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COMMUNICATION

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CuI-catalyzed direct synthesis of diaryl thioethers from aryl boronic acids and arylsulfonyl chlorides

Keke Huang[1] | **Min Yang**[2] | **Xiao-Jing Lai**[1] | **Xin Hu**[2] | **Guanyinsheng Qiu**[3] | **Jin-Biao Liu**[1]

[1]School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, 86 Hongqi Road, Ganzhou, 341000, China

[2]Department of Forensic Science, Gannan Medical University, 1 Yixueyuan Road, Ganzhou, Jiangxi, 341000, China

[3]College of Biological, Chemical Science and Engineering, Jiaxing University, 118 Jiahang Road, Jiaxing, 314001, China

Correspondence
Min Yang, Department of Forensic Science, Gannan Medical University, 1 Yixueyuan Road, Ganzhou, Jiangxi 341000, China.
Email: jiayoudouchi@163.com
Guanyinsheng Qiu, College of Biological, Chemical Science and Engineering, Jiaxing University, 118 Jiahang Road, Jiaxing 314001, China.
Email: qiuguanyinsheng@mail.zjxu.edu
Jin-Biao Liu, School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, 86 Hongqi Road, Ganzhou 341000, China.
Email: liujinbiao@jxust.edu.cn

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A CuI-catalyzed direct coupling of aryl boronic acids with arylsulfonyl chlorides for the preparation of diaryl thioethers was developed. The reaction is initiated by a PPh_3 reduction of the arylsulfonyl chloride, followed by a CuI-catalyzed C–S coupling with an aryl boronic acid. Various arylsulfonyl chlorides can directly serve as a sulfur source in this mild and efficient reaction giving the desired products in moderate to good yields. Moreover, this practical method has also been applied to the thioetherification of aryl iodides and acetylacetones.

KEYWORDS
aryl boronic acid, arylsulfonyl chloride, Cu(I) catalysis, thioether

1 | INTRODUCTION

The thioether functionality is prevalent in numerous natural products and pharmaceutical compounds which possess significant biological activities (Figure 1).[1,2] The structural modification of flavonoids via the introduction of sulfur atoms, such as thio-flavopiridol analogs **1**, has attracted considerable attention due to their antiproliferative activity.[3,4] AZD4407 **2** is being used as an antiallergy/antiasthmatic agent for chronic obstructive pulmonary diseases (COPD).[5] Nelfinavir **3** is employed in the treatment of human immunodeficiency virus (HIV) together with other medications.[6]

Due to the ubiquity of the diaryl thioether motif in pharmaceuticals,[7] novel synthetic protocols have been developed for their preparation[8] and recent attention has focused on transition-metal catalyzed C (sp2)–S bond formation.[9–12] The transition metal-catalyzed C-S coupling of aryl halides or aryl boronic acids with thiols or thiophenols is well developed, and has become one of the most powerful protocols.[13] Recently, other alternative approaches to diaryl thioethers using sulfenylating agents, such as quinone mono-O,S-acetals,[14] disulfides,[15] sulfenyl halides,[16] *N*-thioaryl phthalimides,[17] and thiols in combination with *N*-chlorosuccinimide, Selectflfluor or iron (III) chloride have also been developed.[18]

Among these sulfur sources, arylsulfonyl chlorides have emerged as promising thiol-free sulfur sources in thioether synthesis due to their commercial availability and price. In Vogel's work, arylsulfonyl chlorides have been widely used as leaving groups in C–C bond formation.[19] In 2011, You et al. divulged the first metal-free synthesis of di (hetero)aryl sulfides by directly using sulfonyl chlorides as sulfur sources in the presence of PPh_3 at 130 °C.[20] Quite recently, Fu and co-workers reported a CuI-catalyzed sulfenylation of organozinc reagents with arylsulfonyl chlorides/PPh_3.[21] Despite significant progress, the development of a new, direct and facile sulfenylation of (hetero)arenes to afford diaryl thioethers is still highly desired. In light of our efforts in developing synthetic methodology under mild conditions towards useful molecules,[22] we would like to avoid the use of high temperatures and unstable organometallic reagents for the synthesis of diaryl thioethers. Therefore, we have developed an inexpensive procedure that utilizes arylsulfonyl chlorides which can directly serve as sulfur sources in the construction of diaryl thioethers with aryl boronic acids under mild conditions (Scheme 1).

At the outset of this investigation, optimization of the reaction parameters was performed using *p*-toluenesulfonyl chloride (TsCl) **1a** and 4-methoxyphenylboronic acid **2a** as the model substrates, the results of which are summarized in Table 1. We

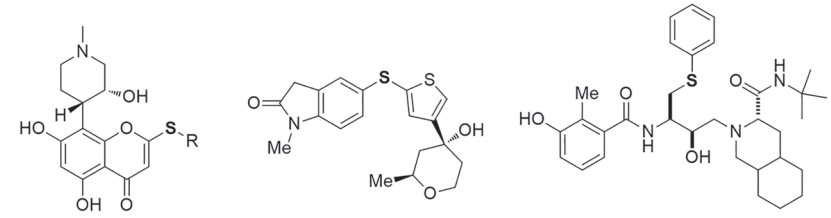
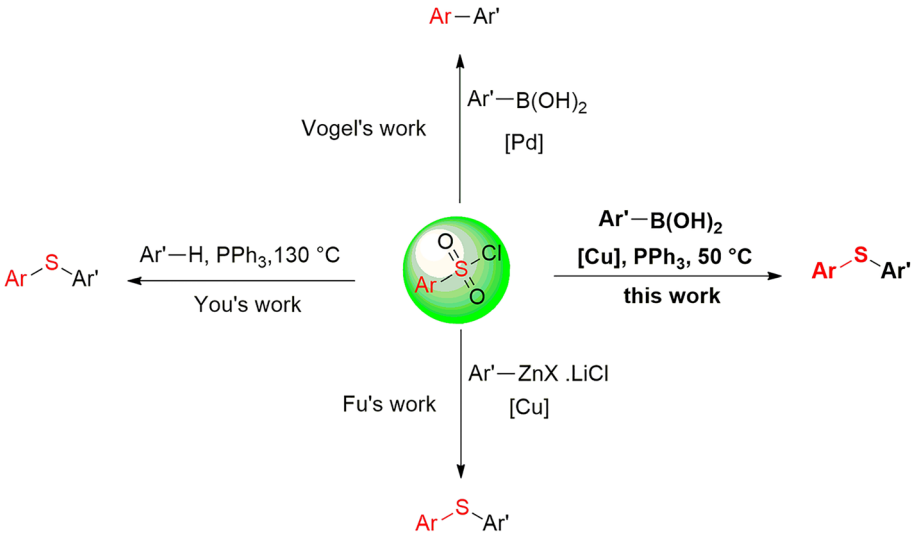


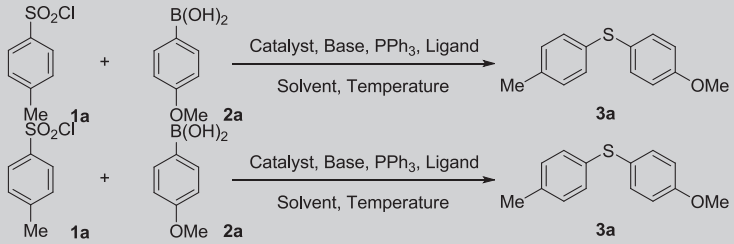
FIGURE 1 Examples of bioactive thioethers



SCHEME 1 Arylsulfonyl chlorides in C–C and C–S bond forming reactions

explored the sulfenylation of TsCl with **2a** in the presence of various catalysts such as CuI, CuBr, Cu_2O, Cu $(OAc)_2$, and $PdCl_2$ with PPh_3, 1,10-phenanthroline (Phen) and K_2CO_3 at 50 °C under air (entries 1-5, Table 1). The reaction of TsCl (1.0 equiv.) and **2a** (1.5 equiv.) in the presence of PPh_3 (2.0 equiv.), CuI (10%), Phen (10%) and K_2CO_3 (3.0 equiv.) in THF/DMSO (*V*/V = 2: 1) at 50 °C, gave (4-methoxyphenyl)(*p*-tolyl)sulfane **3a** in 71% isolated yield (entry 1, Table 1). Alternatively, a trace amount of product was detected in the model reaction with $PdCl_2$ (entry 5, Table 1). To our delight, when the amount of CuI was reduced to 0.01 equiv, the yield of **3a** was increased to 77% (entry 7, Table 1). In order to try and obtain better product yields, different reaction conditions were screened. Firstly, the ratio of THF/DMSO was investigated, and no significant increase in yield was

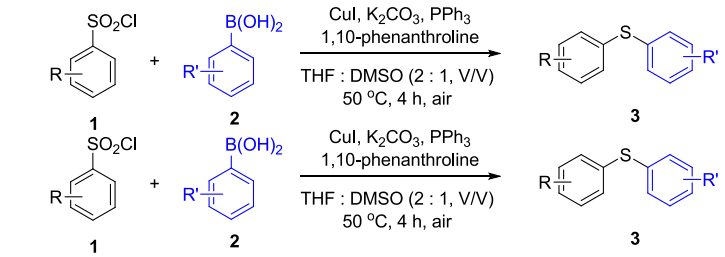
TABLE 1 Initial studies for the reaction of *p*-toluenesulfonyl chloride **1a** with 4-methoxyphenylboronic acid **2a**[a]

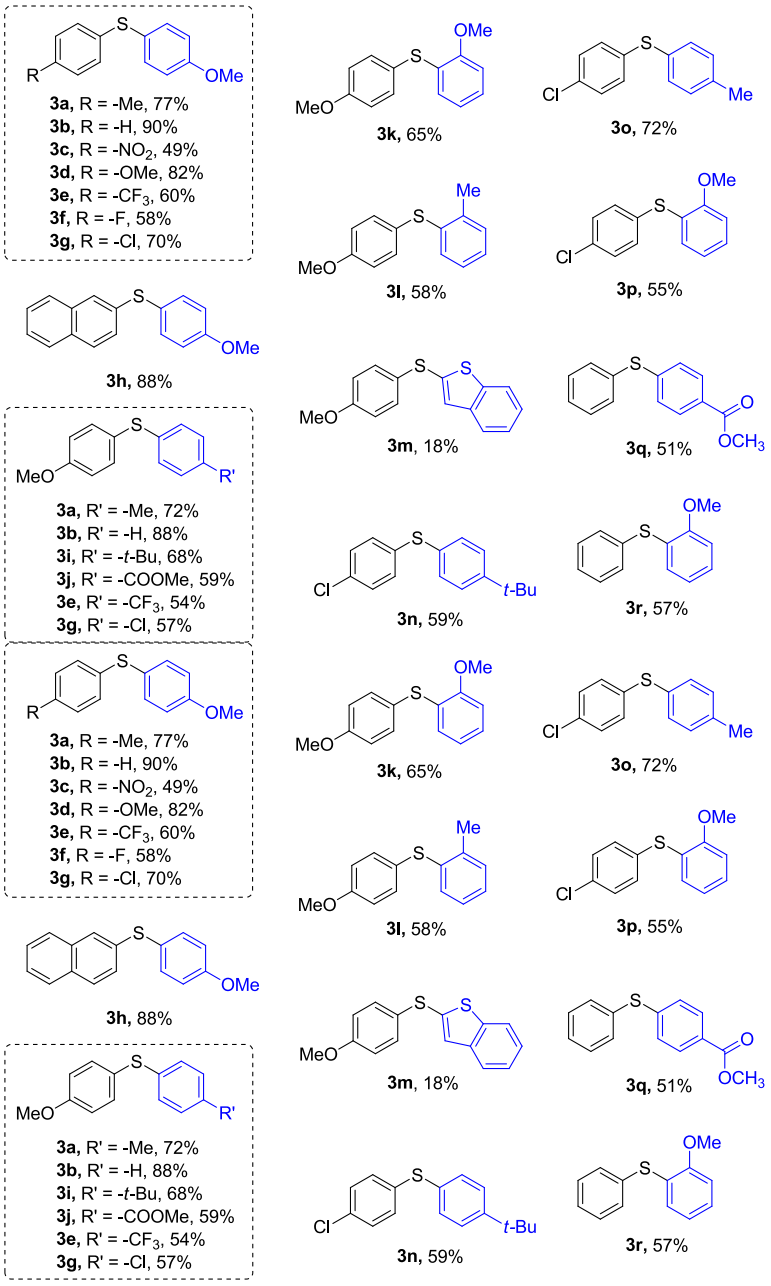


Entry	Base	Catalyst (%)	Ligand	Solvent (*V*/V)	Temperature (°C)	Yield [b]
1	K_2CO_3	CuI (10)	Phen	THF: DMSO (2: 1)	50	71%
2	K_2CO_3	CuBr (10)	Phen	THF: DMSO (2: 1)	50	62%
3	K_2CO_3	Cu_2O (10)	Phen	THF: DMSO (2: 1)	50	40%
4	K_2CO_3	Cu $(OAc)_2$ (10)	Phen	THF: DMSO (2: 1)	50	69%
5	K_2CO_3	$PdCl_2$ (10)	Phen	THF: DMSO (2: 1)	50	trace
6	K_2CO_3	None	Phen	THF: DMSO (2: 1)	50	trace
7	K_2CO_3	CuI (5)	Phen	THF: DMSO (2: 1)	50	77%
8	K_2CO_3	CuI (5)	Phen	THF: DMSO (4: 1)	50	73%
9	K_2CO_3	CuI (5)	Phen	THF: DMSO (1: 1)	50	69%
10	K_2CO_3	CuI (5)	Phen	dioxane: DMSO (2: 1)	50	75%
11	K_2CO_3	CuI (5)	Phen	THF: DMF (2: 1)	50	70%
12	K_2CO_3	CuI (5)	Phen	THF: MeCN (2: 1)	50	49%
13	K_2CO_3	CuI (5)	Phen	THF: MeOH (2: 1)	50	56%
14	K_2CO_3	CuI (5)	Phen	THF: CH_2Cl_2 (2: 1)	50	65%
15	None	CuI (5)	Phen	THF: DMSO (2: 1)	50	trace
16	KOH	CuI (5)	Phen	THF: DMSO (2: 1)	50	70%
17	Cs_2CO_3	CuI (5)	Phen	THF: DMSO (2: 1)	50	trace
18	*t*-BuONa	CuI (5)	Phen	THF: DMSO (2: 1)	50	47%
19	Et_3N	CuI (5)	Phen	THF: DMSO (2: 1)	50	trace
20	K_2CO_3	CuI (5)	None	THF: DMSO (2: 1)	50	5%
21	K_2CO_3	CuI (5)	Bpy	THF: DMSO (2: 1)	50	17%
22	K_2CO_3	CuI (5)	proline	THF: DMSO (2: 1)	50	trace
23	K_2CO_3	CuI (5)	Phen	THF: DMSO (2: 1)	100	76%
24	K_2CO_3	CuI (5)	Phen	THF: DMSO (2: 1)	RT	68%
25	K_2CO_3	CuI (5)	Phen	THF: DMSO (2: 1)	50	37%[c]

Reaction conditions: *a*): TsCl (**1a**, 0.2 mmol), 4-methoxyphenylboronic acid (**2a**, 0.3 mmol), PPh_3 (0.4 mmol), base (0.6 mmol), catalyst/ligand (catalyst: ligand = 1: 1), solvent (3 ml), 4 hr, air; *b*): Isolated yields based on TsCl **1a**. Phen = Phen, 2,2′-bipyridine = Bpy. c) The loading of PPh_3 was reduced to 0.2 mmol.

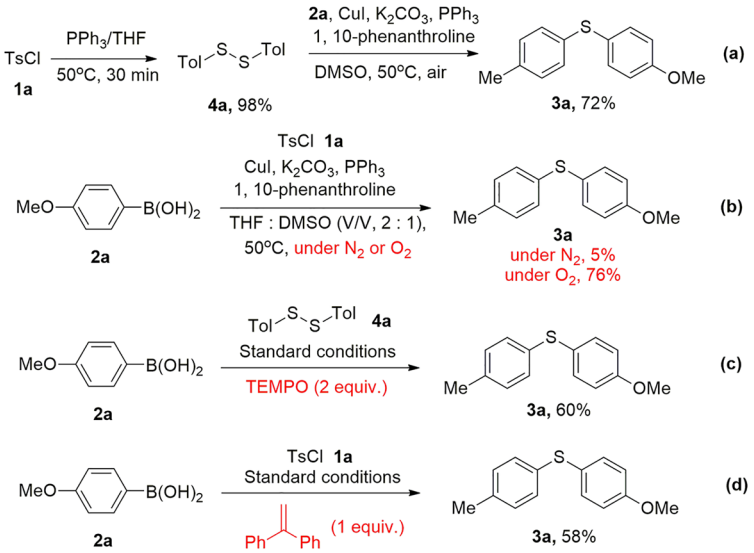
TABLE 2 Reaction of arylsulfonyl chlorides with aryl boronic acids [a]





Reaction conditions: a) **1** (0.2 mmol), **2** (0.3 mmol), PPh_3 (0.4 mmol), K_2CO_3 (0.6 mmol), CuI (5%), 1,10-phenanthroline (5%), THF (2 ml) and DMSO (1 ml), 50 °C, 4 hr, air.

SCHEME 2 Control experiments



observed by adjusting the ratio of solvents (entries 8 and 9, Table 1). Mixed solvent evaluation revealed that no better yields were provided when using dioxane/DMSO, THF/DMF, THF/MeCN, THF/MeOH, and THF/CH_2Cl_2 as the mixed-solvents (entries 10-15, Table 1). Next, several bases such as KOH, Cs_2CO_3, *t*-BuONa and Et_3N, were explored but none of these bases provided better results (entries 16-19, Table 1). Subsequently, several other ligands were tested for this transformation (entries 20-22, Table 1). It was found that 2,2′-bipyridine and proline were not able to promote the reaction. Finally, the effect of temperature was then examined; the results showed that temperatures above or below 50 °C resulted in lower yields of the desired product (entries 23 and 24, Table 1). When 1 equiv. of PPh_3 was further employed, the yield of the corresponding product was dramatically decreased to 37% (entry 25, Table 1). The best reaction conditions were found to be the following: using CuI as the catalyst, Phen as the ligand, K_2CO_3 as the base, PPh_3 as the reducing agent, THF/DMSO as a mixed solvent and conducting the reaction at 50 °C. It should be noted that a trace amount of **3a** was obtained under the model conditions in the absence of CuI (entry 6, Table 1) or K_2CO_3 (entry 15, Table 1). Additionally, no desired product was obtained when the reaction was conducted in the sole THF or DMSO solvent. Other reductants ($NaBH_4$, I_2 or *n*-Bu_4NI instead of PPh_3) and other oxidants (Ag_2CO_3 or H_2O_2 instead of O_2) have also been tested, but no better results were observed (Table S1 in ESI).

The scope and generality of this CuI-catalyzed sulfenylation of various aryl boronic acids with aromatic sulfonyl chlorides/PPh_3 was investigated using the optimized conditions (Table 2). Arylsulfonyl chlorides **1** containing either electron-donating or electron-withdrawing groups were smoothly converted into diaryl thioethers **3a-h** in good to excellent yields via reaction with 4-methoxyphenylboronic acid **2a**. A variety of important functional groups, including nitro (**3c**) and trifluoromethyl (**3e**) substituents were tolerated under the optimized reaction conditions giving their corresponding products in 49% and 60% yield, respectively. In contrast, when using naphthalene-2-sulfonyl chloride, the corresponding product **3h** was obtained in 88% yield. The reaction of 4-methoxybenzene-1-sulfonyl chloride with various aryl boronic acids was then investigated. The results demonstrated that a series of functional substituents, such as methyl, tert-butyl, carboxyl,

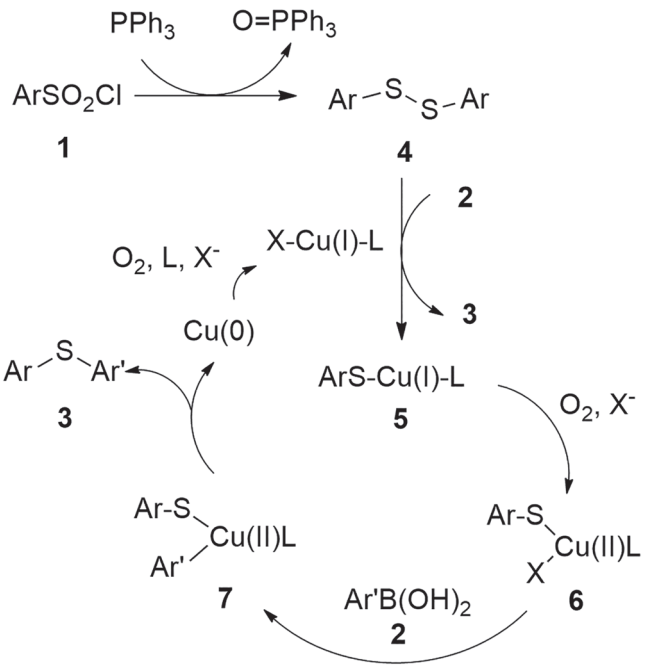
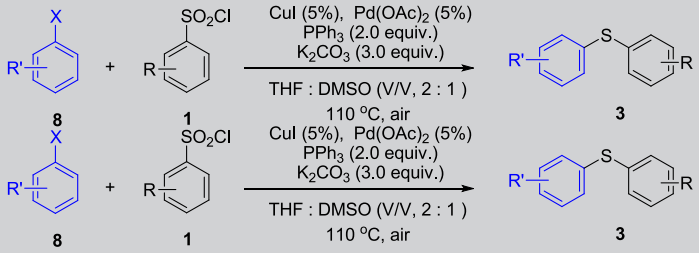


FIGURE 2 Proposed mechanism

trifluoromethyl and chloro groups on the aromatic motif of **2** were tolerated. Interestingly, compared with previous results, there was no obvious difference in yields between **3a**, **3b** and **3e**; however, the diaryl thioether **3g** was obtained in a lower yield of 57%. The influence of steric hindrance on the reaction was not obvious, with the bulky products **3K** and **3I** being obtained in yields of 65% and 58%, respectively. Unfortunately, when a heteroaryl boronic acid was employed for the formation of **3m**, the desired product was obtained in only 18% yield. To further explore the scope and the limitations of the methodology, reactions of 4-chlorobenzene-1-sulfonyl chloride or benzenesulfonyl chloride with different aryl boronic acids were conducted (**3n-3r**). Among the results, the corresponding products were obtained moderate yields, except for **3o**, which was prepared in a good yield (72%). Unfortunately, when aliphatic sulfonyl chlorides or boracic acids were used as the substrates, no anticipated products were observed.

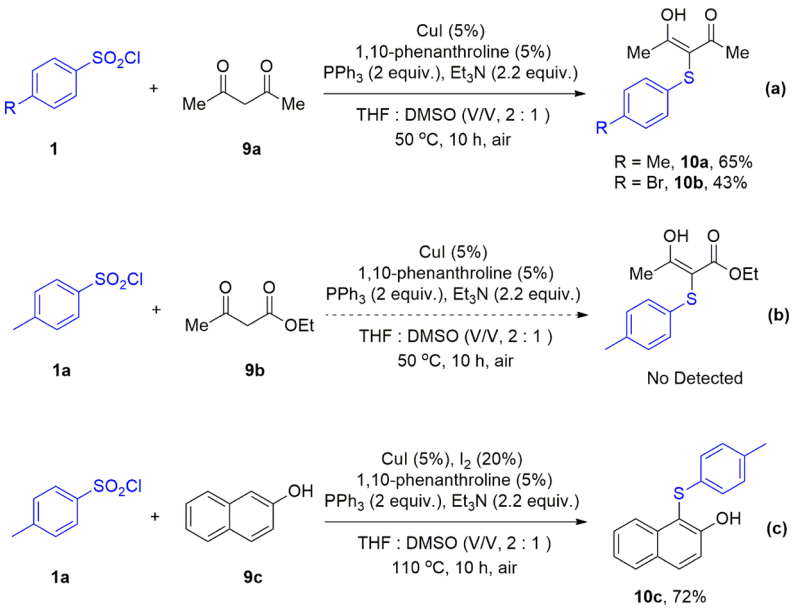
To illustrate a possible mechanism for this transformation, several control experiments were conducted and the results are summarized in Scheme 2. It was observed that TsCl could be reduced by PPh_3, forming the disulfide **4a** in excellent yield. Based on the synthesis of the disulfide **4a**, TsCl may serve as the starting material for further sulfenylation with 4-methoxyphenylboronic acid **2a**,

TABLE 3 Reaction of arylsulfonyl chlorides with aryl boronic acid pinacol ester or aryl iodides **8**[a]



Entry	X	R'	R	Yield
1[b]	boronic acid pinacol ester	4-OMe	H	27%
2	I	4-OMe	H	5%
3	I	H	4-OMe	trace
4	I	4-NO_2	4-OMe	63%
5	I	4-NO_2	4-Me	61%

Reaction conditions: a) **1** (0.2 mmol), **8** (0.3 mmol), PPh_3 (0.4 mmol), K_2CO_3 (0.6 mmol), CuI (5%), Pd $(OAc)_2$ (5%), 1,10-phenanthroline (5%), THF (2 ml) and DMSO (1 ml), 110 °C, 10 hr, air; b) Without Pd $(OAc)_2$.



SCHEME 3 Reactions of aryl sulfonyl chloride with acetylacetone, ethyl acetoacetate and β-naphthol

affording **3a** in 72% yield (Scheme 2a). Compared with the standard conditions, a comparable yield was obtained under an O_2 atmosphere, but the product was obtained in only 5% yield under a N_2 atmosphere, showing the important role of oxygen in this reaction (Scheme 2b). In order to further investigate the reaction mechanism, two commonly used radical scavengers (TEMPO and 1,1-diphenylethylene) were employed. In the presence of the radical scavengers, **3a** was obtained in yields of 60% and 58%, respectively, and no other adducts were detected by GC-MS (**Scheme 2c** and **2d**). This may suggest that this transformation does not occur via a radical process.

Thus, based on the above results and our previous work, we have proposed a plausible mechanism for this transformation (Figure 2).[23] Firstly, the arylsulfonyl chloride is reduced by PPh_3 to give the disulfide **4**. After cleavage by X-Cu(I)-L, Ar-S-Cu(I)L **5** is generated, which is then oxidized by oxygen to give Ar-S-Cu (II)XL **6**.[24] Meanwhile, another half of ArSSAr **4** would react with Ar′B $(OH)_2$ **2** forming the diaryl thioether **3**. Transmetalation of Ar′B $(OH)_2$ **2** occurs to generate Ar-S-Cu (II)-Ar′L **7**, which undergoes reductive elimination to afford the corresponding diaryl thioether **3** and gave Cu(0). Meanwhile, the oxygen in the air regenerated the Cu(I)-catalyst.

To further examine the scope of this method, aryl boronic acid pinacol ester and aryl iodides were employed in the reaction in place of aryl boronic acids (Table 3). The use of a pinacol ester gave in only 27% yield, even at a higher temperature (Entry 1, Table 3). However, the reaction of aryl halides with arylsulfonyl chlorides required additional palladium-catalyst. Only *p*-nitrophenyliodide could be used as the aryl source for smooth coupling with the arylsulfonyl chlorides (Entries 4 and 5, Table 3), and both *p*-methoxyphenyliodide and phenyliodide were unreactive in the thioetherification reaction (Entries 2 and 3, Table 3).

Additionally, acetylacetone, ethyl acetoacetate and *β*-naphthol have been used as reaction substrates (Scheme 3). For instance, treatment of $ArSO_2Cl$ with acetylacetone **9a** in the presence of CuI/Phen, PPh_3, and Et_3N in THF/DMSO at 50 °C for 10 hrs under air, afforded the corresponding thioether **10a** and **10b** in 65% and 43% yields, respectively (Scheme 3a). Acetylacetone thioether was a versatile dual-functionalized synthon.[25] However, ethyl acetoacetate is totally inert in this CuI-catalyzed direct thioetherification reaction (Scheme 3b). We have also investigated the reaction between TsCl and *β*-naphthol under the mediation of molecular iodine, and the corresponding thioether **10c** was obtained in 72% yield (Scheme 3c).

In summary, we have developed an efficient and practical method for the preparation of diaryl thioethers via a CuI-catalyzed direct coupling of aryl boronic acids with arylsulfonyl chlorides. The reaction is initiated via initial reduction of the arylsulfonyl chloride with PPh_3 and subsequent CuI-catalyzed C–S coupling with an aryl boronic acid. Various arylsulfonyl chlorides were used as sulfur sources for smooth coupling with aryl boronic acids; the desired products were obtained in moderate to good yields. Moreover, aryl iodides and acetylacetone could also be employed in the reaction to afford the corresponding thioethers. Work is ongoing to extend the application of this methodology.

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ORCID

Jin-Biao Liu https://orcid.org/0000-0002-5038-6541

REFERENCES

[1] a)J. Hutton, A. D. Jones, S. A. Lee, D. M. G. Martin, B. R. Meyrick, I. Patel, R. F. Peardon, L. Powell, *Org. Process Res. Dev.* **1997**, *1*, 61. b)G. De Martino, M. C. Edler, G. La Regina, A. Coluccia, M. C. Barbera, D. Barrow, R. I. Nicholson, G. Chiosis, A. Brancale, E. Hamel, M. Artico, R. Silvestri, *J. Med. Chem.* **2006**, *49*, 947. c)W. Xie, Y. Wu, J. Zhang, Q. Mei, Y. Zhang, N. Zhu, R. Liu, H. Zhang, *Eur. J. Med. Chem.* **2018**, *145*, 35.

[2] a)S. W. Kaldor, V. J. Kalish, J. F. Davies, B. V. Shetty, J. E. Fritz, K. Appelt, J. A. Burgess, K. M. Campanale, N. Y. Chirgadze, D. K. Clawson, B. A. Dressman, S. D. Hatch, D. A. Khalil, M. B. Kosa, P. P. Lubbehusen, M. A. Muesing, A. K. Patick, S. H. Reich, K. S. Su, J. H. Tatlock, *J. Med. Chem.* **1997**, *40*, 3979. b)G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik, T. W. von Geldern, *J. Med. Chem.* **2001**, *44*, 1202.

[3] H. K. Wang, K. F. Bastow, L. K. Cosentino, K. H. Lee, *J. Med. Chem.* **1996**, *39*, 1975.

[4] T. Kataoka, S. Watanab, E. Mori, R. Kanomoto, S. Tanimura, M. S. Kohno, *Bioorg. Med. Chem.* **2004**, *12*, 2397.

[5] M.-L. Alcaraz, S. Atkinson, P. Cornwall, A. C. Foster, D. M. Gill, L. A. Humphries, P. S. Keegan, R. Kemp, E. Merifield, R. A. Nixon, A. J. Noble, D. O'Beirne, Z. M. Patel, J. Perkins, P. Rowan, P. Sadler, J. T. Singleton, J. Tornos, A. J. Watts, I. A. Woodland, *Org. Process Res. Dev.* **2005**, *9*, 555.

[6] S. Raghavan, B. Sridhar, *J. Org. Chem.* **2010**, *75*, 498.

[7] a)M. Feng, B. Tang, S. H. Liang, X. Jiang, *Curr. Top. Med. Chem.* **2016**, *16*, 1200. b)E. A. Ilardi, E. Vitaku, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 2832.

[8] For recent reviews:a)A. Ghaderi, *Tetrahedron* **2016**, *72*, 4758. b)X.-Q. Pan, J.-P. Zou, W.-B. Yi, W. Zhang, *Tetrahedron* **2015**, *71*, 7481. c)C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. Andy Hor, X. Liu, *Chem. Soc. Rev.* **2015**, *44*, 291. For radical C-S bond formation, see:d)X. Gong, X. Li, W. Xie, J. Wu, S. Ye, *Org. Chem. Front.* **2019**, *6*, 1863. e)J. Zhang, W. Xie, S. Ye, J. Wu, *Org. Chem. Front.* **2019**, *6*, 2254. f)S. Ye, T. Xiang, X. Li, J. Wu, *Org. Chem. Front.* **2019**, *6*, 2183. g)S. Ye, X. Li, W. Xie, J. Wu, *Asian J. Org. Chem.* **2019**, *8*, 893. h)X. Wang, M. Yang, W. Xie, X. Fan, J. Wu, *Chem. Commun.* **2019**, *55*, 6010. i)G. Liu, H. Liu, G. Qiu, S. Pu, J. Wu, *Chem. Commun.* **2012**, *48*, 7049. j) S. Ye, G. Qiu, J. Wu, *Chem. Commun.* **2019**, *55*, 1013. k) X. Gong, M. Wang, S. Ye, J. Wu, *Org. Lett.* **2019**, *21*, 1156. lY. Zong, L. Lang, M. Yang, X. Li, X. Fan, J. Wu, *Org. Lett.* **2019**, *21*, 1935. m)F.-S. He, Y. Wu, X. Li, H. Xia, J. Wu, *Org. Chem. Front.* **2019**, *6*, 1873. nJ. Zhang, X. Li, W. Xie, S. Ye, J. Wu, *Org. Lett.* **2019**, *21*, 4950.

[9] For reviews on transition-metal-catalyzed C-S coupling reaction, see:a)S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed.* **2003**, *42*, 5400. b)T. Kondo, T. Mitsudo, *Chem. Rev.* **2000**, *100*, 3205. c)C. C. Eichman, J. P. Stambuli, *Molecules* **2011**, *16*, 590. d)S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed.* **2003**, *42*, 5400. e)I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596. f)D. J. Procter, *J. Chem. Soc. Perkin. Trans. 1* **2001**, 335. g)I. P. Beletskaya, V. P. Ananikov, *Eur. J. Org. Chem.* **2007**, 3431. h)H. Liu, X. Jiang, *Chem. – Asian J.* **2013**, *8*, 2546.

[10] a)C.-F. Lee, Y.-C. Liu, S. S. Badsara, *Chem. – Asian J.* **2014**, *9*, 706. b)M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *Chem. – Eur. J.* **2006**, *12*, 7782. c)M. A. Fernández-Rodríguez, J. F. Hartwig, *J. Org. Chem.* **2009**, *74*, 1663. d)P. Saravanan, P. Anbarasan, *Org. Lett.* **2014**, *16*, 848. e)L. Cai, J. Cuevas, Y.-Y. Peng, V. W. Pike, *Tetrahedron Lett.* **2006**, *47*, 4449. f) N. Park, K. Park, M. Jang, S. Lee, *J. Org. Chem.* **2011**, *76*, 4371. g)M. Murata, S. L. Buchwald, *Tetrahedron* **2004**, *60*, 7397. h) M. Sayah, M. G. Organ, *Chem. – Eur. J.* **2011**, *17*, 11719. i) F. Y. Kwong, S. L. Buchwald, *Org. Lett.* **2002**, *4*, 3517. j) Y. Jiang, Y. Qin, S. Xie, X. Zhang, J. Dong, D. Ma, *Org. Lett.* **2009**, *11*, 5250. k)F. Ke, Y. Qu, Z. Jiang, Z. Li, D. Wu, X. Zhou, *Org. Lett.* **2011**, *13*, 454. l)L. Rout, T. K. Sen, T. Punniyamurthy, *Angew. Chem. Int. Ed.* **2007**, *46*, 5583. m) H.-J. Xu, Y.-Q. Zhao, T. Feng, Y.-S. Feng, *J. Org. Chem.* **2012**, *77*, 2878. n)C. Uyeda, Y. Tan, G. C. Fu, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 9548. o)V. Percec, J.-Y. Bae, D. H. Hill, *J. Org. Chem.* **1995**, *60*, 6895. p)Y. Zhang, K. C. Ngeow, J. Y. Ying, *Org. Lett.* **2007**, *9*, 3495. q)X.-B. Xu, J. Liu, J.-J. Zhang, Y.-W. Wang, Y. Peng, *Org. Lett.* **2013**, *15*, 550. r) L. B. Junquera, F. E. Fernández, M. C. Puerta, P. Valerga, *Eur. J. Inorg. Chem.* **2017**, *2017*, 2547. s)M. J. Iglesias, A. Prieto, M. C. Nicasio, *Adv. Synth. Catal.* **2010**, *352*, 1949. t) N. Taniguchi, *J. Org. Chem.* **2004**, *69*, 6904.

[11] a)M. A. Fernández-Rodríguez, Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 2180. b)S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed.* **2003**, *42*, 5400.

[12] Y. Liu, H. Wang, J. Zhang, J.-P. Wan, C. Wen, *RSC Adv.* **2014**, *4*, 19472.

[13] For review on Ullmann condensation and modifified reactions, see: a)S. V. Ley, A. W. Thomas, *Angew. Chem. Int. Ed.* **2003**, *42*, 5400. b)F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.* **2009**, *48*, 6954.

[14] M. Matsugi, K. Murata, K. Gotanda, H. Nambu, G. Anilkumar, K. Matsumoto, Y. Kita, *J. Org. Chem.* **2001**, *66*, 2434.

[15] (a)X.-L. Fang, R.-Y. Tang, P. Zhong, J.-H. Li, *Synthesis* **2009**, 4183. (b)S. Zhang, P. Qian, M. Zhang, M. Hu, J. Cheng, *J. Org. Chem.* **2010**, *75*, 6732.

[16] a)I. V. Koval, *Russ. J. Gen. Chem.* **1995**, *64*, 731. b)M. Raban, L.-J. Chern, *J. Org. Chem.* **1980**, *45*, 1688. c)P. Hamel, *J. Org. Chem.* **2002**, *67*, 2854. d)Y. Chen, C.-H. Cho, R. C. Larock, *Org. Lett.* **2009**, *11*, 173.

[17] M. Tudge, M. Tamiya, C. Savarin, G. R. Humphrey, *Org. Lett.* **2006**, *8*, 565.

[18] a)K. M. Schlosser, A. P. Krasutsky, H. W. Hamilton, J. E. Reed, K. Sexton, *Org. Lett.* **2004**, *6*, 819. b)J. S. Yadav, B. V. S. Reddy, Y. J. Reddy, *Tetrahedron Lett.* **2007**, *48*, 7034. c) J. S. Yadav, B. V. S. Reddy, Y. J. Reddy, K. Praneeth, *Synthesis* **2009**, 1520.

[19] For selected examples of arylsulfonyl chlorides used in C–C bond formation, see:a)S. R. Dubbaka, P. Vogel, *J. Am. Chem. Soc.* **2003**, *125*, 15292. b)S. R. Dubbaka, P. Vogel, *Org. Lett.* **2004**, *6*, 95. c)S. R. Dubbaka, P. Vogel, *Chem. – Eur. J.* **2005**, *11*, 2633. d)C. M. R. Volla, P. Vogel, *Angew. Chem. Int. Ed.* **2008**, *47*, 1305. e)J.-B. Liu, H.-P. Zhou, Y.-Y. Peng, *Tetrahedron Lett.* **2014**, *55*, 2872. f)H.-P. Zhou, J.-B. Liu, J.-J. Yuan, Y.-Y. Peng, *RSC Adv.* **2014**, *4*, 25576. g)J.-B. Liu, F.-J. Chen, N. Liu, J. Hu, *RSC Adv.* **2015**, *5*, 45843. h)J. Liu, S. Yuan, X. Song, G. Qiu, *Chin. J. Org. Chem.* **2016**, *36*, 1790.

[20] Q. Wu, D. Zhao, X. Qin, J. Lan, J. You, *Chem. Comm.* **2011**, *47*, 9188.

[21] Y. Fu, Y. Su, Q. S. Xu, Z. Du, Y. Hu, K. H. Wang, D. Huang, *RSC Adv.* **2017**, *7*, 6018.

[22] a)L. Zhang, L. Ma, H. Zhou, J. Yao, X. Li, G. Qiu, *Org. Lett.* **2018**, *20*, 2407. b)D. Chen, Y. Shan, J. Li, J. You, X. Sun, G. Qiu, *Org. Lett.* **2019**, *21*, 4044. c)Y.-C. Wang, R.-X. Wang, G. Qiu, H. Zhou, W. Xie, J.-B. Liu, *Org. Chem. Front.* **2019**, *6*, 2471. d)R. Liu, M. Li, W. Xie, H. Zhou, Y. Zhang, G. Qiu, *J. Org. Chem.* **2019**, *84*, 11763. e)G. Qiu, Z.-F. Chen, W. Xie, H. Zhou, *Eur. J. Org. Chem.* **2019**, 4327. f)Y.-H. Wang, G. Qiu, H. Zhou, W. Xie, J.-B. Liu, *Tetrahedron* **2019**, *75*, 3850. g)Y.-H. Wang, B. Ouyang, G. Qiu, W. Xie, J.-B. Liu, *Org. Biomol. Chem.* **2019**, *17*, 4335. h) M. Yang, X. Hu, B. Ouyang, W. Xie, J.-B. Liu, *Tetrahedron* **2019**, *75*, 3516.

[23] a)G. W. Kabalka, M. S. Reddy, M.-L. Yao, *Tetrahedron Lett.* **2009**, *50*, 7340. b)D. Wan, Y. Yang, X. Liu, M. Li, S. Zhao, J. You, *Eur. J. Org. Chem.* **2016**, 55. (c)R. Wu, K. Huang, G. Qiu, J. B. Liu, *Synthesis* **2019**, 3567.

[24] a)M. M. Kadooka, L. G. Warner, K. Seff, *J. Am. Chem. Soc.* **1976**, *98*, 7569. b)N. Taniguchi, *J. Org. Chem.* **2006**, *71*, 7874. c) N. Taniguchi, *J. Org. Chem.* **2007**, *72*, 1241. d)P. S. Herradura, K. A. Pendola, R. K. Guy, *Org. Lett.* **2000**, *2*, 2019.

[25] For a dual-functional synthon, see:a)C. Wu, Z. Wang, Z. Hu, F. Zeng, X.-Y. Zhang, Z. Cao, Z. Tang, W.-M. He, X.-H. Xu, *Org. Biomol. Chem.* **2018**, *16*, 3177. b)L.-Y. Xie, S. Peng, F. Liu, J.-Y. Yi, M. Wang, Z. Tang, X. Xu, W.-

M. He, *Adv. Synth. Catal.* **2018**, *360*, 4259. c)C. Wu, L.-H. Lu, A.-Z. Peng, G.-K. Jia, C. Peng, Z. Cao, Z. Tang, W.-M. He, X. Xu, *Green Chem.* **2018**, *20*, 3683. d)X. Gong, J. Chen, X. Li, W. Xie, J. Wu, *Chem. – Asian J.* **2018**, *13*, 2543. e)Y. Zhao, Y. Luo, Y. Zhu, H. Wang, H. Zhou, H. Tan, Z. Zhou, *Synlett* **2018**, *29*, 773. f)Y.-H. Zhao, Y. Li, M. Luo, Z. Tang, K. Deng, *Synlett* **2016**, *27*, 2597. g) Y. Zhao, Y. Li, T. Guo, Z. Tang, W. Xie, G. Zhao, *Tetrahedron Lett.* **2016**, *57*, 2257. h)T. Guo, Y. Liu, Y.-H. Zhao, P.-K. Zhang, S.-L. Han, H.-M. Liu, *Tetrahedron Lett.* **2016**, *57*, 4629. i)T. Guo, Y. Liu, Y.-H. Zhao, P.-K. Zhang, S.-L. Han, H.-M. Liu, *Tetrahedron Lett.* **2016**, *57*, 3920. j)L. Zhen, C. Fang, Y. Zheng, G. Qiu, X. Li, H. Zhou, *Tetrahedron Lett.* **2018**, *59*, 3934.

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