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Cu/Fe/O=PPh₃-Catalyzed Etherification for the Synthesis of Aryl 3-Benzo[b]thienyl Ethers

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Cu/Fe-cocatalyzed cross-coupling reactions between 3 bromobenzo[b]thiophene and hydroxyaryls are described
 herein. The combination of Cu and Fe catalysts is important
 for the progress of the reactions, and the use of
 triphenylphosphine oxide as a ligand suppresses the
 dehalogenation of 3-bromobenzo[b]thiophene, and proceeds
 promptly the reaction. The obtained aryl benzo[b]thienyl
 ethers can be converted to π-extended thienobenzofuran
 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.¹ Among the 15 known diaryl ethers, aryl thienyl ethers are important 16 because they can be used as precursors for π -extended 17 thieno[3,2-*b*]furan derivatives,² 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.³ 23 Recently, a breakthrough was accomplished by the 24 discovery of efficient ligands for Ullmann couplings.⁴ 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 reported.⁵ Thus, new possibilities have been reported for the 29 30 synthesis of diaryl ethers; however, applying such reactions to the synthesis of diaryl ethers bearing an electron-rich 31 32 heteroaryl, such as benzo[b]thiophene, is challenging 33 because dehalogenation of the substrate often competes with 34 the desired coupling reaction.⁶ Buchwald and co-workers reported that picolinic acid was an efficient ligand for Cu-35 catalyzed Ullman-type etherifications.7 They reported the 36 37 reaction of 3-bromo-2-formyl-benzo[b]thiophene, but the reaction of 3-bromobenzo[b]thiophene, which could be used 38 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.⁸ 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, which is commercially available and cheaper than 3-47 iodobenzo[b]thiophene. 48

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 arvl 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 copper- or iron-catalyzed Ullmann-type reaction using 58 59 triphenylphosphine oxide as a ligand.9

60 First, we chose 3-bromobenzo[b]thiophene (1) and pcresol as model compounds and performed a screening of 61 copper salts for the Cu/Fe-cocatalyzed etherification 62 63 between them (Table 1). In the presence of a Cu source 64 ([Cu], 5 mol %), Fe(acac)₃ (5 mol %), and K₂CO₃ (2.0 65 equiv), 3-bromobenzo[b]thiophene (1) was treated with pcresol (1.5 equiv). Without the Cu source, only a trace 66 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 dehalogenated compound, benzo[b]thiophene (3) (entry 2). 72 With Cu(I) salts such as CuCl, CuBr, and CuI,^{5f,5h} 2a was 73 74 obtained in the respective yields of 48%, 50%, and 57% 75 (entries 3-5). When the reaction was performed without 76 $Fe(acac)_3$, 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 $Cu(acac)_2$ afforded **2a** in the highest yield (62% yield, entry 83 13).

Then, we examined the effect of the iron source (Table 2) and Fe(acac)₃ was the best iron source among the studied sources. Using FeCl₂•4H₂O, FeCl₃, or FeBr₃, the yield of **2a** decreased to 43%-47% (entries 2-4).

88 The screening of the copper and iron sources revealed 89 that the combination of $Cu(acac)_2$ and $Fe(acac)_3$ 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),⁵ⁱ the yield of **2a** increased to 51%, but **3** was also

obtained in 41% yield (entry 3). The use of 2,2,6,6-1 tetramethylheptane-3,5-dione (TMHD)^{5a,5j} provided a good 2 result (72% yield, entry 4). The use of phosphine ligands 3 was also investigated and found that the triphenylphosphine 4 5 (PPh₃) was also effective, affording 2a in 73% yield and a 15% suppression of the generation of 3 (entry 5). Further 6 screening revealed that electron-donating phosphine ligands 7 such as $P(p-tol)_3$ and PCy_3 were ineffective (entries 6 and 7). 8 9 In contrast, the etherification proceeded smoothly with P(2-10 furyl)₃, which is a slightly electron-deficient ligand (79% yield), but afforded 3 in 18% yield (entry 8). Other electron-11 12 deficient ligands were not effective (entries 9-11). Finally, 13 we found that dehalogenation of **1** was suppressed by the 14 use of triphenylphosphine oxide (O=PPh₃), affording a 10% yield (entry 12). Using 10 mol % of Cu(acac)₂, and 10 15 mol % of Fe(acac)₃, the yield of **2a** increased to 82% (79% 16 isolated yield) with 12 % yield of 3 (entry 13). The ratio of 17 18 $O=PPh_3$ to $Cu(acac)_2$ and $Fe(acac)_3$ is singnificant. 19 Increasing or decreasing the amount of O=PPh₃, the yields 20 of 2a decreased (entries 14 and 15). The temperature highly 21 influenced the reaction, and the yield of 2a decreased to 22 69% at 135 °C (entry 16). While the reason for the 23 suppression of the dehalogenation of 1 is unclear, we 24 assume that a catalyst bearing O=PPh₃ would be highly 25 active and the cross-coupling reaction would proceed faster 26 than the dehalogenation.

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28 Table 1. Cu/Fe-Cocatalyzed etherification of 29 bromobenzo[*b*]thiophene using several catalysts ^a

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

^a Reaction conditions: **1** (0.5 mmol), *p*-cresol (0.75 mmol), [Cu] (5 mol %), Fe(acac)₃ (5 mol %), K₂CO₃ (2.0 equiv), toluene (0.63 M), 145 °C, 24 h. Performed in a sealed tube. ^b Determined by ¹H NMR. ^c Performed without Fe(acac)₃. ^d CuTC = copper thiophene-2carboxylate.

38 Table 2. Effect of the Fe source on the Cu/Fe-cocatalyzed 39 etherification reaction ^a

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3-

	P-cresol (1.5 Br Cu(acac) ₂ (5 [Fe] (5 mo K ₂ CO ₃ (2.0 toluene 145 °C, 2	equiv) mol %) l %) equiv) equiv) e 4 h	2a	+ 5 3	
Entry	[Fe]	Yield of	2a ^b /%	Yield of 3 ^b /%	,
1	Fe(acac) ₃	62		30	
2	FeCl ₂ •4H ₂ O	43		17	
3	FeCl ₃	45		23	
4	FeBr ₃	47		28	
	1 Entry 1 2 3 4	$\begin{array}{c} & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \begin{array}{c} & \end{array} \\ & \end{array} \\ & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \end{array} \\ & \end{array} \\ & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \end{array} \\ & \end{array} \\ & \end{array} \\ & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \end{array} \\ \end{array} \\$	$FeCl_{3} = FeCl_{3} $	$FeCl_{2} \bullet FeCl_{3} $	$\begin{array}{c} & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \begin{array}{c} & \end{array} \\ \end{array} \end{array} \end{array} \end{array} \xrightarrow{\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \end{array} \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \end{array} \\ & \begin{array}{c} & \end{array} \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} & \begin{array}{c} & \end{array} \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} & \begin{array}{c} & \end{array} \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} & \begin{array}{c} & \end{array} \\ \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \\ \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \end{array} \end{array} \xrightarrow{\begin{array}{c} & \end{array} \end{array} \end{array} \begin{array}{c} & \end{array} \end{array} \end{array} \begin{array}{\begin{array}{c} & \end{array} \end{array} \end{array} \end{array} \end{array} \begin{array}{\begin{array}{c} & \end{array} \end{array} \end{array} \end{array} \end{array} \end{array} \begin{array}{\begin{array}{c} & \end{array} $

41 ^a Reaction conditions: **1** (0.5 mmol), *p*-cresol (0.75 42 mmol), Cu(acac)₂ (5 mol %), [Fe] (5 mol %), K₂CO₃ (2.0 43 equiv), toluene (0.63 M), 145 °C, 24 h. Performed in a 44 sealed tube. ^b Determined by ¹H NMR. 45

46 We then examined the scope of the etherification 47 reactions. Several hydroxyaryls were terated with 3bromobenzo[b]thiophene under optimized conditions (Table 48 4). The reaction with phenol afforded the corresponding 49 50 coupling product 2b in 73% yield. Not only p-cresol but 51 also o- and m-cresol could be used for the reaction to give 52 the corresponding coupling products 2c and 2d in the respective yields of 62% and 69%. Hydroxyaryls bearing 53 54 electron-donating groups, such as *t*-Bu and methoxy groups, gave the coupling products in moderate to good yields (2e: 55 56 71%, 2f: 56%). Reactions with hydroxyaryls bearing an 57 electron-withdrawing group were also examined. Reactions 58 with hydroxyaryls bearing a halogen atom, such as F and Cl, at the *p*-position gave the desired coupling products (2g: 59 76%, 2h: 64%). Hydroxylaryls bearing much stronger 60 electron-withdrawing groups at the p-position, such as 61 trifluoromethyl or nitro groups, were unfortunately not 62 applicable, probably due to their electronic effect. In 63 64 contrast, the reaction with *m*-trifluoromethylphenol, which 65 has an electron-withdrawing group at the *m*-position, proceeded smoothly to give the desired coupling product 2k 66 in 62% yield. We performed out the coupling reaction with 67 68 more π -extended hydroxy aryls. *p*-Phenylphenol could be 69 used for the reaction to afford 21 in 71% yield. With 1naphthol or 2-naphthol, the coupling products 2m and 2n 70 71 were obtained in the respective yields of 15% and 54%. 72

75 Table 3. Optimization of ligands ^a

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1		$\begin{array}{c} p\text{-}cresol (1.5 equiv)\\ Cu(acac)_2 (5 mol \%)\\ Fe(acac)_3 (5 mol \%)\\ ligand (20 mol \%)\\ \hline\\ K_2CO_3 (2.0 equiv)\\ toluene\\ 145 \ ^{\circ}\text{C}, 24 \text{ h} \end{array}$		+
-	Entry	Ligand	Yield of 2a ^b /%	Yield of 3 ^b /%
	1	bpy ^c	41	35
	2	phen ^d	39	50
	3	BINOL	51	41
	4	TMHD ^e	72	18
	5	PPh ₃	73	15
	6	P(<i>p</i> -tol)	15	0
	7	PCy ₃	0	0
	8	P(2-furyl) ₃	79	18
	9	$P(C_6F_5)_3$	26	0
	10	$P(C_6H_4-p-CF_3)$	56	14
	11	P(OPh) ₃	26	10
	12	O=PPh ₃	73	10
	$13^{\rm f}$	O=PPh ₃	82 (79) ^g	12
	14 ^h	O=PPh ₃	68	8
	15 ⁱ	O=PPh ₃	63	7
	$16^{\mathrm{f},\mathrm{j}}$	O=PPh ₃	69	9

2 ^a Reaction conditions: 1 (0.5 mmol), p-cresol (0.75 3 mmol), Cu(acac)₂ (5 mol %), Fe(acac)₃ (5 mol %), ligand (bidentate: 10 mol %, monodentate: 20 mol %), K₂CO₃ (2.0 4 equiv), toluene (0.63 M), 145 °C, 24 h. Performed in a sealed tube. ^b Determined by ¹H NMR. ^c bpy = 2,2'-bipyridyl. ^d phen = 1,10-phenanthroline. ^e TMHD = 5 6 7 2,2,6,6-tetramethylheptane-3,5-dione. ^f Performed with 8 9 Cu(acac)₂ (10 mol %), Fe(acac)₃ (10 mol %), O=PPh₃ (40 10 mol %). ^g Isolated yield. ^h Performed with Cu(acac)₂ (10 11 mol %), Fe(acac)₃ (10 mol %), O=PPh₃ (20 mol %). Performed with Cu(acac)₂ (10 mol %), Fe(acac)₃ (10 mol %), 12 O=PPh₃ (60 mol %). ^j Performed at 135 °C. 13

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15 This reaction system could also be applied for the synthesis of diethers (Scheme 1). The Cu/Fe 16

17 -catalyzed reaction between resorcinol 3and 1,3-18 bromobenzo[*b*]thiophene afforded (1) bis(benzo[b]thiophen-3-yloxy)benzene (4) in 54% yield. 19 20 Similarly, the reaction with (1,1'-biphenyl)-4,4'-diol (5) 21 gave the corresponding diether 6 in 74% yield. 22

24 25 Table 4. Scope of the Cu/Fe-cocatalyzed etherification ^a



^a Reaction conditions: **1** (0.5 mmol), hydroxyaryl (0.75 28 mmol), Cu(acac)₂ (10 mol %), Fe(acac)₃ (10 mol %), 29 O=PPh₃ (40 mol %), K₂CO₃ (2.0 equiv), toluene (0.63 M), 30 145 °C, 24 h. Performed in a sealed tube. Isolated yield. 31

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

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35 As an application of the thus-obtained 2, this 36 compound was transformed into thienobenzofurans using a 37 modified Pd-catalyzed dehydrogenative cyclization method, 38 which was reported independently by Satoh and Miura,¹⁰ 39 and by Kanai and Kuninobu.¹¹ In the presence of Pd(OPiv)₂ 40 (10 mol %) and AgOPiv (2.0 equiv) in PivOH, the 41 cyclization of 2f and 2g was performed at 120 °C for 20 h 42 (Scheme 2). The corresponding thienobenzofuran 43 derivatives **7f** and **7g** were obtained in high yields from each 44 precursor, which had an electron-donating or an electron-45 withdrawing group.¹²

1 2 Scheme 2. Representative examples of Pd-catalyzed 3 dehydrogenative cyclization for the synthesis of thienobenzofuran 4 derivatives 7 ^a



7 In summary, we developed Cu/Fe/O=PPh₃-catalyzed etherfication reactions for the 8 synthesis of arvl 9 benzo[b]thienyl ethers. The use of triphenylphosphine oxide 10 a ligand suppresses the dehalogenation of 3as bromobenzo[b]thiopehene, and enables an efficient 11 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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20 Supporting Information available is on http://dx.doi.org/10.1246/cl.*****. 21

22 **References and Notes**

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- 89 For the details of the dehydrogenative cyclization reactions, see 12 90 the Supporting Information.