

## Cu/Fe/O=PPh<sub>3</sub>-Catalyzed Etherification for the Synthesis of Aryl 3-Benzo[*b*]thienyl Ethers

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1 Cu/Fe-cocatalyzed cross-coupling reactions between 3-  
2 bromobenzo[*b*]thiophene and hydroxyaryls are described  
3 herein. The combination of Cu and Fe catalysts is important  
4 for the progress of the reactions, and the use of  
5 triphenylphosphine oxide as a ligand suppresses the  
6 dehalogenation of 3-bromobenzo[*b*]thiophene, and proceeds  
7 promptly the reaction. The obtained aryl benzo[*b*]thienyl  
8 ethers can be converted to  $\pi$ -extended thienobenzofuran  
9 derivatives via Pd-catalyzed dehydrogenative cyclizations.

10 **Keywords:** Aryl thienyl ether, Cu/Fe-cocatalyst, Cross-  
11 **coupling**

12 Diaryl ethers are known as common skeletal motifs of  
13 natural products and bioactive compounds, and several  
14 synthetic methods have been reported thus far.<sup>1</sup> Among the  
15 known diaryl ethers, aryl thienyl ethers are important  
16 because they can be used as precursors for  $\pi$ -extended  
17 thieno[3,2-*b*]furan derivatives,<sup>2</sup> which are potential  
18 candidates for organic materials.

19 While copper-mediated Ullmann couplings have been  
20 used for a long time for the synthesis of diaryl ethers, these  
21 reactions usually require the use of a stoichiometric amount  
22 of copper salts as well as high reaction temperatures.<sup>3</sup>  
23 Recently, a breakthrough was accomplished by the  
24 discovery of efficient ligands for Ullmann couplings.<sup>4</sup> These  
25 ligands realize catalytic Ullmann-type coupling under mild  
26 conditions. Another breakthrough is the use of an iron salt  
27 as a co-catalyst; several excellent works based on the  
28 combination of copper and iron catalysts were recently  
29 reported.<sup>5</sup> Thus, new possibilities have been reported for the  
30 synthesis of diaryl ethers; however, applying such reactions  
31 to the synthesis of diaryl ethers bearing an electron-rich  
32 heteroaryl, such as benzo[*b*]thiophene, is challenging  
33 because dehalogenation of the substrate often competes with  
34 the desired coupling reaction.<sup>6</sup> Buchwald and co-workers  
35 reported that picolinic acid was an efficient ligand for Cu-  
36 catalyzed Ullmann-type etherifications.<sup>7</sup> They reported the  
37 reaction of 3-bromo-2-formyl-benzo[*b*]thiophene, but the  
38 reaction of 3-bromobenzo[*b*]thiophene, which could be used  
39 for thieno[3,2-*b*]furan, was not reported. Quite recently, Ma  
40 and co-workers reported CuI/*N*-(2-phenylphenyl)-*N'*-benzyl  
41 oxalamide-catalyzed diaryl ether syntheses.<sup>8</sup> While the  
42 catalytic system could be used for the synthesis of a wide  
43 variety of diaryl ethers, they used 3-iodobenzo[*b*]thiophene  
44 as the benzo[*b*]thiophene source. To the best of our  
45 knowledge, there has been no efficient method for a Cu-  
46 catalyzed etherification using 3-bromobenzo[*b*]thiophene,  
47 which is commercially available and cheaper than 3-  
48 iodobenzo[*b*]thiophene.

49 We considered that a fine-tuning of the reaction  
50 conditions could enhance the efficiency of the Ullmann-type  
51 coupling reaction of 3-bromobenzo[*b*]thiophene, which  
52 would be a powerful tool for the synthesis of aryl  
53 benzo[*b*]thienyl ethers. We examined the reaction  
54 conditions for an Ullmann-type reaction with 3-  
55 bromobenzo[*b*]thiophene, and found an efficient Cu/Fe  
56 catalytic system, using triphenylphosphine oxide as a ligand.  
57 To the best of our knowledge, there has been no report on a  
58 copper- or iron-catalyzed Ullmann-type reaction using  
59 triphenylphosphine oxide as a ligand.<sup>9</sup>

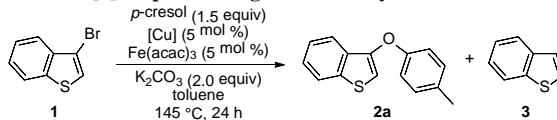
60 First, we chose 3-bromobenzo[*b*]thiophene (**1**) and *p*-  
61 cresol as model compounds and performed a screening of  
62 copper salts for the Cu/Fe-cocatalyzed etherification  
63 between them (Table 1). In the presence of a Cu source  
64 ([Cu], 5 mol %), Fe(acac)<sub>3</sub> (5 mol %), and K<sub>2</sub>CO<sub>3</sub> (2.0  
65 equiv), 3-bromobenzo[*b*]thiophene (**1**) was treated with *p*-  
66 cresol (1.5 equiv). Without the Cu source, only a trace  
67 amount of the desired product was obtained, and most of the  
68 starting material **1** was recovered (entry 1). In contrast, with  
69 copper powder, the coupling reaction between **1** and *p*-  
70 cresol proceeded smoothly to afford the coupling product **2a**  
71 in 55% yield with a considerable amount (41%) of the  
72 dehalogenated compound, benzo[*b*]thiophene (**3**) (entry 2).  
73 With Cu(I) salts such as CuCl, CuBr, and CuI,<sup>5f,5h</sup> **2a** was  
74 obtained in the respective yields of 48%, 50%, and 57%  
75 (entries 3–5). When the reaction was performed without  
76 Fe(acac)<sub>3</sub>, the yield of **2** decreased and that of **3** increased  
77 (entry 4). Among several Cu(I) salts, copper thiophene-2-  
78 carboxylate (CuTC) provided the best result. With CuTC,  
79 the desired compound **2a** was obtained in 60% yield, but **3**  
80 was also obtained in 33% yield (entry 8). We then examined  
81 several Cu(II) salts (entries 9–13) and found that the use of  
82 Cu(acac)<sub>2</sub> afforded **2a** in the highest yield (62% yield, entry  
83 13).

84 Then, we examined the effect of the iron source (Table  
85 2) and Fe(acac)<sub>3</sub> was the best iron source among the studied  
86 sources. Using FeCl<sub>2</sub>•4H<sub>2</sub>O, FeCl<sub>3</sub>, or FeBr<sub>3</sub>, the yield of **2a**  
87 decreased to 43%–47% (entries 2–4).

88 The screening of the copper and iron sources revealed  
89 that the combination of Cu(acac)<sub>2</sub> and Fe(acac)<sub>3</sub> was  
90 efficient for the Cu/Fe-cocatalyzed etherification of **1** and *p*-  
91 cresol; however, dehalogenation of **1** to **3** was still  
92 problematic. Therefore, we investigated the effect of ligands  
93 (Table 3). Diamine ligands such as 2,2'-bipyridyl (bpy) and  
94 1,10-phenanthroline (phen), which are commonly used with  
95 Cu, were ineffective for the reactions, and the yield of **2a**  
96 decreased (entries 1–2). We then evaluated oxygen ligands  
97 (entries 3 and 4) and found that with 1,1'-bi-2-naphthol  
98 (BINOL),<sup>5i</sup> the yield of **2a** increased to 51%, but **3** was also

1 obtained in 41% yield (entry 3). The use of 2,2,6,6-tetramethylheptane-3,5-dione (TMHD)<sup>5a,5j</sup> provided a good result (72% yield, entry 4). The use of phosphine ligands was also investigated and found that the triphenylphosphine (PPh<sub>3</sub>) was also effective, affording **2a** in 73% yield and a 15% suppression of the generation of **3** (entry 5). Further screening revealed that electron-donating phosphine ligands such as P(*p*-tol)<sub>3</sub> and PCy<sub>3</sub> were ineffective (entries 6 and 7). In contrast, the etherification proceeded smoothly with P(2-furyl)<sub>3</sub>, which is a slightly electron-deficient ligand (79% yield), but afforded **3** in 18% yield (entry 8). Other electron-deficient ligands were not effective (entries 9–11). Finally, we found that dehalogenation of **1** was suppressed by the use of triphenylphosphine oxide (O=PPh<sub>3</sub>), affording a 10% yield (entry 12). Using 10 mol % of Cu(acac)<sub>2</sub>, and 10 mol % of Fe(acac)<sub>3</sub>, the yield of **2a** increased to 82% (79% isolated yield) with 12 % yield of **3** (entry 13). The ratio of O=PPh<sub>3</sub> to Cu(acac)<sub>2</sub> and Fe(acac)<sub>3</sub> is significant. Increasing or decreasing the amount of O=PPh<sub>3</sub>, the yields of **2a** decreased (entries 14 and 15). The temperature highly influenced the reaction, and the yield of **2a** decreased to 69% at 135 °C (entry 16). While the reason for the suppression of the dehalogenation of **1** is unclear, we assume that a catalyst bearing O=PPh<sub>3</sub> would be highly active and the cross-coupling reaction would proceed faster than the dehalogenation.

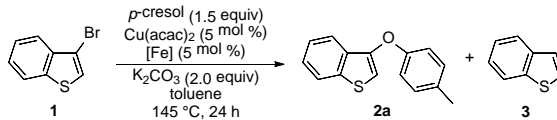
**Table 1. Cu/Fe-Cocatalyzed etherification of 3-bromobenzo[*b*]thiophene using several catalysts<sup>a</sup>**



Entry	[Cu]	Yield of <b>2a</b> <sup>b</sup> /%	Yield of <b>3</b> <sup>b</sup> /%
1	none	<1	<1
2	Cu powder	55	41
3	CuCl	48	25
4	CuBr	50 (42) <sup>c</sup>	32 (45) <sup>c</sup>
5	CuI	57	26
6	Cu <sub>2</sub> O	54	17
7	CuCN	53	33
8	CuTC <sup>d</sup>	60	33
9	CuCl <sub>2</sub>	46	17
10	CuBr <sub>2</sub>	54	40
11	CuO	60	23
12	Cu(OAc) <sub>2</sub>	47	43
13	Cu(acac) <sub>2</sub>	62	30

<sup>a</sup> Reaction conditions: **1** (0.5 mmol), *p*-cresol (0.75 mmol), [Cu] (5 mol %), Fe(acac)<sub>3</sub> (5 mol %), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), toluene (0.63 M), 145 °C, 24 h. Performed in a sealed tube. <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> Performed without Fe(acac)<sub>3</sub>. <sup>d</sup> CuTC = copper thiophene-2-carboxylate.

**Table 2. Effect of the Fe source on the Cu/Fe-cocatalyzed etherification reaction<sup>a</sup>**

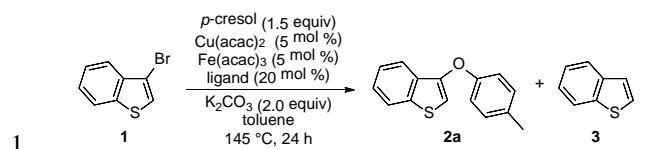


Entry	[Fe]	Yield of <b>2a</b> <sup>b</sup> /%	Yield of <b>3</b> <sup>b</sup> /%
1	Fe(acac) <sub>3</sub>	62	30
2	FeCl <sub>2</sub> •4H <sub>2</sub> O	43	17
3	FeCl <sub>3</sub>	45	23
4	FeBr <sub>3</sub>	47	28

<sup>a</sup> Reaction conditions: **1** (0.5 mmol), *p*-cresol (0.75 mmol), Cu(acac)<sub>2</sub> (5 mol %), [Fe] (5 mol %), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), toluene (0.63 M), 145 °C, 24 h. Performed in a sealed tube. <sup>b</sup> Determined by <sup>1</sup>H NMR.

We then examined the scope of the etherification reactions. Several hydroxyaryls were tested with 3-bromobenzo[*b*]thiophene under optimized conditions (Table 4). The reaction with phenol afforded the corresponding coupling product **2b** in 73% yield. Not only *p*-cresol but also *o*- and *m*-cresol could be used for the reaction to give the corresponding coupling products **2c** and **2d** in the respective yields of 62% and 69%. Hydroxyaryls bearing electron-donating groups, such as *t*-Bu and methoxy groups, gave the coupling products in moderate to good yields (**2e**: 71%, **2f**: 56%). Reactions with hydroxyaryls bearing an electron-withdrawing group were also examined. Reactions with hydroxyaryls bearing a halogen atom, such as F and Cl, at the *p*-position gave the desired coupling products (**2g**: 76%, **2h**: 64%). Hydroxyaryls bearing much stronger electron-withdrawing groups at the *p*-position, such as trifluoromethyl or nitro groups, were unfortunately not applicable, probably due to their electronic effect. In contrast, the reaction with *m*-trifluoromethylphenol, which has an electron-withdrawing group at the *m*-position, proceeded smoothly to give the desired coupling product **2k** in 62% yield. We performed out the coupling reaction with more  $\pi$ -extended hydroxy aryls. *p*-Phenylphenol could be used for the reaction to afford **2l** in 71% yield. With 1-naphthol or 2-naphthol, the coupling products **2m** and **2n** were obtained in the respective yields of 15% and 54%.

**Table 3. Optimization of ligands<sup>a</sup>**

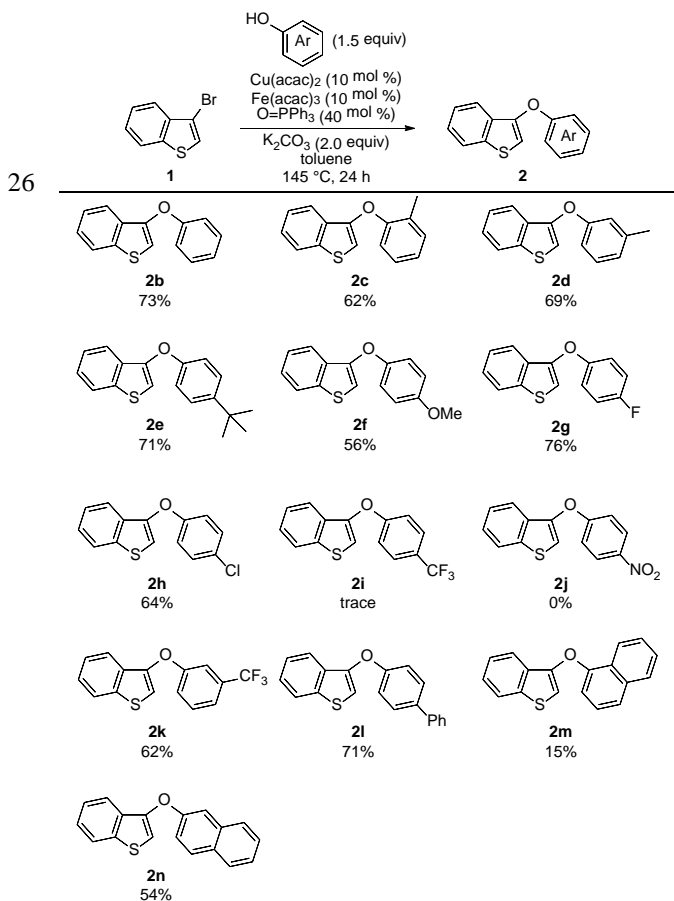


Entry	Ligand	Yield of 2a <sup>b</sup> /%	Yield of 3 <sup>b</sup> /%
1	bpy <sup>c</sup>	41	35
2	phen <sup>d</sup>	39	50
3	BINOL	51	41
4	TMHD <sup>e</sup>	72	18
5	PPh <sub>3</sub>	73	15
6	P( <i>p</i> -tol)	15	0
7	PCy <sub>3</sub>	0	0
8	P(2-furyl) <sub>3</sub>	79	18
9	P(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	26	0
10	P(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -CF <sub>3</sub> )	56	14
11	P(OPh) <sub>3</sub>	26	10
12	O=PPh <sub>3</sub>	73	10
13 <sup>f</sup>	O=PPh <sub>3</sub>	82 (79) <sup>g</sup>	12
14 <sup>h</sup>	O=PPh <sub>3</sub>	68	8
15 <sup>i</sup>	O=PPh <sub>3</sub>	63	7
16 <sup>f,j</sup>	O=PPh <sub>3</sub>	69	9

2 <sup>a</sup> Reaction conditions: **1** (0.5 mmol), *p*-cresol (0.75  
3 mmol), Cu(acac)<sub>2</sub> (5 mol %), Fe(acac)<sub>3</sub> (5 mol %), ligand  
4 (bidentate: 10 mol %, monodentate: 20 mol %), K<sub>2</sub>CO<sub>3</sub> (2.0  
5 equiv), toluene (0.63 M), 145 °C, 24 h. Performed in a  
6 sealed tube. <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> bpy = 2,2'-  
7 bipyridyl. <sup>d</sup> phen = 1,10-phenanthroline. <sup>e</sup> TMHD =  
8 2,2,6,6-tetramethylheptane-3,5-dione. <sup>f</sup> Performed with  
9 Cu(acac)<sub>2</sub> (10 mol %), Fe(acac)<sub>3</sub> (10 mol %), O=PPh<sub>3</sub> (40  
10 mol %). <sup>g</sup> Isolated yield. <sup>h</sup> Performed with Cu(acac)<sub>2</sub> (10  
11 mol %), Fe(acac)<sub>3</sub> (10 mol %), O=PPh<sub>3</sub> (20 mol %). <sup>i</sup>  
12 Performed with Cu(acac)<sub>2</sub> (10 mol %), Fe(acac)<sub>3</sub> (10 mol %),  
13 O=PPh<sub>3</sub> (60 mol %). <sup>j</sup> Performed at 135 °C.

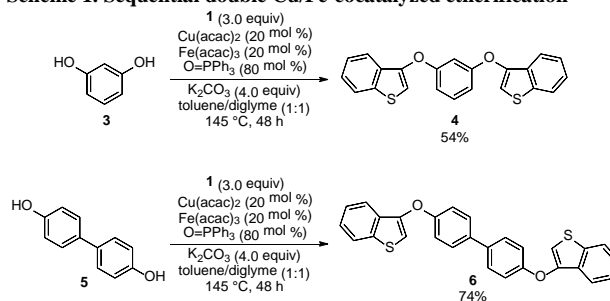
14  
15 This reaction system could also be applied for the  
16 synthesis of diethers (Scheme 1). The Cu/Fe  
17 -catalyzed reaction between resorcinol and 3-  
18 bromobenzo[*b*]thiophene (**1**) afforded 1,3-  
19 bis(benzo[*b*]thiophen-3-yloxy)benzene (**4**) in 54% yield.  
20 Similarly, the reaction with (1,1'-biphenyl)-4,4'-diol (**5**)  
21 gave the corresponding diether **6** in 74% yield.

25 **Table 4. Scope of the Cu/Fe-cocatalyzed etherification** <sup>a</sup>



27 <sup>a</sup> Reaction conditions: **1** (0.5 mmol), hydroxyaryl (0.75  
28 mmol), Cu(acac)<sub>2</sub> (10 mol %), Fe(acac)<sub>3</sub> (10 mol %),  
29 O=PPh<sub>3</sub> (40 mol %), K<sub>2</sub>CO<sub>3</sub> (2.0 equiv), toluene (0.63 M),  
30 145 °C, 24 h. Performed in a sealed tube. Isolated yield.

### 32 Scheme 1. Sequential double Cu/Fe-cocatalyzed etherification



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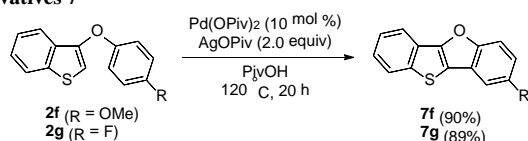
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As an application of the thus-obtained **2**, this  
compound was transformed into thienobenzofurans using a  
modified Pd-catalyzed dehydrogenative cyclization method,  
which was reported independently by Satoh and Miura,<sup>10</sup>  
and by Kanai and Kuninobu.<sup>11</sup> In the presence of Pd(OPiv)<sub>2</sub>  
(10 mol %) and AgOPiv (2.0 equiv) in PivOH, the  
cyclization of **2f** and **2g** was performed at 120 °C for 20 h  
(Scheme 2). The corresponding thienobenzofuran  
derivatives **7f** and **7g** were obtained in high yields from each  
precursor, which had an electron-donating or an electron-  
withdrawing group.<sup>12</sup>

1  
2 **Scheme 2. Representative examples of Pd-catalyzed**  
3 **dehydrogenative cyclization for the synthesis of thienobenzofuran**  
4 **derivatives 7<sup>a</sup>**



5  
6  
7 In summary, we developed Cu/Fe/O=PPh<sub>3</sub>-catalyzed  
8 etherification reactions for the synthesis of aryl  
9 benzo[*b*]thienyl ethers. The use of triphenylphosphine oxide  
10 as a ligand suppresses the dehalogenation of 3-  
11 bromobenzo[*b*]thiophene, and enables an efficient  
12 synthesis of aryl benzo[*b*]thienyl ethers. Further applications  
13 of this strategy for other heteroaryl ethers are on-going in  
14 our laboratory.

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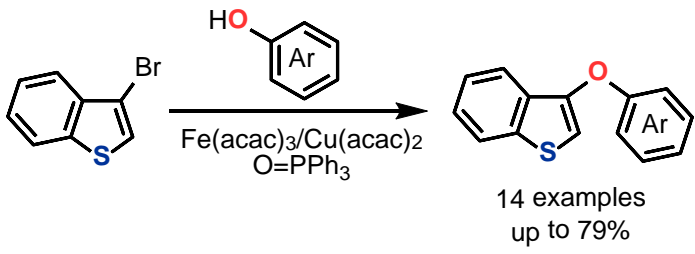
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**NOTE** The diagram is acceptable in a colored form. Publication of the colored G.A. is free of charge.

For publication, electronic data of the colored G.A. should be submitted. Preferred data format is EPS, PS, CDX, PPT, and TIFF.

If the data of your G.A. is "bit-mapped image" data (not "vector data"), note that its print-resolution should be 300 dpi.

You are requested to put a brief abstract (50-60 words, one paragraph style) with the graphical abstract you provided, so that readers can easily understand what the graphic shows.

Graphical Abstract	
Textual Information	
A brief abstract (required)	Cu/Fe-cocatalyzed cross-coupling reactions between 3-bromobenzo[ <i>b</i> ]thiophene and hydroxyaryls are described herein. The combination of Cu and Fe catalysts is important for the progress of the reaction, and the use of triphenylphosphine oxide as a ligand suppresses the dehalogenation of 3-bromobenzo[ <i>b</i> ]thiophene, and proceeds promptly the reaction. The obtained aryl benzo[ <i>b</i> ]thienyl ethers could be converted to $\pi$ -extended thienobenzofuran derivatives via Pd-catalyzed dehydrogenative cyclizations.
Title(required)	Cu/Fe/O=PPh <sub>3</sub> -Catalyzed Etherification for the Synthesis of Aryl 3-Benzo[ <i>b</i> ]thienyl Ethers
Authors' Names(required)	Koichi Mitsudo,* Takuya Asada, Tomohiro Inada, Yuji Kurimoto, Hiroki Mandai, and Seiji Suga*
Graphical Information	
 <p>14 examples up to 79%</p>	