# Copper-Catalyzed Selective Single Arylsulfanylation of Aryl Diiodides with Aryl Thiols

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**Abstract:** Selective single arylsulfanylation reactions of aryl diiodides with aryl or hetaryl thiols to give a broad array of iodine-functionalized sulfides were developed. Further elaboration of the iodine-containing products to provide a variety of aryl and hetaryl sulfides through coupling reactions was also demonstrated.

**Key words:** copper, cross-coupling, iodides, sulfides, catalysis

The copper-catalyzed Ullmann coupling reaction, which includes carbon–carbon and carbon–heteroatom coupling reactions, is now regarded as the basic and most powerful tool for constructing $sp^2$ C–C, C–N, C–O, and C–S bonds in organic synthesis.[1] As a result of the revolutionary discovery of ligand-assisted Ullmann reactions, researches on these reactions have achieved breathtaking progress, and in the last two decades the reactions have permeated almost to every corner of synthetic organic chemistry,[2] including syntheses of natural products,[3] biologically active organic compounds,[3] structurally diverse small heterocyclic molecules,[4] polymers, and many industrial chemical intermediates. In documented versions of the Ullmann coupling reaction, C–S coupling of S-nucleophiles, such as thiophenols or thiols, to aryl or vinyl halides is the major strategy for the synthesis of aryl and vinyl thioethers[5] and, by further tandem reactions, for the synthesis of various sulfur-containing heterocycles.[6] During the last decade, considerable efforts have been made to develop improved protocols for C–S coupling reactions to provide easier access to these sulfur-containing products. The main tactics involve identifying alternative metal catalysts,[7] the development of new ligands,[8] the use of cleaner reaction media[9] or transition-metal-free catalytic systems,[10] and the application of new sources of sulfur.[11] In most reported catalytic C–S coupling reactions of diiodobenzenes, the corresponding double-thiolated sulfides are the major or sole products.[7d,12] Mao and co-workers have systematically investigated the selective double C–S coupling reactions of diiodobenzenes with phenols and thiophenols in the presence of iron and copper cocatalysts.[13] Interestingly, however, there are few examples of selective single C–S coupling reactions of diiodobenzenes with S-nucleophiles. A known route to iodine-functionalized sulfides relies on the addition reaction of arylmagnesium compounds with arynes.[14]

In the context of the versatile reactivity of the iodoaryl backbone for the synthesis of various elaborated aryl products, a straightforward approach to selective single C–S coupling reactions of diiodoaryls would be highly desirable, as this would provide iodoaryl sulfides, useful as precursors of more-complex sulfur-containing products. As a continuation of our longstanding research efforts in copper-catalyzed coupling chemistry,[4,8b,15] we wish to report a simple and efficient method for the synthesis of iodoaryl-functionalized sulfides through copper-catalyzed selective single Ullmann C–S coupling reactions of thiophenols with diiodoaryl compounds.

We focused initially on the model reaction of 1,2-diiodobenzene (**1a**) with benzenethiol (**2a**). On the basis of our previous experiences with enaminone ligand-assisted coupling reactions, we first performed the reaction by using the enaminone ligand **L1** in the presence of copper(I) iodide in dimethyl sulfoxide at 100 °C for 12 hours, and we obtained the monothiolated product **3a** as the major product together with the dithiolated product **4a** in a 62:11 ratio (Table 1, entry 1). The selectivity of this reaction encouraged us to attempt to optimize the reaction conditions for greater selectivity. First, we screened various enaminone ligands **L1**–**4** and the classical ligand 1,10-phenanthroline (**L5**), but we found no improvement (entries 2–5). Furthermore, changing the copper species to copper(II) acetate, copper(I) bromide, copper(II) bromide, or copper(II) oxide also failed to give better results (entries 6–9). Changing the reaction medium and the base additive also failed to enhance the yield or the selectivity of the reaction (entries 10–15). Lowering the reaction temperature led to poor conversion (entry 16), whereas higher temperatures resulted in much lower selectivity (entry 17). However, prolonging the reaction time to 18 hours proved to be effective in providing product **3a** in better yield and greater selectivity (entry 18), although increasing the reaction time further to 21 hours produced no additional improvement (entry 19).

Having identified conditions that permitted highly selective single thiolation of 1,2-diiodobenzene, we went on to examine the reactions of 1,2-, 1,3-, and 1,4-diiodobenzene (**1a**–**c**, respectively) with various thiophenols **2** to demonstrate the general applicability of our approach (Scheme 1).

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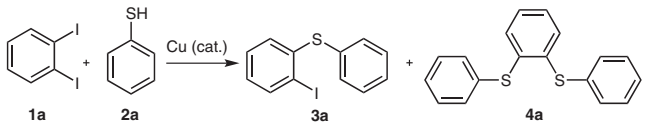
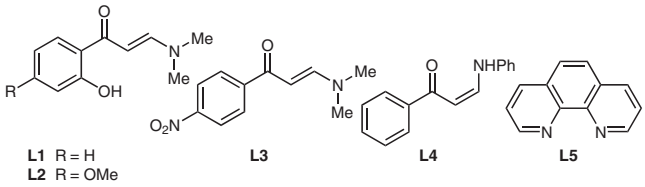
**Table 1** Optimization of Conditions for a Selective Single C–S Coupling Reaction of 1,2-Diiodobenzene



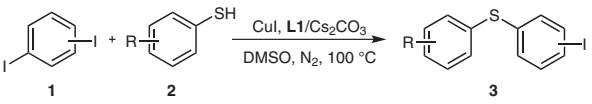

| Entry[a] | Ligand | Copper catalyst | Base | Solvent | Yields of **3a** and **4a** (%)[b] |
|---|---|---|---|---|---|
| 1 | **L1** | CuI | $Cs_2CO_3$ | DMSO | 62:11 |
| 2 | **L2** | CuI | $Cs_2CO_3$ | DMSO | 43:13 |
| 3 | **L3** | CuI | $Cs_2CO_3$ | DMSO | 32:16 |
| 4 | **L4** | CuI | $Cs_2CO_3$ | DMSO | 50:12 |
| 5 | **L5** | CuI | $Cs_2CO_3$ | DMSO | 32:17 |
| 6 | **L1** | $Cu(OAc)_2$ | $Cs_2CO_3$ | DMSO | 35:16 |
| 7 | **L1** | CuBr | $Cs_2CO_3$ | DMSO | 48:12 |
| 8 | **L1** | $CuBr_2$ | $Cs_2CO_3$ | DMSO | 38:13 |
| 9 | **L1** | CuO | $Cs_2CO_3$ | DMSO | 33:19 |
| 10 | **L1** | CuI | $Cs_2CO_3$ | DMF | 17:7 |
| 11 | **L1** | CuI | $Cs_2CO_3$ | 1,4-dioxane | 32:19 |
| 12 | **L1** | CuI | $Cs_2CO_3$ | toluene | 50:26 |
| 13 | **L1** | CuI | *t*-BuOK | DMSO | 43:19 |
| 14 | **L1** | CuI | $Et_3N$ | DMSO | 48:11 |
| 15 | **L1** | CuI | $Na_2CO_3$ | DMSO | 37:17 |
| 16[c] | **L1** | CuI | $Cs_2CO_3$ | DMSO | 48:23 |
| 17[d] | **L1** | CuI | $Cs_2CO_3$ | DMSO | 18:6 |
| 18[e] | **L1** | CuI | $Cs_2CO_3$ | DMSO | 79:7 |
| 19[f] | **L1** | CuI | $Cs_2CO_3$ | DMSO | 76:9 |




[a] *General conditions*: **1a** (0.2 mmol), **2a** (0.3 mmol), Cu catalyst (0.04 mmol), ligand (0.04 mmol), base (0.4 mmol), DMSO (1 mL), 100 °C, 12 h, under $N_2$.
[b] Yield of isolated product, based on **1a**.
[c] At 110 °C.
[d] At 90 °C.
[d] Reaction time 18 h
[e] Reaction time 21 h.

To our delight, the expected reaction occurred with all three diiodobenzenes, and some typical results are listed in Table 2. In general, thiophenols containing various functional groups, such as alkyl, halo, or amino groups, and hetaryl thiols such as 1,3-benzothiazole-2-thiol reacted with diiodobenzenes to give the corresponding monothiolated iodobenzenes with good to excellent selectivities and yields. Although dithiolated byproducts of type **4** were also obtained, their yields were not calculated as they were found in rather small amounts and, in most cases, were difficult to isolate by thin-layer chromatography or column chromatography. Particularly good results were obtained with 1,3-benzothiazole-2-thiol (entries 10 and 18). Arylation of alkylbenzenethiols gave the corresponding sulfides in slightly higher yields than those obtained from halobenzenethiols. However, no significant differences in product yields was observed among the various benzenethiols, probably as a result of the formation of byproducts. All products were characterized by a range of spectroscopic techniques and the structures of products **3a** and **3d** were confirmed by single-crystal X-ray crystallographic analysis (Figure 1).[16]

**Table 2** Synthesis of Iodophenyl Thioethers by Selective C–S Coupling of Aryl Diiodides




| Entry[a] | Diiodobenzene | Thiol | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 1,2-$I_2C_6H_4$ (**1a**) | PhSH | **3a** | 79 |
| 2 | **1a** | 4-TolSH | **3b** | 83 |
| 3 | **1a** | 4-*i*-Pr$C_6H_4$SH | **3c** | 81 |
| 4 | **1a** | 4-F$C_6H_4$SH | **3d** | 69 |
| 5 | **1a** | 4-Cl$C_6H_4$SH | **3e** | 81 |
| 6 | **1a** | 4-Br$C_6H_4$SH | **3f** | 76 |
| 7 | **1a** | 3-TolSH | **3g** | 80 |
| 8 | **1a** | 2-$H_2NC_6H_4$SH | **3h** | 74 |
| 9 | **1a** | naphthalene-2-thiol | **3i** | 81 |
| 10 | **1a** | 1,3-benzothiazole-2-thiol | **3j** | 93 |
| 11 | 1,3-$I_2C_6H_4$ (**1b**) | PhSH | **3k** | 80 |
| 12 | **1b** | 4-TolSH | **3l** | 86 |
| 13 | **1b** | 4-*i*-Pr$C_6H_4$SH | **3m** | 85 |
| 14 | **1b** | 4-F$C_6H_4$SH | **3n** | 71 |
| 15 | **1b** | 4-Br$C_6H_4$SH | **3o** | 78 |
| 16 | **1b** | 3-TolSH | **3p** | 83 |
| 17 | **1b** | naphthalene-2-thiol | **3q** | 72 |
| 18 | **1b** | 1,3-benzothiazole-2-thiol | **3r** | 90 |
| 20 | 1,4-$I_2C_6H_4$ (**1c**) | PhSH | **3s** | 86 |
| 21 | **1c** | 4-TolSH | **3t** | 85 |
| 22 | **1c** | 4-Cl$C_6H_4$SH | **3u** | 83 |

[a] *General conditions*: **1** (0.2 mmol), **2** (0.3 mmol), CuI (0.04 mmol), **L1** (0.04 mmol), $Cs_2CO_3$ (0.4 mmol), DMSO (1 mL), 100 °C, 18 h, under $N_2$.
[b] Yield of isolated product, based on **1**.

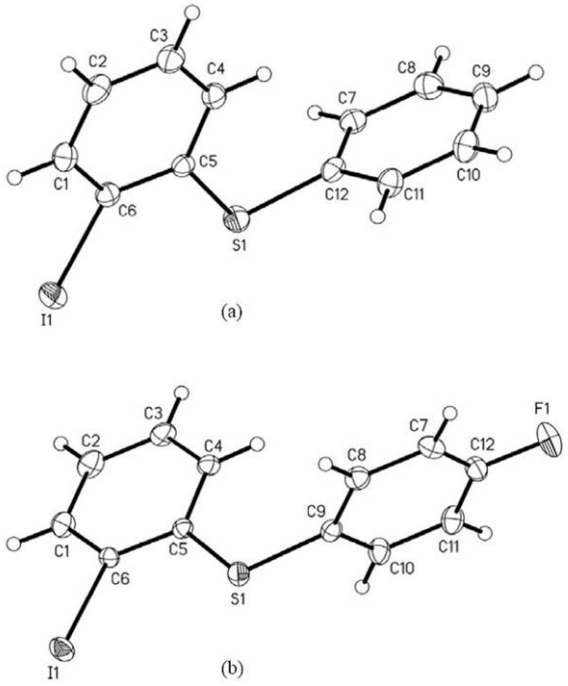
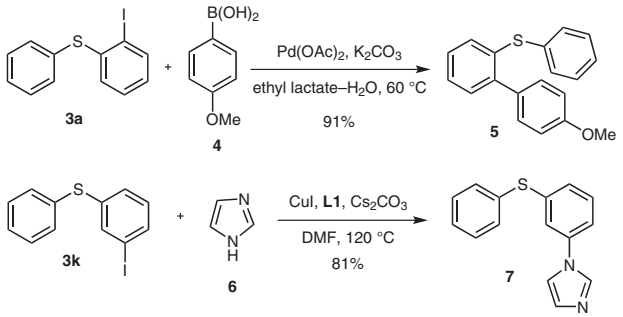



**Figure 1** ORTEP drawings of (a) **3a** and (b) **3d**[16]

Having establishing a method for the synthesis of the iodo(het)aryl sulfides **3**, we then attempted to use the products for the synthesis of more-elaborated sulfides by various coupling reactions of the residual aryl C–I bond. Iodophenyl sulfides **3a** and **3k** were subjected to a typical Suzuki–Miyaura reaction[17] and an Ullmann C–N coupling reaction, respectively (Scheme 1). The corresponding coupled products **5** and **7**, respectively, were obtained in excellent yields.




**Scheme 1** Synthesis of elaborated sulfides from iodophenyl sulfides

In conclusion, we have developed the first generally applicable method for effective synthesis of iodoaryl sulfides by selective single C–S coupling reactions of (het)aryl thiols with 1,2-, 1,3-, or 1,4-diiodobenzene in the presence of a readily available enaminone ligand and copper(I) iodide catalyst to give a broad range of iodine-functionalized sulfides, potentially useful as precursors for syntheses of various elaborated sulfides.

All chemicals were obtained from commercial sources and used as received. Reactions were monitored by TLC. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 spectrometer with $CDCl_3$ as solvent. The reported chemical shifts are relative to TMS as internal standard. Melting points of all solid products were determined in X-4 apparatus and are uncorrected. HRMS data were recorded in the EI or ESI mode on a micrOTOF-QII QTOF mass spectrometer (Bruker).

**(Het)aryl Sulfides 3; General Procedure**

Diiodobenzene **1** (0.2 mmol), (het)aryl thiol **2** (0.3 mmol), CuI (0.04 mmol), ligand **L1** (0.04 mmol), and $Cs_2CO_3$ (0.4 mmol) were added to DMSO (1 mL) in a 25-mL round-bottomed flask equipped with a stirring bar. The mixture was stirred at 100 °C for 18 h under $N_2$ then cooled to r.t. $H_2O$ (8 mL) was added and the resulting residue was extracted with EtOAc (3 × 8 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by silica flash column chromatography (petroleum ether).

**2-Iodophenyl Phenyl Sulfide (3a)**[14]

White solid; yield: 49 mg (79%); mp 55–57 °C (Lit.[14] 55.6–56.0 °C).

IR (KBr): 1564, 1469, 1007, 749, 533 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 1 H), 7.44–7.34 (m, 5 H), 7.19 (t, *J* = 7.6 Hz, 1 H), 6.93 (d, *J* = 8.0 Hz, 1 H), 6.87 (t, *J* = 7.6 Hz, 1 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 142.29, 139.68, 133.89, 133.16, 129.69, 129.43, 128.78, 128.39, 127.49, 99.34.

**2-Iodophenyl 4-Tolyl Sulfide (3b)**

Yellow solid; yield: 54 mg (83%); mp 69–71 °C.

IR (KBr): 2918, 1510, 1450, 1003, 735, 522 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.0 Hz, 1 H), 7.38 (d, *J* = 7.2 Hz, 2 H), 7.22 (d, *J* = 7.6 Hz, 2 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 6.81 (q, *J* = 8.8 Hz, 2 H), 2.38 (s, 3 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 143.33, 139.49, 138.99, 134.10, 130.55, 129.76, 128.61, 128.24, 126.89, 97.82, 21.30.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{13}H_{12}IS$: 326.9704; found: 326.9694.

**2-Iodophenyl 4-Isopropylphenyl Sulfide (3c)**

Yellow oily mass; yield: 57 mg (81%).

IR (KBr): 2959, 2868, 1439, 1008, 744, 556 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.6 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 7.15 (t, *J* = 7.6 Hz, 1 H), 6.87–6.80 (m, 2 H), 2.94–2.89 (m, 1 H), 1.26 (d, *J* = 7.2 Hz, 6 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 149.84, 143.31, 139.47, 134.13, 129.97, 128.64, 128.25, 127.95, 126.89, 97.80, 33.92, 23.89.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{15}H_{16}IS$: 355.0017; found: 355.0018.

**4-Fluorophenyl 2-Iodophenyl Sulfide (3d)**[14]

White solid; yield: 46 mg (69%); mp 94–96 °C (Lit.[14] 93.7–94.7 °C).

IR (KBr): 1530, 1454, 1280, 1006, 741, 528 cm$^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 1 H), 7.45–7.41 (m, 2 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 7.07 (t, *J* = 8.4 Hz, 2 H), 6.85 (q, *J* = 6.8 Hz, 2 H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ = 163.03 (d, $J_{F–C}$ = 248 Hz), 142.71, 139.66, 136.00 (d, $J_{F–C}$ = 8 Hz), 128.78, 128.49, 127.29, 117.09, 116.87, 98.18.

**4-Chlorophenyl 2-Iodophenyl Sulfide (3e)**[14]
White solid; yield: 56 mg (81%); mp 89–91 °C (Lit.[14] 89–90 °C).

IR (KBr): 1521, 1453, 1005, 768, 739, 536 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.0 Hz, 1 H), 7.34 (s, 3 H), 7.26–7.21 (m, 2 H), 6.99 (d, *J* = 8.0 Hz, 1 H), 6.90 (t, *J* = 7.6 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 141.41, 139.88, 134.37, 133.91, 132.78, 130.01, 129.84, 128.92, 127.99, 100.08.

**4-Bromophenyl 2-Iodophenyl Sulfide (3f)**[14]
White solid; yield: 59 mg (76%); mp 89–90 °C (Lit.[14] 88.1–88.8 °C).

IR (KBr): 1563, 1468, 1006, 747, 642, 531 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1 H), 7.50–7.47 (m, 2 H), 7.26–7.21 (m, 3 H), 7.02 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1 H), 6.91 (td, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 141.16, 139.91, 134.00, 133.55, 132.78, 130.25, 128.99, 128.14, 122.39, 100.46.

**2-Iodophenyl 3-Tolyl Sulfide (3g)**
Yellow gummy product; yield: 52 mg (80%).

IR (KBr): 2920, 1440, 1008, 744, 552 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.6 Hz, 1 H), 7.28–7.24 (m, 3 H), 7.18 (s, 2 H), 6.91–6.85 (m, 2 H), 2.35 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 142.63, 139.59, 133.91, 133.43, 130.38, 129.51, 129.34, 129.15, 128.72, 127.26, 98.93, 21.34.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{13}H_{12}IS$: 326.9704; found: 326.9712.

**2-[(2-Iodophenyl)sulfanyl]aniline (3h)**
Brown solid; yield: 48 mg (74%); mp 98–100 °C.

IR (KBr): 3463, 1528, 1456, 1004, 732, 527 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.6 Hz, 1 H), 7.37 (d, *J* = 7.2 Hz, 1 H), 7.22–7.17 (m, 1 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 6.74–6.68 (m, 3 H), 6.52 (d, *J* = 8.0 Hz, 1 H), 3.83 (br s, 2 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 148.81, 141.46, 139.40, 137.69, 131.75, 128.65, 126.49, 125.85, 119.13, 115.66, 114.67, 95.76.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{10}INS$: 326.9579; found: 326.9579.

**2-Iodophenyl 2-Naphthyl Sulfide (3i)**
Yellow solid; yield: 59 mg (81%); mp 59–61 °C.

IR (KBr): 1439, 1009, 748, 525 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1 H), 7.85–7.77 (m, 4 H), 7.53–7.48 (m, 2 H), 7.44 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 6.93 (d, *J* = 8.0 Hz, 1 H), 6.86 (t, *J* = 8.0 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 142.34, 139.72, 133.97, 132.86, 132.57, 131.21, 130.02, 129.55, 129.41, 128.80, 127.86, 127.76, 127.55, 126.84, 126.78, 99.24.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{16}H_{12}IS$: 362.9704; found: 362.9697.

**2-[(2-Iodophenyl)sulfanyl]-1,3-benzothiazole (3j)**
Yellow gummy product; yield: 74 mg (93%).

IR (KBr): 1556, 1459, 1441, 1003, 753, 523 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.77 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 1 H), 7.61 (d, *J* = 7.6 Hz, 1 H), 7.40–7.33 (m, 2 H), 7.24–7.18 (m, 1 H), 7.12–7.08 (m, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 167.73, 153.91, 140.87, 136.32, 135.78, 135.74, 131.66, 129.70, 126.27, 124.57, 122.19, 120.95, 107.56.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{13}H_9INS_2$: 369.9221; found: 369.9220.

**3-Iodophenyl Phenyl Sulfide (3k)**
Yellow gummy product; yield: 50 mg (80%).

IR (KBr): 1570, 1496, 1060, 776, 528 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.38–7.28 (m, 5 H), 7.22 (d, *J* = 8.0 Hz, 1 H), 6.98 (t, *J* = 8.0 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 138.95, 138.31, 135.67, 134.15, 132.06, 130.61, 129.50, 129.26, 127.90, 94.81.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_9IS$: 311.9470; found: 311.9461.

**3-Iodophenyl 4-Tolyl Sulfide (3l)**
Yellow gummy product; yield: 56 mg (86%).

IR (KBr): 2920, 1566, 1491, 1057, 770, 521 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.47 (s, 1 H), 7.40 (d, *J* = 7.2 Hz, 1 H), 7.24 (d, *J* = 7.6 Hz, 2 H), 7.08 (t, *J* = 8.0 Hz, 3 H), 6.87 (t, *J* = 8.0 Hz, 1 H), 2.28 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 140.21, 138.48, 137.14, 135.05, 133.11, 130.45, 130.35, 129.68, 128.08, 94.74, 21.24.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_{11}IS$: 325.9626; found: 325.9637.

**3-Iodophenyl 4-Isopropylphenyl sulfide (3m)**
Yellow gummy product; yield: 60 mg (85%).

IR (KBr): 2967, 2872, 1441, 1008, 743, 559 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 1 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 6.96 (t, *J* = 8.0 Hz, 1 H), 2.94–2.89 (m, 1 H), 1.22 (d, *J* = 6.8 Hz, 6 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 149.22, 139.94, 137.47, 135.19, 132.85, 130.49, 130.19, 128.41, 127.73, 94.73, 33.86, 23.91.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{16}IS$: 355.0017; found: 355.0019.

**4-Fluorophenyl 3-Iodophenyl Sulfide (3n)**
Yellow gummy product; yield: 47 mg (71%).

IR (KBr): 1568, 1486, 1280, 1058, 766, 521 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.52 (t, *J* = 8.0 Hz, 2 H), 7.43–7.39 (m, 2 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.06 (t, *J* = 8.4 Hz, 2 H), 6.98 (t, *J* = 8.0 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 164.04, 161.57, 139.64, 137.30, 135.14 (d, $J_{F-C}$ = 7.0 Hz), 130.59, 128.61, 128.22, 116.87 (d, $J_{F-C}$ = 22.0 Hz), 94.81.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_8FIS$: 329.9375; found: 329.9389.

**4-Bromophenyl 3-Iodophenyl Sulfide (3o)**
Yellow solid; yield: 61 mg (78%); mp 62–64 °C.

IR (KBr): 1565, 1486, 1055, 759, 657, 519 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.56 (s, 1 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.17–7.12 (m, 3 H), 6.93 (t, *J* = 8.0 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 138.81, 137.90, 136.19, 133.83, 133.10, 132.55, 130.79, 129.77, 121.88, 94.95.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_8BrIS$: 389.8575; found: 389.8582.

**3-Iodophenyl 3-Tolyl Sulfide (3p)**
Yellow gummy product; yield: 54 mg (83%).

IR (KBr): 2919, 1569, 1493, 1057, 767, 522 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.23–7.19 (m, 4 H), 7.11 (d, *J* = 7.2 Hz, 1 H), 6.98 (t, *J* = 8.0 Hz, 1 H), 2.33 (s, 3 H)

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 138.89, 138.78, 137.55, 134.97, 133.11, 132.34, 130.05, 128.83, 128.52, 128.36, 94.27, 20.86.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_{11}IS$: 325.9626; found: 325.9631.

**3-Iodophenyl 2-Naphthyl Sulfide (3q)**
Yellow solid; yield: 52 mg (72%); mp 86–88 °C.

IR (KBr): 1434, 1007, 744, 523 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.90 (s, 1 H), 7.83–7.75 (m, 3 H), 7.66 (s, 1 H), 7.55–7.48 (m, 3 H), 7.40 (dd, $J_1$ = 8.8 Hz, $J_2$ = 1.6 Hz, 1 H), 7.24 (d, *J* = 7.2 Hz, 1 H), 6.98 (t, *J* = 8.0 Hz, 1 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 138.99, 138.23, 135.71, 133.78, 132.60, 131.32, 131.28, 130.65, 129.28, 129.27, 129.21, 127.84, 127.63, 126.80, 126.67, 94.87.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{11}IS$: 361.9626; found: 361.9610.

**2-[(3-Iodophenyl)sulfanyl]-1,3-benzothiazole (3r)**
Yellow gummy product; yield: 72 mg (90%).

IR (KBr): 1552, 1453, 1439, 1002, 750, 519 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.23 (d, *J* = 8.0 Hz, 1 H), 7.61–7.55 (m, 2 H), 7.34 (t, *J* = 8.0 Hz, 1 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 7.11 (t, *J* = 8.0 Hz, 1 H).

$^{13}C$ NMR(100 MHz, $CDCl_3$): δ = 167.76, 153.72, 143.09, 139.26, 135.64, 134.11, 132.02, 131.30, 126.36, 124.70, 122.19, 120.95, 94.92.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{13}H_9INS_2$: 369.9221; found: 369.9225.

**4-Iodophenyl Phenyl Sulfide (3s)**
Yellow gummy product; yield: 54 mg (86%).

IR (KBr): 1498, 1479, 1003, 810, 523 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 2 H), 7.40 (s, 1 H), 7.37–7.24 (m, 4 H), 7.01 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 2 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 138.86, 137.64, 136.07, 134.00, 131.55, 128.96, 127.22, 91.46.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_9IS$: 311.9470; found: 311.9484.

**4-Iodophenyl 4-Tolyl Sulfide (3t)**
Yellow solid; yield: 55 mg (85%); mp 100–101 °C.

IR (KBr): 2991, 1491, 1469, 1000, 807, 517 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.53 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 7.6 Hz, 2 H), 6.94 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.6 Hz, 2 H), 2.35 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 137.83, 137.45, 137.39, 132.46, 130.35, 129.81, 129.53, 90.55, 20.76.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{13}H_{11}IS$: 325.9626; found: 325.9640.

**4-Chlorophenyl 4-Iodophenyl Sulfide (3u)**
Yellow solid; yield: 57 mg (83%); mp 80–82 °C.

IR (KBr): 1499, 1479, 1004, 789, 738, 517 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.4 Hz, 2 H), 7.30–7.26 (m, 4 H), 7.02 (d, *J* = 8.4 Hz, 2 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 137.81, 135.33, 133.21, 132.83, 132.29, 131.80, 129.08, 91.97.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_8ClIS$: 345.9080; found: 345.9068.

**4′-Methoxy-2-(phenylsulfanyl)biphenyl (5)**
The reaction of 1,2-diiodobenzene (**3a**; 0.5 mmol) and (4-methoxyphenyl)boronic acid (**4**; 0.75 mmol), performed by following a previously reported procedure,[17] gave a pale yellow gummy product; yield: 133 mg (91%).

IR (KBr): 2834, 1514, 1462, 1038, 756 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.08–7.25 (m, 11 H), 6.83–6.81 (m, 2 H), 3.71 (s, 3 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 157.92, 141.43, 134.51, 134.03, 131.92, 130.81, 129.93, 129.51, 129.44, 128.09, 126.67, 126.08, 125.64, 112.31, 54.13.

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{16}OS$: 292.0922; found: 292.0928.

**1-[3-(Phenylsulfanyl)phenyl]-1*H*-imidazole (7)**
Sulfide **3k** (0.3 mmol), imidazole (**6**; 0.3 mmol), CuI (0.04 mmol), ligand **L1** (0.04 mmol), and $Cs_2CO_3$ (0.6 mol) were added to DMF (1 mL) in a 25-mL round-bottomed flask equipped with a stirring bar. The mixture was stirred at 120 °C for 12 h then cooled to r.t. $H_2O$ (5 mL) was added and the resulting mixture was extracted with EtOAc (3 × 8 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by silica flash column chromatography (EtOAc–petroleum ether, 1:3) to give a yellow gummy product; yield: 61 mg (81%).

IR (KBr): 3442, 1592, 1497, 1057, 742 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.39–7.34 (m, 4 H), 7.23–7.17 (m, 5 H).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 139.28, 137.46, 134.98, 132.76, 132.30, 129.99, 129.88, 129.14, 127.88, 127.59, 121.31, 118.72, 117.60.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{15}H_{13}N_2S$: 253.0799; found: 253.0806.

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**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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(16) Crystallographic data for compounds **3a** and **3d** have been deposited with the accession numbers CCDC 945932 and 945931, respectively, and can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk; Web site: www.ccdc.cam.ac.uk/conts/retrieving.html.
(17) A previously developed catalytic method was used, see: Wan, J.-P.; Wang, C.; Zhou, R.; Liu, Y. *RSC Adv.* **2012**, *2*, 8789.



 