Appendix 2

Appendix to Chapter 3: Evidence for Ligand-Dependent Mechanistic Changes in Nickel-Catalyzed Chain-Growth Polymerizations.

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 and Ni(dppp)Cl_2 was 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. Benzene was distilled from calcium hydride. Compounds **1**, **3**, and **S3** were prepared from literature procedures.[1]

II. General Experimental

<u>*NMR Spectroscopy*</u>: Unless otherwise noted, ^1H, ^{13}C, and ^{31}P NMR spectra for all compounds were acquired in $CDCl_3$ on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 100, and 162 MHz, respectively. For ^1H 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), doublet of quartets (dq), multiplet (m), and broad resonance (br). Unless otherwise indicated, the ^1H, ^{31}P and ^{13}C NMR spectra were recorded at room temperature.

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 or DiComp tip. Unless otherwise indicated, spectra were processed using icIR 4.0 software and raw absorbances were exported into Microsoft Excel or Sigma Plot 10 for analysis.

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

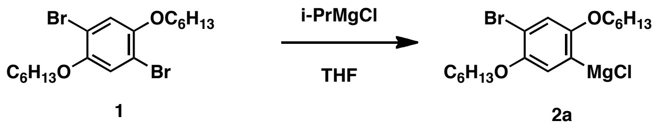
Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed 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.

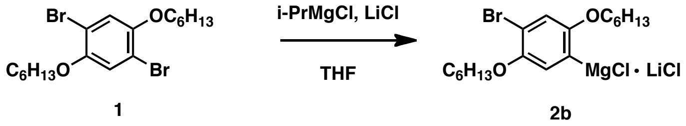
Preparation and Titrations of the Grignards: For **2a** and **2b**: an accurately weighed sample of salicylaldehyde phenylhydrazone[2] (typically between 290-310 mg) was dissolved in 5.00 mL of THF. A 0.20 mL aliquot of this solution was stirred at rt while ArMgCl was added dropwise using a 250 µL syringe. The initial solution is yellow and turns bright orange at the end-point. For **4**: a solution of 25 µL of tridecane in 1.0 mL of the Grignard solution was quenched with methanol. An aliquot of this solution was withdrawn, diluted with $CHCl_3$, analyzed by GC and the concentration determined using a calibration curve (see page S24). To obtain consistent kinetic results Grignards **2a** and **2b** must be prepared the day before use. Grignard **4** must be prepared the day of use. In both cases, titrations are performed immediately before use.

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 data 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.

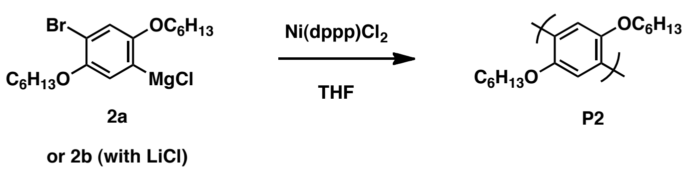
III. Synthetic Procedures



2a.[1] All actions were performed in a glovebox under N_2 atmosphere. A 200 mL flask was equipped with a stir bar. Sequentially, **1** (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.



2b.[1] All actions were performed in a glovebox under N_2 atmosphere. A 200 mL flask was equipped with a stir bar. Sequentially, **1** (14.4 g, 33.0 mmol, 1.00 equiv), THF (35 mL), LiCl (1.3 g, 30 mmol, 0.90 equiv) and *i*-PrMgCl (15 mL, 30 mmol, 0.90 equiv) were added to the flask. The reaction solution was stirred at rt overnight.

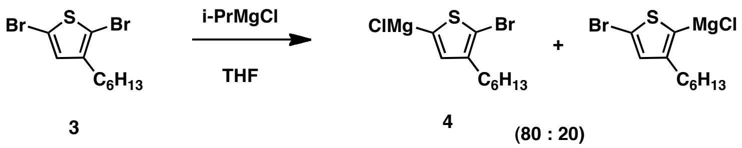


P2.[1] An oven-dried 25 mL Schlenk tube equipped with a stirbar was cooled under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling, the flask was charged with THF (4.6 mL) and cooled to 0 ◦C. After 5 min,

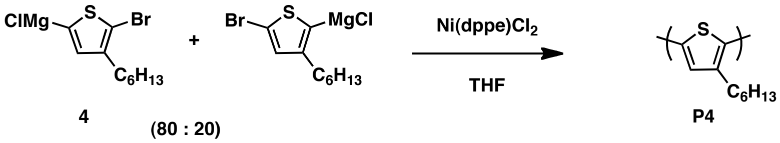
2a or **2b** (4.4 mL, 0.45 M, 1.0 equiv) was added by syringe and allowed to equilibrate for at least 5 min at 0 ◦C. The pre-initiated catalyst solution (1.0 mL, 0.03 M, 0.015 equiv, see section VII) was injected. After 7-8 h, the reaction was quenched with HCl (5 mL, 5 M) and then extracted with $CHCl_3$ (3 x 5 mL). The combined organic layers were washed with water (2 x 5 mL) and brine (1 x 5 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting solid was washed with methanol to give 0.61 g of **P2a** as an off-white solid (quant) or 0.56 g of **P2b** as a white solid (92% yield).

Table S1. Summary of Data for the Preparation of **P2a** and **P2b**

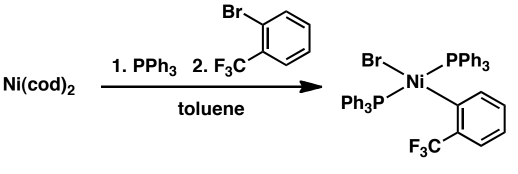
Run	**P2a**		**P2b**	
	M_n (kDa)	PDI	M_n (kDa)	PDI
1	15.1	1.8	25	1.43
2	16.2	1.7	22	1.39
3	16.3	1.6	22	1.46
average	15.9 ± 0.7	1.7 ± 0.7	23 ± 2	1.42 ± 0.04



4.[1] All actions were performed in a glovebox under N_2 atmosphere. A 25 mL Schlenk tube was equipped with a stir bar. Sequentially, **3** (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.

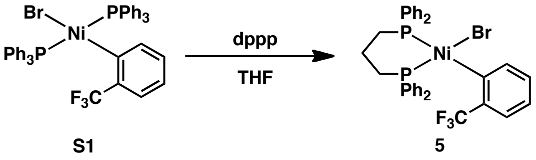


P4.[1] An oven-dried 25 mL Schlenk tube equipped with a stir bar and a rubber septum was cooled under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling the flask was charged with THF (6.8 mL) and **4** (2.2 mL, 0.23 M, 1.0 equiv) and cooled to 0 °C over 2 min. The pre-initiated catalyst solution (1.0 mL, 0.005 M, 0.010 equiv, see section VII) was then injected. After 8 h, the reaction was quenched with HCl (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. The resulting solid was washed with methanol to give 50 mg of **P4** as a dark purple solid (57% yield, M_n = 19 kDa, PDI = 1.4).

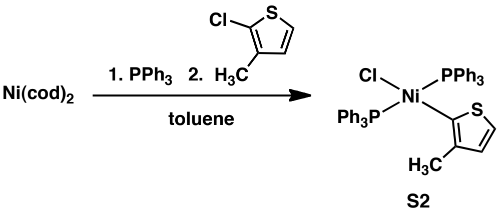


S1

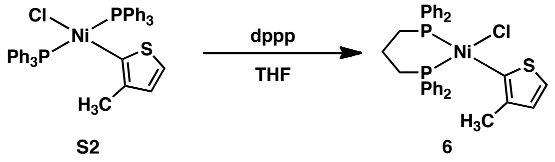
S1.[3] In the glovebox an oven-dried 50 mL flask was equipped with a stir bar and charged with $Ni(cod)_2$ (0.14 g, 0.50 mmol, 1.0 equiv), triphenylphosphine (0.26 g, 1.0 mmol, 2.0 equiv) and toluene (15 mL). 2-Bromo-trifluoromethyltoluene (70 μL, 0.50 mmol, 1.0 equiv) was added by syringe and the solution was allowed to stir at rt until complete conversion was observed by ^{31}P NMR spectroscopy (~15 min). After the solution was partially concentrated (50%), the product was precipitated by adding hexanes (20 mL) and collected by filtration to give 0.28 g of **S1** as an orange solid (70% yield). The product is air-stable. ^{31}P NMR spectrum of **S1** (162 MHz, THF) δ 20.0 (s).



5.[1] In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S1** (0.10 g, 0.12 mmol, 1.0 equiv) and THF (5 mL). Diphenylphosphinopropane (0.050 g, 0.12 mmol, 1.0 equiv) was added and the solution stirred at rt for 5 min. The solution was partially concentrated (50%). The product was precipitated by adding hexanes (15 mL) and collected by filtration to give 0.037 g of **S1** as an orange solid (45% yield). The product is air-sensitive and prone to decomposition over several h even under inert atmosphere. ^{31}P NMR spectrum of **5** (162 MHz, THF) δ 19.9 (dq, $J_{\text{P-P}}$ = 58 Hz, $J_{\text{P-F}}$ = 9.0 Hz), -3.48 (d, $J_{\text{P-P}}$ = 58 Hz).

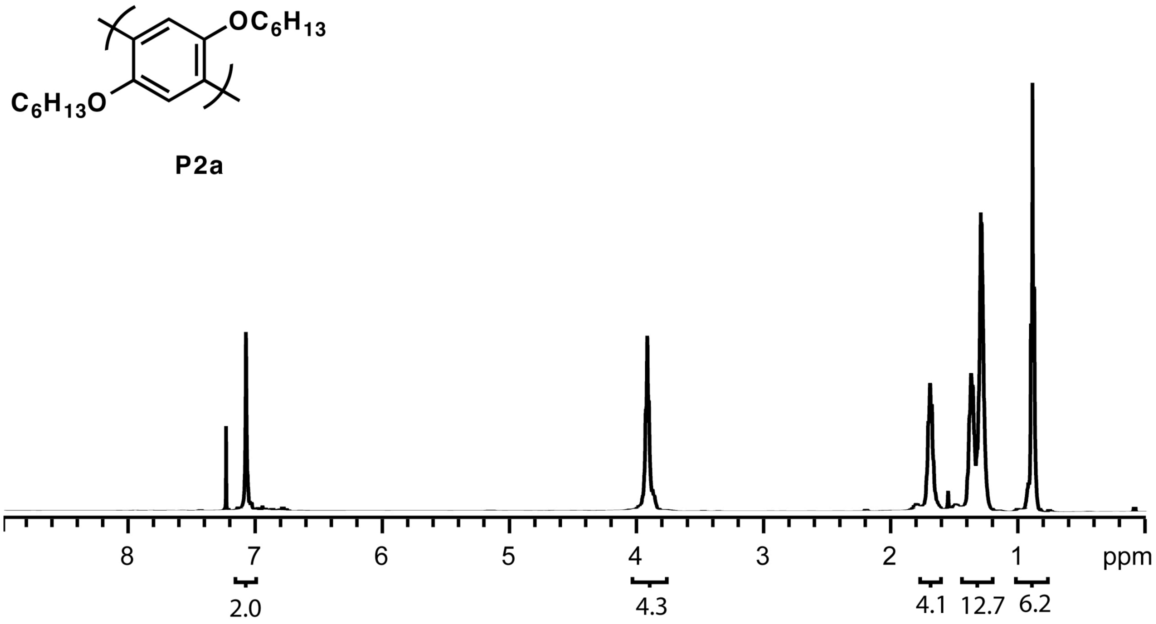


S2.[3] In the glovebox an oven-dried 50 mL Schlenk flask was equipped with a stir bar and charged with Ni(cod)$_2$ (0.14 g, 0.50 mmol, 1.0 equiv), triphenylphosphine (0.26 g, 1.0 mmol, 2.0 equiv) and toluene (15 mL). The flask was removed from the box, placed under N$_2$ and cooled in an ice-water bath. 2-Chloro-3-methylthiophene (60 μL, 0.55 mmol, 1.1 equiv) was added by syringe and the solution was stirred at rt until complete conversion was observed by ^{31}P NMR spectroscopy (~15 min). The solution was loaded onto silica gel, washed with hexanes (100 mL) and then eluted with acetone. After the solution was partially concentrated (50%), the product was precipitated by adding hexanes (20 mL) and collected by filtration to give 0.16 g of **S2** as an orange solid (44% yield). The product is air-stable. ^{31}P NMR spectrum of **S2** (162 MHz, THF) δ 19.7 (s).



6.[1] In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S2** (0.10 g, 0.14 mmol, 1.0 equiv) and THF (5 mL). Diphenylphosphinopropane (0.060 g, 0.14 mmol, 1.0 equiv) was added and the solution stirred at rt for 5 min. The solution was partially concentrated (50%). The product was precipitated by adding hexanes (15 mL) and collected by filtration to give 0.024 g of **6** as a yellow solid (28% yield). The product is air-sensitive and prone to decomposition over several h even under inert atmosphere. ^{31}P NMR spectrum of **6** (162 MHz, THF) δ 18.6 (d, J_{P-P} = 64 Hz), -3.29 (d, J_{P-P} = 64 Hz).

IV. NMR Spectra



P2a

Figure S1. ^{1}H NMR Spectrum of **P2a**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1 (br s, 2H), 3.9 (br m, 4H), 1.7 (br m, 4H), 1.35-1.25 (br m, 12 H), 0.90 (br m, 6H).

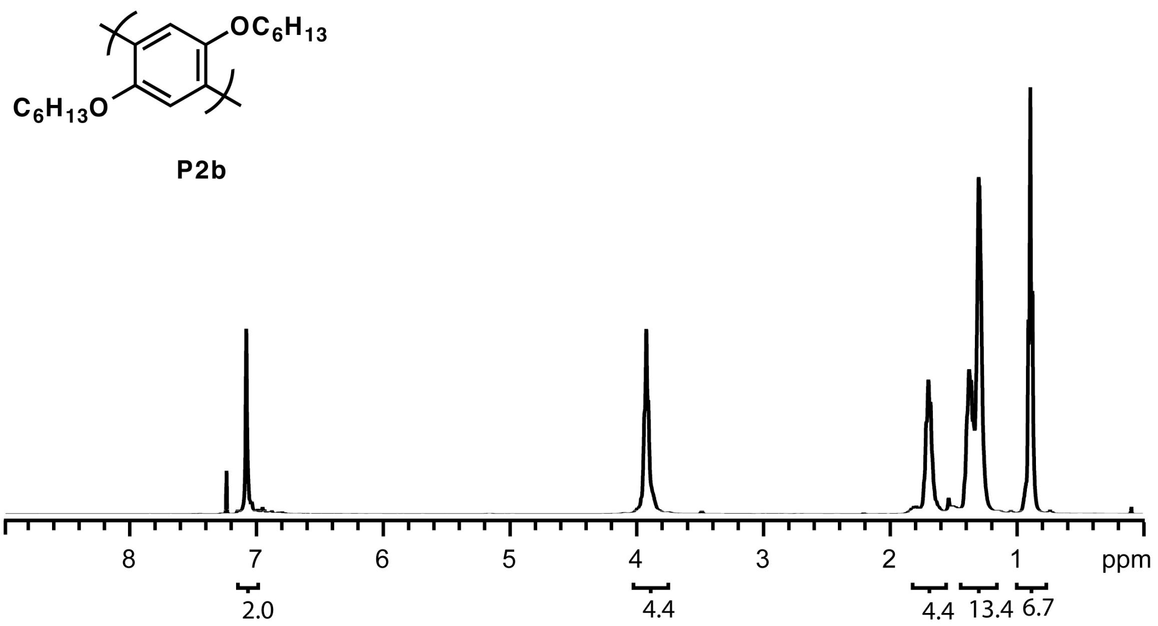


Figure S2. ^{1}H NMR Spectrum of **P2b**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.1 (br s, 2H), 3.9 (br m, 4H), 1.7 (br m, 4H), 1.35-1.25 (br m, 12 H), 0.90 (br m, 6H).

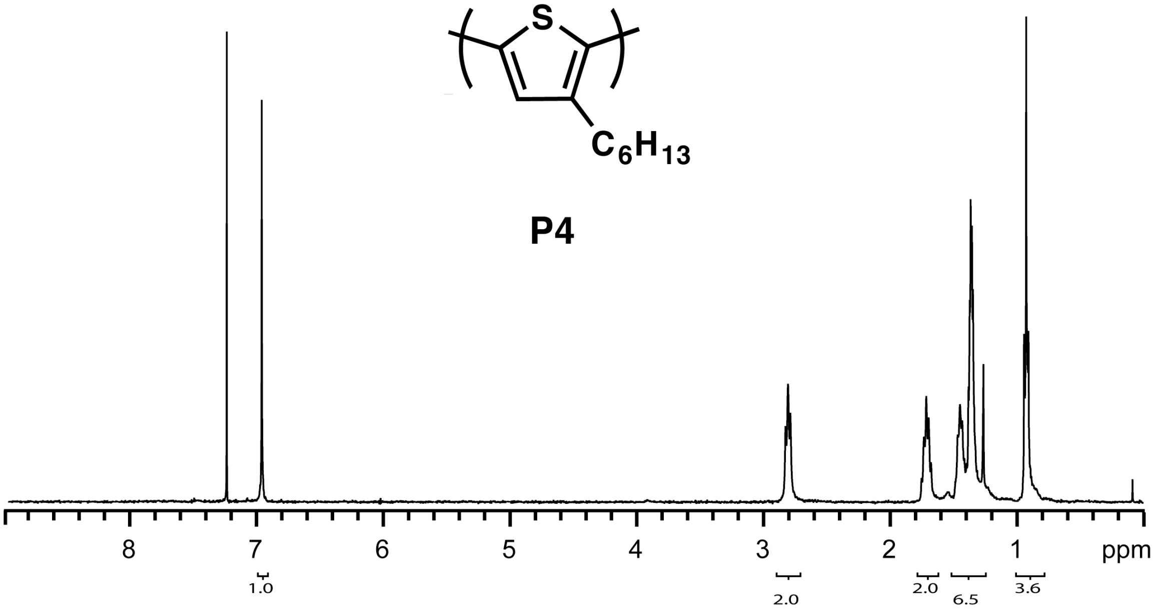


Figure S3. ^{1}H NMR Spectrum of **P4**.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 2.82 (br m, 2H), 1.73 (br m, 2H), 1.45-1.37 (br m, 6 H), 0.93 (br m, 3H).

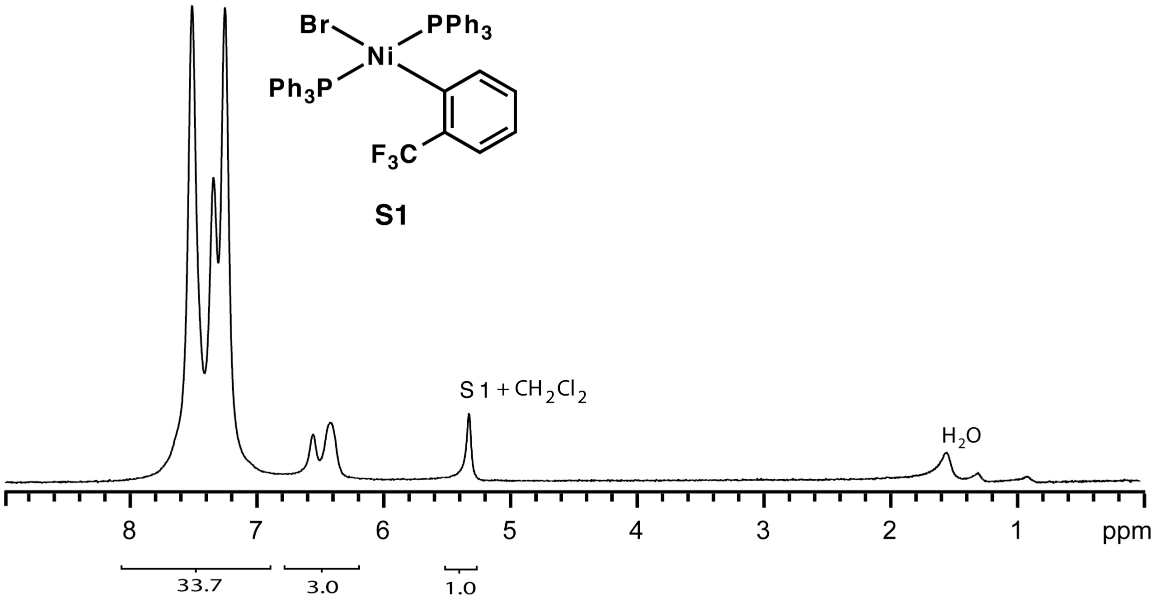


Figure S4. ^{1}H NMR Spectrum of **S1**.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.8-7.0 (br m, 30H), 6.3-6.7 (br m, 3H), 5.32 (br s, 1H + CH_2Cl_2).

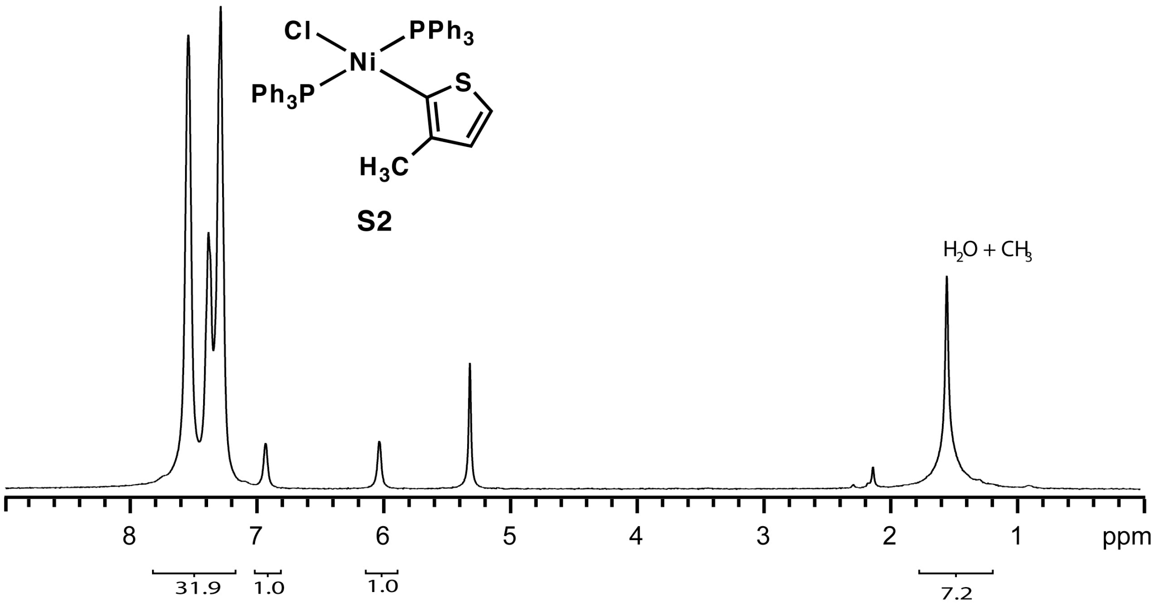


Figure S5. ^{1}H Spectrum of **S2**.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.2-7.7 (br m, 30H), 6.94 (br s, 1H), 6.04 (br s, 1H), 1.54 (br s, 3H).

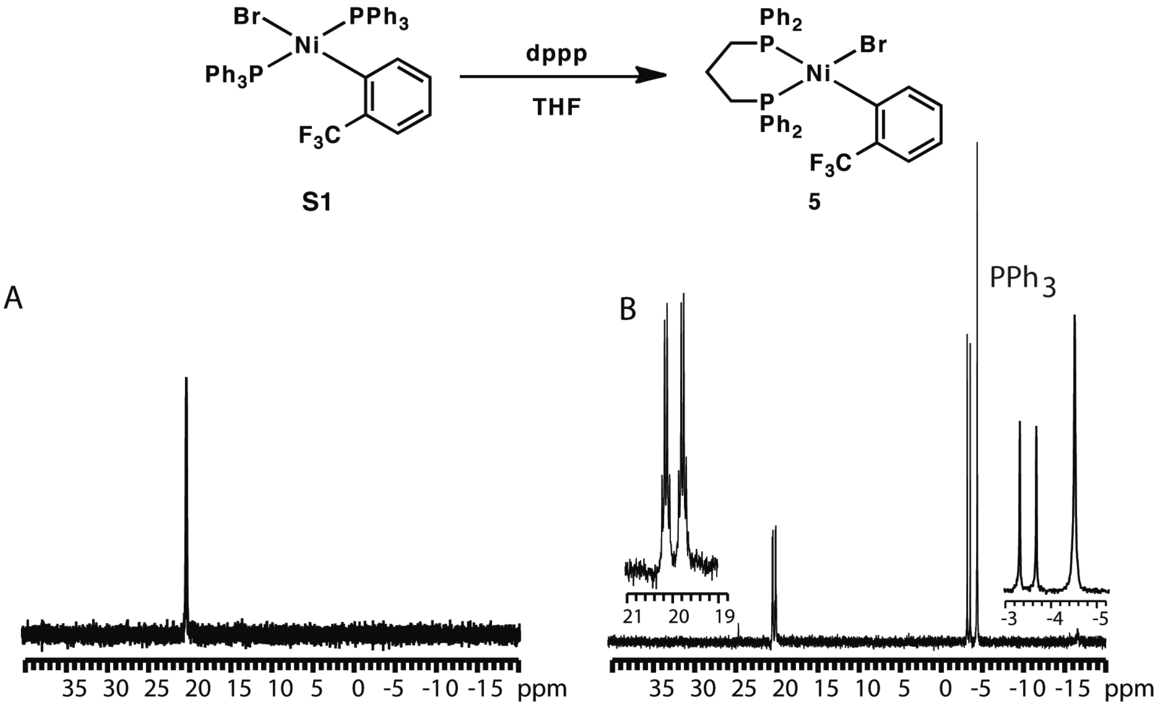


Figure S6. ^{31}P NMR Spectra for the Preparation of **5**.
(A) ^{31}P NMR spectrum of **S1** (162 MHz, THF) δ 20.0 (s). (B) ^{31}P NMR spectrum of **6** (162 MHz, THF) δ 19.9 (dq, $J_{\text{P-P}}$ = 58 Hz, $J_{\text{P-F}}$ = 9.0 Hz), -3.48 (d, $J_{\text{P-P}}$ = 58 Hz).

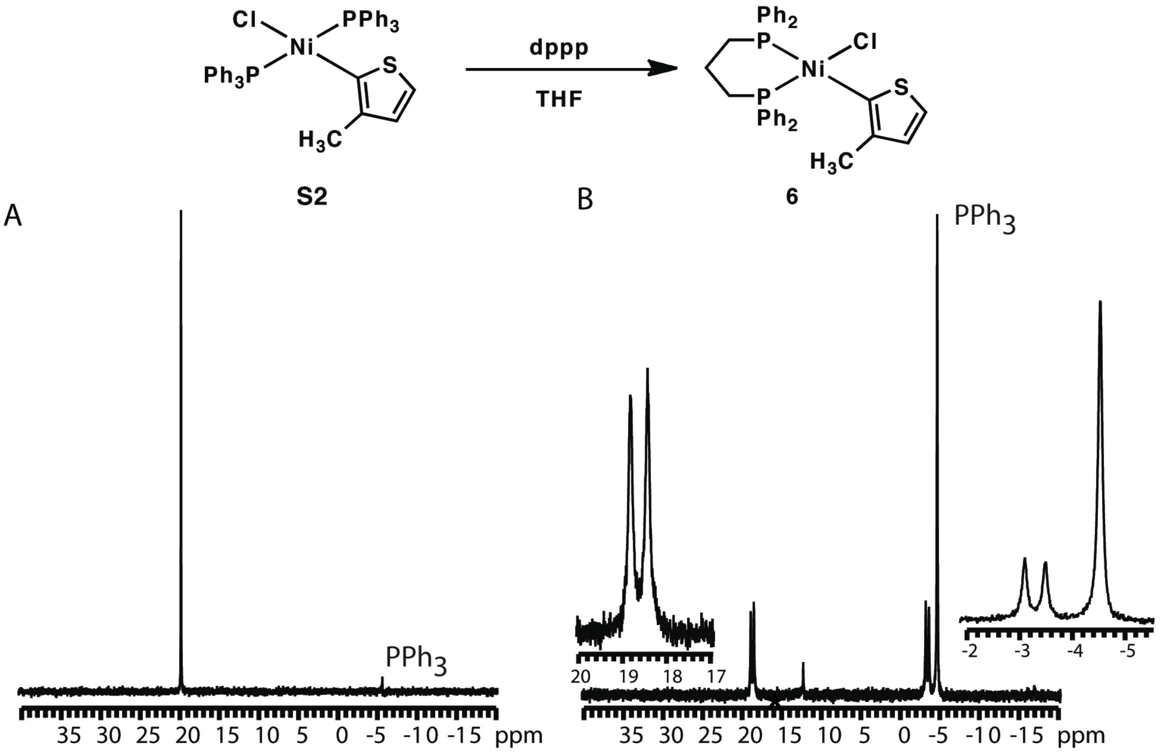


Figure S7. ^{31}P NMR Spectra for the Preparation of **6**.
(A) ^{31}P NMR spectrum of **S2** (162 MHz, THF) δ 19.7 (s). (B) ^{31}P NMR spectrum of **6** (162 MHz, THF) δ 18.6 (d, $J_{P\text{-}P}$ = 64 Hz), -3.29 (d, $J_{P\text{-}P}$ = 64 Hz).
*Corresponds to Ni(dppp)$_2$.[4]

V. Representative IR spectrum and GC Chromatogram

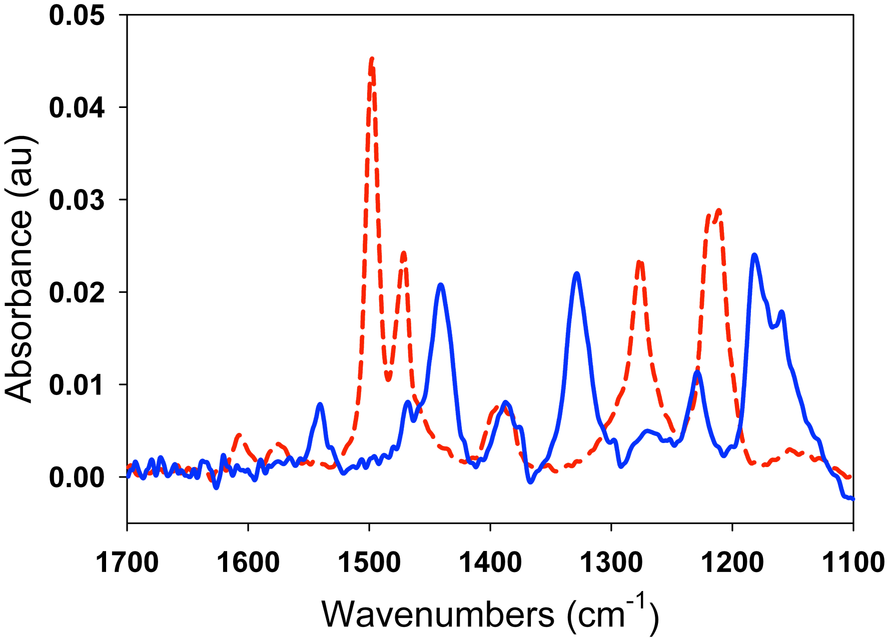


Figure S8. IR spectral overlay of **2b** (red, - - - -) and **P2b** (blue, —).

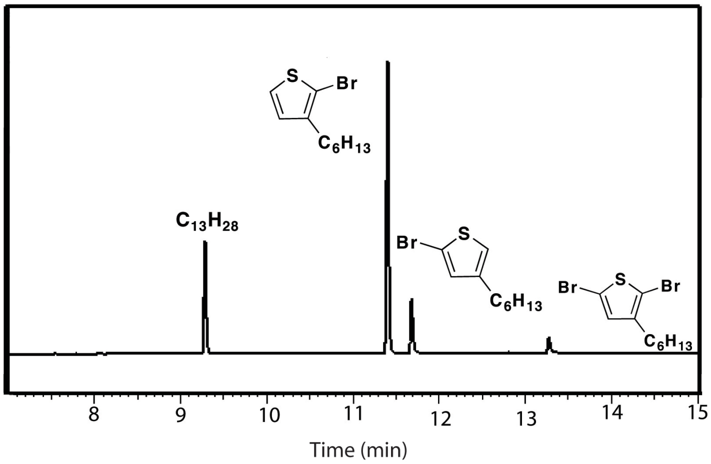


Figure S9. Representative GC trace of thiophene polymerizaton.

VI. Calibration Curves

General procedure for generating a calibration curve utilizing the ReactIR:

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 stir bar. The other neck was equipped with a three-way adapter fitted with a septum for injections and a N_2 line. The oven-dried flask was cooled to rt under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling, the flask was charged with THF and cooled to 0 °C over 5 min. After recording a background spectrum, **2a** or **2b** was added by syringe and allowed to equilibrate for at least 5 min and then the spectra were recorded.

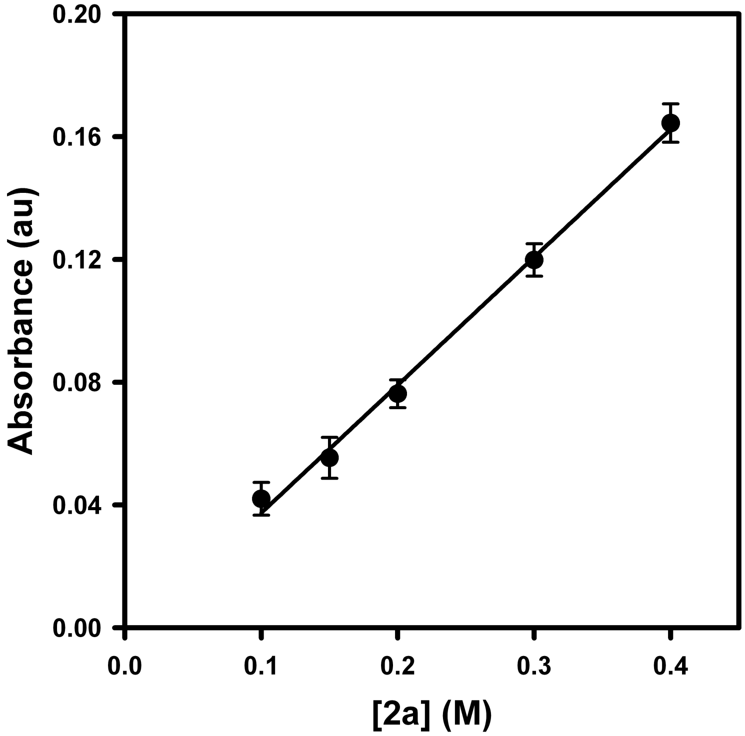


Figure S10. Plot of absorbance versus [**2a**] fitted to y = *m*x + *b* where *m* = 0.42 ± 0.02 and *b* = -0.004 ± 0.004 for the SiComp Probe.

Table S2. Data for the plot in Figure S10.

[**2a**] (M)	Absorbance (au)
0.1	$4.2 \pm 0.5 \times 10^{-2}$
0.15	$5.5 \pm 0.7 \times 10^{-2}$
0.2	$7.6 \pm 0.5 \times 10^{-2}$
0.3	$12 \pm 1 \times 10^{-2}$
0.4	$16 \pm 1 \times 10^{-2}$

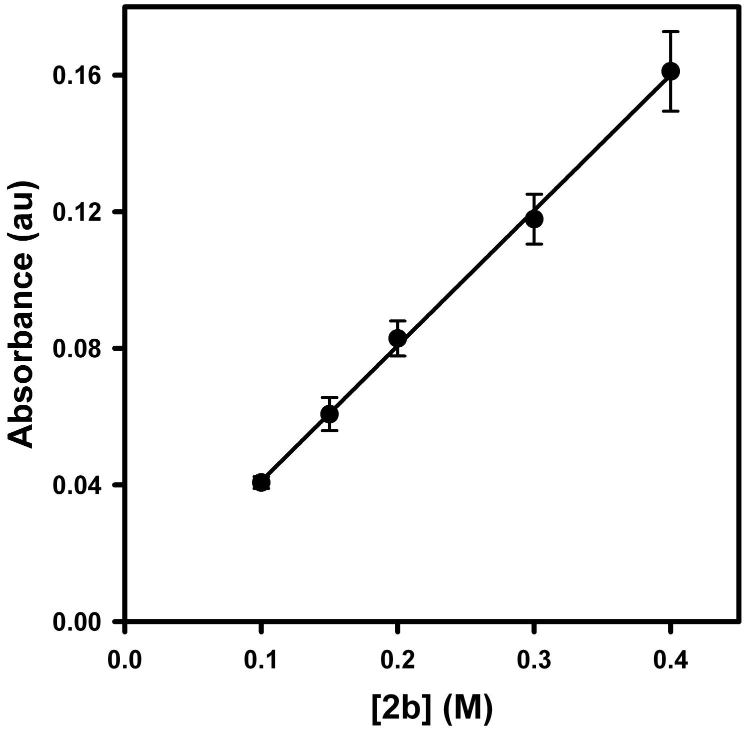


Figure S11. Plot of absorbance versus [**2b**] fitted to y = *m*x + *b* where m = 0.396 ± 0.002 and b = 0.001 ± 0.002 for the SiComp probe.

Table S3. Data for the plot in Figure S11.

[**2b**] (M)	Absorbance (au)
0.1	$4.1 \pm 0.1 \times 10^{-2}$
0.15	$6.1 \pm 0.5 \times 10^{-2}$
0.2	$8.3 \pm 0.5 \times 10^{-2}$
0.3	$11.8 \pm 0.7 \times 10^{-2}$
0.4	$16 \pm 1 \times 10^{-2}$

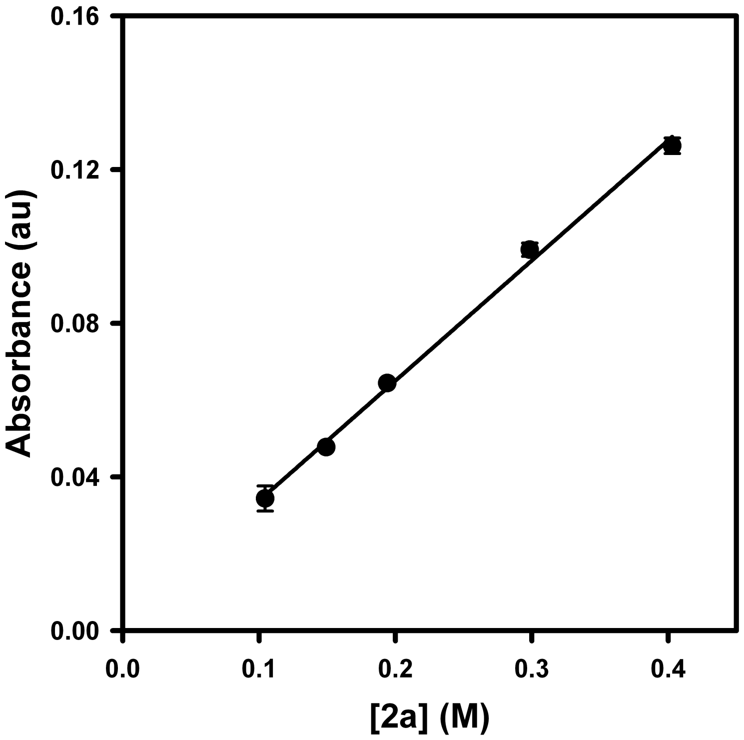


Figure S12. Plot of absorbance versus [**2a**] fitted to y = *m*x + *b* where *m* = 0.31 ± 0.01 and *b* = 0.002 ± 0.003 for the DiComp Probe.

Table S4. Data for the plot in Figure S12.

[**2a**] (M)	Absorbance (au)
0.1	$3.4 \pm 0.3 \times 10^{-2}$
0.15	$4.78 \pm 0.08 \times 10^{-2}$
0.2	$6.44 \pm 0.03 \times 10^{-2}$
0.3	$9.9 \pm 0.2 \times 10^{-2}$
0.4	$12.6 \pm 0.2 \times 10^{-2}$

Procedure for generating a calibration curve utilizing the GC:[5]

Solutions containing a constant concentration of tridecane (2.57 mM) and varying concentrations of **S3** (5.81, 3.48, 2.32, 1.16, and 0.581 mM) were prepared in $CHCl_3$. Each sample was analyzed by GC and the response factor **F** was calculated by fitting the data to the following equation:

$$\frac{\text{Area of thiophene signal}}{\text{Concentration of thiophene}} = \mathbf{F}\left(\frac{\text{Area of tridecane signal}}{\text{Concentration of tridecane}}\right)$$

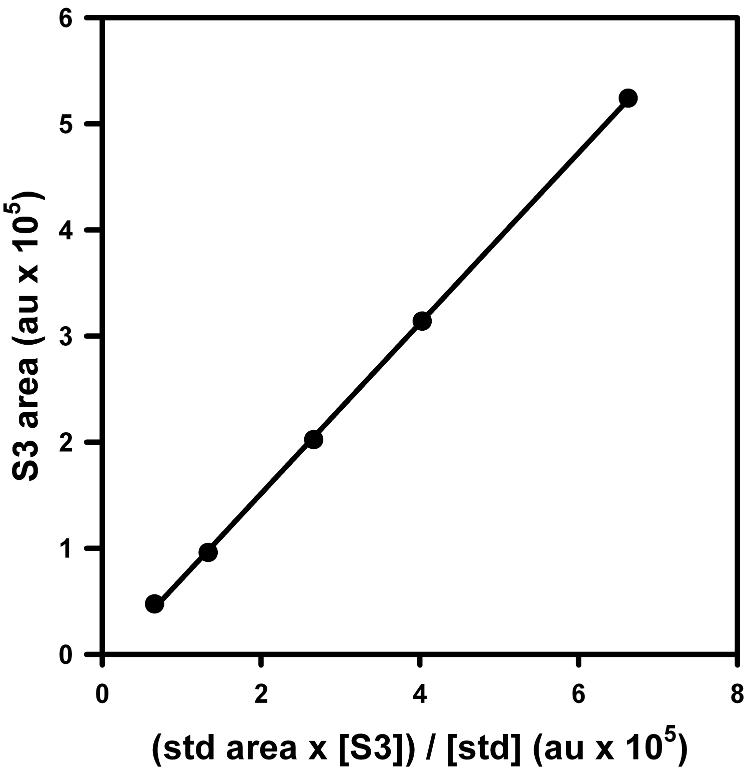


Figure S13. Plot of **S3** area versus (std area x [**S3**]) / [std] fit to y = *m*x + *b* where *m* = 0.803 ± 0.006 and *b* = -9 ± 2 x 10^{3}.

Table S5. Data for the plot in Figure S13.

[**S3**]	area **S3**	area tridecane (std)	(std area x [**S3**]) / [std]
5.80 x 10^{-4}	0.474 x 10^{5}	2.91 x 10^{5}	0.659 x 10^{4}
1.16 x 10^{-3}	0.959 x 10^{5}	2.94 x 10^{5}	1.33 x 10^{5}
2.23 x 10^{-3}	2.02 x 10^{5}	2.95 x 10^{5}	2.66 x 10^{5}
3.48 x 10^{-3}	3.14 x 10^{5}	2.97 x 10^{5}	4.03 x 10^{5}
5.80 x 10^{-3}	5.24 x 10^{5}	2.93 x 10^{5}	6.62 x 10^{5}

VII. Representative Procedure for Preparing the Catalyst Solution

For **2a** and **2b**: All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(dppp)Cl_2 (57 mg, 0.11 mmol, 1.0 equiv), THF (6.0 mL), and **2b** (1.0 mL, 0.52 M, 5.0 equiv) were added to the vial. The reaction mixture was stirred at rt for 10 min until the solution was homogeneous.

For **4**: All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(dppp)Cl_2 (20 mg, 0.038 mmol, 1.0 equiv), THF (14.2 mL), and **4** (0.80 mL, 0.24 M, 5.0 equiv) were added to the flask. The reaction mixture was stirred at rt for 10 min until the solution was homogeneous.

VIII. M_n and PDI versus conversion

(A) Representative procedure for obtaining plots of M_n and PDI versus conversion utilizing the ReactIR:

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 stir bar. The other neck was equipped with a three-way adapter fitted with a septum for injections and an N_2 line. The oven-dried flask was cooled to rt 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, **2b** (4.4 mL, 0.45 M, 1.0 equiv) was added by syringe and allowed to equilibrate for at least 5 min at 0 °C. The pre-initiated catalyst solution (1.0 mL, 0.03 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 30 s of the reaction were discarded. Aliquots (~ 0.5 mL) were withdrawn through the three way adapter via syringe and immediately quenched with 12 M HCl (~ 1 mL). Each aliquot was then extracted with $CHCl_3$ (with mild heating if polymer had precipitated), dried over $MgSO_4$ and filtered, then concentrated. The samples were dissolved in THF (with heating), and passed through a 0.2 μm PTFE filter for GPC analysis.

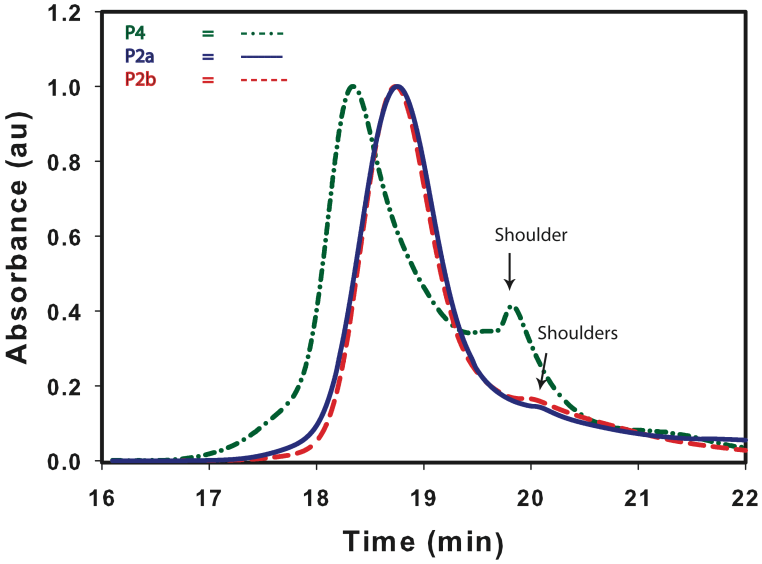


Figure S14. Representative GPC traces for polymerizations of **P2a**, **P2b**, and **P4**. Shoulders appeared toward the end of the polymerizations as noted below (Figures S15, S16 and S17) and were included in the calculation of M_n values reported.

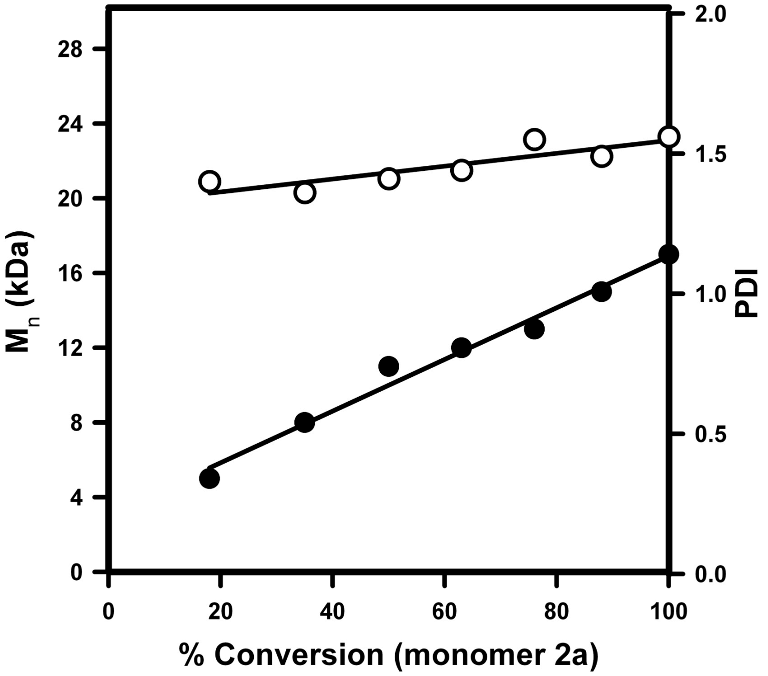


Figure S15. Plot of Mn (●) and PDI (○) versus conversion for **2a** (temp = 0 ◦C, [Ni (dppp)Cl_2] = 0.003 M, [**2a**] = 0.2 M).

Table S6. Data for the plot in Figure S15.

% Conversion (**2a**)	M_n (kDa)	PDI	Note
18	5.1	1.40	
35	8.1	1.36	
50	11	1.41	
63	12	1.44	
76	13	1.55	
88	15	1.49	shoulder
100	17	1.56	shoulder

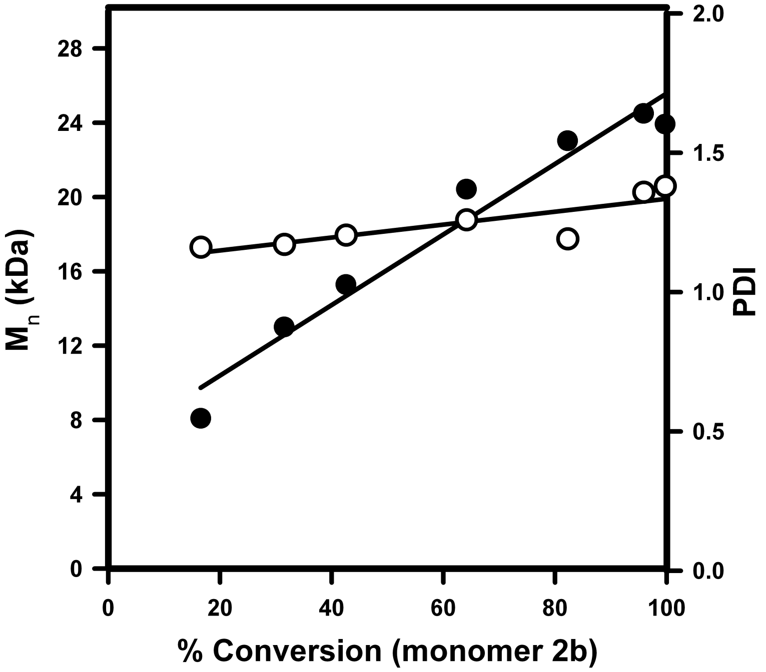


Figure S16. Plot of Mn (●) and PDI (○) versus conversion for **2b** (temp = 0 ◦C, [Ni(dppp)Cl$_2$] = 0.003 M, [**2b**] = 0.2 M).

Table S7. Data for the plot in Figure S16 .

% Conversion (**2b**)	M_n (kDa)	PDI	
17	8.1	1.16	
32	13	1.17	
43	15	1.20	
64	20	1.26	shoulder
82	23	1.19	shoulder
96	24	1.36	shoulder
100	24	1.38	shoulder

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

An oven-dried 10 mL flask equipped with a stir bar and a rubber septum was cooled to rt under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling the flask was charged with tridecane (100 μL), THF (6.8 mL) and **4** (2.2 mL, 0.23 M, 1.0 equiv) and cooled to 0 ◦C over 2 min. The pre-initiated catalyst solution (1.0 mL, 0.005 M, 0.0010 equiv) was then injected. Aliquots (~ 0.5 mL) were withdrawn through the septum and immediately quenched with 5 M HCl (1 mL). Each aliquot was then extracted with $CHCl_3$ (with mild heating if polymer had precipitated) and a portion analyzed by GC. The remainder was 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.

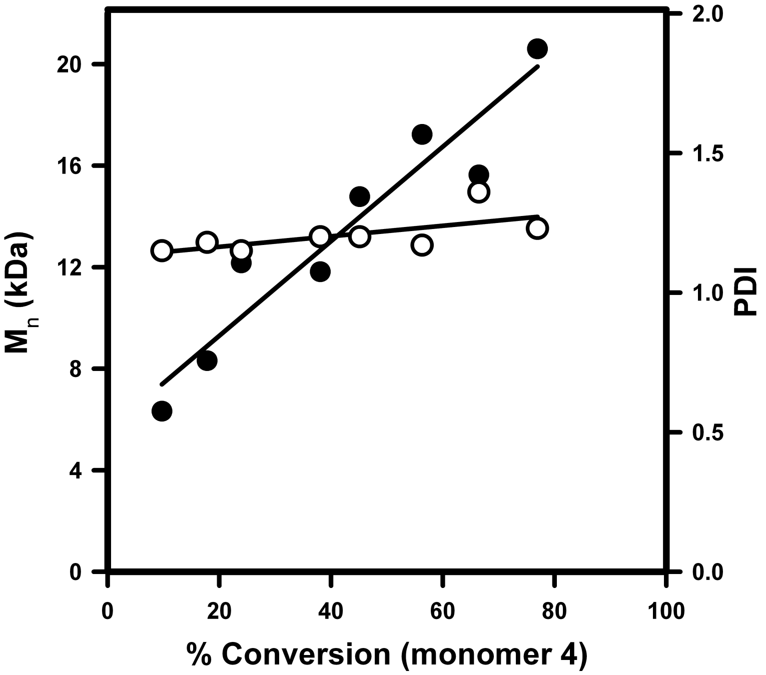


Figure S17. Plot of Mn (●) and PDI (○) versus conversion for **4** (temp = 0 ◦C, [**4**] = 0.05 M, [Ni(dppp)Cl_2] = 0.0005 M).

Table S8. Data for the plot in Figure S17.

% Conversion (**4**)	M_n (kDa)	PDI	Note
9.7	6.3	1.15	
18	8.3	1.18	
24	12	1.15	
38	12	1.20	shoulder
45	15	1.20	shoulder
56	17	1.17	shoulder
66	16	1.36	shoulder
80	21	1.23	shoulder

Note that for monomer **4**, only a single regioisomer is consumed within the first 20% conversion as demonstrated by the following GC traces:

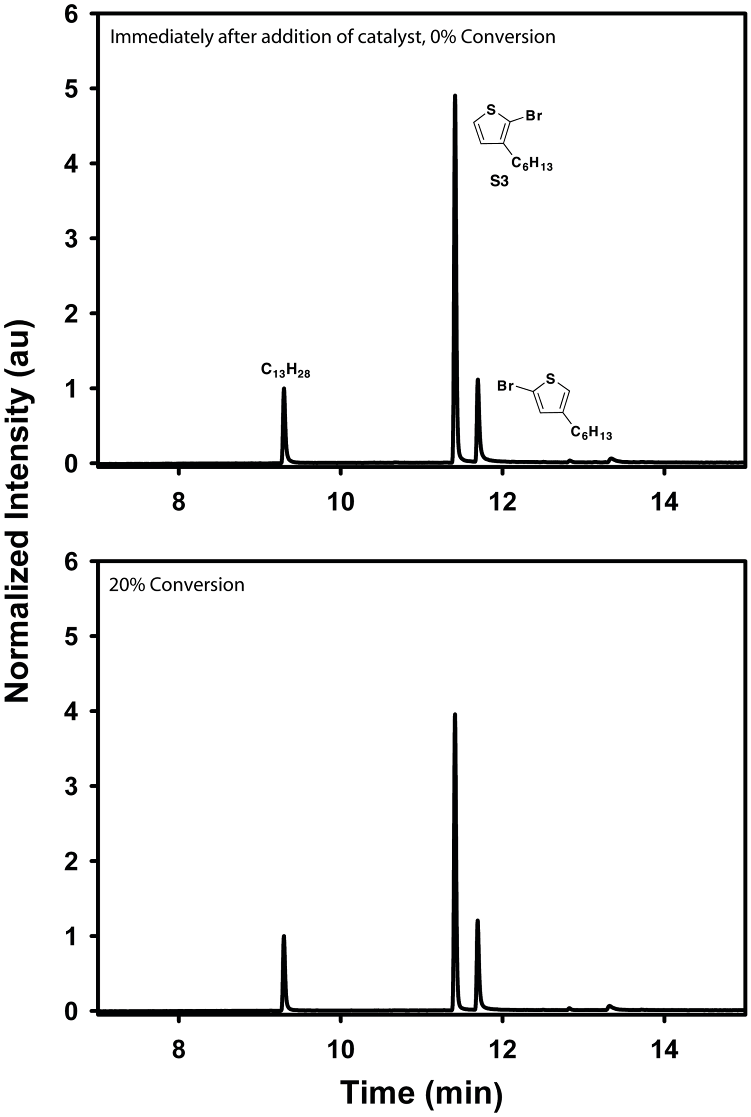


Figure S18. GC trace showing consumption of only a single thiophene regioisomer during the first 20%.

IX. Polymerization Rate Studies

General procedure for polymerization rate studies utilizing the ReactIR:

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 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 to rt under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling, the flask was charged with THF and cooled to 0 °C over 5 min. After recording a background spectrum, **2a** or **2b** (see Synthetic Procedures) was added by syringe and allowed to equilibrate for at least 5 min at 0 °C. The pre-initiated catalyst solution was then injected and spectra were recorded every 30 s over the first 10% conversion. To account for mixing and temperature equilibration, spectra recorded in the first 60 s of the reaction were discarded. The data were converted to concentrations using the appropriate calibration curves (Figures S11, S12 and S13).

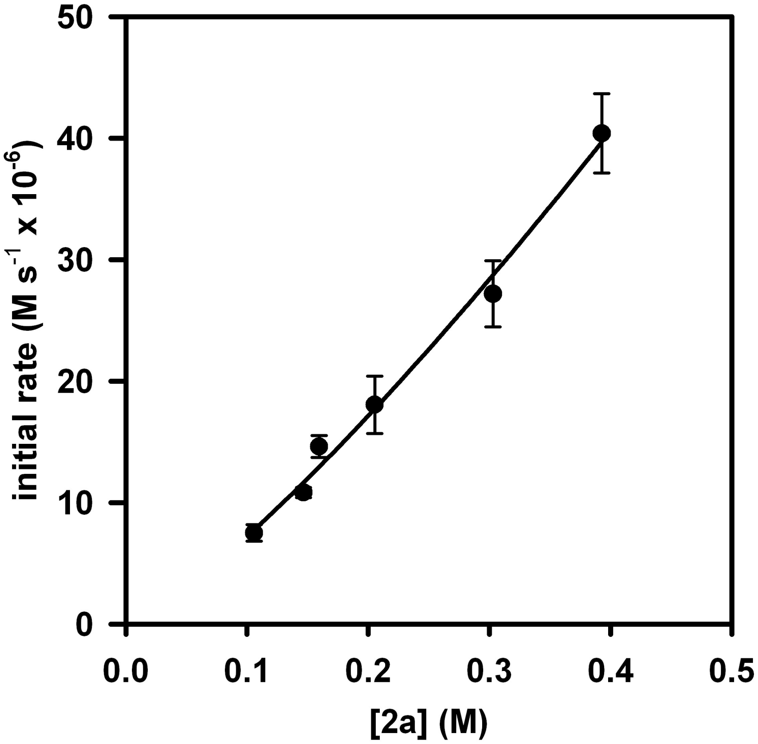


Figure S19. Plot of initial rate versus [monomer] for the polymerization of **2a**. (temp = 0 °C, [Ni(dppp)Cl_2] = 0.0015 M) fitted to initial rate = a[**2a**]^n, where a = 1.3 ± 0.1 x 10^2 and n = 1.24 ± 0.07.

Table S9. Data for the plot in Figure S19.

[**2a**] (M)	initial rate (M s^{-1})
0.1	7.5 ± 0.7 x 10^{-6}
0.15	10.8 ± 0.4 x 10^{-6}
0.16	14.6 ± 0.9 x 10^{-6}
0.2	18 ± 2 x 10^{-6}
0.3	27 ± 3 x 10^{-6}
0.4	40 ± 3 x 10^{-6}

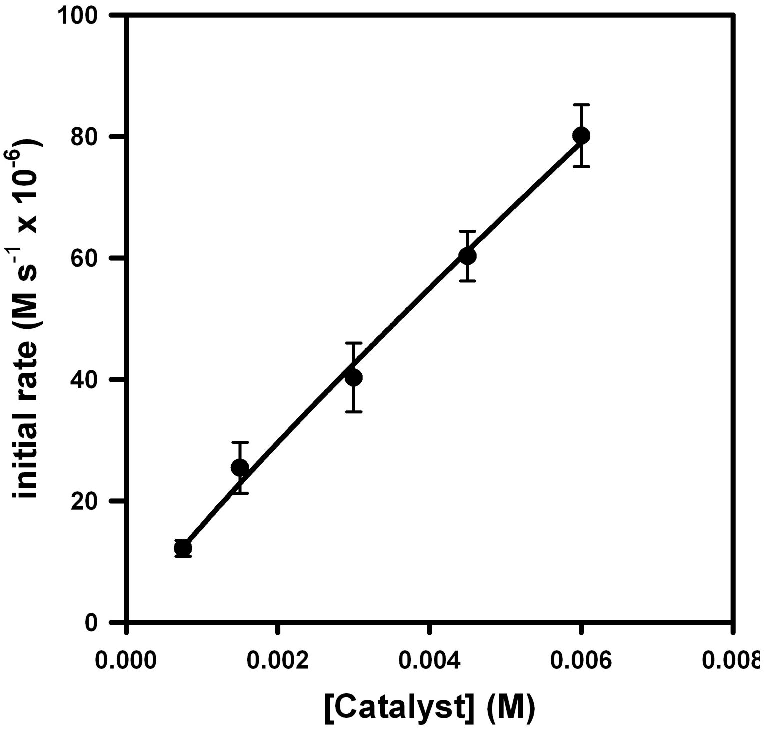


Figure S20. Plot of initial rate versus [catalyst] for the polymerization of **2a** (temp = 0 ◦C, [**2a**] = 0.20 M), fitted to initial rate = *a*[catalyst]^n, where *a* = 8 ± 2 x 10^3 and *n* = 0.89 ± 0.05.

Table S10. Data for the plot in Figure S20.

[Catalyst] (M)	initial rate (M s^{-1})
0.00075	12 ± 1 x 10^{-6}
0.0015	25 ± 4 x 10^{-6}
0.003	40 ± 6 x 10^{-6}
0.0045	60 ± 4 x 10^{-6}
0.006	80 ± 5 x 10^{-6}

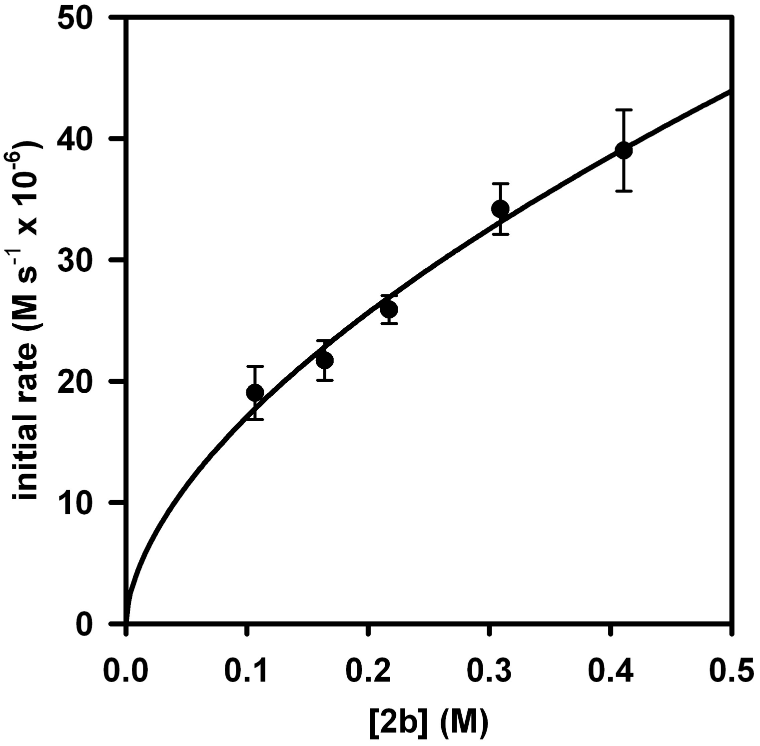


Figure S21. Plot of initial rate versus [monomer] for the polymerization of **2b** (temp = 0 ◦C, [Ni(dppp)Cl$_2$] = 0.0015 M) fitted to initial rate = a[**2b**]^n, where a = 66 ± 4 and n = 0.59 ± 0.05.

Table S11. Data for the plot in Figure S21.

[**2b**] (M)	initial rate (M s^{-1})
0.1	19 ± 2 x 10^{-6}
0.16	21 ± 1 x 10^{-6}
0.2	26 ± 1x 10^{-6}
0.3	34 ± 2 x 10^{-6}
0.4	39 ± 3 x 10^{-6}

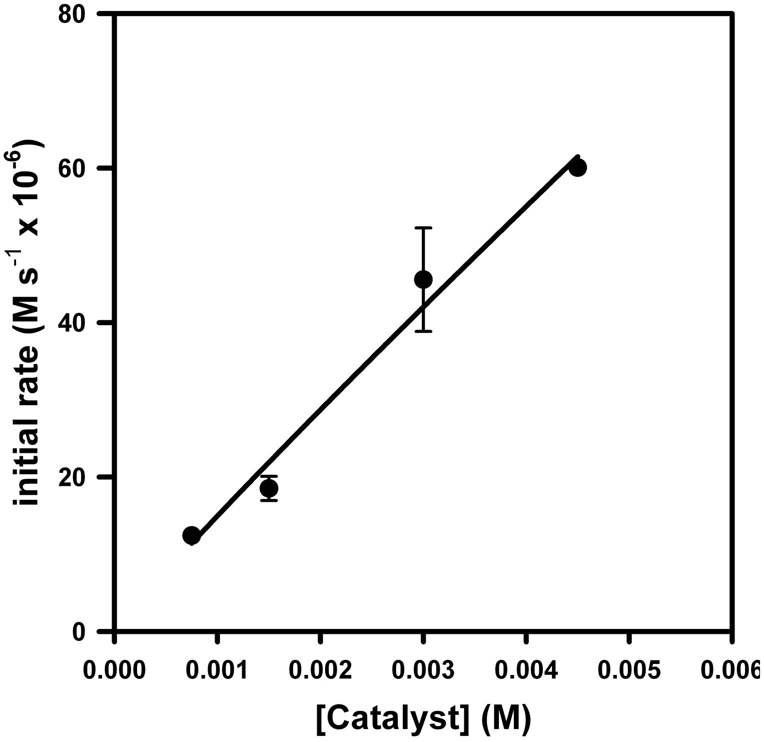


Figure S22. Plot of initial rate versus [catalyst] for the polymerization of **2b** (temp = 0 ◦C, [**2b**] = 0.20 M) fitted to initial rate = *a*[catalyst]^n, where *a* = 1.0 ± 0.7 x 10^4 and *n* = 0.9 ± 0.1.

Table S12. Data for the plot in Figure S22.

[Catalyst] (M)	initial rate (M s^{-1})
0.00075	12.4 ± 0.3 x 10^{-6}
0.0015	18 ± 2 x 10^{-6}
0.003	45 ± 6 x 10^{-6}
0.0045	60 ± 0.2 x 10^{-6}

Changes to the general procedure to determine the order in LiCl:

In the glovebox, a solution of **2a** was prepared and titrated as described above. LiCl (1.0 equiv) was then added and the mixture was stirred until homogeneous to generate **2b**. Separately a 0.6 M solution of LiCl in THF was prepared. The solutions were then removed from the glovebox in 25 mL Schlenk tubes.

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 stir bar. The other neck was equipped with a three-way adapter fitted with a septum for injections and an N_2 line. A 50 mL 2-neck flask was cooled to rt under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling, the flask was charged with THF and the appropriate amount of LiCl solution and cooled to 0 ^{o}C over 5 min. After recording a background spectrum, **2b** was added by syringe and allowed to equilibrate for at least 5 min at 0 ^{o}C. The pre-initiated catalyst solution was then injected and spectra were recorded every 30 s over the first 10% conversion. To account for mixing and temperature equilibration, spectra recorded in the first 60 s of the reaction were discarded. The data were converted to concentrations using the appropriate calibration curves (Figure S12).

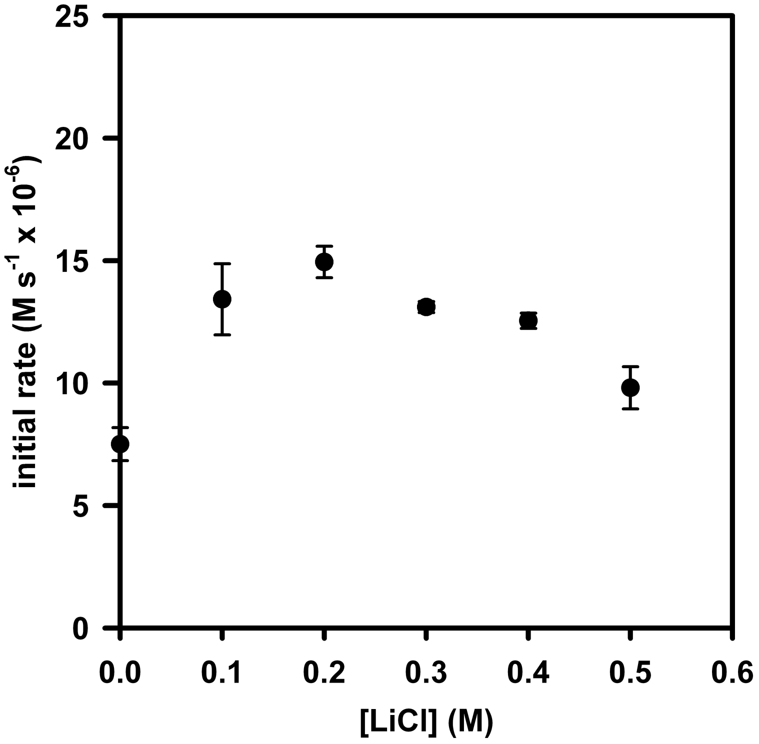


Figure S23. Plot of initial rate versus [LiCl] for the polymerization of **2b** (temp = 0 °C, [**2b**] = 0.20 M, [Ni(dppp)Cl$_2$] = 0.0015 M). Average initial rate = 12 ± 3 x 10^{-6} M s^{-1}.

Table S13. Data for the plot in Figure S23.

[LiCl] (M)	initial rate (M s^{-1})
0	7.5 ± 0.7 x 10^{-6}
0.1	13 ± 1 x 10^{-6}
0.2	14.9 ± 0.6 x 10^{-6}
0.3	13.1 ± 0.2 x 10^{-6}
0.4	12.5 ± 0.3 x 10^{-6}
0.5	9.8 ± 0.9 x 10^{-6}

General procedure for polymerization rate studies utilizing GC:

An oven-dried 10 mL flask was equipped with a stir bar and rubber septum was cooled to rt under vacuum and then refilled with N_2. Following two more cycles of evacuation and refilling the flask was charged with tridecane (25 μL), THF and **4** and cooled to 0 ^{o}C over 2 min. The pre-initiated catalyst solution was then injected. Aliquots (~ 25 μL) were withdrawn through the septum and immediately quenched with methanol (~ 0.5 mL). Each aliquot was then diluted with $CHCl_3$ and analyzed by GC.

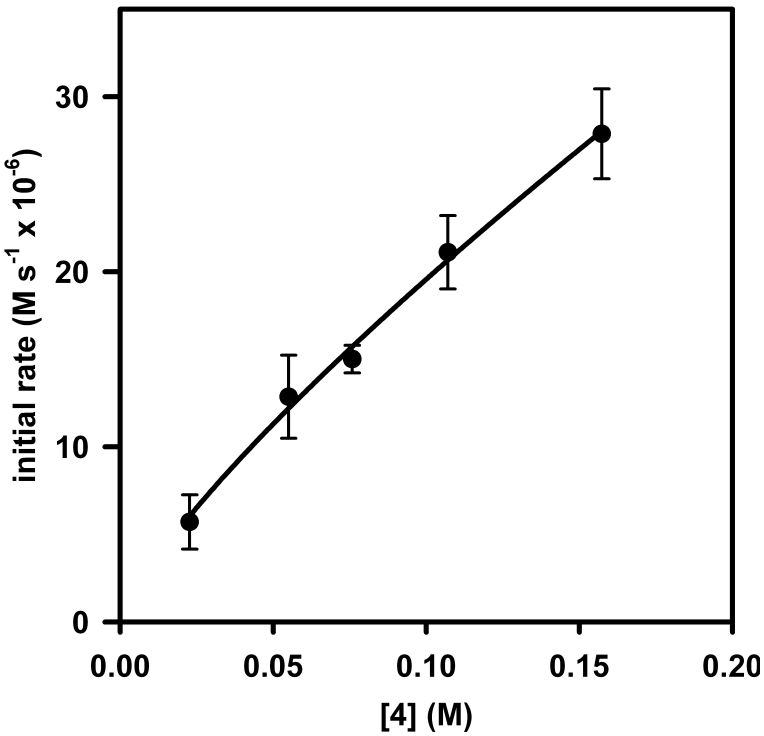


Figure S24. Plot of initial rate versus [monomer] for the polymerization of **4** (temp = 0 ◦C, [Ni(dppp)Cl_2] = 0.00025 M) fitted to initial rate = *a*[**4**]^n, where *a* = 12 ± 1 x 10^1 and *n* = 0.79 ± 0.04.

Table S14. Data for the plot in Figure S24.

[**4**] (M)	initial rate (M s^{-1})
0.02	5.7 ± 1 x 10^{-6}
0.05	13 ± 2 x 10^{-6}
0.07	15 ± 0.8 x 10^{-6}
0.11	21 ± 2 x 10^{-6}
0.16	28 ± 2 x 10^{-6}

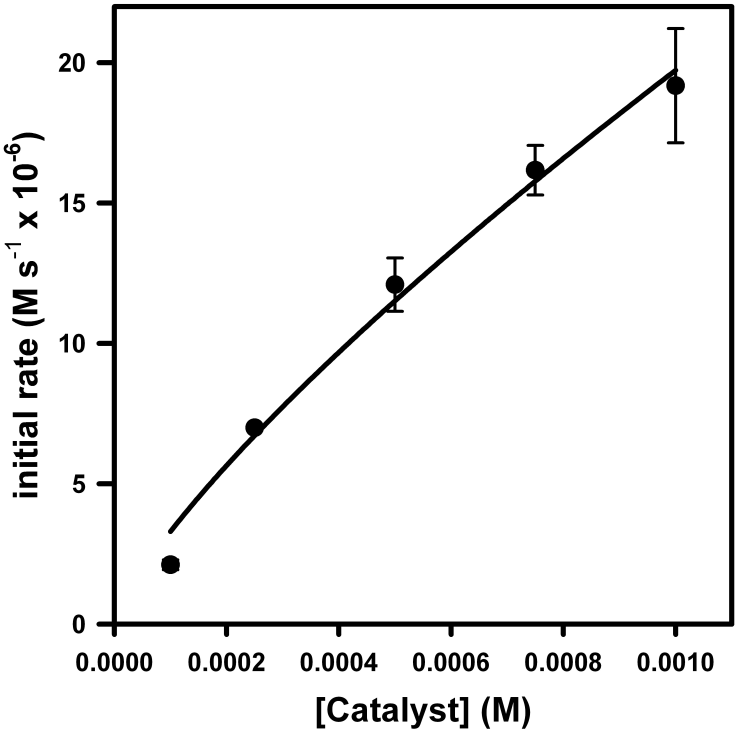


Figure S25. Plot of initial rate versus [catalyst] for the polymerization of **4** (temp = 0 ◦C, [**4**] = 0.05 M) fitted to initial rate = *a*[catalyst]^n, where *a* = 4 ± 2 x 10^3 and *n* = 0.78 ± 0.07.

Table S15. Data for the plot in Figure S25.

[Catalyst] (M)	initial rate (M s^{-1})
0.0001	2.1 ± 0.2 x 10^{-6}
0.00025	6.99 ± 0.05 x 10^{-6}
0.0005	12 ± 1 x 10^{-6}
0.00075	16.1 ± 0.8 x 10^{-6}
0.001	19 ± 2 x 10^{-6}

X. NMR Spectroscopic Studies of Catalyst Resting State

Complexs **IIa** and **IIb** in the presence and absence of monomer **2**

Preparation of the solutions:

All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(dppp)Cl_2 (33 mg, 0.060 mmol, 1.0 equiv), THF (0.5 mL), and **2** (1.5 mL, 0.40 M, 10 equiv) were added to the vial to prepare a 0.030 M solution of the Ni species. The heterogeneous reaction mixture was stirred for 10 min until homogeneous.

Preparation of the NMR spectroscopy samples:

The Ni solution (0.3 mL, 0.02 mmol, 1 equiv) was loaded into a 1 mL syringe. Separately, THF (0.3 mL) and **2** (0.3 mL, 0.1 mmol, 5 equiv) were loaded into an NMR tube sealed with a rubber septum. The NMR tube was removed from the glovebox and cooled in a brine-ice mixture (-15 ◦C) . Immediately before acquiring the spectrum the Ni solution was injected into the NMR tube which was then rapidly inverted. The sample was loaded into the NMR spectrometer pre-cooled at -15 ◦C and ^{31}P and ^{1}H NMR spectra were collected (Figure S26A and S27A). Afterwards the samples were removed from the instrument and allowed to warm to rt. After approximately 30 min a second set of ^{31}P and ^{1}H NMR spectra were collected at rt (Figure S26B and S27B).

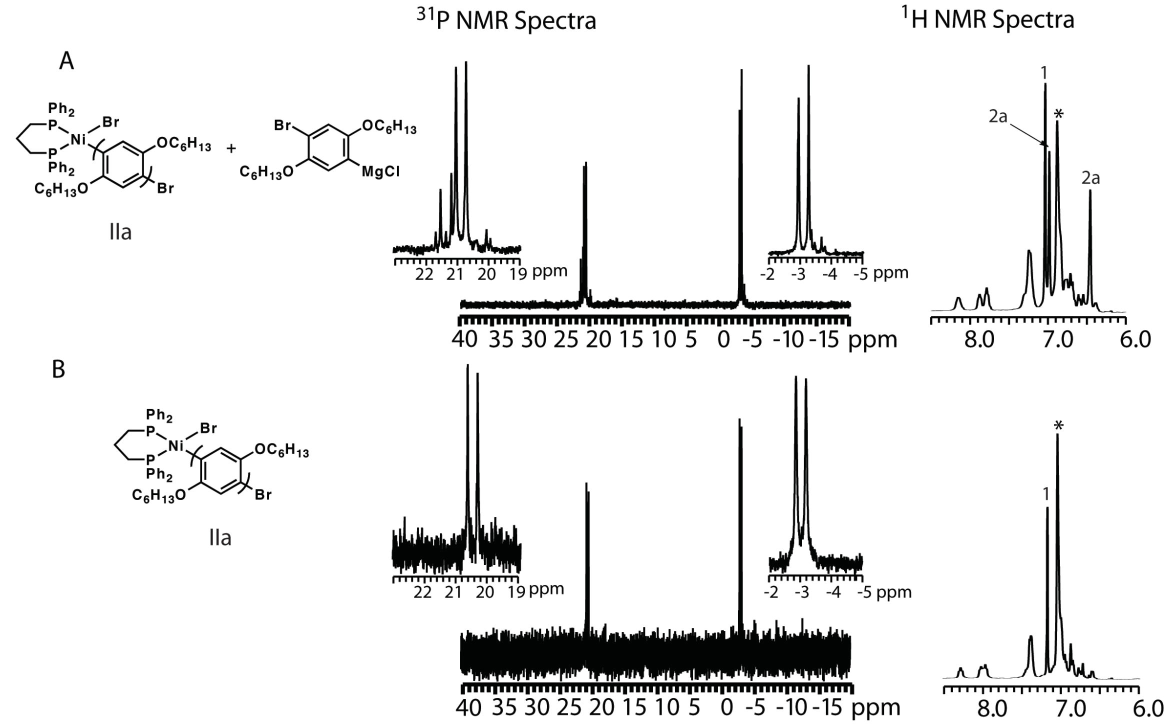


Figure S26. (A) ^{31}P NMR spectrum of complex **IIa** (162 MHz, THF, -15 ◦C) δ 20.9 (d, $J_{P\text{-}P}$ = 52.0 Hz), -3.11 (d, $J_{P\text{-}P}$ = 52.0 Hz) in the presence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectrum. (B) ^{31}P NMR spectrum of complex **IIa** (162 MHz, THF, rt) δ 20.5 (d, $J_{P\text{-}P}$ = 52.2 Hz), -3.11 (d, $J_{P\text{-}P}$ = 51.4 Hz) in the absence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectrum. *Corresponds to polymer **P2a**.

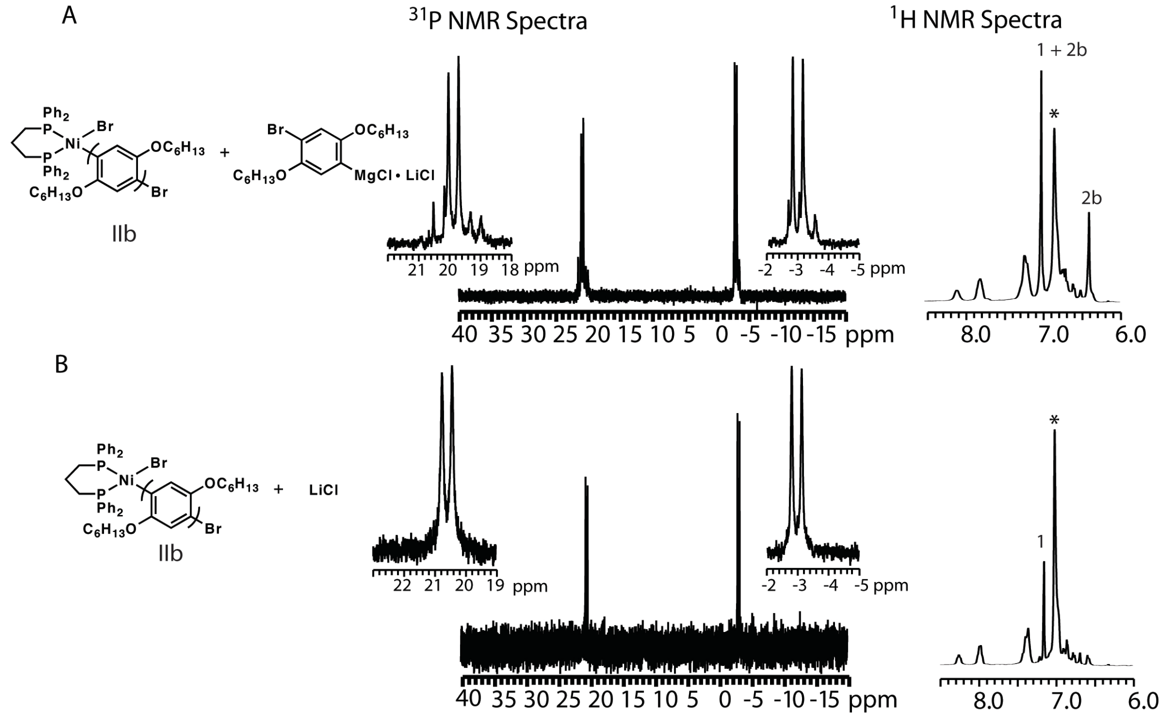


Figure S27. (A) ^{31}P NMR spectrum of complex **IIb** (162 MHz, THF, -15 ◦C) δ 20.9 (d, $J_{P\text{-}P}$ = 52.7 Hz), -2.97 (d, $J_{P\text{-}P}$ = 52.0 Hz) in the presence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectrum. (B) ^{31}P NMR spectrum of complex **IIb** (162 MHz, THF, rt) δ 20.4 (d, $J_{P\text{-}P}$ = 52.8 Hz), -3.03 (d, J = 51.5 Hz) in the absence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectrum. *Corresponds to polymer **P2b**.

Complexe **V** in the presence and absence of monomer **4**

Preparation of the solutions:

All actions were performed in a glovebox under N_2 atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, Ni(dppp)Cl_2 (16 mg, 0.030 mmol, 1.0 equiv), THF (0.5 mL), and **4** (1.5 mL, 0.20 M, 10 equiv) were added to the vial to prepare a 0.015 M solution of the Ni species. The reaction mixture was stirred for 10 min until homogeneous. ^{31}P and ^{1}H NMR spectra were collected at rt (Figure 28A).

Separately, THF (0.5 mL) and **4** (0.2 mL, 0.04 mmol, 7 equiv) were loaded into an NMR tube sealed with a rubber septum. The NMR tube was removed from the glovebox and cooled in a brine-ice mixture (-15 °C). Immediately before acquiring the spectrum the Ni solution (0.4 mL, 0.006 mmol, 1 equiv) was injected into the NMR tube which was then rapidly inverted. The sample was loaded into the NMR spectrometer pre-cooled at -15 °C and ^{31}P and ^{1}H NMR spectra were collected (Figure 28B).

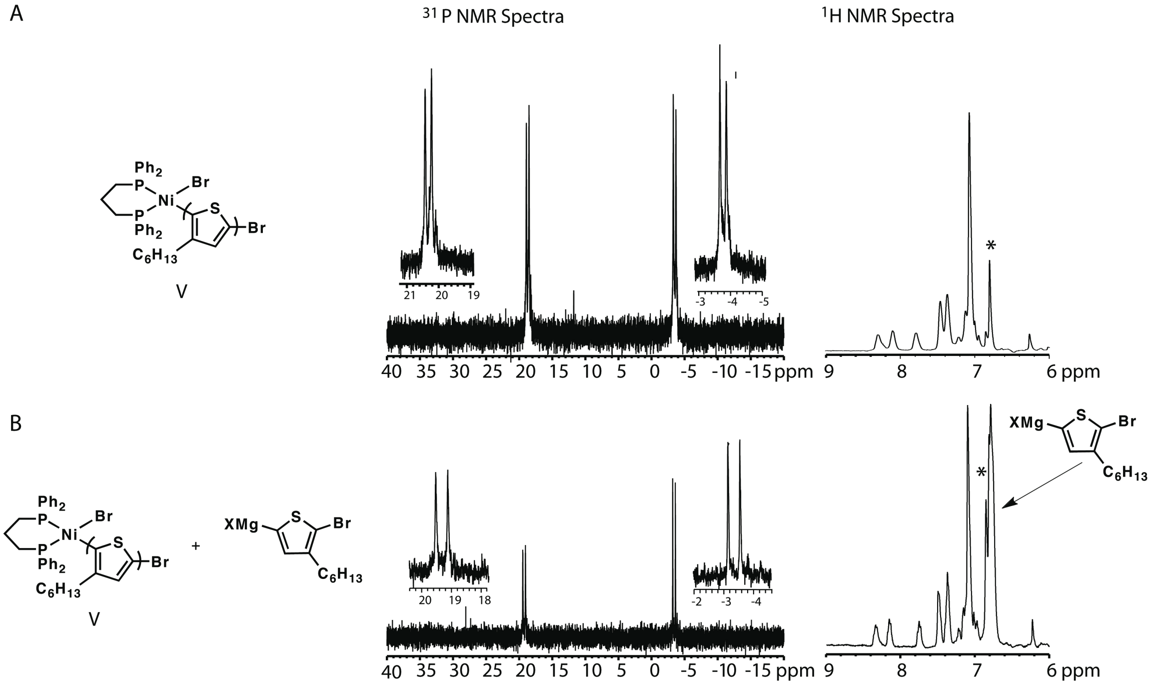


Figure S28. (A) ^{31}P NMR spectrum of complex **V** (162 MHz, THF, rt) δ 18.7 (d, $J_{P\text{-}P}$ = 65.4 Hz), -3.47 (d, $J_{P\text{-}P}$ = 65.4 Hz) in the absence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectrum. (B) ^{31}P NMR spectrum of complex **V** (162 MHz, THF, -15 ◦C) δ 19.3 (d, $J_{P\text{-}P}$ = 66.1 Hz), -3.35 (d, $J_{P\text{-}P}$ = 65.4 Hz) in the presence of monomer as confirmed by the aromatic region of the ^{1}H NMR spectrum. *Corresponds to polymer **P4**.

Note that for monomer **4** only a single regioisomer is consumed under these conditions as demonstrated by the following GC experiment.

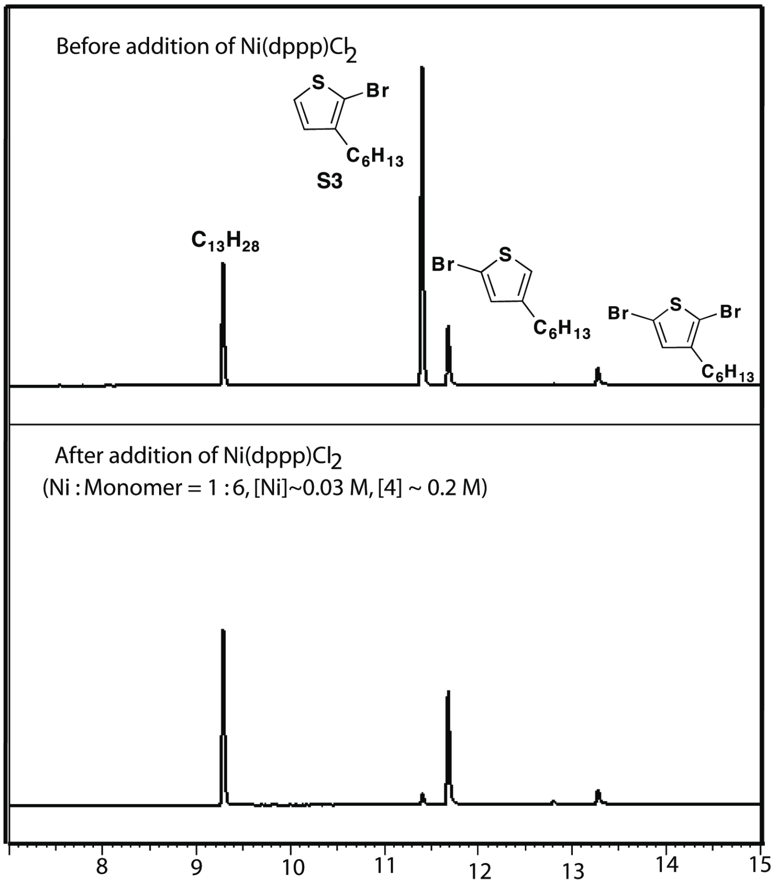


Figure S29. GC trace showing consumption of only a single thiophene regioisomer.

XI. Grignard Aggregation Studies by ^{1}H NMR spectroscopy

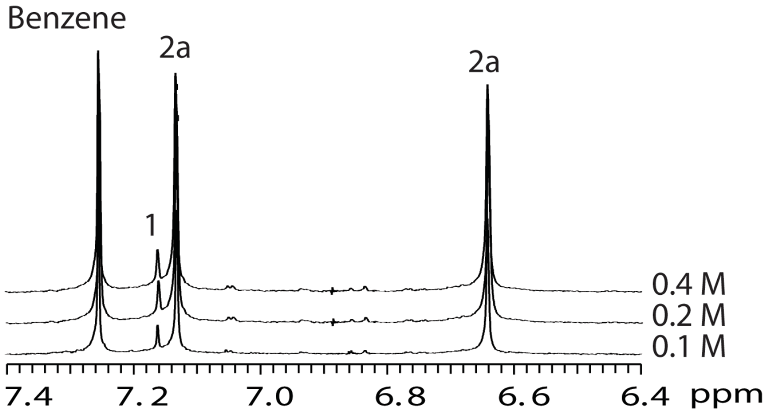


Figure S30. ^{1}H NMR spectra (THF, rt) showing **2a** at increasing concentrations.

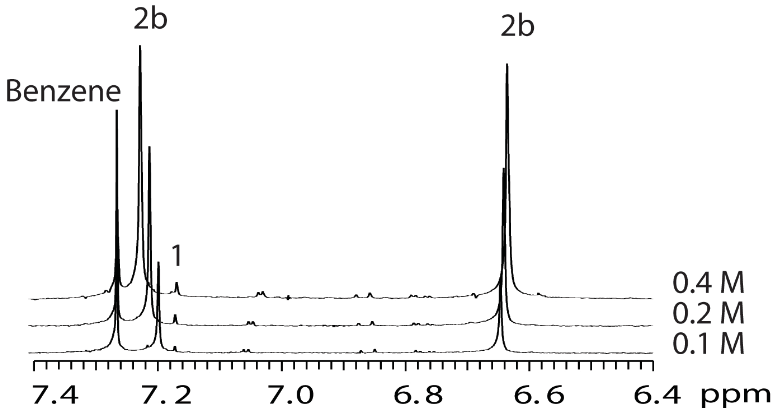


Figure S31. ^{1}H NMR (THF, rt) spectra showing **2b** at increasing concentrations.

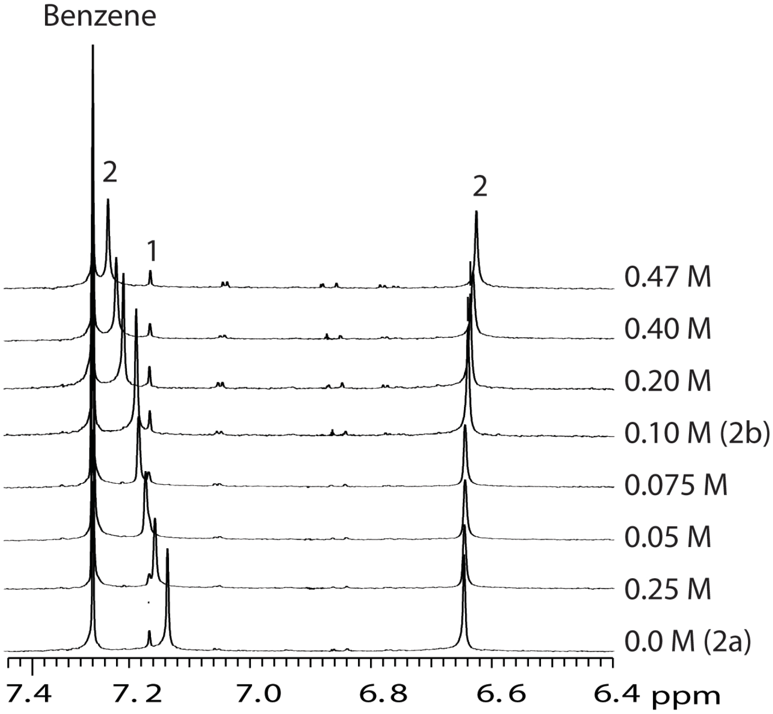


Figure S32. ^{1}H NMR (THF, rt) spectra showing **2** (0.1 M) with increasing concentrations of LiCl.

XII References Cited

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