A New Copper(I)-Catalyzed Cycloetherification/Acid-Catalyzed Allylic Nucleophilic Substitution for One-Pot Synthesis of 2-Substituted Benzofurans

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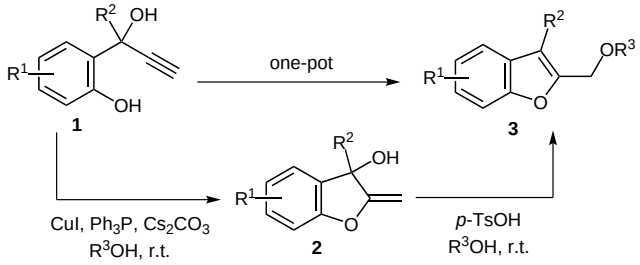
Abstract: A new copper(I)-catalyzed cycloetherification followed by an acid-catalyzed allylic nucleophilic substitution have been developed for the one-pot synthesis of 2-substituted benzofurans. This one-pot reaction proceeds efficiently under extremely mild conditions with simple and inexpensive catalysts, providing diversely substituted benzofurans in good to excellent yields.

Key words: benzofurans, cycloetherifications, allylic nucleophilic substitution, copper, one-pot synthesis

Benzofurans are ubiquitous structural motifs in a wide range of biologically active compounds which display various pharmacological activities such as anti-HIV,[1] anticancer,[2] antifungal,[3] antioxidantive[4] and anti-inflammatory.[5] Thus synthetic access to benzofurans is of considerable interest, and numerous efficient methods have been disclosed in the literature.[6,7] Among them, transition-metal-catalyzed cycloetherification is regarded as one of the most attractive approaches for its high atom-economy and mild reaction conditions.[7] Recently, a novel and efficient two-step procedure synthesis of 2-substituted benzofurans was successfully developed by Gabriele and co-workers.[8] Compared with the traditional stepwise approach, one-pot procedure has received more attention because they could increase the reaction efficiency, avoid the separation of intermediates, save the use of solvents, and reduce the emission of pollutant waste. Herein, we disclose a one-pot approach to the 2-substituted benzofurans via an unprecedented copper-catalyzed cycloetherification followed by an acid-catalyzed allylic nucleophilic substitution (Scheme 1).



Scheme 1 One-pot synthetic approach to 2-substituted benzofurans

Initially, our interest focused on the annulation of 2-(1-hydroxyprop-2-ynyl)phenol derivatives. Although numerous cycloetherifications have been reported, to the best of our knowledge, there are only three papers on the cyclization of these compounds, which was catalyzed by Pd, Au and Ag, respectively.[8a,9] This prompted us to develop a new catalyst system. A model reaction was carried out with 2-(1-hydroxyprop-2-ynyl)phenol (**1a**) in MeOH, using 5 mol% CuI and 10 mol% Cs_2CO_3 as the catalyst. However, after 24 hours of reaction time, no cyclization product was detected (Table 1, entry 1). The reaction mixture was then heated to reflux for nine hours, after which time the desired product **2a** was obtained in 85% yield (entry 2). To our pleasure, the addition of 5 mol% Ph_3P accelerated the reaction greatly and enabled the cycloetherification of **1a** to proceed at room temperature with excellent yield (entry 3). Control experiments suggested that CuI, Cs_2CO_3 and Ph_3P were all necessary for the reaction (entries 4 and 5) and lower CuI or Cs_2CO_3 loading both resulted in a decrease of the yield (entries 6 and 7). Moreover, various copper catalysts and other metal salts were examined. Among them, CuCl, CuBr, $CuCl_2$, $Cu(OTf)_2$, $PtCl_2$, $AgNO_3$ and $InCl_3$ were all less effective than CuI (entries 8–14). $FeCl_3$ and $LaCl_3$ failed to promote the reaction (entries 15 and 16). Interestingly, when a simple acid catalyst *p*-TsOH was employed, an undesired etherification by-product **1g**[10] was formed in high yield (entry 17).

With an optimal set of catalyst system selected, the effects of solvents and bases were examined. These data reveal that the cycloetherifications can be carried out in a broad range of organic solvents at room temperature (Table 2, entries 1–12) or even in water under reflux (entry 13). In addition, a number of bases, including inorganic and organic, were efficient for the reaction (entries 14–21) but pyridine was found to be totally inefficient. This is probably because copper strongly coordinates with pyridine, resulting in the loss of its catalytic activity (entry 22).

With the optimal reaction conditions in hand, the scope of this transformation was evaluated. As can be seen from Table 3, internal alkynes are less active than terminal ones. They required higher catalyst loading, higher temperature and longer reaction time but afforded lower yields (entries 1–3). In addition, phenol **1d** substituted at the terminal alkyne carbon with a TMS groups resulted in desilylation (entry 3). It should be noted that the presence of benzylic OH group plays a crucial role in the cyclo-

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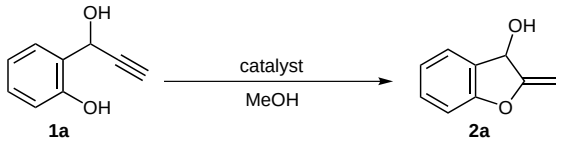
Table 1 Screening of Catalyst

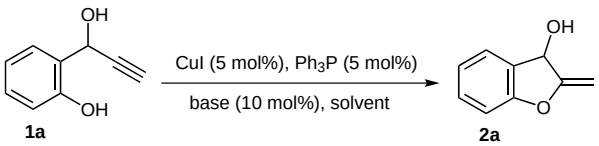


1a **2a**

Entry	Catalyst (mol%)	Condition	Product (yield, %)
1	CuI/Cs_2CO_3 (5:10)	r.t., 24 h	n.r.[a]
2	CuI/Cs_2CO_3 (5:10)	reflux, 9 h	**2a** (85)
3	CuI/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 4 h	**2a** (98)
4	Ph_3P/Cs_2CO_3 (5:10)	r.t., 24 h	n.r.[a]
5	CuI/Ph_3P (5:5)	r.t., 24 h	n.r.[a]
6	CuI/Ph_3P/Cs_2CO_3 (2:5:10)	r.t., 4 h	**2a** (89)
7	CuI/Ph_3P/Cs_2CO_3 (5:5:5)	r.t., 4 h	**2a** (79)
8	CuCl/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 4 h	**2a** (92)
9	CuBr/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 4 h	**2a** (91)
10	$CuCl_2$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 4 h	**2a** (77)
11	$Cu(OTf)_2$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 4 h	**2a** (83)
12	$PtCl_2$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 24 h	**2a** (72)
13	$AgNO_3$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 24 h	**2a** (59)
14	$InCl_3$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 24 h	**2a** (7)
15	$FeCl_3$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 24 h	n.r.[a]
16	$LaCl_3$/Ph_3P/Cs_2CO_3 (5:5:10)	r.t., 24 h	n.r.[a]
17	*p*-TsOH (5)	r.t., 7 h	**1g** (95)

[a] No reaction.

Table 2 Screenings of Solvent and Base



1a **2a**

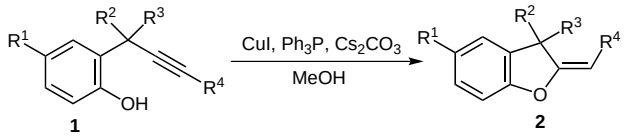
Entry	Solvent	Base	Conditions	Yield (%)
1	EtOH	Cs_2CO_3	r.t., 5 h	94
2	*i*-PrOH	Cs_2CO_3	r.t., 5 h	92
3	*t*-BuOH	Cs_2CO_3	30 °C, 6 h	89
4	CH_2Cl_2	Cs_2CO_3	r.t., 6 h	92
5	$CHCl_3$	Cs_2CO_3	r.t., 8 h	95
6	DMF	Cs_2CO_3	r.t., 24 h	56
7	MeCN	Cs_2CO_3	r.t., 24 h	72
8	benzene	Cs_2CO_3	r.t., 24 h	86
9	1,4-dioxane	Cs_2CO_3	r.t., 11 h	82
10	THF	Cs_2CO_3	r.t., 14 h	65
11	DME	Cs_2CO_3	r.t., 24 h	47
12	hexane	Cs_2CO_3	r.t., 24 h	74
13	H_2O	Cs_2CO_3	reflux, 12 h	71
14	MeOH	K_2CO_3	r.t., 4 h	91
15	MeOH	K_3PO_4	r.t., 4 h	98
16	MeOH	$LiOH·H_2O$	r.t., 4 h	94
17	MeOH	Et_3N	r.t., 12 h	74
18	MeOH	*i*-Pr_2NH	r.t., 4 h	95
19	MeOH	piperidine	r.t., 4 h	97
20	MeOH	TMG	r.t., 4 h	97
21	MeOH	DABCO	r.t., 14 h	62
22	MeOH	pyridine	r.t., 24 h	n.r.[a]

[a] No reaction.

etherifications. When the OH group is replaced by a hydrogen atom or oxidized to a carbonyl, no cycloetherification product was detected even after refluxing the reaction mixture for 24 hours (entries 4 and 5). Furthermore, when the OH group is protected by methyl, higher catalyst loading and higher temperature were required but poor yield was obtained (entry 6). With respect to the terminal alkynes, their cycloetherifications completed in 4–8 hours at ambient temperature with high yields (entries 7–14) and the electron-donating, electron-withdrawing, and halogen substitutions on the aryl ring or alkyl, aryl substitutions at the benzylic position were all tolerated. These data clearly suggest that the presence of a benzylic OH group and a terminal alkyne are both necessary for this copper(I)-catalyzed cycloetherification but the electronic effect of the substituents on the aryl rings and the steric hindrance had little impact on the efficiency of our method.

Having established the cycloetherifications of phenols **1**, we then turned our efforts to realize the one-pot process mentioned in Scheme 1. To our delight, the treatment of the reaction mixture from the cycloetherification process with 1.1 equivalents of acid at room temperature cleanly provided the desired benzofuran in excellent yield (Table 4, entries 1–4). Among these acid tested, *p*-TsOH was found to be most effective (entry 3). Encouraged by the above success, the one-pot procedure was carried out with other alcohols and moderate to good yields were obtained (entries 5–9). These data (Table 1, entry 3, Table 2, entries 1–3 and Table 4, entries 3 and 5–7) showed that steric factor did has deleterious effects on the allylic nucleophilic substitution: primary alcohols underwent the reaction more effectively in terms of lower reaction temperatures and higher yields, as compared to the secondary alcohols, which in turn reacted more efficiently than their tertiary

Table 3 Copper-Catalyzed Cycloetherifications of 2-(1-Hydroxyprop-2-ynyl)phenols[11]



1 2

Entry	Substrates	Conditions	Product (yield, %)
1[a]	**1b** ($R^1 = R^2 = H$, $R^3 = OH$, $R^4 = Ph$)	40 °C, 12 h	**2b** (68)
2[a]	**1c** ($R^1 = NO_2$, $R^2 = H$, $R^3 = OH$, $R^4 = Ph$)	40 °C, 12 h	**2c** (52)
3[a]	**1d** ($R^1 = R^2 = H$, $R^3 = OH$, $R^4 = TMS$)	40 °C, 12 h	**2a** (64)
4	**1e** ($R^1 = R^2 = R^3 = R^4 = H$)	reflux, 24 h	n.r.[b]
5	**1f** ($R^1 = H$, $R^2 = R^3 = O$, $R^4 = H$)	reflux, 24 h	–[c]
6[a]	**1g** ($R^1 = R^2 = H$, $R^3 = OMe$, $R^4 = H$)	50 °C, 12 h	**2g** (59)
7	**1h** ($R^1 = MeO$, $R^2 = H$, $R^3 = OH$, $R^4 = H$)	r.t., 4 h	**2h** (92)
8	**1i** ($R^1 = NO_2$, $R^2 = H$, $R^3 = OH$, $R^4 = H$)	r.t., 6 h	**2i** (85)
9	**1j** ($R^1 = Cl$, $R^2 = H$, $R^3 = OH$, $R^4 = H$)	r.t., 8 h	**2j** (89)
10	**1k** ($R^1 = Br$, $R^2 = H$, $R^3 = OH$, $R^4 = H$)	r.t., 8 h	**2k** (86)
11	**1l** ($R^1 = Me$, $R^2 = H$, $R^3 = OH$, $R^4 = H$)	r.t., 6 h	**2l** (92)
12	**1m** ($R^1 = H$, $R^2 = Me$, $R^3 = OH$, $R^4 = H$)	r.t., 8 h	**2m** (88)
13	**1n** ($R^1 = H$, $R^2 = Et$, $R^3 = OH$, $R^4 = H$)	r.t., 8 h	**2n** (86)
14	**1o** ($R^1 = H$, $R^2 = Ph$, $R^3 = OH$, $R^4 = H$)	r.t., 8 h	**2o** (82)

[a] CuI (10 mol%), Ph_3P (10 mol%) and Cs_2CO_3 (20 mol%) were used.
[b] No reaction.
[c] Decomposition was observed.

counterparts (entries 5–7). Finally, the generality of this one-pot procedure was examined. As expected, a series of diversely substituted benzofurans were obtained with satisfactory yields (entries 10–17). However, halogen substitutions caused an obvious decrease in the yield (entries 12 and 13), although there is no reasonable explanation for the results.

In summary, we have developed a new type of copper(I)-catalyzed cycloetherifications and an acid-catalyzed allylic nucleophilic substitution, which can be carried out in one-pot under mild conditions. This method provides an efficient, straightforward and wide-scope route to diversely substituted benzofurans in high yields. Further studies for construction of other biologically important heterocycles using this method are underway.

Acknowledgment

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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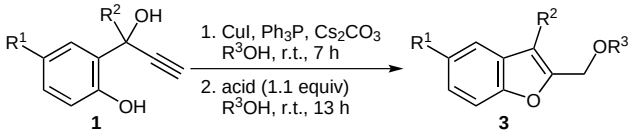
Table 4 One-Pot Synthesis of 2-Substituted Benzofurans[12]



Entry	R^1	R^2	R^3	Acid	Product (yield, %)
1	H	H	Me	CSA	**3a** (79)
2	H	H	Me	PPTS	**3a** (82)
3	H	H	Me	*p*-TsOH	**3a** (95
4	H	H	Me	Amberlyst[a]	**3a** (85)
5	H	H	Et	*p*-TsOH	**3b** (84)
6[b]	H	H	*i*-Pr	*p*-TsOH	**3c** (62)
7[c]	H	H	*t*-Bu	*p*-TsOH	**3d** (49)
8[b,d]	H	H	*c*-Hex	*p*-TsOH	**3e** (88)
9[d]	H	H	Bn	*p*-TsOH	**3f** (83)
10	OMe	H	Me	*p*-TsOH	**3g** (86)
11	NO_2	H	Me	*p*-TsOH	**3h** (83)
12	Cl	H	Me	*p*-TsOH	**3i** (47)
13	Br	H	Me	*p*-TsOH	**3j** (41)
14	Me	H	Me	*p*-TsOH	**3k** (87)
15	H	Me	Me	*p*-TsOH	**3l** (78)
16	H	Et	Me	*p*-TsOH	**3m** (80)
17	H	Ph	Me	*p*-TsOH	**3n** (76)

[a] Amberlyst (100 mg) was used.
[b] Reactions were performed at 35 °C.
[c] Reactions were performed at 45 °C.
[d] Reactions were performed in $CHCl_3$–alcohol (1:1) as solvent.

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(10) See Table 3, entry 6 for detailed structure.

(11) **General Procedure for Copper(I)-Catalyzed Cycloetherification**: CuI (0.005 mmol, 1.0 mg), Ph_3P (0.005 mol, 1.3 mg) and Cs_2CO_3 (0.01 mmol, 3.3 mg) were added to a solution of phenol **1** (0.1 mmol) in MeOH (0.5 mL). The mixture was stirred at r.t. until the reaction was complete (monitored by TLC). After that the solvent was removed and the residue was purified by flash silica gel chromatography using *n*-hexane–EtOAc (4:1) as eluent to give the desired cycloetherification products.

(12) **General Procedure for One-Pot Synthesis of 2-Substituted Benzofurans**: CuI (0.005 mmol, 1.0 mg), Ph_3P (0.005 mol, 1.3 mg) and Cs_2CO_3 (0.01 mmol, 3.3 mg) were added to a solution of phenol **1** (0.1 mmol) in alcohol (0.5 mL). The mixture was stirred at r.t. for 4–6 h. After this time, *p*-TsOH (0.11 mmol, 20.9 mg) was added and the mixture was stirred at r.t. until the starting material was consumed. After that the mixture was diluted with Et_2O and washed with H_2O. The organic phase was separated, dried over Na_2SO_4, then concentrated and purified by silica gel chromatography using *n*-hexane–EtOAc (16:1) as eluent to give the desired benzofurans.

