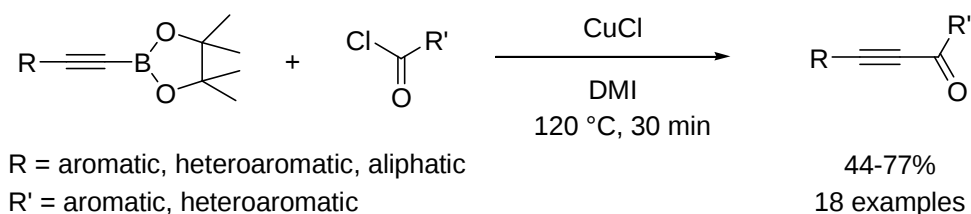


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Palladium- and base-free synthesis of conjugated ynones by cross-coupling reactions of alkynylboronates with acid chlorides mediated by CuCl

Yasushi Nishihara,* Daisuke Saito, Eiji Inoue, Yoshiaki Okada, Mikihiro Miyazaki, Yoshiaki Inoue, and Kentaro Takagi

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Various conjugated ynone derivatives are synthesized by copper-mediated cross-coupling reactions of acid chlorides with alkynylboronates in moderate to high yields.

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Palladium- and base-free synthesis of conjugated ynones by cross-coupling reactions of alkynylboronates with acid chlorides mediated by CuCl

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Abstract— Alkynylboronates can be employed as a practical and versatile precursor for a variety of π -conjugated organic compounds. In the presence of Cu(I) salt, cross-coupling reactions of acid chlorides with alkynylboronates giving rise to the corresponding conjugated ynones takes place readily in aprotic polar solvents such as DMI under neutral conditions.

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Conjugated ynones¹ have been prominently employed as equivalents of valuable intermediates in organic synthesis as well as various functional groups in natural product,² important biologically active heterocycles,³ and acetylenic scaffoldings.⁴ Among most frequently employed methods to access ynones, the palladium and/or copper-catalyzed processes of acid chlorides and terminal alkynes under basic conditions has been widely employed due to the versatile nature of this protocol, increased functional group tolerance and improved yields.^{3f,5,6} But the reactions were limited by undesired side reactions between the acid chlorides and the added tertiary amines, reducing the yields.

Alternatively, the cross-couplings of acid chlorides with the corresponding organometallic reagents such as organosilver,⁷ -silicon,⁸ -cadmium,⁹ -copper,¹⁰ -tin¹¹ -lithium,¹² -magnesium,¹³ -zinc,¹⁴ -aluminum,¹⁵ -thallium,¹⁶ -gallium¹⁷ -antimony,¹⁸ and -indium,¹⁹ have attracted much attention. However, there are limitations with each of them.²⁰

On the other hand, alkynylboronates²¹ have been known to useful synthetic intermediates. Utility of these reagents in transition metal-catalyzed reactions have become the subject of interest due to their enhanced reactivity, and successful transformations involve cycloaddition reactions,²² the synthesis of tetrasubstituted olefins,²³ Suzuki–Miyaura cross-coupling,²⁴ and addition to alkynes.²⁵ On the basis of promising potentialities of alkynylboronates, our

efforts have been made in developing new synthetic methodologies.²⁶ Herein we report the synthesis of conjugated ynones from CuCl-mediated cross-coupling reactions of acid chlorides with alkynylboronates.^{27,28}

Initially, we examined the reaction between phenylethynylboronate **1a** with benzoyl chloride (**2a**) as standard substrates to optimize the reaction conditions. The results employing various copper compounds are listed in Table 1. The cross-coupling reaction was screened with a stoichiometric amount of a copper compound (or salt) in DMI, which is the best solvent for the homocoupling of alkynylsilanes²⁹ and alkynylboronates.^{26a} Counter ions of a halogenated copper salt dramatically affected the yield of 1,3-diphenyl-2-propyn-1-one (**3a**). CuCl was suitable for the present cross-coupling reaction and **3a** was formed in 64% yield (Entry 1). However, 100 mol% of CuCl resulted in the lower yield (31%) of the cross-coupled product. Although CuBr can effect the cross-coupling reaction to give **3a** in 50% yield, CuI was found to be inactive at all (Entries 2 vs 3). Whereas copper (I) thiophene-2-carboxylate (CuTC)³⁰ furnished **3a** in 38% yield (Entry 4), other copper(I) compounds such as Cu₂O, CuCN, and CuOAc were not so effective for the formation of **3a** (Entries 5–7). Although we found that Cu(OAc)₂ was the best additive for the homocoupling reaction of alkynylboronates,^{26a} Cu(OAc)₂ as well as other copper(II) compounds were found to be ineffective for the present reaction (Entries 8–10).

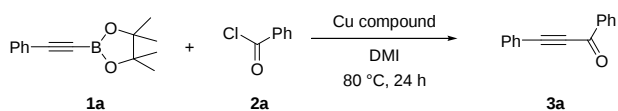


Table 1. Copper-mediated cross-coupling reaction of phenylethynylboronate **1a** with benzoyl chloride (**2a**)^a

Entry	Copper compound	Yield % ^b
1	CuCl	64
2	CuBr	50
3	CuI	0
4	CuTC	38
5	Cu ₂ O	18
6	CuCN	<1
7	CuOAc	0
8	Cu(OTf) ₂	0
9	Cu(OAc) ₂	<1
10	CuCl ₂	0

^a reaction was performed in DMI (3 mL) using **1a** (0.2 mmol) and **2a** (0.22 mmol) at 80 °C for 24 h in the presence of a copper compound (0.4 mmol).

^b Yields were determined by GC.

We next surveyed solvents such as DMSO, DMF, Bu₂O, DMPU, TMU, and toluene using a stoichiometric amount of CuCl. Yields of the cross-coupled product **3a** greatly depend on the nature of the solvent. Among the solvents surveyed in comparison with CuCl-mediated cross-coupling reaction, DMI proved to be by far the most effective and afforded **3a**. In a sharp contrast, no trace of the desired product **3a** was obtained in other organic solvents. It is noteworthy that the present reaction system does not require the palladium catalyst or a base which is normally required for activation of organoboron compounds.³¹

As a result of various combinations of the reaction time and temperature examined, we found that the reaction completed after 30 min at 120 °C in DMI. With the optimized conditions for the facile cross-coupling of **1a** with **2a** in hand, we further explored the tolerance of this process toward a range of alkynylboronates **1** and the results are summarized in Table 2.³² The reactions of acid chlorides bearing electron-withdrawing (Entries 2-4) and electron-donating (Entry 5) groups with **1a** proceeded in moderate to good yields. Since the present cross-coupling reaction proceeds under neutral condition, acid chloride **2f** bearing the ester functionality is compatible to give the corresponding product **3f** in 59% (Entry 6). Acid chlorides having heteroaromatics

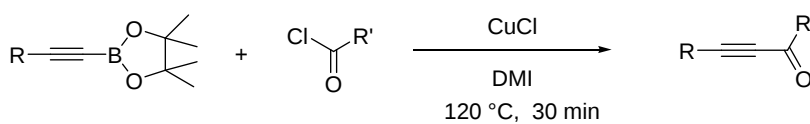
such as 2-furyl and 2-thienyl groups afforded the corresponding cross-coupling products **3g** and **3h** in 58% and 63% isolated yields, respectively (Entries 7 and 8). Acid chloride containing chloride in the ortho position **2i** underwent the reactions to give **3i** in good yield (Entry 9).

On the other hand, the reactions of acid chloride **2a-2c** with alkynylboronates **1b-1e** bearing various functional groups similarly underwent the cross-coupling reactions (Entries 10-17). To this end we have prepared a series of alkynylboronates **1** from isopropoxy(pinacol)borate with alkynyl lithium.³³ These were prepared in situ from the corresponding terminal alkynes with *n*-BuLi at -78 °C, followed by the subsequent treatment with HCl in diethyl ether. For a vast number of derivatives of alkynylboronate, the presence of various substituents, e.g., 4-methoxy (Entries 10-12) and 4-chloro (Entry 13) on the aromatic ring did not diminish the efficiency. Cross-coupling reaction using **1d**, which possesses a sulfur atom gave the corresponding conjugate ynone in 48% yield (Entry 14). Similarly to the case of aliphatic alkynylboronate **1e**, the cross-coupling readily proceeded to provide the corresponding ynones **3o-3q** in good yields (Entries 15-17). Noteworthy is that in all cases no formation of 1,3-diynes was observed in the reaction mixture, derived from homocoupling reaction of alkynylboronates. However, aliphatic and alkenyl acid chlorides completely retarded reaction with **1a** and gave no desired product.

By TLC (hexane: EtOAc = 19:1), the obtained conjugated ynone **3a** (*R*_f = 0.33) were slower moving than the starting acid chloride **2a** (*R*_f = 0.58). All of the cross-coupled products **3** were well characterized by spectroscopic measurements (IR, ¹H and ¹³C{¹H} NMR, and GC-MS) as well as elemental analyses. In IR spectra, conjugated ynones exhibited characteristic strong absorption at 2100-2210 cm⁻¹ for the carbon-carbon triple bond and 1600-1650 cm⁻¹ for the carbonyl group.

Although it has been known that a catalytic amount of CuCl promotes the reaction of alkynylsilanes with acid chlorides,^{8d} a stoichiometric amount of CuCl is required in this reaction. In order to scavenge the contaminating boron-containing species, we conducted the cross-coupling reaction in the presence of Lewis bases such as furan, NEt₃, and THF. However, we found that our attempt to obtain the corresponding conjugated ynones was unsuccessful.

Table 2. Cross-coupling reactions of alkynylboronates **1** with acid chlorides **2**^a

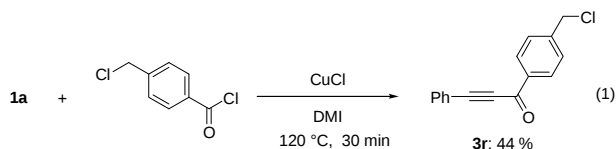


1 + **2** $\xrightarrow[120\text{ }^{\circ}\text{C, 30 min}]{\text{CuCl, DMI}}$ **3**

Entry	R	R'	Products	Yield %
1	C ₆ H ₅ - (1a)	C ₆ H ₅ - (2a)	3a	67
2		4-Cl-C ₆ H ₄ - (2b)	3b	73
3		4-CF ₃ -C ₆ H ₄ - (2c)	3c	70
4		4-NO ₂ -C ₆ H ₄ - (2d)	3d	52
5		4-EtO-C ₆ H ₄ - (2e)	3e	44
6		4-MeOCO-C ₆ H ₄ - (2f)	3f	59
7		2-Furyl (2g)	3g	58
8		2-Thienyl (2h)	3h	63
9		2-Cl-C ₆ H ₄ (2i)	3i	77
10	4-MeO-C ₆ H ₄ - (1b)	2a	3j	73
11		2b	3k	67
12		2c	3l	75
13	4-Cl-C ₆ H ₄ - (1c)	2a	3m	60
14	2-Thienyl (1d)	2a	3n	48
15	n-C ₆ H ₁₃ - (1e)	2a	3o	71
16		2b	3p	75
17		2c	3q	72

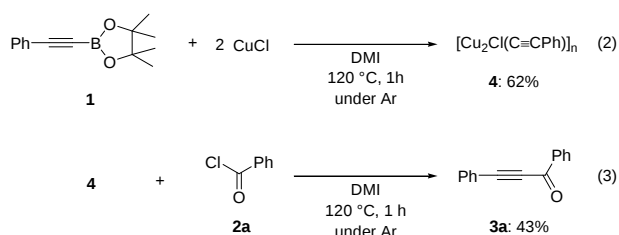
^a Conditions: **1** (1.0 mmol); **2** (1.1 mmol); CuCl (2.0 mmol); DMI (2.5 mL).^b Isolated yields based on **1**.

As one example of the advantage of the Pd-free reaction conditions, the present reaction of 4-chloromethylbenzoyl chloride with **1a** was carried out. In the presence of CuCl under the optimal conditions, the chemoselective cross-coupling occurred to generate the corresponding conjugated ynone **3r** as a sole product in 44% isolated yield (eq 1). The presence of the Pd catalyst resulted in no formation of the desired product **3r** presumably due to the dechlorination at the benzyl position.



In these cross-coupling reactions it is thought that an alkynyl group of alkynylboronates **1** transmetalates from boron to copper without a nucleophilic activator such as a base. To gain an insight into the intermediate alkynylcopper species, the reaction of **1a** with CuCl in 1:2 molar ratio in DMI was carried out. The reaction proceeded at 120 °C for 1 h under an Ar atmosphere to give [Cu₂Cl(C≡CPh)]_n (**4**)³⁴ in 62% yields (eq 2). Alkynylcopper **4** was isolated as a bright yellow solid and elemental analyses (C, H, and Cl) of the product agree with the calculated values from our previously reported alkynylcopper **4** derived from alkynylsilane

with CuCl in DMF.³⁴ Once isolated **4** could react with **2a** cleanly to form the corresponding ynone **3a** in 43% yield (eq 3).



In summary, we have successfully demonstrated copper(I)-mediated cross-coupling reaction of acid chlorides with alkynylboronates leading to various conjugated ynones in aprotic polar solvents such as DMI under Pd-free and neutral reaction conditions. Because the presented method is carried out using the alkynes protected with the boron moiety in the absence of the palladium catalyst, side reactions leading to the conjugated diynes by the Pd-catalyzed homocoupling reactions of terminal alkynes, can be avoided. Smooth transmetalation by CuCl giving rise to the alkynyl copper species is attributed to a strong affinity of a boron atom to chloride rather than bromide or iodide of a counter ion of Cu(I). This reaction is synthetically useful in the sense of being straightforward

carbon-carbon bond formation using a stable, nontoxic, and functional group tolerant alkynylboron compounds.

Further studies on application of the present system to other base-free carbon-carbon bond forming reactions of organoboronates towards new organic molecules bearing a carbon-carbon triple bond are currently ongoing and will be published in due course.

Acknowledgments

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32. Representative procedure: To the 20 mL of a Schlenk tube was successively added CuCl (198 mg, 2 mmol), **1a** (228 mg, 1 mmol), DMI (2.5 mL), and **2a** (128 μ L, 1.1 mmol). After being stirred for 30 min at 120 °C under Ar the reaction mixture was quenched with 1 M hydrochloric acid (2 mL) and extracted with diethyl ether (10 mL x 2). The combined ethereal layer was washed with brine, and dried over MgSO₄. Filtration and concentration afforded pale yellow solid, which was purified by silica gel column chromatography to give 138 mg (0.67 mmol, 67% yield) of **3a** as a white solid.
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