

## Ligand-free highly effective iron/copper co-catalyzed formation of dimeric aryl ethers or sulfides†

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Highly selective coupling of diiodoarenes with phenols or phenthols can be performed by using a low-cost, benign character and readily available Fe/Cu catalytic system in the absence of ligands. It is noteworthy that the desired dimeric aryl ethers or sulfides could be obtained in high yields by coupling between diiodoarenes and phenols, or diphenols with aryl iodides.

The diaryl ether or sulfide linkage is present in numerous natural products and potential pharmaceuticals.<sup>1</sup> Aryl diaryl ether or sulfide oligomers are usually studied as functional materials.<sup>2</sup> Successful examples (Fig. 1) include trifluoromethyl sulfonamido compound **A**, which was discovered as a novel type of protein tyrosine phosphatase inhibitor,<sup>3</sup> compound **B** and its derivatives, which were investigated as candidate anticonvulsants,<sup>4</sup> compound **C**, which was prepared as a water-soluble asterisk molecule and first examined for its colloidal property,<sup>5</sup> compound **D**, which was employed to understand the attractive interaction with electron-deficient molecules and to form a host–guest complex.<sup>6</sup>

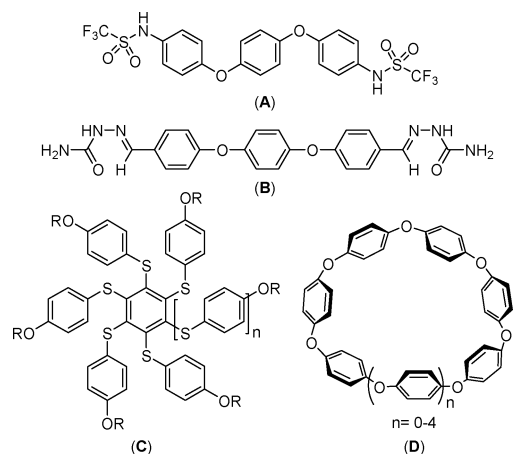


Fig. 1 Selected molecules containing moieties of the aryl ether or sulfide oligomers.

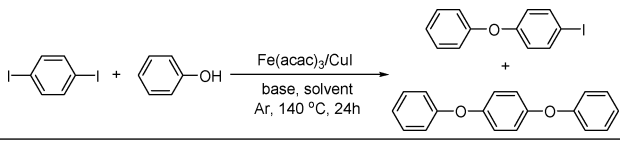
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In the past decades, great efforts have been made on transition metal-catalyzed C–O or C–S formation reactions, which have been regarded as one of the most important methods for the preparation of oxygen- or sulfur-containing compounds.<sup>7</sup> The typical C–O(S) cross-coupling reaction is performed in the presence of Pd catalysts.<sup>8</sup> In addition, in order to reduce the cost of catalytic reactions, nickel-, copper-, and cobalt-based catalysts have been developed as alternative choices.<sup>9</sup> Comparatively, iron as an abundant, economical, and environmental friendly metal shows increasing and promising catalytic abilities in many organic transformations, in particular for C–C bond-forming reactions.<sup>10</sup> Recently, Taillefer *et al.* reported an efficient Fe/Cu catalytic catalyst for *N*-arylation of nitrogen-containing heterocycles with aryl halides.<sup>11</sup> Wakharkar has also developed an efficient C–N coupling between amines and aryl halides in the presence of a heterogeneous recyclable Cu–Fe hydrotalcite catalyst.<sup>12</sup> Independently, Bolm and co-workers reported iron-catalyzed *N*-arylation of *N*-nucleophiles with aryl iodides using *N,N'*-dimethylethylenediamine (dmeda) as the ligand.<sup>13</sup> Subsequently, they successfully applied their methodology to C–O and C–S cross-coupling reactions.<sup>14</sup> In 2007, our research group<sup>15a</sup> and others reported an efficient Fe/Cu co-catalytic system for ligand-free Sonogashira couplings.<sup>15</sup> Extending our interest in improving and simplifying various coupling reactions,<sup>16</sup> we herein describe a high-yielding synthesis of dimeric aryl ethers or sulfides using a low loading of an Fe/Cu co-catalytic system in the absence of ligands.

As a model reaction the coupling between 1,4-diiodobenzene and phenol was investigated. The related results are listed in Table 1. Only Fe(acac)<sub>3</sub> resulted in monosubstituted product (entry 1, Table 1). Only CuI could catalyze the reaction with 32% yield of disubstituted desired product (entry 2). However, combination of Fe(acac)<sub>3</sub> with CuI provided a clearly higher yield of the desired product (68% yield) (entry 3). Enhancement of the amount of phenol resulted in higher yield of the catalytic reaction (entry 4). After screening a variety of bases (*i.e.*, K<sub>3</sub>PO<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KF,<sup>17</sup> Na<sub>2</sub>CO<sub>3</sub> and <sup>t</sup>BuOK) (entries 4–9), K<sub>2</sub>CO<sub>3</sub> was found to be the most effective in the view of conversion and selectivity (entry 5). To our delight, disubstituted product was obtained exclusively. Among the different solvents used, DMSO was clearly proved the best choice (entries 10–11). The dependence of the catalytic productivity on different mole ratios between Fe(acac)<sub>3</sub> and CuI was investigated. It can be seen that equal amounts of Fe and Cu catalysts were the best (entries 12–13). Reducing the loading of the catalyst to 10% and 5% did not change the

**Table 1** Screening catalytic conditions in Fe/Cu co-catalyzed cross-coupling between 1,4-diiodobenzene and phenol<sup>a</sup>



Entry	Fe : Cu <sup>b</sup>	Base	Solvent	Di : mono <sup>c</sup>	yield (%) <sup>d</sup>
1	20 : 0	K <sub>3</sub> PO <sub>4</sub>	DMSO	<1 : >99	—
2	0 : 20	K <sub>3</sub> PO <sub>4</sub>	DMSO	63 : 37	32
3	20 : 20	K <sub>3</sub> PO <sub>4</sub>	DMSO	90 : 10	68
4 <sup>e</sup>	20 : 20	K <sub>3</sub> PO <sub>4</sub>	DMSO	>99 : <1	75
5 <sup>e</sup>	20 : 20	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	91
6 <sup>e</sup>	20 : 20	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	82
7 <sup>e</sup>	20 : 20	KO <sup>t</sup> Bu	DMSO	87 : 13	76
8 <sup>e</sup>	20 : 20	Na <sub>2</sub> CO <sub>3</sub>	DMSO	56 : 44	45
9 <sup>e</sup>	20 : 20	KF	DMSO	21 : 79	17
10 <sup>e</sup>	20 : 20	K <sub>2</sub> CO <sub>3</sub>	DMF	70 : 30	52
11 <sup>e</sup>	20 : 20	K <sub>2</sub> CO <sub>3</sub>	DMAc	41 : 59	33
12 <sup>e</sup>	20 : 10	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	89
13 <sup>e</sup>	10 : 20	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	89
14 <sup>e</sup>	10 : 10	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	91
15 <sup>e</sup>	5 : 5	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	90
16 <sup>e</sup>	2 : 2	K <sub>2</sub> CO <sub>3</sub>	DMSO	63 : 37	57
17 <sup>e,f</sup>	5 : 5	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	99
18 <sup>e,f,g</sup>	5 : 5	K <sub>2</sub> CO <sub>3</sub>	DMSO	>99 : <1	>99

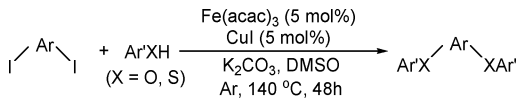
<sup>a</sup> Reaction conditions: Fe(acac)<sub>3</sub> (0.1 mmol), CuI (0.1 mmol), 1,4-diiodobenzene (0.5 mmol), phenol (1.2 mmol), base (2.0 equiv.), solvent (2 mL), Ar, 140 °C, 24 h. <sup>b</sup> Fe(acac)<sub>3</sub> : CuI (mol% : mol%). <sup>c</sup> Ratio based on GC-MS. <sup>d</sup> Isolated yield (based on 1,4-diiodobenzene). <sup>e</sup> 5 equiv. of PhOH was employed. <sup>f</sup> 48 h. <sup>g</sup> Fe(acac)<sub>3</sub> (>99.9%) and CuI (99.999%) from Aldrich were employed into the reaction.

results significantly (entries 14–15). However, only 57% of desired product was obtained in the presence of 2% loading of the catalyst (entry 16). It reached a near maximum (99% yield) when reaction time was extended to 48 h (entry 17). Indeed, using Fe(acac)<sub>3</sub> and CuI with high purity (>99.9% and 99.999%, respectively) yielded quantitative product (entry 18) (see the ESI†).

Thus, this Fe/Cu catalytic system was used to catalyze the reaction of diiodoarenes with a variety of aryl phenols or phenthiols by applying the optimized conditions of entry 17 in Table 1. As shown by the results summarized in Table 2, good to excellent yields (68–99%) of desired products have been achieved for these cross-coupling reactions. It can be seen that the substitution position of the diiodobenzene has a significant effect on the yield of the reactions (entries 1–3, Table 2). In addition, a distinct influence could be seen with different substituents on the *para*-position of the aromatic ring of phenols (entries 4–7). An electron-withdrawing group was found to be inferior (entry 7). When 4,4'-diiodobiphenyl was employed as the substrate, high yields were acquired (entries 8–10). Furthermore, this Fe/Cu catalytic system was applied to the coupling of arene thiols. To our delight, good results were obtained for different substrates (entries 11–17).

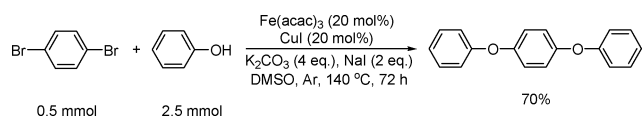
Subsequently, coupling between 1,4-dibromobenzene and phenol was investigated. Under the same catalytic conditions, only 13% of the disubstituted product and 50% of the monosubstituted product were obtained. In order to improve the result, 2 equiv. of NaI as the additive showed to be beneficial for the coupling reaction. Thus, the corresponding product was obtained in 70% yield as shown in Scheme 1.

**Table 2** Fe/Cu co-catalyzed cross-coupling reactions between different aryl diiodoarenes and phenols or phenthiols<sup>a</sup>



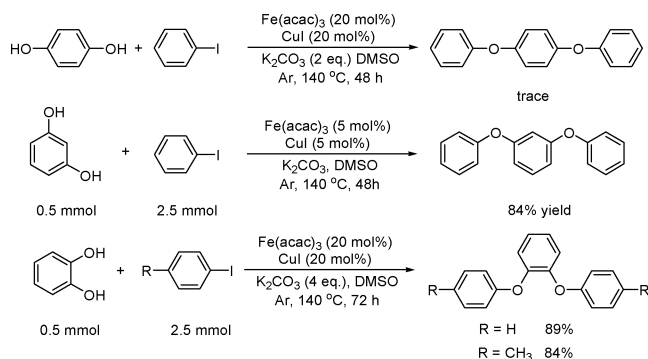
Entry	Aryl halide diiodoarenes	(Thio)phenol	Yield (%) <sup>b</sup>
1			99
2			94
3			77
4			94
5			88
6			86
7			84
8			98
9			90
10			88
11			92
12			85
13			68
14			90
15			82
16			99
17			84

<sup>a</sup> Reaction conditions: Fe(acac)<sub>3</sub> (0.025 mmol), CuI (0.025 mmol), aryl diiodoarene (0.5 mmol), phenol or phenthiol (2.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv.), DMSO (2 mL), Ar, 140 °C, 48 h. <sup>b</sup> Isolated yield based on aryl diiodoarene (average of two runs).



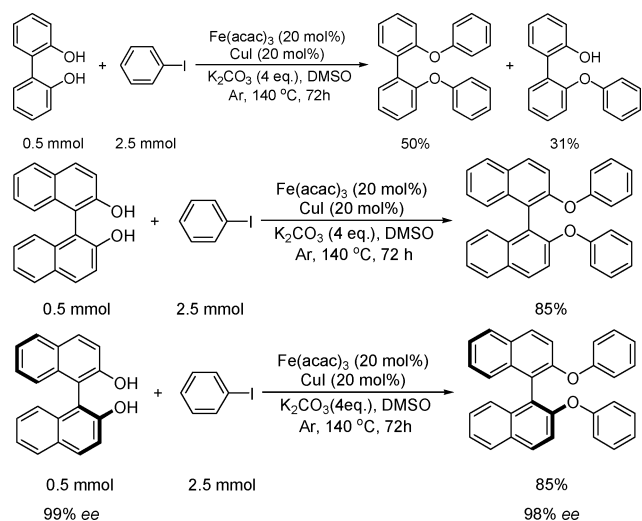
**Scheme 1** Coupling of 1,4-dibromobenzene and phenol using the  $\text{Fe}(\text{acac})_3/\text{CuI}$  catalytic system.

Since the dimeric aryl ethers or sulfides could be prepared by the coupling of diiodobenzene with phenol, the question arises: how about the coupling of diphenol with iodobenzene? As shown in Scheme 2, to our astonishment, the reaction of 1,4-diphenol and iodobenzene could not occur. However, for the coupling of 1,3-diphenol, a good yield of the desired product was obtained (84% yield). When 1,2-diphenol was employed as the substrate, satisfactory results were acquired in the presence of 20% loading of catalysts: 89% and 84% yield of diethers from iodobenzene and 4-methyliodobenzene, respectively.



**Scheme 2** Coupling of diphenols and iodoarenes using the  $\text{Fe}(\text{acac})_3/\text{CuI}$  catalytic system.

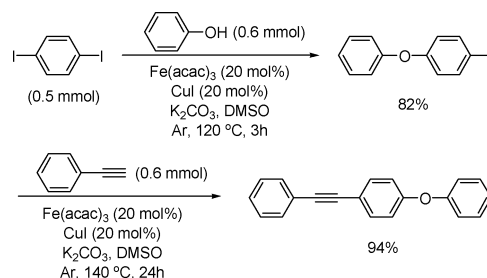
The coupling of 2,2'-biphenol with iodobenzene was studied. The result showed that the desired disubstituted ether was obtained in 50% yield, while the monosubstituted ether was obtained in 31% yield as shown in Scheme 3. The coupling of *rac*-BINOL with iodobenzene afforded the desired product in good yield (85%). It is noteworthy that coupling of (*S*)-BINOL



**Scheme 3** Coupling of 2,2'-biphenol or 1,1'-bi-2-naphthol (BINOL) and iodobenzene using the  $\text{Fe}(\text{acac})_3/\text{CuI}$  catalytic system.

led to the corresponding product in high enantioselectivity (98% ee) (chiral HPLC conditions and data see the ESI†).

The new  $\text{Fe}/\text{Cu}$  co-catalyzed sequential coupling reactions were successfully applied to the synthesis of molecules containing oxygen and alkyne<sup>18</sup> as shown in Scheme 4. The first step is that coupling between 1,4-diiodobenzene and phenol using  $\text{Fe}/\text{Cu}$  catalytic system afforded the monosubstituted product when the catalytic reaction was performed at 120 °C for 3 h. The second step is a Sonogashira-type coupling reaction of phenylacetylene. The desired product could be obtained in 94% yield. Thus, it can be seen that this cheap alternative opens fascinating perspectives towards the use of this versatile methodology on a large scale.



**Scheme 4** The sequential coupling reaction using the  $\text{Fe}(\text{acac})_3/\text{CuI}$  catalytic system.

In summary, we have developed an effective way to prepare dimeric aryl ethers or sulfides catalyzed by an  $\text{Fe}/\text{Cu}$  catalytic system by C–O(S) coupling reactions. The desired products could be achieved in high yields by two ways: coupling of diiodoarenes with phenols and coupling of diphenols with aryl iodides, which could be complimentary in different cases. Features of this protocol worth noting include high selectivity and working with Pd-free and ligand-free conditions. Thus, the low-cost, benign character and easy availability of the catalyst makes this method potentially very useful, which could be amenable to scale-up. Further studies concerning the mechanisms of the catalytic reaction and application of this methodology to other coupling reactions are currently underway.

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