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Cu-catalyzed decarboxylative coupling of propiolic acids with boronic acids

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ABSTRACT

A mild procedure of Cu-catalyzed decarboxylative cross-coupling of aryl- and alkynyl-boronic acids for construction of unsymmetrical substituted alkynes has been developed. The usage of inexpensive copper chloride as catalyst, and employing stable alkynl carboxylic acids and boronic acids as the substrates under oxidative conditions for sp–sp^2 coupling, make this method very easy to operate.

The unsymmetrical substituted alkyne moiety is a ubiquitous structural motif of various bioactive natural products and synthetic pharmaceutical compounds.[1] Hence, developing efficient methods to build unsymmetrical alkynes is a meaningful event.[2] Sonogashira reaction is a powerful and straightforward methodology for construction of aryl alkynes.[3] However, there are some deficiencies in the traditional Sonogashira coupling. For example, homo-coupling reaction can be observed and electron-deficient alkynes do not work well by the Sonogashira reaction.[4] In the past decades, many modifications have been developed for the synthesis of unsymmetrical alkynes, for instance, utilizing 2-methylbut-3-yn-2-ol[5] or silane protected alkynes[6] as coupling reagents, allowing further refinement after the first coupling, thus generating the expected unsymmetrical alkynes.

Carboxylic acids are largely available, stable, and easy to handle and store. They have shown great capacity in catalytic transformations and the protodecarboxylation of carboxylic acids has long existed in organic synthesis.[7,8] Substituted propiolic acids have been employed in the coupling reaction for Csp–C bond and Csp–X bond formation.[9,10] More recently, Loh and co-workers reported a method of Pd-catalyzed decarboxylative cross-coupling of alkynyl carboxylic acids with arylboronic acids in the presence of Ag_2O (**1**, Scheme 1).[11] Our group once reported a strategy of copper(II) chloride catalyzed oxidative amidation of propiolic acids under air via decarboxylative coupling.[12] Therefore, we selected propiolic acids as the alkyne candidates for the construction of unsymmetrical alkyne. Inspired by Loh's work and combined with our previous work, we developed an inexpensive Cu-catalyzed decarboxylative coupling of propiolic acids with boronic acids (**2**, Scheme 1). The advantage of the method is that the copper catalyst is low-toxic, inexpensive, and readily available.[13,14]

Firstly, the coupling reaction between phenylpropiolic acid and (4-methoxyphenyl)boronic acid was investigated and the product **3aa** was obtained with the isolated yield of 24% when copper(II) acetate was used as the catalyst in the presence of oxidant and pyridine (Table 1, entry1). Then different ligands, bases, oxidants, catalysts, and solvents were screened. As shown in Table 1, when 2,2′-bipyridine and 1,10-phenanthroline were used as ligands, no products were obtained (Table 1, entries 2 and 3), indicating that pyridine is important for this coupling reaction. Gratifyingly, when Et_3N was employed as an additional base, the decarboxylative transformation proceeded more efficiently (Table 1, entry 7). Other bases were then screened, but the reactions exhibited lower efficiencies (Table 1, entries 4–6, 8). After screening different oxidants, it was demonstrated that BQ is the most positive oxidant for this coupling reaction (Table 1, entries 10–13). It was found that a catalytic amount of BQ could reduce the yield (Table 1, cf. entries 7 and 9). Furthermore, the control reaction under Ar gave lower yield (Table 1, cf. entries 14 and 15). These results indicate that both BQ and air are required for this decarboxylative coupling. Other Cu-catalysts such as $CuBr_2$, CuCN, and $CuCl_2$ were screened (Table 1, entries 16–18). When the loading of pyridine was decreased from 2.0 to 1.0 equiv, the product **3aa** was obtained in 65% yield (Table 1, entry 19). When some diketones were used as ligands, no desired product was detected (see SI). It is found that $CuCl_2{\cdot}2H_2O$ performed the best catalytic efficiency in dichloromethane (Table 1, entry 14).

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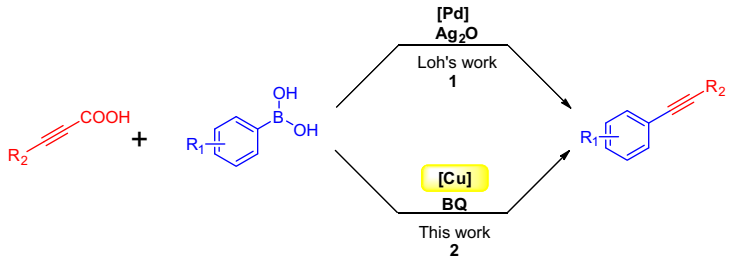
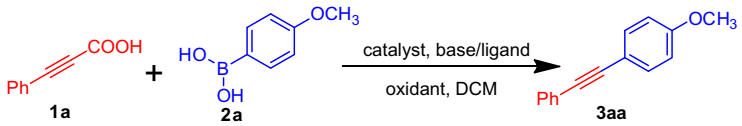


Scheme 1.

Table 1
Optimization of reaction conditions[a]



Entry	Catalyst	Oxidant	Base	Ligand	Yield[b] (%)
1	$Cu(OAc)_2$	BQ	—	Pyridine	24
2	$Cu(OAc)_2$	BQ	—	2,2′-bipyridine	0
3	$Cu(OAc)_2$	BQ	—	1,10-phenanthroline	0
4	$Cu(OAc)_2$	BQ	Na_2CO_3	Pyridine	59
5	$Cu(OAc)_2$	BQ	DABCO	Pyridine	Trace
6	$Cu(OAc)_2$	BQ	DBU	Pyridine	19
7	$Cu(OAc)_2$	BQ	Et_3N	Pyridine	70
8	$Cu(OAc)_2$	BQ	$NaHCO_3$	Pyridine	39
9[c]	$Cu(OAc)_2$	BQ	Et_3N	Pyridine	22
10	$Cu(OAc)_2$	—	Et_3N	Pyridine	Trace
11	$Cu(OAc)_2$	DDQ	Et_3N	Pyridine	0
12	$Cu(OAc)_2$	Oxone	Et_3N	Pyridine	0
13	$Cu(OAc)_2$	O_2	Et_3N	Pyridine	Trace
14	**$CuCl_2·2H_2O$**	**BQ**	**Et_3N**	**Pyridine**	**84**
15[d]	$CuCl_2·2H_2O$	BQ	Et_3N	Pyridine	32
16	$CuBr_2$	BQ	Et_3N	Pyridine	75
17	CuCN	BQ	Et_3N	Pyridine	0
18	$CuCl_2$	BQ	Et_3N	Pyridine	79
19[e]	$CuCl_2·2H_2O$	BQ	Et_3N	Pyridine	65
20	$CuCl_2·2H_2O$	BQ	Et_3N	Pyridine	12
21[f]	$CuCl_2·2H_2O$	BQ	Et_3N	Pyridine	62
22[g]	$CuCl_2·2H_2O$	BQ	Et_3N	Pyridine	Trace

[a] Unless otherwise noted, the reaction was carried out at room temperature using phenylpropiolic acid (0.25 mmol), phenylboronic acid (0.5 mmol), base (0.5 mmol), ligands (0.5 mmol), oxidants (0.25 mmol), catalysts (5 mol %), solvents (3 mL) for 12 h under air atmosphere.
[b] Isolated yield.
[c] 10 mol % BQ was used.
[d] Reaction under Ar.
[e] Pyridine (1.0 equiv) was used in this case.
[f] Benzene was used as solvent.
[g] DMF was used as the solvent.

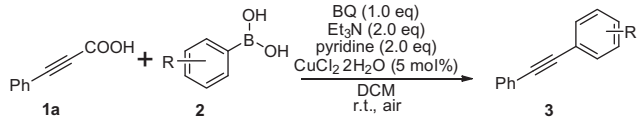
With the optimized conditions in hand, the scope of reaction substrate was investigated. Various arylboronic acids were used to examine the tolerance of this coupling reaction. The electronic properties of the substrates appear to affect the reactivity of coupling. Typical electron-donating groups on the arylboronic acids such as methoxyl, *tert*-butyl gave the desired unsymmetrical alkynes in good yields respectively (Table 2, entries 1 and 8). However, substrates with strong electron-withdrawing groups at the aryl ring of the aryboronic acids gave the products in lower yields (Table 2, entries 5 and 6). It is noteworthy that the halogen group substituted aryboronic acids also could be converted into the desired products smoothly in good yields (Table 2, entries 2, 7, and 10).

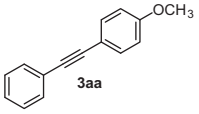
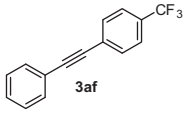
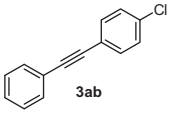
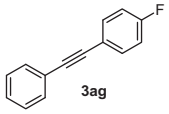
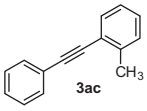
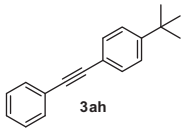
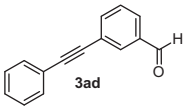
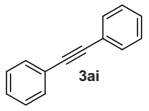
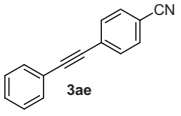
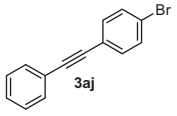
Then, the compatibility of alkynyl carboxylic acids was tested under the standard conditions. As displayed in Table 3, all the coupling reactions using different alkynyl carboxylic acids proceeded smoothly to generate the desired alkynes in moderate to good yields. Phenylpropiolic acid with *meta*-methyl group can be transformed to the corresponding product with good isolated yield (Table 3, entry 1). However, electron-deficient substrates such as 3-(4-cyanophenyl)propiolic acid performed with low efficiency (Table 3, entry 6). Hetero-aromatic ring substituted propiolic acid accomplished the coupling reaction successfully with good yield (Table 3, entry 2). Aliphatic chain substituted propiolic acids are also tolerant in this transformation but with low yields (Table 3, entries 3–5). Although the yields are low to moderate in some cases, no homocoupling products were detected.

A proposed mechanism of this decarboxylative coupling reaction is shown in Scheme 2. The copper(II) intermediate A is initially generated. Followed decarboxylation occurs to form the alkynyl copper(II) intermediate B. Subsequent transmetallation between arylboronic acids and B occurs to form intermediate C. Finally, reductive elimination ensures to form the alkyne products.

In summary, a practical Cu-catalyzed decarboxylative cross-coupling of propiolic acids with boronic acids for the construction

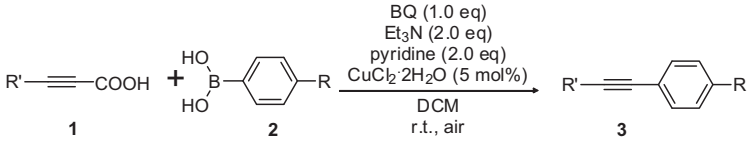
Table 2
Decarboxylative coupling of phenylpropiolic acid with various arylboronic acids[a]

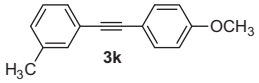
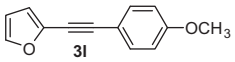
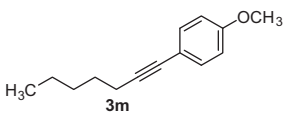
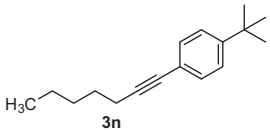


Entry	Product	Yield[b] (%)	Entry	Product	Yield[b] (%)
1	 3aa	84	6	 3af	27
2	 3ab	80	7	 3ag	78
3	 3ac	77	8	 3ah	85
4	 3ad	40	9	 3ai	76
5	 3ae	32	10	 3aj	53

[a] Reaction conditions: **1** (0.25 mmol), **2** (0.5 mmol), $CuCl_2{\cdot}2H_2O$ (0.0125 mmol), BQ (0.25 mmol), Et_3N (0.5 mmol), pyridine (0.5 mmol), solvent (3 mL), rt, 12 h. For the detail, see experimental section.
[b] Isolated yields.

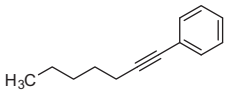
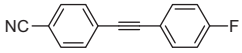
Table 3
Decarboxylative coupling of arylboronic acids with alkynyl carboxylic acids[a]



Entry	Product	Yield[b] (%)
1	 3k	75
2	 3l	71
3	 3m	37
4	 3n	38

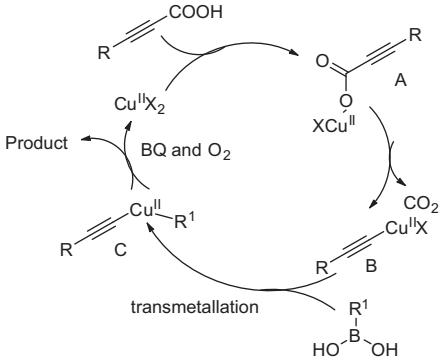
(*continued on next page*)

Table 3 (*continued*)

Entry	Product	Yield[b] (%)
5	 **3o**	33
6	 **3p**	26

[a] Reaction conditions: **4** (0.25 mmol), **2** (0.5 mmol), $CuCl_2{\cdot}2H_2O$ (0.0125 mmol), BQ (0.25 mmol), Et_3N (0.5 mmol), pyridine (0.5 mmol), solvent (3 mL), rt, 12 h. For the detail, see experimental section.

[b] The yield was isolated.



Scheme 2. Proposed mechanism for this transformation.

of unsymmetrical substituted alkynes has been developed. The usage of inexpensive copper chloride as catalyst, and employing stable alkynl carboxylic acids and boronic acids as the substrates under oxidative conditions for sp–sp^2 coupling, make this method very easy to operate. The application of this transformation in organic synthesis is ongoing in our laboratory.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.01.118.

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