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Microwave-Assisted Copper-Catalyzed Cross-Coupling Reaction of Thiols with Aryl Iodides in Water

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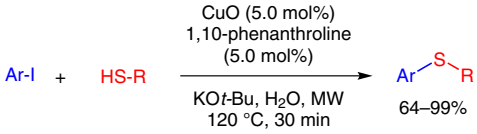

Ar = aryl; R = aryl, alkyl

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Abstract Microwave-promoted C–S bond formation from thiols and aryl iodides in the presence of a copper catalyst is reported. A combination of copper(II) oxide and 1,10-phenanthroline catalyzes this reaction. A variety of aryl iodides react smoothly with thiols to provide the corresponding aryl sulfides in good to excellent yields. Notably, the reactions proceed in water with a short reaction time (30 minutes). This system shows broad functional-group tolerance; amino, chloro, bromo, acetyl, and nitro groups are unaffected by the reaction conditions.

Key words microwave heating, copper, cross-coupling, thiols, aryl iodides, sulfides

The preparation of aryl sulfides has developed into an interesting topic for synthetic organic chemists, as these molecules play important roles in organic synthesis, materials science, and chemical biology.[2–4] Whereas conventional methods for preparing aryl sulfides require harsh reaction conditions,[5] the transition-metal-catalyzed formation of C–S bond from thiols and aryl halides proceeds under mild conditions.[6–15] Palladium,[7] copper,[8] nickel,[9] iron,[10] indium,[11] cobalt,[12] gold,[13] manganese,[14] and silver[15] have all been used as catalysts for this transformation. Remarkably, copper is the most popular of these metals because of the low cost of its salts. However, most copper-catalyzed C–S coupling reactions are performed in organic solvents.[8] Environmentally friendly catalytic systems in which water is used as the reaction medium are attractive because water is safe and abundant.[16a–d] As a result, water has been used in many transition-metal-catalyzed cross-coupling reactions[16e] including C–S bond-forming process.[16f–r] However, such reactions have two major limitations. The first is that long reaction times (24–48 hours)[16f–r] are required and, secondly, activated aryl chlorides couple only with aryl thiols: alkyl thiols cannot be used.[16r]

The microwave-assisted technique has gained much attention because of its high efficiency and short reaction times.[16n,17] Although the microwave-assisted copper-catalyzed C–S coupling reaction is known,[18] it does have several limitations in that reaction times of 120–180 minutes are required and these reactions are performed in organic solvents.[18] As part of our ongoing studies on C–S coupling reactions,[6a,8c,d,10a,d,14,19] we report a microwave-assisted copper-catalyzed C–S bond-formation reaction of aryl iodides with thiols in water with a short reaction time (30 minutes).

We chose 1-iodo-4-methylbenzene (**1a**) and benzenethiol (**2a**) as starting materials for determining the optimal reaction conditions. A 22% yield of sulfide **3a** was obtained when the reaction was performed in water in the presence of copper(II) oxide with 1,10-phenanthroline (**L1**; Figure 1) as a ligand and cesium carbonate as a base at 120 °C in an oil bath for 24 hours (Table 1, entry 1). To our delight, however, we obtained a 90% yield of sulfide **3a** within 30 minutes when microwave heating was applied instead of conventional heating in an oil bath (entry 2). A study of the effect of various ligands (Figure 1) showed that **L1** is among the best ligands (entries 3–8). We also studied the effect of various bases (entries 9–14), and we found that potassium *tert*-butoxide is superior to other bases, giving a 99% isolated yield of the product (entry 9). A lower reaction temperature (entry 15) or a shorter reaction time (entry 16) gave a reduced yield of the product. A control experiment showed that only traces of product were detected when the reaction was carried out in the absence of copper(II) oxide (entry 17). When we used copper(I) oxide or copper(II) acetate as the catalyst for the coupling reaction in the presence of **L1** as the ligand and potassium *tert*-butoxide as the base, sulfide **3a** was obtained in 89% and 65% yield, respectively.

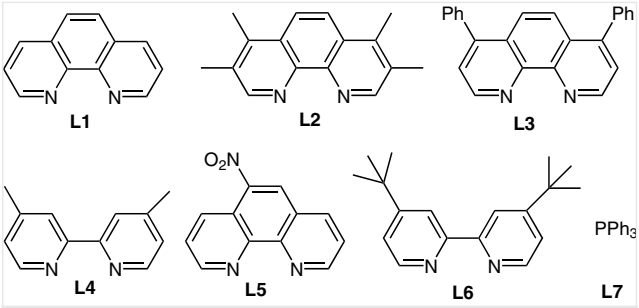
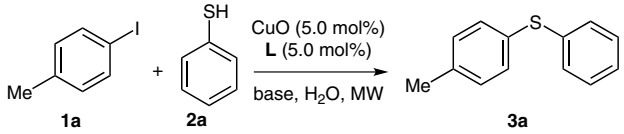


Figure 1 Structures of ligands **L1**–**L7**

Table 1 Optimization of the Reaction Conditions[a]

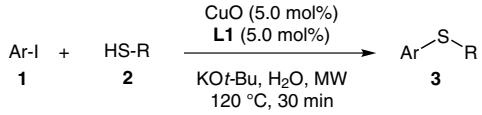


Entry	Ligand	Base	Temp (°C)	Time (min)	Yield[d] (%)
1	**L1**	Cs_2CO_3	120[b]	720	22
2	**L1**	Cs_2CO_3	120	30	90
3	**L2**	Cs_2CO_3	120	30	77
4	**L3**	Cs_2CO_3	120	30	88
5	**L4**	Cs_2CO_3	120	30	14
6	**L5**	Cs_2CO_3	120	30	66
7	**L6**	Cs_2CO_3	120	30	34
8	**L7**	Cs_2CO_3	120	30	22
9	**L1**	**KO*t*-Bu**	**120**	**30**	**99**
10	**L1**	KOH	120	30	63
11	**L1**	NaO*t*-Bu	120	30	57
12	**L1**	K_2CO_3	120	30	81
13	**L1**	NaOH	120	30	69
14	**L1**	Et_3N	120	30	78
15	**L1**	KO*t*-Bu	110	30	71
16	**L1**	KO*t*-Bu	120	10	69
17[c]	**L1**	KO*t*-Bu	120	30	trace

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), CuO (0.025 mmol, 5 mol%), ligand (0.025 mmol, 5 mol%), base (0.75 mmol), H_2O (0.5 mL).
[b] The reaction was performed in an oil bath.
[c] No catalyst was used.
[d] Isolated yield.

Having identified the optimal conditions, we studied the scope of this catalytic system with various substrates; the results are summarized in Table 2.[20] Aryl iodides **1** containing electron-donating groups (Table 2, entries 4, 7, and 13) or electron-withdrawing groups (entries 9, 11–12) coupled with aryl thiols **2** to give good yields of the corresponding sulfides **3**. Functional groups including chloro (entries 3, 6, and 7), bromo (entry 5), acetyl (entries 11 and 12), and amino (entry 10) were unaffected by the catalytic reaction. Alkyl thiols **2** (entries 13–21) also reacted smoothly with aryl iodides **1** to give the corresponding sulfides **3** in in good to excellent yields. However, 2-iodopyridine gave only a trace of the corresponding sulfide in its reaction with 4-methylbenzenethiol (entry 22).

Table 2 Microwave-Assisted Copper-Catalyzed Coupling Reaction of Thiols with Iodides[a]



Entry	Ar	R	Product	Yield[b] (%)
1	3-Tol	Ph	**3b**	87
2	2-Tol	Ph	**3c**	93
3	4-Tol	4-ClC_6H_4	**3d**	93
4	3-$MeOC_6H_4$	Ph	**3e**	81
5	4-BrC_6H_4	Ph	**3f**	91
6	4-ClC_6H_4	Ph	**3g**	84
7	4-$MeOC_6H_4$	4-ClC_6H_4	**3h**	88
8	4-Tol	4-$MeOC_6H_4$	**3i**	96
9	3-$O_2NC_6H_4$	Ph	**3j**	82
10	4-Tol	2-$H_2NC_6H_4$	**3k**	83
11	4-$MeCOC_6H_4$	Ph	**3l**	97
12	3-$MeCOC_6H_4$	Ph	**3m**	78
13	4-$MeOC_6H_4$	$(CH_2)_{11}Me$	**3n**	82
14	4-ClC_6H_4	$(CH_2)_{11}Me$	**3o**	83
15	4-Tol	Bn	**3p**	88
16	4-BrC_6H_4	$(CH_2)_{11}Me$	**3q**	88
17	4-Tol	$(CH_2)_{11}Me$	**3r**	72
18	Ph	Bn	**3s**	71
19	Ph	$(CH_2)_{11}Me$	**3t**	69
20	4-Tol	$CH_2CH(Me)Et$	**3u**	65
21	4-Tol	Cy	**3v**	64
22	2-pyridyl	4-Tol	**3w**	trace[c]

[a] Reaction conditions: **1** (0.6 mmol), **2** (0.5 mmol), CuO (0.025 mmol, 5 mol%), **L1** (0.025 mmol, 5 mol%), KO*t*-Bu (0.75 mmol), H_2O (0.5 mL).
[b] Isolated yield based on thiol.
[c] Detected by GC/MS.

We also carried out similar C–S coupling reactions of other aryl halides with benzenethiol by using the same catalytic system under similar reaction conditions. However, neither aryl chlorides nor aryl bromides were suitable substrates for C–S coupling with benzenethiol, as the thiol was converted into the corresponding disulfide in the reaction system.

In summary, we have developed an efficient microwave-assisted copper(II) oxide catalyzed cross-coupling reaction of thiols with aryl iodides in water that gives the cor-

responding sulfides in good to excellent yields within a short reaction time. Functional groups such as amino, chloro, bromo, and acetyl are all tolerated under the conditions employed. Applications of this catalytic system to other cross-coupling reactions are in progress in our laboratory.

All chemicals were purchased from commercial suppliers and were used without further purification. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh). NMR spectra were recorded on a Varian Mercury-400 instrument using $CDCl_3$ as the solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Melting points were determined by using a Büchi 535 apparatus and are uncorrected. The microwave-heated reactions were carried out on a CEM-Discover SP instrument (Model No. 908005; Serial No. DU9209).

Aryl Sulfides 3a–v; General Procedure

A 4-mL sealable vial equipped with a magnetic stirrer bar was charged with KO*t*-Bu (85.7 mg, 0.75 mmol), CuO (1.99 mg, 0.025 mmol), ligand **L1** (0.025 mmol), and the appropriate aryl iodide (0.6 mmol) under N_2. The vial was sealed with a cap containing a PTFE septum, and the thiol (0.5 mmol) and H_2O (0.5 mL) were added by syringe. The mixture was heated at 120 °C by microwave irradiation with stirring for 30 min, then cooled to r.t. and diluted with EtOAc (20 mL). The resulting solution was filtered through a pad of silica gel that was washed with EtOAc (20 mL). The organic phase was concentrated to give a crude material that was purified by column chromatography (silica gel, hexane).

Phenyl 4-Tolyl Sulfide (3a)[20a]

Prepared by following the general procedure from 4-iodotoluene (**1a**, 131.4 mg, 0.6 mmol) and thiophenol (**2a**, 0.0525 mL, 0.5 mmol) as a colorless oil; yield: 99.3 mg (99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 7.11–7.30 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.3, 129.0, 129.7, 130.0, 131.2, 132.2, 137.1, 137.5.

Phenyl 3-Tolyl Sulfide (3b)[20a]

Prepared by following the general procedure from 3-iodotoluene (0.078 ml, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a colorless oil; yield: 87.3 mg (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 7.03–7.33 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 126.8, 128.0, 128.3, 129.0, 129.1, 130.7, 131.8, 135.2, 136.0, 139.0.

Phenyl 2-Tolyl Sulfide (3c)[20a]

Prepared by following the general procedure from 2-iodotoluene (0.078 ml, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a colorless oil; yield: 92.9 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 7.11–7.29 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5, 126.3, 126.7, 127.9, 129.1, 129.6, 130.5, 132.9, 133.7, 136.1, 139.9.

4-Chlorophenyl 4-Tolyl Sulfide (3d)[20a]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and 4-chlorothiophenol (72.25 mg, 0.5 mmol) as a colorless oil; yield: 108.8 mg (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 7.12–7.29 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 129.1, 130.2, 130.6, 130.7, 132.2, 132.5, 135.9, 138.0.

4-Methoxyphenyl Phenyl Sulfide (3e)[20a]

Prepared by following the general procedure from 4-iodoanisole (143.3 mg, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a colorless oil; yield: 87.8 mg (81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3 H), 6.88 (dd, *J* = 6.4, 2.0 Hz, 2 H), 7.12–7.24 (m, 5 H), 7.41 (dd, *J* = 6.8, 2.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.9, 124.2, 125.7, 128.1, 128.9, 135.3, 138.6, 159.8.

4-Bromophenyl Phenyl Sulfide (3f)[20a]

Prepared by following the general procedure from 1-bromo-4-iodobenzene (173.3 mg, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a colorless oil; yield: 120.6 mg (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.18 (m, 2 H), 7.25–7.41 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.8, 127.5, 128.3, 131.5, 132.0, 132.2, 134.8, 135.4.

4-Chlorophenyl Phenyl Sulfide (3g)[20a]

Prepared by following the general procedure from 1-chloro4-iodobenzene (144.3 mg, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a colorless oil; yield: 92.1 mg (84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.34 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 127.4, 129.23, 129.27, 131.2, 131.9, 132.8, 134.6, 135.0.

4-Chlorophenyl 4-Methoxyphenyl Sulfide (3h)[19c]

Prepared by following the general procedure from 4-iodoanisole (143.3 mg, 0.6 mmol) and 4-chlorothiophenol (74.5 mg, 0.5 mmol) as a colorless oil; yield: 109.9 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 6.90 (dd, *J* = 6.8, 2.4 Hz, 2 H), 7.07 (dd, *J* = 6.8, 2.0 Hz, 2 H), 7.18 (dd, *J* = 6.8, 2.4 Hz, 2 H), 7.40 (dd, *J* = 6.8, 2.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 115.1, 123.6, 129.0, 129.2, 131.5, 135.5, 137.3, 160.0.

4-Methoxyphenyl 4-Tolyl Sulfide (3i)[14]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and 4-methoxythiophenol (0.0633 mL, 0.5 mmol) as a colorless oil; yield: 220.7 mg (96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 3.74 (s, 3 H), 6.83 (dd, *J* = 6.8, 2.0 Hz, 2 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 7.34 (dd, *J* = 6.8, 2.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 55.2, 114.7, 125.5, 129.2, 129.7, 134.2, 134.3, 135.9, 159.3.

3-Nitrophenyl Phenyl Sulfide (3j)[20c]

Prepared by following the general procedure from 1-iodo-3-nitrobenzene (150.9 mg, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a light-yellow liquid; yield: 102.4 mg (82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.43 (m, 4 H), 7.46–7.50 (m, 3 H), 7.98–8.03 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 120.8, 123.0, 128.9, 129.6, 129.8, 132.0, 133.4, 134.2, 140.5, 148.6.

2-(4-Tolylsulfanyl)aniline (3k)[20b]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and 2-aminothiophenol (0.0539 mL, 0.5 mmol) as a light-yellow oil; yield: 89.1 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 4.17 (br s, 2 H), 6.70–6.75 (m, 2 H), 6.99–7.04 (m, 4 H), 7.17–7.21 (m, 1 H), 7.43 (dd, *J* =8.0, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 115.1, 115.3, 118.6, 126.9, 129.7, 130.8, 132.9, 135.4, 137.0, 148.5.

1-[4-(Phenylsulfanyl)phenyl]ethanone (3l)[10a]

Prepared by following the general procedure from 1-(4-iodophenyl)ethanone (148.0 mg, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a white solid; yield: 111.1 mg (97%); mp 65–66 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.55 (s, 3 H), 7.21 (dd, *J* = 6.6, 1.8 Hz, 2 H), 7.39–7.41 (m, 3 H), 7.49–7.51 (m, 2 H), 7.82 (dd, *J* = 6.8, 2.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.5, 127.4, 128.8, 128.9, 129.7, 132.0, 133.9, 134.4, 144.9, 197.1.

1-[3-(Phenylsulfanyl)phenyl]ethanone (3m)[19e]

Prepared by following the general procedure from 1-(3-iodophenyl)ethanone (0.0863 mL, 0.6 mmol) and thiophenol (0.0525 mL, 0.5 mmol) as a yellow oil; yield: 89.0 mg (78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.54 (s, 3 H), 7.28–7.39 (m, 6 H), 7.43–7.46 (m, 1 H), 7.77–7.80 (m, 1 H), 7.89–7.90 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 126.5, 127.7, 129.3, 129.4, 129.8, 131.7, 134.2, 134.5, 137.4, 137.8, 197.4.

1-(Dodecylsulfanyl)-4-methoxybenzene (3n)[19e]

Prepared by following the general procedure from 4-iodoanisole (143.3 mg, 0.6 mmol) and 1-dodecanethiol (0.1225 mL, 0.5 mmol) as a colorless solid; yield: 126.4 mg (82%); mp 46–47 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.2 Hz, 3 H), 1.32–1.45 (m, 18 H), 1.61–1.66 (m, 2 H), 2.88 (t, *J* = 7.4 Hz, 2 H), 3.85 (s, 3 H), 6.88–6.92 (m, 2 H), 7.38–7.41 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.7, 29.2, 29.3, 29.3, 29.5, 29.6, 29.6, 31.9, 35.8, 55.2, 114.4, 126.9, 132.8, 158.6.

1-Chloro-4-(dodecylsulfanyl)benzene (3o)[20d]

Prepared by following the general procedure from 1-chloro-4-iodobenzene (144.3 mg, 0.6 mmol) and 1-dodecanethiol (0.120 mL, 0.5 mmol) as a colorless oil; yield: 129.0 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25–1.42 (m, 18 H), 1.58–1.65 (m, 2 H), 2.88 (t, *J* = 7.2 Hz, 2 H), 7.22–7.25 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.7, 29.0, 29.1, 29.3, 29.5, 29.6, 29.6, 31.9, 33.8, 128.9, 130.1, 131.5, 135.6.

Benzyl 4-Tolyl Sulfide (3p)[20e]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and phenylmethanethiol (0.062 mL, 0.5 mmol) as a colorless oil; yield: 94.6 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 3.97 (s, 2 H), 6.96 (d, *J* = 8.4 Hz, 2 H), 7.10–7.18 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 39.7, 127.0, 128.4, 128.8, 129.5, 130.6, 132.4, 136.5, 137.7.

1-Bromo-4-(dodecylsulfanyl)benzene (3q)[19c]

Prepared by following the general procedure from 1-bromo-4-iodobenzene (173.3 mg, 0.6 mmol) and 1-dodecanethiol (0.120 mL, 0.5 mmol) as a colorless oil; yield: 156.4 mg (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25–1.41 (m, 18 H), 1.58–1.64 (m, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.8, 28.9, 29.1, 29.3, 29.5, 29.5, 29.6, 29.6, 31.9, 33.6, 119.2, 130.2, 131.7, 136.3.

Dodecyl 4-Tolyl Sulfide (3r)[14]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and 1-dodecanethiol (0.1225 mL, 0.5 mmol) as a colorless oil; yield: 104.8 mg (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.25–1.30 (m, 16 H), 1.38–1.41 (m, 2 H), 1.57–1.63 (m, 2 H), 2.31 (s, 3 H), 2.86 (t, *J* = 7.4 Hz, 2 H), 7.08 (d, *J* = 7.6 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.0, 22.7, 28.8, 29.2, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 34.3, 129.6, 129.7, 133.1, 135.7.

Benzyl Phenyl Sulfide (3s)[10a]

Prepared by following the general procedure from iodobenzene (0.06863 ml, 0.6 mmol) and phenylmethanethiol (0.062 mL, 0.5 mmol) as a colorless oil; yield: 71.3 mg (71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.09 (s, 2 H), 7.13–7.30 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.9, 126.2, 127.1, 128.4, 128.7, 128.8, 129.6, 136.3, 137.3.

Dodecyl Phenyl Sulfide (3t)[10a]

Prepared by following the general procedure from iodobenzene (0.06863 ml, 0.6 mmol) and 1-dodecanethiol (0.120 mL, 0.5 mmol) as a colorless oil; yield: 95.7 mg (69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.25–1.43 (m, 18 H), 1.60–1.67 (m, 2 H), 2.90 (t, *J* = 7.2 Hz, 2 H), 7.13–7.16 (m, 1 H), 7.24–7.32 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.8, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 31.9, 33.5, 33.6, 125.5, 128.8, 137.1.

2-Methylbutyl 4-Tolyl Sulfide (3u)[19e]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and 2-methylbutane-1-thiol (0.0645 mL, 0.5 mmol) as a colorless oil; yield: 63.0 mg (65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 1.00 (d, *J* = 6.8 Hz, 3 H), 1.21–1.28 (m, 1 H), 1.49–1.65 (m, 2 H), 2.30 (s, 3 H), 2.70 (dd, *J* = 12.4, 7.6 Hz, 1 H), 2.90 (dd, *J* = 7.6, 12.4 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 18.8, 20.9, 28.7, 34.4, 41.4, 129.5, 129.5, 133.6, 135.6.

Cyclohexyl 4-Tolyl Sulfide (3v)[19e]

Prepared by following the general procedure from 4-iodotoluene (131.4 mg, 0.6 mmol) and cyclohexanethiol (0.0615 mL, 0.5 mmol) as a colorless oil; yield: 65.9 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22–1.39 (m, 5 H), 1.58–1.97 (m, 5 H), 2.32 (s, 3 H), 2.99–3.04 (m, 1 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 25.7, 26.0, 33.3, 47.0, 129.4, 131.2, 132.7, 136.8.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1379206. Included are ^{1}H and ^{13}C NMR spectra for compounds **3a**–**v**.

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