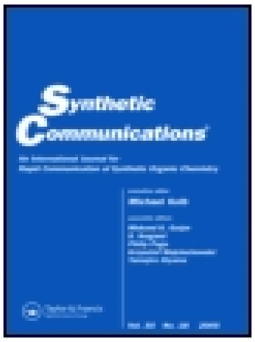

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Primary sulfonamide as a coupling partner: Copper(I)-catalyzed regioselective cross-coupling of 2-nitro benzenesulfonamides with thiol through the cleavage of Ar–SO_2NH_2 bonds

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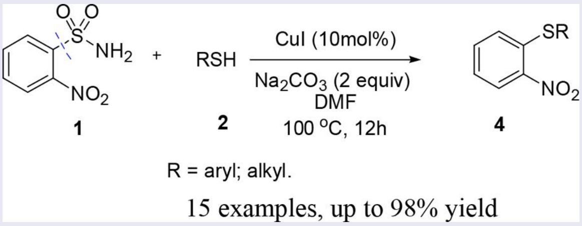
ABSTRACT

In this article, we have presented a novel and efficient method for the direct synthesis of unsymmetrical sulfides through the copper(I)-catalyzed cross-coupling of 2-nitro benzenesulfonamides with thiols in the presence of catalytic amount of CuI in DMF as solvent at 100 °C. In addition, the products were obtained in high to excellent yields. More importantly, the novel system showed the primary 2-nitro benzenesulfonamides as a new coupling partner and regioselectively promoted C–S bond-forming transformations through the cleavage of Ar–SO_2NH_2 bonds.

GRAPHICAL ABSTRACT



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KEYWORDS
Copper(I)-catalyzed; cross-coupling; regioselective; sulfonamide; thiol

Introduction

Sulfides and their derivatives were important and were widely used in pharmaceutical, biological molecules, and chemical materials.[1–3] Since Migita et al.[4] first reported the palladium-catalyzed C(aryl)–S bond formation from the corresponding aryl halides and thiols, transition metal-catalyzed cross-coupling reaction is the most common and powerful method for the formation of C–S bonds.[5] Up to now, different transition metal-catalyzed systems including Pd,[6] Cu,[7] Ni,[8] Co,[9] Fe,[10] and other metals[11] have been reported. In general, the cross-coupling reactions are conducted between aryl donors and thiols or disulfides, the aryl halides were the most common electrophilic counterparts.

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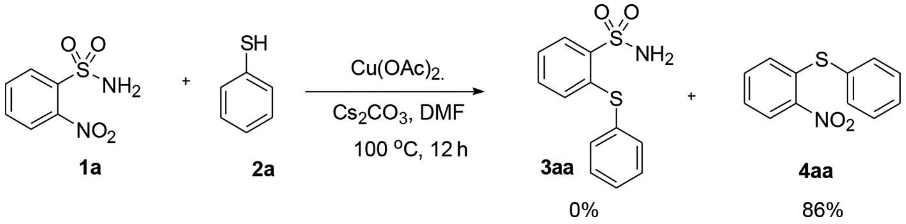
Supplemental data (Characterization data, and copies of 1H spectra for all of the products 4) can be accessed on the publisher's website.

The copper-catalyzed cross-coupling reactions with the use of diaryl disulfides and aryl boric acids or silicones as substrates have been disclosed.[12] Recently, the direct thiolation of arene C–H bonds has been developed as an attractive method to form C–S bonds from unfunctionalized arenes. However, the activity and selectivity observed in these systems rely on either the use of directing groups[13] or activated or acidic arene C–H bonds.[14] Very recently, Wu et al.[15] reported for first time that the cross-coupling of activated nitroarenes and arylboronic acids in the presence of rhodium(I) complex produces unsymmetrical diaryl ethers in excellent yields. Nitroarenes have also been used as a new coupling partner for the unsymmetrical diaryl sulfides using thiophenols,[16] sulfinates[17], and also the synthesis of alkyl aryl sulfides using alkyl halides (Br, Cl), triphenyltin chloride, and arylboronic acids as the coupling partners in the presence of $Na_2S_2O_3 \cdot 5H_2O$ or S8 as sulfur source under ligand-free conditions.[18] More recently, nitroarenes have also been reported to be active as an electrophilic coupling partner in the synthesis of biaryls through the palladium-catalyzed Suzuki–Miyaura coupling reaction through the cleavage of Ar–NO_2 bonds.[19] Similarly, sulfonamides are valuable intermediates in synthetic organic chemistry and were extensively used as pharmaceutical agents because of their diverse biological properties. Therefore, the search for new methodologies for the conversion of sulfonamide functional group is very important in organic chemistry. Significantly, desulfonative couplings have become attractive alternatives to the use of prefunctionalized organometallic reagents. However, the reactions mainly focused on the development of C–C bond-forming transformations through the cross-coupling of vinyl sulfones or aryl sulfonates with Grignard reagents.[20] Nevertheless, aryl sulfonamides have not yet been reported to undergo the transition metal-catalyzed cross-coupling reactions with the SO_2NH_2 group serving as a leaving group. Herein we report a novel copper(I)-catalyzed regioselective cross-coupling of 2-nitro benzenesulfonamides with thiol under mild conditions through the cleavage of Ar–SO_2NH_2 bonds.

Results and discussion

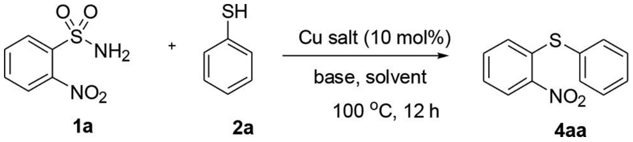
Recently, Shinde et al.[16] reported a novel copper(I)-catalyzed cross-coupling of nitroarenes with thiol through the cleavage of Ar–NO_2 bonds. Based on the aforementioned availability, we attempt to extend this analogous strategy to get the corresponding 2-phenylsulfanyl-benzenesulfonamide substrates **3**. Initially, the reaction of **1a** with thiophenol **2a** was investigated in the presence of $Cu(OAc)_2$ as a catalyst and Cs_2CO_3 as a base in DMF at 100 °C for 12 h (Scheme 1). Curiously, the product **3aa** through the cleavage of Ar–NO_2 bonds was not detected, the Ar–SO_2NH_2 bond was cleaved and the corresponding cross-coupling product **4aa** was obtained in 86% yield.



Scheme 1. Synthesis of unsymmetrical sulfides through the cleavage of Ar–SO_2NH_2 bonds.

Inspired by the above positive results, we then considered screening the reaction conditions. The primary 2-nitro benzylsulfonamide (**1a**) and thiophenol (**2a**) were first chosen as the substrates for the model reaction to optimize the reaction conditions. The reaction was screened with several copper salts, solvents, and reaction temperature to enhance the competence of the coupling reactions, and the results are summarized in Table 1. Initially, the base was investigated under similar conditions (Table 1, entry 1), the trace amount of product was obtained using Ag_2CO_3 as a base (Table 1, entry 2); furthermore, K_3PO_4 only gave the desired product in 11% yield (Table 1, entry 3). KOAc or K_2CO_3 produces the desired product in 72 and 80% yields, respectively (Table 1, entries 4 and 5), and the yields are less compared to Cs_2CO_3. To our delight, the 92% yield was obtained when Na_2CO_3 was a base under similar conditions (Table 1, entry 6). To further optimize the reaction conditions, the copper courses were screened in the presence of Na_2CO_3 (2 equiv.) with DMF as solvent under air for 12 h. Cu_2O, CuO, and $CuCl_2$ produced the desired product in moderate yield (Table 1, entries 7–9). Significantly, the yield was dramatically improved to 96% in presence of CuI (Table 1, entry 10). Finally, the solvents were screened, it was found that reaction works in various solvents such as DMA, DMSO, CH_3CN, or 1,4-dioxane but yields are less compared to DMF under the identical conditions (Table 1, entries 11–14). DMF was turnout as the best solvent among those examined. In addition, the amounts of copper salts were investigated, and the 82%

Table 1. Optimization of conditions.



Entry[a]	Cu salt	Base	Solvent	Yield/%[b]
1	$Cu(OAc)_2$	Cs_2CO_3	DMF	86
2	$Cu(OAc)_2$	Ag_2CO_3	DMF	Trace
3	$Cu(OAc)_2$	K_3PO_4	DMF	11
4	$Cu(OAc)_2$	KOAc	DMF	72
5	$Cu(OAc)_2$	K_2CO_3	DMF	80
6	$Cu(OAc)_2$	Na_2CO_3	DMF	92
7	Cu_2O	Na_2CO_3	DMF	41
8	CuO	Na_2CO_3	DMF	43
9	$CuCl_2$	Na_2CO_3	DMF	60
10	CuI	Na_2CO_3	DMF	96
11	CuI	Na_2CO_3	DMA	46
12	CuI	Na_2CO_3	DMSO	74
13	CuI	Na_2CO_3	CH_3CN	69
14	CuI	Na_2CO_3	1,4-dioxane	78
15[c]	CuI	Na_2CO_3	DMF	82
16[d]	CuI	Na_2CO_3	DMF	75
17[e]	CuI	Na_2CO_3	DMF	50
18[f]	CuI	Na_2CO_3	DMF	21
19	/	Na_2CO_3	DMF	Trace

[a] Reaction conditions: 2-nitro benzylsulfonamide (**1a**) (0.25 mmol), thiophenol (**2a**) (0.5 mmol), copper salt (10 mol%), base (0.5 mmol), and solvent (0.5 mL), at 100 °C for 12 h.

[b] Isolated yield.

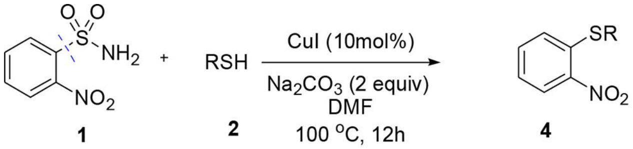
[c] In presence of 5 mol% CuI.

[d] Reaction at 75 °C.

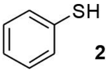
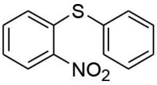
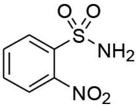
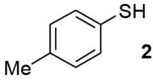
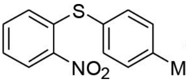
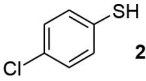
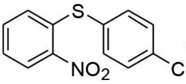
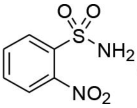
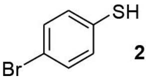
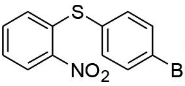
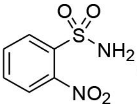
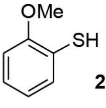
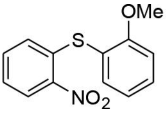
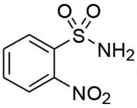
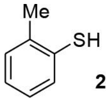
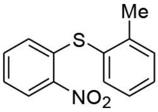
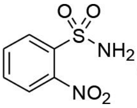
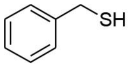
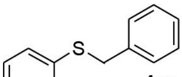
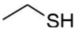
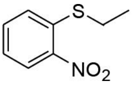
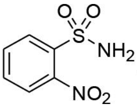
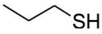
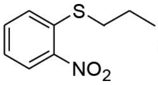
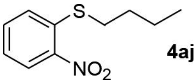
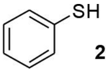
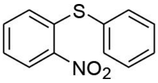
[e] Reaction at 50 °C.

[f] Reaction at 25 °C.

Table 2. Copper(I)-catalyzed regioselective cross coupling of 2-nitro benzenesulfonamide 1 with various thiols 2.

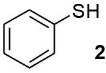
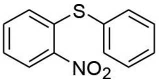


R = aryl; alkyl.

Entry[a]	Substrate **1**	Substrate **2**	Product **4**	Yield (%)[b]
1	 **1a**	 **2a**	 **4aa**	96
2	 **1a**	 **2b**	 **4ab**	91
3	 **1a**	 **2c**	 **4ac**	86
4	 **1a**	 **2d**	 **4ad**	89
5	 **1a**	 **2e**	 **4ae**	93
6	 **1a**	 **2f**	 **4af**	86
7	 **1a**	 **2g**	 **4ag**	95
8	 **1a**	 **2h**	 **4ah**	97
9	 **1a**	 **2i**	 **4ai**	98
10	 **1a**	 **2j**	 **4aj**	94
11	 **1b**	 **2a**	 **4aa**	96

(*Continued*)

Table 2. Continued.

Entry[a]	Substrate 1	Substrate 2	Product 4	Yield (%)[b]
12	 **1c**	 **2a**	 **4aa**	93

[a]Reaction conditions: 2-nitro benzenesulfonamides (**1**) (0.25 mmol), thiol (**2**) (0.5 mmol), CuI (10 mol%), $NaCO_3$ (0.5 mmol), and DMF (0.5 mL), at 100 °C for 12 h under air.
[b]Isolated yield.

yield was obtained in presence of 5 mol% CuI (Table 1, entry 15). The reaction temperature was also screened; the desired product was obtained in 75 and 51% yield in 75 and 50 °C, respectively (Table 1, entries 16 and 17). In further decrease to 25 °C, only 21% yield was obtained (Table 1, entry 18). It should be mentioned that in the absence of Cu salt, a trace amount of desired product was formed (Table 1, entry 19), which also further proved that the present reaction was not aromatic nucleophilic substitution (SNAr) reactions. Finally, these experiments suggest that CuI is the choice of transition metal catalyst and that Na_2CO_3 serves as the base in DMF at 100 °C for 12 h under air.

After having the set of optimized conditions, we focused our attention on extending the scope of this process using 2-nitro benzenesulfonamide **1** and various thiols (**2**) (-Table 2). Primarily, we set on to evaluate 2-nitro benzenesulfonamide **1a** and different aryl thiols **2**. The 2-nitro benzenesulfonamide **1a** reacted with 4-methyl-benzenethiol **2b** to give the desired product in 91% yield (Table 2, entry 2), it should be mentioned that halo-substituted aryl thiols have tolerated well to give the corresponding products, for example, 4-chlorobenzethiol **2c** and 4-bromobenzetyhiol **2d** can offer the corresponding product in 86 and 89% yields, respectively (Table 2, entries 3 and 4). Interestingly, it turned out that ortho-substituted benzylthiol, such as 2-methylbenzethiol **2e** and 2-methoxyl benzetyhiol **2f**, can afford 93 and 86% yields of the desired products, respectively (Table 2, entries 5 and 6). To our delight, alkyl thiols were also active substrates under the present reaction conditions and gave excellent yields of the desired products. For example, the reaction of 2-nitro benzenesulfonamide **1a** with benzyl thiol **2g** gave the desired product in 95% yield (Table 2, entry 7). Furthermore, *n*-ethyl thiol **2h**, *n*-propyl thiol **2i**, and *n*-butyl thiol **2j** can also afford the expected products in excellent yields (Table 2, entries 8–10). It is also interesting to note that the secondary and tertiary 2-nitro benzenesulfonamide derivatives **1c–d** served as good substrates provided the corresponding products in excellent yields (Table 2, entries 11 and 12). However, we attempted to use various benzenesulfonamide **1** bearing nitro group at *meta*- or *para*-position as the substrate with thiophenol (**2a**), and only trace amount of product was obtained.

Conclusion

In summary, we have successfully developed the first copper(I)-catalyzed cross-coupling of 2-nitro benzenesulfonamides with thiol to form unsymmetrical sulfides under mild conditions with excellent yields. Notably, this method furnished the direct synthesis of unsymmetrical sulfides through the regiochemical cleavage of $C–SO_2NH_2$ without the cleavage of $C–NO_2$. This study illustrates the potential of sulfonamides to act as versatile electrophiles in new types of catalytic C–S forming reactions. Further studies toward investigating the detail reaction mechanism and expanding the scope of this reaction are under way in our laboratory.

Experimental

All reactions were performed under air. Chemicals were purchased from Aldrich, Acros, or Alfa Asar, and, unless otherwise noted, were used without further purification. Flash chromatography was performed on silica gel (silica gel, 200–300 mesh). ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometers with $CDCl_3$ as the solvent. Compounds **1b** and **1c** were prepared according to the literature.[20]

General procedure for the synthesis of unsymmetrical sulfides 4

A mixture of 2-nitro benzylsulfonamide 1 (0.25 mmol), thiol 2 (0.5 mmol), CuI (0.025 mmol), $NaCO_3$ (0.5 mmol), and DMSO (0.5 mL) was placed in a 25-mL round-bottom flask. The mixture was stirred for 12 h at 100 °C under air. Then, the reaction mixture was cooled, diluted with ethyl acetate, filtered through celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography with ethyl acetate/petroleum ether to afford the desired product 4.

Funding

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