

Supporting Information for:

## Study and Modular Synthesis of Unsymmetrical Bis(phosphino)pyrrole Ligands

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## I. General Information

**General Considerations.** All reactions were carried out in a nitrogen-filled MBraun LABstar Pro glovebox unless otherwise stated. All glassware was oven-dried overnight at greater than 110 °C and cooled under vacuum prior to use. Anhydrous hexane, pentane, and dichloroethane (DCE) were purchased from Aldrich and stored over 3 Å molecular sieves prior to use. All other solvents were collected from a Glass Contour Solvent Purification System, degassed, and stored over 3 Å molecular sieves in a glovebox. Dichloromethane-*d*<sub>2</sub> (CD<sub>2</sub>Cl<sub>2</sub>) was purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves. Lithium 2-(diphenylphosphino)pyrrolide<sup>1</sup> and 1-(diphenylphosphino)-2-(diisopropylphosphino)benzene<sup>2</sup> were prepared according to literature procedures. Tetrabutylammonium hexafluorophosphate ([*n*-Bu<sub>4</sub>N][PF<sub>6</sub>]) for electrochemical studies was recrystallized three times from ethanol. Filtrations were performed using PTFE syringe filters with 0.45 μm pores. The chlorophosphines *i*-Pr<sub>2</sub>PCl (Fisher or Sigma Aldrich), (*o*-tolyl)<sub>2</sub>PCl (Strem), (EtO)<sub>2</sub>PCl (Fisher), Cy<sub>2</sub>PCl (Acros), Ph(*t*-Bu)PCl (Strem), (2,4,6-trimethylphenyl)<sub>2</sub>PCl (Sigma-Aldrich), (*p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCl (Alfa Aesar), (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCl (Alfa Aesar), (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)PCl (Fisher), (MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>PCl, *t*-Bu<sub>2</sub>PCl (Alfa Aesar), and Ph<sub>2</sub>PCl (Aldrich) were used as received from their respective vendors. The transition metal complexes (DME)NiCl<sub>2</sub>, CuCl, Pd(COD)Cl<sub>2</sub>, Pt(COD)Cl<sub>2</sub>, (TMEDA)Ni(*o*-tolyl)Cl, and (Ph<sub>3</sub>P)<sub>2</sub>Ni(CO)<sub>2</sub> were used as received from Strem Chemicals. For catalytic studies, furfurylamine (Fisher) was distilled from CaH<sub>2</sub> and stored over 3 Å molecular sieves, and 4-chlorobenzonitrile (Oakwood) and ferrocene (99%, Strem) were used as received.

**Spectroscopy.** <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>19</sup>F{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} spectra were collected on Bruker AV-300, AV-400, and AV-500 NMR spectrometers at ambient temperature. <sup>1</sup>H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the solvent (5.32 ppm for CDHCl<sub>2</sub>). <sup>13</sup>C NMR spectra were referenced relative to the solvent signal (53.84 ppm for CD<sub>2</sub>Cl<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>H} were referenced using the absolute reference function of the Mnova 9.0.1 NMR software package. Infrared spectra were recorded on a Nicolet iS10 FT-IR spectrometer. UV-vis data were acquired using a Cary 60 UV-vis spectrophotometer.

**X-ray Crystallography.** X-ray crystallographic data were collected on a Rigaku Oxford Diffraction Supernova diffractometer. Crystal samples were handled under immersion oil and quickly transferred to a cold nitrogen stream.

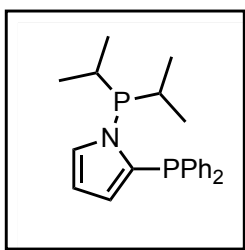
**Electrochemistry.** Electrochemical experiments were performed inside a glovebox in tetrahydrofuran (THF) with 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] and 1 mM analyte. A CH Instruments 660E potentiostat was used with a 3 mm glassy carbon working electrode and a platinum wire auxiliary electrode. The silver wire reference electrode was referenced to the ferrocene-ferrocenium couple.

**Elemental Analysis.** Elemental analyses were performed by Midwest Microlab, LLC.

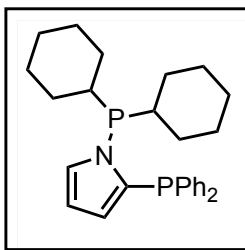
**Mass Spectrometry.** High resolution mass spectrometric data were collected using a Shimadzu IT-TOF spectrometer.

## II. Synthesis and Characterization of Bis(phosphino)pyrrole Ligands

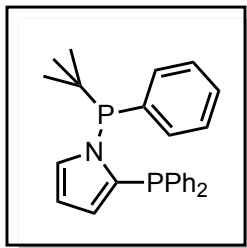
**General Procedure:** In a nitrogen-filled glovebox, lithium 2-(diphenylphosphino)pyrrolide (128.6 mg, 0.500 mmol, 1.0 equiv.) was dissolved in diethyl ether (7 mL). Chlorophosphine (0.500 mmol, 1.0 equiv.) was added as a solid or *via* syringe. The reaction mixture was stirred for the indicated amount of time at 23 °C in a 20-mL scintillation vial and then filtered through a syringe filter. The desired compound was then isolated by crystallization or concentration. *Note:* For some reactions that yielded crystalline material, crystallization was unnecessary to achieve spectroscopic purity but was performed for the sake of thoroughness.



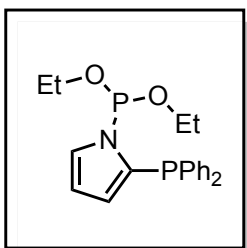
**2-diphenylphosphino-1-diisopropylphosphino-pyrrole (L1).** The general procedure was followed using *i*-Pr<sub>2</sub>PCl (80 μL, 0.502 mmol, 1.0 equiv.) and with stirring for 16 h. The product was crystallized from pentane at -35 °C to yield colorless crystals (142.8 mg, 0.389 mmol). The solution yielded additional crystals upon cooling a second time (16.9 mg, 0.046 mmol; Combined yield: 159.7 mg, 0.435 mmol, 87% yield). *Note:* The reaction can be run for as little as four hours without compromising product yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.35 – 7.26 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 7.09 – 7.05 (m, 1H, pyrrole), 6.34 – 6.30 (m, 1H, pyrrole), 5.82 – 5.77 (m, 1H, pyrrole), 2.23 – 2.13 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.07 (dd, *J* = 16.5, 7.0 Hz, 6H, CH<sub>3</sub>), 0.86 (dd, *J* = 11.6, 7.0 Hz, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 138.6 (dd, *J* = 9.5, 4.2 Hz), 136.7 (d, *J* = 23.0 Hz), 134.2 (d, *J* = 19.8 Hz), 128.9, 128.7 (d, *J* = 6.9 Hz), 127.5, 119.7, 112.6, 28.2 (dd, *J* = 16.3, 2.8 Hz), 19.4 – 18.5 (m); <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 62.6 (d, *J* = 111.6 Hz), -29.1 (d, *J* = 109.0 Hz). IR (ATR, cm<sup>-1</sup>): 3055, 2967, 2951, 2864, 1434, 1159, 746, 726, 699; HRMS (ESI, TOF): exact mass calcd for C<sub>22</sub>H<sub>28</sub>NP<sub>2</sub> [M + H]<sup>+</sup> 368.1691, found 368.1676.



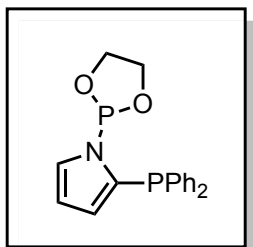
**2-diphenylphosphino-1-dicyclohexylphosphino-pyrrole (L2).** The general procedure was followed using Cy<sub>2</sub>PCl (110 μL, 0.498 mmol, 1.0 equiv.) and with stirring for 18 h. The product was crystallized from diethyl ether at -35 °C to yield colorless crystals (125.3 mg, 0.280 mmol, 56% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.35 – 7.23 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 7.08 – 7.03 (m, 1H, pyrrole), 6.32 – 6.26 (m, 1H, pyrrole), 5.75 (br s, 1H, pyrrole), 1.96 (br s, 2H, C<sub>6</sub>H<sub>11</sub>), 1.85 – 1.70 (m, 4H, C<sub>6</sub>H<sub>11</sub>), 1.70 – 1.56 (m, 4H, C<sub>6</sub>H<sub>11</sub>), 1.42 (d, *J* = 13.0 Hz, 2H, C<sub>6</sub>H<sub>11</sub>), 1.34 – 1.22 (m, 2H, C<sub>6</sub>H<sub>11</sub>), 1.22 – 1.04 (m, 6H, C<sub>6</sub>H<sub>11</sub>), 1.04 – 0.92 (m, 2H, C<sub>6</sub>H<sub>11</sub>); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 138.7 (dd, *J* = 9.6, 4.3 Hz), 136.8, 134.2 (d, *J* = 19.9 Hz), 128.9, 128.7 (d, *J* = 6.8 Hz), 127.7, 119.5, 112.4, 37.8 (dd, *J* = 16.7, 2.9 Hz), 29.6 (d, *J* = 19.4 Hz), 28.7 (d, *J* = 7.3 Hz), 27.4 – 27.1 (m), 26.8 (*Note:* An additional aliphatic signal was observed due to hindered motion<sup>3</sup>); <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 55.3 (d, *J* = 112 Hz), -29.2 (d, *J* = 112 Hz); IR (ATR, cm<sup>-1</sup>): 2925, 1433, 1162, 1062, 726, 695; HRMS (ESI, TOF): exact mass calcd for C<sub>28</sub>H<sub>36</sub>NP<sub>2</sub> [M + H]<sup>+</sup> 448.2317, found 448.2401. The difference between calculated and found mass exceeded 5 ppm despite multiple attempts.



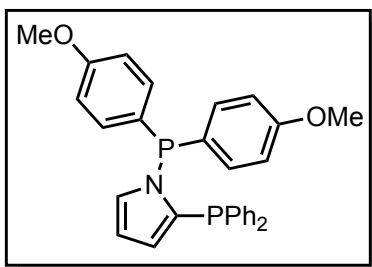
**2-diphenylphosphino-1-(phenyl, *t*-butyl)phosphino pyrrole (L3).** The reaction was performed following the general procedure, using Ph(*t*-Bu)PCl (94  $\mu$ L, 0.498 mmol, 1.0 equiv.) and with stirring for 18 h. Following crystallization from diethyl ether at  $-35$   $^{\circ}$ C, the product was isolated as a colorless solid (157.1 mg, 0.378 mmol, 76% yield).  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.38 – 7.25 (m, 11H,  $\text{C}_6\text{H}_5$  and pyrrole), 7.25 – 7.16 (m, 5H,  $\text{C}_6\text{H}_5$ ), 6.39 – 6.35 (m, 1H, pyrrole), 5.82 (td,  $J = 3.1, 1.4$  Hz, 1H, pyrrole), 1.13 (d,  $J = 13.6$  Hz, 9H,  $\text{C}(\text{CH}_3)_3$ );  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  138.7 – 138.2 (m), 137.7 – 137.0 (m), 134.5 (d,  $J = 20.4$  Hz), 133.8 (d,  $J = 19.8$  Hz), 131.8 (d,  $J = 20.0$  Hz), 129.5 (d,  $J = 7.7$  Hz), 129.1 (d,  $J = 1.9$  Hz), 128.9 – 128.5 (m, 3 superimposed signals), 119.9 (d,  $J = 5.0$  Hz), 113.0, 34.7 (dd,  $J = 20.1, 2.7$  Hz), 28.2 (d,  $J = 16.6$  Hz);  $^{31}\text{P NMR}$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  58.9 (d,  $J = 122.9$  Hz),  $-28.3$  (d,  $J = 123.1$  Hz); **IR** (ATR,  $\text{cm}^{-1}$ ): 3051, 2864, 1485, 1434, 1362, 1158, 1092, 1060, 738, 692; **HRMS** (ESI, TOF): exact mass calcd for  $\text{C}_{26}\text{H}_{28}\text{NP}_2$  [ $\text{M} + \text{H}$ ] $^+$  416.1691, found 416.1701.



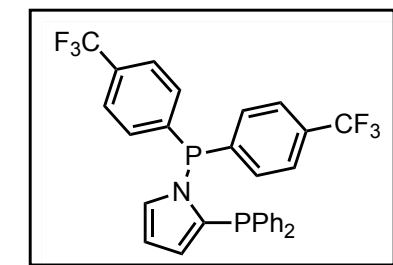
**2-diphenylphosphino-1-diethoxyphosphino pyrrole (L4).** The reaction was performed using a modification of the general procedure. Lithium 2-(diphenylphosphino)pyrrolide (128.6 mg, 0.500 mmol, 1.0 equiv.) was transferred to a Schlenk bomb using diethyl ether (7 mL). The bomb was removed from the glovebox and affixed to the Schlenk line.  $(\text{EtO})_2\text{PCl}$  (94  $\mu$ L, 0.65 mmol, 1.3 equiv.) was added and the reaction mixture was stirred for 17 h at which point the bomb was returned to the glovebox. The reaction mixture was filtered *via* syringe filter and the resulting solution was concentrated to a clear, colorless oil (172.6 mg, 0.465 mmol, 93% yield). *Note:* The reaction was performed on a Schlenk line due to the volatility of diethyl chlorophosphite.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.38 – 7.35 (m, 1H, pyrrole), 7.35 – 7.29 (m, 10H,  $\text{C}_6\text{H}_5$ ), 6.31 – 6.26 (m, 1H, pyrrole), 6.02 – 5.59 (m, 1H), 3.87 – 3.77 (m, 2H,  $\text{CH}_2$ ), 3.71 – 3.61 (m, 2H,  $\text{CH}_2$ ), 1.11 (t,  $J = 7.1$ , 6H,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  138.0 (dd,  $J = 7.4, 4.0$  Hz), 133.9 (d,  $J = 19.7$  Hz), 131.3 (dd,  $J = 20.3, 2.2$  Hz), 129.1, 128.8 (d,  $J = 7.1$  Hz), 125.1 (d,  $J = 3.4$  Hz), 121.5, 111.5 (d,  $J = 1.8$  Hz), 61.2 (d,  $J = 12.8$  Hz), 16.8 (d,  $J = 5.5$  Hz);  $^{31}\text{P NMR}$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  123.9 (d,  $J = 122.7$  Hz),  $-30.7$  (d,  $J = 122.9$  Hz). **IR** (ATR,  $\text{cm}^{-1}$ ): 2983, 1156, 1029, 743, 694; **HRMS** (ESI, TOF): The molecular ion was not observed, potentially due to hydrolysis.



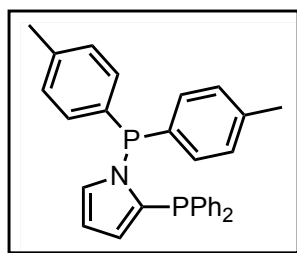
**2-diphenylphosphino-1-(1,3,2-dioxaphospholane)pyrrole (L5).** The reaction was performed following the general procedure, using ethylene chlorophosphite (44.5  $\mu$ L, 0.500 mmol, 1.0 equiv.) and with stirring for 25 h. The product was isolated as a clear, colorless oil following concentration. (163.8 mg, 0.480 mmol, 96% yield). *Note:* Approx. 1% by mass  $\text{Et}_2\text{O}$  is present despite prolonged exposure to vacuum.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.40 – 7.28 (m, 10H,  $\text{C}_6\text{H}_5$ ), 7.01 (tt,  $J = 2.9, 1.5$  Hz, 1H, pyrrole), 6.29 – 6.26 (m, 1H, pyrrole), 6.03 – 6.00 (m, 1H, pyrrole), 4.20 – 4.02 (m, 4H,  $\text{C}_2\text{H}_4\text{O}_2$ );  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  137.7 (dd,  $J = 6.6, 4.0$  Hz), 133.8 (d,  $J = 19.5$  Hz), 131.4 (dd,  $J = 15.8, 2.4$  Hz), 129.2, 128.9 (d,  $J = 7.2$  Hz), 124.7 (d,  $J = 3.7$  Hz), 122.0, 112.1 (d,  $J = 1.8$  Hz), 65.3 (d,  $J = 8.7$  Hz);  $^{31}\text{P NMR}$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  125.1 (d,  $J = 120.4$  Hz),  $-30.3$  (d,  $J = 121.4$  Hz); **IR** (ATR,  $\text{cm}^{-1}$ ): 3051, 2975, 2911, 1426, 1155, 1005, 921, 730; **HRMS** (ESI, TOF): exact mass calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}_2\text{P}_2$  [ $\text{M} + \text{H}$ ] $^+$  342.0807, found 342.0789.



**2-diphenylphosphino-1-bis(4-methoxyphenyl)phosphino pyrrole (L6).** The reaction was performed following the general procedure using bis(4-methoxyphenyl)chlorophosphine (140.3 mg, 0.500 mmol, 1.0 equiv.) and with stirring for 24 h. Residual chlorophosphine was dissolved in additional diethyl ether (3 mL) to ensure complete transfer. The product was isolated as a colorless solid (233.9, 0.472 mmol, 94% yield) following concentration of the diethyl ether solution.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.36 – 7.24 (m, 10H,  $\text{C}_6\text{H}_5$ ), 7.16 – 7.01 (m, 4H,  $\text{C}_6\text{H}_4\text{Ome}$ ), 6.91 – 6.83 (m, 4H,  $\text{C}_6\text{H}_4\text{Ome}$ ), 6.72 (tt,  $J = 2.7, 1.4$  Hz, 1H, pyrrole), 6.26 (m, 1H, pyrrole), 5.89 – 5.86 (m, 1H, pyrrole), 3.80 (s, 6H,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  161.5 (MeOC), 138.1 (dd,  $J = 8.6, 4.3$  Hz), 135.1 (d,  $J = 24.9$  Hz), 134.6 – 133.9 (m, overlapping aryl signals), 133.3 (d,  $J = 18.8$  Hz), 129.2 – 128.1 (m, overlapping aryl signals), 120.6 (d,  $J = 3.9$  Hz), 114.7 (d,  $J = 7.5$  Hz), 112.9, 55.8;  $^{31}\text{P NMR}$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  38.9 (d,  $J = 113.2$  Hz), -29.0 (d,  $J = 113.1$  Hz); **IR** (ATR,  $\text{cm}^{-1}$ ): 1591, 1499, 1245, 1157, 1093, 1028, 823, 698; **HRMS** (ESI, TOF): exact mass calcd for  $\text{C}_{30}\text{H}_{28}\text{NO}_2\text{P}_2$  [ $\text{M} + \text{H}$ ] $^+$  496.1590, found 496.1614.



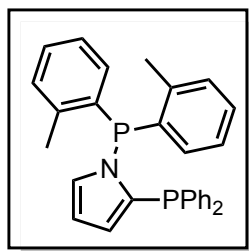
**2-diphenylphosphino-1-bis(4-trifluoromethylphenyl)phosphino pyrrole (L7).** The reaction was performed following the general procedure, using bis(4-trifluorophenyl)chlorophosphine (125  $\mu\text{L}$ , 0.499 mmol, 1.0 equiv.) and with stirring for 13 h. The product was isolated as a colorless solid (281.3 mg, 0.492 mmol, 98% yield) following evaporation from filtered diethyl ether solution and then concentration from a pentane solution.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.65 – 7.56 (m, 4H,  $\text{C}_6\text{H}_4\text{CF}_3$ ), 7.40 – 7.18 (m, 14H,  $\text{C}_6\text{H}_4\text{CF}_3$  and  $\text{C}_6\text{H}_5$ ), 6.69 (tt,  $J = 2.7, 1.4$  Hz, 1H, pyrrole), 6.36 – 6.33 (m, 1H, pyrrole), 6.00 – 5.97 (m, 1H, pyrrole).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  141.4 (d,  $J = 16.9$  Hz), 137.3 (dd,  $J = 8.1, 4.2$  Hz), 136.5 (d,  $J = 25.6$  Hz), 134.2 (d,  $J = 20.0$  Hz), 133.1 (d,  $J = 21.4$  Hz), 132.2 (q,  $J = 32.5$  Hz), 129.4, 129.0 (d,  $J = 6.9$  Hz), 126.2 – 125.8 (m, two superimposed resonances), 123.2, 121.4 (d,  $J = 4.5$  Hz), 114.3;  $^{31}\text{P NMR}$  (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  36.0 (d,  $J = 110.1$  Hz), -29.1 (d,  $J = 109.6$  Hz);  $^{19}\text{F NMR}$  (282 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -63.3; **IR** (ATR,  $\text{cm}^{-1}$ ): 1608, 1436, 1320, 1162, 1058, 745, 692; **HRMS** (ESI, TOF): exact mass calcd for  $\text{C}_{30}\text{H}_{22}\text{F}_6\text{NP}_2$  [ $\text{M} + \text{H}$ ] $^+$  572.1126, found 572.1200. The difference between calculated and found mass exceeded 5 ppm despite multiple attempts.



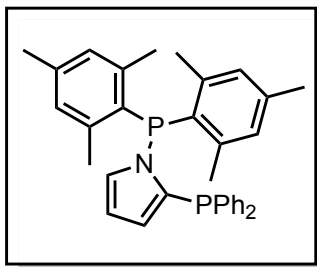
**2-diphenylphosphino-1-bis(4-methylphenyl)phosphino pyrrole (L8).** The reaction was performed following the general procedure, using bis(4-methylphenyl)chlorophosphine (113  $\mu\text{L}$ , 0.500 mmol, 1.0 equiv.) and with stirring for 13 h. The product was isolated as a colorless solid (193.6 mg, 0.418 mmol, 84% yield) following precipitation from pentane at  $-35$   $^\circ\text{C}$ .  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.36 – 7.26 (m, 10H), 7.18 – 7.14 (m, 4H), 7.09 – 7.03 (m, 4H), 6.72 (tt,  $J = 2.8, 1.4$  Hz, 1H), 6.26 (td,  $J = 3.1, 1.2$  Hz, 1H), 5.90 – 5.86 (m, 1H),

2.35 (s, 6H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  140.5, 138.1 (dd,  $J = 8.6, 4.4$  Hz), 135.3 (dd,  $J = 25.5, 1.6$  Hz), 134.1 (d,  $J = 20.0$  Hz), 133.9 (d,  $J = 2.8$  Hz), 132.7 (d,  $J = 21.4$  Hz), 129.83 (d,  $J = 6.9$  Hz), 129.0, 128.8 (d,  $J = 7.1$  Hz), 120.6 (d,  $J = 3.9$  Hz), 113.0 (d,  $J = 1.9$  Hz), 21.6 (*Note*: One

aromatic signal was not observed);  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  39.1 (d,  $J = 112.7$  Hz), -28.89 (d,  $J = 112.1$  Hz); IR (ATR,  $\text{cm}^{-1}$ ): 3047, 2923, 2852, 1434, 1163, 1088, 810, 691; HRMS (ESI, TOF): exact mass calcd for  $\text{C}_{30}\text{H}_{27}\text{NP}_2$   $[\text{M} + \text{H}]^+$  464.1691, found 464.1701.

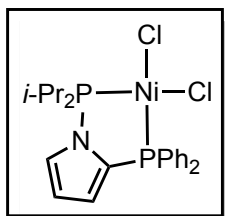


**2-diphenylphosphino-1-di(*o*-tolyl)phosphino pyrrole (L9).** The reaction was performed following the general procedure but with excess chlorophosphine, using (*o*-tolyl) $_2\text{PCl}$  (136.8 mg, 0.550 mmol, 1.1 equiv.) and with stirring for 22 h. The product was crystallized from diethyl ether at  $-35$  °C to yield colorless crystals (142.5 mg, 0.307 mmol, 61% yield). *Note:* Crystallization is essential for isolating spectroscopically pure material.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.36 – 7.24 (m, 12H,  $\text{C}_6\text{H}_5$  and *o*-tolyl), 7.22 – 7.17 (m, 2H, *o*-tolyl), 7.13 (t,  $J = 7.5$  Hz, 2H, *o*-tolyl), 6.68 (ddd,  $J = 7.7, 4.3, 1.3$  Hz, 2H, *o*-tolyl), 6.51 (tt,  $J = 2.8, 1.4$  Hz, 1H, pyrrole), 6.31 – 6.28 (m, 1H, pyrrole), 6.01 – 5.98 (m, 1H, pyrrole), 2.17 (d,  $J = 1.4$  Hz, 6H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  142.3 (d,  $J = 27.8$  Hz), 137.9 (dd,  $J = 8.3, 4.2$  Hz), 135.3 (dd,  $J = 24.1, 2.4$  Hz), 134.9 (dd,  $J = 14.8, 2.9$  Hz), 134.0 (d,  $J = 20.0$  Hz), 132.1 – 131.7 (m), 130.8 (d,  $J = 4.3$  Hz), 130.3, 129.6 (dd,  $J = 7.2, 1.9$  Hz), 129.0, 128.7 (d,  $J = 7.0$  Hz), 126.7, 121.0 (d,  $J = 3.6$  Hz), 113.2 (d,  $J = 1.9$  Hz), 20.9 (d,  $J = 21.0$  Hz).  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  29.3 (d,  $J = 113.9$  Hz), -30.0 (d,  $J = 114.3$  Hz); IR (ATR,  $\text{cm}^{-1}$ ): 2860, 2355, 1434, 1158, 1096, 1060, 738, 692; HRMS (ESI, TOF): exact mass calcd for  $\text{C}_{30}\text{H}_{28}\text{NP}_2$   $[\text{M} + \text{H}]^+$  464.1691, found 464.1672.

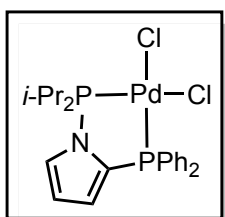


**2-diphenylphosphino-1-dimesityl phosphino pyrrole (L10).** The reaction was performed following the general procedure, using (2,4,6-trimethylphenyl) $_2\text{PCl}$  (152.4 mg, 0.500 mmol, 1.0 equiv.) and with stirring for 18 h. Residual chlorophosphine was dissolved in additional diethyl ether (3 mL) to ensure complete transfer. Additional diethyl ether (10 mL) was used during the filtration step. The product was isolated as a colorless solid following concentration (140.3 mg, 0.270 mmol, 54% yield). The supernatant yielded additional crystals upon cooling a second time (13.9 mg, 0.027 mmol, 5% yield; Combined yield: 154.2 mg, 0.297 mmol, 59% yield). *Note:* The low yield may be attributed in part to the low solubility of the title compound.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.42 – 7.27 (m, 10H,  $\text{C}_6\text{H}_5$ ), 6.82 (d,  $J = 3.2$  Hz, 4H, mesityl), 6.71 – 6.67 (m, 1H, pyrrole), 6.25 – 6.21 (m, 1H, pyrrole), 6.03 – 5.99 (m, 1H, pyrrole), 2.26 (s, 6H, *p*- $\text{CH}_3$ ), 1.91 (d,  $J = 1.6$  Hz, 12H, *o*- $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  142.0 (d,  $J = 18.1$  Hz), 139.7, 138.1 (dd,  $J = 7.9, 5.1$  Hz), 136.3 (dd,  $J = 28.0, 5.0$  Hz), 134.2 (d,  $J = 19.8$  Hz), 133.3 (d,  $J = 18.9$  Hz), 131.4 – 131.0 (m), 130.9 (d,  $J = 3.1$  Hz), 129.0, 128.8 (d,  $J = 6.9$  Hz), 121.4 (t,  $J = 2.8$  Hz), 113.1 (d,  $J = 2.0$  Hz), 21.3 (d,  $J = 16.8$  Hz), 21.2;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  29.4 (d,  $J = 136.0$  Hz), -30.1 (d,  $J = 135.2$  Hz); IR (ATR,  $\text{cm}^{-1}$ ): 2955, 2915, 1608, 1434, 1159, 750, 695; HRMS (ESI, TOF): exact mass calcd for  $\text{C}_{34}\text{H}_{36}\text{NP}_2$   $[\text{M} + \text{H}]^+$  520.2317, found 520.2352. The difference between calculated and found mass exceeded 5 ppm despite multiple attempts.

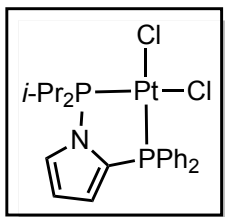
### III. Synthesis and Characterization of Transition Metal Complexes



**(L1)NiCl<sub>2</sub>.** NiCl<sub>2</sub>(DME) (22.0 mg, 0.100 mmol, 1.0 equiv.) was suspended in DCM (1 mL). Ligand **L1** (36.7 mg, 0.100 mmol, 1.0 equiv.) was added dropwise to the suspension using additional DCM (3 mL). The reaction mixture was stirred for 1 h, during which time it became a yellow and homogeneous solution. The reaction mixture was filtered *via* syringe filter and concentrated to an orange solid. The solid was washed with pentane to yield the desired product as an orange, analytically pure solid (46.6 mg, 0.094 mmol, 94% yield). X-ray quality crystals of **(L1)NiCl<sub>2</sub>** were grown from a saturated toluene solution at -35 °C. *Note:* This compound is air-stable. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.89 – 7.74 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.60 – 7.51 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.49 – 7.42 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.09 – 7.05 (m, 1H, pyrrole), 6.79 – 6.75 (m, 1H, pyrrole), 6.48 – 6.43 (m, 1H, pyrrole), 2.90 – 2.78 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.52 (dd, *J* = 18.4, 7.1 Hz, 6H, CH<sub>3</sub>), 1.37 (dd, *J* = 16.7, 7.1 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 134.3 (d, *J* = 10.6 Hz), 132.1 (d, *J* = 2.9 Hz), 130.3, 129.8, 129.1 (d, *J* = 11.9 Hz), 126.1 (dd, *J* = 9.3, 4.1 Hz), 122.0 (dd, *J* = 6.7, 1.9 Hz), 118.6 (dd, *J* = 9.3, 3.8 Hz), 30.0 (d, *J* = 26.9 Hz), 19.1 (d, *J* = 2.4 Hz), 18.1 (d, *J* = 2.4 Hz). <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 128.0 (d, *J* = 79.9 Hz), 18.8 (d, *J* = 79.7 Hz); **IR** (ATR, cm<sup>-1</sup>): 2970, 2925, 1438, 1225, 1172, 1103, 747, 689, 653, 588, 535; **EA:** Anal. Calcd. for C<sub>22</sub>H<sub>27</sub>Cl<sub>2</sub>NNiP<sub>2</sub>: C, 53.17; H, 5.48; N, 2.82. Found: C, 53.04; H, 5.54; N, 2.59. **UV-vis** (CHCl<sub>3</sub>): λ<sub>max</sub> = 456 nm, ε<sub>456</sub> = 1.50 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup>.

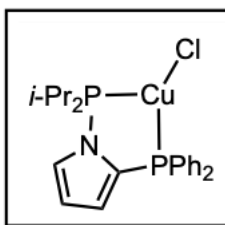


**(L1)PdCl<sub>2</sub>.** Pd(cod)Cl<sub>2</sub> (28.6 mg, 0.100 mmol, 1.0 equiv.) was dissolved in DCM (1 mL). Ligand **L1** (36.7 mg, 0.100 mmol, 1.0 equiv.) was added using DCM (3 mL). The reaction mixture was stirred for 1 h and then concentrated. The resulting solid was washed with pentane (2 mL). The solid was dissolved in DCE and filtered through glass fiber. Pentane was diffused in to the DCE solution at room temperature over two days, resulting in crystals. The supernatant was decanted and residual solvent was removed from the yellow crystals under vacuum. The desired product was isolated as analytically pure, yellow crystals. (41.5 mg, 0.076 mmol, 76% yield). X-ray quality crystals of **(L1)PdCl<sub>2</sub>** were grown by layering a DCM solution of the complex with hexane and storing at room temperature. *Note:* This compound is air-stable. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.90 – 7.72 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.64 – 7.53 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.50 – 7.44 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.17 – 7.13 (m, 1H, pyrrole), 6.89 – 6.82 (m, 1H, pyrrole), 6.62 – 6.59 (m, 1H, pyrrole), 3.12 – 2.81 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (dd, *J* = 19.7, 7.1 Hz, 6H, CH<sub>3</sub>), 1.25 (dd, *J* = 17.5, 7.1 Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 134.3 (d, *J* = 11.9 Hz), 133.6 (d, *J* = 24.0 Hz), 132.5 (d, *J* = 3.3 Hz), 129.7 (d, *J* = 65.9 Hz), 129.3 (d, *J* = 12.5 Hz), 126.6 (dd, *J* = 11.5, 2.7 Hz), 122.7 (dd, *J* = 7.1, 2.2 Hz), 119.6 (dd, *J* = 11.9, 5.4 Hz), 30.7 (d, *J* = 26.3 Hz), 18.5 (d, *J* = 3.2 Hz), 18.0 (d, *J* = 2.4 Hz). <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 135.4 (d, *J* = 18.5 Hz), 26.8 (d, *J* = 18.5 Hz); **IR** (ATR, cm<sup>-1</sup>): 3105, 2978, 2925, 1438, 1172, 1103, 751, 690, 592, 543; **EA:** Anal. Calcd. for C<sub>22</sub>H<sub>27</sub>Cl<sub>2</sub>NP<sub>2</sub>Pd: C, 48.51; H, 5.00; N, 2.57. Found: C, 48.71; H, 4.95; N, 2.54.



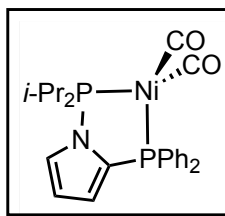
**(L1)PtCl<sub>2</sub>**. Pt(cod)Cl<sub>2</sub> (37.4 mg, 0.100 mmol) was dissolved in DCM (1 mL). Ligand **L1** (36.7 mg, 0.100 mmol, 1.0 equiv.) was added using DCM (3 mL). The reaction mixture was stirred for 1 h at 23 °C. The reaction mixture was filtered through a syringe filter and concentrated. The resulting colorless solid was washed with pentane (2 mL). The desired product was isolated as spectroscopically pure, colorless crystals (42.5 mg, 0.067 mmol, 67% yield) by diffusion of pentane into a DCE solution of (**L1**)PtCl<sub>2</sub> at room

temperature. X-ray quality crystals were grown in the same manner. *Note:* This compound is air-stable. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.82 – 7.73 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.58 – 7.50 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.49 – 7.40 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.19 – 7.12 (m, 1H, pyrrole), 7.07 – 6.95 (m, 1H, pyrrole), 6.64 – 6.58 (m, 1H, pyrrole), 3.04 – 2.96 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.39 (dd, *J* = 19.2, 7.1 Hz, 6H, CH<sub>3</sub>), 1.18 (dd, *J* = 17.3, 7.0 Hz, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 134.2 (d, *J* = 11.6 Hz), 133.3 (dd, *J* = 89.6, 18.1 Hz), 132.4 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 12.5 Hz), 129.0 (d, *J* = 73.5 Hz), 125.6 (d, *J* = 9.8 Hz), 122.1 (dd, *J* = 7.8, 2.8 Hz), 118.6 (dd, *J* = 9.7, 7.2 Hz), 29.4 (d, *J* = 34.8 Hz), 18.0 (d, *J* = 2.3 Hz), 17.7 (d, *J* = 2.7 Hz); <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 105.3 (d with Pt satellites, *J*<sub>PP</sub> = 9.9 Hz, *J*<sub>Pt-P</sub> = 3874 Hz), 5.5 (d with Pt satellites, *J*<sub>PP</sub> = 10.0 Hz, *J*<sub>Pt-P</sub> = 3422 Hz); IR (ATR, cm<sup>-1</sup>): 2966, 2929, 1434, 1230, 1176, 1103, 751, 596, 543; EA: Anal. Calcd. for C<sub>22</sub>H<sub>27</sub>Cl<sub>2</sub>NP<sub>2</sub>Pt: C, 41.72; H, 4.30; N, 2.21. Found: C, 39.25; H, 4.17; N, 1.83. Combustion analysis was consistently low in carbon despite four attempts using various purification methods.



**[(L1)CuCl]<sub>2</sub>**. CuCl (9.9 mg, 0.100 mmol, 1.0 equiv.) was suspended in DCM (1 mL). To the suspension was added **L1** (36.7 mg, 0.100 mmol, 1.0 equiv.) using DCM (3 mL). The reaction mixture was stirred for 26 h at 23 °C. The reaction mixture was filtered using a syringe filter and the resulting filtrate was concentrated. The crude product was washed with pentane (2 mL). The product was isolated as colorless crystals (32.4 mg, 0.069 mmol, 69% yield) by layering a DCM solution of the product with hexane. X-ray

quality crystals of [(**L1**)CuCl]<sub>2</sub> were grown by layering a DCM solution of the complex with pentane at room temperature. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.60 – 7.51 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.37 – 7.31 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.30 – 7.24 (m, 4H, C<sub>6</sub>H<sub>5</sub>), 7.15 – 7.09 (m, 1H, pyrrole), 6.53 – 6.50 (m, 1H, pyrrole), 6.48 – 6.45 (m, 1H, pyrrole), 2.46 – 2.35 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (dd, *J* = 19.0, 7.0 Hz, 6H, CH<sub>3</sub>), 0.98 (dd, *J* = 13.9, 7.0 Hz, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 134.6 (dd, *J* = 26.4, 6.9 Hz), 133.8 (d, *J* = 16.0 Hz), 129.7, 128.8 (d, *J* = 9.5 Hz), 127.0 (dd, *J* = 5.8, 2.5 Hz), 120.0, 115.7 (d, *J* = 4.8 Hz), 27.9 (t, *J* = 5.8 Hz), 18.2 (d, *J* = 14.8 Hz), 17.8 (d, *J* = 2.6 Hz). (*Note:* One aromatic signal could not be located); <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 61.2 (br), -37.0 (br); IR (ATR, cm<sup>-1</sup>): 2870, 1163, 1102, 730, 669, 561, 517; EA: Anal. Calcd. for C<sub>22</sub>H<sub>27</sub>ClCuN: C, 56.65; H, 5.84; N, 3.00. Found: C, 56.41; H, 5.93; N, 3.03.

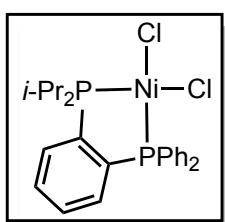


**(L1)Ni(CO)<sub>2</sub>**. (Ph<sub>3</sub>P)<sub>2</sub>Ni(CO)<sub>2</sub> (38.4 mg, 0.060 mmol, 1.0 equiv.) was dissolved in THF (3 mL). Ligand **L1** (26.5 mg, 0.072 mmol, 1.2 equiv.) was added using additional THF (6 mL). The reaction mixture was stirred at 23 °C for 24 h, during which time it became a yellow and homogeneous solution. The reaction mixture was concentrated in the glovebox and was recrystallized from pentane at -35 °C overnight. The first crystallization yielded crystals of (Ph<sub>3</sub>P)<sub>2</sub>Ni(CO)<sub>2</sub> starting material. The reaction mixture

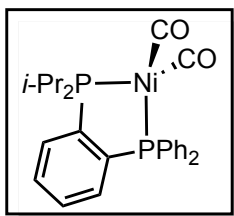
was then pipetted into a second scintillation vial and placed in a freezer at -35 °C overnight. This



second crystallization yielded the final product as colorless, spectroscopically pure crystals (11.0 mg, 0.023 mmol, 38% yield). *Note:* This compound is air-sensitive.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.56 – 7.45 (m, 4H,  $\text{C}_6\text{H}_5$ ), 7.38 – 7.32 (m, 6H,  $\text{C}_6\text{H}_5$ ), 7.10 – 7.04 (m, 1H, pyrrole), 6.66 – 6.59 (m, 1H, pyrrole), 6.42 – 6.34 (m, 1H, pyrrole), 2.46 (dhept,  $J = 8.5, 6.9$  Hz, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.14 (dd,  $J = 18.5, 6.9$  Hz, 6H,  $\text{CH}_3$ ), 0.80 (dd,  $J = 14.7, 6.9$  Hz, 6H,  $\text{CH}_3$ ).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  201.7 (dd,  $J = 7.2, 2.3$  Hz), 138.0 (dd,  $J = 36.2, 5.0$  Hz), 137.2 (dd,  $J = 61.7, 31.2$  Hz), 132.5 (d,  $J = 14.8$  Hz), 129.6 (d,  $J = 1.8$  Hz), 128.8 (d,  $J = 9.7$  Hz), 124.8 (dd,  $J = 7.4, 5.0$  Hz), 118.1 (d,  $J = 4.9$  Hz), 116.9 (d,  $J = 7.0$  Hz), 30.3 (dd,  $J = 13.4, 3.9$  Hz), 18.6 (d,  $J = 13.7$  Hz), 17.9 (d,  $J = 2.8$  Hz).  $^{31}\text{P NMR}$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  127.12 (d,  $J = 6.1$  Hz), 17.65 (d,  $J = 6.1$  Hz). **IR** (ATR,  $\text{cm}^{-1}$ ): 3062, 1996 (C=O), 1934 (C=O), 1477, 1434, 742, 695; **EA:** Anal. Calcd. for  $\text{C}_{24}\text{H}_{27}\text{NNiO}_2\text{P}_2$ : C, 59.79; H, 5.64; N, 2.91. Found: C, 58.23; H, 5.55; N, 2.77. Analytically pure material was not acquired despite multiple attempts.

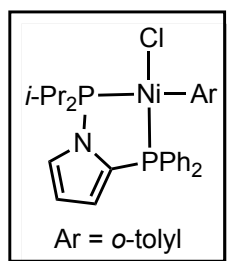


**(L11)NiCl<sub>2</sub>.**  $\text{NiCl}_2(\text{DME})$  (22.0 mg, 0.100 mmol, 1.0 equiv.) was suspended in DCM (1 mL). Ligand **L11** (37.8 mg, 0.100 mmol, 1.0 equiv.) was transferred to the suspension using additional DCM (3 mL). The reaction mixture was stirred at 23 °C until homogenous (approx. 5 h), during which time the solution became orange. The reaction mixture was filtered *via* syringe filter and concentrated to an orange solid, which was then washed with pentane (approx. 3 mL). The desired product was isolated as orange analytically pure crystals (44.4 mg, 0.087 mmol, 87% yield) by diffusion of pentane to a DCE solution of **(L11)NiCl<sub>2</sub>**. X-ray quality crystals were grown in the same manner. *Note:* This compound is air-stable.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.84 – 7.77 (m, 4H), 7.75 – 7.70 (m, 1H), 7.68 – 7.62 (m, 1H), 7.62 – 7.51 (m, 3H), 7.49 – 7.39 (m, 5H), 2.90 – 2.76 (m, 2H), 1.51 (dd,  $J = 17.5, 7.0$  Hz, 1H), 1.34 (dd,  $J = 16.0, 7.1$  Hz, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  143.9 (dd,  $J = 52.7, 31.7$  Hz), 138.7 (dd,  $J = 40.2, 37.5$  Hz), 134.4 (d,  $J = 10.1$  Hz), 133.8 (dd,  $J = 13.8, 1.8$  Hz), 133.4 (dd,  $J = 6.3, 2.1$  Hz), 132.9 (dd,  $J = 5.3, 2.2$  Hz), 132.28 – 131.81 (m), 130.32 (d,  $J = 55.5$  Hz), 129.2 (d,  $J = 11.2$  Hz), 28.0 (d,  $J = 27.0$  Hz), 19.8 (d,  $J = 2.2$  Hz), 18.8 (d,  $J = 2.1$  Hz);  $^{31}\text{P NMR}$  (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  84.4 (d,  $J = 71.0$  Hz), 55.2 (d,  $J = 70.3$  Hz); **IR** (ATR,  $\text{cm}^{-1}$ ): 2967, 2923, 2869, 1439, 1249, 1100, 747, 700, 547; **EA:** Anal. Calcd. for  $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{NiP}_2$ : C, 56.74; H, 5.56; N: 0.00. Found: C, 56.35; H, 5.03; N, 0.00. **UV-vis** ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}} = 454$  nm,  $\epsilon_{456} = 1.52 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ .



**(L11)Ni(CO)<sub>2</sub>.**  $(\text{Ph}_3\text{P})_2\text{Ni}(\text{CO})_2$  (38.4 mg, 0.060 mmol, 1.0 equiv.) was dissolved in THF (3 mL) in a 20-mL scintillation vial. Ligand **L1** (25.0 mg, 0.066 mmol, 1.1 equiv.) was added to the nickel solution using additional THF (6 mL). The reaction mixture was sealed, removed from the glovebox, and heated at 50 °C for 22 h, during which time it became a light yellow, homogeneous solution. (*Note:* Elevated temperatures were required to ensure complete consumption of nickel starting material) The reaction mixture was opened to air and concentrated under reduced pressure. The product was isolated as a spectroscopically pure, colorless solid (18.8 mg, 0.064 mmol, 64% yield) following two recrystallizations from pentane at -25 °C. *Note:* This compound is air-stable.  $^1\text{H NMR}$  (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.74 – 7.69 (m, 1H, phenylene), 7.51 – 7.46 (m, 1H, phenylene), 7.44 – 7.30 (m, 12H), 2.41 (dhept,  $J = 9.3, 6.9$  Hz, 2H), 1.14 (dd,  $J = 16.9, 6.9$  Hz, 6H), 0.76 (dd,  $J = 14.5, 6.9$  Hz, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  202.6 (t,  $J = 4.1$  Hz), 146.7 (t,  $J = 39.0$  Hz), 145.4 (dd,  $J = 44.5,$

30.0 Hz), 138.4 (dd,  $J = 27.9, 6.2$  Hz), 134.2 (d,  $J = 11.6$  Hz), 132.6 (d,  $J = 14.3$  Hz), 131.1 (d,  $J = 13.5$  Hz), 130.3 (t,  $J = 5.2$  Hz), 129.4 (d,  $J = 1.7$  Hz), 128.8 (d,  $J = 9.1$  Hz), 27.7 (dd,  $J = 15.1, 5.5$  Hz), 19.9 (d,  $J = 10.8$  Hz), 19.0 (d,  $J = 3.7$  Hz) (*Note*: One aromatic signal was not observed);  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  76.1 (d,  $J = 24.8$  Hz), 47.7 (d,  $J = 25.1$  Hz); IR (ATR,  $\text{cm}^{-1}$ ): 2693, 1986 (C=O), 1923 (C=O), 1438, 744, 629; EA: Anal. Calcd. for  $\text{C}_{26}\text{H}_{28}\text{NiO}_2\text{P}_2$ : C, 63.32; H, 5.72; N, 0.00. Found: C, 62.54; H, 6.01; N, 0.00. Combustion analysis was low in carbon despite multiple attempts.

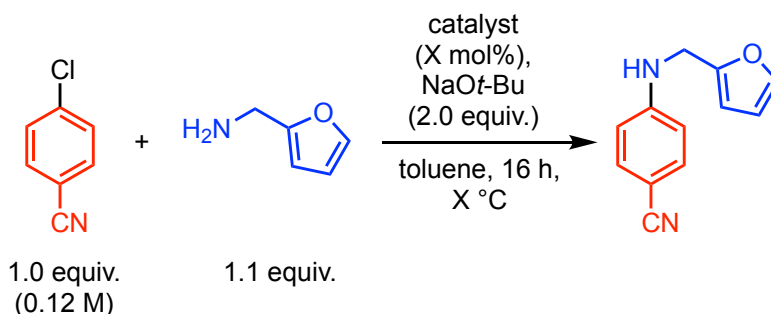


**(L1)Ni(*o*-tolyl)Cl.** A 20-mL scintillation vial was charged with **L1** (38.6 mg, 0.105 mmol, 1.05 equiv.), (TMEDA)Ni(*o*-tolyl)Cl (30.1 mg, 0.100 mmol, 1.0 equiv), and THF (4 mL). The vial was sealed, removed from the glovebox, and heated at 50 °C for 3 h. The orange, homogeneous reaction mixture was opened to air and concentrated by rotary evaporation. The resulting orange foam was dissolved in DCM, filtered, and concentrated to approximately ~0.5 mL. To the solution was added pentane (~15 mL), which immediately resulted in a turbid solution. The solution was stored at -35 °C

to induce crystallization. The product was isolated as orange crystals (42.4 mg, 0.077 mmol, 77% yield). X-ray quality crystals were grown from a dilute DCM/pentane solution (~1:15) at -35 °C. *Note*: This complex is air-stable.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.01 – 7.94 (m, 2H), 7.51 – 7.37 (m, 4H), 7.16 – 7.06 (m, 4H), 6.70 – 6.62 (m, 4H), 6.57 – 6.48 (m, 2H), 6.29 – 6.26 (m, 1 H), 2.86 – 2.74 (m, 2H), 2.08 (s, 3H), 1.63 – 1.44 (m, 3H), 1.32 (ddd,  $J = 14.5, 7.0, 2.0$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  157.2 (dd,  $J = 91.8, 39.5$  Hz), 145.2, 138.2 – 137.5 (m), 137.3 – 137.1 (m), 133.7 (dd,  $J = 95.5, 10.9$  Hz), 132.5 (d,  $J = 60.9$  Hz), 131.4 (d,  $J = 2.8$  Hz), 130.8 (d,  $J = 2.8$  Hz), 129.6 – 129.1 (m) 128.7 (dd,  $J = 134.3, 11.1$  Hz), 125.7 (dd,  $J = 7.9, 5.3$  Hz), 123.3 (d,  $J = 3.2$  Hz), 120.4 (d,  $J = 6.2$  Hz), 117.4 (dd,  $J = 9.4, 3.1$  Hz), 27.7 (dd,  $J = 58.1, 15.6$  Hz), 24.6 (d,  $J = 2.0$  Hz), 18.6 (dd,  $J = 36.1, 5.7$  Hz), 18.1 (d,  $J = 22.5$  Hz).  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  111.7 (d,  $J = 34.4$  Hz), 21.9 (d,  $J = 33.7$  Hz). IR (ATR,  $\text{cm}^{-1}$ ): 3056, 2960, 1571, 1436, 1217, 1177, 1100, 1057, 1026, 959, 882, 740, 694, 574. EA: Anal. Calcd. for  $\text{C}_{29}\text{H}_{34}\text{ClNiNP}_2$ : C, 63.03; H, 6.20; N, 2.53. Found: C, 62.92; H, 6.31; N, 2.62.

## IV. Catalytic Studies

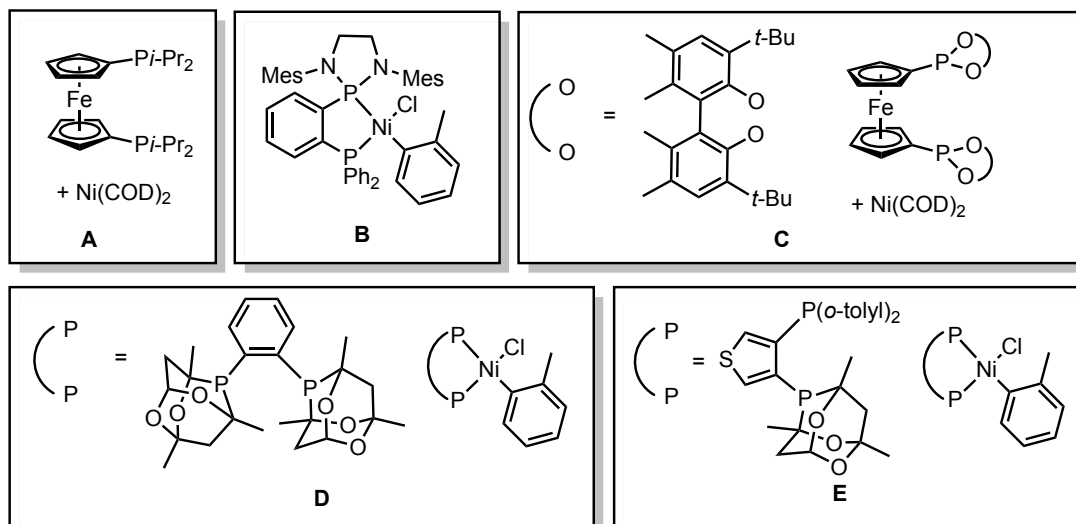
A 20-mL scintillation vial was charged with 4-chlorobenzonitrile (34.4 mg, 0.250 mmol, 1.0 equiv.), furfurylamine (25  $\mu$ L, 0.0282 mmol), (**L1**)Ni(*o*-tolyl)Cl (6.5 mg, 0.012 mmol, 5 mol%), NaO*t*-Bu (48.1 mg, 0.501 mmol, 2.0 equiv.), and toluene (2.5 mL). The vial was sealed, removed from the glovebox, and heated at the reported temperature for 16 h in a temperature-controlled aluminum block. The reaction mixture was filtered through cotton and then a syringe filter, each of which was washed with DCM. A chloroform solution of ferrocene (1.0 mL, 0.0250 M) was added to the filtered reaction mixture. An aliquot of the new solution was concentrated by rotary evaporation and analyzed by  $^1\text{H}$  NMR spectroscopy to determine the yield. Spectral data of the product match that previously reported in the literature.<sup>4</sup> A representative spectrum is provided on S-47.



**Table S1.** Comparative nickel-catalyzed cross-coupling of 4-chlorobenzonitrile and furfurylamine

Reference	Catalyst	Catalyst Loading (mol%)	Temperature (°C)	Yield (%)
<b>4</b>	<b>A</b>	5	110	82
<b>5</b>	<b>B</b>	5	25	85
<b>6</b>	<b>C</b>	5	80	57
<b>7</b>	<b>D</b>	1.75	25	>95
<b>8</b>	<b>E</b>	2.25	25	77
<i>This Work</i> <sup>a</sup>	( <b>L1</b> )Ni( <i>o</i> -tolyl)Cl	5	25	71 $\pm$ 2 <sup>b</sup>
<i>This Work</i> <sup>a</sup>	( <b>L1</b> )Ni( <i>o</i> -tolyl)Cl	5	40	>99

<sup>a</sup> 0.10 M in electrophile; <sup>b</sup> Standard deviation reported of three independent runs: 70%, 70%, 73%



## V. Examination of Air- and Water-Stability of Ligand L1

To gain insight into the reactivity of the reported bis(phosphino)pyrrole ligands toward water and ambient oxygen, an experiment was conducted to measure the degradation of **L1** under various conditions.

In a nitrogen-filled glovebox, Compound **L1** (15.0 mg, 0.041 mmol) and the internal standard trimethoxybenzene (5 mg) was dissolved in DCM-d<sub>2</sub> (1.8 mL). Three NMR tubes were charged with 0.5 mL of the solution. Each sample was sealed with parafilm and a <sup>1</sup>H NMR spectrum was acquired for each solution. The following manipulations were then performed with each solution:

**Tube A:** The sample was left sealed and undisturbed.

**Tube B:** The sample was poured into a vial open to air and returned to the NMR tube.

**Tube C:** Deionized water (5 μL) was injected into the sample.

The samples were analyzed by <sup>1</sup>H NMR over 24 h. Over the course of that time period, the following percentage of **L1** remained compared to the internal standard:

Tube	Percentage of L1 Remaining
A	96%
B	88%
C	96%

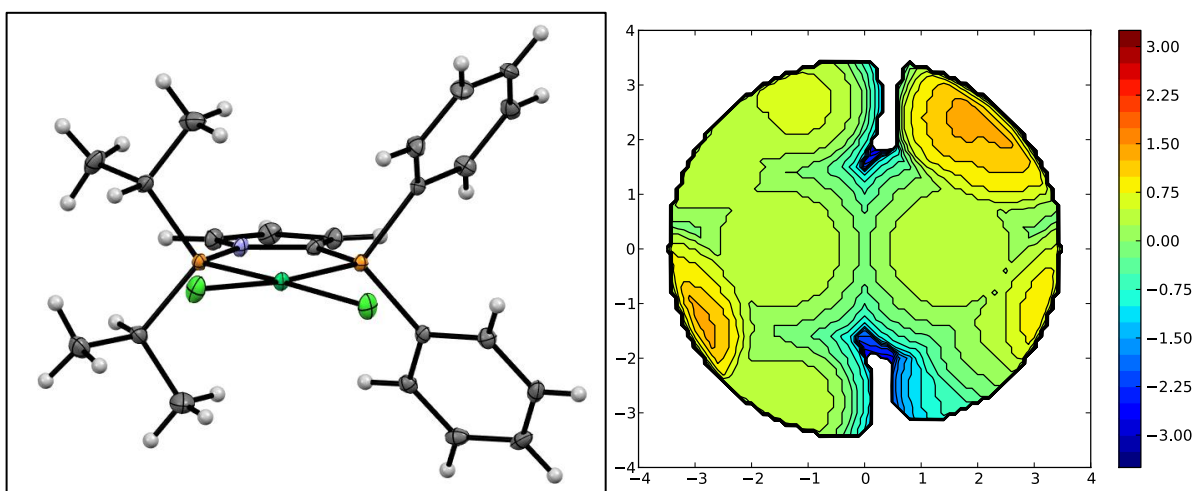
In no case were new peaks observed to account for the mass balance.

## VI. Buried Volume Details for (L1)NiCl<sub>2</sub> and (L11)NiCl<sub>2</sub>

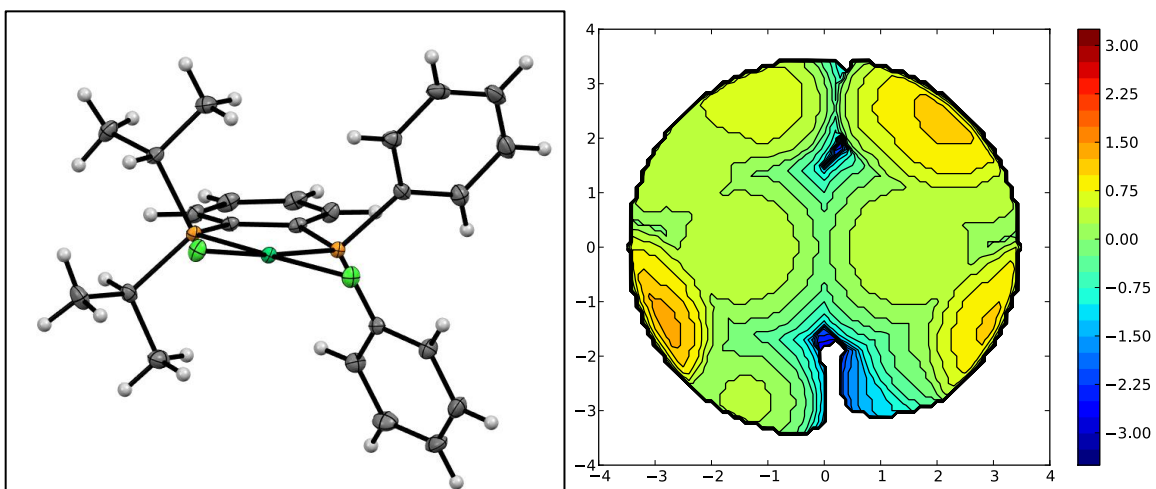
Buried volume ( $\%V_{\text{Bur}}$ ) calculations were performed for both (L1)NiCl<sub>2</sub> and (L11)NiCl<sub>2</sub> using the SambVca 2.0 web application<sup>9</sup> and the solid state structures of each compound based on the following parameters:

*Atomic radii:* 1.17  
*Sphere radius:* 3.5  
*Mesh:* 0.10  
*H Atoms:* included

Nickel and chloride atoms were omitted for each calculation. The ORTEP diagram is oriented to match the corresponding steric map.

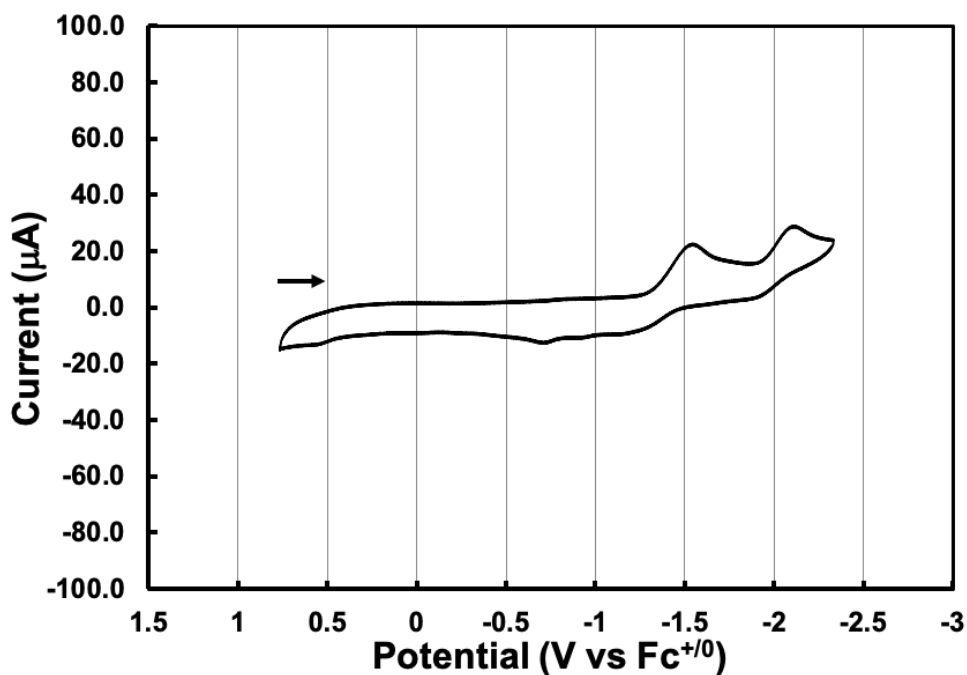


**Figure S1.** Steric map of (L1)NiCl<sub>2</sub>;  $\%V_{\text{Bur}} = 54.5\%$ .

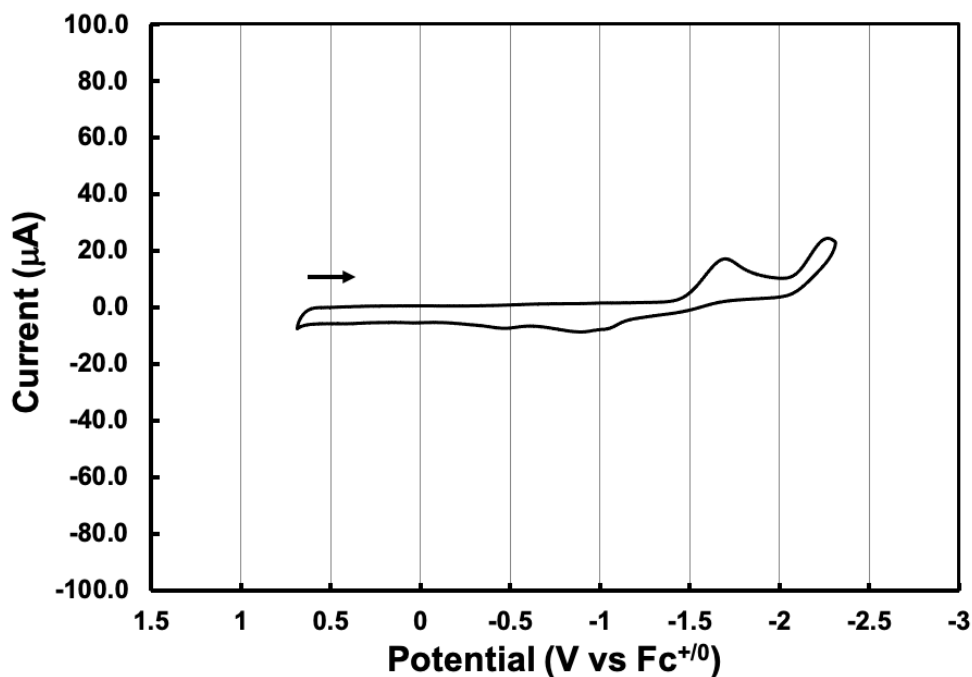


**Figure S2.** Steric map of (L11)NiCl<sub>2</sub>;  $\%V_{\text{Bur}} = 55.2\%$ .

## VII. Cyclic Voltammograms of (L1)NiCl<sub>2</sub> and (L11)NiCl<sub>2</sub>



**Figure S3.** Cyclic voltammogram of (L1)NiCl<sub>2</sub> in THF. Conditions: scan rate: 300 mV/s; supporting electrolyte: 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>]; working electrode: glassy carbon; auxiliary electrode: platinum wire; reference: silver wire referenced to the Fc<sup>+0</sup> couple. *Note:* Both reductions are irreversible.



**Figure S4.** Cyclic voltammogram of (L11)NiCl<sub>2</sub> in THF. Conditions: scan rate: 300 mV/s; supporting electrolyte: 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>]; working electrode: glassy carbon; auxiliary electrode: platinum wire; reference: silver wire referenced to the Fc<sup>+0</sup> couple. *Note:* Both reductions are irreversible.

### VIII. Infrared Spectra for (L1)Ni(CO)<sub>2</sub> and (L11)Ni(CO)<sub>2</sub>

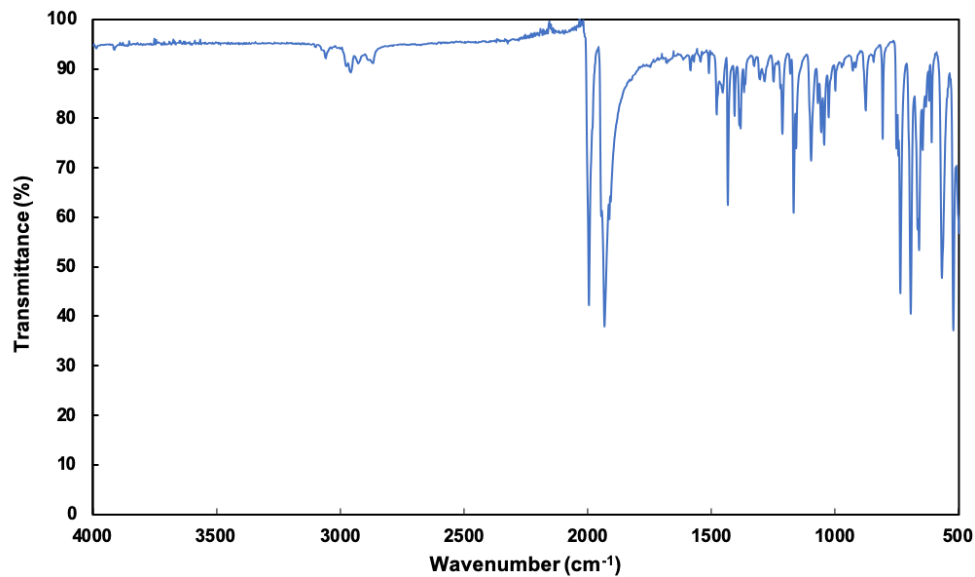


Figure S5. Infrared spectrum of (L1)Ni(CO)<sub>2</sub>.

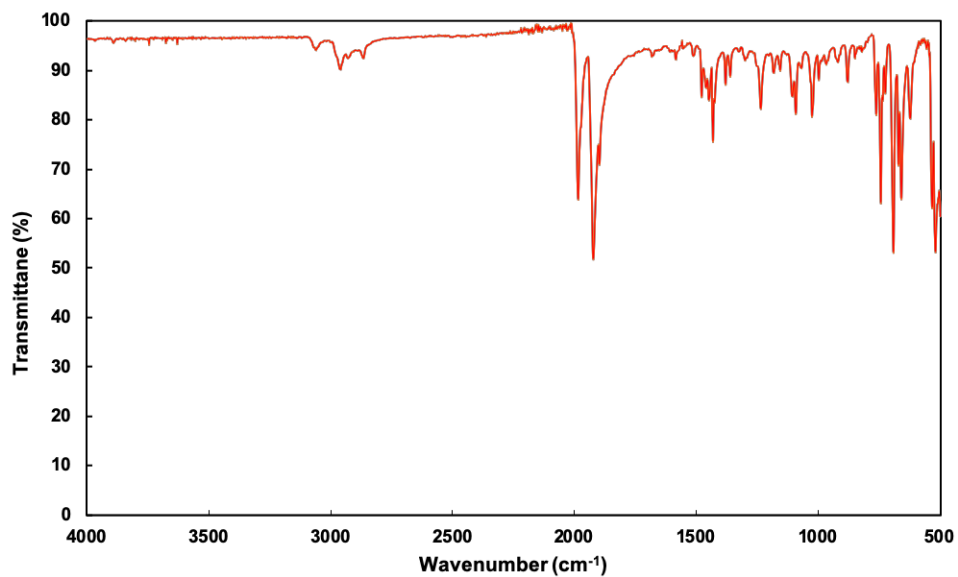
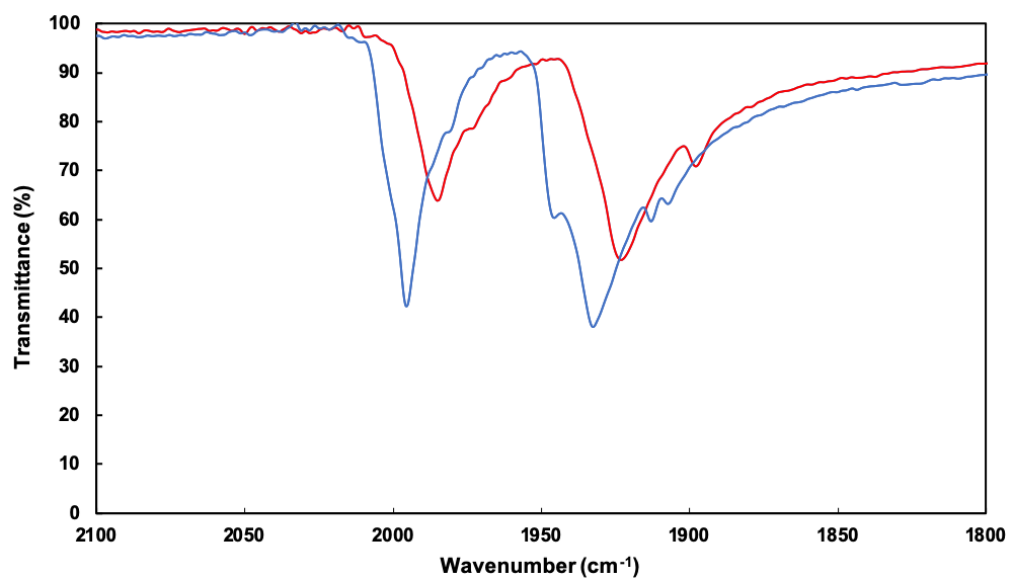


Figure S6. Infrared spectrum of (L11)Ni(CO)<sub>2</sub>.



**Figure S7.** Superimposed IR spectra of (L1)Ni(CO)<sub>2</sub> (blue) and (L11)Ni(CO)<sub>2</sub> (red).



### IX. UV-vis Data for (L1)NiCl<sub>2</sub> and (L11)NiCl<sub>2</sub>

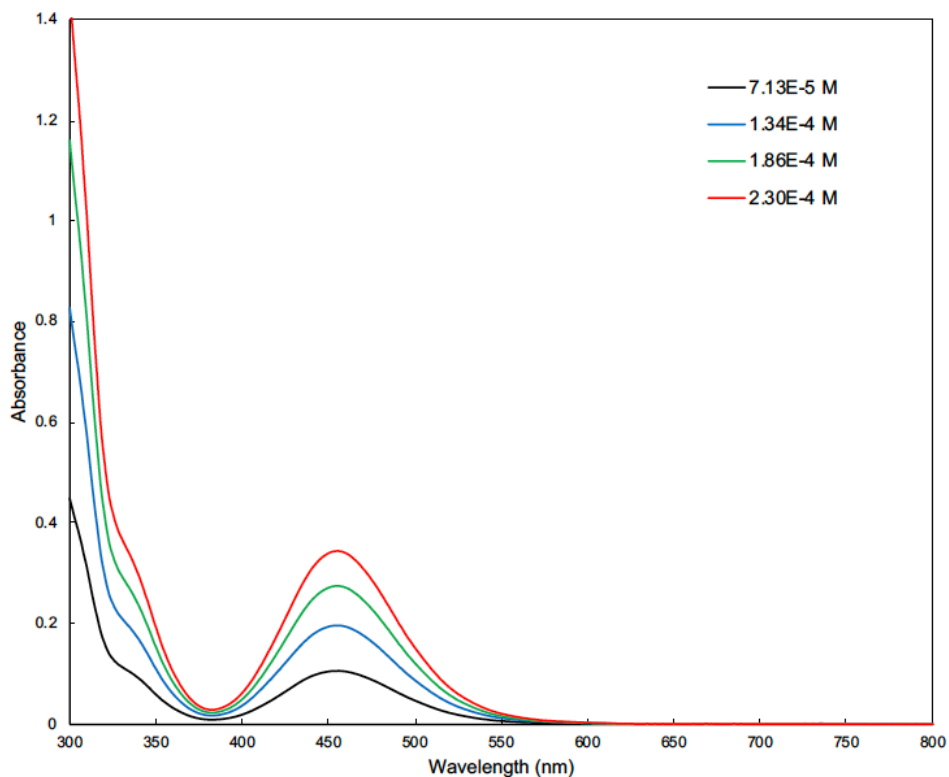
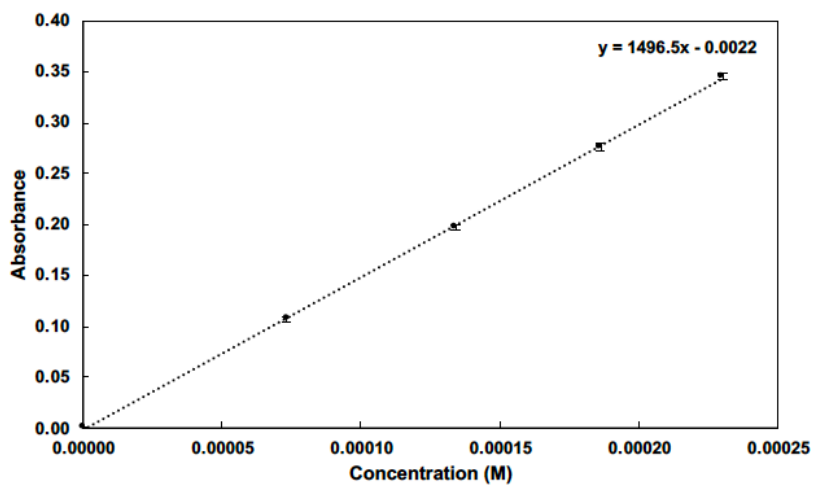


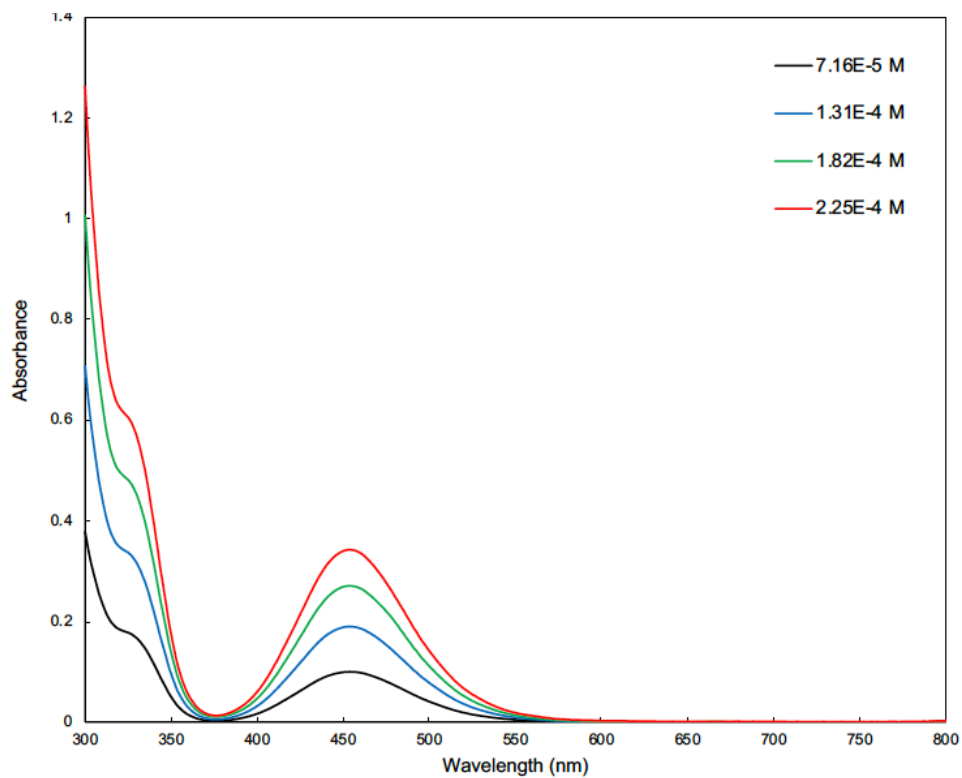
Figure S8. UV-vis spectra for (L1)NiCl<sub>2</sub> over various concentrations.



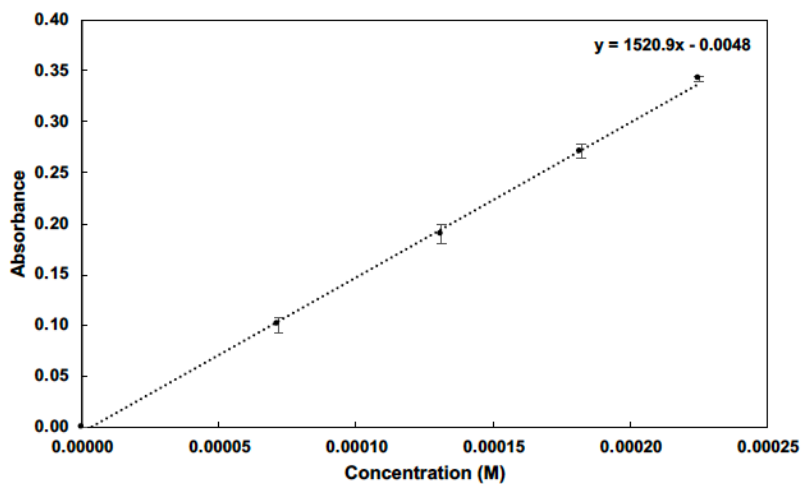
$$\epsilon_{456} = 1,497 \pm 12 \text{ M}^{-1}\text{cm}^{-1}$$

(standard error reported)

Figure S9. Extinction coefficient determination for (L1)NiCl<sub>2</sub> at 456 nm.



**Figure S10.** UV-vis spectra for (L11)NiCl<sub>2</sub> over various concentrations.

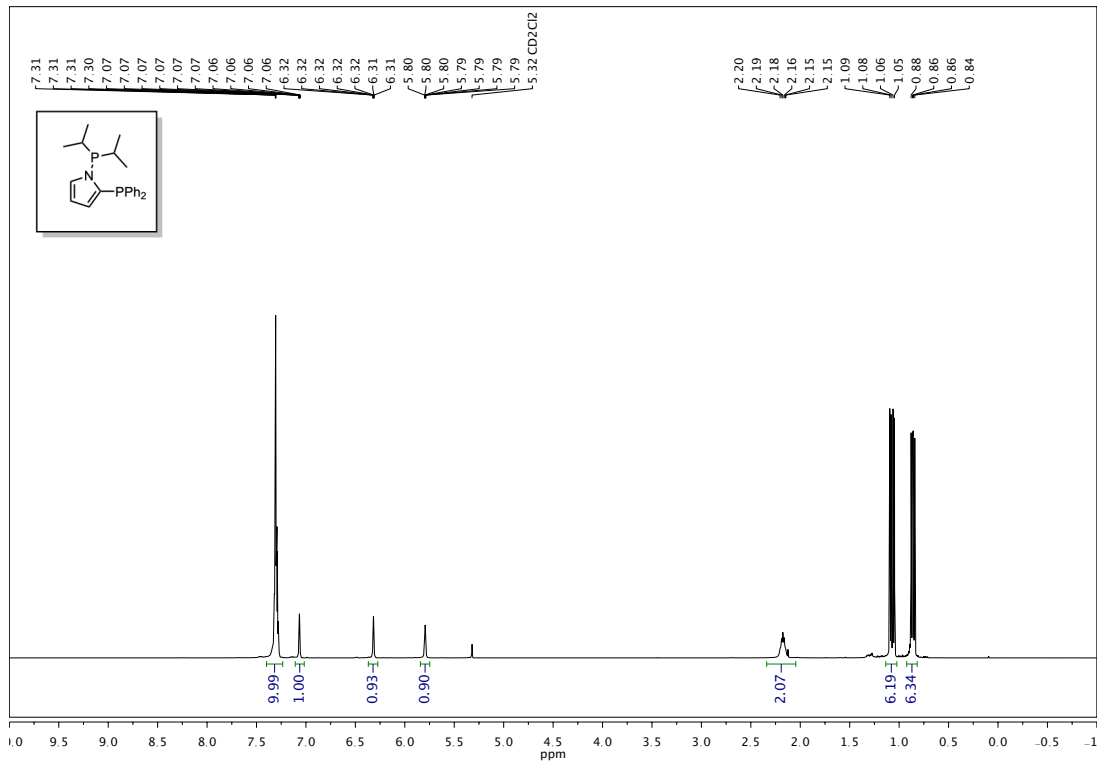


$$\epsilon_{454} = 1,521 \pm 31 \text{ M}^{-1}\text{cm}^{-1}$$

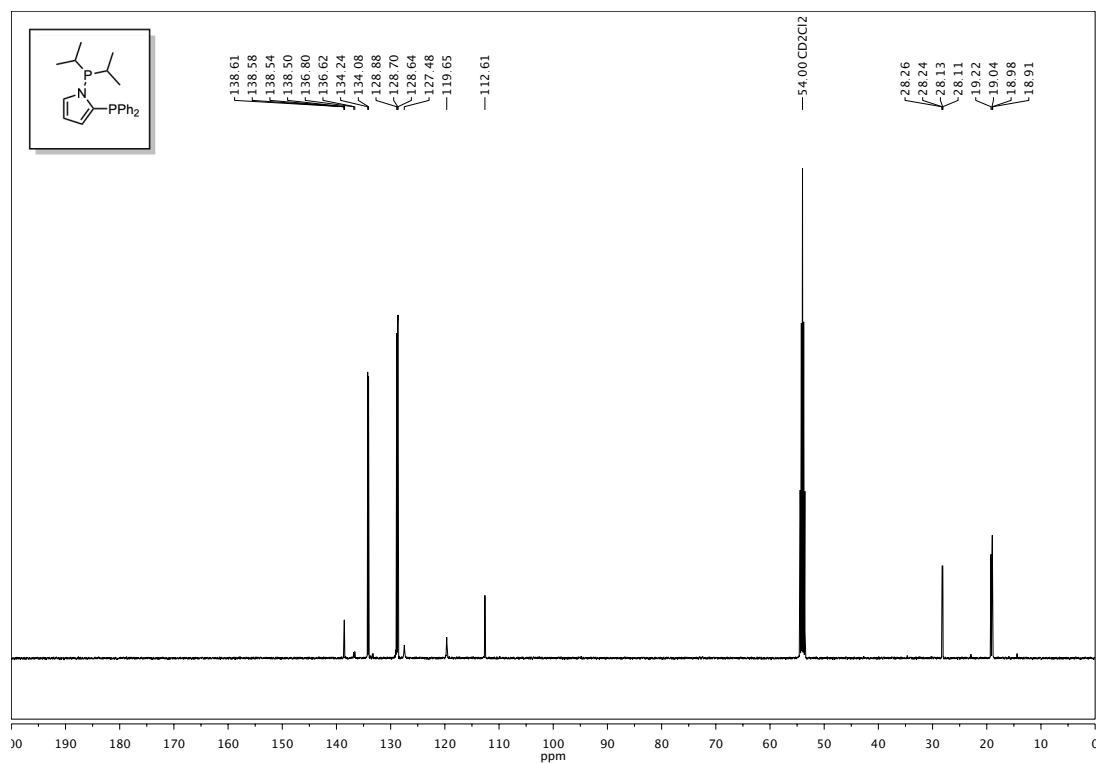
(standard error reported)

**Figure S11.** Extinction coefficient determination for (L11)NiCl<sub>2</sub>.

## X. NMR Spectra of Bis(phosphino)pyrrole Ligands



**Figure S12.**  $^1\text{H}$  NMR spectrum of L1.



**Figure S13.**  $^{13}\text{C}$  NMR spectrum of L1.

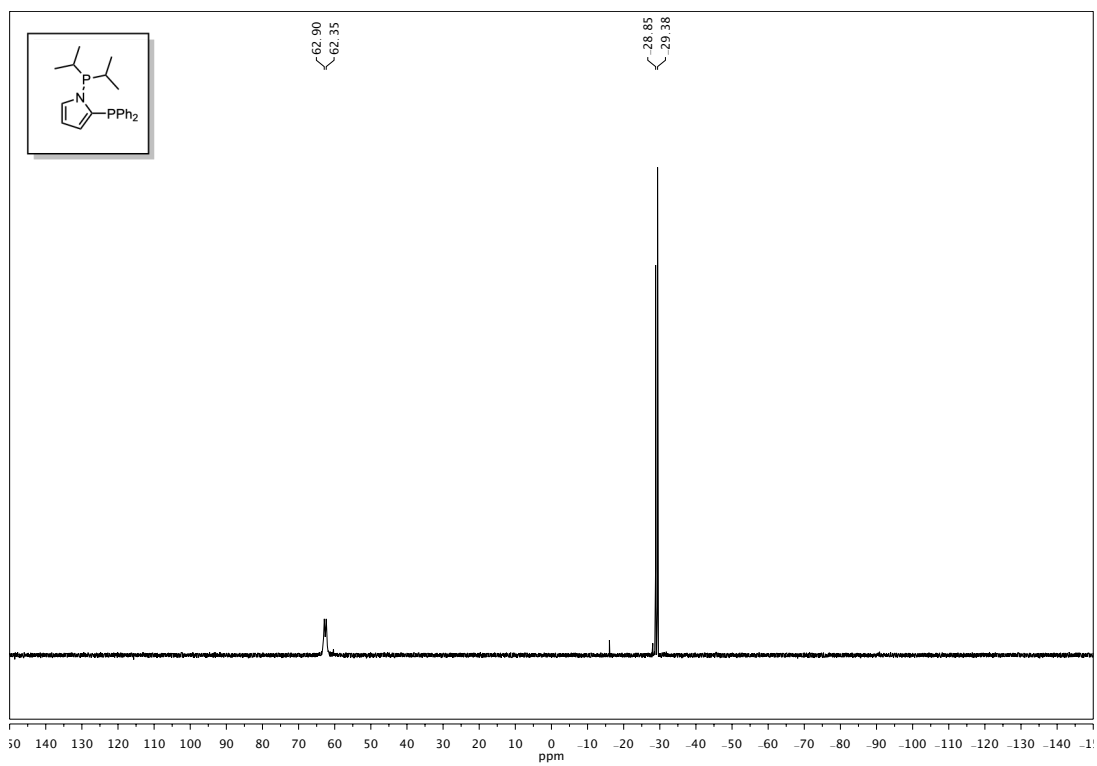


Figure S14.  $^{31}\text{P}$  NMR spectrum of L1.

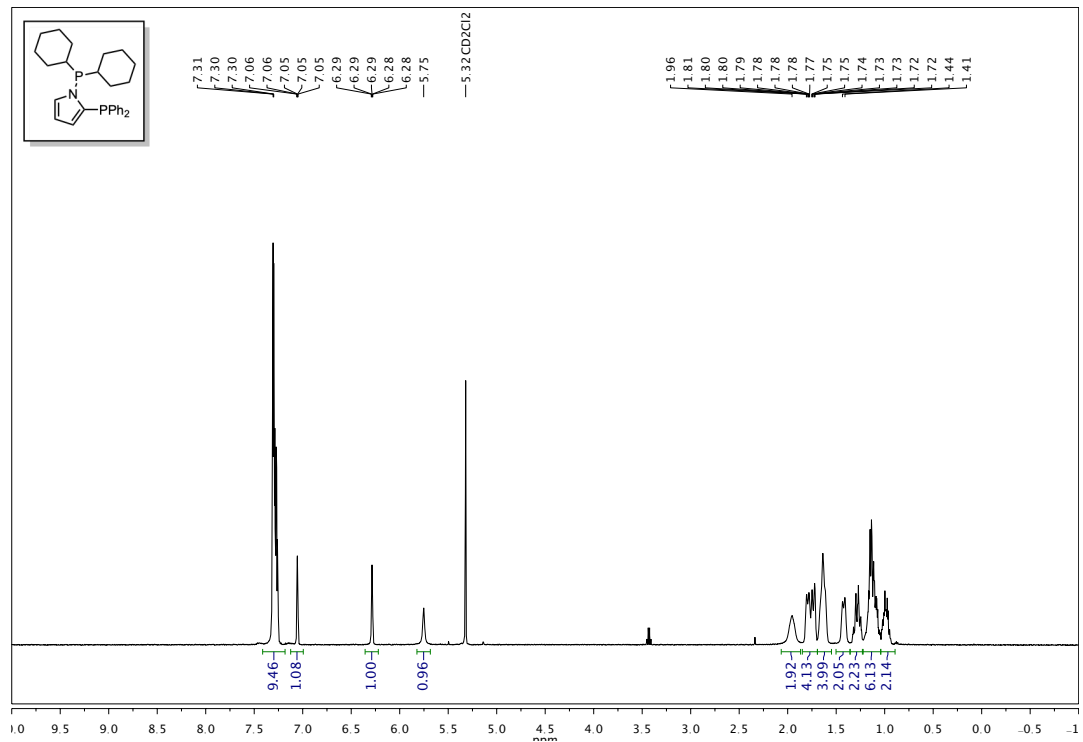


Figure S15.  $^1\text{H}$  NMR spectrum of L2.

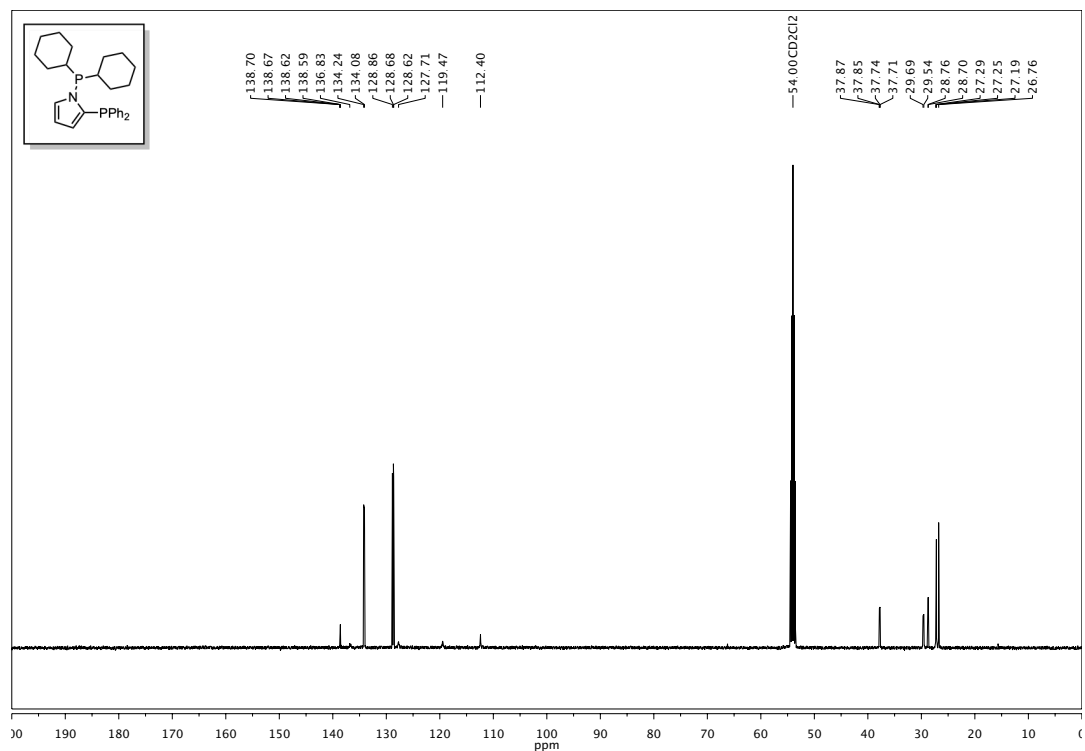


Figure S16.  $^{13}\text{C}$  NMR spectrum of L2.

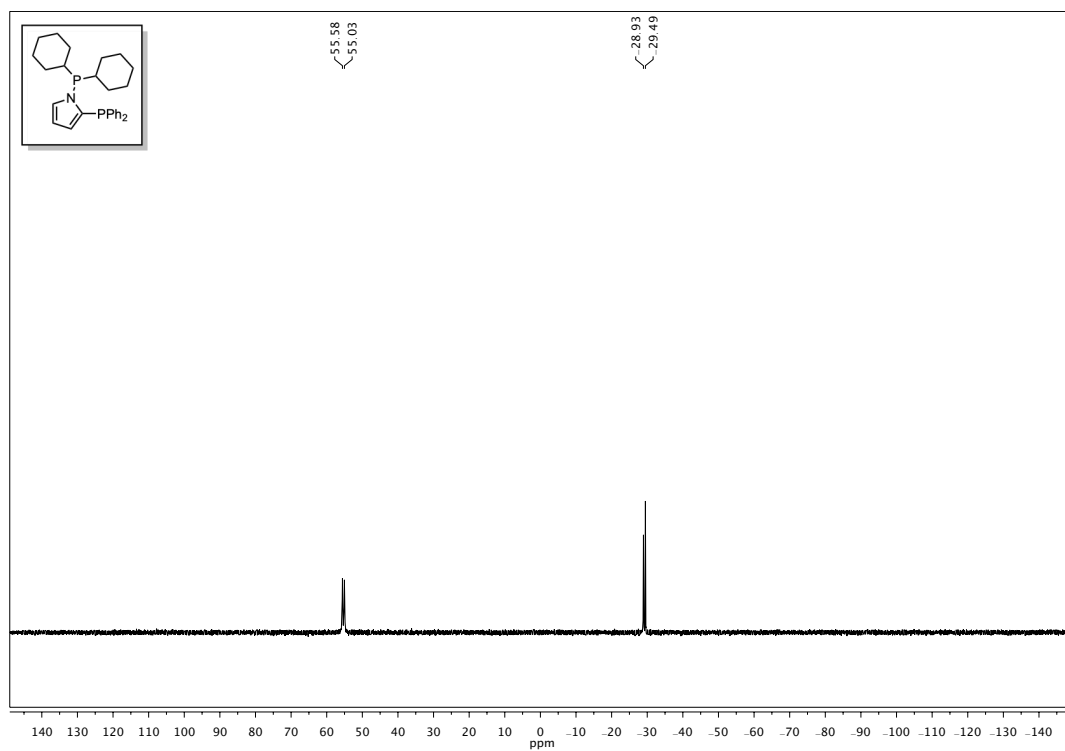


Figure S17.  $^{31}\text{P}$  NMR spectrum of L2.

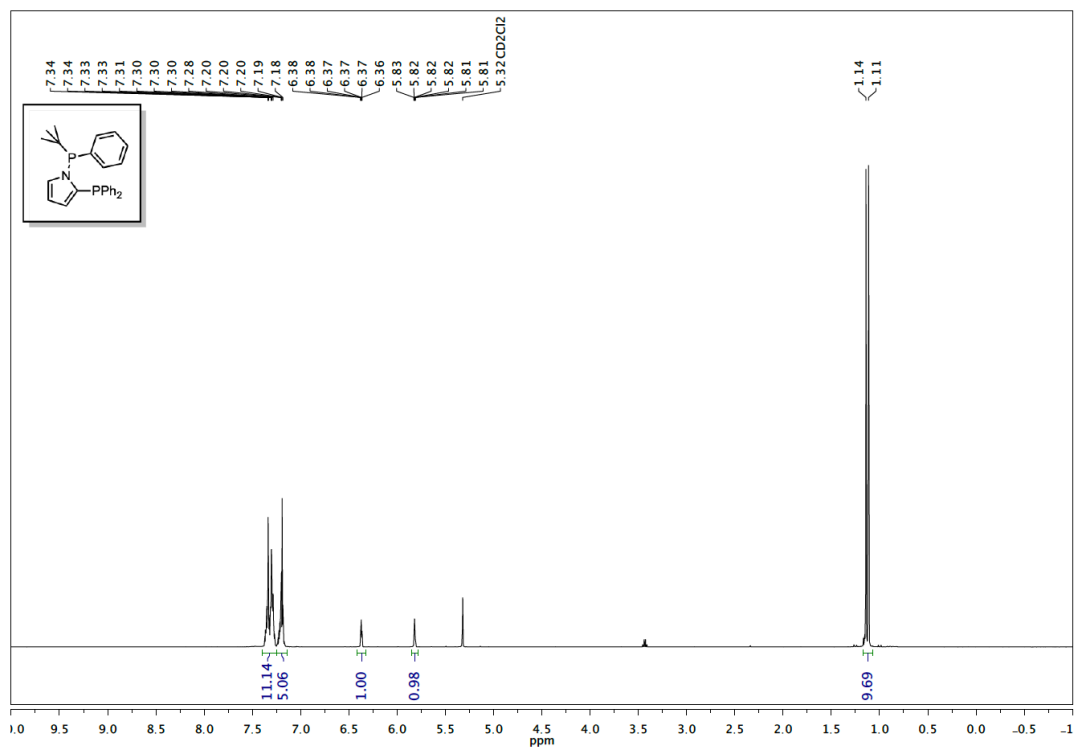


Figure S18. <sup>1</sup>H NMR spectrum of L3.

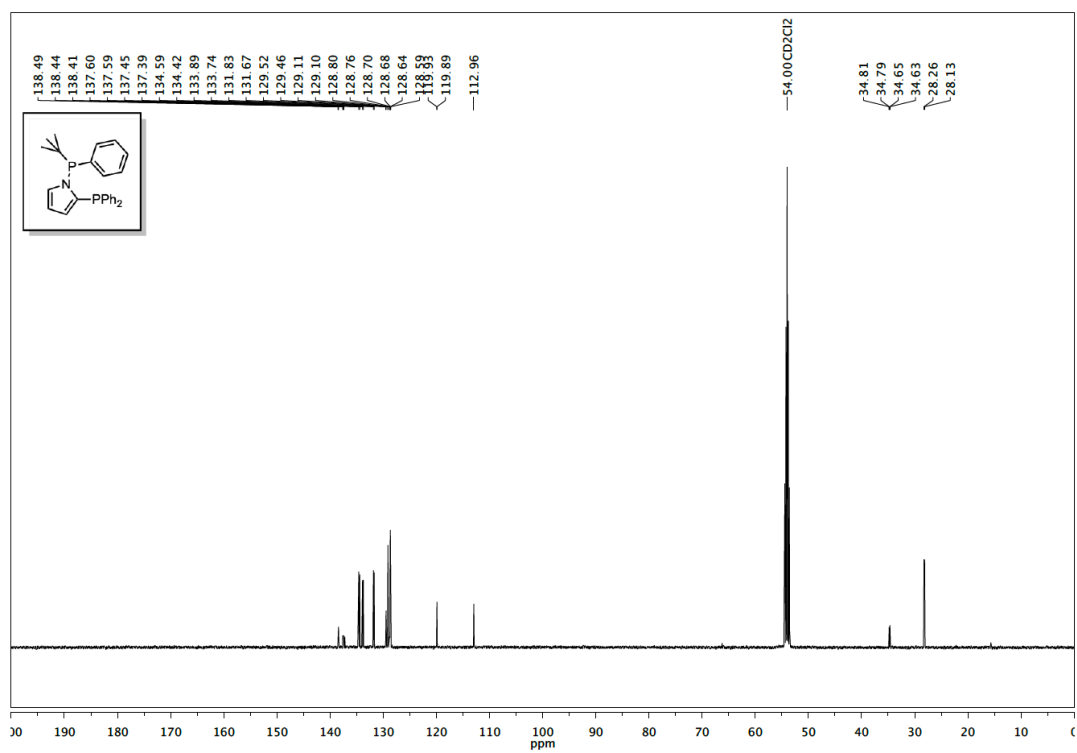


Figure S19. <sup>13</sup>C NMR spectrum of L3.

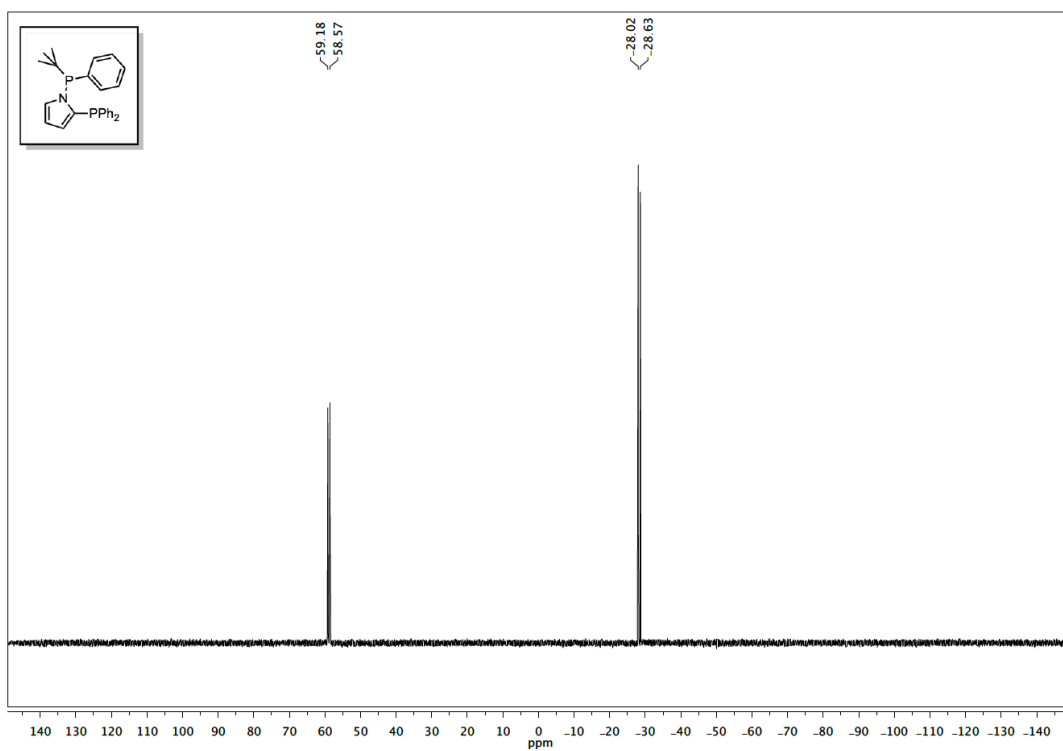


Figure S20.  $^{31}\text{P}$  NMR spectrum of L3.

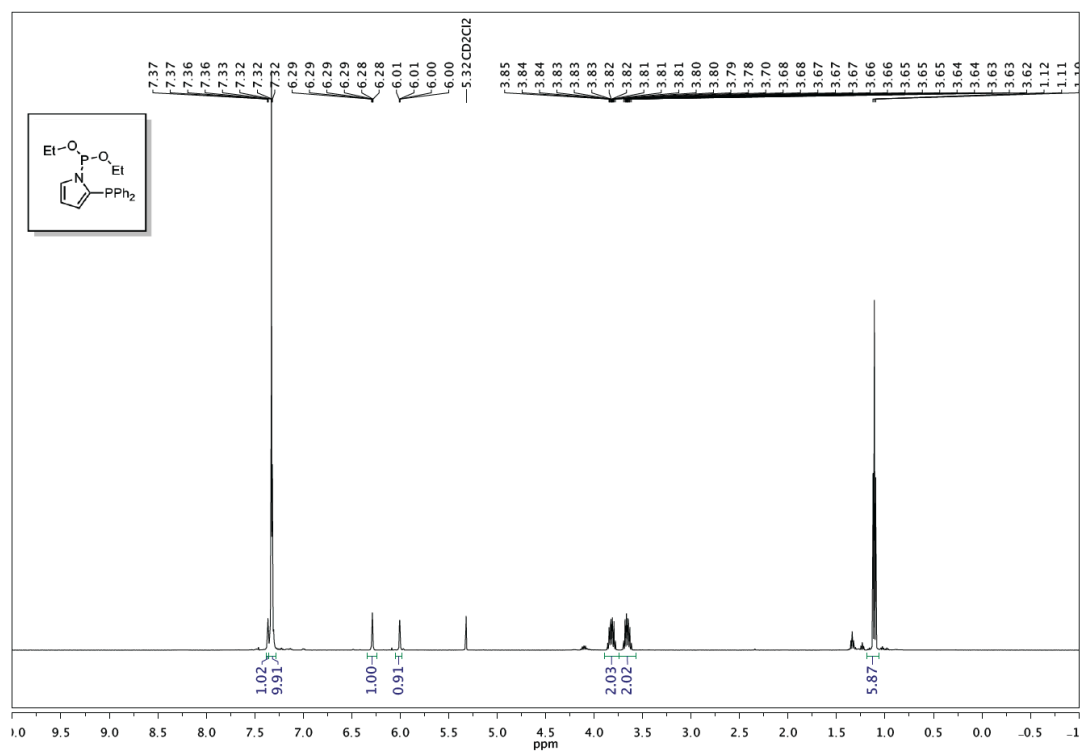


Figure S21.  $^1\text{H}$  NMR spectrum of L4.

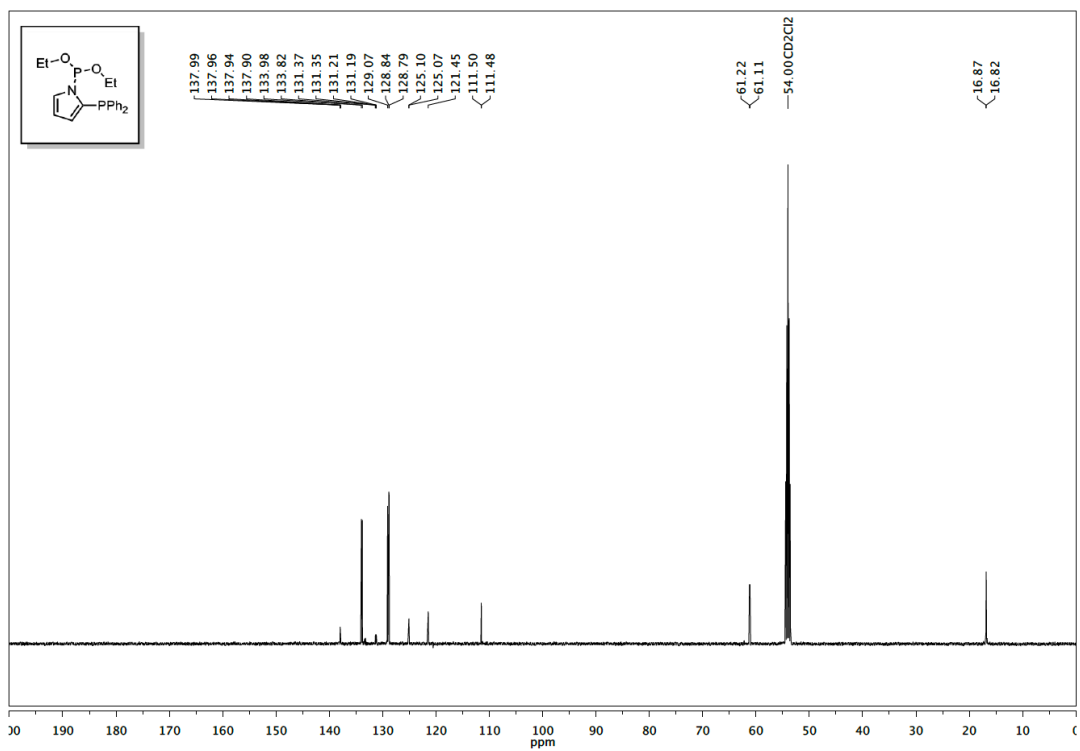


Figure S22. <sup>13</sup>C NMR spectrum of L4.

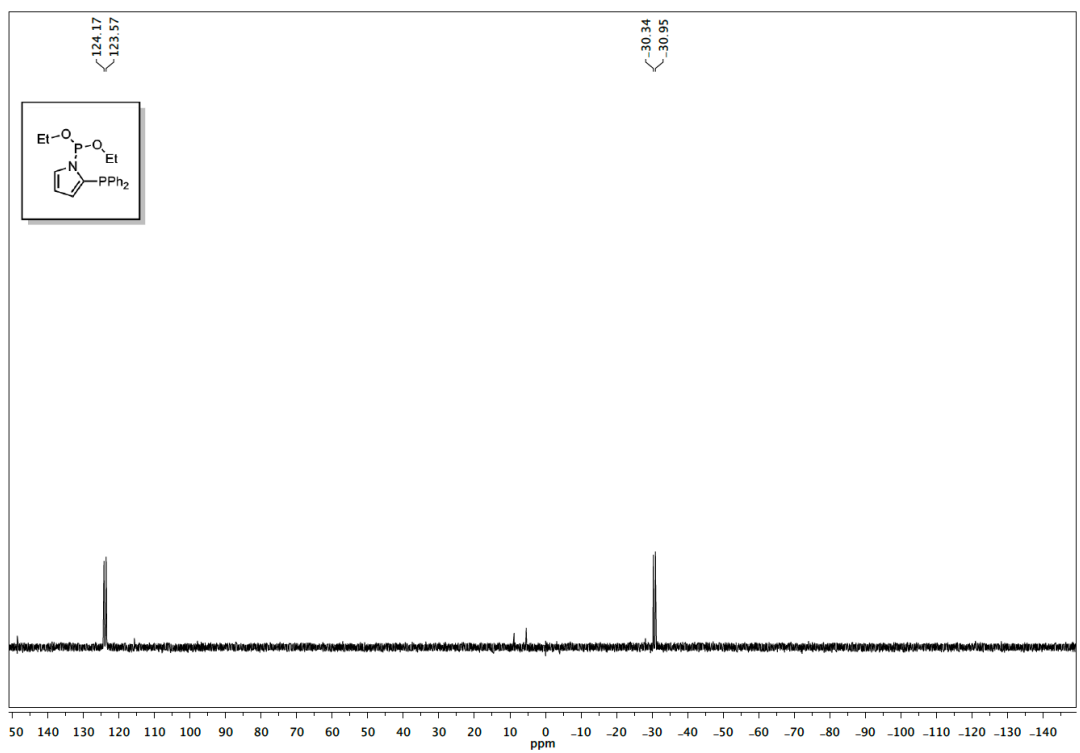


Figure S23. <sup>31</sup>P NMR spectrum of L4.



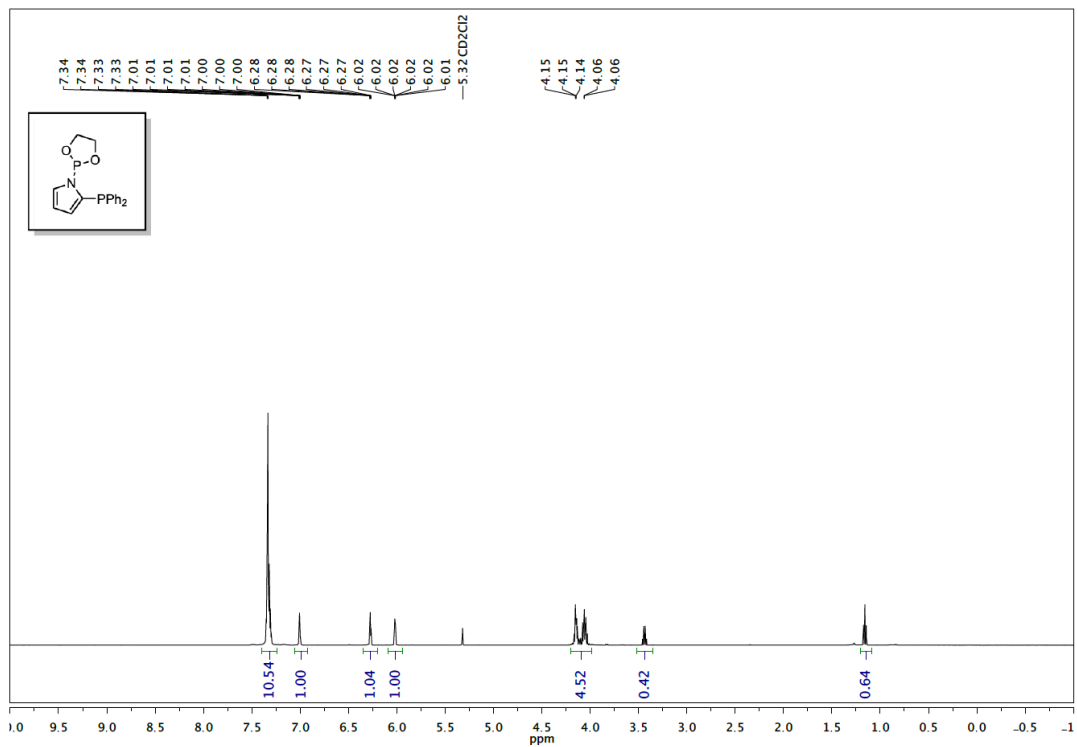


Figure S24.  $^1\text{H}$  NMR spectrum of L5.

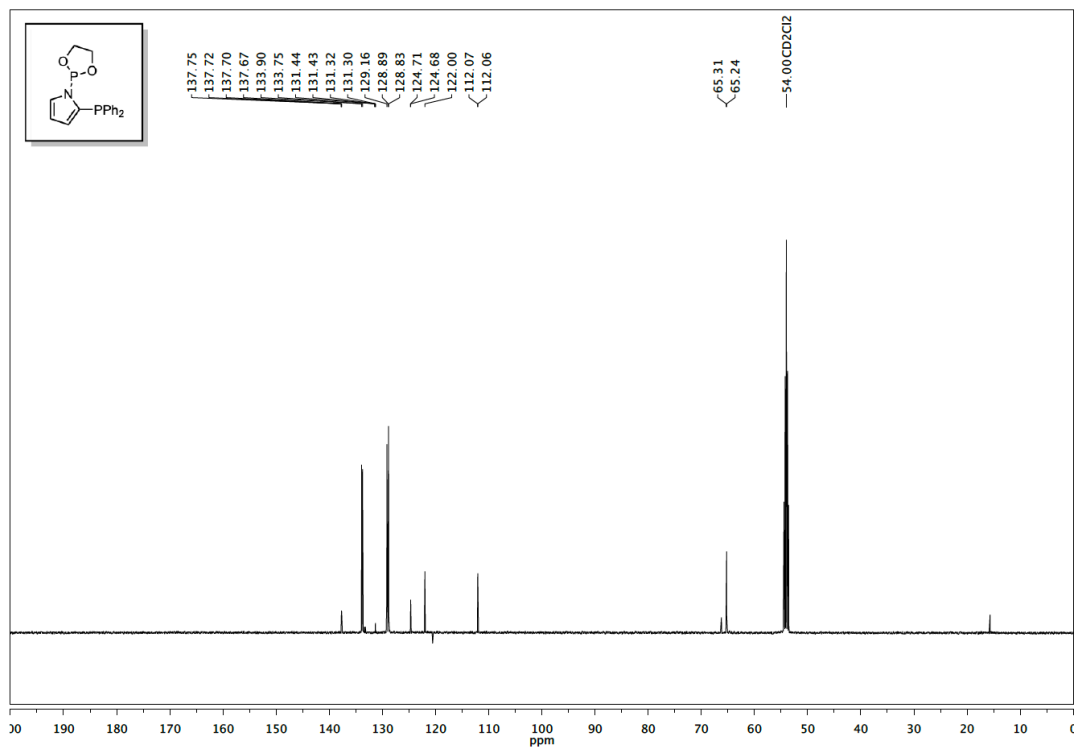


Figure S25.  $^{13}\text{C}$  NMR spectrum of L5.

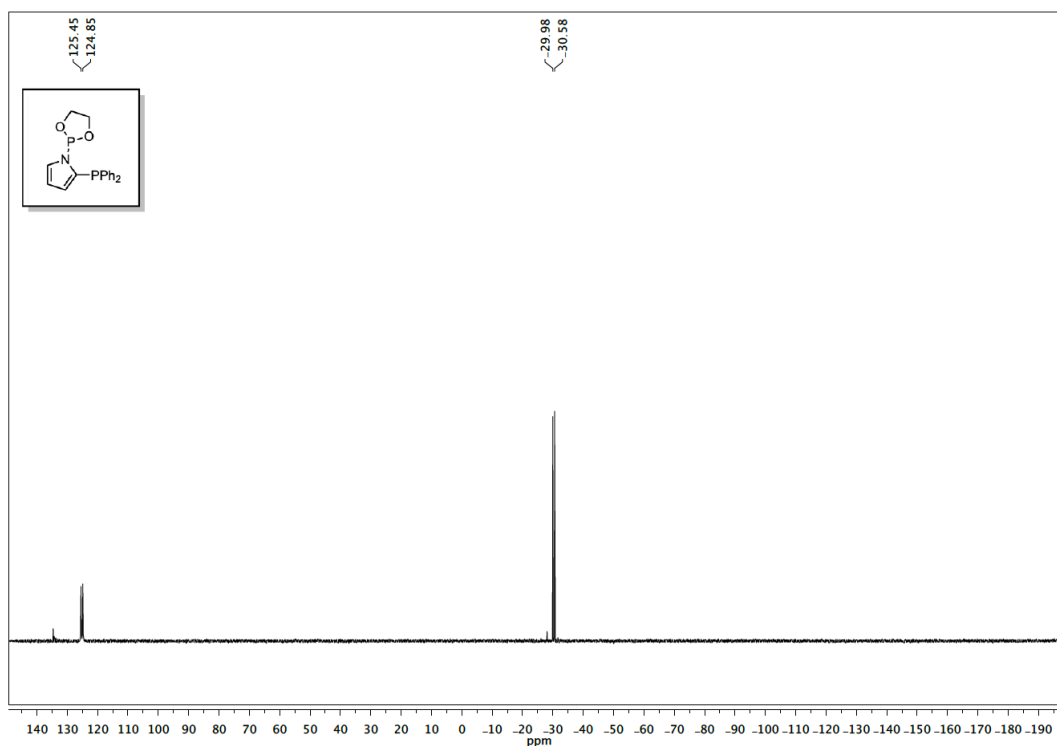


Figure S26.  $^{31}\text{P}$  NMR spectrum of L5.

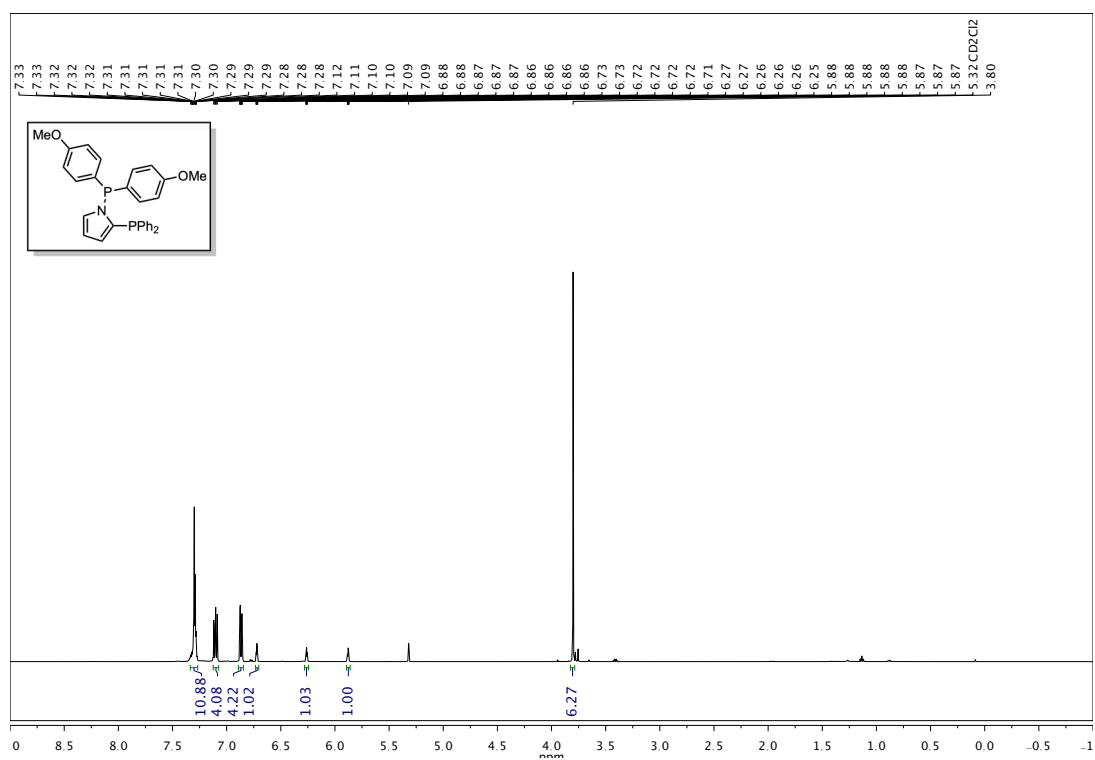


Figure S27.  $^1\text{H}$  NMR spectrum of L6.

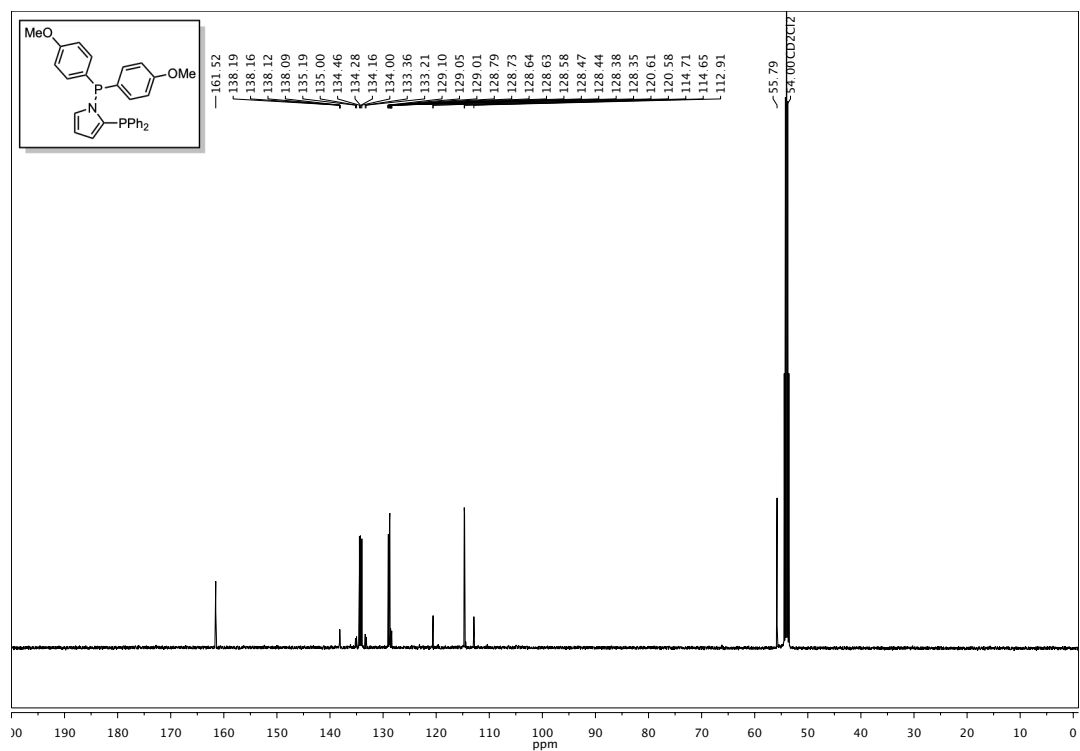


Figure S28.  $^{13}\text{C}$  NMR spectrum of L6.

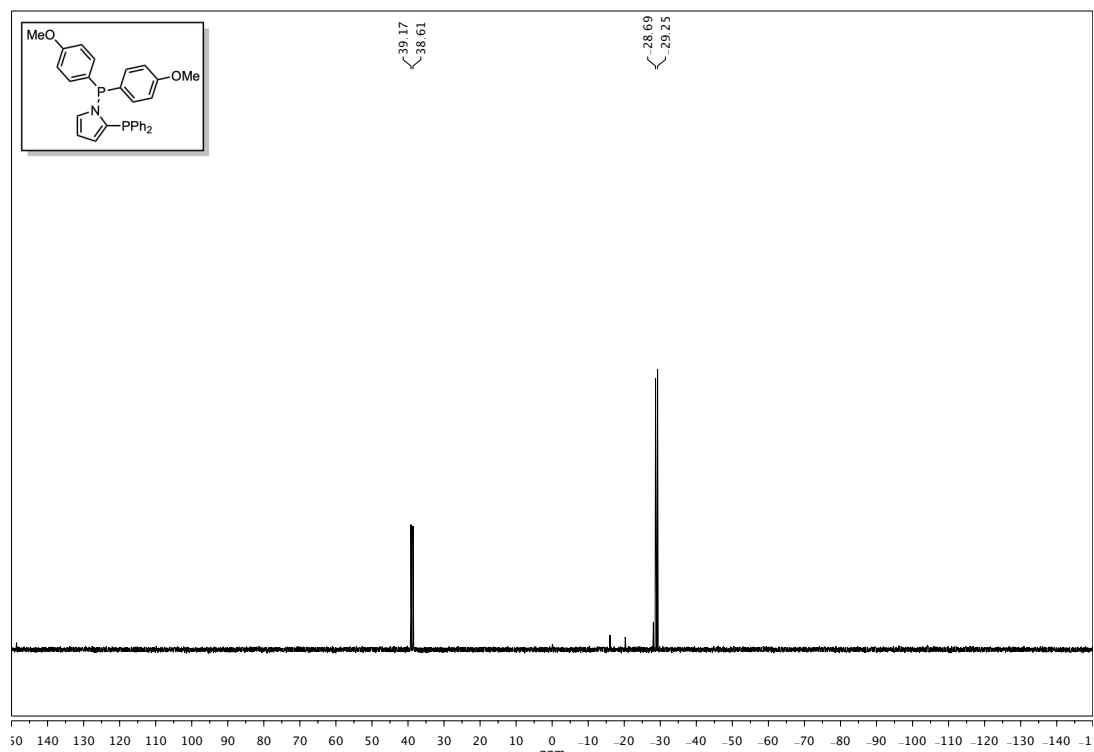


Figure S29.  $^{31}\text{P}$  NMR spectrum of L6.

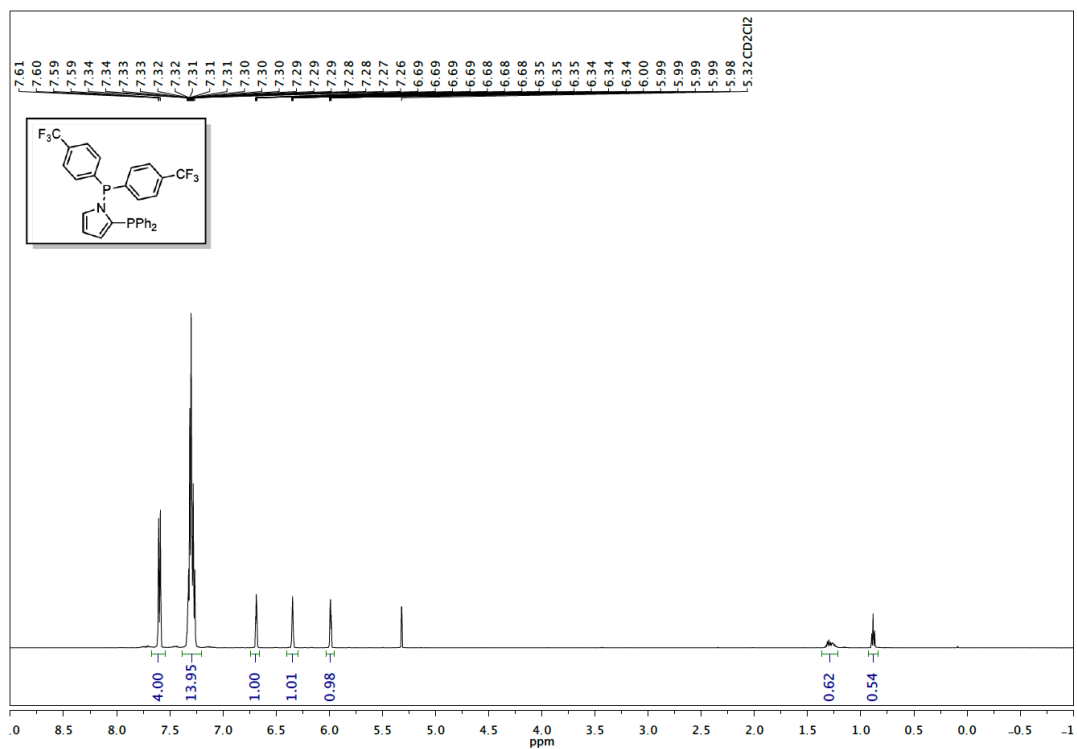


Figure S30. <sup>1</sup>H NMR spectrum of L7.

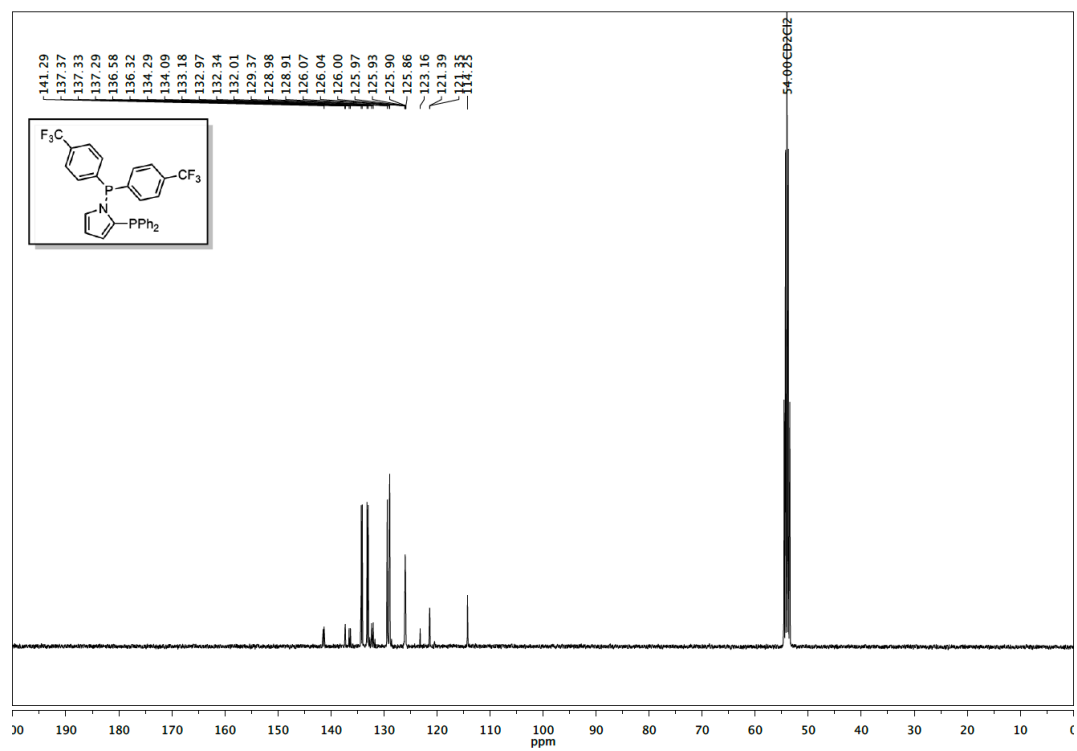


Figure S31. <sup>13</sup>C NMR spectrum of L7.

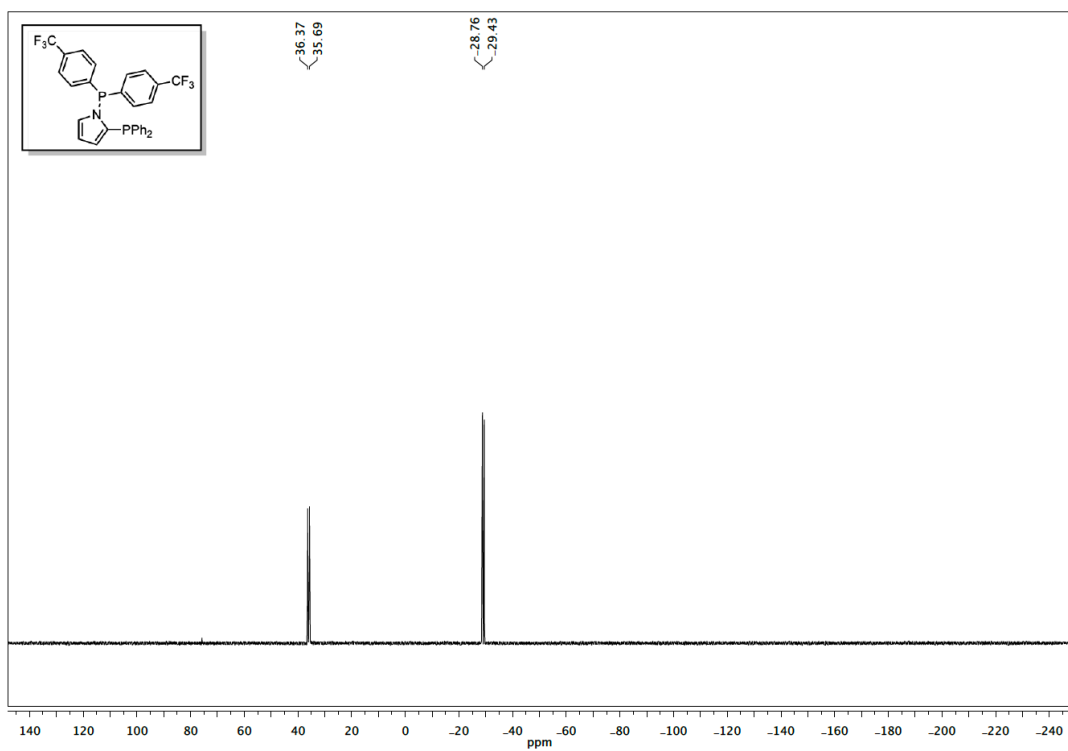


Figure S32. <sup>31</sup>P NMR spectrum of L7.

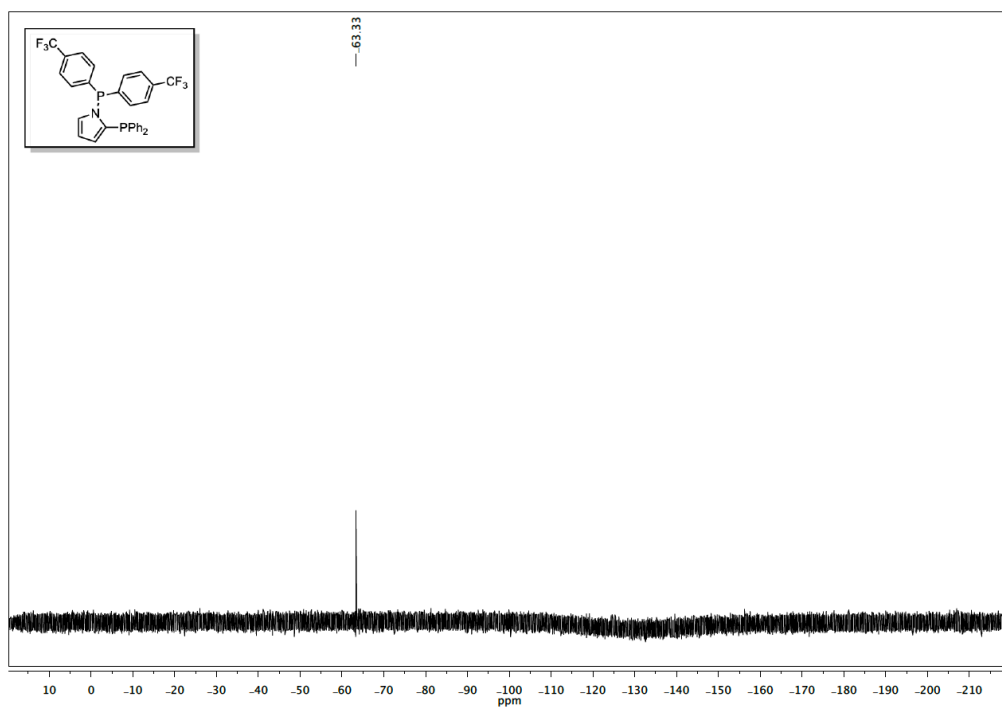


Figure S33. <sup>19</sup>F NMR spectrum of L7.

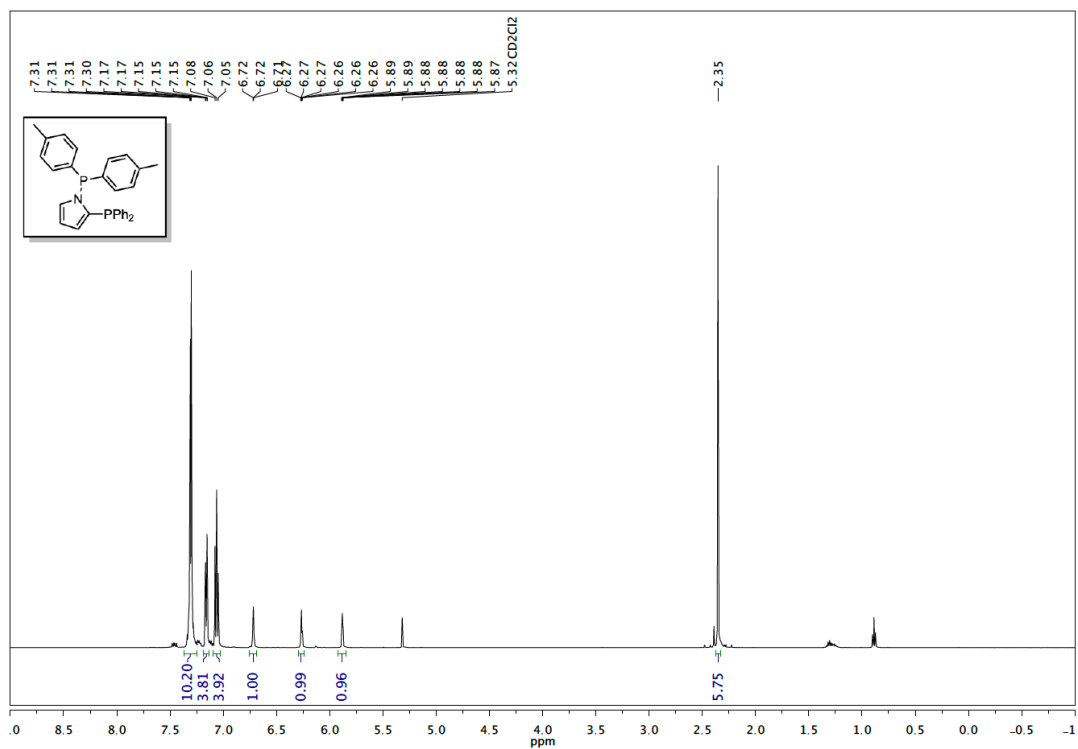


Figure S34.  $^1\text{H}$  NMR spectrum of L8.

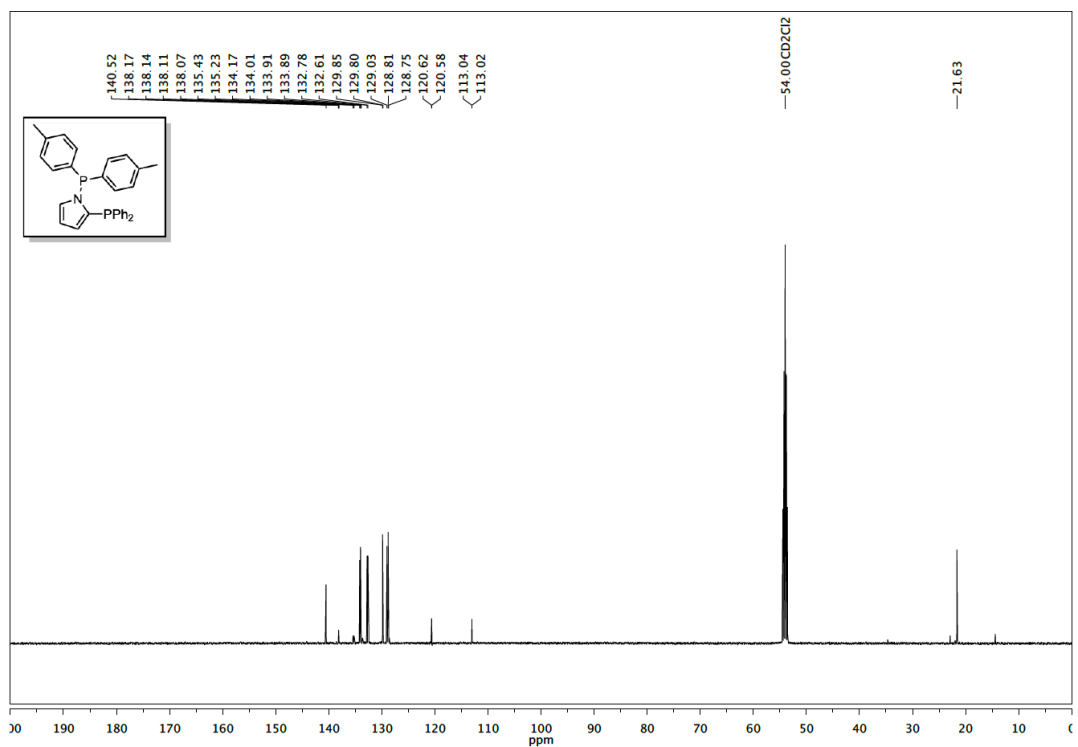
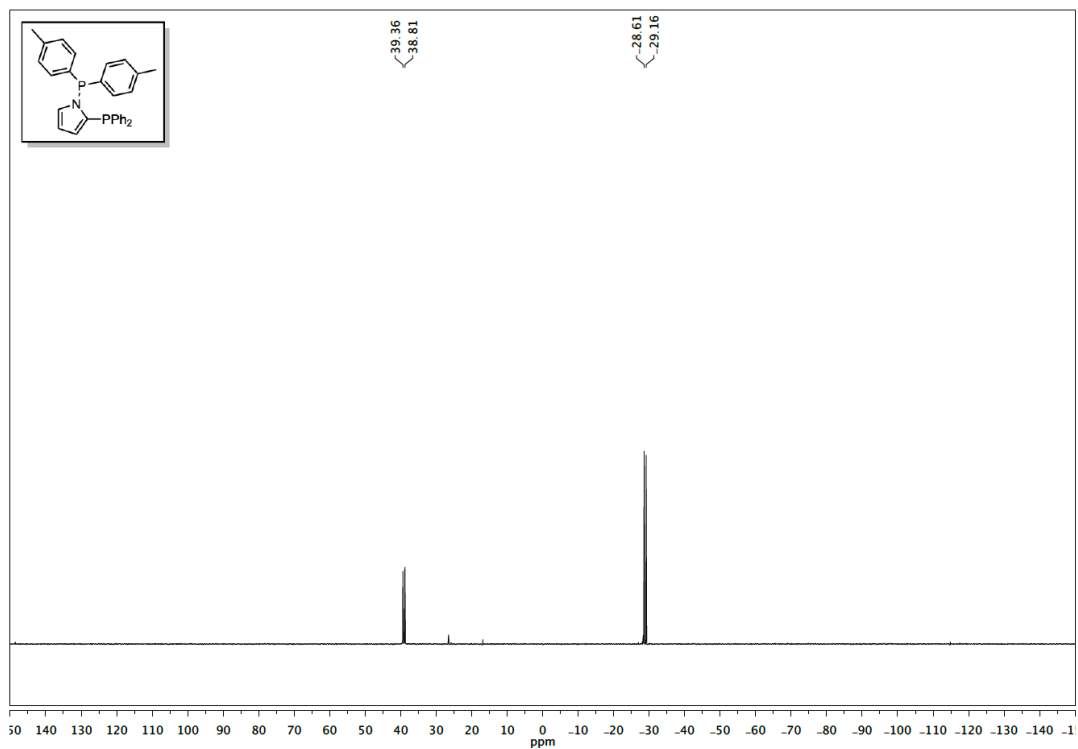
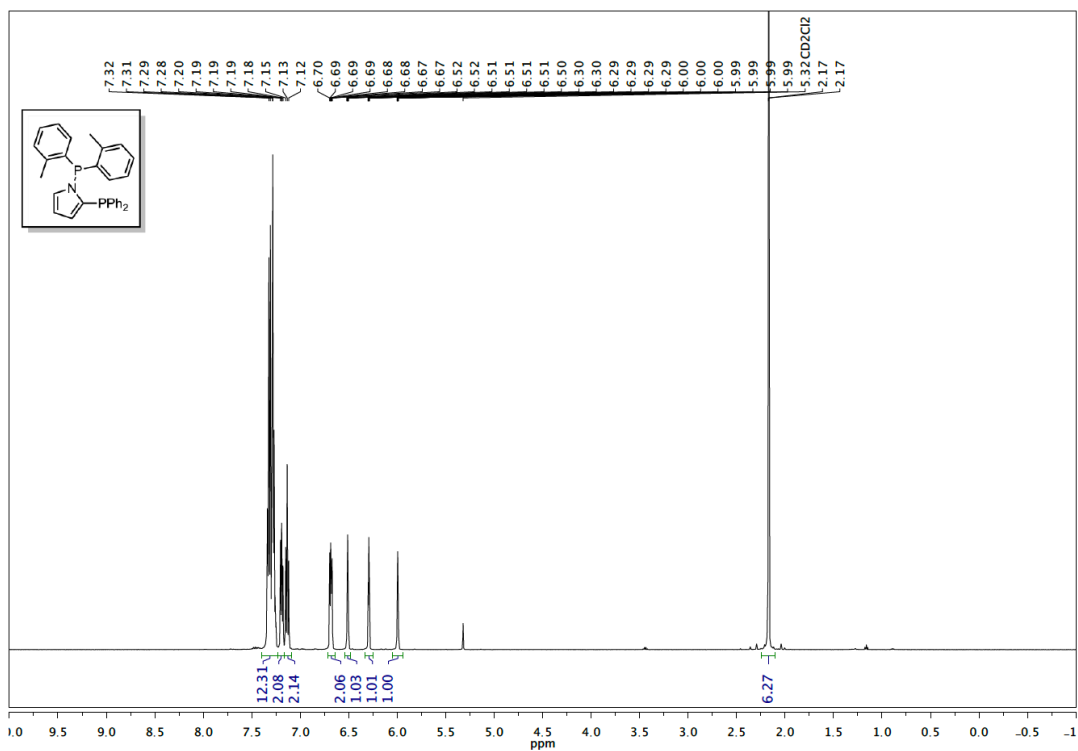


Figure S35.  $^{13}\text{C}$  NMR spectrum of L8.



**Figure S36.** <sup>31</sup>P NMR spectrum of L8.



**Figure S37.** <sup>1</sup>H NMR spectrum of L9.

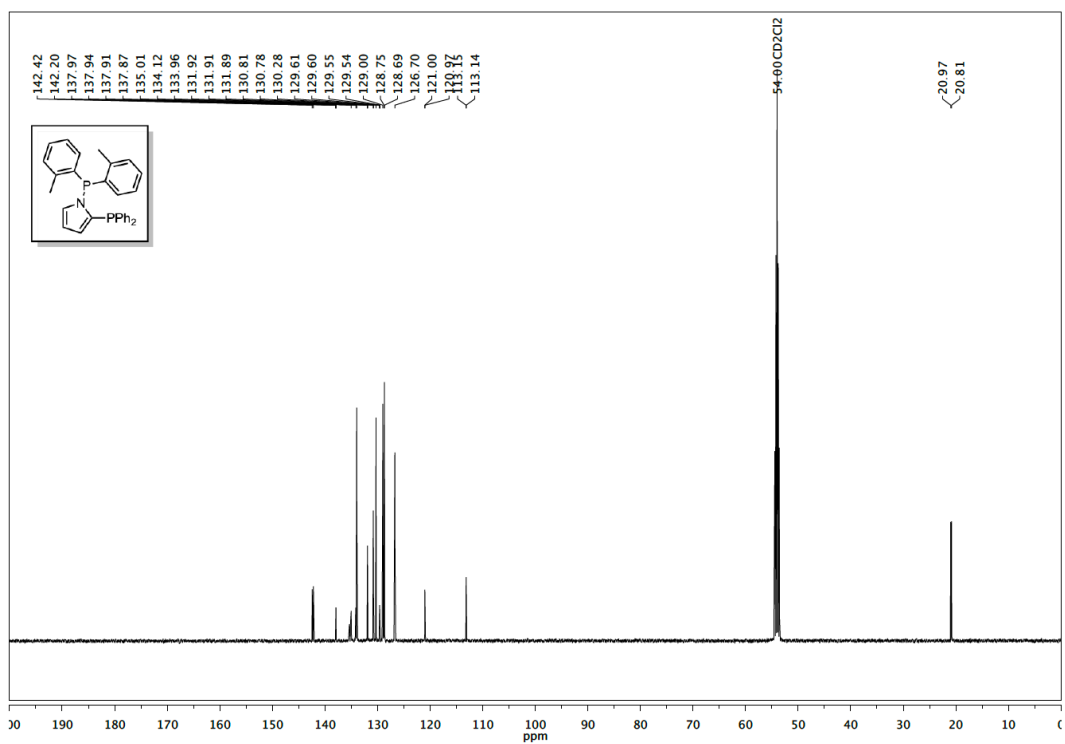


Figure S38.  $^{13}\text{C}$  NMR spectrum of L9.

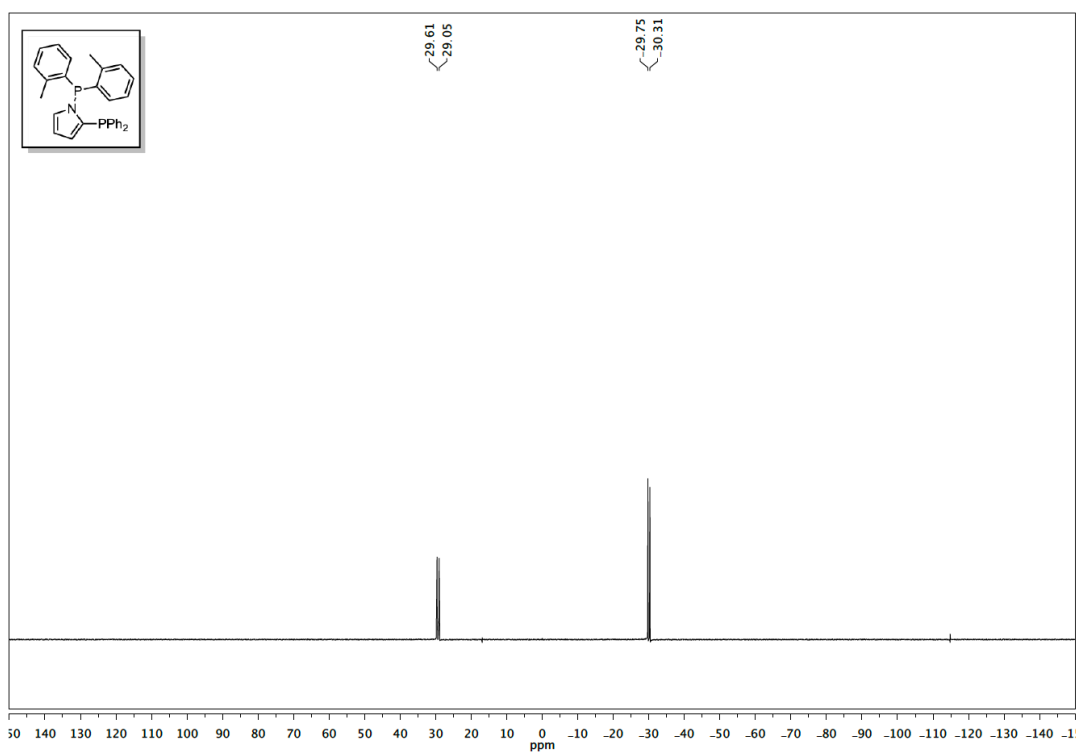


Figure S39.  $^{31}\text{P}$  NMR spectrum of L9.



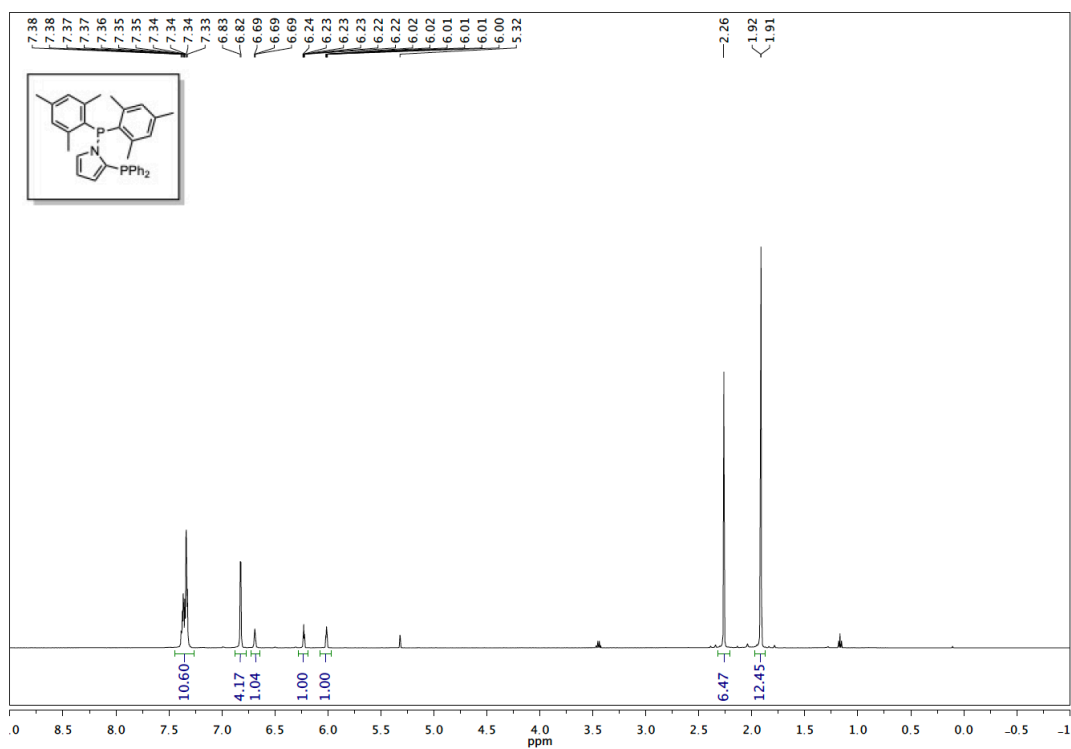


Figure S40.  $^1\text{H}$  NMR spectrum of L10.

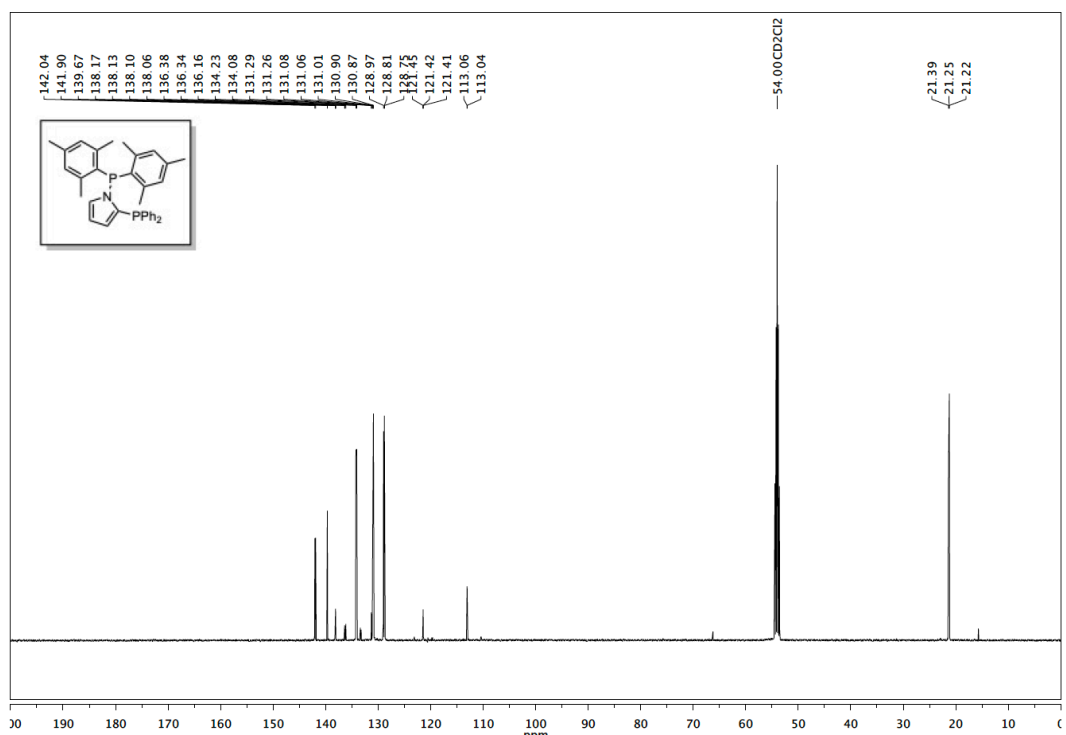
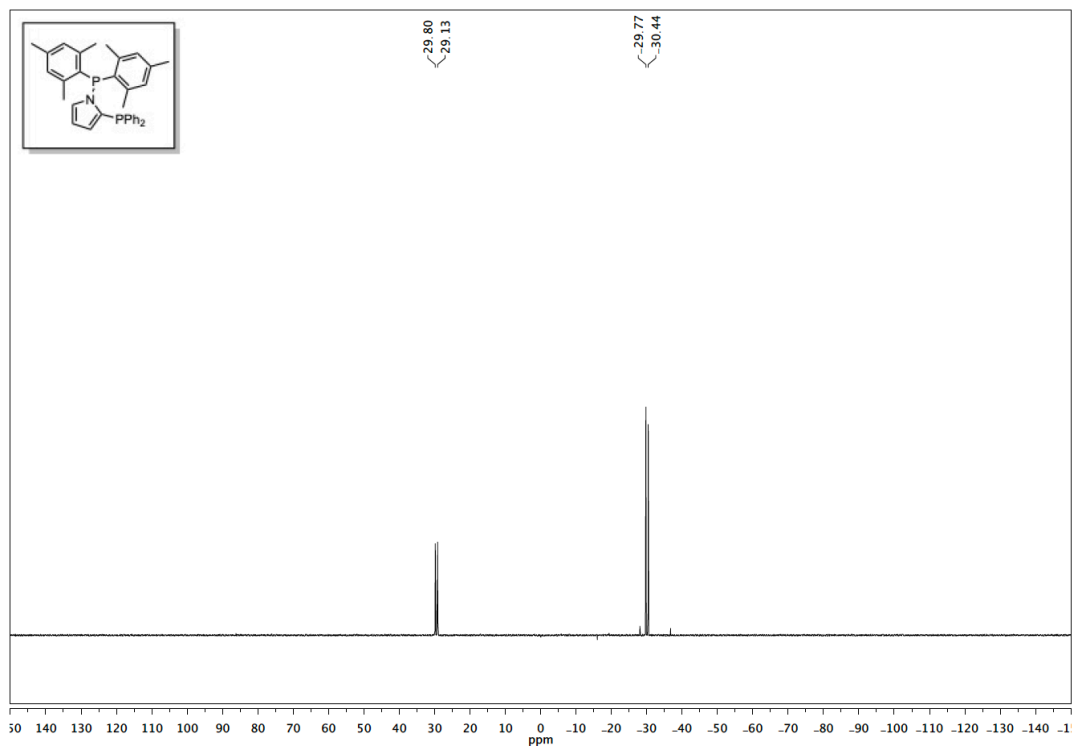


Figure S41.  $^{13}\text{C}$  NMR spectrum of L10.



**Figure S42.**  $^{31}\text{P}$  NMR spectrum of L10.

## XI. NMR Spectra of Transition Metal Complexes

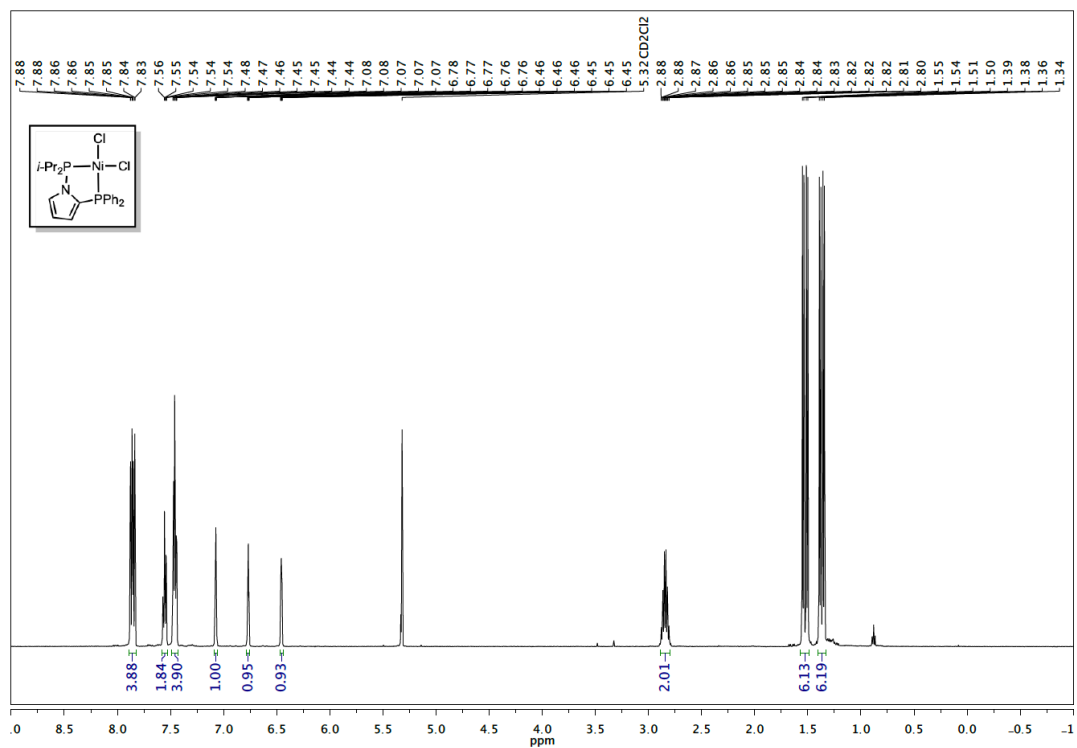


Figure S43. <sup>1</sup>H NMR spectrum of (L1)NiCl<sub>2</sub>.

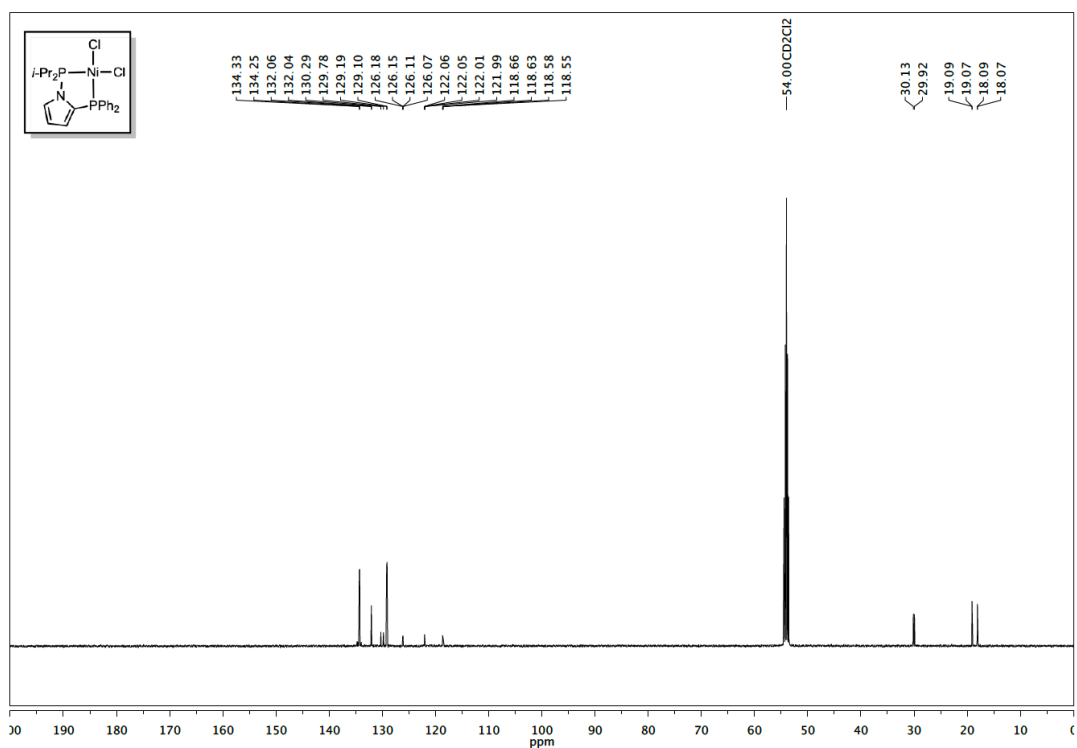


Figure S44. <sup>13</sup>C NMR spectrum of (L1)NiCl<sub>2</sub>.

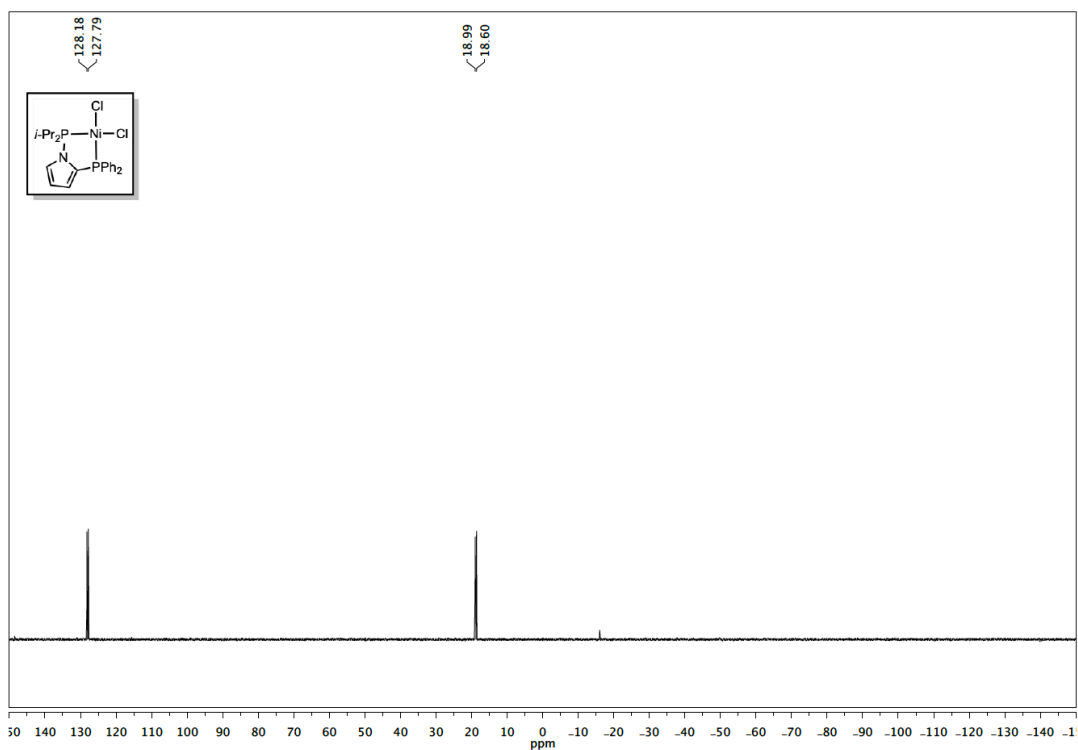


Figure S45.  $^{31}P$  NMR spectrum of  $(L1)NiCl_2$ .

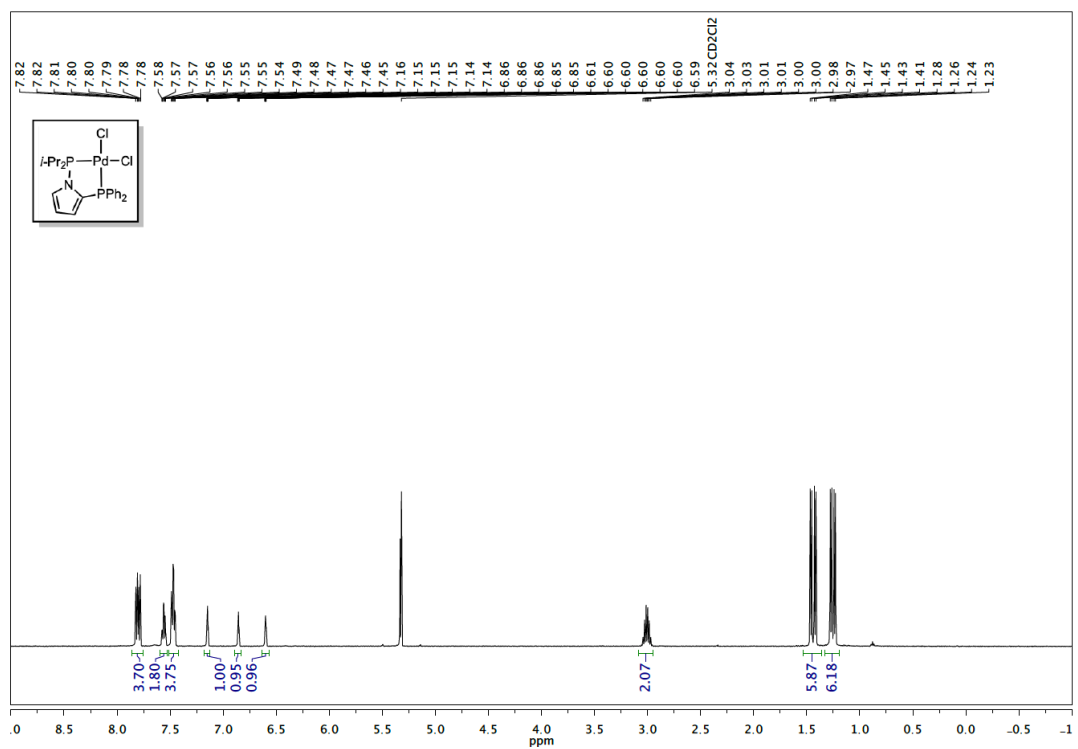


Figure S46.  $^1H$  NMR spectrum of  $(L1)PdCl_2$ .

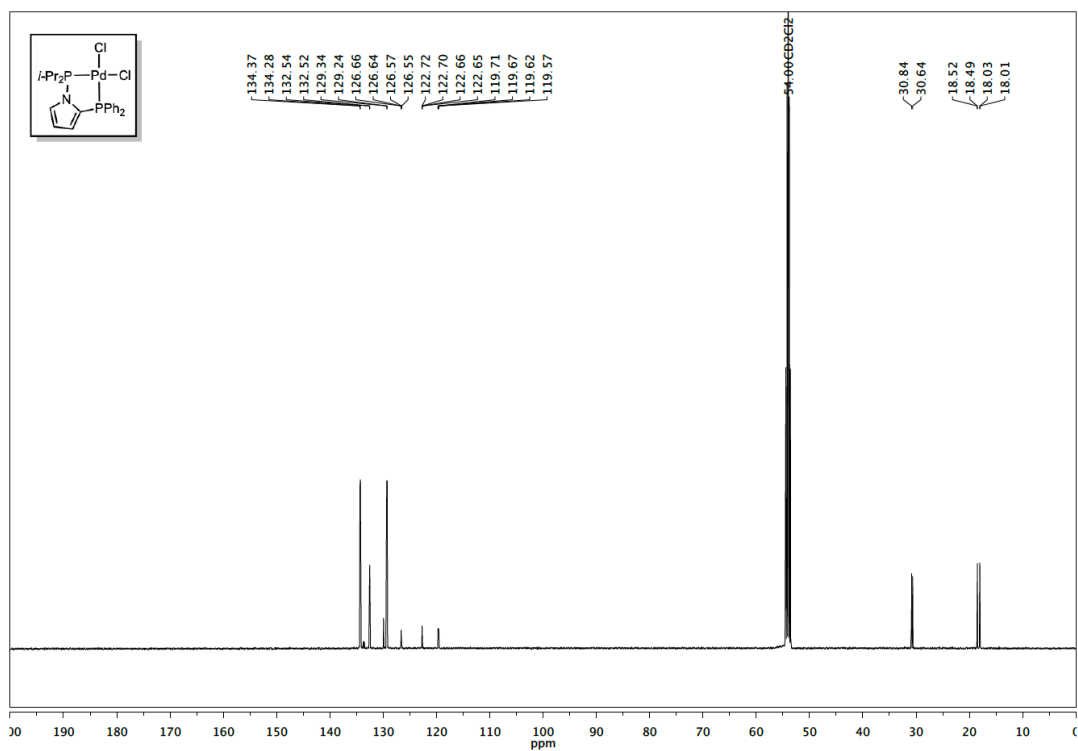


Figure S47.  $^{13}C$  NMR spectrum of  $(L1)PdCl_2$ .

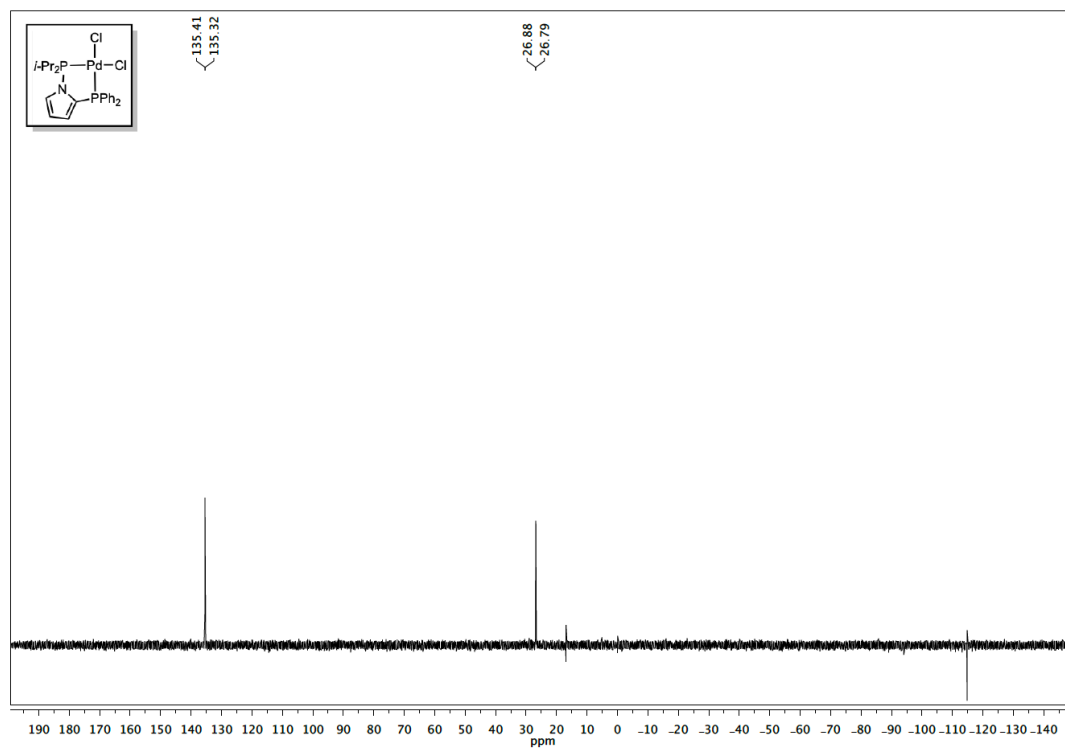


Figure S48.  $^{31}P$  NMR spectrum of  $(L1)PdCl_2$ .

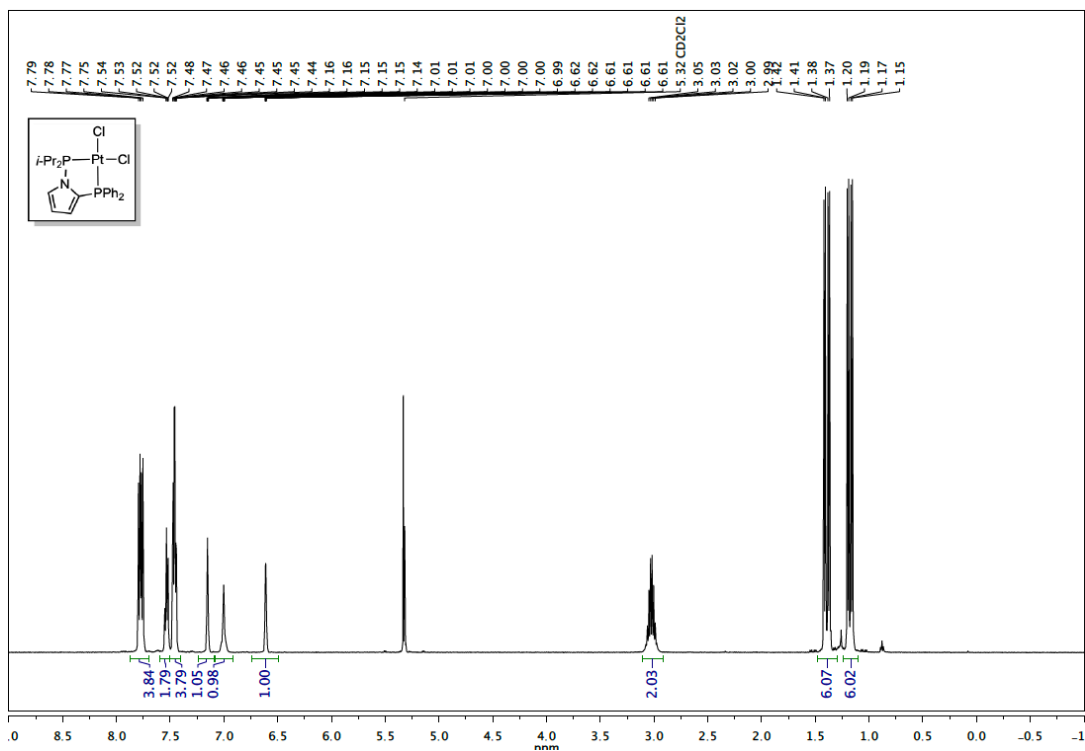


Figure S49.  $^1\text{H}$  NMR spectrum of  $(\text{L1})\text{PtCl}_2$ .

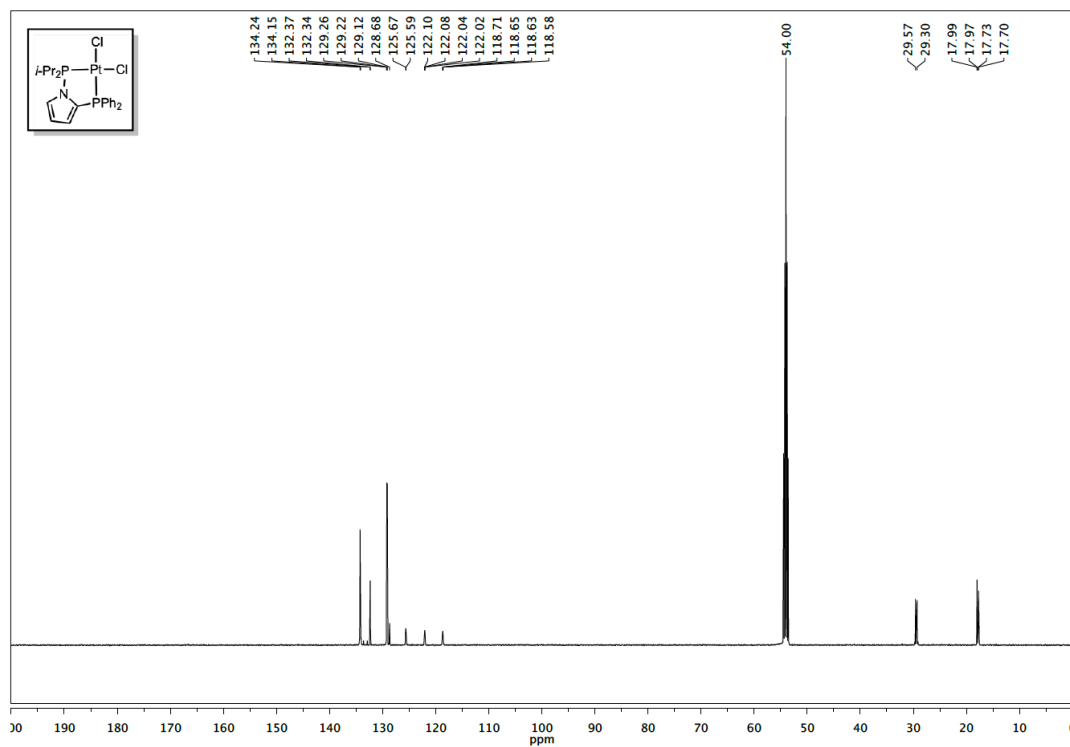


Figure S50.  $^{13}\text{C}$  NMR spectrum of  $(\text{L1})\text{PtCl}_2$ .

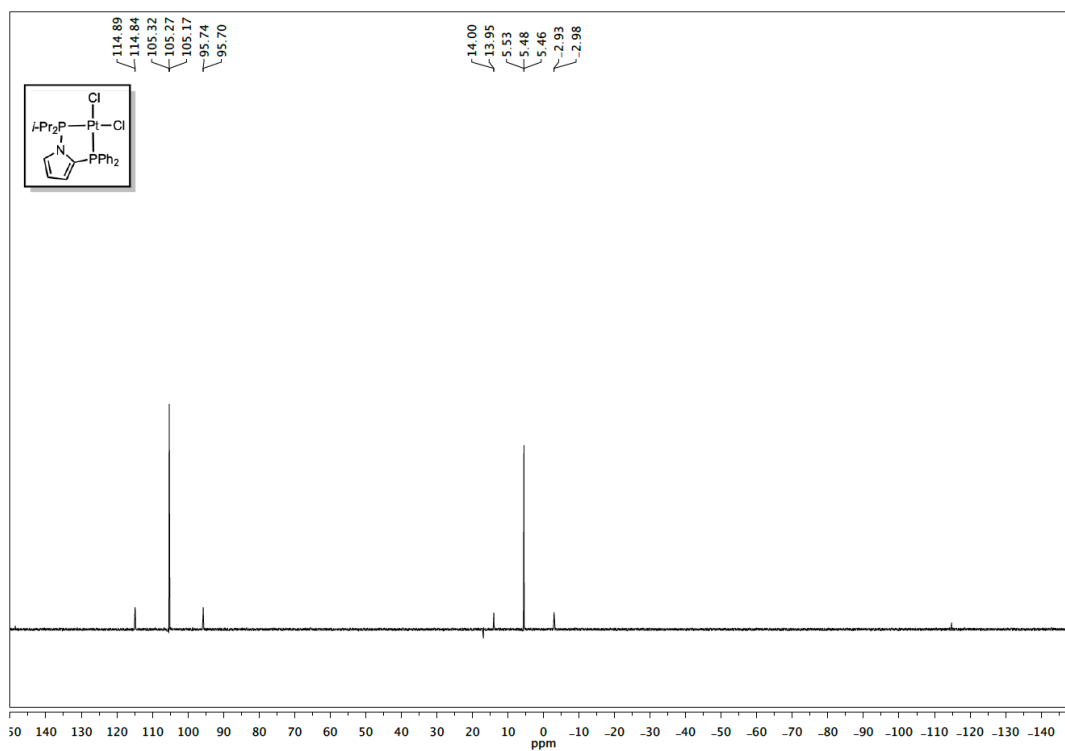


Figure S51.  $^{31}P$  NMR spectrum of  $(L1)PtCl_2$ .

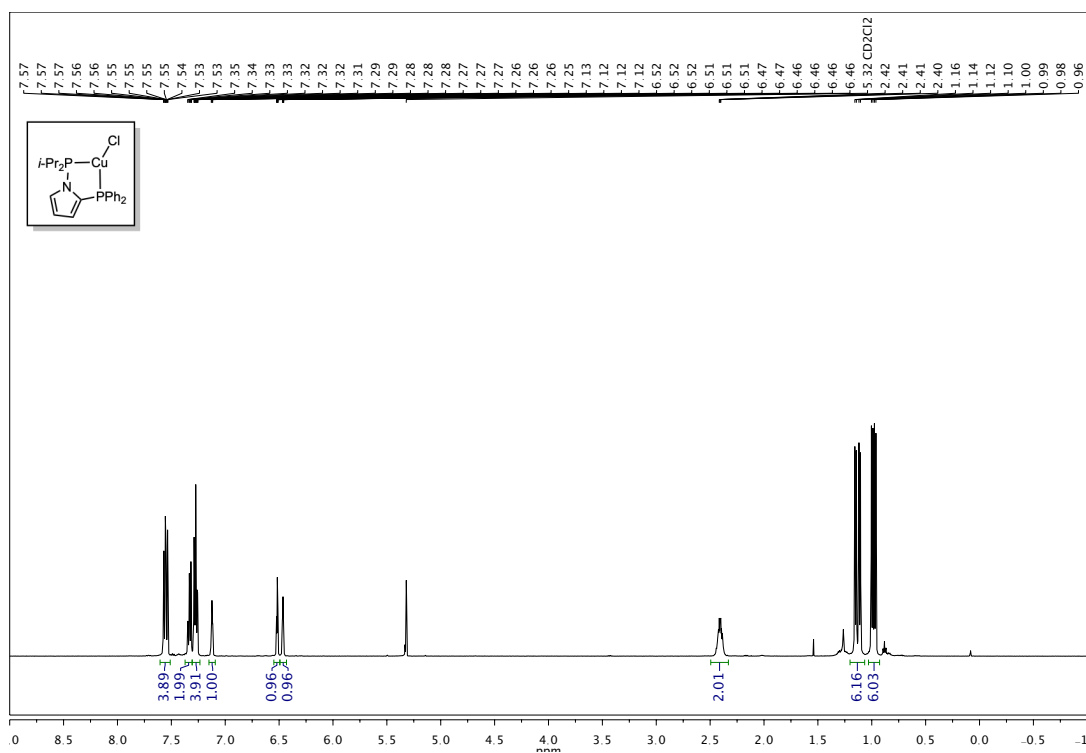


Figure S52.  $^1H$  NMR spectrum of  $[(L1)CuCl]_2$ .

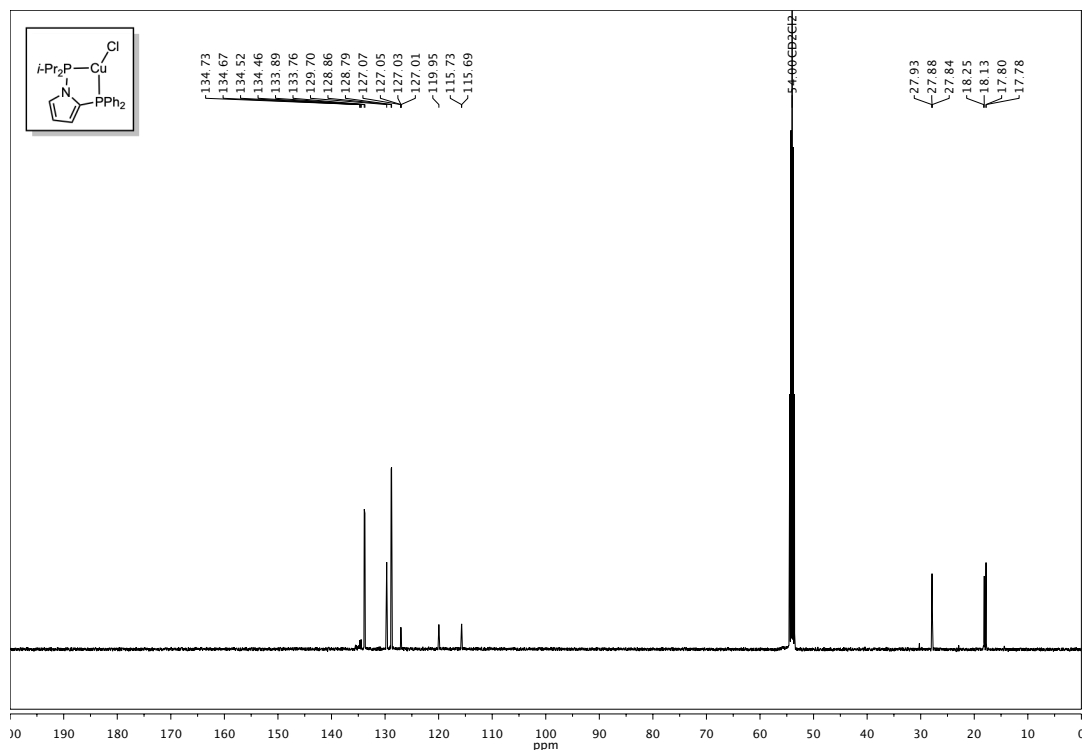


Figure S53.  $^{13}\text{C}$  NMR spectrum of  $[(\text{L1})\text{CuCl}]_2$ .

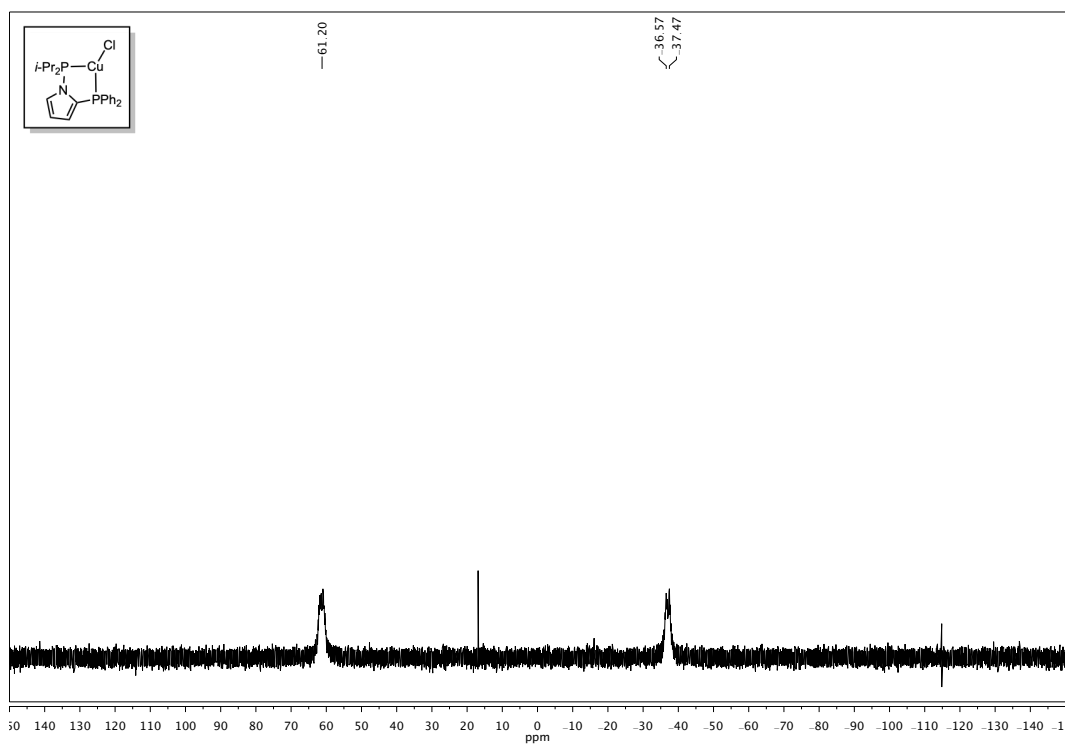


Figure S54.  $^{31}\text{P}$  NMR spectrum of  $[(\text{L1})\text{CuCl}]_2$ .



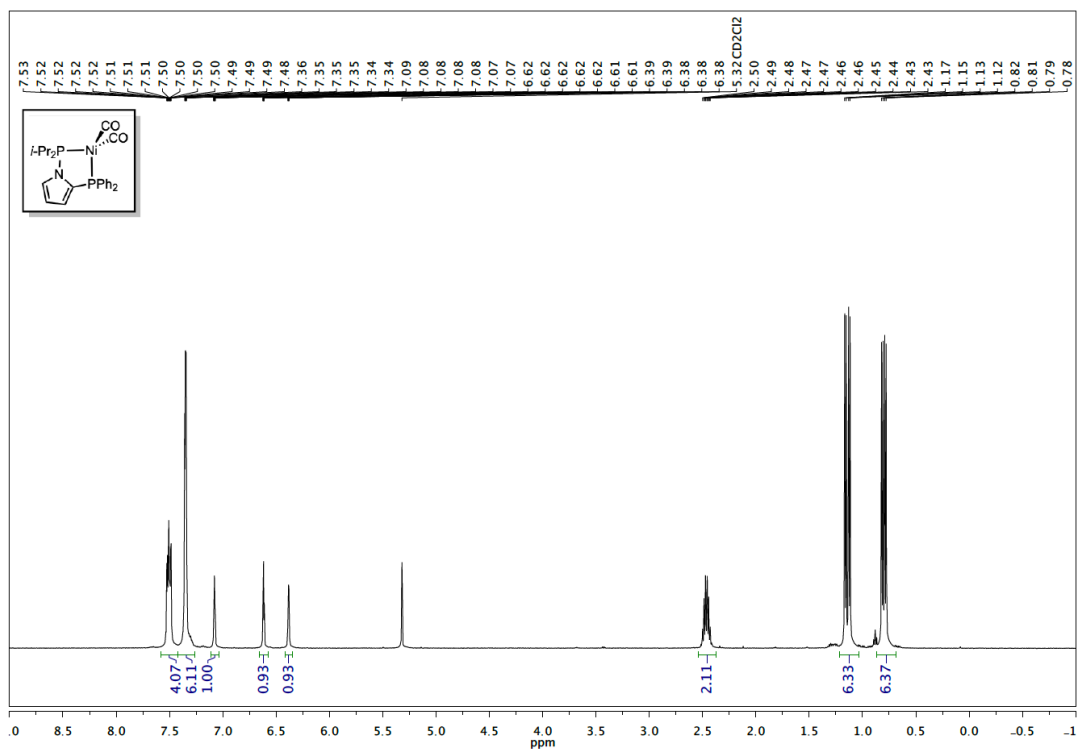


Figure S55. <sup>1</sup>H NMR spectrum of (L1)Ni(CO)<sub>2</sub>.

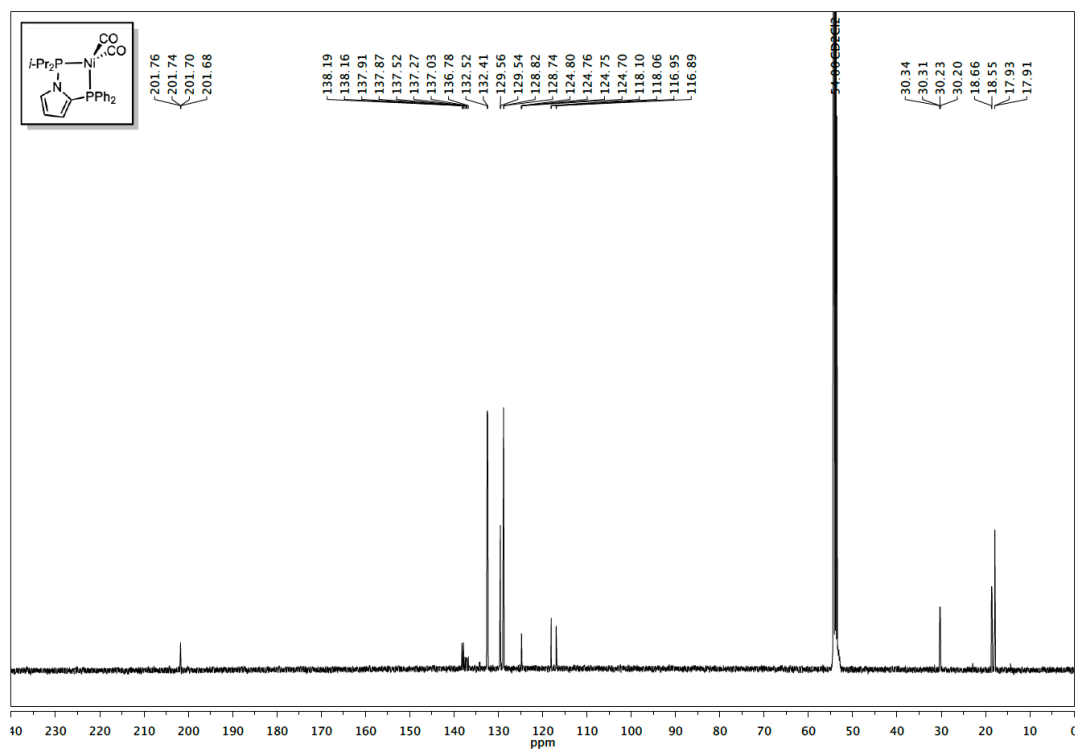


Figure S56. <sup>13</sup>C NMR spectrum of (L1)Ni(CO)<sub>2</sub>.

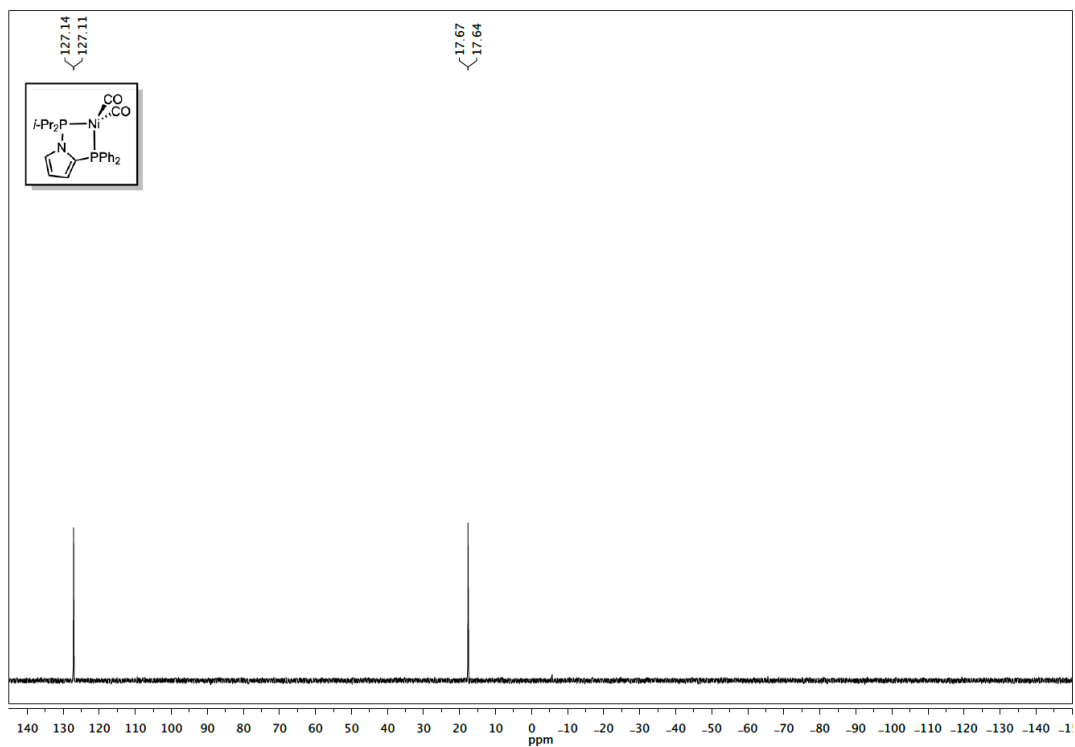


Figure S57.  $^{31}\text{P}$  NMR spectrum of  $(\text{L1})\text{Ni}(\text{CO})_2$ .

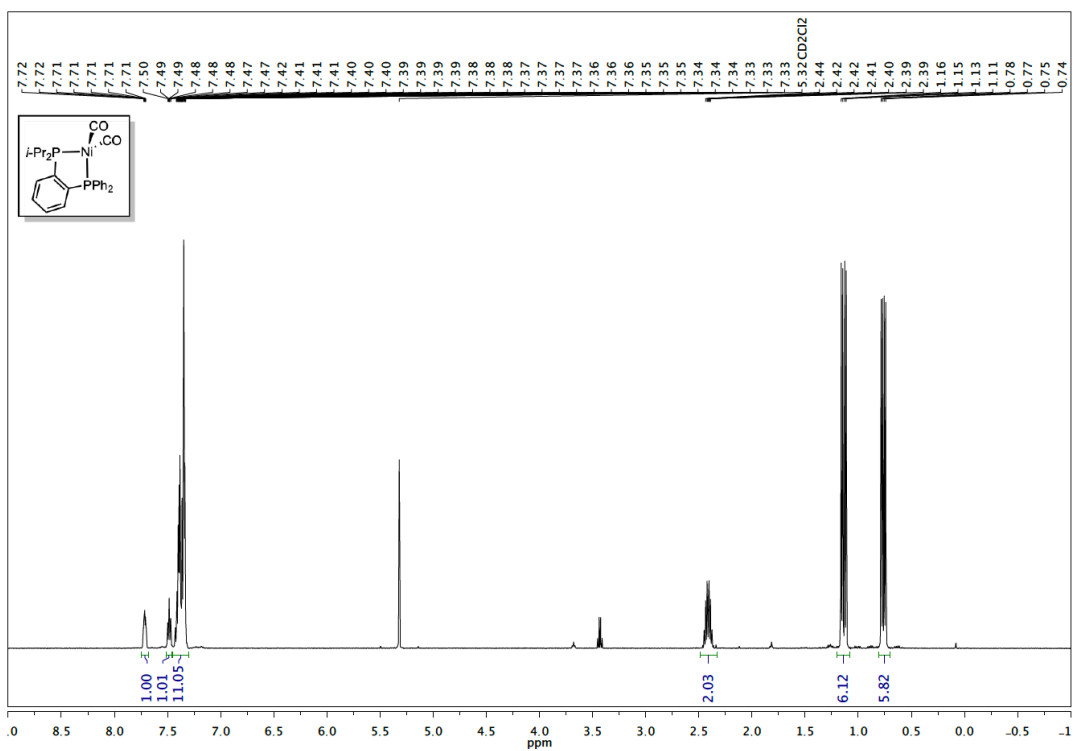


Figure S58.  $^1\text{H}$  NMR spectrum of  $(\text{L11})\text{Ni}(\text{CO})_2$ .

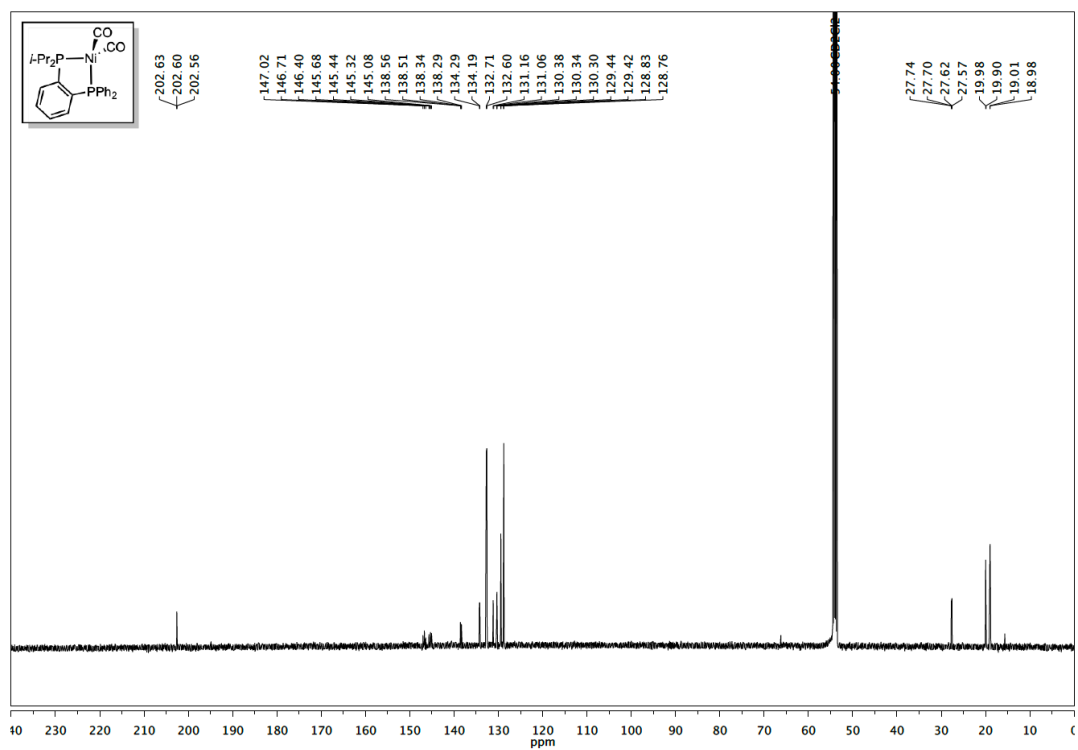


Figure S59.  $^{13}C$  NMR spectrum of  $(L11)Ni(CO)_2$ .

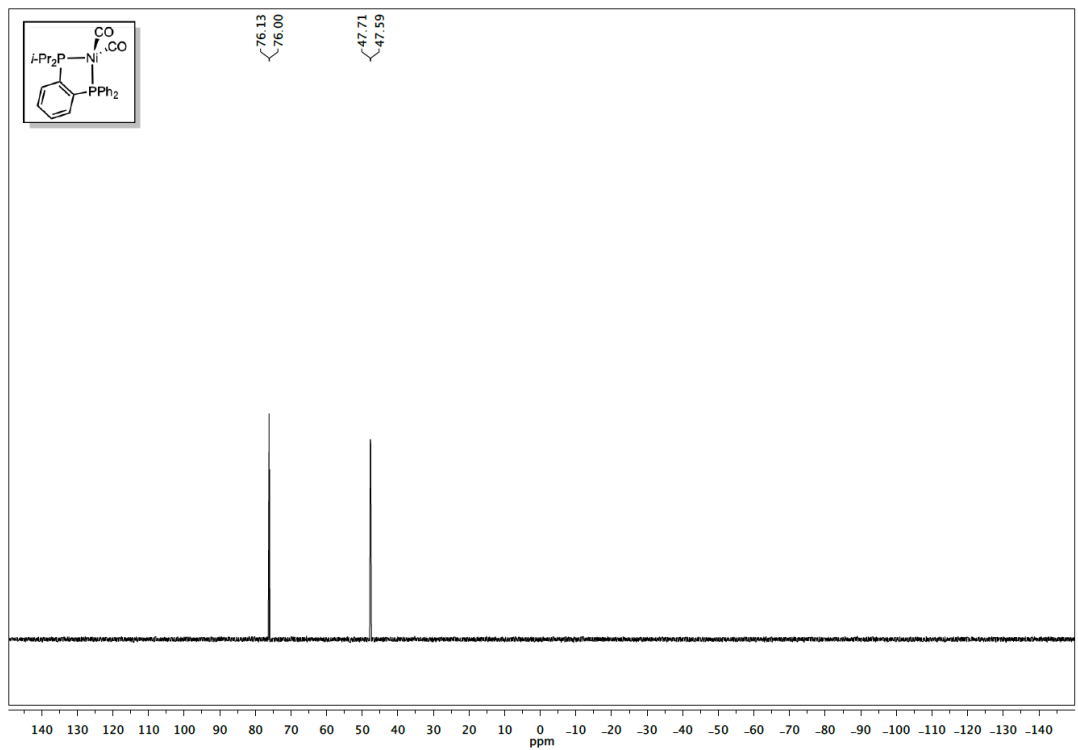


Figure S60.  $^{31}P$  NMR spectrum of  $(L11)Ni(CO)_2$ .

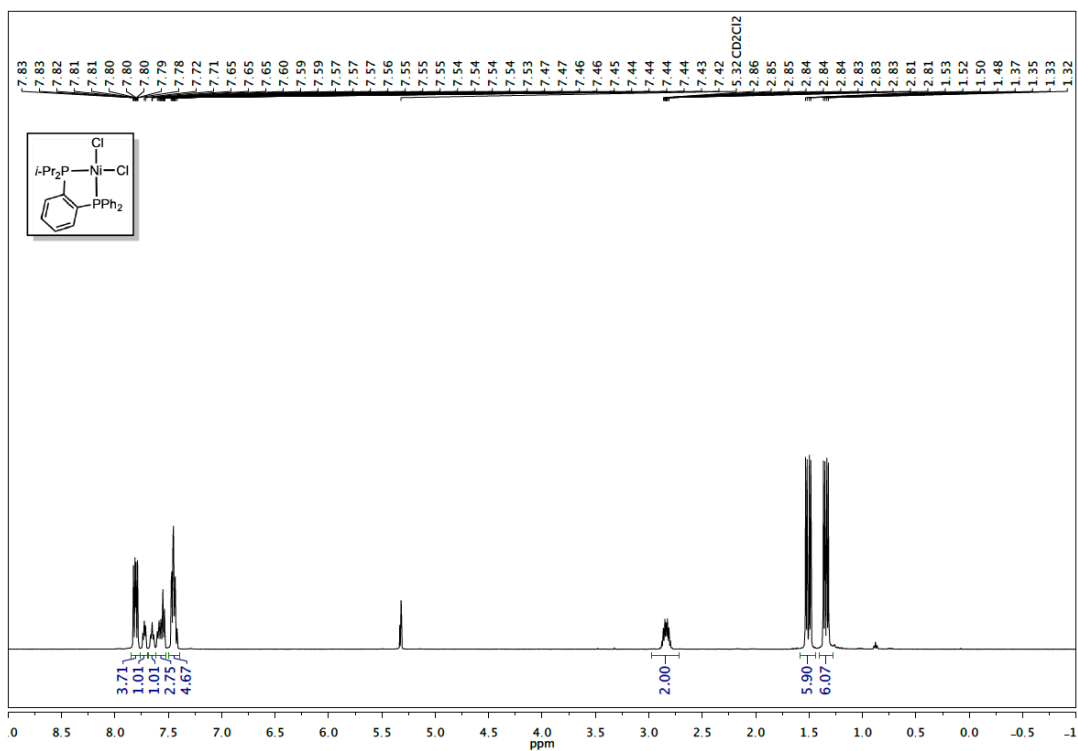


Figure S61.  $^1H$  NMR spectrum of  $(L11)NiCl_2$ .

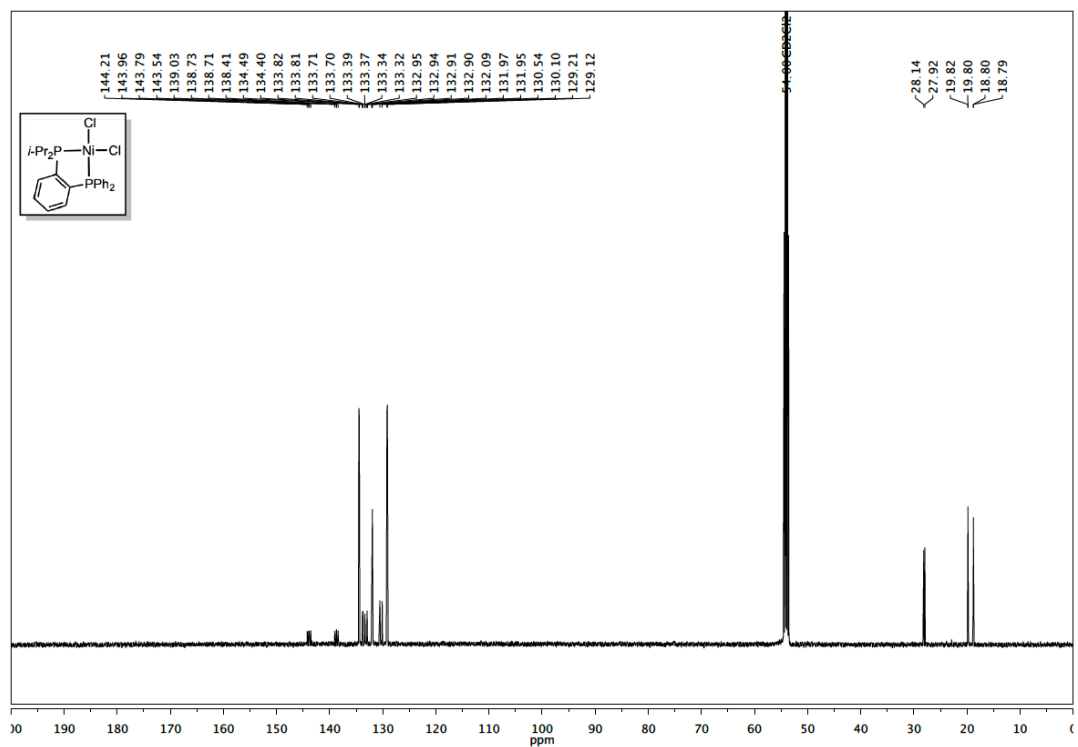


Figure S62.  $^{13}C$  NMR spectrum of  $(L11)NiCl_2$ .

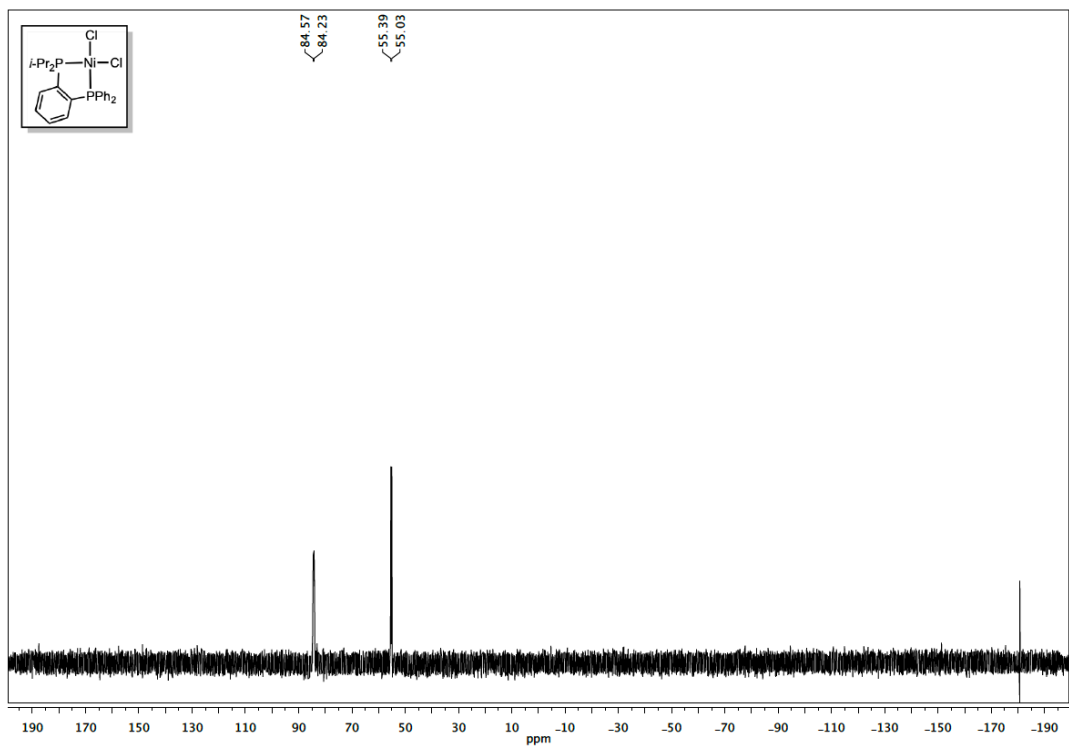


Figure S63.  $^{31}\text{P}$  NMR spectrum of  $(L11)NiCl_2$ .

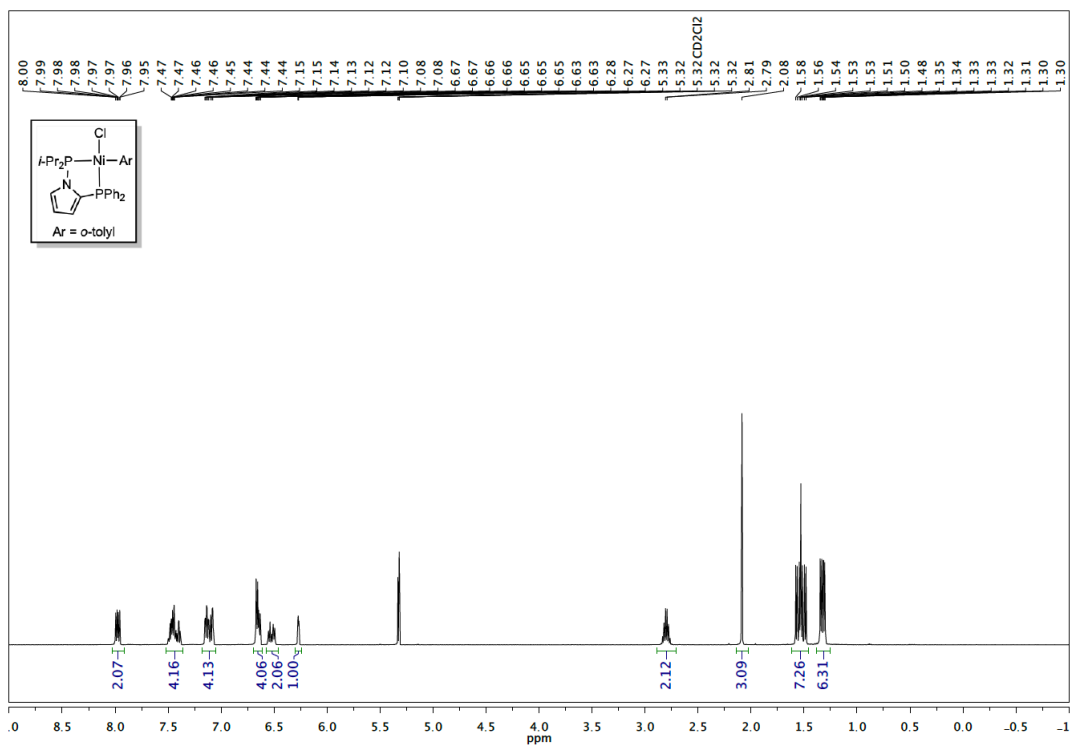


Figure S64.  $^1\text{H}$  NMR spectrum of  $(L1)Ni(o\text{-tolyl})Cl$ .

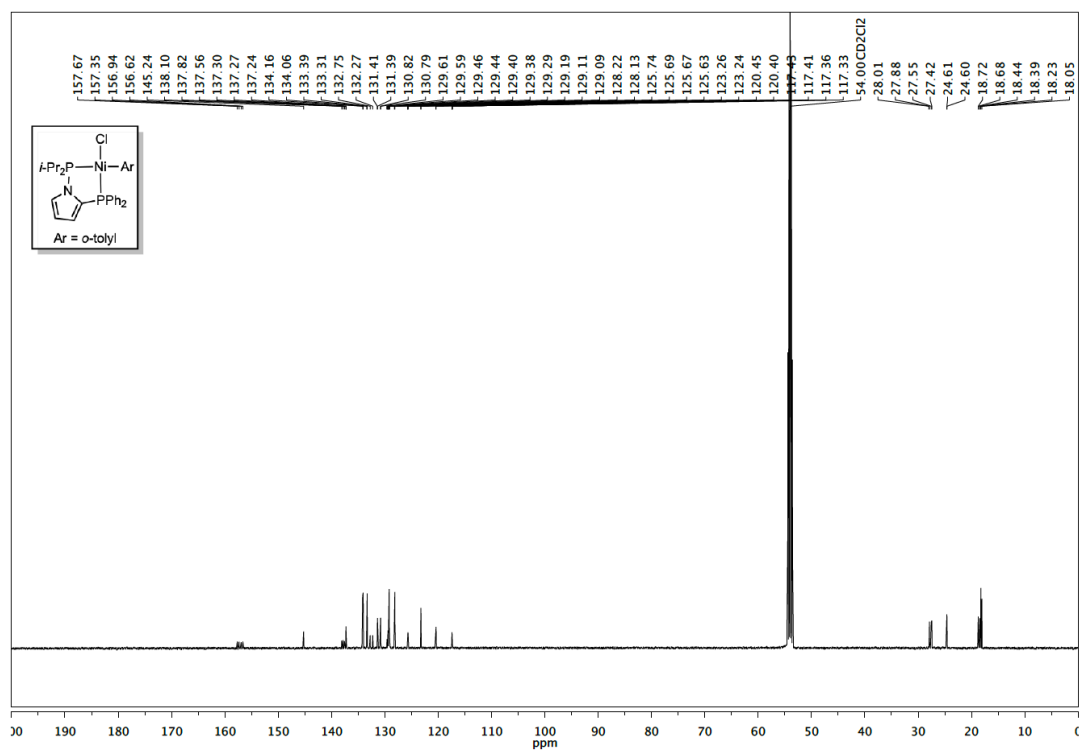


Figure S65. <sup>13</sup>C NMR spectrum of (L1)Ni(*o*-tolyl)Cl.

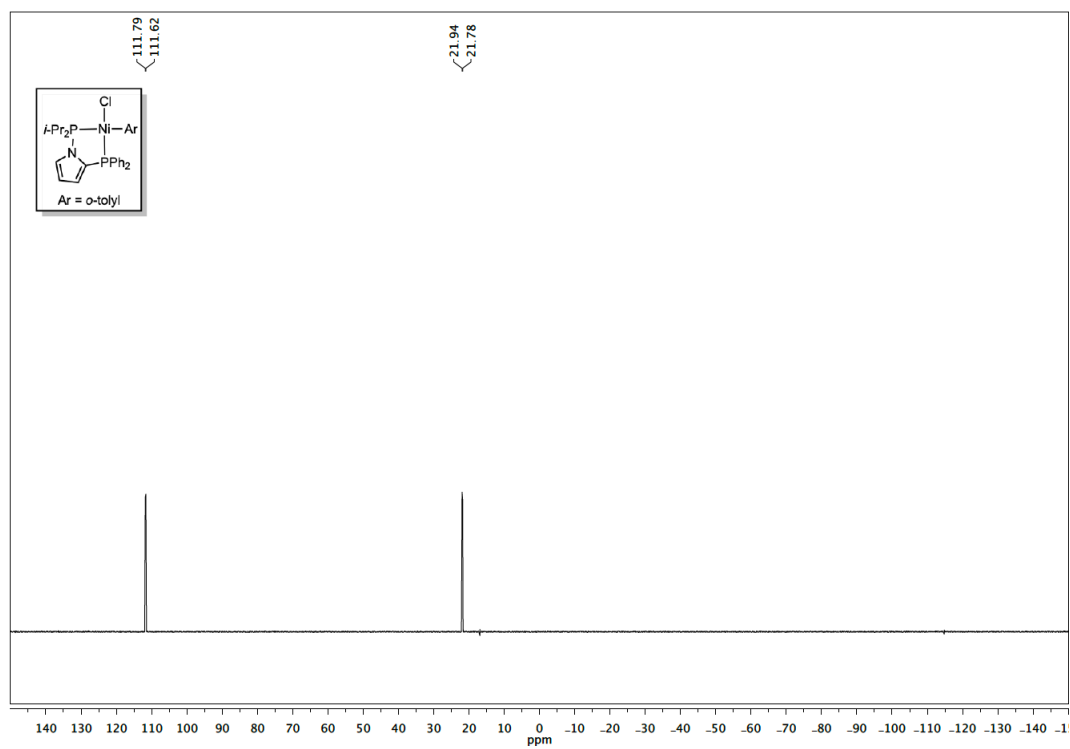


Figure S66. <sup>31</sup>P NMR spectrum of (L1)Ni(*o*-tolyl)Cl.

## XII. NMR Spectrum of Cross-Coupled Product

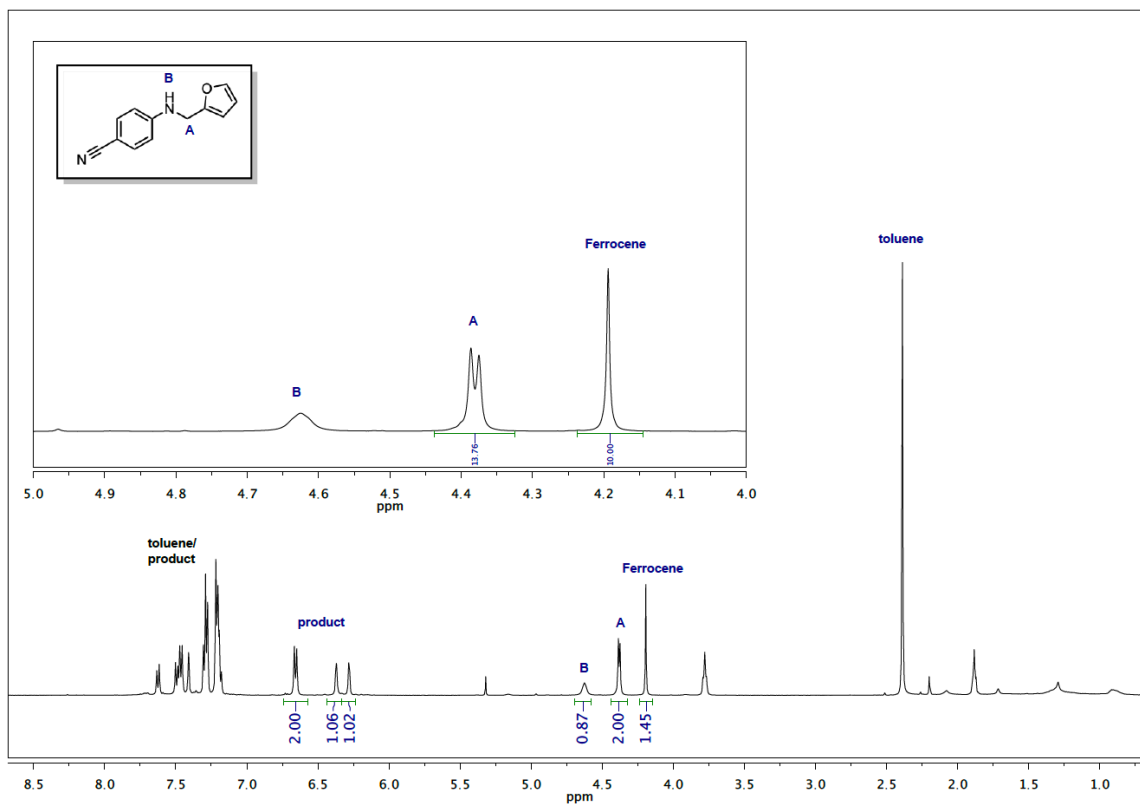


Figure S67.  $^1\text{H}$  NMR spectrum of catalytic reaction mixture with internal standard (ferrocene).

### XIII. X-Ray Crystallographic Data

*Details of crystallographic refinement for (L1)NiCl<sub>2</sub>, (L1)PdCl<sub>2</sub>, (L1)PtCl<sub>2</sub>, [(L1)CuCl]<sub>2</sub>, (L11)NiCl<sub>2</sub>, and (L1)Ni(o-tolyl)Cl*

*General Methods.* A suitable crystal of each sample was selected for analysis and mounted in a polyimide loop. All measurements were made on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Cu-K $\alpha$  or Mo-K $\alpha$  radiation at a temperature of 100 K. Using Olex2,<sup>10</sup> the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package<sup>11</sup> using Least Squares minimization.

All complexes were refined without restraint.



**Table S2.** Crystal data and structure refinement for (L1)NiCl<sub>2</sub>.

Identification code	hdf-ii-04	
Empirical formula	C <sub>22</sub> H <sub>27</sub> Cl <sub>2</sub> NNiP <sub>2</sub>	
Formula weight	496.99	
Temperature	100.01(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 9.7449(2) Å	α = 90°
	b = 13.8069(4) Å	β = 95.441(2)°
	c = 16.9460(4) Å	γ = 90°
Volume	2269.76(9) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.454 Mg/m <sup>3</sup>	
Absorption coefficient	1.240 mm <sup>-1</sup>	
F(000)	1032	
Crystal size	0.209 x 0.101 x 0.063 mm <sup>3</sup>	
Theta range for data collection	2.415 to 29.966°.	
Index ranges	-13<=h<=13, -17<=k<=17, -23<=l<=23	
Reflections collected	13749	
Independent reflections	5488 [R(int) = 0.0280]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.685	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5488 / 2 / 257	
Goodness-of-fit on F <sup>2</sup>	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0263, wR2 = 0.0556	
R indices (all data)	R1 = 0.0278, wR2 = 0.0564	
Absolute structure parameter	-0.003(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.347 and -0.341 e/Å <sup>-3</sup>	

**Table S3.** Crystal data and structure refinement for (L1)PdCl<sub>2</sub>.

Identification code	scw-ii-30a	
Empirical formula	C <sub>22</sub> H <sub>27</sub> ClNP <sub>2</sub> Pd · ½(CH <sub>2</sub> Cl <sub>2</sub> )	
Formula weight	587.15	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 28.03203(16) Å	α = 90°
	b = 9.55406(6) Å	β = 93.0442(5)°
	c = 18.39924(10) Å	γ = 90°
Volume	4920.72(5) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.585 Mg/m <sup>3</sup>	
Absorption coefficient	10.388 mm <sup>-1</sup>	
F(000)	2376	
Crystal size	0.319 x 0.132 x 0.101 mm <sup>3</sup>	
Theta range for data collection	3.157 to 72.360°.	
Index ranges	-34<=h<=34, -10<=k<=11, -22<=l<=22	
Reflections collected	47966	
Independent reflections	9646 [R(int) = 0.0357]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.578 and 0.142	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	9646 / 0 / 540	
Goodness-of-fit on F <sup>2</sup>	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0327, wR2 = 0.0837	
R indices (all data)	R1 = 0.0336, wR2 = 0.0843	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.345 and -1.916 e/Å <sup>-3</sup>	

**Table S4.** Crystal data and structure refinement for (L1)PtCl<sub>2</sub>.

Identification code	scw-ii-31	
Empirical formula	C <sub>22</sub> H <sub>27</sub> Cl <sub>2</sub> NP <sub>2</sub> Pt	
Formula weight	633.37	
Temperature	99.96(12) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.9874(2) Å	α = 90°
	b = 16.6163(3) Å	β = 97.565(2)°
	c = 14.1086(3) Å	γ = 90°
Volume	2320.99(8) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.813 Mg/m <sup>3</sup>	
Absorption coefficient	6.422 mm <sup>-1</sup>	
F(000)	1232	
Crystal size	0.303 x 0.119 x 0.103 mm <sup>3</sup>	
Theta range for data collection	2.359 to 29.948°.	
Index ranges	-12<=h<=13, -23<=k<=22, -18<=l<=18	
Reflections collected	28248	
Independent reflections	6054 [R(int) = 0.0472]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.977 and 0.549	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6054 / 0 / 257	
Goodness-of-fit on F <sup>2</sup>	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0472	
R indices (all data)	R1 = 0.0274, wR2 = 0.0488	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.904 and -1.204 e/Å <sup>-3</sup>	

**Table S5.** Crystal data and structure refinement for [(L1)CuCl]<sub>2</sub>.

Identification code	idd-ii-63	
Empirical formula	C <sub>44</sub> H <sub>54</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>2</sub> P <sub>4</sub>	
Formula weight	932.75	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6486(3) Å	α = 75.136(3)°
	b = 10.1503(3) Å	β = 73.244(3)°
	c = 13.6583(5) Å	γ = 62.259(3)°
Volume	1121.76(7) Å <sup>3</sup>	
Z	1	
Density (calculated)	1.381 Mg/m <sup>3</sup>	
Absorption coefficient	3.858 mm <sup>-1</sup>	
F(000)	484	
Crystal size	0.366 x 0.229 x 0.08 mm <sup>3</sup>	
Theta range for data collection	3.415 to 72.410°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -16 ≤ l ≤ 16	
Reflections collected	21063	
Independent reflections	4381 [R(int) = 0.0195]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.323	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4381 / 0 / 248	
Goodness-of-fit on F <sup>2</sup>	1.075	
Final R indices [I > 2σ(I)]	R1 = 0.0221, wR2 = 0.0593	
R indices (all data)	R1 = 0.0226, wR2 = 0.0596	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.283 and -0.369 e/Å <sup>-3</sup>	

**Table S6.** Crystal data and structure refinement for (L11)NiCl<sub>2</sub>.

Identification code	jfv-i-007	
Empirical formula	C <sub>26</sub> H <sub>32</sub> Cl <sub>6</sub> NiP <sub>2</sub>	
Formula weight	677.86	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.43393(15) Å	α = 83.8079(17)°
	b = 10.5673(2) Å	β = 86.3096(16)°
	c = 17.8435(4) Å	γ = 73.1764(18)°
Volume	1512.42(5) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.489 Mg/m <sup>3</sup>	
Absorption coefficient	6.919 mm <sup>-1</sup>	
F(000)	696	
Crystal size	0.406 x 0.231 x 0.167 mm <sup>3</sup>	
Theta range for data collection	2.492 to 72.271°.	
Index ranges	-10 ≤ h ≤ 10, -11 ≤ k ≤ 12, -22 ≤ l ≤ 22	
Reflections collected	22626	
Independent reflections	5910 [R(int) = 0.0217]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.885 and 0.182	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5910 / 0 / 320	
Goodness-of-fit on F <sup>2</sup>	1.092	
Final R indices [I > 2σ(I)]	R1 = 0.0249, wR2 = 0.0633	
R indices (all data)	R1 = 0.0255, wR2 = 0.0637	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.363 and -0.381 e/Å <sup>-3</sup>	

**Table S7.** Crystal data and structure refinement for (L1)Ni(o-tolyl)Cl.

Identification code	mwj-2-018	
Empirical formula	C <sub>29</sub> H <sub>34</sub> ClNNiP <sub>2</sub>	
Formula weight	552.67	
Temperature	100.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 17.7452(6) Å	α = 90°
	b = 10.5763(4) Å	β = 96.599(3)°
	c = 29.5471(11) Å	γ = 90°
Volume	5508.6(3) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.333 Mg/m <sup>3</sup>	
Absorption coefficient	0.936 mm <sup>-1</sup>	
F(000)	2320	
Crystal size	0.284 x 0.198 x 0.13 mm <sup>3</sup>	
Theta range for data collection	2.246 to 29.979°.	
Index ranges	-24 ≤ h ≤ 24, -14 ≤ k ≤ 14, -39 ≤ l ≤ 40	
Reflections collected	79588	
Independent reflections	14653 [R(int) = 0.0844]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.637	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	14653 / 0 / 623	
Goodness-of-fit on F <sup>2</sup>	1.131	
Final R indices [I > 2σ(I)]	R1 = 0.0730, wR2 = 0.1142	
R indices (all data)	R1 = 0.1103, wR2 = 0.1265	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.579 and -0.488 e/Å <sup>-3</sup>	

#### XIV. References

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