DOI: 10.1002/adsc.201600642

Copper-Catalyzed Three-Component One-Pot Synthesis of Aryl Sulfides with Sulfur Powder under Aqueous Conditions

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Received: June 20, 2016; Revised: September 5, 2016; Published online: ■■ ■■, 0000

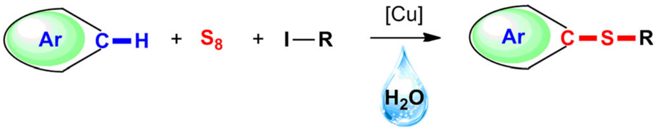
Supporting information for this article can be found under: http://dx.doi.org/10.1002/adsc.201600642.

Abstract: A copper-catalyzed three-component (arenes, iodohydrocarbon, and sulfur powder) synthesis of substituted aryl sulfides has been developed. Water is used as the green solvent in a simple and environmentally friendly procedure. Various functional groups attached to the substrates were well tolerated in this process to afford the corresponding products in moderate to good yields.

Keywords: aryl sulfides; copper-catalyzed reaction; sulfur powder; three-component reaction; water

Aryl sulfides are ubiquitous structural motifs found in numerous pharmaceutically active compounds and medicinally important natural products.[1] Therefore, various methods for the formation of C–S bonds to synthesize aryl sulfides have been developed. On the basis of the sulfur source, there are two common methods for the synthesis of aryl sulfides *via* cross-coupling reactions. The first approach is based on the transition metal-catalyzed cross-coupling reactions of organic halides with organosulfur sources, and disulfides[2] or thiols[3] are the most popular reagents in these reactions. Sulfuryl chloride,[4] sulfonylhydrazide[5] and sodium sulfinates[6] have also been reported as sources of the sulfide group. Another typical method is based on inorganic sulfur reagents, in which sulfur powder (S_8), which is abundant and smell-free in nature, has been extensively investigated for introducing sulfur atoms into organic molecules.[7] Also, a variety of inorganic metal sulfides, such as Na_2S,[8] K_2S[9] and Na_2SO_3[10] have been successfully used as a sulfur source.

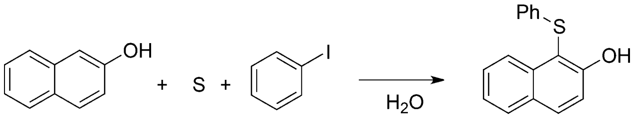
In recent years, the transition metal-catalyzed direct sulfenylation of C–H bonds using inorganic sulfur as the sulfur source has attracted considerable interest, since this strategy provides a more atom-economic route to construct the C–S bond by omitting substrate pre-activation. Recently, we and others have developed various approaches for C–H sulfuration using sulfur powder as sulfur source,[11] whereby most of the procedures described above were carried out in organic solvents. From the perspective of green chemistry, water is a desirable reaction medium because of its inexpensive, non-toxic nature and environmental friendliness. As part of our continuing efforts using water as an ideal solvent for C–H sulfenylation,[12] herein we disclose a novel and environmentally-friendly protocol for the synthesis of aryl sulfides *via* C–H bond functionalization of arenes with iodohydrocarbons and sulfur powder under aqueous conditions (Scheme 1).



Scheme 1. Sulfenylation of arenes with iodohydrocarbons and sulfur powder.

Our initial efforts were focused on searching for an efficient catalytic system using 2-naphthol (**1a**), iodobenzene (**2a**), and sulfur powder as model substrates under aqueous conditions (Table 1). To our delight, an 80% yield of the desired product was obtained in the presence of 10 mol% $Cu(OAc)_2$, 10 mol% 1,10-phen and 1 equiv. of K_2CO_3 in H_2O at 120 °C for 24 h (entry 1). A variety of the other copper catalysts including $CuCl_2$, $CuSO_4$, $Cu(OTf)_2$, CuI was examined (entries 2–5), Among the catalysts screened, $Cu(OTf)_2$ showed the best efficiency to give the corresponding product **3a** in 89% yield (entry 5). The ligands play an important role in this kind of transformation. Among the various ligands screened, 1,10-phen showed the best efficiency (entries 6–10). The

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



1a **2a** **3aa**

Entry	Catalyst	Ligand	Base	Yield [%][b]
1	$Cu(OAc)_2$	1,10-phen	K_2CO_3	80
2	$CuCl_2$	1,10-phen	K_2CO_3	78
3	$CuSO_4$	1,10-phen	K_2CO_3	75
4	CuI	1,10-phen	K_2CO_3	74
5	$Cu(OTf)_2$	1,10-phen	K_2CO_3	89
6	$Cu(OTf)_2$	**L1**	K_2CO_3	30
7	$Cu(OTf)_2$	TMEDA	K_2CO_3	2
8	$Cu(OTf)_2$	**L2**	K_2CO_3	79
9	$Cu(OTf)_2$	**L3**	K_2CO_3	43
10	$Cu(OTf)_2$	Ph_3P	K_2CO_3	0
11	$Cu(OTf)_2$	1,10-phen	KOH	64
12	$Cu(OTf)_2$	1,10-phen	$KHCO_3$	52
13	$Cu(OTf)_2$	1,10-phen	KO-*t*-Bu	26
14	$Cu(OTf)_2$	1,10-phen	Na_2CO_3	84
15	$Cu(OTf)_2$	1,10-phen	Cs_2CO_3	83
16[c]	$Cu(OTf)_2$	1,10-phen	K_2CO_3	98
17	$Cu(OTf)_2$	1,10-phen	K_2CO_3	12
18	$Cu(OTf)_2$	1,10-phen	K_2CO_3	trace
19[d]	$Cu(OTf)_2$	1,10-phen	K_2CO_3	86
20[f]	$Cu(OTf)_2$	1,10-phen	K_2CO_3	10
21[g]	–	–	K_2CO_3	trace

[a] *Conditions*: **1a** (0.5 mmol), **2a** (0.75 mmol), sulfur (1.0 mmol), catalyst (10 mol%), ligand (10 mol%), base (0.5 mmol), H_2O (1.0 mL), 120 °C, 24 h, under air; **L1** = 2,2-bipyridine, **L2** = 4,5-diazafluoren-9-one, **L3** = 1,10-phenanthroline-5,6-dione.

[b] GC yield.

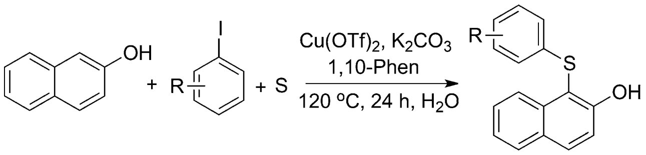
[c] K_2CO_3 (0.75 mmol).

[d] Under argon.

[e] Bromobenzene instead of iodobenzene.

[f] Chlorobenzene instead of iodobenzene.

Table 2. Reaction of 2-naphthol with aryl halides.[a]



1a **2** **3**

Entry	Aryl halide	No.	Product	Yield [%][b]
1	R = 4-Me	**2b**	**3ab**	75
2	R = 4-OCH_3	**2c**	**3ac**	80
3	R = 4-F	**2d**	**3ad**	75
4	R = 4-Cl	**2e**	**3ae**	90
5	R = 4-Br	**2f**	**3af**	73
6	R = 4-I	**2g**	**3ag**	40
7	R = 4-CF_3	**2h**	**3ah**	80
8	R = 4-NH_2	**2i**	**3ai**	70
9	R = 4-NO_2	**2j**	**3aj**	68
10	R = 4-CN	**2k**	**3ak**	78
11	R = 4-CHO	**2l**	**3al**	77
12	R = 4-$COCH_3$	**2m**	**3am**	66
13	R = 4-$COOCH_3$	**2n**	**3an**	71
14	R = 4-Ph	**2o**	**3ao**	85
15	R = 2-Me	**2p**	**3ap**	83
16	R = 2-OMe	**2q**	**3aq**	77
17	R = 2-NH_2	**2r**	**3ar**	80
18	R = 3-Me	**2s**	**3as**	90
19	R = 3-OMe	**2t**	**3at**	83
20	R = 3-NO_2	**2u**	**3au**	73
21	1-iodonaphthalene	**2v**	**3av**	80

[a] *Conditions*: **1a** (0.5 mmol), **2** (0.75 mmol), sulfur (1.0 mmol), copper triflate (10 mol%), 1,10-Phen (10 mol%), K_2CO_3 (150 mol%), in H_2O (1 mL), 120 °C, air, 24 h.

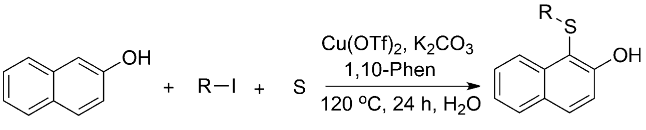
[b] Isolated yield.

reaction was less efficient when other base were tested (entries 11–15). The yield can be improved to 98% by increasing the amount of K_2CO_3 to 1.5 equiv. (entry 16). Copper triflate as catalyst and 1,10-phen as ligand are both necessary, and very low yields were obtained when the reaction was carried out in the absence either one (entries 17 and 18). The yield did not change when the reaction was carried out under argon (entry 19). Unfortunately, Bromobenzene and chlorobenzene are not suitable for this transformation under the optimal conditions (entries 20 and 21). It should be noted that no 2-phenoxynaphthalene by-product was observed with the present system.

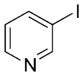
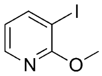
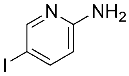
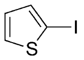
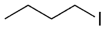
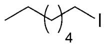
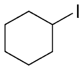
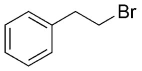
With the optimized conditions in hand, a variety of aryl iodides was examined under the optimized reaction conditions to explore the scope of the substrates, as summarized in Table 2. Methyl- and methoxyiodobenzenes reacted smoothly with **1a** to give the corresponding products in reasonable yields (entries 1 and 2). Halogen substituents such as trifluoromethyl, fluoro, chloro, bromo and iodo were all well tolerated under the optimized reaction conditions (entries 3–7), and the desired product **3ae** was isolated in 90% yield when 1-chloro-4-iodobenzene (**2e**) was used (entry 4). It should be noted that 1,4-diiodobenzene was also able to couple with **1a** to give the desired monosulfuration product (entry 6) in 40% yield, and the carbon-iodine bond may be cleavable. Therefore, there are many by-products generated. Moreover, an active amino group substituent on iodobenzene was well tolerated, and the desired product (**3ai**) was obtained in 70% yield (entry 8). Other substrates bearing electron-withdrawing groups such as nitro, cyano, aldehyde, acetyl and aliphatic groups remained effective and gave the corresponding arylsulfonamides in good yields (entries 9–13). There seems to be little effect of the substituent position (*ortho* or *meta*) of the benzene ring on the reaction yield. For example, when the methyl was located in an *ortho* (**2p**) and in a *meta* (**2s**) position on the benzene ring, the corresponding products **3ap** and **3as** were obtained in 83% and 90% yields, respectively (entry 15, entry 18). Similarly, when a methoxy groups was located at the *ortho* (**2q**) and *meta* (**2t**) position on the benzene ring, the corresponding products **3ap** and **3as** were obtained in 77% and 83% yields, respectively (entry 16, entry 19). When 2-iodoaniline (**2r**) and 1-iodo-3-nitrobenzene (**2u**) were employed, the corresponding products **3ar** and **3au** were obtained in 80% and 73% yields, respectively (entry 17, entry 20). In addition, more bulky substrates such as iodonaphthalene also reacted with **1a** and gave the product **3av** in 80% yield (entry 21).

To our delight, besides iodobenzenes, this reaction system could also be applied to the direct sulfenylation of heterocyclic halogen derivatives and alkyl halides with **1a** (Table 3). Moderate to good yields were achieved when the heteroaromatic iodine-containing compounds such as 3-iodopyridine (**2w**), 3-iodo-2-methoxypyridine (**2x**) and 5-iodopyridin-2-amine (**2y**) were used (entries 1–3). When 2-iodothiophene (**2z**) was used, the desired product **3az** was observed, albeit in 35% yield (entry 4). Furthermore, noteworthy is that an alkyl iodide coupled with **1a** to give the corresponding sulfide product (entries 5–7), and (2-bromoethyl)benzene also worked with **1a** to afford the corresponding sulfide product **3ada** in 35% yield (entry 8).

Table 3. Sulfenylation of 2-naphthol with halides.[a] <



1a **2** **3**

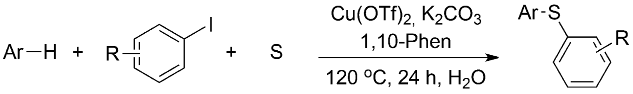
Entry	Aryl halide	No.	Product	Yield [%][b]
1		**2w**	**3aw**	82
2		**2x**	**3ax**	80
3		**2y**	**3ay**	68
4		**2z**	**3az**	35
5		**2aa**	**3aaa**	55
6		**2ab**	**3aba**	48
7		**2ac**	**3aca**	21
8		**2ad**	**3ada**	35

[a] *Conditions*: **1a** (0.5 mmol), **2** (0.75 mmol), sulfur (1.0 mmol), copper triflate (10 mol%), 1,10-Phen (10 mol%), K_2CO_3 (150 mol%), in H_2O (1 mL), 120 °C, air, 24 h.

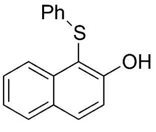
[b] Isolated yield.

To further examine the scope and limitations of the sulfenylation reaction, we tested various arene derivatives for this kind of reaction (Table 4). 2-Naphthols with a bromo group at C-6 or C-7 both smoothly coupled with **2a** and gave the desired products **3ba** and **3ca** in 60% and 68% yields, respectively. Besides 7-bromonaphthalen-2-ol which reacted smoothly with iodobenzene, other substrates bearing functional groups such as **2c**, **2e**, and **2l** gave the aryl sulfides **3cc**, **3ce** and **3cl**, respectively, in moderate to good yields. Promising results from naphthalen-2-ol motivated us to further extend this new protocol to naphthalen-2-amine derivatives. It is noteworthy that the compounds **1d** and **1e** were tolerated in this reaction and afforded the corresponding products **3da** and **3ea** in 41% and 60% yields, respectively. We further tested this method with naphthalen-1-ol under the op-

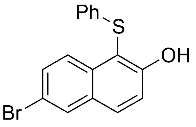
Table 4. Substrate scope.[a]



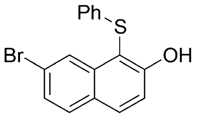
1 **2** **3**



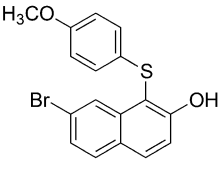
3aa 86%



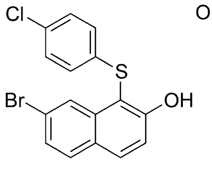
3ba 60%



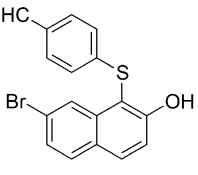
3ca 68%



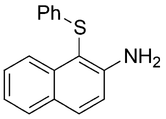
3cc 70%



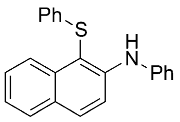
3ce 55%



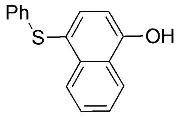
3cl 68%



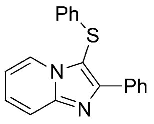
3da 41%



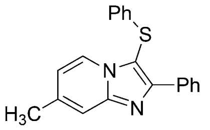
3ea 60%



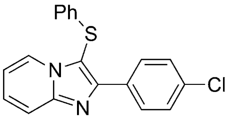
3fa 50%



3ga 79%



3ha 75%

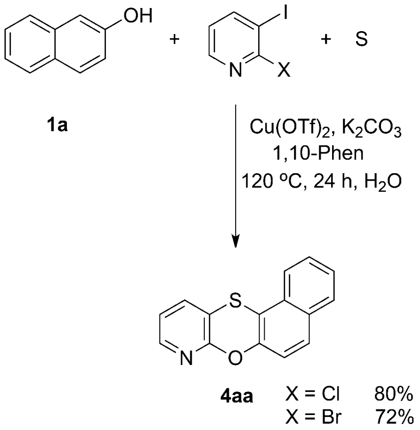


3ia 61%

[a] *Conditions*: **1** (0.5 mmol), **2** (0.75 mmol), sulfur (1.0 mmol), copper triflate (10 mol%), 1,10-Phen (10 mol%), K_2CO_3 (150 mol%), in H_2O (1 mL), 120 °C, air, 24 h.

[b] Isolated yield.

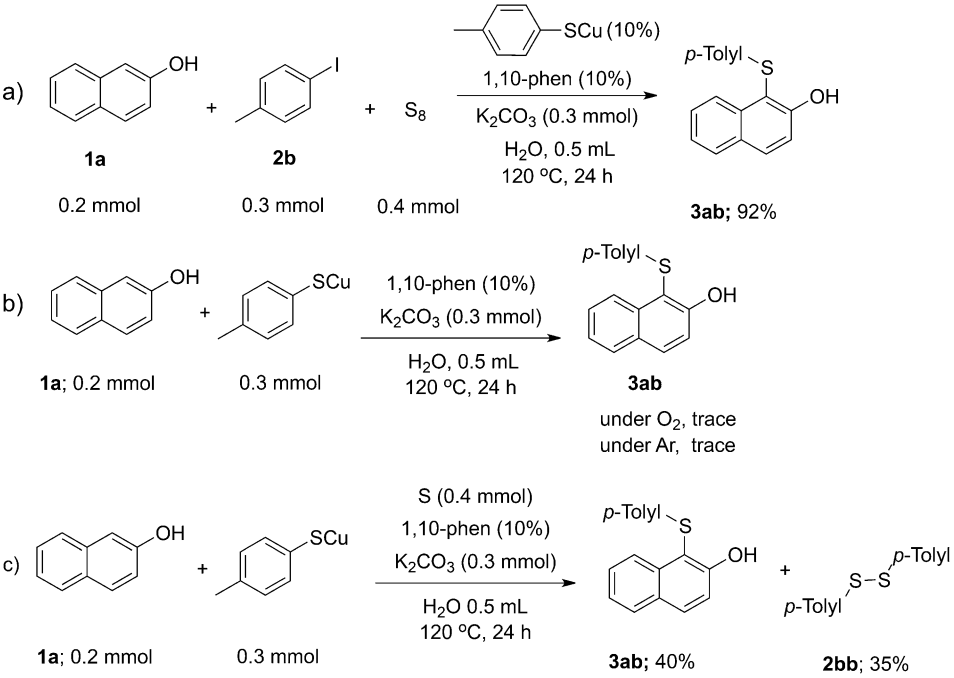
timized conditions. Encouragingly, the reactions furnished the corresponding 4-(phenylthio)naphthalen-1-ol **3fa** in 50% yield. On the basis of results obtained in the case of electron-rich arenes, we have further extended this strategy to 2-phenylimidazo[1,2-*a*]pyridine derivatives (**1g–1i**). We carried out the reactions of 2-phenylimidazo[1,2-*a*]pyridine derivatives with **2a** under the aforementioned conditions. It was found that the 2-phenylimidazo[1,2-*a*]pyridine derivatives were well tolerated in this transformation to give the corresponding products in good yields (**3ga**, **3ha**, **3ia**). To our surprise, the naphtho[1′,2′:5,6]-[1,4]oxathiino[2,3-*b*]pyridine (**4aa**) was obtained in 80% and 72% yields when using 2-fluoro-3-iodopyridine or 2-chloro-3-iodopyridine as the substrate (Scheme 2).



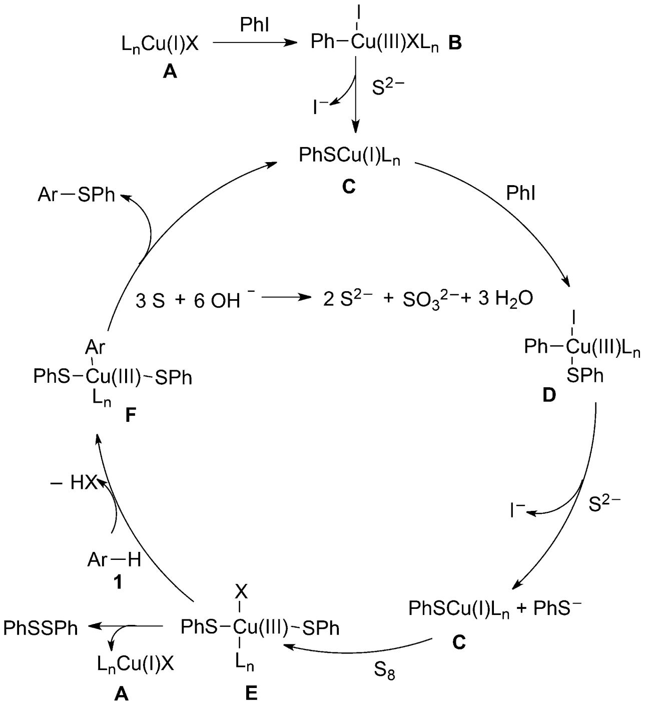
Scheme 2. Cyclic reaction of 2-naphthol.

Control experiments were carried out to gain preliminary insights into the mechanism of the catalytic procedure. The product **3ab** could be gained in 92% yield when catalyzed by 10 mol% of *p*-tolylSCu (Scheme 3a), however, a stoichiometric reaction of *p*-tolylSCu with 2-naphthol did not proceed under an N_2 or an O_2 atmosphere (Scheme 3b). These results indicate that *p*-tolylSCu would not be an intermediate but be an active catalyst in the catalytic cycle. It is interesting that the 1-(*p*-tolylthio)naphthalen-2-ol (**3ab**) was obtained in 40% and the by-product 1,2-di-*p*-tolyl disulfide (**2bb**) was obtained in 35% when 2 equiv. of S_8 powder was added (Scheme 3c), which suggests that the (*p*-tolylS)$_2$Cu complex would be formed during the procedure and elemental S could serve as an oxidant. That also is in agreement with the observation that the reaction could proceed smoothly under an argon atmosphere (Table 1, entry 16).

According to our above control experiments and related references, a proposed mechanism is illustrated in Scheme 4. It is known that sulfur could undergo a disproportionation reaction in the presence of a base to produce sulfide anion and sulfite.[13] The first step of the catalytic cycle would be an oxidative addition of copper with iodobenzene to afford complex **B**. Then **B** undergoes ligand exchange with S^{2-} followed by reductive elimination and further ligand exchange of X^- with PhS^- species to produce the complex **C**, which is the catalytically active species and proceeds through a 2nd oxidative addition/ligand exchange/reductive elimination sequence to regenerate the complex **C** and molecular PhS^-. Then the S_8-



Scheme 3. Control experiments.



Scheme 4. Proposed catalytic cycle.

initiated oxidation affords the complex **E**,[14] which could undergo reductive elimination to generate the 1,2-diphenyl disulfide. This could also rationalize why small amounts of disulfides were detected in the reaction. Subsuquently, the electrophilic metallation of **1** with **E** occurs to give intermediate **F**. Finally, the intermediate **F** undergoes reductive elimination to generate the sulfenylation product and the catalyst **C**.

In summary, we have developed a simple and efficient method for preparing aryl sulfides from arenes, iodohydrocarbon, and sulfur powder under aqueous conditions. Copper triflate acted as an efficient catalyst for this kind of transformation. Halogen, nitro, cyano, aldehyde, acetyl and amino functional groups were well tolerated under the optimized reaction conditions. This method affords an efficient alternative approach for the synthesis of biologically important heterodiaryl sulfides from sulfur powder.

Experimental Section

General Procedure

A 10-mL oven-dried reaction vessel was charged with naphthalen-2-ol (**1a**, 72 mg, 0.5 mmol), sulfur (32 mg, 1.0 mmol), $Cu(OTf)_2$ (18 mg, 0.05 mmol), 1,10-phen (9 mg, 0.05 mmol), K_2CO_3 (103.7 mg, 0.75 mmol), iodobenzene (**2a**, 83.5 μL, 0.75 mmol) and H_2O (1.0 mL) under air. The resulting solution was stirred at 120 °C for 24 h. After cooling to room temperature the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **3aa** as white solid; yield: 108 mg (86%).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21372187, 21502160, 21572194), Hunan Provincial Natural Science Foundation of China (16JJ3112), the Scientific Research Fund of Hunan Provincial Education Department (15C1311, YB2016B024), and the China Postdoctoral Science Foundation Funded Project (2015M572257).

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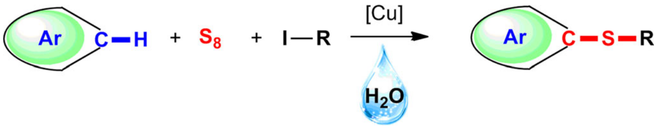
Copper-Catalyzed Three-Component One-Pot Synthesis of Aryl Sulfides with Sulfur Powder under Aqueous Conditions



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