

A General Method for the Formation of Aryl-Sulfur Bonds using Copper(I)

Catalysts

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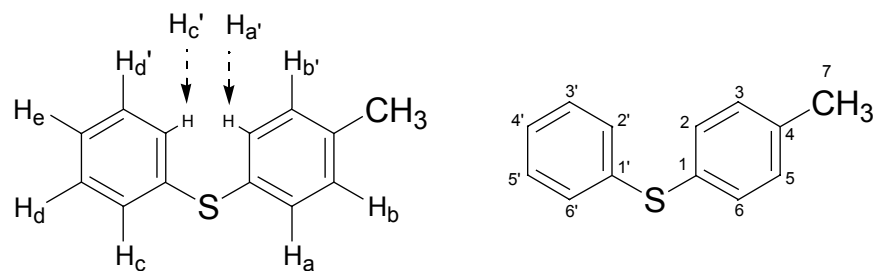
Supporting Information

General. All of the reactions reported herein were conducted under an inert atmosphere of argon in oven-dried glassware. All reagents and solvents were obtained from Acros or from Aldrich and were used without further purification. Sodium *tert*-Butoxide (Acros, 99%) was stored in an argon filled glove box. Purification was performed by flash chromatography using ICN Flash Silica Gel, 230-400 mesh. The yields given refer to isolated yields of the characterized compounds, deemed pure by elemental analyses, ^1H NMR and ^{13}C NMR. NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. Chemical shifts were reported in parts per million (δ). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; and m, multiplet. The coupling constants, J , are reported in Hertz (Hz). The residual solvent peak was used as the internal reference. All proton and ^{13}C NMR assignments for the diphenylsulfides were made using the work done by Perumal et. al. (*Magn. Reson. Chem.* 1987, 25, 1001-1006; *Magn. Reson. Chem.* 1995, 33, 779-790.) as a reference. Elemental analyses were performed at the Microanalysis Laboratory, University of Massachusetts at Amherst by Dr. Greg Dabkowski. The reported melting points were uncorrected.

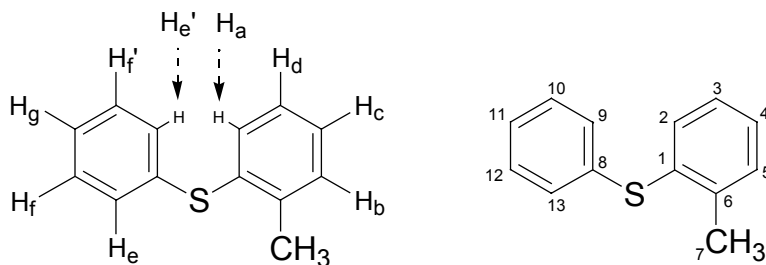
Cu-Catalyzed Coupling of thiophenols with aryl iodides

General Procedure: In an argon-filled glove box, a Pyrex glass tube (2.5 cm in diameter) equipped with a Teflon stir bar, was charged with sodium *tert*-butoxide (Acros, 3.0 mmol), CuI (10 mol% with respect to the aryl iodide), and neocuproine (10 mol% with respect to the aryl iodide). The tube was then sealed with a rubber septum, taken out of the glove box and thiophenol (2.2 mmol), the aryl iodide (2.00 mmol) and toluene (6.0 mL) were injected into the tube through the septum. The contents were then stirred at 110 °C for 24 hours. The reaction mixture was then cooled to room temperature and filtered to remove any insoluble residues. The filtrate was concentrated in vacuo; the residue was purified by flash column chromatography on silica gel to obtain the analytically pure product. Due to the stench of the thiols, all glassware and syringes used were washed with bleach to reduce the odor of the thiols.

***p*-Tolylthiophenol (entry 1, Table 1):** The general procedure was used to convert 4-iodotoluene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (379 mg, 94% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.22-7.08 (m, 7H; H_a, H_{a'}, H_c, H_{c'}, H_d, H_{d'}, H_e) 7.04-7.00 (d, *J* = 7.91, 2H; H_b, H_{b'}), 2.25 (s, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 137.54 (C₄), 137.09 (C_{1'}), 132.24 (C₂, C₆), 131.24 (C₁), 130.03 (C₃, C₅), 129.72 (C_{2'}, C_{6'}), 128.99 (C_{3'}, C_{5'}), 126.35 (C_{4'}), 21.09 (C₇). Anal. Calcd. for C₁₃H₁₂S: C, 77.95; H, 6.04; S, 16.01; Found C, 78.00; H, 6.06; S, 15.88.

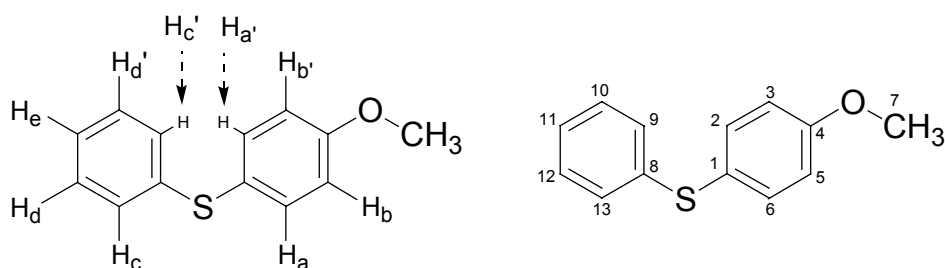


***o*-Tolylthiophenol (entry 2, Table 1):** The general procedure was used to convert 2-iodotoluene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (386 mg, 96% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.20-7.00 (m, 9H; H_a , H_b , H_c , H_d , H_e , H_e' , H_f , H_f' , H_g), 2.26 (s, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 139.88 (C_8), 136.08 (C_6), 133.69 (C_1), 132.93 (C_2), 130.54 (C_5), 129.55 (C_9 , C_{13}), 129.07, (C_{10} , C_{12}), 127.84 (C_3), 126.66 (C_{11}), 126.27 (C_4), 20.55 (C_7). Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{S}$: C, 77.95; H, 6.04; S, 16.01; Found C, 77.87; H, 6.06; S, 15.81.

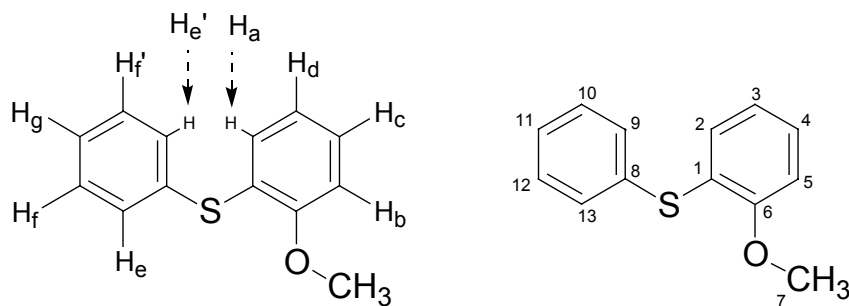


1-Methoxy-4-(phenylthio)benzene (entry 3, Table 1): The general procedure was used to convert 4-iodoanisole and thiophenol to the title product. Purification by flash chromatography (hexane / CH_2Cl_2 [3:1] as the eluent) gave the analytically pure product as a clear oil (416 mg, 96% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.29 (dt, J = 7.72, 2H; H_a , H_a'), 7.13-6.97 (m, 5H; H_c , H_c' , H_d , H_d' , H_e), 6.77 (d, J =7.54, 2H; H_b , H_b'), 3.67 (s,

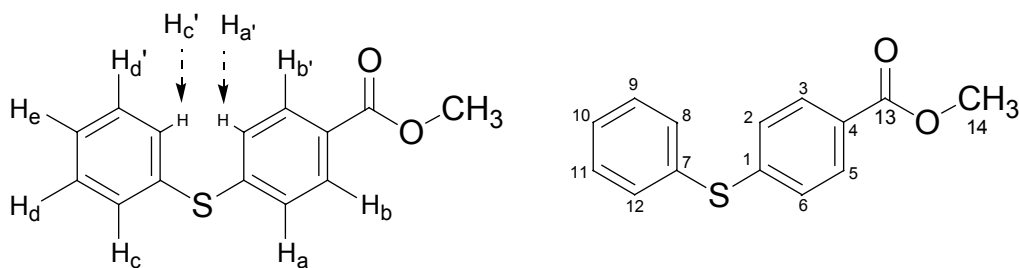
3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 159.74 (C_4), 138.54 (C_8), 135.29 (C_2 , C_6), 128.85 (C_9 , C_{13}), 128.08 (C_{10} , C_{12}), 125.66 (C_{11}), 124.17 (C_1), 114.90 (C_3 , C_5), 55.23 (C_7). Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{OS}$: C, 72.19; H, 5.59; S, 14.82; Found C, 72.34; H, 5.70; S, 14.81.



1-Methoxy-2-(phenylthio)benzene (entry 4, Table 1): The general procedure was used to convert 2-iodoanisole and thiophenol to the title product. Purification by flash chromatography (hexane / CH_2Cl_2 [3:1] as the eluent) gave the analytically pure product as a clear oil (412 mg, 95% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.25 (m, 6H; H_c , H_e , H_e' , H_f , H_f' , H_g), 7.12 (dd, $J=6.03$, 1H; H_a), 6.96-6.89 (m, 2H; H_b , H_d), 3.90 (s, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 157.21 (C_6), 134.39 (C_8), 131.50 (C_2), 131.35 (C_9 , C_{13}), 129.07 (C_{10} , C_{12}), 128.27 (C_4), 126.99 (C_{11}), 123.96 (C_1), 121.16 (C_3), 110.76 (C_5), 55.78 (C_7). Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{OS}$: C, 72.19; H, 5.59; S, 14.82; Found C, 72.23; H, 5.70; S, 14.67.

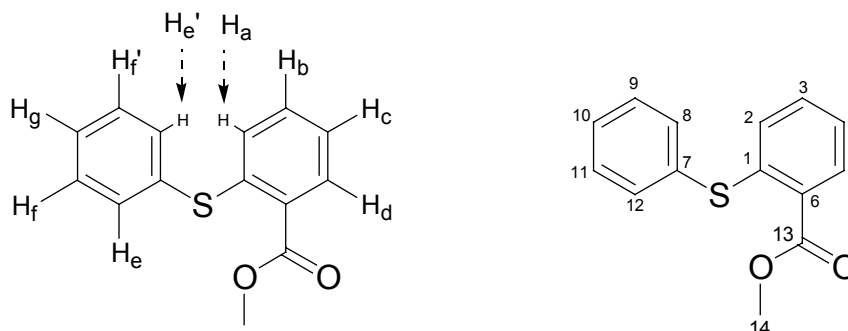


4-Phenylsulfanyl-benzoic acid methyl ester (entry 5, Table 1): The general procedure was used to convert Methyl-4-iodobenzoate and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate [6:1] as the eluent) gave the analytically pure product as a white solid (411 mg, 84% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.88 (dt, $J=8.67$, 2H; H_b , $\text{H}_{b'}$), 7.51-7.47 (m, 2H; H_c , $\text{H}_{c'}$), 7.39-7.37 (m, 3H; H_d , $\text{H}_{d'}$, H_e), 7.21 (dt, $J=8.67$, 2H; H_a , $\text{H}_{a'}$), 3.89 (s, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 166.60 (C_{13}), 144.33 (C_1), 133.63 (C_4), 132.29 (C_8 , C_{12}), 130.03 (C_7), 129.58 (C_9 , C_{11}), 128.60 (C_3 , C_5), 127.47 (C_{10}), 127.39 (C_2 , C_6), 52.02 (C_{14}). Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}$: C, 68.83; H, 4.95; S, 13.13; Found C, 68.87; H, 4.95; S, 12.96. mp found: 70-71 $^\circ\text{C}$.

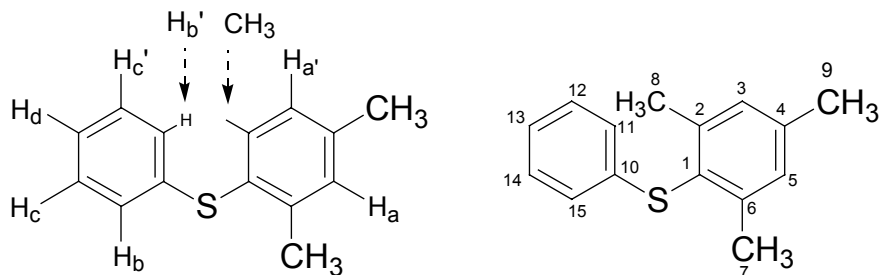


2-Phenylsulfanyl-benzoic acid methyl ester (entry 6, Table 1): The general procedure was used to convert Methyl-2-iodobenzoate and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate [6:1] as the eluent) gave the analytically pure product as a clear oil (397 mg, 81% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.88 (dd, $J=6.22$, 1H; H_d), 7.47 (m, 2H; H_a , H_b), 7.33 (m, 3H; H_e , $\text{H}_{e'}$, H_f), 7.14 (td, $J=5.4$, 1H; H_c), 7.04 (td, $J=6.02$, 1H; H_f), 6.73 (dd, $J=6.78$, 1H; H_g), 3.85 (s, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 166.79 (C_{13}), 143.15 (C_1), 135.47 (C_6), 132.39 (C_3), 132.22 (C_2), 130.93 (C_5), 129.65 (C_7), 129.02 (C_8 , C_{12}), 127.28 (C_9 , C_{11}), 126.58

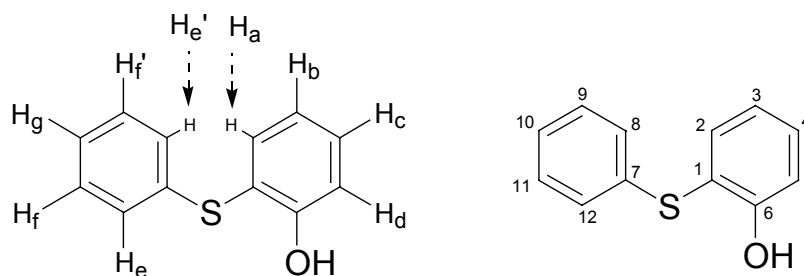
(C₁₀), 124.19 (C₄), 52.10 (C₁₄). Anal. Calcd. for C₁₄H₁₂O₂S: C, 68.83; H, 4.95; S, 13.13; Found C, 68.94; H, 5.10; S, 12.90.



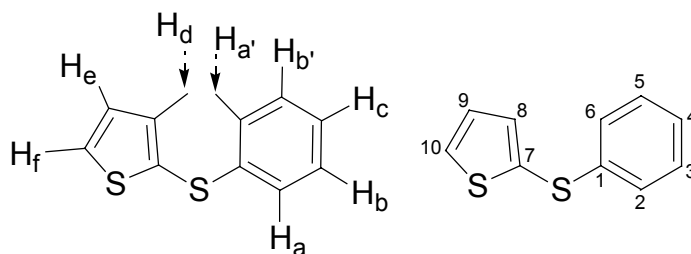
(2,4,6-trimethylphenyl)-phenyl sulfide (entry 7, Table 1): The general procedure was used to convert 2,4,6-trimethyliodobenzene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (444 mg, 97% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.20 (m, 2H; H_b, H_b'), 7.09 (m, 3H; H_c, H_c', H_d), 6.96 (m, 2H; H_a, H_a') 2.44 (s, 6H; *ortho* methyl protons), 2.37 (s, 3H, *para* methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 143.67 (C₂, C₆), 139.21 (C₄), 138.35 (C₁), 129.29 (C₁₀), 128.81 (C₁₁, C₁₅), 127.20 (C₁₂, C₁₄), 125.39 (C₃, C₅), 124.41 (C₁₃), 21.67 (C₇, C₈), 21.10 (C₉). Anal. Calcd. for C₁₅H₁₆S: C, 78.90; H, 7.06; S, 14.04; Found C, 78.76; H, 7.23; S, 14.10.



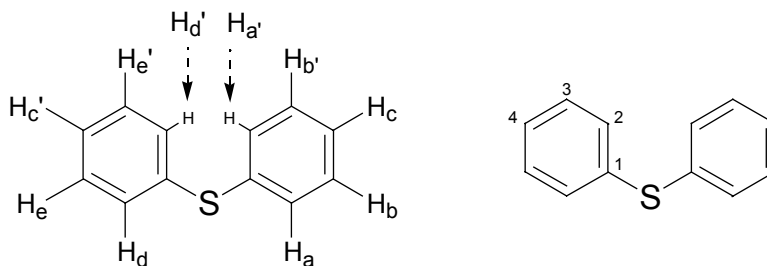
2-Phenylsulfanyl-phenol (entry 8, Table 1): The general procedure was used to convert 2-iodothiophene and thiophenol to the title product. Purification by flash chromatography (hexane / ethyl acetate (6:1) as the eluent) gave the analytically pure product as a light brown oil (328 mg, 81% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.43 (dd, $J=5.65$, 1H; $\text{H}_{\text{e}'}$), 7.28 (m, 1H; H_{e}), 7.14 (m, 2H; H_{f} , $\text{H}_{\text{f}'}$), 7.07-6.97 (m, 4H; H_{a} , H_{b} , H_{c} , H_{g}), 6.86 (td, $J=6.02$, 1H; H_{d}), 6.44 (s, 1H, alcohol proton). ^{13}C NMR (75 MHz, CDCl_3) δ 157.22 (C_6), 136.89 (C_2), 135.80 (C_7), 132.26 (C_8 , C_{12}), 129.17 (C_9 , C_{11}), 126.78 (C_4), 126.07 (C_{10}), 121.25 (C_3), 116.20 (C_1), 115.51 (C_5). Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{S}$: C, 71.25; H, 4.98; S, 15.85; Found C, 71.25; H, 5.01; S, 15.82.



2-Phenylsulfanyl-thiophene (entry 9, Table 1): The general procedure was used to convert 2-iodophenol and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (349 mg, 91% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.52 (dd, $J=4.14$, 2H; H_{a} , $\text{H}_{\text{a}'}$), 7.36-7.21 (m, 6H; H_{b} , $\text{H}_{\text{b}'}$, H_{c} , H_{d} , H_{f}), 7.12 (m, 1H; H_{e}). ^{13}C NMR (75 MHz, CDCl_3) δ 138.59 (C_1), 136.03 (C_7), 131.24 (C_2 , C_6), 131.02 (C_9), 128.91 (C_3 , C_5), 127.88 (C_8), 127.03 (C_{10}), 125.98 (C_4). Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{S}_2$: C, 62.46; H, 4.19; S, 33.35; Found C, 62.56; H, 4.21; S, 33.13.



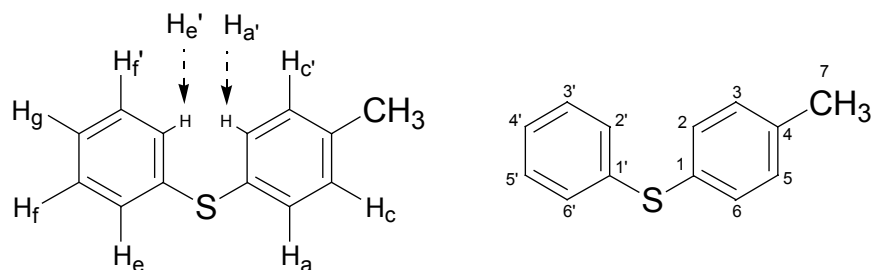
Diphenylsulfide (entry 1, Table 2): The general procedure was used to convert iodobenzene and thiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (360 mg, 98% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.48-7.44 (m, 4H; H_a , $\text{H}_{a'}$, H_d , $\text{H}_{d'}$), 7.42-7.39 (m, 4H; H_b , $\text{H}_{b'}$, H_e , $\text{H}_{e'}$), 7.37-7.31 (m, 2H; H_c , $\text{H}_{c'}$). ^{13}C NMR (75 MHz, CDCl_3) δ 135.70 (C_1), 130.94 (C_2), 129.10 (C_3), 126.94 (C_4). Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{S}$: C, 77.37; H, 5.41; S, 17.21; Found C, 77.50; H, 5.45; S, 17.00.



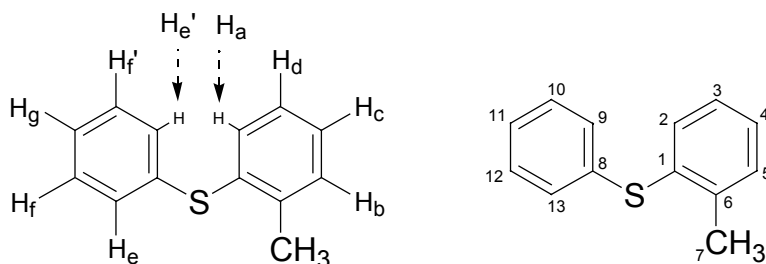
***p*-Tolylthiophenol (entry 2, Table 2):** The general procedure was used to convert iodobenzene and *p*-toluenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (388 mg, 97.0% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.18 (dt, $J=8.1$, 2H; H_a , $\text{H}_{a'}$), 7.15-7.12 (m, 4H; H_e , $\text{H}_{e'}$, H_f , $\text{H}_{f'}$), 7.08 (m, 1H; H_g), 7.04-7.00 (d, $J=7.34$, 2H; H_c , $\text{H}_{c'}$), 2.22 (s, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 138.05 (C_4), 137.62 ($\text{C}_{1'}$), 132.77 (C_2 , C_6),

131.76 (C₁), 130.55 (C₃, C₅), 130.23 (C_{2'}, C_{6'}), 129.52 (C_{3'}, C_{5'}), 126.87 (C_{4'}), 21.62 (C₇).

Anal. Calcd. for C₁₃H₁₂S: C, 77.95; H, 6.04; S, 16.01; Found C, 77.78; H, 6.01; S, 16.19.

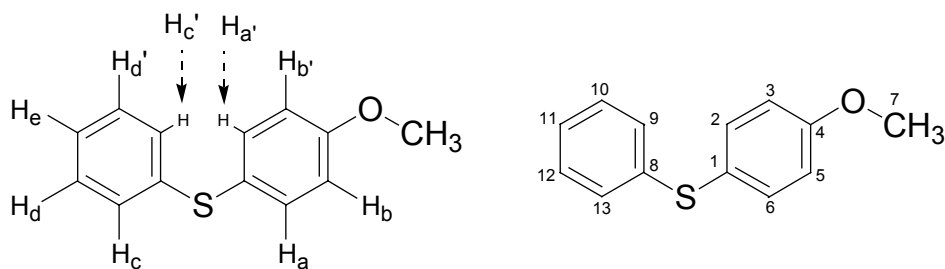


***o*-Tolylthiophenol (entry 3, Table 2):** The general procedure was used to convert iodobenzene and *o*-toluenethiol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (383 mg, 95% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.20-6.98 (m, 9H; H_a, H_b, H_c, H_d, H_e, H_{e'}, H_f, H_{f'}, H_g), 2.27 (s, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 139.90 (C₈), 136.10 (C₆), 133.70 (C₁), 132.94 (C₂), 130.54 (C₅), 129.55 (C₉, C₁₃), 129.07, (C₁₀, C₁₂), 127.85 (C₃), 126.66 (C₁₁), 126.27 (C₄), 20.54 (C₇). Anal. Calcd. for C₁₃H₁₂S: C, 77.95; H, 6.04; S, 16.01; Found C, 78.02; H, 6.01; S, 16.01.

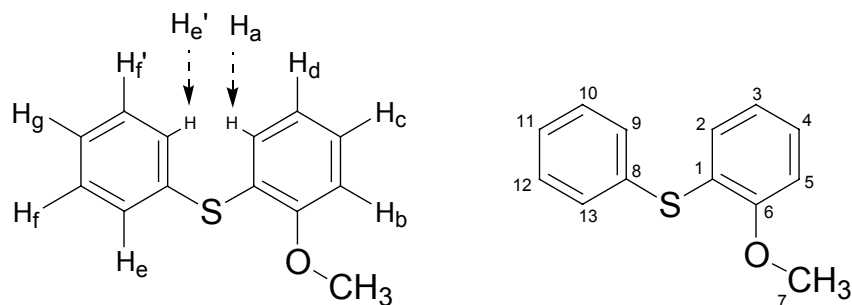


1-Methoxy-4-(phenylthio)benzene (entry 4, Table 2): The general procedure was used to convert iodobenzene and 4-methoxybenzenethiol to the title product. Purification by

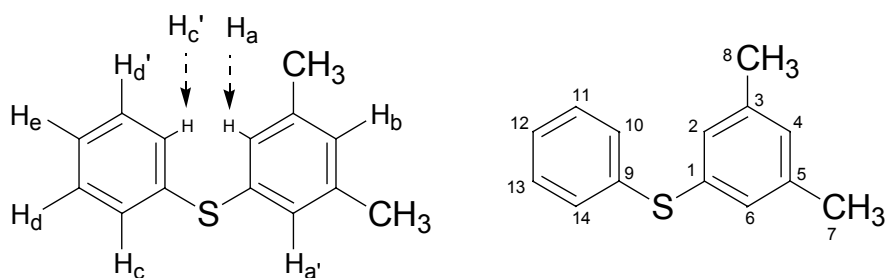
flash chromatography (hexane / CH₂Cl₂ [3:1] as the eluent) gave the analytically pure product as a clear oil (410 mg, 95% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.27 (dt, *J*= 8.85, 2H; H_a, H_{a'}), 7.12-6.96 (m, 5H; H_c, H_{c'}, H_d, H_{d'}, H_e), 6.75 (dt, 2H; H_b, H_{b'}), 3.67 (s, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 159.76 (C₄), 138.56 (C₈), 135.32 (C₂, C₆), 128.86 (C₉, C₁₃), 128.10 (C₁₀, C₁₂), 125.68 (C₁₁), 124.19 (C₁), 114.92 (C₃, C₅), 55.27 (C₇). Anal. Calcd. for C₁₃H₁₂OS: C, 72.19; H, 5.59; S, 14.82; Found C, 72.26; H, 5.59; S, 14.65.



1-Methoxy-2-(phenylthio)benzene (entry 5, Table 2): The general procedure was used to convert iodobenzene and 2-methoxybenzenethiol to the title product. Purification by flash chromatography (hexane / CH₂Cl₂ [3:1] as the eluent) gave the analytically pure product as a clear oil (406 mg, 94% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.25 (m, 6H; H_c, H_e, H_{e'}, H_f, H_{f'}, H_g), 7.14 (dd, 1H; H_a), 6.96-6.89 (m, 2H; H_b, H_d), 3.90 (s, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 157.20 (C₆), 134.38 (C₈), 131.88 (C₂), 131.35 (C₉, C₁₃), 129.15 (C₁₀, C₁₂), 128.25 (C₄), 127.40 (C₁₁), 123.93 (C₁), 121.14 (C₃), 110.75 (C₅), 55.76 (C₇). Anal. Calcd. for C₁₃H₁₂OS: C, 72.19; H, 5.59; S, 14.82; Found C, 72.22; H, 5.70; S, 14.63.

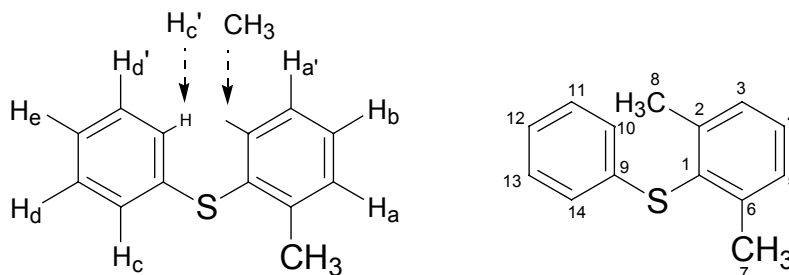


(3,5-dimethyl-phenyl)-phenyl sulfide (entry 6, Table 2): The general procedure was used to convert iodobenzene and 3,5-dimethylthiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (417 mg, 97% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.17-7.01 (m, 5H; H_c , H_c' , H_d , H_d' , H_e), 6.84 (s, 2H; H_a , H_a'), 6.72 (s, 1H; H_b), 2.10 (s, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 138.81 (C_3 , C_5), 136.35 (C_9), 134.69 (C_1), 130.44 (C_{10} , C_{14}), 129.10 (C_{11} , C_{13}), 129.02 (C_2 , C_6), 128.68 (C_4), 126.61 (C_{12}), 21.13 (C_7 , C_8). Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{S}$: C, 78.45; H, 6.58; S, 14.96; Found C, 78.53; H, 6.62; S, 14.89.



(2,6-dimethyl-phenyl)-phenyl sulfide (entry 7, Table 2): The general procedure was used to convert iodobenzene and 2,6-dimethylthiophenol to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (409 mg, 95% yield). ^1H NMR (300 MHz, CDCl_3) δ 7.1-6.98 (m, 5H; H_c , H_c' ,

H_d, H_{d'}, H_e), 6.93-6.86 (m, 1H; H_b), 6.77 (d, *J* = 7.16, 2H; H_a, H_{a'}) 2.34 (s, 6H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 143.86 (C₂, C₆), 137.98 (C₉), 130.43 (C₁), 129.22 (C₄), 128.86 (C₁₀, C₁₄), 128.40 (C₁₁, C₁₃), 125.59 (C₃, C₅), 124.57 (C₁₂), 21.82 (C₇, C₈).
 Anal. Calcd. for C₁₄H₁₄S: C, 78.45; H, 6.58; S, 14.96; Found C, 78.58; H, 6.71; S, 14.98.

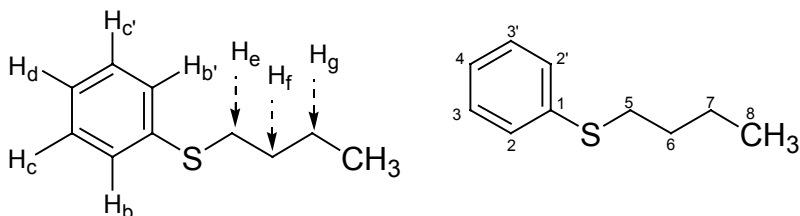


Cu-Catalyzed Coupling of *n*-Butyl sulfides with aryl iodides.

General Procedure: In an argon-filled glove box, a Pyrex glass tube (2.5 cm in diameter) equipped with a Teflon stir bar, was charged with sodium *tert*-butoxide (Acros, 3.0 mmol), CuI (10 mol% with respect to the aryl iodide), and neocuproine (10 mol % with respect to the aryl iodide). The tube was then sealed with a rubber septum, taken out of the glove box and *n*-butyl sulfide (2.2 mmol), the aryl iodide (2.00 mmol) and toluene (5.0 mL) were injected into the tube through the septum. The contents were then stirred at 110 °C for 24 hours. The reaction mixture was then cooled to room temperature and filtered to remove any insoluble residues. The filtrate was concentrated in vacuo; the residue was purified by flash column chromatography on silica gel to obtain the

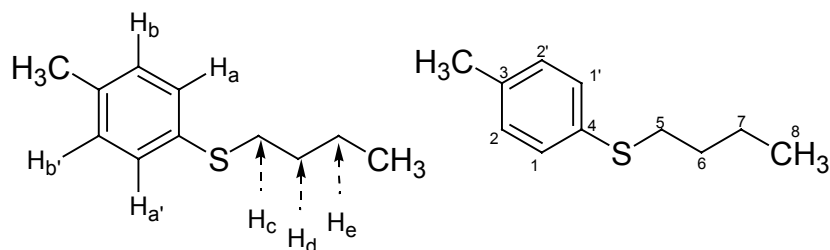
analytically pure product. Due to the stench of the *n*-butyl sulfides, all glassware and syringes used were washed with bleach to reduce the odor of the thiols.

***n*-Butyl Phenyl Sulfide (entry 1, Table 3):** The general procedure was used to convert iodobenzene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (310 mg, 95 % yield). ^1H NMR (300 MHz, CDCl_3) δ 7.26-7.09 (m, 5H; H_b , $\text{H}_{b'}$, H_c , $\text{H}_{c'}$, H_d), 2.88-2.82 (t, $J=4.0$, 2H; H_e), 1.60-1.46 (m, 2H; H_f), 1.42-1.30 (m, 2H; H_g), 0.88-0.82 (t, $J=3.9$, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 136.9 (C_1), 128.7 ($\text{C}_{3'}$, C_3 , C_2 , $\text{C}_{2'}$), 125.5 (C_4), 33.1 (C_5), 31.1 (C_6), 21.9 (C_7), 13.6 (C_8). Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{S}$: C, 72.23; H, 8.49; S, 19.28; Found C, 71.97; H, 8.67; S, 19.07.

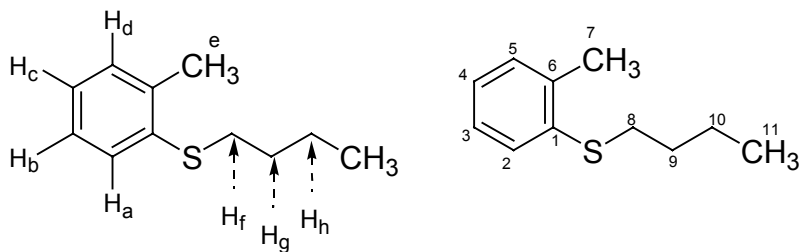


***n*-Butyl 4-Methylphenyl Sulfide (entry 2, Table 3):** The general procedure was used to convert 4-iodotoluene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (331 mg, 94 % yield). ^1H NMR (300 MHz, CDCl_3) δ 7.15-7.12 (d, $J=8.2$, 2H; H_a , $\text{H}_{a'}$), 6.98-6.96 (d, $J=7.9$, 2H; H_b , $\text{H}_{b'}$), 2.79-2.74 (t, $J=7.1$, 2H; H_c), 2.20 (Methyl Protons), 1.55-1.45 (m, 2H; H_d), 1.39-1.15 (m, 2H; H_e), 0.83-0.78 (t, $J=7.1$, 3H; H_f). ^{13}C NMR (75 MHz, CDCl_3) δ 135.6 (C_4), 133 (C_3), 129.6 (C_1 , $\text{C}_{1'}$), 129.47 (C_2 , $\text{C}_{2'}$), 33.8 (methyl

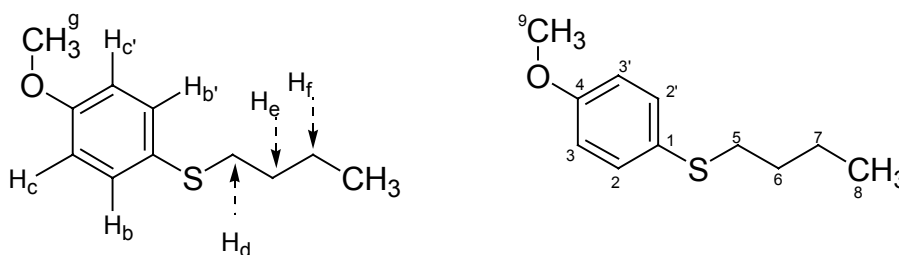
protons), 31.2 (C₅), 21.8 (C₆), 20.8 (C₇), 13.54 (C₈). Anal. Calcd. for C₁₁H₁₆S: C, 73.27; H, 8.94; S, 17.78; Found C, 73.21; H, 9.15; S, 17.57.



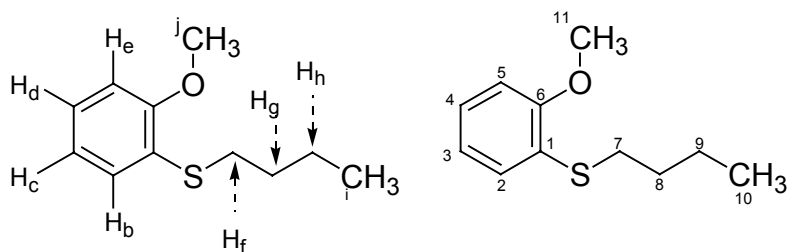
***n*-Butyl 2-Methylphenyl Sulfide (entry 3, Table 3):** The general procedure was used to convert 2-iodotoluene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (331 mg, 93 % yield). ¹H NMR (300 MHz, CDCl₃) δ 7.17-6.97 (m, 4H; H_a, H_b, H_c, H_d), 2.80-2.78 (t, *J*= 7.3, 2H; H_f), 2.27 (s, 3H; H_e), 1.61-1.51 (m, 2H; H_g), 1.44-1.17 (m, 2H; H_h), 0.87-0.82 (t, *J*= 7.3, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 137 (C₁), 136.3 (C₆), 129.9 (C₅), 127.1 (C₂), 126.2 (C₃), 125.1 (C₄), 32.3 (C₈), 31 (C₉), 22 (C₁₀), 20.2 (C₇), 13.6 (C₁₁). Anal. Calcd. for C₁₁H₁₆S: C, 73.27; H, 8.94; S, 17.78; Found C, 73.23; H, 9.16; S, 17.57.



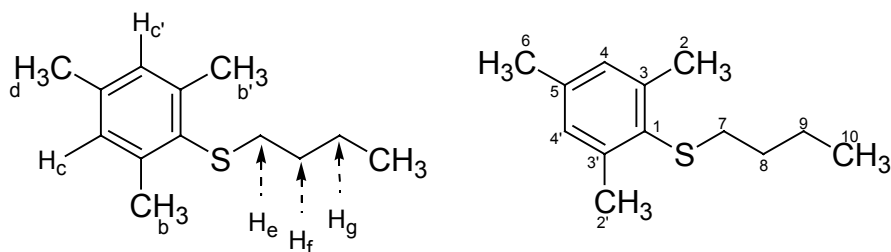
***n*-Butyl 4-Methoxyphenyl Sulfide (entry 4, Table 3):** The general procedure was used to convert 4-methoxy iodobenzene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (370 mg, 95 % yield). ^1H NMR (300 MHz, CDCl_3) δ 7.26-7.23 (d, J = 9.0, 2H; H_b , $\text{H}_{b'}$), 6.76-6.73 (d, J = 8.8, 2H; H_c , $\text{H}_{c'}$), 3.69 (s, 3H; H_g), 2.75-2.70 (t, 2H; H_d), 1.50-1.43 (m, 2H; H_e), 1.36-1.28 (m, 2H; H_f), 0.83-0.78 (t, 3H; methyl protons). ^{13}C NMR (75 MHz, CDCl_3) δ 158.62 (C_4), 132.81 (C_1), 126.85 (C_2 , $\text{C}_{2'}$), 114.39 (C_3 , $\text{C}_{3'}$), 55.21 (C_9), 35.04 (C_5), 31.63 (C_6), 21.75 (C_7), 13.59 (C_8). Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{SO}$: C, 67.30; H, 8.22; S, 16.33; Found C, 66.87; H, 8.28; S, 16.21.



***n*-Butyl 2-Methoxyphenyl Sulfide (entry 5, Table 3):** The general procedure was used to convert 2-iodoanisole and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a light yellow oil (329 mg, 84 % yield). ^1H NMR (300 MHz, CDCl_3) δ 7.18-6.75 (m, 4H; H_b , H_c , H_d , H_e), 3.82 (s, 3H; H_i), 2.84-2.79 (t, J = 7.3, 2H; H_f), 1.60-1.52 (m, 2H; H_g), 1.43-1.36 (m, 2H; H_h), 0.87-0.82 (t, J = 7.3, 3H; H_j). ^{13}C NMR (75 MHz, CDCl_3) δ 156.98 (C_6), 128.56 (C_2), 126.54 (C_4), 125.22 (C_1), 120.98 (C_3), 110.28 (C_5), 55.73 (C_{11}), 31.49 (C_7), 30.94 (C_8), 22.06 (C_9), 13.66 (C_{10}). Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{OS}$: C, 67.30; H, 8.22; S, 16.33; Found C, 67.43; H, 8.28; S, 16.10.

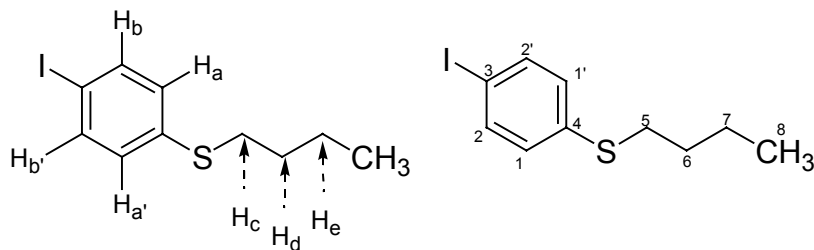


***n*-Butyl 2,2'-Dimethyl-4-methylphenyl Sulfide (entry 6, Table 3):** The general procedure was used to convert 2,2'-Dimethyl-4-methyl iodobenzene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (405 mg, 98 % yield). ^1H NMR (300 MHz, CDCl_3) δ 6.93 (s, 2H; H_c , $\text{H}_{c'}$), 2.64-2.59 (t, $J=7.1$, 2H; H_e), 2.50 (s, 6H; H_b , $\text{H}_{b'}$), 2.26 (s, 3H; H_d), 1.39-1.51 (m, 4H; H_f , H_g), 0.91-0.86 (t, $J=7.1$, 3H; H_h). ^{13}C NMR (75 MHz, CDCl_3) δ 142.8 (C_5), 137.7 (C_3 , $\text{C}_{3'}$), 130.5 (C_1), 128.8 (C_4 , C_4'), 35.2 (C_2 , $\text{C}_{2'}$), 31.9 (C_6), 22.0 (C_7), 21.9 (C_8), 20.9 (C_9), 13.69 (C_{10}). Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{S}$: C, 74.94; H, 9.67; S, 15.39; Found C, 74.66; H, 9.90; S, 15.32.

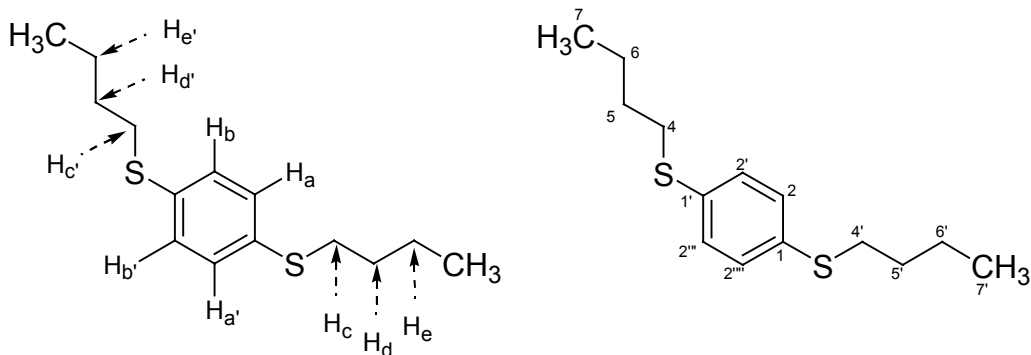


***n*-Butyl 4-Iodophenyl Sulfide (entry 7, Table 3):** The general procedure was used to convert diiodobenzene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a pale yellow oil (512 mg, 88 % yield). ^1H NMR (300 MHz, CDCl_3) δ 7.58-7.55 (d, $J=8.4$, 2H; H_a , $\text{H}_{a'}$), 7.05-7.02 (d, $J=8.2$, 2H; H_b , $\text{H}_{b'}$), 2.91-2.86 (t, $J=7.3$, 2H; H_c), 1.67-1.49 (m,

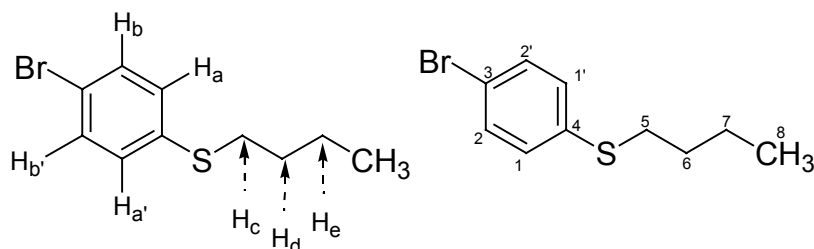
2H; H_d), 1.42-1.30 (m, 2H; H_e), 0.94-0.89 (t, $J=7.3$, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 137.6 (C₁, C_{1'}), 137.2 (C₄), 130.2 (C₂, C_{2'}), 90.0 (C₃), 32.9 (C₅), 30.9 (C₆), 21.9 (C₇), 13.6 (C₈). High Resolution Mass. Spec. for C₁₀H₁₃S; Expected, 291.9783; Found, 291.9796



1,4-Bis-Butylsulfanyl-benzene (entry 8, Table 3): The general procedure was used to convert Diiodobenzene and 2 equiv. of *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a transparent oil (497 mg, 98 % yield). ¹H NMR (300 MHz, CDCl₃) δ 7.15 (d, $J_p=0.3$, 4H; H_a, H_{a'}, H_b, H_{b'}), 2.83-2.78 (t, $J=7.3$, 4H; H_c, H_{c'}), 1.56-1.48 (m, 4H; H_d, H_{d'}), 1.39-1.18 (m, 4H; H_e, H_{e'}), 0.86-0.81 (t, $J=7.3$, 6H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 134.2 (C₁, C_{1'}), 129.5 (C₂, C_{2'}, C_{2'''}, C_{2''''}), 33.5 (C₄, C_{4'}), 31.1 (C₅, C_{5'}), 21.8 (C₆, C_{6'}), 13.5 (C₇, C_{7'}). High Resolution Mass. Spec. for C₁₄H₂₂S₂; Expected, 254.1163; Found, 254.1162

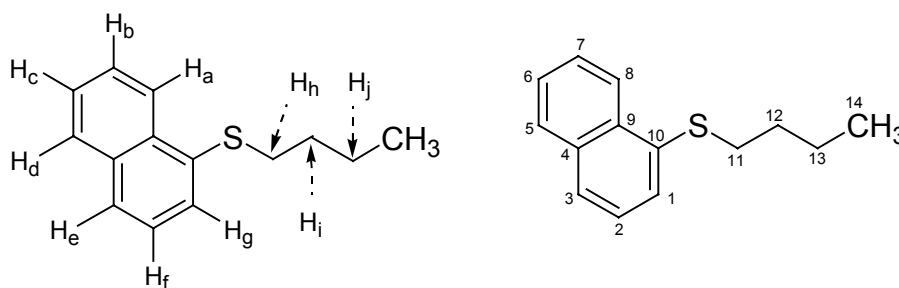


***n*-Butyl 4-Bromophenyl Sulfide (entry 9, Table 3):** The general procedure was used to convert 4-iodo bromobenzene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (450 mg, 92 % yield). ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.36 (d, J =8.6, 2H; H_a , H_a'), 7.19-7.15 (d, J = 8.28, 2H; H_b , H_b'), 2.91-2.86 (t, J =7.1, 2H; H_c), 1.57-1.47 (m, 2H; H_d), 1.41-1.31 (m, 2H; H_e), 0.94-0.89 (t, J =7.3, 3H; H_f). ^{13}C NMR (75 MHz, CDCl_3) δ 136.2 (C_4), 131.7 (C_1 , C_1'), 130.2 (C_2 , C_2'), 119.2 (C_3), 33.2 (C_5), 30.9 (C_6), 21.8 (C_7), 13.5(C_8). Anal. Calcd. for $\text{C}_{10}\text{H}_{13}\text{Br}$ C, 48.99; H, 5.34; S, 13.08; Found C, 49.09; H, 5.44; S, 12.96.



***n*-Butyl 2-Naphthalene Sulfide (entry 10, Table 3):** The general procedure was used to convert 2-Iodonaphthalene and *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane) gave the analytically pure product as a clear oil (410 mg, 95 % yield). ^1H NMR (300 MHz, CDCl_3) δ 8.46-8.44 (d, J =8.1, 1H; H_a), 7.88-7.85 (d, J = 7.1,

1H; H_d), 7.75-7.73 (d, 1H; H_e), 7.61-7.40 (m, 4H; H_g, H_f, H_b, H_c), 2.89-2.84 (t, 2H; H_h), 1.60-1.50 (m, 4H; H_i), 1.42-1.30 (m, 4H; H_j), 0.98-0.93 (t, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 134.17 (C₄), 133.81 (C₁₀), 132.78 (C₉), 128.47 (C₈), 127.27 (C₅), 126.72 (C₂), 126.17 (C₆), 126.09 (C₇), 125.50 (C₁), 124.95 (C₃), 33.7 (C₁₁), 31.16 (C₁₂), 21.98 (C₁₃), 13.63 (C₁₄). Anal. Calcd. for C₁₄H₁₆S: C, 77.72; H, 7.45; S, 14.82; Found C, 77.44; H, 7.63; S, 14.56.



4-Pyrrole *n*-Butyl phenyl sulfide (entry 11, Table 3): The general procedure was used to convert Diiodobenzene and 2 equiv. of *n*-butyl sulfide to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a white solid (430 mg, 95% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.45-7.37 (d, *J*=8.8, 2H; H_a, H_a), 7.32-7.25 (d, *J*= 8.8, 2H; H_b, H_b'), 7.07-7.05 (t, *J*=2.2, 2H; H_g, H_g'), 6.35-6.33 (t, *J*=2.07, 2H; H_f, H_f'), 2.95-2.90 (t, *J*=7.15, 2H; H_c), 1.59-1.52 (m, 2H; H_d), 1.45-1.18 (m, 2H; H_e), 0.95-0.90 (t, *J*=7.3, 3H; methyl protons). ¹³C NMR (75 MHz, CDCl₃) δ 133.8 (C₃), 130.5 (C₄), 120.8 (C₁, C₁'), 119.2 (C₂, C₂'), 118.2 (C₈, C₈'), 110.4 (C₉, C₉'), 33.9 (C₅), 31.1 (C₆), 21.9 (C₇), 13.5 (C₁₀). High Resolution Mass. Spec. for C₁₄H₁₇NS; Expected, 231.1082; Found, 231.1099.

Cyclohexyl-phenyl sulfide (entry 12, Table 3): The general procedure was used to convert iodobenzene and cyclohexylmercaptan to the title product. Purification by flash chromatography (hexane as the eluent) gave the analytically pure product as a clear oil (297 mg, 77% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.44 (dd, *J*=6.97, 2H; H_a, H_{a'}), 7.35-7.22 (m, 3H; H_b, H_{b'}, H_c), 3.19-3.11 (m, 1H; H_d), 2.04 (m, 2H; H_e, H_i), 1.82 (m, 2H; H_{e'}, H_{i'}), 1.65 (m, 1H; H_g), 1.48-1.26 (m, 5H; H_h, H_f, H_{h'}, H_{f'}, H_{g'}). ¹³C NMR (75 MHz, CDCl₃) δ 135.11 (C₁), 131.75 (C₃, C₅), 128.64 (C₂, C₆), 126.46 (C₄), 46.44 (C₇), 33.26 (C₈, C₁₂), 25.97 (C₁₀), 25.69 (C₉, C₁₁). Anal. Calcd. for C₁₂H₁₆S: C, 74.94; H, 8.39; S, 16.67; Found C, 75.06; H, 8.40; S, 16.54.

