Electronic Supplementary Information

Phosphine-functionalized NHC Ni(II) and Ni(0) complexes: synthesis, characterization and catalytic properties

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General Methods. All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques or under nitrogen atmosphere in an Mbraun glovebox. All substrates were purchased from Aldrich and used without further purification. Solvents were distilled and degassed before use. The $Ni(cod)_2$,[1] $[Ni(allyl)Cl]_2$[2] and the phosphine-functionalized $NHCPPh_2$ ligands[3] were prepared according to literature methods. NMR spectra were recorded on Agilent 400 MR or Agilent 500 DD2. FTIR spectra were recorded on a Nicolet IR200 FTIR spectrometer. ^1H and ^{13}C NMR shifts were measured relative to deuterated solvents peaks but are reported relative to tetramethylsilane. Elemental analyses were performed on a PerkinElmer Series II CHNS/O Analyzer 2400.

Synthesis of complexes [Ni(ArNHCPPh$_2$)(allyl)]Cl (Ar = Mes (1a), (2,6-*i*Pr-C$_6$H$_3$ (1b)). The imidazolium salt (1.5 mmol) and potassium bis(trimethylsilyl)amide (0.3 g, 1.5 mmol) were stirred in THF (10 mL) at -30 ºC for 2 hours. A solution of $[Ni(allyl)Cl]_2$ (0.2 g, 0.75 mmol) in THF (5 mL) cooled at -30 ºC was added to the former suspension, and the mixture was allowed to reach room temperature. The solvent was removed under vacuum and the residue was dissolved in dichloromethane and filtered through a Celite pad. The solution was taken to dryness and the solid washed with diethyl ether and dried under vacuum. Recrystallization from toluene afforded the complexes as dark orange solids. Yields: 0.72 g, 90 % for **1a**; 0.81 g, 87 % for **1b**. Data for **1a**: ^1H NMR (500 MHz, CD_2Cl_2, -30 ºC) δ 8.13 (s, 1H, C*H*$_{imid}$), 7.56-7.41 (m, 10 H, C*H*$_{Ar}$), 7.03 (s, 1 H, C*H*$_{imid}$), 7.01 (s, 1 H, C*H*$_{Ar}$), 6.95 (s, 1 H, C*H*$_{Ar}$), 5.11 (m, 1 H, NC*H*$_2$), 4.99 (m, 1 H, H$_{meso}$), 4.48 (m, 1 H, NC*H*$_2$), 3.53 (m, 1 H, H$_{syn}$), 3.45 (m, 1 H, H$_{syn}$), 2.65 (m, 1 H, PC*H*$_2$), 2.53 (m, 1 H, PC*H*$_2$), 2.32 (s, 3 H, C*H*$_3$), 1.94 (s, 3 H, C*H*$_3$), 1.92 (s, 3H, C*H*$_3$), 1.88-1.80 (m, 2 H, H$_{anti}$). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, -30 ºC) δ 171.0 (d, J_{CP} = 20 Hz, N*C*N), 139.6 (*C*$_{Ar}$), 136.3 (*C*$_{Ar}$), 133.4 (d, J_{CP} = 13 Hz, *C*$_{Ar}$), 131.8 (*C*$_{Ar}$), 131.6 (*C*$_{Ar}$), 131.1 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 129.5 (*C*$_{Ar}$), 129.4 (*C*$_{Ar}$), 129.2 (d, J_{CP} = 3 Hz, *C*$_{Ar}$), 125.0 (*C*$_{Ar}$), 122.6 (*C*$_{Ar}$), 115.5 (*C*H$_{allyl}$), 67.1 (d, J_{CP} = 29 Hz, *C*H$_{2allyl}$), 63.1 (*C*H$_{2allyl}$), 46.6 (d, J_{CP} = 3 Hz, N*C*H$_2$), 26.7 (d, J_{CP} = 26 Hz, P*C*H$_2$), 21.2 (*C*H$_{3Ar}$), 18.4 (*C*H$_{3Ar}$), 18.2 (*C*H$_{3Ar}$). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2) δ 20.6. Anal. Calcd for $C_{29}H_{32}N_2PNiCl$: C, 65.26; H, 6.04; N, 5.25. Found: C, 64.74; H, 5.96; N, 5.21. Data for **1b**: ^1H NMR (500 MHz, CD_2Cl_2, -50 ºC) δ 8.31 (s, 1 H, C*H*$_{imid}$), 7.59-7.41 (m, 11 H, C*H*$_{Ar}$), 7.31-7.14 (m, 2 H, C*H*$_{Ar}$), 7.10 (s, 1 H, C*H*$_{imid}$), 5.16 (m, 1 H, NC*H*$_2$), 4.99 (m, 1 H, H$_{meso}$), 4.38 (m, 1 H, NC*H*$_2$), 3.53 (m, 1 H, H$_{syn}$), 3.41 (m, 1 H, H$_{syn}$), 2.66 (m, 1 H, PC*H*$_2$), 2.53-2.41 (m, 3 H, C*H*-*i*Pr and PC*H*$_2$), 1.76 (m, 1 H, H$_{anti}$), 1.69 (m, 1 H, H$_{anti}$), 1.19 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, C*H*$_3$-*i*Pr), 1.05 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, C*H*$_3$-*i*Pr), 1.01 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, C*H*$_3$-*i*Pr),

0.82 (d, 3 H, $^{3}J_{HH}$ = 6.9 Hz, C*H*$_3$-*i*Pr). ^{13}C{1H} NMR (125 MHz, CD_2Cl_2, -70 ºC) δ 172.5, (d, J_{CP} = 24 Hz, N*C*N), 145.1 (*C*$_{Ar}$), 144.6 (*C*$_{Ar}$), 137.7 (*C*$_{Ar}$), 135.5 (*C*$_{Ar}$), 133.1 (d, J_{CP} = 13 Hz, *C*$_{Ar}$), 131.5 (*C*$_{Ar}$), 131.0 (*C*$_{Ar}$), 130.9 (*C*$_{Ar}$), 130.6 (*C*$_{Ar}$), 129.9 (*C*$_{Ar}$), 129.1-128.9 (m, *C*$_{Ar}$), 128.7 (*C*$_{Ar}$), 127.9 (*C*$_{Ar}$), 124.9 (*C*$_{Ar}$), 124.5 (*C*$_{Ar}$), 123.8 (*C*$_{Ar}$), 123.6 (d, J_{CP} = 16 Hz, *C*$_{Ar}$), 114.7 (*C*H$_{allyl}$), 66.4 (d, J_{CP} = 22 Hz, *C*H$_{2allyl}$), 62.8 (*C*H$_{2allyl}$), 45.8 (N*C*H$_2$), 28.0 (*C*H-*i*Pr), 27.9 (*C*H-*i*Pr), 26.2 (d, J_{CP} = 27 Hz, P*C*H$_2$), 25.6 (*C*H$_3$-*i*Pr), 22.9 (*C*H$_3$-*i*Pr), 22.2 (*C*H$_3$-*i*Pr), 21.1 (*C*H$_3$-*i*Pr). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 22.9. Anal. Calcd for $C_{32}H_{38}N_2PNiCl$•0.5C_7H_8: C, 68.57; H, 6.81; N, 4.50. Found: C, 68.94; H, 6.79; N, 4.25.

Synthesis of [Ni(ArNHCPPh$_2$)(allyl)]SbF$_6$ (Ar = 2,6-*i*Pr-C$_6$H$_3$ (1b-SbF$_6$)). One equivalent of $AgSbF_6$ (0.123 g, 0.35 mmol) was added to a solution of complex **1b** (0.2 g, 0.35 mmol) in dichloromethane (5 mL). The reaction stirred for 10 min and then filtered through a pad of Celite. The solvent was removed under reduce pressure to afford a pale yellow solid in quantitative yield. .Data for **1b-SbF$_6$**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.63-7.44 (m, 10 H, C*H*$_{Ar}$), 7.36-7.28 (m, 2 H, C*H*$_{Ar}$), 7.16 (d, 1 H, $^{3}J_{HH}$ = 1.8 Hz, C*H*$_{imid}$), 5.00 (m, 1 H, H$_{meso}$), 4.65 (m, 1 H, NC*H*$_2$), 4.35 (m, 1 H, NC*H*$_2$), 3.59 (m, 1 H, H$_{syn}$), 3.54 (m, 1 H, H$_{syn}$), 2.68 (m, 1 H, PC*H*$_2$), 2.57-2.44 (m, 3 H, C*H*-*i*Pr and PC*H*$_2$), 1.90-1.85 (m, 2 H, H$_{anti}$), 1.21 (d, 3 H, $^{3}J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr), 1.09 (d, 3 H, $^{3}J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr), 1.07 (d, 3 H, $^{3}J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr), 0,95 (d, 3 H, $^{3}J_{HH}$ = 6.8 Hz, CH$_3$-*i*Pr). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 172.9, (d, J_{CP} = 19 Hz, N*C*N), 145.6 (*C*$_{Ar}$), 145.1 (*C*$_{Ar}$), 136.0 (*C*$_{Ar}$), 132.9 (d, J_{CP} = 14 Hz, *C*$_{Ar}$), 131.9 (d, J_{CP} = 3 Hz, *C*$_{Ar}$), 131.5 (d, J_{CP} = 11 Hz, *C*$_{Ar}$), 131.3 (d, J_{CP} = 3 Hz, *C*$_{Ar}$), 130.6 (*C*$_{Ar}$), 129.6, (d, J_{CP} = 2 Hz, *C*$_{Ar}$), 129.5 (d, J_{CP} = 2 Hz, *C*$_{Ar}$), 124.9 (*C*$_{Ar}$), 124.3 (d, J_{CP} = 6 Hz, *C*$_{Ar}$), 123.6 (*C*$_{Ar}$), 115.3 (*C*H$_{allyl}$), 67.6 (d, J_{CP} = 18 Hz, *C*H$_{2allyl}$), 63.2 (d, J_{CP} = 5 Hz, *C*H$_{2allyl}$), 47.1 (d, J_{CP} = 4 Hz, N*C*H$_2$), 28.5 (d, J_{CP} = 18 Hz, P*C*H$_2$), 27.0 (*C*H-*i*Pr), 26.8 (*C*H-*i*Pr), 25.4 (*C*H$_3$-*i*Pr), 24.9 (*C*H$_3$-*i*Pr), 22.9 (*C*H$_3$-*i*Pr), 22.6 (*C*H$_3$-*i*Pr). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 21.3. Anal. Calcd for $C_{32}H_{38}F_6N_2PNiSb$•0.4CH_2Cl_2: C, 48.04; H, 4.83; N, 3.46. Found: C, 47.83; H, 4.83; N, 3.46.

Synthesis of complexes [Ni(ArNHCPPh$_2$)(alkene)] (Ar = (2,6-iPr-C$_6$H$_3$; alkene = styrene (2a), diethyl fumarate, (2b)). The imidazolium salt (0.48g, 1 mmol), potassium bis(trimethylsilyl)amide (0.2 g, 1 mmol), $Ni(cod)_2$ (0.27 g, 1 mmol) and 3 equivalents of the corresponding alkene were dissolved in THF (5 mL). The mixture was stirred for 90 minutes at room temperature and then, it was filtered through a pad of Celite. The volatiles were removed under reduced pressure. The yellow-orange solid was washed with hexane to give the desired product. Yield: 0.54 g, 90 % for **2a**; 0.57 g, 85 % for **2b**. Data for **2a**: ^{1}H NMR

(500 MHz, C_6D_6) δ 7.60 (t, 2 H, J_{HH} = 8.5 Hz, CH_{Ar}), 7.27-7.14 (m, 3 H, CH_{Ar}), 7.10-6.85 (m, 13 H, CH_{Ar}), 6.41 (s, 1 H, CH_{imid}), 6.13 (s, 1 H, CH_{imid}), 3.78-3.68 (m, 1 H, NCH_2 and CH_{olefin}), 3.39 (m, 1 H, NCH_2), 2.95 (sept, 1 H, $^3J_{HH}$ = 7 Hz, CH-*i*Pr), 2.66 (sept, 1 H, $^3J_{HH}$ = 7 Hz, CH-*i*Pr), 2.15 (m, 1H, CH_{olefin}), 1.94-1.85 (m, 2 H, PCH_2 and CH_{olefin}), 1.57 (m, 1 H, PCH_2), 1.30 (d, 3 H, $^3J_{HH}$ = 7 Hz, CH_3-*i*Pr), 1.11 (d, 3 H, $^3J_{HH}$ = 7 Hz, CH_3-*i*Pr), 1.05 (d, 3 H, $^3J_{HH}$ = 7 Hz, CH_3-*i*Pr), 0.89 (d, 3 H, $^3J_{HH}$ = 7 Hz, CH_3-*i*Pr). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 195.5 (d, J_{CP} = 8 Hz, NCN), 150.3 (C_{Ar}), 146.3 (C_{Ar}), 145.8 (C_{Ar}), 139.6 (d, J_{CP} = 23 Hz, C_{Ar}), 138.1 (C_{Ar}), 135.9 (d, J_{CP} = 25 Hz, C_{Ar}), 133.3 (d, J_{CP} = 15 Hz, C_{Ar}), 131.7 (d, J_{CP} = 13 Hz, C_{Ar}), 129.1 (C_{Ar}), 128.3 (C_{Ar}), 128.0 (C_{Ar}), 127.6 (C_{Ar}), 123.6 (C_{Ar}), 123.3 (C_{Ar}), 123.2 (C_{Ar}), 121.0 (C_{Ar}), 120.1 (C_{Ar}), 119.8 (C_{Ar}), 52.2 (CH$_{2olefin}$), 47.0 (d, J_{CP} = 8 Hz, NCH$_2$), 33.4 (d, J_{CP} = 24 Hz, CH$_{olefin}$), 28.4 (CH-*i*Pr), 28.3 (CH-*i*Pr), 27.7 (d, J_{CP} = 23 Hz, PCH$_2$), 25.4 (CH$_3$-*i*Pr), 24.6 (CH$_3$-*i*Pr), 23.7 (CH$_3$-*i*Pr), 22.6 (CH$_3$-*i*Pr). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6) δ 15.2. Data for **2b**: ^{1}H NMR (500 MHz, C_6D_6): δ 8.07 (t, 2 H, $^3J_{HH}$ = 8.7 Hz, CH_{Ar}), 7.49 (t, 2 H, $^3J_{HH}$ = 8.7 Hz, CH_{Ar}), 7.24-7.12 (m, 7 H, CH_{Ar}), 7.08-7.01 (m, 2 H, CH_{Ar}), 6.46 (s, 1H, CH_{imid}), 6.09 (br. s, 1 H, CH_{imid}), 4.05 (dq, 1 H, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, COOCH_2CH$_3$), 3.97 (dq, 1 H, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, COOCH_2CH$_3$), 3.90-3.81 (m, 2 H, COOCH_2CH$_3$ and NCH_2), 3.71 (dq, 1 H, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, COOCH_2CH$_3$), 3.54 (m, 1 H, CH_{olefin}), 3.33-3.21 (m, 2 H, CH_{olefin} and NCH_2), 3.09 (sept, 1 H, $^3J_{HH}$ = 6.5 Hz, CH-*i*Pr), 3.08 (sept, 1 H, $^3J_{HH}$ = 6.5 Hz, CH-*i*Pr), 1.72 (m, 1 H, PCH_2), 1.60 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH$_3$-*i*Pr), 1.39 (m, 1 H, PCH_2), 1.12 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH$_3$-*i*Pr), 0.99 (d, 3 H, $^3J_{HH}$ = 6.5 Hz, CH$_3$-*i*Pr), 0.97 (t, 3 H, $^3J_{HH}$ = 7 Hz, COOCH$_2$CH_3), 0.84 (t, 3 H, $^3J_{HH}$ = 7 Hz, COOCH_2CH_3), 0.70 (d, 3H, $^3J_{HH}$ = 7 Hz, CH$_3$-*i*Pr). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 192.0 (NCN), 173.8 (d, J_{CP} = 5 Hz, C=O), 145.9 (C_{Ar}), 144.9 (C_{Ar}), 137.4 (C_{Ar}), 137.2 (C_{Ar}), 136.9 (C_{Ar}), 135.1 (d, J_{CP} = 31 Hz, C_{Ar}), 133.3 (d, J_{CP} = 14 Hz, C_{Ar}), 132.2 (d, J_{CP} = 13 Hz, C_{Ar}), 129.4 (C_{Ar}), 129.1 (C_{Ar}), 128.9 (C_{Ar}), 128.4 (d, J_{CP} = 9 Hz, C_{Ar}), 128.1 (d, J_{CP} = 9 Hz, C_{Ar}), 128.0 (C_{Ar}), 127.2 (C_{Ar}), 123.8 (d, J_{CP} = 5 Hz, C_{Ar}), 123.3 (C_{Ar}), 119.8 (C_{Ar}), 57.9 (COOCH$_2$CH$_3$), 57.8 (CH$_{olefin}$), 46.2 (d, J_{CP} = 7 Hz, NCH$_2$), 41.2 (d, J_{CP} = 20 Hz, CH$_{olefin}$), 34.0 (COOCH$_2$CH$_3$), 27.4 (d, J_{CP} = 25 Hz, PCH$_2$), 26.3 (CH-*i*Pr), 24.5 (CH-*i*Pr), 23.3 (CH$_3$-*i*Pr), 22.4 (CH$_3$-*i*Pr), 22.3 (CH$_3$-*i*Pr), 21.8 (CH$_3$-*i*Pr), 14.4 (d, J_{CP} = 20 Hz, COOCH$_2C$H$_3$), 13.9 (COOCH$_2C$H$_3$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 23.7. IR (KBr): ν(C-O) = 1668 cm^{-1} (str). Anal. Calcd for $C_{37}H_{45}N_2O_4PNi$: C, 66.19; H, 6.76; N, 4.17. Found: C, 66.28; H, 6.49; N, 4.29.

Alternative synthetic procedure for the preparation of 2a.

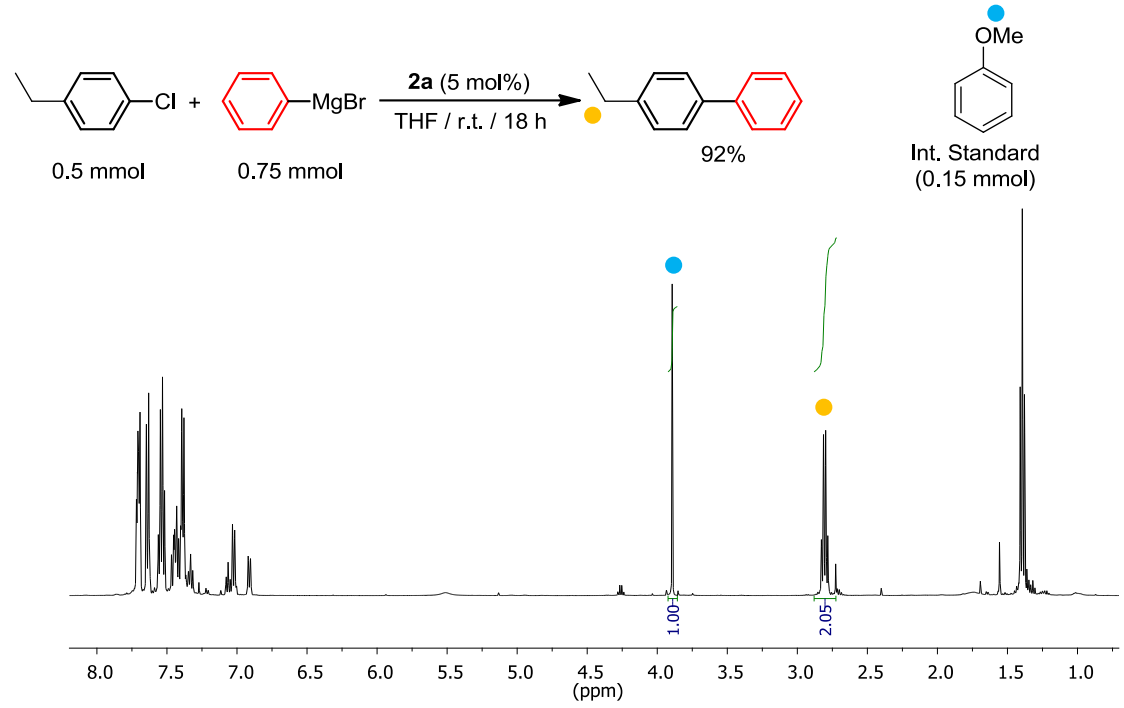
Di-*n*-butylmagnesium (0.53 mmol, solution 1 M in heptane) was added slowly to a solution of **1b** (0.5 g, 0.8 mmol) and styrene (0.18 mL, 1.6 mmol) in THF (5 mL) at -78ºC. The mixture was stirred for 1 hour at -78ºC and then, at room temperature for additional 90 min. The solvent was removed under vacuum and the solid washed with distilled water to remove the magnesium salts, and finally with petroleum ether to afford **2a** as yellow solid (0.48 g, 87 %).

Typical catalytic procedure for Kumada-Tamao-Corriu reactions. To a mixture of the catalyst (0.1 to 5 mol%) and the (hetero)aryl chloride (0.5 mmol) in THF (1 mL), phenylmagnesium chloride (0.75 mmol, 1 M in THF) was added under a nitrogen atmosphere. The reaction mixture was stirred at a room temperature for a given time (1 h or 16 h). A saturated solution of NH_4Cl was added and the mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was evaporated to dryness. The yield of product was determined by ^{1}H NMR using anisole as internal standard.

Typical catalytic procedure for Suzuki-Miyaura reactions. The catalyst (1 or 3 mol%), the base K_3PO_4 (1.3 mmol), phenylboronic acid (0.65 mmol) and toluene (2 mL) were added in turn to a vial equipped with a J Young tap and containing a magnetic bar. The aryl chloride (0.5 mmol) was added under a nitrogen atmosphere. The reaction mixture was stirred for 18 h at 80 ºC in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through celite. After evaporation of the solvent, the crude was analyzed by ^{1}H NMR using anisole as internal standard.

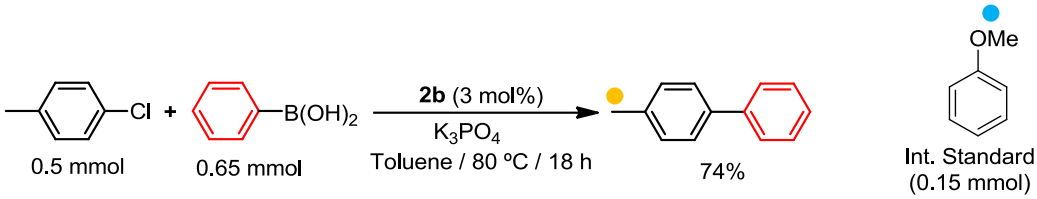
Typical catalytic procedure for Buchwald-Hartwig amination reactions. The catalyst (5 or 10 mol%), the base NaO*t*Bu or LiO*t*Bu (0.6 mmol) and dioxane (1 mL) were added in turn to a vial equipped with a J Young tap and containing a magnetic bar. The *N*-nucleophile (0.6 mmol) and the (hetero)aryl chloride (0.5 mmol) were added under a nitrogen atmosphere. The reaction mixture was stirred at 110ºC for 16 h in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through celite. The clean solution was evaporated to dryness, and the residue was analyzed by ^{1}H NMR using anisole as internal standard.

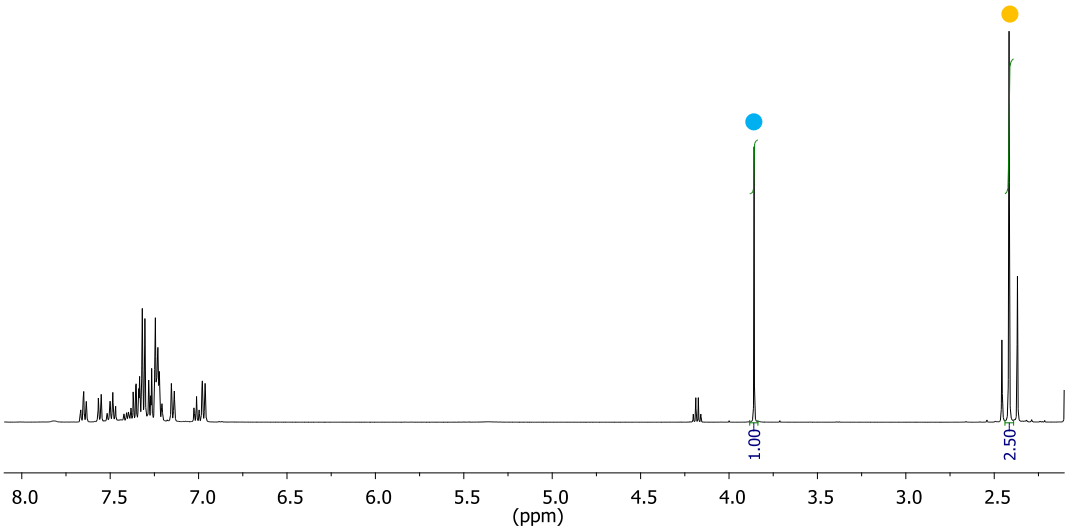
Example of the yield determination by ^{1}H NMR in the Kumada-Tamao-Corriu reaction.



$$\text{Yield} = \frac{\frac{2.05}{2H} \cdot 0.15\ \text{mmol}}{\frac{1.00}{3H}} = 0.46\ \text{mmol} \Big/ 0.5\ \text{mmol} \cdot 100 = \mathbf{92\%}$$

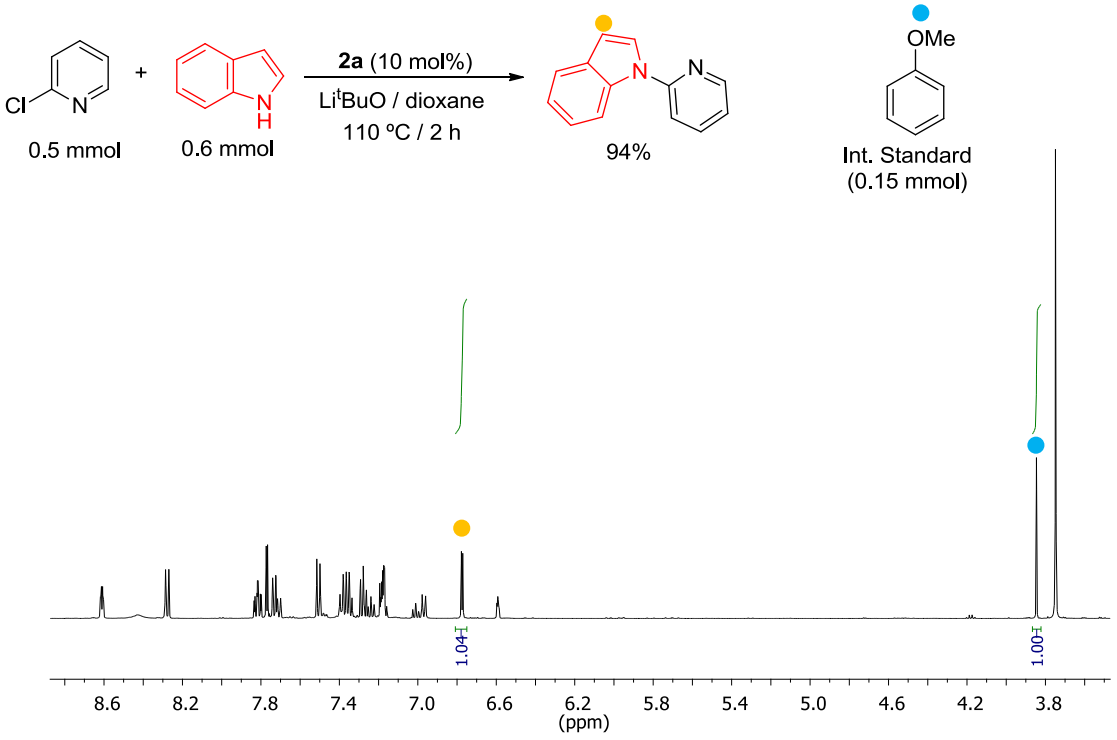
Example of the yield determination by ^{1}H NMR in the Suzuki-Miyaura reaction.





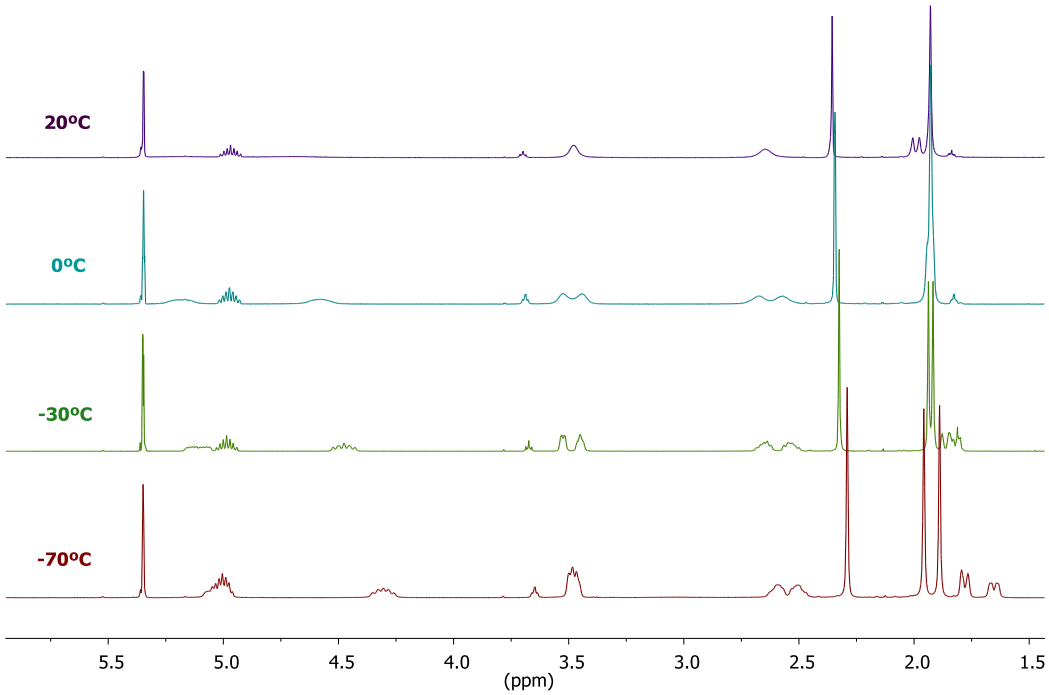
$$\text{Yield} = \frac{\frac{2.50}{3H} \cdot 0.15\ \text{mmol}}{\frac{1.00}{3H}} = 0.37\ \text{mmol} \,/\, 0.5\ \text{mmol} \cdot 100 = \mathbf{74\%}$$

Example of the yield determination by ^{1}H NMR in the Buchwald-Hartwig reaction.

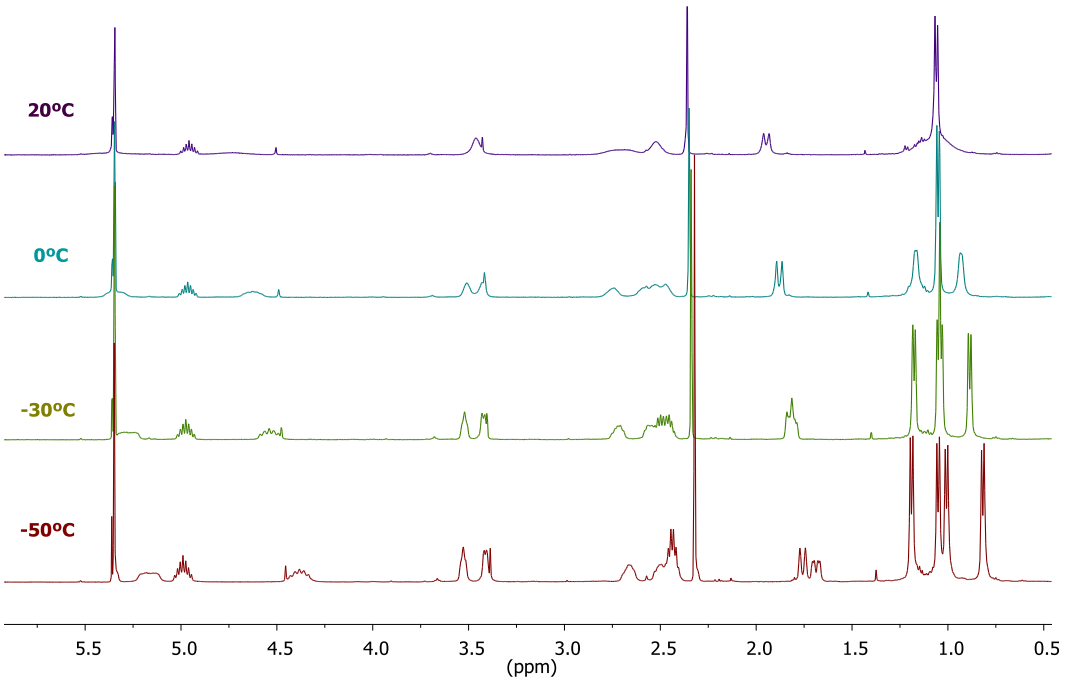


$$\text{Yield} = \frac{\frac{1.04}{1H} \cdot 0.15\ \text{mmol}}{\frac{1.00}{3H}} = 0.47\ \text{mmol} \,/\, 0.5\ \text{mmol} \cdot 100 = \mathbf{94\%}$$

Variable temperature ^{1}H NMR studies carried out with 1a in CD_2Cl_2.



Variable temperature ^{1}H NMR studies carried out with 1b in CD_2Cl_2.



With the coalescence temperatures (*Tc*) and the separation (δν) of the corresponding two signals at low temperature, the $\Delta G^{\ddagger}$ values of interconversion processes *syn-syn* and *anti-anti* were determined.[4] It was not possible to determine the coalescence of the *anti* proton resonances for **1a** due to strong overlap with the signal of the methyl groups.

Table S1. δν, *T*c and $\Delta G^{\ddagger}$ data for complexes **1a** and **1b**.[a]

Complex	Exchanging protons	δν (Hz)	*Tc* (K)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
1a	*syn-syn*	55.1	288	58.9
1b	*anti-anti*	37.5	258	53.3
1b	*syn-syn*	62.4	283	57.5

[a]Complex concentration: 1.50 $x10^{-2}$ M (in 0.7 mL of CD_2Cl_2); ^{1}H NMR spectra recorded in 500 MHz spectrometer.

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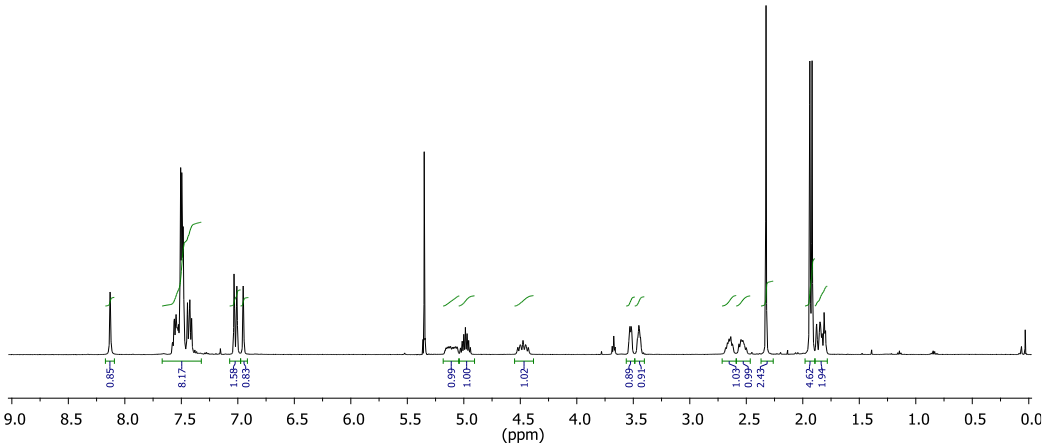
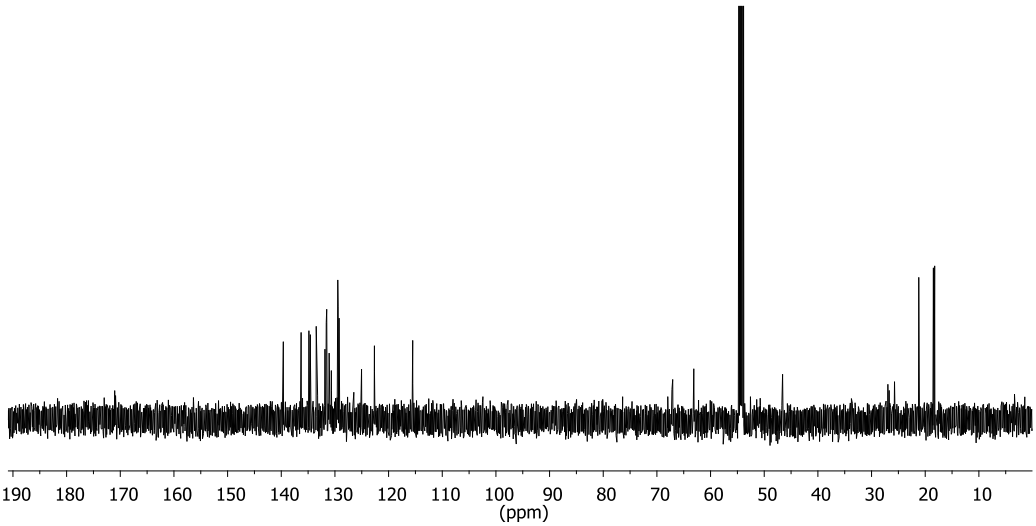
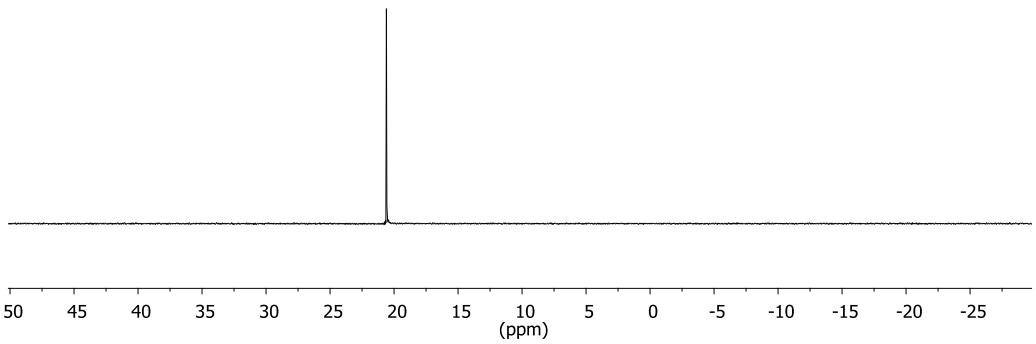
Low temperature (-30 °C) ^{1}H NMR spectrum of 1a.



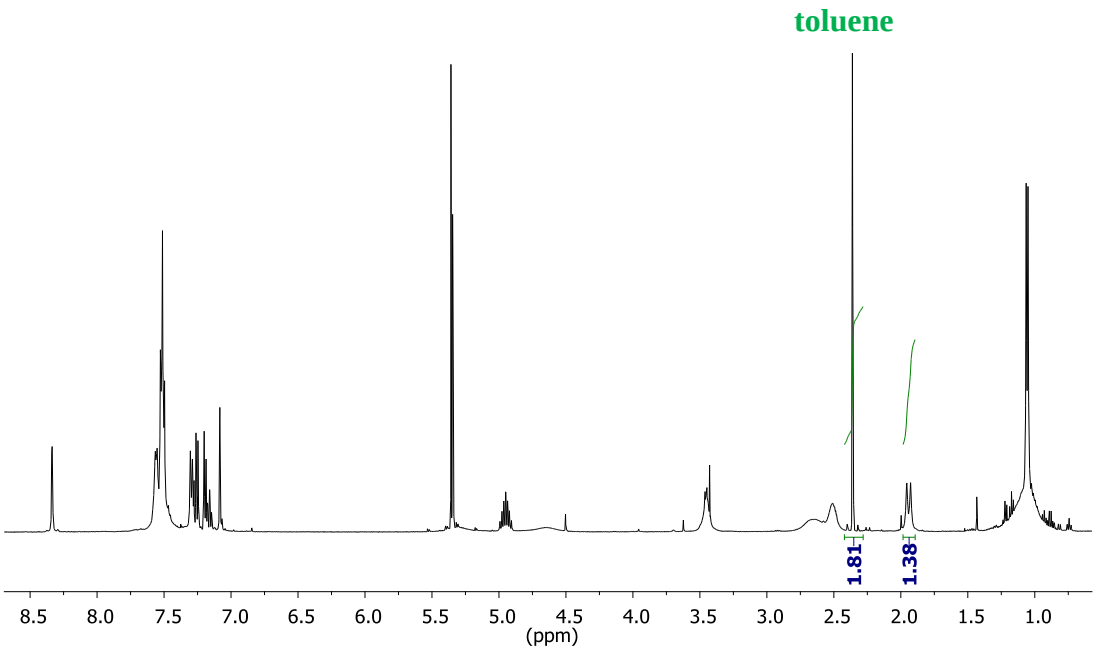
Low temperature (-70 °C) ^{13}C{^{1}H} NMR spectrum of 1a.



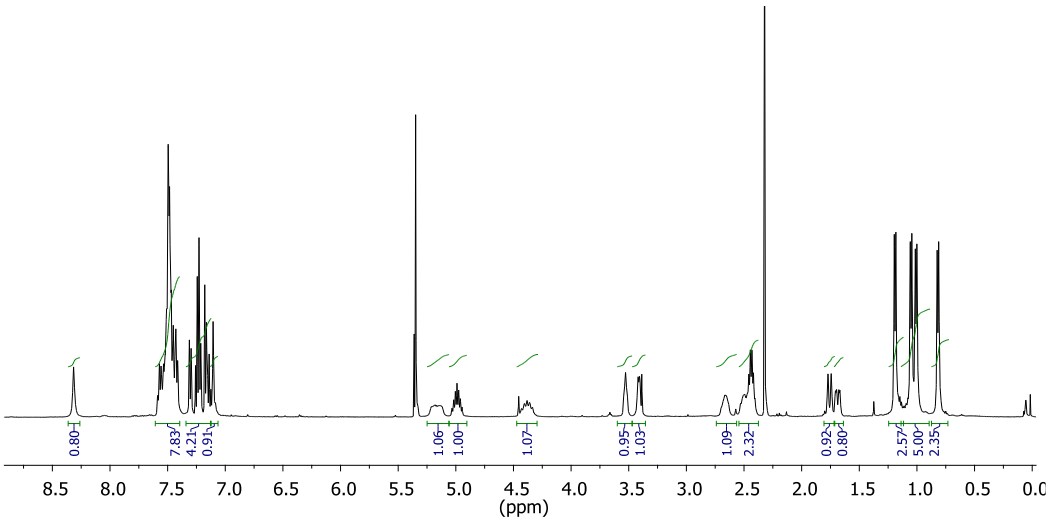
^{31}P{^{1}H} NMR spectrum of 1a.



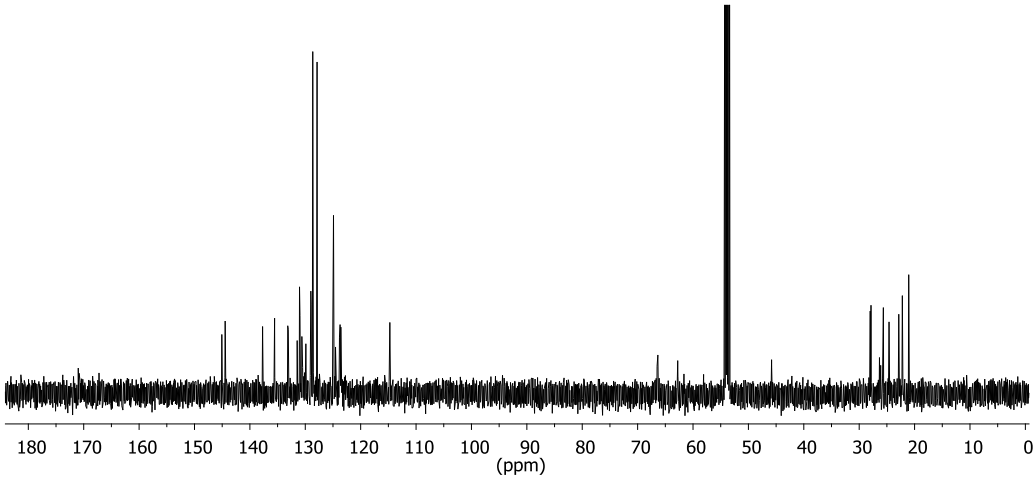
^{1}H NMR spectrum of 1b.



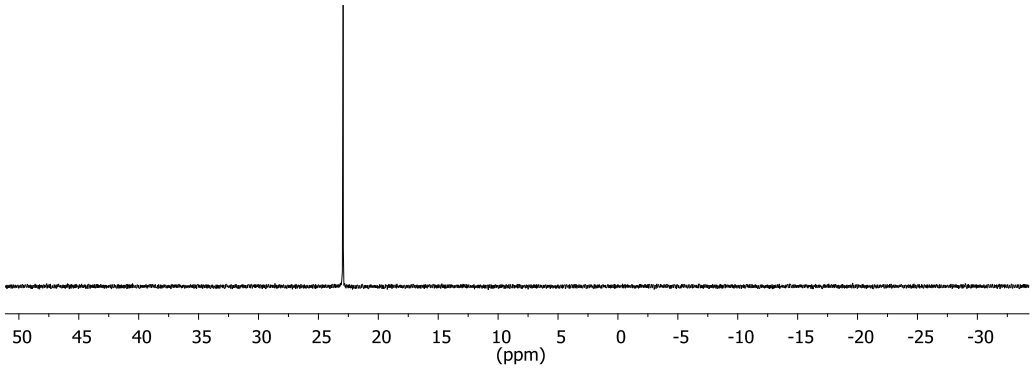
Low temperature (-50 °C) ^{1}H NMR spectrum of 1b.



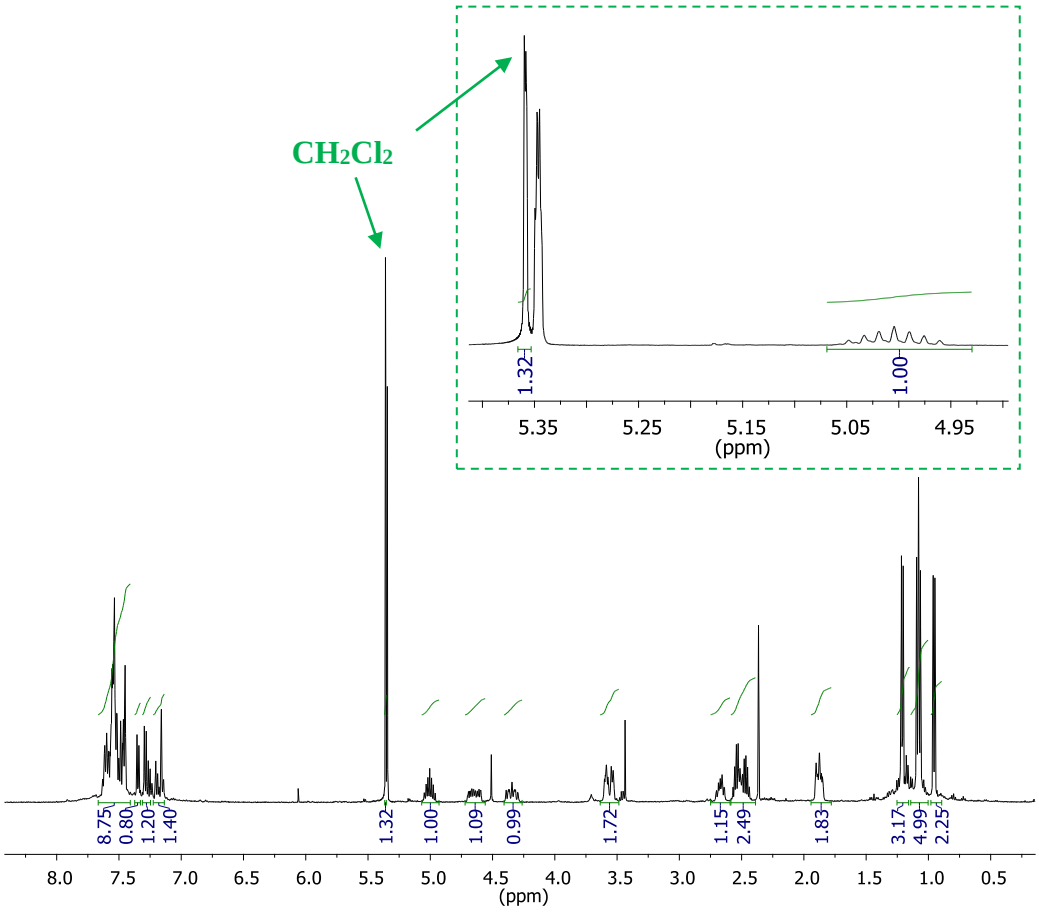
Low temperature (-70 ºC) $^{13}C\{^{1}H\}$ NMR spectrum of 1b.



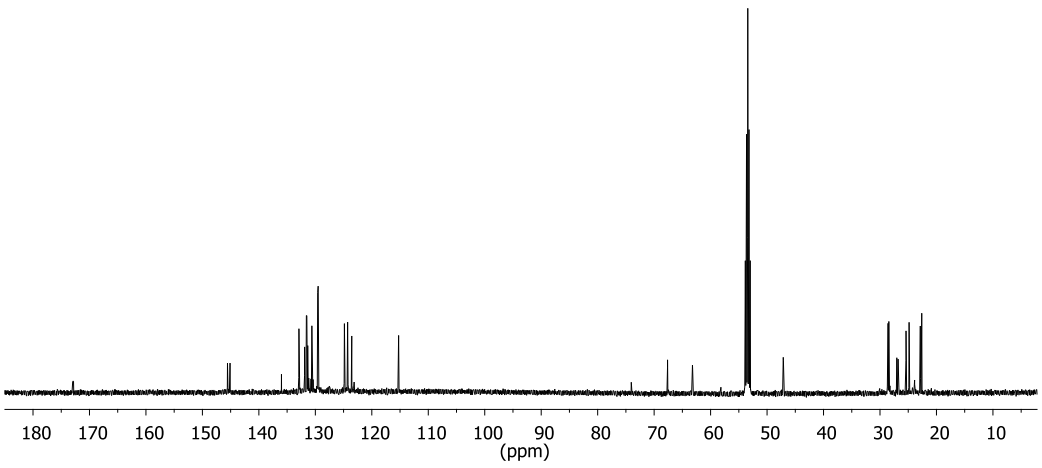
$^{31}P\{^{1}H\}$ NMR spectrum of 1b.



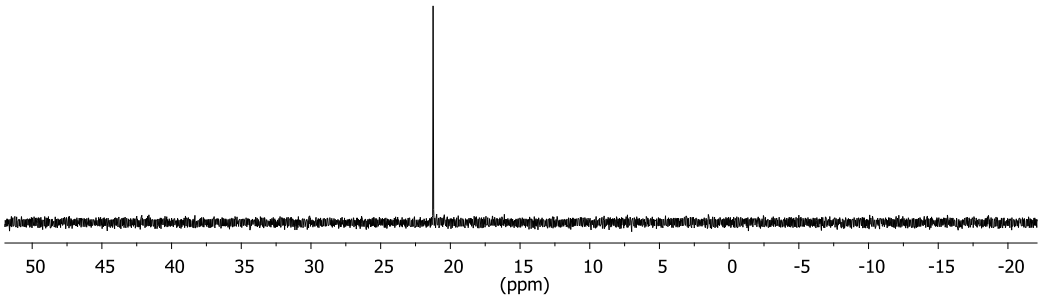
^{1}H NMR spectrum of 1b-SbF_6



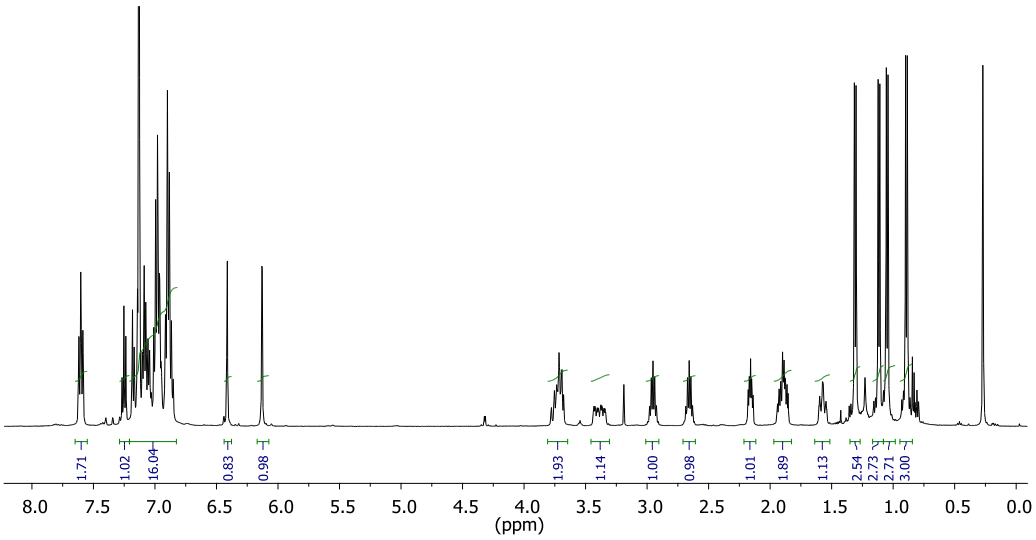
^{13}C NMR spectrum of 1b-SbF_6.



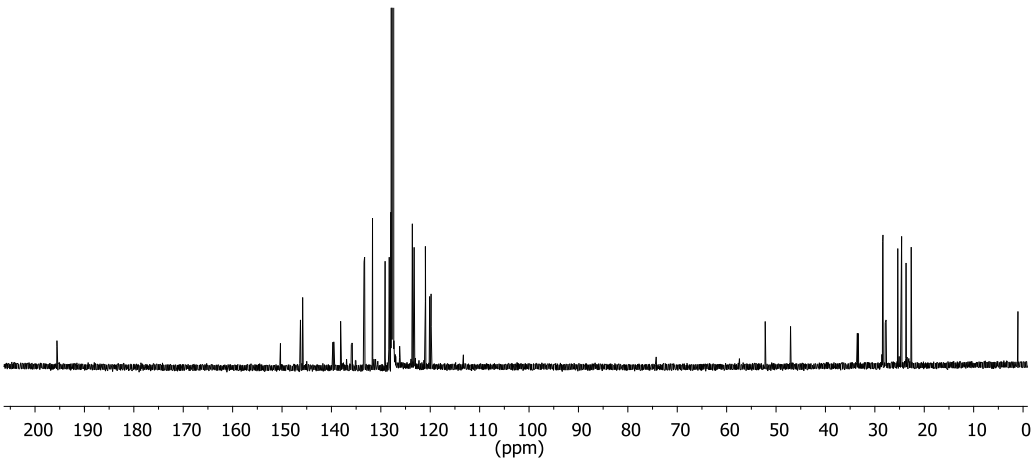
^{31}P NMR spectrum of 1b-SbF_6.



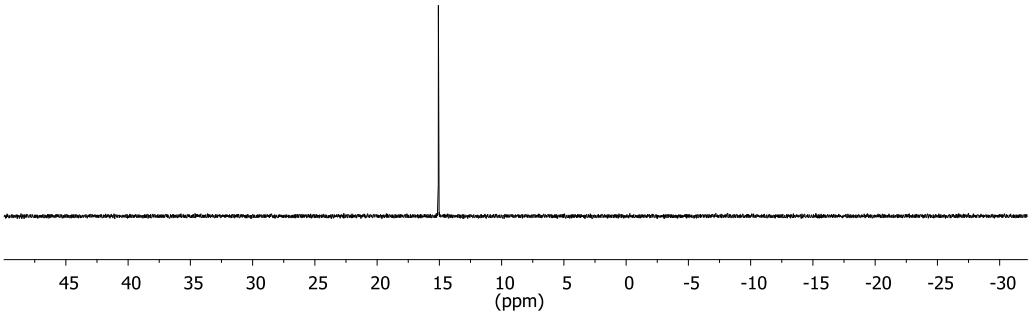
^{1}H NMR spectrum of 2a.



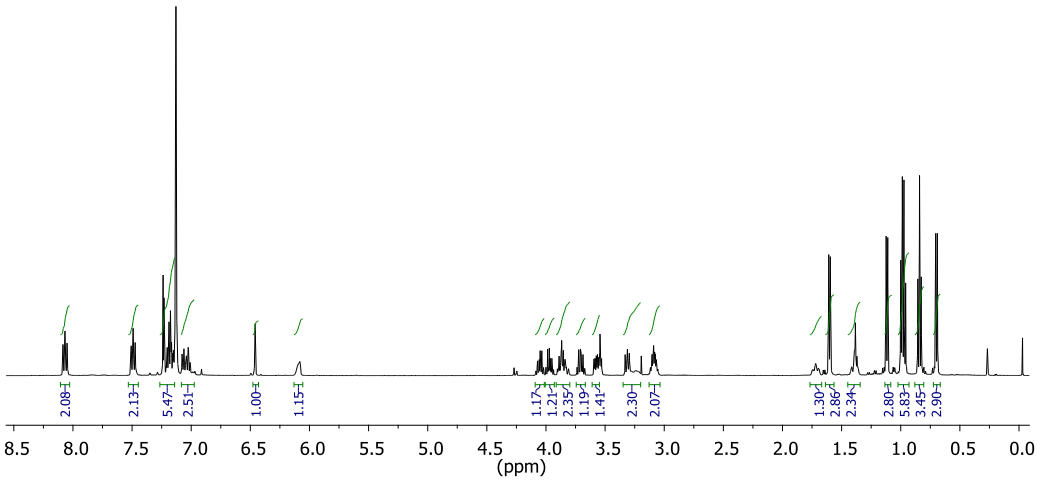
^{13}C{^{1}H} NMR spectrum of 2a.



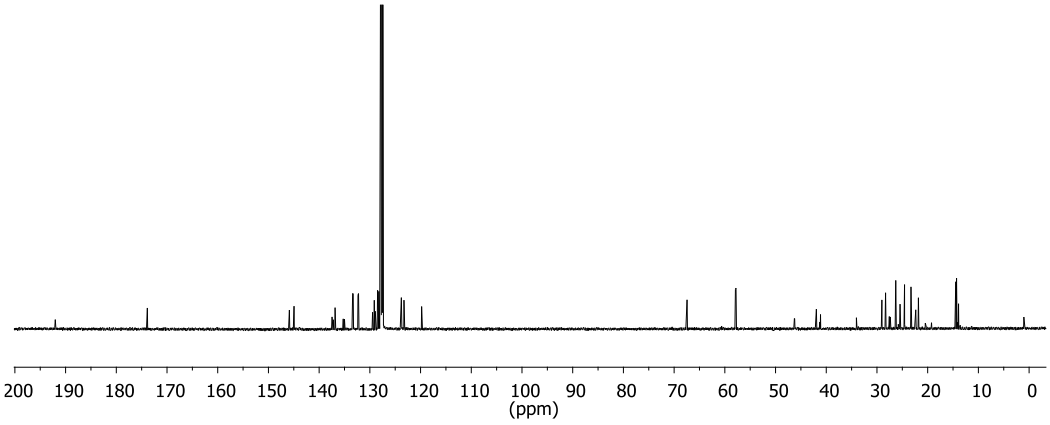
^{31}P{^{1}H} NMR spectrum of 2a.



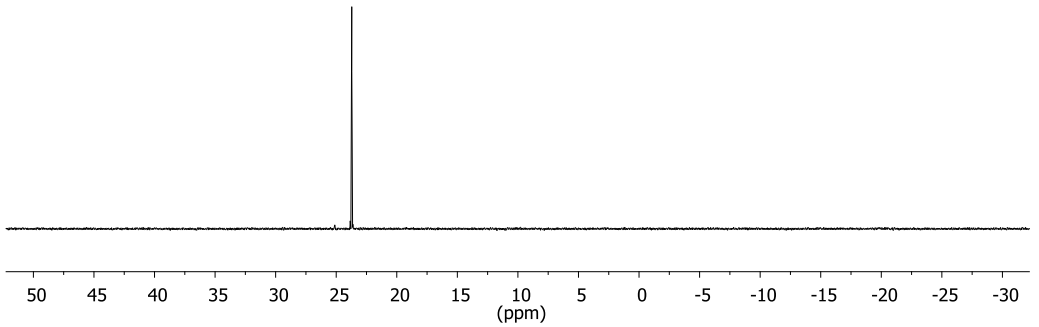
^{1}H NMR spectrum of 2b.



^{13}C{^{1}H} NMR spectrum of 2b.



^{31}P{^{1}H} NMR spectrum of 2b.



X-crystallographic data for 2b.

A summary of the crystallographic data and structure refinement results for **2b** is given in ***Table S1***. One crystal coated with dry perfluoropolyether was mounted on a glass fiber and fixed under a cold nitrogen stream. The intensity data were collected on a Bruker-Nonius X8ApexII CCD area detector diffractometer using Mo-K_α radiation source (λ = 0.71073 Å) fitted with a graphite monochromator. The data collection strategy used was ω and ϕ rotations with narrow frames (width of 0.50 degree). Instrument and crystal stability were evaluated from the measurement of equivalent reflections at different measuring times and no decay was observed. The data were reduced using SAINT[1] and corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied (SADABS)[2]. The structures were solved by direct methods using SIR-2002[3] and refined against all F^2 data by full-matrix least-squares techniques using SHELXL-2016/6[4] minimizing $w[Fo^2-Fc^2]^2$. All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and allowed to ride on the attached atoms with isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) those U_{eq} values of the corresponding attached atoms.

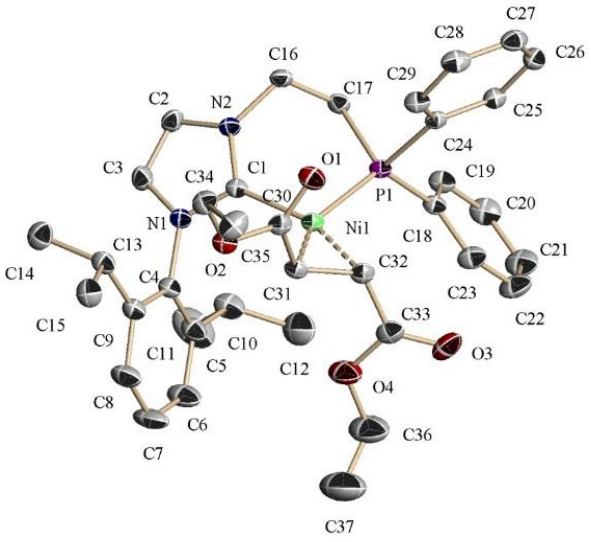
References

1 Bruker. APEX2. Bruker AXS Inc., Madison, Wisconsin, USA, **2007**.

2 Bruker Advanced X-ray Solutions, SAINT and SADABS programs, Bruker AXS Inc., Madison, WI, **2004**.

3 C. M. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. **2003**, 36, 1103.

4 G. M. Sheldrick, *Acta Cryst.,* **2015**, C71, 3-8.



ORTEP view of **2b** with the thermal ellipsoids set at 30 % probability level. The hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for **2b**

Empirical formula	$C_{37}H_{45}N_2NiO_4P$	
Formula weight	671.43	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.7746(4) Å	α= 83.689(2)°.
	b = 11.0588(5) Å	β= 82.032(2)°.
	c = 18.2168(8) Å	γ = 79.558(2)°.
Volume	1715.10(13) $Å^3$	
Z	2	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.653 mm^{-1}	
F(000)	712	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	2.278 to 25.245°.	
Index ranges	-10<=h<=10, -13<=k<=12, -21<=l<=15	
Reflections collected	32713	
Independent reflections	6194 [R(int) = 0.0450]	
Completeness to theta = 25.242°	99.4 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9375 and 0.8804
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6194 / 35 / 412
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.1056
R indices (all data)	R1 = 0.0570, wR2 = 0.1130
Extinction coefficient	n/a
Largest diff. peak and hole	0.754 and -0.476 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	4613(1)	561(1)	2959(1)	29(1)
P(1)	6549(1)	-945(1)	2909(1)	29(1)
O(1)	2315(2)	505(2)	4529(1)	46(1)
O(2)	1074(2)	2379(2)	4141(1)	41(1)
O(3)	2229(3)	-1477(2)	2165(1)	65(1)
O(4)	2269(3)	513(2)	1789(1)	72(1)
N(1)	5673(2)	2985(2)	2587(1)	33(1)
N(2)	7164(2)	1721(2)	3265(1)	32(1)
C(1)	5801(3)	1835(2)	2959(1)	29(1)
C(2)	7874(3)	2752(3)	3065(2)	40(1)
C(3)	6949(3)	3535(3)	2638(2)	42(1)
C(4)	4507(3)	3459(2)	2089(1)	36(1)
C(5)	4828(4)	3126(3)	1360(2)	47(1)
C(6)	3693(4)	3562(3)	892(2)	67(1)
C(7)	2324(5)	4299(4)	1135(2)	74(1)
C(8)	2060(4)	4637(3)	1850(2)	58(1)
C(9)	3144(3)	4238(3)	2349(2)	39(1)
C(10)	6334(4)	2339(3)	1068(2)	55(1)
C(11)	7173(5)	3052(5)	425(2)	103(2)
C(12)	6070(5)	1118(4)	848(2)	82(1)
C(13)	2878(3)	4668(3)	3123(2)	40(1)
C(14)	3740(4)	5737(3)	3156(2)	53(1)
C(15)	1169(3)	5087(3)	3399(2)	51(1)
C(16)	7917(3)	573(2)	3638(1)	35(1)
C(17)	8334(3)	-433(2)	3101(2)	34(1)
C(18)	7217(3)	-1865(2)	2116(1)	33(1)
C(19)	8768(3)	-2129(3)	1803(2)	42(1)
C(20)	9173(4)	-2856(3)	1211(2)	55(1)
C(21)	8071(4)	-3335(4)	933(2)	65(1)
C(22)	6531(4)	-3093(4)	1238(2)	64(1)
C(23)	6107(3)	-2354(3)	1819(2)	47(1)
C(24)	6332(3)	-2140(2)	3682(1)	30(1)
C(25)	7137(3)	-3335(2)	3654(1)	36(1)
C(26)	7004(4)	-4199(3)	4261(2)	46(1)
C(27)	6076(4)	-3852(3)	4907(2)	47(1)
C(28)	5285(3)	-2669(3)	4941(2)	46(1)
C(29)	5383(3)	-1811(3)	4328(1)	39(1)
C(30)	1959(3)	1262(3)	4022(1)	34(1)
C(31)	2348(3)	1095(2)	3230(1)	32(1)
C(32)	2697(3)	-147(3)	3019(1)	35(1)
C(33)	2377(3)	-463(3)	2310(2)	45(1)
C(34)	593(3)	2642(3)	4905(2)	45(1)
C(35)	-899(4)	2224(3)	5195(2)	56(1)
C(36)	2069(6)	258(5)	1066(2)	99(1)
C(37)	693(7)	982(6)	825(3)	142(2)

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

Ni(1)-C(1)	1.898(3)	C(15)-H(15B)	0.9700
Ni(1)-C(32)	1.965(2)	C(15)-H(15C)	0.9700
Ni(1)-C(31)	1.977(2)	C(16)-C(17)	1.524(4)
Ni(1)-P(1)	2.1527(7)	C(16)-H(16A)	0.9800
P(1)-C(18)	1.827(3)	C(16)-H(16B)	0.9800
P(1)-C(24)	1.836(2)	C(17)-H(17A)	0.9800
P(1)-C(17)	1.847(2)	C(17)-H(17B)	0.9800
O(1)-C(30)	1.211(3)	C(18)-C(23)	1.392(4)
O(2)-C(30)	1.357(3)	C(18)-C(19)	1.392(4)
O(2)-C(34)	1.442(3)	C(19)-C(20)	1.385(4)
O(3)-C(33)	1.214(4)	C(19)-H(19)	0.9400
O(4)-C(33)	1.354(4)	C(20)-C(21)	1.361(5)
O(4)-C(36)	1.417(3)	C(20)-H(20)	0.9400
N(1)-C(1)	1.367(3)	C(21)-C(22)	1.378(5)
N(1)-C(3)	1.386(3)	C(21)-H(21)	0.9400
N(1)-C(4)	1.451(3)	C(22)-C(23)	1.378(4)
N(2)-C(1)	1.369(3)	C(22)-H(22)	0.9400
N(2)-C(2)	1.386(3)	C(23)-H(23)	0.9400
N(2)-C(16)	1.464(3)	C(24)-C(25)	1.384(4)
C(2)-C(3)	1.337(4)	C(24)-C(29)	1.387(3)
C(2)-H(2)	0.9400	C(25)-C(26)	1.386(4)
C(3)-H(3)	0.9400	C(25)-H(25)	0.9400
C(4)-C(5)	1.396(4)	C(26)-C(27)	1.383(4)
C(4)-C(9)	1.398(4)	C(26)-H(26)	0.9400
C(5)-C(6)	1.385(4)	C(27)-C(28)	1.369(4)
C(5)-C(10)	1.509(4)	C(27)-H(27)	0.9400
C(6)-C(7)	1.372(5)	C(28)-C(29)	1.387(4)
C(6)-H(6)	0.9400	C(28)-H(28)	0.9400
C(7)-C(8)	1.371(4)	C(29)-H(29)	0.9400
C(7)-H(7)	0.9400	C(30)-C(31)	1.461(3)
C(8)-C(9)	1.388(4)	C(31)-C(32)	1.435(4)
C(8)-H(8)	0.9400	C(31)-H(31)	0.9900
C(9)-C(13)	1.511(4)	C(32)-C(33)	1.450(4)
C(10)-C(12)	1.515(5)	C(32)-H(32)	0.9900
C(10)-C(11)	1.518(5)	C(34)-C(35)	1.476(4)
C(10)-H(10)	0.9900	C(34)-H(34A)	0.9800
C(11)-H(11A)	0.9700	C(34)-H(34B)	0.9800
C(11)-H(11B)	0.9700	C(35)-H(35A)	0.9700
C(11)-H(11C)	0.9700	C(35)-H(35B)	0.9700
C(12)-H(12A)	0.9700	C(35)-H(35C)	0.9700
C(12)-H(12B)	0.9700	C(36)-C(37)	1.418(4)
C(12)-H(12C)	0.9700	C(36)-H(36A)	0.9800
C(13)-C(15)	1.519(4)	C(36)-H(36B)	0.9800
C(13)-C(14)	1.525(4)	C(37)-H(37A)	0.9700
C(13)-H(13)	0.9900	C(37)-H(37B)	0.9700
C(14)-H(14A)	0.9700	C(37)-H(37C)	0.9700
C(14)-H(14B)	0.9700		
C(14)-H(14C)	0.9700	C(1)-Ni(1)-C(32)	155.78(11)
C(15)-H(15A)	0.9700	C(1)-Ni(1)-C(31)	113.39(11)

C(32)-Ni(1)-C(31)	42.69(11)	H(11A)-C(11)-H(11B)	109.5
C(1)-Ni(1)-P(1)	96.78(7)	C(10)-C(11)-H(11C)	109.5
C(32)-Ni(1)-P(1)	107.35(8)	H(11A)-C(11)-H(11C)	109.5
C(31)-Ni(1)-P(1)	147.23(8)	H(11B)-C(11)-H(11C)	109.5
C(18)-P(1)-C(24)	102.10(12)	C(10)-C(12)-H(12A)	109.5
C(18)-P(1)-C(17)	103.80(12)	C(10)-C(12)-H(12B)	109.5
C(24)-P(1)-C(17)	100.47(11)	H(12A)-C(12)-H(12B)	109.5
C(18)-P(1)-Ni(1)	125.04(8)	C(10)-C(12)-H(12C)	109.5
C(24)-P(1)-Ni(1)	112.12(8)	H(12A)-C(12)-H(12C)	109.5
C(17)-P(1)-Ni(1)	110.31(9)	H(12B)-C(12)-H(12C)	109.5
C(30)-O(2)-C(34)	116.9(2)	C(9)-C(13)-C(15)	113.6(2)
C(33)-O(4)-C(36)	116.2(3)	C(9)-C(13)-C(14)	110.8(2)
C(1)-N(1)-C(3)	111.4(2)	C(15)-C(13)-C(14)	107.7(2)
C(1)-N(1)-C(4)	123.5(2)	C(9)-C(13)-H(13)	108.2
C(3)-N(1)-C(4)	124.1(2)	C(15)-C(13)-H(13)	108.2
C(1)-N(2)-C(2)	111.5(2)	C(14)-C(13)-H(13)	108.2
C(1)-N(2)-C(16)	123.8(2)	C(13)-C(14)-H(14A)	109.5
C(2)-N(2)-C(16)	123.8(2)	C(13)-C(14)-H(14B)	109.5
N(1)-C(1)-N(2)	103.2(2)	H(14A)-C(14)-H(14B)	109.5
N(1)-C(1)-Ni(1)	130.46(18)	C(13)-C(14)-H(14C)	109.5
N(2)-C(1)-Ni(1)	125.80(18)	H(14A)-C(14)-H(14C)	109.5
C(3)-C(2)-N(2)	106.8(2)	H(14B)-C(14)-H(14C)	109.5
C(3)-C(2)-H(2)	126.6	C(13)-C(15)-H(15A)	109.5
N(2)-C(2)-H(2)	126.6	C(13)-C(15)-H(15B)	109.5
C(2)-C(3)-N(1)	107.0(2)	H(15A)-C(15)-H(15B)	109.5
C(2)-C(3)-H(3)	126.5	C(13)-C(15)-H(15C)	109.5
N(1)-C(3)-H(3)	126.5	H(15A)-C(15)-H(15C)	109.5
C(5)-C(4)-C(9)	123.1(2)	H(15B)-C(15)-H(15C)	109.5
C(5)-C(4)-N(1)	117.5(2)	N(2)-C(16)-C(17)	110.2(2)
C(9)-C(4)-N(1)	119.4(2)	N(2)-C(16)-H(16A)	109.6
C(6)-C(5)-C(4)	117.0(3)	C(17)-C(16)-H(16A)	109.6
C(6)-C(5)-C(10)	119.8(3)	N(2)-C(16)-H(16B)	109.6
C(4)-C(5)-C(10)	123.1(3)	C(17)-C(16)-H(16B)	109.6
C(7)-C(6)-C(5)	121.3(3)	H(16A)-C(16)-H(16B)	108.1
C(7)-C(6)-H(6)	119.3	C(16)-C(17)-P(1)	110.29(17)
C(5)-C(6)-H(6)	119.3	C(16)-C(17)-H(17A)	109.6
C(8)-C(7)-C(6)	120.2(3)	P(1)-C(17)-H(17A)	109.6
C(8)-C(7)-H(7)	119.9	C(16)-C(17)-H(17B)	109.6
C(6)-C(7)-H(7)	119.9	P(1)-C(17)-H(17B)	109.6
C(7)-C(8)-C(9)	121.7(3)	H(17A)-C(17)-H(17B)	108.1
C(7)-C(8)-H(8)	119.2	C(23)-C(18)-C(19)	118.2(2)
C(9)-C(8)-H(8)	119.2	C(23)-C(18)-P(1)	117.67(19)
C(8)-C(9)-C(4)	116.6(3)	C(19)-C(18)-P(1)	124.1(2)
C(8)-C(9)-C(13)	121.2(3)	C(20)-C(19)-C(18)	120.2(3)
C(4)-C(9)-C(13)	122.2(2)	C(20)-C(19)-H(19)	119.9
C(5)-C(10)-C(12)	112.0(3)	C(18)-C(19)-H(19)	119.9
C(5)-C(10)-C(11)	109.8(3)	C(21)-C(20)-C(19)	120.7(3)
C(12)-C(10)-C(11)	111.5(3)	C(21)-C(20)-H(20)	119.6
C(5)-C(10)-H(10)	107.7	C(19)-C(20)-H(20)	119.6
C(12)-C(10)-H(10)	107.7	C(20)-C(21)-C(22)	120.1(3)
C(11)-C(10)-H(10)	107.7	C(20)-C(21)-H(21)	120.0
C(10)-C(11)-H(11A)	109.5	C(22)-C(21)-H(21)	120.0
C(10)-C(11)-H(11B)	109.5	C(23)-C(22)-C(21)	119.9(3)

C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
C(22)-C(23)-C(18)	121.0(3)
C(22)-C(23)-H(23)	119.5
C(18)-C(23)-H(23)	119.5
C(25)-C(24)-C(29)	119.1(2)
C(25)-C(24)-P(1)	122.32(19)
C(29)-C(24)-P(1)	118.5(2)
C(24)-C(25)-C(26)	120.9(3)
C(24)-C(25)-H(25)	119.6
C(26)-C(25)-H(25)	119.6
C(27)-C(26)-C(25)	119.4(3)
C(27)-C(26)-H(26)	120.3
C(25)-C(26)-H(26)	120.3
C(28)-C(27)-C(26)	120.1(3)
C(28)-C(27)-H(27)	119.9
C(26)-C(27)-H(27)	119.9
C(27)-C(28)-C(29)	120.6(3)
C(27)-C(28)-H(28)	119.7
C(29)-C(28)-H(28)	119.7
C(24)-C(29)-C(28)	119.9(3)
C(24)-C(29)-H(29)	120.1
C(28)-C(29)-H(29)	120.1
O(1)-C(30)-O(2)	122.1(2)
O(1)-C(30)-C(31)	126.0(2)
O(2)-C(30)-C(31)	111.9(2)
C(32)-C(31)-C(30)	117.4(2)
C(32)-C(31)-Ni(1)	68.21(13)
C(30)-C(31)-Ni(1)	111.92(17)
C(32)-C(31)-H(31)	116.7
C(30)-C(31)-H(31)	116.7
Ni(1)-C(31)-H(31)	116.7
C(31)-C(32)-C(33)	122.2(2)
C(31)-C(32)-Ni(1)	69.10(14)
C(33)-C(32)-Ni(1)	113.90(19)
C(31)-C(32)-H(32)	114.6
C(33)-C(32)-H(32)	114.6
Ni(1)-C(32)-H(32)	114.6
O(3)-C(33)-O(4)	121.0(3)
O(3)-C(33)-C(32)	126.1(3)
O(4)-C(33)-C(32)	112.9(3)
O(2)-C(34)-C(35)	111.6(2)
O(2)-C(34)-H(34A)	109.3
C(35)-C(34)-H(34A)	109.3
O(2)-C(34)-H(34B)	109.3
C(35)-C(34)-H(34B)	109.3
H(34A)-C(34)-H(34B)	108.0
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
O(4)-C(36)-C(37)	111.3(4)
O(4)-C(36)-H(36A)	109.4
C(37)-C(36)-H(36A)	109.4
O(4)-C(36)-H(36B)	109.4
C(37)-C(36)-H(36B)	109.4
H(36A)-C(36)-H(36B)	108.0
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	19(1)	38(1)	27(1)	-1(1)	-2(1)	-4(1)
P(1)	21(1)	38(1)	28(1)	-3(1)	-2(1)	-4(1)
O(1)	49(1)	52(1)	35(1)	2(1)	-3(1)	-3(1)
O(2)	35(1)	49(1)	35(1)	-6(1)	0(1)	-1(1)
O(3)	46(1)	76(2)	81(2)	-34(1)	-16(1)	-13(1)
O(4)	87(2)	84(2)	42(1)	-13(1)	-24(1)	7(1)
N(1)	28(1)	36(1)	33(1)	-2(1)	-5(1)	-3(1)
N(2)	26(1)	36(1)	32(1)	-4(1)	-7(1)	-4(1)
C(1)	25(1)	38(1)	22(1)	-3(1)	1(1)	-2(1)
C(2)	31(1)	42(2)	50(2)	-7(1)	-9(1)	-11(1)
C(3)	36(2)	36(2)	57(2)	0(1)	-7(1)	-11(1)
C(4)	36(2)	36(2)	33(1)	2(1)	-7(1)	-3(1)
C(5)	52(2)	49(2)	34(2)	-1(1)	-4(1)	4(1)
C(6)	76(2)	80(3)	36(2)	-13(2)	-18(2)	20(2)
C(7)	75(3)	89(3)	52(2)	-15(2)	-35(2)	30(2)
C(8)	54(2)	65(2)	50(2)	-9(2)	-19(2)	18(2)
C(9)	36(2)	40(2)	39(2)	0(1)	-7(1)	-2(1)
C(10)	55(2)	69(2)	34(2)	-6(1)	2(1)	7(2)
C(11)	83(3)	118(4)	79(3)	24(3)	29(2)	9(3)
C(12)	80(3)	79(3)	81(3)	-28(2)	-8(2)	14(2)
C(13)	37(2)	41(2)	37(1)	-2(1)	-3(1)	1(1)
C(14)	49(2)	53(2)	58(2)	-14(2)	-1(2)	-7(2)
C(15)	45(2)	51(2)	54(2)	-8(2)	4(1)	-4(1)
C(16)	28(1)	41(2)	37(1)	0(1)	-12(1)	-5(1)
C(17)	22(1)	38(2)	42(1)	0(1)	-7(1)	-3(1)
C(18)	30(1)	40(2)	26(1)	0(1)	-2(1)	-2(1)
C(19)	31(1)	53(2)	37(1)	-4(1)	-1(1)	-1(1)
C(20)	43(2)	74(2)	40(2)	-11(2)	8(1)	4(2)
C(21)	69(2)	84(3)	38(2)	-24(2)	-4(2)	4(2)
C(22)	63(2)	87(3)	46(2)	-26(2)	-14(2)	-7(2)
C(23)	38(2)	65(2)	38(2)	-12(1)	-4(1)	-6(1)
C(24)	25(1)	39(2)	29(1)	-1(1)	-6(1)	-9(1)
C(25)	35(1)	41(2)	34(1)	-4(1)	-6(1)	-8(1)
C(26)	56(2)	40(2)	44(2)	2(1)	-16(1)	-12(1)
C(27)	52(2)	59(2)	36(2)	9(1)	-13(1)	-27(2)
C(28)	39(2)	70(2)	30(1)	0(1)	0(1)	-17(2)
C(29)	30(1)	51(2)	34(1)	-5(1)	-2(1)	-5(1)
C(30)	21(1)	44(2)	37(1)	-2(1)	-1(1)	-11(1)
C(31)	21(1)	41(2)	33(1)	1(1)	-4(1)	-3(1)
C(32)	22(1)	45(2)	39(1)	-2(1)	-4(1)	-8(1)
C(33)	24(1)	62(2)	51(2)	-15(2)	-5(1)	0(1)
C(34)	45(2)	51(2)	38(2)	-12(1)	-1(1)	-7(1)
C(35)	47(2)	72(2)	51(2)	-17(2)	8(1)	-20(2)
C(36)	112(3)	123(3)	60(2)	-24(2)	-32(2)	13(2)
C(37)	151(4)	175(5)	100(3)	-25(3)	-75(3)	28(4)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2b**. .

	x	y	z	U(eq)
H(2)	8824	2875	3203	48
H(3)	7130	4312	2414	51
H(6)	3865	3349	398	80
H(7)	1563	4573	811	89
H(8)	1122	5152	2006	70
H(10)	7008	2158	1473	67
H(11A)	6519	3267	26	154
H(11B)	8147	2546	245	154
H(11C)	7388	3800	593	154
H(12A)	5463	714	1257	123
H(12B)	7069	594	730	123
H(12C)	5509	1263	415	123
H(13)	3300	3973	3469	48
H(14A)	4844	5485	2998	80
H(14B)	3600	5970	3662	80
H(14C)	3326	6436	2829	80
H(15A)	781	5853	3120	77
H(15B)	1063	5216	3923	77
H(15C)	572	4459	3331	77
H(16A)	7210	309	4067	42
H(16B)	8866	711	3820	42
H(17A)	9031	-1136	3316	41
H(17B)	8883	-115	2634	41
H(19)	9542	-1813	1995	50
H(20)	10220	-3021	999	66
H(21)	8360	-3830	532	78
H(22)	5772	-3433	1050	76
H(23)	5052	-2178	2018	56
H(25)	7781	-3564	3218	44
H(26)	7540	-5013	4234	55
H(27)	5989	-4430	5322	56
H(28)	4670	-2435	5384	55
H(29)	4808	-1009	4351	46
H(31)	1807	1725	2882	39
H(32)	2568	-789	3436	42
H(34A)	476	3533	4940	54
H(34B)	1402	2229	5211	54
H(35A)	-1701	2630	4892	84
H(35B)	-1199	2429	5705	84
H(35C)	-775	1337	5179	84
H(36A)	2010	-619	1068	119
H(36B)	2974	431	717	119
H(37A)	-212	761	1146	214
H(37B)	624	832	317	214
H(37C)	725	1849	848	214

Table S7. Torsion angles [°] for **2b**.

C(3)-N(1)-C(1)-N(2)	2.6(3)
C(4)-N(1)-C(1)-N(2)	171.5(2)
C(3)-N(1)-C(1)-Ni(1)	-169.00(19)
C(4)-N(1)-C(1)-Ni(1)	-0.1(3)
C(2)-N(2)-C(1)-N(1)	-2.1(3)
C(16)-N(2)-C(1)-N(1)	-171.5(2)
C(2)-N(2)-C(1)-Ni(1)	169.97(18)
C(16)-N(2)-C(1)-Ni(1)	0.6(3)
C(32)-Ni(1)-C(1)-N(1)	-47.5(4)
C(31)-Ni(1)-C(1)-N(1)	-55.4(2)
P(1)-Ni(1)-C(1)-N(1)	137.7(2)
C(32)-Ni(1)-C(1)-N(2)	142.6(2)
C(31)-Ni(1)-C(1)-N(2)	134.7(2)
P(1)-Ni(1)-C(1)-N(2)	-32.2(2)
C(1)-N(2)-C(2)-C(3)	0.9(3)
C(16)-N(2)-C(2)-C(3)	170.3(2)
N(2)-C(2)-C(3)-N(1)	0.7(3)
C(1)-N(1)-C(3)-C(2)	-2.1(3)
C(4)-N(1)-C(3)-C(2)	-171.0(2)
C(1)-N(1)-C(4)-C(5)	-82.8(3)
C(3)-N(1)-C(4)-C(5)	84.7(3)
C(1)-N(1)-C(4)-C(9)	98.5(3)
C(3)-N(1)-C(4)-C(9)	-94.0(3)
C(9)-C(4)-C(5)-C(6)	-2.6(5)
N(1)-C(4)-C(5)-C(6)	178.7(3)
C(9)-C(4)-C(5)-C(10)	176.8(3)
N(1)-C(4)-C(5)-C(10)	-1.9(4)
C(4)-C(5)-C(6)-C(7)	0.7(6)
C(10)-C(5)-C(6)-C(7)	-178.8(4)
C(5)-C(6)-C(7)-C(8)	1.0(7)
C(6)-C(7)-C(8)-C(9)	-0.9(6)
C(7)-C(8)-C(9)-C(4)	-0.9(5)
C(7)-C(8)-C(9)-C(13)	176.8(3)
C(5)-C(4)-C(9)-C(8)	2.7(4)
N(1)-C(4)-C(9)-C(8)	-178.6(3)
C(5)-C(4)-C(9)-C(13)	-175.0(3)

N(1)-C(4)-C(9)-C(13)	3.7(4)
C(6)-C(5)-C(10)-C(12)	-64.6(4)
C(4)-C(5)-C(10)-C(12)	115.9(4)
C(6)-C(5)-C(10)-C(11)	59.9(5)
C(4)-C(5)-C(10)-C(11)	-119.5(4)
C(8)-C(9)-C(13)-C(15)	23.8(4)
C(4)-C(9)-C(13)-C(15)	-158.6(3)
C(8)-C(9)-C(13)-C(14)	-97.6(3)
C(4)-C(9)-C(13)-C(14)	80.0(3)
C(1)-N(2)-C(16)-C(17)	60.2(3)
C(2)-N(2)-C(16)-C(17)	-107.9(3)
N(2)-C(16)-C(17)-P(1)	-71.5(2)
C(18)-P(1)-C(17)-C(16)	167.70(18)
C(24)-P(1)-C(17)-C(16)	-86.94(19)
Ni(1)-P(1)-C(17)-C(16)	31.5(2)
C(24)-P(1)-C(18)-C(23)	78.0(2)
C(17)-P(1)-C(18)-C(23)	-177.8(2)
Ni(1)-P(1)-C(18)-C(23)	-50.3(2)
C(24)-P(1)-C(18)-C(19)	-100.3(2)
C(17)-P(1)-C(18)-C(19)	3.8(3)
Ni(1)-P(1)-C(18)-C(19)	131.3(2)
C(23)-C(18)-C(19)-C(20)	0.3(4)
P(1)-C(18)-C(19)-C(20)	178.7(2)
C(18)-C(19)-C(20)-C(21)	-0.8(5)
C(19)-C(20)-C(21)-C(22)	0.3(6)
C(20)-C(21)-C(22)-C(23)	0.8(6)
C(21)-C(22)-C(23)-C(18)	-1.4(5)
C(19)-C(18)-C(23)-C(22)	0.8(4)
P(1)-C(18)-C(23)-C(22)	-177.7(3)
C(18)-P(1)-C(24)-C(25)	23.6(2)
C(17)-P(1)-C(24)-C(25)	-83.2(2)
Ni(1)-P(1)-C(24)-C(25)	159.70(18)
C(18)-P(1)-C(24)-C(29)	-159.5(2)
C(17)-P(1)-C(24)-C(29)	93.8(2)
Ni(1)-P(1)-C(24)-C(29)	-23.4(2)
C(29)-C(24)-C(25)-C(26)	-0.1(4)
P(1)-C(24)-C(25)-C(26)	176.8(2)
C(24)-C(25)-C(26)-C(27)	-1.1(4)

C(25)-C(26)-C(27)-C(28)	0.6(4)
C(26)-C(27)-C(28)-C(29)	1.0(4)
C(25)-C(24)-C(29)-C(28)	1.7(4)
P(1)-C(24)-C(29)-C(28)	-175.3(2)
C(27)-C(28)-C(29)-C(24)	-2.2(4)
C(34)-O(2)-C(30)-O(1)	1.1(3)
C(34)-O(2)-C(30)-C(31)	178.9(2)
O(1)-C(30)-C(31)-C(32)	22.4(4)
O(2)-C(30)-C(31)-C(32)	-155.3(2)
O(1)-C(30)-C(31)-Ni(1)	-53.5(3)
O(2)-C(30)-C(31)-Ni(1)	128.77(18)
C(30)-C(31)-C(32)-C(33)	150.0(2)
Ni(1)-C(31)-C(32)-C(33)	-105.8(2)
C(30)-C(31)-C(32)-Ni(1)	-104.2(2)
C(36)-O(4)-C(33)-O(3)	-3.6(4)
C(36)-O(4)-C(33)-C(32)	175.6(3)
C(31)-C(32)-C(33)-O(3)	-158.7(3)
Ni(1)-C(32)-C(33)-O(3)	121.8(3)
C(31)-C(32)-C(33)-O(4)	22.1(4)
Ni(1)-C(32)-C(33)-O(4)	-57.4(3)
C(30)-O(2)-C(34)-C(35)	-88.7(3)
C(33)-O(4)-C(36)-C(37)	122.6(5)

Symmetry transformations used to generate equivalent atoms: