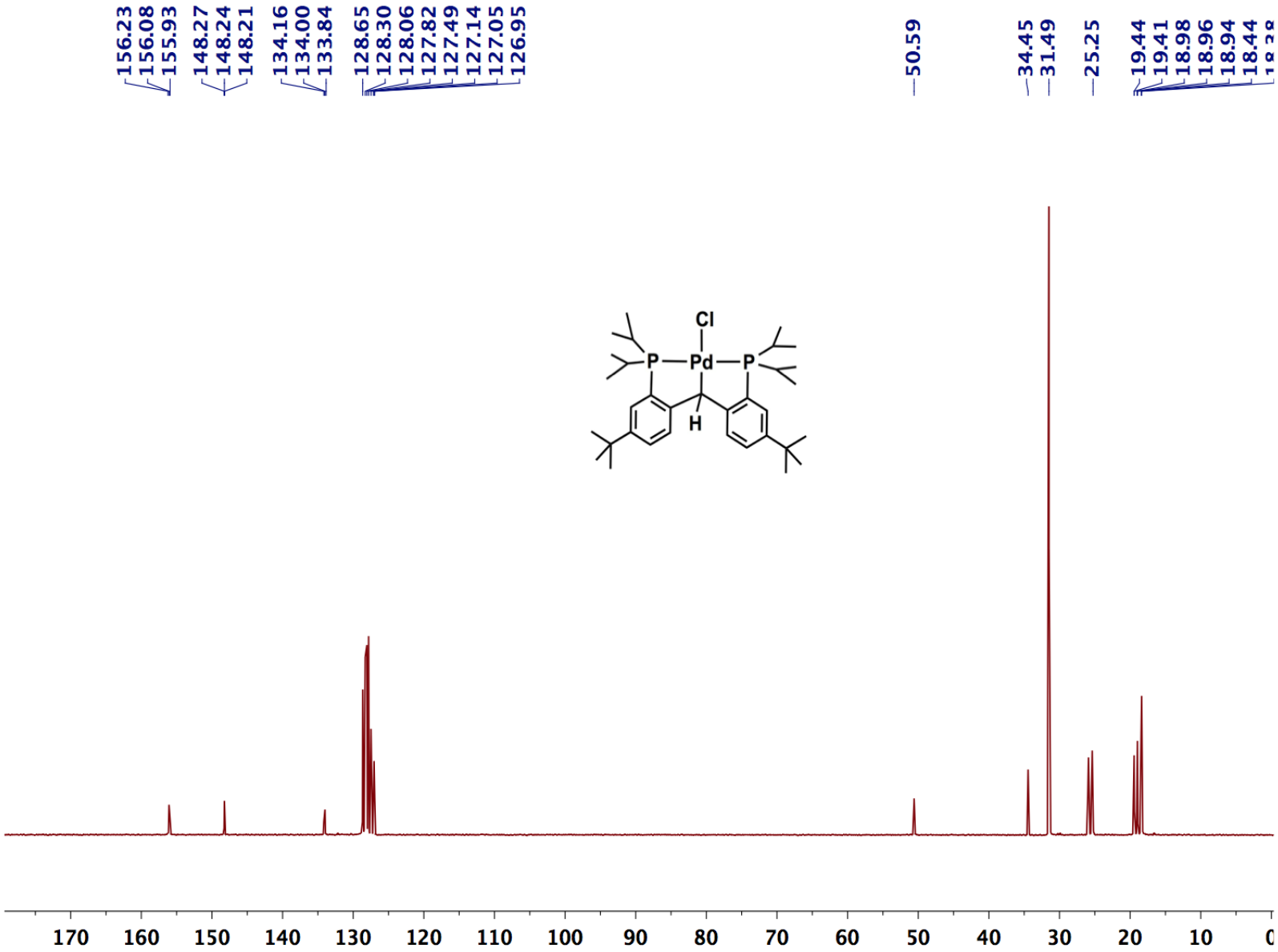


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**).

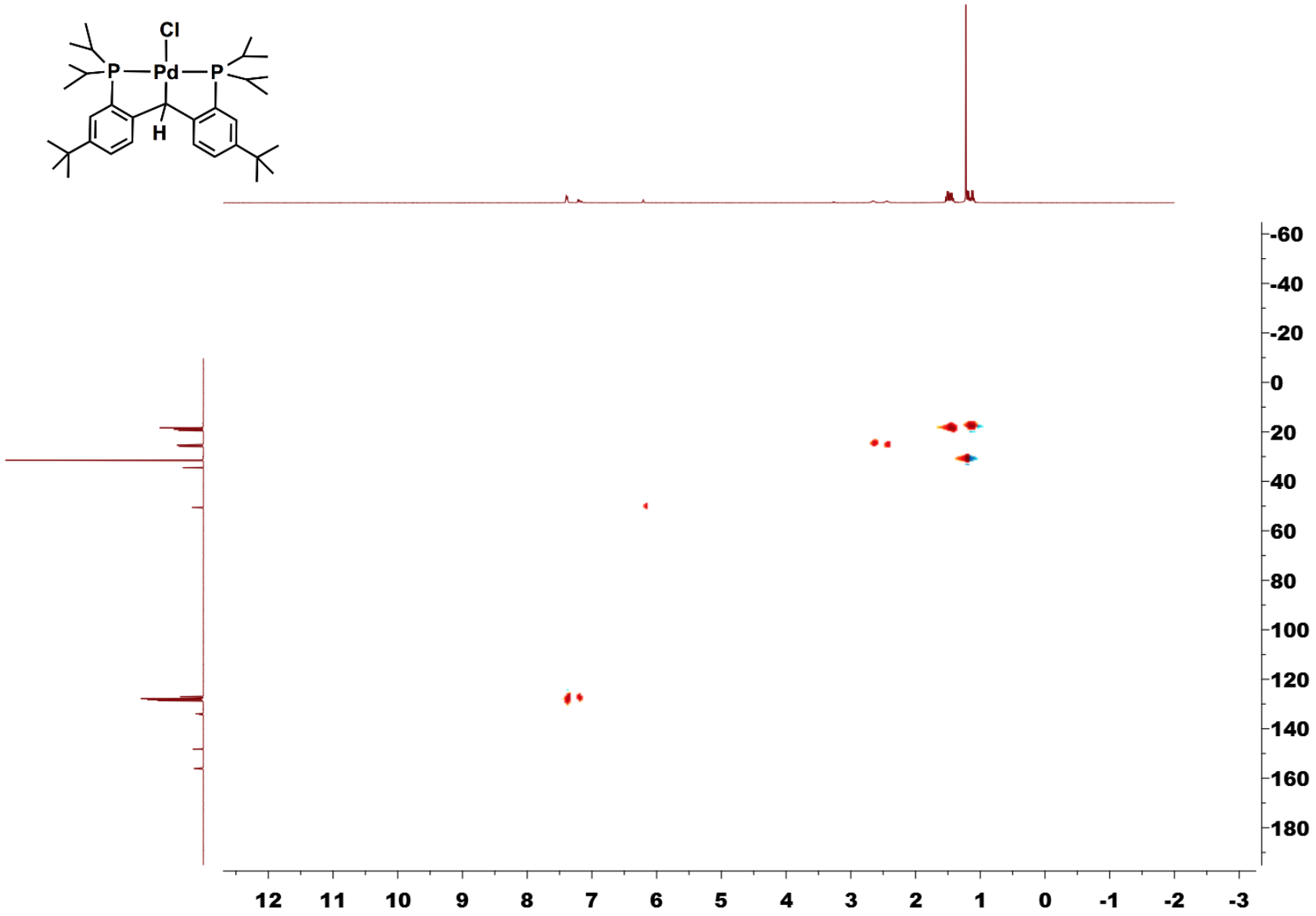


Figure S22. ^{1}H-^{13}C HSQC NMR spectrum for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**).

3.4 NMR Spectra for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (3)

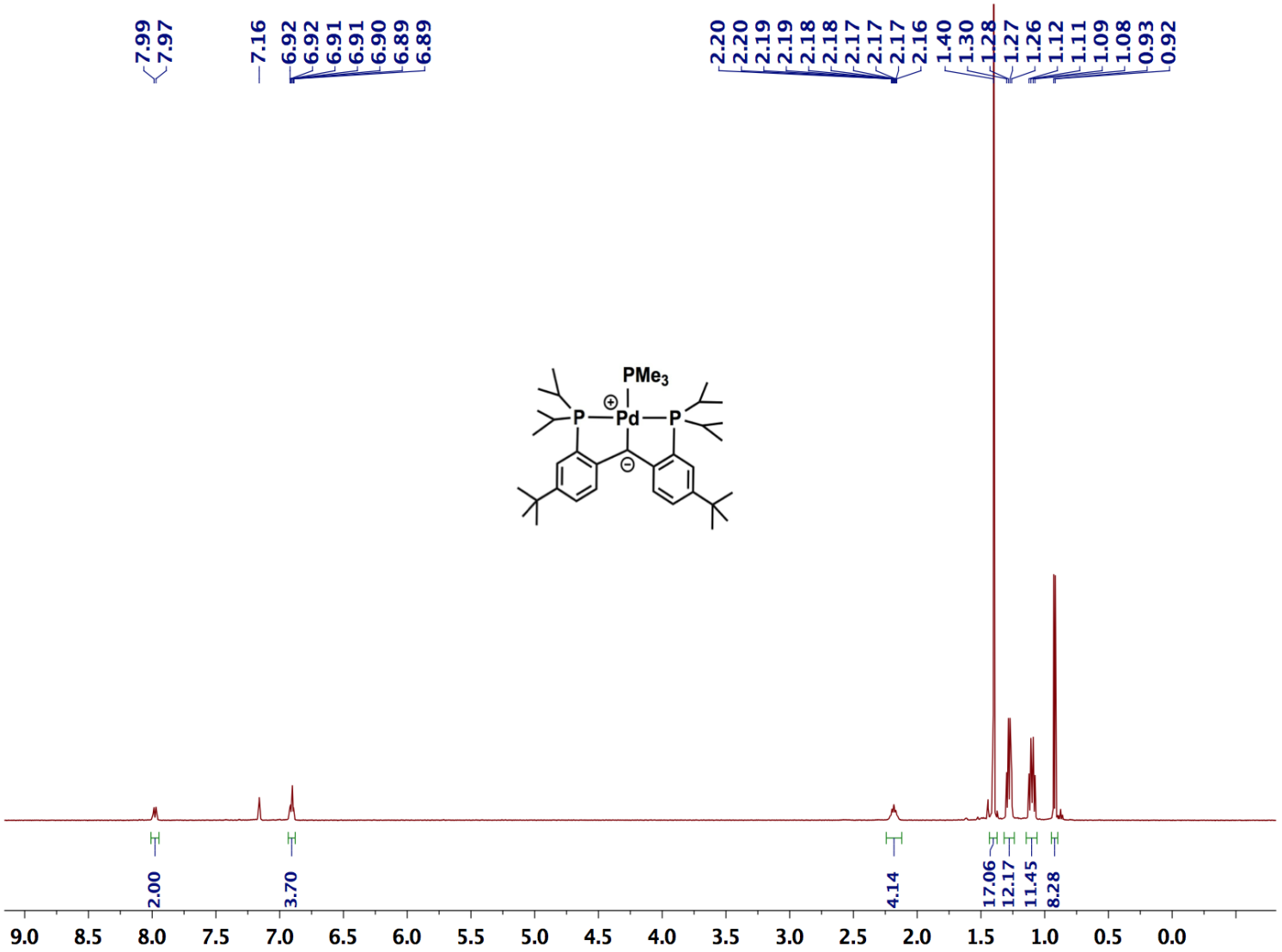


Figure S23. ^{1}H NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**).

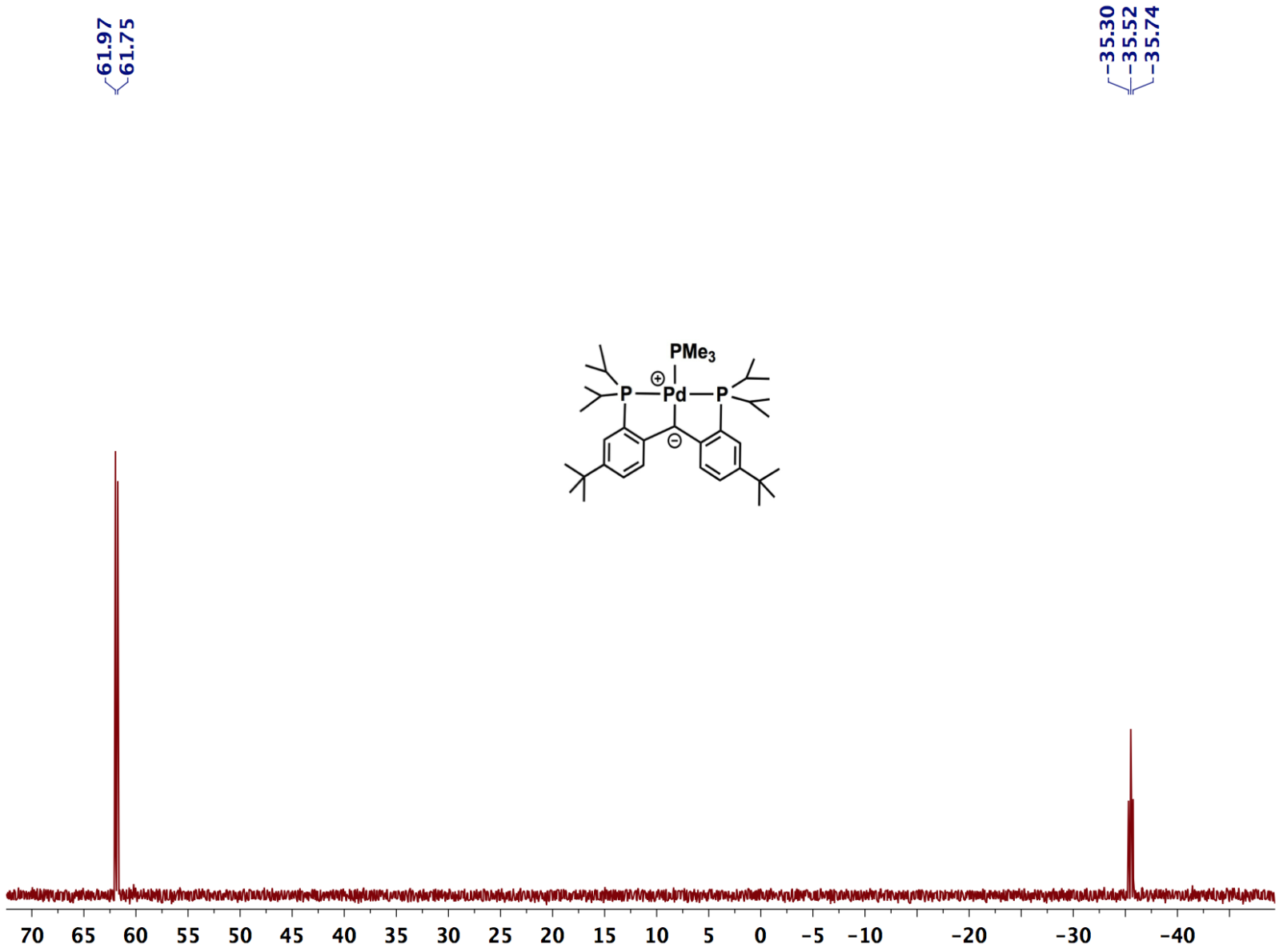


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe_3) (**3**).

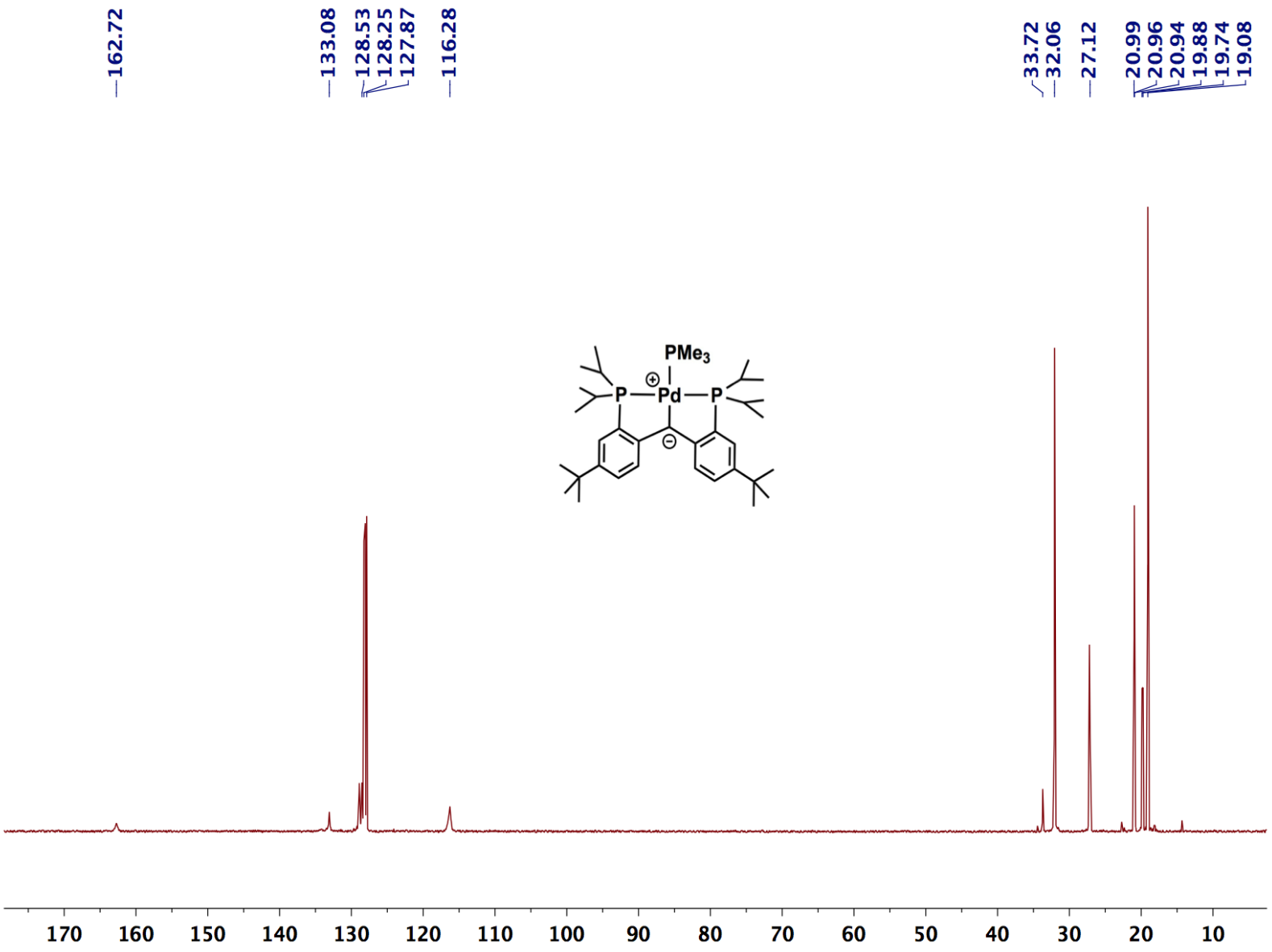


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe_3) (**3**).

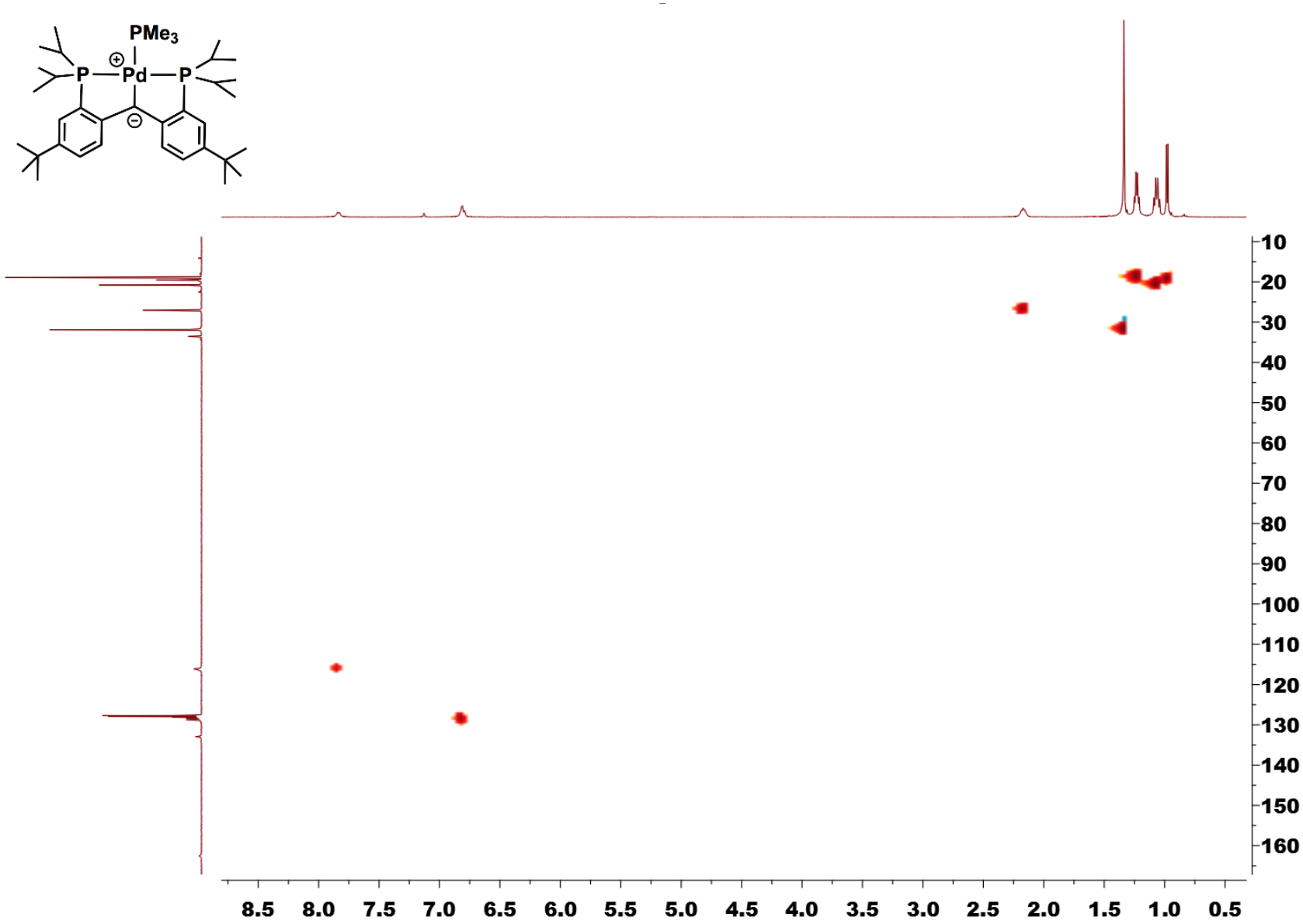


Figure S26. ^{1}H-^{13}C HSQC NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**).

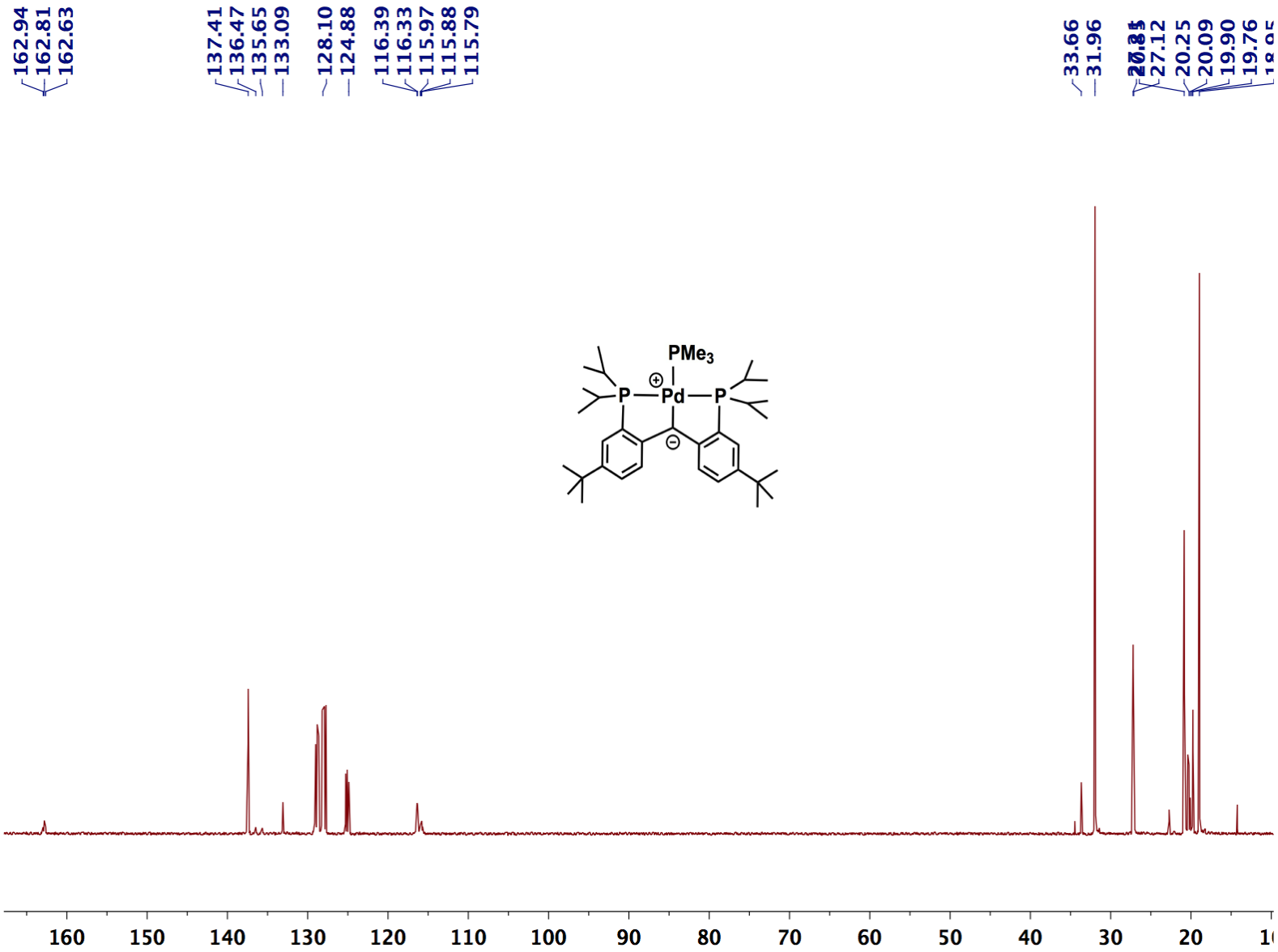


Figure S27. 25 °C $^{13}C\{^{1}H\}$ NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe_3) (**3**) in deuterated toluene.

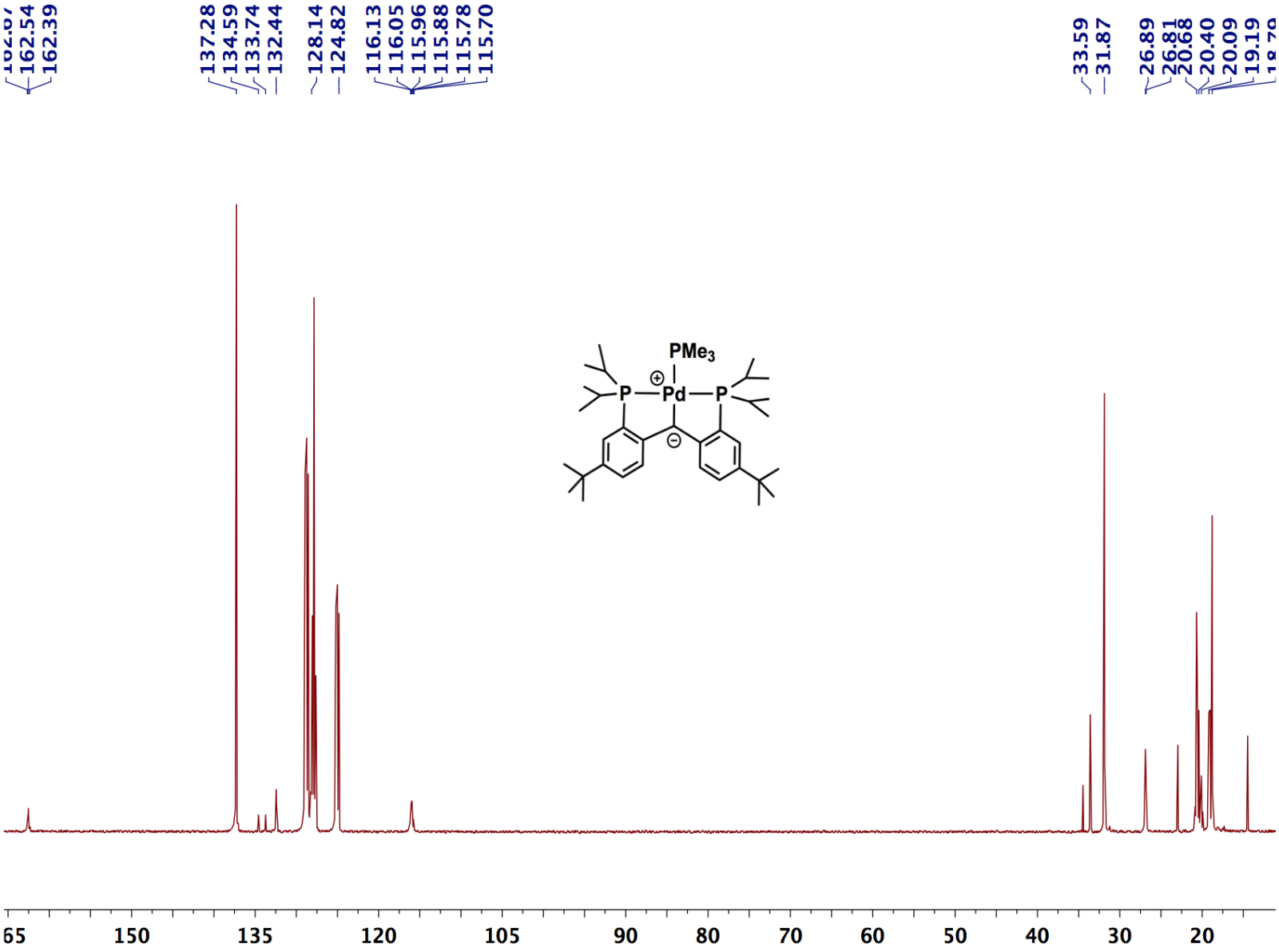


Figure S28. −40 °C $^{13}C\{^{1}H\}$ NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe_3) (**3**) in deuterated toluene.

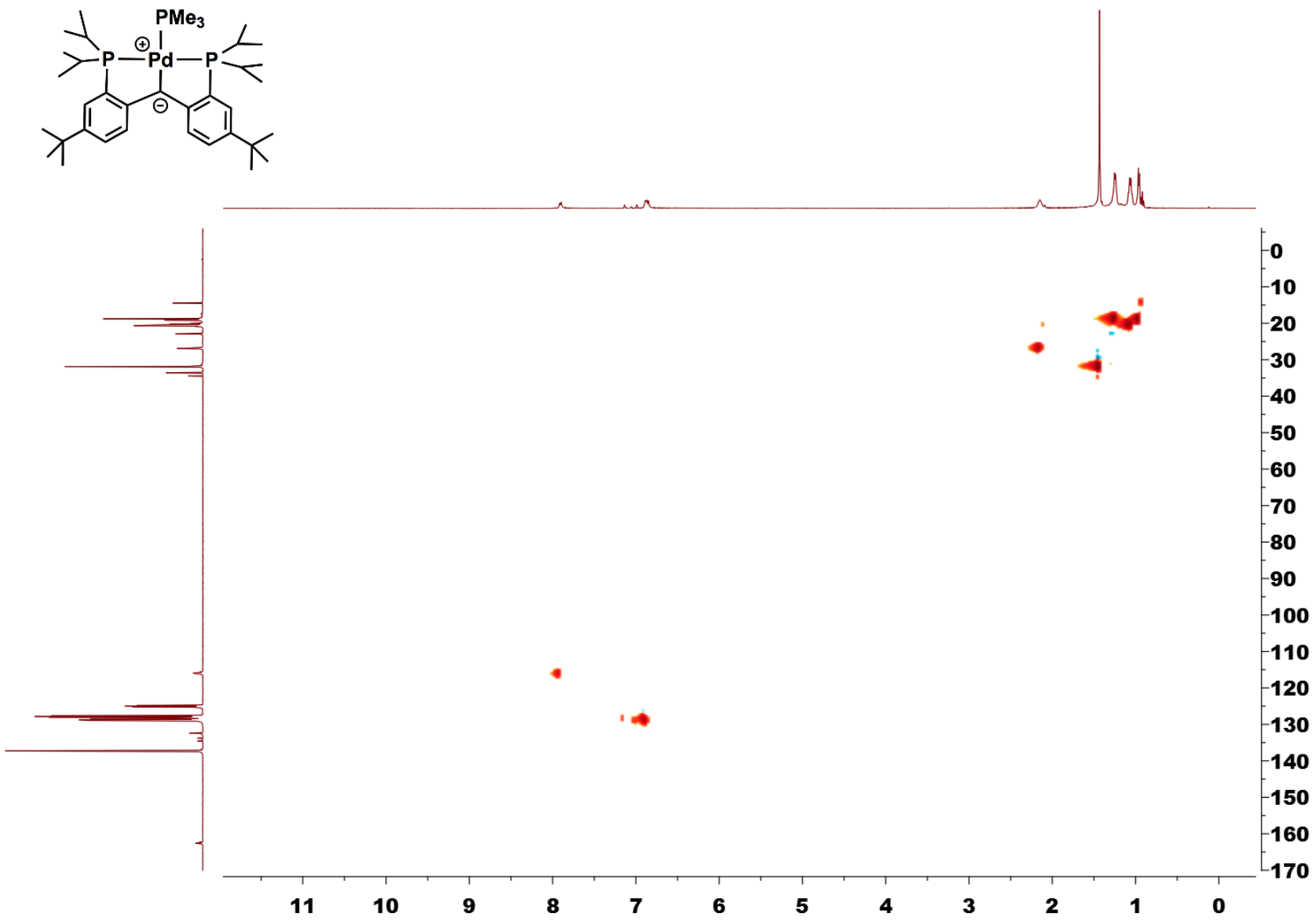


Figure S29. −40 °C ^{1}H-^{13}C HSQC NMR spectrum for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**) in deuterated toluene.

3.5 NMR Spectra for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (5)

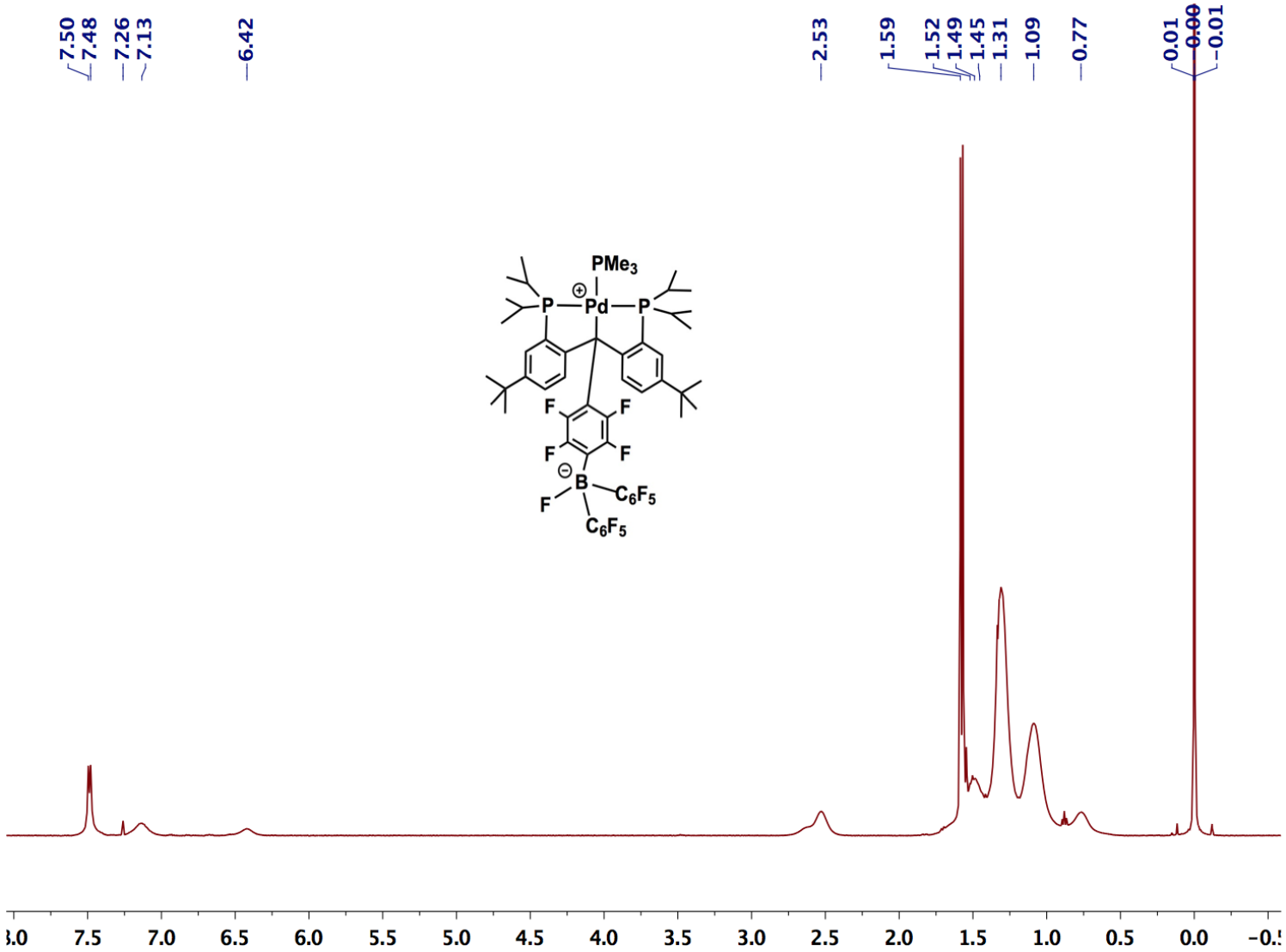


Figure S30. 25 °C ^{1}H NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

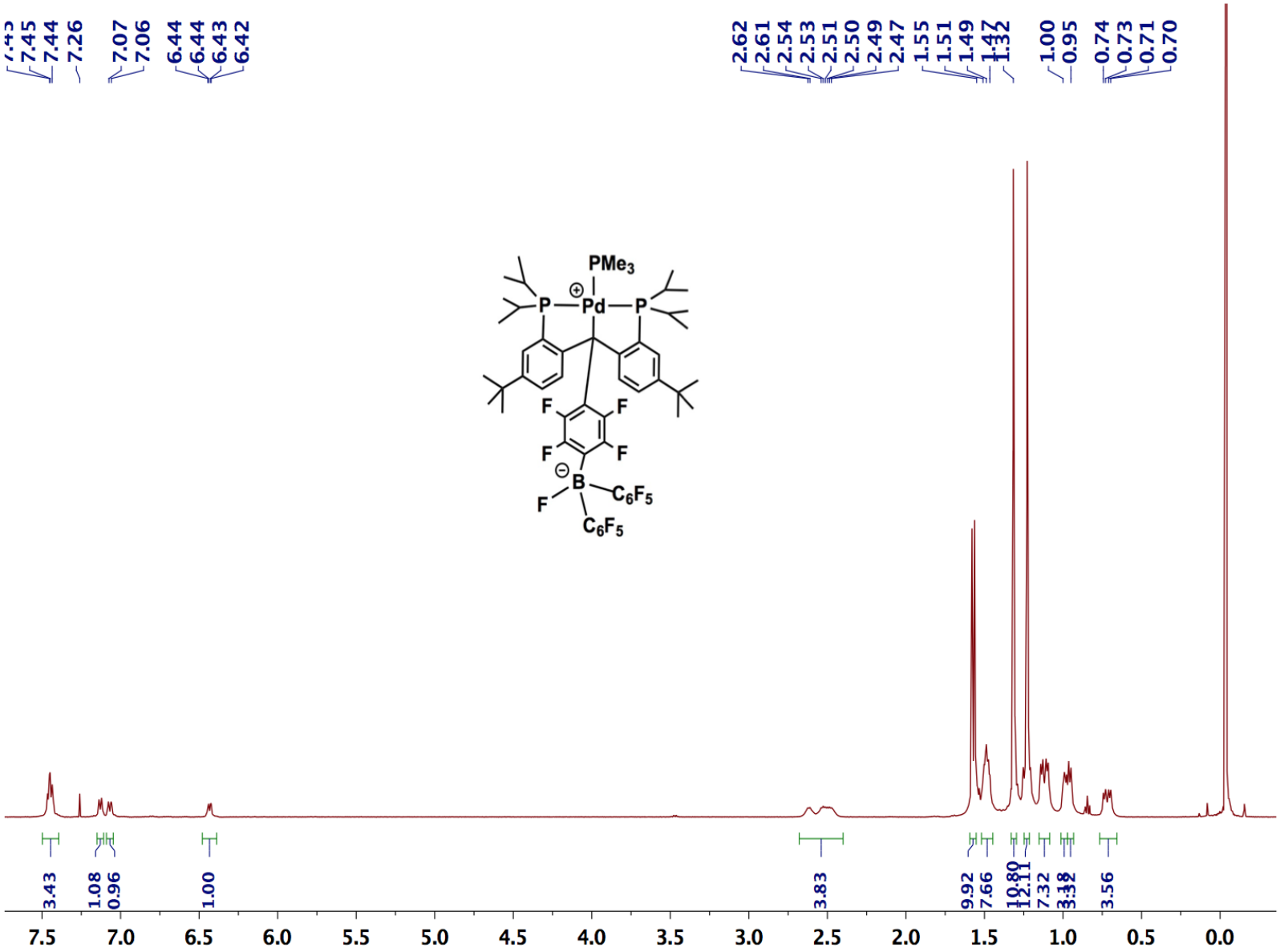


Figure S31. −35 °C ^{1}H NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

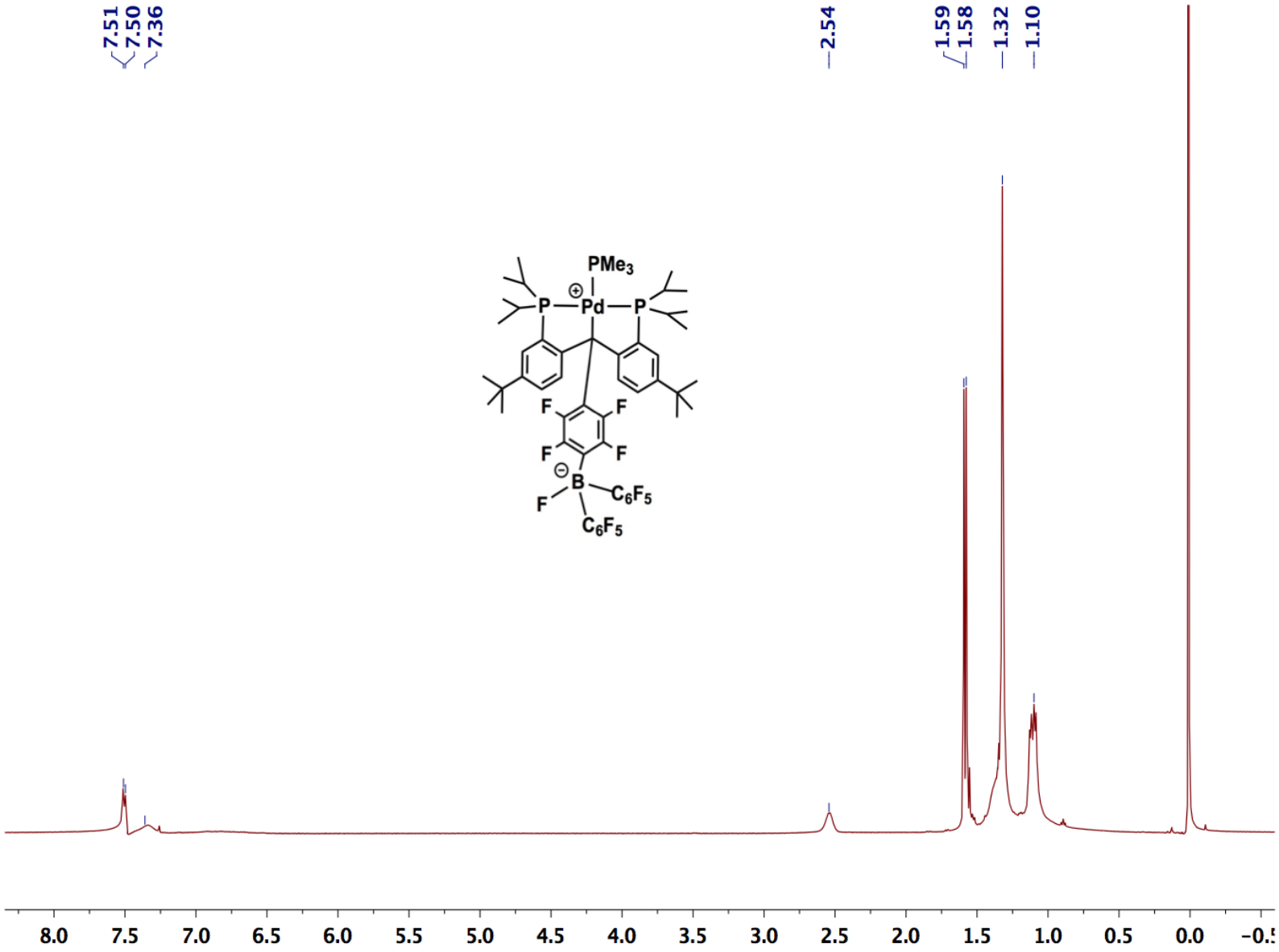


Figure S32. 55 °C ^{1}H NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

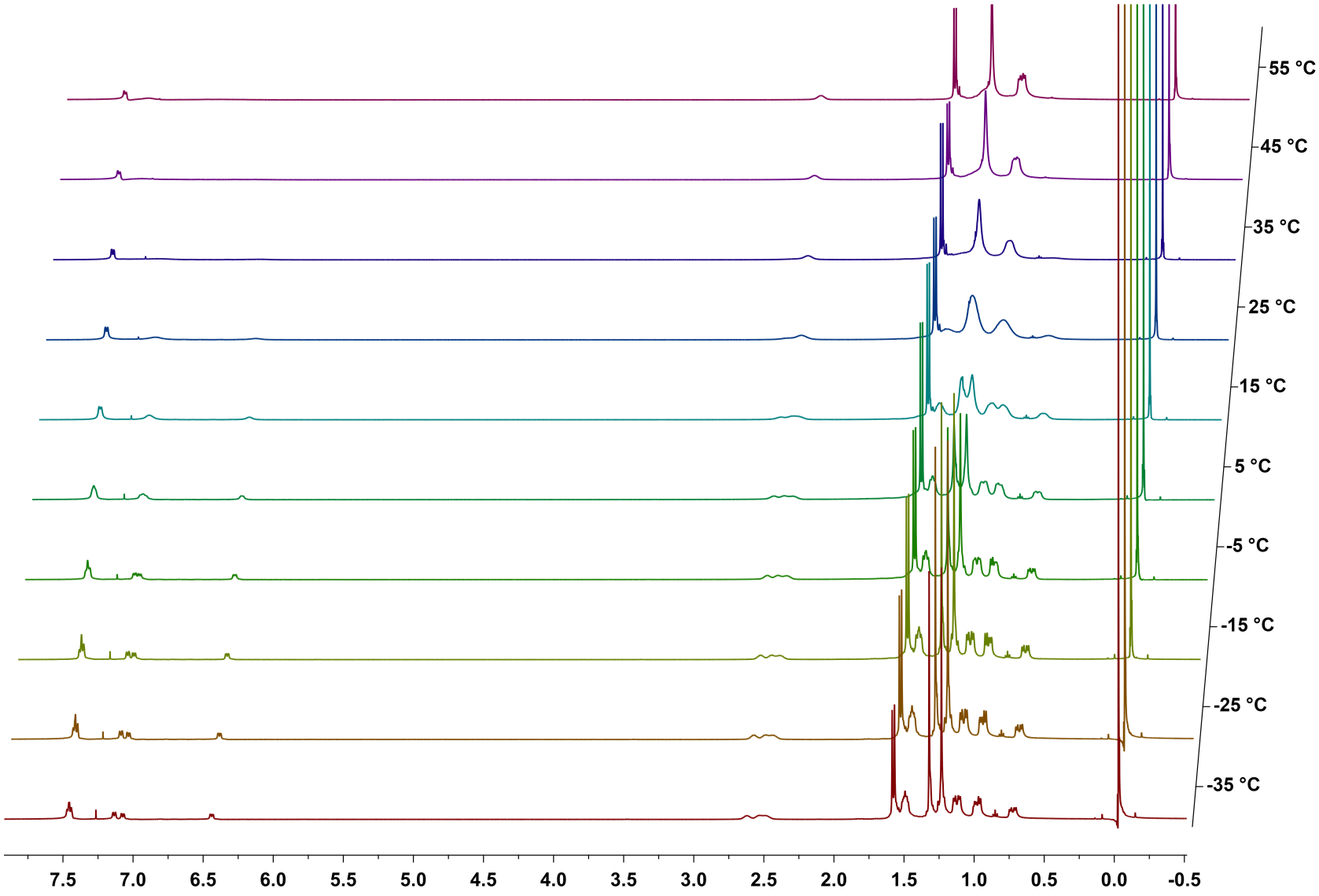


Figure S33. Variable temperature ^{1}H NMR spectra for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

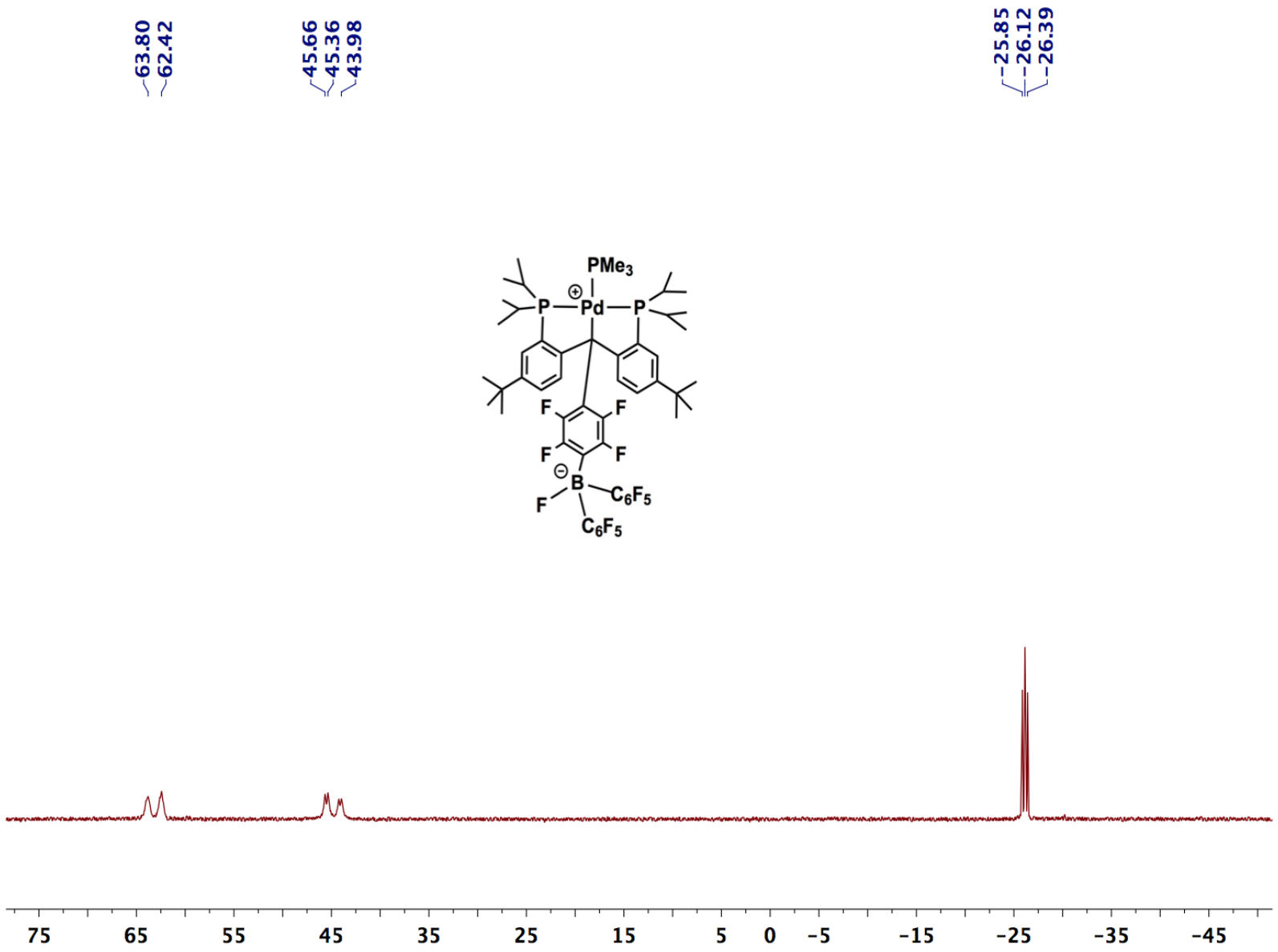


Figure S34. 25 °C $^{31}P\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

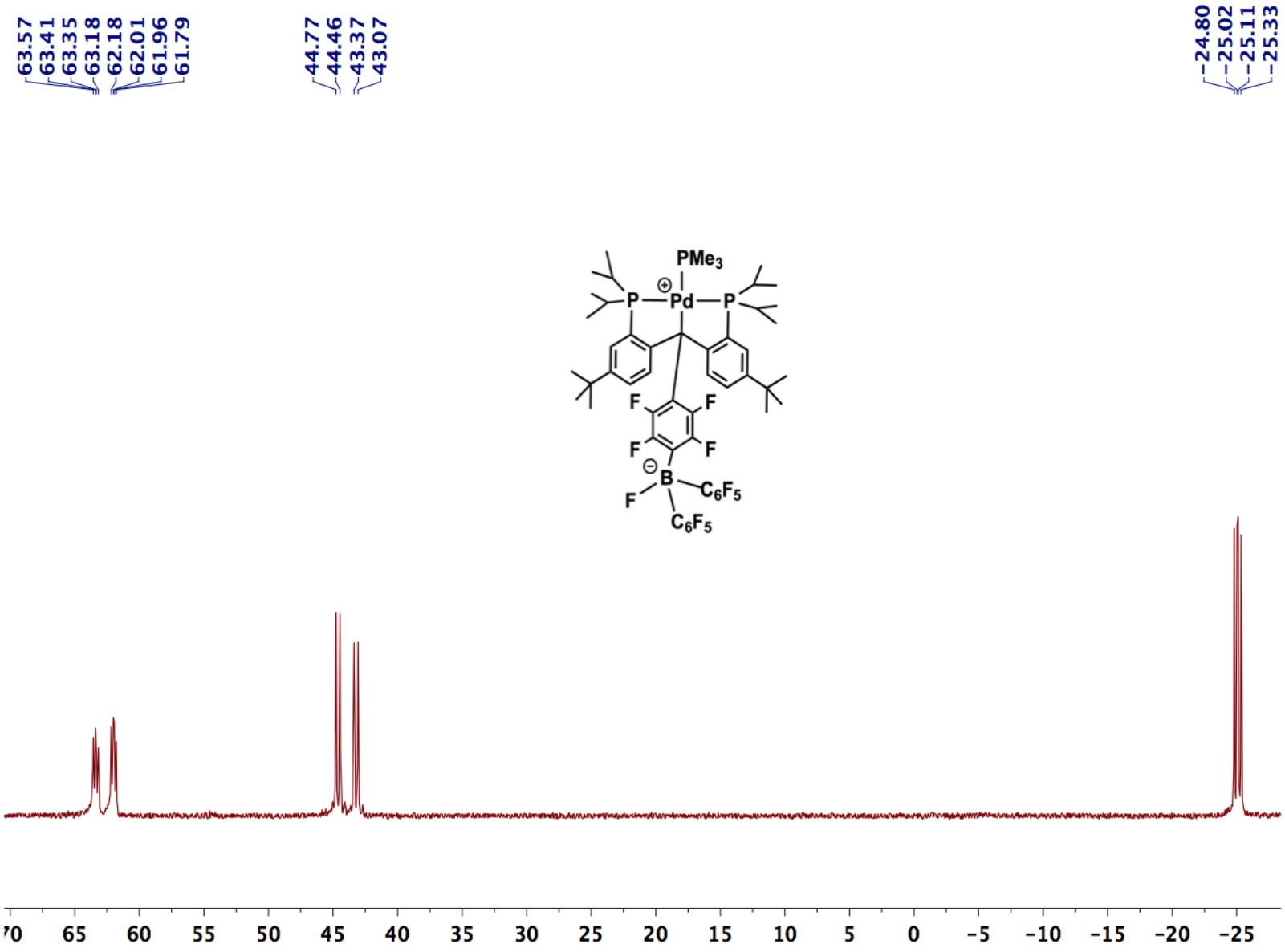


Figure S35. −35 °C $^{31}P\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

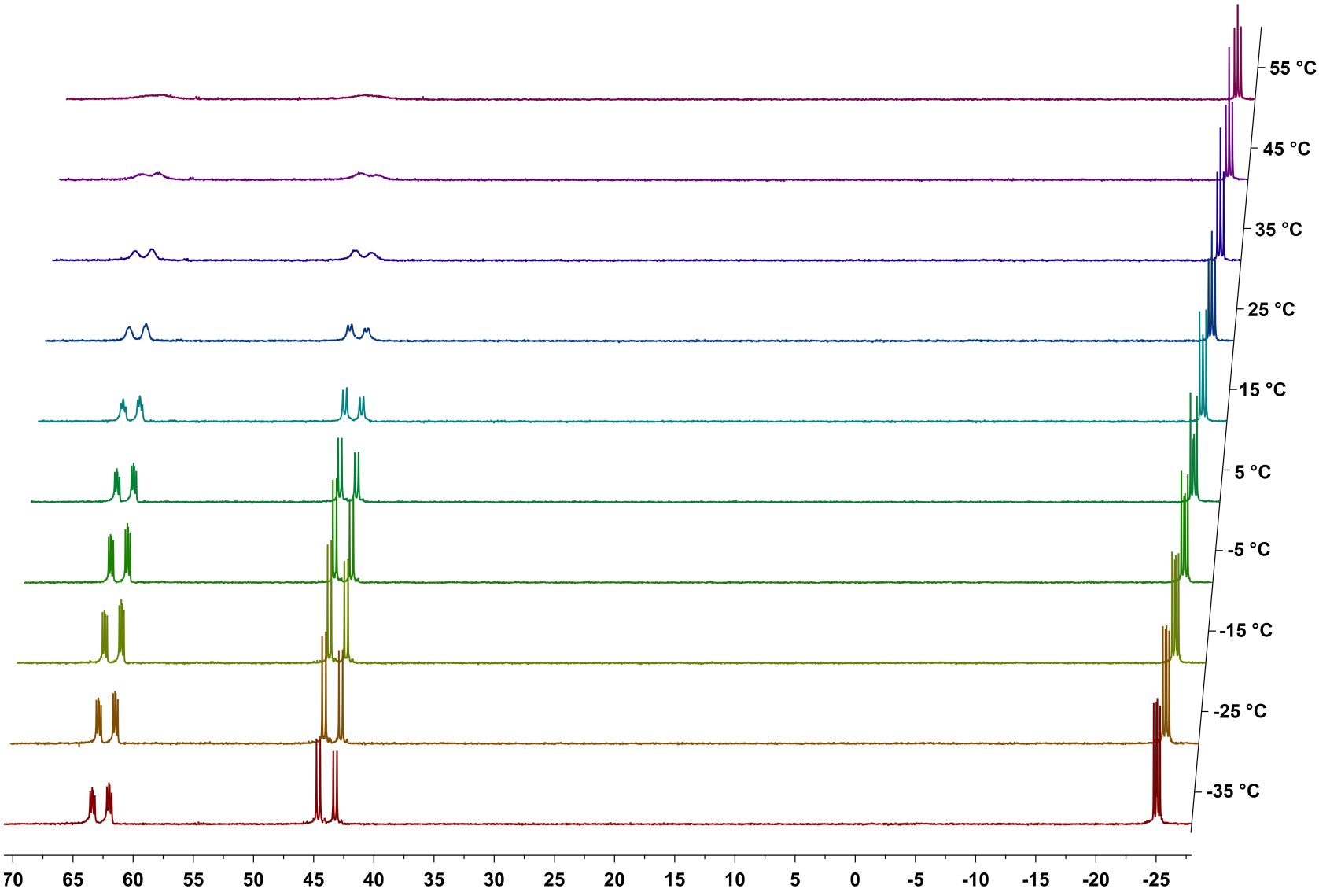


Figure S36. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

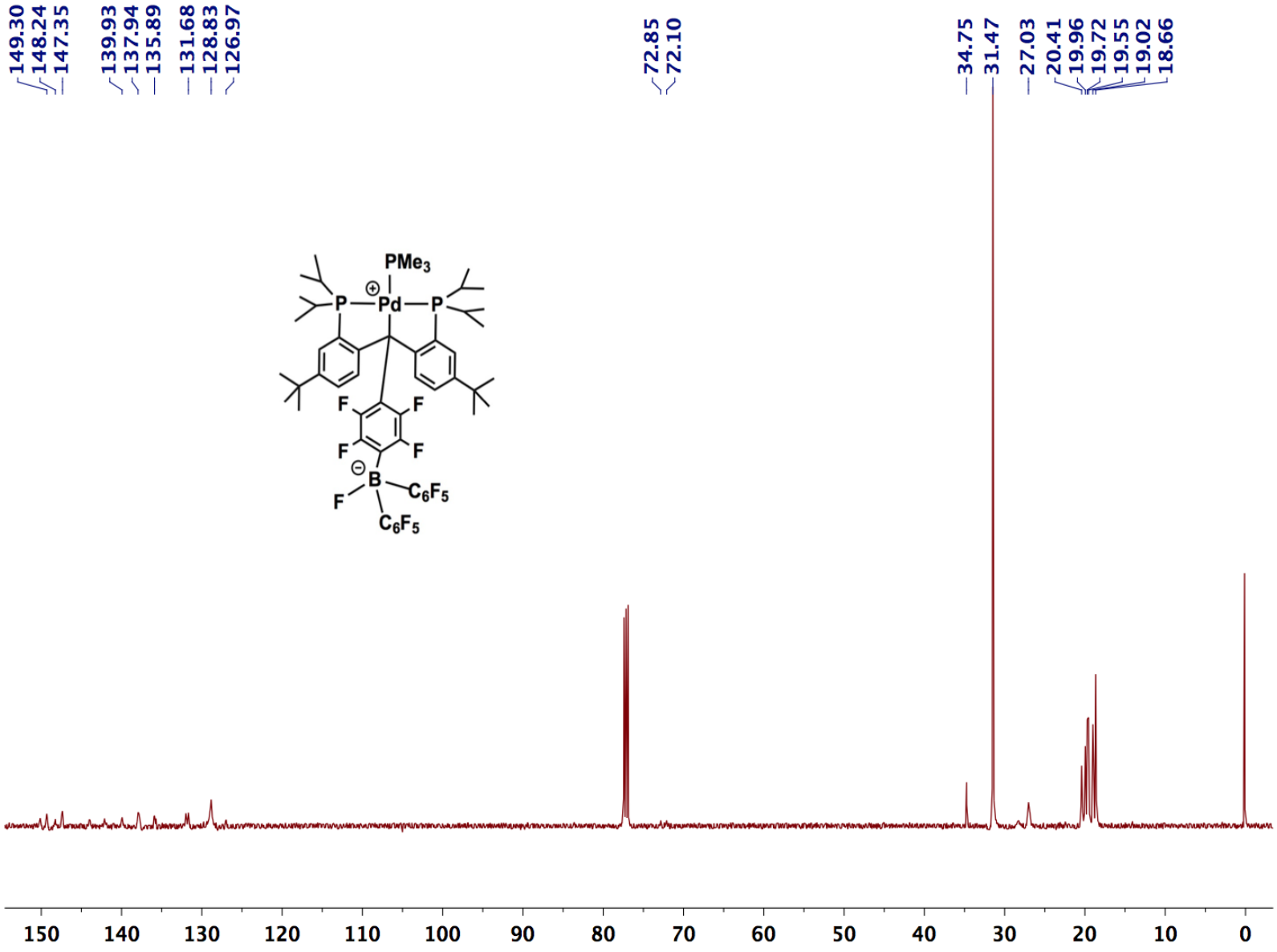


Figure S37. 55 °C $^{13}C\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

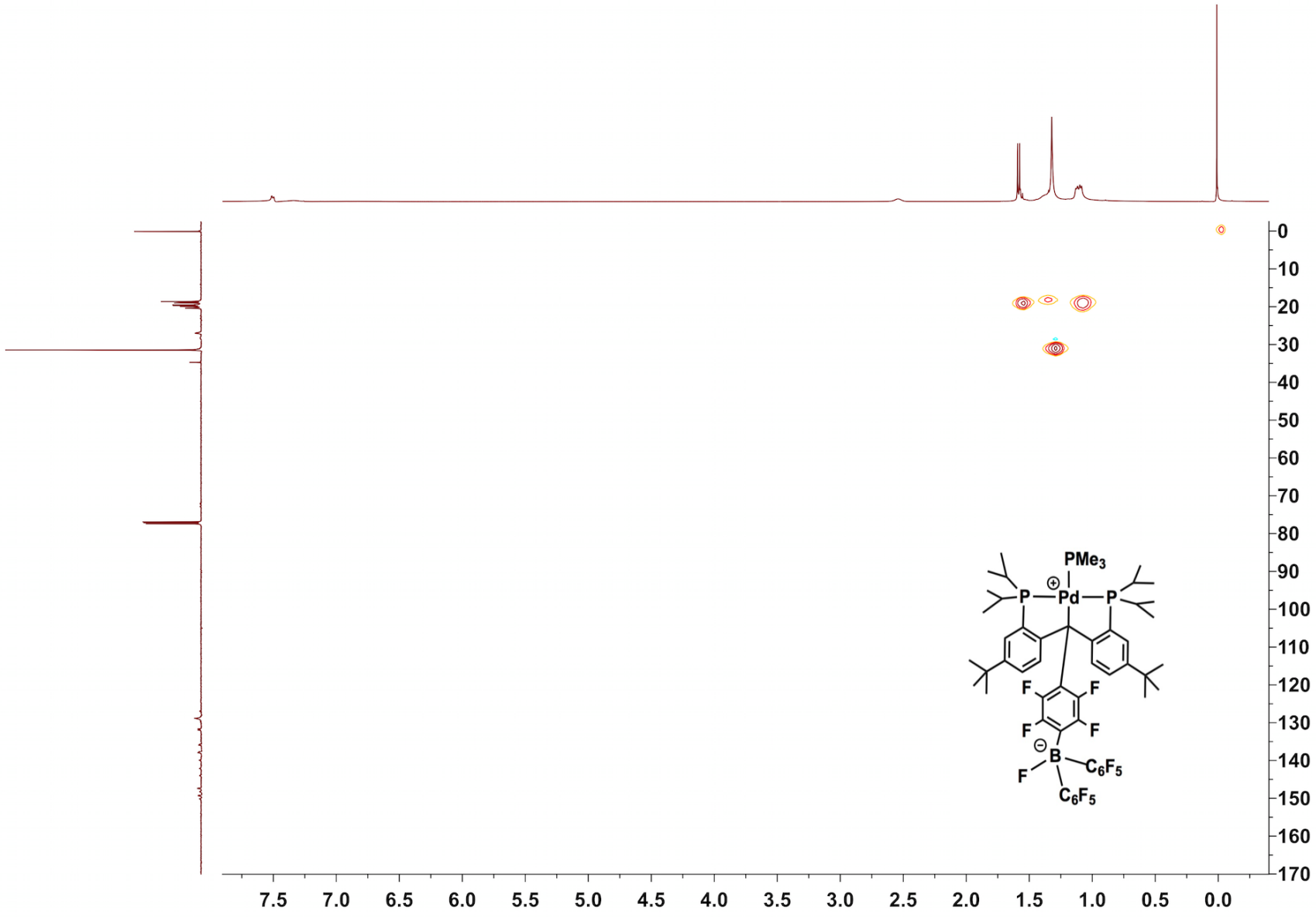


Figure S38. 55 °C ^{1}H-^{13}C HSQC NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

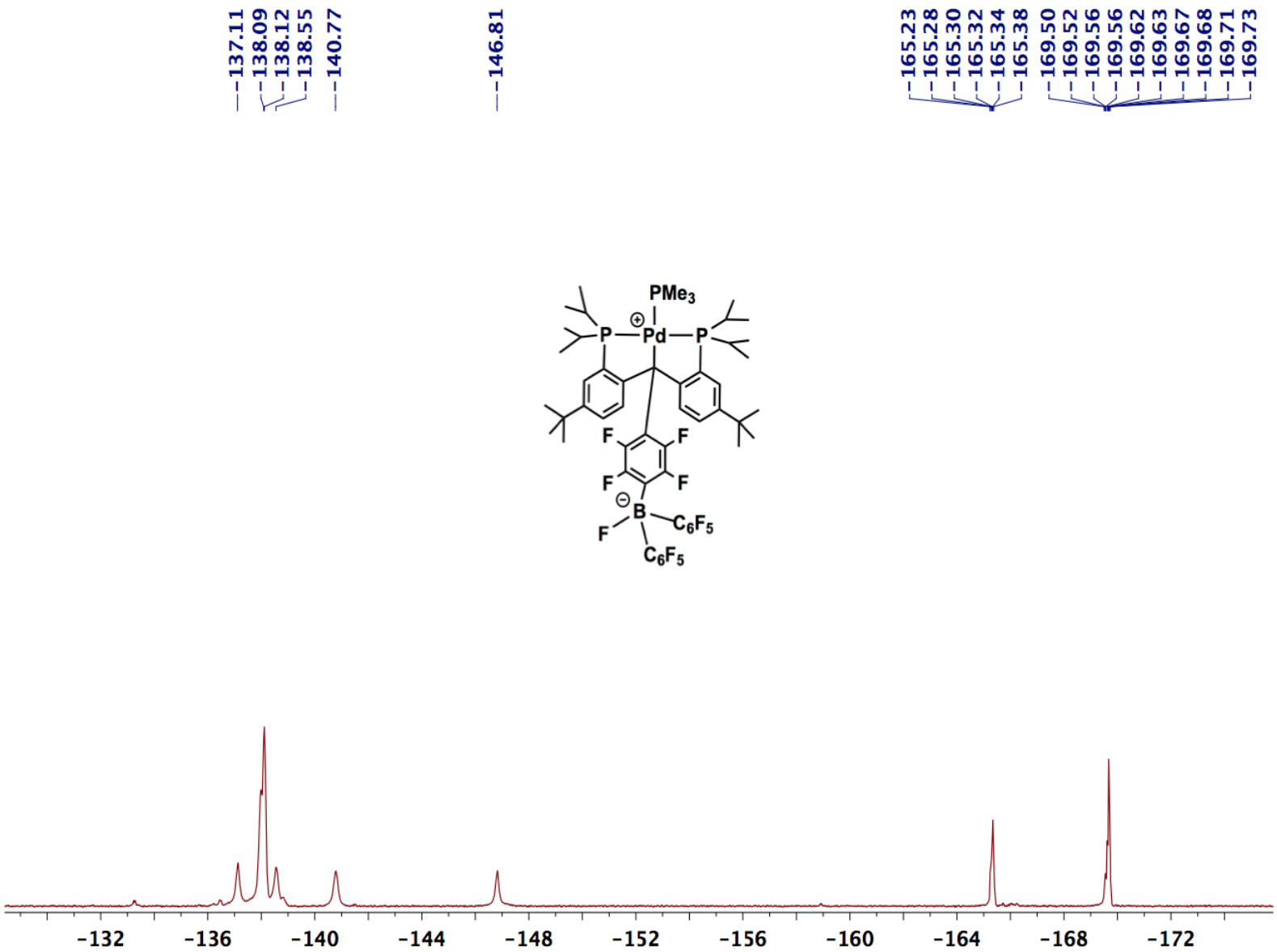


Figure S39. 25 °C $^{19}F\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

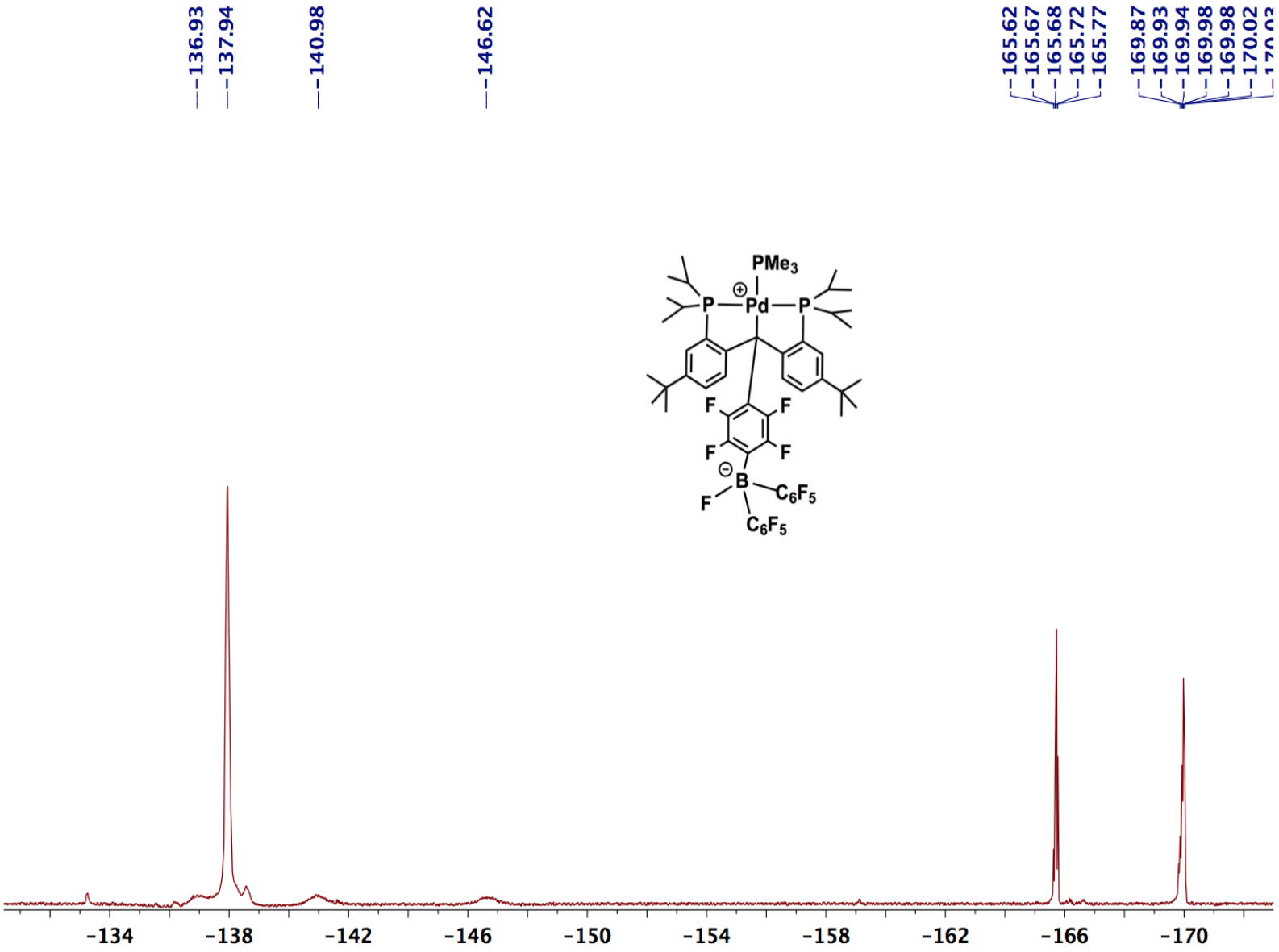


Figure S40. 55 °C $^{19}F\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

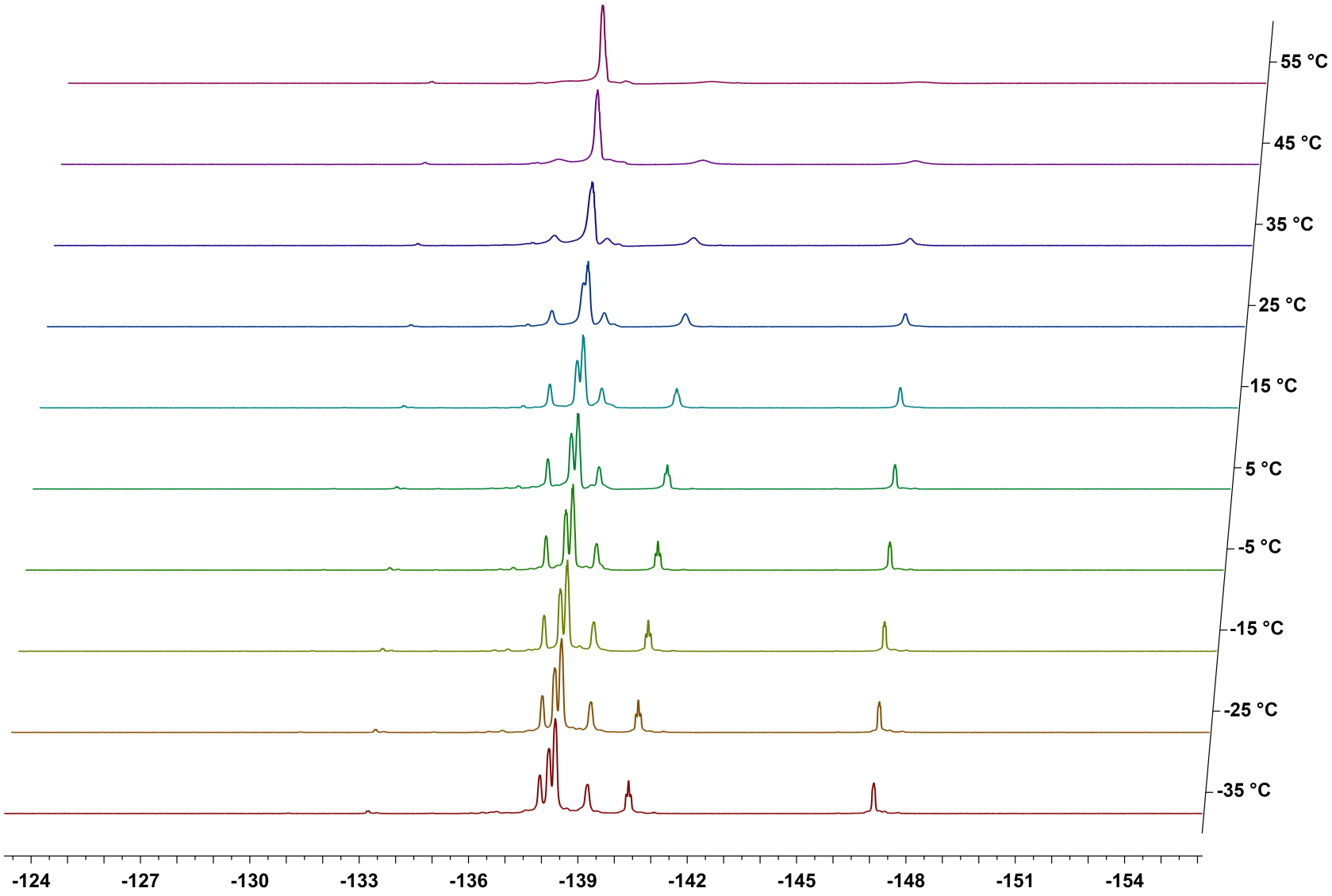


Figure S41. Variable temperature $^{19}F\{^{1}H\}$ NMR spectra for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

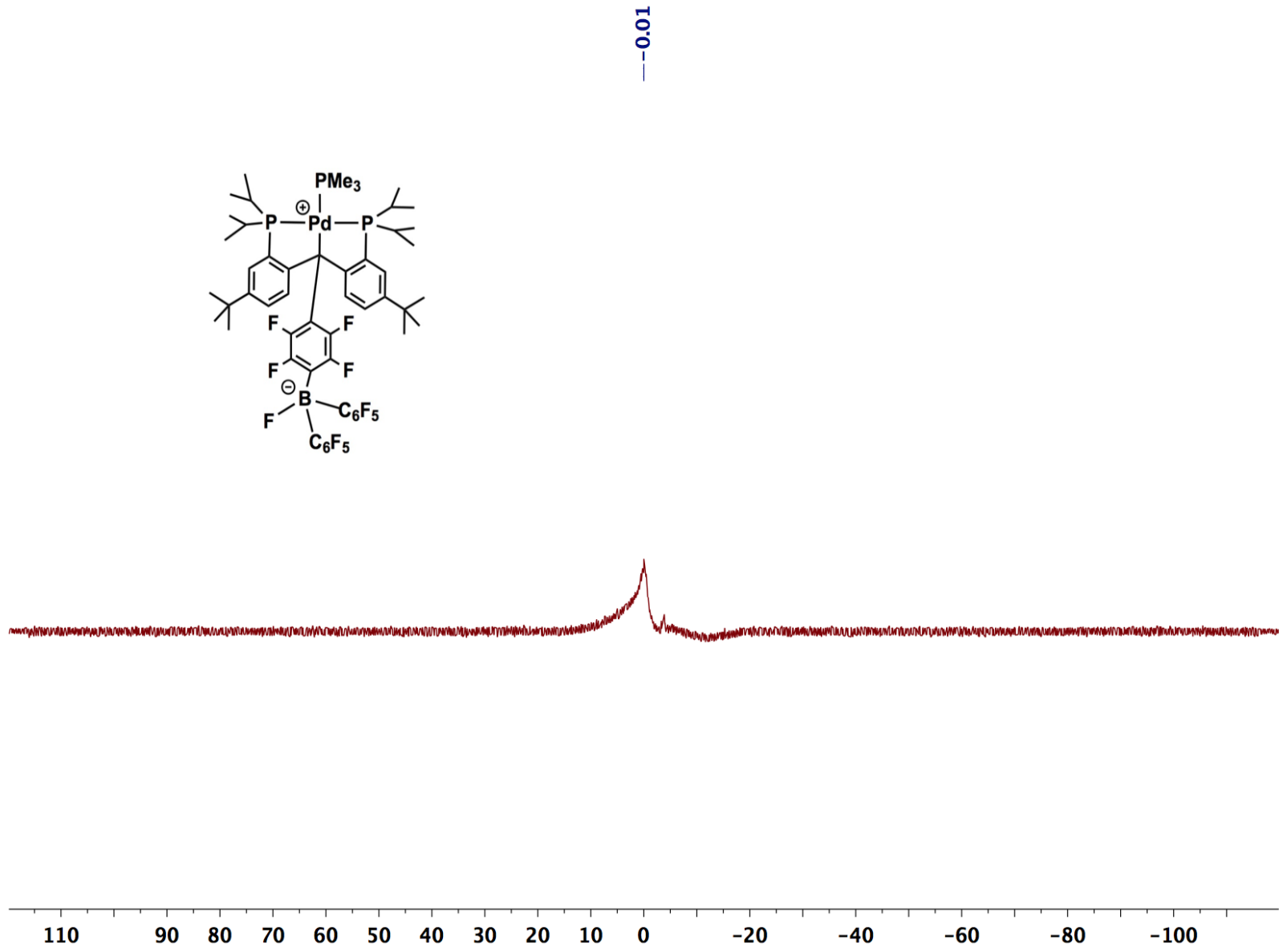


Figure S42. 25 °C $^{11}B\{^{1}H\}$ NMR spectrum for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

3.6 NMR Spectra for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] ([8][BAr$^F_4$])

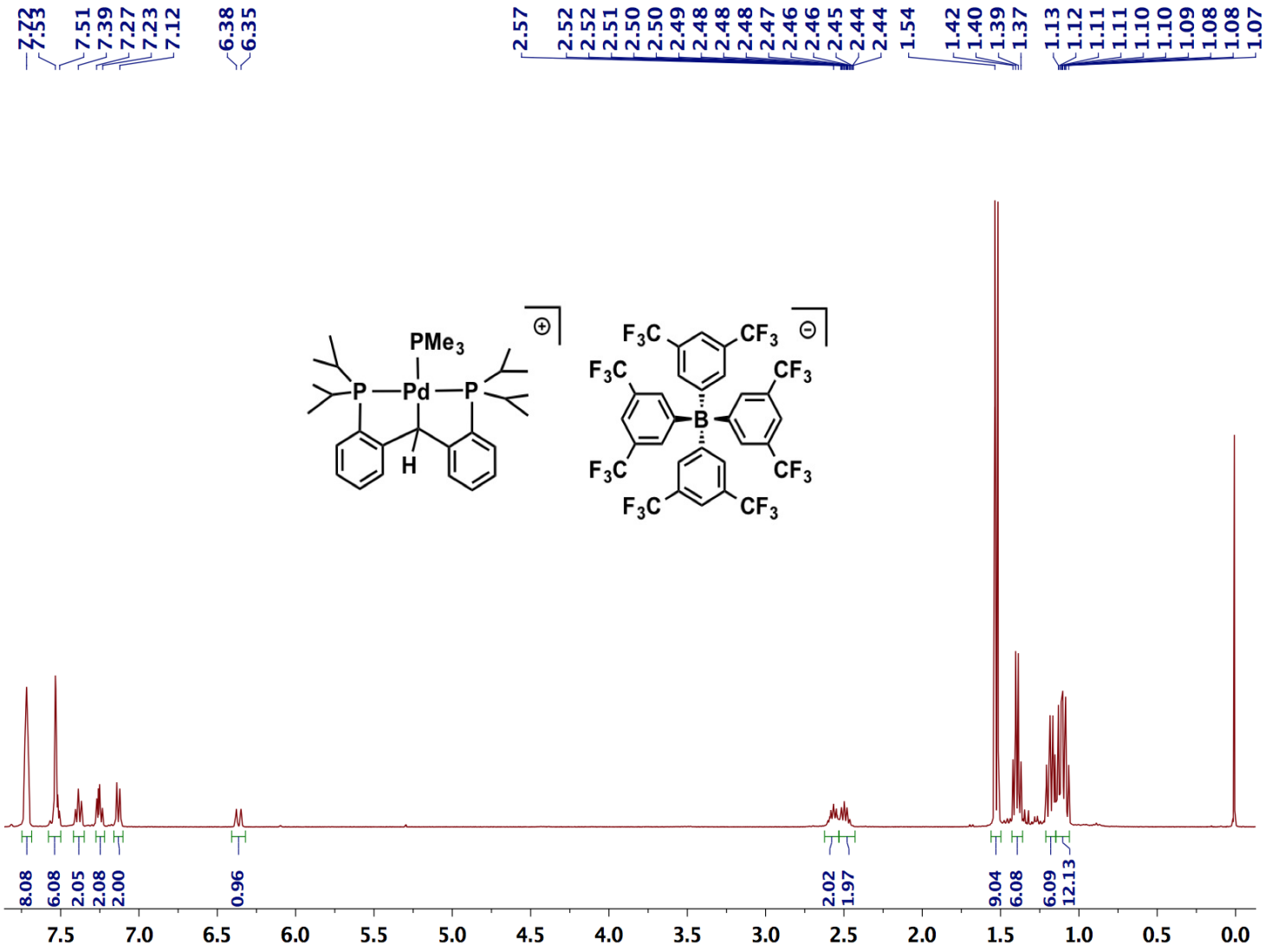


Figure S43. ^{1}H NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

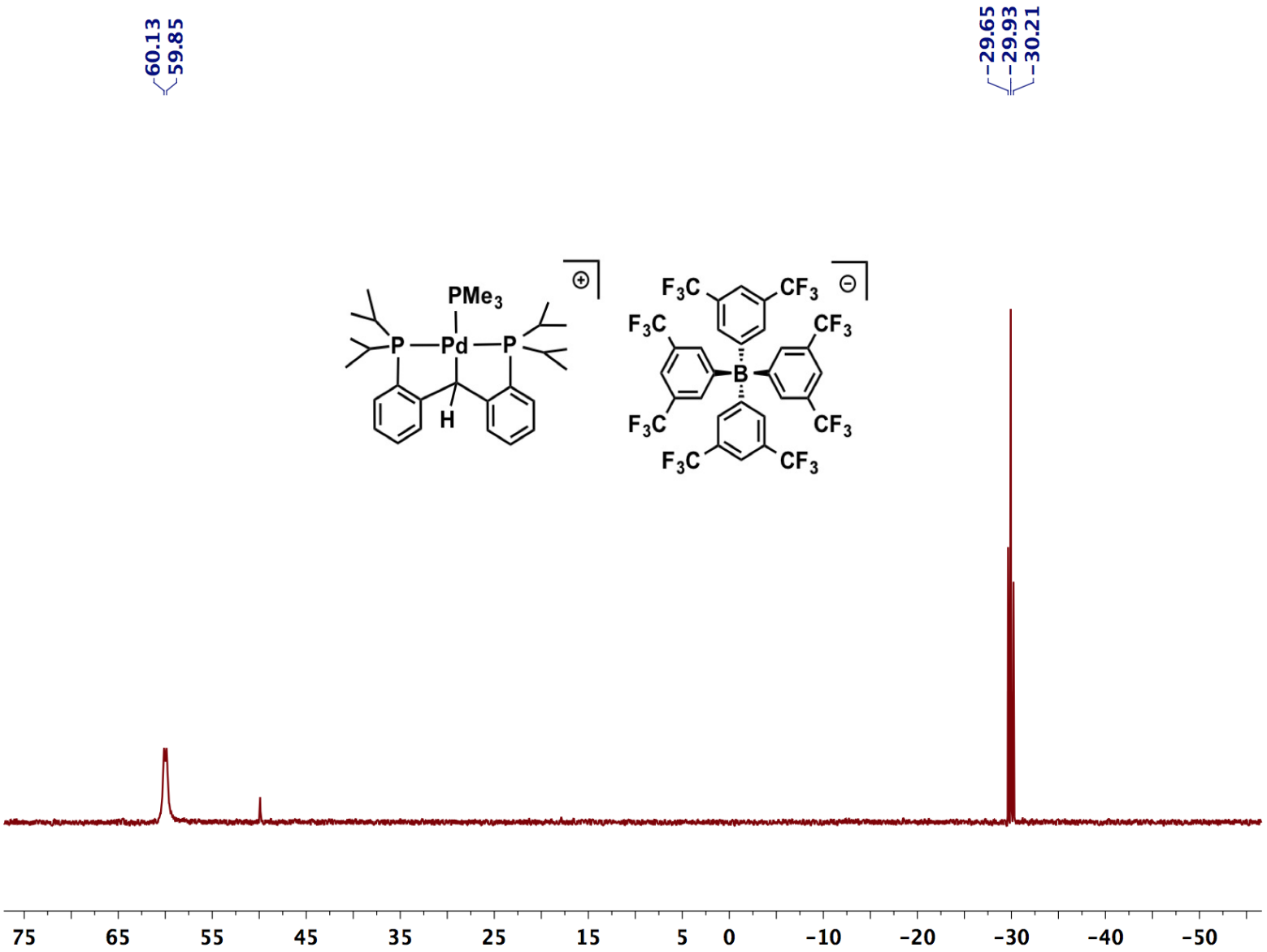


Figure S44. $^{31}P\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

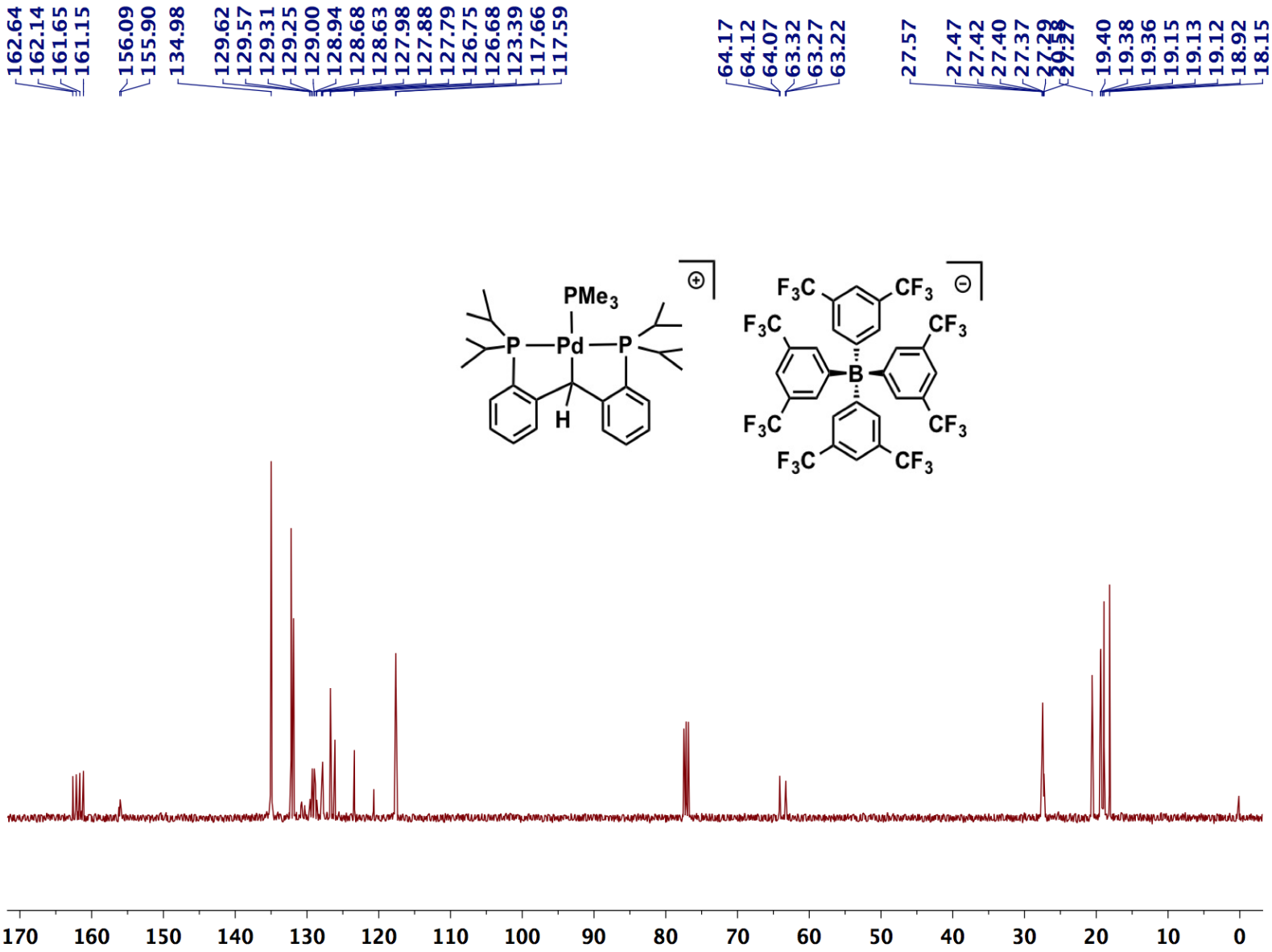


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

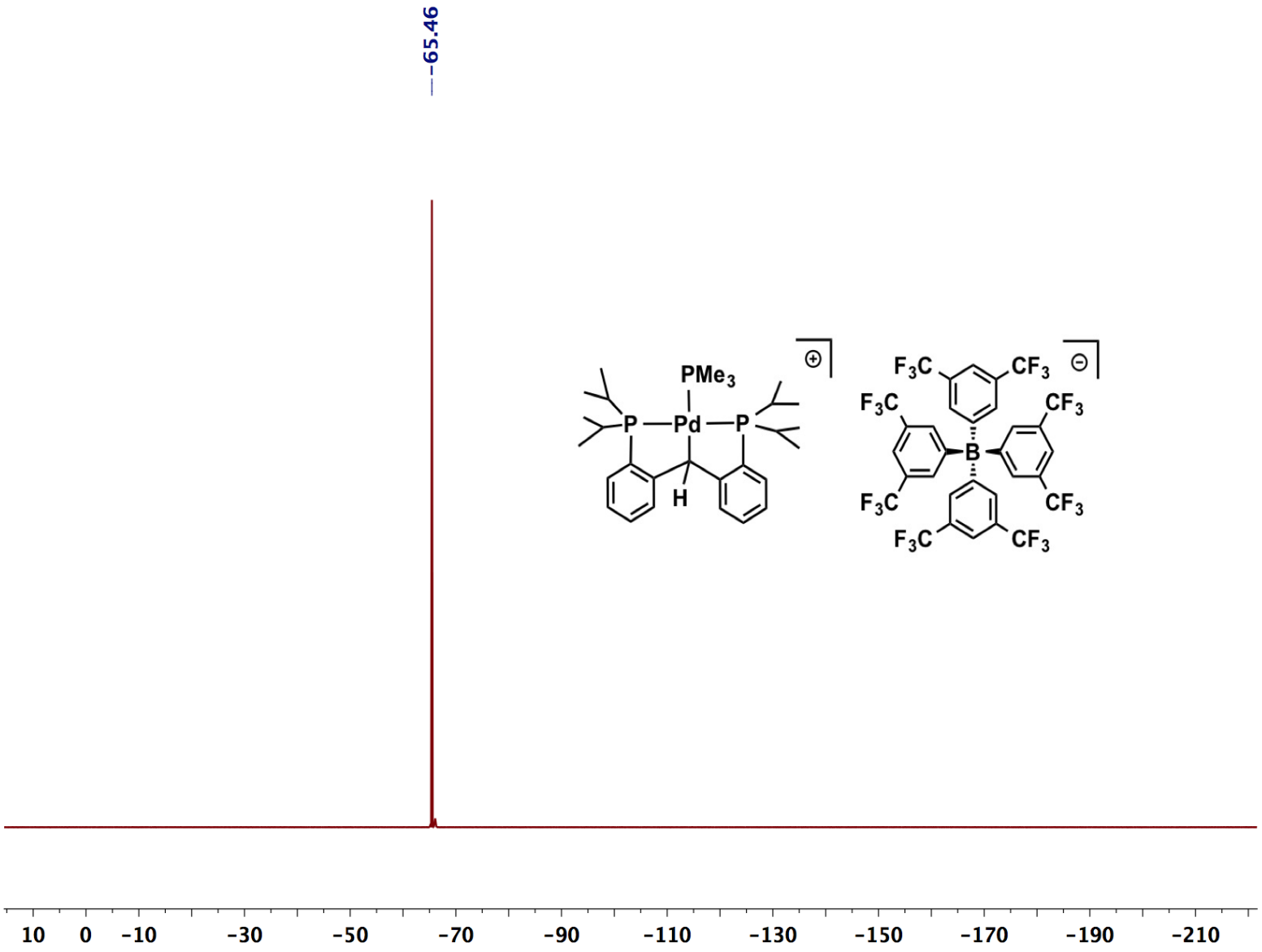


Figure S46. $^{19}F\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

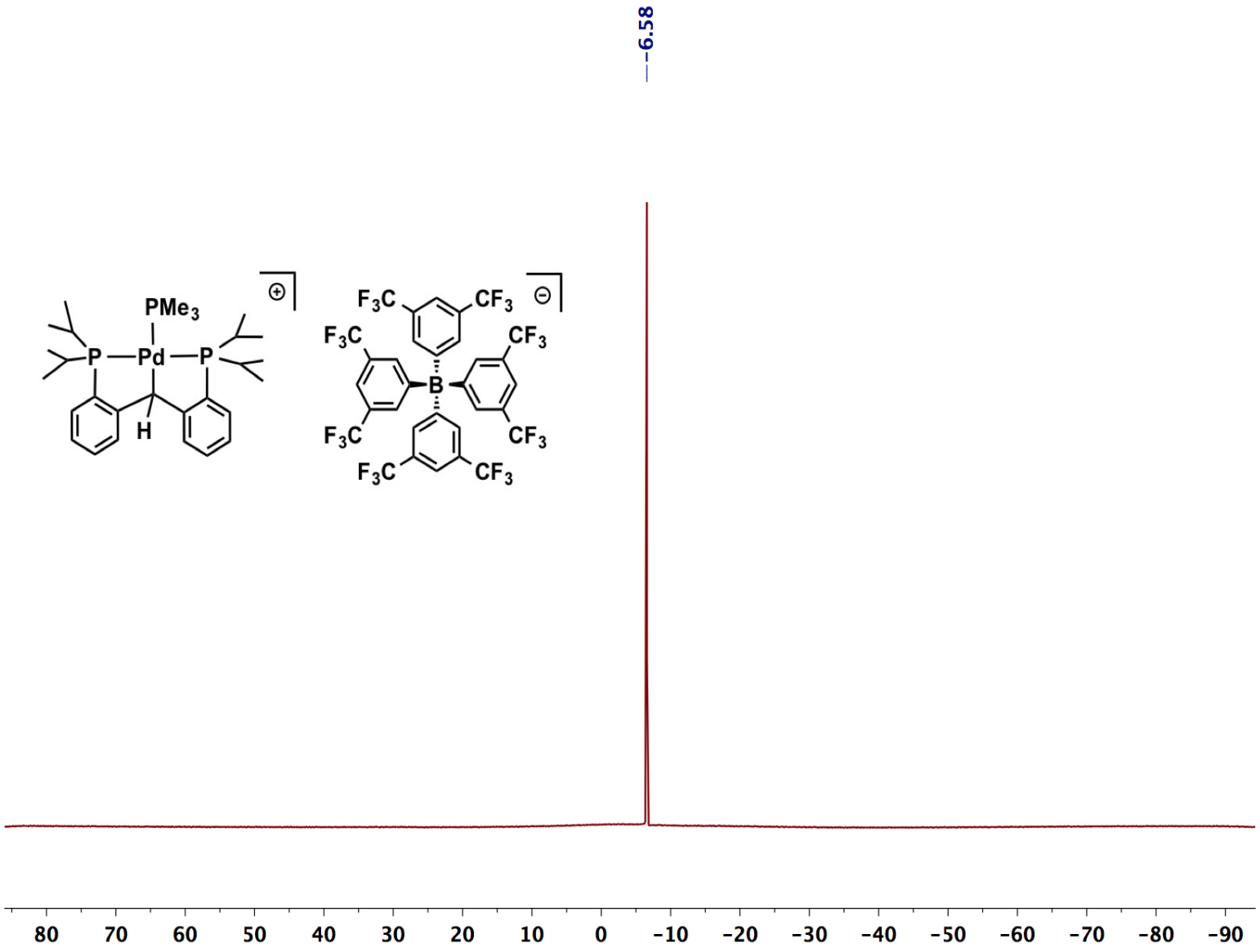


Figure S47. $^{11}B\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

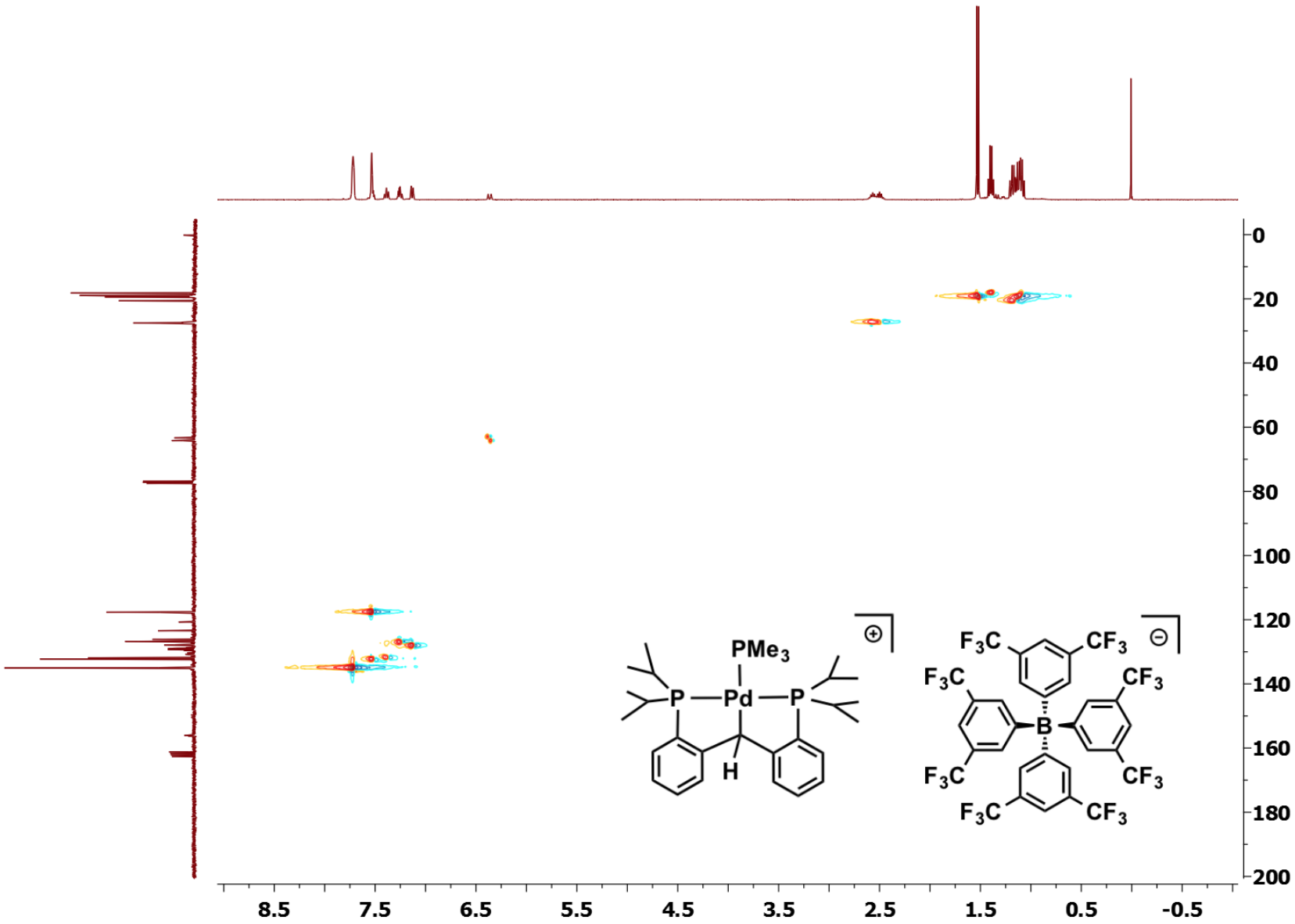


Figure S48. ^{1}H-^{13}C HSQC NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

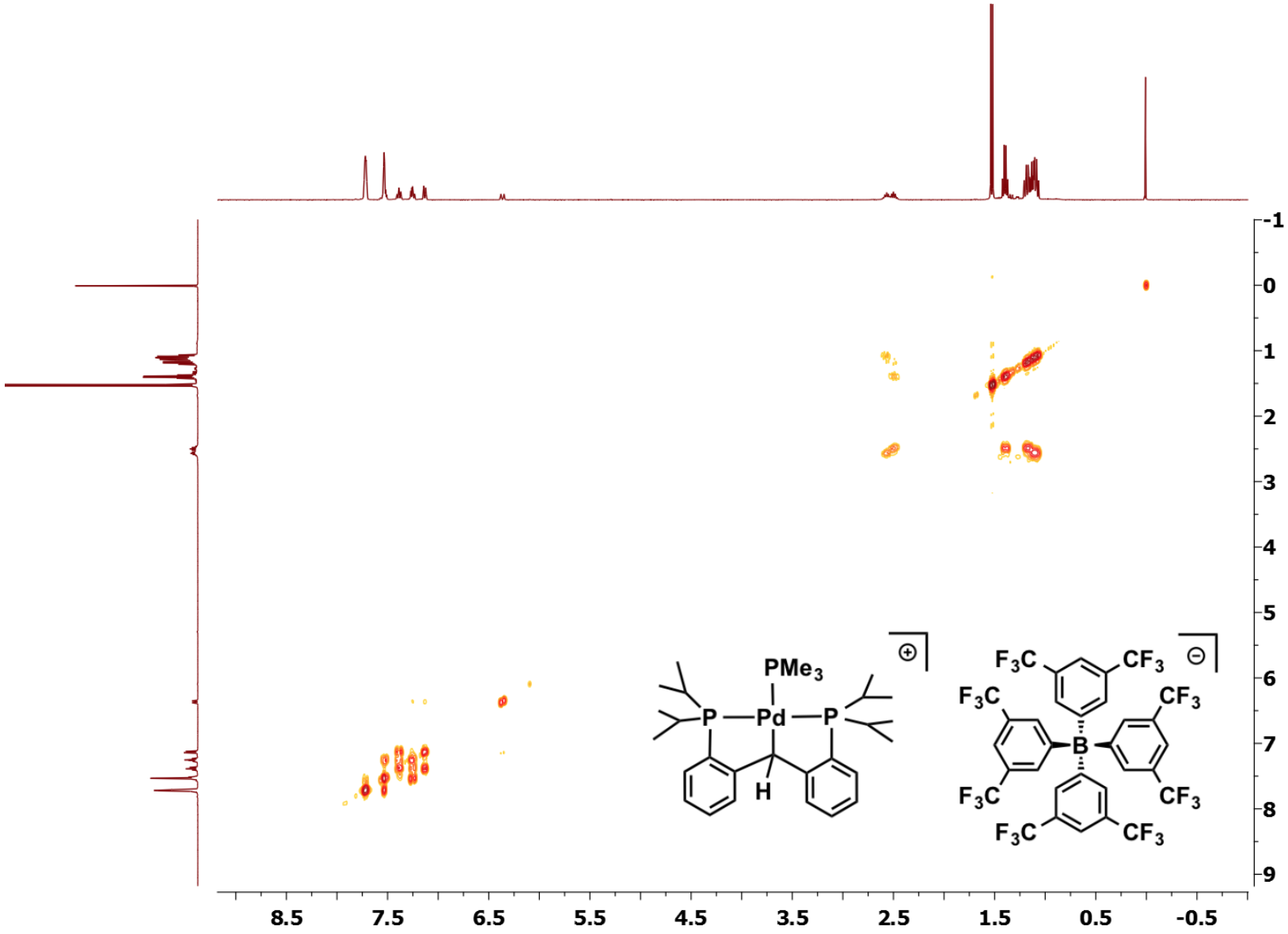


Figure S49. ^{1}H-^{1}H COSY NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

3.7 NMR Spectra for [{PC(sp^3)HP}PdPMe$_3$][HB(C_6F_5)$_3$] ([8][HB(C_6F_5)$_3$])

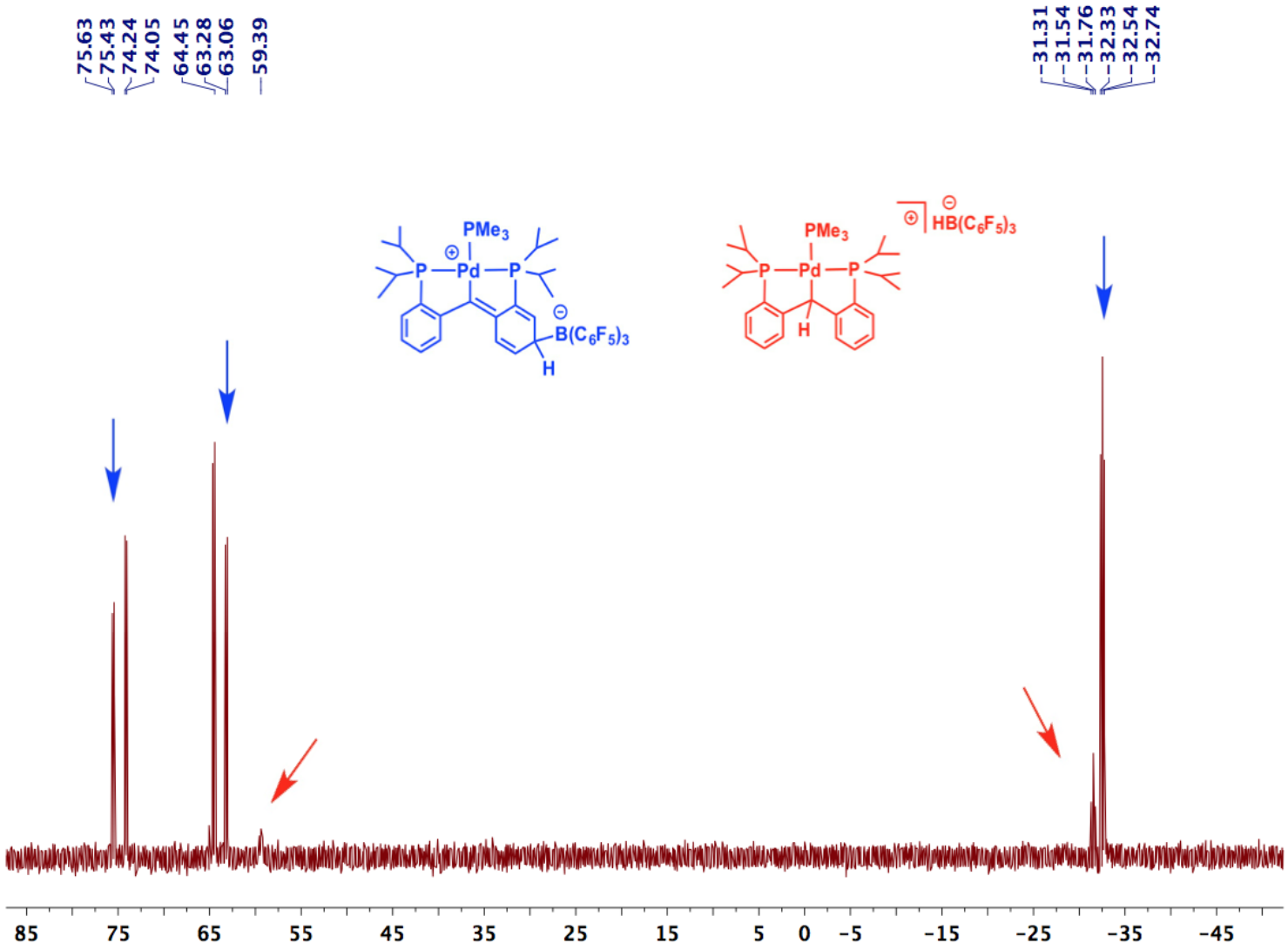


Figure S50. $^{31}P\{^1H\}$ NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][HB(C_6F_5)$_3$] (**[8][HB(C_6F_5)$_3$]**).

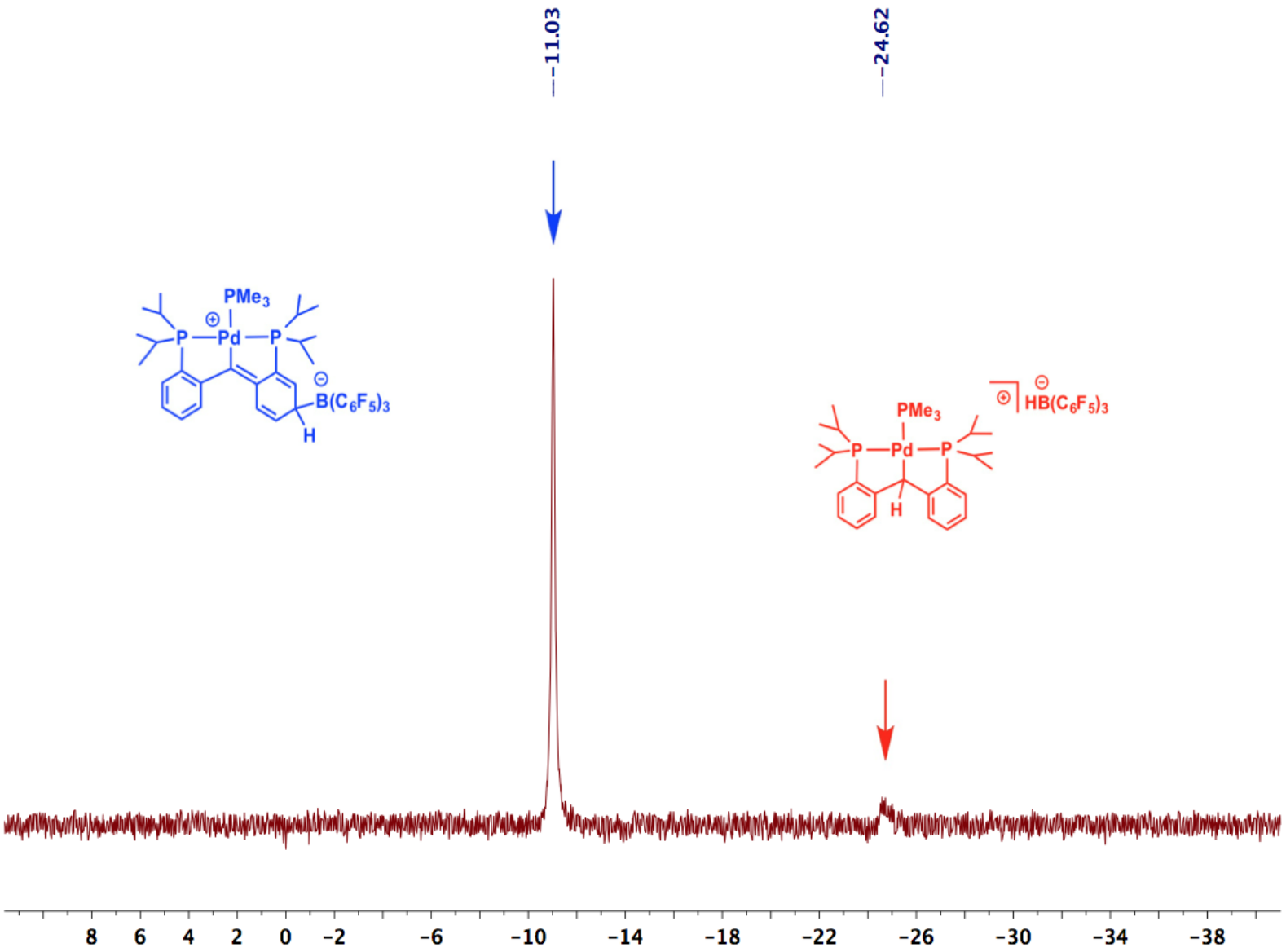


Figure S51. $^{11}B\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}PdPMe$_3$][HB(C$_6$F$_5$)$_3$] (**[8][HB(C$_6$F$_5$)$_3$]**).

3.8 NMR Spectra for [{PC(sp^3)HP}^{tBu}PdPMe$_3$][BAr$^F_4$] ([9][BAr$^F_4$])

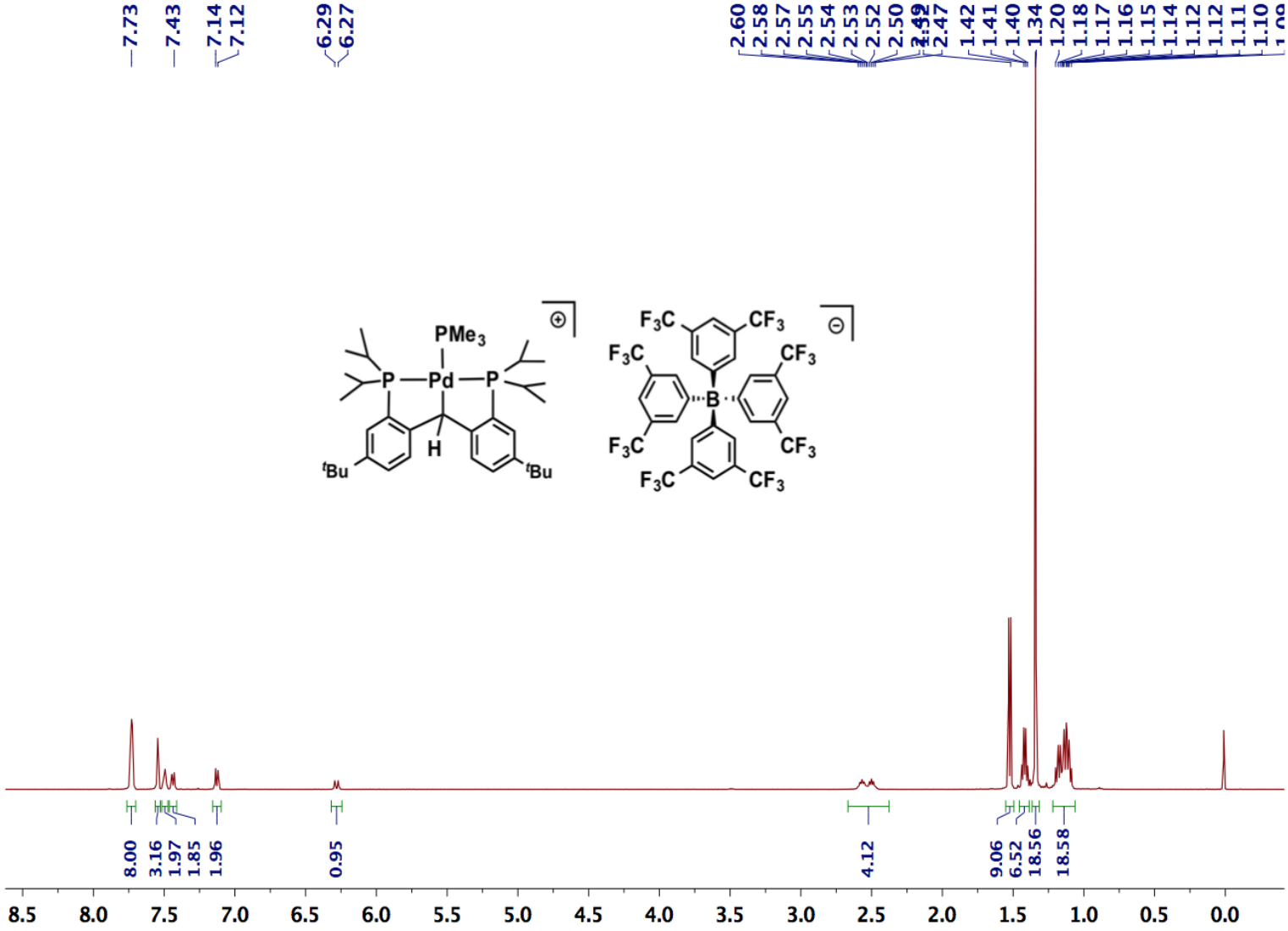


Figure S52. ^{1}H NMR spectrum for [{PC(sp^3)HP}^{tBu}PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**).

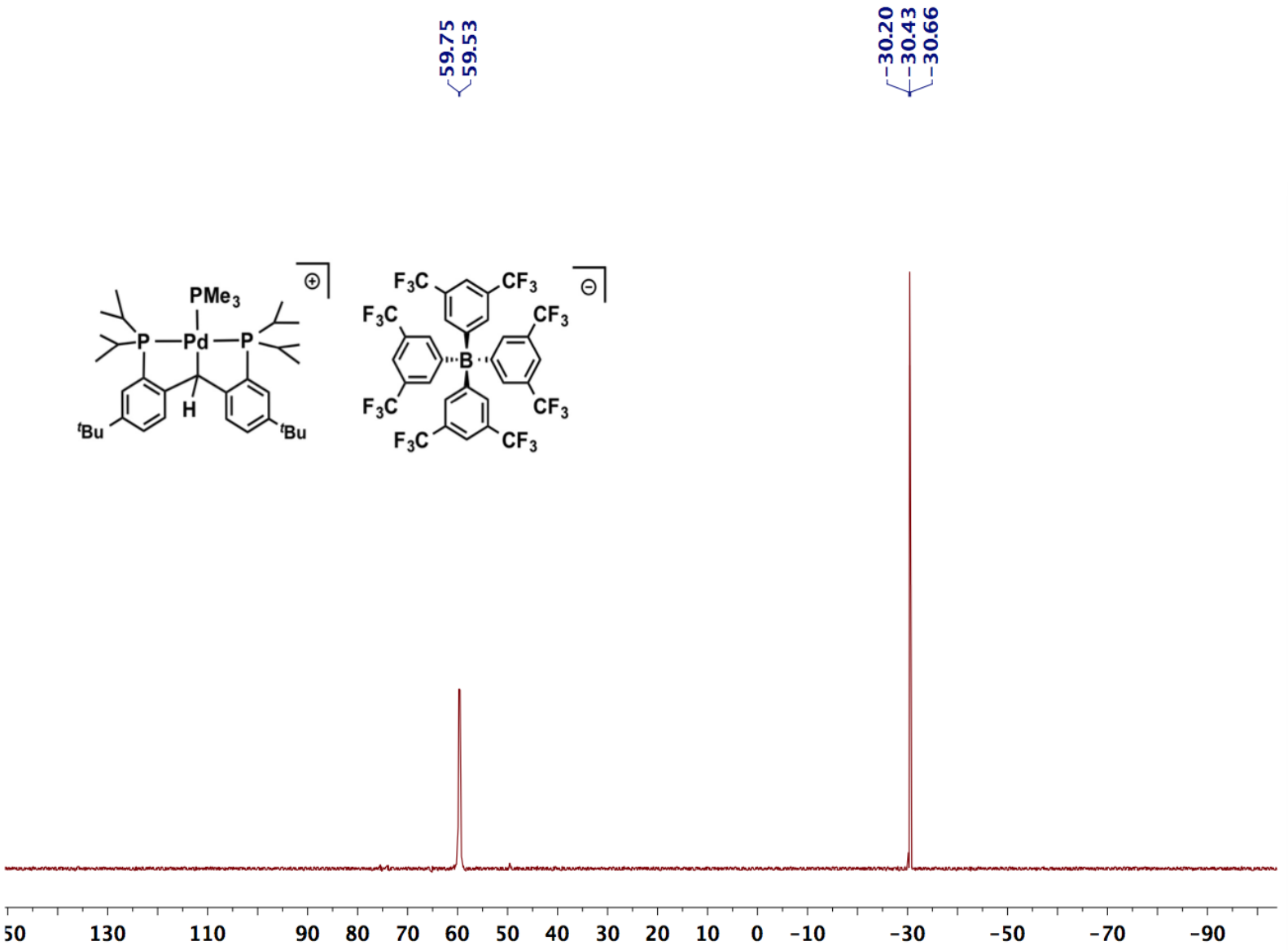


Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**).

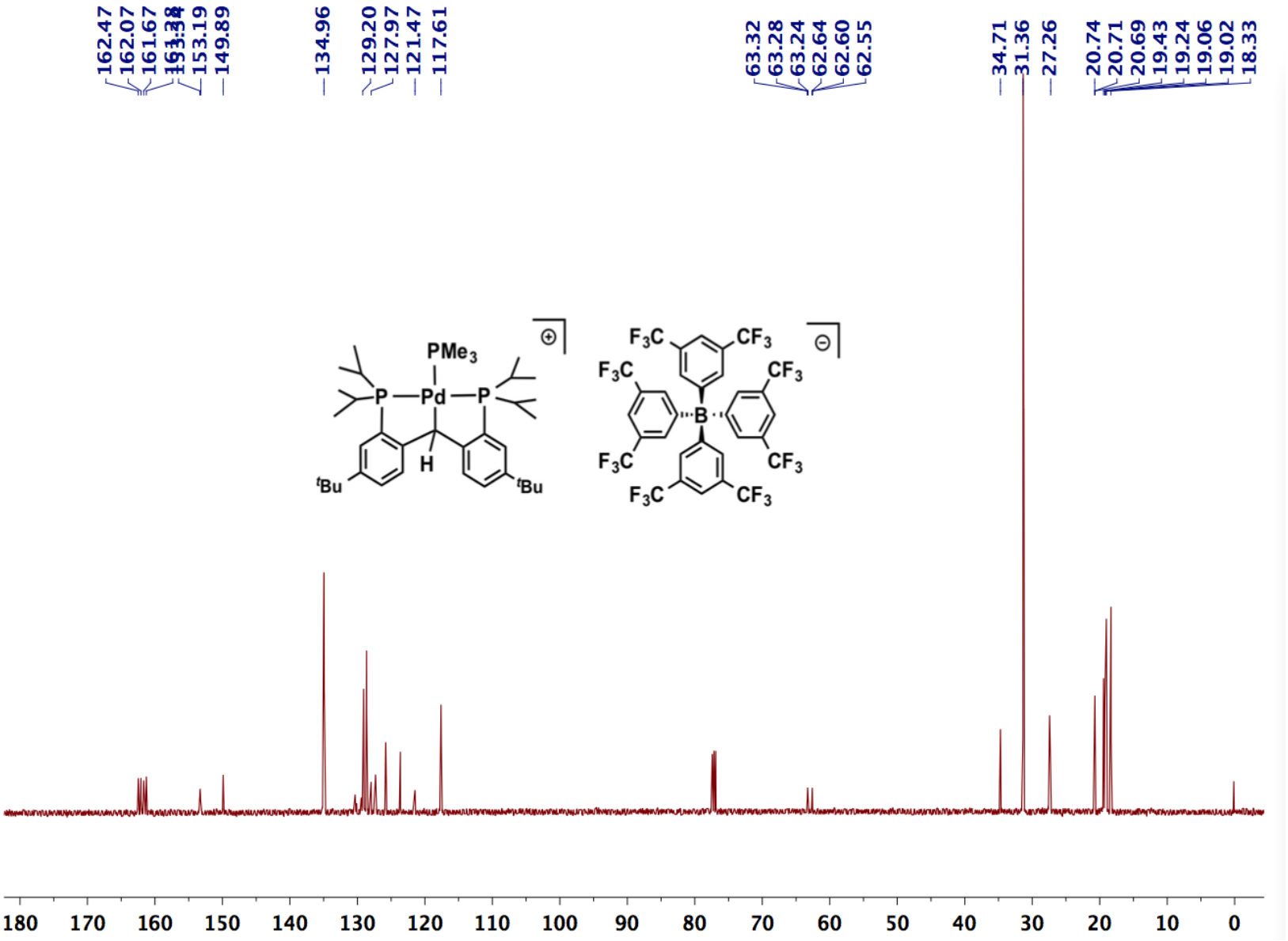


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**).

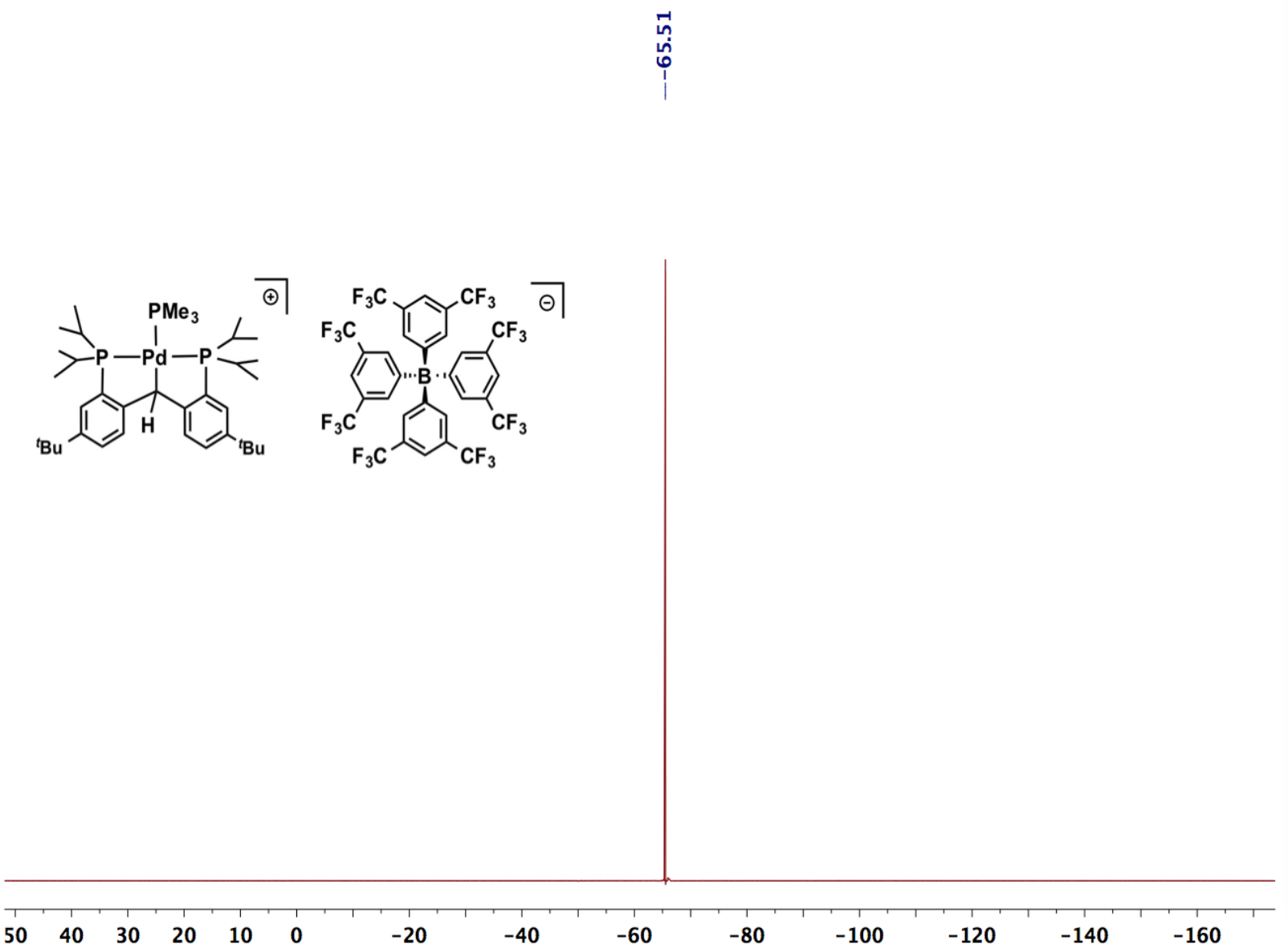


Figure S55. $^{19}F\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^{F}_4$] (**[9][BAr$^{F}_4$]**).

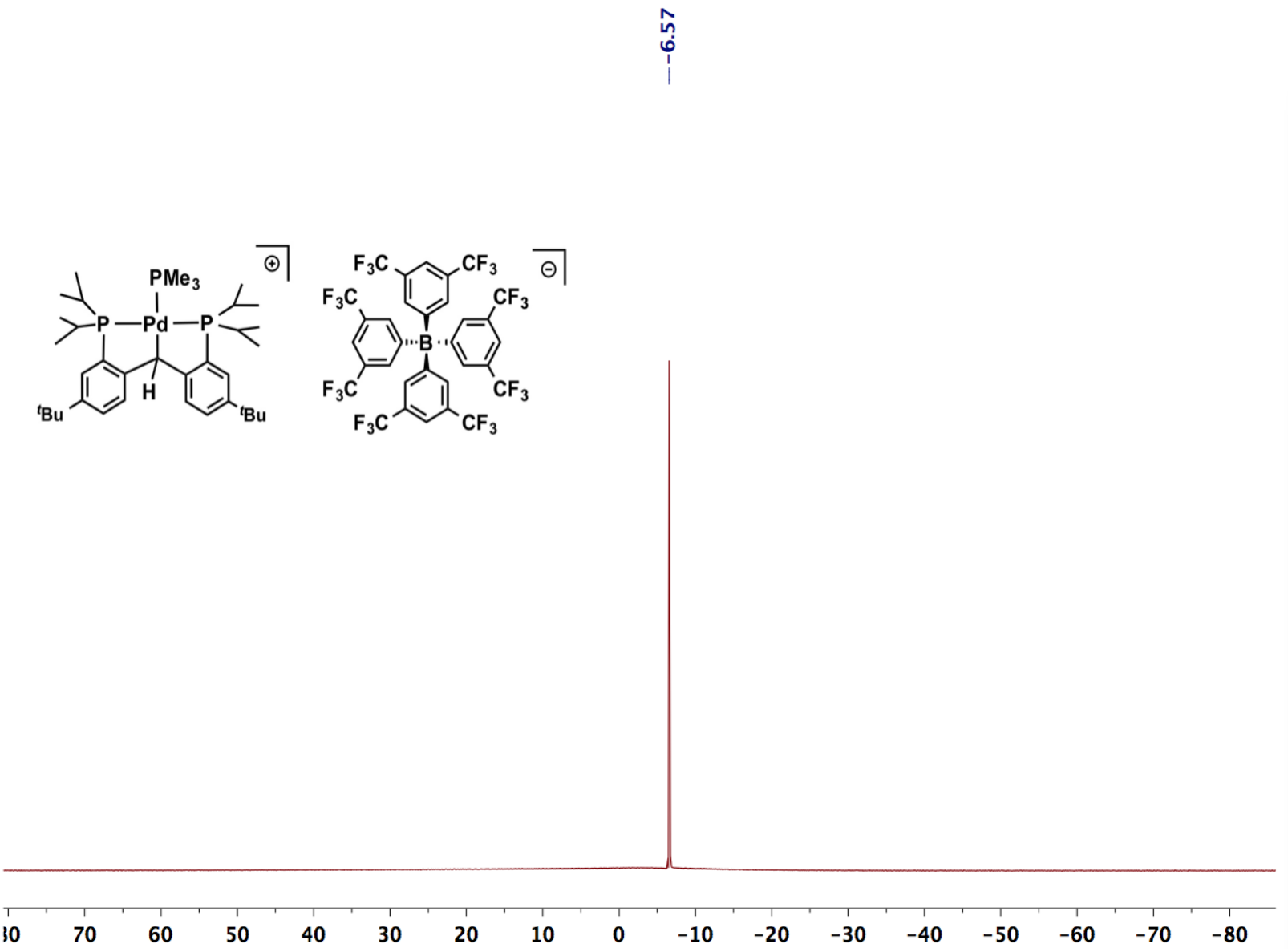


Figure S56. $^{11}B\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**).

3.9 NMR Spectra for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][HB(C$_6$F$_5$)$_3$] ([9][HB(C$_6$F$_5$)$_3$])

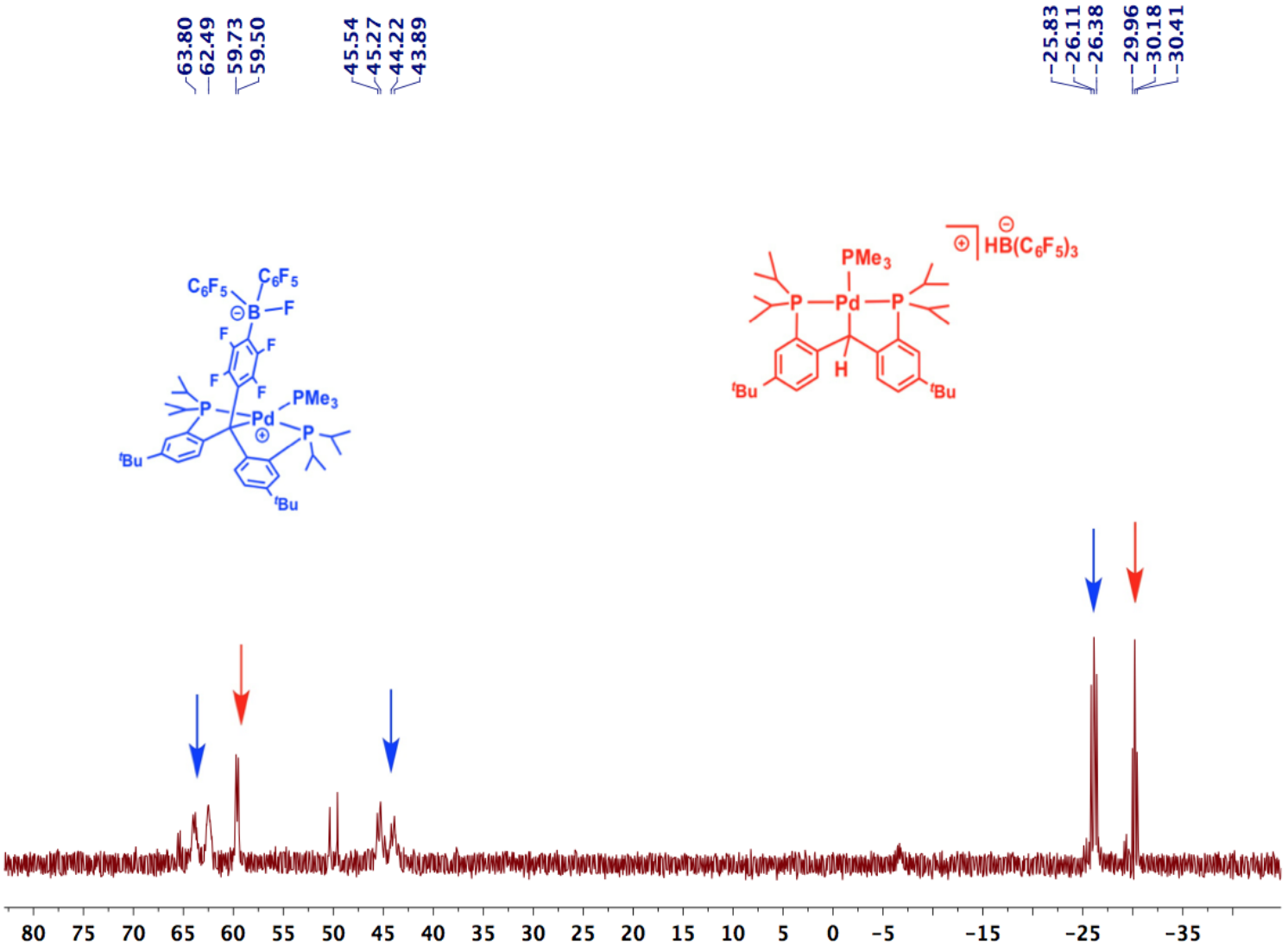


Figure S57. ^{31}P{^{1}H} NMR spectrum for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][HB(C$_6$F$_5$)$_3$] (**[9][HB(C$_6$F$_5$)$_3$]**).

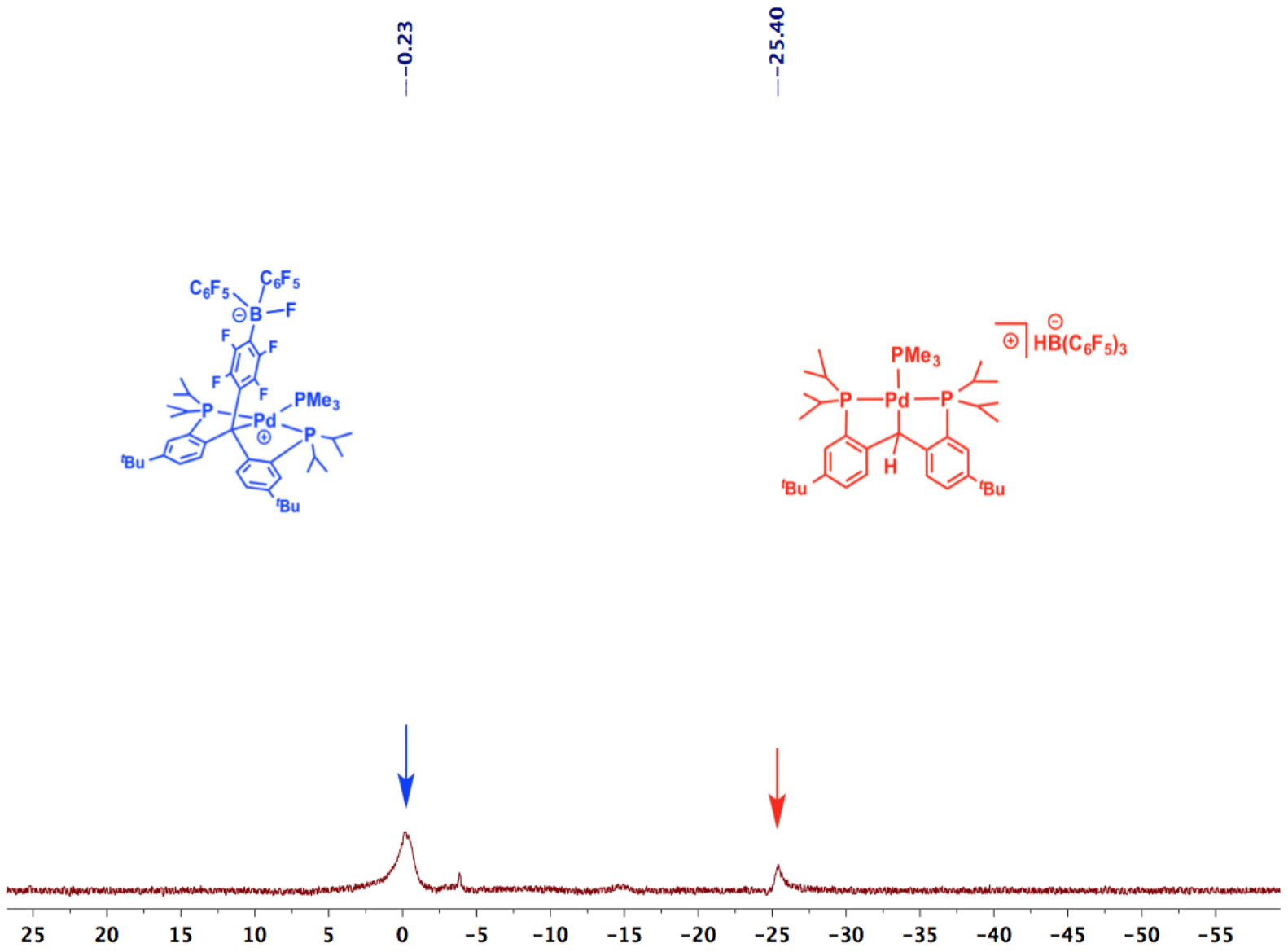


Figure S58. $^{11}B\{^{1}H\}$ NMR spectrum for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][HB(C_6F_5)$_3$] (**[9][HB(C_6F_5)$_3$]**).

4 Crystal Data

4.1 Crystal data for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (4)

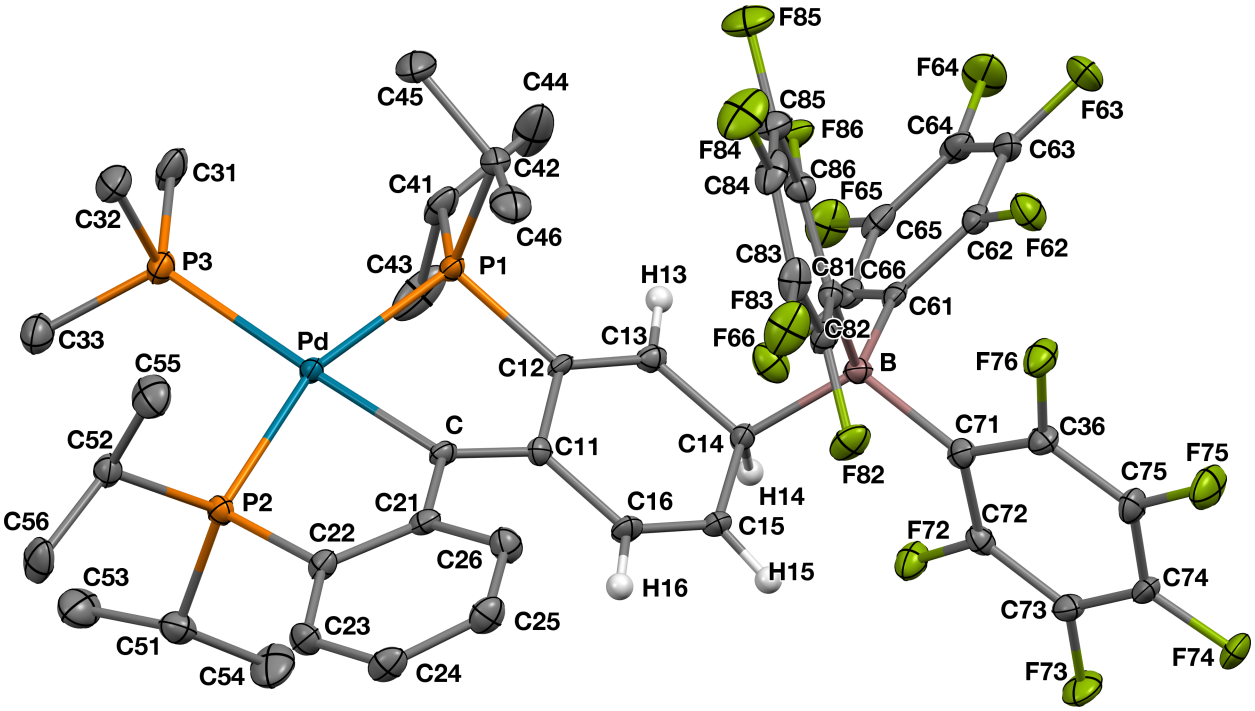


Figure S59. Thermal-ellipsoid (50% probability) representation of $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**). Most hydrogen atoms were omitted for clarity.

Table S7. Crystal data and structure refinement for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**).

Identification code:	cc197	
Empirical formula:	$C_{46}H_{45}BF_{15}P_3Pd$	
Formula weight:	1092.94	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/n$	
Unit cell dimensions:	a = 9.7351(4) Å	α = 90°
	b = 29.7778(12) Å	β = 104.9431(16)°
	c = 16.3484(6) Å	γ = 90°
Volume:	4579.0(3) Å^3	
Z:	4	
Density (calculated):	1.585 g·cm^{-3}	
Absorption coefficient (μ):	0.605 mm^{-1}	
F(000):	2208	
Crystal size:	0.08 × 0.05 × 0.02 mm^3	
θ range for data collection:	1.46 to 28.13°	
Index ranges:	$-12 \le h \le 7$, $-39 \le k \le 39$, $-21 \le l \le 21$	
Reflections collected:	88562	
Independent reflections:	11118 [R_{int} = 0.1029]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.9874 and 0.9809	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	11118 / 0 / 606	
Goodness-of-fit on F^2:	1.005	
Final R indices [I>2σ(I)]:	R_1 = 0.0399, wR_2 = 0.0651	
R indices (all data):	R_1 = 0.0814, wR_2 = 0.0749	
Largest diff. peak and hole:	0.486 and −0.604 e$^-$·Å^{-3}	

Table S8. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [$(C_6F_5)_3$B-PC(sp^2)P]^{H}Pd(PMe_3) (**4**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.04085(2)	0.86548(1)	0.76206(1)	0.011(1)
C	−0.1143(3)	0.83814(9)	0.81312(16)	0.012(1)
P(1)	0.08894(7)	0.78995(2)	0.75638(4)	0.013(1)
P(2)	−0.07381(8)	0.93128(2)	0.78231(4)	0.014(1)
P(3)	0.22990(8)	0.89747(2)	0.71584(5)	0.017(1)
C(11)	−0.1650(3)	0.79604(9)	0.79098(16)	0.013(1)
C(12)	−0.0818(3)	0.76522(9)	0.75394(16)	0.012(1)
C(13)	−0.1249(3)	0.72377(9)	0.72888(16)	0.014(1)
C(14)	−0.2630(3)	0.70389(8)	0.73445(17)	0.014(1)
C(15)	−0.3449(3)	0.73668(9)	0.77139(17)	0.015(1)
C(16)	−0.3003(3)	0.77775(9)	0.79883(17)	0.016(1)
C(21)	−0.1748(3)	0.86742(9)	0.86715(16)	0.014(1)
C(25)	−0.2943(3)	0.87930(10)	0.97793(18)	0.021(1)
C(24)	−0.3054(3)	0.92464(10)	0.95987(17)	0.020(1)
C(23)	−0.2457(3)	0.94189(9)	0.89884(17)	0.019(1)
C(22)	−0.1759(3)	0.91364(9)	0.85492(16)	0.014(1)
C(26)	−0.2306(3)	0.85075(9)	0.93218(17)	0.019(1)
C(31)	0.3291(3)	0.86472(10)	0.65720(19)	0.027(1)
C(32)	0.3708(3)	0.91530(10)	0.80586(19)	0.027(1)
C(33)	0.2019(3)	0.94762(10)	0.65048(19)	0.025(1)
C(36)	−0.3920(3)	0.60960(9)	0.87385(17)	0.016(1)
C(41)	0.1505(3)	0.76721(10)	0.66769(18)	0.022(1)
C(42)	0.2123(3)	0.76880(9)	0.85347(18)	0.019(1)
C(43)	0.0425(3)	0.77857(13)	0.58476(18)	0.037(1)
C(44)	0.1937(4)	0.71753(11)	0.6720(2)	0.040(1)
C(46)	0.1694(3)	0.78426(10)	0.93173(18)	0.026(1)
C(45)	0.3652(3)	0.78286(11)	0.8581(2)	0.032(1)
C(51)	−0.2085(3)	0.95525(10)	0.69220(18)	0.022(1)
C(52)	0.0414(3)	0.97719(9)	0.83649(17)	0.017(1)
C(53)	−0.1482(3)	0.97935(11)	0.6271(2)	0.031(1)
C(54)	−0.3101(3)	0.91813(11)	0.6505(2)	0.034(1)
C(55)	0.1237(3)	0.96073(10)	0.92394(18)	0.027(1)
C(56)	−0.0281(3)	1.02242(9)	0.8427(2)	0.027(1)
C(61)	−0.1736(3)	0.61597(9)	0.72866(17)	0.013(1)
C(62)	−0.1185(3)	0.57591(9)	0.76599(17)	0.015(1)
F(62)	−0.12013(17)	0.56754(5)	0.84709(10)	0.023(1)
C(63)	−0.0567(3)	0.54345(9)	0.72821(19)	0.019(1)
F(63)	−0.00088(17)	0.50615(5)	0.77089(11)	0.029(1)
C(64)	−0.0478(3)	0.54954(9)	0.6465(2)	0.022(1)

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Table S8. – continued from previous page

atom	x	y	x	U(eq)
F(64)	0.01618(19)	0.51862(6)	0.60862(12)	0.034(1)
C(65)	−0.1034(3)	0.58754(10)	0.60523(18)	0.019(1)
F(65)	−0.09543(18)	0.59445(6)	0.52488(10)	0.029(1)
C(66)	−0.1659(3)	0.61916(9)	0.64529(17)	0.016(1)
F(66)	−0.21694(17)	0.65528(5)	0.59682(9)	0.023(1)
B	−0.2334(3)	0.65435(10)	0.78526(19)	0.013(1)
C(71)	−0.3806(3)	0.63189(9)	0.80117(16)	0.014(1)
C(72)	−0.5055(3)	0.63006(9)	0.73677(16)	0.014(1)
F(72)	−0.51001(16)	0.64818(5)	0.66038(9)	0.022(1)
C(73)	−0.6286(3)	0.60933(9)	0.74327(18)	0.017(1)
F(73)	−0.74421(16)	0.60803(6)	0.67679(10)	0.027(1)
C(74)	−0.6328(3)	0.58790(9)	0.81636(18)	0.018(1)
F(74)	−0.74904(16)	0.56539(6)	0.82273(11)	0.026(1)
C(75)	−0.5134(3)	0.58836(9)	0.88228(17)	0.018(1)
F(76)	−0.27987(16)	0.60651(6)	0.94260(10)	0.023(1)
C(81)	−0.1123(3)	0.66568(9)	0.87376(16)	0.014(1)
C(82)	−0.1458(3)	0.68757(9)	0.94111(17)	0.017(1)
F(82)	−0.28359(16)	0.69685(5)	0.93801(10)	0.022(1)
C(83)	−0.0490(3)	0.70073(10)	1.01404(17)	0.021(1)
F(83)	−0.08992(19)	0.72309(6)	1.07497(10)	0.031(1)
C(84)	0.0922(3)	0.69091(10)	1.02467(17)	0.023(1)
F(84)	0.18930(18)	0.70317(6)	1.09544(10)	0.036(1)
C(85)	0.1330(3)	0.67013(10)	0.95981(18)	0.021(1)
F(85)	0.27153(17)	0.66190(6)	0.96700(11)	0.032(1)
C(86)	0.0329(3)	0.65946(9)	0.88688(17)	0.016(1)
F(86)	0.08590(16)	0.64206(5)	0.82485(10)	0.022(1)
F(75)	−0.51527(17)	0.56733(6)	0.95474(10)	0.029(1)
H(13)	−0.0636	0.7057	0.7059	0.016
H(14)	−0.3196	0.6976	0.6753	0.016
H(15)	−0.4364	0.7278	0.7759	0.018
H(16)	−0.3586	0.7957	0.8243	0.019
H(25)	−0.3308	0.8676	1.0222	0.025
H(24)	−0.3541	0.9439	0.9894	0.024
H(23)	−0.2521	0.9731	0.8867	0.023
H(26)	−0.2244	0.8196	0.9448	0.022
H(31A)	0.2633	0.8513	0.6076	0.040
H(31B)	0.3813	0.8409	0.6935	0.040
H(31C)	0.3964	0.8842	0.6388	0.040
H(32A)	0.4513	0.9265	0.7861	0.040
H(32B)	0.4016	0.8898	0.8440	0.040
H(32C)	0.3355	0.9393	0.8361	0.040
H(33A)	0.2935	0.9586	0.6443	0.037

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Table S8. – continued from previous page

atom	x	y	x	U(eq)
H(33B)	0.1569	0.9708	0.6773	0.037
H(33C)	0.1400	0.9405	0.5945	0.037
H(41)	0.2383	0.7845	0.6671	0.026
H(42)	0.2081	0.7352	0.8519	0.023
H(43A)	0.0814	0.7704	0.5371	0.055
H(43B)	0.0223	0.8109	0.5828	0.055
H(43C)	−0.0454	0.7618	0.5810	0.055
H(44A)	0.1084	0.6987	0.6618	0.060
H(44B)	0.2556	0.7109	0.7282	0.060
H(44C)	0.2447	0.7113	0.6289	0.060
H(46A)	0.1753	0.8171	0.9356	0.039
H(46B)	0.2335	0.7710	0.9822	0.039
H(46C)	0.0716	0.7747	0.9280	0.039
H(45A)	0.3902	0.7734	0.8063	0.048
H(45B)	0.4299	0.7687	0.9072	0.048
H(45C)	0.3736	0.8156	0.8636	0.048
H(51)	−0.2647	0.9777	0.7156	0.026
H(52)	0.1134	0.9825	0.8036	0.020
H(53A)	−0.1022	0.9575	0.5980	0.047
H(53B)	−0.0783	1.0017	0.6556	0.047
H(53C)	−0.2254	0.9944	0.5857	0.047
H(54A)	−0.3897	0.9312	0.6078	0.052
H(54B)	−0.3465	0.9026	0.6935	0.052
H(54C)	−0.2597	0.8966	0.6233	0.052
H(55A)	0.1621	0.9307	0.9189	0.041
H(55B)	0.0598	0.9594	0.9614	0.041
H(55C)	0.2020	0.9815	0.9476	0.041
H(56A)	−0.0790	1.0325	0.7859	0.040
H(56B)	0.0452	1.0444	0.8682	0.040
H(56C)	−0.0953	1.0194	0.8778	0.040

Table S9. Anisotropic displacement parameters (Å^2) for [$(C_6F_5)_3$B-PC(sp^2)P]^{H}Pd(PMe_3) (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0105(1)	0.0102(1)	0.0147(1)	−0.0013(1)	0.0050(1)	−0.0014(1)
C	0.0097(14)	0.0151(14)	0.0134(13)	0.0017(11)	0.0053(11)	0.0006(11)
P(1)	0.0101(3)	0.0116(4)	0.0178(4)	−0.0021(3)	0.0058(3)	−0.0012(3)
P(2)	0.0146(4)	0.0108(4)	0.0171(4)	−0.0014(3)	0.0051(3)	−0.0005(3)
P(3)	0.0158(4)	0.0165(4)	0.0200(4)	−0.0002(3)	0.0072(3)	−0.0034(3)
C(11)	0.0130(14)	0.0128(14)	0.0147(13)	0.0035(11)	0.0052(11)	0.0007(11)
C(12)	0.0062(13)	0.0145(14)	0.0145(14)	0.0008(11)	0.0038(11)	−0.0013(11)
C(13)	0.0121(14)	0.0164(15)	0.0136(14)	0.0011(11)	0.0052(11)	0.0011(11)
C(14)	0.0118(14)	0.0111(14)	0.0194(14)	−0.0010(11)	0.0067(12)	−0.0018(11)
C(15)	0.0096(14)	0.0146(15)	0.0222(15)	0.0013(12)	0.0061(12)	0.0004(11)
C(16)	0.0122(15)	0.0158(15)	0.0238(15)	−0.0011(12)	0.0101(12)	0.0006(12)
C(21)	0.0087(13)	0.0172(14)	0.0162(13)	−0.0026(12)	0.0030(11)	−0.0011(12)
C(25)	0.0206(16)	0.0251(17)	0.0187(15)	−0.0016(12)	0.0103(13)	−0.0023(13)
C(24)	0.0185(16)	0.0227(17)	0.0209(15)	−0.0079(12)	0.0100(13)	−0.0017(13)
C(23)	0.0190(16)	0.0126(14)	0.0258(16)	−0.0044(12)	0.0074(13)	0.0007(12)
C(22)	0.0131(14)	0.0147(14)	0.0159(14)	−0.0035(11)	0.0061(12)	−0.0031(11)
C(26)	0.0225(16)	0.0162(15)	0.0190(15)	0.0014(12)	0.0080(13)	0.0009(12)
C(31)	0.0238(17)	0.0247(16)	0.0381(18)	−0.0032(15)	0.0199(14)	−0.0081(15)
C(32)	0.0197(16)	0.0248(18)	0.0338(18)	0.0031(14)	0.0035(14)	−0.0053(14)
C(33)	0.0240(17)	0.0238(17)	0.0263(17)	0.0046(13)	0.0072(14)	−0.0043(14)
C(36)	0.0125(14)	0.0163(15)	0.0190(15)	−0.0007(12)	0.0012(12)	−0.0012(12)
C(41)	0.0181(16)	0.0226(16)	0.0300(17)	−0.0086(13)	0.0154(14)	−0.0058(13)
C(42)	0.0119(15)	0.0149(15)	0.0296(17)	0.0044(12)	0.0028(13)	0.0004(12)
C(43)	0.0298(19)	0.066(3)	0.0201(17)	−0.0166(17)	0.0154(15)	−0.0200(18)
C(44)	0.042(2)	0.0248(19)	0.068(3)	−0.0181(18)	0.041(2)	−0.0080(16)
C(46)	0.0243(17)	0.0270(18)	0.0219(16)	0.0036(13)	−0.0027(14)	0.0008(14)
C(45)	0.0144(16)	0.0334(19)	0.044(2)	0.0121(16)	0.0002(15)	−0.0003(14)
C(51)	0.0191(16)	0.0203(16)	0.0247(16)	0.0007(13)	0.0050(13)	0.0042(13)
C(52)	0.0177(15)	0.0137(15)	0.0206(15)	−0.0005(12)	0.0073(12)	−0.0024(12)
C(53)	0.0271(18)	0.037(2)	0.0272(18)	0.0110(15)	0.0038(15)	0.0030(15)
C(54)	0.0237(18)	0.040(2)	0.0316(19)	0.0046(16)	−0.0083(15)	−0.0096(16)
C(55)	0.0280(18)	0.0249(18)	0.0259(17)	−0.0039(14)	0.0004(14)	−0.0053(14)
C(56)	0.0314(18)	0.0139(15)	0.0390(19)	−0.0081(14)	0.0173(15)	−0.0063(14)
C(61)	0.0079(13)	0.0128(13)	0.0185(14)	−0.0020(11)	0.0028(11)	−0.0034(11)
C(62)	0.0118(14)	0.0146(14)	0.0192(15)	−0.0010(12)	0.0034(12)	−0.0022(11)
F(62)	0.0287(10)	0.0185(9)	0.0225(9)	0.0056(7)	0.0081(8)	0.0040(7)
C(63)	0.0134(15)	0.0118(14)	0.0323(18)	0.0009(13)	0.0072(13)	−0.0002(12)
F(63)	0.0269(10)	0.0144(9)	0.0478(11)	0.0051(8)	0.0118(9)	0.0067(7)
C(64)	0.0150(15)	0.0154(15)	0.0375(19)	−0.0107(13)	0.0128(14)	−0.0031(12)
F(64)	0.0356(11)	0.0218(10)	0.0530(12)	−0.0120(9)	0.0266(10)	0.0039(8)

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Table S9. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(65)	0.0126(15)	0.0236(16)	0.0218(16)	−0.0046(13)	0.0069(12)	−0.0071(12)
F(65)	0.0354(11)	0.0323(10)	0.0232(9)	−0.0084(8)	0.0172(8)	−0.0043(9)
C(66)	0.0119(14)	0.0138(14)	0.0204(15)	−0.0016(12)	0.0016(12)	−0.0025(11)
F(66)	0.0304(10)	0.0202(9)	0.0178(9)	0.0015(7)	0.0072(8)	0.0039(8)
B	0.0104(16)	0.0130(15)	0.0153(16)	−0.0006(13)	0.0034(13)	0.0010(13)
C(71)	0.0138(14)	0.0120(13)	0.0172(14)	−0.0032(12)	0.0038(11)	−0.0010(12)
C(72)	0.0175(15)	0.0129(14)	0.0134(13)	0.0023(11)	0.0058(11)	0.0025(12)
F(72)	0.0193(9)	0.0265(10)	0.0172(8)	0.0041(7)	0.0019(7)	−0.0063(7)
C(73)	0.0108(14)	0.0171(15)	0.0228(15)	−0.0001(12)	0.0017(12)	0.0008(12)
F(73)	0.0135(9)	0.0347(11)	0.0284(10)	0.0042(8)	−0.0042(8)	−0.0066(8)
C(74)	0.0099(14)	0.0151(15)	0.0295(16)	0.0004(12)	0.0074(13)	−0.0018(12)
F(74)	0.0139(9)	0.0265(10)	0.0402(11)	0.0081(8)	0.0091(8)	−0.0064(8)
C(75)	0.0189(16)	0.0182(15)	0.0204(15)	0.0043(12)	0.0103(13)	−0.0021(12)
F(76)	0.0178(9)	0.0308(10)	0.0196(9)	0.0064(7)	0.0006(7)	−0.0066(8)
C(81)	0.0138(15)	0.0112(14)	0.0162(14)	0.0006(11)	0.0048(12)	−0.0026(11)
C(82)	0.0156(15)	0.0162(15)	0.0215(15)	−0.0009(12)	0.0096(12)	−0.0031(12)
F(82)	0.0182(9)	0.0273(10)	0.0246(9)	−0.0075(7)	0.0120(7)	−0.0022(7)
C(83)	0.0300(18)	0.0213(16)	0.0141(14)	−0.0025(12)	0.0111(13)	−0.0058(13)
F(83)	0.0385(11)	0.0387(11)	0.0193(9)	−0.0130(8)	0.0143(8)	−0.0120(9)
C(84)	0.0235(17)	0.0272(17)	0.0130(14)	−0.0003(13)	−0.0019(13)	−0.0117(14)
F(84)	0.0314(11)	0.0529(13)	0.0178(9)	−0.0070(8)	−0.0029(8)	−0.0142(9)
C(85)	0.0131(15)	0.0240(16)	0.0237(16)	0.0026(13)	0.0030(13)	−0.0002(13)
F(85)	0.0134(9)	0.0442(12)	0.0338(10)	−0.0031(9)	−0.0018(8)	0.0013(8)
C(86)	0.0173(15)	0.0148(15)	0.0171(14)	0.0002(11)	0.0043(12)	−0.0001(12)
F(86)	0.0124(8)	0.0284(10)	0.0262(9)	−0.0094(8)	0.0066(7)	−0.0003(7)
F(75)	0.0246(10)	0.0390(11)	0.0257(10)	0.0130(8)	0.0084(8)	−0.0072(8)

Table S10. Distances [Å] for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**).

atom – atom	distance	atom – atom	distance
Pd – C	2.071(3)	Pd – P(1)	2.3039(7)
Pd – P(2)	2.3208(7)	Pd – P(3)	2.3627(8)
C – C(11)	1.362(4)	C – C(21)	1.468(4)
P(1) – C(12)	1.809(3)	P(1) – C(41)	1.835(3)
P(1) – C(42)	1.837(3)	P(2) – C(22)	1.812(3)
P(2) – C(52)	1.843(3)	P(2) – C(51)	1.845(3)
P(3) – C(31)	1.811(3)	P(3) – C(32)	1.813(3)
P(3) – C(33)	1.815(3)	C(11) – C(12)	1.455(4)
C(11) – C(16)	1.462(4)	C(12) – C(13)	1.334(4)
C(13) – C(14)	1.492(4)	C(13) – H(13)	0.9500
C(14) – C(15)	1.484(4)	C(14) – B	1.681(4)
C(14) – H(14)	1.0000	C(15) – C(16)	1.336(4)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(22)	1.391(4)	C(21) – C(26)	1.403(4)
C(25) – C(24)	1.380(4)	C(25) – C(26)	1.381(4)
C(25) – H(25)	0.9500	C(24) – C(23)	1.378(4)
C(24) – H(24)	0.9500	C(23) – C(22)	1.391(4)
C(23) – H(23)	0.9500	C(26) – H(26)	0.9500
C(31) – H(31A)	0.9800	C(31) – H(31B)	0.9800
C(31) – H(31C)	0.9800	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(36) – F(76)	1.353(3)
C(36) – C(75)	1.378(4)	C(36) – C(71)	1.390(4)
C(41) – C(43)	1.524(4)	C(41) – C(44)	1.535(4)
C(41) – H(41)	1.0000	C(42) – C(46)	1.516(4)
C(42) – C(45)	1.529(4)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(51) – C(53)	1.521(4)	C(51) – C(54)	1.523(4)
C(51) – H(51)	1.0000	C(52) – C(56)	1.522(4)
C(52) – C(55)	1.528(4)	C(52) – H(52)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(55) – H(55C)	0.9800	C(56) – H(56A)	0.9800

Continued on next page

Table S10. – continued from previous page

atom – atom	distance	atom – atom	distance
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800
C(61) – C(62)	1.384(4)	C(61) – C(66)	1.387(4)
C(61) – B	1.667(4)	C(62) – F(62)	1.353(3)
C(62) – C(63)	1.367(4)	C(63) – F(63)	1.349(3)
C(63) – C(64)	1.372(4)	C(64) – F(64)	1.349(3)
C(64) – C(65)	1.357(4)	C(65) – F(65)	1.352(3)
C(65) – C(66)	1.375(4)	C(66) – F(66)	1.352(3)
B – C(81)	1.648(4)	B – C(71)	1.662(4)
C(71) – C(72)	1.389(4)	C(72) – F(72)	1.351(3)
C(72) – C(73)	1.376(4)	C(73) – F(73)	1.349(3)
C(73) – C(74)	1.365(4)	C(74) – F(74)	1.342(3)
C(74) – C(75)	1.367(4)	C(75) – F(75)	1.344(3)
C(81) – C(86)	1.386(4)	C(81) – C(82)	1.389(4)
C(82) – F(82)	1.358(3)	C(82) – C(83)	1.372(4)
C(83) – F(83)	1.341(3)	C(83) – C(84)	1.372(4)
C(84) – F(84)	1.342(3)	C(84) – C(85)	1.372(4)
C(85) – F(85)	1.346(3)	C(85) – C(86)	1.368(4)
C(86) – F(86)	1.354(3)		

Table S11. Angles [°] for $[(C_6F_5)_3B\text{-}PC(sp^2)P]^HPd(PMe_3)$ (**4**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	79.01(7)	C – Pd – P(2)	81.19(7)
P(1) – Pd – P(2)	160.08(3)	C – Pd – P(3)	175.08(7)
P(1) – Pd – P(3)	101.40(3)	P(2) – Pd – P(3)	98.52(3)
C(11) – C – C(21)	122.2(2)	C(11) – C – Pd	120.44(19)
C(21) – C – Pd	117.17(18)	C(12) – P(1) – C(41)	108.52(13)
C(12) – P(1) – C(42)	105.76(12)	C(41) – P(1) – C(42)	106.40(14)
C(12) – P(1) – Pd	101.72(9)	C(41) – P(1) – Pd	120.21(10)
C(42) – P(1) – Pd	113.22(10)	C(22) – P(2) – C(52)	105.60(12)
C(22) – P(2) – C(51)	103.78(13)	C(52) – P(2) – C(51)	108.41(13)
C(22) – P(2) – Pd	102.36(9)	C(52) – P(2) – Pd	116.06(9)
C(51) – P(2) – Pd	118.80(10)	C(31) – P(3) – C(32)	101.09(15)
C(31) – P(3) – C(33)	98.69(14)	C(32) – P(3) – C(33)	101.79(14)
C(31) – P(3) – Pd	121.18(10)	C(32) – P(3) – Pd	110.30(10)
C(33) – P(3) – Pd	120.57(10)	C – C(11) – C(12)	119.3(2)
C – C(11) – C(16)	126.4(2)	C(12) – C(11) – C(16)	114.4(2)
C(13) – C(12) – C(11)	123.1(2)	C(13) – C(12) – P(1)	126.7(2)
C(11) – C(12) – P(1)	109.93(18)	C(12) – C(13) – C(14)	124.4(2)
C(12) – C(13) – H(13)	117.8	C(14) – C(13) – H(13)	117.8
C(15) – C(14) – C(13)	110.5(2)	C(15) – C(14) – B	114.7(2)
C(13) – C(14) – B	109.6(2)	C(15) – C(14) – H(14)	107.2
C(13) – C(14) – H(14)	107.2	B – C(14) – H(14)	107.2
C(16) – C(15) – C(14)	125.2(2)	C(16) – C(15) – H(15)	117.4
C(14) – C(15) – H(15)	117.4	C(15) – C(16) – C(11)	122.2(2)
C(15) – C(16) – H(16)	118.9	C(11) – C(16) – H(16)	118.9
C(22) – C(21) – C(26)	118.0(2)	C(22) – C(21) – C	119.4(2)
C(26) – C(21) – C	122.6(3)	C(24) – C(25) – C(26)	120.5(3)
C(24) – C(25) – H(25)	119.7	C(26) – C(25) – H(25)	119.7
C(23) – C(24) – C(25)	119.7(3)	C(23) – C(24) – H(24)	120.2
C(25) – C(24) – H(24)	120.2	C(24) – C(23) – C(22)	120.1(3)
C(24) – C(23) – H(23)	119.9	C(22) – C(23) – H(23)	119.9
C(21) – C(22) – C(23)	120.7(2)	C(21) – C(22) – P(2)	113.33(19)
C(23) – C(22) – P(2)	125.9(2)	C(25) – C(26) – C(21)	120.5(3)
C(25) – C(26) – H(26)	119.7	C(21) – C(26) – H(26)	119.7
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5

Continued on next page

Table S11. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
F(76) – C(36) – C(75)	114.5(2)	F(76) – C(36) – C(71)	121.2(2)
C(75) – C(36) – C(71)	124.3(3)	C(43) – C(41) – C(44)	111.9(3)
C(43) – C(41) – P(1)	109.3(2)	C(44) – C(41) – P(1)	117.4(2)
C(43) – C(41) – H(41)	105.8	C(44) – C(41) – H(41)	105.8
P(1) – C(41) – H(41)	105.8	C(46) – C(42) – C(45)	110.6(2)
C(46) – C(42) – P(1)	111.33(19)	C(45) – C(42) – P(1)	111.1(2)
C(46) – C(42) – H(42)	107.9	C(45) – C(42) – H(42)	107.9
P(1) – C(42) – H(42)	107.9	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(53) – C(51) – C(54)	110.6(3)
C(53) – C(51) – P(2)	114.7(2)	C(54) – C(51) – P(2)	108.8(2)
C(53) – C(51) – H(51)	107.4	C(54) – C(51) – H(51)	107.4
P(2) – C(51) – H(51)	107.4	C(56) – C(52) – C(55)	110.9(2)
C(56) – C(52) – P(2)	117.5(2)	C(55) – C(52) – P(2)	108.60(19)
C(56) – C(52) – H(52)	106.4	C(55) – C(52) – H(52)	106.4
P(2) – C(52) – H(52)	106.4	C(51) – C(53) – H(53A)	109.5
C(51) – C(53) – H(53B)	109.5	H(53A) – C(53) – H(53B)	109.5
C(51) – C(53) – H(53C)	109.5	H(53A) – C(53) – H(53C)	109.5
H(53B) – C(53) – H(53C)	109.5	C(51) – C(54) – H(54A)	109.5
C(51) – C(54) – H(54B)	109.5	H(54A) – C(54) – H(54B)	109.5
C(51) – C(54) – H(54C)	109.5	H(54A) – C(54) – H(54C)	109.5
H(54B) – C(54) – H(54C)	109.5	C(52) – C(55) – H(55A)	109.5
C(52) – C(55) – H(55B)	109.5	H(55A) – C(55) – H(55B)	109.5
C(52) – C(55) – H(55C)	109.5	H(55A) – C(55) – H(55C)	109.5
H(55B) – C(55) – H(55C)	109.5	C(52) – C(56) – H(56A)	109.5
C(52) – C(56) – H(56B)	109.5	H(56A) – C(56) – H(56B)	109.5
C(52) – C(56) – H(56C)	109.5	H(56A) – C(56) – H(56C)	109.5
H(56B) – C(56) – H(56C)	109.5	C(62) – C(61) – C(66)	112.3(2)
C(62) – C(61) – B	119.8(2)	C(66) – C(61) – B	127.8(2)
F(62) – C(62) – C(63)	115.5(2)	F(62) – C(62) – C(61)	119.3(2)
C(63) – C(62) – C(61)	125.2(3)	F(63) – C(63) – C(62)	120.9(3)

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Table S11. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
F(63) – C(63) – C(64)	119.6(3)	C(62) – C(63) – C(64)	119.4(3)
F(64) – C(64) – C(65)	120.9(3)	F(64) – C(64) – C(63)	120.6(3)
C(65) – C(64) – C(63)	118.5(3)	F(65) – C(65) – C(64)	119.7(3)
F(65) – C(65) – C(66)	120.1(3)	C(64) – C(65) – C(66)	120.2(3)
F(66) – C(66) – C(65)	114.0(2)	F(66) – C(66) – C(61)	121.7(2)
C(65) – C(66) – C(61)	124.3(3)	C(81) – B – C(71)	113.3(2)
C(81) – B – C(61)	110.8(2)	C(71) – B – C(61)	104.5(2)
C(81) – B – C(14)	104.3(2)	C(71) – B – C(14)	112.7(2)
C(61) – B – C(14)	111.5(2)	C(72) – C(71) – C(36)	112.5(2)
C(72) – C(71) – B	121.3(2)	C(36) – C(71) – B	126.0(2)
F(72) – C(72) – C(73)	115.4(2)	F(72) – C(72) – C(71)	119.9(2)
C(73) – C(72) – C(71)	124.6(2)	F(73) – C(73) – C(74)	119.0(2)
F(73) – C(73) – C(72)	120.9(2)	C(74) – C(73) – C(72)	120.1(3)
F(74) – C(74) – C(73)	121.2(2)	F(74) – C(74) – C(75)	120.5(3)
C(73) – C(74) – C(75)	118.3(3)	F(75) – C(75) – C(74)	119.2(2)
F(75) – C(75) – C(36)	120.6(2)	C(74) – C(75) – C(36)	120.2(3)
C(86) – C(81) – C(82)	112.2(2)	C(86) – C(81) – B	125.3(2)
C(82) – C(81) – B	122.1(2)	F(82) – C(82) – C(83)	115.1(2)
F(82) – C(82) – C(81)	119.8(2)	C(83) – C(82) – C(81)	125.0(3)
F(83) – C(83) – C(84)	119.4(3)	F(83) – C(83) – C(82)	121.2(3)
C(84) – C(83) – C(82)	119.4(3)	F(84) – C(84) – C(83)	120.8(3)
F(84) – C(84) – C(85)	120.6(3)	C(83) – C(84) – C(85)	118.6(3)
F(85) – C(85) – C(86)	120.4(3)	F(85) – C(85) – C(84)	119.9(3)
C(86) – C(85) – C(84)	119.7(3)	F(86) – C(86) – C(85)	114.7(2)
F(86) – C(86) – C(81)	120.4(2)	C(85) – C(86) – C(81)	124.9(3)

4.2 Crystal data for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (6)

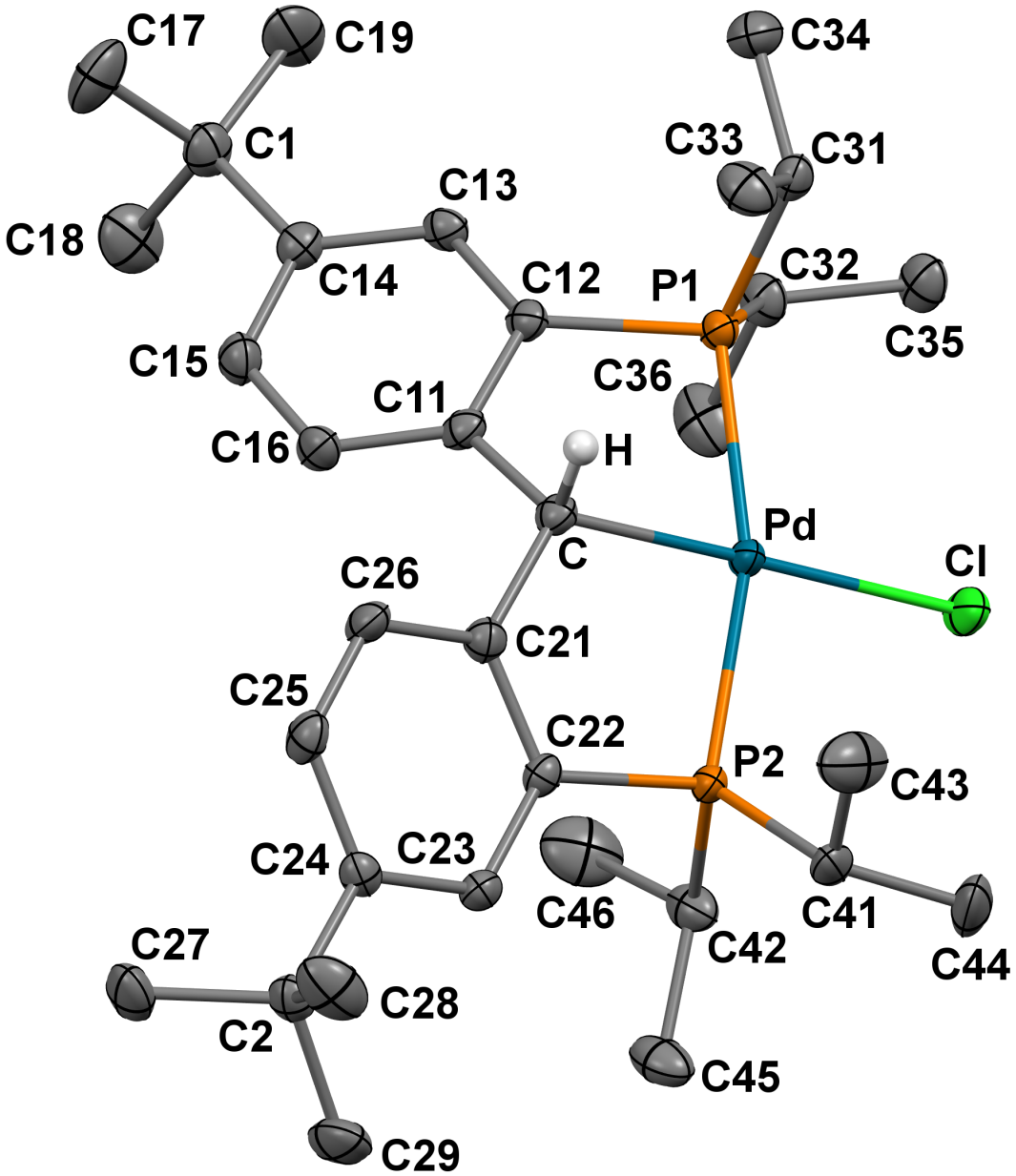

Figure S60. Thermal-ellipsoid (50% probability) representation of [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**). Most hydrogen atoms were omitted for clarity.

Table S12. Crystal data and structure refinement for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**).

Identification code:	pc21	
Empirical formula:	$C_{33}H_{53}ClP_2Pd$	
Formula weight:	653.54	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 12.3466(7) Å	α = 90°
	b = 11.6819(7) Å	β = 91.4208(9)°
	c = 23.5089(14) Å	γ = 90°
Volume:	3389.7(3) Å^3	
Z:	4	
Density (calculated):	1.281 g·cm^{-3}	
Absorption coefficient (μ):	0.740 mm^{-1}	
F(000):	1376	
Crystal size:	0.15 × 0.11 × 0.09 mm^3	
θ range for data collection:	1.65 to 25.00°	
Index ranges:	$-14 \le h \le 14$, $-13 \le k \le 13$, $-27 \le l \le 27$	
Reflections collected:	45195	
Independent reflections:	5975 [R_{int} = 0.0509]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.7033	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	5975 / 0 / 348	
Goodness-of-fit on F^2:	1.041	
Final R indices [I>2σ(I)]:	R_1 = 0.0300, wR_2 = 0.0706	
R indices (all data):	R_1 = 0.0356, wR_2 = 0.0731	
Largest diff. peak and hole:	1.846 and −1.555 e$^-$·Å^{-3}	

Table S13. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(sp^3)HP]$^{t\text{Bu}}$PdCl (**6**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.25809(1)	0.18347(2)	0.00762(1)	0.017(1)
C(1)	0.4307(2)	0.5698(2)	−0.19201(11)	0.026(1)
P(1)	0.38503(5)	0.18862(5)	−0.06302(3)	0.016(1)
C(11)	0.33696(19)	0.4065(2)	−0.03259(10)	0.018(1)
C(12)	0.38722(19)	0.3429(2)	−0.07529(10)	0.017(1)
C(13)	0.41867(19)	0.3948(2)	−0.12586(10)	0.018(1)
C(14)	0.39849(19)	0.5100(2)	−0.13708(10)	0.020(1)
C(15)	0.3435(2)	0.5703(2)	−0.09558(11)	0.023(1)
C(16)	0.3135(2)	0.5207(2)	−0.04462(10)	0.021(1)
C(22)	0.15767(18)	0.3736(2)	0.09020(10)	0.016(1)
C(21)	0.25181(19)	0.4171(2)	0.06699(10)	0.019(1)
C(19)	0.4857(3)	0.4883(3)	−0.23319(12)	0.040(1)
C(18)	0.3291(3)	0.6191(3)	−0.22207(12)	0.039(1)
C(17)	0.5092(3)	0.6680(3)	−0.17763(13)	0.042(1)
C(24)	0.13543(19)	0.5412(2)	0.14995(9)	0.017(1)
C(23)	0.10060(19)	0.4350(2)	0.13102(10)	0.018(1)
C(25)	0.2325(2)	0.5820(2)	0.12832(10)	0.022(1)
C(26)	0.2896(2)	0.5217(2)	0.08790(10)	0.022(1)
C(31)	0.52586(19)	0.1381(2)	−0.04898(10)	0.019(1)
C	0.31575(19)	0.3475(2)	0.02411(10)	0.018(1)
C(29)	−0.0414(2)	0.5672(3)	0.20144(13)	0.036(1)
C(28)	0.1364(3)	0.5973(3)	0.25196(11)	0.038(1)
C(27)	0.0702(2)	0.7369(2)	0.17994(12)	0.032(1)
C(32)	0.3438(2)	0.1283(2)	−0.13289(11)	0.023(1)
C(33)	0.5689(2)	0.1953(2)	0.00540(12)	0.030(1)
C(34)	0.6013(2)	0.1569(2)	−0.09824(12)	0.029(1)
C(36)	0.2290(2)	0.1670(3)	−0.14840(13)	0.036(1)
C(41)	0.1176(2)	0.1490(2)	0.13600(11)	0.024(1)
C(42)	−0.0104(2)	0.2258(2)	0.03521(11)	0.025(1)
C(43)	0.2301(2)	0.1456(3)	0.16419(13)	0.043(1)
C(44)	0.0708(3)	0.0291(2)	0.12749(13)	0.039(1)
C(45)	−0.1028(2)	0.2594(3)	0.07405(13)	0.032(1)
C(46)	−0.0102(3)	0.2997(3)	−0.01818(13)	0.046(1)
C(35)	0.3535(2)	−0.0025(2)	−0.13316(11)	0.027(1)
Cl	0.19180(5)	−0.00503(5)	−0.00835(3)	0.030(1)
P(2)	0.12535(5)	0.22817(5)	0.06852(3)	0.016(1)
C(2)	0.0749(2)	0.6097(2)	0.19524(10)	0.021(1)
H(13)	0.4548	0.3502	−0.1533	0.022
H(15)	0.3258	0.6483	−0.1024	0.027

Continued on next page

Table S13. – continued from previous page

atom	x	y	x	U(eq)
H(16)	0.2763	0.5654	−0.0176	0.026
H(19A)	0.4362	0.4253	−0.2430	0.060
H(19B)	0.5518	0.4574	−0.2151	0.060
H(19C)	0.5041	0.5298	−0.2678	0.060
H(18A)	0.3494	0.6550	−0.2580	0.058
H(18B)	0.2960	0.6765	−0.1975	0.058
H(18C)	0.2772	0.5573	−0.2299	0.058
H(17A)	0.5292	0.7071	−0.2127	0.063
H(17B)	0.5744	0.6372	−0.1586	0.063
H(17C)	0.4740	0.7225	−0.1523	0.063
H(23)	0.0366	0.4030	0.1460	0.021
H(25)	0.2603	0.6532	0.1417	0.027
H(26)	0.3554	0.5523	0.0743	0.026
H(31)	0.5226	0.0539	−0.0417	0.023
H	0.3890	0.3363	0.0424	0.021
H(29A)	−0.0784	0.5670	0.1641	0.054
H(29B)	−0.0799	0.6181	0.2272	0.054
H(29C)	−0.0405	0.4894	0.2170	0.054
H(28A)	0.1381	0.5165	0.2632	0.058
H(28B)	0.1000	0.6421	0.2811	0.058
H(28C)	0.2106	0.6253	0.2481	0.058
H(27A)	0.1440	0.7672	0.1778	0.047
H(27B)	0.0309	0.7785	0.2092	0.047
H(27C)	0.0327	0.7464	0.1430	0.047
H(32)	0.3935	0.1594	−0.1621	0.028
H(33A)	0.6412	0.1653	0.0150	0.044
H(33B)	0.5200	0.1790	0.0366	0.044
H(33C)	0.5732	0.2782	−0.0005	0.044
H(34A)	0.5746	0.1138	−0.1315	0.044
H(34B)	0.6743	0.1304	−0.0874	0.044
H(34C)	0.6037	0.2386	−0.1076	0.044
H(36A)	0.2107	0.1437	−0.1875	0.054
H(36B)	0.2244	0.2505	−0.1453	0.054
H(36C)	0.1780	0.1317	−0.1223	0.054
H(41)	0.0687	0.1923	0.1616	0.028
H(42)	−0.0245	0.1453	0.0226	0.030
H(43A)	0.2801	0.1056	0.1393	0.064
H(43B)	0.2266	0.1052	0.2006	0.064
H(43C)	0.2558	0.2240	0.1708	0.064
H(44A)	−0.0039	0.0349	0.1126	0.059
H(44B)	0.0715	−0.0114	0.1640	0.059
H(44C)	0.1146	−0.0131	0.1004	0.059

Continued on next page

Table S13. – continued from previous page

atom	x	y	x	U(eq)
H(45A)	−0.1724	0.2454	0.0544	0.049
H(45B)	−0.0967	0.3408	0.0837	0.049
H(45C)	−0.0984	0.2137	0.1090	0.049
H(46A)	0.0479	0.2744	−0.0429	0.069
H(46B)	0.0018	0.3799	−0.0075	0.069
H(46C)	−0.0801	0.2925	−0.0385	0.069
H(35A)	0.3298	−0.0321	−0.1704	0.040
H(35B)	0.3078	−0.0347	−0.1037	0.040
H(35C)	0.4291	−0.0244	−0.1255	0.040

Table S14. Anisotropic displacement parameters (Å^2) for [PC(sp^3)HP]$^{t\mathrm{Bu}}$PdCl (**6**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0177(1)	0.0117(1)	0.0207(1)	−0.0026(1)	0.0067(1)	−0.0029(1)
C(1)	0.0338(15)	0.0236(14)	0.0196(14)	0.0035(11)	0.0034(11)	0.0024(12)
P(1)	0.0187(3)	0.0135(3)	0.0172(3)	−0.0034(2)	0.0039(2)	−0.0020(2)
C(11)	0.0180(12)	0.0178(13)	0.0191(13)	−0.0019(10)	0.0029(10)	−0.0056(10)
C(12)	0.0167(12)	0.0155(13)	0.0200(13)	−0.0034(10)	0.0022(10)	−0.0030(10)
C(13)	0.0197(12)	0.0188(13)	0.0169(12)	−0.0044(10)	0.0026(9)	−0.0008(10)
C(14)	0.0202(12)	0.0206(13)	0.0186(13)	0.0006(10)	−0.0002(10)	−0.0013(10)
C(15)	0.0284(14)	0.0163(13)	0.0241(14)	−0.0009(10)	0.0026(11)	−0.0002(11)
C(16)	0.0256(13)	0.0173(13)	0.0213(13)	−0.0053(10)	0.0065(10)	−0.0013(10)
C(22)	0.0180(12)	0.0156(12)	0.0141(12)	0.0017(10)	0.0004(9)	−0.0020(10)
C(21)	0.0213(12)	0.0166(13)	0.0179(12)	−0.0002(10)	0.0019(10)	−0.0007(10)
C(19)	0.057(2)	0.0416(19)	0.0226(15)	0.0114(13)	0.0178(14)	0.0102(16)
C(18)	0.0475(18)	0.0450(19)	0.0237(15)	0.0082(13)	−0.0018(13)	0.0089(15)
C(17)	0.056(2)	0.0363(19)	0.0339(17)	0.0130(14)	0.0045(15)	−0.0159(15)
C(24)	0.0221(12)	0.0168(13)	0.0118(12)	0.0001(9)	0.0008(9)	0.0029(10)
C(23)	0.0175(12)	0.0171(13)	0.0180(12)	0.0019(10)	0.0033(9)	−0.0011(10)
C(25)	0.0292(14)	0.0162(13)	0.0210(13)	−0.0026(10)	0.0020(11)	−0.0058(11)
C(26)	0.0237(13)	0.0189(13)	0.0230(13)	−0.0016(10)	0.0081(10)	−0.0070(11)
C(31)	0.0246(13)	0.0152(12)	0.0180(12)	0.0006(10)	0.0030(10)	−0.0025(10)
C	0.0160(12)	0.0166(12)	0.0198(13)	−0.0017(10)	0.0021(10)	−0.0033(10)
C(29)	0.0319(15)	0.0340(17)	0.0438(18)	−0.0137(14)	0.0184(13)	0.0002(13)
C(28)	0.0485(18)	0.0479(19)	0.0190(14)	−0.0035(13)	0.0023(13)	0.0155(15)
C(27)	0.0437(17)	0.0211(14)	0.0304(15)	−0.0035(12)	0.0113(13)	0.0076(13)
C(32)	0.0288(14)	0.0198(14)	0.0208(13)	−0.0062(11)	0.0008(11)	−0.0022(11)
C(33)	0.0252(14)	0.0325(16)	0.0307(15)	−0.0043(12)	−0.0037(11)	0.0035(12)
C(34)	0.0239(14)	0.0306(16)	0.0331(16)	0.0036(12)	0.0075(12)	−0.0003(12)
C(36)	0.0370(16)	0.0325(17)	0.0385(17)	−0.0118(13)	−0.0158(13)	0.0021(13)
C(41)	0.0275(14)	0.0190(13)	0.0253(14)	0.0069(11)	0.0124(11)	0.0024(11)
C(42)	0.0188(12)	0.0238(14)	0.0314(15)	−0.0089(12)	−0.0005(11)	−0.0011(11)
C(43)	0.0352(17)	0.055(2)	0.0372(18)	0.0215(16)	0.0024(13)	0.0086(15)
C(44)	0.058(2)	0.0162(14)	0.0444(18)	0.0060(13)	0.0241(15)	−0.0019(14)
C(45)	0.0189(13)	0.0351(17)	0.0435(17)	−0.0136(14)	−0.0008(12)	0.0018(12)
C(46)	0.0380(17)	0.067(2)	0.0324(17)	0.0021(16)	−0.0113(14)	0.0089(16)
C(35)	0.0366(15)	0.0209(14)	0.0230(14)	−0.0074(11)	0.0033(11)	−0.0049(12)
Cl	0.0296(3)	0.0163(3)	0.0439(4)	−0.0100(3)	0.0143(3)	−0.0082(3)
P(2)	0.0167(3)	0.0122(3)	0.0198(3)	−0.0003(2)	0.0052(2)	−0.0021(2)
C(2)	0.0257(13)	0.0198(13)	0.0172(12)	−0.0012(10)	0.0042(10)	0.0032(11)

Table S15. Distances [Å] for [PC(sp^3)HP]$^{t\mathrm{Bu}}$PdCl (**6**).

atom – atom	distance	atom – atom	distance
Pd – C	2.078(2)	Pd – P(2)	2.2638(6)
Pd – P(1)	2.3125(6)	Pd – Cl	2.3758(6)
C(1) – C(19)	1.529(4)	C(1) – C(14)	1.530(3)
C(1) – C(17)	1.534(4)	C(1) – C(18)	1.537(4)
P(1) – C(12)	1.825(2)	P(1) – C(32)	1.847(2)
P(1) – C(31)	1.858(3)	C(11) – C(16)	1.393(4)
C(11) – C(12)	1.406(3)	C(11) – C	1.529(3)
C(12) – C(13)	1.398(3)	C(13) – C(14)	1.393(3)
C(13) – H(13)	0.9500	C(14) – C(15)	1.393(3)
C(15) – C(16)	1.389(3)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(22) – C(21)	1.392(3)
C(22) – C(23)	1.402(3)	C(22) – P(2)	1.815(2)
C(21) – C(26)	1.394(3)	C(21) – C	1.529(3)
C(19) – H(19A)	0.9800	C(19) – H(19B)	0.9800
C(19) – H(19C)	0.9800	C(18) – H(18A)	0.9800
C(18) – H(18B)	0.9800	C(18) – H(18C)	0.9800
C(17) – H(17A)	0.9800	C(17) – H(17B)	0.9800
C(17) – H(17C)	0.9800	C(24) – C(23)	1.383(3)
C(24) – C(25)	1.397(3)	C(24) – C(2)	1.540(3)
C(23) – H(23)	0.9500	C(25) – C(26)	1.389(3)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(31) – C(34)	1.520(3)	C(31) – C(33)	1.526(4)
C(31) – H(31)	1.0000	C – H	1.0000
C(29) – C(2)	1.530(4)	C(29) – H(29A)	0.9800
C(29) – H(29B)	0.9800	C(29) – H(29C)	0.9800
C(28) – C(2)	1.525(4)	C(28) – H(28A)	0.9800
C(28) – H(28B)	0.9800	C(28) – H(28C)	0.9800
C(27) – C(2)	1.530(4)	C(27) – H(27A)	0.9800
C(27) – H(27B)	0.9800	C(27) – H(27C)	0.9800
C(32) – C(36)	1.524(4)	C(32) – C(35)	1.532(4)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(43)	1.524(4)	C(41) – C(44)	1.527(4)
C(41) – P(2)	1.841(2)	C(41) – H(41)	1.0000
C(42) – C(46)	1.524(4)	C(42) – C(45)	1.530(4)
C(42) – P(2)	1.833(3)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800

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Table S15. – continued from previous page

atom – atom	distance	atom – atom	distance
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800		

Table S16. Angles [°] for [PC(sp^3)HP]$^{t\mathrm{Bu}}$PdCl (**6**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	85.38(6)	C – Pd – P(1)	82.81(6)
P(2) – Pd – P(1)	164.24(2)	C – Pd – Cl	178.34(7)
P(2) – Pd – Cl	93.54(2)	P(1) – Pd – Cl	98.48(2)
C(19) – C(1) – C(14)	112.3(2)	C(19) – C(1) – C(17)	108.6(2)
C(14) – C(1) – C(17)	109.4(2)	C(19) – C(1) – C(18)	108.2(2)
C(14) – C(1) – C(18)	109.4(2)	C(17) – C(1) – C(18)	109.0(2)
C(12) – P(1) – C(32)	103.96(12)	C(12) – P(1) – C(31)	108.91(11)
C(32) – P(1) – C(31)	105.82(11)	C(12) – P(1) – Pd	98.75(8)
C(32) – P(1) – Pd	116.88(9)	C(31) – P(1) – Pd	120.81(8)
C(16) – C(11) – C(12)	117.0(2)	C(16) – C(11) – C	124.7(2)
C(12) – C(11) – C	118.2(2)	C(13) – C(12) – C(11)	121.0(2)
C(13) – C(12) – P(1)	124.60(18)	C(11) – C(12) – P(1)	113.61(17)
C(14) – C(13) – C(12)	121.9(2)	C(14) – C(13) – H(13)	119.1
C(12) – C(13) – H(13)	119.1	C(15) – C(14) – C(13)	116.3(2)
C(15) – C(14) – C(1)	120.2(2)	C(13) – C(14) – C(1)	123.5(2)
C(16) – C(15) – C(14)	122.6(2)	C(16) – C(15) – H(15)	118.7
C(14) – C(15) – H(15)	118.7	C(15) – C(16) – C(11)	121.1(2)
C(15) – C(16) – H(16)	119.5	C(11) – C(16) – H(16)	119.5
C(21) – C(22) – C(23)	121.3(2)	C(21) – C(22) – P(2)	114.28(17)
C(23) – C(22) – P(2)	124.08(17)	C(22) – C(21) – C(26)	117.2(2)
C(22) – C(21) – C	120.9(2)	C(26) – C(21) – C	121.6(2)
C(1) – C(19) – H(19A)	109.5	C(1) – C(19) – H(19B)	109.5
H(19A) – C(19) – H(19B)	109.5	C(1) – C(19) – H(19C)	109.5
H(19A) – C(19) – H(19C)	109.5	H(19B) – C(19) – H(19C)	109.5
C(1) – C(18) – H(18A)	109.5	C(1) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	C(1) – C(18) – H(18C)	109.5
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5
C(1) – C(17) – H(17A)	109.5	C(1) – C(17) – H(17B)	109.5
H(17A) – C(17) – H(17B)	109.5	C(1) – C(17) – H(17C)	109.5
H(17A) – C(17) – H(17C)	109.5	H(17B) – C(17) – H(17C)	109.5
C(23) – C(24) – C(25)	116.8(2)	C(23) – C(24) – C(2)	122.4(2)
C(25) – C(24) – C(2)	120.7(2)	C(24) – C(23) – C(22)	121.4(2)
C(24) – C(23) – H(23)	119.3	C(22) – C(23) – H(23)	119.3
C(26) – C(25) – C(24)	122.1(2)	C(26) – C(25) – H(25)	119.0
C(24) – C(25) – H(25)	119.0	C(25) – C(26) – C(21)	121.0(2)
C(25) – C(26) – H(26)	119.5	C(21) – C(26) – H(26)	119.5
C(34) – C(31) – C(33)	111.6(2)	C(34) – C(31) – P(1)	114.05(18)
C(33) – C(31) – P(1)	108.34(17)	C(34) – C(31) – H(31)	107.5
C(33) – C(31) – H(31)	107.5	P(1) – C(31) – H(31)	107.5
C(11) – C – C(21)	116.0(2)	C(11) – C – Pd	108.56(15)
C(21) – C – Pd	115.65(15)	C(11) – C – H	105.2

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Table S16. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(21) – C – H	105.2	Pd – C – H	105.2
C(2) – C(29) – H(29A)	109.5	C(2) – C(29) – H(29B)	109.5
H(29A) – C(29) – H(29B)	109.5	C(2) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
C(2) – C(28) – H(28A)	109.5	C(2) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	C(2) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
C(2) – C(27) – H(27A)	109.5	C(2) – C(27) – H(27B)	109.5
H(27A) – C(27) – H(27B)	109.5	C(2) – C(27) – H(27C)	109.5
H(27A) – C(27) – H(27C)	109.5	H(27B) – C(27) – H(27C)	109.5
C(36) – C(32) – C(35)	111.5(2)	C(36) – C(32) – P(1)	109.47(18)
C(35) – C(32) – P(1)	111.37(18)	C(36) – C(32) – H(32)	108.1
C(35) – C(32) – H(32)	108.1	P(1) – C(32) – H(32)	108.1
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(43) – C(41) – C(44)	111.8(2)	C(43) – C(41) – P(2)	108.78(18)
C(44) – C(41) – P(2)	112.0(2)	C(43) – C(41) – H(41)	108.0
C(44) – C(41) – H(41)	108.0	P(2) – C(41) – H(41)	108.0
C(46) – C(42) – C(45)	111.3(2)	C(46) – C(42) – P(2)	108.85(19)
C(45) – C(42) – P(2)	115.36(19)	C(46) – C(42) – H(42)	107.0
C(45) – C(42) – H(42)	107.0	P(2) – C(42) – H(42)	107.0
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5

Continued on next page

Table S16. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(22) – P(2) – C(42)	109.06(12)	C(22) – P(2) – C(41)	104.11(11)
C(42) – P(2) – C(41)	107.13(12)	C(22) – P(2) – Pd	103.64(8)
C(42) – P(2) – Pd	113.27(9)	C(41) – P(2) – Pd	118.88(8)
C(28) – C(2) – C(27)	108.2(2)	C(28) – C(2) – C(29)	109.5(2)
C(27) – C(2) – C(29)	107.9(2)	C(28) – C(2) – C(24)	108.4(2)
C(27) – C(2) – C(24)	111.0(2)	C(29) – C(2) – C(24)	111.8(2)

4.3 Crystal data for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (3)

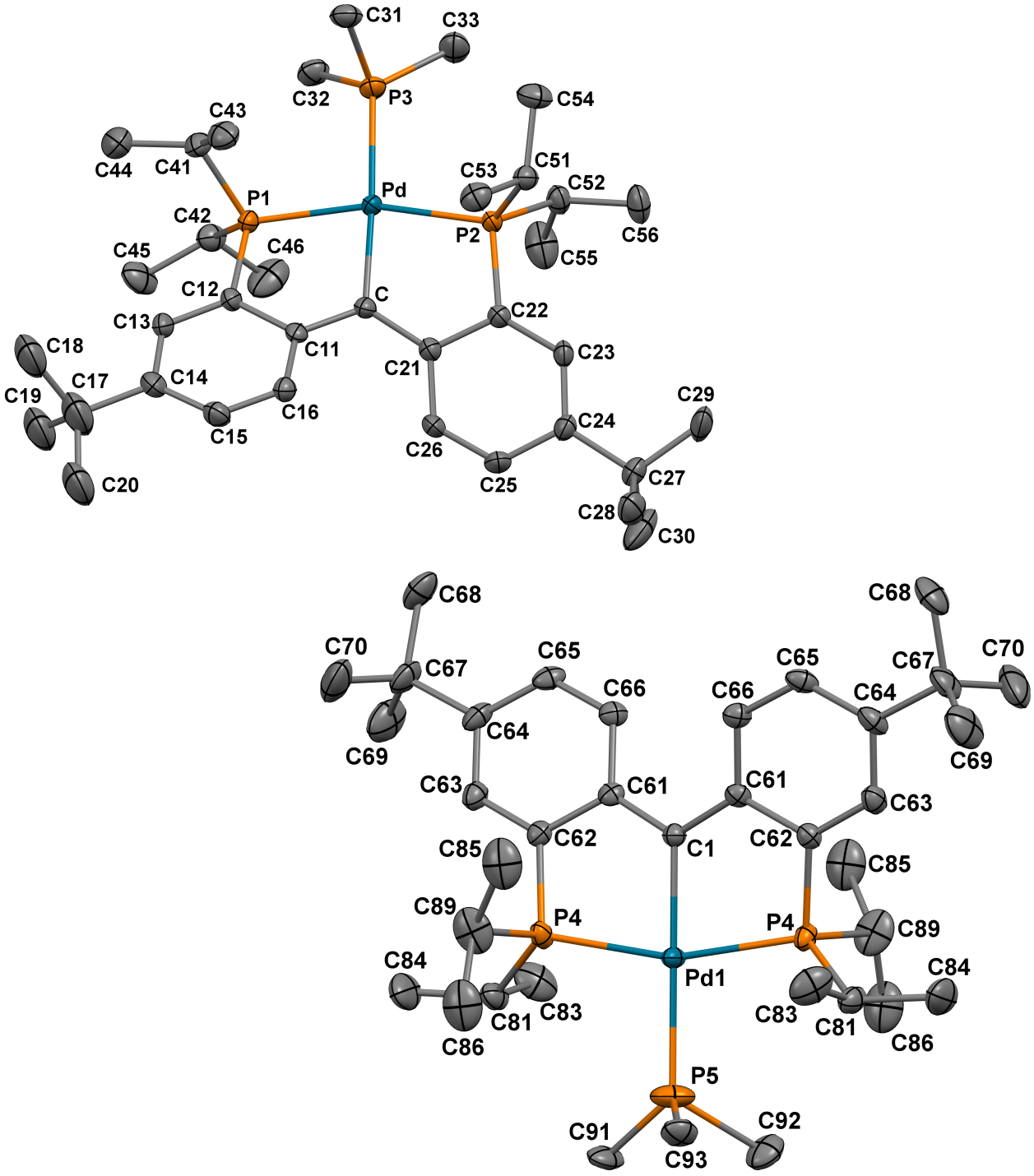

Figure S61. Thermal-ellipsoid (50% probability) representation of the two crystallographically independent molecules of[PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**). Hydrogen atoms were omitted for clarity.

Table S17. Crystal data and structure refinement for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**).

Identification code:	pc23	
Empirical formula:	$C_{36}H_{61}P_3Pd$	
Formula weight:	693.16	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$C2/c$	
Unit cell dimensions:	a = 28.976(3) Å	α = 90°
	b = 14.6255(14) Å	β = 106.946(2)°
	c = 31.853(4) Å	γ = 90°
Volume:	12913(2) Å^3	
Z:	12	
Density (calculated):	1.070 g·cm^{-3}	
Absorption coefficient (μ):	0.561 mm^{-1}	
F(000):	4416	
Crystal size:	0.13 × 0.10 × 0.09 mm^3	
θ range for data collection:	1.34 to 25.00°	
Index ranges:	$-34 \le h \le 34$, $-17 \le k \le 17$, $-37 \le l \le 37$	
Reflections collected:	103779	
Independent reflections:	11379 [R_{int} = 0.0366]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.8393 and 0.7062	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	11379 / 0 / 570	
Goodness-of-fit on F^2:	1.038	
Final R indices [I>2σ(I)]:	R_1 = 0.0347, wR_2 = 0.0835	
R indices (all data):	R_1 = 0.0395, wR_2 = 0.0858	
Largest diff. peak and hole:	1.525 and −0.772 e$^-$·Å^{-3}	

Table S18. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PC(sp^2)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (**3**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.25640(1)	0.59937(1)	0.21152(1)	0.019(1)
C	0.31971(9)	0.64729(19)	0.20130(8)	0.021(1)
P(1)	0.30355(2)	0.60537(5)	0.28383(2)	0.021(1)
C(1)	0.5000	0.1709(2)	0.2500	0.018(1)
Pd(1)	0.5000	0.31270(2)	0.2500	0.019(1)
P(2)	0.22986(2)	0.61514(5)	0.13612(2)	0.020(1)
P(3)	0.18574(2)	0.54685(5)	0.22705(2)	0.025(1)
P(4)	0.54528(2)	0.28762(5)	0.32165(2)	0.020(1)
P(5)	0.5000	0.47313(7)	0.2500	0.035(1)
C(11)	0.35564(9)	0.68681(18)	0.23758(8)	0.020(1)
C(12)	0.35547(9)	0.66985(19)	0.28171(8)	0.022(1)
C(13)	0.39170(9)	0.7015(2)	0.31803(9)	0.026(1)
C(14)	0.43012(10)	0.7538(2)	0.31402(9)	0.031(1)
C(18)	0.45070(15)	0.8359(4)	0.38625(13)	0.070(1)
C(82)	0.5156(5)	0.2990(11)	0.3628(4)	0.050(2)
C(87)	0.4649(2)	0.2536(6)	0.3460(2)	0.042(1)
C(88)	0.5064(3)	0.4032(6)	0.3727(3)	0.042(1)
C(17)	0.47068(15)	0.7820(4)	0.35504(14)	0.070(1)
C(16)	0.39331(9)	0.74759(19)	0.23464(9)	0.023(1)
C(15)	0.42875(10)	0.7785(2)	0.27107(9)	0.029(1)
C(19)	0.49080(15)	0.6935(3)	0.38189(13)	0.070(1)
C(20)	0.51244(14)	0.8212(4)	0.34447(13)	0.070(1)
C(21)	0.32498(9)	0.64261(19)	0.15790(8)	0.022(1)
C(22)	0.28420(9)	0.62894(19)	0.12065(8)	0.022(1)
C(23)	0.28713(10)	0.62927(19)	0.07767(8)	0.024(1)
C(24)	0.33054(10)	0.63583(19)	0.06818(9)	0.025(1)
C(25)	0.37171(10)	0.6425(2)	0.10478(9)	0.029(1)
C(26)	0.36948(9)	0.6468(2)	0.14710(9)	0.029(1)
C(27)	0.33592(10)	0.6356(2)	0.02177(9)	0.029(1)
C(28)	0.35903(12)	0.7253(2)	0.01359(10)	0.041(1)
C(29)	0.28706(12)	0.6263(3)	−0.01318(10)	0.044(1)
C(31)	0.15144(10)	0.6353(2)	0.24524(10)	0.032(1)
C(30)	0.36836(16)	0.5560(3)	0.01691(12)	0.058(1)
C(32)	0.19423(11)	0.4605(2)	0.27007(10)	0.033(1)
C(33)	0.13669(11)	0.4912(2)	0.18560(10)	0.039(1)
C(41)	0.27332(11)	0.6682(2)	0.31866(9)	0.031(1)
C(42)	0.32384(10)	0.4948(2)	0.31158(9)	0.031(1)
C(43)	0.26055(11)	0.7631(2)	0.29834(10)	0.035(1)
C(44)	0.29676(12)	0.6716(3)	0.36772(10)	0.042(1)

Continued on next page

Table S18. – continued from previous page

atom	x	y	x	U(eq)
C(45)	0.36961(11)	0.4972(3)	0.35042(11)	0.045(1)
C(46)	0.33036(15)	0.4268(3)	0.27707(13)	0.055(1)
C(51)	0.19391(9)	0.71761(19)	0.11394(9)	0.025(1)
C(52)	0.19605(10)	0.5177(2)	0.10445(9)	0.028(1)
C(53)	0.22088(11)	0.8025(2)	0.13657(10)	0.033(1)
C(54)	0.14255(10)	0.7140(2)	0.11774(11)	0.036(1)
C(55)	0.22791(14)	0.4333(2)	0.11507(12)	0.051(1)
C(56)	0.17456(12)	0.5292(2)	0.05492(10)	0.038(1)
C(61)	0.53692(8)	0.12409(17)	0.28287(8)	0.017(1)
C(62)	0.56387(9)	0.17047(17)	0.32141(8)	0.019(1)
C(63)	0.59824(9)	0.12740(19)	0.35524(9)	0.024(1)
C(64)	0.61089(9)	0.03592(19)	0.35291(9)	0.025(1)
C(65)	0.58673(9)	−0.00939(18)	0.31428(9)	0.023(1)
C(66)	0.55149(9)	0.03140(17)	0.28056(9)	0.020(1)
C(67)	0.64963(11)	−0.0088(2)	0.39079(10)	0.034(1)
C(68)	0.65810(12)	−0.1092(2)	0.38171(11)	0.041(1)
C(69)	0.69792(12)	0.0418(3)	0.39673(12)	0.052(1)
C(70)	0.63450(16)	−0.0048(3)	0.43223(11)	0.057(1)
C(81)	0.59973(10)	0.35952(19)	0.34326(9)	0.028(1)
C(83)	0.63413(11)	0.3430(2)	0.31590(12)	0.044(1)
C(84)	0.62641(13)	0.3548(2)	0.39211(11)	0.050(1)
C(89)	0.5106(4)	0.2824(10)	0.3647(4)	0.042(1)
C(85)	0.4729(3)	0.2044(7)	0.3520(3)	0.050(2)
C(86)	0.4890(3)	0.3688(6)	0.3727(3)	0.050(2)
C(91)	0.5401(2)	0.5451(4)	0.2844(2)	0.037(2)
C(92)	0.5002(2)	0.5371(5)	0.1963(2)	0.041(2)
C(93)	0.4406(2)	0.5144(4)	0.2520(2)	0.033(1)
H(13)	0.3900	0.6867	0.3466	0.031
H(18A)	0.4238	0.8023	0.3917	0.105
H(18B)	0.4393	0.8955	0.3733	0.105
H(18C)	0.4761	0.8449	0.4140	0.105
H(82)	0.5348	0.2682	0.3904	0.060
H(87A)	0.4448	0.2888	0.3212	0.063
H(87B)	0.4496	0.2524	0.3697	0.063
H(87C)	0.4684	0.1909	0.3364	0.063
H(88A)	0.5374	0.4354	0.3827	0.063
H(88B)	0.4901	0.4062	0.3956	0.063
H(88C)	0.4862	0.4322	0.3459	0.063
H(16)	0.3940	0.7675	0.2064	0.028
H(15)	0.4531	0.8180	0.2669	0.035
H(19A)	0.5161	0.7102	0.4086	0.105
H(19B)	0.5042	0.6527	0.3640	0.105

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Table S18. – continued from previous page

atom	x	y	x	U(eq)
H(19C)	0.4646	0.6622	0.3898	0.105
H(20A)	0.5385	0.8318	0.3716	0.105
H(20B)	0.5032	0.8794	0.3290	0.105
H(20C)	0.5236	0.7788	0.3257	0.105
H(23)	0.2582	0.6248	0.0541	0.028
H(25)	0.4025	0.6441	0.0999	0.035
H(26)	0.3987	0.6528	0.1702	0.034
H(28A)	0.3378	0.7765	0.0152	0.062
H(28B)	0.3639	0.7238	−0.0156	0.062
H(28C)	0.3902	0.7330	0.0359	0.062
H(29A)	0.2715	0.5692	−0.0085	0.067
H(29B)	0.2919	0.6255	−0.0424	0.067
H(29C)	0.2665	0.6781	−0.0110	0.067
H(31A)	0.1248	0.6070	0.2536	0.047
H(31B)	0.1385	0.6789	0.2213	0.047
H(31C)	0.1726	0.6675	0.2706	0.047
H(30A)	0.3995	0.5608	0.0395	0.087
H(30B)	0.3734	0.5584	−0.0122	0.087
H(30C)	0.3529	0.4980	0.0203	0.087
H(32A)	0.2134	0.4863	0.2981	0.049
H(32B)	0.2111	0.4076	0.2627	0.049
H(32C)	0.1627	0.4412	0.2725	0.049
H(33A)	0.1113	0.4734	0.1987	0.058
H(33B)	0.1490	0.4367	0.1746	0.058
H(33C)	0.1234	0.5337	0.1613	0.058
H(41)	0.2418	0.6364	0.3146	0.037
H(42)	0.2972	0.4713	0.3227	0.037
H(43A)	0.2383	0.7934	0.3119	0.052
H(43B)	0.2451	0.7569	0.2667	0.052
H(43C)	0.2900	0.7996	0.3034	0.052
H(44A)	0.2757	0.7044	0.3817	0.063
H(44B)	0.3278	0.7033	0.3739	0.063
H(44C)	0.3020	0.6091	0.3793	0.063
H(45A)	0.3645	0.5372	0.3733	0.067
H(45B)	0.3965	0.5205	0.3407	0.067
H(45C)	0.3772	0.4352	0.3622	0.067
H(46A)	0.3552	0.4494	0.2644	0.083
H(46B)	0.2998	0.4202	0.2538	0.083
H(46C)	0.3402	0.3673	0.2909	0.083
H(51)	0.1916	0.7218	0.0820	0.030
H(52)	0.1683	0.5061	0.1164	0.034
H(53A)	0.2218	0.8025	0.1676	0.050

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Table S18. – continued from previous page

atom	x	y	x	U(eq)
H(53B)	0.2042	0.8576	0.1223	0.050
H(53C)	0.2539	0.8019	0.1343	0.050
H(54A)	0.1437	0.7106	0.1488	0.054
H(54B)	0.1260	0.6600	0.1023	0.054
H(54C)	0.1250	0.7692	0.1046	0.054
H(55A)	0.2429	0.4295	0.1469	0.076
H(55B)	0.2531	0.4374	0.1003	0.076
H(55C)	0.2083	0.3786	0.1049	0.076
H(56A)	0.1523	0.4786	0.0433	0.057
H(56B)	0.2005	0.5290	0.0409	0.057
H(56C)	0.1570	0.5873	0.0488	0.057
H(63)	0.6137	0.1614	0.3809	0.028
H(65)	0.5949	−0.0713	0.3109	0.027
H(66)	0.5365	−0.0034	0.2550	0.024
H(68A)	0.6826	−0.1351	0.4069	0.061
H(68B)	0.6693	−0.1135	0.3555	0.061
H(68C)	0.6279	−0.1433	0.3768	0.061
H(69A)	0.7234	0.0114	0.4196	0.078
H(69B)	0.6948	0.1053	0.4054	0.078
H(69C)	0.7062	0.0409	0.3690	0.078
H(70A)	0.6588	−0.0352	0.4561	0.085
H(70B)	0.6034	−0.0357	0.4274	0.085
H(70C)	0.6314	0.0592	0.4401	0.085
H(81)	0.5886	0.4242	0.3374	0.034
H(83A)	0.6576	0.3930	0.3207	0.066
H(83B)	0.6158	0.3403	0.2848	0.066
H(83C)	0.6511	0.2849	0.3247	0.066
H(84A)	0.6032	0.3602	0.4091	0.075
H(84B)	0.6498	0.4049	0.4000	0.075
H(84C)	0.6434	0.2962	0.3987	0.075
H(89)	0.5344	0.2643	0.3931	0.050
H(85A)	0.4491	0.2189	0.3240	0.075
H(85B)	0.4565	0.1980	0.3748	0.075
H(85C)	0.4892	0.1470	0.3493	0.075
H(86A)	0.4668	0.3910	0.3452	0.075
H(86B)	0.5146	0.4141	0.3840	0.075
H(86C)	0.4714	0.3591	0.3943	0.075
H(91A)	0.5309	0.6086	0.2763	0.044
H(91B)	0.5725	0.5337	0.2819	0.044
H(91C)	0.5399	0.5342	0.3147	0.044
H(92A)	0.4944	0.6024	0.1995	0.061
H(92B)	0.4747	0.5123	0.1716	0.061

Continued on next page

Table S18. – continued from previous page

atom	x	y	x	U(eq)
H(92C)	0.5315	0.5288	0.1909	0.061
H(93A)	0.4329	0.4869	0.2772	0.049
H(93B)	0.4160	0.4971	0.2249	0.049
H(93C)	0.4415	0.5811	0.2550	0.049

Table S19. Anisotropic displacement parameters (Å^2) for [PC(sp^2)P]$^{t\text{Bu}}$Pd(PMe$_3$) (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0160(1)	0.0270(1)	0.0149(1)	0.0022(1)	0.0048(1)	−0.0005(1)
C	0.0156(12)	0.0302(15)	0.0182(13)	0.0026(11)	0.0053(10)	0.0025(11)
P(1)	0.0194(3)	0.0300(4)	0.0153(3)	0.0034(3)	0.0057(3)	0.0034(3)
C(1)	0.0176(17)	0.0159(17)	0.0182(18)	0.000	0.0024(14)	0.000
Pd(1)	0.0171(1)	0.0132(1)	0.0207(2)	0.000	−0.0035(1)	0.000
P(2)	0.0154(3)	0.0269(4)	0.0157(3)	0.0013(3)	0.0031(3)	−0.0022(3)
P(3)	0.0210(3)	0.0317(4)	0.0236(4)	0.0023(3)	0.0089(3)	−0.0040(3)
P(4)	0.0168(3)	0.0228(3)	0.0176(3)	−0.0040(3)	−0.0006(3)	0.0034(3)
P(5)	0.0302(6)	0.0147(5)	0.0615(8)	0.000	0.0161(5)	0.000
C(11)	0.0156(12)	0.0261(14)	0.0187(13)	0.0017(11)	0.0045(10)	0.0061(10)
C(12)	0.0175(13)	0.0297(15)	0.0175(13)	0.0022(11)	0.0037(10)	0.0032(11)
C(13)	0.0205(13)	0.0401(17)	0.0167(13)	0.0025(12)	0.0037(11)	0.0044(12)
C(14)	0.0196(14)	0.0450(18)	0.0260(15)	−0.0007(13)	0.0030(12)	0.0036(13)
C(18)	0.0455(11)	0.1050(19)	0.0446(12)	−0.0024(11)	−0.0088(9)	−0.0157(12)
C(82)	0.030(2)	0.079(5)	0.045(3)	−0.005(3)	0.019(2)	0.002(2)
C(87)	0.0222(19)	0.065(4)	0.046(3)	−0.012(2)	0.0208(19)	0.002(2)
C(88)	0.0222(19)	0.065(4)	0.046(3)	−0.012(2)	0.0208(19)	0.002(2)
C(17)	0.0455(11)	0.1050(19)	0.0446(12)	−0.0024(11)	−0.0088(9)	−0.0157(12)
C(16)	0.0217(13)	0.0298(15)	0.0188(13)	0.0036(11)	0.0059(11)	0.0030(11)
C(15)	0.0202(14)	0.0356(16)	0.0297(15)	0.0014(13)	0.0052(12)	−0.0037(12)
C(19)	0.0455(11)	0.1050(19)	0.0446(12)	−0.0024(11)	−0.0088(9)	−0.0157(12)
C(20)	0.0455(11)	0.1050(19)	0.0446(12)	−0.0024(11)	−0.0088(9)	−0.0157(12)
C(21)	0.0183(13)	0.0290(15)	0.0188(13)	0.0013(11)	0.0038(11)	0.0000(11)
C(22)	0.0181(13)	0.0286(14)	0.0191(13)	0.0005(11)	0.0046(10)	−0.0015(11)
C(23)	0.0241(14)	0.0299(15)	0.0147(13)	−0.0020(11)	0.0020(11)	−0.0035(11)
C(24)	0.0277(14)	0.0304(15)	0.0175(13)	−0.0020(11)	0.0082(11)	−0.0025(12)
C(25)	0.0203(14)	0.0446(18)	0.0247(15)	−0.0016(13)	0.0104(12)	−0.0041(12)
C(26)	0.0148(13)	0.0489(18)	0.0206(14)	−0.0021(13)	0.0023(11)	−0.0003(12)
C(27)	0.0326(16)	0.0366(17)	0.0190(14)	−0.0003(12)	0.0107(12)	0.0002(13)
C(28)	0.0396(18)	0.058(2)	0.0262(16)	0.0087(15)	0.0091(14)	−0.0082(16)
C(29)	0.047(2)	0.070(2)	0.0171(15)	−0.0073(15)	0.0097(14)	−0.0198(18)
C(31)	0.0228(14)	0.0389(17)	0.0368(17)	0.0052(14)	0.0146(13)	0.0005(12)
C(30)	0.086(3)	0.065(3)	0.0330(19)	0.0023(18)	0.031(2)	0.026(2)
C(32)	0.0315(16)	0.0368(17)	0.0337(16)	0.0053(13)	0.0162(13)	−0.0037(13)
C(33)	0.0335(17)	0.050(2)	0.0328(17)	0.0007(15)	0.0105(14)	−0.0162(15)
C(41)	0.0279(15)	0.0415(18)	0.0252(15)	−0.0006(13)	0.0116(12)	0.0067(13)
C(42)	0.0283(15)	0.0353(16)	0.0297(15)	0.0110(13)	0.0101(12)	0.0071(13)
C(43)	0.0339(16)	0.0343(17)	0.0377(17)	−0.0069(14)	0.0136(14)	0.0032(13)
C(44)	0.0378(18)	0.057(2)	0.0337(18)	−0.0070(16)	0.0126(15)	0.0000(16)
C(45)	0.0306(17)	0.054(2)	0.044(2)	0.0250(17)	0.0032(15)	0.0090(15)

Continued on next page

Table S19. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(46)	0.075(3)	0.046(2)	0.052(2)	0.0114(18)	0.030(2)	0.031(2)
C(51)	0.0216(14)	0.0314(15)	0.0222(14)	0.0052(12)	0.0068(11)	0.0026(11)
C(52)	0.0274(14)	0.0329(16)	0.0215(14)	0.0000(12)	0.0038(12)	−0.0087(12)
C(53)	0.0361(17)	0.0294(16)	0.0358(17)	−0.0004(13)	0.0140(14)	0.0004(13)
C(54)	0.0235(15)	0.0400(18)	0.0465(19)	0.0069(15)	0.0122(14)	0.0050(13)
C(55)	0.065(2)	0.0312(18)	0.044(2)	−0.0004(15)	−0.0032(18)	0.0023(17)
C(56)	0.0432(18)	0.0401(18)	0.0237(15)	−0.0013(13)	−0.0029(14)	−0.0133(15)
C(61)	0.0144(12)	0.0175(12)	0.0204(13)	0.0020(10)	0.0057(10)	−0.0022(10)
C(62)	0.0158(12)	0.0197(13)	0.0196(13)	0.0028(10)	0.0042(10)	−0.0006(10)
C(63)	0.0206(13)	0.0249(14)	0.0218(14)	0.0032(11)	0.0001(11)	−0.0028(11)
C(64)	0.0192(13)	0.0253(14)	0.0284(15)	0.0114(12)	0.0025(11)	0.0011(11)
C(65)	0.0167(12)	0.0181(13)	0.0337(15)	0.0057(11)	0.0070(11)	−0.0008(10)
C(66)	0.0144(12)	0.0187(13)	0.0260(14)	0.0005(11)	0.0043(10)	−0.0013(10)
C(67)	0.0306(16)	0.0334(17)	0.0324(16)	0.0150(13)	−0.0021(13)	0.0064(13)
C(68)	0.0374(18)	0.0423(19)	0.0388(18)	0.0180(15)	0.0061(14)	0.0155(15)
C(69)	0.0326(18)	0.057(2)	0.052(2)	0.0164(18)	−0.0108(16)	0.0019(16)
C(70)	0.076(3)	0.058(2)	0.0311(18)	0.0150(17)	0.0085(18)	0.031(2)
C(81)	0.0253(14)	0.0224(14)	0.0288(15)	−0.0047(12)	−0.0049(12)	0.0006(11)
C(83)	0.0235(16)	0.046(2)	0.060(2)	−0.0124(17)	0.0091(15)	−0.0087(14)
C(84)	0.052(2)	0.041(2)	0.0386(19)	−0.0049(16)	−0.0167(16)	−0.0104(17)
C(89)	0.0222(19)	0.065(4)	0.046(3)	−0.012(2)	0.0208(19)	0.002(2)
C(85)	0.030(2)	0.079(5)	0.045(3)	−0.005(3)	0.019(2)	0.002(2)
C(86)	0.030(2)	0.079(5)	0.045(3)	−0.005(3)	0.019(2)	0.002(2)
C(91)	0.033(3)	0.017(3)	0.047(4)	−0.005(3)	−0.009(3)	−0.006(2)
C(92)	0.039(4)	0.037(4)	0.044(4)	0.016(3)	0.010(3)	−0.011(3)
C(93)	0.028(3)	0.024(3)	0.042(4)	−0.002(3)	0.004(3)	0.010(2)

Table S20. Distances [Å] for [PC(sp^2)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (**3**).

atom – atom	distance	atom – atom	distance
Pd – C	2.076(3)	Pd – P(2)	2.3099(7)
Pd – P(1)	2.3120(7)	Pd – P(3)	2.3701(7)
C – C(11)	1.433(4)	C – C(21)	1.436(4)
P(1) – C(12)	1.794(3)	P(1) – C(41)	1.846(3)
P(1) – C(42)	1.854(3)	C(1) – C(61)#1	1.434(3)
C(1) – C(61)	1.434(3)	C(1) – Pd(1)	2.074(3)
Pd(1) – P(4)#1	2.3063(7)	Pd(1) – P(4)	2.3063(7)
Pd(1) – P(5)	2.3463(11)	P(2) – C(22)	1.793(3)
P(2) – C(51)	1.844(3)	P(2) – C(52)	1.852(3)
P(3) – C(33)	1.825(3)	P(3) – C(31)	1.826(3)
P(3) – C(32)	1.827(3)	P(4) – C(82)	1.775(11)
P(4) – C(62)	1.797(3)	P(4) – C(81)	1.854(3)
P(4) – C(89)	1.925(9)	P(5) – C(91)	1.707(5)
P(5) – C(91)#1	1.707(5)	P(5) – C(93)#1	1.841(6)
P(5) – C(93)	1.841(6)	P(5) – C(92)#1	1.950(6)
P(5) – C(92)	1.950(6)	C(11) – C(12)	1.429(4)
C(11) – C(16)	1.432(4)	C(12) – C(13)	1.395(4)
C(13) – C(14)	1.387(4)	C(13) – H(13)	0.9500
C(14) – C(15)	1.405(4)	C(14) – C(17)	1.537(5)
C(18) – C(17)	1.510(7)	C(18) – H(18A)	0.9800
C(18) – H(18B)	0.9800	C(18) – H(18C)	0.9800
C(82) – C(87)	1.558(14)	C(82) – C(88)	1.594(17)
C(82) – H(82)	1.0000	C(87) – H(87A)	0.9800
C(87) – H(87B)	0.9800	C(87) – H(87C)	0.9800
C(88) – H(88A)	0.9800	C(88) – H(88B)	0.9800
C(88) – H(88C)	0.9800	C(17) – C(20)	1.464(6)
C(17) – C(19)	1.568(7)	C(16) – C(15)	1.382(4)
C(16) – H(16)	0.9500	C(15) – H(15)	0.9500
C(19) – H(19A)	0.9800	C(19) – H(19B)	0.9800
C(19) – H(19C)	0.9800	C(20) – H(20A)	0.9800
C(20) – H(20B)	0.9800	C(20) – H(20C)	0.9800
C(21) – C(22)	1.424(4)	C(21) – C(26)	1.430(4)
C(22) – C(23)	1.396(4)	C(23) – C(24)	1.380(4)
C(23) – H(23)	0.9500	C(24) – C(25)	1.407(4)
C(24) – C(27)	1.531(4)	C(25) – C(26)	1.370(4)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(27) – C(28)	1.529(4)	C(27) – C(29)	1.531(4)
C(27) – C(30)	1.532(5)	C(28) – H(28A)	0.9800
C(28) – H(28B)	0.9800	C(28) – H(28C)	0.9800
C(29) – H(29A)	0.9800	C(29) – H(29B)	0.9800
C(29) – H(29C)	0.9800	C(31) – H(31A)	0.9800

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Table S20. – continued from previous page

atom – atom	distance	atom – atom	distance
C(31) – H(31B)	0.9800	C(31) – H(31C)	0.9800
C(30) – H(30A)	0.9800	C(30) – H(30B)	0.9800
C(30) – H(30C)	0.9800	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(41) – C(44)	1.512(4)
C(41) – C(43)	1.530(4)	C(41) – H(41)	1.0000
C(42) – C(45)	1.528(4)	C(42) – C(46)	1.535(5)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(54)	1.529(4)
C(51) – C(53)	1.531(4)	C(51) – H(51)	1.0000
C(52) – C(55)	1.519(4)	C(52) – C(56)	1.527(4)
C(52) – H(52)	1.0000	C(53) – H(53A)	0.9800
C(53) – H(53B)	0.9800	C(53) – H(53C)	0.9800
C(54) – H(54A)	0.9800	C(54) – H(54B)	0.9800
C(54) – H(54C)	0.9800	C(55) – H(55A)	0.9800
C(55) – H(55B)	0.9800	C(55) – H(55C)	0.9800
C(56) – H(56A)	0.9800	C(56) – H(56B)	0.9800
C(56) – H(56C)	0.9800	C(61) – C(62)	1.421(3)
C(61) – C(66)	1.428(4)	C(62) – C(63)	1.387(4)
C(63) – C(64)	1.395(4)	C(63) – H(63)	0.9500
C(64) – C(65)	1.393(4)	C(64) – C(67)	1.535(4)
C(65) – C(66)	1.383(4)	C(65) – H(65)	0.9500
C(66) – H(66)	0.9500	C(67) – C(70)	1.508(5)
C(67) – C(68)	1.530(5)	C(67) – C(69)	1.546(5)
C(68) – H(68A)	0.9800	C(68) – H(68B)	0.9800
C(68) – H(68C)	0.9800	C(69) – H(69A)	0.9800
C(69) – H(69B)	0.9800	C(69) – H(69C)	0.9800
C(70) – H(70A)	0.9800	C(70) – H(70B)	0.9800
C(70) – H(70C)	0.9800	C(81) – C(83)	1.522(4)
C(81) – C(84)	1.524(4)	C(81) – H(81)	1.0000
C(83) – H(83A)	0.9800	C(83) – H(83B)	0.9800
C(83) – H(83C)	0.9800	C(84) – H(84A)	0.9800
C(84) – H(84B)	0.9800	C(84) – H(84C)	0.9800
C(89) – C(86)	1.464(15)	C(89) – C(85)	1.548(14)
C(89) – H(89)	1.0000	C(85) – H(85A)	0.9800
C(85) – H(85B)	0.9800	C(85) – H(85C)	0.9800

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Table S20. – continued from previous page

atom – atom	distance	atom – atom	distance
C(86) – H(86A)	0.9800	C(86) – H(86B)	0.9800
C(86) – H(86C)	0.9800	C(91) – H(91A)	0.9800
C(91) – H(91B)	0.9800	C(91) – H(91C)	0.9800
C(92) – H(92A)	0.9800	C(92) – H(92B)	0.9800
C(92) – H(92C)	0.9800	C(93) – H(93A)	0.9800
C(93) – H(93B)	0.9800	C(93) – H(93C)	0.9800

Table S21. Angles [°] for [PC(sp^2)P]$^{t\mathrm{Bu}}$Pd(PMe$_3$) (**3**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	81.08(7)	C – Pd – P(1)	81.43(7)
P(2) – Pd – P(1)	162.38(3)	C – Pd – P(3)	177.04(7)
P(2) – Pd – P(3)	101.73(3)	P(1) – Pd – P(3)	95.73(3)
C(11) – C – C(21)	122.7(2)	C(11) – C – Pd	118.51(18)
C(21) – C – Pd	118.79(18)	C(12) – P(1) – C(41)	108.12(14)
C(12) – P(1) – C(42)	108.88(13)	C(41) – P(1) – C(42)	106.72(14)
C(12) – P(1) – Pd	103.94(9)	C(41) – P(1) – Pd	111.80(10)
C(42) – P(1) – Pd	117.07(10)	C(61)#1 – C(1) – C(61)	123.0(3)
C(61)#1 – C(1) – Pd(1)	118.51(16)	C(61) – C(1) – Pd(1)	118.51(16)
C(1) – Pd(1) – P(4)#1	80.846(18)	C(1) – Pd(1) – P(4)	80.846(18)
P(4)#1 – Pd(1) – P(4)	161.69(4)	C(1) – Pd(1) – P(5)	180.0
P(4)#1 – Pd(1) – P(5)	99.154(18)	P(4) – Pd(1) – P(5)	99.154(18)
C(22) – P(2) – C(51)	104.26(12)	C(22) – P(2) – C(52)	107.71(13)
C(51) – P(2) – C(52)	105.45(13)	C(22) – P(2) – Pd	104.12(9)
C(51) – P(2) – Pd	117.33(9)	C(52) – P(2) – Pd	116.91(9)
C(33) – P(3) – C(31)	99.45(15)	C(33) – P(3) – C(32)	98.08(15)
C(31) – P(3) – C(32)	102.62(14)	C(33) – P(3) – Pd	122.11(10)
C(31) – P(3) – Pd	114.83(10)	C(32) – P(3) – Pd	116.43(10)
C(82) – P(4) – C(62)	107.7(5)	C(82) – P(4) – C(81)	102.5(5)
C(62) – P(4) – C(81)	108.59(12)	C(62) – P(4) – C(89)	100.7(4)
C(81) – P(4) – C(89)	108.8(4)	C(82) – P(4) – Pd(1)	117.3(5)
C(62) – P(4) – Pd(1)	103.44(9)	C(81) – P(4) – Pd(1)	117.02(10)
C(89) – P(4) – Pd(1)	116.6(4)	C(91) – P(5) – C(91)#1	103.9(4)
C(91) – P(5) – C(93)#1	49.6(3)	C(91)#1 – P(5) – C(93)#1	104.1(3)
C(91) – P(5) – C(93)	104.1(3)	C(91)#1 – P(5) – C(93)	49.6(3)
C(93)#1 – P(5) – C(93)	141.7(4)	C(91) – P(5) – C(92)#1	47.0(3)
C(91)#1 – P(5) – C(92)#1	95.2(3)	C(93)#1 – P(5) – C(92)#1	96.6(3)
C(93) – P(5) – C(92)#1	64.6(3)	C(91) – P(5) – C(92)	95.2(3)
C(91)#1 – P(5) – C(92)	47.0(3)	C(93)#1 – P(5) – C(92)	64.6(3)
C(93) – P(5) – C(92)	96.6(3)	C(92)#1 – P(5) – C(92)	122.7(4)
C(91) – P(5) – Pd(1)	128.0(2)	C(91)#1 – P(5) – Pd(1)	128.0(2)
C(93)#1 – P(5) – Pd(1)	109.13(19)	C(93) – P(5) – Pd(1)	109.13(19)
C(92)#1 – P(5) – Pd(1)	118.7(2)	C(92) – P(5) – Pd(1)	118.7(2)
C(12) – C(11) – C(16)	113.2(2)	C(12) – C(11) – C	120.9(2)
C(16) – C(11) – C	125.9(2)	C(13) – C(12) – C(11)	122.7(2)
C(13) – C(12) – P(1)	125.4(2)	C(11) – C(12) – P(1)	111.83(19)
C(14) – C(13) – C(12)	122.5(3)	C(14) – C(13) – H(13)	118.8
C(12) – C(13) – H(13)	118.8	C(13) – C(14) – C(15)	115.9(3)
C(13) – C(14) – C(17)	120.4(3)	C(15) – C(14) – C(17)	123.8(3)
C(17) – C(18) – H(18A)	109.5	C(17) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	C(17) – C(18) – H(18C)	109.5

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Table S21. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5
C(87) – C(82) – C(88)	106.4(9)	C(87) – C(82) – P(4)	108.4(9)
C(88) – C(82) – P(4)	112.3(7)	C(87) – C(82) – H(82)	109.9
C(88) – C(82) – H(82)	110.2	P(4) – C(82) – H(82)	109.5
C(82) – C(87) – H(87A)	109.5	C(82) – C(87) – H(87B)	110.0
H(87A) – C(87) – H(87B)	109.5	C(82) – C(87) – H(87C)	109.6
H(87A) – C(87) – H(87C)	109.5	H(87B) – C(87) – H(87C)	109.5
C(82) – C(88) – H(88A)	108.4	C(82) – C(88) – H(88B)	110.0
H(88A) – C(88) – H(88B)	109.5	C(82) – C(88) – H(88C)	109.0
H(88A) – C(88) – H(88C)	109.5	H(88B) – C(88) – H(88C)	109.5
C(20) – C(17) – C(18)	116.6(4)	C(20) – C(17) – C(14)	112.8(3)
C(18) – C(17) – C(14)	110.8(3)	C(20) – C(17) – C(19)	104.4(4)
C(18) – C(17) – C(19)	103.0(4)	C(14) – C(17) – C(19)	108.2(4)
C(15) – C(16) – C(11)	122.9(3)	C(15) – C(16) – H(16)	118.6
C(11) – C(16) – H(16)	118.6	C(16) – C(15) – C(14)	122.4(3)
C(16) – C(15) – H(15)	118.8	C(14) – C(15) – H(15)	118.8
C(17) – C(19) – H(19A)	109.5	C(17) – C(19) – H(19B)	109.5
H(19A) – C(19) – H(19B)	109.5	C(17) – C(19) – H(19C)	109.5
H(19A) – C(19) – H(19C)	109.5	H(19B) – C(19) – H(19C)	109.5
C(17) – C(20) – H(20A)	109.5	C(17) – C(20) – H(20B)	109.5
H(20A) – C(20) – H(20B)	109.5	C(17) – C(20) – H(20C)	109.5
H(20A) – C(20) – H(20C)	109.5	H(20B) – C(20) – H(20C)	109.5
C(22) – C(21) – C(26)	113.2(2)	C(22) – C(21) – C	120.9(2)
C(26) – C(21) – C	125.9(2)	C(23) – C(22) – C(21)	122.9(2)
C(23) – C(22) – P(2)	125.4(2)	C(21) – C(22) – P(2)	111.64(19)
C(24) – C(23) – C(22)	122.3(2)	C(24) – C(23) – H(23)	118.8
C(22) – C(23) – H(23)	118.8	C(23) – C(24) – C(25)	115.5(2)
C(23) – C(24) – C(27)	124.6(2)	C(25) – C(24) – C(27)	120.0(2)
C(26) – C(25) – C(24)	123.1(3)	C(26) – C(25) – H(25)	118.4
C(24) – C(25) – H(25)	118.4	C(25) – C(26) – C(21)	122.6(2)
C(25) – C(26) – H(26)	118.7	C(21) – C(26) – H(26)	118.7
C(28) – C(27) – C(24)	109.6(2)	C(28) – C(27) – C(29)	108.1(3)
C(24) – C(27) – C(29)	111.7(2)	C(28) – C(27) – C(30)	108.8(3)
C(24) – C(27) – C(30)	109.7(2)	C(29) – C(27) – C(30)	108.9(3)
C(27) – C(28) – H(28A)	109.5	C(27) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	C(27) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
C(27) – C(29) – H(29A)	109.5	C(27) – C(29) – H(29B)	109.5
H(29A) – C(29) – H(29B)	109.5	C(27) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5

Continued on next page

Table S21. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5
C(27) – C(30) – H(30A)	109.5	C(27) – C(30) – H(30B)	109.5
H(30A) – C(30) – H(30B)	109.5	C(27) – C(30) – H(30C)	109.5
H(30A) – C(30) – H(30C)	109.5	H(30B) – C(30) – H(30C)	109.5
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(44) – C(41) – C(43)	112.9(3)	C(44) – C(41) – P(1)	119.2(2)
C(43) – C(41) – P(1)	107.2(2)	C(44) – C(41) – H(41)	105.5
C(43) – C(41) – H(41)	105.5	P(1) – C(41) – H(41)	105.5
C(45) – C(42) – C(46)	109.6(3)	C(45) – C(42) – P(1)	116.5(2)
C(46) – C(42) – P(1)	108.2(2)	C(45) – C(42) – H(42)	107.4
C(46) – C(42) – H(42)	107.4	P(1) – C(42) – H(42)	107.4
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(54) – C(51) – C(53)	111.4(2)	C(54) – C(51) – P(2)	113.3(2)
C(53) – C(51) – P(2)	108.97(19)	C(54) – C(51) – H(51)	107.6
C(53) – C(51) – H(51)	107.6	P(2) – C(51) – H(51)	107.6
C(55) – C(52) – C(56)	110.9(3)	C(55) – C(52) – P(2)	108.2(2)
C(56) – C(52) – P(2)	118.1(2)	C(55) – C(52) – H(52)	106.3
C(56) – C(52) – H(52)	106.3	P(2) – C(52) – H(52)	106.3
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5

Continued on next page

Table S21. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5
C(62) – C(61) – C(66)	113.7(2)	C(62) – C(61) – C(1)	120.6(2)
C(66) – C(61) – C(1)	125.7(2)	C(63) – C(62) – C(61)	122.9(2)
C(63) – C(62) – P(4)	125.3(2)	C(61) – C(62) – P(4)	111.65(18)
C(62) – C(63) – C(64)	122.3(3)	C(62) – C(63) – H(63)	118.8
C(64) – C(63) – H(63)	118.8	C(65) – C(64) – C(63)	115.5(2)
C(65) – C(64) – C(67)	123.8(3)	C(63) – C(64) – C(67)	120.7(3)
C(66) – C(65) – C(64)	123.2(3)	C(66) – C(65) – H(65)	118.4
C(64) – C(65) – H(65)	118.4	C(65) – C(66) – C(61)	122.1(2)
C(65) – C(66) – H(66)	118.9	C(61) – C(66) – H(66)	118.9
C(70) – C(67) – C(68)	107.9(3)	C(70) – C(67) – C(64)	109.8(3)
C(68) – C(67) – C(64)	112.4(3)	C(70) – C(67) – C(69)	111.0(3)
C(68) – C(67) – C(69)	107.1(3)	C(64) – C(67) – C(69)	108.7(2)
C(67) – C(68) – H(68A)	109.5	C(67) – C(68) – H(68B)	109.5
H(68A) – C(68) – H(68B)	109.5	C(67) – C(68) – H(68C)	109.5
H(68A) – C(68) – H(68C)	109.5	H(68B) – C(68) – H(68C)	109.5
C(67) – C(69) – H(69A)	109.5	C(67) – C(69) – H(69B)	109.5
H(69A) – C(69) – H(69B)	109.5	C(67) – C(69) – H(69C)	109.5
H(69A) – C(69) – H(69C)	109.5	H(69B) – C(69) – H(69C)	109.5
C(67) – C(70) – H(70A)	109.5	C(67) – C(70) – H(70B)	109.5
H(70A) – C(70) – H(70B)	109.5	C(67) – C(70) – H(70C)	109.5
H(70A) – C(70) – H(70C)	109.5	H(70B) – C(70) – H(70C)	109.5
C(83) – C(81) – C(84)	110.8(3)	C(83) – C(81) – P(4)	109.0(2)
C(84) – C(81) – P(4)	118.5(2)	C(83) – C(81) – H(81)	105.9
C(84) – C(81) – H(81)	105.9	P(4) – C(81) – H(81)	105.9
C(81) – C(83) – H(83A)	109.5	C(81) – C(83) – H(83B)	109.5
H(83A) – C(83) – H(83B)	109.5	C(81) – C(83) – H(83C)	109.5
H(83A) – C(83) – H(83C)	109.5	H(83B) – C(83) – H(83C)	109.5
C(81) – C(84) – H(84A)	109.5	C(81) – C(84) – H(84B)	109.5
H(84A) – C(84) – H(84B)	109.5	C(81) – C(84) – H(84C)	109.5
H(84A) – C(84) – H(84C)	109.5	H(84B) – C(84) – H(84C)	109.5
C(86) – C(89) – C(85)	112.2(8)	C(86) – C(89) – P(4)	115.3(7)
C(85) – C(89) – P(4)	108.5(8)	C(86) – C(89) – H(89)	106.4
C(85) – C(89) – H(89)	106.8	P(4) – C(89) – H(89)	107.2
P(5) – C(91) – H(91A)	109.5	P(5) – C(91) – H(91B)	109.5
P(5) – C(91) – H(91C)	109.5	P(5) – C(92) – H(92A)	109.5
P(5) – C(92) – H(92B)	109.5	P(5) – C(92) – H(92C)	109.5
P(5) – C(93) – H(93A)	109.5	P(5) – C(93) – H(93B)	109.5
P(5) – C(93) – H(93C)	109.5		

4.4 Crystal data for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{tBu}Pd(PMe_3)$ (5)

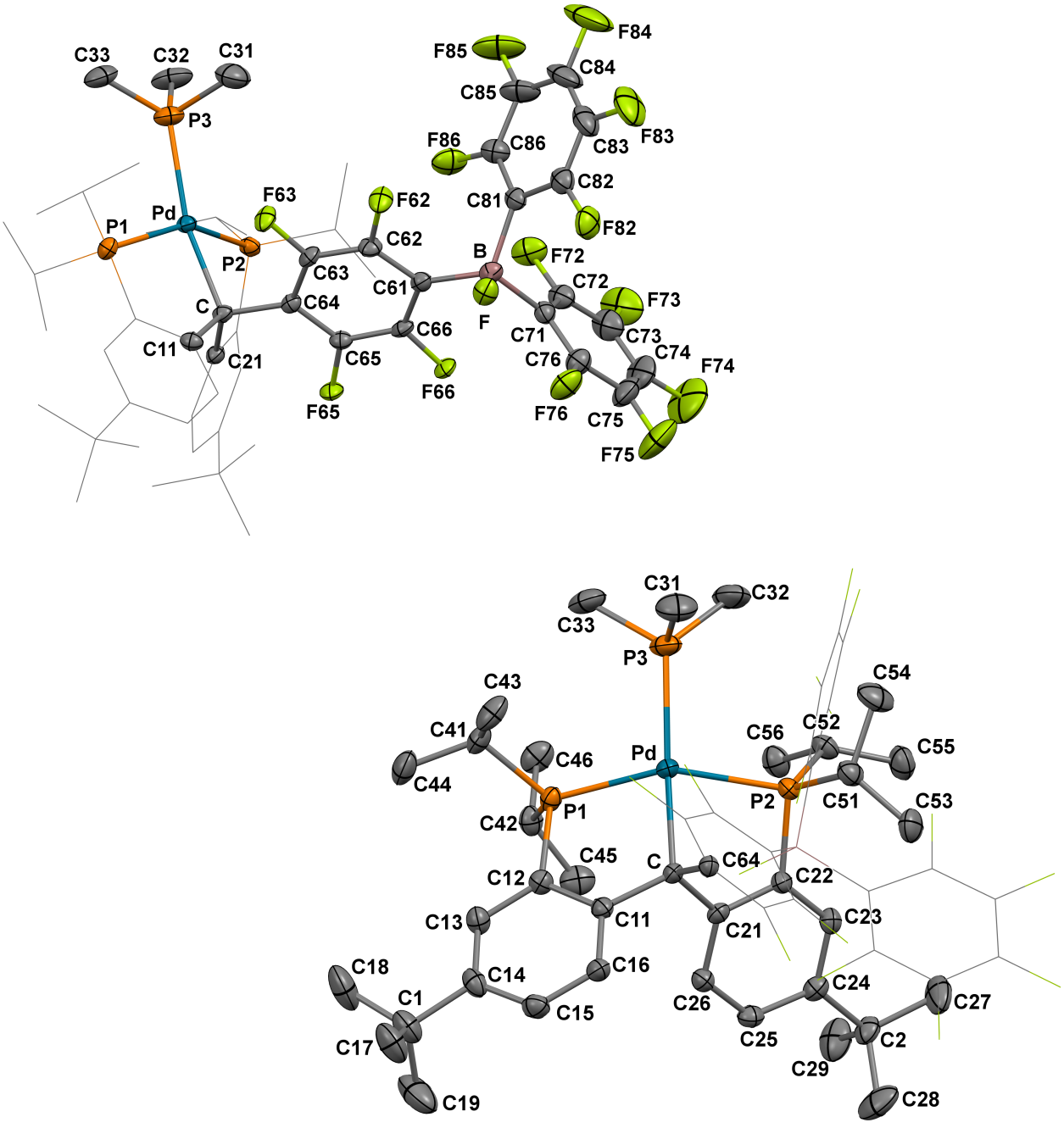

Figure S62. Thermal-ellipsoid representation of $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{tBu}Pd(PMe_3)$ (**5**) at 50% probability. Hydrogen atoms were omitted for clarity.

Table S22. Crystal data and structure refinement for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

Identification code:	pc26	
Empirical formula:	$C_{54}H_{61}BF_{15}P_3Pd$	
Formula weight:	1205.15	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	a = 14.7706(10) Å	α = 90°
	b = 13.9199(9) Å	β = 93.208(2)°
	c = 28.5994(19) Å	γ = 90°
Volume:	5871.0(7) Å^3	
Z:	4	
Density (calculated):	1.363 g·cm^{-3}	
Absorption coefficient (μ):	0.479 mm^{-1}	
F(000):	2464	
Crystal size:	0.09 × 0.08 × 0.08 mm^3	
θ range for data collection:	1.38 to 25.00°	
Index ranges:	$-17 \le h \le 17$, $-13 \le k \le 16$, $-33 \le l \le 34$	
Reflections collected:	92881	
Independent reflections:	10345 [R_{int} = 0.0419]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.9876 and 0.9029	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	10345 / 0 / 685	
Goodness-of-fit on F^2:	1.066	
Final R indices [I>2σ(I)]:	R_1 = 0.0379, wR_2 = 0.0880	
R indices (all data):	R_1 = 0.0481, wR_2 = 0.0917	
Largest diff. peak and hole:	0.600 and −0.364 e$^-$·Å^{-3}	

Table S23. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $[(C_6F_5)_2BF(C_6F_4)$-PC(sp^3)P]$^{t\text{Bu}}$Pd(PMe_3) (**5**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.91902(1)	0.21635(2)	0.33807(1)	0.019(1)
C(1)	1.3489(2)	−0.0048(2)	0.38490(12)	0.035(1)
P(1)	1.06856(5)	0.21494(5)	0.31722(2)	0.021(1)
C(2)	0.9218(2)	0.3319(2)	0.56875(10)	0.029(1)
P(2)	0.80699(5)	0.23980(5)	0.39204(2)	0.020(1)
P(3)	0.84292(6)	0.28242(6)	0.27057(3)	0.032(1)
C(11)	1.06663(18)	0.0860(2)	0.38726(9)	0.020(1)
C(12)	1.12250(18)	0.12541(19)	0.35525(9)	0.021(1)
C(14)	1.24891(19)	0.0257(2)	0.38403(11)	0.027(1)
C(13)	1.21361(19)	0.0970(2)	0.35460(10)	0.026(1)
C(15)	1.1909(2)	−0.0165(2)	0.41451(10)	0.027(1)
C(17)	1.3547(2)	−0.1137(3)	0.37983(15)	0.048(1)
C(16)	1.10166(19)	0.0125(2)	0.41624(9)	0.024(1)
C(18)	1.3983(2)	0.0381(3)	0.34469(16)	0.056(1)
C(19)	1.3947(3)	0.0268(3)	0.43096(16)	0.065(1)
C(21)	0.96488(17)	0.18424(19)	0.43736(9)	0.018(1)
C(22)	0.88289(17)	0.23096(19)	0.44420(9)	0.020(1)
C(23)	0.86761(18)	0.2740(2)	0.48690(9)	0.022(1)
C(24)	0.93541(19)	0.2795(2)	0.52236(9)	0.023(1)
C(25)	1.01896(19)	0.2403(2)	0.51382(10)	0.024(1)
C(26)	1.03356(18)	0.1922(2)	0.47251(9)	0.022(1)
C(27)	0.8241(2)	0.3610(3)	0.57379(13)	0.053(1)
C(28)	0.9499(3)	0.2665(3)	0.60927(12)	0.055(1)
C(29)	0.9823(3)	0.4199(3)	0.57145(13)	0.049(1)
C(31)	0.7811(3)	0.1822(3)	0.24294(13)	0.052(1)
C(32)	0.7537(3)	0.3726(3)	0.27134(12)	0.051(1)
C(33)	0.9051(3)	0.3286(3)	0.22246(11)	0.043(1)
C	0.97156(17)	0.12453(19)	0.39355(9)	0.018(1)
C(41)	1.0973(2)	0.1894(2)	0.25628(10)	0.027(1)
C(42)	1.13049(19)	0.3265(2)	0.33325(10)	0.026(1)
C(43)	1.0447(2)	0.1030(2)	0.23742(11)	0.039(1)
C(44)	1.1971(2)	0.1778(3)	0.24702(12)	0.040(1)
C(46)	1.0945(2)	0.4125(2)	0.30521(11)	0.036(1)
C(45)	1.1285(2)	0.3449(2)	0.38545(11)	0.034(1)
C(51)	0.70997(19)	0.1560(2)	0.39591(10)	0.028(1)
C(52)	0.76229(19)	0.3637(2)	0.39032(11)	0.027(1)
F	0.80846(11)	−0.30447(12)	0.37846(6)	0.030(1)
C(54)	0.6320(2)	0.1848(3)	0.36193(13)	0.045(1)
C(53)	0.6797(2)	0.1387(3)	0.44539(11)	0.037(1)

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Table S23. – continued from previous page

atom	x	y	x	U(eq)
C(55)	0.6972(2)	0.3948(2)	0.42761(12)	0.038(1)
C(56)	0.8416(2)	0.4344(2)	0.38884(12)	0.033(1)
C(61)	0.79361(18)	−0.1326(2)	0.39081(9)	0.021(1)
C(62)	0.83480(19)	−0.0947(2)	0.35208(9)	0.023(1)
F(62)	0.82115(12)	−0.13894(12)	0.30996(5)	0.032(1)
C(63)	0.88822(18)	−0.0148(2)	0.35324(9)	0.022(1)
F(63)	0.92340(11)	0.01303(11)	0.31246(5)	0.028(1)
C(64)	0.90893(17)	0.03786(19)	0.39369(9)	0.018(1)
C(65)	0.87157(18)	−0.00149(19)	0.43291(9)	0.020(1)
F(65)	0.89045(11)	0.03528(12)	0.47611(5)	0.026(1)
C(66)	0.81544(18)	−0.0807(2)	0.43078(9)	0.020(1)
F(66)	0.78335(11)	−0.10797(11)	0.47231(5)	0.026(1)
C(71)	0.68901(19)	−0.2617(2)	0.43495(10)	0.025(1)
C(72)	0.6145(2)	−0.2084(2)	0.44731(10)	0.033(1)
F(72)	0.58987(12)	−0.13048(14)	0.42161(7)	0.043(1)
C(73)	0.5643(2)	−0.2279(3)	0.48451(13)	0.046(1)
F(73)	0.49189(14)	−0.1735(2)	0.49371(8)	0.070(1)
C(74)	0.5874(3)	−0.3042(3)	0.51284(13)	0.055(1)
F(74)	0.5382(2)	−0.3251(2)	0.54954(9)	0.095(1)
C(76)	0.7112(2)	−0.3363(2)	0.46510(11)	0.033(1)
F(76)	0.78388(14)	−0.39240(13)	0.45911(7)	0.044(1)
C(81)	0.66178(19)	−0.2414(2)	0.34423(10)	0.025(1)
C(82)	0.6336(2)	−0.3305(2)	0.32751(11)	0.033(1)
F(82)	0.67027(13)	−0.41134(13)	0.34649(7)	0.043(1)
C(83)	0.5698(2)	−0.3439(3)	0.29162(13)	0.047(1)
F(83)	0.54889(17)	−0.43279(19)	0.27609(8)	0.072(1)
C(84)	0.5265(3)	−0.2665(4)	0.27186(13)	0.056(1)
F(84)	0.46127(18)	−0.2781(2)	0.23774(9)	0.095(1)
C(85)	0.5492(2)	−0.1773(3)	0.28725(13)	0.050(1)
F(85)	0.50709(18)	−0.1000(2)	0.26799(9)	0.080(1)
C(86)	0.6166(2)	−0.1655(2)	0.32225(11)	0.033(1)
F(86)	0.63713(13)	−0.07388(13)	0.33447(7)	0.043(1)
C(75)	0.6615(3)	−0.3584(3)	0.50347(12)	0.048(1)
F(75)	0.68666(19)	−0.43324(19)	0.53107(9)	0.079(1)
B	0.7405(2)	−0.2355(2)	0.38736(11)	0.023(1)
H(13)	1.2519	0.1274	0.3335	0.031
H(15)	1.2130	−0.0665	0.4347	0.033
H(17A)	1.4184	−0.1328	0.3784	0.071
H(17B)	1.3209	−0.1337	0.3510	0.071
H(17C)	1.3287	−0.1445	0.4068	0.071
H(16)	1.0636	−0.0180	0.4374	0.029
H(18A)	1.4002	0.1081	0.3479	0.085

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Table S23. – continued from previous page

atom	x	y	x	U(eq)
H(18B)	1.3662	0.0209	0.3149	0.085
H(18C)	1.4603	0.0128	0.3453	0.085
H(19A)	1.3917	0.0969	0.4335	0.097
H(19B)	1.4583	0.0063	0.4324	0.097
H(19C)	1.3637	−0.0024	0.4569	0.097
H(23)	0.8096	0.3003	0.4919	0.027
H(25)	1.0675	0.2464	0.5369	0.028
H(26)	1.0912	0.1642	0.4681	0.026
H(27A)	0.7851	0.3041	0.5707	0.079
H(27B)	0.8059	0.4075	0.5493	0.079
H(27C)	0.8180	0.3902	0.6046	0.079
H(28A)	0.9433	0.3006	0.6389	0.082
H(28B)	1.0133	0.2473	0.6069	0.082
H(28C)	0.9113	0.2092	0.6083	0.082
H(29A)	0.9777	0.4511	0.6019	0.074
H(29B)	0.9630	0.4649	0.5465	0.074
H(29C)	1.0453	0.4006	0.5677	0.074
H(31A)	0.8239	0.1312	0.2357	0.078
H(31B)	0.7492	0.2042	0.2139	0.078
H(31C)	0.7371	0.1573	0.2643	0.078
H(32A)	0.7028	0.3472	0.2881	0.076
H(32B)	0.7329	0.3885	0.2391	0.076
H(32C)	0.7774	0.4305	0.2872	0.076
H(33A)	0.9416	0.3839	0.2332	0.065
H(33B)	0.8623	0.3485	0.1969	0.065
H(33C)	0.9450	0.2783	0.2113	0.065
H(41)	1.0750	0.2456	0.2371	0.033
H(42)	1.1953	0.3170	0.3258	0.032
H(43A)	1.0659	0.0452	0.2542	0.058
H(43B)	1.0540	0.0956	0.2040	0.058
H(43C)	0.9799	0.1123	0.2419	0.058
H(44A)	1.2316	0.2317	0.2611	0.060
H(44B)	1.2044	0.1769	0.2132	0.060
H(44C)	1.2198	0.1174	0.2608	0.060
H(46A)	1.0309	0.4236	0.3118	0.053
H(46B)	1.0990	0.3999	0.2717	0.053
H(46C)	1.1303	0.4696	0.3141	0.053
H(45A)	1.1549	0.2899	0.4027	0.051
H(45B)	1.0656	0.3539	0.3938	0.051
H(45C)	1.1636	0.4029	0.3936	0.051
H(51)	0.7317	0.0924	0.3847	0.034
H(52)	0.7274	0.3702	0.3595	0.032

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Table S23. – continued from previous page

atom	x	y	x	U(eq)
H(54A)	0.5864	0.1336	0.3602	0.067
H(54B)	0.6548	0.1953	0.3308	0.067
H(54C)	0.6044	0.2442	0.3728	0.067
H(53A)	0.7323	0.1205	0.4659	0.055
H(53B)	0.6347	0.0869	0.4448	0.055
H(53C)	0.6528	0.1977	0.4572	0.055
H(55A)	0.7313	0.4036	0.4577	0.057
H(55B)	0.6509	0.3451	0.4308	0.057
H(55C)	0.6678	0.4554	0.4181	0.057
H(56A)	0.8182	0.4990	0.3819	0.050
H(56B)	0.8817	0.4147	0.3644	0.050
H(56C)	0.8757	0.4346	0.4192	0.050

Table S24. Anisotropic displacement parameters (Å^2) for [$(C_6F_5)_2BF(C_6F_4)$-PC(sp^3)P]$^{t\text{Bu}}$Pd(PMe_3) (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0193(1)	0.0212(1)	0.0150(1)	0.0020(1)	0.0001(1)	0.0011(1)
C(1)	0.0225(16)	0.0330(18)	0.050(2)	−0.0021(15)	−0.0005(14)	0.0041(14)
P(1)	0.0230(4)	0.0199(4)	0.0204(4)	0.0022(3)	0.0054(3)	0.0004(3)
C(2)	0.0322(16)	0.0349(18)	0.0209(15)	−0.0086(13)	0.0053(12)	−0.0014(14)
P(2)	0.0156(3)	0.0245(4)	0.0202(4)	0.0004(3)	−0.0002(3)	0.0016(3)
P(3)	0.0384(5)	0.0366(5)	0.0212(4)	0.0039(3)	−0.0062(3)	0.0063(4)
C(11)	0.0202(14)	0.0234(14)	0.0174(14)	−0.0024(11)	−0.0002(11)	0.0024(11)
C(12)	0.0231(14)	0.0191(14)	0.0220(14)	−0.0001(11)	0.0021(11)	0.0000(11)
C(14)	0.0208(14)	0.0267(16)	0.0338(17)	−0.0076(13)	0.0015(12)	0.0040(12)
C(13)	0.0218(14)	0.0253(16)	0.0307(16)	0.0007(13)	0.0052(12)	0.0009(12)
C(15)	0.0300(16)	0.0260(16)	0.0253(15)	0.0020(12)	−0.0010(12)	0.0071(13)
C(17)	0.0287(18)	0.041(2)	0.074(3)	−0.0024(19)	0.0033(17)	0.0099(15)
C(16)	0.0252(15)	0.0295(16)	0.0185(14)	0.0028(12)	0.0022(11)	0.0042(12)
C(18)	0.0245(18)	0.053(2)	0.093(3)	0.002(2)	0.0123(19)	0.0072(17)
C(19)	0.035(2)	0.081(3)	0.076(3)	−0.029(2)	−0.018(2)	0.014(2)
C(21)	0.0211(14)	0.0191(13)	0.0152(13)	0.0023(11)	0.0023(11)	−0.0010(11)
C(22)	0.0177(13)	0.0230(15)	0.0180(13)	0.0010(11)	0.0008(10)	−0.0012(11)
C(23)	0.0208(14)	0.0229(15)	0.0234(14)	−0.0017(12)	0.0042(11)	0.0009(12)
C(24)	0.0286(15)	0.0216(14)	0.0200(14)	−0.0005(12)	0.0031(12)	−0.0009(12)
C(25)	0.0237(14)	0.0258(15)	0.0208(14)	0.0001(12)	−0.0033(11)	−0.0016(12)
C(26)	0.0200(14)	0.0244(15)	0.0217(14)	0.0001(12)	0.0002(11)	0.0024(11)
C(27)	0.038(2)	0.082(3)	0.039(2)	−0.029(2)	0.0094(16)	0.003(2)
C(28)	0.088(3)	0.054(2)	0.0234(18)	−0.0067(17)	0.0096(18)	0.008(2)
C(29)	0.056(2)	0.045(2)	0.048(2)	−0.0230(18)	0.0157(18)	−0.0085(18)
C(31)	0.054(2)	0.061(2)	0.038(2)	−0.0024(18)	−0.0154(17)	−0.003(2)
C(32)	0.057(2)	0.063(3)	0.0318(19)	0.0106(18)	−0.0076(17)	0.025(2)
C(33)	0.059(2)	0.047(2)	0.0226(17)	0.0089(15)	−0.0047(15)	0.0054(18)
C	0.0178(13)	0.0220(14)	0.0147(13)	0.0025(11)	0.0027(10)	0.0020(11)
C(41)	0.0368(17)	0.0256(16)	0.0203(15)	0.0024(12)	0.0105(12)	0.0013(13)
C(42)	0.0243(15)	0.0224(15)	0.0327(17)	0.0011(13)	0.0066(12)	−0.0018(12)
C(43)	0.058(2)	0.0351(19)	0.0244(16)	−0.0042(14)	0.0142(15)	−0.0068(16)
C(44)	0.045(2)	0.0425(19)	0.0331(18)	0.0052(15)	0.0195(15)	0.0051(16)
C(46)	0.049(2)	0.0239(16)	0.0342(18)	0.0023(14)	0.0064(15)	−0.0041(15)
C(45)	0.0418(18)	0.0248(17)	0.0347(18)	−0.0015(13)	−0.0043(14)	−0.0074(14)
C(51)	0.0208(14)	0.0313(17)	0.0321(16)	0.0029(13)	−0.0013(12)	−0.0015(13)
C(52)	0.0233(15)	0.0257(16)	0.0312(16)	0.0018(13)	−0.0015(12)	0.0065(12)
F	0.0278(9)	0.0280(9)	0.0362(10)	0.0027(7)	0.0079(7)	0.0058(7)
C(54)	0.0272(17)	0.050(2)	0.054(2)	0.0071(18)	−0.0130(16)	−0.0078(16)
C(53)	0.0262(16)	0.044(2)	0.0407(19)	0.0036(16)	0.0106(14)	−0.0048(15)

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Table S24. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(55)	0.0319(17)	0.0376(19)	0.046(2)	0.0008(16)	0.0105(15)	0.0103(15)
C(56)	0.0309(17)	0.0270(17)	0.0421(19)	0.0005(14)	0.0039(14)	0.0039(13)
C(61)	0.0188(13)	0.0242(15)	0.0200(14)	0.0027(11)	0.0022(11)	0.0024(11)
C(62)	0.0281(15)	0.0246(15)	0.0151(14)	−0.0036(11)	0.0013(11)	−0.0002(12)
F(62)	0.0475(11)	0.0312(9)	0.0181(8)	−0.0085(7)	0.0086(7)	−0.0118(8)
C(63)	0.0255(14)	0.0247(15)	0.0169(14)	0.0045(12)	0.0061(11)	−0.0007(12)
F(63)	0.0406(10)	0.0284(9)	0.0167(8)	−0.0029(7)	0.0115(7)	−0.0087(8)
C(64)	0.0179(13)	0.0194(14)	0.0165(13)	0.0009(11)	0.0033(10)	0.0030(11)
C(65)	0.0222(14)	0.0225(14)	0.0155(13)	−0.0020(11)	0.0008(11)	0.0025(12)
F(65)	0.0346(9)	0.0328(9)	0.0118(8)	0.0004(7)	−0.0002(7)	−0.0066(7)
C(66)	0.0203(14)	0.0268(15)	0.0137(13)	0.0049(11)	0.0043(11)	0.0052(12)
F(66)	0.0311(9)	0.0321(9)	0.0144(8)	0.0045(7)	0.0053(7)	−0.0058(7)
C(71)	0.0242(15)	0.0264(16)	0.0237(15)	−0.0025(12)	0.0023(12)	−0.0043(12)
C(72)	0.0277(16)	0.045(2)	0.0255(16)	−0.0023(15)	0.0043(13)	0.0009(15)
F(72)	0.0351(10)	0.0559(12)	0.0398(11)	0.0027(10)	0.0076(8)	0.0206(9)
C(73)	0.0306(18)	0.068(3)	0.040(2)	−0.0051(19)	0.0115(15)	0.0047(18)
F(73)	0.0382(12)	0.119(2)	0.0552(14)	−0.0090(14)	0.0227(10)	0.0180(13)
C(74)	0.048(2)	0.081(3)	0.038(2)	0.010(2)	0.0237(18)	−0.007(2)
F(74)	0.0871(19)	0.140(3)	0.0634(17)	0.0263(18)	0.0499(15)	−0.0043(19)
C(76)	0.0354(17)	0.0325(18)	0.0316(17)	0.0009(14)	0.0059(14)	0.0013(14)
F(76)	0.0563(12)	0.0344(11)	0.0422(11)	0.0115(9)	0.0105(9)	0.0140(9)
C(81)	0.0213(14)	0.0328(17)	0.0215(15)	−0.0015(12)	0.0045(12)	−0.0021(12)
C(82)	0.0294(16)	0.0406(19)	0.0289(17)	−0.0022(15)	0.0065(13)	−0.0046(15)
F(82)	0.0533(12)	0.0271(10)	0.0499(12)	−0.0018(9)	0.0042(10)	−0.0097(9)
C(83)	0.043(2)	0.057(2)	0.040(2)	−0.0153(18)	0.0014(17)	−0.0208(19)
F(83)	0.0768(17)	0.0761(17)	0.0638(15)	−0.0282(13)	0.0006(13)	−0.0405(14)
C(84)	0.039(2)	0.089(3)	0.036(2)	−0.011(2)	−0.0152(17)	−0.009(2)
F(84)	0.0652(17)	0.154(3)	0.0620(17)	−0.0151(18)	−0.0391(14)	−0.0090(18)
C(85)	0.043(2)	0.068(3)	0.038(2)	0.0025(19)	−0.0126(16)	0.021(2)
F(85)	0.0777(17)	0.101(2)	0.0583(15)	0.0085(14)	−0.0277(13)	0.0424(16)
C(86)	0.0314(17)	0.0380(19)	0.0287(17)	−0.0024(14)	−0.0015(13)	0.0041(14)
F(86)	0.0507(12)	0.0350(11)	0.0428(11)	0.0035(9)	−0.0065(9)	0.0153(9)
C(75)	0.063(2)	0.049(2)	0.0339(19)	0.0155(17)	0.0106(17)	−0.0064(19)
F(75)	0.107(2)	0.0742(17)	0.0588(16)	0.0387(13)	0.0268(15)	0.0038(15)
B	0.0238(16)	0.0238(17)	0.0214(16)	0.0017(13)	0.0029(13)	0.0039(13)

Table S25. Distances [Å] for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

atom – atom	distance	atom – atom	distance
Pd – C	2.148(3)	Pd – P(1)	2.3200(7)
Pd – P(2)	2.3478(7)	Pd – P(3)	2.3651(8)
C(1) – C(19)	1.512(5)	C(1) – C(18)	1.518(5)
C(1) – C(17)	1.525(5)	C(1) – C(14)	1.536(4)
P(1) – C(12)	1.809(3)	P(1) – C(42)	1.847(3)
P(1) – C(41)	1.851(3)	C(2) – C(28)	1.514(5)
C(2) – C(27)	1.514(4)	C(2) – C(29)	1.516(5)
C(2) – C(24)	1.537(4)	P(2) – C(22)	1.819(3)
P(2) – C(52)	1.846(3)	P(2) – C(51)	1.856(3)
P(3) – C(33)	1.814(3)	P(3) – C(32)	1.821(4)
P(3) – C(31)	1.823(4)	C(11) – C(12)	1.380(4)
C(11) – C(16)	1.398(4)	C(11) – C	1.523(4)
C(12) – C(13)	1.404(4)	C(14) – C(13)	1.384(4)
C(14) – C(15)	1.387(4)	C(13) – H(13)	0.9500
C(15) – C(16)	1.382(4)	C(15) – H(15)	0.9500
C(17) – H(17A)	0.9800	C(17) – H(17B)	0.9800
C(17) – H(17C)	0.9800	C(16) – H(16)	0.9500
C(18) – H(18A)	0.9800	C(18) – H(18B)	0.9800
C(18) – H(18C)	0.9800	C(19) – H(19A)	0.9800
C(19) – H(19B)	0.9800	C(19) – H(19C)	0.9800
C(21) – C(26)	1.392(4)	C(21) – C(22)	1.398(4)
C(21) – C	1.512(4)	C(22) – C(23)	1.390(4)
C(23) – C(24)	1.387(4)	C(23) – H(23)	0.9500
C(24) – C(25)	1.384(4)	C(25) – C(26)	1.385(4)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(27) – H(27A)	0.9800	C(27) – H(27B)	0.9800
C(27) – H(27C)	0.9800	C(28) – H(28A)	0.9800
C(28) – H(28B)	0.9800	C(28) – H(28C)	0.9800
C(29) – H(29A)	0.9800	C(29) – H(29B)	0.9800
C(29) – H(29C)	0.9800	C(31) – H(31A)	0.9800
C(31) – H(31B)	0.9800	C(31) – H(31C)	0.9800
C(32) – H(32A)	0.9800	C(32) – H(32B)	0.9800
C(32) – H(32C)	0.9800	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C – C(64)	1.520(4)	C(41) – C(43)	1.515(4)
C(41) – C(44)	1.521(4)	C(41) – H(41)	1.0000
C(42) – C(45)	1.517(4)	C(42) – C(46)	1.520(4)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(46) – H(46A)	0.9800

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Table S25. – continued from previous page

atom – atom	distance	atom – atom	distance
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(51) – C(54)	1.519(4)
C(51) – C(53)	1.527(4)	C(51) – H(51)	1.0000
C(52) – C(56)	1.532(4)	C(52) – C(55)	1.538(4)
C(52) – H(52)	1.0000	F – B	1.422(4)
C(54) – H(54A)	0.9800	C(54) – H(54B)	0.9800
C(54) – H(54C)	0.9800	C(53) – H(53A)	0.9800
C(53) – H(53B)	0.9800	C(53) – H(53C)	0.9800
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(55) – H(55C)	0.9800	C(56) – H(56A)	0.9800
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800
C(61) – C(66)	1.375(4)	C(61) – C(62)	1.397(4)
C(61) – B	1.633(4)	C(62) – F(62)	1.358(3)
C(62) – C(63)	1.363(4)	C(63) – F(63)	1.360(3)
C(63) – C(64)	1.389(4)	C(64) – C(65)	1.390(4)
C(65) – F(65)	1.352(3)	C(65) – C(66)	1.379(4)
C(66) – F(66)	1.357(3)	C(71) – C(76)	1.377(4)
C(71) – C(72)	1.389(4)	C(71) – B	1.637(4)
C(72) – F(72)	1.349(4)	C(72) – C(73)	1.358(5)
C(73) – F(73)	1.348(4)	C(73) – C(74)	1.368(5)
C(74) – F(74)	1.341(4)	C(74) – C(75)	1.368(5)
C(76) – F(76)	1.346(4)	C(76) – C(75)	1.388(5)
C(81) – C(86)	1.381(4)	C(81) – C(82)	1.385(4)
C(81) – B	1.649(4)	C(82) – F(82)	1.349(4)
C(82) – C(83)	1.367(5)	C(83) – F(83)	1.345(4)
C(83) – C(84)	1.360(6)	C(84) – F(84)	1.342(4)
C(84) – C(85)	1.353(6)	C(85) – F(85)	1.346(4)
C(85) – C(86)	1.381(5)	C(86) – F(86)	1.353(4)
C(75) – F(75)	1.347(4)		

Table S26. Angles [°] for $[(C_6F_5)_2BF(C_6F_4)\text{-}PC(sp^3)P]^{t\text{Bu}}Pd(PMe_3)$ (**5**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	82.82(7)	C – Pd – P(2)	80.56(7)
P(1) – Pd – P(2)	152.41(3)	C – Pd – P(3)	165.87(8)
P(1) – Pd – P(3)	102.08(3)	P(2) – Pd – P(3)	99.34(3)
C(19) – C(1) – C(18)	109.6(3)	C(19) – C(1) – C(17)	110.3(3)
C(18) – C(1) – C(17)	106.7(3)	C(19) – C(1) – C(14)	108.4(3)
C(18) – C(1) – C(14)	112.4(3)	C(17) – C(1) – C(14)	109.4(3)
C(12) – P(1) – C(42)	103.57(13)	C(12) – P(1) – C(41)	108.48(13)
C(42) – P(1) – C(41)	105.01(13)	C(12) – P(1) – Pd	104.18(9)
C(42) – P(1) – Pd	113.23(9)	C(41) – P(1) – Pd	121.02(10)
C(28) – C(2) – C(27)	108.1(3)	C(28) – C(2) – C(29)	108.2(3)
C(27) – C(2) – C(29)	109.9(3)	C(28) – C(2) – C(24)	109.4(3)
C(27) – C(2) – C(24)	112.4(2)	C(29) – C(2) – C(24)	108.8(2)
C(22) – P(2) – C(52)	106.74(13)	C(22) – P(2) – C(51)	110.54(13)
C(52) – P(2) – C(51)	108.22(13)	C(22) – P(2) – Pd	96.03(9)
C(52) – P(2) – Pd	112.12(10)	C(51) – P(2) – Pd	121.78(10)
C(33) – P(3) – C(32)	99.34(17)	C(33) – P(3) – C(31)	101.82(18)
C(32) – P(3) – C(31)	100.82(19)	C(33) – P(3) – Pd	121.29(12)
C(32) – P(3) – Pd	124.70(12)	C(31) – P(3) – Pd	105.06(13)
C(12) – C(11) – C(16)	118.0(2)	C(12) – C(11) – C	121.8(2)
C(16) – C(11) – C	120.1(2)	C(11) – C(12) – C(13)	120.4(3)
C(11) – C(12) – P(1)	114.4(2)	C(13) – C(12) – P(1)	125.2(2)
C(13) – C(14) – C(15)	117.4(3)	C(13) – C(14) – C(1)	122.5(3)
C(15) – C(14) – C(1)	120.0(3)	C(14) – C(13) – C(12)	121.5(3)
C(14) – C(13) – H(13)	119.2	C(12) – C(13) – H(13)	119.2
C(16) – C(15) – C(14)	121.6(3)	C(16) – C(15) – H(15)	119.2
C(14) – C(15) – H(15)	119.2	C(1) – C(17) – H(17A)	109.5
C(1) – C(17) – H(17B)	109.5	H(17A) – C(17) – H(17B)	109.5
C(1) – C(17) – H(17C)	109.5	H(17A) – C(17) – H(17C)	109.5
H(17B) – C(17) – H(17C)	109.5	C(15) – C(16) – C(11)	121.0(3)
C(15) – C(16) – H(16)	119.5	C(11) – C(16) – H(16)	119.5
C(1) – C(18) – H(18A)	109.5	C(1) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	C(1) – C(18) – H(18C)	109.5
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5
C(1) – C(19) – H(19A)	109.5	C(1) – C(19) – H(19B)	109.5
H(19A) – C(19) – H(19B)	109.5	C(1) – C(19) – H(19C)	109.5
H(19A) – C(19) – H(19C)	109.5	H(19B) – C(19) – H(19C)	109.5
C(26) – C(21) – C(22)	117.7(2)	C(26) – C(21) – C	124.3(2)
C(22) – C(21) – C	118.0(2)	C(23) – C(22) – C(21)	120.5(2)
C(23) – C(22) – P(2)	124.6(2)	C(21) – C(22) – P(2)	114.55(19)
C(24) – C(23) – C(22)	121.3(3)	C(24) – C(23) – H(23)	119.3
C(22) – C(23) – H(23)	119.3	C(25) – C(24) – C(23)	117.7(2)

Continued on next page

Table S26. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(25) – C(24) – C(2)	120.0(2)	C(23) – C(24) – C(2)	122.2(2)
C(24) – C(25) – C(26)	121.6(3)	C(24) – C(25) – H(25)	119.2
C(26) – C(25) – H(25)	119.2	C(25) – C(26) – C(21)	120.8(3)
C(25) – C(26) – H(26)	119.6	C(21) – C(26) – H(26)	119.6
C(2) – C(27) – H(27A)	109.5	C(2) – C(27) – H(27B)	109.5
H(27A) – C(27) – H(27B)	109.5	C(2) – C(27) – H(27C)	109.5
H(27A) – C(27) – H(27C)	109.5	H(27B) – C(27) – H(27C)	109.5
C(2) – C(28) – H(28A)	109.5	C(2) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	C(2) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
C(2) – C(29) – H(29A)	109.5	C(2) – C(29) – H(29B)	109.5
H(29A) – C(29) – H(29B)	109.5	C(2) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(21) – C – C(64)	111.5(2)	C(21) – C – C(11)	113.3(2)
C(64) – C – C(11)	106.6(2)	C(21) – C – Pd	104.32(17)
C(64) – C – Pd	106.22(16)	C(11) – C – Pd	114.82(17)
C(43) – C(41) – C(44)	109.7(3)	C(43) – C(41) – P(1)	110.3(2)
C(44) – C(41) – P(1)	117.4(2)	C(43) – C(41) – H(41)	106.2
C(44) – C(41) – H(41)	106.2	P(1) – C(41) – H(41)	106.2
C(45) – C(42) – C(46)	111.1(3)	C(45) – C(42) – P(1)	110.5(2)
C(46) – C(42) – P(1)	112.2(2)	C(45) – C(42) – H(42)	107.6
C(46) – C(42) – H(42)	107.6	P(1) – C(42) – H(42)	107.6
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5

Continued on next page

Table S26. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(54) – C(51) – C(53)	112.6(3)	C(54) – C(51) – P(2)	110.9(2)
C(53) – C(51) – P(2)	114.9(2)	C(54) – C(51) – H(51)	105.9
C(53) – C(51) – H(51)	105.9	P(2) – C(51) – H(51)	105.9
C(56) – C(52) – C(55)	110.3(3)	C(56) – C(52) – P(2)	109.11(19)
C(55) – C(52) – P(2)	118.8(2)	C(56) – C(52) – H(52)	105.9
C(55) – C(52) – H(52)	105.9	P(2) – C(52) – H(52)	105.9
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5
C(66) – C(61) – C(62)	111.6(2)	C(66) – C(61) – B	126.9(2)
C(62) – C(61) – B	120.8(2)	F(62) – C(62) – C(63)	116.7(2)
F(62) – C(62) – C(61)	118.8(2)	C(63) – C(62) – C(61)	124.5(3)
F(63) – C(63) – C(62)	117.4(2)	F(63) – C(63) – C(64)	119.1(2)
C(62) – C(63) – C(64)	123.4(2)	C(63) – C(64) – C(65)	112.7(2)
C(63) – C(64) – C	121.5(2)	C(65) – C(64) – C	125.7(2)
F(65) – C(65) – C(66)	115.9(2)	F(65) – C(65) – C(64)	121.2(2)
C(66) – C(65) – C(64)	123.0(2)	F(66) – C(66) – C(61)	120.2(2)
F(66) – C(66) – C(65)	115.0(2)	C(61) – C(66) – C(65)	124.7(2)
C(76) – C(71) – C(72)	114.0(3)	C(76) – C(71) – B	125.7(3)
C(72) – C(71) – B	120.3(3)	F(72) – C(72) – C(73)	116.4(3)
F(72) – C(72) – C(71)	118.9(3)	C(73) – C(72) – C(71)	124.6(3)
F(73) – C(73) – C(72)	121.0(3)	F(73) – C(73) – C(74)	119.7(3)
C(72) – C(73) – C(74)	119.3(3)	F(74) – C(74) – C(73)	120.2(4)
F(74) – C(74) – C(75)	120.6(4)	C(73) – C(74) – C(75)	119.2(3)
F(76) – C(76) – C(71)	121.4(3)	F(76) – C(76) – C(75)	115.6(3)
C(71) – C(76) – C(75)	122.9(3)	C(86) – C(81) – C(82)	113.5(3)
C(86) – C(81) – B	127.2(3)	C(82) – C(81) – B	119.2(3)
F(82) – C(82) – C(83)	115.6(3)	F(82) – C(82) – C(81)	120.1(3)
C(83) – C(82) – C(81)	124.2(3)	F(83) – C(83) – C(84)	119.8(3)
F(83) – C(83) – C(82)	120.6(4)	C(84) – C(83) – C(82)	119.6(3)
F(84) – C(84) – C(85)	120.2(4)	F(84) – C(84) – C(83)	120.6(4)
C(85) – C(84) – C(83)	119.2(3)	F(85) – C(85) – C(84)	120.0(3)

Continued on next page

Table S26. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
F(85) – C(85) – C(86)	120.0(4)	C(84) – C(85) – C(86)	120.0(3)
F(86) – C(86) – C(85)	116.2(3)	F(86) – C(86) – C(81)	120.5(3)
C(85) – C(86) – C(81)	123.3(3)	F(75) – C(75) – C(74)	120.6(3)
F(75) – C(75) – C(76)	119.6(3)	C(74) – C(75) – C(76)	119.8(3)
F – B – C(61)	105.1(2)	F – B – C(71)	111.3(2)
C(61) – B – C(71)	112.9(2)	F – B – C(81)	107.9(2)
C(61) – B – C(81)	113.9(2)	C(71) – B – C(81)	105.7(2)

4.5 Crystal data for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] ([8][BAr$^F_4$])

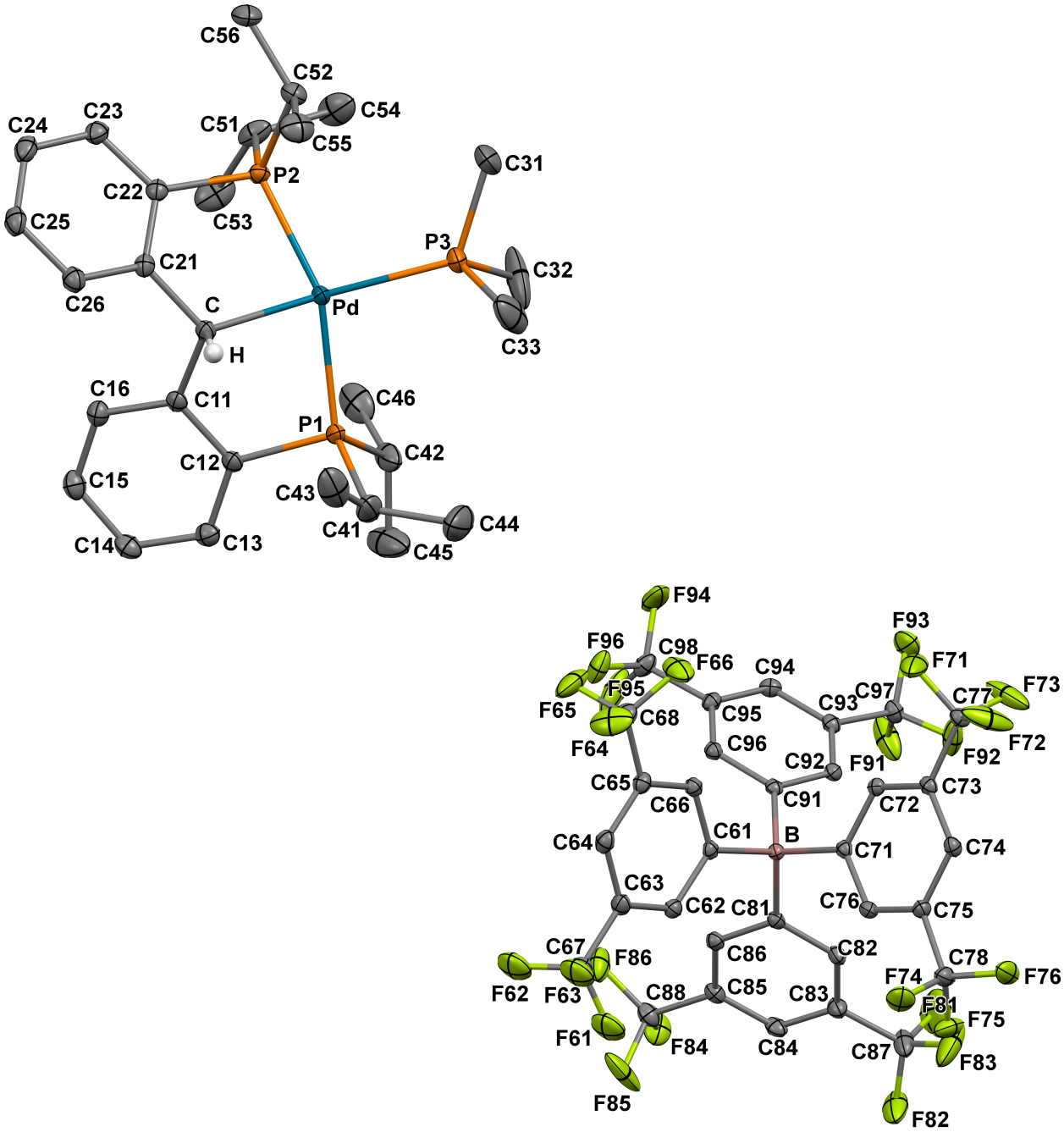

Figure S63. Thermal-ellipsoid representation of [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S27. Crystal data and structure refinement for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

Identification code:	cc273	
Empirical formula:	$C_{60}H_{58}BF_{24}P_3Pd$	
Formula weight:	1445.18	
Temperature:	120(2) K	
Wavelength:	1.54178 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/n$	
Unit cell dimensions:	a = 13.1862(3) Å	α = 90°
	b = 12.7167(3) Å	β = 94.9670(9)°
	c = 37.1231(8) Å	γ = 90°
Volume:	6201.6(2) Å^3	
Z:	4	
Density (calculated):	1.548 g·cm^{-3}	
Absorption coefficient (μ):	4.145 mm^{-1}	
F(000):	2920	
Crystal size:	0.09 × 0.08 × 0.07 mm^3	
θ range for data collection:	2.39 to 68.29°	
Index ranges:	$-15 \le h \le 15$, $-15 \le k \le 14$, $-44 \le l \le 44$	
Reflections collected:	112788	
Independent reflections:	11345 [R_{int} = 0.0404]	
Completeness to θ = 68.29°:	99.8 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7531 and 0.5916	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	11345 / 0 / 817	
Goodness-of-fit on F^2:	1.036	
Final R indices [I>2σ(I)]:	R_1 = 0.0453, wR_2 = 0.1137	
R indices (all data):	R_1 = 0.0465, wR_2 = 0.1146	
Largest diff. peak and hole:	1.245 and −1.122 e$^-$·Å^{-3}	

Table S28. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

atom	x	y	z	U(eq)
Pd	0.65220(2)	0.73636(2)	0.35881(1)	0.019(1)
P(1)	0.77598(6)	0.68631(7)	0.40521(2)	0.024(1)
P(2)	0.57053(6)	0.84993(6)	0.31740(2)	0.020(1)
P(3)	0.51565(6)	0.63384(7)	0.37675(2)	0.028(1)
C	0.7827(2)	0.7939(2)	0.33625(8)	0.019(1)
C(11)	0.8595(2)	0.8379(2)	0.36505(8)	0.020(1)
C(12)	0.8741(2)	0.7825(2)	0.39790(8)	0.021(1)
C(13)	0.9560(2)	0.8057(3)	0.42295(9)	0.025(1)
C(14)	1.0198(2)	0.8896(3)	0.41693(9)	0.028(1)
C(15)	1.0008(3)	0.9494(3)	0.38595(9)	0.029(1)
C(16)	0.9223(2)	0.9239(3)	0.36017(9)	0.024(1)
B	0.1839(2)	0.2770(3)	0.38313(9)	0.016(1)
C(21)	0.7656(2)	0.8614(2)	0.30260(8)	0.020(1)
C(22)	0.6709(2)	0.9076(2)	0.29360(8)	0.021(1)
C(23)	0.6576(3)	0.9810(3)	0.26550(8)	0.026(1)
C(25)	0.8297(3)	0.9504(3)	0.25172(9)	0.030(1)
C(24)	0.7378(3)	1.0028(3)	0.24496(9)	0.031(1)
C(26)	0.8444(2)	0.8810(3)	0.28053(9)	0.026(1)
C(31)	0.4004(3)	0.6188(4)	0.34651(15)	0.060(1)
C(32)	0.4624(5)	0.6516(6)	0.41932(15)	0.090(2)
C(33)	0.5543(4)	0.4968(4)	0.37934(19)	0.070(2)
C(41)	0.8490(3)	0.5626(3)	0.41062(13)	0.046(1)
C(42)	0.7317(3)	0.7164(4)	0.44991(10)	0.045(1)
C(43)	0.8788(3)	0.5285(3)	0.37371(16)	0.057(1)
C(44)	0.7997(5)	0.4740(5)	0.43064(19)	0.086(2)
C(45)	0.8072(4)	0.7128(6)	0.48308(13)	0.079(2)
C(46)	0.6800(3)	0.8236(4)	0.44827(12)	0.054(1)
C(51)	0.5016(3)	0.9608(3)	0.33539(9)	0.033(1)
C(52)	0.4859(2)	0.7868(3)	0.28137(9)	0.028(1)
C(53)	0.5741(4)	1.0248(3)	0.36147(11)	0.049(1)
C(54)	0.4082(3)	0.9250(4)	0.35372(12)	0.052(1)
C(55)	0.5440(3)	0.6951(3)	0.26628(11)	0.041(1)
C(56)	0.4414(3)	0.8583(3)	0.25063(10)	0.036(1)
F(611)	−0.0858(11)	0.2122(9)	0.4875(3)	0.076(3)
F(621)	−0.0160(10)	0.0823(9)	0.4803(2)	0.076(3)
F(631)	−0.1700(11)	0.0675(10)	0.4580(3)	0.076(3)
C(61)	0.0678(2)	0.2399(2)	0.38942(8)	0.017(1)
F(61)	−0.0298(3)	0.1598(4)	0.48986(10)	0.057(1)
C(62)	0.0364(2)	0.2063(2)	0.42262(8)	0.020(1)

Continued on next page

Table S28. – continued from previous page

atom	x	y	x	U(eq)
F(62)	−0.1283(3)	0.0468(4)	0.46197(12)	0.057(1)
C(63)	−0.0654(2)	0.1832(3)	0.42707(9)	0.025(1)
F(63)	−0.1809(3)	0.2008(3)	0.47207(9)	0.057(1)
C(64)	−0.1401(2)	0.1946(3)	0.39857(9)	0.026(1)
F(64)	−0.27750(18)	0.2811(3)	0.34500(7)	0.061(1)
C(65)	−0.1111(2)	0.2297(2)	0.36567(9)	0.022(1)
F(65)	−0.2134(2)	0.1537(2)	0.31778(8)	0.065(1)
C(66)	−0.0094(2)	0.2516(2)	0.36122(8)	0.019(1)
F(66)	−0.16277(18)	0.3097(2)	0.30970(7)	0.057(1)
C(67)	−0.0969(3)	0.1463(3)	0.46244(9)	0.036(1)
C(68)	−0.1907(3)	0.2429(3)	0.33454(10)	0.031(1)
C(71)	0.1779(2)	0.4052(2)	0.38444(8)	0.017(1)
F(71)	0.0521(3)	0.5855(2)	0.29773(7)	0.076(1)
C(72)	0.1547(2)	0.4678(2)	0.35374(8)	0.017(1)
F(72)	0.0607(3)	0.7243(2)	0.32814(7)	0.080(1)
C(73)	0.1374(2)	0.5754(2)	0.35628(8)	0.018(1)
F(73)	0.18936(19)	0.6641(3)	0.30560(7)	0.078(1)
C(74)	0.1455(2)	0.6266(2)	0.38945(8)	0.020(1)
F(74)	0.09431(18)	0.59984(19)	0.47444(6)	0.046(1)
C(75)	0.1693(2)	0.5657(2)	0.42024(8)	0.021(1)
F(75)	0.25531(19)	0.57664(18)	0.47838(6)	0.045(1)
C(76)	0.1835(2)	0.4583(2)	0.41766(8)	0.020(1)
F(76)	0.1913(2)	0.71926(16)	0.45573(6)	0.044(1)
C(77)	0.1104(2)	0.6383(2)	0.32256(8)	0.022(1)
C(78)	0.1777(3)	0.6157(3)	0.45691(9)	0.028(1)
C(81)	0.2707(2)	0.2287(2)	0.41309(8)	0.018(1)
F(81)	0.5984(2)	0.3035(3)	0.44070(11)	0.096(1)
C(82)	0.3564(2)	0.2859(2)	0.42704(8)	0.022(1)
F(82)	0.5692(3)	0.2706(3)	0.49392(10)	0.089(1)
C(83)	0.4356(3)	0.2397(3)	0.44897(9)	0.027(1)
F(83)	0.5050(2)	0.4047(2)	0.46703(11)	0.086(1)
C(84)	0.4330(2)	0.1340(3)	0.45758(9)	0.025(1)
F(84)	0.43564(17)	−0.08526(17)	0.45441(7)	0.045(1)
C(85)	0.3491(2)	0.0754(2)	0.44411(8)	0.022(1)
F(85)	0.3145(3)	−0.0527(2)	0.48655(8)	0.076(1)
C(86)	0.2702(2)	0.1218(2)	0.42240(8)	0.019(1)
F(86)	0.28394(17)	−0.09428(16)	0.43020(7)	0.048(1)
C(87)	0.5255(3)	0.3046(3)	0.46308(12)	0.041(1)
C(88)	0.3446(3)	−0.0382(3)	0.45395(9)	0.030(1)
C(91)	0.2214(2)	0.2326(2)	0.34490(8)	0.017(1)
F(91)	0.52615(17)	0.2104(2)	0.29716(9)	0.065(1)
C(92)	0.3092(2)	0.2742(2)	0.33145(8)	0.019(1)

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Table S28. – continued from previous page

atom	x	y	x	U(eq)
F(92)	0.47323(19)	0.3676(2)	0.30276(7)	0.055(1)
C(93)	0.3513(2)	0.2306(2)	0.30167(8)	0.020(1)
F(93)	0.44215(18)	0.2868(2)	0.25328(6)	0.047(1)
C(94)	0.3063(2)	0.1440(2)	0.28381(8)	0.021(1)
F(94)	0.1712(2)	0.0121(3)	0.24266(6)	0.072(1)
C(95)	0.2195(2)	0.1018(2)	0.29659(8)	0.020(1)
F(95)	0.22314(19)	−0.08127(19)	0.28753(9)	0.069(1)
C(96)	0.1783(2)	0.1450(2)	0.32665(8)	0.019(1)
F(96)	0.07758(15)	−0.00963(17)	0.28567(6)	0.041(1)
C(97)	0.4481(2)	0.2734(3)	0.28921(9)	0.025(1)
C(98)	0.1723(2)	0.0062(3)	0.27844(9)	0.028(1)
H	0.8163	0.7292	0.3277	0.023
H(13)	0.9682	0.7640	0.4441	0.031
H(14)	1.0757	0.9058	0.4339	0.034
H(15)	1.0423	1.0088	0.3823	0.035
H(16)	0.9111	0.9655	0.3389	0.029
H(23)	0.5941	1.0157	0.2606	0.031
H(25)	0.8830	0.9621	0.2365	0.036
H(24)	0.7299	1.0537	0.2262	0.037
H(26)	0.9081	0.8466	0.2853	0.031
H(31A)	0.4186	0.5992	0.3224	0.090
H(31B)	0.3629	0.6854	0.3451	0.090
H(31C)	0.3576	0.5637	0.3558	0.090
H(32A)	0.4311	0.7214	0.4200	0.134
H(32B)	0.5164	0.6454	0.4391	0.134
H(32C)	0.4106	0.5976	0.4221	0.134
H(33A)	0.4949	0.4526	0.3824	0.105
H(33B)	0.6049	0.4870	0.4000	0.105
H(33C)	0.5842	0.4770	0.3570	0.105
H(41)	0.9139	0.5803	0.4253	0.056
H(42)	0.6776	0.6637	0.4540	0.054
H(43A)	0.8177	0.5083	0.3584	0.086
H(43B)	0.9253	0.4684	0.3766	0.086
H(43C)	0.9128	0.5869	0.3624	0.086
H(44A)	0.7478	0.4394	0.4142	0.130
H(44B)	0.7678	0.5031	0.4514	0.130
H(44C)	0.8518	0.4227	0.4392	0.130
H(45A)	0.8519	0.6517	0.4816	0.118
H(45B)	0.7704	0.7074	0.5048	0.118
H(45C)	0.8483	0.7772	0.4843	0.118
H(46A)	0.7300	0.8780	0.4438	0.082
H(46B)	0.6516	0.8378	0.4713	0.082

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Table S28. – continued from previous page

atom	x	y	x	U(eq)
H(46C)	0.6252	0.8240	0.4287	0.082
H(51)	0.4779	1.0074	0.3147	0.040
H(52)	0.4272	0.7561	0.2931	0.034
H(53A)	0.6330	1.0474	0.3490	0.074
H(53B)	0.5972	0.9812	0.3823	0.074
H(53C)	0.5384	1.0867	0.3697	0.074
H(54A)	0.3642	0.8826	0.3368	0.078
H(54B)	0.3705	0.9867	0.3611	0.078
H(54C)	0.4299	0.8827	0.3751	0.078
H(55A)	0.5001	0.6589	0.2476	0.062
H(55B)	0.5647	0.6457	0.2858	0.062
H(55C)	0.6046	0.7219	0.2558	0.062
H(56A)	0.4950	0.8769	0.2350	0.054
H(56B)	0.4144	0.9224	0.2609	0.054
H(56C)	0.3865	0.8212	0.2364	0.054
H(62)	0.0857	0.1989	0.4427	0.024
H(64)	−0.2092	0.1788	0.4016	0.031
H(66)	0.0083	0.2752	0.3383	0.023
H(72)	0.1506	0.4359	0.3305	0.021
H(74)	0.1354	0.7004	0.3911	0.024
H(76)	0.1976	0.4189	0.4393	0.023
H(82)	0.3607	0.3585	0.4214	0.027
H(84)	0.4870	0.1023	0.4723	0.030
H(86)	0.2140	0.0796	0.4136	0.023
H(92)	0.3410	0.3338	0.3430	0.022
H(94)	0.3344	0.1145	0.2634	0.025
H(96)	0.1192	0.1140	0.3350	0.022

Table S29. Anisotropic displacement parameters (Å^2) for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ...+ 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0137(1)	0.0213(1)	0.0219(1)	0.0057(1)	0.0024(1)	−0.0004(1)
P(1)	0.0154(3)	0.0306(4)	0.0257(4)	0.0121(3)	0.0027(3)	0.0008(3)
P(2)	0.0168(3)	0.0226(4)	0.0197(4)	0.0028(3)	0.0018(3)	0.0029(3)
P(3)	0.0208(4)	0.0333(5)	0.0310(4)	0.0075(3)	0.0025(3)	−0.0079(3)
C	0.0160(14)	0.0196(14)	0.0225(15)	0.0018(12)	0.0040(11)	0.0006(11)
C(11)	0.0156(13)	0.0202(15)	0.0238(15)	0.0015(12)	0.0052(11)	0.0031(11)
C(12)	0.0157(14)	0.0220(15)	0.0245(15)	0.0024(12)	0.0045(12)	0.0018(11)
C(13)	0.0236(15)	0.0299(17)	0.0233(15)	0.0013(13)	0.0035(12)	0.0037(13)
C(14)	0.0244(16)	0.0325(18)	0.0270(16)	−0.0067(14)	−0.0006(13)	−0.0023(13)
C(15)	0.0309(17)	0.0237(16)	0.0328(17)	−0.0041(13)	0.0061(14)	−0.0059(13)
C(16)	0.0263(16)	0.0217(15)	0.0261(16)	0.0014(12)	0.0050(12)	−0.0007(12)
B	0.0171(15)	0.0156(15)	0.0168(15)	0.0015(12)	0.0007(12)	−0.0015(12)
C(21)	0.0221(15)	0.0193(15)	0.0201(14)	0.0000(11)	0.0033(11)	−0.0027(12)
C(22)	0.0231(15)	0.0216(15)	0.0187(14)	−0.0008(12)	0.0012(11)	−0.0024(12)
C(23)	0.0285(16)	0.0257(16)	0.0221(15)	0.0021(12)	−0.0021(12)	−0.0019(13)
C(25)	0.0333(18)	0.0353(19)	0.0229(16)	0.0022(14)	0.0082(13)	−0.0091(15)
C(24)	0.0395(19)	0.0304(18)	0.0213(15)	0.0052(13)	−0.0002(14)	−0.0085(15)
C(26)	0.0244(16)	0.0299(17)	0.0246(15)	0.0001(13)	0.0053(12)	−0.0030(13)
C(31)	0.029(2)	0.070(3)	0.078(3)	0.030(3)	−0.009(2)	−0.020(2)
C(32)	0.105(5)	0.111(5)	0.060(3)	−0.031(3)	0.053(3)	−0.078(4)
C(33)	0.043(3)	0.032(2)	0.133(5)	0.005(3)	−0.005(3)	−0.0121(19)
C(41)	0.033(2)	0.033(2)	0.072(3)	0.026(2)	0.0005(19)	0.0017(16)
C(42)	0.0294(19)	0.080(3)	0.0258(18)	0.0117(19)	0.0054(15)	−0.0110(19)
C(43)	0.042(2)	0.025(2)	0.107(4)	0.002(2)	0.019(2)	0.0063(17)
C(44)	0.081(4)	0.064(4)	0.108(5)	0.052(3)	−0.028(4)	−0.028(3)
C(45)	0.044(3)	0.160(6)	0.033(2)	0.019(3)	0.002(2)	0.000(3)
C(46)	0.047(2)	0.082(3)	0.037(2)	−0.019(2)	0.0203(19)	−0.008(2)
C(51)	0.042(2)	0.0361(19)	0.0233(16)	0.0035(14)	0.0081(14)	0.0190(16)
C(52)	0.0215(16)	0.0321(18)	0.0300(17)	0.0014(14)	−0.0025(13)	−0.0026(13)
C(53)	0.075(3)	0.037(2)	0.035(2)	−0.0107(17)	0.003(2)	0.015(2)
C(54)	0.046(2)	0.069(3)	0.045(2)	0.010(2)	0.0228(19)	0.028(2)
C(55)	0.047(2)	0.035(2)	0.040(2)	−0.0103(17)	−0.0071(17)	−0.0012(17)
C(56)	0.0276(17)	0.047(2)	0.0324(18)	0.0053(16)	−0.0094(14)	−0.0020(16)
F(611)	0.129(7)	0.060(4)	0.043(3)	0.019(3)	0.038(4)	0.006(4)
F(621)	0.129(7)	0.060(4)	0.043(3)	0.019(3)	0.038(4)	0.006(4)
F(631)	0.129(7)	0.060(4)	0.043(3)	0.019(3)	0.038(4)	0.006(4)
C(61)	0.0203(14)	0.0118(13)	0.0196(14)	−0.0009(10)	0.0026(11)	−0.0006(10)
F(61)	0.0616(16)	0.076(2)	0.0365(12)	0.0102(11)	0.0239(11)	−0.0029(13)
C(62)	0.0223(15)	0.0193(14)	0.0194(14)	−0.0009(11)	0.0014(11)	−0.0006(12)

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Table S29. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(62)	0.0616(16)	0.076(2)	0.0365(12)	0.0102(11)	0.0239(11)	−0.0029(13)
C(63)	0.0264(16)	0.0264(17)	0.0241(16)	−0.0037(13)	0.0073(13)	−0.0053(13)
F(63)	0.0616(16)	0.076(2)	0.0365(12)	0.0102(11)	0.0239(11)	−0.0029(13)
C(64)	0.0202(15)	0.0281(17)	0.0292(16)	−0.0041(13)	0.0056(12)	−0.0045(13)
F(64)	0.0260(12)	0.105(2)	0.0511(15)	−0.0062(15)	−0.0051(10)	0.0219(13)
C(65)	0.0200(15)	0.0195(15)	0.0269(16)	−0.0015(12)	0.0006(12)	0.0002(11)
F(65)	0.0787(19)	0.0459(15)	0.0623(16)	−0.0150(13)	−0.0405(15)	−0.0025(13)
C(66)	0.0210(15)	0.0168(14)	0.0195(14)	−0.0001(11)	0.0036(12)	0.0003(11)
F(66)	0.0376(13)	0.0817(19)	0.0472(14)	0.0320(13)	−0.0156(10)	−0.0103(12)
C(67)	0.039(2)	0.048(2)	0.0225(17)	−0.0024(15)	0.0094(15)	−0.0151(17)
C(68)	0.0228(17)	0.0356(19)	0.0333(18)	0.0004(14)	−0.0022(14)	−0.0013(14)
C(71)	0.0139(13)	0.0177(14)	0.0187(13)	0.0014(11)	0.0017(10)	−0.0017(10)
F(71)	0.113(2)	0.0526(16)	0.0519(15)	0.0257(13)	−0.0507(16)	−0.0328(16)
C(72)	0.0146(13)	0.0200(15)	0.0173(13)	−0.0001(11)	0.0018(10)	0.0000(11)
F(72)	0.151(3)	0.0610(18)	0.0312(13)	0.0150(12)	0.0162(16)	0.070(2)
C(73)	0.0149(13)	0.0208(15)	0.0193(14)	0.0028(11)	0.0032(11)	0.0000(11)
F(73)	0.0376(13)	0.144(3)	0.0541(16)	0.0651(19)	0.0105(12)	0.0097(16)
C(74)	0.0227(15)	0.0162(14)	0.0223(15)	0.0011(11)	0.0050(12)	−0.0003(11)
F(74)	0.0583(14)	0.0544(14)	0.0271(10)	−0.0111(10)	0.0188(10)	−0.0108(11)
C(75)	0.0238(15)	0.0193(15)	0.0187(14)	−0.0010(11)	0.0031(11)	−0.0020(12)
F(75)	0.0608(15)	0.0432(13)	0.0271(10)	−0.0092(9)	−0.0153(10)	0.0046(11)
C(76)	0.0223(14)	0.0202(15)	0.0160(13)	0.0035(11)	0.0005(11)	−0.0016(12)
F(76)	0.0851(18)	0.0202(10)	0.0275(10)	−0.0061(8)	0.0056(11)	−0.0072(10)
C(77)	0.0240(15)	0.0200(15)	0.0217(15)	0.0023(12)	0.0028(12)	0.0030(12)
C(78)	0.0422(19)	0.0204(16)	0.0212(15)	−0.0005(12)	0.0007(14)	−0.0010(14)
C(81)	0.0196(14)	0.0190(15)	0.0156(13)	0.0014(11)	0.0042(11)	0.0007(11)
F(81)	0.0538(18)	0.127(3)	0.109(3)	0.001(2)	0.0153(18)	−0.053(2)
C(82)	0.0233(15)	0.0197(15)	0.0232(15)	0.0069(12)	0.0004(12)	−0.0024(12)
F(82)	0.086(2)	0.074(2)	0.094(2)	0.0457(18)	−0.066(2)	−0.0465(17)
C(83)	0.0227(16)	0.0285(17)	0.0281(17)	0.0073(13)	−0.0021(13)	−0.0037(13)
F(83)	0.0656(19)	0.0435(16)	0.139(3)	−0.0098(18)	−0.054(2)	−0.0113(14)
C(84)	0.0216(15)	0.0292(17)	0.0246(15)	0.0087(13)	−0.0007(12)	0.0032(13)
F(84)	0.0373(12)	0.0280(11)	0.0668(15)	0.0065(10)	−0.0053(11)	0.0126(9)
C(85)	0.0236(15)	0.0202(15)	0.0222(15)	0.0038(12)	0.0064(12)	0.0037(12)
F(85)	0.140(3)	0.0344(13)	0.0644(17)	0.0246(12)	0.0658(19)	0.0170(16)
C(86)	0.0199(14)	0.0204(15)	0.0182(14)	0.0006(11)	0.0038(11)	−0.0003(11)
F(86)	0.0407(12)	0.0223(11)	0.0775(17)	0.0116(11)	−0.0148(11)	−0.0051(9)
C(87)	0.0304(19)	0.036(2)	0.055(2)	0.0210(18)	−0.0160(17)	−0.0106(16)
C(88)	0.0311(17)	0.0256(17)	0.0336(18)	0.0082(14)	0.0049(14)	0.0049(14)
C(91)	0.0175(14)	0.0162(14)	0.0169(14)	0.0039(11)	−0.0004(11)	0.0022(11)
F(91)	0.0227(11)	0.0606(16)	0.114(2)	0.0470(17)	0.0155(13)	0.0077(11)
C(92)	0.0199(14)	0.0173(14)	0.0186(14)	0.0011(11)	0.0007(11)	−0.0003(11)

Continued on next page

Table S29. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F(92)	0.0543(15)	0.0474(14)	0.0686(16)	−0.0212(12)	0.0356(13)	−0.0283(12)
C(93)	0.0203(15)	0.0188(15)	0.0207(14)	0.0042(11)	0.0013(12)	0.0019(11)
F(93)	0.0474(13)	0.0638(16)	0.0326(11)	0.0056(11)	0.0149(10)	−0.0167(12)
C(94)	0.0199(14)	0.0240(15)	0.0187(14)	0.0001(12)	0.0017(11)	0.0045(12)
F(94)	0.097(2)	0.092(2)	0.0303(12)	−0.0263(13)	0.0131(13)	−0.0574(18)
C(95)	0.0198(14)	0.0197(15)	0.0209(14)	−0.0013(12)	−0.0009(11)	0.0013(11)
F(95)	0.0436(14)	0.0292(12)	0.129(3)	−0.0284(15)	−0.0278(15)	0.0075(10)
C(96)	0.0170(13)	0.0197(14)	0.0189(14)	0.0021(11)	0.0018(11)	−0.0009(11)
F(96)	0.0278(10)	0.0398(12)	0.0582(14)	−0.0228(10)	0.0108(9)	−0.0115(9)
C(97)	0.0247(16)	0.0233(16)	0.0271(16)	0.0021(12)	0.0074(13)	−0.0006(12)
C(98)	0.0235(16)	0.0305(17)	0.0296(17)	−0.0107(14)	0.0034(13)	−0.0006(13)

Table S30. Distances [Å] for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

atom – atom	distance	atom – atom	distance
Pd – C	2.109(3)	Pd – P(2)	2.3070(8)
Pd – P(1)	2.3557(8)	Pd – P(3)	2.3648(8)
P(1) – C(12)	1.818(3)	P(1) – C(42)	1.847(4)
P(1) – C(41)	1.847(4)	P(2) – C(22)	1.809(3)
P(2) – C(51)	1.834(3)	P(2) – C(52)	1.850(3)
P(3) – C(32)	1.798(5)	P(3) – C(33)	1.816(5)
P(3) – C(31)	1.820(4)	C – C(11)	1.515(4)
C – C(21)	1.517(4)	C – H	1.0000
C(11) – C(16)	1.393(4)	C(11) – C(12)	1.407(4)
C(12) – C(13)	1.394(4)	C(13) – C(14)	1.389(5)
C(13) – H(13)	0.9500	C(14) – C(15)	1.383(5)
C(14) – H(14)	0.9500	C(15) – C(16)	1.387(5)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
B – C(71)	1.634(4)	B – C(61)	1.639(4)
B – C(91)	1.642(4)	B – C(81)	1.644(4)
C(21) – C(22)	1.395(4)	C(21) – C(26)	1.400(4)
C(22) – C(23)	1.400(4)	C(23) – C(24)	1.384(5)
C(23) – H(23)	0.9500	C(25) – C(24)	1.387(5)
C(25) – C(26)	1.387(5)	C(25) – H(25)	0.9500
C(24) – H(24)	0.9500	C(26) – H(26)	0.9500
C(31) – H(31A)	0.9800	C(31) – H(31B)	0.9800
C(31) – H(31C)	0.9800	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(41) – C(43)	1.521(7)
C(41) – C(44)	1.525(6)	C(41) – H(41)	1.0000
C(42) – C(45)	1.516(6)	C(42) – C(46)	1.523(7)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(54)	1.528(6)
C(51) – C(53)	1.534(6)	C(51) – H(51)	1.0000
C(52) – C(55)	1.528(5)	C(52) – C(56)	1.536(5)
C(52) – H(52)	1.0000	C(53) – H(53A)	0.9800
C(53) – H(53B)	0.9800	C(53) – H(53C)	0.9800
C(54) – H(54A)	0.9800	C(54) – H(54B)	0.9800
C(54) – H(54C)	0.9800	C(55) – H(55A)	0.9800
C(55) – H(55B)	0.9800	C(55) – H(55C)	0.9800

Continued on next page

Table S30. – continued from previous page

atom – atom	distance	atom – atom	distance
C(56) – H(56A)	0.9800	C(56) – H(56B)	0.9800
C(56) – H(56C)	0.9800	F(611) – F(61)	0.993(12)
F(611) – C(67)	1.250(12)	F(611) – F(63)	1.341(14)
F(621) – F(61)	1.069(11)	F(621) – C(67)	1.455(12)
F(621) – F(62)	1.638(13)	F(631) – F(62)	0.616(13)
F(631) – C(67)	1.390(15)	C(61) – C(62)	1.400(4)
C(61) – C(66)	1.403(4)	F(61) – C(67)	1.301(6)
C(62) – C(63)	1.398(4)	C(62) – H(62)	0.9500
F(62) – C(67)	1.332(7)	C(63) – C(64)	1.389(5)
C(63) – C(67)	1.487(4)	F(63) – C(67)	1.379(6)
C(64) – C(65)	1.385(5)	C(64) – H(64)	0.9500
F(64) – C(68)	1.332(4)	C(65) – C(66)	1.392(4)
C(65) – C(68)	1.502(5)	F(65) – C(68)	1.316(4)
C(66) – H(66)	0.9500	F(66) – C(68)	1.329(4)
C(71) – C(76)	1.402(4)	C(71) – C(72)	1.402(4)
F(71) – C(77)	1.330(4)	C(72) – C(73)	1.392(4)
C(72) – H(72)	0.9500	F(72) – C(77)	1.300(4)
C(73) – C(74)	1.389(4)	C(73) – C(77)	1.502(4)
F(73) – C(77)	1.305(4)	C(74) – C(75)	1.394(4)
C(74) – H(74)	0.9500	F(74) – C(78)	1.341(4)
C(75) – C(76)	1.383(4)	C(75) – C(78)	1.498(4)
F(75) – C(78)	1.337(4)	C(76) – H(76)	0.9500
F(76) – C(78)	1.330(4)	C(81) – C(86)	1.403(4)
C(81) – C(82)	1.404(4)	F(81) – C(87)	1.325(6)
C(82) – C(83)	1.396(4)	C(82) – H(82)	0.9500
F(82) – C(87)	1.310(5)	C(83) – C(84)	1.383(5)
C(83) – C(87)	1.500(5)	F(83) – C(87)	1.312(5)
C(84) – C(85)	1.390(5)	C(84) – H(84)	0.9500
F(84) – C(88)	1.341(4)	C(85) – C(86)	1.391(4)
C(85) – C(88)	1.493(4)	F(85) – C(88)	1.319(4)
C(86) – H(86)	0.9500	F(86) – C(88)	1.343(4)
C(91) – C(96)	1.397(4)	C(91) – C(92)	1.404(4)
F(91) – C(97)	1.317(4)	C(92) – C(93)	1.394(4)
C(92) – H(92)	0.9500	F(92) – C(97)	1.329(4)
C(93) – C(94)	1.392(4)	C(93) – C(97)	1.498(4)
F(93) – C(97)	1.340(4)	C(94) – C(95)	1.384(4)
C(94) – H(94)	0.9500	F(94) – C(98)	1.329(4)
C(95) – C(96)	1.395(4)	C(95) – C(98)	1.499(4)
F(95) – C(98)	1.327(4)	C(96) – H(96)	0.9500
F(96) – C(98)	1.316(4)		

Table S31. Angles [°] for [{PC(sp^3)HP}PdPMe$_3$][BAr$^F_4$] (**[8][BAr$^F_4$]**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	82.42(8)	C – Pd – P(1)	81.17(8)
P(2) – Pd – P(1)	155.55(3)	C – Pd – P(3)	166.01(9)
P(2) – Pd – P(3)	102.12(3)	P(1) – Pd – P(3)	98.13(3)
C(12) – P(1) – C(42)	106.23(18)	C(12) – P(1) – C(41)	102.63(16)
C(42) – P(1) – C(41)	106.3(2)	C(12) – P(1) – Pd	99.56(10)
C(42) – P(1) – Pd	110.36(13)	C(41) – P(1) – Pd	129.16(16)
C(22) – P(2) – C(51)	105.82(16)	C(22) – P(2) – C(52)	104.13(15)
C(51) – P(2) – C(52)	108.08(16)	C(22) – P(2) – Pd	105.08(10)
C(51) – P(2) – Pd	117.12(11)	C(52) – P(2) – Pd	115.31(11)
C(32) – P(3) – C(33)	101.7(3)	C(32) – P(3) – C(31)	100.7(3)
C(33) – P(3) – C(31)	98.5(2)	C(32) – P(3) – Pd	122.90(17)
C(33) – P(3) – Pd	109.06(17)	C(31) – P(3) – Pd	119.99(15)
C(11) – C – C(21)	114.5(2)	C(11) – C – Pd	111.49(19)
C(21) – C – Pd	117.1(2)	C(11) – C – H	104.0
C(21) – C – H	104.0	Pd – C – H	104.0
C(16) – C(11) – C(12)	117.9(3)	C(16) – C(11) – C	124.5(3)
C(12) – C(11) – C	117.4(3)	C(13) – C(12) – C(11)	120.9(3)
C(13) – C(12) – P(1)	124.2(2)	C(11) – C(12) – P(1)	114.8(2)
C(14) – C(13) – C(12)	120.0(3)	C(14) – C(13) – H(13)	120.0
C(12) – C(13) – H(13)	120.0	C(15) – C(14) – C(13)	119.2(3)
C(15) – C(14) – H(14)	120.4	C(13) – C(14) – H(14)	120.4
C(14) – C(15) – C(16)	121.0(3)	C(14) – C(15) – H(15)	119.5
C(16) – C(15) – H(15)	119.5	C(15) – C(16) – C(11)	120.7(3)
C(15) – C(16) – H(16)	119.7	C(11) – C(16) – H(16)	119.6
C(71) – B – C(61)	103.6(2)	C(71) – B – C(91)	112.8(2)
C(61) – B – C(91)	112.3(2)	C(71) – B – C(81)	112.6(2)
C(61) – B – C(81)	113.6(2)	C(91) – B – C(81)	102.3(2)
C(22) – C(21) – C(26)	118.6(3)	C(22) – C(21) – C	120.1(3)
C(26) – C(21) – C	121.2(3)	C(21) – C(22) – C(23)	120.7(3)
C(21) – C(22) – P(2)	113.0(2)	C(23) – C(22) – P(2)	125.8(2)
C(24) – C(23) – C(22)	119.4(3)	C(24) – C(23) – H(23)	120.3
C(22) – C(23) – H(23)	120.3	C(24) – C(25) – C(26)	120.4(3)
C(24) – C(25) – H(25)	119.8	C(26) – C(25) – H(25)	119.8
C(23) – C(24) – C(25)	120.1(3)	C(23) – C(24) – H(24)	119.9
C(25) – C(24) – H(24)	119.9	C(25) – C(26) – C(21)	120.2(3)
C(25) – C(26) – H(26)	119.9	C(21) – C(26) – H(26)	119.9
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5

Continued on next page

Table S31. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(43) – C(41) – C(44)	112.5(5)	C(43) – C(41) – P(1)	108.5(3)
C(44) – C(41) – P(1)	116.2(4)	C(43) – C(41) – H(41)	106.3
C(44) – C(41) – H(41)	106.3	P(1) – C(41) – H(41)	106.3
C(45) – C(42) – C(46)	108.6(5)	C(45) – C(42) – P(1)	119.1(3)
C(46) – C(42) – P(1)	108.9(3)	C(45) – C(42) – H(42)	106.5
C(46) – C(42) – H(42)	106.5	P(1) – C(42) – H(42)	106.5
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(54) – C(51) – C(53)	111.1(3)	C(54) – C(51) – P(2)	112.2(3)
C(53) – C(51) – P(2)	109.7(3)	C(54) – C(51) – H(51)	107.9
C(53) – C(51) – H(51)	107.9	P(2) – C(51) – H(51)	107.9
C(55) – C(52) – C(56)	110.6(3)	C(55) – C(52) – P(2)	107.8(2)
C(56) – C(52) – P(2)	116.6(3)	C(55) – C(52) – H(52)	107.2
C(56) – C(52) – H(52)	107.2	P(2) – C(52) – H(52)	107.2
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5
F(61) – F(611) – C(67)	69.8(8)	F(61) – F(611) – F(63)	128.8(12)
C(67) – F(611) – F(63)	64.2(7)	F(61) – F(621) – C(67)	59.7(6)

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Table S31. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
F(61) – F(621) – F(62)	102.6(9)	C(67) – F(621) – F(62)	50.6(5)
F(62) – F(631) – C(67)	71.7(17)	C(62) – C(61) – C(66)	116.0(3)
C(62) – C(61) – B	124.3(3)	C(66) – C(61) – B	119.3(3)
F(611) – F(61) – F(621)	137.4(12)	F(611) – F(61) – C(67)	64.4(8)
F(621) – F(61) – C(67)	75.1(7)	C(63) – C(62) – C(61)	121.8(3)
C(63) – C(62) – H(62)	119.1	C(61) – C(62) – H(62)	119.1
F(631) – F(62) – C(67)	82.3(17)	F(631) – F(62) – F(621)	137.4(19)
C(67) – F(62) – F(621)	57.6(5)	C(64) – C(63) – C(62)	120.9(3)
C(64) – C(63) – C(67)	118.2(3)	C(62) – C(63) – C(67)	121.0(3)
F(611) – F(63) – C(67)	54.7(5)	C(65) – C(64) – C(63)	118.3(3)
C(65) – C(64) – H(64)	120.9	C(63) – C(64) – H(64)	120.9
C(64) – C(65) – C(66)	120.7(3)	C(64) – C(65) – C(68)	119.1(3)
C(66) – C(65) – C(68)	120.1(3)	C(65) – C(66) – C(61)	122.2(3)
C(65) – C(66) – H(66)	118.9	C(61) – C(66) – H(66)	118.9
F(611) – C(67) – F(61)	45.7(6)	F(611) – C(67) – F(62)	131.5(5)
F(61) – C(67) – F(62)	109.0(4)	F(611) – C(67) – F(63)	61.1(7)
F(61) – C(67) – F(63)	103.8(4)	F(62) – C(67) – F(63)	103.0(4)
F(611) – C(67) – F(631)	127.3(8)	F(61) – C(67) – F(631)	127.2(6)
F(63) – C(67) – F(631)	80.1(6)	F(611) – C(67) – F(621)	90.1(8)
F(61) – C(67) – F(621)	45.2(5)	F(62) – C(67) – F(621)	71.8(5)
F(63) – C(67) – F(621)	137.5(5)	F(631) – C(67) – F(621)	97.1(7)
F(611) – C(67) – C(63)	114.9(5)	F(61) – C(67) – C(63)	115.3(3)
F(62) – C(67) – C(63)	113.5(3)	F(63) – C(67) – C(63)	111.2(3)
F(631) – C(67) – C(63)	111.6(5)	F(621) – C(67) – C(63)	109.2(4)
F(65) – C(68) – F(66)	106.8(3)	F(65) – C(68) – F(64)	106.6(3)
F(66) – C(68) – F(64)	105.4(3)	F(65) – C(68) – C(65)	112.5(3)
F(66) – C(68) – C(65)	112.8(3)	F(64) – C(68) – C(65)	112.2(3)
C(76) – C(71) – C(72)	115.7(3)	C(76) – C(71) – B	120.5(3)
C(72) – C(71) – B	123.4(3)	C(73) – C(72) – C(71)	121.9(3)
C(73) – C(72) – H(72)	119.0	C(71) – C(72) – H(72)	119.0
C(74) – C(73) – C(72)	121.4(3)	C(74) – C(73) – C(77)	119.0(3)
C(72) – C(73) – C(77)	119.7(3)	C(73) – C(74) – C(75)	117.4(3)
C(73) – C(74) – H(74)	121.3	C(75) – C(74) – H(74)	121.3
C(76) – C(75) – C(74)	121.0(3)	C(76) – C(75) – C(78)	118.9(3)
C(74) – C(75) – C(78)	120.2(3)	C(75) – C(76) – C(71)	122.6(3)
C(75) – C(76) – H(76)	118.7	C(71) – C(76) – H(76)	118.7
F(72) – C(77) – F(73)	107.4(3)	F(72) – C(77) – F(71)	105.5(3)
F(73) – C(77) – F(71)	103.3(3)	F(72) – C(77) – C(73)	113.6(3)
F(73) – C(77) – C(73)	113.3(3)	F(71) – C(77) – C(73)	112.9(3)
F(76) – C(78) – F(75)	106.8(3)	F(76) – C(78) – F(74)	106.4(3)
F(75) – C(78) – F(74)	105.8(3)	F(76) – C(78) – C(75)	113.0(3)
F(75) – C(78) – C(75)	112.1(3)	F(74) – C(78) – C(75)	112.2(3)

Continued on next page

Table S31. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(86) – C(81) – C(82)	115.6(3)	C(86) – C(81) – B	120.7(3)
C(82) – C(81) – B	123.2(3)	C(83) – C(82) – C(81)	122.3(3)
C(83) – C(82) – H(82)	118.8	C(81) – C(82) – H(82)	118.8
C(84) – C(83) – C(82)	120.7(3)	C(84) – C(83) – C(87)	119.2(3)
C(82) – C(83) – C(87)	120.0(3)	C(83) – C(84) – C(85)	118.2(3)
C(83) – C(84) – H(84)	120.9	C(85) – C(84) – H(84)	120.9
C(84) – C(85) – C(86)	120.9(3)	C(84) – C(85) – C(88)	118.6(3)
C(86) – C(85) – C(88)	120.5(3)	C(85) – C(86) – C(81)	122.3(3)
C(85) – C(86) – H(86)	118.9	C(81) – C(86) – H(86)	118.9
F(82) – C(87) – F(83)	107.5(4)	F(82) – C(87) – F(81)	104.9(4)
F(83) – C(87) – F(81)	104.4(4)	F(82) – C(87) – C(83)	113.5(3)
F(83) – C(87) – C(83)	114.1(3)	F(81) – C(87) – C(83)	111.7(4)
F(85) – C(88) – F(84)	105.4(3)	F(85) – C(88) – F(86)	108.6(3)
F(84) – C(88) – F(86)	104.7(3)	F(85) – C(88) – C(85)	112.4(3)
F(84) – C(88) – C(85)	112.4(3)	F(86) – C(88) – C(85)	112.8(3)
C(96) – C(91) – C(92)	116.1(3)	C(96) – C(91) – B	123.6(3)
C(92) – C(91) – B	119.8(3)	C(93) – C(92) – C(91)	122.0(3)
C(93) – C(92) – H(92)	119.0	C(91) – C(92) – H(92)	119.0
C(94) – C(93) – C(92)	120.6(3)	C(94) – C(93) – C(97)	118.7(3)
C(92) – C(93) – C(97)	120.6(3)	C(95) – C(94) – C(93)	118.3(3)
C(95) – C(94) – H(94)	120.8	C(93) – C(94) – H(94)	120.8
C(94) – C(95) – C(96)	120.8(3)	C(94) – C(95) – C(98)	118.9(3)
C(96) – C(95) – C(98)	120.2(3)	C(95) – C(96) – C(91)	122.1(3)
C(95) – C(96) – H(96)	118.9	C(91) – C(96) – H(96)	118.9
F(91) – C(97) – F(92)	107.4(3)	F(91) – C(97) – F(93)	106.1(3)
F(92) – C(97) – F(93)	104.7(3)	F(91) – C(97) – C(93)	112.3(3)
F(92) – C(97) – C(93)	113.7(3)	F(93) – C(97) – C(93)	112.0(3)
F(96) – C(98) – F(95)	106.7(3)	F(96) – C(98) – F(94)	106.5(3)
F(95) – C(98) – F(94)	105.2(3)	F(96) – C(98) – C(95)	113.4(3)
F(95) – C(98) – C(95)	112.6(3)	F(94) – C(98) – C(95)	111.9(3)

4.6 Crystal data for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] ([9][BAr$^F_4$])

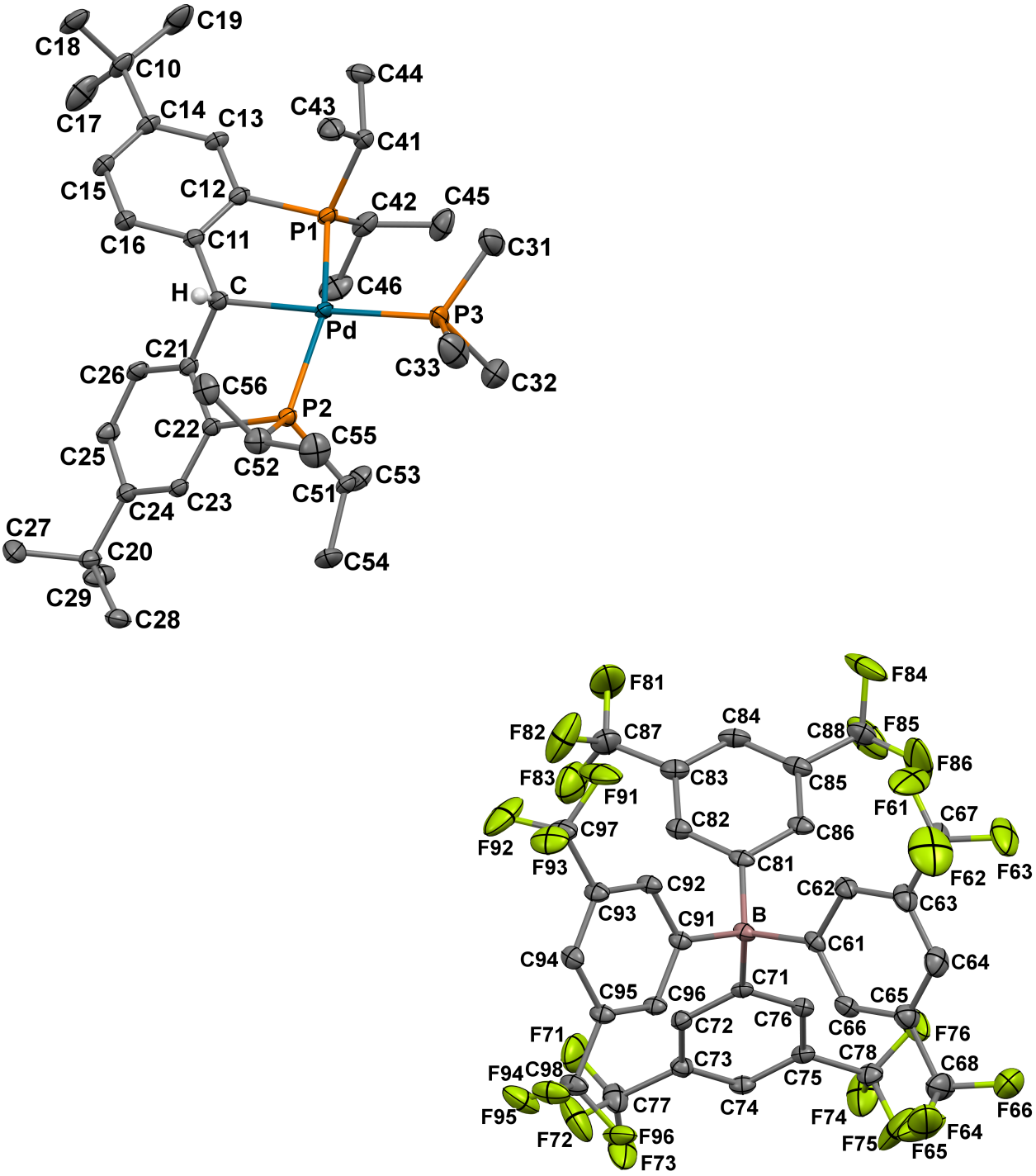

Figure S64. Thermal-ellipsoid representation of [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S32. Crystal data and structure refinement for [{PC(sp^3)HP}$^{t\mathrm{Bu}}$PdPMe$_3$][BAr$^{\mathrm{F}}_4$] (**[9][BAr$^{\mathrm{F}}_4$]**).

Identification code:	pc41	
Empirical formula:	$C_{68}H_{74}BF_{24}P_3Pd$	
Formula weight:	1557.39	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Triclinic	
Space group:	$P\bar{1}$	
Unit cell dimensions:	a = 13.7002(14) Å	α = 65.531(3)°
	b = 17.7228(18) Å	β = 74.700(3)°
	c = 18.5200(19) Å	γ = 88.259(3)°
Volume:	3931.8(7) Å^3	
Z:	2	
Density (calculated):	1.315 g·cm^{-3}	
Absorption coefficient (μ):	0.390 mm^{-1}	
F(000):	1588	
Crystal size:	0.09 × 0.08 × 0.05 mm^3	
θ range for data collection:	1.55 to 25.00°	
Index ranges:	$-16 \le h \le 16$, $-21 \le k \le 21$, $-22 \le l \le 22$	
Reflections collected:	71970	
Independent reflections:	13848 [R_{int} = 0.0347]	
Completeness to θ = 25.00°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.7138	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	13848 / 0 / 891	
Goodness-of-fit on F^2:	1.065	
Final R indices [I>2σ(I)]:	R_1 = 0.0492, wR_2 = 0.1270	
R indices (all data):	R_1 = 0.0575, wR_2 = 0.1325	
Largest diff. peak and hole:	2.142 and −1.161 e$^-$·Å^{-3}	

Table S33. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}$^{t\mathrm{Bu}}$PdPMe$_3$][BAr$^{\mathrm{F}}_4$] (**[9][BAr$^{\mathrm{F}}_4$]**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

atom	x	y	z	U(eq)
Pd	0.32223(2)	0.73427(1)	0.20636(2)	0.024(1)
P(1)	0.19690(6)	0.78475(5)	0.28063(5)	0.024(1)
P(2)	0.48672(6)	0.72477(5)	0.13234(5)	0.023(1)
P(3)	0.25908(7)	0.59265(5)	0.26444(6)	0.034(1)
C(10)	0.1232(3)	1.1026(2)	0.2240(2)	0.038(1)
C(11)	0.3060(2)	0.9231(2)	0.1573(2)	0.027(1)
C(12)	0.2242(2)	0.89670(19)	0.2281(2)	0.026(1)
C(13)	0.1658(2)	0.9537(2)	0.2505(2)	0.027(1)
C(14)	0.1846(3)	1.0383(2)	0.2012(2)	0.029(1)
C(16)	0.3231(2)	1.0084(2)	0.1061(2)	0.030(1)
C(15)	0.2639(3)	1.0640(2)	0.1282(2)	0.031(1)
C(17)	0.1907(4)	1.1515(3)	0.2466(3)	0.063(1)
C(18)	0.0878(3)	1.1621(3)	0.1505(2)	0.049(1)
C(19)	0.0291(4)	1.0624(3)	0.2960(3)	0.060(1)
C	0.3735(2)	0.86201(19)	0.1368(2)	0.026(1)
C(20)	0.8106(2)	0.9245(2)	0.0834(2)	0.031(1)
C(21)	0.4836(2)	0.87618(19)	0.13309(19)	0.025(1)
C(22)	0.5499(2)	0.81959(18)	0.11919(18)	0.022(1)
C(23)	0.6542(2)	0.83606(19)	0.10059(18)	0.023(1)
C(24)	0.6965(2)	0.90492(19)	0.1023(2)	0.026(1)
C(26)	0.5249(2)	0.9442(2)	0.1369(2)	0.029(1)
C(25)	0.6287(3)	0.9577(2)	0.1229(2)	0.031(1)
C(27)	0.8438(3)	1.0095(2)	0.0101(3)	0.045(1)
C(28)	0.8710(3)	0.8592(2)	0.0621(3)	0.038(1)
B	0.1409(3)	0.6337(2)	0.7333(2)	0.023(1)
C(29)	0.8342(3)	0.9267(3)	0.1584(3)	0.045(1)
C(31)	0.1252(3)	0.5621(3)	0.3107(3)	0.063(1)
C(32)	0.3075(4)	0.5197(3)	0.3505(3)	0.060(1)
C(33)	0.2894(4)	0.5429(3)	0.1958(4)	0.068(1)
C(41)	0.0670(2)	0.7640(2)	0.2790(2)	0.028(1)
C(42)	0.1934(3)	0.7601(2)	0.3880(2)	0.034(1)
C(43)	0.0667(3)	0.7877(3)	0.1903(2)	0.041(1)
C(44)	−0.0166(3)	0.8036(3)	0.3206(3)	0.044(1)
C(45)	0.1477(4)	0.6722(2)	0.4478(2)	0.049(1)
C(46)	0.3003(3)	0.7769(3)	0.3912(3)	0.049(1)
C(51)	0.5460(2)	0.6380(2)	0.1976(2)	0.029(1)
C(52)	0.5289(3)	0.7272(2)	0.0270(2)	0.038(1)
C(53)	0.5364(3)	0.6449(2)	0.2783(2)	0.040(1)
C(54)	0.6555(3)	0.6246(2)	0.1613(3)	0.047(1)

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Table S33. – continued from previous page

atom	x	y	x	U(eq)
C(55)	0.5033(4)	0.6463(3)	0.0237(3)	0.054(1)
C(56)	0.4872(3)	0.8000(3)	−0.0325(2)	0.043(1)
C(61)	0.2163(2)	0.66688(19)	0.77129(18)	0.024(1)
F(61)	0.1621(3)	0.8666(2)	0.8337(3)	0.120(2)
C(62)	0.1973(3)	0.7335(2)	0.7928(2)	0.030(1)
F(62)	0.2164(3)	0.8018(3)	0.9352(2)	0.109(1)
C(63)	0.2613(3)	0.7597(2)	0.8269(2)	0.038(1)
F(63)	0.3180(2)	0.88257(19)	0.8271(2)	0.086(1)
C(64)	0.3481(3)	0.7212(3)	0.8392(2)	0.042(1)
F(64)	0.4911(3)	0.5697(3)	0.7852(3)	0.115(2)
C(65)	0.3692(3)	0.6546(2)	0.8188(2)	0.037(1)
F(65)	0.4541(2)	0.55803(19)	0.9074(2)	0.089(1)
C(66)	0.3032(3)	0.6277(2)	0.7873(2)	0.030(1)
F(66)	0.54190(19)	0.66495(17)	0.81275(18)	0.064(1)
C(67)	0.2389(3)	0.8303(3)	0.8500(3)	0.060(1)
C(68)	0.4640(4)	0.6124(3)	0.8298(3)	0.052(1)
C(71)	0.2055(2)	0.58918(18)	0.67571(18)	0.021(1)
F(71)	0.1055(2)	0.4334(2)	0.5748(2)	0.081(1)
C(72)	0.1669(2)	0.52097(19)	0.66945(19)	0.025(1)
F(72)	0.1294(3)	0.35684(17)	0.68936(18)	0.084(1)
C(73)	0.2233(2)	0.4870(2)	0.6178(2)	0.027(1)
F(73)	0.2427(2)	0.37655(18)	0.5776(2)	0.078(1)
C(74)	0.3205(2)	0.5198(2)	0.56993(19)	0.027(1)
F(74)	0.4958(2)	0.6131(2)	0.45610(18)	0.078(1)
C(75)	0.3598(2)	0.58872(19)	0.57346(19)	0.025(1)
F(75)	0.53193(19)	0.5867(2)	0.56473(19)	0.097(1)
C(76)	0.3033(2)	0.62270(19)	0.62443(18)	0.023(1)
F(76)	0.4809(2)	0.70366(16)	0.5009(2)	0.082(1)
C(77)	0.1775(3)	0.4136(3)	0.6151(3)	0.045(1)
C(78)	0.4661(3)	0.6237(2)	0.5254(2)	0.033(1)
C(81)	0.0927(2)	0.70870(19)	0.66894(19)	0.025(1)
F(81)	−0.1699(3)	0.7981(2)	0.5336(3)	0.116(2)
C(82)	0.0019(3)	0.6947(2)	0.6541(2)	0.029(1)
F(82)	−0.2058(2)	0.6982(3)	0.65340(19)	0.094(1)
C(83)	−0.0368(3)	0.7550(2)	0.5946(2)	0.034(1)
F(83)	−0.1267(2)	0.6795(2)	0.5514(2)	0.088(1)
C(84)	0.0164(3)	0.8322(2)	0.5457(2)	0.036(1)
F(84)	0.1138(3)	0.99323(15)	0.5027(2)	0.089(1)
C(85)	0.1076(3)	0.8476(2)	0.5580(2)	0.033(1)
F(85)	0.1995(3)	0.94222(17)	0.42645(16)	0.084(1)
C(86)	0.1448(3)	0.7872(2)	0.61815(19)	0.028(1)
F(86)	0.2470(3)	0.94029(19)	0.5245(2)	0.118(2)

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Table S33. – continued from previous page

atom	x	y	x	U(eq)
C(87)	−0.1344(3)	0.7346(3)	0.5837(3)	0.047(1)
C(88)	0.1661(3)	0.9297(2)	0.5047(2)	0.042(1)
C(91)	0.0531(2)	0.56927(19)	0.81305(18)	0.023(1)
F(91)	−0.2117(2)	0.64889(16)	0.92039(19)	0.081(1)
C(92)	−0.0395(2)	0.59400(19)	0.84575(19)	0.026(1)
F(92)	−0.2844(2)	0.5427(2)	0.9243(2)	0.086(1)
C(93)	−0.1118(3)	0.5397(2)	0.9153(2)	0.028(1)
F(93)	−0.24317(19)	0.53668(16)	1.02806(14)	0.057(1)
C(94)	−0.0943(3)	0.4575(2)	0.9561(2)	0.028(1)
F(94)	−0.02709(18)	0.30677(13)	1.04507(12)	0.050(1)
C(95)	−0.0024(3)	0.4317(2)	0.92510(19)	0.027(1)
F(95)	−0.0209(2)	0.29727(14)	0.93323(16)	0.063(1)
C(96)	0.0691(2)	0.48643(19)	0.85575(19)	0.024(1)
F(96)	0.11392(17)	0.32980(13)	0.95314(15)	0.056(1)
C(97)	−0.2120(3)	0.5675(2)	0.9458(2)	0.037(1)
C(98)	0.0159(3)	0.3421(2)	0.9639(2)	0.034(1)
H(13)	0.1124	0.9340	0.3003	0.033
H(16)	0.3758	1.0282	0.0558	0.036
H(15)	0.2775	1.1217	0.0927	0.037
H(17A)	0.2502	1.1792	0.1996	0.095
H(17B)	0.2129	1.1133	0.2941	0.095
H(17C)	0.1522	1.1934	0.2607	0.095
H(18A)	0.1470	1.1915	0.1038	0.074
H(18B)	0.0472	1.2026	0.1656	0.074
H(18C)	0.0463	1.1305	0.1350	0.074
H(19A)	−0.0083	1.1057	0.3082	0.090
H(19B)	0.0495	1.0245	0.3447	0.090
H(19C)	−0.0144	1.0312	0.2817	0.090
H	0.3745	0.8736	0.0790	0.031
H(23)	0.6979	0.7988	0.0862	0.027
H(26)	0.4813	0.9825	0.1494	0.035
H(25)	0.6543	1.0043	0.1274	0.037
H(27A)	0.8325	1.0072	−0.0391	0.067
H(27B)	0.9161	1.0239	0.0000	0.067
H(27C)	0.8040	1.0517	0.0224	0.067
H(28A)	0.8568	0.8573	0.0137	0.057
H(28B)	0.8513	0.8046	0.1090	0.057
H(28C)	0.9438	0.8738	0.0499	0.057
H(29A)	0.9068	0.9425	0.1452	0.068
H(29B)	0.8162	0.8716	0.2047	0.068
H(29C)	0.7947	0.9676	0.1736	0.068
H(31A)	0.0875	0.5958	0.2719	0.094

Continued on next page

Table S33. – continued from previous page

atom	x	y	x	U(eq)
H(31B)	0.1033	0.5706	0.3613	0.094
H(31C)	0.1118	0.5032	0.3239	0.094
H(32A)	0.2738	0.4638	0.3716	0.091
H(32B)	0.2934	0.5384	0.3948	0.091
H(32C)	0.3810	0.5185	0.3304	0.091
H(33A)	0.2617	0.5723	0.1487	0.101
H(33B)	0.2597	0.4850	0.2250	0.101
H(33C)	0.3633	0.5442	0.1760	0.101
H(41)	0.0500	0.7024	0.3091	0.033
H(42)	0.1496	0.7994	0.4049	0.041
H(43A)	0.0796	0.8483	0.1591	0.062
H(43B)	0.0004	0.7696	0.1893	0.062
H(43C)	0.1199	0.7607	0.1653	0.062
H(44A)	−0.0082	0.8641	0.2884	0.066
H(44B)	−0.0122	0.7904	0.3764	0.066
H(44C)	−0.0831	0.7817	0.3236	0.066
H(45A)	0.0785	0.6646	0.4451	0.074
H(45B)	0.1460	0.6633	0.5041	0.074
H(45C)	0.1893	0.6321	0.4330	0.074
H(46A)	0.3451	0.7389	0.3754	0.073
H(46B)	0.2984	0.7682	0.4474	0.073
H(46C)	0.3261	0.8345	0.3530	0.073
H(51)	0.5037	0.5860	0.2121	0.034
H(52)	0.6047	0.7379	0.0081	0.045
H(53A)	0.5794	0.6937	0.2676	0.060
H(53B)	0.5581	0.5946	0.3167	0.060
H(53C)	0.4654	0.6510	0.3025	0.060
H(54A)	0.6623	0.6241	0.1075	0.070
H(54B)	0.6729	0.5712	0.1987	0.070
H(54C)	0.7015	0.6698	0.1546	0.070
H(55A)	0.5380	0.6489	−0.0309	0.080
H(55B)	0.4297	0.6378	0.0338	0.080
H(55C)	0.5257	0.6000	0.0660	0.080
H(56A)	0.5154	0.8047	−0.0887	0.065
H(56B)	0.5064	0.8515	−0.0300	0.065
H(56C)	0.4130	0.7908	−0.0170	0.065
H(62)	0.1387	0.7620	0.7840	0.036
H(64)	0.3925	0.7401	0.8612	0.051
H(66)	0.3177	0.5802	0.7761	0.036
H(72)	0.0999	0.4969	0.7015	0.030
H(74)	0.3594	0.4958	0.5355	0.033
H(76)	0.3320	0.6707	0.6247	0.028

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Table S33. – continued from previous page

atom	x	y	x	U(eq)
H(82)	−0.0353	0.6417	0.6860	0.035
H(84)	−0.0092	0.8738	0.5047	0.044
H(86)	0.2078	0.7996	0.6250	0.034
H(92)	−0.0536	0.6502	0.8194	0.031
H(94)	−0.1436	0.4199	1.0036	0.034
H(96)	0.1315	0.4668	0.8365	0.029

Table S34. Anisotropic displacement parameters (Å^2) for [{PC(sp^3)HP}$^{t\text{Bu}}$PdPMe$_3$][BAr$^F_4$] (**[9][BAr$^F_4$]**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}$ + ...+ 2hka*b*U_{12}].

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.0237(4)	0.0199(4)	0.0317(4)	−0.0117(3)	−0.0108(3)	0.0086(3)
P(2)	0.0229(4)	0.0204(4)	0.0288(4)	−0.0113(3)	−0.0086(3)	0.0051(3)
P(3)	0.0283(5)	0.0208(4)	0.0485(6)	−0.0162(4)	−0.0016(4)	0.0009(3)
C(10)	0.050(2)	0.0264(18)	0.036(2)	−0.0155(16)	−0.0107(17)	0.0199(16)
C(11)	0.0229(16)	0.0241(16)	0.0346(18)	−0.0129(14)	−0.0097(14)	0.0073(13)
C(12)	0.0250(16)	0.0220(16)	0.0366(18)	−0.0151(14)	−0.0132(14)	0.0080(13)
C(13)	0.0280(17)	0.0261(17)	0.0321(18)	−0.0153(14)	−0.0108(14)	0.0109(13)
C(14)	0.0337(18)	0.0228(16)	0.0364(19)	−0.0153(15)	−0.0151(15)	0.0127(14)
C(16)	0.0252(17)	0.0245(17)	0.0349(19)	−0.0088(14)	−0.0068(14)	0.0052(13)
C(15)	0.0315(18)	0.0204(16)	0.0367(19)	−0.0094(14)	−0.0095(15)	0.0081(13)
C(17)	0.103(4)	0.038(2)	0.072(3)	−0.037(2)	−0.040(3)	0.029(2)
C(18)	0.059(3)	0.041(2)	0.043(2)	−0.0154(18)	−0.011(2)	0.033(2)
C(19)	0.080(3)	0.042(2)	0.044(2)	−0.016(2)	0.000(2)	0.035(2)
C	0.0258(16)	0.0241(16)	0.0254(16)	−0.0090(13)	−0.0069(13)	0.0064(13)
C(20)	0.0229(17)	0.0272(17)	0.048(2)	−0.0169(16)	−0.0140(15)	0.0063(13)
C(21)	0.0254(16)	0.0213(15)	0.0251(16)	−0.0085(13)	−0.0063(13)	0.0066(13)
C(22)	0.0221(15)	0.0197(15)	0.0225(15)	−0.0085(12)	−0.0056(12)	0.0041(12)
C(23)	0.0234(16)	0.0208(15)	0.0244(16)	−0.0098(13)	−0.0071(13)	0.0078(12)
C(24)	0.0237(16)	0.0226(16)	0.0316(17)	−0.0116(14)	−0.0095(13)	0.0052(13)
C(26)	0.0286(17)	0.0235(16)	0.0379(19)	−0.0173(15)	−0.0088(14)	0.0092(13)
C(25)	0.0320(18)	0.0249(17)	0.044(2)	−0.0199(15)	−0.0149(16)	0.0069(14)
C(27)	0.030(2)	0.034(2)	0.063(3)	−0.0103(19)	−0.0156(18)	−0.0017(16)
C(28)	0.0203(17)	0.038(2)	0.059(2)	−0.0247(18)	−0.0096(16)	0.0054(15)
B	0.0277(18)	0.0187(17)	0.0201(17)	−0.0080(14)	−0.0030(14)	0.0045(14)
C(29)	0.040(2)	0.049(2)	0.067(3)	−0.035(2)	−0.030(2)	0.0141(18)
C(31)	0.039(2)	0.038(2)	0.099(4)	−0.029(2)	0.001(2)	−0.0045(19)
C(32)	0.054(3)	0.041(2)	0.071(3)	−0.009(2)	−0.016(2)	0.008(2)
C(33)	0.062(3)	0.055(3)	0.094(4)	−0.052(3)	0.001(3)	−0.009(2)
C(41)	0.0233(16)	0.0213(16)	0.0349(18)	−0.0096(14)	−0.0063(14)	0.0042(13)
C(42)	0.047(2)	0.0307(18)	0.0302(18)	−0.0148(15)	−0.0159(16)	0.0156(16)
C(43)	0.034(2)	0.048(2)	0.040(2)	−0.0131(18)	−0.0170(17)	0.0058(17)
C(44)	0.0231(18)	0.046(2)	0.063(3)	−0.028(2)	−0.0062(17)	0.0075(16)
C(45)	0.073(3)	0.035(2)	0.029(2)	−0.0066(17)	−0.0103(19)	0.012(2)
C(46)	0.059(3)	0.057(3)	0.050(2)	−0.029(2)	−0.036(2)	0.022(2)
C(51)	0.0256(17)	0.0200(15)	0.0405(19)	−0.0129(14)	−0.0101(14)	0.0079(13)
C(52)	0.041(2)	0.040(2)	0.039(2)	−0.0227(17)	−0.0126(17)	0.0048(16)
C(53)	0.047(2)	0.035(2)	0.040(2)	−0.0117(17)	−0.0236(18)	0.0140(17)
C(54)	0.033(2)	0.037(2)	0.066(3)	−0.022(2)	−0.0082(19)	0.0162(17)
C(55)	0.069(3)	0.054(3)	0.050(3)	−0.035(2)	−0.014(2)	0.002(2)

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Table S34. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(56)	0.052(2)	0.048(2)	0.031(2)	−0.0168(18)	−0.0096(17)	−0.0031(19)
C(61)	0.0307(17)	0.0189(15)	0.0181(15)	−0.0064(12)	−0.0013(13)	−0.0007(13)
F(61)	0.099(3)	0.107(3)	0.264(5)	−0.155(4)	−0.100(3)	0.066(2)
C(62)	0.0291(17)	0.0283(17)	0.0320(18)	−0.0166(15)	−0.0009(14)	0.0024(14)
F(62)	0.122(3)	0.131(3)	0.105(3)	−0.098(3)	0.001(2)	0.001(2)
C(63)	0.040(2)	0.038(2)	0.043(2)	−0.0284(18)	−0.0026(17)	−0.0010(16)
F(63)	0.0641(18)	0.0714(19)	0.143(3)	−0.083(2)	0.0011(18)	−0.0094(15)
C(64)	0.043(2)	0.050(2)	0.047(2)	−0.032(2)	−0.0141(18)	0.0000(18)
F(64)	0.105(3)	0.153(3)	0.210(4)	−0.154(4)	−0.120(3)	0.097(3)
C(65)	0.043(2)	0.0339(19)	0.041(2)	−0.0187(17)	−0.0163(17)	0.0050(16)
F(65)	0.080(2)	0.0600(18)	0.108(3)	0.0019(17)	−0.059(2)	0.0038(15)
C(66)	0.041(2)	0.0203(16)	0.0292(18)	−0.0098(14)	−0.0126(15)	0.0052(14)
F(66)	0.0464(15)	0.0614(16)	0.0841(19)	−0.0266(15)	−0.0273(14)	0.0086(13)
C(67)	0.042(2)	0.073(3)	0.093(4)	−0.069(3)	−0.005(2)	0.001(2)
C(68)	0.057(3)	0.051(3)	0.069(3)	−0.033(2)	−0.040(2)	0.015(2)
C(71)	0.0226(15)	0.0194(15)	0.0186(15)	−0.0060(12)	−0.0069(12)	0.0072(12)
F(71)	0.0620(18)	0.094(2)	0.130(3)	−0.079(2)	−0.0445(19)	0.0050(16)
C(72)	0.0221(16)	0.0258(16)	0.0260(16)	−0.0109(13)	−0.0058(13)	0.0045(13)
F(72)	0.121(3)	0.0493(16)	0.0699(19)	−0.0328(15)	0.0089(18)	−0.0379(17)
C(73)	0.0292(17)	0.0264(17)	0.0298(17)	−0.0148(14)	−0.0087(14)	0.0056(13)
F(73)	0.0523(16)	0.0758(19)	0.133(3)	−0.087(2)	0.0047(16)	−0.0018(14)
C(74)	0.0304(18)	0.0291(17)	0.0237(16)	−0.0132(14)	−0.0067(14)	0.0115(14)
F(74)	0.0541(16)	0.115(3)	0.0637(18)	−0.0570(18)	0.0216(14)	−0.0171(16)
C(75)	0.0248(16)	0.0246(16)	0.0223(16)	−0.0081(13)	−0.0063(13)	0.0078(13)
F(75)	0.0275(13)	0.138(3)	0.0666(19)	0.0150(19)	−0.0151(13)	0.0013(16)
C(76)	0.0266(16)	0.0208(15)	0.0226(16)	−0.0091(13)	−0.0077(13)	0.0052(12)
F(76)	0.0435(15)	0.0462(15)	0.125(3)	−0.0378(16)	0.0323(16)	−0.0113(12)
C(77)	0.042(2)	0.044(2)	0.055(3)	−0.034(2)	−0.0012(19)	−0.0019(18)
C(78)	0.0292(18)	0.036(2)	0.0339(19)	−0.0180(16)	−0.0042(15)	0.0084(15)
C(81)	0.0321(17)	0.0207(15)	0.0202(15)	−0.0102(13)	−0.0015(13)	0.0086(13)
F(81)	0.097(3)	0.065(2)	0.174(4)	0.001(2)	−0.103(3)	0.0099(18)
C(82)	0.0339(18)	0.0261(17)	0.0255(17)	−0.0102(14)	−0.0056(14)	0.0076(14)
F(82)	0.0390(15)	0.166(4)	0.0644(19)	−0.036(2)	−0.0114(14)	−0.0120(18)
C(83)	0.039(2)	0.0324(19)	0.0341(19)	−0.0162(16)	−0.0118(16)	0.0139(16)
F(83)	0.0675(19)	0.114(3)	0.120(3)	−0.078(2)	−0.0404(19)	0.0084(18)
C(84)	0.048(2)	0.0299(18)	0.0282(18)	−0.0096(15)	−0.0127(16)	0.0184(16)
F(84)	0.103(2)	0.0222(12)	0.098(2)	−0.0133(13)	0.0199(19)	0.0112(14)
C(85)	0.044(2)	0.0226(17)	0.0247(17)	−0.0082(14)	−0.0037(15)	0.0109(15)
F(85)	0.132(3)	0.0451(15)	0.0418(15)	−0.0103(12)	0.0173(16)	−0.0190(16)
C(86)	0.0333(18)	0.0244(16)	0.0251(17)	−0.0122(14)	−0.0025(14)	0.0097(14)
F(86)	0.124(3)	0.0535(18)	0.124(3)	0.0423(19)	−0.077(3)	−0.0453(19)
C(87)	0.047(2)	0.046(2)	0.049(2)	−0.015(2)	−0.023(2)	0.0110(19)

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Table S34. – continued from previous page

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(88)	0.053(2)	0.0265(19)	0.038(2)	−0.0044(16)	−0.0151(18)	0.0066(17)
C(91)	0.0285(16)	0.0220(15)	0.0203(15)	−0.0112(13)	−0.0060(13)	0.0056(13)
F(91)	0.0613(17)	0.0414(14)	0.094(2)	−0.0125(14)	0.0239(15)	0.0253(13)
C(92)	0.0322(17)	0.0209(15)	0.0213(16)	−0.0088(13)	−0.0043(13)	0.0075(13)
F(92)	0.0383(15)	0.157(3)	0.112(3)	−0.101(3)	−0.0289(16)	0.0403(18)
C(93)	0.0291(17)	0.0273(17)	0.0267(17)	−0.0131(14)	−0.0021(14)	0.0073(14)
F(93)	0.0532(15)	0.0651(16)	0.0410(13)	−0.0242(12)	0.0058(11)	0.0205(12)
C(94)	0.0294(17)	0.0258(17)	0.0220(16)	−0.0086(13)	0.0020(13)	0.0006(13)
F(94)	0.0631(15)	0.0338(11)	0.0262(11)	0.0022(9)	0.0036(10)	0.0163(11)
C(95)	0.0322(18)	0.0249(16)	0.0232(16)	−0.0115(13)	−0.0054(14)	0.0078(14)
F(95)	0.106(2)	0.0289(12)	0.0650(17)	−0.0219(12)	−0.0374(16)	0.0136(13)
C(96)	0.0264(16)	0.0243(16)	0.0225(16)	−0.0117(13)	−0.0036(13)	0.0069(13)
F(96)	0.0416(13)	0.0308(12)	0.0629(15)	0.0010(11)	0.0028(11)	0.0157(10)
C(97)	0.034(2)	0.035(2)	0.034(2)	−0.0133(16)	0.0004(16)	0.0095(16)
C(98)	0.040(2)	0.0259(17)	0.0257(18)	−0.0066(14)	−0.0010(15)	0.0068(15)

Table S35. Distances [Å] for [{PC(sp^3)HP}$^{t\mathrm{Bu}}$PdPMe$_3$][BAr$^{\mathrm{F}}_4$] (**[9][BAr$^{\mathbf{F}}_4$]**).

atom – atom	distance	atom – atom	distance
Pd – C	2.117(3)	Pd – P(1)	2.3067(8)
Pd – P(2)	2.3501(9)	Pd – P(3)	2.3684(9)
P(1) – C(12)	1.810(3)	P(1) – C(42)	1.838(3)
P(1) – C(41)	1.839(3)	P(2) – C(22)	1.808(3)
P(2) – C(51)	1.840(3)	P(2) – C(52)	1.865(4)
P(3) – C(33)	1.787(5)	P(3) – C(31)	1.800(4)
P(3) – C(32)	1.857(5)	C(10) – C(19)	1.520(6)
C(10) – C(18)	1.525(5)	C(10) – C(14)	1.528(4)
C(10) – C(17)	1.528(6)	C(11) – C(12)	1.393(5)
C(11) – C(16)	1.399(5)	C(11) – C	1.505(4)
C(12) – C(13)	1.398(4)	C(13) – C(14)	1.384(5)
C(13) – H(13)	0.9500	C(14) – C(15)	1.400(5)
C(16) – C(15)	1.381(5)	C(16) – H(16)	0.9500
C(15) – H(15)	0.9500	C(17) – H(17A)	0.9800
C(17) – H(17B)	0.9800	C(17) – H(17C)	0.9800
C(18) – H(18A)	0.9800	C(18) – H(18B)	0.9800
C(18) – H(18C)	0.9800	C(19) – H(19A)	0.9800
C(19) – H(19B)	0.9800	C(19) – H(19C)	0.9800
C – C(21)	1.515(4)	C – H	1.0000
C(20) – C(29)	1.522(5)	C(20) – C(28)	1.525(5)
C(20) – C(24)	1.527(4)	C(20) – C(27)	1.530(5)
C(21) – C(26)	1.384(5)	C(21) – C(22)	1.390(4)
C(22) – C(23)	1.389(4)	C(23) – C(24)	1.382(4)
C(23) – H(23)	0.9500	C(24) – C(25)	1.392(4)
C(26) – C(25)	1.385(5)	C(26) – H(26)	0.9500
C(25) – H(25)	0.9500	C(27) – H(27A)	0.9800
C(27) – H(27B)	0.9800	C(27) – H(27C)	0.9800
C(28) – H(28A)	0.9800	C(28) – H(28B)	0.9800
C(28) – H(28C)	0.9800	B – C(61)	1.634(5)
B – C(81)	1.635(4)	B – C(91)	1.637(5)
B – C(71)	1.644(4)	C(29) – H(29A)	0.9800
C(29) – H(29B)	0.9800	C(29) – H(29C)	0.9800
C(31) – H(31A)	0.9800	C(31) – H(31B)	0.9800
C(31) – H(31C)	0.9800	C(32) – H(32A)	0.9800
C(32) – H(32B)	0.9800	C(32) – H(32C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(41) – C(43)	1.518(5)
C(41) – C(44)	1.527(5)	C(41) – H(41)	1.0000
C(42) – C(45)	1.520(5)	C(42) – C(46)	1.525(6)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800

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Table S35. – continued from previous page

atom – atom	distance	atom – atom	distance
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(53)	1.521(5)
C(51) – C(54)	1.529(5)	C(51) – H(51)	1.0000
C(52) – C(55)	1.515(5)	C(52) – C(56)	1.522(5)
C(52) – H(52)	1.0000	C(53) – H(53A)	0.9800
C(53) – H(53B)	0.9800	C(53) – H(53C)	0.9800
C(54) – H(54A)	0.9800	C(54) – H(54B)	0.9800
C(54) – H(54C)	0.9800	C(55) – H(55A)	0.9800
C(55) – H(55B)	0.9800	C(55) – H(55C)	0.9800
C(56) – H(56A)	0.9800	C(56) – H(56B)	0.9800
C(56) – H(56C)	0.9800	C(61) – C(62)	1.391(4)
C(61) – C(66)	1.397(5)	F(61) – C(67)	1.255(6)
C(62) – C(63)	1.393(5)	C(62) – H(62)	0.9500
F(62) – C(67)	1.390(6)	C(63) – C(64)	1.377(6)
C(63) – C(67)	1.483(5)	F(63) – C(67)	1.306(5)
C(64) – C(65)	1.383(5)	C(64) – H(64)	0.9500
F(64) – C(68)	1.317(5)	C(65) – C(66)	1.386(5)
C(65) – C(68)	1.498(6)	F(65) – C(68)	1.330(5)
C(66) – H(66)	0.9500	F(66) – C(68)	1.321(5)
C(71) – C(72)	1.393(4)	C(71) – C(76)	1.401(4)
F(71) – C(77)	1.342(5)	C(72) – C(73)	1.389(4)
C(72) – H(72)	0.9500	F(72) – C(77)	1.324(5)
C(73) – C(74)	1.377(5)	C(73) – C(77)	1.487(5)
F(73) – C(77)	1.315(4)	C(74) – C(75)	1.382(5)
C(74) – H(74)	0.9500	F(74) – C(78)	1.330(4)
C(75) – C(76)	1.382(4)	C(75) – C(78)	1.486(5)
F(75) – C(78)	1.300(4)	C(76) – H(76)	0.9500
F(76) – C(78)	1.300(4)	C(81) – C(82)	1.393(5)
C(81) – C(86)	1.397(5)	F(81) – C(87)	1.305(5)
C(82) – C(83)	1.392(5)	C(82) – H(82)	0.9500
F(82) – C(87)	1.313(5)	C(83) – C(84)	1.382(5)
C(83) – C(87)	1.480(6)	F(83) – C(87)	1.328(5)
C(84) – C(85)	1.382(5)	C(84) – H(84)	0.9500
F(84) – C(88)	1.309(5)	C(85) – C(86)	1.387(5)
C(85) – C(88)	1.484(5)	F(85) – C(88)	1.322(5)
C(86) – H(86)	0.9500	F(86) – C(88)	1.296(5)
C(91) – C(96)	1.392(4)	C(91) – C(92)	1.397(4)
F(91) – C(97)	1.320(4)	C(92) – C(93)	1.387(5)
C(92) – H(92)	0.9500	F(92) – C(97)	1.308(5)

Continued on next page

Table S35. – continued from previous page

atom – atom	distance	atom – atom	distance
C(93) – C(94)	1.383(5)	C(93) – C(97)	1.492(5)
F(93) – C(97)	1.336(4)	C(94) – C(95)	1.387(5)
C(94) – H(94)	0.9500	F(94) – C(98)	1.331(4)
C(95) – C(96)	1.382(5)	C(95) – C(98)	1.493(4)
F(95) – C(98)	1.327(4)	C(96) – H(96)	0.9500
F(96) – C(98)	1.329(4)		

Table S36. Angles [°] for [{PC(sp^3)HP}$^{t\mathrm{Bu}}$PdPMe$_3$][BAr$^{\mathrm{F}}_4$] (**[9][BAr$^{\mathbf{F}}_4$]**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	82.93(9)	C – Pd – P(2)	79.55(9)
P(1) – Pd – P(2)	157.28(3)	C – Pd – P(3)	170.68(9)
P(1) – Pd – P(3)	100.61(3)	P(2) – Pd – P(3)	98.96(3)
C(12) – P(1) – C(42)	104.04(16)	C(12) – P(1) – C(41)	105.73(14)
C(42) – P(1) – C(41)	107.59(16)	C(12) – P(1) – Pd	104.53(11)
C(42) – P(1) – Pd	118.42(12)	C(41) – P(1) – Pd	115.14(11)
C(22) – P(2) – C(51)	106.69(15)	C(22) – P(2) – C(52)	103.14(16)
C(51) – P(2) – C(52)	106.04(16)	C(22) – P(2) – Pd	99.71(10)
C(51) – P(2) – Pd	110.81(11)	C(52) – P(2) – Pd	128.23(13)
C(33) – P(3) – C(31)	101.6(2)	C(33) – P(3) – C(32)	100.3(3)
C(31) – P(3) – C(32)	99.1(2)	C(33) – P(3) – Pd	115.37(17)
C(31) – P(3) – Pd	120.67(15)	C(32) – P(3) – Pd	116.44(16)
C(19) – C(10) – C(18)	107.4(3)	C(19) – C(10) – C(14)	112.1(3)
C(18) – C(10) – C(14)	109.6(3)	C(19) – C(10) – C(17)	109.2(4)
C(18) – C(10) – C(17)	109.6(3)	C(14) – C(10) – C(17)	108.9(3)
C(12) – C(11) – C(16)	117.6(3)	C(12) – C(11) – C	121.2(3)
C(16) – C(11) – C	121.3(3)	C(11) – C(12) – C(13)	121.3(3)
C(11) – C(12) – P(1)	113.7(2)	C(13) – C(12) – P(1)	124.8(3)
C(14) – C(13) – C(12)	121.1(3)	C(14) – C(13) – H(13)	119.4
C(12) – C(13) – H(13)	119.4	C(13) – C(14) – C(15)	117.1(3)
C(13) – C(14) – C(10)	122.7(3)	C(15) – C(14) – C(10)	120.2(3)
C(15) – C(16) – C(11)	120.5(3)	C(15) – C(16) – H(16)	119.8
C(11) – C(16) – H(16)	119.8	C(16) – C(15) – C(14)	122.3(3)
C(16) – C(15) – H(15)	118.9	C(14) – C(15) – H(15)	118.9
C(10) – C(17) – H(17A)	109.5	C(10) – C(17) – H(17B)	109.5
H(17A) – C(17) – H(17B)	109.5	C(10) – C(17) – H(17C)	109.5
H(17A) – C(17) – H(17C)	109.5	H(17B) – C(17) – H(17C)	109.5
C(10) – C(18) – H(18A)	109.5	C(10) – C(18) – H(18B)	109.5
H(18A) – C(18) – H(18B)	109.5	C(10) – C(18) – H(18C)	109.5
H(18A) – C(18) – H(18C)	109.5	H(18B) – C(18) – H(18C)	109.5
C(10) – C(19) – H(19A)	109.5	C(10) – C(19) – H(19B)	109.5
H(19A) – C(19) – H(19B)	109.5	C(10) – C(19) – H(19C)	109.5
H(19A) – C(19) – H(19C)	109.5	H(19B) – C(19) – H(19C)	109.5
C(11) – C – C(21)	114.1(3)	C(11) – C – Pd	116.8(2)
C(21) – C – Pd	110.1(2)	C(11) – C – H	104.9
C(21) – C – H	104.9	Pd – C – H	104.9
C(29) – C(20) – C(28)	108.6(3)	C(29) – C(20) – C(24)	109.5(3)
C(28) – C(20) – C(24)	111.6(3)	C(29) – C(20) – C(27)	109.3(3)
C(28) – C(20) – C(27)	108.7(3)	C(24) – C(20) – C(27)	109.2(3)
C(26) – C(21) – C(22)	117.1(3)	C(26) – C(21) – C	125.0(3)
C(22) – C(21) – C	117.7(3)	C(23) – C(22) – C(21)	120.9(3)

Continued on next page

Table S36. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(23) – C(22) – P(2)	125.3(2)	C(21) – C(22) – P(2)	113.7(2)
C(24) – C(23) – C(22)	122.1(3)	C(24) – C(23) – H(23)	118.9
C(22) – C(23) – H(23)	118.9	C(23) – C(24) – C(25)	116.3(3)
C(23) – C(24) – C(20)	123.7(3)	C(25) – C(24) – C(20)	120.0(3)
C(21) – C(26) – C(25)	121.3(3)	C(21) – C(26) – H(26)	119.4
C(25) – C(26) – H(26)	119.4	C(26) – C(25) – C(24)	121.9(3)
C(26) – C(25) – H(25)	119.0	C(24) – C(25) – H(25)	119.0
C(20) – C(27) – H(27A)	109.5	C(20) – C(27) – H(27B)	109.5
H(27A) – C(27) – H(27B)	109.5	C(20) – C(27) – H(27C)	109.5
H(27A) – C(27) – H(27C)	109.5	H(27B) – C(27) – H(27C)	109.5
C(20) – C(28) – H(28A)	109.5	C(20) – C(28) – H(28B)	109.5
H(28A) – C(28) – H(28B)	109.5	C(20) – C(28) – H(28C)	109.5
H(28A) – C(28) – H(28C)	109.5	H(28B) – C(28) – H(28C)	109.5
C(61) – B – C(81)	113.4(3)	C(61) – B – C(91)	105.8(2)
C(81) – B – C(91)	112.2(3)	C(61) – B – C(71)	110.1(3)
C(81) – B – C(71)	102.9(2)	C(91) – B – C(71)	112.6(2)
C(20) – C(29) – H(29A)	109.5	C(20) – C(29) – H(29B)	109.5
H(29A) – C(29) – H(29B)	109.5	C(20) – C(29) – H(29C)	109.5
H(29A) – C(29) – H(29C)	109.5	H(29B) – C(29) – H(29C)	109.5
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(43) – C(41) – C(44)	110.9(3)	C(43) – C(41) – P(1)	108.7(2)
C(44) – C(41) – P(1)	116.5(2)	C(43) – C(41) – H(41)	106.7
C(44) – C(41) – H(41)	106.7	P(1) – C(41) – H(41)	106.7
C(45) – C(42) – C(46)	112.1(3)	C(45) – C(42) – P(1)	113.2(3)
C(46) – C(42) – P(1)	108.8(3)	C(45) – C(42) – H(42)	107.5
C(46) – C(42) – H(42)	107.5	P(1) – C(42) – H(42)	107.5
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5

Continued on next page

Table S36. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(53) – C(51) – C(54)	109.9(3)	C(53) – C(51) – P(2)	108.9(2)
C(54) – C(51) – P(2)	118.4(3)	C(53) – C(51) – H(51)	106.3
C(54) – C(51) – H(51)	106.3	P(2) – C(51) – H(51)	106.3
C(55) – C(52) – C(56)	111.3(3)	C(55) – C(52) – P(2)	114.2(3)
C(56) – C(52) – P(2)	109.7(3)	C(55) – C(52) – H(52)	107.1
C(56) – C(52) – H(52)	107.1	P(2) – C(52) – H(52)	107.1
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5
C(62) – C(61) – C(66)	115.2(3)	C(62) – C(61) – B	123.0(3)
C(66) – C(61) – B	121.7(3)	C(61) – C(62) – C(63)	122.2(3)
C(61) – C(62) – H(62)	118.9	C(63) – C(62) – H(62)	118.9
C(64) – C(63) – C(62)	120.9(3)	C(64) – C(63) – C(67)	117.9(4)
C(62) – C(63) – C(67)	121.2(4)	C(63) – C(64) – C(65)	118.4(3)
C(63) – C(64) – H(64)	120.8	C(65) – C(64) – H(64)	120.8
C(64) – C(65) – C(66)	120.0(3)	C(64) – C(65) – C(68)	119.9(3)
C(66) – C(65) – C(68)	120.2(3)	C(65) – C(66) – C(61)	123.2(3)
C(65) – C(66) – H(66)	118.4	C(61) – C(66) – H(66)	118.4
F(61) – C(67) – F(63)	112.3(5)	F(61) – C(67) – F(62)	103.2(4)
F(63) – C(67) – F(62)	100.1(4)	F(61) – C(67) – C(63)	116.0(4)
F(63) – C(67) – C(63)	113.7(4)	F(62) – C(67) – C(63)	109.8(4)
F(64) – C(68) – F(66)	108.2(4)	F(64) – C(68) – F(65)	105.5(4)
F(66) – C(68) – F(65)	104.3(3)	F(64) – C(68) – C(65)	113.0(3)
F(66) – C(68) – C(65)	112.7(4)	F(65) – C(68) – C(65)	112.5(4)
C(72) – C(71) – C(76)	115.4(3)	C(72) – C(71) – B	124.1(3)
C(76) – C(71) – B	120.4(3)	C(73) – C(72) – C(71)	122.1(3)
C(73) – C(72) – H(72)	119.0	C(71) – C(72) – H(72)	119.0
C(74) – C(73) – C(72)	121.2(3)	C(74) – C(73) – C(77)	119.8(3)
C(72) – C(73) – C(77)	119.0(3)	C(73) – C(74) – C(75)	118.0(3)

Continued on next page

Table S36. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(73) – C(74) – H(74)	121.0	C(75) – C(74) – H(74)	121.0
C(74) – C(75) – C(76)	120.7(3)	C(74) – C(75) – C(78)	119.5(3)
C(76) – C(75) – C(78)	119.7(3)	C(75) – C(76) – C(71)	122.6(3)
C(75) – C(76) – H(76)	118.7	C(71) – C(76) – H(76)	118.7
F(73) – C(77) – F(72)	108.0(4)	F(73) – C(77) – F(71)	105.0(3)
F(72) – C(77) – F(71)	103.8(4)	F(73) – C(77) – C(73)	114.1(3)
F(72) – C(77) – C(73)	112.7(3)	F(71) – C(77) – C(73)	112.5(3)
F(76) – C(78) – F(75)	109.4(4)	F(76) – C(78) – F(74)	104.1(3)
F(75) – C(78) – F(74)	103.1(3)	F(76) – C(78) – C(75)	113.9(3)
F(75) – C(78) – C(75)	112.6(3)	F(74) – C(78) – C(75)	112.9(3)
C(82) – C(81) – C(86)	115.5(3)	C(82) – C(81) – B	121.4(3)
C(86) – C(81) – B	122.7(3)	C(83) – C(82) – C(81)	122.9(3)
C(83) – C(82) – H(82)	118.5	C(81) – C(82) – H(82)	118.5
C(84) – C(83) – C(82)	120.1(3)	C(84) – C(83) – C(87)	120.9(3)
C(82) – C(83) – C(87)	119.0(3)	C(85) – C(84) – C(83)	118.4(3)
C(85) – C(84) – H(84)	120.8	C(83) – C(84) – H(84)	120.8
C(84) – C(85) – C(86)	120.9(3)	C(84) – C(85) – C(88)	118.7(3)
C(86) – C(85) – C(88)	120.4(3)	C(85) – C(86) – C(81)	122.2(3)
C(85) – C(86) – H(86)	118.9	C(81) – C(86) – H(86)	118.9
F(81) – C(87) – F(82)	108.6(4)	F(81) – C(87) – F(83)	104.5(4)
F(82) – C(87) – F(83)	103.0(4)	F(81) – C(87) – C(83)	114.0(4)
F(82) – C(87) – C(83)	113.5(3)	F(83) – C(87) – C(83)	112.3(3)
F(86) – C(88) – F(84)	106.3(4)	F(86) – C(88) – F(85)	104.6(4)
F(84) – C(88) – F(85)	104.2(3)	F(86) – C(88) – C(85)	114.1(3)
F(84) – C(88) – C(85)	114.1(3)	F(85) – C(88) – C(85)	112.6(3)
C(96) – C(91) – C(92)	115.5(3)	C(96) – C(91) – B	121.5(3)
C(92) – C(91) – B	122.9(3)	C(93) – C(92) – C(91)	122.5(3)
C(93) – C(92) – H(92)	118.7	C(91) – C(92) – H(92)	118.7
C(94) – C(93) – C(92)	120.7(3)	C(94) – C(93) – C(97)	118.3(3)
C(92) – C(93) – C(97)	120.9(3)	C(93) – C(94) – C(95)	117.7(3)
C(93) – C(94) – H(94)	121.1	C(95) – C(94) – H(94)	121.1
C(96) – C(95) – C(94)	121.0(3)	C(96) – C(95) – C(98)	119.7(3)
C(94) – C(95) – C(98)	119.1(3)	C(95) – C(96) – C(91)	122.5(3)
C(95) – C(96) – H(96)	118.8	C(91) – C(96) – H(96)	118.8
F(92) – C(97) – F(91)	107.7(4)	F(92) – C(97) – F(93)	105.3(3)
F(91) – C(97) – F(93)	104.9(3)	F(92) – C(97) – C(93)	112.2(3)
F(91) – C(97) – C(93)	113.7(3)	F(93) – C(97) – C(93)	112.5(3)
F(95) – C(98) – F(96)	105.7(3)	F(95) – C(98) – F(94)	106.2(3)
F(96) – C(98) – F(94)	106.3(3)	F(95) – C(98) – C(95)	112.2(3)
F(96) – C(98) – C(95)	113.2(3)	F(94) – C(98) – C(95)	112.6(3)