

Appendix 2
Supporting Information for Chapter 3
Cross-propagation in Ni-catalyzed copolymerizations of 3-alkylthiophenes and 2,5-dialkoxybenzenes

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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 (2M in THF) was purchased in 100 mL quantities from Aldrich and Ni(cod)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 P₂O₅. Decane was distilled from CaH₂. Compounds **1a**¹, **2a**¹, 1,2-bis(di-4-chlorophenylphosphino)ethane², and 1,2-bis(di-4-methoxyphenylphosphino)ethane², were prepared by literature procedures. Monomers were titrated by the method of Love and Jones³ before use.

II. General Experimental

NMR Spectroscopy: Unless otherwise noted, ¹H, ¹³C, and ³¹P NMR spectra for all compounds were acquired in CDCl₃ on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 100, and 161 MHz, respectively. For ¹H and ¹³C NMR spectra the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. ³¹P NMR spectra were referenced to external H₃PO₄ (85% aq). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonance (br). Unless otherwise indicated, the ¹H, ³¹P and ¹³C NMR spectra were recorded at room temperature. Note that integrations for protons on the alkyl chains of some compounds are high due to insufficient relaxation time.

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 and 350 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 mmID, 0.25 µm df) column.

III. General and Representative Procedures

Representative procedure for obtaining plots of M_n and PDI versus conversion

An oven-dried 10 mL flask equipped with a stir bar and a rubber septum was cooled under vacuum and then refilled with N₂. Following two more cycles of evacuation and refilling the flask was charged with docosane (0.1 mL, 0.1 M in THF), THF (7.0), **1a** (0.50 mL, 0.25 M, 0.125 mmol, 1.0 equiv) and **2a** (0.29 mL, 0.44 M, 0.125 mmol, 1.0 equiv). A solution of **3b** (0.500 mL, 0.0125 mmol 0.01 equiv) was injected. Aliquots (~0.2 mL) were withdrawn through the septum and immediately quenched with 5 M HCl (~1 mL). Each aliquot was then extracted with CHCl₃ (with mild heating if polymer had precipitated) and a portion analyzed by GC. The remainder was dried over MgSO₄, filtered, 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 conducting block copolymerizations

In the glovebox, **1a** (0.55 mL, 0.250 M, 0.125 mmol, 1.00 equiv) was combined with THF (11 mL) in a 20 mL vial with a stir bar. A solution of **3b** (0.5 mL, 0.025 M, 0.0125 mmol 0.01 equiv) was added with vigorous stirring and the reaction stirred for 3 h. An aliquot (~0.100 mL) was taken from the reaction, removed from the glovebox, quenched with 5 M HCl (1 mL), extracted with CHCl₃ (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC analysis. A solution of **2a** (0.260 mL, 0.450 M, 0.125 mmol, 1.00 equiv) was then added to the reaction and the reaction stirred for an additional 3 h. The reaction was then removed from the glovebox and quenched with 5 M HCl (10 mL). It was then extracted with hot CHCl₃ (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant purple solid was then removed for GPC analysis.

Representative procedure for conducting batch copolymerizations

In the glovebox, **1a** (0.55 mL, 0.250 M, 0.125 mmol, 1.00 equiv) and **2a** (0.26 mL, 0.45 M, 0.125 mmol, 1.00 equiv) were combined with THF (11 mL) in a 20 mL vial with a stir bar. A solution of **3b** (0.5 mL, 0.025 M, 0.0125 mmol 0.01 equiv) was added with vigorous stirring and the reaction stirred for 4 h. The reaction was then removed from the glovebox and quenched with 5 M HCl (10 mL). It was then extracted with hot CHCl₃ (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant purple solid was then removed for GPC analysis.

Representative procedure for conducting crossover studies

In the glovebox, **4b** (0.0198 g, 0.0263 mmol, 1.00 equiv) was dissolved in THF (1.9 mL) in a 4 mL vial with equipped with a stir bar. Decane (0.100 mL, 0.1 M) and dppe (0.0105 g, 0.0263 mmol, 1.00 equiv) were added and the reaction stirred for 1 min to combine. **1b** (0.087 mL, 0.0237 mmol, 0.90 equiv) was added and the reaction stirred for 15 min. The reaction was then removed from the glovebox and quenched with 12 MHCl (1 mL,). H₂O (2 mL) was added and the reaction extracted with CHCl₃ (3 x 1 mL). The combined organic extracts were then analyzed by GC.

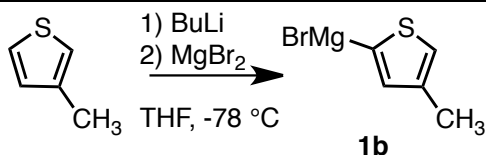
Representative procedure for conducting chain-extension studies

In the glovebox, **4b** (0.0303 g, 0.0402 mmol, 1.00 equiv) was dissolved in THF (2.0 mL) in a 4 mL vial with equipped with a stir bar. Decane (0.100 mL, 0.1 M) and dppe (0.0160 g, 0.0402 mmol, 1.00 equiv) were added and the reaction stirred for 1 min to combine. **2b** (0.086 mL, 0.037 mmol, 0.90 equiv) was added and the reaction stirred for 15 min. The reaction was then removed from the glovebox and quenched with HCl (1mL, 12 M). H₂O (2 mL) was added and the reaction extracted with CHCl₃ (3 x 1 mL). The combined organic extracts were then analyzed by GC.

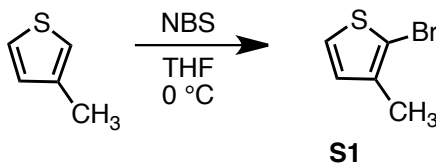
Representative procedure for conducting competition studies

In the glovebox, **4b** (0.0303 g, 0.0402 mmol, 1.00 equiv) was dissolved in THF (2.0 mL) in a 4 mL vial with equipped with a stir bar. Decane (0.100 mL, 0.1 M) and dppe (0.0160 g, 0.0402 mmol, 1.00 equiv) were added and the reaction stirred for 1 min to combine. **2c** (0.086 mL, 0.037 mmol, 0.90 equiv) was added and the reaction stirred for 15 min. The reaction was then removed from the glovebox and quenched with HCl (1mL, 12 M). H₂O (2 mL) was added and the reaction extracted with CHCl₃ (3 x 1 mL). The combined organic extracts were then analyzed by GC.

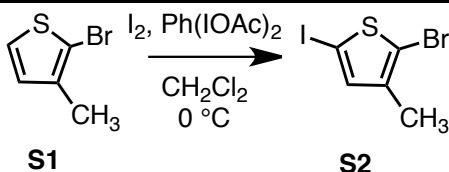
IV. Synthetic Procedures



1b: An oven-dried 20 mL Schlenk flask equipped with a stir bar and septum was cooled under vacuum then filled with N₂. 3-methylthiophene (0.0966 mL, 1.00 mmol, 1.00 equiv) and THF (2.4 mL) were added and the flask cooled to -78 °C and equilibrated for 5 min. *n*-BuLi (0.625 mL, 1.6 M, 1.00 mmol, 1.00 equiv) was added dropwise and the reaction maintained at -78 °C for 3 h. The solution was then cannula transferred to a second vacuum-dried, N₂ filled 20 mL Schlenk flask equipped with a stir bar and septum containing MgBr₂ at -78 °C and the reaction maintained at -78 °C for 30 min, then warmed to rt.

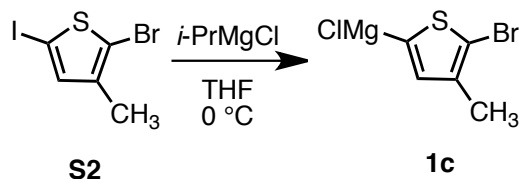


2-bromo-3-methylthiophene (S1): An oven-dried 100 mL Schlenk flask equipped with a stir bar and septum was cooled under a positive flow of N₂, then 3-methylthiophene (0.48 mL, 5.0 mmol, 1.00 equiv) and THF (10 mL) were added. The flask was then cooled to 0 °C for 5 min, after which NBS (0.9293 g, 5.25 mol, 1.05 equiv) was added under positive N₂. After 6 h the reaction was quenched with 10% aq Na₂CO₃ (10 mL) and extracted with hexanes (3 x 10 mL). The combined organics were washed with brine (1 x 15 mL), dried over decolorizing carbon and MgSO₄, filtered and concentrated in vacuo. The resulting yellow oil was chromatographed through silica gel using hexanes as the eluent then purified via distillation to yield 2-bromo-3-methylthiophene (**S1**) (0.4301 g, 49% yield) as a clear oil. HRMS (EI): Calcd. for C₅H₅BrS [M⁺] 175.92953; found, 175.9292.

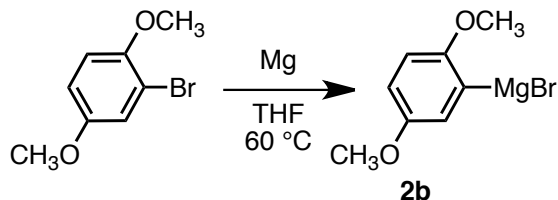


2-bromo-3-methyl-5-iodothiophene (S2): An oven-dried 50 mL Schlenk flask equipped with a stir bar and septum was cooled under a positive flow of N₂. **S1** (0.4301 g, 2.43 mmol, 1.00 equiv) and CH₂Cl₂ (10 mL) were added to the flask and the flask was cooled

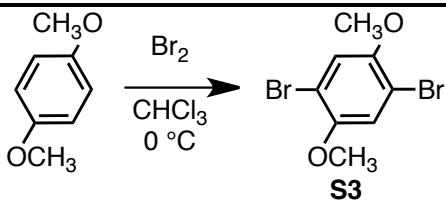
to 0 °C. I₂ (0.3390 g, 1.34 mmol, 0.550 equiv) and PhI(OAc)₂ (0.4450 g, 1.34 mmol, 0.550 equiv) were added under positive N₂. The reaction was stirred at 0 °C for 4 h in the dark after which it was quenched with saturated aq Na₂SO₃ (~10 mL) and extracted with CH₂Cl₂ (3 x 10 mL). The combined organics were then washed with brine (1 x 20 mL), dried over decolorizing carbon and MgSO₄, filtered and concentrated in vacuo. The resulting yellow oil was chromatographed through silica using hexanes as the eluent and then purified via distillation to yield 2-bromo-3-methyl-5-iodothiophene (**S2**) (2.40 g, 61% yield) as a clear oil. HRMS (EI): Calcd. for C₅H₄BrIS [M⁺] 301.82618; found, 301.8252.



1c: **S2** (0.1577 g, 0.520 mmol, 1.05 equiv) was dissolved in THF (1.75 mL) in a 25 mL Schlenk tube equipped with a stir bar and septum under an N₂ atmosphere. The tube was sealed and cooled to 0 °C. *i*-PrMgCl (0.250 mL, 0.500 mmol, 1.00 equiv) was added under N₂ and the reaction stirred at 0 °C for 30 min, then warmed to rt.

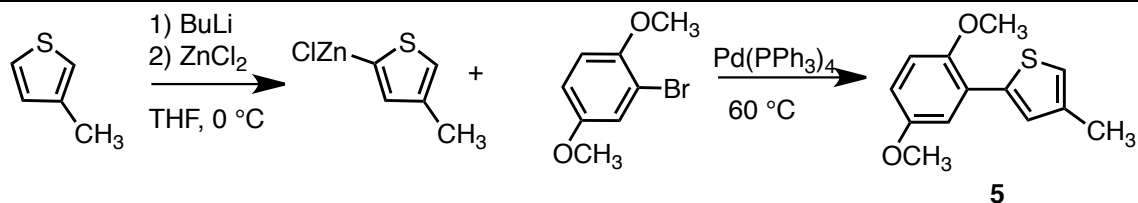


2b: Bromo-2,5-dimethoxybenzene (0.6512 g, 3.00 mmol, 1.00 equiv) and Mg (0.0729 g, 3.00 mmol, 1.0 equiv) were combined in THF (6 mL) in a 25 mL Schlenk tube equipped with a stir bar and septum under an N₂ atmosphere. The tube was sonicated for 5 h then heated to 65 °C overnight.

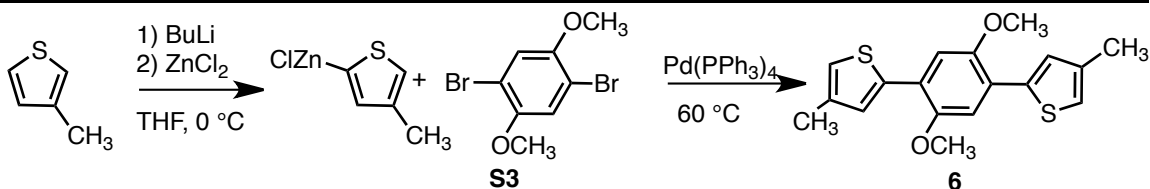


1,4-dibromo-2,5-dimethoxybenzene (S3): *p*-Dimethoxybenzene (1.000 g, 7.237 mmol, 1.00 equiv) was dissolved in 15 mL CHCl₃ in a 30 mL flask equipped with a stir bar. The flask was cooled to 0 °C and Br₂ (0.9327 mL, 1.809 mmol, 2.5 equiv) was added dropwise. After 2 h the reaction was quenched with aq Na₂SO₃ (~10 mL) then extracted with CH₂Cl₂ (2 x 10 mL) and the solvent removed in vacuo. The resulting white powder was recrystallized from CHCl₃/ EtOH and dried under vacuum to yield 1,4-dibromo-2,5-

dimethoxybenzene (1.8208 g, 85%) as white crystals. HRMS (EI): Calcd. for C₈H₈Br₂O₂ [M⁺] 293.8891; found, 283.8892.

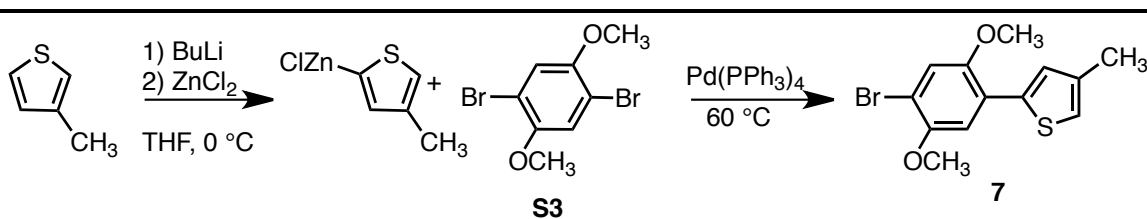


2-(2,5-dimethoxyphenyl)-4-methylthiophene (5): A 50 mL oven-dried Schlenk flask equipped with stir bar and septum was cooled under vacuum. Once cool, the flask was filled with N₂ then re-evacuated. This procedure was repeated twice, then the flask was refilled with N₂ and charged with 3-methylthiophene (0.193 mL, 2.0 mmol, 1.0 equiv). THF (4 mL) was added and the flask cooled to 0 °C. BuLi (1.25 mL, 2.0 mmol, 1.0 equiv) was added dropwise and the reaction maintained at 0 °C for 2 h. A solution of ZnCl₂ (0.2726 g, 2.0 mmol, 1.0 equiv) in THF (4 mL) was added to the flask and the solution stirred at 0 °C for 30 min. Then a solution of 1-bromo-2,5-dimethoxybenzene (0.301 mL, 2.0 mmol, 1.0 equiv) and Pd(PPh₃)₄ (0.0920 g, 0.08 mmol) in THF (8 mL) was added and the reaction brought to 60 °C and stirred overnight. The reaction was cooled to rt then quenched with H₂SO₄ (10 mL, 5% in H₂O), then extracted with Et₂O (3 x 10 mL). The combined organics were washed with 10 mL brine and dried over MgSO₄, filtered and the solvent removed in vacuo. The resulting brown oil was chromatographed on silica eluting with 5% EtOAc in hexanes, then *p*-dimethoxybenzene removed by sublimation to yield **5** (0.0258 g, 11% yield) as a clear oil. HRMS (EI): C₁₃H₁₄O₂S [M⁺] 234.0715; found, 234.0707.

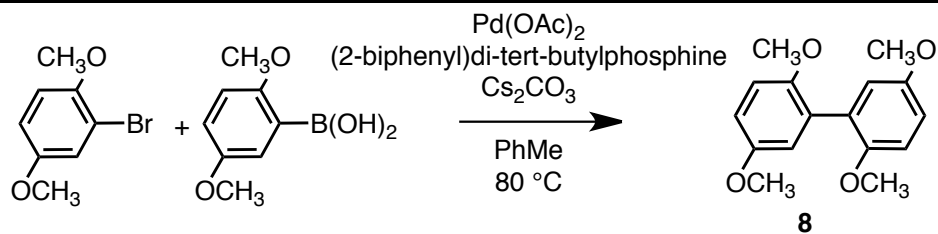


5,5'-(2,5-dimethoxy-1,4-phenylene)bis(3-methylthiophene) (6): A 50 mL oven-dried Schlenk flask equipped with stir bar and septum was cooled under vacuum. Once cool, the flask was filled with N₂ then re-evacuated. This procedure was repeated twice, then the flask was refilled with N₂ and charged with 3-methylthiophene (0.193 mL, 2.0 mmol, 1.0 equiv). THF (4 mL) was added and the flask cooled to 0 °C. BuLi (1.25 mL, 2.0 mmol, 1.0 equiv) was added dropwise and the reaction maintained at 0 °C for 3 h. A solution of ZnCl₂ (0.2726 g, 2.0 mmol, 1.0 equiv) in THF (4 mL) was added to the flask and the solution stirred at 0 °C for 30 min. Then a solution of 1,4-dibromo-2,5-dimethoxybenzene (0.2950 g, 1.0 mmol, 0.5 equiv) and Pd(PPh₃)₄ (0.0920 g, 0.08 mmol) in THF (8 mL) was added and the reaction brought to 60 °C and stirred for 48 h. The reaction was cooled to rt then quenched with H₂SO₄ (20 mL, 5% in H₂O), then extracted with Et₂O (3 x 15 mL). The combined organics were washed with 10 mL brine and dried over MgSO₄, filtered and the solvent removed in vacuo. The resulting yellow solid was

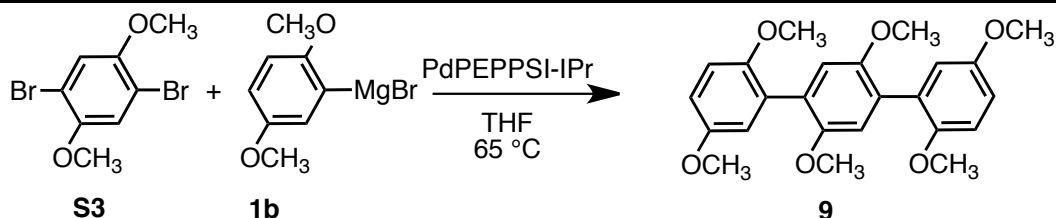
chromatographed on silica eluting with 5% EtOAc in hexanes, then recrystallized from hot CHCl₃ to yield **6** (0.0410 g, 12% yield) as yellow powder. HRMS (EI): C₁₈H₁₈O₂S₂ [M+] 330.0748; found, 330.0743.



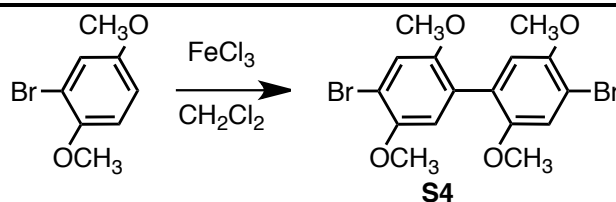
2-(4-bromo-2,5-dimethoxyphenyl)-4-methylthiophene (7): A 50 mL oven-dried Schlenk flask equipped with stir bar and septum was cooled under vacuum. Once cool, the flask was filled with N₂ then re-evacuated. This was repeated twice, then the flask was refilled with N₂ and charged with 3-methylthiophene (0.193 mL, 2.00 mmol, 1.0 equiv). THF (4 mL) was added and the flask cooled to 0 °C. BuLi (1.25 mL, 2.0 mmol, 1.0 equiv) was added dropwise and the reaction maintained at 0 °C for 2 h. A solution of ZnCl₂ (0.2726 g, 2.00 mmol, 1.0 equiv) in THF (4 mL) was added to the flask and the solution stirred at 0 °C for 30 min. Then a solution of **S3** (0.6000 g, 1.0 mmol, 1.0 equiv) and Pd(PPh₃)₄ (0.0920 g, 0.08 mmol) in THF (8 mL) was added and the reaction brought to 60 °C and stirred for 24 h. The reaction was cooled to rt then quenched with H₂SO₄ (15 mL, 5% in H₂O), then extracted with CH₂Cl₂ (3 x 10 mL). The combined organics were washed with brine (10 mL) and dried over MgSO₄, filtered and the solvent removed in vacuo. The resulting yellow solid was chromatographed on silica eluting with 15% CH₂Cl₂ in hexanes then residual *p*-dimethoxybenzene removed by sublimation and the resulting white solid recrystallized from CHCl₃/CH₃OH to yield **7** (0.0940 g, 15% yield) as a colorless wax. HRMS (EI): C₁₃H₁₃BrO₂S [M+] 311.9820; found, 311.9824.



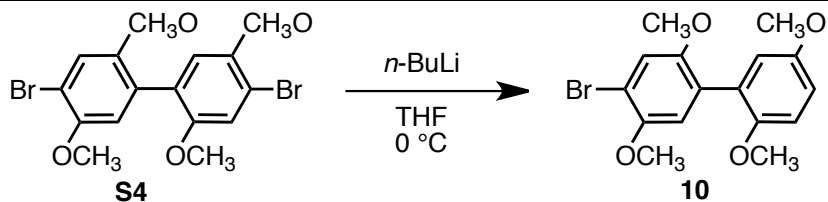
2,2',5,5'-tetramethoxy-1,1'-biphenyl (8): A 25 mL oven-dried Schlenk flask equipped with a septum and stir bar was cooled under N₂. The vessel was charged with 1-bromo-2,5-dimethoxybenzene (0.3255 g, 1.50 mmol, 1.0 equiv), 2,5-dimethoxyphenylboronic acid (0.3275 g, 1.80 mmol, 1.2 equiv), Cs₂CO₃ (1.466 g, 4.50 mmol, 3.0 equiv), Pd(OAc)₂ (0.0168 g, 0.075 mmol, 0.05 equiv), (2-biphenyl)di-tert-butylphosphine (0.0223 g, 0.075 mmol, 0.05 equiv) and PhMe (7 mL). The solution was sparged with N₂ for 10 min, then heated to 80 °C overnight. The reaction was cooled to rt, then H₂O (15 mL) was added and extracted with CH₂Cl₂ (4 x 15 mL). The combined organics were washed with brine (10 mL) then dried over MgSO₄ and the volatiles removed in vacuo. The resultant oil was chromatographed on silica eluting with 15% CH₂Cl₂ in hexanes to yield a white solid (0.154 g, 37%). HRMS (APCI): C₁₆H₁₈O₄ [M+H]⁺ 275.1287; found,



2,2',2'',5,5',5''-hexamethoxy-1,1':4',1''-terphenyl (9): A 25 mL oven-dried Schlenk flask which had been cooled under vacuum then filled with N₂ was equipped with a stirbar and septum was charged with **S3** (0.074 g, 0.25 mmol, 1.0 equiv), 2,5-dimethoxyphenylmagnesium bromide (1.2 mL, 0.42 M in THF, 0.50 mmol, 2.1 equiv), [1,3-bis(2,6-Diisopropylphenyl)imidazol-2-ylidene] (3-chloropyridyl)palladium(II) dichloride (7.4 mg, 0.0109 mmol, 0.044 equiv) and THF (4 mL). The flask was then heated to 65 °C overnight. After 12 h the flask was cooled to rt and saturated aq NH₄Cl (10 mL) added then extracted with CH₂Cl₂ (3 x 10 mL). The combined organics were washed with brine (10 mL) then dried over MgSO₄. The solvent was removed en vacuo and the residue chromatographed on silica eluting with 15% CH₂Cl₂ in hexanes. HRMS (APCI): C₂₄H₂₆O₆ [M+H]⁺ 411.1802; found, 411.1800.

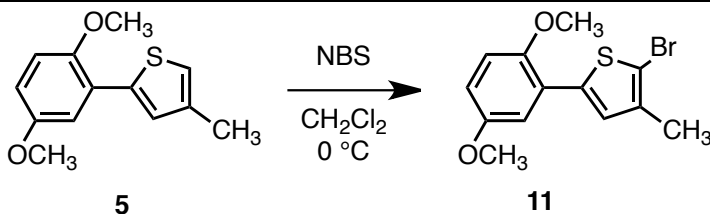


4,4'-dibromo-2,2',5,5'-tetramethoxy-1,1'-biphenyl (S4): Bromo-2,5-dimethoxybenzene (0.181 mL, 1.2 mmol, 1.2 equiv) was dissolved in CH₂Cl₂ (3 mL) in a 25 mL round-bottom flask equipped with a stir bar. FeCl₃ (0.1622 g, 1.00 mmol, 1.0 equiv) was dissolved in CH₂Cl₂ (2 mL) was added to the flask and the reaction placed under N₂ overnight. The reaction was quenched with H₂O (10 mL), extracted with CH₂Cl₂ (3 x 15 mL) and the combined organics dried over MgSO₄. The solvent was removed in vacuo to yield a red powder, which was chromatographed through silica eluting with 20% CH₂Cl₂ in hexanes to yield a grayish powder, which was recrystallized from hot MeOH to yield a white powder (0.1142 g, 44%) HRMS (EI): C₁₆H₁₆Br₂O₄ [M⁺] 429.9413; found, 429.9430.

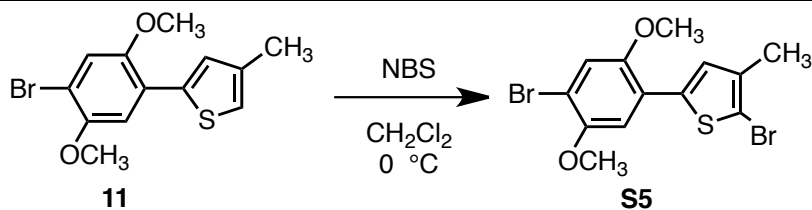


4-bromo-2,2',5,5'-tetramethoxy-1,1'-biphenyl (10): A 25 mL oven-dried Schlenk flask

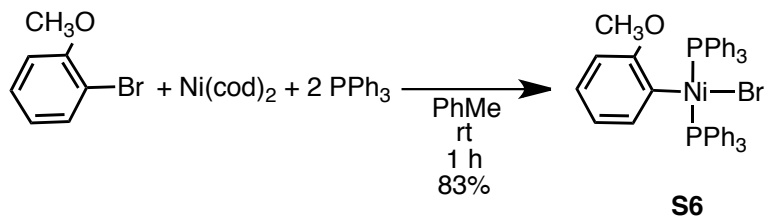
equipped with stir bar and septum was cooled under vacuum. Once cool the flask was filled with N₂, charged with **S4** (0.1865 g, 0.4316 mmol, 1.0 equiv), re-evacuated and filled with N₂. THF (4 mL) was added and the flask cooled to 0 °C, then *n*-BuLi (0.27 mL, 0.4316 mmol, 1.0 equiv) was added and the reaction kept at 0 °C for 2 h. The reaction was quenched with H₂O (10 mL) then extracted with Et₂O (3 x 5 mL), the combined organics were washed with brine (5 mL) then dried over MgSO₄ and solvent removed in vacuo to yield a yellow wax. The product was chromatographed on silica eluting with 9:1 hexanes : EtOAc to yield **10** as a white powder (0.0166 g, 11 %). HRMS C₁₆H₁₇BrO₄ [M⁺] 352.0310; found, 352.0313.



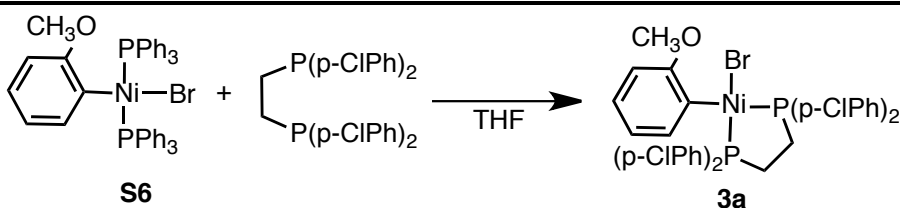
2-bromo-5-(2,5-dimethoxyphenyl)-3-methylthiophene (11) An oven-dried 20 mL Schlenk flask equipped with a stir bar was cooled under N₂ then charged with **5** (0.1671 g, 0.713 mmol, 1.00 equiv) and CH₂Cl₂ (1.5 mL) under N₂. The flask was cooled to 0 °C then NBS (0.1262 g, 0.713 mmol, 1.00 equiv) was added and the reaction kept at to 0 °C for 3 h. The reaction was quenched with aq Na₂CO₃ (10 mL) then extracted with CH₂Cl₂ (3 x 5 mL). The combined organics were washed with aq Na₂SO₃ (10 mL), brine (10 mL), then dried over MgSO₄. The solvent was removed in vacuo and the residue chromatographed on silica eluting with 10% CH₂Cl₂ in hexanes to yield **11** as a colorless wax (0.2041 g, 90% yield). HRMS (EI): C₁₃H₁₃BrO₂S [M⁺] 311.9820; found, 311.9824.



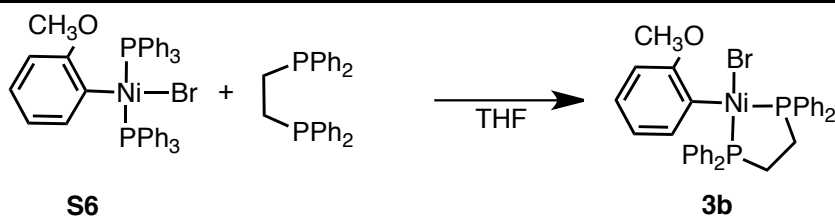
2-bromo-5-(4-bromo-2,5-dimethoxyphenyl)-3-methylthiophene (S5): **11** (0.0711 g, 0.227 mmol, 1.00 equiv) was dissolved in CH₂Cl₂ (2 mL) in an oven dried 50 mL Schlenk flask equipped with a stir bar under N₂. The flask was cooled to 0 °C then NBS (0.0441 g, 0.250 mmol, 1.1 equiv) was added and the reaction kept at to 0 °C for 2 h. The reaction was quenched with aq Na₂CO₃ (5 mL) then extracted with CH₂Cl₂ (3 x 5 mL). The organics were washed with brine (5 mL) then dried over Na₂SO₄. The solvent was removed in vacuo and the residue chromatographed on silica eluting with 15% CH₂Cl₂ in hexanes to yield **S5** as a white powder (0.0594 g, 67% yield). HRMS (EI): C₁₃H₁₂Br₂O₂S [M⁺] 389.8925; found, 389.8922.



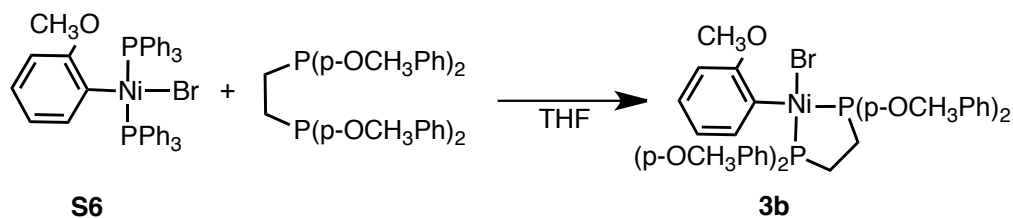
S6: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with Ni(cod)₂ (550.1 mg, 2.00 mmol, 1.0 equiv), PPh₃ (1.0490 g, 4.00 mmol, 2.0 equiv) and PhMe (6.0 mL). 2-Bromoanisole (0.374 mL, 3.00 mmol, 1.5 equiv) was added by syringe and the solution was allowed to stir at rt for 45 min. The product was precipitated by adding hexanes (20 mL), cooled to -35 °C for 15 min then collected by filtration and washed with hexanes (20 mL) and cold MeOH (15 mL) to give 1.2740 of **S6** as a yellow solid (83% yield). The product is air-stable.



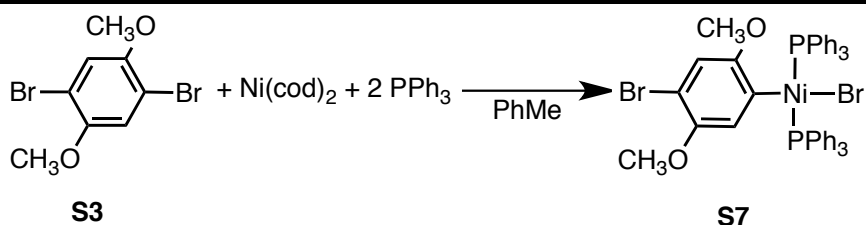
3a In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S6** (0.250 g, 0.325 mmol, 1.00 equiv) and THF (4 mL). 1,2-Bis(di-4-chlorophenylphosphino)ethane (0.1827 g, 0.341 mmol, 1.05 equiv) was added and the reaction stirred for 20 min, then hexanes (15 mL) was added and the vial cooled to -35 °C for 15 min. The yellow precipitate was collected by filtration and washed with hexanes (20 mL). The product was then recrystallized from THF/hexanes to yield orange needles (0.2356 g, 93%).



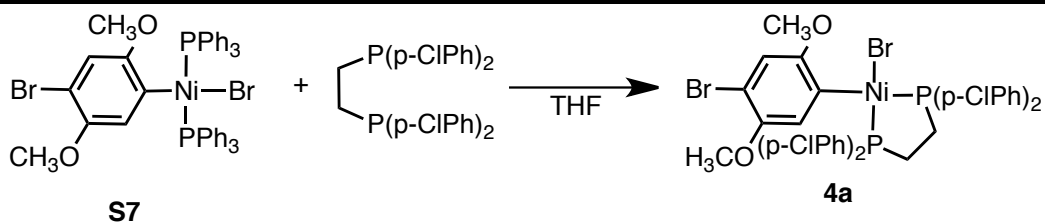
3b: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S6** (0.250 g, 0.325 mmol, 1.00 equiv) and THF (4 mL). 1,2-Bis(diphenylphosphino)ethane (0.1422 g, 0.357 mmol, 1.10 equiv) was added and the reaction stirred for 20 min, then hexanes (15 mL) was added and the vial cooled to -35 °C for 15 min. The yellow precipitate was collected by filtration and washed with hexanes (10 mL) and cold Et₂O. The product was then recrystallized from THF/hexanes to yield orange needles. (0.1629 g, 78 %)



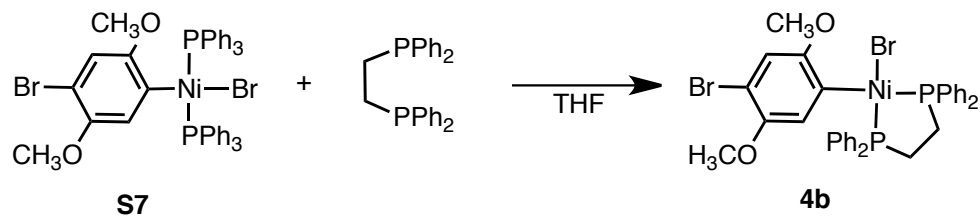
3c: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S6** (0.250 g, 0.325 mmol, 1.00 equiv) and THF (4 mL). 1,2-Bis(di-4-methoxyphenylphosphino)ethane (0.1767 g, 0.341 mmol, 1.05 equiv) was added and the reaction stirred for 20 min, then hexanes (15 mL) was added and the vial cooled to $-35\text{ }^{\circ}\text{C}$ for 15 min. The yellow precipitate was collected by filtration and washed with hexanes (20 mL) to yield a yellow powder. (0.2213 g, 89 %).



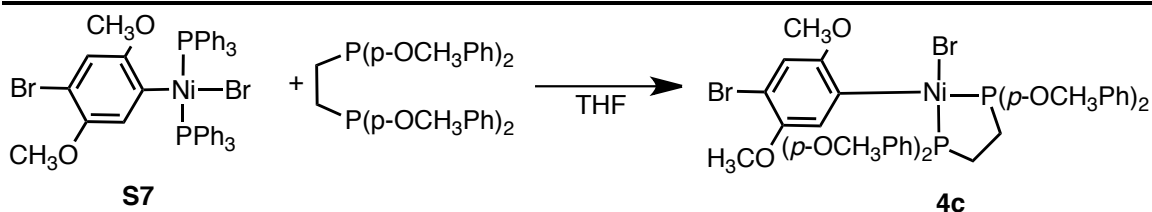
S7: In the glovebox, an oven-dried 20 mL vial was equipped with a stir bar and charged with $\text{Ni}(\text{cod})_2$ (0.6090 g, 2.21 mmol, 1.00 equiv), PPh_3 (1.1613 g, 4.42 mmol, 2.00 equiv) and PhMe (10 mL). A solution of **S3** (0.8749 g, 3.33 mmol, 1.5 equiv) in 1:1 THF:PhMe (4 mL) was added to the vial and the mixture stirred for 1 h. Then 5 mL of hexanes was added to the reaction and the resulting suspension triturated. The reaction was then filtered and washed with hexanes (3 x 20 mL) then cold MeOH (2 x 20 mL) and the resulting yellow powder dried in vacuo (1.1628 g, 60%).



4a: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S7** (0.300 g, 0.341 mmol, 1.00 equiv) and THF (4 mL). 1,2-bis(di-4-chlorophenylphosphino)ethane (0.1857 g, 0.358 mmol, 1.05 equiv) was added and the reaction stirred for 30 min, then hexanes (16 mL) was added. The yellow precipitate was collected by filtration and recrystallized from THF/hexanes to yield a yellow powder (0.2233 g, 75 %).



4b: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S7** (0.2500 g, 0.2843 mmol, 1.00 equiv) and THF (7 mL). A solution of 1,2-bis(diphenylphosphino)ethane (0.1132 g, 0.2843 mmol, 1.00 equiv) in THF (1 mL) was added and the reaction stirred for 10 min, then hexanes (10 mL) was added and the vial cooled to -35 °C for 15 min.. The yellow precipitate was collected by filtration and washed with hexanes (20 mL) to yield a yellow powder (0.1677 g, 78 %).



4c: In the glovebox an oven-dried 20 mL vial was equipped with a stir bar and charged with **S7** (0.300 g, 0.341 mmol, 1.00 equiv) and THF (4 mL). 1,2-bis(di-4-methoxyphenylphosphino)ethane (0.1910 g, 0.358 mmol, 1.05 equiv) was added and the reaction stirred for 30 min, then hexanes (16 mL) was added. The yellow precipitate was collected by filtration and recrystallized from THF/hexanes to yield a yellow powder (0.1947 g, 64 %).

V. NMR Spectra

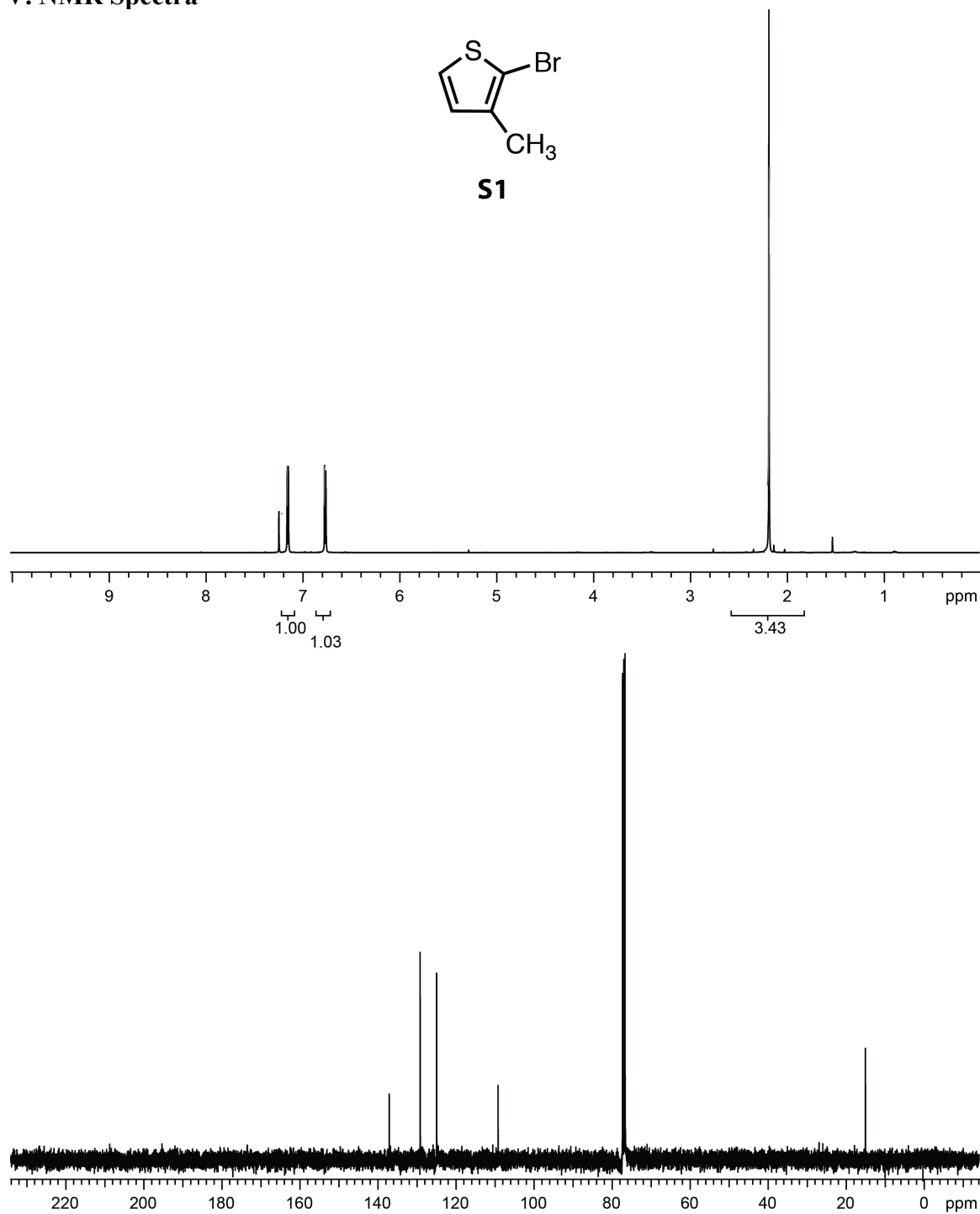


Figure S1 ^1H and ^{13}C NMR spectra for **S1**

^1H NMR (400 MHz, CDCl_3) δ 7.15 (d, $J = 5.6$ Hz, 1H), 6.76 (d, $J = 5.6$ Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.112, 129.188, 124.969, 109.212, 15.063.

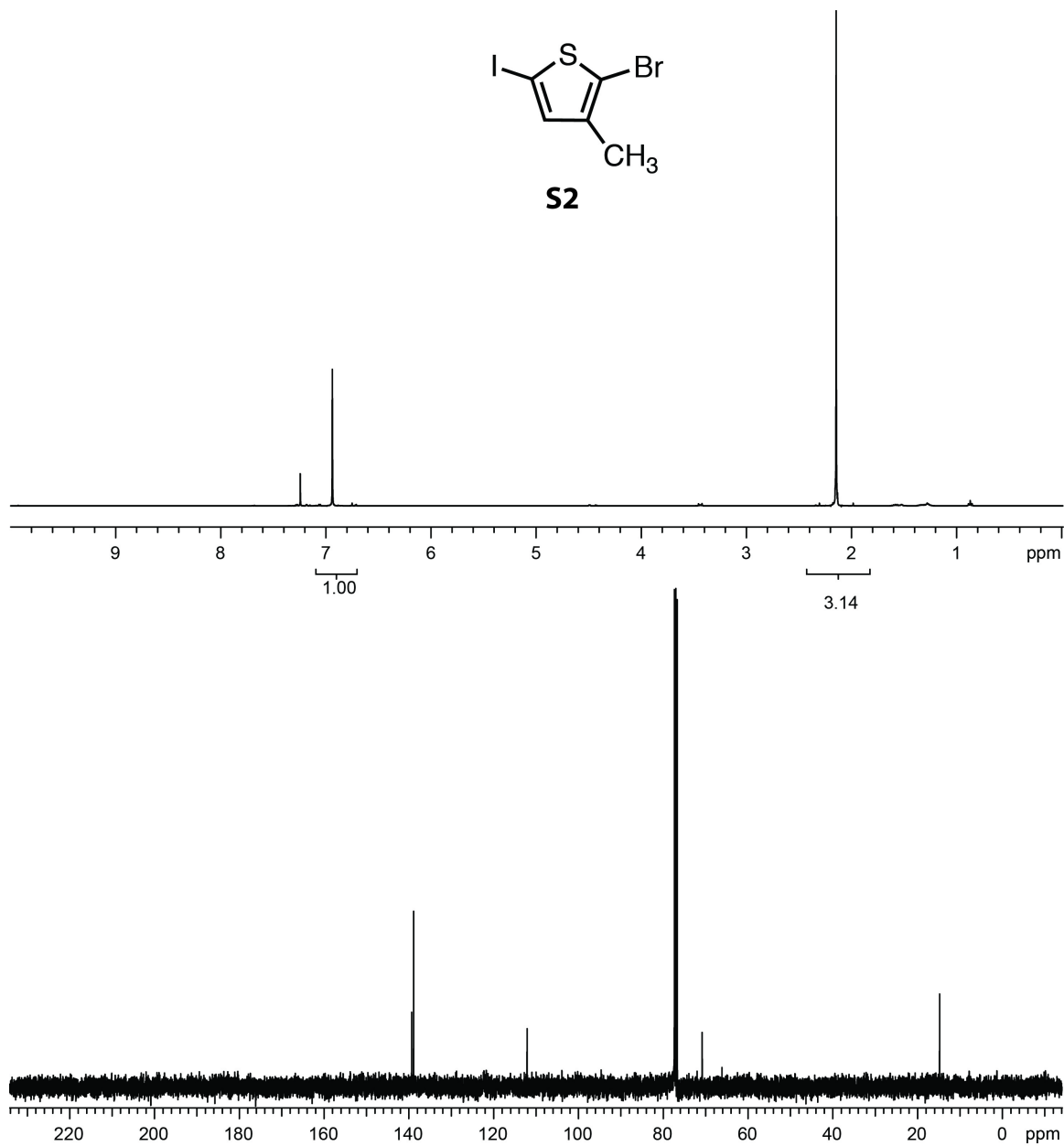


Figure S2 ¹H and ¹³C NMR spectra for **S2**
¹H NMR (400 MHz, CDCl₃) δ 6.938 (s, 1H), 2.145 (s, 3H). ¹³C NMR (100 MHz, CDCl₃)
δ 139.317, 138.866, 112.106, 70.800, 14.794.

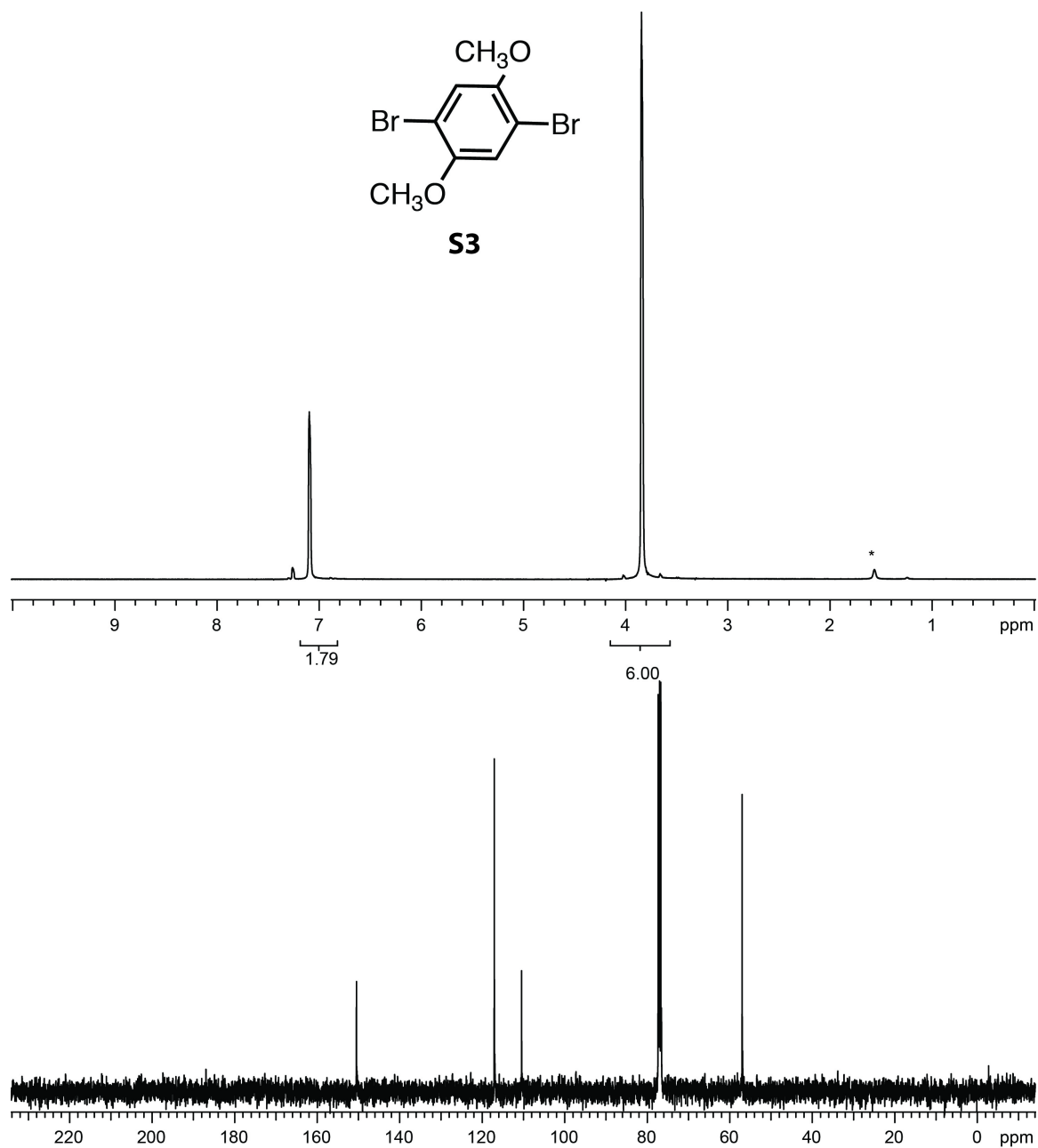


Figure S3 ¹H and ¹³C NMR spectra for **S3**
¹H NMR (400 MHz, CDCl₃) δ 7.096 (s, 2H), 3.844 (s, 6H). ¹³C NMR (100 MHz, CDCl₃)
δ 150.468, 117.060, 110.439, 56.986.
* denotes H₂O present in solvent

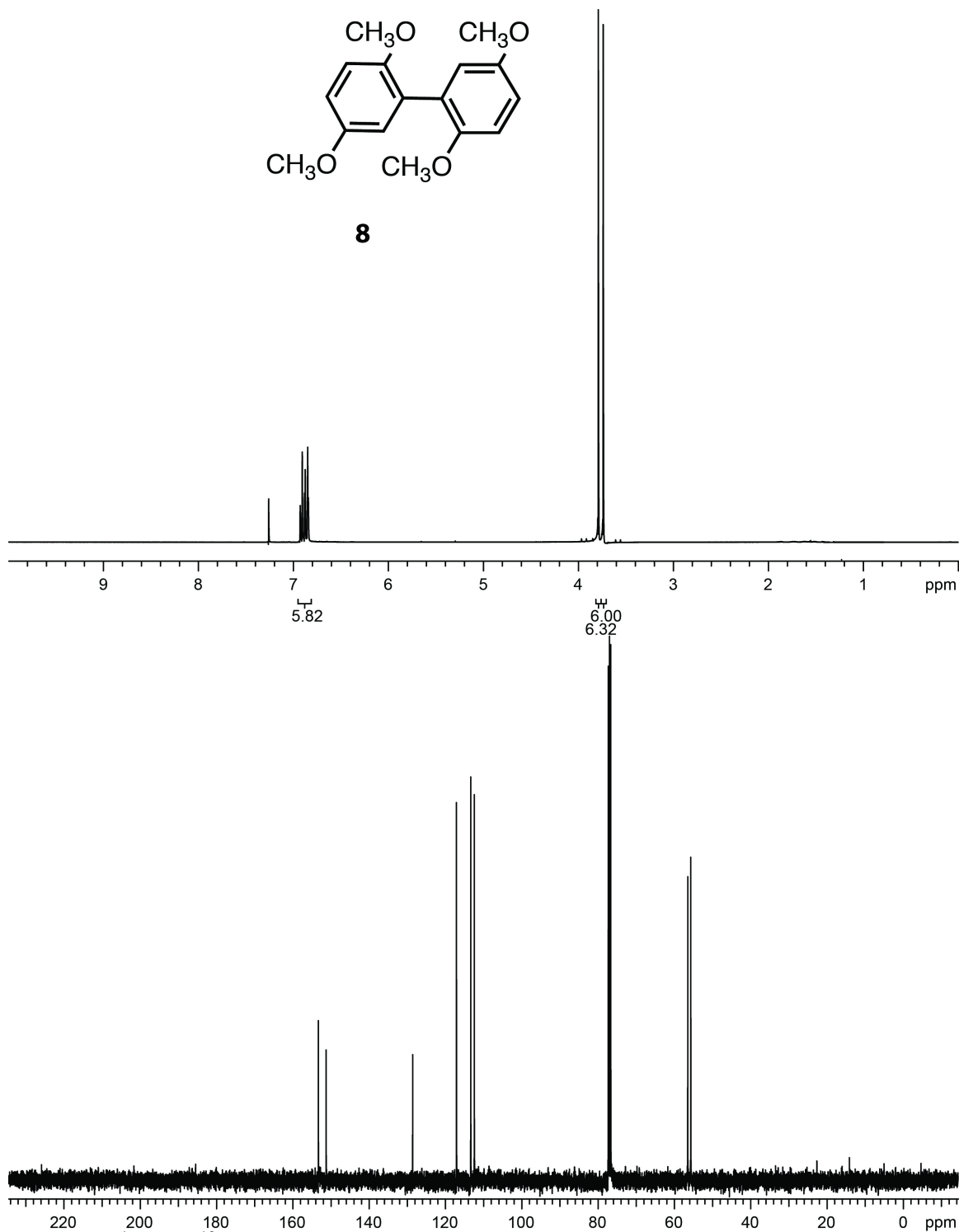


Figure S4 ¹H and ¹³C NMR spectra for **8**
¹H NMR (400 MHz, CDCl₃) δ 6.906-6.843 (m, 6H), 3.789 (s, 6H), 3.738 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.299, 151.271, 128.591, 117.108, 113.368, 112.434, 56.483, 55.701.

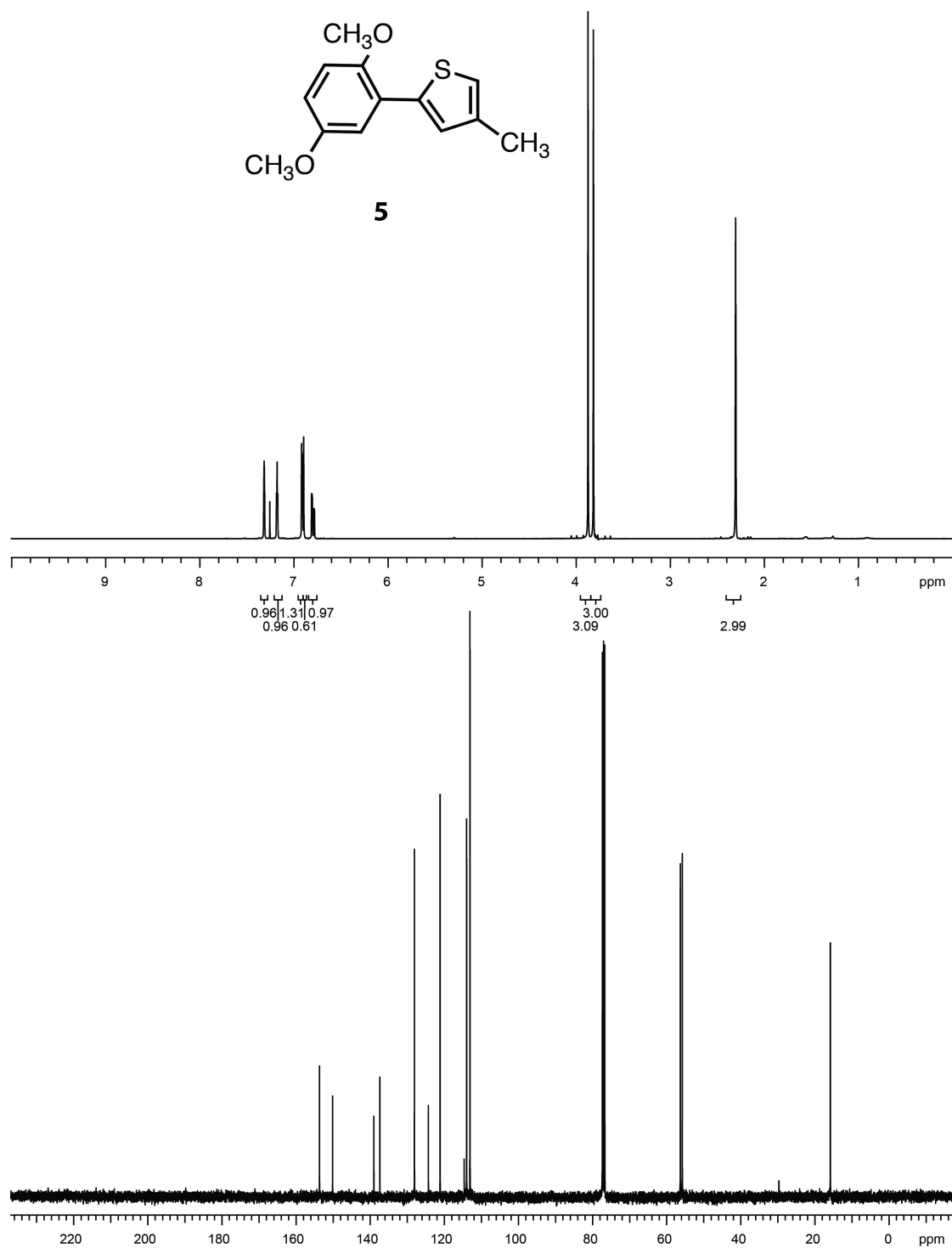


Figure S5 ¹H and ¹³C NMR spectra for **5**

¹H NMR (400 MHz, CDCl₃) δ 7.316 (s, 1H), 7.178 (d, *J* = 2.8 Hz, 1H), 6.914 (br, 1H), 6.896 (s, 1H), 6.803 (dd, *J* = 5.6, 2.8 Hz), 3.874 (s, 3H), 3.817 (s, 3H), 2.305 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 153.682, 149.786, 138.053, 136.443, 126.548, 123.377, 113.345, 113.026, 112.688, 110.270, 56.210, 55.709, 15.125.

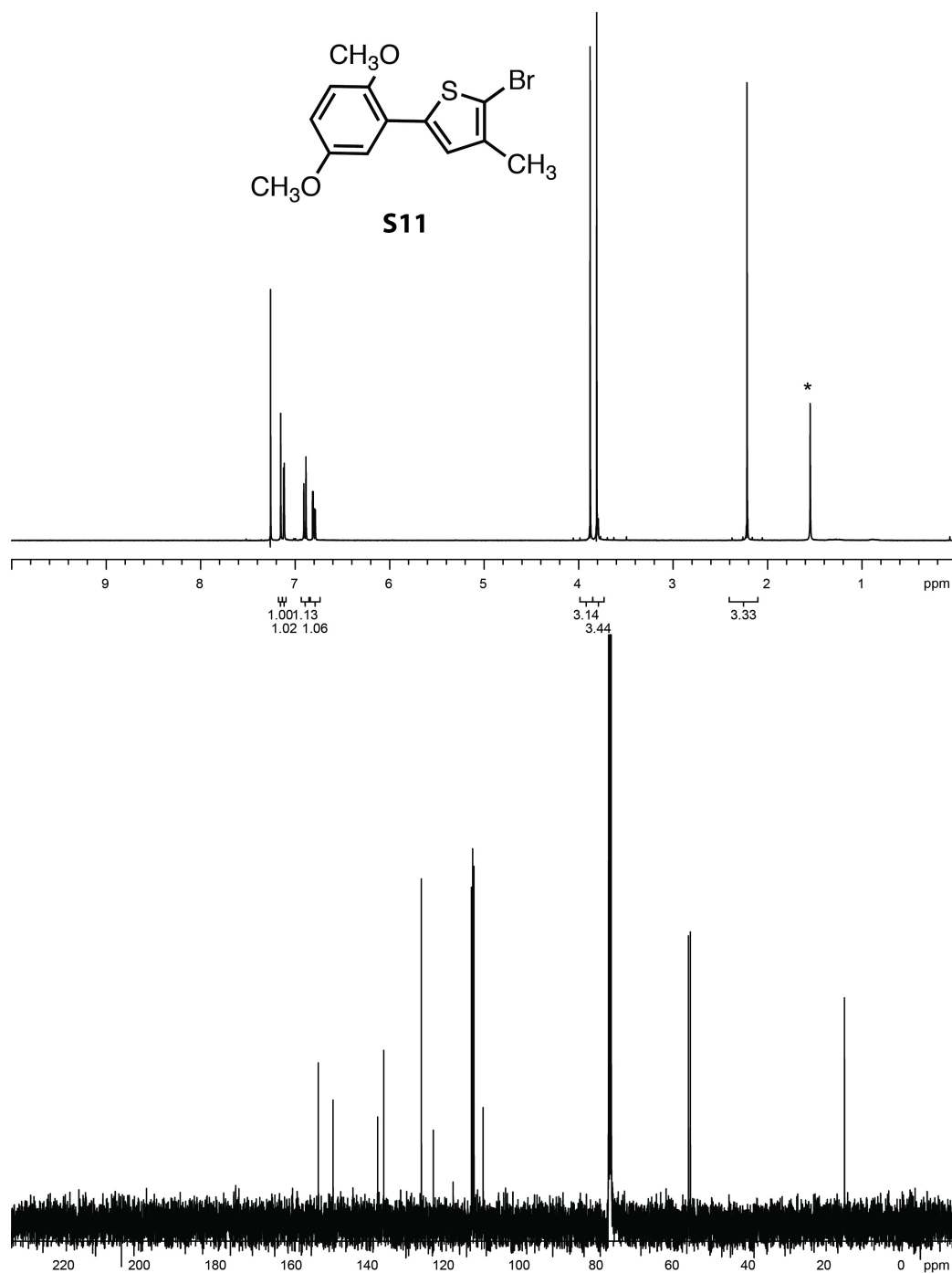


Figure S6 ^1H and ^{13}C NMR spectra for **S11**

^1H NMR (400 MHz, CDCl_3) δ 7.153 (s, 1H), 7.123 (d, J = 3.2 Hz, 1H), 6.908 (d, J = 9.2 Hz, 1H), 6.801 (dd, J = 8.8, 3.2 Hz, 1H), 3.878 (s, 3H), 3.808 (s, 3H), 2.217 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.164, 150.102, 138.323, 137.537, 128.187, 123.371, 121.395, 117.265, 112.023, 110.260, 56.891, 56.433, 15.816.

* denotes H_2O present in solvent

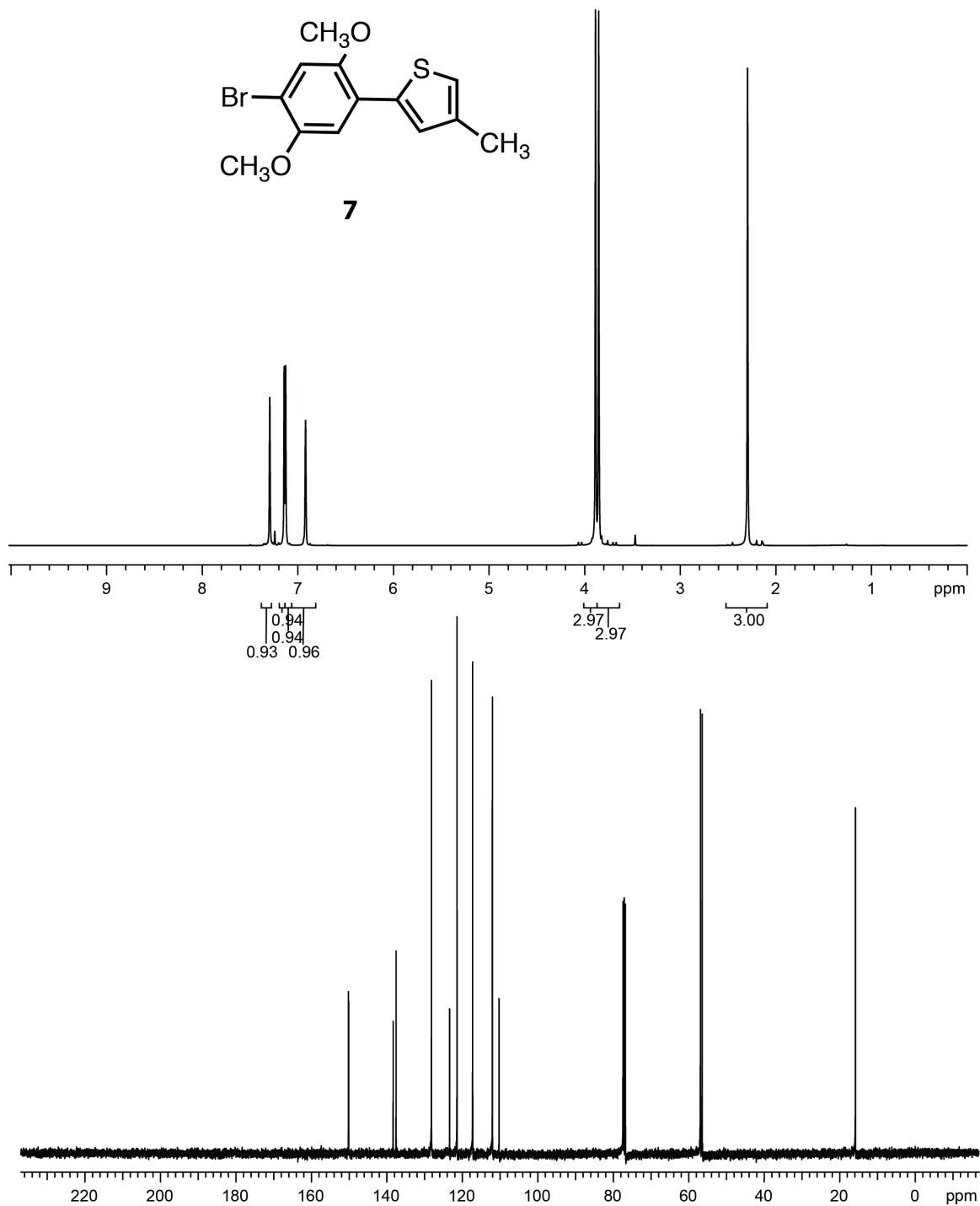


Figure S7 ¹H and ¹³C NMR spectra for **7**

¹H NMR (400 MHz, CDCl₃) δ 7.294 (s, 1H), 7.143 (s, 1H), 7.127 (s, 1H), 6.919 (s, 1H), 3.886 (s, 3H), 3.853 (s, 3H), 2.296 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.164, 150.102, 138.323, 137.537, 128.187, 123.371, 121.395, 117.265, 112.023, 110.260, 56.891, 56.433, 15.816

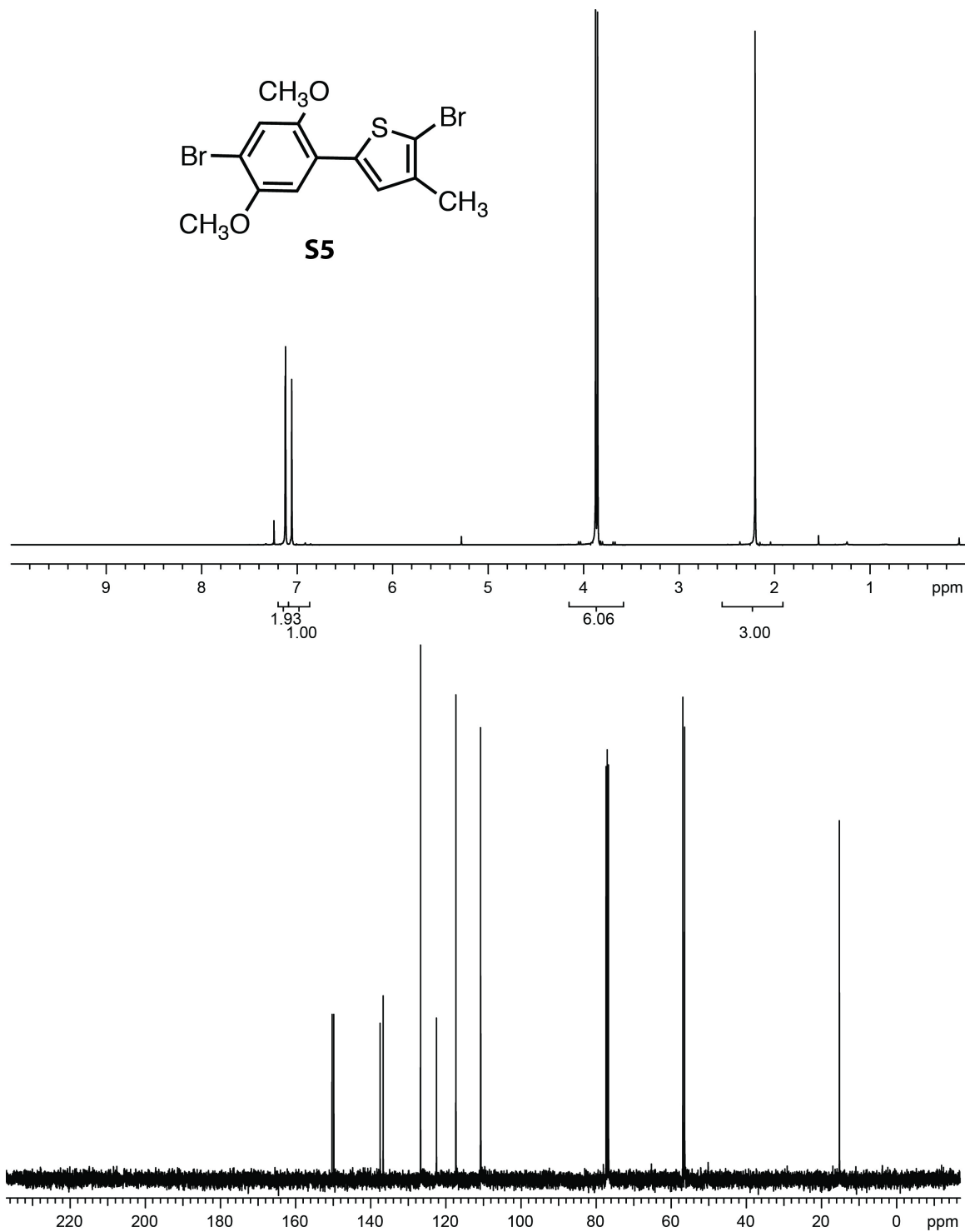


Figure S8 ¹H and ¹³C NMR spectra for **S5**
¹H NMR (400 MHz, CDCl₃) δ 7.137 (s, 2H), 7.065 (s, 1H), 3.890 (s, 3H), 3.869 (s, 3H), 2.220 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.277, 149.816, 137.494, 136.684, 126.723, 122/488, 117.319, 110.756, 110.717, 110.663, 56.898, 56.433, 15.219.

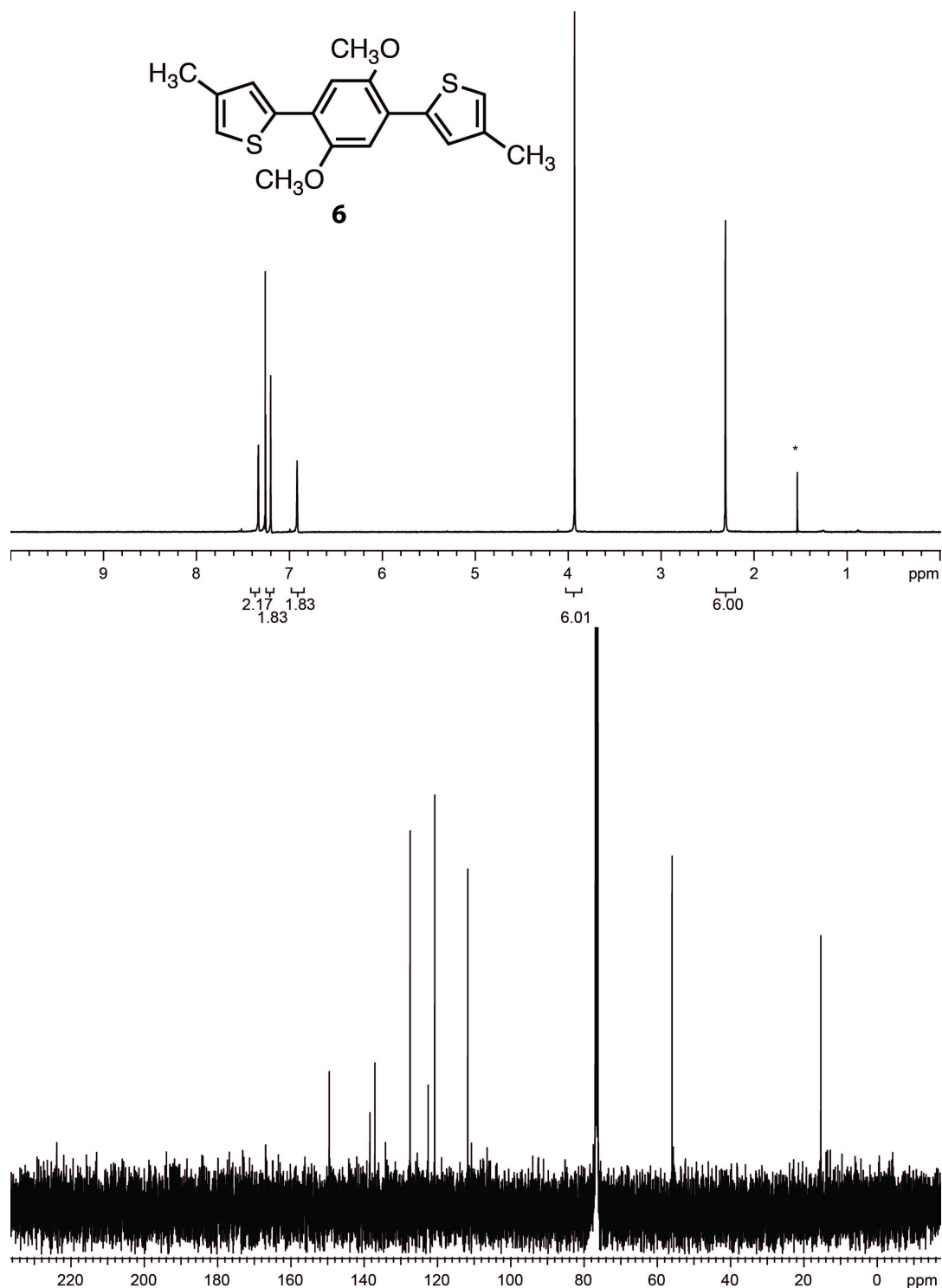


Figure S9 ¹H and ¹³C NMR spectra for **6**
¹H NMR (400 MHz, CDCl₃) δ 7.338 (s, 2H), 7.203 (s, 2H), 6.919 (s, 2H), 3.933 (s, 6H), 2.310 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 149.970, 138.843, 137.510, 127.897, 122.961, 121.163, 112.146, 56.391, 15.808.
 * denotes H₂O present in solvent

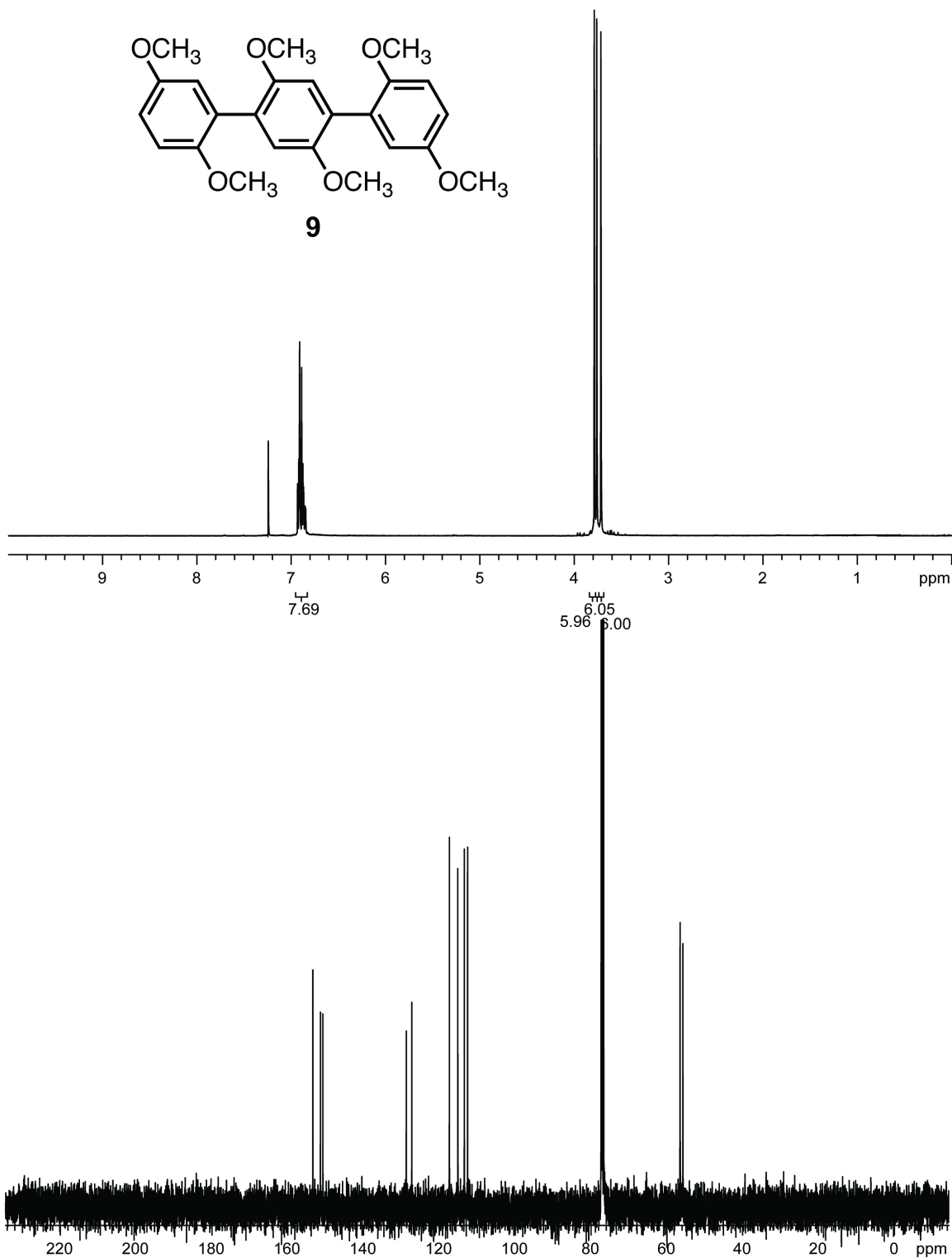


Figure S10 ¹H and ¹³C NMR spectra for **9**

¹H NMR (400 MHz, CDCl₃) δ 6.910 (m, 8H), 3.787 (s, 6H), 3.761 (s, 6H), 3.717 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 153.363, 151.370, 150.717, 128.716, 127.273, 117.340, 115.126, 113.406, 112.533, 56.517, 56.476, 55.473.

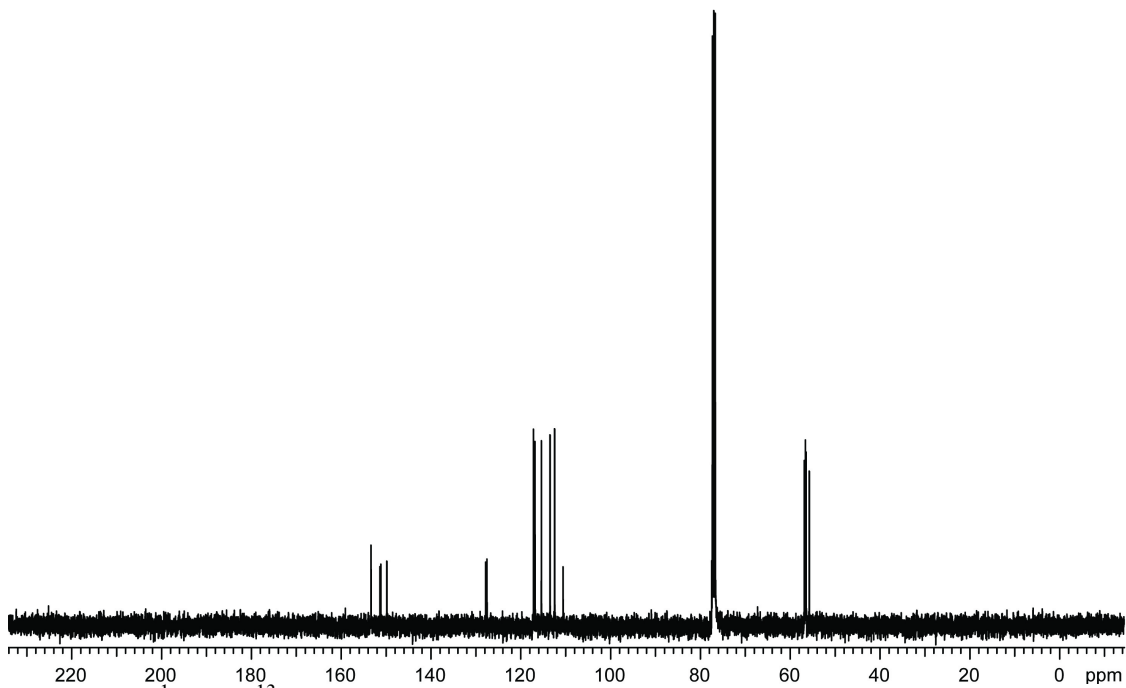
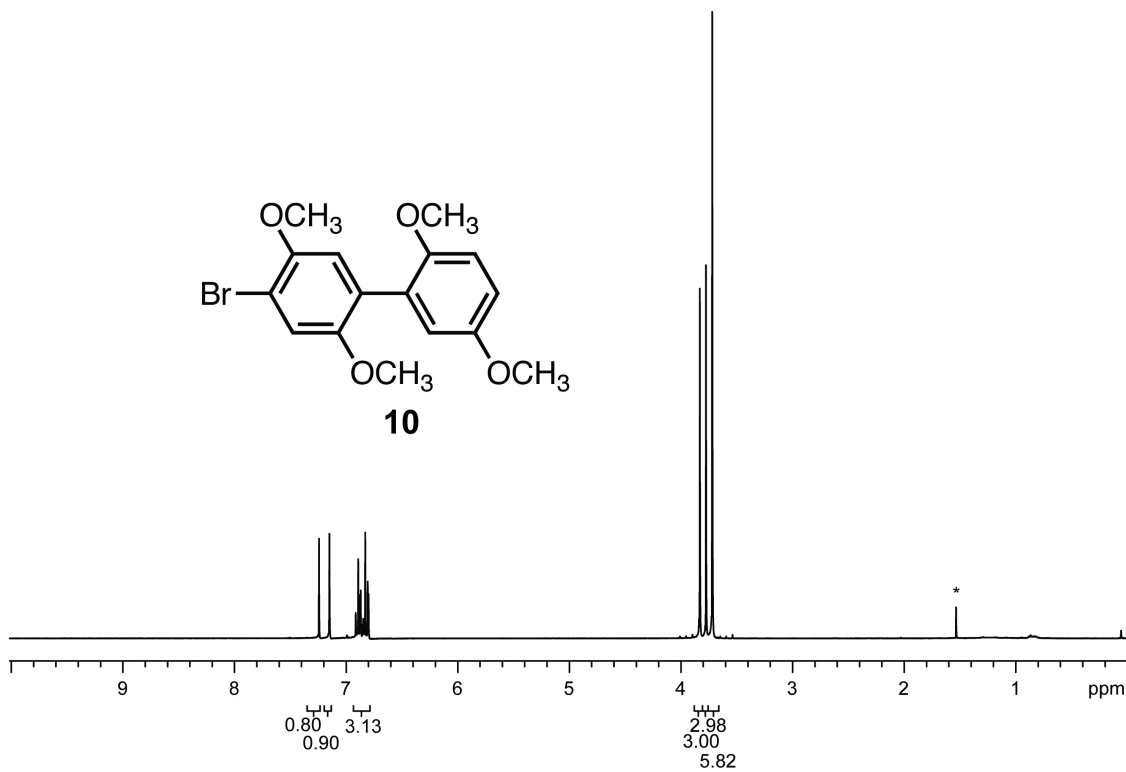
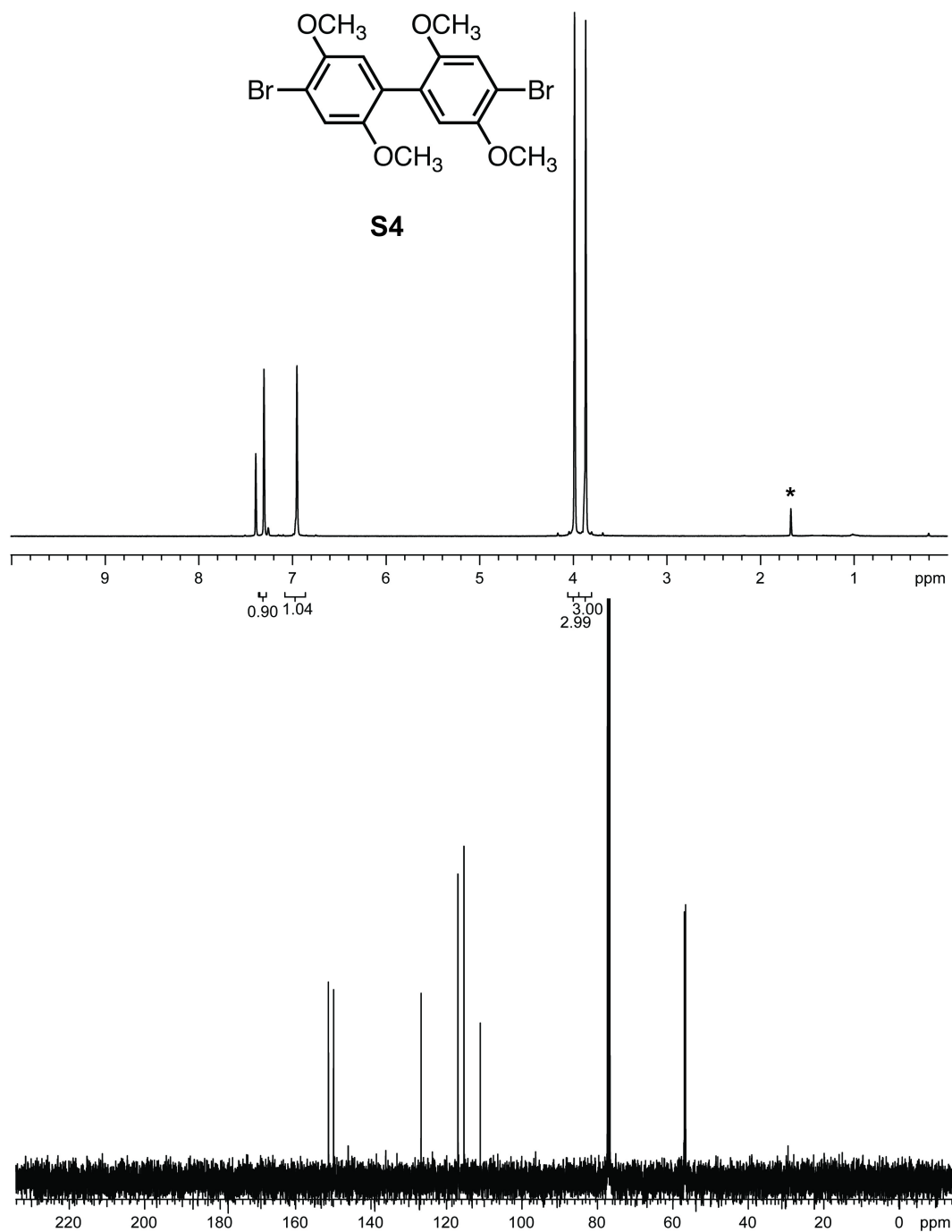


Figure S11 ^1H and ^{13}C NMR spectra for **10**

^1H NMR (400 MHz, CDCl_3) δ 7.242 (s, 1H), 7.149 (s, 1H), 6.828 (m, 3H), 3.830 (s, 3H), 3.775 (s, 3H), 3.719 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.325, 151.358, 151.138, 149.813, 127.808, 127.512, 17.158, 116.816, 115.399, 113.467, 112.453, 110.558, 56.840, 56.597, 56.453, 55.735.

* denotes H_2O present in solvent



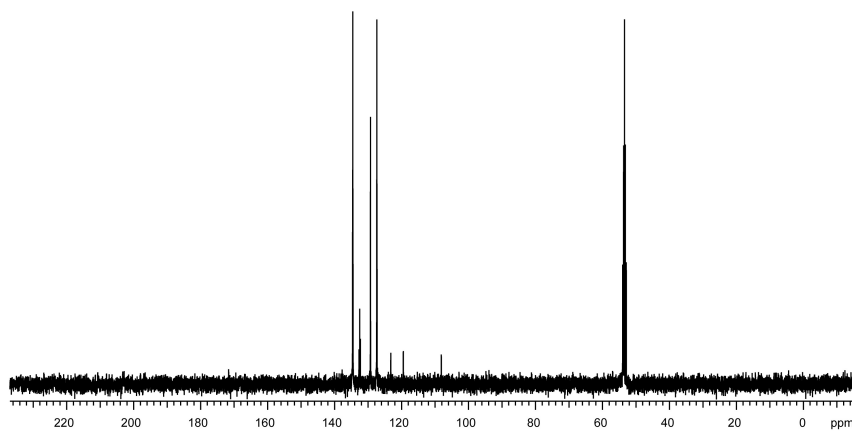
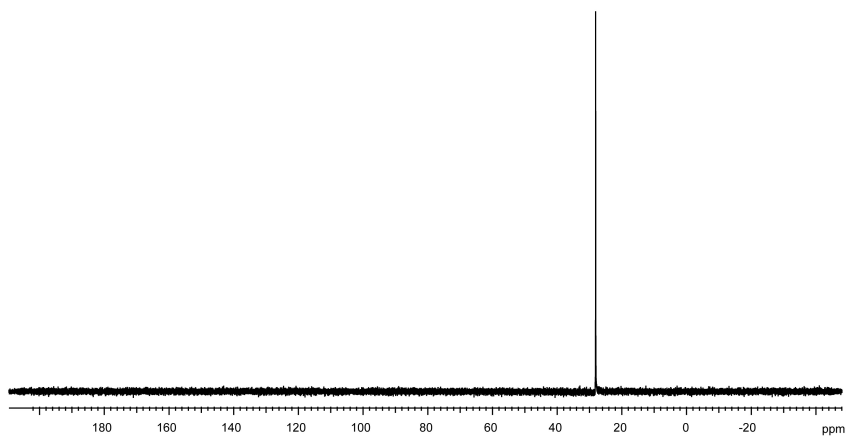
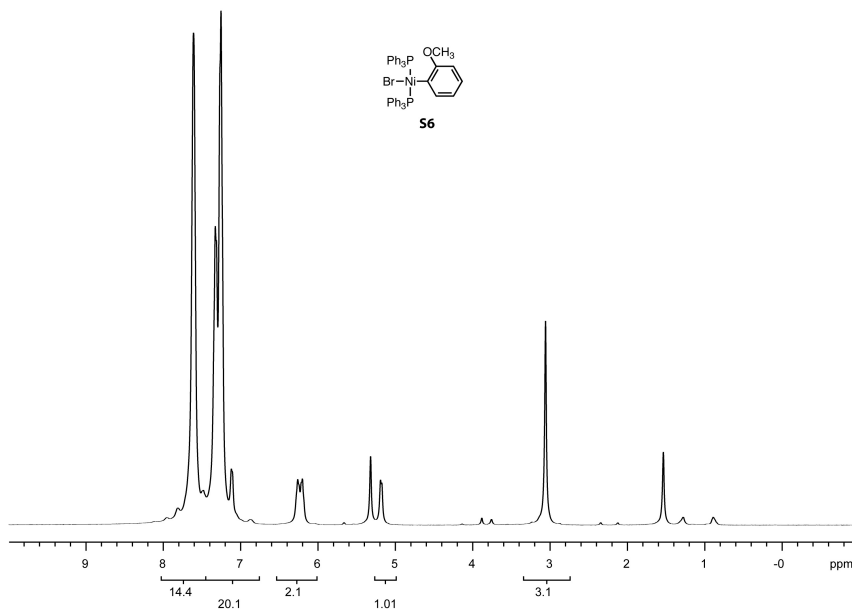
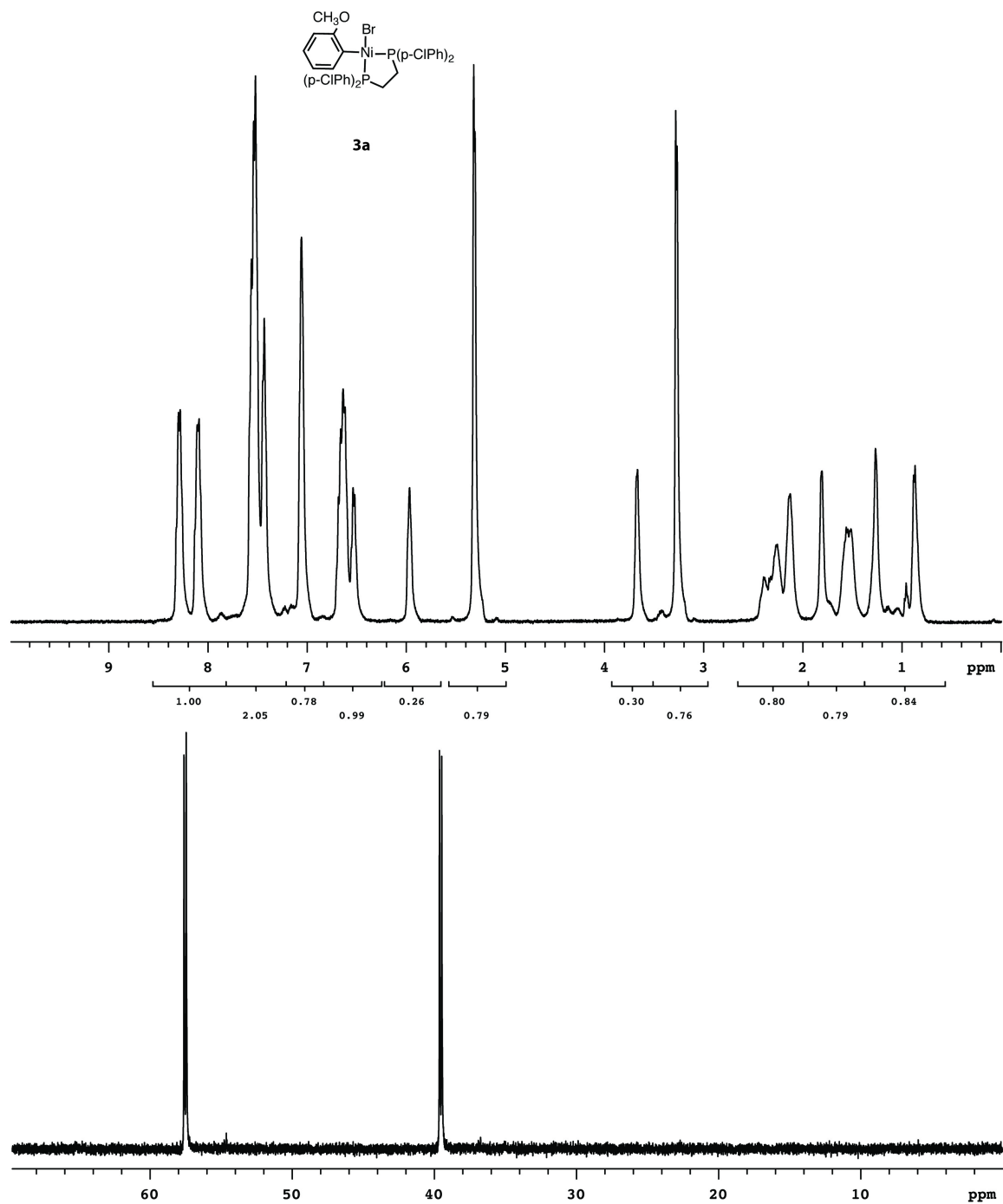


Figure S13. ^1H , ^{31}P and ^{13}C NMR spectra for **S6**

^1H NMR (400 MHz, CD_2Cl_2) δ 7.61 (br, 12 H), 7.31 (br m, 19 H), 6.24 (m, 2H), 5.19 (br, 1H), 3.06 (br, 3H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 22.42 (s). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 134.60, 134.54, 134.49, 132.70, 132.48, 132.27, 129.26, 127.40, 127.13, 127.31, 123.20, 119.46, 108.11.



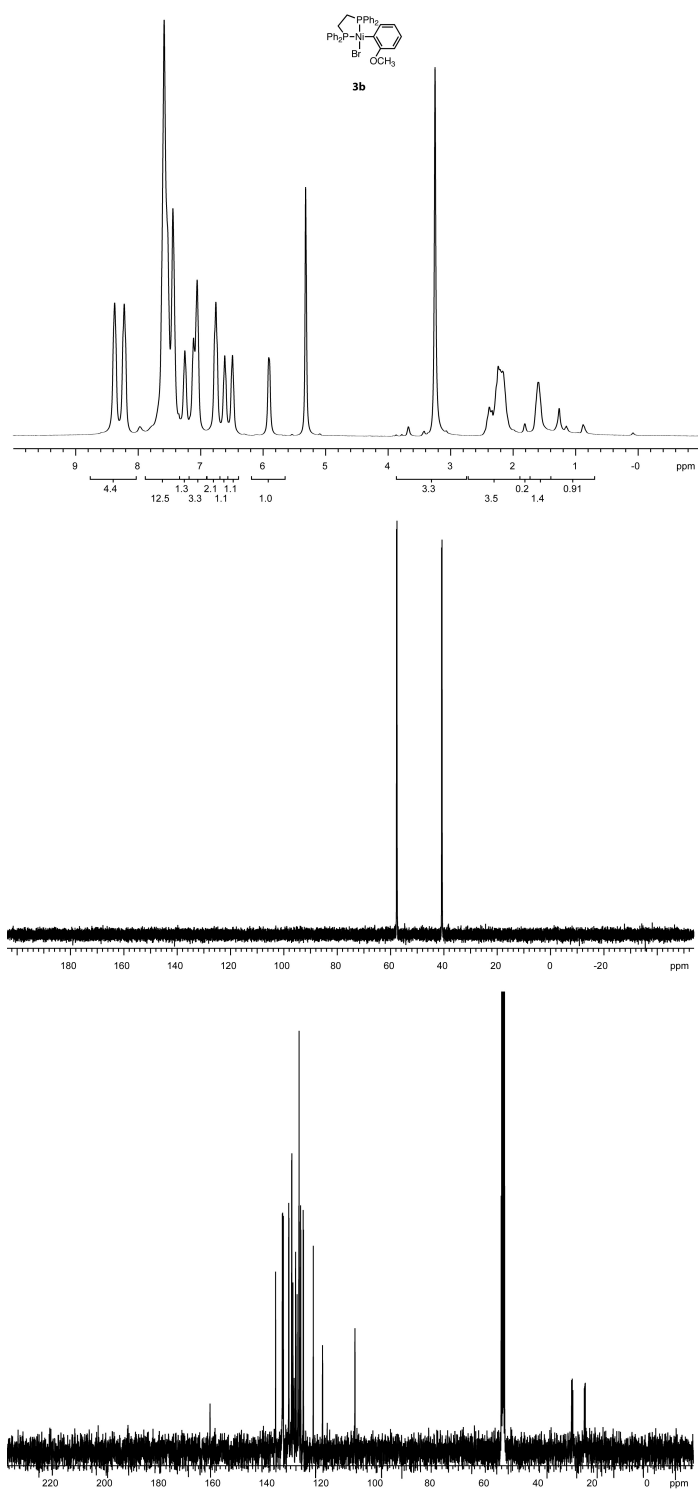
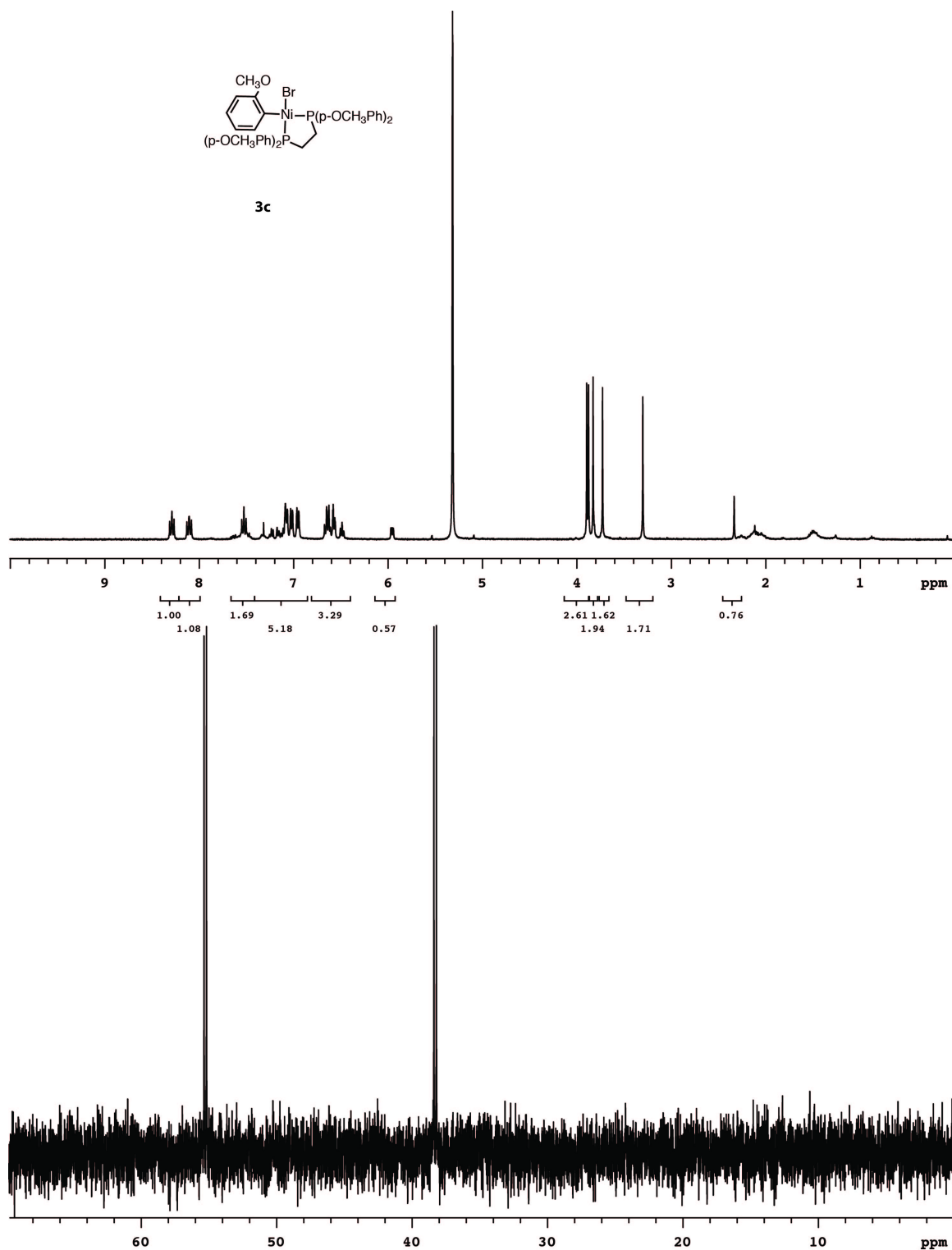
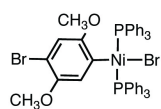


Figure S15. ¹H, ³¹P and ¹³C, NMR spectra for **3b**

¹H NMR (400 MHz, CD₂Cl₂) δ 8.38 (s, 1H), 8.22 (s, 2H), 7.58 (br m, 12H), 7.25 (s, 1H), 7.11 (m, 3H), 6.76 (br, 2H), 6.61 (br, 1H), 6.49 (br, 1H), 5.91 (br, 1H) 3.25 (br 3H), 2.24 (br m, 4H). ³¹P NMR (162 MHz, CD₂Cl₂) δ 57.64 (d, *J* = 27.3 Hz), 40.75 (d, *J* = 27.3 Hz). ¹³C NMR (100 MHz, CD₂Cl₂) δ 161.7, 137.51, 135.03, 134.91, 134.74, 134.63, 132.67, 132.57, 131.58, 131.50, 131.11, 130.13, 129.56, 128.92, 128.82, 128.73, 128.28, 128.18, 127.30, 127.20, 123.57, 120.18, 108.17, 28.12 (dd, *J*_{PC} = 26.4, 20.7 Hz), 23.2 (dd, *J*_{PC} = 12.5, 11.7 Hz).





S7

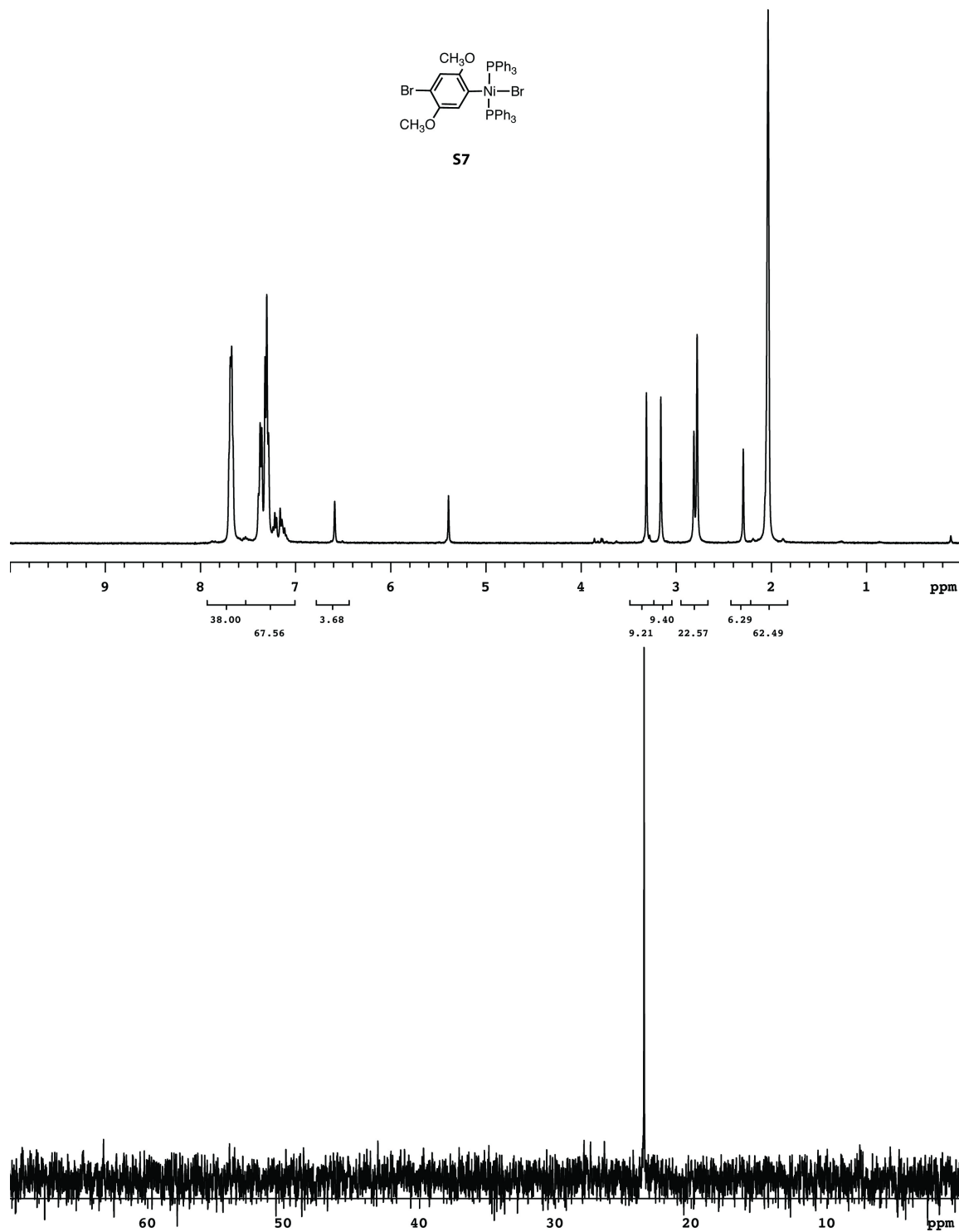


Figure S17. ^1H , ^{31}P NMR spectra for **S7**
 ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 7.685 (br, 10H), 7.355 (m, 20 H) 6.589 (s, 1H), 5.393 (s, 1H) 3.312 (s, 2H), 3.161 (s, 2H), 2.780 (m, 6H), 2.295 (s, 2H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 23.469

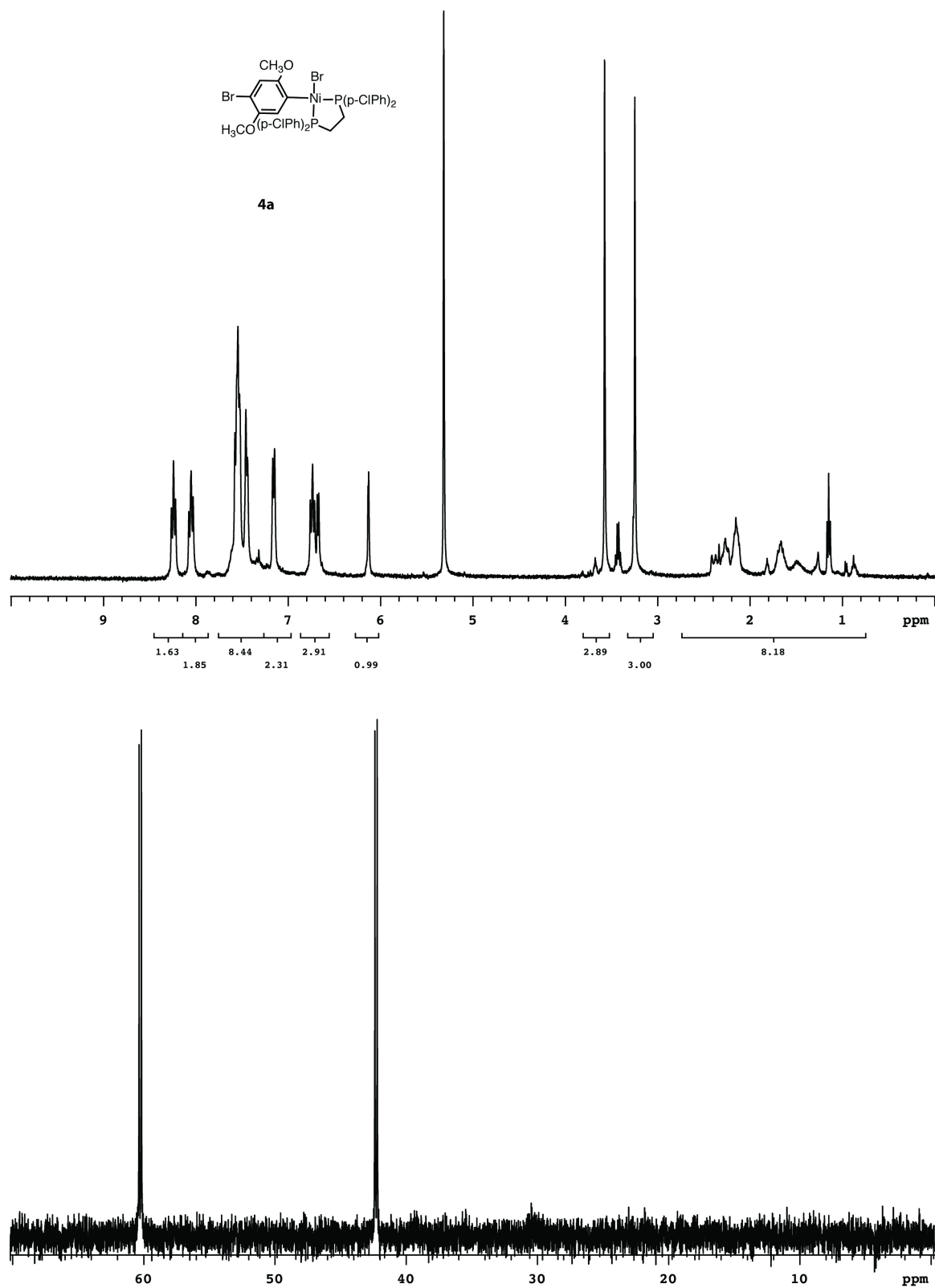


Figure S18. ^1H , ^{31}P NMR spectra for **4a**

^1H NMR (400 MHz, CDCl_3) δ 8.242 (t, $J = 9.2$ Hz, 2H), 8.051 (t, $J = 10.4$ Hz, 2H), 7.544 (m, 8 H), 7.167 (d, $J = 7.6$ Hz, 2H), 6.761 (t, $J = 9.6$ Hz, 2H), 6.686 (d, $J = 6.8$ Hz, 1H), 6.136 (s, 1H) 3.575 (s, 3H), 3.248 (s 3H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 60.613 (d, $J = 25$ Hz), 42.637 (d, $J = 25$ Hz)

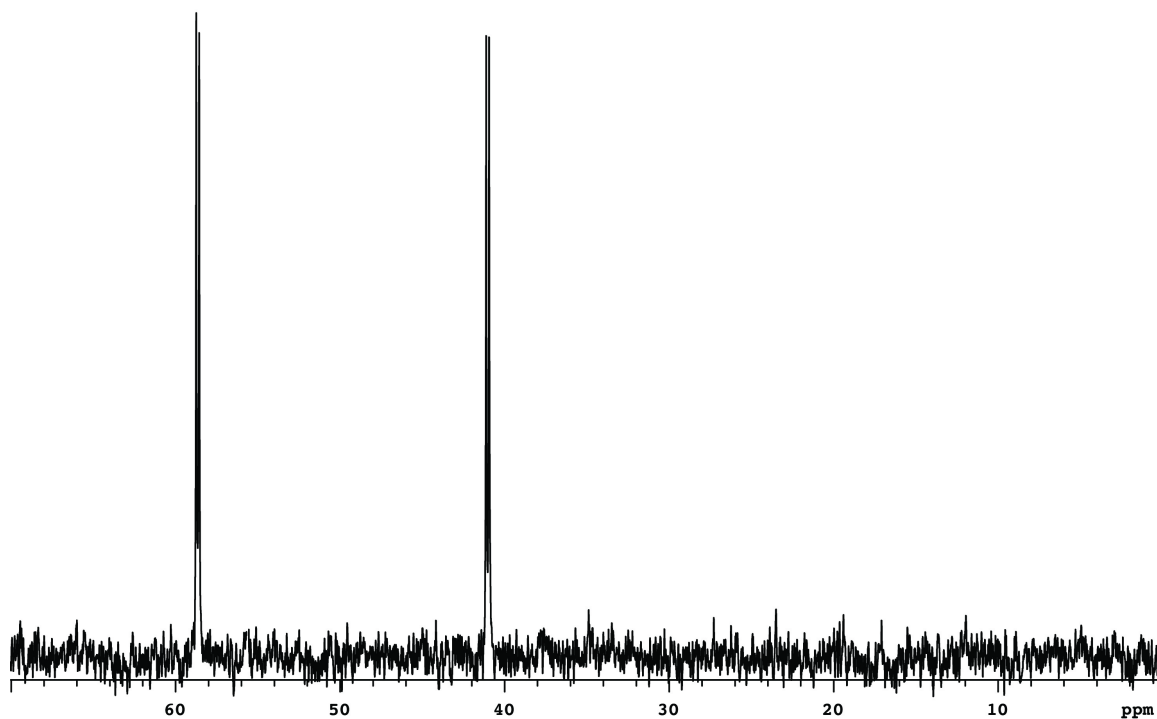
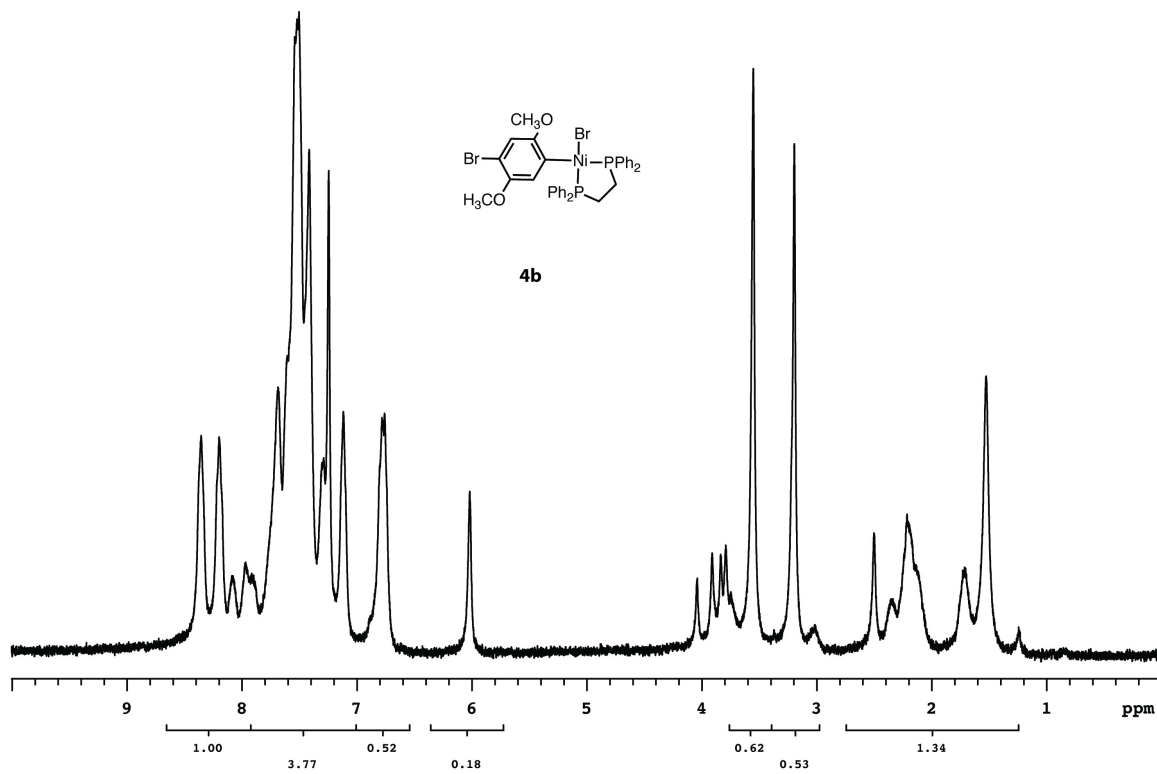


Figure S19. ^1H , ^{31}P NMR spectra for **4b**

^1H NMR (400 MHz, CDCl_3) δ 8.355 (s, 2H), 8.199 (s, 2H), 7.96 (br, 2 H) 7.522 (m, 16H), 7.290 (br, 3H), 7.120 (s, 2 H), 6.783 (2, 3 H), 6.019 (s, 1H), 3.910 (m, 3H), 3.522 (s, 3H), 3.196 (s, 3H), 2.503 (s, 1H), 2.215 (br, 3H), 1.716 (br, 1H) 1.527 (s, 3H). ^{31}P NMR (162 MHz, CDCl_3) δ 58.703 (d, $J = 28$ Hz), 41.076 (d, $J = 28$ Hz)

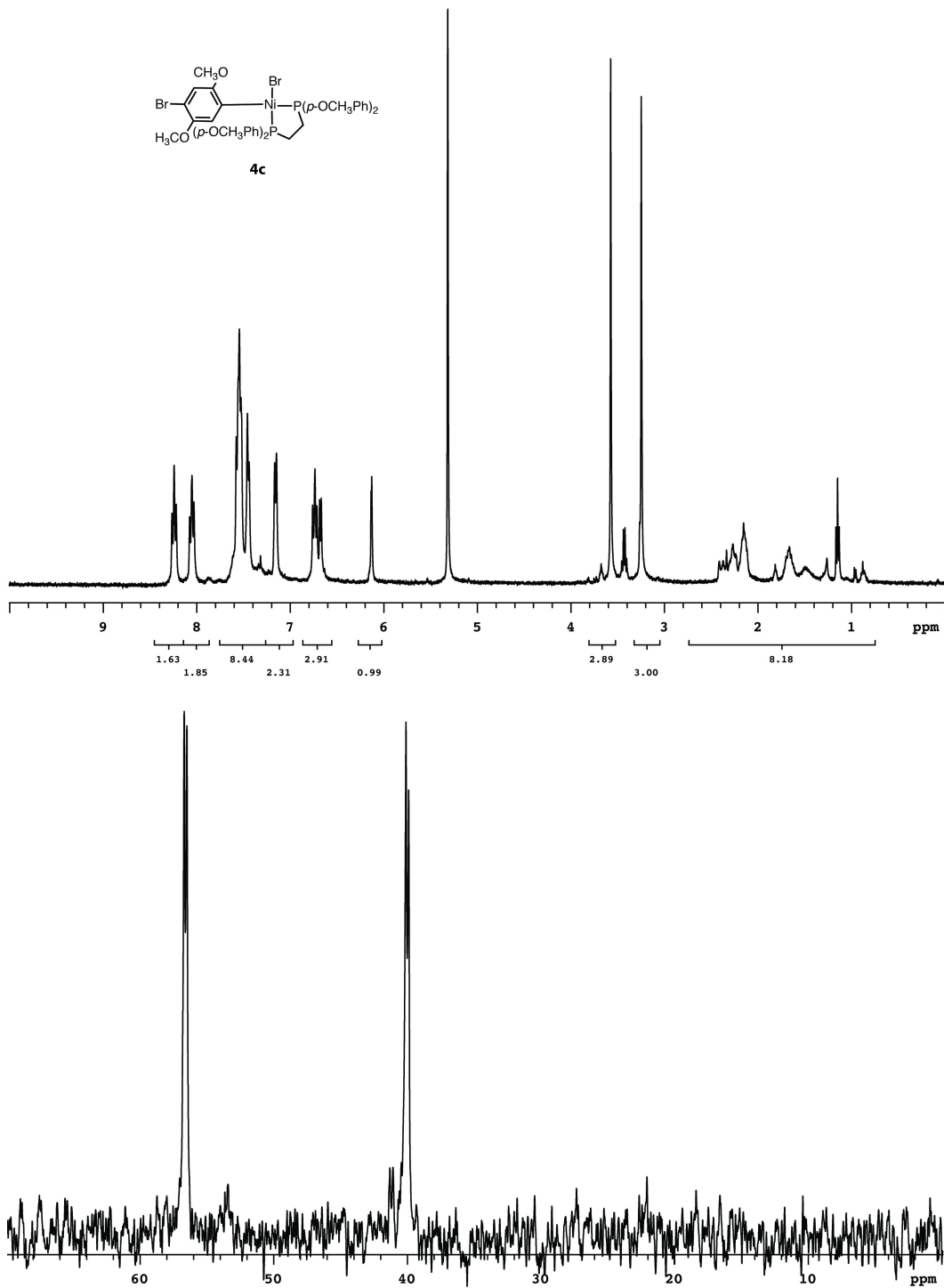


Figure S20. ^1H , ^{31}P NMR spectra for **4c**

^1H NMR (400 MHz, CDCl_3) δ 8.273 (s, 2H), 8.104 (s, 2H), 7.878 (s, 2H), 7.527 (br, 4 H), 7.248 (s, 2 H), 6.990 (m, 8 H), 6.701 (m, 5 H), 6.031 (s, 1H), 3.875 (m, 20H) 4.585 (s, 3 H), 3.279 (s, 3H), 2.110 (br, 4 H), 1.838 (s, 3H), 1.584 (s, 3H) ^{31}P NMR (162 MHz, CD_2Cl_2) δ 56.697 (d, $J = 32$ Hz), 40.099 (d, $J = 32$ Hz).

VI. Block Copolymerizations

Table S1 Summary of block copolymerization data

Initiator	p-PP M_n (kDa)	p-PP PDI	p-PP-b-3HT M_n (kDa)	p-PP-b-3HT PDI
3a	28.3	2.02	48.0	1.96
3a	27.6	1.98	47.9	2.10
3b	26.5	1.29	57.8	1.55
3b	28.5	1.25	55.6	1.49
3c	31.2	1.33	59.5	1.31
3c	30.5	1.29	55.8	1.32
	p3HT M_n (kDa)	p3HT PDI	p3HT-b-PP M_n (kDa)	p3HT-b-PP PDI
3a	31.5	1.12	39.7	2.44
3a	25.7	1.13	37.6	2.50
3b	25.4	1.07	41.5	1.68
3b	26.5	1.10	40.7	1.56
3c	27.9	1.04	38.2	1.71
3c	28.1	1.09	39.9	1.61

VIII. Batch Copolymerizations

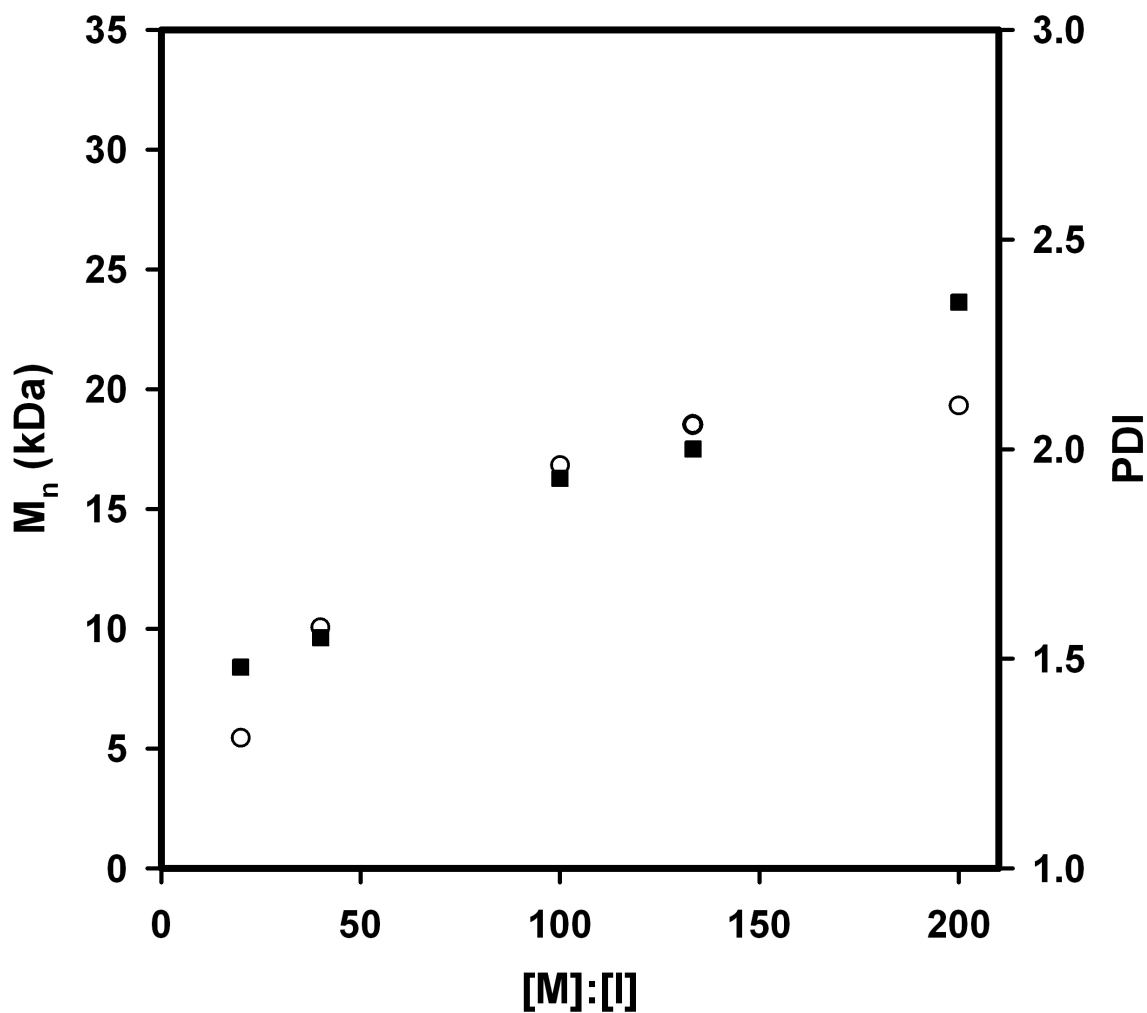


Figure S21 Plot of M_n (○) and PDI (■) versus monomer-to-initiator ratio (M:I) for the batch copolymerization of **1a** and **2a** initiated by **3a** ($[1a] = [2a] = 0.04$ M).

Table S2 Data used for Figure S21

[M]:3a	M _n (kDa)	PDI
20	5.4	1.48
40	10.0	1.55
100	16.8	1.93
133.3	18.5	2
200	19.3	2.35

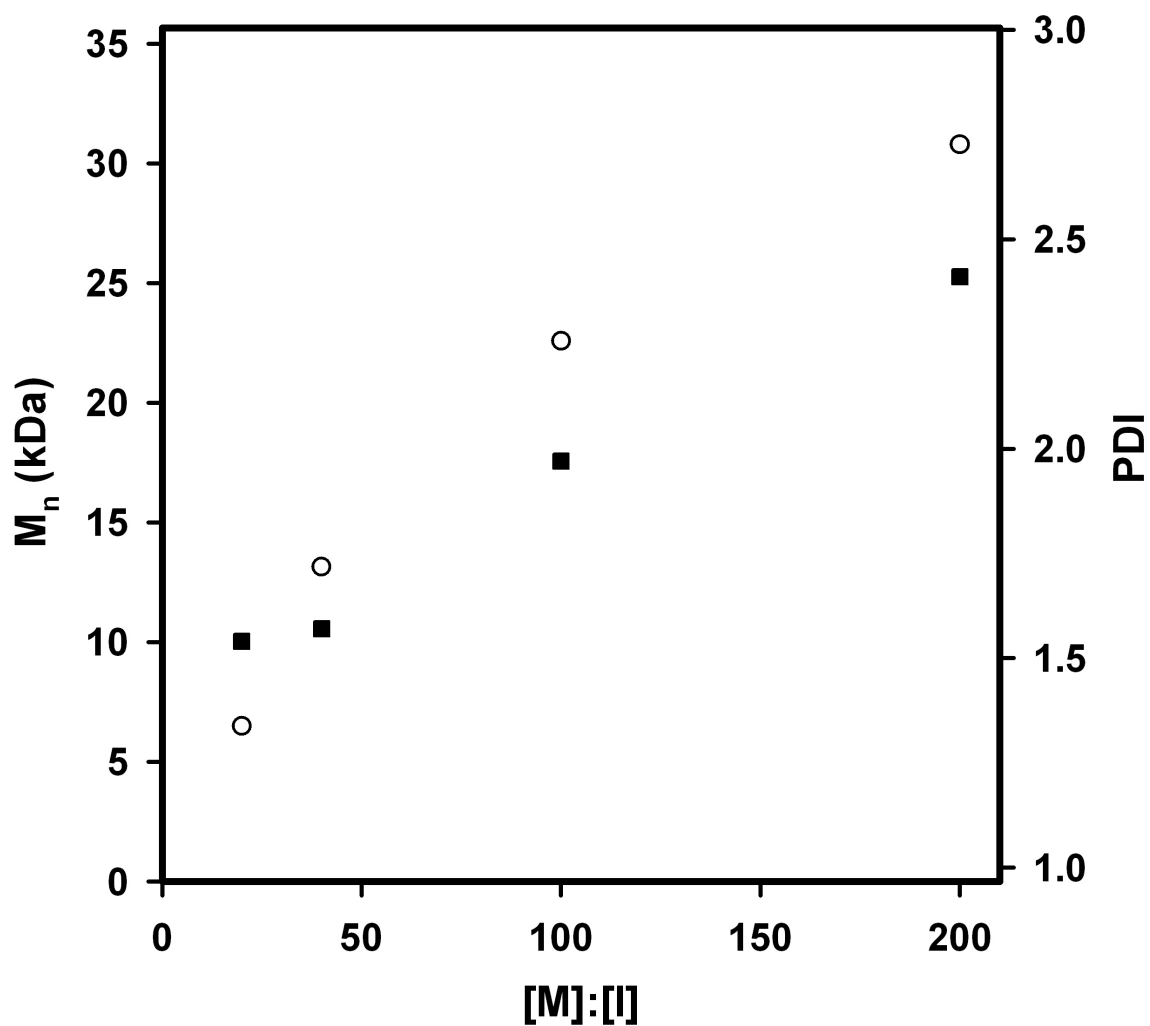


Figure 3.3B Plot of M_n (○) and PDI (■) versus monomer-to-initiator ratio (M:I) for the batch copolymerization of **1a** and **2a** initiated by **3b** ($[1a] = [2a] = 0.04$ M).

Table S2 Data used for Figure 3.3B

[M]: 3b	M_n (kDa)	PDI
200	51.7	1.15
100	31.1	1.10
40	11.9	1.27
20	5.4	1.43

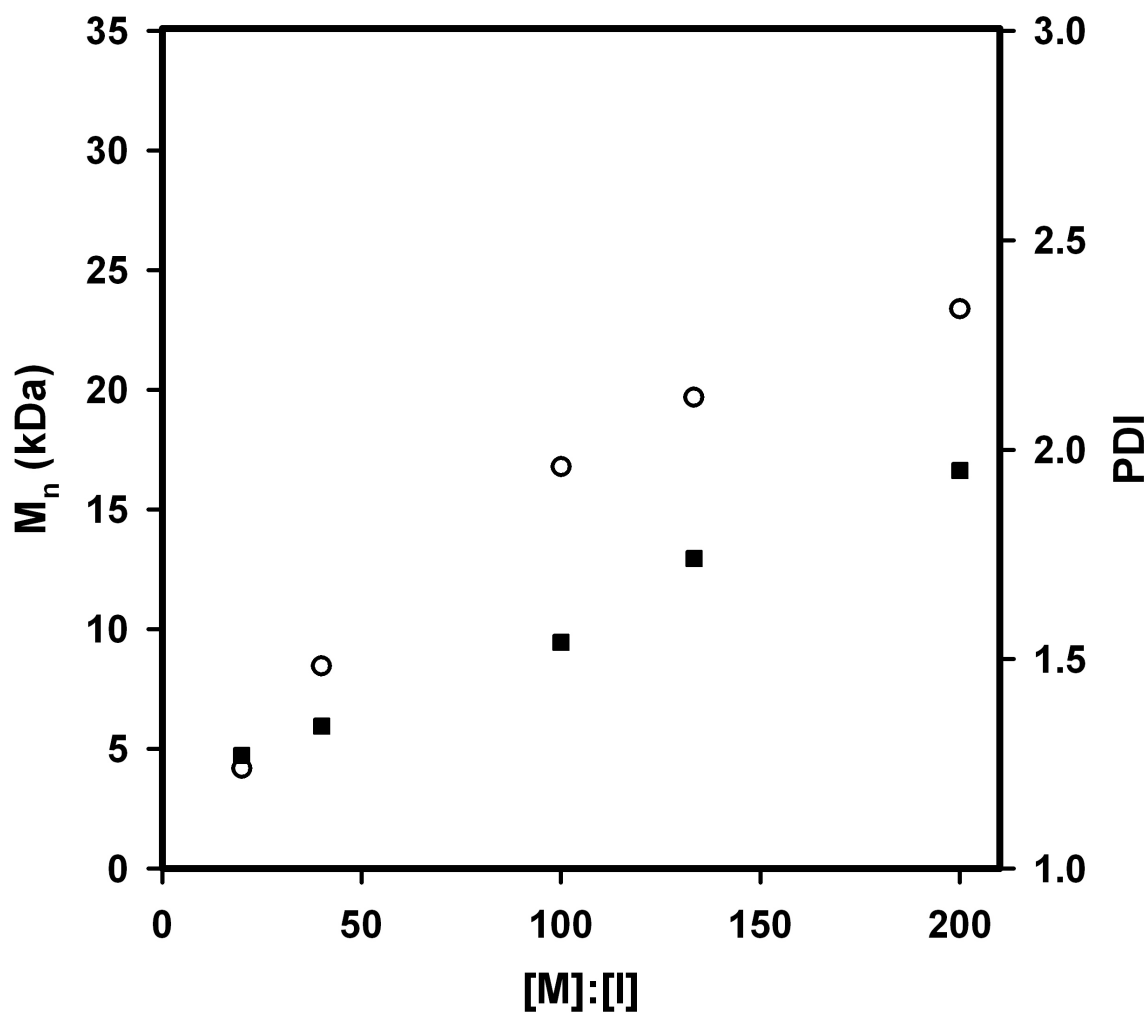


Figure 3.3C Plot of M_n (○) and PDI (■) versus monomer-to-initiator ratio (M:I) for the batch copolymerization of **1a** and **2a** initiated by **3c** ($[1a] = [2a] = 0.04$ M).

Table S3 Data used for Figure 3.3C

[M]: 3c	M_n (kDa)	PDI
20	4.2	1.27
40	8.4	1.34
100	16.8	1.54
133	19.7	1.74
200	23.4	1.95

IX. Calibration Curves

Solutions containing a constant concentration of decane (0.010 M) and varying concentrations of **S4, S5, 5, 6, 7, 8, 9, 10, 11** were prepared in CHCl₃. Each was analyzed by GC and the response factor **F** calculated by fitting the data to the following equation:

$$\frac{\text{analyte area}}{[\text{analyte}]} = F \frac{\text{decane area}}{[\text{decane}]}$$

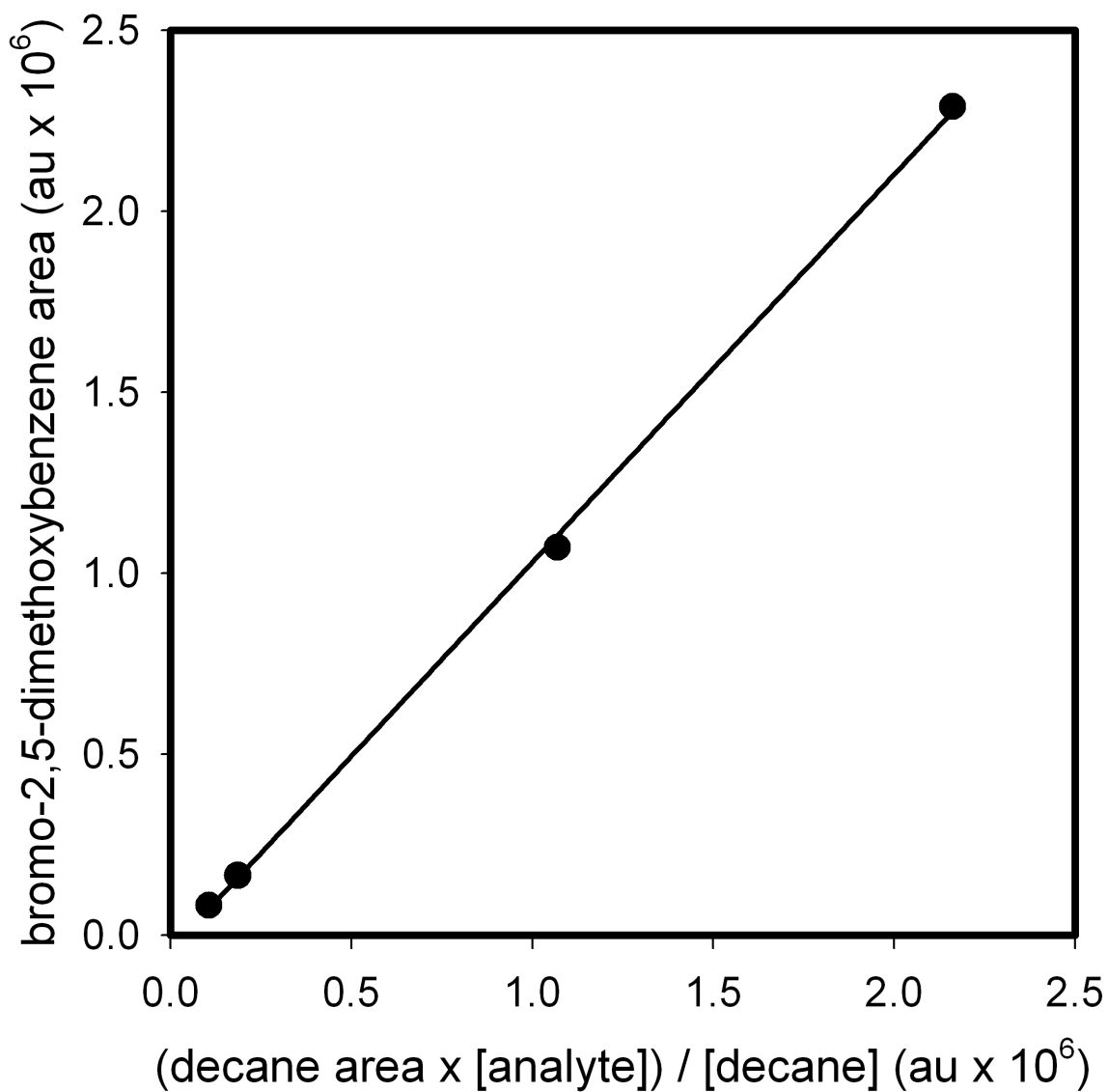


Figure S18 Plot of bromo-2,5-dimethoxybenzene area versus $(\text{decane area} \times [\text{bromo-2,5-dimethoxybenzene}]) / [\text{decane}]$ fitted to $y = mx + b$ where $m = 1.07 \pm 0.02$ and $b = -0.042 \pm 0.001 \times 10^6$.

Table S4 Data for the plot in Figure S18

[bromo-2,5-dimethoxybenzene] (M)	Area bromo-2,5-dimethoxybenzene (au x 10 ⁶)	Area decane (au x 10 ⁶)	(docosane area x [bromo-2,5-dimethoxybenzene]) / [docosane]
0.00007675	0.003170	0.286338	0.002198
0.0001535	0.007631	0.262090	0.004023
0.0007675	0.044692	0.227986	0.017497
0.001535	0.088341	0.212714	0.032651
0.007675	0.484289	0.227143	0.174332

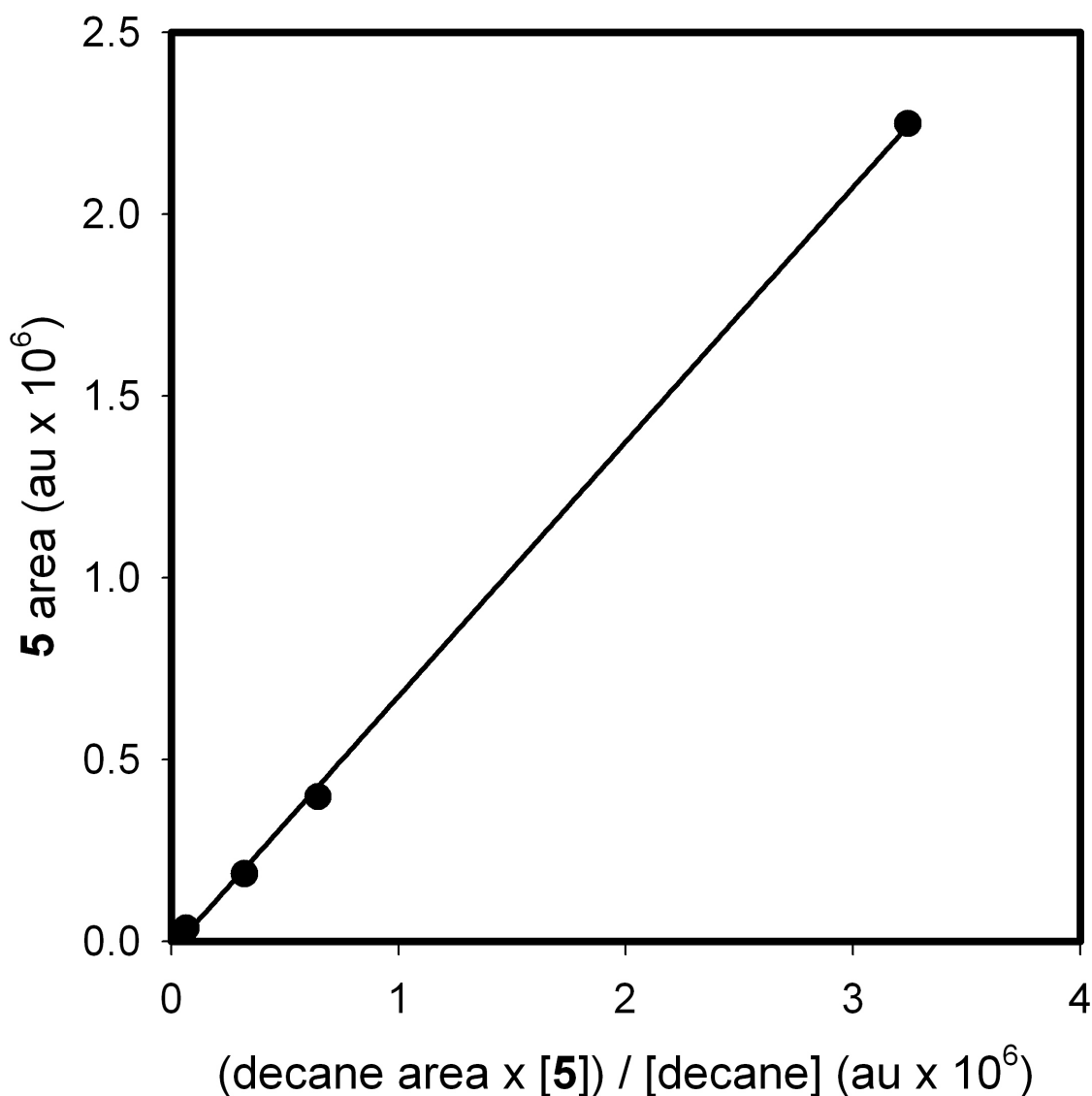


Figure S19 Plot of 5 area versus (decane area x [5]) / [decane] fitted to $y = mx + b$ where $m = 0.77 \pm 0.02$ and $b = -0.029 \pm 0.001 \times 10^6$.

Table S5 Data for the plot in Figure S19

[5] (M)	Area 5 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [5]) / [decane]
0.001395	0.025600	0.3353354	0.046797
0.002791	0.035660	0.2365828	0.066033
0.013955	0.185003	0.231063	0.322460
0.027911	0.397512	0.2315583	0.646302
0.139555	2.249090	0.2323087	3.241984

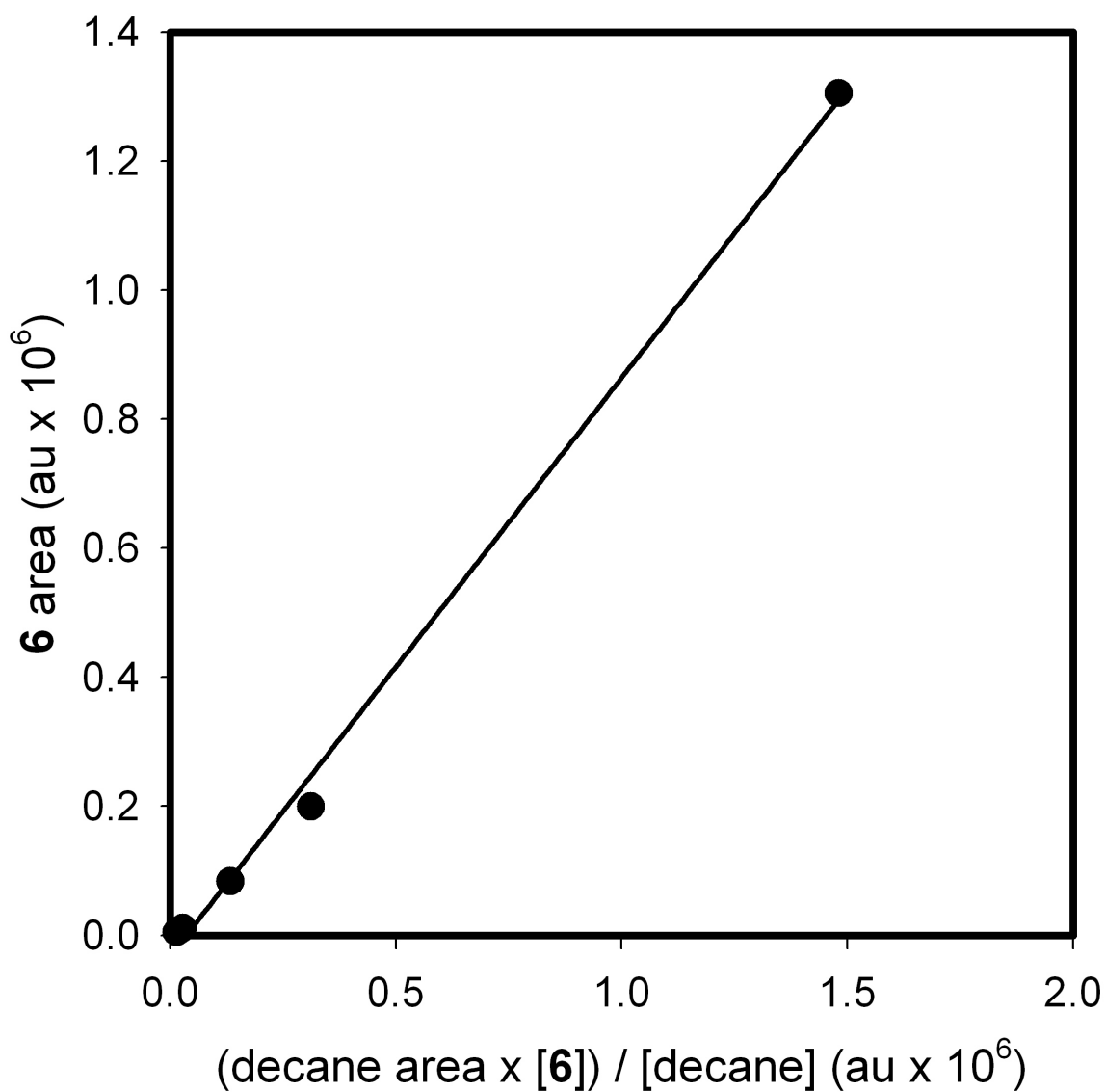


Figure S20 Plot of **6** area versus (decane area x **[6]**) / [decane] fitted to $y = mx + b$ where $m = 2.798 \pm 0.004$ and $b = -0.0322 \pm 0.02 \times 10^6$.

Table S6 Data for the plot in Figure S20

[6] (M)	Area 6 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [6]) / [decane]
6.975E-07	0.0047014	0.2082496	0.01452541
0.000001395	0.0112747	0.2072297	0.028908543
0.000006975	0.0836397	0.1913225	0.133447444
0.00001395	0.1995605	0.2234205	0.311671598
0.00006975	1.3050664	0.2123266	1.480978035

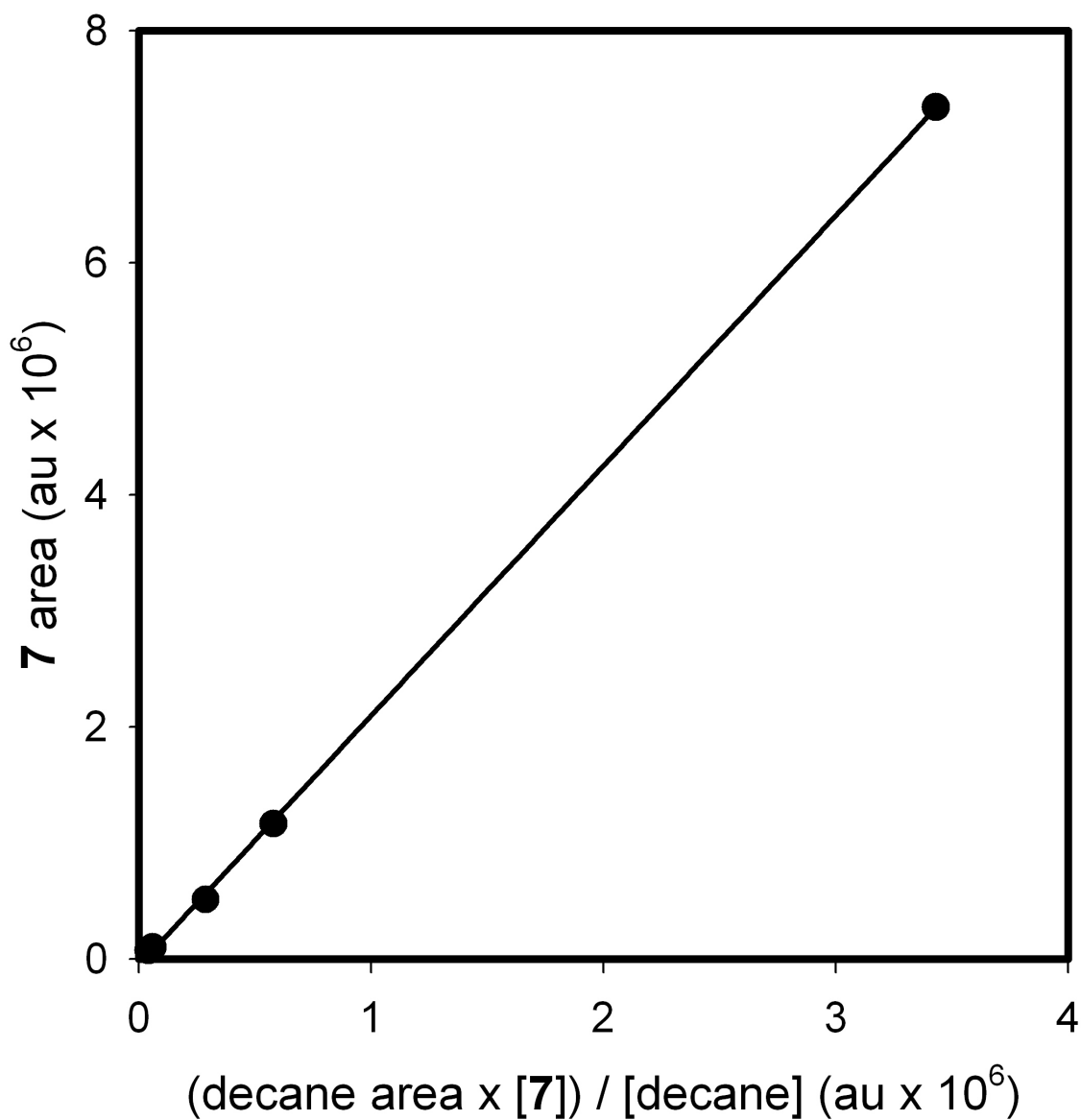


Figure S21 Plot of 7 area versus (decane area x [7]) / [decane] fitted to $y = mx + b$ where $m = 1.86 \pm 0.05$ and $b = 0.115 \pm 0.01 \times 10^6$.

Table S7 Data for the plot in Figure S21

[7] (M)	Area 7 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [7]) / [decane]
0.003113	0.071510	0.218939	0.0681666
0.006227	0.16985	0.189294	0.117873
0.031135	1.07051	0.260103	0.809833
0.062270	2.49093	0.172453	1.073864
0.311350	14.3662	0.247392	7.702562

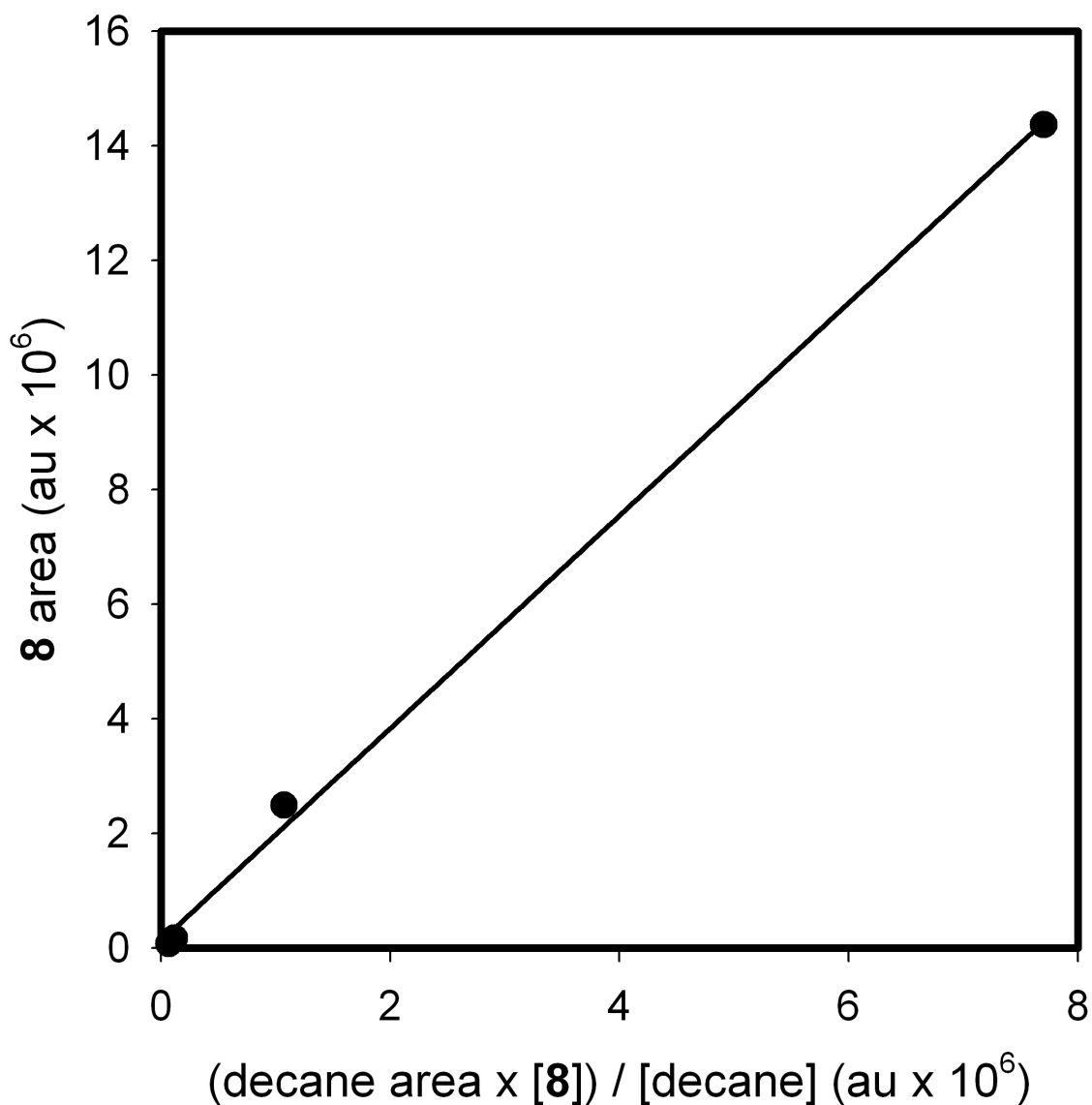


Figure S22 Plot of **8** area versus (decane area x **[8]**) / [decane] fitted to $y = mx + b$ where $m = 1.86 \pm 0.05$ and $b = 0.115 \pm 0.01 \times 10^6$.

Table S8 Data for the plot in Figure S22

[8] (M)	Area 8 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [8]) / [decane]
0.003113	0.071510	0.218939	0.0681666
0.006227	0.16985	0.189294	0.117873
0.031135	1.07051	0.260103	0.809833
0.062270	2.49093	0.172453	1.073864
0.311350	14.3662	0.247392	7.702562

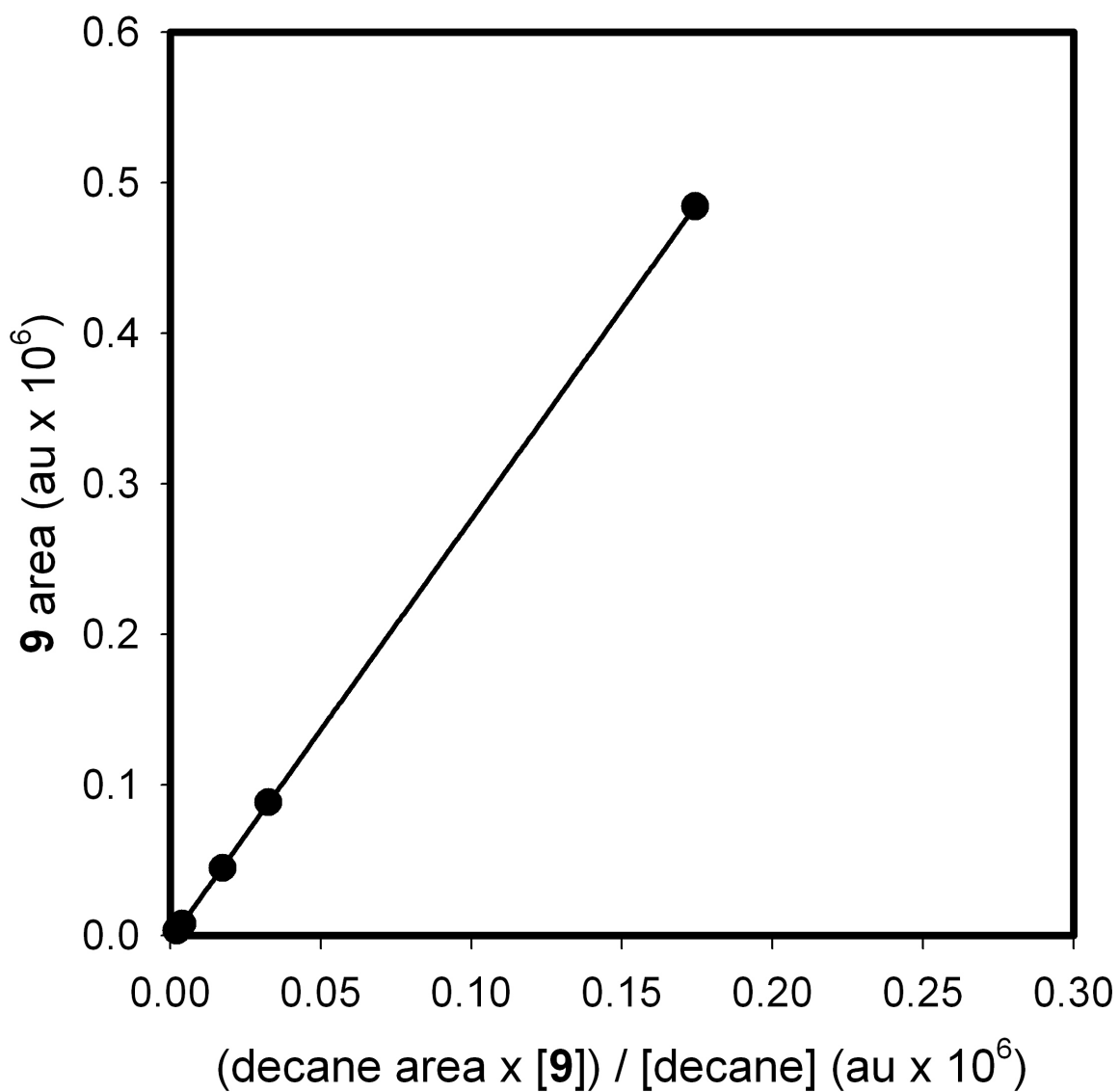


Figure S23 Plot of **9** area versus (decane area x **[9]**) / [decane] fitted to $y = mx + b$ where $m = 2.798 \pm 0.004$ and $b = -0.0035 \pm 0.0003 \times 10^6$.

Table S9 Data for the plot in Figure S23

[9] (M)	Area 9 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [9]) / [decane]
7.675E-08	0.2863379	0.0031702	0.002197643
1.535E-07	0.2620905	0.0076308	0.004023089
7.675E-07	0.2279863	0.0446921	0.017497949
0.000001535	0.2127142	0.0883407	0.03265163
0.000007675	0.2271426	0.4842895	0.174331946

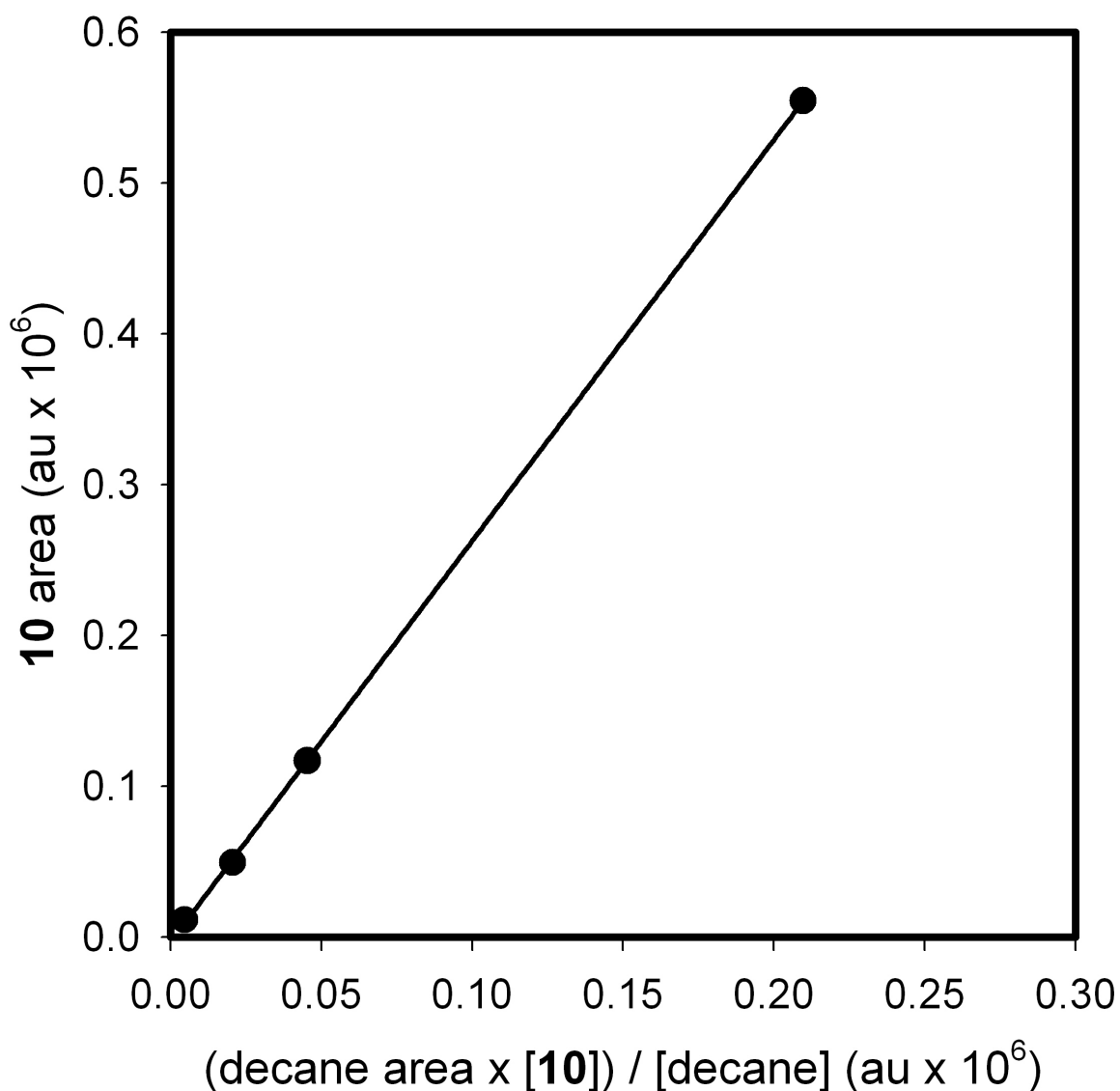


Figure S24 Plot of **10** area versus $(\text{decane area} \times [\mathbf{10}]) / [\text{decane}]$ fitted to $y = mx + b$ where $m = 1.86 \pm 0.05$ and $b = 0.115 \pm 0.01 \times 10^6$.

Table S10 Data for the plot in Figure S24

[10] (M)	Area 10 (au x 10 ⁶)	Area decane (au x 10 ⁶)	$(\text{decane area} \times [\mathbf{10}]) / [\text{decane}]$
2.322E-07	0.201092	0.0112873	0.004669356
0.000001161	0.1775401	0.0492814	0.020612406
0.000002322	0.1953252	0.1168265	0.045354511
0.00001161	0.1806269	0.5545728	0.209707831
2.322E-07	0.201092	0.0112873	0.004669356

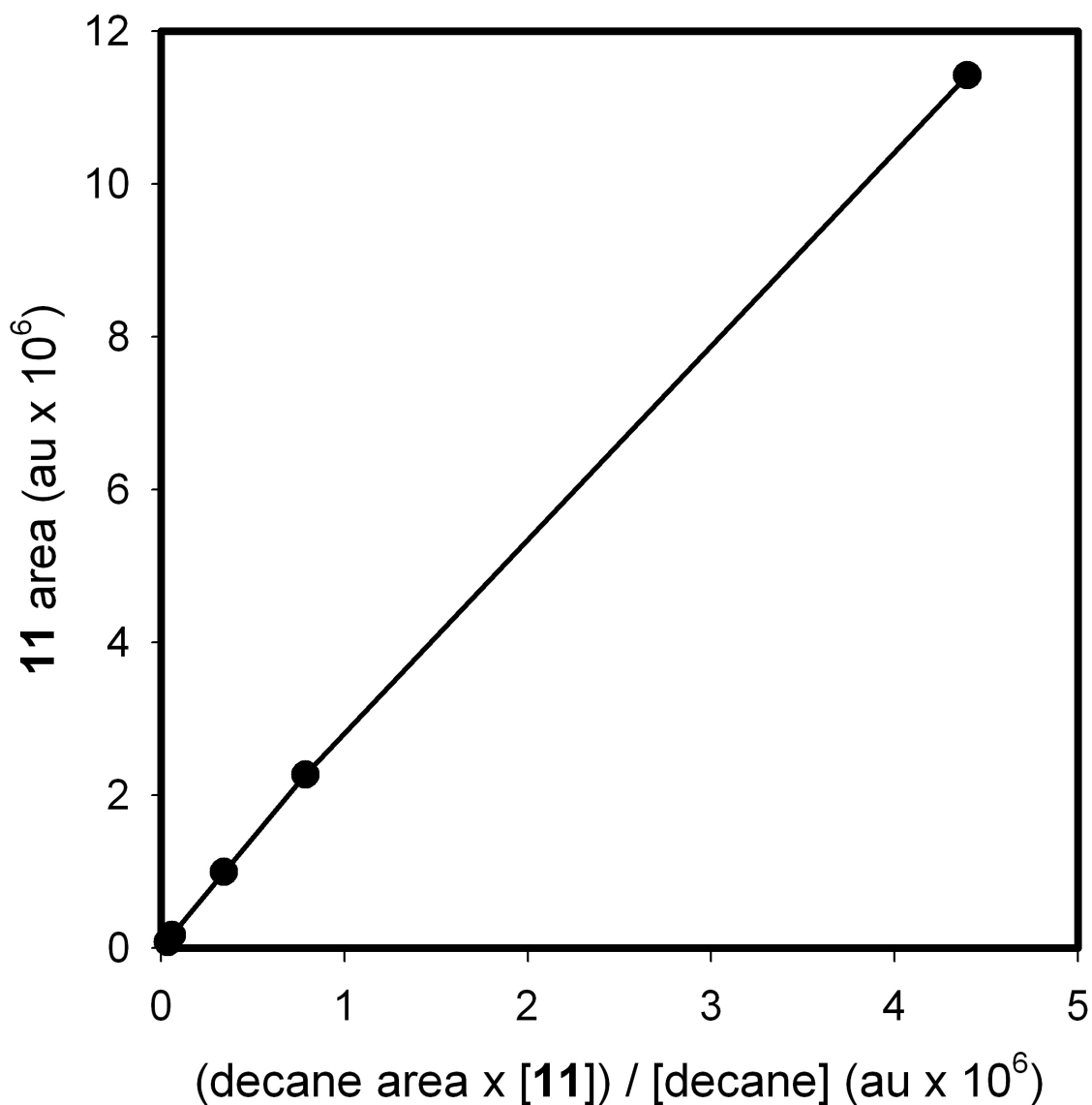


Figure S25 Plot of **11** area versus (decane area x **[11]**) / [decane] fitted to $y = mx + b$ where $m = 2.5863 \pm 0.03$ and $b = 0.073 \pm 0.06 \times 10^6$.

Table S11 Data for the plot in Figure S25

[11] (M)	Area 11 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [11]) / [decane]
1.50538E-06	0.2442017	0.0765738	0.036761629
3.01076E-06	0.1992621	0.1663903	0.059993026
1.50538E-05	0.2287574	0.9922743	0.344366758
3.01076E-05	0.2620049	2.265544	0.788833742
0.000150538	0.2921184	11.4180246	4.39749124

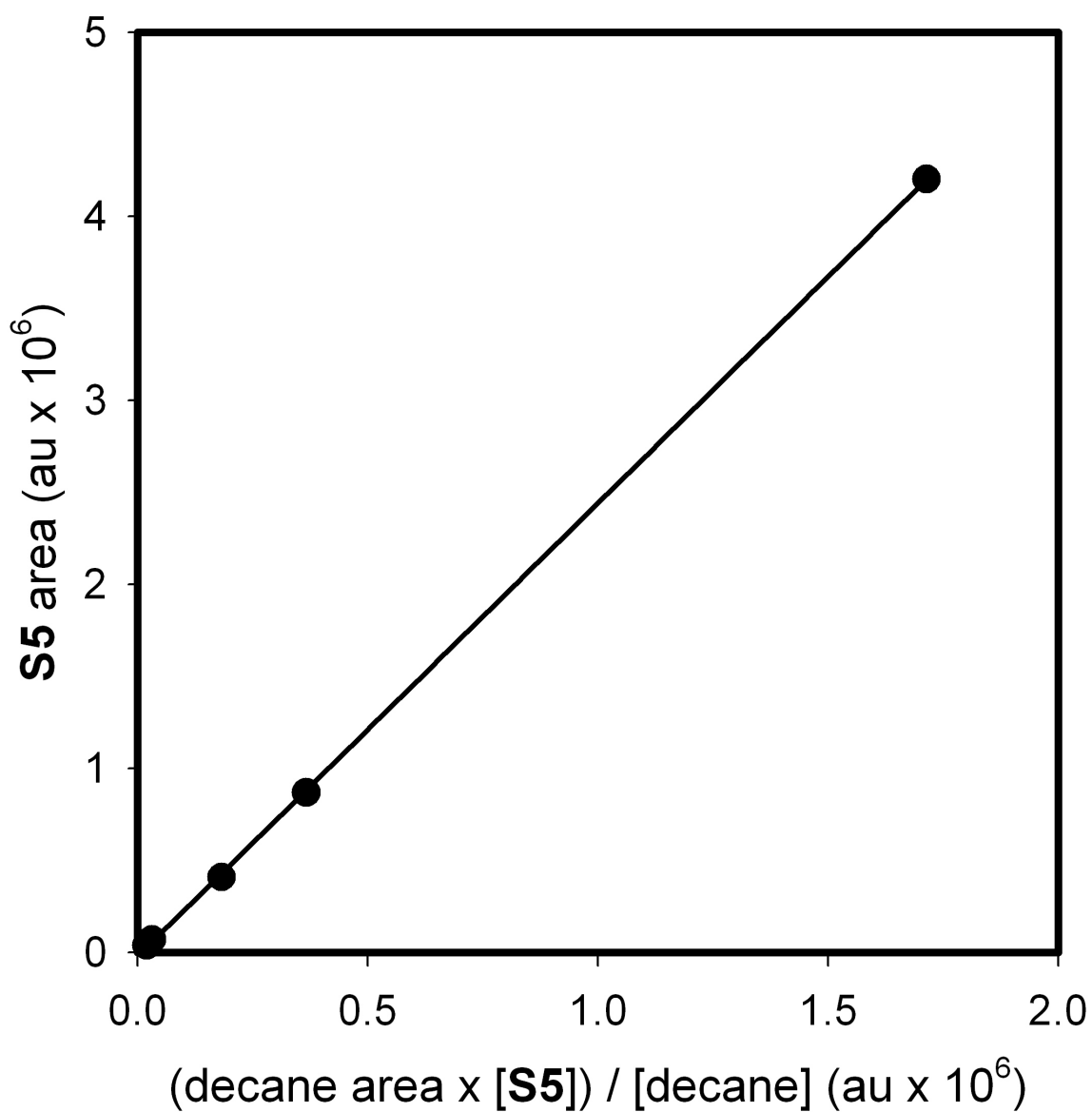


Figure S26 Plot of S5 area versus (decane area x [S5]) / [decane] fitted to $y = mx + b$ where $m = 2.462 \pm 0.01$ and $b = -0.0223 \pm 0.009 \times 10^6$.

Table S12 Data for the plot in Figure S26

[S5] (M)	Area S5 (au x 10 ⁶)	Area decane (au x 10 ⁶)	(decane area x [S5]) / [decane]
8.174E-07	0.0368447	0.236905	0.0193646
1.6348E-06	0.0690864	0.189644	0.0310030
0.000008174	0.408340	0.223262	0.182494
0.000016348	0.867896	0.224081	0.366328
0.00008174	4.202393	0.209709	1.7141613

M_n and PDI versus conversion

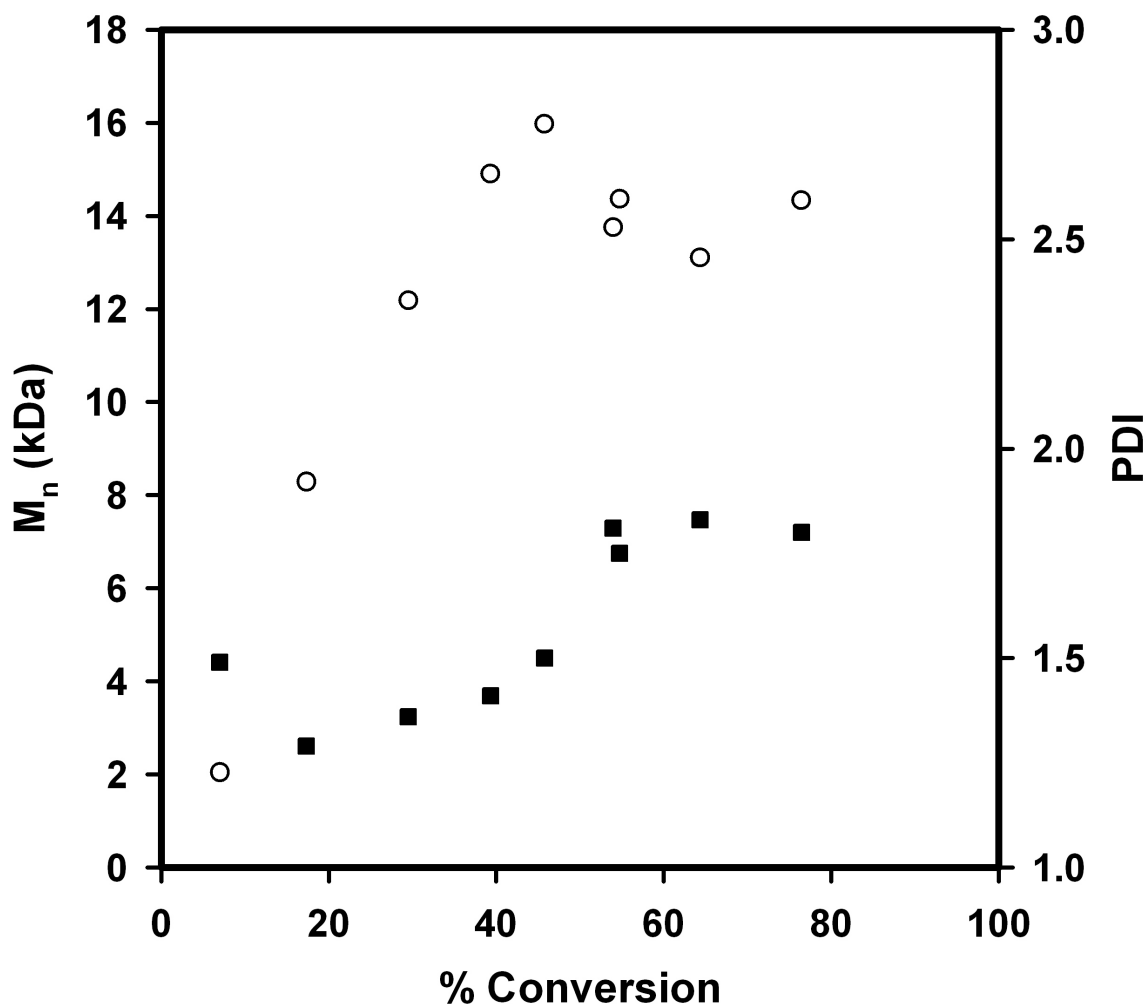


Figure S27 Plot of M_n (○) and PDI (■) versus time for the batch copolymerization of **1a** and **2a** initiated by **3b** ($[1a] = [2a] = 0.10$ M $[3b] = 0.0025$ M).

Table S13 Data used to create Figure S27

% conversion	M_n (kDa)	PDI
7.0	2.0	1.49
17.3	8.3	1.29
29.5	12.2	1.36
39.3	14.9	1.41
45.7	16.0	1.5
54.7	14.4	1.75
53.9	13.7	1.81
64.3	13.1	1.83
76.4	14.3	1.80

Small molecule studies

Table S23 Crossover experiments

[Ni]	Initial moles Ni (x 10 ⁵)	Moles quenched [Ni] (x 10 ⁵)	Moles 5 (x 10 ⁵)	Moles 6 (x 10 ⁵)	Moles 7 (x 10 ⁵)	% associative
4a	4.15	0.685	1.29	2.04	0.0855	97
4a	2.97	0.617	1.42	0.571	0.338	85
4a	4.80	0.578	1.29	2.79	0.115	97
4a	5.50	1.05	2.33	1.94	0.176	96
4b	3.91	0.303	1.73	1.53	0.291	92
4b	2.97	0.617	1.42	0.571	0.338	85
4b	5.01	0.507	1.52	0.203	2.74	95
4b	6.13	0.261	0.728	2.21	3.35	90
4c	4.80	0.256	1.55	2.73	0.232	97
4c	2.97	0.617	1.42	0.571	0.338	85
4c	5.20	0.243	1.48	0.392	3.09	92
4c	13.7	0.256	6.30	7.61	0.61	96

Table S24 Chain Extension Experiments

[Ni]	Initial moles Ni (x 10 ⁵)	Moles quenched [Ni] (x 10 ⁵)	Moles 8 (x 10 ⁵)	Moles 9 (x 10 ⁵)	Moles 10 (x 10 ⁵)	% associative
4a	4.19	1.50	0.489	1.179	0.348	87
4a	2.02	0.712	0.234	0.875	0.179	86
4a	1.07	0.291	0.107	0.00747	0.607	90
4b	1.97	0.800	0.393	0.659	0.109	91
4b	2.65	1.18	0.598	0.420	0.443	70
4b	6.10	0.923	0.451	2.10	2.21	55
4c	2.81	0.927	0.830	0.870	0.165	91
4c	2.66	1.18	0.598	0.420	0.443	70
4c	1.72	0.244	0.062	0.165	1.18	88

Table S25 Competition Experiments

[Ni]	Initial moles [Ni] (x 10 ⁵)	Moles quenched [Ni] (x 10 ⁵)	Moles 7 (x 10 ⁵)	Moles 11 (x 10 ⁵)	Moles S5 (x 10 ⁵)
4a	2.37	0.17	2.16	n.d.	n.d.
4a	2.02	0.712	1.24	n.d.	n.d.
4a	1.87	0.241	1.58	n.d.	n.d.
4b	1.99	0.130	1.81	n.d.	n.d.
4b	1.75	0.58	1.08	n.d.	n.d.
4b	2.14	0.923	1.19	n.d.	n.d.
4c	2.34	0.927	1.42	n.d.	n.d.
4c	1.92	0.742	1.21	n.d.	n.d.
4c	1.89	0.276	1.51	n.d.	n.d.

References Cited

(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) Lee, S.R.; Bryan, Z.J.; Wagner, A.M.; McNeil, A.J. *Chem. Sci.* **2012**, *3*, 1562-1566.

(3) Love, B.E.; Jones, E.G. *J. Org. Chem.* **1999**, *64*, 3755-3756.

Appendix 3
Supporting Information for Chapter 4
Challenges in Ni-catalyzed Controlled Copolymerizations

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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 (2M in THF) was purchased in 100 mL quantities from Aldrich and Ni(cod)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 P₂O₅. Decane was distilled from CaH₂. Compounds Ni(depe)Cl₂¹, Ni(dppe)(Ph)Cl,² Ni(dppe)(*o*-anisyl)Br,³ **1**,⁴ **3**,⁴ were prepared by literature procedures. Monomers were titrated by the method of Love and Jones before use.⁵

II. General Experimental

NMR Spectroscopy: Unless otherwise noted, ¹H, ¹³C, and ³¹P NMR spectra for all compounds were acquired in CDCl₃ on a Varian MR400 or a Varian Inova 400 Spectrometer operating at 400, 100, and 161 MHz, respectively. For ¹H and ¹³C NMR spectra the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. ³¹P NMR spectra were referenced to external H₃PO₄ (85% aq). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and broad resonance (br). Unless otherwise indicated, the ¹H, ³¹P and ¹³C NMR spectra were recorded at room temperature. Note that integrations for protons on the alkyl chains of some compounds are high due to insufficient relaxation time.

IR Spectroscopy: Samples were recorded using a Mettler Toledo ReactIR iC10 fitted with a Mercury Cadmium Telluride (MCT) detector, and AgX (9.5 mm x 1.5 mm) probe 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.

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

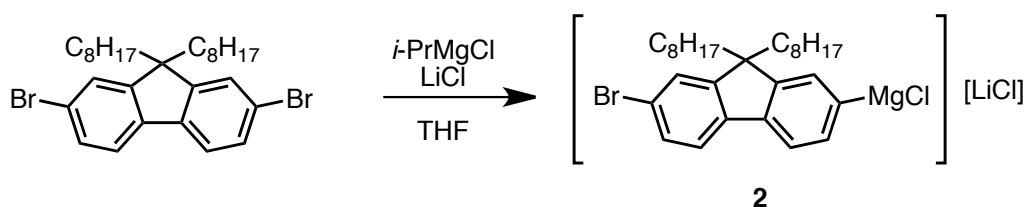
Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with Waters Styragel® (7.8 x 300 mm) THF HR 0.5, THF HR 1, and THF HR 4 type columns in sequence and analyzed with Waters 2487 dual absorbance detector (254 and 350 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 mmID, 0.25 µm df) column.

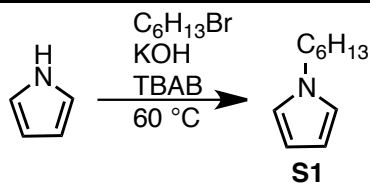
UV-vis Spectroscopy: UV-vis spectra were acquired using a Perkin Elmer Lambda 850 UV-vis Spectrometer. Solution samples were prepared at 1×10^{-4} M in CHCl_3 . Thin-films were spin-cast on glass slides from 1 mg/mL solutions in CHCl_3 .

Fluorescence Spectroscopy: Fluorescence spectra were recorded on a Fluoromax-2 fluorimeter. Solution samples were prepared in at 1×10^{-4} M in CHCl_3 . Thin-films were spin-cast on glass slides from 1 mg/mL solutions in CHCl_3 .

III. Synthetic Procedures

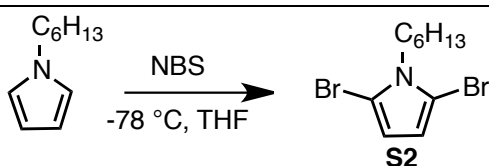


2: All actions were performed in a glovebox under N_2 atmosphere. A 20 mL flask was equipped with a stir bar. 2,7-Dibromo-9,9-bis(octyl)fluorene (1.00 g, 1.80 mmol, 1.00 eq), LiCl (0.077 g, 1.80 mmol, 1.00 eq) and THF (2.70 mL) were added and stirred until a homogeneous solution was obtained. Then *i*-PrMgCl (0.960 mL, 1.80 mmol, 1.00 eq) was added to the flask. The reaction mixture was stirred overnight and then titrated.

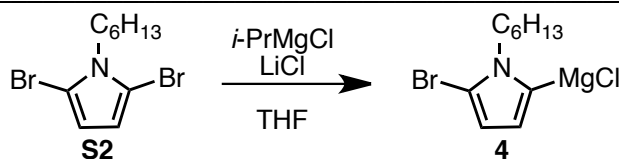


S1: A 100-mL oven-dried Schlenk flask equipped with a stir bar and septum was cooled under N_2 . Tetrabutylammonium bromide (2.40 g, 75.5 mmol, 0.500 equiv), KOH (9.70 g, 160 mmol, 1.10 equiv) and pyrrole (10.3 mL, 149 mmol, 1.00 equiv) were added to the

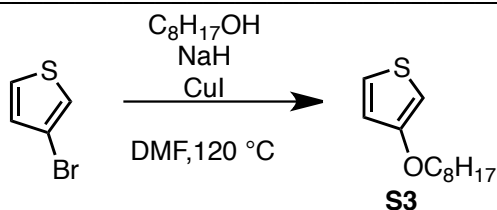
flask and heated to 80 °C. Then 1-bromohexane (31.4 mL, 224 mmol, 1.50 equiv) was added and the reaction stirred overnight. The reaction was cooled to rt, then filtered and the solids washed with hexanes. The filtrate was washed with H₂O, then brine, dried over MgSO₄, then filtered and solvent removed in vacuo. The resultant brown oil was chromatographed on silica, eluting with hexanes and then distilled (98 °C, 0.30 torr) to yield a colorless oil (17.9 g, 79% yield). Calcd. for C₁₀H₁₇N, 151.1361 [M]⁺; found, 151.1356.



S2: A 50-mL oven-dried Schlenk flask equipped with a stir bar and septum was cooled under N₂. *N*-hexylpyrrole (2 g, 0.01 mol, 1 equiv) and THF (20 mL) were added via syringe. The solution was cooled to -78 °C. NBS (4.67 g, 27.0 mmol, 2.05 equiv) was added portion-wise (~0.5 g) over 20 min. After 5 h, the reaction mixture was then warmed to -10 °C and stirred vigorously. After 30 min the reaction was quenched with a mixture of saturated aq. Na₂SO₃ (15 mL) and 10% aq. Na₂CO₃ (5 mL), then extracted with hexanes. The combined organics were dried over Na₂SO₃/Na₂SO₄. The solvent was reduced in vacuo to ~10 mL and then filtered through basic alumina. The crude product was then chromatographed through silica eluting with hexanes to yield a colorless oil (2.4411 g, 60% yield). Calcd. for C₁₀H₁₅NBr₂, 306.9571 [M]⁺; found, 306.9581.

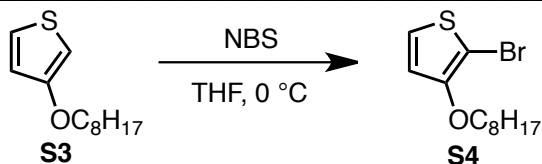


4: All actions were performed in a glovebox under N₂ atmosphere. A 20 mL vial was equipped with a stir bar. Sequentially, **S2** (973 mg, 3.15 mmol, 1.05 equiv), THF (3.5 mL), LiCl (126 mg, 3.40 mmol, 1.05 equiv) and *i*-PrMgCl (1.5 mL, 2.5 mmol, 1.0 equiv) were added to the flask. The reaction mixture was stirred at rt overnight.

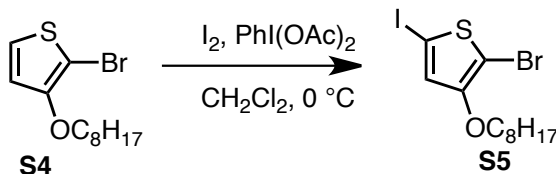


S3: A 50 mL oven-dried Schlenk flask equipped with a stir bar and septum was cooled under N₂. Once cool, NaH (1.296 g, 54 mmol, 1.50 equiv) was added and suspended in DMF (12 mL). *n*-Octanol (28.4 mL, 189 mmol, 5.40 equiv) was added dropwise over 1 h and the suspension stirred for 1 h. The flask was then charged with 3-bromothiophene (3.38 mL, 35.0 mmol, 1.00 equiv) and heated to 120 °C. CuI (1.01 g, 70.1 mmol, 2.00

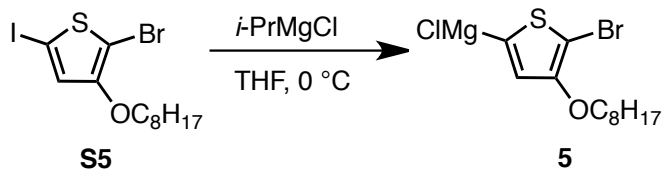
equiv) was added and the reaction maintained at 120 °C for 4 h. The reaction was cooled to rt then filtered through a celite pad. The celite was washed with H₂O (3 x 30 mL), then hexanes (4 x 15 mL). The combined organics were washed with H₂O (2 x 10 mL) then brine (20 mL) and dried over MgSO₄. The solvent was removed in vacuo and the product chromatographed on silica eluting with hexanes. The resultant oil was distilled (70 °C, 0.150 torr) to yield **S3** (6.20 g, 44%).



S4: A 50 mL oven-dried Schlenk flask equipped with a stir bar and septum was cooled under N₂. Once cool, **S3** (1.00 g, 4.71 mmol, 1.00 equiv) was added and the flask cooled to 0 °C. NBS (0.838 g, 4.71 mmol, 1.00 equiv) was added and the reaction maintained at 0 °C for 3 h. The reaction was quenched with 10% aq. Na₂CO₃ (5 mL), then extracted with hexanes. The combined organics were washed with brine, dried over Na₂SO₄ and the solvent removed in vacuo. The residue was chromatographed on silica eluting with hexanes to yield **S4** (1.146 g, 84%).

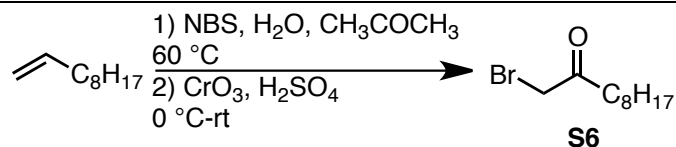


S5: A 15 mL oven-dried Schlenk flask equipped with a stir bar and septum was cooled under N₂. Once cool, **S4** (0.178 g, 0.600 mmol, 1.00 equiv) and CH₂Cl₂ (1.7 mL) was added and the flask cooled to 0 °C. I₂ (0.085 g, 0.336 mmol, 0.550 equiv) and PhI(OAc)₂ (0.108 g, 0.336 mmol, 0.550 equiv) were added and the reaction maintained at 0 °C for 12 h. The reaction was quenched with a mixture of saturated aq. Na₂SO₃ (15 mL) and 10% aq. Na₂CO₃ (5 mL), then extracted with CH₂Cl₂. The combined organics were washed with brine (10 mL) then dried over MgSO₄ and activated carbon, then the solvent removed in vacuo to yield an orange oil. The oil was chromatographed eluting with hexanes then distilled under vacuum (105 °C, 0.030 torr) to yield **S5** (0.1926 g, 86%). as a clear oil.

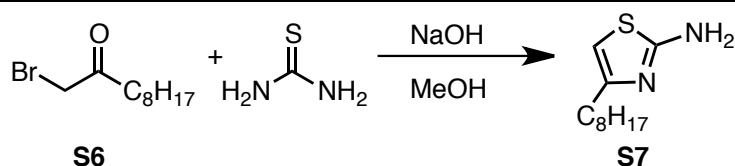


5: All actions were performed under N₂ atmosphere. A 20 Schlenk tube was equipped with a stir bar and septum. Sequentially, **S5** (229 mg, 5.50 mmol, 1.05 equiv) and THF (2 mL), were added to the flask and the reaction cooled to 0 °C. *i*-PrMgCl (0.250 mL, 2 M,

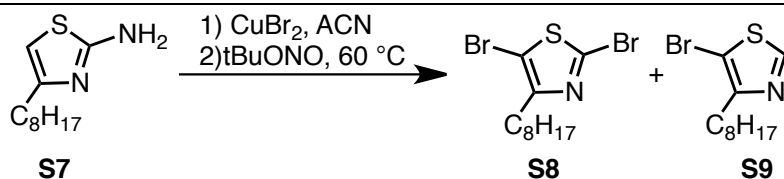
5 mmol, 1.00 equiv) and the reaction stirred at 0 °C for 45 min.



S6: Decene (5.00 g, 6.75 mL, 35.6 mmol, 1.0 equiv) was dissolved in H₂O (5 mL) and acetone (7 mL) in a 100 mL round-bottomed flask equipped with a stir bar. NBS (6.92 g, 39.1 mmol, 1.10 equiv) was added and a reflux condenser attached. The flask was heated to 60 °C for 2 h, after which all NBS had been consumed and the reaction was complete by TLC. CrO₃ (4.60 g, 46.0 mmol, 1.30 equiv) was dissolved in H₂O (10 mL) and H₂SO₄ (3.2 mL). The flask was cooled to 0 °C, then the Cr solution was added, the reaction stirred overnight and allowed to come to rt. The reaction was extracted with Et₂O (3 x 30 mL), the organics washed with brine (20 mL) then dried over Na₂SO₄. Solvents were removed in vacuo and run through a silica plug eluting with 5% EtOAc to yield **S6** as a clear oil.

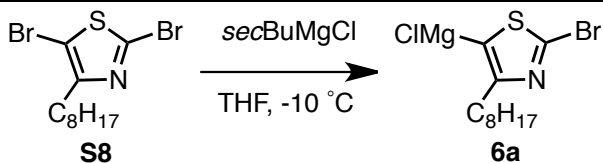


S7: Thiourea (1.616 g, 0.021 mol) 1.0 equiv) and **S6** (5.00 g 0.021 mol, 1.0 equiv) were dissolved in MeOH (3.5 mL) in a 100 mL round-bottomed flask equipped with a stir bar and the flask heated to 100 °C. After 2 h the reaction was cooled and NaOH (1.27 g, 0.0318 mol, 1.5 equiv) was added and the reaction heated to 100 °C. The reaction was stirred for another 2 h then cooled to rt and diluted with H₂O (10 mL), extracted with Et₂O (3 x 10 mL). The combined organics were washed with brine and dried over MgSO₄ then the solvents removed in vacuo. The resulting brown liquid was chromatographed on silica with 50% EtOAc in hexanes, then on neutral alumina with 50 % EtOAc in hexanes to yield **S7** (2.816 g 63%) as a yellow wax.

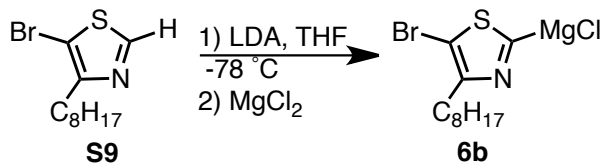


2,5-dibromo-4-octylthiazole (S8), 5-bromo-4-octylthiazole (S9): **S6** (0.150 g, 0.707 mmol, 1.00 equiv) was added to a dry 25 mL Schlenk flask equipped with a stir bar which had been cooled under N₂. CH₃CN (8.8 mL) and CuBr₂ (0.237 g, 1.06 mmol, 1.50 equiv) were added and the reaction stirred at rt for 20 minutes or until reaction was

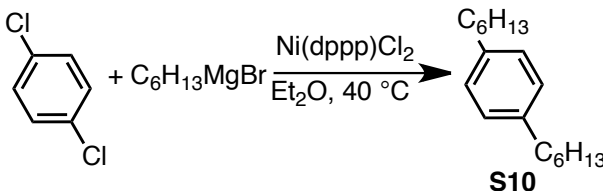
complete by TLC. Then *t*BuONO (0.127 g, 1.06 mmol, 1.50 equiv) was added and the reaction heated to 65 °C. After 20 min the reaction was cooled to rt and solvent removed in vacuo. The residue was taken up in Et₂O (15 mL) then washed with aq NH₄Cl (10 mL) then H₂O (10 mL) then brine (10 mL). The organic layer was dried over MgSO₄ then volatiles removed en vacuo and the resulting brown oil chromatographed on silica eluting with 20 % EtOAc to yield 2,5-dibromo-4-octylthiazole (**S8**) (0.1833 g, 72%) as a clear oil and 5-bromo-4-octylthiazole (0.0332 g, 17 %) as a clear oil.



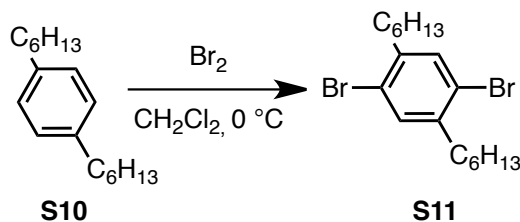
6a: All actions were performed under N₂ atmosphere. A 20 mL Schlenk tube was equipped with a stir bar and septum and 2,5-dibromo-4-octylthiazole (0.1775 g, 0.500 mmol, 1.00 equiv) and THF (2 mL) was added and the reaction cooled to -10 °C. *sec*BuMgCl (0.250 mL, 0.500 mmol, 1.00 equiv) was added and the reaction stirred at -10 °C for 10 min.



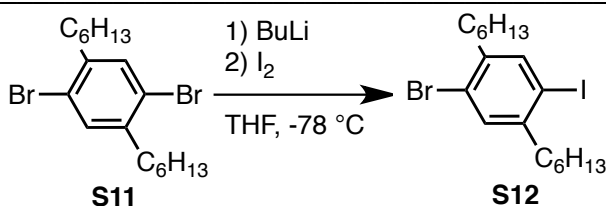
6b: An oven-dried, 20 mL Schlenk flask equipped with a stir bar and septum was cooled under N₂. 5-bromo-4-octylthiazole (0.1279 g, 0.463 mmol, 1.05 equiv) and THF (0.8 mL) were added to the flask and the flask cooled to -78 °C. LDA (0.882 mL, 0.50 M, 0.44 mmol, 1.00 equiv) was added and the reaction maintained at -78 °C for 30 min then warmed to rt.



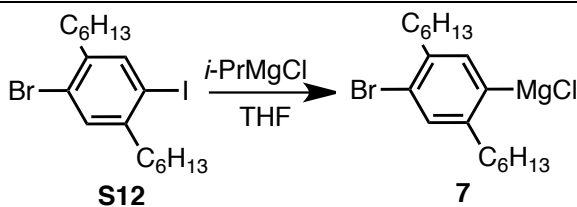
S10: An oven-dried 50 mL Schlenk flask was cooled equipped with a stir bar and septum was cooled under N₂. Once cool the flask was charged with *p*-dichlorobenzene (1.57 g, 10.7 mmol, 0.50 equiv), Et₂O (10 mL) and Ni(dppp)Cl₂ (0.3471 g, 0.641 mmol, 0.030 equiv). *n*-Hexylmagnesium bromide (22 mL, 21.4 mmol, 2.00 equiv) was added and the reaction refluxed overnight. The reaction was quenched with H₂O (20 mL) then extracted with Et₂O (3 x 20 mL). The combined organics were washed with brine (15 mL), dried over MgSO₄ and solvent removed in vacuo. The product was chromatographed eluting with hexanes to yield **S10** (1.968 g, 75%) as a clear oil.



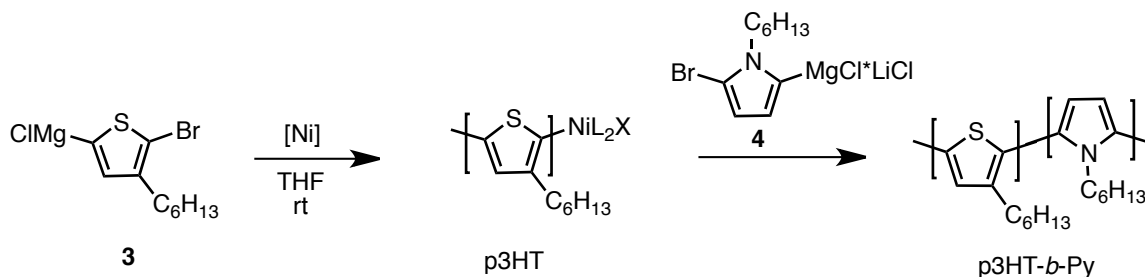
S11: An oven-dried 25 mL Schlenk flask equipped with a stir bar and septum was cooled under N₂. Once cool the flask was charged with **S10** (0.500 g, 2.03 mmol, 1.00 equiv) and CH₂Cl₂ (2 mL) and the flask cooled to 0 °C. Br₂ (0.262 g, 5.08 mmol, 2.5 equiv) was added and the reaction allowed to warm to rt overnight. The reaction was quenched with saturated aq. Na₂SO₃ (8 mL) and extracted with CH₂Cl₂ (3 x 15 mL). The organic layer was washed with brine (10 mL) and dried over MgSO₄. The yellow solid was recrystallized from EtOH to yield **S11** (0.753 g, 92%) as a white solid.



S12: An oven-dried 50 mL Schlenk flask equipped with a stir bar and septum was cooled under vacuum. Once cool the flask filled with N₂ and charged with **S11** (0.3000 g, 0.742 mmol, 1.00 equiv) and THF (7 mL) then cooled to -78 °C. BuLi (0.518 mL, 1.6 M, 0.816 mmol, 1.10 equiv) was added dropwise and the reaction maintained at -78 °C for 1 h. The reaction was then transferred to a solution of I₂ (0.207 g, 0.816 mmol 1.10 equiv) in THF (5 mL) at -78 °C. The reaction was quenched with saturated aq. Na₂SO₃ (8 mL) and extracted with CH₂Cl₂ (3 x 5 mL). The combined organics were washed with brine (10 mL), dried over MgSO₄ and solvents removed in vacuo. The product was chromatographed on silica eluting with hexanes to yield **S12** (0.2573 g, 77%) as a white solid.



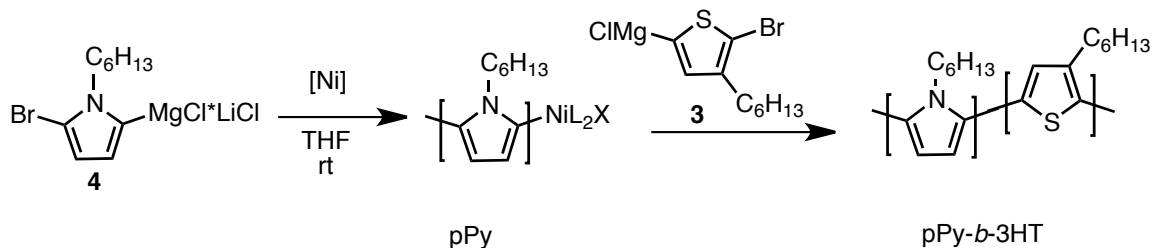
7: In the glovebox, **S12** (0.100 g, 0.222 mmol, 1.2 equiv) was dissolved in THF (0.915 mL) in a 20 mL vial equipped with a stir bar. *i*-PrMgCl (0.0925 mL, 0.185 mmol, 1.0 equiv) was added and the reaction stirred for 1 h.



p3HT-*b*-Py: In the glovebox, **3** (2.00 mL, 0.250 M, 0.500 mmol, 1.00 equiv) was added to a 20 mL vial with a stir bar. [Ni] (0.0125 mmol 0.025 equiv) was added with vigorous stirring and the reaction stirred for 2 h. An aliquot (~0.100 mL) was taken from the reaction, removed from the glovebox, quenched with 5 M HCl (1 mL), extracted with CHCl₃ (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC analysis. A solution of **4** (1.00 mL, 0.500 M, 0.125 mmol, 1.00 equiv) was then added to the vial and the reaction stirred for an additional 3 h. The reaction was then removed from the glovebox and quenched with aq Na₂CO₃ (10 mL). It was then extracted with hot CHCl₃ (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant purple solid was then removed for GPC analysis.

Table S1: Summary of block copolymerizations for p3HT-*b*-Py

[Ni]	p3HT		p3HT- <i>b</i> -Py	
	M _n (kDa)	PDI	M _n (kDa)	PDI
Ni(dppe)Cl ₂	8.7	1.4	13.9	1.6
Ni(dppp)Cl ₂	5.5	1.3	14.0	1.6
Ni(depe)Cl ₂	5.7	1.2	6.8	1.3

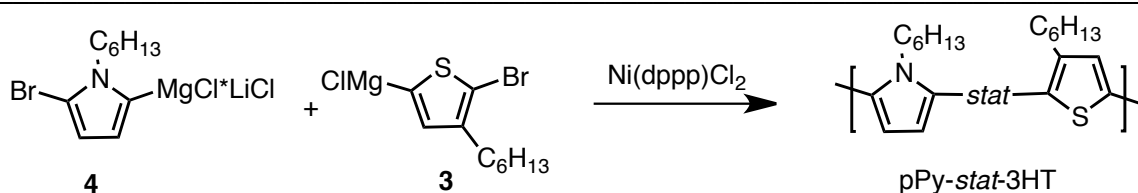


pPy-*b*-3HT: In the glovebox, **4** (1.0 mL, 0.500 M, 0.500 mmol, 1.00 equiv) was added to a 20 mL vial with a stir bar and combined with THF (1 mL). [Ni] (0.0125 mmol 0.025 equiv) was added with vigorous stirring and the reaction stirred for 2 h. An aliquot (~0.100 mL) was taken from the reaction, removed from the glovebox, quenched with aq Na₂CO₃ (1 mL), extracted with CHCl₃ (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC analysis. A solution of **3** (2.0 mL, 0.250 M, 0.500 mmol, 1.00 equiv) was then added to the vial and the reaction stirred for an additional 3 h. The reaction was then removed from the glovebox and quenched with aq Na₂CO₃ (10

mL). It was then extracted with hot CHCl_3 (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant purple solid was then removed for GPC analysis.

Table S2 Summary of block copolymerizations for pPy-*b*-3HT

	pPy		pPy- <i>b</i> -3HT	
	M_n (kDa)	PDI	M_n (kDa)	PDI
Ni(dppe) Cl_2	8.7	1.4	8.7	1.7
Ni(dppp) Cl_2	6.3	1.3	10.5	1.4
Ni(depe) Cl_2	8.4	1.3	6.2	1.5



pPy-*b*-3HT: Solutions of **4** (1.0 mL, 0.5 M, 0.500 mmol, 1.00 equiv) and **3** (2.0 mL, 0.500 M, 0.125 mmol, 1.00 equiv) were added under N_2 to an oven-dried 20 mL Schlenk flask with a stir bar and combined with THF (1 mL). A suspension of Ni(dppp) Cl_2 (06.8 mg, 0.0125 mmol 0.025 equiv) in THF (0.100 mL) was added with vigorous stirring and the reaction stirred for 6 h. Aliquots (~0.100 mL) were taken from the reaction via syringe, quenched with aq Na_2CO_3 (1 mL), extracted with CHCl_3 (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC and ^1H NMR analysis.

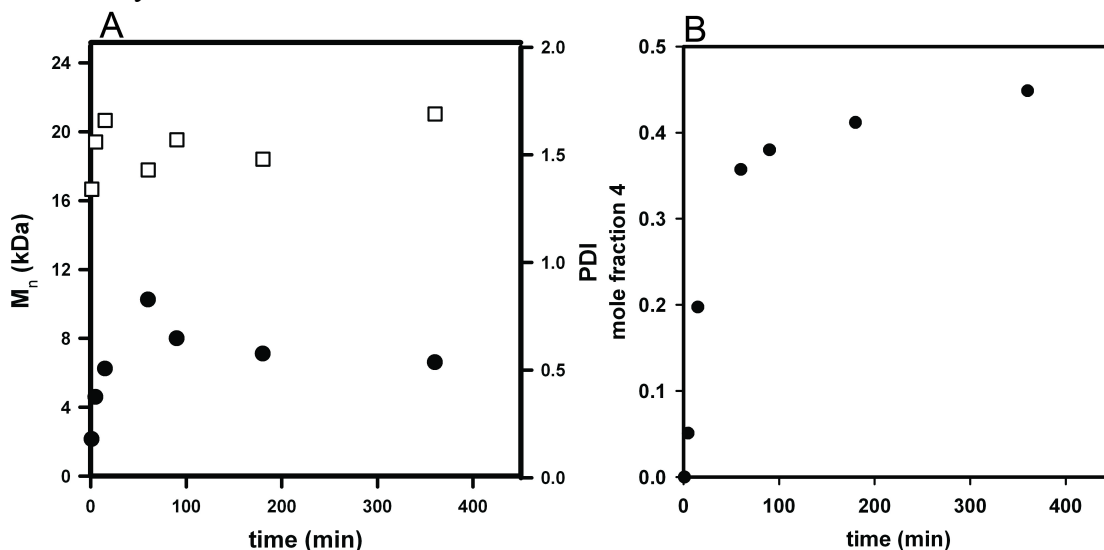
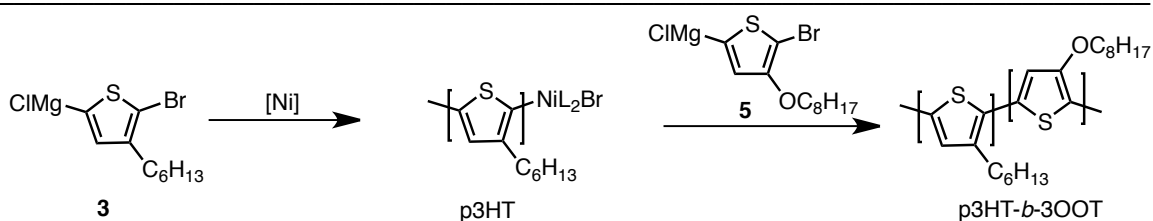


Figure S1 (A) Plot of M_n (●) and PDI (□) versus time for the batch copolymerization of **3** and **4** initiated by Ni(dppp) Cl_2 ($[\mathbf{3}] = [\mathbf{4}] = 0.25$ M, $[\text{Ni}] = 6.3$ mM). (B) Plot of the mole fraction of **4** in the copolymer versus time during the batch copolymerization of **3** and **4**.

Table S3 Data used for Figure S1A and B

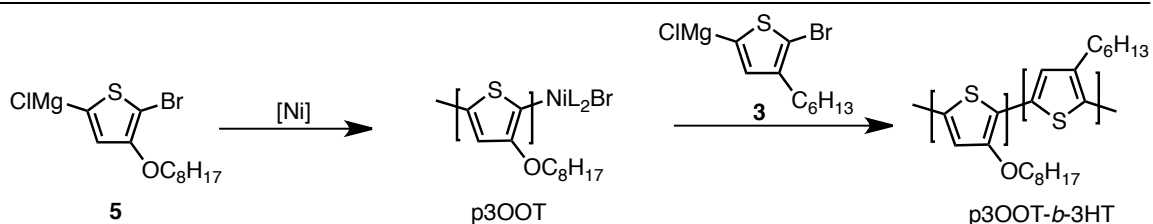
Time (min)	M _n	PDI	mole fraction 4
1	2.157	1.34	0
5	4.602	1.56	0.051
15	6.243	1.66	0.197
60	10.25	1.43	0.357
90	8.007	1.57	0.380
180	7.109	1.48	0.412
360	6.616	1.69	0.448



p3HT-*b*-3OOT: In the glovebox, **3** (2.00 mL, 0.250 M, 0.500 mmol, 1.00 equiv) was added to a 20 mL vial with a stir bar. [Ni] (0.0125 mmol 0.025 equiv) was added with vigorous stirring and the reaction stirred for 2 h. An aliquot (~0.100 mL) was taken from the reaction, removed from the glovebox, quenched with 5 M HCl (1 mL), extracted with CHCl₃ (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC analysis. A solution of **5** (2.20 mL, 0.222 M, 0.500 mmol, 1.00 equiv) was then added to the vial and the reaction stirred for an additional 3 h. The reaction was then removed from the glovebox and quenched with 5 M HCl (10 mL). It was then extracted with hot CHCl₃ (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant purple solid was then removed for GPC analysis.

Table S4 Summary of block copolymerizations for p3HT-*b*-3OOT

[Ni]	p3HT		p3HT- <i>b</i> -3OOT	
	M _n (kDa)	PDI	M _n (kDa)	PDI
Ni(dppe)Cl ₂	3.3	1.2	3.5	1.5
Ni(dppp)Cl ₂	3.5	1.2	4.5	1.5

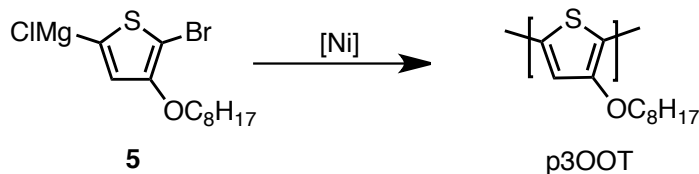


p3OOT-*b*-3HT: In the glovebox, **5** (2.20 mL, 0.250 M, 0.500 mmol, 1.00 equiv) was added to a 20 mL vial with a stir bar. [Ni] (0.0125 mmol 0.025 equiv) was added with

vigorous stirring and the reaction stirred for 2 h. An aliquot (~0.100 mL) was taken from the reaction, removed from the glovebox, quenched with 5 M HCl (1 mL), extracted with CHCl₃ (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC analysis. A solution of **3** (2.00 mL, 0.250 M, 0.500 mmol, 1.00 equiv) was then added to the vial and the reaction stirred for an additional 3 h. The reaction was then removed from the glovebox and quenched with 5 M HCl (10 mL). It was then extracted with hot CHCl₃ (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant purple solid was then removed for GPC analysis.

Table S5 Summary of block copolymerizations for p3OOT-*b*-3HT

	p3OOT		p3OOT- <i>b</i> -3HT	
	M _n (kDa)	PDI	M _n (kDa)	PDI
Ni(dppe)Cl ₂	1.7	1.2	2.4	1.4
Ni(dppp)Cl ₂	1.5	1.3	2.1	1.5



p3OOT: A solution of **5** (2.20 mL, 0.250 M, 0.500 mmol, 1.00 equiv) was added under N₂ to an oven-dried 20 mL Schlenk flask with a stir bar and combined with THF (1 mL). A suspension of Ni(dppp)Cl₂ (06.8 mg, 0.0125 mmol 0.025 equiv) in THF (0.100 mL) was added with vigorous stirring and the reaction stirred for 6 h. Aliquots (~0.100 mL) were taken from the reaction via syringe, quenched with 5M HCl (1 mL), extracted with CHCl₃ (3 x 1 mL), the solvent removed in vacuo and the resulting polymer prepared for GPC and ¹H NMR analysis.

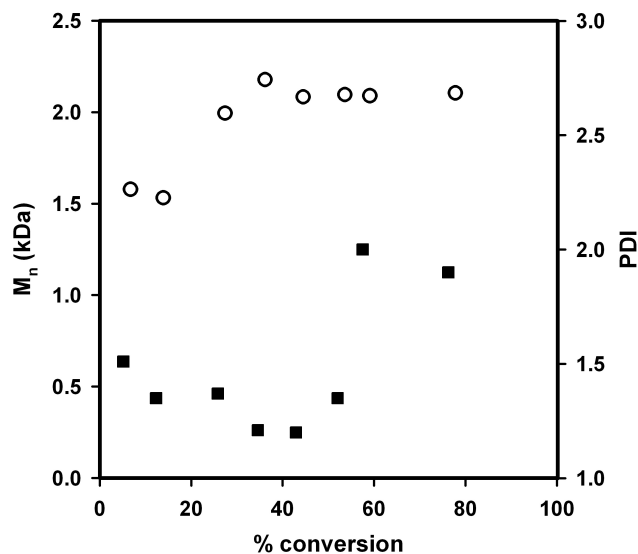


Figure S2 Plot of M_n (○) and PDI (■) versus conversion for the Ni(dppp)Cl₂ initiated polymerization of **5** ([**5**] = 0.10 M, [Ni] = 1.5 mM).

Table S6 Data used for Figure S2

% Conversion	M _n (kDa)	PDI
6.7	1.6	1.51
13.9	1.5	1.35
27.4	2.0	1.37
36.2	2.2	1.21
44.5	2.1	1.20
53.6	2.1	1.35
59.1	2.1	2.00
77.8	2.1	1.90

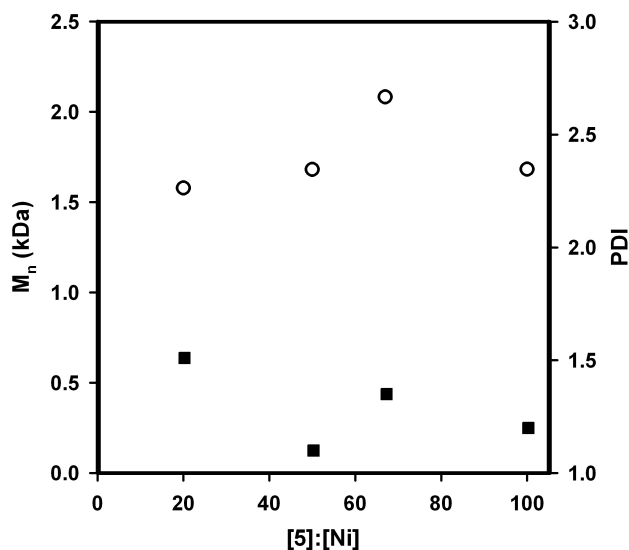
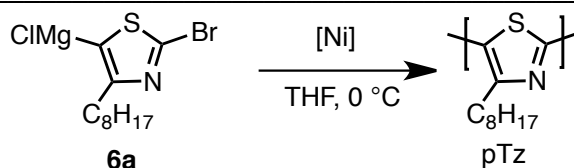


Figure S3 Plot of M_n (○) and PDI (■) versus monomer to initiator ratio for the Ni(dppp)Cl₂ initiated polymerization of **5** ([**5**] = 0.10 M).

Table S7 Data used for Figure S3

[5]:[Ni]	M _n	PDI
20	1.6	1.51
50	1.7	1.10
67	2.1	1.35
100	1.7	1.20

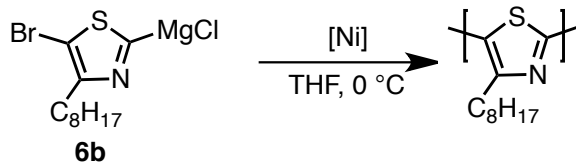


pTz: An oven-dried 50 mL Schlenk flask equipped with a stir bar and three-way adapter with septum was evacuated and cooled under vacuum. Once cool, the flask was filled with N₂ and re-evacuated: this process was repeated twice and the flask filled with N₂.

THF (3 mL) was added to the flask and cooled to 0 °C. **6a** (2.00 mL, 0.500 mmol 1.00 equiv) was added by syringe and the solution stirred for 1 min. A suspension of [Ni] (0.001 mmol, 0.01 equiv) in THF (0.1 mL) was added to the flask and the reaction maintained at 0 °C for 3 h. The reaction was quenched with 5 M HCl (10 mL), extracted with CHCl₃ (3 x 10 mL) and the solvent removed in vacuo. A sample of the resultant brown solid (~ 1mg) was then prepared for GPC analysis.

Table S8 Summary of polymerization data for pTz

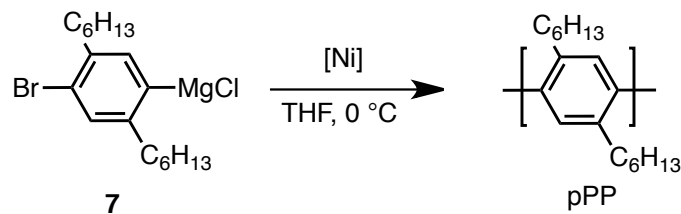
[Ni]	M _n (kDa)	PDI	% Conversion
Ni(dppp)Cl ₂	2.5	1.8	71
Ni(dppe)Cl ₂	2.8	1.6	65
Ni(depe)Cl ₂	3.2	1.9	63
Ni(dppe)(<i>o</i> -anisyl)Br	2.5	2.2	65
Ni(dppe)(Ph)Br	5.6	2.2	77



pTz: An oven-dried 50 mL Schlenk flask equipped with a stir bar and three-way adapter with septum was evacuated and cooled under vacuum. Once cool, the flask was filled with N₂ and re-evacuated: this process was repeated twice and the flask filled with N₂. THF (3 mL) was added to the flask and cooled to 0 °C. **6b** (1.6 mL, 0.46 mmol 1.00 equiv) was added by syringe and the solution stirred for 1 min. A suspension of [Ni] (0.0046 mmol, 0.01 equiv) in THF (0.1 mL) was added to the flask and the reaction maintained at 0 °C for 3 h. The reaction was quenched with 5 M HCl (10 mL), extracted with CHCl₃ (3 x 10 mL) and the solvent removed in vacuo. A sample of the resultant brown solid (~ 1mg) was then prepared for GPC analysis.

Table S9 Summary of polymerization data for pTz

Ni(dppp)Cl ₂	2.7	1.7	59
Ni(dppe)Cl ₂	2.1	1.6	63
Ni(dppe)(<i>o</i> -anisyl)Br	2.2	1.5	65



pPP: In the glovebox, **7** (1.00 mL, 0.222 mmol, 1.00 equiv) was added to a 20 mL vial with a stir bar. [Ni] (0.0125 mmol 0.025 equiv) was added with vigorous stirring and the reaction stirred for 5 h. The reaction was then removed from the glovebox and quenched with 5 M HCl (10 mL). It was then extracted with hot CHCl₃ (4 x 5 mL), and the solvent removed in vacuo. A sample (~1 mg) of the resultant white solid was then removed for GPC analysis.

Table S10 Summary of polymerization data for pPP

[Ni]	M _n (kDa)	PDI	% Conversion
Ni(dppp)Cl ₂	0.7	1.1	89
Ni(dppe)Cl ₂	0.8	1.1	85

M_n and PDI versus conversion

General procedure for obtaining plots of M_n and PDI vs. conversion:

The nickel initiator was suspended in THF within a 50 mL 2-neck round bottom flask. The IR probe was then inserted through an O-ring sealed 14/20 ground glass adapter (custom made) into the flask under positive N_2 from a three-way adapter fitted with a septum for injections and an N_2 line. The flask and monomer solutions was then cooled to 0 °C over ~ 5 min. After recording a background spectrum, **1** and **2** (see Synthetic Procedures) were added by syringe and spectra were recorded every 15 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 via syringe through the three-way adaptor and quenched with 5 M HCl (~ 1 mL). Each aliquot was then extracted with $CHCl_3$ with mild heating, dried over $MgSO_4$, filtered, then concentrated. The samples were then dissolved in THF and passed through a 0.2 μm PTFE filter for GPC analysis.

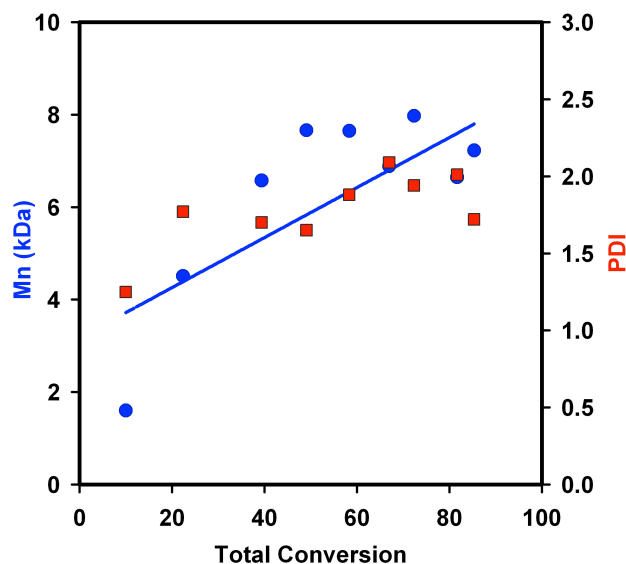


Figure S4 Plot of M_n (●) and PDI (■) versus conversion for the batch copolymerization of **1** and **2** with $[Ni] = Ni(dppp)Cl_2$

Table S11 Data for Figure S4

% Conversion	M_n (kDa)	PDI
10	1.6	1.2
22	4.5	1.8
39	6.6	1.7
49	7.7	1.7
58	7.6	1.9
67	6.9	2.1
72	8	1.9
82	6.6	2
85	7.2	1.7

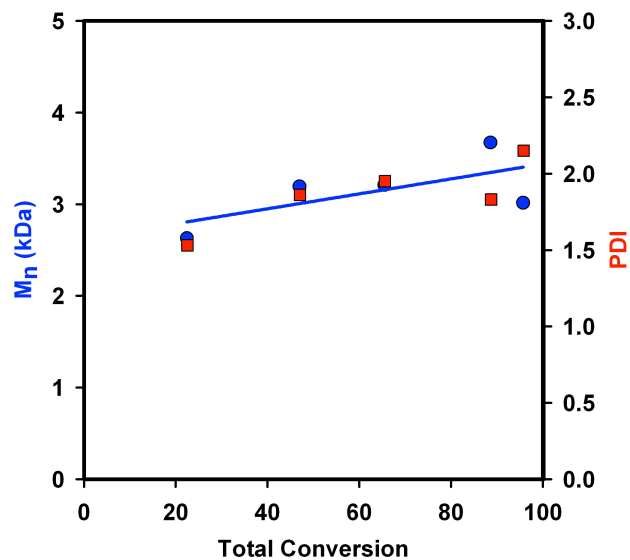


Figure S5 Plot of M_n (●) and PDI (■) versus conversion for the batch copolymerization of **1** and **2** with $[Ni] = Ni(PPh_3)_2Cl_2$

Table S12 Data for Figure S5

Conversion	M _n (kDa)	PDI
22	2.6	1.5
47	3.2	1.9
65	3.2	1.9
87	3.7	1.8
96	3	2.2

General procedure for semi-batch polymerizations:

The nickel initiator was suspended in THF within a 50 mL 2-neck round bottom flask. The IR probe was then inserted through an O-ring sealed 14/20 ground glass adapter (custom made) into the flask under positive N₂ from a three-way adapter fitted with a septum for injections and an N₂ line. The flask and monomer solutions was then cooled to 0 °C over ~ 5 min. After recording a background spectrum, a solution of **2** was taken up into a syringe. The stainless steel needle inserted through the septum and into the reaction vessel and the syringe placed into a syringe pump. **1** was added by syringe and spectra were recorded every 15 s over the entire reaction and **2** added to the reaction mixture via syringe pump at a constant rate. 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 via syringe through the three-way adapter and quenched with 5 M HCl (~1 mL). Each aliquot was then extracted with CHCl₃ with mild heating, dried over MgSO₄, filtered, then concentrated. The samples were then dissolved in CDCl₃ for ¹H NMR analysis to determine the composition of the copolymer. After NMR analysis the polymer samples were concentrated to dryness, taken up in hot THF and passed through a 0.2 μm PTFE filter for GPC analysis.

Reactivity Ratios

General Procedure for Determining Reactivity Ratios via ReactIR

Solutions of **1** and **2** were pre-mixed in varying molar ratios and the mole ratio checked by ¹H NMR. Ni(dppe)Cl₂ was suspended in THF in a 50 mL 2-neck round bottom flask with a magnetic stir bar. A three-way adapter fitted with a septum and an N₂ line was inserted into the flask and the IR probe inserted through an O-ring sealed 14/20 ground glass adapter into the other neck under positive nitrogen flow. The flask was then cooled to 0 °C and allowed to equilibrate. After recording a background spectrum the pre-mixed monomer solution, which had been cooled to 0 °C, was added by syringe and spectra were recorded every 15s over the first 30-40% 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. From these the mole ratio of monomers was calculated and the data from 10-30% conversion fit to the integrated copolymerization (Eq S1) where 1-[M]/[M]₀ is conversion, f₁ is the mole fraction of monomer **1** at that conversion and (f₁)₀ is the initial mole fraction of monomer **1** using least-squares regression in SigmaPlot 10.

$$1 - \frac{[M]}{[M]_0} = 1 - \left(\frac{f_1}{(f_1)_0} \right)^{\frac{r_2}{1-r_2}} \left(\frac{1-f_1}{1-(f_1)_0} \right)^{\frac{r_1}{1-r_1}} \left(\frac{(f_1)_0 - \frac{1-r_2}{2-r_1-r_2}}{f_1 - \frac{1-r_2}{2-r_1-r_2}} \right)^{\frac{1-r_1 r_2}{(1-r_1)(1-r_2)}}$$

Equation S1 The integrated copolymerization equation

Procedure for inputting the copolymerization equation in SigmaPlot 10

Input your data for 1-[M]/[M]₀, f₁ and (f₁)₀ into a Sigmaplot data file. Go to the Statistics toolbar, choose Dynamic Fit Wizard, Equation Category: User Defined => New and input the following:

Equation: f = 1 - ((x/z)^(b/(1-b))) * (((1-x)/(1-z))^(a/(1-a))) * (((z - ((1-b)/(2-a-b))))^(1-a*b)) / ((1-a)*(1-b)))

fit f to y

Constraints a > 0, b > 0

Variables x = col(1)

z = col(2)

y = col(3)

Initial Parameters a=1, b=1

Press Next, then, then Next again.

From this equation

Table S13 Reactivity ratio data used to find reactivity ratios.

f ₂	(f ₂) ₀	1-[M]/[M] ₀
0.42037157	0.528	0.191238139
0.416410628	0.528	0.201411287
0.409698551	0.528	0.218855041
0.418832298	0.528	0.203158363
0.41392164	0.528	0.198427772
0.394146747	0.528	0.22554736
0.405739341	0.528	0.216321279

0.39476968	0.528	0.238282701
0.387277313	0.528	0.235215505
0.387174922	0.528	0.241299679
0.408589333	0.528	0.220837476
0.384039254	0.528	0.246040693
0.397259114	0.528	0.231628704
0.386692123	0.528	0.256354477
0.389067885	0.528	0.224849081
0.389731044	0.528	0.242718542
0.382494539	0.528	0.250745558
0.496175606	0.561	0.130035083
0.486812762	0.561	0.145834662
0.502057508	0.561	0.134532376
0.481631676	0.561	0.164983495
0.479347789	0.561	0.169955686
0.493259295	0.561	0.162862561
0.463761866	0.561	0.201788327
0.446080865	0.561	0.234054629
0.480792127	0.561	0.178911139
0.472794445	0.561	0.196815229
0.470936269	0.561	0.197981596
0.454437637	0.561	0.220306389
0.451754795	0.561	0.241465839
0.464391716	0.561	0.213428102
0.466348189	0.561	0.20585092
0.456640352	0.561	0.218724428
0.334702044	0.49	0.262240311
0.325768652	0.49	0.27999107
0.314731331	0.49	0.302155191
0.332588828	0.49	0.307151669
0.315750316	0.49	0.323379317
0.322384498	0.49	0.341863114
0.538807682	0.606	0.168542741
0.531629038	0.606	0.178163681
0.52948323	0.606	0.181316825
0.524879277	0.606	0.180213245
0.523552351	0.606	0.190459784
0.508844372	0.606	0.215438309
0.516141393	0.606	0.20167085
0.515508728	0.606	0.203247031
0.528738062	0.606	0.188154672
0.514246426	0.606	0.212707626
0.516633911	0.606	0.205403452
0.511361622	0.606	0.204841128
0.510763682	0.606	0.218786184
0.506216967	0.606	0.223382873
0.50677773	0.606	0.2244834
0.497637071	0.606	0.237485169
0.503471777	0.606	0.239276421
0.498869679	0.606	0.239980356
0.497869874	0.606	0.231925548
0.497373049	0.606	0.255510954
0.497346974	0.606	0.241771835

0.540101418	0.606	0.164735045
0.532370014	0.606	0.169910278
0.528050415	0.606	0.181407819
0.531283813	0.606	0.171279989
0.530165462	0.606	0.180422024
0.513762141	0.606	0.200790612
0.506180805	0.606	0.216222034
0.519261964	0.606	0.189957592
0.516656004	0.606	0.199226861
0.52260176	0.606	0.191615751
0.502336093	0.606	0.225402247
0.489996097	0.606	0.241504781
0.48716439	0.606	0.247078106
0.510110265	0.606	0.211988771
0.512551172	0.606	0.21767967
0.506848917	0.606	0.216918623
0.505714591	0.606	0.226050558
0.505380843	0.606	0.23099221
0.487940442	0.606	0.255815234
0.48493714	0.606	0.252155628
0.496889407	0.606	0.239943384
0.50019109	0.606	0.230039808
0.502252941	0.606	0.231567374
0.481144376	0.606	0.258416642
0.47748149	0.606	0.263713582
0.434260874	0.497	0.151998667
0.426443218	0.497	0.151095916
0.410985842	0.497	0.181428834
0.415721666	0.497	0.202316501
0.39352473	0.497	0.204371072
0.385274249	0.497	0.203805238
0.38133104	0.497	0.212716197
0.395342471	0.497	0.227629649
0.384010306	0.497	0.241473345
0.379217346	0.497	0.235049777
0.357774876	0.497	0.247003103
0.369402544	0.497	0.258650487
0.348806635	0.497	0.269681229
0.356397318	0.497	0.256611739
0.342582332	0.497	0.271059801
0.349858138	0.497	0.272774226
0.351635712	0.497	0.258236791
0.346289294	0.497	0.262100731
0.354858873	0.497	0.304186514
0.414983677	0.497	0.157452816
0.401019661	0.497	0.183048034
0.376588238	0.497	0.220393127
0.378252451	0.497	0.228600787
0.359710926	0.497	0.244263273
0.364809402	0.497	0.242395189
0.353562164	0.497	0.246851647
0.335170036	0.497	0.268697529
0.347655967	0.497	0.261515242

0.354583332	0.497	0.261696331
0.350170307	0.497	0.267528143
0.332882207	0.497	0.287806812
0.314418505	0.497	0.298620426
0.320362227	0.497	0.302025771
0.328008283	0.497	0.287883683
0.320482102	0.497	0.307132639
0.318060636	0.497	0.29559112
0.309597529	0.497	0.310994505
0.511028824	0.569	0.110754281
0.447195775	0.569	0.186581662
0.431956234	0.569	0.239133203
0.413008704	0.569	0.245380264
0.434062096	0.569	0.252570352
0.387181821	0.569	0.301252857
0.404856395	0.569	0.298933581
0.373831587	0.569	0.326637866
0.423127357	0.569	0.282307437
0.363911009	0.569	0.334235388
0.364399	0.569	0.342353144
0.493218613	0.569	0.123710374
0.466269881	0.569	0.14212664
0.464790285	0.569	0.174042333
0.423236974	0.569	0.229935632
0.441883494	0.569	0.235607651
0.422634445	0.569	0.247309113
0.383872295	0.569	0.284537811
0.401829064	0.569	0.275388795
0.368868421	0.569	0.330942912
0.359005283	0.569	0.313284282
0.418213129	0.569	0.297621655
0.421180564	0.569	0.263951611
0.385989668	0.569	0.30685227
0.257243591	0.355	0.164117285
0.271672614	0.355	0.158358291
0.282613582	0.355	0.172881688
0.236232887	0.355	0.221322439
0.231230844	0.355	0.235281573
0.216996773	0.355	0.254371656
0.282760177	0.355	0.111001993
0.282817703	0.355	0.156265207
0.280631485	0.355	0.154009469
0.262313043	0.355	0.182792292
0.27788299	0.355	0.165522158
0.251608861	0.355	0.217534747
0.275315913	0.355	0.213861717
0.235938551	0.355	0.27339855
0.244225126	0.355	0.257895531
0.258132353	0.355	0.276432267
0.239820029	0.355	0.267740532
0.292095173	0.33	0.22093368
0.259331142	0.33	0.292201744
0.481144376	0.606	0.258416642

0.47748149	0.606	0.263713582
0.434260874	0.497	0.151998667
0.426443218	0.497	0.151095916
0.410985842	0.497	0.181428834
0.415721666	0.497	0.202316501
0.39352473	0.497	0.204371072
0.385274249	0.497	0.203805238
0.38133104	0.497	0.212716197
0.395342471	0.497	0.227629649
0.384010306	0.497	0.241473345
0.379217346	0.497	0.235049777
0.357774876	0.497	0.247003103
0.369402544	0.497	0.258650487
0.348806635	0.497	0.269681229
0.356397318	0.497	0.256611739
0.342582332	0.497	0.271059801
0.238170884	0.33	0.331137388
0.243500549	0.33	0.337353234
0.20581763	0.33	0.392739739
0.207718122	0.33	0.388241049
0.228079433	0.33	0.367008413
0.178121431	0.33	0.42544181
0.184723686	0.33	0.435640565
0.182596769	0.33	0.446482284
0.178242336	0.33	0.458029581
0.183997267	0.33	0.445090164
0.180094965	0.33	0.444829072
0.177725753	0.33	0.456137843
0.17245693	0.33	0.457809188
0.176557431	0.33	0.469211465
0.142853088	0.33	0.493824242
0.150265972	0.33	0.488874761
0.176460723	0.33	0.464493741
0.139286792	0.33	0.497299957
0.132282062	0.33	0.497989773
0.169631825	0.33	0.465287172
0.133364284	0.33	0.486914359
0.153494053	0.33	0.498361508
0.13722863	0.33	0.499456195
0.182529447	0.33	0.490272439
0.22416903	0.33	0.146472502
0.216553461	0.33	0.155479822
0.21333616	0.33	0.166285403
0.197730465	0.33	0.192259825
0.211252206	0.33	0.161001304
0.217325658	0.33	0.174405292
0.209745977	0.33	0.198523597
0.20004659	0.33	0.194244286
0.192748069	0.33	0.204897752
0.207942196	0.33	0.20649243
0.193310545	0.33	0.210674184
0.223766234	0.29	0.124358364
0.211315264	0.29	0.151529844

0.222278677	0.29	0.138926331
0.218048543	0.29	0.150002445
0.210094944	0.29	0.170319742
0.211523513	0.29	0.175283297
0.208440171	0.29	0.186633838
0.221460182	0.29	0.164878125
0.198291539	0.29	0.201072263
0.186511085	0.29	0.223175175
0.215033837	0.29	0.188677318
0.191929252	0.29	0.203784245
0.212618909	0.29	0.201276447
0.199992511	0.29	0.214713276
0.198292963	0.29	0.212883774
0.228859285	0.29	0.175852505
0.208886891	0.29	0.208451588
0.186878821	0.29	0.232245691
0.209448021	0.29	0.202967471
0.163704949	0.29	0.262282546
0.198343652	0.29	0.22005524
0.214458334	0.254	0.063917594
0.200358637	0.254	0.086105931
0.19712507	0.254	0.096706763
0.19979826	0.254	0.091933346
0.209686851	0.254	0.082199309
0.198931623	0.254	0.095867249
0.199333185	0.254	0.09618994
0.188928816	0.254	0.113288545
0.218238561	0.254	0.076686748
0.205129798	0.254	0.095194894
0.193997483	0.254	0.116860809
0.191111428	0.254	0.115126154
0.204060538	0.254	0.099300417
0.201464444	0.254	0.104141364
0.198342168	0.254	0.110766399
0.19695212	0.254	0.110738597
0.198637213	0.254	0.113489996
0.206091243	0.254	0.10181415
0.20528438	0.254	0.111852972
0.203499147	0.254	0.107213095
0.177350742	0.254	0.129224218
0.159519925	0.219	0.104908375
0.147983614	0.219	0.129432738
0.160064999	0.219	0.114052858
0.15599818	0.219	0.128868727
0.168804846	0.219	0.119643952
0.163208761	0.219	0.127370654
0.167715562	0.219	0.105439083
0.162245387	0.219	0.113233163
0.154627238	0.219	0.134485957
0.163171766	0.219	0.130188534
0.170607246	0.219	0.123996199
0.170564975	0.219	0.118981626
0.149521153	0.219	0.140919768

0.175874108	0.219	0.111201152
0.154488307	0.219	0.13611302
0.161396904	0.219	0.129293409
0.173445626	0.219	0.11769736
0.172507697	0.219	0.128500449
0.159107711	0.219	0.1418982
0.166942837	0.219	0.131612651
0.158486519	0.219	0.141516932
0.199479097	0.219	0.157985201
0.186531858	0.219	0.182424398
0.182791693	0.219	0.197048118
0.201552565	0.219	0.186482754
0.174643965	0.219	0.213162948
0.187293628	0.219	0.206275926
0.180308731	0.219	0.211296956
0.172867138	0.219	0.215571785
0.174007464	0.219	0.217354088
0.164072111	0.219	0.227077884
0.176719662	0.219	0.214885416
0.162318901	0.219	0.230171061
0.158305489	0.219	0.237800278
0.158935917	0.219	0.233197235
0.174488952	0.219	0.232764605
0.15615101	0.219	0.250331748
0.171687929	0.219	0.234802438
0.153455665	0.219	0.25178802
0.169090206	0.219	0.232811043
0.170544149	0.219	0.239468918
0.158891232	0.219	0.241046715
0.126512637	0.13	0.171994694
0.116627016	0.13	0.253979389
0.113745523	0.13	0.2810862
0.11339161	0.13	0.28058626
0.110557126	0.13	0.316653309
0.108099415	0.13	0.339323962
0.090794047	0.13	0.431981642
0.099089651	0.13	0.380837803
0.092303234	0.13	0.420423248
0.099140867	0.13	0.406118802
0.109713682	0.13	0.33858713
0.111527232	0.13	0.347117646
0.096406941	0.13	0.425813743
0.093252689	0.13	0.4506784
0.107345433	0.13	0.374733487
0.092505321	0.13	0.455733792
0.094995396	0.13	0.437390908
0.103009845	0.13	0.403284766
0.110091582	0.13	0.384017933
0.105979659	0.13	0.407788391
0.098582632	0.13	0.443282432
0.066713931	0.0909	0.094271847
0.067116868	0.0909	0.098887456
0.06548761	0.0909	0.093994802

0.059970295	0.0909	0.101379633
0.063866945	0.0909	0.10892681
0.055511815	0.0909	0.103392993
0.055255144	0.0909	0.118002806
0.058961325	0.0909	0.128905431
0.053451194	0.0909	0.127564722
0.056003331	0.0909	0.126876164
0.061215367	0.0909	0.118944797
0.057050775	0.0909	0.147478701
0.05736629	0.0909	0.145727763
0.052196662	0.0909	0.1439312
0.063127212	0.0909	0.142022881
0.061846817	0.0909	0.151438663
0.051239591	0.0909	0.165273951
0.061352479	0.0909	0.16873254
0.042364873	0.0909	0.184979841
0.049372399	0.0909	0.179720449
0.046365505	0.0909	0.208918201
0.102698215	0.13	0.051222358
0.110015531	0.13	0.045723209
0.099823243	0.13	0.062843276
0.09435083	0.13	0.071014643
0.097187671	0.13	0.071238294
0.090663789	0.13	0.079583742
0.100996233	0.13	0.078460339
0.091750255	0.13	0.08833706
0.091419478	0.13	0.092555551
0.092662743	0.13	0.088624671
0.092554161	0.13	0.08954357
0.098217148	0.13	0.086517175
0.102364668	0.13	0.092566779
0.087688327	0.13	0.109401861
0.084110277	0.13	0.112450406
0.081921842	0.13	0.117010441
0.086264094	0.13	0.117222608
0.088395252	0.13	0.106364891
0.088059866	0.13	0.113433576
0.091143659	0.13	0.108697313
0.088615223	0.13	0.130413353
0.088637315	0.13	0.127325516
0.088595807	0.13	0.120395237
0.079953495	0.13	0.12882758
0.089270843	0.13	0.118092519
0.087326201	0.13	0.119217624
0.085481477	0.13	0.134883677
0.083869247	0.13	0.130400224
0.097115593	0.13	0.118320213
0.084405633	0.13	0.137585272
0.082428968	0.13	0.15043454
0.094051929	0.13	0.13391954
0.089573018	0.13	0.138064742
0.088524321	0.13	0.139046824
0.077471489	0.13	0.151349477

0.088205071	0.13	0.143435877
0.080682627	0.13	0.150716595
0.086424414	0.13	0.145185375
0.090280932	0.13	0.142624789
0.085940296	0.13	0.158716093
0.08488379	0.14	0.112905547
0.081872426	0.14	0.114795459
0.109749928	0.14	0.086047686
0.093617007	0.14	0.1021144
0.099318873	0.14	0.101616678
0.07118746	0.14	0.124995963
0.089285938	0.14	0.117639471
0.08548475	0.14	0.131619068
0.070961745	0.14	0.139152869
0.076570553	0.14	0.141605623
0.08002357	0.14	0.128007869
0.08505815	0.14	0.141252117
0.073641353	0.14	0.147563858
0.088875346	0.14	0.137252823
0.087007062	0.14	0.145772636
0.089617047	0.14	0.144820529
0.076439323	0.14	0.15370306
0.08694347	0.14	0.145882872
0.073814384	0.14	0.167294502
0.077822363	0.14	0.170319154
0.07189153	0.14	0.179707455
0.08434243	0.14	0.157430596
0.065807314	0.14	0.165036303
0.063594538	0.14	0.19168271
0.080822966	0.14	0.172574602
0.076734638	0.14	0.171916094
0.071020692	0.14	0.177073084
0.082000642	0.14	0.175881244
0.075484849	0.14	0.184613279
0.07730881	0.14	0.186640921
0.054760308	0.14	0.204747104
0.110749699	0.14	0.065364953
0.118018987	0.14	0.060869834
0.108958192	0.14	0.06657918
0.105577709	0.14	0.083415973
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0.099764638	0.14	0.088613222
0.096364846	0.14	0.101545505
0.110088329	0.14	0.080024005
0.09078187	0.14	0.099479867
0.100735985	0.14	0.102164134
0.10534681	0.14	0.08695314
0.090237385	0.14	0.118536817
0.094698795	0.14	0.10914595
0.099235772	0.14	0.111383896
0.101249299	0.14	0.110061349
0.095370416	0.14	0.110095678

0.097104286	0.14	0.115288092
0.091510131	0.14	0.126935052
0.082142102	0.14	0.142572703
0.094444985	0.14	0.122436133
0.20330552	0.27	0.125491513
0.181677263	0.27	0.142462974
0.191597223	0.27	0.124725302
0.179400789	0.27	0.136734838
0.174258766	0.27	0.156974816
0.182497987	0.27	0.149911971
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0.151777783	0.27	0.191532773
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0.158629641	0.27	0.195441828
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0.162099921	0.27	0.19153418
0.131819422	0.27	0.229062846
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0.17596983	0.27	0.171546101
0.17654771	0.27	0.161942405
0.190647592	0.27	0.155951954
0.17457039	0.27	0.166251222
0.183081721	0.27	0.17049088
0.147429669	0.27	0.195202644

Calibration Curves

General Procedure for Creating Calibration Curves for in-situ IR spectroscopy

An oven-dried 50 mL 2-neck round-bottom flask was equipped with a magnetic stir bar and the IR probe inserted through an O-ring sealed 14/20 ground glass adapter inserted into the neck. Into the other neck was inserted a three-way adapter fitted with a septum and an N₂ line. The hot flask was cooled under vacuum and then refilled with N₂. After two more cycles of evacuation and refilling the flask was charged with THF and cooled to 0 °C in an ice/water bath. After 5 minutes a background spectrum was recorded, then a solution of **1** or **2** was added and the solution equilibrated for several minutes after which a spectrum was taken.

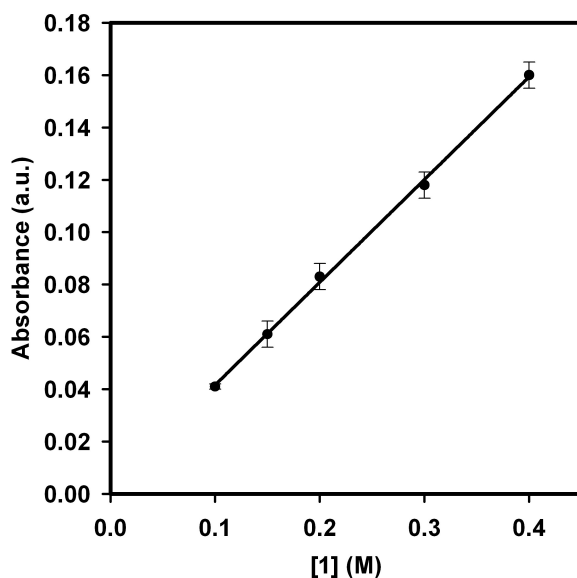


Figure S6 Plot of absorbance versus [1] fitted to $y = mx + b$ where $m = 0.396 \pm 0.002$ and $b = 0.001 \pm 0.002$.

Table S14. Data for the plot in **Figure S6**

[1] (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	$11.8 \pm 0.5 \times 10^{-2}$
0.4	$16 \pm 1 \times 10^{-2}$

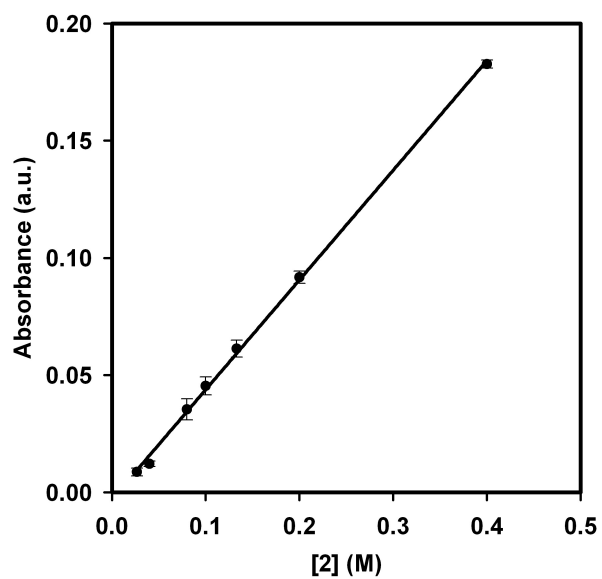
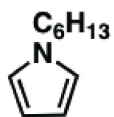


Figure S7 Plot of absorbance versus [2] fitted to $y = mx + b$ where $m = 0.468 \pm 0.007$ and $b = -0.003 \pm 0.001$.

Table S15 Data for plot in **Figure S7**

[2] (M)	Absorbance (au)
0.4	$18 \pm 0.2 \times 10^{-2}$
0.2	$9.2 \pm 0.3 \times 10^{-2}$
0.13	$6.1 \pm 0.3 \times 10^{-2}$
0.1	$4.5 \pm 0.4 \times 10^{-2}$

NMR Spectra



S1

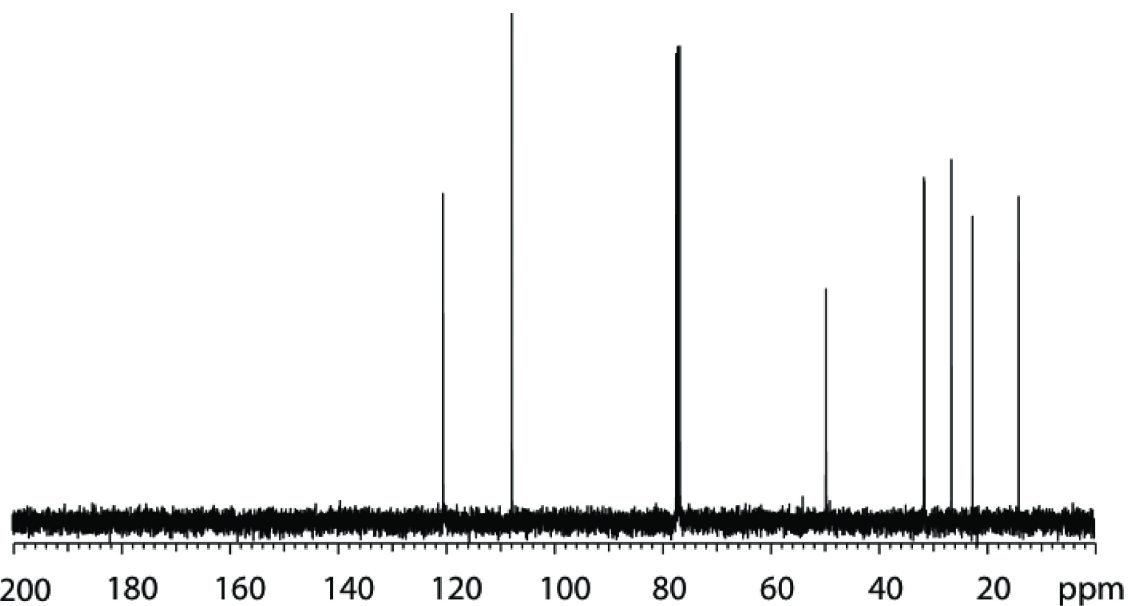
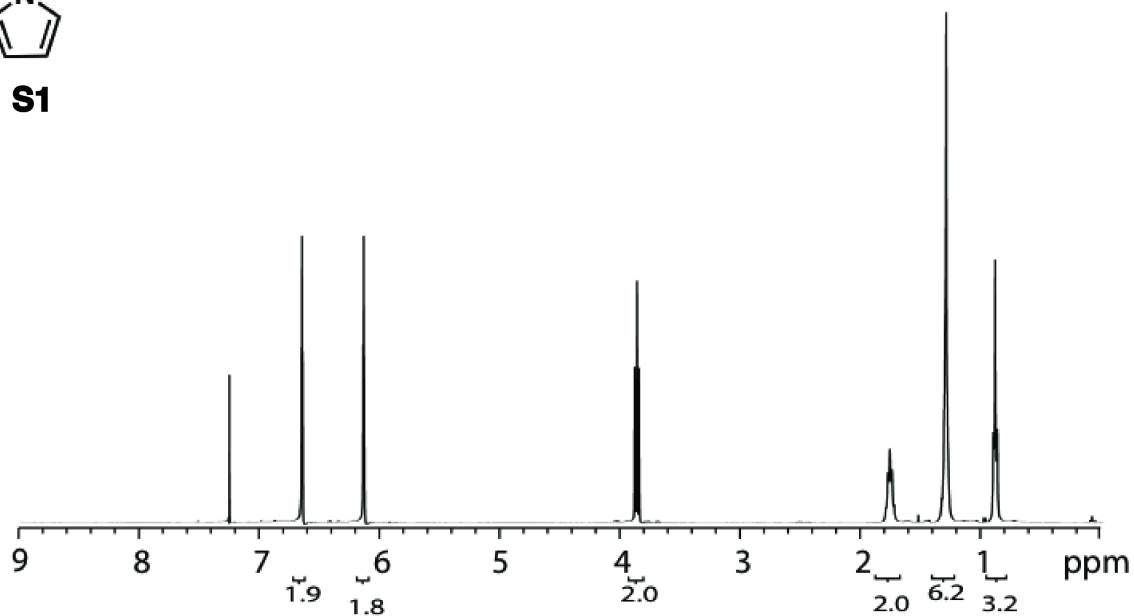


Figure S7 1H and ^{13}C NMR spectra for **S1**

1H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 2H), 6.16 (m, 2H), 3.88 (t, $J = 7.4$ Hz, 2H), 1.84-1.73 (m, 2H), 1.38-1.25 (m, 6H), 0.95-0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.43, 107.71, 49.62, 31.53, 31.48, 26.43, 22.51, 12.99.

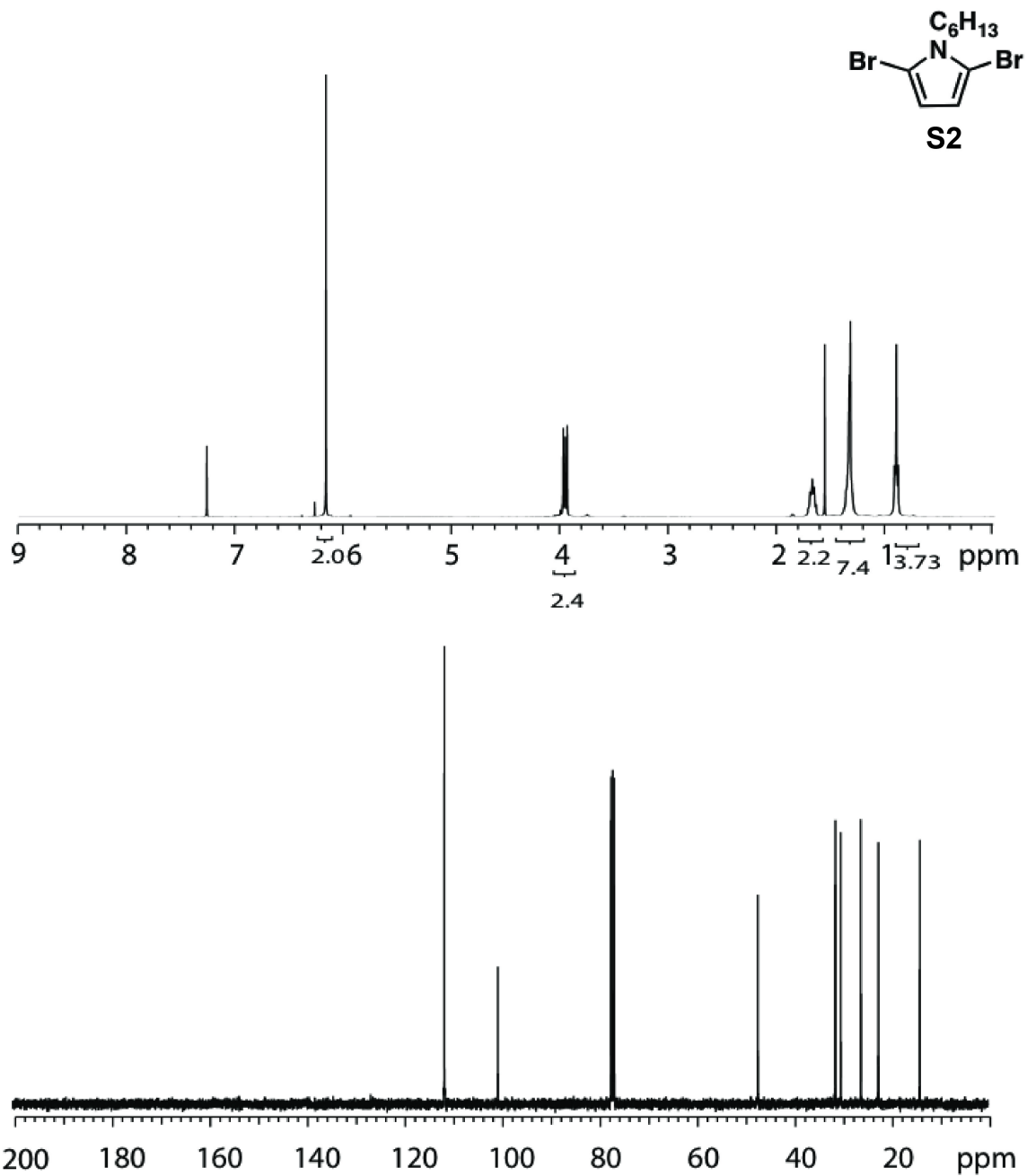


Figure S8 ¹H and ¹³C NMR spectra for **S2**

¹H NMR (400 MHz, CDCl₃) δ 6.17 (m, 2H), 3.96 (m, 2H), 1.74-1.62 (m, 2H), 1.41-1.27 (m, 6H), 0.95-0.85 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 111.55, 100.56, 47.25, 31.33, 30.23, 26.12, 22.51, 13.98.

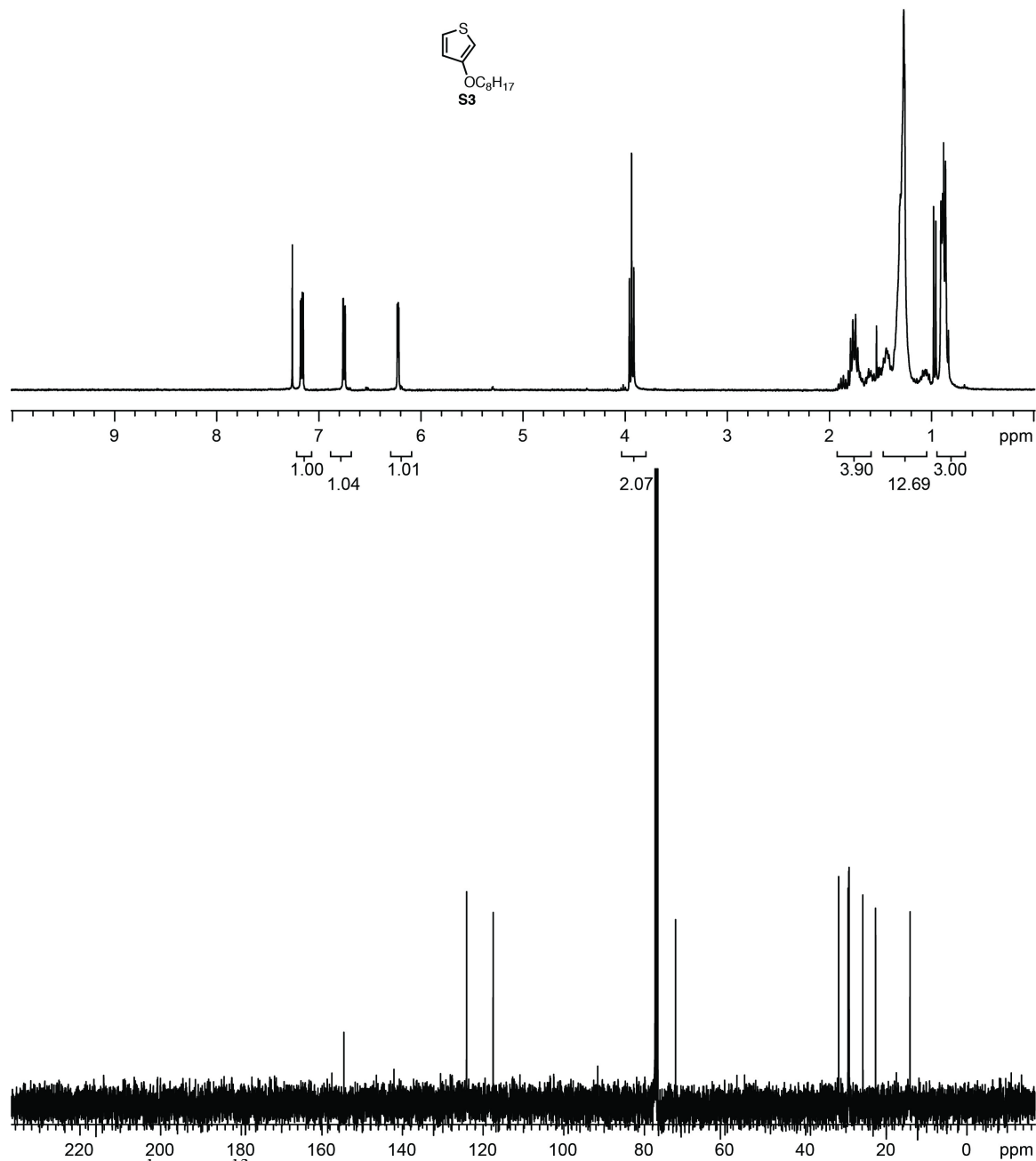


Figure S10 ¹H and ¹³C NMR spectra for S3

¹H NMR (400 MHz, CDCl₃) δ 7.169 (dd, *J* = 2.8, 8 Hz, 1 H) 6.759 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.227 (dd, *J* = 2.4, 1.6 Hz 1H), 3.937 (t, *J* = 8.8 Hz, 2H), 1.760 (m, 2H) 1.262 (br, 10H), 0.908 (t, *J* = 9.2 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 154.531, 124.092, 117.501, 72.246, 31.773, 29.452, 29.274, 29.192, 25.790, 22.622, 14.082.

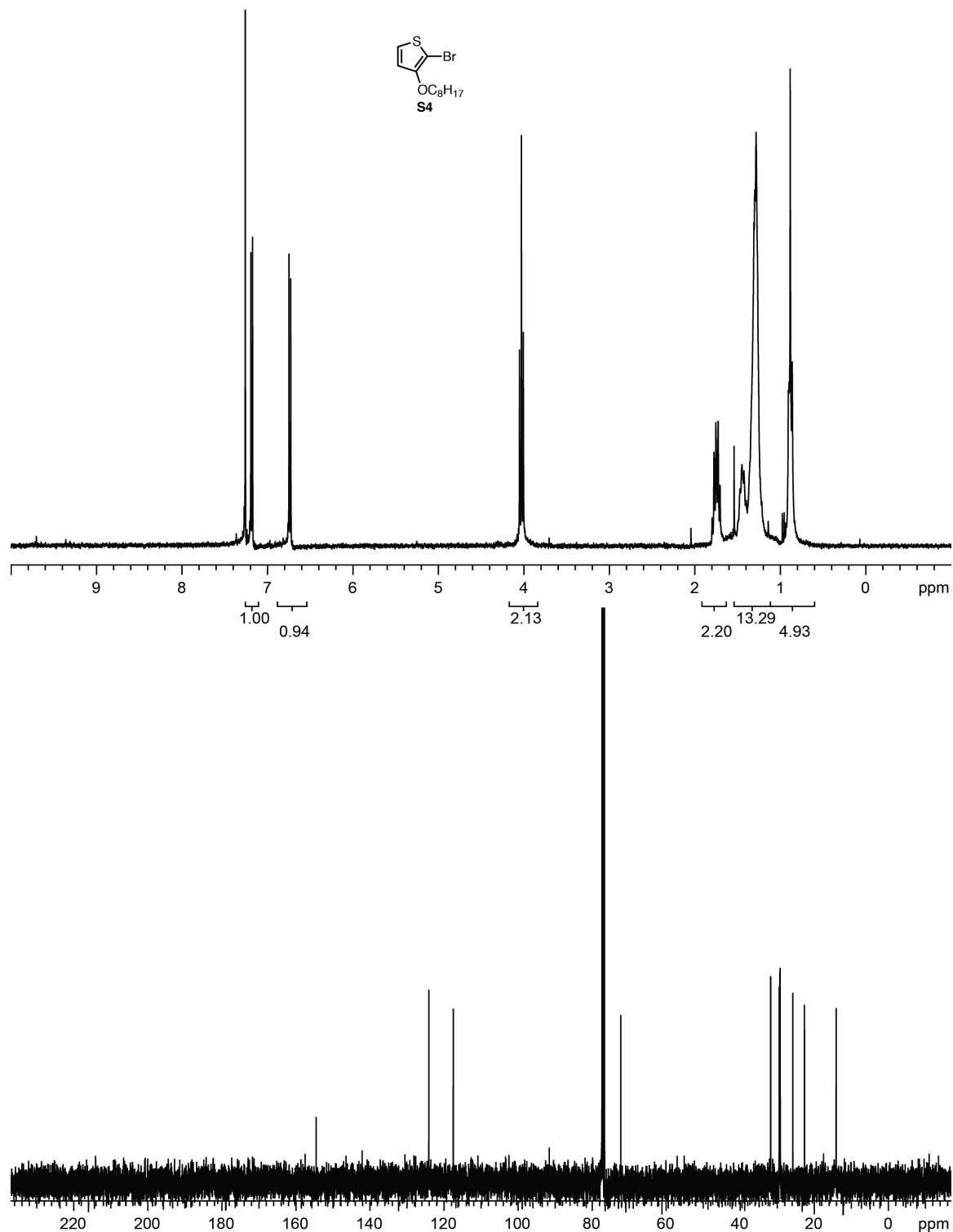
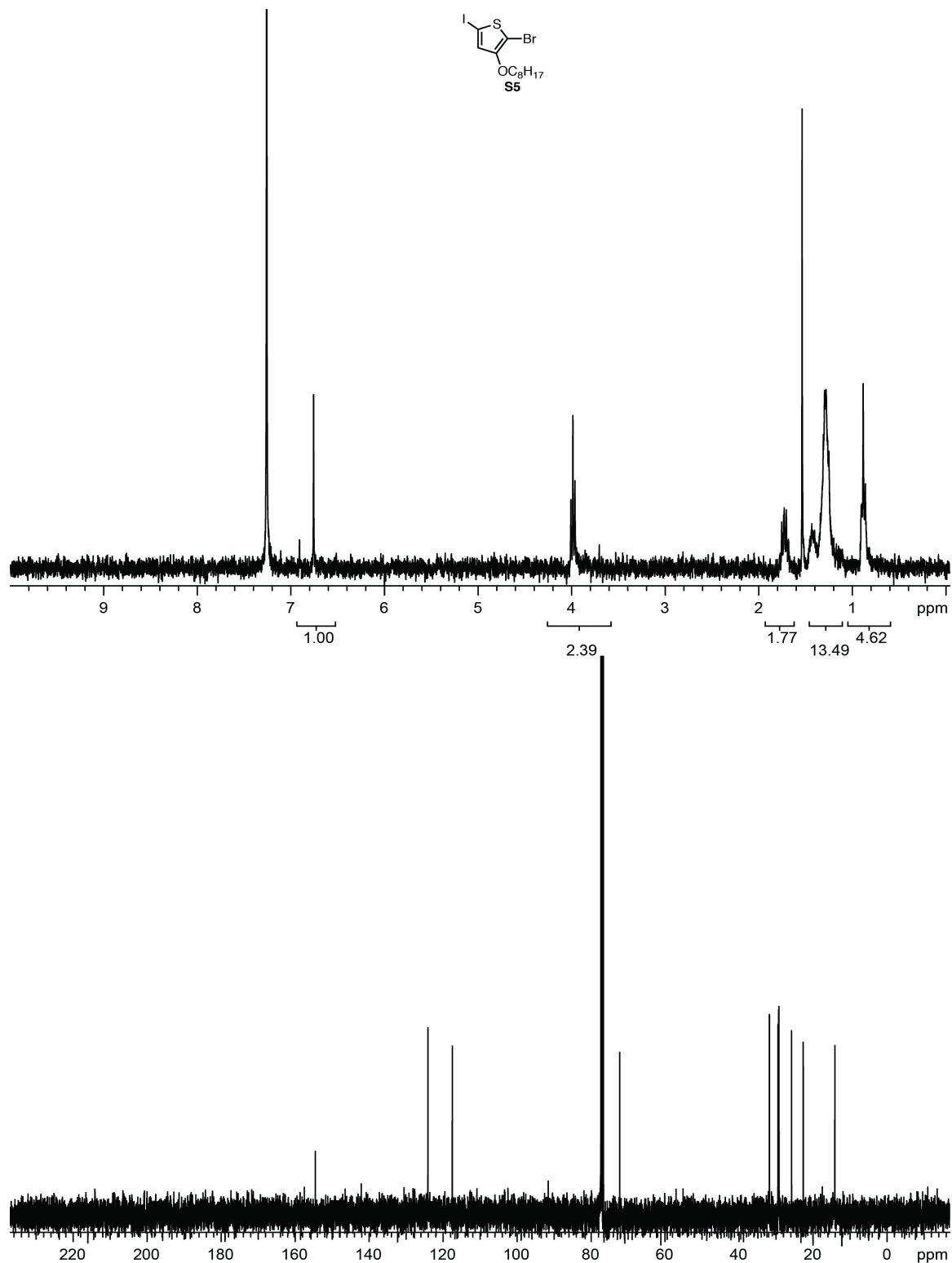


Figure S11 ¹H and ¹³C NMR spectra for S4

¹H NMR (300 MHz, CDCl₃) δ 7.174 (d, *J* = 6 Hz, 1H), 6.747 (d, *J* = 6 Hz, 1H), 4.028 (t, *J* = 6.6 Hz, 2 H), 1.753 (m, 2 H), 1.298 (br, 14 H), 0.884 (t, *J* = 7.2 Hz) ¹³C NMR (100 MHz, CDCl₃) δ 154.531, 124.092, 117.501, 72.246, 31.773, 29.452, 29.274, 29.192, 25.790, 22.622, 14.082.



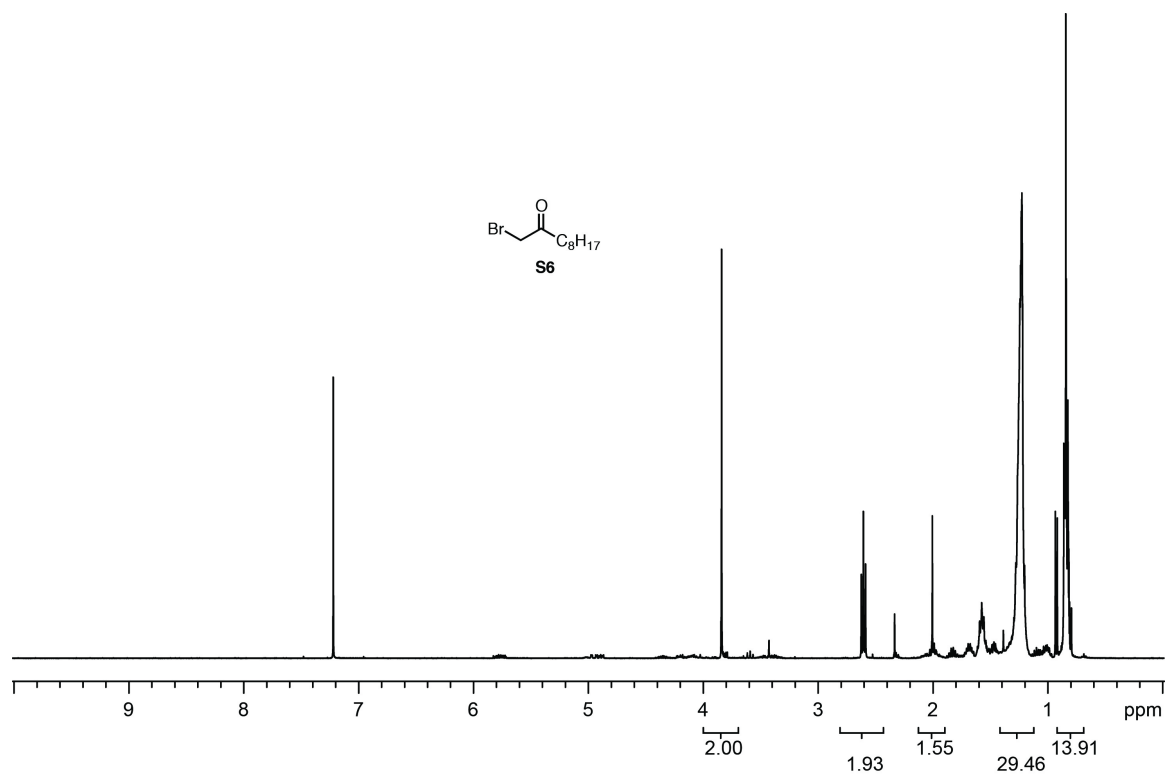


Figure S13 $^1\text{H NMR}$ spectrum for **S6**

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.840 (s, 2H), 2.605 (t, $J = 7.2$ Hz, 2H), 1.219 (br, 12H), 0.826 (t, $J = 4$ Hz, 3H).

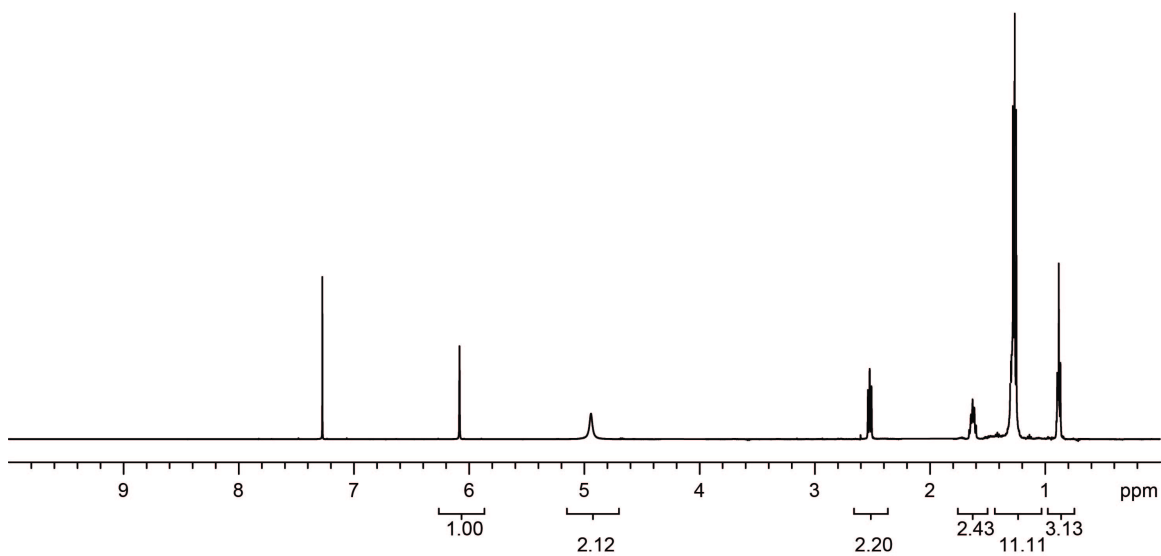
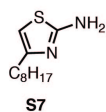


Figure S14 ¹H NMR spectrum for **S7**

¹H NMR (400 MHz, CDCl₃) 6.083 (s, 1H), 4.900 (br, 2H), 2.539 (t, *J* = 6.4 Hz, 2H), 1.630 (m, 2H), 1.250 (br, 10H), 0.889 (t, *J* = 2.8 Hz, 3H)

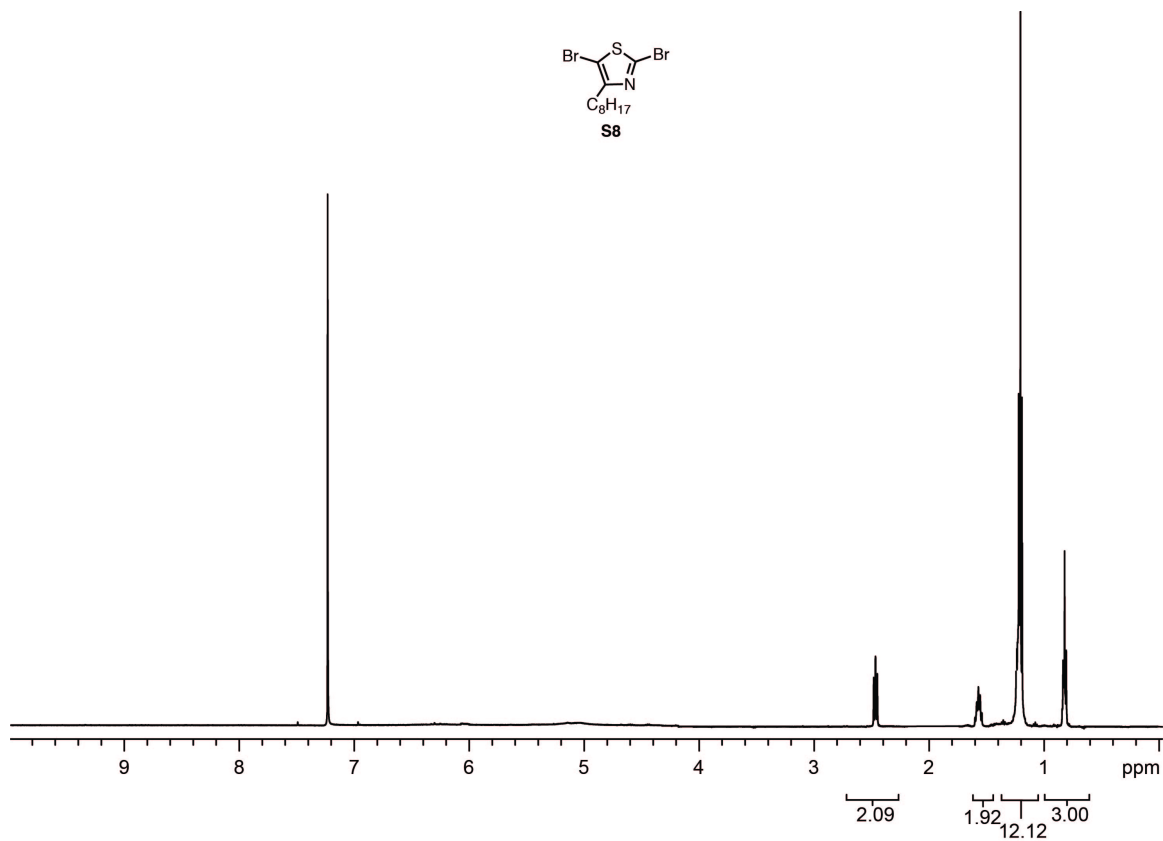
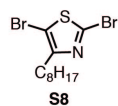


Figure S15 ^1H NMR spectrum for **S8**

^1H NMR (400 MHz, CDCl_3) 2.539 (t, $J = 6.4$ Hz, 2H), 1.630 (m, 2H), 1.250 (br, 10H), 0.889 (t, $J = 2.8$ Hz, 3H)

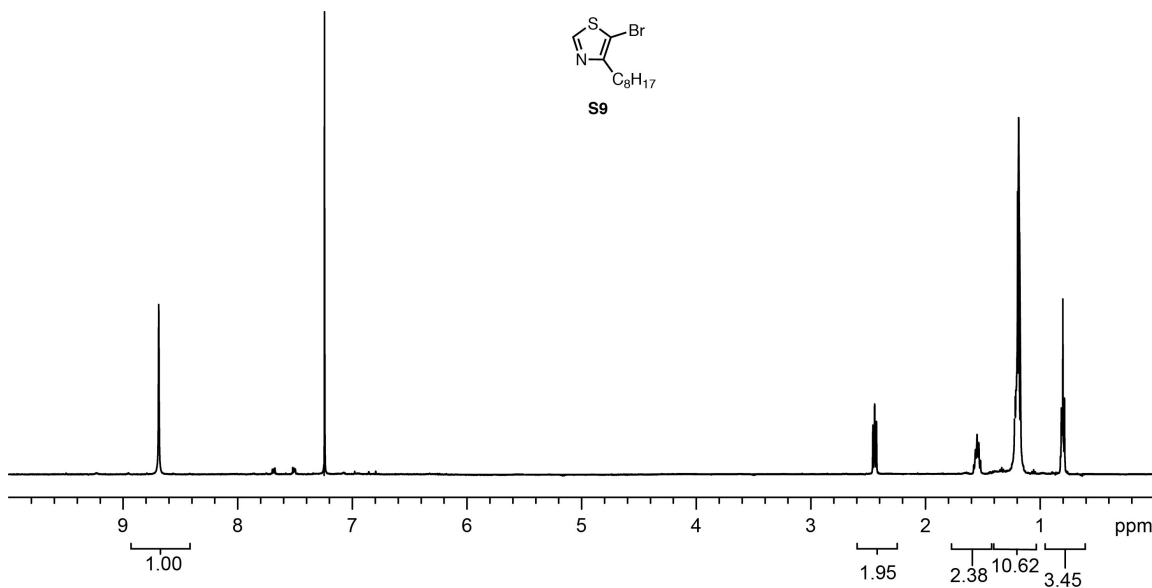


Figure S16 ^1H NMR spectrum for **S9**

^1H NMR (400 MHz, CDCl_3) 8.689 (s, 1H) 2.549 (t, $J = 7.6$ Hz, 2H), 1.681 (br, 2H), 1.341 (br, 10H), 0.856 (t, $J = 2.8$ Hz, 3H)

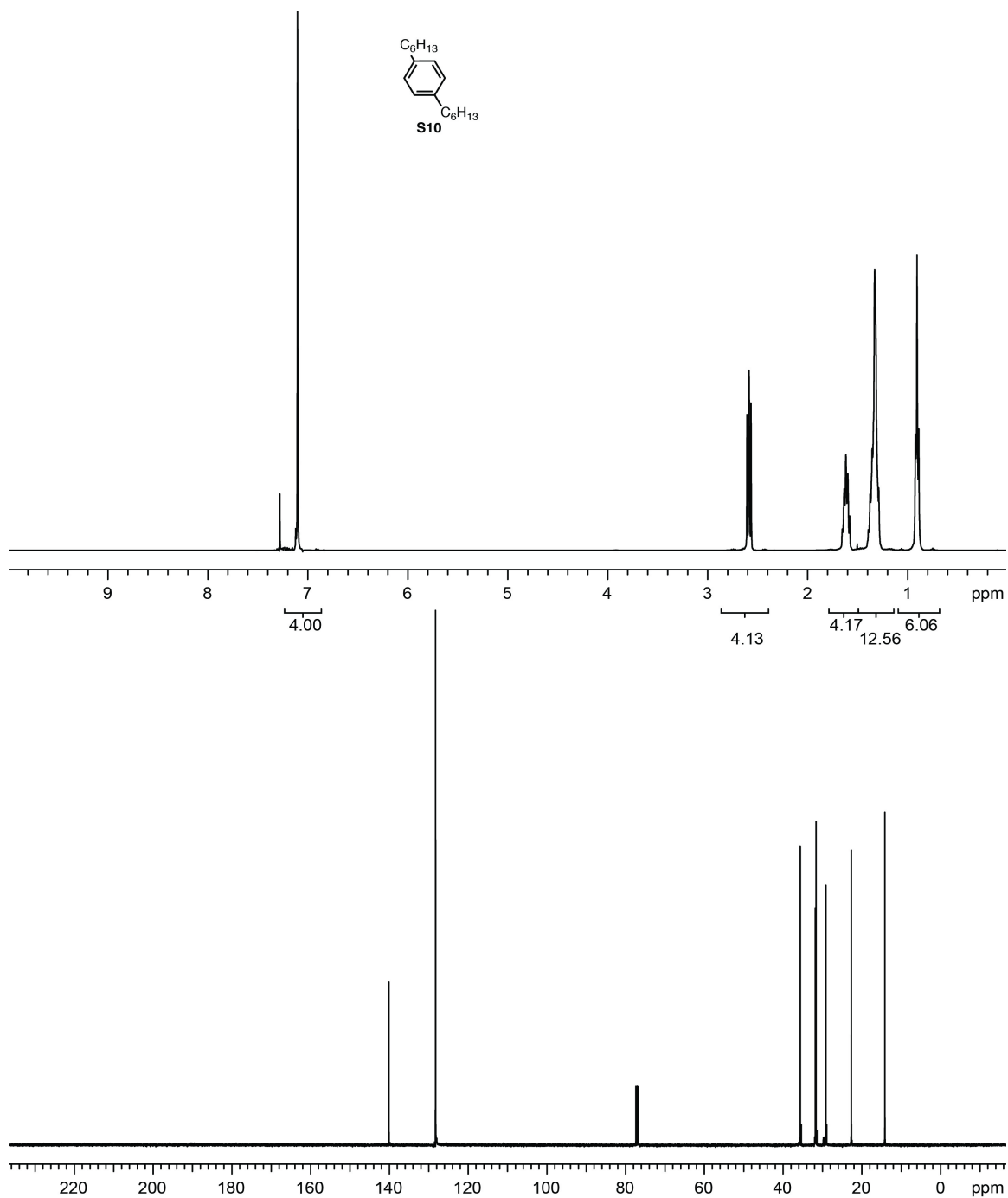


Figure S17 ¹H and ¹³C NMR spectra for **S10**

¹H NMR (400 MHz, CDCl₃) δ 7.084 (s, 4H), 2.566 (t, *J* = 7.6 Hz, 4H), 1.597 (m, 4H), 1.308 (br, 12 H), 0.885 (t, *J* = 7.2 Hz) ¹³C NMR (100 MHz, CDCl₃) δ 140.062, 128.219, 35.591, 31.773, 31.587, 29.090, 22.636, 14.102.

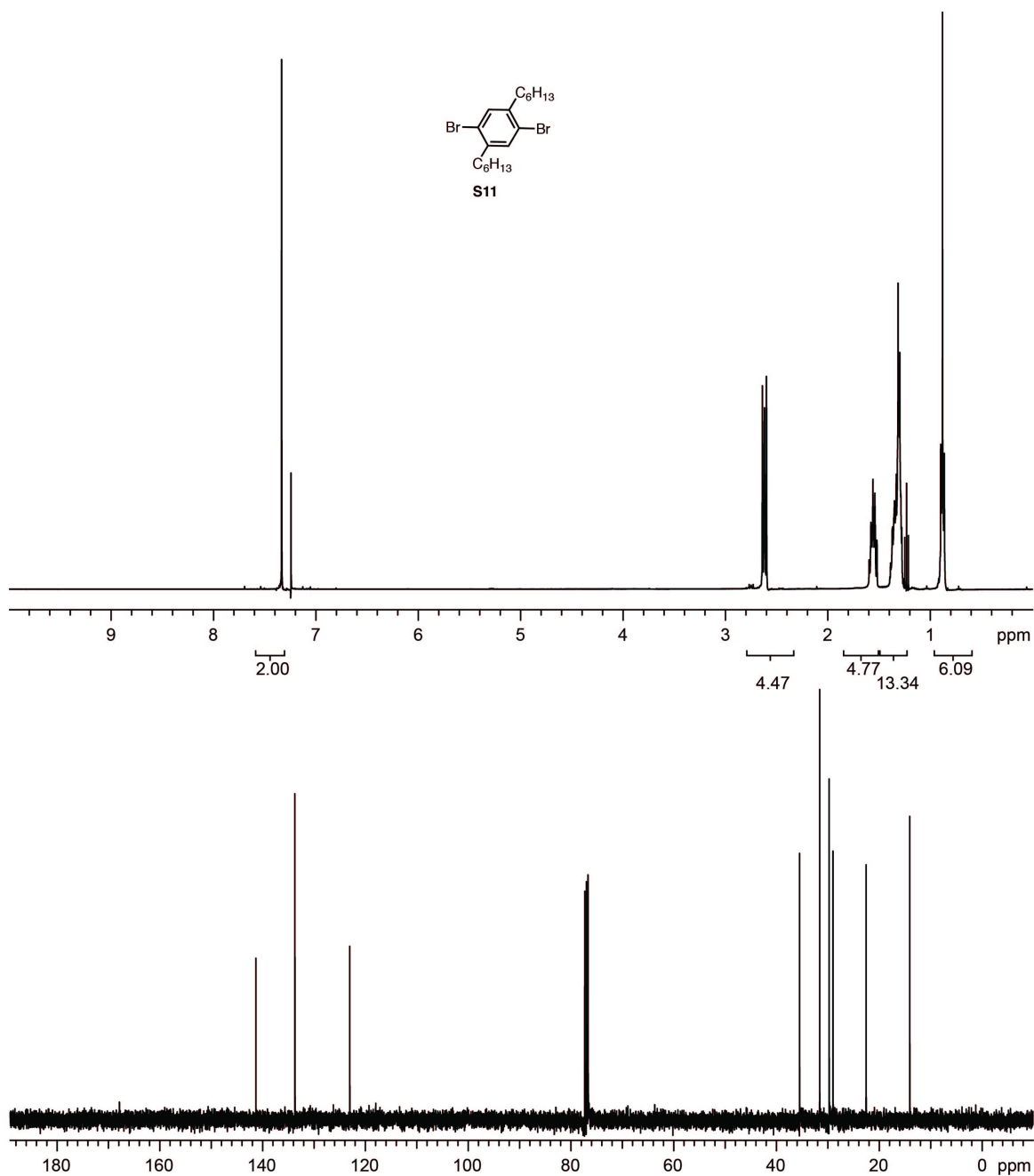
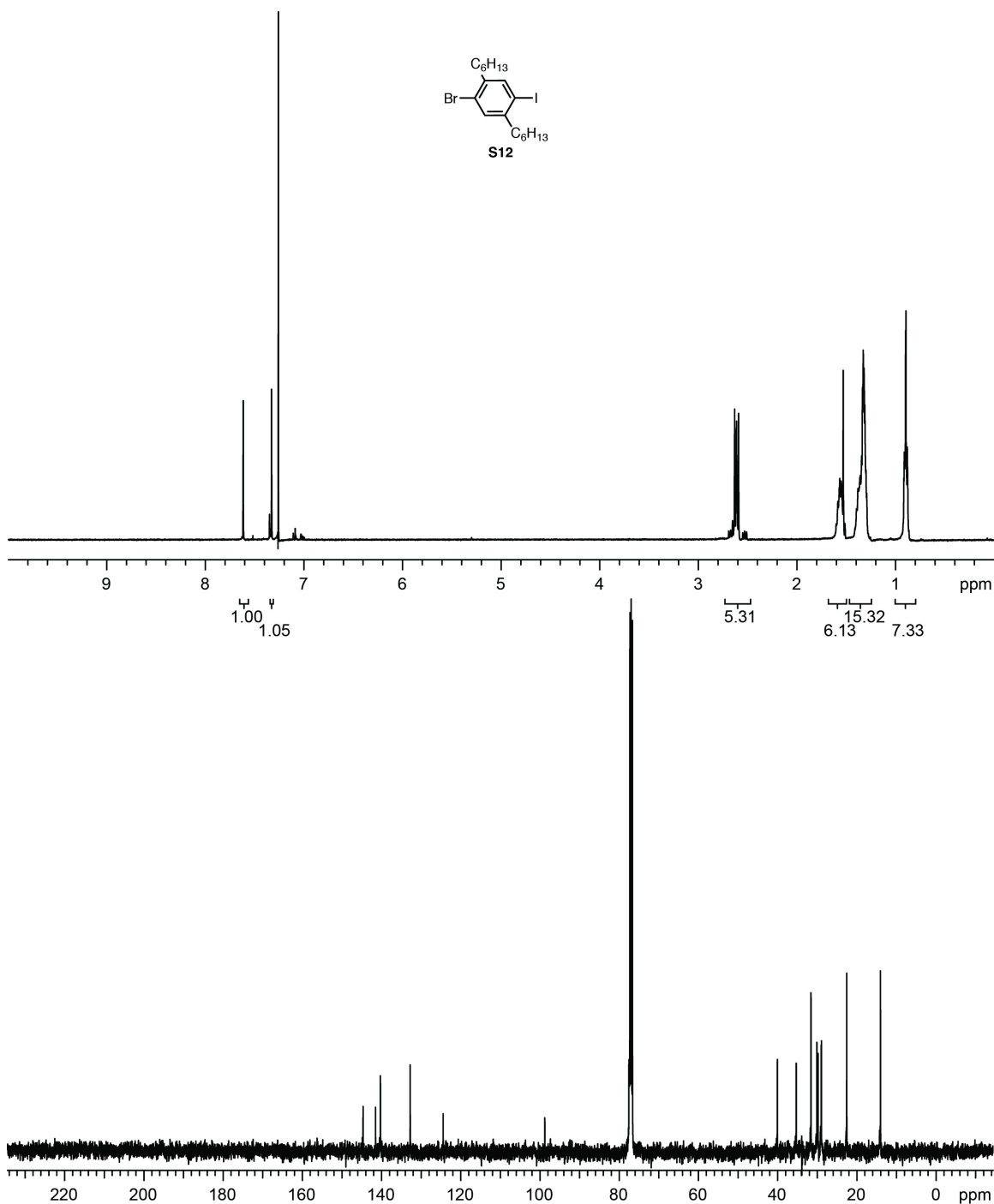


Figure S18 ¹H and ¹³C NMR spectra for **S11**

¹H NMR (400 MHz, CDCl₃) δ 7.352 (s, 2H), 2.656 (t, *J* = 6.4 Hz, 4H), 1.557 (m, 4H), 1.314 (br, 12 H), 0.901 (t, *J* = 7.6 Hz) ¹³C NMR (100 MHz, CDCl₃) δ 141.299, 133.713, 123.027, 35.500, 31.579, 29.750, 28.991, 22.599, 14.051.



^1H NMR (400 MHz, CDCl_3) δ 7.616 (s, 1H), 7.328 (s, 1H), 2.611 (m, 4 H), 1.564 (m, 4 H), 1.318 (br, 14 H), 0.897 (m, 6 H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.649, 141.508, 140.267, 132.756, 124.433, 98.764, 40.053, 35.280, 33.879, 31.563, 30.082, 29.786, 28.985, 28.935, 22.541, 14.028.

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