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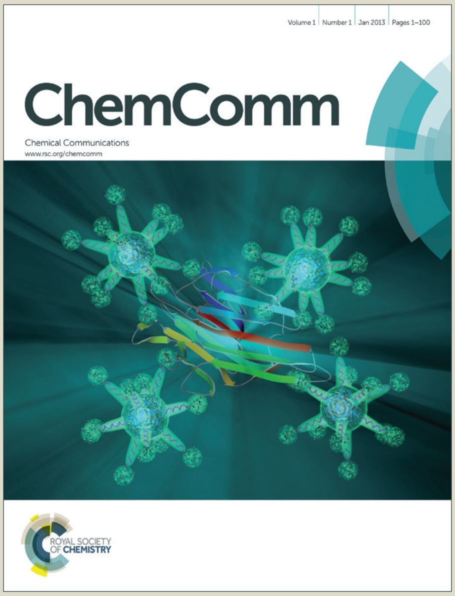

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A mild and facile synthesis of aryl and alkenyl sulfides via copper-catalyzed deborylthiolation of organoborons with thiosulfonates

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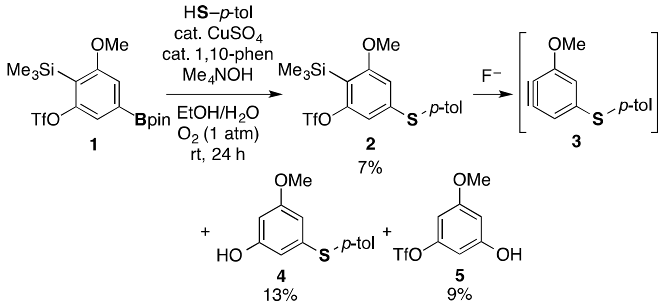
An efficient deborylthiolation of aryl- and alkenylborons with thiosulfonates has been achieved under mild conditions using a copper catalyst. All steps of the experimental process were free from unpleasant odors. The mild reaction conditions as well as ready availability of boron compounds and thiosulfonates enabled easy access to an array of sulfides, including those bearing sensitive functional groups.

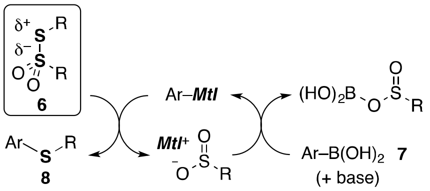
Aromatic sulfur compounds are widely used in a variety of disciplines, including materials science and pharmaceutical chemistry.[1–3] The most popular methods for preparing aromatic sulfides include the nucleophilic displacement of disulfides with carbon nucleophiles, such as aryl Grignard reagents, and transition-metal-catalyzed coupling reactions of aryl halides or boronic acids with thiols or disulfides.[4,5] Although numerous alternative methods for sulfide synthesis have been developed, reliable aromatic C–S bond forming reactions are still limited, particularly those applicable to the synthesis of sulfides bearing sensitive functional groups and free from unpleasant organosulfurous odors. Here we report an odorless copper-catalyzed thiolation of boronic acid derivatives with readily available thiosulfonates that allows for the facile preparation of diverse sulfides under mild conditions.



Scheme 1 The Chan–Lam–Evans-type thiolation of arylboronic ester **1**.

In the course of our recent studies on aryne chemistry,[6] we faced the limitation of the conventional methods for transition-metal-catalyzed deborylthiolation. For example, an attempt to transform arylboronic ester **1**[6i,7] to sulfide **2**, which we designed as a precursor of thiolated aryne **3**, via the Chan–Lam–Evans-type thiolation[5e] with *p*-toluenethiol resulted in a low efficiency, and desilylated side products, such as **4** and **5**, were also obtained (Scheme 1). Furthermore, an attempt to prepare **2** via the copper-catalyzed deborylthiolation of **1** with *N*-*p*-tolylthiosuccinimide[5a] also failed without producing any of the desired product. These unfavorable results motivated us to develop a novel method with higher functional group tolerance that is applicable to the synthesis of a wider range of sulfides.

We focused on thiosulfonate **6**[6c,8,9] as a readily available, odorless electrophilic sulfur source to provide sulfides by reaction with carbon nucleophiles accompanied by the liberation of an odorless and water-soluble sulfinate (Scheme 2). Considering the good leaving ability of the sulfonyl group,[10] we designed a catalytic thiolation reaction of boronic acids **7** using thiosulfonate **6**. The hypothetical catalytic cycle included a formal substitution reaction between thiosulfonate **6** and organometallic species generated from boronic acid **7** via a metal exchange reaction with or without a base, affording the desired sulfide **8** and regenerating the catalyst.



Scheme 2 Design of catalytic thiolation of arylboronic acids **7** using thiosulfonate **6**.

After extensive screening of the reaction conditions, we found that a copper salt in the presence of a weak base efficiently catalyzed the thiolation of phenylboronic acid (**7a**) with *S*-*p*-tolyl *p*-toluenethiosulfonate (**6a**) at room temperature to afford sulfide **8a** (Table 1). Initial screening for the metal salt indicated that copper salts, including copper sulfate, were most suitable for the desired

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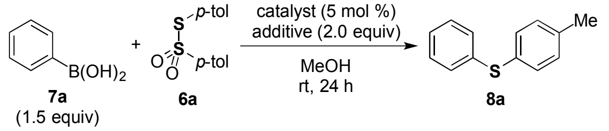
transformation (entries 1–5). Further studies showed that addition of a base was quite effective (entries 6–10). In particular, the use of a weak base, such as sodium bicarbonate or cesium fluoride, in combination with copper sulfate dramatically improved the reaction efficiencies to afford **8a** in excellent yields (entries 9 and 10). On the other hand, reactions in the presence of potassium *tert*-butoxide or potassium carbonate resulted in low efficiencies at room temperature (entries 6 and 7), while heating at 50 °C moderately improved the yield of **8a** for the latter case (entry 8). It is worth noting that the thiolation was achieved free from unpleasant odors during all steps of the experimental process.

Table 1 Optimization of the reaction conditions



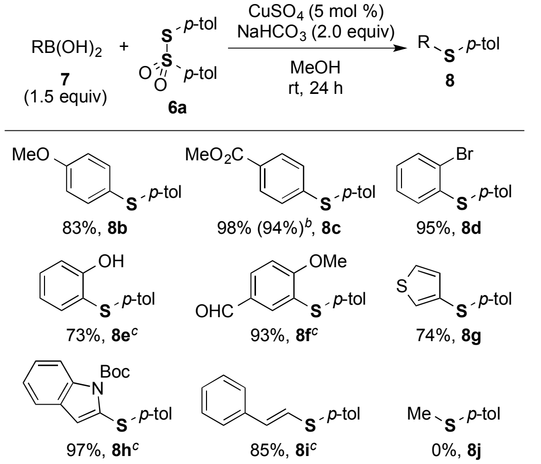
Entry	Catalyst	Additive	Yield of **8a** (%)[a]
1	Pd(OAc)$_2$	—	2
2	Ni(OAc)$_2$	—	0
3	CuOAc	—	16
4	Cu(OAc)$_2$	—	17
5	CuSO$_4$	—	16
6	CuSO$_4$	KO*t*-Bu	11
7	CuSO$_4$	K$_2$CO$_3$	7
8[b]	CuSO$_4$	K$_2$CO$_3$	53
9	CuSO$_4$	NaHCO$_3$	quant[c]
10	CuSO$_4$	CsF	98

[a] Yields were determined based on GC analyses unless otherwise noted. [b] The reaction was performed at 50 °C. [c] Isolated yield.

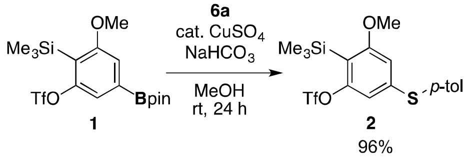
The optimized conditions were applicable to thiolations of a broad range of boronic acids **7** using thiosulfonate **6a**, with a slight modification of the conditions depending on the substrates (Table 2). Thiolations of *para*-substituted phenyl boronic acid bearing an electron-donating methoxy group or an electron-withdrawing ester moiety proceeded efficiently to afford sulfide **8b** or **8c**, respectively, in high yields. Furthermore, the reaction was scalable, as successfully demonstrated in the gram-scale synthesis of sulfide **8c** without exposure to unpleasant odors during the synthetic process. *ortho*-Bromophenylboronic acid was also thiolated efficiently with **6a** to yield sulfide **8d** without diminishing the bromo group. Sulfide **8e** having an unprotected phenolic hydroxy group was obtained in high yield from 2-hydroxyphenylboronic acid using potassium carbonate instead of sodium bicarbonate and heating at 50 °C, which effectively suppressed undesired deborylprotonation of the boronic acid. Thiolation of borylbenzaldehyde also proceeded efficiently to afford sulfide **8f**, leaving the electrophilic formyl group untouched. Heteroaromatic boronic acids also served as good substrates to provide thienyl or indolyl sulfides **8g** or **8h** in high yields. While alkenylboronic acid was thiolated smoothly to afford alkenyl sulfide **8i**, thiolation of methylboronic acid did not proceed under any of the conditions examined. The mild reaction conditions also enabled the deborylthiolation of borylated aryne precursor **1** to afford desired **2** in an excellent yield without producing desilylated side products (Scheme 3). These results clearly demonstrated the high functional group tolerance of this method.

The ready availability of various thiosulfonates also gives the method a distinctive advantage. For example, thiosulfonates such as **6b**–**6f**, which were easily prepared by selective oxidation of symmetric disulfides, were applicable to the thiolation, as demonstrated in the reaction with boronic acid **7c** (Table 3). *para*-Methoxyphenyl- and *para*-chlorophenylthiolated products **8k** and **8l** were obtained in high yields using thiosulfonates **6b** and **6c**, respectively (entries 1 and 2). The reaction with *ortho*-substituted substrate **6d** also proceeded smoothly to afford sulfide **8m** in an excellent yield (entry 3). Furyl- and benzylthiolation using

Table 2 Thiolations of various boronic acids **7** with thiosulfonate **6a**[a]

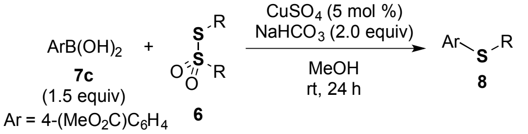


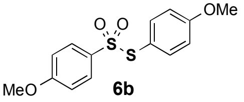
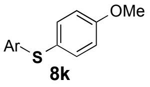
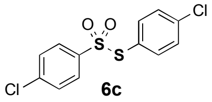
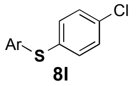
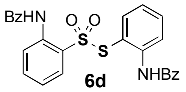
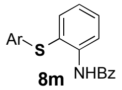
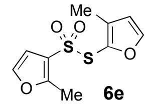
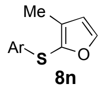
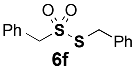
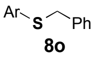
[a] Isolated yields. [b] A yield when the reaction was performed using 10 mmol of **6a** (2.8 g) and 15 mmol of **7c** (2.7 g) in parentheses. [c] K$_2$CO$_3$ (2.0 equiv) was used instead of NaHCO$_3$, and the reaction was performed at 50 °C for 24 h.



Scheme 3 Copper-catalyzed deborythiolation of arylboronic ester **1** with thiosulfonate **6a**.

Table 3 Thiolations of boronic acid **7c** with various thiosulfonates **6**



Entry	Thiosulfonate **6**	Product **8**	Yield (%)[a]
1	 **6b**	 **8k**	82
2	 **6c**	 **8l**	93
3	 **6d**	 **8m**	94
4	 **6e**	 **8n**	93
5	 **6f**	 **8o**	93

[a] Isolated yield.

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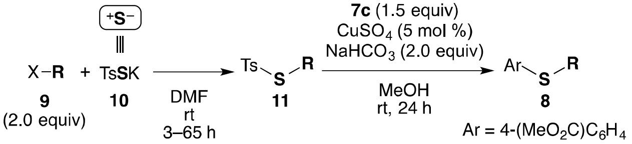
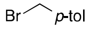
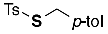
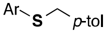
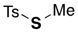
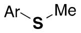
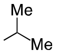
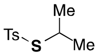
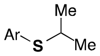
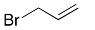
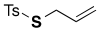
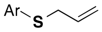
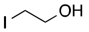
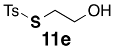
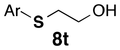
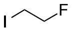
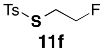
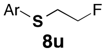
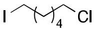
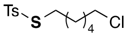
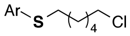
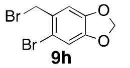
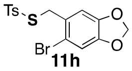
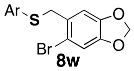
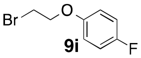
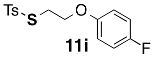
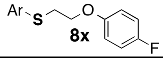
thiosulfonates **6e** and **6f** efficiently afforded sulfides **8n** and **8o**, respectively, showing the broad scope of the method (entries 4 and 5).

Table 4 Sulfide syntheses from alkyl halides **9**, potassium thiosulfonate **10**, and boronic acid **7c**



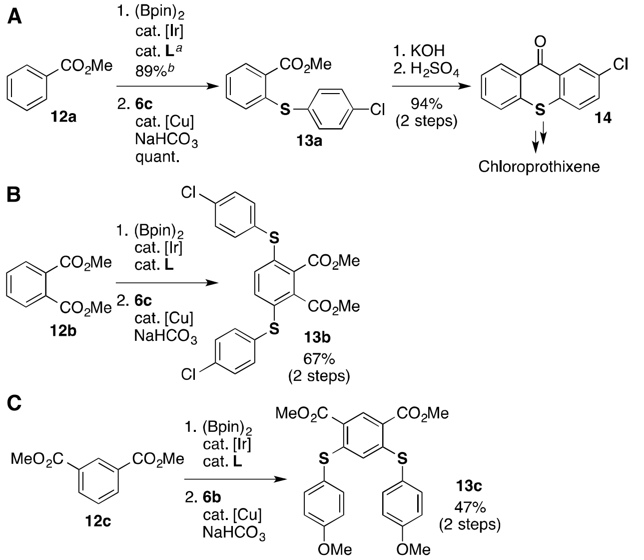
Ar = 4-$(MeO_2C)C_6H_4$

Entry	9	11	Yield (%)[a]	8	Yield (%)[a]
1	 **9a**	 **11a**	94	 **8p**	77
2	I–Me **9b**	 **11b**	86	 **8q**	97
3[b]	 **9c**	 **11c**	83	 **8r**	82
4	 **9d**	 **11d**	88	 **8s**	89
5	 **9e**	 **11e**	70	 **8t**	94
6	 **9f**	 **11f**	95	 **8u**	99
7	 **9g**	 **11g**	88	 **8v**	91
8	 **9h**	 **11h**	92	 **8w**	74
9	 **9i**	 **11i**	90	 **8x**	86

[a]Isolated yield. [b]K_2CO_3 (2.0 equiv) was used instead of $NaHCO_3$, and the reaction was performed at 50 °C for 24 h.

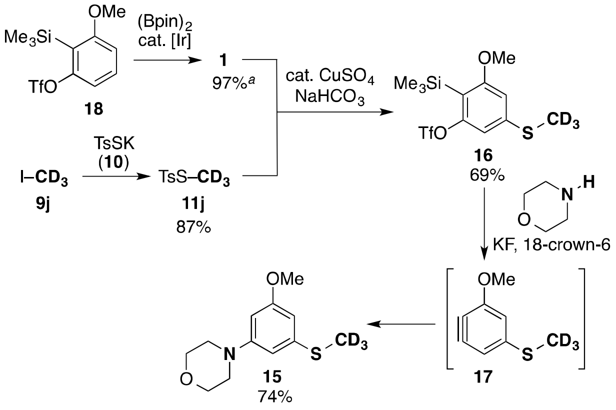
The use of readily available alkyl thiosulfonates further expanded the scope of the reaction. Nucleophilic substitution reactions of alkyl halides **9a**–**9i** with potassium *p*-toluenethiosulfonate (**10**)[11] efficiently provided the corresponding alkyl thiosulfonates **11a**–**11i** in high yields (Table 4). Subsequent copper-catalyzed thiolation of boronic acid **7c** with these thiosulfonates also proceeded efficiently, affording alkyl aryl sulfides **8p**–**8x** in high yields. These results clearly demonstrated the wide functional group tolerance of this two-step transformation, as not only the simple alkyl halides **9a** and **9b** but also the sterically-hindered secondary alkyl halide **9c** and allyl bromide (**9d**) participated in the sulfide synthesis (entries 1–4). Alkyl halides bearing an unprotected hydroxy group (entry 5), other halides (entries 6–9), or ether moieties (entries 8 and 9) also served as good substrates, efficiently affording the corresponding alkyl aryl sulfides without damaging these functionalities. It is worth noting that the reagent **10** acted overall as a "$^{+}S^{-}$" equivalent in this transformation.

A formal C–H thiolation[12,13] of simple aromatic compounds was achieved via iridium-catalyzed C–H borylation of arenes,[14,15] followed by the copper-catalyzed thiolation, enabling facile access to an array of sulfides (Scheme 4). For example, *ortho*-selective borylation of methyl benzoate (**12a**) using Ir–Silica-SMAP catalyst[15a] and subsequent deborylthiolation with **6c** afforded sulfide **13a** in high overall yield (Scheme 4A). Hydrolysis of **13a** followed by acidic cyclization furnished thioxanthone **14**, which is a key intermediate for various antipsychotics.[16] This approach enabled the double thiolation of *ortho*- and *meta*-phthalate diester **12b** and **12c**, easily providing di(sulfanyl) diesters **13b** or **13c**, respectively (Schemes 4B and 4C).



Scheme 4 Formal C–H thiolation of aryl esters **12a**–**12c**. Yields are those of isolated products. [a]**L** = Silica-SMAP. [b]See, ref. 15a.

The combined use of the methods developed in this study and a multi-component coupling based on the aryne chemistry[17] enabled the facile and efficient preparation of sulfides that were previously difficult to access. For example, the sequential assembly of various modules, such as iodomethane-d_3 (**9j**), potassium thiosulfonate (**10**), borylated aryne precursor **1**,[6i] and morpholine, allowed to furnish 1,3,5-trisubstituted aryl sulfide **15** in high efficiency (Scheme 5). The thiolated aryne precursors, such as **16**, would serve as platform molecules for preparing diverse highly functionalized aryl sulfides through the generation of arynes, such as **17**, and their reactions with various arynophiles and nucleophiles.[6,17]



Scheme 5 Synthesis of 1,3,5-trisubstituted aryl sulfide **15** via formal C–H thiolation of aryne precursor **18**. Yields are those of isolated products. [a]See, ref. 6i.

In summary, we have developed a simple, efficient, and odorless deborylthiolation method of organoboron compounds with thiosulfonates catalyzed by copper. The ready availability of diverse boronic acid derivatives and thiosulfonates, as well as the mild reaction conditions allowed us to prepare a variety of sulfides, including those with sensitive functionalities. Further studies are currently underway in our laboratory.

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Notes and references

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A mild and facile synthesis of aryl and alkenyl sulfides via copper-catalyzed deborylthiolation of organoborons with thiosulfonates

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A simple, efficient, and oderless deborylthiolation of aryl- and alkenylborons with thiosulfonates has been achieved under mild conditions using a copper catalyst.