Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information For:

Versatile (η^6-arene)Ni(PCy_3) nickel monophosphine precursors

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S1: General Procedures

Experimental Details

All experiments were performed under an N_2 atmosphere using either standard Schlenk techniques or a glovebox. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and α,α,α-trifluorotoluene were purchased from Alfa Aesar and used as received. Anisole, mesitylene, hexamethyldisiloxane (HMDSO) and 1,3-bis(trifluoromethyl)benzene were purchased from Sigma Aldrich, deoxygenated by freeze-pump-thaw three times and dried by passing through a column of activated alumina. ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded on a Bruker AMX spectrometer operating at 500 MHz. All chemical shifts are recorded in parts per million, and all coupling constants are reported in hertz. ^{1}H NMR spectra were referenced to $(Me_3Si)_2O$ (δ 0.065)[1-3] with respect to tetramethylsilane at δ 0.00. ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4 at δ 0.00. ^{13}C{^{1}H} NMR spectra were referenced to solvent resonances ($(Me_3Si)_2O$, δ 1.94). ^{19}F{1H} NMR spectra were referenced to an external sample of 80% CCl_3F in $CDCl_3$ at δ 0.00. Elemental analyses were performed by the Center for Catalysis and Materials Research, Windsor, Ontario. Trimethylaluminum solution (2.0 M in toluene) was purchased from Sigma Aldrich and used as received. Nickel(II) acetylacetonate was purchased from Alfa Aesar. *N*-Methylmorpholine *N*-oxide (NMO) and tricyclohexylphosphine (PCy_3) was purchased from Oakwood Products, Inc. $Ni_2N_2(PCy_3)_4$ (**1**) was prepared according to the method of Jolly.[4] All of the solid compounds mentioned above were deoxygenated under vacuum before use.

S2: Synthesis, Characterization and NMR spectra

Synthesis and Characterization of $(Cy_3P)Ni(\eta^6\text{-}C_7H_8)$ (2a) To a stirring solution of $Ni_2N_2(PCy_3)_4$ (**1**) (2.00 g, 1.58 mmol) in 50 mL toluene, *N*-methylmorpholine *N*-oxide (NMO) (0.370 g, 3.16 mmol) was added over the course of 20 min. The solution turned from dark red to orange over the course of the addition. All volatiles were removed under vacuum and the remaining residue was dissolved in 50 mL of *n*-pentane. The mixture was filtered through Celite and the solution was cooled to –40 °C for 12 h. Tricyclohexylphosphine oxide ($O{=}PCy_3$) precipitated from solution as an off-white solid and was removed by cold filtration through Celite. The filtrate was dried under vacuum, and then redissolved in 5 mL pentane and filtered through Celite. Cooling to –40 °C for 12 h provided **2a** as orange crystals suitable for single crystal X-ray diffraction. The product was collected by filtration and dried under vacuum (yield 0.468 g, 34.4 %). ^{1}H NMR (HMDSO, 500 MHz, 298 K): δ 1.13-1.28 (m, 18H, $PCHCH_2C\mathit{H}_2C\mathit{H}_2$), 1.66-1.74 (m, 15H, $PC\mathit{H}C\mathit{H}_2CH_2CH_2$), 2.22 (s, 3H, $C_6H_5C\mathit{H}_3$), 5.75 (accidentally coincident s, 5H, $C_6\mathit{H}_5CH_3$). ^{31}P{^{1}H} NMR (HMDSO, 202.5 MHz, 298 K): δ 47.6 (s). ^{13}C{^{1}H} (HMDSO, 125.8 MHz, 298 K): δ 22.01 (s, $C_6H_5\mathit{C}H_3$), 27.15 (s, $PCHCH_2CH_2\mathit{C}H_2$), 28.10 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, $PCHCH_2\mathit{C}H_2$), 31.27 (d, $^{2}J_{C\text{-}P}$ = 5.7 Hz, $PCH\mathit{C}H_2$), 35.02 (d, $^{1}J_{C\text{-}P}$ = 17.6 Hz, P*C*H), 89.47 (s, *m*-toluene *C*), 89.97 (s, *p*-toluene *C*), 92.29 (s, *o*-toluene *C*), 102.00 (s, ipso-*C*CH_3). Anal. Calcd for $C_{25}H_{41}NiP$ (MW 431.26): C, 69.63; H, 9.58. Found: C, 69.68; H, 9.50.

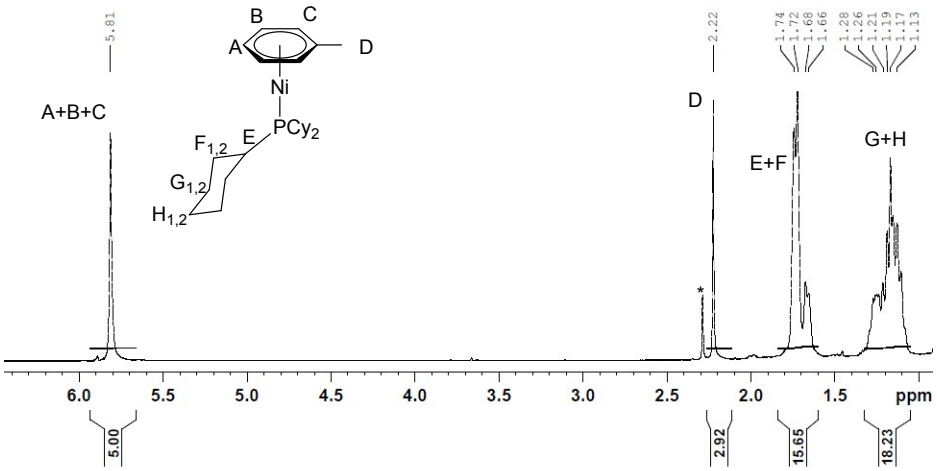

Figure S1. ^{1}H NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}C_7H_8)$ (**2a**) in $(Me_3Si)_2O$. *toluene impurity from slow decomposition of **2a**.

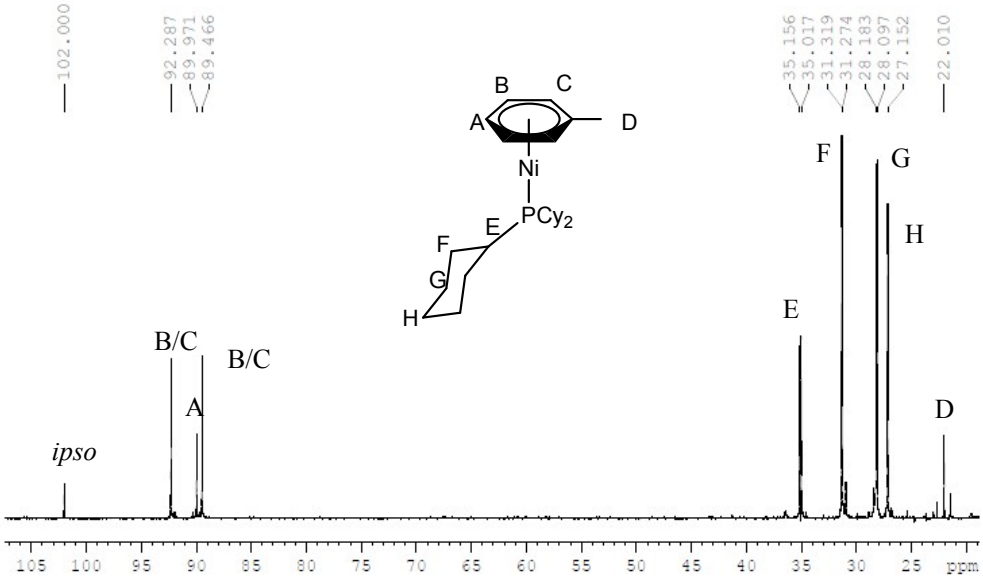

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}C_7H_8)$ (**2a**) in $(Me_3Si)_2O$.

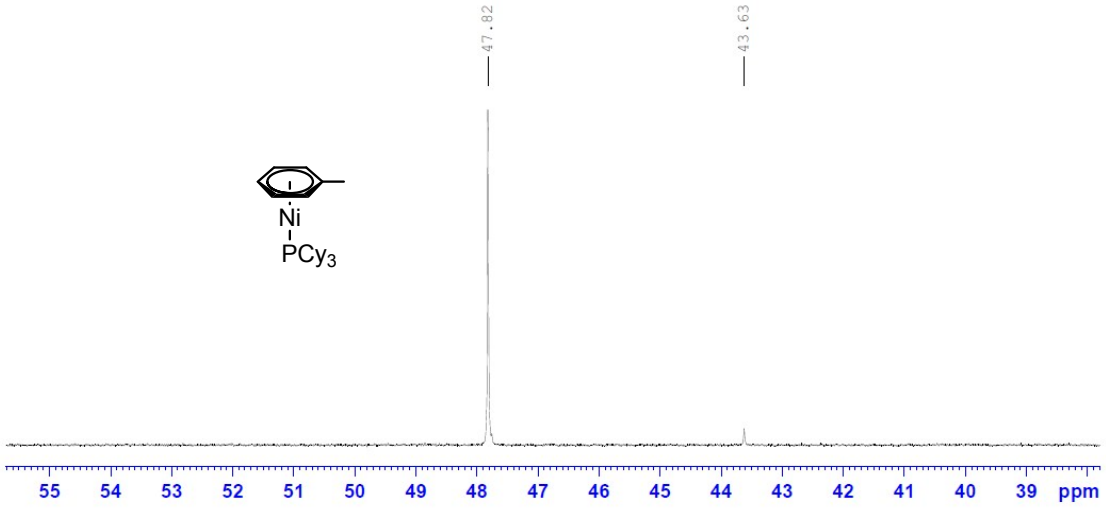

Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}C_7H_8)$ (**2a**) in $(Me_3Si)_2O$.

Synthesis and Characterization of $(Cy_3P)Ni(\eta^6\text{-}C_6H_6)$ (2b)

Complex **2a** (400 mg, 0.93 mmol) was dissolved in 15 mL of benzene. After 10 min of stirring, all volatiles were removed under vacuum. The remaining residue was dissolved in 10 mL of *n*-pentane and filtered through a plug of Celite, then cooled to –40 °C for 16 h. Yellow crystals of **2b** were isolated, washed with –40 °C *n*-pentane, and dried under vacuum (yield 117 mg, 30.2%). ^{1}H NMR (HMDSO, 500 MHz, 298 K): δ 1.10-1.28 (m, 18H, PCHCH$_2$C*H*$_2$C*H*$_2$), 1.57-1.82 (m, 15H, PC*H*C*H*$_2$), 5.85 (s, 6H, benzene-C*H*). $^{31}P\{^{1}H\}$ NMR (HMDSO, 202.5 MHz, 298 K): δ 46.5 (s). $^{13}C\{^{1}H\}$ (HMDSO, 125.8 MHz, 298K): δ 27.19 (s, PCHCH$_2$CH$_2$*C*H$_2$), 28.19 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, PCHCH$_2$*C*H$_2$), 31.37 (d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, PCH*C*H$_2$), 35.03 (d, $^{1}J_{C\text{-}P}$ = 18.2 Hz, P*C*H), 90.39 (s, benzene-*C*H). Anal. Calcd for $C_{25}H_{41}ONiP$ (MW 417.23): C, 69.09; H, 9.42. Found: C, 69.37; H, 9.56.

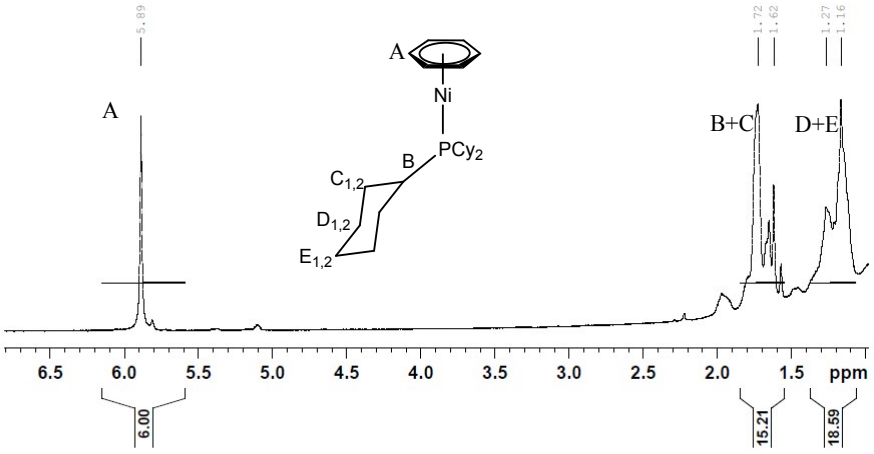

Figure S4. ^{1}H NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}C_6H_6)$ (**2b**) in $(Me_3Si)_2O$.

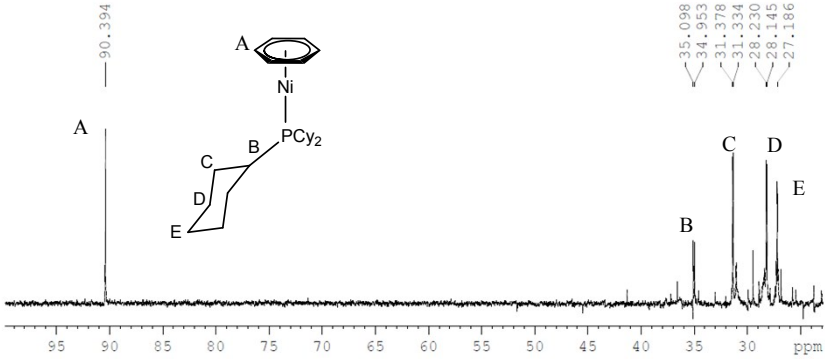

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}C_6H_6)$ (**2b**) in $(Me_3Si)_2O$.

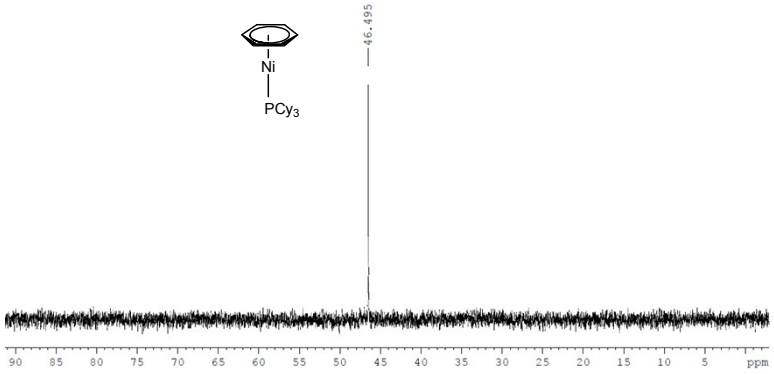

Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}C_6H_6)$ (**2b**) in $(Me_3Si)_2O$.

Synthesis and Characterization of $(Cy_3P)Ni(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)$ (**2c**). To a stirring solution of **1** (520 mg, 0.410 mmol) in 10 mL mesitylene and 5 mL pentane, *N*-methylmorpholine *N*-oxide (NMO) (96 mg, 0.821 mmol) was added over the course of 20 min. The solution was stirred for an additional 30 min, at which point all volatiles were removed. The residue was dissolved in 30 mL pentane and filtered the solution through Celite. The filtrate was cooled to –40 °C for 6 h, then filtered through Celite to remove $O{=}PCy_3$. The volume of solution was reduced to 2 mL under vacuum and filtered through a plug of Celite. The solution was then cooled to –40 °C for 16 h which yielded orange cubic crystals suitable for single crystal X-Ray diffraction. Crystals of **2c** were collected, washed with cold pentane and dried under vacuum (87 mg, yield 23.1 %). ^{1}H NMR (HMDSO, 500 MHz, 298 K): δ 1.08-1.26 (m, 18H, $PCHCH_2CH_2CH_2$), 1.65-1.73 (m, 15H, $PCHCH_2CH_2CH_2$), 2.17 (s, 9H, CCH_3), 5.63 (s, 3H, mesitylene *CH*). $^{31}P\{^{1}H\}$ NMR (HMDSO, 202.5 MHz, 298 K): δ 49.5 (s). $^{13}C\{^{1}H\}$ (HMDSO, 125.8 MHz, 298 K): δ 21.9 (s, CCH_3), 27.2 (s, $PCHCH_2CH_2CH_2$), 28.1 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, $PCHCH_2CH_2$), 31.3 (d, $^{2}J_{C\text{-}P}$ = 6.0 Hz, $PCHCH_2$), 35.3 (d, $^{1}J_{C\text{-}P}$ = 17 Hz, *PC*H), 94.2 (s, mesitylene *C*H), 100.2(s, mesitylene *C*CH). Anal. Calcd for $C_{25}H_{41}ONiP$ (MW 447.26): C, 67.13; H, 9.24. Found: C, 66.92; H, 9.27.

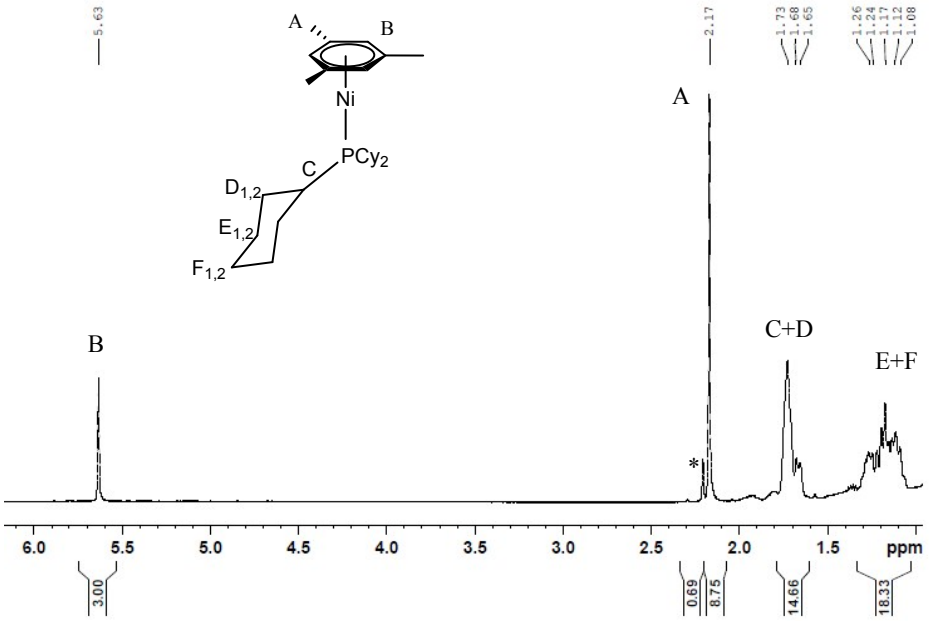

Figure S7. ^{1}H NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)$ (**2c**) in $(Me_3Si)_2O$. * mesitylene impurity from slow decomposition of **2c**

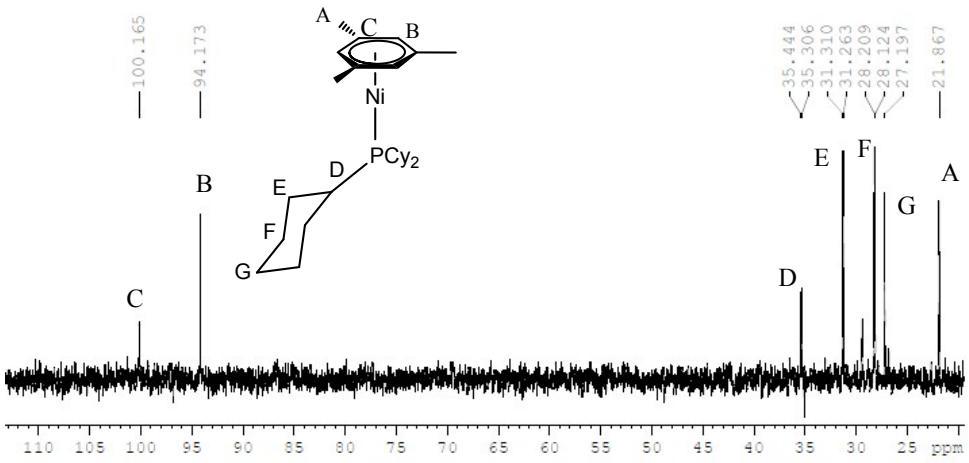

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)$ (**2c**) in $(Me_3Si)_2O$.

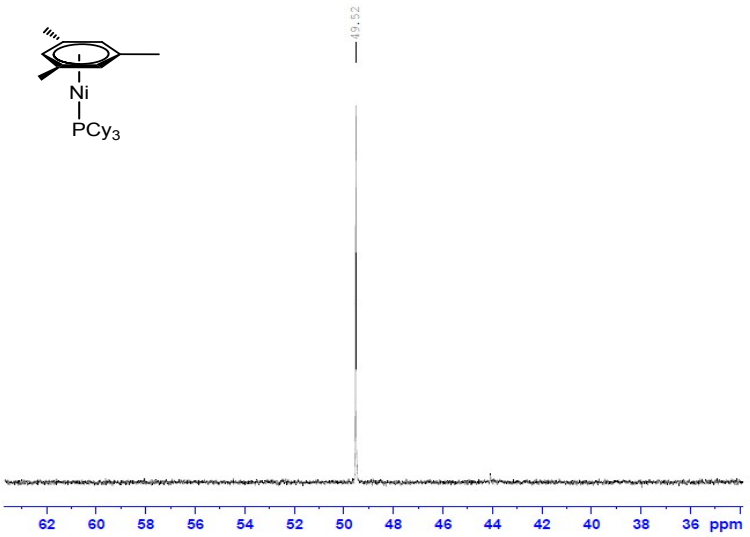

Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)$ (**2c**) in $(Me_3Si)_2O$.

Synthesis and Characterization of $(Cy_3P)Ni(\eta^6\text{-}CF_3C_6H_5)$ (2d). Complex **2a** (400 mg, 0.93 mmol) was dissolved in 15 mL of *α, α, α*-trifluorotoluene. After 10 min of stirring, the solution was evaporated under vacuum. The residue was dissolved in 6 mL of *n*-pentane, filtered through a plug of Celite, and cooled to –40 °C for 12 h. Dark yellow-orange crystals of **2d** precipitated. The crystals were collected and washed with cold pentane and dried under vacuum (121 mg, yield 26.9%). ^{1}H NMR (HMDSO, 500 MHz, 298 K): δ 1.13-1.20 (m, 18H, $PCHCH_2CH_2CH_2$), 1.70-1.73 (m, 15H, $PCHCH_2$), 6.02 (m, 3H, *m*- and *p*-trifluorotoluene H), 6.14 (m, 2H, *o*-trifluotoluene H). $^{31}P\{^{1}H\}$ NMR (HMDSO, 202.5 MHz, 298 K): δ 45.5 (s). $^{13}C\{^{1}H\}$ (HMDSO, 125.8 MHz, 298 K): δ 27.0 (s, $PCHCH_2CH_2CH_2$), 28.0 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, $PCHCH_2CH_2$), 31.1 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz, $PCHCH_2$), 34.5 (d, $^{1}J_{C\text{-}P}$ = 18 Hz, PCH), 86.1 (s), 89.4 (s), 89.7 (s). $^{19}F\{^{1}H\}$ (HMDSO, 470.6 MHz, 298 K): δ –61.05 (s). Anal. Calcd for $C_{25}H_{38}F_3NiP$ (MW 485.23): C, 61.88; H, 7.89. Found: C, 61.57; H, 8.21.

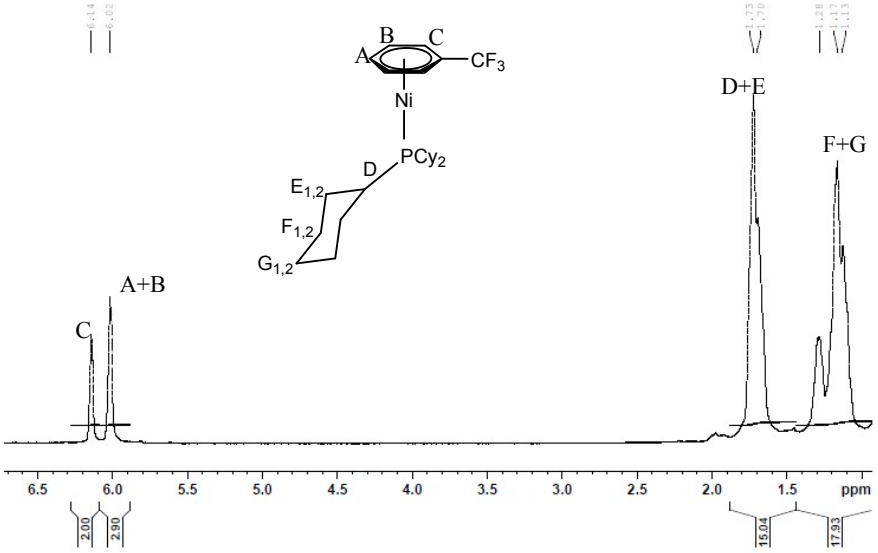

Figure S10. ^{1}H NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}CF_3C_6H_5)$ (**2d**) in $(Me_3Si)_2O$.

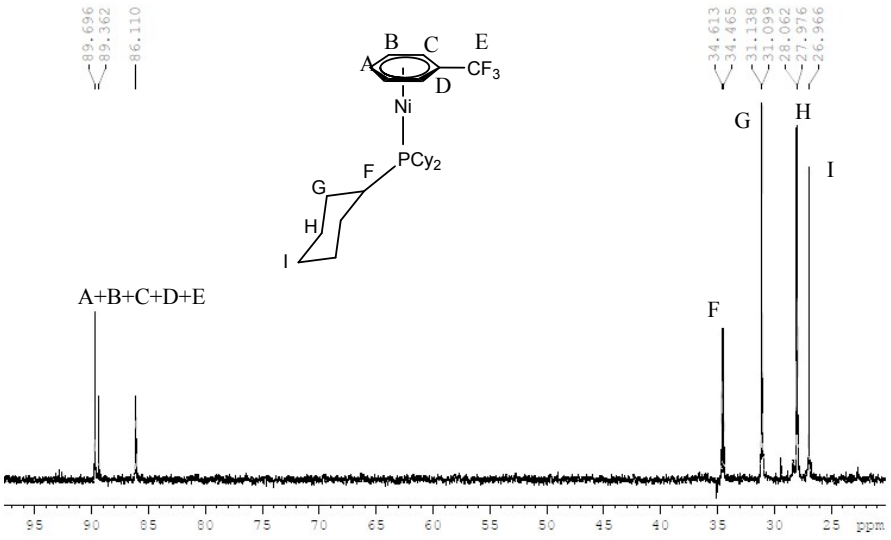

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}CF_3C_6H_5)$ (**2d**) in $(Me_3Si)_2O$.

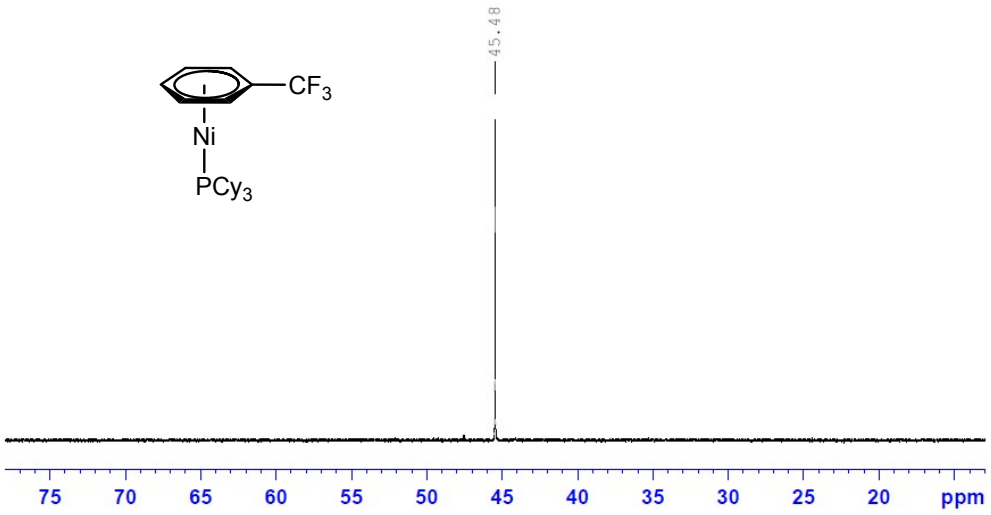

Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}CF_3C_6H_5)$ (**2d**) in $(Me_3Si)_2O$.

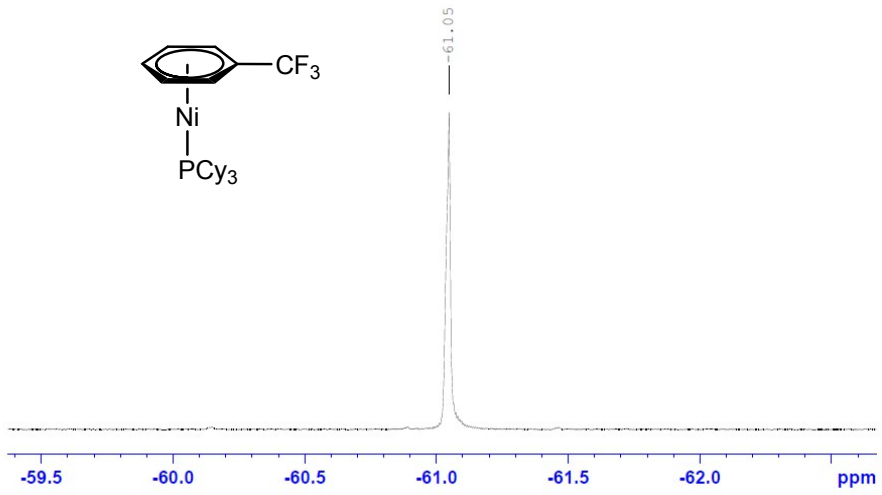

Figure S13. $^{19}F\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}CF_3C_6H_5)$ (**2d**) in $(Me_3Si)_2O$.

Synthesis and Characterization of $(Cy_3P)Ni[\eta^6\text{-}1,3\text{-}(CF_3)_2C_6H_4]$ (2e). Complex **2a** (400 mg, 0.93 mmol) was dissolved in 15 mL of 1,3-bis-(trifluoromethyl)benzene. After 10 min of stirring, all volatiles were removed under vacuum. The remaining residue was dissolved in 5 mL of *n*-pentane, filtered through a plug of Celite, and cooled to –40 °C for 16 h. Complex **2e** was isolated as orange-red crystals (142 mg, 27.7 %). ^{1}H NMR (HMDSO, 500 MHz, 298 K): δ 1.11-1.32 (m, 18H, $PCH_2CH_2CH_2CH_2$), 1.68-1.74 (m, 15H, $PCHCH_2$), 6.16 (m, 1H, CF_3CCHCH), 6.26 (m, 2H, $CF_3CCHCHCH$), 6.41 (1H, $CF_3CCHCCF_3$). $^{31}P\{^{1}H\}$ NMR (HMDSO, 202.5 MHz, 298 K): δ 43.1 (s). $^{13}C\{^{1}H\}$ (HMDSO, 125.8 MHz, 298K): δ 24.9 (s, 3C), 26.0 (d, $^{3}J_{C\text{-}P}$ = 10.8 Hz), 29.0 (d, $^{2}J_{C\text{-}P}$ = 4.2 Hz), 32.2 (d, $^{1}J_{C\text{-}P}$ = 19.6 Hz), 80.3 (s), 83.1 (s), 83.4 (s), 87.2 (s). $^{19}F\{^{1}H\}$ (HMDSO, 470.6 MHz, 298 K): δ -61.80 (s). Anal. Calcd for $C_{25}H_{38}F_3NiP$ (MW 553.23): C, 56.45; H, 6.74. Found: C, 56.53; H, 6.94.

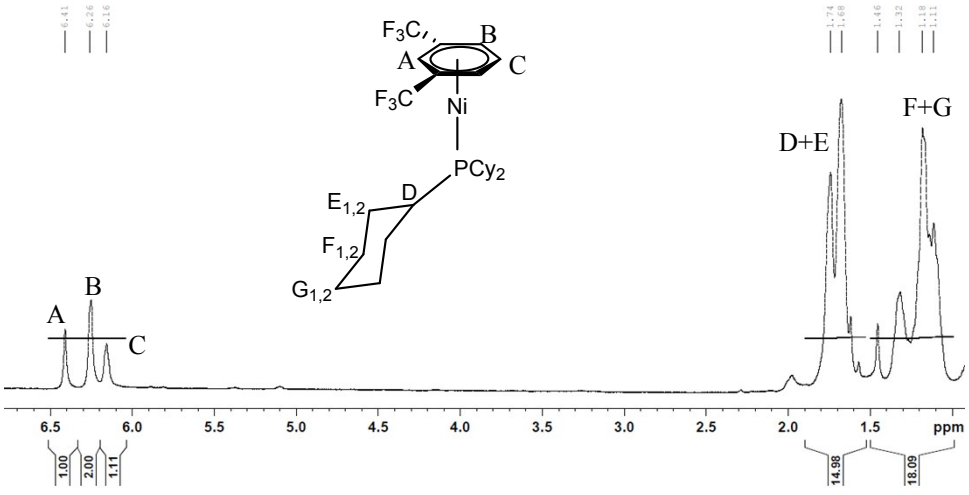

Figure S14. ^{1}H NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}1,3\text{-}(CF_3)C_6H_4)$ (**2e**) in $(Me_3Si)_2O$.

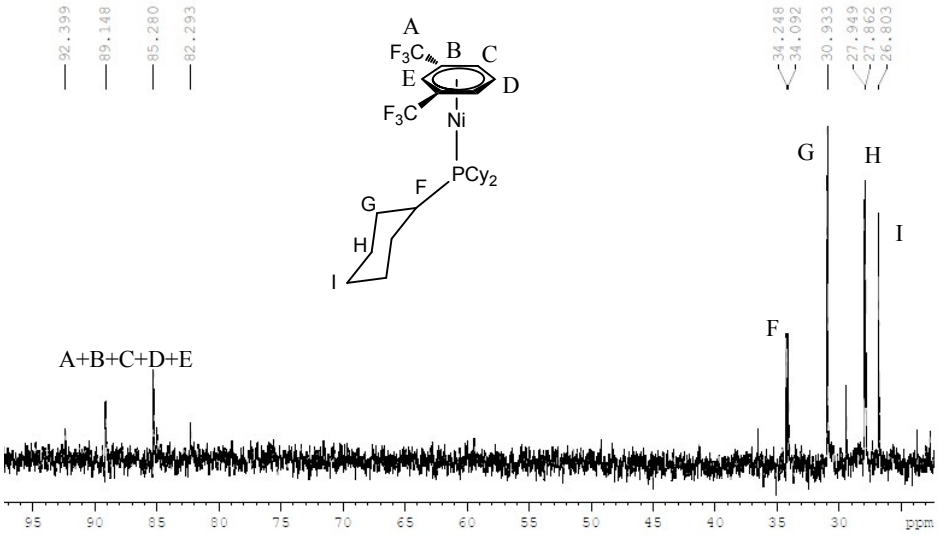

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}1,3\text{-}(CF_3)C_6H_4)$ (**2e**) in $(Me_3Si)_2O$.

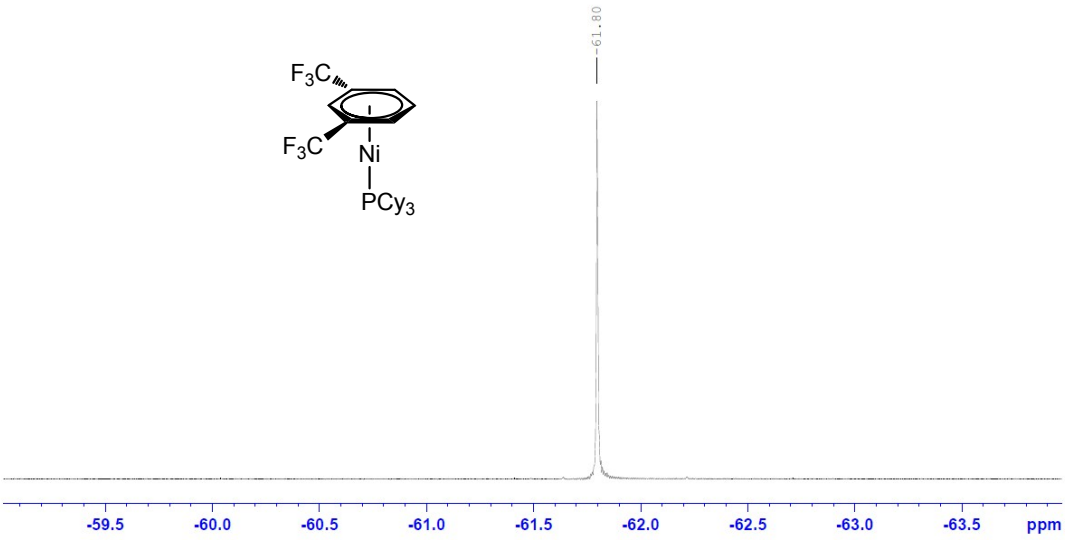

Figure S16. $^{19}F\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}1,3\text{-}(CF_3)C_6H_4)$ (**2e**) in $(Me_3Si)_2O$.

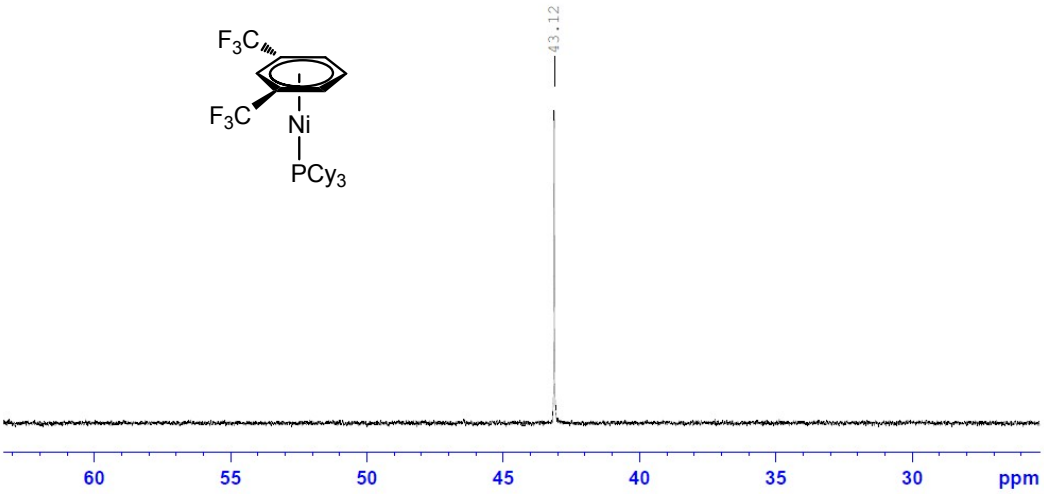

Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of $((Cy_3P)Ni(\eta^6\text{-}1,3\text{-}(CF_3)C_6H_4)$ (**2e**) in $(Me_3Si)_2O$.

Synthesis and Characterization of $(Cy_3P)Ni(\eta^6\text{-}MeOC_6H_5)$ (2f)

Complex **2a** (500 mg, 1.11 mmol) was dissolved in 15 mL of anisole. After 15 min of stirring, all volatiles were removed under vacuum. The remaining residue was dissolved in 5 mL of *n*-pentane, filtered through a plug of Celite, and cooled to –40 °C for 16 h. Complex **2f** was isolated as dark yellow-orange crystals and dried under vacuum (yield 0.129 g, 24.9%). ^{1}H NMR (HMDSO, 500 MHz, 298 K): δ 1.17-1.27 (m, 18H, $PCHCH_2CH_2CH_2$), 1.67-1.74 (m, 15H, $PCHCH_2$), 3.62 (s, 3H, OCH_3), 5.69 (m, 1H, *p*-anisole C*H*), 5.73 (m, 2H, *o*-anisole C*H*), 5.79 (m, 2H, *m*-anisole C*H*). $^{31}P\{^{1}H\}$ NMR (HMDSO, 202.5 MHz, 298 K): δ 48.3 (s). $^{13}C\{^{1}H\}$ (HMDSO, 125.8 MHz, 298K): δ 27.1 (s, $PCHCH_2CH_2CH_2$), 28.1 (d, $^{3}J_{C\text{-}P}$ = 11 Hz, $PCHCH_2CH_2$), 31.3(d, $^{2}J_{C\text{-}P}$ = 5.6 Hz, $PCHCH_2$), 35.1 (d, $^{1}J_{C\text{-}P}$ = 17.8 Hz, PCH), 54.6 (s, OCH_3), 80.9 (s, *m*-toluene *C*), 87.0 (s, *o*-toluene *C*), 88.5 (s, C, *p*-toluene *C*), 102.9 (s, $COCH_3$). Anal. Calcd for $C_{25}H_{41}ONiP$ (MW 447.26): C, 67.14; H, 9.24. Found: C, 66.92; H, 9.27.

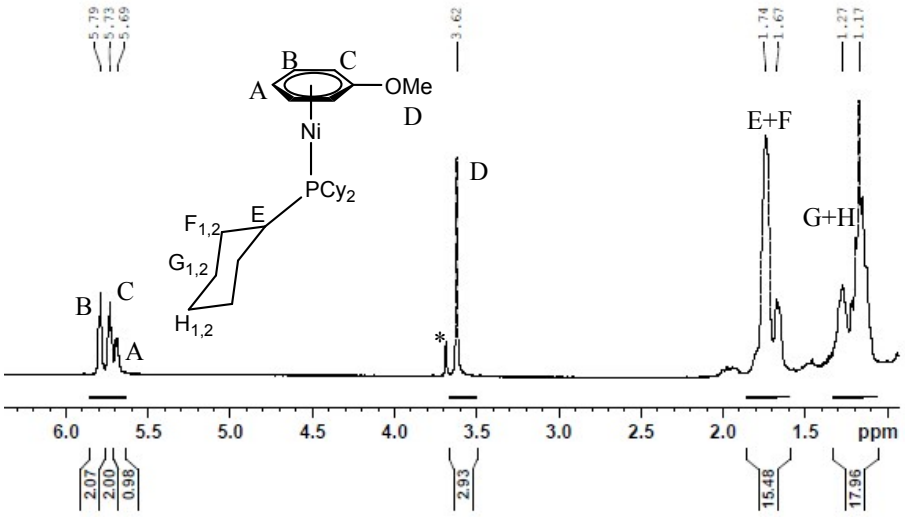

Figure S18. ^{1}H NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}MeOC_6H_5)$ (**2f**) in $(Me_3Si)_2O$. * anisole impurity from slow decomposition of **2f**.

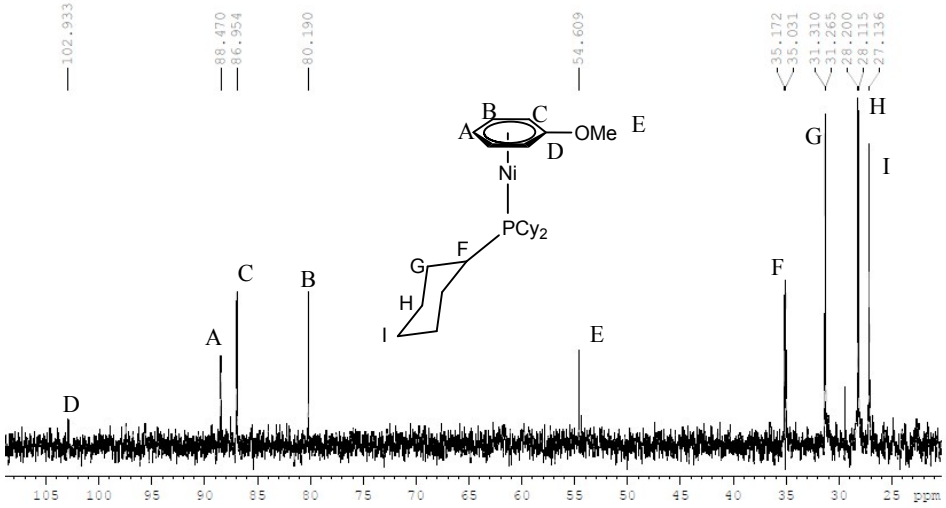

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}MeOC_6H_5)$ (**2f**) in $(Me_3Si)_2O$.

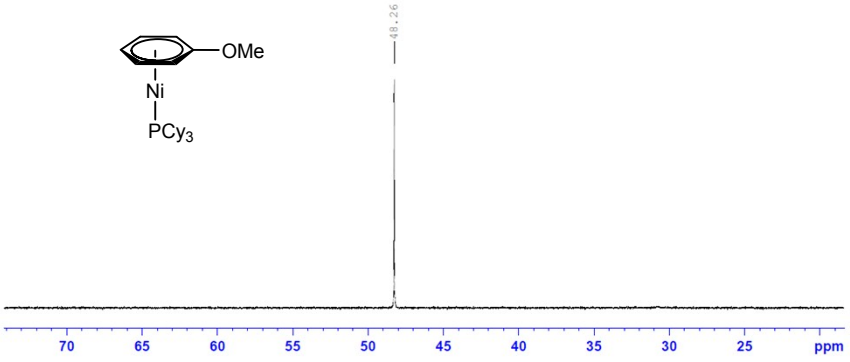

Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of $(Cy_3P)Ni(\eta^6\text{-}MeOC_6H_5)$ (**2f**) in $(Me_3Si)_2O$.

S3: Equilibrium Studies of **1 and 1-P^{i}Pr$_3$**

NMR scale reaction of $N_2[Ni(P^iPr_3)_2]_2$ (1-P^iPr_3) and toluene in the absence of NMO

1-P^iPr_3 was prepared according to the literature method[5]. 10 mg of **1**-P^iPr_3 (0.0127 mmol) was dissolved in 0.6 mL of pentane and only one singlet peak at δ 43.8 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum (Figure S21). When 10 mg of $N_2[Ni(P^iPr_3)_2]_2$ was dissolved in toluene (0.6 mL, 5.65 mmol) at room temperature, the resonance corresponding to P^iPr_3 (δ 19.8 ppm) and ($^iPr_3P$)Ni(C_7H_8) appear in the $^{31}P\{^1H\}$ NMR spectrum (Figure S22).

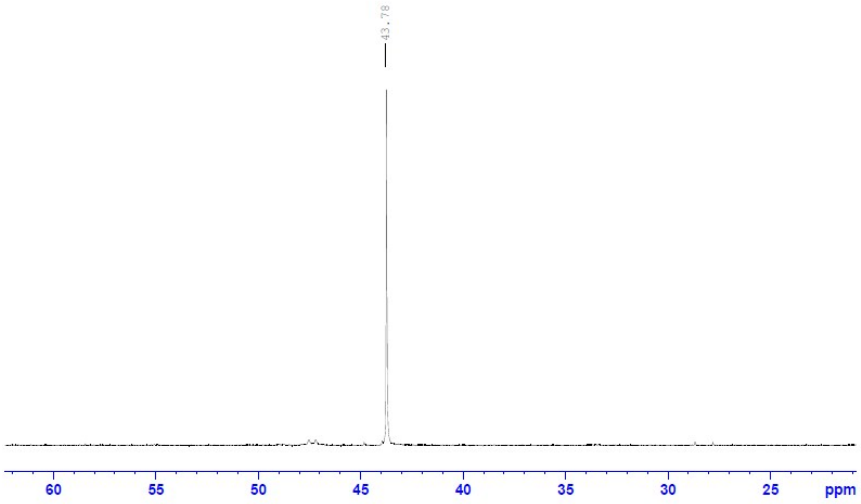

Figure S21. $^{31}P\{^1H\}$ NMR spectrum of [($^iPr_3P$)Ni]$_2N_2$ (**1-P^iPr_3**) in pentane.

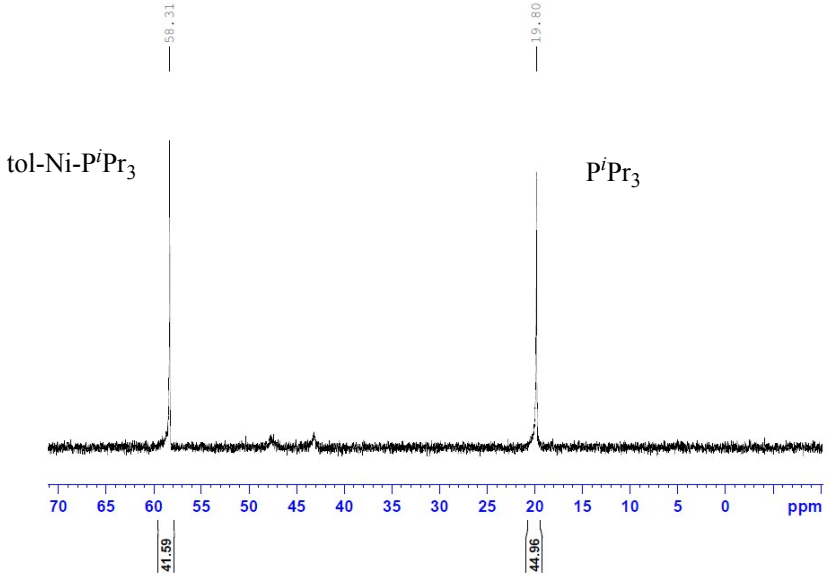

Figure 22. $^{31}P\{^1H\}$ NMR spectrum of **1-P^iPr_3** in toluene.

NMR scale reaction of 1 and toluene in the absence of NMO

A solution of **1** (10 mg, 0.00789 mmol) in 0.6 mL pentane was analyzed by $^{31}P\{^{1}H\}$ NMR and features one singlet resonance at δ 31.1 (Figure S23). When 10 mg of **1** was dissolved in 0.6 mL of toluene in a J. Young tube, two singlet resonances were observed at δ 46.5 and δ 10.3 (Figure S24) which correpsond to **2a** and PCy_3, respectively. Degassing the solution by three freeze-pump-thaw cycles did not affect these two resonances.

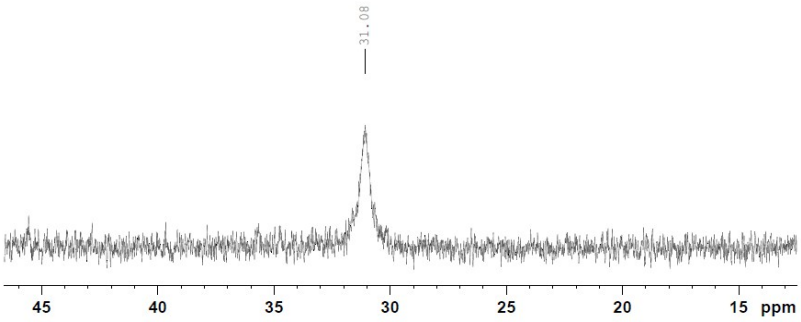

Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum of $Ni_2N_2(PCy_3)_4$ (**1**) in pentane.

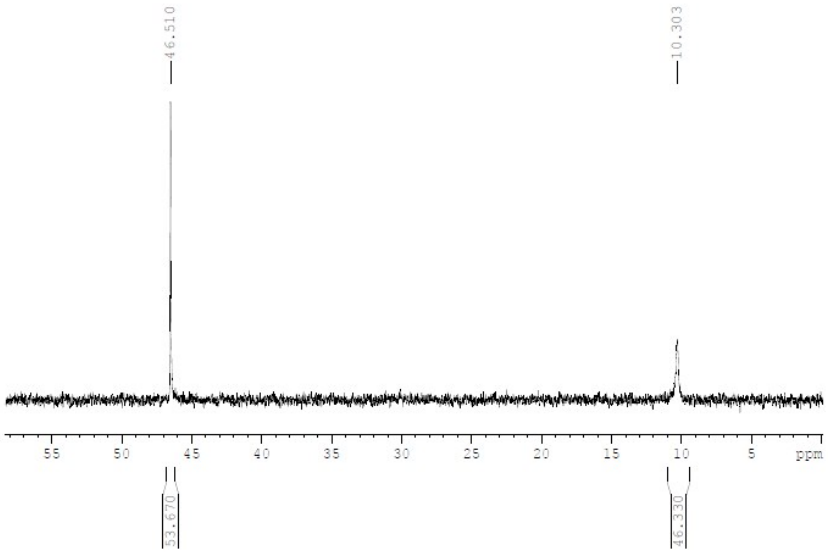

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of $Ni_2N_2(PCy_3)_4$ in toluene.

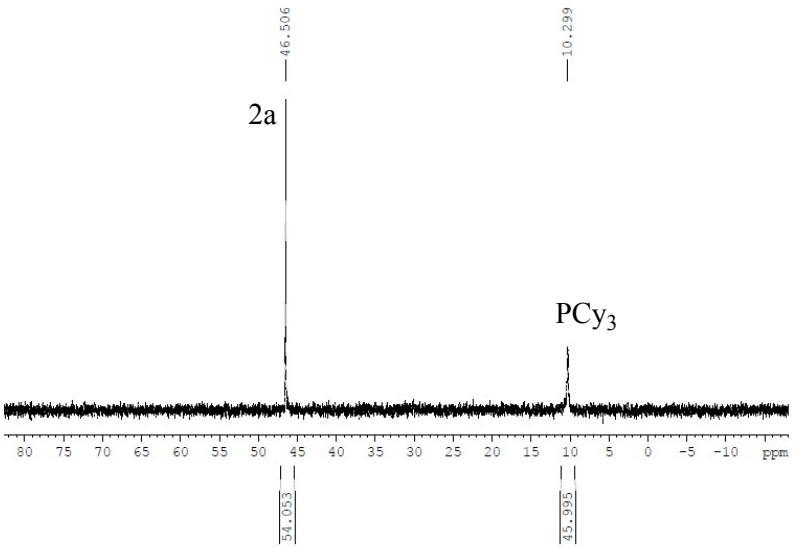

Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in toluene under vacuum.

NMR scale reaction of 2a and PCy_3 under 1 atm of N_2

6 mg (0.014 mmol) of **2a** and 4 mg (0.014 mmol) of PCy_3 was dissovled in pentane at room temperature under 1 atm N_2. The reaction reached equilibrium in 1 h. A resonance corresponding to **1** was observed at δ 31.0 as shown in Figure S26.

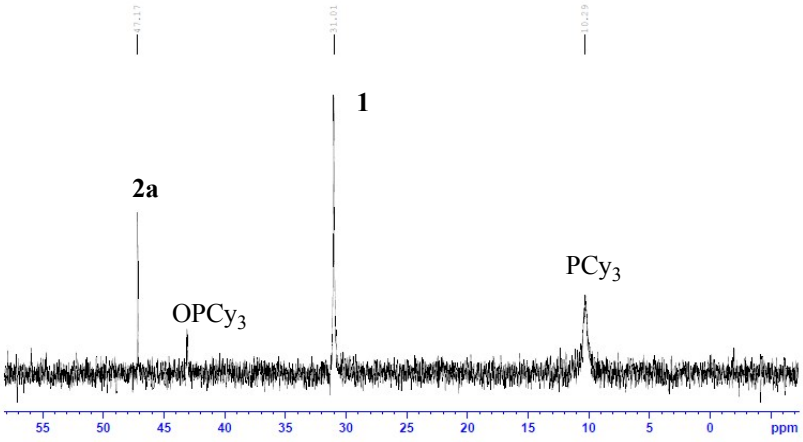

Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** and PCy_3 in pentane under 1 atm N_2.

Variable-temperature NMR of 1 in toluene

10 mg of **1** was fully dissolved in 0.6 mL toluene and $^{31}P\{^{1}H\}$ MMR data was collected at 283, 293, 293 and 303 K (Figure S27).

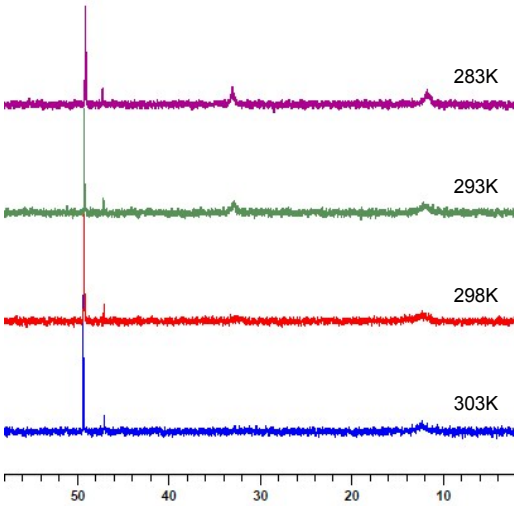

Figure S27. VT-NMR of **1** in toluene

Equilibrium between $N_2[Ni(PCy_3)_2]_2$ and $N_2Ni(PCy_3)_2$

A solution of **1** (10 mg, 0.023 mmol) was dissovled in 0.6 mL of THF and transferred to a J. Young NMR tube. A $^{31}P\{^1H\}$ NMR spectrum of the solution was collected at room temperature and featured a broad resonance ($W_{1/2}$ =121 Hz) at δ 30.6 ppm. The J. Young NMR tube was cooled in liquid nitrogen and the N_2 atmosphere was removed under vacuum. The $^{31}P\{^1H\}$ NMR spectrum was then recollected in the absence of N_2. A much sharper singlet ($W_{1/2}$= 15 Hz) was observed at δ 30.9 (Figure S28).

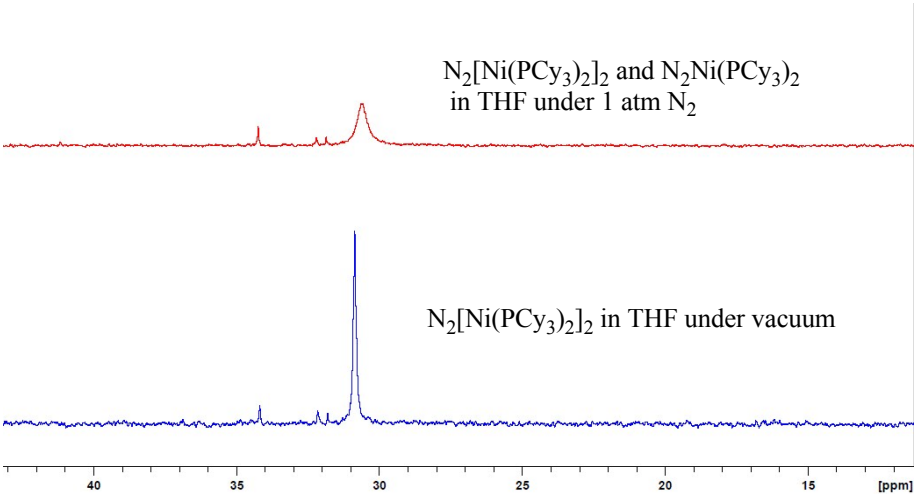

Figure S28. Equilibrium of **1** and $N_2Ni(PCy_3)_2$ in THF

Arene competition reactions with 2a

10 mg of **2a** (0.0232 mmol) was dissolved in a mixture of anisole (25.1 mg, 0.232 mmol), dimethylaniline (28.1 mg, 0.232 mmol), fluorobenzene (22.3 mg, 0.232 mmol) and *n*-pentane (0.60 mL) in an NMR tube. The reaction was monitored through $^{31}P\{^1H\}$ NMR at room temperature over a period of 6 h. The reaction reached equilibrium in 30 min. The spectrum was simulated using line-fitting in TopSpin 3.5pl7.

The ratio of **2a**, **2f**, (Cy_3P)Ni(η^6-C_6H_5F) (**2g**) and (Cy_3P)Ni(η^6-$Me_2NC_6H_5$) (**2h**) at equilibrium was 1:3.40:3.28:6.77 (Figure S29). In another experiment, 8 mg of **2a** was dissolved in a mixture of benzene (0.170 mL, 1.89 mmol), mesitylene (0.260 mL, 1.89 mmol) and toluene (0.200 mL, 1.89 mmol). The reaction was monitored through $^{31}P\{^1H\}$ NMR at room temperature over a period of 6 h and the reaction reached equilibrium in 30 min. The integral ratio of **2a**, **2b** and **2c** was 1:1.19:0.98, respectively (Figure S30). In a third experiment, a similar method as described above was used to compete **2a** (8 mg), with 0.200 mL toluene, 0.230 mL α, α, α trifluorotoluene (1.89 mmol) and 0.290 mL 1,3 bis(trifluoromethyl) benzene (1.89 mmol). The ratio of the integrals of these three analogues was determined to be 1:2:12 (Figure S31). The Gibbs free energy of the reaction was calculated using the equation $\Delta G = -RTlnK$ (R = 8.314 KJ/mol).

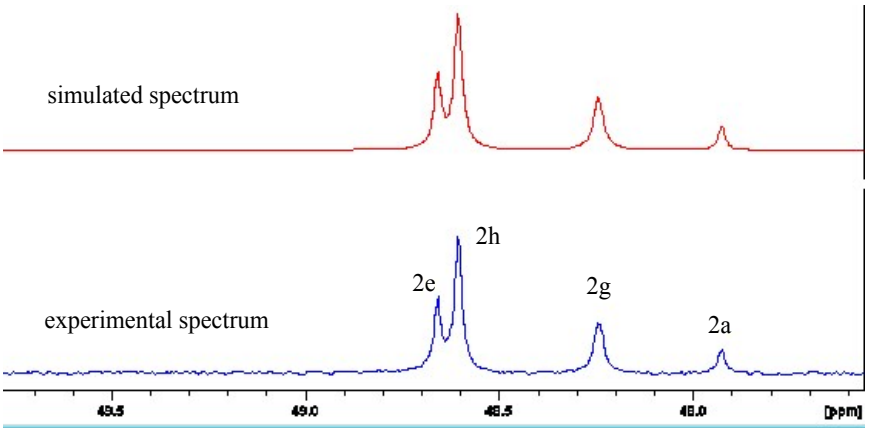

Figure S29. $^{31}P\{^1H\}$ NMR spectrum of competition of **2a** with toluene, anisole, and dimethylaniline

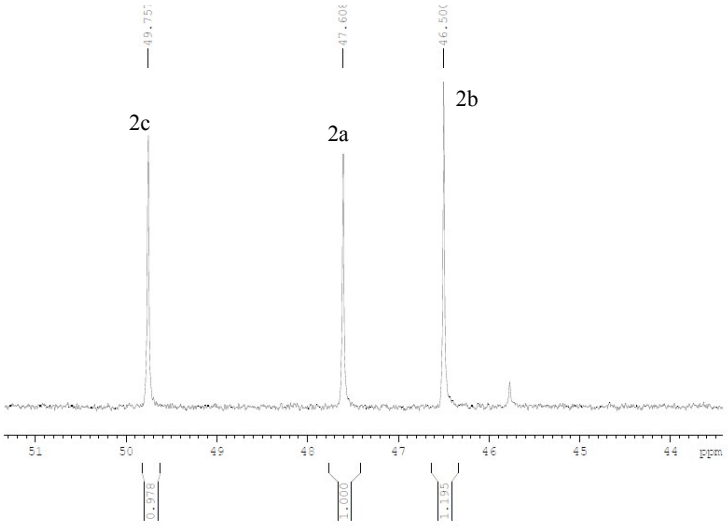

Figure S30. $^{31}P\{^1H\}$ NMR spectrum of competition of **2a** with toluene, mesitylene, and benzene

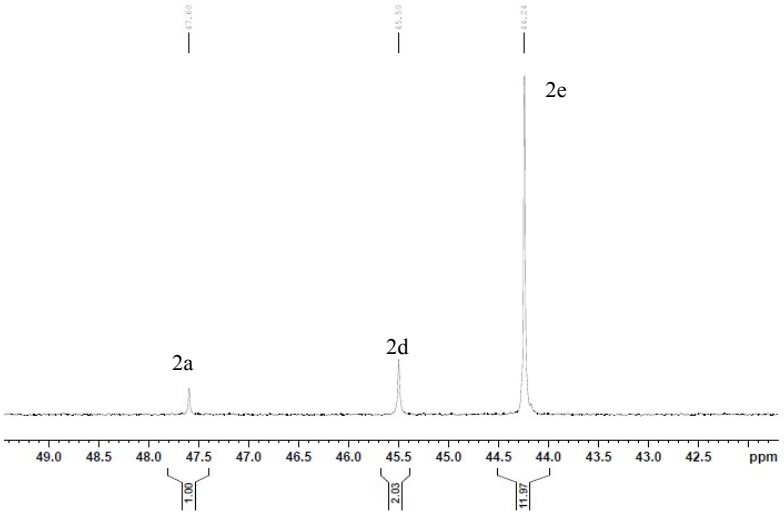

Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of competition of **2a** with toluene, α, α, α trilfluorotoluene, and 1,3 bis(trifluoromethyl) benzene

S4: Selective bond lengths in molecular structures of **2a-f**

Table 1. Experimental parameters

Arene	Average Ni-C(arene) bond length (Å)	Ni-*ipso*-C bond length(Å)	Ni-arene centre distance (Å)
anisole	2.129	2.157	1.596
mesitylene	2.131	2.136	1.597
toluene	2.127	2.136	1.594
benzene	2.119	n/a	1.587
α,α,α-trifluorotoluene	2.114	2.083	1.582
1,3-bis(trifluoromethyl)benzene	2.114	2.101(2.103)	1.579

* Ni-C(substituted) bond lengths of 1,3-bis(trifluoromethyl)benzene analogue are the average of the two Ni-C(substituted) bonds.

** Numbers in brackets are the bond lengths to the 2-C of 1,3-bis(trifluoromethyl)benzene and Ni.

S5: Crystallographic Data of **2a-f**

Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
Chemical Formula	$C_{25}H_{41}NiP$	$C_{24}H_{39}NiP$	$C_{27}H_{45}NiP$	$C_{25}H_{38}F_3NiP$	$C_{26}H_{37}F_6NiP$	$C_{25}H_{41}NiOP$
Formula Weight	431.26	417.23	459.31	485.23	553.23	447.26
Temp	173(2) K	173(2) K	173(2) K	173(2) K	173(2) K	173(2) K
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P -1	P2(1)/n	P2(1)/c	P2(1)/c	C2/c	P -1
a/ Å	8.6764(6)	9.8511(11)	12.7379(14)	11.8792(7)	16.921(4)	8.6352(5)
b/ Å	9.5709(7)	22.745(2)	9.3650(11)	9.2062(6)	9.399(2)	9.7092(6)
c/ Å	15.6496(11)	9.8693(10)	21.990(3)	22.9722(15)	32.999(8)	15.6942(10)
α/ °	96.519(2)	90	90	90	90	97.5800(10)
β/ °	99.003(2)	92.166(2)	104.542(2)	104.1810(10)	99.990(4)	99.4610(10)
γ/ °	115.531(2)	90	90	90	90	115.0380(10)
V/ $Å^3$	1134.08(14)	2209.7(4)	2539.2(5)	2435.7(3)	5169(2)	1145.68(12)
Z	2	4	4	4	8	2
D_{calc}/g cm^{-3}	1.263	1.254	1.201	1.323	1.422	1.297
μ(Mo-Kα) / mm^{-1}	0.933	0.956	0.838	0.894	0.868	0.93
F(000)	468	904	4256	1032	2320	484
Reflection collected	56664	72724	8145	60724	49098	32139
Independent reflections	9957	9693	6405	8797	7542	25298
R(int)	4.42	4.35	twinned	3.90	7.54	twinned
R1 ($I > 2\sigma(I)$)[a]	3.37	3.07	5.52	3.60	4.34	6.38
R1(all)	5.47	4.57	7.78	5.62	8.79	9.18
wR2(all)	7.19	6.65	14.53	9.04	8.66	10.95
GOF	1.0210	1.0560	1.1440	1.0430	1.0340	1.0920

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