Supporting Information

Nickel-Catalyzed Direct Formation of C-S Bond of Aryl Sulfides from Arylsulfonyl Chlorides and Aryl Iodides Using Mn as a Reducing Agent

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1. General Information

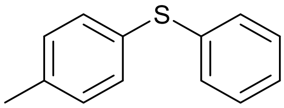
All chemicals were purchased from commercial suppliers and used without further purification. Solvent DMF was dried over CaH_2 and stored in the presence of activated molecular sieve. All reactions were carried out under an atmosphere of nitrogen using tube with a Teflon screwcap. Flash chromatography was performed on silica gel (200-300 mesh). The single crystal data of compounds were collected by a Cu-Kα or Mo-Kα rotating anode source at 100 K, using a Supernova diffractometer with the ω-scan method. ^1H NMR spectra were recorded on Bruker Avance III (400 MHz) and chemical shifts are expressed in δ ppm values with reference to tetramethylsilane (TMS) as internal standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet. Coupling constants (J) are expressed in Hz. Product yields refer to isolated yields after column chromatography. All commercial reagents were purchased from Alfa, Sigma Aldrich, Energy Chemical or TCI.

2. General Experimental Procedure

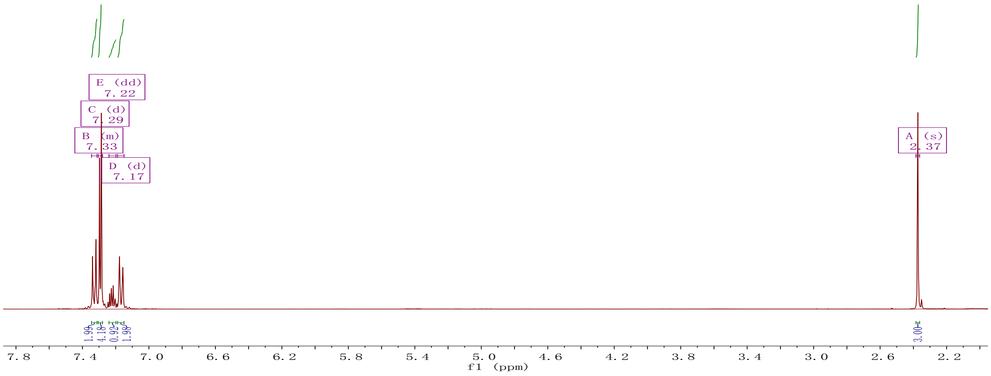
$NiCl_2$**.**glyme (0.02 mmol, 4.4 mg), neocuproine (L_4) (0.03 mmol, 6.3 mg), NaI (0.3 mmol, 45 mg), KF (0.3 mmol, 17.4 mg), Mn dust (1 mmol, 55 mg), arysulfonyl chlorides (0.6 mmol) and aryl iodides (0.2 mmol) were mixed in dried DMF (1ml) in a 35 ml Teflon screwcap sealed tube. The tube was charged with N_2 and the mixture was vigorously stirred at 80 ^oC for 24 h. After cooling to RT, the reaction mixture was diluted with dichloromethane (20 mL), filtered through a pad of silica gel and further concentrated under reduced pressure. The crude product was purified on a silica gel column.

3. Detailed Procedure and characterization of compounds in Table 2

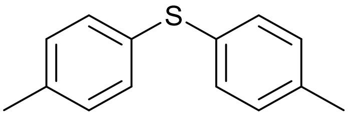
1) (4-Methylphenyl) (phenyl) sulfane (3a) [1]:



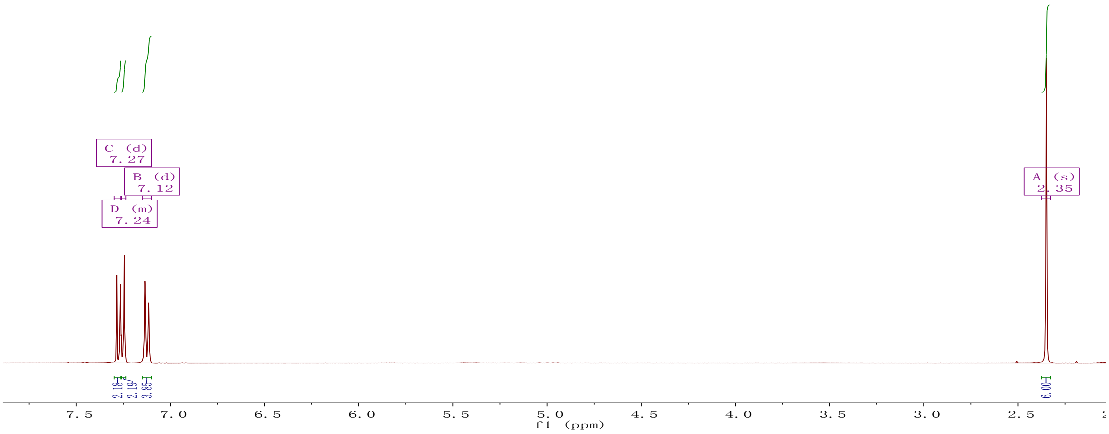
Following the general experimental procedure presented above, using Iodobenzene (0.2 mmol, 41 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether eluted with petroleum ether to provide **3a** as a colorless oil (57% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.31 (m, 2H), 7.29 (d, J = 4.3 Hz, 4H), 7.22 (dd, J = 9.0, 4.3 Hz, 1H), 7.17 (d, J = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.62, 137.14, 132.29, 131.30, 131.07, 130.08, 129.80, 129.05, 128.56, 126.42, 21.15.



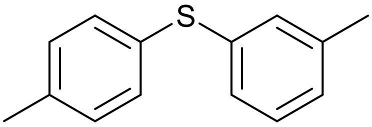
2) Di-(p-tolyl) sulfane (3b) [2]:



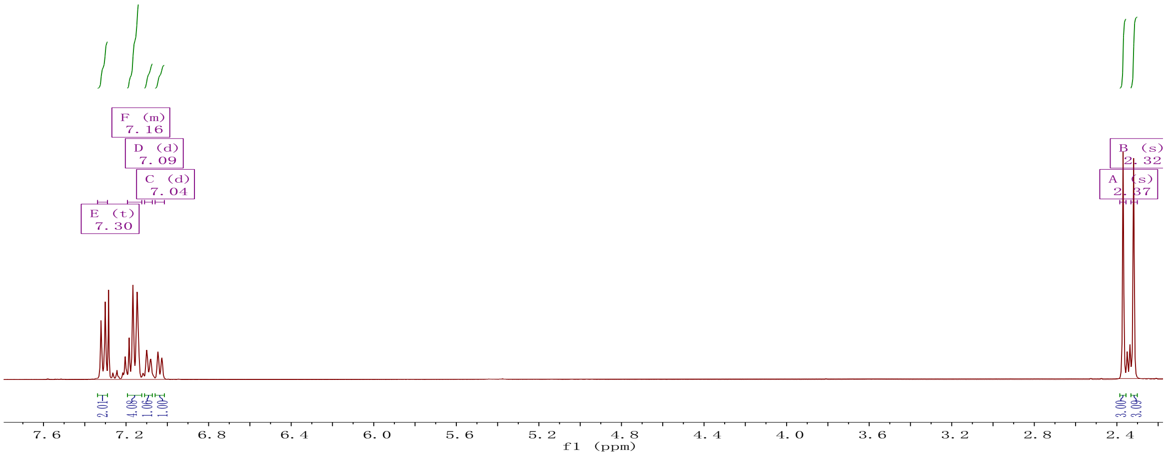
Following the general experimental procedure presented above, using 4-Iodotoluene (0.2 mmol, 43.6 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3b as a white solid (81% yield); m.p. 55–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 7.5 Hz, 2H), 7.26 – 7.24 (m, 2H), 7.12 (d, J = 8.0 Hz, 4H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.90, 132.67, 131.06, 129.91, 21.07.



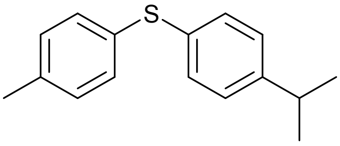
3) (3-Methylphenyl) (4-methylphenyl) sulfane (3c) [1]:



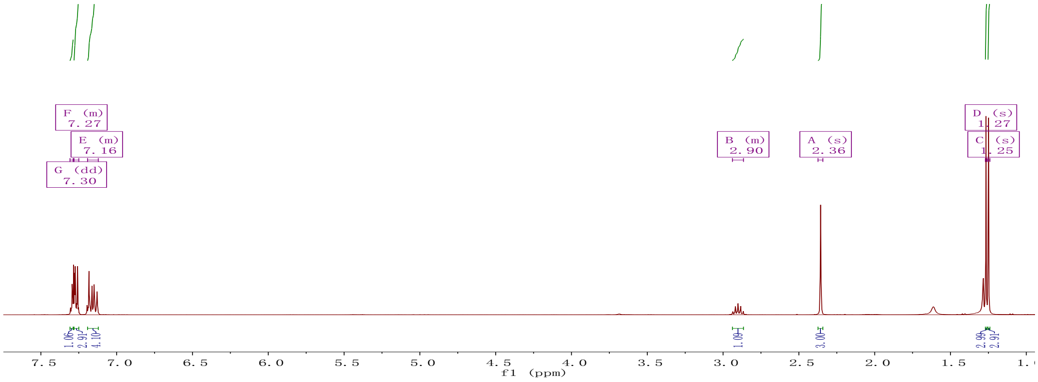
Following the general experimental procedure presented above, using 3-Iodotoluene (0.2 mmol, 43.6 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3c as a colorless oil (48% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 6.2 Hz, 2H), 7.19 – 7.12 (m, 4H), 7.09 (d, J = 7.7 Hz, 1H), 7.04 (d, J = 7.5 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.89, 137.39, 136.61, 132.01, 131.62, 130.63, 130.02, 128.91, 127.42, 127.12, 21.31, 21.14.



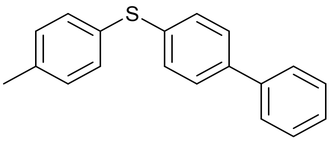
4) (4-Isopropylphenyl) (4-methylphenyl) sulfane (3d):



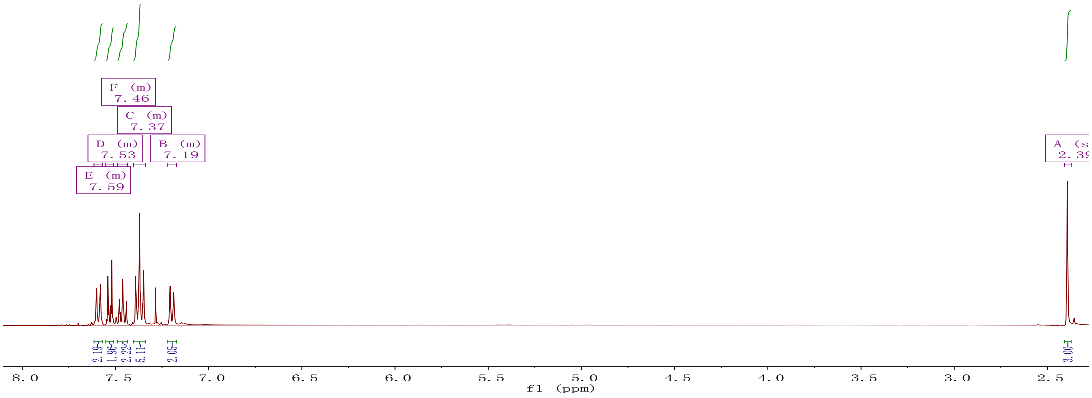
Following the general experimental procedure presented above, using 1-Iodo-4-isopropylbenzene (0.2 mmol, 49 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3d as a colorless oil (60% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30 (dd, J = 4.4, 2.0 Hz, 1H), 7.28 – 7.25 (m, 3H), 7.19 – 7.12 (m, 4H), 2.94 – 2.87 (m, 1H), 2.36 (s, 3H), 1.27 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.75, 137.04, 133.18, 132.39, 131.41, 131.07, 130.75, 129.94, 127.29, 33.75, 23.93, 21.10. Anal. Calcd. for $C_{16}H_{18}S$: C, 79.30; H, 7.49. Found C, 78.18; H, 7.26.



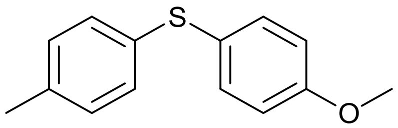
5) (4-Phenylphenyl) (4-methylphenyl) sulfane (3e)[3]:



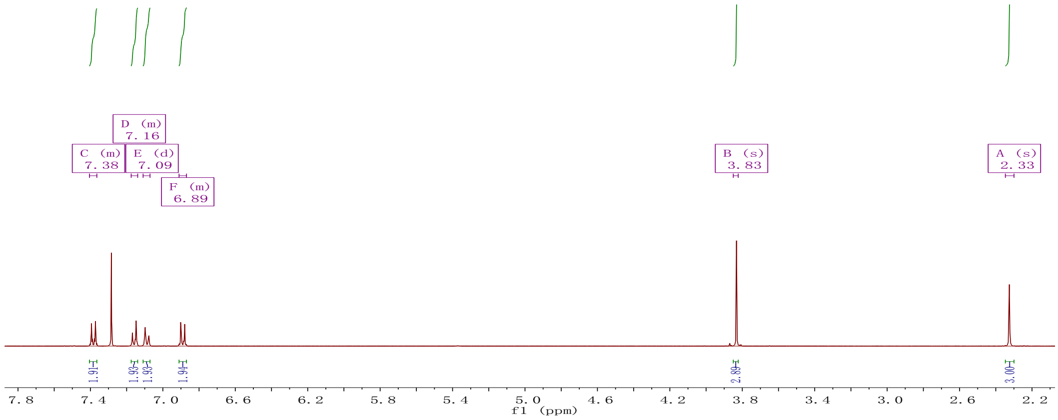
Following the general experimental procedure presented above, using 4-Iodobiphenyl (0.2mmol, 56mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3e as a white solid (51% yield); m.p. 106–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.57 (m, 2H), 7.55 – 7.51 (m, 2H), 7.49 – 7.44 (m, 2H), 7.40 – 7.34 (m, 5H), 7.22 – 7.17 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.43, 139.39, 137.75, 136.31, 132.41, 131.20, 130.15, 130.07, 128.84, 127.74, 127.39, 126.94, 21.18.



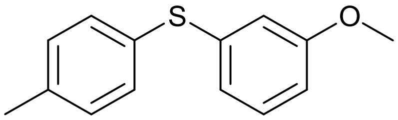
6) (4-Methoxyphenyl) (4-methylphenyl) sulfane (3f) [2]:



Following the general experimental procedure presented above, using 4-Iodoanisole (0.2mmol, 47.4mg) and p-toluenesulfonyl chloride (0.6mmol, 114mg) as substrates instead, purified by column chromatography (40:1 PE:EtOAc) to provide 3f as a colorless oil (92% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 2H), 7.17 – 7.14 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.91 – 6.87 (m, 2H), 3.83 (s, 3H), 2.33 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 159.46, 136.14, 134.37, 129.78, 129.39, 127.75, 125.65, 114.88, 55.37, 21.00.

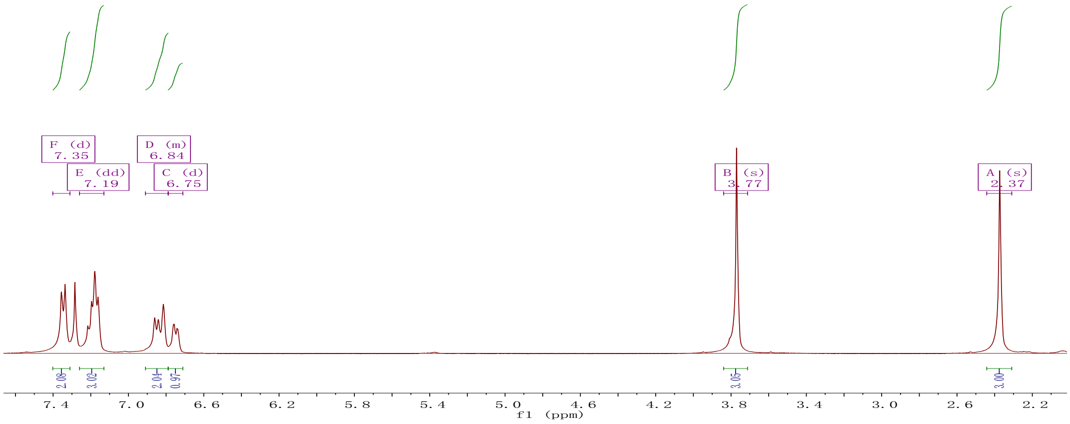


7) (3-Methoxyphenyl) (4-methylphenyl) sulfane (3g) [4]:

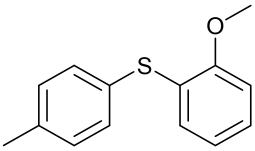


Following the general experimental procedure presented above, using 3-Iodoanisole (0.2mmol, 47.4mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (40:1 PE:EtOAc) to provide 3g as a colorless oil (81%

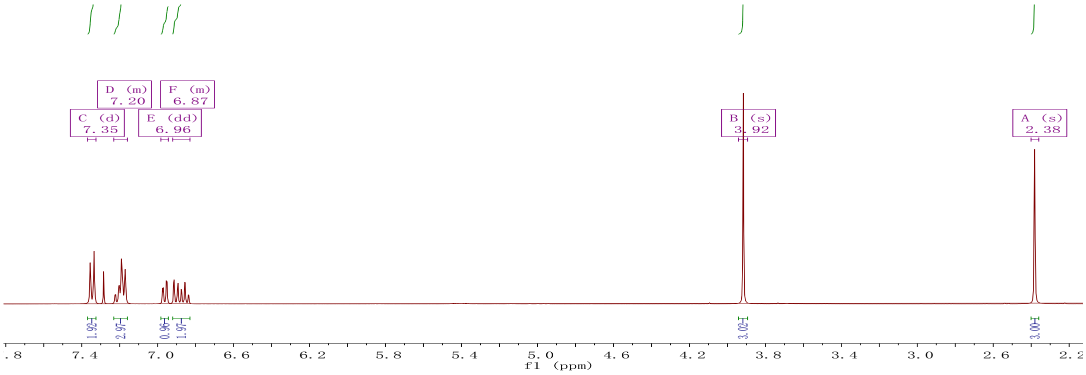
yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.9 Hz, 2H), 7.19 (dd, J = 14.4, 7.6 Hz, 3H), 6.91 – 6.79 (m, 2H), 6.75 (d, J = 6.4 Hz, 1H), 3.77 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.00, 138.63, 137.84, 132.64, 130.75, 130.11, 129.82, 121.76, 114.80, 112.07, 55.26, 21.17.



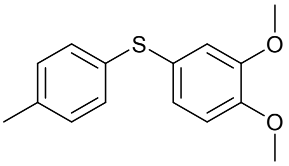
8) (2-Methoxyphenyl) (4-methylphenyl) sulfane (3h) [5]:



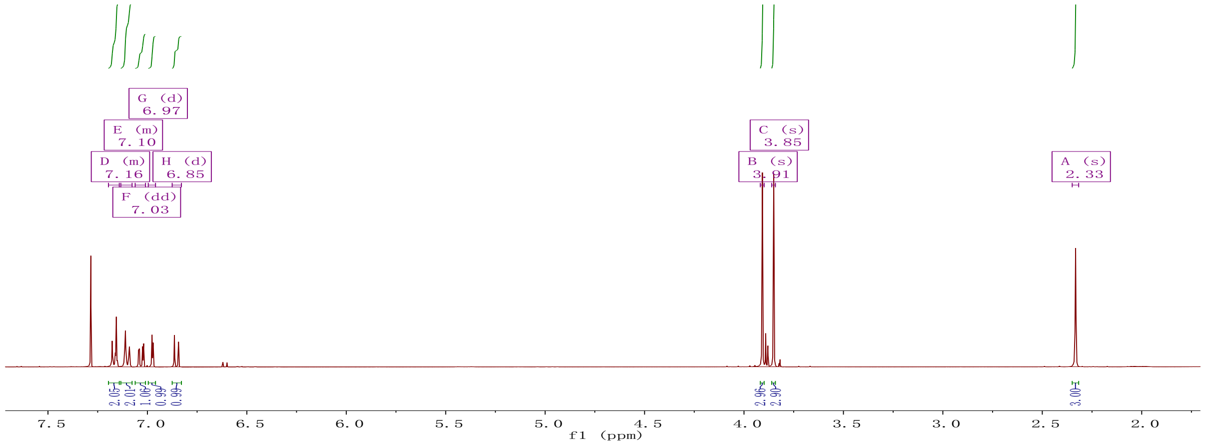
Following the general experimental procedure presented above, using 2-Iodoanisole (0.2mmol, 47.4mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (40:1 PE:EtOAc) to provide 3h as a colorless oil (22% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.1 Hz, 2H), 7.23 – 7.16 (m, 3H), 6.96 (dd, J = 7.7, 1.6 Hz, 1H), 6.92 – 6.83 (m, 2H), 3.92 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.55, 137.75, 132.98, 130.12, 129.91, 129.82, 127.44, 125.73, 121.22, 110.63, 55.89, 21.19.



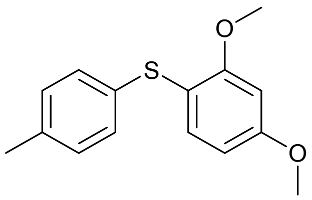
9) (3, 4-Dimethoxyphenyl) (4-methylphenyl) sulfane (3i):



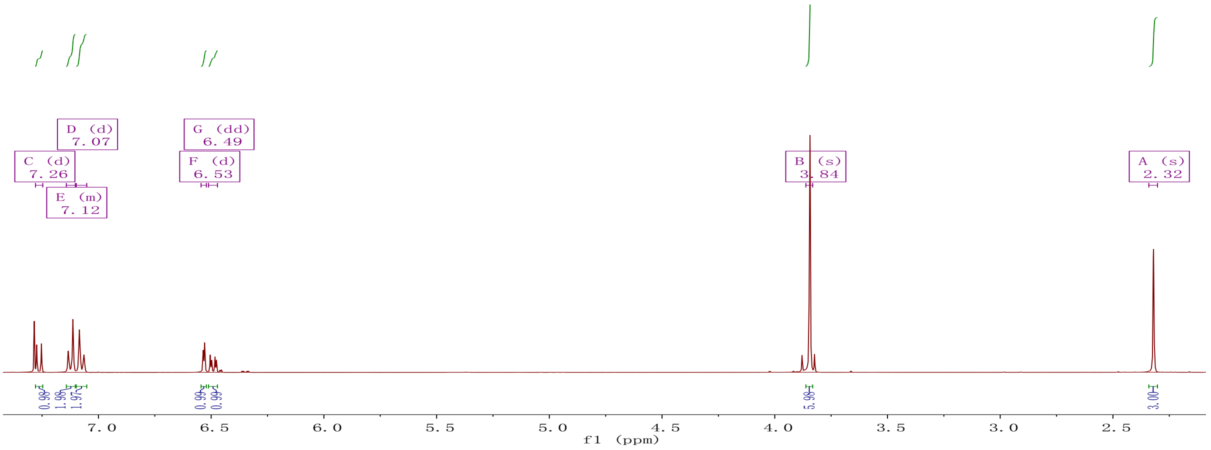
Following the general experimental procedure presented above, using 4-Iodo-1,2-dimethoxybenzene (0.2mmol, 53.4mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg)as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 3i as a colorless oil (90% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.14 (m, 2H), 7.13 – 7.08 (m, 2H), 7.03 (dd, J = 8.3, 2.1 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.35, 149.00, 136.24, 134.06, 129.81, 129.36, 125.87, 125.64, 120.84, 115.77, 111.72, 111.31, 55.97, 21.01. Anal. Calcd. for $C_{15}H_{16}SO_2$: C, 69.21; H, 6.20. Found: C, 70.86; H, 6.37.



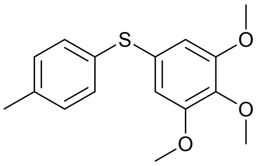
10) (2, 4-Dimethoxyphenyl) (4-methylphenyl) sulfane (3j)[6]:



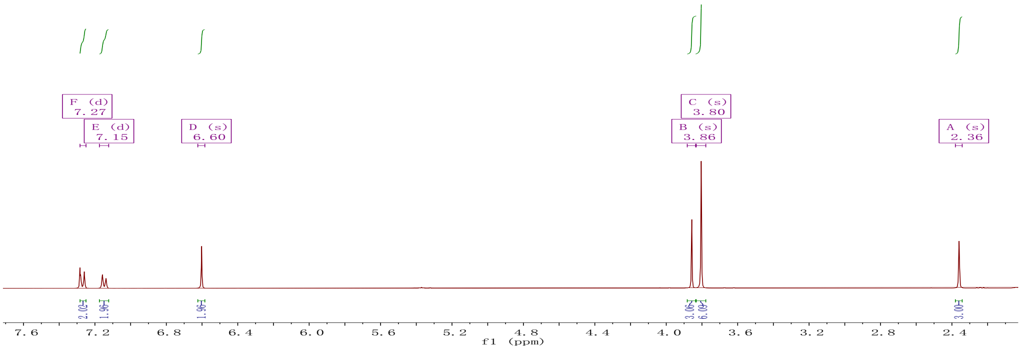
Following the general experimental procedure presented above, using 1-Iodo-2,4-dimethoxybenzene (0.2mmol, 53.4mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (25:1 PE:EtOAc) to provide 3j as a white solid (29% yield); m.p. 71−73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.4 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 6.53 (d, J = 2.5 Hz, 1H), 6.49 (dd, J = 8.5, 2.5 Hz, 1H), 3.84 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.36, 159.79, 135.78, 135.48, 133.38, 129.66, 129.01, 113.62, 105.28, 99.20, 55.96, 55.49, 21.00.



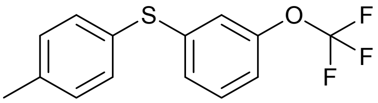
11) (3, 4, 5-trimethoxyphenyl) (4-methylphenyl) sulfane (3k):



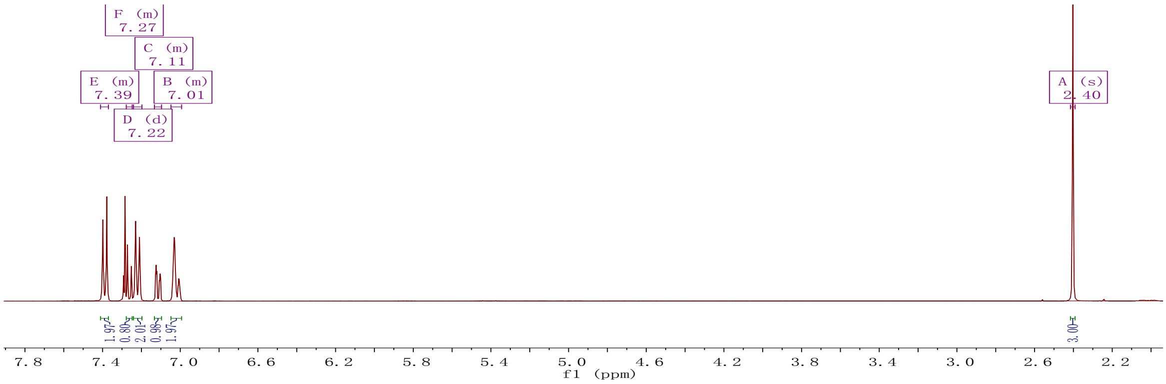
Following the general experimental procedure presented above, using 5-Iodo-1,2,3-trimethoxybenzene (0.2 mmol, 59 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 3k as a white solid (82% yield); m.p. 81-83 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.60 (s, 2H), 3.86 (s, 3H), 3.80 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)：δ 153.55, 137.39, 137.14, 132.29, 130.92, 130.75, 129.97, 108.32, 60.92, 56.17, 21.10. Anal. Calcd. for $C_{16}H_{18}SO_3$: C, 66.18; H, 6.25. Found: C, 65.77; H, 6.20.



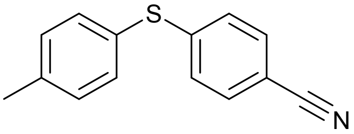
12) (3-(trifluoromethoxy) phenyl) (4-methylphenyl) sulfane (3l):



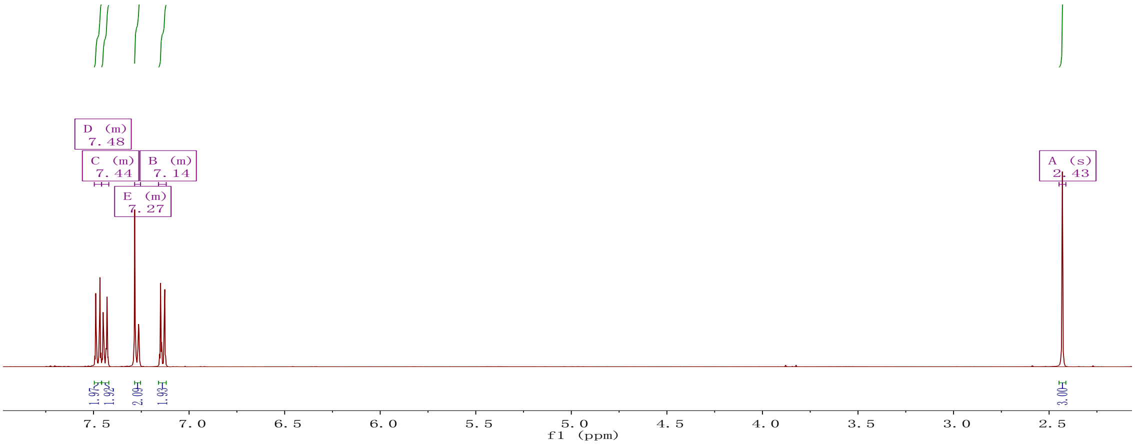
Following the general experimental procedure presented above, using 1-Iodo-3-(trifluoromethoxy) benzene (0.2mmol, 57.6mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3l as a colorless oil (60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.37 (m, 2H), 7.28 – 7.25 (m, 1H), 7.22 (d, J = 7.9 Hz, 2H), 7.13 – 7.10 (m, 1H), 7.05 – 6.99 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.62, 140.68, 138.83, 133.59, 130.41, 129.97, 129.06, 126.48, 120.63, 119.10, 118.08, 21.21. Anal. Calcd. for $C_{14}H_{11}SOF_3$: C, 59.14; H, 3.90. Found: C, 58.33; H, 3.83.



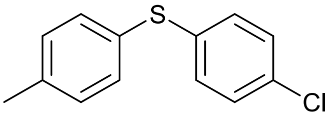
13) 4-(p-tolylthio)benzonitrile (3m) [7]:



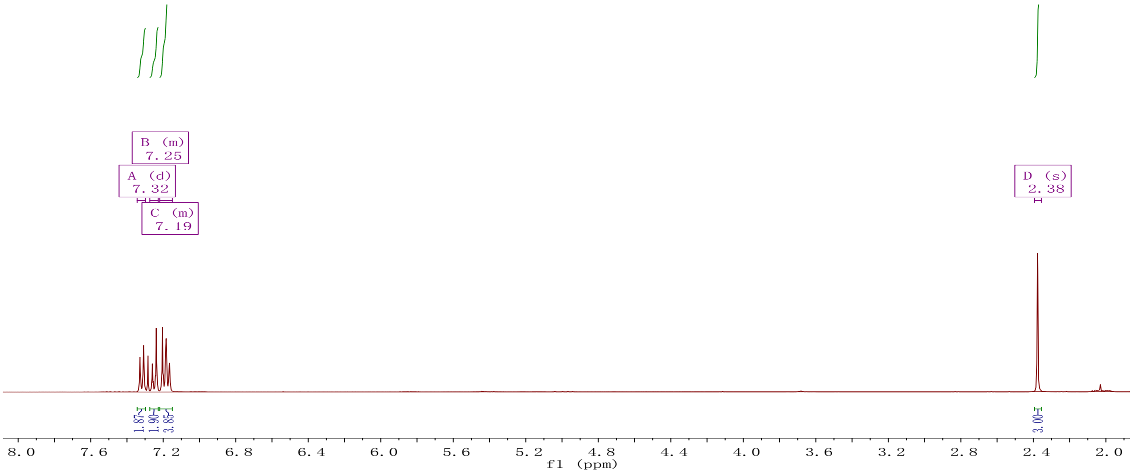
Following the general experimental procedure presented above, using 4 -Iodobenzonitrile benzene (0.2 mmol, 45.8 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 3m as a white solid (80% yield); m.p. 100-102 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 – 7.46 (m, 2H), 7.46 – 7.42 (m, 2H), 7.28 – 7.25 (m, 2H), 7.16 – 7.12 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.61, 139.97, 134.96, 132.30, 130.77, 126.80, 126.70, 118.92, 108.30, 21.33.



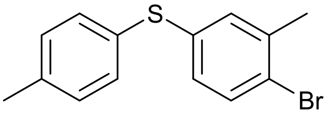
14) (4-Chlorophenyl) (4-methylphenyl) sulfane (3n)[8]:



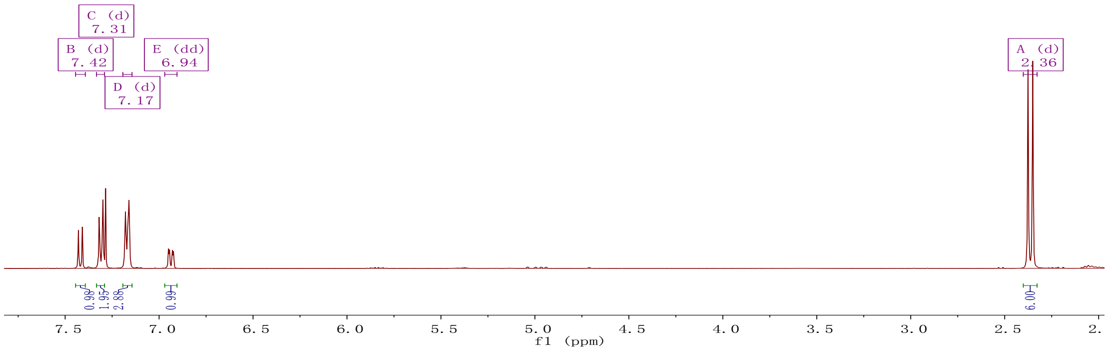
Following the general experimental procedure presented above, using 1-Chloro-4-iodobenzene (0.2mmol, 47.6mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3n as a white solid (50% yield); m.p. 71–72 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 2H), 7.19 (dt, J = 12.4, 4.1 Hz, 4H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 138.06, 135.96, 132.50, 132.30, 130.81, 130.69, 130.22, 129.15, 21.15.



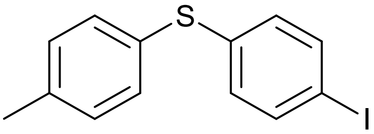
15) (4-Bromo-3-methylphenyl) (4-methoxyphenyl) sulfane (3o):



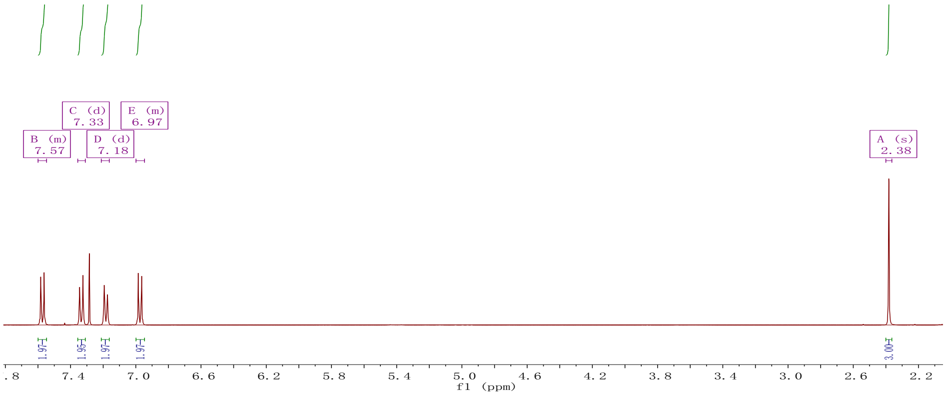
Following the general experimental procedure presented above, using 2-Bromo-5-iodotoluene (0.2 mmol, 59.4 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3o as a colorless oil (36% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.42 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.5 Hz, 3H), 6.94 (dd, J = 8.3, 2.2 Hz, 1H), 2.36 (d, J = 10.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 138.90, 137.40, 136.60, 132.01, 131.07, 130.61, 130.02, 128.56, 127.42, 127.11, 21.32, 21.14. Anal. Calcd. for $C_{14}H_{13}SBr$: C, 57.35; H, 4.47. Found C, 55.98; H, 4.41.



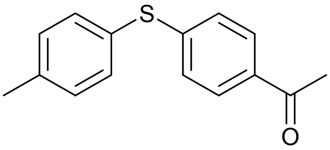
16) (4-Iodophenyl) (4-methylphenyl) sulfane (3p)[9]:



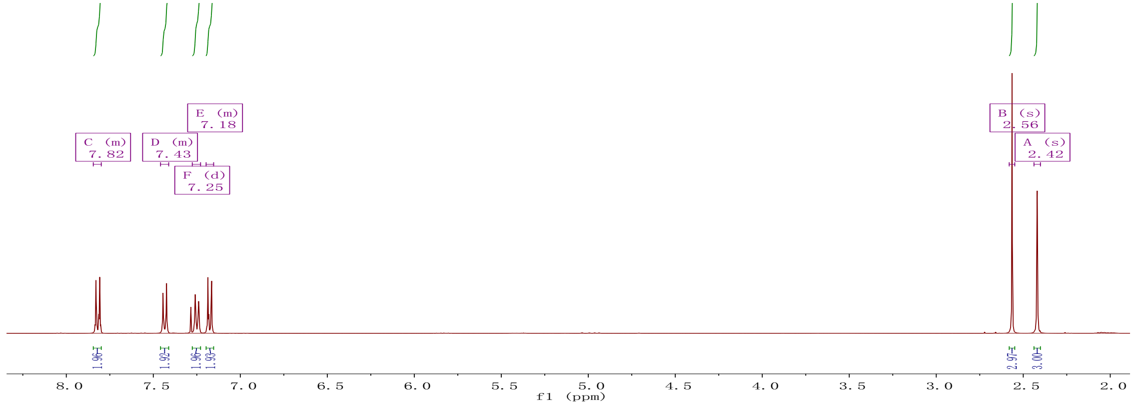
Following the general experimental procedure presented above, using 1,4-Diiodobenzene (0.2mmol, 66mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 3p as a white solid (39% yield); mp 100–101 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.60 – 7.55 (m, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.00 – 6.95 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 138.30, 137.95, 137.88, 132.91, 130.89, 130.28, 130.09, 129.81, 128.56, 91.00, 21.21.



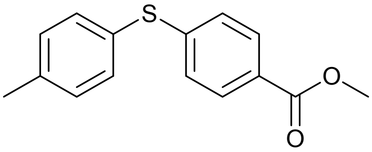
17) 1-(4-(P-Tolylthio) phenyl) ethanone (3q) [10]:



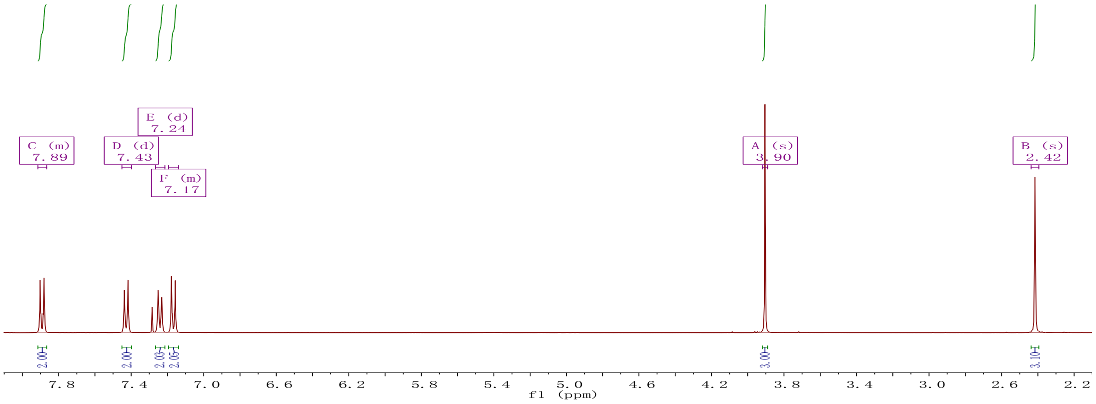
Following the general experimental procedure presented above, using 4-Iodoacetophenone (0.2 mmol, 49 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 3q as a white solid (42% yield); m.p. 90-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 – 7.80 (m, 2H), 7.46 – 7.41 (m, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.20 – 7.15 (m, 2H), 2.56 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.16, 145.96, 139.36, 134.51, 134.15, 130.55, 128.84, 127.92, 126.66, 26.46, 21.29.



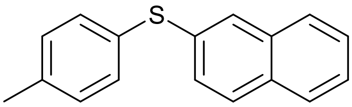
18) Methyl-4-(p-tolylthio) benzoate (3r) [11]:



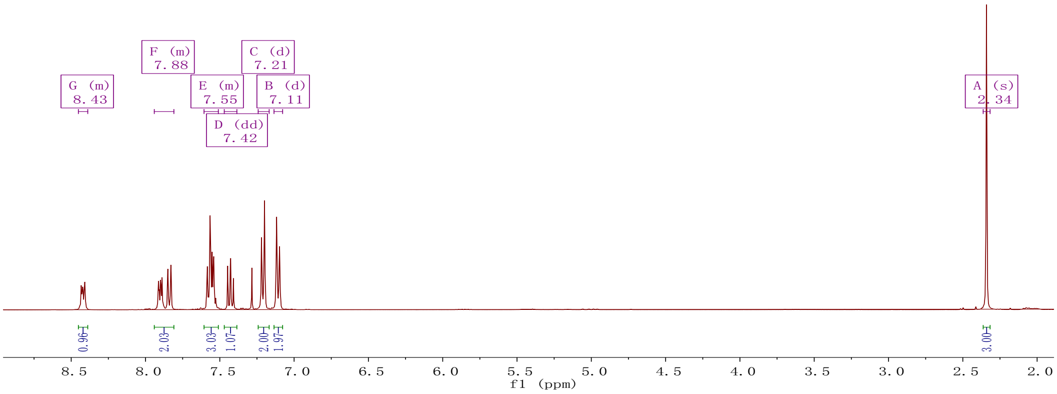
Following the general experimental procedure presented above, using Methyl 4-iodobenzoate (0.2 mmol, 52.4 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 3r as a white solid (46% yield); m.p. 45–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.87 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.19 – 7.14 (m, 2H), 3.90 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.77, 145.42, 139.22, 134.38, 130.50, 130.01, 128.16, 127.05, 126.71, 52.04, 21.27.



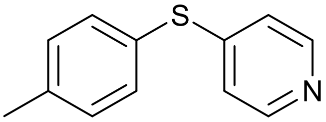
19) (4-Methylphenyl) (naphthalen-2-yl) sulfane (3v) [12]:



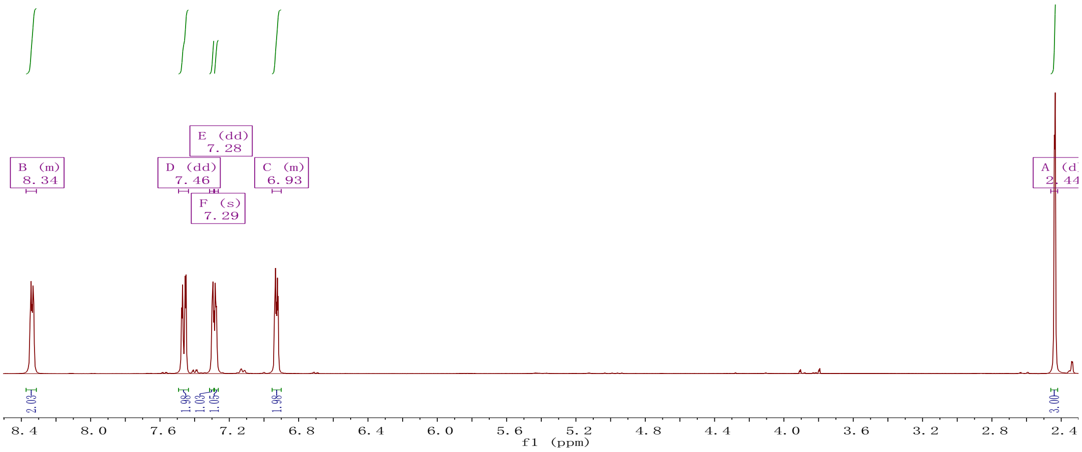
Following the general experimental procedure presented above, using 2-Iodonaphthalene (0.2 mmol, 50.8 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 3v as a white solid (70% yield); m.p. 67–68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 – 8.39 (m, 1H), 7.93 – 7.87 (m, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.46 – 7.40 (m, 1H), 7.21 (d, J = 8.2 Hz, 2H), 7.12 (t, J = 9.9 Hz, 2H), 2.35 (d, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.64, 134.14, 133.11, 132.67, 132.46, 130.99, 130.29, 129.99, 128.53, 128.45, 126.76, 126.37, 125.80, 125.41, 21.06.



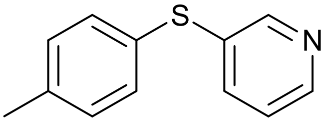
20) 4-(P-tolylthio) pyridine (3w) [13]:



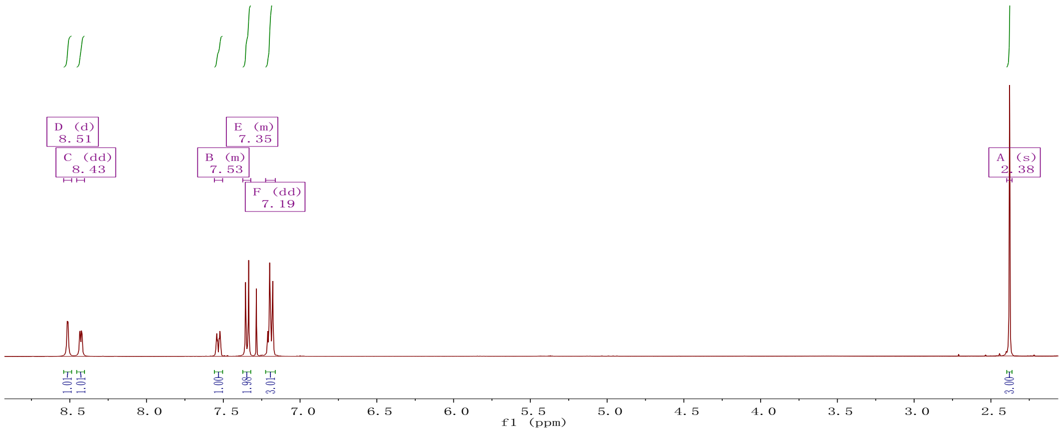
Following the general experimental procedure presented above, using 4-Iodopyridine (0.2 mmol, 41 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (10:1 PE:EtOAc) to provide 3w as a Colorless oil (63% yield); 1H NMR (400 MHz, $CDCl_3$): δ 8.37 – 8.31 (m, 2H), 7.46 (dd, J = 8.2, 2.0 Hz, 2H), 7.29 (s, 1H), 7.28 (dd, J = 2.3, 0.8 Hz, 1H), 6.95 – 6.90 (m, 2H), 2.44 (d, J = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.09, 149.32, 140.18, 135.43, 130.76, 125.54, 120.49, 21.35.



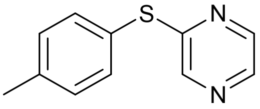
21) 3-(P-tolylthio) pyridine (3x) [14]:



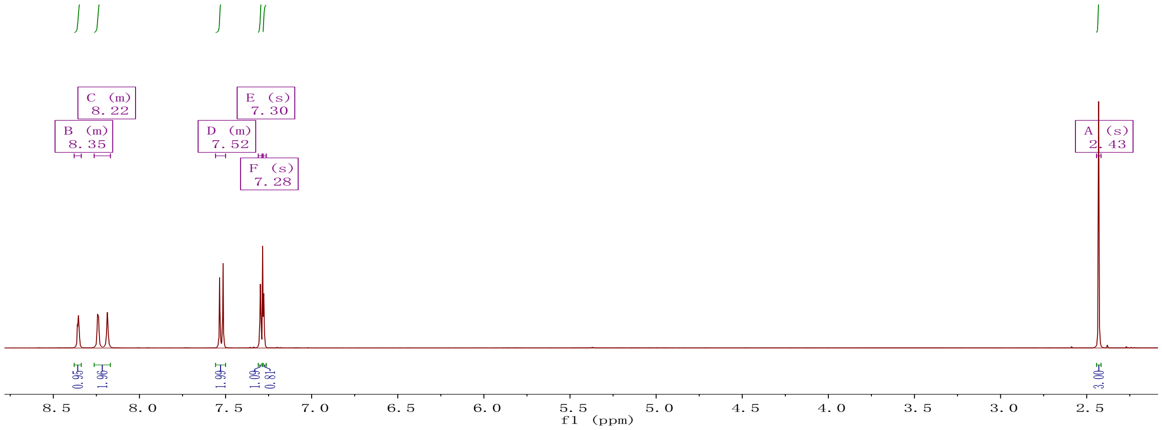
Following the general experimental procedure presented above, using 3-Iodopyridine (0.2mmol, 41mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (10:1 PE:EtOAc) to provide 3x as a Colorless oil (55% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.51 (d, J = 1.8 Hz, 1H), 8.43 (dd, J = 4.7, 1.1 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.37 – 7.32 (m, 2H), 7.19 (dd, J = 7.7, 5.4 Hz, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 150.02, 147.25, 138.49, 136.80, 134.84, 132.81, 130.37, 129.50, 123.78, 21.17.



22) 2-(P-Tolylthio) pyrazine (3y) [15]:

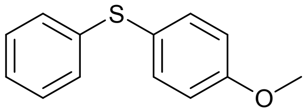


Following the general experimental procedure presented above, using Iodopyrazine (0.2 mmol, 41.2 mg) and p-toluenesulfonyl chloride (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography (10:1 PE:EtOAc) to provide 3y as a Colorless oil (92% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 – 8.34 (m, 1H), 8.26 – 8.17 (m, 2H), 7.56 – 7.50 (m, 2H), 7.30 (s, 1H), 7.28 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 159.26, 143.77, 142.52, 140.14, 139.90, 135.27, 130.72, 125.15, 21.37.

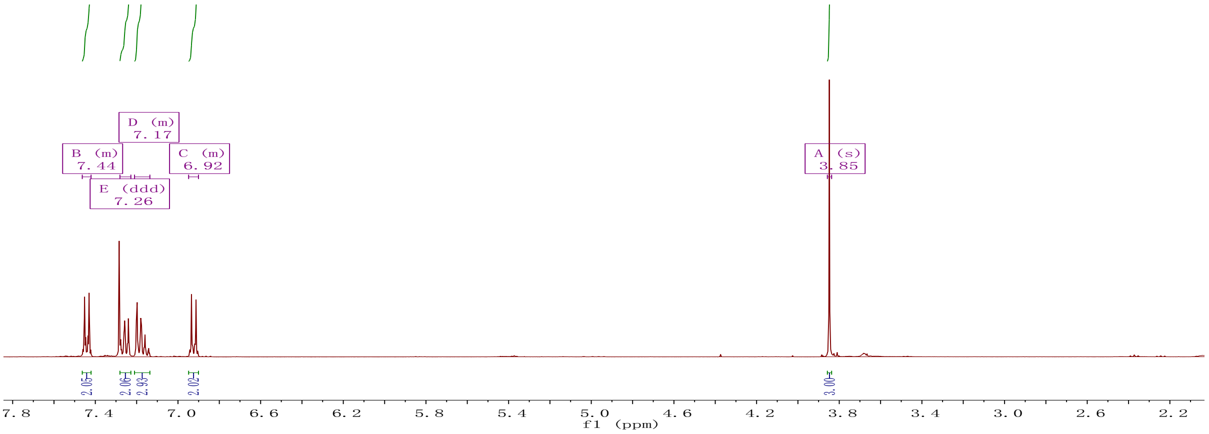


4. Detailed Procedure and characterization of compounds in Table 3.

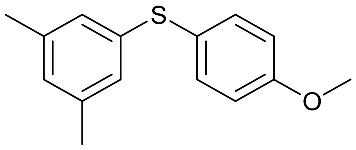
23) (4-Methoxyphenyl) (phenyl) sulfane (4a) [16]:



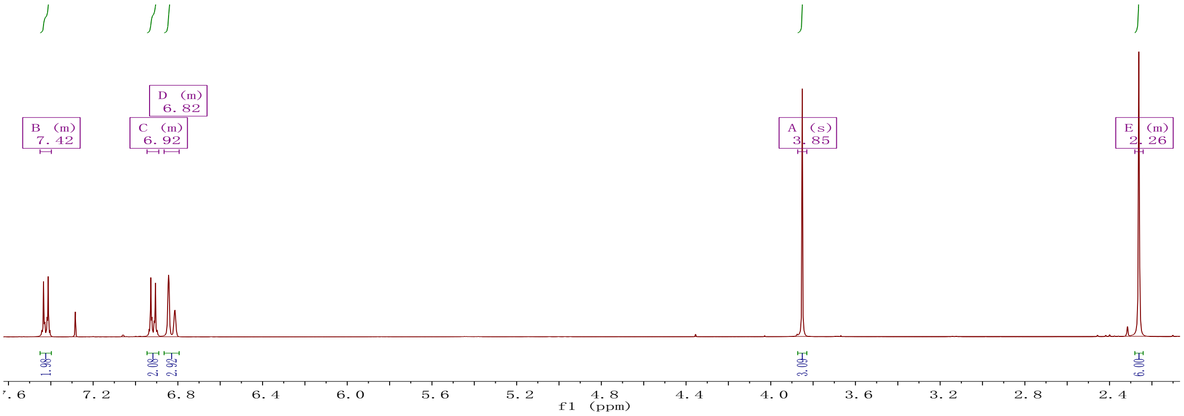
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and benzenesulfonyl chloride (0.6 mmol, 106 mg)as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4a as a colorless oil (62% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.26 (ddd, J = 7.2, 4.5, 1.4 Hz, 2H), 7.21 – 7.14 (m, 3H), 6.95 – 6.90 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.84, 138.61, 135.38, 128.94, 128.22, 125.77, 124.32, 115.00, 55.38.



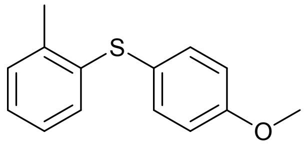
24) (3, 5-Dimethylphenyl) (4-methoxyphenyl) sulfane (4c) [4]:



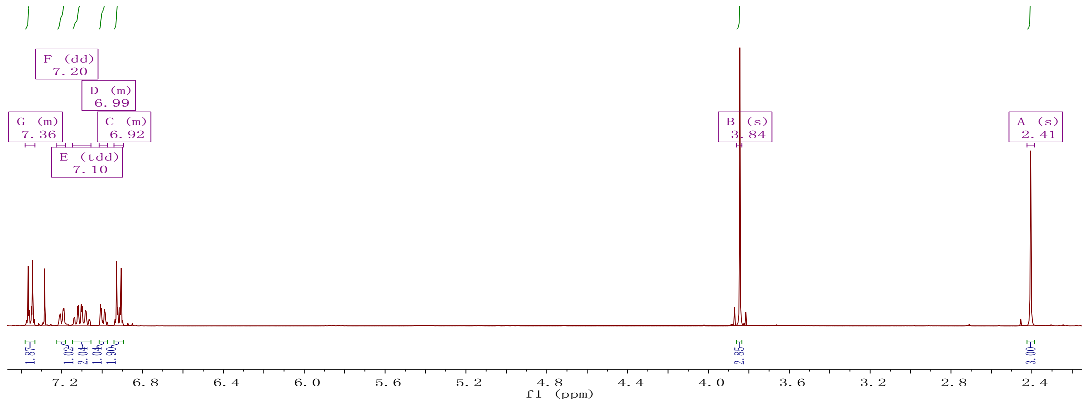
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 3,5-dimethylbenzenesulfonyl chlorid (0.6 mmol, 123 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4c as a colorless oil (59% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 2H), 6.95 – 6.89 (m, 2H), 6.86 – 6.79 (m, 3H), 3.85 (s, 3H), 2.28 – 2.24 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.63, 138.63, 138.21, 137.78, 135.01, 127.88, 126.24, 124.82, 116.37, 114.90, 55.37, 21.23.



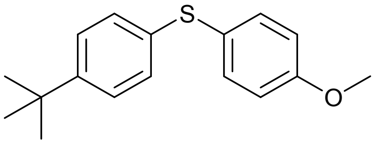
25) (4-Methoxyphenyl) (2-methylphenyl) sulfane (4d)[17]:



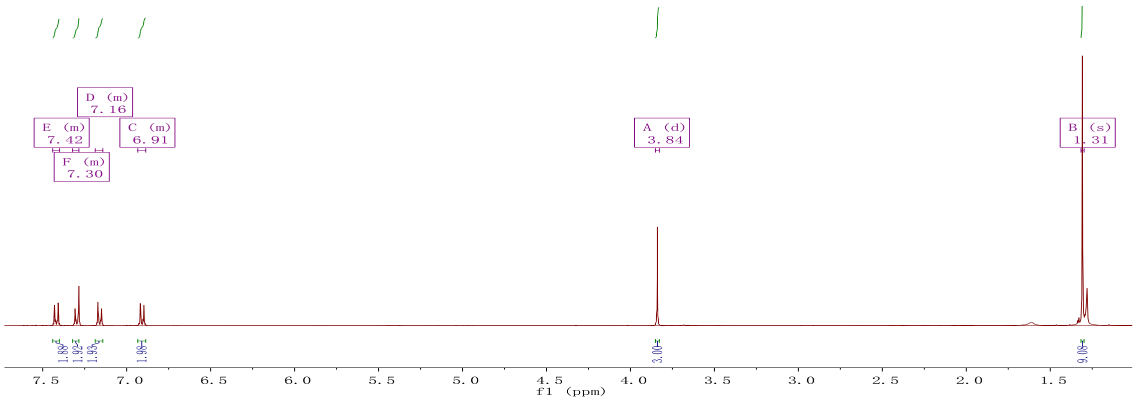
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 2-methylbenzenesulfonyl chloride chlorid (0.6 mmol, 114 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4d as a colorless oil (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.33 (m, 2H), 7.20 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.10 (tdd, *J* = 8.9, 7.3, 1.5 Hz, 2H), 7.01 – 6.97 (m, 1H), 6.94 – 6.89 (m, 2H), 3.84 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.53, 137.03, 134.59, 130.21, 129.05, 126.47, 126.12, 124.44, 115.03, 55.37, 20.31.



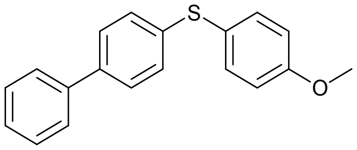
26) (4-(Tert-butyl) phenyl) (4-methoxyphenyl) sulfane (4e) [8]:



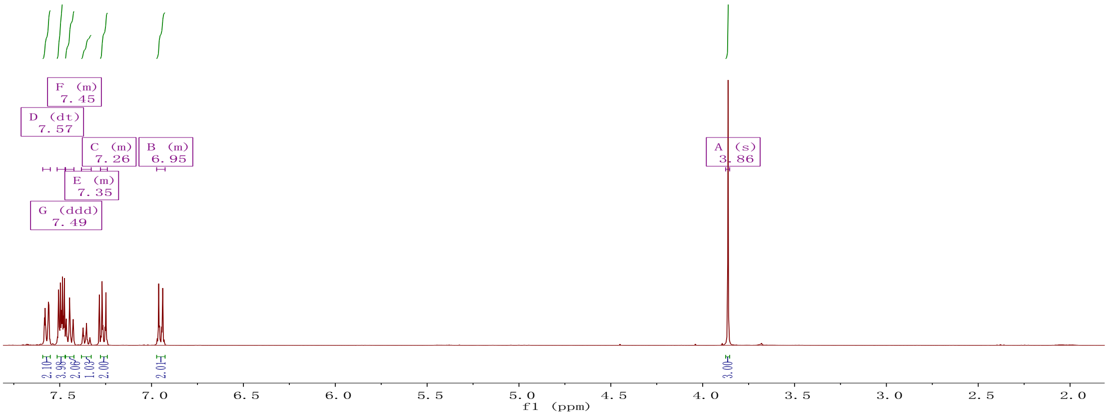
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2mmol, 47.4mg) and 4-tert-Butylbenzenesulfonyl chloride (0.6mmol, 140mg)as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4e as a colorless oil (51% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 7.19 – 7.14 (m, 2H), 6.93 – 6.89 (m, 2H), 3.84 (d, *J* = 2.6 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.60, 149.21, 134.82, 134.66, 128.57, 128.37, 126.72, 126.04, 125.13, 114.90, 34.44, 31.29.



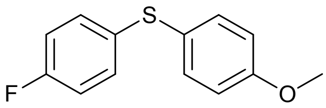
27) (4-Phenylphenyl) (4-methoxyphenyl) sulfane (4f)[18]:



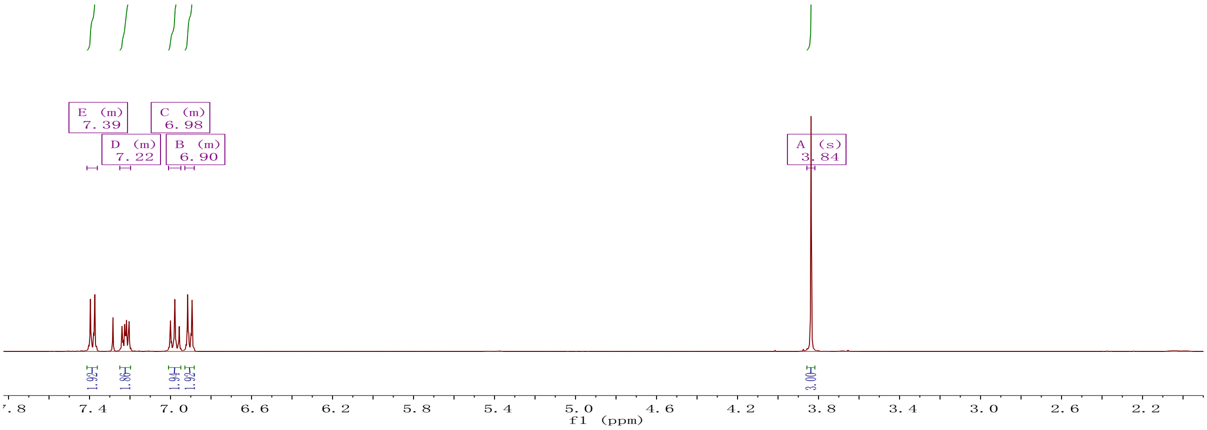
Following the general procedure for Table 3, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 4-biphenylsulfonyl chloride (0.6 mmol, 152 mg) as substrates instead, purified by column chromatography (40:1 PE:EtOAc) to provide 4f as a white solid (46% yield); m.p. 94-95 ° C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dt, *J* = 3.1, 1.9 Hz, 2H), 7.49 (dd, *J* = 8.9, 4.2, 2.2 Hz, 4H), 7.47 – 7.42 (m, 2H), 7.38 – 7.33 (m, 1H), 7.28 – 7.24 (m, 2H), 6.97 – 6.93 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.92, 140.48, 138.76, 137.80, 135.58, 135.37, 128.64, 128.41, 127.72, 127.53, 127.00, 126.76, 124.18, 115.13, 115.00, 55.52.



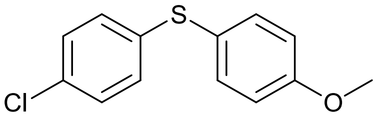
28) (4-Fluorophenyl) (4-methoxyphenyl) sulfane (4g)[18]:



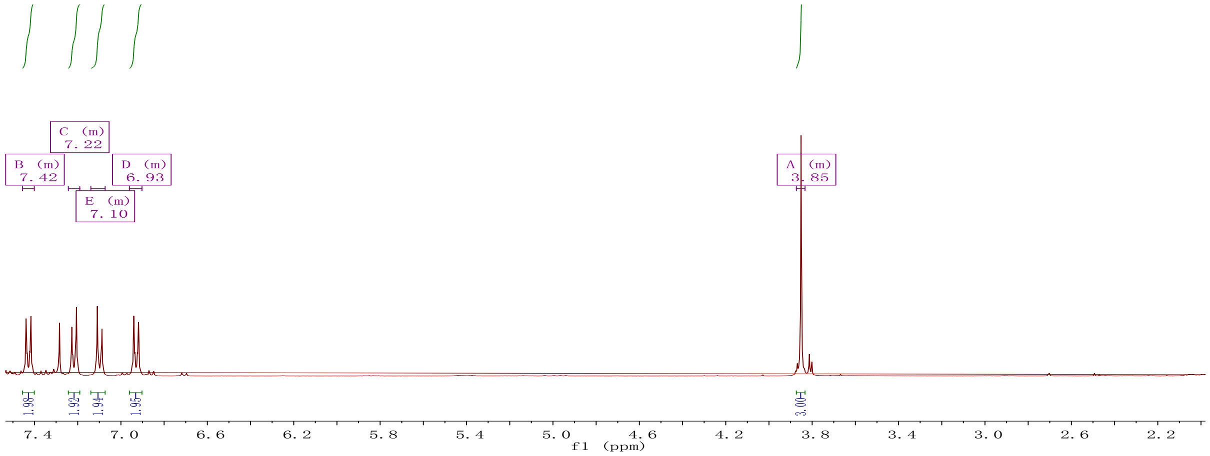
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 4-fluorobenzenesulfonyl chloride (0.6 mmol, 117 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4g as a Colorless oil (48% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 2H), 7.25 – 7.20 (m, 2H), 7.01 – 6.95 (m, 2H), 6.93 – 6.88 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.84, 160.39, 159.69, 134.51, 133.13, 133.10, 131.11, 131.03, 125.27, 116.18, 115.96, 115.00, 55.38.



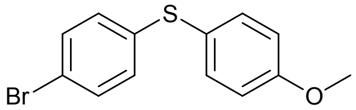
29) (4-Chlorophenyl) (4-methoxyphenyl) sulfane (4h)[19]:



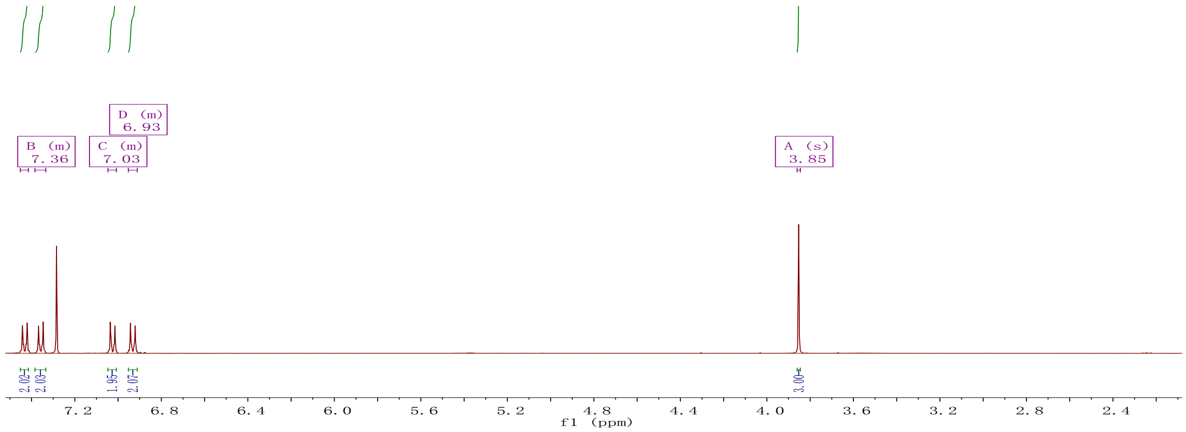
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 4-chlorobenzenesulfonyl chloride (0.6 mmol, 126.6 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4h as a white solid (40% yield); m.p. 65-66 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 – 7.40 (m, 2H), 7.24 – 7.19 (m, 2H), 7.14 – 7.07 (m, 2H), 6.96 – 6.90 (m, 2H), 3.87 – 3.83 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.07, 137.38, 135.51, 131.61, 129.32, 129.02, 123.77, 115.14, 55.40.



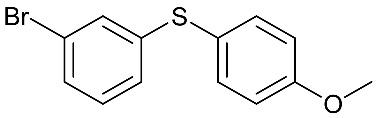
30) (4-Bromophenyl) (4-methoxyphenyl) sulfane (4i) [20]:



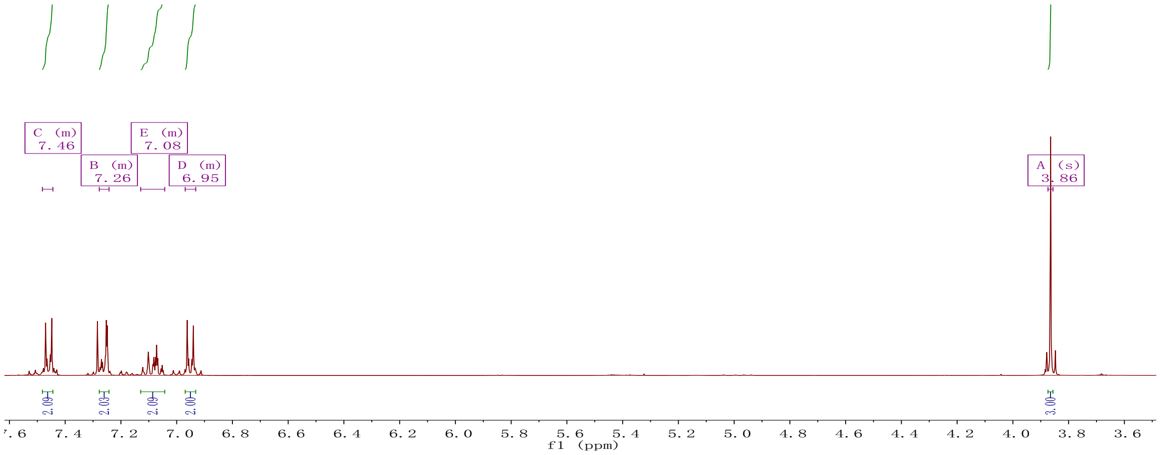
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 4-bromobenzenesulfonyl chloride (0.6 mmol, 153 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4i as a white solid (63% yield); m.p. 57-59 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.05 – 7.01 (m, 2H), 6.95 – 6.91 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.13, 138.18, 135.65, 132.21, 131.91, 129.47, 123.52, 119.39, 115.16, 55.40.



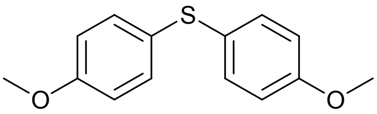
31) (3-Bromophenyl) (4-methoxyphenyl) sulfane (4j):



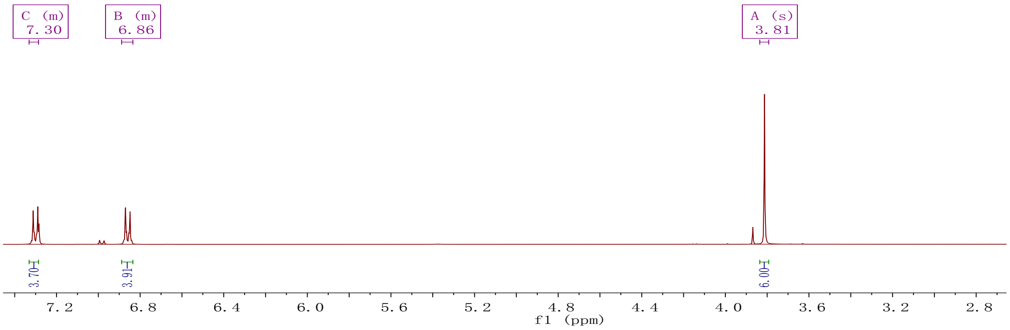
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 3-bromobenzenesulfonyl chloride (0.6 mmol, 153 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4j as a colorless oil (38% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.48 – 7.44 (m, 2H), 7.28 – 7.24 (m, 2H), 7.13 – 7.04 (m, 2H), 6.97 – 6.93 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 160.32, 141.60, 136.11, 130.15, 129.88, 128.51, 125.96, 122.94, 122.68, 115.24, 55.41. Anal. Calcd. for $C_{13}H_{11}SOBr$: C, 52.89; H, 3.77. Found: C, 53.58; H, 3.72.



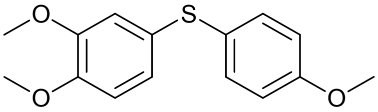
32) Bis(4-methoxyphenyl) sulfane (4k)[21]:



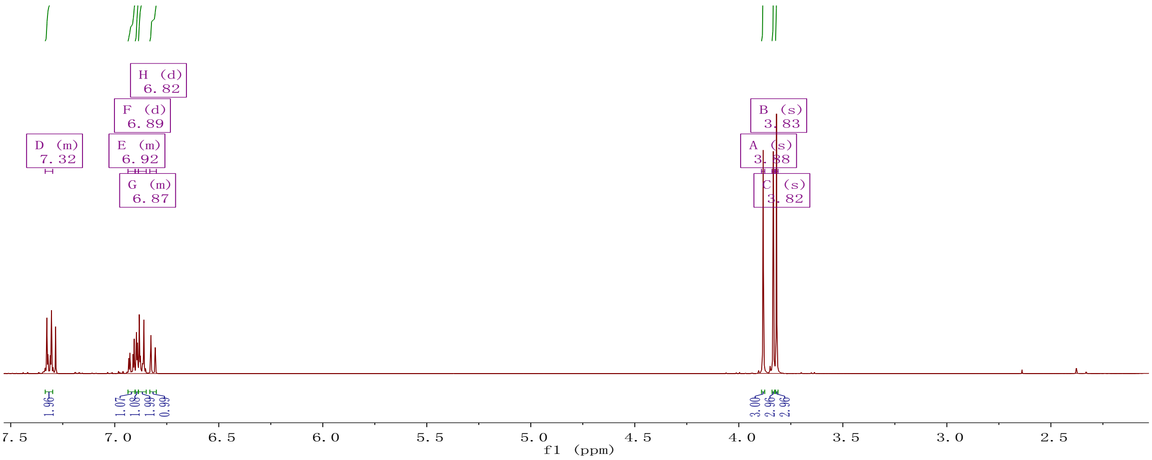
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 4-methoxybenzenesulfonyl chloride (0.6 mmol, 124 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4k as a white solid (88% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.44 – 7.40 (m, 2H), 7.32 – 7.29 (m, 3H), 6.88 – 6.84 (m, 4H), 3.82 (d, J = 4.4 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 158.98, 132.74, 127.44, 114.76, 55.36.



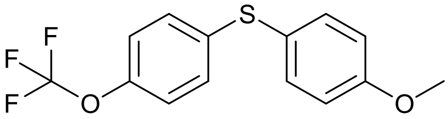
33) (3,4-Dimethoxyphenyl) (4-methoxyphenyl) sulfane (4l)[22]:



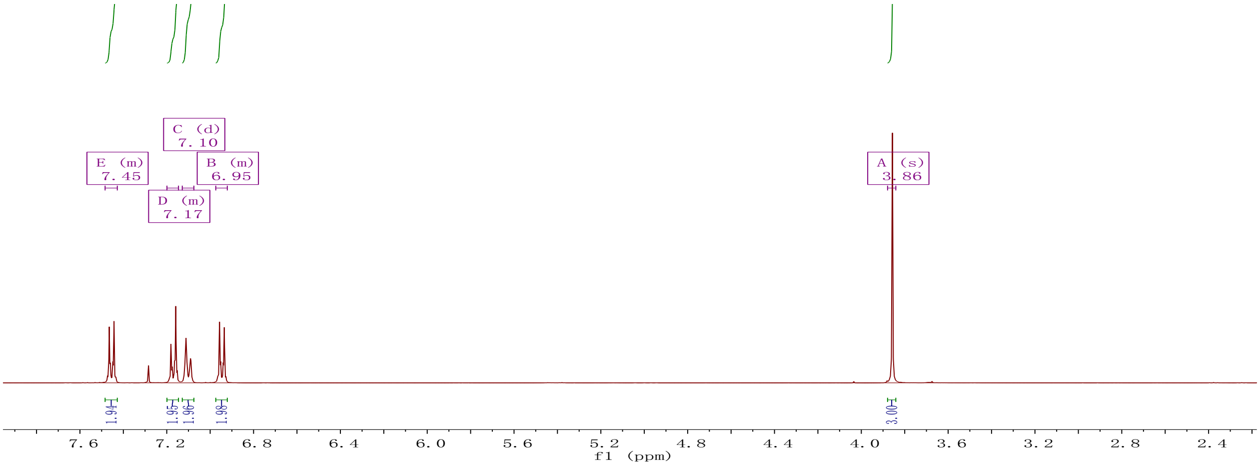
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 3,4-dimethoxybenzenesulfonyl chloride (0.6 mmol, 142 mg)as substrates instead, purified by column chromatography (5:1 PE:EtOAc) to provide 4l as a white solid (68% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.30 (m, 2H), 6.94 – 6.90 (m, 1H), 6.89 (d, J = 2.1 Hz, 1H), 6.89 – 6.85 (m, 2H), 6.82 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.07, 149.31, 148.47, 132.83, 127.84, 127.06, 123.77, 114.79, 114.31, 111.73, 55.98, 55.94, 55.37.



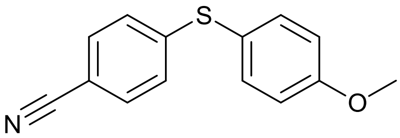
34) (4-Methoxyphenyl) (4-(trifluoromethoxy)phenyl) sulfane (4m):



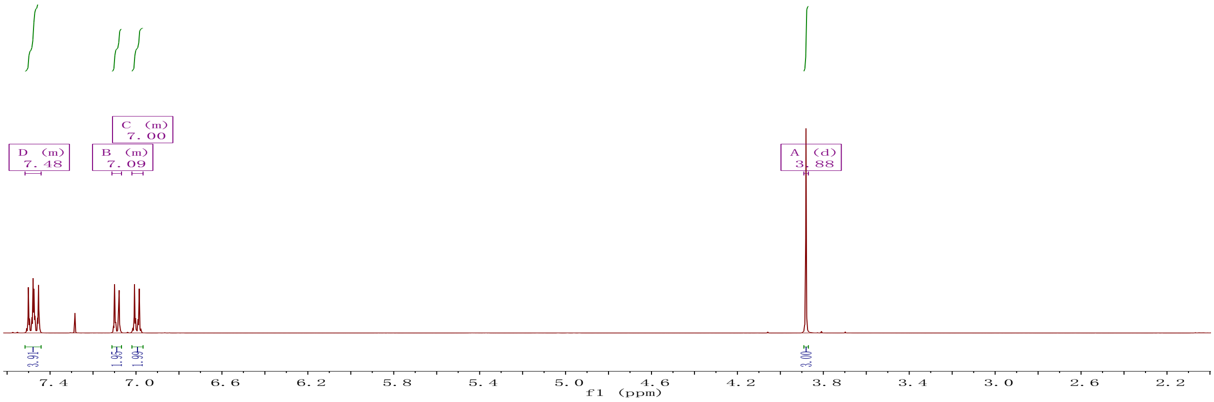
Following the general procedure for Table 3, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 3-(Trifluoromethoxy)benzenesulfonyl chloride (0.6 mmol, 156 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4m as a colorless oil (42% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.43 (m, 2H), 7.20 – 7.15 (m, 2H), 7.10 (d, J = 8.3 Hz, 2H), 6.97 – 6.92 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.19, 137.75, 135.78, 128.99, 123.45, 121.59, 115.19, 5.41. Anal. Calcd. for $C_{14}H_{11}SO_2F_3$: C, 55.99; H, 3.69. Found C, 56.42; H, 3.74.



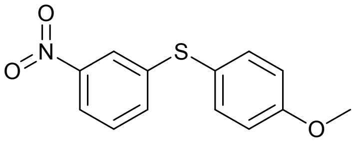
35) 4-((4-Methoxyphenyl)thio) benzonitrile (4n)[23]:



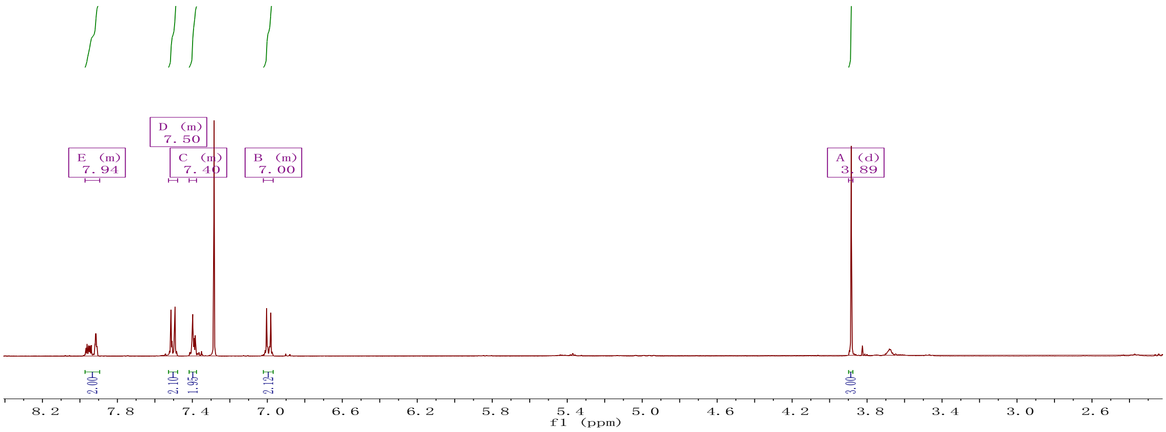
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 4-cyanobenzenesulfonyl chloride (0.6 mmol, 121 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 4n as a white solid (68% yield); m.p. 87-88 ºC; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52 – 7.44 (m, 4H), 7.11 – 7.07 (m, 2H), 7.02 – 6.97 (m, 2H), 3.88 (d, J = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.60, 139.97, 134.96, 132.29, 130.76, 126.81, 126.70, 118.91, 108.30, 21.33.



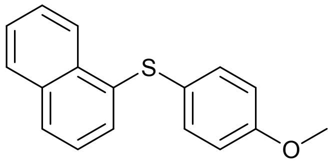
36) (4-Methoxyphenyl)(3-nitrophenyl) sulfane (4o):



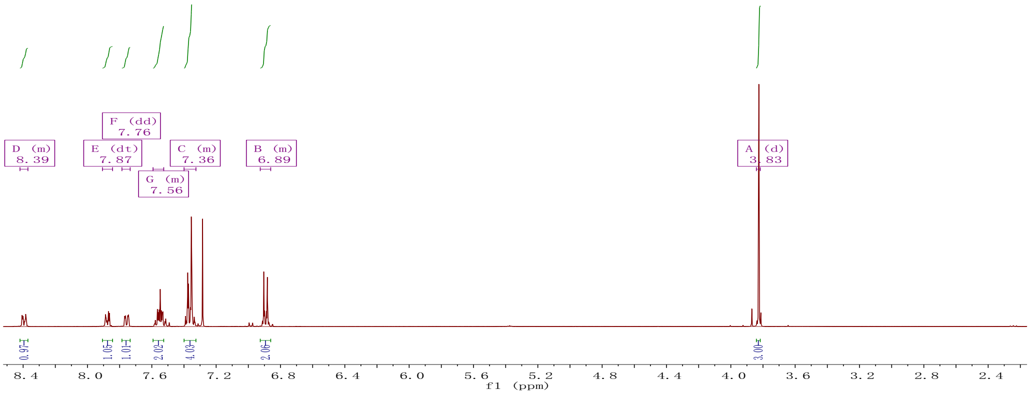
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2mmol, 47.4mg) and 3-nitrobenzenesulfonyl chloride (0.6 mmol, 133 mg) as substrates instead, purified by column chromatography eluted with petroleum ether to provide 4p as a colorless oil (10% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.97 – 7.89 (m, 2H), 7.53 – 7.48 (m, 2H), 7.42 – 7.38 (m, 2H), 7.02 – 6.97 (m, 2H), 3.89 (d, J = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ156.90, 138.20, 136.69, 132.35, 129.46, 122.98, 121.26, 120.07, 116.36, 115.58, 55.45. Anal. Calcd. for $C_{13}H_{11}SO_3N$: C, 59.76; H, 4.25; N, 5.36. Found C, 57.87; H, 4.09; N, 5.22.



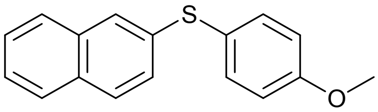
37) (4-Methoxyphenyl) (naphthalen-1-yl) sulfane (4q)[24]:



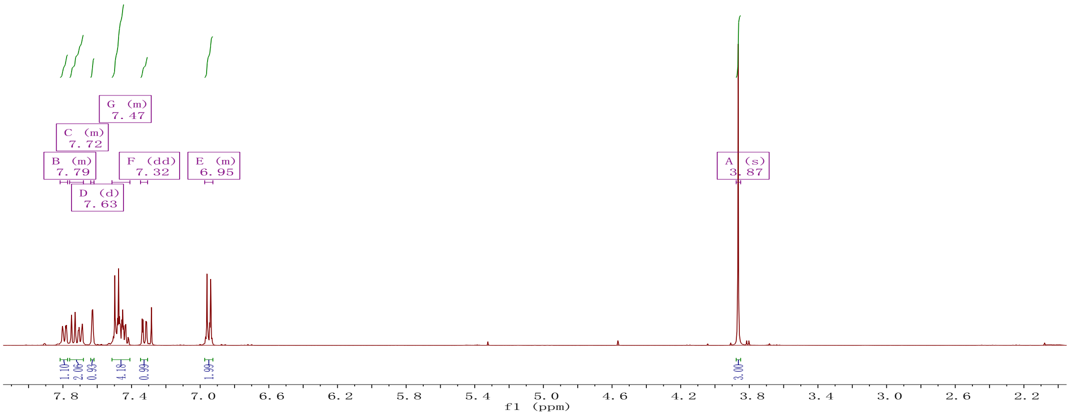
Following the general experimental procedure presented above, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 1-naphthalenesulfonyl chloride (0.6 mmol, 121 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 4q as a white solid (78% yield); mp 106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 – 8.37 (m, 1H), 7.87 (dt, J = 6.9, 2.9 Hz, 1H), 7.76 (dd, J = 7.4, 1.8 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.40 – 7.33 (m, 4H), 6.93 – 6.86 (m, 2H), 3.83 (d, J = 4.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.38, 134.63, 133.98, 133.83, 128.49, 127.41, 126.50, 126.30, 125.73, 125.19, 124.91, 115.02, 55.36.



38) (4-Methoxyphenyl) (naphthalen-2-yl) sulfane (4r)[5]:

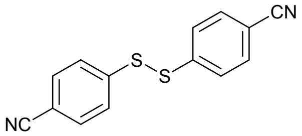


Following the general procedure for Table 3, using 4-Iodoanisole (0.2 mmol, 47.4 mg) and 2-naphthalenesulfonyl chloride (0.6 mmol, 136 mg) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 4r as a white solid (56% yield); m.p. 75-76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.77 (m, 1H), 7.76 – 7.68 (m, 2H), 7.63 (d, J = 1.4 Hz, 1H), 7.51 – 7.41 (m, 4H), 7.32 (dd, J = 8.6, 1.9 Hz, 1H), 6.97 – 6.93 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.87, 135.93, 135.25, 133.78, 132.75, 131.74, 128.56, 127.72, 127.17, 126.73, 126.53, 126.46, 125.64, 124.43, 115.07, 55.41.

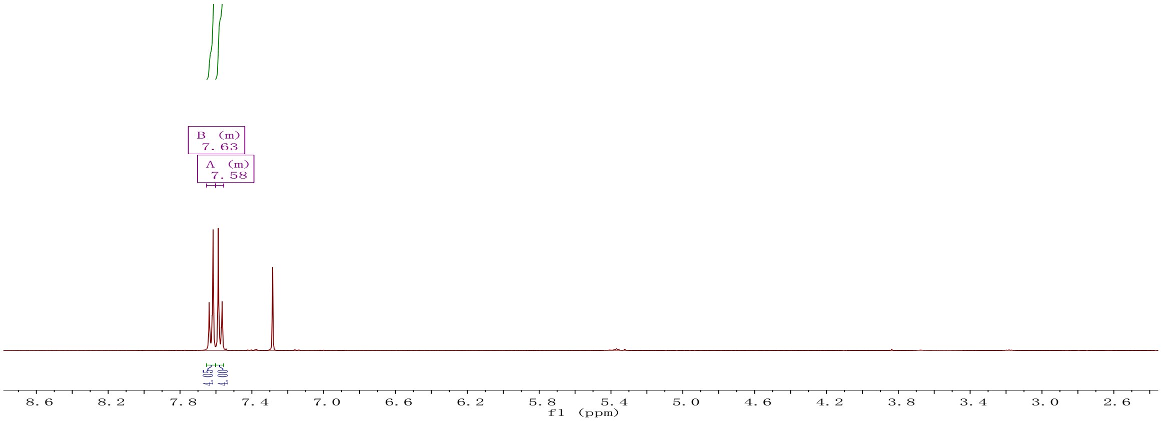


5. Detailed Procedure and characterization of compounds in scheme 2.

(a) Bis(4-cyanophenyl) disulfide (5a)[25]:



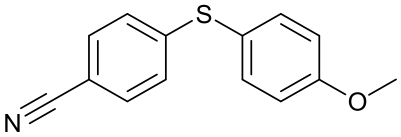
Following the general experimental procedure presented above, using Mn dust (0.2 mmol, 11 mg), 4-cyanobenzenesulfonyl chloride (0.2 mmol, 40 mg), and DMF (anhydrous, 1 ml) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 5a as a white solid (63% yield); m.p. 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.60 (m, 4H), 7.60 – 7.56 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.11, 132.80, 126.51, 118.19, 110.92.



(b) Following the general experimental procedure presented above, using $NiCl_2$.glyme (0.01 mmol, 2.3 mg), L_4 (0.015 mmol, 3.2 mg), Bis(4-cyanophenyl)disulfide (0.1 mmol, 26.4 mg), 4-Iodoanisole (0.1 mmol, 23.7 mg) and DMF (anhydrous, 1 ml). No product was found.

(c) Following the general experimental procedure presented above, using L_4 (0.015 mmol, 3.2 mg), Mn dust (0.1 mol, 5.5 mg), Bis(4-cyanophenyl)disulfide (0.1 mmol, 26.4 mg), 4-Iodoanisole (0.1 mmol, 23.7 mg) and DMF (anhydrous, 1 ml). No product was found.

(d) 4-((4-Methoxyphenyl)thio) benzonitrile



Following the general experimental procedure presented above, using $NiCl_2$.glyme (0.01 mmol, 2.2 mg), L_4 (0.015 mmol, 3.2 mg), Mn dust (0.1 mol, 5.5 mg), Bis(4-cyanophenyl)disulfide (0.1 mmol, 26.4 mg), 4-Iodoanisole (0.1 mmol, 23.7 mg) and DMF (anhydrous, 1ml) as substrates instead, purified by column chromatography (20:1 PE:EtOAc) to provide 4-((4-methoxyphenyl)thio)benzonitrile as a white solid (Compound 4n, 83% yield); See compound 4n for the characterization of complex. (page 20)

6. References:

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7. Crystal data and structure refinement for Compound 3j (CCDC 1494572).

Compound 3j

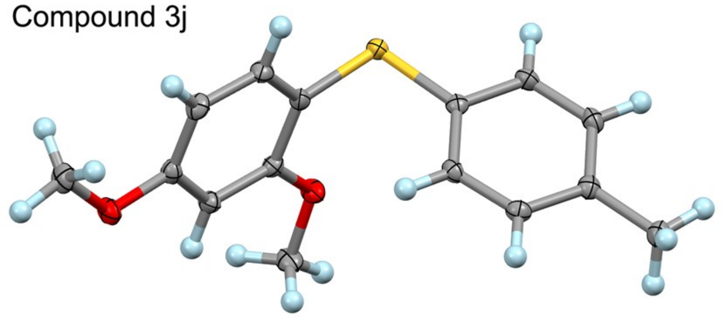


Figure S1

Empirical formula	C15 H16 O2 S	
Formula weight	260.34	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.68603(16) Å	α= 90°.
	b = 23.9176(4) Å	β= 111.053(3)°.
	c = 7.76261(17) Å	γ = 90°.
Volume	1331.76(5) Å^3	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	2.084 mm^{-1}	
F(000)	552	
Crystal size	0.32 x 0.22 x 0.15 mm^3	
Theta range for data collection	3.70 to 69.98°.	
Index ranges	-6<=h<=9, -26<=k<=29, -9<=l<=8	
Reflections collected	8328	
Independent reflections	2513 [R(int) = 0.0161]	
Completeness to theta = 69.98°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5553	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2513 / 0 / 163	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0287, wR2 = 0.0772	
R indices (all data)	R1 = 0.0309, wR2 = 0.0786	
Largest diff. peak and hole	0.270 and -0.228 e.Å^{-3}	

8. Crystal data and structure refinement for Compound 3k (CCDC 1494571).

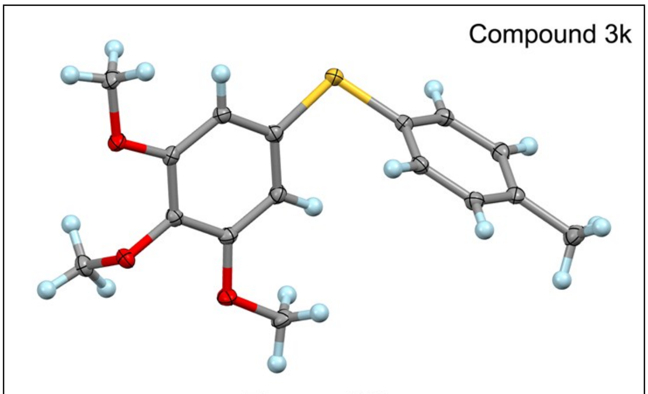


Figure S2

Empirical formula	$C_{16}H_{18}O_3S$	
Formula weight	290.36	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.9478(5) Å	α= 82.206(6)°.
	b = 9.1969(5) Å	β= 81.643(7)°.
	c = 11.8012(10) Å	γ = 75.220(6)°.
Volume	717.54(9) Å^3	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	2.044 mm^{-1}	
F(000)	308	
Crystal size	0.25 x 0.20 x 0.12 mm^3	
Theta range for data collection	3.81 to 69.98°.	
Index ranges	-7<=h<=8, -11<=k<=9, -14<=l<=14	
Reflections collected	4482	
Independent reflections	2692 [R(int) = 0.0311]	
Completeness to theta = 69.98°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7915 and 0.6290	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2692 / 0 / 184	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0923	
R indices (all data)	R1 = 0.0488, wR2 = 0.0976	
Largest diff. peak and hole	0.304 and -0.302 e.Å^{-3}	

9. Crystal data and structure refinement for Compound 3m (CCDC 1494573).

Compound 3m

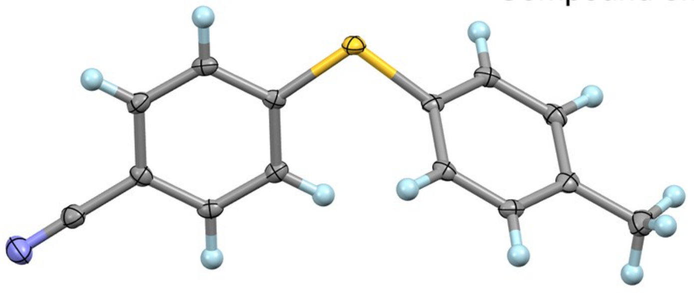
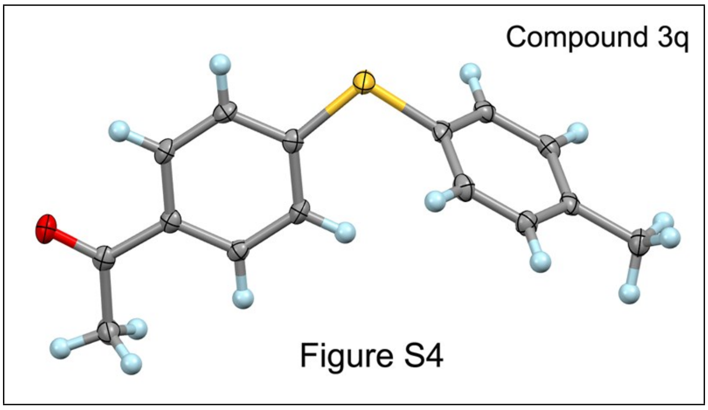


Figure S3

Empirical formula	C14 H11 N S	
Formula weight	225.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.7042(3) Å	α= 90°.
	b = 25.743(2) Å	β= 94.590(5)°.
	c = 7.8069(4) Å	γ = 90°.
Volume	1142.70(13) Å^3	
Z	4	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.252 mm^{-1}	
F(000)	472	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	3.53 to 26.00°.	
Index ranges	-6<=h<=7, -31<=k<=29, -8<=l<=9	
Reflections collected	4848	
Independent reflections	2240 [R(int) = 0.0240]	
Completeness to theta = 26.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9753 and 0.9283	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2240 / 0 / 145	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.0937	
R indices (all data)	R1 = 0.0490, wR2 = 0.0967	
Largest diff. peak and hole	0.346 and -0.378 e.Å^{-3}	

10. Crystal data and structure refinement for Compound 3q (CCDC 1494574).



Compound 3q

Figure S4

Empirical formula	C15 H14 O S	
Formula weight	242.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.7958(3) Å	α= 90°.
	b = 25.4544(12) Å	β= 93.626(4)°.
	c = 8.3123(4) Å	γ = 90°.
Volume	1223.84(10) Å^3	
Z	4	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.244 mm^{-1}	
F(000)	512	
Crystal size	0.40 x 0.20 x 0.20 mm^3	
Theta range for data collection	3.43 to 26.00°.	
Index ranges	-6<=h<=7, -28<=k<=31, -8<=l<=10	
Reflections collected	5356	
Independent reflections	2393 [R(int) = 0.0230]	
Completeness to theta = 26.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9529 and 0.9088	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2393 / 0 / 154	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0856	
R indices (all data)	R1 = 0.0442, wR2 = 0.0903	
Largest diff. peak and hole	0.265 and -0.270 e.Å^{-3}	

11. Crystal data and structure refinement for Compound 3r (CCDC 1494575).

Compound 3r

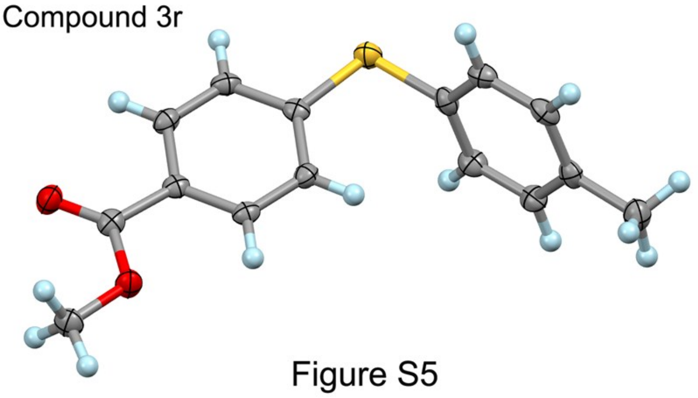


Figure S5

Empirical formula	C15 H14 O2 S	
Formula weight	258.32	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.6110(3) Å	α= 90°.
	b = 25.6833(13) Å	β= 98.982(4)°.
	c = 8.9910(4) Å	γ = 90°.
Volume	1279.79(11) Å^3	
Z	4	
Density (calculated)	1.341 Mg/m^3	
Absorption coefficient	2.168 mm^{-1}	
F(000)	544	
Crystal size	0.22 x 0.18 x 0.12 mm^3	
Theta range for data collection	5.27 to 70.93°.	
Index ranges	-4<=h<=6, -31<=k<=27, -11<=l<=10	
Reflections collected	4586	
Independent reflections	2415 [R(int) = 0.0311]	
Completeness to theta = 70.93°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7809 and 0.6470	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2415 / 0 / 163	
Goodness-of-fit on F^2	1.180	
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1475	
R indices (all data)	R1 = 0.0725, wR2 = 0.1531	
Largest diff. peak and hole	0.531 and -0.532 e.Å^{-3}	

12. Crystal data and structure refinement for Compound 4n (CCDC 1494576).

Compound 4n

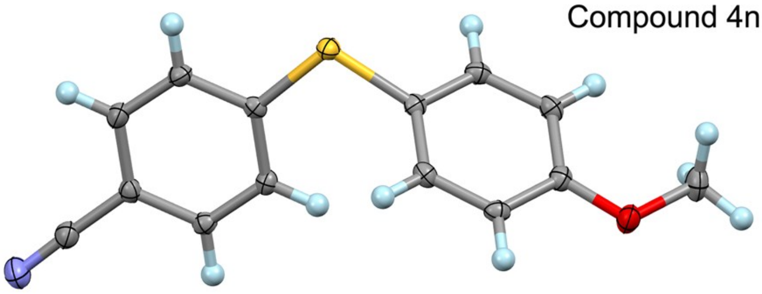


Figure S6

Empirical formula	C14 H11 N O S	
Formula weight	241.30	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.67633(18) Å	α= 90°.
	b = 26.8781(8) Å	β= 95.042(3)°.
	c = 7.7875(2) Å	γ = 90°.
Volume	1183.54(6) Å^3	
Z	4	
Density (calculated)	1.354 Mg/m^3	
Absorption coefficient	2.269 mm^{-1}	
F(000)	504	
Crystal size	0.24 x 0.16 x 0.14 mm^3	
Theta range for data collection	5.94 to 69.99°.	
Index ranges	-6<=h<=6, -32<=k<=32, -9<=l<=7	
Reflections collected	4295	
Independent reflections	2215 [R(int) = 0.0204]	
Completeness to theta = 69.99°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7418 and 0.6120	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2215 / 0 / 154	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0332, wR2 = 0.0883	
R indices (all data)	R1 = 0.0356, wR2 = 0.0899	
Largest diff. peak and hole	0.272 and -0.417 e.Å^{-3}	

13. Crystal data and structure refinement for Compound 5a (CCDC 1494577).

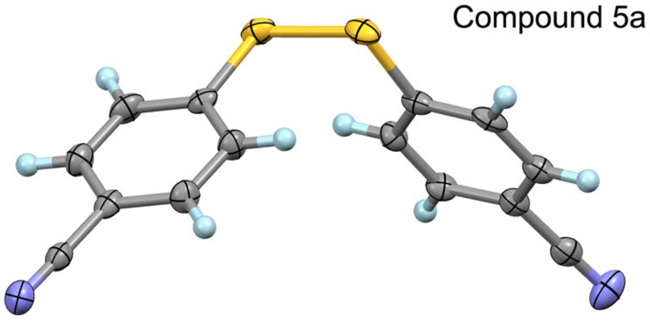


Figure S7

Empirical formula	C14 H8 N2 S2	
Formula weight	268.34	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.8232(4) Å	α= 84.863(4)°.
	b = 11.6428(5) Å	β= 83.654(4)°.
	c = 14.5818(7) Å	γ = 73.557(4)°.
Volume	1263.68(10) Å^3	
Z	4	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	3.656 mm^{-1}	
F(000)	552	
Crystal size	0.22 x 0.18 x 0.12 mm^3	
Theta range for data collection	3.97 to 69.99°.	
Index ranges	-9<=h<=5, -14<=k<=14, -17<=l<=16	
Reflections collected	8569	
Independent reflections	4710 [R(int) = 0.0461]	
Completeness to theta = 69.99°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6681 and 0.5001	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4710 / 0 / 325	
Goodness-of-fit on F^2	1.119	
Final R indices [I>2sigma(I)]	R1 = 0.0691, wR2 = 0.2121	
R indices (all data)	R1 = 0.0784, wR2 = 0.2166	
Largest diff. peak and hole	1.016 and -0.569 e.Å^{-3}	