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Synthesis of Benzyl-, Allyl-, and Allenyl-boronates via Copper-Catalyzed Borylation of Alcohols

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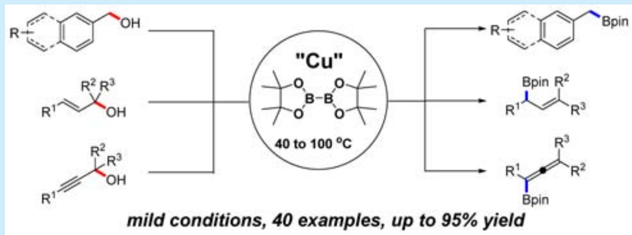
Supporting Information

ABSTRACT: Alcohols are among the most abundant and readily available organic feedstocks in industrial processes. The direct catalytic functionalization of sp^3 C−O bonds of alcohols remains the main challenge in this field. Here, we report a copper-catalyzed synthesis of benzyl-, allyl-, and allenyl-boronates from benzylic, allylic, and propargylic alcohols, respectively. This protocol exhibits a broad reaction scope (40 examples) and high efficiency (up to 95% yield) under mild conditions, including for the preparation of secondary allylic boronates. Preliminarily mechanistic studies suggest that nucleophilic substitution is involved in this reaction.

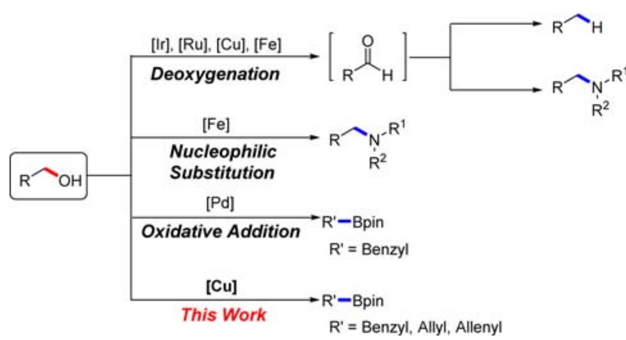


Concerns about environmental and economic issues have promoted synthetic chemistry toward the development of efficient methods for forming desired products from readily available and environmentally benign feedstocks. From this point of view, alcohols constitute a highly attractive class of starting material, as they are inexpensive and often easily derived from natural sources.[1] The main challenge lies in the activation of sp^3 C−O bonds of alcohols by metal catalysts, as the OH group is not readily replaced by other nucleophiles.[2a] In recent years, metal-catalyzed deoxygenation and functionalization (alkylation[2a−d] and amination[2e]) of alcohols have been successfully developed. Saito and co-workers reported an iron-catalyzed amination of alcohols via nucleophilic substitution.[3]

Organoboron compounds have found widespread application in organic synthesis.[4] For example, benzylic trifluoroborates can release benzyl radicals through a single-electron transfer pathway,[5] and both allyl-[4] and allenyl-[4,6] boronates are useful synthetic intermediates in organic synthesis. However, the preparation of benzyl-, allyl-, and allenyl-boronates still remains a challenge,[4] due to the poor substrate scope of the classic methodology using Grignard or lithium reagents.[7] In the past 15 years, metal-catalyzed direct borylation[8] of benzylic[9] and allylic[10] C−X (X = H, halogen) bonds has been developed. Marder and others have recently focused on the development of copper-[11a−e] or zinc-catalyzed[11f−i] direct borylation of organic halides to synthesize various organoboron compounds including benzyl- and allyl-boronates.[11b] Alternatively, the borylation of sp^3 C−O bonds, which is more desirable, has emerged as an efficient way to construct sp^3 C−B bonds. Palladium catalysts have been found capable of borylation of both benzylic[12a] and allylic[12b−j] sp^3 C−O bonds. Recently, a few examples have established that nickel catalysts have the same potential for the borylation of sp^3 C−O bonds.[13] Ito and Sawamura developed the copper-catalyzed synthesis of allyl- and allenyl-boronates from organic carbonates.[14] Szabó and co-workers reported bimetallic (Pd and Cu) catalysis to prepare allenylboronates, in which CuI was employed as the cocatalyst.[15] Nevertheless, the borylations of benzyl and allyl alcohols require different Pd catalysts and different conditions.[12] Pd-catalyzed borylation of acyclic allylic alcohols gives preferentially linear products.[12b−j] The development of a general and straightforward methodology for direct borylation of alcohols to obtain branched acyclic products is highly desirable. We present herein the first copper-catalyzed direct borylation of alcohols to synthesize allyl-, benzyl-, and allenyl-boronates under mild conditions (Scheme 1).

Optimized conditions were found by employing **1a** as the model substrate, as it is less volatile than benzyl alcohols, 5.0

Scheme 1. Transition-metal-catalyzed functionalization of sp^3 C−O bonds of alcohols



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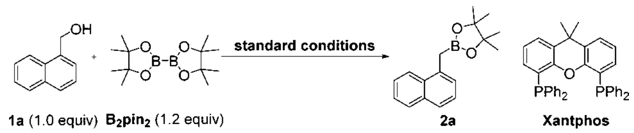
mol % $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$, and 6.5 mol % Xantphos, using 1.0 equiv of $Ti(O^iPr)_4$, and the desired product **2a** was obtained in a 94% yield (Table 1, entry 1). When we used the

Table 1. Condition Screening for Benzylic Alcohols[a]



entry	variation from the standard conditions	yield (%)
1	no change	94 (87[c])
2	$[Cu(CH_3CN)_4]^+[BF_4]^-$ instead of $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$	81
3	without catalyst or ligand or $Ti(O^iPr)_4$	N.D.[d]
4	PCy_3 instead of Xantphos	52
5	$AlCl_3$ instead of $Ti(O^iPr)_4$	N.D.[d]

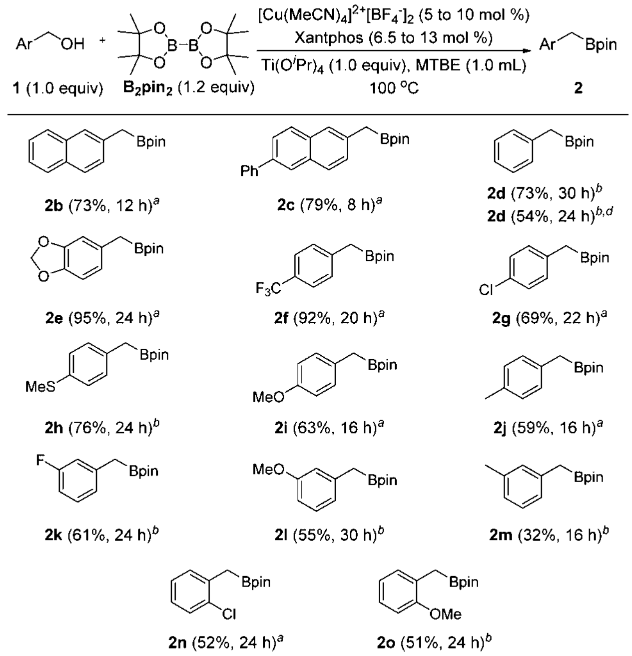
[a]Standard conditions: **1a** (0.20 mmol), B_2pin_2 (0.24 mmol), $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (5.0 mol %), Xantphos (6.5 mol %), $Ti(O^iPr)_4$ (0.20 mmol), MTBE (1.0 mL), 100 °C, 12 h. [b]Yields were determined by GC-MS analysis vs a calibrated internal standard and are averages of two experiments. [c]Isolated yield. [d]N.D. = not detected.

analogous Cu^I source, $[Cu(CH_3CN)_4]^+[BF_4]^-$, **2a** was also obtained in an 81% yield (Table 1, entry 2). Control experiments suggest that the benzylic sp^3 C–O activation and borylation are catalyzed by $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$, in combination with Xantphos, and that the additive, $Ti(O^iPr)_4$, is also crucial for the reaction, as it enhances the leaving group ability of the OH moiety[12a] (Table 1, entry 3). When Xantphos was replaced by PCy_3, **2a** was formed in a lower yield of 52% (Table 1, entry 4). No desired product **2a** was formed with $AlCl_3$ as the additive (Table 1, entry 5; for additional screening experiments, see Supporting Information (SI)).

With the optimized conditions in hand, we next studied the substrate scope for the borylation reaction of benzylic alcohols (Scheme 2). Thus, naphthalen-2-ylmethanol (**1b**) and its derivative **1c** gave the corresponding products **2b** and **2c** in yields of 73% and 79%, respectively. Benzyl alcohol (**1d**) gave **2d** in a 73% yield with 10 mol % catalyst after 30 h. When we employed benzyl acetate (**1d′**) as the starting material, **2d** was also obtained in a 56% yield. The compound 3,4-(methylenedioxy)benzyl alcohol (**1e**) worked efficiently, giving **2e** in an excellent yield of 95%. Compound **2f** was isolated in a 92% yield, when we employed 4-(trifluoromethyl)benzyl alcohol (**1f**) as starting material. With (4-chlorophenyl)methanol (**1g**) as a substrate, the desired product **2g** was isolated in a 69% yield. When 4-methylthiobenzyl alcohol (**1h**), 4-methoxy benzyl alcohol (**1i**), and 4-methyl benzyl alcohol (**1j**) were employed in this borylation reaction, the isolated yields of **2h**, **2i**, and **2j** were 76%, 63%, and 59%, respectively. We also isolated the *meta* substituted benzyl boronates **2k–m** in modest yields of 32%–61%. With *ortho* substituted benzylic alcohols **1n** and **1o**, **2n** and **2o** were isolated in yields of 52% and 51%, respectively. Due to the fact that benzyl boronates are unstable on silica gel, and they are volatile compounds as well, flash chromatography and rotary evaporation of solvents contribute to yield losses to varying extents.[12a]

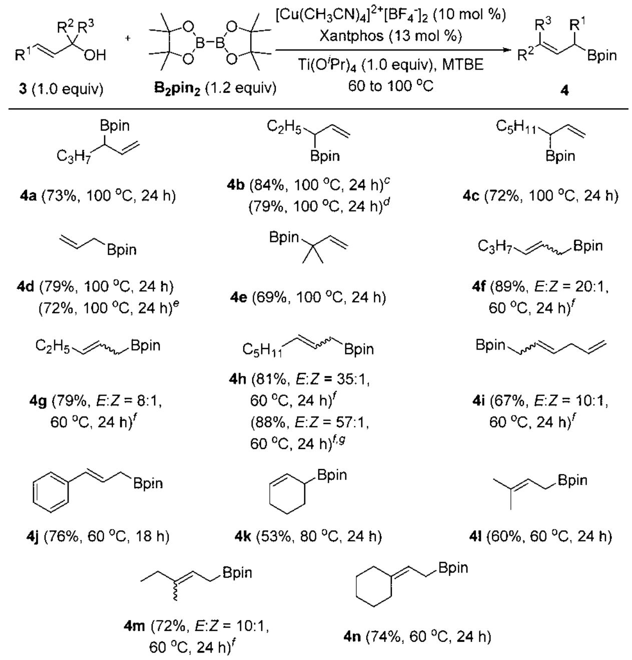
With primary allylic alcohols, such as **3a–c**, (Scheme 3) secondary allyl boronates **4a–c** were obtained as the sole products in yields of 72% to 84%. This is a unique feature of the current Cu-catalyzed method, as Pd-catalyzed borylation of

Scheme 2. Synthesis of Benzyl Boronates[a,b,c]



[a]Condition A: **1** (0.20 mmol), B_2pin_2 (0.24 mmol), $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (5 mol %), Xantphos (6.5 mol %), $Ti(O^iPr)_4$ (0.20 inmol), MTBE (1.0 mL). [b]Condition B: **1** (0.20 mmol), B_2pin_2 (0.24 mmol), $[Cu(MeCN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (0.20 mmol), MTBE (1.0 mL). [c]Isolated yields. [d]Benzyl acetate was used as the substrate.

Scheme 3. Synthesis of Allyl Boronates[a,b]



[a]Standard conditions: **3** (0.20 mmol), B_2pin_2 (0.24 mmol), $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (0.20 mmol), MTBE (1.0 mL), 60 to 100 °C. [b]Isolated yield. [c](*E*)-Pent-2-en-l-ol was used as the substrate. [d](*Z*)-Pent-2-en-l-ol was used as the substrate. [e]Allyl acetate was used as the substrate. [f]*E*/*Z* isomer ratios were determined by ^1H NMR spectroscopy of the crude product. [g]Oct-l-en-3-yl acetate was used as the substrate.

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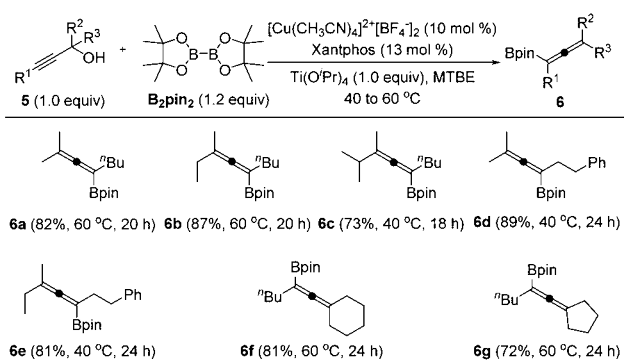
allylic alcohols **3a−c** gives the corresponding linear allylboronate isomer.[12c−f] The reason is that the Pd-catalyzed reaction proceeds via an η^3-allyl palladium complex,[12h] while the present Cu-catalyzed reaction apparently follows another mechanism (see below). The double bond geometry of the starting material did not affect this reaction. Compound **4b** was obtained in 79% yield, when we replaced (*E*)-pent-2-en-1-ol (**3b**) with its isomer (*Z*)-pent-2-en-1-ol (**3b′**) as the substrate. Both allylic alcohol (**3d**) and acetate (**3d′**) were suitable substrates for this reaction, giving allyl boronate **4d** in yields of 79% and 72%, respectively. With 3-methylbut-2-en-1-ol (**3e**), the tertiary allylic boronate **4e** was obtained in 69% yield. Formation of **4a−c** and **4e** from **3a−c** and **3e** indicates an S_N2' mechanism for the borylation reaction. Similar regioselectivity was reported by Ito and Sawamura for the Cu-catalyzed borylation of allylic carbonates.[15] This suggests that our process could potentially be extended to the catalytic asymmetric borylation of allylic alcohols. Secondary allylic alcohols, such as **3f** to **3j**, can be borylated at 60 °C, giving the corresponding primary boronates **4f** to **4j** in yields of 67% to 89%. Oct-1-en-3-yl acetate (**3h′**) was also a suitable substrate for the borylation reaction giving **4h** in 88% yield. With cyclohex-2-en-1-ol (**3k**) as the substrate, **4k** was obtained in a yield of 53%. Next, we tested tertiary allylic alcohols **3l**, **3m**, and **3n** for this reaction at 60 °C, and the linear boronates **4l**, **4m**, and **4n** were obtained in moderate yields of 60%, 72%, and 74%, respectively. The above results also suggested that a nucleophilic substitution pathway is probably involved in this reaction.

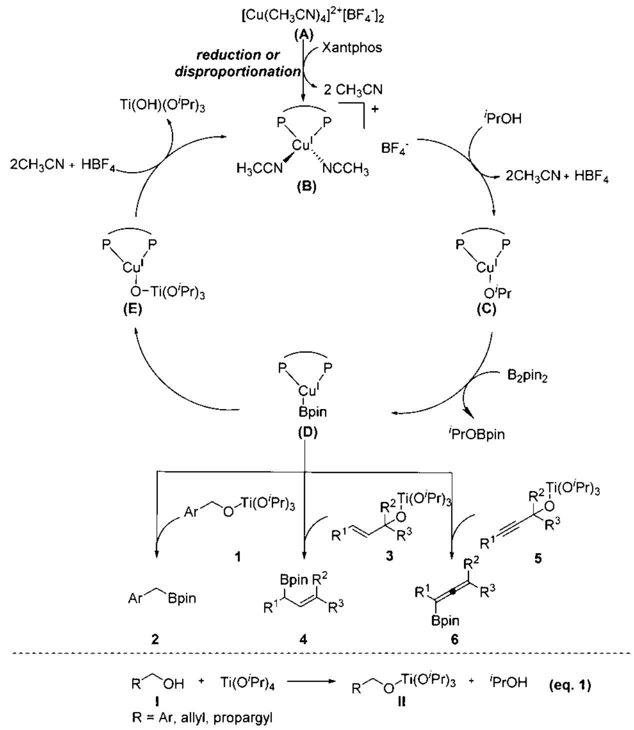
Few examples have been reported for the synthesis of allenyl boronates,[14c,15,16] which are useful reagents for the preparation of stereo- and regio-defined allenes via C−C bond formation.[4,6] The Cu-catalyzed borylation reaction can be also applied to the synthesis of allenylboronates from propargylic alcohols (Scheme 4). This is again a unique feature of the present study. Palladium catalysis cannot be used for the synthesis of allenylboronates from propargylic alcohols.[15] Thus, at 60 °C, **5a** and **5b** gave the allenyl boronates **6a** and **6b** in yields of 82% and 87%, respectively, and at 40 °C, the desired products **6c−e** were also obtained in yields of 73%−89%. The cyclohexyl (**5f**) and cyclopentyl (**5g**) derivatives gave the corresponding products **6f** and **6g** in yields of 81% and 72%, respectively. The observed regioselectivity with propargyl alcohols also suggests that the reaction proceeds via an S_N2'-type pathway (Scheme 5).[17]

Scheme 4. Synthesis of Allenyl Boronates[a,b]



[a]Standard conditions: **5** (0.20 mmol), B_2pin_2 (0.24 mmol), $[Cu(CH_3CN)_4]^{2+}[BF_4^-]_2$ (10 mol %), Xantphos (13 mol %), $Ti(O^iPr)_4$ (0.20 mmol), MTBE (1.0 mL), 40 to 60 °C. [b]Isolated yield.

Scheme 5. Plausible Mechanism for the Catalytic Borylation



We hypothesize that the active catalyst, for example, is a Cu^I species.[18] The active Cu^I species **B** could be generated either via reduction by a boryl anion nucleophile[19] or by dispropotionation of Cu^{II} (Table S3, SI).[20] Alcohols (**I**) can be activated by $Ti(O^iPr)_4$ to generate **1**, **3**, **5** (**II**), and ^{i}PrOH (eq 1). Next, Cu species (**B**) could react with ^{i}PrOH to give **C** followed by transmetalation with B_2pin_2 to generate the Cu^I−Bpin species (**D**).[21] Nucleophilic substitution involving **II** (**1**, **3**, or **5**) and Cu^I−Bpin (**D**) would form the borylation products (**2**, **4**, or **6**) and intermediate **E**. Finally, **E** could react with HBF_4 and CH_3CN to regenerate **B**.

In summary, we have developed the first example of a Cu-catalyzed direct borylation of alcohols, which offers an efficient methodology to synthesize a broad range of benzyl-, allyl-, and allenyl-boronates under mild conditions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00256.

Experimental procedures and compound characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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