

Supporting Information for

Limitations of Using Small Molecules to Identify Catalyst-Transfer Polycondensation Reactions

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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. 4-*t*-Butylphenylmagnesium bromide (**S6**) (0.5 M in THF), Pd-PEPPSI-IPr, and Buchwald precatalysts were purchased from Aldrich. All other reagent grade materials and solvents were purchased from Aldrich, Acros, EMD, Strem, 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. THF was dried and deoxygenated using an MBraun solvent purification system composed of activated alumina, copper catalyst, and molecular sieves. All glassware was oven-dried at 120 $^{\circ}\text{C}$ for at least 1 h before use. Compounds **S2**¹, **S3**², **1**², **S1**³, **6**³, **S7**⁴, **S8**⁴, **S9**⁴, and **S10**⁵ were prepared according to modified literature procedures.

II. General Experimental

NMR Spectroscopy: ¹H, ¹³C NMR, and ³¹P spectra for all compounds were acquired at rt in CDCl₃, CD₂Cl₂, or C₆D₆ on a Varian VNMRS 500 operating at 500, 126, and 202 MHz or a Varian VNMRS 700 operating at 700 and 176 MHz. For ¹H, ¹³C NMR, and ³¹P spectra in deuterated solvents, the chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS) and referenced with residual solvent. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). * indicates residual H₂O

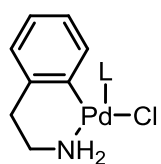
Gel-Permeation Chromatography: Polymer molecular weights were determined by comparison with polystyrene standards (Varian, EasiCal PS-2 MW 580-377,400) on a Waters 1515 HPLC instrument equipped with column guard and three Phenogel columns (4.6 x 30 cm, 10² Å, 10³ Å, 10⁴ Å) in sequence and analyzed with Waters 2487 dual absorbance detector (254 nm), or on a Malvern Viscotek GPCMax VE2001 equipped with two Viscotek LT-5000L 8 mm (ID) x 300 mm (L) columns and analyzed with Viscotek TDA 305 (with R.I., UV-PDA Detector Model 2600 (190-500 nm), RALS/LALS, and viscometer). Samples were dissolved in THF (with mild heating) and passed through a 0.2 μm PTFE filter prior to analysis.

Titrations of the Grignard Reagents: In the glovebox, an accurately weighed sample of salicylaldehyde phenylhydrazone (typically between 290-310 mg) was added to a 5 mL volumetric flask and dissolved with THF. Next, 0.50 mL of this solution was transferred to a 4 mL vial and stirred at rt while ArMgBr was added dropwise using a 500 μL syringe. The initial solution was yellow and turns bright orange at the end-point.⁶

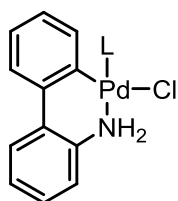
Gas Chromatography: Gas chromatography was carried out using a Shimadzu GC 2010 containing a Shimadzu SHRX5 (crossbound 5% diphenyl – 95% dimethyl polysiloxane; 15 m, 0.25 mm ID, 0.25 μm df) column.

III. Structure Chart

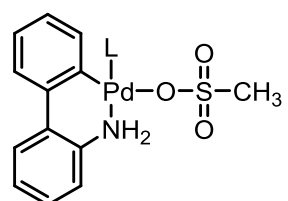
Generation 1-3 precatalysts



Gen 1

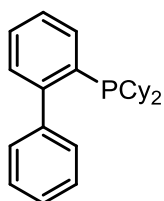


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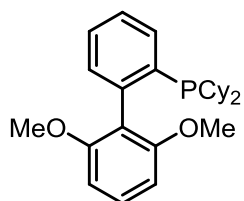


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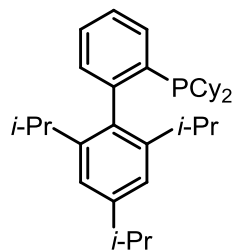
Buchwald phosphine ligands



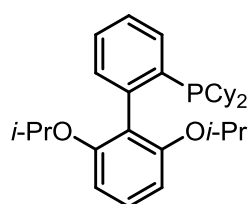
CyJohnPhos



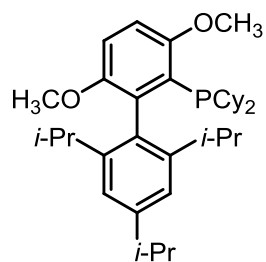
SPhos



XPhos

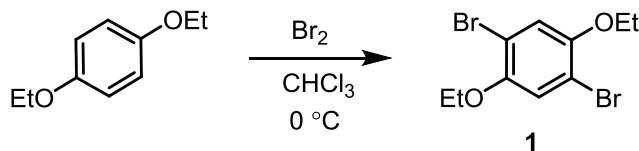


RuPhos

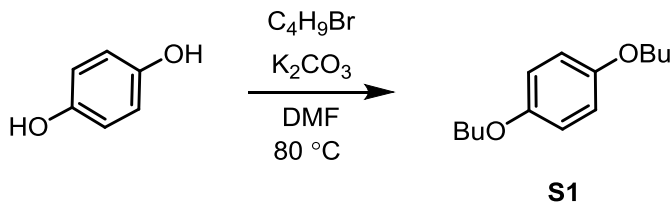


BrettPhos

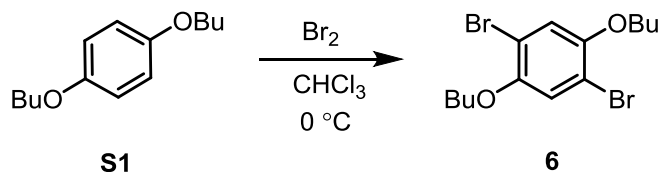
IV. Synthetic Procedures



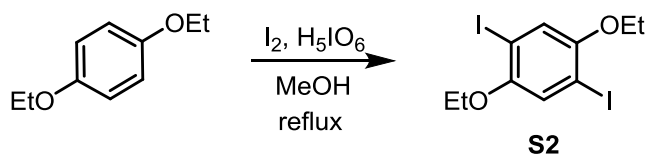
1.² A 500 mL round-bottom flask was equipped with a stir bar. Sequentially, 1,4-diethoxybenzene (13.0 g, 78.2 mmol, 1.0 equiv), and CHCl₃ (90 mL) were added to the flask. The reaction flask was cooled to 0 °C in an ice/water bath and fitted with an addition funnel. Bromine (10.0 mL, 195 mmol, 2.5 equiv) was added dropwise under N₂ and the pressure was vented through a solution of aq satd Na₂SO₃ and NaHCO₃ (50:50). After 3 h, the reaction was quenched with an aq satd solution of Na₂SO₃ (100 mL) and stirred vigorously until colorless. The aqueous mixture was extracted with DCM (3 x 100 mL). The organic layers were combined and washed with water (2 x 200 mL) and brine (1 x 200 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The residue was recrystallized from DCM/methanol to produce 21.3 g of **1** as a white solid (84% yield). HRMS (EI): Calculated for C₁₀H₁₂O₂Br₂, 321.9204 [M⁺]; found, 321.9197.



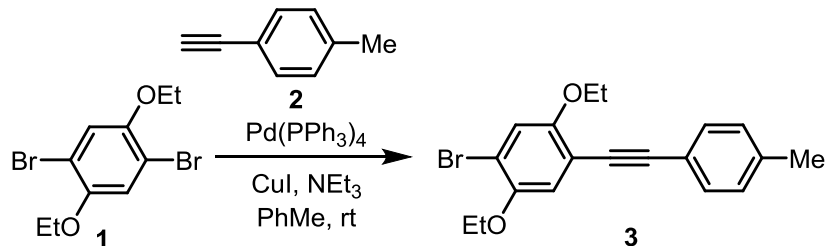
S1.³ A 500 mL round-bottom flask was equipped with a stir bar. Sequentially, hydroquinone (20.0 g, 0.182 mol, 1.0 equiv), anhydrous DMF (120 mL), and 1-bromobutane (49.0 mL, 0.454 mol, 2.5 equiv) were added to the flask. The flask was put under N₂ and stirred vigorously while heated to 80 °C. Once at 80 °C, K₂CO₃ (62.2 g, 0.454 mmol, 2.5 equiv) was slowly added over 10 min and subsequently put under N₂ again for 5 d. After cooling to rt, the reaction mixture was poured into water (400 mL). The reaction mixture was extracted with hexanes (3 x 200 mL). The organic layers were combined and washed with water (2 x 200 mL) and brine (1 x 200 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The resulting oil was passed through silica gel with 100% DCM as the eluent. Recrystallization from hot methanol produced 34.7 g of **S1** as a white crystalline solid (86% yield). HRMS (EI): Calculated for C₁₄H₂₂O₂, 222.1620 [M⁺]; found, 222.1626.



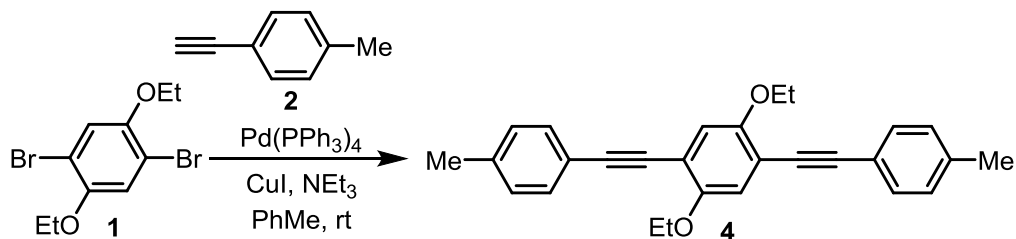
6.³ A 500 mL round-bottom flask was equipped with a stir bar. Sequentially, **S1** (17.3 g, 77.7 mmol, 1.0 equiv), and CHCl_3 (90 mL) were added to the flask. The reaction flask was cooled to $0\text{ }^\circ\text{C}$ in an ice/water bath and fitted with an addition funnel. Bromine (10.0 mL, 194 mmol, 2.5 equiv) was added dropwise under N_2 and the pressure was vented through a solution of aq satd Na_2SO_3 and NaHCO_3 (50:50). After 3 h, the reaction was quenched with an aq satd solution of Na_2SO_3 (100 mL) and stirred vigorously until colorless. The aqueous mixture was extracted with DCM (3 x 100 mL). The organic layers were combined and washed with water (2 x 200 mL) and brine (1 x 200 mL), dried over MgSO_4 , filtered, and concentrated in vacuo. The residue was recrystallized from DCM/methanol to produce 23.3 g of **6** as a white solid (79% yield). HRMS (EI): Calculated for $\text{C}_{14}\text{H}_{20}\text{Br}_2\text{O}_2$, 377.9830 [M⁺]; found, 377.9824.



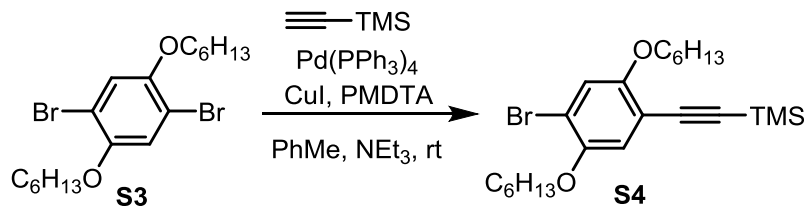
S2.¹ A 100 mL round-bottom flask was equipped with a stir bar. Sequentially, 1,4-diethoxybenzene (5.00 g, 30.1 mmol, 1.0 equiv), and MeOH (50 mL) were added to the flask. Iodine (7.64 g, 30.1 mmol, 1.0 equiv) and periodic acid (6.86 g, 30.1 mol, 1.0 equiv) were added with stirring. This was then heated to reflux and put under N_2 atmosphere. After 4 h, the reaction was quenched with an aq satd solution of Na_2SO_3 (50 mL) and stirred vigorously until colorless. The aqueous mixture was extracted with DCM (3 x 50 mL). The organic layers were combined and washed with water (2 x 50 mL) and brine (1 x 50 mL), dried over MgSO_4 , filtered, and concentrated in vacuo. The residue was recrystallized from DCM/methanol to produce 7.29 g of **S2** as a white solid (58% yield). HRMS (EI): Calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{I}_2$, 417.8927 [M⁺]; found, 417.8927.



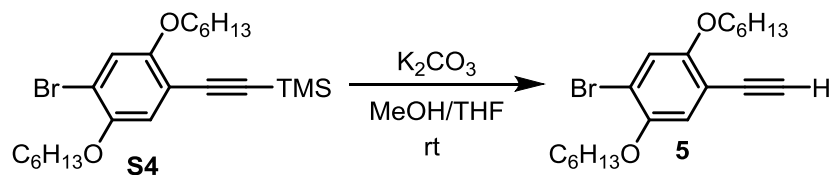
3. A 200 mL Schlenk flask was equipped with a stir bar, the chamber was evacuated for 5 min, and then charged with N₂. Sequentially, **1** (2.00 g, 6.17 mmol, 1.0 equiv), Pd(PPh₃)₄ (360 mg, 0.312 mmol, 5 mol %), CuI (120 mg, 0.620 mmol, 10 mol %) were all added and placed under vac for 20 min. The flask was then placed under N₂ atmosphere. Next, PhMe (60 mL) was added with stirring. Once dissolved, NEt₃ (30 mL, 33% by volume), and **2** (0.78 mL, 6.2 mmol, 1.0 equiv) were added. The reaction was left for 14 h at rt. This reaction was quenched with aq satd NH₄Cl (50 mL) and extracted with DCM (3 x 50 mL), the organic layers were combined and washed with brine (50 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The resulting oil was passed through silica gel with DCM/hexanes (20:80) as the eluent to produce 1.22 g of **3** as an off-white solid (55% yield). HRMS (ESI⁺): Calculated for C₁₉H₁₉BrO₂, 359.0641 [M+H]⁺; found, 359.0641.



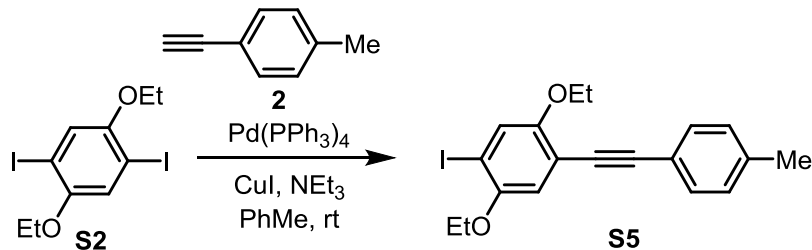
4. A 200 mL Schlenk flask was equipped with a stir bar, the chamber was evacuated for 5 min, and then and charged with N₂. Sequentially, **1** (2.00 g, 6.17 mmol, 1.0 equiv), Pd(PPh₃)₄ (360 mg, 0.312 mmol, 5 mol %), CuI (120 mg, 0.620 mmol, 10 mol %) were all added and placed under vac for 20 min. The flask was then placed under N₂ atmosphere. Next, PhMe (60 mL) was added with stirring. Once dissolved, NEt₃ (30 mL, 33% by volume), and **2** (1.95 mL, 15.4 mmol, 2.5 equiv) were added. The reaction was left for 14 h at rt. This reaction was quenched with aq satd NH₄Cl (50 mL) and extracted with DCM (3 x 50 mL), the organic layers were combined and washed with brine (50 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The resulting oil was passed through silica gel with DCM/hexanes (20:80) as the eluent to produce 1.98 g of **4** as an off-white solid (81% yield). HRMS (ESI⁺): Calculated for C₂₈H₂₆O₂, 395.2006 [M+H]⁺; found, 395.2010.



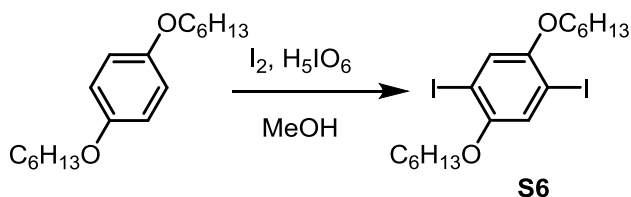
S4. In the glovebox, a 20 mL vial was equipped with a stir bar. Then, **S3** (500 mg, 1.15 mmol, 1.5 equiv), trimethylsilylacetylene (0.11 mL, 0.76 mmol, 1.0 equiv), Pd(PPh₃)₄ (44 mg, 0.038 mmol, 5 mol %), CuI (14 mg, 0.076 mmol, 10 mol %), PMDTA (16 μL, 0.076 mmol, 10 mol %), PhMe (10 mL), and NEt₃ (5 mL) were all added. The reaction was left to stir overnight at rt. The solution was quenched with aq satd NH₄Cl (10 mL). The solution was extracted with DCM (3 x 25 mL). The organic layers were combined and washed with water (2 x 25 mL) and brine (1 x 25 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The product was purified by column chromatography (20% DCM/80% hexanes) to produce 252 mg of **S4** (73% yield). HRMS (ESI⁺): Calculated for C₂₃H₃₇BrO₂Si, 453.1819 [M+H]⁺; found, 453.1821.



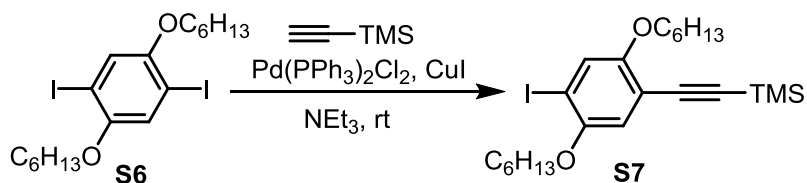
5. A 250 mL round bottom flask was equipped with a stir bar and charged with **S4** (2.00 g, 4.41 mmol, 1.0 equiv), K₂CO₃ (10 g, excess), THF (50 mL), and MeOH (50 mL). The reaction was stirred for 2 h at rt. The reaction was filtered and washed with THF (25 mL), the filtrate was then concentrated in vacuo. This oil was purified by column chromatography (20% DCM/80% hexanes) to produce 1.56 g of **5** (93% yield). HRMS (ESI⁺): Calculated for C₂₀H₂₉BrO₂, 381.1424 [M+H]⁺; found, 381.1423.



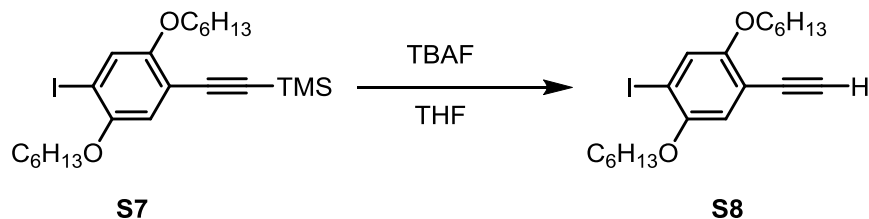
S5. A 200 mL Schlenk flask was equipped with a stir bar, the chamber was evacuated for 5 min, and then charged with N₂. Sequentially, **S2** (2.00 g, 4.78 mmol, 1.0 equiv), Pd(PPh₃)₄ (276 mg, 0.239 mmol, 5 mol %), CuI (91.1 mg, 0.478 mmol, 10 mol %) were all added and placed under vac for 20 min. The flask was then placed under N₂ atmosphere. Next, PhMe (60 mL) was added with stirring. Once dissolved, NEt₃ (30 mL, 33% by volume), and tolyl-acetylene (0.61 mL, 4.8 mmol, 1.0 equiv) were added. The reaction was left for 14 h at rt. This reaction was quenched with aq satd NH₄Cl (50 mL) and extracted with DCM (3 x 50 mL), the organic layers were combined and washed with brine (50 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The resulting oil was passed through silica gel with DCM/hexanes (20:80) as the eluent to produce 932 mg of **S5** as an off-white solid (48% yield). HRMS (ESI⁺): Calculated for C₁₉H₁₉O₂, 407.0502 [M+H]⁺; found, 407.0512.



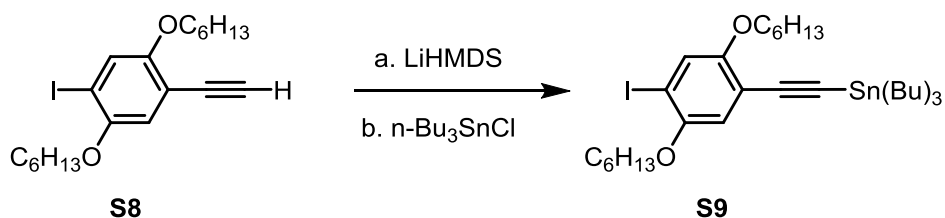
S6.¹ A 25 mL round-bottom flask was equipped with a stir bar and reflux condenser. Sequentially, 1,4-dihexyloxybenzene (1.12 g, 4.01 mmol, 1.0 equiv), and MeOH (7 mL) were added to the flask. Iodine (1.07 g, 4.01 mmol, 1.0 equiv) and periodic acid (0.914 g, 4.01 mol, 1.0 equiv) were added with stirring. The reaction mixture was then heated to reflux and placed under N₂ atmosphere. After 6 h, the reaction was quenched with an aq satd solution of Na₂SO₃ (30 mL) and stirred vigorously until colorless. The aqueous mixture was extracted with DCM (3 x 25 mL). The organic layers were combined and washed with water (1 x 25 mL) and brine (1 x 25 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The residue was recrystallized from DCM/methanol to produce 1.41 g of **S2** as a white solid (66% yield). HRMS (EI): Calculated for C₁₈H₂₈O₂I₂, 530.0179 [M⁺]; found, 530.0192.



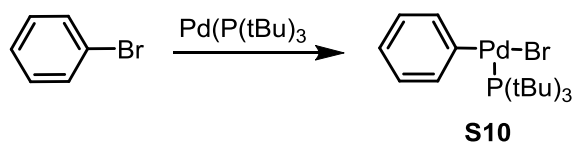
S7. In the glovebox, a 20 mL vial was equipped with a stir bar. Then, **S6** (532 mg, 1.00 mmol, 1.5 equiv), trimethylsilylacetylene (0.10 mL, 0.70 mmol, 0.7 equiv), Pd(PPh₃)₂Cl₂ (35 mg, 0.05 mmol, 5 mol%), CuI (1.9 mg, 0.01 mmol, 1 mol %), and NEt₃ (11.5 mL) were all added. The reaction was stirred for 6 h at rt. The solution was quenched with aq satd NH₄Cl (30 mL), then extracted with hexanes (3 x 25 mL). The organic layers were combined and washed with water (1 x 25 mL) and brine (1 x 25 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The product was purified by column chromatography with PhMe/hexanes(20:80) as the eluent to produce 187.6 mg of **S7** (53% yield) as a yellow oil. HRMS (EI): Calculated for C₂₃H₃₇IO₂Si, 500.1608 [M⁺]; found, 500.1607



S8. In a 25 mL round-bottom flask, **S7** (319.0 mg, 0.64 mmol, 1 equiv) was dissolved in THF (8 mL), then tetrabutyl ammonium fluoride (1 M in THF, 0.96 mL, 1.5 equiv) was added and the solution was stirred 10 min at rt. DI water (10 mL) was added and the aqueous solution was extracted with diethyl ether (3 x 20 mL). The organic layers were combined and washed with water (1 x 20 mL) and brine (1 x 20 mL), dried over MgSO₄, filtered, and concentrated in vacuo. The product was purified by column chromatography with DCM/hexanes (10:90) as the eluent to produce 220.10 mg of **S8** (81% yield) as a yellow solid. HRMS (EI⁺): Calculated for C₂₀H₂₉IO₂, 428.1212 [M⁺]; found, 428.1199.



S8. In a 50 mL Schlenk flask, **S8** (190.1 mg, 0.44 mmol, 1 equiv) was dissolved in anhydrous THF (8 mL), and cooled to $-78\text{ }^{\circ}\text{C}$. Then, LiHMDS (0.75 M in THF, 0.77 mL, 1.3 equiv) was added dropwise, and the solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h. Tri-*n*-butyltin chloride (0.16 mL, 0.58 mmol, 1.3 equiv) was added, then the dry ice bath was removed and the solution was stirred for 90 min. The reaction was quenched with sat. aqueous NH_4Cl (5 mL), then extracted with diethyl ether (2 x 15 mL). The organic layers were combined and washed with water (1 x 15 mL) and brine (1 x 15 mL), dried over MgSO_4 , filtered, and concentrated in vacuo. The product was dried under vacuum overnight, giving 303.2 mg of a yellow oil (95%), and used without further purification. HRMS (EI): Calculated for $\text{C}_{32}\text{H}_{55}\text{I}\text{O}_2\text{Sn}$, 661.1564 [M-Bu] $^{+}$; found, 661.1567



S10. In a glovebox, a 20 mL vial was charged with bis(tri-*t*-butylphosphine)palladium (153.3 mg, 0.300 mmol, 1 equiv) and bromobenzene (1.5 mL, 14.1 mmol, 47 equiv). The reaction mixture was stirred at $70\text{ }^{\circ}\text{C}$ for 2.5 h, then poured into cold pentane, causing immediate precipitation of a yellow solid. The product was isolated by vacuum filtration, then washed with pentane (5 x 3 mL), giving 41.3 mg of a yellow solid (29%).

V. NMR Spectra

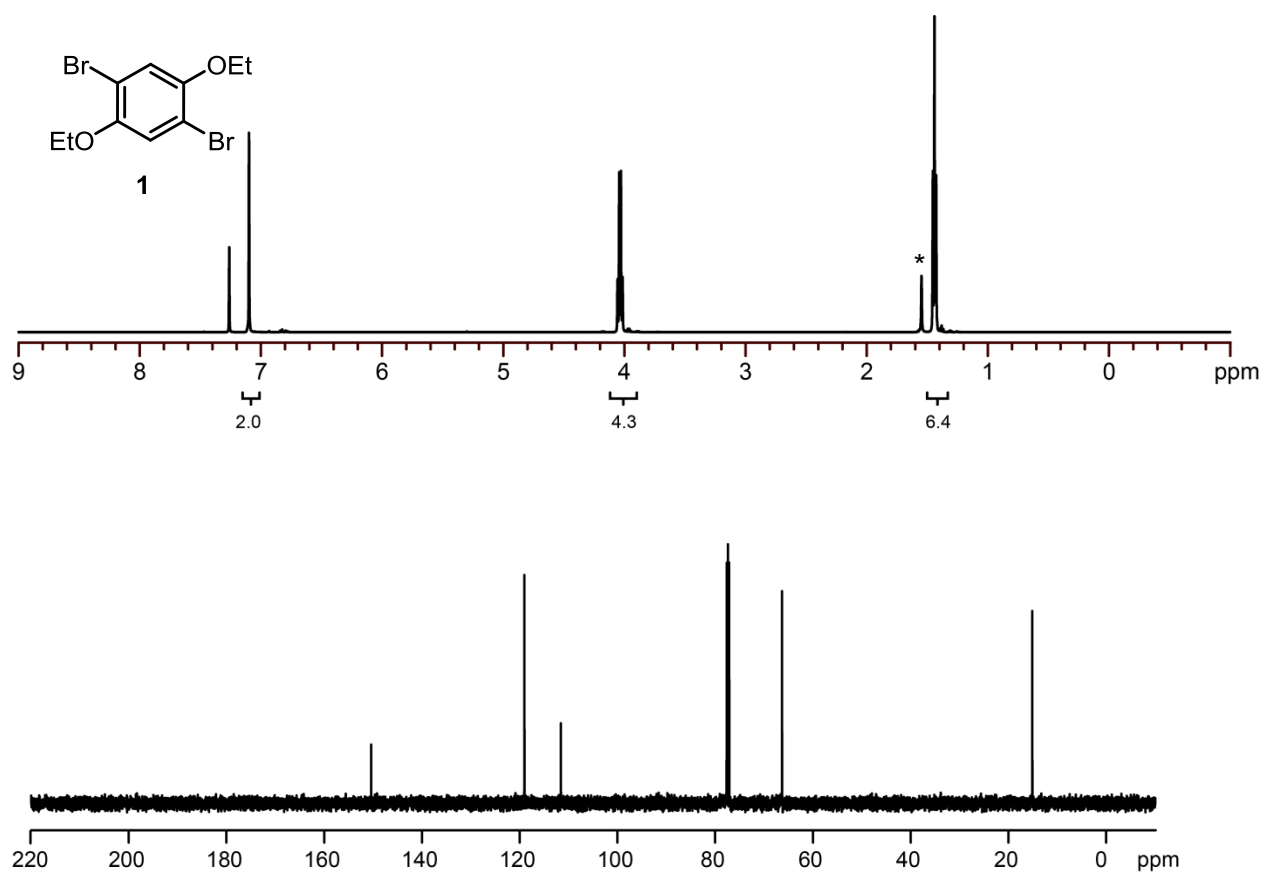


Figure S1. ¹H and ¹³C NMR spectra for **1**. ¹H NMR (500 MHz, CDCl₃) δ 7.10 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 4H), 1.47 (t, *J* = 7.1 Hz, 6H). * indicates residual H₂O. ¹³C NMR (126 MHz, CDCl₃) δ 150.00, 118.65, 111.85, 65.94, 14.73.

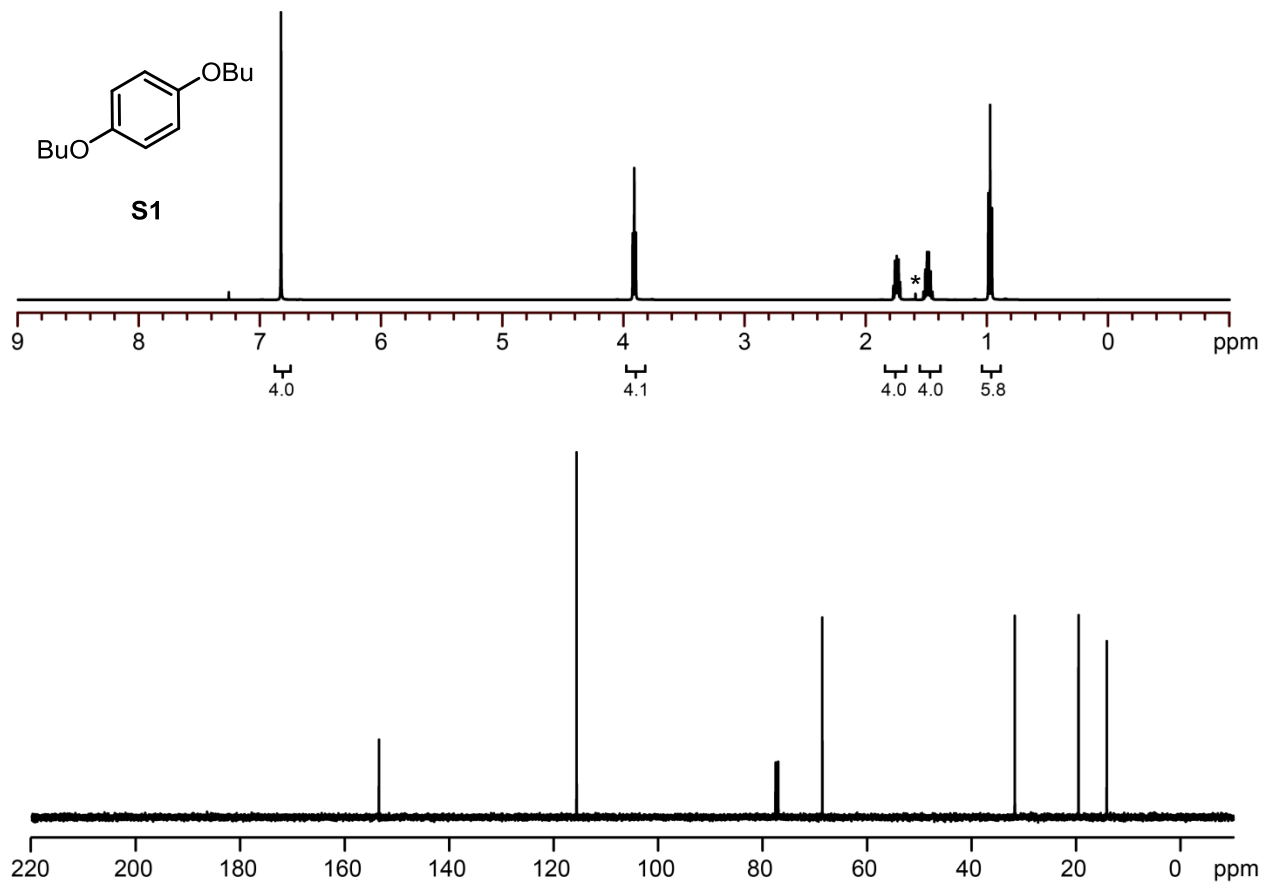


Figure S2. ^1H and ^{13}C NMR spectra for **S1**. ^1H NMR (500 MHz, CDCl_3) δ 6.83 (s, 4H), 3.92 (t, $J = 7.0$ Hz, 4H), 1.80–1.73 (m, 4H), 1.55–1.46 (m, 4H), 0.98 (t, $J = 7.3$ Hz, 6H). * indicates residual H_2O . ^{13}C NMR (126 MHz, CDCl_3) δ 153.19, 115.36, 68.30, 31.45, 19.24, 13.84.

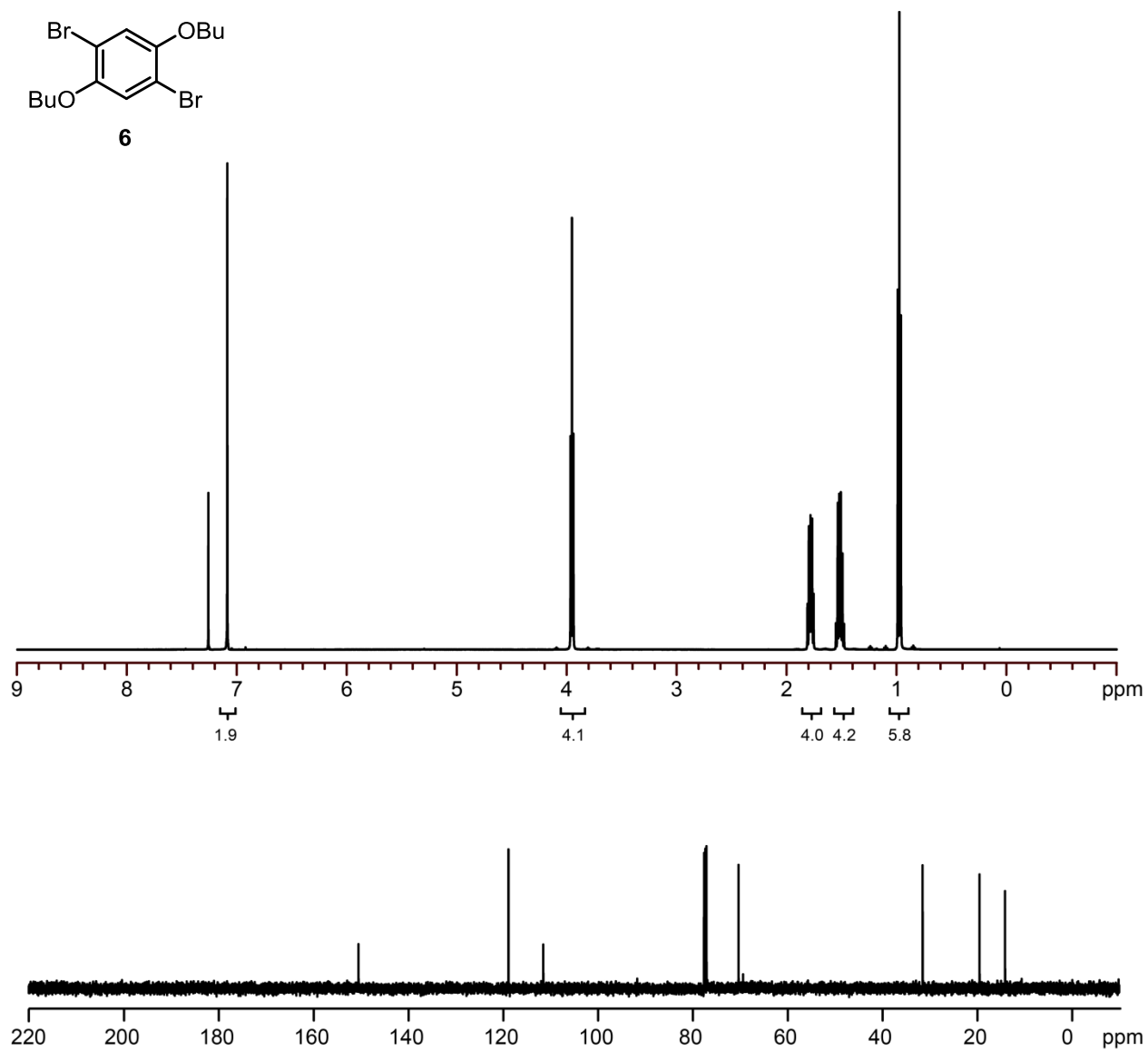


Figure S3. ¹H and ¹³C NMR spectra for **6**. ¹H NMR (500 MHz, CDCl₃) δ 7.09 (s, 2H), 3.96 (t, *J* = 6.7 Hz, 4H), 1.84–1.77 (m, 4H), 1.58–1.49 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 150.08, 118.46, 111.13, 69.99, 31.19, 19.19, 13.81.

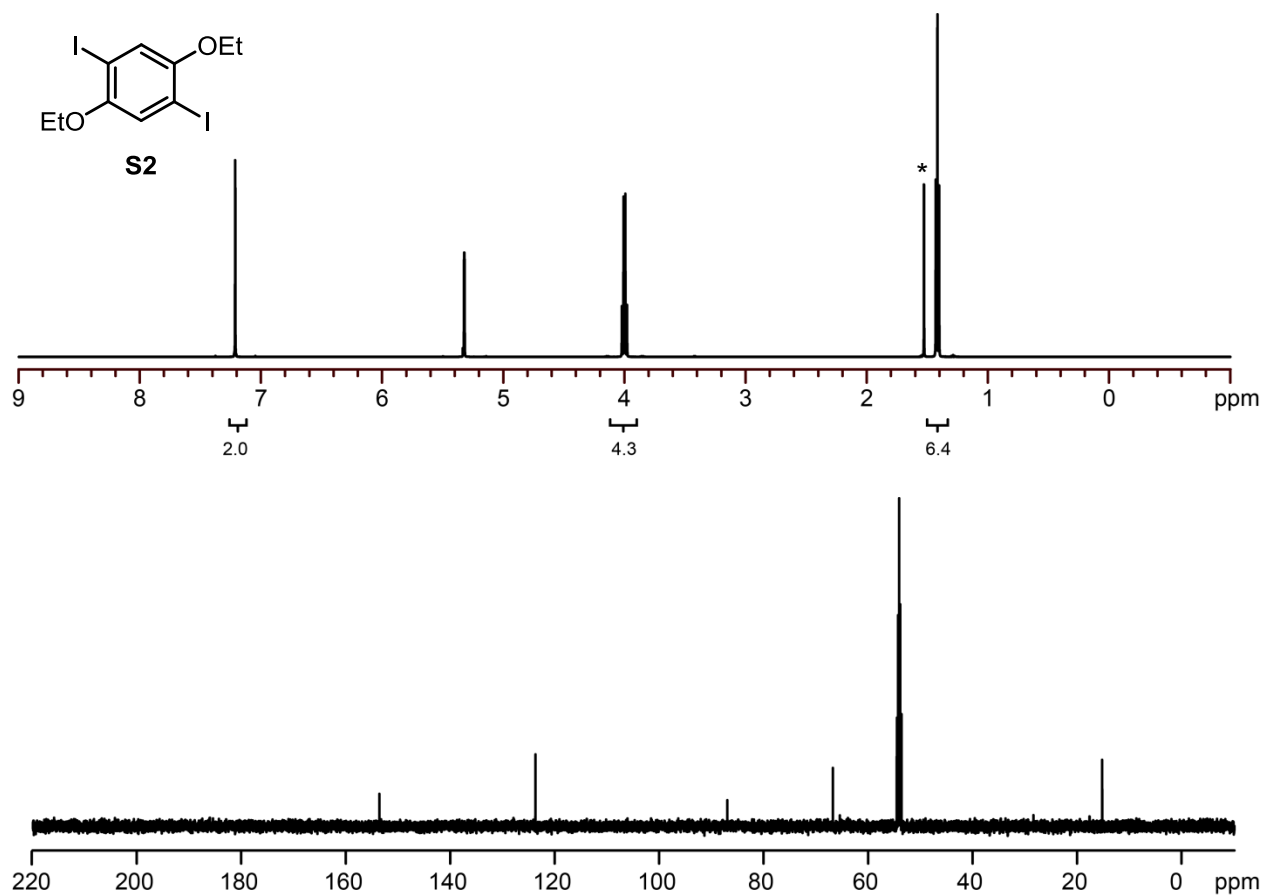


Figure S4. ^1H and ^{13}C NMR spectra for **S2**. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.21 (s, 2H), 4.01 (q, $J = 7.0$ Hz, 4H), 1.42 (t, $J = 7.0$ Hz, 6H), * indicates residual H_2O . ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.66, 123.80, 87.09, 66.92, 15.40.

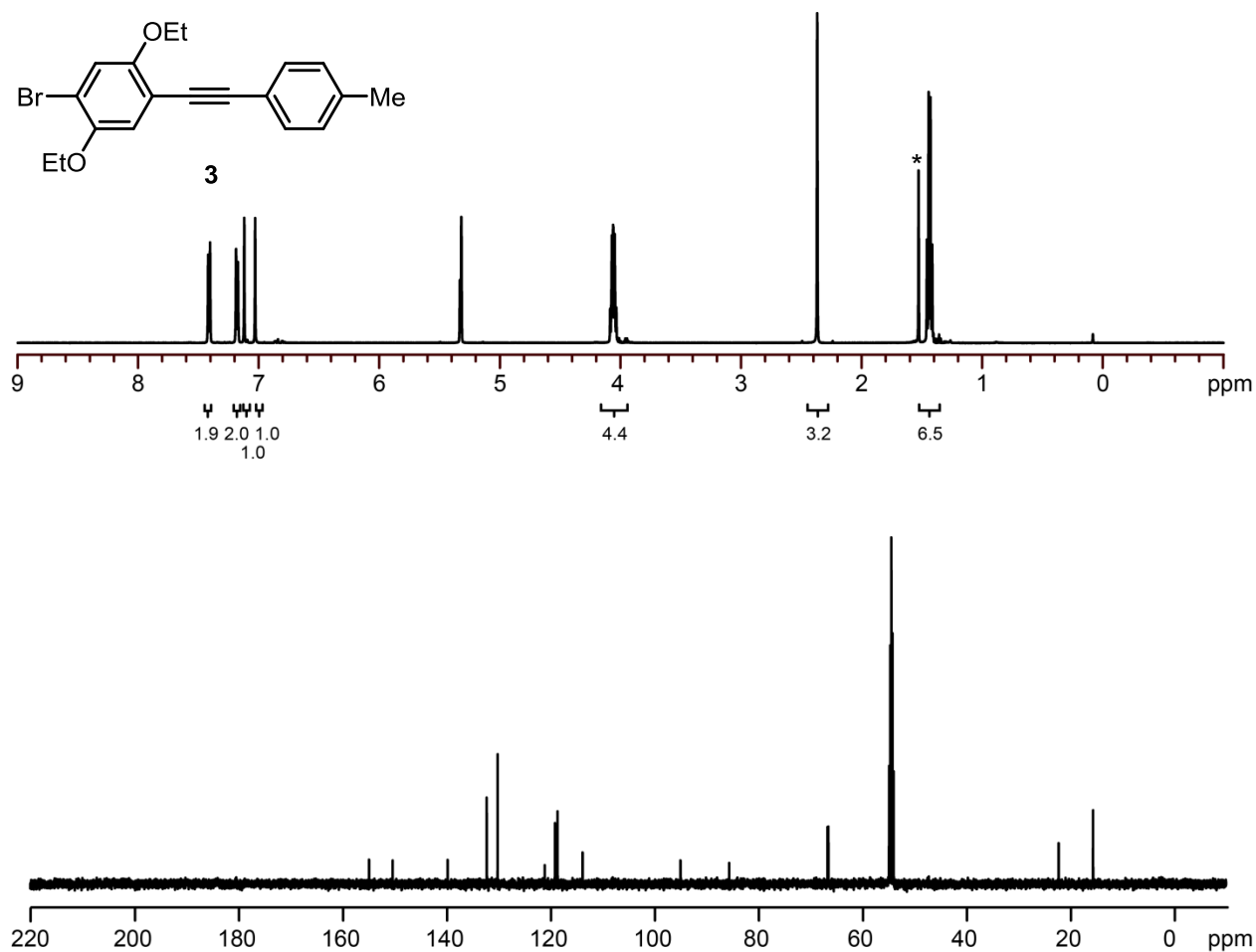


Figure S5. ¹H and ¹³C NMR spectra for **3**. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 7.03 (s, 1H), 4.09–4.03 (m, 4H), 2.37 (s, 3H), 1.46–1.41 (m, 6H). * indicates residual H₂O. ¹³C NMR (126 MHz, CD₂Cl₂) δ 154.73, 150.20, 139.62, 132.11, 129.99, 120.94, 118.96, 118.46, 113.71, 113.65, 94.82, 85.46, 66.50, 66.34, 22.04, 15.43, 15.42.

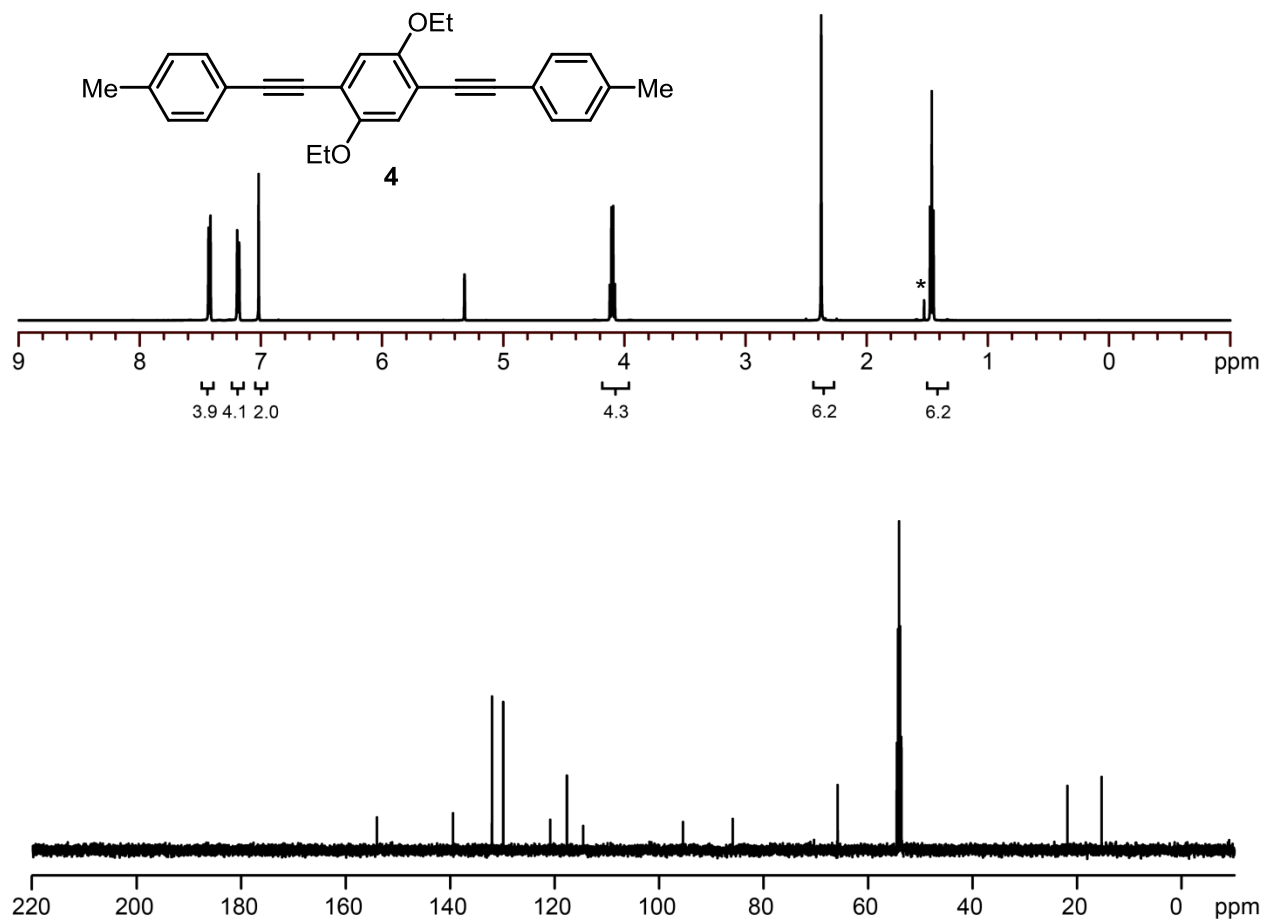


Figure S6. ^1H and ^{13}C NMR spectra for **4**. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.42 (d, J = 8.4 Hz, 4H), 7.19 (d, J = 7.9 Hz, 4H), 7.02 (s, 2H), 4.12–4.08 (m, 4H), 2.38 (s, 6H), 1.46 (t, J = 7.0 Hz, 6H). * indicates residual H_2O . ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.35, 138.79, 131.33, 129.18, 120.18, 116.99, 113.88, 94.79, 85.27, 65.19, 21.23, 14.69.

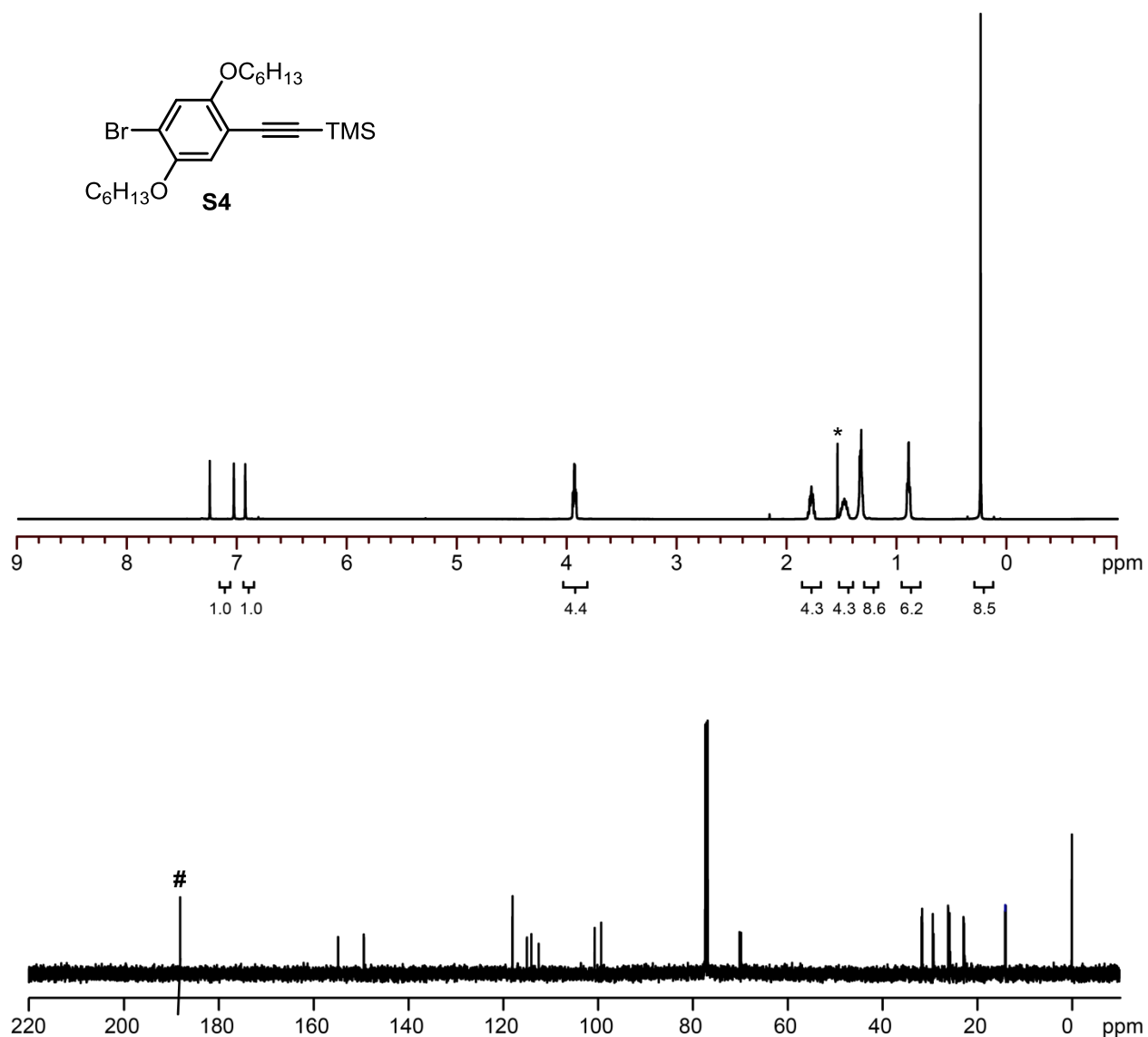


Figure S7. ¹H and ¹³C NMR spectra for **S4**. ¹H NMR (500 MHz, CDCl₃) δ 7.04 (s, 1H), 6.94 (s, 1H), 3.97-3.91 (m, 4H), 1.83-1.75 (m, 4H), 1.54-1.43 (m, 4H), 1.39-1.30 (m, 8H), 0.95-0.87 (m, 6H), 0.26 (s, 9H). * indicates residual H₂O. ¹³C NMR (126 MHz, CDCl₃) δ 154.71, 149.29, 117.93, 114.89, 113.56, 112.40, 100.61, 99.22, 70.08, 69.72, 31.60, 31.58, 29.25, 29.24, 25.67, 25.65, 22.58, 22.57, 14.05, 14.02, -0.06. # indicates NMR instrument artifact

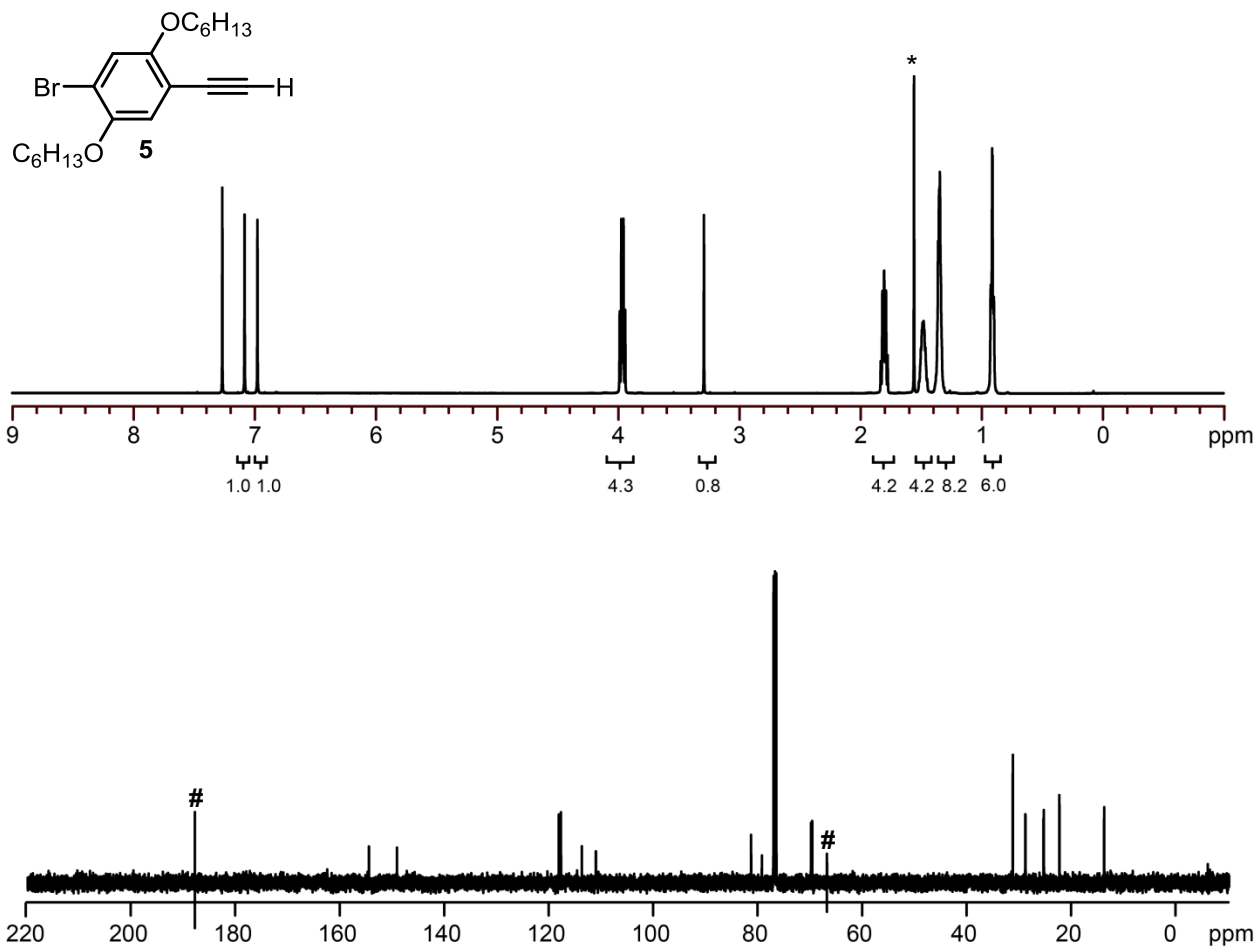


Figure S8. ¹H and ¹³C NMR spectra for **5**. ¹H NMR (500 MHz, CDCl₃) δ 7.08 (s, 1H), 6.97 (s, 1H), 3.99–3.93 (m, 4H), 3.29 (s, 1H), 1.84–1.76 (m, 4H), 1.52–1.43 (m, 4H), 1.39–1.31 (m, 8H), 0.94–0.88 (m, 6H). * indicates residual H₂O. ¹³C NMR (126 MHz, CD₂Cl₂) δ 154.72, 149.34, 118.38, 117.96, 113.96, 111.28, 81.58, 79.52, 70.13, 69.89, 31.50, 29.94, 29.11, 29.05, 25.63, 25.55, 22.57, 22.57, 14.02, 14.00. # indicates NMR instrument artifact

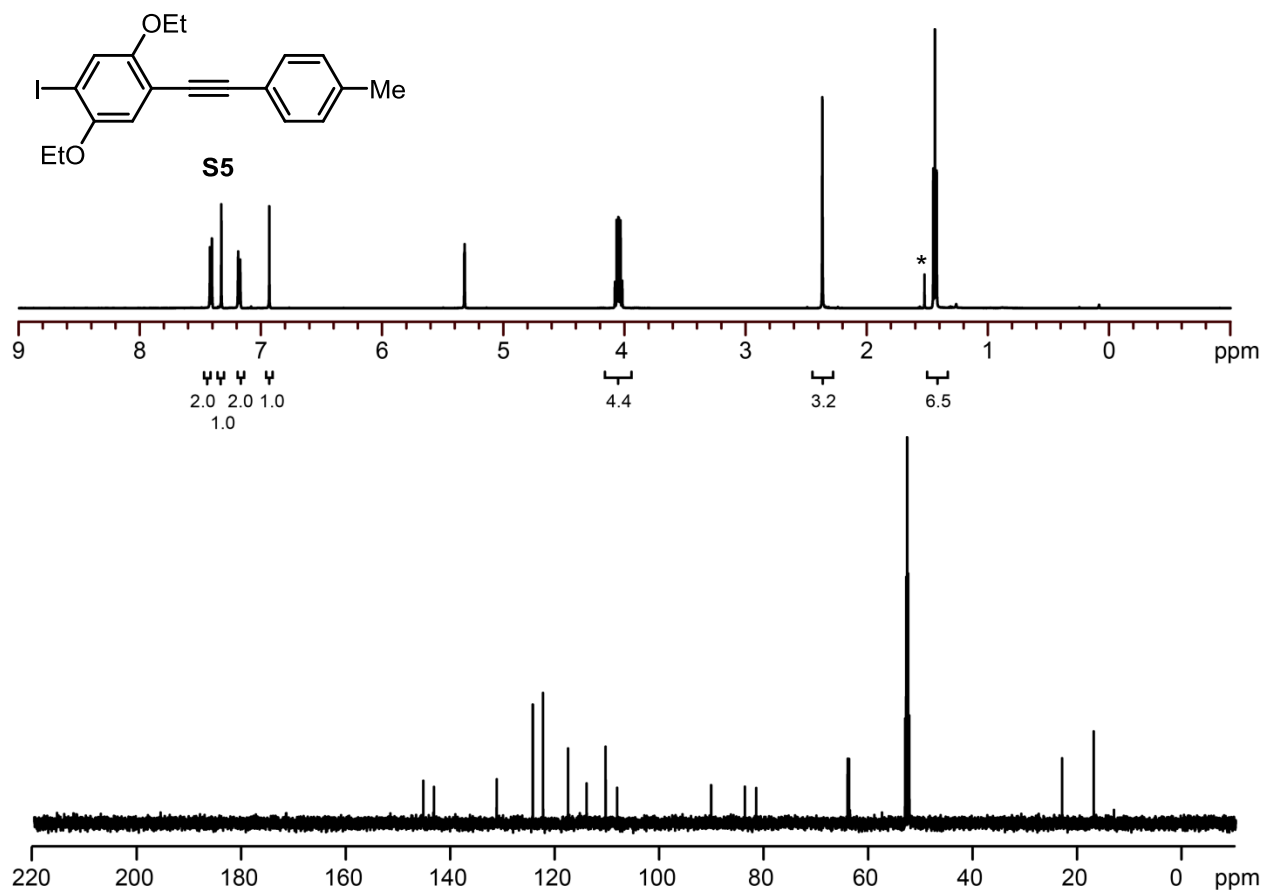


Figure S9. ¹H and ¹³C NMR spectra for **S5**. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.33 (s, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.93 (s, 1H), 4.08–4.01 (m, 4H), 2.37 (s, 3H), 1.44 (t, *J* = 7.0 Hz, 6H). * indicates residual H₂O. ¹³C NMR (126 MHz, CD₂Cl₂) δ 154.87, 152.64, 139.62, 132.09, 129.97, 124.76, 120.90, 116.95, 114.56, 95.00, 87.99, 85.62, 66.10, 66.32, 22.03, 15.45.

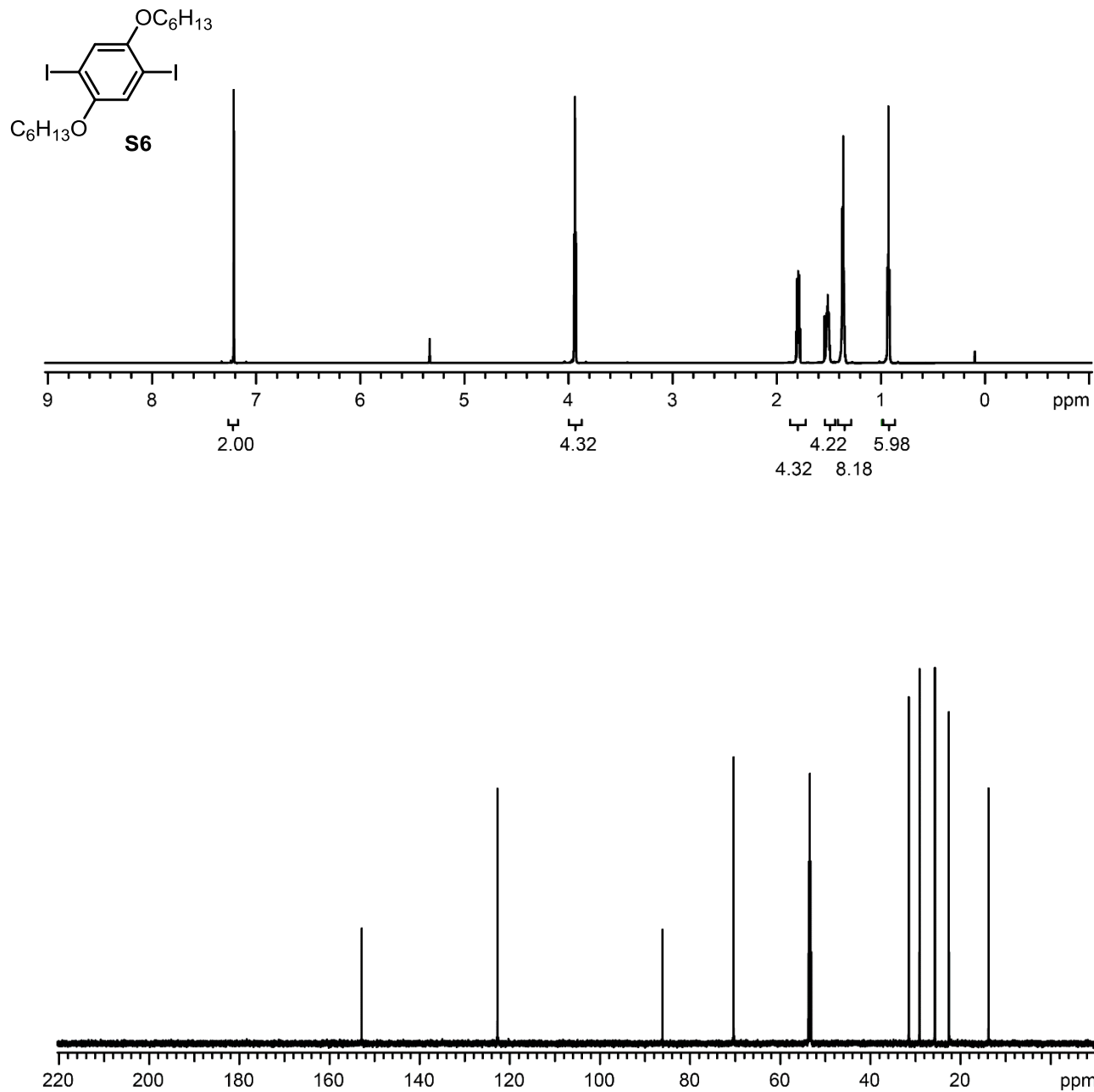


Figure S9. ¹H and ¹³C NMR spectra for **S6**. ¹H NMR (700 MHz, CD₂Cl₂) δ 7.21 (s, 2H), 3.94 (t, *J* = 6.3, 4H), 1.81–1.77 (m, 4H), 1.53–1.49 (m, 4H), 1.39–1.34 (m, 8H), 0.94–0.91 (m, 6H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 152.84, 122.72, 86.10, 70.35, 31.45, 29.09, 25.67, 22.57, 13.79.

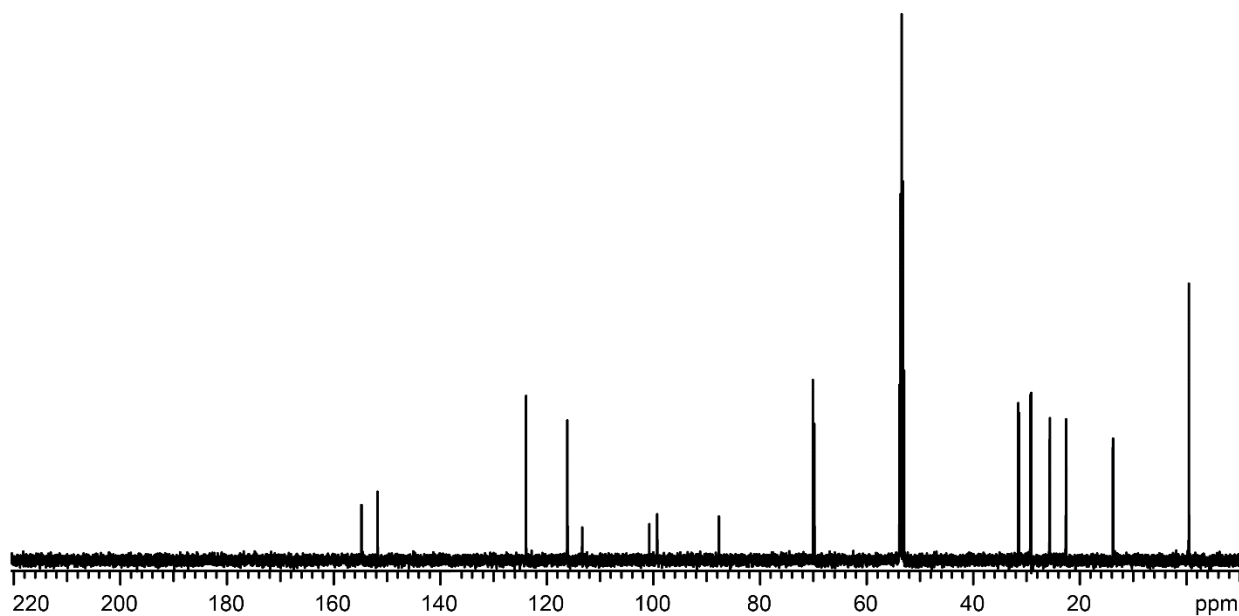
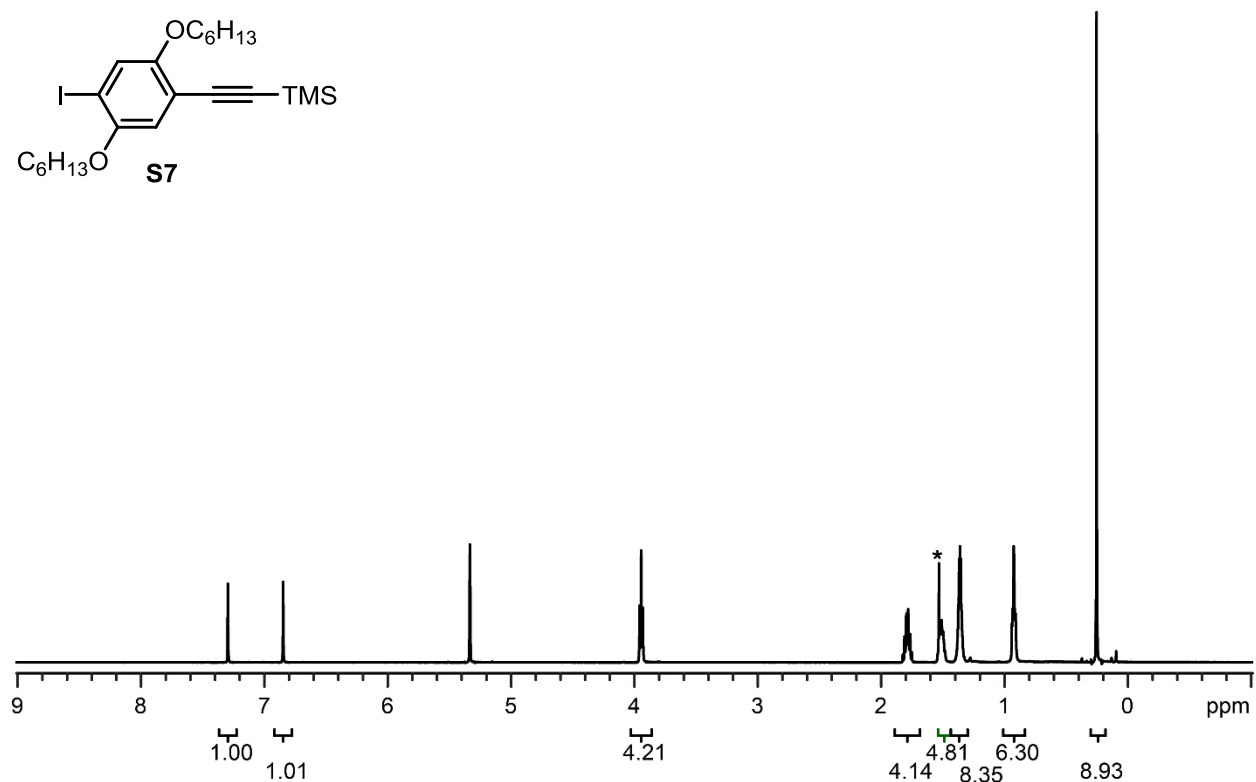
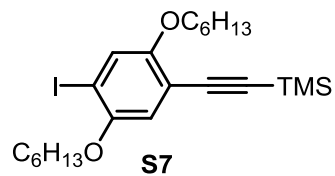
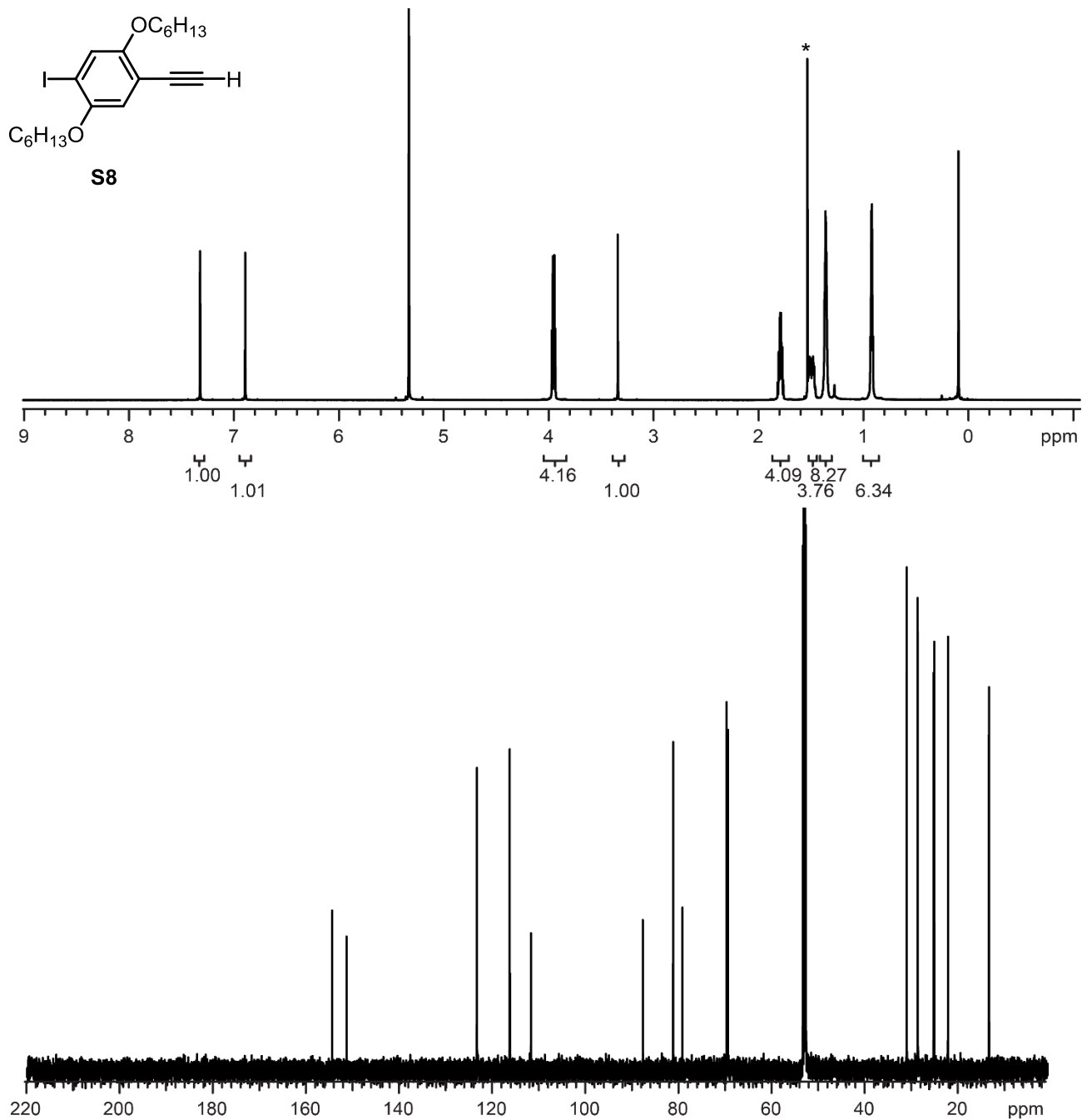
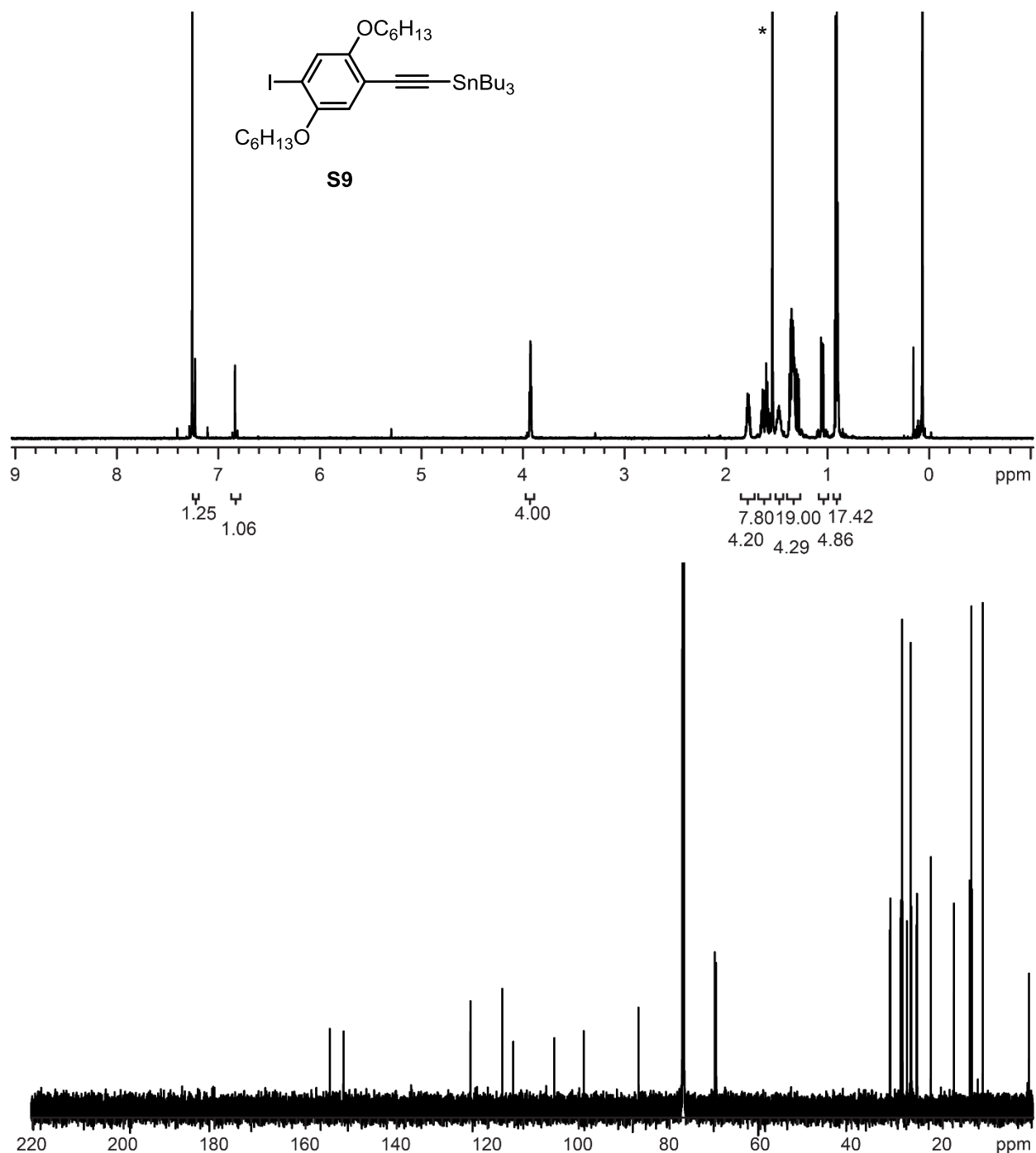


Figure S10. ^1H and ^{13}C NMR spectra for **S6**. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.27 (s, 1H), 6.82 (s, 1H), 3.92 (t, $J = 5.8$ Hz, 4H), 1.80–1.73 (m, 4H), 1.51–1.47 (m, 4H), 1.35–1.32 (m, 8H), 0.92–0.89 (m, 6H), 0.24 (s, 9H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 1549.76, 151.72, 123.88, 116.14, 113.34, 100.76, 99.27, 87.68, 70.08, 69.80, 31.54, 31.45, 29.24, 29.10, 25.68, 25.61, 22.60, 22.57, 13.79, 13.76, 0.47.





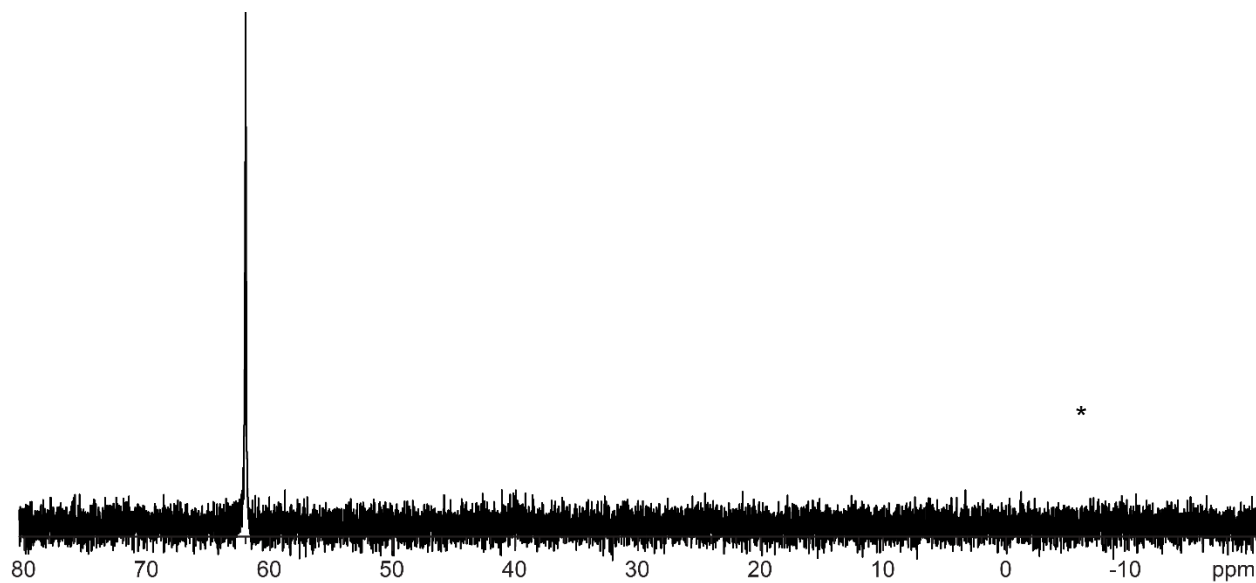
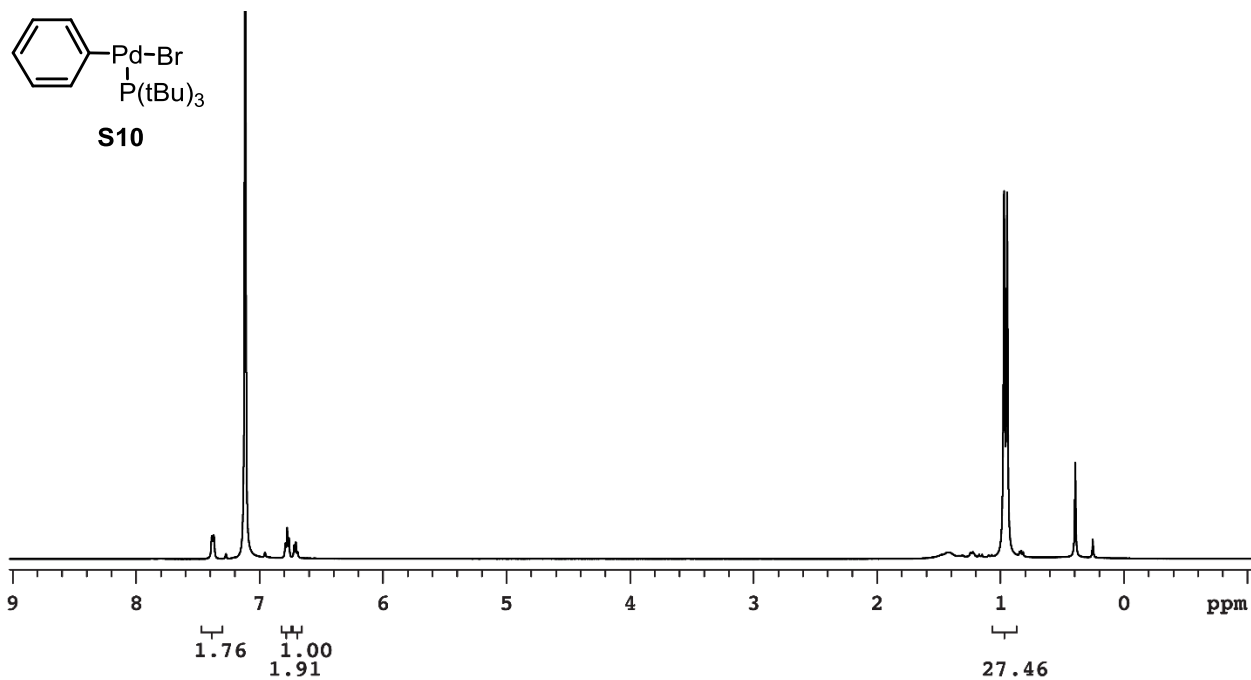
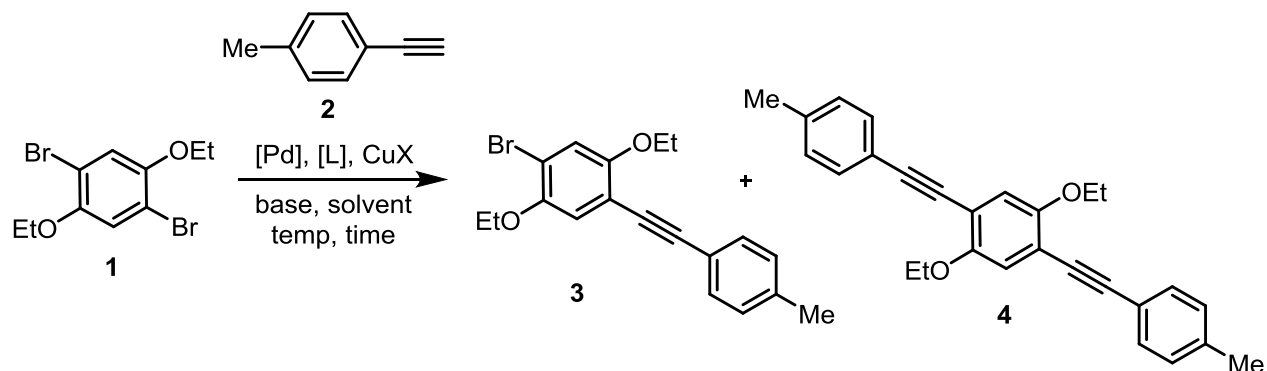
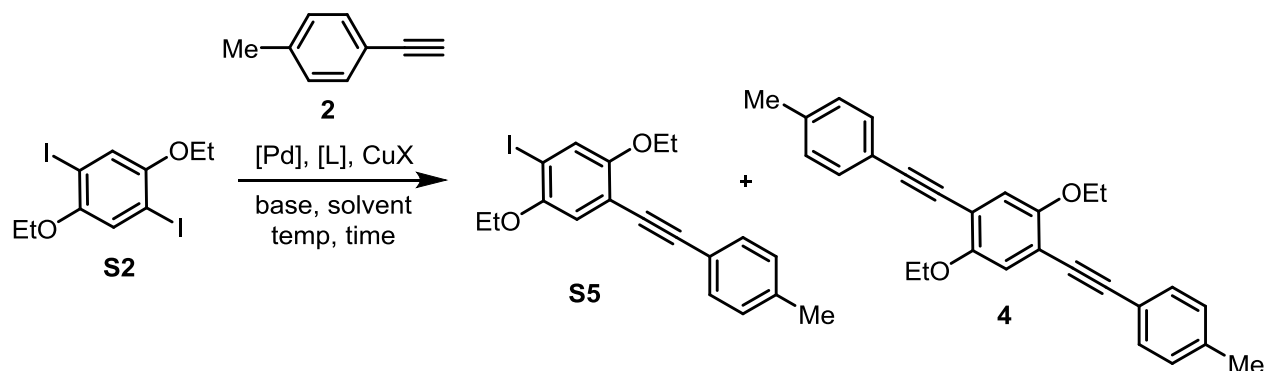


Figure S13. ^1H and ^{31}P NMR spectra for **S10**. ^1H NMR (500 MHz, C_6D_6) δ 7.42 (d, $J = 6.5$ Hz, 2H), 6.82 (t, $J = 7.5$ Hz, 2H), 6.75 (t, $J = 7.0$ Hz, 1H), 1.00 (d, $J_{\text{P-H}} = 12.5$, 27 H). ^{31}P NMR (202 MHz, C_6C_6) δ 61.98.

VI. Small Molecule Screens

The small molecule screens outlined in this section reflect a small percentage of the total number performed. We initially began screening small molecules utilizing 1,4-diiodo-2,5-diethoxybenzene (**S2**), however we observed aryl iodide decomposition in solution over time. We switched to 1,4-dibromo-2,5-diethoxybenzene (**1**) and observed higher selectivity for the di-functional product (**4**). All small molecule screens listed are using **S2** unless noted. The amount of 1,1'-(1,2-ethynediyl)bis(4-methylbenzene) formed was less than 3% unless stated otherwise.



Representative Procedure for Small Molecule Screens:

Prior to starting each batch of reactions, separate stock solutions in PhMe were made for C₁₉H₄₀ internal standard (0.050 M), **1** (0.20 M), CuI/PMDTA (0.050 M). Similarly, a stock solution of the phosphine ligand (0.020 M) was also prepared when needed.

In the glovebox, a 4 mL vial was equipped with a stir bar. Pd catalyst (0.0025 mmol, 1.0 equiv) was then carefully measured out in the vial, and the mass was recorded. Sequentially phosphine ligand* (0.25 mL of 0.02 M stock solution, 2.0 equiv), CuI/PMDTA (0.25 mL of 0.050 M stock solution, 5.0 equiv), **1** (1.0 mL of 0.20 M stock solution, 80

equiv), C₁₉H₄₀ internal standard (0.25 mL of 0.050 M stock solution, 5.0 equiv), and 0.25 mL PhMe were added with stirring to reach a total volume of 2.0 mL PhMe. Next, NEt₃ (1 mL, 33% by volume) and **2** (13 μL, 0.10 mmol, 40 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 2 days at rt. The vial was removed from the glovebox and the reaction was quenched with HCl (12.1 M, 3 mL) and subsequently diluted with water (8 mL). The reaction mixture was then extracted with DCM (3 x 3 mL), and the combined organic layers were dried over MgSO₄, filtered through a 0.2 μm PTFE filter, and subjected to GC analysis.

Table S1. Data for reactions with 0-2 equiv of SPhos.

Conditions: Solvent = PhMe/NEt₃ (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (1 equiv) + **n** SPhos, CuI/PMDTA = 5 equiv (1:1 ratio).

SPhos (equiv)	% Conv. 2	μmol S5	μmol 4	S5/4 ratio
0	100	13.6	56.4	20/80
1	63	12.0	8.2	60/40
2	52	8.5	2.0	81/19

Table S2. Data for reactions with variable Pd precatalysts.

Conditions: Solvent = PhMe/NEt₃ (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = **precatalyst** (1 equiv), CuI/PMDTA = 5 equiv (1:1 ratio).

Catalyst	% Conv. 2	μmol S5	μmol 4	S5/4 ratio
Gen 1 SPhos	80	19.0	39.0	33/67
Gen 2 SPhos	100	11.9	76.1	14/84
Gen 3 SPhos	100	13.9	68.7	17/83
Gen 1 XPhos	100	25.0	38.4	39/61
Gen 2 XPhos	100	26.1	40.1	39/61
Gen 3 XPhos	100	34.6	68.8	33/67
Gen 1 BrettPhos	100	38.8	19.3	67/33
Gen 2 BrettPhos	100	40.1	25.6	61/39
Gen 2 RuPhos	100	18.9	33.1	36/64

Table S3. Data for reactions with variable Pd catalysts.

Conditions: Solvent = PhMe/NEt₃ (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = **precatalyst** (1 equiv) or **PdL₂** (1 equiv), CuI/PMDTA = 5 equiv (1:1 ratio).

ArX ₂	Catalyst	% Conv. 2	μmol 3 or S5	μmol 4	3/4 or S5/4 ratio
S2	Gen 1 SPhos	80	16.3	28.1	37/63
S2	Gen 2 SPhos	100	11.8	37.9	24/76
S2	Gen 1 XPhos	100	25.5	45.1	36/64
S2	Gen 2 XPhos	100	21.5	45.5	32/68
S2	Pd(PhCN)Cl ₂ + XPhos	70	26.0	36.3	36/64
S2	Pd(OAc) ₂ + XPhos	100*	17.1	19.4	47/53
1	Pd(OAc) ₂ + CyJohnPhos	100 [^]	64.8	25.2	72/28

*This reaction produced 12% yield of 1,1'-(1,2-ethynediyl)bis(4-methylbenzene) as a side-product.

[^]These conditions resulted in 51% isolated yield of **3** when scaled to a 1 g of **1**.

Table S4. Data for reactions with 5-20 equiv PMDTA.

Conditions: Solvent = PhMe/NEt₃ (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (1 equiv), CuI/PMDTA (1:n ratio) = 5 equiv.

PMDTA (equiv)	% Conv. 2	μmol S5	μmol 4	S5/4 ratio
5	100	9.0	25.3	26/74
10	100	9.1	20.6	31/69
15	93	8.8	25.1	31/69
20	94	9.1	19.4	32/68

Table S5. Data for reactions with 1-20 equiv Cul/PMDTA (1:1 ratio).

Conditions: Solvent = PhMe/NEt₃ (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (1 equiv), Cul/PMDTA = n equiv (1:1 ratio).

Cul + PMDTA (equiv)	% Conv. 2	μmol S5	μmol 4	S5/4 ratio
1	95	16.6	60.6	22/78
5	100	14.0	44.3	24/76
10	100	13.3	34.3	28/72
20	100	13.3	30.3	31/69

Table S6. Data for reactions with 0.2-5 equiv of Gen 2 SPhos

Conditions: Solvent = PhMe/NEt₃ (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (n equiv), Cul/PMDTA = 5 equiv (1:1 ratio).

Gen 2 SPhos (equiv)	% Conv. 2	μmol S5	μmol 4	S5/4 ratio
0.2	100	21.3	61.1	26/74
1	100	13.6	56.3	20/80
5	100	7.4	18.3	29/71

Table S7. Data for reactions with various bases.

Conditions: Solvent = PhMe/**base** (67/33 vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (1 equiv), Cul/PMDTA = 5 equiv (1:1 ratio).

Base	pKa	% Conv. 2	μmol S5	μmol 4	S5/4 ratio
HNPh ₂	1	42	2.8	0.0	100/0
NBn ₃	4	71	5.4	0.1	97/3
NEt ₃	9	100	11.8	37.9	24/76
NHiPr ₂	11	100	11.1	27.5	29/71
DBU	14	100	25.8	11.8	69/31
KOtBu	18	83*	6.1	1.1	85/15

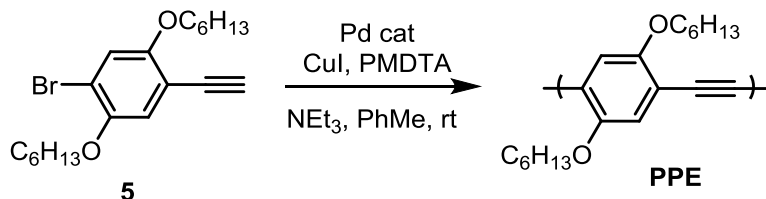
*This reaction produced 17% yield of 1,1'-(1,2-ethynediyl)bis(4-methylbenzene) as a side-product.

Table S8. Data for reactions with 15-100% NEt₃ volume ratio.

Conditions: Solvent = PhMe/NEt₃ (**n** vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (1 equiv), CuI/PMDTA = 5 equiv (1:1 ratio).

ArX ₂	NEt ₃ (% vol)	% Conv. 2	μmol 3 or S5	μmol 4	3/4 or S5/4 ratio
S2	15	12	18.1	8.3	69/31
S2	25	46	24.7	30.1	45/55
S2	33	69	22.1	40.6	35/65
S2	50	94	16.0	58.8	21/79
S2	75	100	11.0	63.4	15/85
S2	100 (neat)	100	6.5	76.0	8/92
1	100 (neat)	100	1.2	55.5	4/96
1	100 (neat)	100	1.0	56.0	2/98

VII. Polymerization Results



Representative Procedure for PPE Polymerizations:

Prior to starting each batch of reactions, separate stock solutions in PhMe were made for **5** (0.050 M) with added internal standard (C₂₂H₄₆, ~3 mg), and CuI/PMDTA (0.050 M).

In the glovebox, a 4 mL vial was equipped with a stir bar. Gen 2 SPhos (1.3 μmol, 0.94 mg, 1.0 equiv) was then carefully measured out in the vial, and the mass was recorded. Sequentially, CuI/PMDTA (0.13 mL of 0.050 M stock solution, 5.0 equiv), and 0.11 mL PhMe were added with stirring to reach a total volume of 0.24 mL PhMe. Next, NEt₃ (1 mL, 33% by volume) and **5** (1.76 mL of 0.050 M stock solution, 67 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 2 days at rt. The vial was removed from the glovebox, quenched with HCl (12.1 M, 1 mL), and subsequently diluted with water (4 mL). The reaction was then extracted with DCM (3 x 3 mL). The combined organic layers were dried over MgSO₄. Conversion was determined relative to the initial concentration, using the internal standard as a reference via GC. To measure molecular weight and molecular weight distribution, the organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

Table S9. Data for polymerization screens with NEt₃ (variable volume)

Conditions: Solvent = PhMe/NEt₃ (n vol. ratio, 3 mL total vol.), temperature = rt, Pd = Gen 2 SPhos (1 equiv), CuI/PMDTA = 5 equiv (1:1 ratio).

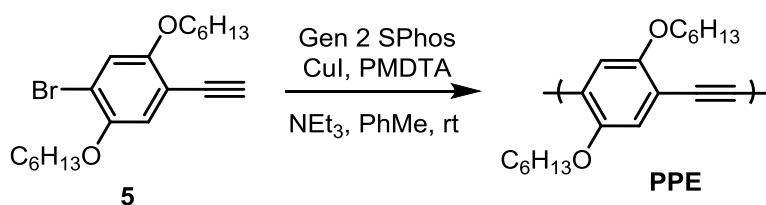
NEt ₃ (% vol)	% Conv. 5	M _n (predicted)	M _n (measured)	Đ
33	100	20.2	7.2	1.57
50	100	20.2	7.8	1.61

Table S10. Data for reactions with variable Pd precatalysts.

Conditions: Solvent = PhMe/NEt₃ (50/50 vol. ratio, 3 mL total vol.), temperature = rt, Pd = **precatalyst** (1 equiv), CuI/PMDTA = 5 equiv (1:1 ratio).

Catalyst	% Conv. 5	M _n (predicted)	M _n (measured)	Đ
Gen 1 SPhos	100	15.1	4.6	4.29
Gen 2 SPhos	100	24.8	10.1	4.76
Gen 3 SPhos	100	23.3	10.3	6.08
Gen 1 XPhos	100	22.0	8.2	1.99
Gen 2 XPhos	100	23.6	12.5	2.79
Gen 3 XPhos	100	25.4	11.9	3.00

VIII. M_n and \bar{D} versus Conversion



Representative Procedure for M_n and \bar{D} versus Conversion Studies utilizing GC analysis:

Prior to starting each batch of reactions, separate stock solutions in PhMe were made for **5** (0.50 M) with added internal standard (C₂₂H₄₆, ~3 mg), and CuI/PMDTA (0.050 M).

In the glovebox, a 20 mL vial was equipped with a stir bar. Gen 2 SPhos (0.013 mmol, 9.1 mg, 1.0 equiv) was then carefully measured out in the vial, and the mass was recorded. Sequentially, CuI/PMDTA (1.26 mL of 0.050 M stock solution, 5.0 equiv), and 4.54 mL PhMe were added with stirring to reach a total volume of 5.80 mL PhMe. Next, NEt₃ (2.5 mL, 25% by volume) and **5** (1.70 mL of a 0.50 M stock solution, 67 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 30 h at rt. Samples (~0.5 mL) were taken periodically and removed from the glovebox, quenched with HCl (12.1 M, 1 mL), and subsequently diluted with water (4 mL). The sample was then extracted with DCM (3 x 3 mL). The combined organic layers were dried over MgSO₄. Conversion was determined relative to the initial concentration, using the internal standard as a reference via GC. To measure molecular weight and molecular weight distribution, the organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

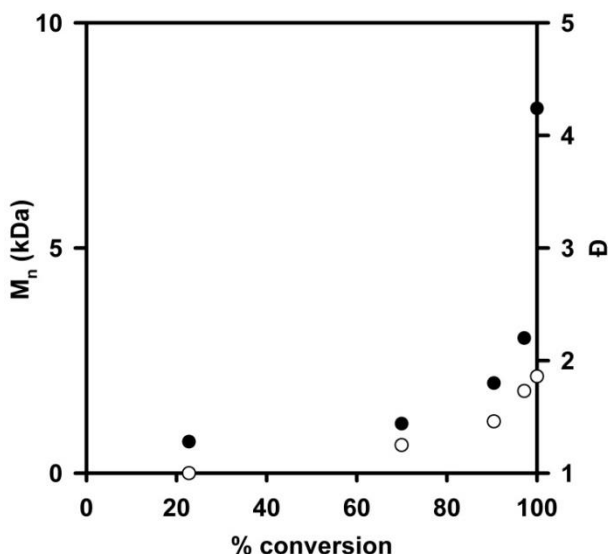


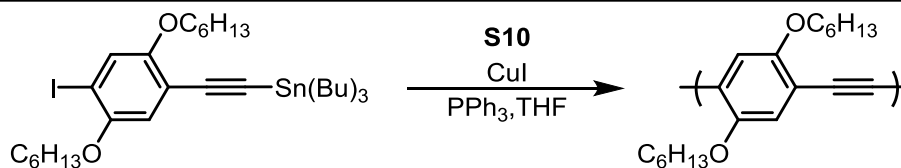
Figure S14. Plot of M_n (•) and \bar{D} (°) versus conversion utilizing the most favorable small molecule conditions.

Table S11. Data for the plot in **Figure S14**.

Time (min)	% Conv. 5	M_n	\bar{D}
50	23	0.7	1.00
125	70	1.1	1.25
190	90	2.0	1.46
240	97	3.0	1.73
1770	100	8.1	1.86

Procedures for M_n and \bar{D} versus Time Studies utilizing **S9** Monomer:

Method A:



In the glovebox, a 20 mL vial was equipped with a stir bar and charged with CuI (1.9 mg, 0.01 mmol, 0.1 equiv) and triphenylphosphine (2.6 mg, 0.1 mmol, 0.1 equiv), then **S9** (4 mL of a 0.025 M stock solution in THF, 0.10 mmol, 1 equiv) and **S10** (0.2 mL of a 0.01 M solution in THF, 0.02 equiv) were added. The reaction was stirred for 12 h at rt. Samples (~0.5 mL) were taken periodically and removed from the glovebox, quenched with DI water/MeOH (1:4, 1 mL), and subsequently extracted with DCM (2 x 3 mL). The combined

organic layers were dried over MgSO_4 . To measure molecular weight and molecular weight distribution, the organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

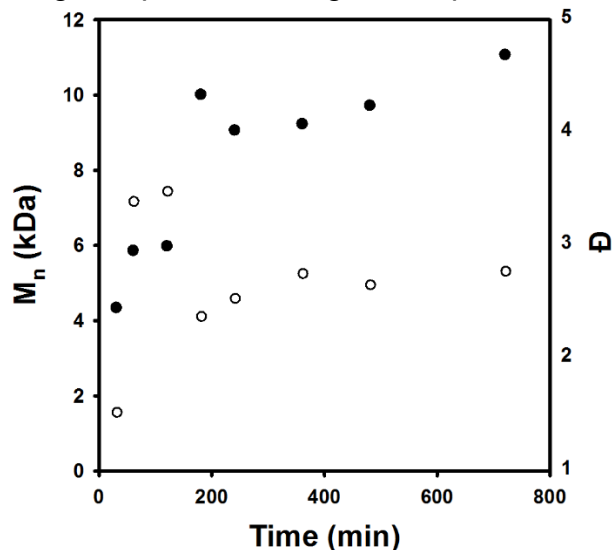
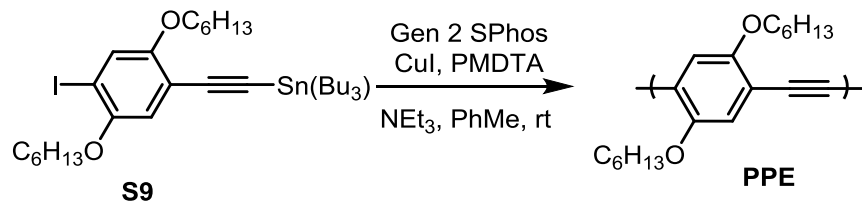


Figure S15. Plot of M_n (•) and \bar{D} (°) versus time utilizing **S9** monomer and previously reported chain-growth conditions.⁴

Table S12. Data for the plot in **Figure S15**.

Time (min)	M_n	\bar{D}
30	4.4	1.49
60	5.9	3.36
120	6.0	3.45
180	10.0	2.34
240	9.1	2.50
360	9.2	2.72
480	9.7	2.62
720	11.1	2.74

Method B:



In the glovebox, a 20 mL vial was equipped with a stir bar. Gen 2 SPhos (0.0026 mmol, 1.9 mg, 1.0 equiv) was then carefully measured out in the vial. Sequentially, an aliquot of a stock solution (0.19 mL) containing CuI (0.050 M) and PMDTA (0.050 M) and PhMe (1.6 mL) were added with stirring to reach a total volume of 1.79 mL PhMe. Next, NEt₃ (1.47 mL, 25% by volume) and **S9** (2.6 mL of a 0.050 M stock solution, 50 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 12 h at rt. Samples (~0.5 mL) were taken periodically and removed from the glovebox, quenched with HCl (12.1 M, 1 mL), and subsequently diluted with water (4 mL). The sample was then extracted with DCM (3 x 3 mL). The combined organic layers were dried over MgSO₄. To measure molecular weight and molecular weight distribution, the organic phase was concentrated in vacuo, redissolved in THF (~1.5 mL) with mild heating and passed through a 0.2 μm PTFE filter for GPC analysis.

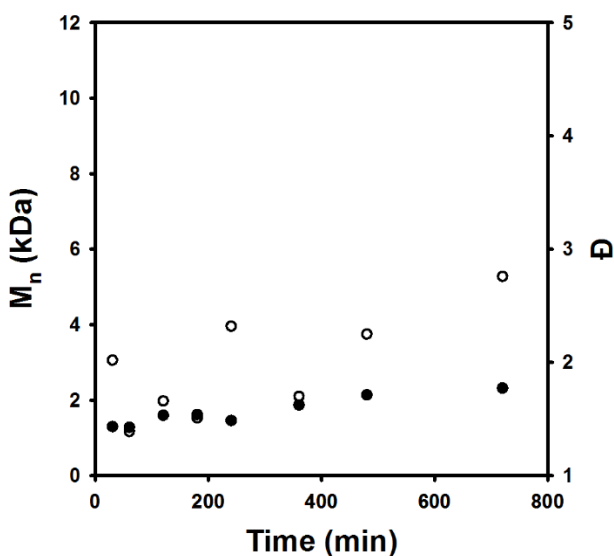
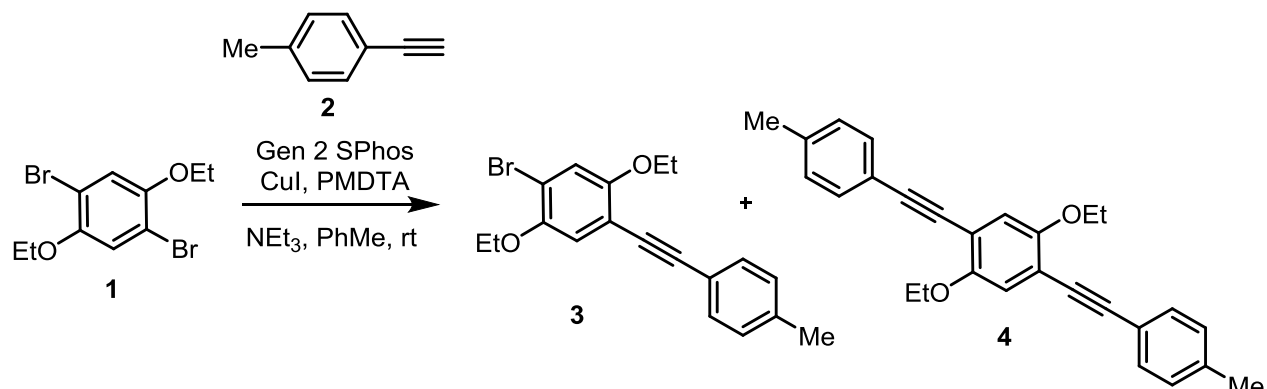


Figure S16. Plot of M_n (•) and Đ (°) versus time utilizing **S9** monomer and the most favorable small molecule conditions.

Table S13. Data for the plot in **Figure S16**

Time (min)	M_n	\bar{D}
30	1.3	2.02
60	1.3	1.39
120	1.6	1.66
180	1.6	1.51
240	1.5	2.32
360	1.9	1.7
480	2.1	2.25
720	2.3	2.76

IX. Small Molecule Reaction Profiles



Representative Procedure for Sonogashira Small Molecule Reaction Profile utilizing GC analysis:

Prior to starting each batch of reactions, separate stock solutions in PhMe were made for **1** (0.50 M), **2** (0.50 M) with added internal standard (C₂₂H₄₆, ~3 mg), and CuI/PMDTA (0.050 M).

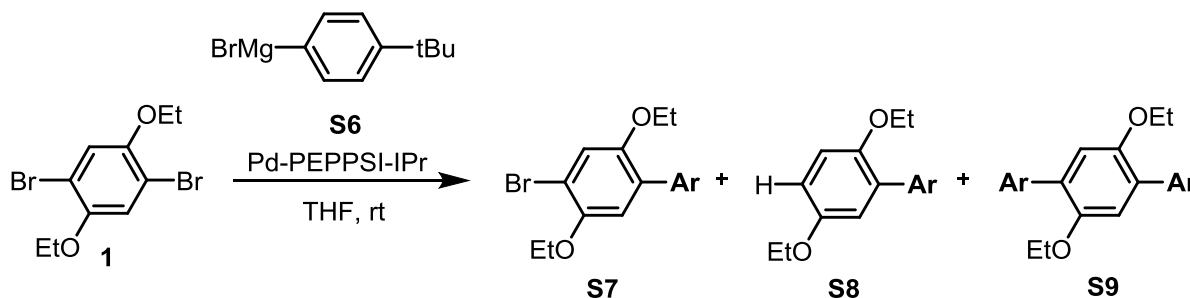
In the glovebox, a 20 mL vial was equipped with a stir bar. Gen 2 SPhos (5.8 mg, 0.0075 mmol, 1.0 equiv) was then carefully measured out in the vial, and the mass was recorded. Sequentially CuI/PMDTA (0.76 mL of 0.050 M stock solution, 5.0 equiv), **1** (1.2 mL of 0.50 M stock solution, 80 equiv), and 3.84 mL PhMe were added with stirring to reach a total volume of 5.80 mL PhMe. Next, NEt₃ (6 mL, 50% by volume) and **2** (0.2 mL of 0.50 M stock solution, 40 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 24 h at rt. Samples (~0.5 mL) were taken periodically and removed from the glovebox, quenched with HCl (12.1 M, 1 mL), and subsequently diluted with water (4 mL). The sample was then extracted with DCM (2 x 3 mL). The combined organic layers were dried over MgSO₄. Conversion was determined relative to the initial concentration, using the internal standard as a reference via GC.

Table S14. Data for Sonogashira small molecule reaction profile, trial 1.

Time (h)	% Conv. 2	% 3	% 4
1	6	100	0
2	19	92	8
3	27	77	23
5	46	37	63
22	100	9	91

Table S15. Data for Sonogashira small molecule reaction profile, trial 2.

Time (h)	% Conv. 2	% 3	% 4
2	18	100	0
3	28	95	5
4	52	50	50
5	57	36	64
22	100	9	91



Representative Procedure for Sonogashira Small Molecule Reaction Profile utilizing GC analysis:

Prior to starting each batch of reactions, separate stock solutions in THF were made for **1** (0.50 M), Pd-PEPPSI-IPr (0.050 M), and **S6** (0.25 M) with added internal standard (C₂₂H₄₆, ~3 mg).

In the glovebox, a 20 mL vial was equipped with a stir bar. Pd-PEPPSI-IPr (0.15 mL of 0.050 M stock solution, 1.0 equiv) was then added to the vial with stirring. Sequentially **1** (1.2 mL of 0.50 M stock solution, 80 equiv), and 9.45 mL THF were added with stirring to reach a total volume of 10.80 mL THF. Next, **S6** (1.2 mL of 0.25 M stock solution, 40 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 60 min at rt. Samples (~0.5 mL) were taken periodically and removed from the glovebox, quenched with HCl (12.1 M, 1 mL), and subsequently diluted with water (4 mL). The sample was then extracted with DCM (2 x 3 mL). The combined organic layers were dried over MgSO₄. Conversion was determined relative to the initial concentration, using the internal standard as a reference via GC.

Table S16. Data for Kumada small molecule reaction profile, trial 1.

Time (min)	% Conv. S6	% S7	% S8 + S9
0.5	25	0	100
1.5	32	1	99
2.5	39	0	100
3.5	45	5	95
5	49	6	94
7	53	7	93
60	100	8	92

Table S17. Data for Kumada small molecule reaction profile, trial 2.

Time (min)	% Conv. S6	% S7	% S8 + S9
0.5	30	0	100
2	44	0	100
2.5	50	3	97
3	55	4	96
3.5	60	7	93
4.5	64	8	92
5	77	8	92
60	100	9	91

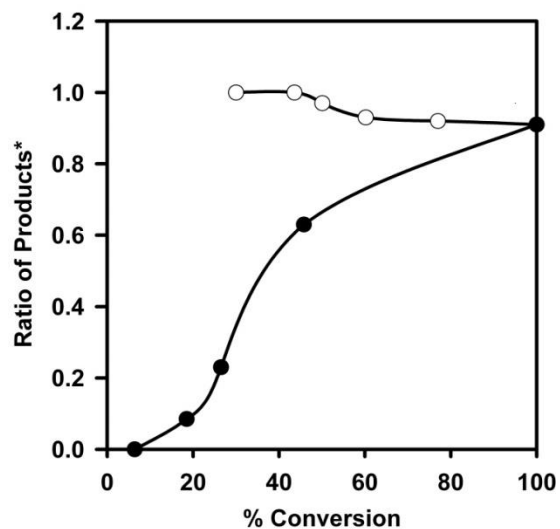


Figure S17. Plot of product ratios versus conversion from **Table 14** and **Table 17**. For Sonogashira (•) small molecule reactions, the product ratio is of compounds **4:3**. For Kumada (°) small molecule reactions, the product ratio is of compounds (**S8 + S9**):**S7** as both **S8** and **S9** stem from intramolecular pathways.

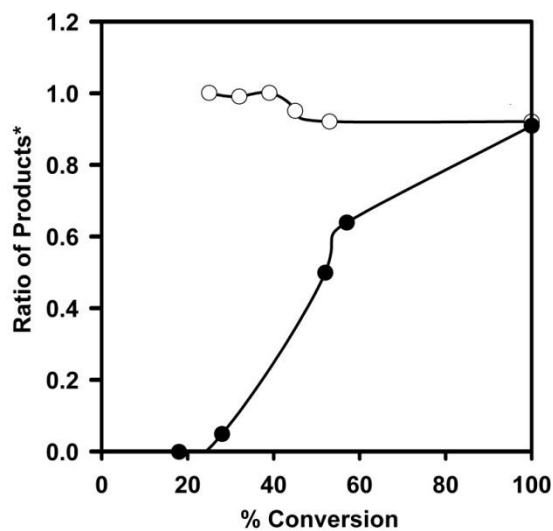
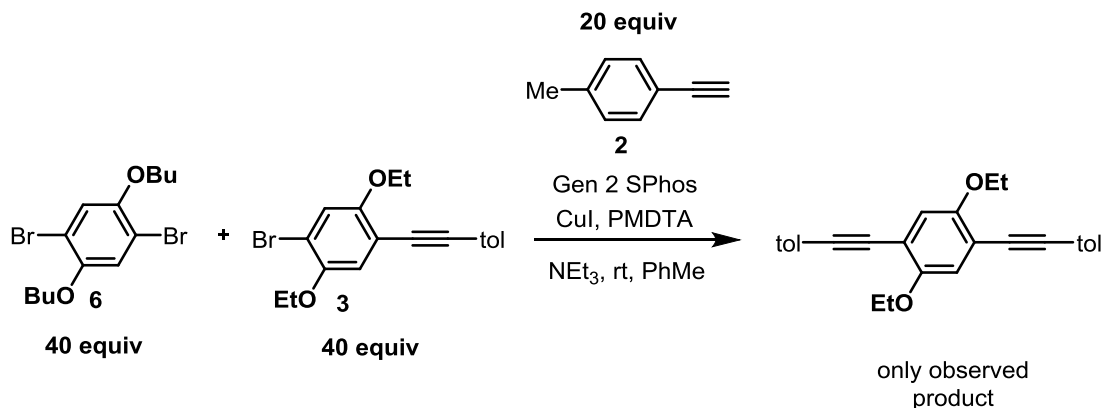


Figure S18. Plot of product ratios versus conversion from **Table 15** and **Table 16**. For Sonogashira (•) small molecule reactions, the product ratio is of compounds **4:3**. For Kumada (°) small molecule reactions, the product ratio is of compounds (**S8 + S9**):**S7** as both **S8** and **S9** stem from intramolecular pathways.

X. Competition Experiments



Representative Procedure for Sonogashira Reactivity Competition Experiments:

Prior to starting each batch of reactions, separate stock solutions in PhMe were made for C₁₉H₄₀ internal standard (0.050 M), **6** (0.20 M), **3** (0.20 M), and CuI/PMDTA (0.050 M).

In the glovebox, a 4 mL vial was equipped with a stir bar. Pd catalyst (1.9 mg, 0.0025 mmol, 1.0 equiv) was then carefully measured out in the vial, and the mass was recorded. Sequentially, CuI/PMDTA (0.25 mL of 0.050 M stock solution, 5.0 equiv), **6** (0.50 mL of 0.20 M stock solution, 40 equiv), **3** (0.50 mL of 0.20 M stock solution, 40 equiv), C₁₉H₄₀ internal standard (0.25 mL of 0.050 M stock solution, 5.0 equiv), and 0.50 mL PhMe were added with stirring to reach a total volume of 2.0 mL PhMe. Next, NEt₃ (1 mL, 33% by volume) and **2** (13 μ L, 0.10 mmol, 40 equiv) were added to the vial. The cap was secured tightly and the reaction was stirred for 2 days at rt. The vial was removed from the glovebox and the reaction was quenched with HCl (12.1 M, 3 mL) and subsequently diluted with water (8 mL). The reaction mixture was then extracted with DCM (2 x 3 mL), and the combined organic layers were dried over MgSO₄, filtered through a 0.2 μ m PTFE filter, and subjected to GC analysis.

GC analysis showed exclusively conversion of the mono-functionalized starting material (**3**), and also showed only formation of the di-functionalized product (**4**) labeled with ethoxy side-chains, indicating that it originated from **3**. This experiment was performed twice with the same results.

XI. Calibration Curves

Representative Procedure for Preparing Calibration Curves:

A stock solution was made by weighing ~75 mg of each compound into a 25 mL volumetric flask which was then filled with DCM. A separate stock solution of internal standard ($C_{19}H_{40}$) was also made by placing ~75 mg into a 25 mL volumetric flask and then diluting with DCM. These stock solutions were used to make 5 samples with known concentrations within the expected range of concentrations of the experiment (0.05 mmol – 0.0005 mmol for compounds **4**, 0.1 mmol – 0.01 mmol for compound **3**). Each of these samples was analyzed by GC and the areas plotted against the known concentrations to produce a calibration curve. The process was performed twice per compound and the ratios were averaged.

These calibration curves were used to convert the GC product area ratio of **3:4** into mol product ratios of **3:4**. These calibration curves were also used to determine the conversion of **2**, the μmol of **S5**, the μmol of **3**, and μmol of **4** found in **VI** (small molecule screens).

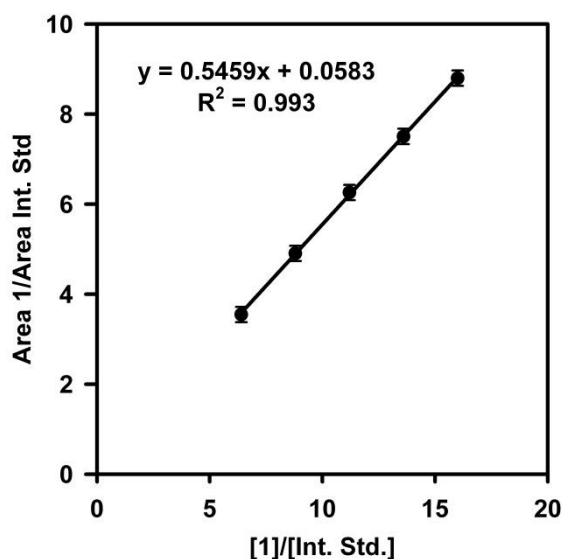


Figure S19. Calibration curve for **1**, points include error bars.

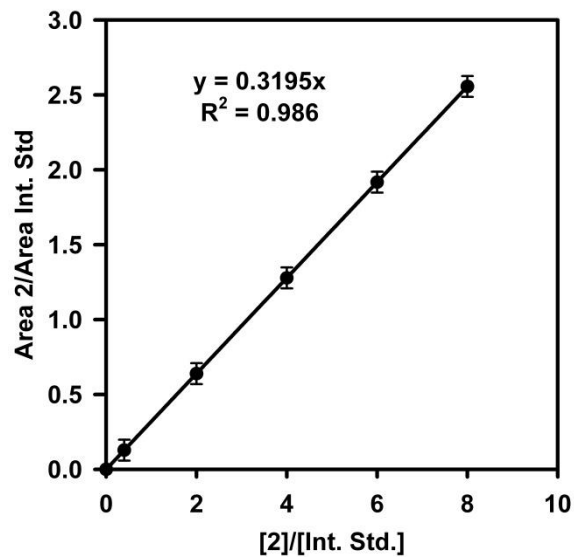


Figure S20. Calibration curve for 2, points include error bars.

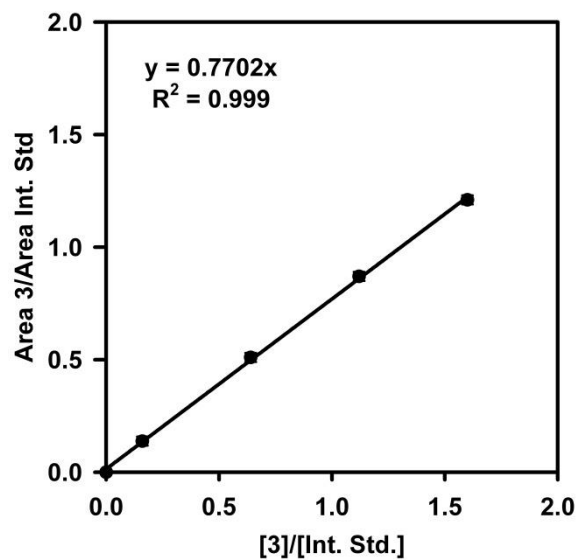


Figure S21. Calibration curve for 3, points include error bars.

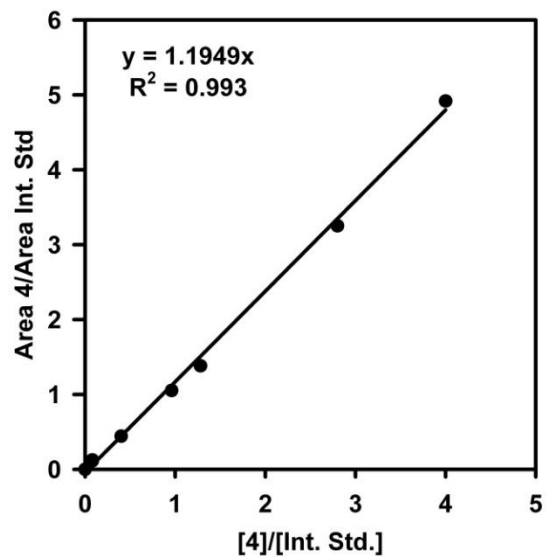


Figure S22. Calibration curve for 4.

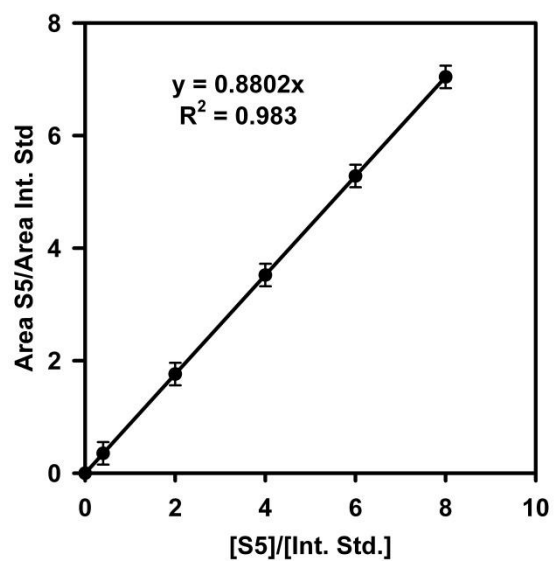


Figure S23. Calibration curve for S5, points include error bars.

XII. References

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