

**Importance of co-donor field strength in the preparation of tetradentate  $\alpha$ -diimine nickel hydrosilylation catalysts**

*Supplementary Information*

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## Experimental Procedures

**General Considerations.** All synthetic reactions were performed within an MBraun glove box under an atmosphere of purified nitrogen. Aldrich or Acros anhydrous solvents were purified using a Pure Process Technology solvent system and stored in the glovebox over activated 4Å molecular sieves and sodium prior to use. Benzene-*d*<sub>6</sub> was purchased from Cambridge Isotope Laboratories and dried over 4Å molecular sieves prior to use. (COD)<sub>2</sub>Ni was purchased from Strem and used as received, while 2-(diphenylphosphino)-1-ethylamine and 3-(diphenylphosphino)-1-propylamine were used as received from Strem. 2,3-Butanedione, *p*-toluenesulfonic acid, *N,N*-dimethyl-1,3-propanediamine, 2-(2-aminoethyl)pyridine were purchased from TCI America. Hydrosilylation substrates phenylacetylene, 2,4-dimethyl-3-pentanone, and cyclohexanone were purchased from Sigma-Aldrich, while phenylsilane was purchased from Oakwood Chemical. All of the gases used in this study were obtained from Praxair. <sup>Ph<sub>2</sub>PEt</sup>DI was prepared in a similar fashion to <sup>Ph<sub>2</sub>PPr</sup>DI, using a slightly modified procedure from that reported in T. D. DuBois, *Inorg. Chem.*, 1972, **11**, 718.

Solution <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Varian 400-MR 400 MHz NMR spectrometer. All <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts (ppm) are reported relative to SiMe<sub>4</sub> using <sup>1</sup>H (residual) and <sup>13</sup>C chemical shifts of the solvent as secondary standards. <sup>31</sup>P NMR data (ppm) is reported relative to H<sub>3</sub>PO<sub>4</sub>. Elemental analyses were performed at Robertson Microlit Laboratories Inc. (Ledgewood, NJ) and the Arizona State University CLAS Goldwater Environmental Laboratory (Tempe, AZ).

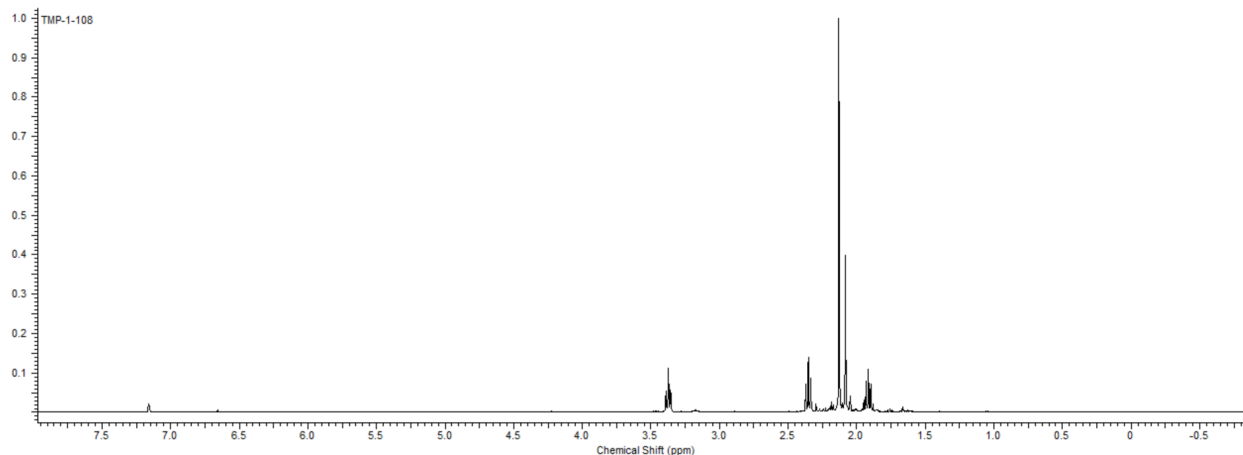
**X-ray Crystallography.** Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a glove box and transferred to a glass fiber with Apiezon N grease, which was then mounted on the goniometer head of a Bruker APEX (Arizona State University) or APEX II diffractometer (University of Arizona) equipped with Mo  $K_{\alpha}$  radiation. A hemisphere routine was used for data collection and determination of the lattice constants. The space group was identified and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS), completed by subsequent Fourier synthesis, and refined by full-matrix, least-squares procedures on  $|F|^2$  (SHELXL). The solid-state structure of **4** was found to have two positionally disordered chelate arm carbon atoms that were successfully modeled.

**Electrochemistry.** Electrochemical experiments were conducted using a 1210B handheld potentiostat purchased from CH Instruments Inc. All experiments were performed under a nitrogen atmosphere using a glassy carbon working electrode (3 mm diameter), a silver/silver ion reference electrode, and a platinum counter electrode that were purchased from BAS Inc. Approximately 2 mg of ferrocene (reference, purchased from Sigma-Aldrich) and/or nickel complex (sample) were added to 5 mL of a 0.1 M acetonitrile or tetrahydrofuran solution of tetrabutylammonium hexafluorophosphate (Fluka) directly before data collection. All cyclic voltammograms are reported relative to  $Fc^+/Fc$ . The  $E_{1/2}$  values provided were determined by averaging the potentials of maximum anodic and cathodic current.

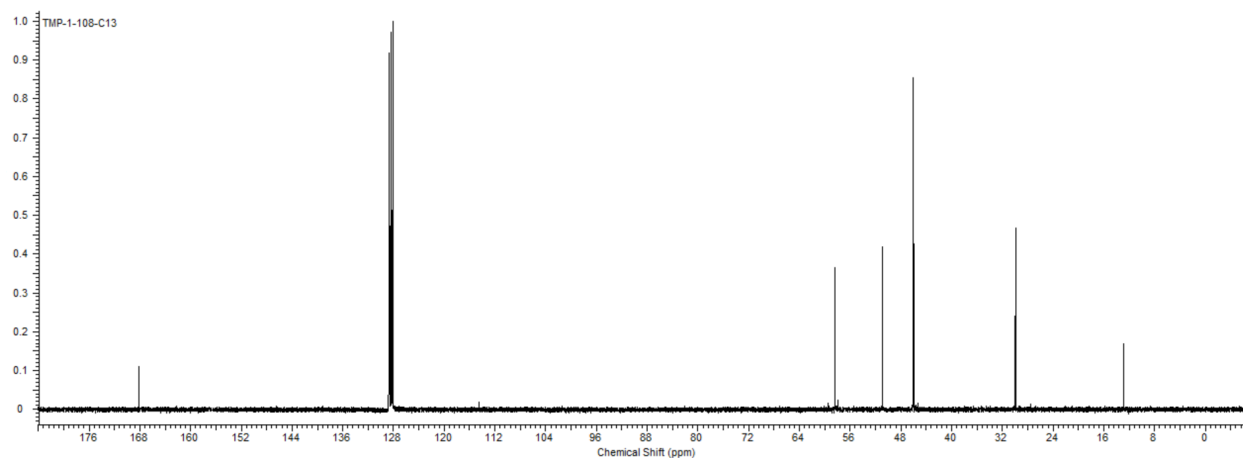
**UV-Visible Spectroscopy.** All UV/Vis spectra were collected on a Perkin-Elmer Lambda 18 Spectrometer using a two-beam liquid cell. The spectrometer utilized both deuterium and halogen lamps with a change-over occurring at 300 nm.

### Improved Preparation of

$(\text{H}_3\text{C})_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  ( $^{\text{Me}_2\text{NPrDI}}$ ). A 100 mL thick-walled glass bomb was charged with 0.021 g (0.123 mmol) of *p*-toluenesulfonic acid, 0.143 g (1.66 mmol) of 2,3-butanedione, 5 cm<sup>3</sup> of 4Å molecular sieves, and approximately 10 mL of toluene. After stirring at 23 °C for five minutes, a solution of 0.343 g (3.36 mmols) of 3-*N,N*-dimethyl-1-propylamine in 10 mL of toluene was added dropwise to the reaction mixture. The glass bomb was then sealed under nitrogen and set to stir in a 70 °C oil bath for 18 hours. The resulting light brown solution was then cooled to 23 °C and filtered under a nitrogen atmosphere. The toluene was then removed *in vacuo* to afford 0.370 g (88%) of a dark yellow oil identified as  $^{\text{Me}_2\text{NPrDI}}$ . Analysis for C<sub>14</sub>H<sub>30</sub>N<sub>4</sub>: Calcd. C, 66.09%; H, 11.89%; N, 22.02%. Found: C, 66.33%; H, 12.00%; N, 21.85%. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ = 3.35 (t, *J* = 7.0 Hz, 4H, NCH<sub>2</sub>), 2.34 (t, *J* = 7.0 Hz, 4H, NCH<sub>2</sub>), 2.11 (s, 12H, N(CH<sub>3</sub>)<sub>2</sub>), 2.07 (s, 6H, N=C(CH<sub>3</sub>)), 1.89 (pseudo quintet, *J* = 7.0 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): δ = 168.14 (N=CCH<sub>3</sub>), 58.35 (C=NCH<sub>2</sub>CH<sub>2</sub>), 50.88 (CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>), 46.02 (N(CH<sub>3</sub>)<sub>2</sub>), 29.89 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 12.81 (N=CCH<sub>3</sub>).



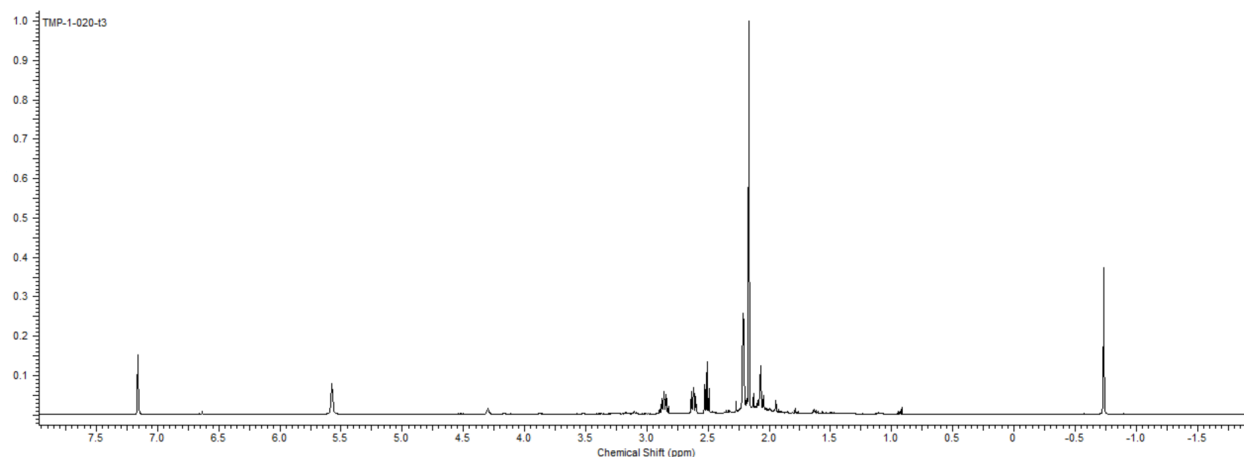
**Figure S1.** <sup>1</sup>H NMR spectrum of <sup>Me</sup><sub>2</sub>NPrDI in benzene-*d*<sub>6</sub>.



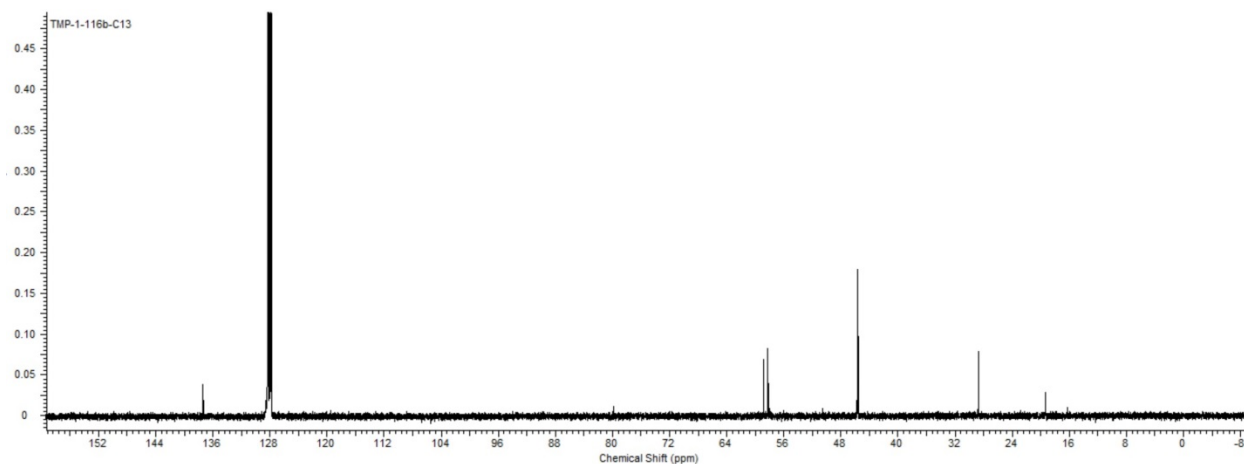
**Figure S2.** <sup>13</sup>C NMR spectrum of <sup>Me</sup><sub>2</sub>NPrDI in benzene-*d*<sub>6</sub>.

**Preparation of (<sup>Me</sup><sub>2</sub>NPrDI)<sub>2</sub>Ni (**1**).** Under a nitrogen atmosphere, a 20 mL scintillation vial was charged with 0.054 g (0.532 mmol) of <sup>Me</sup><sub>2</sub>NPrDI, 0.029 g (0.262 mmol) of (COD)<sub>2</sub>Ni, and approximately 10 mL of toluene. The resulting solution turned deep red after approximately one minute and continued to darken while stirring at ambient temperature for 24 hours. The solution was then filtered through Celite and the toluene was removed *in vacuo* to afford 0.093 g (77%) a glossy red solid identified as **1**. Recrystallization from a pentane solution at -35 °C afforded 10

mg (7%) of red crystals. Analysis for  $C_{28}H_{60}N_8Ni$ : Calcd. C, 59.26%; H, 10.66%. Found: C, 59.32%; H, 10.40%. Values determined for N were consistently low.  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  2.86 (pseudo quintet,  $J = 7.0$  Hz, 8H,  $CH_2CH_2CH_2$ ), 2.62 (t,  $J = 7.0$  Hz, 8H,  $C=NCH_2$ ), 2.51 (t,  $J = 7.0$  Hz, 8H,  $CH_2N$ ), 2.17 (s, 24H,  $N(CH_3)_2$ ), -0.73 (s, 12H,  $N=C(CH_3)$ ).  $^{13}C$  NMR (benzene- $d_6$ ):  $\delta$  137.39 (s,  $N=C(CH_3)$ ), 58.83 (s,  $CH_2$ ), 58.23 (s,  $CH_2$ ), 45.61 (s,  $N(CH_3)_2$ ), 28.70 (s,  $CH_2CH_2CH_2$ ), 19.35 (s,  $C(CH_3)$ ).



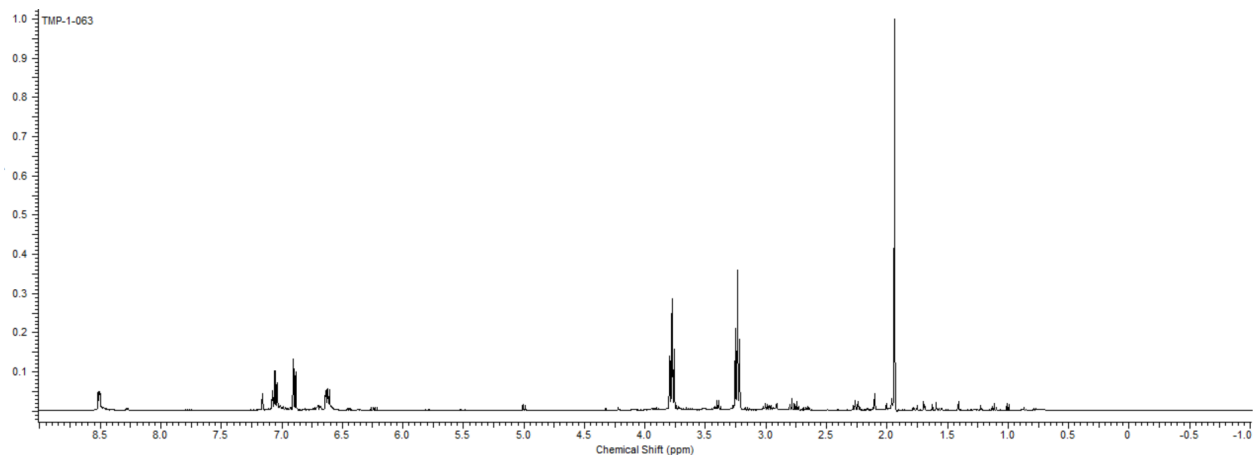
**Figure S3.**  $^1H$  NMR spectrum of **1** in benzene- $d_6$ .



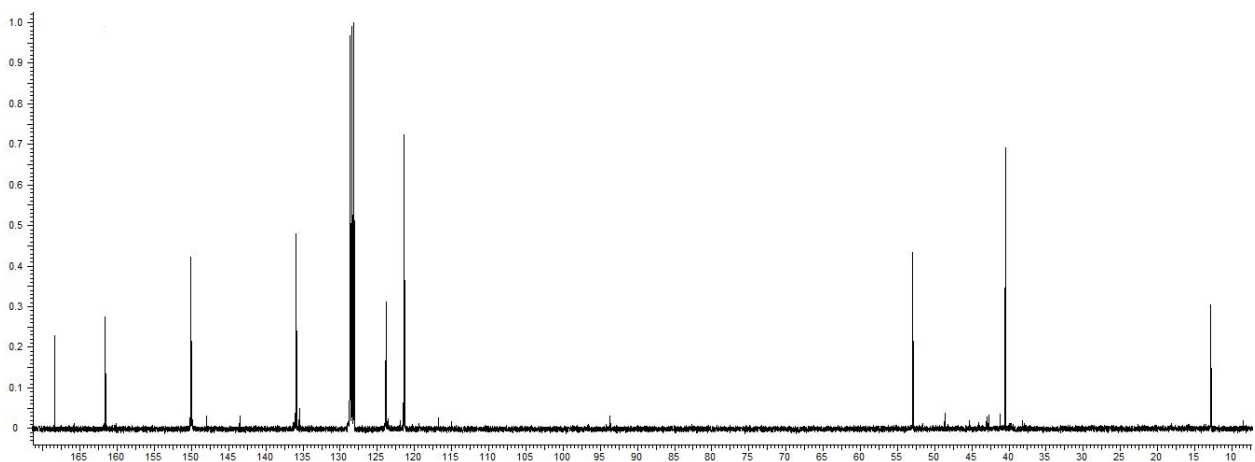
**Figure S4.**  $^{13}C$  NMR spectrum of **1** in benzene- $d_6$ .

**Preparation of (2-NC<sub>5</sub>H<sub>4</sub>)CH<sub>2</sub>CH<sub>2</sub>N=C(CH<sub>3</sub>)C(CH<sub>3</sub>)=NCH<sub>2</sub>CH<sub>2</sub>(2-NC<sub>5</sub>H<sub>4</sub>) (Py<sup>Et</sup>DI).**

A 100 mL thick-walled glass bomb was charged with 0.352 g (4.09 mmol) of 2,3-butanedione, 0.013 g (0.073 mmol) of *p*-toluenesulfonic acid, and approximately 40 mL of toluene. The bomb was then set to stir at ambient temperature for five minutes, after which time 1.00 g (8.20 mmol) of 2-(2-aminoethyl)pyridine was added dropwise to the 2,3-butanedione solution along with approximately 5 cm<sup>3</sup> of 4 Å molecular sieves. The resulting reaction mixture was then sealed under a nitrogen atmosphere and set to stir in an oil bath at 100 °C. After 24 hours the reaction was removed from the oil bath and cooled to ambient temperature before being moved into a glove box. The solution was then filtered through Celite and the toluene was removed *in vacuo* to yield 0.976 g (81%) of a viscous brown oil identified as Py<sup>Et</sup>DI. Analysis for C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>: Calcd. C, 73.44%; H, 7.53%; N, 19.03%. Found: C, 73.16 %; H, 7.42%; N, 18.79%. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>): δ 8.51 (d, *J* = 6.0 Hz, 2H, *pyridine*), 7.05 (td, *J* = 7.5, 2.0 Hz, 2H, *pyridine*), 6.89 (d, *J* = 7.8 Hz, 2H, *pyridine*), 6.62 (m, 2H, *pyridine*), 3.78 (t, *J* = 7.0 Hz, 4H, C=NCH<sub>2</sub>), 3.24 (t, *J* = 7.0 Hz, 4H, PyCH<sub>2</sub>), 1.94 (s, 6H, N=C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (benzene-*d*<sub>6</sub>): δ 168.46 (C=NCH<sub>2</sub>), 161.60 (*pyridine*), 150.07 (*pyridine*), 135.89 (*pyridine*), 123.84 (*pyridine*), 121.36 (*pyridine*), 52.94 (C=NCH<sub>2</sub>), 40.46 (PyCH<sub>2</sub>), 12.83 (N=CCH<sub>3</sub>).



**Figure S5.**  $^1\text{H}$  NMR spectrum of  $\text{PyEtDI}$  in benzene- $d_6$ .

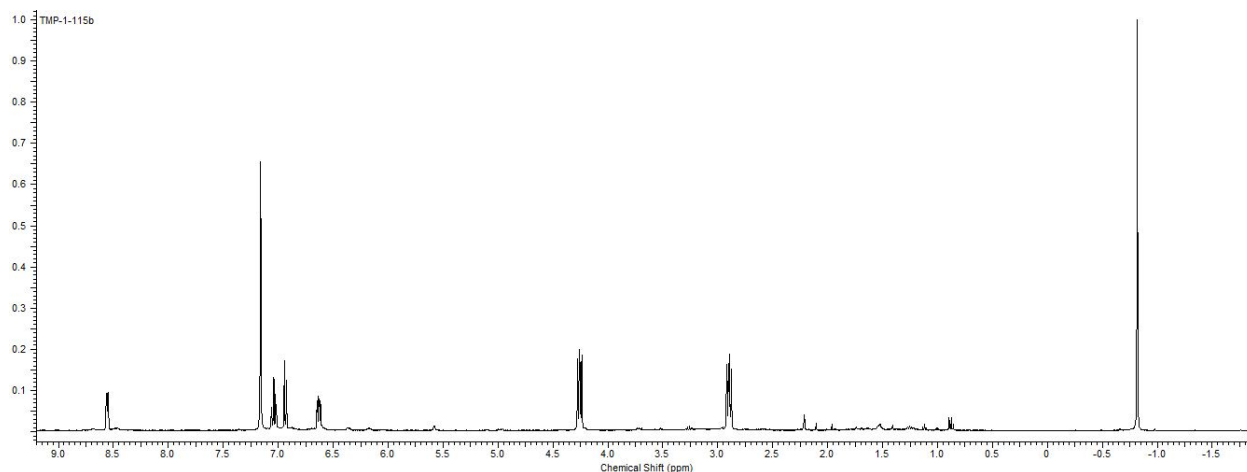


**Figure S6.**  $^{13}\text{C}$  NMR spectrum of  $\text{PyEtDI}$  in benzene- $d_6$ .

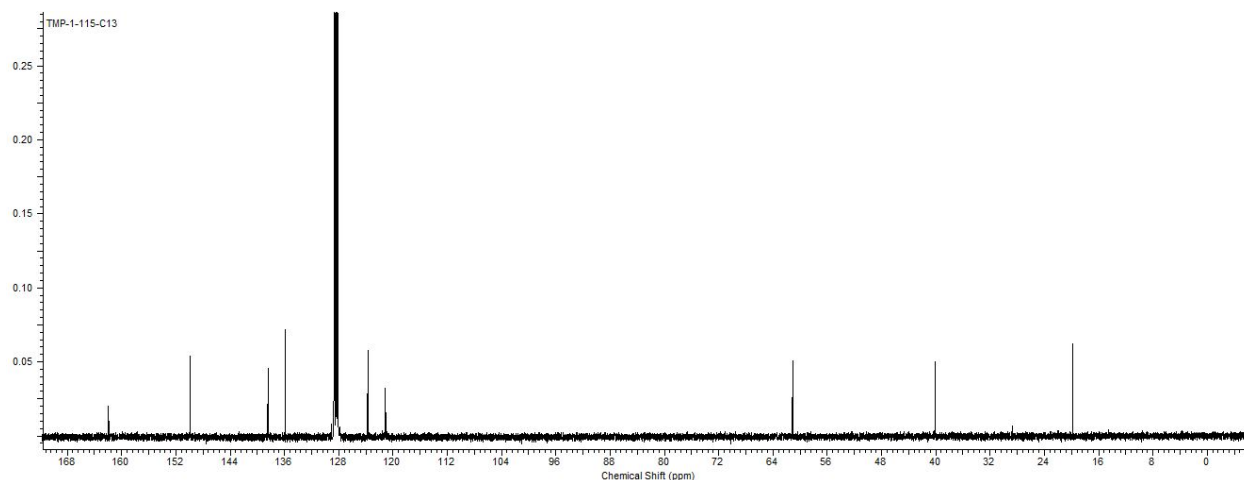
**Preparation of  $(\text{PyEtDI})_2\text{Ni}$  (2).** Under a nitrogen atmosphere, a 20 mL scintillation vial was charged with 0.056 g (0.203 mmol) of  $(\text{COD})_2\text{Ni}$  and approximately 7 mL of THF. A separate 20 mL scintillation vial was charged with 0.120 g (0.406 mmol) of  $\text{PyEtDI}$  and approximately 7 mL of THF. The light brown solution of  $\text{PyEtDI}$  was then added to the light yellow solution of  $(\text{COD})_2\text{Ni}$  which began to turn red over a course of 10 minutes. The reaction mixture was then allowed to stir at 23 °C for 5 hours. The resulting red solution was filtered through Celite and the



THF was removed *in vacuo* to give 0.122 g of crude **2** (93%). The product was purified by repeated extraction into pentane followed by recrystallization at  $-35\text{ }^{\circ}\text{C}$ , yielding 0.053 g (40%) of **2** as red crystals. Analysis for  $\text{C}_{36}\text{H}_{44}\text{N}_8\text{Ni}$ : Calcd. C, 66.78%; H, 6.85%; N, 17.31%. Found: C, 66.50%; H, 6.86%; N, 17.07%.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  8.55 (d,  $J = 5.0$  Hz, 4H, *pyridine*), 7.04 (td,  $J = 9.5, 8.0$  Hz, 4H, *pyridine*), 6.93 (d,  $J = 8.0$  Hz, 4H, *pyridine*), 6.64 (m, 4H, *pyridine*), 4.26 (t,  $J = 7.8$  Hz, 8H,  $\text{CH}_2$ ), 2.90 (t,  $J = 7.8$  Hz, 8H,  $\text{CH}_2$ ), -0.82 (s, 12H,  $\text{C}(\text{CH}_3)$ ).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  161.97 (s,  $\text{N}=\text{C}(\text{CH}_3)$ ), 149.94 (s, *pyridine*), 138.43 (s, *pyridine*), 135.91 (s, *pyridine*), 123.72 (s, *pyridine*), 121.12 (s, *pyridine*), 61.08 (s,  $\text{CH}_2$ ), 40.09 (s,  $\text{CH}_2$ ), 19.79 (s,  $\text{C}(\text{CH}_3)$ ).



**Figure S7.**  $^1\text{H}$  NMR spectrum of  $(^{\text{PyEt}}\text{DI})_2\text{Ni}$  in benzene- $d_6$ .



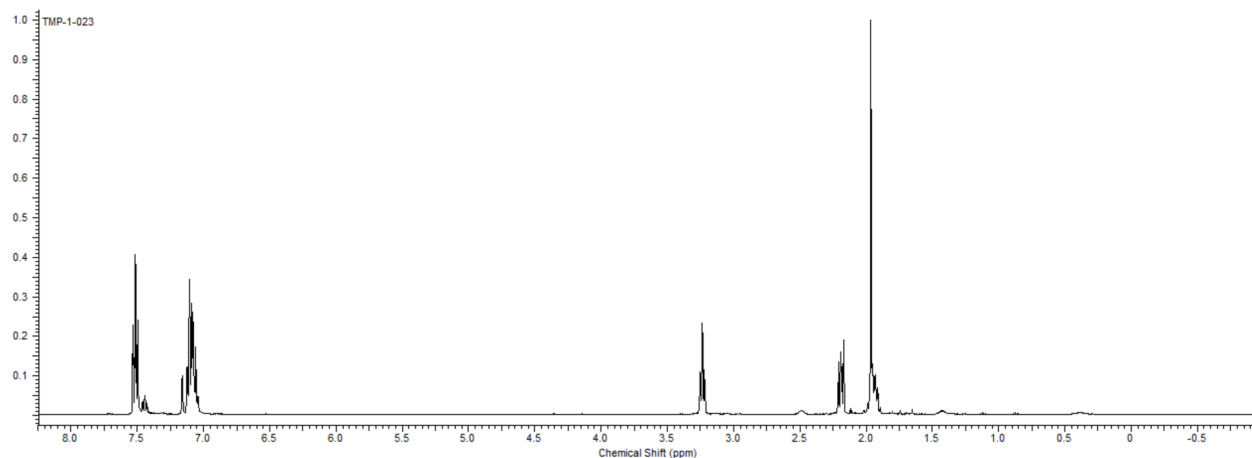
**Figure S8.**  $^{13}\text{C}$  NMR spectrum of  $(\text{Py}^{\text{Et}}\text{DI})_2\text{Ni}$  in benzene- $d_6$ .

**Preparation of  $(\text{H}_5\text{C}_6)_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{N}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NCH}_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$   
 $(\text{Ph}_2\text{PPrDI})$ .**

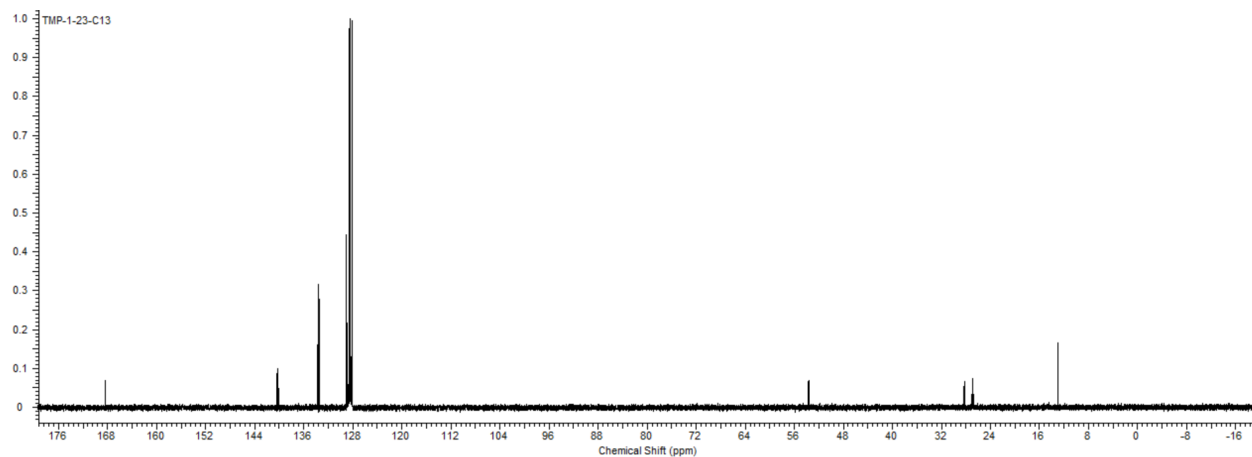
Under  $\text{N}_2$ , a 100 mL thick-walled glass bomb was charged with 0.038 g (0.429 mmol) of 2,3-butanedione, 0.004 g (0.029 mmol) of *p*-toluenesulfonic acid, and approximately 5 mL of toluene and set to stir for five minutes at ambient temperature. At that time, 0.204 g (0.872 mmols) of 3-(diphenylphosphino)-1-propylamine was added dropwise to the 2,3-butanedione solution along with approximately 4  $\text{cm}^3$  of 4 Å molecular sieves. The initial pale yellow solution was then set to stir in an oil bath at 80 °C. After 20 minutes, the reaction mixture turned colorless. After 22 hours the reaction was stopped, allowed to cool to ambient temperature, and then moved into a glove box. The solution was vacuum filtered through Celite and the toluene was removed *in vacuo* to yield 0.196 g (83%) of a yellow, waxy solid identified as  $\text{Ph}_2\text{PPrDI}$ .

Analysis for  $\text{C}_{34}\text{H}_{38}\text{N}_2\text{P}_2$ : Calcd. C, 76.10%; H, 7.14%; N, 5.22%. Found: C, 76.27%; H, 7.39%; N, 5.40%.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  7.51 (td,  $J = 8.0, 1.5$  Hz, 8H, *phenyl*), 7.12-7.06 (m, 12H, *phenyl*), 3.23 (t,  $J = 7.0$  Hz, 4H,  $\text{C}=\text{NCH}_2$ ), 2.19 (m, 4H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.96 (s, 6H,  $\text{N}=\text{C}(\text{CH}_3)_2$ ), 1.93 (m, 4H,  $\text{CH}_2\text{P}$ ).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  168.38 ( $\text{N}=\text{C}(\text{CH}_3)$ ), 140.28 (d,  $J$

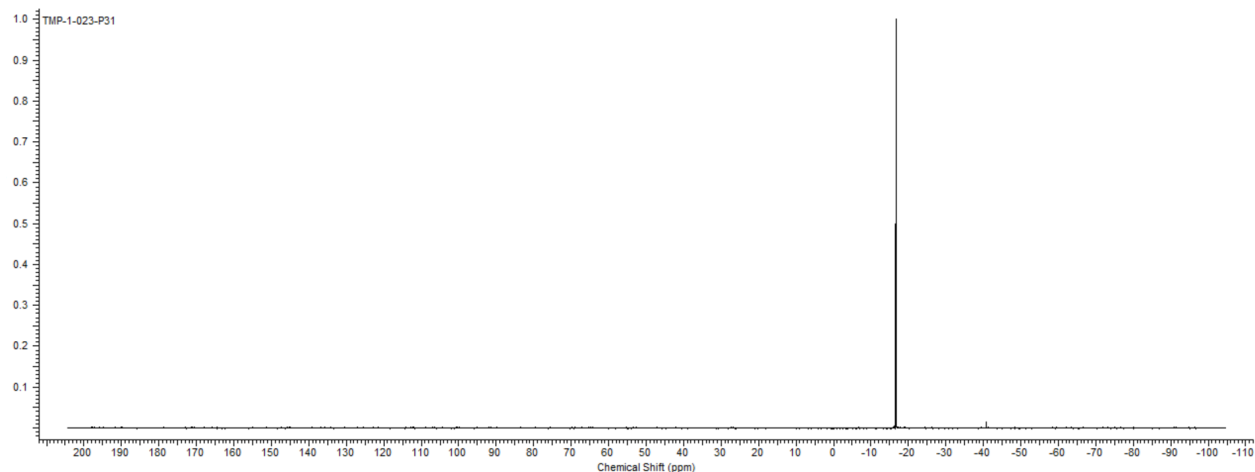
= 14.5 Hz, *phenyl*), 133.53 (d,  $J = 18.5$  Hz, *phenyl*), 129.05 (d,  $J = 6.0$  Hz, *phenyl*), 128.96 (s, *phenyl*), 55.60 (d,  $J = 13.5$  Hz, C=NCH<sub>2</sub>), 28.27 (d,  $J = 16.5$  Hz, CH<sub>2</sub>P), 26.87 (d,  $J = 12.5$  Hz, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 12.95 (s, C(CH<sub>3</sub>)). <sup>31</sup>P (benzene-*d*<sub>6</sub>):  $\delta$  -16.61 (s, PPh<sub>2</sub>).



**Figure S9.** <sup>1</sup>H NMR spectrum of Ph<sub>2</sub>PPrDI in benzene-*d*<sub>6</sub>.

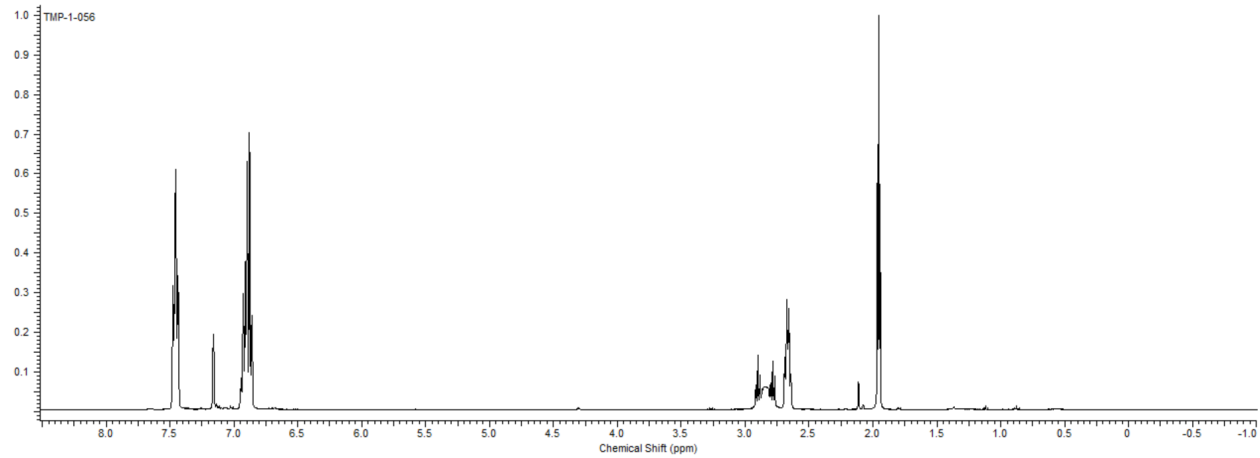


**Figure S10.** <sup>13</sup>C NMR spectrum of Ph<sub>2</sub>PPrDI in benzene-*d*<sub>6</sub>.

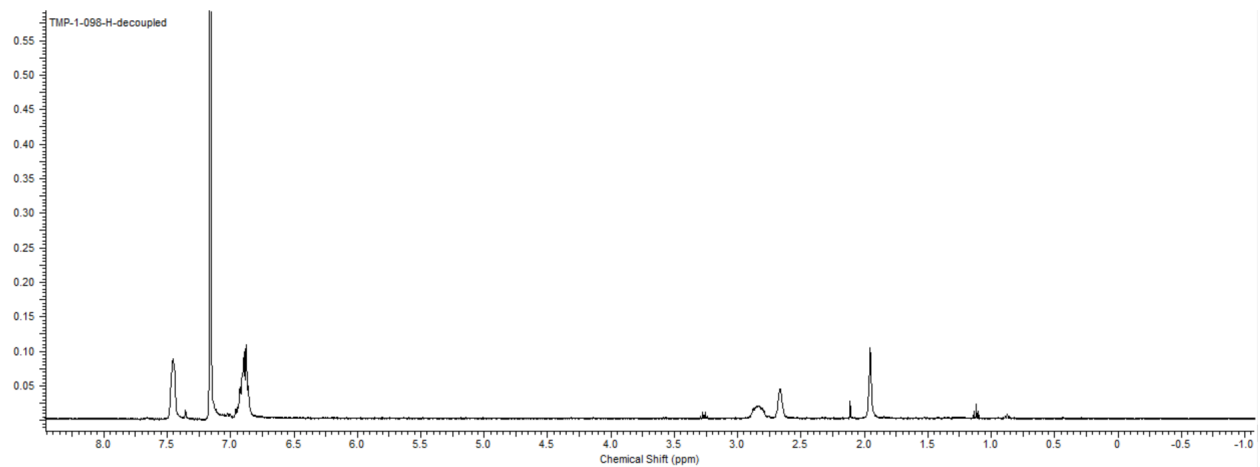


**Figure S11.**  $^{31}\text{P}$  NMR spectrum of  $\text{Ph}_2\text{PPrDI}$  in benzene- $d_6$ .

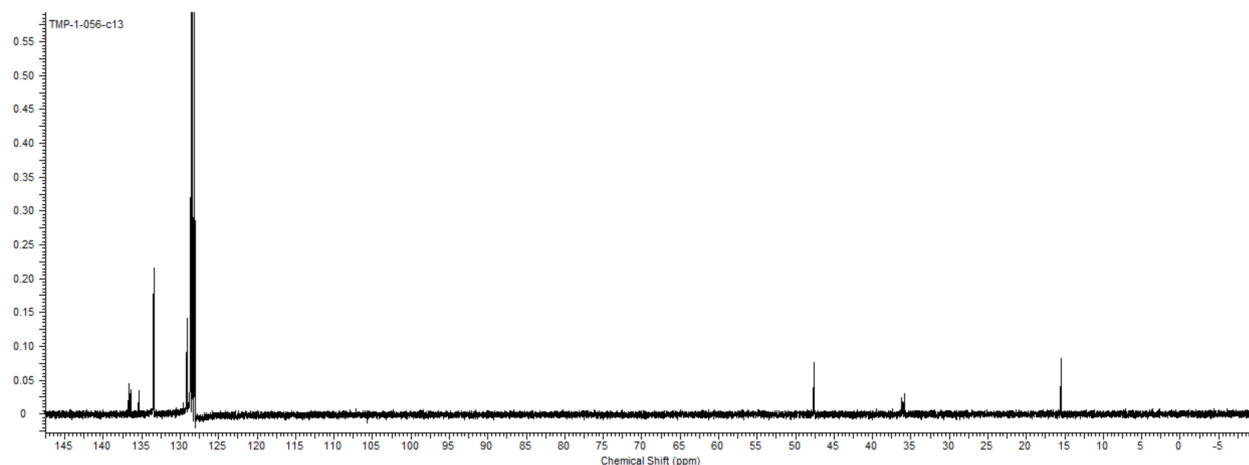
**Preparation of ( $\text{Ph}_2\text{PEtDI}$ )Ni (**3**).** Under a nitrogen atmosphere, a 20 mL scintillation vial was charged with 0.033 g (0.119 mmol) of  $\text{Ni}(\text{COD})_2$ , 0.062 g (0.123 mmol) of  $\text{Ph}_2\text{PEtDI}$ , and approximately 14 mL of toluene. Upon the addition of  $\text{Ph}_2\text{PEtDI}$  to the solution of  $\text{Ni}(\text{COD})_2$ , the color instantly transitioned from a light yellow to a deep green. The resulting deep green solution was then stirred for 24 hours at 23 °C and the color persisted. After 24 hours the solution was then filtered through Celite and the toluene was removed *in vacuo* to yield 0.067 g (96%) of a red micro-crystalline solid identified as **3**. Analysis for  $\text{C}_{32}\text{H}_{34}\text{N}_2\text{P}_2\text{Ni}$ : Calcd C, 67.75%; H, 6.04%; N, 4.94%. Found: C, 67.62%; H, 5.81%; N, 5.33%.  $^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  7.46 (t,  $J$  = 7.8 Hz, 4H, *phenyl*), 6.94-6.86 (m, 8H, *phenyl*), 2.84 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.67 (pseudo q,  $J$  = 6.3 Hz, 4H,  $\text{C}=\text{NCH}_2$ ), 1.96 (t,  $J$  = 4.3 Hz, 6H,  $\text{C}(\text{CH}_3)_2$ ).  $\{^{31}\text{P}\}^1\text{H}$  NMR (benzene- $d_6$ ):  $\delta$  7.46 (broad s, 4H, *phenyl*), 6.96-6.86 (m, 8H, *phenyl*), 2.84 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.66 (broad s, 4H,  $\text{NCH}_2$ ), 1.96 (broad s, 6H,  $\text{C}(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR (benzene- $d_6$ ):  $\delta$  136.57 (dd,  $J$  = 16.0, 14.5 Hz, *phenyl*), 135.41 (t,  $J$  = 3.0 Hz,  $\text{N}=\text{C}(\text{CH}_3)$ ), 133.47 (t,  $J$  = 6.0 Hz, *phenyl*), 129.16 (s, *phenyl*), 128.45 (s, *phenyl*), 47.62 (s,  $\text{CH}_2$ ) 36.07 (t,  $J$  = 15.0 Hz,  $\text{CH}_2$ ), 15.52 (s,  $\text{C}(\text{CH}_3)_2$ ).  $^{31}\text{P}$  NMR (benzene- $d_6$ ):  $\delta$  56.36 (s,  $\text{PPh}_2$ ).



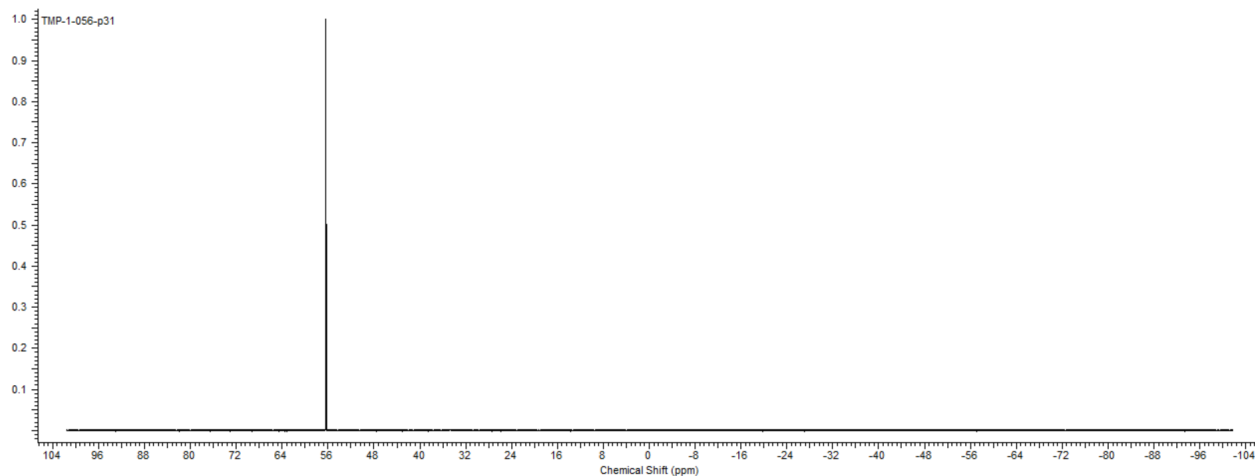
**Figure S12.**  $^1\text{H}$  NMR spectrum of **3** in benzene- $d_6$ .



**Figure S13.**  $\{^{31}\text{P}\}^1\text{H}$  NMR spectrum of **3** in benzene- $d_6$ .



**Figure S14.**  $^{13}\text{C}$  NMR spectrum of **3** in benzene- $d_6$ .



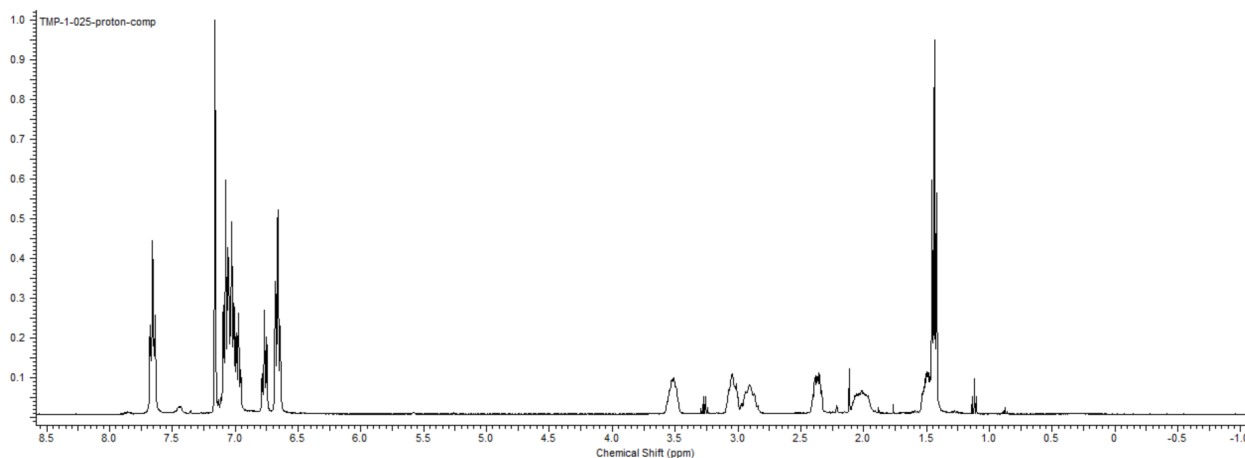
**Figure S15.**  $^{31}\text{P}$  NMR spectrum of **3** in benzene- $d_6$ .

**Preparation of ( $\text{Ph}_2\text{PPrDI}$ )Ni (**4**).** Under a nitrogen atmosphere a 20 mL scintillation vial was charged with 0.089 g (0.165 mmol) of  $\text{Ph}_2\text{PPrDI}$  and approximately 5 mL of toluene. A separate solution consisting of 0.045 g (0.164 mmol) of  $\text{Ni}(\text{COD})_2$  in approximately 5 mL of toluene was then added dropwise to the solution of  $\text{Ph}_2\text{PPrDI}$ . Upon the addition of  $\text{Ni}(\text{COD})_2$ , the solution immediately changed from the clear color indicative of  $\text{Ph}_2\text{PPrDI}$  to a deep red solution. The resulting reaction mixture was then capped and sealed under nitrogen and allowed to stir at 23 °C

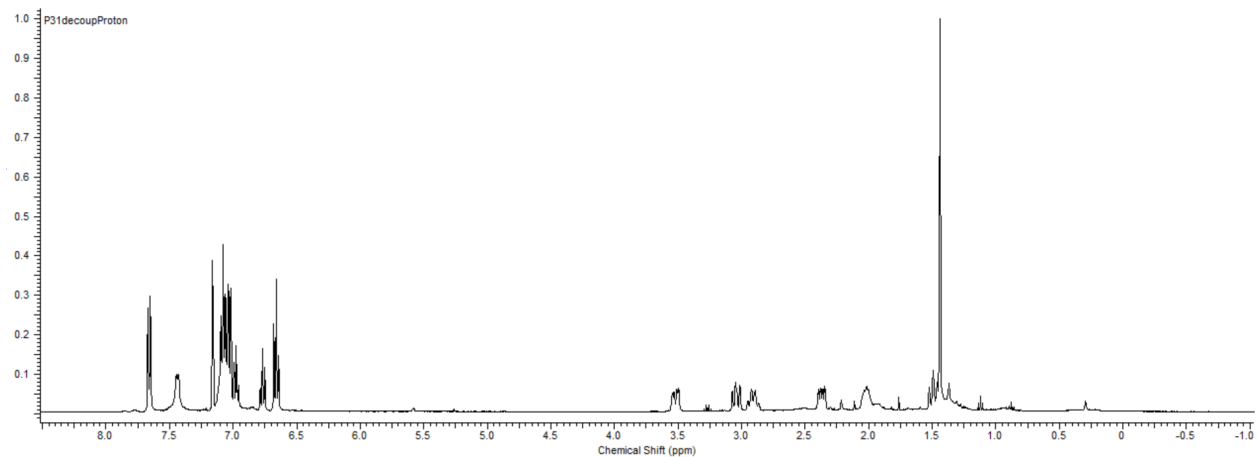
for 24 hours. After stirring, the resulting deep red solution was filtered through Celite and the toluene was removed *in vacuo* to yield 0.082 g (84%) of a red solid identified as **4**.

Recrystallization from an ether/pentane solution afforded 0.047 g (48%) of clear red crystals.

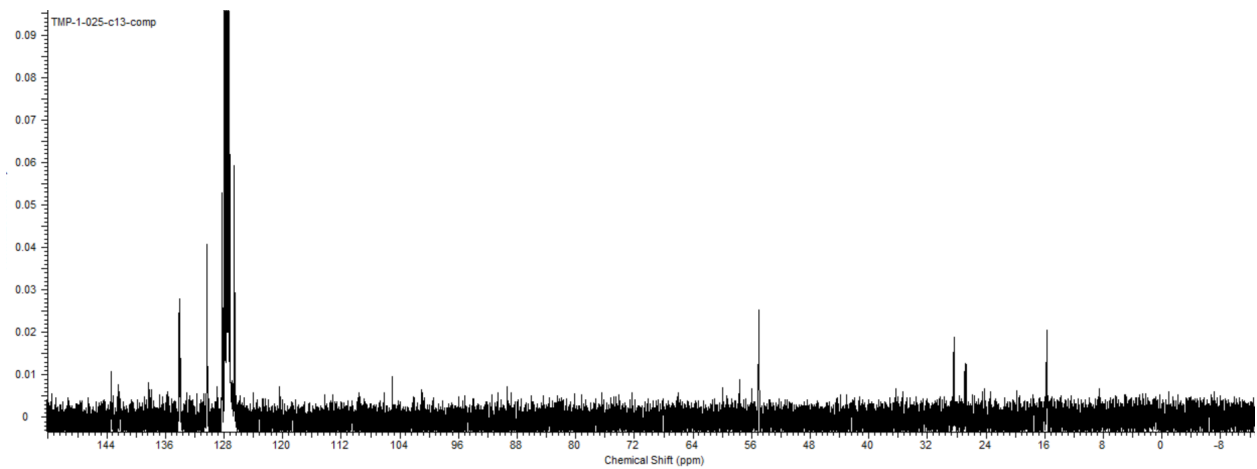
Analysis for  $C_{34}H_{36}N_2P_2Ni$ : Calcd C, 68.60%; H, 6.43%; N, 4.71%. Found: C, 68.32 %; H, 6.49%; N, 5.08%.  $^1H$  NMR (benzene- $d_6$ ):  $\delta$  7.66 (t,  $J = 7.8$  Hz, *phenyl*), 7.03 (m, *phenyl*), 6.77 (t,  $J = 7.0$  Hz, *phenyl*), 6.66 (t,  $J = 7.0$  Hz, *phenyl*), 3.52 (m, 2H,  $CH_2$ ), 3.05 (m, 2H,  $CH_2$ ), 2.90 (m, 2H,  $CH_2$ ), 2.37 (m, 2H,  $CH_2$ ), 2.01 (m, 2H,  $CH_2$ ), 1.49 (m, 2H,  $CH_2$ ), 1.44 (t,  $J = 7.0$  Hz, 6H,  $N=C(CH_3)$ ).  $\{^{31}P\}^1H$  NMR (benzene- $d_6$ ):  $\delta$  7.66 (d,  $J = 7.4$  Hz, 4H, *phenyl*), 7.44 (d,  $J = 7.0$  Hz, 4H, *phenyl*), 7.06 (m, 4H, *phenyl*), 6.77 (t,  $J = 7.4$  Hz, 4H, *phenyl*), 6.66 (t,  $J = 7.0$  Hz, 4H, *phenyl*), 3.52 (dd,  $J = 8.6$  Hz, 5.5 Hz, 2H,  $CH_2$ ), 3.05 (t,  $J = 13.3$  Hz, 2H,  $CH_2$ ), 2.91 (pseudo q,  $J = 11.0$  Hz, 2H,  $CH_2$ ), 2.36 (m, 2H,  $CH_2$ ), 2.02 (m, 2H,  $CH_2$ ), 1.49 (m, 2H,  $CH_2$ ), 1.44 (s, 6H,  $N=C(CH_3)$ ).  $^{13}C$  NMR (benzene- $d_6$ ):  $\delta$  134.83 (t,  $J = 7.5$  Hz, *phenyl*), 131.10 (t,  $J = 5.2$  Hz, *phenyl*), 128.99 (s, *phenyl*), 127.98 (t,  $J = 4.5$  Hz, *phenyl*), 127.35 (s, *phenyl*), 55.81 (broad s,  $CH_2$ ), 29.16 (t,  $J = 8.9$  Hz,  $CH_2$ ), 27.62 (dd,  $J = 12.6, 10.9$  Hz,  $CH_2$ ), 16.51 (s,  $C(CH_3)$ ), two resonances not located.  $^{31}P$  NMR (benzene- $d_6$ ):  $\delta$  39.03 (s,  $PPh_2$ ).



**Figure S16.**  $^1H$  NMR spectrum of **4** in benzene- $d_6$ .

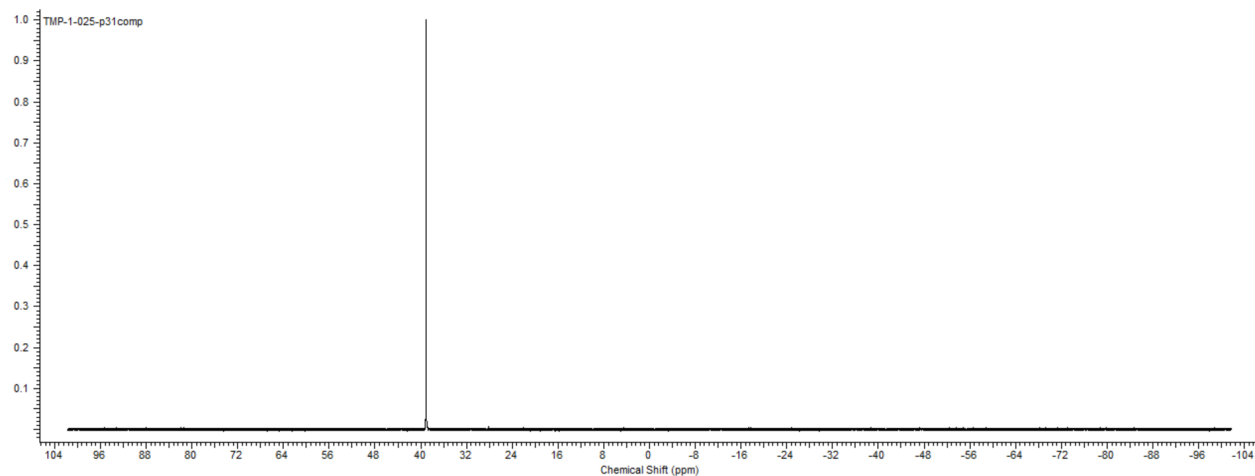


**Figure S17.**  $\{^{31}\text{P}\}^1\text{H}$  NMR spectrum of **4** in benzene- $d_6$ .



**Figure S18.**  $^{13}\text{C}$  NMR spectrum of **4** in benzene- $d_6$ .





**Figure S19.**  $^{31}\text{P}$  NMR spectrum of **4** in benzene- $d_6$ .

**Hydrosilylation of cyclohexanone with ( $\text{Ph}_2\text{PEtDI}$ )Ni:** A 20 mL scintillation vial was charged with 11.9 mg (0.0210 mmol) of ( $\text{Ph}_2\text{PEtDI}$ )Ni and approximately 0.5 mL of benzene- $d_6$ . A separate 20 mL vial was then charged with 0.5 mL of benzene- $d_6$ , 52  $\mu\text{L}$  (0.42 mmol) of phenylsilane, and 43  $\mu\text{L}$  (0.42 mmol) of cyclohexanone. The two solutions were then added to a J. Young NMR tube and sealed under a nitrogen atmosphere. The reaction mixture was allowed to sit at 23  $^\circ\text{C}$  for 24 hours after which time a  $^1\text{H}$  NMR spectrum was collected.

**Hydrosilylation of cyclohexanone with ( $\text{Ph}_2\text{PPrDI}$ )Ni:** A 20 mL scintillation vial was charged with 9.6 mg (0.016 mmol) of ( $\text{Ph}_2\text{PPrDI}$ )Ni and approximately 0.5 mL of benzene- $d_6$ . A separate 20 mL vial was then charged with 0.5 mL of benzene- $d_6$ , 40  $\mu\text{L}$  (0.32 mmol) of phenylsilane, and 34  $\mu\text{L}$  (0.32 mmol) of cyclohexanone. The two solutions were then added to a J. Young NMR tube and sealed under a nitrogen atmosphere. The reaction mixture was allowed to sit at 23  $^\circ\text{C}$  for 24 hours after which time a  $^1\text{H}$  NMR spectrum was collected.

**Hydrosilylation of 2,4-dimethyl-3-pentanone with (<sup>Ph<sub>2</sub>PEt</sup>DI)Ni:** A 20 mL scintillation vial was charged with 4.7 mg (0.0083 mmol) of (<sup>Ph<sub>2</sub>PEt</sup>DI)Ni and approximately 0.5 mL of benzene-*d*<sub>6</sub>. A separate 20 mL scintillation vial was then charged with 0.5 mL of benzene-*d*<sub>6</sub>, 21 μL (0.17 mmol) of phenylsilane, and 24 μL (0.17 mmol) of 2,4-dimethyl-3-pentanone. The two solutions were then added to a J.Young NMR tube and sealed under a nitrogen atmosphere. The reaction mixture was then allowed to sit at 23 °C for 24 hours after which time a <sup>1</sup>H NMR spectrum was collected.

**Hydrosilylation of 2,4-dimethyl-3-pentanone with (<sup>Ph<sub>2</sub>PPr</sup>DI)Ni:** A 20 mL scintillation vial was charged with 5.0 mg (0.0084 mmol) of (<sup>Ph<sub>2</sub>PPr</sup>DI)Ni and approximately 0.5 mL of benzene-*d*<sub>6</sub>. A separate 20 mL scintillation vial was then charged with 0.5 mL of benzene-*d*<sub>6</sub>, 21 μL (0.17 mmol) of phenylsilane, and 24 μL (0.17 mmol) of 2,4-dimethyl-3-pentanone. The two solutions were then added to a J.Young style NMR tube and sealed under a nitrogen atmosphere. The reaction mixture was then allowed to sit at 23 °C for 24 hours after which time a <sup>1</sup>H NMR spectrum was collected.

**Hydrosilylation of phenylacetylene with (<sup>Ph<sub>2</sub>PEt</sup>DI)Ni:** A 20 mL scintillation vial was charged with 7.0 mg (0.12 mmol) of (<sup>Ph<sub>2</sub>PEt</sup>DI)Ni and approximately 0.5 mL of benzene-*d*<sub>6</sub>. A separate 20 mL scintillation vial was then charged with 0.5 mL of benzene-*d*<sub>6</sub>, 30 μL (0.24 mmol) of phenylsilane, and 26 μL (0.24 mmol) of phenylacetylene. The two solutions were then added to a J.Young NMR tube and sealed under a nitrogen atmosphere. The reaction mixture was then allowed to sit at 23 °C for 24 hours after which time a <sup>1</sup>H NMR spectrum was collected.

Although *trans*-(Ph)HC=CH(SiH<sub>2</sub>Ph) was identified as the major product, small quantities of secondary olefin containing compounds were also observed by <sup>1</sup>H NMR spectroscopy.

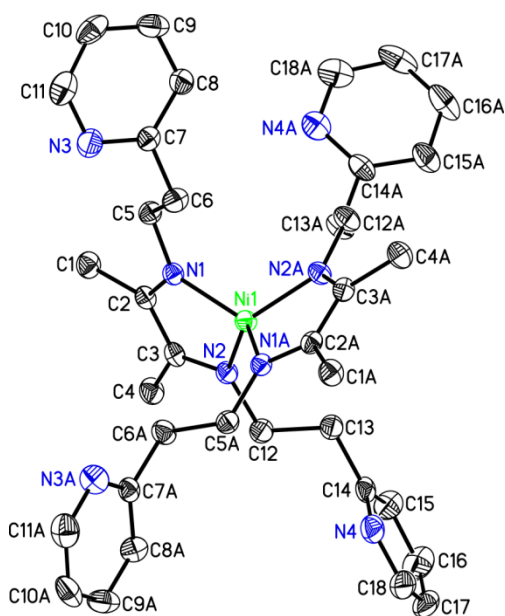
**Hydrosilylation of phenylacetylene with (<sup>Ph<sub>2</sub>PPrDI</sup>)Ni:** A 20 mL scintillation vial was charged with 4.2 mg (0.0071 mmol) of (<sup>Ph<sub>2</sub>PPrDI</sup>)Ni and approximately 0.5 mL of benzene-*d*<sub>6</sub>. A separate 20 mL scintillation vial was then charged with 0.5 mL of benzene-*d*<sub>6</sub>, 18 μL (0.14 mmol) of phenylsilane, and 18 μL (0.16 mmol) of phenylacetylene. The two solutions were then pipetted into a J-Young style NMR tube and sealed under a nitrogen atmosphere. The reaction mixture was then allowed to sit at 23 °C for 24 hours after which time a <sup>1</sup>H NMR spectrum was collected. Although *trans*-(Ph)HC=CH(SiH<sub>2</sub>Ph) was identified as the major product, small quantities of secondary olefin containing compounds were also observed by <sup>1</sup>H NMR spectroscopy.

**Table S1.** Crystallographic Data for (<sup>PyEt</sup>DI)<sub>2</sub>Ni, (<sup>Ph<sub>2</sub>PEt</sup>DI)Ni, and (<sup>Ph<sub>2</sub>PPr</sup>DI)Ni.

	( <sup>PyEt</sup> DI) <sub>2</sub> Ni	( <sup>Ph<sub>2</sub>PEt</sup> DI)Ni	( <sup>Ph<sub>2</sub>PPr</sup> DI)Ni
Chemical formula	C <sub>36</sub> H <sub>44</sub> N <sub>8</sub> Ni	C <sub>32</sub> H <sub>34</sub> N <sub>2</sub> P <sub>2</sub> Ni	C <sub>34</sub> H <sub>36</sub> N <sub>2</sub> P <sub>2</sub> Ni
Formula weight	647.50	567.26	595.31
crystal dimensions	0.160x0.140x0.060	0.370 x 0.120 x 0.080	0.276 x 0.183 x 0.129
crystal system	monoclinic	triclinic	triclinic
space group	C <sub>12</sub> /C <sub>1</sub>	P-1	P-1
<i>a</i> (Å)	9.3548(8)	11.2266(10)	7.7544(6)
<i>b</i> (Å)	20.4687(17)	11.4080(10)	11.1974(8)
<i>c</i> (Å)	17.6111(15)	12.5302(11)	17.6096(13)
<i>α</i> (deg)	90	65.0460(2)	88.050(3)
<i>β</i> (deg)	94.424(2)	75.784(2)	87.795(3)
<i>γ</i> (deg)	90	89.781(2)	71.604(4)
<i>V</i> (Å <sup>3</sup> )	3362.1(5)	1401.3(2)	1449.43(19)
<i>Z</i>	4	2	2
<i>T</i> (°C)	123.(2)	123.(2)	100.(2)
<i>ρ</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.279	1.344	1.359
<i>μ</i> (mm <sup>-1</sup> )	0.615	0.830	0.806
reflections collected	13867	11233	27313
data/restraints/parameters	3114/0/206	11233/0/338	5316/6/367
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0457	0.0484	0.0298
w <i>R</i> <sub>2</sub> (all data)	0.0946	0.1064	0.0725
Goodness-of-fit	1.031	1.027	1.048
Largest peak, hole (eÅ <sup>-3</sup> )	0.289, -0.202	0.617, -0.368	0.368, -0.267

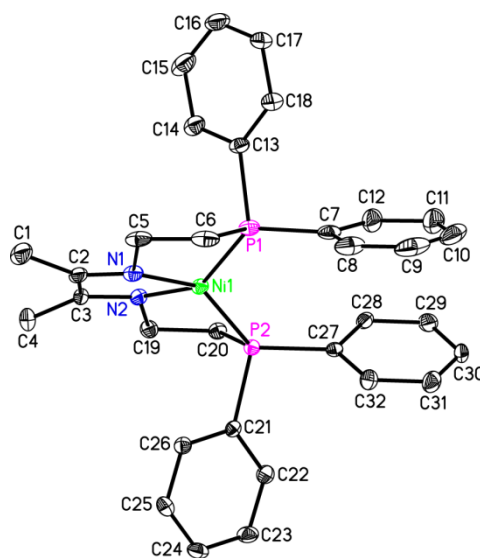
**Table S2.** Metrical parameters determined for (PyEtDI)<sub>2</sub>Ni.

Ni(1)-N(1)	1.904(2)	N(1)-Ni(1)-N(1A)	131.74(13)
Ni(1)-N(2)	1.912(2)	N(1)-Ni(1)-N(2A)	117.59(9)
N(1)-C(2)	1.344(3)	N(1)-Ni(1)-N(2)	81.83(9)
N(1)-C(5)	1.460(3)	N(2)-Ni(1)-N(2A)	133.77(14)
N(2)-C(3)	1.341(3)	C(2)-N(1)-C(5)	119.0(2)
N(2)-C(12)	1.456(3)	C(2)-N(1)-Ni(1)	115.20(18)
N(3)-C(11)	1.337(4)	C(5)-N(1)-Ni(1)	125.57(16)
N(3)-C(7)	1.340(4)	C(3)-N(2)-C(12)	119.8(2)
N(4)-C(14)	1.331(4)	C(3)-N(2)-Ni(1)	115.33(18)
N(4)-C(18)	1.338(4)	C(12)-N(2)-Ni(1)	124.67(17)
C(1)-C(2)	1.505(4)	C(11)-N(3)-C(7)	117.0(3)
C(2)-C(3)	1.416(4)	C(14)-N(4)-C(18)	116.6(3)
C(3)-C(4)	1.501(4)	N(1)-C(2)-C(3)	114.1(2)
C(5)-C(6)	1.517(4)	N(1)-C(2)-C(1)	121.8(2)
C(6)-C(7)	1.497(4)	C(3)-C(2)-C(1)	124.2(2)
C(7)-C(8)	1.369(4)	N(2)-C(3)-C(2)	113.5(2)
C(8)-C(9)	1.384(4)	N(2)-C(3)-C(4)	122.2(2)
C(9)-C(10)	1.371(5)	C(2)-C(3)-C(4)	124.3(2)
C(10)-C(11)	1.358(5)	N(1)-C(5)-C(6)	112.4(2)
C(12)-C(13)	1.498(4)	C(7)-C(6)-C(5)	111.0(2)
C(13)-C(14)	1.499(4)	N(3)-C(7)-C(8)	122.5(3)
C(14)-C(15)	1.383(4)	N(3)-C(7)-C(6)	115.5(3)
C(15)-C(16)	1.372(5)	C(8)-C(7)-C(6)	122.0(3)
C(16)-C(17)	1.362(5)	C(7)-C(8)-C(9)	119.2(3)
C(17)-C(18)	1.355(5)	C(10)-C(9)-C(8)	118.5(3)
		C(11)-C(10)-C(9)	118.7(3)
		N(3)-C(11)-C(10)	124.1(3)
		N(2)-C(12)-C(13)	112.0(2)
		C(12)-C(13)-C(14)	112.0(2)
		N(4)-C(14)-C(15)	122.3(3)
		N(4)-C(14)-C(13)	116.9(3)
		C(15)-C(14)-C(13)	120.8(3)
		C(16)-C(15)-C(14)	119.1(3)
		C(17)-C(16)-C(15)	119.2(4)
		C(18)-C(17)-C(16)	118.1(3)
		N(4)-C(18)-C(17)	124.8(4)



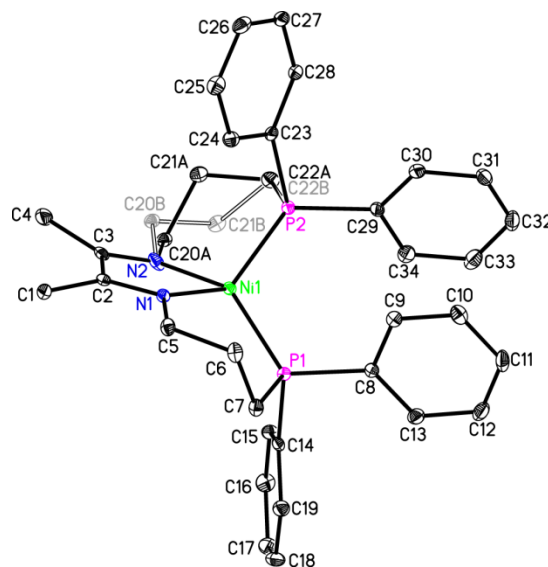
**Table S3.** Metrical parameters determined for ( $\text{Ph}_2\text{PEtDI}$ )Ni.

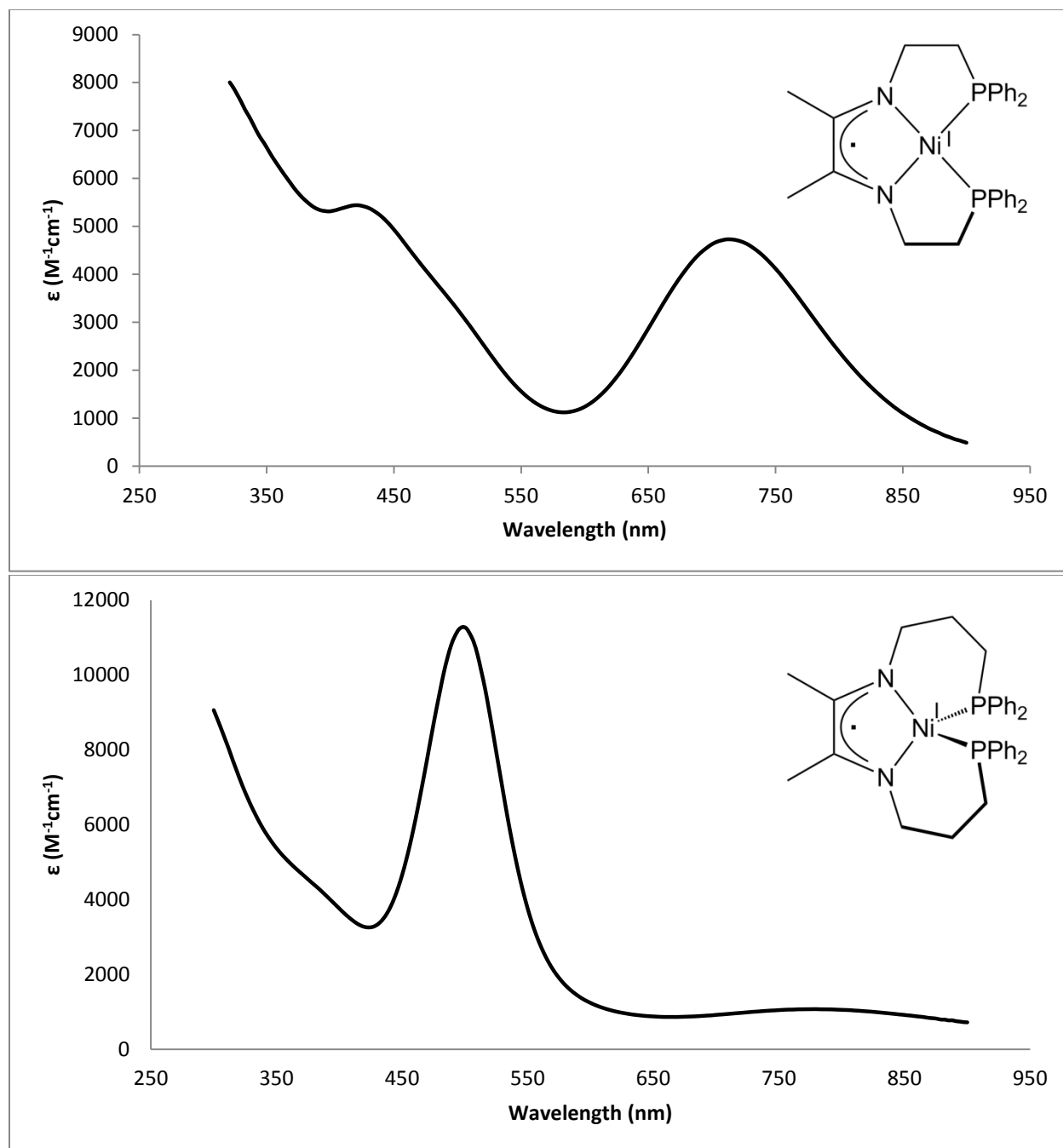
Ni(1)-N(2)	1.885(2)	N(2)-Ni(1)-N(1)	83.77(10)	C(15)-C(14)-C(13)	120.9(3)
Ni(1)-N(1)	1.896(2)	N(2)-Ni(1)-P(2)	85.13(7)	C(14)-C(15)-C(16)	119.7(3)
Ni(1)-P(2)	2.1283(8)	N(1)-Ni(1)-P(2)	149.02(7)	C(17)-C(16)-C(15)	120.1(3)
Ni(1)-P(1)	2.1290(8)	N(2)-Ni(1)-P(1)	149.37(7)	C(16)-C(17)-C(18)	120.2(3)
P(1)-C(7)	1.817(3)	N(1)-Ni(1)-P(1)	85.40(8)	C(17)-C(18)-C(13)	120.8(3)
P(1)-C(6)	1.826(3)	P(2)-Ni(1)-P(1)	117.15(3)	N(2)-C(19)-C(20)	108.9(2)
P(1)-C(13)	1.840(3)	C(7)-P(1)-C(6)	106.64(15)	C(19)-C(20)-P(2)	104.18(18)
P(2)-C(27)	1.819(3)	C(7)-P(1)-C(13)	101.54(13)	C(26)-C(21)-C(22)	118.3(2)
P(2)-C(21)	1.835(3)	C(6)-P(1)-C(13)	100.81(12)	C(26)-C(21)-P(2)	118.36(19)
P(2)-C(20)	1.840(3)	C(7)-P(1)-Ni(1)	127.99(10)	C(22)-C(21)-P(2)	123.2(2)
N(1)-C(2)	1.360(4)	C(6)-P(1)-Ni(1)	99.96(10)	C(23)-C(22)-C(21)	120.4(3)
N(1)-C(5)	1.469(3)	C(13)-P(1)-Ni(1)	116.40(10)	C(22)-C(23)-C(24)	120.8(3)
N(2)-C(3)	1.373(3)	C(27)-P(2)-C(21)	101.91(12)	C(25)-C(24)-C(23)	119.6(3)
N(2)-C(19)	1.466(3)	C(27)-P(2)-C(20)	108.71(12)	C(24)-C(25)-C(26)	120.0(3)
C(1)-C(2)	1.503(4)	C(21)-P(2)-C(20)	99.43(12)	C(21)-C(26)-C(25)	120.8(2)
C(2)-C(3)	1.388(4)	C(27)-P(2)-Ni(1)	127.27(9)	C(28)-C(27)-C(32)	118.3(2)
C(3)-C(4)	1.506(4)	C(21)-P(2)-Ni(1)	116.62(9)	C(28)-C(27)-P(2)	123.1(2)
C(5)-C(6)	1.522(4)	C(20)-P(2)-Ni(1)	99.35(8)	C(32)-C(27)-P(2)	118.5(2)
C(7)-C(12)	1.384(4)	C(2)-N(1)-C(5)	118.8(2)	C(27)-C(28)-C(29)	120.4(3)
C(7)-C(8)	1.392(4)	C(2)-N(1)-Ni(1)	113.36(18)	C(30)-C(29)-C(28)	120.9(3)
C(8)-C(9)	1.393(5)	C(5)-N(1)-Ni(1)	122.70(19)	C(31)-C(30)-C(29)	119.3(3)
C(9)-C(10)	1.368(6)	C(3)-N(2)-C(19)	119.0(2)	C(30)-C(31)-C(32)	120.6(3)
C(10)-C(11)	1.364(6)	C(3)-N(2)-Ni(1)	112.81(19)	C(31)-C(32)-C(27)	120.5(3)
C(11)-C(12)	1.374(4)	C(19)-N(2)-Ni(1)	122.84(16)		
C(13)-C(14)	1.387(4)	N(1)-C(2)-C(3)	113.8(2)		
C(13)-C(18)	1.390(4)	N(1)-C(2)-C(1)	120.8(3)		
C(14)-C(15)	1.376(4)	C(3)-C(2)-C(1)	125.3(3)		
C(15)-C(16)	1.380(5)	N(2)-C(3)-C(2)	114.2(3)		
C(16)-C(17)	1.365(5)	N(2)-C(3)-C(4)	120.4(3)		
C(17)-C(18)	1.375(4)	C(2)-C(3)-C(4)	125.4(3)		
C(19)-C(20)	1.529(3)	N(1)-C(5)-C(6)	108.6(2)		
C(21)-C(26)	1.388(3)	C(5)-C(6)-P(1)	105.74(19)		
C(21)-C(22)	1.394(3)	C(12)-C(7)-C(8)	118.1(3)		
C(22)-C(23)	1.377(4)	C(12)-C(7)-P(1)	117.9(2)		
C(23)-C(24)	1.380(4)	C(8)-C(7)-P(1)	124.1(3)		
C(24)-C(25)	1.372(4)	C(10)-C(9)-C(8)	120.1(4)		
C(25)-C(26)	1.391(4)	C(7)-C(8)-C(9)	119.9(4)		
C(27)-C(28)	1.382(4)	C(11)-C(10)-C(9)	120.8(4)		
C(27)-C(32)	1.398(4)	C(10)-C(11)-C(12)	119.3(4)		
C(28)-C(29)	1.384(4)	C(11)-C(12)-C(7)	121.8(3)		
C(29)-C(30)	1.373(4)	C(14)-C(13)-C(18)	118.2(3)		
C(30)-C(31)	1.372(4)	C(14)-C(13)-P(1)	118.7(2)		
C(31)-C(32)	1.381(4)	C(18)-C(13)-P(1)	123.0(2)		



**Table S4.** Metrical parameters determined for ( $\text{Ph}_2\text{PPrDI}$ )Ni.

Ni(1)-N(2)	1.9250(18)	N(2)-Ni(1)-N(1)	81.88(7)	C(17)-C(16)-C(15)	119.8(2)
Ni(1)-N(1)	1.9369(17)	N(2)-Ni(1)-P(1)	139.80(6)	C(16)-C(17)-C(18)	120.2(2)
Ni(1)-P(1)	2.1343(6)	N(1)-Ni(1)-P(1)	99.09(5)	C(17)-C(18)-C(19)	119.9(2)
Ni(1)-P(2)	2.1345(6)	N(2)-Ni(1)-P(2)	94.14(5)	C(18)-C(19)-C(14)	120.7(2)
P(1)-C(14)	1.829(2)	N(1)-Ni(1)-P(2)	130.67(5)	N(2)-C(20A)-C(21A)	111.7(4)
P(1)-C(8)	1.839(2)	P(1)-Ni(1)-P(2)	113.58(2)	N(2)-C(20B)-C(21B)	107.5(7)
P(1)-C(7)	1.846(2)	C(14)-P(1)-C(8)	102.07(9)	C(22A)-C(21A)-C(20A)	112.4(3)
P(2)-C(29)	1.834(2)	C(14)-P(1)-C(7)	102.66(10)	C(21A)-C(22A)-P(2)	112.90(18)
P(2)-C(23)	1.842(2)	C(8)-P(1)-C(7)	99.19(9)	C(24)-C(23)-C(28)	118.67(19)
P(2)-C(22A)	1.847(2)	C(14)-P(1)-Ni(1)	119.05(7)	C(24)-C(23)-P(2)	117.84(15)
N(1)-C(2)	1.340(3)	C(8)-P(1)-Ni(1)	121.44(7)	C(28)-C(23)-P(2)	123.47(16)
N(1)-C(5)	1.465(3)	C(7)-P(1)-Ni(1)	109.27(7)	C(25)-C(24)-C(23)	120.8(2)
N(2)-C(3)	1.341(3)	C(29)-P(2)-C(23)	102.90(9)	C(24)-C(25)-C(26)	120.2(2)
N(2)-C(20B)	1.458(13)	C(29)-P(2)-C(22A)	99.98(10)	C(27)-C(26)-C(25)	119.6(2)
N(2)-C(20A)	1.497(6)	C(23)-P(2)-C(22A)	101.45(10)	C(26)-C(27)-C(28)	120.4(2)
C(1)-C(2)	1.504(3)	C(29)-P(2)-Ni(1)	124.15(7)	C(27)-C(28)-C(23)	120.2(2)
C(2)-C(3)	1.414(3)	C(23)-P(2)-Ni(1)	113.12(7)	C(30)-C(29)-C(34)	118.2(2)
C(3)-C(4)	1.510(3)	C(22A)-P(2)-Ni(1)	112.25(7)	C(30)-C(29)-P(2)	124.02(17)
C(5)-C(6)	1.515(3)	C(2)-N(1)-C(5)	116.58(17)	C(34)-C(29)-P(2)	117.74(16)
C(6)-C(7)	1.529(3)	C(2)-N(1)-Ni(1)	114.15(14)	C(29)-C(30)-C(31)	120.3(2)
C(8)-C(13)	1.391(3)	C(5)-N(1)-Ni(1)	128.24(13)	C(32)-C(31)-C(30)	120.8(2)
C(8)-C(9)	1.394(3)	C(3)-N(2)-C(20B)	107.7(4)	C(31)-C(32)-C(33)	119.5(2)
C(9)-C(10)	1.382(3)	C(3)-N(2)-C(20A)	123.5(3)	C(32)-C(33)-C(34)	120.2(2)
C(10)-C(11)	1.380(3)	C(3)-N(2)-Ni(1)	113.91(15)	C(33)-C(34)-C(29)	121.0(2)
C(11)-C(12)	1.377(3)	C(20B)-N(2)-Ni(1)	131.6(5)		
C(12)-C(13)	1.386(3)	C(20A)-N(2)-Ni(1)	121.6(2)		
C(14)-C(15)	1.386(3)	N(1)-C(2)-C(3)	114.09(19)		
C(14)-C(19)	1.396(3)	N(1)-C(2)-C(1)	122.10(19)		
C(15)-C(16)	1.385(3)	C(3)-C(2)-C(1)	123.75(19)		
C(16)-C(17)	1.380(3)	N(2)-C(3)-C(2)	114.41(19)		
C(17)-C(18)	1.381(3)	N(2)-C(3)-C(4)	122.1(2)		
C(18)-C(19)	1.385(3)	C(2)-C(3)-C(4)	123.4(2)		
C(20A)-C(21A)	1.525(7)	N(1)-C(5)-C(6)	113.68(16)		
C(20B)-C(21B)	1.508(13)	C(5)-C(6)-C(7)	112.69(17)		
C(21A)-C(22A)	1.503(4)	C(6)-C(7)-P(1)	110.10(15)		
C(23)-C(24)	1.392(3)	C(13)-C(8)-C(9)	118.44(19)		
C(23)-C(28)	1.397(3)	C(13)-C(8)-P(1)	123.95(16)		
C(24)-C(25)	1.383(3)	C(9)-C(8)-P(1)	117.57(15)		
C(25)-C(26)	1.384(3)	C(10)-C(9)-C(8)	120.8(2)		
C(26)-C(27)	1.383(3)	C(11)-C(10)-C(9)	120.1(2)		
C(27)-C(28)	1.388(3)	C(12)-C(11)-C(10)	119.7(2)		
C(29)-C(30)	1.389(3)	C(11)-C(12)-C(13)	120.6(2)		
C(29)-C(34)	1.394(3)	C(12)-C(13)-C(8)	120.4(2)		
C(30)-C(31)	1.391(3)	C(15)-C(14)-C(19)	118.35(19)		
C(31)-C(32)	1.368(4)	C(15)-C(14)-P(1)	117.92(15)		
C(32)-C(33)	1.381(4)	C(19)-C(14)-P(1)	123.72(16)		
C(33)-C(34)	1.381(3)	C(16)-C(15)-C(14)	121.1(2)		



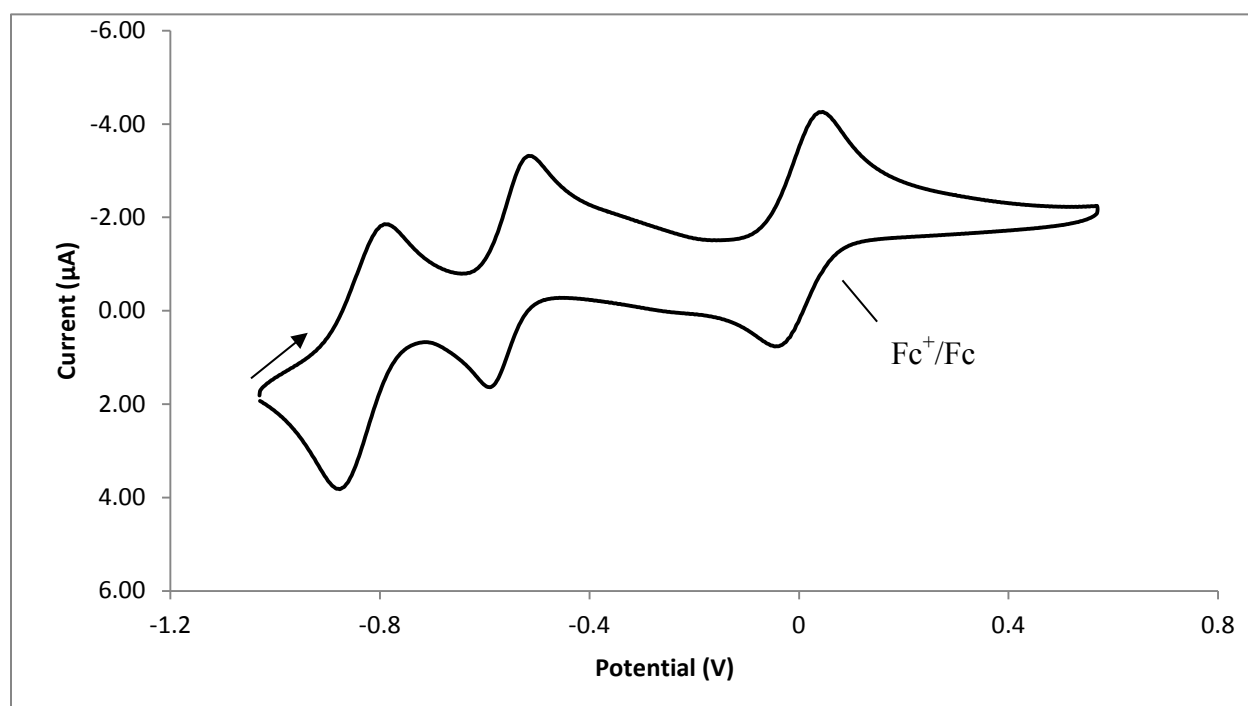


**Figure S20.** The UV-visible spectrum of **3** (top) and **4** (bottom) in toluene.

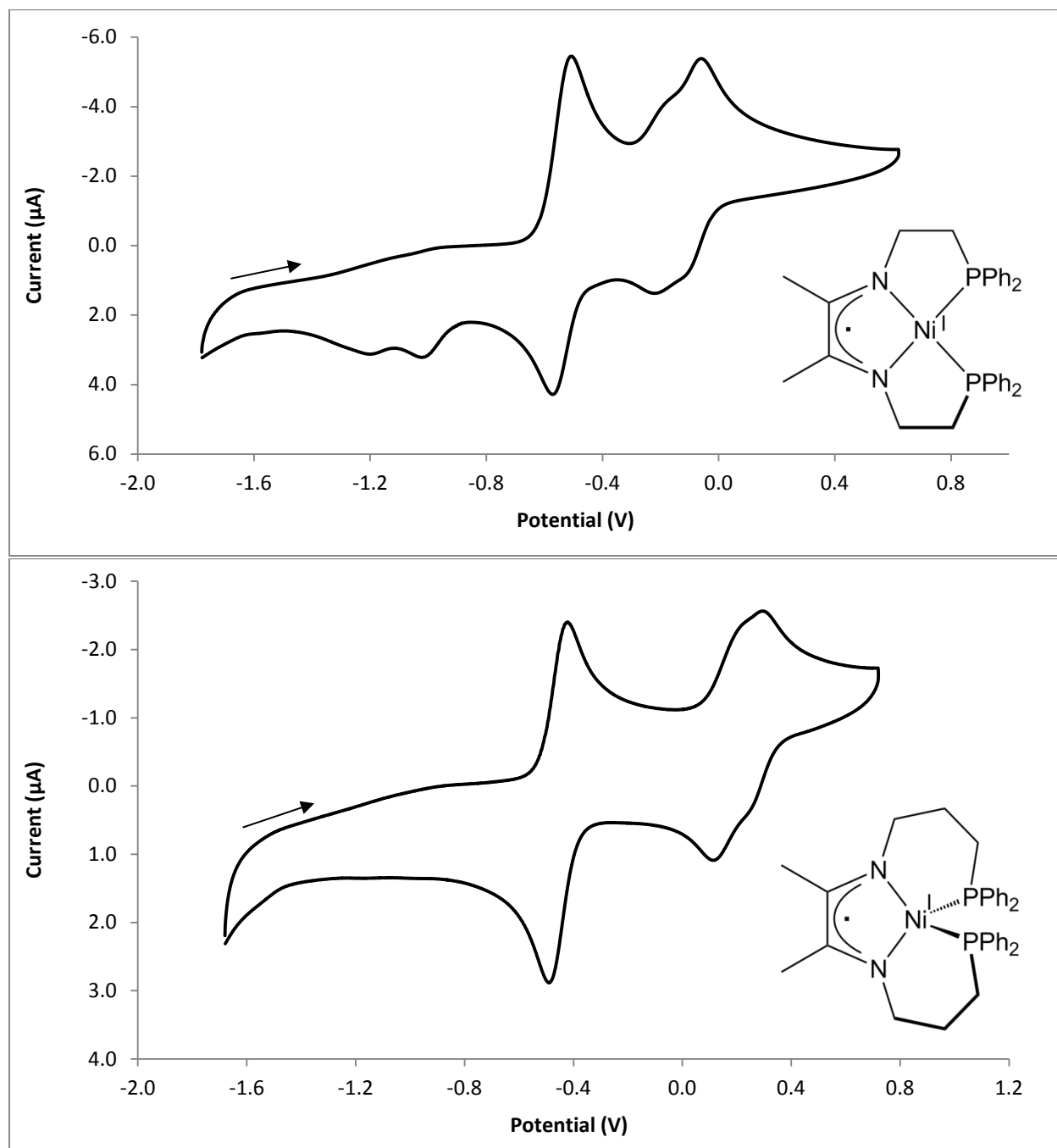


Complex	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )
<b>3</b>	422	5450
	714	4750
<b>4</b>	499	11310
	776	1080

**Table S5.** The wavelengths of maximum absorption ( $\lambda_{\text{max}}$ ) and extinction coefficient ( $\epsilon$ ) for each complex analyzed by UV-visible spectroscopy.



**Figure S21.** Cyclic voltammogram of **2** relative to Fc<sup>+</sup>/Fc (internal standard) in tetrahydrofuran (scan rate = 25 mV/s).



**Figure S22.** Cyclic voltammograms of **3** (top) and **4** (bottom) relative to  $\text{Fc}^+/\text{Fc}$  in acetonitrile (scan rate = 50 mV/s).