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Manganese-Catalyzed Cross-Coupling of Thiols with Aryl Iodides

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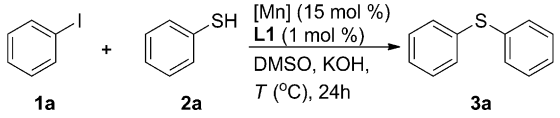
Abstract: A manganese-catalyzed cross-coupling reaction of thiols with aryl iodides, furnishing aryl thioethers in good to excellent yields has been reported; the system shows good functional group tolerance and enables the sterically demanding aryl iodides to couple with thiols.

Keywords: aryl iodide · cross-coupling · N ligands · manganese · thiol

Introduction

Aryl thioethers are important motifs found in biological compounds.[1] While many reliable methods have been achieved for preparing such molecules,[1–12] the palladium-catalyzed cross-coupling of thiols with aryl halides and pseudo halides is one of the most popular methods in this transformation.[3] Besides palladium, other catalytic systems using copper,[4] nickel,[5] cobalt,[6] indium,[7] gold,[8] rhodium,[9] iron,[10] and manganese[11] have also been reported for the same purpose. Unfortunately, most of the metals listed above are expensive and toxic; therefore, it is desirable to find an alternative metal for preparation of aryl thioethers. Economically and environmentally benign manganese salts are attractive because manganese is one of the most abundant metals in the world. Although manganese salts have been used for many transformations,[13,14] their use as a catalyst in cross-coupling reactions is relatively unexplored.[15] Recently, Yadavalli et al. reported the manganese-catalyzed cross-coupling reaction between thiols and aryl iodides by using a combination of $MnCl_2{\cdot}4H_2O$ with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), **L1** as the catalyst, and KOH as a base in dimethyl sulfoxide (DMSO) at 110 °C for 24 h (Table 1, entry 1).[11] Metal contaminants that trigger catalysis are a serious issue in recent transition metal catalysis,[16,17] and the presence of trace amounts of transition metals in the base may actually be responsible for the cross-coupling reaction.[18] In our hands, using high purity KOH, the product was obtained in poor yield when the reaction was carried out using Yadavalli's conditions (Table 1, entry 2). In addition, even when the reaction temperature was raised to 135 °C, the desired product was formed in only 29% yield (Table 1, entry 3). These results indicated that KOH might contain an impurity, which could promote the C–S coupling reaction. To clarify the nature of this C–S bond formation using manganese we combined $MnCl_2$ with 1,10-phenanthroline as a reactive catalytic system for the coupling of aryl iodides with thiols. Moreover, the purity of manganese salts has also been extensively examined.

Table 1. Influence of KOH for manganese-catalyzed cross-coupling of iodobenzene with thiophenol.[a]



1a 2a 3a

Entry	[Mn]	Source of KOH	*T* [°C]	Yield [%]
1	$MnCl_2{\cdot}4H_2O$	KOH	110	82[11]
2	$MnCl_2$ (99.99%)[b]	KOH (99.99%)	110	19
3	$MnCl_2$ (99.99%)[b]	KOH (99.99%)	135	29

[a] Reaction conditions: Mn source (0.15 mmol, 15 mol%), ligand (0.01 mmol, 1 mol%), iodobenzene (1.2 mmol), thiophenol (1.0 mmol), KOH (1.5 mmol) in DMSO (2.0 mL). [b] Copper, palladium, and nickel are not detected by inductively coupled plasma mass spectrometry (ICP-MS).

Results and Discussion

To determine the optimized reaction conditions, 4-iodotoluene and thiophenol were chosen as the model substrates. The results are summarized in Table 2. A series of ligands (Figure 1) were examined (Table 2, entries 1–9), and **L3**–**L5**, **L8**, and **L9** proved to be efficient ligands for this transformation in 1,4-dioxane. We then studied the solvent effect (Table 2, entries 10–18) for ligands **L3**–**L5**, **L8**, and **L9**. We found toluene to be the most suitable solvent for this reaction; the product was obtained in excellent yields when **L3** and **L4** were used as the ligands (Table 2, entries 10 and 11, respectively). Other solvents such as DMSO, *N,N*-dimethylformamide (DMF), and tetrahydrofuran (THF) did not provide good results. We also examined the source of base (Table 2, entries 19–23). We found that Cs_2CO_3 is superior to Na_2CO_3, KO*t*Bu, NaO*t*Bu, K_3PO_4, and K_2CO_3. Screening of the manganese source (Table 2, entries 24–28) indicated that $MnCl_2$ is still the best salt for the reaction. The product

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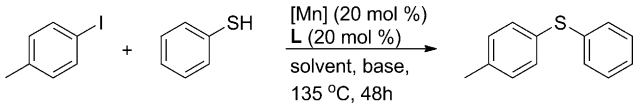
Table 2. Optimized reaction conditions.[a]



1b 2b 3b

Entry	[Mn]	Ligand	Base	Solvent	Yield [%]
1	$MnCl_2$	**L1**	Cs_2CO_3	1,4-dioxane	57
2	$MnCl_2$	**L2**	Cs_2CO_3	1,4-dioxane	62
3	$MnCl_2$	**L3**	Cs_2CO_3	1,4-dioxane	81
4	$MnCl_2$	**L4**	Cs_2CO_3	1,4-dioxane	99
5	$MnCl_2$	**L5**	Cs_2CO_3	1,4-dioxane	83
6	$MnCl_2$	**L6**	Cs_2CO_3	1,4-dioxane	78
7	$MnCl_2$	**L7**	Cs_2CO_3	1,4-dioxane	67
8	$MnCl_2$	**L8**	Cs_2CO_3	1,4-dioxane	89
9	$MnCl_2$	**L9**	Cs_2CO_3	1,4-dioxane	81
10	$MnCl_2$	**L3**	Cs_2CO_3	1,4-toluene	99
11	$MnCl_2$	**L4**	Cs_2CO_3	1,4-toluene	89
12	$MnCl_2$	**L5**	Cs_2CO_3	1,4-toluene	20
13	$MnCl_2$	**L8**	Cs_2CO_3	1,4-toluene	5
14	$MnCl_2$	**L9**	Cs_2CO_3	1,4-toluene	15
15	$MnCl_2$	**L3**	Cs_2CO_3	DMSO	65
16	$MnCl_2$	**L3**	Cs_2CO_3	DMF	40
17	$MnCl_2$	**L3**	Cs_2CO_3	NMP	22
18	$MnCl_2$	**L3**	Cs_2CO_3	THF	29
19	$MnCl_2$	**L3**	Na_2CO_3	toluene	75
20	$MnCl_2$	**L3**	KO*t*Bu	toluene	59
21	$MnCl_2$	**L3**	NaO*t*Bu	toluene	30
22	$MnCl_2$	**L3**	K_3PO_4	toluene	72
23	$MnCl_2$	**L3**	K_2CO_3	toluene	87
24	$MnBr_2$	**L3**	Cs_2CO_3	toluene	88
25	$Mn(OAc)_2{\cdot}4H_2O$	**L3**	Cs_2CO_3	toluene	76
26	MnO	**L3**	Cs_2CO_3	toluene	30
27	$MnSO_4{\cdot}H_2O$	**L3**	Cs_2CO_3	toluene	52
28	$MnCl_2{\cdot}4H_2O$	**L3**	Cs_2CO_3	toluene	90
29	$MnCl_2$	**L3**	Cs_2CO_3	toluene	35[b]
30	$MnCl_2$	**L3**	Cs_2CO_3	toluene	99[c]

[a] Reaction conditions: Mn source (0.2 mmol, 20 mol%), ligand (0.2 mmol, 20 mol%), 4-iodotoluene (1.2 mmol), thiophenol (1.0 mmol), base (1.5 mmol) in solvent (1.0 mL). [b] 1 equivalent of TEMPO was added. [c] Reaction was conducted on a larger scale with 10 mmol of thiophenol. NMP = *N*-methylpyrollidone.

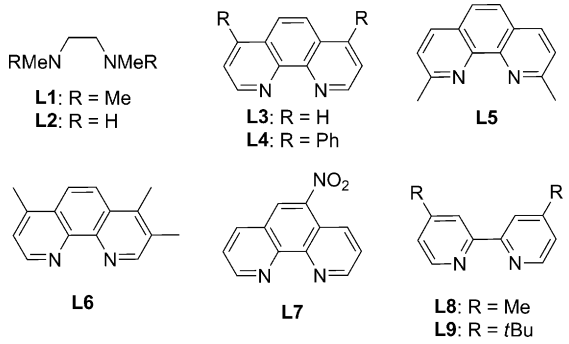
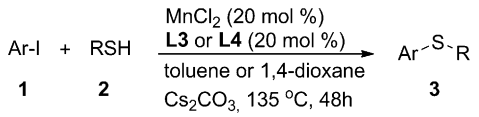


Figure 1. Structures of the ligands **L1**–**L9**.

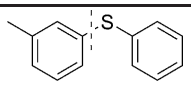
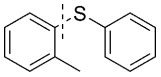
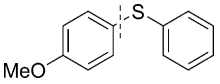
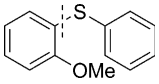
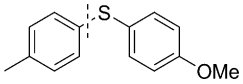
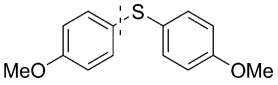
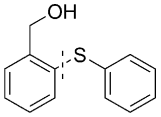
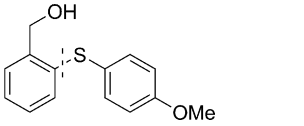
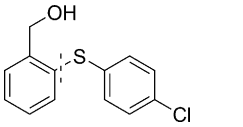
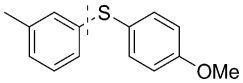
3b was obtained in only 35% yield when the reaction was carried out in the presence of 2,2,6,6-tetramethylpiperidine *N*-oxyl radical (TEMPO) (Table 2, entry 29). This result implies that the reaction might go through a radical mechanism. The reaction was also performed on larger scale by using 10 mmol of thiophenol; this furnished the product in 99% yield (Table 2, entry 30).

Based on the optimized reaction conditions, we then studied the scope of this catalytic system. The results are summarized in Table 3, a variety of aryl iodides coupled smoothly with aryl thiols, thus affording the corresponding diaryl thioethers in good to excellent yields. Meanwhile, the sterically demanding aryl iodides were also shown to be good coupling partners to provide **3d**, **3f**, **3i**–**3k** (Table 3, entries 2, 4, 7–9). Furthermore, functional groups such as unprotected alcohols (Table 3, entries 7–9) and chloro substituents (Table 3, entry 9) were both tolerated under the reaction conditions.

Table 3. Manganese-catalyzed S-arylation of aryl iodides with aryl thiols.[a]



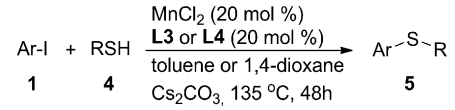
1 2 3

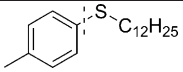
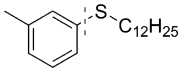
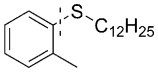
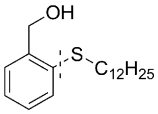
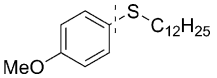
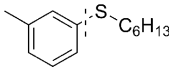
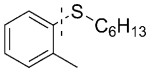
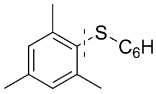
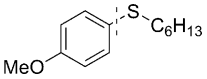
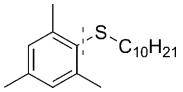
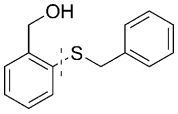
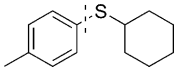
Entry	Product		Yield [%]
1		**3c**	99 98[b]
2		**3d**	91
3		**3e**	99
4		**3f**	80
5		**3g**	99 99[b]
6		**3h**	88
7		**3i**	99
8		**3j**	89
9		**3k**	76
10		**3l**	67[c]

[a] Reaction conditions unless otherwise stated: $MnCl_2$ (0.2 mmol, 20 mol%), **L3** (0.2 mmol, 20 mol%), aryl iodide (1.2 mmol), aryl thiol (1.0 mmol), Cs_2CO_3 (1.5 mmol) in toluene (1.0 mL). [b] Reaction was conducted on a larger scale with 10 mmol of thiol. [c] **L4** (0.2 mmol, 20 mol%) in 1,4-dioxane (1.0 mL).

We then studied the cross-coupling reaction of aryl iodides with a series of alkyl thiols. The results are listed in Table 4, alkyl thiols including 1-dodecanethiol (Table 4, en-

Table 4. Manganese-catalyzed S-arylation of aryl iodides with alkyl thiols.[a]



Entry	Product		Yield [%]
1		**5a**	81
2		**5b**	78[b]
3		**5c**	71
4		**5d**	82
5		**5e**	63
6		**5f**	84
7		**5g**	78
8		**5h**	60[b]
9		**5i**	64
10		**5j**	68[b]
11		**5k**	64
12		**5l**	63[b]

[a] Reaction conditions unless otherwise stated: $MnCl_2$ (0.2 mmol, 20 mol%), **L3** (0.2 mmol, 20 mol%), aryl iodide (1.2 mmol), alkyl thiol (1.0 mmol), Cs_2CO_3 (1.5 mmol) in toluene (1.0 mL). [b] **L4** (0.2 mmol, 20 mol%) in 1,4-dioxane (1.0 mL).

tries 1–5), 1-hexanethiol (Table 4, entries 6–9), 1-decanethiol (Table 4, entry 10), benzyl mercaptan (Table 4, entry 11), and cyclohexanethiol (Table 4, entry 12) are coupled with a wide spectrum of aryl iodides, thereby affording the aryl–alkyl thioethers in moderate to good yields. It is important to note that the aryl iodides that have sterically demanding substituents do not reduce the efficiency of the reactions (Table 4, entries 3, 4, 7, 8, 10, and 11).

Conclusions

In conclusion, we have reported the manganese-catalyzed cross-coupling reaction of thiols with aryl iodides. The purity of KOH and metal source has been extensively examined. Functional groups such as unprotected alcohols and chloro substituents are tolerated under the optimized reaction conditions. Moreover, this catalytic system enables the sterically demanding aryl iodides to couple with thiols. A detailed mechanistic study of this catalytic system and applications to other cross-coupling reactions are under progress in our laboratory.

Experimental Section

General information

All chemicals were purchased from commercial suppliers and used without further purification. Toluene was dried over sodium; 1,4-dioxane and DMF were dried over CaH_2 and stored in the presence of activated molecular sieves. All reactions were carried out under an inert atmosphere. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh).

Spectroscopic analysis

NMR spectra were recorded on a Varian Unity Inova-600 or 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. Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, br = broad. Melting points (m.p.) were determined using a Büchi 535 apparatus and are reported uncorrected. GC-MS analyses were performed on a GC-MS analysis on HP 5890 GC equipped with HP 5972 MS. High-resolution mass spectra were carried out on a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

General procedure for Table 1

A sealable vial equipped with a magnetic stirrer bar was charged with $MnCl_2$ (18.6 mg, 0.15 mmol), KOH (84 mg, 1.5 mmol), and TMEDA (1.5 μL, 0.01 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum. Under a nitrogen atmosphere, thiophenol (0.104 mL, 1.0 mmol), iodobenzene (0.138 mL, 1.2 mmol), and DMSO (2.0 mL) were added with a syringe. The septum was then replaced by a screw cap containing a PTFE septum, and the reaction vessel was heated at 110 °C and then at 135 °C in an oil bath. After stirring at this temperature for 24 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was filtered through a pad of Celite then washed with ethyl acetate (20 mL) and concentrated under reduced pressure to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to yield the product **3a**.

*Diphenyl sulfide **3a** (Table 1, entry 3)*[3c]

3a was afforded by following the general procedure from Table 1. The product was then purified by column chromatography (SiO_2, hexane) to provide **3a** as a colorless oil (54 mg, 29%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.21$–7.36 ppm (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 127.0$, 129.2, 131.0, 135.7 ppm.

General procedure for Table 2

A sealable vial equipped with a magnetic stirrer bar was charged with $MnCl_2$ (24.8 mg, 0.20 mmol), base (1.5 mmol), and ligand (0.20 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum. Under a nitrogen atmosphere, thiophenol (0.104 mL, 1.0 mmol), 4-iodotoluene (262 mg, 1.2 mmol), and the solvent (1.0 mL) were added with a syringe. The septum was then replaced by a screw cap containing a PTFE septum, and the reaction vessel was heated at 135 °C in an oil bath. After stirring at this temperature for 48 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was filtered through

a pad of Celite then washed with ethyl acetate (20 mL) and concentrated under reduced pressure to give the crude material, which was then purified by column chromatography (SiO_2, hexane) to yield **3b**.

*4-Methylphenyl phenyl sulfide **3b** (Table 2, entry 10)[3c]*

Following the general procedure for Table 2, using Cs_2CO_3 (488 mg, 1.5 mmol), **L3** (36.0 mg, 0.2 mmol), and toluene (1.0 mL) afforded **3b** as a colorless oil (198 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 7.09–7.18 (m, 3H), 7.20–7.29 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.3, 129.0, 129.6, 130.0, 131.2, 132.2, 137.1, 137.5 ppm.

General procedure for Table 3

A sealable vial equipped with a magnetic stirrer bar was charged with $MnCl_2$ (24.8 mg, 0.2 mmol), Cs_2CO_3 (488 mg, 1.5 mmol), **L3** (36.0 mg, 0.2 mmol) or **L4** (67.2 mg, 0.2 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum, aryl iodide (1.20 mmol), toluene (1.0 mL) or 1,4-dioxane (1.0 mL) were added with a syringe. The arylthiol (1.0 mmol) was then added by syringe, and the vial was sealed with a cap containing a PTFE septum and the reaction vessel was heated at 135 °C in an oil bath. After stirring at this temperature for 48 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of Celite then washed with ethyl acetate (20 mL) and concentrated under vacuum to give the crude material, which was then purified by column chromatography (SiO_2, hexane or hexane/EtOAc 9:1) to yield **3**.

*3-Methylphenyl phenyl sulfide **3c** (Table 3, entry 1)[3c]*

Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **3c** as a colorless oil (198 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 7.04–7.33 ppm (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 126.8, 128.0, 128.3, 129.0, 129.1, 130.7, 131.8, 135.2, 136.0, 139.0 ppm.

*2-Methylphenyl phenyl sulfide **3d** (Table 3, entry 2)[3c]*

Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 2-iodotoluene (0.156 mL, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **3d** as a colorless oil (182 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 7.10–7.29 ppm (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 126.3, 126.7, 127.9, 129.1, 129.6, 130.5, 132.9, 133.7, 136.1, 139.9 ppm.

*4-Methoxyphenyl phenyl sulfide **3e** (Table 3, entry 3)[3c]*

Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **3e** as a colorless oil (214 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3H), 6.85 (dd, J = 2.4, 6.8 Hz, 2H), 7.07–7.21 (m, 5H), 7.39 ppm (dd, J = 2.0, 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 114.9, 124.1, 125.6, 128.0, 128.8, 135.2, 138.5, 159.7 ppm.

*2-Methoxyphenyl phenyl sulfide **3f** (Table 3, entry 4)[3c]*

Following the general procedure for Table 3, using thiophenol (0.104 mL, 1.0 mmol), 2-iodoanisole (0.156 mL, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **3f** as a colorless oil (173 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.83–6.90 (m, 2H), 7.08 (dd, J = 1.4, 7.8 Hz, 1H), 7.19–7.40 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 110.8, 121.2, 124.0, 127.0, 128.3, 129.1, 131.4, 131.5, 134.4, 157.2 ppm.

*4-Methylphenyl 4-methoxyphenyl sulfide **3g** (Table 3, entry 5)[3c]*

Following the general procedure for Table 3, using 4-methoxythiophenol (0.126 mL, 1.0 mmol), 4-iodotoluene (262 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **3g** as a colorless oil (228 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 3.74 (s, 3H), 6.83 (dd, J = 2.0, 6.8 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.34 ppm (dd, J = 2.4, 6.8 Hz, 2H); ^{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 ppm.

*Di-4-methoxyphenyl sulfide **3h** (Table 3, entry 6)[3c]*

Following the general procedure for Table 3, using 4-iodoanisole (287 mg, 1.2 mmol), 4-methoxythiophenol (0.126 mL, 1.0 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane/EtOAc 9:1) to provide **3h** as a white solid (217 mg, 88% yield). M.p.: 45–46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 6H), 6.80 (d, J = 6.8 Hz, 4H), 7.26 ppm (d, J = 6.8 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.7, 127.4, 132.7, 158.9 ppm.

*(2-(Phenylthio)phenyl)methanol **3i** (Table 3, entry 7)[4d]*

Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), thiophenol (0.104 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane/EtOAc 9:1) to provide **3i** as a colorless oil (214 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.31 (brs, 1H), 4.74 (s, 2H), 7.16–7.19 (m, 3H), 7.21–7.4 (m, 3H), 7.25–7.36 (m, 2H), 7.48 ppm (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.3, 126.5, 128.4, 128.4, 129.1, 129.4, 132.3, 133.9, 135.9, 142.3 ppm.

*(2-(4-Methoxyphenylthio)phenyl)methanol **3j** (Table 2, entry 8)[4g]*

Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), 4-methoxythiophenol (0.126 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 9:1) to provide **3j** as a colorless oil (219 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.48 (brs, 1H), 3.78 (s, 3H), 4.76 (s, 2H), 6.86 (dt, J = 4.0, 9.2 Hz, 2H), 7.09 (dd, J = 1.4, 8.0 Hz, 1H), 7.13–7.24 (m, 2H), 7.29 (dt, J = 4.0, 8.0 Hz, 2H), 7.41 ppm (dd, J = 1.2, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 63.3, 115.0, 124.3, 126.8, 128.1, 128.2, 130.4, 134.1, 135.6, 139.8, 159.5 ppm.

*(2-(4-Chlorophenylthio)phenyl)methanol **3k** (Table 3, entry 9)[19]*

Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), 4-chlorothiophenol (145 mg, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc 9:1) to provide **3k** as a colorless oil (190 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.79 (brs, 1H), 4.70 (s, 2H), 7.07 (dd, J = 4.0, 8.0 Hz, 2H), 7.17–7.25 (m, 3H), 7.30–7.33 (m, 2H), 7.48 ppm (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.1, 128.3, 128.4, 128.6, 129.2, 130.5, 131.7, 132.4, 133.8, 134.6, 132.3 ppm.

*3-Methylphenyl 4-methoxyphenyl sulfide **3l** (Table 3, entry 10)[3c]*

Following the general procedure for Table 3, using Cs_2CO_3 (812 mg, 2.5 mmol), 4-methoxythiophenol (0.126 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), and **L4** (67.2 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL). The crude product was purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (154 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.75 (s, 3H), 6.85 (dd, J = 2.0, 6.8 Hz, 2H), 6.90–6.97 (m, 2H), 7.01 (s, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.38 ppm (dd, J = 2.0, 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 55.2, 114.8, 124.4, 125.4, 126.6, 128.7, 128.8, 135.0, 138.1, 138.6, 159.6 ppm.

General procedure for Table 4

A sealable vial equipped with a magnetic stirrer bar was charged with $MnCl_2$ (24.8 mg, 0.2 mmol), Cs_2CO_3 (488 mg, 1.5 mmol), and **L3** (36.0 mg, 0.2 mmol) or **L4** (67.2 mg, 0.2 mmol) under a nitrogen atmosphere. The aperture of the vial was then covered with a rubber septum, aryl iodide (1.20 mmol), toluene (1.0 mL) or 1,4-dioxane (1.0 mL) were added by sy-

ringe. The alkyl thiol (1.0 mmol) was then added by syringe, and the vial sealed with a cap containing a PTFE septum and the reaction vessel was heated at 135 °C in an oil bath. After stirring at this temperature for 48 h, the heterogeneous mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of Celite then washed with ethyl acetate (20 mL) and concentrated under reduced pressure to give the crude material, which was then purified by column chromatography (SiO_2, hexane or hexane/EtOAc 9:1) to yield **5**.

*Dodecyl 4-methylphenyl sulfide **5a** (Table 4, entry 1)*[4a]

Following the general procedure for Table 4, using 1-dodecanethiol (0.240 mL, 1.0 mmol), 4-iodotoluene (261 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was purified by column chromatography (SiO_2, hexane) to provide **5a** as a colorless oil (237 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3H), 1.25–1.31 (m, 16H), 1.37–1.40 (m, 2H), 1.56–1.62 (m, 2H), 2.28 (s, 3H), 2.84 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.22 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.9, 22.6, 28.8, 29.1, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 34.2, 129.5, 129.6, 133.2, 135.5 ppm.

*Dodecyl 3-methylphenyl sulfide **5b** (Table 4, entry 2)*

Following the general procedure for Table 4, using 1-dodecanethiol (0.240 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), and **L4** (67.2 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL). The crude product was then purified by column chromatography (SiO_2, hexane) to provide **3l** as a colorless oil (228 mg, 78% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3H), 1.25–1.30 (m, 16H), 1.37–1.43 (m, 2H), 1.59–1.68 (m, 2H), 2.32 (s, 3H), 2.90 (t, J = 7.4 Hz, 2H), 6.96 (d, J = 6.8 Hz, 1H), 7.10–7.25 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 21.3, 22.7, 28.8, 29.1, 29.1, 29.3, 29.5, 29.6, 29.6, 31.9, 33.5, 125.7, 126.4, 128.6, 129.4, 136.7, 138.5 ppm. HREI-MS calcd. for $C_{19}H_{32}S$: 292.2225, found: 292.2228.

*Dodecyl 2-methylphenyl sulfide **5c** (Table 4, entry 3)*[20]

Following the general procedure for Table 4, using 1-dodecanethiol (0.240 mL, 1.0 mmol), 2-iodotoluene (0.156 mL, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5c** as a colorless oil (207 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.8 Hz, 3H), 1.29–1.33 (m, 16H), 1.43–1.47 (m, 2H), 1.64–1.72 (m, 2H), 2.38 (s, 3H), 2.89 (t, J = 7.4 Hz, 2H), 7.05–7.09 (m, 1H), 7.13–7.17 (m, 2H), 7.24–7.27 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 20.2, 22.7, 29.0, 29.2, 29.3, 29.5, 29.6, 29.6, 29.7, 31.9, 32.7, 32.8, 125.1, 126.2, 127.2, 129.9, 136.4, 137.1 ppm.

*(2-(Dodecylthio)phenyl)methanol **5d** (Table 4, entry 4)*[4d]

Following the general procedure for Table 4, using Cs_2CO_3 (812 mg, 2.5 mmol), 1-dodecanethiol (0.240 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane/EtOAc 9:1) to provide **5d** as a white solid (205 mg, 82% yield): M.p.: 38–39 °C (lit.[4d] 38–39 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3H), 1.25–1.31 (m, 16H), 1.38 (m, 2H), 1.60–1.68 (m, 2H), 2.37 (br s, 1H), 2.91 (t, J = 7.4 Hz, 2H), 4.76 (d, J = 6.0 Hz, 2H), 7.18–7.28 (m, 2H), 7.34–7.38 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 28.8, 29.1, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 33.9, 63.6, 126.1, 128.1, 128.1, 129.2, 135.1, 140.3 ppm.

*Dodecyl 4-methoxyphenyl sulfide **5e** (Table 4, entry 5)*[4a]

Following the general procedure for Table 4, using 1-dodecanethiol (0.240 mL, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5e** as a colorless solid (194 mg, 63% yield): M.p.: 44–45 °C (lit.[4a] 44–45 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3H), 1.30–1.39 (m, 18H), 1.53–1.62 (m, 2H), 2.80 (t, J = 7.4 Hz, 2H), 3.78 (s, 3H), 6.81–6.84 (m, 2H), 7.31–7.34 ppm (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 22.7, 28.7, 29.2, 29.3, 29.5, 29.6, 29.6, 29.6, 31.9, 35.8, 55.2, 114.4, 126.9, 132.8, 158.6 ppm.

*Hexyl 3-methylphenyl sulfide **5f** (Table 4, entry 6)*

Following the general procedure for Table 4, 1-hexanethiol (0.141 mL, 1.0 mmol), 3-iodotoluene (0.156 mL, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5f** as a colorless oil (175 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.89 (m, 3H), 1.27–1.33 (m, 4H), 1.37–1.44 (m, 2H), 1.58–1.66 (m, 2H), 2.29 (s, 3H), 2.86–2.91 (m, 2H), 6.92–6.95 (m, 1H), 7.08–7.16 ppm (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 21.2, 22.5, 28.5, 29.0, 31.3, 33.4, 125.6, 126.4, 128.5, 129.3, 136.7, 138.4 ppm. HREI-MS calcd. for $C_{13}H_{20}S$: 208.1285, found: 208.1279.

*Hexyl 2-methylphenyl sulfide **5g** (Table 4, entry 7)*

Following the general procedure for Table 4, using 1-hexanethiol (0.141 mL, 1.0 mmol), 2-iodotoluene (0.156 mL, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene. The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5g** as a colorless oil (162 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85–0.90 (m, 3H), 1.26–1.32 (m, 4H), 1.39–1.46 (m, 2H), 1.61–1.69 (m, 2H), 2.33 (s, 3H), 2.82–2.89 (m, 2H), 7.02–7.06 (m, 1H), 7.11–7.14 (m, 2H), 7.18–7.23 ppm (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 20.2, 22.5, 28.6, 28.9, 31.4, 32.6, 125.1, 126.2, 127.0, 129.9, 136.4, 136.9 ppm. HREI-MS calcd. for $C_{13}H_{20}S$: 208.1285, found: 208.1278.

*Hexyl 2,4,6-trimethylphenyl sulfide **5h** (Table 4, entry 8)*

Following the general procedure for Table 4, using 1-hexanethiol (0.141 mL, 1.0 mmol), 2-iodo-1,3,5-trimethylbenzene (295 mg, 1.2 mmol), and **L4** (67.2 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL). The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5h** as a colorless oil (142 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, J = 6.8 Hz, 3H), 1.28–1.44 (m, 6H), 1.53–1.59 (m, 2H), 2.30 (s, 3H), 2.55 (s, 6H), 2.65 (t, J = 7.4 Hz, 2H), 6.96 ppm (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.0, 20.9, 21.9, 22.5, 28.6, 29.9, 31.5, 35.6, 128.8, 130.6, 137.7, 142.8 ppm. HREI-MS calcd. for $C_{15}H_{24}S$: 236.1598, found: 236.1605.

*Decyl 2,4,6-trimethylphenyl sulfide **5i** (Table 4, entry 9)*

Following the general procedure for Table 4, using 1-decanethiol (0.220 mL, 1.0 mmol), 2-iodo-1,3,5-trimethylbenzene (295 mg, 1.2 mmol), and **L4** (67.2 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL). The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5i** as a colorless oil (199 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, J = 6.8 Hz, 3H), 1.30–1.43 (m, 14H), 1.53–1.60 (m, 2H), 2.31 (s, 3H), 2.55 (s, 6H), 2.65 (t, J = 7.4 Hz, 2H), 6.70 ppm (s, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.1, 20.9, 21.9, 22.7, 29.0, 29.1, 29.2, 29.3, 29.5, 29.9, 31.9, 35.5, 128.8, 130.6, 137.7, 142.8 ppm. HREI-MS calcd. for $C_{19}H_{32}S$: 292.2224, found: 292.2216.

*Hexyl 4-methoxyphenyl sulfide **5j** (Table 4, entry 10)*[21]

Following the general procedure for Table 4, using 1-hexanethiol (0.141 mL, 1.0 mmol), 4-iodoanisole (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene (1.0 mL). The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5j** as a colorless oil (144 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.4 Hz, 3 H), 1.22–1.34 (m, 4H), 1.36–1.41 (m, 2H), 1.52–1.60 (m, 2H), 2.78–2.82 (m, 2H), 3.77 (s, 3H), 6.81–6.84 (m, 2H), 7.30–7.34 ppm (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.9, 22.5, 28.3, 29.2, 31.3, 35.7, 55.2, 114.4, 126.9, 132.8, 158.6 ppm.

*(2-(Benzylthio)phenyl)methanol **5k** (Table 4, entry 11)*[22]

Following the general procedure for Table 4, using Cs_2CO_3 (812 mg, 2.5 mmol), benzyl mercaptan (0.118 mL, 1.0 mmol), 2-iodobenzyl alcohol (281 mg, 1.2 mmol), and **L3** (36.0 mg, 0.2 mmol) in toluene (1.0 mL). The product was then purified by column chromatography (SiO_2, hexane/EtOAc 9:1) to provide **5k** as a colorless oil (147 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.24$ (br s, 1H), 4.03 (s, 2H), 4.59 (s, 2H), 7.16–7.24 (m, 7H), 7.32–7.38 ppm (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 39.6$, 63.3, 127.2, 127.2, 128.2, 128.2, 128.4, 128.7, 131.5, 133.9, 137.2, 141.6 ppm.

Cyclohexyl 4-methylphenyl sulfide ***5l*** *(Table 4, entry 12)*[3c]

Following the general procedure for Table 4, using cyclohexyl mercaptan (0.126 mL, 1.0 mmol), 4-iodotoluene (261 mg, 1.2 mmol), and **L4** (67.2 mg, 0.2 mmol) in 1,4-dioxane (1.0 mL). The crude product was then purified by column chromatography (SiO_2, hexane) to provide **5l** as a colorless oil (130 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.20$–1.40 (m, 5H), 1.57–1.61 (m, 1H), 1.73–1.77 (m, 2H), 1.94–1.99 (m, 2H), 2.32 (s, 3H), 2.98–3.04 (m, 1H), 7.09 (d, $J = 7.6$ Hz, 2H), 7.31 ppm (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 21.0$, 25.7, 26.0, 33.3, 47.0, 129.4, 131.1, 132.7, 136.8 ppm.

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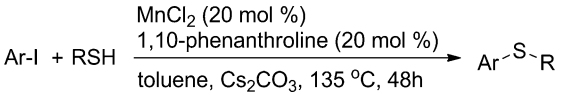

Coming up for ArI: A manganese-catalyzed cross-coupling reaction of thiols with aryl iodides that furnishes aryl thioethers in good to excellent yields has been reported. Functional groups such as unprotected alcohols and chloro substituents are tolerated under these reaction conditions. Moreover, this catalytic system enables the sterically demanding aryl iodides to couple with thiols (see scheme; R = aryl or alkyl).

Cross-Coupling Reactions

*Tsung-Jui Liu, Chih-Lun Yi, Chien-Ching Chan, Chin-Fa Lee** ____ ▮▮▮▮–▮▮▮▮

Manganese-Catalyzed Cross-Coupling of Thiols with Aryl Iodides