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Cu-Catalyzed Synthesis of Diaryl Thioethers and *S*-Cycles by Reaction of Aryl Iodides with Carbon Disulfide in the Presence of DBU

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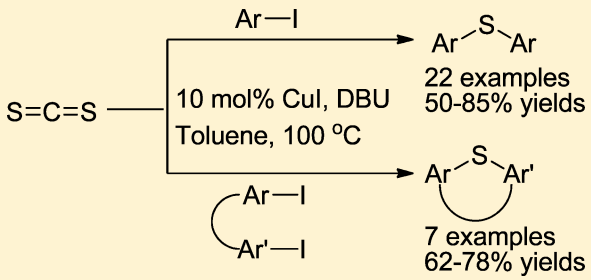
Supporting Information

ABSTRACT: Diaryl thioethers and *S*-cycles were obtained on the basis of the copper-catalyzed reaction of carbon disulfide and aryl iodides in the presence of DBU. This reaction enables the one-pot synthesis of diaryl thioethers by employing cheap, available, and easy-to-handle carbon disulfide with aryl iodides. The reaction was successfully employed in the construction of sulfur-containing cyclic molecules.



INTRODUCTION

Sulfur-containing organic molecules are a very important motif; particularly, diaryl thioethers and their derivatives have been recognized as imperative molecules in biological, pharmaceutical, and material interest.[1,2] The traditional methods for the synthesis of diaryl thioethers involve condensation of arenethiols with aryl halides[3] and treatment of aryl lithium or Grignard reagents with sulfurated electrophiles.[4] However, these methods often require harsh reaction conditions and are not suitable for molecules containing sensitive functional groups.[5] The development of transition-metal-catalyzed coupling of arenethiols with aryl halides or pseudohalides has overcome these difficulties to a great extent. A number of reactions have been developed for the synthesis of diaryl thioethers using Pd,[6] Cu,[7] Fe,[8] and other metal catalysts.[9] However, these metal-catalyzed reactions require foul-smelling, expensive, and less available arenethiols. In addition, arenethiols are prone to undergo oxidative homocoupling to produce disulfides as byproducts. To solve these drawbacks, persulfides have been employed,[10] but these require a stoichiometric amount of reductant. Recently, thiourea,[11] thiolates,[12] and metal sulfides[13,14] have been reported as sulfur sources in the formation of diaryl thioethers. However, using thiourea and thiolates as sulfur source are limited to use Pd/P-ligand as catalyst, and using metal sulfides as sulfur source requires high temperature and long reaction time. Therefore, the development of a foul-smell-free, cheap, and easy-to-handle method using a sulfur surrogate for the synthesis of diaryl sulfides is still desirable. As part of our continuous effort toward copper-catalyzed C−S bond formation and its application in heterocyclic synthesis using CS_2,[15] herein, we report a simple, mild, functional group-tolerant system for the synthesis of the diaryl thioethers and *S*-cyclic compounds based on Cu-catalyzed reaction of CS_2 and aryl iodides under ligand-free conditions.

RESULTS AND DISCUSSION

In the preliminary experiment, we used iodobenzene **1a** and carbon disulfide as starting materials and Cs_2CO_3 as base in toluene at 100 °C; diphenyl sulfide **2a** was not obtained (Table 1, entry 1). Then several bases were screened under the same reaction conditions. Clearly, inorganic bases such as K_3PO_4, KOH, and ^{t}BuONa as well as organic bases such as Et_3N and 1,4-diazabicyclo[2.2.2]octane (DABCO) were ineffective under the condition (entries 2−6). To our delight, when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as base, the reaction proceeded smoothly, and **2a** was obtained in 91% yield (entry 7). We then examined the effect of different solvents, such as dioxane, THF, MeCN, and dimethyl formamide (DMF) (entries 8−11). Of all the solvents tested, toluene as solvent afforded satisfying yield (entry 7). The reactiveness also depended on reaction temperature. When the reaction temperature was reduced to 80 °C, the yield of product was decreased to 21% (entry 12). On the other hand, without CuI, the reaction did not proceed (entry 13). Furthermore, the effect of other copper salts was also examined. CuBr and CuCl as catalyst gave product in 65 and 49% yields, respectively (entries 14−15). CuI proved to be the best choice among the screened copper salts under the reaction conditions (entry 7). The reaction also showed a strong dependence on the amount of DBU. When the DBU was used in 1 and 3 equiv, the desired product was formed in 27 and 61% yields, respectively (entry 16−17).

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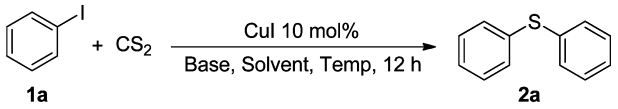
Table 1. Optimization between Iodobenzene 1a and Carbon Disulfide[a]



1a 2a

entry	base	solvent	temp (°C)	yield (%)[b]
1	Cs_2CO_3	toluene	100	NR
2	K_3PO_4	toluene	100	NR
3	KOH	toluene	100	NR
4	^tBuONa	toluene	100	NR
5	Et_3N	toluene	100	NR
6	DABCO	toluene	100	NR
7	DBU	toluene	100	91 (85)
8	DBU	dioxane	100	89 (81)
9	DBU	THF	100	16
10	DBU	CH_3CN	100	68
11	DBU	DMF	100	3
12	DBU	toluene	80	21
13	DBU	toluene	100	NR[c]
14	DBU	toluene	100	65[d]
15	DBU	toluene	100	49[e]
16	DBU	toluene	100	27[f]
17	DBU	toluene	100	61[g]

[a]Reaction condition: 1 mmol of 4-iodobenzene, 1 mmol of carbon disulfide, 0.1 mmol of CuI, and 2 mmol of base in 1.5 mL of solvent for 12 h. [b]Yield was determined by the GC using *n*-dodecane as the internal standard; isolated yield was given in brackets. [c]Without using CuI. [d]CuBr (10 mol %) was employed. [e]CuCl (10 mol %) was employed. [f]DBU (1 mmol) was used. [g]DBU (3 mmol) was used.

On the basis of these results, the optimal conditions involved the following parameters: CuI as catalyst, DBU as base, toluene as solvent, and reaction temperature at 100 °C. Under the optimized condition, a study on the substrate scope was carried out, and the representative results are summarized in Table 2. Different aryl iodides were transformed into corresponding diaryl sulfides in moderate to excellent yields ranging from 50 to 85%. Both an electron-donating and an electron-withdrawing group at *ortho*-position of aryl iodides afforded the corresponding diaryl sulfides in good yields (entries 2−6). To our delight, the crystal of **2d** was suitable for single crystal analysis, and its structure was fully characterized by X-ray diffraction analysis. Under the same reaction conditions, 1-iodo-3-methylbenzene **1g** and methyl 3-iodobenzoate **1h** showed 65 and 67% yields, respectively (entries 7 and 8). Furthermore, substitution at the *para*-position of iodobenze did not affect the reaction either (entries 9−14). Even with stronger electron-withdrawing group such as CO_2Me or CF_3 group on *para*-position of the iodobenzene could also succeed to generate desired product in 65 and 78% isolated yields, respectively (entries 13−14). When 1-iodonaphthalene **1o** was used as a substrate, the desired product **2o** was also formed in 84% yield (entry 15). 4-Iodo-1,1′-biphenyl **1p** also afforded the corresponding diaryl sulfide in 56% yield (entry 16). Multisubstituent on iodobenzene could also give the corresponding products in satisfying yield with prolonged reaction time to 48 h. For instance, when 1-iodo-2,4-dimethylbenzene **1q** and 2-iodo-1,4-dimethylbenzene **1r** were used, the desired product **2q** and **2r** were obtained in 70 and 68% yields, respectively (entries 17−18). Sterically hindered mesityl iodide **1s** was transformed into the corresponding diaryl sulfide **2s** in 50% (entry 19). It is noteworthy that heteroaromatic substrates such as 4-iodopyridine **1t**, 2-iodopyridine **1u**, and 2-iodothiophene **1v** were employed to afford the corresponding product in good yields (entries 20−22). In the cases where *p*-chloroiodobenzene and *p*-bromoiodobenzene were employed, the corresponding diaryl sulfides were obtained (entries 11−12). This result implied that there was good chemoselectivity between iodide, bromide, and chloride functional groups, although bromobenzene and chlorobenzene did not perform the reaction to afford diphenyl sulfide under the optimal conditions.

Next, we tried the possibility of applying this catalytic system in the reaction of two different aryl iodides by using iodobenzene **1a** and 1-iodo-4-methoxybenzene **1i**. When the ratio of two substrates was 1:1, 49% cross-coupling product **2ai** was obtained, while homocoupling products **2a** and **2i** were obtained in 22 and 20% yields, respectively (Scheme 1).

Having established an effective catalytic system for the coupling reactions of aryl iodides with CS_2, we also tried a variety of diiodoaryl compounds. The results are summarized in Table 3. When 2,2′-diiodobiphenyl **3a** and 2-iodo-1-(2-iodophenyl)-1*H*-pyrrole **3b** were used, the desired product **4a** and **4b** were formed in 75 and 62% yields, respectively (entries 1−2). When 1,2-diiodobenzene **3c** and 2,2′-oxybis(iodobenzene) **3d** were employed, thianthrene **4c** and phenoxathiine **4d** were formed in 65 and 72% yields, respectively (entries 3−4). Furthermore, (*Z*)-1-iodo-2-(2-iodovinyl)benzene derivatives were used to displace diioaryl compounds, and benzo[*b*]thiophene **4e**, **4f** were obtained in good yields (entry 5−6). Finally, diiododiene **3g** was used in the reaction, and thiophene **4g** was also obtained in 78% yield (entry 7).

On the basis of the above results, the mechanism of this reaction is proposed as shown in Scheme 2. It is reported that DBU reacted with CS_2 to yield compound **5** and $DBUH^+SH^-$ **6**.[16] CuI reacts with $DBUH^+SH^-$ **6** to generate CuSH **7**,[7i] which reacts with aryl iodide by oxidative addition to form intermediate **8**. Then the intermediate **8** transforms into complex **9**[7i] via reductive elimination and ligand exchange in the presence of DBU. Aryl iodide reacts with complex **9** by oxidative addition to form compound **10**, which undergoes reductive elimination to afford product **2** and releases CuI.

CONCLUSIONS

An efficient methodology for the C−S coupling of aryl iodides applying carbon disulfide as a cheap, available and easy-to-handle sulfide surrogate was developed. The new methodology could be used to synthesize symmetrical diaryl thioethers in high to excellent yields. The reaction was successfully transferred to synthesis of dibenzo[*b*,*d*]thiophene, benzo[*d*]-pyrrolo[2,1-*b*]thiazole, thianthrene, phenoxathiine, dibenzothiophene, and thiophene in high yields. This unprecedented reaction provides potential access to valuable structures for drug discovery and material sciences.

EXPERIMENTAL SECTION

General Comments. All the reactions were carried out in predried screwcapped tubes with Teflon-lined septum under N_2 atmosphere. Unless indicated, all materials were obtained from commercial sources and used as received. Dioxane, THF, toluene and CH_3CN were fresh distilled, while DMF was dried by molecular sieve. Column chromatography was performed on silica gel (particle size 200−300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on 300 or 400 MHz at ambient temperature with $CDCl_3$ or DMSO-d_6 as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual

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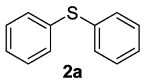
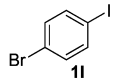
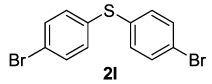
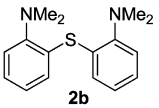
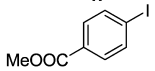
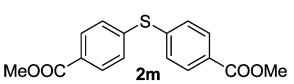
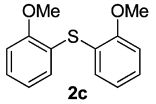
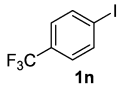
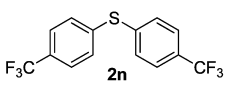
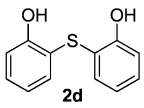
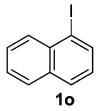
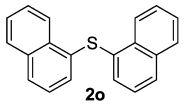
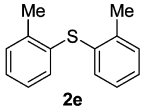
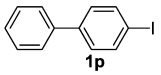
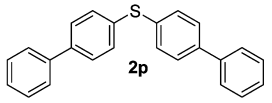
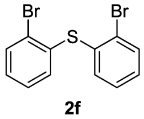
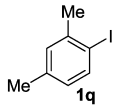
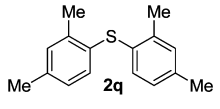
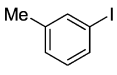
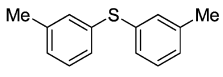
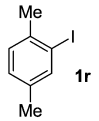
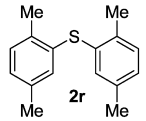
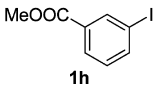
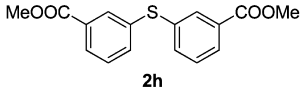
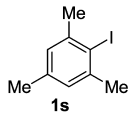
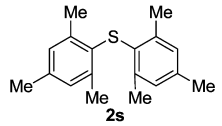
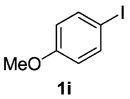
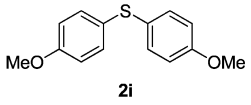
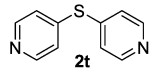
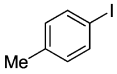
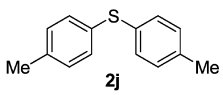
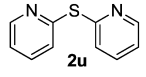
Table 2. Copper-Catalyzed Reaction of Different Aryl Iodides with CS_2[a]

entry	substrate **1**	product	yield (%)[b]	entry	substrate **1**	product	yield (%)[b]
1	 **1a**	 **2a**	85	12	 **1l**	 **2l**	74
2	 **1b**	 **2b**	78	13	 **1m**	 **2m**	65
3	 **1c**	 **2c**	83	14	 **1n**	 **2n**	78
4	 **1d**	 **2d**	81	15	 **1o**	 **2o**	84
5	 **1e**	 **2e**	75	16	 **1p**	 **2p**	56
6	 **1f**	 **2f**	67	17	 **1q**	 **2q**	70[c]
7	 **1g**	 **2g**	65	18	 **1r**	 **2r**	68[c]
8	 **1h**	 **2h**	67	19	 **1s**	 **2s**	50[c]
9	 **1i**	 **2i**	80	20	 **1t**	 **2t**	75
10	 **1j**	 **2j**	68	21	 **1u**	 **2u**	66
11	**1k**	**2k**	70	22	**1v**	**2v**	70

[a]Reaction conditions: 1 mmol of aryl iodides, 1 mmol of carbon disulfide, 0.1 mmol of CuI, and 2 mmol of DBU in 1.5 mL of toluene at 100 °C for 12 h. [b]Isolated yields. [c]Reaction time is 48 h.

Scheme 1. Reaction of Two Different Aryl Iodides and Carbon Disulfide

proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (J) were given in Hertz (Hz). The mass analyzer type was Q-TOF used for the HRMS measurements. The term m, q, d, s referred to multiplet, quartet, doublet, and singlet. The reaction progress was monitored by GC. GC yields, using *n*-dodecane as the internal standard, were obtained in proportion to the integral area of *n*-dodecane signal. 2,2′-Diiodobiphenyl **3a**, 2-iodo-1-(2-iodophenyl)-1*H*-pyrrole **3b**, 2,2′-oxybis(iodobenzene) **3d** were formed according to literature reports.[17] (*Z*)-1-Iodo-2-(4-iodohex-3-en-3-yl)benzene **3e**, (*Z*)-1-iodo-2-(1-iodo-1-phenylhex-1-en-2-yl)benzene **3f**, (3*Z*,5*Z*)-4,5-diethyl-3,6-diiodoocta-3,5-diene **3g** were obtained according to literature reports.[18]

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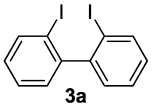
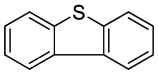
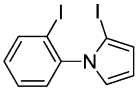
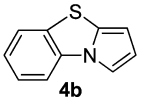
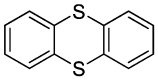
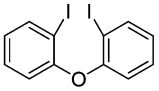
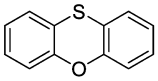
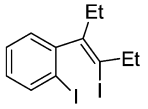
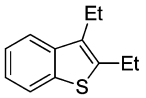
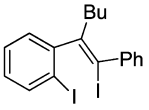
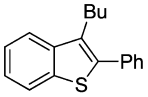
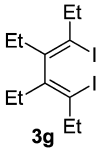
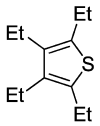
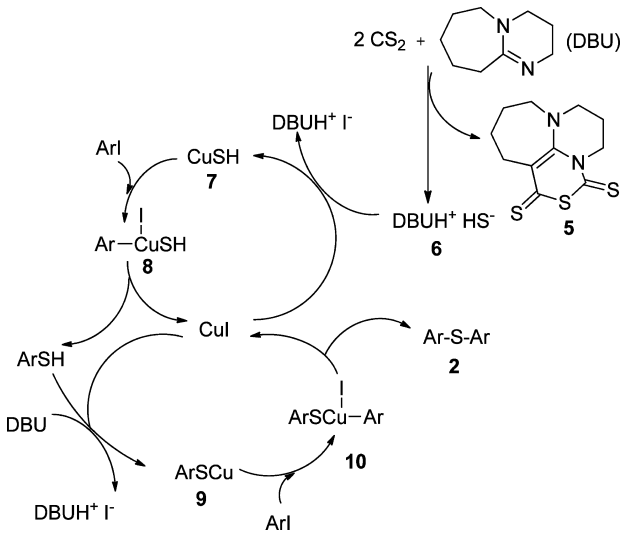
Table 3. Synthesis of Various Sulfide-Containing Cyclic Compounds[a]

entry	substrate	product	yield (%)[b]
1	 **3a**	 **4a**	75
2	 **3b**	 **4b**	62
3	 **3c**	 **4c**	65
4	 **3d**	 **4d**	72
5	 **3e**	 **4e**	74
6	 **3f**	 **4f**	68
7	 **3g**	 **4g**	78

[a]Reaction conditions: 0.5 mmol of diiodoaryls, 1 mmol of carbon disulfide, 0.1 mmol of CuI, and 2 mmol of DBU in 1.5 mL of toluene at 100 °C for 12 h. [b]Isolated yields.

Scheme 2. Proposed Mechanism



General Procedure for the Synthesis of Product 2. A sealed tube was charged with the mixture of aryl iodide **1** (1 mmol), carbon disulfide (1 mmol), CuI (0.1 mmol), DBU (2 mmol) and then stirred in toluene (1.5 mL) at 100 °C under nitrogen atmosphere for indicated time. After completion, H_2O (5 mL) was added, and the mixture was extracted with EtOAc (5 mL × 3) and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether) provided the corresponding product **2**.

*Diphenyl sulfide (**2a**).*[13a] Colorless liquid: 158 mg (85% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.36 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.2, 129.3, 131.2, 135.9.

*2,2′-Thiobis(N,N-dimethylaniline) (**2b**).* Yellow solid: 212 mg (78% yield), mp 54−56 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.84 (s, 12 H), 6.93−7.21 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.6, 119.3, 123.4, 127.5, 130.4, 132.5, 153.6; HRMS (ESI positive mode) calcd for $C_{16}H_{20}N_2S$ + H^+ 273.1425, found 273.1430; ESI-MS $[M + H]^+$ m/z 273.2.

*2,2′-Dimethoxy diphenyl sulfide (**2c**).*[13a] Yellow liquid: 204 mg (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 6H), 6.85−6.92 (m, 4H), 7.04−7.07 (m, 2H), 7.22−7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.0, 110.9, 121.3, 122.7, 128.5, 132.0, 157.9.

*2,2′-Thiodiphenol (**2d**).*[19] Light yellow solid: 177 mg (81% yield); ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.72−6.77 (m, 2 H), 6.88−6.93 (m, 4 H), 7.08−7.13 (m, 2 H), 9.81 (br, 2 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 115.4, 119.7, 120.0, 128.3, 131.6, 156.0.

*Di-o-tolyl sulfide (**2e**).*[13a] White solid: 161 mg (75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 6H), 7.05−7.11 (m, 4H), 7.15−7.19 (m, 2H), 7.24 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 126.8, 127.2, 130.6, 131.2, 134.4, 139.0.

*2,2′-Dibromo diphenyl sulfide (**2f**).*[13b] Light yellow solid: 230 mg (67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11−7.16 (m, 4 H), 7.21−7.25 (m, 2 H), 7.63 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.9, 128.3, 128.9, 132.5, 133.6, 135.8.

*Di-m-tolyl sulfide (**2g**).*[20] Yellow liquid: 137 mg (64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 6H), 6.95 (d, J = 7.3 Hz, 2H), 7.04 (d, J = 7.8 Hz, 2H), 7.34−7.38 (m, 1H), 7.07−7.11 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 128.0, 128.2, 129.1, 131.7, 135.7, 139.1.

*Bis(m-dimethoxycarbonylphenyl) sulfide (**2h**).* Yellow solid: 202 mg (67% yield), mp 79−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 6H), 7.34−7.37 (m, 2H), 7.47 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 8.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 128.6, 129.5, 131.4, 132.2, 135.5, 136.0, 166.3; HRMS (ESI positive mode) calcd for $C_{16}H_{14}O_4S$ + H^+ 303.0687, found 303.0685; ESI-MS $[M + Na]^+$ m/z 325.1.

*4,4′-Dimethoxy diphenyl sulfide (**2i**).*[13a] Yellow liquid: 197 mg (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 6H), 6.83 (d, J = 8.7 Hz, 4H), 7.28 (d, J = 8.7 Hz, 4H),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 114.9, 127.5, 132.8, 159.1.

*Di-p-tolyl sulfide (**2j**).*[13a] White solid: 146 mg (68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 7.10 (d, J = 7.8 Hz, 2H), 7.22−7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 130.0, 131.2, 132.8, 137.0.

*4,4′-Dichloro diphenyl sulfide (**2k**).*[13a] White solid: 178 mg (70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.29 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.6, 132.4, 133.6, 134.0.

*4,4′-Dibromo diphenyl sulfide (**2l**).*[13a] White solid: 255 mg (74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.3 Hz, 4H), 7.43 (d, J = 8.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.6, 132.6, 132.7, 134.6.

*Bis(p-dimethoxycarbonylphenyl) sulfide (**2m**).* White solid: 196 mg (65% yield), mp 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 6H), 7.36 (d, J = 8.2 Hz, 4H), 7.95 (d, J = 8.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 129.1, 130.5, 140.9, 166.5; HRMS (ESI positive mode) calcd for $C_{16}H_{14}O_4S$ + H^+ 303.0689, found 303.0687; ESI-MS $[M + Na]^+$ m/z 325.1.

*4,4′-Trifluoromethyl diphenyl sulfide (**2n**).*[11] White solid: 251 mg (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.1 (q,

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J_{F-C} = 272.2 Hz), 126.4 (q, J_{F-C} = 3.8 Hz), 129.8 (q, J_{F-C} = 33.6 Hz), 131.2, 139.7.

*Bis(1-naphthyl) sulfide (**2o**).*[13a] Light yellow solid: 240 mg (84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.35 (m, 4H), 7.54−7.58 (m, 4H), 7.79−7.81 (m, 2H), 7.90−7.92 (m, 2H), 8.45−7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.2, 126.0, 126.5, 126.9, 128.1, 128.7, 130.0, 132.5, 132.7, 134.2.

*Bis([1,1′-biphenyl]-4-yl) sulfide (**2p**).*[21] White solid: 189 mg (56% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36−7.40 (m, 2H), 7.45−7.49 (m, 8H), 7.63−7.72 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 126.6, 127.8, 127.8, 129.0, 131.3, 133.9, 139.2, 139.3.

*Bis(2,4-dimethylphenyl) sulfide (**2q**).*[11] Colorless liquid: 169 mg (70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 6H), 2.36 (s, 6H), 6.91−6.98 (m, 4H), 7.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.1, 127.5, 131.2, 131.3, 131.4, 137.0, 138.8.

*Bis(2,5-dimethylphenyl) sulfide (**2r**).*[11] White solid: 165 mg (68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 6H), 2.36 (s, 6H), 6.92 (s, 2H), 6.99 (d, J = 10.1 Hz, 2H), 7.14 (d, J = 10.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 21.0, 128.0, 130.4, 131.7, 134.1, 135.8, 136.4.

*Dimesityl sulfide (**2s**).*[22] White solid: 135 mg (50% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 12 H), 2.24 (s, 6 H), 6.83 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 21.8, 129.4, 131.2, 136.6, 140.4.

*Bis(4-pyridyl) sulfide (**2t**).*[13b] Yellow solid: 141 mg (75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 4.6 Hz, 2H), 8.47 (d, J = 4.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.8, 144.0, 150.4.

*Bis(2-pyridyl) sulfide (**2u**).* Red solid: 124 mg (66% yield), mp 218−220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08−7.13 (m, 2 H), 7.37−7.40 (m, 2 H), 7.54−7.59 (m, 2 H), 8.47−8.49 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.8, 125.8, 137.1, 150.2, 156.8, $[M + H]^+$ m/z 189.4.

*Bis(2-thiophenyl) sulfide (**2v**):*[11] Light yellow liquid: 139 mg (70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95−6.97 (m, 2H), 7.21−7.22 (m, 2H), 7.33−7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.6, 129.8, 132.9, 135.6.

General Procedure for the Synthesis of Product 4. A sealed tube was charged with the mixture of diiodoaryl compound **3** (0.5 mmol), carbon disulfide (1 mmol), CuI (0.1 mmol), DBU (2 mmol) and then stirred in toluene (1.5 mL) at 100 °C under nitrogen atmosphere for indicated time. After completion, H_2O (5 mL) was added, and the mixture was extracted with EtOAc (5 mL × 3) and dried by anhydrous Na_2SO_4. Evaporation of the solvent followed by purification on silica gel (petroleum ether) provided the corresponding product **4**.

*Dibenzo[b,d]thiophene (**4a**).*[14a] White solid: 69 mg (75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.33 (m, 2H), 7.70−7.73 (m, 1H), 7.99−8.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.7, 122.9, 124.4, 126.8, 135.6, 139.5.

*Benzo[d]pyrrolo[2,1-b]thiazole (**4b**).*[23] White solid: 54 mg (62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, J = 3.6 Hz, 1 H), 6.58−6.59 (m, 1H), 7.17−7.21 (m, 1H), 7.29−7.33 (m, 1H), 7.42−7.43 (m, 1H), 7.50 (d, J = 7.8 Hz, 1 H), 7.56 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 98.9, 110.4, 111.7, 114.9, 123.7, 123.9, 125.5, 127.8, 131.7, 134.7.

*Thianthrene (**4c**).*[24] White solid: 70 mg (65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15−7.18 (m, 4H), 7.40−7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.8, 128.9, 135.7.

*Phenoxathiine (**4d**).* White solid: 72 mg (72% yield), mp 54−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.6 Hz, 3 H), 1.39 (t, J = 7.5 Hz, 3 H), 2.86 (q, J = 7.6 Hz, 2 H), 2.94 (q, J = 7.5 Hz, 2 H), 7.28−7.33 (m, 1 H), 7.36−7.41 (m, 1 H), 7.69 (d, J = 7.5 Hz, 1 H), 7.82 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 117.9, 120.2, 124.6, 126.9, 127.8, 152.3, M^+ m/z 200.3.

*2,3-Diethylbenzo[b]thiophene (**4e**).*[14a] Colorless liquid: 70 mg (74% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, J = 7.6 Hz, 3 H), 1.39 (t, J = 7.5 Hz, 3 H), 2.86 (q, J = 7.6 Hz, 2 H), 2.94 (q, J = 7.5 Hz, 2 H), 7.28−7.33 (m, 1 H), 7.36−7.41 (m, 1 H), 7.69 (d, J = 7.5 Hz, 1 H), 7.82 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 16.4, 19.7, 21.9, 121.3, 122.4, 123.4, 123.8, 132.6, 138.5, 140.2, 141.4.

*3-Butyl-2-phenylbenzo[b]thiophene (**4f**).*[14a] Colorless liquid: 90 mg (68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (q, J = 7.2 Hz, 3H), 1.35−1.47 (m, 2H), 1.64−1.76 (m, 2H), 2.87−2.94 (m, 2H), 7.35 (m, 1H), 7.38−7.44 (m, 2H), 7.47 (m, 2H), 7.55 (m, 2H), 7.78 (m, 1H), 7.83−7.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 23.0, 26.8, 32.6, 122.4, 122.4, 124.2, 124.2, 128.0, 128.7, 129.8, 132.9, 135.0, 138.3, 139.4, 140.6.

*2,3,4,5-Tetraethylthiophene (**4g**).*[14a] Colorless liquid: 77 mg (78% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (t, J = 7.5 Hz, 6 H), 1.28 (t, J = 7.6 Hz, 6 H), 2.50 (q, J = 7.6 Hz, 4 H), 2.76 (q, J = 7.4 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.7, 16.5, 20.3, 21.4, 136.8, 138.0.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of spectra for all compounds and the crystallographic data of product **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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