Electronic Supporting Information (ESI) for:

Evidence for a preferential intramolecular oxidative addition in Ni-catalyzed cross-coupling reactions and their impact on chain-growth polymerizations

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I. Materials

Flash chromatography was performed on SiliCycle silica gel (40-63 μm) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F254. *i*-PrMgCl (2 M in THF), **2** (1 M in THF), and *i*-PrMgBr (2.7 M in 2-MeTHF) were purchased in 100 mL quantities from Aldrich. $Ni(cod)_2$, depe, and dppe were purchased from Strem. All other reagent grade materials and solvents were purchased from Aldrich, Acros, EMD, or Fisher and used without further purification unless otherwise noted. THF was dried and deoxygenated using an Innovative Technology (IT) solvent purification system composed of activated alumina, copper catalyst, and molecular sieves. *N*-Bromosuccinimide was recrystallized from hot water and dried over P_2O_5. All glassware was oven-dried at 120 °C for at least 1 h before use. Compounds **S11**[1] and **S12**[1] were prepared according to modified literature procedures.

II. General Experimental

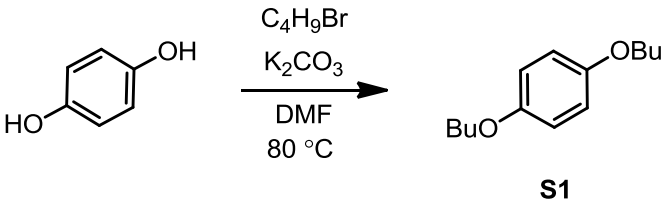
NMR Spectroscopy: Unless otherwise noted, ^1H, ^{13}C, and ^{31}P NMR spectra for all compounds were acquired at rt in $CDCl_3$ or CD_2Cl_2 on a Varian vnmrs 500 operating at 500, 126, and 202 MHz or a Varian MR 400 operating at 400, 100 and 162 MHz, respectively. For ^1H, and ^{13}C NMR spectra in deuterated solvents, the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. For ^{31}P NMR spectra in deuterated solvents, the chemical shift data are reported in units of δ (ppm) relative to H_3PO_4 and referenced with residual solvent. For ^1H and ^{31}P NMR spectra in non-deuterated THF, the chemical shift data are reported in units of δ (ppm) and referenced with the THF peak at 3.58 ppm in the ^1H NMR spectrum, which is then applied to all nuclei. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m), and broad resonance (br).

Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed with Waters 2487 dual absorbance detector (254 nm). Samples were dissolved in THF (with mild heating) and passed through a 0.2 μm PTFE filter prior to analysis.

Titrations of the Grignard Reagents: An accurately weighed sample of salicylaldehyde phenylhydrazone (typically between 290-310 mg) was dissolved in 5.00 mL of THF. A 0.50 mL aliquot of this solution was stirred at rt while ArMgBr was added dropwise using a 500 μL syringe. The initial solution is yellow and turns bright orange at the end-point.[2]

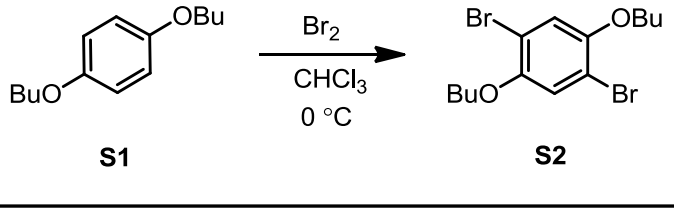
Gas Chromatography: Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHRX5 (crossbound 5% diphenyl – 95% dimethyl polysiloxane; 15 m 0.25 mm ID, 0.25 μm df) column.

III. Synthetic Procedures



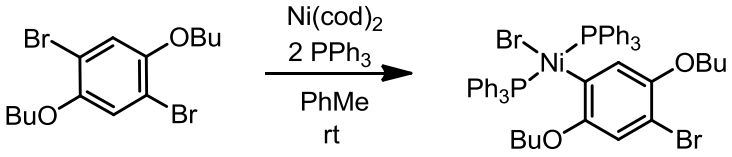
S1

S1.[1] A 500 mL round-bottom flask was equipped with a stir bar. Sequentially, hydroquinone (20. g, 0.20 mol, 1.0 equiv), anhydrous DMF (120 mL), and 1-bromobutane (49 mL, 0.45 mol, 2.5 equiv) were added to the flask. The flask was put under N_2 atmosphere and stirred vigorously while heated to 80 °C. Once at 80 °C, potassium carbonate (63 g, 0.45 mmol, 2.5 equiv) was slowly added and subsequently put under N_2 atmosphere again for 5 d. After cooling to rt, the reaction mixture was poured into water (400 mL). The reaction mixture was extracted with hexanes (3 x 200 mL). The organic layers were combined and washed with water (2 x 200 mL) and brine (1 x 200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting oil was passed though silica gel with neat DCM as the eluent. Recrystallization from hot methanol produced 35 g of **S1** as a white crystalline solid (86% yield). HRMS (EI): Calcd. For $C_{14}H_{22}O_2$, 222.1620 [M+]; found, 222.1626.



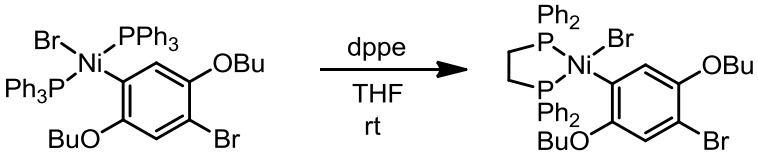
S1 **S2**

S2.[1] A 500 mL round-bottom flask was equipped with a stir bar. Sequentially, **S1** (17 g, 0.078 mol, 1.0 equiv), and $CHCl_3$ (90 mL) were added to the flask. The reaction flask was cooled to 0 °C in an ice/water bath and fitted with an addition funnel. Bromine (10 mL, 0.19 mol, 2.5 equiv) was added dropwise under N_2 and the pressure was vented through a solution of aq saturated Na_2SO_3 and $NaHCO_3$ (50:50). After 3 h, the reaction was quenched with an aq saturated solution of Na_2CO_3 (100 mL) and stirred vigorously until colorless. The aqueous mixture was extracted with DCM (3 x 100 mL). The organic layers were combined and washed with water (2 x 200 mL) and brine (1 x 200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was recrystallized from DCM/methanol to produce 23 g of **S2** as a white solid (79% yield). HRMS (EI): Calcd. For $C_{14}H_{20}Br_2O_2$, 377.9830 [M+]; found, 377.9824.



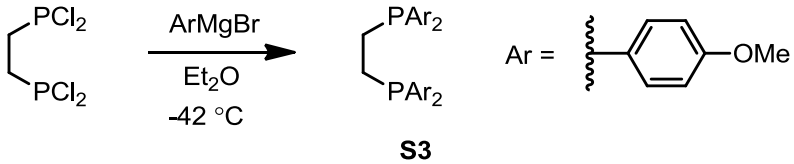
S2 **1b**

1b.[3] In the glovebox, an oven-dried 25 mL flask was equipped with a stir bar and charged with $Ni(cod)_2$ (0.25 g, 0.91 mmol, 1.0 equiv), PPh_3 (0.48 g, 1.8 mmol, 2.0 equiv), and toluene (10 mL). After 30 min of stirring, **S2** (0.68 g, 1.8 mmol, 2.0 equiv) was dissolved in a minimal amount of toluene and added dropwise to the flask and allowed to stir for 1 h at rt. Once the reaction was complete as observed by ^{31}P NMR spectroscopy, the product was precipitated with hexanes (25 mL) and removed from the glovebox. The air-stable solid was collected by filtration and washed with MeOH to produce 0.58 g of yellow-orange solid (66% yield). Elemental Analysis: Calcd for $C_{50}H_{50}Br_2NiO_2P_2$, C, 62.34, H, 5.23, Br 16.59; Found C, 62.26, H, 5.08, Br, 16.42. ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.50.



1b **1a**

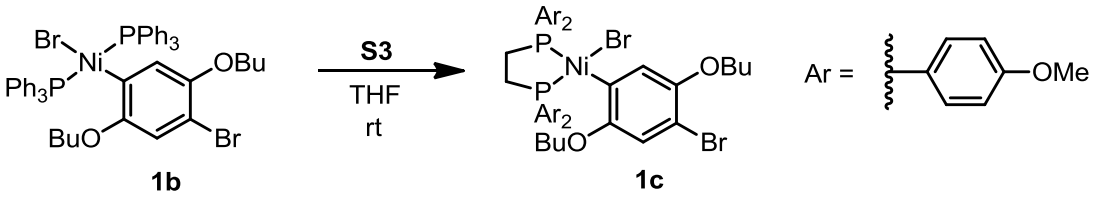
1a.[3] In the glovebox a 20 mL vial was equipped with a stir bar and charged with **1b** (0.25 g, 0.26 mmol, 1.0 equiv), dppe (0.10 g, 0.26 mmol, 1.0 equiv), and THF (5 mL). The reaction was left to stir for 1 h at rt. The solution was partially concentrated (50%) and hexanes (15 mL) was added. The resulting orange solid was then recrystallized from THF/hexanes and filtered to produce 0.16 g of **1a** (73% yield). Elemental Analysis: Calcd for $C_{40}H_{44}Br_2NiO_2P_2$, C, 57.38, H, 5.30, Br 19.09; Found C, 57.33, H, 5.39, Br, 18.98. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 57.69 (d, J = 29.2 Hz), 41.15 (d, J = 29.2 Hz).



S3

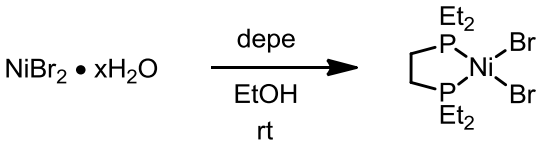
S3.[4] In the glovebox an oven-dried 50 mL Schlenk flask was equipped with a stir bar and charged with 1,2-bis(dichlorophosphino)ethane (0.39 mL, 2.6 mmol, 1.0 equiv) and anhydrous

Et_2O (15 mL). The flask was removed, placed under an N_2 atmosphere on a Schlenk line, and then cooled to -42 °C in a MeCN/CO_2 bath. Once cooled, *p*-methoxyphenylmagnesium bromide, 0.5 M solution in THF (31 mL, 15 mmol, 6.0 equiv) was added dropwise over the course of an hour. The reaction was stirred for an additional 1 h at -42 °C and warmed to rt over 1.5 h. Additional *p*-methoxyphenylmagnesium bromide, 0.5 M solution in THF (10 mL, 5.1 mmol, 2.0 equiv) was then added dropwise and the reaction was warmed to 45 °C for 4 h. Upon completion as determined by ^{31}P NMR spectroscopy, the reaction was cooled to rt and quenched with saturated aq NH_4Cl (50 mL). The mixture was extracted with Et_2O (3 x 25 mL) and the organic layers were combined, dried over $MgSO_4$, filtered and concentrated in vacuo. Recrystallization in methanol/THF produced 0.42 g of white crystalline solid (32% yield). ^{31}P NMR (202 MHz, $CDCl_3$) δ 16.50.



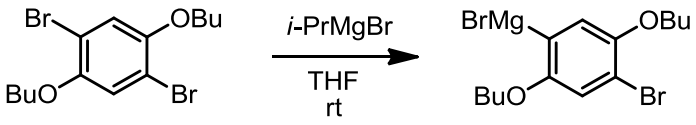
1b **1c**

1c.[5] In the glovebox a 20 mL vial was equipped with a stir bar and charged with **1b** (0.25 g, 0.26 mmol, 1.0 equiv), **S3** (0.14 g, 0.26 mmol, 1.0 equiv), and THF (5 mL). The reaction was left to stir for 1 h at rt. The solution was concentrated and precipitated with hexanes (18 mL). The orange solid was then recrystallized from THF/hexanes, filtered, and triturated with hexanes to produce 0.15 g of **1c** (61% yield). Elemental Analysis: Calcd for $C_{44}H_{52}Br_2NiO_6P_2$, C, 55.20, H, 5.47, Br 16.69; Found C, 55.30, H, 5.50, Br, 16.41. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 55.77 (d, J = 32.8 Hz), 39.75 (d, J = 32.8 Hz).



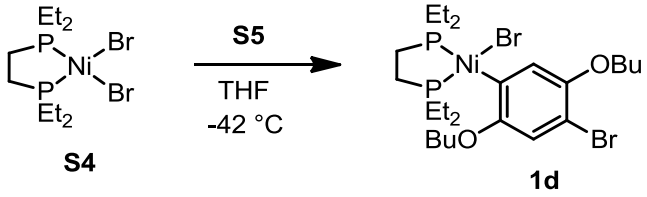
S4

S4.[4] A 25 mL Schlenk flask was placed under N_2 and equipped with a stir bar. Sequentially, $NiBr_2$•xH_2O (0.20 g, 0.69 mmol, 1.0 equiv) and ethanol (13 mL) were added to the flask and the solution was sparged with N_2 for 15 min. Then, 1,2-bis(diethylphosphino)ethane (depe) (0.14 g, 0.69 mmol, 1.0 equiv) was taken from the glovebox in a syringe and injected directly into the flask. The reaction was stirred for 25 min and a dark red solid formed. The reaction was left overnight uncapped to crystallize, filtered, and washed with cold EtOH to produce 0.16 g of **S4** (55% yield). HRMS (EI): Calcd. For $NiC_{10}H_{24}Br_2$, 421.9073 [M+]; found, 421.9066. ^{31}P NMR (202 MHz, $CDCl_3$) δ 82.58.



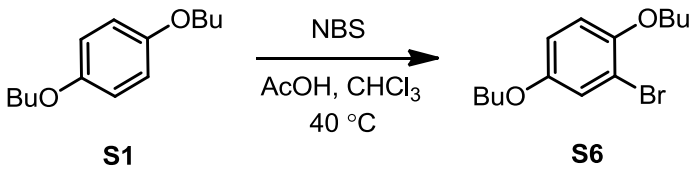
S2 **S5**

S5.[1] All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, **S2** (0.90 g, 2.3 mmol, 1.0 equiv), THF (2.5 mL), and *i*-PrMgBr (0.79 mL, 2.1 mmol, 0.9 equiv) were added to the flask. The reaction was stirred at rt overnight. Concentration was determined by titration immediately before use as described in the general experimental (page S2).



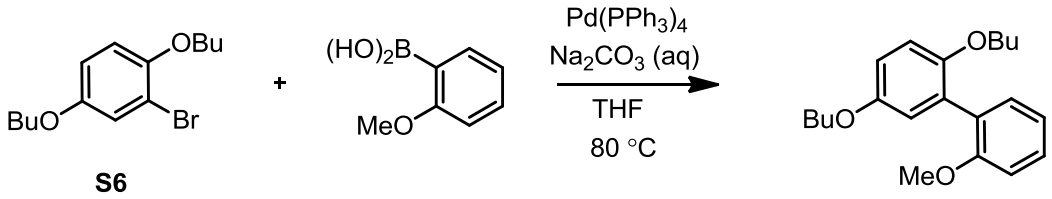
S4 **1d**

1d. In the glovebox an oven-dried 50 mL Schlenk flask was equipped with a stir bar. Sequentially, **S4** (0.15 g, 0.37 mmol, 1.0 equiv) and THF (12 mL) were added and the flask was equipped with a septum secured with copper wire. Freshly prepared **S5** (0.84 mL, 0.44 M, 0.37 mmol, 1.0 equiv) was placed in an oven-dried Schlenk tube, diluted with THF (12 mL), and sealed. Both flasks were removed from the glovebox and placed under N_2 atmosphere. The Schlenk flask containing **S4** was then cooled to -42 °C in a MeCN/CO_2 bath. Next, the solution of **S5** was cannula transferred to the Schlenk flask containing **S4** dropwise over the course of 5 min and stirred for 1 h. Upon completion as determined by ^{31}P NMR spectroscopy, the reaction was warmed to rt and quenched with saturated aq NaBr (25 mL). The mixture was extracted with hexanes (3 x 25 mL) and the organic layers were combined, dried over $MgSO_4$, filtered, concentrated in vacuo, and taken back into the glovebox. Recrystallization in THF/hexanes produced 0.12 g of yellow-orange crystalline solid (50% yield). Elemental Analysis: Calcd for $C_{24}H_{44}Br_2NiO_2P_2$, C, 44.69, H, 6.88, Br 24.77; Found C, 44.58, H, 6.85, Br, 24.97. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 65.48 (d, J = 33.6 Hz), 58.80 (d, J = 33.6 Hz).



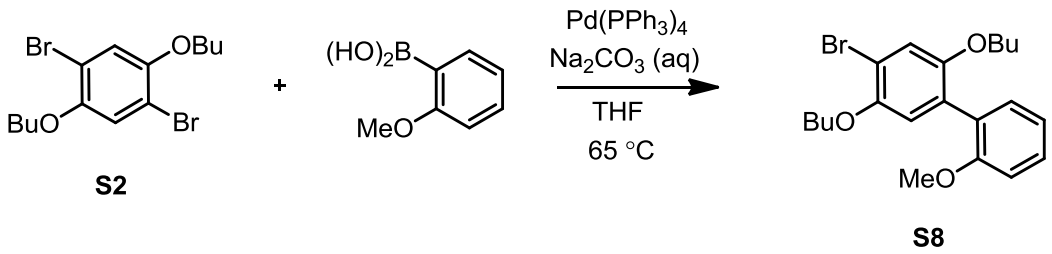
S1 **S6**

S6.[1] A 150 mL round-bottom flask was equipped with a stir bar. Sequentially, **S1** (5.0 g, 23 mmol, 1.0 equiv), $CHCl_3$ (85 mL), N-bromosuccinimide (NBS) (4.0 g, 23 mmol, 1.0 equiv), and acetic acid (43 mL) were added. The mixture was stirred at 40 °C for 24 h. Upon completion, the reaction solution was quenched with H_2O (50 mL). The aqueous layer was then extracted with $CHCl_3$ (2 x 50 mL), and the combined organic layers were washed with 20% w/v aq NaOH (1 x 50 mL), water (3 x 125 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Distillation (158 °C , 0.2 torr) produced 2.7 g of **S6** as a light yellow oil (40% yield). HRMS (EI): Calcd. For $C_{14}H_{21}Br$, 300.0725 [M+]; found, 300.0730.



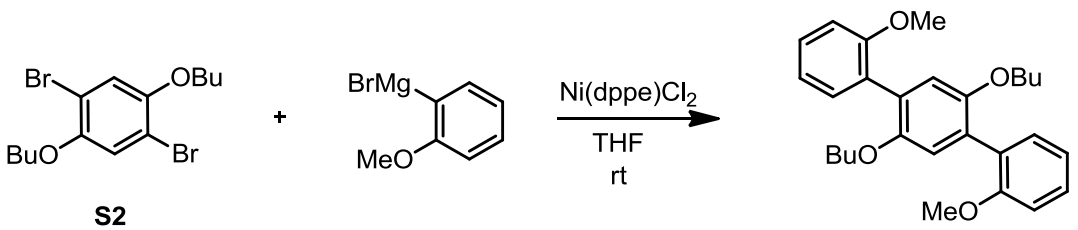
S6 **S7**

S7. A 250 mL Schlenk flask was equipped with a stir bar and placed under N_2 atmosphere. Sequentially, **S6** (1.4 g, 4.6 mmol, 1.0 equiv), 2-methoxyphenylboronic acid (0.6 g, 4.2 mmol, 0.9 equiv), THF (85 mL), tetrakis(triphenylphosphine)palladium(0) (0.3 g, 0.2 mmol, 0.05 equiv), and aq Na_2CO_3 (2 M, 80 mL) were added with stirring. This Schlenk flask was then equipped with a reflux condenser, heated to 80 °C for 36 h. Upon completion, the reaction was cooled to rt and extracted with DCM (3 x 50 mL). The combined organic layers were washed with water (2 x 75 mL) and brine (1 x 75 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography (85% hexanes, 15% DCM) gave 0.6 g of the product as a clear oil (42% yield). HRMS (EI): Calcd. For $C_{21}H_{28}O_3$, 329.2111 [M+]; found, 329.2105.



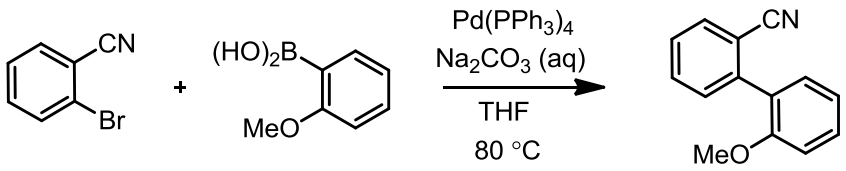
S2 **S8**

S8. A 50 mL Schlenk flask was equipped with a stir bar and placed under N_2 atmosphere. Sequentially, **S2** (0.50 g, 1.3 mmol, 1.0 equiv), 2-methoxyphenylboronic acid (0.15 g, 0.99 mmol, 0.75 equiv), THF (15 mL), tetrakis(triphenylphosphine)palladium(0) (0.08 g, 0.07 mmol, 0.05 equiv), and aq Na_2CO_3 (2 M, 10 mL) were added with stirring. This Schlenk flask was then equipped with a reflux condenser, heated to 65 °C for 18 h. Upon completion, the reaction was cooled, and extracted with DCM (3 x 25 mL). The combined organic layers were washed with water (2 x 50 mL) and brine (1 x 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography (85% hexanes, 15% DCM) gave 0.09 g of the product as a clear oil (22% yield). HRMS (EI): Calcd. For $C_{21}H_{27}BrO_3$, 407.1216 [M+]; found, 407.1215.



S2 **S9**

S9. In the glovebox, a 20 mL vial was equipped with a stir bar. Sequentially, **S2** (1.0 g, 2.6 mmol, 1.0 equiv), 2-methoxyphenylmagnesium bromide (1 M, 6.6 mmol, 2.5 equiv), THF (15 mL), and Ni(dppe)Cl_2 (0.07 g, 0.1 mmol, 0.05 equiv) were added with stirring. This mixture was then stirred at rt for 2 h. Upon completion, the vial was removed from the glovebox and quenched with hydrochloric acid (12.1 M, 5 mL) and subsequently diluted with water (25 mL). The reaction was then extracted with DCM (3 x 25 mL). The combined organic layers were washed with aq saturated $NaHCO_3$ (1 x 50 mL), water (2 x 50 mL) and brine (1 x 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography (85% hexanes, 15% DCM) gave 0.11 g of the product as a clear oil (10% yield). HRMS (EI): Calcd. For $C_{28}H_{34}O_4$, 407.1216 [M+]; found, 407.1215.



S10

S10. A 50 mL Schlenk flask was equipped with a stir bar and placed under N_2 atmosphere. Sequentially, 2-bromobenzonitrile (0.50 g, 2.8 mmol, 1.0 equiv), 2-methoxyphenylboronic acid (0.42 g, 2.8 mmol, 1.0 equiv), THF (15 mL), tetrakis(triphenylphosphine)palladium(0) (0.16 g, 0.14 mmol, 0.050 equiv), and aq Na_2CO_3 (2 M, 10 mL) were added with stirring. This Schlenk flask was then equipped with a reflux condenser and heated to 80 °C for 36 h. Upon completion, the reaction was cooled and extracted with DCM (3 x 25 mL). The combined organic layers were washed with water (2 x 50 mL) and brine (1 x 50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography (85% hexanes, 15% DCM) gave 0.32 g of the colorless oil as a product (55% yield). HRMS (EI): Calcd. For $C_{14}H_{11}NO$, 210.0913 [M+]; found, 210.0907.

IV. NMR Spectra

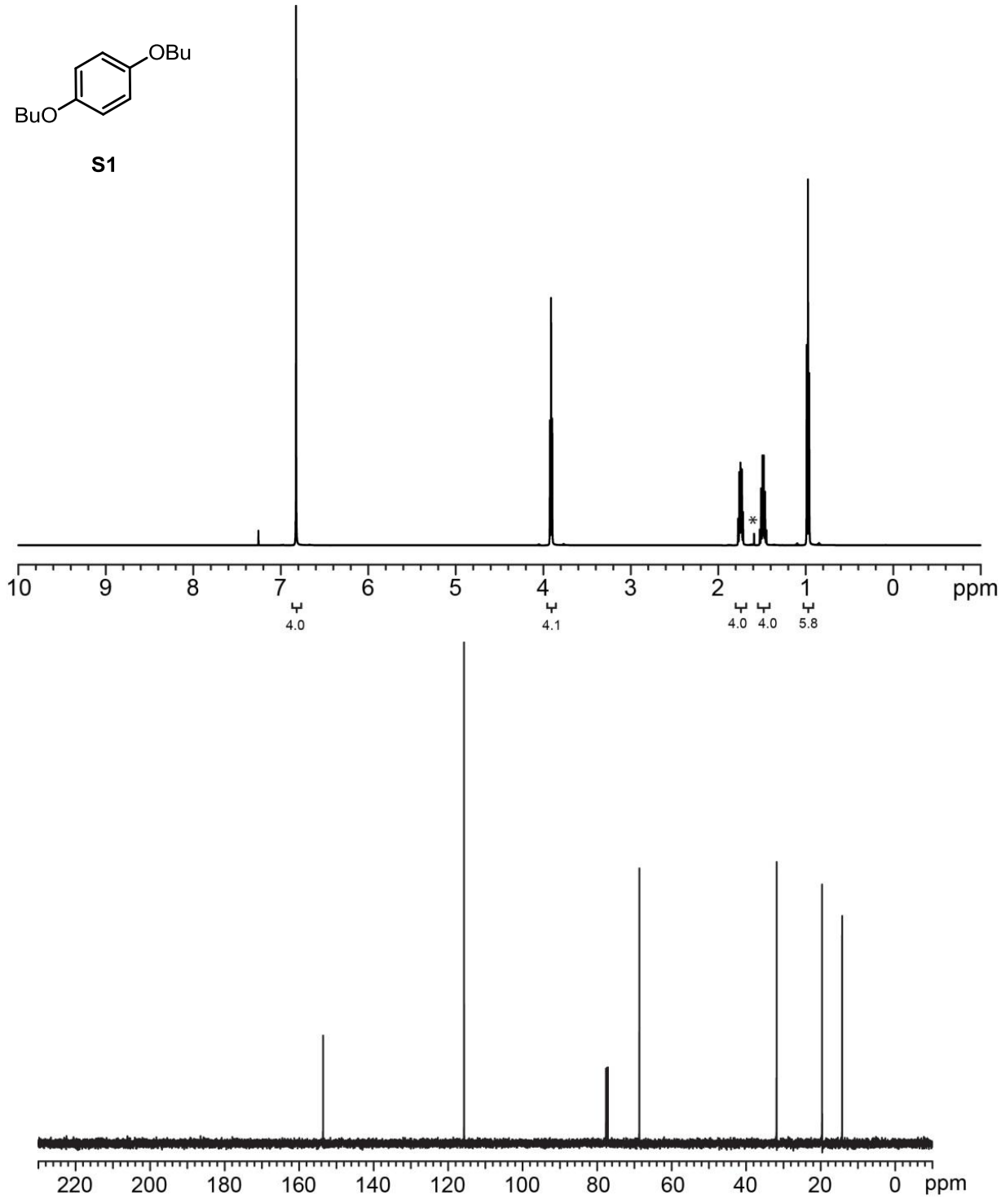
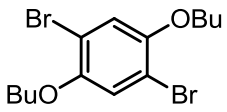


Figure S1. ^{1}H and ^{13}C NMR spectra for **S1**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 4H), 3.92 (t, J = 7.0 Hz, 4H), 1.75 (m, 4H), 1.49 (m, 4H), 0.98 (t, J = 7.3 Hz, 6H). * indicates residual H_2O. ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.19, 115.36, 68.30, 31.45, 19.24, 13.84.



S2

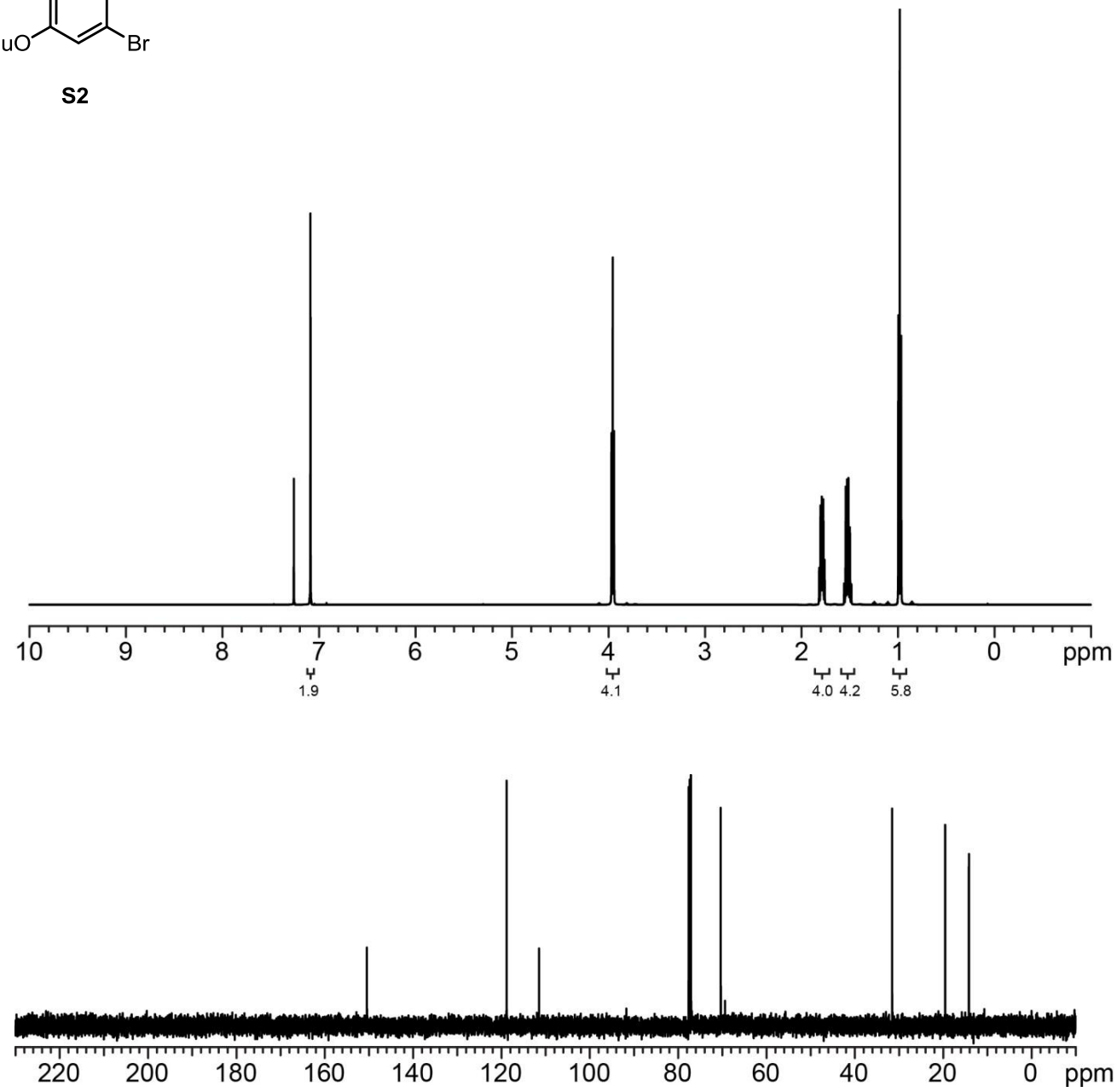


Figure S2. ^{1}H and ^{13}C NMR spectra for **S2**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 2H), 3.96 (t, *J* = 6.7 Hz, 4H), 1.79 (m, 4H), 1.53 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.08, 118.46, 111.13, 69.99, 31.19, 19.19, 13.81.

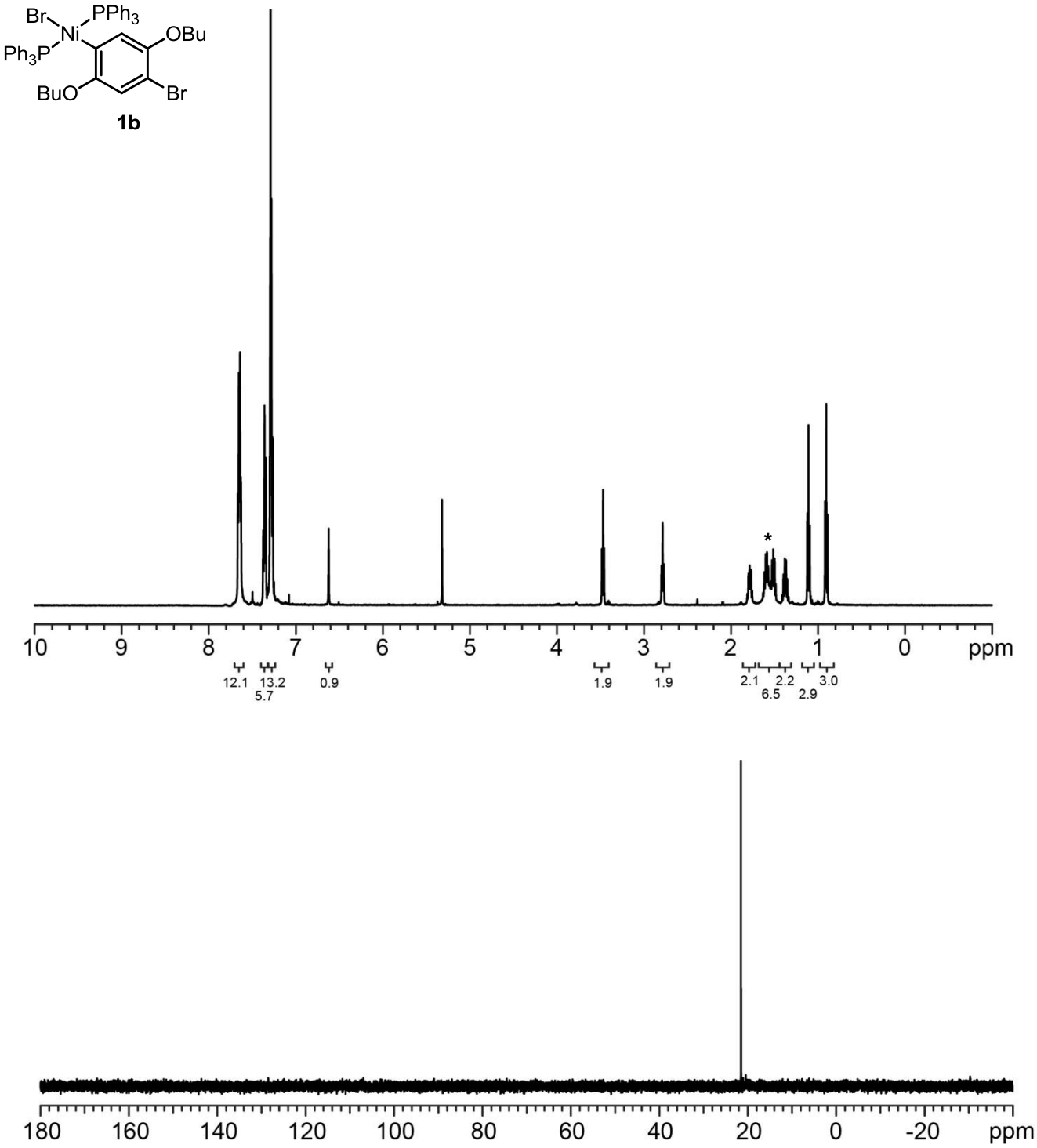


Figure S3. ^{1}H and ^{31}P NMR spectra for **1b**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66-7.63 (br, 12H), 7.37-7.34 (br m, 6H), 7.29-7.27 (br m, 13H), 6.62 (s, 1H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 6.6 Hz, 2H), 1.79 (m, 2H), 1.61-1.45 (br m, 4H), 1.37 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H). * indicates residual H_2O. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 21.50.

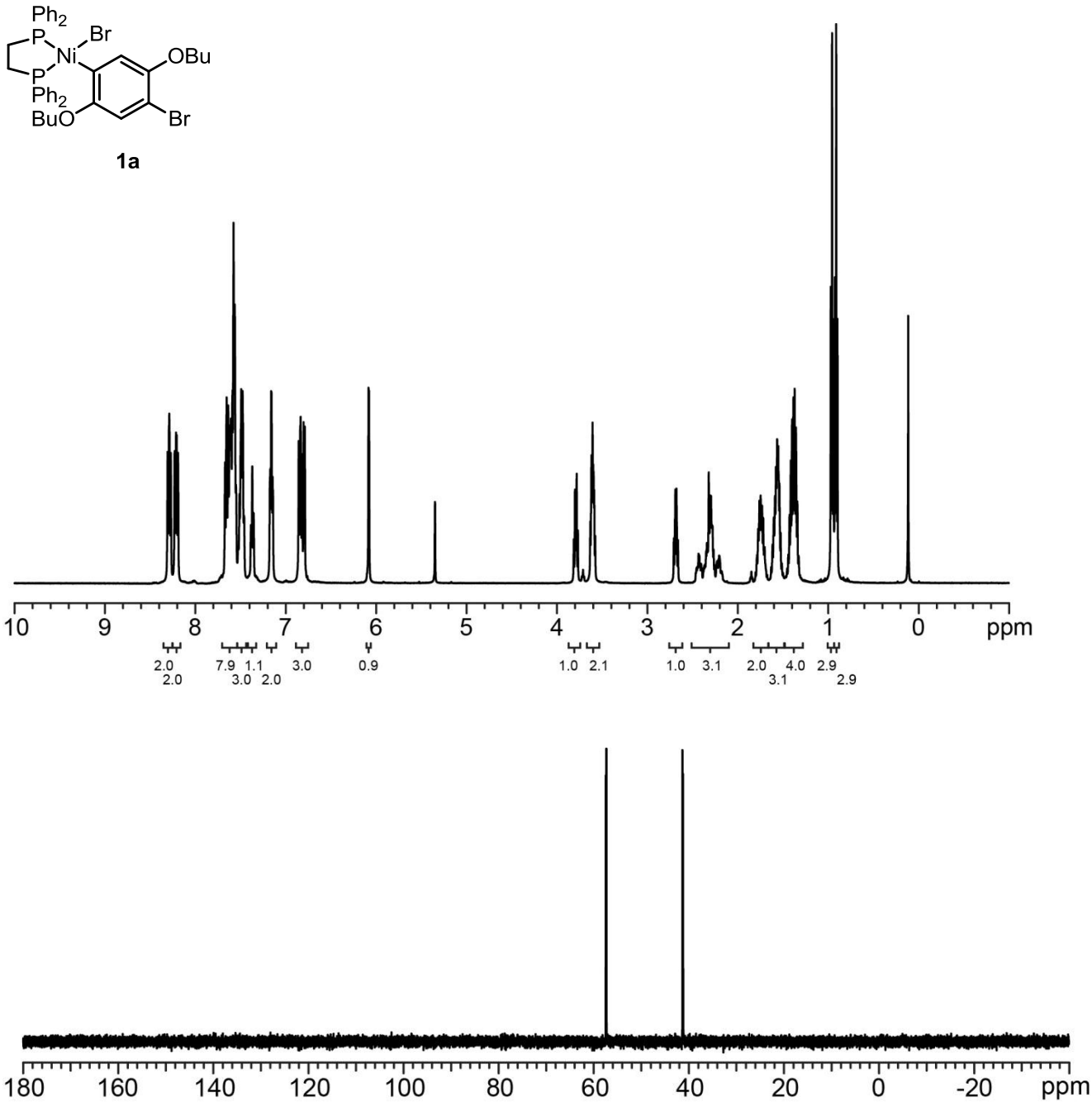


Figure S4. ^{1}H and ^{31}P NMR spectra for **1a**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.29 (t, *J* = 8.7 Hz, 2H), 8.21 (t, *J* = 9.2 Hz, 2H), 7.67-7.56 (m, 8H), 7.52-7.45 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 2H), 6.86-6.79 (m, 3H), 6.08 (s, 1H), 3.79 (q, *J* = 6.6 Hz, 1H), 3.64-3.57 (m, 2H), 2.68 (q, *J* = 5.9 Hz, 1H), 2.48-2.18 (m, 3H), 1.75 (m, 2H), 1.57 (m, 3H), 1.39 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H) . ^{31}P NMR (202 MHz, CD_2Cl_2) δ 57.69 (d, *J* = 29.2 Hz), 42.15 (d, *J* = 29.2 Hz).

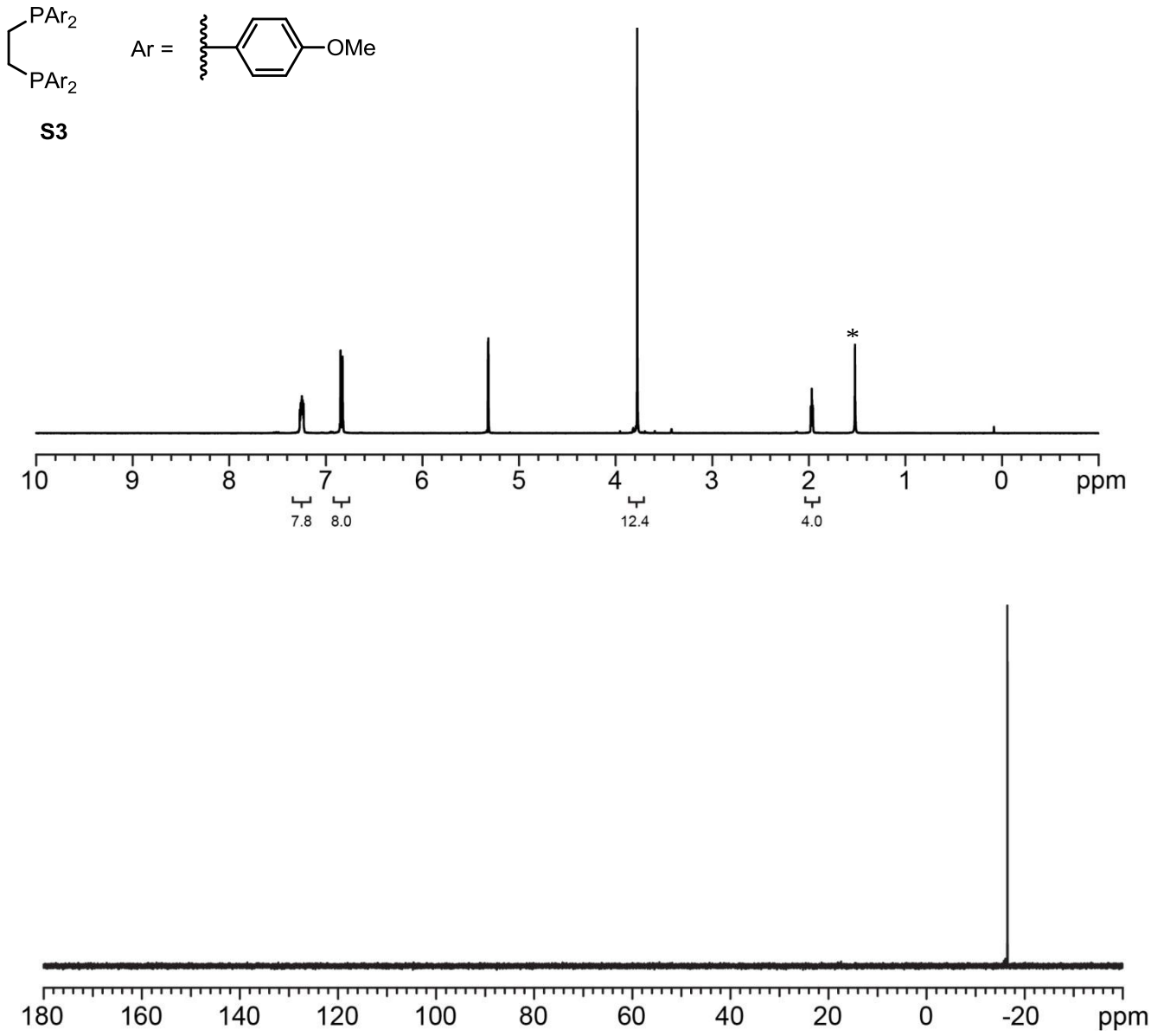


Figure S5. ^{1}H and ^{31}P NMR spectra for **S3**. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26-7.24 (m, 8H), 6.84 (d, *J* = 8.6 Hz, 8H), 3.78 (s, 12H), 1.97 (t, *J* = 4.7, 4H). * indicates residual H_2O. ^{31}P NMR (162 MHz, CD_2Cl_2) δ -16.50.

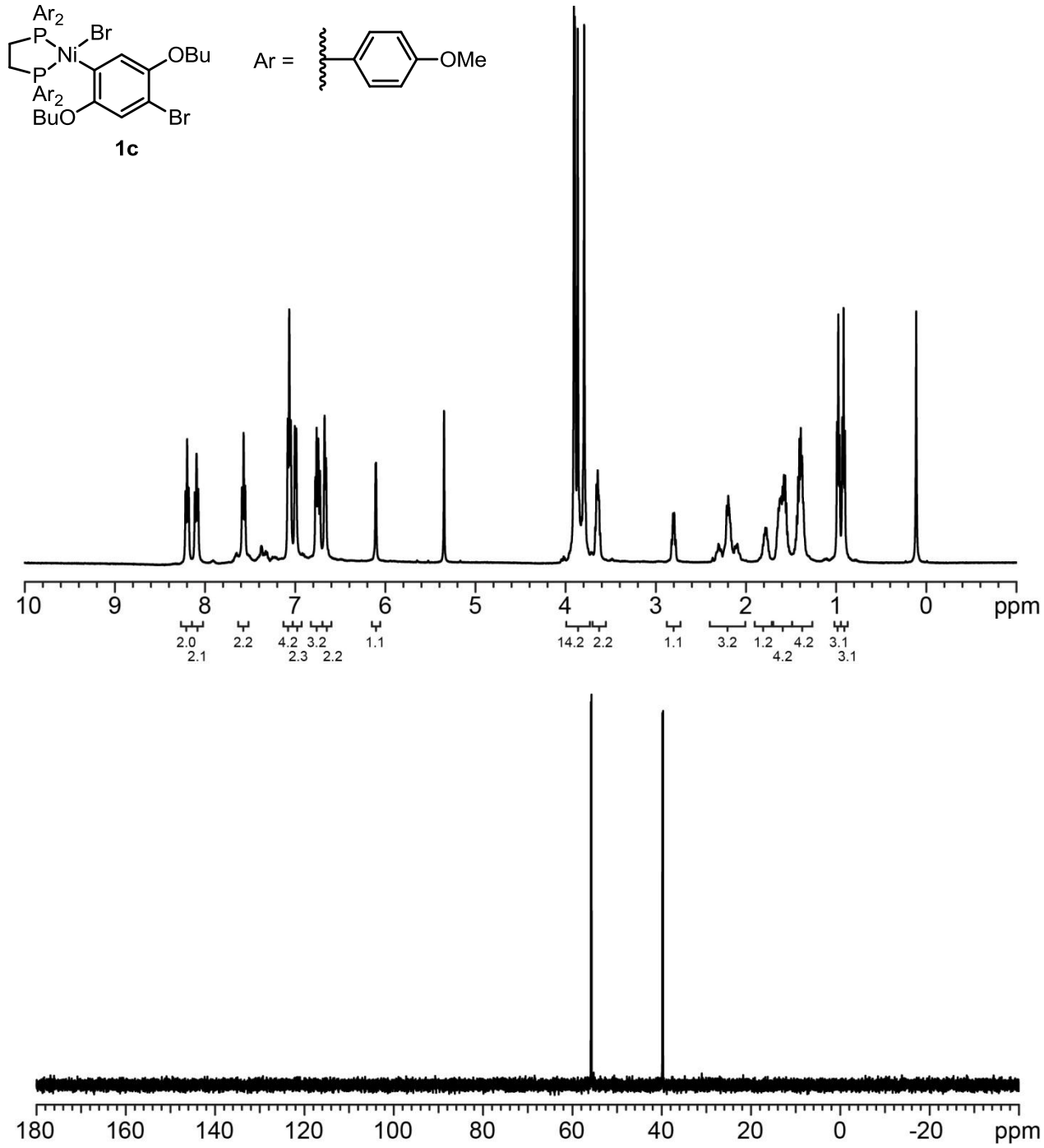


Figure S6. ^{1}H and ^{31}P NMR spectra for **1c**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.20 (t, *J* = 9.2 Hz, 2H), 8.10 (t, *J* = 9.7 Hz, 2H), 7.57 (t, *J* = 9.0 Hz, 2H), 7.07 (t, *J* = 8.5 Hz, 4H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.77-6.71 (m, 3H), 6.66 (d, *J* = 7.8 Hz, 2H), 6.10 (s, 1H), 3.91-3.79 (m, 14H), 3.66-3.63 (m, 2H), 2.80 (q, *J* = 6.6 Hz, 1H), 2.38-2.05 (m, 2H), 1.83-1.72 (m, 1H), 1.64-1.55 (m, 4H), 1.40 (m, 4H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H) . ^{31}P NMR (202 MHz, CD_2Cl_2) δ 55.77 (d, *J* = 32.8 Hz), 39.75 (d, *J* = 32.8 Hz).

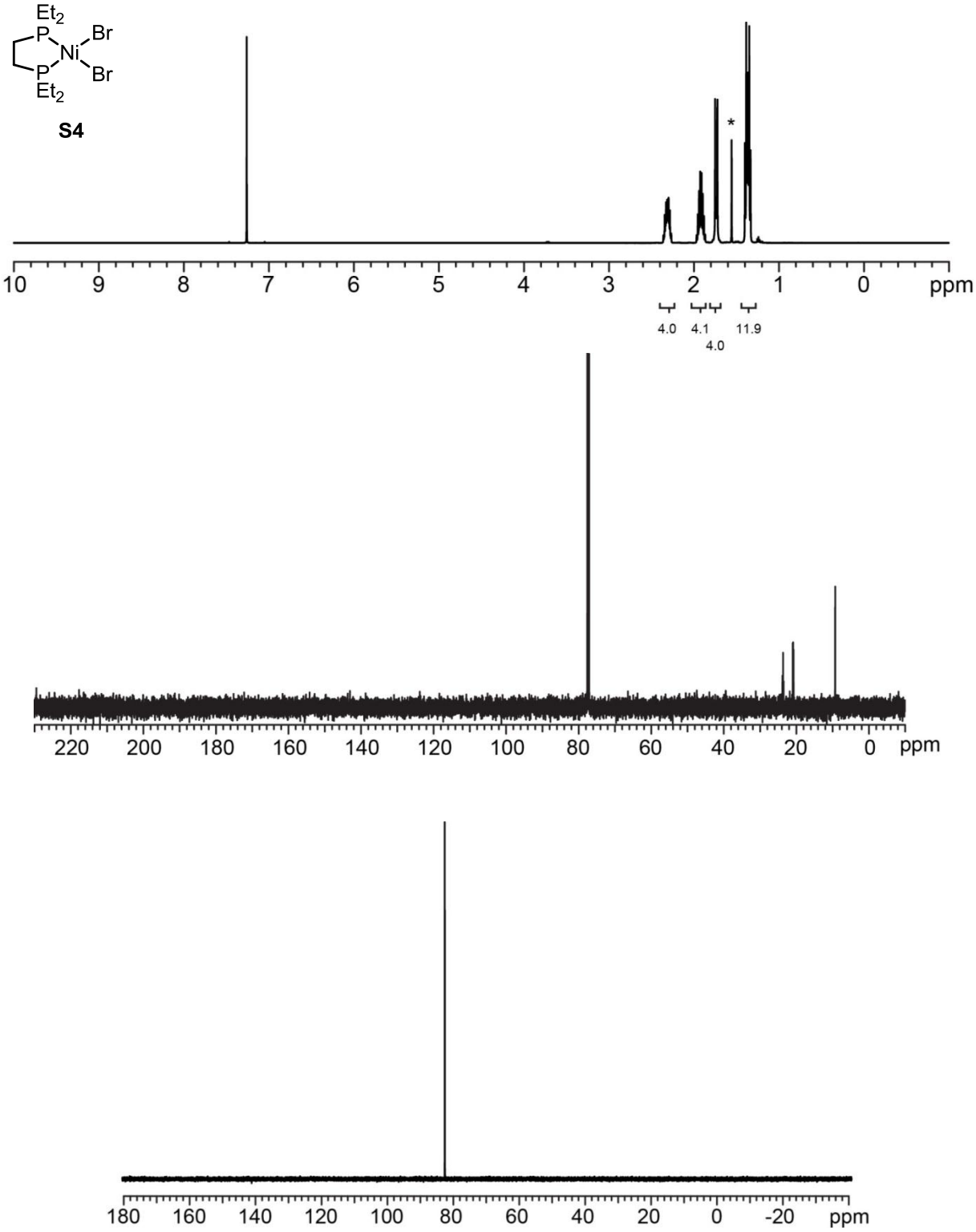


Figure S7. ^{1}H, ^{13}C, and ^{31}P NMR spectra for **S4**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.26 (m, 4H), 1.90 (m, 4H), 1.71 (br, 4H), 1.39-1.30 (m, 12H). * indicates residual H_2O. ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.32 (m), 20.53 (t, J = 15.5 Hz), 8.93. ^{31}P NMR (202 MHz, $CDCl_3$) δ 82.58.

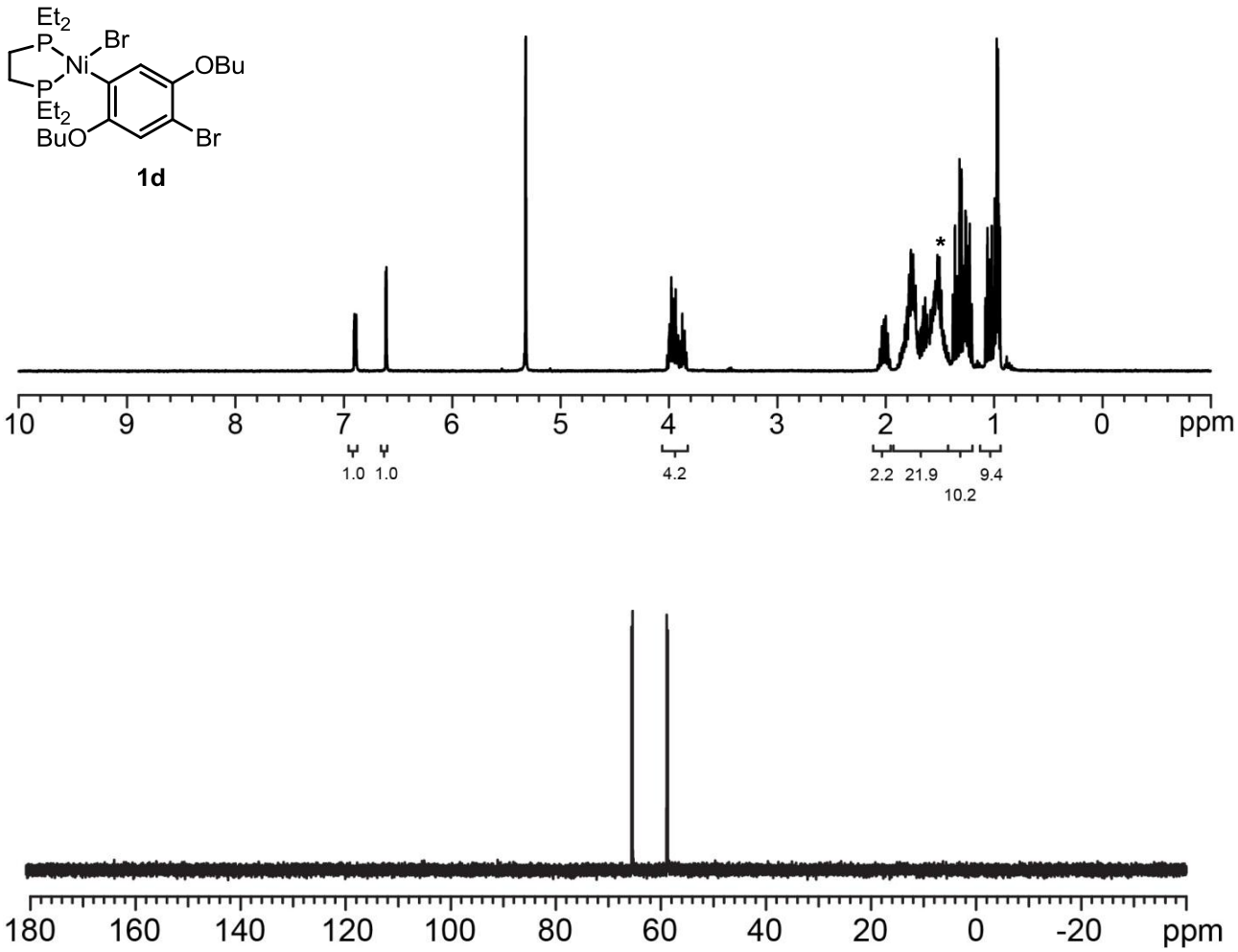
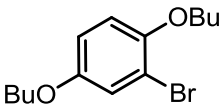


Figure S8. ^{1}H and ^{31}P NMR spectra for **1d**. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.96 (d, *J* = 6.6 Hz, 1H), 6.61 (d, *J* = 3.1 Hz, 1H), 4.02-3.84 (m, 4H), 2.01 (m, 2H), 1.89-1.42 (m, 16H), 1.38-1.21 (m, 10H), 1.08-0.94 (m, 10H). * indicates residual H_2O. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 64.48 (d, *J* = 33.6 Hz), 58.80 (d, *J* = 33.6 Hz).



S6

Figure S9. ^{1}H and ^{13}C NMR spectra for **S6**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.07 (d, *J* = 2.9 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.80 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.95 (t, *J* = 6.6 Hz, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.80-1.69 (m, 4H), 1.55-1.42 (m, 4H), 0.97 (t, *J* = 7.8 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.59, 149.72, 119.38, 114.53, 114.31, 112.38, 69.76, 68.52, 31.35, 31.29, 19.23, 19.16, 13.60, 13.58.

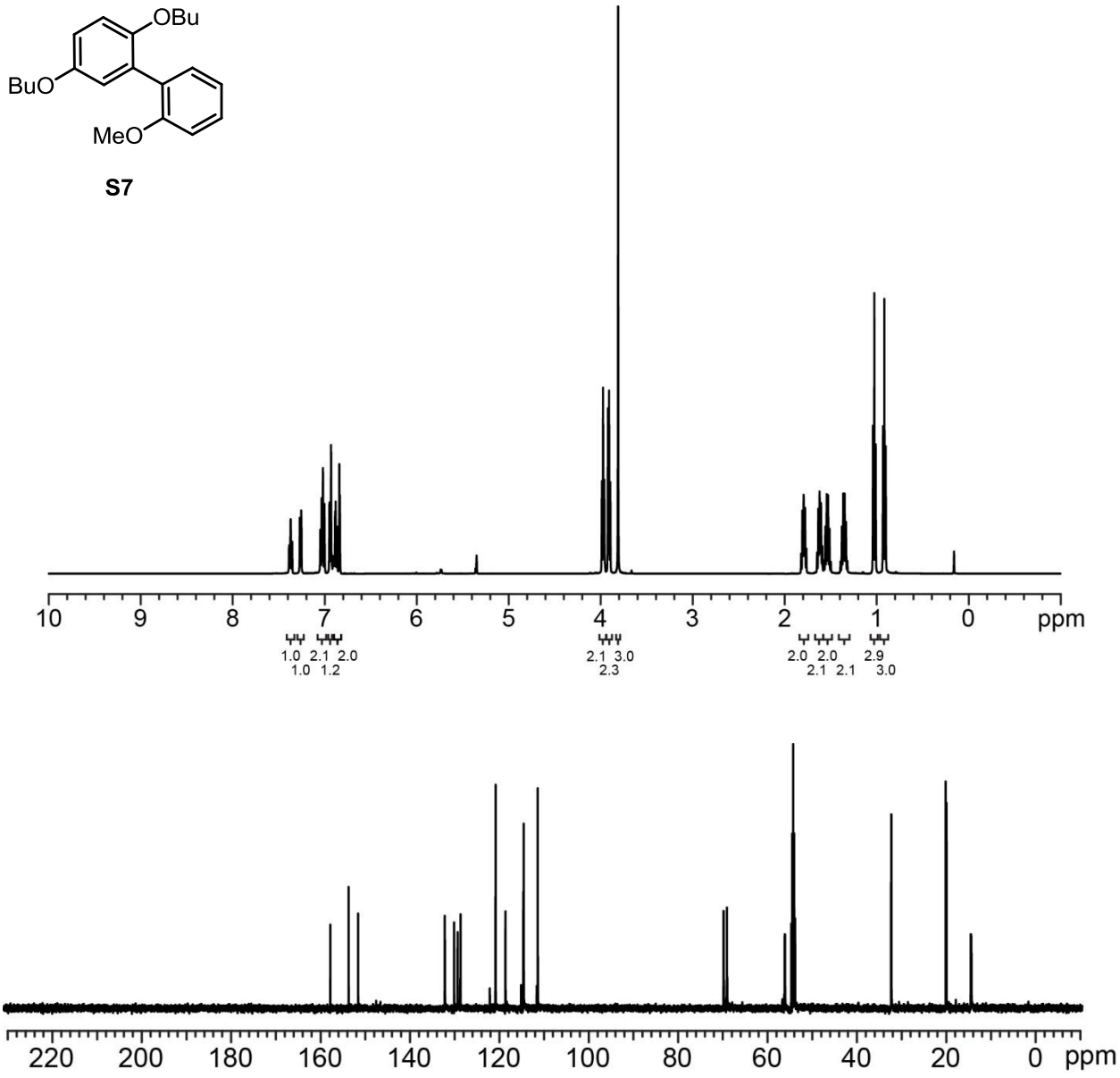
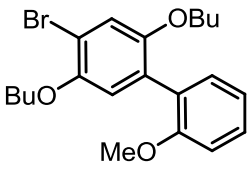


Figure S10. ^{1}H and ^{13}C NMR spectra for **S7**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.02-6.97 (m, 2H), 6.92-6.90 (m, 1H), 6.86-6.80 (m, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 3.88 (t, *J* = 6.0 Hz, 2H), 3.72 (s, 3H), 1.77 (m, 2H), 1.59 (m, 2H), 1.50 (m, 2H), 1.33 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.96, 152.87, 150.75, 131.35, 129.27, 128.48, 127.84, 120.99, 117.78, 113.79, 113.69, 110.54, 68.97, 68.22, 55.32, 31.48, 31.43, 19.25, 19.08, 13.65, 13.52.



4

Figure S11. ^{1}H and ^{13}C NMR spectra for **4**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.33 (t, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 6.98 (m, 2H), 6.83 (s, 1H), 3.96 (t, *J* = 6.4 Hz, 2H), 3.84 (t, *J* = 6.5 Hz, 2H), 3.75 (s, 3H), 1.77 (m, 2H), 1.59-1.49 (m, 4H), 1.29 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.81, 150.94, 149.22, 131.17, 128.77, 128.17, 126.94, 120.00, 117.62, 117.04, 110.65, 110.59, 69.70, 69.09, 55.29, 31.30, 31.20, 19.19, 18.98, 13.58, 13.44.

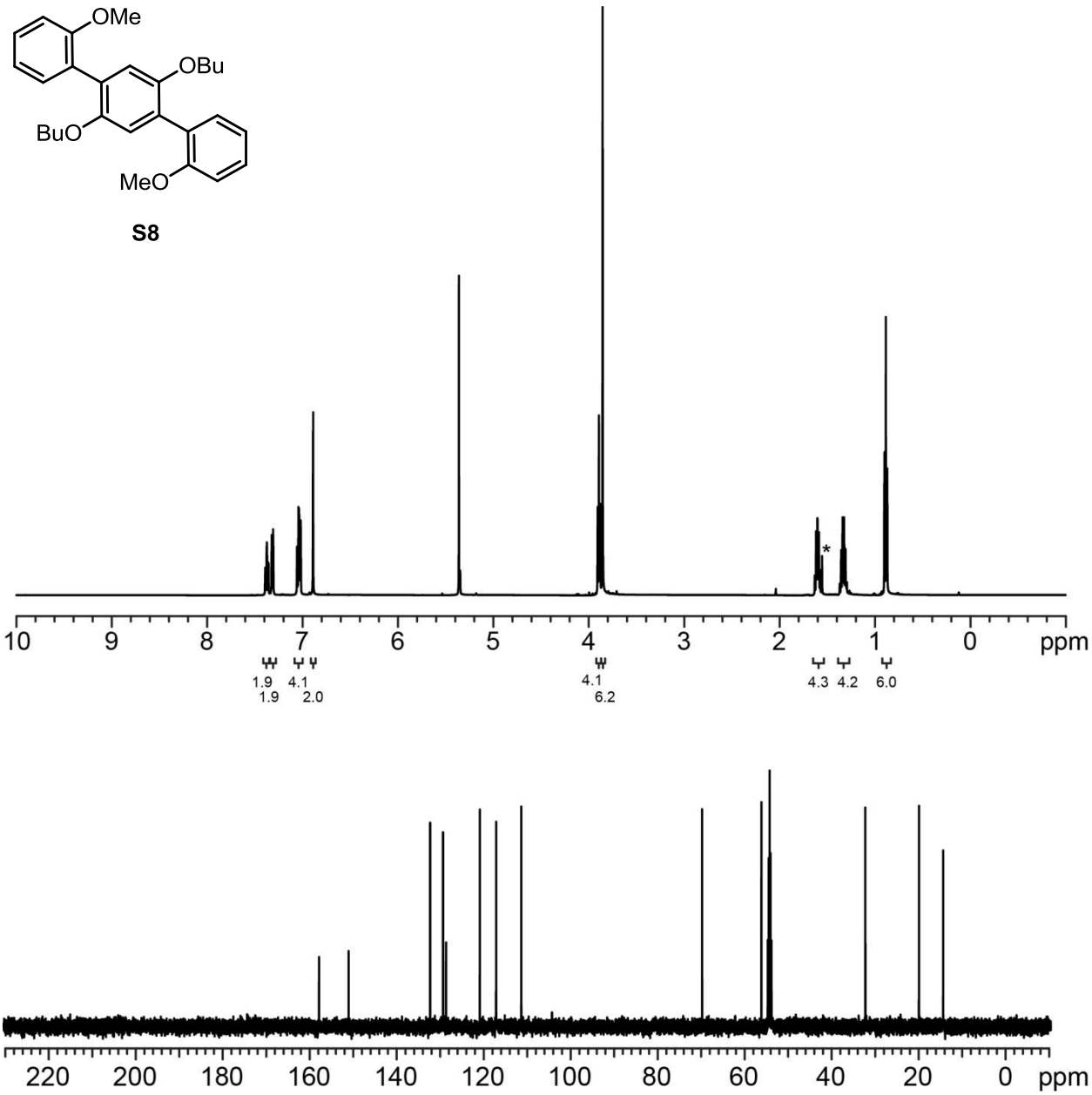


Figure S12. ^{1}H and ^{13}C NMR spectra for **S8**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.34 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 7.03-6.99 (m, 4H), 6.86 (s, 2H), 3.86 (t, *J* = 6.7 Hz, 4H), 3.83 (s, 6H), 1.57 (m, 4H), 1.30 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 6H). * indicates residual H_2O. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 157.41, 150.60, 131.86, 128.89, 128.20, 128.18, 120.43, 116.69, 110.91, 69.33, 55.69, 31.80, 19.46, 13.91.

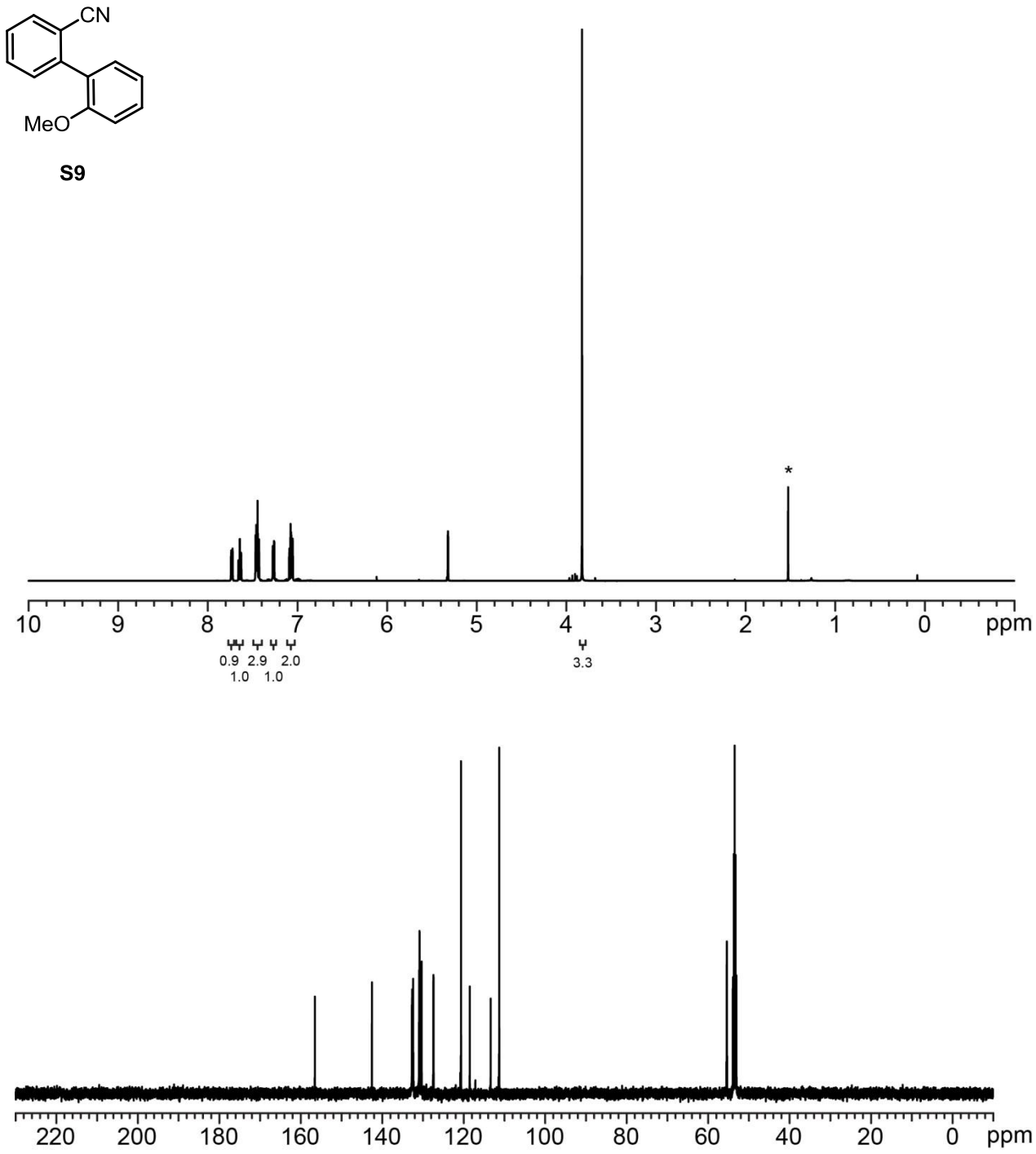
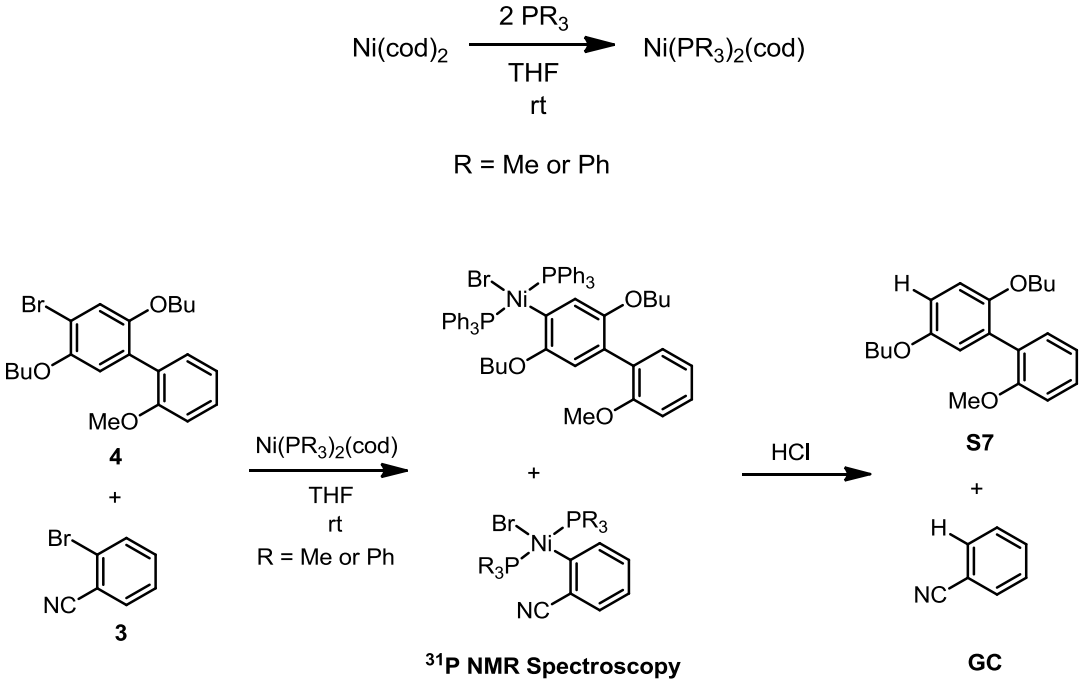


Figure S13. ^{1}H and ^{13}C NMR spectra for **S9**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.47-7.43 (m, 3H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.09-7.05 (m, 2H), 3.82 (s, 3H). * indicates residual H_2O. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 156.86, 142.85, 133.03, 132.98, 132.73, 131.24, 130.66, 127.77, 127.71, 120.98, 118.83, 113.69, 111.61, 55.74.

V. Oxidative Addition Comparison

To determine the reactive preference for Ni(0) towards aryl bromides **3** and **4**, $Ni(cod)(PR_3)_2$ was utilized as a model with PPh_3 and PMe_3.



Representative Procedure for Oxidative Addition Comparisons:

In the glovebox, a 20 mL vial was equipped with a stir bar. Sequentially, $Ni(cod)_2$ (25 mg, 0.091 mmol, 1 equiv), PPh_3 (48 mg, 0.18 mmol, 2 equiv), and THF (3 mL) were added. This mixture was then stirred at rt for 1 h. Then, **3** (37 mg, 0.091 mmol, 1 equiv) and **4** (17 mg, 0.091 mmol, 1 equiv) were dissolved in THF (1 mL). This solution was subsequently taken up in a syringe and quickly added to the vial containing $Ni(cod)(PPh_3)_2$. This solution was left stirring for 1 h at rt. An aliquot was then removed and placed in a J. Young NMR tube for ^{31}P NMR Spectroscopic analysis. The remaining solution was removed from the glovebox and quenched with hydrochloric acid (12.1 M, 3 mL) and subsequently diluted with water (8 mL). The reaction was then extracted with DCM (3 x 3 mL). The combined organic layers were dried over $MgSO_4$, filtered through a 0.2 μm PTFE filter, and subjected to GC analysis.

^{31}P NMR Spectrum of the comparison ofPPh_3

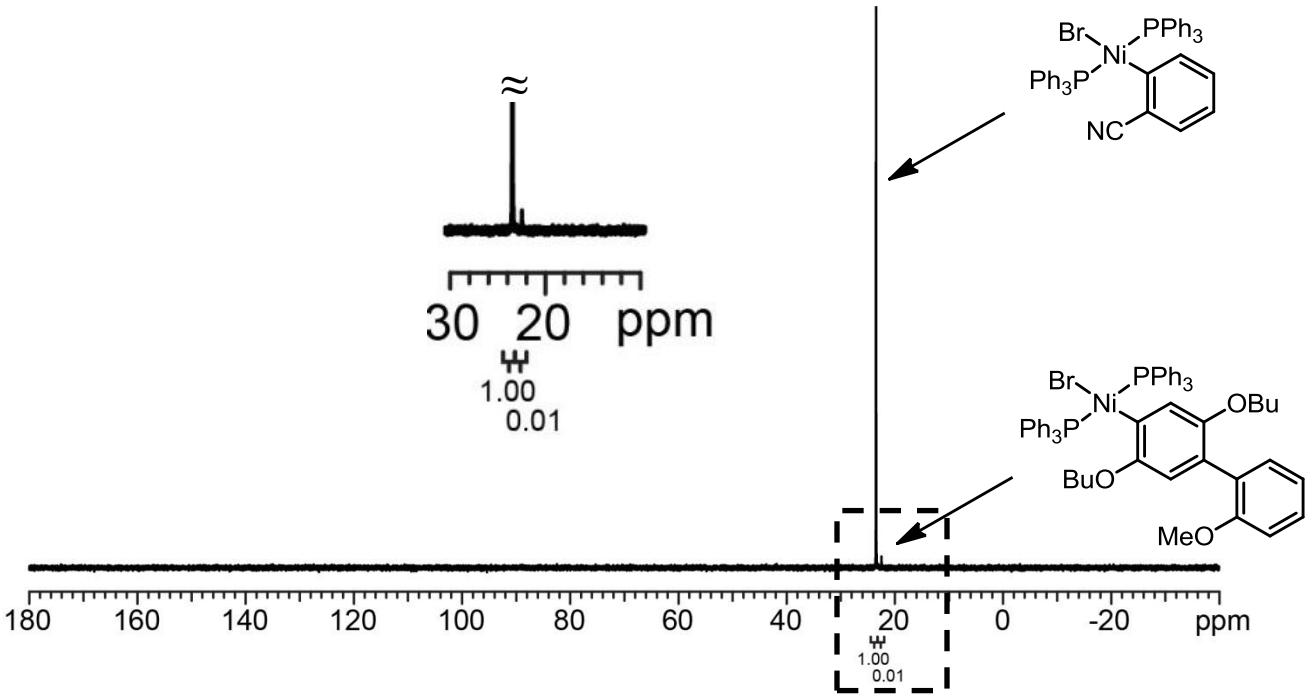


Figure S14. ^{31}P NMR Spectrum for the oxidative addition comparison using PPh_3

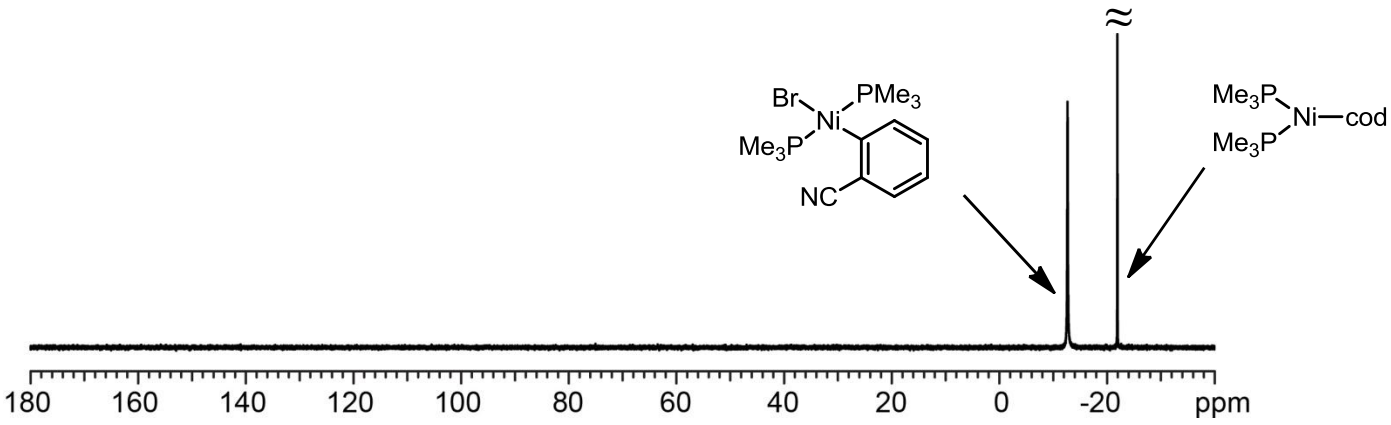


Figure S15. ^{31}P NMR Spectrum for the oxidative addition comparison using PMe_3

Table S1. Data for oxidative addition comparisons in **Figure S14** and **Figure S15**.

Ligand	Conversion of **3*** (%)	% Conversion of **4*** (%)	Ratio of **3**:**4** - GC	Ratio of **3**:**4** - NMR
PPh_3	98.3	0.9	99.1:0.9	99:1
PMe_3	36.4	0.2	99.2:0.8	>99.9:0.1

* Based on relative areas as determined by GC

VI. Calibration Curves

Representative Procedure for Preparing Calibration Curves:

A stock solution was made by weighing ~25 mg of each compound into a 5 mL volumetric flask which was then filled with CH_2Cl_2. A separate stock solution of internal standard (nonadecane) was also made by placing ~25 mg into a 5 mL volumetric flask and filling with CH_2Cl_2. These stock solutions were then used to make 5 samples with known dilutions within the expected range of concentrations of the experiment (0.02 M – 0.001 M for compounds **S6**, **S7**, **4**, **S8**, **S9**, and PhCN, 0.2 M – 0.002 M for compound **3**). Each of these samples were analyzed by GC and the areas plotted against the known concentrations, producing a calibration curve. The process was performed twice per compound and the ratios were averaged. Error bars are included in figures.

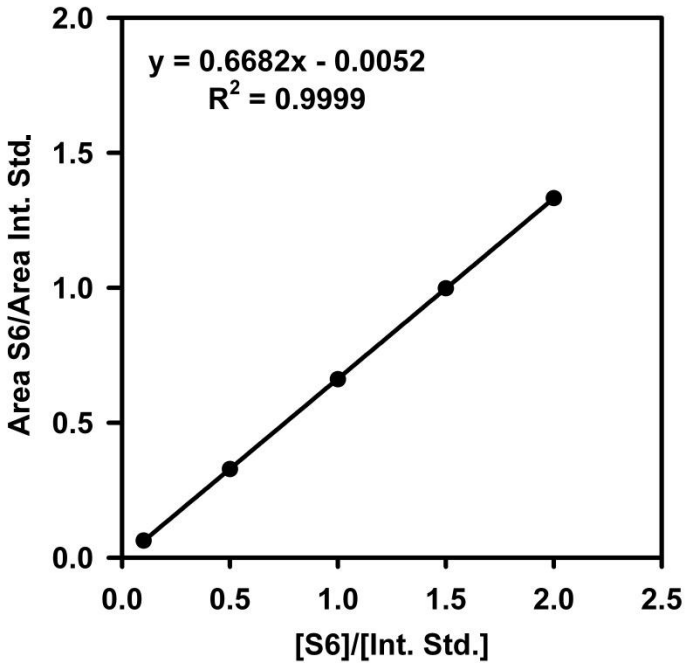


Figure S16. Calibration curve for **S6**.

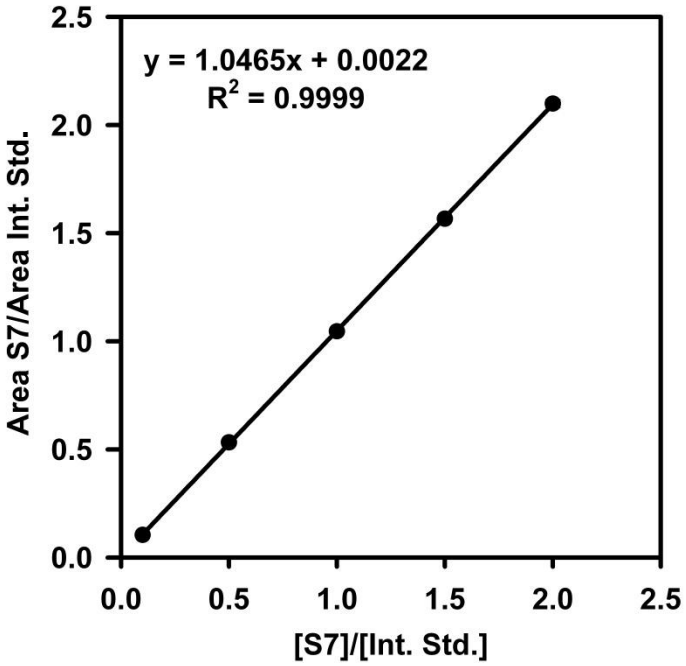


Figure S17. Calibration curve for **S7**.

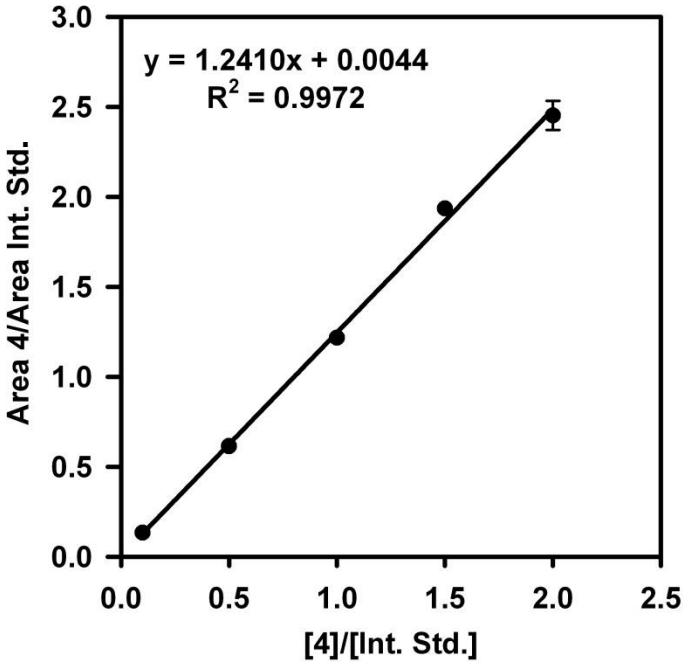


Figure S18. Calibration curve for **4**.

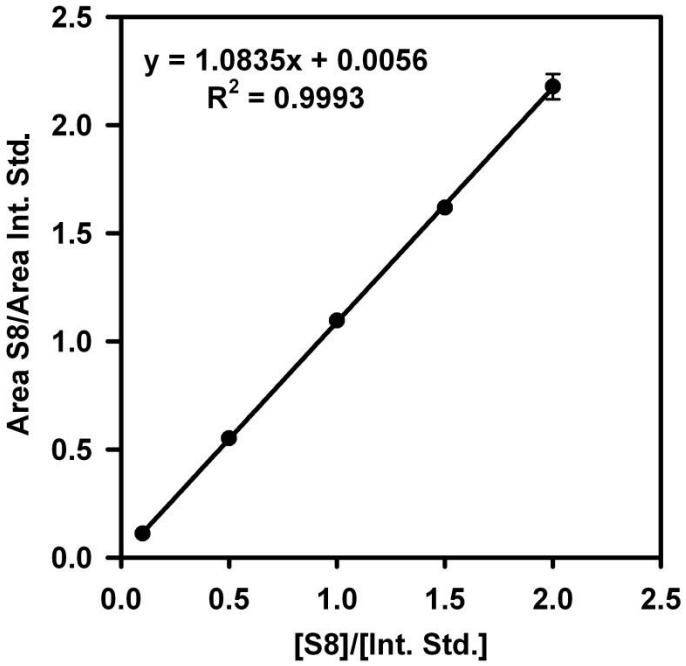


Figure S19. Calibration curve for **S8**.

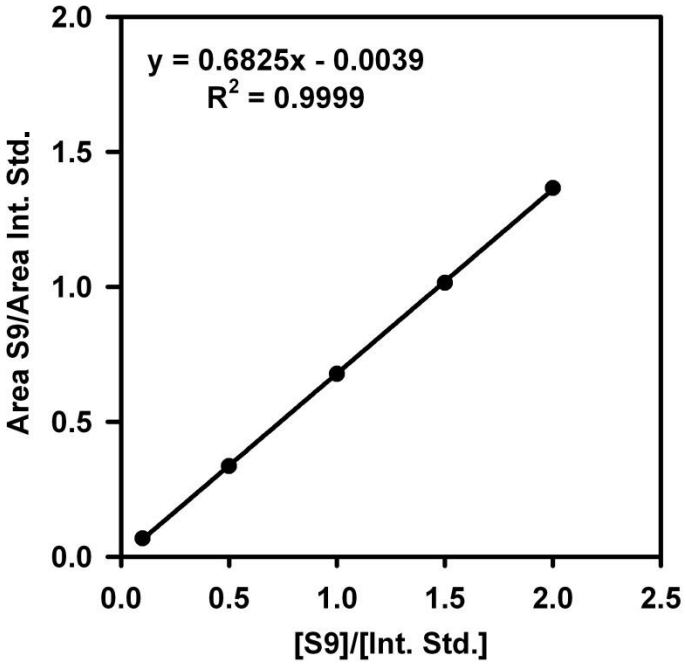


Figure S20. Calibration curve for **S9**.

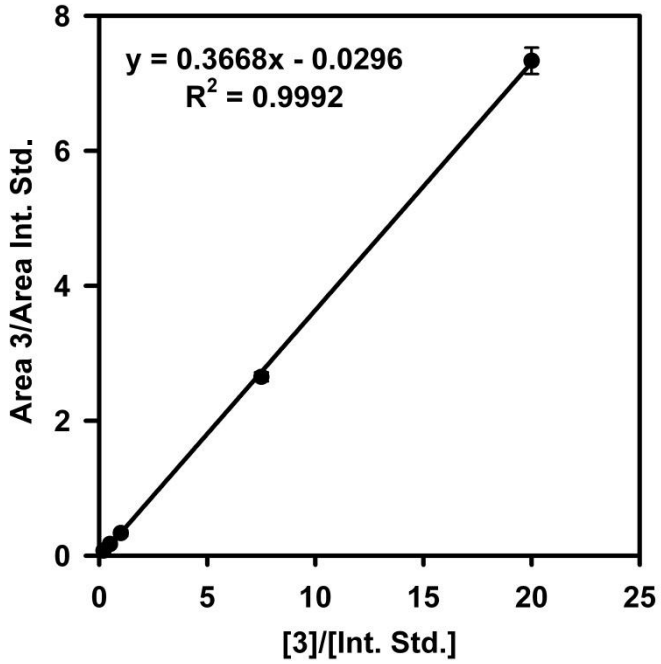


Figure S21. Calibration curve for **3**.

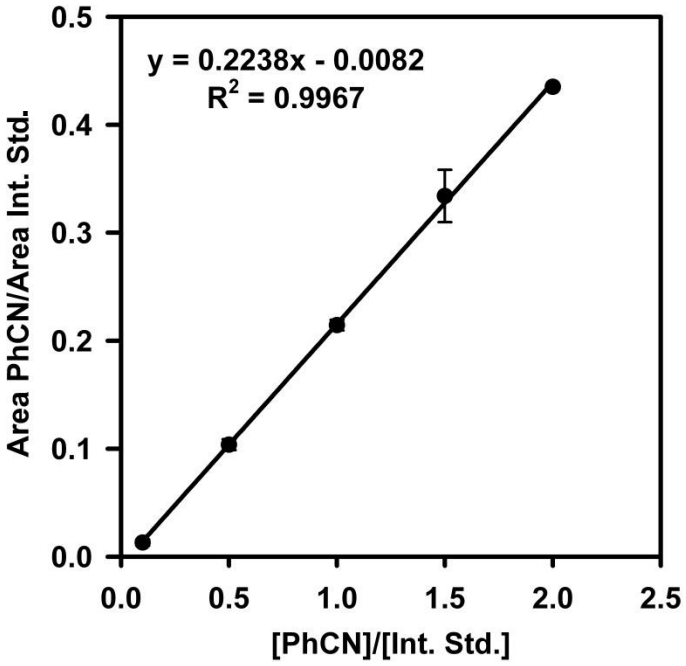
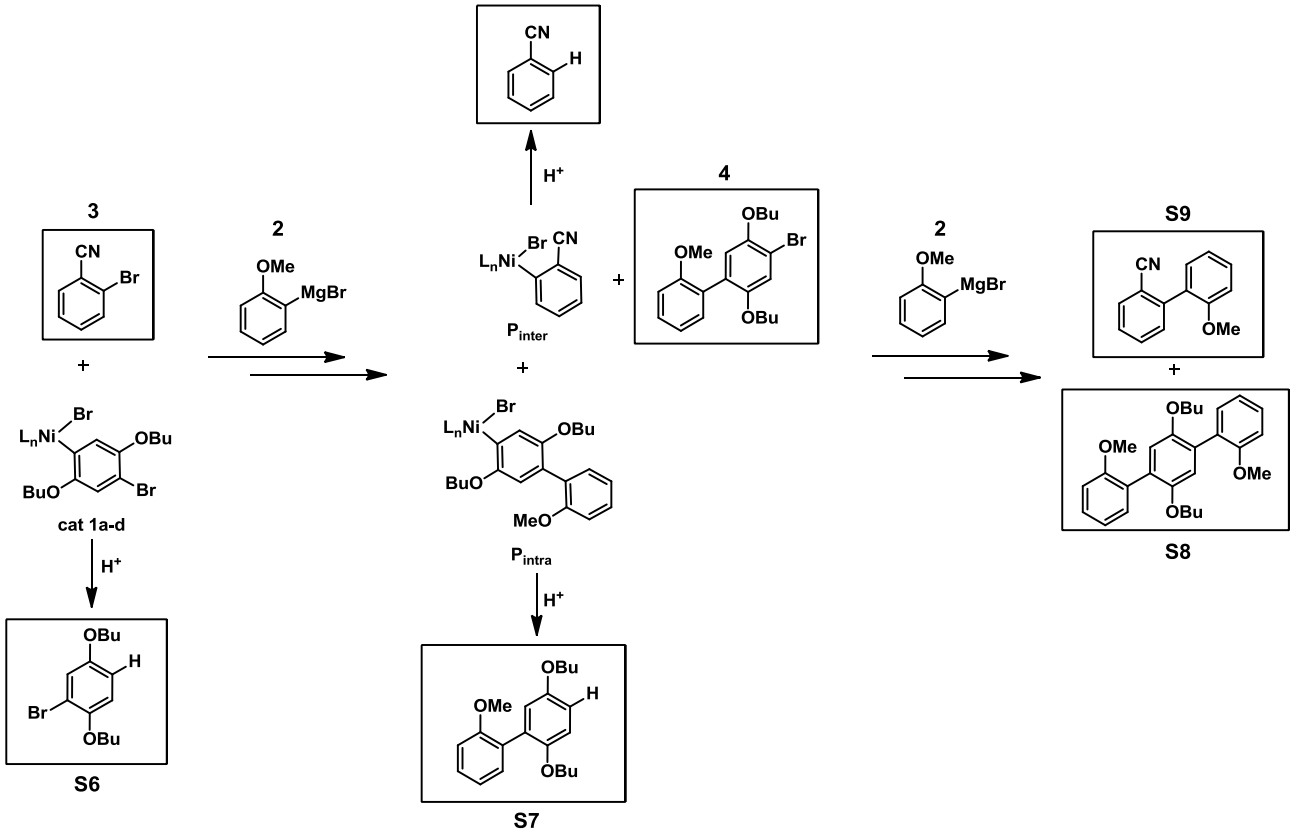


Figure S22. Calibration curve for **PhCN**.

VII. Competition Experiments

Representative Procedure for Performing Competition Experiments:

Prior to starting, separate stock solutions of catalysts **1a-d**, internal standard (nonadecane), and **3** were made. In the glovebox, a 4 mL vial was equipped with a stir bar. Sequentially, **1a** (12.9 mg, 0.020 mmol, 1.0 equiv), **3** (2.9 mg, 0.016 mmol, 0.8 equiv), and nonadecane (internal standard) (2.7 mg, 0.010 mmol, 0.5 equiv) were added with stirring resulting in a total volume of 1 mL (THF). With a microsyringe, **2** (0.16 µL, 0.016 mmol, 0.8 equiv) was added and stirred for 2 h at rt. Upon completion, the vial was removed from the glovebox and quenched with hydrochloric acid (12.1 M, 1 mL) and subsequently diluted with water (1 mL). The reaction was then extracted with DCM (3 x 2 mL). The combined organic layers were dried over $MgSO_4$, filtered through a 0.2 µm PTFE filter, and subjected to GC analysis.



Description of Competition Experiments:

Shown above is a diagram of the reactions that occur during the competition experiments. Along the bottom is the pathway that is consistent with intramolecular oxidative addition. The products along the top are those that correspond to intermolecular oxidative addition. The compounds with boxes around them are those that can be quantified by GC following the hydrolysis of the nickel containing compounds with conc. HCl. As shown above, both P_{inter} and P_{intra} can undergo an additional cycle of transmetallation and reductive elimination producing **S8**, **S9**, and Ni(0). This "free" Ni(0) will react with **3** to generate additional P_{inter}. Therefore, P_{intra} was quantified by **S7** and **S8**, whereas P_{inter} was determined from **4**.

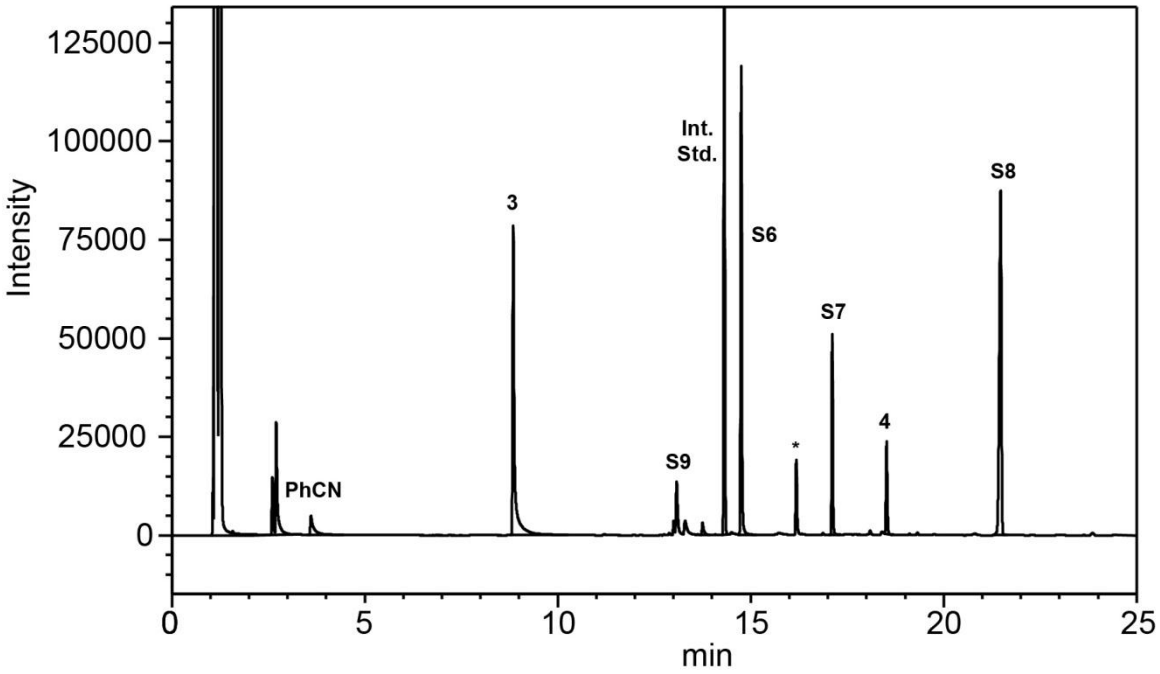


Figure S23. Representative GC of competition experiment using catalyst **1a** and 2 equiv of **3**. * indicates peaks from the corresponding ligand.

Table S2. Summary of competition experiments for catalyst **1a**, with 1 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	95.14	4.86	116
Run 2	95.14	4.86	130
Run 3	94.27	5.73	99
Average	94.9 ± 0.5	5.1 ± 0.5	115 ± 16

Table S3. Summary of competition experiments for catalyst **1a**, with 2 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	90.75	9.25	109
Run 2	90.68	9.32	103
Run 3	90.63	9.37	104
Average	90.69 ± 0.06	9.31 ± 0.06	105 ± 3

Table S4. Summary of competition experiments for catalyst **1a**, with 10 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	68.08	31.92	114
Run 2	68.21	31.79	116
Run 3	70.59	29.41	98
Average	69 ± 1	31 ± 1	109 ± 10

Table S5. Summary of competition experiments for catalyst **1a**, with 50 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	39.31	60.69	106
Run 2	39.49	60.51	112
Run 3	41.22	58.78	103
Average	40 ± 1	60 ± 1	107 ± 5

Table S6. Summary of competition experiments for catalyst **1a**, with 100 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	32.05	67.95	103
Run 2	31.53	68.47	106
Run 3	32.05	67.95	98
Average	31.9 ± 0.3	68.1 ± 0.3	102 ± 4

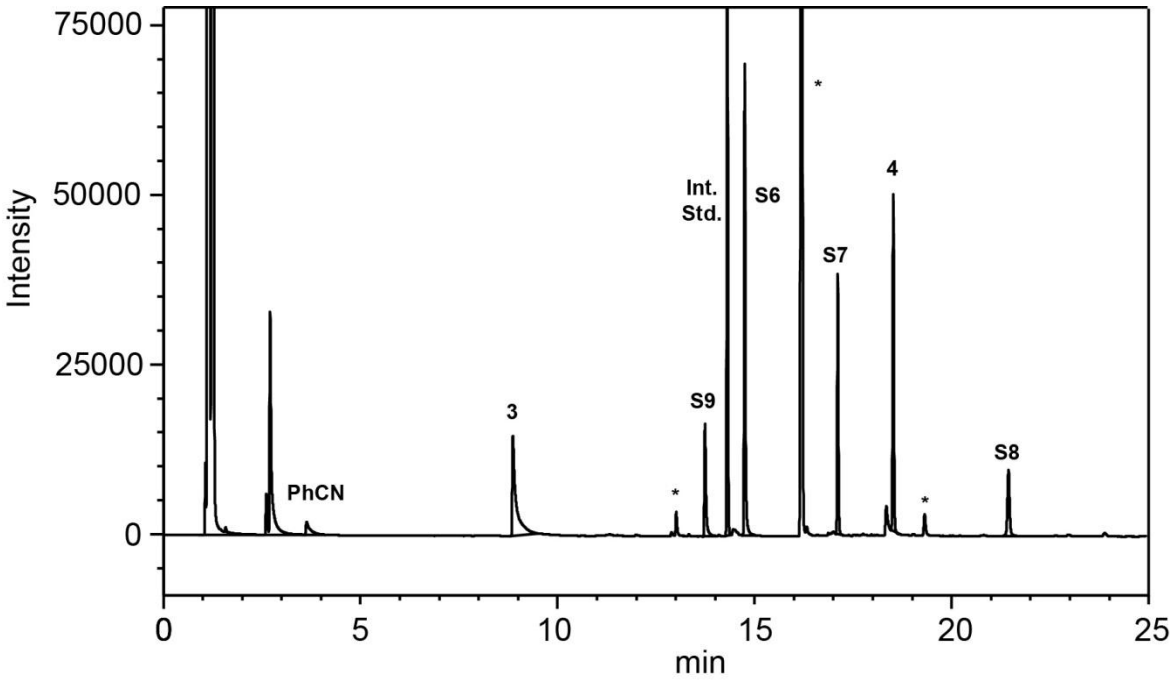


Figure S24. Representative GC of competition experiment using catalyst **1b** and 2 equiv of **3**. * indicates peaks from the corresponding ligand.

Table S7. Summary of competition experiments for catalyst **1b**, with 1 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	65.38	34.62	105
Run 2	64.56	35.44	99
Run 3	66.26	33.74	97
Average	65.4 ± 0.9	34.6 ± 0.9	100 ± 4

Table S8. Summary of competition experiments for catalyst **1b**, with 2 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	55.05	44.95	96
Run 2	55.23	44.77	103
Run 3	55.82	44.18	97
Average	55.4 ± 0.4	44.6 ± 0.4	99 ± 4

Table S9. Summary of competition experiments for catalyst **1b**, with 10 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	26.80	73.20	102
Run 2	27.20	72.81	99
Run 3	28.66	71.34	95
Average	28 ± 1	72 ± 1	99 ± 4

Table S10. Summary of competition experiments for catalyst **1b**, with 50 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	13.27	86.74	96
Run 2	13.31	86.69	97
Run 3	11.86	88.14	95
Average	12.8 ± 0.8	87.2 ± 0.8	96 ± 1

Table S11. Summary of competition experiments for catalyst **1b**, with 100 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	11.27	88.73	92
Run 2	11.10	88.90	96
Run 3	9.27	90.73	94
Average	11 ± 1	89 ± 1	94 ± 2

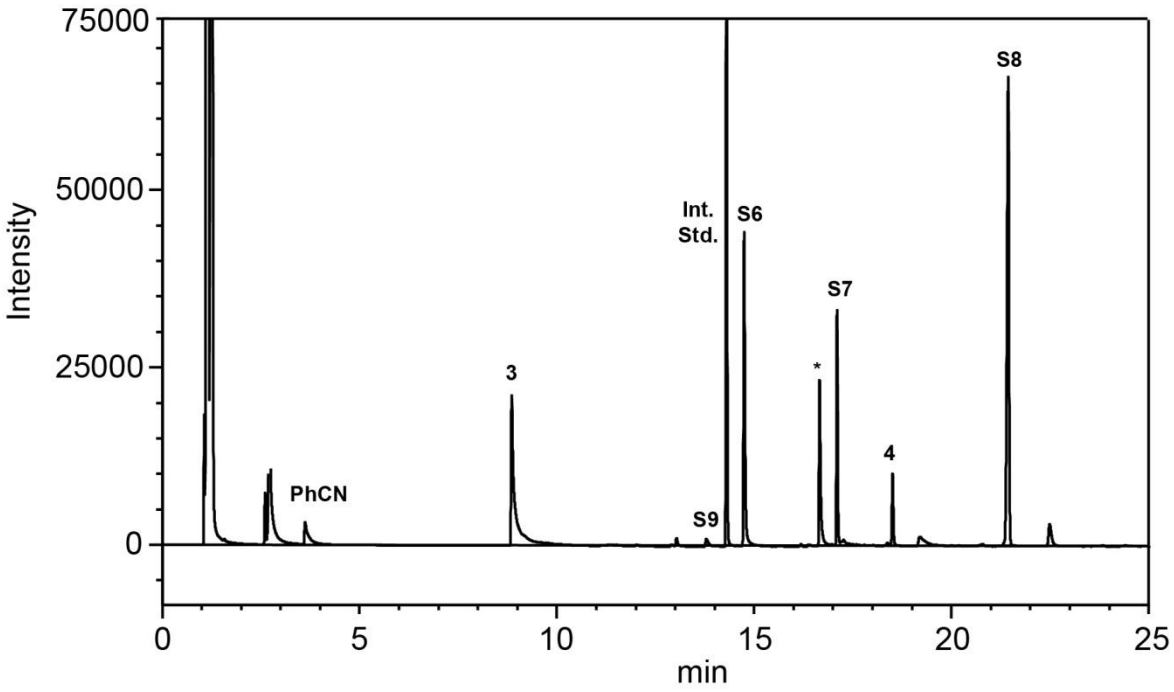


Figure S25. Representative GC of competition experiment using catalyst **1c** and 2 equiv of **3.** * indicates peaks from the corresponding ligand.

Table S12. Summary of competition experiments for catalyst **1c**, with 1 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	96.46	3.54	115
Run 2	97.25	2.75	110
Run 3	95.65	4.35	112
Average	96.5 ± 0.8	3.6 ± 0.8	112 ± 3

Table S13. Summary of competition experiments for catalyst **1c**, with 2 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	93.91	6.09	111
Run 2	94.34	5.66	103
Run 3	92.35	7.65	106
Average	94 ± 1	6 ± 1	107 ± 4

Table S14. Summary of competition experiments for catalyst **1c**, with 10 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	77.39	22.61	111
Run 2	77.62	22.38	115
Run 3	78.25	21.75	105
Average	77.8 ± 0.5	22.2 ± 0.5	110 ± 5

Table S15. Summary of competition experiments for catalyst **1c**, with 50 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	48.46	51.54	104
Run 2	50.04	49.96	101
Run 3	45.37	54.63	98
Average	48 ± 2	52 ± 0.2	101 ± 3

Table S16. Summary of competition experiments for catalyst **1c**, with 100 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	39.86	60.14	94
Run 2	41.08	58.92	95
Run 3	37.20	62.80	94
Average	39 ± 2	61 ± 2	94.3 ± 0.6

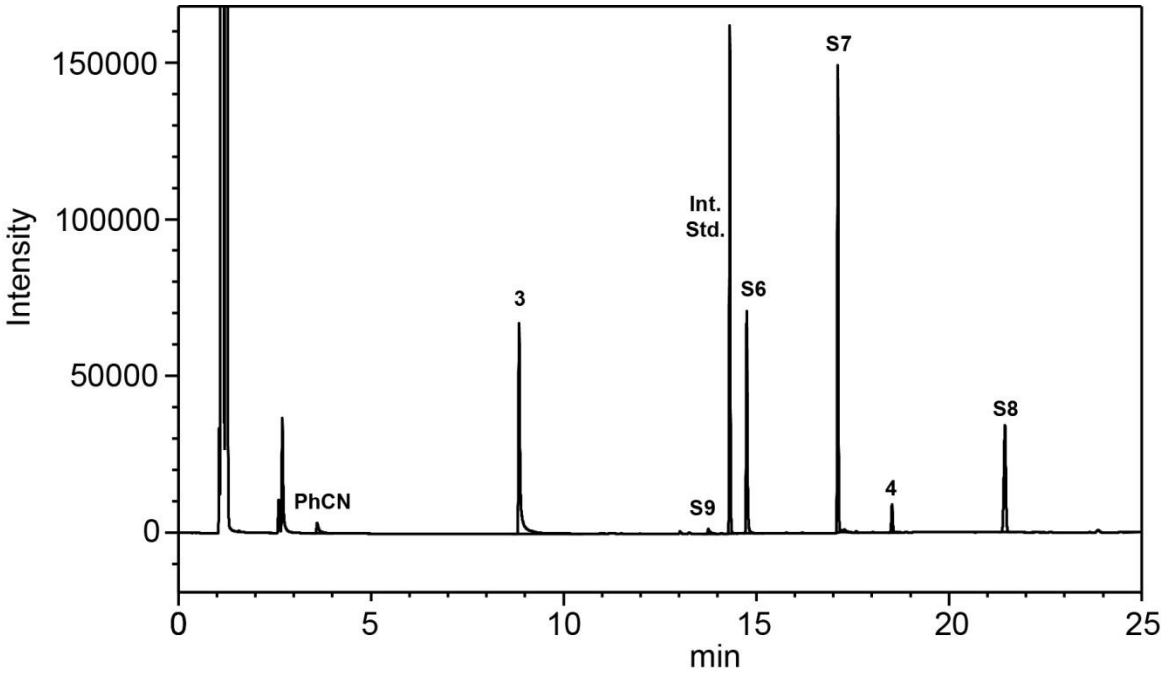


Figure S26. Representative GC of competition experiment using catalyst **1d** and 2 equiv of **3.**

Table S17. Summary of competition experiments for catalyst **1d**, with 1 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	98.08	1.92	102
Run 2	98.37	1.63	105
Run 3	97.99	2.01	110
Average	98.1 ± 0.2	1.9 ± 0.2	106 ± 4

Table S18. Summary of competition experiments for catalyst **1d**, with 2 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	95.90	4.10	112
Run 2	96.29	3.71	103
Run 3	96.35	3.65	105
Average	96.2 ± 0.2	3.8 ± 0.2	106 ± 5

Table S19. Summary of competition experiments for catalyst **1d**, with 10 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	86.43	13.57	105
Run 2	86.12	13.88	109
Run 3	87.25	12.75	97
Average	86.6 ± 0.6	13.4 ± 0.6	104 ± 6

Table S20. Summary of competition experiments for catalyst **1d**, with 50 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	70.11	29.89	105
Run 2	70.52	29.48	102
Run 3	71.69	28.31	108
Average	70.8 ± 0.8	29.2 ± 0.8	105 ± 3

Table S21. Summary of competition experiments for catalyst **1d**, with 100 equiv of **3**.

	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	62.93	37.07	94
Run 2	64.43	35.57	97
Run 3	64.89	35.11	96
Average	64 ± 1	34 ± 1	96 ± 2

VIII. Relative Rate Constants for Intra- versus Intermolecular Pathways

$$\mathbf{I}_{intra} \xrightarrow{k_{intra}} \mathbf{P}_{intra} \quad (2)$$

$$\mathbf{I}_{intra} + \mathbf{3} \xrightarrow{k_{inter}} \mathbf{P}_{inter} \quad (3)$$

$$\frac{d[\mathbf{P}_{intra}]}{dt} = k_{intra}[\mathbf{I}_{intra}] \quad (4)$$

$$\frac{d[\mathbf{P}_{inter}]}{dt} = k_{inter}[\mathbf{I}_{intra}][\mathbf{3}] \quad (5)$$

$$\frac{[\mathbf{P}_{intra}]}{[\mathbf{P}_{inter}]} = \frac{k_{intra}}{k_{inter}[\mathbf{3}]} \quad (6)$$

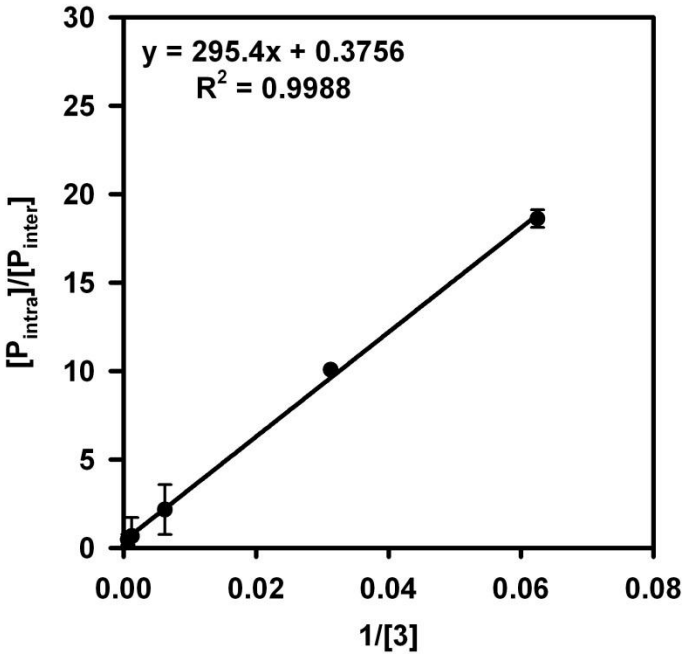


Figure S27. Plot of the relative rate constants for intra- versus intermolecular pathways versus concentration of **3** for **1a**.

Table S22. Data for the plot in Figure S27.

3 (equiv)	$[P_{intra}]$	$[P_{inter}]$	$[P_{intra}]/[P_{inter}]$	1/[**3**]
1	94.9	5.1	18.6	0.0625
2	90.7	9.3	10.1	0.03125
10	69.0	31.0	2.16	0.00625
50	40.0	61.0	0.66	0.00125
100	31.9	68.1	0.47	0.000625

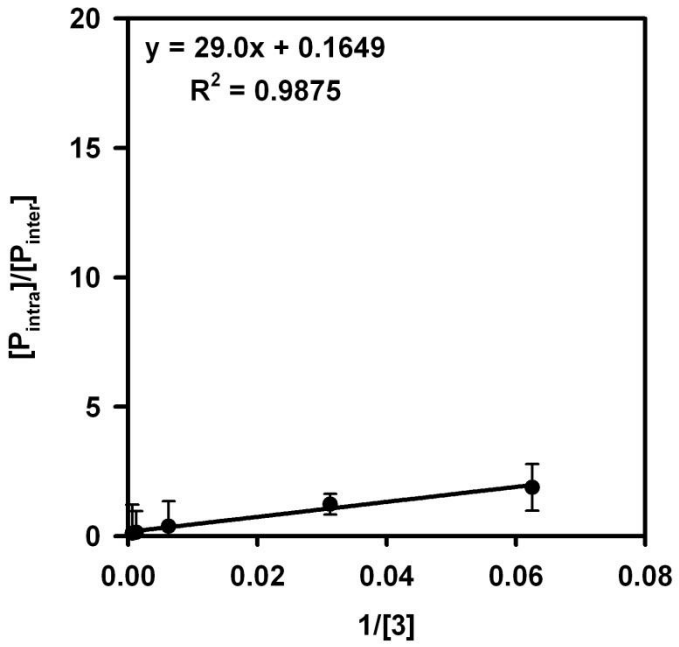


Figure S28. Plot of the relative rate constants for intra- versus intermolecular pathways versus concentration of **3** for **1b**.

Table S23. Data for the plot in Figure S28.

3 (equiv)	[P_{intra}]	[P_{inter}]	[P_{intra}]/[P_{inter}]	1/[**3**]
1	65.4	34.6	1.89	0.0625
2	55.4	44.6	1.24	0.03125
10	27.6	72.4	0.38	0.00625
50	12.8	87.2	0.15	0.00125
100	10.6	89.4	0.12	0.000625

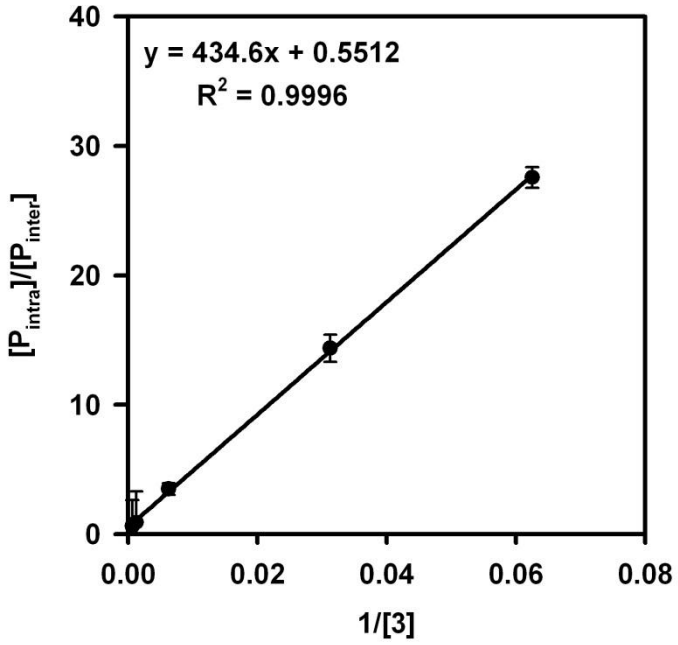


Figure S29. Plot of the relative rate constants for intra- versus intermolecular pathways versus concentration of **3** for **1c**.

Table S24. Data for the plot in Figure S29.

3 (equiv)	[P_{intra}]	[P_{inter}]	[P_{intra}]/[P_{inter}]	1/[**3**]
1	96.5	3.5	27.6	0.0625
2	93.5	6.5	14.4	0.03125
10	77.8	22.2	3.50	0.00625
50	48.0	52.0	0.92	0.00125
100	39.4	60.6	0.65	0.000625

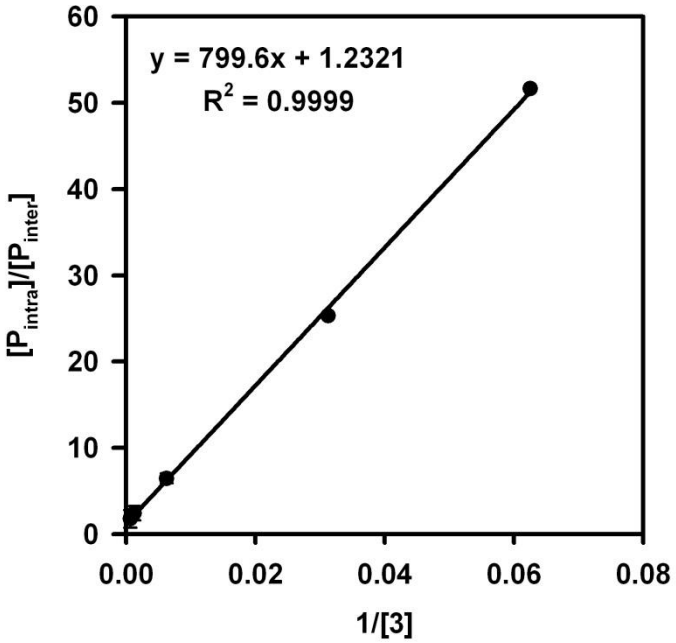


Figure S30. Plot of the relative rate constants for intra- versus intermolecular pathways versus concentration of **3** for **1d**.

Table S25. Data for the plot in Figure S30.

3 (equiv)	[P_{intra}]	[P_{inter}]	[P_{intra}]/[P_{inter}]	1/[**3**]
1	98.1	1.9	51.6	0.0625
2	96.2	3.8	25.3	0.03125
10	86.6	13.4	6.46	0.00625
50	70.8	29.2	2.42	0.00125
100	64.1	35.9	1.79	0.000625

IX. Evidence for Irreversible Dissociation

To determine whether the dissociation of I_{intra} is irreversible (see Scheme 1), a competition experiment was performed as described previously (page S30) for catalysts **1a** and **1d** with an additional 100 equiv **4** added.

Scheme S1

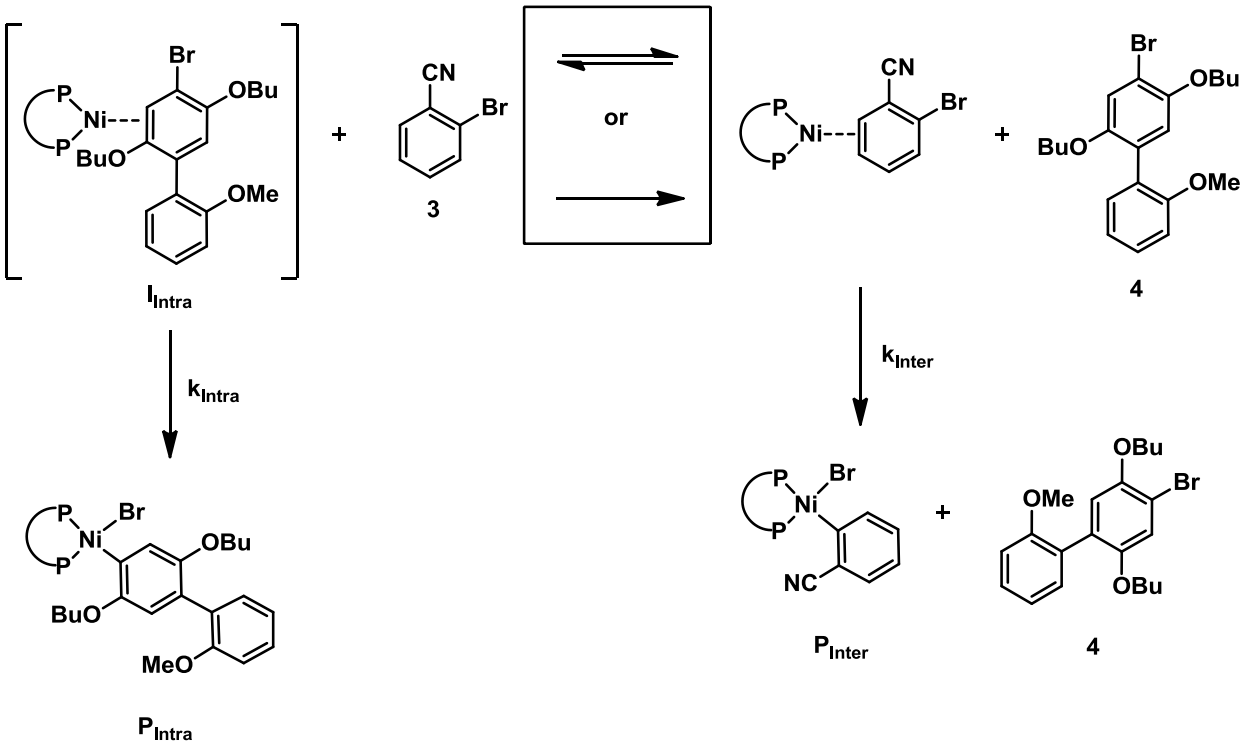


Table S26. Summary of competition experiments for catalyst **1a**, with 100 equiv of **3** and variable equiv of **4**.

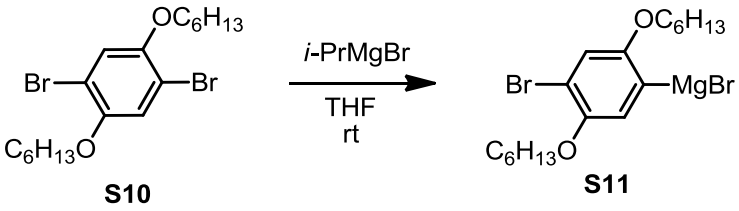
	4 (equiv)	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	0	32.05	67.95	103
Run 2	0	31.53	68.47	106
Run 3	0	32.05	67.95	98
Average of 1-3	0	31.9 ± 0.3	68.1 ± 0.3	102 ± 4
Run 4	100	29.71	70.29	124
Run 5	100	27.85	72.15	116
Average of 4 and 5	100	29 ± 1	71 ± 1	120 ± 6

Table S27. Summary of competition experiments for catalyst **1d**, with 100 equiv of **3** and variable equiv of **4**.

	4 (equiv)	P_{intra}	P_{inter}	Mass Balance (%)
Run 1	0	62.93	37.07	94
Run 2	0	64.43	35.57	97
Run 3	0	64.89	35.11	96
Average of 1-3	0	64 ± 1	36 ± 1	96 ± 2
Run 4	100	63.09	36.91	110
Run 5	100	64.63	35.37	116
Average of 4 and 5	100	64 ± 1	36 ± 1	113 ± 4

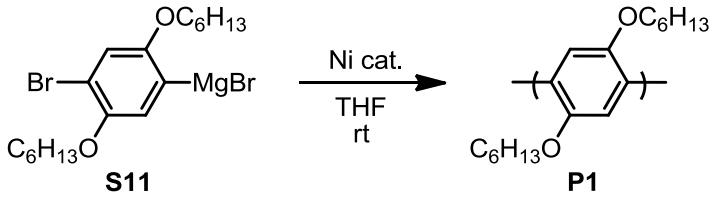
X. Summary of Polymerization Results

Representative Procedure for Preparing Monomer for Polymerizations:



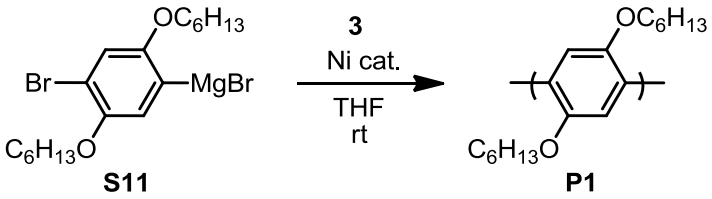
S11. In the glovebox, **S10** (2.00 g, 4.32 mmol, 1.0 equiv) was dissolved in THF (4 mL) in a 20 mL vial equipped with a stir bar. Then, *i*-PrMgBr (1.44 mL, 3.89 mmol, 0.9 equiv) was added via syringe, the vial was capped, and the reaction was stirred overnight at rt.

Representative Procedure for Polymerizations:



S12. All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, catalyst **1a** (6.3 mg, 0.0075 mmol, 1.0 equiv), THF (3.60 mL), and **S11** (1.40 mL, 0.359 M, 0.5025 mmol, 67 equiv), with docosane added (as an internal standard), were added to the vial with stirring. After 24 h, the reaction was removed from the glovebox, and poured into aq. HCl (12.1 M, 5 mL). This mixture was then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. To monitor conversion, GC samples were prepared by taking aliquots (~0.25 mL) of this organic phase and diluting with CH_2Cl_2 (~0.75 mL). Conversion was determined relative to the initial concentration, using the internal standard as a reference. To measure molecular weight and molecular weight distribution, the remaining organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

Representative Procedure for Competitive Polymerizations:



S13. All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, catalyst **1a** (6.3 mg, 0.0075 mmol, 1.0 equiv), THF (3.60 mL), **3** (137.5 mg, 0.75 mmol, 100 equiv), and **S11** (1.40 mL, 0.359 M, 0.5025 mmol, 67 equiv), with docosane added (as an internal standard), were added to the vial with stirring. After 24 h, the reaction was removed from the glovebox, and poured into aq. HCl (12.1 M, 5 mL). This mixture was then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. To monitor conversion, GC samples were prepared by taking aliquots (~0.25 mL) of this organic phase and diluting with CH_2Cl_2 (~0.75 mL). Conversion was determined relative to the initial concentration, using the internal standard as a reference. To measure molecular weight and molecular weight distribution, the remaining organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

Table S28. Summary of results with 0 equiv **3** added.

Catalyst	Experiment	% Conversion **S11**	% Conversion **S10**	M_n (kDa)	Đ
1a	Run 1	89	0	31.2	1.36
	Run 2	93	0	27.1	1.39
	Average	91	0	29 ± 3	1.38 ± 0.02
1b	Run 1	59	51	2.1	2.40
	Run 2	72	66	2	2.44
	Average	66	59	2.05 ± 0.07	2.42 ± 0.03
1c	Run 1	88	0	37.8	1.27
	Run 2	93	0	28.5	1.31
	Average	91	0	33 ± 6	1.29 ± 0.03
1d	Run 1	89	0	30.5	1.43
	Run 2	93	0	26.7	1.45
	Average	91	0	29 ± 3	1.44 ± 0.01

Table S29. Summary of results with 50 equiv **3** added.

Catalyst	Experiment	% Conversion **S11**	% Conversion **S10**	% Conversion **3**	M_n (kDa)	Đ
	Run 1	93	0	24	25.5	2.30
1a	Run 2	93	0	24	24.4	2.29
	Average	93	0	24	25.0 ± 0.8	2.30 ± 0.01
	Run 1	66	59	64	1.1	2.61
1b	Run 2	67	61	69	1	2.33
	Average	67	60	67	1.05 ± 0.07	2.50 ± 0.2
	Run 1	93	0	12	28.3	1.87
1c	Run 2	94	0	19	29.4	1.90
	Average	94	0	16	28.9 ± 0.8	1.89 ± 0.02
	Run 1	92	0	27	22.8	1.97
1d	Run 2	93	0	10	23.9	1.99
	Average	93	0	19	23.4 ± 0.8	1.98 ± 0.01

Table S30. Summary of results with 100 equiv **3** added.

Catalyst	Experiment	% Conversion **S11**	% Conversion **S10**	% Conversion **3**	M_n (kDa)	Đ
	Run 1	92	0	10	17.4	2.33
1a	Run 2	92	0	6	16.3	2.36
	Average	92	0	8	16.9 ± 0.8	2.35 ± 0.02
	Run 1	69	61	68	1.0	2.47
1b	Run 2	71	63	65	1.1	2.36
	Average	70	62	67	1.05 ± 0.07	2.42 ± 0.08
	Run 1	93	0	17	21.5	2.29
1c	Run 2	93	0	19	29.4	2.26
	Average	93	0	18	25 ± 6	2.28 ± 0.02
	Run 1	93	0	8	19.1	2.17
1d	Run 2	93	0	6	19.7	2.12
	Average	93	0	7	19.4 ± 0.4	2.15 ± 0.04

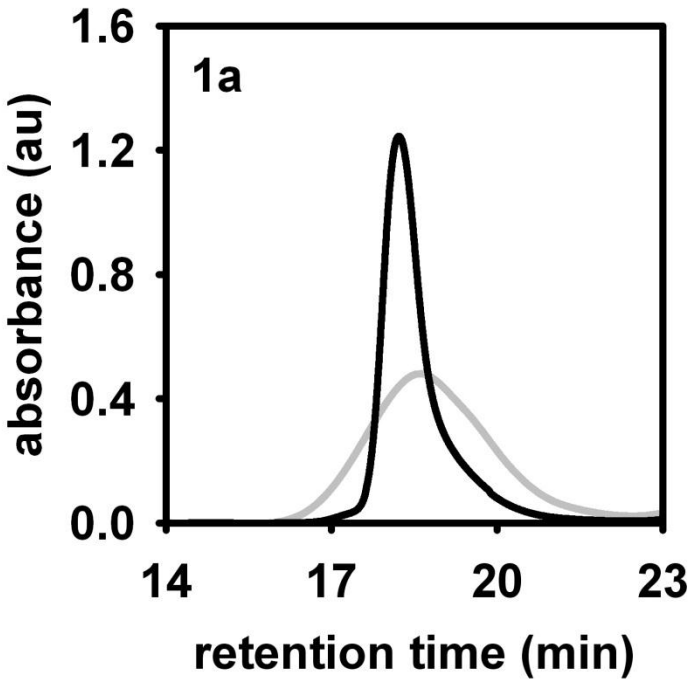


Figure S31. Representative GPC traces of polymer formed by catalyst **1a** with 0 equiv (black) and 100 equiv (grey) **3**.

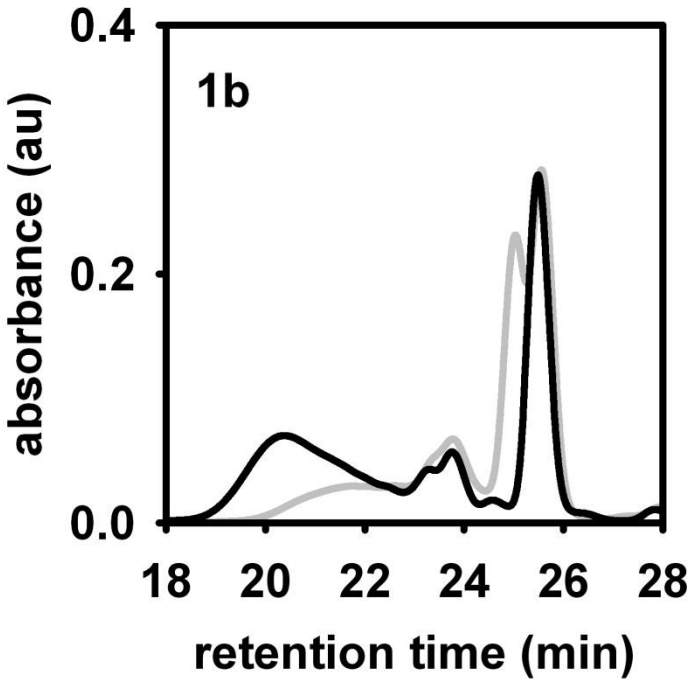


Figure S32. Representative GPC traces of polymer formed by catalyst **1b** with 0 equiv (black) and 100 equiv (grey) **3**.

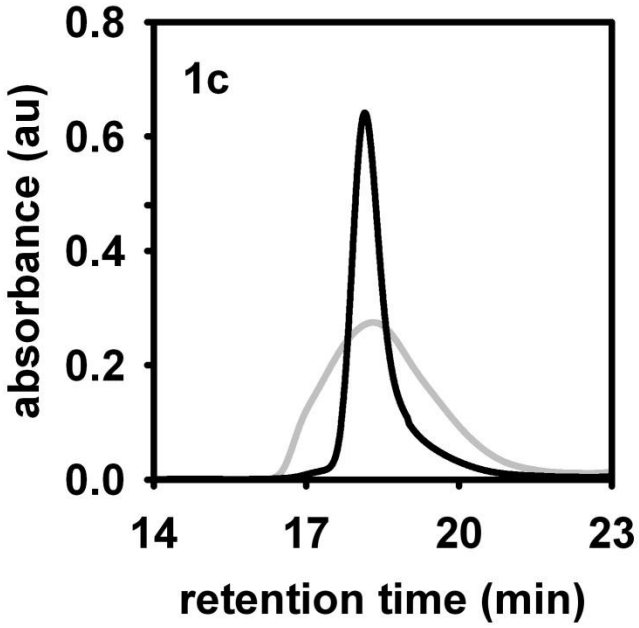


Figure S33. Representative GPC traces of polymer formed by catalyst **1c** with 0 equiv (black) and 100 equiv (grey) **3**.

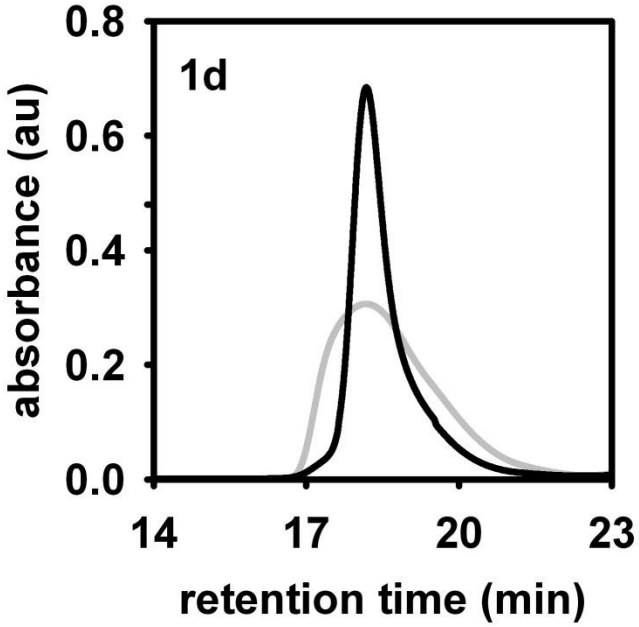


Figure S34. Representative GPC traces of polymer formed by catalyst **1d** with 0 equiv (black) and 100 equiv (grey) **3**.

XI. Crystal Structure of S4.

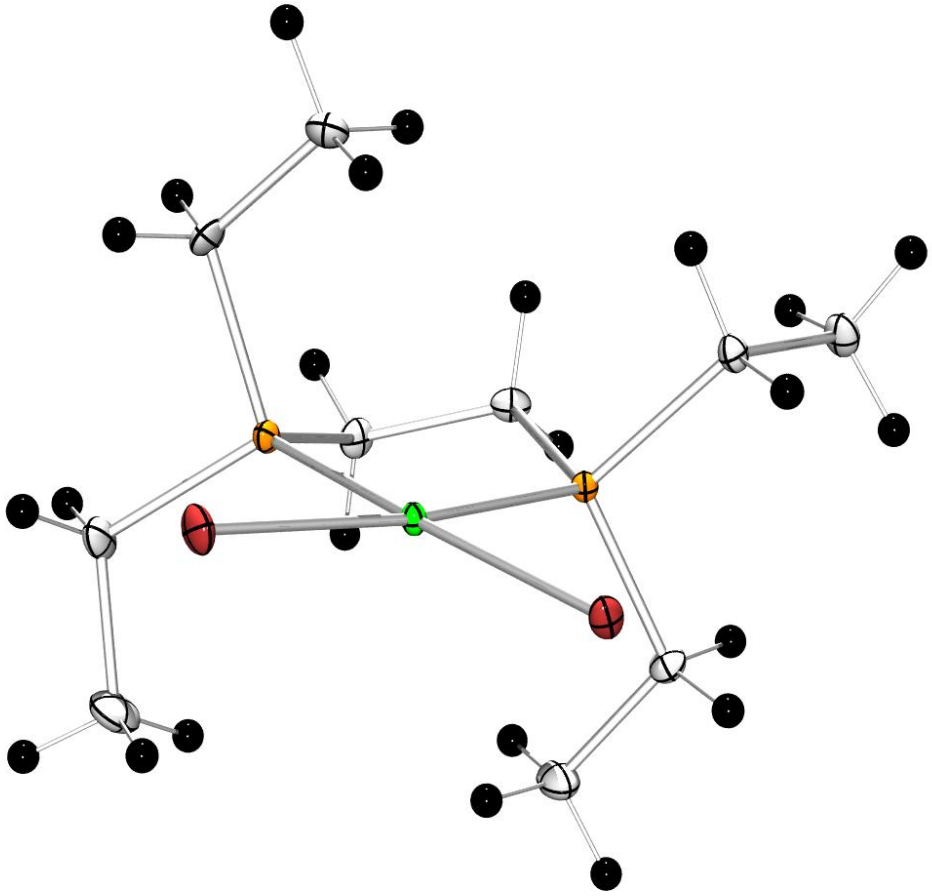
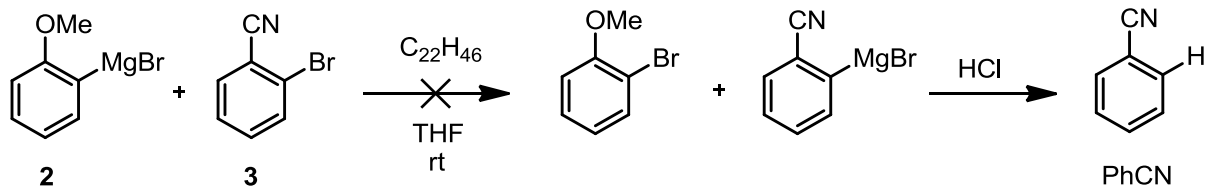


Figure S35. Crystal structure of **S4**. The Ni-P bond lengths are 2.14, 2.15 Å, the Ni-Br bond lengths are 2.34, 2.35 Å. The P-Ni-P bond angle is 87.53°. The Br-Ni-Br bond angle is 96.10°.

XII. Schlenk Equilibrium between 2 and 3



*Representative Procedure for Investigating the Schlenk Equilibrium of **2** and **3**:*
All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, **3** (18 mg, 0.10 mmol, 1.0 equiv) and THF (3.0 mL), with docosane added (as an internal standard), were added to the vial with stirring. Once dissolved, **2** (0.10 mL, 0.10 mmol, 1.0 equiv) was added and the vial was capped. After 2 h, the reaction was removed from the glovebox, and poured into aq. HCl (12.1 M, 3 mL). This mixture was then extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were dried over $MgSO_4$ and filtered. Conversion was determined relative to the initial concentration, using the internal standard as a reference.

Sample	Production of PhCN (%)
Run 1	0.0
Run 2	0.0
Run 3	0.0
Run 4	0.0

XIII. References

(1) E. L. Lanni and A. J. McNeil, *J. Am. Chem. Soc.* 2009, **131**, 16573-16579.
(2) B. D. Love and E. G. Jones, *J. Org. Chem.* 1999, **64**, 3755-3756.
(3) E. L. Lanni and A. J. McNeil, *Macromolecules* 2010, **43**, 8039-8044.
(4) S. R. Lee, Z. J. Bryan, A. M. Wagner, and A. J. McNeil, *Chem. Sci.* 2012, **3**, 1562-1566.
(5) E. L. Lanni, J. R. Locke, C. M. Gleave, and A. J. McNeil, *Macromolecules* 2011, **44**, 5136-5145.