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Simple, efficient and recyclable catalytic system for performing copper-catalyzed C–S coupling of thiols with aryl iodides in PEG and PEG–H_2O

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ABSTRACT

A new protocol for the coupling of aryl iodides with thiophenols or alkanethiols is reported. The reaction is catalyzed by CuI–PEG or CuI–PEG–H_2O system in the absence of ligands and volatile organic solvents. A variety of functionalized aryl sulfides are prepared in excellent yields. The isolation of the products is readily performed by the extraction with diethyl ether or petroleum ether, and the CuI–PEG catalyst can be reused without significant loss in activity. The simple catalytic system is economically competitive and environmentally friendly.

The formation of C–S bonds is one of the most important reactions in numerous synthesis of intermediates and targets with biological and pharmaceutical impact, and in molecular precursors for the development of materials.[1] The classical methods for the synthesis of aryl sulfides involving condensation of thiols with aryl halides often require harsh reaction conditions such as strong bases and elevated temperatures. However, these methods are not suitable for molecules containing sensitive functional groups. To overcome these difficulties, Migita and co-workers reported palladium-catalyzed C–S coupling of iodo and bromo arenes with thiols using $Pd(PPh_3)_4$ as the catalyst under mild conditions,[2] and many ligands have now been developed for this reaction.[3] Other transition metal-based catalytic systems have also been studied, such as nickel,[4] cobalt,[5] copper,[6] and iron.[7]

From an industrial view point, the low cost of copper and the use of readily accessible and stable ligands provide an indisputable advantage than the other catalytic systems. The general approach for the copper-mediated C–S coupling requires a catalytic amount of copper (5–10 mol %) and the presence of a ligand (10–20 mol %). Some ligand-free copper-catalyzed C–S coupling reactions have also been developed.[6l–n,s] However, many of these ligand-free methods suffer from certain drawbacks, such as the use of nano-copper particles,[6l,m] the requirement of microwave irradiation,[6m] and poor efficiency with aliphatic thiols[6m,s] or electron-rich aryl iodides.[6l] In addition, of limited number of methods available employing copper catalysts, most involve the use of non-recyclable catalytic system and toxic organic solvents. Hence, the development of simple and green chemical methods for the C–S coupling reaction is of particular value.

The preliminary studies have revealed that PEG could be used as a reaction medium for selective reactions with easy recycle ability of solvents and catalysts.[8] Unlike several of the 'neoteric solvents' such as ionic liquids whose toxicity and environmental burden data are for most part unknown, complete toxicity profiles are available for a range of PEG molecular weights, and a number of reviews have also covered PEG chemistry and its application in biotechnology and medicine.[9]

Table 1
Coupling of thiophenol with iodobenzene in different conditions[a]

$$\text{PhSH} \quad + \quad \text{PhI} \xrightarrow[\text{Base, PEG, 12 h,110 }^{\circ}\text{C}]{\text{[Cu]}} \text{PhSPh}$$

Entry	PEG	[Cu] (mol)	Base	Yield[b] (%)
1	PEG_{1000}	Cu (10%)	K_3PO_4	94
2	PEG_{1000}	Cu_2O (10%)	K_3PO_4	96
3	PEG_{1000}	CuO (10%)	K_3PO_4	93
4	PEG_{1000}	CuI (10%)	K_3PO_4	97
5	PEG_{1000}	CuI (2%)	K_3PO_4	84
6	PEG_{1000}	CuI (5%)	K_3PO_4	97
7	PEG_{1000}	CuI (5%)	K_2CO_3	95
8	PEG_{1000}	CuI (5%)	NaOH	97
9	PEG_{1000}	CuI (5%)	K_3PO_4	21[c]
10	PEG_{600}	CuI (5%)	K_3PO_4	96
11	PEG_{2000}	CuI (5%)	K_3PO_4	97
12	PEG_{1000}	CuI (5%)	$K_3PO_4{\cdot}3H_2O$	97
13	PEG_{1000}	CuI (5%)	$K_3PO_4{\cdot}3H_2O$	96[d]
14	—	CuI (5%)	$K_3PO_4{\cdot}3H_2O$	93[e]
15	—	CuI (5%)	$K_3PO_4{\cdot}3H_2O$	19[f]
16	PEG_{1000}	—	$K_3PO_4{\cdot}3H_2O$	N.D.

[a] Reaction conditions: Iodobenzene (2.4 mmol), benzenethiol (2 mmol), Cu salt, base (4 mmol), and PEG (2 g) were stirred for 12 h at 110 °C.
[b] Yield of the isolated product.
[c] At 80 °C.
[d] H_2O (0.5 mL) was added.
[e] 2% (w/w) PEG_{1000}–H_2O (2 mL) was used instead of PEG_{1000}.
[f] Pure water (2 mL) was used.

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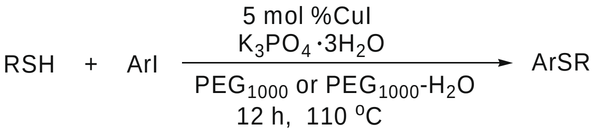
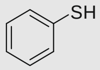
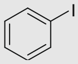
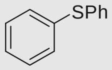
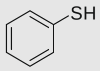
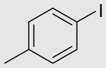
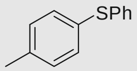
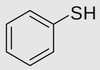
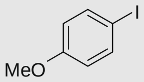
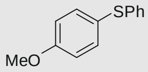
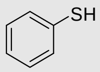
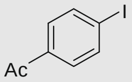
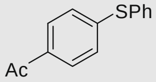
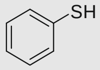
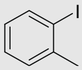
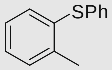
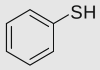
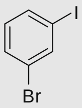
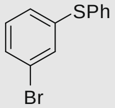
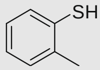
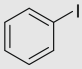
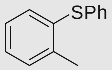
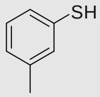
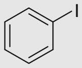
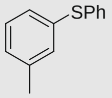
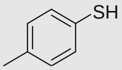
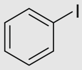
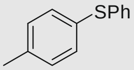
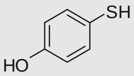
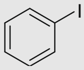
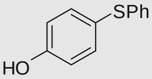
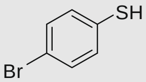
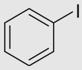
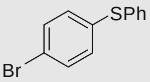
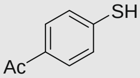
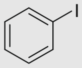
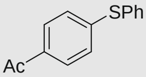
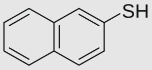
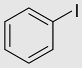
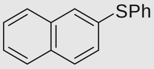
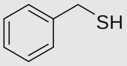
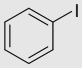
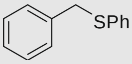
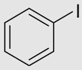
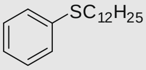
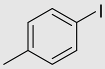
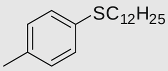
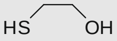
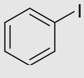
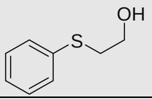
Table 2
CuI–PEG-catalyzed S-arylation of thiols[a]



Entry	Thiol	Aryl-I	Product	Yield[b] (%)	
				A	B
1				97	93
2				93	81
3				93	86
4				85	78
5				94	93
6				97	95
7				95	99
8				98	99
9				97	99
10				96[c]	24[c]
11				95	94
12				87	81
13				94	82
14				96	83
15	$C_{12}H_{25}SH$			97	79
16	$C_{12}H_{25}SH$			88	28
17				95[c]	15[c]

[a] Method A: aryl iodide (2.4 mmol), thiol (2 mmol), CuI (0.1 mmol), $K_3PO_4 \cdot 3H_2O$ (4 mmol), and PEG_{1000} (2 g) were stirred for 12 h at 110 °C. Method B: iodobenzene (2.4 mmol), thiol (2 mmol), CuI (0.1 mmol), $K_3PO_4 \cdot 3H_2O$ (4 mmol), and 2 mL 2% (w/w) PEG_{1000}–H_2O solution were stirred for 12 h at 110 °C.
[b] Yield of the isolated product.
[c] Aryl iodide (2 mmol)and thiol (2 mmol) were used.

Considering our previous work in the field with the application of PEG to the generation of C–C bond,[8b,10] we tried the C–S coupling which would allow the construction of aryl thioether derivatives in PEG. The reactions are effective at 110 °C in pure PEG or even in PEG–H_2O solution. To the best of our knowledge, there have been only two examples which allowed the C–S cross-coupling in aqueous medium.[6p,s]

As a model study, we chose thiophenol and iodobenzene as the coupling partners, and the efficiency of several copper(0), (I) and (II) sources, base, and commercially available PEGs was tested. The results are summarized in Table 1.

Exhilaratingly, all the Cu^0, Cu^I, and Cu^{II} sources tested resulted in satisfactory yields (Table 1, entries 1–3), which are in agreement with the previously reported results that copper compounds in various oxidation states are catalytically active.[11] As CuI turned out to give the best result, it was chosen as the standard Cu source for subsequent experiments. Various bases were found to be highly effective (Table 1, entries 5–7). All the PEGs tested had similar results (Table 1, entries 6 and 10–11). When the reaction was performed with 5 mol % CuI in the presence of K_3PO_4 as a base in PEG_{1000} at 80 °C for 12 h, the expected coupling product of diphenyl sulfide was afforded in only 21% yield (Table 1, entry 9). We also investigated the reaction in the presence of water (Table 1, entries 12–14). Interestingly, the aqueous medium containing only 2% PEG_{1000} without other additives or ligands furnished target compound in excellent yield (Table 1, entry 14).

Thus, the optimized reaction conditions utilized 5 mol % of CuI, K_3PO_4 or $K_3PO_4 \cdot 3H_2O$ or NaOH (2 equiv) in PEG_{1000} as a solvent at 110 °C for 12 h. Since $K_3PO_4 \cdot 3H_2O$ provides milder condition than NaOH and is easier to be maintained than K_3PO_4, it was chosen as the standard base. To minimize the chemical waste, we investigated the reaction in aqueous medium containing 2% PEG_{1000}.

Next, the scope of this novel protocol in coupling reactions of various thiols and iodobenzenes was evaluated in CuI–PEG and CuI–PEG–H_2O systems (Table 2). In general, all reactions were very clean in CuI–PEG system, and the thioethers were obtained in good to excellent yields under the previously optimized conditions. The coupling reactions tolerated a wide scope of functional groups, including free hydroxyl moieties (Table 2, entries 10 and 17, method A[13]) which readily couple with aryl halides in the presence of a copper catalyst.[6i,q,14] The CuI–PEG system efficiently coupled thiols with electron-rich, electron-neutral, and electron-deficient aryl iodides (85–98% yield, Table 2, method A). The steric hindrance of *ortho*-substituents on both partners of the reaction did not affect the outcome (Table 2, entries 5 and 7, method A).

Most of the thiophenols could couple with aryl iodides in CuI–PEG–H_2O system, furnishing target diaryl thioethers in good to excellent yield except for 4-mercaptophenol (Table 2, entry 10, method B[13]). Unfortunately, compared to CuI–PEG system, all attempts to couple aliphatic thiols with aryl iodides led to sharply degressive coupling efficiency in CuI–PEG–H_2O system (Table 2, entries 14–17, method B). The different coupling efficiency between thiophenols and aliphatic thiols in CuI–PEG–H_2O system may be due to the different nucleophilic abilities between thiolates and aliphatic thiols. Minimization of chemical waste, of which 80% is estimated to be solvents,[12] is a constant challenge as environmental concerns are increasingly brought into focus. With this purpose, PEG–H_2O may be a seemly choice.

Extension of this C–S coupling process was carried out using aryl bromides. The results are shown in Table 3. The catalytic system efficiently coupled thiophenol with electron-deficient aryl bromide (62% yield, Table 3, entry 3), but it did not work well with electron-rich and electron-neutral aryl bromides.

The recycle experiment was carried out on the coupling of iodobenzene with benzenethiol in the CuI–PEG_{1000} system (Table 4). In order to reduce the amount of salt generated in the reaction, NaOH was used as the base. After the completion of the reaction, the product was isolated from the reaction mixture by extracting with petroleum ether. The insoluble CuI–PEG system was reused without additional CuI and PEG in the first six recycles to afford excellent yields.

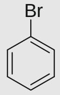
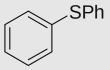
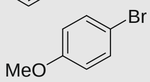
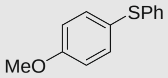
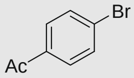
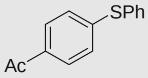
When we were preparing this manuscript, Sperotto et al. reported a ligand-free CuI-catalyzed C–S coupling of aryl iodides and thiols,[15] Compared to this literature method, our procedure brings two significant improvements: (1) the coupling for aliphatic thiols is more efficient and (2) the catalytic system can be recovered and reused.

We propose a possible mechanism for the copper-catalyzed S-arylation of thiols (Scheme 1). It is presumed that PEG works not only as the reaction medium or phase transfer catalyst but also as a ligand.[8] Cu(I) or Cu(II) was reduced by PEG to form Cu(0), which conjugates with PEG to form a reactive species **A**.[16] The subsequent oxidative addition of the **A** with aryl iodides leads to the intermediate **B**. In the presence of base, thiols react with **B** readily to afford complex **C**, which undergoes a reductive elimination to provide the target product and to regenerate the reactive species **A**.

In summary, we have demonstrated a selective, efficient, and general protocol for the synthesis of aryl sulfides via a CuI–PEG catalyzed coupling of aryl iodides with thiophenols or alkanethiols. Compared with the published methods, our procedure possesses several advantages: (1) the volatile organic solvent-free and ligand-free reactions are economically competitive and environmental friendly; (2) the catalytic system is applicable for both aryl thiols and aliphatic thiols; (3) the catalyst could be recovered and reused; and (4) the workup of the reaction mixture and isolation of the desired product are simple and convenient. Because of these issues, we believe that our protocol could find its applications in organic synthesis.

Table 3
CuI–PEG_{1000}-catalyzed C–S coupling between aryl bromides and thiophenol[a]

$$\text{PhSH} + \text{ArBr} \xrightarrow[\substack{\text{2 eq } K_3PO_4\bullet 3H_2O \\ PEG_{1000},\ 12\ h,\ 110\ ^oC}]{\text{5 mol \%CuI}} \text{ArSPh}$$

Entry	ArBr	Product	Yield[b] (%)
1	 	 	Trace
2	 	 	Trace
3	 	 	62

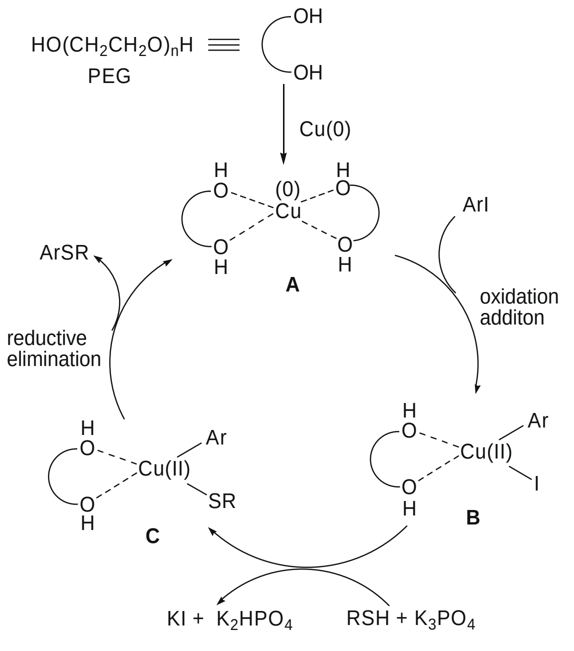
[a] Reaction conditions: Aryl bromide (2.4 mmol), thiol (2 mmol), CuI (0.1 mmol), $K_3PO_4 \cdot 3H_2O$ (4 mmol), and PEG_{1000} (2 g) were stirred for 12 h at 110 °C.
[b] Isolated yield.

Table 4
Recycle experiment of CuI–PEG_{1000}[a]

$$\text{PhSH} + \text{PhI} \xrightarrow[\substack{\text{2 eq NaOH} \\ PEG_{1000},\ 12\ h,\ 110\ ^oC}]{\text{5 mol \%CuI}} \text{PhSPh}$$

Run	Product (yield, %)[b]
1	97
2	98
3	98
4	97
5	95
6	95

[a] Reaction conditions: Iodobenzene (2.4 mmol), benzenethiol (2 mmol), CuI (0.1 mmol), NaOH (4 mmol), and PEG_{1000} (2 g) were stirred for 12 h at 110 °C.
[b] Isolated yield.



Scheme 1. Proposed mechanism for the coupling reaction.

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Supplementary data

Supplementary data (detailed experimental procedures, characterization data, copies of ^1H and ^{13}C NMR spectra for all products.) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.11.082.

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13. *Typical procedure for the coupling reaction*. *Method A*: A mixture of aryl iodides (2.4 mmol), thiols (2 mmol), CuI (19 mg, 0.1 mmol), $K_3PO_4 \cdot 3H_2O$ (1.064 g, 4 mmol), and PEG_{1000} (2 g) was stirred for 12 h at 110 °C. Then, the solution was cooled to room temperature and the resulting solid was extracted with diethyl ether or petroleum ether (5 mL × 6). The residue was subjected to a second run with the same substrates. The combined diethyl ether or petroleum ether phase was concentrated. Further purification of the product was achieved by flash chromatography on a silica gel column. *Method B*: A suspension of aryl iodides (2.4 mmol), thiols (2 mmol), CuI (19 mg, 0.1 mmol), and $K_3PO_4 \cdot 3H_2O$ (1.064 g, 4 mmol) in 2% (w/w) PEG_{1000}–H_2O solution (2 mL) was stirred for 12 h at 110 °C. Then, the solution was cooled to room temperature and extracted with diethyl ether or petroleum ether (5 mL × 6). The combined diethyl ether or petroleum ether phase was dried over anhydrous Na_2SO_4 and then concentrated. Further purification of the product was achieved by flash chromatography on a silica gel column.
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