Supporting Information for

Effect of ligand electronic properties on precatalyst initiation and propagation in Ni-catalyzed cross-coupling 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) was purchased in 100 mL quantities from Aldrich. $Ni(cod)_2$ 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. Compounds **S1**,[1] **S2**,[1] **S3**,[2] **S4**,[3] **1a-c**,[2] **S5**,[2] **S6**,[3] and **3a-c**[2] were prepared from modified literature procedures.

II. General Experimental

NMR Spectroscopy: Unless otherwise noted, ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra for all compounds were acquired at rt in acetone-d_6 or $CDCl_3$ on a Varian vnmrs 700 operating at 700, 176, 660, and 283 MHz, Varian vnmrs 500 operating at 500, 126, 470, and 202 MHz or a Varian MR 400 operating at 400, 100, 376 and 162 MHz, respectively. For ^1H, ^{13}C, ^{19}F, and ^{31}P 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 ^1H, ^{19}F and ^{31}P NMR spectra in non-deuterated THF, the chemical shift data are reported in units of δ (ppm) and referenced with 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), quintet (quin), multiplet (m), broad resonance (br), and apparent triplet (at).

Mass Spectrometry: HRMS data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer.

IR Spectroscopy: Samples were recorded using a Mettler Toledo ReactIR iC10 fitted with a Mercury Cadmium Telluride (MCT) detector, and AgX probe (9.5 mm x 1.5 mm) with a SiComp tip. The spectra were processed using icIR 4.0 software and raw absorbances were exported into Microsoft Excel or Sigma Plot 10 for analysis.

MALDI-TOF MS: MALDI-TOF mass spectra were recorded using Waters Tofspec-2E in reflectron mode at a unit mass resolution of 4000. The matrix, α-cyano-4-hydroxy-cinnamic acid (CHCA), was prepared at a concentration of 10 mg/mL in a solution of 50/50 (v/v) CH_3CN/EtOH. The instrument was mass calibrated with a mixture of peptides in the CHCA matrix. The polymer sample was dissolved in CH_2Cl_2 to obtain a ~1 mg/mL solution. A 3 μL aliquot of polymer solution was mixed with 3 μL of the matrix solution. 1 μL of this mixture was placed on the target plate and then air-dried.

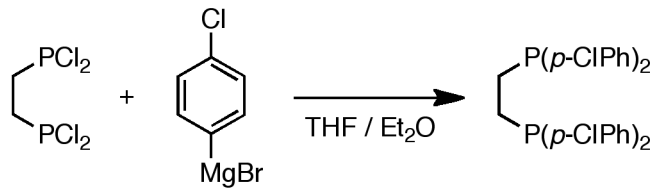
Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR

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 ArMgCl was added dropwise using a 500 μL syringe. The initial solution is yellow and turns bright orange at the end-point.[4]

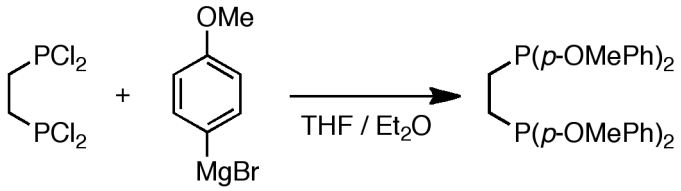
Statistical Analysis: Reported quantitative data represents the average of 2-3 experiments and the error bars represent the standard deviation in these measurements.

III. Synthetic Procedures



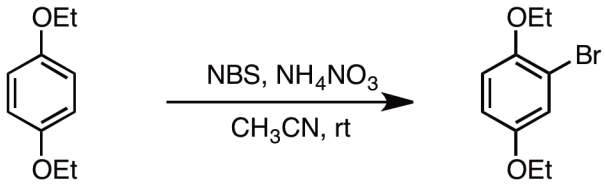
S1

S1. An oven-dried Schlenk flask was brought into the glovebox and equipped with a stir bar,1,2-bis(dichlorophosphino)ethane (0.39 mL, 2.6 mmol, 1.0 equiv) and anhydrous THF (15 mL). The flask was then brought out of the glovebox and placed under N_2. After cooling to -40 °C, 4-chlorophenylmagnesium bromide (16.0 mL, 1 M in Et_2O, 6.0 equiv) was added dropwise over 15 min. The reaction mixture was stirred for 1 h at -40 °C and then warmed to rt. The clear yellow soln was quenched with an aq satd soln of NH_4Cl (50 mL). The mixture was extracted with Et_2O (3 x 30 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo until ~2 mL of soln was left. Methanol (200 mL) was added to give a white solid which was recrystallized in THF/MeOH to give 0.998 g of **S1** (73% yield). HRMS (EI): [M+] Calcd. for $C_{26}H_{20}P_2Cl_4$, 533.9794; found, 533.9793. ^{31}P NMR (162 MHz, $CDCl_3$) δ -14.9.



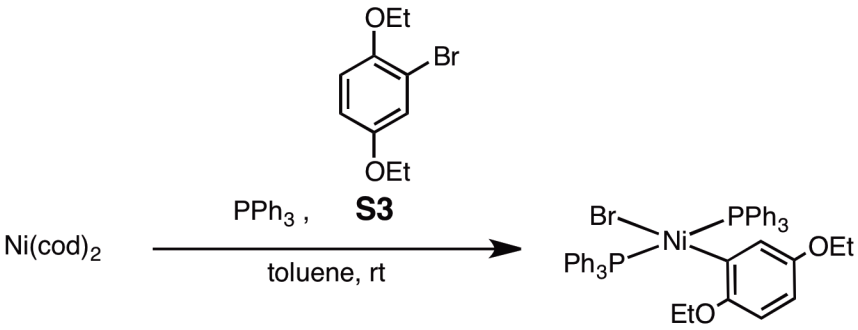
S2

S2. An oven-dried Schlenk flask was brought into the glovebox and equipped with a stir bar, 1,2-bis(dichlorophosphino)ethane (0.39 mL, 2.6 mmol, 1.0 equiv) and anhydrous Et_2O (15 mL). The flask was then brought out of the glovebox and placed under N_2. After cooling to -40 °C, 4-methoxyphenylmagnesium bromide (30.0 mL, 0.5 M in THF, 6.0 equiv) was added dropwise over 15 min. The reaction mixture was stirred for 1 h at -40 °C and warmed to rt. Additional 4-methoxyphenylmagnesium bromide (10.0 mL, 0.5 M in THF, 2.0 equiv) was added dropwise and the mixture was stirred at 45 °C for 3 h. After cooling to rt, the clear yellow soln was quenched with an aq satd soln of NH_4Cl (50 mL). The mixture was extracted with Et_2O (3 x 30 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo until ~2 mL of soln was left. Methanol (200 mL) was added to give a white solid which was recrystallized in THF/MeOH to give 0.550 g of **S2** (42% yield). HRMS (EI): [M+] Calcd. for $C_{30}H_{32}O_4P_2$, 518.1776; found, 518.1787. ^{31}P NMR (162 MHz, $CDCl_3$) δ -16.1.



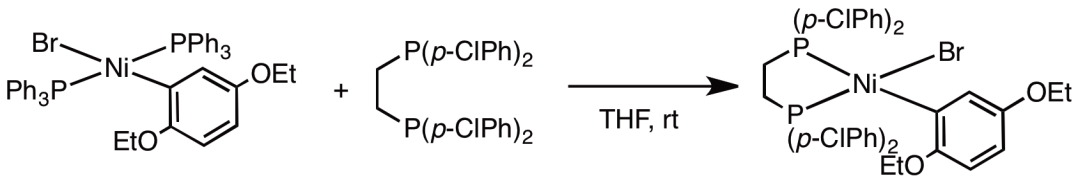
S3

S3. A 25 mL round bottom flask was equipped with a stir bar. Sequentially, 1,4 diethoxybenzene (2.490 g, 15.00 mmol, 1.0 equiv), acetonitrile (7.5 mL), *N*-bromosuccinimide (2.670 g, 15.00 mmol, 1.0 equiv), and NH_4NO_3 (240.0 mg, 3.000 mmol, 0.2 equiv) were added. The solution was stirred at rt under N_2. After 30 min, the dark red solution was quenched with water (40 mL) and the mixture was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with water (2 x 150 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting oil was purified with silica gel chromatography, using 80/20 (v/v) hexanes/toluene as the eluent to give 1.980 g of **S3** as a clear colorless oil (54% yield). HRMS (EI): [M+] Calcd. for $C_{10}H_{13}BrO_2$, 244.0099; found, 244.0091.



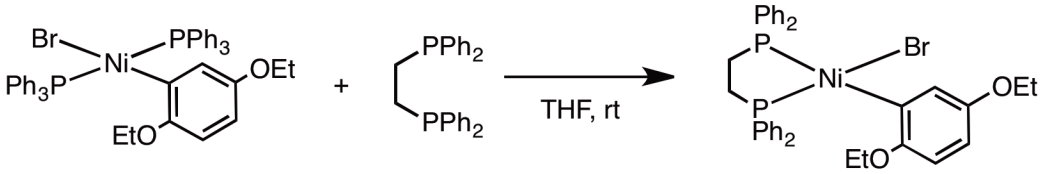
S4

S4. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, $Ni(cod)_2$ (550.6 mg, 2.002 mmol, 1.0 equiv), PPh_3 (1.050 g, 4.003 mmol, 2.0 equiv), **S3** (735.0 mg, 2.999 mmol, 1.5 equiv), and toluene (15 mL) were added. The solution was stirred at rt for 1 h. The reaction was removed from the glovebox and transferred to a 250 mL round bottom flask. Addition of hexanes (200 mL) led to an yellowish orange precipitate. The solid was filtered and washed with hexanes (20 mL) and cold MeOH (5 mL). The resulting solid was recrystallized in THF/hexanes to give 1.175 g of **S4** as a yellow solid (71% yield). Elemental Analysis: Calcd for $C_{46}H_{43}BrNiO_2P_2$, C, 66.7; H, 5.2; Found C, 66.5; H, 5.3. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 22.55.



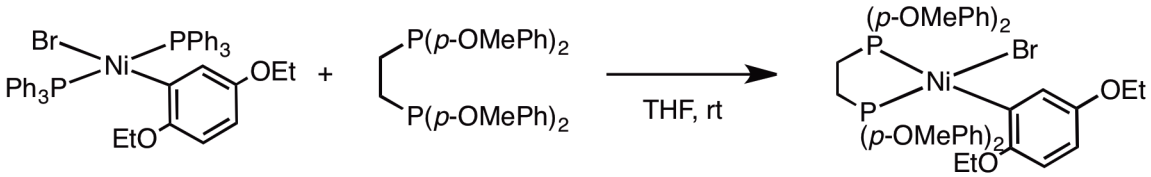
S3 **S1** **1a**

1a. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, **S3** (415.1 mg, 0.5011 mmol, 1.0 equiv), **S1** (294.2 mg, 0.5510 mmol, 1.1 equiv), and THF (10 mL) were added. The solution was stirred at rt for 1.5 h. The deep red soln was concentrated in vacuo until ~2 mL of soln was left. Addition of hexanes (18 mL) led to a yellowish orange precipitate. The solid was filtered and washed with hexanes (20 mL). The resulting solid was recrystallized in THF/hexanes to give an orange solid. The solids were then redissolved in THF (~50 mL), passed through a 0.2 μm PTFE filter to remove any undissolved solids, and concentrated in vacuo to give 323.7 mg of **1a** as an orange solid (77% yield). Elemental Analysis: Calcd for $C_{36}H_{33}BrCl_4NiO_2P_2$, C, 51.5; H, 4.0; Cl, 16.9; Found C, 51.6; H, 4.0; Cl, 16.6. ^{31}P NMR (202 MHz, acetone-d_6) δ 57.31 (d, J = 24.6 Hz), 39.23 (d, J = 24.6 Hz).



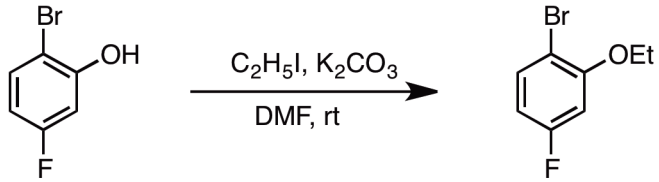
S3 **1b**

1b. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, **S3** (414.2 mg, 0.5000 mmol, 1.0 equiv), 1,2-bis(diphenylphosphino)ethane (dppe) (219.1 mg, 0.5500 mmol, 1.1 equiv), and THF (10 mL) were added. The solution was stirred at rt for 1 h. The deep red soln was concentrated in vacuo until ~2 mL of soln was left. Addition of hexanes (18 mL) led to a yellowish orange precipitate. The solid was filtered and washed with hexanes (20 mL). The resulting solid was recrystallized in THF/hexanes to give an orange solid. The solids were then redissolved in THF (~50 mL), passed through a 0.2 μm PTFE filter to remove any undissolved solids, and concentrated in vacuo to give 281.1 mg of **1b** as an orange solid (80% yield). Elemental Analysis: Calcd for $C_{36}H_{37}BrNiO_2P_2$, C, 61.6; H, 5.3; Found C, 61.5; H, 5.4. ^{31}P NMR (202 MHz, acetone-d_6) δ 57.12 (d, J = 26.4 Hz), 39.69 (d, J = 26.4 Hz).



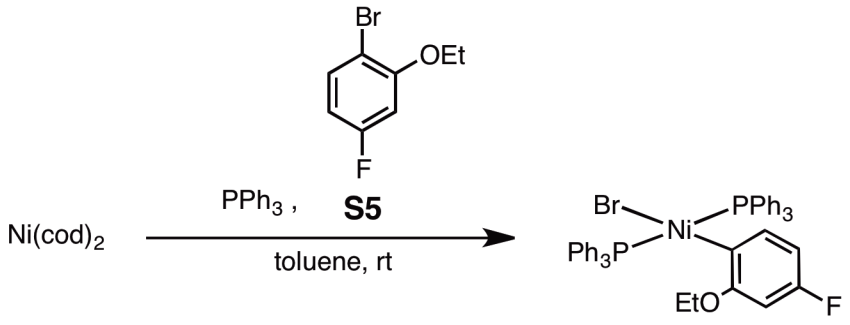
S3 **S2** **1c**

1c. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, **S3** (414.2 mg, 0.5000 mmol, 1.0 equiv), **S2** (285.1 mg, 0.5502 mmol, 1.1 equiv), and THF (10 mL) were added. The solution was stirred at rt for 1.5 h. The deep red soln was concentrated in vacuo until ~2 mL of soln was left. Addition of hexanes (18 mL) led to a yellowish orange precipitate. The solid was filtered and washed with hexanes (20 mL) and Et_2O (10 mL). The resulting solid was recrystallized in THF/hexanes to give an orange solid. The solids were then redissolved in THF (~40 mL), passed through a 0.2 μm PTFE filter to remove any undissolved solids, and concentrated in vacuo to give 261.9 mg of **1c** as an orange solid (64% yield). Elemental Analysis: Calcd for $C_{40}H_{45}BrNiO_6P_2$, C, 58.4; H, 5.5; Found C, 58.6; H, 5.8. ^{31}P NMR (160 MHz, acetone-d_6) δ 54.79 (d, J = 29.2 Hz), 37.17 (d, J = 29.2 Hz).



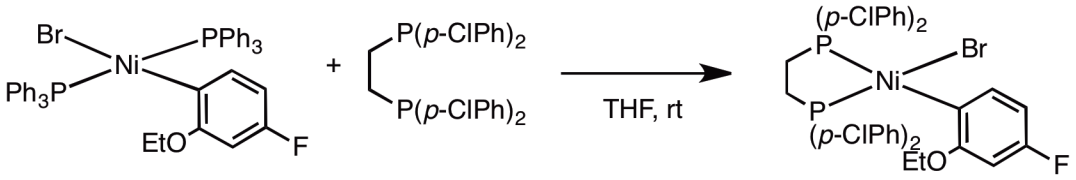
S5

S5. A 100 mL round bottom flask was equipped with a stir bar. Sequentially, 2-bromo-5-fluorophenol (2.580 g, 13.51 mmol, 1.0 equiv), anhydrous DMF (30 mL), iodoethane (8.410 g, 53.92 mmol, 4.0 equiv), and K_2CO_3 (4.660 g, 33.72 mmol, 2.5 equiv) were added. The solution was stirred at rt under N_2. After 2 h, the reaction mixture was filtered and the solid was washed with hexanes (60 mL). The filtrate was poured into water (90 mL) and extracted with hexanes (3 x 50 mL). The combined organic layers were washed with water (2 x 50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting oil was purified with silica gel chromatography, using hexanes as the eluent to give 2.762 g of **S5** as a clear colorless oil (93% yield). HRMS (EI): [M+] Calcd. for C_8H_8BrFO, 217.9743; found, 217.9753. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.10 (m).



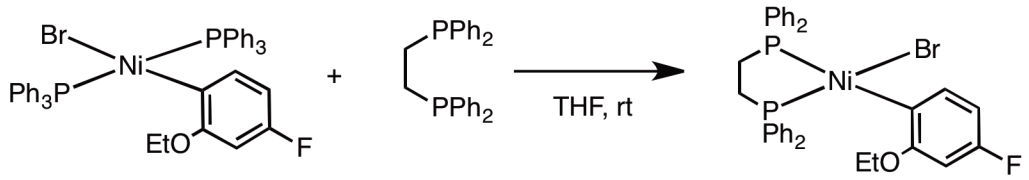
S6

S6. A 100 mL oven-dried round bottom flask was equipped with a stir bar in the glovebox. Sequentially, $Ni(cod)_2$ (275.4 mg, 1.001 mmol, 1.0 equiv), PPh_3 (525.5 mg, 2.004 mmol, 2.0 equiv), **S5** (299.2 mg, 1.501 mmol, 1.5 equiv), and toluene (10 mL) were added. The solution was stirred at rt for 1 h. The reaction was removed from the glovebox. Addition of hexanes (80 mL) led to a yellow precipitate. The solid was filtered and washed with hexanes (20 mL) and cold MeOH (10 mL). The resulting solid was recrystallized in THF/hexanes to give 647.4 mg of **S6** as a yellow solid (81% yield). Elemental Analysis: Calcd for $C_{44}H_{38}BrFNiOP_2$, C, 65.9; H, 4.8; F, 2.4; Found C, 65.9; H, 4.8; F, 2.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -124.65. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 22.06.



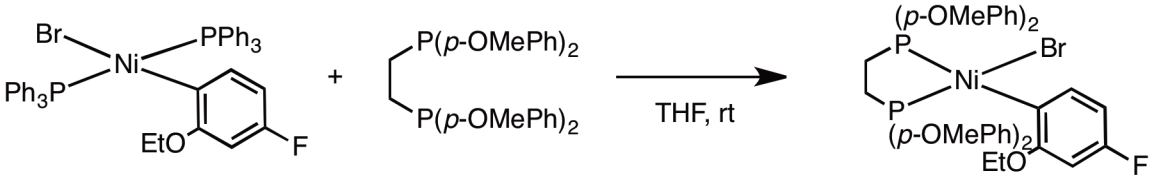
S6 **S1** **3a**

3a. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, **S6** (320.9 mg, 0.4000 mmol, 1.0 equiv), **S1** (235.0 mg, 0.4400 mmol, 1.1 equiv), and THF (8 mL) were added. The solution was stirred at rt for 1 h. The deep red soln was concentrated in vacuo until ~2 mL of soln was left. Addition of hexanes (18 mL) led to a yellowish orange precipitate. The solid was filtered and washed with hexanes (20 mL). The resulting solid was recrystallized in THF/hexanes to give an orange solid. The solids were then redissolved in THF (~40 mL), passed through a 0.2 μm PTFE filter to remove any undissolved solids, and concentrated in vacuo to give 259.4 mg of **3a** as an orange solid (80% yield). Elemental Analysis: Calcd for $C_{34}H_{28}BrCl_4FNiOP_2$, C, 50.2; H, 3.5; Cl, 17.4; Found C, 50.4; H, 3.4; Cl, 17.1. ^{19}F NMR (470 MHz, acetone-d_6) δ -123.22 (m). ^{31}P NMR (200 MHz, acetone-d_6) δ 57.95 (d, J = 26.4 Hz), 40.28 (d, J = 26.4 Hz).



S6 **3b**

3b. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, **S6** (324.0 mg, 0.4000 mmol, 1.0 equiv), 1,2-bis(diphenylphosphino)ethane (dppe) (175.3 mg, 0.4400 mmol, 1.1 equiv), and THF (8 mL) were added. The solution was stirred at rt for 1 h. The deep red soln was concentrated in vacuo until ~2 mL of soln was left. Addition of hexanes (18 mL) led to a yellow precipitate. The solid was filtered and washed with hexanes (20 mL). The resulting solid was recrystallized in THF/hexanes to give an orange solid. The solids were then redissolved in THF (~40 mL), passed through a 0.2 µm PTFE filter to remove any undissolved solids, and concentrated in vacuo to give 208.5 mg of **3b** as an orange solid (77% yield). Elemental Analysis: Calcd for $C_{34}H_{32}BrFNiOP_2$, C, 60.4; H, 4.8; F, 2.8; Found C, 60.3; H, 5.1; F, 2.4. ^{19}F NMR (470 MHz, acetone-d_6) δ -124.05 (m). ^{31}P NMR (202 MHz, acetone-d_6) δ 57.82 (d, J = 28.5 Hz), 40.61 (d, J = 28.5 Hz).



S6 **S2** **3c**

3c. A 20 mL vial was equipped with a stir bar in the glovebox. Sequentially, **S6** (321.0 mg, 0.4000 mmol, 1.0 equiv), **S2** (228.3 mg, 0.4400 mmol, 1.1 equiv), and THF (8 mL) were added. The solution was stirred at rt for 1 h. The deep red soln was concentrated in vacuo until ~2 mL of soln was left. Addition of hexanes (18 mL) led to a yellowish orange precipitate. The solid was filtered and washed with hexanes (20 mL) and cold MeOH (5 mL). The resulting solid was recrystallized in THF/hexanes to give an orange solid. The solids were then redissolved in THF (~50 mL), passed through a 0.2 µm PTFE filter to remove any undissolved solids, and concentrated in vacuo to give 102.9 mg of **3c** as an orange solid (32% yield). Elemental Analysis: Calcd for $C_{39}H_{40}BrFNiO_5P_2$, C, 57.3; H, 5.1; F, 2.4; Found C, 57.7; H, 5.3; F, 2.1. ^{19}F NMR (660 MHz, $CDCl_3$) δ -124.15 (m). ^{31}P NMR (283 MHz, $CDCl_3$) 55.21 (d, J = 30.7 Hz), 38.75 (d, J = 30.7 Hz).

IV. NMR Spectra

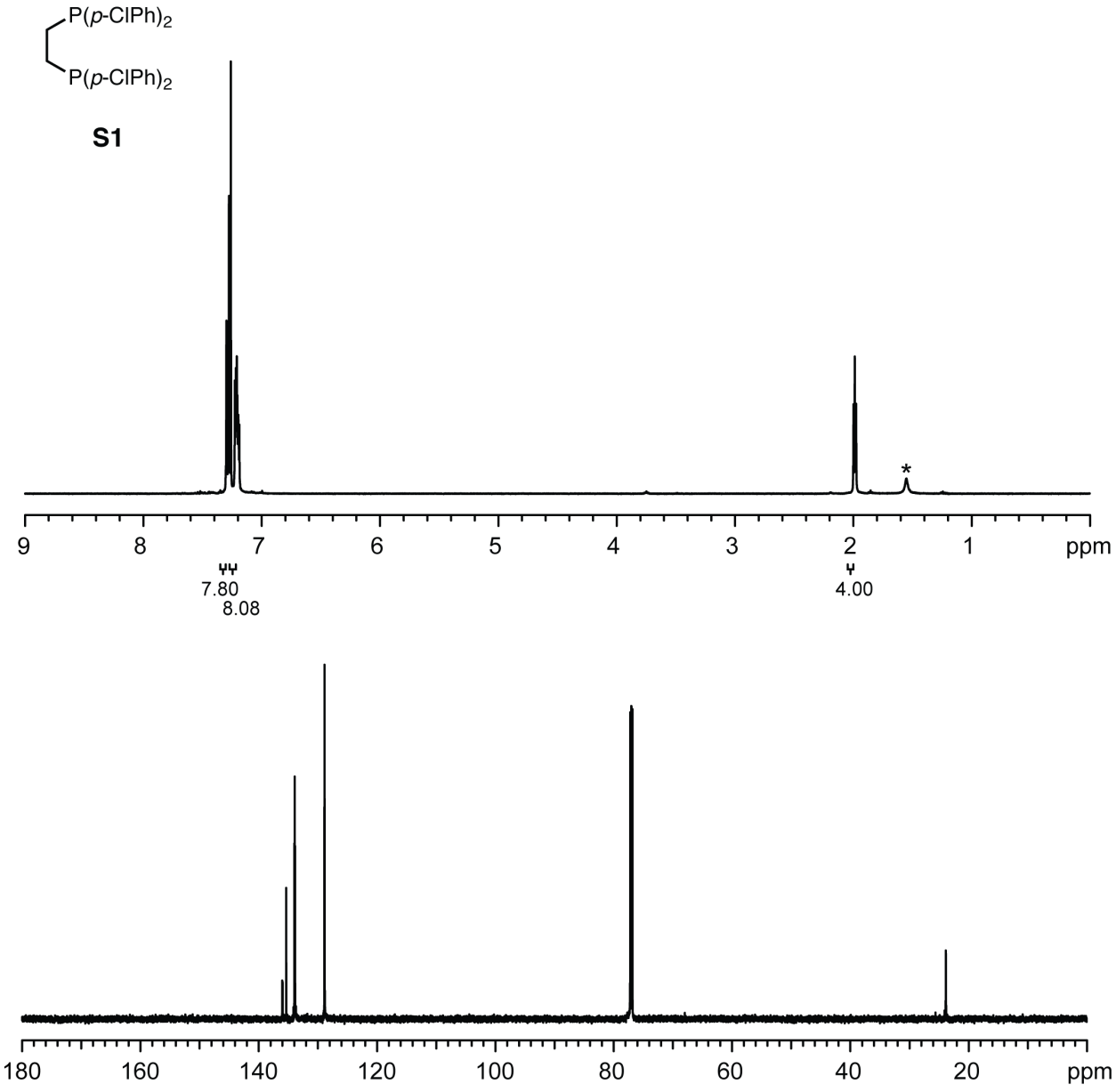


Figure S1. ^{1}H and ^{13}C NMR spectra of **S1**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 8H), 7.23-7.19 (m, 8H), 1.99 (dd, *J* = 4.4, 4.2 Hz, 4H). *residual H_2O. ^{13}C NMR (176 MHz, $CDCl_3$) δ 135.98 (dd, *J* = 8.8, 6.2 Hz), 135.34, 133.90 (at, *J* = 9.9 Hz), 128.87 (at, *J* = 3.4 Hz), 23.85 (d, *J* = 2.5 Hz).

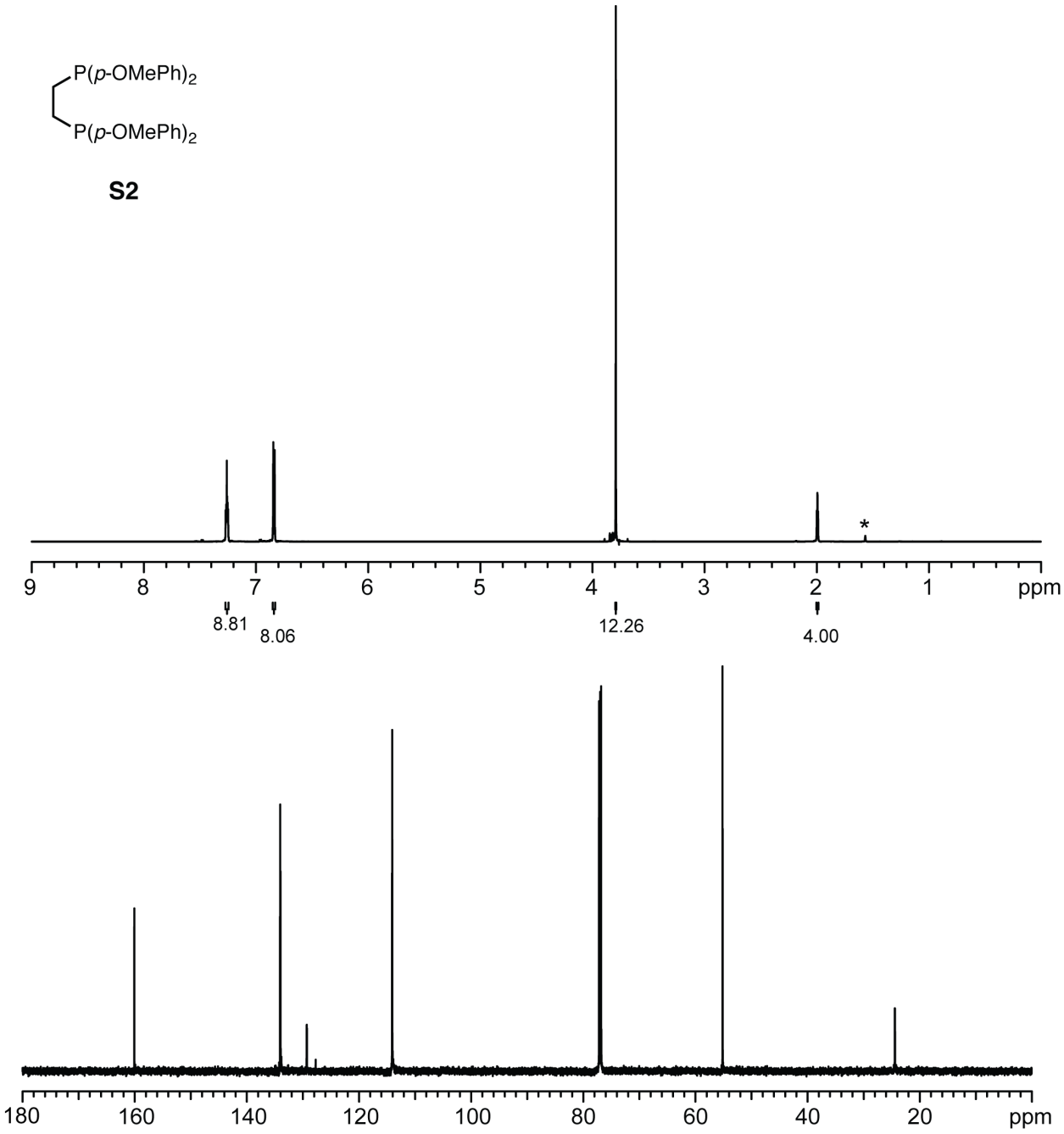


Figure S2. ^{1}H and ^{13}C NMR spectra of **S2**. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.27-7.25 (m, 8H), 6.84 (d, *J* = 8.6 Hz, 8H), 3.79 (s, 12H), 1.99 (dd, *J* = 4.2, 3.5 Hz, 4H). *residual H_2O. ^{13}C NMR (176 MHz, $CDCl_3$) δ 160.06, 134.04 (at, *J* = 9.9 Hz), 129.30 (at, *J* = 5.5 Hz), 114.07 (at, *J* = 3.7 Hz), 55.15, 24.41 (d, *J* = 3.3 Hz).

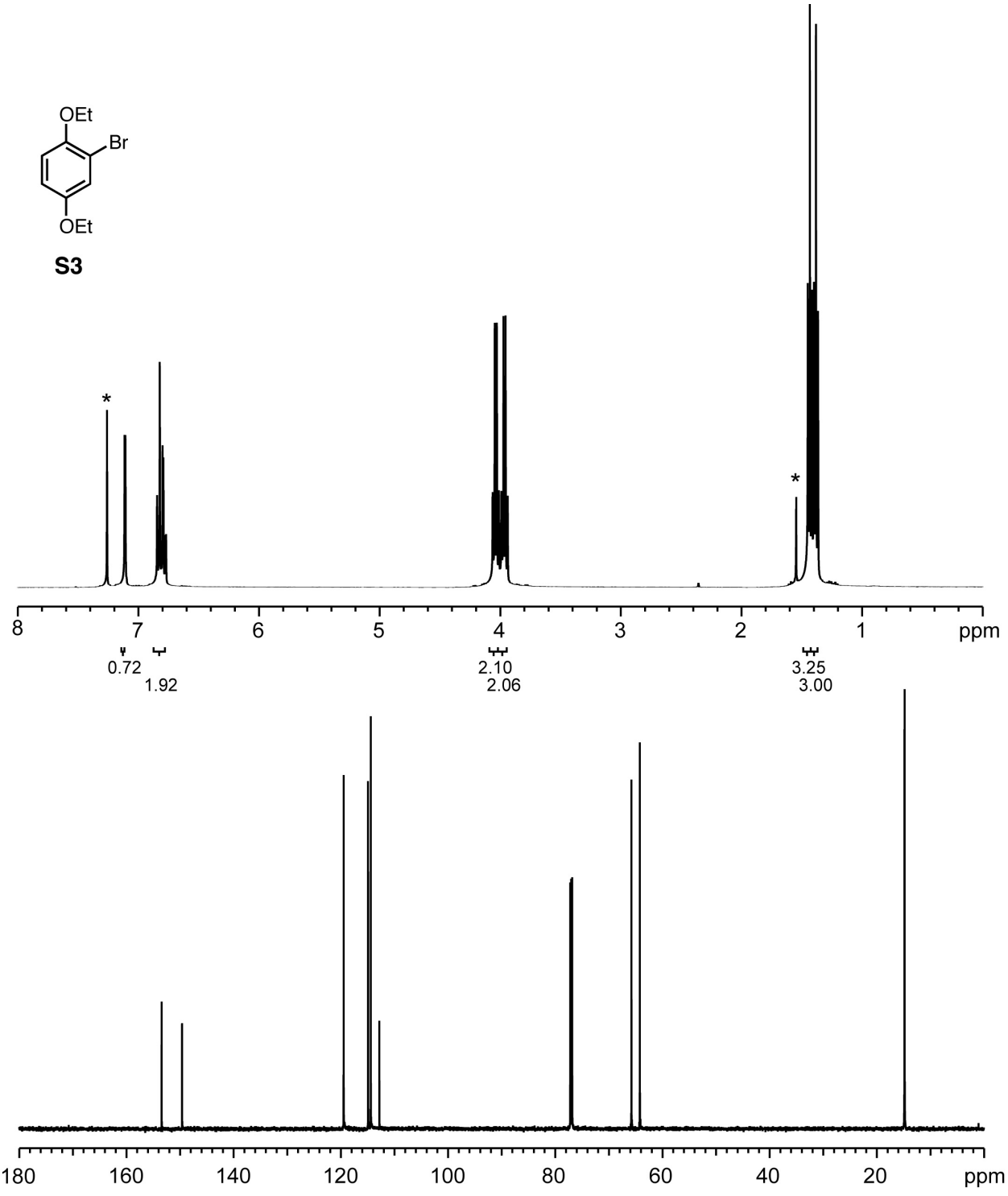


Figure S3. ^{1}H and ^{13}C NMR spectra of **S3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 2.8 Hz, 1H), 6.85-6.77 (m, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.38 (t, *J* = 7.0 Hz, 3H). *residual H_2O. ^{13}C NMR (176 MHz, $CDCl_3$) δ 153.43, 149.62, 119.48, 114.91, 114.41, 112.82, 65.78, 64.21, 14.86, 14.80.

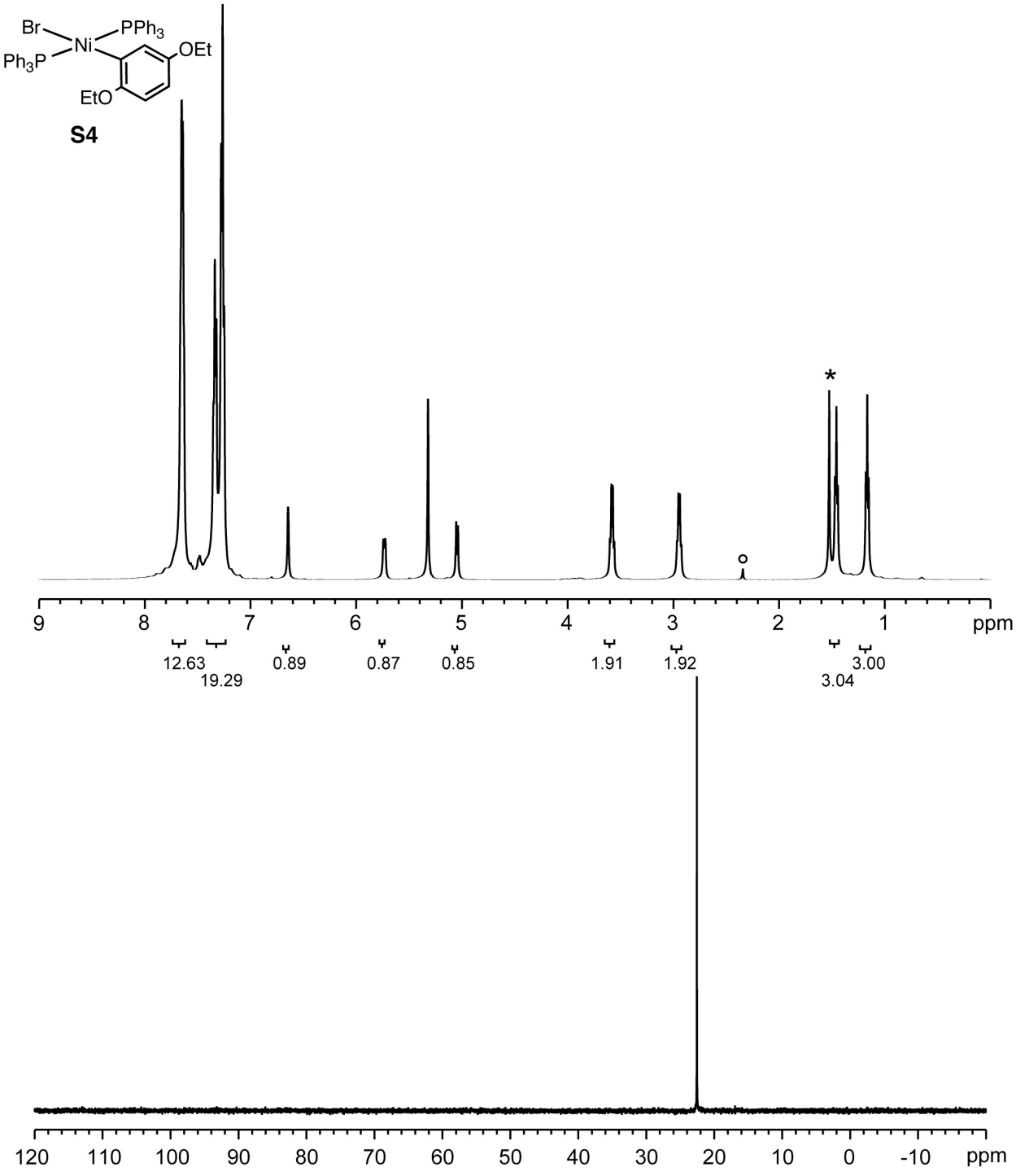


Figure S4. ^{1}H and ^{31}P NMR spectra of **S4**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.64 (bs, 12H), 7.35-7.25 (m, 18H), 6.65 (s, 1H), 5.73 (t, *J* = 7.8 Hz, 1H), 5.05 (d, *J* = 8.8 Hz, 1H) 3.58 (q, *J* = 6.9 Hz, 2H), 2.94 (q, *J* = 6.9 Hz, 2H), 1.46 (t, *J* = 6.8 Hz, 3H), 1.17 (t, *J* = 6.8 Hz, 3H). residual *H_2O and °toluene. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 22.55.

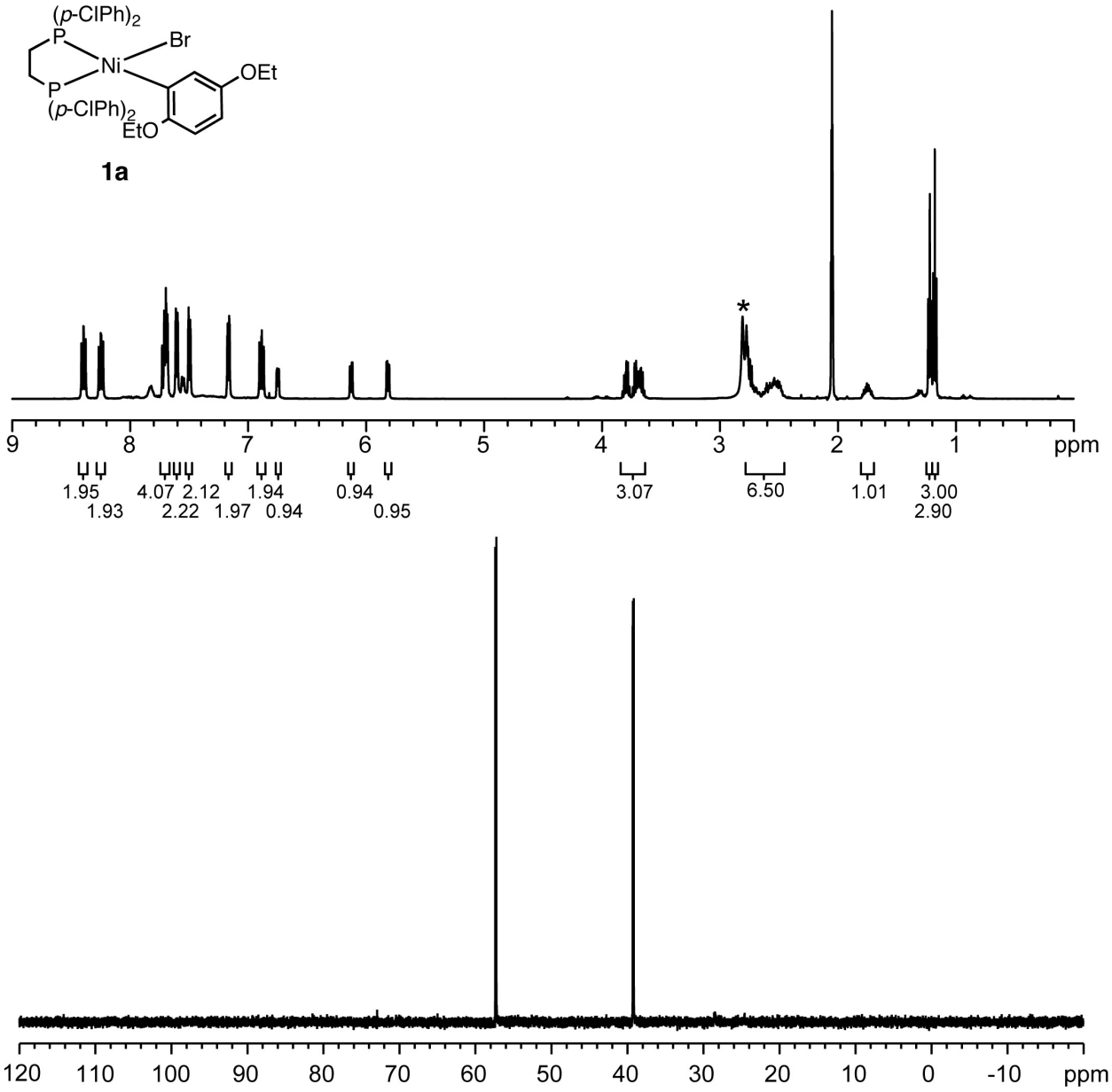


Figure S5. ^{1}H and ^{31}P NMR spectra of **1a**. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.41-8.38 (m, 2H), 8.27-8.23 (m, 2H), 7.73-7.68 (m, 4H), 7.61 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.50 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.18 (dd, *J* = 8.5, 1.9 Hz, 2H), 6.90-6.87 (m, 2H), 6.75 (dd, *J* = 7.1, 1.9 Hz, 1H), 6.13 (dd, *J* = 8.6, 2.8 Hz, 1H), 5.82 (dd, *J* = 8.6, 3.4 Hz, 1H), 3.83-3.64 (m, 3H), 2.80-2.47 (m, 4H), 1.79-1.70 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). *residual H_2O. ^{31}P NMR (202 MHz, acetone-d_6) δ 57.31 (d, *J* = 24.6 Hz), 39.23 (d, *J* = 24.6 Hz).

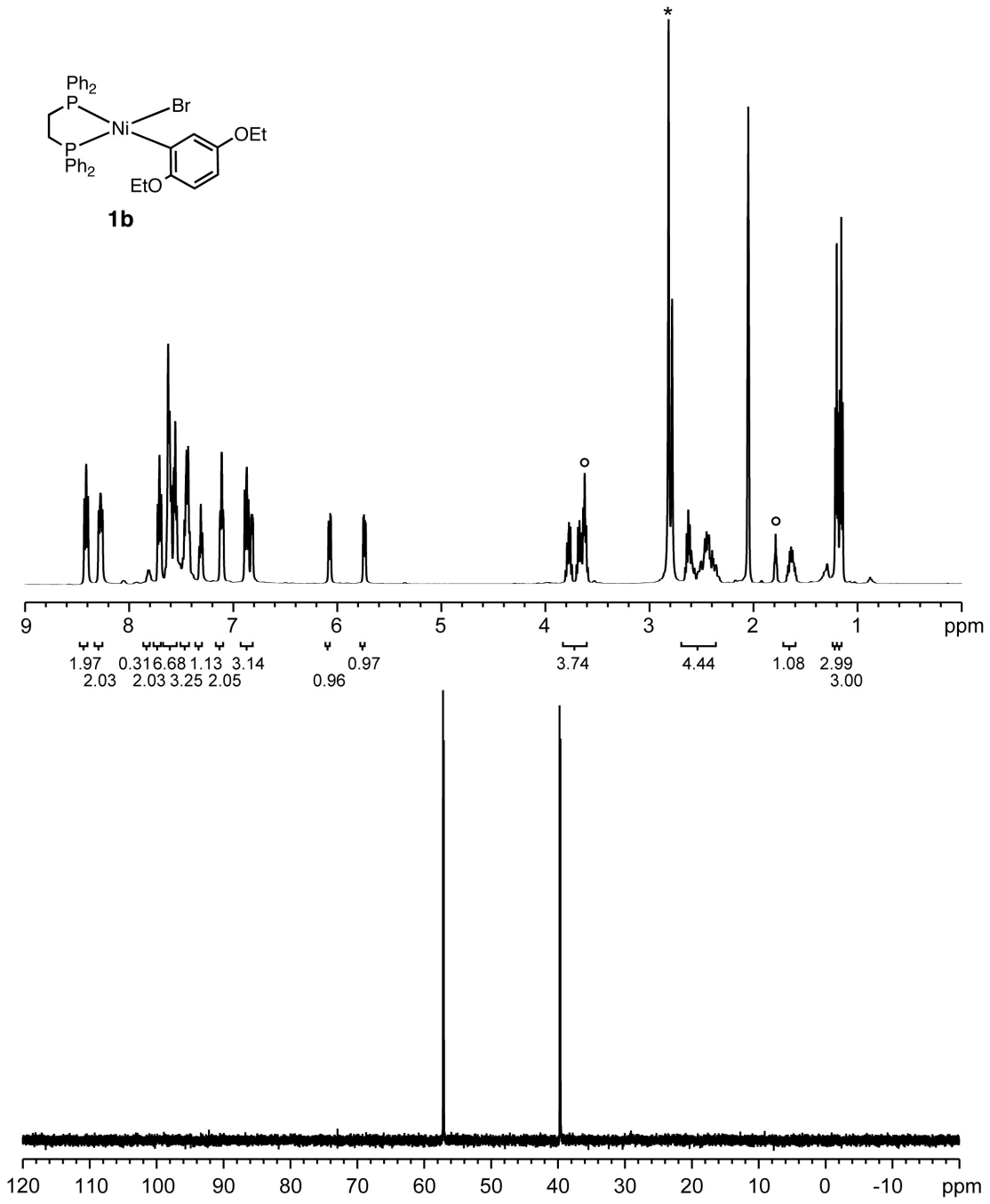


Figure S6. ^{1}H and ^{31}P NMR spectra of **1b**. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.41 (t, J = 8.5 Hz, 2H), 8.27 (t, J = 8.5 Hz, 2H), 7.71 (t, J = 8.5 Hz, 2H), 7.62-7.54 (m, 6H), 7.47-7.42 (m, 3H), 7.31 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 6.8 Hz, 2H), 6.89-6.81 (m, 3H), 6.07 (dd, J = 8.5, 2.5 Hz, 1H), 5.74 (dd, J = 8.5, 3.2 Hz, 1H), 3.81-3.59 (m, 4H), 2.66-2.33 (m, 3H), 1.68-1.59 (m, 1H), 1.20 (t, J = 6.9 Hz, 3H), 1.16 (t, J = 6.9 Hz, 3H). residual *H_2O and °THF. ^{31}P NMR (202 MHz, acetone-d_6) δ 57.12 (d, J = 26.4 Hz), 39.69 (d, J = 26.4 Hz).

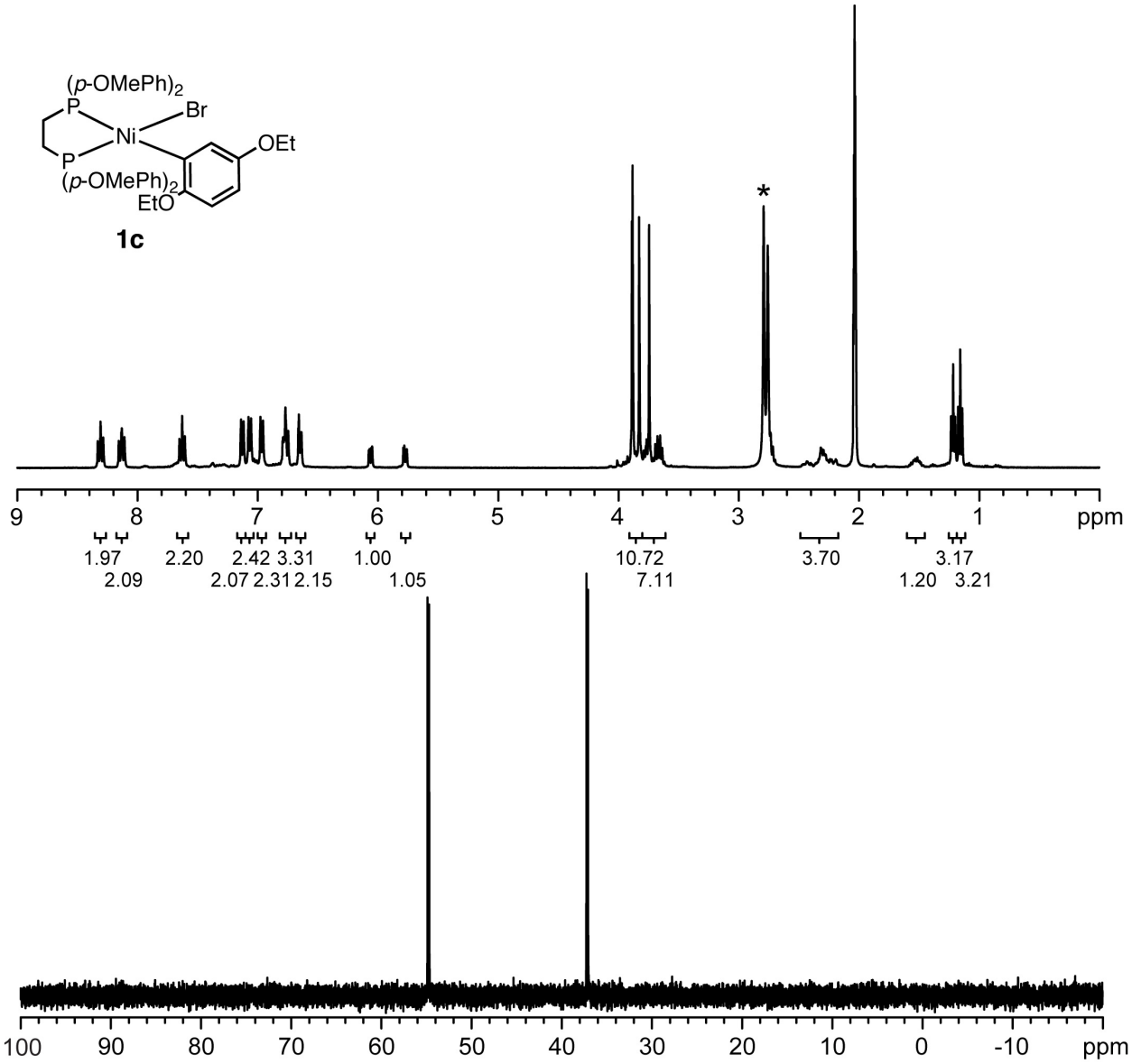


Figure S7. ^{1}H and ^{13}C NMR spectra of **1c**. ^{1}H NMR (400 MHz, acetone-d_6) δ 8.32 (t, J = 8.7 Hz, 2H), 8.15 (t, J = 9.3 Hz, 2H), 7.64 (t, J = 9.1 Hz, 2H), 7.14 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.2 Hz, 2H), 6.80-6.76 (m, 3H), 6.66 (dd, J = 8.7, 1.7 Hz, 2H), 6.08 (dd, J = 8.3, 2.7 Hz, 1H), 5.79 (dd, J = 8.5, 3.2 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.81 (s, 3H), 3.79-3.77 (m, 2H), 3.76 (s, 3H), 3.71-3.65 (m, 2H), 2.47-2.19 (m, 3H), 1.59-1.44 (m, 1H), 1.23 (t, J = 7.0 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H).*residual H_2O. ^{31}P NMR (160 MHz, acetone-d_6) δ 54.79 (d, J = 29.2 Hz), 37.17 (d, J = 29.2 Hz).

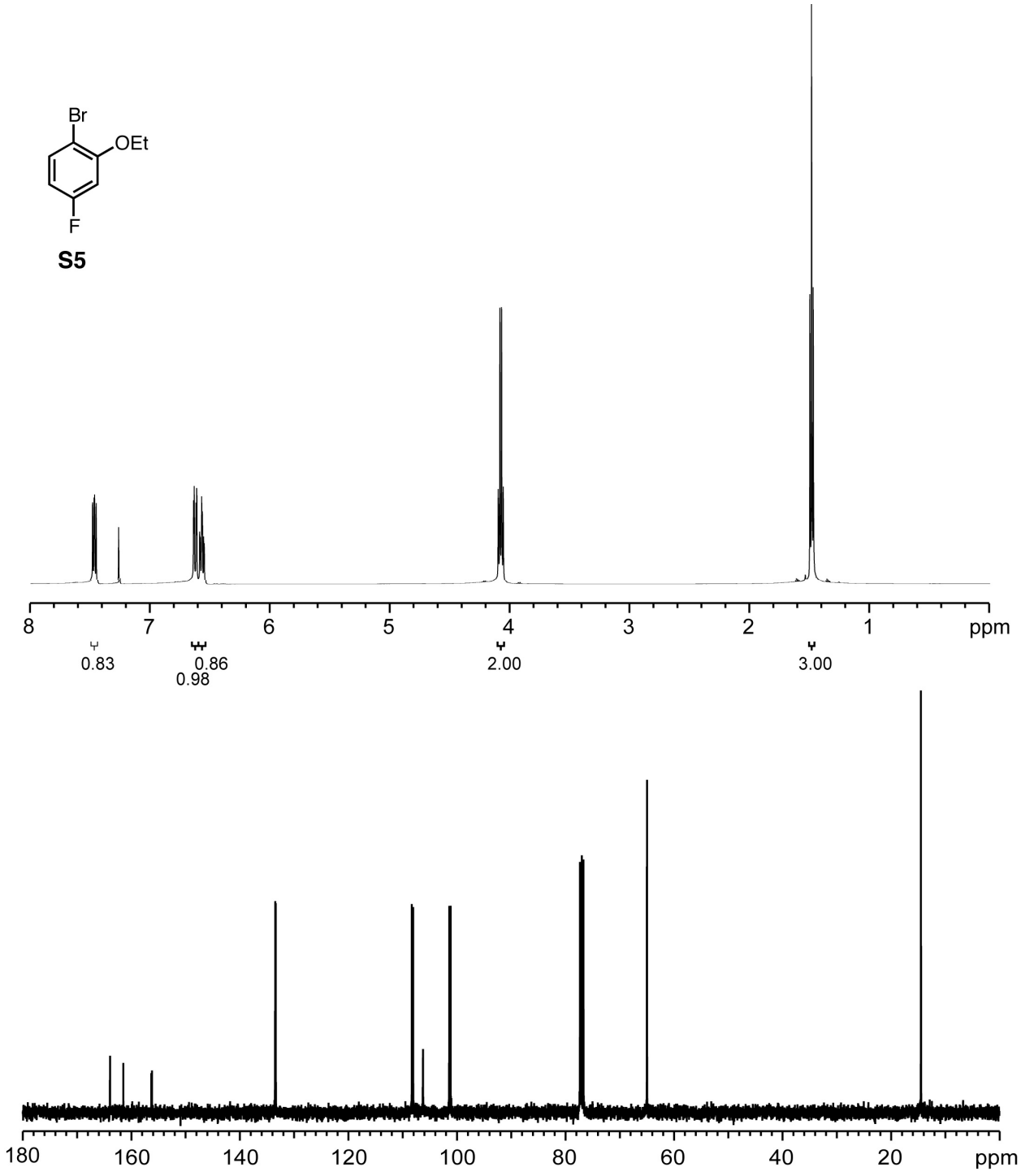


Figure S8. ^{1}H and ^{13}C NMR spectra of **S5**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.43 (m, 1H), 6.60 (dd, *J* = 10.6, 2.8 Hz, 1H), 6.55 (dt, *J* = 8.2, 2.8 Hz, 1H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.70 (d, *J* = 245 Hz), 156.25 (d, *J* = 10.2 Hz), 133.42 (d, *J* = 9.8 Hz), 108.20 (d, *J* = 22.5 Hz), 106.25 (d, *J* = 3.6 Hz), 101.29 (d, *J* = 26.7 Hz), 64.98, 14.49.

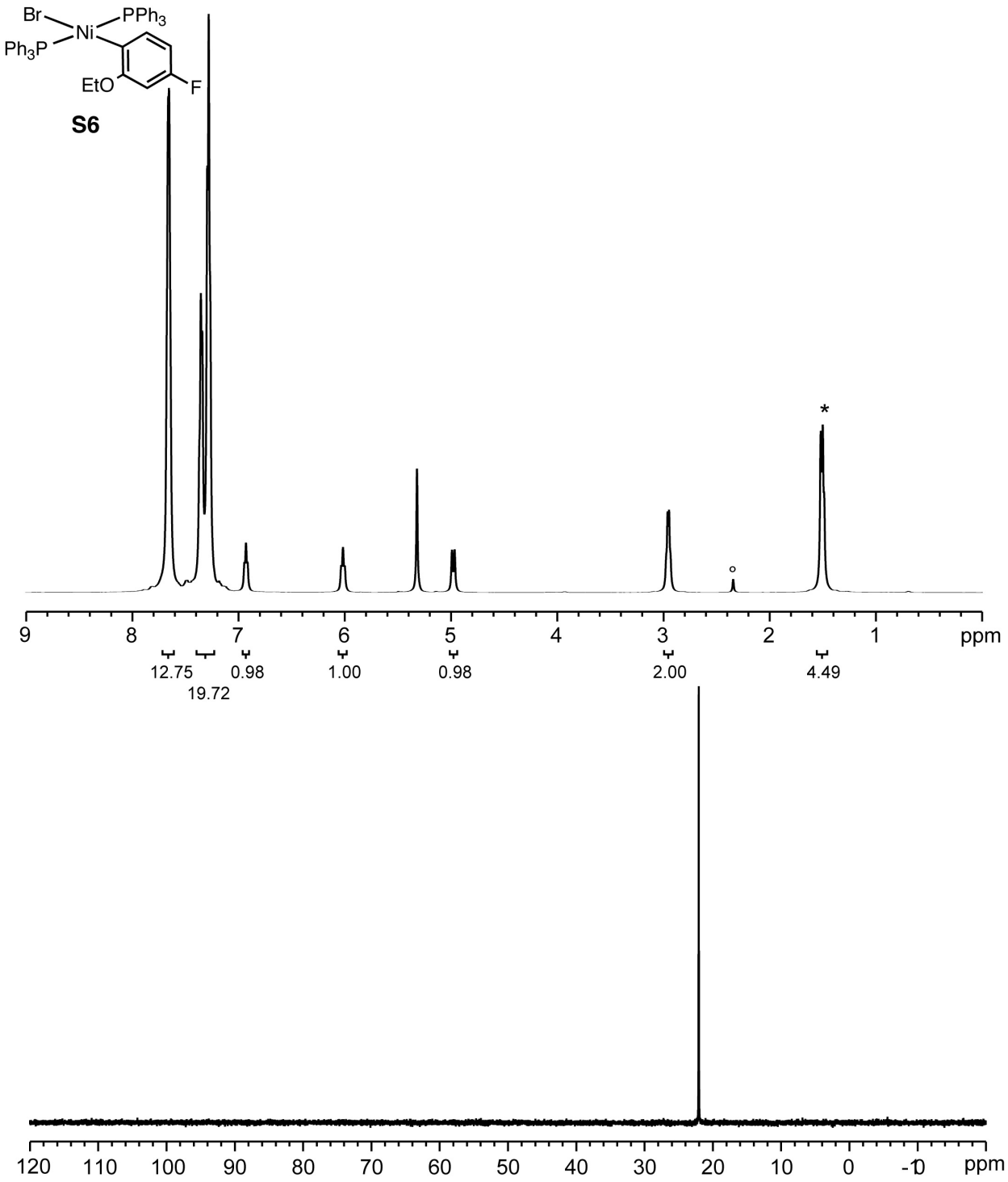


Figure S9. ^{1}H and ^{31}P NMR spectra of **S6**. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 (bs, 12H), 7.37-7.26 (m, 18H), 6.93 (t, *J* = 7.0 Hz, 1H), 6.02 (t, *J* = 8.3 Hz, 1H), 4.98 (d, *J* = 12.7 Hz, 1H) 2.95 (q, *J* = 6.6 Hz, 2H), 1.50 (t, *J* = 5.9 Hz, 3H). residual *H_2O and °Toluene. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 22.06.

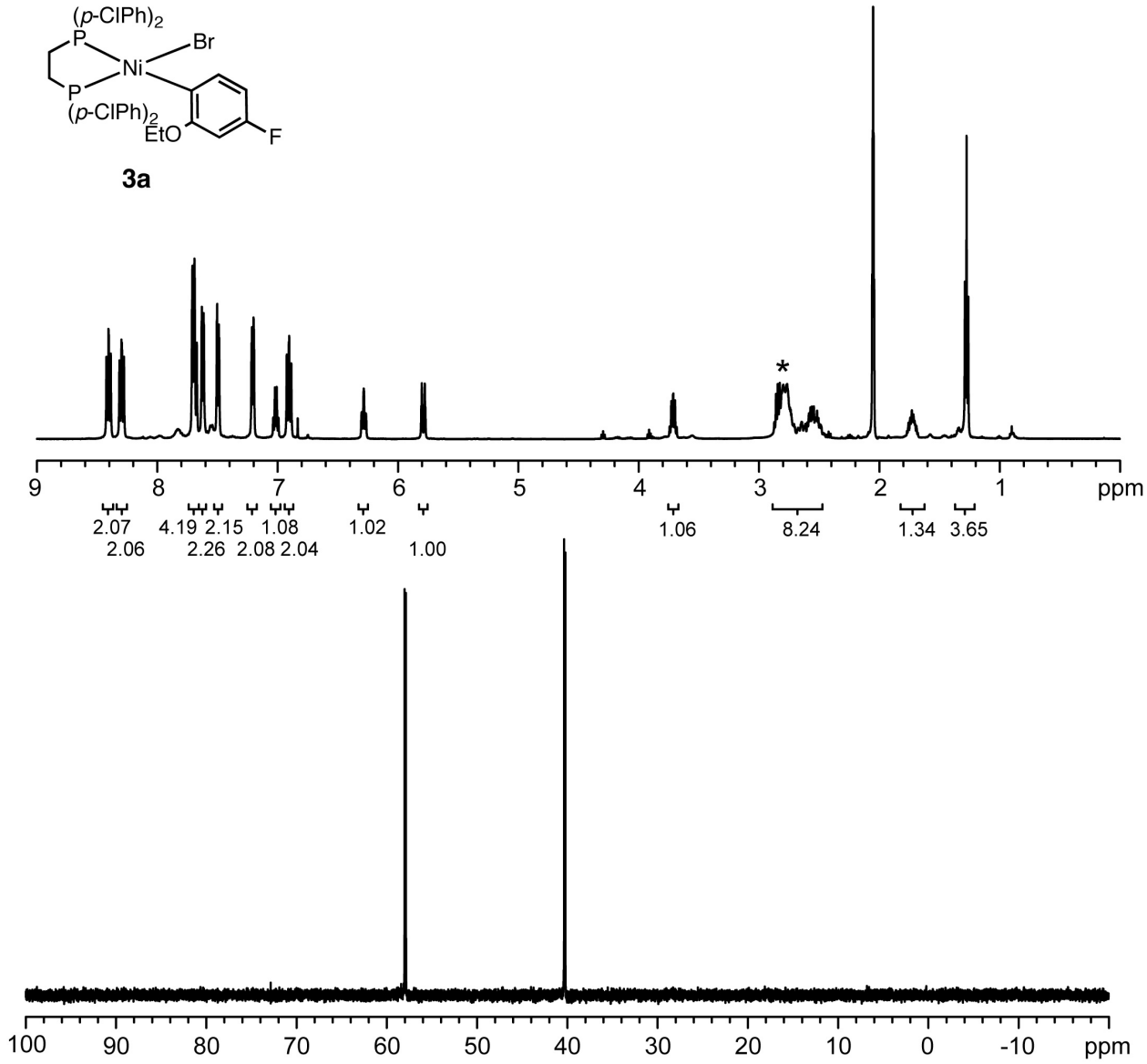


Figure S10. ^{1}H and ^{31}P NMR spectra of **3a**. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.43-8.39 (m, 2H), 8.32-8.28 (m, 2H), 7.71-7.67 (m, 4H), 7.63-7.62 (m, 2H), 7.51-7.49 (m, 2H), 7.22-7.20 (m, 2H), 7.04-7.00 (m, 1H), 6.92-6.89 (m, 2H), 6.30-6.27 (m, 1H), 5.81-5.77 (m, 1H), 3.75-3.68 (m, 1H), 2.86-2.46 (m, 4H), 1.80-1.69 (m, 1H), 1.28 (t, J = 7.0 Hz, 3H). *residual H_2O. ^{31}P NMR (200 MHz, acetone-d_6) δ 57.95 (d, J = 26.4 Hz), 40.28 (d, J = 26.4 Hz).

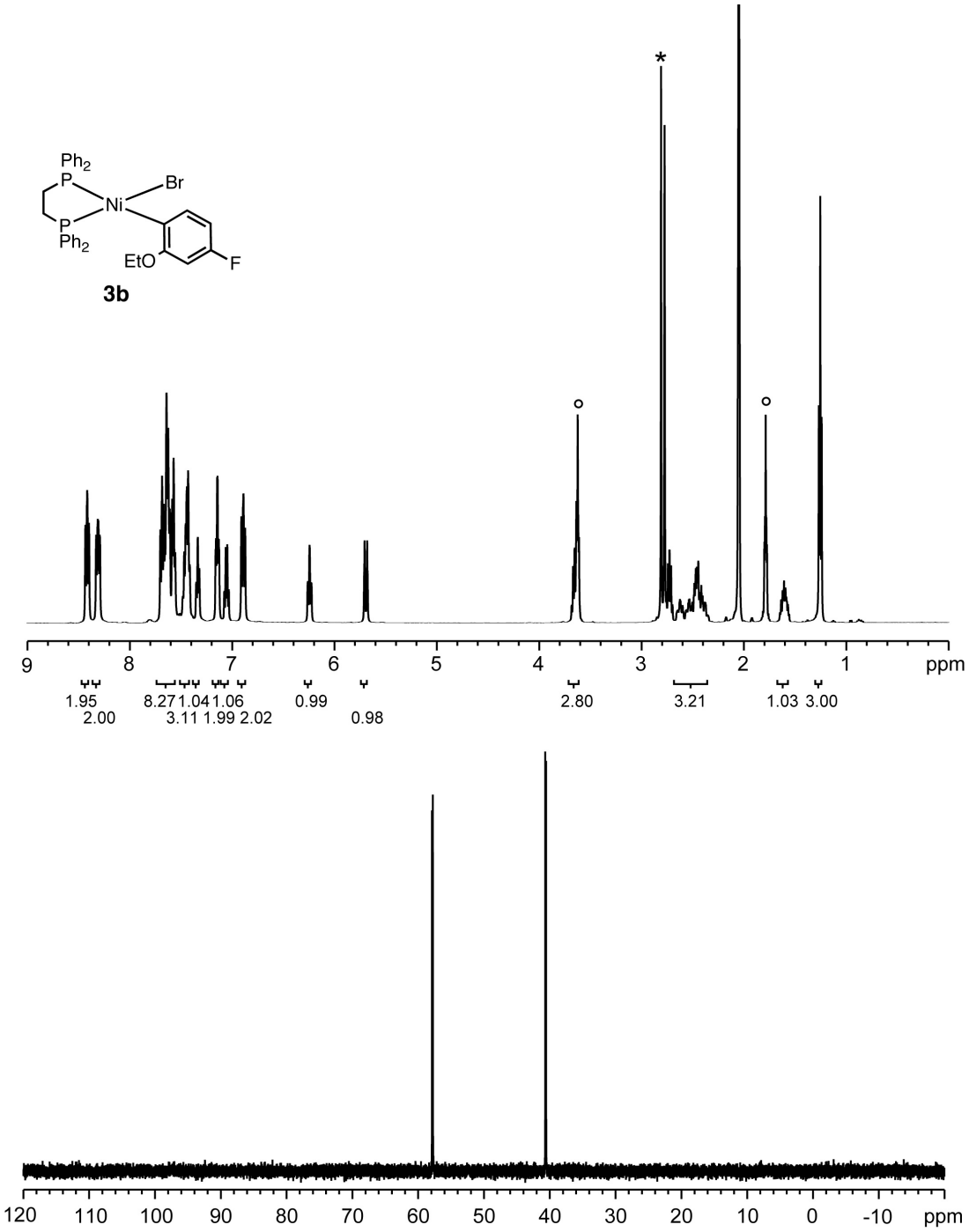


Figure S11. ^{1}H and ^{31}P NMR spectra of **3b**. ^{1}H NMR (500 MHz, acetone-d_6) δ 8.42 (t, J = 8.6 Hz, 2H), 8.31 (t, J = 8.6 Hz, 2H), 7.70-7.56 (m, 8H), 7.47-7.41 (m, 3H), 7.34 (t, J = 7.3 Hz, 1H), 7.15 (td, J = 7.7, 2.1 Hz, 2H), 7.05 (q, J = 7.4 Hz, 1H), 6.89 (t, J = 9.0 Hz, 2H), 6.24 (t, J = 8.4 Hz, 1H), 5.69 (dt, J = 12.6, 2.4 Hz, 1H), 3.68-3.61 (m, 2H), 2.76-2.37 (m, 3H), 1.64-1.57 (m, 1H), 1.25 (t, J = 6.9 Hz, 3H). residual *H_2O and °THF. ^{31}P NMR (202 MHz, acetone-d_6) δ 57.82 (d, J = 28.5 Hz), 40.61 (d, J = 28.5 Hz).

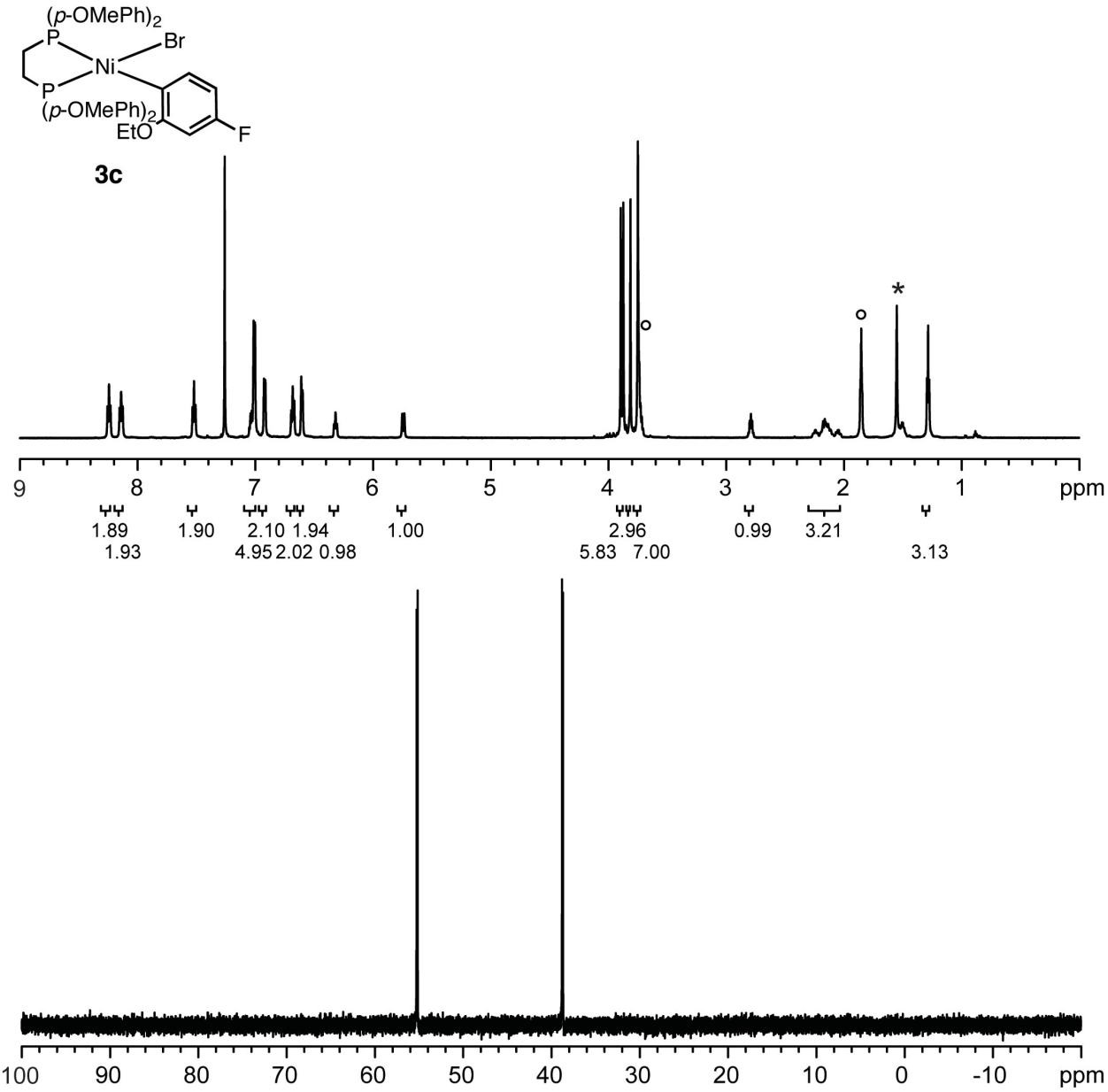
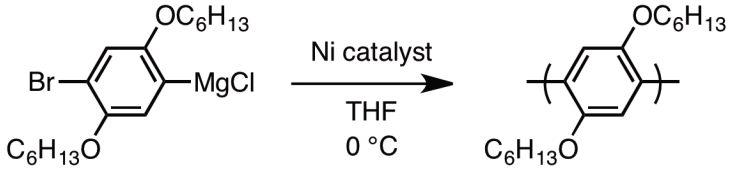


Figure S12. ^{1}H and ^{31}P NMR spectra of **3c**. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.24 (t, *J* = 9.0 Hz, 2H), 8.14 (t, *J* = 9.3 Hz, 2H), 7.52 (t, *J* = 8.9 Hz, 2H), 7.05-7.00 (m, 5H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.68 (t, *J* = 9.7 Hz, 2H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.32 (t, *J* = 8.5 Hz, 1H), 5.74 (d, *J* = 12.5 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 3.74-3.72 (m, 2H), 2.79 (quin, *J* = 7.9 Hz, 1H), 2.26-2.03 (m, 3H), 1.29 (t, *J* = 6.8 Hz, 3H). residual *H_2O and °THF. ^{31}P NMR (283 MHz, $CDCl_3$) 55.21 (d, *J* = 30.7 Hz), 38.75 (d, *J* = 30.7 Hz).

V. Propagation Rate Studies

Representatitve Procedure for Performing Propagation Rate Studies:

The IR probe was inserted through an O-ring sealed 14/20 ground glass adapter (custom made) into an oven-dried 50 mL 2-neck flask containing a Teflon magnetic stir bar. The other neck was equipped with a three-way adapter fitted with a septum for injections and an N_2 line. The flask was cooled under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling, the flask was charged with THF (4.6 mL) and cooled to 0 °C over ~5 min. After recording a background spectrum, monomer **2** (4.4 mL, 0.46 M in THF) was added by syringe and allowed to equilibrate for at least 5 min at 0 °C. After 5 min, the solution of **1b** (1 mL, 0.015 M in THF) was injected and spectra were recorded every 15 s over the first 15-20% conversion. To account for mixing and temperature equilibration, spectra recorded in the first 60 s of the reaction were discarded. The data for first 10% conversion were converted to concentrations using the appropriate calibration curve prepared as previously reported.[2]



2 **P2**

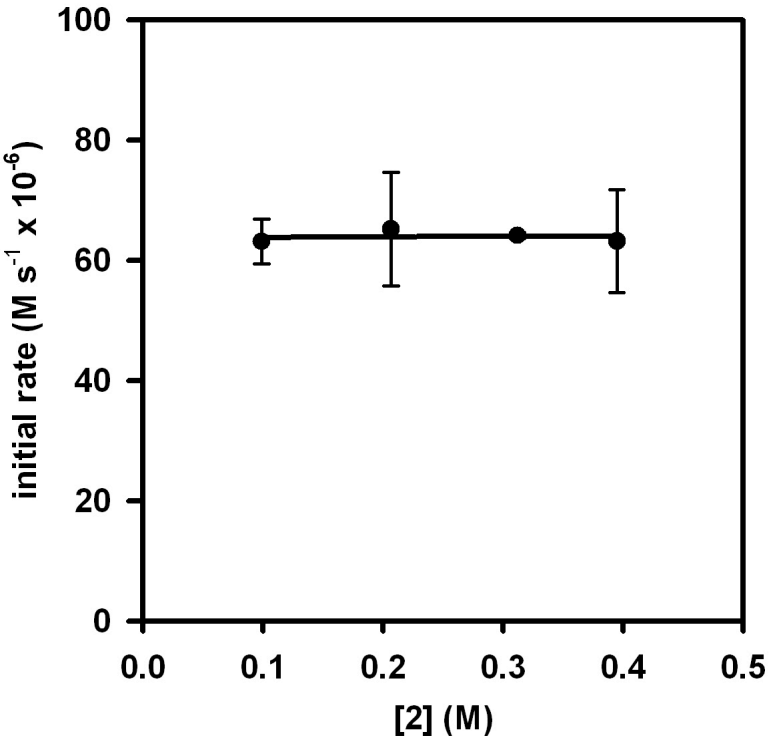


Figure S13. Plot of initial rate versus [monomer] for the polymerization of **2** with catalyst **1a**. (temp = 0 °C, [**1a**] = 0.0015 M) fitted to y = a[monomer]^n, where a = 64 ± 2 and n = 0.00 ± 0.02.

Table S1. Data for the plot in Figure S13.

[**2**] (M)	Initial rate (M s^{-1})
0.1	63 ± 4 x 10^{-6}
0.2	65 ± 9 x 10^{-6}
0.3	64.1 ± 0.5 x 10^{-6}
0.4	63 ± 9 x 10^{-6}

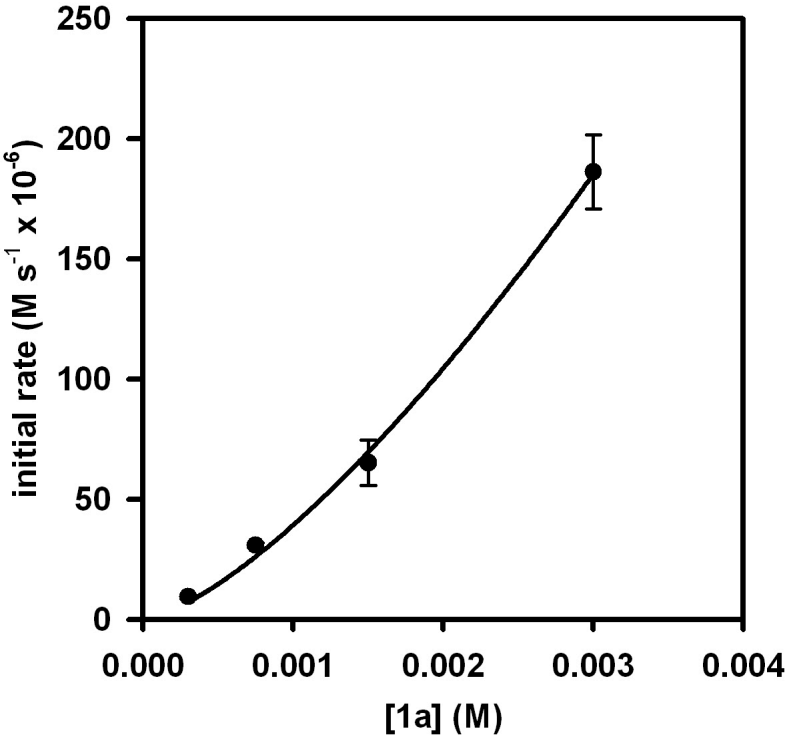


Figure S14. Plot of initial rate versus [**1a**] for the polymerization of **2** with catalyst **1a**. (temp = 0 °C, [**2**] = 0.02 M) fitted to $y = a[\mathbf{1a}]^n$, where $a = 7 \pm 3 \times 10^5$ and $n = 1.41 \pm 0.08$.

Table S2. Data for the plot in Figure S14.

[**1a**] (M)	Initial rate (M s^{-1})
0.00030	$9.5 \pm 0.8 \times 10^{-6}$
0.00075	$30.9 \pm 0.9 \times 10^{-6}$
0.0015	$65 \pm 9 \times 10^{-6}$
0.0030	$190 \pm 20 \times 10^{-6}$

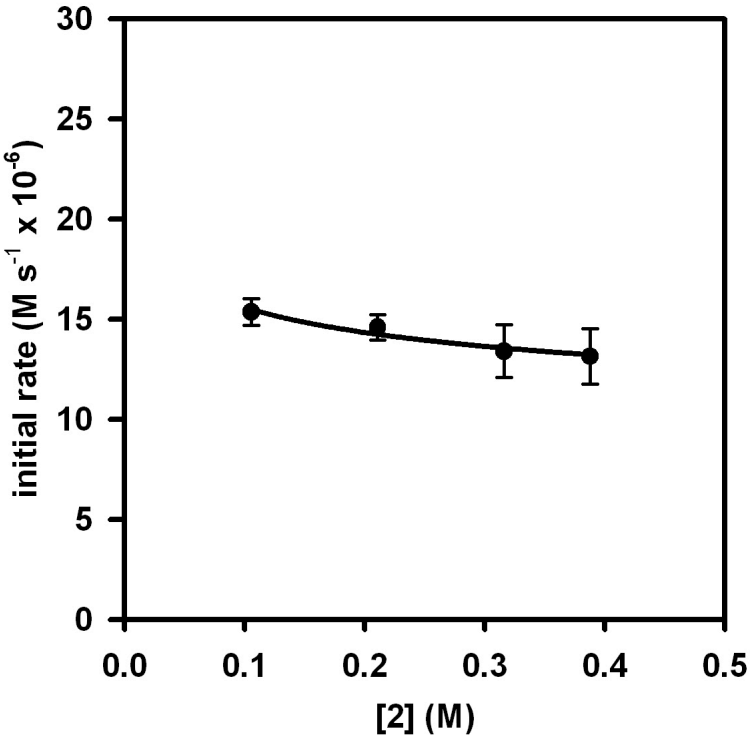


Figure S15. Plot of initial rate versus [monomer] for the polymerization of **2** with catalyst **1b**. (temp = 0 °C, [**1b**] = 0.0015 M) fitted to y = a[monomer]^n, where a = 11.8 ± 0.4 and n = -0.12 ± 0.02.

Table S3. Data for the plot in Figure S15.

[**2**] (M)	initial rate (M s^{-1})
0.1	15.4 ± 0.7 x 10^{-6}
0.2	14.6 ± 0.6 x 10^{-6}
0.3	13 ± 1 x 10^{-6}
0.4	13 ± 1 x 10^{-6}

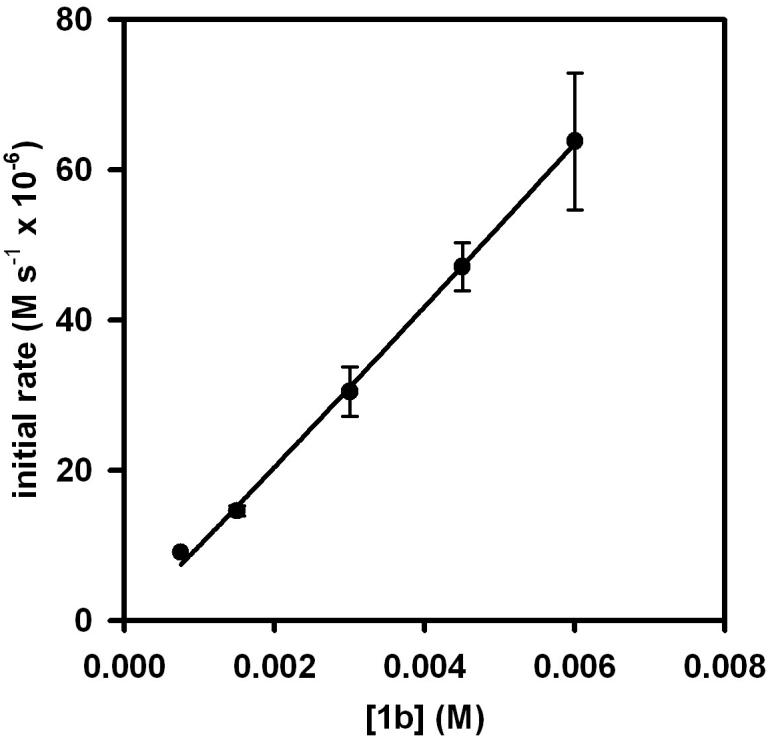


Figure S16. Plot of initial rate versus [**1b**] for the polymerization of **2** with catalyst **1b**. (temp = 0 °C, [**2**] = 0.02 M) fitted to $y = a[\mathbf{1b}]^n$, where $a = 1.3 \pm 0.2 \times 10^4$ and $n = 1.03 \pm 0.04$.

Table S4. Data for the plot in Figure S16.

[**1b**] (M)	Initial rate ($M\ s^{-1}$)
0.00075	9.1×10^{-6}
0.0015	$14.6 \pm 0.6 \times 10^{-6}$
0.0030	$30 \pm 3 \times 10^{-6}$
0.0045	$47 \pm 3 \times 10^{-6}$
0.0060	$64 \pm 9 \times 10^{-6}$

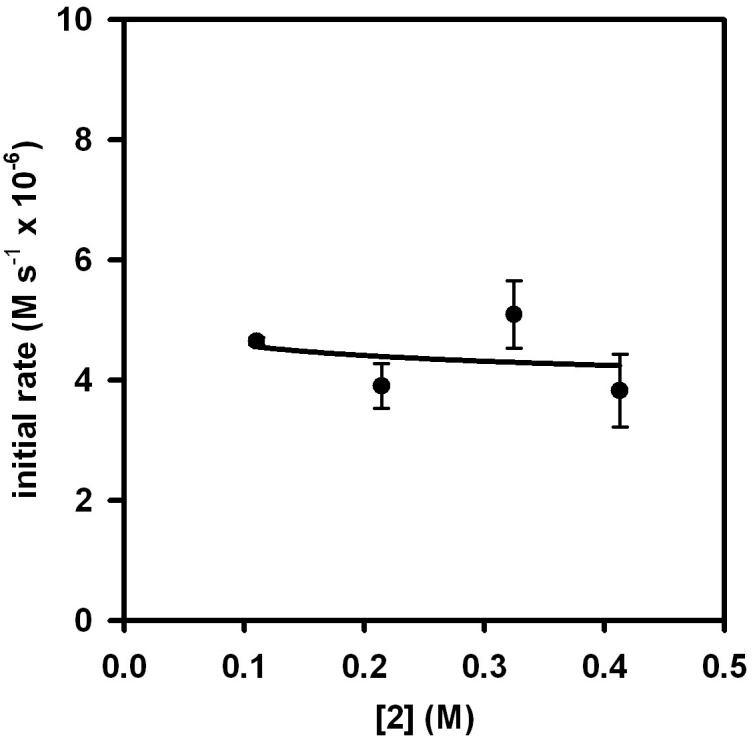


Figure S17. Plot of initial rate versus [monomer] for the polymerization of **2** with catalyst **1c**. (temp = 0 °C, [**1c**] = 0.0015 M) fitted to y = a[monomer]^n, where a = 4 ± 1 and n = -0.1 ± 0.2.

Table S5. Data for the plot in Figure S17.

[**2**] (M)	Initial rate (M s^{-1})
0.1	4.65 ± 0.06 x 10^{-6}
0.2	3.9 ± 0.4 x 10^{-6}
0.3	5.1 ± 0.6 x 10^{-6}
0.4	3.8 ± 0.6 x 10^{-6}

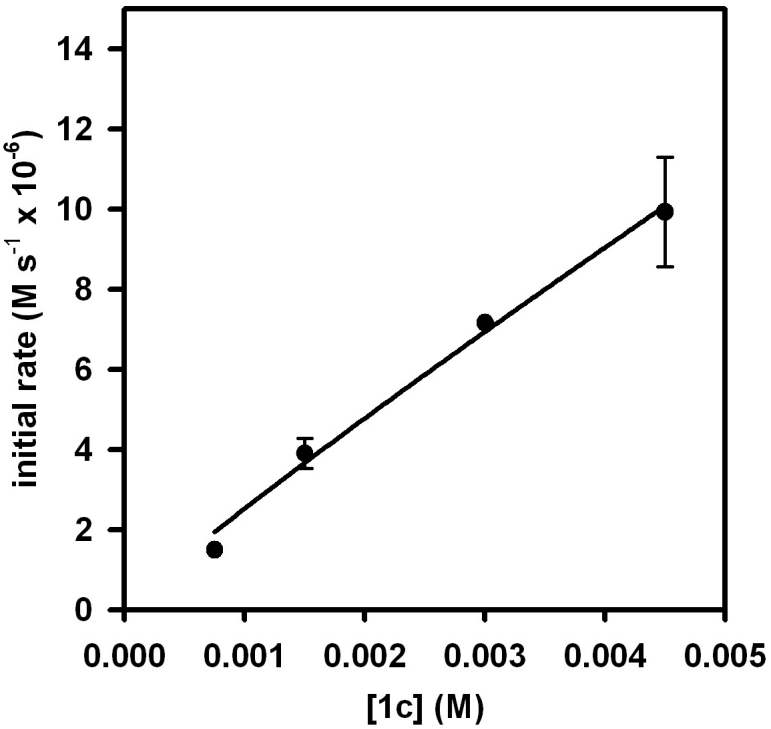


Figure S18. Plot of initial rate versus [**1c**] for the polymerization of **2** with catalyst **1c**. (temp = 0 °C, [**2**] = 0.02 M) fitted to $y = a[\mathbf{1c}]^n$, where $a = 9.1 \pm 0.7 \times 10^2$ and $n = 0.92 \pm 0.08$.

Table S6. Data for the plot in Figure S18.

[**1c**] (M)	Initial rate (M s^{-1})
0.00075	1.5×10^{-6}
0.0015	$3.9 \pm 0.4 \times 10^{-6}$
0.0030	$7.16 \pm 0.03 \times 10^{-6}$
0.0045	$10 \pm 1 \times 10^{-6}$

VI. Spectroscopic Studies for Catalyst Resting States

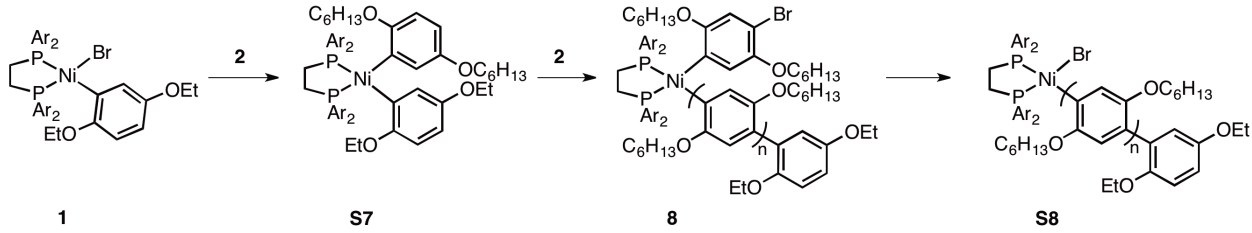
Representative Procedure for Performing NMR Spectroscopic Studies on the Catalyst Resting States:

Initiation Studies:
In the glovebox, catalyst **1a** (16.8 mg, 0.0200 mmol, 1.0 equiv) was dissolved in THF (0.5 mL) and loaded into a J. Young NMR tube equipped with a rubber septum. Separately, 1.5 mL of **2** (0.40 M in THF) was placed in a 1.5 mL vial equipped with a septum. Once removed from the glovebox, these samples were immediately sealed with parafilm, and the solution of **2** was placed on dry ice.

The NMR tube was cooled to -20 °C in the NMR spectrometer, and both ^{1}H and ^{31}P NMR spectra were recorded. Then, 0.25 mL of **2** (0.40 M, 0.10 mmol, 5.0 equiv) was injected into the NMR tube, and spectra were recorded for both nuclei (Figure S19A). The sample was then removed from the spectrometer and allowed to warm to rt. After 30 min, a second set of ^{31}P and ^{1}H NMR spectra were collected at rt.

Propagation Studies:
In the glovebox, catalyst **1a** (16.8 mg, 0.0200 mmol, 1.0 equiv) was partially dissolved in THF (0.3 mL) followed by 0.75 mL of **2** (0.40 M, 0.30 mmol, 15 equiv) with vigorous mixing. After 30 min at rt, this solution was loaded into a J. Young NMR tube equipped with a septum. Separately, 1.5 mL of **2** (0.40 M in THF) was placed in a 1.5 mL vial equipped with a septum. Once removed from the glovebox, these samples were immediately sealed with parafilm, and the solution of **2** was placed on dry ice.

The NMR tube was cooled to -20 °C in the NMR spectrometer, and both ^{1}H and ^{31}P NMR spectra were recorded. Then, 0.50 mL of **2** (0.40 M, 0.20 mmol, 10 equiv) was injected into the NMR tube, and spectra were recorded for both nuclei (Figure S19B). The sample was then removed from the spectrometer and allowed to warm to rt. After 30 min, a second set of ^{31}P and ^{1}H NMR spectra were collected at rt (Figure S19C).



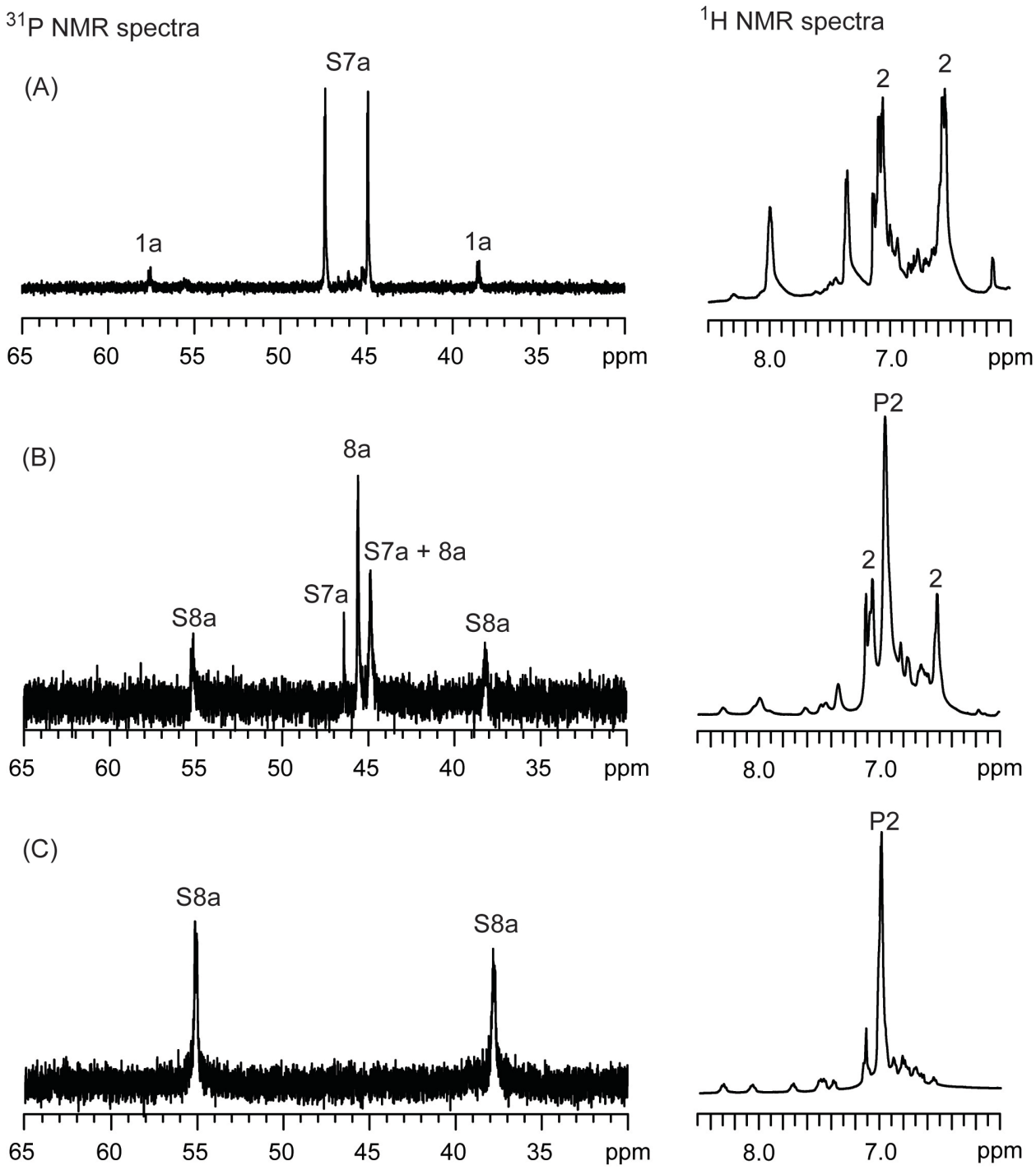


Figure S19. ^{31}P NMR spectra (162 MHz, THF, -20 °C) of (A) complex **S7a** δ 47.42 (d, *J* = 9.1 Hz), 44.93 (d, *J* = 9.0 Hz), (B) complex **8a** δ 45.59 (d, *J* = 7.5 Hz), 44.91 (br), (C) complex **S8a** δ 55.08 (d, *J* = 21.9 Hz), 37.82 (d, *J* = 20.9 Hz) in the presence or absence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectra (500 MHz, THF, -20 °C).

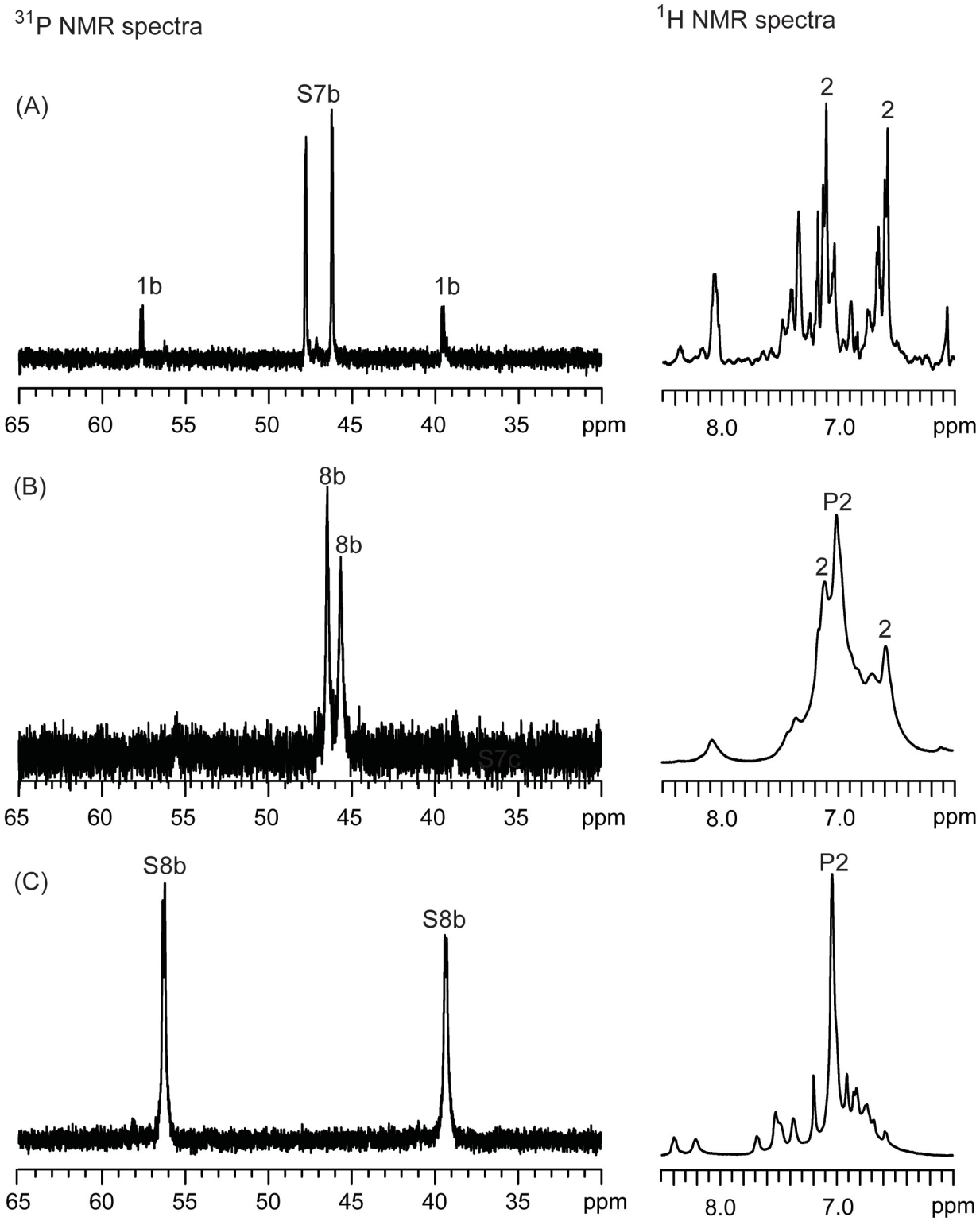


Figure S20. ^{31}P NMR spectra (162 MHz, THF, -20 °C) of (A) complex **S7b** δ 47.74 (d, *J* = 9.9 Hz), 46.18 (d, *J* = 10.9 Hz), (B) complex **8b** δ 46.46 (br), 45.66 (br), (C) complex **S8b** δ 56.27 (d, *J* = 26.0 Hz), 39.34 (d, *J* = 23.4 Hz) in the presence or absence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectra (500 MHz, THF, -20 °C).

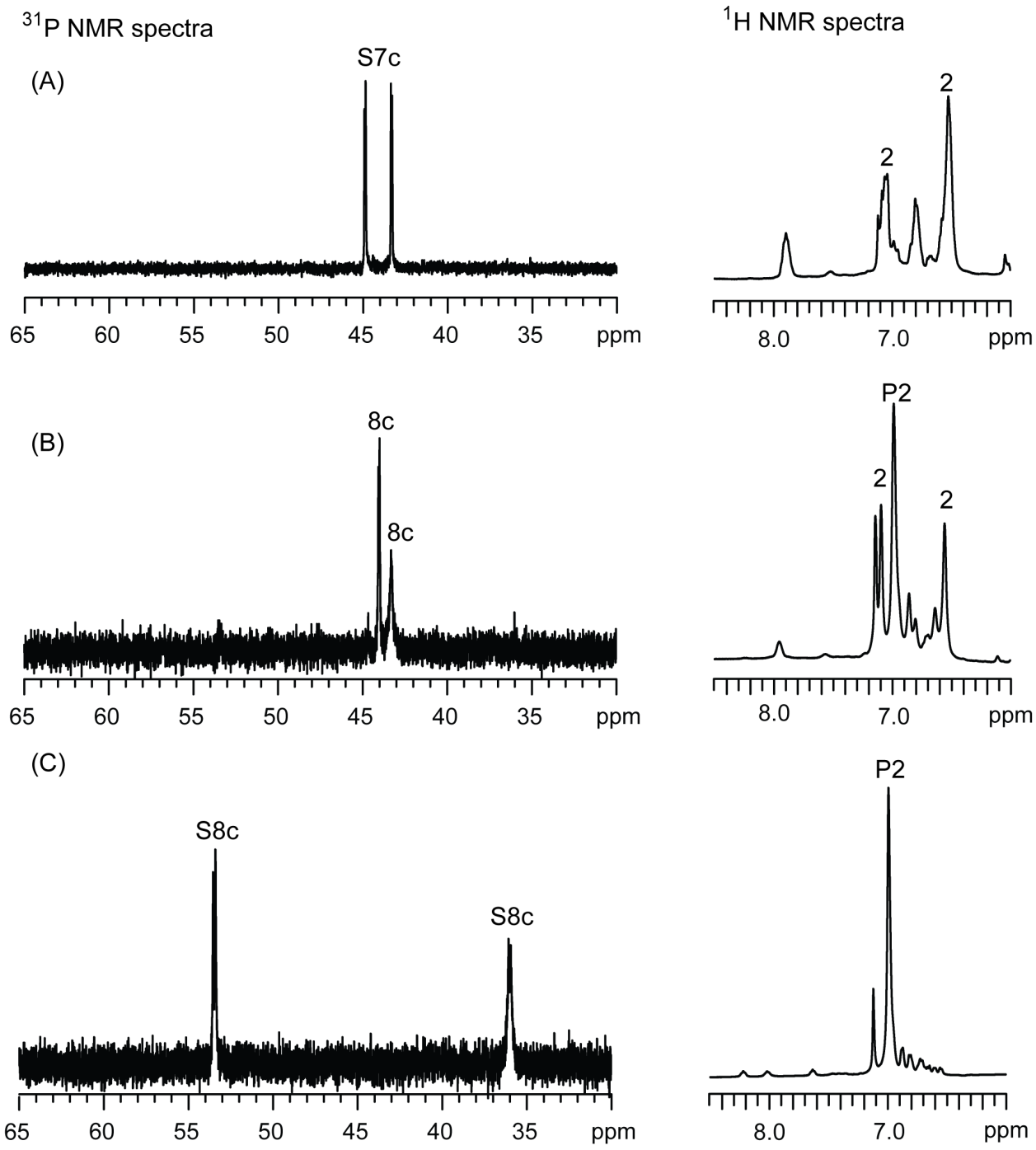
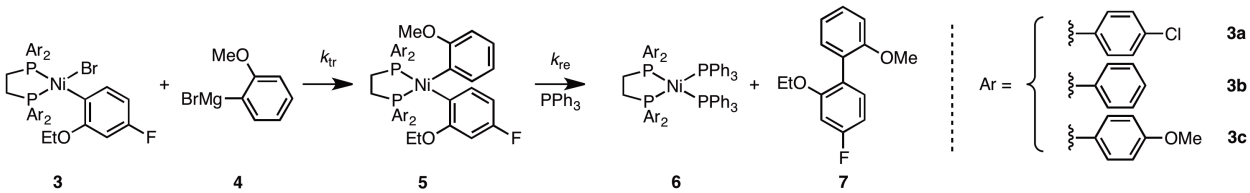


Figure S21. ^{31}P NMR spectra (162 MHz, THF, -10 °C) of (A) complex **S7c** δ 44.89 (d, *J* = 13.8 Hz), 43.32 (d, *J* = 14.3 Hz), (B) complex **8c** δ 44.03 (d, *J* = 12.7 Hz), 43.32 (br), (C) complex **S8c** δ 53.47 (d, *J* = 27.7 Hz), 36.07 (d, *J* = 22.2 Hz) in the presence or absence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectra (500 MHz, THF, -10 °C).

VII. Initiation Rate Studies

Representative Procedure for Performing NMR Spectroscopic Initiation Rate Studies:
All actions were performed in a glovebox under N_2 atmosphere. In 4 mL vial, nickel stock solution was prepared by dissolving **3b** (15.3 mg, 0.0226 mmol, 1.0 equiv) and PPh_3 (11.9 mg, 0.0454 mmol, 2.0 equiv) in THF (0.88 mL). Then, trifluoromethyl benzene (22 µL, 0.34 M in THF, 0.33 equiv) was added as an internal standard. An NMR tube was charged with this solution (0.8 mL), sealed with a septum, and removed from the glovebox. The tube was cooled to -5 °C in the NMR spectrometer for ~40 min. Immediately prior to acquiring kinetic data, **4** (0.2 mL, 0.2 M in THF, 2.0 equiv, kept at 0 °C) was injected into the tube. The tube was rapidly inverted once and then inserted into the spectrometer at -5 °C. Each spectrum was taken with the following parameters using Varian vnmr 500; acquisition time = 1.5 s, relaxation time = 3.0 s, scan size = 4, and pre-acquisition delay = 120 s.

Representative Procedure for Performing Igor Pro Analysis:
The integrated peak values of **3**, **5**, and **7** were converted to concentration using internal standard. The concentration was fitted to equations below using Igor Pro v6.22A. 'CollumKinetic 5000' was used as the master procedure file and the analysis was performed using same procedure reported in 'Fitting to Differential equations in Igor Pro' provided by the Collum group.[5]



3 4 5 6 7

$$\frac{d\,[\mathbf{3}]}{dt} = -\,k_{tr}\,[\mathbf{3}]\,[\mathbf{4}]$$

$$\frac{d\,[\mathbf{5}]}{dt} = k_{tr}\,[\mathbf{3}]\,[\mathbf{4}] - k_{re}\,[\mathbf{5}]$$

$$\frac{d\,[\mathbf{7}]}{dt} = k_{re}\,[\mathbf{5}]$$

The precatalyst initiation was observed using ^{19}F and ^{31}P NMR spectroscopy to support the peak assignments.

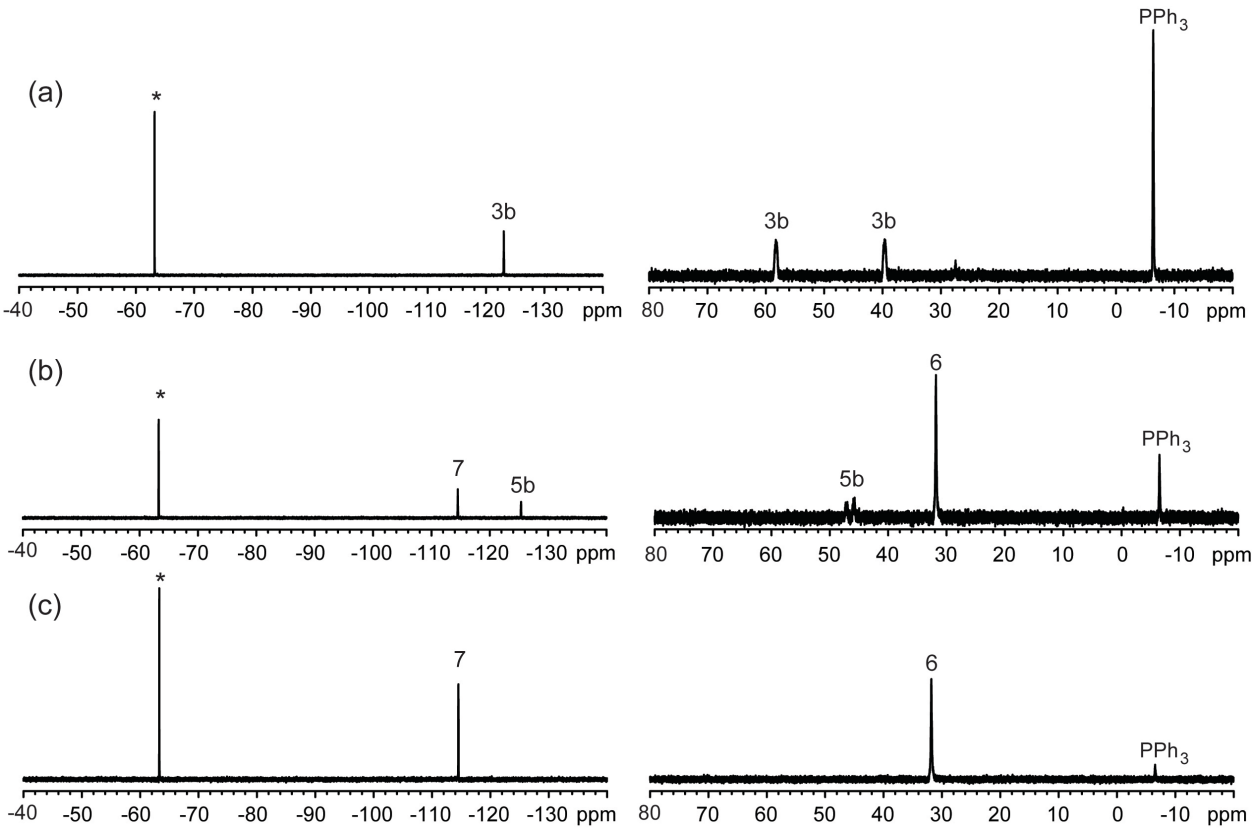


Figure S22. Representative ^{19}F and ^{31}P NMR spectra of initiation rate study for catalyst **3b** at the (a) beginning, (b) middle, and (c) end of the reaction. * represents the internal standard, trifluoromethyl benzene.

Control experiment

Initiation rate studies were performed with varying [PPh_3] to determine its effect on the rates of transmetalation and reductive elimination. (temp = -5 °C, [**3b**] = 0.02 M, and [monomer] = 0.04 M)

Table S7. Rate data for catalyst **3b** with varying [PPh_3].

[PPh_3] (M)	k_{tr} (M^{-1} s^{-1} x 10^{-3})	k_{re} (s^{-1} x 10^{-3})
0.04	26 ± 3	0.43 ± 0.07
0.08	16.0 ± 0.6	0.46 ± 0.01
0.16	22.4 ± 0.6	0.57 ± 0.02

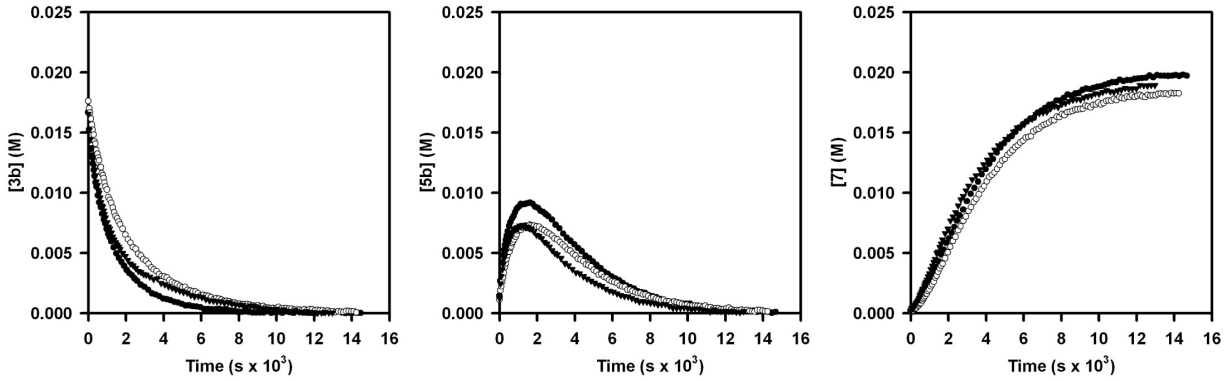


Figure S23. Plot of concentration versus time for catalyst **3b** with varying [PPh_3], (●= 0.04 M, ○= 0.08 M, ▼= 0.16 M)

Initiation rate studies were performed with varying [**4**] to determine its effect on the rates of transmetalation and reductive elimination. (temp = -5 °C, [**3b**] = 0.02 M, and [PPh_3] = 0.04 M)

Table S8. Rate data for catalyst **3b** with varying [**4**].

[**4**] (M)	k_{tr} (M^{-1} s^{-1} x 10^{-3})	k_{re} (s^{-1} x 10^{-3})
0.04	26 ± 3	0.43 ± 0.07
0.08	18.3 ± 0.7	0.457 ± 0.006
0.16	22.5 ± 0.6	0.575 ± 0.006

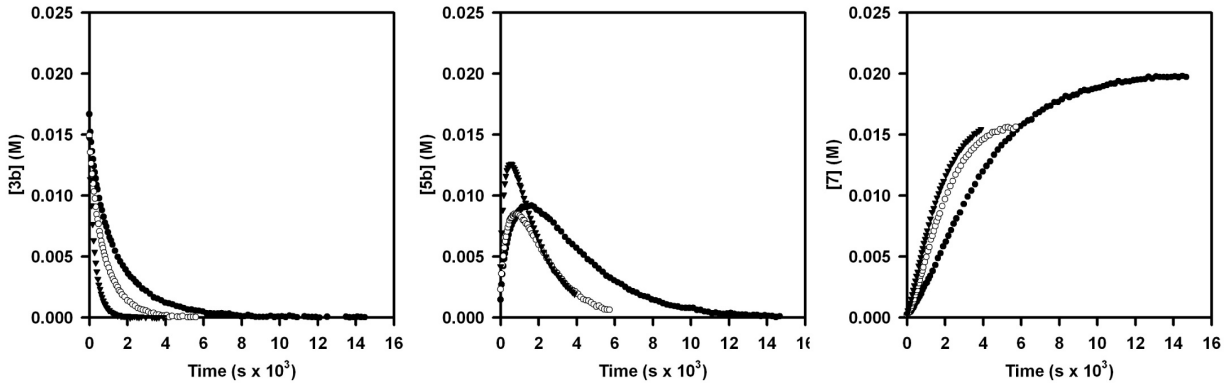


Figure S24. Plot of concentration versus time for catalyst **3b** with varying [**4**], (●= 0.04 M, ○= 0.08 M, ▼= 0.16 M)

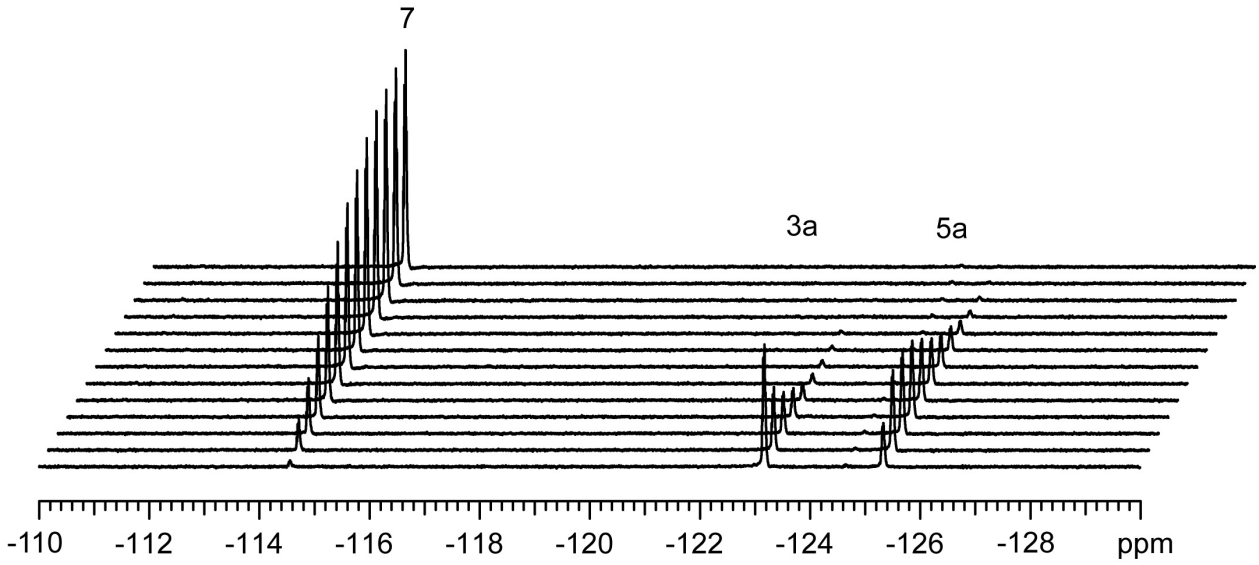


Figure S25. Representative ^{19}F NMR spectral array for catalyst **3a**. The internal standard, trifluoromethyl benzene, was observed at -63.33 ppm and is not shown.

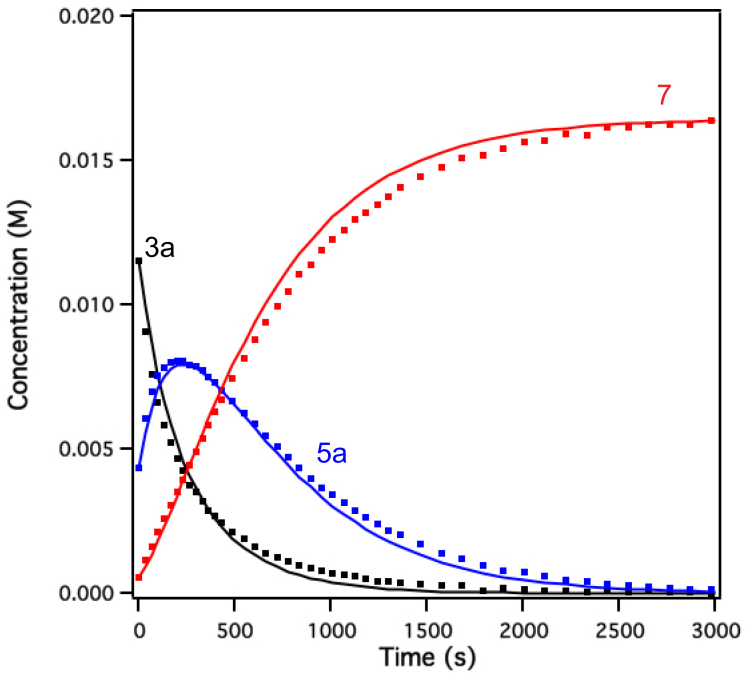


Figure S26. Plot of concentration versus time for data in Figure S25.

Table S9. Rate data for catalyst **3a**.

Trial	k_{tr} (M^{-1} s^{-1} x 10^{-3})	k_{re} (s^{-1} x 10^{-3})
1	127	1.66
2	173	1.94
3	128	1.90
Average	140 ± 30	1.8 ± 0.2

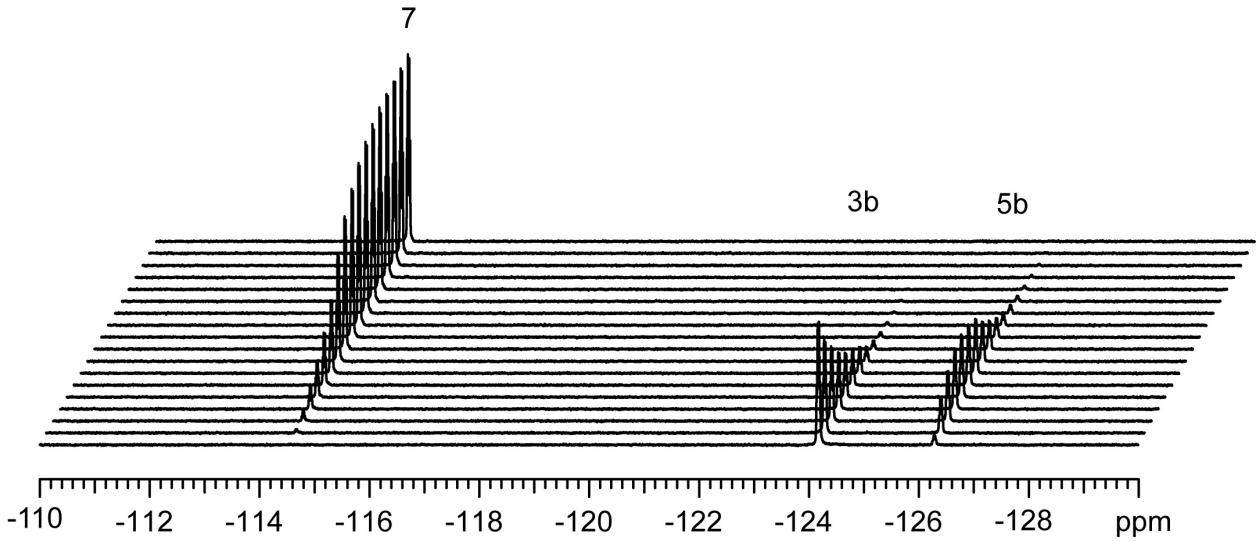


Figure S27. Representative ^{19}F NMR spectral array for catalyst **3b**. The internal standard, trifluoromethyl benzene, was observed at -63.33 ppm and is not shown.

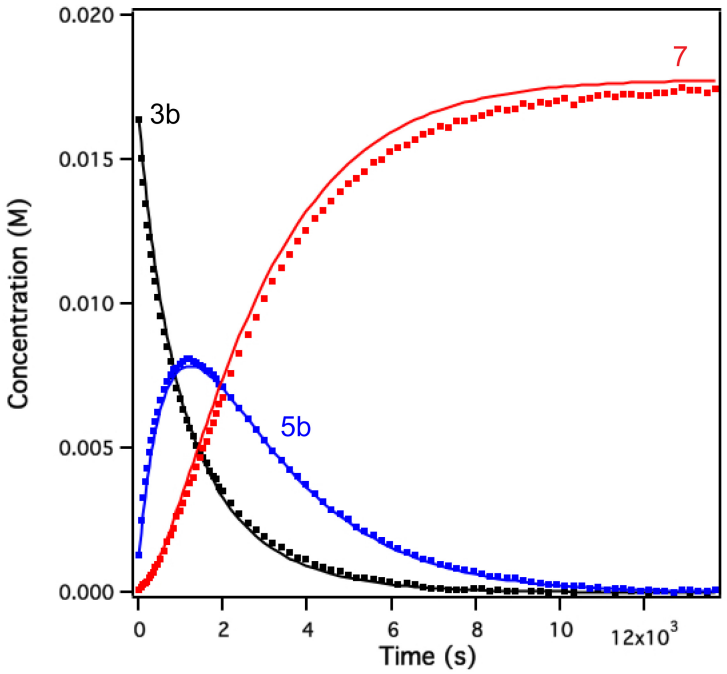


Figure S28. Plot of concentration versus time for Figure S27.

Table S10. Rate data for catalyst **3b**.

Trial	k_{tr} (M^{-1} s^{-1} x 10^{-3})	k_{re} (s^{-1} x 10^{-3})
1	26.8	0.504
2	28.0	0.406
3	21.9	0.374
Average	26 ± 3	0.43 ± 0.07

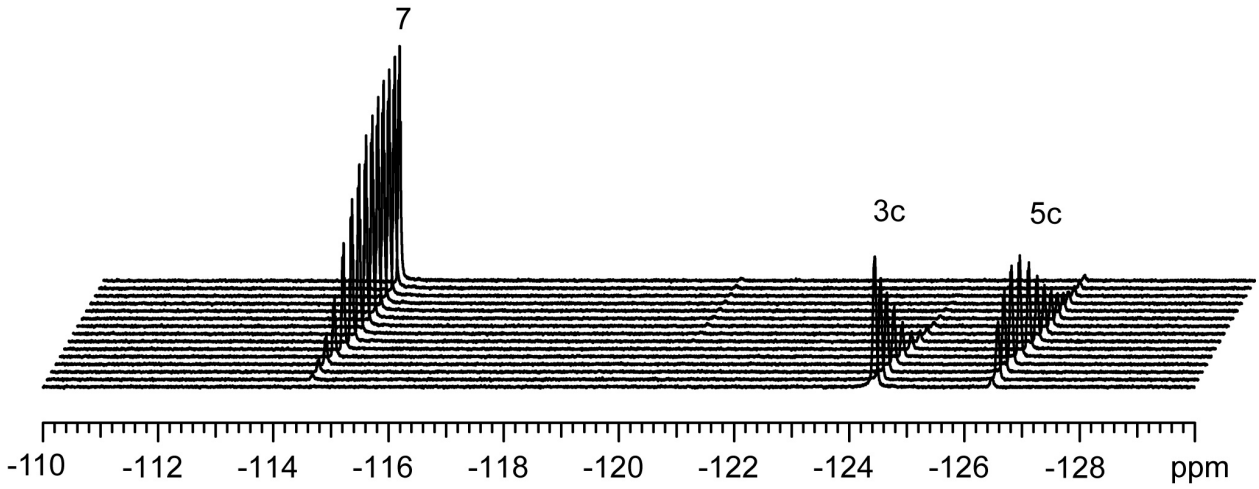


Figure S29. Representative ^{19}F NMR spectral array for catalyst **3c**. The internal standard, trifluoromethyl benzene, was observed at -63.36 ppm and is not shown.

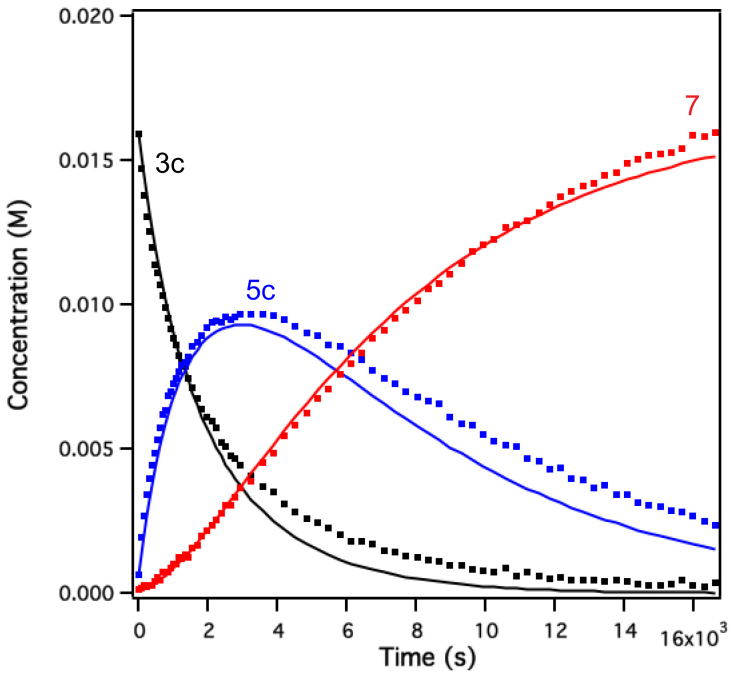


Figure S30. Plot of concentration versus time for Figure S29.

Table S11. Rate data for catalyst **3c**.

Trial	k_{tr} (M^{-1} s^{-1} x 10^{-3})	k_{re} (s^{-1} x 10^{-3})
1	10.9	0.183
2	10.5	0.195
3	15.8	0.162
4	11.3	0.190
Average	12 ± 2	0.18 ± 0.01

VIII. Hammett Plots

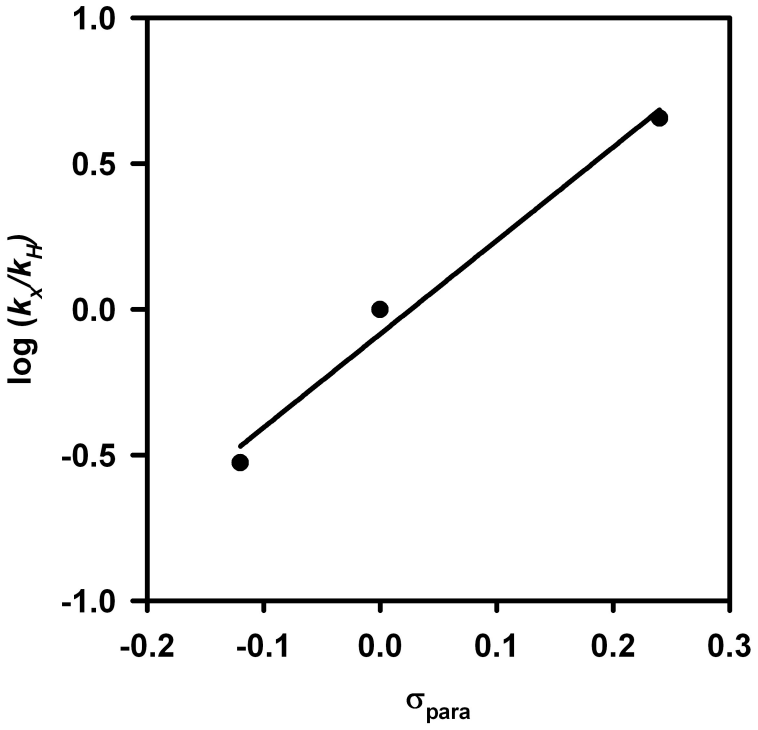


Figure S31. Plot of log(k_X /k_H) versus σ_{para} for reductive elimination during propagation. Fitted to log(k_X/k_H) = ρ x σ_{para}, where ρ = 3.2 ± 0.4.

Table S12. Data for the plot in Figure S31.

Catalyst	σ_{para}	log (k_X /k_H)
1a	0.24	0.66
1b	0	0
1c	-0.12	-0.53

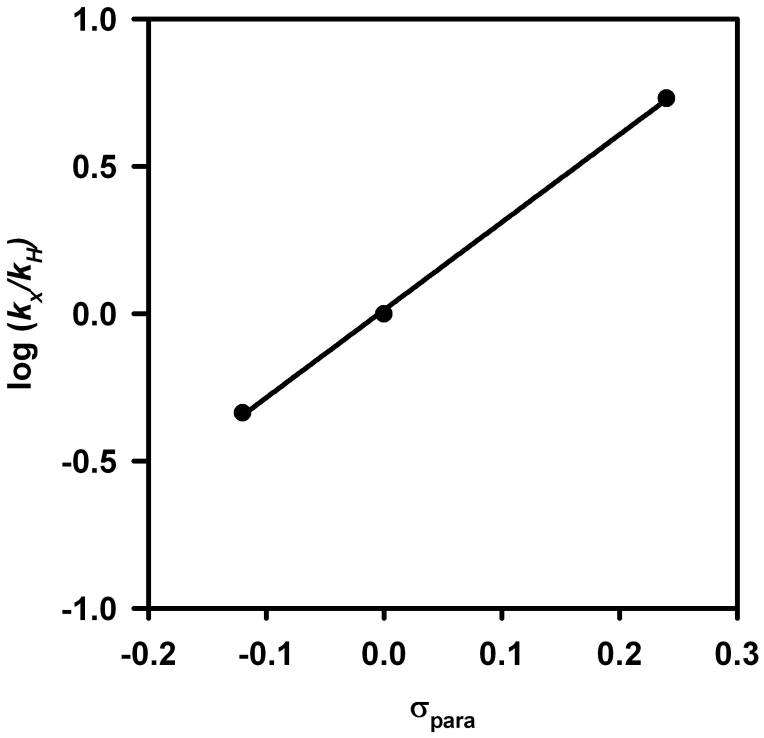


Figure S32. Plot of log(k_X/k_H) versus σ_{para} for transmetalation during precatalyst initiation. Fitted to log(k_X/k_H) = ρ x σ_{para}, where ρ = 2.98 ± 0.06.

Table S13. Data for the plot in Figure S32.

Catalyst	σ_{para}	log (k_X/k_H)
3a	0.24	0.73
3b	0	0
3c	-0.12	-0.34

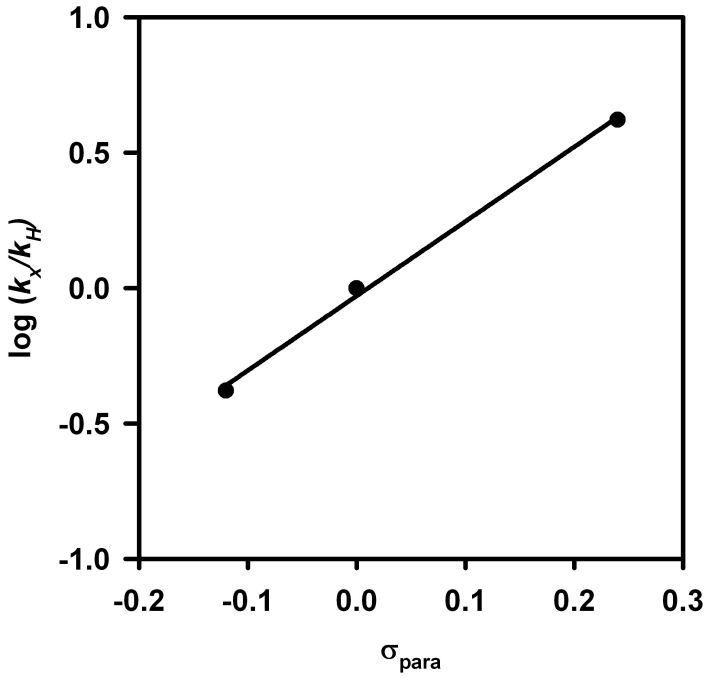


Figure S33. Plot of log(k_X/k_H) versus σ_{para} for reductive elimination during precatalyst initiation. Fitted to log(k_X/k_H) = ρ x σ_{para}, where ρ = 2.8 ± 0.1.

Table S14. Data for the plot in Figure S33.

Catalyst	σ_{para}	log (k_X/k_H)
3a	0.24	0.62
3b	0	0
3c	-0.12	-0.38

IX. Chain-growth Polymerization Data

Representative Procedure for M_n and PDI versus Conversion Studies utilizing React IR:
The IR probe was inserted through an O-ring sealed 14/20 ground glass adapter (custom-made) into an oven-dried 50 mL 2-neck flask equipped with a stir bar. The other neck was fitted with a three-way adapter fitted with a septum for injections/aliquot sampling and an N_2 line. The oven-dried flask was cooled under vacuum. The flask was then filled with N_2 and evacuated again for a total of three cycles. The flask was charged with THF (6.5 mL) and cooled to 0 °C over 15 min. After recording a background spectrum, monomer **2** (2.5 mL, 0.41 M, 1.0 equiv) was added by syringe and allowed to equilibrate for at least 10 min at 0 °C before proceeding. The catalyst solution (1.0 mL, 0.015 M, 0.015 equiv) was then injected and spectra were recorded every 30 s over the entire reaction. To account for mixing and temperature equilibration, spectra recorded in the first 60 s of the reaction were discarded. Aliquots (~0.5 mL) were taken through the three way adapter via syringe and immediately quenched with 12 M HCl (~1 mL). Each aliquot was then extracted with CH_2Cl_2 (2 x 1.5 mL) (with mild heating if polymer had precipitated), dried over $MgSO_4$, filtered, and then concentrated. The samples were dissolved in THF (with heating), and passed through a 0.2 μm PTFE filter for GPC analysis.

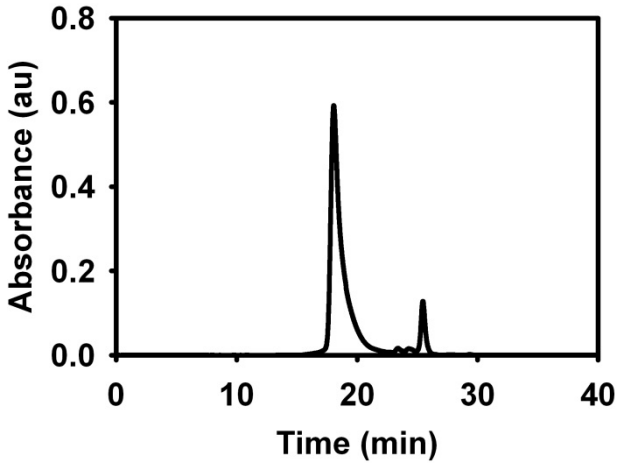


Figure S34. Representative GPC trace of **P2** at 60% conversion with catalyst **1a** (M_n: 20.7 kDa, PDI: 1.63).

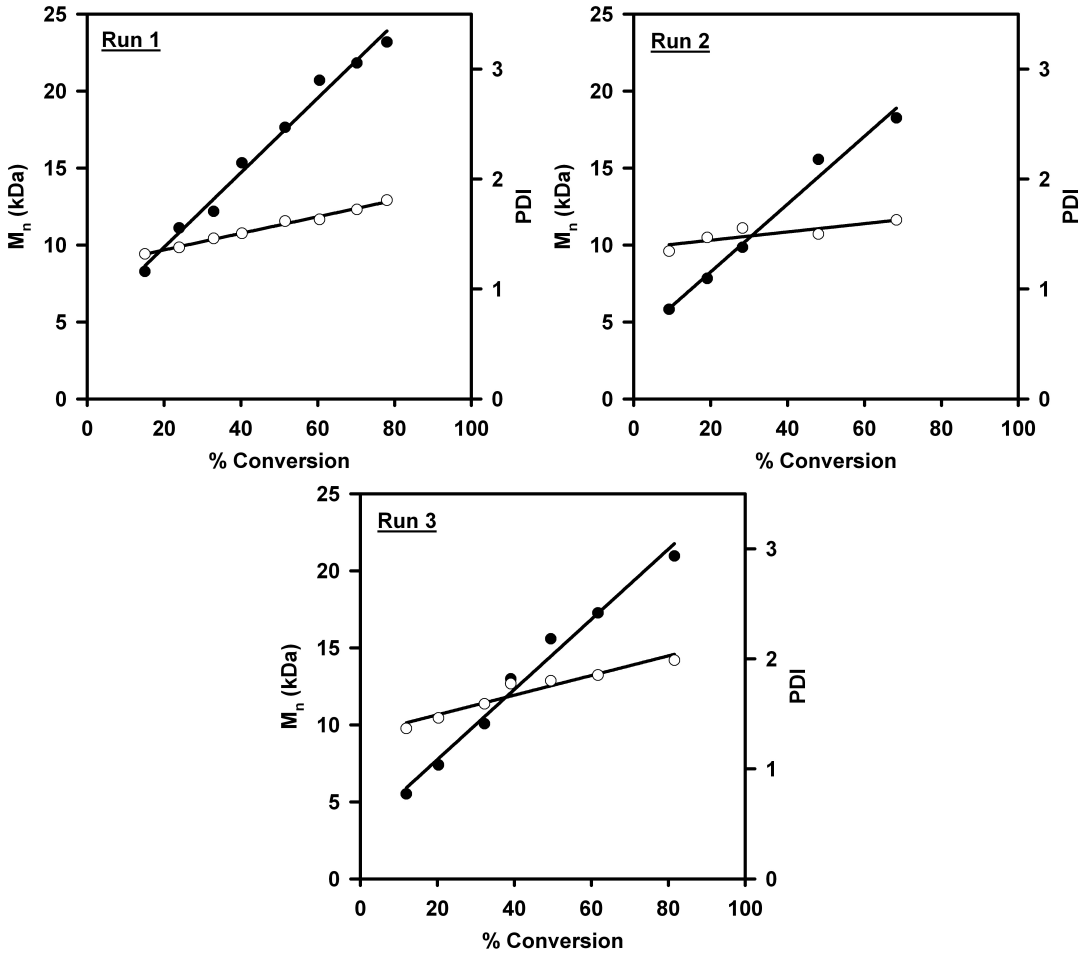


Figure S35. Plot of Mn (●) and PDI (o) versus conversion for **2** (temp = 0 °C, [**1a**] = 0.0015 M, [**2**] = 0.10 M (run 1), 0.10 M (run 2), 0.10 M (run 3)).

Table S15. Data for the plot in Figure S35, run 1.

% Conversion	M_n (kDa)	PDI
15	8.3	1.32
24	11.1	1.38
33	12.2	1.46
40	15.3	1.51
52	17.6	1.62
60	20.7	1.63
70	21.8	1.72
78	23.2	1.81

Table S16. Data for the plot in Figure S35, run 2.

% Conversion	M_n (kDa)	PDI
9	5.8	1.34
19	7.8	1.47
28	9.8	1.55
48	15.6	1.50
68	18.3	1.63

Table S17. Data for the plot in Figure S35, run 3.

% Conversion	M_n (kDa)	PDI
12	5.5	1.37
20	7.4	1.46
32	10.1	1.59
39	13.0	1.77
49	15.6	1.80
62	17.3	1.85
82	21.0	1.99

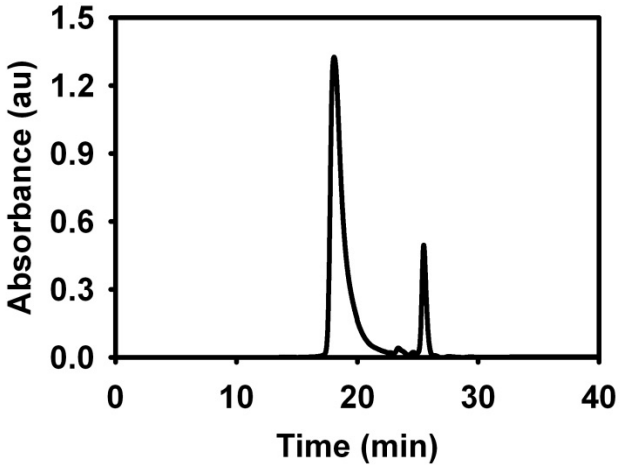


Figure S36. Representative GPC trace of **P2** at 60% conversion with catalyst **1b** (M_n: 19.1 kDa, PDI: 1.67).

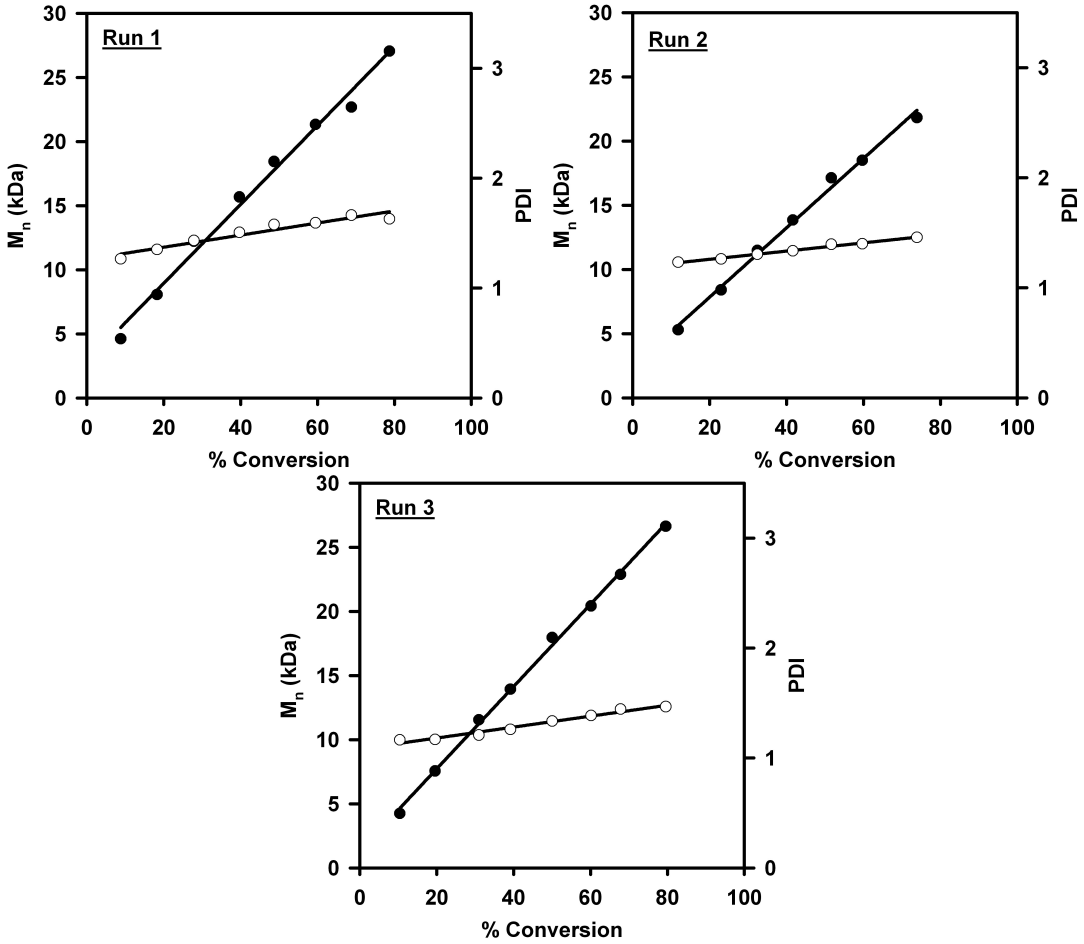


Figure S37. Plot of Mn (●) and PDI (o) versus conversion for **2** (temp = 0 °C, [**1b**] = 0.0015 M, [**2**] = 0.11 M (run 1), 0.11 M (run 2), 0.10 M (run 3)).

Table S18. Data for the plot in Figure S37, run 1.

% Conversion	M_n (kDa)	PDI
9	4.6	1.27
18	8.1	1.35
28	12.2	1.43
40	15.7	1.51
49	18.4	1.58
59	21.3	1.59
69	22.7	1.66
79	27.1	1.63

Table S19. Data for the plot in Figure S37, run 2.

% Conversion	M_n (kDa)	PDI
12	5.3	1.23
23	8.4	1.26
32	11.5	1.31
42	13.8	1.34
52	17.1	1.39
60	18.5	1.40
74	21.8	1.46

Table S20. Data for the plot in Figure S37, run 3.

% Conversion	M_n (kDa)	PDI
10	4.3	1.17
20	7.6	1.17
31	11.6	1.21
39	13.9	1.26
50	18.0	1.34
60	20.4	1.39
68	22.9	1.45
80	26.6	1.47

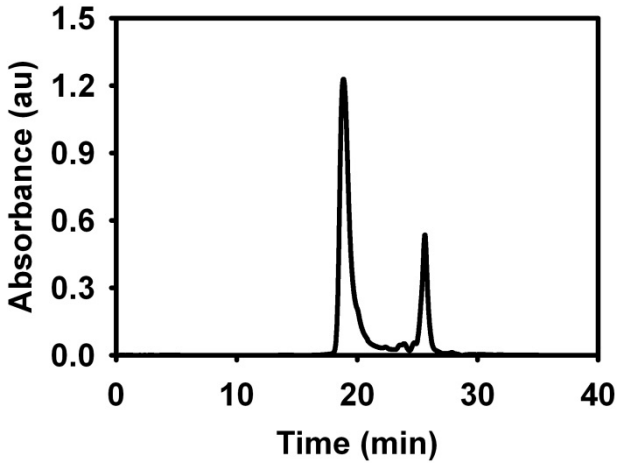


Figure S38. Representative GPC trace of **P2** at 60% conversion with catalyst **1c** (M_n: 14.0 kDa, PDI: 1.28).

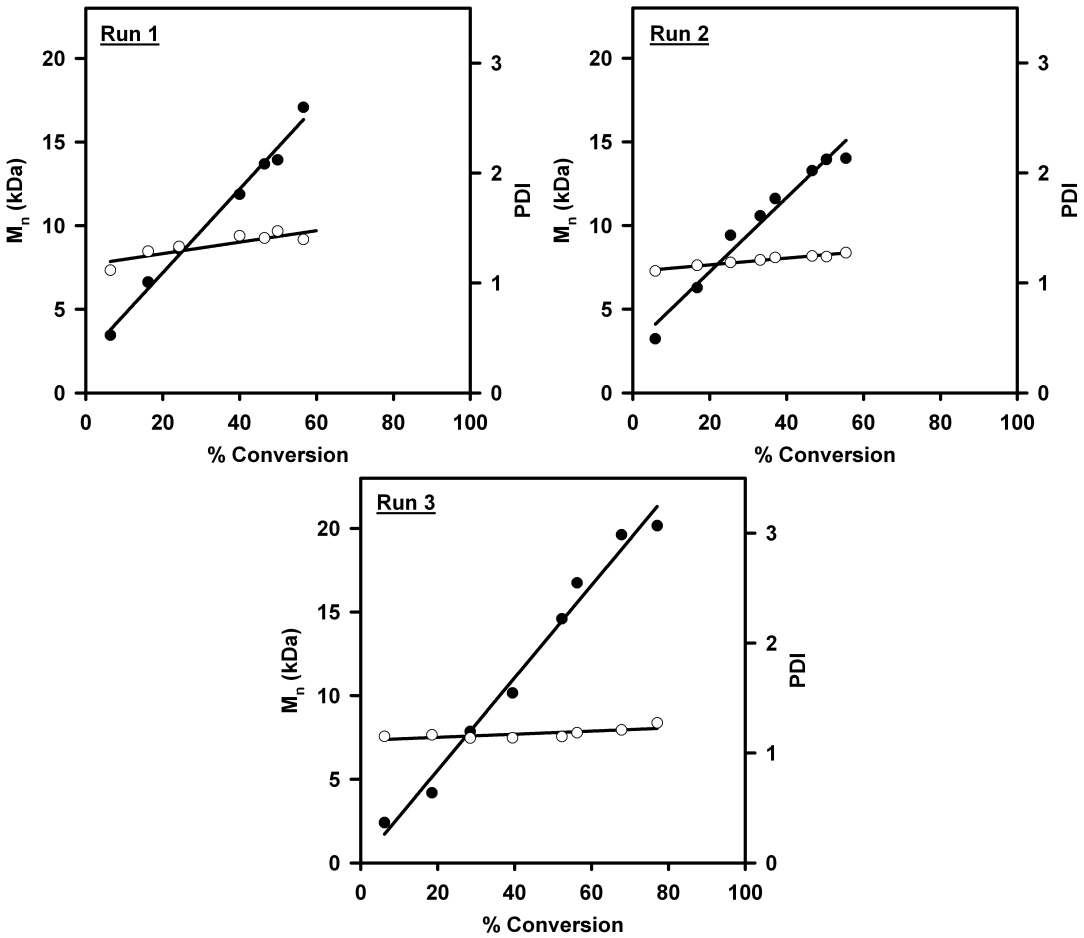


Figure S39. Plot of Mn (●) and PDI (o) versus conversion for **2** (temp = 0 °C, [**1c**] = 0.0015 M, [**2**] = 0.095 M (run 1), 0.099 M (run 2), 0.10 M (run 3)).

Table S21. Data for the plot in Figure S39, run 1.

% Conversion	M_n (kDa)	PDI
6	3.5	1.12
16	6.6	1.29
24	8.6	1.33
40	11.9	1.43
46	13.7	1.41
50	13.9	1.47
57	17.1	1.40

Table S22. Data for the plot in Figure S39, run 2.

% Conversion	M_n (kDa)	PDI
6	3.2	1.11
17	6.3	1.16
25	9.4	1.19
33	10.6	1.21
37	11.6	1.23
47	13.3	1.24
50	13.9	1.24
55	14.0	1.28

Table S23. Data for the plot in Figure S39, run 3.

% Conversion	M_n (kDa)	PDI
6	2.4	1.15
19	4.2	1.16
28	7.9	1.14
39	10.2	1.14
52	14.6	1.15
56	16.7	1.18
68	19.6	1.21
77	20.2	1.27

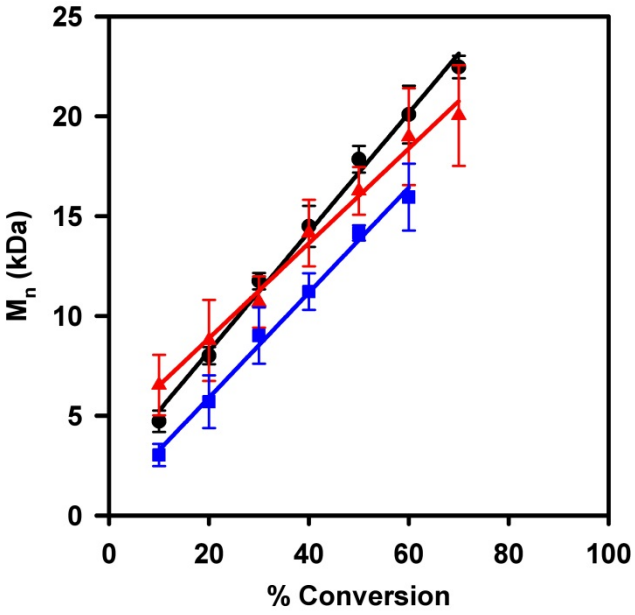


Figure S40. Plot of average M_n versus conversion for all three catalysts with error bars. Samples within ±4% of target conversion were included (▲= **1a**, ● = **1b**, ■ = **1c**).

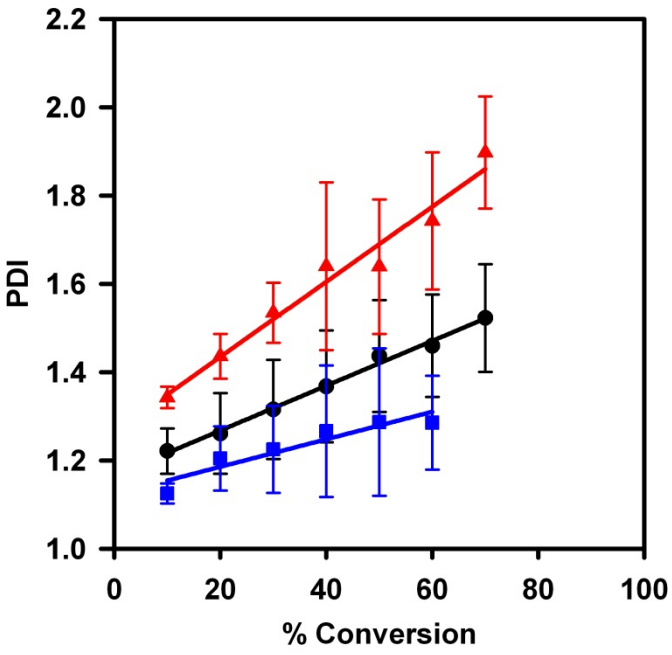


Figure S41. Plot of average average PDI versus conversion for all three catalysts with error bars. Samples within ±4% of target conversion were included (▲= **1a**, ● = **1b**, ■ = **1c**).

Representative Procedure for Preparation of Oligomers for MALDI-TOF MS Studies:
All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, **1b** (11.0 mg, 0.015 mmol, 1.0 equiv), THF (4.75 mL), and **2** (0.25 mL, 0.44 M, 7 equiv) were added to the flask. After 1 h, the reaction was removed from the glovebox and poured into HCl (aq., 5 mL, 5 M) and then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were concentrated in vacuo. The resulting solid was washed with MeOH (50 mL) to give **P2** as an off-white solid: M_n: 1.76 kDa, PDI: 1.15 (GPC). For MS sample a small amount of polymer dissolved in $CHCl_3$ was first filtered through a pipet column of basic, acidic, and neutral alumina to remove Ni and the solution was concentrated in vacuo. The general procedure was followed for MALDI-TOF MS sample preparation (see General Experimental pS2). For **P2**: M_n: 1.84 kDa, PDI: 1.03 (MALDI-TOF MS)

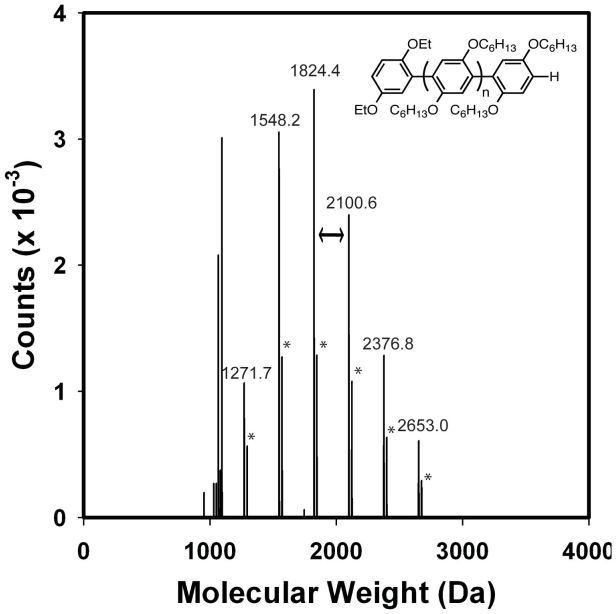


Figure S42. MALDI-TOF MS spectrum of **P2** initiated with **1a**. * represents $[M + Na]^+$.

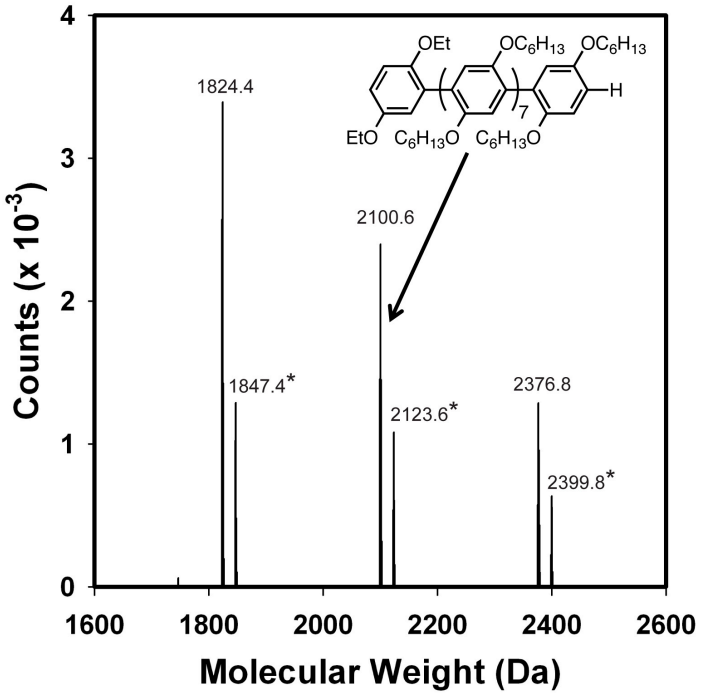


Figure S43. Expanded view of Figure S42. * represents $[M + Na]^+$.

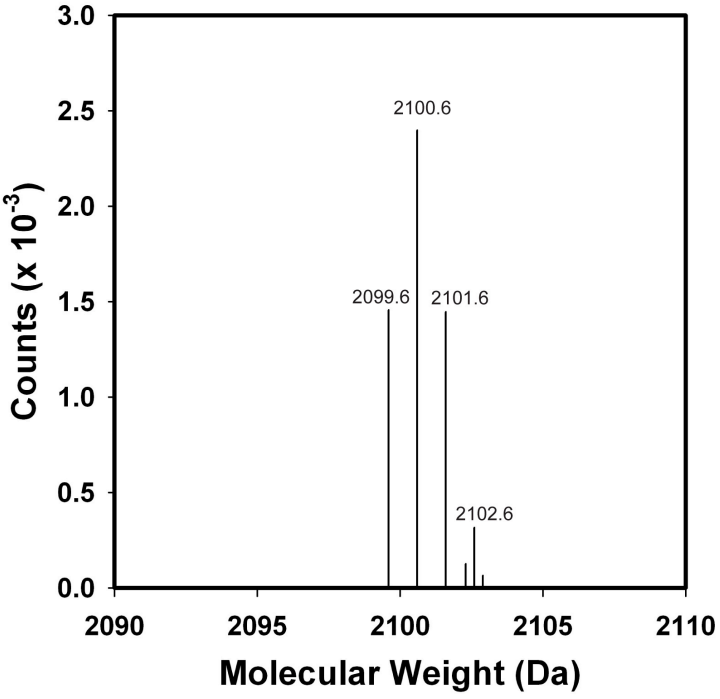


Figure S44. Expanded view of Figure S43.

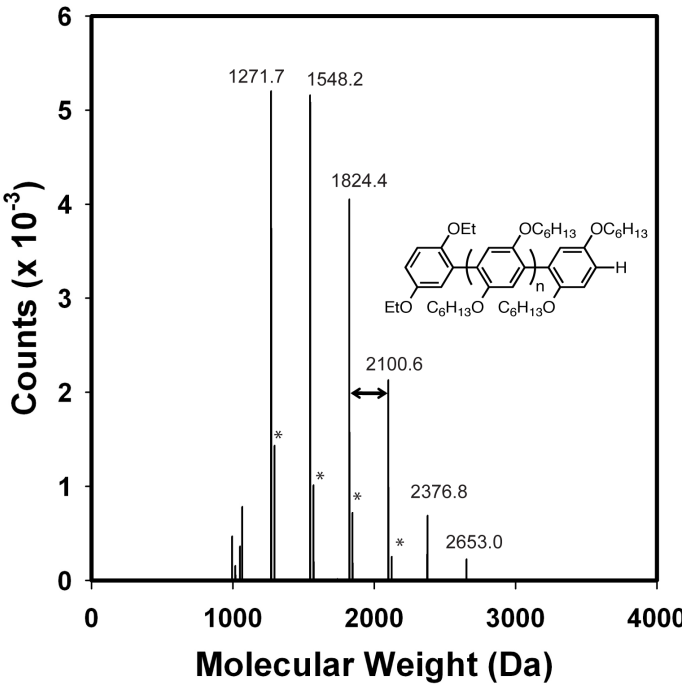


Figure S44. MALDI-TOF MS spectrum of **P2** initiated with **1b**. * represents $[M + Na]^+$.

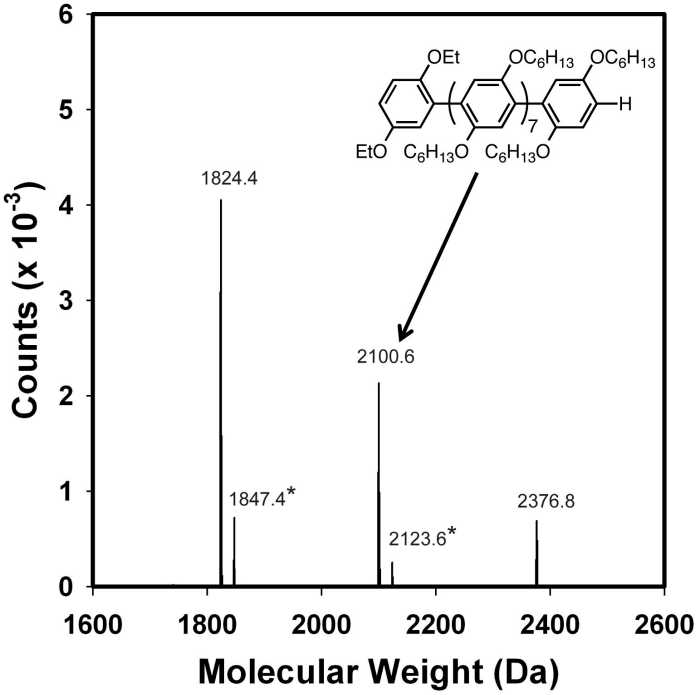


Figure S45. Expanded view of Figure S44. * represents $[M + Na]^+$.

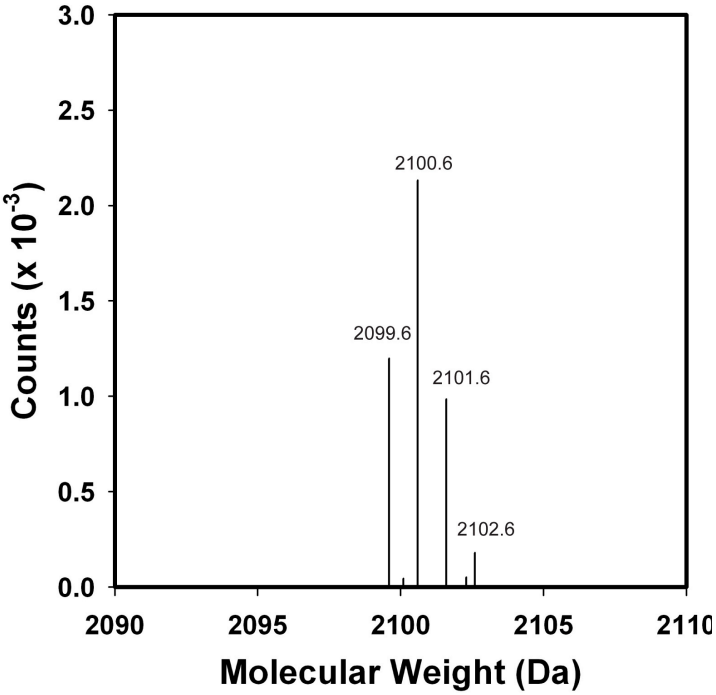


Figure S46. Expanded view of Figure S45.

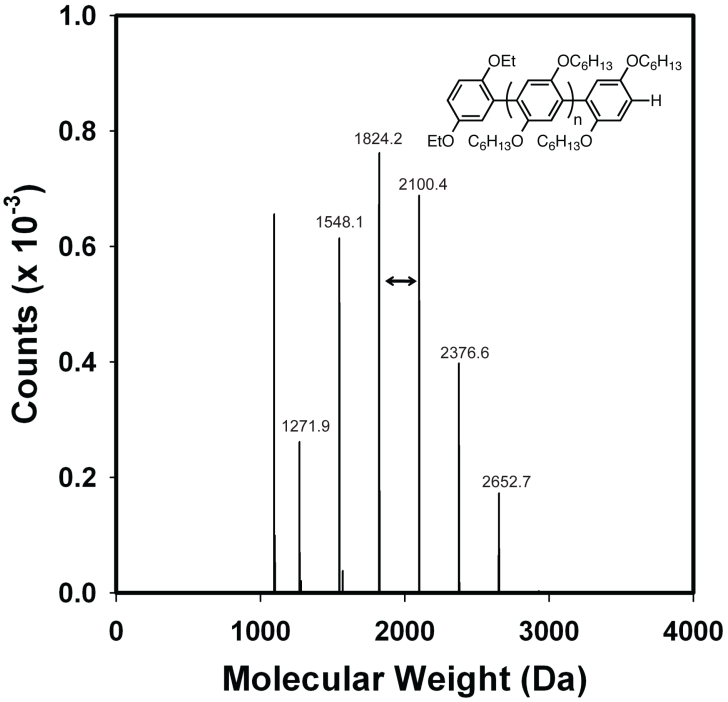


Figure S47. MALDI-TOF MS spectrum of **P2** initiated with **1c**.

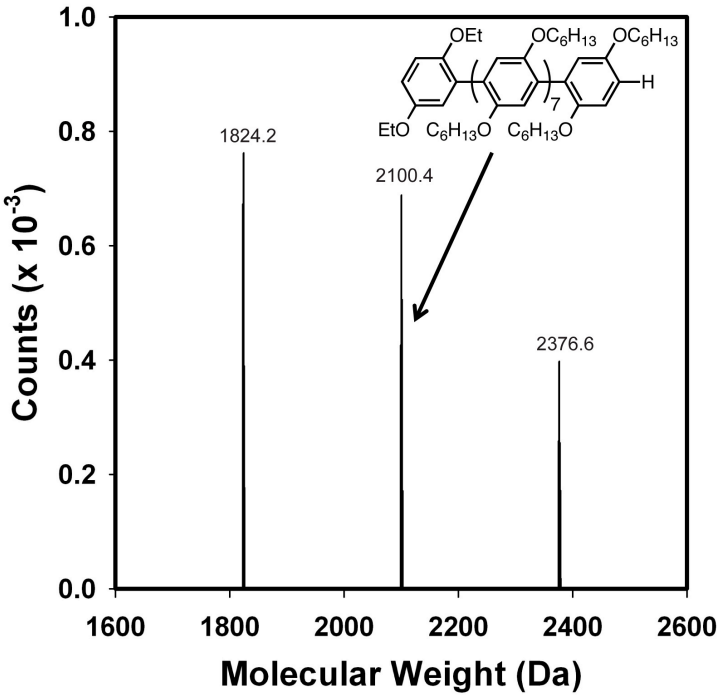


Figure S48. Expanded view of Figure S47.

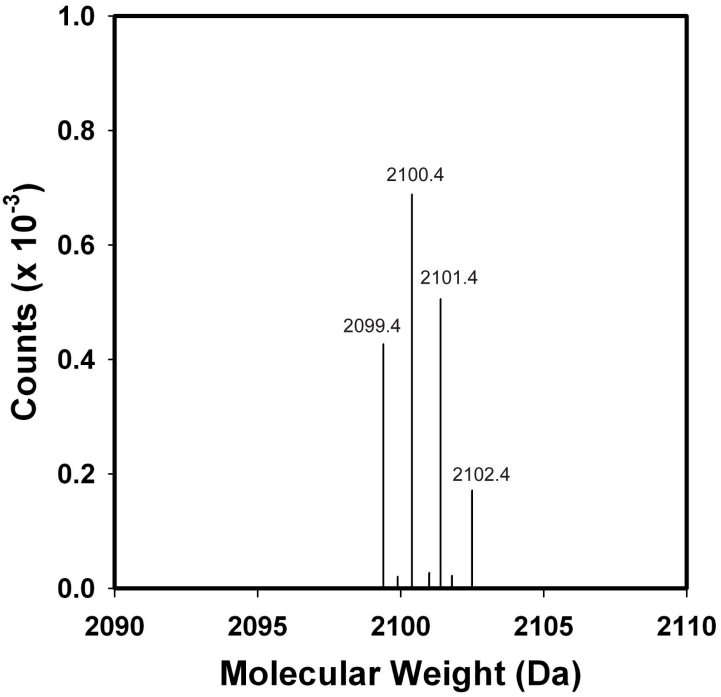


Figure S49. Expanded view of Figure S48.

Representative Procedure for Obtaining High Molecular Weight Polymer Samples:
An oven-dried 50 mL Schlenk flask was charged with the solution of **1b** (6.8 mL, 0.022 M in THF) and a stir bar in a glovebox. The flask was equipped with a two-way adapter fitted with a septum for injection and brought out of the glovebox. After introducing N_2 through the two-way adaptor and the side-arm of the flask (2 lines), the solution was cooled to 0 °C over 15 min. Then, monomer **2** (3.2 mL, 0.46 M in THF), with docosane added as an internal standard, was added by syringe. After 8 h, an aliquot (~0.5 mL) was taken through the two-way adaptor via syringe and immediately quenched with 12 M HCl (~1 mL). It was then extracted with CH_2Cl_2 (2 x 1.5 mL) with mild heating, dried over $MgSO_4$, filtered, and then concentrated. The sample was then dissolved in THF (with heating), and passed through a 0.2 μm PTFE filter for GPC analysis. The remainder of reaction was quenched with 12 M HCl (~10 mL) followed by the same work-up procedure. The resulting polymer was washed with MeOH (~200 mL) and dried in vacuo. Conversion was determined relative to the initial concentration, using the internal standard as a reference by GC analysis.

Table S24. Polymerization data for catalysts **1a-c**.

Catalyst	Reaction Time (h)	M_n (kDa)	PDI	Monomer Conversion (%)	Isolated Yield (%)
1a	4	29.1	2.36	93	67
1b	8	40.0	1.71	90	48
1c	11	41.3	1.56	71	54

X. References

(1) J. Chatt, W. Hussain, G. J. Leigh, H. M. Ali, C. J. Pickett, D. A. Rankin, *J. Chem. Soc., Dalton Trans.*, 1985, 1131.
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(5) For the numerical integration procedure, see: http://www.chem.cornell.edu/dbc6/Site_2/Group_Resources.html . For leading references on this procedure, see: (a) A. C. Hoepker, L. Gupta, Y. Ma, M. F. Faggin, D. B. Collum, *J. Am. Chem. Soc.*, 2011, **133**, 7135. (b) Y. Ma, A. C. Hoepker, L. Gupta, M. F. Faggin, D. B. Collum, *J. Am. Chem. Soc.*, 2010, **132**, 15610.