A General, Efficient and Functional-Group-Tolerant Catalyst System for the Palladium-Catalyzed Thioetherification of Aryl Bromides and Iodides

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General Methods: All reactions were assembled under an inert atmosphere. Reactions were conducted in 4 mL vials sealed with a cap containing a PTFE septum. All glassware was oven-dried, evacuated and purged with nitrogen immediately prior to use. All reaction temperatures refer to bath temperatures. All common reagents were obtained from commercial suppliers and used without further purification. CyPF-*t*Bu (1-dicyclohexylphosphino-2-di-*tert*-butylphosphinoethylferrocene) was obtained from commercial suppliers and used without purification. Toluene was degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column of activated alumina. 1,2-Dimethoxyethane (DME, 99.9% purity, HPLC grade) was used without further purification, but was stored under nitrogen. Other solvents were dried by standard methods. Reactions performed at 110 °C in DME (b.p. = 85 °C) were conducted using the standard vials and caps cited above; no loss of solvent was observed. All other chemicals were used as received from commercial sources. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ on 400 MHz or 500 MHz spectrometers with tetramethylsilane or residual protiated solvent used as a reference. Abbreviations for ^{1}H NMR splitting patterns are: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; oct, octet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; tt, triplet of triplets; m, multiplet. The coupling constants are reported in hertz (Hz). Flash column chromatography was carried out on silica gel (230-240 mesh). The yields of the coupled products included in all tables refer to isolated yields and are the average of two runs. Products that had been reported previously were isolated in greater than 95% purity, as determined by ^{1}H NMR spectroscopy and capillary gas chromatography (GC). GC and GC/MS analyses were conducted with an HP-1 methyl silicone column.

Preparation of stock solution A (1.0 x 10^{-2} M): DME (1.0 mL) was added to a mixture of $Pd(OAc)_2$ (2.2 mg) and CyPF-*t*Bu (5.5 mg). The resulting orange solution was stirred at room temperature for 1 min before using.

Preparation of stock solution B (1.0 x 10^{-4} M): 10 μL of stock solution **A** was diluted to 1.0 mL with DME. The resulting pale yellow solution was stirred at room temperature for 1 min before using.

General procedure for the coupling of *p*-halotoluenes with 1-octanethiol and thiophenol; compared rates and catalytic activity of the different haloarenes: The appropriate quantity of stock solution **A** or **B** was added to a 4 mL vial containing the aryl halide (1.00 mmol) and NaO*t*Bu (106 mg, 1.10 mmol) in 1.5 mL of DME. The thiol (1.00 mmol) was then added, and the vial sealed with a cap containing a PTFE septum. The mixture was heated at 110 ºC until the haloarene was consumed, as determined by GC (reaction times reported in Scheme 2). Silica gel (0.5 g) was added, and the solvents were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane as eluent. The corresponding sulfide was isolated in the yields reported in Scheme 2 and Table 1.

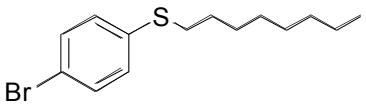
4-Methylphenyl octyl sulfide.[1] Colorless liquid. ^{1}H and ^{13}C NMR spectra are the same as those given later for the product in Table 4, entry 1.

4-Methylphenyl phenyl sulfide.[2] Colorless liquid. ^{1}H and ^{13}C NMR spectra are the same as those given later for the product in Table 5, entry 1.

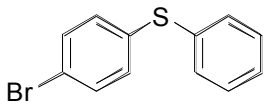
General procedure for the coupling of *p*-halotoluenes with 1-octanethiol and thiophenol; competition experiments: 100 μL of stock solution **A** was added to a 4 mL vial containing an equimolecular mixture (1.00 mmol) of aryl iodide and bromide (Scheme 3, eq. 1) or aryl bromide and chloride (Scheme 3, eq. 2) and NaO*t*Bu (106 mg, 1.10 mmol) in 1.5 mL of DME. The thiol

(1.00 mmol) was then added, and the vial sealed with a cap containing a PTFE septum. The mixture was heated 1 hour at 110 ºC. Reaction conversions were determined by GC or GC/MS and are summarized in Scheme 3 (eq. 1 and 2).

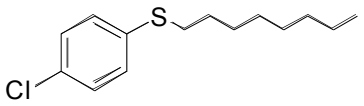
General procedure for the coupling of 1-bromo-4-iodobencene and 4-bromo-1-chlorobencene with 1-octanethiol and thiophenol; competition experiments: 100 μL of stock solution **A** was added to a 4 mL vial containing 1-bromo-4-iodobencene (Scheme 3, eq. 3) or 4-bromo-1-chlorobencene (Scheme 3, eq. 4) (1.00 mmol) and NaO*t*Bu (106 mg, 1.10 mmol) in 1.5 mL of DME. The thiol (1.00 mmol) was then added, and the vial sealed with a cap containing a PTFE septum. The mixture was heated 1 hour at 110 ºC. Reaction conversions were determined by GC or GC/MS and are summarized in Scheme 3 (eq. 3 and 4). Silica gel (0.5 g) was added, and the solvents were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane as eluent. Sulfides were isolated in the yields reported in Scheme 3 (eq. 3 and 4).



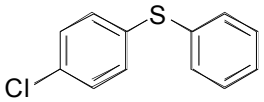
4-Bromophenyl octyl sulfide.[2] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.29 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 1.54 (quint, J = 7.6 Hz, 2H), 1.35-1.29 (m, 2H), 1.23-1.17 (m, 8 H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 136.2, 131.7 (2C), 130.2 (2C), 119.2, 33.6, 31.7, 29.1, 29.0, 28.9, 28.7, 22.5, 14.0.



4-Bromophenyl phenyl sulfide.[2] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.29 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 6.9 Hz, 2H), 7.21-7.16 (m, 3H), 7.07 (d, J = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 135.4, 134.7, 132.1 (2C), 132.0 (2C), 131.4 (2C), 129.3 (2C), 127.4, 120.8.



4-Chlorophenyl octyl sulfide.[3] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.14 (s, 4H), 2.79 (t, J = 7.3 Hz, 2H), 1.54 (quint, J = 7.5 Hz, 2H), 1.36-1.29 (m, 2H), 1.23-1.16 (m, 8 H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 135.6, 131.5, 130.1 (2C), 128.8 (2C), 33.8, 31.7, 29.1, 29.02, 28.96, 28.7, 22.5, 14.0.



4-Chlorophenyl phenyl sulfide.[2] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.25-7.19 (m, 4H), 7.18-7.12 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 135.0, 134.6, 132.9, 131.9 (2C), 131.2 (2C), 129.24 (2C), 129.22 (2C), 127.3.

General procedure for the coupling of aryl halides with thiols; temperature and base influence: The appropriate quantity of stock solution **A** was added to a 4 mL vial containing the aryl bromide or iodide (1.00 mmol) and base (1.10 mmol) in 1.5 mL of DME. The thiol (1.00 mmol) was then added, and the vial sealed with a cap containing a PTFE septum. The mixture was heated at the temperature indicated in Tables 2 and 3 until the aryl halide was consumed or no further reaction evolution was observed, as determined by GC. Silica gel (0.5 g) was added, and the solvents were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane as eluent. The corresponding sulfide was formed in conversions and isolated yields reported in Tables 2 and 3.

4-Methylphenyl octyl sulfide.[1] Colorless liquid. ^{1}H and ^{13}C NMR spectra are the same as those given later for the product in Table 4, entry 1.

4-Methylphenyl phenyl sulfide.[2] Colorless liquid. ^{1}H and ^{13}C NMR spectra are the same as those given later for the product in Table 5, entry 1.

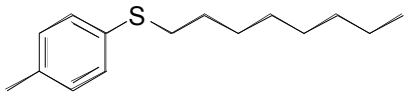
1-Methylpropyl phenyl sulfide.[4] Colorless liquid. ^{1}H and ^{13}C NMR spectra are the same as those given later for the product in Table 4, entry 12.

Cyclohexyl 4-methylphenyl sulfide.[5] Colorless liquid. ^{1}H and ^{13}C NMR spectra are the same as those given later for the product in Table 4, entry 14.

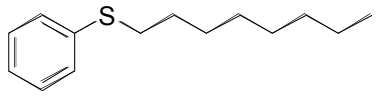
General procedure for the coupling of aryl bromides and iodides with aliphatic and aromatic thiols: The appropriate quantity of stock solution **A** or **B** was added to a 4 mL vial containing the aryl bromide or iodide (1.00 mmol) and NaO*t*Bu (106 mg, 1.10 mmol) in DME (1.5 mL). The thiol (1.00 mmol) was then added, and the vial sealed with a cap containing a PTFE septum. The mixture was heated at the temperature indicated in Tables 4 and 5 until the aryl halide was consumed, as determined by GC. Silica gel (0.5 g) was added, and the solvents were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane or a mixture of hexane and ethyl acetate as eluent. Aryl sulfides were isolated in the yields reported in Tables 4 and 5.

Representative procedures without using a drybox (Table 4 and Table 5 entry 2): An oven-dried test tube with a screw cap containing a PTFE-lined septum was evacuated and backfilled with N_2. To the flask was added NaO*t*Bu (106 mg, 1.10 mmol) and a stir bar. The flask was evacuated and heated to remove the moisture present in the base; then evacuated and backfilled with N_2 three times. To the flask was then added *p*-bromotoluene (121 μL, 1.00 mmol), DME (2.0 mL), the suitable amount of stock solution **A** (50 μL for coupling 1-

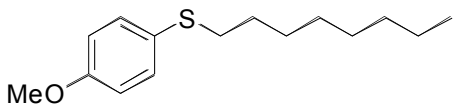
octanethiol and 10 μL for thiophenol), and the thiol (1.00 mmol), which were stored and handled under an inert atmosphere. The resulting mixture was stirred at 90 °C for 1-octanethiol and at 110 °C for thiophenol until the bromide was consumed, as determined by GC. Silica gel (0.5 g) was then added, and solvents were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane as eluent to give the corresponding sulfides in the yields reported in Table 4 (entry 2) and Table 5 (entry 2).



4-Methylphenyl octyl sulfide (Table 4, entries 1−3).[1] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.10 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.17 (s, 3H), 1.48 (quint, *J* = 7.4 Hz, 2H), 1.26 (quint, *J* = 7.4 Hz, 2H), 1.17-1.08 (m, 8H), 0.74 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 135.7, 133.1, 129.7 (2C), 129.5 (2C), 34.3, 31.7, 29.2, 29.10, 29.06, 28.7, 22.6, 20.9, 14.0.

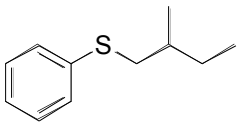


Octyl phenyl sulfide (Table 4, entries 4−5).[6] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.25-7.23 (m, 2H), 7.21-7.16 (m, 2H), 7.09-7.06 (m, 1H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.57 (quint, *J* = 7.4 Hz, 2H), 1.34 (quint, *J* = 7.4 Hz, 2H), 1.21-1.18 (m, 8H), 0.80 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.0, 128.7 (4C), 125.5, 33.5, 31.7, 29.09, 29.06 (2C), 28.8, 22.6, 14.0.

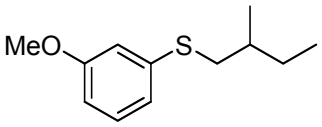


4-Methoxyphenyl octyl sulfide (Table 4, entries 6−7).[2] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 3.71 (s, 3H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.50 (quint, *J* = 7.4 Hz, 2H), 1.30 (quint, *J* = 7.4 Hz, 2H), 1.22-1.14 (m, 8H), 0.80 (t, *J* = 7.1 Hz, 3H).

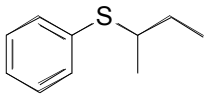
^{13}C NMR ($CDCl_3$): δ 158.6, 132.8 (2C), 126.9, 114.4 (2C), 55.2, 35.7, 31.7, 29.3, 29.09, 29.06, 28.6, 22.6, 14.0.



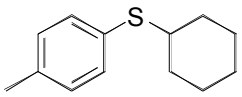
2-Methylbutyl phenyl sulfide (Table 4, entries 8−9).[7] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.25-7.22 (m, 2H), 7.20-7.15 (m, 2H), 7.08-7.04 (m, 1H), 2.86 (dd, *J* = 6.0 Hz and 12.6 Hz, 1H), 2.66 (dd, *J* = 7.6 Hz and 12.6 Hz, 1H), 1.57 (m, 1H), 1.45 (m, 1H), 1.18 (m, 1 H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.5, 128.7 (2C), 128.6 (2C), 125.4, 40.6, 34.4, 28.7, 18.8, 11.2.



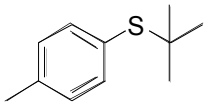
2-Methylbutyl 3-methoxyphenyl sulfide (Table 4, entries 10−11).[8] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.07 (t, *J* = 7.9 Hz, 1H), 6.80-6.76 (m, 2H), 6.59-6.56 (m, 1H), 3.67 (s, 3H), 2.84 (dd, *J* = 12.5 Hz and 5.9 Hz, 1H), 2.64 (dd, *J* = 12.5 Hz and 7.6 Hz, 1H), 1.60-1.52 (m, 1H), 1.49-1.39 (m, 1H), 1.22-1.11 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 159.6, 138.8, 129.4, 120.5, 113.7, 110.9, 55.0, 40.2, 34.3, 28.7, 18.8, 11.1.



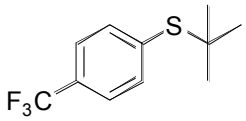
1-Methylpropyl phenyl sulfide (Table 4, entries 12−13).[4] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.32-7.29 (m, 2H), 7.20-7.16 (m, 2H), 7.13-7.09 (m, 1H), 3.07 (sext, *J* = 6.6 Hz, 1H), 1.57 (m, 1H), 1.45 (m, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 135.4, 131.7 (2C), 128.6 (2C), 126.4, 44.7, 29.4, 20.4, 11.4.



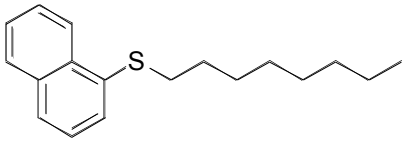
Cyclohexyl 4-methylphenyl sulfide (Table 4, entries 14−15).[5] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.23 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.93 (tt, J = 10.5 Hz and 3.8 Hz, 1H), 2.24 (s, 3H), 1.89-1.86 (m, 2H), 1.69-1.66 (m, 2 H), 1.53-1.49 (m, 1H), 1.30-1.11 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 136.7, 132.7 (2C), 131.1, 129.4 (2C), 47.0, 33.3 (2C), 26.0, 25.7 (2C), 21.0.



4-Methyl-phenyl 2-methyl-2-propyl sulfide (Table 4, entry 16).[9] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.32 (d, J = 7.7 Hz, 2H), 7.04 (d, J = 7.7 Hz, 2H), 2.27 (s, 3H), 1.18 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 138.6, 137.3 (2C), 129.1 (2C), 120.0, 45.4, 30.8 (3C), 21.1.

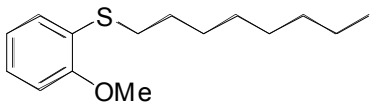


2-Methyl-2-propyl 4-trifluoromethylphenyl sulfide (Table 4, entry 17).[8] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.56 (d, J = 7.9 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 1.23 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.6, 137.3 (2C), 130.5 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 125.2 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 124.5 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 46.6, 30.9 (3C).

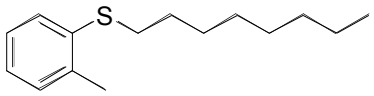


1-Naphthyl octyl sulfide (Table 4, entries 18−19).[10] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 8.45 (d, J = 8.8 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.60-7.52 (m, 3H), 7.43 (t, J = 8.2 Hz, 1H), 3.0 (t, J = 7.5 Hz, 2H), 1.71 (quint, J = 7.5 Hz, 2H), 1.49-1.45 (m, 2H),

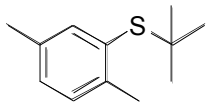
1.30 (bs, 8H), 0.92 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 134.2, 133.8, 132.8, 128.4, 127.3, 126.7, 126.1, 126.0, 125.5, 124.9, 34.1, 31.7, 29.1 (3C), 28.8, 22.6, 14.0.



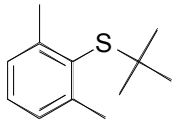
2-Methoxyphenyl octyl sulfide (Table 4, entries 20−21).[8] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.23 (dd, J = 7.6 Hz and 1.6 Hz, 1H), 7.15-7.12 (m, 1H), 6.90 (td, J = 7.6 Hz and 1.3 Hz, 1H), 6.82 (dd, J = 8.0 Hz and 1.3 Hz, 1H), 3.86 (s, 3H), 2.87 (t, J = 7.6 Hz, 2H), 1.65 (quint, J = 7.6 Hz, 2H), 1.43 (m, 2H), 1.31-1.22 (m, 8 H), 0.87 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 156.9, 128.4, 126.4, 125.1, 120.8, 110.1, 55.5, 31.7, 31.6, 29.0 (2C), 28.8, 28.7, 22.5, 13.9.



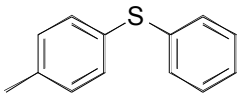
2-Methylphenyl octyl sulfide (Table 4, entries 22−23).[8] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.15 (d, J = 8.2 Hz, 1H), 7.06-7.03 (m, 2H), 6.98-6.95 (m, 1H), 2.79 (t, J = 7.4 Hz, 2H), 2.27 (s, 3H), 1.57 (quint, J = 7.5 Hz, 2H), 1.38-1.32 (m, 2H), 1.19 (bs, 8H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.0, 136.4, 129.9, 127.1, 126.2, 125.1, 32.7, 31.7, 29.1 (2C), 28.9 (2C), 22.6, 20.2, 14.0.



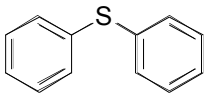
2,5-Dimethylphenyl 2-methyl-2-propyl sulfide (Table 4, entry 24).[11] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.26 (s, 1H), 7.06 (d, J = 7.9 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 140.5, 139.4, 135.0, 131.7, 130.0, 129.6, 46.9, 31.0 (3C), 21.2, 20.6.



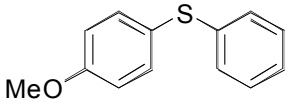
2,6-Dimethylphenyl 2-methyl-2-propyl sulfide (Table 4, entries 25−26).[11] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.04 (bs, 3H), 2.49 (s, 6H), 1.21 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 145.2 (2C), 132.1, 128.2, 127.9 (2C), 49.1, 31.5 (3C), 23.0 (2C).



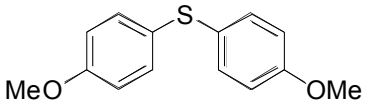
4-Methylphenyl phenyl sulfide (Table 5, entries 1−4 and 7−8).[2] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.19-7.14 (m, 4H), 7.11-7.05 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 137.5, 137.0, 132.2 (2C), 131.2, 130.0 (2C), 129.7 (2C), 128.9 (2C), 126.3, 21.0.



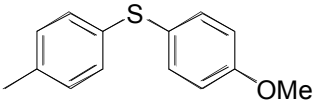
Diphenyl sulfide (Table 5, entries 5−6).[5] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.26-7.24 (m, 4H), 7.21-7.18 (m, 4H), 7.16-7.13 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 135.7 (2C), 130.9 (4C), 129.1 (4C), 126.9 (2C).



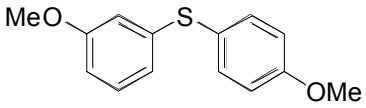
4-Methoxyphenyl phenyl sulfide (Table 5, entries 9−10).[5] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.23 (d, *J* = 8.8 Hz, 2H), 7.06-7.02 (m, 2H), 7.00-6.93 (m, 3H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.7, 138.5, 135.3 (2C), 128.8 (2C), 128.1 (2C), 125.7, 124.2, 114.9 (2C), 55.3.



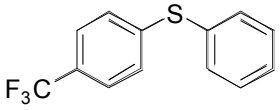
Di-4-methoxyphenyl sulfide (Table 5, entries 11−12).[12] White solid. ^{1}H NMR ($CDCl_3$): δ 7.26 (d, J = 8.8 Hz, 4H), 6.81 (d, J = 8.8 Hz, 4H), 3.76 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 158.8 (2C), 132.6 (4C), 127.3 (2C), 114.6 (4C), 55.2 (2C).



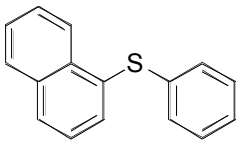
4-Methylphenyl 4-methoxyphenyl sulfide (Table 5, entries 13−14).[13] White solid. ^{1}H NMR ($CDCl_3$): δ 7.47 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.3, 135.9, 134.21 (2C), 134.15, 129.6 (2C), 129.2 (2C), 125.4, 114.7 (2C), 55.1, 20.8.



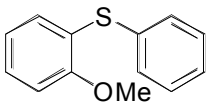
3-Methoxyphenyl 4-methoxyphenyl sulfide (Table 5, entries 15−16).[12] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.50 (d, J = 8.8 Hz, 2H), 7.20 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 6.82-6.72 (m, 3H), 3.86 (s, 3H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.8 (2C), 140.0, 135.5 (2C), 129.6, 123.6, 120.0, 114.8 (2C), 113.2, 111.1, 55.2, 55.0.



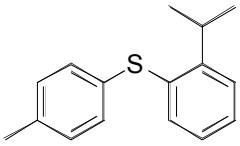
Phenyl 4-trifluoromethylphenyl sulfide (Table 5, entry 17).[14] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.47-7.45 (m, 4H), 7.39-7.35 (m, 3H), 7.28-7.24 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 142.8, 133.5 (2C), 132.4, 129.6 (2C), 128.6, 128.2 (2C), 128.1 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 125.7 (d, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 271.6 Hz).



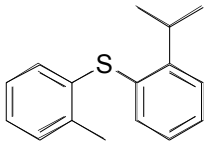
1-Naphthyl phenyl sulfide (Table 5, entries 18−19).[10] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 8.26 (s, 1H), 7.71-7.53 (m, 3H), 7.37-7.0 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 136.8, 134.1, 133.5, 132.4, 131.1, 129.1, 129.0 (2C), 128.9 (2C), 128.5, 126.8, 126.3, 126.0, 125.7, 125.5.



2-Methoxyphenyl phenyl sulfide (Table 5, entries 20−21).[5] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.42-7.40 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.32-7.27 (m, 2H), 7.14 (dt, *J* = 7.8 Hz and 1.7 Hz, 1H), 6.96-6.90 (m, 2H), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.1, 134.3, 131.4, 131.3 (2C), 129.0 (2C), 128.2, 126.9, 123.9, 121.1, 110.7, 55.7.

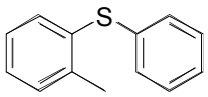


2-Isopropylphenyl 4-methylphenyl sulfide (Table 5, entries 22−24).[8] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.32 (dd, *J* = 7.7 Hz and 1.4 Hz, 1H), 7.26-7.14 (m, 4H), 7.11-7.06 (m, 3H), 3.54 (sept, *J* = 6.8 Hz, 1H), 2.32 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 149.2, 136.4, 133.8, 132.7, 132.3, 130.6 (2C), 129.8 (2C), 127.6, 126.4, 125.7, 30.4, 23.4 (2C), 20.9.

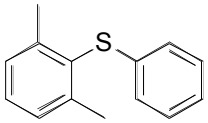


2-Isopropylphenyl 2-methylphenyl sulfide (Table 5, entries 25−26).[15] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.26 (d, *J* = 7.6 Hz, 1H), 7.19-7.14 (m, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 7.02-6.99 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 3.43 (sept, *J* = 6.7 Hz, 1H), 2.31 (s, 3H), 1.17 (d, *J* = 6.7 Hz,

6H). ^{13}C NMR ($CDCl_3$): δ 149.3, 138.3, 135.3, 132.9, 131.9, 130.9, 130.3, 127.6, 126.7, 126.54, 126.49, 125.8, 30.5, 23.4 (2C), 20.3.



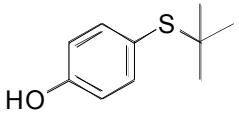
2-Methylphenyl phenyl sulfide (Table 5, entries 27−28).[5] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.47-7.19 (m, 9H), 2.50 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 136.0, 133.6, 132.9, 130.9, 130.5, 129.5 (2C), 129.0 (2C), 127.8, 126.6, 126.2, 20.5.



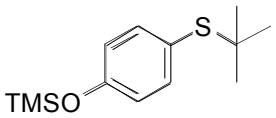
2,6-Dimethylphenyl phenyl sulfide (Table 5, entries 29−30).[11] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.33-7.29 (m, 1H), 7.27-7.23 (m, 4H), 7.15-7.11 (m, 1H), 7.02-6.99 (m, 2H), 2.51 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 143.8 (2C), 137.9, 130.4, 129.2, 128.8 (2C), 128.4 (2C), 125.5 (2C), 124.5, 21.8 (2C).

General procedure for the coupling of functionalized aryl bromides and iodides with aliphatic and aromatic thiols: The appropriate quantity of stock solution **A** or **B** was added to a 4 mL vial containing the aryl bromide or iodide (1.00 mmol) and base LiHMDS or Cs_2CO_3 (2.4 mmol), unless otherwise stated, in DME (1.5 mL). The thiol (1.00 mmol) was then added, and the vial sealed with a cap containing a PTFE septum. The mixture was heated at the temperature indicated in Tables 6 and 7 until the aryl halide was consumed, as determined by GC. Silica gel (0.5 g) was added, and the solvents were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel using hexane or a mixture of hexane and ethyl acetate as eluent. Aryl sulfides were isolated in the yields reported in Tables 6 and 7. Reactions of haloarenes bearing aromatic or aliphatic hydroxyl groups using LiHMDS as base

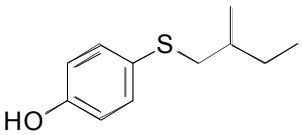
initially form the corresponding sulfide protected by a TMS group, however the silyl group was removed by an acid treatment (HCl 1N) prior to the chromatographic purification.



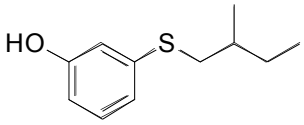
4-(2-Methyl-2-propylsulfanyl)phenol (Table 6, entries 1 and 4).[16] White solid. ^{1}H NMR ($CDCl_3$): δ 7.39 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.62 (bs, 1 H), 1.26 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.3, 139.0 (2C), 123.4, 115.5 (2C), 45.6, 30.6 (3C).



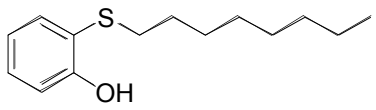
(4-(2-Methyl-2-propylsulfanyl)phenoxytrimethylsilane (Table 6, entry 2). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 1.18 (s, 9H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 156.0, 138.8 (2C), 124.4, 120.0 (2C), 45.5, 30.7 (3C), 0.1 (3C). Elem. Anal. Calcd for $C_{13}H_{22}OSSi$: C, 61.36; H, 8.71. Found: C, 61.48; H, 8.46.



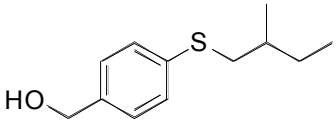
4-(2-Methylbutylsulfanyl)phenol (Table 6, entry 3). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.20 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 4.92 (bs, 1H), 2.76 (dd, *J* = 12.6 Hz and 5.7 Hz, 1H), 2.58 (dd, *J* = 12.6 Hz and 7.6 Hz, 1H), 1.50 (oct, *J* = 6.6 Hz, 1H), 1.45-1.38 (m, 1H), 1.20-1.11 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 154.4, 132.8 (2C), 127.6, 115.9 (2C), 43.0, 34.4, 28.5, 18.7, 11.1. Elem. Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.09; H, 8.17.



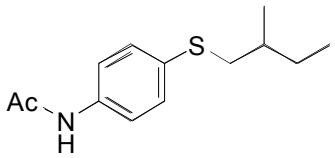
3-(2-Methylbutylsulfanyl)phenol (Table 6, entries 5−6).[8] Yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.04 (t, *J* = 7.9 Hz, 1H), 6.80 (m, 1H), 6.72 (t, *J* = 2.1 Hz, 1H), 6.53 (m, 1H), 5.90-4.20 (bs, 1H), 2.84 (dd, *J* = 12.3 Hz and 5.7 Hz, 1H), 2.65 (dd, *J* = 12.3 Hz and 7.6 Hz, 1H), 1.58 (oct, *J* = 6.6 Hz, 1H), 1.49-1.40 (m, 1H), 1.22-1.13 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 155.6, 139.1, 129.8, 120.7, 115.0, 112.5, 40.2, 34.3, 28.7, 18.8, 11.1.



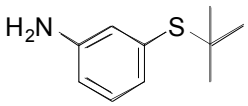
2-Octylsulfanylphenol (Table 6, entries 7−8).[17] Yellow liquid. ^{1}H NMR ($CDCl_3$): δ 7.38 (dd, *J* = 7.6 Hz and 1.5 Hz, 1H), 7.17 (dt, *J* = 7.6 Hz and 1.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.80-6.76 (m, 1H), 6.70 (bs, 1 H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.50-1.43 (m, 2H), 1.31-1.17 (m, 10H), 0.79 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 156.8, 135.8, 130.8, 120.6, 119.1, 114.6, 36.7, 31.7, 29.5, 29.04, 28.98, 28.5, 22.5, 14.0.



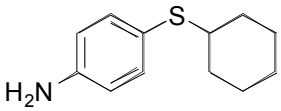
2-Methylbutyl 4-hydroxymethylphenyl sulfide (Table 6, entries 9−12). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.15 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 4.45 (s, 2H), 2.78 (dd, *J* = 12.6 Hz and 5.8 Hz, 1H), 2.59 (dd, *J* = 12.6 Hz and 7.6 Hz, 1H), 2.00 (bs, 1H), 1.54-1.33 (m, 2H), 1.17-1.07 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.75 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 138.1, 136.6, 128.8 (2C), 127.4 (2C), 64.6, 40.6, 34.3, 28.6, 18.8, 11.1. Elem. Anal. Calcd for $C_{12}H_{18}OS$: C, 68.52; H, 8.63. Found: C, 68.62; H, 8.73.



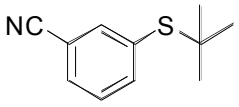
N-(4-(2-Methylbutylsulfanyl)phenyl) acetamide (Table 6, entry 13). White solid. ^{1}H NMR ($CDCl_3$): δ 7.66 (bs, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 2.81 (dd, *J* = 5.8 Hz and 12.6 Hz, 1H), 2.62 (dd, *J* = 7.6 Hz and 12.6 Hz, 1H), 2.07 (s, 3H), 1.54 (oct, *J* = 6.6 Hz, 1H), 1.48-1.40 (m, 1H), 1.21-1.13 (m, 1H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.81 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 168.5, 136.0, 132.4, 130.2 (2C), 120.4 (2C), 41.6, 34.4, 28.6, 24.4, 18.7, 11.1. Elem. Anal. Calcd for $C_{13}H_{19}NOS$: C, 65.78; H, 8.07; N, 5.90. Found: C, 65.57; H, 7.92; N, 5.91.



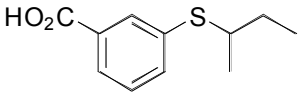
3-(2-Methyl-2-propylsulfanyl)aniline (Table 6, entry 14).[8] Yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.10 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.67 (dd, *J* = 7.8 Hz and 2.5 Hz, 1H), 3.71 (bs, 2H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 146.1, 133.2, 129.0, 127.5, 123.7, 115.4, 45.6, 30.9 (3C).



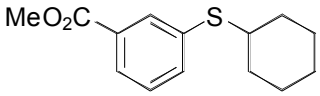
4-Cyclohexylsulfanylaniline (Table 6, entry 15).[18] Yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 8.5 Hz, 2H), 3.75 (bs, 2H), 2.78-2.72 (m, 1H) 1.86-1.83 (m, 2H), 1.71-1.64 (m, 2H), 1.53-1.48 (m, 1H), 1.49-1.10 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 146.1, 135.9 (2C), 121.5, 115.1 (2C), 47.9, 33.2 (2C), 26.0, 25.6(2C).



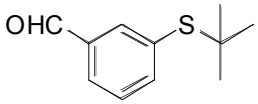
3-Cyanophenyl 2-methyl-2-propyl sulfide (Table 6, entries 16−19).[8] White solid. ^{1}H NMR ($CDCl_3$): δ 7.82 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 141.5, 140.2, 134.7, 132.0, 129.1, 118.1, 112.6, 46.7, 30.8 (3C).



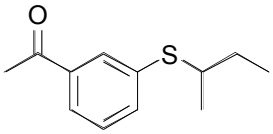
3-(1-Methylpropylsulfanyl)benzoic acid (Table 6, entries 20−21).[8] Pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 11.92 (bs, 1H), 8.12 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 3.25 (sext, *J* = 6.6 Hz, 1H), 1.73-1.64 (m, 1H), 1.62-1.53 (m, 1H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 171.9, 136.8, 136.5, 132.5, 129.8, 128.8, 128.1, 44.7, 29.4, 20.4, 11.3.



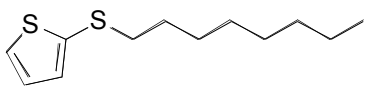
Methyl 3-cyclohexylsulfanylbenzoate (Table 6, entry 22).[11] Pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.28-7.24 (m, 1H), 3.83 (s, 3H), 3.10-3.05 (m, 1H), 1.90-1.86 (m, 2H), 1.69-1.67 (m, 2H), 1.54-1.51 (m, 1H), 1.33-1.15 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 166.5, 136.0, 135.8, 132.3, 130.6, 128.6, 127.5, 52.0, 46.4, 33.1 (2C), 25.8, 25.6 (2C).



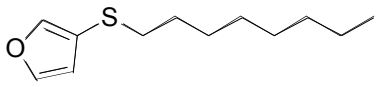
3-(2-Methyl-2-propylsulfanyl)benzaldehyde (Table 6, entry 23).[8] Colorless oil. ^{1}H NMR ($CDCl_3$): δ 10.03 (s, 1H), 8.02 (t, *J* = 1.6 Hz, 1H), 7.88 (dt, *J* = 7.6 Hz and 1.6 Hz, 1H), 7.79 (dt, *J* = 7.6 Hz and 1.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 191.5, 143.0, 138.2, 136.5, 134.2, 129.4, 128.9, 46.2, 30.7 (3C).



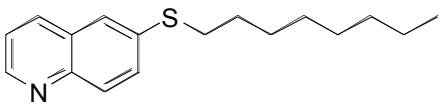
3-Acetylphenyl 1-Methylpropyl sulfide (Table 6, entry 24). Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.89 (t, *J* = 1.8 Hz, 2H), 7.71 (m, 1H), 7.50 (m, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 3.17 (hex, *J* = 6.7 Hz, 1H), 2.53 (s, 3H), 1.66-1.44 (m, 2H), 1.22 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 197.4, 137.5, 136.8, 135.6, 130.7, 128.8, 126.2, 44.6, 29.3, 26.5, 20.3, 11.3. Elem. Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H, 7.74. Found: C, 69.15; H, 7.75.



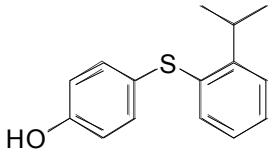
Octyl 2-thiophenyl sulfide (Table 6, entries 25−26).[19] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.23 (dd, *J* = 5.4 Hz and 1.3 Hz, 1H), 7.02 (dd, *J* = 3.5 Hz and 1.3 Hz, 1H), 6.88 (dd, *J* = 5.4 Hz and 3.5 Hz, 1H), 2.70 (t, *J* = 7.3 Hz, 2H), 1.53 (quint, *J* = 7.3 Hz, 2H), 1.33-1.27 (m, 2H), 1.20 (bs, 8H), 0.80 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 134.9, 133.1, 128.7, 127.3, 38.9, 31.7, 29.3, 29.1, 29.0, 28.3, 22.6, 14.0.



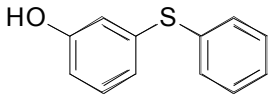
3-Furyl octyl sulfide (Table 6, entry 27). Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.32 (m, 2H), 6.32 (m, 1H), 2.60 (t, *J* = 7.4 Hz, 2H), 1.50 (quint, *J* = 7.3 Hz, 2H), 1.33-1.27 (m, 2H), 1.23-1.16 (m, 8H), 0.80 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 143.3 (2C), 116.6, 113.7, 35.4, 31.7, 29.4, 29.1, 29.0, 28.5, 22.5, 14.0. Elem. Anal. Calcd for $C_{12}H_{20}OS$: C, 67.87; H, 9.49. Found: C, 67.83; H, 9.31.



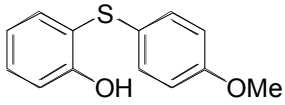
Octyl 6-quinolyl sulfide (Table 6, entry 28). Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 8.73 (dd, J = 4.1 Hz and J = 1.6 Hz, 1H), 7.91 (m, 2H), 7.54-7.51 (m, 2H), 7.25 (dd, J = 9.1 Hz and J = 4.1 Hz, 1H), 2.93 (t, J = 7.4 Hz, 2H), 1.61 (quint, J = 7.4 Hz, 2H), 1.36 (quint, J = 7.3 Hz, 2H), 1.23-1.16 (m, 8H), 0.78 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 149.5, 146.6, 136.1, 134.7, 130.2, 129.6, 128.6, 124.9, 121.4, 33.1, 31.6, 29.00, 28.98, 28.8, 28.7, 22.5, 13.9.



4-(2-Isopropylphenylsulfanyl)phenol (Table 7, entries 1−2).[8] Pale yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.22-7.16 (m, 3H), 7.13-7.08 (m, 1H), 7.00-6.93 (m, 2H), 6.74-6.70 (m, 2H), 5.28 (bs, 1 H), 3.43 (m, 1H), 1.16 (dd, J = 6.8 Hz and 1.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 155.3, 147.7, 135.5, 134.4 (2C), 130.1, 126.7, 126.3, 125.6, 125.5, 116.4 (2C), 30.2, 23.2 (2C).

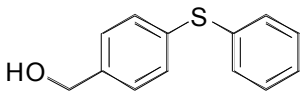


3-Phenylsulfanylphenol (Table 7, entries 3−4). Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.33-7.28 (m, 2H), 7.24-7.14 (m, 3H), 7.05 (t, J = 7.8 Hz, 1H), 6.81-6.77 (m, 1H), 6.64-6.62 (m, 1H), 6.59-6.56 (m, 1H), 5.00 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 155.8, 137.7, 134.5, 131.8 (2C), 130.1, 129.2 (2C), 127.4, 122.6, 116.7, 113.8. Elem. Anal. Calcd for $C_{12}H_{10}OS$: C, 71.25; H, 4.98. Found: C, 71.01; H, 5.02.

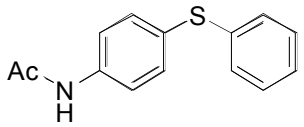


2-(4-Methoxyphenylsulfanyl)phenol (Table 7, entries 5−6).[20] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.41 (dd, J = 7.7 Hz and 1.6 Hz, 1H), 7.23 (td, J = 7.7 Hz and 1.6 Hz, 1H), 7.05 (d, J = 9.0 Hz, 2H), 6.94 (dd, J = 8.3 Hz and 1.3 Hz, 1H), 6.83 (dt, J = 7.6 Hz and 1.3 Hz, 1H), 6.71 (d,

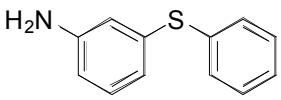
J = 9.0 Hz, 2H), 6.48 (s, 1H), 3.67 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.7, 156.6, 136.1, 131.6, 130.0 (2C), 126.0, 121.1, 118.4, 115.3, 114.9 (2C), 55.3.



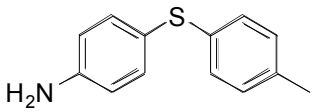
4-Hydroxymethylphenyl phenyl sulfide (Table 7, entries 7−9). White solid. ^{1}H NMR ($CDCl_3$): δ 7.27-7.11 (m, 9H), 4.53 (s, 2H), 2.06 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 139.8, 135.7, 134.8, 131.2 (2C), 130.8 (2C), 129.1 (2C), 127.7 (2C), 126.9, 64.6. Elem. Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.03; H, 5.59.



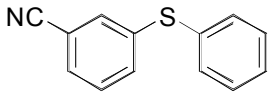
***N*-(4-Phenylsulfanyl)phenyl acetamide (Table 7, entries 10−11).** White solid. ^{1}H NMR ($CDCl_3$): δ 7.42-7.37 (m, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.20-7.17 (m, 4H), 7.15-7.09 (m, 1H), 2.09 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 168.9, 138.6, 136.8, 134.9, 131.5 (2C), 129.5, 129.1 (2C), 127.3, 126.1, 121.4, 118.4, 24.4. Elem. Anal. Calcd for $C_{14}H_{13}NOS$: C, 69.11; H, 5.39; N, 5.76. Found: C, 68.91; H, 5.38; N, 5.73.



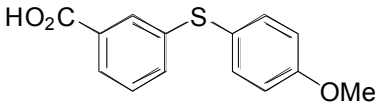
3-Phenylsulfanylaniline (Table 7, entry 12).[21] Yellow oil. ^{1}H NMR ($CDCl_3$): δ 7.35-7.32 (m, 2H), 7.29-7.20 (m, 3H), 7.05 (t, *J* = 8.1 Hz, 1H), 6.73-6.68 (m, 1H), 6.61-6.09 (m, 1H), 6.53-6.50 (m, 1H), 3.60 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ 147.0, 136.3, 135.6, 130.9 (2C), 129.8, 129.0 (2C), 126.8, 120.8, 116.9, 113.8.



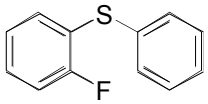
4-(4-Methylphenylsulfanyl)aniline (Table 7, entry 13).[18] Colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.19 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 6.56 (d, J = 8.6 Hz, 2H), 3.67 (bs, 2H), 2.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 146.6, 135.5, 135.3, 135.2 (2C), 129.5 (2C), 128.2 (2C), 121.6, 115.7 (2C), 20.8.



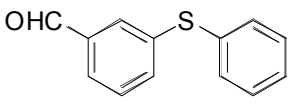
3-Cyanophenyl phenyl sulfide (Table 7, entries 14−16).[15] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.46-7.31 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 139.8, 133.2 (2C), 132.7, 132.0, 131.5, 129.7 (2C), 129.5, 129.4, 128.7, 118.1, 113.2.



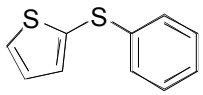
3-(4-Methoxyphenylsulfanyl)benzoic acid (Table 7, entries 17−19).[15] White solid. ^{1}H NMR ($CDCl_3$): δ 7.90 (bs, 1H), 7.86-7.83 (m, 1H), 7.45 (d, J = 9.0 Hz, 2H), 7.36-7.31 (m, 2H), 6.92 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 171.8, 160.1, 140.1, 135.9 (2C), 132.6, 129.9, 129.0, 128.9, 127.2, 122.8, 115.2 (2C), 55.3.



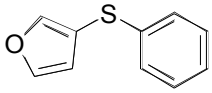
2-Fluorophenyl phenyl sulfide (Table 7, entry 20).[22] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.18-7.05 (m, 7H), 6.94-6.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 161.0 (d, $^1J_{C\text{-}F}$ = 246.9 Hz), 134.0, 133.3, 130.8 (2C), 129.3, 129.2 (2C), 127.2, 124.6 (d, $^3J_{C\text{-}F}$ = 10.7 Hz), 122.6 (d, $^2J_{C\text{-}F}$ = 17.6 Hz), 115.8 (d, $^2J_{C\text{-}F}$ = 22.23 Hz).



3-Phenylsulfanylbenzaldehyde (Table 7, entry 21).[23] Colorless oil. ^{1}H NMR ($CDCl_3$): δ 9.83 (s, 1H), 7.66 (t, *J* = 1.8 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.35-7.31 (m, 2H), 7.28-7.20 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 191.5, 138.6, 137.0, 135.2, 133.5, 132.3 (2C), 130.4, 129.6, 129.4 (2C), 128.0, 127.5.



Phenyl thiophen-2-yl sulfide (Table 7, entries 22−23).[5] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.32 (d, *J* = 5.1 Hz, 1H), 7.18-7.00 (m, 6H), 6.95-6.93 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 138.5, 135.9, 131.2, 130.9, 128.9 (2C), 127.8, 127.0 (2C), 125.9.



3-Furyl phenyl sulfide (Table 7, entry 24).[24] Colorless liquid. ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 1H), 7.40 (m, 1H), 7.16-7.10 (m, 4H), 7.06-7.03 (m, 1H), 6.34 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 146.1, 144.1, 137.2, 128.8 (2C), 127.2 (2C), 125.7, 114.6, 113.9.

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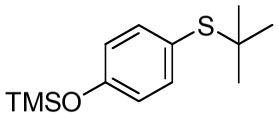

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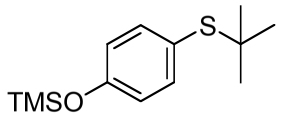

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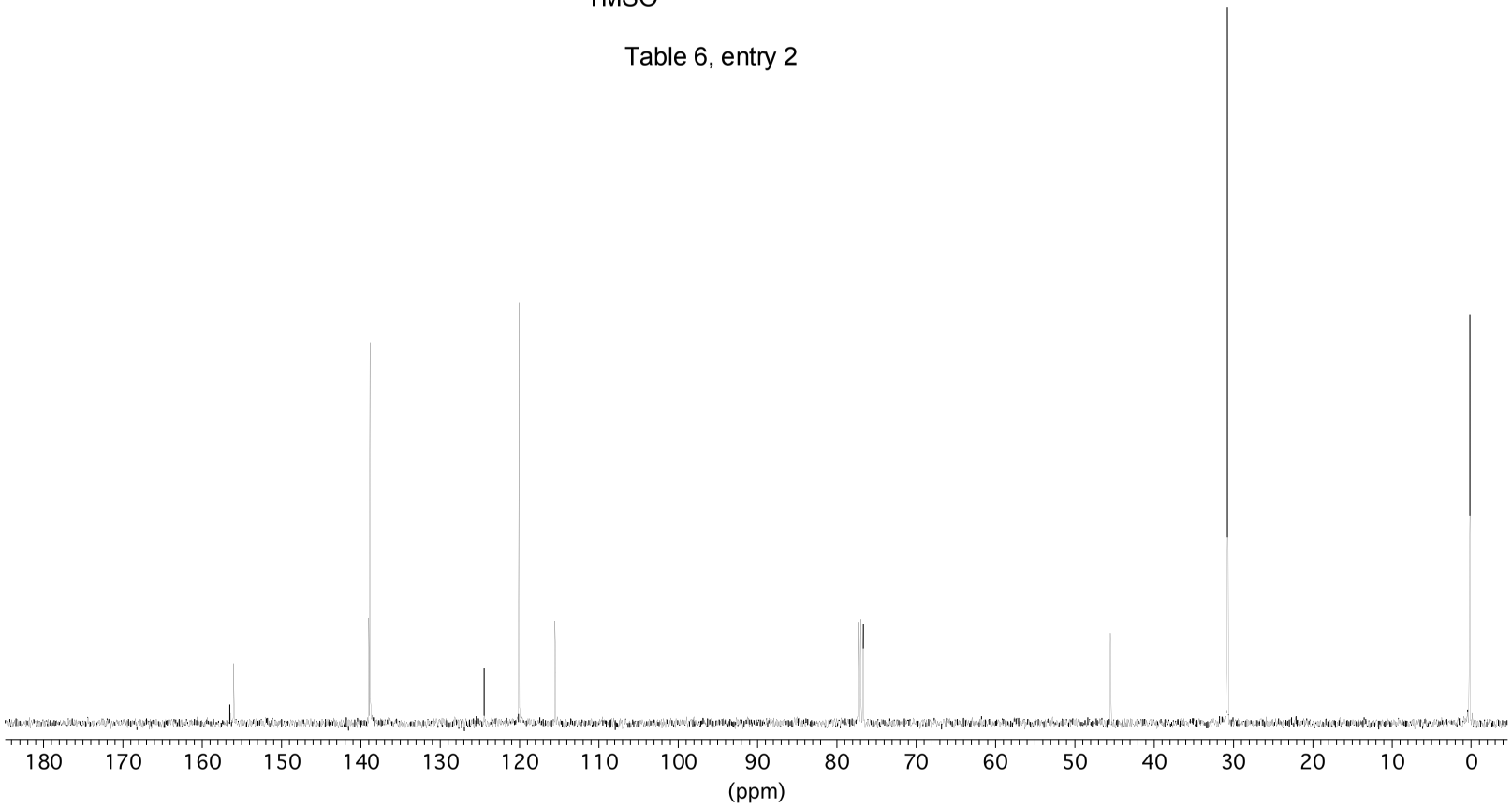

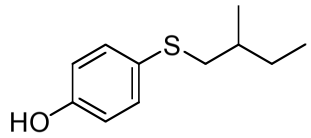

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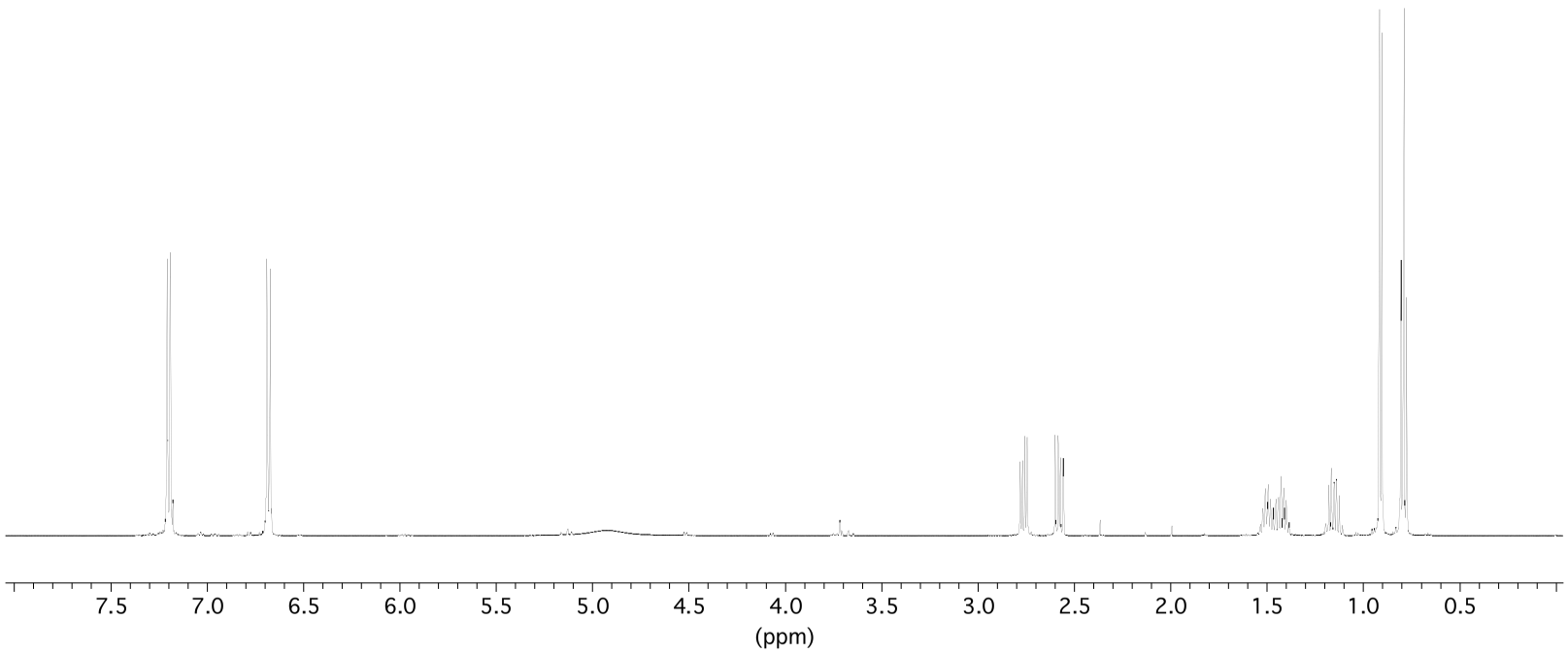

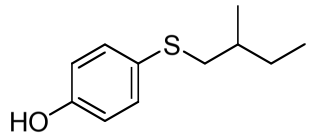

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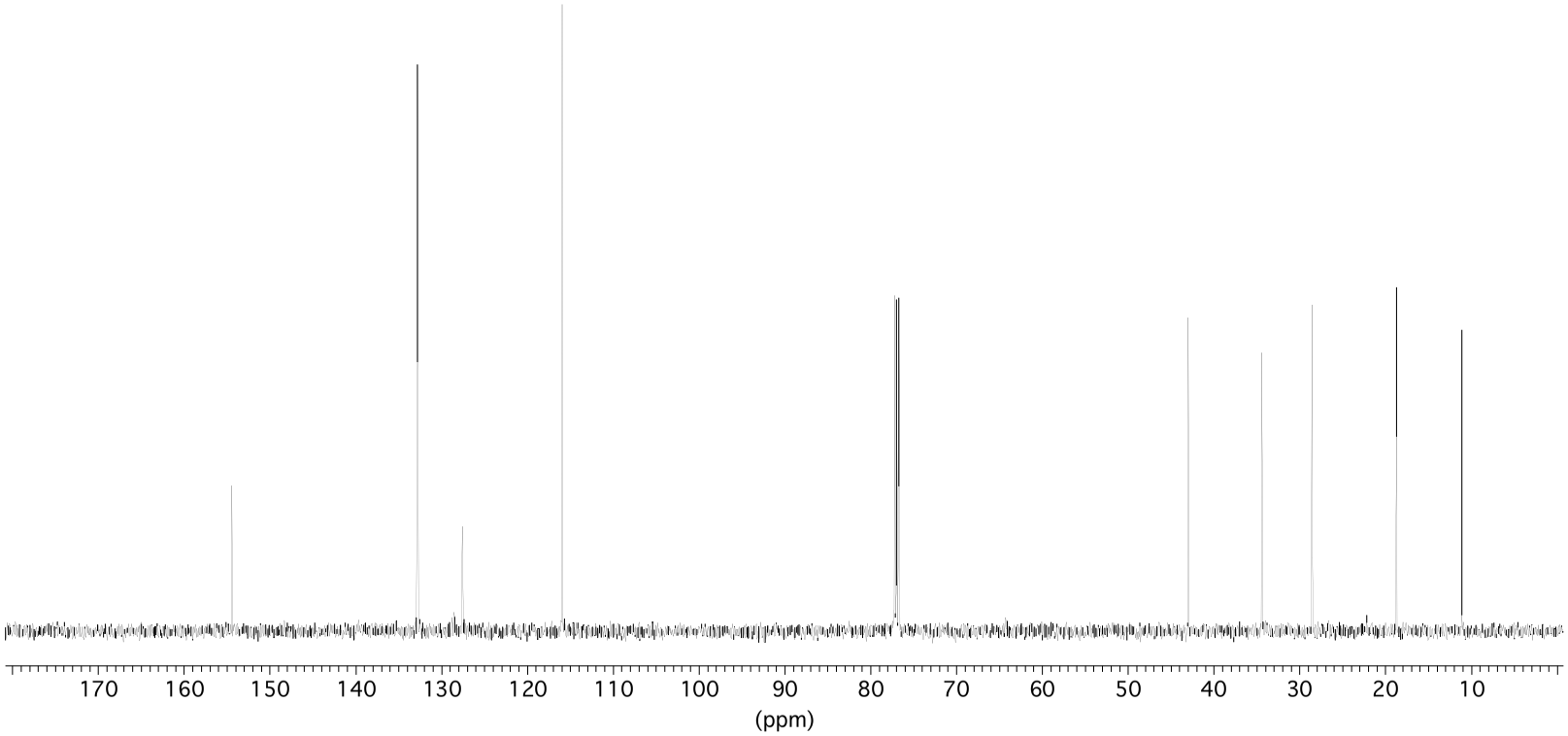

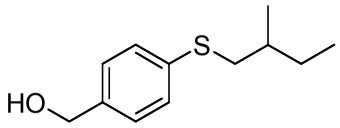

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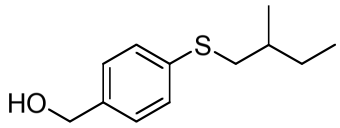

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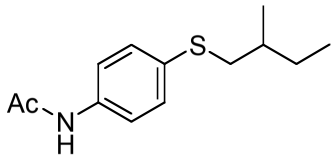

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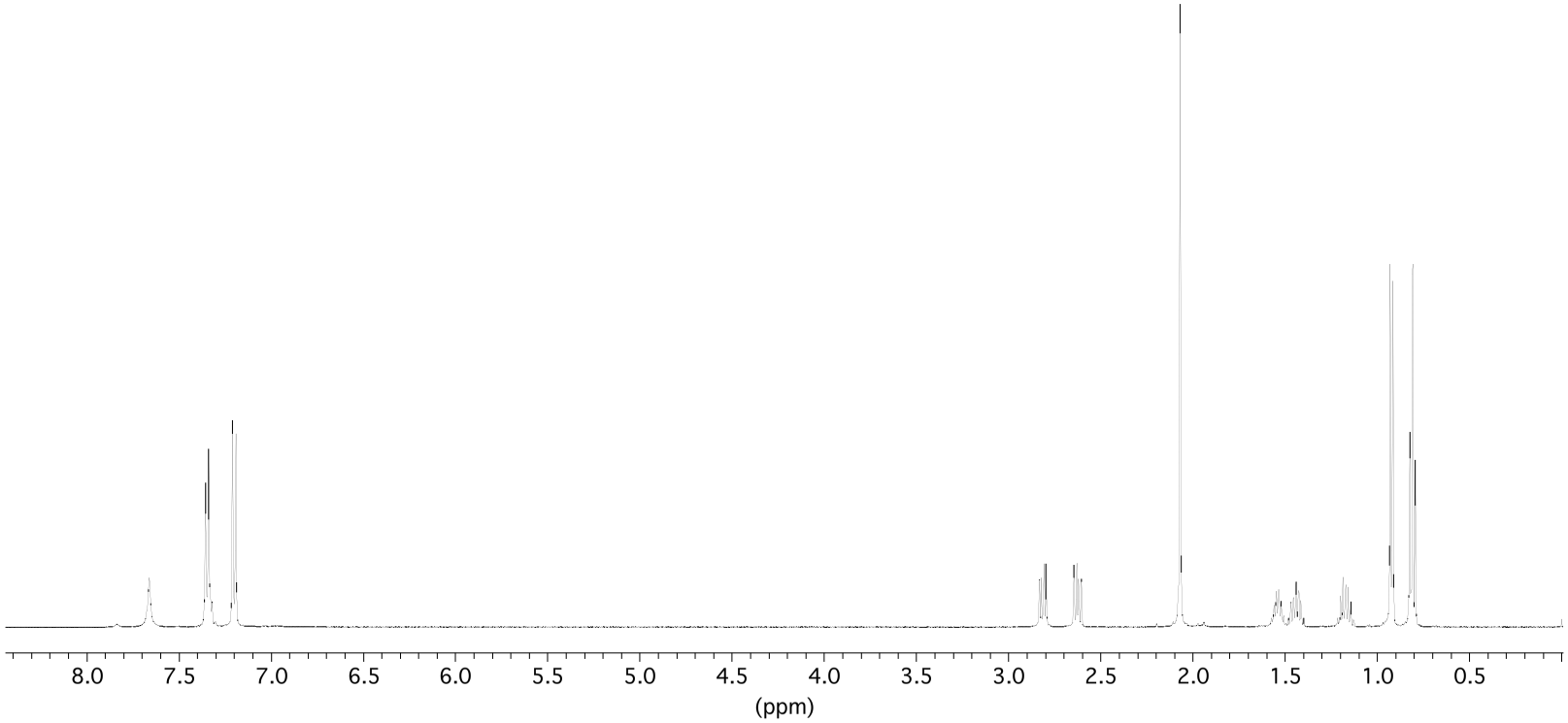

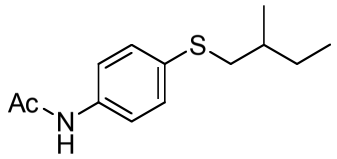

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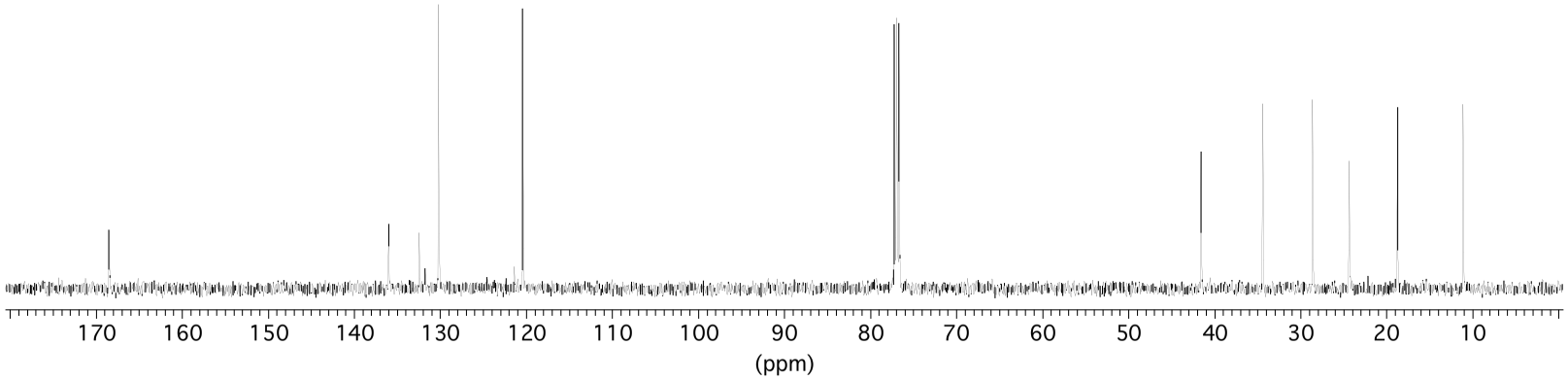

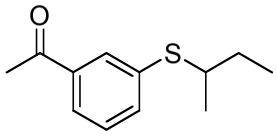

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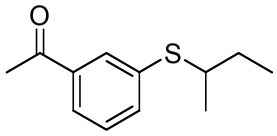

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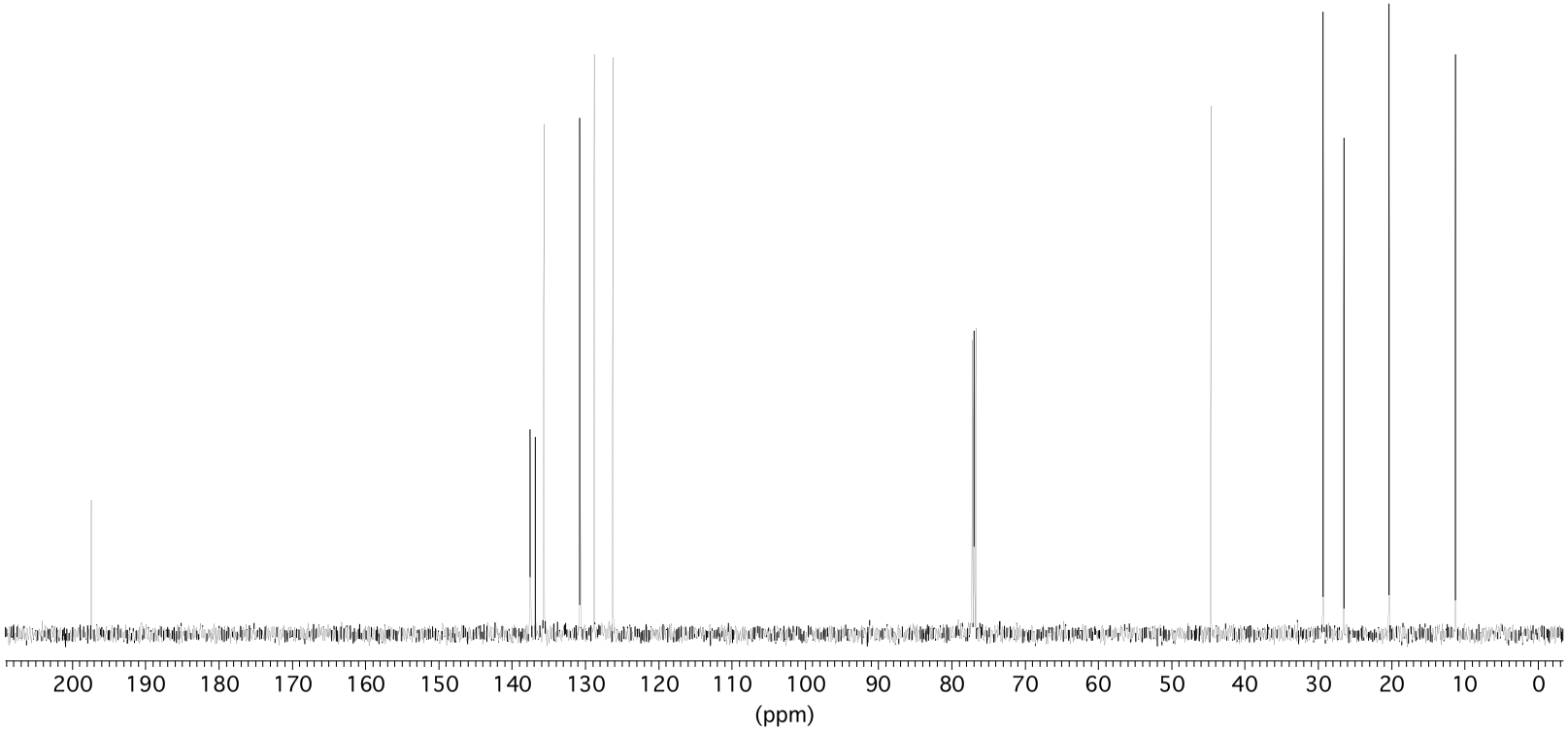

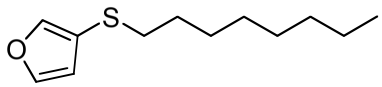

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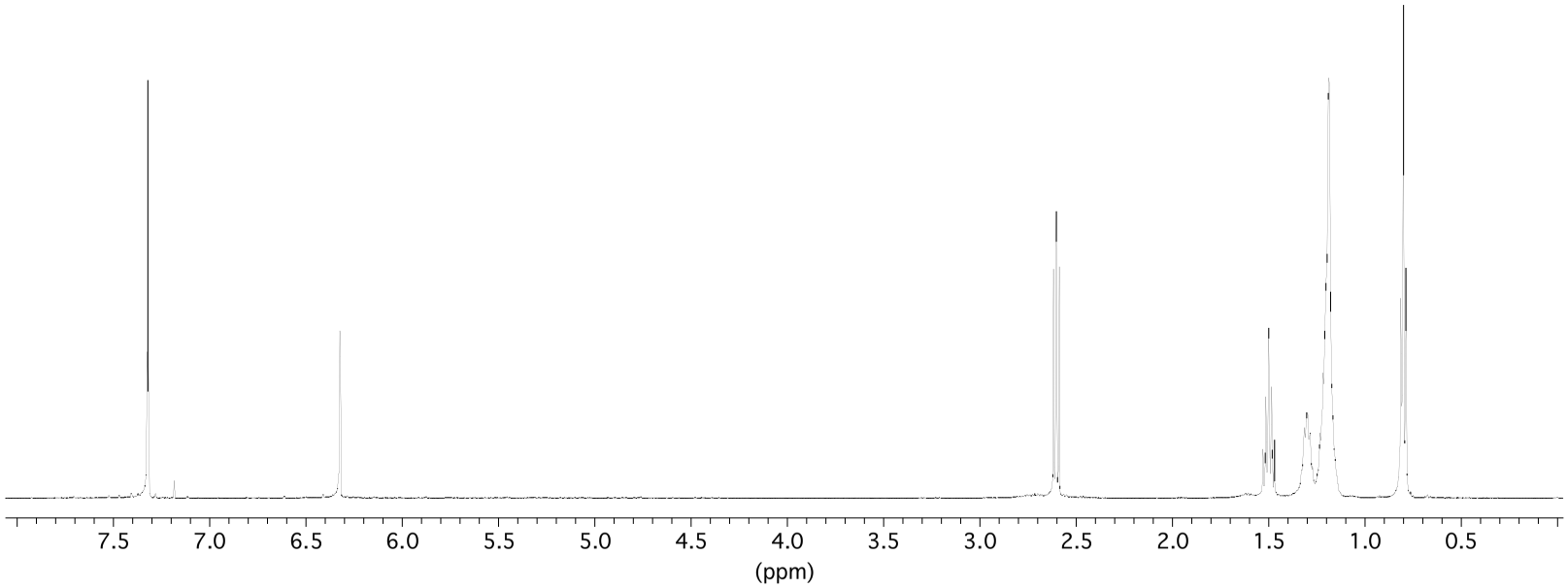

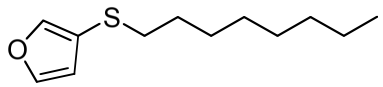

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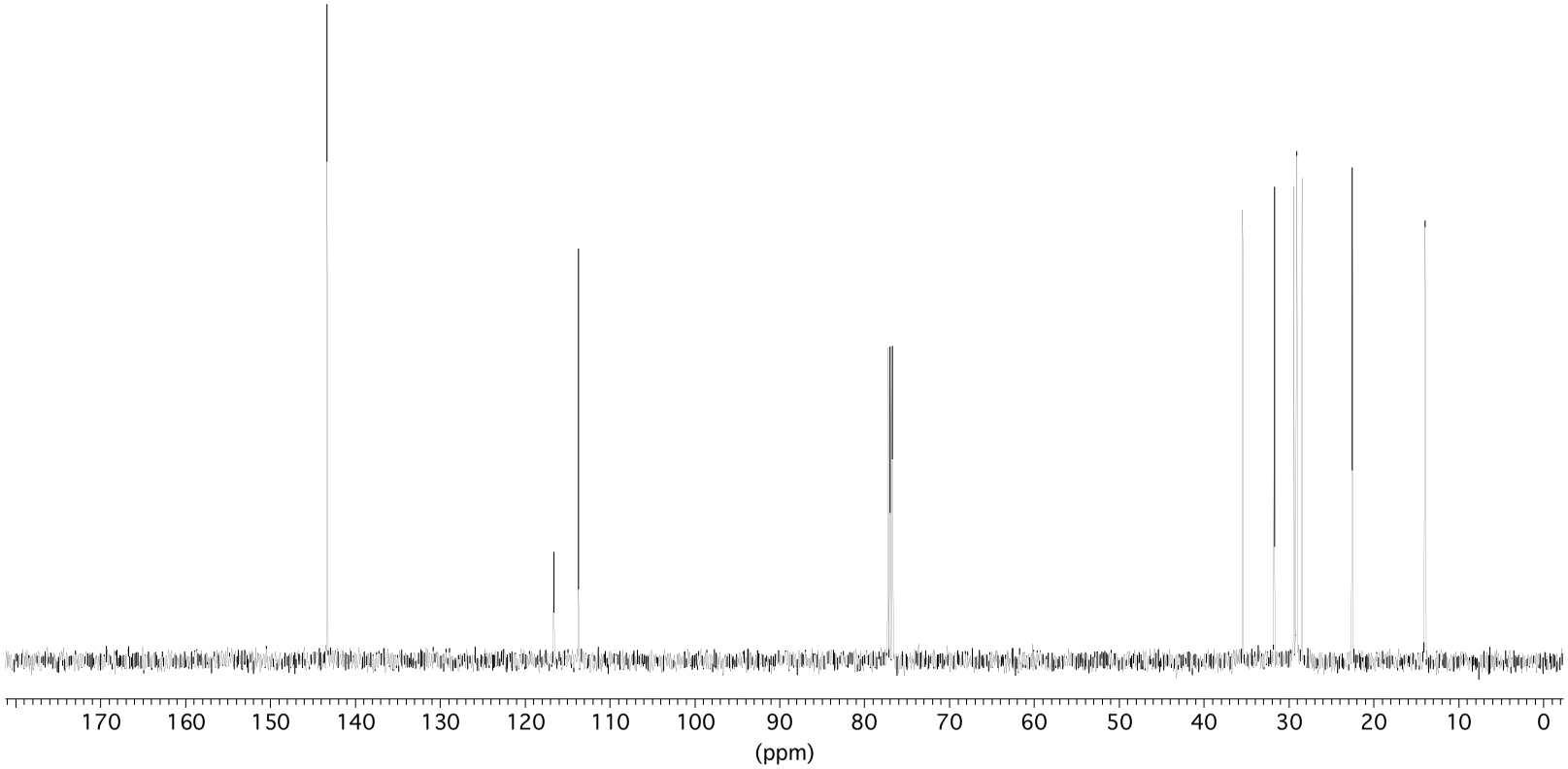

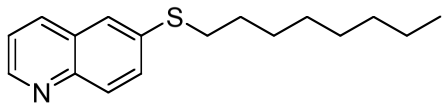

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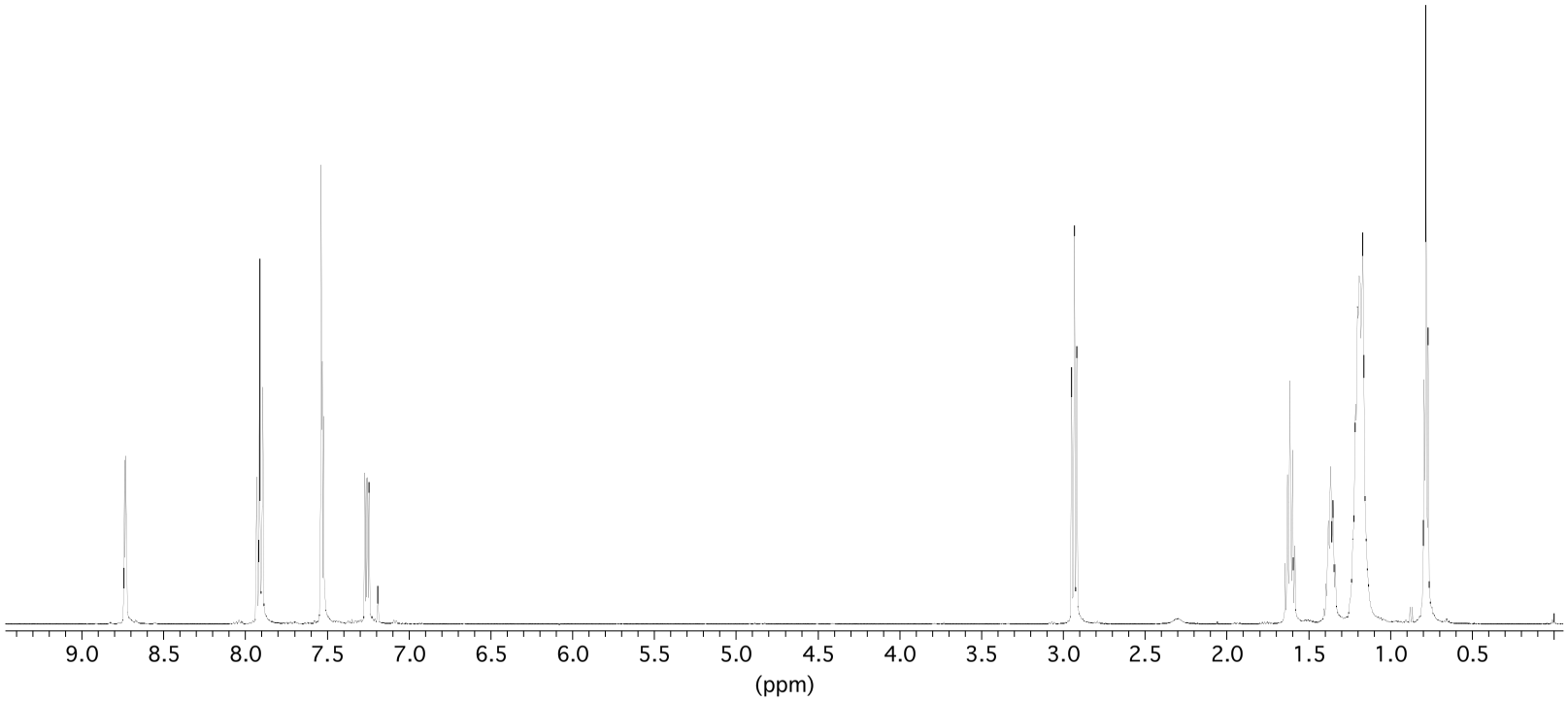

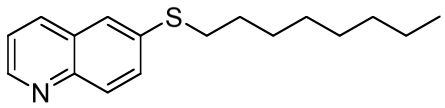

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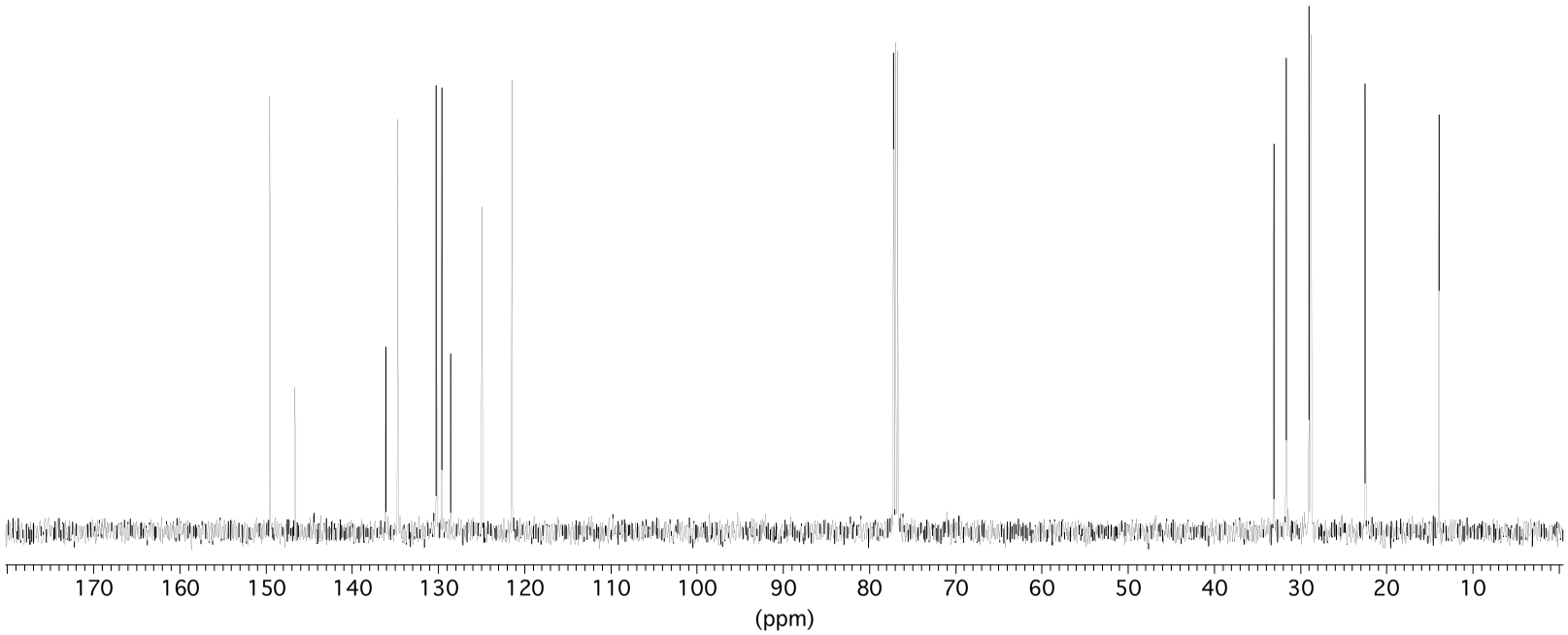

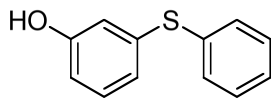

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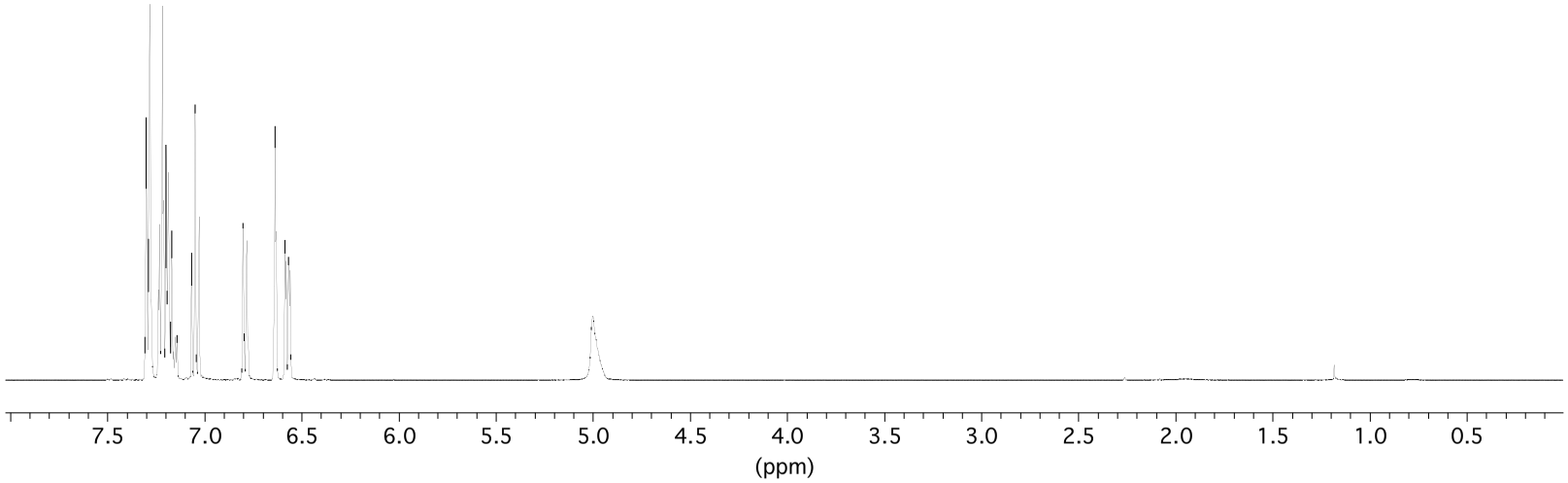

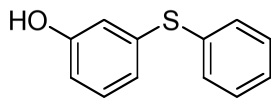

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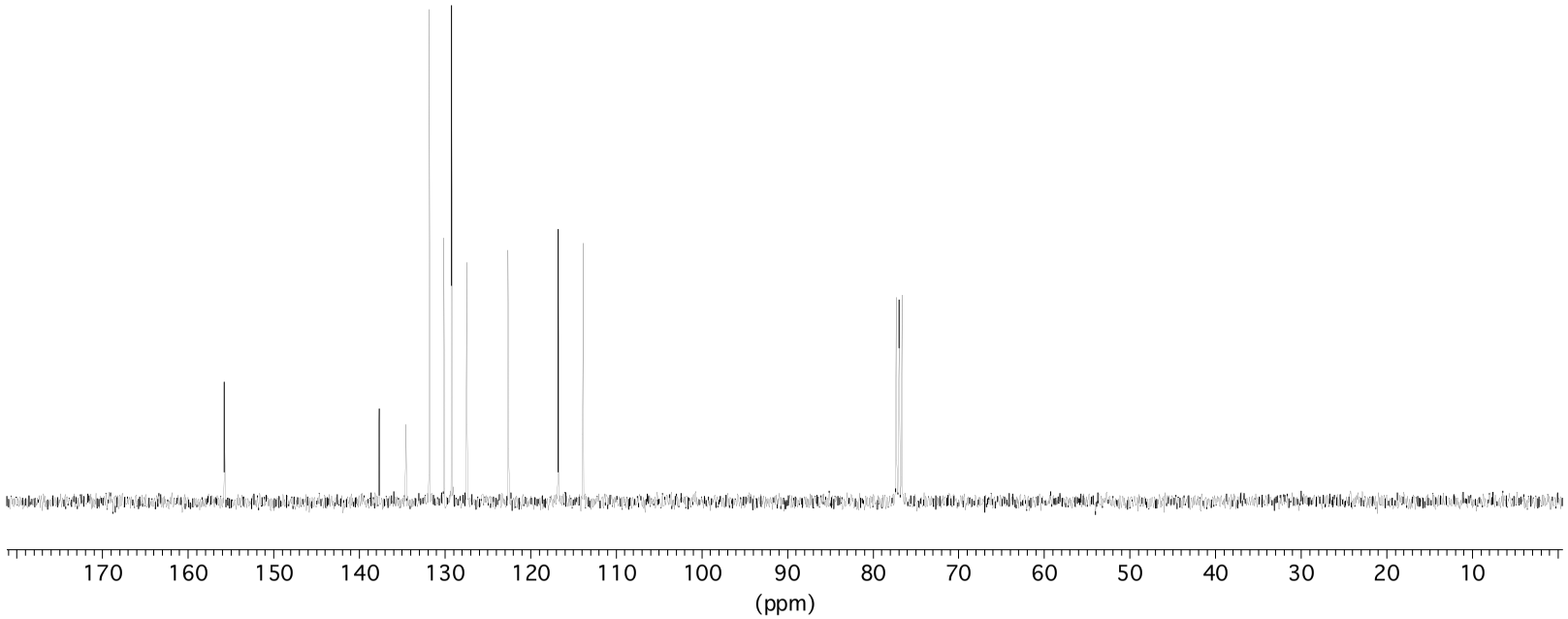

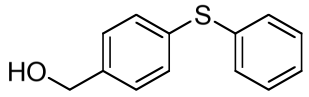

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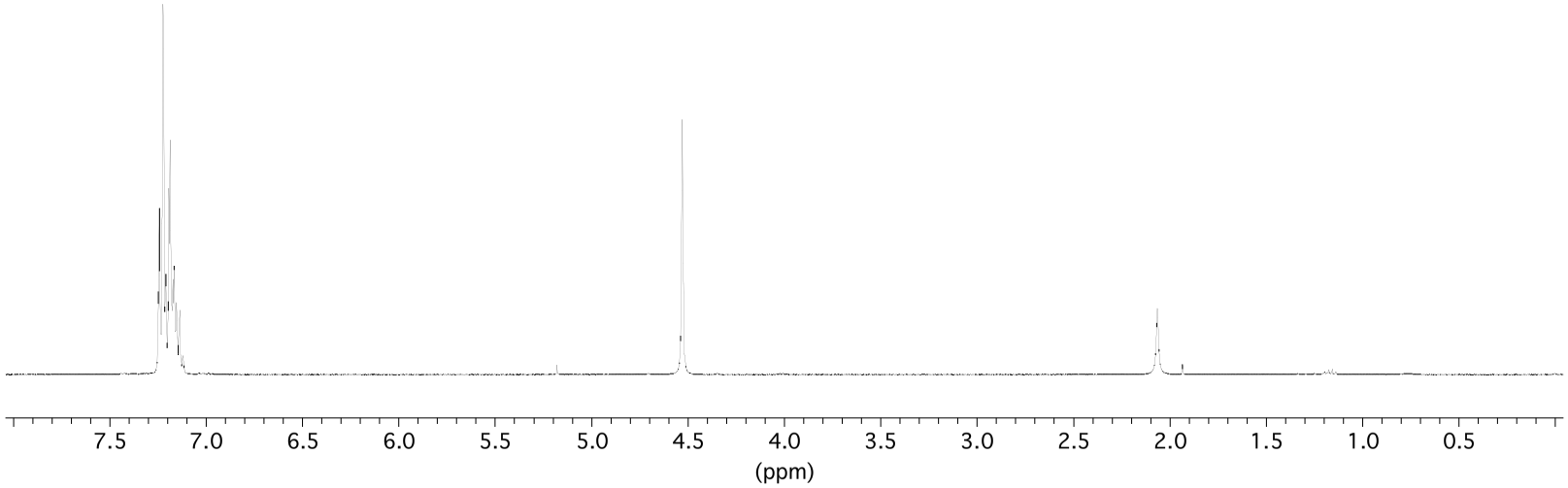

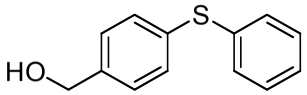

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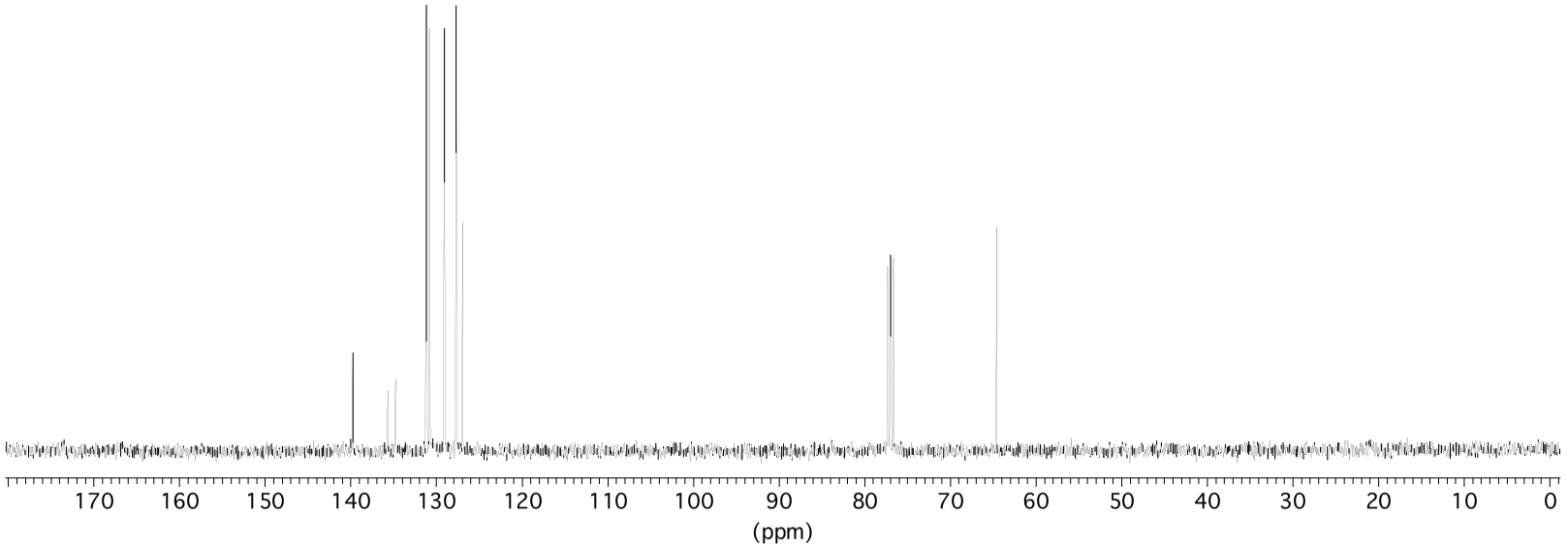

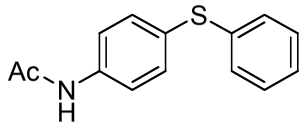

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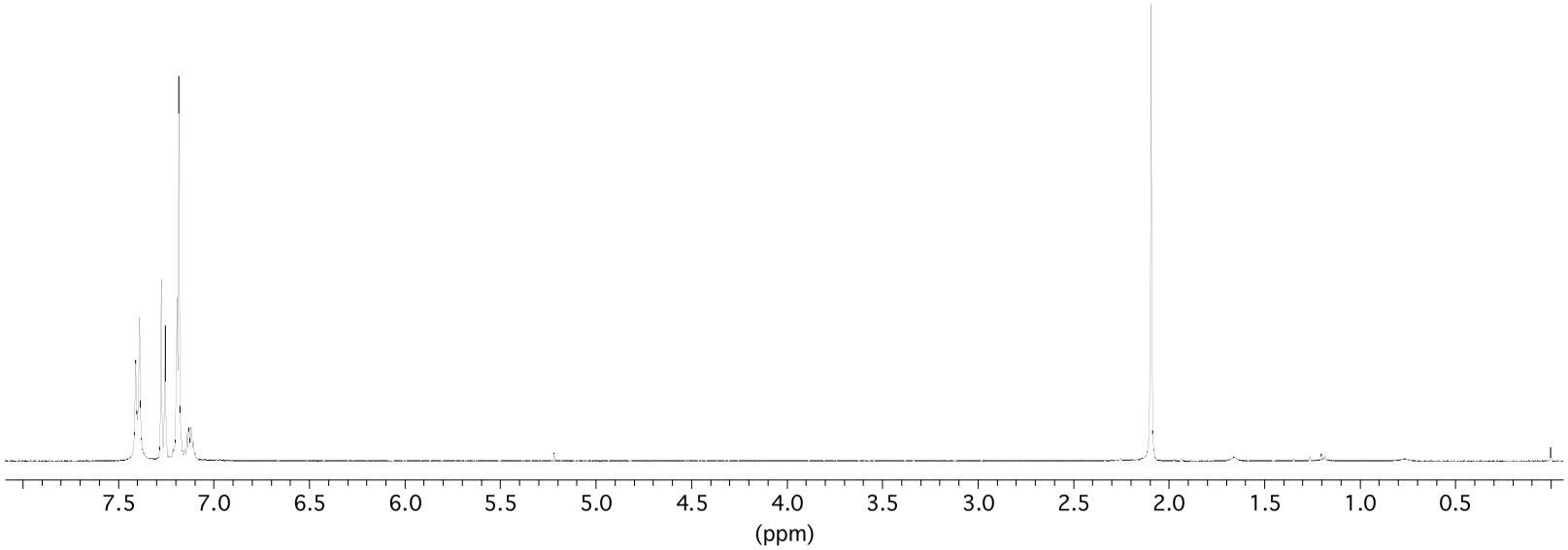

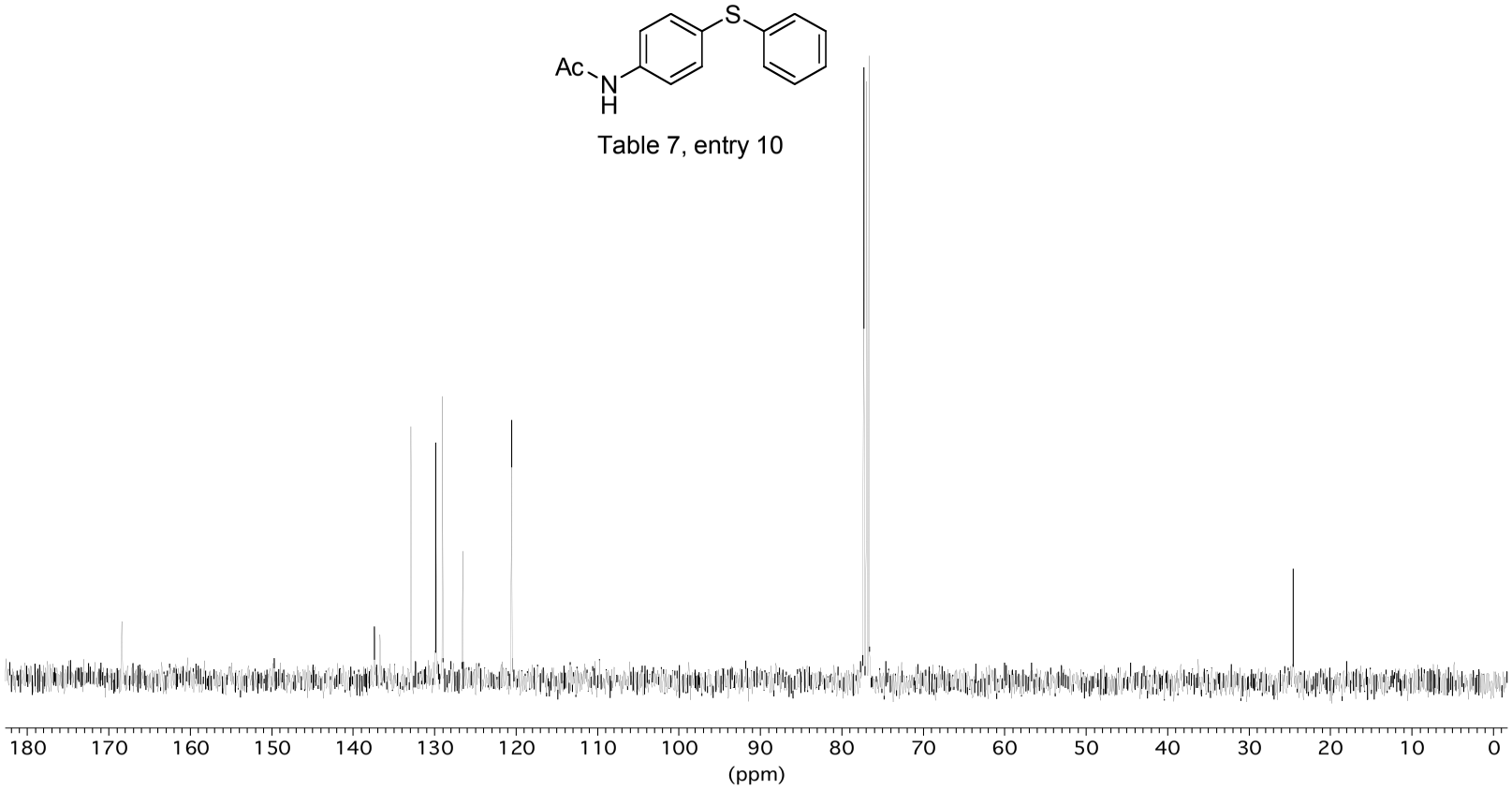

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