A New Family of Nucleophiles for Photoinduced, Copper-Catalyzed Cross-Couplings via Single-Electron Transfer: Reactions of Thiols with Aryl Halides Under Mild Conditions (0 °C)

Christopher Uyeda, Yichen Tan, Gregory C. Fu,* and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information

Table of Contents

I. General Information

Unless specified otherwise, all reagents were purchased from commercial vendors and used without further purification. CH_3CN was dried and degassed by passage through a column of activated alumina and sparging with N_2 gas. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc.

^{1}H and ^{13}C spectra were collected at room temperature on Varian 300, 400, or 500 MHz NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in ppm relative to tetramethylsilane, using the residual solvent resonance as an internal standard.

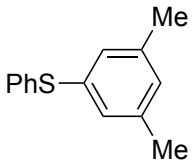
Single-crystal X-ray diffraction studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker KAPPA APEX II diffractometer. Data were collected at 100 K using Mo Kα radiation (λ = 0.71073 Å). Structures were solved by the direct method using SHELXS and refined against F2 on all data by full-matrix least-squares with SHELXL-97.

Elemental analysis was performed by Robertson Microlit Laboratories (Ledgewood, NJ). Fluorescence measurements (excitation and emission spectra) were taken in dry, degassed acetonitrile in a 1-cm quartz cuvette using a Horiba Jobin Yvon Fluorolog-3 instrument in the Beckmann Institute Laser Resource Center at Caltech.

II. Photoinduced, Copper-Catalyzed C–S Cross Couplings

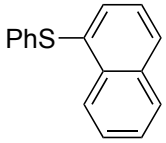
General procedure, Table 1. Under an atmosphere of N_2, a borosilicate glass tube was charged in turn with CuI (0.033 mmol, 10%), NaO*t*-Bu (0.33 mmol, 1.0 equiv), CH_3CN (1.0 mL), 1-iodo-3,5-dimethylbenzene (48 μL, 0.33 mmol, 1.0 equiv), and thiophenol (34 μL, 0.33 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5 h, Et_2O (10 mL) and dodecane (76 μL) were added, and the reaction was analyzed by GC.

General procedure, Table 2, 3, and 4. Under an atmosphere of N_2, a borosilicate glass tube was charged in turn with CuI (0.10 mmol, 10%), NaO*t*-Bu (1.0 mmol, 1.0 equiv), CH_3CN (3.0 mL), the aryl halide (1.0 mmol, 1.0 equiv), and the aryl thiol (1.0 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5–24 h, the volatiles were removed under reduced pressure. The residue was suspended in Et_2O, and the mixture was filtered through a short plug of Celite. The filtrate was concentrated, and the residue was purified by column chromatography.

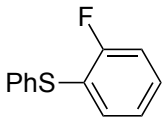


3,5-Dimethylphenyl phenyl sulfide (Table 2, entry 1) [457625-29-5]. According to the general procedure, 1-iodo-3,5-dimethylbenzene (144 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 194 mg (91% yield). Run 2: 180 mg (84% yield).

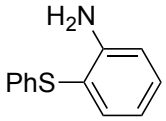
Gram-scale reaction (Table 2, entry 1). According to the general procedure, 1-iodo-3,5-dimethylbenzene (1.54 mL, 8.0 mmol, 1.0 equiv) and thiophenol (822 μL, 8.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. After purification by column chromatography (SiO_2, hexanes), 1.40 g (82% yield) of 3,5-dimethylphenyl phenyl sulfide was isolated as a colorless oil.



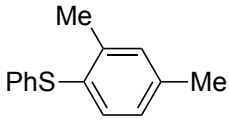
1-Naphthyl phenyl sulfide (Table 2, entry 2) [7570-98-1]. According to the general procedure, 1-iodonaphthalene (146 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 198 mg (84% yield). Run 2: 189 mg (80% yield).



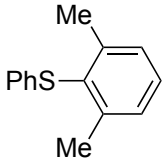
2-Fluorophenyl phenyl sulfide (Table 2, entry 3) [61900-51-4]. According to the general procedure, 2-fluoroiodobenzene (117 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 161 mg (79% yield). Run 2: 158 mg (77% yield).



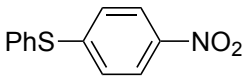
2-Aminophenyl phenyl sulfide (Table 2, entry 4) [134-94-7]. According to the general procedure, 2-aminoiodobenzene (219 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 8 h. The product (yellow oil) was purified by column chromatography (SiO_2, hexanes → 1:10 Et_2O:hexanes). Run 1: 149 mg (74% yield). Run 2: 152 mg (76% yield).



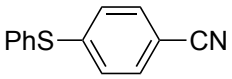
2,4-Dimethylphenyl phenyl sulfide (Table 2, entry 5) [16704-47-5]. According to the general procedure, 1-iodo-2,4-dimethylbenzene (144 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 172 mg (80% yield). Run 2: 161 mg (75% yield).



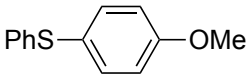
2,6-Dimethylphenyl phenyl sulfide (Table 2, entry 6) [54088-93-6]. According to the general procedure, 1-iodo-2,6-dimethylbenzene (144 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 8 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes): 158 mg (74% yield). Run 2: 152 mg (71% yield)



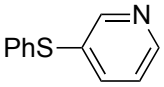
4-Nitrophenyl phenyl sulfide (Table 2, entry 7) [952-97-6]. According to the general procedure, 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (pale-yellow oil) was purified by column chromatography (SiO_2, hexanes → 1:1 Et_2O:hexanes). Run 1: 207 mg (90% yield). Run 2: 206 mg (89% yield).



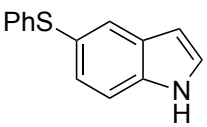
4-Cyanophenyl phenyl sulfide (Table 2, entry 8) [51238-46-1]. According to the general procedure, 4-iodo-benzonitrile (229 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes → 1:10 Et_2O:hexanes). Run 1: 174 mg (82% yield). Run 2: 163 mg (76% yield).



4-Methoxyphenyl phenyl sulfide (Table 2, entry 9) [5633-57-8]. According to the general procedure, 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 171 mg (79% yield). Run 2: 169 mg (78% yield).

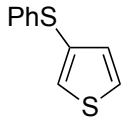


3-(Phenylthio)pyridine (Table 2, entry 10) [28856-77-1]. According to the general procedure, 3-iodopyridine (205 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, 1:5 EtOAc:hexanes). Run 1: 155 mg (83% yield). Run 2: 150 mg (80% yield).

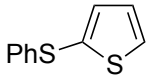


5-(Phenylthio)-1*H*-indole (Table 2, entry 11) [163258-14-8]. According to the general procedure, 5-iodoindole (243 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0

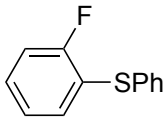
equiv) were reacted at 0 °C for 5 h. The product (colorless solid) was purified by column chromatography (SiO_2, 1:10 EtOAc:hexanes). Run 1: 145 mg (64% yield). Run 2: 138 mg (61% yield).



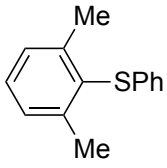
3-(Phenylthio)thiophene (Table 2, entry 12) [16718-11-9]. According to the general procedure, 3-iodothiophene (210 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 138 mg (72% yield). Run 2: 135 mg (70% yield)



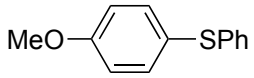
2-(Phenylthio)thiophene (Table 2, entry 13) [16718-12-0]. According to the general procedure, 2-iodothiophene (210 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 121 mg (63% yield). Run 2: 126 mg (66% yield).



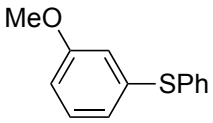
2-Fluorophenyl phenyl sulfide (Table 3, entry 1) [61900-51-4]. According to the general procedure, iodobenzene (112 μL, 1.0 mmol, 1.0 equiv) and 2-fluorothiophenol (107 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 152 mg (74% yield). Run 2: 147 mg (72% yield).



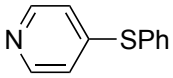
2,6-Dimethylphenyl phenyl sulfide (Table 3, entry 2) [54088-93-6]. According to the general procedure, iodobenzene (112 μL, 1.0 mmol, 1.0 equiv) and 2,6-dimethylbenzenethiol (133 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 8 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 154 mg (72% yield). Run 2: 148 mg (69% yield).



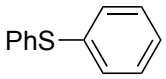
4-Methoxyphenyl phenyl sulfide (Table 3, entry 3) [5633-57-8]. According to the general procedure, iodobenzene (112 μL, 1.0 mmol, 1.0 equiv) and 4-methoxythiophenol (123 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 172 mg (80% yield). Run 2: 178 mg (82% yield)



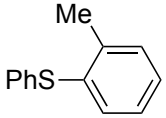
3-Methoxyphenyl phenyl sulfide (Table 3, entry 4) [30723-54-7]. According to the general procedure, iodobenzene (112 μL, 1.0 mmol, 1.0 equiv) and 3-methoxythiophenol (124 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, 1:50 EtOAc:hexanes). Run 1: 140 mg (65% yield). Run 2: 139 mg (64% yield).



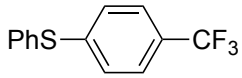
4-(Phenylthio)pyridine (Table 3, entry 5) [33399-48-3]. According to the general procedure, iodobenzene (112 μL, 1.0 mmol, 1.0 equiv) and 4-mercaptopyridine (111 mg, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 5 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes → Et_2O). Run 1: 139 mg (74% yield). Run 2: 136 mg (73% yield)



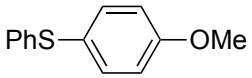
Diphenylsulfide (Table 4, entry 1) [139-66-2]. According to the general procedure, bromobenzene (105 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 139 mg (75% yield). Run 2: 131 mg (70% yield).



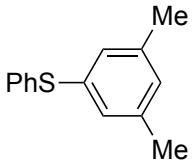
Phenyl *o*-tolyl sulfide (Table 4, entry 2) [13963-35-4]. According to the general procedure, 2-bromotoluene (120 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 119 mg (59% yield). Run 2: 119 mg (59% yield).



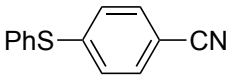
Phenyl 4-trifluoromethylphenyl sulfide (Table 4, entry 3) [53451-90-4]. According to the general procedure, 1-bromo-4-(trifluoromethyl)benzene (140 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 178 mg (70% yield). Run 2: 177 mg (70% yield).



4-Methoxyphenyl phenyl sulfide (Table 4, entry 4) [5633-57-8]. According to the general procedure, 4-bromoanisole (187 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 24 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes). Run 1: 138 mg (64% yield). Run 2: 135 mg (63% yield).

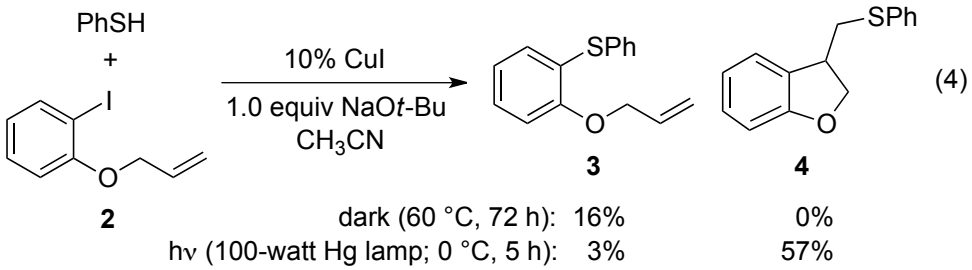


3,5-Dimethylphenyl phenyl sulfide (Eq. (2)) [457625-29-5]. According to the general procedure, 1-iodo-3,5-dimethylbenzene (144 μL, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at –40 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO_2, hexanes): 170 mg (80% yield).



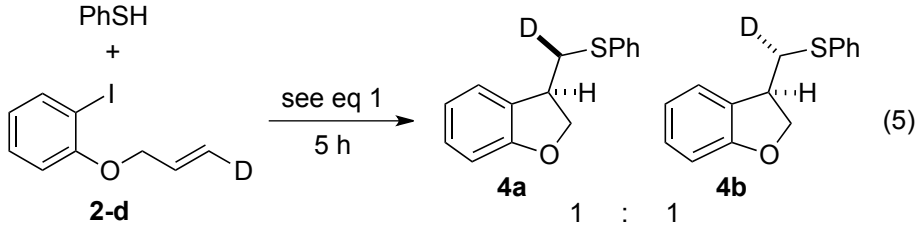
4-Cyanophenyl phenyl sulfide (Eq. (3)) [51238-46-1]. According to the general procedure, 4-chlorobenzonitrile (138 mg, 1.0 mmol, 1.0 equiv) and thiophenol (103 μL, 1.0 mmol, 1.0 equiv) were reacted at 0 °C for 12 h. The product (colorless oil) was purified by column chromatography (SiO_2, 1:20 EtOAc:hexanes): 162 mg (77% yield).

III. Cyclization and Isotopic Labeling Experiments [Eq. (4) and Eq. (5)]

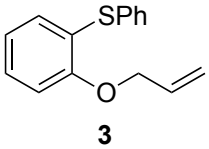


Under an atmosphere of N_2, a borosilicate glass tube was charged in turn with CuI (3.8 mg, 0.020 mmol, 10%), NaO*t*-Bu (19.2 mg, 0.20 mmol, 1.0 equiv), 2-allyloxy-1-iodobenzene (52.0 mg, 0.20 mmol, 1.0 equiv) in CH_3CN (0.50 mL), and thiophenol (22.0 mg, 0.20 mmol, 1.0 equiv) in CH_3CN (0.50 mL). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5 h, 1,3,5-trimethoxybenzene (33.6 mg, 0.20 mmol, 1.0 equiv) was added, and the volatiles were removed under reduced pressure. The residue was suspended in Et_2O, and the mixture was filtered through a short plug of Celite. The filtrate was concentrated, and the residue was then suspended in hexanes. The mixture was filtered through a short plug of Celite, and the filtrate was concentrated. Next, the reaction mixture was analyzed by ^{1}H NMR spectroscopy.

This procedure was repeated in the dark with a reaction time of 72 h at 60 °C.



The procedure above was repeated using the mono-deuterated substrate (**2-d**).[1] The reaction mixture was analyzed by ^{2}H{^{1}H} NMR.



2-(Allyloxy)phenyl phenyl sulfide (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 2 H), 7.34–7.28 (m, 2 H), 7.28–7.23 (m, 1 H), 7.20 (ddd, *J* = 1.8, 7.4, 8.2 Hz, 1 H), 7.09 (dd, *J* = 1.6, 7.6 Hz, 1 H), 6.93–6.83 (m, 2 H), 6.04–5.90 (m, 1 H), 5.38 (qd, *J* = 1.7, 17.2 Hz, 1 H), 5.24 (qd, *J* = 1.5, 10.6 Hz, 1 H), 4.59 (td, *J* = 1.7, 5.0 Hz, 2 H).

(1) For a preparation of **2-d**, see: S. E. Creutz, K. J. Lotito, G. C. Fu, J. C. Peters, *Science* **2012**, *338*, 647–651.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.4, 134.7, 133.0, 131.9, 131.6, 129.2, 128.2, 127.2, 125.1, 121.6, 117.6, 112.6, 69.5.

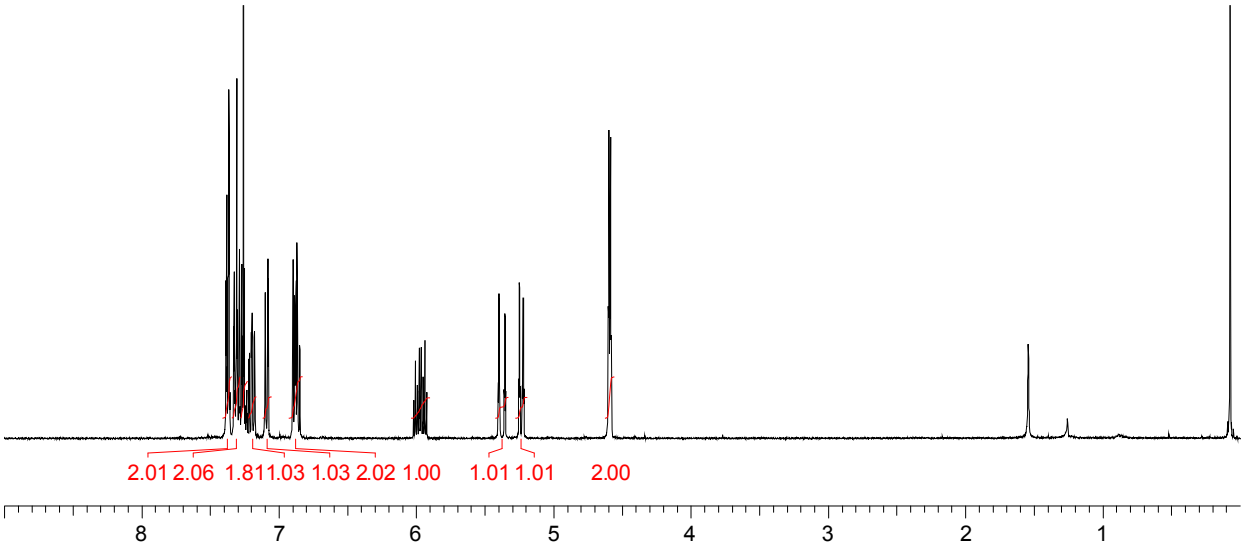


Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of **3**.

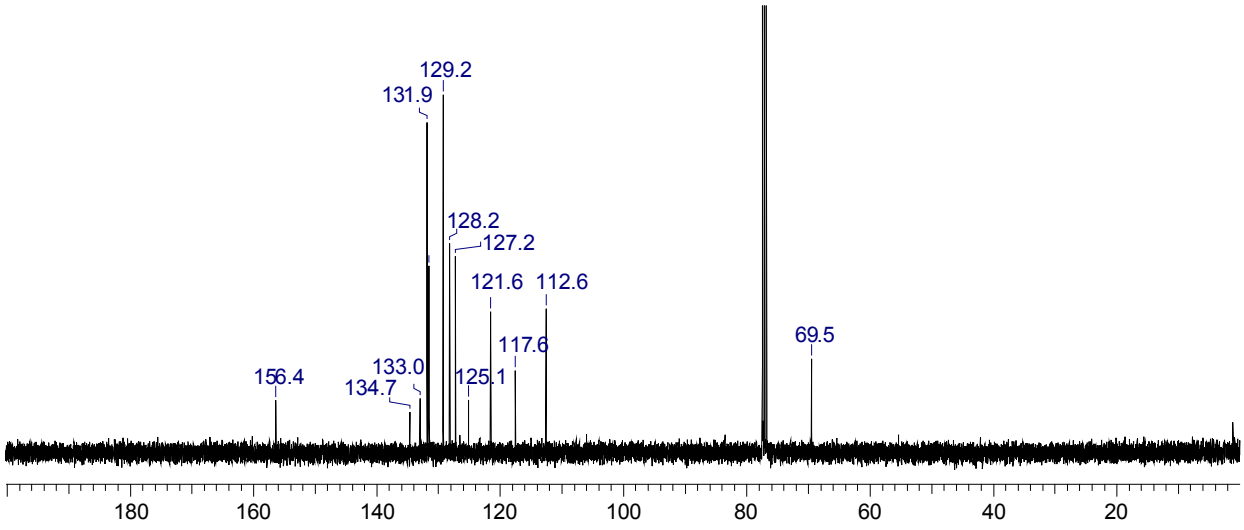
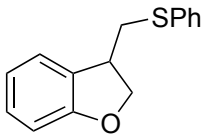


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **3.**



4

3-(Phenylthiomethyl)-2,3-dihydrobenzofuran (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.37 (m, 2 H), 7.36–7.28 (m, 2 H), 7.28–7.19 (m, 2 H), 7.19–7.12 (m, 1 H), 6.88 (dt, *J* = 0.9, 7.5 Hz, 1 H), 6.81 (d, *J* = 8.1 Hz, 1 H), 4.63 (t, *J* = 9.0 Hz, 1 H), 4.45 (dd, *J* = 5.7, 9.2 Hz, 1 H), 3.64 (tt, *J* = 5.2, 9.4 Hz, 1 H), 3.33 (dd, *J* = 4.9, 12.7 Hz, 1 H), 3.02 (dd, *J* = 9.7, 13.0 Hz, 1 H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.1, 135.6, 130.1, 129.2, 129.0, 126.7, 124.7, 120.7, 110.0, 76.2, 41.8, 39.0.

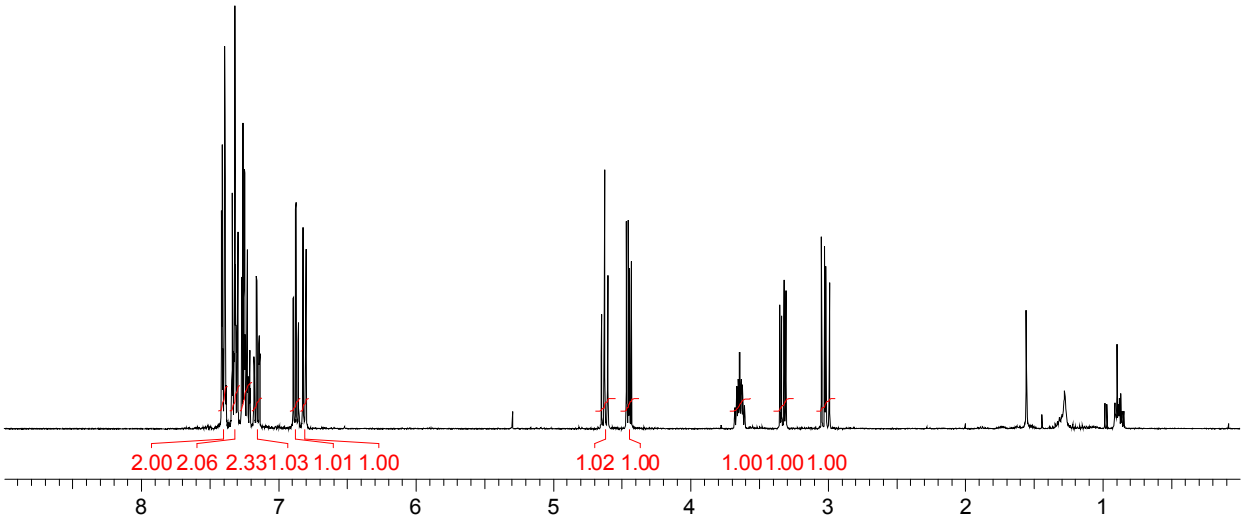


Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of **4**.

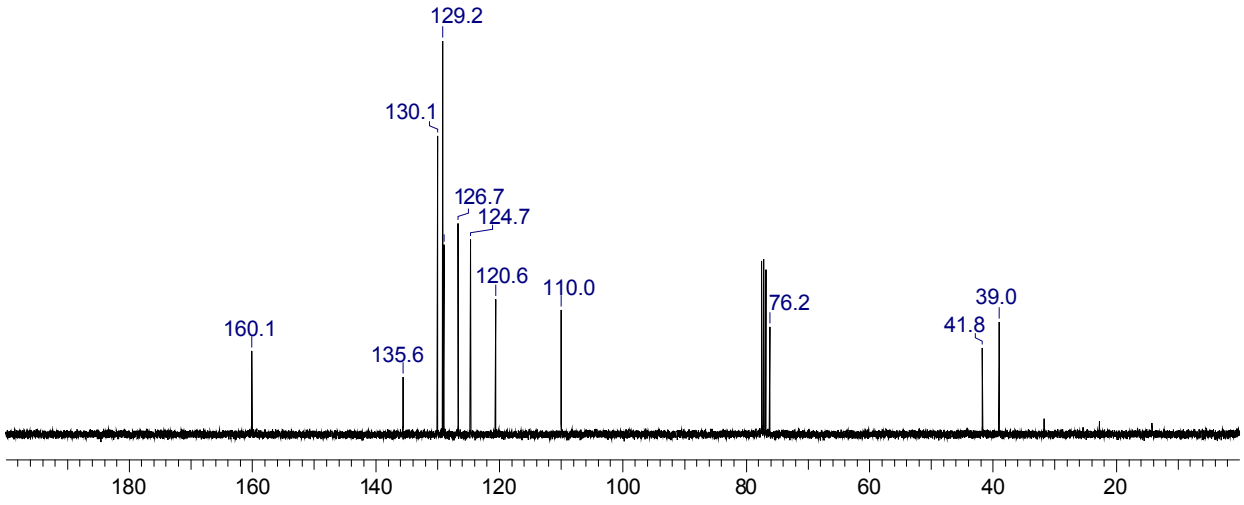


Figure S4. ^{13}C{^{1}H} NMR spectrum ($CDCl_3$) of **4.**

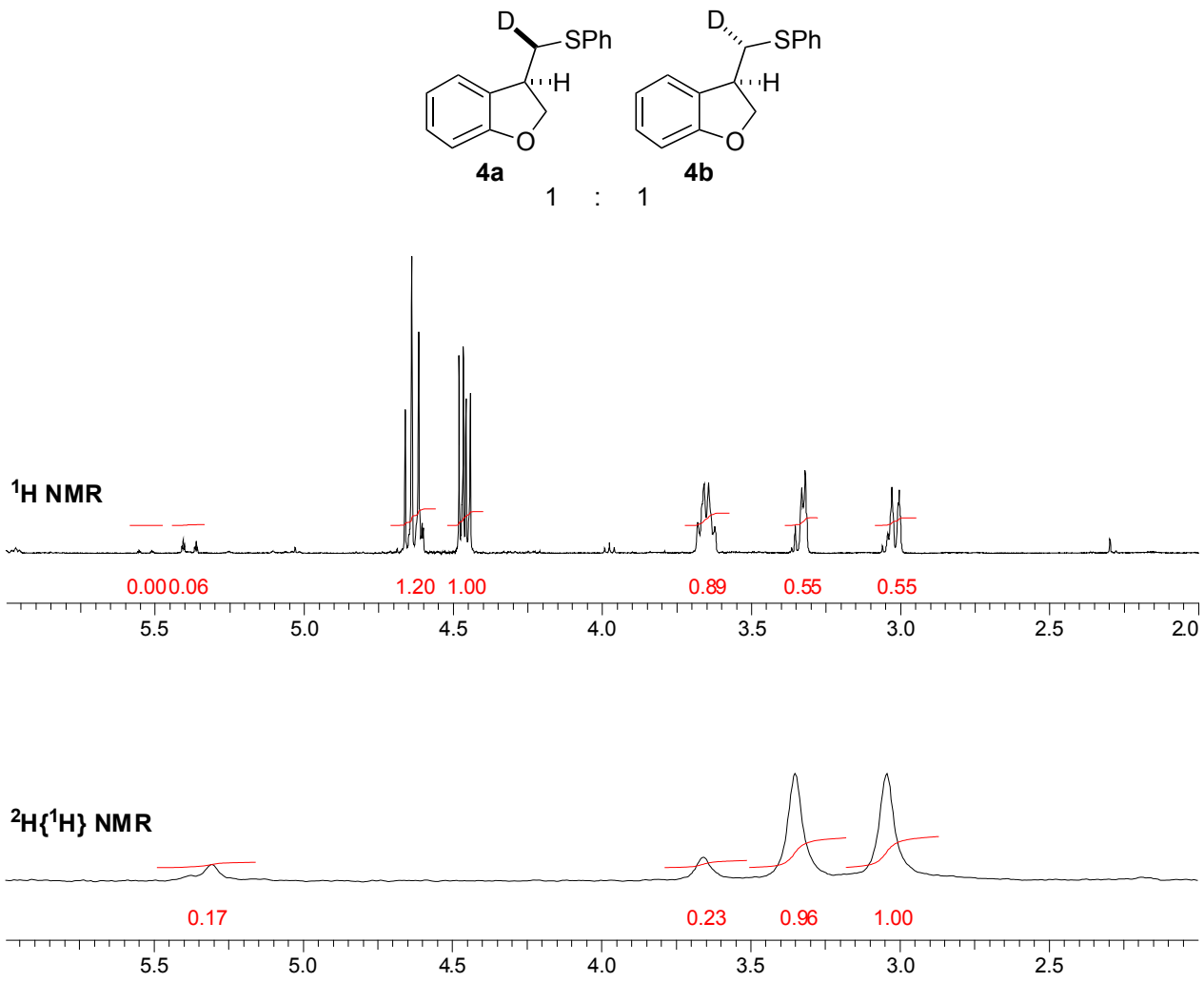
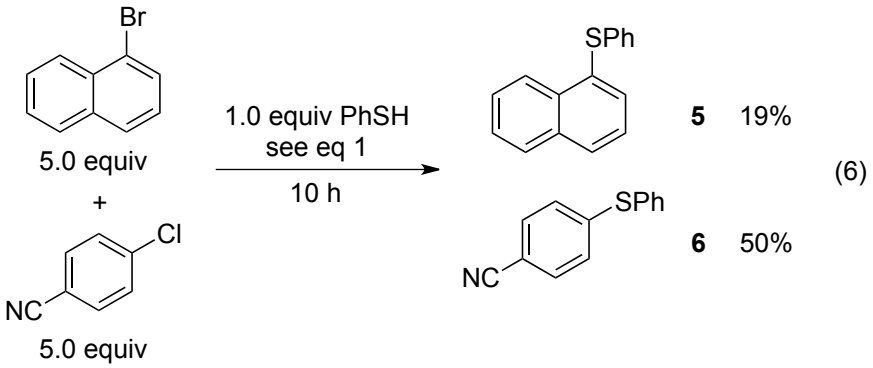


Figure S5. ^{1}H NMR and $^{2}H\{^{1}H\}$ NMR spectra ($CDCl_3/CHCl_3$) of the unpurified reaction mixture from the cross-coupling of **2-d**. Unreacted **2-d** is at 5.3 ppm.

IV. Competition Experiment [Eq. (6)]



Under an atmosphere of N_2, a borosilicate glass tube was charged in turn with CuI (9.5 mg, 0.050 mmol, 10%), NaO*t*-Bu (48.1 mg, 0.50 mmol, 1.0 equiv), 4-chlorobenzonitrile (344 mg, 2.5 mmol, 5.0 equiv), CH_3CN (1.5 mL), 1-bromonaphthalene (350 μL, 2.5 mmol, 5.0 equiv), and thiophenol (51 μL, 0.50 mmol, 1.0 equiv). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 10 h, Et_2O (10 mL) and dodecane (114 μL) were added, and then the mixture was analyzed by GC.

V. Synthesis and Reactivity of $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$

$[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$. Under an atmosphere of N_2, a vial was charged with CuI (190 mg, 1.0 mmol, 1.0 equiv), NaO*t*-Bu (96.1 mg, 1.0 mmol, 1.0 equiv), CH_3CN (1.0 mL), and thiophenol (103 μL, 1.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 15 min, and then it was filtered through a short plug of Celite. 12-Crown-4 (352 mg, 2.0 mmol, 2.0 equiv) was added to the filtrate, and then the mixture was filtered through a short plug of Celite. The filtrate (total volume: 2 mL) was allowed to stand at room temperature. After 12 h, X-ray quality crystals of $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$ had formed (yellow crystalline solid; see Section VI).

$[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$. Under an atmosphere of N_2, a vial was charged with CuCl (99 mg, 1.0 mmol, 1.0 equiv), NaO*t*-Bu (96.1 mg, 1.0 mmol, 1.0 equiv), CH_3CN (1.0 mL), and thiophenol (103 μL, 1.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature for 15 min, and then it was filtered through a short plug of Celite. 12-Crown-4 (352 mg, 2.0 mmol, 2.0 equiv) was added to the filtrate, and then the mixture was filtered through a short plug of Celite. The filtrate (total volume: 2 mL) was allowed to stand at room temperature. After 12 h, analytically pure $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$ (82 mg, 32% yield) was isolated as a yellow crystalline solid (X-ray quality crystals had the same unit cell as the crystals obtained in the previous paragraph with CuI as the starting material).

Elemental analysis calcd for $C_{74}H_{99}Cu_5Na_2O_{16}S_7$: C, 48.50; H, 5.44. Found: C, 48.27; H, 5.40.

Reaction of $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$ with 1-iodo-3,5-dimethylbenzene. Under an atmosphere of N_2, a tube was charged with $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$ (24.4 mg, 0.013 mmol, 1.0 equiv) and then a solution of 1-iodo-3,5-dimethylbenzene (22.0 mg, 0.093 mmol, 7.0 equiv) in CH_3CN (1.0 mL). The tube was sealed with a rubber septum, and then the heterogeneous reaction mixture was stirred at 0 °C, irradiating with a 100-watt Hg lamp. After 5 h, Et_2O (10 mL) and dodecane (20 μL) were added, and the reaction was analyzed by GC.

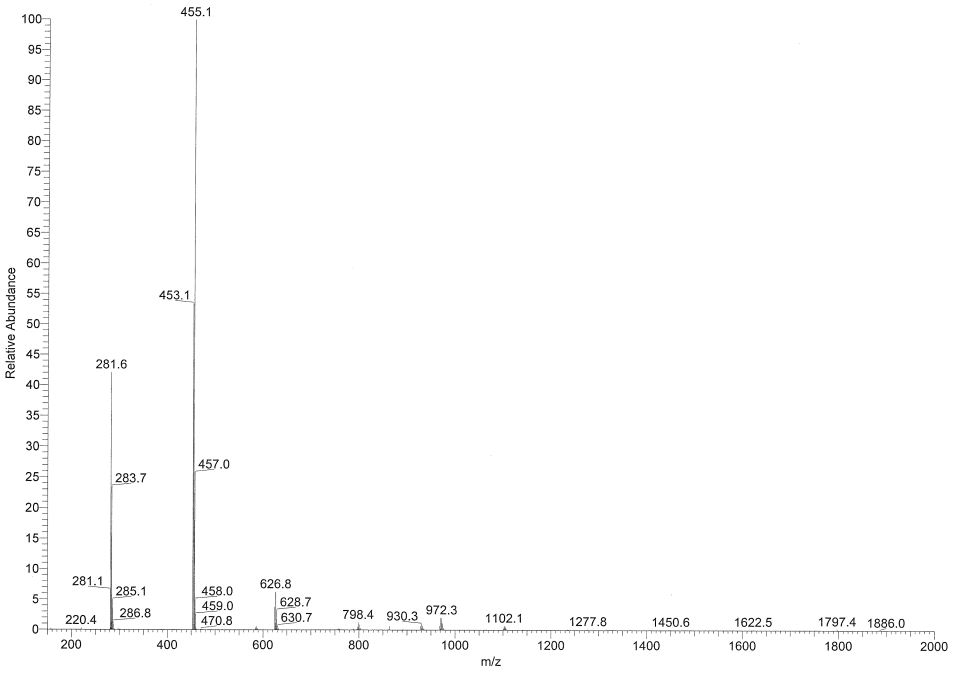


Figure S6. ESI–MS (negative) of $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$ (**1**) dissolved in CH_3CN.

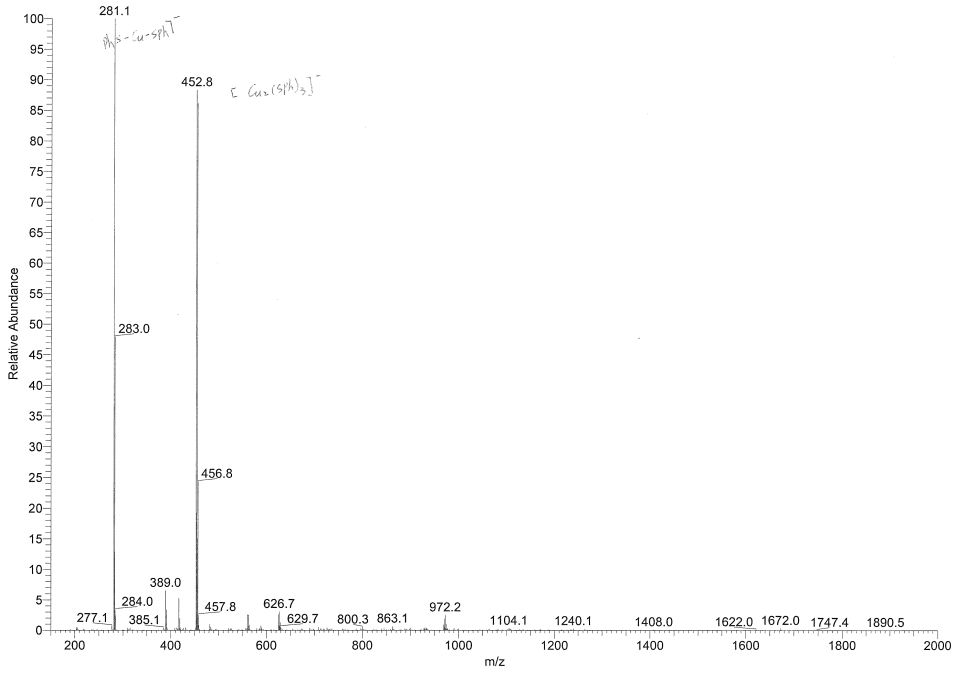
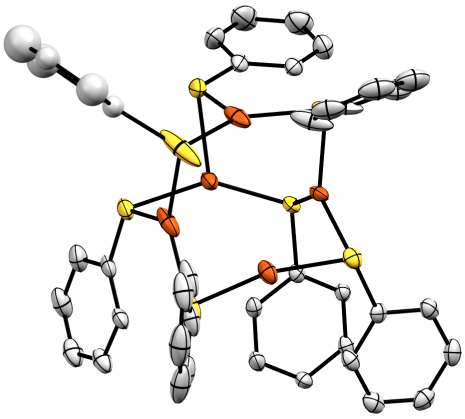


Figure S7. ESI–MS (negative) of an aliquot of a cross-coupling reaction mixture (PhSH, 1-iodo-3,5-dimethylbenzene, NaO*t*-Bu, 10% CuI, CH_3CN, 1 h, 0 °C, 100-watt Hg lamp).

VI. X-Ray Crystallographic Data for $[Cu_5(SPh)_7][Na(12\text{-crown-}4)_2]_2$



Empirical formula	$C_{74}H_{62}Cu_5Na_2O_{16}S_7$
Formula weight	1795.34
Temperature/K	373(2)
Crystal system	triclinic
Space group	P-1
a/Å	15.7407(6)
b/Å	15.7841(6)
c/Å	19.5588(8)
α/°	85.530(3)
β/°	71.368(2)
γ/°	61.411(2)
Volume/Å3	4026.9(3)
Z	2
ϱcalcmg/mm3	1.481
m/mm‐ 1	1.553
F(000)	1826.0
Crystal size/mm3	0.21 × 0.12 × 0.10
2Θ range for data collection	2.96 to 71.26°
Index ranges	-25 ≤ h ≤ 25, -23 ≤ k ≤ 25, -31 ≤ l ≤ 31
Reflections collected	150135
Independent reflections	33743[R(int) =0.0871]
Data/restraints/parameters	33743/0/874
Goodness-of-fit on F2	1.027
Final R indexes [I>=2σ (I)]	R1 = 0.1403, wR2 = 0.3776
Final R indexes [all data]	R1 = 0.2124, wR2 = 0.4232
Largest diff. peak/hole / e Å-3	9.48/-2. 26

VII. ^{1}H NMR Spectra of Cross-Coupling Products

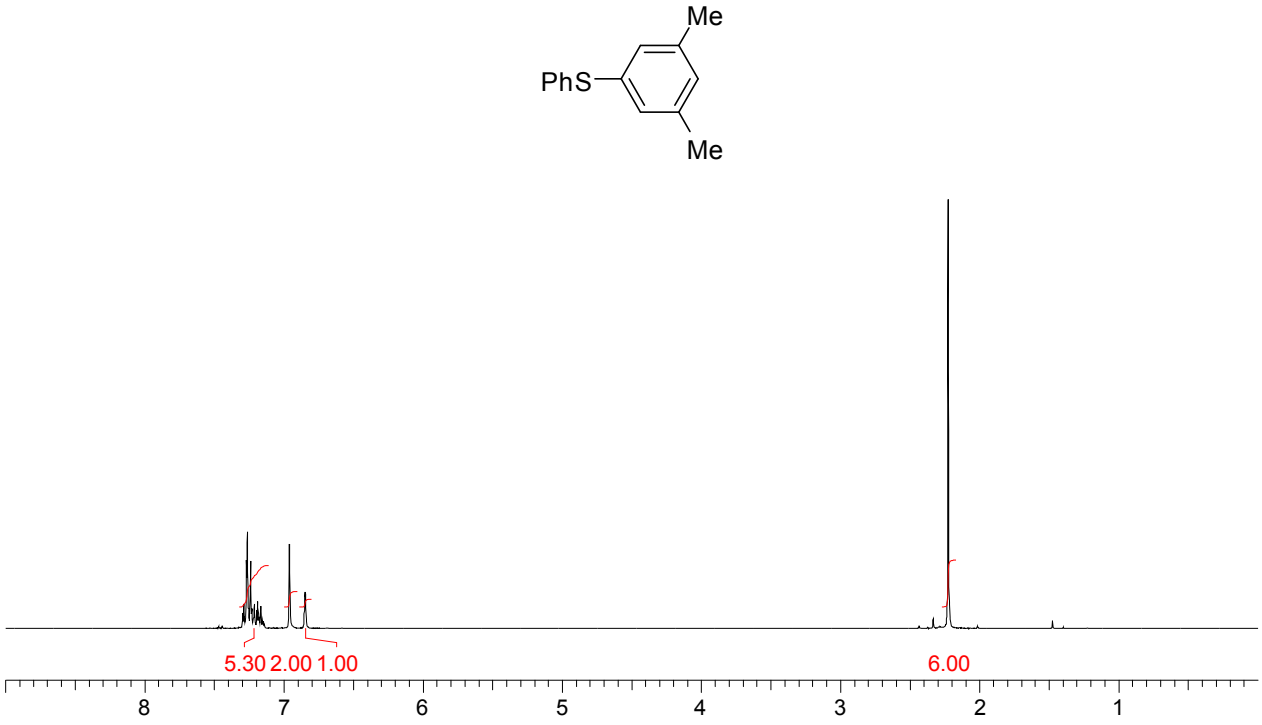


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 1.

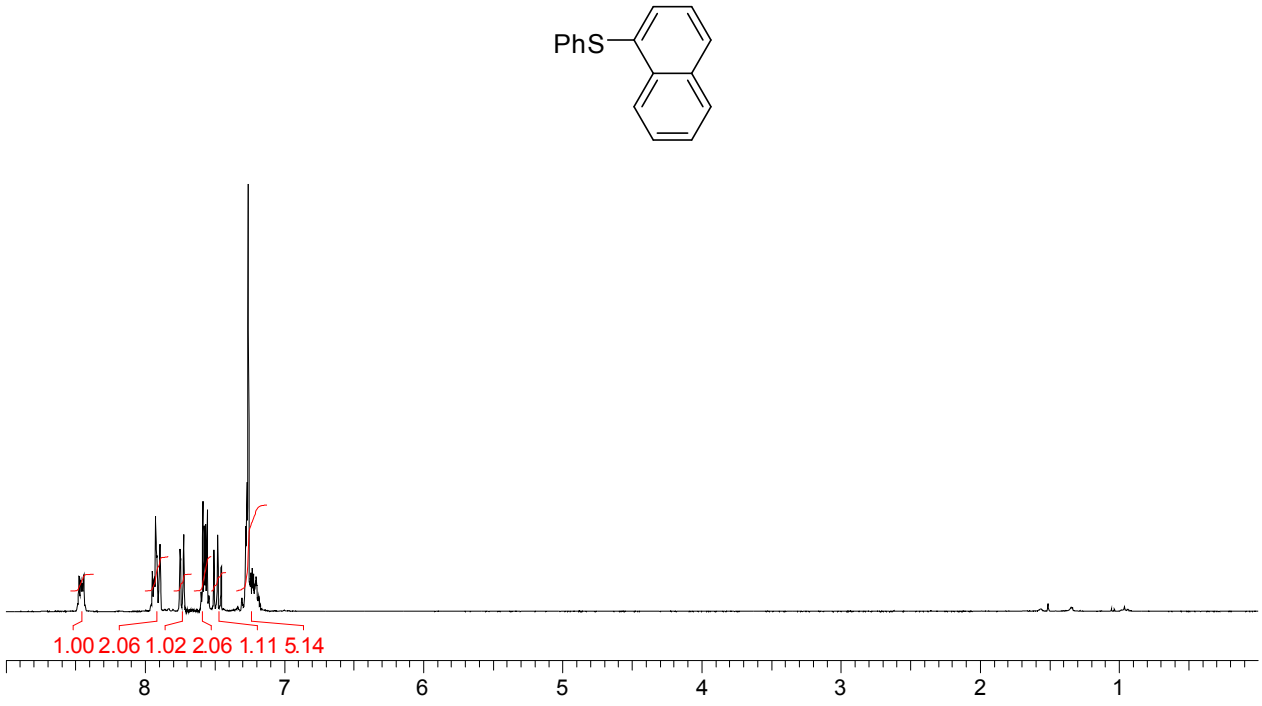


Figure S9. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 2.

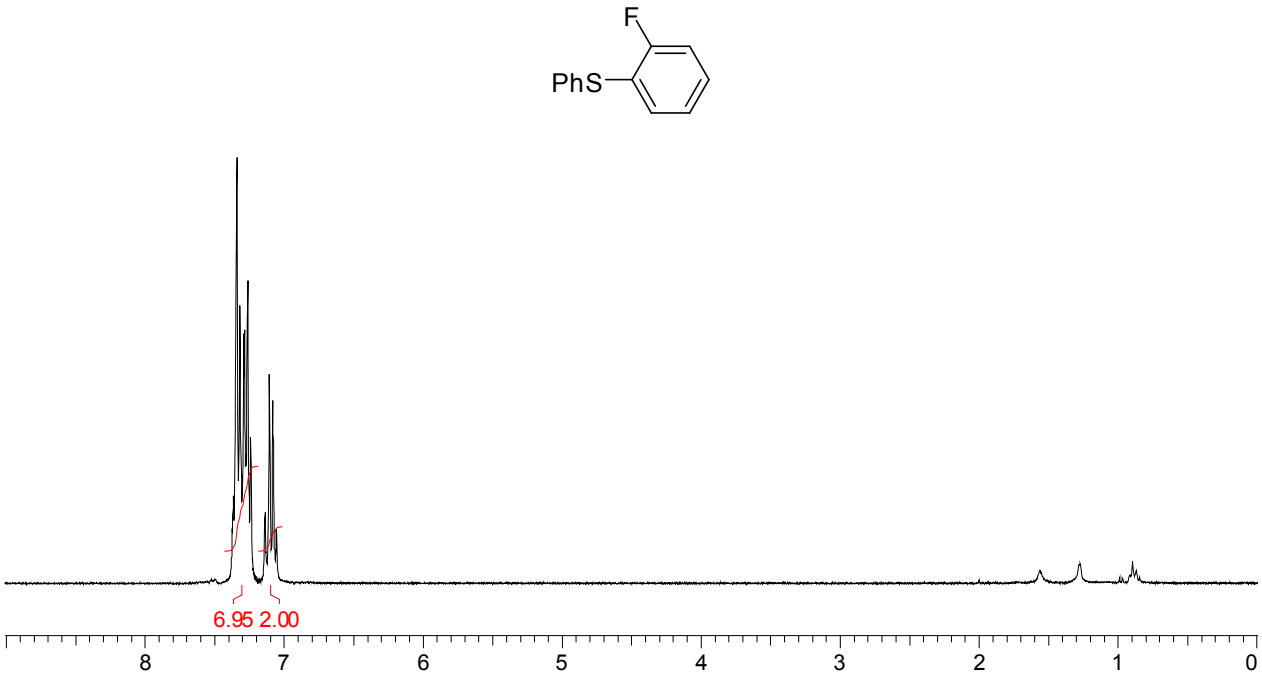


Figure S10. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 3.

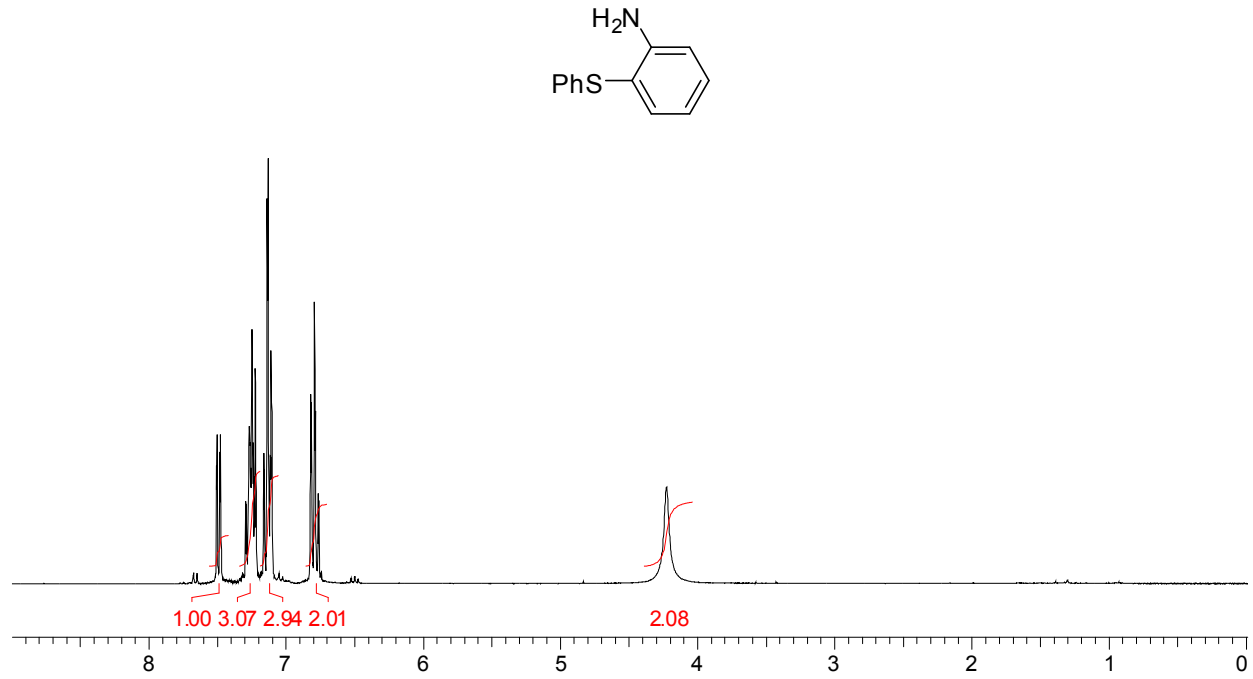


Figure S11. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 4.

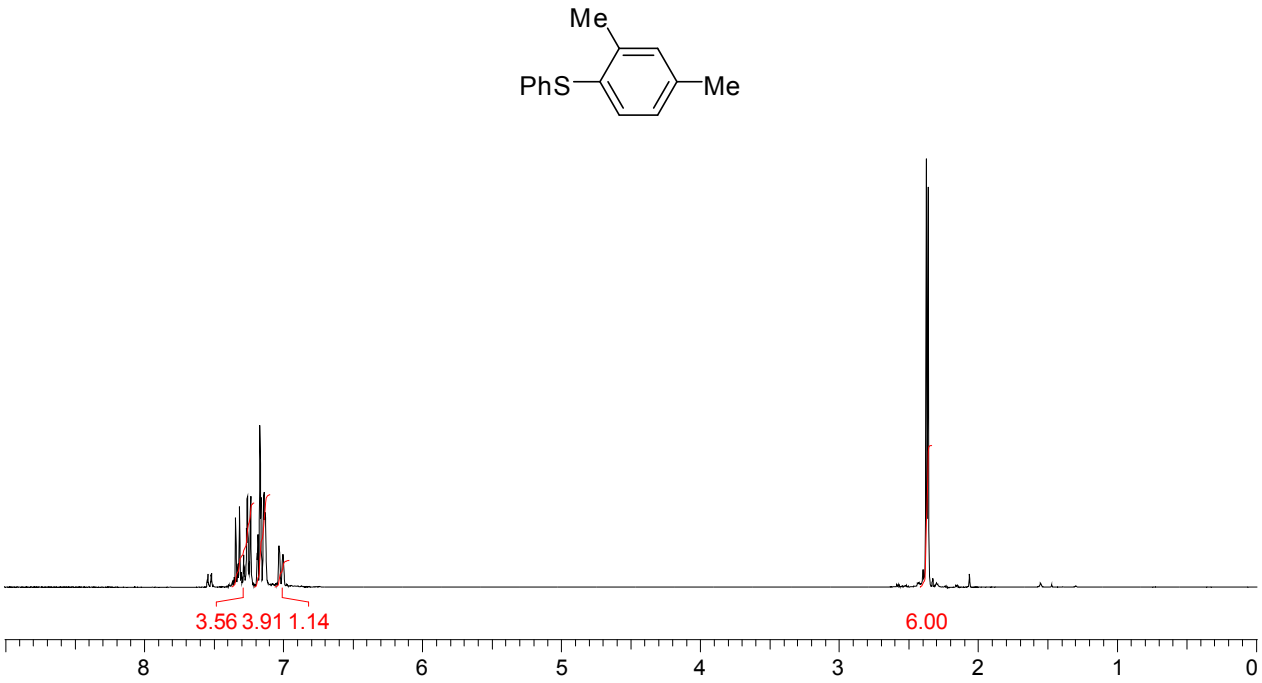


Figure S12. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 5.

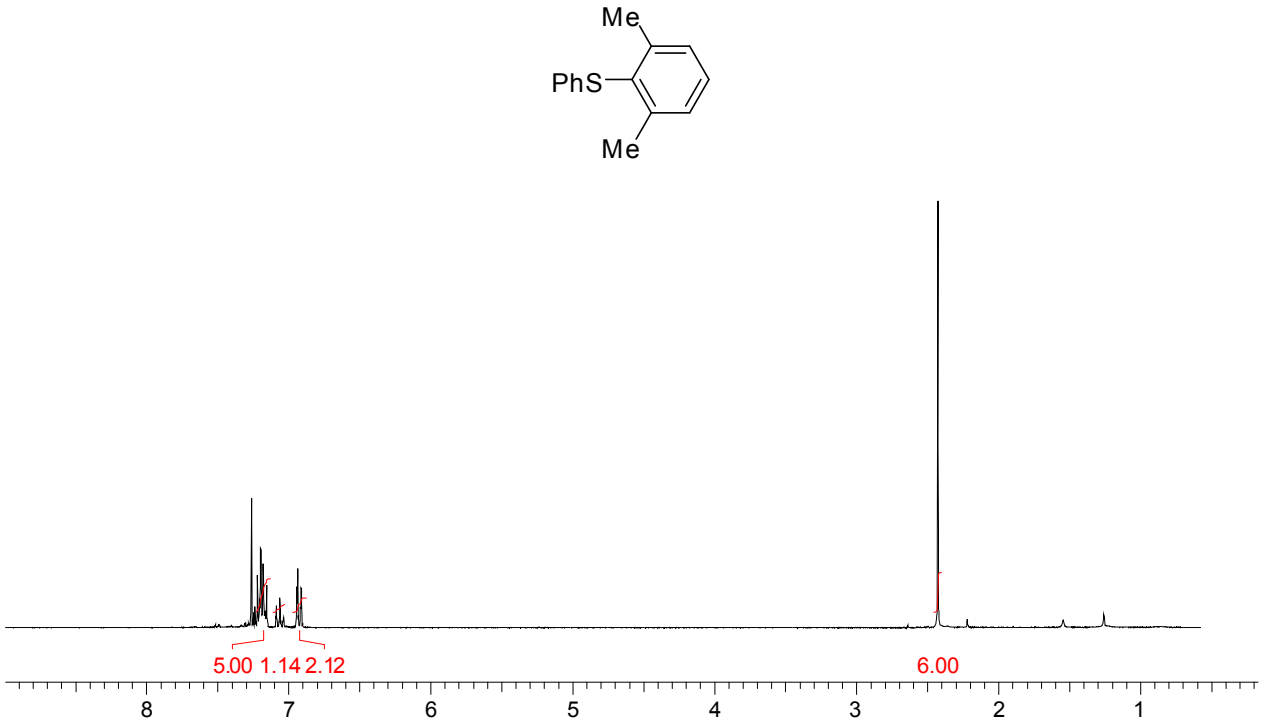


Figure S13. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 6.

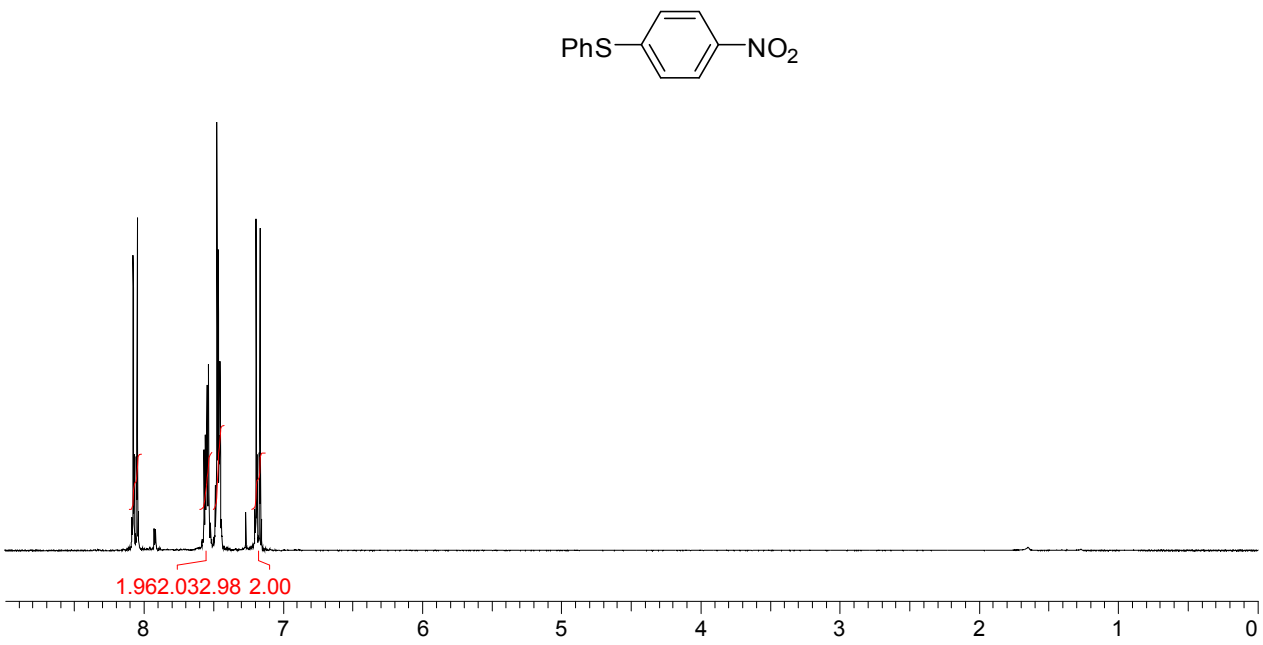


Figure S14. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 7.

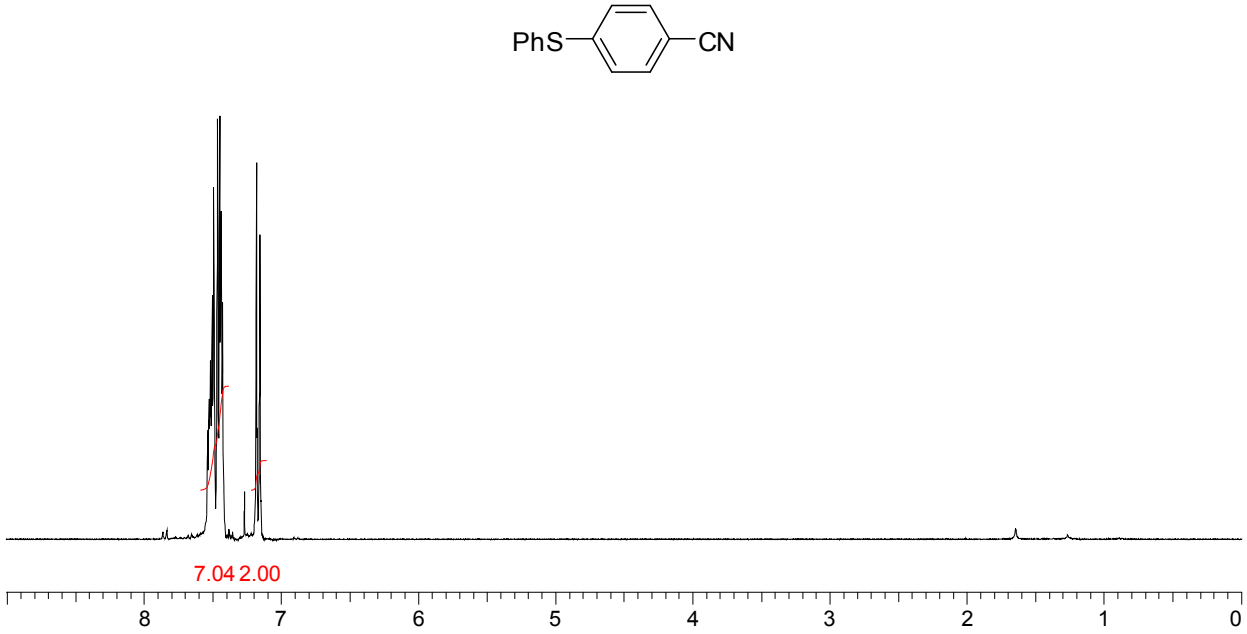


Figure S15. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 8.

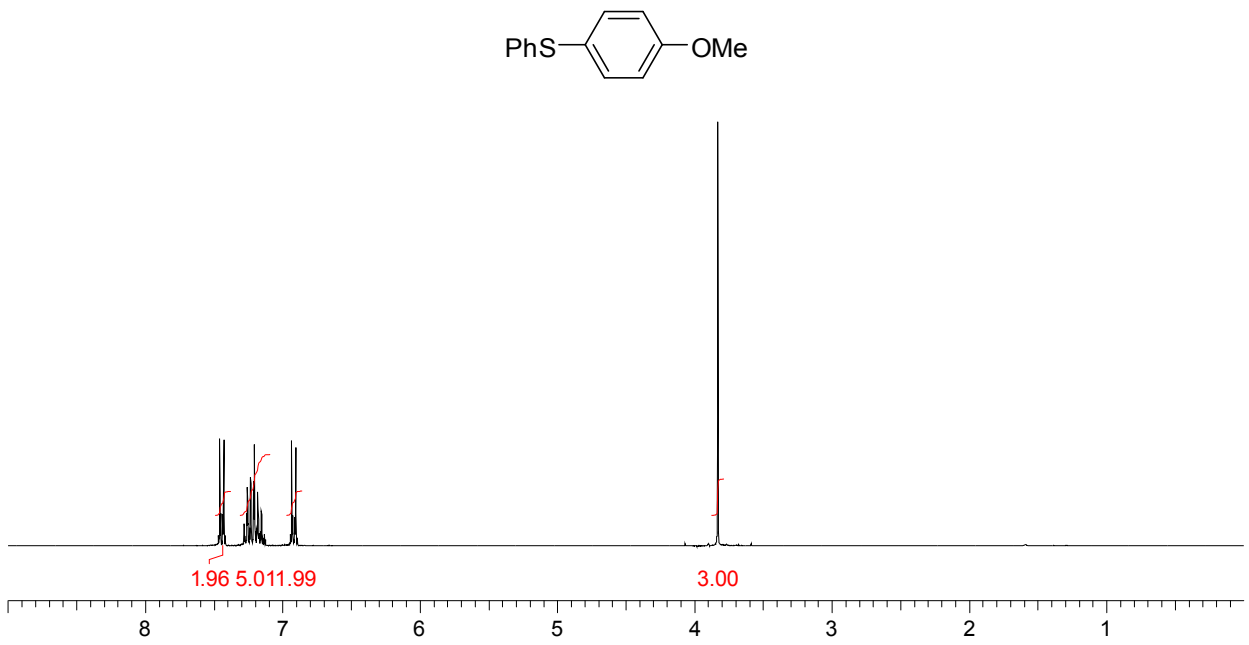


Figure S16. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 9.

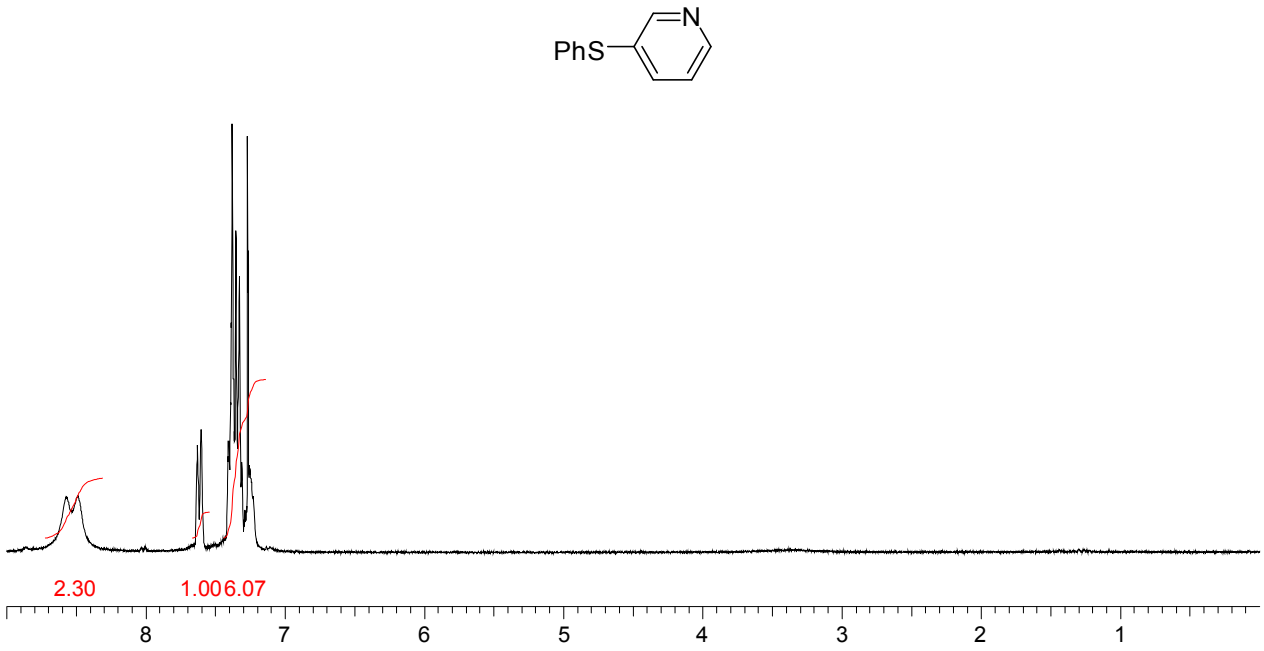


Figure S17. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 10.

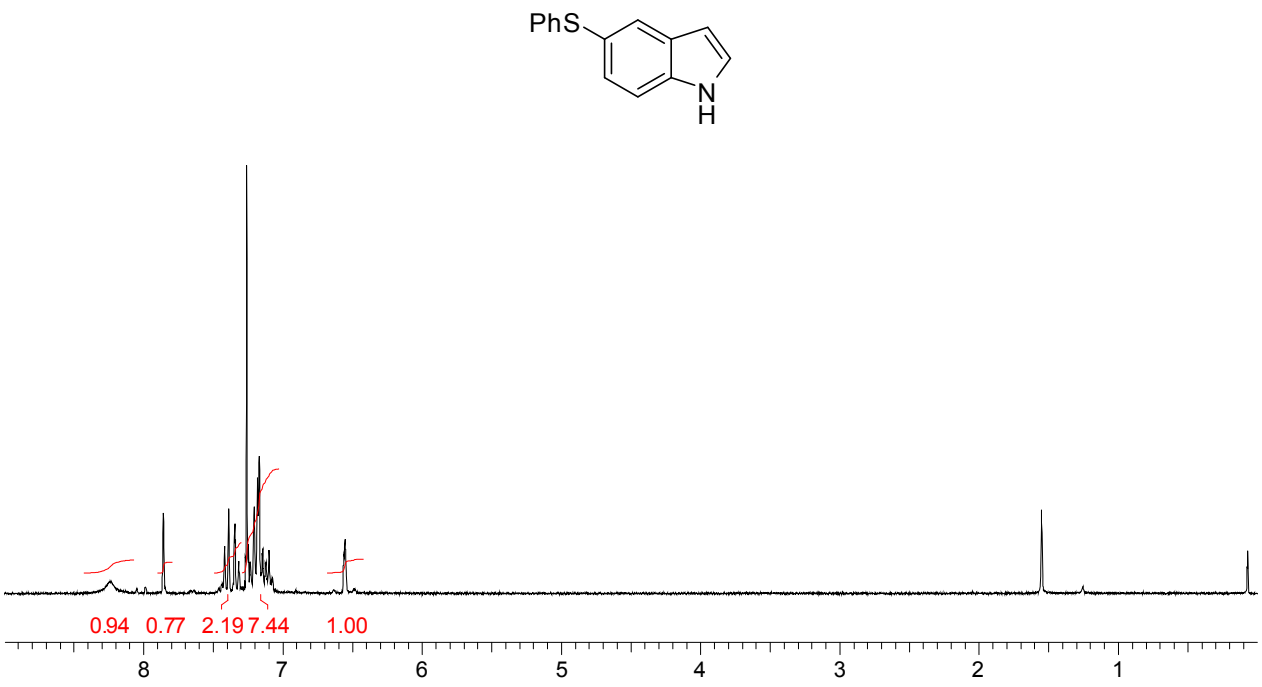


Figure S18. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 11.

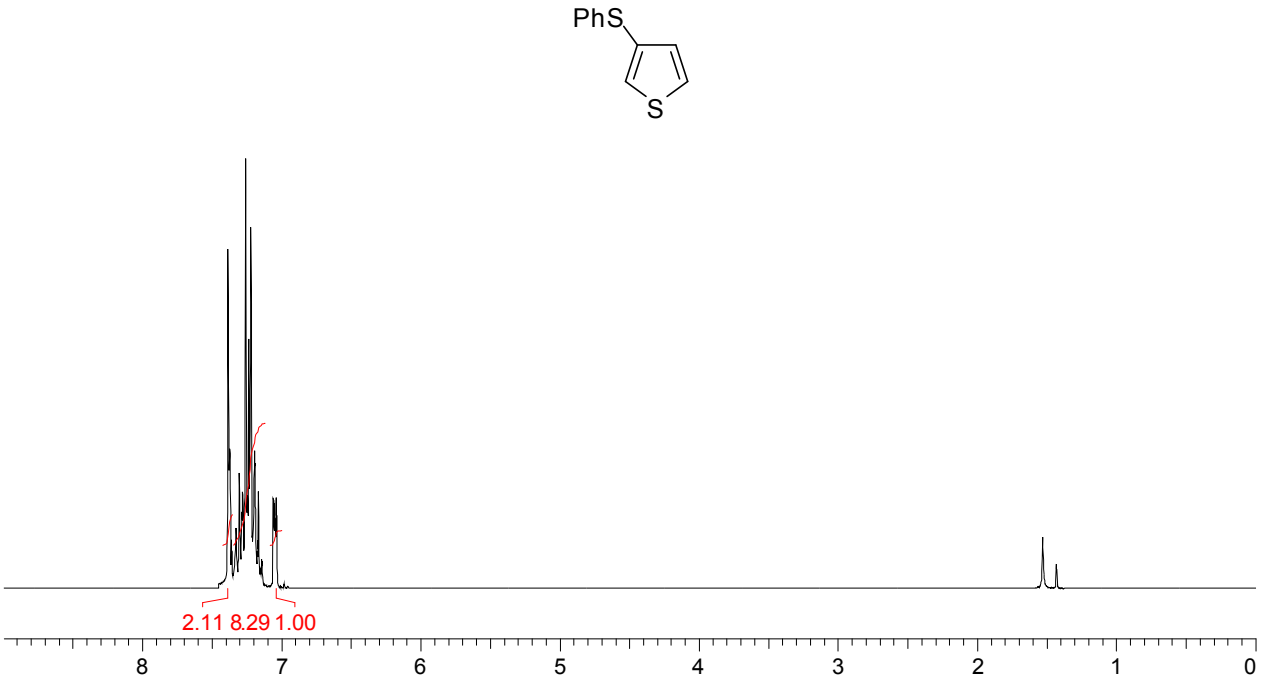


Figure S19. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 12.

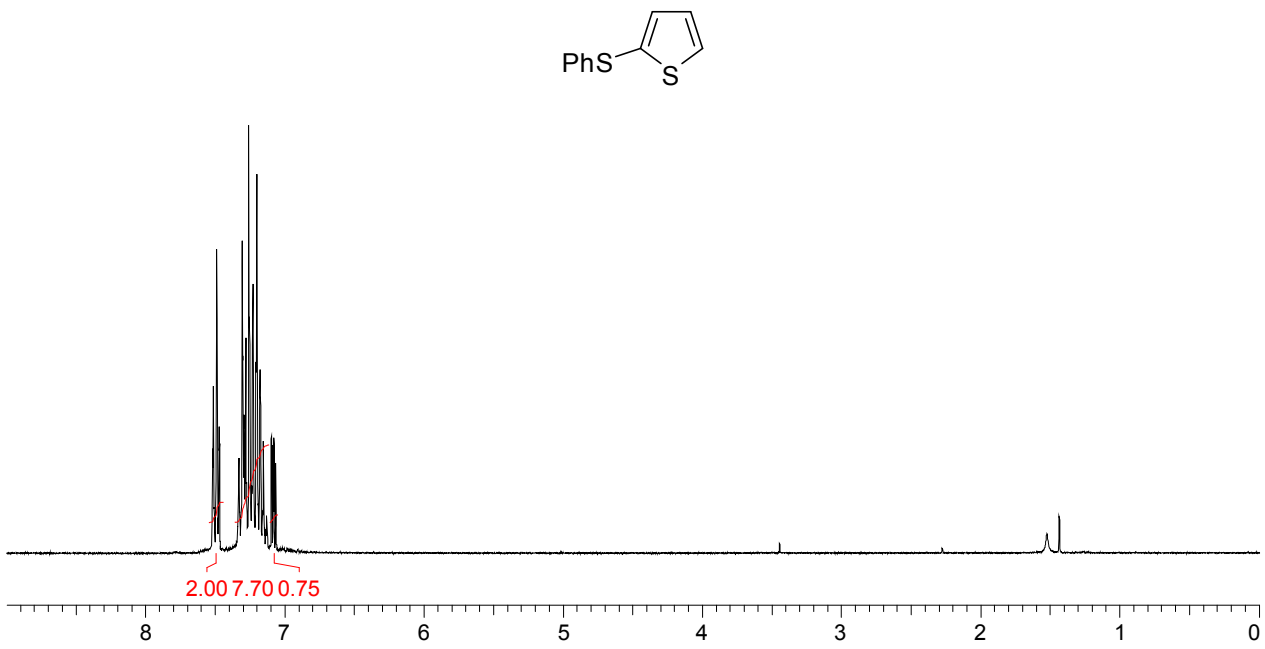


Figure S20. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 2, entry 13.

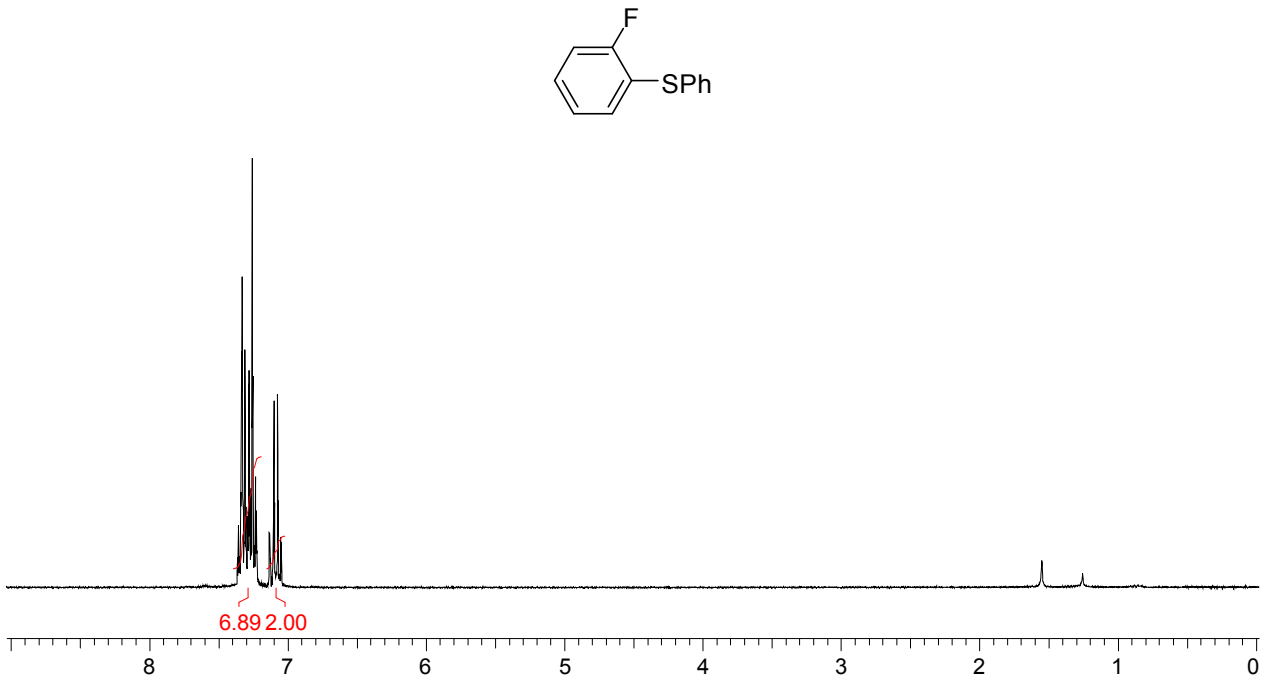


Figure S21. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 1.

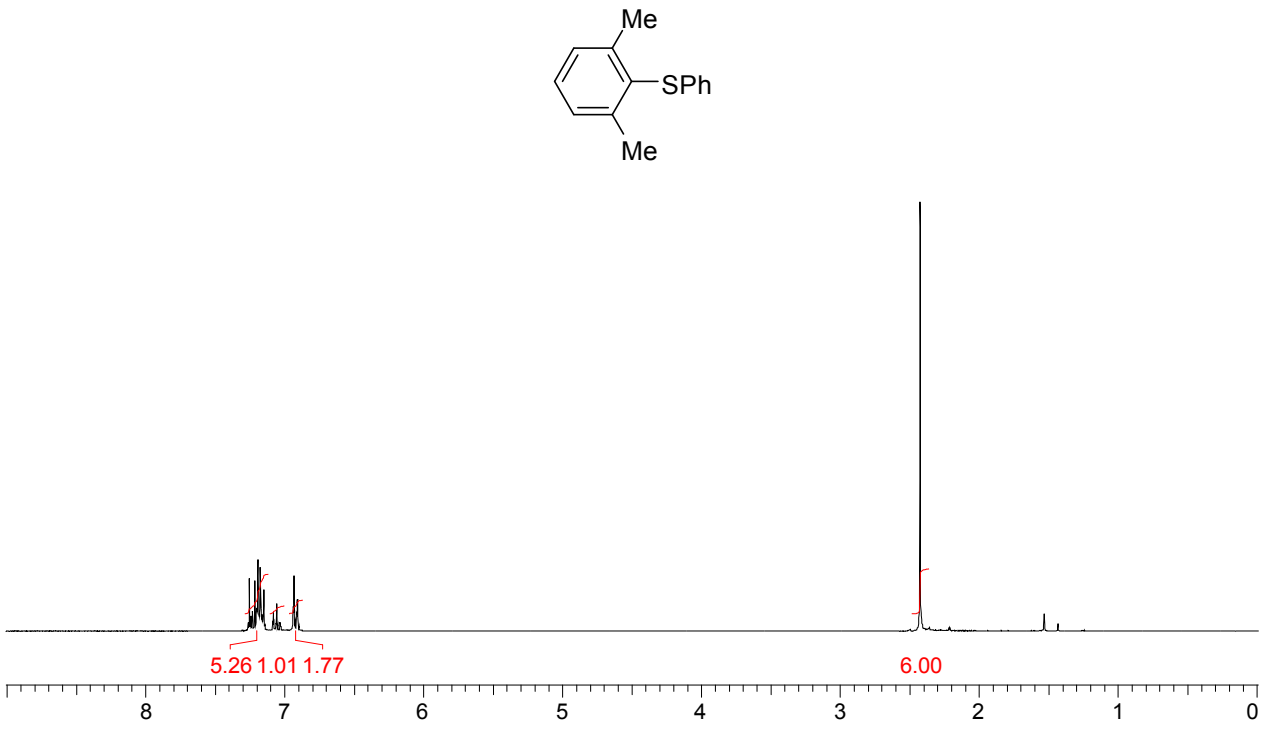


Figure S22. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 2.

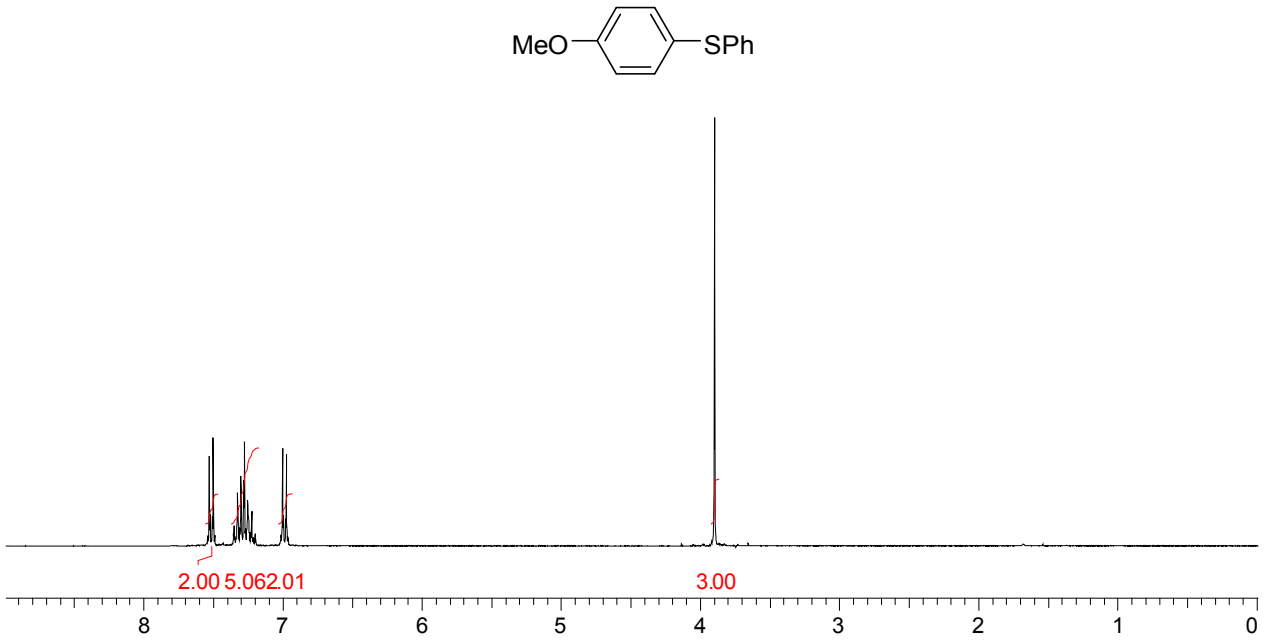


Figure S23. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 3.

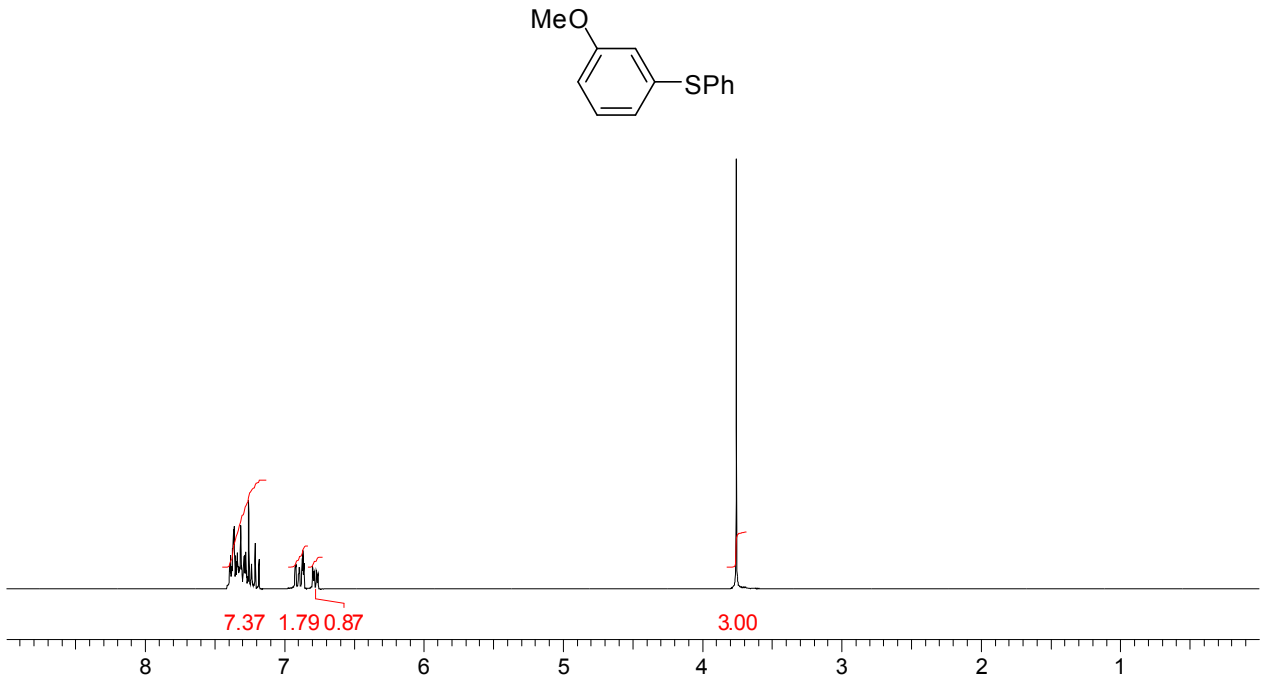


Figure S24. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 4.

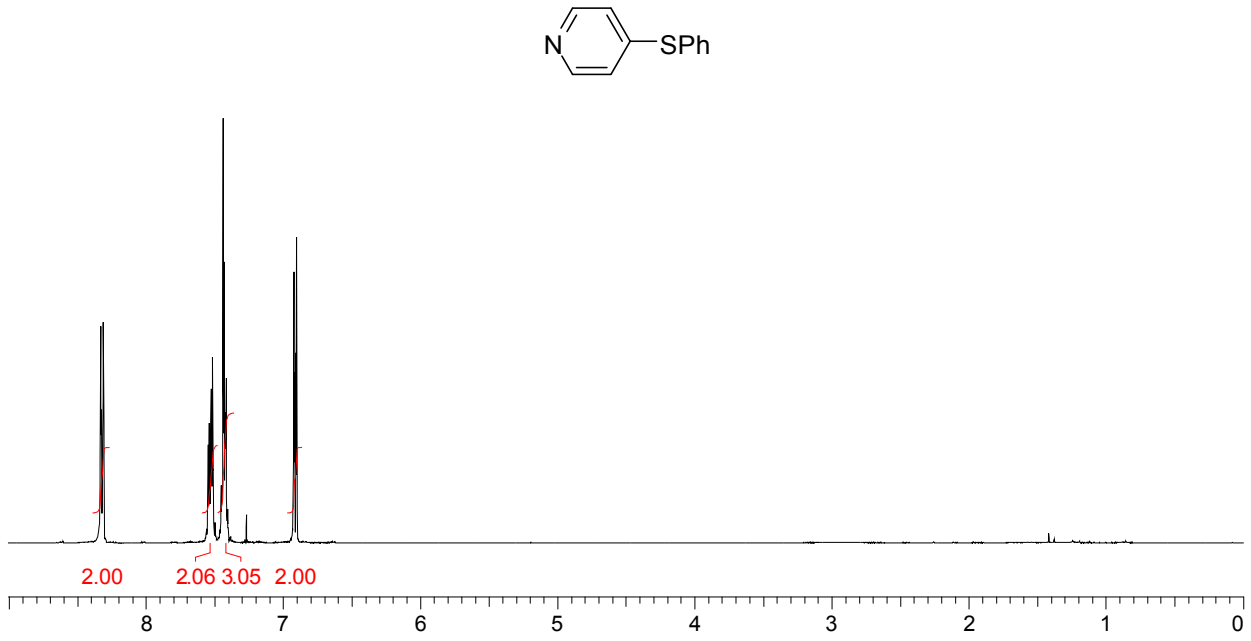


Figure S25. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 3, entry 5.

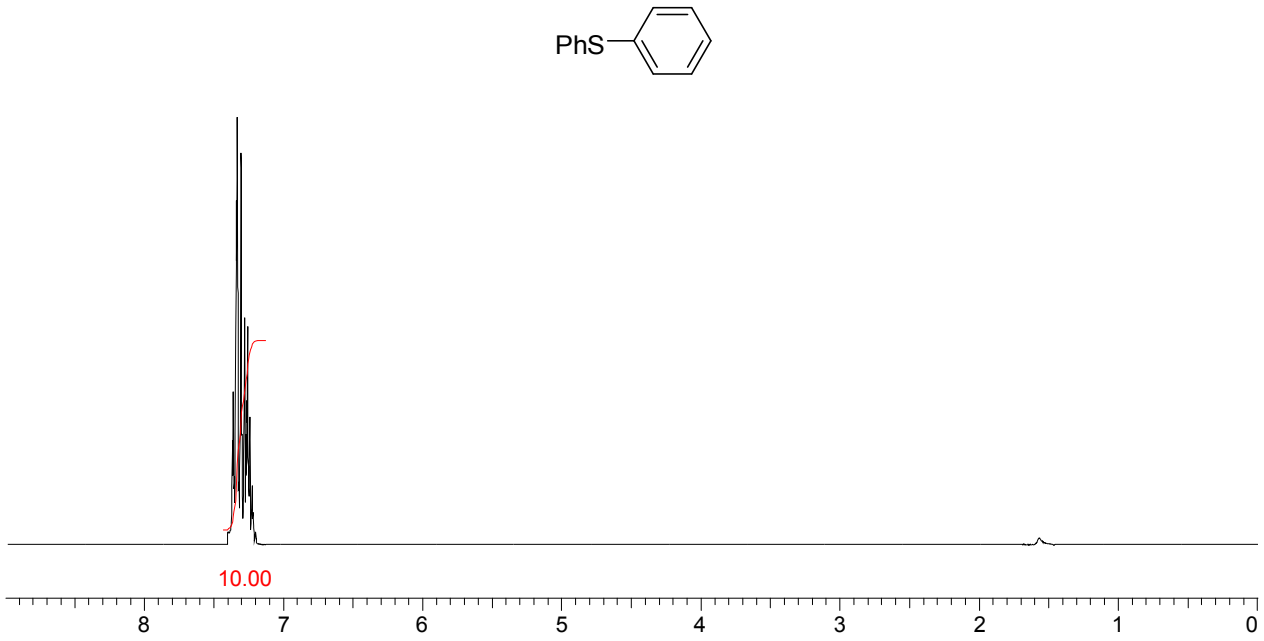


Figure S26. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 4, entry 1.

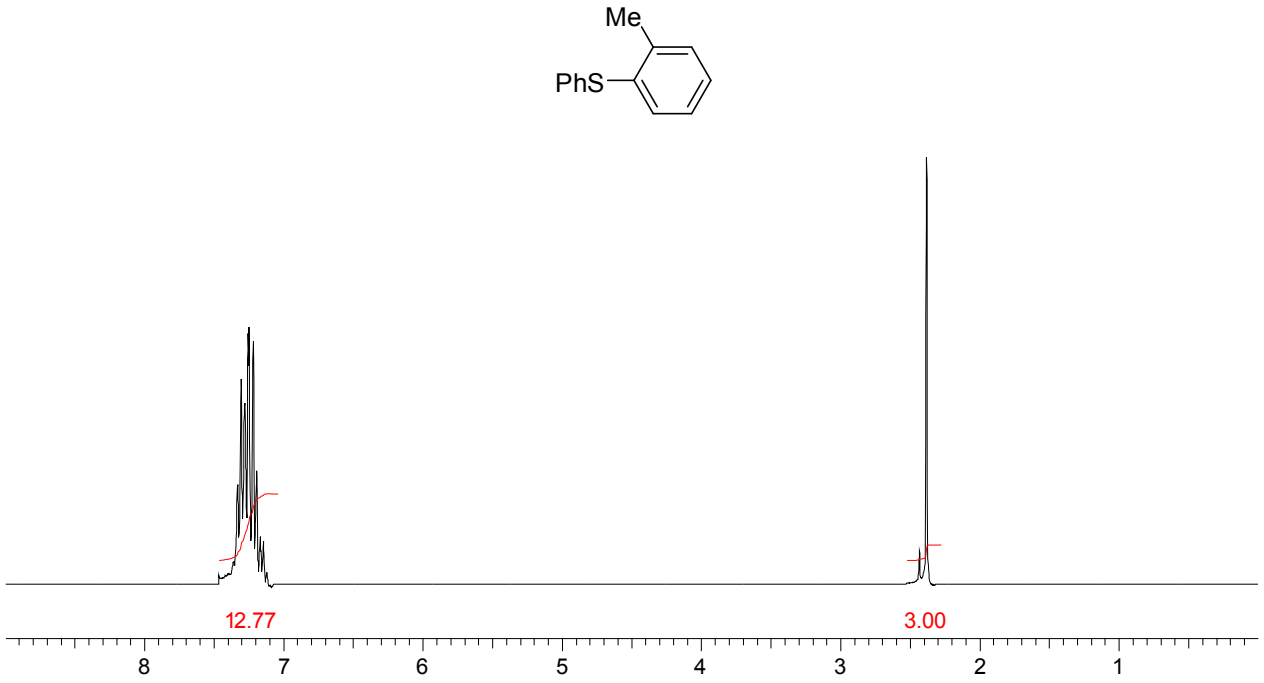


Figure S27. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 4, entry 2.

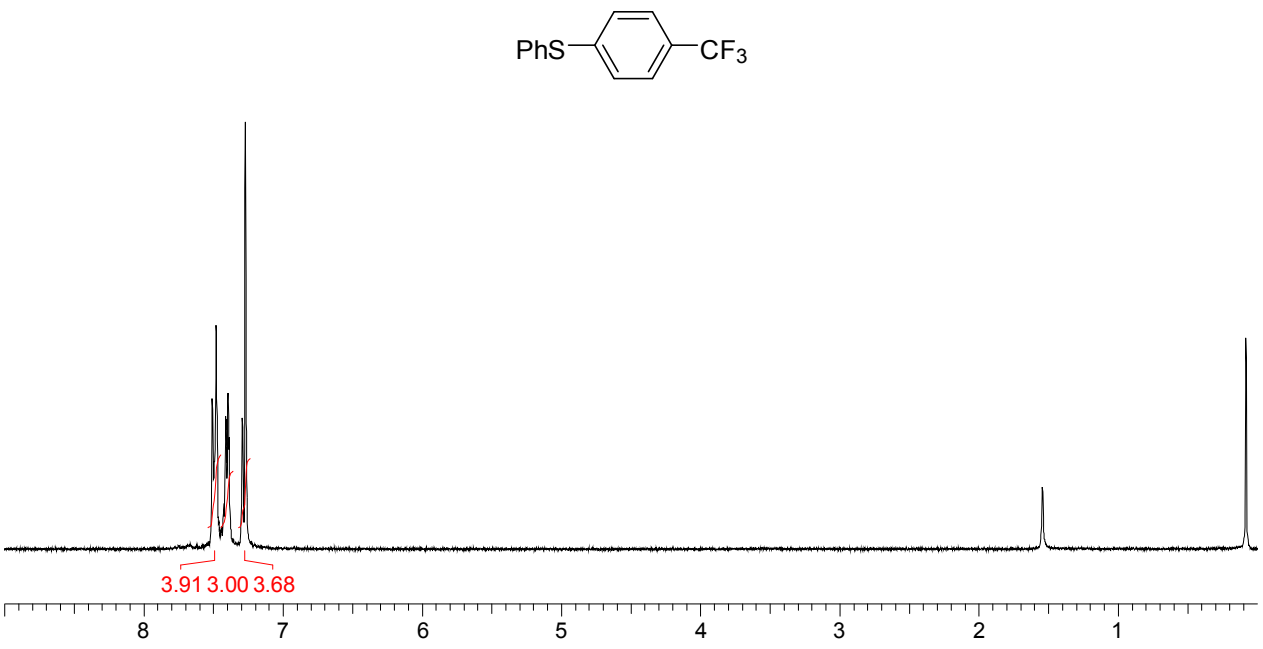


Figure S28. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 4, entry 3.

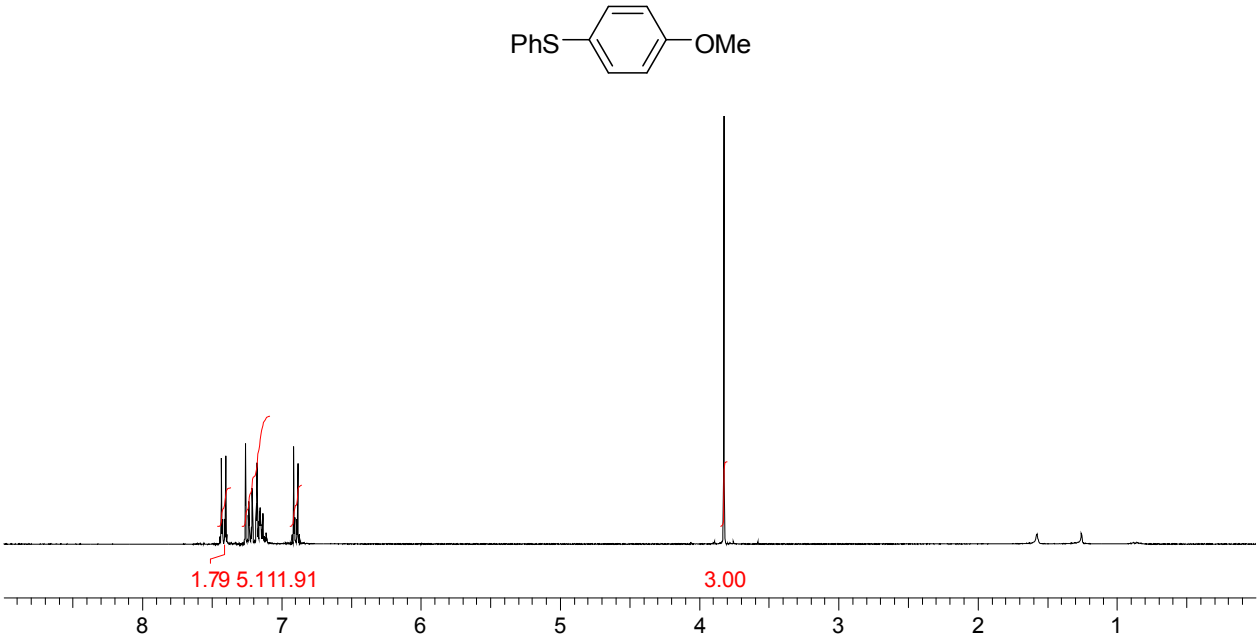


Figure S29. ^{1}H NMR spectrum ($CDCl_3$) for the product in Table 4, entry 4.

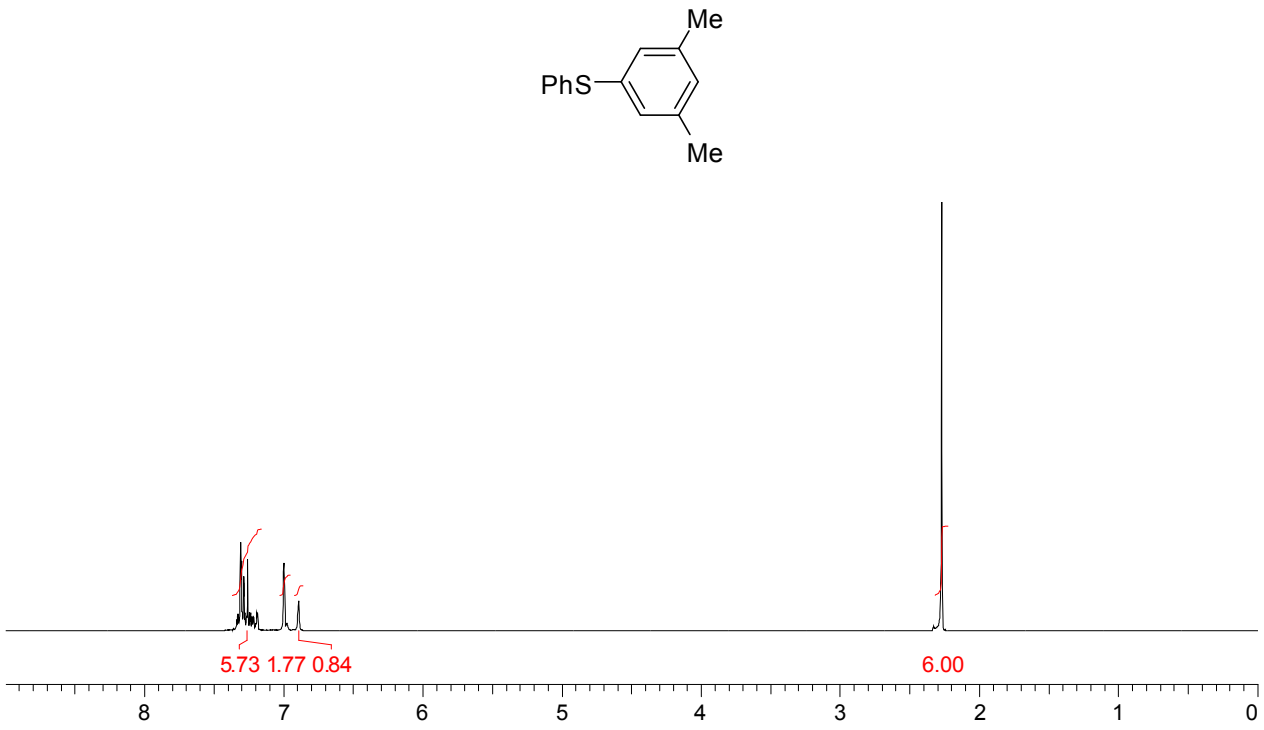


Figure S30. ^{1}H NMR spectrum ($CDCl_3$) for the product in Eq. (2).

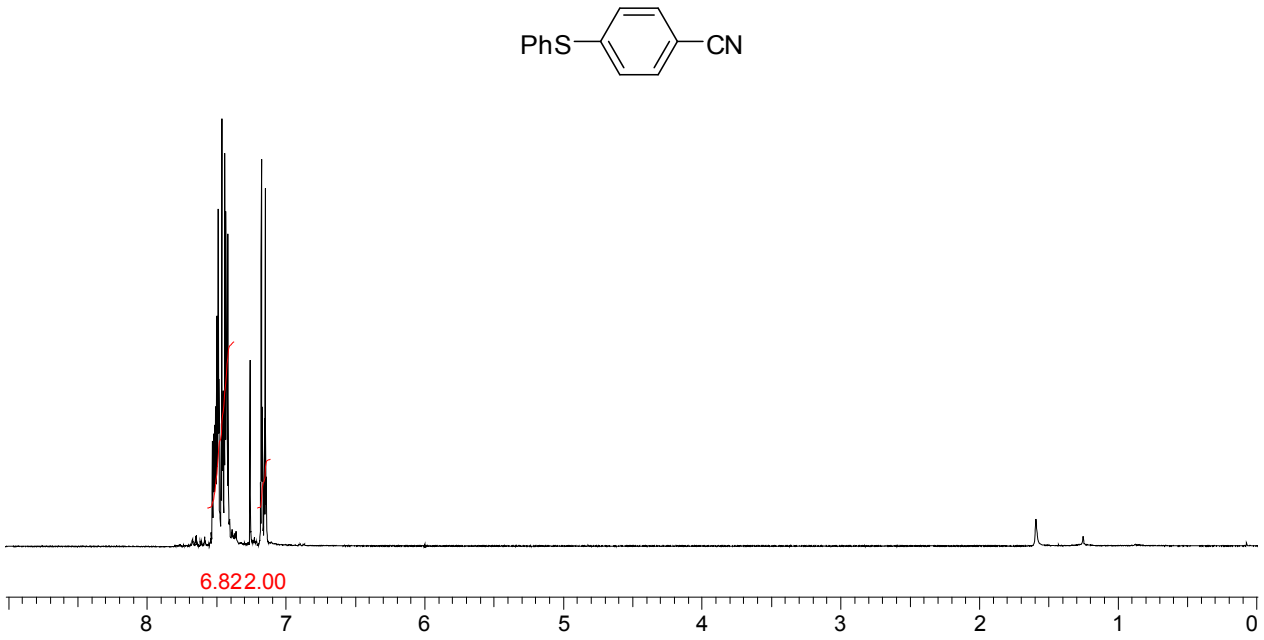


Figure S31. ^{1}H NMR spectrum ($CDCl_3$) for the product in Eq. (3).