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Communication

Cross Coupling

Copper(II)-Catalyzed C–S Cross-Coupling with Thiazolidine-2-thiones and Boronic Acids: Synthesis of Azole Sulfides

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Abstract: The copper(II)-catalyzed C–S cross coupling of thiazolidine-2-thiones with organoboronic acids towards the synthesis of azole sulfides was investigated. This mild and base-free protocol has the advantages of short reaction times and excellent yields with no need for an ancillary ligand.

Introduction

In recent years, transition-metal-catalyzed carbon–heteroatom cross couplings have emerged as successful organic synthetic strategies.[1] Transition-metal catalysts have been extensively used for the construction of C–S bonds to yield organosulfur compounds that find applications in the biological, pharmaceutical, and materials fields.[2,3] Azole sulfide motifs, in particular, can be found in a vast number of pharmaceutically active molecules (Figure 1).[4] 2-Thio-substituted 1,3-benzothiazoles can

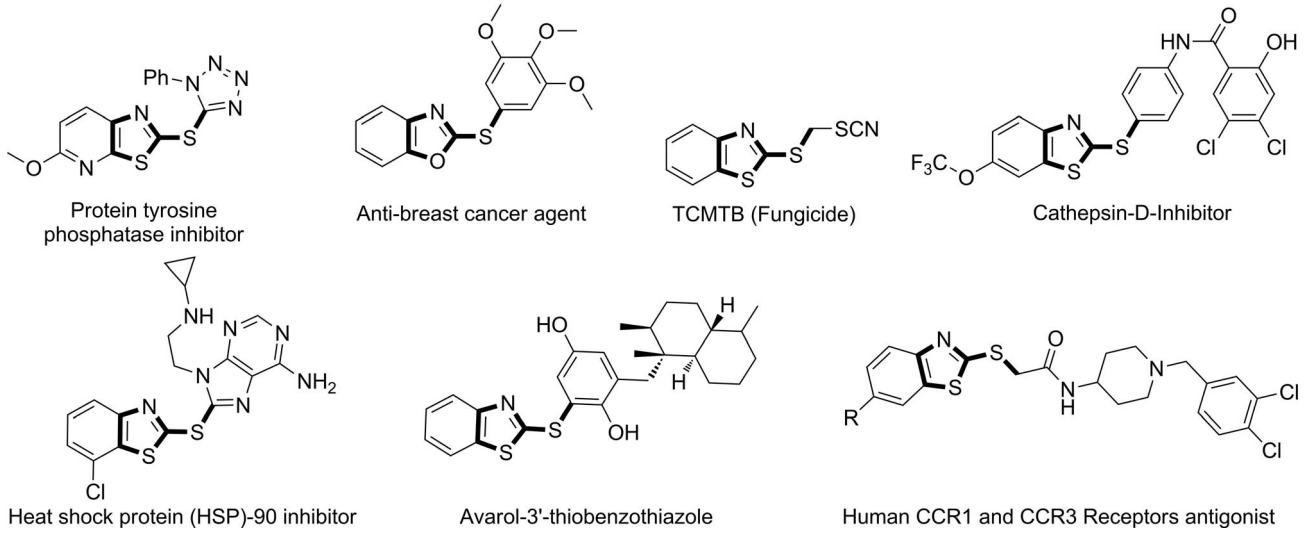

Figure 1. Various pharmaceutically active benzo-fused thiazole sulfides.

be used as vulcanization catalysts and corrosion inhibitors and as reagents for metal-catalyzed cross coupling reactions.[1a–1c,5]

Aryl sulfides can act as anti-inflammatory agents, and they are also used for the treatment of Parkinson's disease, Alzheimer's disease, and obstructive pulmonary diseases.[6] In the past two decades, numerous advancements have been made in C–S bond-formation reactions by using several excellent metal catalysts such as Fe,[7] Pd,[8] Cu,[9] and Ni,[10] and this has resulted in the generation of various functional molecules.[11] Several attempts at C–S bond formation through the coupling of thiols or disulfides with aryl halides have been made.[12] How-

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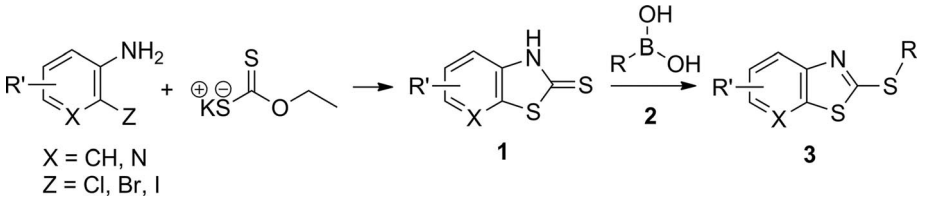


Scheme 1. Strategy for the synthesis of azole sulfides.

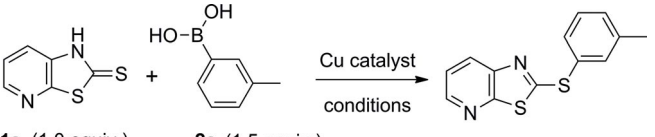
ever, very few reports are available for the synthesis of heteroaryl sulfides through the copper-catalyzed C–S cross coupling of thiols, thioamides, and diaryl disulfides with organoboronic acids.[13–16] Savarin et al. described the Cu^{I}–carboxylate-catalyzed base-free synthesis of thioethers by reaction of boronic acids with aryl, heteroaryl, and alkyl *N*-thioimides.[14] Taniguchi and Li also reported[15] the copper(I)-catalyzed C–S cross coupling of diaryl disulfides with boronic acids to give aryl and heteroaryl sulfides. Xu et al. reported[16] the copper(II)-catalyzed *S*-arylation of thiols by oxidative coupling of thiols with boronic acids at room temperature under basic conditions with the use of an ancillary ligand. Chan–Lam-type cross coupling is emerging as an alternative to traditional cross coupling reactions.[17] Notably, the reported routes for the construction of heteroaryl-fused azole sulfides require tedious reaction conditions and long reaction times; hence, to overcome these limitations, the present investigation was undertaken.

Recently, we reported an expedient approach for the synthesis of fused thiazoles from organoborons and thiazolidine-2-thiones under a desulfitative coupling strategy.[18] In continuation of our enduring curiosity in the development of oxidative C–S cross coupling reactions under mild conditions, we report the synthesis of azole sulfides by direct C–S bond formation between aryl/vinyl boronic acids and thiazolidine-2-thiones in the presence of copper(II) acetylacetonate [$Cu(acac)_2$] under base-free and ligand-free condition (Scheme 1). The thiazolidine-2-thiones were first prepared from readily available 2-haloanilines and potassium ethyl xanthate.[19]

Results and Discussion

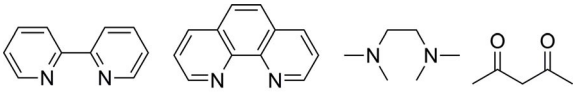
To start, we inspected the C–S cross coupling of thiazolo[5,4-*b*]pyridine-2(1*H*)-thione (**1a**, 1.0 equiv.) with a stoichiometric amount of (3-methylphenyl)boronic acid (**2a**, 1.5 equiv.) in the presence of a stoichiometric amount of cupric bromide (10 mol-%) and 2,2′-bipyridine (10 mol-%) as a ligand in dioxane under aerobic conditions at 100 °C. After 8 h, 2-thio-substituted thiazole **3c** was obtained (22 %; Table 1, entry 1). The conversion was not effective even with 1,10-phenanthroline as the ligand (26 %; Table 1, entry 2). Other copper(II) salts and ligand systems were also examined, but the desired product was obtained in low yields (Table 1, entries 3–6). An appreciable yield was obtained with the combination of $Cu(OAc)_2$ (10 mol-%) and 2,2′-bipyridine (10 mol-%) at 80 °C in 1,2-dichloroethane (DCE) as the solvent, and full conversion was accomplished in 2 h under aerobic conditions (Table 1, entry 7). Upon using the $Cu(OAc)_2$ (10 mol-%)/acetylacetonate (10 mol-%) system, the yield increased to 85 % (Table 1, entry 8). To our delight, the yield of the reaction increased to 89 % by using $Cu(acac)_2$ at a higher loading (20 mol-%) without the addition of an ancillary ligand (Table 1, entry 9). However, lowering the reaction temperature led to poor yields and longer reaction times were required (Table 1, entries 13 and 14). No substantial increase in the yield of anticipated product **3a** was noticed upon testing other metal acetylacetonate catalytic systems, including $Fe(acac)_2$, $Fe(acac)_3$, $Ni(acac)_2$, and $Pd(acac)_2$ (Table 1, entries 9–11). Among the numerous solvents screened, 1,2-dichloroethane was ideal.

Table 1. Optimization of the reaction conditions.[a]



1a (1.0 equiv.) **2a** (1.5 equiv.) **3c**

Entry	Catalyst (mol-%)	Ligand	Solvent	Time [h]	Temp. [°C]	Yield[b] [%]
1	$CuBr_2$ (10)	L1	dioxane	8	100	22
2	$CuBr_2$ (10)	L2	dioxane	8	100	26
3	$Cu(NO_3)_2{\cdot}3H_2O$ (10)	L2	DCE	16	80	12
4	$CuSO_4{\cdot}5H_2O$ (5)	L1	dioxane	5	80	46
5	$CuSO_4{\cdot}5H_2O$ (5)	L3	THF	5	80	37
6	$CuSO_4{\cdot}5H_2O$ (5)	L4	dioxane	5	80	62
7	$Cu(OAc)_2$ (10)	L1	DCE	2	80	71
8	$Cu(OAc)_2$ (10)	L4	DCE	2	80	85
9	$Cu(acac)_2$ (20)	–	DCE	0.5	80	89
10	$Cu(acac)_2$ (20)	–	dioxane	0.5	80	83
11	$Cu(acac)_2$ (20)	–	DMF	0.5	80	72
12	$Cu(acac)_2$ (20)	–	THF	0.5	80	80
13	$Cu(acac)_2$ (20)	–	DCE	12	50	43
14	$Cu(acac)_2$ (20)	–	DCE	24	r.t.	12
15	$Ni(acac)_2$ (20)	–	DCE	8	80	–
16	$Fe(acac)_2$ (20)	–	DCE	8	80	–
17	$Fe(acac)_3$ (20)	–	DCE	24	80	–
18	$Pd(acac)_2$ (5)	–	dioxane	16	100	–



L1 **L2** **L3** **L4**

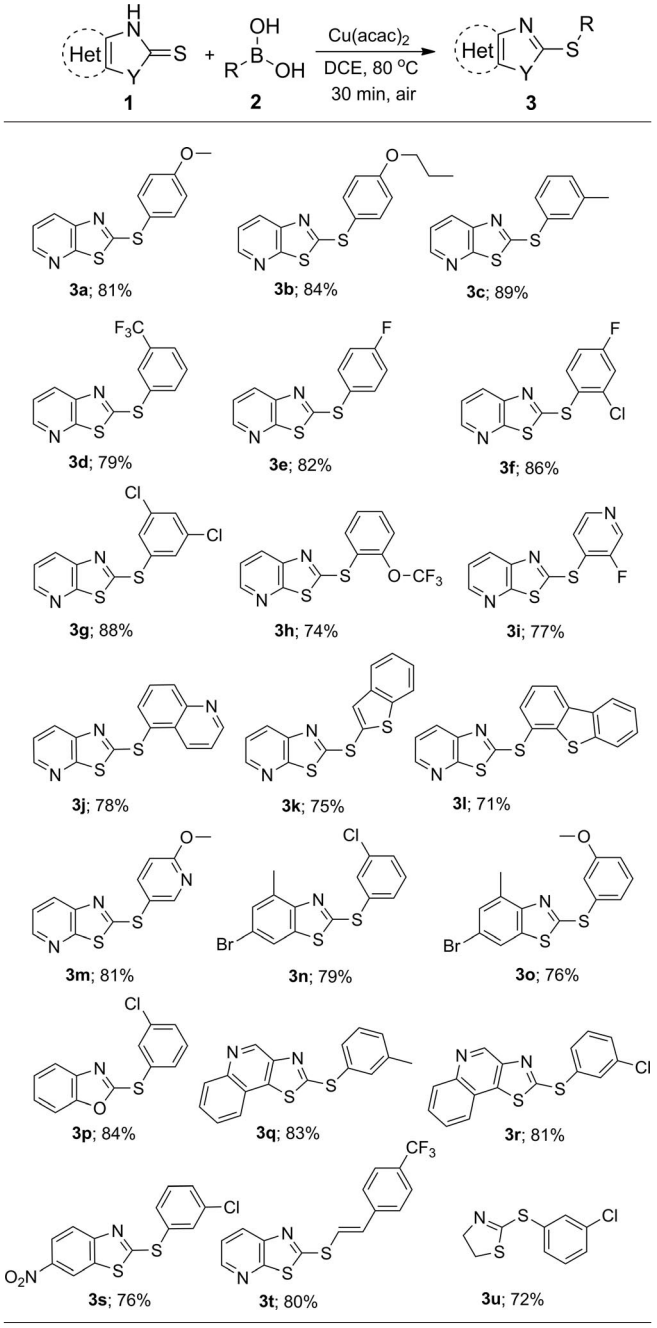
[a] Reaction conditions: Thiazolidine-2-thione **1** (0.10 mmol), R–$B(OH)_2$ **2** (0.15 mmol), catalyst (5–20 mol-%), and ligand (5–20 mol-%) in solvent (5 mL) heated for the specified time open to air. [b] Isolated yield.

Under the optimized conditions, we inspected the scope of this C–S coupling reaction in terms of the arylboronic acid to obtain products **3**, which were obtained in good yields, as depicted in Table 2. Generally, reactions with arylboronic acids having both electron-withdrawing and electron-donating

groups in the *para*, *meta*, or *ortho* position gave products **3a**–**h** in excellent yields (74–89 %). In addition, the reaction was investigated with heteroarylboronic acids, and products **3i**–**m** were afforded in decent yields (71–81 %). The coupling of thiazolo[5,4-*b*]pyridine-2(1*H*)-thione and (*E*)-β-styrylboronic acid was also successfully achieved to give **3t** in good yield (80 %). The scope of the reaction was extended to simple aryl-, heteroaryl-, and fused heteroarylthiazolidine-2-thiones, and corresponding cross-coupled azole sulfides **3n**–**u** were obtained (Table 2). It was ultimately found that electronic effects – either in the thione component or in the arylboronic acid – did not affect the course of the reaction.

However, the transformation was not fruitful with some functionalized or sterically hindering arylboronic acids or alkylboronic acids under the optimized conditions. All the synthesized compounds were characterized by NMR spectroscopy, and the structures of **3k**[20] and **3p**[20] were further confirmed by single-crystal X-ray analysis (Figure 2).

Table 2. Synthesis of azole sulfides **3a**–**u**.[a]



[a] Reaction conditions: Thiazolidine-2-thione **1** (0.10 mmol), R–B(OH)$_2$ **2** (0.15 mmol) and Cu(acac)$_2$ (20 mol-%) in dichloromethane (5 mL) heated at 80 °C for 30 min open to air.

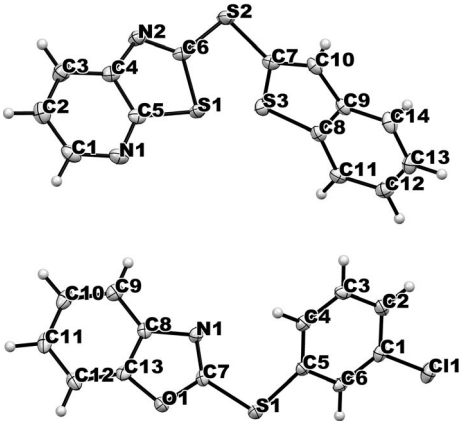
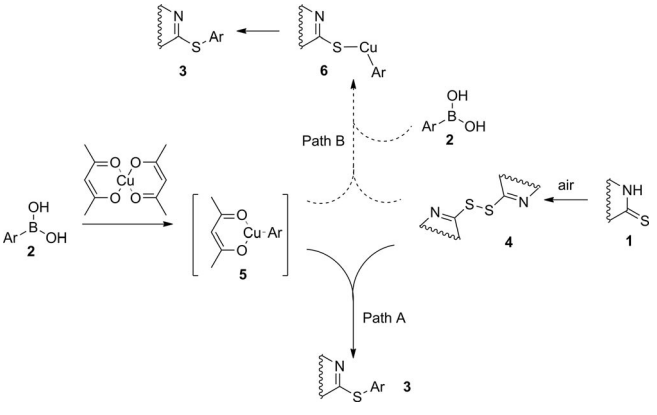


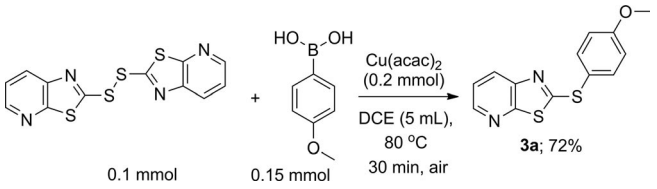
Figure 2. X-ray analysis of **3k** (top) and **3p** (bottom). Thermal ellipsoids are shown at the 50 % probability level.

It is believed that the thioamide system is readily oxidized to give disulfide **4** stimulated by the Cu^{II} reagent in the presence of air.[14] The arylboronic acid may then react with Cu^{II} acetylacetonate through a transmetalation step to form Cu^{II} intermediate **5**, which can react with disulfide **4** to give **3** (Scheme 2, path A). As an alternative possible mechanism, disulfide **4** and intermediate **5** may undergo transmetalation with the arylboronic acid to generate intermediate **6**, which ultimately delivers aryl sulfide **3** (Scheme 2, path B).



Scheme 2. Plausible mechanism.

The reaction of (4-methoxyphenyl)boronic acid with a 1,2-diaryl disulfide under the optimized conditions resulted in thiazole sulfide **3a** in good yield (Scheme 3); this result ensured that the reaction proceeds through the formation of disulfide intermediate **4**.



Scheme 3. Reaction of a 1,2-diaryl disulfide with (4-methoxyphenyl)boronic acid.

Conclusions

A simple and efficient protocol for the synthesis of a library of azole sulfides from easily available organoboronic acids and thiazolidine-2-thiones under mild, nonbasic conditions without an ancillary ligand and within short reaction times was established.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded with a 300 MHz spectrometer in $CDCl_3$ by using tetramethylsilane as an internal standard. Chemical shifts are reported in parts per million (δ), coupling constants (J values) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), p (pentet), m (multiplet). ^{13}C NMR spectra were routinely run with broadband decoupling. Aluminum plates precoated with silica gel (Merck) were used for TLC analysis with a mixture of petroleum ether (60–80 °C) and ethyl acetate as the eluent. Elemental analyses were performed with a Perkin–Elmer 2400 Series II Elemental CHNS analyzer. Mass spectra were recorded with a LCQ Fleet spectrometer, Thermo Fisher Instruments Ltd., USA. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed in the positive ion and negative ion modes with a liquid chromatography ion trap.

Typical Procedure for the Synthesis of Fused Azole Sulfides 3: R–B(OH)$_2$ **2** (0.15 mmol) and Cu(acac)$_2$ (0.02 mmol, 20 mol-%) were added to a stirred solution of thiazolidine-2-thione **1** (0.10 mmol) in DCE (5 mL), and the mixture was heated at 80 °C for 0.5 h in open air. Completion of the reaction was monitored by TLC. After cooling to room temperature, the mixture was filtered through Celite. Then, the filtrate was washed with a saturated solution of NH_4Cl (3 × 10 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was then purified by column chromatography on silica gel (hexanes/ethyl acetate, 4.5:0.5) to yield azole sulfide **3**.

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Keywords: Synthetic methods · Cross coupling · Copper · Sulfur heterocycles · Nitrogen heterocycles · Boronic acids

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[20] CCDC 1450789 (for **3k**) and 1450790 (for **3p**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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