Appendix 3

Appendix to Chapter 4: Preliminary Results for Ligand-based Steric Effects in Ni-catalyzed Chain-Growth Polymerizations using Bis(dialkylphosphino)ethanes

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(dppp)Cl_2, Ni(dppe)Cl_2, dmpe, depe, and dcpe 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. Tridecane was distilled from sodium/ benzophenone. 1-bromo-2,5-(bishexyloxy)benzene (**S1**),[1] and compounds **S4**,[1] **S7**,[1] **1**,[2] **2**,[3] **3**,[4] **4a-b**,[1] **5a**-**b**,[5] **6a-d**,[1] amd **7**,[2] were prepared from literature procedures.

II. General Experimental

NMR Spectroscopy: Unless otherwise noted, ^{1}H, ^{13}C, and ^{31}P NMR spectra for all compounds were acquired at rt in $CDCl_3$ on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 100, and 132 MHz, respectively. For ^{1}H and ^{13}C NMR spectra the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. ^{31}P NMR spectra were referenced to external H_3PO_4 (85% aq). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), quintet (quin), multiplet (m), and broad resonance (br).

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. 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 acetonitrile/ethanol. 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 was mixed with 3 µL of the matrix solution. 1 µL of the 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.

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

Titrations of the Grignard Reagents: An accurately weighed sample of salicylaldehyde phenylhydrazone[6] (typically between 290-310 mg) was dissolved in 5.00 mL of THF. A 0.20 mL aliquot of this solution was stirred at rt while ArMgCl was added dropwise using a 250 µL syringe. The initial solution is yellow and turns bright orange at the end-point.

Statistical Analysis: Reported quantitative data represents the average of 2-3 experiments and the error bars represent the standard deviation in these measurements. In cases where the error was greater than 10% of the average value, the experiments were repeated an additional 2-3 times and these values were included in the average and standard deviation calculations.

III. General and Representative Procedures

Calibration Curves: The calibration curve for monomer **7** was reported previously.[1] For monomer **4a**, a calibration curves were prepared as previously reported.[1] GC solutions containing a constant concentration of docosane (0.00120 M) and varying concentrations of 1-bromo-2,5-(bishexyloxy)benzene (**S1**) (0.00300, 0.00180, 0.00119, 0.000593, and 0.000297 M) were prepared in $CHCl_3$. Each was analyzed by GC and the response factor **F** calculated by fitting the data to the equation of Hernández et al.[7]

Rate Studies: Rate studies using the ReactIR were performed using same procedure reported previously,[1] except the ice bath was replaced with an oil bath set to 50 °C and the reactions were run under Argon.

Representative procedure for preparing the catalyst solution: All actions were performed in a glovebox under N_2 atmosphere. An 8 mL vial was equipped with a stir bar. Sequentially, Ni(depe)Cl_2 (20 mg, 0.060 mmol, 1.0 equiv), THF (3.3 mL), and **4a** (0.67 mL, 0.45 M, 5 equiv) were added to the flask. The reaction mixture was stirred for 5 min until homogeneous, then transferred to a Schlenk tube and kept in a brine/ice bath at -15 °C.

M_n and PDI versus Conversion Studies: Plots of M_n and PDI versus conversion utilizing GC and GPC were obtained as previously reported with the following changes:[1] 1) the entire process was performed in a glovebox. 2) the catalyst was combined with THF as solid and heated to 60 °C. 3) The monomer was added last.

*Representative Procedure for Screening using **4a**:* All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(depe)Cl_2 (2.5 mg, 0.0075 mmol, 0.0015 equiv), THF (4.0 mL), and **4a** (1.0 mL, 0.5 mmol, 60 equiv) were added to the vial. The reaction solution was stirred at 60 °C or rt for 6-7 h. An aliquot was taken and quenched with CH_3OH (0.2 mL), diluted with $CHCl_3$ and analyzed by GC. The remainder of the reaction was removed from the glovebox and quenched with HCl (aq., 5 mL, 5 M) extracted with $CHCl_3$ (5 mL, with mild heating if polymer had precipitated) and then concentrated. The samples were dissolved in THF (with heating) and passed through a 0.2 μm PTFE filter for GPC analysis.

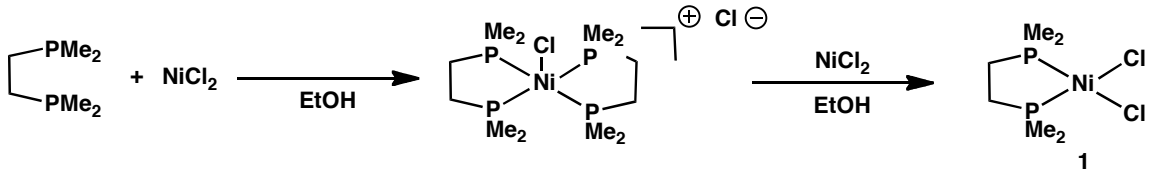
Representative Procedure for Performing NMR Spectroscopic Studies: All actions were performed in a glovebox under N_2 atmosphere. An NMR tube was charged with **2** (10 mg, 0.030 mmol, 1.0 equiv) and THF (0.2 mL). The tube was sealed with a septum removed from the glovebox. Immediately prior to acquiring data, **4a** (1.0 mL, 0.45 M in THF, 15 equiv) was injected into the tube. The tube was rapidly inverted twice and then inserted into the spectrometer at 60 °C.

Procedure for Performing 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, **6a** (6 mg, 0.014 mmol, 1.0 equiv), THF (9.8 mL), and **4a** (0.23 mL, 0.45 M, 7 equiv) were added to the flask. After 90 min, the reaction was removed from the glovebox and quenched with HCl (aq., 5 mL, 5 M) and then extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers concentrated in vacuo. The

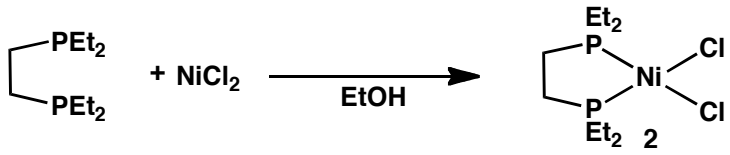
resulting solid was washed with CH_3OH (50 mL) to give **P4** as an off-white solid: M_n: 2.4 kDa, PDI: 1.16 (GPC). For MS sample a small amount of polymer was first filtered through a pipet column of neutral alumina and then the general procedure was followed (see General Experimental).

Ligand Exchange Experiments: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar. **5a** or **5b** (~20 mg, 1.0 equiv), THF (1 mL) and depe or dcpe (1.0 - 1.4 equiv) were added and the mixture was stirred at rt for 5 min. The solution was transferred to an NMR tube and analyzed by ^{31}P NMR spectroscopy.

III. Synthetic Procedures

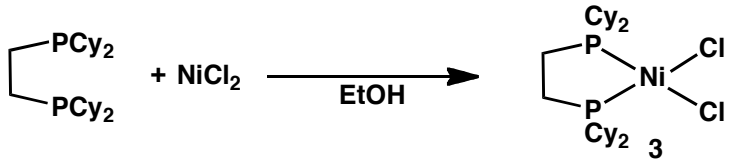


A Schlenk flask was placed under N_2 and equipped with a stir bar. EtOH and acetone were sparged for 30 min prior to starting the reaction. $NiCl_2$•$6H_2O$ (0.4 g, 2 mmol, 1.0 equiv) was added to the flask. Next, EtOH (11 mL) was added using a double-sided needle. Finally, 1,2-bis(dimethylphosphino)ethane (dmpe) (0.55 mL, 3.3 mmol, 2.0 equiv) was added to the flask by syringe. After 30 min, acetone (8 mL) and toluene (16 mL) were added. A precipitate formed which was collected by filtration under N_2 using a Schlenk filter frit (^{31}P NMR (132 MHz, $CDCl_3$) δ 43.32 ppm). Next, 0.52g of the precipitate was combined with another portion of $NiCl_2$•$6H_2O$ (0.52 g) in 26 mL of EtOH. The reaction was refluxed at 85 °C for 45 min and the solution turned red/brown. After cooling to rt an orange precipitate formed. The solid was filtered and washed with hexanes to give 0.35 g of **1** as a orange/brown solid (75% yield). HRMS (EI): Calcd. for $C_6H_{16}Cl_2NiP_2$, 277.9458 [M]+; found, 277.9470. ^{31}P NMR (132 MHz, $CDCl_3$) δ 50.32 ppm.



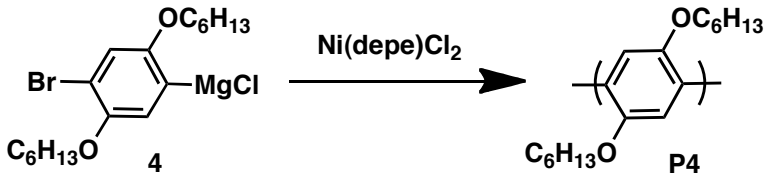
2. A 25 mL Schlenk flask was placed under N_2 and equipped with a stir bar. Sequentially, $NiCl_2$•$6H_2O$ (0.36 g, 1.5 mmol, 1.0 equiv), EtOH (10 mL), and 1,2-bis(diethylphosphino)ethane (depe) (0.25 mL, 1 mmol, 1.0 equiv) were added to the flask. The reaction stirred at rt for 10 min and an orange solution formed. The solution was partially concentrated and cooled in the freezer at -30 °C until

crystals formed. The solid was filtered and washed with EtOH (100 mL) to give 0.23 g of **2** as an orange solid (70% yield). HRMS (EI): Calcd. for $C_{10}H_{24}Cl_2NiP_2$, 334.0084 [M]+; found, 334.0078. ^{31}P NMR (132 MHz, $CDCl_3$) δ 76.88 ppm. Elemental Analysis: Calcd for $C_{10}H_{24}Cl_2NiP_2$, C, 35.76; H, 7.20; Cl, 21.11; Found C, 35.94; H, 7.18; Cl, 20.84.



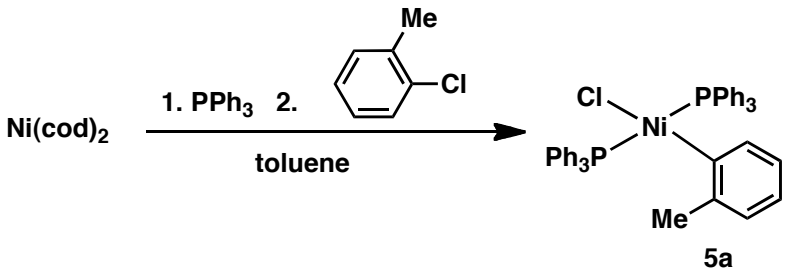
---

3. A 200 mL flask was placed under N_2 and equipped with a stir bar. Sequentially, $NiCl_2$•$6H_2O$ (0.36 g, 1.5 mmol, 1.5 equiv), EtOH (30 mL), and 1,2-bis (dicyclohexylphosphino)ethane (dcpe) (0.42 g, 1.0 mmol, 1.0 equiv) were added to the flask. The reaction stirred at rt for 10 min and an orange precipitate formed. The solid was filtered and washed with EtOH to give 0.37 g of **3** as an orange solid (67% yield). HRMS (EI): Calcd. for $C_{26}H_{48}Cl_2NiP_2$, 550.1962 [M]+; found, 550.1964. ^{31}P NMR (132 MHz, $CDCl_3$) δ 72.43 ppm.



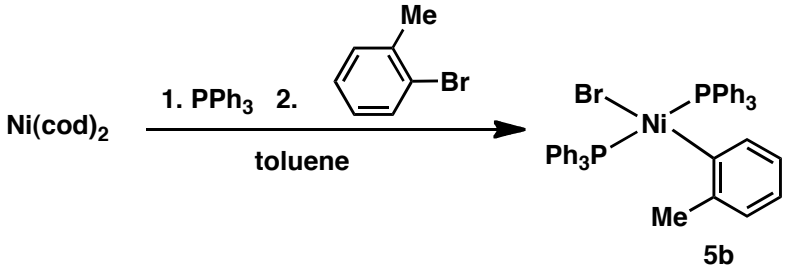
P4a. All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Ni(depe)Cl_2 (2.7 mg, 0.0075 mmol, 0.0015 equiv) and THF (4.0 mL) were combined and heated to 60 °C. **4a** (1.0 mL, 0.5 mmol, 1.0 equiv) was added to the vial and the reaction solution was stirred at 60 °C for 45 min. After 45 min the reaction was removed from the glovebox and quenched with HCl (aq., 5 mL, 5 M) and then extracted with $CHCl_3$ (3 x 5 mL). The combined organic layers were concentrated in vacuo. A sample was taken for

GPC analysis (M_n: 9.5 kDa, PDI: 2.12) and then the resulting solid was precipitated from THF/methanol to give 0.1161 g of **P4a** as an off-white solid (64% yield).



5a

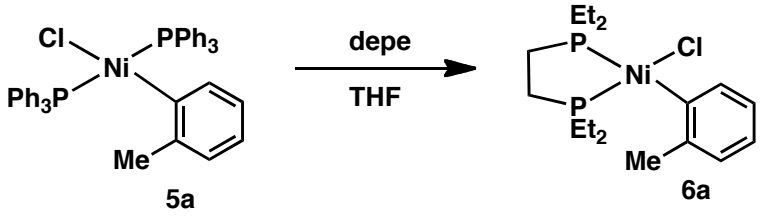
5a. In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with $Ni(cod)_2$ (134.7 mg, 4.897 x 10^{-4} mol, 1.0 equiv), PPh_3 (264.5 mg, 1.008 mmol, 2.0 equiv) and toluene (5.0 mL). 2-Chlorotoluene (87 µL, 6.9 x 10^{-1} mmol, 1.5 equiv) was added by syringe and the solution was allowed to stir at rt for 20 min. The product was precipitated by adding hexanes (20 mL), collected by filtration and washed with hexanes and cold MeOH to give 201.3 mg of **5a** as a yellow solid (58% yield). The product is air-stable. ^{31}P NMR spectrum of **5a** (162 MHz, $CDCl_3$) δ 21.19 (s).



5b

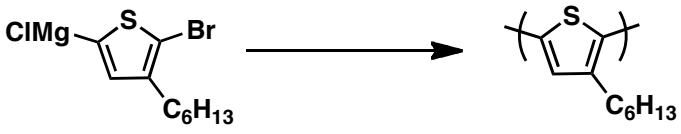
5b. In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with $Ni(cod)_2$ (142.2 mg, 5.170 x 10^{-1} mmol, 1.0 equiv), PPh_3 (268.0 mg, 1.022 mmol, 2.0 equiv) and toluene (5.0 mL). 2-Bromotoluene (90 µL, 7.483 x 10^{-1} mmol, 1.5 equiv) was added by syringe and the solution was allowed to stir

at rt for 20 min. The product was precipitated by adding hexanes (20 mL), collected by filtration and washed with hexanes and cold MeOH to give 297.2 mg of **5b** as a yellow solid (76% yield). The product is air-stable. ^{31}P NMR spectrum of **5b** (162 MHz, $CDCl_3$) δ 20.2 (s).



5a 6a

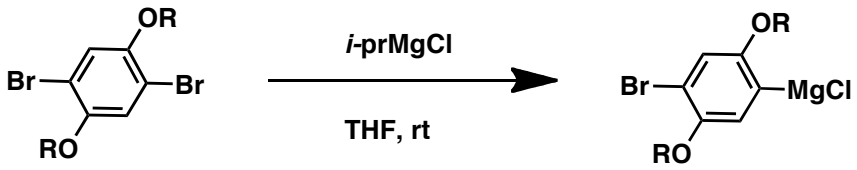
6a. In the glovebox an oven-dried 20 mL vial was equipped with a stir bar. **5a** (68.2 mg, 9.61 x 10^{-2} mmol, 1.0 equiv), THF (3 mL) and depe (32 µL, 1.4 x 10^{-2} mmol, 1.4 equiv) was added and the mixture was stirred at rt for 5 min. Hexanes (15 mL) was added and the reaction mixture cooled at -30 °C in the glovebox freezer. After 15 min the product was filtered, washed with hexanes (20 mL) and recrystallized twice from THF/hexanes to give 7 mg of **6a** as an orange solid (6% yield). The product is unstable in THF solution at high concentrations (>0.015 M) Calcd. for $C_{17}H_{31}ClNiP_2$, 390.0943 [M]+; found, 390.0954. ^{31}P NMR (132 MHz, $CDCl_3$) δ 72.43 ppm.



7 P7

P7. All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(depe)Cl_2 (5.4 mg, 0.015 mmol, 0.0015 equiv), THF (2.5 mL), and **7** (2.5 mL, 0.50 mmol, 1 equiv) were added to the vial. The reaction solution was stirred at 60 °C for 1 h. After 1 h, the reaction

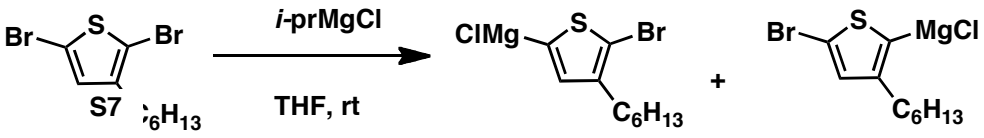
was quenched with HCl (aq., 5 mL, 5 M) and then extracted with $CHCl_3$ (3 x 5 mL). The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL) and concentrated in vacuo. A sample was taken for GPC analysis (M_n: 7.5 kDa, PDI: 2.26) and then the resulting solid was precipitated from THF/ methanol to give 0.05091 g of **P7** as a purple solid (38% yield).



S4a: R = C_6H_{13}
S4b: R = CH_3

4a: R = C_6H_{13}
4b: R = CH_3

4a/b.[1] All actions were performed in a glovebox under N_2 atmosphere. A 200 mL flask was equipped with a stir bar. Sequentially, **S4a** (14.4 g, 33.0 mmol, 1.00 equiv), THF (35 mL), and *i*-PrMgCl (15 mL, 30 mmol, 0.90 equiv) were added to the flask. The reaction solution was stirred at rt overnight. **4b** was prepared in the same manner starting from 1,4-dibromo-2,5-dimethoxybenzene (commercial).



S5

7 (80:20)

7.[1] All actions were performed in a glovebox under N_2 atmosphere. A 25 mL Schlenk tube was equipped with a stir bar. Sequentially, **S5** (2.4 g, 7.4 mmol, 1.0 equiv), THF (21 mL), and *i*-PrMgCl (3.7 mL, 7.4 mmol, 1.0 equiv) were added to the tube. The reaction solution was stirred for 1 h at rt.

IV. NMR Spectra

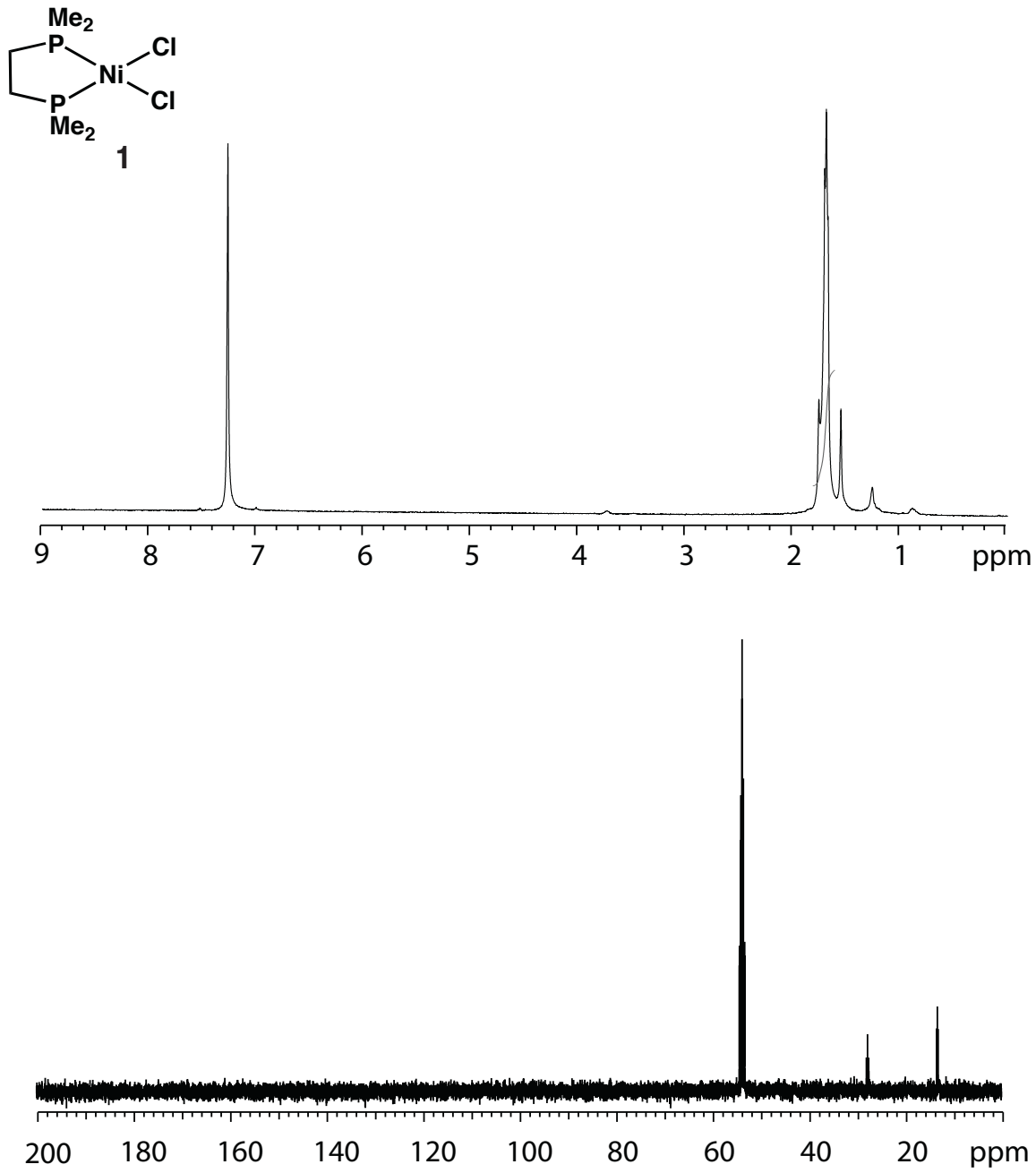


Figure S1.^{1}H and ^{13}C NMR Spectra of **Ni(dmpe)Cl$_2$** (**1**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81-1.64 (br m).
^{13}C NMR (100 MHz, $CDCl_3$) δ 27.79 (t, $J_{C\text{-}P}$ = 24.2 Hz), 13.3 (t, $J_{C\text{-}P}$ = 16.0 Hz).

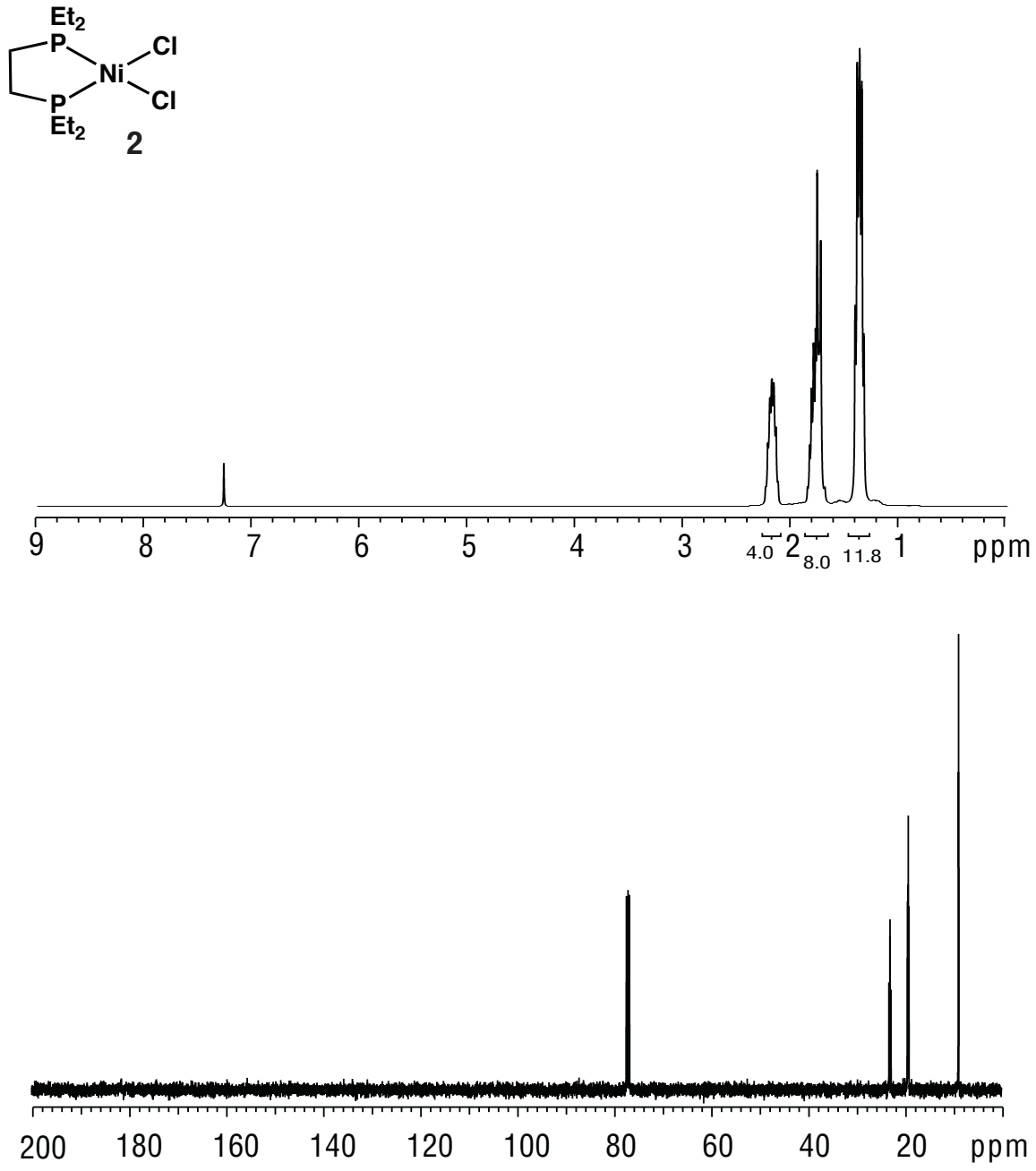


Figure S2. ^{1}H and ^{13}C NMR Spectra of **Ni(depe)Cl$_2$** (**2**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.2-2.1 (m, 4H), 1.9-1.6 (br m, 8H), 1.4-1.2 (m, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 22.98 (t, J_{C-P} = 21.9 Hz), 19.21 (t, J_{C-P} =14.4 Hz), 8.84.

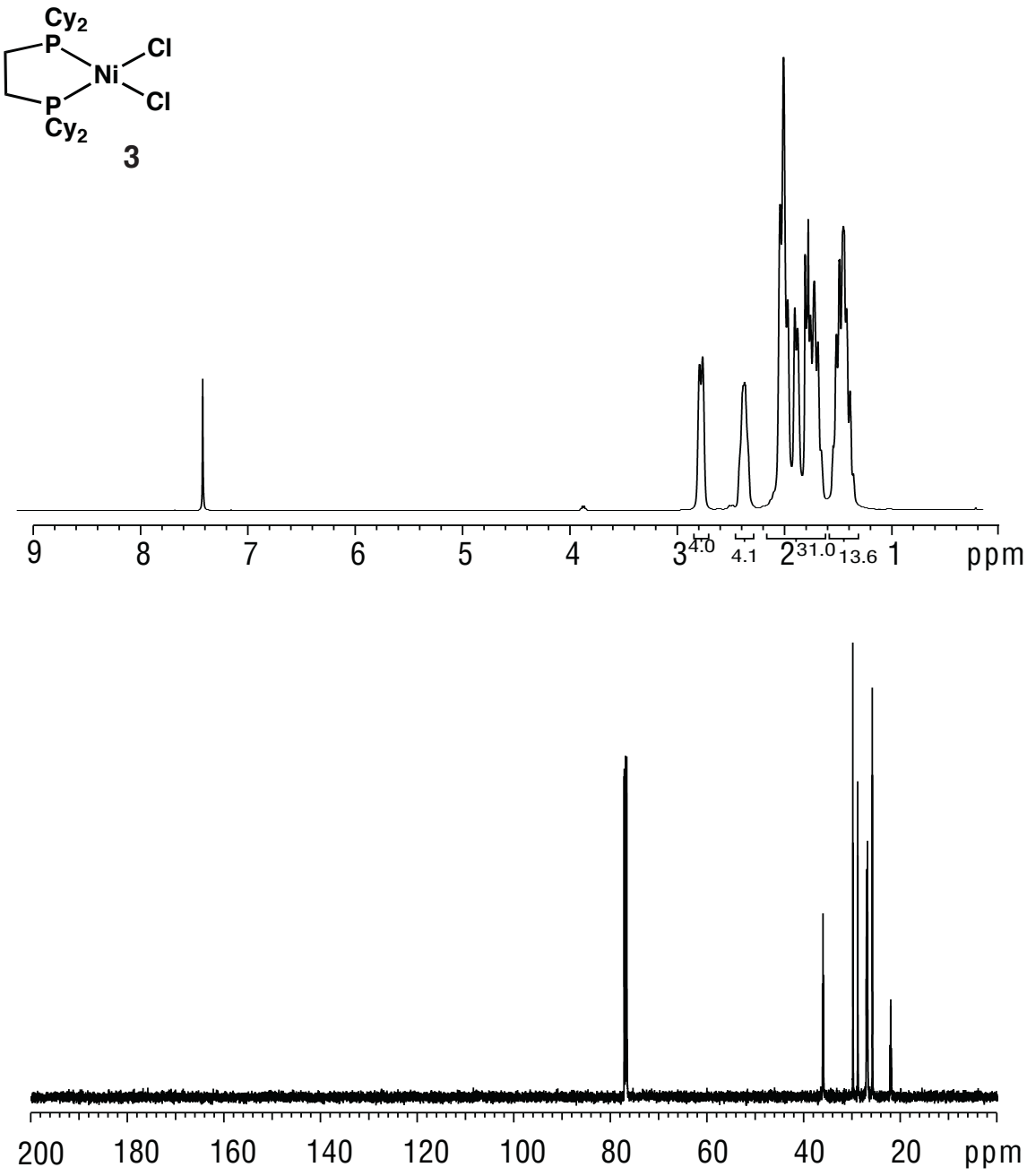


Figure S3. ^{1}H and ^{13}C NMR Spectra of **Ni(dcpe)Cl$_2$** (**3**).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.70-2.55 (m, 4H), 2.35-2.10 (m, 4H), 2.0-1.1 (m, 40H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 36.10 (t, J_{C-P} = 13.2 Hz), 29.93, 28.92, 27.10 (t, J_{C-P} = 6.4 Hz), 26.90 (t, J_{C-P} = 4.2 Hz), 25.89, 22.08 (t, J_{C-P} = 20.2 Hz).

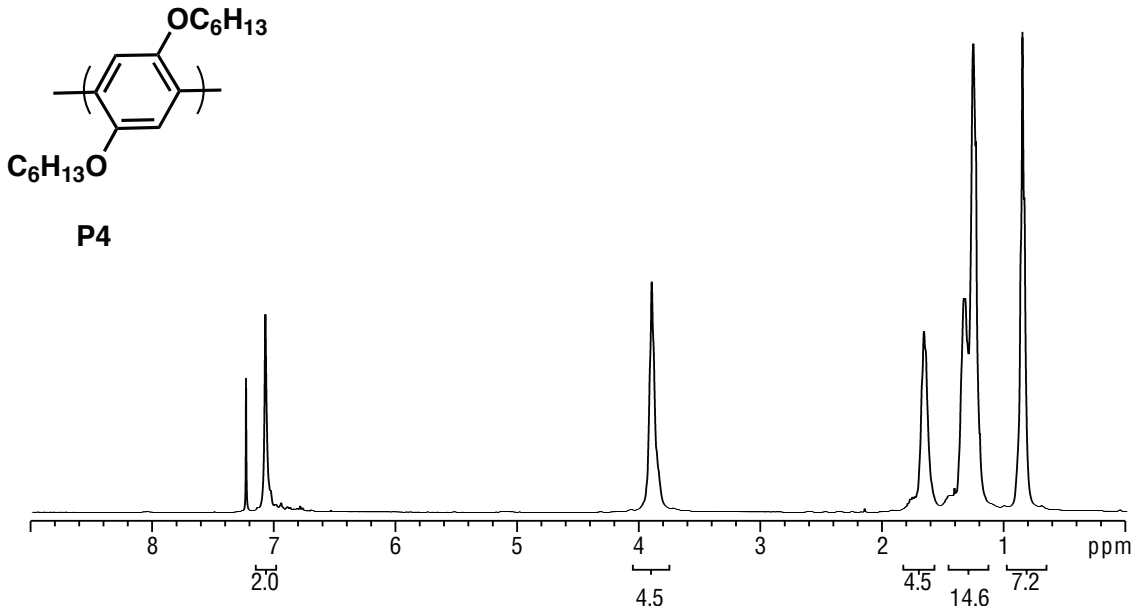


Figure S4. ^{1}H NMR Spectrum of **P4a.**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 3.90 (br m, 4H), 1.66 (br m, 4H), 1.34-1.26 (br m, 12 H), 0.85 (br m, 6H).

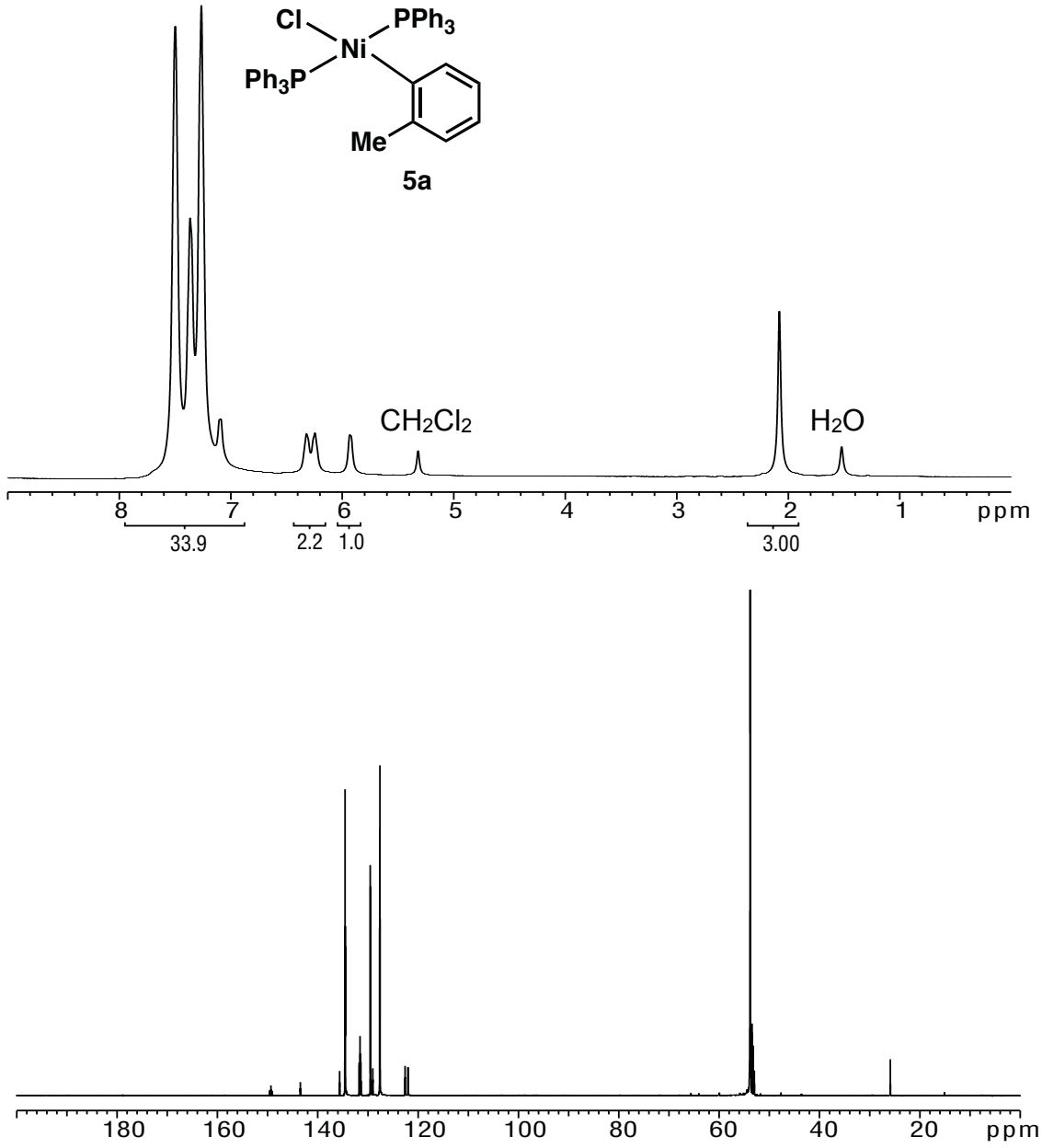


Figure S5. ^{1}H and ^{13}C NMR Spectra of **5a**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7-6.9 (m, 31H), 6.4-6.1 (m, 2H), 5.9 (br s, 1H), 2.08 (br s, 3H). ^{13}C NMR (100 MHz, CH_2Cl_2:CD_2Cl_2 (1:1)) δ 149.71 (t, J_{C-P} = 32.66 Hz), 143.86 (t, J_{C-P} = 3.49 Hz), 136.02 (t, J_{C-P} = 4.27 Hz), 134.93 (t, J_{C-P} = 5.80 Hz), 131.96 (t, J_{C-P} = 21.79 Hz), 129.91, 129.38 (t, J_{C-P} = 2.93 Hz), 128.01 (t, J_{C-P} = 4.91 Hz), 122.98 (t, J_{C-P} = 2.27 Hz), 122.39 (t, J_{C-P} = 2.22 Hz), 26.26.

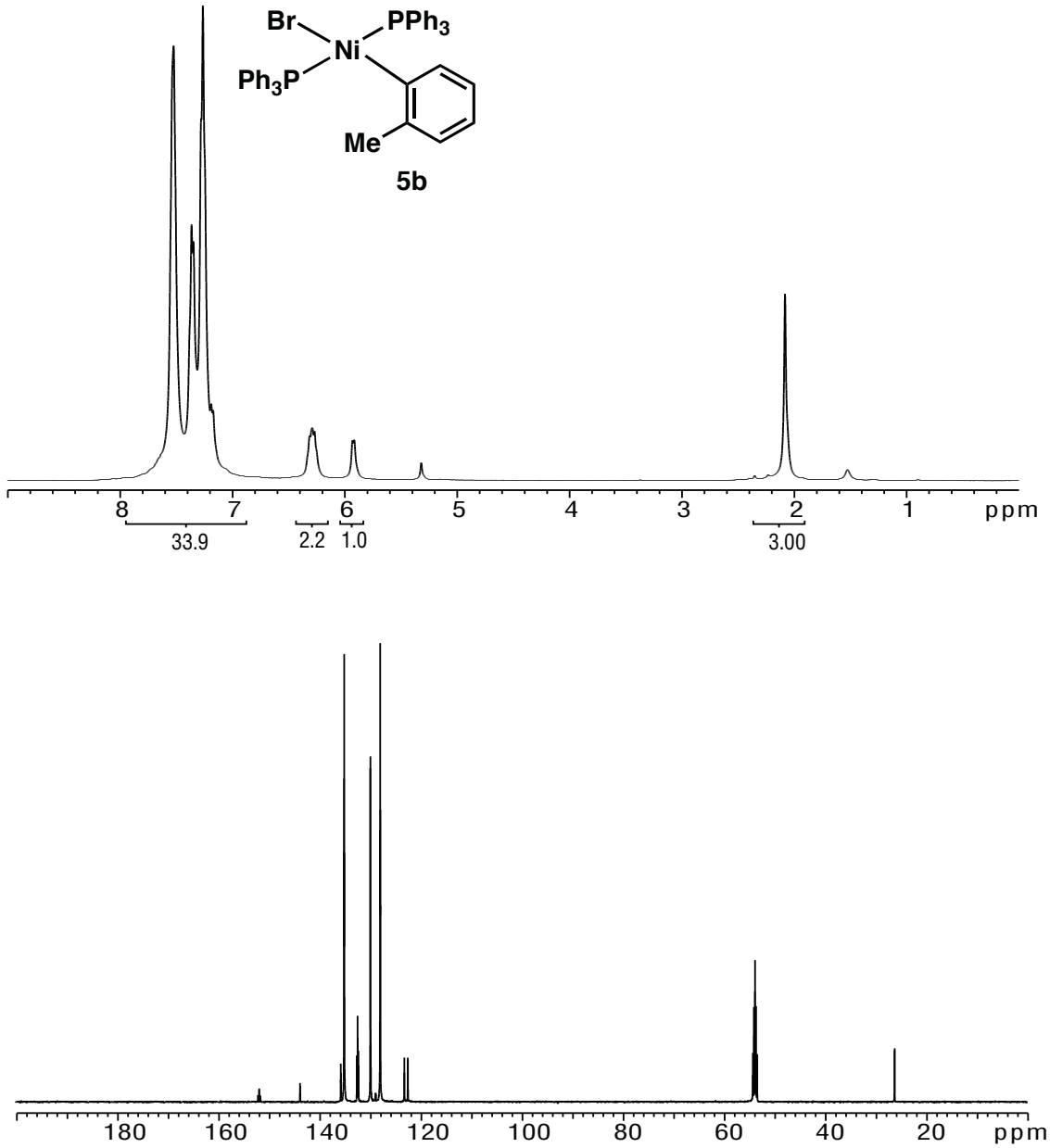


Figure S6. ^{1}H and ^{13}C NMR Spectra of **5b**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7-7.1 (m, 31H), 6.29 (m, 2H), 5.92 (br s, 1H), 2.08 (br s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 151.87 (t, J_{C-P} = 32.75 Hz), 143.78 (t, J_{C-P} = 3.76 Hz), 135.72 (t, J_{C-P} = 3.90 Hz), 135.06 (t, J_{C-P} = 5.26 Hz), 132.40 (t, J_{C-P} = 20.86 Hz), 129.88,
128.84 (d, J_{C-P} = 11.08 Hz), 127.93 (t, J_{C-P} = 4.93 Hz), 123.16, 122.42, 26.18.

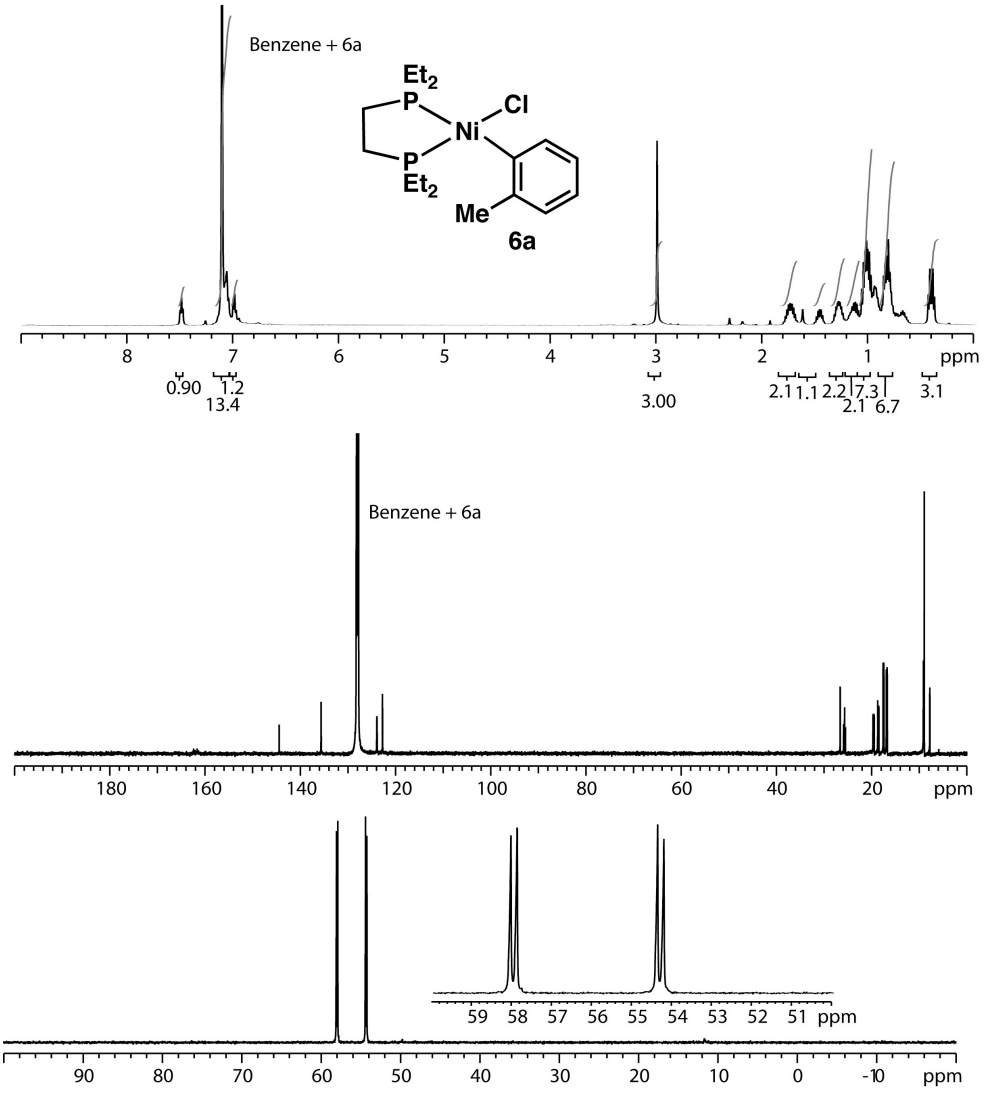


Figure S7. ^{1}H, ^{13}C and ^{31}P NMR Spectra of **6a**.
^{1}H NMR (400 MHz, C_6D_6) δ 7.5-7.4 (m, 1H), 7.2-7.0 (m, 2H), 7.0-6.9 (m, 1H), 3.0 (br s, 3H), 1.8-1.7 (m, 2H), 1.5-1.4 (m, 1H), 1.4-1.2 (m, 2H), 1.2-1.1 (m, 2H), 1.1-1.0 (m, 2H), 0.88-0.76 (m 6H), 0.48-0.31 (m, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 162.06 (d, J_{C-P} = 91.8 Hz), 135.65 (dd, J_{C-P} = 2.4, 1.5 Hz), 128.29, 123.95 (dd, J_{C-P} = 2.5, 4.4 Hz), 122.75 (d, J_{C-P} = 3.8 Hz), 26.63 (d, J_{C-P} = 1.5 Hz), 25.71 (t, J_{C-P} = 24.2 Hz), 19.61 (dd, J_{C-P} = 21.4, 11.5 Hz), 18.61 (dd, J_{C-P} = 2.3, 31.7 Hz), 17.5 (d, J_{C-P} = 20.9 Hz), 16.83 (dd, J_{C-P} = 4.5, 25.3 Hz), 9.16, 8.97, 7.8 (d, J_{C-P} = 5.0 Hz))

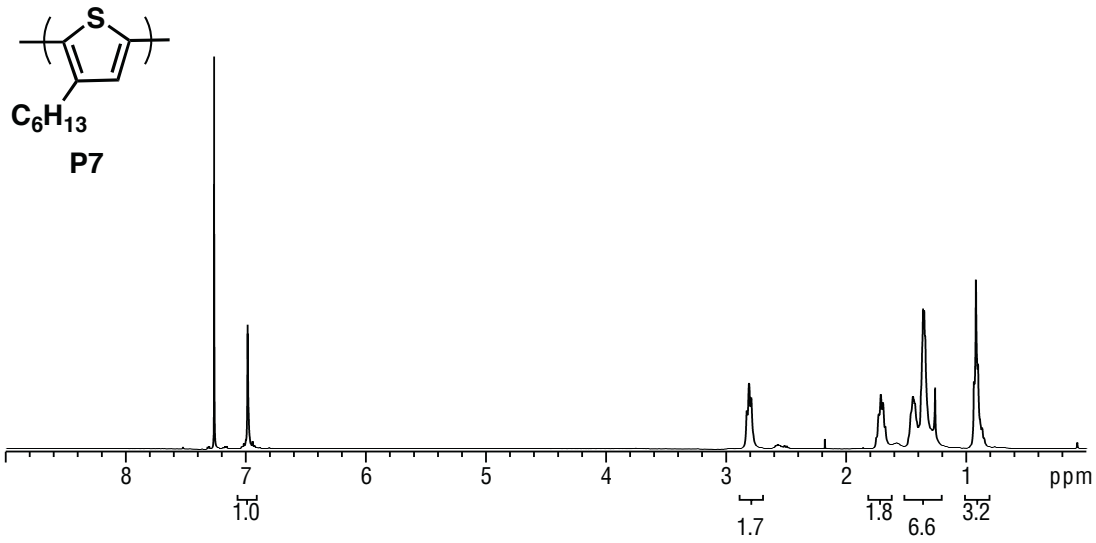


Figure S8. ^{1}H NMR Spectrum of **P7**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 2.78 (br m, 2H), 1.69 (br m, 2H), 1.44-1.23 (br m, 6 H), 0.89 (br m, 3H).

V. Representative GPC Traces

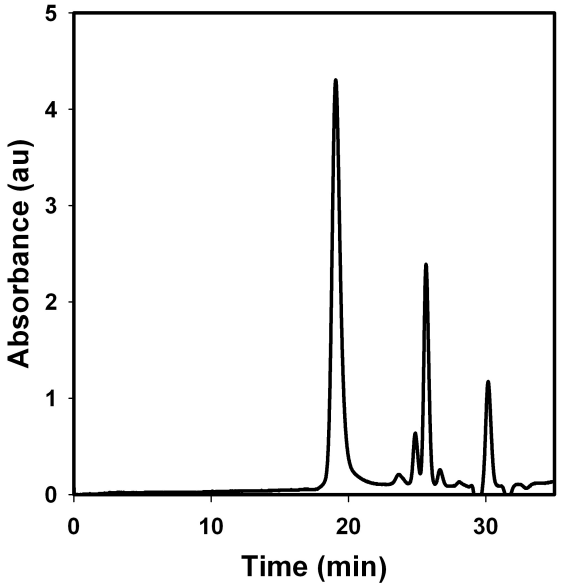


Figure S9. Representative GPC trace of **P4a** with catalyst **2** (M_n: 21.5 kDa; PDI: 1.18) performed by the author.

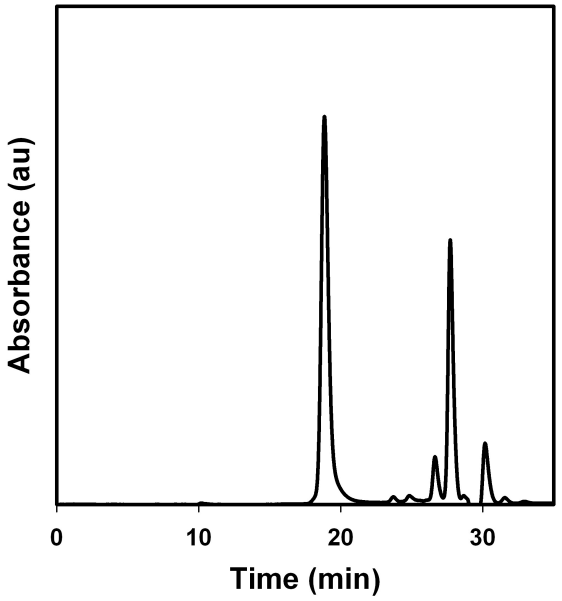


Figure S10. Representative GPC trace of **P7** with catalyst **2** (M_n: 19.3 kDa; PDI: 1.20) performed by the author.

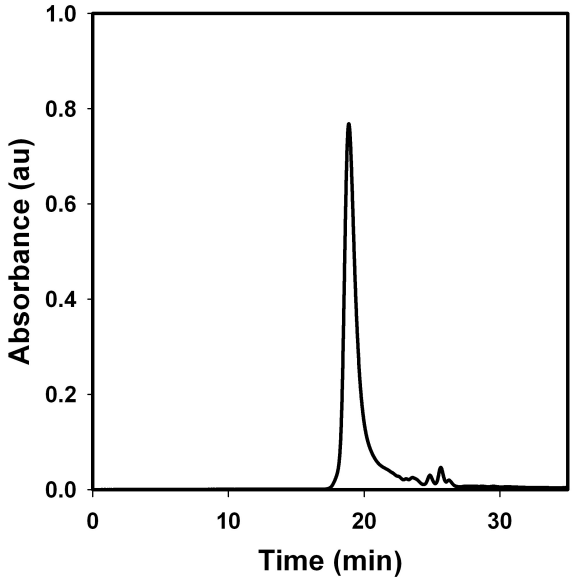


Figure S11. Representative GPC trace of **P4a** with catalyst **2** (M_n: 9.5 kDa, PDI: 2.12) performed by Jonas Locke.

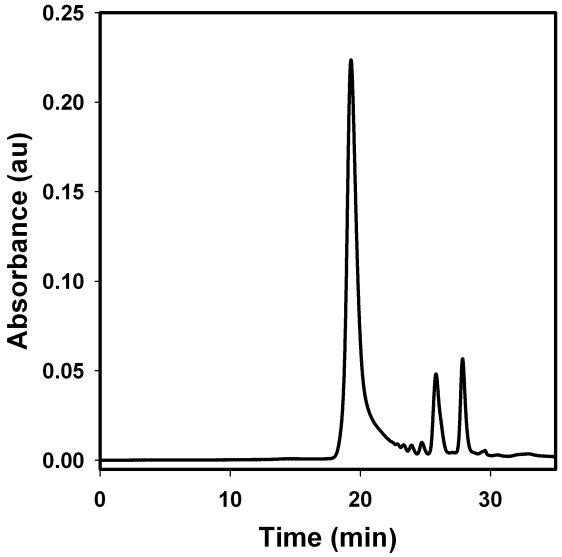


Figure S12. Representative GPC trace of **P7** (M_n: 7.5 kDa, PDI: 2.26) performed by Jonas Locke.

VI. Calibration Curve

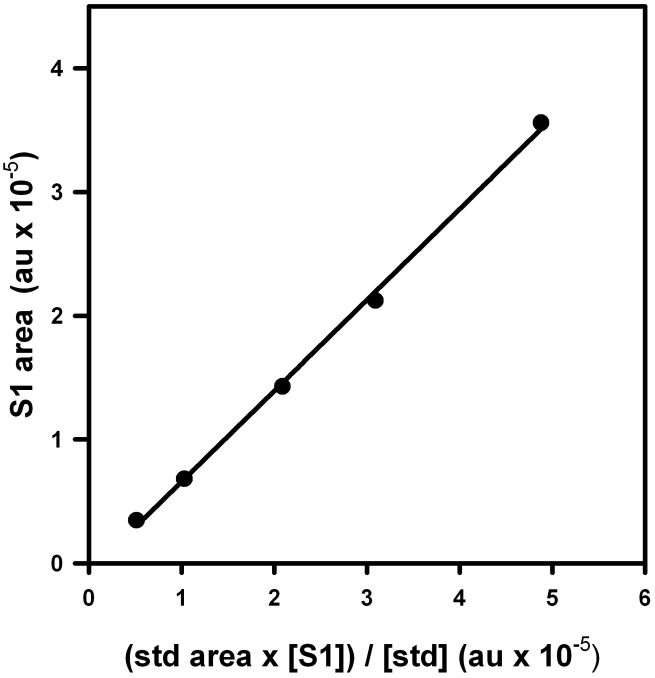


Figure S13. Plot of analyte area versus (std area x [**S1**]) / [std] fit to y = *m*x + *b* where *m* = 0.803 ± 0.006 and *b* = -73 ± 2.

Table S1. Data for the plot in Figure S13.

[**S1**]	area **S1** (analyte)	area docosane (std)	(std area x [**S1**]) / [std]
2.97×10^{-3}	3.58×10^{5}	16.4×10^{6}	4.88×10^{5}
1.78×10^{-3}	2.18×10^{5}	17.4×10^{6}	3.09×10^{5}
1.19×10^{-3}	1.42×10^{5}	17.6×10^{6}	2.08×10^{5}
0.593×10^{-3}	0.680×10^{5}	17.4×10^{6}	1.03×10^{5}
0.297×10^{-3}	0.347×10^{5}	17.3×10^{6}	0.514×10^{5}

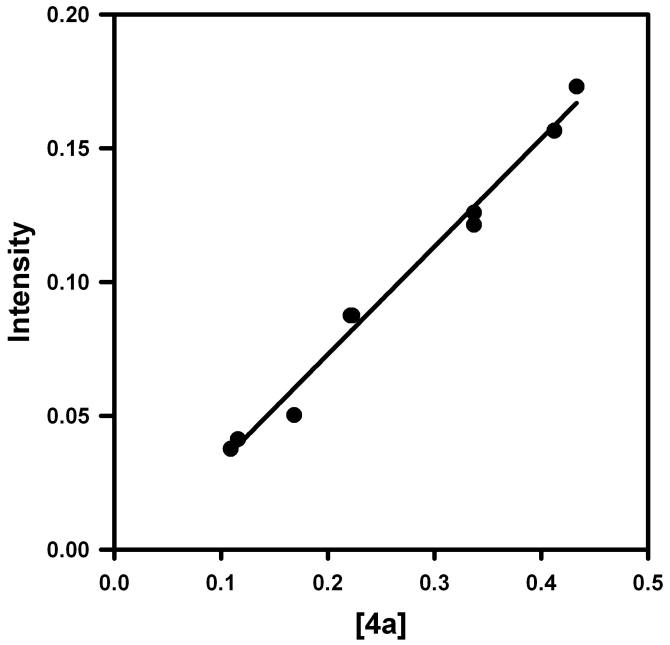


Figure S14. Plot of absorbance versus [**4a**] (temp = 50 °C) fit to y = *m*x + *b* where *m* = 0.40 ± 0.02 and *b* = -0.008 ± 0.005.

Table S2. Data for the plot in Figure S14.

Intensity	[4a]
0.0376	0.109
0.0412	0.116
0.0502	0.168
0.0874	0.223
0.0874	0.221
0.121	0.337
0.126	0.337
0.157	0.412
0.173	0.433

VII. Representative GC Traces

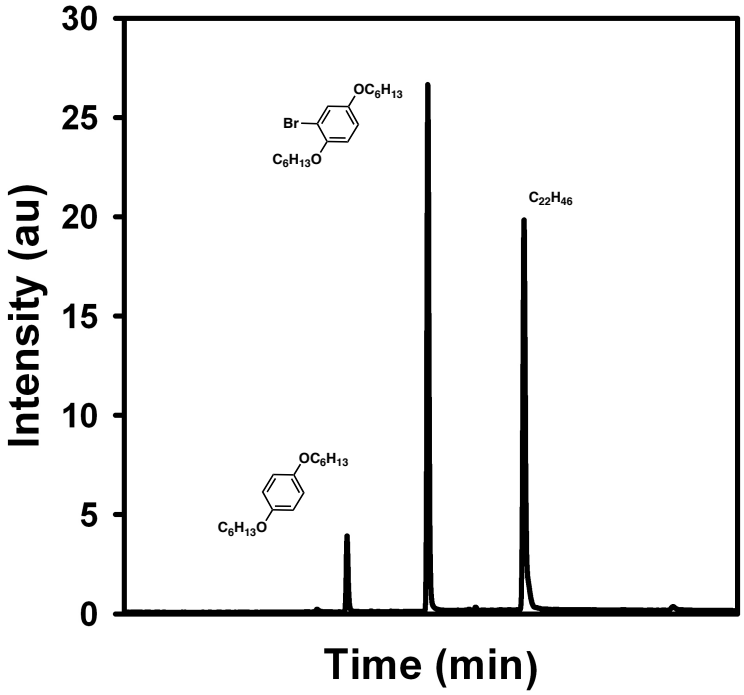


Figure S15. Representative GC trace of the polymerization of **4a** with **2**.

.

VIII.Reaction Screens

Table S3: Summary of screening reactions using **4a** (left: trial 1; right: trial 2, [Ni(depe)Cl_2] = 0.0015 M, [**4a**] = 0.10 M) performed by the author.

Temperature	rt					rt			
Catalyst	**Conv (%)**	**Yield (%)**	**Mn (kDa)**	**PDI**		**Conv (%)**	**Yield (%)**	**Mn (kDa)**	**PDI**
dppe	97	--	25	1.2		97	--	27	1.2
dppp	94	--	29	1.6		96	--	16	1.3
1	6	--	--	--		6	--	--	--
2	81	--	21	1.2		71	--	19	1.1
3	4	--	--	--		5	--	--	--
4	4	--	--	--		4	--	--	--

Temperature	60 °C					60 °C			
Catalyst	**Conv**	**Yield**	Mn	PDI		**Conv**	**Yield**	Mn	PDI
dppe	97	--	28	1.4		96	--	28	1.5
dppp	97	--	16	1.9		97	--	12	1.5
1	97	60	23	1.4		97	60	23	1.2
2	97	73	23	1.1		97	54	24	1.4
3	20	--	3.1	16		17	--	3.6	13
4	25	--	5.7	11		21	--	4.9	11

Table S4: Summary of screening reactions using **4a** (left: trial 1; right: trial 2, [Ni(depe)Cl_2] = 0.0015 M, [**4a**] = 0.10 M) performed by Jonas Locke

Temp	rt (6-7 h)				rt (6-7 h)			
Cat.	**Conv (%)**	**Yield (%)**	**M_n (kDa)**	**PDI**	**Conv (%)**	**Yield (%)**	**M_n (kDa)**	**PDI**
Ni(dppe)Cl_2	97	-	15	1.56	97	-	16	1.54
Ni(dppp)Cl_2	94	-	15.4	2.37	96	-	8.2	1.97
1	6	-	-	-	6	-	-	-
2	81	-	13	1.40	71	-	13	1.33
3	4	-	-	-	4	-	-	-

Temp	60 °C (1 h)				60 °C (1 h)			
Cat.	**Conv (%)**	**Yield (%)**	**M_n (kDa)**	**PDI**	**Conv (%)**	**Yield (%)**	**M_n (kDa)**	**PDI**
Ni(dppe)Cl_2	95	50	8.6	2.42	95.3	53	8.5	2.52
Ni(dppp)Cl_2	94	51	5.0	3.59	94	50	5.0	3.35
1	32	21	1.6	1.51	1.8	-	1.8	1.56
2	95	64	9.5	2.12	94	50	15	1.98
3	25	10	0.8	1.02	23	0	0.8	1.01

Table S5: Summary of screening reactions using **7** (left: trial 1; right: trial 2, [Ni(depe)Cl_2] = 0.0015 M, [**Monomer**] = 0.10 M) performed by Jonas Locke.

Monomer	7 (60 °C, 1 h)				7 (60 °C, 1 h)			
Cat.	**Conv (%)**	**Yield (%)**	**M_n (kDa)**	**PDI**	**Conv (%)**	**Yield (%)**	**M_n (kDa)**	**PDI**
Ni(dppe)Cl_2	93	54	6.5	2.29	93	39	6.3	2.59
Ni(dppp)Cl_2	91	61	10.6	1.77	91	62	6.6	2.30
2	94	38	7.6	2.26	94	67	6.4	2.1

IX. M_n and PDI versus Conversion Studies

Representative procedure for obtaining plots of M_n and PDI versus conversion utilizing GC:

All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(depe)Cl_2 (2.5 mg, 0.0075 mmol, 0.0015 equiv), THF (4.0 mL), and **5** (1.0 mL, 0.5 mmol, 1.0 equiv) were added to the vial. The vial was sealed with a septum cap and heated to 60 °C. Aliquots (~ 0.025 mL) were withdrawn through the septum and a portion rapidly quenched with MeOH (0.2 mL), diluted with $CHCl_3$ and analyzed by GC. The remainder of the aliquot was quenched with HCl (aq., 1 mL, 5 M) extracted with $CHCl_3$ (3 mL, with mild heating if polymer had precipitated) and then concentrated. The samples were dissolved in THF (with heating) and passed through a 0.2 μm PTFE filter for GPC analysis.

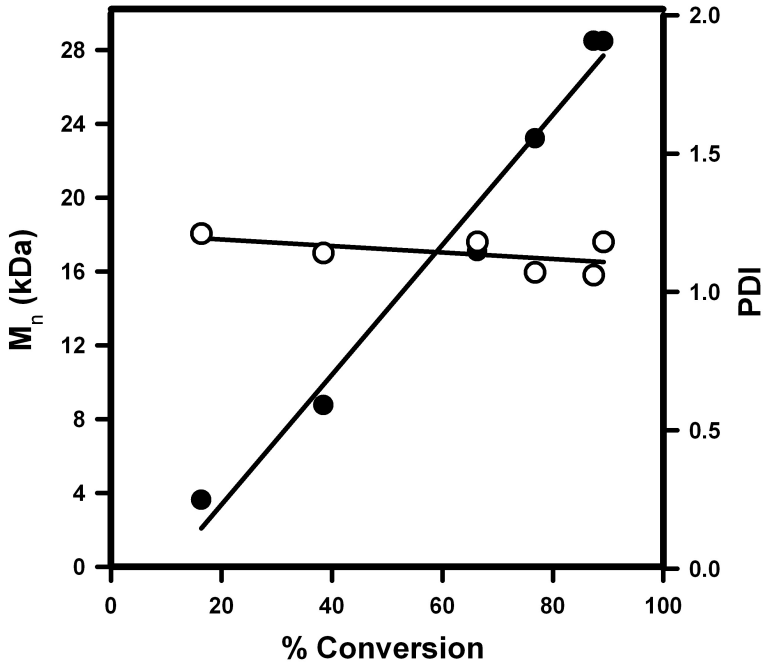


Figure S16. Plot of Mn (●) and PDI (○) versus conversion for **4a** (temp = 60 °C, [Ni(depe)Cl_2] = 0.0015 M, [**4a**] = 0.1 M).

Table S6. Data for the plot in Figure S16.

% Conversion (**4a**)	M_n (kDa)	PDI
16	3.6	1.21
38	8.8	1.14
66	17	1.18
76	23	1.07
87	28	1.06
88	28	1.18

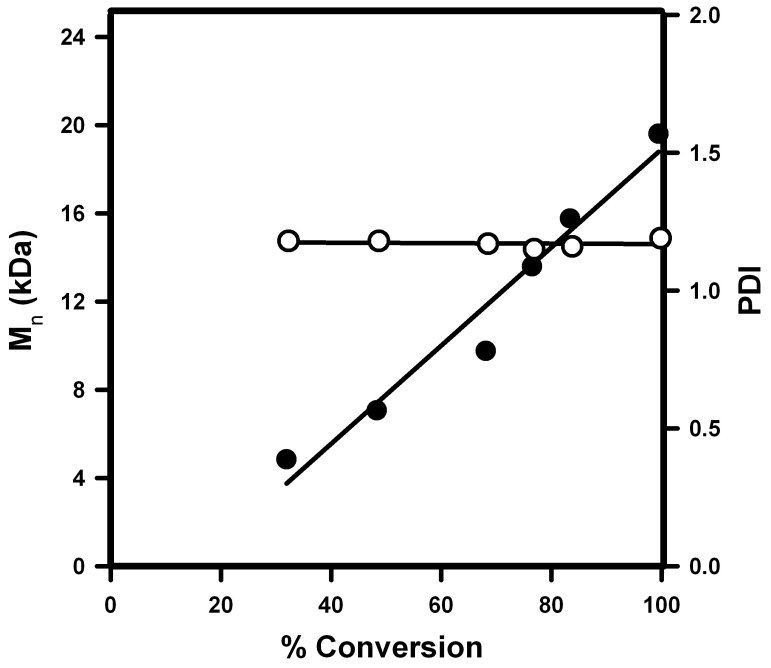


Figure S17. Plot of Mn (●) and PDI (○) versus conversion for **7** (temp = 60◦°C, [Ni(depe)Cl_2] = 0.0015 M, [**7**] = 0.1 M).

Table S7. Data for the plot in Figure S17.

% Conversion (**7**)	M_n (kDa)	PDI
32	4.8	1.18
48	7.1	1.18
68	9.7	1.17
76	13	1.15
83	16	1.16
99	20.0	1.19

X. Rate Studies

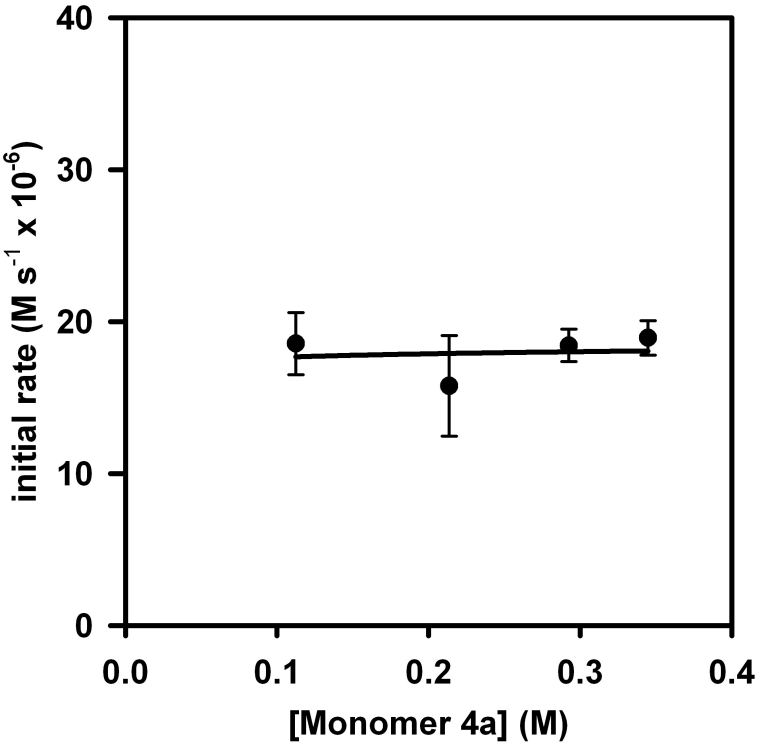


Figure S18. Plot of initial rate versus [monomer] for the polymerization of **4a** (temp = 50 °C**,** [**Ni**] = 0.0015 M in THF). The curve depicts an unweighted least-squares fit to the expression initial rate = *a*[monomer]^{n} that gave *a* = 18 ± 3 and *n* = -0.02 ± 0.01.

Table S8. Data for the plot in Figure S18.

[**4a**] (M)	initial rate (M s^{-1})
0.11	19 ± 2 x 10^{-6}
0.22	15 ± 3 x 10^{-6}
0.30	18 ± 1 x 10^{-6}
0.34	19 ± 1 x 10^{-6}

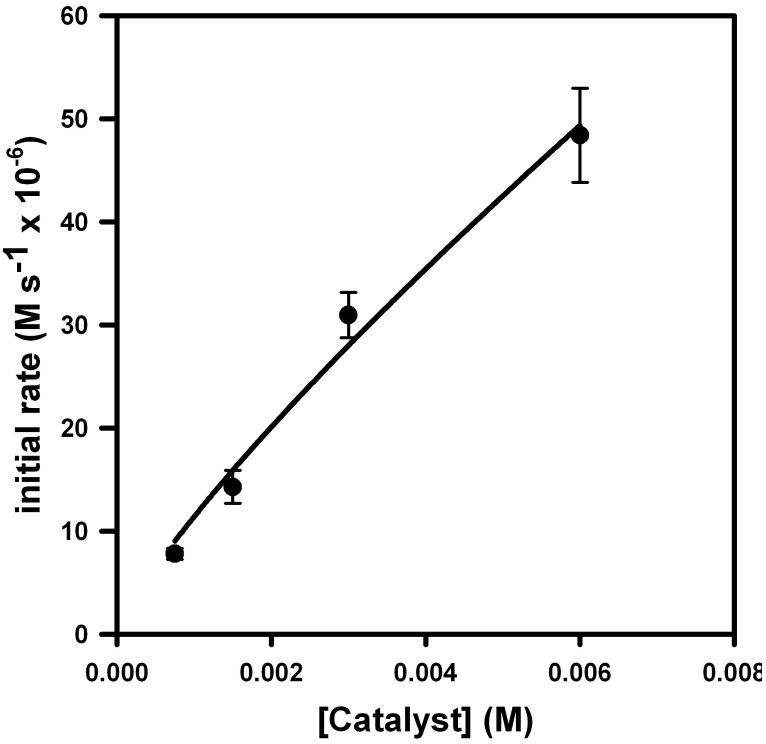


Figure S19. Plot of initial rate versus [catalyst] for the polymerization of **4a** (temp = 50 °C, [**4a**] = 0.30 M in THF). The curve depicts an unweighted least-squares fit to the expression initial rate = a[catalyst]^n that gave a = (3 ± 1) x 10^3 and n = 0.82 ± 0.09.

Table S9. Data for the plot in Figure S19.

[**Cat.**] (M)	initial rate (M s^{-1})
0.00075	7.8 ± 0.5 x 10^{-6}
0.0015	14 ± 2 x 10^{-6}
0.003	31 ± 2 x 10^{-6}
0.006	48 ± 5 x 10^{-6}

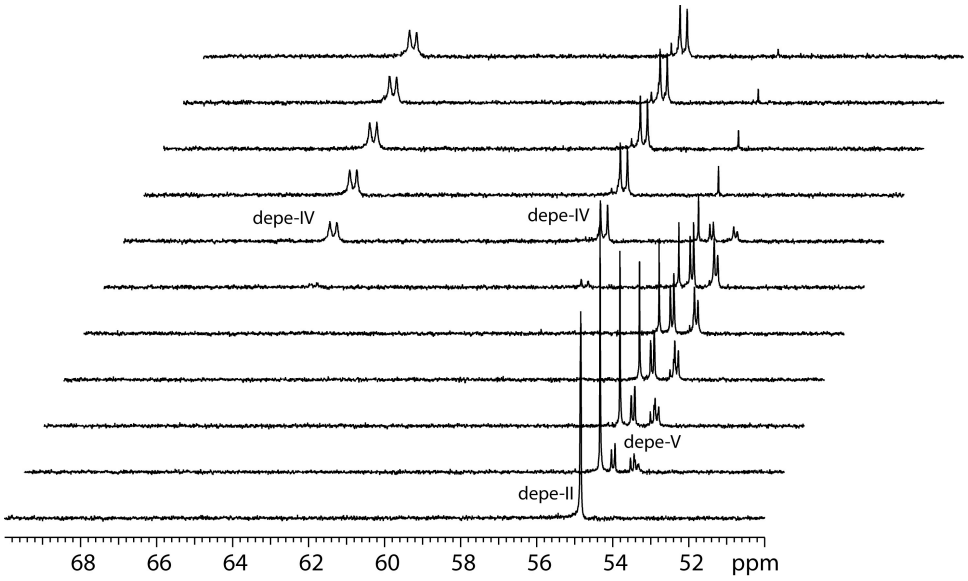


Figure S20. ^{31}P NMR (162 MHz, THF, rt), spectra of the reaction of **4a** with **2** (were averaged over 16 scans (33s) and were acquired every 35 min).

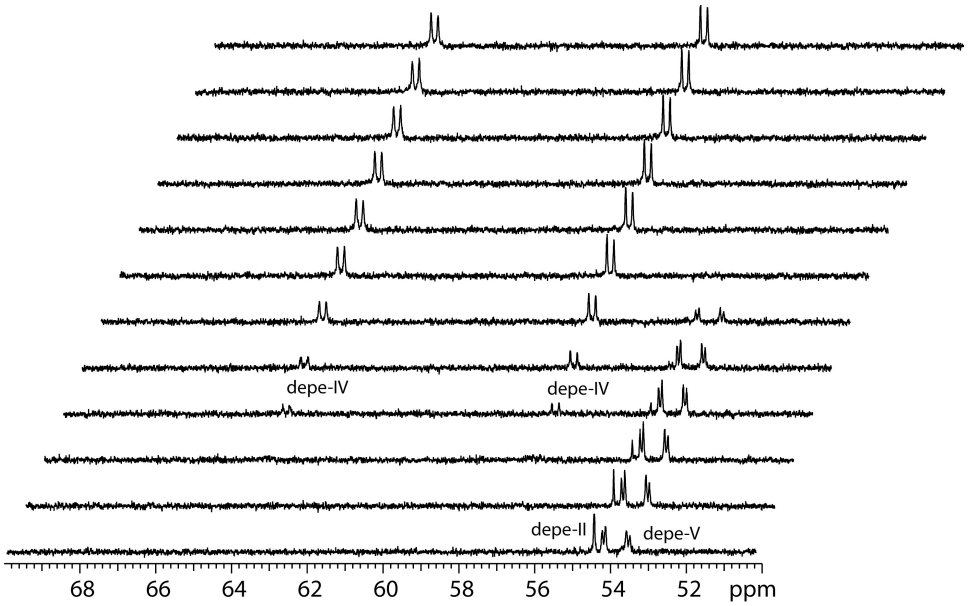


Figure S21. ^{31}P NMR (162 MHz, THF, 60 °C) spectra of the reaction of **4a** with **2** (were averaged over 16 scans (33s) and were acquired every 35 min).

XII. NMR Spectroscopic Studies

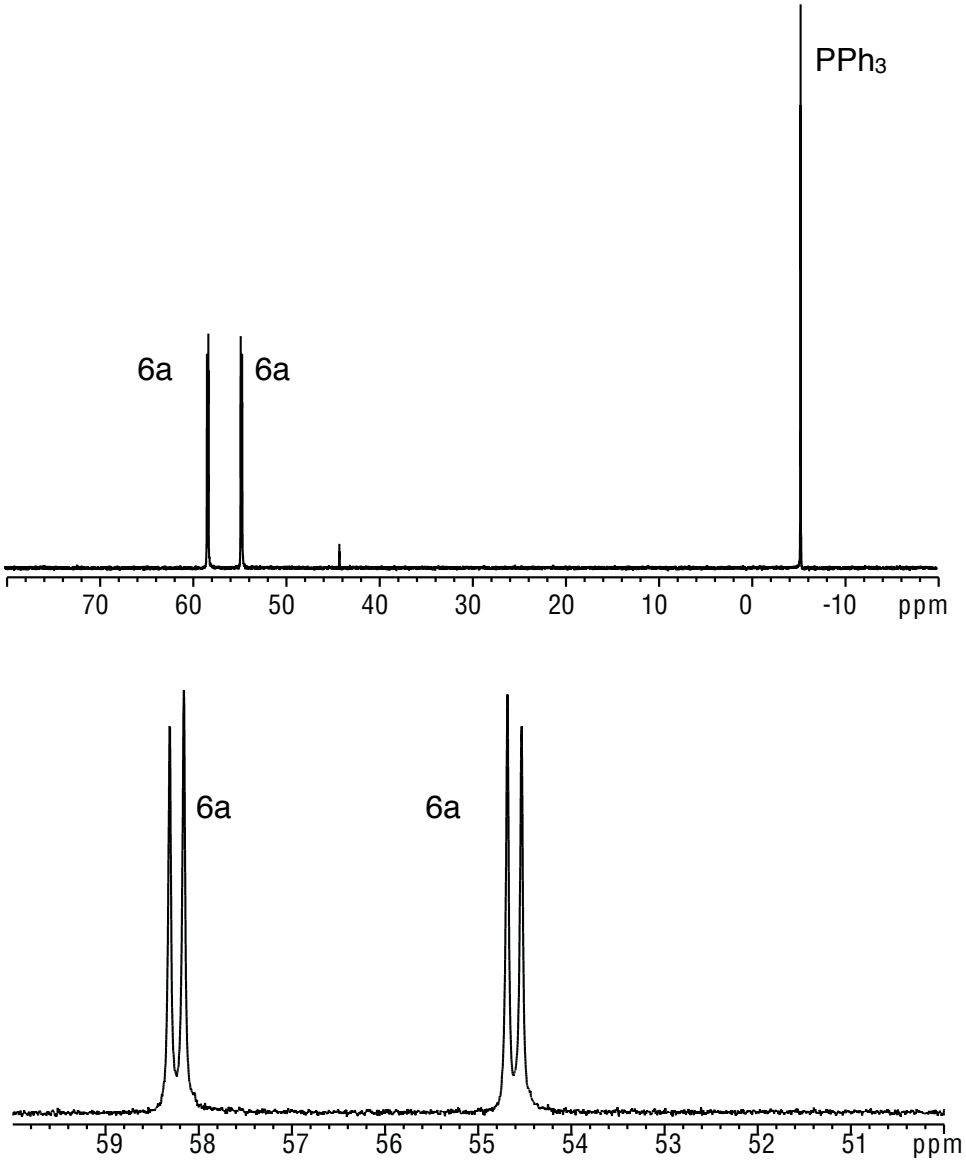


Figure S22. ^{31}P NMR spectra of complex **5a** combined with depe to form complex **6a**, (162 MHz, THF, rt) δ 58.2 (d, $J_{P\text{-}P}$ = 25.7 Hz), 54.6 (d, $J_{P\text{-}P}$ = 25.7 Hz).

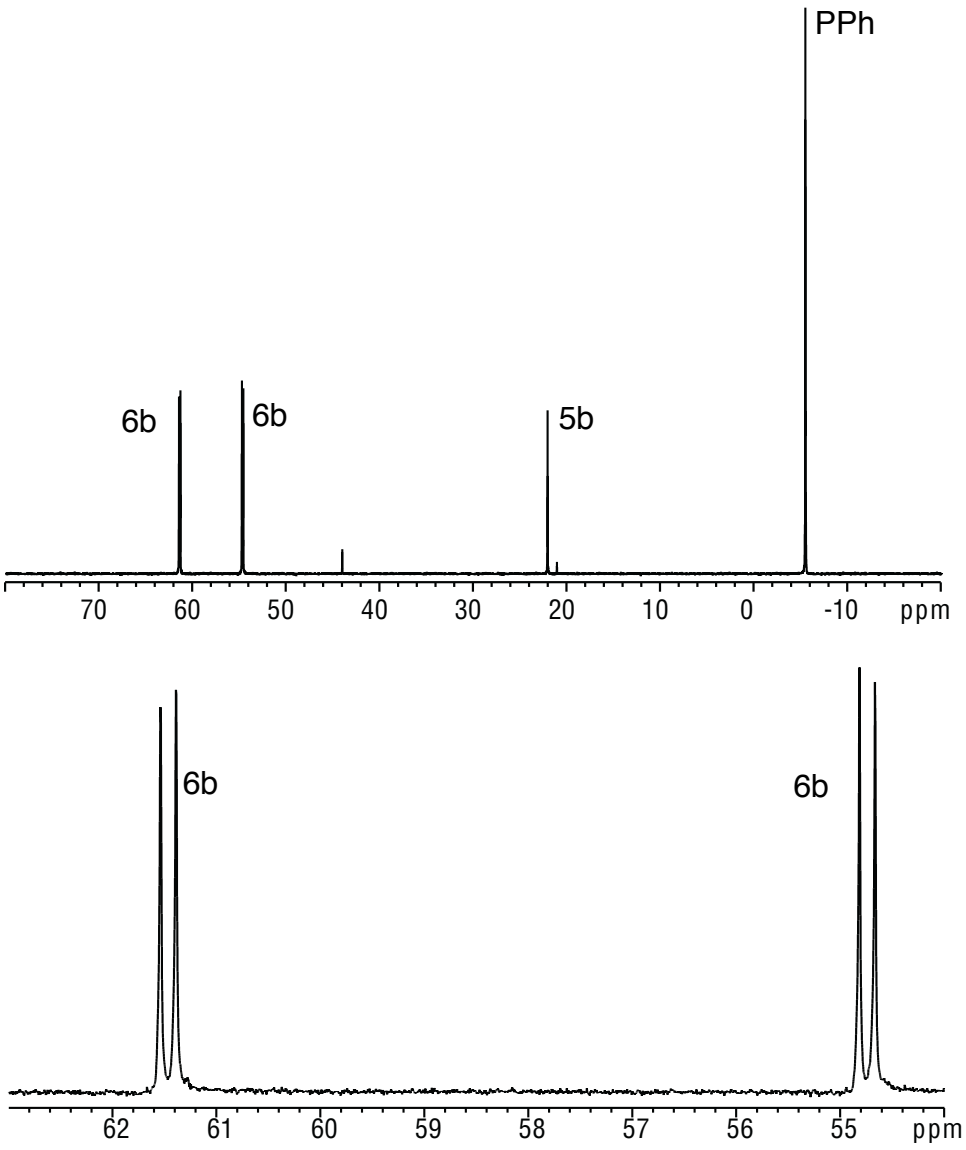


Figure S23. ^{31}P NMR spectra of complex **5b** combined with depe to form complex **6b**, (162 MHz, THF, rt) δ 61.5 (d, $J_{P\text{-}P}$ = 24.3 Hz), 54.8 (d, $J_{P\text{-}P}$ = 24.3 Hz).

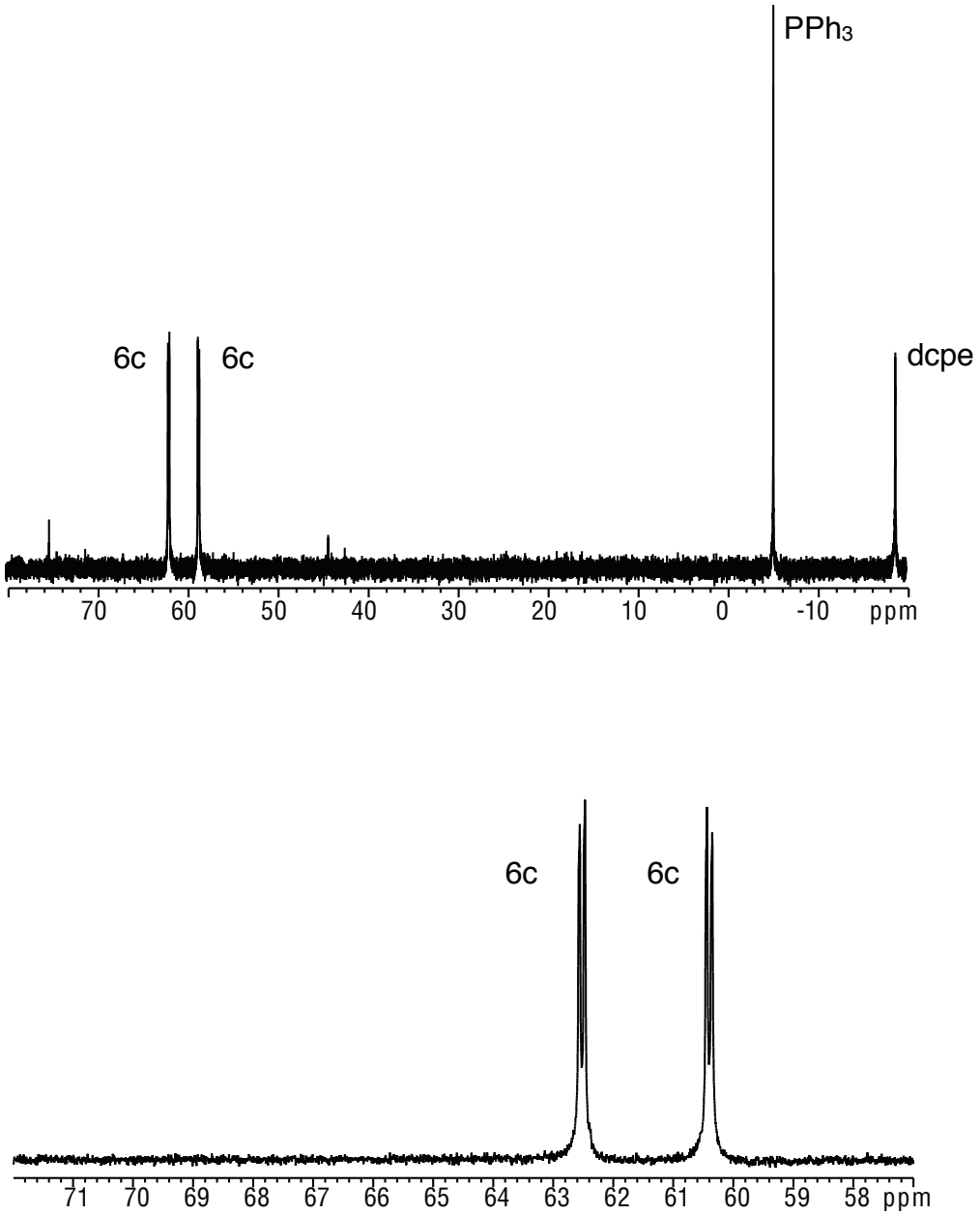


Figure S24. ^{31}P NMR spectra of complex **5a** combined with dcpe to form complex **6c** (162 MHz, THF, rt) δ 62.9 (d, $J_{P\text{-}P}$ = 17.8 Hz), 60.76 (d, $J_{P\text{-}P}$ = 17.8 Hz).

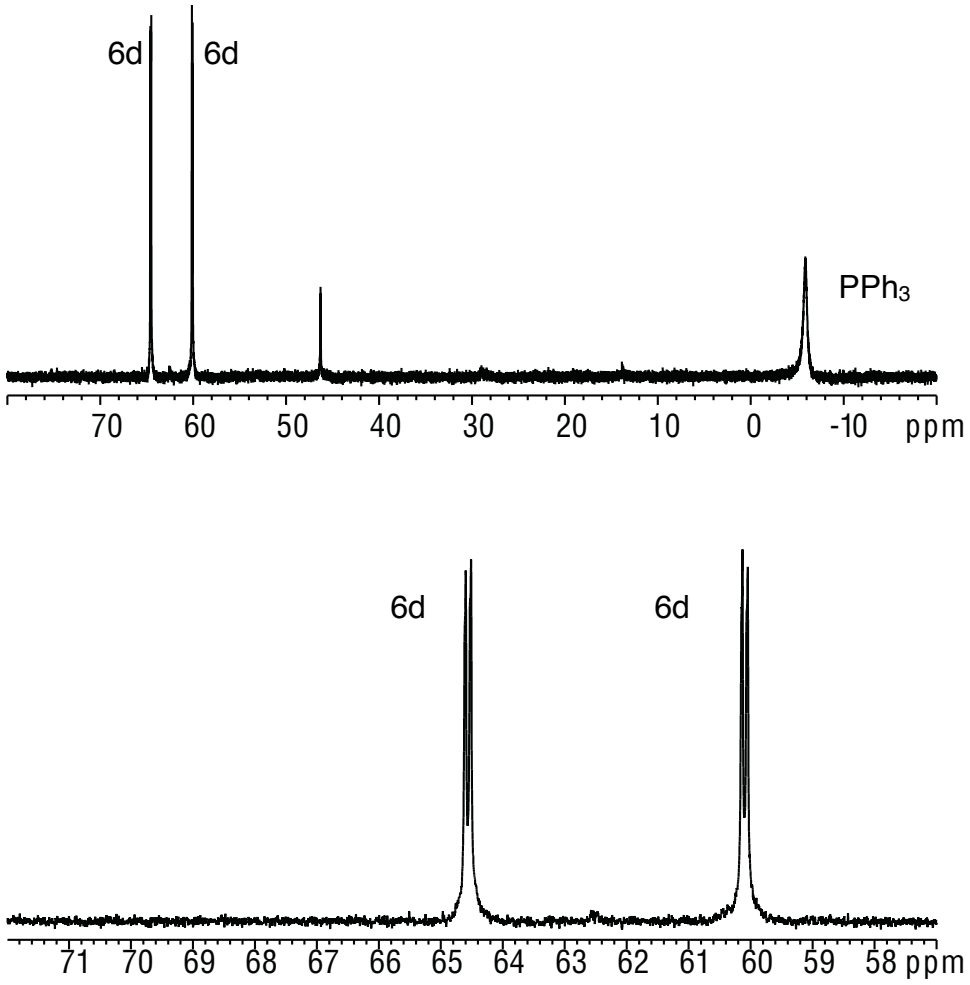


Figure S25. ^{31}P NMR spectra of complex **5d** combined with dcpe to form complex **6d** (162 MHz, THF, rt) δ 64.9 (d, $J_{P\text{-}P}$ = 17.3 Hz), 60.5 (d, $J_{P\text{-}P}$ = 17.2 Hz).

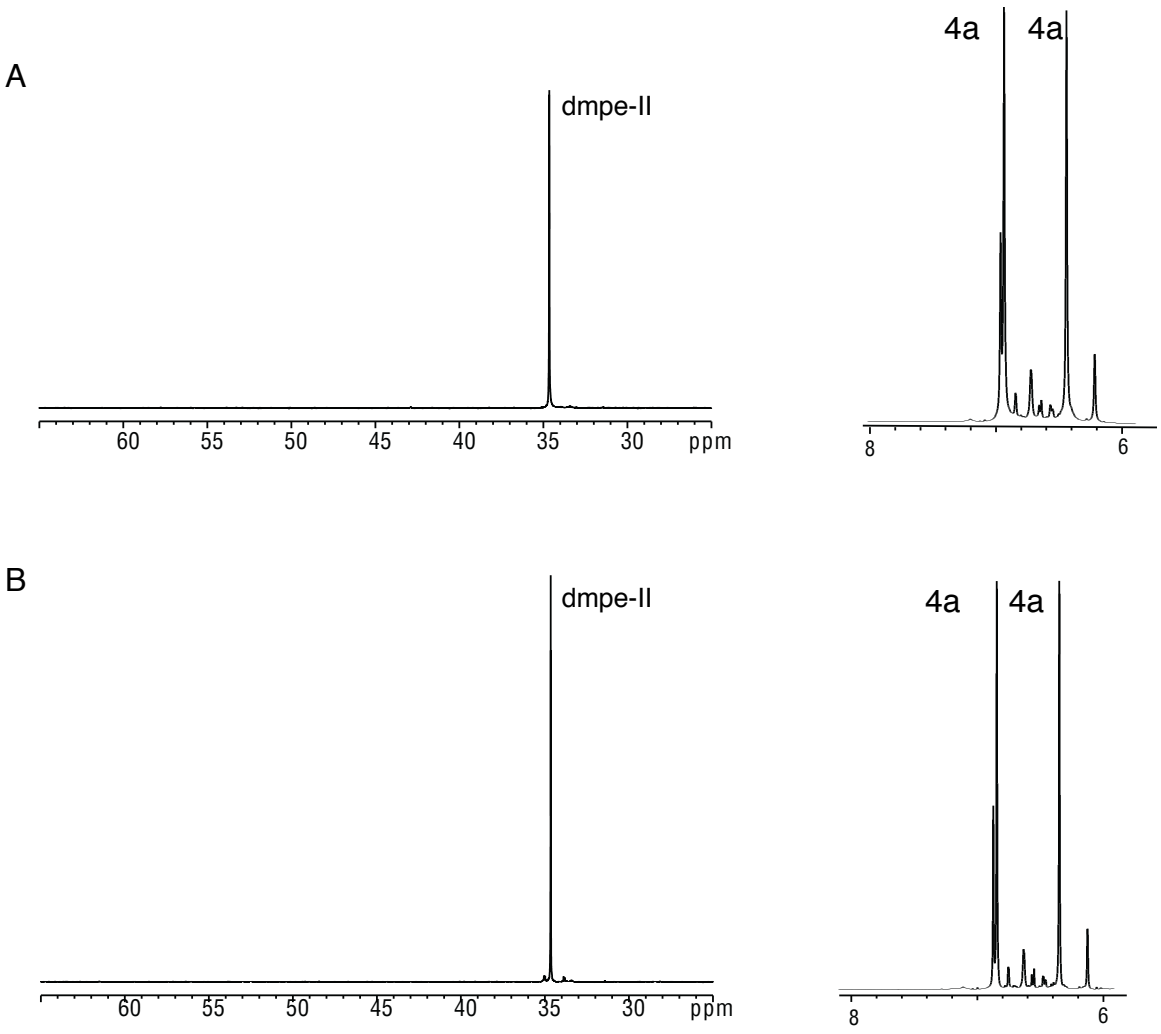


Figure S26. (A) ^{31}P NMR spectrum (202 MHz, THF, rt) for the reaction of monomer **4a** with catalyst **1** showing the complex observed during initiation (δ 34.2) and selected portions of the ^{1}H NMR spectrum. (B) ^{31}P NMR spectrum (202 MHz, THF, rt) for the catalyst resting state after 150 min at rt (δ 34.2) and selected portions of the ^{1}H NMR spectrum.

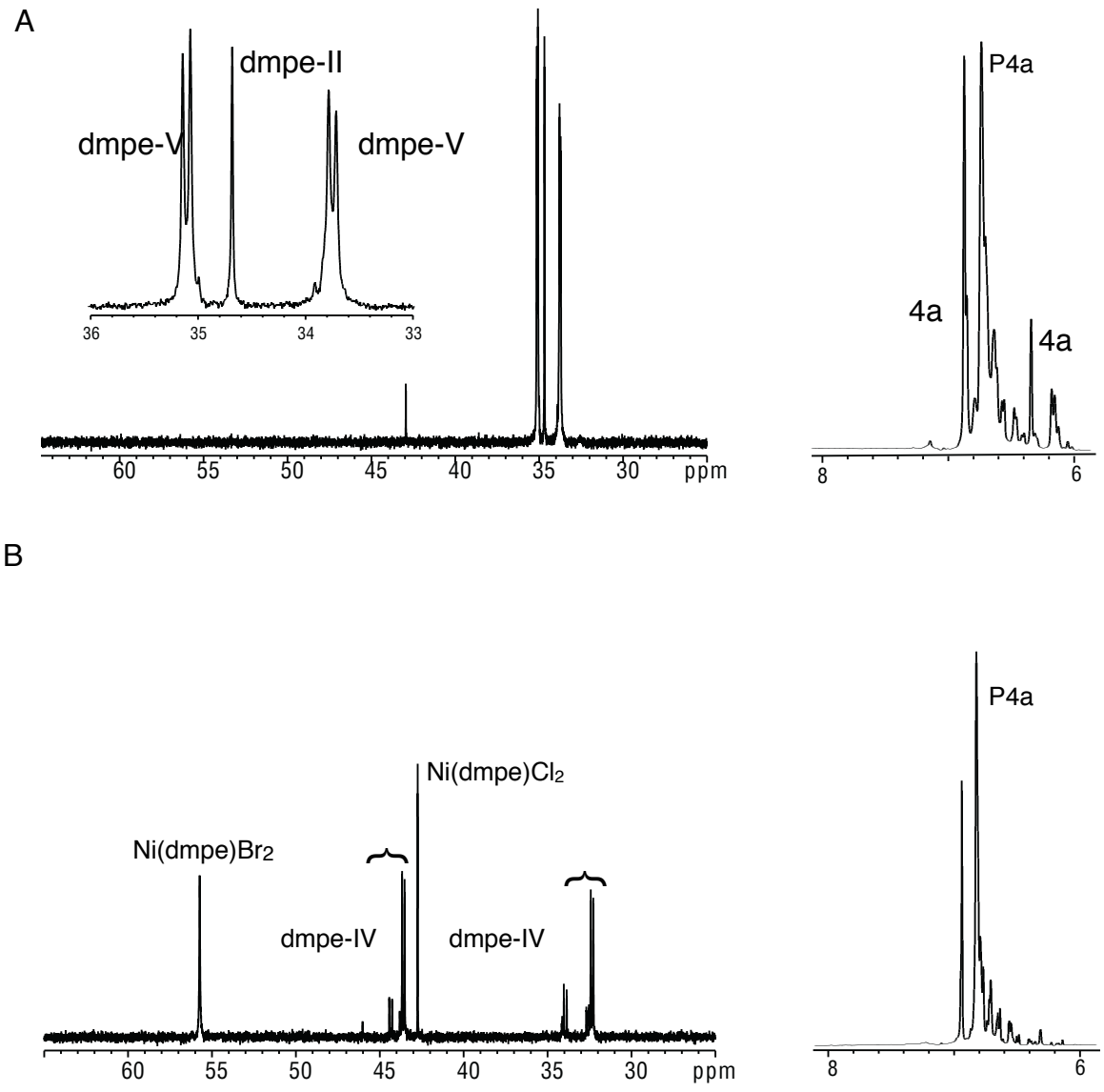


Figure S27. (A) ^{31}P NMR Spectra (202 MHz, THF, rt) showing the catalyst resting state for the reaction of monomer **4a** with catalyst **1** after heating at 60 °C for 60 min (δ 35.1 (d, $J_{P\text{-}P}$ = 14.8 Hz), 34.2, 33.8 (d, $J_{P\text{-}P}$ = 14.8 Hz)) and selected portions of the ^{1}H NMR spectrum. (B) ^{31}P NMR spectrum (202 MHz, THF, 60 °C) for the catalyst resting state after heating at 60 °C for 90 min (δ 55.8, 44.4 (d, $J_{P\text{-}P}$ = 34.5 Hz), 43.8 (d, $J_{P\text{-}P}$ = 30.8 Hz), 43.5 (d, $J_{P\text{-}P}$ = 30.8 Hz), 42.8, 33.9 (d, $J_{P\text{-}P}$ = 34.5 Hz), 32.5 (d, $J_{P\text{-}P}$ = 30.8 Hz), 32.4 (d, $J_{P\text{-}P}$ = 30.8 Hz)) and selected portions of the ^{1}H NMR spectrum.

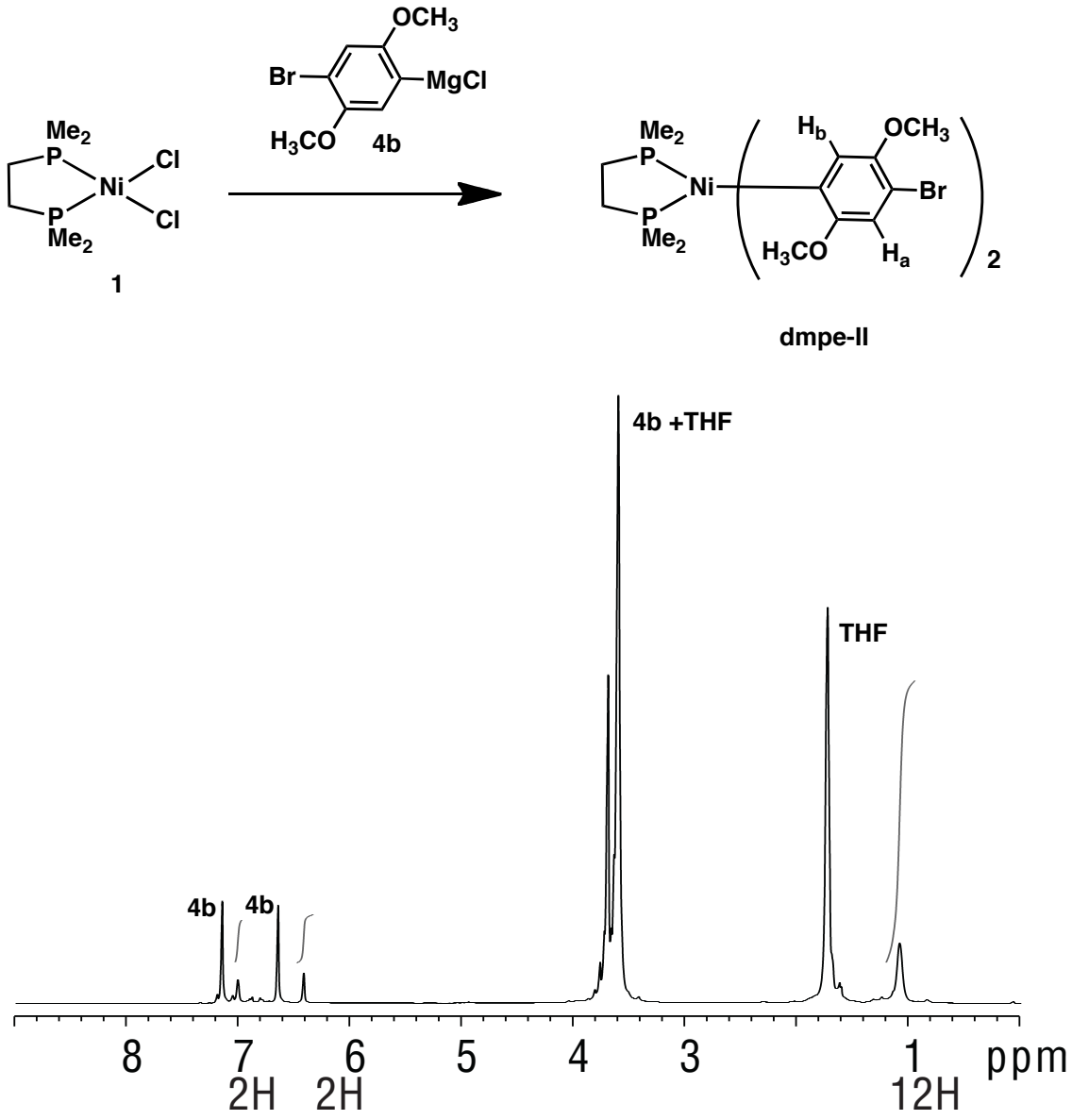


Figure S28.[1]H NMR Spectrum of **Ni(dmpe)Cl$_2$** with **4b** in d^8 THF.
4b (0.8 mL, 0.42M (d^8 THF), 1.9 mmol, 46.0 equiv) was added to a suspension of **1** (0.0093 g, 0.0041 mmol, 1.00 equiv) in d^8 THF (0.2 mL) at rt and stirred for 5 min, then placed in a J-Young NMR tube.

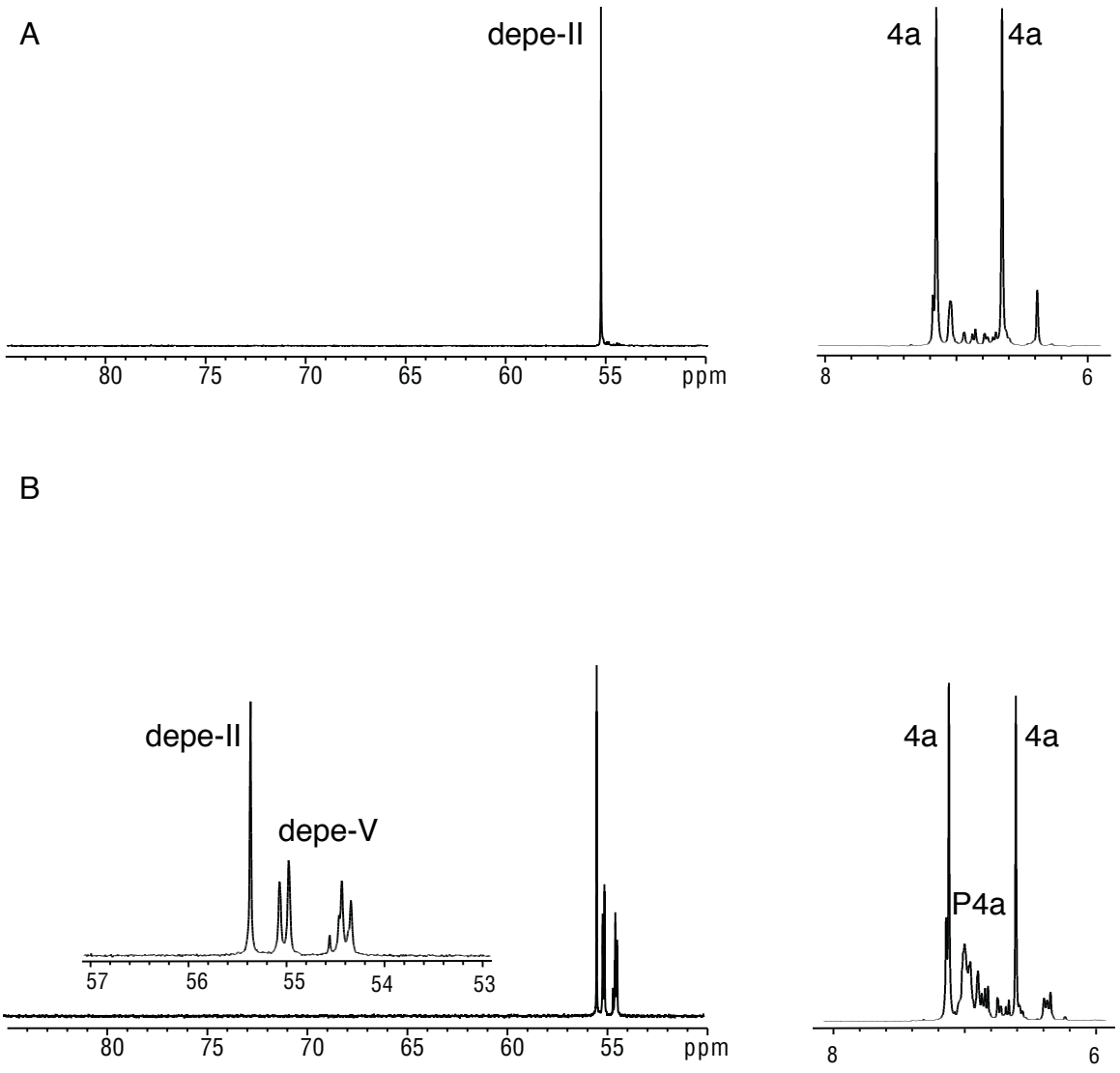


Figure S29. (A) ^{31}P NMR spectrum (162 MHz, THF, rt) for the reaction of monomer **4a** with catalyst **2** showing the complex observed during initiation at rt (δ 55.3) and selected portions of the ^{1}H NMR spectrum. (B) ^{31}P NMR spectrum (162 MHz, THF, rt) for the catalyst resting state after 40 min at rt (δ 55.3, 55.0 (d, $J_{P\text{-}P}$ = 14.5 Hz), 54.4 (d, $J_{P\text{-}P}$ = 14.5 Hz)) and selected portions of the ^{1}H NMR spectrum.

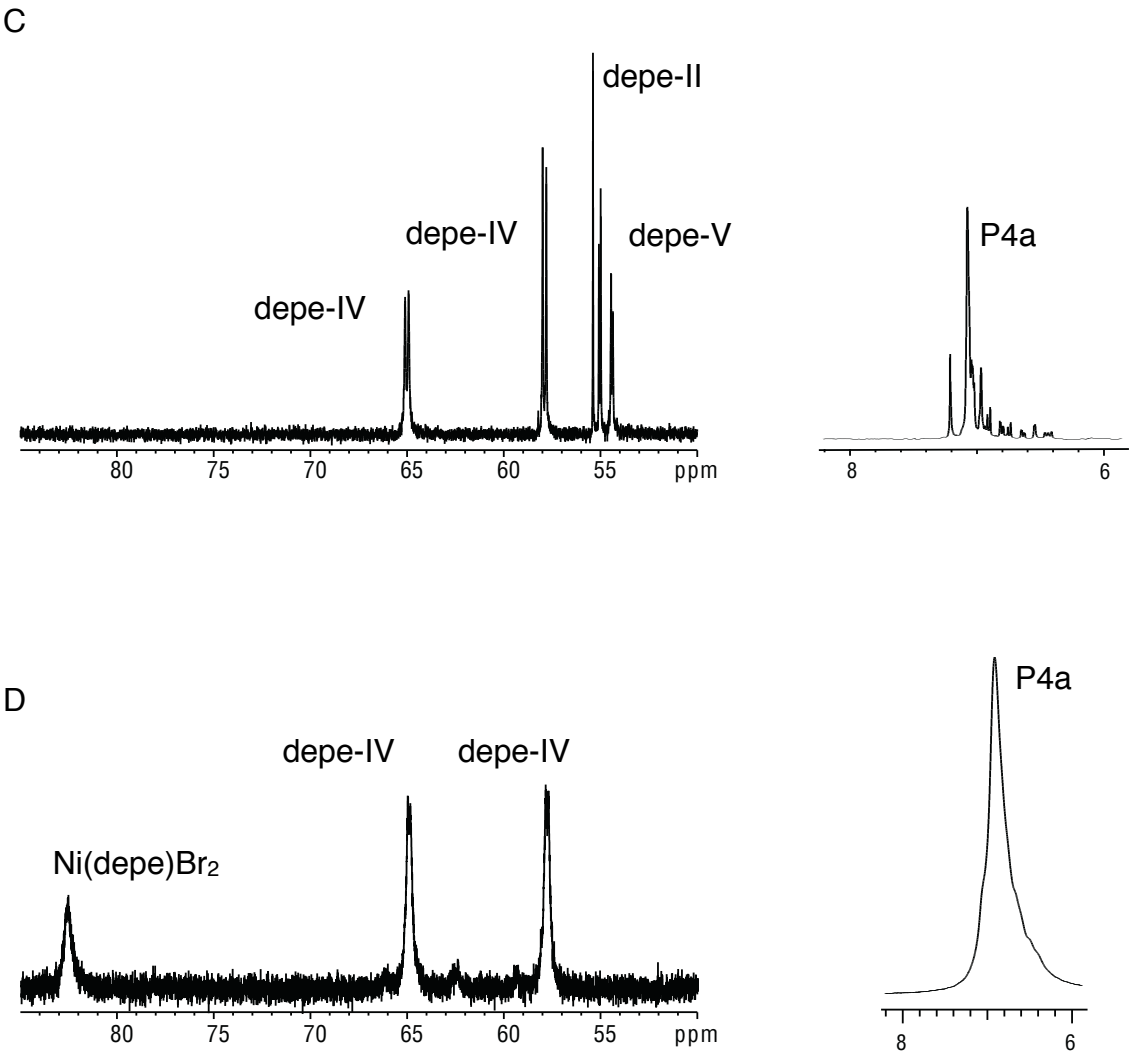


Figure S30. (C) ^{31}P NMR spectrum (162 MHz, THF, rt) for the catalyst resting state after 5.5 h at rt (δ 65.0 (d, $J_{P\text{-}P}$ = 30.6 Hz), 57.9 (d, $J_{P\text{-}P}$ = 30.6 Hz) 55.3, 55.0 (d, $J_{P\text{-}P}$ = 14.5 Hz), 54.4 (d, $J_{P\text{-}P}$ = 14.5 Hz)) and selected portions of the ^{1}H NMR spectrum. (D) ^{31}P NMR spectrum (162 MHz, THF, rt) for the catalyst resting state after 26 h at rt (δ 82.6, 65.0 (d, $J_{P\text{-}P}$ = 30.6 Hz), 57.9 (d, $J_{P\text{-}P}$ = 30.6 Hz)) and selected portions of the ^{1}H NMR spectrum.

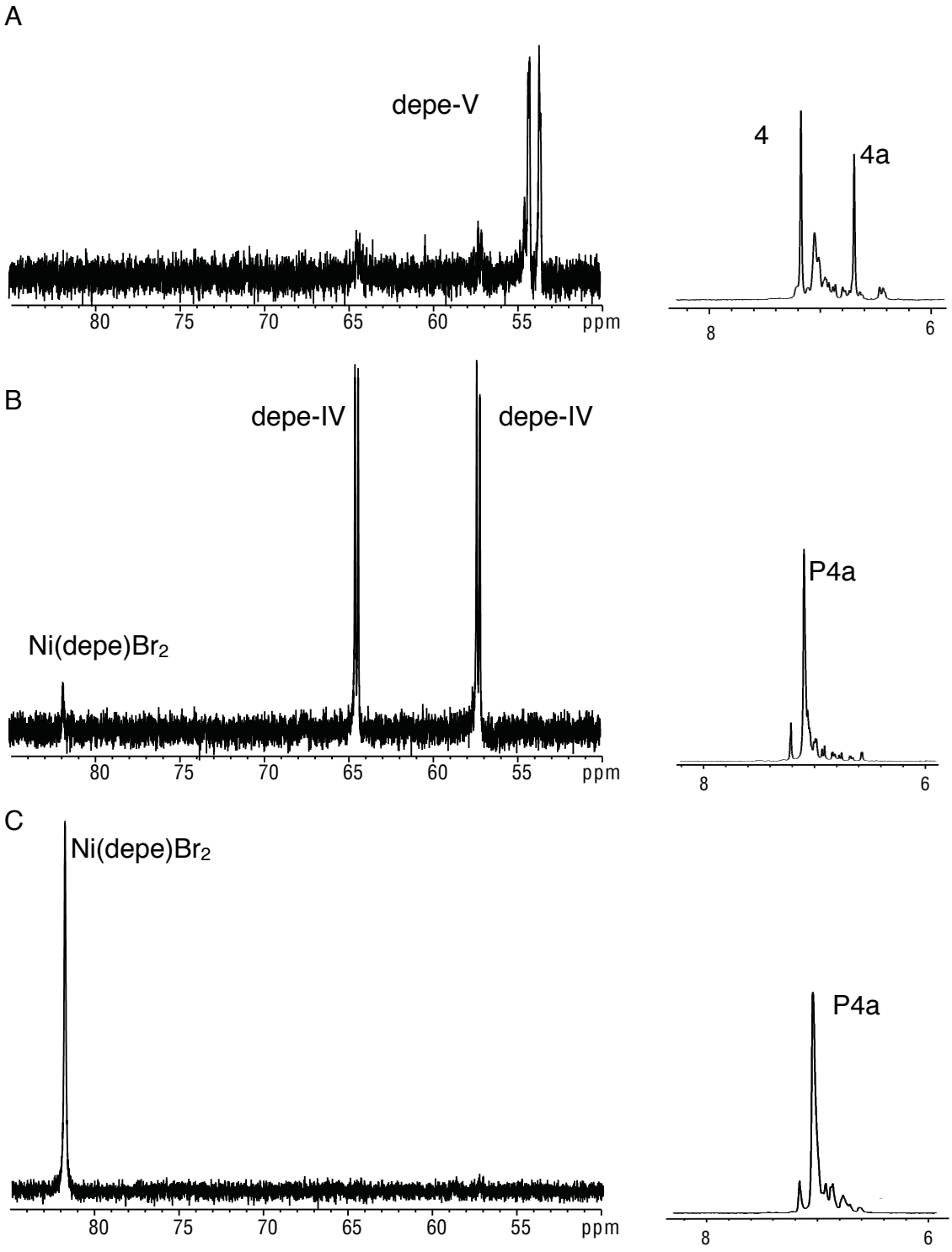


Figure S31. (A) ^{31}P NMR spectra (162 MHz, THF, 60 °C) for the reaction of monomer **4a** with catalyst **2** showing the complex observed during initiation at 60 °C. (B) ^{31}P NMR spectra (162 MHz, THF, 60 °C) for the catalyst resting state after 10 minutes at 60 °C (C) ^{31}P NMR spectra (162 MHz, THF, 60 °C) for the catalyst resting state after 3 hours at 60 °C and selected portions of the ^{1}H NMR spectrum.

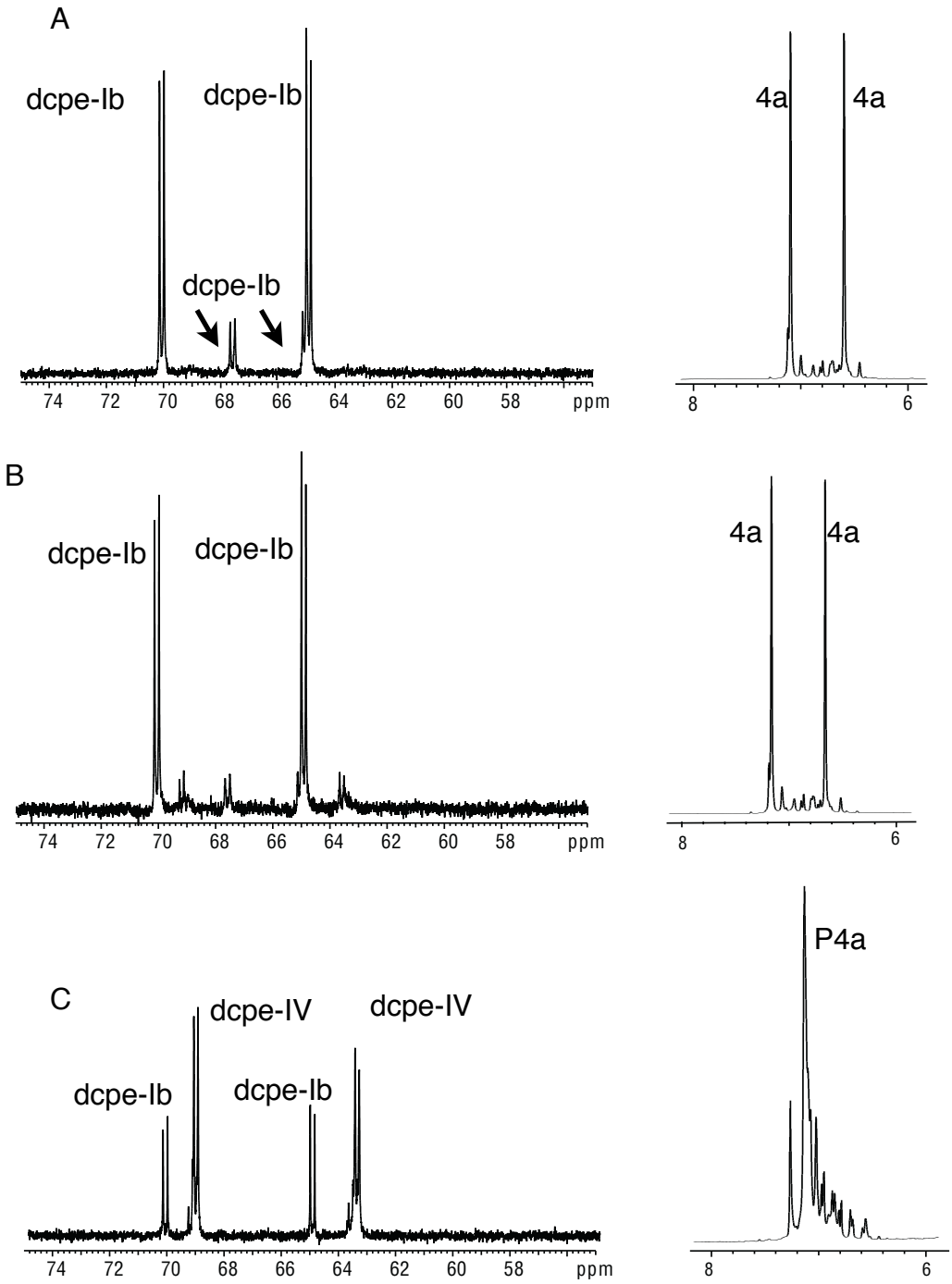


Figure S32. (A) ^{31}P NMR spectrum (162 MHz, THF, rt) for the reaction of monomer **4a** with catalyst **3** showing the complexes observed during initiation at rt (δ 70.1 (d, $J_{P\text{-}P}$ = 27.1 Hz), 67.6 (d, $J_{P\text{-}P}$ = 25.7 Hz), 65.1 (d, $J_{P\text{-}P}$ = 25.7 Hz), 64.9 (d, $J_{P\text{-}P}$ = 27.1 Hz)) and selected portions of the ^{1}H NMR spectrum. (B) ^{31}P NMR Spectrum (162 MHz, THF, rt) for the catalyst resting state after 5 h at rt δ 70.1 (d, $J_{P\text{-}P}$ = 27.1 Hz), 69.2 (d, $J_{P\text{-}P}$ = 23.6 Hz) 67.6 (d, $J_{P\text{-}P}$ = 25.7 Hz), 65.1 (d, $J_{P\text{-}P}$ = 25.7 Hz), 64.9 (d, $J_{P\text{-}P}$ = 27.1 Hz), 63.6 (d, $J_{P\text{-}P}$ = 23.6 Hz) and selected portions of the ^{1}H NMR spectrum. (C) ^{31}P NMR Spectrum for the catalyst resting state after 25 hours at 60 °C (162 MHz, THF, rt) δ 70.1 (d, $J_{P\text{-}P}$ = 27.1 Hz), 69.2 (d, $J_{P\text{-}P}$ = 23.6 Hz), 64.9 (d, $J_{P\text{-}P}$ = 27.1 Hz), 63.6 (d, $J_{P\text{-}P}$ = 23.6 Hz) and selected portions of the ^{1}H NMR spectrum.

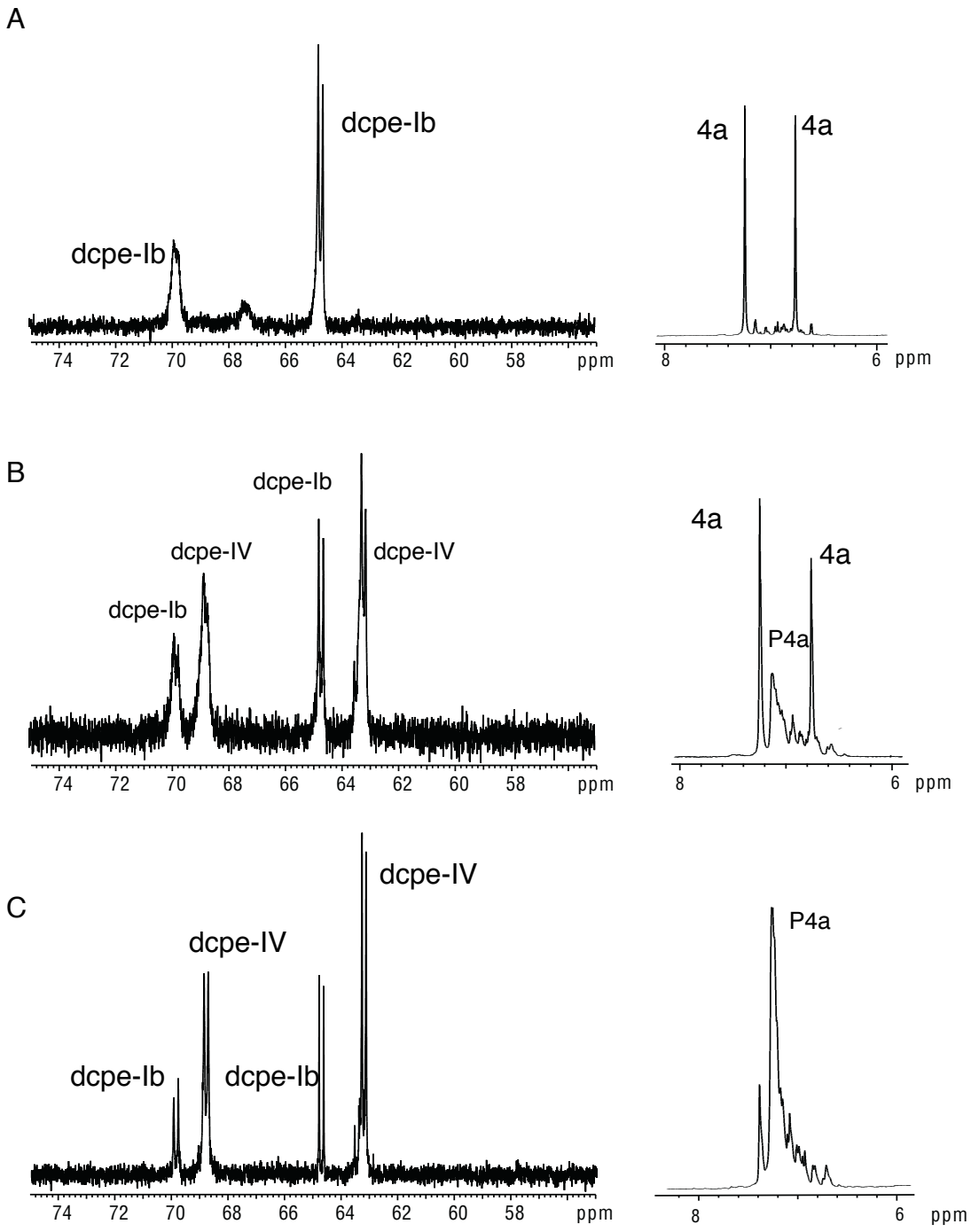


Figure S34. (A) ^{31}P NMR spectrum (162 MHz, THF, 60 °C) for the reaction of monomer **4a** with catalyst **3** showing the complexes observed during initiation at 60 °C. (B) ^{31}P NMR spectrum (162 MHz, THF, 60 °C) for the catalyst resting state after 3 h at 60 °C and selected portions of the ^{1}H NMR spectrum. (C) ^{31}P NMR spectrum (162 MHz, THF, 60 °C) for the catalyst resting state after 24 h at 60 °C and selected portions of the ^{1}H NMR spectrum.

XI. MALDI-TOF MS Data

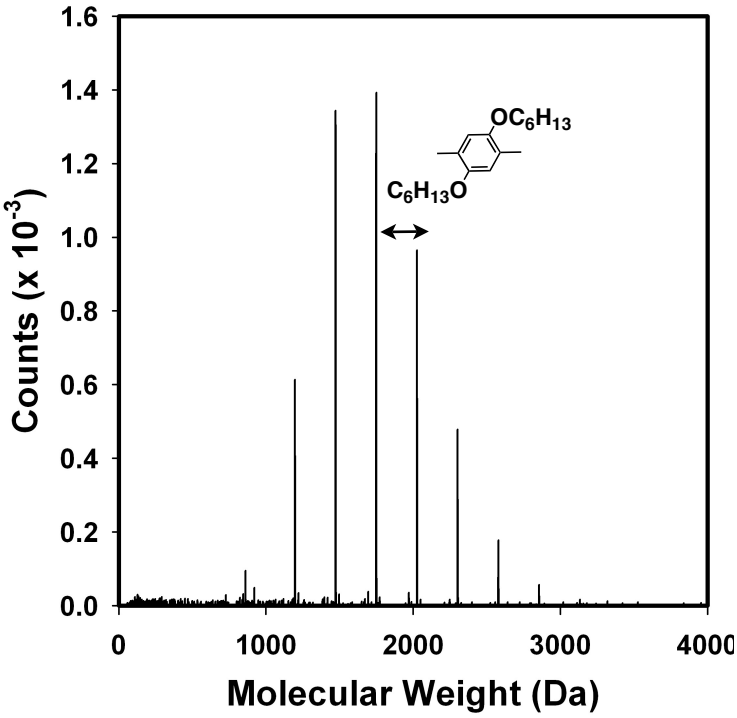


Figure S35. MALDI-TOF MS spectrum of **P4a** initiated with **6a**.

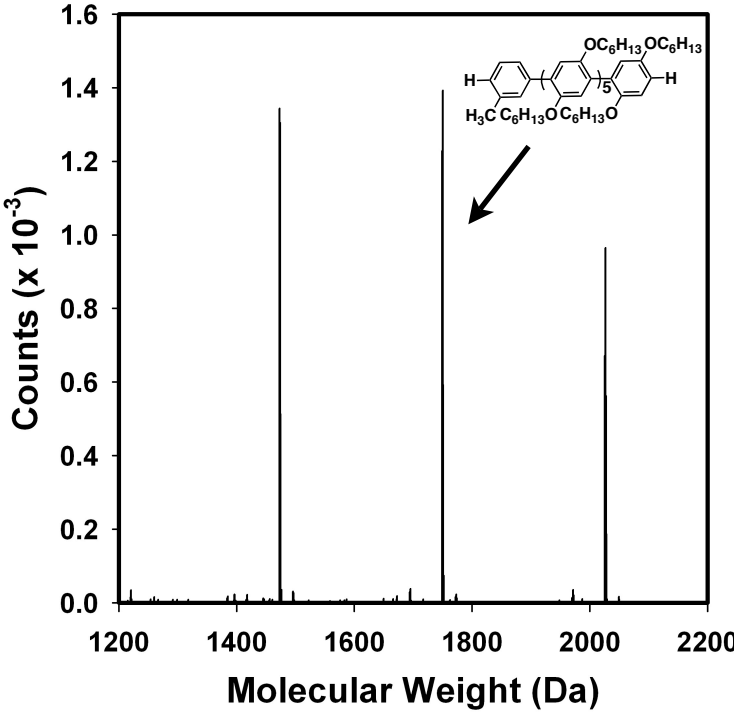


Figure S36. Expanded view of Figure S43.

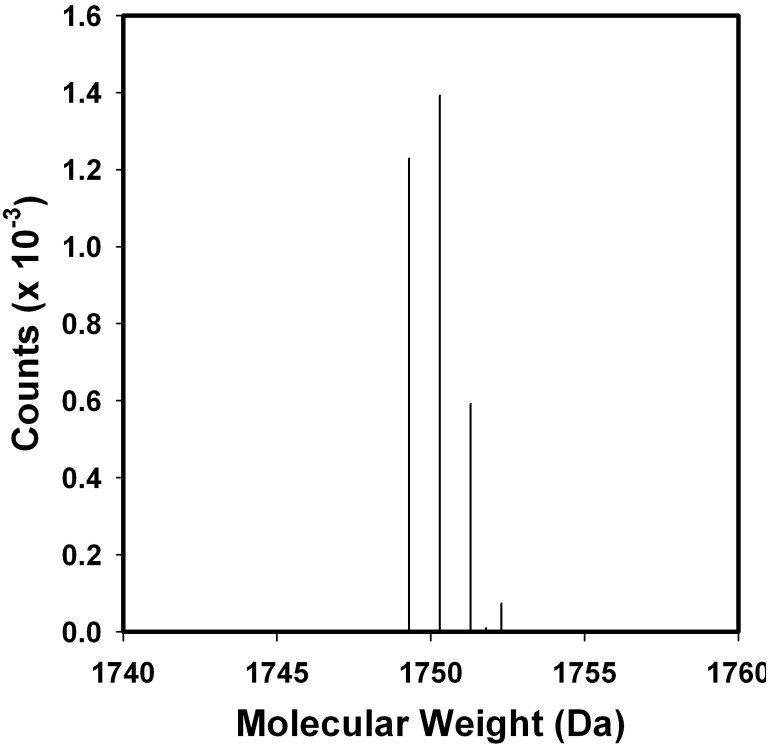


Figure S37. Expanded view of Figure S43

References:

1. (a) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573. (b) Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8039.

2. Booth, G.; Chatt, J. *J. Chem. Soc.* **1965**, 3238.

3. Alyea, E. C.; Meek, D. W. *Inorg. Chem.* **1972**, *11*, 1029.

4. Angulo, I. M.; Bouwman, E.; van Gorkum, R.; Lok, S. M.; Lutz, M. Spek, A. L. *J. Mol Cat. A: Chem* **2003**, *202*, 97.

5. Locke, J. R.; McNeil, A. J. *Macromolecules* **2010**, 43, 8709.

6. Love, B. E.; Jones, E. G. *J. Org. Chem.* **1999**, *64*, 3755.

7. Hernández, M.; Miralrio, G.; Arévalo, A.; Bernès, S.; García, J. J; López, C.; Maitlis, P. M.; del Rio, F. *Organometallics* **2001**, *20*, 4061.