Nickel-Mediated Hydrogenolysis of C-O Bonds of Aryl Ethers: What Is the Source of the Hydrogen?

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Supporting Information

I. Experimental Details

General considerations: Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs' method.[1] Benzene-d_6 was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. Chloroform-*d* was also purchased from Cambridge Isotope Laboratories and vacuum distilled from calcium hydride. Alumina and Celite were activated by heating under vacuum at 200 °C for 12 h. 4-(tert-butyl)-2,6-diiodophenol, 5-(tert-butyl)-1,3-diiodo-2-methoxybenzene, its isotopolog with a deuterated methoxy ether, 2,6-diiodo-4-nitrophenol, 1,3-diiodo-2-methoxy-5-nitrobenzene, and its isotopolog with a deuterated methoxy ether were synthesized following literature procedures[2-5]. All other materials were used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at ambient temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C$_6$D$_6$) and 7.26 ppm and 77.16 ppm (CDCl$_3$) for ^{1}H and ^{13}C NMR data, respectively. ^{31}P NMR chemical shifts are reported with respect to the instrument solvent lock when a deuterated solvent was used. IR spectra were recorded on a Thermo-Fisher Scientific Nicolet 6700 FT-IR spectrometer. Gas chromatography-mass spectrometry (GC-MS) analysis was performed upon filtering the sample through a plug of silica gel. Fast atom bombardment-mass spectrometry (FAB-MS) analysis was performed with a JEOL JMS-600H high resolution mass spectrometer. Elemental analysis was conducted by Midwest Microlab, LLC (Indianapolis, IN). In the following complexes, the carbons of the terphenyl backbone are assigned using the following scheme:
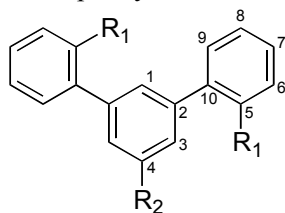
Synthesis of bis(2'-bromophenyl)-4-tert-butyl-2-methoxybenzene.
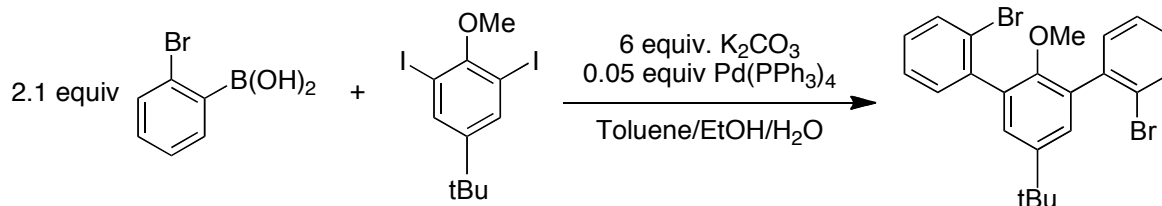
Suzuki coupling conditions were adapted from a previously published procedure.[6] 5-(tert-butyl)-1,3-diiodo-2-methoxybenzene (2.48 g, 6.58 mmol, 1 equiv), 2-bromo-phenylboronic acid (2.77 g, 13.80 mmol, 2.1 equiv), K$_2$CO$_3$ (5.46 g, 39.47 mmol, 6 equiv), 140 mL toluene, 40 mL ethanol, and 40 mL water were added to a 500 mL Schlenk tube fitted with a screw-in Teflon stopper. The mixture was degassed by three freeze-pump-thaw cycles, after which Pd(PPh$_3$)$_4$ (380 mg, 0.38 mmol, 0.05 equiv) was added as a solid with a counterflow of nitrogen. The reaction vessel was then placed in an oil bath pre-heated to 65°C. After stirring for 12 h, the reaction mixture was allowed to cool to room temperature, concentrated via rotary evaporation and diluted with 200 mL H$_2$O. The solution was extracted with three portions of CH$_2$Cl$_2$. The combined organic fractions were dried over MgSO$_4$, filtered and concentrated via rotary evaporation. The product (Kugelrohr, 10 mTorr, 200°C) was then distilled from biphenyl impurities (Kugelrohr, 10 mTorr, 90°C) to afford 2.48 g (79% yield, 5.22 mmol) of the desired terphenyl dibromide as a white solid. ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 7.69 (d, 2H, Ar-H_6), 7.46 (d, 2H, Ar-H_9), 7.35 (t, 2H, Ar-H_7), 7.29 (s, 2H, Ar-H_3), 7.20 (td, 2H, Ar-H_8), 3.15 (s, 3H, OCH_3), 1.37 (s, 2H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz) δ 152.49 (s, Ar-C_2), 145.50 (s, Ar-C_1), 140.17 (s, Ar-C_4), 133.92 (s, Ar-C_{10}), 132.78 (s, Ar-C_6), 131.89 (s, Ar-C_9), 128.83 (s, Ar-C_7), 128.49 (s, Ar-C_3), 127.01 (s, Ar-C_8), 124.05 (s,

Ar-C_5), 60.69 (s, OCH_3), 34.56 (s, C(CH$_3$)$_3$), 31.54 (s, C(CH_3)$_3$). MS (m/z): calcd, 474.0017 (M+); found 474.0031 (FAB+, M+$^•$).

Synthesis of [1,3-bis(2'-diisopropylphosphino)-4-tert-butyl-2-methoxybenzene] (1a).
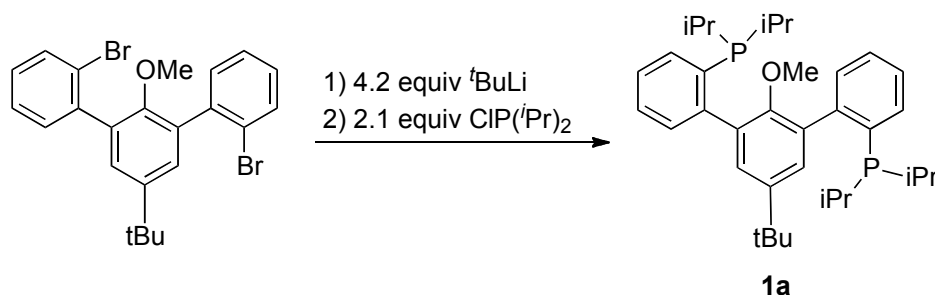
A mixture of bis(2'-bromophenyl)-4-tert-butyl-2-methoxybenzene (1.00 g, 2.11 mmol, 1 equiv) and THF (30 mL) in a 100 mL round bottom was frozen in a cold well. The vial was removed from the cold well and ^{t}BuLi in pentane (1.7 M, 5.2 mL, 8.86 mmol, 4.2 equiv) was added via syringe to the thawing solution. The resulting dark orange solution was allowed to warm to room temperature while stirring for 20 minutes before being frozen again. Separately, a 20 mL scintillation vial was charged with a solution of chlorodiisopropylphosphine (0.68 g, 4.43 mmol, 2.1 equiv) in hexanes (5 mL) and frozen. The thawing chlorophosphine solution was added dropwise to the just-thawed lithiation reaction mixture. The reaction mixture was allowed to warm to and stir at room temperature for 2 hours. The volatile materials were then removed under vacuum and the residue was dissolved in hexanes and filtered through Celite. The volatiles were removed from the filtrate under reduced pressure, and the resulting yellow oil was redissolved in hexanes and filtered through Celite a second time. The volatiles were removed from the filtrate under reduced pressure once more, and the resulting yellow oil was redissolved in hexanes and filtered through a bed of alumina. Removal of volatile materials *in vacuo* yielded **1a** as a colorless oil (0.68 g, 1.20 mmol) in 57% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, 2H, Ar-H), 7.48 (m, 2H, Ar-H), 7.35 (m, 4H, Ar-H), 7.11 (m, 2H, Ar-H), 3.02 (m, 3H, OCH_3), 2.17 (hept, 2H, CH(CH$_3$)$_2$), 1.98 (sept, 2H, CH(CH$_2$)$_3$), 1.33 (s, 9H, C(CH_3)$_3$), 1.06 (m, 18H, CH(CH_3)$_3$), 0.89 (qr, 6H, CH(CH_3)$_3$). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 152.66 (s, Ar-C), 148.03 (s, Ar-C), 147.73 (s, Ar-C), 143.19 (s, Ar-C), 136.30 (d, Ar-C), 134.79 (d, Ar-C), 132.36 (s, Ar-C), 132.34 (d, Ar-C), 131.29 (d, Ar-C), 130.92 (s, Ar-C), 129.53 (s, Ar-C), 129.14 (d, Ar-C), 128.02 (s, Ar-C), 127.77, (s, Ar-C), 126.38 (s, Ar-C), 59.81 (s, OCH_3), 34.41 (s, C(CH$_3$)$_3$), 31.74 (s, C(CH_3)$_3$), 26.38 (d, CH(CH$_3$)$_3$), 24.64 (d, CH(CH_3)$_3$), 20.45 (m, CH(CH$_2$)$_3$). ^{31}P{^{1}H} NMR (121 MHz, C$_6$D$_6$) δ -3.10 (s), -4.13 (s). MS (m/z): calcd, 549.3415 (M+); found 549.3431 (FAB+, M+).

Synthesis of [1,3-bis(2'-diisopropylphosphino)-4-tert-butyl-2-methoxybenzene]nickel(0) (2a).
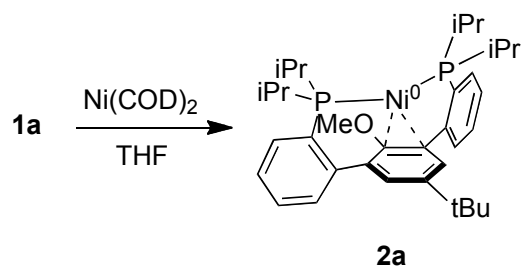
A colorless solution of diphosphine **1a** (0.51 g, 0.92 mmol, 1 equiv) in THF (3 mL) was added dropwise to a slurry of Ni(COD)$_2$ (0.25 g, 0.92 mmol, 1 equiv) in THF (2 mL) in a 20 mL scintillation vial charged

with a magnetic stir bar. Upon addition, a light orange color was observed. After 30 min., the reaction mixture had changed color to dark red. The mixture was stirred at room temperature for 4 h, at which time volatiles were removed under reduced pressure. The dark red residue was triturated twice with THF (3 mL) and solvent was removed *en vacuo* both times to afford a dark red powder. This powder was redissolved in THF and allowed to stir at room temperature for an additional 4 h, at which time volaties were removed under reduced pressure. The dark red residue was triturated twice with THF (3 mL) and solvent was removed *en vacuo* both times to afford a dark red powder. This dark red powder was washed with three portions of acetonitrile (4 mL) and solvent removed *en vacuo* to afford **6a** (0.32 g, 0.53 mmol) in 58% yield and approximately 90% purity. To date, an analytically pure sample has yet to be obtained to date due to $Ni(COD)_2$ contamination, the following data was obtained using material of approximately 90% purity (^{1}H NMR). ^{1}H NMR (500 MHz, C_6D_6) δ 7.68 (d, 2H, Ar-H_6), 7.32 (d, 2H, Ar-H_9), 7.23 (q, 4H, Ar-H_7 & Ar-H_8), 6.31 (t, 2H, Ar-H_3), 4.30 (s, 4H, $Ni(COD)_2$), 3.14 (s, 3H, OCH_3), 2.32 (m, 2H, $CH(CH_3)_2$), 2.08 (s, 8H. $Ni(COD)_2$), 2.04 (q, 2H, $CH(CH_3)_2$), 1.29 (s, 9H, $C(CH_3)$), 1.20 (qr, 6H, $CH(CH_3)_3$), 1.12 (m, 12H, $CH(CH_3)_3$), 1.02 (qr, 6H, $CH(CH_3)_3$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 151.64 (t, Ar-C_5), 139.78 (t, Ar-C_{10}), 138.03 (s, Ar-C_4), 130.85 (s, Ar-C_9), 129.70 (t, Ar-C_6), 129.16 (s, Ar-C_7), 127.00 (s, Ar-C_8), 119.67 (s, Ar-C_3), 113.57 (t, Ar-C_2), 101.45 (t, Ar-C_1), 89.72 (s, $Ni(COD)_2$), 59.26 (s, OCH_3), 34.25 (s, $C(CH_3)$), 31.35 (s, $C(CH_3)$), 30.89 (s, $Ni(COD)_2$), 27.25 (t, $CH(CH_3)_2$), 21.70 (t, $CH(CH_3)_2$), 19.99 (m, $CH(CH_3)_2$), 19.79 (t, $CH(CH_3)_2$), 19.23 (t, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121, MHz, C_6D_6) δ 41.04 (s).

Synthesis of [1,3-bis(2'-diisopropylphosphino)-4-tert-butyl-2-methoxybenzene]nickel(0) (6a).

6a
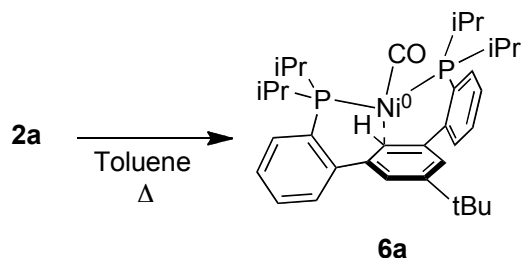
A 100 mL Schlenk tube fitted with a screw-in Teflon stopper was charged with a magnetic stir bar and a dark red solution of crude **2a** (0.09 g, 0.15 mmol, 1 equiv) in toluene (6 mL). The reaction vessel was removed from the glovebox and placed in an oil bath pre-heated to 100°C. After stirring for 2 h the reaction mixture was allowed to cool to room temperature. A black precipitate was observed on the walls of the reaction vessel. The reaction mixture was brought in the glovebox and filtered through Celite. The volatiles were removed from the filtrate under reduced pressure. NMR spectra indicated that the residue contained ca 90% **6a**. The dark red material was redissolved in the minimum volume of toluene (2 mL) and chilled to -35°C. After 8 hours, solvent was decanted with a pipette and a darkly colored precipitate was washed twice with toluene chilled to -35°C. The precipitate was ground to a powder to afford **6a** as an orange solid (0.60 g, 0.10 mmol, 60% yield). X-ray quality crystals were grown from a saturated solution in acetonitrile at room temperature. ^{1}H NMR (300 MHz, C_6D_6). δ 7.42 (m, 4H, Ar-H_6 & Ar-H_9), δ 7.26 (s, 2H, Ar-H_3), 7.16 (m, 4H, Ar-H_7 & Ar-H_8), 6.82 (tt, 1H, Ar-H_1), 2.38 (hept, 2H, $CH(CH_3)_2$), 2.14 (hept, 2H, $CH(CH_3)_2$), 1.44 (s, 9H, $C(CH_3)_3$), 1.11 (m, 18H, $CH(CH_3)_2$), 0.95 (q, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 196.33 (s, Ni-CO), 151.46 (s, Ar-C_4), 150.95 (t, Ar-C_{10}), 141.01 (t, Ar-C_2), 135.86 (t, Ar-C_5), 131.20 (s, Ar-C_9), 130.69 (t, Ar-C_6), 129.07 (s, Ar-C_8), 127.31 (s, Ar-C_7), 122.97 (s, Ar-C_3), 89.92 (s, Ar-C_1), 34.95 (s, $C(CH_3)_3$), 31.70 (s, $C(CH_3)_3$), 29.39 (t, $CH(CH_3)_2$), 26.52 (t, $CH(CH_3)_2$), 20.32 (t, $CH(CH_3)_2$), 19.48 (t, $CH(CH_3)_2$), 18.77 (s, $CH(CH_3)_2$), 18.37 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6). δ 33.64 (s). Anal. Calcd. for $C_{35}H_{48}OP_2Ni$ (%): C, 69.44; H, 7.99 Found: C, 69.26; H, 7.72. IR (hexanes) : ν_{CO} = 1929 cm^{-1}.

1,3-bis(2′-bromophenyl)-2-methoxy-4-nitrobenzene
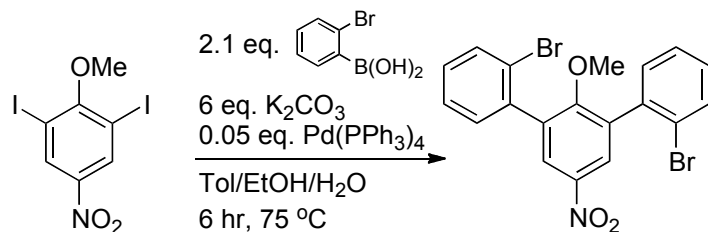
1,3-bis(2′-bromophenyl)-2-methoxy-4-nitrobenzene was synthesized according to the procedure for 1,3-bis(2'-bromophenyl)-4-tert-butyl-2-methoxybenzene listed above[6]. The crude 1,3-bis(2'-bromophenyl)-2-methoxy-4-nitrobenzene was reduced without purification. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.17 (s, 2H, central Ar-H), 7.71 (d, 2H, Ar-H), 7.40 (m, 4H, Ar-H), 7.30 (d, 2H, Ar-H), 3.27 (s, 3H, OCH_3)

4-amino-1,3-bis(2'-bromophenyl)-2-methoxybenzene
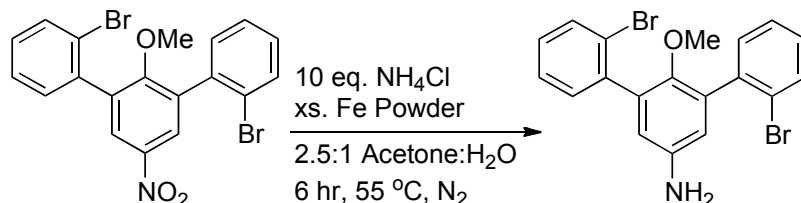
4-amino-1,3-bis(2'-bromophenyl)-2-methoxybenzene was synthesized using a modified literature procedure[7]. The crude 4-amino-1,3-bis(2'-bromophenyl)-2-methoxybenzene was methylated without purification. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.65 (d, 2H, Ar-H), 7.36 (m, 4H, Ar-H), 7.20 (t, 2H, Ar-H), 6.59 (s, 2H, central Ar-H), 3.63 (s, 2H, NH_2), 3.27 (s, 3H, OCH_3)

1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene
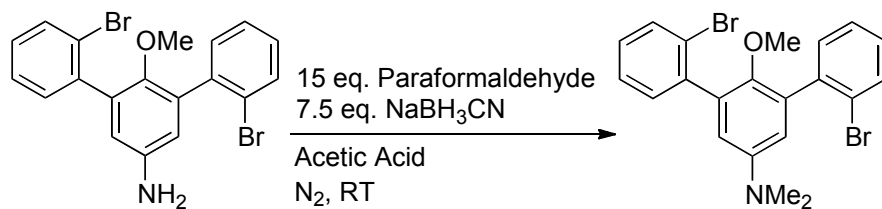
1,3-bis(2'-bromophenyl)-4-dimethylamino-2-methoxybenzene was synthesized using a literature procedure[8]. The product was purified by Flash chromatography (dichloromethane) and isolated as a colorless solid. Yield: 41.9% ^{1}H NMR (C$_6$D$_6$, 399.80 MHz) δ 7.57 (d, 2H, Ar-H_6), 7.41 (d, 2H, Ar-H_9), 7.01 (t, 2H, Ar-H_7), 6.81 (t, 2H, Ar-H_8), 6.68 (s, 2H, Ar-H_3), 3.12 (s, 3H, OCH_3), 2.48 (s, 6H, N(CH_3)$_2$), ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz) δ 146.72 (s, Ar-C_1), 146.66 (s, Ar-C_4), 141.21 (s, Ar-C_{10}), 135.74 (s, Ar-C_2), 132.98 (s, Ar-C_9), 132.31 (s, Ar-C_6), 128.97 (s, Ar-C_7), 127.09 (s, Ar-C_8), 124.54 (s, Ar-C_5), 115.73 (s, Ar-C_3), 60.77 (s, O-CH_3), 40.69 (N(CH_3)$_2$), MS (m/z): calcd, 460.9813 (M+); found, 460.9822 (FAB+, M+).

1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (1b)
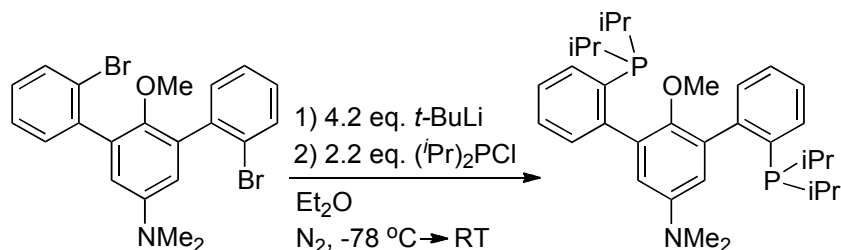
In a glovebox a 100 mL schlenk tube was charged with a colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (50.1 mg, 0.11 mmol) in Et_2O (30 mL) and a stir bar. The schlenk tube was removed from the glove box and cooled to -78°C in a dry ice/acetone bath. Under N2, ^{t}BuLi in pentane (1.5 M, 303.5 µL, 0.46 mmol) was added via syringe slowly to the cold solution. The resulting dark yellow mixture was stirred for one hour at -78°C. After an hour chlorodiisopropylphosphine (36.5 µl, 0.23 mmol) was added to the cold solution slowly via syringe. After addition the reaction mixture was allowed to warm to and stir at room temperature for 8 hours. The volatile materials were then removed under vacuum and the pale yellow/white residue was mixed in hexanes and filtered through Celite. The volatiles were removed from the filtrate *in vacuo*, and the resulting pale yellow/colorless oil was redissolved in pentane and stirred with alumina. The mixture was filtered through a bed of alumina and the alumina was rinsed with toluene. Removal of volatile materials under vacuum yielded 1b as a white solid (0.68 g, 1.20 mmol) in 92.9% yield. ^{1}H NMR (C_6D_6, 300 MHz, 75°C) δ 7.65 (m, 2H, Ar-H_6), 7.48 (m, 2H, Ar-H_9), 7.19 (m, 4H, Ar-H_{7-8}), 6.73 (s, 2H, Ar-H_3), 3.14 (s, 3H, OCH_3), 2.65 (s, 6H, N(CH_3)$_2$), 2.06 (m, 2H, CH(CH$_3$)$_2$) , 1.92 (m, 2H, CH(CH$_3$)$_2$) , 1.08 (m, 24H, CH(CH_3)$_2$) ^{13}C{^{1}H} NMR (C_6D_6, 100.54 MHz) δ 148.52 (m, Ar-C_{10}), 147.49 (s, Ar-C_1), 145.61 (s, Ar-C_4), 136.85 (d, Ar-C_5), 136.44 (d, Ar-C_2), 132.43 (s, Ar-C_9), 131.68 (d, Ar-C_6), 128.19 (s, Ar-C_8), 126.68 (s, Ar-C_7), 117.41 (s, Ar-C_3), 60.18 (s, O-CH_3), 41.21 (N(CH_3)$_2$), 26.79 (CH-(CH_3)$_2$), 24.96 (CH-(CH_3)$_2$), 20.83 (CH-(CH_3)$_2$), ^{31}P{^{1}H} NMR (C_6D_6, 121.48 MHz) δ -2.72 (s), -4.09 (s) MS (m/z): calcd, 535.3133 (M+); found, 535.3134 (FAB+, M+).

[1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (2b)
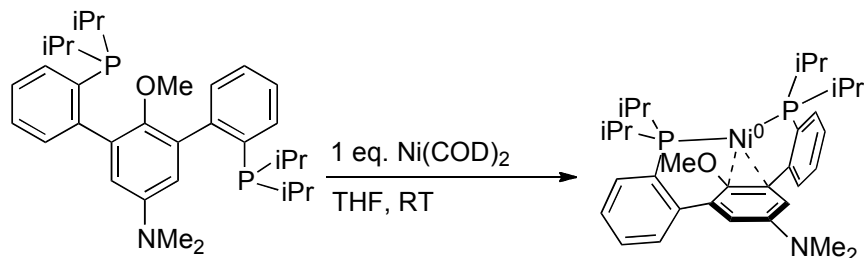
A colorless solution of 1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene (937.2mg, 1.74 mmol) in THF (35 ml) was mixed with a yellow slurry of Ni(COD)$_2$ (477.7 mg, 1.74 mmol) in THF (5 ml) at RT. The mixture changed color to dark red and was stirred for 11 hours. Volatiles were removed *in vacuo* yielding a dark red solid. The crude solid was taken up in MeCN and filtered through celite to remove solids. MeCN was removed from the filtrate under vacuum. The dark red solid was dissolved in hexanes and cooled to neigh freezing temperatures in a liquid nitrogen cooled cold well and filtered through a celite packed frit. The hexanes were removed under vacuum yielding a dark red solid. Yield: 872.9 mg, 84.4% ^{1}H NMR (C_6D_6, 399.80 MHz) δ 7.70 (d, 2H, Ar-H_6), 7.32 (m, 2H, Ar-H_9), 7.24 (mm, 4H, Ar-H_{7-8}), 5.84 (t, 2H, Ar-H_3), 3.17 (s, 3H, OCH_3), 2.58 (s, 6H, N(CH_3)$_2$), 2.33 (m, 2H, CH(CH$_3$)$_2$), 2.04 (m, 2H, CH(CH$_3$)$_2$), 1.25 (mm, 6H, CH(CH_3)$_2$), 1.16 (mm, 12H, CH(CH_3)$_2$), 1.06 (m, 6H, CH(CH_3)$_2$) ^{13}C{^{1}H} NMR (C_6D_6, 100.54 MHz) δ 151.42 (t, Ar-C_{10}), 143.50 (s, Ar-C_4), 140.43 (t, Ar-C_5), 130.82 (s,

Ar-C_6), 129.74 (t, Ar-C_9), 128.95 (s, Ar-C_8), 127.11 (s, Ar-C_7), 115.72 (t, Ar-C_2), 109.32 (t, Ar-C_3), 100.69 (t, Ar-C_1), 59.55 (s, O-CH_3), 42.03 (N(CH_3)$_2$), 27.25 (CH-(CH_3)$_2$), 21.82 (CH-(CH$_3$)$_2$), 20.15 (CH-(CH_3)$_2$), 20.09 (CH-(CH_3)$_2$), 19.80 (CH-(CH_3)$_2$), 19.33 (CH-(CH_3)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 40.65 (s) Anal. Calcd. for C$_{33}$H$_{47}$NNiOP$_2$ (%): C, 66.68; H, 7.97; N, 2.36 Found C, 66.45; H, 7.94; N, 2.11.

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)methoxide (3b)

A dark red solution of purified [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (105.2 mg, 0.18 mmol) in C$_6$H$_6$ was warmed to 45°C in a schlenk tube. After 14 hours the solvent was removed under vacuum. The resulting red orange solid was washed with pentane and extracted with ether. The ether was pumped off resulting in an orange solid (**3b**). Yield: 82.7 mg, 78.6% ^{1}H NMR (C$_6$D$_6$, 399.80 MHz) δ 7.76 (d, 2H, Ar-H_6), 7.44 (d, 2H, Ar-H_9), 7.37 (t, 2H, Ar-H_7), 7.17 (t, 2H, Ar-H_8), 6.78 (s, 2H, Ar-H_3), 3.67 (s, 3H, OCH_3), 2.56 (s, 6H, N(CH_3)$_2$), 2.52 (br, 2H, CH(CH$_3$)$_2$), 1.76 (br, 2H, CH(CH$_3$)$_2$), 1.66 (br, 6H, CH(CH_3)$_2$), 1.28 (br, 6H, CH(CH_3)$_2$), 0.96 (br, 6H, CH(CH_3)$_2$), 0.80 (br, 6H, CH(CH_3)$_2$) ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.54 MHz) δ 153.23 (t, Ar-C_{10}), 150.95 (s, Ar-C_4), 147.19 (t, Ar-C_5), 130.26 (s, Ar-C_7), 129.41 (s, Ar-C_9), 128.40 (s, Ar-C_2), 128.35 (s, Ar-C_6), 126.99 (s, Ar-C_1), 126.60 (s, Ar-C_8), 113.59 (s, Ar-C_3), 54.84 (s, OCH_3), 40.56 (s, N(CH_3)$_2$), 23.83 (s, CH(CH$_3$)$_2$), 21.09 (s, CH(CH_3)$_2$), 20.45 (s, CH(CH_3)$_2$), 19.77 (s, CH(CH_3)$_2$), 18.90 (s, CH(CH_3)$_2$), 18.12 (s, CH(CH_3)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 161.85 MHz) δ 27.26 (s) Anal. Calcd. for C$_{33}$H$_{47}$NNiOP$_2$ (%): C, 66.68; H, 7.97; N, 2.36 Found C, 66.60; H, 8.10; N, 2.23.

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)hydride (4b)
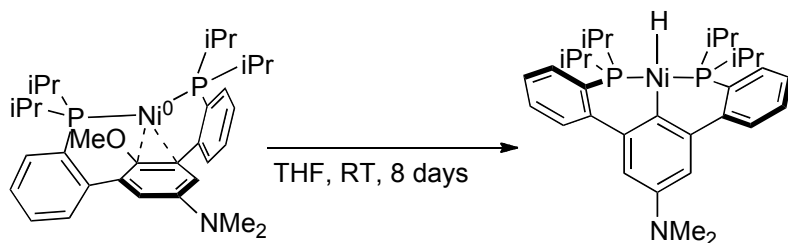
A dark red solution of crude [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (100.1 mg, 0.17 mmol) in THF (10 ml) was stirred at RT for 8 days. Over the course of 8 days a yellow solid precipitated. The solid was collected on a pad of celite. The solid was extracted from the celite with toluene. Removal of solvent under vacuum yielded a yellow solid. Yield: 52.3 mg, 55% ^{1}H NMR (C$_6$D$_6$, 300 MHz) δ 7.87 (d, 2H, Ar-H_6), 7.44 (t, 2H, Ar-H_7), 7.29 (d, 2H, Ar-H_9), 7.14 (t, 2H, Ar-H_8), 6.79 (s, 2H, Ar-H_3), 2.54 (t, 6H, N(CH_3)$_2$), 2.27 (br m, 2H, CH(CH$_3$)$_2$), 1.70 (br m, 6H, CH(CH_3)$_2$), 1.61 (br m, 2H, CH(CH$_3$)$_2$), 1.28 (mm, 6H, CH(CH_3)$_2$), 1.12 (mm, 6H, CH(CH_3)$_2$), 0.70 (m, 6H, CH(CH_3)$_2$), -2.80 (t, 1H, Ni-H), ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.54 MHz) δ 152.69 (t, Ar-C_{10}), 150.79 (s, Ar-C_4), 147.09 (t, Ar-C_5), 130.40 (s, Ar-C_7), 129.13 (s, Ar-C_9), 128.70 (s, Ar-C_2), 128.15 (s, Ar-C_6), 126.61 (s, Ar-C_8), 126.41 (s, Ar-C_1), 114.03 (s, Ar-C_3), 41.07 (s, N(CH_3)$_2$), 24.08 (s, CH(CH$_3$)$_2$), 20.48 (s, CH(CH_3)$_2$), 20.34 (s, CH(CH_3)$_2$), 20.08 (s, CH(CH_3)$_2$), 18.75 (s, CH(CH_3)$_2$), 18.08 (s, CH(CH_3)$_2$), ^{31}P{^{1}H} NMR (C$_6$D$_6$, 121.48 MHz) δ 30.41 (s) Anal. Calcd. for C$_{32}$H$_{45}$NNiP$_2$ (%): C, 68.10; H, 8.04; N, 2.48 Found. C, 67.63; H, 7.85; N, 2.05

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)iodide (5)
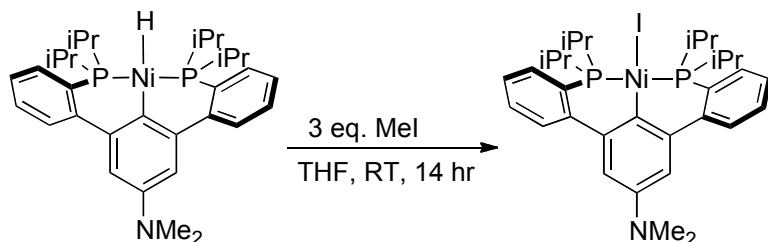
A yellow solution of [1,3-bis(2'-diisopropylphosphino)-4-dimethylaminophenyl]nickel(II)hydride (35.3 mg, 0.063 mmol) was made in THF (7 ml). To this solution was added dry methyl iodide (28.5 mg, 0.20 mmol) at room temperature. The solution was stirred for 14 hours at room temperature in the dark. After 14 hours the volatiles were removed under vacuum leaving a red orange residue. The residue was washed with hexanes and extracted with ether. The ether was removed under vacuum yielding a red orange solid. X-ray quality crystals were grown from a concentrated solution in ether. Yield: 27.4 mg, 63.5%^{1}H NMR (C_6D_6, 399.80 MHz) δ 7.72 (d, 2H, Ar-H_6), 7.40 (d, 2H, Ar-H_9), 7.37 (t, 2H, Ar-H_8), 7.13 (t, 2H, Ar-H_7), 6.78 (s, 2H, Ar-H_3), 3.03 (m, 2H, CH(CH$_3$)$_2$), 2.52 (m, 6H, N(CH_3)$_2$), 1.77 (m, 2H, CH(CH$_3$)$_2$), 1.51 (q, 6H, CH(CH_3)$_2$), 1.31 (m, 6H, CH(CH_3)$_2$), 0.91 (m, 6H, CH(CH_3)$_2$), 0.77 (m, 6H, CH(CH_3)$_2$), ^{13}C{^{1}H} NMR (C_6D_6, 100.54 MHz), δ 151.38 (t, Ar-C_{10}), 151.20 (s, Ar-C_4), 146.92 (t, Ar-C_5), 130.39 (s, Ar-C_8), 129.78 (t, Ar-C_9), 127.98 (s, Ar-C_2), 127.95 (s, Ar-C_6), 127.16 (s, Ar-C_7), 126.19 (t, Ar-C_1), 113.86 (t, Ar-C_3), 40.28 (N(CH$_3$)$_2$), 24.29 (CH-(CH$_3$)$_2$), 23.59 (CH-(CH$_3$)$_2$), 20.55 (CH-(CH$_3$)$_2$), 20.21 (CH-(CH$_3$)$_2$), 19.39 (CH-(CH$_3$)$_2$), 18.91 (CH-(CH$_3$)$_2$), ^{31}P{^{1}H} NMR (C_6D_6, 121.48 MHz) δ 34.35 (s) Anal. Calcd. for $C_{32}H_{44}NNiP_2$ (%): C, 58.01; H, 6.51; N, 1.90 Found. C, 58.23; H, 6.62; N, 2.00

[1,3-bis(2'-diisopropylphosphino)-4-dimethylaminobenzenel]nickel(0)carbonyl (6b)
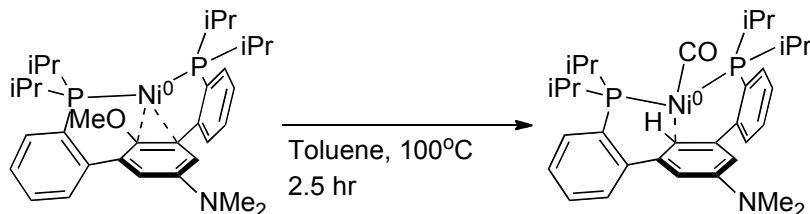
A dark red solution of crude [1,3-bis(2'-diisopropylphosphino)-4-dimethylamino-2-methoxybenzene]nickel(0) (96.9 mg, 0.16 mmol) in toluene was heated to 100 °C in a sealed schlenk tube. The tube was heated for 2.5 hours. After 2.5 hours the solvent was removed under vacuum giving an orange solid. NMR spectra indicated that this material contained ca 95% **6b**. The solid was washed with hexanes and dried under vacuum yielding a red orange solid. Yield: 83.8 mg, 86.7%. ^{1}H NMR (C_6D_6, 399.80 MHz) δ 7.49 (br m, 2H, Ar-H_6), 7.44 (br m, 2H, Ar-H_9), 7.18 (m, 4H, Ar-H_{7-8}), 6.56 (s, 2H, Ar-H_3), 6.51 (t, 1H, Ar-H_1), 2.65 (s, 6H, N(CH_3)$_2$), 2.40 (m, 2H, CH(CH$_3$)$_2$), 2.18 (m, 2H, CH(CH$_3$)$_2$), 1.24 (q, 6H, CH(CH_3)$_2$), 1.16 (q, 6H, CH(CH_3)$_2$), 1.10 (q, 6H, CH(CH_3)$_2$), 1.02 (q, 6H, CH(CH_3)$_2$) ^{13}C{^{1}H} NMR (C_6D_6, 100.54 MHz) δ 195.98 (t, Ni-CO), 152.54 (s, Ar-C_4), 151.06 (t, Ar-C_{10}), 145.58 (s, Ar-C_2), 136.50 (t, Ar-C_5), 131.26 (s, Ar-C_9), 130.81 (s, Ar-C_6), 128.90 (s, Ar-C_8), 127.29 (s, Ar-C_7), 110.03 (s, Ar-C_3), 84.65 (s, Ar-C_1), 40.68 (N(CH$_3$)$_2$), 29.44 (CH-(CH$_3$)$_2$), 26.79 (CH-(CH$_3$)$_2$), 20.40 (CH-(CH$_3$)$_2$), 19.62 (CH-(CH$_3$)$_2$), 18.90 (CH-(CH$_3$)$_2$), 18.60 (CH-(CH$_3$)$_2$) ^{31}P{^{1}H} NMR (C_6D_6, 121.48 MHz) δ 34.17 (s) EA Calcd. C, 66.91; H, 7.66; N, 2.36 Found. C, 67.13; H, 7.67; N, 2.38 IR (C_6D_6): ν_{CO} = 1917 cm^{-1}.

Reaction of 2b with d_1-triethylsilane

A J. Young tube was charged with a dark red solution of **2b** (5.3 mg, 0.009 mmol) in C_6D_6. To this solution was added d_1-triethylsilane by syringe (3 μL, 0.019 mmol) and the solution heated to 80 °C. After two and a half hours the formation of **6b** was confirmed by ^{1}H and ^{31}P NMR spectroscopy. Based on the integration of the Ar-H_3 peak at 6.56 and the Ar-H_1 peak at 6.51 ppm in the ^{1}H-NMR spectrum, the isotopolog distribution consisted of 7% d_1-**6b** (deuterium atom being incorporated into the ipso carbon [Ar-H_1] of the central arene) and 93% d_0-**6b**. Increasing the equivalents of triethylsilane led to an increase in deuteration of Ar-H_1. Thirteen equivalents of d_1-triethylsilane under the same conditions led to 18% d_1-**6b** and 82% **6b**. Starting with d_3-**2b** and two equivalents of triethylsilane, the product after five hours at 80 °C was found to contain 47% d_1-**6b** and 53% **6b**. An unidentified species was observed by ^{1}H and ^{31}P NMR spectroscopy, in amount roughly proportional to the label incorporation from SiX (X=D or H). This is consistent with decreased generation of formaldehyde and hence lower formation of the nickel carbonyl species upon reductive elimination / decarbonylation. The increased label incorporation from SiH vs SiD in the experiments above is consistent with normal isotope effects for β-H elimination from the intermediate nickel methoxide species (**3**) and for transmetallation in the reaction of the silane with **3**.

Reaction of 4b with methanol

A J. Young tube was charged with a yellow slurry of **4b** (4.7 mg, 0.008 mmol) in C_6D_6. To this slurry was added (0.3 mg, 0.008 mmol) of methanol. The J. Young tube was sealed, inverted several times, and allowed to react at 20 °C for 15 minutes. After the allotted time the solution contained 20% **3b** by ^{31}P and ^{1}H NMR spectroscopy. Longer reaction times and increasing the amount of methanol added (10 eq.) did not change the percentage of **3b** produced.

Reaction of 4b with formaldehyde

A J. Young tube was charged with a yellow slurry of **4b** (5.2 mg, 0.009 mmol) in C_6D_6. To this slurry was added paraformaldehyde (1 mg, 0.033 mmol). The J. Young tube was sealed and heated to 60°C for two and a half hours. During the first 30 minutes of heating everything became soluble and the color of the solution changed to orange. After the allotted time the solution contained 85% **6b** by ^{31}P and ^{1}H NMR spectroscopy.

Reaction of 4b with carbon monoxide

A J. Young tube (2.9 ml) was charged with a yellow slurry of **4b** (4.8 mg, 0.009 mmol) in C_6D_6 (0.6 ml). The slurry was degassed by three freeze-pump-thaw cycles and left under static vacuum. Using a schlenk line equipped with a mercury manometer, the evacuated gas manifold was pressurized with carbon monoxide (53 Torr). Using the gas manifold the J. Young tube containing a frozen benzene solution under static vacuum was pressurized with carbon monoxide corresponding to ca. 0.8 equiv of carbon monoxide for the free volume of the tube. The tube was thawed and inverted several times then heated at 60 °C for 64 hours with periodic mixing. Over time the color of the solution changed to a light orange. After the allotted time the solution contained ca. 50% **6b** by ^{31}P and ^{1}H NMR spectroscopy as part of a mixture with unidentified species.

Reaction of 5 with sodium methoxide

A vial was charged with a red orange solution of **5** (18.7 mg, 0.027 mmol) in THF (ca. 5 ml). To this solution was added a slurry of sodium methoxide (4.4 mg, 0.081 mmol) in THF (ca. 1 ml). The mixture was stirred at 20 °C for four hours. After four hours the solution contained 64% **3b** by ^{31}P and ^{1}H NMR spectroscopy along with unreacted **5** and β-H elimination product, **4b**.

Quantification of H$_2$ in the conversion of 2b to 6b

In a Schlenk tube 25.8 mg (0.043 mmol) of **2b** was dissolved in toluene (ca. 5 ml). The solution was degassed by three freeze-pump-thaw cycles and left under static vacuum. The solution of **2b** was heated to 100 °C for 12 hours. After 12 hours the solution was frozen and the gas in the Schlenk flask was pumped through a liquid nitrogen cooled trap and collected in a calibrated volume (24 ml) using a Toepler pump. After 20 minutes (ca. 25 cycles of the Toepler pump) the Schlenk flask was sealed and thawed. Upon thawing the solution was re-frozen and the aforementioned Toepler pump process was repeated. After three of the described freeze-Toepler pump-thaw cycles, the pressure of gas collected was found to be 29 Torr. Using the Toepler pump the gas was pumped through a CuO filled tube. The tube was heated and kept between a range of 300 and 375 °C. After 40 minutes of pumping the gas through the CuO tube, the pressure of gas was found to be 1 Torr. The measurements corresponded to 0.037 mmol combustible gas (H$_2$) released from the reaction of **2b** to form **6b**. The amount of hydrogen released was found to be 0.9 equivalents (based on two independent determinations 0.88 and 0.93 equivalents) after correcting for 91% **6b** being formed (determined by ^{1}H and ^{31}P NMR spectroscopy) under the conditions described.

II. Crystallographic Data

Table S1. Crystal and refinement data for **2b**, **5**, and **6a**

	2b	**5**	**6a**
CCDC Deposition #	859840	859841	857167
Empirical formula	C$_{33}$H$_{47}$NOP$_2$Ni	C$_{32}$H$_{44}$NP$_2$INi • C$_4$H$_{10}$O	0.96(C$_{35}$H$_{48}$OP$_2$Ni) 0.04(C$_{34}$H$_{48}$P$_2$ClNi)
Formula weight	594.37	764.35	605.66
Crystallization Solvent	Hexamethyldisiloxane	Diethyl ether	Acetonitrile
Crystal Habit	Block	Plate	Block
Crystal size, mm^3	0.25 x 0.16 x 0.09	0.36 x 0.23 x 0.04	0.31 x 0.24 x 0.22
Crystal color	Red	Red	Dark orange
θ range for lattice determination	2.35 to 30.25°	2.85 to 36.20°	2.37 to 44.55°
a, Å	10.6162(4)	9.0551(6)	19.1875(10)
b, Å	19.6007(8)	17.5696(12)	9.6032(5)
c, Å	15.6192(6)	11.5133(8)	17.5086(9)
a, °	90	90	90
b, °	103.887(2)	102.374(3)	93.098(3)
g, °	90	90	90
Volume, Å^3	3155.1(2)	1789.2(2)	3221.4(3)
Z	4	2	4
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2$_1$/n	P 2$_1$	C c
Density (calculated)	1.251 Mg/m^3	1.419 Mg/m^3	1.249 Mg/m^3
F(000)	1272	792	1296

θ range for data collection, °	2.08 to 33.20	1.81 to 36.41	2.13 to 47.45
Completeness to θ = 26.43°	97.3%	100.0%	99.7%
Index ranges	$-16 \leq h \leq 16$ $-30 \leq k \leq 30$ $-23 \leq l \leq 21$	$-15 \leq h \leq 15$ $-29 \leq k \leq 29$ $-19 \leq l \leq 19$	$-39 \leq h \leq 39$ $-19 \leq k \leq 19$ $-35 \leq l \leq 36$
Data collection scan type	ω scans; 9 settings	ω scans; 15 settings	ω scans; 16 settings
Reflections collected	78843	109962	120762
Independent reflections	11768 [R_{int}= 0.0695]	17397 [R_{int}= 0.0392]	24726 [R_{int}= 0.0365]
Absorption coefficient, mm^{-1}	0.743	1.522	0.730
Absorption correction	None	Semi-empirical from equivalents	None
Max. and min. transmission	0.9362 and 0.8363	0.9569 and 0.6479	0.8559 and 0.8053
Hydrogen placement	Geometric positions	Geometric positions	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data / restraints / parameters	11768 / 0 / 354	17397 / 7 / 417	24726 / 2 / 373
Treatment of hydrogen atoms	Riding	Riding	Riding
Goodness-of-fit on F2	1.604	1.924	1.711
Final R indices [I>2s(I), 4802 reflections]	R1 = 0.0489 wR2 = 0.0501	R1 = 0.0266 wR2 = 0.0483	R1 = 0.0259 wR2 = 0.0427
R indices (all data)	R1 = 0.0934 wR2 = 0.0514	R1 = 0.0312 wR2 = 0.0488	R1 = 0.0334 wR2 = 0.0429
Type of weighting scheme used	Sigma	Sigma	Sigma
Weighting scheme used	$w=1/s^2(Fo^2)$	$w=1/s^2(Fo^2)$	$w=1/s^2(Fo^2)$
Max shift/error	0.001	0.006	0.002
Average shift/error	0	0	0
Largest diff. peak and hole, e.Å^{-3}	1.838 and -1.065	1.668 and -0.753	0.428 and -0.607
Type of diffractometer	Bruker KAPPA APEX II	Bruker KAPPA APEX II	Bruker KAPPA APEX II
Wavelength, Å MoKa	0.71073	0.71073	0.71073
Data Collection Temperature	100(2) K	100(2) K	100(2) K
Structure solution program	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods	Direct methods	Direct methods
Secondary solution method	Difference Fourier map	Difference Fourier map	Difference Fourier map
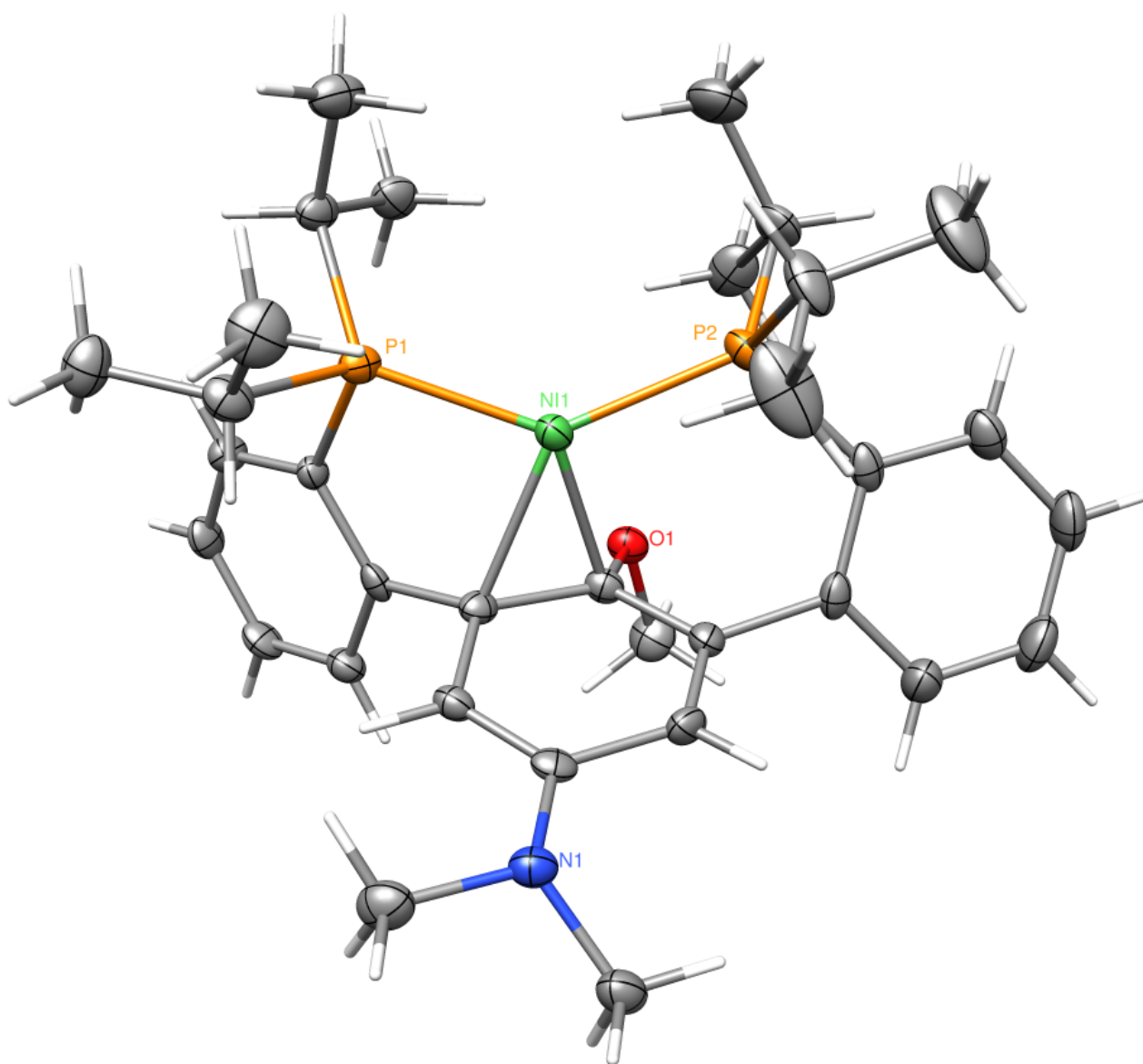
Figure S1. Structural drawing of **2b** with 50% thermal probability ellipsoids.

Special Refinement Details for 2b. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2s(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2b**. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Ni(1)	9252(1)	2504(1)	3704(1)	18(1)
P(1)	8688(1)	1534(1)	4155(1)	20(1)
P(2)	10268(1)	2868(1)	2734(1)	22(1)
O(1)	11102(1)	3154(1)	4912(1)	21(1)
N(1)	5974(1)	4118(1)	4063(1)	20(1)
C(1)	9168(1)	1691(1)	5340(1)	15(1)
C(2)	9522(2)	1210(1)	6016(1)	23(1)
C(3)	9827(2)	1408(1)	6888(1)	23(1)
C(4)	9777(2)	2086(1)	7101(1)	23(1)
C(5)	9432(1)	2572(1)	6439(1)	21(1)
C(6)	9154(1)	2379(1)	5560(1)	17(1)
C(7)	8804(2)	2903(1)	4836(1)	17(1)
C(8)	7542(1)	3227(1)	4707(1)	18(1)
C(9)	7230(2)	3818(1)	4239(1)	18(1)
C(10)	8183(2)	4124(1)	3861(1)	20(1)
C(11)	9404(2)	3867(1)	3996(1)	18(1)
C(12)	10367(2)	4159(1)	3545(1)	20(1)
C(13)	10773(2)	4829(1)	3707(1)	30(1)
C(14)	11668(2)	5115(1)	3298(1)	37(1)
C(15)	12148(2)	4725(1)	2712(1)	35(1)
C(16)	11749(2)	4059(1)	2544(1)	28(1)
C(17)	10845(2)	3756(1)	2944(1)	21(1)
C(18)	9772(2)	3268(1)	4526(1)	17(1)
C(19)	5030(2)	3778(1)	4446(1)	29(1)
C(20)	5946(2)	4853(1)	4177(1)	26(1)
C(21)	11628(2)	3637(1)	5591(1)	32(1)
C(22)	9450(2)	707(1)	4024(1)	22(1)
C(23)	10930(2)	790(1)	4300(1)	29(1)
C(24)	9010(2)	456(1)	3064(1)	31(1)
C(25)	6933(2)	1340(1)	4026(1)	26(1)
C(26)	6632(2)	707(1)	4495(1)	33(1)
C(27)	6192(2)	1341(1)	3068(1)	37(1)
C(28)	11766(2)	2434(1)	2630(1)	31(1)
C(29)	11464(2)	1732(1)	2199(1)	45(1)
C(30)	12678(2)	2375(1)	3546(1) _	36(1)
C(31)	9252(2)	2895(1)	1597(1) ‾	36(1)
C(32)	9855(2)	3198(1)	890(1)	54(1)
C(33)	7977(2)	3240(1)	1596(1)	54(1)

Table S3. Selected bond lengths [Å] and angles [°] for **2b**.

Ni(1)-C(18)	1.9628(16)	C(18)-Ni(1)-C(7)	41.11(6)
Ni(1)-C(7)	2.0907(16)	C(18)-Ni(1)-P(1)	120.95(5)
Ni(1)-P(1)	2.1614(5)	C(7)-Ni(1)-P(1)	85.23(5)
Ni(1)-P(2)	2.1799(5)	C(18)-Ni(1)-P(2)	95.53(5)
		C(7)-Ni(1)-P(2)	135.74(5)
		P(1)-Ni(1)-P(2)	137.43(2)

Table S4. Bond lengths [Å] and angles [°] for **2b.**

Ni(1)-C(18)	1.9628(16)	C(6)-C(1)-C(2)	118.89(14)
Ni(1)-C(7)	2.0907(16)	C(6)-C(1)-P(1)	113.37(12)
Ni(1)-P(1)	2.1614(5)	C(2)-C(1)-P(1)	127.74(13)
Ni(1)-P(2)	2.1799(5)	C(3)-C(2)-C(1)	120.94(16)
P(1)-C(1)	1.8242(15)	C(4)-C(3)-C(2)	119.87(16)
P(1)-C(22)	1.8451(17)	C(3)-C(4)-C(5)	120.11(16)
P(1)-C(25)	1.8649(17)	C(6)-C(5)-C(4)	120.36(17)
P(2)-C(31)	1.8440(17)	C(5)-C(6)-C(1)	119.77(15)
P(2)-C(28)	1.8445(17)	C(5)-C(6)-C(7)	120.82(16)
P(2)-C(17)	1.8480(18)	C(1)-C(6)-C(7)	119.38(14)
O(1)-C(18)	1.4137(17)	C(18)-C(7)-C(8)	116.69(15)
O(1)-C(21)	1.4310(18)	C(18)-C(7)-C(6)	121.82(14)
N(1)-C(9)	1.4219(19)	C(8)-C(7)-C(6)	117.13(14)
N(1)-C(19)	1.448(2)	C(18)-C(7)-Ni(1)	64.64(9)
N(1)-C(20)	1.452(2)	C(8)-C(7)-Ni(1)	115.84(11)
C(1)-C(6)	1.393(2)	C(6)-C(7)-Ni(1)	108.28(11)
C(1)-C(2)	1.397(2)	C(9)-C(8)-C(7)	122.83(16)
C(2)-C(3)	1.377(2)	C(8)-C(9)-C(10)	118.30(15)
C(3)-C(4)	1.374(2)	C(8)-C(9)-N(1)	123.36(16)
C(4)-C(5)	1.389(2)	C(10)-C(9)-N(1)	118.20(15)
C(5)-C(6)	1.3856(19)	C(11)-C(10)-C(9)	121.73(16)
C(6)-C(7)	1.507(2)	C(10)-C(11)-C(18)	120.73(15)
C(7)-C(18)	1.428(2)	C(10)-C(11)-C(12)	121.35(15)
C(7)-C(8)	1.452(2)	C(18)-C(11)-C(12)	117.74(14)
C(8)-C(9)	1.368(2)	C(13)-C(12)-C(17)	120.43(16)
C(9)-C(10)	1.421(2)	C(13)-C(12)-C(11)	119.82(16)
C(10)-C(11)	1.360(2)	C(17)-C(12)-C(11)	119.75(16)
C(11)-C(18)	1.436(2)	C(14)-C(13)-C(12)	121.13(18)
C(11)-C(12)	1.489(2)	C(15)-C(14)-C(13)	119.05(19)
C(12)-C(13)	1.386(2)	C(16)-C(15)-C(14)	120.33(18)
C(12)-C(17)	1.411(2)	C(15)-C(16)-C(17)	122.05(18)
C(13)-C(14)	1.384(2)	C(16)-C(17)-C(12)	117.01(17)
C(14)-C(15)	1.381(2)	C(16)-C(17)-P(2)	123.74(14)
C(15)-C(16)	1.378(2)	C(12)-C(17)-P(2)	119.25(13)
C(16)-C(17)	1.398(2)	O(1)-C(18)-C(7)	120.18(14)
C(22)-C(23)	1.535(2)	O(1)-C(18)-C(11)	118.72(14)
C(22)-C(24)	1.540(2)	C(7)-C(18)-C(11)	119.07(14)
C(25)-C(26)	1.514(2)	O(1)-C(18)-Ni(1)	104.73(10)
C(25)-C(27)	1.514(2)	C(7)-C(18)-Ni(1)	74.25(10)
C(28)-C(30)	1.527(2)	C(11)-C(18)-Ni(1)	104.60(11)
C(28)-C(29)	1.531(2)	C(23)-C(22)-C(24)	110.98(14)
C(31)-C(33)	1.512(2)	C(23)-C(22)-P(1)	108.80(12)
C(31)-C(32)	1.524(2)	C(24)-C(22)-P(1)	110.45(11)
C(18)-Ni(1)-C(7)	41.11(6)	C(26)-C(25)-C(27)	111.05(14)
C(18)-Ni(1)-P(1)	120.95(5)	C(26)-C(25)-P(1)	115.83(12)
C(7)-Ni(1)-P(1)	85.23(5)	C(27)-C(25)-P(1)	112.03(12)
C(18)-Ni(1)-P(2)	95.53(5)	C(30)-C(28)-C(29)	111.28(16)
C(7)-Ni(1)-P(2)	135.74(5)	C(30)-C(28)-P(2)	108.60(11)
P(1)-Ni(1)-P(2)	137.43(2)	C(29)-C(28)-P(2)	111.07(12)
C(1)-P(1)-C(22)	103.76(7)	C(33)-C(31)-C(32)	110.87(17)
C(1)-P(1)-C(25)	99.94(7)	C(33)-C(31)-P(2)	109.31(13)
C(22)-P(1)-C(25)	105.23(8)	C(32)-C(31)-P(2)	117.32(13)
C(1)-P(1)-Ni(1)	98.66(5)		
C(22)-P(1)-Ni(1)	125.00(6)		
C(25)-P(1)-Ni(1)	119.44(6)		
C(31)-P(2)-C(28)	104.23(8)		
C(31)-P(2)-C(17)	103.67(8)		
C(28)-P(2)-C(17)	101.17(8)		
C(31)-P(2)-Ni(1)	113.96(6)		
C(28)-P(2)-Ni(1)	119.38(6)		
C(17)-P(2)-Ni(1)	112.55(6)		
C(18)-O(1)-C(21)	112.62(12)		
C(9)-N(1)-C(19)	116.04(14)		
C(9)-N(1)-C(20)	115.62(13)		
C(19)-N(1)-C(20)	111.68(13)		

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Table S5. Anisotropic displacement parameters ($Å^2$ x 10^4) for **2b**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a*^2U^{11} + ... + 2 h k a* b* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	184(1)	191(1)	188(1)	0(1)	70(1)	11(1)
P(1)	223(2)	184(3)	188(3)	-9(2)	39(2)	11(2)
P(2)	185(2)	292(3)	196(3)	-18(2)	84(2)	-10(2)
O(1)	176(6)	229(7)	220(7)	-12(5)	43(5)	14(5)
N(1)	180(7)	206(9)	213(9)	-19(7)	40(7)	27(7)
C(1)	162(8)	155(10)	153(10)	12(7)	54(7)	3(7)
C(2)	256(9)	196(11)	241(11)	-10(8)	76(8)	-4(8)
C(3)	245(10)	258(12)	198(11)	66(8)	73(8)	21(8)
C(4)	232(9)	323(12)	154(10)	-21(8)	66(8)	2(9)
C(5)	199(8)	234(11)	213(10)	-33(9)	81(7)	-4(8)
C(6)	118(7)	236(11)	177(10)	28(8)	76(7)	-1(7)
C(7)	204(9)	168(10)	144(10)	-16(7)	44(7)	12(7)
C(8)	148(8)	213(10)	188(10)	-37(8)	63(7)	-1(7)
C(9)	198(9)	207(11)	129(10)	-47(8)	40(7)	21(8)
C(10)	254(9)	140(9)	221(10)	32(8)	73(8)	45(8)
C(11)	208(9)	167(10)	164(10)	-11(7)	75(8)	-3(8)
C(12)	166(9)	190(11)	240(11)	94(8)	42(8)	7(8)
C(13)	338(11)	223(12)	383(13)	46(9)	175(10)	27(9)
C(14)	387(12)	224(12)	511(14)	100(10)	140(11)	-40(10)
C(15)	300(11)	358(14)	422(13)	158(11)	158(10)	-20(10)
C(16)	221(9)	339(13)	300(11)	71(9)	119(9)	30(9)
C(17)	160(8)	264(11)	212(11)	105(8)	50(8)	34(8)
C(18)	148(8)	196(10)	178(10)	-10(8)	40(7)	16(7)
C(19)	184(9)	277(12)	412(13)	-32(9)	75(9)	24(8)
C(20)	254(10)	257(11)	287(11)	36(8)	116(9)	77(8)
C(21)	250(10)	330(13)	339(12)	-21(9)	25(9)	-56(9)
C(22)	293(10)	184(10)	191(10)	5(8)	63(8)	14(8)
C(23)	327(11)	239(12)	317(12)	20(9)	93(9)	57(9)
C(24)	411(12)	243(12)	257(11)	-18(9)	54(9)	45(9)
C(25)	250(10)	302(12)	211(11)	-11(9)	48(8)	7(9)
C(26)	256(10)	314(13)	409(13)	39(10)	31(9)	-55(9)
C(27)	292(11)	407(14)	371(13)	34(10)	-17(10)	7(10)
C(28)	295(9)	339(12)	382(11)	-34(11)	232(8)	-1(10)
C(29)	500(13)	409(15)	521(15)	-129(11)	300(12)	6(11)
C(30)	209(9)	322(14)	566(13)	18(10)	121(9)	30(9)
C(31)	387(12)	532(15)	180(11)	29(10)	91(9)	-103(11)
C(32)	482(14)	920(20)	210(12)	57(12)	80(10)	-182(14)
C(33)	275(11)	990(20)	300(13)	182(13)	-23(10)	6(13)
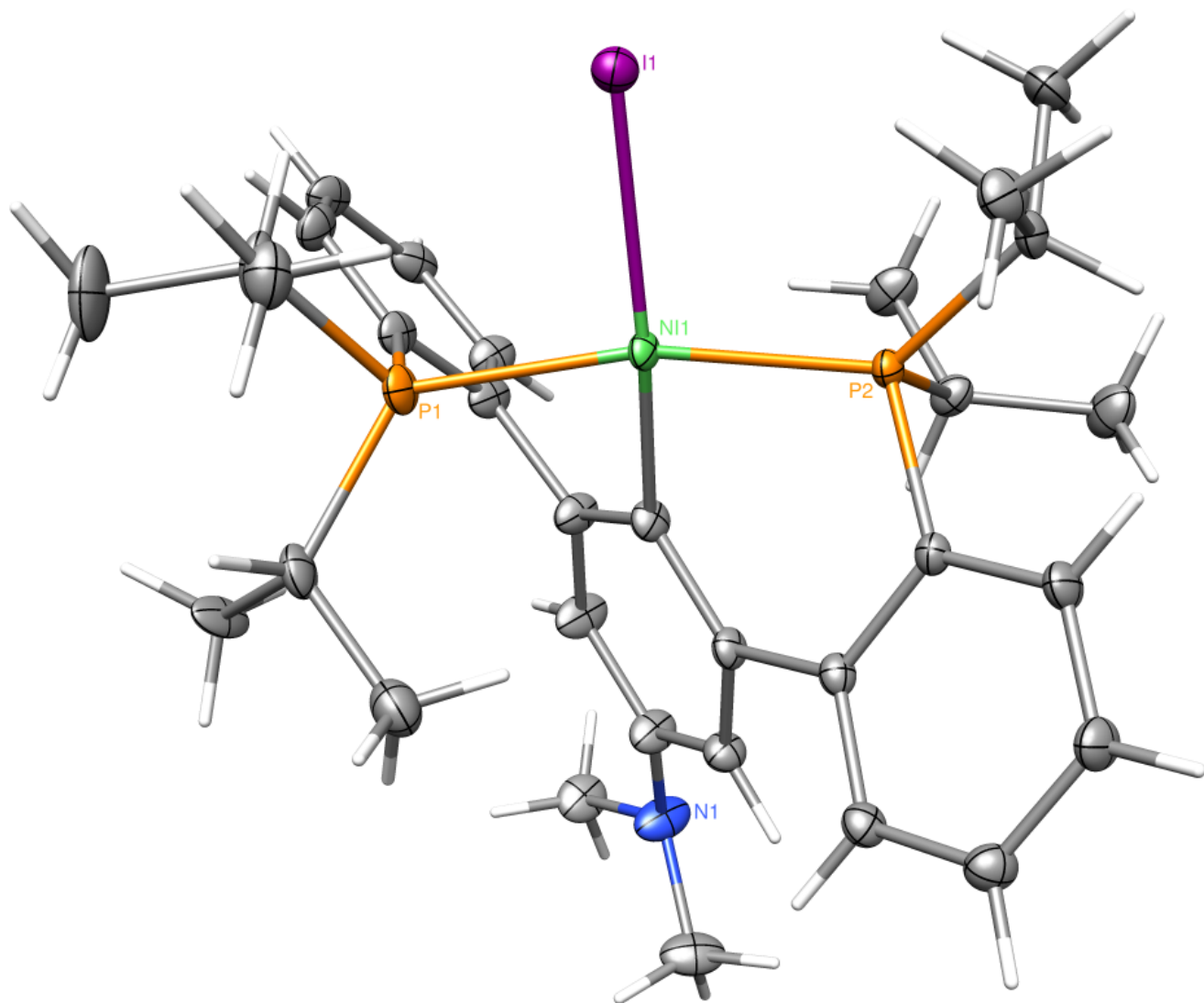
Figure S2. Structural drawing of **5** with 50% thermal probability ellipsoids.
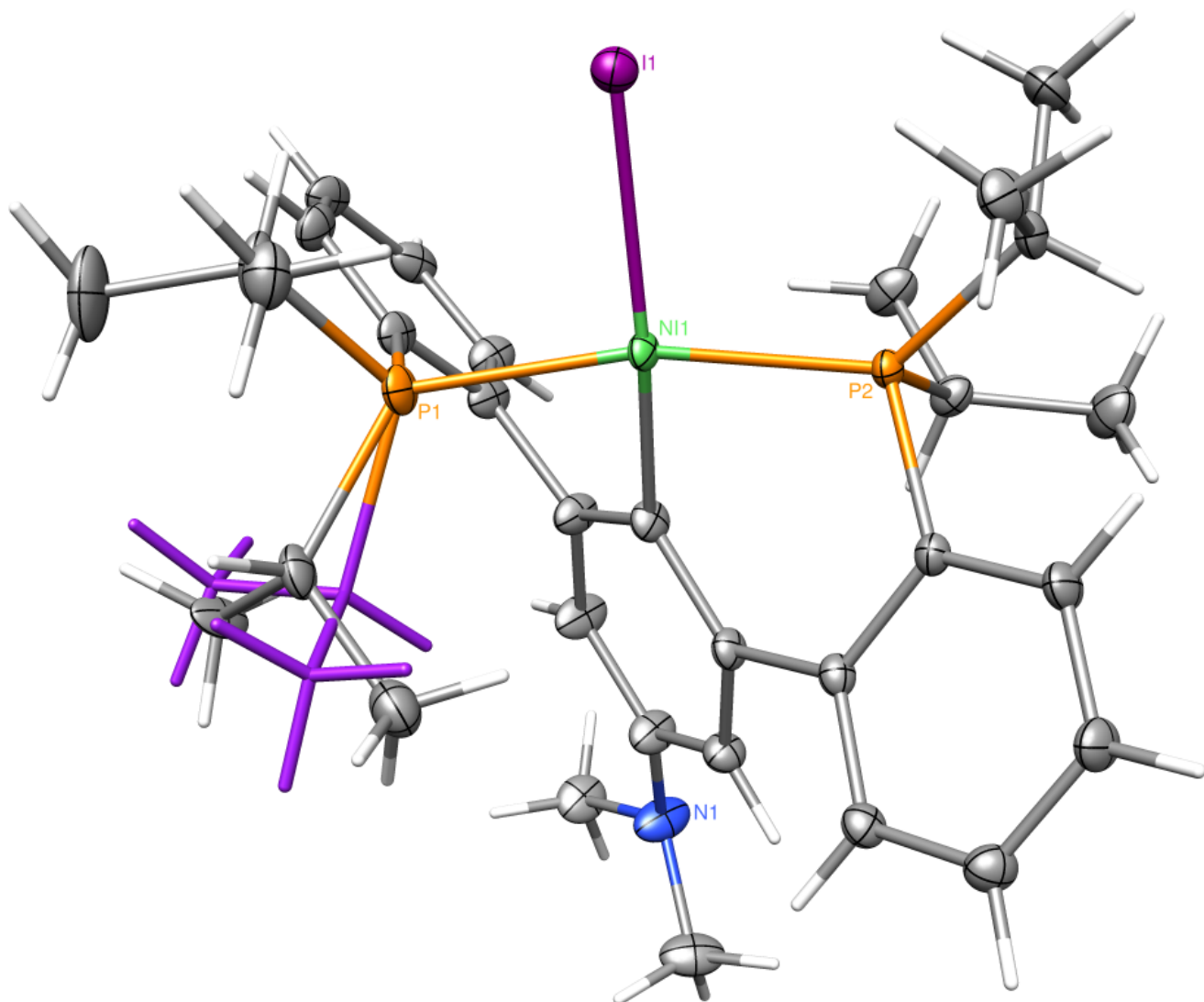
Figure S3. Structural drawing of **5** with 50% thermal probability ellipsoids showing disorder in isopropyl group.

Special Refinement Details for 5. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. One of the isopropyl groups on P1 is disordered and the model includes anisotropic refinement the disordered atoms without restraints in the least-squares. The two orientations of the disordered group were constrained to have a total occupancy of one. Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2s(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2x 10^3) for **5**. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U$_{eq}$	Occ
Ni(1)	10947(1)	943(1)	1261(1)	12(1)	1
I(1)	12720(1)	2063(1)	1760(1)	18(1)	1
N(1)	4918(2)	-832(1)	438(1)	26(1)	1
P(1)	11101(1)	650(1)	3148(1)	17(1)	1
P(2)	10524(1)	980(1)	-677(1)	13(1)	1
C(1)	9562(2)	1278(1)	3307(1)	18(1)	1
C(2)	9694(2)	1873(1)	4132(1)	22(1)	1
C(3)	8487(2)	2348(1)	4157(1)	24(1)	1
C(4)	7133(2)	2252(1)	3354(1)	22(1)	1
C(5)	6994(2)	1681(1)	2508(1)	22(1)	1
C(6)	8196(2)	1186(1)	2475(1)	18(1)	1
C(7)	8006(2)	546(1)	1600(1)	19(1)	1
C(8)	6627(2)	153(1)	1423(2)	23(1)	1
C(9)	6328(2)	-474(1)	673(1)	20(1)	1
C(10)	7473(2)	-703(1)	111(1)	17(1)	1
C(11)	8838(2)	-304(1)	245(1)	14(1)	1
C(12)	9870(2)	-554(1)	-526(1)	13(1)	1
C(13)	9997(2)	-1322(1)	-789(1)	16(1)	1
C(14)	10799(2)	-1569(1)	-1611(1)	19(1)	1
C(15)	11522(2)	-1036(1)	-2184(1)	19(1)	1
C(16)	11435(2)	-274(1)	-1921(1)	17(1)	1
C(17)	10634(2)	-17(1)	-1092(1)	13(1)	1
C(18)	9144(2)	336(1)	1002(1)	15(1)	1
C(19)	3864(2)	-628(1)	1165(2)	25(1)	1
C(20)	4827(2)	-1615(1)	48(2)	29(1)	1
C(21)	12765(2)	945(1)	4291(1)	25(1)	1
C(22)	14202(2)	577(1)	4061(2)	24(1)	1
C(23)	12630(2)	798(1)	5579(2)	42(1)	1
C(24A)	10839(4)	-306(2)	3773(3)	21(1)	0.635(6)
C(25A)	9526(9)	-383(3)	4464(7)	25(1)	0.635(6)
C(26A)	10588(4)	-952(2)	2875(3)	27(1)	0.635(6)
C(24B)	10309(6)	-334(3)	3409(5)	17(1)	0.365(6)
C(25B)	9676(15)	-224(6)	4541(11)	26(2)	0.365(6)
C(26B)	11535(6)	-930(3)	3517(5)	24(1)	0.365(6)
C(27)	11788(2)	1453(1)	-1524(1)	18(1)	1
C(28)	11576(2)	2313(1)	-1618(2)	23(1)	1
C(29)	13459(2)	1252(1)	-1048(1)	22(1)	1
C(30)	8570(2)	1232(1)	-1447(1)	18(1)	1
C(31)	8316(2)	1226(1)	-2798(1)	26(1)	1
C(32)	8011(2)	1964(1)	-958(1)	24(1)	1
C(41)	5764(3)	9430(2)	7114(2)	61(1)	1
C(42)	6484(3)	9045(1)	6250(2)	49(1)	1
O(41)	5392(2)	8616(1)	5452(1)	37(1)	1
C(43)	6010(3)	8221(1)	4598(3)	53(1)	1
C(44)	4831(3)	7720(2)	3896(3)	60(1)	1

Table S7. Selected bond lengths [Å] and angles [°] for **5**.

Ni(1)-C(18)	1.9188(14)	C(18)-Ni(1)-P(2)	84.30(4)
Ni(1)-P(2)	2.1827(4)	C(18)-Ni(1)-P(1)	83.98(4)
Ni(1)-P(1)	2.2075(4)	P(2)-Ni(1)-P(1)	166.680(17)
Ni(1)-I(1)	2.5268(2)	C(18)-Ni(1)-I(1)	161.06(4)
		P(2)-Ni(1)-I(1)	99.972(12)
		P(1)-Ni(1)-I(1)	93.156(13)

Table S8. Bond lengths [Å] and angles [°] for **5**.

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Ni(1)-C(18)	1.9188(14)	C(17)-P(2)-C(27)	102.65(7)
Ni(1)-P(2)	2.1827(4)	C(17)-P(2)-C(30)	101.79(6)
Ni(1)-P(1)	2.2075(4)	C(27)-P(2)-C(30)	105.95(7)
Ni(1)-I(1)	2.5268(2)	C(17)-P(2)-Ni(1)	103.40(4)
N(1)-C(9)	1.397(2)	C(27)-P(2)-Ni(1)	123.96(5)
N(1)-C(19)	1.443(2)	C(30)-P(2)-Ni(1)	115.85(5)
N(1)-C(20)	1.444(2)	C(2)-C(1)-C(6)	118.95(14)
P(1)-C(1)	1.8173(16)	C(2)-C(1)-P(1)	124.47(12)
P(1)-C(21)	1.8504(17)	C(6)-C(1)-P(1)	116.39(11)
P(1)-C(24A)	1.862(3)	C(3)-C(2)-C(1)	120.82(15)
P(1)-C(24B)	1.920(6)	C(4)-C(3)-C(2)	120.44(14)
P(2)-C(17)	1.8230(14)	C(3)-C(4)-C(5)	119.56(14)
P(2)-C(27)	1.8522(15)	C(4)-C(5)-C(6)	121.01(15)
P(2)-C(30)	1.8553(15)	C(5)-C(6)-C(1)	119.19(13)
C(1)-C(2)	1.400(2)	C(5)-C(6)-C(7)	120.48(14)
C(1)-C(6)	1.402(2)	C(1)-C(6)-C(7)	120.28(13)
C(2)-C(3)	1.380(2)	C(8)-C(7)-C(18)	121.52(14)
C(3)-C(4)	1.379(2)	C(8)-C(7)-C(6)	116.01(13)
C(4)-C(5)	1.385(2)	C(18)-C(7)-C(6)	122.45(13)
C(5)-C(6)	1.399(2)	C(9)-C(8)-C(7)	121.96(14)
C(6)-C(7)	1.496(2)	C(8)-C(9)-C(10)	116.83(13)
C(7)-C(8)	1.404(2)	C(8)-C(9)-N(1)	121.70(13)
C(7)-C(18)	1.405(2)	C(10)-C(9)-N(1)	121.37(14)
C(8)-C(9)	1.390(2)	C(9)-C(10)-C(11)	122.11(14)
C(9)-C(10)	1.394(2)	C(10)-C(11)-C(18)	121.20(13)
C(10)-C(11)	1.4001(19)	C(10)-C(11)-C(12)	116.07(12)
C(11)-C(18)	1.414(2)	C(18)-C(11)-C(12)	122.54(12)
C(11)-C(12)	1.4862(19)	C(13)-C(12)-C(17)	118.43(12)
C(12)-C(13)	1.393(2)	C(13)-C(12)-C(11)	120.53(12)
C(12)-C(17)	1.4094(19)	C(17)-C(12)-C(11)	120.78(12)
C(13)-C(14)	1.381(2)	C(14)-C(13)-C(12)	122.31(13)
C(14)-C(15)	1.388(2)	C(13)-C(14)-C(15)	118.94(14)
C(15)-C(16)	1.379(2)	C(16)-C(15)-C(14)	119.75(14)
C(16)-C(17)	1.3923(19)	C(15)-C(16)-C(17)	121.91(13)
C(21)-C(22)	1.526(2)	C(16)-C(17)-C(12)	118.61(13)
C(21)-C(23)	1.535(2)	C(16)-C(17)-P(2)	123.85(11)
C(24A)-C(25A)	1.572(7)	C(12)-C(17)-P(2)	117.53(10)
C(24A)-C(26A)	1.519(5)	C(7)-C(18)-C(11)	116.30(13)
C(24B)-C(26B)	1.511(7)	C(7)-C(18)-Ni(1)	117.85(11)
C(24B)-C(25B)	1.544(15)	C(11)-C(18)-Ni(1)	125.84(10)
C(27)-C(28)	1.524(2)	C(22)-C(21)-C(23)	110.09(14)
C(27)-C(29)	1.536(2)	C(22)-C(21)-P(1)	110.63(11)
C(30)-C(31)	1.523(2)	C(23)-C(21)-P(1)	114.73(13)
C(30)-C(32)	1.532(2)	C(25A)-C(24A)-C(26A)	105.1(3)
C(41)-C(42)	1.466(4)	C(25A)-C(24A)-P(1)	116.5(3)
C(42)-O(41)	1.415(3)	C(26A)-C(24A)-P(1)	115.1(2)
O(41)-C(43)	1.413(3)	C(26B)-C(24B)-C(25B)	114.6(6)
C(43)-C(44)	1.483(4)	C(26B)-C(24B)-P(1)	110.2(4)
C(18)-Ni(1)-P(2)	84.30(4)	C(25B)-C(24B)-P(1)	103.8(5)
C(18)-Ni(1)-P(1)	83.98(4)	C(28)-C(27)-C(29)	110.65(14)
P(2)-Ni(1)-P(1)	166.680(17)	C(28)-C(27)-P(2)	113.57(11)
C(18)-Ni(1)-I(1)	161.06(4)	C(29)-C(27)-P(2)	112.42(11)
P(2)-Ni(1)-I(1)	99.972(12)	C(31)-C(30)-C(32)	113.03(13)
P(1)-Ni(1)-I(1)	93.156(13)	C(31)-C(30)-P(2)	113.97(11)
C(9)-N(1)-C(19)	117.81(13)	C(32)-C(30)-P(2)	112.40(10)
C(9)-N(1)-C(20)	118.54(13)	O(41)-C(42)-C(41)	109.6(2)
C(19)-N(1)-C(20)	114.64(13)	C(43)-O(41)-C(42)	112.79(18)
C(1)-P(1)-C(21)	106.43(7)	O(41)-C(43)-C(44)	109.0(2)
C(1)-P(1)-C(24A)	110.21(11)		
C(21)-P(1)-C(24A)	97.44(14)		
C(1)-P(1)-C(24B)	102.20(17)		
C(21)-P(1)-C(24B)	114.54(19)		
C(1)-P(1)-Ni(1)	93.98(5)		
C(21)-P(1)-Ni(1)	120.31(5)		
C(24A)-P(1)-Ni(1)	127.17(11)		
C(24B)-P(1)-Ni(1)	114.68(17)		

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Table S9. Anisotropic displacement parameters ($Å^2$x 10^4) for **5**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	109(1)	165(1)	92(1)	-8(1)	46(1)	-24(1)
I(1)	165(1)	205(1)	183(1)	-3(1)	41(1)	-28(1)
N(1)	161(6)	288(7)	368(8)	-110(6)	126(6)	-74(5)
P(1)	197(2)	222(2)	115(2)	12(1)	83(1)	5(2)
P(2)	142(2)	144(2)	100(1)	-5(1)	45(1)	-13(1)
C(1)	210(7)	219(7)	145(6)	-20(5)	112(5)	-22(6)
C(2)	253(7)	271(8)	144(6)	-49(5)	83(6)	-34(6)
C(3)	329(9)	219(7)	203(7)	-67(6)	151(7)	-37(6)
C(4)	253(8)	201(8)	269(8)	-6(6)	165(6)	0(5)
C(5)	166(7)	267(8)	251(8)	-50(6)	109(6)	-38(6)
C(6)	175(7)	219(7)	190(7)	-43(5)	122(6)	-35(5)
C(7)	167(7)	222(7)	199(7)	-62(6)	100(6)	-48(5)
C(8)	159(7)	289(8)	299(8)	-98(7)	152(6)	-65(6)
C(9)	133(6)	258(8)	244(7)	-50(6)	96(6)	-56(6)
C(10)	132(6)	183(7)	191(7)	-5(5)	53(5)	-28(5)
C(11)	119(6)	182(6)	124(6)	5(5)	53(5)	-13(5)
C(12)	108(6)	168(6)	121(6)	8(5)	31(5)	-7(5)
C(13)	144(6)	168(6)	169(6)	9(5)	55(5)	-9(5)
C(14)	192(7)	164(6)	227(7)	-16(6)	76(6)	11(5)
C(15)	218(7)	208(7)	181(7)	-28(6)	118(6)	-5(6)
C(16)	210(7)	186(7)	153(6)	4(5)	102(5)	-12(5)
C(17)	134(6)	153(6)	109(6)	-4(5)	34(5)	1(5)
C(18)	118(6)	195(7)	155(6)	-4(5)	63(5)	-21(5)
C(19)	127(7)	337(9)	317(9)	-38(7)	99(6)	-40(6)
C(20)	180(8)	234(8)	487(11)	-43(7)	122(7)	-44(6)
C(21)	277(8)	366(9)	97(6)	-8(6)	30(5)	46(7)
C(22)	216(8)	328(9)	177(7)	15(6)	21(6)	18(7)
C(23)	421(11)	699(15)	130(7)	46(8)	70(7)	127(11)
C(24A)	217(16)	280(14)	134(14)	62(12)	58(11)	-23(13)
C(25A)	360(30)	190(20)	287(19)	4(16)	256(18)	-71(17)
C(26A)	289(16)	278(14)	240(14)	65(11)	39(12)	-12(11)
C(24B)	140(20)	250(20)	120(20)	63(19)	17(17)	-19(19)
C(25B)	250(30)	260(40)	260(30)	150(30)	40(20)	-80(30)
C(26B)	270(30)	210(20)	310(30)	75(18)	180(20)	25(17)
C(27)	233(7)	205(7)	119(6)	-7(5)	92(5)	-35(6)
C(28)	321(9)	187(7)	202(7)	16(6)	93(6)	-59(6)
C(29)	207(7)	256(8)	217(7)	-25(6)	122(6)	-41(6)
C(30)	168(7)	181(6)	167(7)	-22(5)	2(5)	6(5)
C(31)	297(9)	272(8)	186(7)	-13(6)	-27(6)	34(7)
C(32)	228(7)	224(9)	265(7)	-38(7)	13(6)	60(6)
C(41)	703(18)	656(17)	342(12)	41(12)	-152(12)	-206(15)
C(42)	379(12)	374(12)	613(15)	151(11)	-135(11)	-117(10)
O(41)	324(8)	364(7)	387(8)	45(6)	-26(6)	-78(6)
C(43)	407(12)	389(12)	815(19)	-32(13)	165(12)	-50(10)
C(44)	647(17)	532(15)	675(17)	-220(13)	280(14)	-185(13)
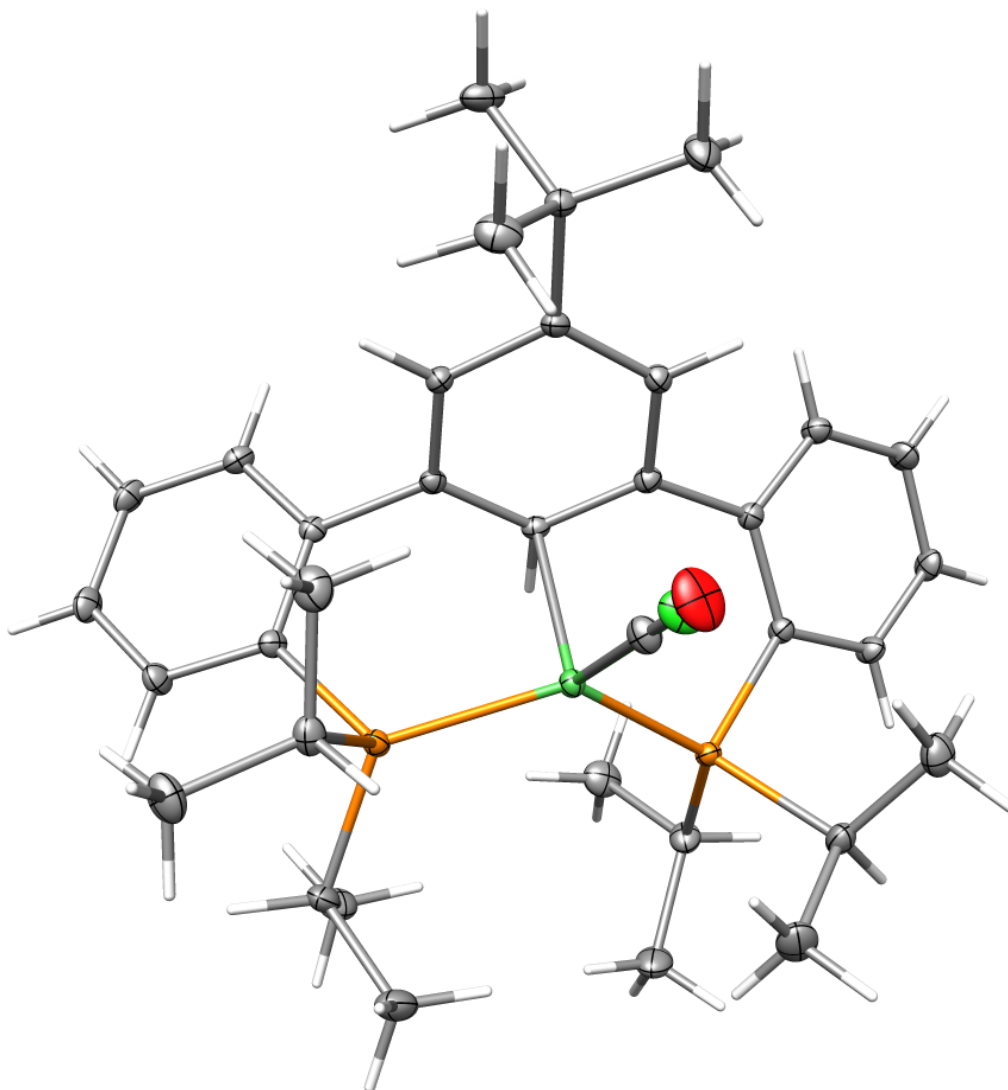
Figure S4. Structural drawing of **6a** with 50% thermal probability ellipsoids.

Special Refinement Details for 6a. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The crystal is disordered at the carbonyl position with a 0.04% impurity of chlorine present. All components were refined without restraint other than setting total occupancy to equal unity. Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2s(\ F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6a** (CCDC 857167). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Ni(1)	5193(1)	7496(1)	6109(1)	10(1)	1
P(1)	4561(1)	6027(1)	5395(1)	10(1)	1
P(2)	6099(1)	8746(1)	5816(1)	10(1)	1
C(1)	3720(1)	6738(1)	5029(1)	11(1)	1
C(2)	3321(1)	6135(1)	4424(1)	14(1)	1
C(3)	2676(1)	6671(1)	4177(1)	15(1)	1
C(4)	2415(1)	7833(1)	4536(1)	15(1)	1
C(5)	2803(1)	8448(1)	5137(1)	13(1)	1
C(6)	3452(1)	7926(1)	5389(1)	10(1)	1
C(7)	3828(1)	8590(1)	6062(1)	10(1)	1
C(8)	3527(1)	8492(1)	6767(1)	11(1)	1
C(9)	3842(1)	9093(1)	7431(1)	10(1)	1
C(10)	4467(1)	9784(1)	7369(1)	11(1)	1
C(11)	4784(1)	9931(1)	6661(1)	11(1)	1
C(12)	5403(1)	10843(1)	6625(1)	10(1)	1
C(13)	5390(1)	12125(1)	7010(1)	13(1)	1
C(14)	5931(1)	13072(1)	6984(1)	15(1)	1
C(15)	6506(1)	12757(1)	6562(1)	14(1)	1
C(16)	6536(1)	11479(1)	6196(1)	13(1)	1
C(17)	5998(1)	10503(1)	6223(1)	10(1)	1
C(18)	4450(1)	9342(1)	6000(1)	10(1)	1
C(19)	3492(1)	8891(1)	8192(1)	12(1)	1
C(20)	3427(1)	7320(1)	8346(1)	18(1)	1
C(21)	2764(1)	9550(1)	8140(1)	19(1)	1
C(22)	3917(1)	9541(1)	8866(1)	20(1)	1
C(23)	4292(1)	4491(1)	5968(1)	14(1)	1
C(24)	3838(1)	4944(1)	6616(1)	19(1)	1
C(25)	3944(1)	3276(1)	5530(1)	22(1)	1
C(26)	4886(1)	5172(1)	4531(1)	15(1)	1
C(27)	4977(1)	6228(1)	3886(1)	19(1)	1
C(28)	5570(1)	4412(1)	4742(1)	22(1)	1
C(29)	6386(1)	9267(1)	4851(1)	15(1)	1
C(30)	5784(1)	9947(1)	4389(1)	21(1)	1
C(31)	6710(1)	8072(1)	4415(1)	23(1)	1
C(32)	6947(1)	8187(1)	6297(1)	14(1)	1
C(33)	7009(1)	8547(1)	7150(1)	20(1)	1
C(34)	7039(1)	6613(1)	6200(1)	23(1)	1
C(35)	5309(1)	6931(1)	7056(1)	14(1)	0.964(3)
O(1)	5387(1)	6565(1)	7684(1)	29(1)	0.964(3)
Cl(1)	5375(5)	6771(8)	7456(5)	19(3)	0.036(3)

Table S11. Selected bond lengths [Å] and angles [°] for **6a**.

Ni(1)-C(35)	1.7472(10)	C(35)-Ni(1)-P(2)	109.28(3)
Ni(1)-P(2)	2.1950(2)	C(35)-Ni(1)-P(1)	112.14(3)
Ni(1)-P(1)	2.2048(2)	P(2)-Ni(1)-P(1)	129.471(8)
Ni(1)-C(18)	2.2763(7)	C(35)-Ni(1)-C(18)	111.58(3)
Ni(1)-Cl(1)	2.465(8)	P(2)-Ni(1)-C(18)	93.132(18)
		P(1)-Ni(1)-C(18)	97.360(18)
		C(35)-Ni(1)-Cl(1)	1.9(2)
		P(2)-Ni(1)-Cl(1)	107.7(2)
		P(1)-Ni(1)-Cl(1)	114.0(2)
		C(18)-Ni(1)-Cl(1)	110.80(19)

Table S12. Bond lengths [Å] and angles [°] for **6a**.

Ni(1)-C(35)	1.7472(10)	Ni(1)-C(18)	2.2763(7)
Ni(1)-P(2)	2.1950(2)	Ni(1)-Cl(1)	2.465(8)
Ni(1)-P(1)	2.2048(2)	P(1)-C(1)	1.8354(7)

|			
P(1)-C(26)	1.8582(7)	C(1)-C(6)-C(7)	121.69(6)
P(1)-C(23)	1.8723(7)	C(8)-C(7)-C(18)	119.77(6)
P(2)-C(17)	1.8452(7)	C(8)-C(7)-C(6)	117.75(6)
P(2)-C(32)	1.8693(7)	C(18)-C(7)-C(6)	122.43(5)
P(2)-C(29)	1.8745(7)	C(7)-C(8)-C(9)	121.65(6)
C(1)-C(2)	1.3983(9)	C(10)-C(9)-C(8)	118.03(6)
C(1)-C(6)	1.4148(9)	C(10)-C(9)-C(19)	123.50(6)
C(2)-C(3)	1.3881(10)	C(8)-C(9)-C(19)	118.42(6)
C(3)-C(4)	1.3877(11)	C(9)-C(10)-C(11)	122.23(6)
C(4)-C(5)	1.3879(10)	C(18)-C(11)-C(10)	118.66(6)
C(5)-C(6)	1.3924(10)	C(18)-C(11)-C(12)	122.10(5)
C(6)-C(7)	1.4907(9)	C(10)-C(11)-C(12)	118.78(5)
C(7)-C(8)	1.3942(8)	C(13)-C(12)-C(17)	118.63(6)
C(7)-C(18)	1.4054(9)	C(13)-C(12)-C(11)	117.49(6)
C(8)-C(9)	1.4043(9)	C(17)-C(12)-C(11)	123.88(6)
C(9)-C(10)	1.3791(10)	C(14)-C(13)-C(12)	121.81(6)
C(9)-C(19)	1.5367(9)	C(13)-C(14)-C(15)	119.43(6)
C(10)-C(11)	1.4166(8)	C(16)-C(15)-C(14)	119.45(7)
C(11)-C(18)	1.4106(9)	C(15)-C(16)-C(17)	121.84(6)
C(11)-C(12)	1.4798(9)	C(16)-C(17)-C(12)	118.76(6)
C(12)-C(13)	1.4044(9)	C(16)-C(17)-P(2)	120.42(5)
C(12)-C(17)	1.4101(9)	C(12)-C(17)-P(2)	120.58(5)
C(13)-C(14)	1.3837(10)	C(7)-C(18)-C(11)	119.58(5)
C(14)-C(15)	1.3936(10)	C(7)-C(18)-Ni(1)	97.16(4)
C(15)-C(16)	1.3874(10)	C(11)-C(18)-Ni(1)	89.38(4)
C(16)-C(17)	1.3979(10)	C(21)-C(19)-C(22)	108.86(6)
C(19)-C(21)	1.5307(11)	C(21)-C(19)-C(9)	109.67(5)
C(19)-C(22)	1.5315(10)	C(22)-C(19)-C(9)	112.16(6)
C(19)-C(20)	1.5384(10)	C(21)-C(19)-C(20)	109.47(6)
C(23)-C(25)	1.5301(10)	C(22)-C(19)-C(20)	108.03(6)
C(23)-C(24)	1.5311(11)	C(9)-C(19)-C(20)	108.60(5)
C(26)-C(28)	1.5288(11)	C(25)-C(23)-C(24)	109.70(7)
C(26)-C(27)	1.5343(10)	C(25)-C(23)-P(1)	117.25(5)
C(29)-C(30)	1.5223(11)	C(24)-C(23)-P(1)	111.00(5)
C(29)-C(31)	1.5288(11)	C(28)-C(26)-C(27)	111.34(6)
C(32)-C(33)	1.5318(10)	C(28)-C(26)-P(1)	109.58(5)
C(32)-C(34)	1.5327(11)	C(27)-C(26)-P(1)	111.30(5)
C(35)-O(1)	1.157(2)	C(30)-C(29)-C(31)	111.98(6)
		C(30)-C(29)-P(2)	109.98(5)
C(35)-Ni(1)-P(2)	109.28(3)	C(31)-C(29)-P(2)	113.42(5)
C(35)-Ni(1)-P(1)	112.14(3)	C(33)-C(32)-C(34)	109.10(6)
P(2)-Ni(1)-P(1)	129.471(8)	C(33)-C(32)-P(2)	113.20(5)
C(35)-Ni(1)-C(18)	111.58(3)	C(34)-C(32)-P(2)	109.71(5)
P(2)-Ni(1)-C(18)	93.132(18)	O(1)-C(35)-Ni(1)	179.55(9)
P(1)-Ni(1)-C(18)	97.360(18)		
C(35)-Ni(1)-Cl(1)	1.9(2)		
P(2)-Ni(1)-Cl(1)	107.7(2)		
P(1)-Ni(1)-Cl(1)	114.0(2)		
C(18)-Ni(1)-Cl(1)	110.80(19)		
C(1)-P(1)-C(26)	101.98(3)		
C(1)-P(1)-C(23)	102.54(3)		
C(26)-P(1)-C(23)	101.69(3)		
C(1)-P(1)-Ni(1)	113.99(2)		
C(26)-P(1)-Ni(1)	123.08(3)		
C(23)-P(1)-Ni(1)	111.05(2)		
C(17)-P(2)-C(32)	101.33(3)		
C(17)-P(2)-C(29)	98.40(3)		
C(32)-P(2)-C(29)	101.03(3)		
C(17)-P(2)-Ni(1)	107.99(2)		
C(32)-P(2)-Ni(1)	114.72(2)		
C(29)-P(2)-Ni(1)	129.17(2)		
C(2)-C(1)-C(6)	118.30(6)		
C(2)-C(1)-P(1)	123.09(5)		
C(6)-C(1)-P(1)	118.58(5)		
C(3)-C(2)-C(1)	121.71(7)		
C(4)-C(3)-C(2)	119.64(6)		
C(5)-C(4)-C(3)	119.61(7)		
C(4)-C(5)-C(6)	121.42(7)		
C(5)-C(6)-C(1)	119.32(6)		
C(5)-C(6)-C(7)	118.90(6)		

Table S13. Anisotropic displacement parameters (Å^2 x 10^4) for **6a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\,h^2a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	100(1)	95(1)	102(1)	-1(1)	4(1)	-9(1)
P(1)	102(1)	90(1)	105(1)	-10(1)	-5(1)	9(1)
P(2)	85(1)	91(1)	111(1)	-6(1)	12(1)	4(1)
C(1)	108(3)	112(3)	98(2)	2(2)	2(2)	7(2)
C(2)	153(3)	142(3)	120(2)	-19(2)	-10(2)	-5(2)
C(3)	136(3)	188(3)	115(2)	12(2)	-23(2)	-24(3)
C(4)	100(3)	195(3)	145(3)	42(2)	-11(2)	3(2)
C(5)	109(3)	139(3)	139(3)	13(2)	20(2)	10(2)
C(6)	104(3)	105(2)	89(2)	12(2)	17(2)	-7(2)
C(7)	92(3)	91(2)	104(2)	-2(2)	8(2)	10(2)
C(8)	93(3)	120(3)	110(2)	-7(2)	18(2)	-12(2)
C(9)	102(3)	112(3)	98(2)	-8(2)	15(2)	6(2)
C(10)	112(3)	129(3)	102(2)	-10(2)	9(2)	-12(2)
C(11)	99(3)	104(3)	115(2)	6(2)	18(2)	-5(2)
C(12)	99(3)	102(3)	105(2)	11(2)	4(2)	-5(2)
C(13)	123(3)	117(3)	150(3)	-6(2)	24(2)	9(2)
C(14)	156(3)	95(3)	185(3)	-26(2)	9(2)	-4(2)
C(15)	119(3)	117(3)	194(3)	5(2)	3(2)	-32(2)
C(16)	106(3)	123(3)	167(3)	-5(2)	30(2)	-15(2)
C(17)	97(3)	88(3)	124(2)	4(2)	7(2)	0(2)
C(18)	98(3)	98(2)	100(2)	6(2)	27(2)	4(2)
C(19)	112(3)	150(3)	97(2)	-9(2)	26(2)	-11(2)
C(20)	232(4)	183(4)	139(3)	36(2)	57(2)	-4(3)
C(21)	176(4)	240(4)	145(3)	-7(3)	51(2)	52(3)
C(22)	199(4)	282(4)	109(3)	-28(2)	28(2)	-59(3)
C(23)	152(3)	114(3)	158(3)	15(2)	-26(2)	-8(2)
C(24)	221(4)	173(3)	178(3)	22(2)	26(3)	-53(3)
C(25)	272(4)	131(3)	246(3)	-11(3)	-4(3)	-60(3)
C(26)	146(3)	144(3)	149(3)	-48(2)	10(2)	19(2)
C(27)	205(4)	212(4)	148(3)	-23(2)	43(2)	13(3)
C(28)	191(4)	222(4)	237(3)	-63(3)	12(3)	71(3)
C(29)	142(3)	185(3)	130(3)	1(2)	35(2)	-26(3)
C(30)	258(4)	230(4)	149(3)	29(3)	1(3)	24(3)
C(31)	175(4)	319(4)	188(3)	-69(3)	55(3)	12(3)
C(32)	109(3)	135(3)	183(3)	-12(2)	-16(2)	18(2)
C(33)	200(4)	207(4)	179(3)	13(3)	-55(3)	9(3)
C(34)	215(4)	156(3)	314(4)	-21(3)	-58(3)	77(3)
C(35)	174(4)	113(3)	145(4)	6(3)	2(3)	-15(3)
O(1)	435(6)	277(5)	143(4)	87(3)	-36(4)	-49(4)
Cl(1)	280(30)	160(30)	140(50)	80(20)	10(30)	30(20)

III. Nuclear Magnetic Resonance Spectra

Figure S5. ^{1}H NMR spectrum of **1a** in CDCl$_3$.
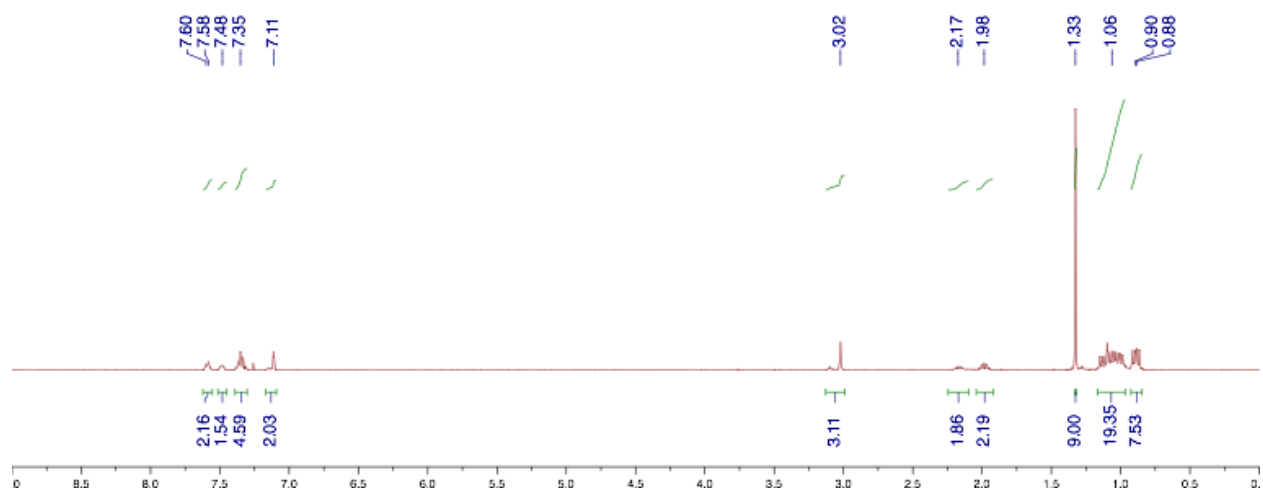
Figure S6. ^{13}C{^{1}H} NMR spectrum of **1a** in CDCl$_3$.
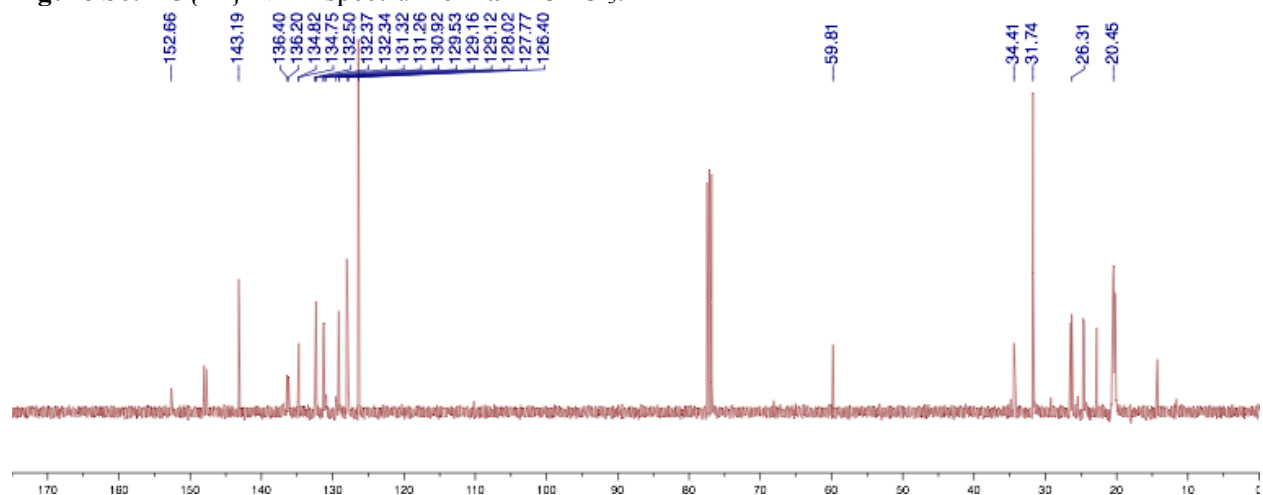
Figure S7. ^{31}P{^{1}H} NMR spectrum of **1a** in C$_6$D$_6$.
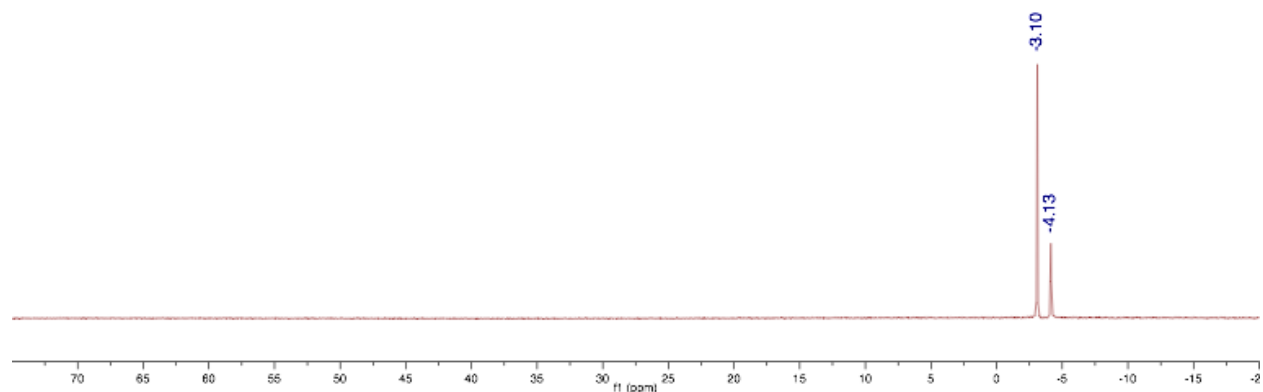
Figure S8. ^{1}H NMR spectrum of **2a** in C_6D_6.
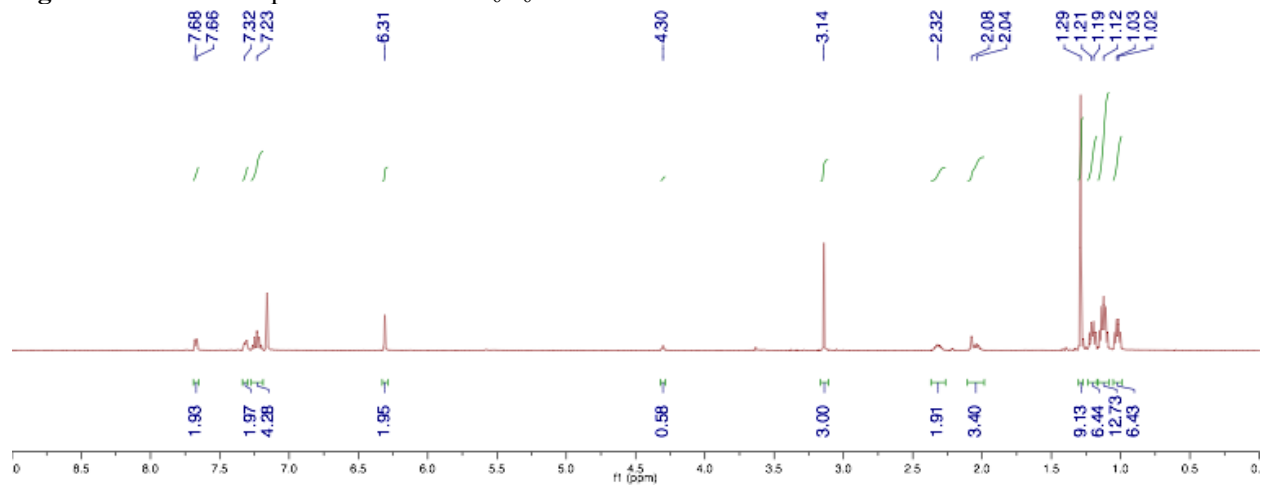
Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.
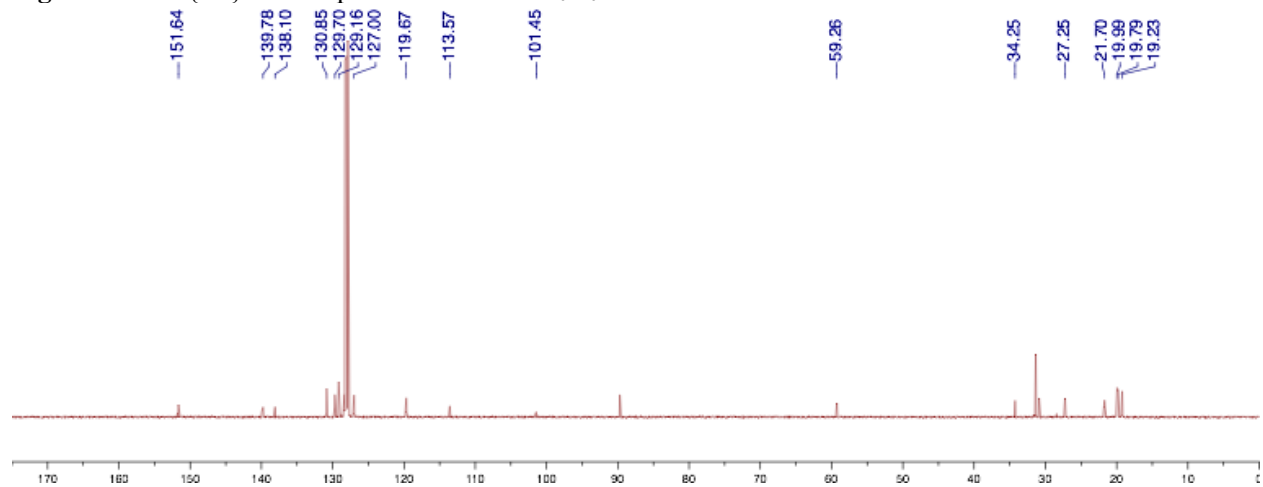
Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6.
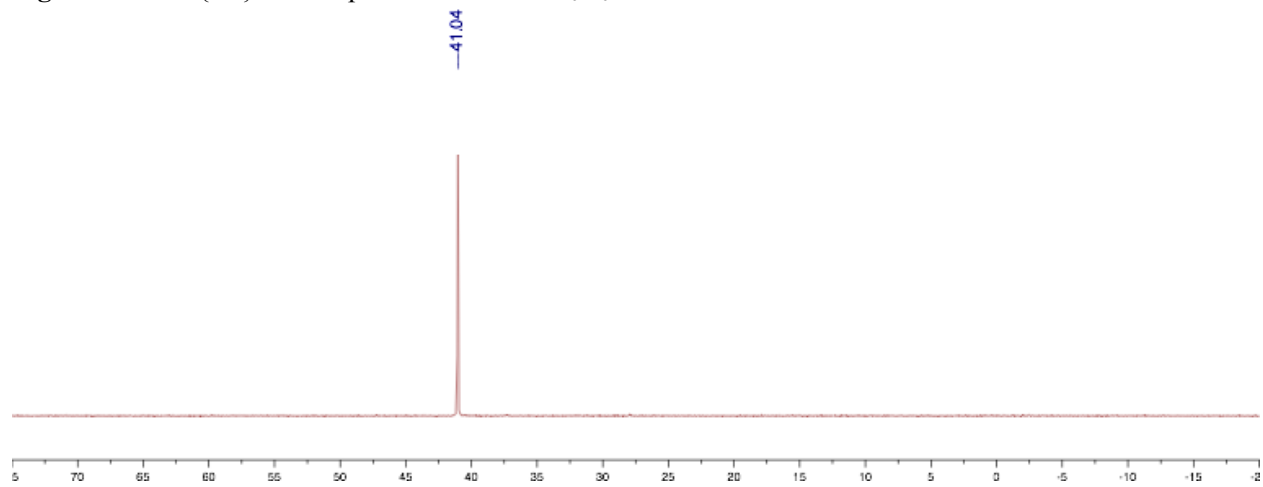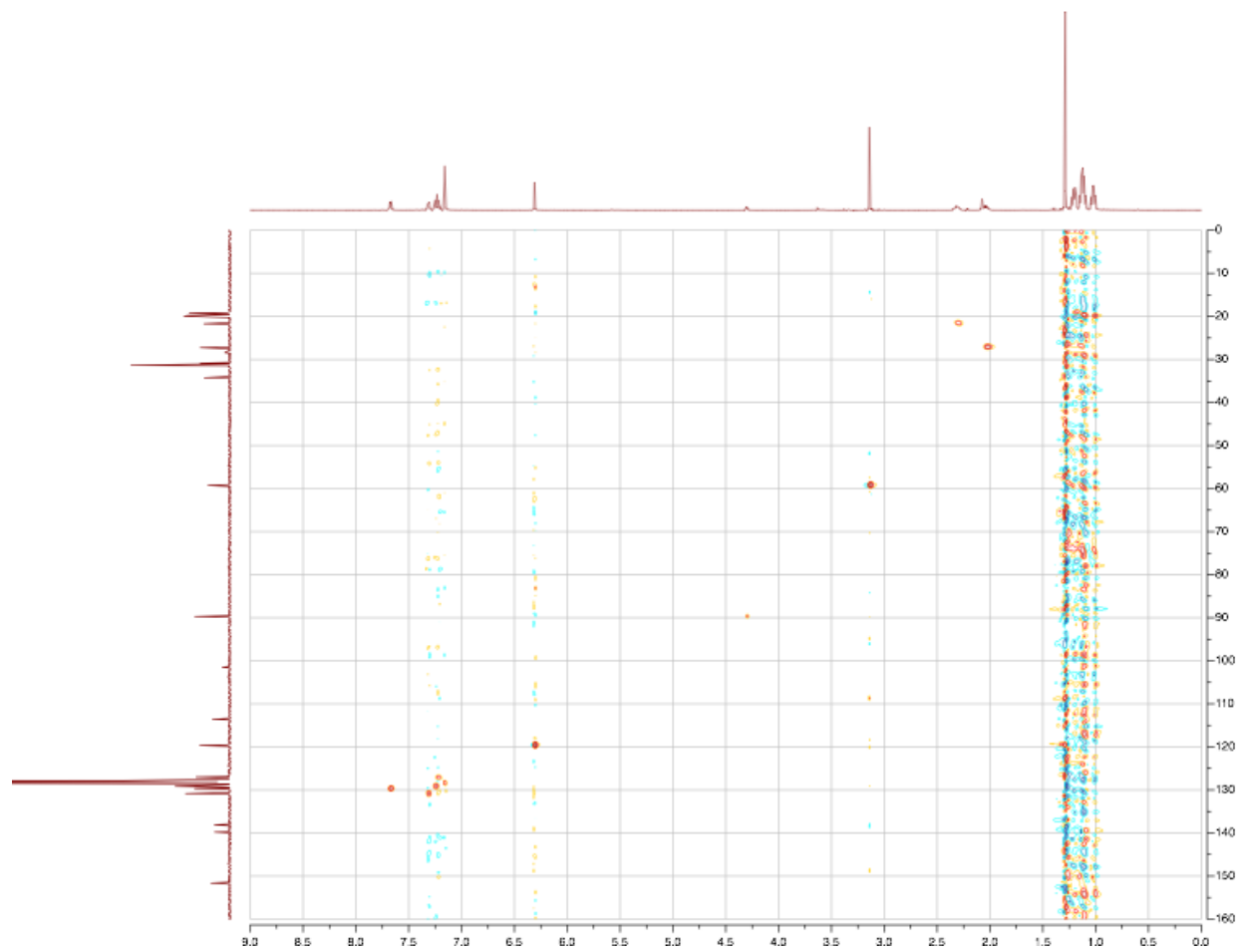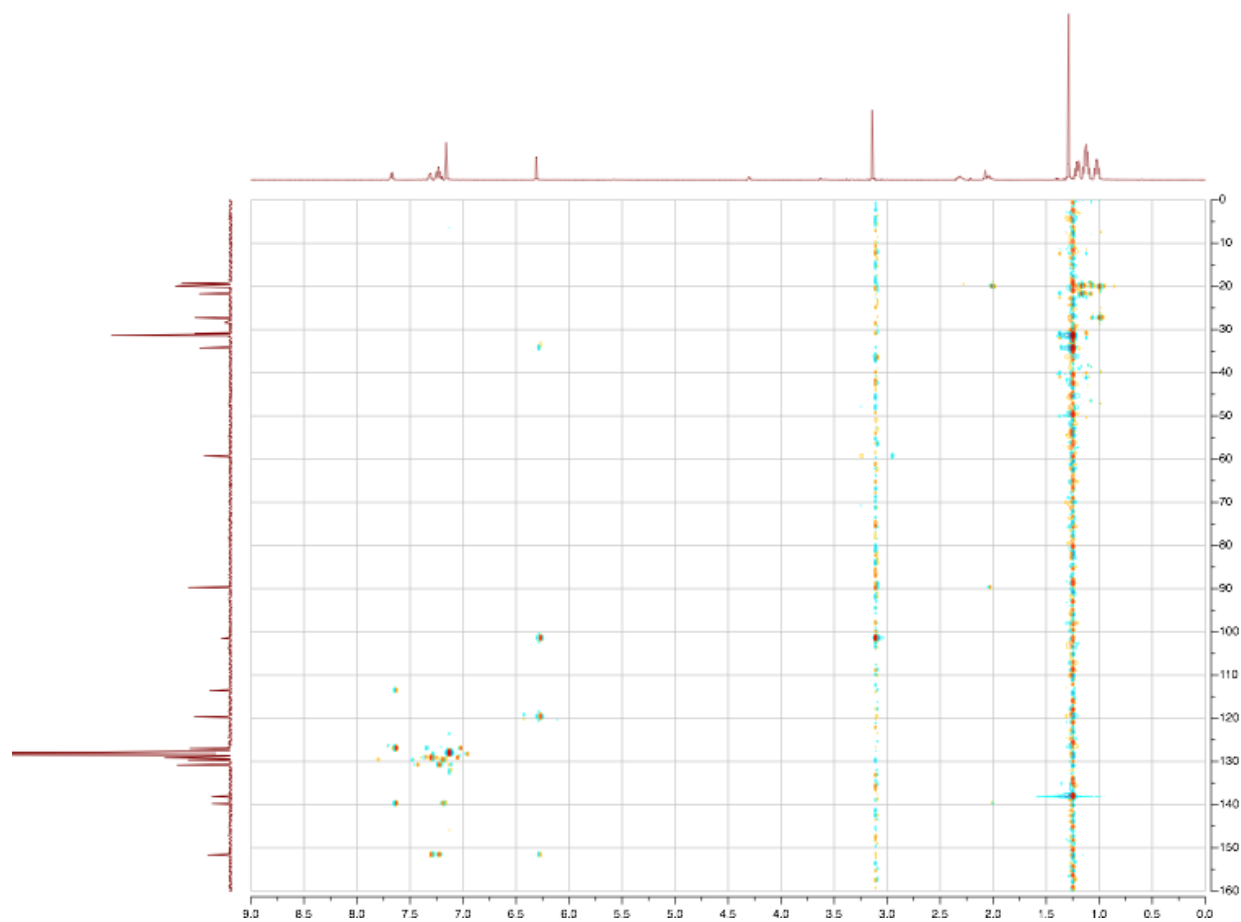
Figure S13. ^{1}H NMR spectrum of **6a** in C$_6$D$_6$.
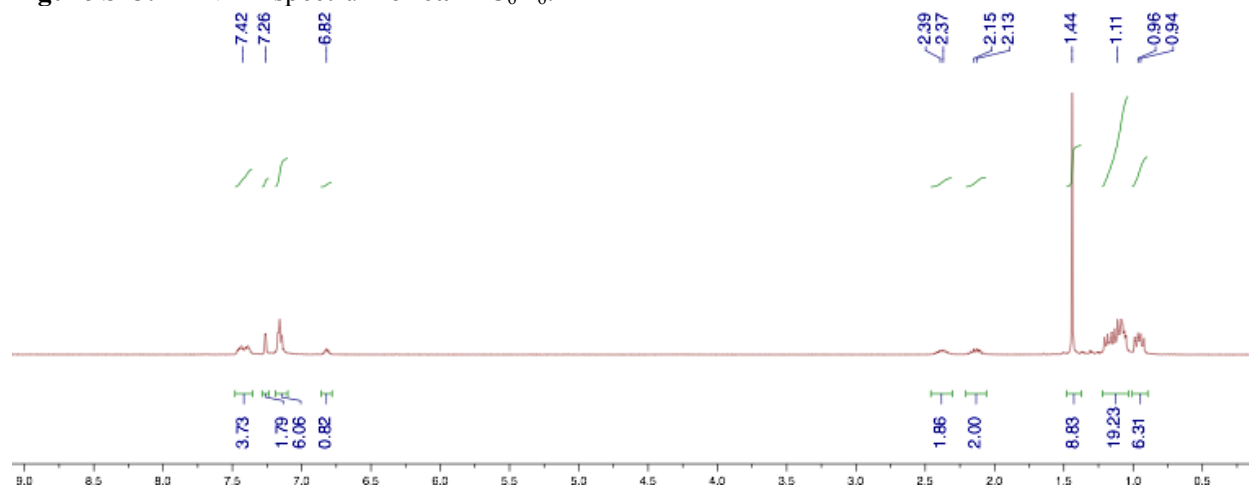
Figure S14. ^{13}C{^{1}H} NMR spectrum of **6a** in C$_6$D$_6$.
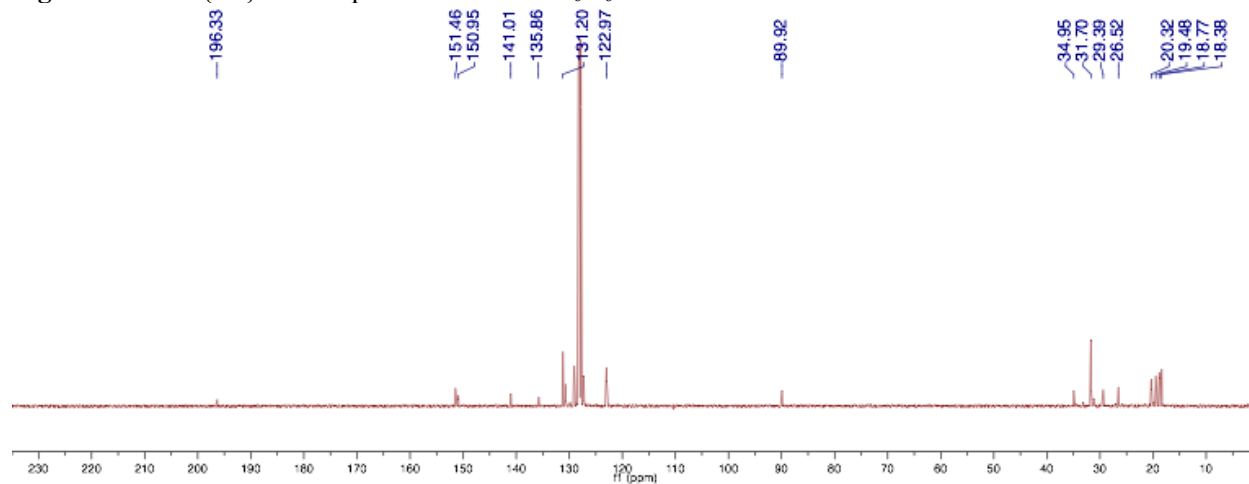
Figure S15. ^{31}P{^{1}H} spectrum of **6a** in C$_6$D$_6$.

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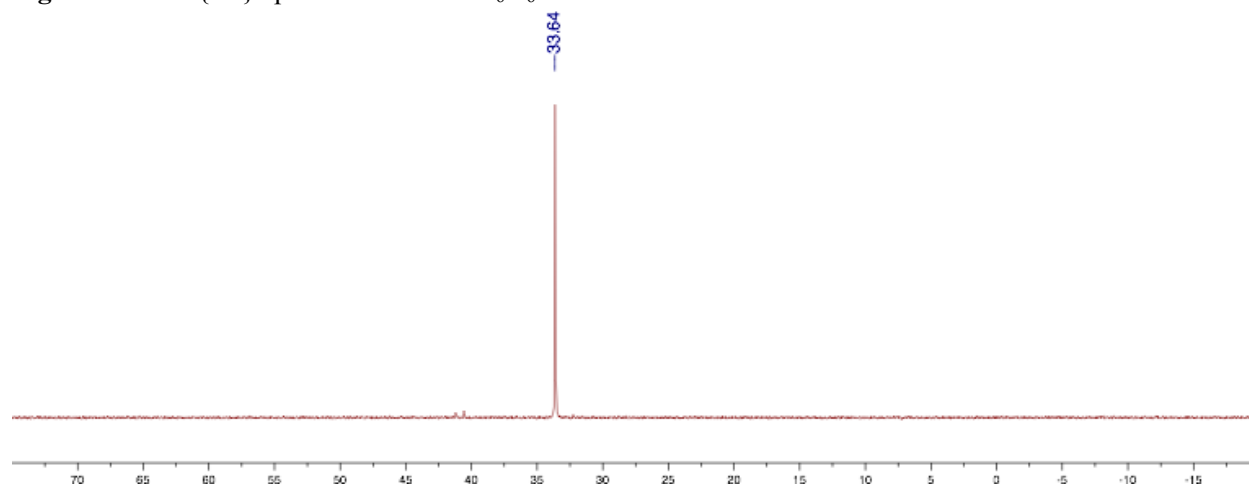
Figure S16. ^{1}H NMR spectrum of **1b** in C$_6$D$_6$ at 25°C
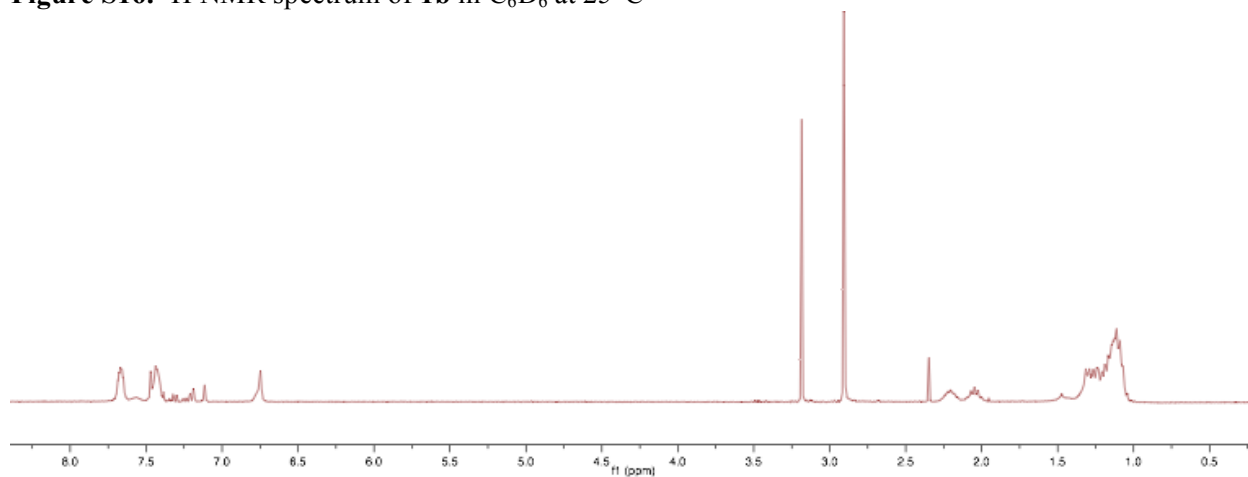
Figure S17. ^{1}H NMR spectrum of **1b** in C$_6$D$_6$ at 75°C
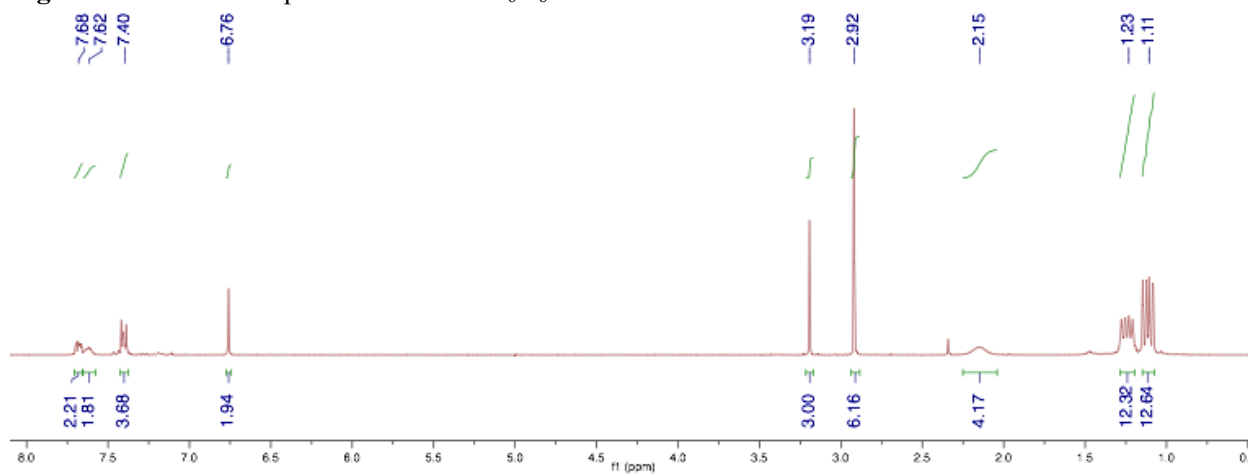
Figure S18. ^{13}C{^{1}H} NMR spectrum of **1b** in C$_6$D$_6$ at 25°C

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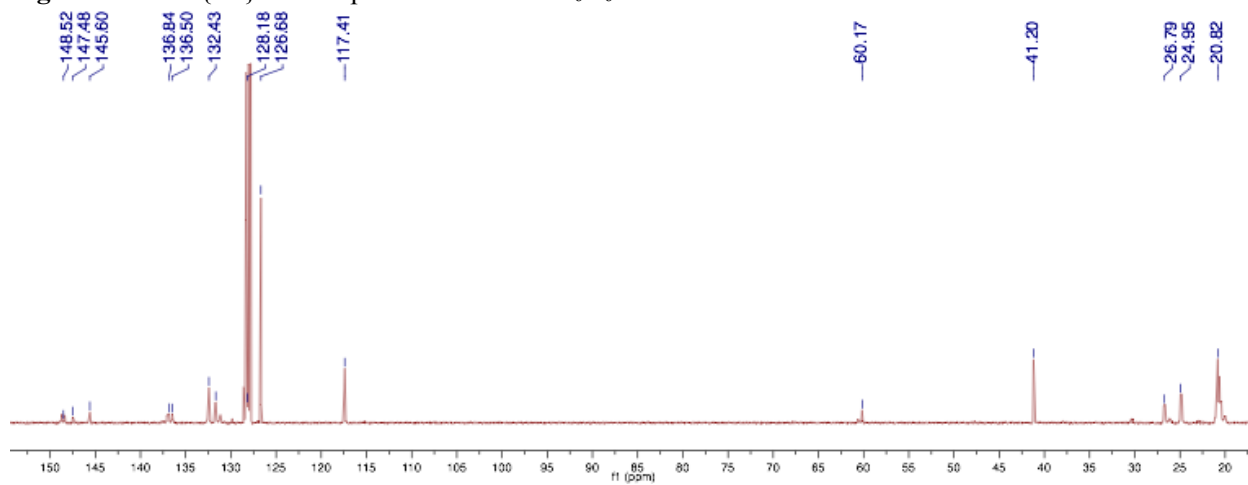
Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 25°C
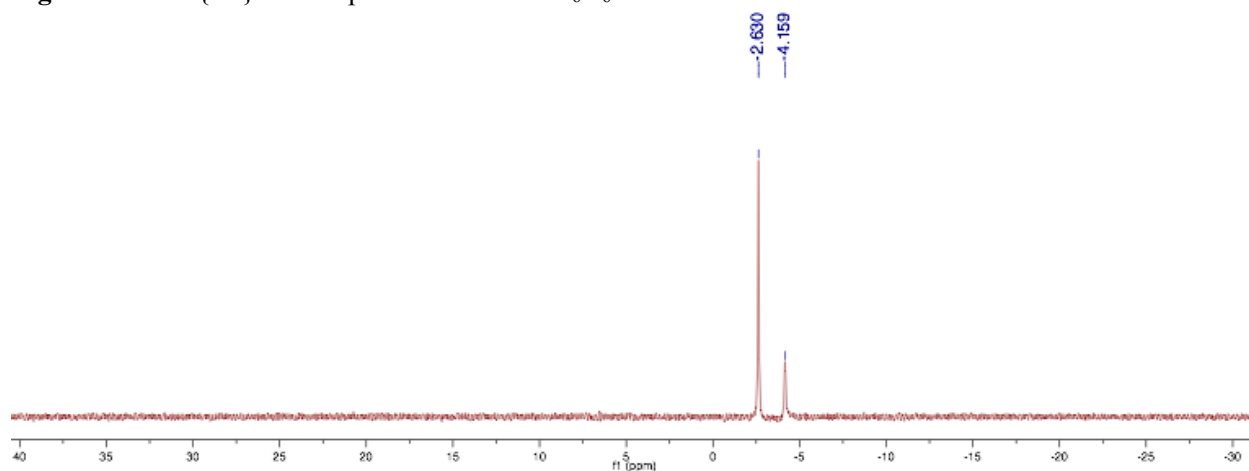
Figure 20. $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in C_6D_6 at 75°C
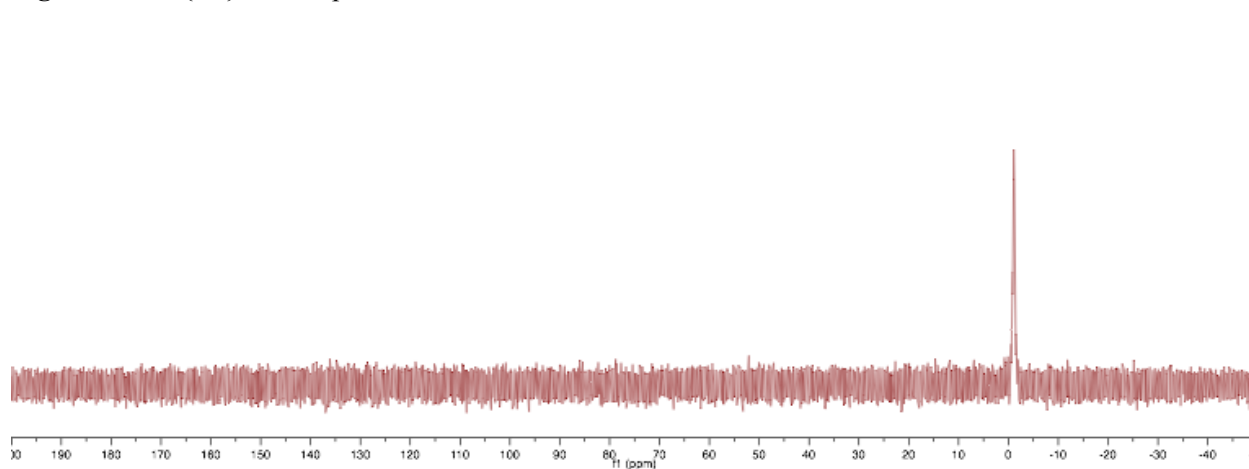
Figure 21. ^{1}H NMR spectrum of **2b** in C_6D_6
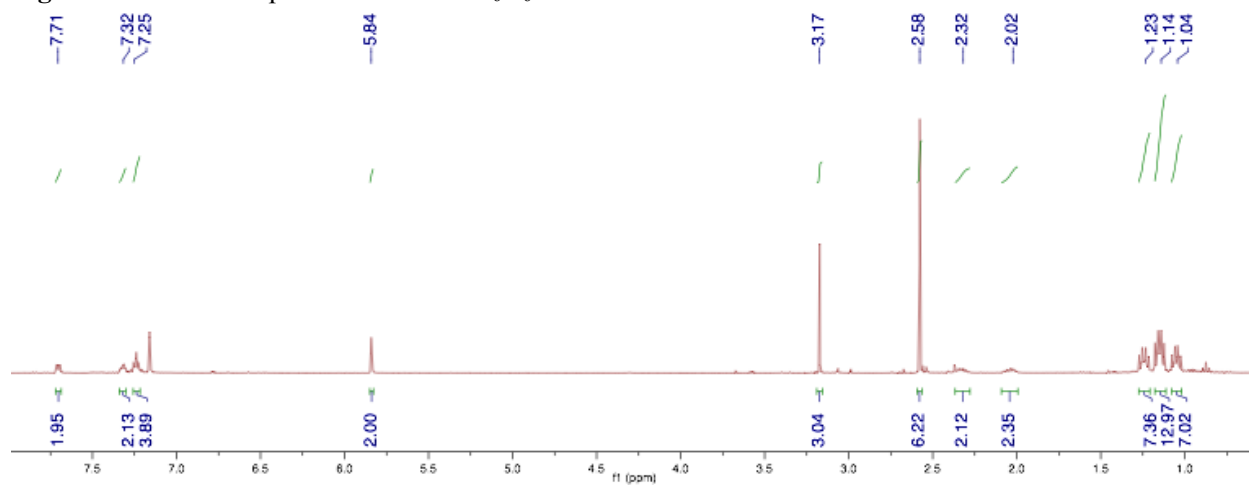
Figure 22. $^{13}C\{^1H\}$ NMR spectrum of **2b** in C_6D_6

151.41
143.49
140.43
130.81
129.75
128.94
127.10
115.71
109.32
100.69
59.55
42.02
27.25
21.81
20.15
20.08
19.79
19.33

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
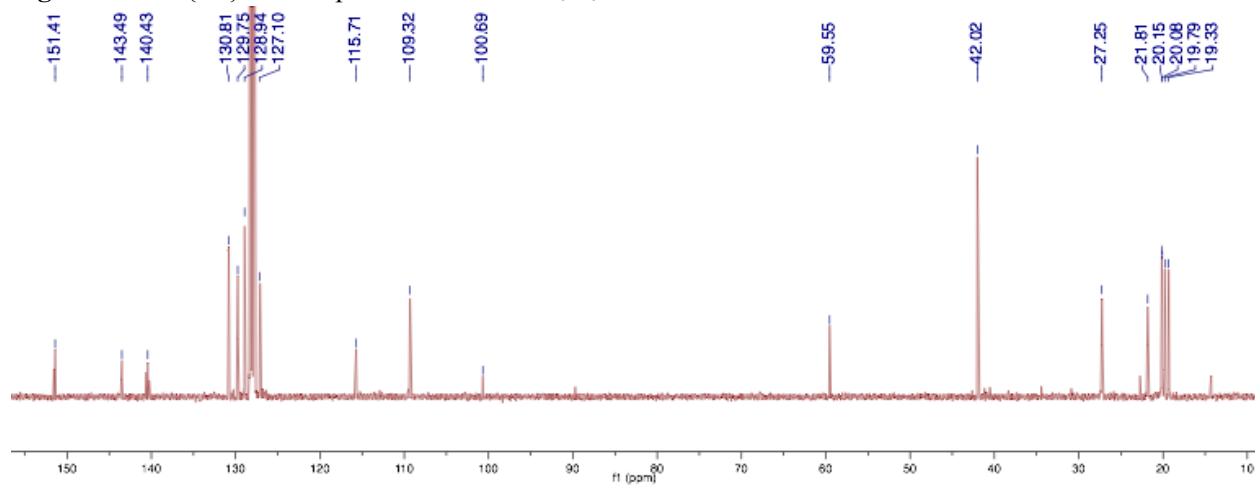
Figure S23. $^{31}P\{^1H\}$ NMR spectrum of **2b** in C_6D_6

40.65

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
f1 (ppm)
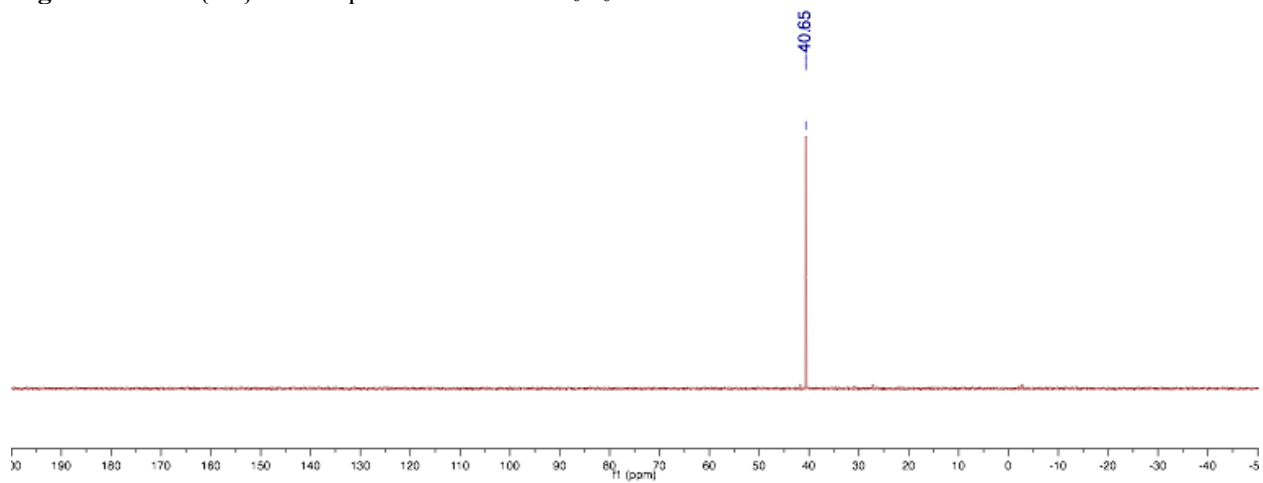
Figure S24. ^1H NMR spectrum of **3b** in C_6D_6

7.77
7.38
7.17
6.78
3.67
2.56
2.53
1.77
1.67
1.28
0.97
0.80

2.17
2.24
2.43
2.00
3.22
6.26
1.59
2.50
7.03
7.28
6.40
6.04

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
f1 (ppm)

33
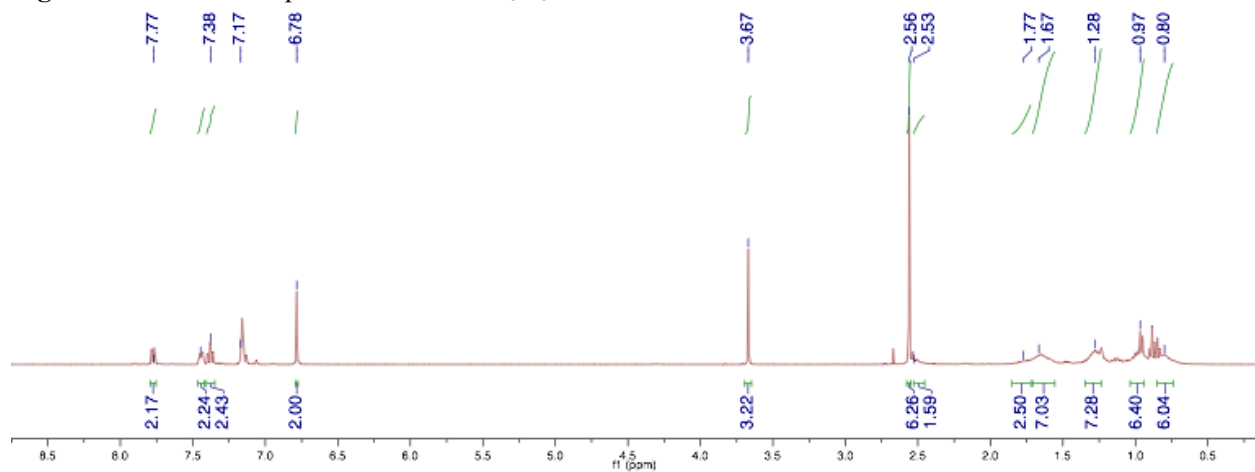
Figure S25. $^{13}C\{^1H\}$ NMR spectrum of **3b** in C_6D_6
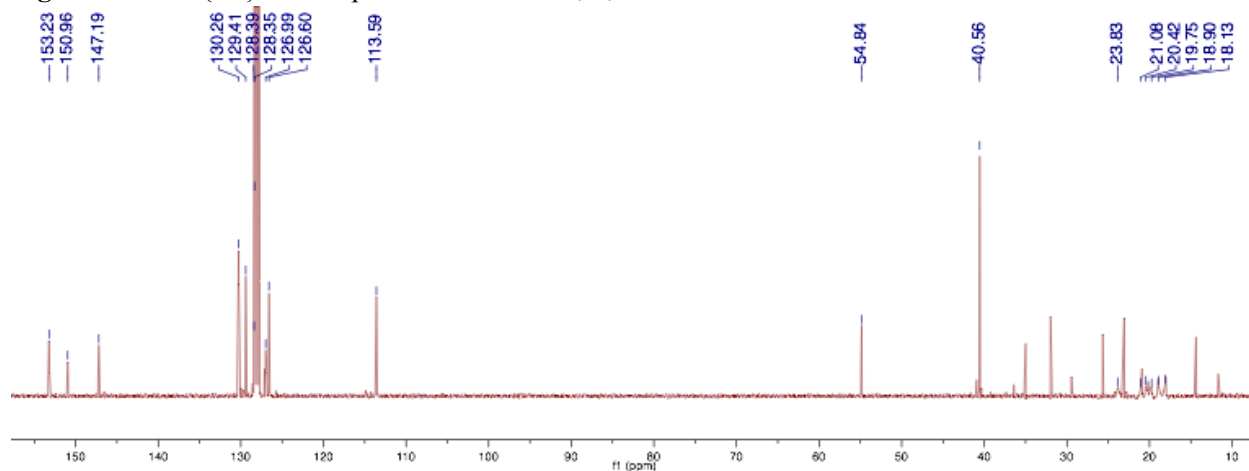
Figure S26. $^{31}P\{^1H\}$ NMR spectrum of **3b** in C_6D_6
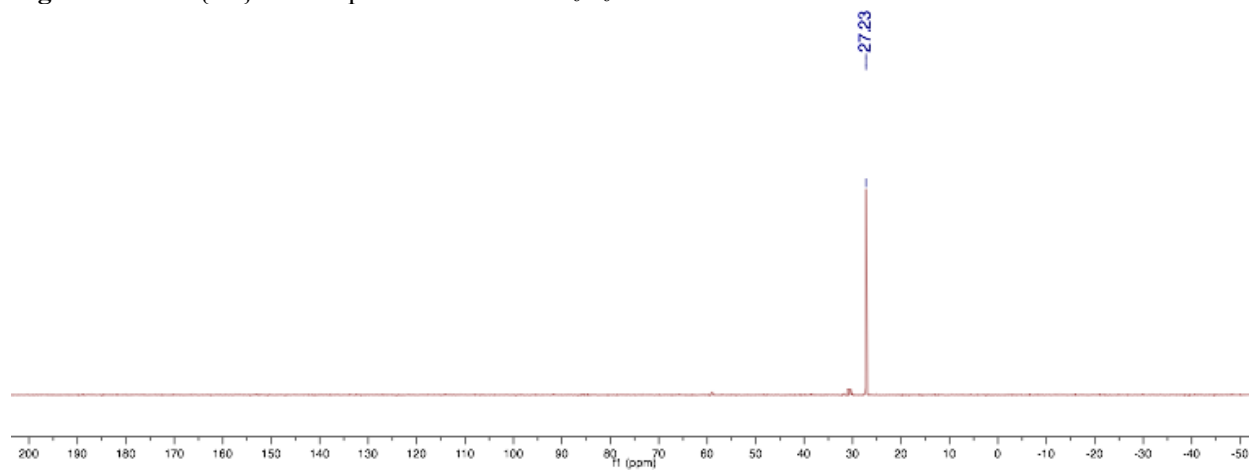
Figure S27. ^1H NMR spectrum of **4b** in C_6D_6
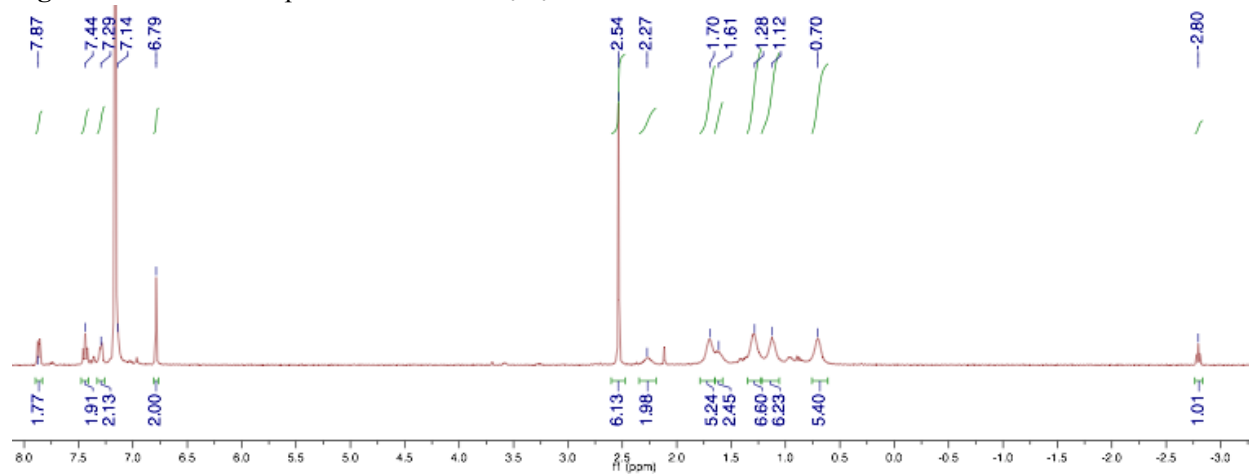
Figure S28. ^{1}H NMR spectrum of **4b** in CD_2Cl_2
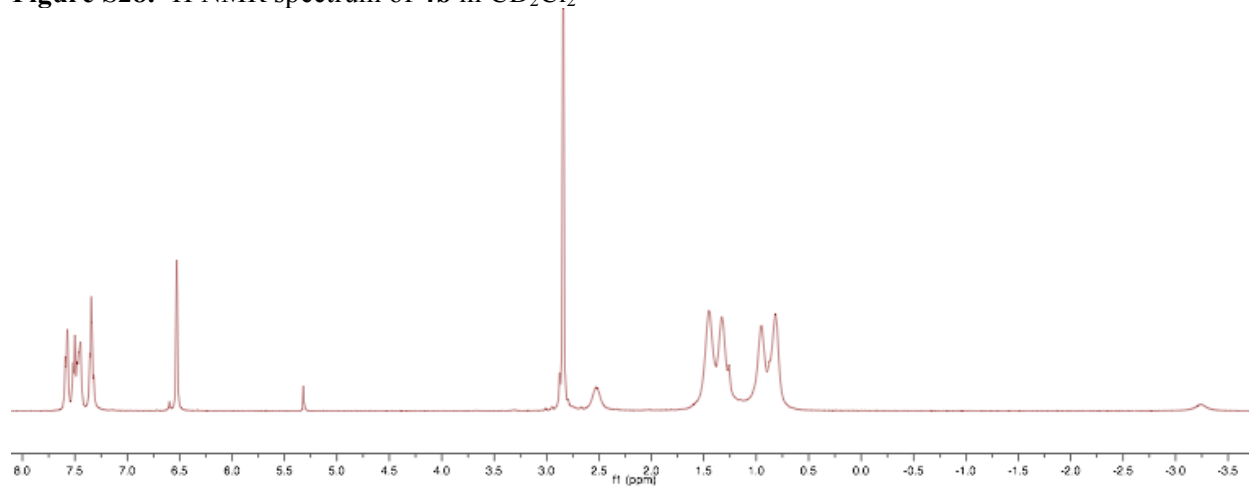
Figure S29. $^{13}C\{^1H\}$ NMR spectrum of **4b** in CD_2Cl_2
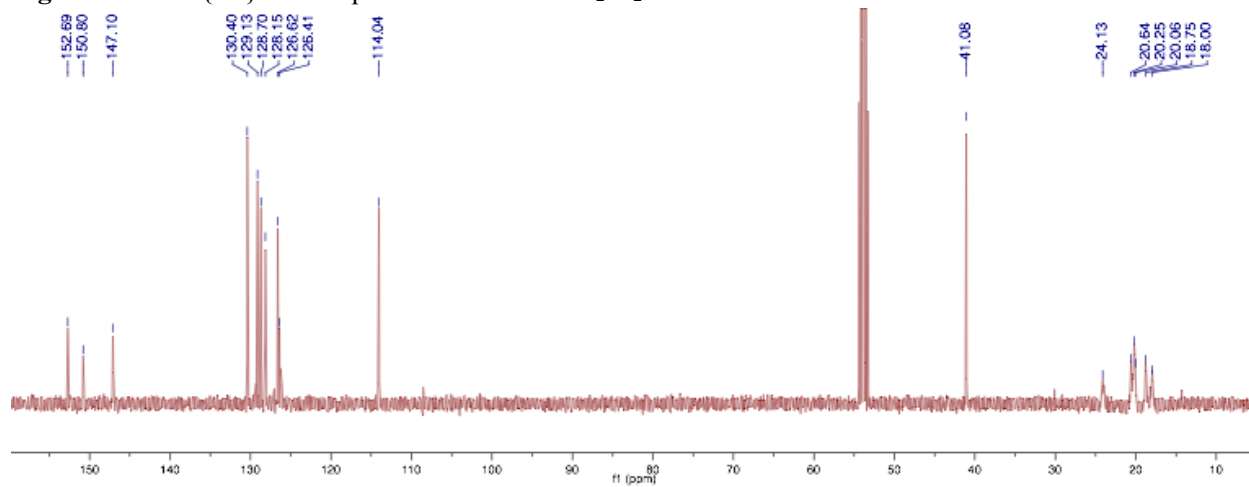
Figure S30. $^{31}P\{^1H\}$ NMR spectrum of **4b** in C_6D_6
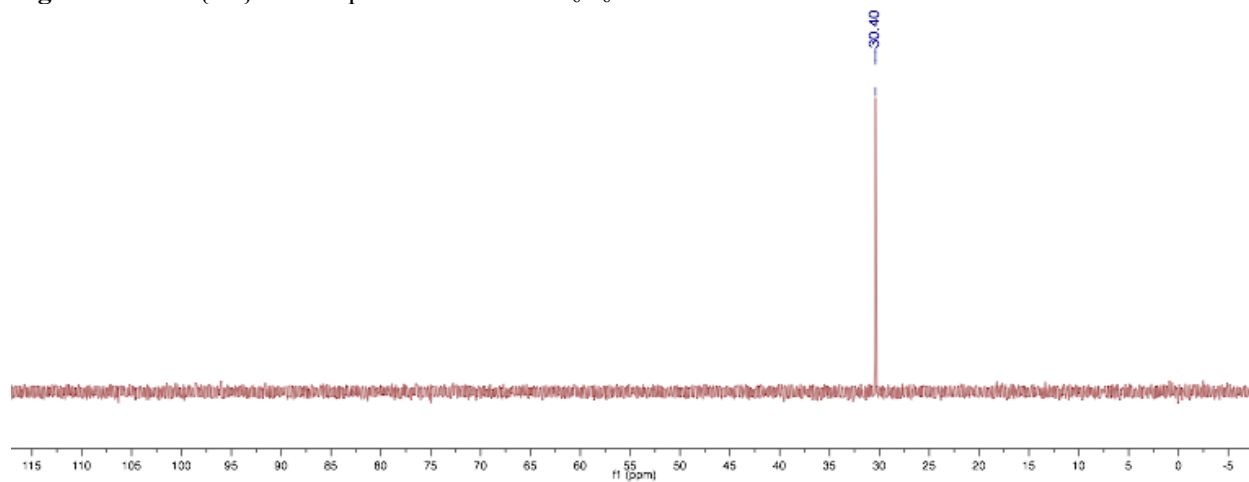
Figure S31. ^{1}H NMR spectrum of **5** in C$_6$D$_6$
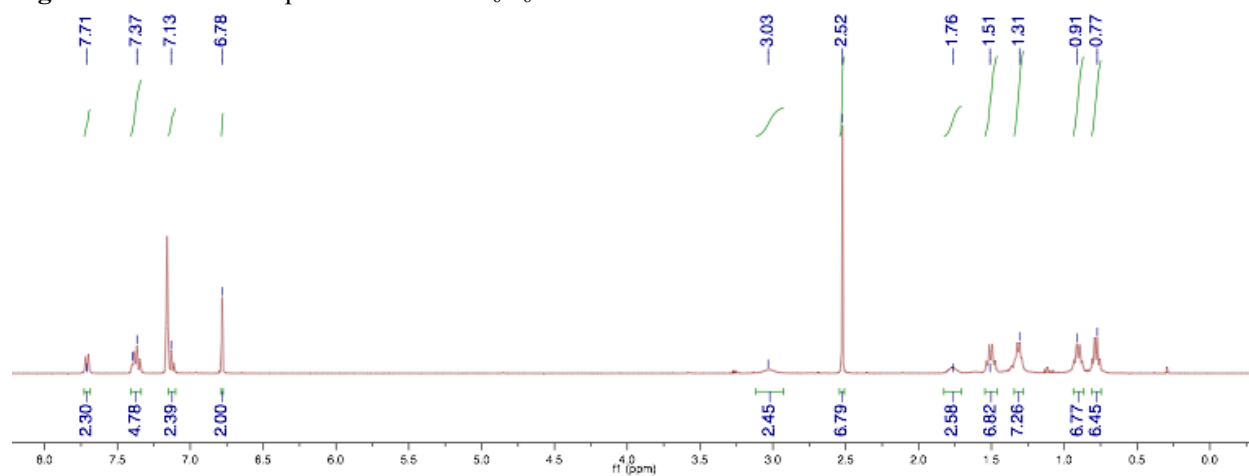
Figure S32. ^{13}C{^{1}H} NMR spectrum of **5** in C$_6$D$_6$
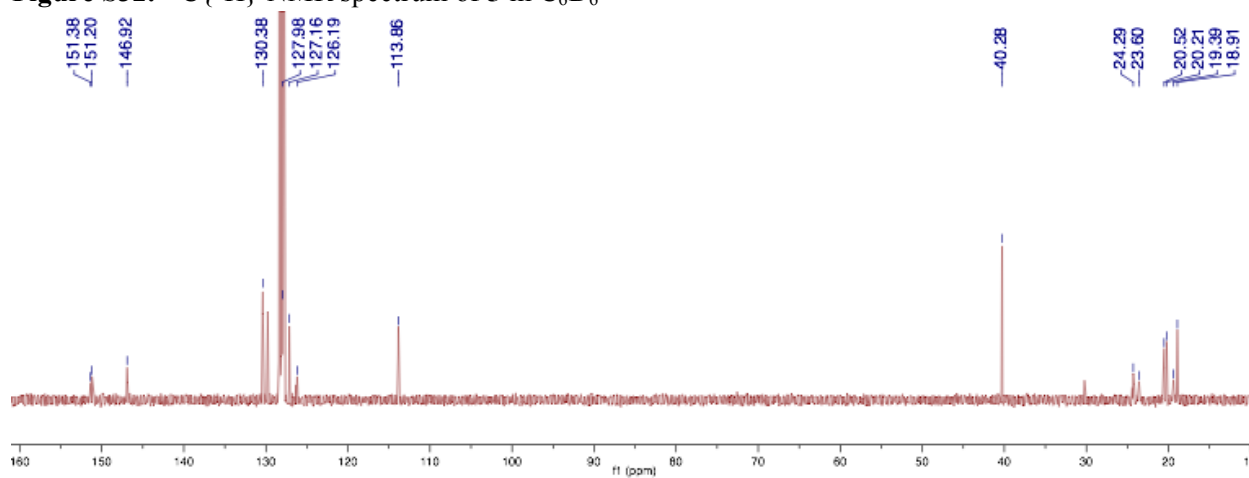
Figure S33. ^{31}P{^{1}H} NMR spectrum of **5** in C$_6$D$_6$
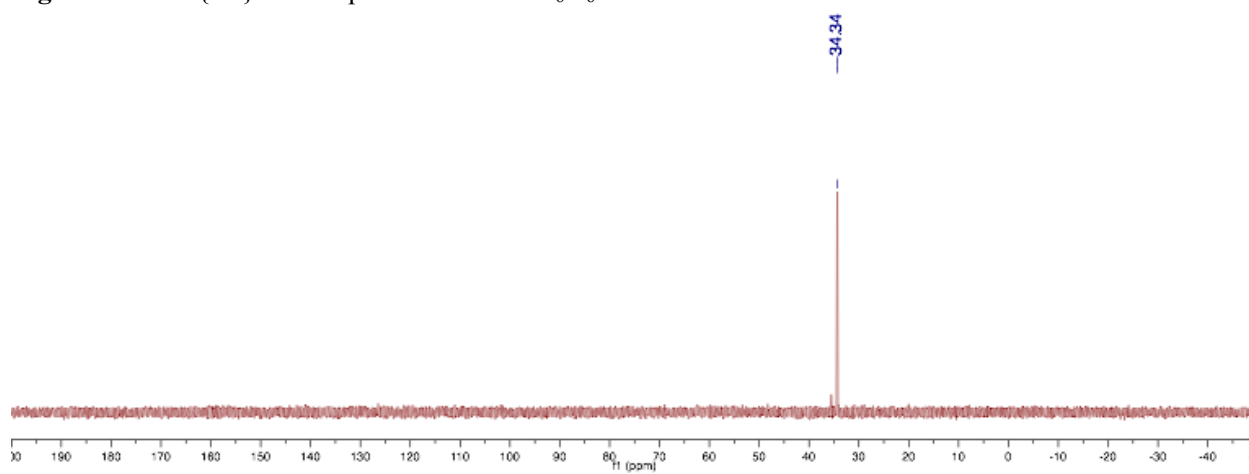
Figure S34. ^{1}H NMR spectrum of **6b** in C_6D_6
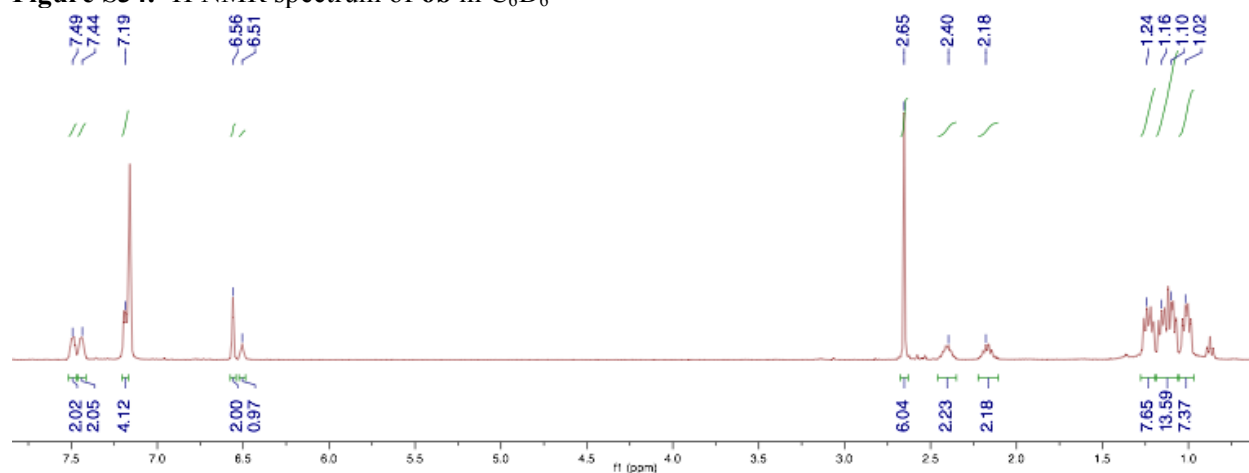
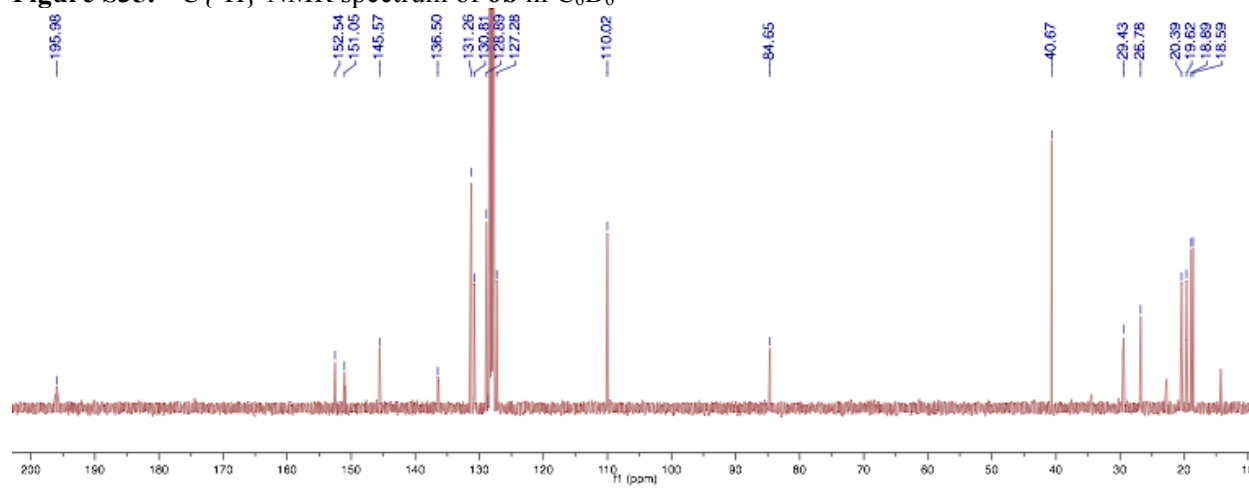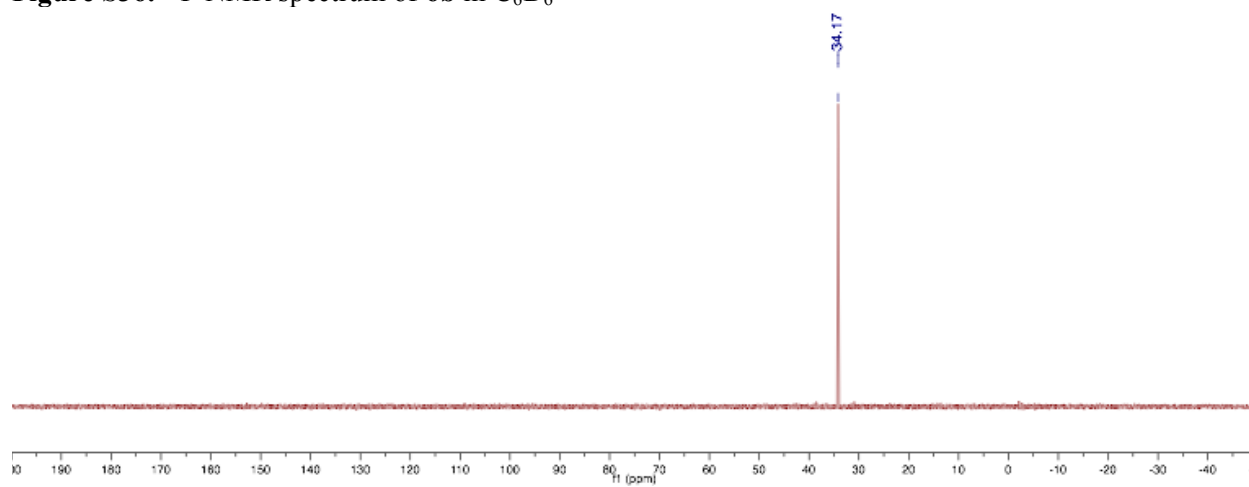

Figure S35. $^{13}C\{^1H\}$ NMR spectrum of **6b** in C_6D_6

**Figure S36.** ^{31}P NMR spectrum of **6b** in C_6D_6

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IV. Hydrogenolysis Studies

General considerations. Syntheses of 2-(trideutromethoxy)naphthalene,[9] 2-(hexyloxy)naphthalene,[10] 1,1-dideuteroiodohexane,[11] and 1,3-bis(2,6-diisopropylphenyl)-imadzolinium chloride[12] (SIPr·HCl) were performed as described in the literature. m-Xylene was dried with sodium benzophenone ketyl and stored in an inert atmosphere glovebox. Hexanol was dried with sodium, distilled, and used in an inert atmosphere glovebox.

Synthesis of 2-(1,1-dideuterohexyloxy)naphthalene. A procedure was adapted from the literature.[10] A Schlenk tube was charged with a stir bar, 2-hydroxynaphthalene (0.72 g, 5.0 mmol), K_2CO_3 (1.05 g, 7.6 mmol), 1,1-dideuteroiodohexane (1.65 g, 7.7 mmol), and acetone (7.5 mL) under a N_2 counterflow. The tube was sealed with a Teflon screw-stopper and heated at 70 °C for 14h. The reaction mixture was washed with hexanes and the combined organic washes were concentrated under vacuum to an orange oil. The organics were run through a silica gel plug with hexanes and concentrated under vacuum to obtain pure product as an oil (1.04 g, 91%). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 7.80-7.67 (m, 3H), 7.47-7.39 (app td, 1H), 7.35-7.29 (app td, 1H), 7.18-7.11 (m, 2H), 1.84 (app t, 2H), 1.59-1.31 (m, 8H),1.02-0.81 (m, 3H). GC-MS (m/z): calcd, 230.16 (M+); found 230.2.

**Synthesis of 2-deuteronaphthalene**. A Schlenk tube was charged with 2-bromonaphthalene (100 mg, 0.780 mmol), a stir bar, and Et$_2$O (10 mL) and stirred at -78 °C under N_2. A solution of 1.7 M ^{t}BuLi (0.96 mL, 1.638 mmol) was added dropwise. After 30 min, the reaction mixture was allowed to warm to room temperature over 10 min. Then D$_2$O (0.16 mL, 7.8 mmol) was added to the reaction. The reaction mixture was washed with H$_2$O, extracted with DCM, dried with MgSO$_4$, and filtered. After removing volatiles via rotary evaporation and redissolution in DCM, the mixture was analyzed by GC-MS and ^{2}H NMR. GC-MS (m/z): calcd, 129.07 (M+); found 129.1. ^{2}H NMR (74 MHz, CH$_2$Cl$_2$ with internal CD$_2$Cl$_2$ standard): 7.52 (s).
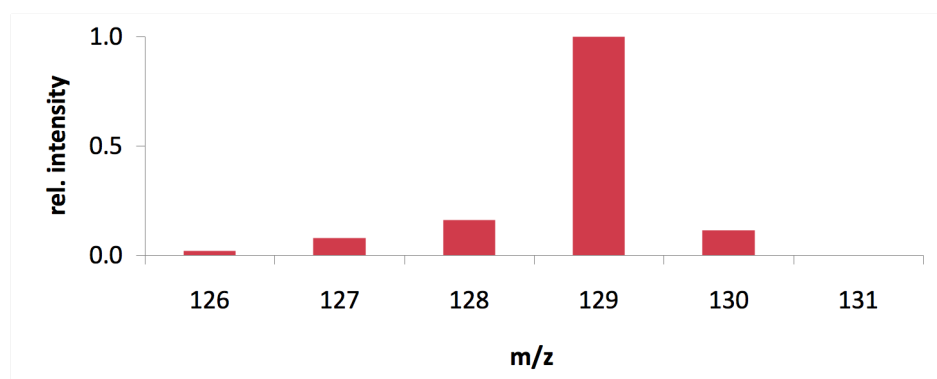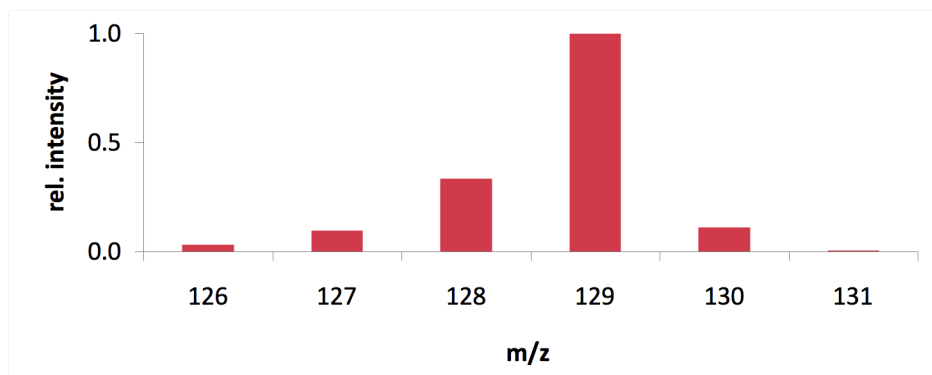

Figure S37. MS of 2-deuteronaphthalene.

Hydrogenolysis of 2-methoxynaphthalene (and deuterated variants). A procedure was adapted from the literature.[10] In a N_2-atmosphere glovebox, a Schlenk tube was carefully charged with a stir bar, SIPr·HCl (27.5 mg, 0.062 mmol), and NaO^{t}Bu (37.5 mg, 0.389 mmol) with the aid of weighing paper and an anti-static bar. Ni(COD)$_2$ (8.5 mg, 0.031 mmol) was affected by static too much to consistently transfer as a solid, so for reproducibility a suspension in minimal hexanes was employed to add to the reaction mixture. Immediately thereafter, the reaction flask was placed under vacuum to remove hexanes.

A solution (0.8 mL) of 2-methoxynaphthalene (23.5 mg, 0.149 mmol) and tetradecane (8.1 μL, 0.031 mmol) in m-xylene was added with a pipette. The reaction mixture was sealed with a Teflon screw-stopper and stirred for 10 minutes at room temperature. The mixture was degassed with two freeze-pump-thaw cycles, warmed to room temperature, and treated with 1 atm H_2 (as regulated by a mercury bubbler). The reaction mixture was once again sealed with a Teflon screw-stopper and placed in a 120 °C oil bath for 16h. The reaction flask was removed from heat, allowed to cool to room temperature, and quenched with 1 mL Et_2O and 1.5 mL 1M HCl aqueous solution. After 5 minutes of vigorous stirring, the top organic phase was separated via pipet. The aqueous phase was washed with 1 mL Et_2O. The combined organic solutions were pushed through successive $MgSO_4$ and Celite plugs, and analyzed by GC-MS and GC. Naphthalene yield relative to internal tetradecane standard (GC FID): 74%. Analogous reactions with 2-(trideuteromethoxy)naphthalene or D_2 were performed by the same procedure.
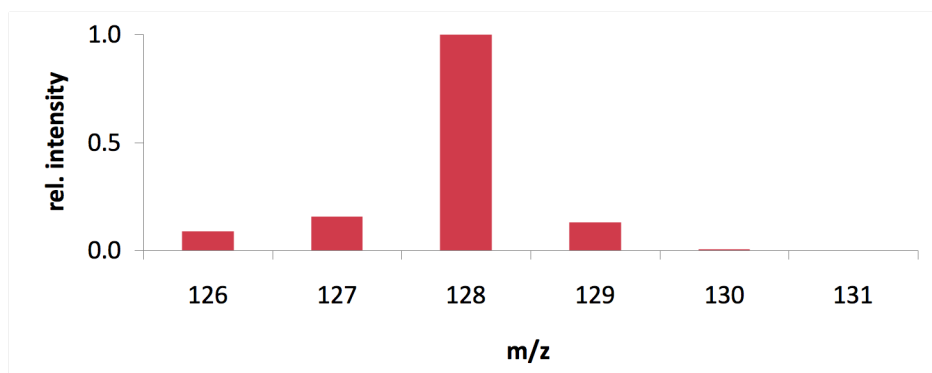
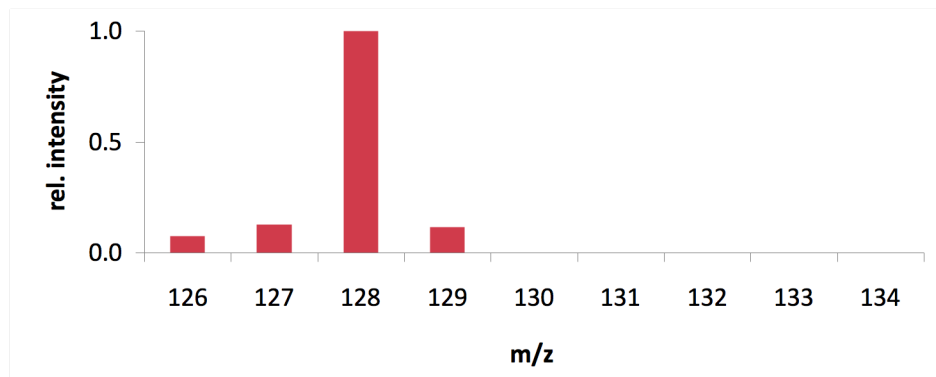**Figure S38.** MS of naphthalene from hydrogenolysis of 2-methoxynaphthalene under H_2.

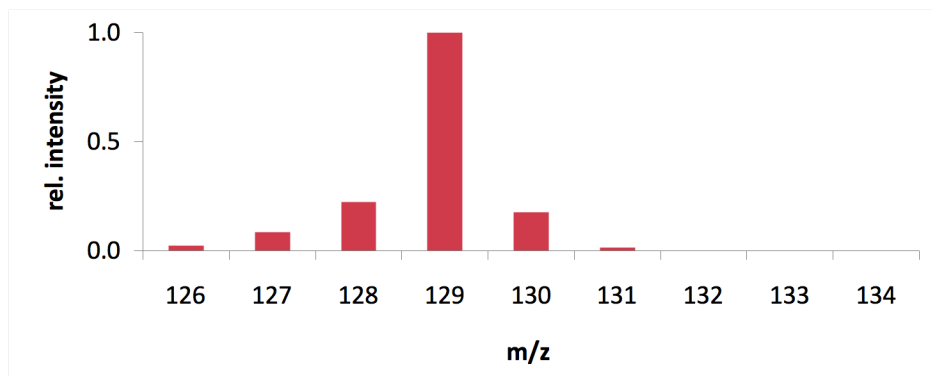**Figure S39.** MS of naphthalene from hydrogenolysis of 2-(trideuteromethoxy)naphthalene under H_2.

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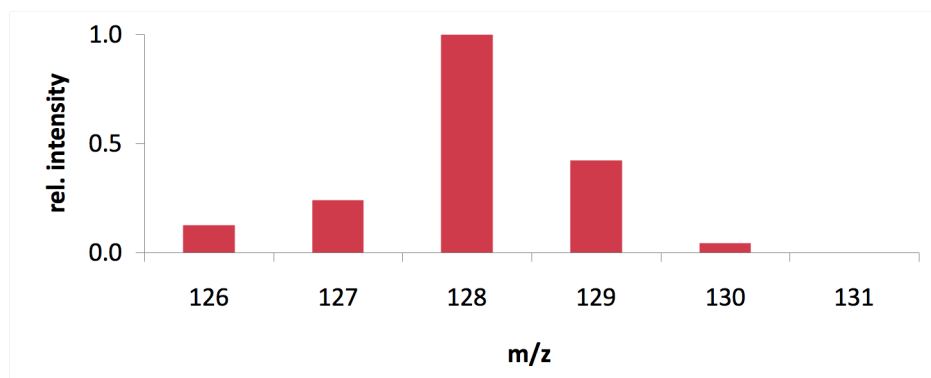
Figure S40. MS of naphthalene from hydrogenolysis of 2-methoxynaphthalene under D_2.

Hydrogenolysis of 2-(n-hexyloxy)naphthalene (and deuterated variants). A procedure was adapted from the literature.[10] In a N_2-atmosphere glovebox, a Schlenk tube was carefully charged with a stir bar, SIPr·HCl (25.8 mg, 0.060 mmol), and NaO^{t}Bu (37.4 mg, 0.389 mmol) with the aid of weighing paper and an anti-static bar. Ni(COD)$_2$ (8.5 mg, 0.031 mmol) was affected by static too much to consistently transfer as a solid, so for reproducibility a suspension in minimal hexanes was employed to add to the reaction mixture. Immediately thereafter, the reaction flask was placed under vacuum to remove hexanes. A solution (0.8 mL) of 2-(n-hexyloxy)naphthalene (33.9 mg, 0.148 mmol) and tetradecane (8.1 μL, 0.031 mmol) in m-xylene was added with a pipette. The reaction mixture was sealed with a Teflon screw-stopper and stirred for 10 minutes at room temperature. The mixture was degassed with two freeze-pump-thaw cycles, warmed to room temperature, and treated with 1 atm H_2 (as regulated by a mercury bubbler). The reaction mixture was once again sealed with a Teflon screw-stopper and placed in a 120 °C oil bath for 16h. The reaction flask was removed from heat, allowed to cool to room temperature, and quenched with 1 mL Et$_2$O and 1.5 mL 1M HCl aqueous solution. After 5 minutes of vigorous stirring, the top organic phase was separated via pipet. The aqueous phase was washed with 1 mL Et$_2$O. The combined organic solutions were pushed through successive MgSO$_4$ and Celite plugs and analyzed by GC and GC-MS. Naphthalene yield relative to internal tetradecane standard (GC FID): 98%. ^{2}H NMR spectra (74 MHz, CH$_2$Cl$_2$ with CD$_2$Cl$_2$ internal standard), although broad, indicated ^{2}H incorporation at the 2-position of naphthalene product. Analogous reactions with 2-(trideuteromethoxy)naphthalene or D_2 were performed by the same procedure.
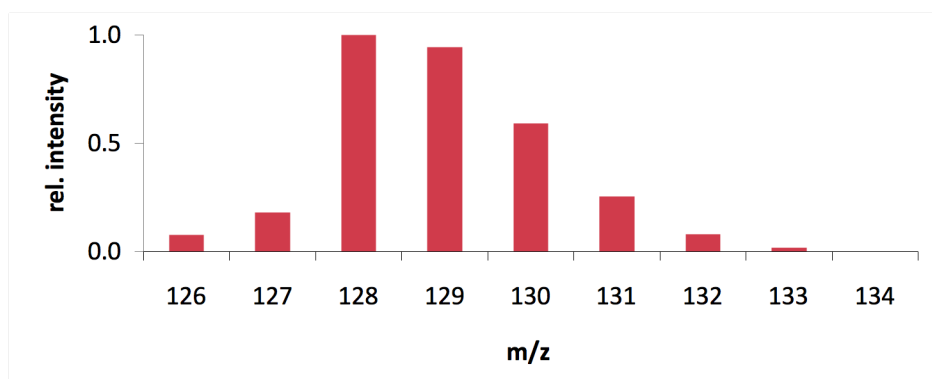

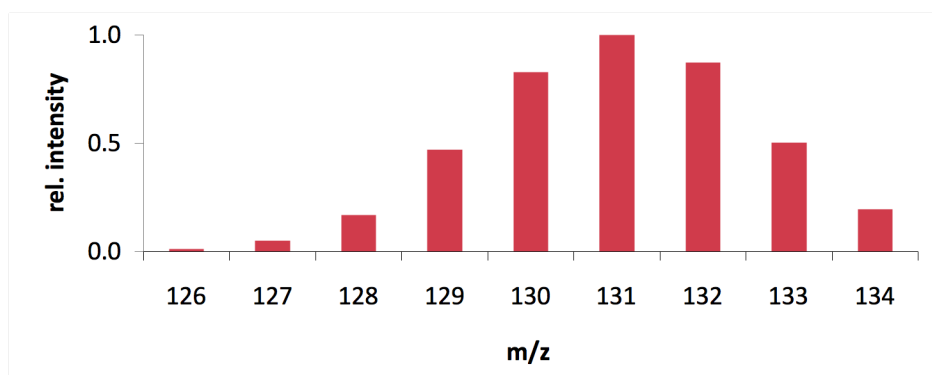**Figure S41.** MS of naphthalene from hydrogenolysis of 2-(n-hexyloxy)naphthalene under H_2.

Figure S42. MS of naphthalene from hydrogenolysis of 2-(1,1-d_2-n-hexyloxy)naphthalene under H_2.

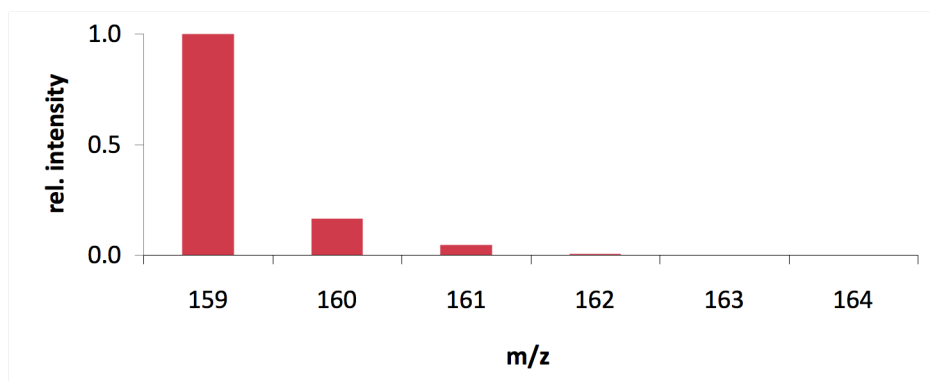**Figure S43.** MS of naphthalene from hydrogenolysis of 2-(n-hexyloxy)naphthalene under D_2.

Exposure of naphthalene to hydrogenolysis conditions under D_2. Naphthalene was submitted to hydrogenolysis conditions under D_2 (vide supra) in place of alkylnaphtylether substrate. The reaction mixture was analyzed by GC and GC-MS.


Figure S44. MS of naphthalene from exposure to hydrogenation conditions under D_2.

Derivatization of hexanol byproducts. A procedure was adapted from the literature.[10] Authentic hexanol or the organic extracts from hydrogenolysis of 2-(n-hexyloxy)naphthalene (and deuterated variants) were pushed through a $MgSO_4$ plug into a Schlenk tube under N_2 counterflow. N-methyl-N-

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(trimethylsilyl)trifluoroacetamide (0.10 mL) was added to the tube. The tube was sealed and heated to 60 °C for 1h to derivatize hexanol into (n-hexyloxy)trimethylsilane. The reaction mixture was analyzed by GC-MS and GC without further purification. The base peak in the mass spectrum of (n-hexyloxy)trimethylsilane (for d_0, m/z = 159) corresponds to fragmentation of a methyl off of the molecular ion. Near quantitative methyl fragmentation is also observed for this compound in the NIST database reference spectrum. It is assumed that the fragmented methyl group is not ^{2}H-enriched. Products derived from under D_2 display d_{0-4} isotopologues. Two C-D bonds could be formed from reversible hydrogenation of an aldehyde intermediate. Another two C-D bonds could be formed from β-position deuteration via enolates formed from an aldehyde intermediate under the basic reaction conditions.

Figure S45. MS of (n-hexyloxy)trimethylsilane from hydrogenolysis of 2-(n-hexyloxy)naphthalene under H_2 and derivatization.
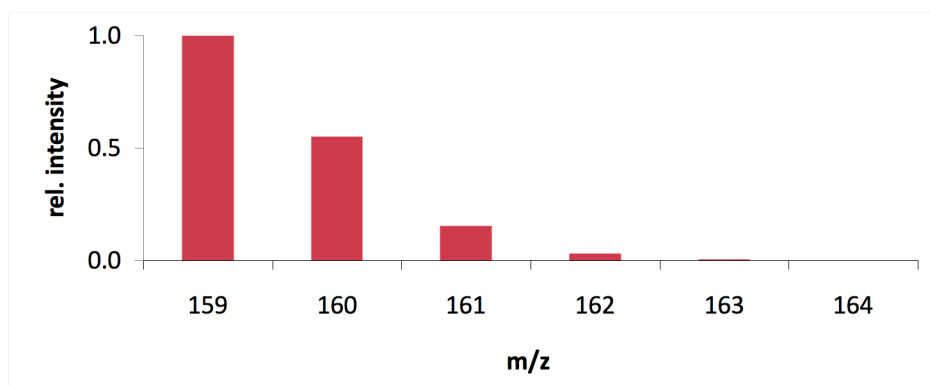
Figure S46. MS of (n-hexyloxy)trimethylsilane from hydrogenolysis of 2-(1,1-d_2-n-hexyloxy)naphthalene under H_2 and derivatization.
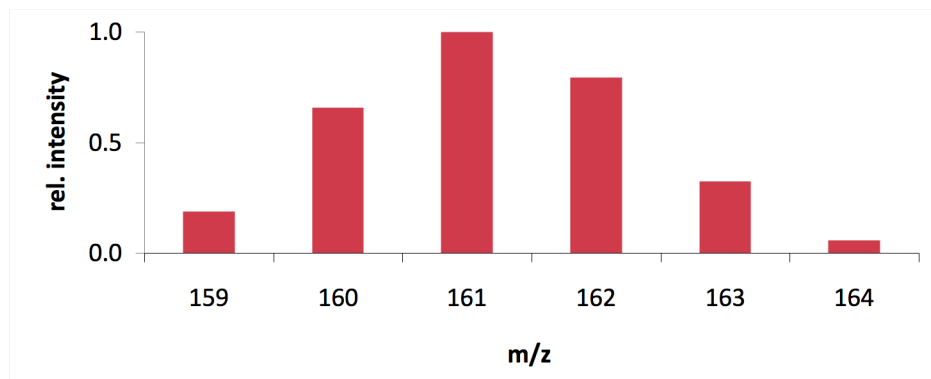
Figure S47. MS of (n-hexyloxy)trimethylsilane from hydrogenolysis of 2-(n-hexyloxy)naphthalene under D_2 and derivatization.

Reaction of 2-methoxynaphthalene under hydrogenolysis conditions with H_2 pre-activation. In a N_2-atmosphere glovebox, a Schlenk tube was carefully charged with a stir bar, SIPr·HCl (27.5 mg, 0.0618 mmol), and NaO^{t}Bu (37.5 mg, 0.3894 mmol) with the aid of weighing paper and an anti-static bar. Ni(COD)$_2$ (8.5 mg, 0.0309 mmol) was transferred as a suspension in minimal toluene (ca. 1 mL) to the reaction mixture. The reaction mixture was sealed with a Teflon screw-stopper and stirred for 10 minutes at room temperature. The mixture was degassed with two freeze-pump-thaw cycles, warmed to room temperature, and treated with 1 atm H_2 (as regulated by a mercury bubbler). The reaction mixture was once again sealed with a Teflon screw-stopper and placed in a 120 °C oil bath for 5h. The reaction mixture was placed under vacuum, removing all volatiles and leaving a dark red crude mixture. The reaction flask was brought back into a glovebox, and a solution (0.8 mL) of 2-methoxynaphthalene (23.5 mg, 0.1485 mmol) and tetradecane (8.1 mL, 0.0309 mmol) in m-xylene was added with a pipette. The reaction mixture was then sealed and placed in a 120 °C oil bath for 16h. The reaction flask was removed from heat, allowed to cool to room temperature, and quenched with 1 mL Et$_2$O and 1.5 mL 1M HCl aqueous solution. After 5 minutes of vigorous stirring, the top organic phase was separated via pipet. The aqueous phase was washed with 1 mL Et$_2$O. The combined organic solutions were pushed through successive MgSO$_4$ and Celite plugs, and analyzed by GC-MS and GC. Naphthalene yield relative to internal tetradecane standard: 49% (GC FID).

V. Reductive Cleavage Studies with Triethylsilane

General Procedure. A procedure was adapted from the literature.[10] In a N_2-atmosphere glovebox, a Schlenk tube was carefully charged with a stir bar, SIPr·HCl (25.8 mg, 0.062 mmol), and NaO^{t}Bu (37.4 mg, 0.389 mmol) with the aid of weighing paper and an anti-static bar. Ni(COD)$_2$ (8.5 mg, 0.031 mmol) was affected by static too much to consistently transfer as a solid, so for reproducibility a suspension in minimal hexanes was employed to add to the reaction mixture. Immediately thereafter, the reaction flask was placed under vacuum to remove hexanes. A solution (0.8 mL) of 2-methoxynaphthalene (23.6 mg, 0.149 mmol) and tetradecane (8.1 µL, 0.031 mmol) in m-xylene was added with a pipette. Then Et$_3$SiD (48.9 µL, 0.297 mmol) was added via microsyringe. The reaction mixture was sealed with a Teflon screw-stopper and placed in a 120 °C oil bath for 24h. The reaction flask was removed from heat, allowed to cool to room temperature, and quenched with 1 mL Et$_2$O and 1.5 mL 1M HCl aqueous solution. After 5 minutes of vigorous stirring, the top organic phase was separated via pipet. The aqueous phase was washed with 1 mL Et$_2$O. The combined organic solutions were pushed through successive MgSO$_4$ and Celite plugs, and analyzed by GC-MS and GC. These isotopic labeling studies suggest that hydrogens from moieties other than OCX$_3$ and SiX (X = H or D) are incorporated into the arene product. Studies beyond the subject of this paper are necessary to fully elucidate the mechanism of isotopic scrambling.

Table S14. Results of various labeling studies with triethylsilane

Substrate	Silane	Naphthalene yield (%)	d_0 (% vs d_1)
NaphOCD$_3$	2 equiv. Et$_3$SiH	81	95
NaphOCH$_3$	2 equiv. Et$_3$SiD	56	> 95
NaphOCH$_3$	8.3 equiv. Et$_3$SiD	85	81*
NaphOCD$_3$	2 equiv. Et$_3$SiD	68	85*

*Schlenk tube was successively rinsed three times with D$_2$O under N$_2$ and flame-dried under vacuum prior to use for this reaction.

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