

Evidence for In Situ Catalyst Modification During the Pd-Catalyzed Conversion of Aryl Triflates to Aryl Fluorides

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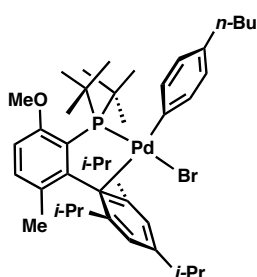
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SUPPORTING INFORMATION

General Procedures. All reactions were carried out in a nitrogen-filled glovebox using oven-dried glassware and anhydrous degassed solvents unless otherwise noted. Dry, oxygen-free toluene, DCM, THF, and Et₂O were obtained by passage through activated alumina columns followed by purging with argon. Anhydrous pentane and cyclohexane were purchased from Aldrich in sure-seal™ bottles and were purged with argon before use. CD₂Cl₂ (99.9%) was purchased in sealed ampules from Cambridge Isotopes. Celite was dried at 200 °C under high vacuum before use. The preparation of *t*-BuBrettPhos and RockPhos have been previously described.^{1,2} [(cinnamyl)PdCl]₂ was purchased from Aldrich and used as received. Cesium fluoride (99.9%) was purchased from Aldrich (or Strem) and was dried at 200°C under high-vacuum for 24 hours. The dried CsF was then transferred to a nitrogen-filled glovebox where it was thoroughly ground using an oven-dried mortar and pestle. The finely ground CsF was then filtered through a 45 μm stainless-steel sieve (purchased from Cole Parmer) and the smaller particles collected.

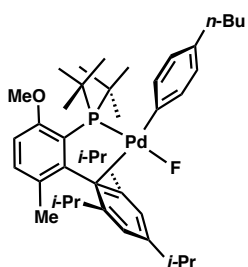
Yields refer to spectroscopically (^1H , ^{31}P , ^{19}F NMR) homogeneous materials, unless otherwise stated. Single crystal X-ray diffraction analyses were obtained for most compounds (**4**, **7**, **8**, and **9**). All yields stated for fluorination reactions are based on ^{19}F NMR relative to an internal standard of 1-fluoronaphthalene, 3-fluoroanisole, or 4-fluorobenzonitrile. NMR spectra were recorded on a Bruker AMX 400 (for ^1H , ^{13}C , and ^{31}P) and Varian XL 300 MHz NMR spectrometer (for ^{19}F and ^{31}P) spectrometer and were calibrated using residual solvent as an internal reference (CD_2Cl_2 : 5.32 ppm for ^1H NMR and 53.84 ppm for ^{13}C NMR). ^{19}F NMR spectra were calibrated to an internal standard of 1-fluoronaphthalene (δ -124.0 ppm), 3-fluoroanisole (δ -112.2 ppm), or 4-fluorobenzonitrile (δ -104.3 ppm) for experiments requiring yields and an external standard of CFCl_3 for all others (δ 0.0 ppm). Proton decoupled ^{31}P NMR spectra are referenced to an external *aq.* H_3PO_4 standard (δ 0.0 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, at = apparent triplet, ad = apparent doublet.

Synthesis of Complexes 4-8, 11



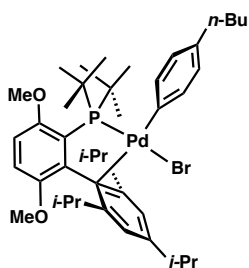
Complex 4: To an oven-dried vial was added RockPhos (**3**) (250 mg, 0.53 mmol, 1.1 equiv.) and 4-bromo-*n*butylbenzene (565 mg, 2.65 mmol, 5 equiv.). With rapid stirring, cyclohexane was added dropwise until all reagents had completely dissolved (2 mL total). $(\text{COD})\text{Pd}(\text{CH}_2\text{TMS})_2$ (205 mg, 0.53 mmol, 1 equiv.) was added rapidly in one portion and the mixture was vigorously stirred at room temperature for 16 hours, during which period a precipitate formed. Pentane (2 mL) was added and the mixture placed in a $-20\text{ }^\circ\text{C}$ freezer for 1 hour. The mixture was filtered through a sintered glass frit, washed

with pentane (3 X 3 mL), and dried under reduced pressure to afford **4** as a yellow solid (320 mg, 76%). To obtain X-ray quality crystals, a small sample (10 mg) was dissolved in a minimal quantity of DCM, layered with pentane, and cooled to -20 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.26 (d, *J* = 8.8 Hz, 1 H), 7.11 (s, 2 H), 6.93 (d, *J* = 7.4 Hz, 2 H), 6.87 (d, *J* = 7.8 Hz, 1 H), 6.63 (d, *J* = 7.9 Hz, 2 H), 3.81 (s, 3 H), 3.07 (septet, *J* = 6.8 Hz, 1 H), 2.69 (septet, *J* = 6.8 Hz, 2 H), 2.45 (t, *J* = 7.6 Hz, 2 H), 1.66 (d, *J* = 6.7 Hz, 6 H), 1.55 – 1.47 (m, 2H), 1.41 (s, 9 H), 1.37 (d, *J* = 6.8 Hz, 6 H), 1.37 (s, 9 H), 1.32 – 1.25 (m, 2 H), 1.18 (s, 3 H), 0.93 (d, *J* = 6.6 Hz, 6 H), 0.89 (t, *J* = 7.3 Hz, 3 H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 159.5, 157.8, 152.7, 148.5, 148.3, 139.8, 139.7, 136.7, 135.5, 133.0, 132.9, 129.8, 129.7, 126.2, 126.1, 126.0, 125.6, 122.7, 122.6, 110.2, 54.0, 41.6, 41.5, 34.9, 34.8, 34.2, 32.9, 32.9, 31.7, 27.3, 26.9, 24.9, 24.5, 22.7, 19.9, 14.2 (observed complexity is due to C—P splitting); ³¹P NMR (121 MHz, CD₂Cl₂) δ 70.8.



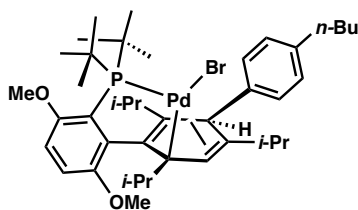
Complex 5: Complex **4** (150 mg, 0.19 mmol, 1 equiv.) was dissolved in DCM (5 mL) in an oven-dried vial. The vial was wrapped in aluminum foil, AgF (180 mg, 1.43 mmol, 7.5 equiv.) was added in one portion, and the mixture was rapidly stirred for 7 hours while protected from light. Pentane (10 ml) was added and the mixture placed in a -20 °C freezer for 12 hours [this step precipitates unwanted black particles]. The mixture was filtered through a small (1 cm), tightly packed plug of celite and the solvent removed under reduced pressure to yield a brown film. Pentane (5 mL) was added and the solvent removed under reduced pressure. This process was repeated two more times [this ensures complete removal of DCM] to afford **5** as a dark yellow solid (120 mg, 88%). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.31 (d, *J* = 7.4 Hz, 1 H), 7.14 (s, 2 H), 7.03 (dd, *J* = 8.0, 1.6 Hz, 2

H), 6.90 (d, $J = 8.6$ Hz, 1 H), 6.66 (d, $J = 6.2$ Hz, 2 H), 3.83 (s, 3 H), 2.94 (septet, $J = 7.3$ Hz, 1 H), 2.69 (septet, $J = 6.7$ Hz, 2 H), 2.44 (t, $J = 7.2$ Hz, 2 H), 1.74 (d, $J = 7.4$ Hz, 6 H), 1.54 – 1.24 (m, 13 H), 1.44 (s, 9 H), 1.41 (s, 9 H), 0.99 (d, $J = 6.4$ Hz, 6 H), 0.88 (t, $J = 6.5$ Hz, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 159.0, 157.9, 152.8, 148.5 (b), 142.0 (b), 137.2, 135.6, 132.4, 132.3, 129.2, 127.0, 126.2, 124.5, 120.5, 110.4, 66.0, 40.7 (b), 35.0, 34.9, 34.3, 32.9, 32.8, 31.7, 28.8, 28.6, 27.1, 24.8, 24.2 (b), 22.7, 20.4, 15.5, 14.2, 14.1 (observed complexity is due to C—P splitting); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 78.1 (d, $J = 163.1$ Hz); ^{19}F NMR (282 MHz, CD_2Cl_2) δ -215.1 (d, $J = 165.3$ Hz).



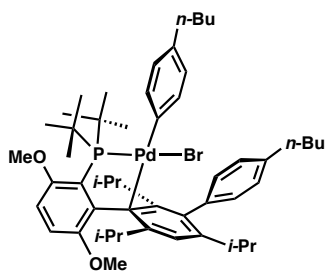
Complex 6: To an oven-dried vial was added *t*-BuBrettPhos (**2**) (500 mg, 1.03 mmol, 1.05 equiv.) and 4-bromo-*n*butylbenzene (1.1 g, 5.16 mmol, 5 equiv.). With rapid stirring, cyclohexane was added dropwise until all reagents had dissolved (10 mL).

(COD)Pd(CH_2TMS)₂ (400 mg, 1.03 mmol, 1 equiv.) was added rapidly in one portion and the mixture was vigorously stirred at room temperature for 16 hours, during which period the solution had become slightly red colored and a yellow precipitate had formed. The mixture was filtered through a sintered glass frit, washed with pentane (3 x 5 mL), and dried under reduced pressure to afford **6** as a bright yellow solid (490 mg, 61%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.04 (s, 2 H), 6.93 – 6.92 (m, 3 H), 6.87 (d, $J = 8.8$, 1 H), 6.61 (d, $J = 8.0$ Hz, 2 H), 3.78 (s, 3 H), 3.34 (s, 3 H), 3.01 (bs, 1 H), 2.62 – 2.52 (m, 2 H), 2.43 (at, $J = 7.7$ Hz, 2 H), 1.57 (d, $J = 6.7$ Hz, 6 H), 1.54 – 1.47 (m, 4 H), 1.38 (s, 9 H), 1.34 (s, 9 H), 1.33 (d, $J = 7.2$ Hz, 6 H), 0.88 (t, $J = 7.3$ Hz, 3 H), 0.82 (d, $J = 6.6$ Hz, 6 H); ^{31}P NMR (121 MHz, CD_2Cl_2) δ 67.6 (broad); [Note: a ^{13}C NMR spectra of **6** could not be obtained due to its rapid isomerization to **7** in solution].

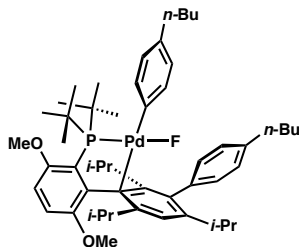


Complex 7: Complex **6** (490 mg, 0.61 mmol, 1.0 equiv.)

was dissolved in DCM (or THF) (10 mL) and allowed to stand for 12 hours, during which period a color change from yellow to dark red was observed. The solvent was removed under reduced pressure, and the resulting dark-red solid was triturated with pentane (2 mL) and filtered. The solid was washed with pentane (2 x 5 mL) and dried under reduced pressure to afford **7** as a red solid (420 mg, 86%), which contained small amounts of **6**. Trituration with a minimal quantity of DCM afforded **7** (purity > 95%) as a red crystalline solid. To obtain X-ray quality crystals a small sample (10 mg) was dissolved in a minimal quantity of DCM, layered with pentane, and cooled to -20 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 8.60 (dd, *J* = 8.0, 1.7 Hz, 1 H), 7.30 (dd, *J* = 7.5, 1.9 Hz, 1 H), 7.19 (dd, *J* = 8.0, 2.0 Hz, 1 H), 7.10 (dd, *J* = 7.8, 2.0 Hz, 1 H), 7.05 (d, *J* = 9.0 Hz, 1 H), 6.93 (dd, *J* = 9.0, 2.4 Hz, 1 H), 5.79 (s, 1 H), 3.80 (s, 3 H), 3.71 (s, 3 H), 3.08 (d, *J* = 39.3 Hz, 1 H), 2.60 (t, *J* = 7.7 Hz, 2 H), 2.37 (septet, *J* = 6.8 Hz, 1 H), 1.91 (septet, *J* = 6.8 Hz, 1 H), 1.63 – 1.57 (m, 2 H), 1.52 (d, *J* = 15.0 Hz, 9 H), 1.41 (d, *J* = 14.8 Hz, 9 H), 1.36 – 1.30 (m, 3 H), 1.23 (d, *J* = 6.7 Hz, 3 H), 1.15 (d, *J* = 6.8 Hz, 6 H), 1.07 (d, *J* = 6.9 Hz, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 0.73 (d, *J* = 6.5 Hz, 3 H), - 0.06 (d, *J* = 6.9 Hz, 3 H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 174.9, 174.9, 155.2, 155.2, 151.7, 151.6, 142.2, 136.8, 136.6, 136.3, 136.3, 136.2, 136.0, 131.7, 129.0, 128.7, 127.8, 119.1, 118.9, 114.1, 110.5, 98.6, 68.3, 68.2, 55.1, 54.5, 52.2, 52.2, 40.1, 39.9, 39.4, 39.4, 35.5, 33.0, 32.8 (b), 32.5, 30.5, 30.5, 22.7, 22.6, 22.3, 21.4, 21.4, 20.2, 20.0, 19.9, 14.1 (observed complexity is due to C—P splitting); ³¹P NMR (121 MHz, CD₂Cl₂) δ 82.6.



Complex 8: Complex **7** (152 mg, 0.19 mmol, 1.0 eq.) was dissolved in THF (3 mL). 4-bromo-*n*butylbenzene (100 μ L, 0.57 mmol, 3.0 eq.) was added, followed by 1,8-diazabicycloundec-7-ene (34.5 μ L, 0.23 mmol, 1.2 eq.). The mixture was allowed to stir at room temperature for 12 hours, during which period a color change from dark red to yellow was observed, along with formation of an insoluble white solid. The crude reaction mixture was filtered through an oven-dried glass frit, and the solvent was removed under reduced pressure to afford a yellow oil. Ether (3 mL) was added and then removed under reduced pressure. This process was repeated two additional times to afford a yellow solid that was further washed with pentane (3 x 5 mL), giving **8** as a bright yellow solid (158 mg, 90%). Vapor diffusion of an Et₂O/DCM solution of **8** with pentane afforded X-ray quality crystals. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.72 (d, J = 9.4 Hz, 1 H), 7.17 – 7.12 (m, 3 H), 7.08 (d, J = 7.6 Hz, 1 H), 6.96 (d, J = 9.4 Hz, 2 H), 6.93 – 6.85 (m, 2 H), 6.64 (d, J = 7.6 Hz, 2 H), 3.78 (s, 3 H), 3.40 (s, 3 H), 2.94 (septet, J = 7.3 Hz, 1 H), 2.66 (t, J = 7.8 Hz, 2 H), 2.58 (septet, J = 6.4 Hz, 1 H), 2.51 – 2.44 (m, 3 H), 1.69 – 1.63 (m, 2 H), 1.60 (d, J = 7.7 Hz, 3 H), 1.56 – 1.48 (m, 2 H), 1.47 – 1.25 (m, 25 H), 1.04 – 1.00 (m, 6 H), 0.95 (t, J = 7.7 Hz, 3 H), 0.89 (t, J = 6.4 Hz, 3 H), 0.78 (d, J = 6.4 Hz, 3 H), 0.64 (d, J = 7.7 Hz, 3 H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 158.0, 154.4, 154.4, 153.8, 152.3, 152.2, 151.8, 141.5, 140.3, 139.6, 139.4, 139.4, 138.5, 136.6, 132.4, 131.8, 130.0, 129.9, 127.9, 127.8, 127.2, 126.5, 126.0, 123.7, 118.3, 118.3, 113.7, 110.6, 110.5, 66.0, 54.7, 41.7, 41.5, 41.4, 41.2, 35.8, 34.9, 34.3, 34.1, 33.5, 33.0, 33.0, 32.7, 32.6, 31.6, 30.3, 25.6, 25.4, 25.2, 24.6, 22.8, 22.7, 22.3, 15.5, 14.2, 14.2 (observed complexity is due to C—P splitting); ³¹P NMR (121 MHz, CD₂Cl₂) δ 71.7.



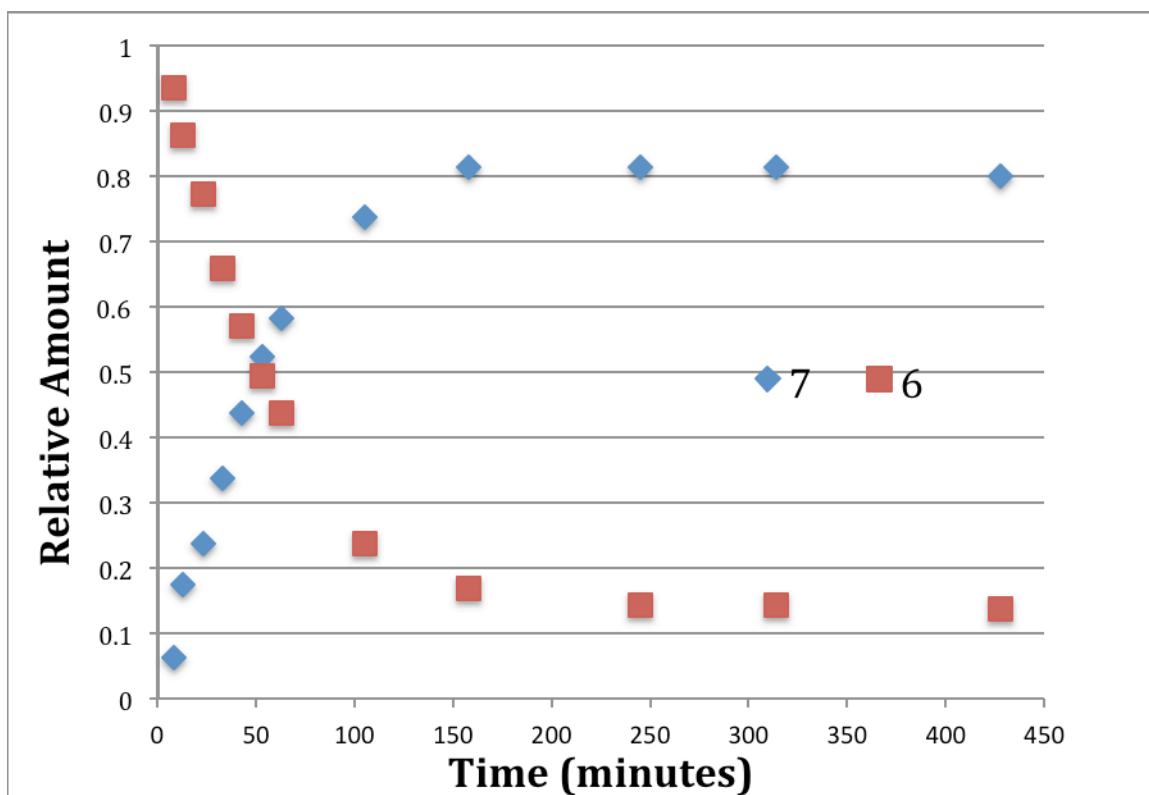
Complex 11: Complex **8** (145 mg, 0.16 mmol, 1 equiv.) was dissolved in DCM (5 mL) in an oven-dried vial. The vial was wrapped in aluminum foil and AgF (100 mg, 0.79 mmol, 5.0 equiv.) was added in one portion. The mixture was rapidly stirred for 4 hours while protected from light. Pentane (10 mL) was then added, and the vial was placed in a -20 °C freezer for 12 hours [this step precipitates unwanted black particles]. The mixture was filtered through a small (1 cm), tightly-packed plug of celite and the solvent removed under reduced pressure to afford a light brown oil. Pentane (5 mL) was added and then removed under reduced pressure; this process was repeated two additional times to afford **11** as a yellow solid (117 mg, 86%). ¹H NMR (400 MHz, CD₂Cl₂) δ 7.52 (d, *J* = 8.5 Hz, 1 H), 7.20 – 7.10 (m, 6 H), 6.93 (s, 2 H), 6.70 (d, *J* = 7.6 Hz, 2 H), 3.79 (s, 3 H), 3.48 (s, 3 H), 2.89 (septet, *J* = 6.7 Hz, 1 H), 2.67 (t, *J* = 7.8 Hz, 2 H), 2.54 – 2.48 (m, 2 H), 2.47 (t, *J* = 7.8 Hz 2 H), 1.71 – 1.63 (m, 2 H), 1.65 (d, *J* = 7.5 Hz, 3 H), 1.57 – 1.53 (m, 2 H), 1.48 (d, *J* = 15.5 Hz, 9 H), 1.30 (d, *J* = 15.0 Hz, 9 H), 1.43 – 1.34 (m, 4 H), 1.07 (at, *J* = 6.0 Hz 6 H), 1.01 (d, *J* = 7.5 Hz, 3 H), 0.97 (t, *J* = 7.9 Hz, 3 H), 0.92 (t, *J* = 7.5 Hz, 3 H), 0.88 (d, *J* = 7.2 Hz, 3 H), 0.81 (d, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CD₂Cl₂) δ 157.4, 154.1, 152.3, 152.1, 148.9, 142.5, 141.9, 141.3, 139.9, 139.7, 139.5, 138.9, 137.4, 137.1, 133.9, 131.5, 130.8, 130.6, 128.2, 127.9, 127.4, 126.4, 126.2, 122.6, 118.2, 113.7, 110.5, 54.6, 40.9, 40.7, 40.4, 40.2, 35.9, 35.3, 35.1, 34.4, 34.2, 33.9, 33.4, 33.0, 32.9, 32.6, 32.5, 31.6, 30.4, 26.2, 25.9, 25.0, 24.9, 24.1, 22.9, 22.8, 22.6, 14.2, 14.2 (observed complexity is due to C—P splitting); ³¹P NMR (121 MHz, CD₂Cl₂) δ 78.1 (d, *J* = 163.7 Hz); ¹⁹F NMR (282 MHz, CD₂Cl₂) δ -210.6 (d, *J* = 166.9 Hz).

General Procedure for a Catalytic Fluorination Reaction Using 2 or 3 (Figure 3)

In a nitrogen-filled glovebox, an oven-dried screw cap vial was charged with CsF (90 mg, 0.60 mmol, 3 equiv). [(cinnamyl)PdCl]₂ (2.6 mg, 0.005 mmol, 5 mol % “Pd”), **2** or **3** (0.0075 mmol, 7.5 mol%), aryl triflate (0.2 mmol, 1 equiv.), and toluene (2 mL). The vial was sealed, removed from the glovebox and placed into a pre-heated 120 °C oil bath for 20 hours with vigorous stirring. Upon cooling to room temperature, an internal standard (1-fluoronaphthalene) was added and the reaction mixture analyzed by ¹⁹F NMR spectroscopy.

Procedure to Monitor the Kinetics of Rearrangement of 6 to 7 (Figure 4)

In a nitrogen-filled glovebox, an oven-dried vial was charged with complex **6** (10 mg, 0.012 mmol, 1 equiv.) and an internal standard of 1,3,5-trimethoxybenzene (5 mg, 0.03 mmol, 2.4 equiv). CD₂Cl₂ (750 µL) was added rapidly and the contents of the vial were quickly transferred to an oven-dried screw cap NMR tube. The conversion of **6** to **7** was monitored by ¹H NMR at room temperature with the first spectra recorded at T = 8 minutes after dissolution. Spectra were recorded periodically thereafter at T = 13, 23, 33, 43, 53, 63, 105, 158, 245, 314, and 428 minute time points. The normalized quantities of **6** and **7** relative to the internal standard were then plotted (SI Figure 1)



SI Figure 1. Isomerization of *t*-BuBrettPhos oxidative addition complex **6** to dearomatized complex **7**.

Isolation of **9** from a Catalytic Fluorination Reaction (Figure 7)

To an oven-dried schlenk tube was added 4-*n*-BuPhOTf (744 mg, 2.63 mmol, 1.0 equiv.), RockPhos (**3**) (250 mg, 0.53 mmol, 0.20 equiv.), [(cinnamyl)PdCl]₂ (138 mg, 0.27 mmol, 0.10 equiv.), CsF (1.22 g, 8.0 mmol, 3 equiv.) and toluene (25 ml). The tube was sealed and placed into a preheated 120 °C oil bath with vigorous stirring. After 20 hours of heating at 120 °C, the reaction was cooled to room temperature and diluted with EtOAc (50 mL). The organic layer was washed with NaHCO₃ (100 mL), brine (100 mL) and dried (MgSO₄). Volatiles were removed *in vacuo* and the crude reaction mixture was purified by silica gel chromatography [gradient: hexanes→DCM→Et₂O] to obtain a light brown foam (245 mg) which contained an approximate 5:1 mixture of **9** (δ 37.0 ppm) and

3 (δ 35.8 ppm) as determined by ^{31}P NMR. Recrystallization from hot MeOH/EtOAc afforded analytically pure **9** (75 mg) as an off-white solid. X-ray quality crystals (fine white needles) were obtained by vapor diffusion of a MeOH/Et₂O solution of **9** with pentane. [Note: under identical experimental conditions, *t*-buBrettPhos (**2**) (δ 34.8 ppm) is quantitatively converted to a new ligand (δ 36.0 ppm); however all re-crystallization attempts have failed to deliver analytically pure arylated **2**].

Data for **9**: ^1H NMR (400 MHz, CD_2Cl_2) δ 7.25 – 7.21 (m, 3 H), 7.17 (d, J = 9.1 Hz, 2 H), 7.10 (d, J = 8.0 Hz, 1 H), 6.83 (d, J = 8.3 Hz, 1 H), 3.81 (s, 3 H), 2.77 (septet, J = 8.2 Hz, 1 H), 2.68 (t, J = 6.8 Hz, 2 H), 2.56 – 2.45 (m, 2 H), 1.80 (s, 3 H), 1.71 – 1.65 (m, 2 H), 1.43 – 1.38 (m, 2 H), 1.28 – 1.13 (m, 24 H), 1.03 (d, J = 6.8 Hz, 3 H), 0.99 – 0.93 (m, 6 H), 0.81 (d, J = 7.2 Hz, 3 H), 0.61 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 160.7, 160.7, 152.0, 151.7, 147.6, 145.8, 142.8, 141.4, 139.1, 138.8, 138.8, 132.9, 132.3, 131.8, 131.0, 130.9, 127.2, 127.1, 125.3, 124.9, 120.4, 108.8, 54.0, 35.8, 34.7, 34.6, 34.4, 34.3, 34.2, 32.8, 32.8, 32.4, 32.4, 32.3, 32.2, 31.3, 31.3, 29.8, 25.4, 25.4, 24.9, 24.7, 24.3, 23.6, 22.9, 22.5, 22.5, 14.2 (observed complexity is due to C—P splitting); ^{31}P NMR (121 MHz, CD_2Cl_2) δ : 36.9.

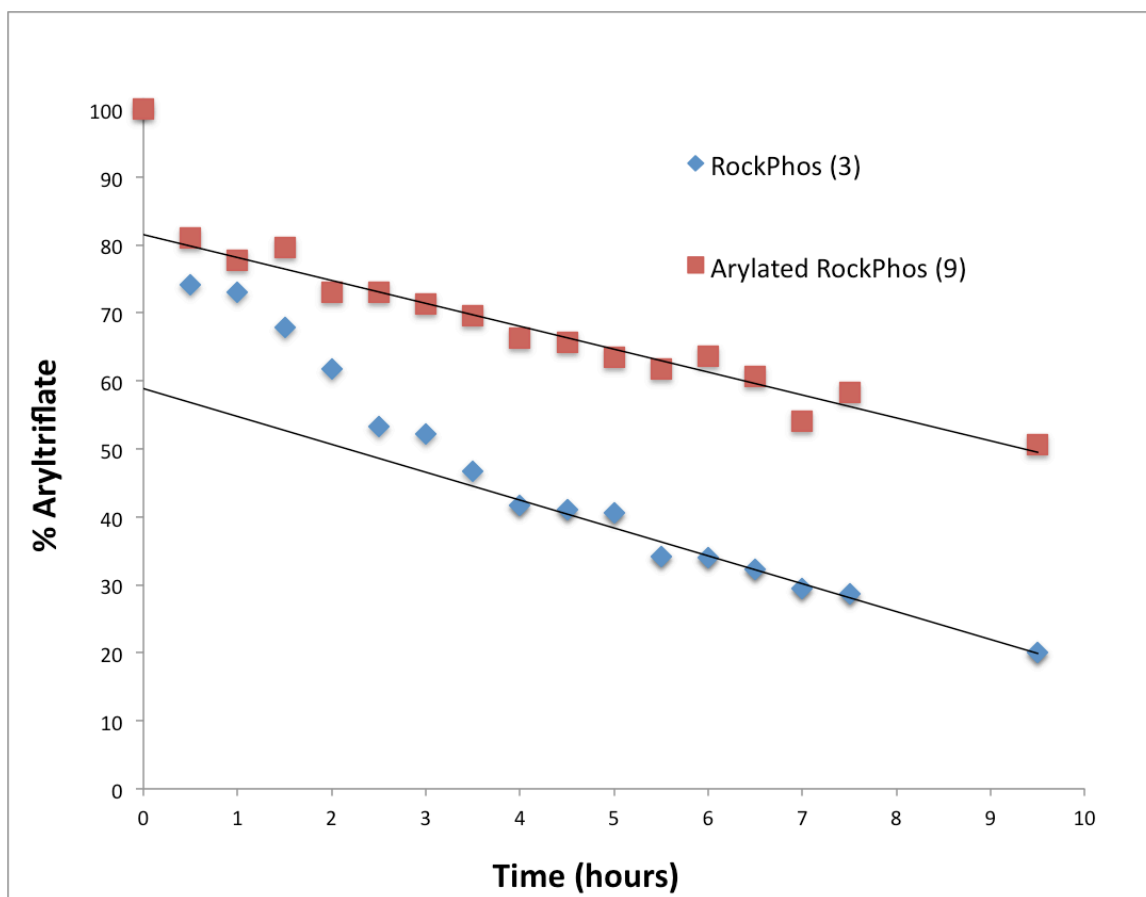
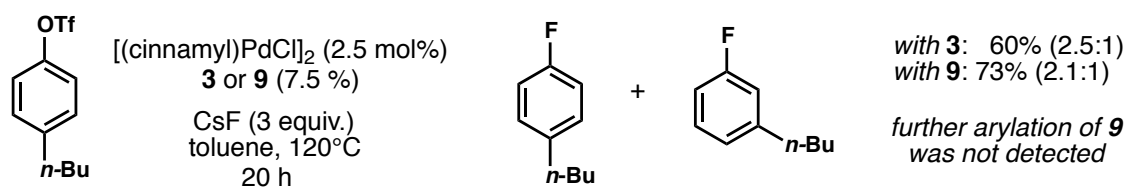
**Procedure for an Initial Rate Comparison Between RockPhos (3) and Arylated
RockPhos (9)**

To an oven-dried vial was added [(cinnamyl)PdCl]₂ (32.5 mg, 0.062 mmol) and toluene (25 mL). The vial was vigorously shaken to obtain complete dissolution and the resulting mixture was used as a stock solution. Meanwhile, two oven-dried screw top vials were charged with the following:

Vial #1: CsF (455 mg, 2.99 mmol, 3 equiv.), RockPhos (**3**) (35 mg, 0.075 mmol, 7.5 mol%), 1-fluoronaphthalene (110 μ l, 0.85 mmol, 0.85 equiv), and 4-*n*BuPhOTf (227.5 μ l, 1 mmol, 1 equiv).

Vial #2: CsF (455 mg, 2.99 mmol, 3 equiv.), arylated RockPhos (**9**) (45 mg, 0.075 mmol, 7.5 mol%), 1-fluoronaphthalene (110 μ l, 1.0 mmol, 1 equiv), and 4-*n*BuPhOTf (227.5 μ l, 1 mmol, 1 equiv).

To each vial was added 10 mL of the [(cinnamyl)PdCl]₂ stock solution (this corresponds to 5 mol% “Pd”). The vials were sealed, removed from the glovebox, and placed into a pre-heated 120 °C oil bath with vigorous stirring maintaining a bath temperature of 120 – 125°C. Every 30 minutes, samples (~ 200-300 μ l) were rapidly removed, quenched with EtOAc, and directly analyzed for conversion against the internal standard by ¹⁹F NMR spectroscopy (SI figure 2).



SI Figure 2. Initial rate comparison between RockPhos (**3**) and aryated RockPhos (**9**) in the Pd-catalyzed fluorination of 4-*n*BuPhOTf.

General Procedure for Thermolysis Experiments of Complex **11** (Table 2)

In a nitrogen-filled glovebox, an oven-dried screw cap NMR tube was charged with LPd(Ar)F complex **11** (15-35 mg), toluene (or cyclohexane) (800 μ L), and additive (where appropriate) (10 equiv.). The tube was removed from the glovebox and placed in a 120 °C oil bath. After 2-3 hours at 120 °C, the reaction was cooled, the internal standard (1-fluoronaphthalene, 3-fluoroanisole, or 4-fluorobenzonitrile, 1 equiv.) added, and the product mixture analyzed by ^{19}F NMR spectroscopy.

Entry 1 (toluene): Following the general procedure, **11** (12.5 mg, 0.01 mmol, 1 equiv.) was heated at 120 °C in toluene for 3 hours. After cooling and addition of 1-fluoronaphthalene, ^{19}F NMR analysis showed 15% of 4-*n*BuPhF (δ -118.4 ppm).

Entry 1 (cyclohexane): Following the general procedure, **11** (15 mg, 0.02 mmol, 1 equiv.) was heated at 120 °C in toluene for 3 hours. After cooling and addition of 1-fluoronaphthalene, ^{19}F NMR analysis showed 20% of 4-*n*BuPhF (δ -118.4 ppm).

Entry 2: Following the general procedure, **11** (19 mg, 0.02 mmol, 1 equiv.) and bromobenzene (34 mg, 0.2 mmol, 10 equiv.) were heated at 120 °C in toluene for 3 hours. After cooling and addition of 1-fluoronaphthalene, ^{19}F NMR analysis showed 40% of fluorobenzene (δ -113.3 ppm) and 7% of 4-*n*BuPhF (δ -118.4 ppm).

Entry 3: Following the general procedure, **11** (34 mg, 0.04 mmol, 1 equiv.) and 1-naphthyltriflate (107 mg, 0.40 mmol, 10 equiv.) were heated at 120 °C in toluene for 2 hours. After cooling and addition of 3-fluoroanisole, ^{19}F NMR analysis showed 75% of 1-fluoronaphthalene (δ -124.0 ppm) and a trace (~3%) of 4-*n*BuPhF (δ -118.4 ppm).

Entry 4 (toluene): Following the general procedure, **11** (19 mg, 0.022 mmol, 1 equiv.) and 4-*n*-BuPhOTf (61 mg, 0.22 mmol, 10 equiv.) were heated at 120 °C in toluene for 3 hours. After cooling and addition of 1-fluoronaphthalene, ¹⁹F NMR analysis showed 32% of 4-*n*BuPhF (δ -118.4 ppm) and 20% of 3-*n*BuPhF (δ -114.4 ppm).

Entry 4 (cyclohexane): Following the general procedure, complex **11** (20 mg, 0.023 mmol, 1 equiv.) and 4-*n*-BuPhOTf (64 mg, 0.23 mmol, 10 equiv.) were heated at 120 °C in cyclohexane for 3 hours (significant boiling of the solvent was observed). After cooling and addition of 1-fluoronaphthalene, ¹⁹F NMR analysis showed 27% of 4-*n*BuPhF (δ -118.4 ppm) and 17% of 3-*n*BuPhF (δ -114.4 ppm).

Entry 5: Following the general procedure, complex **11** (25 mg, 0.03 mmol, 1 equiv.) and 4-*n*-BuPhBr (61 mg, 0.3 mmol, 10 equiv.) were heated at 120 °C in toluene for 3 hours. After cooling and addition of 1-fluoronaphthalene, ¹⁹F NMR analysis showed 24% of 4-*n*BuPhF (δ -118.4 ppm), 3% of 3-*n*BuPhF (δ -114.4 ppm).

Entry 6: Following the general procedure, complex **11** (9.5 mg, 0.01 mmol, 1 equiv.) and 4-OMePhOTf (28 mg, 0.1 mmol, 10 equiv) were heated at 120 °C in toluene for 3 hours. After cooling and addition of 4-fluorobenzonitrile, ¹⁹F NMR analysis showed 30% of 4-*n*BuPhF (δ -118.4 ppm), 18% of 3-*n*BuPhF (δ -114.4 ppm), and 7% of 3-OMePhF (δ -112.2 ppm).

Procedure For a Catalytic Fluorination using **11** (Figure 10)

In a nitrogen-filled glovebox, an oven-dried screw cap vial was charged with CsF (90 mg, 0.60 mmol, 3 equiv), **11** (8.6 mg, 0.01 mmol, 5 mol%), 4-*n*BuPhBr (56 mg, 0.20 mmol, 1 equiv.), and toluene (2 mL). The vial was sealed, removed from the glovebox and placed into a pre-heated 120 °C oil bath for 16 hours with vigorous stirring. Upon cooling to

room temperature, the internal standard (1-fluoronaphthalene) was added, and ^{19}F NMR analysis indicated 54% of 4-*n*BuPhF (δ -118.4 ppm) and 30% of 3-*n*BuPhF (δ -114.4 ppm).

X-Ray Structure Determination

Low-temperature diffraction data (ϕ - and ω -scans) were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) for the structure of compound **8** and on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from an *I μ S* micro-source for the structure of compounds **4**, **7**, and **9**. All structures were solved by direct methods using SHELXS³ and refined against F^2 on all data by full-matrix least squares with SHELXL-97⁴ using established refinement techniques.⁵ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters unless otherwise noted below.

Compound **9** crystallizes in the triclinic space group $P-1$ with one molecule in the asymmetric unit.

Compound **7** crystallizes in the triclinic space group $P-1$ with one molecule in the asymmetric unit. The highest residual electron density maximum was significantly higher than the next highest one (9.5 v/s 1.1 electrons) and was modeled as a second

palladium atom position (4.7% occupancy). This improved the model significantly and the remaining atoms in the molecule were observed in the difference Fourier map indicating a whole molecule disorder. Unfortunately, refinement of this whole molecule disorder was not stable and only the palladium atom was disordered while the remaining atoms were refined as fully occupied.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The butyl group on the phenyl ligand is disordered over two positions and restrained appropriately.

Compound **8** crystallizes in the orthorhombic space group $Pbca$ with one molecule in the asymmetric unit.

Table 1. Crystal data and structure refinement for 4.

| | | |
|---------------------------------|-------------------------------------------|------------------|
| Identification code | x11038 | |
| Empirical formula | C ₄₁ H ₆₂ Br O P Pd | |
| Formula weight | 788.19 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | a = 18.4713(17) Å | a = 90°. |
| | b = 11.6250(11) Å | b = 103.472(2)°. |
| | c = 18.7030(18) Å | g = 90°. |
| Volume | 3905.6(6) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.340 Mg/m ³ | |
| Absorption coefficient | 1.568 mm ⁻¹ | |
| F(000) | 1648 | |
| Crystal size | 0.15 x 0.15 x 0.05 mm ³ | |
| Theta range for data collection | 1.40 to 30.03°. | |
| Index ranges | -26 ≤ h ≤ 25, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26 | |
| Reflections collected | 88255 | |
| Independent reflections | 11416 [R(int) = 0.0673] | |

| | |
|-----------------------------------|---------------------------------------------|
| Completeness to theta = 30.03° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9257 and 0.7988 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 11416 / 101 / 457 |
| Goodness-of-fit on F ² | 1.016 |
| Final R indices [I>2sigma(I)] | R1 = 0.0319, wR2 = 0.0659 |
| R indices (all data) | R1 = 0.0529, wR2 = 0.0733 |
| Largest diff. peak and hole | 0.473 and -0.785 e.Å ⁻³ |

Table 2. Crystal data and structure refinement for 7.

| | | |
|---------------------------------|--------------------------------------------------------|-----------------|
| Identification code | x11058 | |
| Empirical formula | C ₄₁ H ₆₂ Br O ₂ P Pd | |
| Formula weight | 804.19 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | <i>P</i> -1 | |
| Unit cell dimensions | a = 11.7544(10) Å | a = 75.412(2)°. |
| | b = 11.9376(10) Å | b = 71.071(2)°. |
| | c = 16.5466(14) Å | g = 62.967(2)°. |
| Volume | 1941.2(3) Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.376 Mg/m ³ | |
| Absorption coefficient | 1.581 mm ⁻¹ | |
| F(000) | 840 | |
| Crystal size | 0.15 x 0.10 x 0.05 mm ³ | |
| Theta range for data collection | 1.31 to 30.31°. | |
| Index ranges | -16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23 | |
| Reflections collected | 85025 | |
| Independent reflections | 11637 [R(int) = 0.0373] | |
| Completeness to theta = 30.31° | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9251 and 0.7974 | |
| Refinement method | Full-matrix least-squares on F ² | |

| | |
|--------------------------------------|---------------------------------------|
| Data / restraints / parameters | 11637 / 0 / 440 |
| Goodness-of-fit on F^2 | 1.030 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0264$, $wR2 = 0.0602$ |
| R indices (all data) | $R1 = 0.0336$, $wR2 = 0.0628$ |
| Largest diff. peak and hole | 0.739 and -0.525 e. \AA^{-3} |

Table 3. Crystal data and structure refinement for 8.

| | | |
|----------------------------------------|--------------------------------------------------------------------|------------------|
| Identification code | 11148 | |
| Empirical formula | $C_{51} H_{74} Br O_2 P Pd$ | |
| Formula weight | 936.38 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 \AA | |
| Crystal system | Orthorhombic | |
| Space group | $Pbca$ | |
| Unit cell dimensions | $a = 19.9808(17) \text{\AA}$ | $a = 90^\circ$. |
| | $b = 20.8738(18) \text{\AA}$ | $b = 90^\circ$. |
| | $c = 22.375(2) \text{\AA}$ | $c = 90^\circ$. |
| Volume | $9331.9(14) \text{\AA}^3$ | |
| Z | 8 | |
| Density (calculated) | 1.333 Mg/m^3 | |
| Absorption coefficient | 1.326 mm^{-1} | |
| F(000) | 3936 | |
| Crystal size | $0.30 \times 0.20 \times 0.15 \text{ mm}^3$ | |
| Theta range for data collection | 1.68 to 30.32° . | |
| Index ranges | $-28 \leq h \leq 28$, $-29 \leq k \leq 29$, $-31 \leq l \leq 31$ | |
| Reflections collected | 251395 | |
| Independent reflections | 13999 [$R(\text{int}) = 0.0629$] | |
| Completeness to $\theta = 30.32^\circ$ | 100.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.8259 and 0.6918 | |
| Refinement method | Full-matrix least-squares on F^2 | |
| Data / restraints / parameters | 13999 / 0 / 521 | |
| Goodness-of-fit on F^2 | 1.046 | |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0433$, $wR2 = 0.1083$ | |
| R indices (all data) | $R1 = 0.0550$, $wR2 = 0.1148$ | |

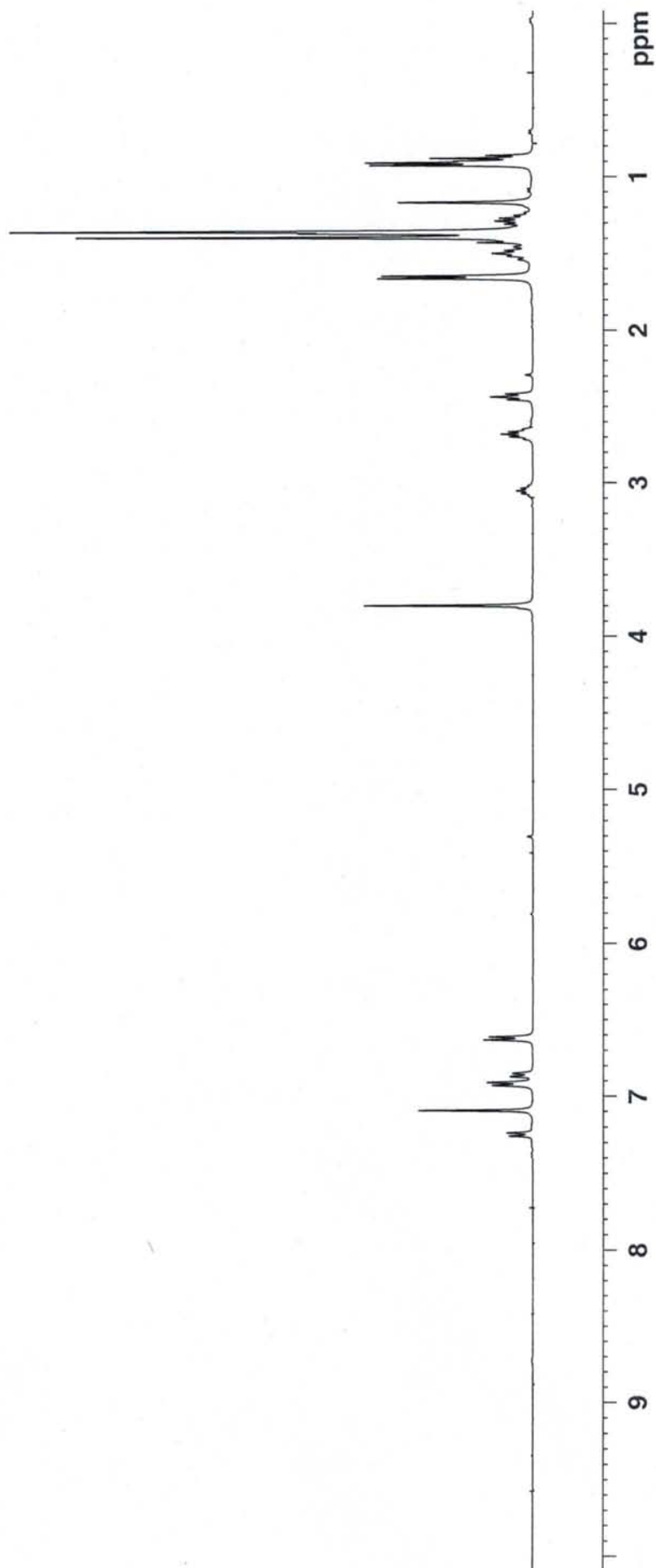
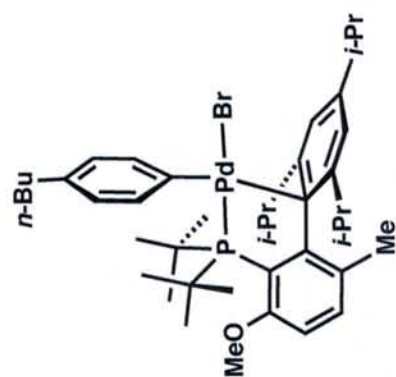
Largest diff. peak and hole 2.924 and -1.201 e.Å⁻³

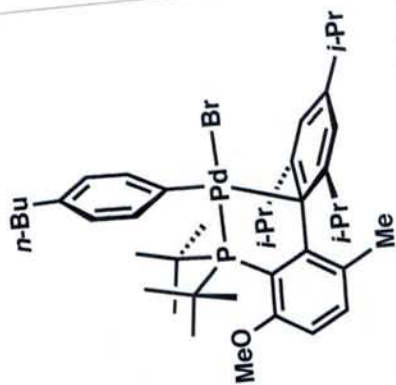
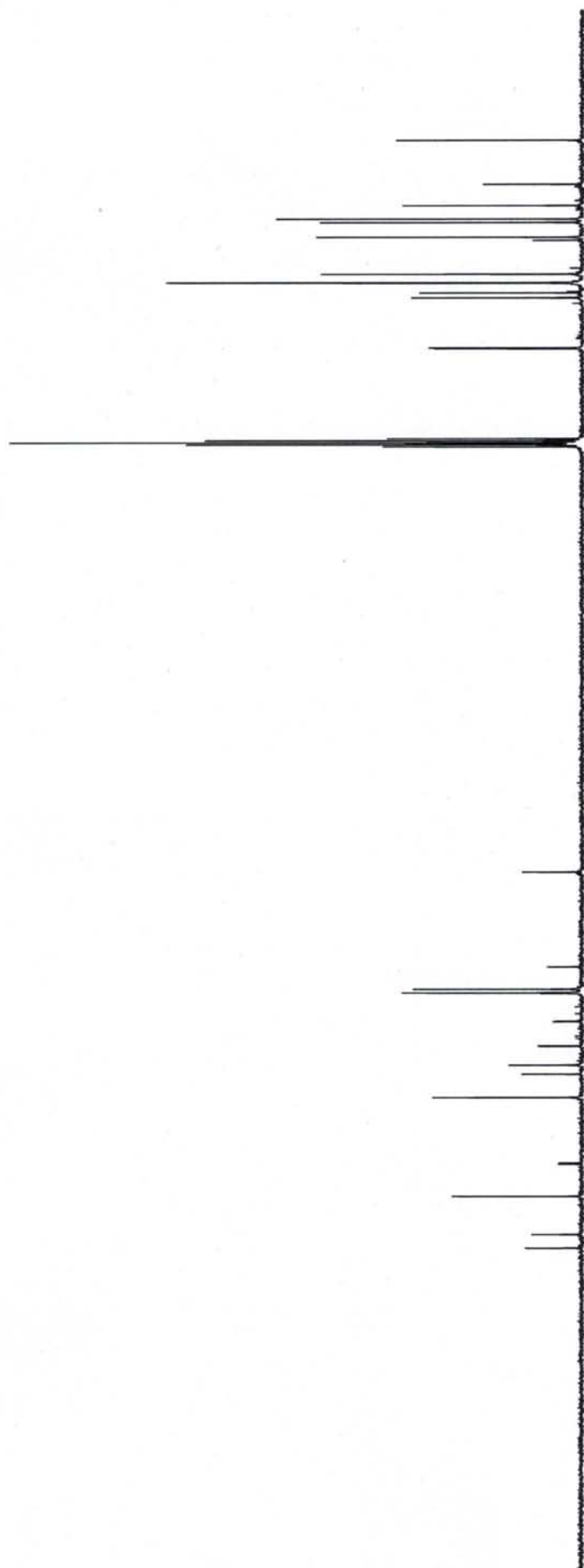
Table 4. Crystal data and structure refinement for 9.

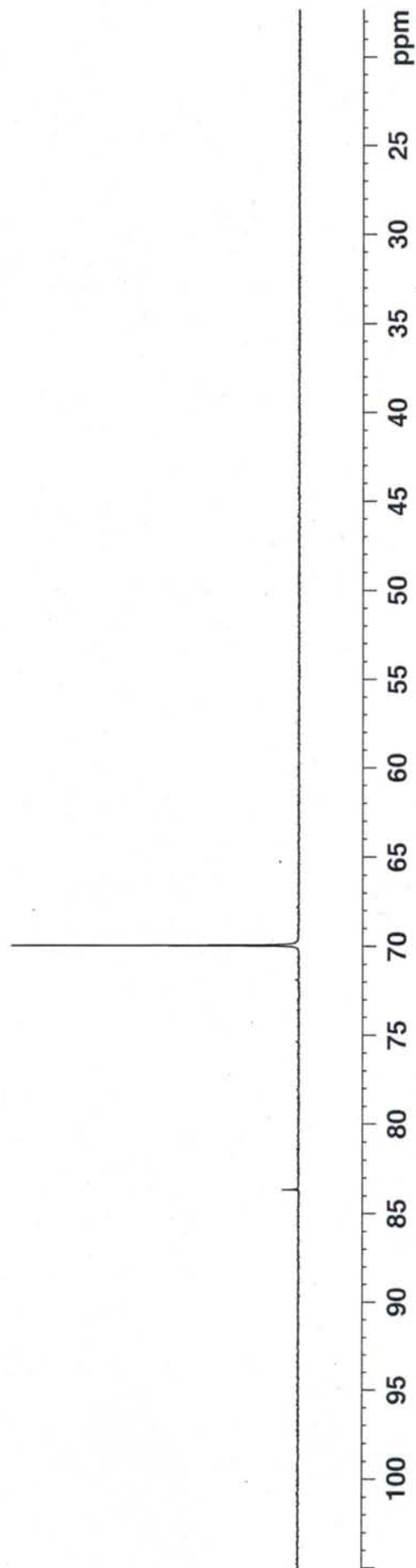
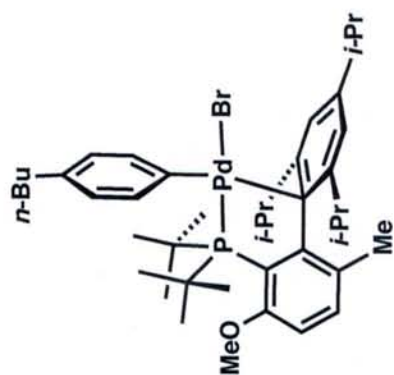
| | | |
|-----------------------------------|---------------------------------------------|------------------|
| Identification code | x11088 | |
| Empirical formula | C ₄₁ H ₆₁ O P | |
| Formula weight | 600.87 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | <i>P</i> -1 | |
| Unit cell dimensions | a = 10.633(4) Å | a = 107.083(7)°. |
| | b = 11.053(4) Å | b = 102.721(8)°. |
| | c = 16.941(6) Å | g = 96.416(10)°. |
| Volume | 1822.8(12) Å ³ | |
| Z | 2 | |
| Density (calculated) | 1.095 Mg/m ³ | |
| Absorption coefficient | 0.104 mm ⁻¹ | |
| F(000) | 660 | |
| Crystal size | 0.15 x 0.10 x 0.10 mm ³ | |
| Theta range for data collection | 1.30 to 30.03°. | |
| Index ranges | -14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23 | |
| Reflections collected | 77306 | |
| Independent reflections | 10657 [R(int) = 0.0590] | |
| Completeness to theta = 30.03° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9896 and 0.9845 | |
| Refinement method | Full-matrix least-squares on F ² | |
| Data / restraints / parameters | 10657 / 0 / 403 | |
| Goodness-of-fit on F ² | 1.049 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0464, wR2 = 0.1112 | |
| R indices (all data) | R1 = 0.0674, wR2 = 0.1233 | |
| Largest diff. peak and hole | 0.635 and -0.283 e.Å ⁻³ | |

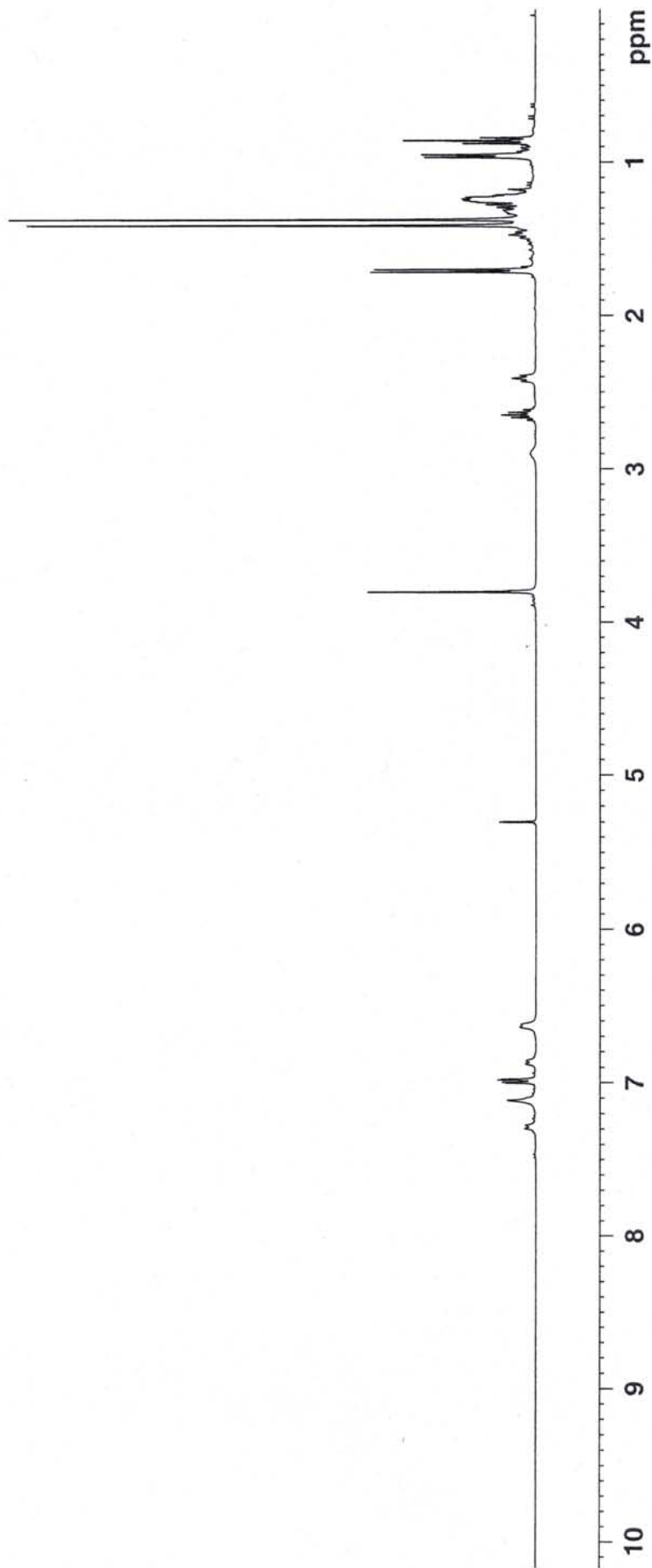
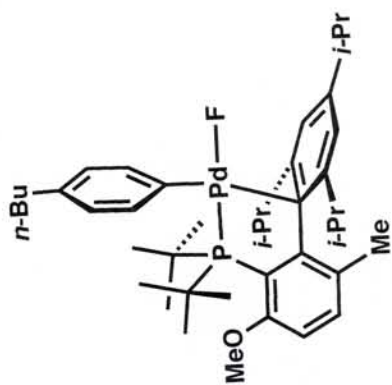
References

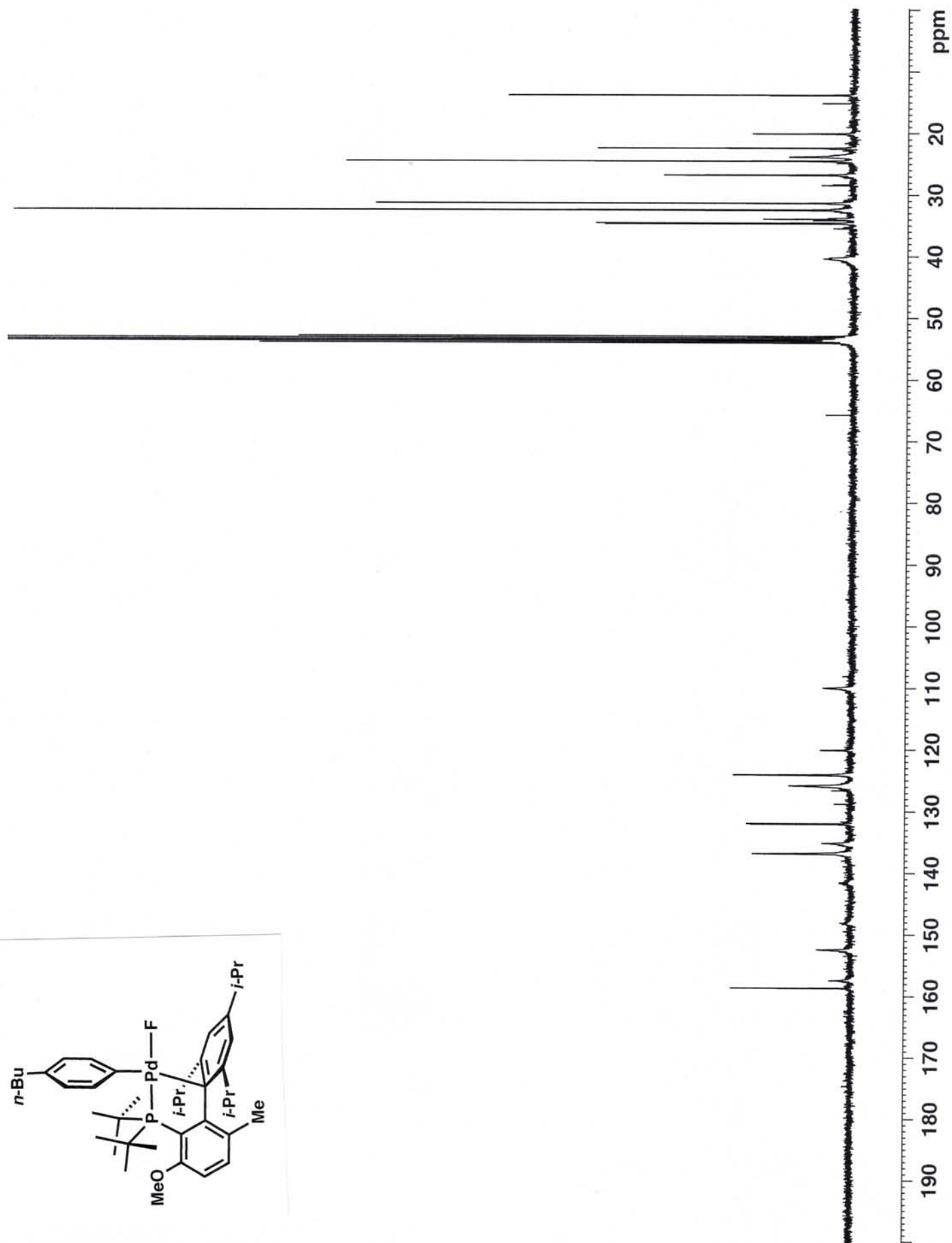
- (1) Fors, B. P.; Dooleweerd, K.; Zeng, Q.; Buchwald, S. L. *Tetrahedron* **2009**, *65*, 6576-6583.
- (2) Wu, X.; Fors, B. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 9943.
- (3) Sheldrick, G. M. *Acta Cryst.* **1990**, A46, 467-473.
- (4) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.
- (5) Müller, P. *Crystallography Reviews* **2009**, *15*, 57-83.

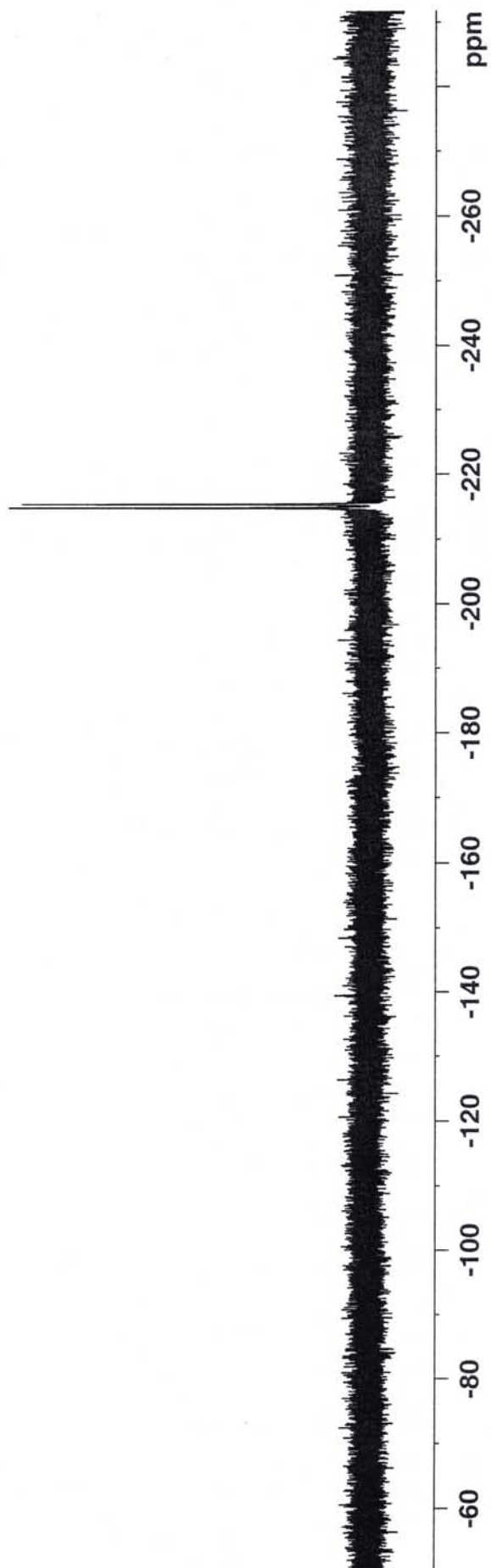
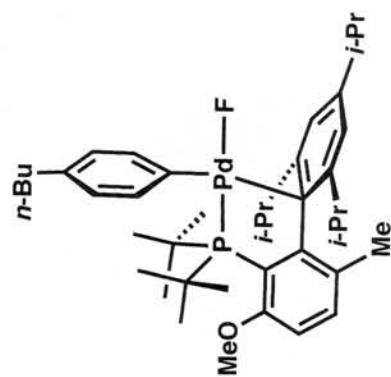


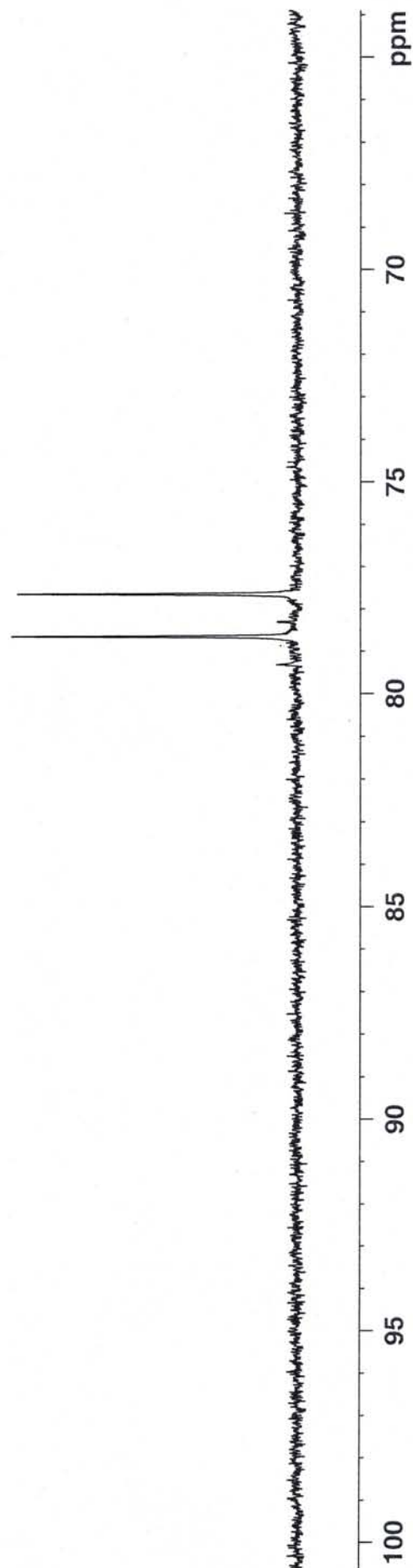
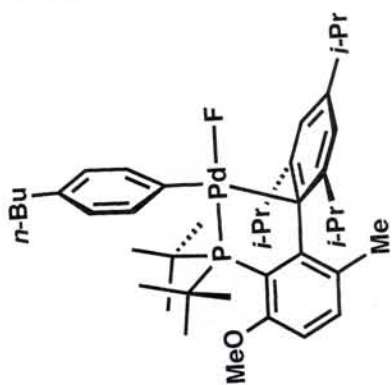


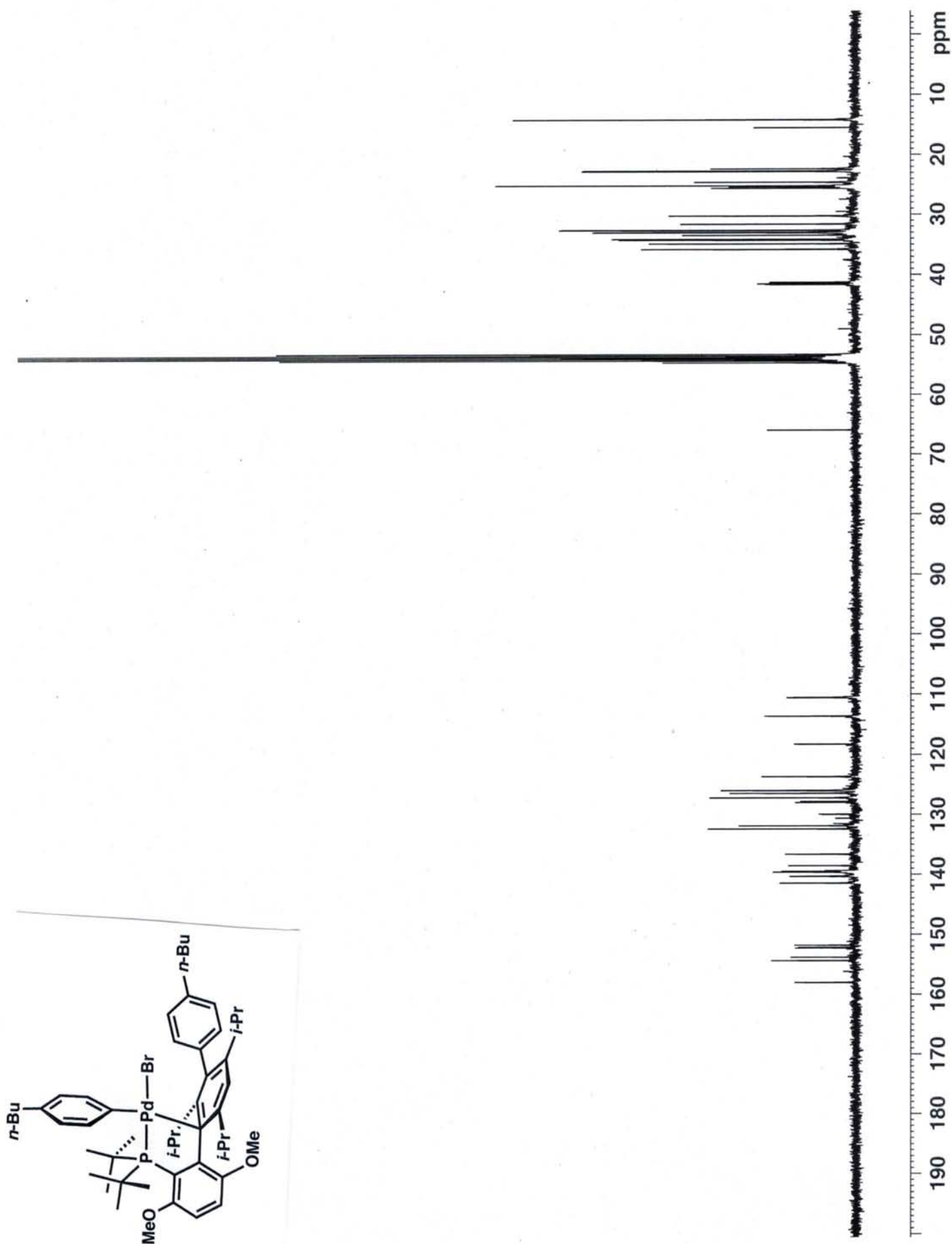


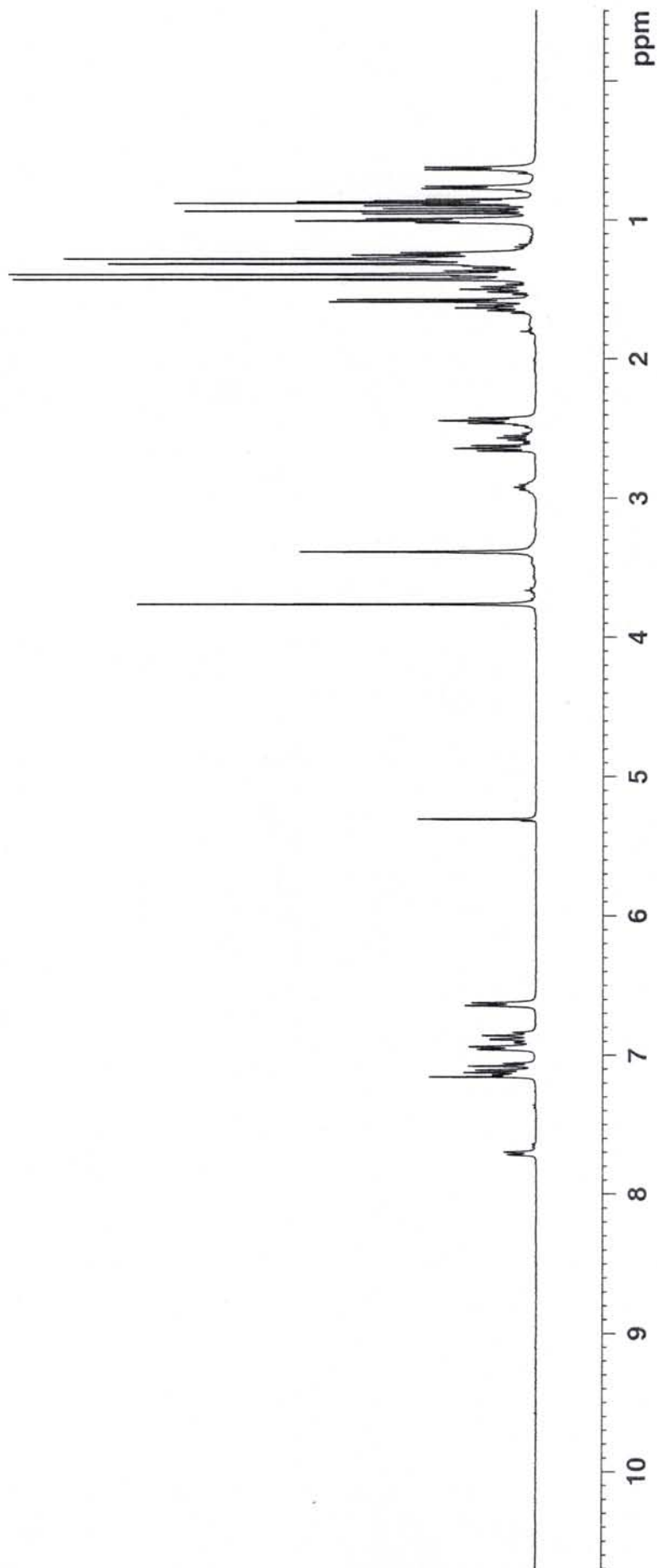
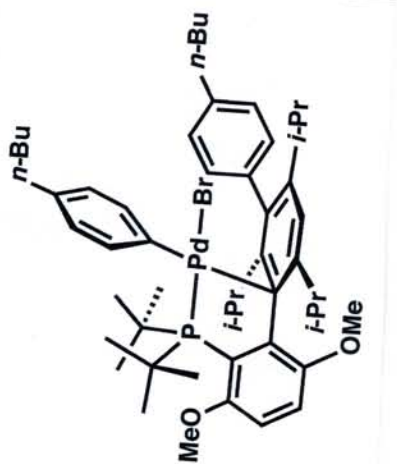


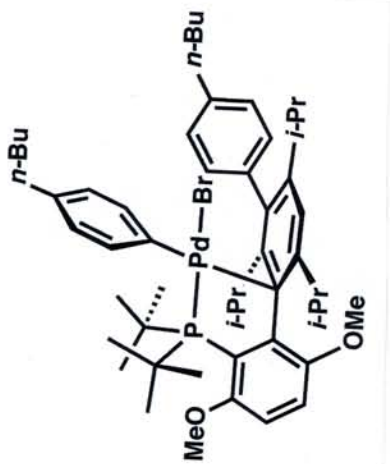


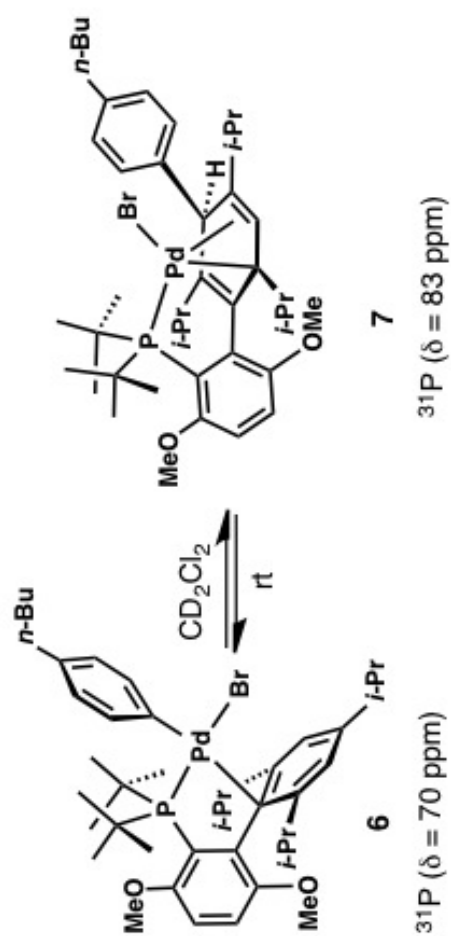




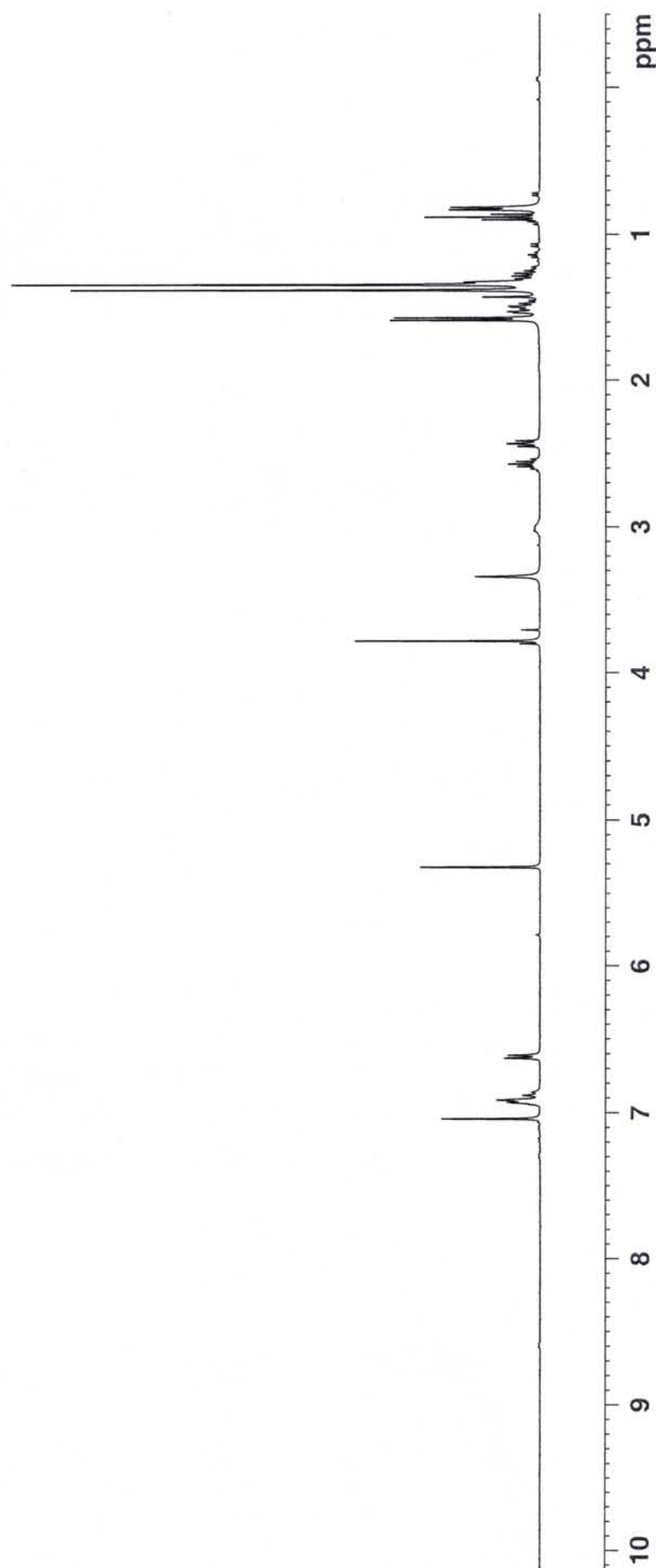


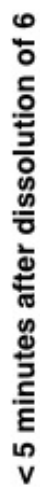


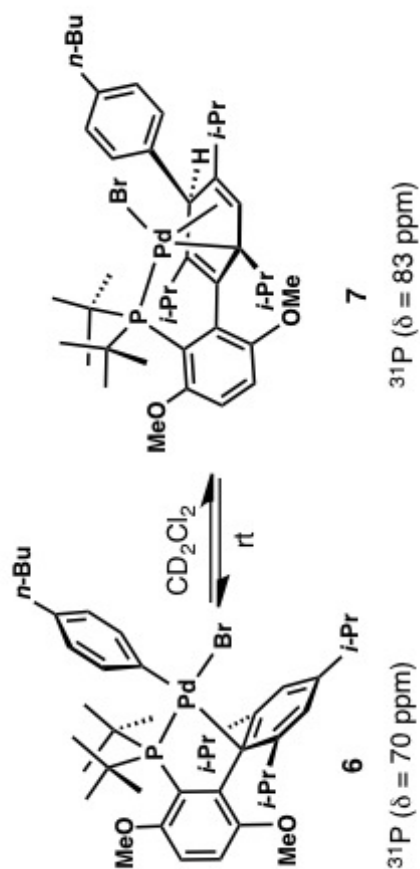




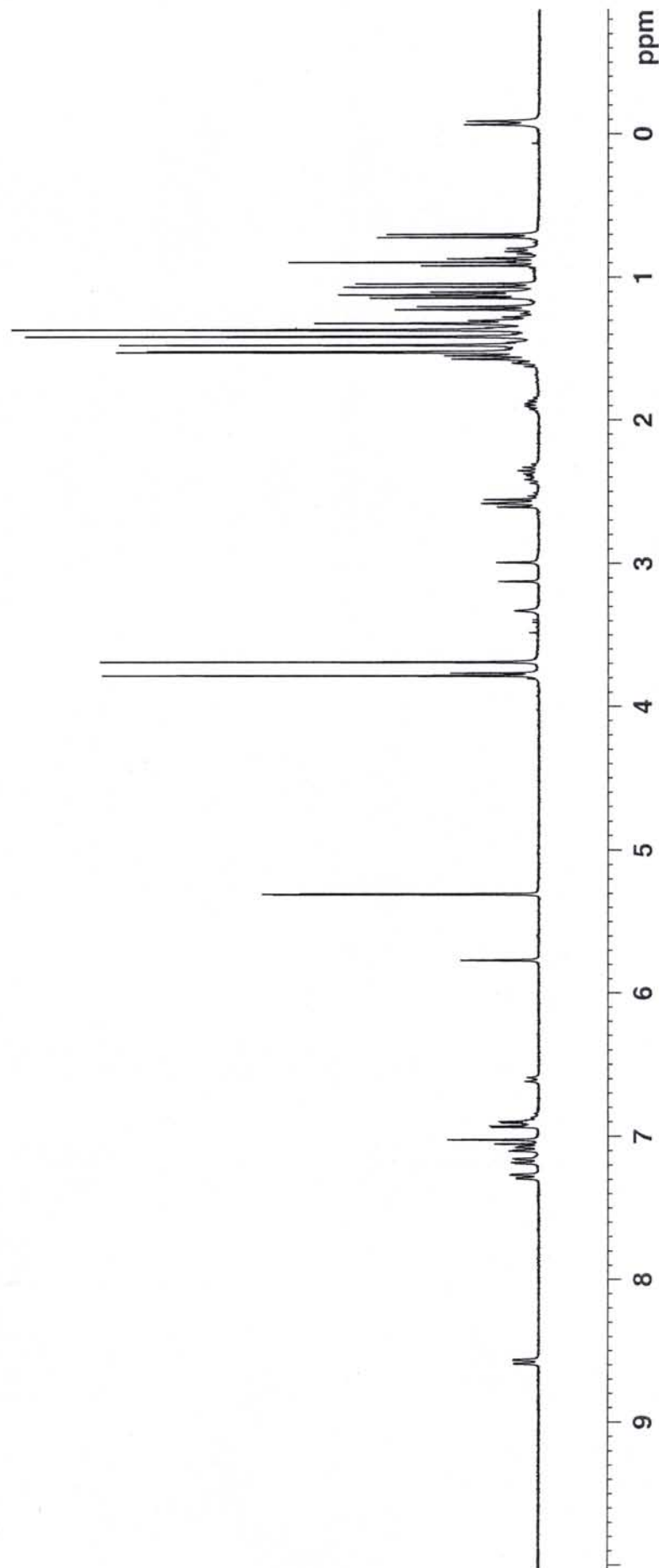
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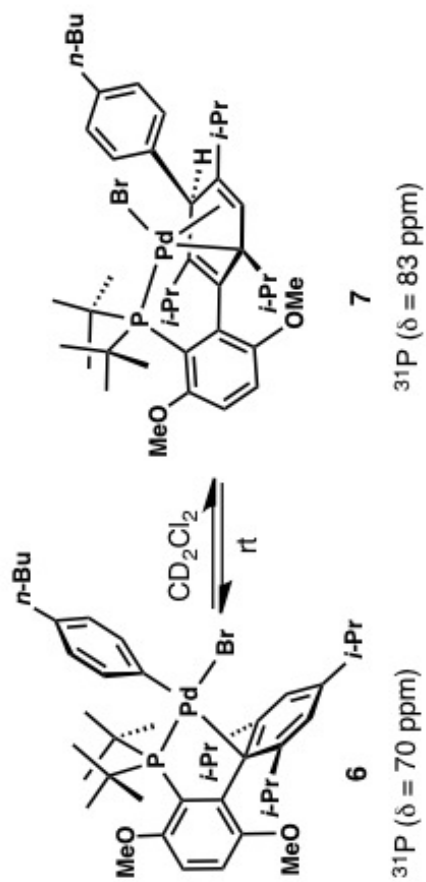




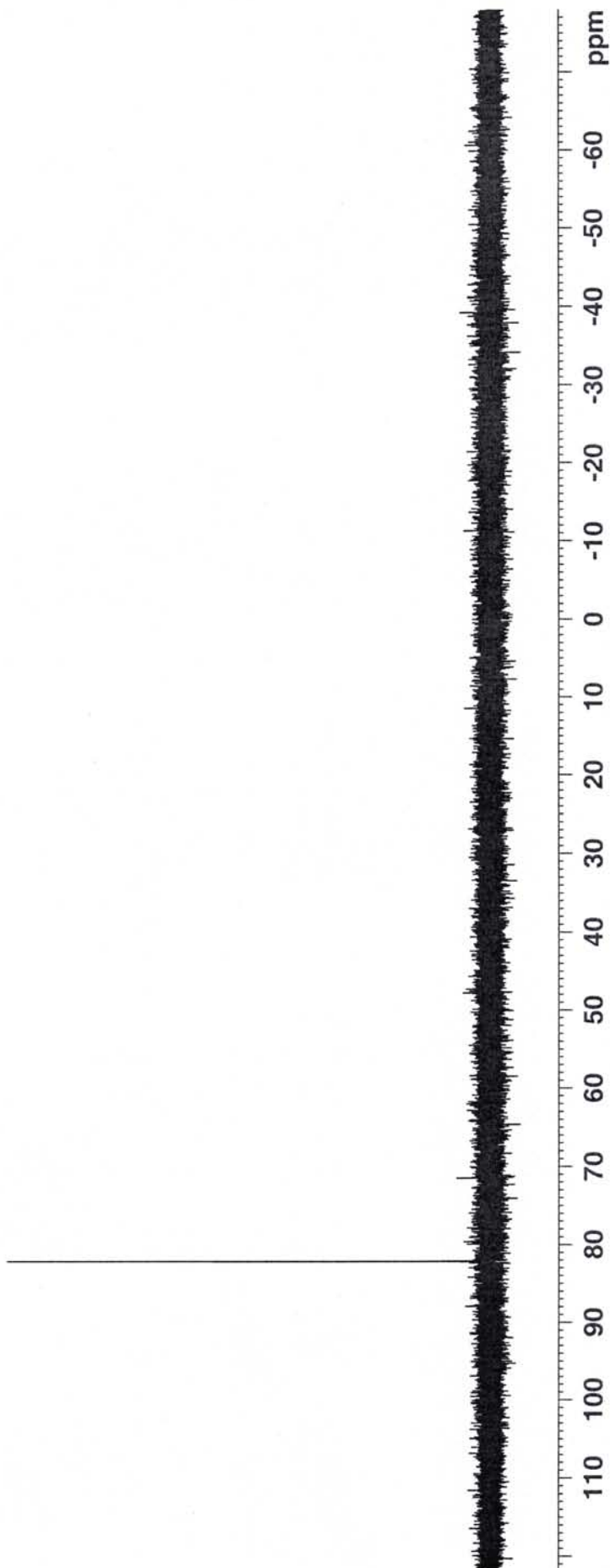


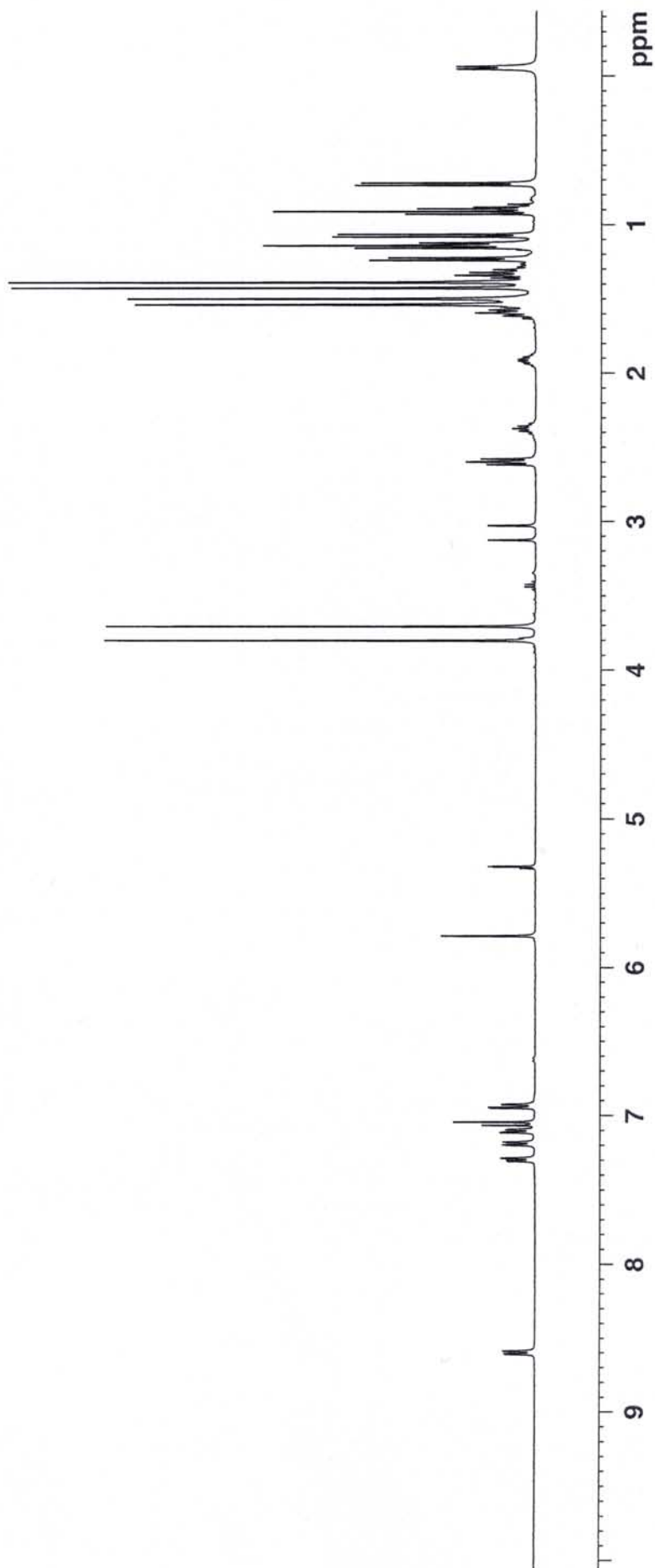
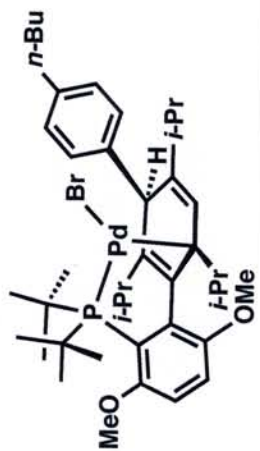
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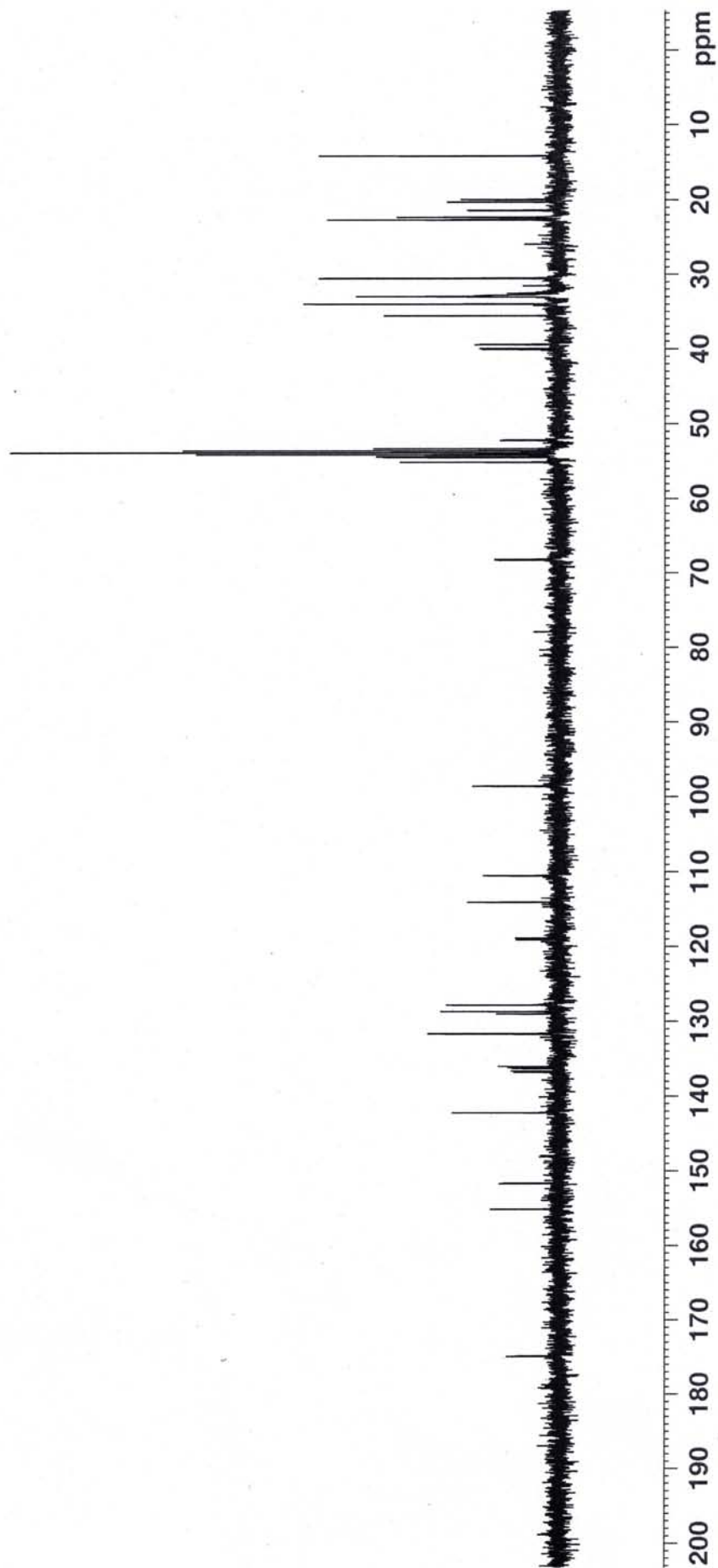
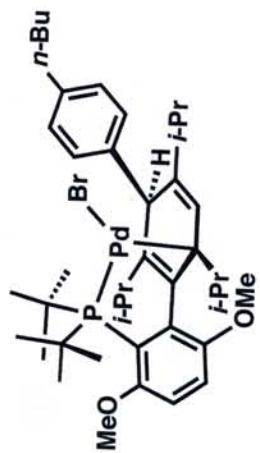


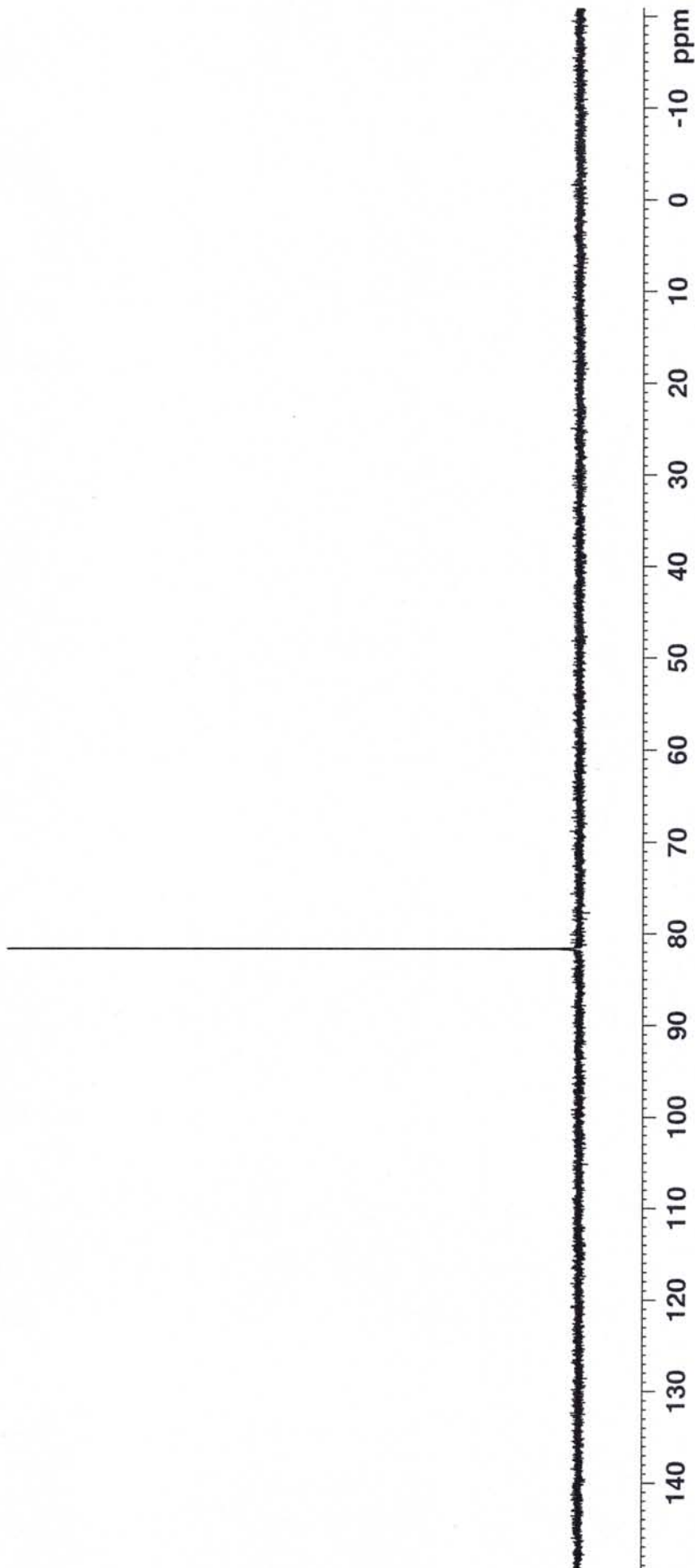
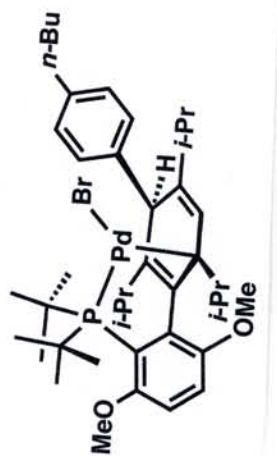


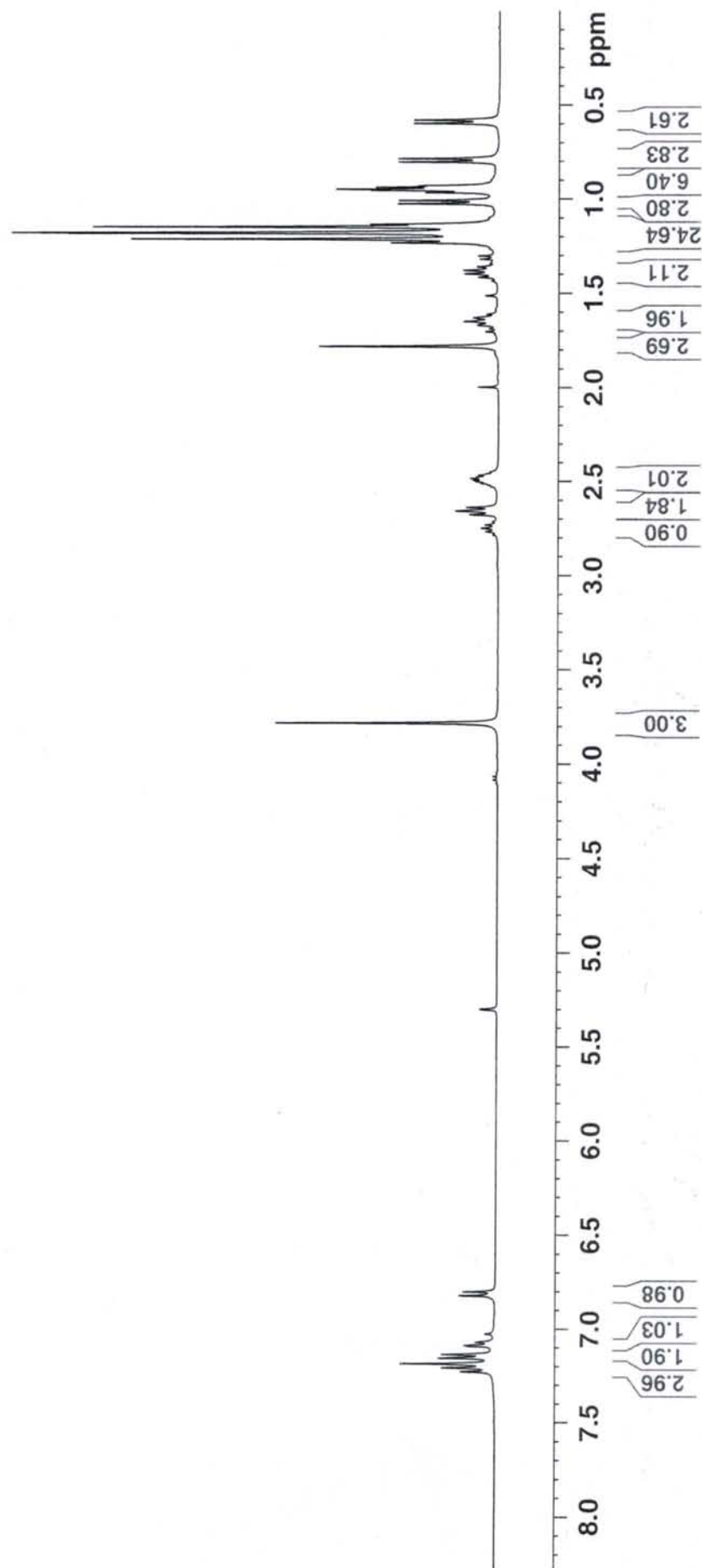
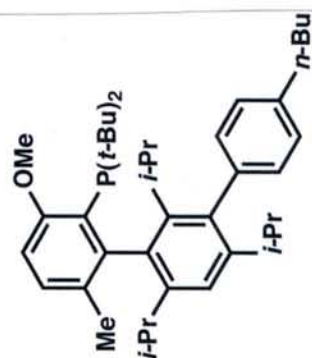
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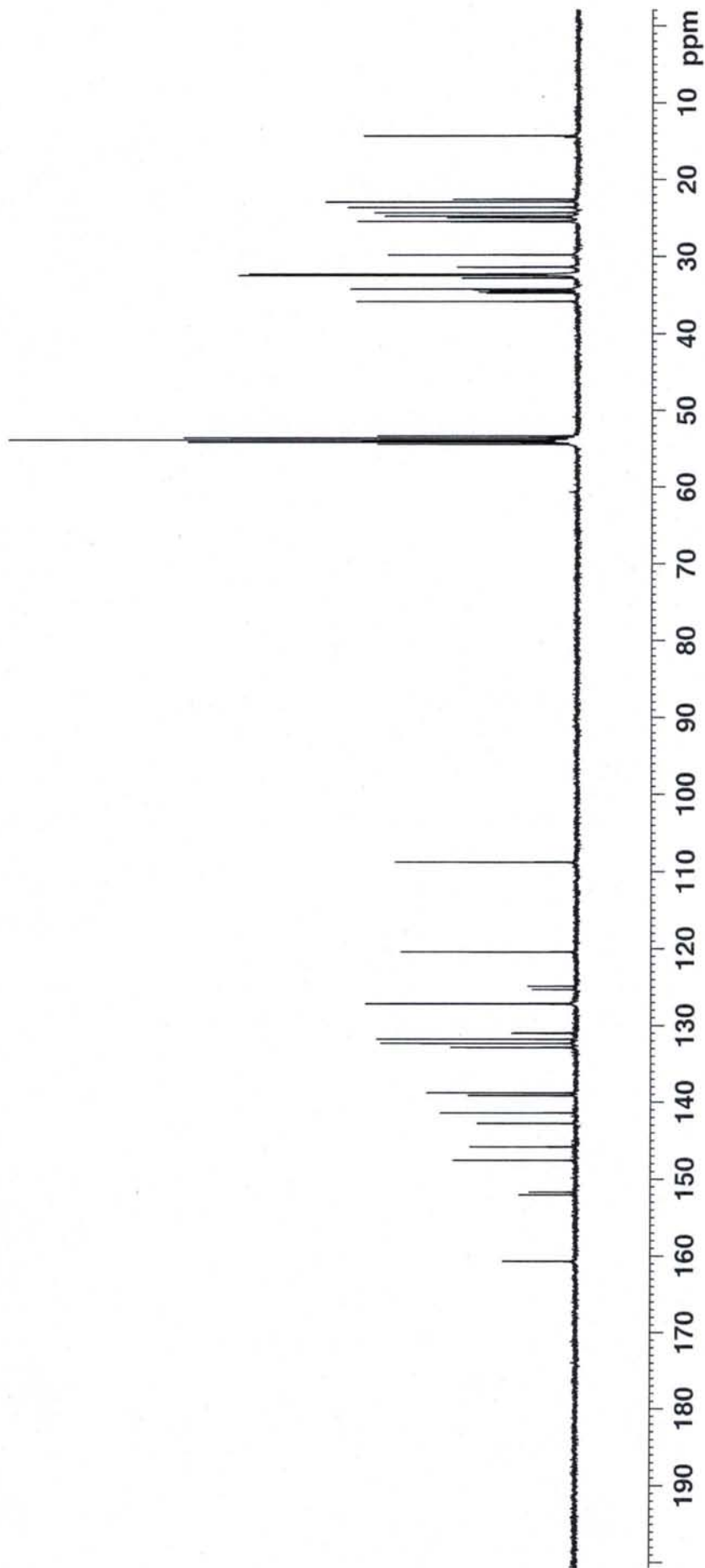
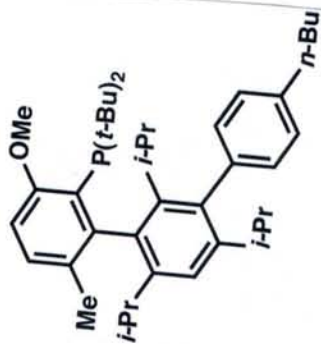


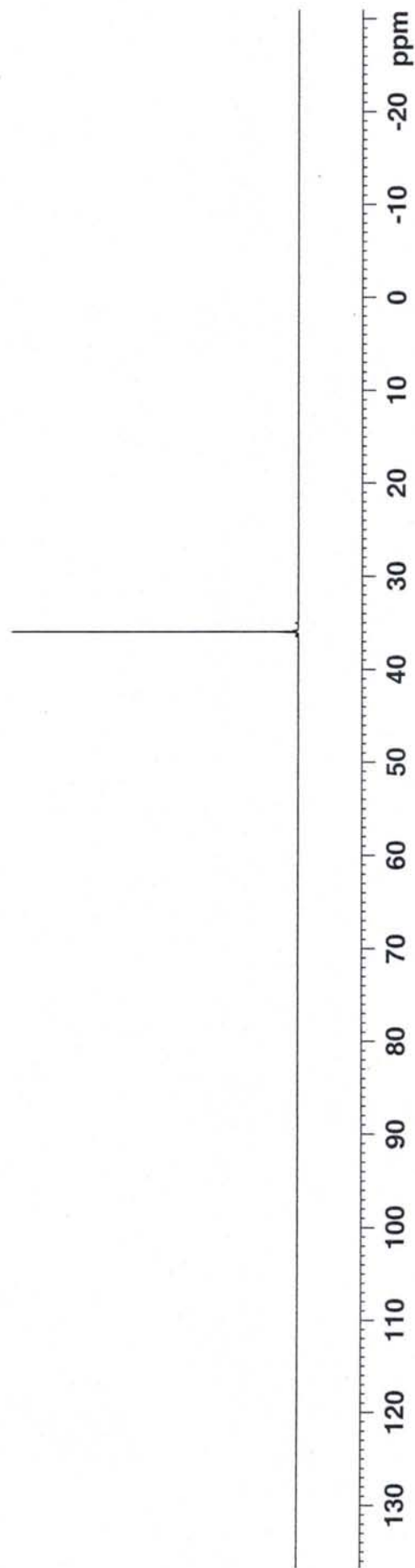
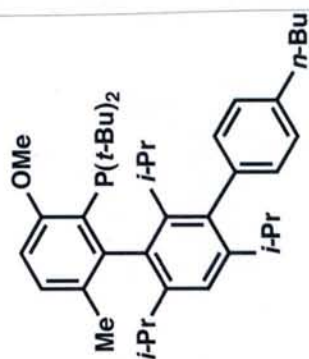


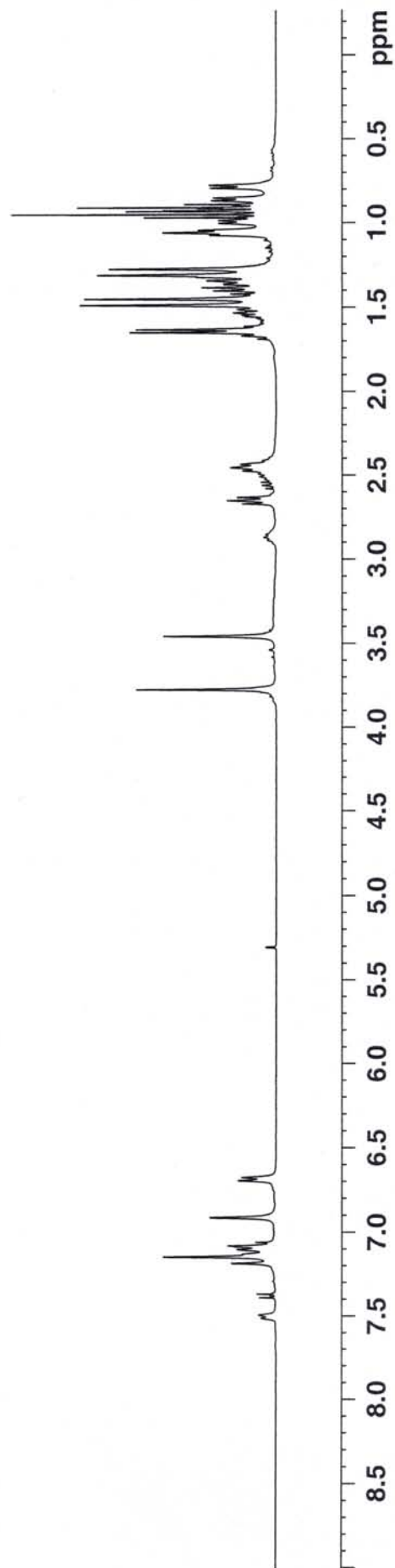
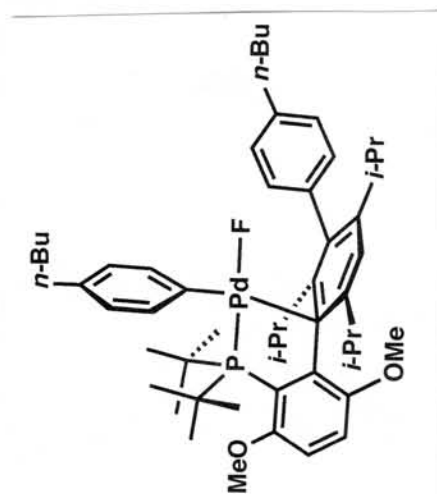


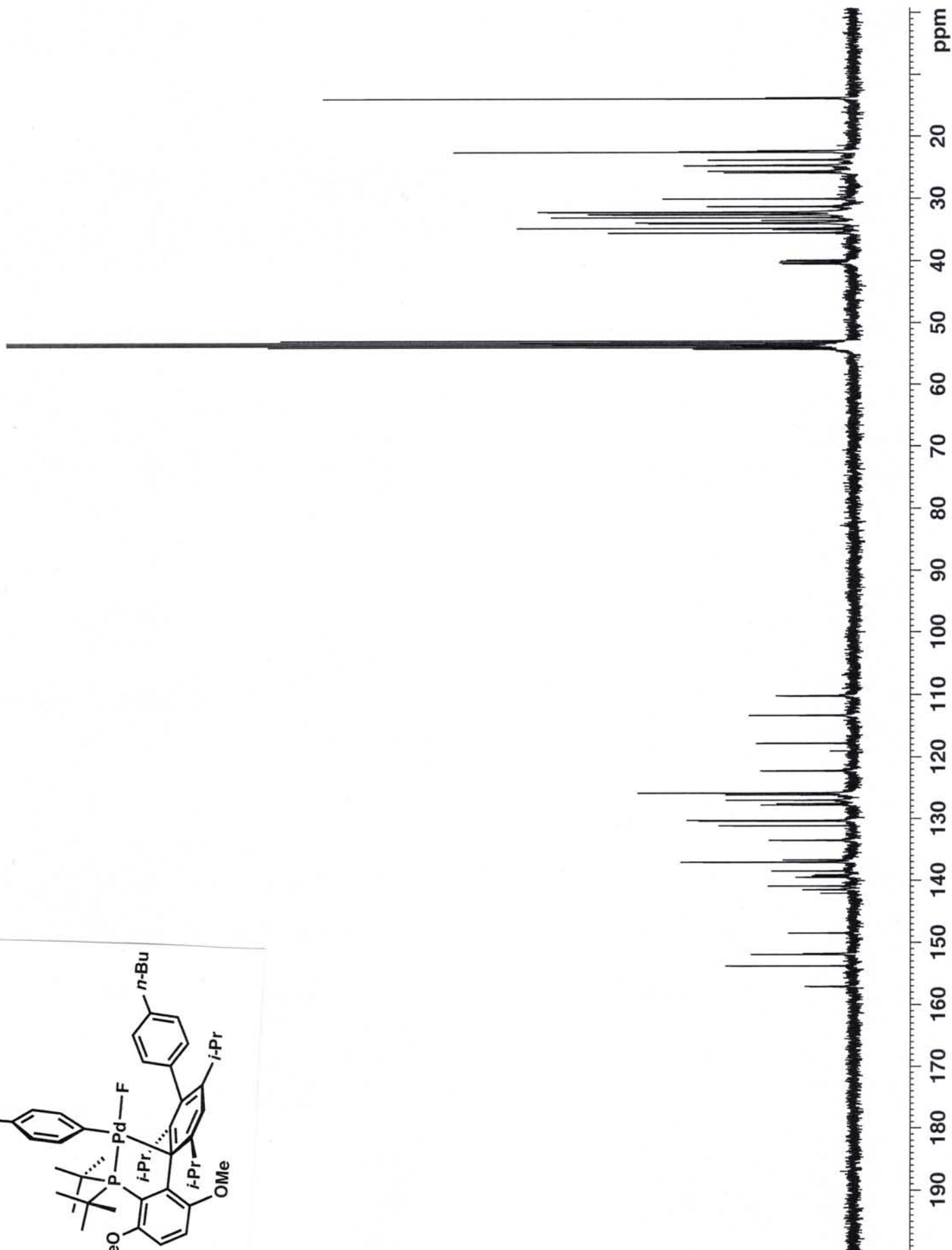
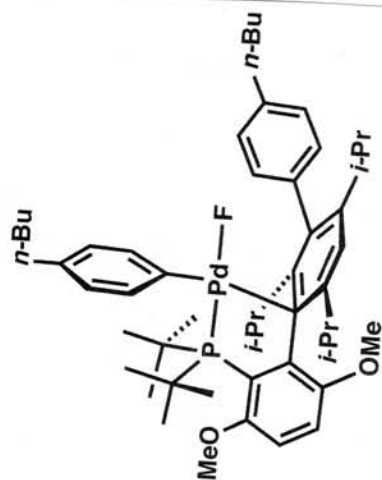


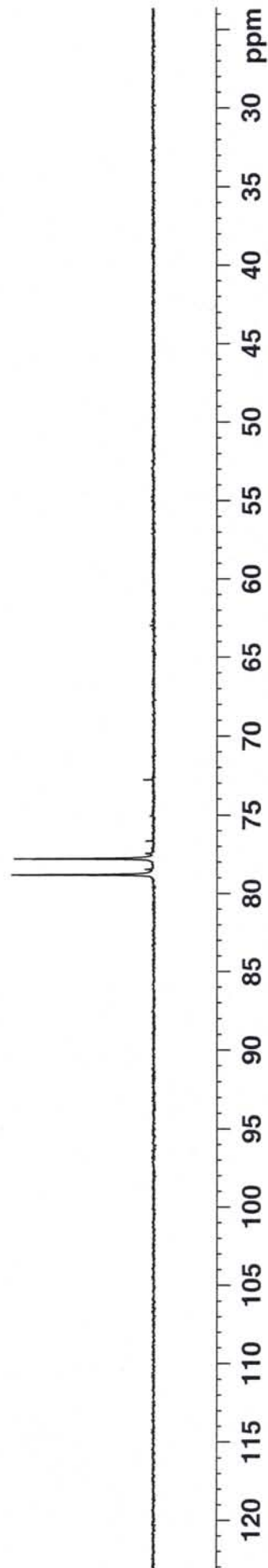
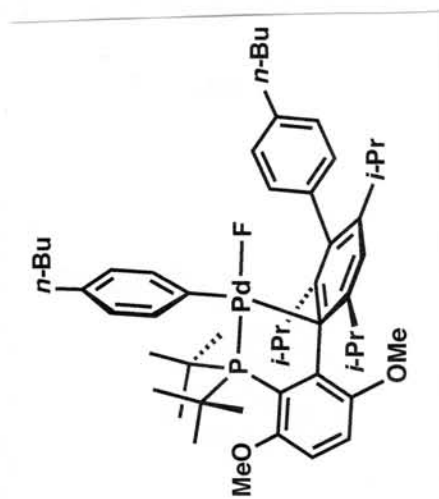












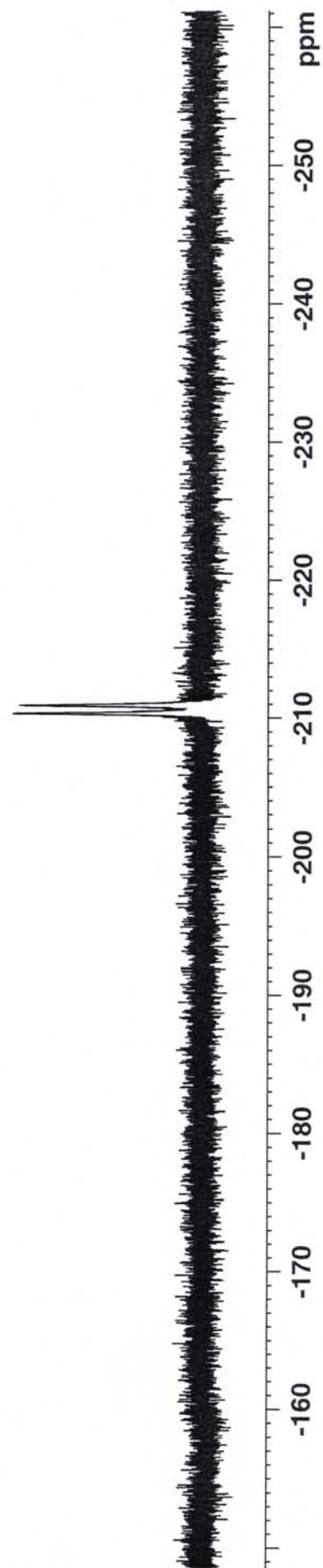
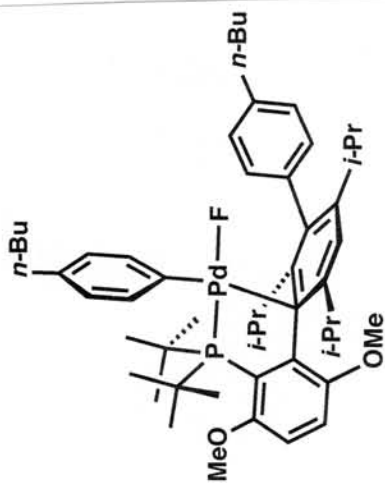


Figure 9. Fate of ligand (**3**) after failed thermolysis experiments (free phosphine region shown)

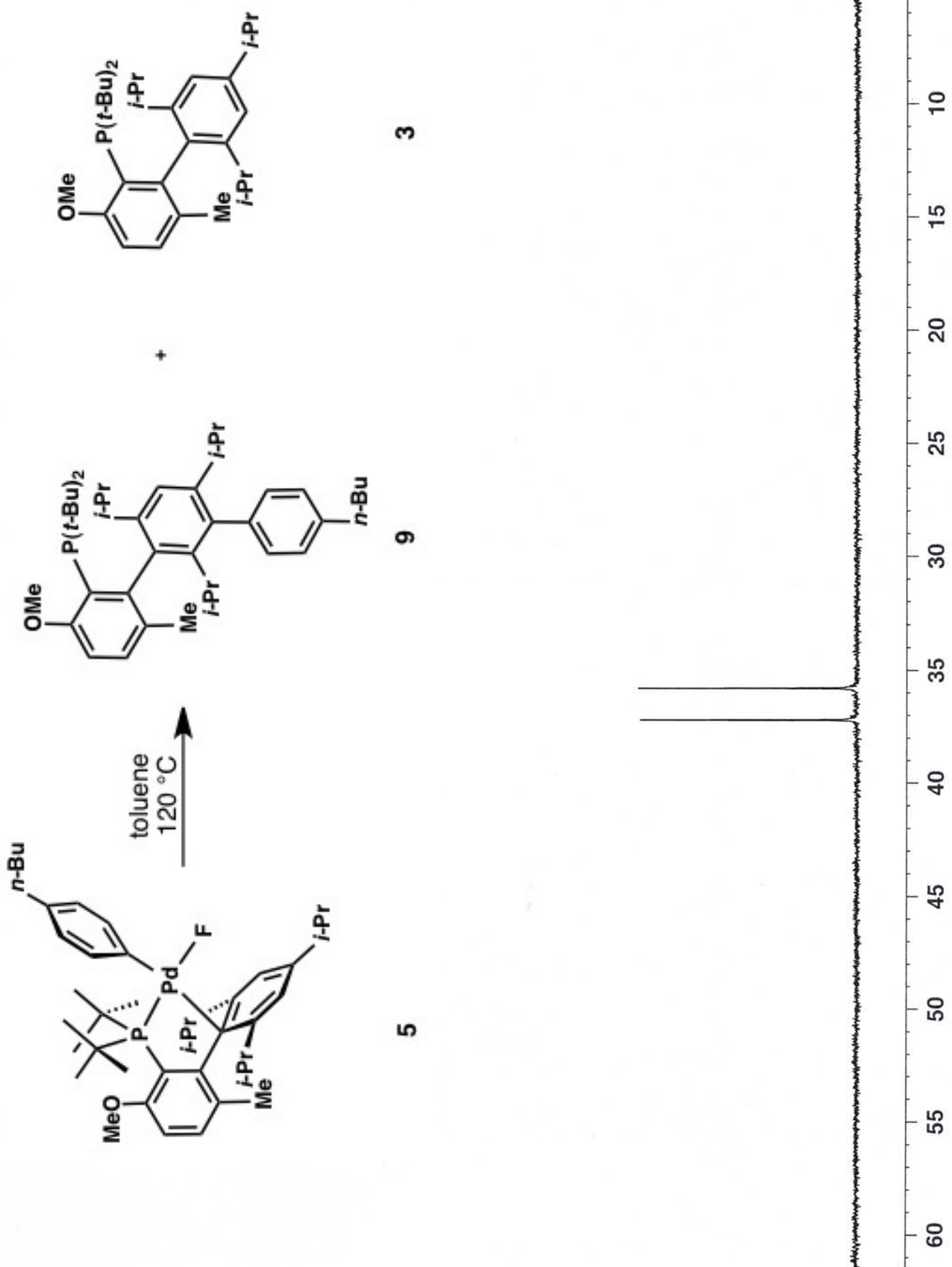


Figure 9. Fate of ligand (**3**) after failed thermolysis experiments (free phosphine region shown)

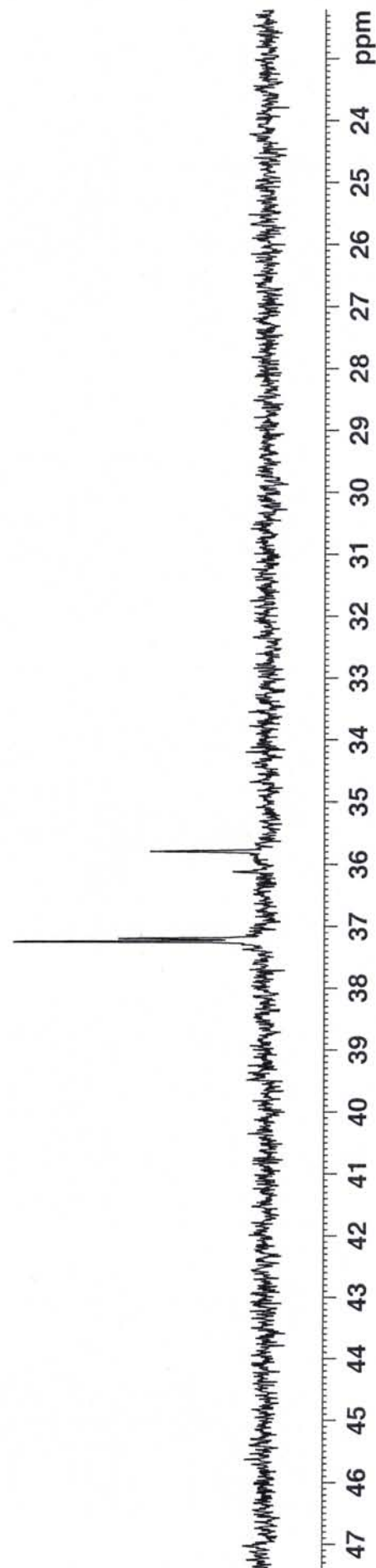
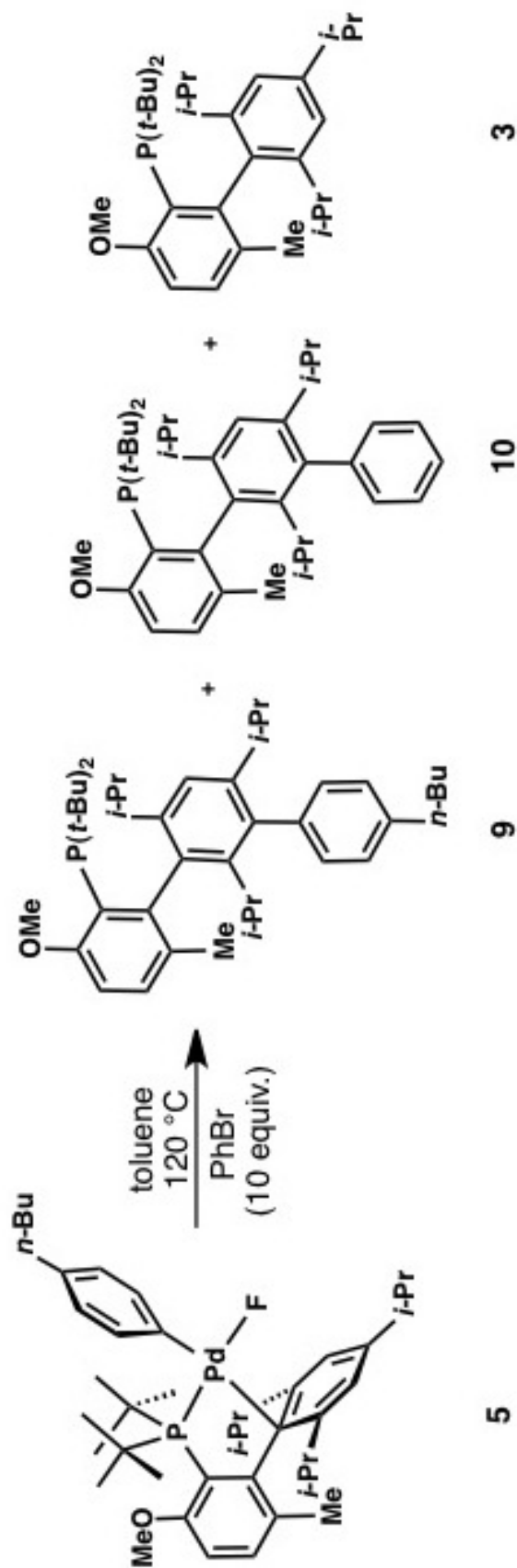
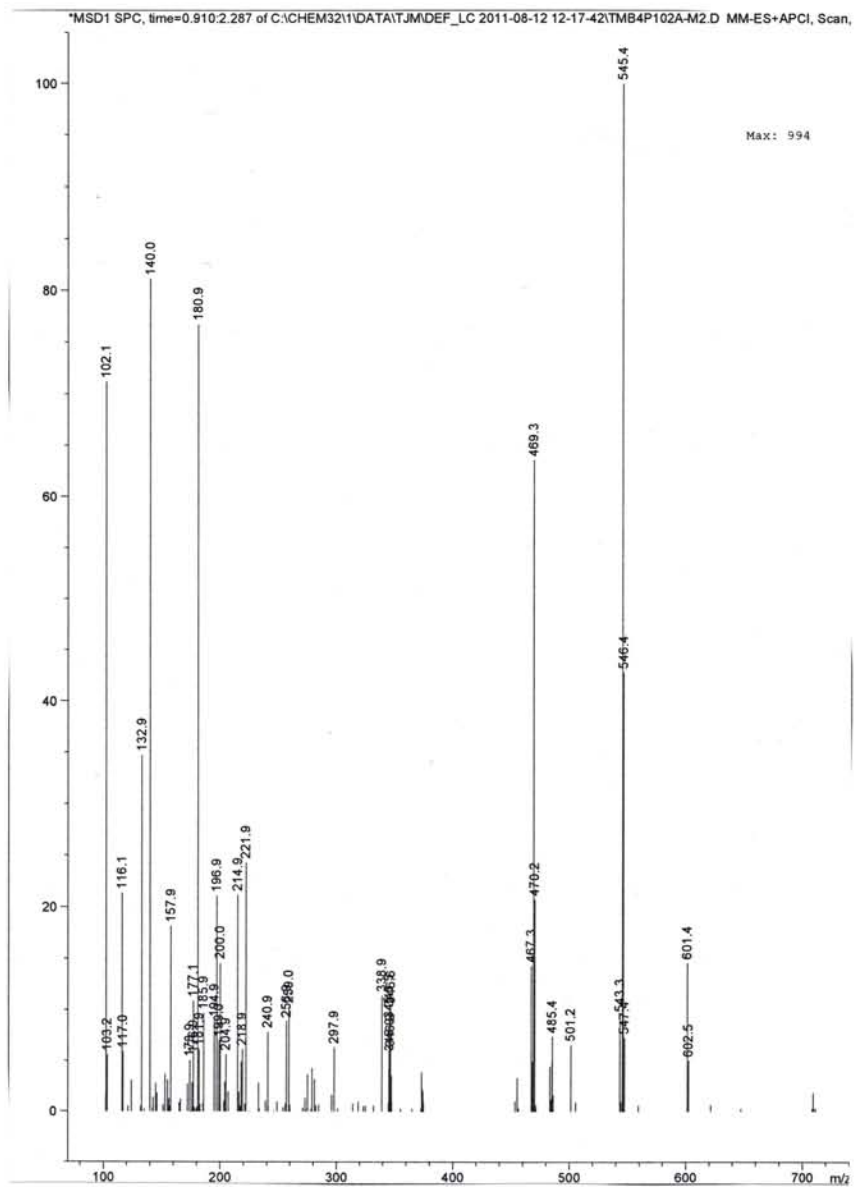
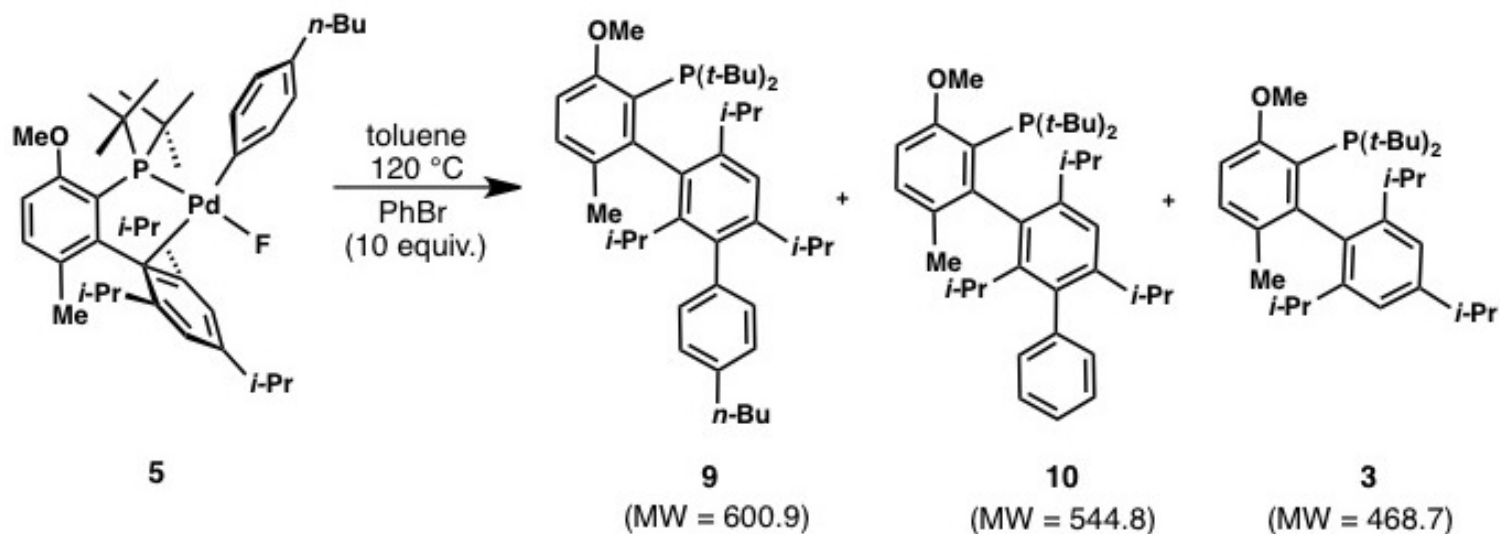
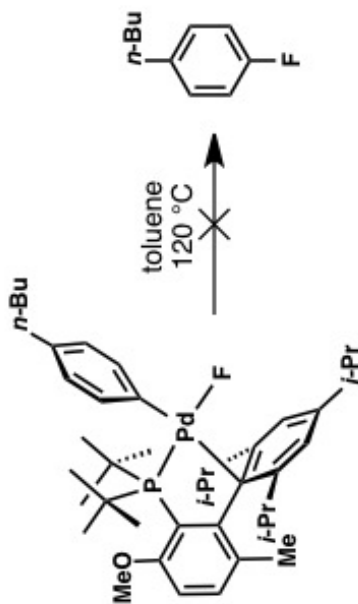


Figure 9. Fate of ligand (**3**) after failed thermolysis experiments (LC-MS detection of **3**, **9**, **10**)

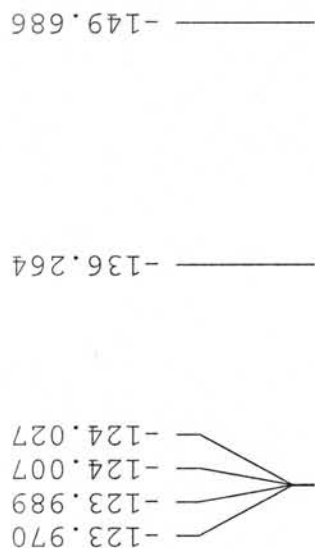


^{19}F NMR analysis of a crude thermolysis experiment of complex **5**
 (The peak at -124 ppm is the internal standard (1-fluoronaphthalene))

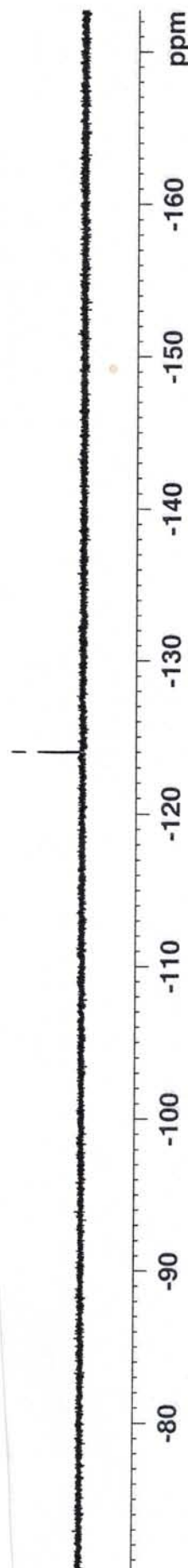


5

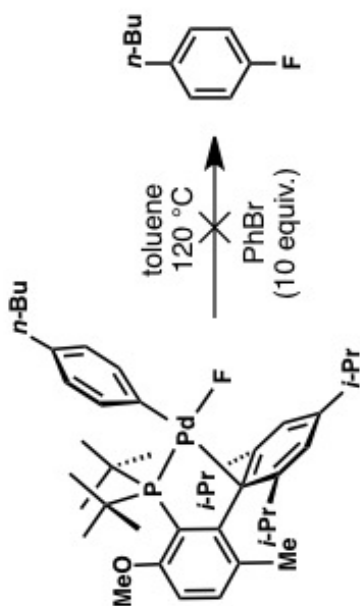
Before addition of Et_3N :



After addition of Et_3N :

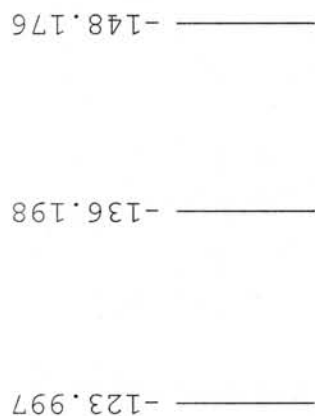


^{19}F NMR analysis of a crude thermolysis experiment of complex **5**
 (The peak at -124 ppm is the internal standard (1-fluoronaphthalene))



5

Before addition of Et_3N :



After addition of Et_3N :

