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Chan–Lam-Type C–S Coupling Reaction by Sodium Aryl Sulfinates and Organoboron Compounds

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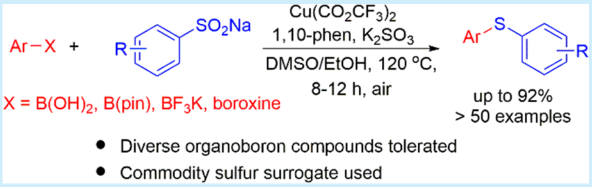
ABSTRACT: A Chan–Lam-type C–S coupling reaction using sodium aryl sulfinates has been developed to provide diaryl thioethers in up to 92% yields in the presence of a copper catalyst and potassium sulfite. Both electron-rich and electron-poor sodium aryl sulfinates and diverse organoboron compounds were tolerated for the synthesis of aryl and heteroaryl thioethers and dithioethers. The mechanistic study suggested that potassium sulfite was involved in the deoxygenation of sulfinate through a radical process.



Thioethers are represented in various bioactive compounds and natural products and contribute to the third-largest constituent of sulfur-containing drugs.[1] Regarding the predominant role of the thioether scaffold in pharmaceutical development, the construction of a C–S bond became a major research topic in synthetic chemistry, and diverse synthetic protocols have been developed. In general, aryl sulfide is prepared via the cross-coupling reaction between a thiol and an organohalide.[2] However, the large-scale utilization of thiols is often complicated by their repulsive odor and the associated toxicity.

Scheme 1. C–S Coupling Reactions for the Synthesis of Diaryl Thioethers

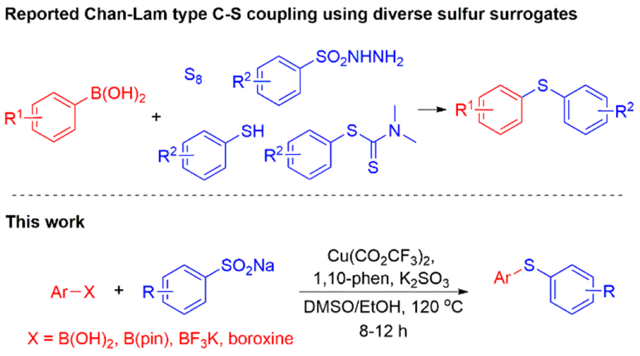
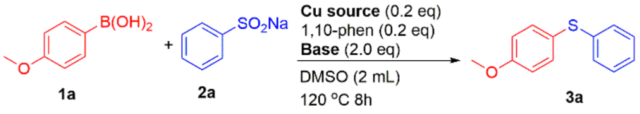


Table 1. Optimization of Bases and the Catalyst[a]



entry	base (*x*)	[Cu]	yield (%)[b]
1	DABCO	CuI	5
2	DMAP	CuI	trace
3	TMP	CuI	19
4	Na_2SO_3	CuI	38
5	$CaSO_3$	CuI	27
6	$(NH_4)_2SO_3$	CuI	38
7	K_2SO_3	CuI	61
8	K_2SO_3	$Cu(OTf)_2$	58
9	K_2SO_3	$Cu(ClO_4)_2$	54
10	K_2SO_3	$Cu(CO_2CF_3)_2$	64
11[c]	K_2SO_3	$Cu(CO_2CF_3)_2$	33
12[d]	K_2SO_3	$Cu(CO_2CF_3)_2$	69
13[e]	K_2SO_3	$Cu(CO_2CF_3)_2$	65

[a] Reaction conditions are as follows: **1a** (0.3 mmol), **2a** (1.2 mmol), base, Cu source (20 mol %), ligand (20 mol %), and DMSO (2.0 mL) were stirred at 120 °C for 8 h. [b] NMR yield using CH_2Br_2 as an internal standard. [c] Used 0.45 mmol of K_2SO_3. [d] Used 0.75 mmol of K_2SO_3. [e] Used 0.9 mmol of K_2SO_3.

Table 2. Optimization of the Ligand and Additive[a]

entry	ligand	additives (*y*)	yield (%)[b]
1	1,10-Phen		64
2	2,2′-bpy		50

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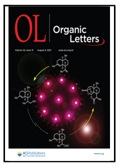

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Table 2. continued

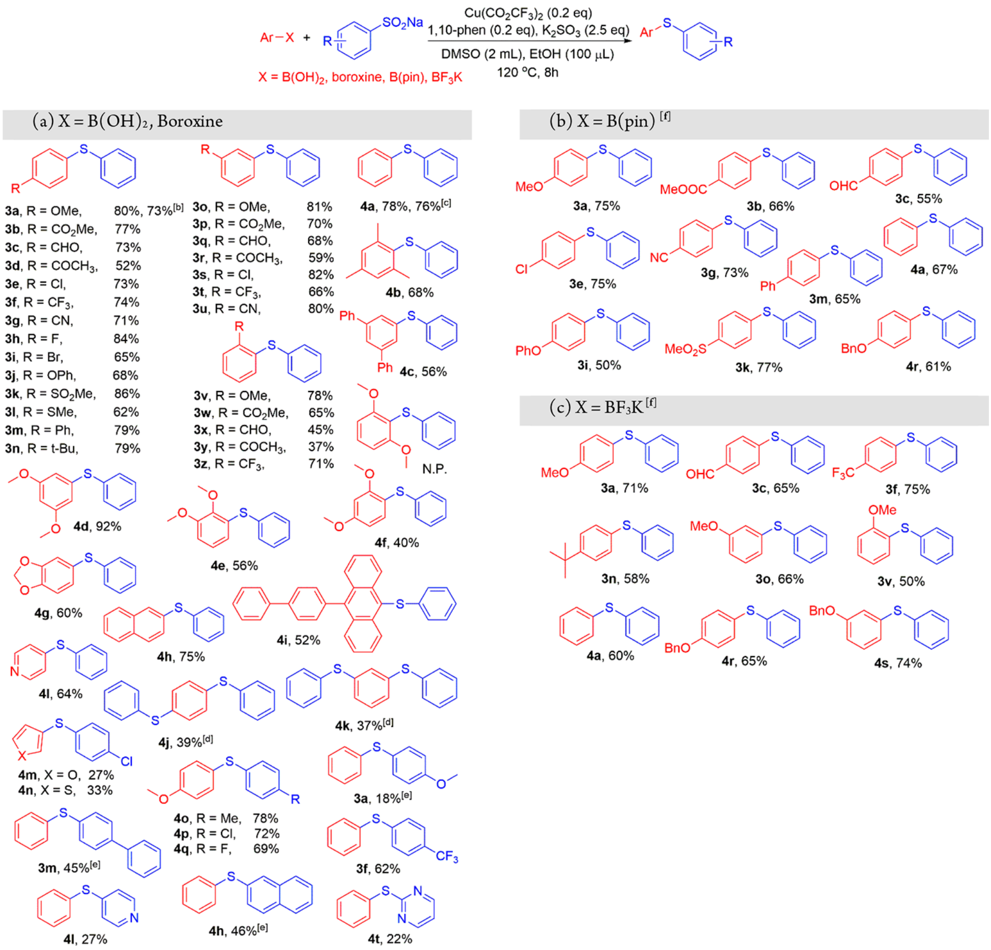
entry	ligand	additives (y)	yield (%)[b]
3	DMEDA		9
4	L-proline		9
5	L-ascorbic acid		21
6	neocuproine		4
7	4,7-$(MeO)_2$Phen		56
8	3,4,7,8-Me_4Phen		38
9	1,10-Phen	MeOH (100 μL)	65
10	1,10-Phen	EtOH (100 μL)	82
11	1,10-Phen	t-BuOH (100 μL)	67
12	1,10-Phen	EtOH (20 μL)	67
13	1,10-Phen	EtOH (200 μL)	66
14[c]	1,10-Phen	EtOH (200 μL)	n.p.
15		EtOH (200 μL)	50
16[d]	1,10-Phen	EtOH (200 μL)	7

[a] Reaction conditions are as follows: **1a** (0.3 mmol), **2a** (1.2 mmol), K_2SO_3 (0.75 mmol), $Cu(CO_2CF_3)_2$ (20 mol %), ligand (20 mol %), DMSO (2.0 mL), and additives were stirred at 120 °C for 8 h. [b] NMR yield using CH_2Br_2 as an internal standard. [c] Without catalyst. [d] Without K_2SO_3.

To circumvent this problem, different sulfur surrogates, such as sulfonyl chloride,[3] Bunte salt,[4] S_8,[5] and xanthate,[6] were used as alternatives to thiols for thioether preparation. Despite the effectiveness of using these sulfur surrogates, the use of reactive reagents, the need for specialized reaction conditions, or the multiple synthetic steps used often limits their application.

Among the various sulfur surrogates, sodium sulfinate is considered an ideal sulfur donor due to its low volatility and ease of handling and storage. Although sodium sulfinate has been used predominantly in sulfonylation,[7] sulfenylation using sodium sulfinate has been limited to specific heteroarenes, i.e., indole and imidazopyridine.[8] Previously, we reported a new method for diaryl thioether synthesis that is promoted by DABCO and uses aryl iodide and sodium aryl sulfinate,[9] indicating the potential for using aryl sulfinate as a sulfenylation agent. This result encouraged us to explore other possible reaction partners besides aryl halides. Chan–Lam couplings for preparation of thioether using thiols, S_8, disulfides, phenyldithiocarbamates, and sulfonyl hydrazines have been reported (Scheme 1)[10] despite the safety and hazard issues. In this study, we attempted to use commercially available sodium aryl sulfinates as sulfenylating agents to couple with diverse organoboron compounds, such as aryl boronic acids, esters, trifluoroborates, and boroxine. As the result, we disclose herein an alternative method for the preparation of thioethers via Chan–Lam

Scheme 2. Substrate Scope[a]



[a] Isolated yields. Reaction conditions are as follows: arylboronic acid (0.3 mmol), sodium arylsulfinate (1.2 mmol), K_2SO_3 (0.75 mmol), $Cu(CO_2CF_3)_2$ (20 mol %), 1,10-Phen (20 mol %), DMSO (2.0 mL), and EtOH (100 μL) were stirred at 120 °C. [b] One mmol scale. [c] Used 0.1 mmol of triphenylboroxine. [d] Used sodium benzenesulfinate (2.4 mmol) and K_2SO_3 (1.5 mmol). [e] Sodium arylsulfinate was synthesized in the laboratory. [f] Twelve hours.

coupling using sodium aryl sulfinates as relatively safe commodity sulfur surrogates (Scheme 1).

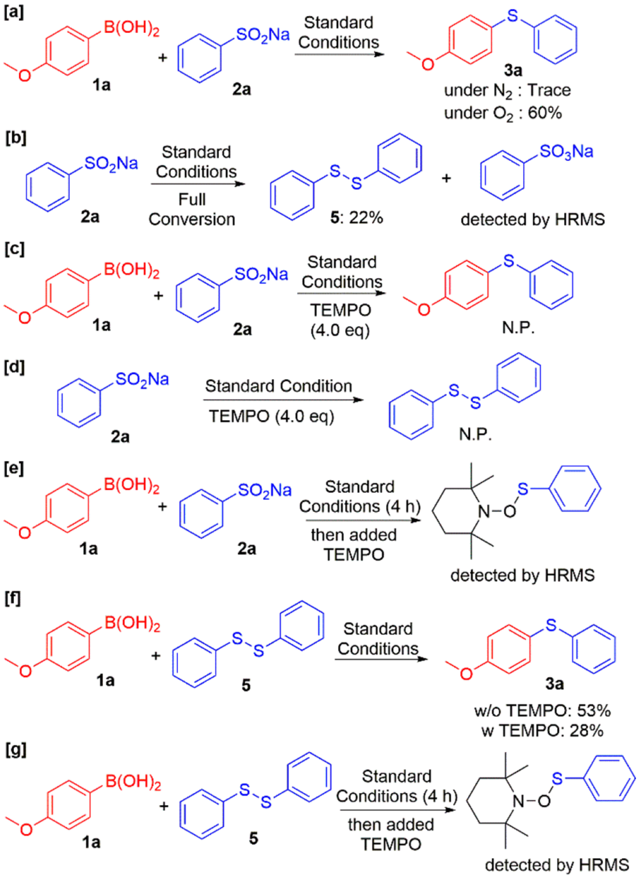
4-Methoxyphenyl boronic acid **1a** and sodium benzenesulfinate **2a** were chosen as model substrates to optimize the reaction conditions (Tables 1, 2, S1, and S2). The initial reactions were performed under our previous conditions for the coupling between sulfinates and iodoarenes,[9] and the new conditions were based on the literature for the coupling between thiols and boronic acids[11] plus DABCO as the base, which was shown to be critical for the deoxygenation of sulfinates (Table 1, entry 1). 5% of the desired thioether **3a** was obtained under the new conditions. Encouraged by the result, we performed the further screening of amine bases, which showed no obvious improvement in the reaction yield while the best result was obtained in the presence of 2,2,6,6-tetramethylpiperidine (TMP) (Table 1, entries 2 and 3). By turning to inorganic reducing agents, we observed that the yield of the coupling product **3a** increased significantly to 38% when Na_2SO_3 was used (Table 1, entry 4). Subsequently, different sulfite salts were screened (Table 1, entries 4−7), and K_2SO_3 gave the highest yield of 61% (Table 1, entry 7), probably because of its relatively higher solubility in the solvent compared to those of other sulfites. Using K_2SO_3 as the base, various types of copper catalysts were tested (Table 1, entry 8−10). $Cu(CO_2CF_3)_2$ provided a slightly higher yield of **3a** (Table 1, entry 10), and the yield increased to 69% when 2.5 equiv of K_2SO_3 was used (Table 1, entry 12).

Further exploration on the choice of ligands demonstrated that 1,10-phenanthroline (1,10-Phen) was an appropriate coordination agent in this reaction system, while other bidentate *N*,*N*- and *N*,*O*-ligands were less effective (Table 2, entries 2−8). Finally, the reaction performance was enhanced with the addition of alcohol (Table 2, entries 9−11). Notably, the yield of **3a** increased significantly to 82% when 100 μL of EtOH was added (Table 2, entry 10), probably due to the improved solubilities of both K_2SO_3 and sodium benzenesulfinate in the reaction mixture.

With the establishment of the optimized conditions, the scope of the reaction was then explored with an array of substituted aryl boronic acids (Scheme 2a). In the presence of *para*-substituted aryl boronic acids, the reaction was compatible with a series of electron-donating groups and electron-withdrawing groups, with the yields from 52% to 86% (**3a**−**3n**). Substituents at the *meta*-position displayed a similar substituent−reactivity relationship with an improved isolated yield, especially for 2-cyano and 2-chloro groups (**3o**−**3u**). For *ortho*-substituted substrates (**3v**−**3z**), similar isolated yields were obtained from the reaction. While boroxine showed a similar reactivity compared to those of boronic acid (**4a**) and 2,4,6-trimethyl-substituted aryl boronic acid gave the corresponding product in a good yield (**4b**), the effect of the substitution position toward the reactivity was more significant when dimethoxy-substituted aryl boronic acids underwent sulfenylation. 3,5-Dimethoxyphenyl boronic acid underwent the reaction with an excellent isolated yield of 92% (**4d**), whereas the yields diminished for the 2,3- and 2,4-dimethoxy-substituted substrate(**4e** and **4f**, respectively), and no desired product was isolated for the 2,6-dimethoxy-substituted substrate, reflecting the steric impact on the reaction.

Attempts for the one-pot disulfenylation of aryl diboronic acid were also successful with phenyl diboronic acid despite the product yield decreasing to ∼40% (**4j** and **4k**). Additionally, heteroaryl boronic acids can also be used as the coupling partner (**4l**−**4n**) except 2-heteroaryl boronic acids, probably due to their instability. Finally, a series of substituted sodium benzenesulfinates were tested. 4-Methyl, 4-chloro, and 4-fluoro benzenesulfinates could be used as sulfenylating agents to afford the desired thioethers in 69−78% yields (**4o**−**4q**, respectively). Other aryl- and heteroarylsulfinates also gave reasonable yields. We then assessed the tolerance for different aryl boron reagents as coupling partners. Both aryl boronic acid pinacol esters and potassium aryl trifluoroborates can be converted to the corresponding thioethers with ≥50% yields (Scheme 2b and c).

Scheme 3. Control Experiments

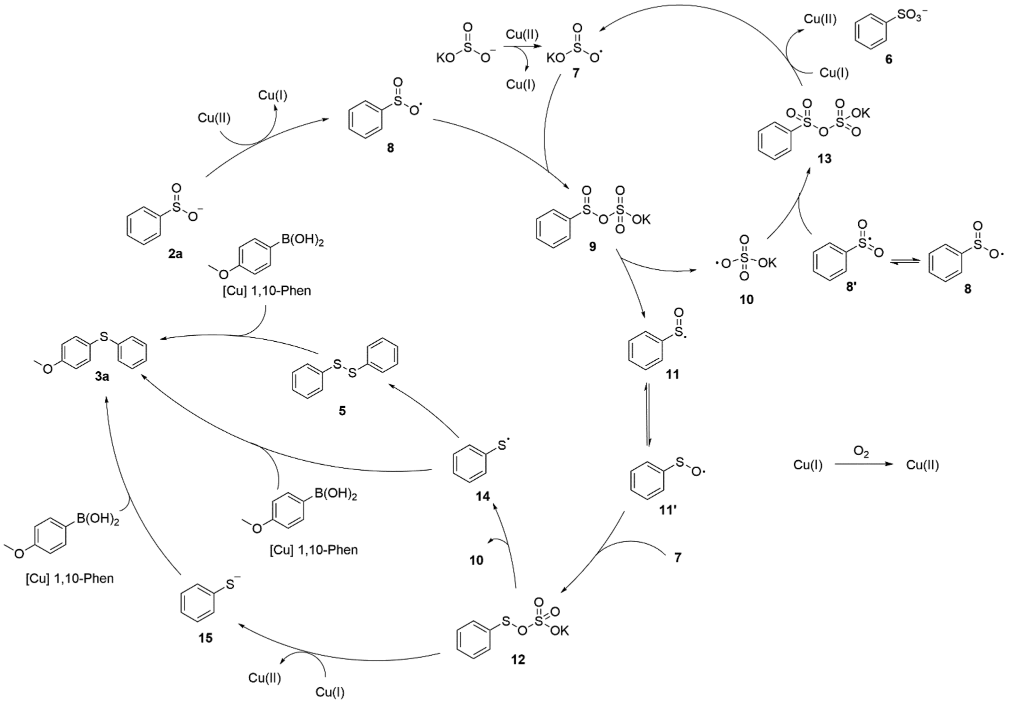


A series of control experiments were performed to elucidate the reaction mechanism (Scheme 3). Oxygen gas or air was shown to be important for this reaction (Schemes 2 and 3a). When sodium benzenesulfinate **2a** was treated under the standard conditions, disulfide **5** was isolated in only a 22% yield (Scheme 3b) and sodium benzenesulfonate **6** was detected in the HRMS analysis (Figure S1). With the addition of TEMPO, no desired product can be obtained with or without the presence of boronic acid **1a** (Scheme 3c and d), suggesting a radical mechanism for the deoxygenation process of sulfinate.

By adding TEMPO to the standard reaction while stirring after 4 h, the thiyl radicals were trapped by TEMPO (Scheme 3e and Figure S2). By treating disulfide **5** with **1a**, **3a** was formed with only a 53% yield. The reaction yield decreased to 28% with the addition of TEMPO (Scheme 3f), indicating multiple coupling mechanisms. The thiyl radicals were also trapped when TEMPO was added to the reaction mixture between disulfide **5** and **1a** after 4 h (Scheme 3g and Figure S3). These results suggest a radical mechanism in parallel to the coupling reaction with the aryl boronic acid.

Based on the results, the following reaction mechanism is proposed (Scheme 4). Through oxidation by copper(II), sulfite

Scheme 4. Proposed Mechanism



and sodium benzenesulfinate **2a** can be respectively oxidized to give the sulfite radical **7**[12] and the sulfonyl radical **8**, which can couple to afford sulfinyl sulfonate **9**. Upon the departure of sulfate radical **10**, the resulting sulfinyl radical **11** reacts with the sulfite radical **7** furnish the sulfenyl sulfonate **12**. This process is validated by the detection of benzenesulfonate **6** through the formation of sulfonyl sulfate **13**. Intermediate **12** can undergo homolytic cleavage to give the thiyl radical **14**[13] to either directly react with or possibly form disulfide **5** for the coupling with boronic acid in the presence of copper catalyst to give product **3a**. By a reduction with copper, the sulfenyl anion **15** can be generated from **12** to undergo the coupling reaction.

In summary, a Chan–Lam-type C–S coupling reaction protocol for diaryl thioether formation is reported using aryl boronic acid and sodium aryl sulfinate as the sulfenylating agent. In the presence of a commonly used copper catalyst, diverse thioethers can be prepared in this one-step reaction using commodity chemicals. Furthermore, aryl boronic acid esters and borates are also competent coupling partners under the reaction conditions. The mechanistic study suggested a radical pathway in both the deoxygenation of aryl sulfinate and the coupling reaction, with the aid of potassium sulfite as a mild reducing agent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02299.

Procedures, figures, characterization, full optimization conditions and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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