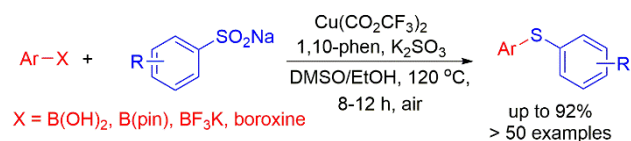


# Chan-Lam Type C-S Coupling Reaction by Sodium Aryl Sulfinates and Organoboron Compounds

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Supporting Information Placeholder



- Diverse organoboron compounds tolerated
- Commodity sulfur surrogate used

**ABSTRACT:** A Chan-Lam type C-S coupling reaction using sodium aryl sulfinates has been developed to provide diaryl thioethers with 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.

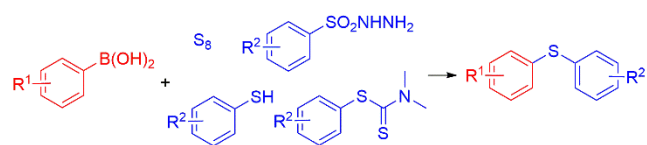
Thioethers are represented in various bioactive compounds and natural products, and contribute to the third-largest constituent of sulfur-containing drugs.<sup>1</sup> Regarding the predominant role of thioether scaffold in pharmaceutical development, construction of C-S bond became a major research topic in synthetic chemistry, and diverse synthetic protocol has been developed. In general, aryl sulfide is prepared via the cross-coupling reaction between a thiol and an organohalide.<sup>2</sup> However, large-scale utilization of thiols is often complicated by the repulsive odor and the toxicity associated. To circumvent this problem, different sulfur surrogates, such as sulfonyl chloride,<sup>3</sup> Bunte salt,<sup>4</sup> S<sub>8</sub>,<sup>5</sup> and xanthate<sup>6</sup>, were used as alternatives of thiols for thioether preparation. Despite the effectiveness of using these sulfur surrogates, the use of reactive reagents, the needs for specialized reaction conditions, or the multiple synthetic steps often limit their application.

Among various sulfur surrogates, sodium sulfinate is considered an ideal sulfur donor due to the low volatility and ease of handling and storage. Although sodium sulfinate has been used predominantly in sulfonylation<sup>7</sup>, sulfonylation using sodium sulfinate was limited to specific heteroarenes, i.e., indole and imidazopyridine<sup>8</sup>. Previously, we reported a new method for diaryl thioether synthesis promoted by DABCO using aryl iodide and sodium aryl sulfinate,<sup>9</sup> indicating the potential of using aryl sulfinate as a sulfonylation agent. This result encouraged us to explore other possible reaction partners besides aryl halides. Chan-Lam coupling for preparation of thioether using thiols, S<sub>8</sub>, disulfides, phenyldithiocarbamates and sulfonyl hydrazines have been reported (Scheme 1),<sup>10</sup> despite of safety and hazard issues. In this study, we attempted to use commercially available sodium aryl sulfinates as the sulfonylating agent to couple with diverse organoboron compounds, such as aryl boronic ac-

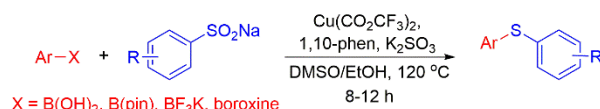
ids, esters, trifluoroborates and boroxine. As the result, we disclosed herein an alternative method for the preparation of thioethers via Chan-Lam coupling using sodium aryl sulfinates as a relatively safe commodity sulfur surrogate (Scheme 1).

## Scheme 1. C-S Coupling Reactions for Synthesis of Diaryl Thioethers

Reported Chan-Lam type C-S coupling using diverse sulfur surrogates



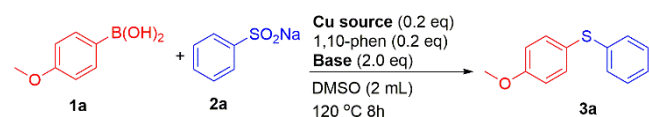
This work



4-methoxyphenyl boronic acid **1a** and sodium benzenesulfinate **2a** were chosen as model substrates for optimization of reaction conditions (Table 1, 2, S1, and S2). The initial reactions were performed under our previous conditions for the coupling between sulfonates and iodoarenes,<sup>9</sup> and the new conditions based on the literature for the coupling between thiols and boronic acids,<sup>11</sup> 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 further screening of amine bases showing 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, entry 2 and 3).

By turning to inorganic reducing agents, we observed that the yield of coupling product **3a** increased significantly to 38% when Na<sub>2</sub>SO<sub>3</sub> was used (Table 1, entry 4). Subsequently, different sulfite salts were screened (Table 1, entry 4-7), and K<sub>2</sub>SO<sub>3</sub> gave the highest yield of 61% (Table 1, entry 7), probably because of relatively higher solubility than other sulfites in the solvent. Using K<sub>2</sub>SO<sub>3</sub> as the base, various types of copper catalysts were tested (Table 1, entry 8-10), in which Cu(CO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> provided a slightly higher yield of **3a** (Table 1, entry 10), and the yield has increased to 69% when 2.5 equivalent of K<sub>2</sub>SO<sub>3</sub> was used (Table 1, entry 12).

**Table 1. Optimization of Bases and Catalyst** <sup>[a]</sup>

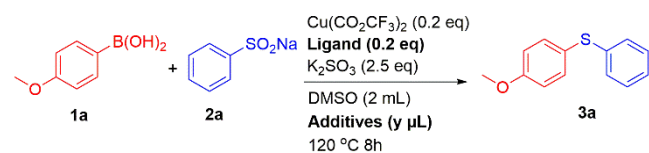


Entry	Base (x)	[Cu]	Yield (%) <sup>[b]</sup>
1	DABCO	CuI	5
2	DMAP	CuI	Trace
3	TMP	CuI	19
4	Na <sub>2</sub> SO <sub>3</sub>	CuI	38
5	CaSO <sub>3</sub>	CuI	27
6	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>	CuI	38
7	K <sub>2</sub> SO <sub>3</sub>	CuI	61
8	K <sub>2</sub> SO <sub>3</sub>	Cu(OTf) <sub>2</sub>	58
9	K <sub>2</sub> SO <sub>3</sub>	Cu(ClO <sub>4</sub> ) <sub>2</sub>	54
10	K <sub>2</sub> SO <sub>3</sub>	Cu(CO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	64
11 <sup>[c]</sup>	K <sub>2</sub> SO <sub>3</sub>	Cu(CO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	33
12 <sup>[d]</sup>	K <sub>2</sub> SO <sub>3</sub>	Cu(CO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	69
13 <sup>[e]</sup>	K <sub>2</sub> SO <sub>3</sub>	Cu(CO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	65

<sup>[a]</sup>Reaction condition: **1a** (0.3 mmol), **2a** (1.2 mmol), base, Cu source (20 mol%), ligand (20 mol%), DMSO (2.0 mL) were stirred at 120 °C for 8h. <sup>[b]</sup>NMR yield using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>[c]</sup>0.45 mmol of K<sub>2</sub>SO<sub>3</sub> is used. <sup>[d]</sup>0.75 mmol of K<sub>2</sub>SO<sub>3</sub> is used. <sup>[e]</sup>0.9 mmol of K<sub>2</sub>SO<sub>3</sub> is used.

Further exploration on the choice of ligands demonstrated that 1,10-phenanthroline was an appropriate coordination agent in this reaction system, while other bidentate *N,N'*- and *N,O*-ligands were less effective (Table 2, entry 2-8). Finally, with the addition of alcohol, the reaction performance was enhanced (Table 2, entry 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 solubility of both K<sub>2</sub>SO<sub>3</sub> and sodium benzenesulfinate in the reaction mixture.

**Table 2. Optimization of Ligand and additive** <sup>[a]</sup>



Entry	Ligand	Additives (y)	Yield (%) <sup>[b]</sup>
1	1,10-Phen	/	64
2	2,2'-bpy	/	50
3	DMEDA	/	9
4	L-proline	/	9
5	L-ascorbic acid	/	21

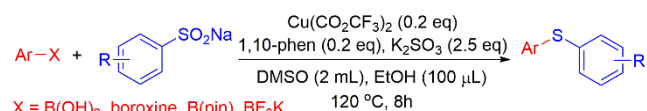
6	neocuproine	/	4
7	4,7-(MeO) <sub>2</sub> phen	/	56
8	3,4,7,8-Me <sub>4</sub> phen	/	38
9	1,10-Phen	MeOH (100 μL)	65
10	1,10-Phen	EtOH (100 μL)	82
11	1,10-Phen	t-BuOH (100 μL)	67
12	1,10-Phen	EtOH (20 μL)	67
13	1,10-Phen	EtOH (200 μL)	66
14 <sup>[c]</sup>	1,10-Phen	EtOH (200 μL)	N. P.
15	/	EtOH (200 μL)	50
16 <sup>[d]</sup>	1,10-Phen	EtOH (200 μL)	7

<sup>[a]</sup>Reaction condition: **1a** (0.3 mmol), **2a** (1.2 mmol), K<sub>2</sub>SO<sub>3</sub> (0.75 mmol), Cu(CO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (20 mol%), ligand (20 mol%), DMSO (2.0 mL), additives were stirred at 120 °C for 8h. <sup>[b]</sup>NMR yield using CH<sub>2</sub>Br<sub>2</sub> as internal standard. <sup>[c]</sup>Without catalyst. <sup>[d]</sup>Without K<sub>2</sub>SO<sub>3</sub>.

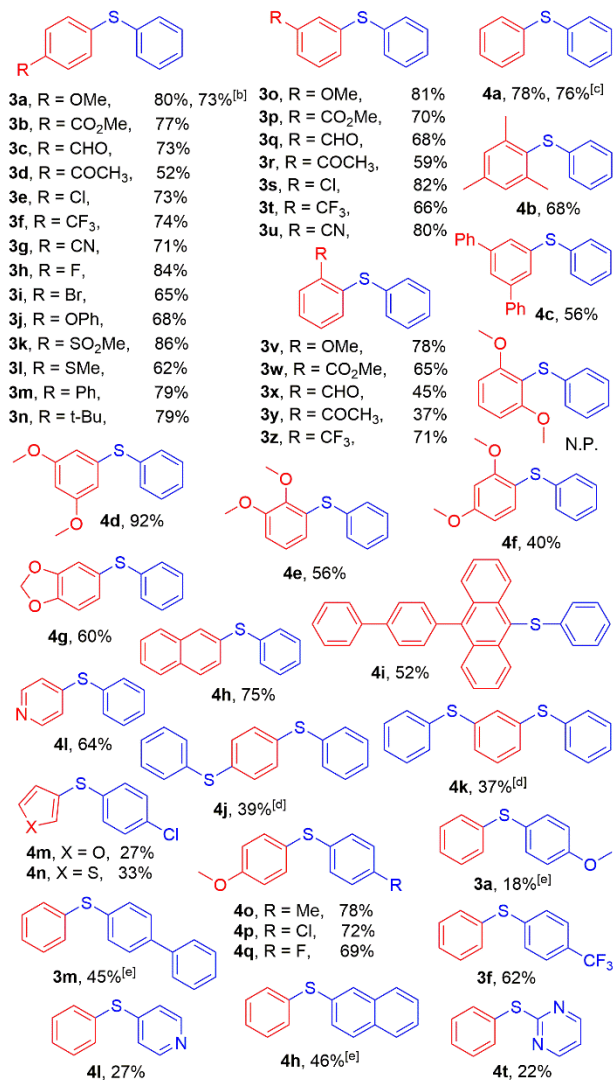
With the establishment of the optimized conditions, the scope of the reaction was then explored with an array of substituted aryl boronic acid (Scheme 2a). In the presence of *para*-substituted aryl boronic acids, the reaction was compatible with a series of electron-donating groups and electron-withdrawing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

Attempts on one-pot disulfenylation of aryl diboronic acid were also successful with phenyl diboronic acid, despite the product yield decreased 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 instability. Finally, a series of substituted sodium benzenesulfonates were tested. 4-methyl, 4-chloro and 4-fluoro benzenesulfonates could be used as sulfenyating agents to afford the desired thioethers in 69% - 78% yields (**4o-4q**). Other aryl- and heteroarylsulfonates also gave reasonable yields. We then assessed the tolerance of different aryl boron reagents as coupling partner. Both aryl boronic acid pinacol esters and potassium aryl trifluoroborates can be converted into the corresponding thioethers with ≥ 50% yields (Scheme 2b and 2c).

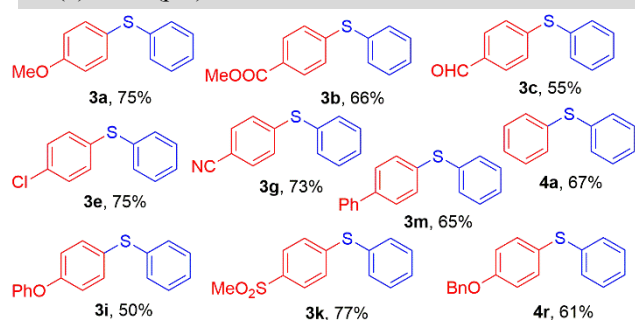
**Scheme 2. Substrate scope** <sup>[a]</sup>



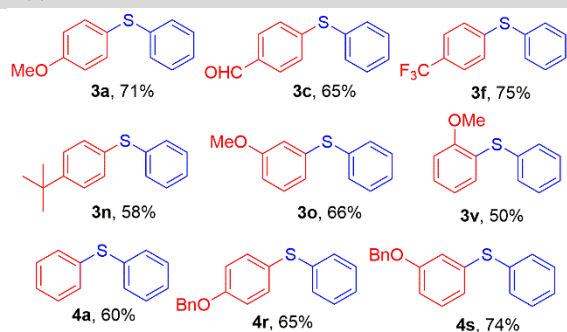
(a) X = B(OH)<sub>2</sub>, Boroxine



(b) X = B(pin)<sup>[f]</sup>



(c) X = BF<sub>3</sub>K<sup>[f]</sup>

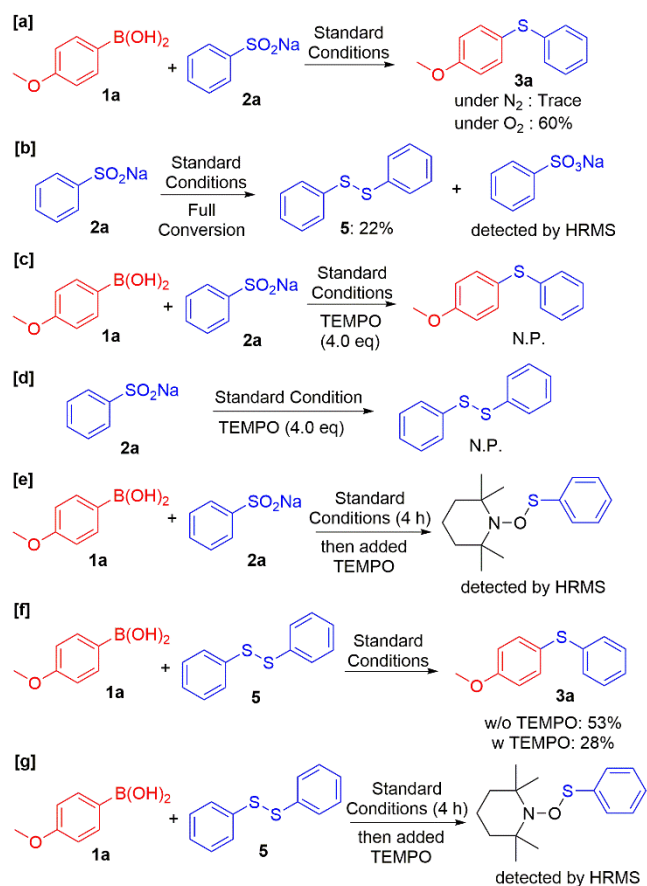


<sup>[a]</sup>Isolated yields. Reaction condition: arylboronic acid (0.3 mmol), sodium arylsulfinate (1.2 mmol), K<sub>2</sub>SO<sub>3</sub> (0.75 mmol),

Cu(CO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (20 mol%), 1,10-Phen (20 mol%), DMSO (2.0 mL) and EtOH (100 μL) were stirred at 120 °C. <sup>[b]</sup>1 mmol scale <sup>[c]</sup>0.1 mmol of triphenylboroxine was used. <sup>[d]</sup>sodium benzenesulfinate (2.4 mmol), K<sub>2</sub>SO<sub>3</sub> (1.5 mmol) was used. <sup>[e]</sup>Sodium arylsulfinate was synthesized in the laboratory. <sup>[f]</sup>12 h.

A series of control experiments were performed to elucidate the reaction mechanism (Scheme 3). Oxygen gas or air showed to be important for this reaction (Scheme 2 and 3a). When sodium benzenesulfinate **2a** was treated under the standard conditions, disulfide **5** was isolated in only 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 3d), suggesting a radical mechanism in the deoxygenation process of sulfinate.

**Scheme 3. Control experiments**

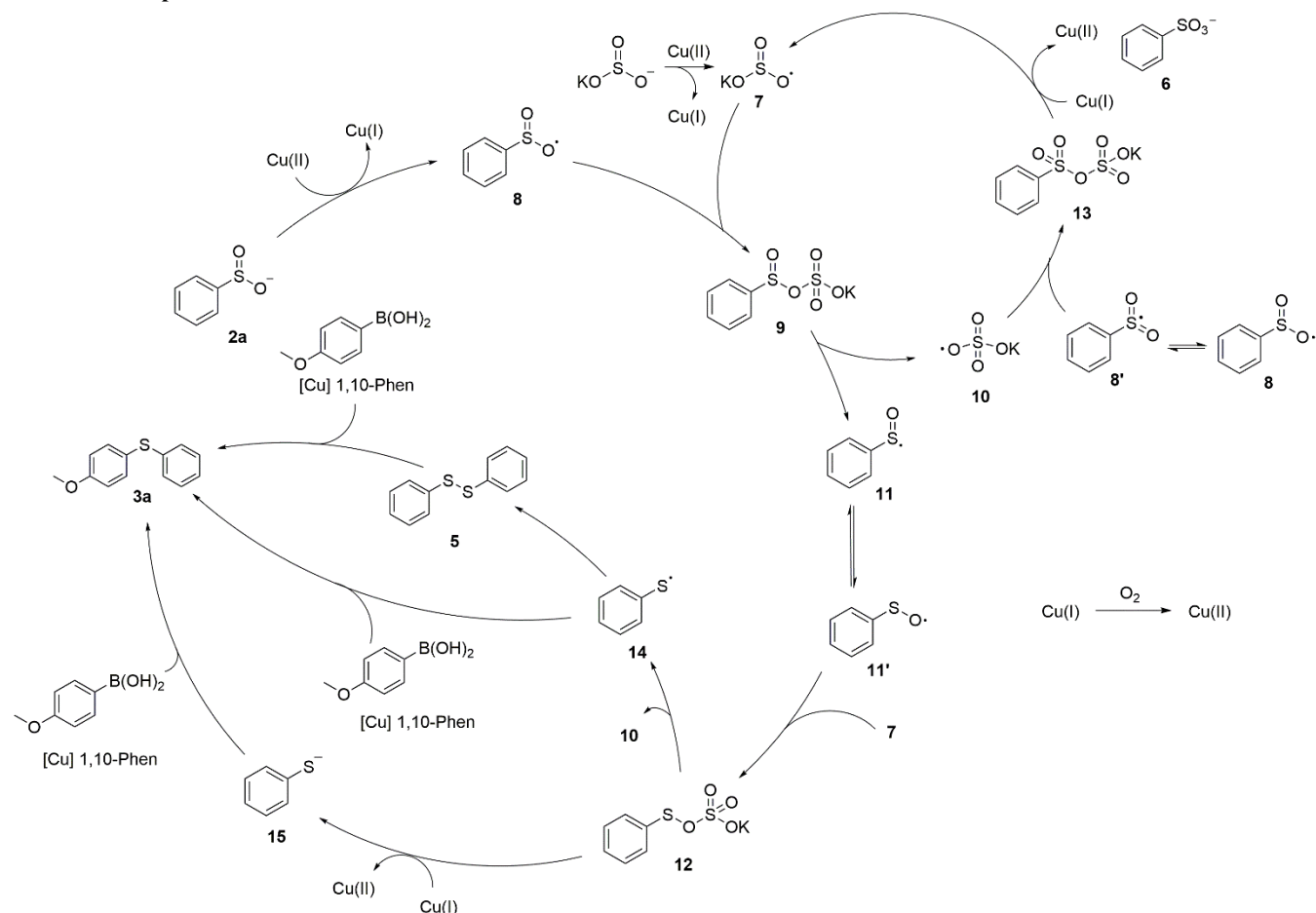


By adding TEMPO to the standard reaction stirring after 4 hours, the thiyl radicals were trapped by TEMPO (Scheme 3e and Figure S2). By treating disulfide **5** with **1a**, **3a** was formed with only 53% yield, and the reaction yield decreased to 28% with addition of TEMPO (Scheme 3f), indicating multiple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

Based on the results, the following reaction mechanism is proposed (Scheme 4): Through the oxidation by copper(II), sulfite and sodium benzenesulfinate **2a** can be respectively oxidized to give sulfite radical **7**<sup>12</sup> and sulfonyl radical **8**, which couple together to afford sulfinyl sulfonate **9**. Upon the departure of sulfate radical **10**, the resulting sulfinyl radical **11** reacts

with sulfite radical **7** furnish the sulfenyl sulfonate **12**. This process is validated by the detection of benzenesulfonate **6** through formation of sulfonyl sulfate **13**. Intermediate **12** can undergo homolytic cleavage to give thiyl radical **14**<sup>13</sup> to directly react or

#### Scheme 4. Proposed mechanism



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 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 on the ACS Publications website.

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

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possibly form disulfide **5** for coupling with boronic acid in the presence of copper catalyst to give product **3a**. By reduction with copper, sulfenyl anion **15** can be generated from **12** to undergo the coupling reaction.

#### Notes

The authors declare no conflict of interest.

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