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Oxidative Coupling of Dichalcogenides with Sodium Sulfinates via Copper-Catalyzed Cleavage of S−S and Se−Se Bonds

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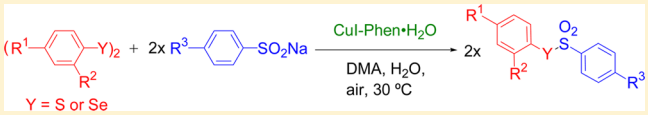
Supporting Information

ABSTRACT: A copper-catalyzed sulfonylation of disulfides was achieved using sodium sulfinates in air. The reaction formed various sulfur−sulfone bonds efficiently and afforded thiosulfonates in good yields. Selenosulfonates could also be prepared with this procedure. Furthermore, both chalcogenide groups on the dichalcogenides were available in these reactions.



INTRODUCTION

The development of transition metal-catalyzed organosulfur syntheses is of much importance in organic chemistry.[1] In particular, the formation of sulfur−carbon bonds has already been investigated. The products of these reactions have found widespread use as reagents or intermediates.[2,3]

However, exploration of the construction of a sulfur−heteroatom bond has been slow.[1,4] The synthetic method remains unchanged. Similarly, the formation of thiosulfonates having sulfur−sulfone bonds, which are still generally prepared by traditional procedures, is difficult.

It is known that the oxidation of symmetrical disulfides[5] or the coupling of a disulfide with sodium thiosulfinate occurs in the presence of excess $AgNO_3$[6] or oxidants such as iodine[7c,d] or NBS[7e] (Figure 1). These oxidants work via the production of a radical or cation species.[7] Unfortunately, the catalytic procedure using disulfides has not been explored. A similar reaction using thioimide has recently been performed using a $Sc(OTf)_2$ catalyst.[8]

Notably, the reaction of a thiol with sulfonyl chloride cannot be used to prepare the corresponding thiosulfonates, unlike the analogous synthesis of sulfonamide. The procedure usually affords disulfide as a major product owing to the rapid reaction of thiols with thiosulfonates.[9] Therefore, the development of such a convenient catalytic method using disulfides or thiols is desirable.

Thiols and disulfides are well-known to be poisons for transition metals. The employment of these compounds often gives transition metal−thiolate complexes that are stable and inactive.[10] Consequently, the combination of transition metals with thiols stops reactions. To activate the metal−thiolates, the conversion of oxidation states is required.

For example, the reactions of copper-thiolates with aryl halides give aryl sulfides in good yields.[11] This indicates that the oxidation of metal−thiolates can promote the reaction and that oxidative reaction conditions are necessary for transition metal-catalyzed sulfonylation using disulfides or thiols. However, sulfonylation using disulfides has yet to be developed.

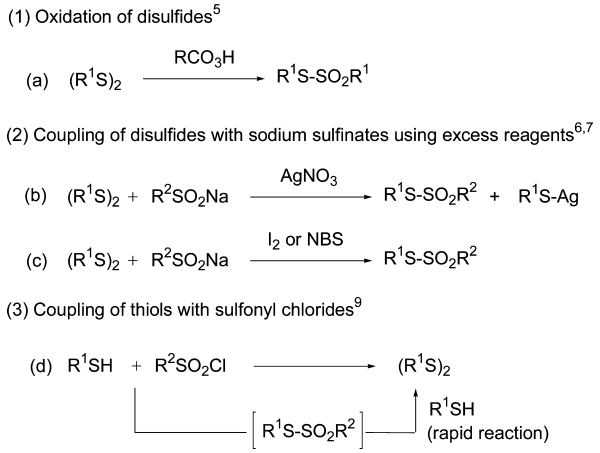


Figure 1. Sulfonylation of disulfides.

As a general rule, disulfides are more stable than thiols, which are air-sensitive and have rank odors. Accordingly, the exploitation of reactions using disulfides is justified.

Recently, it was found that a copper-catalyzed synthesis of thiosulfonates from thiols with sodium sulfinates could be performed under an oxygen atmosphere.[12] This method can suppress the formation of disulfides as byproducts. In addition, copper salts are able to cleave disulfide bonds.[13] These facts show that the sulfonylation of disulfides is enabled by the presence of a copper catalyst (Figure 2). It would seem that the oxidation of $R^1SCu(I)$ as an intermediate would produce active $R^1SCu(II)$; however, a catalytic method toward this end has not been established to date.

One approach to solve this problem may be to perform this reaction under mild oxidative conditions. With this, the copper-catalyzed sulfonylation of disulfides was achieved under air. Furthermore, diselenides were also reactive under these conditions. The procedure consumed both chalcogenide groups

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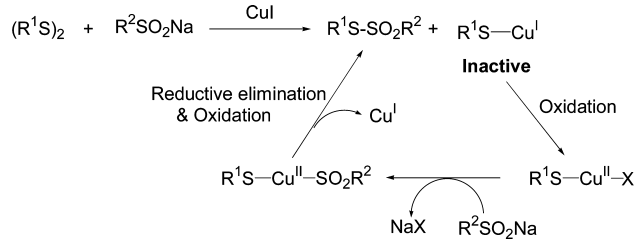


Figure 2. Strategy for a copper-catalyzed sulfonylation of disulfides.

on the dichalcogenides completely. In this article, this methodology will be described.

RESULTS AND DISCUSSION

Preparation of Thiosulfonates from Disulfides and Sodium Sulfinates. Initially, to establish suitable conditions, a mixture of bis(4-methylphenyl)disulfide **1a** with sodium benzenesulfinate **2a** was surveyed in air. As shown in Table 1, in the absence of CuI catalyst, the reaction did not occur, and disulfide was recovered (entry 1). Similarly, CuI itself gave the same result (entry 2). Fortunately, the addition of amine ligands such as 1,10-phenanthroline·H_2O (Phen·H_2O) or *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TMEDA) increased the yield of thiosulfonate **3aa** to 72 or 67%, respectively (entries 3 and 4). Then, to improve the reactivity of copper catalyst, NH_4BF_4 was added, which led to an 80% yield of **3aa** without recovery of disulfide (entry 5).[14] The reaction afforded the best result at 30 °C (entry 6). Although other additives such as NH_4PF_6 or Cs_2CO_3 were tested, these salts could not promote the reactivity satisfactorily (entries 7 and 8). In the evaluation of other solvents or copper catalysts, desired results were not obtained (entries 9−15).

On the basis of the previously described method, the scope and limitations of the optimized conditions were screened (Table 2). When the mixture of diaryl disulfides **1** with sodium sulfinates **2** was treated by CuI-Phen·H_2O in air, the expected thiosulfonates **3** were obtained in excellent yields. The use of sodium sulfinates or disulfides having electron-withdrawing groups slightly decreased the reactivity (entries 4, 5, and 12−14). Unfortunately, the reaction using diaryl disulfides with a nonprotected group did not give the corresponding products, and a complex mixture was detected (entries 10 and 11). On the contrary, dialkyl disulfides were successful reagents under the reaction conditions (entries 18−20). However, the reaction of bis(*t*-butyl) disulfide was not successful under an oxygen atmosphere (entry 21).

Application to Preparation of Selenosulfonates using Diselenides. Attention was then focused toward the coupling of diselenides (**4**) with sodium sulfinates (**2**). As shown in Table 3, numerous combinations of diselenides with sodium sulfinates gave good results. These reactions required 20 mol % of CuI-Phen·H_2O catalyst and are successful in DMA without the addition of H_2O (0.1 mL). However, some reactions required the addition of water to promote the reactivity (entries 4, 11, and 13).

Thus, the copper-catalyzed sulfonylation of disulfides or diselenides using sodium sulfinates could be used effectively to synthesize thiosulfonates or selenosulfonates and could efficiently use the two chalcogenide groups on the dichalcogenide reagents.

Although the coupling of ditelluride with sodium sulfinate was attempted, the expected reaction ultimately did not proceed, and the production of complex mixtures was observed (Scheme 1).

Scheme 1. Reactivity of Ditellureide

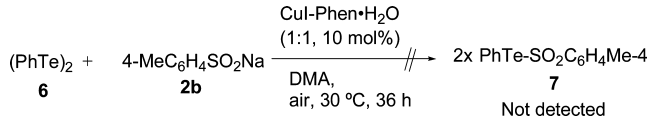
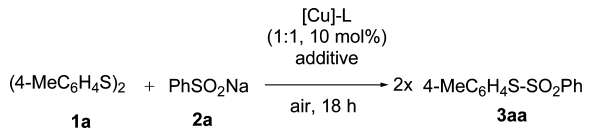


Table 1. Investigation of Conditions[a]



entry	[Cu] (mol %)	solvent	add.	temp. (°C)	3aa/1a[b]	3aa (%)
1	none	DMA/H_2O (3:1)	none	30	0:100	0
2	CuI	DMA/H_2O (3:1)	none	30	0:100	0
3	CuI-Phen·H_2O	DMA/H_2O (3:1)	none	30	95:5	72
4	CuI-TMEDA	DMA/H_2O (3:1)	none	30	90:10	67
5	CuI-Phen·H_2O	DMA/H_2O (3:1)	NH_4BF_4	30	100:0	80
6		DMA/H_2O (3:1)	NH_4BF_4	100	80:20	49
7		DMA/H_2O (3:1)	NH_4PF_4	30	70:30	51
8		DMA/H_2O (3:1)	Cs_2CO_3	30	100:0	36
9		DMF/H_2O (3:1)	NH_4BF_4	30	77:23	65
10		DMSO/H_2O (3:1)	NH_4BF_4	30	100:0	58
11	CuCl-Phen·H_2O	DMA/H_2O (3:1)	NH_4BF_4	30	91:9	64
12	CuBr-Phen·H_2O	DMA/H_2O (3:1)	NH_4BF_4	30	83:17	61
13	$CuCl_2$-Phen·H_2O	DMA/H_2O (3:1)	NH_4BF_4	30	91:9	77
14	$CuBr_2$-Phen·H_2O	DMA/H_2O (3:1)	NH_4BF_4	30	79:21	52
15	$Cu(OAc)_2$-Phen·H_2O	DMA/H_2O (3:1)	NH_4BF_4	30	83:17	53

[a]A mixture of **1a** (0.15 mmol), **2a** (0.33 mmol), and additive (0.15 mmol) in DMA (0.3 mL) and H_2O (0.1 mL) was treated in air. [b]The ratio was determined by ^1H NMR.

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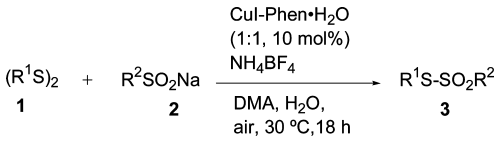
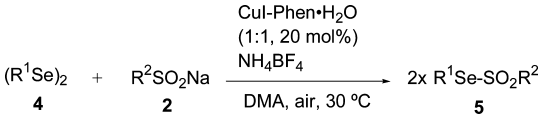
Table 2. Copper-Catalyzed Coupling of Disulfides with Sodium Sulfinates[a]



entry	R^1	R^2	time (h)	3	3 (%)
1	$(4\text{-MeC}_6H_4S)_2$	$PhSO_2Na$	18	**3aa**	81
2		$4\text{-MeC}_6H_4SO_2Na$	18	**3ab**	80
3[c]		$4\text{-MeOC}_6H_4SO_2Na$	18	**3ac**	77
4[c]		$4\text{-ClC}_6H_4SO_2Na$	36	**3ad**	66
5		$4\text{-FC}_6H_4SO_2Na$	36	**3ae**	72
6		$4\text{-AcHNC}_6H_4SO_2Na$	18	**3af**	65
7		$MeSO_2Na$	18	**3ag**	71
8	$(PhS)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3ba**	94
9	$(4\text{-MeOC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3ca**	74
10	$(4\text{-H}_2NC_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3da**	trace
11	$(4\text{-HOC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3ea**	trace
12	$(4\text{-ClC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**3fa**	65
13	$(4\text{-BrC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	19	**3ga**	61
14	$(4\text{-O}_2NC_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**3ha**	69[b]
15	$(2\text{-MeC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3ia**	78
16	$(2\text{-MeOC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**3ja**	70
17	$(2\text{-BrC}_6H_4S)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3ka**	54
18	$(MeS)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**3la**	79
19	$(PhCH_2S)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**3ma**	60[b]
20	$(n\text{-BuS})_2$	$4\text{-MeC}_6H_4SO_2Na$	48	**3na**	58[b]
21	$(t\text{-BuS})_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**3oa**	trace[b]

[a]Conditions: a mixture of **1** (0.15 mmol), **2** (0.33 mmol), and NH_4BF_4 (0.15 mmol) in DMA (0.3 mL) and H_2O (0.1 mL) was treated with CuI-Phen·H_2O under air. [b]The reaction was performed under an oxygen atmosphere.

Table 3. Copper-Catalyzed Sulfonylation of Diselenides[a]

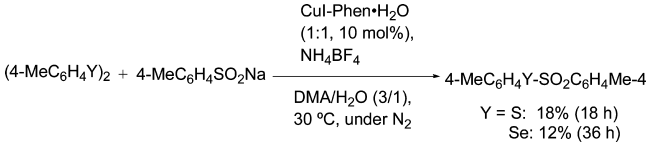


entry	R^1	R^2	time (h)	5	5 (%)
1	$(PhSe)_2$	$PhSO_2Na$	18	**5aa**	71
2		$PhSO_2Na$	18	**5aa**	51[b]
3		$4\text{-MeC}_6H_4SO_2Na$	18	**5ab**	66
4		$4\text{-MeC}_6H_4SO_2Na$	18	**5ab**	75[b]
5		$4\text{-MeC}_6H_4SO_2Na$	18	**5ab**	65[c]
6		$4\text{-MeOC}_6H_4SO_2Na$	36	**5ac**	68
7		$4\text{-ClC}_6H_4SO_2Na$	18	**5ad**	65
8		$4\text{-FC}_6H_4SO_2Na$	18	**5ae**	61
9		$4\text{-AcHNC}_6H_4SO_2Na$	18	**5af**	59
10	$(4\text{-MeC}_6H_4Se)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**5bb**	63
11	$(4\text{-MeOC}_6H_4Se)_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**5cb**	70[b]
12	$(1\text{-NaphthylSe})_2$	$4\text{-MeC}_6H_4SO_2Na$	36	**5db**	57
13	$(PhCH_2Se)_2$	$4\text{-MeC}_6H_4SO_2Na$	18	**5eb**	50[b]

[a]Conditions: a mixture of **4** (0.15 mmol), **2** (0.33 mmol), and NH_4BF_4 (0.15 mmol) in DMA (0.6 mL) was treated with CuI-Phen·H_2O under air. [b]The reaction was performed in DMA (0.3 mL) and H_2O (0.1 mL). [c]Phen was used instead of Phen·H_2O.

Proposed Reaction Mechanism of the Copper-Catalyzed Coupling of Dichalcogenides with Sodium Sulfinates. To elucidate the reaction mechanism, further experimentation was attempted. In the absence of oxygen, where the reaction was investigated under a nitrogen atmosphere, the corresponding products were produced at lower yields with the recovery of dichalcogenides (Scheme 2).

Scheme 2. Sulfonylation in the Absence of Oxygen



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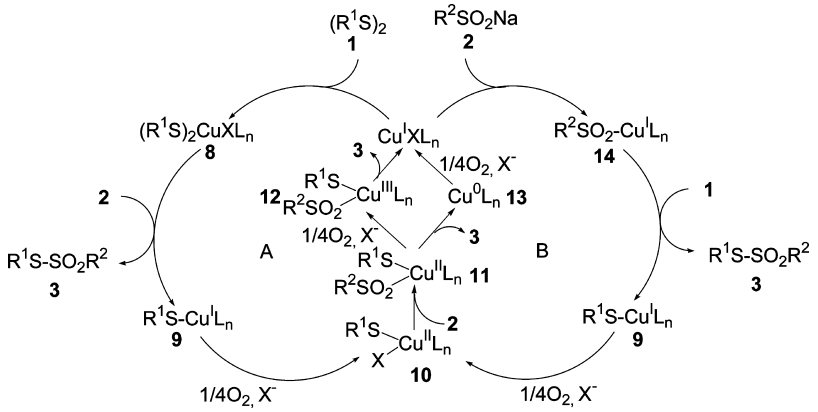
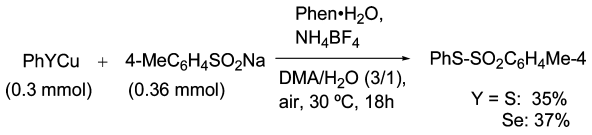


Figure 3. Plausible mechanism.

The reactivity of PhYCu(I) (Y = S or Se) was also examined (Scheme 3).[15] The reaction of PhYCu(I) with sodium 4-toluenesulfinate gave the corresponding thiosulfonate and selenosulfonate at yields of 35 and 37%, respectively.

Scheme 3. Reactivity of PhYCu(I)



These facts show that the procedure requires oxygen and that PhYCu(I) is formed as a reaction intermediate.

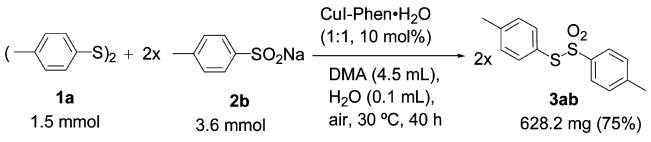
Given these results, a plausible mechanism was considered, as shown in Figure 3.[16] In cycle A, after the formation of complex **8** from disulfide **1** with Cu(I)X,[13] the reaction of **8** with sodium sulfinate **2** gives thiosulfinate **3** and copper thiolate **9** via reductive elimination. Subsequently, the oxidation of **9** produces $R^1SCu(II)X$ **10**[11], and $R^1S(R^2SO_2)Cu(II)$ **11** is obtained by the transmetalation. Finally, complex **11** gives thiosulfonate **3** and Cu(I)X after oxidation and then reductive elimination.

However, in cycle B, after the generation of sulfonyl copper complex **14** from sodium sulfinate **2** with Cu(I)X, the reaction of **14** with disulfide **1** affords thiosulfonate **3** and thiolate copper complex **9**. Consequently, the catalytic cycle is achieved and is able to consume both sulfide groups on the disulfides. Similarly, the same process is able to accommodate diselenide reagents.

In addition, it is expected that the rates of these two processes are different according to the distribution of substrates.

This developed procedure can be scaled up as follows (Scheme 4). When the amount of sulfonylation using bis(4-tolyl) disulfide was increased from 0.15 to 1.5 mmol, the corresponding thiosulfonate **3ab** was produced in 75% yield. To promote the reaction, the use of 0.1 mL of water was most important. However, a large quantity of water decreased the formation of **3ab**.[17] As a result, it was apparent that the presence of a small amount of water could promote the reaction.

Scheme 4. Large-Scale Sulfonylation of Disulfide



CONCLUSIONS

The sulfonylation of disulfides was achieved using sodium sulfinates under air. The procedure afforded numerous thiosulfonates in good yields. Furthermore, selenosulfonates could be readily synthesized. These reactions were able to use both chalcogenide groups on the dichalcogenide reagents. Although they were tested, ditellurides did not successfully yield the desired products under these conditions

EXPERIMENTAL SECTION

General Procedure and Chemicals. All reactions were carried out in air. ^1H and ^{13}C NMR spectra were recorded at 270 and 67.5 MHz, respectively. Chemical shifts are reported in δ ppm, referenced to an internal tetramethylsilane standard for ^1H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR. Compounds **3aa**,[7] **3ab**,[7] **3ac**,[5c] **3ad**,[5c,7] **3ae**,[7] **3ag**,[7] **3ba**,[7] **3ca**,[5c,7] **3fa**,[7] **3ga**,[7] **3ha**,[18] **3la**,[5] **3ma**,[6e] **5aa**,[3c] **5ab**,[3c] and **5ad**[3c] showed identical spectra to those reported in the literature.

Typical Procedure for Copper-Catalyzed Sulfonylation of Disulfides: Synthesis of *S*-4-Tolyl Benzenethiosulfonate (3aa) (Table 2, Entry 1). To a mixture of bis(4-tolyl) disulfide (37.0 mg, 0.15 mmol), sodium phenylsulfinate (54.2 mg, 0.33 mmol), and NH_4BF_4 (15.7 mg, 0.15 mmol) in DMA (0.3 mL) and H_2O (0.1 mL) were added CuI (2.9 mg, 0.015 mmol) and Phen·H_2O (3.0 mg, 0.015 mmol), and the mixture was stirred at 30 °C for 18 h in air using a balloon. After the residue was dissolved in Et_2O, the solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (30% diethyl ether/hexane) gave **3aa** (64.5 mg, 81%) as a white solid. mp 48−51 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.60−7.55 (m, 3H, Ar−H), 7.44 (d, J = 8.1 Hz, 2H, Ar−H), 7.24−7.21 (m, 2H, Ar−H), 7.13 (d, J = 8.1 Hz, 2H, Ar−H), 2.37 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 142.9, 142.1, 136.4, 133.5, 130.2, 128.7, 127.5, 124.3, 21.4; IR ($CHCl_3$) 1595, 1490, 1325, 1145 cm^{-1}; Anal. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58. Found: C, 59.00; H, 4.51.

*S-4-Tolyl 4-Toluenethiosulfonate (**3ab**).* The title compound was obtained as a white solid (67.1 mg, 80%). M: colorless crystals. mp 73−75 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 2H, Ar−H), 7.26−7.19 (m, 4H, Ar−H), 7.14 (d, J = 8.2 Hz, 2H, Ar−H), 2.42 (s, 3H, CH_3), 2.37 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.6, 142.0, 140.4, 136.4, 130.1, 129.3, 127.5, 124.5, 21.6, 21.4; IR ($CHCl_3$) 1595, 1491, 1327, 1143 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.31; H, 5.05.

*S-4-Tolyl 4-Methoxybenzenethiosulfonate (**3ac**).* The title compound was obtained as a white solid (68.0 mg, 77%). mp 54−55 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.51 (d, J = 8.5 Hz, 2H, Ar−H), 7.25

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(d, J = 8.5 Hz, 2H, Ar−H), 7.15 (d, J = 8.5 Hz, 2H, Ar−H), 6.87 (d, J = 8.5 Hz, 2H, Ar−H), 3.87 (s, 3H, CH_3), 2.38 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 163.5, 141.9, 136.5, 135.0, 130.2, 129.9, 124.7, 113.8, 55.7, 21.5; IR ($CHCl_3$) 1593, 1495, 1327, 1140 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_3S_2$: C, 57.12; H, 4.79. Found: C, 57.08; H, 4.76.

*S-4-Tolyl 4-Chlorobenzenethiosulfonate (**3ad**).* The title compound was obtained as a white solid (59.6 mg, 66%). mp 127−128 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 2H, Ar−H), 7.40 (d, J = 8.8 Hz, 2H, Ar−H), 7.25 (d, J = 8.8 Hz, 2H, Ar−H), 7.17 (d, J = 8.2 Hz, 2H, Ar−H), 2.39 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 142.4, 141.5, 140.1, 136.4, 130.4, 129.1, 128.9, 124.0, 21.5; IR ($CHCl_3$) 1582, 1475, 1331, 1146 cm^{-1}; Anal. Calcd for $C_{13}H_{11}ClO_2S_2$: C, 52.25; H, 3.71. Found: C, 55.21; H, 3.67.

*S-4-Tolyl 4-Fluorobenzenethiosulfonate (**3ae**).* The title compound was obtained as a white solid (61.5 mg, 72%). mp 103−105 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.62−7.56 (m, 2H, Ar−H), 7.27−7.22 (m, 2H, Ar−H), 7.17−7.06 (m, 4H, Ar−H), 2.39 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 165.4 (d, $^1J_{(C-F)}$ = 254 Hz), 142.3, 139.0 (d, $^4J_{(C-F)}$ = 3 Hz), 136.4, 130.4 (d, $^3J_{(C-F)}$ = 9 Hz), 127.5, 124.2, 116.0 (d, $^2J_{(C-F)}$ = 23 Hz), 21.5; IR ($CHCl_3$) 1588, 1491, 1331, 1142 cm^{-1}; Anal. Calcd for $C_{13}H_{11}FO_2S_2$: C, 55.44; H, 3.95. Found: C, 55.50; H, 3.91.

*S-4-Tolyl 4-Acetylaminobenzenethiosulfonate (**3af**).* The title compound was obtained as a white solid (62.7 mg, 65%). mp 175−176 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.73 (br, 1H, NH), 7.59 (d, J = 8.8 Hz, 2H, Ar−H), 7.49 (d, J = 8.8 Hz, 2H, Ar−H), 7.24 (d, J = 8.1 Hz, 2H, Ar−H), 7.14 (d, J = 8.1 Hz, 2H, Ar−H), 2.37 (s, 3H, CH_3), 2.22 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 168.8, 142.8, 142.3, 137.6, 136.5, 130.3, 128.9, 124.3, 118.7, 24.8, 21.5; IR ($CHCl_3$) 1703, 1513, 1326, 1142 cm^{-1}; Anal. Calcd for $C_{15}H_{15}NO_3S_2$: C, 56.05; H, 4.70; N, 4.30. Found: C, 56.00; H, 4.69; N, 4.23.

*S-4-Tolyl 4-Methanethiosulfonate (**3ag**).* The title compound was obtained as a colorless oil (43.2 mg, 71%). ^1H NMR (270 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H, Ar−H), 7.29 (d, J = 8.1 Hz, 2H, Ar−H), 3.16 (s, 3H, CH_3), 2.42 (s, 3H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 142.5, 136.1, 130.7, 124.4, 47.1, 21.4; IR ($CHCl_3$) 1594, 1490, 1325, 1136 cm^{-1}; Anal. Calcd for $C_8H_{10}O_2S_2$: C, 47.50; H, 4.98. Found: C, 47.54; H, 4.94.

*S-4-Phenyl 4-Toluenethiosulfonate (**3ba**).* The title compound was obtained as a white solid (74.6 mg, 94%). mp 75−76 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.47−7.42 (m, 3H, Ar−H), 7.38−7.33 (m, 4H, Ar−H), 7.20 (d, J = 8.1 Hz, 2H, Ar−H), 2.41 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.7, 140.3, 136.5, 131.3, 129.4, 129.3, 128.0, 127.5, 21.6; IR ($CHCl_3$) 1594, 1442, 1328, 1143 cm^{-1}; Anal. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58. Found: C, 58.94; H, 4.54.

*S-4-Metoxyphenyl 4-Toluenethiosulfonate (**3ca**).* The title compound was obtained as a white solid (65.3 mg, 74%). mp 67−68 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H, Ar−H), 7.29−7.20 (m, 4H, Ar−H), 6.84 (d, J = 8.5 Hz, 2H, Ar−H), 3.83 (s, 3H, OCH_3), 2.42 (s, 3H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 162.2, 144.5, 140.3, 138.3, 129.3, 127.6, 118.7, 114.9, 55.4, 21.6; IR ($CHCl_3$) 1590, 1493, 1325, 1141 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_3S_2$: C, 57.12; H, 4.79. Found: C, 57.08; H, 4.75.

*S-4-Chlorophenyl 4-Toluenethiosulfonate (**3fa**).* The title compound was obtained as a white solid (58.3 mg, 65%). mp 89−90 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.46 (d, J = 7.9 Hz, 2H, Ar−H), 7.34−7.36 (brs, 4H, Ar−H), 7.23 (d, J = 8.2 Hz, 2H, Ar−H), 2.43 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.9, 140.1, 138.1, 137.7, 129.7, 129.5, 127.6, 126.5, 21.7; IR ($CHCl_3$) 1573, 1331, 1420, 1145 cm^{-1}; Anal. Calcd for $C_{13}H_{11}ClO_2S_2$: C, 52.25; H, 3.71. Found: C, 52.20; H, 3.69.

*S-4-Bromophenyl 4-Toluenethiosulfonate (**3ga**).* The title compound was obtained as a white solid (63.1 mg, 61%). mp 99−100 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.50−7.45 (m, 4H, Ar−H), 7.26−7.20 (m, 4H, Ar−H), 2.43 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 145.0, 140.1, 137.8, 132.6, 129.5, 127.5, 127.1, 126.6, 21.7; IR ($CHCl_3$) 1521, 1423, 1332, 1145 cm^{-1}; Anal. Calcd for $C_{13}H_{11}BrO_2S_2$: C, 45.49; H, 3.23. Found: C, 45.50; H, 3.20.

*S-4-Nitrophenyl 4-Toluenethiosulfonate (**3ha**).* The title compound was obtained as a yellow solid (79.1 mg, 69%). mp 129−131 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 8.18 (d, J = 8.8 Hz, 2H, Ar−H), 7.59 (d, J = 8.8 Hz, 2H, Ar−H), 7.49 (d, J = 8.3 Hz, 2H, Ar−H), 7.25 (d, J = 8.3 Hz, 2H, Ar−H), 2.44 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 145.6, 140.1, 137.0, 135.7, 129.7, 127.5, 126.4, 124.4, 21.7; IR ($CHCl_3$) 1599, 1344, 1214, 1146 cm^{-1}; Anal. Calcd for $C_{13}H_{11}NO_4S_2$: C, 50.47; H, 3.58; N, 4.53. Found: C, 50.23; H, 3.46; N, 4.35.

*S-2-Tolyl 4-Toluenethiosulfonate (**3ia**).* The title compound was obtained as a white solid (65.2 mg, 78%). mp 98−99 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.43 (d, J = 8.2 Hz, 2H, Ar−H), 7.39−7.15 (m, 6H, Ar−H), 2.42 (s, 3H, CH_3), 2.15 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.7, 144.2, 140.7, 138.3, 131.8, 130.9, 129.4, 127.5, 127.2, 126.8, 21.6, 20.6; IR ($CHCl_3$) 1592, 1471, 1327, 1143 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.07. Found: C, 60.36; H, 5.03.

*S-2-Methoxyphenyl 4-Toluenethiosulfonate (**3ja**).* The title compound was obtained as a white solid (61.7 mg, 70%). mp 98−99 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.51−7.41 (m, 4H, Ar−H), 7.20 (d, J = 7.9 Hz, 2H, Ar−H), 6.96 (t, J = 8.6 Hz, 1H, Ar−H), 6.79 (d, J = 8.6 Hz, 1H, Ar−H), 3.47 (s, 3H, OCH_3), 2.41 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 160.2, 144.2, 141.5, 139.5, 133.8, 129.1, 127.6, 121.2, 115.6, 111.3, 55.4, 21.6; IR ($CHCl_3$) 1585, 1478, 1326, 1142 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_3S_2$: C, 57.12; H, 4.79. Found: C, 57.20; H, 4.74.

*S-2-Bromophenyl 4-Toluenethiosulfonate (**3ka**).* The title compound was obtained as a white solid (55.4 mg, 54%). mp 119−120 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.71 (d, J = 7.6 Hz, 1H, Ar−H), 7.57 (d, J = 7.3 Hz, 1H, Ar−H), 7.46 (t, J = 8.2 Hz, 2H, Ar−H), 7.40−7.27 (m, 4H, Ar−H), 2.43 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 145.1, 140.7, 139.4, 133.6, 132.7, 131.1, 129.6, 129.4, 128.3, 127.5, 21.7; IR ($CHCl_3$) 1594, 1447, 1330, 1144 cm^{-1}; Anal. Calcd for $C_{13}H_{11}BrO_2S_2$: C, 45.49; H, 3.23. Found: C, 45.43; H, 3.22.

*S-Methyl 4-Toluenethiosulfonate (**3la**).* The title compound was obtained as a white solid (23.8 mg, 79%). mp 57−58 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.81 (d, J = 8.6 Hz, 2H, Ar−H), 7.35 (d, J = 8.6 Hz, 2H, Ar−H), 2.50 (s, 3H, CH_3), 2.46 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.8, 140.8, 129.8, 127.1, 21.6, 18.0; IR ($CHCl_3$) 1596, 1333, 1215, 1143 cm^{-1}; Anal. Calcd for $C_8H_{10}O_2S_2$: C, 47.50; H, 4.98. Found: C, 47.66; H, 4.89.

*S-Benzyl 4-Toluenethiosulfonate (**3ma**).* The title compound was obtained as a white solid (50.2 mg, 60%). mp 31−33 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 7.72 (d, J = 8.2 Hz, 2H, Ar−H), 7.28−7.19 (m, 7H, Ar−H), 4.24 (s, 2H, CH_2), 2.43 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.6, 142.0, 133.7, 129.7, 129.1, 128.7, 127.9, 127.0, 40.3, 21.6; IR ($CHCl_3$) 1594, 1494, 1454, 1326, 1140 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.40; H, 5.06. Found: C, 60.53; H, 4.99.

*S-n-Butyl 4-Toluenethiosulfonate (**3na**).* The title compound was obtained as a colorless oil (42.5 mg, 58%). ^1H NMR (270 MHz, $CDCl_3$) δ 7.82 (d, J = 8.2 Hz, 2H, Ar−H), 7.35 (d, J = 8.2 Hz, 2H, Ar−H), 2.98 (t, J = 6.8 Hz, 2H, CH_2), 2.45 (s, 3H, Ar−CH_3), 1.64−1.53 (m, 2H, CH_2), 1.40−1.26 (m, 2H, CH_2), 0.85 (d, J = 6.8 Hz, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.6, 141.9, 129.7, 126.9, 35.6, 30.5, 21.7, 21.6, 13.3; IR (neat) 2960, 1594, 1455, 1326, 1142 cm^{-1}; Anal. Calcd for $C_{11}H_{16}O_2S_2$: C, 54.06; H, 6.60. Found: C, 53.92; H, 6.52.

Typical Procedure for Copper-Catalyzed Sulfonylation of Diselenides: Synthesis of Se-Phenyl Benzeneselenosulfonate (5aa) (Table 3, Entry 1). To a mixture of diphenyl diselenide (46.8 mg, 0.15 mmol), sodium phenylsulfinate (54.2 mg, 0.33 mmol), and NH_4BF_4 (15.7 mg, 0.15 mmol) in DMA (0.6 mL) were added CuI (5.7 mg, 0.03 mmol) and Phen·H_2O (5.9 mg, 0.03 mmol), and the mixture was stirred at 30 °C for 18 h in air using a balloon. After the residue was dissolved in Et_2O, the solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (20% diethyl ether/hexane) gave

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5aa (63.1 mg, 71%) as a white solid. mp 53−54 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55−7.26 (m, 10H, Ar−H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 145.2, 137.2, 133.5, 130.9, 129.6, 128.7, 127.9, 127.0; IR ($CHCl_3$) 1447, 1307, 1215, 1135 cm^{-1}; Anal. Calcd for $C_{12}H_{10}O_2SSe$: C, 48.49; H, 3.39. Found: C, 48.16; H, 3.50.

*Se-4-Phenyl 4-Tolueneselenosulfonate (**5ab**).* The title compound was obtained as a white solid (61.5 mg, 66%). mp 79−80 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.52−7.31 (m, 7H, Ar−H), 7.18 (d, J = 8.2 Hz, 2H, Ar−H), 2.41 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.5, 142.6, 137.2, 130.8, 129.5, 129.2, 128.0, 127.0, 21.6; IR ($CHCl_3$) 1594, 1440, 1318, 1215, 1134 cm^{-1}; Anal. Calcd for $C_{13}H_{12}O_2SSe$: C, 50.16; H, 3.89. Found: C, 50.09; H, 3.85.

*Se-Phenyl 4-Methoxybenzeneselenosulfonate (**5ac**).* The title compound was obtained as a white solid (66.8 mg, 68%). mp 58−60 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.52−7.31 (m, 7H, Ar−H), 6.83 (d, J = 9.2 Hz, 2H, Ar−H), 3.85 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 163.4, 137.4, 137.2, 130.8, 129.5, 129.3, 128.1, 113.7, 55.7; IR ($CHCl_3$) 1586, 1490, 1292, 1212, 1174 cm^{-1}; Anal. Calcd for $C_{13}H_{12}O_3SSe$: C, 47.71; H, 3.70. Found: C, 47.59; H, 3.69.

*Se-4-Phenyl 4-Chlorobenzeneselenosulfonate (**5ad**).* The title compound was obtained as a white solid (64.8 mg, 65%). mp 95−97 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.52−7.34 (m, 9H, Ar−H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 143.5, 140.0, 137.2, 131.1, 129.7, 128.9, 128.3, 127.6; IR ($CHCl_3$) 1578, 1474, 1213, 1136 cm^{-1}; Anal. Calcd for $C_{12}H_9ClO_2SSe$: C, 43.45; H, 2.74. Found: C, 43.28; H, 2.71.

*Se-Phenyl 4-Fluorobenzeneselenosulfonate (**5ae**).* The title compound was obtained as a white solid (60.1 mg, 61%). mp 105−106 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.54−7.46 (m, 5H, Ar−H), 7.38−7.33 (m, 2H, Ar−H), 7.09−7.03 (m, 2H, Ar−H); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 165.3 (d, J = 256 Hz), 141.1 (d, J = 3 Hz), 137.2, 131.1, 129.8 (d, J = 10 Hz), 129.7, 127.7, 115.9 (d, J = 23 Hz); IR ($CHCl_3$) 1590, 1490, 1323, 1216, 1134 cm^{-1}; Anal. Calcd for $C_{12}H_9FO_2SSe$: C, 45.72; H, 2.88. Found: C, 45.69; H, 2.89.

*Se-Phenyl 4-Acetylaminobenzeneselenosulfonate (**5af**).* The title compound was obtained as a white solid (62.6 mg, 59%). mp 112−113 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.65 (br, 1H, NH), 7.57−7.31 (m, 9H, Ar−H), 2.21 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 168.7, 142.7, 139.9, 137.2, 131.0, 129.6, 128.4, 127.8, 118.6, 24.8; IR ($CHCl_3$) 3430, 1701, 1589, 1513, 1319, 1215, 1133 cm^{-1}; Anal. Calcd for $C_{14}H_{13}NO_3SSe$: C, 47.46; H, 3.70; N, 3.95. Found: C, 47.56; H, 3.42; N, 3.56.

*Se-4-Tolyl 4-Tolueneselenosulfonate (**5bb**).* The title compound was obtained as a white solid (61.9 mg, 63%). mp 107−108 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.41 (d, J = 8.5 Hz, 2H, Ar−H), 7.38 (d, J = 8.3 Hz, 2H, Ar−H), 7.20 (d, J = 8.5 Hz, 2H, Ar−H), 7.15 (d, J = 8.3 Hz, 2H, Ar−H), 2.41 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.4, 142.8, 141.5, 137.2, 130.3, 129.2, 127.0, 124.7, 21.6, 21.5; IR ($CHCl_3$) 1594, 1318, 1214, 1133 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_2SSe$: C, 51.69; H, 4.34. Found: C, 51.51; H, 4.24.

*Se-4-Methoxyphenyl 4-Tolueneselenosulfonate (**5cb**).* The title compound was obtained as a white solid (68.7 mg, 70%). mp 77−79 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.40 (d, J = 7.9 Hz, 2H, Ar−H), 7.40 (d, J = 8.8 Hz, 2H, Ar−H), 7.20 (d, J = 7.9 Hz, 2H, Ar−H), 6.84 (d, J = 8.8 Hz, 2H, Ar−H), 3.84 (s, 3H, CH_3), 2.41 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 161.9, 144.4, 142.7, 139.0, 129.3, 127.0, 118.9, 115.1, 55.4, 21.6; IR ($CHCl_3$) 1592, 1494, 1211, 1130 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_3SSe$: C, 49.27; H, 4.13. Found: C, 49.49; H, 4.07.

*Se-1-Naphtyl 4-Tolueneselenosulfonate (**5db**).* The title compound was obtained as a yellow solid (61.9 mg, 57%). mp 119−121 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.03−7.95 (m, 2H, Ar−H), 7.85−7.80 (m, 2H, Ar−H), 7.46−7.35 (m, 3H, Ar−H), 7.24 (d, J = 8.1 Hz, 2H, Ar−H), 6.99 (d, J = 8.1 Hz, 2H, Ar−H), 2.30 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.4, 142.3, 138.7, 134.6, 134.0, 132.4, 129.1, 128.4, 127.9, 127.7, 127.3, 127.0, 126.5, 125.8, 21.5; IR ($CHCl_3$) 1595, 1445, 1214, 1134 cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2SSe$: C, 56.51; H, 3.91. Found: C, 56.58; H, 3.96.

*Se-Benzyl 4-Tolueneselenosulfonate (**5eb**).* The title compound was obtained as a pale yellow oil (48.9 mg, 50%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H, Ar−H), 7.29−7.23 (m, 7H, Ar−H), 4.49 (s, 2H, CH_2), 2.44 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 144.5, 144.5, 135.0, 129.7, 129.3, 128.8, 127.8, 126.4, 36.9, 21.6; IR (neat) 3061, 1594, 1493, 1454, 1301, 1133 cm^{-1}; Anal. Calcd for $C_{14}H_{14}O_2SSe$: C, 51.69; H, 4.34. Found: C, 51.29; H, 4.32.

Large-Scale of Sulfonylation of Disulfide (Scheme 4). To a mixture of bis(4-tolyl) disulfide (369.6 mg, 1.5 mmol), sodium phenylsulfinate (641.5 mg, 3.6 mmol), and NH_4BF_4 (157.2 mg, 1.5 mmol) in DMA (0.3 mL) and H_2O (0.1 mL) were added CuI (28.6 mg, 0.15 mmol) and Phen·H_2O (29.7 mg, 0.15 mmol), and the mixture was stirred at 30 °C for 40 h in air using a balloon. After the residue was dissolved in Et_2O, the solution was washed with H_2O and saturated sodium chloride and dried over anhydrous magnesium sulfate. Chromatography on silica gel (30% diethyl ether/hexane) gave *S*-4-tolyl 4-toluenethiosulfonate (**3ab**) (628.2 mg, 75%).

■ ASSOCIATED CONTENT

Supporting Information

Copies of the ^{1}H NMR and ^{13}C NMR spectra. 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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