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A Highly Efficient, Ligand-Free, and Recyclable Cu_2S-Catalyzed Coupling of Aryl Iodides with Diaryl Disulfides

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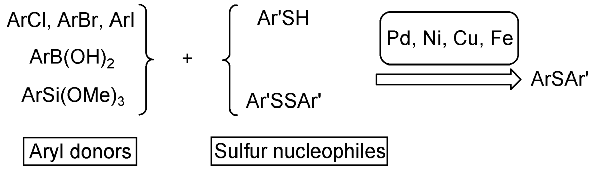
A highly efficient and ligand-free copper(I) sulfide catalyzed cross-coupling reaction of aryl iodides with diaryl disulfides was developed. With only 1 mol-% of Cu_2S as the catalyst, iron powder as the reductant, and K_2CO_3 as the base, aryl iodides reacted with disulfides in DMSO at 90–110 °C for 18–24 h under an atmosphere of argon to give the corresponding aryl sulfides in good to excellent yields. In addition, the catalyst is recyclable and reusable with some loss of activity.

Introduction

Aryl sulfides are widely used in pharmaceuticals, functional materials, and synthetic chemistry. Among the numerous methods developed in the past decades, the most common and powerful approach is the transition-metal-catalyzed C(aryl)–S coupling reaction.[1] Generally, the cross-coupling reactions are conducted between aryl donors and thiols (Scheme 1). Up to now, different transition-metal-catalyzed systems including palladium,[2] nickel,[3] copper,[4] and iron[5] have been reported. These important processes enable the efficient formation of aryl sulfides with a wide functional group tolerance However, thiols (most have offensive odors) are easily oxidized to diaryl disulfides even in air. Thus, diaryl disulfides often accompany the cross-coupling products as byproducts, and for the effective conversion of thiols, aryl donors are used in excess.[6]



Scheme 1. Transition-metal-catalyzed C–S coupling reactions.

On the contrary, diaryl disulfides are structure symmetric, air stable, and easy to handle. However, the transition-metal-catalyzed cross-coupling reaction of diaryl disulfides as sulfur nucleophile has rarely been reported. Among the countable reports, Pd and Ni catalysts are employed for the efficient conversion of diaryl disulfides.[7] The limitation of these metals could easily result in residual toxicity after work-up of the reaction mixtures. Copper-catalyzed cross-coupling reactions with the use of diaryl disulfides and aryl boric acids or silicones as substrates have been disclosed.[8] Further, more economical aryl halides as substrates have also been demonstrated by Taniguchi and Engman.[9] However, a large amount of copper catalyst, an appropriate ligand, and two equivalents of the reductant were all necessary.

In the environmental context of today, one of the challenging issues for chemists is to develop a simple, effective, and green system under environmentally friendly conditions. Most recently, Rao disclosed a new, efficient, and ligand-free cross-coupling reaction of aryl halides and diaryl diselenides by using a catalytic amount of nano-CuO as a recyclable catalyst.[10] This was followed by a report from Wang disclosing an iron-catalyzed ligand-free coupling of aryl boronic acids with diselenides and ditellurides.[11] These processes were important advances for the synthesis of a variety of aryl chalcogens. Unfortunately, by using diaryl disulfides as the chalcogen source for direct C–S coupling these protocols were unsuccessful, probably due to the stronger S–S bond.

Herein, we report a novel, efficient, and ligand-free Cu_2S-catalyzed cross-coupling reaction of aryl iodides with diaryl disulfides.

Results and Discussion

We began the study by examining the cross-coupling reaction of diphenyl disulfide with 1-iodo-4-methylbenzene. The coupling reaction afforded the desired product, phenyl (*p*-tolyl) sulfide, and a small amount of diphenyl sulfide as a byproduct when the substrates were stirred at 110 °C for 18 h under an atmosphere of argon (Table 1, Entry 1). Of the following copper catalysts tested, Cu powder and Cu_2S gave complete conversion; CuI, Cu_2O, $CuCl_2$, and CuO

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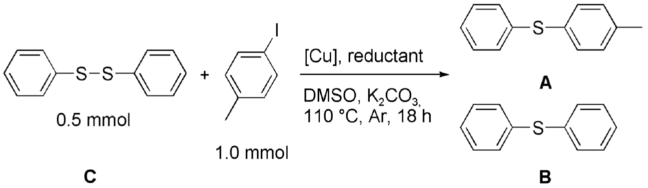
were found to be inferior. Interestingly, in the presence of Fe powder, the reaction was dramatically accelerated, especially with the use of Cu_2S, which gave the desired product in nearly quantitative yield. Besides, we observed that the addition of Fe reduced the formation of symmetrical sulfide byproducts, which is advantageous as these byproducts are not easily separated from the desired unsymmetrical sulfides (Table 1, Entry 10). Other common reductants such as Zn, Mg, and Al powder gave the desired products in lower yields. It was surprising that Fe showed more efficient catalyst activity than the stronger reductants tested. We postulated that binding of the Fe ion with ArS^- played a critical role in the catalyst process (Scheme 3). Further study indicated that Fe powder had nearly no catalytic effect (Table 1, Entry 14). Although the presence of base did not seem to be essential on the basis of the reaction equation, it was demonstrated that the reaction without base proceeded with lower conversion (Table 1, Entry 15). It was also noted that the polar donor solvent DMF was slightly inferior to DMSO.

Table 1. Optimization of the reaction condition.[a]

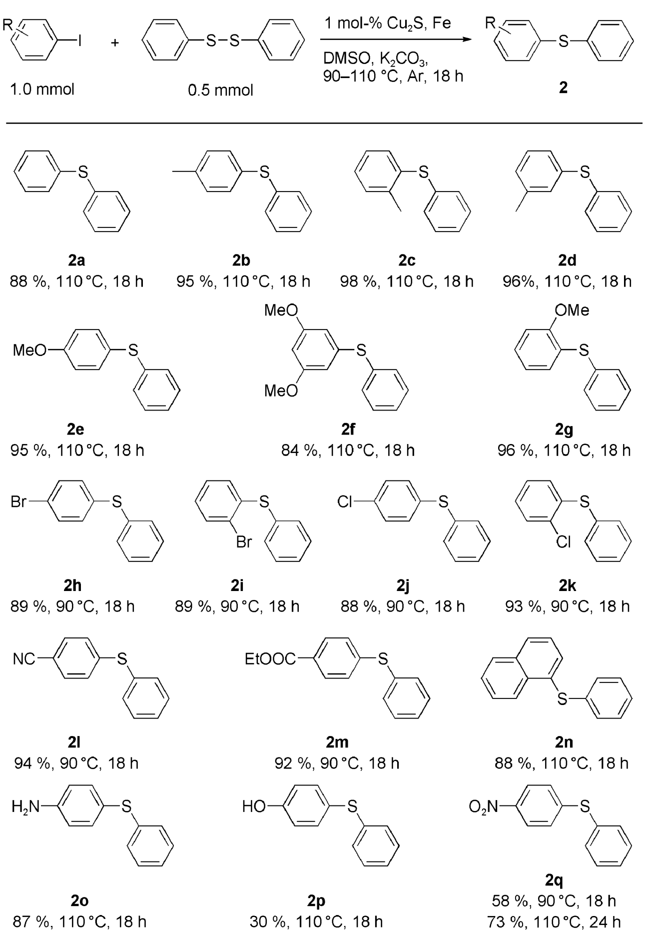


Entry	[Cu]	mol-%	Reductant	GC yield [%] A	B	C
1	CuBr	10	–	89	8	3
2	Cu_2O	10	–	87	3	10
3	$CuCl_2$	10	–	84	9	7
4	CuO	10	–	47	3	50
5	CuI	10	–	88	7	5
6	CuI	1	Fe	95	5	0
7	Cu	10	–	93	7	0
8	Cu	1	Fe	94	6	0
9	Cu_2S	10	–	93	6	1
10	Cu_2S	1	Fe	99.5	0.5	0
11	Cu_2S	1	Mg	90	1	9
12	Cu_2S	1	Zn	92	3	5
13	Cu_2S	1	Al	90	6	4
14	–	–	Fe	5	–	95
15	Cu_2S	1	Fe	24[b]	0	76

[a] Reaction conditions: 1-iodo-4-methylbenzene (1.0 mmol), diphenyl disulfide (0.5 mmol), [Cu] (1 or 10 mol-%), reductant (0.6 mmol), K_2CO_3 (1 mmol), and DMSO (1 mL) stirred at 110 °C for 18 h under an atmosphere of argon. GC yield was calculated by the area integrals of **A**, **B**, and **C**. [b] Without K_2CO_3.

We next investigated the influence of various aryl iodides on this coupling reaction. As shown in Table 2, the catalyst system has substantial substrate scope. A variety of electron-rich, electron-neutral, and electron-deficient aryl iodides underwent the cross-coupling reaction smoothly to generate the corresponding aryl sulfides. Generally, products formed in high yield at 110 °C within 18 h, and electron-deficient aryl iodides transformed efficiently at 90 °C (Table 2, **2h**–**m**). However, the aryl iodide with a strong electron-withdrawing nitro group gave only moderate yield. GC analysis indicated that amount of the starting materials were left (Table 2, **2q**). Elevating the reaction temperature to 110 °C and prolonging the reaction time to 24 h enhanced the yield to 73 %.

Table 2. The cross-coupling reaction between aryl iodides and diphenyl disulfide.[a]



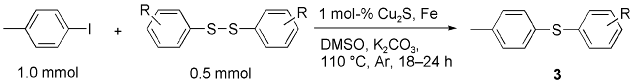
[a] Reaction conditions: Aryl iodide (1.0 mmol), diphenyl sulfide (0.5 mmol), Cu_2S (1 mol-%), Fe (0.6 mmol), K_2CO_3 (1 mmol), and DMSO (1 mL) stirred at 90–110 °C for 18 h under an atmosphere of argon. Isolated yield.

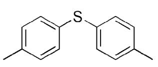
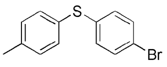
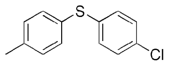
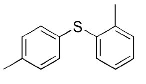
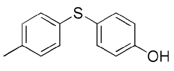
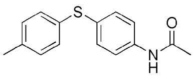
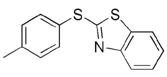
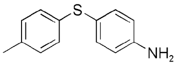
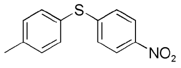
A more remarkable observation was that the cross-coupling reactions gave excellent yields, regardless of whether the substitution was at the *para*, *meta*, or *ortho* position (Table 2, **2b**–**d**), which showed that the steric hindrance effect was not significant.

The functional tolerance results showed that a series of functional groups, including methyl, methoxy, chloro, bromo, nitro, amino, and cyano groups, were perfectly tolerated. An aryl iodide bearing an ester group, which undergoes hydrolysis easily, was also well tolerated (Table 2, **2m**). Moreover, the coupling reaction showed interesting chemoselectivity. Aryl iodides coupled with disulfides in the presence of chloro and bromo groups at the aryl ring (Table 2, **2h**–**k**). The free $–NH_2$ group was well tolerated, and the coupling reaction took place at the –SS– group rather than the $-NH_2$ group (Table 2, **2o**). However, the free –OH group was not efficient, presumably because the Lewis basic group (ArO^-) could compete with the –SS– group for binding to the copper center, preventing the coordination of the –SS– groups (Table 2, **2p**). GC–MS indicated that some staring materials were left and approximately 30% reduction product (phenol) was observed.

Finally, we investigated the reaction of various diaryl disulfides with 1-iodo-4-methylbenzene (Table 3). Diaryl disulfides containing methyl, chloro, bromo, and amide groups underwent reactions in good to excellent yields and no significant electron or steric effect was found. Similar results were observed with dibenzothiazole disulfide as substrate (Table 3, **3g**). The free $-NH_2$ and –OH groups were not very efficient for the same reason explained above (Table 3, **3e**, **3h**). The nitro group weakened the nucleophilicity of the –SS– bond, resulting in less coordination with the copper center and therefore a moderate yield was obtained (Table 3, **3i**).

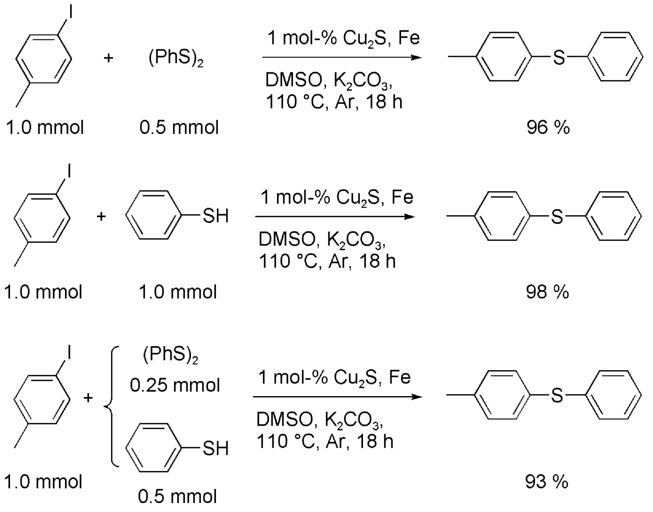
Table 3. The cross-coupling reaction between 1-iodo-4-methylbenzene and diaryl disulfides.[a]



 **3a** 89 %, 110 °C, 18 h	 **3b** 89 %, 110 °C, 18 h	 **3c** 92 %, 110 °C,18 h
 **3d** 96 %, 110 °C, 18 h	 **3e** 32 %, 110 °C, 24 h	 **3f** 82 %, 110 °C, 18 h
 **3g** 85 %, 110 °C, 18 h	 **3h** 57 %, 110 °C, 24 h	 **3i** 48 %, 110 °C, 24 h

[a] Reaction conditions: 1-iodo-4-methylbenzene (1.0 mmol), disulfide (0.5 mmol), Cu_2S (1 mol-%), Fe (0.6 mmol), K_2CO_3 (1 mmol), and DMSO (1 mL) stirred at 110 °C for 18–24 h under an atmosphere of argon. Isolated yield.

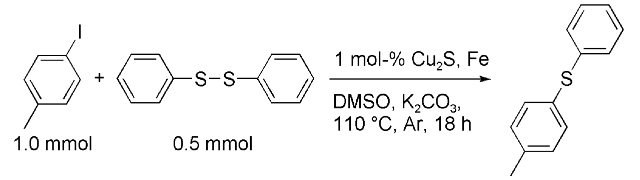
As typically observed for metal-catalyzed C–S cross-coupling reactions, diaryl disulfides as byproducts often accompany the cross-coupling products even with an excess amount of the aryl donors. As shown in Scheme 2, with only a theoretical amount of raw materials, and with either disulfide or thiol as the nucleophile, the coupling reactions proceeded well. Further, even when a mixture of disulfide and thiol was used as the starting material, the reaction proceeded smoothly to generate the desired product in excellent yield.



Scheme 2. Compatibility of diphenyl disulfide and thiol (GC yield).

To develop novel and efficient systems that are recoverable and reusable is one of the major goals of C–S coupling reactions.[12] Previous research focused on homogeneous catalyst with supporting ligands, and the catalyst was used only once. However, the Cu_2S system here is heterogeneous and recyclable. The catalyst could be recovered from the aqueous solution by simple centrifugation and then reused for the fresh cross-coupling reaction. The desired product was formed in 86% yield after reusing the medium three times (Table 4, Entry 3).

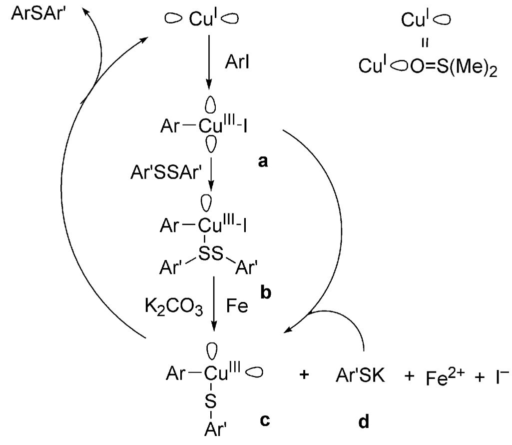
Table 4. Recyclability experiments of the Cu_2S system.[a]



Entry	Recycle	GC yield [%]
1	run 1	96
2	run 2	90
3	run 3	86

[a] Reaction conditions: After completion of the reaction, the resulting mixture was treated with H_2O and ethyl acetate (3 × 5 mL). The catalyst was recovered from the solution by centrifugation, dried under vacuum, and reused for the next run. The combined organic layer was detected by GC.

Finally, the possible mechanism is depicted in Scheme 3. In this heterogeneous system, it seems that the solvent acts as a ligand and coordinates with the copper center first;[13] oxidative addition of the aryl iodide with the catalyst may provide intermediate **a**. Then, disulfide coordinates with the catalyst to provide intermediate **b**, which undergoes a bond breaking reaction to generate activating species intermediate **c** and thiol anion intermediate **d**. Intermediate **c** easily provides the desired C–S cross-coupled product by reductive elimination. Intermediate **d** together with intermediate **a** regenerate activating species **c** and then provide the desired unsymmetrical sulfide. K_2CO_3, which seems to be unnecessary, actually stabilizes the thiol anion. The generation of Fe^{2+} may bind to thiol anion **d** to accelerate the coordination with intermediate **a**, which is not possible for other common reductants.



Scheme 3. Possible mechanism for cross-coupling reactions of aryl iodides and disulfides.

Conclusions

In summary, we developed a highly efficient and ligand-free copper(I) sulfide catalyzed cross-coupling reaction of aryl iodides with diaryl disulfides. With only 1 mol-% of Cu_2S as the catalyst, iron powder as the reductant, and K_2CO_3 as the base, aryl iodides reacted with disulfides in DMSO at 90–110 °C for 18–24 h under an atmosphere of argon to give the corresponding aryl sulfides in good to excellent yields. In addition, the novel system showed wide functional group tolerance and was chemoselective. Furthermore, the catalyst system was demonstrated to be recyclable and reusable with some loss of activity.

Experimental Section

General Information: All reagents unless otherwise noted were obtained from commercial sources (purity >99%) and used without further purification. The reactions were carried out under an argon atmosphere, and the products were isolated by column chromatography on silica gel (200–300 mesh) by using petroleum ether (60–90 °C) and ethyl acetate as eluents. Compounds described in the literature were characterized by comparing their ^1H and ^{13}C NMR spectra and MS data to the reported data. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and chemical shifts are reported in parts per million relative to TMS. Gas chromatography analyses were performed with an FID detector. High-resolution mass spectrometric data (HRMS) were performed with an HPLC-Q-Tof MS.

Preparation of Copper(I) Sulfide: Cu_2S can be prepared by slowly adding a solution of CuCl and $Na_2S_2O_3$ to an aqueous solution of Na_2S. Precipitated Cu_2S was produced by filtration and washing sequentially with H_2O, EtOH, and EtOAc and drying in vacuo for 24 h. The block Cu_2S was ground up into a fine powder prior to use.

General Procedure for the Coupling of Aryl Iodides with Diphenyl Disulfides: A flame-dried test tube with a magnetic stirring bar was charged with Cu_2S (1.6 mg, 0.01 mmol), Fe powder (33.6 mg, 0.6 mmol), K_2CO_3 (138 mg, 1.0 mmol), disulfide (0.5 mmol), aryl iodide (1.0 mmol), and DMSO (1 mL). The mixture was stirred at the indicated temperature under an atmosphere of argon for 18–24 h and cooled to room temperature. The resulting mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic layer was dried with Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate or dichloromethane). All the physical data of the known compounds were in agreement with those reported in the literature.

General Procedure for the Recyclability Experiments of Cu_2S: Following the general procedure, the resulting mixture was treated with H_2O and ethyl acetate (3 × 5 mL). The catalyst was recovered from the solution by centrifugation, dried under vacuum, and reused for the next run. The combined organic layer was detected by GC. To the catalyst, Cu_2S, and some residual Fe powder was added the new Fe powder (33.6 mg, 0.6 mmol), K_2CO_3 (138 mg, 1.0 mmol), disulfide (0.5 mmol), aryl iodide (1.0 mmol), and DMSO (1 mL) under an atmosphere of argon for the next run.

Diphenyl Thioether (2a): The product was obtained (petroleum ether) as a colorless oil in 88% yield. CAS: 139-66-2. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.21 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 131.2, 129.4, 127.2 ppm. GC–MS (EI): m/z = 186 $[M]^+$.

4-Tolyl Phenyl Thioether (2b): The product was obtained (petroleum ether) as a colorless oil in 95% yield. CAS: 3699-01-2. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.12 (m, 9 H, Ar-H), 2.34 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 137.3, 132.4, 131.5, 130.2, 130.0, 129.2, 126.6, 21.2 ppm. GC–MS (EI): m/z = 200 $[M]^+$.

2-Tolyl Phenyl Thioether (2c): The product was obtained as colorless oil in 98% yield. CAS: 13963–35–4. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.12 (m, 9 H, Ar-H), 2.38 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1, 136.3, 133.9, 133.1, 130.8, 129.8, 129.3, 128.1, 126.9, 126.5, 20.8 ppm. GC–MS (EI): m/z = 200 $[M]^+$.

3-Tolyl Phenyl Thioether (2d): The product was obtained (petroleum ether) as a colorless oil in 96% yield. CAS: 13865-48-0. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.05 (m, 9 H, Ar-H), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 136.3, 135.4, 132.0, 130.9, 129.3, 129.2, 128.5, 128.2, 127.0, 21.5 ppm. GC–MS (EI): m/z = 200 $[M]^+$.

4-Phenylsulfanylanisol (2e): The product was obtained (ethyl acetate/petroleum ether, 1:50) as a slightly yellow oil in 95% yield. CAS: 5633-57-8. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.8 Hz, 2 H, Ar-H), 7.25–7.11 (m, 5 H, Ar-H), 6.89 (d, J = 8.8 Hz, 2 H, Ar-H), 3.81 (s, 3 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 138.8, 135.6, 129.1, 128.3, 125.9, 124.4, 115.1, 55.5 ppm. GC–MS (EI): m/z = 216 $[M]^+$.

(3,5-Dimethoxyphenyl)(phenyl)sulfane (2f): The product was obtained (ethyl acetate/petroleum ether, 1:10) as a slightly yellow oil in 84% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, J = 8.4 Hz, 2 H, Ar-H), 7.24–7.38 (m, 3 H, Ar-H), 6.45 (d, J = 2.4 Hz, 2 H, Ar-H), 6.32 (t, J = 2.4 Hz, 1 H, Ar-H), 3.73 (s, 6 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 138.3, 134.9, 121.9, 129.4, 127.6, 108.3, 99.5, 55.5 ppm. GC–MS (EI): m/z = 246 $[M]^+$. HRMS (ESI): calcd. for $C_{15}H_{15}NOS$ $[M + Na]^+$ 269.0612; found 269.0616.

(2-Methoxyphenyl)(phenyl)sulfane (2g): The product was obtained (ethyl acetate/petroleum ether, 1:50) as a colorless oil in 96% yield.

CAS: 14065-22-6. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.36–7.21 (m, 6 H, Ar-H), 7.08 (d, J = 8.0 Hz, 1 H, Ar-H), 6.88 (m, 2 H, 1-H, Ar-H), 3.87 (s, 6 H, OCH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 157.6, 134.8, 131.9, 131.6, 129.3, 128.5, 127.2, 124.3, 121.4, 111.1, 56.1 ppm. GC–MS (EI): *m*/*z* = 216 [M]$^+$.

4-Bromophenyl Phenyl Thioether (2h): The product was obtained (petroleum ether) as a colorless oil in 89% yield. CAS: 65662-88-6. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.39 (d, J = 8.4 Hz, 2 H, Ar-H), 7.36–7.24 (m, 5 H, Ar-H), 7.16 (d, J = 8.4 Hz, 2 H, 2-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.7, 135.0, 132.4, 132.3, 131.7, 129.5, 127.7, 121.0 ppm. GC–MS (EI): *m*/*z* = 264 [M]$^+$, 266 [M + 2]$^+$.

2-Bromophenyl Phenyl Thioether (2i): The product was obtained (petroleum ether) as a slightly yellow solid in 89% yield. CAS: 15861-48-0. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.55 (d, J = 8.0 Hz, 1 H, Ar-H), 7.46–7.37 (m, 5 H, Ar-H), 7.13 (t, J = 7.6 Hz, 1 H, Ar-H), 7.02 (t, J = 7.6 Hz, 1 H, Ar-H), 6.92 (d, J = 8.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.9, 133.7, 133.2, 133.0, 129.9, 129.8, 128.6, 128.0, 127.4, 123.1 ppm. GC–MS (EI): *m*/*z* = 264 [M]$^+$, 266 [M + 2]$^+$.

4-Chlorophenyl Phenyl Thioether (2j): The product was obtained (petroleum ether) as a colorless oil in 88% yield. CAS: 13343-26-5. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.35–7.25 (m, 9 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 135.3, 134.8, 133.2, 132.2, 131.5, 129.49, 129.48, 127.6 ppm. GC–MS (EI): *m*/*z* = 220 [M]$^+$, 222 [M + 2]$^+$.

(2-Chlorophenyl)(phenyl)sulfane(2k): The product was obtained (petroleum ether) as a colorless oil in 93% yield. CAS: 33667-82-2. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.44 (d, J = 8.0 Hz, 2 H, Ar-H), 7.37–7.32 (m, 4 H, Ar-H), 7.14–7.08 (m, 2 H, Ar-H), 6.98 (d, J = 8.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 136.5, 133.4, 133.1, 132.9, 130.3, 129.8, 129.6, 128.2, 127.3, 127.2 ppm. GC–MS (EI): *m*/*z* = 220 [M]$^+$, 222 [M + 2]$^+$.

4-(Phenylthio)benzonitrile (2l): The product was obtained (ethyl acetate/petroleum ether, 1:20) as a colorless oil in 94% yield. CAS: 51238-46-1. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.52–7.41 (m, 7 H, Ar-H), 7.16 (d, J = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 145.9, 134.6, 132.5, 131.0, 130.1, 129.5, 127.5, 118.9, 108.9 ppm. GC–MS (EI): *m*/*z* = 211 [M]$^+$.

Ethyl 4-(Phenylthio)benzoate (2m): The product was obtained (CH$_2$Cl$_2$/petroleum ether, 1:10) as a colorless oil in 92% yield. CAS: 10129-07-4. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.90 (d, J = 8.8 Hz, 2 H, Ar-H), 7.47 (d, J = 9.2 Hz, 2 H, Ar-H), 7.38–7.36 (m, 3 H, Ar-H), 7.20 (d, J = 8.8 Hz, 2 H, Ar-H), 4.37 (q, J = 7.6 Hz, 2 H, CH$_2$), 1.36 (t, J = 7.6 Hz, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 166.3, 144.2, 133.7, 132.9, 130.2, 129.7, 128.7, 128.2, 128.0, 61.1, 14.5 ppm. GC–MS (EI): *m*/*z* = 258 [M]$^+$.

1-Naphyl Phenyl Thioether (2n): The product was obtained (petroleum ether) as a colorless oil in 88% yield. CAS: 7570-98-1. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.39–8.36 (m, 1 H, Ar-H), 7.85–7.83 (m, 2 H, Ar-H), 7.65 (d, J = 7.2 Hz, 1 H, Ar-H), 7.51–7.49 (m, 2 H, Ar-H), 7.41 (t, J = 7.2 Hz, 1 H, Ar-H), 7.22–7.14 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 137.1, 134.4, 133.8, 132.7, 131.4, 129.4, 129.2, 129.1, 128.7, 127.1, 126.6, 126.3, 126.0, 125.8 ppm. GC–MS (EI): *m*/*z* = 236 [M]$^+$.

4-Aminophenyl Phenyl Thioether (2o): The product was obtained (ethyl acetate/petroleum ether, 1:3) as a pale solid in 87% yield. CAS: 1135-14-4. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.31 (d, J = 8.4 Hz, 2 H, Ar-H), 7.22 (t, J = 7.2 Hz, 2 H, Ar-H), 7.14–7.08 (m, 3 H, Ar-H), 6.69 (d, J = 8.4 Hz, 2 H, Ar-H), 3.87 (br. s, 2 H, NH$_2$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 146.4, 139.6, 136.1, 129.0, 127.6, 125.5, 121.3, 116.4 ppm. GC–MS (EI): *m*/*z* = 201 [M]$^+$.

4-(Phenylsulfanyl)Phenol (2p): The product was obtained (ethyl acetate/petroleum ether, 1:20) as a colorless oil in 30% yield. CAS: 5633-55-6. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.36 (d, J = 8.8 Hz, 2 H, Ar-H), 7.24–7.13 (m, 5 H, Ar-H), 6.83 (d, J = 8.8 Hz, 2 H, Ar-H), 5.86 (br. s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 156.1, 138.6, 135.7, 129.1, 128.5, 126.0, 124.7, 116.7 ppm. GC–MS (EI): *m*/*z* = 202 [M]$^+$.

4-Nitrophenyl Phenyl Thioether (2q): The product was obtained (ethyl acetate/petroleum ether, 1:20) as a yellow solid in 58% yield (90 °C, 18 h) or in 73% yield (110 °C, 24 h). CAS: 952-97-6. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.06 (d, J = 9.2 Hz, 2 H, Ar-H), 7.56–7.54 (m, 2 H, Ar-H), 7.47–7.45 (m, 3 H, Ar-H), 7.18 (d, J = 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 148.7, 145.5, 134.9, 130.5, 130.2, 129.9, 126.8, 124.2 ppm. GC–MS (EI): *m*/*z* = 231 [M]$^+$.

Di-*p*-tolylsulfane (3a): The product was obtained (petroleum ether) as a white solid in 89% yield. CAS: 620-94-0. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.20 (d, J = 8.0 Hz, 4 H, Ar-H), 7.07 (d, J = 8.0 Hz, 4 H, Ar-H), 2.29 (s, 6 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 137.1, 132.8, 131.2, 130.1, 21.2 ppm. GC–MS (EI): *m*/*z* = 214 [M]$^+$.

(4-Bromophenyl)(*p*-tolyl)sulfane (3b): The product was obtained (petroleum ether) as a white solid in 89% yield. CAS: 22865-54-9. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.36 (d, J = 8.4 Hz, 2 H, Ar-H), 7.30 (d, J = 8.4 Hz, 2 H, Ar-H), 7.15 (d, J = 8.0 Hz, 2 H, Ar-H), 7.09 (d, J = 8.8 Hz, 2 H, Ar-H), 2.35 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.3, 137.0, 132.8, 132.2, 131.1, 130.7, 130.4, 120.3, 21.3 ppm. GC–MS (EI): *m*/*z* = 278 [M]$^+$, 280 [M + 2]$^+$.

(4-Chlorophenyl)(*p*-tolyl)sulfane (3c): The product was obtained (petroleum ether) as a white solid in 92% yield. CAS: 22865-55-0. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.29 (d, J = 8.0 Hz, 2 H, Ar-H), 7.22 (d, J = 8.8 Hz, 2 H, Ar-H), 7.18–7.14 (m, 4 H, 3-H, 1-H), 2.35 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 138.2, 136.2, 132.7, 132.5, 131.1, 131.0, 130.4, 129.3, 21.3 ppm. GC–MS (EI): *m*/*z* = 234 [M]$^+$, 236 [M + 2]$^+$.

o-Tolyl(*p*-tolyl)sulfane (3d): The product was obtained (petroleum ether) as a colorless liquid in 96% yield. CAS: 4279-70-3. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.20–7.06 (m, 8 H, Ar-H), 2.37 (s, 3 H, CH$_3$), 2.31 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 139.0, 137.0, 135.4, 131.9, 131.7, 131.2, 130.6, 130.2, 127.3, 126.7, 21.2, 20.6 ppm. GC–MS (EI): *m*/*z* = 214 [M]$^+$.

4-(*p*-Tolylthio)phenol (3e): The product was obtained (ethyl acetate/petroleum ether, 1:20) as a white solid in 32% yield. CAS: 5633-56-7. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.30 (d, J = 8.4 Hz, 2 H, Ar-H), 7.14 (d, J = 8.0 Hz, 2 H, Ar-H), 7.06 (d, J = 8.0 Hz, 2 H, Ar-H), 6.78 (d, J = 8.8 Hz, 2 H, Ar-H), 4.96 (br. s, 1 H, OH), 2.30 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 155.6, 136.5, 134.6, 134.3, 130.0, 129.8, 126.3, 116.5, 21.1 ppm. GC–MS (EI): *m*/*z* = 216 [M]$^+$.

***N*-[4-(*p*-Tolylthio)phenyl]acetamide (3f):** The product was obtained (ethyl acetate/petroleum ether, 3:2) as a white solid in 82% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.43 (d, J = 8.4 Hz, 2 H, Ar-H), 7.33 (br. s, 1 H, NH), 7.27 (m, 2 H, Ar-H), 7.22 (d, J = 8.4 Hz, 2 H, Ar-H), 7.10 (d, J = 8.0 Hz, 2 H, Ar-H), 2.32 (s, 3 H, CH$_3$), 2.16 (s, 3 H, CH$_3$) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 168.4, 137.3, 137.1, 132.5, 131.9, 131.6, 131.3, 130.1, 120.7, 24.7, 21.2 ppm. GC–

MS (EI): m/z = 257 $[M]^+$. HRMS (ESI): calcd. for $C_{14}H_{14}O_2S$ $[M + Na]^+$ 280.0772; found 280.0771.

2-(*p*-Tolylthio)benzo[*d*]thiazole (3g): The product was obtained (petroleum ether/CH_2Cl_2, 3:1) as a yellow solid in 85% yield. CAS: 39544-84-8. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.0 Hz, 1 H, Ar-H), 7.61–7.67 (m, 3 H, Ar-H), 7.38 (td, J = 8.0, 0.8 Hz, 1 H, Ar-H), 7.28–7.21 (m, 3 H, Ar-H), 2.42 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 154.2, 141.2, 135.7, 135.6, 130.9, 126.5, 126.2, 124.3, 122.0, 120.9, 21.5 ppm. GC–MS (EI): m/z = 257 $[M]^+$.

4-(*p*-Tolylthio)aniline (3h): The product was obtained (ethyl acetate/petroleum ether, 1:3) as a slightly yellow solid in 57% yield. CAS: 22865-52-7. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.4 Hz, 2 H, Ar-H), 7.08–7.06 (m, 4 H, 1-H, Ar-H), 6.65 (d, J = 8.8 Hz, 2 H, Ar-H), 3.81 (br. s, 1 H, NH_2), 2.28 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 135.69, 135.68, 135.4, 129.8, 128.6, 122.3, 116.1, 21.1 ppm. GC–MS (EI): m/z = 215 $[M]^+$.

(4-Nitrophenyl)(*p*-tolyl)sulfane (3i): The product was obtained (ethyl acetate/petroleum ether, 1:20) as a yellow solid in 48% yield. CAS: 22865-48-1. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 9.2 Hz, 2 H, Ar-H), 7.44 (d, J = 8.0 Hz, 2 H, Ar-H), 7.27 (d, J = 8.0 Hz, 2 H, Ar-H), 7.13 (d, J = 8.8 Hz, 2 H, Ar-H), 2.42 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 145.5, 140.4, 135.2, 131.0, 126.8, 126.4, 124.2, 21.5 ppm. GC–MS (EI): m/z = 245 $[M]^+$.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and copies of the original ^1H and ^{13}C NMR spectra of all compounds.

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