Reductive Elimination from Arylpalladium Cyanide Complexes

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Supporting Information

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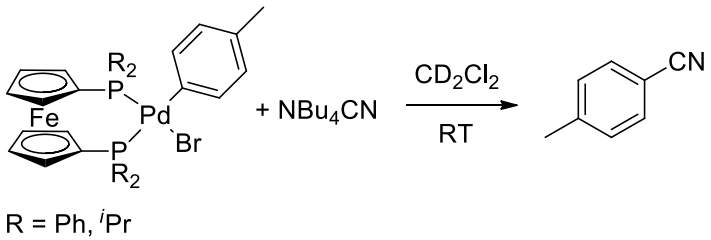
General Procedures. All manipulations were conducted under an inert atmosphere. ^{1}H, ^{19}F, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Varian 400 or 500 MHz spectrometer with tetramethylsilane or residual protiated solvent as a reference. All ^{31}P NMR chemical shifts are reported in parts per million relative to an 85% H_3PO_4 external standard. All ^{19}F NMR chemical shifts are reported in parts per million relative to a $CFCl_3$ external standard. Elemental analyses were performed at the University of Illinois Microanalysis Lab or by Robertson Microlab, Inc., Ledgewood, NJ. Analytical gas chromatography (GC) was performed using a Hewlett-Packard 5890 Gas Chromatograph fitted with a flame ionization detector and a Hewlett-Packard HP5 (30m x 0.32 mm) capillary column. GC-MS analyses were obtained on an Agilent 6890-N Gas Chromatograph equipped with an HP-5 30 m × 0.25 mm × 0.25 μm capillary column (Agilent). The GC was directly interfaced to an Agilent 5973 mass selective detector (EI, 70 eV). CyPF-*t*-Bu (1-dicyclohexylphosphino-2-di-*t*-butylphosphinoethylferrocene) was obtained from Solvias AG and Strem and used without further purification. The complexes $(PPh_3)_2Pd(C_6H_5)(F)$,[1] $(PPh_3)_2Pd(C_6H_4$-*p*-OMe$)(F)$,[1] $(PPh_3)_2Pd(C_6H_4$-*p*-Cl$)(F)$,[1] $(PPh_3)_2Pd(C_6H_4$-*p*-$CF_3)(F)$[1], (DPPF)Pd(C_6H_4-*p*-Me)(Br),[2] (D^{i}PPF)Pd(C_6H_4-*p*-Me)(Br),[3] (CyPF-*t*-Bu)Pd(C_6H_4-*p*-Me)(Br),[3] (dppdmp)$PdCl_2$,[14] and Pd(dppdmp)$_2$[14] have been previously synthesized and characterized. $NBu_4{}^{13}CN$ was prepared according to a previous report.[4] The synthesis of dppdmp has been reported elsewhere.[5] All other chemicals were used as received from commercial sources.

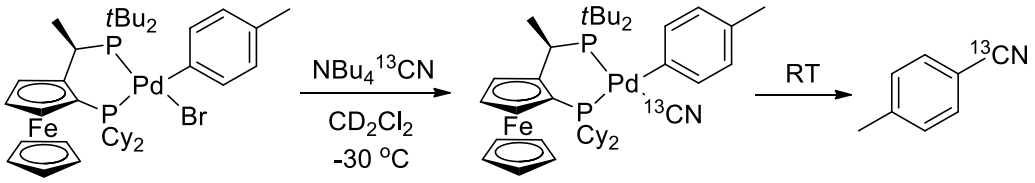
Computational Details. All DFT calculations were performed using the hybrid, three-parameter exchange functional of Becke (B3)[6] and the correlation functional of Lee, Yang, and Parr (LYP)][7](B3LYP) as implemented in Gaussian 09.[8] The palladium and phosphorus atoms were modeled with the effective core potential and associated triple ζ basis sets of Hay and Wadt (LANL2TZ).[9-11] For the palladium atom, an f polarization function was added to the basis set. All other atoms were calculated with the 6-311G** basis set.[12, 13] Unless otherwise noted, all geometries are fully optimized and confirmed as minima or n-order saddle points by analytical frequency calculations at the same level.



Reaction of NBu_4CN with bisphosphine-ligated arylpalladium bromide complexes
In the glovebox, (DPPF)Pd(C_6H_4-*p*-Me)(Br) (0.013 g, 0.016 mmol) and trimethoxybenzene (0.0029 g, 0.017 mmol) were weighed into a 4 mL scintillation vial and dissolved in 0.4 mL CD_2Cl_2. The solution was transferred to a screw-topped NMR tube with a septum-lined cap. In a separate vial, NBu_4CN (0.0064 g, 0.024 mmol) was dissolved in 0.1 mL CD_2Cl_2. This solution was then drawn into an airtight syringe, which was capped with a silicone stopper. The NMR tube was then cooled to -78 °C, and the NBu_4CN solution was added. The reaction mixture was then warmed to room temperature, and ^{1}H and ^{31}P NMR spectra were recorded. The ^{1}H NMR spectrum indicated that *p*-tolylnitrile had formed in 89% yield based on the integration of an aromatic peak of the organic product versus integration of the aromatic resonance of the internal standard. The ^{31}P NMR spectrum indicated > 95% conversion of the arylpalladium bromide

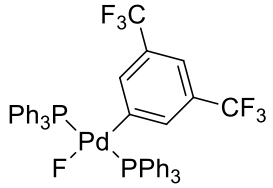
complex to unidentified products with two singlet resonances at 10.37 and 8.22 ppm in a ratio of 2:1.

The reaction of (D^{i}PPF)Pd(C_6H_4-*p*-Me)(Br) with NBu_4CN was performed in the same manner as the reaction of (DPPF)Pd(C_6H_4-*p*-Me)(Br) described above with the following amounts of reagents: (D^{i}PPF)Pd(C_6H_4-*p*-Me)(Br) (0.011 g, 0.016 mmol), trimethoxybenzene (0.0030 g, 0.017 mmol), NBu_4CN (0.0065 g, 0.024 mmol). *p*-Tolylnitrile was formed in 98% yield. The ^{31}P NMR spectrum indicated > 95% conversion of the arylpalladium bromide complex to unidentified products with two singlet resonances at 27.15 and -1.40 ppm in a ratio of 1:1.3.



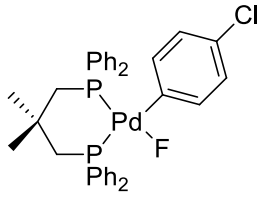
Generation, low temperature characterization, and reductive elimination of (CyPF-*t*-Bu)Pd(C_6H_4-*p*-Me)(^{13}CN)

In the glovebox, (CyPF-*t*-Bu)Pd(C_6H_4-*p*-Me)(Br) (0.0066 g, 0.0079 mmol) and trimethoxybenzene (0.0011 g, 0.0065 mmol) were weighed into a 4 mL vial and dissolved in 0.4 ml of CD_2Cl_2. The solution was transferred to a screw-topped NMR tube with a septum-lined cap. Into a separate vial, $NBu_4{}^{13}CN$ (0.0055 g, 0.020 mmol) was weighed and dissolved in 0.1 ml of CD_2Cl_2. This solution was then drawn into an airtight syringe, which was capped with a silicone stopper. A ^1H NMR spectrum was recorded of the palladium complex and internal standard. The NMR tube was then cooled to -78 °C, and the $NBu_4{}^{13}CN$ solution was added. The tube was inserted into the NMR probe that had been cooled to -40 °C, and ^1H and ^{31}P NMR spectra were recorded. The yield of (CyPF-*t*-Bu)Pd(C_6H_4-*p*-Me)(^{13}CN) was determined to be 96 % based on integration of the most downfield aryl proton peak, relative to that of the aryl resonances of the trimethoxybenzene standard. ^{31}P NMR (CD_2Cl_2) δ 79.54 (dd, J_{PP} = 27.5 Hz, J_{PC} = 11.7 Hz), 9.64 (dd, J_{PP} = 31.3 Hz, J_{PC} = 122.9 Hz). ^1H NMR (CD_2Cl_2) δ 7.31 (m, 1H), 7.06 (m, 1H), 6.94 (d, *J* = 2.0 Hz, 1H) 6.79 (d, *J* = 5.2 Hz, 1H) , 4.84 (s, 1H), 4.51 (s, 1H), 4.43 (s, 1H), 4.22 (s, 5H), 3.08 (m, 1H), 2.22 (s, 3H), 1.82 (s, 3H), 1.58 (d, *J* =10.7 Hz, 9H), 1.37 (d, *J* = 14.0 Hz, 9H), 0.8-2.1 (alkyl H from CyPF-*t*-Bu). The sample was then warmed to room temperature for 30 min. The yield of *p*-tolunitrile was 88%, according to the integration of the arylnitrile doublet resonance at 7.30 ppm compared to those of the aromatic resonances of the trimethoxybenzene standard.

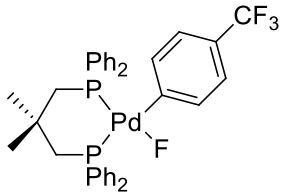


$(PPh_3)_2$Pd(C_6H_3-3,5-CF_3)(F): $(PPh_3)_2$Pd(C_6H_3-3,5-CF_3)(F) was synthesized by a procedure described previously for the preparation of PPh_3-ligated arylpalladium fluoride complexes.[1] The reagents were added in the following amounts: $(PPh_3)_2$Pd(C_6H_3-3,5-CF_3)(I) (0.104 g, 0.108

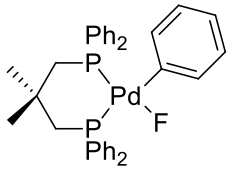
mmol), AgF (0.027 g, 0.213 mmol) and benzene (5 mL). The reaction yield was 0.078 g (84%). ^{31}P NMR (CD_2Cl_2) δ 20.07 (s). ^{1}H NMR (CD_2Cl_2) δ 7.62 (m, 12 H), 7.41 (m, 6H), 7.32 (m, 12 H), 7.09 (s, 2H), 6.75 (s, 1H). ^{19}F NMR (-40 °C, CD_2Cl_2) δ -288.50 (br s), -63.91 (s). Anal. Calc. for $PdP_2C_{44}H_{33}F$: C, 61.23; H, 3.85. Found C, 61.76; H, 4.17.



(dppdmp)Pd(C_6H_4-*p*-Cl)(F): (PPh_3)$_2$Pd(C_6H_4-*p*-Cl)(F) (0.175 g, 0.230 mmol) and dppdmp (0.101 g, 0.230 mmol) were weighed into a 20 mL vial, and 2 mL of toluene was added. The white suspension was stirred at room temperature for 30 min. After that time, the white solid product was collected on a frit and washed with additional toluene to yield 0.139 g (89%) of (dppdmp)Pd(C_6H_4-*p*-Cl)(F). ^{31}P NMR ($CDCl_3$) δ 24.9 (dd, J_{PP} = 45.6 Hz, J_{PF} = 167.6 Hz), -7.99 (dd, J_{PP} = 45.6 Hz, J_{PF} = 17.6 Hz). ^{1}H NMR ($CDCl_3$) δ 8.12-8.08 (m, 4H), 7.59 (dd, J = 7.5 Hz, 8.0 Hz, 4H), 7.45-7.37 (m, 8H), 7.32-7.29 (m, 4H), 6.94 (dd, J = 5.9, 8.0 Hz, 2H), 6.65 (dd, J = 1.9 Hz, 8.3 Hz, 8H), 2.35-2.32 (m, 4H), 0.83 (s, 6H). ^{19}F NMR (-40 °C, $CDCl_3$) δ -251.30 (d J_{PF} = 166.9 Hz). Anal. Calc. for $PdP_2C_{35}H_{34}FCl$: C, 62.05; H, 5.06. Found C, 62.09; H, 5.09.

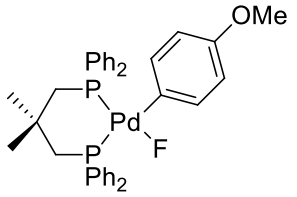


(dppdmp)Pd(C_6H_4-*p*-CF_3)(F): (PPh_3)$_2$Pd(C_6H_4-*p*-CF_3)(F) (0.077 g, 0.097 mmol) and dppdmp (0.044 g, 0.099 mmol) were weighed into a 20 mL vial, and 2 mL of toluene were added. The white suspension was stirred at room temperature for 30 min. After that time, the white solid was collected on a frit and washed with additional toluene, yielding 0.049 g (71%) of (dppdmp)Pd(C_6H_4-*p*-CF_3)(F). ^{31}P NMR (CD_2Cl_2) δ 24.20 (dd, J_{PP} = 46.4 Hz, J_{PF} = 165.4 Hz), -7.69 (dd, J_{PP} = 46.2 Hz, J_{PF} = 13.6 Hz). ^{1}H NMR (CD_2Cl_2) δ 8.12 (m, 4H), 7.31-7.58 (m, 16H), 7.17 (d, J = 3.6 Hz, 2H), 6.89 (d, J = 7.5 Hz, 2H), 2.37 (m, 4H), 0.86 (s, 6H). ^{19}F NMR (-40 °C, $CDCl_3$) δ -254.12 (d J_{PF} = 163 Hz), -61.71 (s). Anal. Calc. for $PdP_2C_{36}H_{34}F_4$: C: 60.81, H: 6.79; Found C: 60.71, H: 4.72.

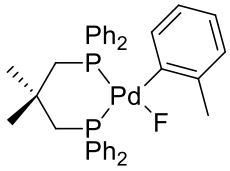


(dppdmp)Pd(C_6H_5)(F): (PPh_3)$_2$Pd(C_6H_5)(F) (0.037 g, 0.051 mmol) and dppdmp (0.025 g, 0.057 mmol) were weighed into a 20 mL vial, and 2 mL of toluene were added. The white suspension was stirred at room temperature for 30 min. After that time, the white solid was collected on a frit and washed with additional toluene, yielding 0.032 g (99%) of (dppdmp)Pd(C_6H_5)(F). ^{31}P NMR (CD_2Cl_2) δ 24.86 (dd, J_{PP} = 46.4 Hz, J_{PF} = 157.5 Hz), -8.77 (dd, J_{PP} = 47.1 Hz, J_{PF} = 4.6 Hz). ^{1}H NMR (CD_2Cl_2) δ 8.15 (m, 4H), 7.30-7.59 (m, 16H), 7.01

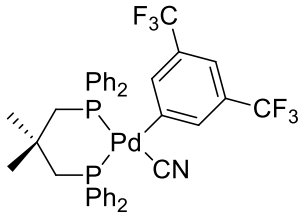
(m, 2H), 6.66 (br s, 3H), 2.33 (dd, J = 3.0, 9.9 Hz, 4H), 0.78 (s, 6H). ^{19}F NMR (-40 °C, $CDCl_3$) δ -249.38 (d J_{PF} = 163.0 Hz). Anal. Calc. for $PdP_2C_{35}H_{35}F$: C: 65.38, H: 5.49; Found C: 64.76, H: 5.64.



(dppdmp)Pd(C_6H_4-*p*-OMe)(F): $(PPh_3)_2Pd(C_6H_4$-*p*-OMe)(F) (0.055 g, 0.072 mmol) and dppdmp (0.032 g, 0.73 mmol) were weighed into a 20 mL vial, and 2 mL of CH_2Cl_2 were added. The solution was stirred at room temperature for 30 min. After that time, 5 mL of pentane were added to precipitate a white solid. The solid was collected on a frit and washed with additional pentane and ether, yielding 0.037 g (78%) of (dppdmp)Pd(C_6H_4-*p*-OMe)(F). ^{31}P NMR (CD_2Cl_2) δ 25.01 (dd, J_{PP} = 44.0 Hz, J_{PF} = 168.3 Hz), -7.15 (dd, J_{PP} = 46.3 Hz, J_{PF} = 19.7 Hz). ^{1}H NMR (CD_2Cl_2) δ 8.18 (m, 4H), 7.51-7.35 (m, 16H), 6.90 (t, J = 7.1 Hz, 2H), 6.34 (d, J = 7.0 Hz, 2H), 3.62 (s, 3H), 2.36 (dd, J = 5.2, 9.8 Hz, 4H), 0.80 (s, 6H). ^{19}F NMR (-40 °C, $CDCl_3$) δ -267.44 (d J_{PF} = 170.2 Hz). Anal. Calc. for $PdP_2C_{36}H_{37}OF$: C: 64.10, H: 5.50; Found C: 64.30, H: 5.42.



(dppdmp)Pd(C_6H_4-*o*-Me)(F):$(PPh_3)_2Pd(C_6H_4$-*o*-Me)(F) (0.044 g, 0.059 mmol) and dppdmp (0.028 g, 0.063 mmol) were weighed into a 20 mL vial, and 2 mL of toluene were added. The white suspension was stirred at room temperature for 30 min. After that time, the white solid was collected on a frit and washed with additional toluene, yielding 0.029 g (75%) of (dppdmp)Pd(C_6H_4-*o*-Me)(F). ^{31}P NMR (CD_2Cl_2) δ 25.91 (dd, J_{PP} = 45.3 Hz, J_{PF} = 164.8 Hz), -6.03 (dd, J_{PP} = 45.1 Hz, J_{PF} = 19.3 Hz). ^{1}H NMR (CD_2Cl_2) δ 8.20 (m, 2H), 8.04 (m, 2H), 7.52-7.37 (m, 16H), 7.00 (m, 1H), 6.85 (m, 1H), 6.61 (m, 1H), 6.46 (d, J = 6.8 Hz, 1H), 2.32 (br s, 2H), 2.21 (br s, 2H), 1.13 (s, 3H), 0.42 (s, 3H). ^{19}F NMR (-40 °C, $CDCl_3$) δ -264.00 (d J_{PF} = 163.8 Hz). Anal. Calc. for $PdP_2C_{36}H_{37}F$: C: 65.81, H: 5.68; Found C: 66.09, H: 5.96

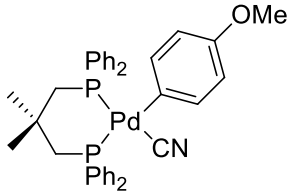


(dppdmp)Pd(C_6H_3-3,5-CF_3)(CN): $(PPh_3)_2Pd(C_6H_3$-3,5-CF_3)(F) (0.050 g, 0.058 mmol) and dppdmp (0.026 g, 0.059 mmol) were weighed in a 20 mL vial and dissolved in 2 mL toluene. The solution was stirred for 30 min at room temperature, at which time a white solid precipitated. TMSCN (11.5 μL) was then added to the reaction, as well as 0.5 mL CH_2Cl_2 to assist in the dissolution of the white solid. The reaction was stirred for 5 min. Addition of pentane (2 mL) led to precipitation of the product as a white solid. The solid was collected on a frit and washed

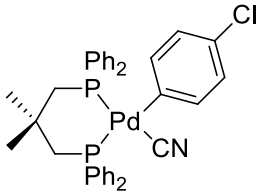
with pentane to yield 0.042 g (91%) of (dppdmp)Pd(C_6H_3-3,5-CF_3)(CN). Single crystals of the complex suitable for X-ray diffraction were obtained by dissolving the solid in a minimal amount of CH_2Cl_2, layering the solution with pentane and storing the solution at -35 °C overnight. ^{31}P NMR (CD_2Cl_2) δ 13.89 (d, J = 45.9 Hz), 3.09 (d, J = 46.3 Hz). ^{1}H NMR (CD_2Cl_2) δ 7.87 (m, 4H), 7.54 (m, 2H), 7.44 (s, 1H), 7.43 (s, 1H), 7.26 (m, 14H), 7.13 (s, 1H), 2.38 (t, J = 10.6 Hz, 4H), 0.82 (s, 6H). ^{19}F NMR (CD_2Cl_2) δ -63.29 (s). Anal. Calc. for $PdP_2C_{38}H_{33}F_6$: C, 58.06; H, 4.23; N, 1.78. Found: C, 57.93; H, 4.13; N, 2.30.

General procedure for the characterization of the bisphosphine-ligated arylpalladium cyanide complexes (3a-3e) at low temperature

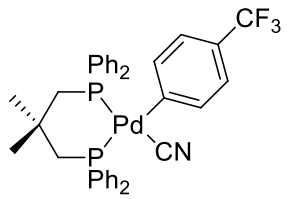
The bisphosphine arylpalladium fluoride precursor and trimethoxybenzene were weighed into a 4 mL vial and dissolved in 0.4 mL of CD_2Cl_2. The solution was then transferred to a screw-topped NMR tube with a septum-lined cap. In a separate 4 mL vial, 1.5 equiv of TMSCN were dissolved in 0.1 ml CD_2Cl_2 and taken up in a 1 mL gastight syringe, which was sealed with a silicone stopper. The two solutions were exported from the glovebox. An initial ^{1}H NMR spectrum of the arylpalladium fluoride complex was recorded. The NMR tube was then cooled to -78 °C, and the TMSCN solution was added. ^{31}P and ^{1}H spectra were then recorded in an NMR probe that had been precooled to -40 °C. The yield of the complex was calculated based on integration of an aryl peak of the complex versus the integration of the resonances of the trimethoxybenzene standard (at 6.08 ppm and 3.78 ppm). Note: the peaks in the ^{1}H NMR spectra at 0.35 (s), 0.22 (d, J = 7.45 Hz), and 0.06 (s) ppm correspond to TMSCN, TMSF, and HMDSO (present in the TMSCN solution), respectively.



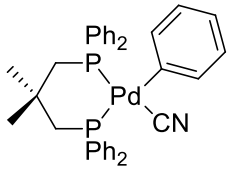
The complex (dppdmp)Pd(C_6H_4-*p*-OMe)(CN) was generated in 78% yield, according to the procedure listed above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-OMe)(F) (0.0090 g, 0.013 mmol); TMSCN (2.7 μL, 0.020 mmol), trimethoxybenzene (0.0020 g, 0.012 mmol). ^{31}P NMR (CD_2Cl_2) δ 9.90 (d, J = 46.1 Hz), -2.12 (d, J = 46.2 Hz). ^{1}H NMR (CD_2Cl_2) δ 7.88-7.90 (m, 4H), 7.29-7.51 (m, 16H), 6.70 (d, J = 7.6 Hz, 2H), 6.29 (d, J = 7.2 Hz, 2H), 3.56 (s, 3H), 2.36 (m, 4H), 0.71 (s, 6H).



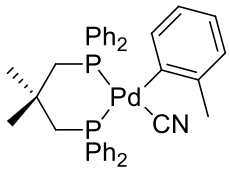
The complex (dppdmp)Pd(C_6H_4-*p*-Cl)(CN) was generated in 99% yield, according to the procedure listed above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-Cl)(F) (0.0060 g, 0.0088 mmol); TMSCN (1.8 μL, 0.013 mmol), trimethoxybenzene (0.0016 g, 0.010 mmol). ^{31}P NMR (CD_2Cl_2) δ 11.25 (d, J = 46.4 Hz), -0.21 (d, J = 46.6 Hz). ^{1}H NMR (CD_2Cl_2) δ 7.84 (m, 4H), 7.51 (m, 4H), 7.34 (m, 12H), 6.80 (app t, J = 7.2 Hz, 2H), 6.61 (d, J = 7.2 Hz, 2H), 2.35 (app d, J = 9.7 Hz, 4H), 0.70 (s, 6H).



The complex (dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) was generated in 95% yield according to the procedure listed above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-CF_3)(F) (0.0062 g, 0.0087 mmol), TMSCN (1.8 μL, 0.016 mmol), trimethoxybenzene (0.0023 g, 0.014 mmol). ^{31}P NMR (CD_2Cl_2) δ 11.51 (d, *J* = 47.0 Hz), -0.21 (d, *J* = 47.0 Hz). ^{1}H NMR (CD_2Cl_2) δ 7.86 (m, 4H), 7.52 (d, *J* = 2.1 Hz, 4H), 7.31 (m, 12H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 2.36 (d, *J* = 9.9 Hz, 4H), 0.69 (s, 6H). IR ν_{CN} = 2129 cm^{-1}.

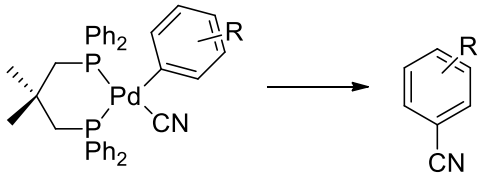


The complex (dppdmp)Pd(C_6H_5)(CN) was generated in 99% yield according to the procedure listed above with the following amounts of reagents: (dppdmp)Pd(C_6H_5)(F) (0.0058 g, 0.0090 mmol); TMSCN (1.8 μL, 0.014 mmol), trimethoxybenzene (0.0019 g, 0.011 mmol). ^{31}P NMR (CD_2Cl_2) δ 11.91 (d, *J* = 47.0 Hz), -0.28 (d, *J* = 47.0 Hz). ^{1}H NMR (CD_2Cl_2) δ 7.86 (dd, *J* = 9.6, 4.9 Hz, 4H), 7.50 (br s, 4H), 7.37 (m, 12H), 7.27 (m, 1H), 6.83 (t, *J* = 6.1 Hz, 2H), 6.59 (m, 2H), 2.34 (dd, *J* = 15.9 Hz, 7.9 Hz, 4H), 0.66 (s, 6H).



The complex (dppdmp)Pd(C_6H_4-*o*-Me)(CN) was generated in 99% yield according to the procedure listed above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*o*-Me)(F) (0.0057 g, 0.0087 mmol); TMSCN (1.7 μL, 0.013 mmol), trimethoxybenzene (0.0024 g, 0.014 mmol). ^{31}P NMR (CD_2Cl_2) δ 14.07 (d, *J* = 46.0 Hz), 0.90 (d, *J* = 46.0 Hz). ^{1}H NMR (CD_2Cl_2) δ 7.90 (m, 4H), 7.50 (m, 4H), 7.24 (m, 12H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.41 (t, *J* = 6.7 Hz, 1H), 6.08 (d, *J* = 5.1 Hz, 1H), 2.31 (s, 3H), 2.40 (dd, *J* = 24.8 Hz, 14.7 Hz, 4H), 0.84 (s, 6H).

General procedure for the determination of the rates and yields of reductive elimination from bisphosphine-ligated arylpalladium cyanide complexes in CD_2Cl_2 and DMF (3a-3e)



Rates of reductive elimination in CD_2Cl_2:
The bisphosphine arylpalladium fluoride precursor and trimethoxybenzene were weighed into a 4 mL vial and dissolved in 0.4 mL of CD_2Cl_2. The solution was then transferred to a screw-topped NMR tube with a septum-lined cap. In a separate 4 mL vial, 1.5 equiv of TMSCN were dissolved in 0.1 ml of CD_2Cl_2 and taken up in a 1 mL gastight syringe, which was sealed with a silicone stopper. The two solutions were exported from the glovebox. The NMR tube was then cooled to -78 °C, and the TMSCN solution was then added. An initial ^1H NMR spectrum of the arylpalladium cyanide complex was recorded. ^1H spectra were then recorded every minute for 4-14 h runs in an NMR probe that had been preset at the specified temperature. The reductive elimination was monitored until less than 5% of the starting complex remained. The yield of the organic product was calculated based on the ratio of the integration of a set of arylnitrile peaks versus the internal standard relative to the ratio of the integration of the peaks in the starting spectrum of the arylpalladium cyanide complex versus the internal standard.

(dppdmp)Pd(C_6H_4-*p*-OMe)(CN): The rate of reductive was monitored at 20 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-OMe)(CN) (0.0076 g, 0.011 mmol), trimethoxybenzene (0.0016 g, 0.0095 mmol), TMSCN (3.1 μL, 0.22 mmol). *p*-methoxybenzonitrile was generated in 94% yield.

(dppdmp)Pd(C_6H_4-*p*-Cl)(CN): The rate of reductive elimination was monitored at 20 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-Cl)(F) (0.0066 g, 0.010 mmol), trimethoxybenzene (0.0033 g, 0.020 mmol), TMSCN (2.0 μL, 0.015 mmol). *p*-Chlorobenzonitrile was generated in 67% yield at 87% conversion of the arylpalladium cyanide complex after 14 h.

The rate of reductive elimination was also monitored at 40 °C with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-Cl)(F) (0.0054 g, 0.0080 mmol), trimethoxybenzene (0.0025 g, 0.015 mmol), TMSCN (1.6 μL, 0.012 mmol). *p*-chlorobenzonitrile was generated in 98% yield.

(dppdmp)Pd(C_6H_4-*p*-CF_3)(CN): The rate of reductive was monitored at 40 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) (0.0077 g, 0.011 mmol), trimethoxybenzene (0.0025 g, 0.015 mmol), TMSCN (2.2 μL, 0.017 mmol). *p*-Trifluoromethylbenzonitrile was generated in 94% yield.

The rate of reductive was also monitored at 20 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) (0.0075 g, 0.011 mmol), trimethoxybenzene (0.0013 g, 0.0077 mmol), TMSCN (2.2 μL, 0.017 mmol). *p*-Trifluoromethylbenzonitrile was formed in 81% yield at 81% conversion of the cyanide complex after 56 h.

The rate of reductive elimination with added $B(C_6F_5)_3$ (0.0066 g, 0.013 mmol) was determined at 40 °C with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) (0.0057 g, 0.0080 mmol), trimethoxybenzene (0.0024 g, 0.014 mmol), TMSCN (2.0 μL, 0.012 mmol). *p*-Trifluoromethylbenzonitrile was generated in 81% yield.

(dppdmp)Pd(C_6H_5)(CN): The rate of reductive elimination was monitored at 20 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_5)(CN) (0.0058 g, 0.0090 mmol), trimethoxybenzene (0.0015 g, 0.0089 mmol), TMSCN (1.8 μL, 0.014 mmol). Benzonitrile was generated in 80 % yield.

(dppdmp)Pd(C_6H_4-*o*-Me)(CN): The rate of reductive elimination was monitored at 20 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*o*-Me)(CN) (0.0062 g, 0.0094 mmol), trimethoxybenzene (0.0021 g, 0.012 mmol), TMSCN (1.9 μL, 0.014 mmol. *o*-Methylbenzonitrile was generated in 93% yield.

(dppdmp)Pd(C_6H_3-3,5-CF_3)(CN): (dppdmp)Pd(C_6H_3-3,5-CF_3)(CN) (0.0067 g, 0.0086 mmol) and trimethoxybenzene (0.0029 g, 0.017 mmol) were dissolved in 0.4 mL of CD_2Cl_2, and the solution was transferred to a septum-lined screw top NMR tube. The solution was heated in an oil bath at 80 °C. After 2 h, a ^{1}H NMR spectrum was recorded, and less than 10% of the starting complex had reacted according to integration of the starting peaks of the complex versus the added standard. After 16 hours, < 5% of the starting complex remained. The yield of 3,5-trifluoromethylbenzonitrile was determined to be 45% based on integration of the product peaks versus the integration of the added standard according to ^{1}H NMR spectroscopy.

Rates of reductive elimination in DMF:
The bisphosphine arylpalladium fluoride precursor and dppdmp were weighed into a 4 mL vial and dissolved in 0.4 mL of DMF. The solution was then transferred to a screw-topped NMR tube with a septum-lined cap. In a separate 4 mL vial, 1.5 equiv of TMSCN were dissolved in 0.1 ml of DMF and taken up in a 1 mL gastight syringe, which was sealed with a silicone stopper. The two solutions were exported from the glovebox. The NMR tube was then cooled to -78 °C, and the TMSCN solution was added. An initial ^{31}P NMR spectrum of the arylpalladium cyanide complex was recorded. ^{31}P NMR spectra were then recorded every minute for 2-6 h in an NMR probe that had been preset at the specified temperature. The reductive elimination was monitored until less than 5% of the starting complex remained. At the end of the reaction, 5 μL of dodecane was added. The yield of the organic product was calculated based on the ratio of the integration of the arylnitrile peak versus the internal dodecane standard as determined by GC/MS analysis. The arylnitrile products are all known compounds and were identified using GC/MS and GC by comparison of the mass spectra and retention times of the products with those of authentic compounds.

(dppdmp)Pd(C_6H_4-*p*-OMe)(CN): The rate of reductive was monitored at 40 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-OMe)(CN) (0.0099 g, 0.015 mmol), dppdmp (0.0077 g, 0.0017 mmol), TMSCN (2.9 μL, 0.22 mmol). *p*-methoxybenzonitrile was generated in 67% yield.

(dppdmp)Pd(C_6H_4-*p*-Cl)(CN): The rate of reductive elimination was monitored at 40 °C with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-Cl)(F) (0.0080 g, 0.0011 mmol), dppdmp (0.0067 g, 0.015 mmol), TMSCN (2.4 μL, 0.018 mmol). *p*-chlorobenzonitrile was generated in 95% yield.

(dppdmp)Pd(C_6H_4-*p*-CF_3)(CN): The rate of reductive was monitored at 40 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) (0.010 g, 0.014 mmol), dppdmp (0.0067 g, 0.015 mmol), TMSCN (2.9 μL, 0.021 mmol). *p*-Trifluoromethylbenzonitrile was generated in 92% yield.

The rate of reductive elimination with added $B(C_6F_5)_3$ (0.014 g, 0.028 mmol) was determined at 40 °C with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) (0.010 g, 0.014 mmol), dppdmp (0.0070 g, 0.016 mmol), TMSCN (3.7 μL, 0.021 mmol). *p*-Trifluoromethylbenzonitrile was generated in 76% yield.

(dppdmp)Pd(C_6H_5)(CN): The rate of reductive elimination was monitored at 40 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_5)(CN) (0.0070 g, 0.011 mmol), dppdmp (0.0048 g, 0.011 mmol), TMSCN (2.2 μL, 0.017 mmol). Benzonitrile was generated in 80% yield.

(dppdmp)Pd(C_6H_4-*o*-Me)(CN): The rate of reductive elimination was monitored at 40 °C according to the procedure described above with the following amounts of reagents: (dppdmp)Pd(C_6H_4-*o*-Me)(CN) (0.011 g, 0.016 mmol), dppdmp (0.0087 g, 0.020 mmol), TMSCN (3.3 μL, 0.024 mmol. *o*-Methylbenzonitrile was generated in 95% yield.

Independent synthesis of (dppdmp)$PdCl_2$

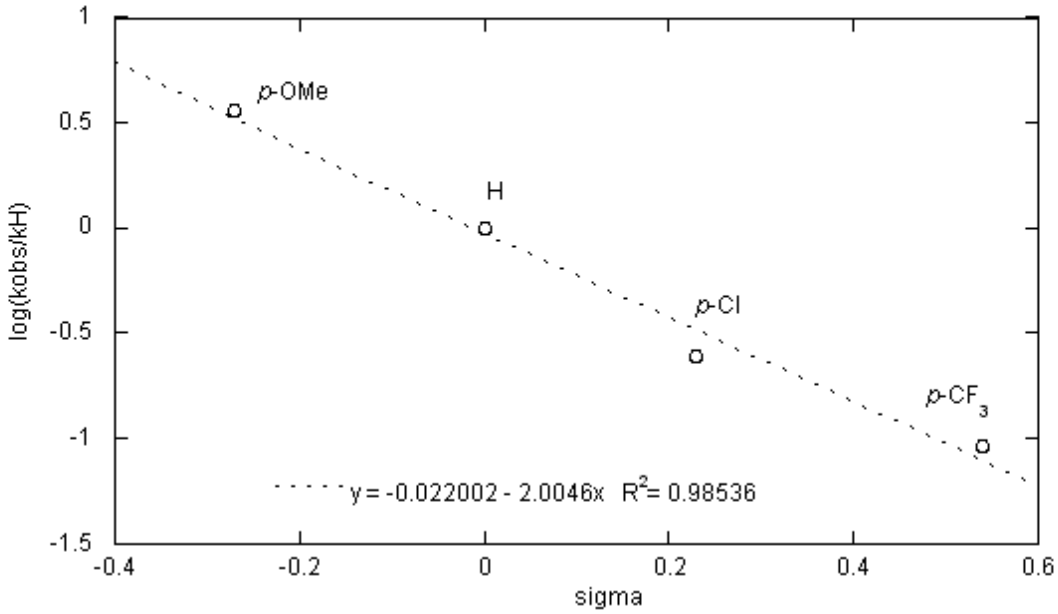
In a 20 mL vial, $(CH_3CN)_2PdCl_2$ (0.098 g, 0.38 mol) and dppdmp (0.17 g, 0.38 mmol) were stirred in 5 mL of THF. The yellow suspension gradually turned white after stirring at room temperature overnight. After 16 h, 5 mL of pentane was added, and the white solid was collected on a fritted funnel to yield 0.20 g (86%) of the previously reported compound (dppdmp)$PdCl_2$.[14] ^{31}P NMR (DMSO-d_6) δ 14.95 (s). ^{1}H NMR (DMSO-d_6) δ 7.95 (m, 4 H), 7.51 (m, 8H), 7.37 (m, 8H), 2.64 (m, 4H), 0.48 (s, 6H).

Trapping of the Pd(0) product from reductive elimination of 3a in DMF

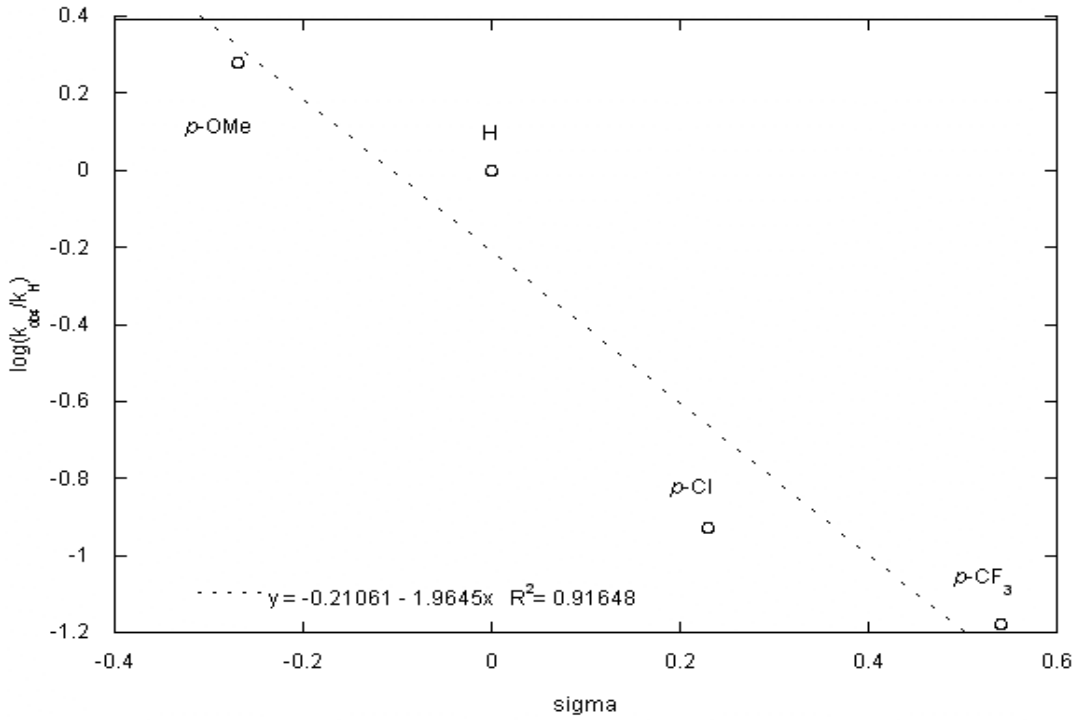
In a 4 ml vial, (dppdmp)Pd(C_6H_4-*p*-CF_3)(F) (0.034 g, 0.047 mmol) and dppdmp (0.021 g, 0.049 mmol) were dissolved in 1 mL of DMF. TMSCN (9.5 μL, 0.071 mmol) was added to the solution, and the reaction mixture was heated at 80 °C for 30 min. After 30 min, fine yellow needles precipitated from solution. The reaction was cooled to RT, and the yellow solid was filtered, washed with DMF, and dried to yield 0.033 g (72%) of the previously reported compound Pd(dppdmp)$_2$.[14] ^{31}P NMR (CD_2Cl_2) δ 1.31 (s). ^{1}H NMR (CD_2Cl_2) δ 7.32 (m, 8H), 7.14 (m, 16H), 7.08 (m, 16H), 2.14 (m, 8H), 0.24 (s, 12H).

Hammett analysis plots

In CD_2Cl_2:



In DMF:



Structure Coordinates

***cis*-$(PMe_3)_2Pd(C_6H_4$-*p*-$CF_3)(CN)$**

Pd	1.357280000	-0.067172000	4.200839000
P	0.854684000	1.383801000	2.488225000
P	1.090952000	-1.868760000	2.795463000
C	1.618172000	1.631553000	5.281125000
C	0.686301000	3.141329000	2.911818000
C	-0.670341000	1.036007000	1.549278000
C	2.122746000	1.384872000	1.202620000
C	-0.295045000	-1.909289000	1.620504000
C	1.003136000	-3.511350000	3.526542000
C	2.528548000	-1.949511000	1.694937000
C	1.776465000	-1.428246000	5.644978000
C	3.077817000	-1.904292000	5.909337000
C	3.367795000	-2.717463000	6.990755000
C	2.338680000	-3.087302000	7.858834000
C	1.057448000	-2.642369000	7.603399000
C	0.797033000	-1.817473000	6.516084000
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H	0.417766000	3.635180000	2.131787000
H	1.527818000	3.475011000	3.227100000
H	-1.420883000	1.013952000	2.149426000
H	-0.590618000	0.185716000	1.109059000
H	-0.810793000	1.722528000	0.891204000
H	2.284106000	0.484519000	0.911286000
H	2.938247000	1.754890000	1.556066000
H	1.828195000	1.915059000	0.460753000
H	-0.351626000	-1.067441000	1.161204000
H	-1.116063000	-2.064843000	2.098447000
H	-0.157408000	-2.613133000	0.985828000
H	1.701892000	-3.609365000	4.179190000
H	1.109050000	-4.174246000	2.842422000
H	0.150436000	-3.625981000	3.955139000
H	3.336162000	-1.933773000	2.215873000
H	2.516073000	-1.194587000	1.102888000
H	2.493750000	-2.759974000	1.183856000
H	3.790926000	-1.648183000	5.317188000
H	4.265697000	-3.024590000	7.139734000
C	2.738729353	-3.879866064	9.117099177
H	0.341434000	-2.908663000	8.183690000
H	-0.104328000	-1.512331000	6.375833000
N	1.811508000	2.893966000	6.084166000
F	4.186008611	-3.664374441	9.398331693
F	2.485496341	-5.331265676	8.893802953
F	1.931816185	-3.408605257	10.277639519

***cis*-$(PMe_3)_2Pd(C_6H_4$-*p*-$CF_3)$(CN) Transition State**

Pd	1.473923336	-0.305130137	-0.000059293
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P	0.998481847	2.023005447	-0.000067513
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C	4.068304105	-2.251524388	1.450516574
C	5.299884159	-0.090723138	0.000225811
C	4.068538454	-2.251531391	-1.450361430
C	2.378960949	3.265432628	-0.000412657
C	-0.003279168	2.591878557	1.449346627
C	-0.003929600	2.591864139	-1.449035365
C	-0.492806206	-0.929896327	-0.000112028
C	-1.172982315	-1.178985120	-1.199435379
C	-2.494000063	-1.622486657	-1.205092943
C	-3.161673516	-1.838405762	-0.000004788
C	-2.493909843	-1.622490820	1.205025059
C	-1.172881767	-1.179001754	1.199261622
H	4.006539084	-1.673366940	2.374595168
H	5.053101067	-2.720963417	1.383749537
H	3.291798667	-3.016271237	1.465875414
H	5.323015743	0.544926088	0.886459728
H	5.323313662	0.544852166	-0.886040277
H	6.189534546	-0.725703092	0.000403538
H	4.006185789	-1.673533488	-2.374498829
H	3.292449740	-3.016722628	-1.465413600
H	5.053618998	-2.720411070	-1.383777465
H	3.001037322	3.130970609	-0.886116176
H	3.001488722	3.130968876	0.884977819
H	1.978236484	4.282262449	-0.000300321
H	-0.931786887	2.022995373	1.491938688
H	-0.229441367	3.657951303	1.368555306
H	0.554199662	2.411791725	2.370498354
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H	0.553289489	2.412090453	-2.370409638
H	-0.230332652	3.657860744	-1.367976682
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H	-0.667242673	-1.044366044	2.149331087
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F	-4.933300010	-2.979182548	-1.087760054
F	-5.434919630	-1.169810521	-0.001007715
F	-4.933785658	-2.977567521	1.088665953

***cis*-$(PMe_3)_2Pd(C_6H_4$-*p*-$NH_2)$(CN)**

Pd	1.357280000	-0.067172000	4.200839000
P	0.854684000	1.383801000	2.488225000
P	1.090952000	-1.868760000	2.795463000
C	1.618172000	1.631553000	5.281125000
C	0.686301000	3.141329000	2.911818000
C	-0.670341000	1.036007000	1.549278000
C	2.122746000	1.384872000	1.202620000
C	-0.295045000	-1.909289000	1.620504000
C	1.003136000	-3.511350000	3.526542000
C	2.528548000	-1.949511000	1.694937000
C	1.776465000	-1.428246000	5.644978000
C	3.077817000	-1.904292000	5.909337000
C	3.367795000	-2.717463000	6.990755000
C	2.338680000	-3.087302000	7.858834000
C	1.057448000	-2.642369000	7.603399000
C	0.797033000	-1.817473000	6.516084000
H	0.022025000	3.244838000	3.597663000
H	0.417766000	3.635180000	2.131787000
H	1.527818000	3.475011000	3.227100000
H	-1.420883000	1.013952000	2.149426000
H	-0.590618000	0.185716000	1.109059000
H	-0.810793000	1.722528000	0.891204000
H	2.284106000	0.484519000	0.911286000
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H	2.493750000	-2.759974000	1.183856000
H	3.790926000	-1.648183000	5.317188000
H	4.265697000	-3.024590000	7.139734000
N	2.567361306	-3.916442518	9.099924526
H	0.341434000	-2.908663000	8.183690000
H	-0.104328000	-1.512331000	6.375833000
N	1.811508000	2.893966000	6.084166000
H	2.869690512	-4.980564237	9.008563554
H	2.433048299	-3.461847395	10.103620659

cis-(PMe_3)$_2$Pd(C_6H_4-_p_-NH_2)(CN) Transition State

Pd	1.234660000	-0.180653000	-0.001313000
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C	4.043266000	-1.814117000	1.414237000
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C	4.039035000	-1.780236000	-1.464190000
C	2.250421000	3.437564000	-0.199166000
C	0.039542000	2.852086000	1.546144000
C	-0.327190000	2.815842000	-1.310717000
C	-0.789927000	-0.926710000	0.011887000
C	-1.507121000	-0.867979000	-1.198964000
C	-2.880193000	-0.666104000	-1.203547000
C	-3.575407000	-0.533463000	0.001355000
C	-2.883342000	-0.621292000	1.211745000
C	-1.510097000	-0.824927000	1.217958000
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H	3.920808000	-1.210613000	-2.388022000
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H	-0.190838000	3.918450000	1.474202000
H	0.700035000	2.684017000	2.399156000
H	-1.254844000	2.245543000	-1.241414000
H	0.106381000	2.639356000	-2.297226000
H	-0.546835000	3.881263000	-1.200583000
H	-0.982170000	-0.996781000	-2.137731000
H	-3.417915000	-0.622197000	-2.143167000
N	-5.078246147	-0.386516380	-0.001621069
H	-3.423538000	-0.542220000	2.147451000
H	-0.987850000	-0.922072000	2.162068000
N	0.702779000	-3.235851000	0.052823000
H	-5.633574759	-0.381881813	-0.962745422
H	-5.627722508	-0.283127214	0.957328618

***cis*-$(PMe_3)_2Pd(C_6H_5)(CN)$**

Pd	1.357280446	-0.067172445	4.200839093
P	0.854684465	1.383801248	2.488225080
P	1.090952362	-1.868760350	2.795462781
C	1.618171856	1.631553090	5.281124970

C	0.686301259	3.141328591	2.911818382
C	-0.670340732	1.036006990	1.549278217
C	2.122745702	1.384872150	1.202619941
C	-0.295045106	-1.909289448	1.620503798
C	1.003136317	-3.511349528	3.526541568
C	2.528547879	-1.949511055	1.694936996
C	1.776465092	-1.428245592	5.644978352
C	3.077817274	-1.904291569	5.909337108
C	3.367794621	-2.717463297	6.990755366
C	2.338679741	-3.087302301	7.858834227
C	1.057447852	-2.642369135	7.603399113
C	0.797032727	-1.817472589	6.516083671
H	0.022025482	3.244838442	3.597662751
H	0.417765923	3.635179543	2.131786747
H	1.527818272	3.475010501	3.227099773
H	-1.420882937	1.013951700	2.149426069
H	-0.590618072	0.185715760	1.109058949
H	-0.810793078	1.722528432	0.891203850
H	2.284106387	0.484519277	0.911286384
H	2.938247039	1.754890005	1.556065855
H	1.828194809	1.915058888	0.460752810
H	-0.351625970	-1.067440718	1.161203779
H	-1.116063243	-2.064843382	2.098447261
H	-0.157408122	-2.613133059	0.985827582
H	1.701892124	-3.609364855	4.179189754
H	1.109049586	-4.174246112	2.842422460
H	0.150435905	-3.625980609	3.955138617
H	3.336161683	-1.933773101	2.215873064
H	2.516073469	-1.194587215	1.102887827
H	2.493750007	-2.759974004	1.183856013
H	3.790925984	-1.648182796	5.317188484
H	4.265697322	-3.024590162	7.139733824
H	2.519506555	-3.642383997	8.621476401
H	0.341434364	-2.908663318	8.183689976
H	-0.104327592	-1.512330796	6.375833415
N	1.811508411	2.893965985	6.084166147

cis-(PMe_3)$_2$Pd(C_6H_5)(CN) Transition State

Pd	1.473923336	-0.305130137	-0.000059293
P	3.764364945	-1.140949729	0.000057953
P	0.998481847	2.023005447	-0.000067513
C	1.024844000	-2.264283000	-0.000211000
C	4.068304105	-2.251524388	1.450516574
C	5.299884159	-0.090723138	0.000225811
C	4.068538454	-2.251531391	-1.450361430
C	2.378960949	3.265432628	-0.000412657

C	-0.003279168	2.591878557	1.449346627
C	-0.003929600	2.591864139	-1.449035365
C	-0.492806206	-0.929896327	-0.000112028
C	-1.172982315	-1.178985120	-1.199435379
C	-2.494000063	-1.622486657	-1.205092943
C	-3.212427778	-1.912035990	-0.002071224
C	-2.493909843	-1.622490820	1.205025059
C	-1.172881767	-1.179001754	1.199261622
H	4.006539084	-1.673366940	2.374595168
H	5.053101067	-2.720963417	1.383749537
H	3.291798667	-3.016271237	1.465875414
H	5.323015743	0.544926088	0.886459728
H	5.323313662	0.544852166	-0.886040277
H	6.189534546	-0.725703092	0.000403538
H	4.006185789	-1.673533488	-2.374498829
H	3.292449740	-3.016722628	-1.465413600
H	5.053618998	-2.720411070	-1.383777465
H	3.001037322	3.130970609	-0.886116176
H	3.001488722	3.130968876	0.884977819
H	1.978236484	4.282262449	-0.000300321
H	-0.931786887	2.022995373	1.491938688
H	-0.229441367	3.657951303	1.368555306
H	0.554199662	2.411791725	2.370498354
H	-0.932299839	2.022742328	-1.491430303
H	0.553289489	2.412090453	-2.370409638
H	-0.230332652	3.657860744	-1.367976682
H	-0.667426664	-1.044313878	-2.149545916
H	-2.999485043	-1.817096993	-2.143676952
H	-2.999334592	-1.817090372	2.143639051
H	-0.667242673	-1.044366044	2.149331087
N	1.039205000	-3.426373000	-0.000327000
H	-4.246364953	-2.189157290	-0.004224691

***cis*-$(PMe_3)_2Pd(C_6H_5)(CO)^+$**

Pd	1.357280446	-0.067172445	4.200839093
P	0.854684465	1.383801248	2.488225080
P	1.090952362	-1.868760350	2.795462781
C	1.618171856	1.631553090	5.281124970
C	0.686301259	3.141328591	2.911818382
C	-0.670340732	1.036006990	1.549278217
C	2.122745702	1.384872150	1.202619941
C	-0.295045106	-1.909289448	1.620503798
C	1.003136317	-3.511349528	3.526541568
C	2.528547879	-1.949511055	1.694936996
C	1.776465092	-1.428245592	5.644978352
C	3.077817274	-1.904291569	5.909337108

C	3.367794621	-2.717463297	6.990755366
C	2.338679741	-3.087302301	7.858834227
C	1.057447852	-2.642369135	7.603399113
C	0.797032727	-1.817472589	6.516083671
H	0.022025482	3.244838442	3.597662751
H	0.417765923	3.635179543	2.131786747
H	1.527818272	3.475010501	3.227099773
H	-1.420882937	1.013951700	2.149426069
H	-0.590618072	0.185715760	1.109058949
H	-0.810793078	1.722528432	0.891203850
H	2.284106387	0.484519277	0.911286384
H	2.938247039	1.754890005	1.556065855
H	1.828194809	1.915058888	0.460752810
H	-0.351625970	-1.067440718	1.161203779
H	-1.116063243	-2.064843382	2.098447261
H	-0.157408122	-2.613133059	0.985827582
H	1.701892124	-3.609364855	4.179189754
H	1.109049586	-4.174246112	2.842422460
H	0.150435905	-3.625980609	3.955138617
H	3.336161683	-1.933773101	2.215873064
H	2.516073469	-1.194587215	1.102887827
H	2.493750007	-2.759974004	1.183856013
H	3.790925984	-1.648182796	5.317188484
H	4.265697322	-3.024590162	7.139733824
H	2.519506555	-3.642383997	8.621476401
H	0.341434364	-2.908663318	8.183689976
H	-0.104327592	-1.512330796	6.375833415
O	1.811508411	2.893965985	6.084166147

cis-$(PMe_3)_2Pd(C_6H_5)(CO)^+$ Transition State

Pd	1.375364887	0.040903430	3.728705465
P	0.752501552	1.985598590	2.389783059
P	0.951988338	-2.186632157	3.026388357
C	2.149842000	1.277752000	5.113420000
C	-0.282164643	3.167757162	3.371664497
C	-0.178613838	1.929711614	0.778067748
C	2.231273027	3.004836707	1.937574703
C	0.264098632	-2.525238379	1.333732327
C	-0.241857896	-3.106521234	4.102186204
C	2.444417196	-3.282529227	3.030260642
C	2.222686736	-0.660715949	5.477282045
C	3.601366233	-0.882785855	5.580187111
C	4.180775189	-1.466337402	6.816772024
C	3.325040490	-1.951085667	7.986784219
C	1.844418588	-1.661739668	7.863918150
C	1.436398203	-0.878792864	6.615185609

H	-1.236282226	2.698852137	3.620509610
H	-0.467021002	4.086351877	2.808829209
H	0.244049928	3.396442769	4.298388550
H	-1.150247124	1.454427403	0.923618564
H	0.380802793	1.357923537	0.036529858
H	-0.337846162	2.941346253	0.395581316
H	2.877084485	2.437062756	1.264878224
H	2.786282370	3.224548105	2.849808265
H	1.932240576	3.936503470	1.450427995
H	0.935886835	-2.121488017	0.574754740
H	-0.709910327	-2.047684369	1.224242135
H	0.152793355	-3.600408838	1.172083930
H	0.123010265	-3.092026420	5.129087597
H	-0.353028130	-4.140270342	3.765498469
H	-1.214513578	-2.611626455	4.073474756
H	2.884382029	-3.287585133	4.027039311
H	3.184088668	-2.888347962	2.330632148
H	2.177427011	-4.300806311	2.736429572
H	4.248184696	-0.687107328	4.731159958
H	5.243788175	-1.498122181	6.825650798
H	1.090602701	-1.985870801	8.655138077
H	0.370027980	-0.678247037	6.586359361
O	2.532636000	2.188766000	5.747815000
H	3.772503474	-2.468919191	8.898594679

$Pd(PMe_3)_2$

Pd	1.357280446	-0.067172445	4.200839093
P	0.854684465	1.383801248	2.488225080
P	1.864450059	-1.487999154	5.937434226
C	0.686301259	3.141328591	2.911818382
C	-0.670340732	1.036006990	1.549278217
C	2.122745702	1.384872150	1.202619941
C	0.906766409	-3.014498792	6.173656756
C	1.899698755	-0.812591294	7.605627503
C	3.541965442	-2.124053008	5.681043533
H	0.022025482	3.244838442	3.597662751
H	0.417765923	3.635179543	2.131786747
H	1.527818272	3.475010501	3.227099773
H	-1.420882937	1.013951700	2.149426069
H	-0.590618072	0.185715760	1.109058949
H	-0.810793078	1.722528432	0.891203850
H	2.284106387	0.484519277	0.911286384
H	2.938247039	1.754890005	1.556065855
H	1.828194809	1.915058888	0.460752810
H	0.817489181	-3.471100246	5.333173637
H	0.031545551	-2.795187950	6.509199548

H	1.355958524	-3.581410289	6.801344150
H	2.388846310	0.014784570	7.606056837
H	2.325085339	-1.436054010	8.196397297
H	1.000688578	-0.649727301	7.904273998
H	4.148140475	-1.391228886	5.541821545
H	3.549057570	-2.694831663	4.909843648
H	3.815393001	-2.622630944	6.453003548

***p*-Aminobenzonitrile**

C	-2.220801179	0.224327421	1.161468233
C	0.073181368	1.503090394	1.627998272
H	-0.497018599	2.420290363	1.622698704
C	1.426381327	1.522190464	1.986498753
H	1.900081373	2.454090488	2.257598797
C	2.165581442	0.333290351	1.993398587
N	3.624775235	0.353665030	2.380140338
C	1.551481462	-0.874809640	1.641899029
H	2.121681429	-1.792009580	1.647198597
C	0.198281504	-0.893909621	1.283498684
H	-0.275418543	-1.825809586	1.012298504
C	-0.693659871	0.275831599	1.355113699
H	4.347209857	-0.306053196	1.855501314
H	3.975122325	1.028135181	3.188861142
N	-3.717954467	0.174662798	0.970269663

Benzonitrile

H	-2.188421077	-0.064682395	0.999998967
C	-0.530520982	1.158117622	1.627998272
H	-1.100720949	2.075317591	1.622698704
C	0.822678976	1.177217692	1.986498753
H	1.296379023	2.109117716	2.257598797
C	1.561879092	-0.011682421	1.993398587
C	0.947779112	-1.219782413	1.641899029
H	1.517979079	-2.136982352	1.647198597
C	-0.405420847	-1.238882393	1.283498684
H	-0.879120893	-2.170782358	1.012298504
C	-1.144520826	-0.049882383	1.276498715
C	3.050405890	0.009278721	2.387668143
N	4.171615835	0.025000046	2.684635024

***p*-Trifluoromethylbenzonitrile**

C	-2.220801179	0.224327421	1.161468233
C	0.073181368	1.503090394	1.627998272
H	-0.497018599	2.420290363	1.622698704
C	1.426381327	1.522190464	1.986498753
H	1.900081373	2.454090488	2.257598797

C	2.165581442	0.333290351	1.993398587
C	3.654147486	0.353857123	2.387739417
C	1.551481462	-0.874809640	1.641899029
H	2.121681429	-1.792009580	1.647198597
C	0.198281504	-0.893909621	1.283498684
H	-0.275418543	-1.825809586	1.012298504
C	-0.693659871	0.275831599	1.355113699
N	-3.717954467	0.174662798	0.970269663
F	4.474542076	0.749479609	1.208735310
F	4.064900696	-1.002751638	2.846510922
F	3.862046633	1.335205129	3.489688227

Aniline

H	-2.190481939	1.180932625	0.885351103
C	-0.412232014	2.525139310	1.562204719
H	-1.015914947	3.492425098	1.563974154
C	1.081087851	2.549210596	1.936031868
H	1.584974524	3.534707528	2.209309871
C	1.896765769	1.243395763	1.928214621
N	3.365526459	1.270753974	2.276033665
C	1.218331059	-0.087341296	1.552075228
H	1.823544842	-1.053305148	1.544152825
C	-0.275466203	-0.110964770	1.177690417
H	-0.778070409	-1.094765141	0.896482680
C	-1.088053630	1.196457749	1.175177079
H	3.854990464	2.231147999	2.542207496
H	3.957006838	0.331486204	2.262064669

Benzene

H	-1.698183868	1.190180155	0.999998967
C	-0.040283773	2.412980171	1.627998272
H	-0.610483739	3.330180140	1.622698704
C	1.312916186	2.432080241	1.986498753
H	1.786616233	3.363980265	2.257598797
C	2.052116301	1.243180128	1.993398587
H	3.096016314	1.257880123	2.269898812
C	1.438016322	0.035080137	1.641899029
H	2.008216288	-0.882119803	1.647198597
C	0.084816363	0.015980156	1.283498684
H	-0.388883683	-0.915919809	1.012298504
C	-0.654283616	1.204980167	1.276498715

Trifluoromethylbenzene

H	-2.191394172	1.180532558	0.884143329
C	-0.412869534	2.525841594	1.558586163
H	-1.016513272	3.493269007	1.563207731

C	1.078508291	2.548395927	1.942382669
H	1.577384046	3.530055598	2.238004257
C	1.898414602	1.245069334	1.923198102
C	3.379654815	1.262455642	2.340792990
C	1.217679297	-0.087112689	1.557744446
H	1.819258649	-1.055842312	1.568617104
C	-0.273957421	-0.109923839	1.174830941
H	-0.775181249	-1.095182919	0.895478075
C	-1.088346929	1.197327020	1.170901312
F	4.217578261	1.654055119	1.172500570
F	3.778110517	-0.096047407	2.805501011
F	3.572973422	2.244732231	3.443551851

Table 1: B3LYP Computed Energies

Molecule	ΔG (Hartree)
cis-$(PMe_3)_2Pd(C_6H_4$-*p*-$CF_3)(CN)$	-1040.862563
cis-$(PMe_3)_2Pd(C_6H_4$-*p*-$CF_3)(CN)$ TS	-1040.835152
cis-$(PMe_3)_2Pd(C_6H_4$-*p*-$NH_2)(CN)$	-759.075200
cis-$(PMe_3)_2Pd(C_6H_4$-*p*-$NH_2)(CN)$ TS	-759.049470
cis-$(PMe_3)_2Pd(C_6H_5)(CN)$	-703.718681
cis-$(PMe_3)_2Pd(C_6H_5)(CN)$ TS	-703.692044
cis-$(PMe_3)_2Pd(C_6H_5)(CO)^+$	-724.011368
cis-$(PMe_3)_2Pd(C_6H_5)(CO)^+$ TS	-723.997913
$Pd(PMe_3)_2$	-379.244888
p-Aminobenzonitrile	-379.866497
Benzonitrile	-324.504547
p-Trifluoromethylbenzonitrile	-661.643085
Aniline	-287.594068
Benzene	-232.235840
Trifluoromethylbenzene	-569.377363

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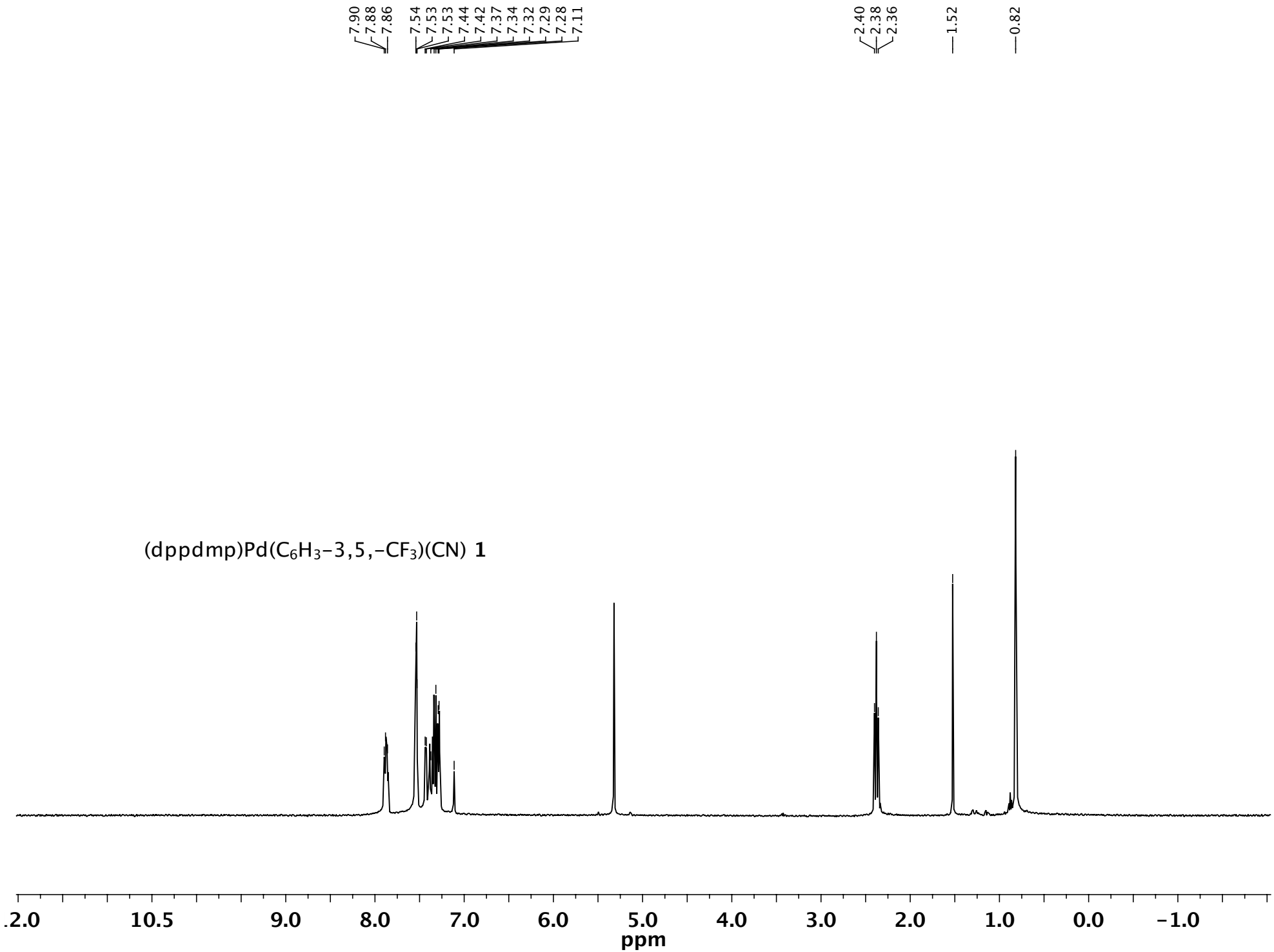
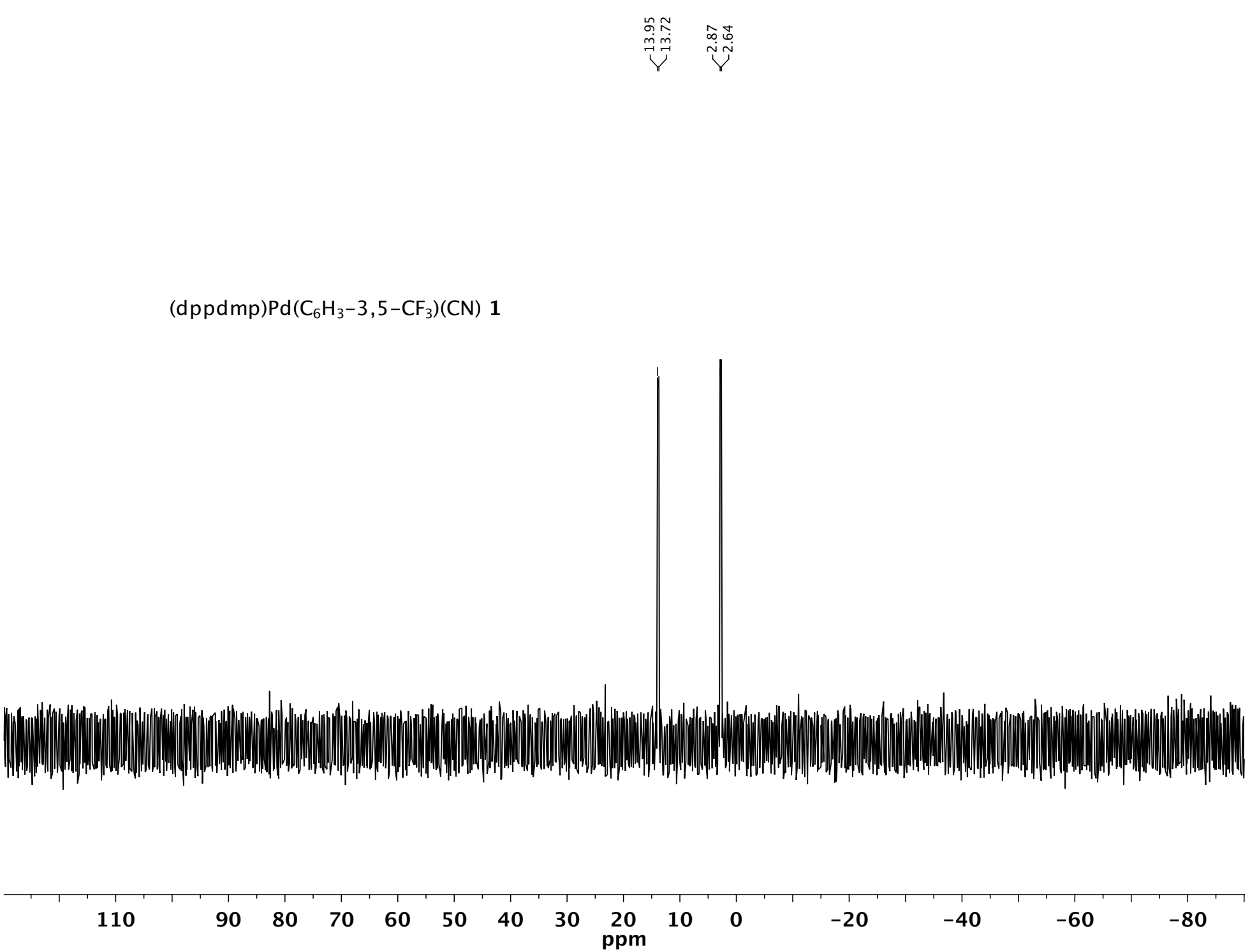
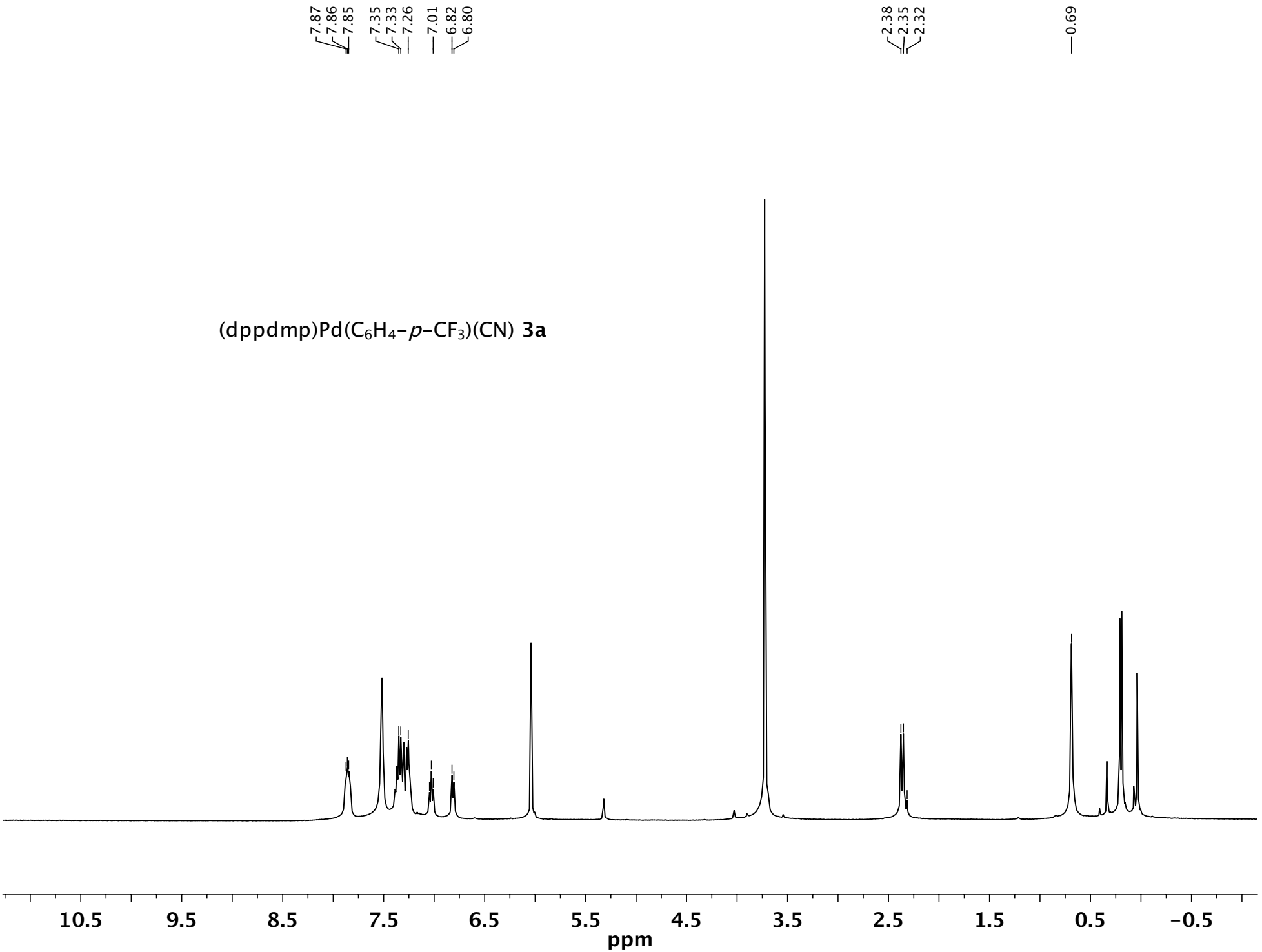
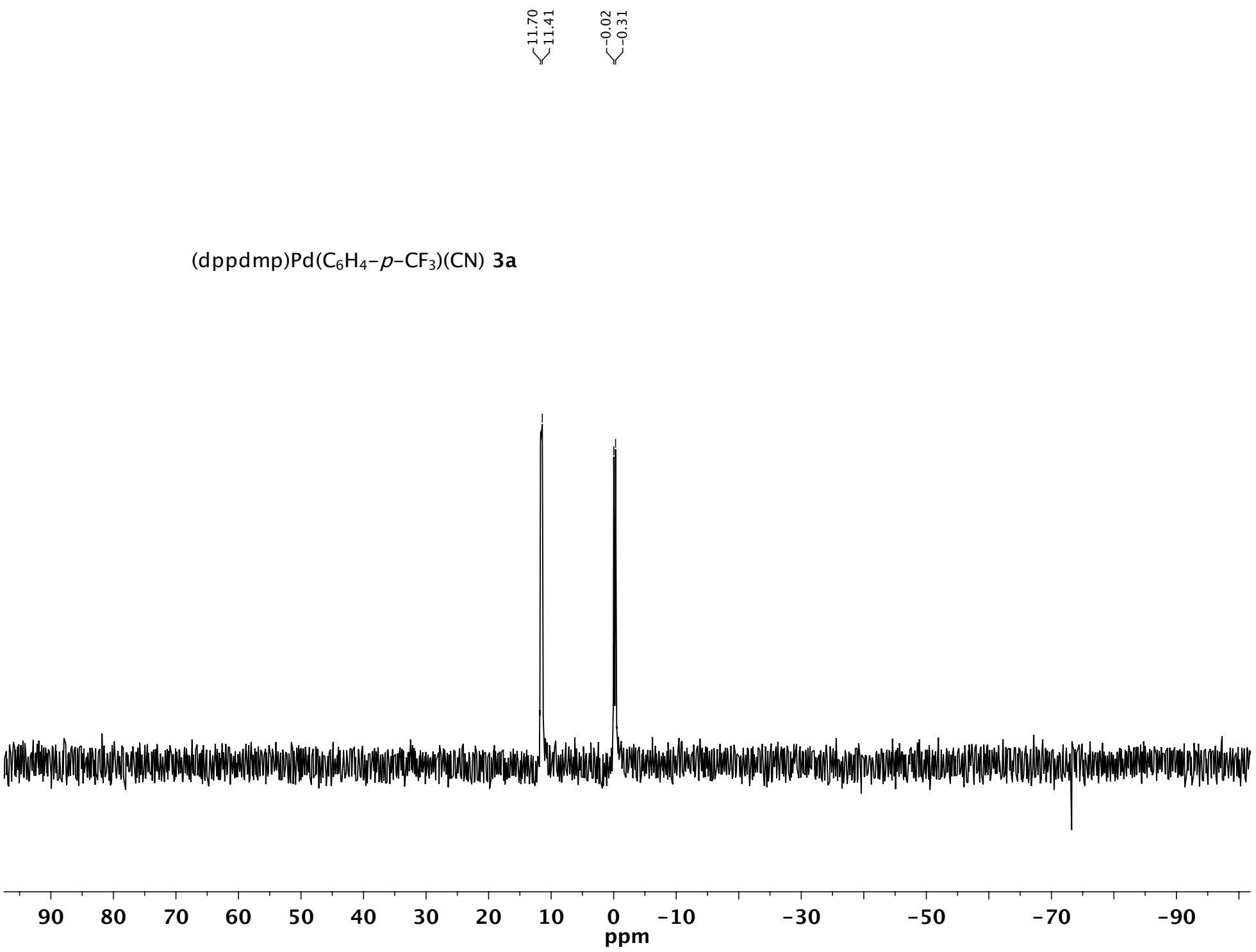
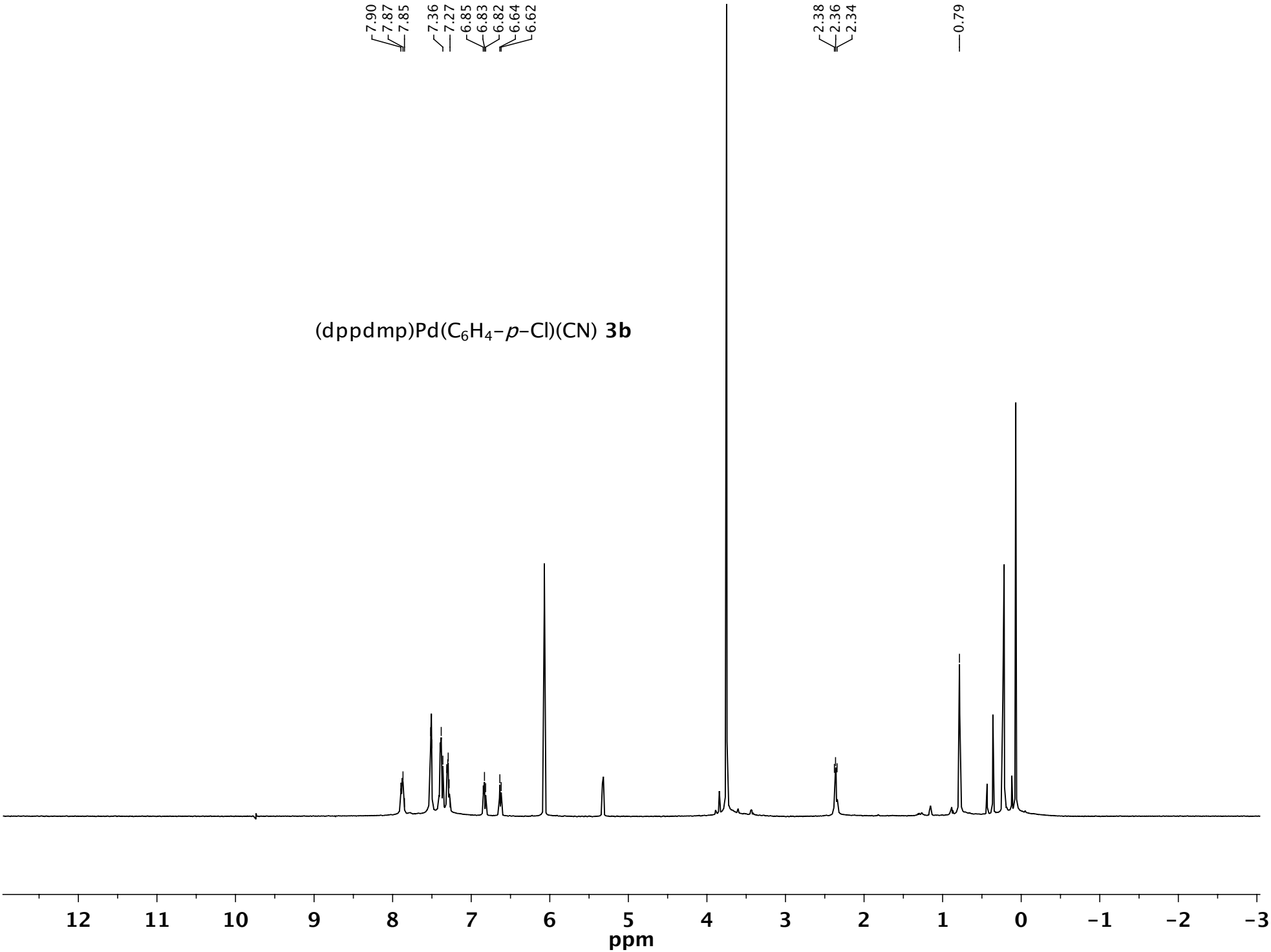

7.90
7.88
7.86
7.54
7.53
7.53
7.44
7.42
7.37
7.34
7.32
7.29
7.28
7.11
2.40
2.38
2.36
1.52
0.82
(dppdmp)Pd(C6H3-3,5,-CF3)(CN) 1
.2.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm

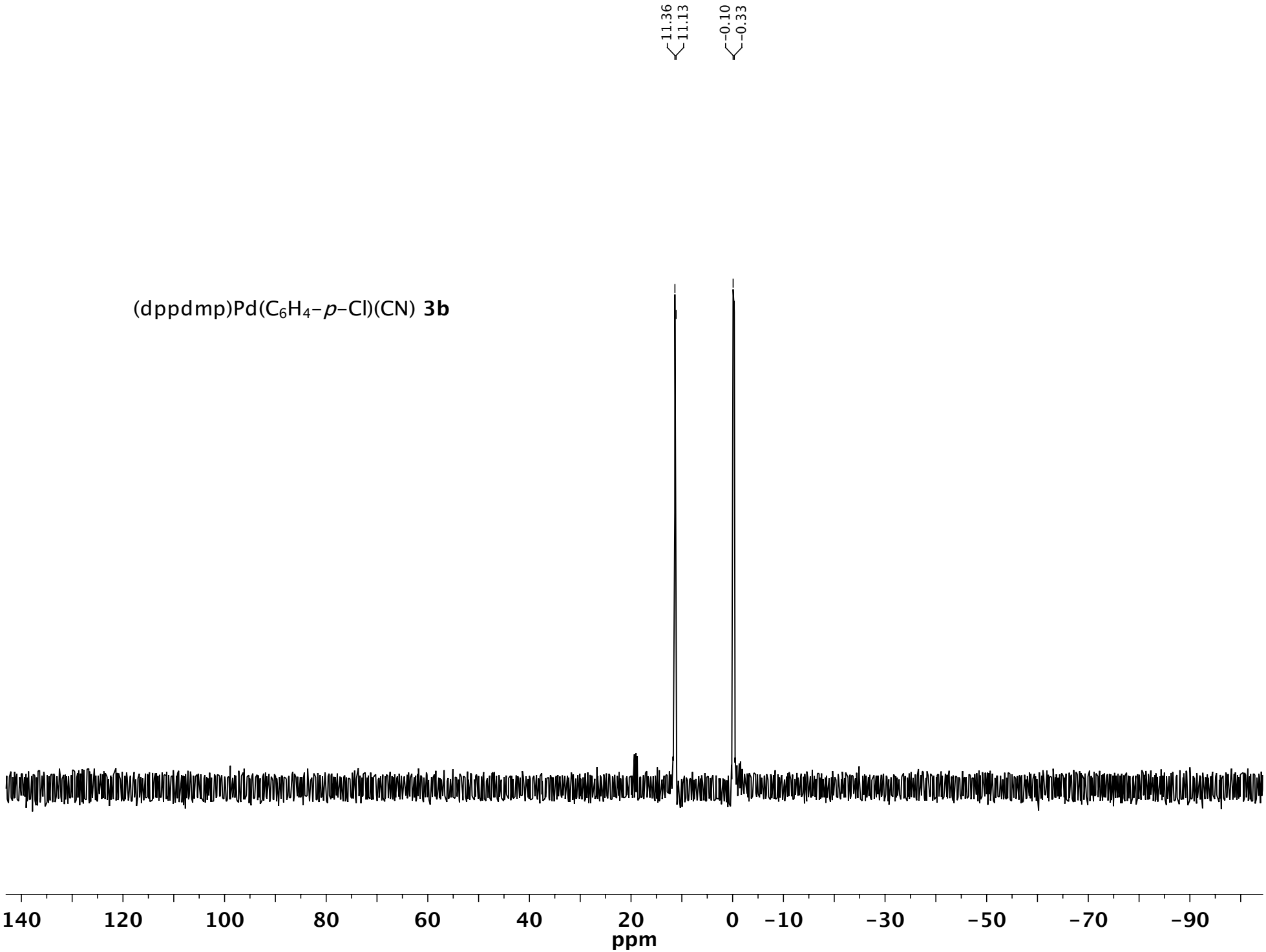

13.95
13.72
2.87
2.64
(dppdmp)Pd(C6H3-3,5-CF3)(CN) 1
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
ppm

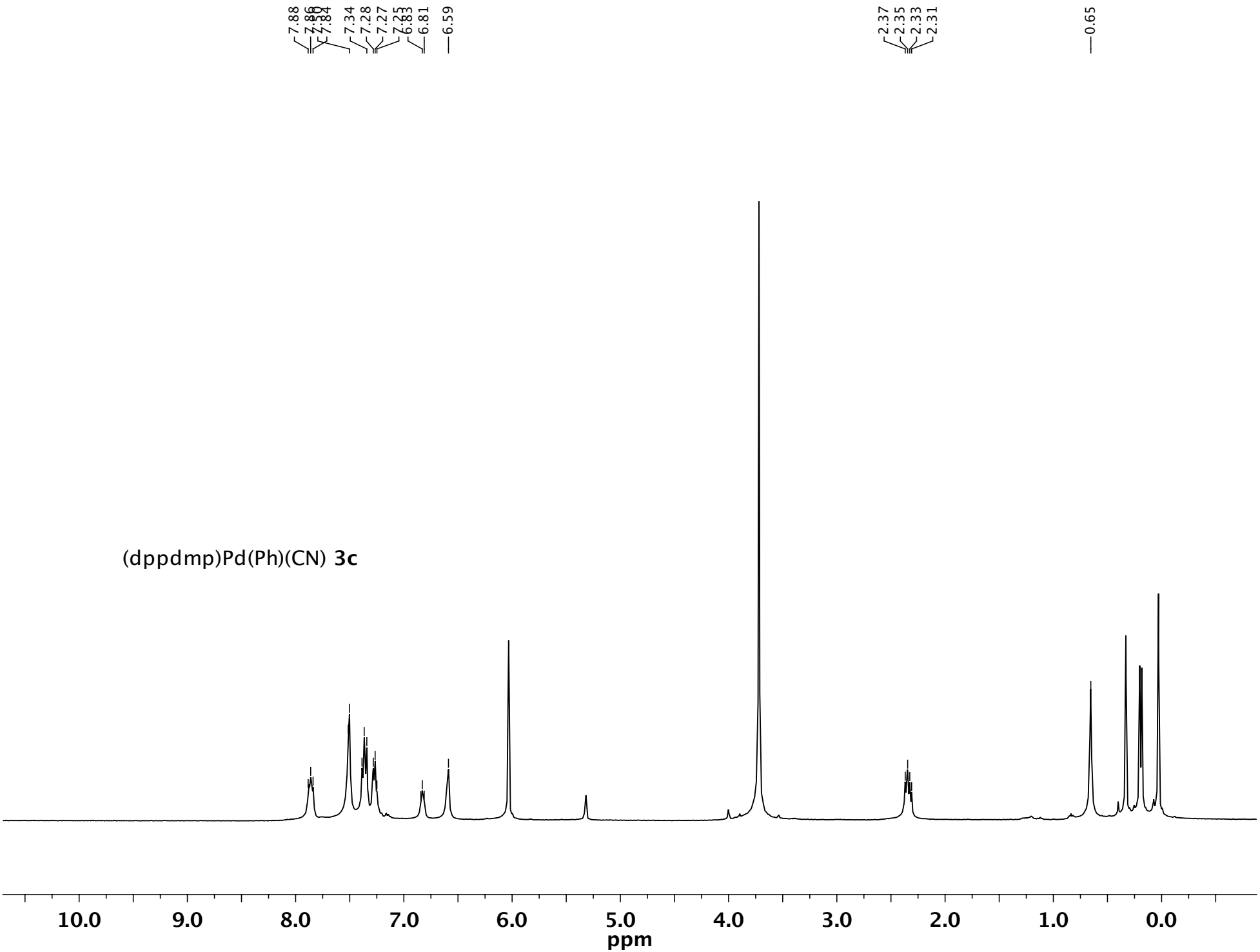

7.87
7.86
7.85
7.35
7.33
7.26
7.01
6.82
6.80
2.38
2.35
2.32
0.69
(dppdmp)Pd(C6H4–p–CF3)(CN) 3a
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
–0.5
ppm

(dppdmp)Pd(C_6H_4-*p*-CF_3)(CN) **3a**

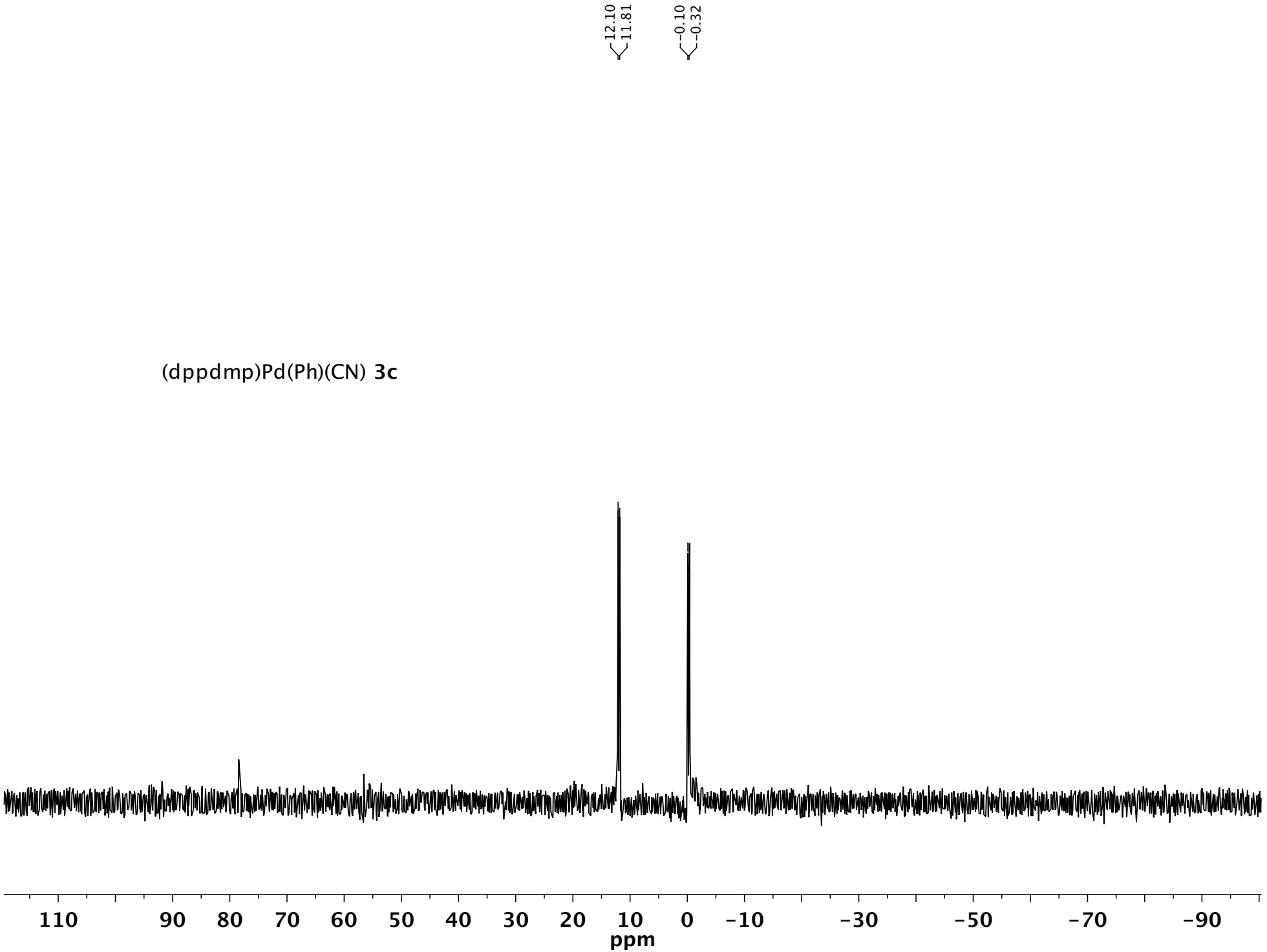


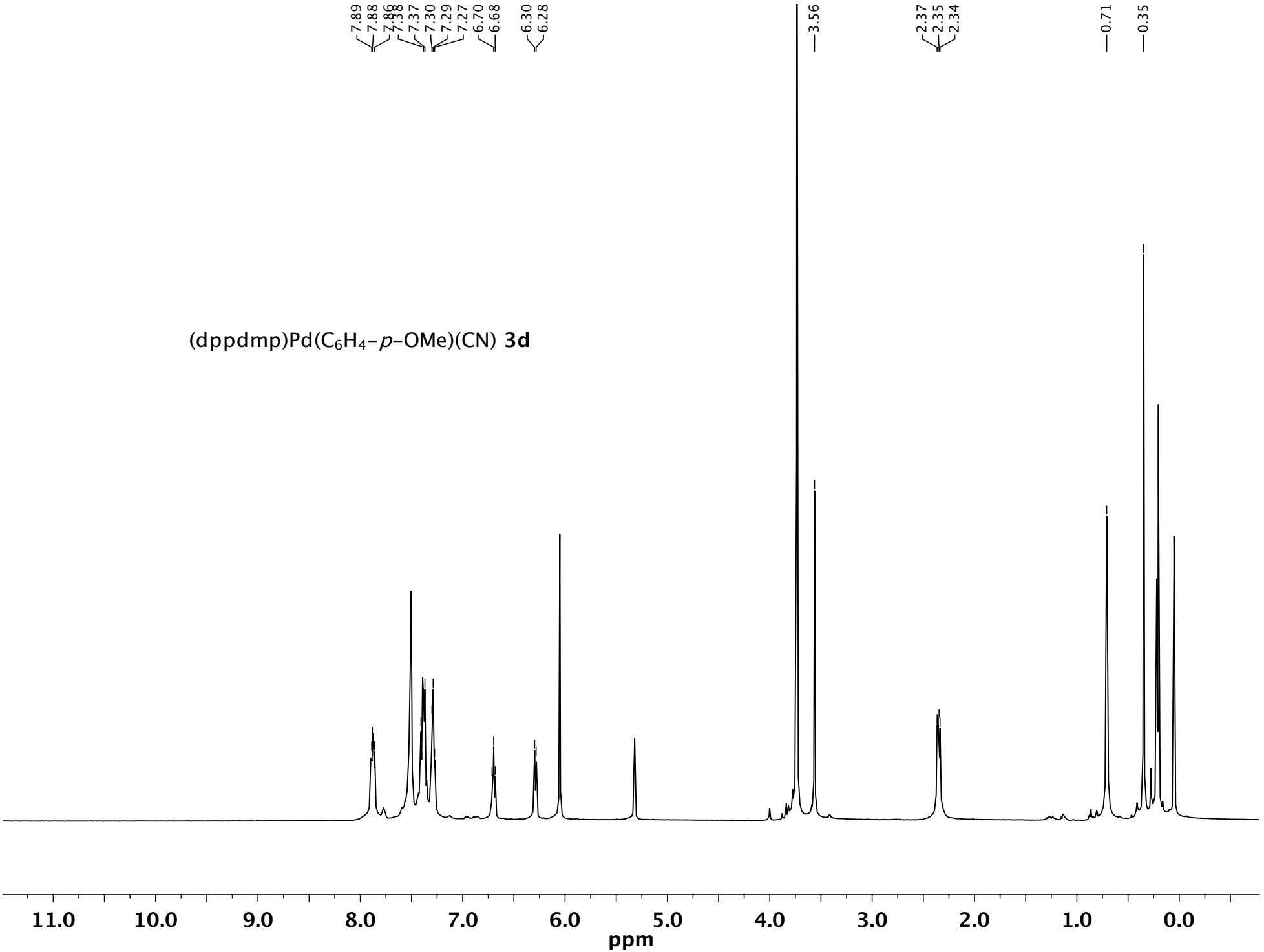

7.90
7.87
7.85
7.36
7.27
6.85
6.83
6.82
6.64
6.62
2.38
2.36
2.34
0.79
(dppdmp)Pd(C6H4–p–Cl)(CN) 3b
12
11
10
9
8
7
6
5
4
3
2
1
0
–1
–2
–3
ppm

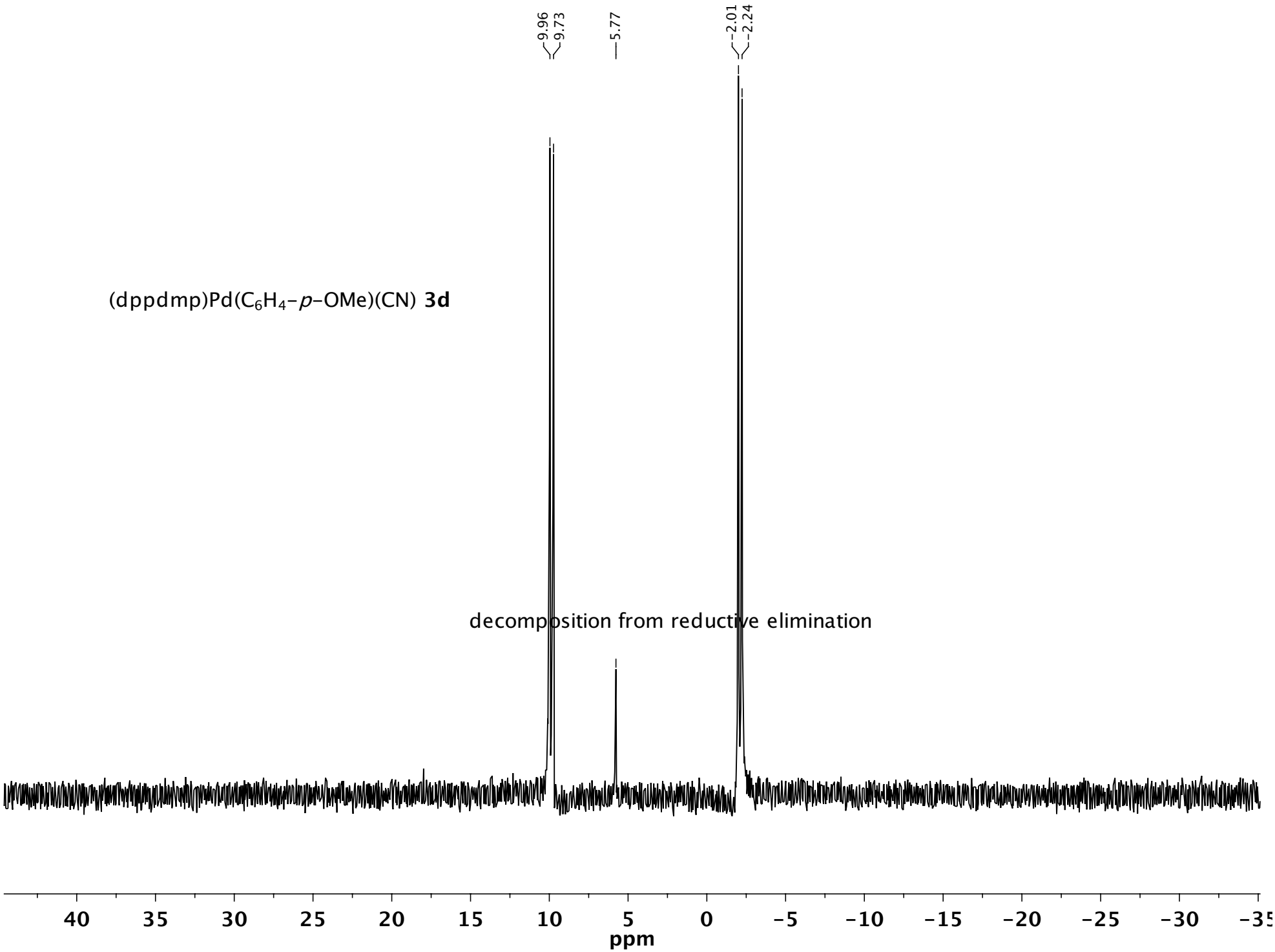

11.36
11.13
-0.10
-0.33
(dppdmp)Pd(C6H4-p-Cl)(CN) 3b
140
120
100
80
60
40
20
0
-10
-30
-50
-70
-90
ppm

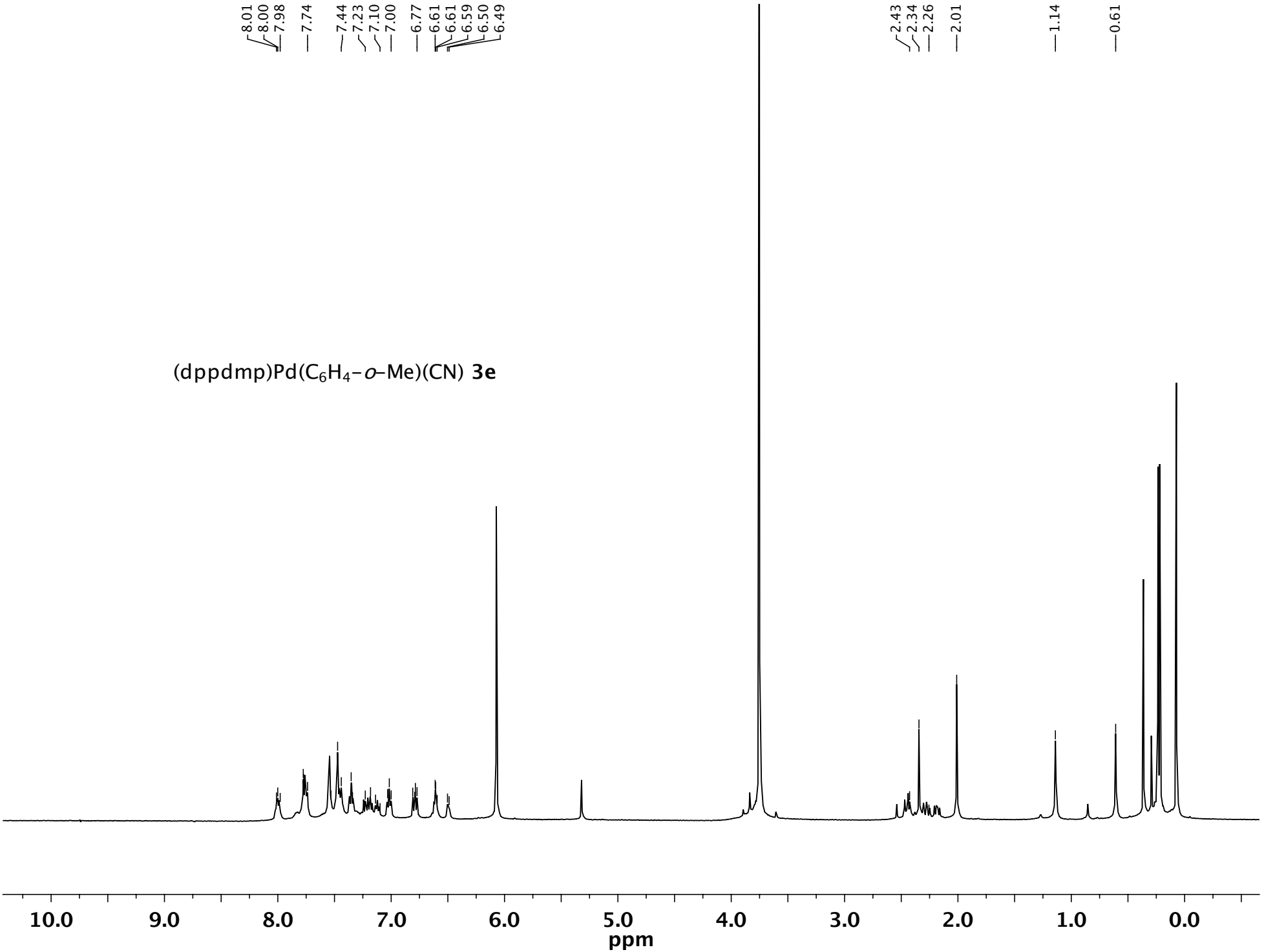

7.88
7.86
7.84
7.34
7.28
7.27
7.25
6.83
6.81
6.59
2.37
2.35
2.33
2.31
0.65
(dppdmp)Pd(Ph)(CN) 3c
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

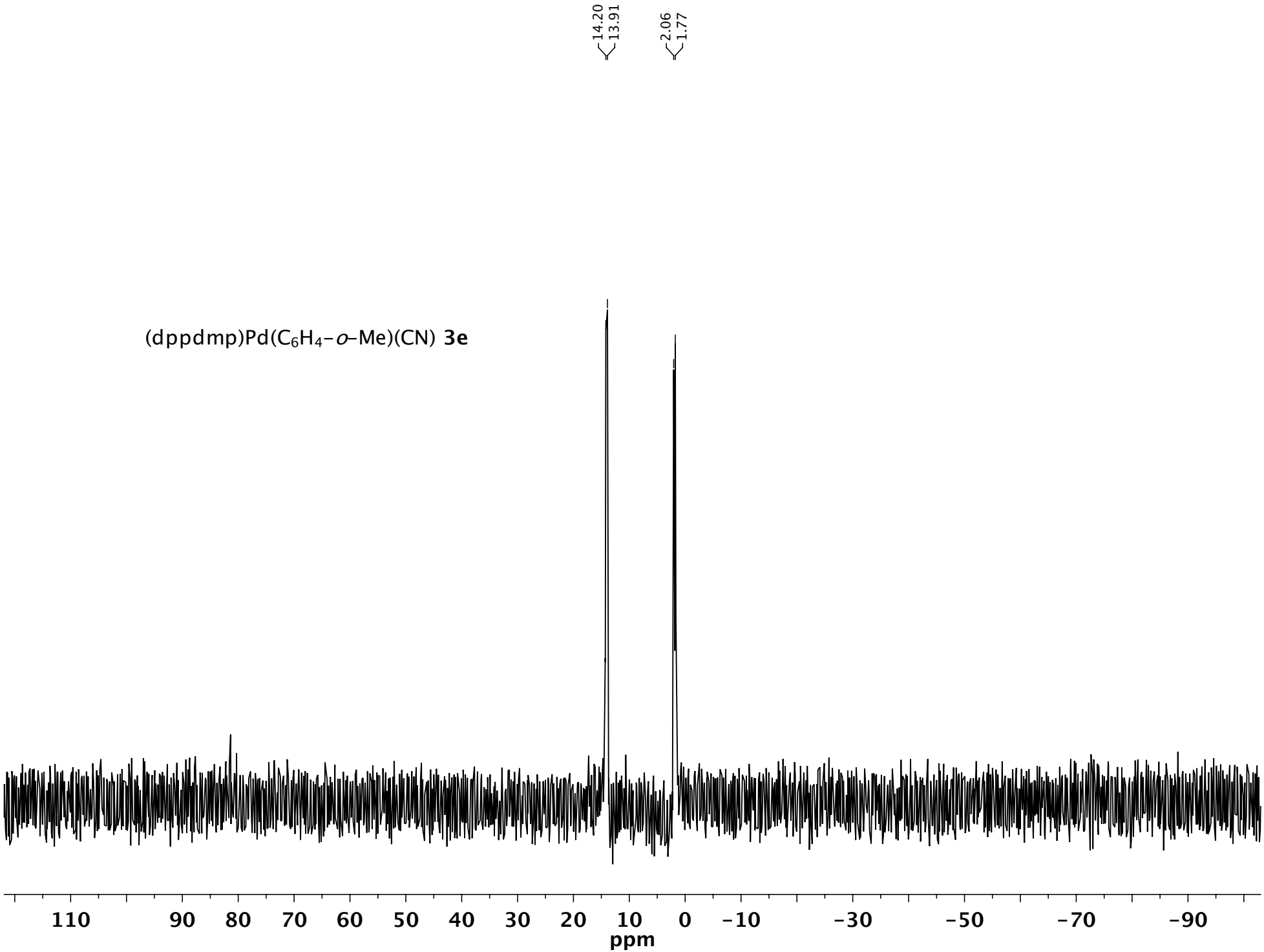
(dppdmp)Pd(Ph)(CN) **3c**

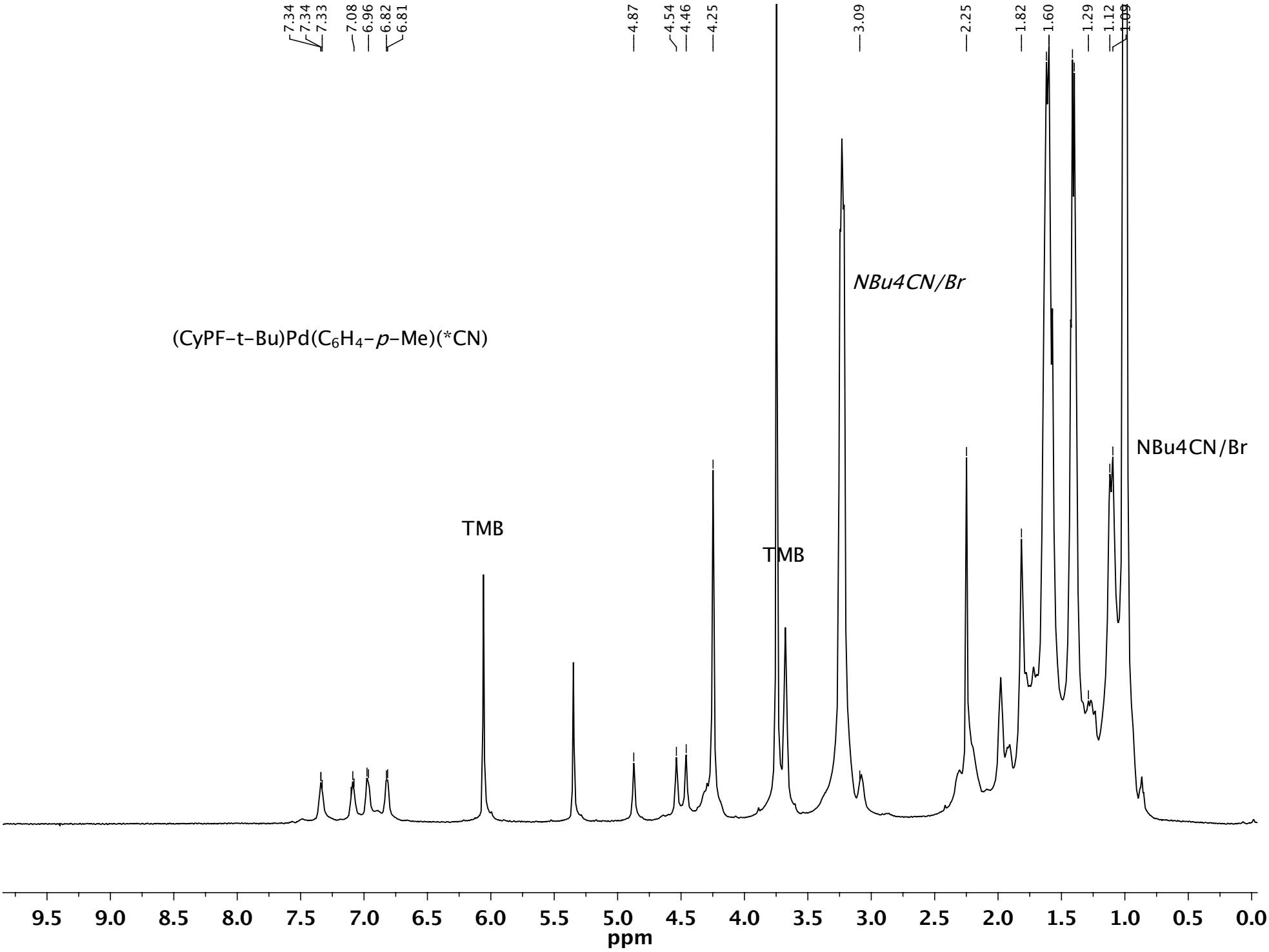


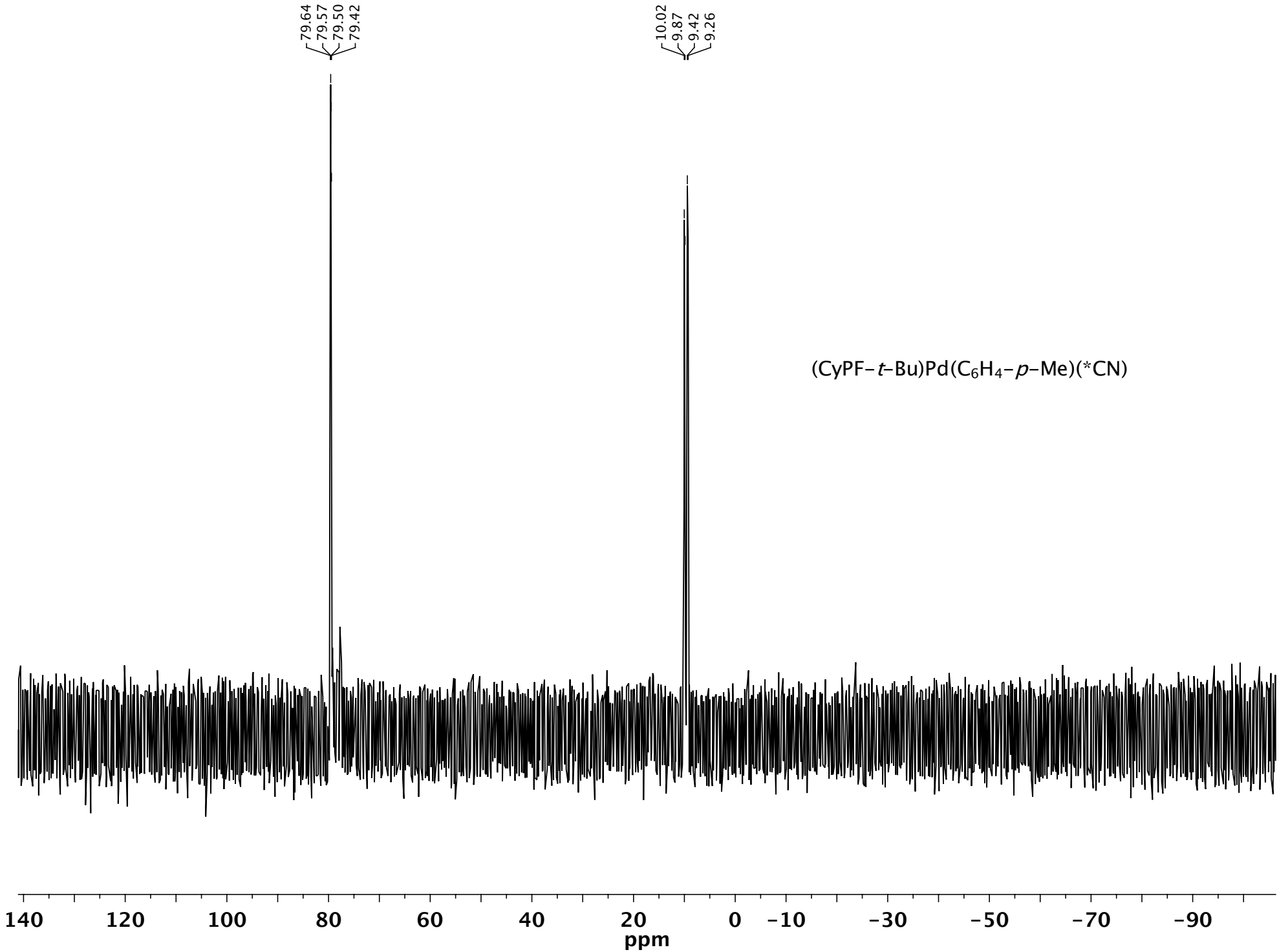

7.89
7.88
7.38
7.37
7.30
7.29
7.27
6.70
6.68
6.30
6.28
3.56
2.37
2.35
2.34
0.71
0.35
(dppdmp)Pd(C6H4–p–OMe)(CN) 3d
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


9.96
9.73
5.77
-2.01
-2.24
(dppdmp)Pd(C6H4–p–OMe)(CN) 3d
decomposition from reductive elimination
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
ppm


8.01
8.00
7.98
7.74
7.44
7.23
7.10
7.00
6.77
6.61
6.61
6.59
6.50
6.49
2.43
2.34
2.26
2.01
1.14
0.61
(dppdmp)Pd(C6H4–o–Me)(CN) 3e
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


14.20
13.91
2.06
1.77
(dppdmp)Pd(C6H4–o–Me)(CN) 3e
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
ppm


7.34
7.34
7.33
7.08
6.96
6.82
6.81
4.87
4.54
4.46
4.25
3.09
2.25
1.82
1.60
1.29
1.12
1.09
(CyPF-t-Bu)Pd(C6H4-p-Me)(*CN)
TMB
TMB
NBu4CN/Br
NBu4CN/Br
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


79.64
79.57
79.50
79.42
10.02
9.87
9.42
9.26
(CyPF–t–Bu)Pd(C6H4–p–Me)(*CN)
140
120
100
80
60
40
20
0
–10
–30
–50
–70
–90
ppm