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Practical procedure for copper(I)-catalyzed allylic boryl substitution with stoichiometric alkoxide base

Hajime Ito[a,*], Takanori Miya[b], Masaya Sawamura[b]

[a] Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan
[b] Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan

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ABSTRACT

We have developed a useful procedure for borylation using catalytic CuCl/Xantphos and stoichiometric K(O-*t*-Bu): the highly versatile method is suitable for the synthesis of allylboronates including those with terminal and internal allylic systems, cyclic structures, and functional groups. Optically active allylboronates were synthesized from prochiral substrates with a chiral diphosphine ligand using this procedure. The reaction rate is generally higher than the original Cu(O-*t*-Bu)/ligand catalyst system, which we previously reported.

1. Introduction

Allylboronates are very useful organoboron reagents that undergo stereoselective C–C bond formation in an aldehyde addition with high selectivity.[1] Simple allylboronates, such as (2-propenyl) boronate [allyl–B(OR)$_2$] or 2-(methyl-2-propenyl)boronate [crotyl–B(OR)$_2$], are easily prepared from the allyl or crotyllithium reagent and the corresponding Grignard reagents; however, synthesis of allylboronates that have more complicated structures, such as α-substituted chiral C–B bonds, asymmetrically substituted allyl systems (RCH=CHCH$_2$R′, R≠R′) and functional groups sensitive to organometallic nucleophiles is challenging. There are many excellent approaches for the synthesis of complicated allylboronates; however, the methods usually require chiral auxiliary on the boron atom,[2] multistep reaction procedures, and the use of lithium or Grignard reagents, which still causes low functional group compatibility.

Since copper(I)-catalyzed borylation was first reported by two independent groups (Ito and Hosomi; Ishiyama and Miyaura),[3] many useful reactions for organoboron synthesis with the relevant copper(I)/diboron catalyst systems have been repotrted.[4] γ-Selective boryl substitution of allylic carbonates was reported by us in 2005 as a useful method for the synthesis of various allylic boronates.[5,6,7c] The reaction, free from a lithium or Grignard nucleophile, includes formal nucleophilic substitution of allylic carbonates by the borylcopper(I) intermediate, which is generated from a σ-bond metathesis reaction between copper(I) alkoxide and a diboron compound. By using this catalysis, allylic boronates with internal allylic systems can be synthesized from the corresponding allylic carbonates through an *anti*-S$_N$2′ reaction with high stereoselectivity. The reaction has broad substrate scope and good functional group tolerance; when optically active allylic carbonates are used, the corresponding optically active α-substituted allylboronates are produced with high selectivity. By using the catalyst with a chiral phosphine ligand, the enantioselective borylation of prochiral allylic carbonates can be conducted.[5b,7c]

One significant drawback of this procedure is that sublimed Cu(O-*t*-Bu) should be used as the catalyst precursor to obtain high reactivity. Cu(O-*t*-Bu) is very air sensitive and a cumbersome glovebox treatment is required.[8] Since our original paper was published, we have been aware of the necessity to improve the usability of this reaction. For copper(I)-catalyzed borylation of α,β-unsaturated carbonyl compounds, many researchers reported excellent procedures, which can be carried out without the use of a glove-box. Yun and co-workers carefully examined the mixing ratio of CuCl and Na(O-*t*-Bu) in their seminal paper for asymmetric borylation of α,β-unsaturated esters and nitriles; a slight excess of Na(O-*t*-Bu) (4.5 mol %) against CuCl (typically, 3 mol %) is required for obtaining good reactivity and reproducibility.[4b] Many other loading conditions for CuX (0.01–15 mol %) and alkoxide bases (0.01–80 mol %) in the generation of borylcopper intermediates have been reported[4,6].

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* Corresponding author. Tel./fax: +81 11 706 6561; e-mail address: hajito@eng.hokudai.ac.jp (H. Ito).

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However, we experienced that the simple application of such conditions [for example, CuCl (5 mol %), Na(O-*t*-Bu) (30 mol %), ligand (5 mol %)] to our borylation reaction for allylic carbonates failed and gave only low product yields. Recently we have reported a borylation-cyclization reaction of γ-aryl substituted allylic phosphonates for stereoselective synthesis of cyclobutyl boronates and optically active aryl-substituted cyclopropyl boronates, respectively. Excess use of a K(O-*t*-Bu) solution relative to the copper(I) salt is crucial in these reactions.

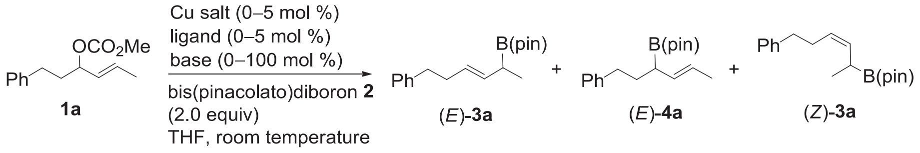
These findings prompted us to re-examine the reaction conditions in terms of a large amount of K(O-*t*-Bu). In this paper, we report a new procedure that has high usability as well as higher activity when compared to the original Cu(O-*t*-Bu) based reaction. The applicability of the new CuCl/excess K(O-*t*-Bu)/ligand conditions was validated by using the substrates we previously reported in the Cu(O-*t*-Bu)/ligand catalysis. The procedure showed comparable reactivity, regio- and stereoselectivity. In addition, all reagents used in this glove-box free procedure are commercially available.

2. Results and discussion

We examined the combination catalyst of CuCl/K(O-*t*-Bu) using various mixing ratios with the same substrate concentration (0.5 M in THF) (Table 1). The reaction with 5 mol % of Cu(O-*t*-Bu)/Xantphos catalyst, which is the most reactive combination in our previous study,[5a] was carried out with allylic carbonate **1a** and bis(pinacolato) diboron **2**. The reaction proceeded well and gave the corresponding product (*E*)-**3a** in a high yield with high regio- and *E*/*Z* selectivities [**3a**/**4a**=>99:<1, *E*/*Z* (for **3a**)=99:1]. However, the reaction required 24 h to complete under these conditions (entry 1).[9] The reaction with 5 mol % of CuCl/Xantphos did not proceed (entry 2). Combination of catalytic amounts of CuX (X=Cl, Br, I) and K(O-*t*-Bu) was commonly used as a substitution for Cu(O-*t*-Bu).[4,6,7] We thus tried to use 10 mol % of K(O-*t*-Bu) with 5 mol % of CuCl; however, the product was obtained only in 15% yield after 1 h and 44% after 48 h (entry 3). Use of 50 mol % of K(O-*t*-Bu) improved the reactivity (entry 4), but the reaction did not reach completion. Combination of 5 mol % of CuCl/Xantphos and 100 mol % of K(O-*t*-Bu) resulted in sufficient activity enhancement, giving the desired product in a high yield of 96% within 1 h (entry 5).[10] Loadings of copper(I) salt and ligand as low as 1 mol % still gave good reactivity without significant loss of the regio and *E*/*Z* selectivities [89%, 1 h, 98%, 24 h, **3a**/**4a**=97:3, *E*/*Z* (for **3a**)=96:4] (entry 6). We checked whether the copper(I) salt is necessary for the reaction (entry 7).[11] The reaction without a phosphine ligand gave the allylboronate, but with low regio and *E*/*Z* selectivities [**3a**/**4a**=67:33, *E*/*Z* (for **3a**)=69:31] as well as a low yield (56%) (entry 8). This contrasts with the original reaction featuring Cu(O-*t*-Bu), wherein diphosphine ligands were necessary for the reaction.[12] Use of PPh_3 ligand significantly reduced the reaction rate; only 18% product was detected after 24 h with low selectivities (**3a**/**4a**=78:22, *E*/*Z* (for **3a**)=67:33, entry 9). Both dppp (58%, 1 h, 98%, 8 h, entry 10) and dppf (59%, 1 h, 84%, 8 h, entry 11) showed lower reactivities with comparable selectivity as compared to those with Xantphos. Other copper(I) and copper(II) salts, CuI, CuCN, Cu(OAc), $Cu(OAc)_2$, and $CuCl_2$ afforded good reactivity and selectivities (entries 11–15).

Given the optimized conditions, we next examined the applicability of this new convenient procedure by applying this approach to various substrates including those that we have previously reported (Table 2).[5a,b] The reaction of allylic carbonate **1b**, which has a terminal allylic system with a terminal carbon–carbon double bond, resulted in the corresponding allylboronate (*E*)-**3b** in a good yield of 78% with high γ-regioselectivity (entry 1). The reaction of allylic carbonate **1c** with a terminal allylic system with an internal carbon–carbon double bond gave the corresponding γ-substituted product (entry 2). Substrates with five or seven-membered ring structures (**1d**–**f**) afforded cyclic allylboronates in good yields (67–94%) under the reaction conditions at a slightly higher temperature of 40 °C (entries 3–5). The newly developed CuCl/Xantphos/excess K(O-*t*-Bu) catalyst procedure showed the same or slightly higher reactivity and almost comparable yields and selectivities as compared to the original Cu(O-*t*-Bu)/Xantphos system; however, a substrate with a pivalate moiety [(*E*)-**1g**] afforded the allylboronate in high yield, although a longer reaction time (>24 h) resulted in low yield (approx.<10%) because of the high sensitivity of the ester under basic conditions (entry 6).

Table 1
Copper(I)-catalyzed boryl substitution of allylic carbonate **1a**[a]



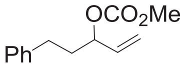
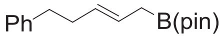
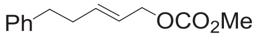
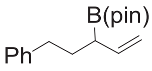
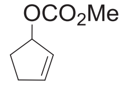
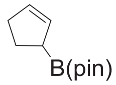
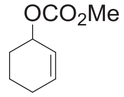
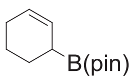
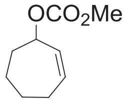
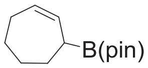
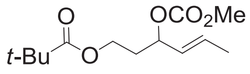
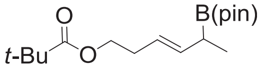
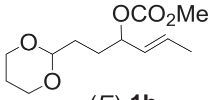
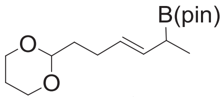
Entry	Copper salt (mol %)	Base (mol %)	Ligand (mol %)	Yield (%),[b] reaction time	**3a**/**4a**[b,c]	*E*/*Z* for **3a**[b,c]
1	Cu(O-*t*-Bu) (5)	None	Xantphos (5)	32 (1 h), 86 (24 h)	>99:<1	99:1
2	CuCl (5)	None	Xantphos (5)	0 (48 h)	—	—
3	CuCl (5)	K(O-*t*-Bu) (10)	Xantphos (5)	15 (1 h), 44 (48 h)	98:2	98:2
4	CuCl (5)	K(O-*t*-Bu) (50)	Xantphos (5)	49 (1 h), 78 (48 h)	98:2	96:4
5	CuCl (5)	K(O-*t*-Bu) (100)	Xantphos (5)	96 (1 h)	99:1	98:2
6	CuCl (1)	K(O-*t*-Bu) (100)	Xantphos (1)	89 (1 h), 98 (24 h)	97:3	96:4
7	None	K(O-*t*-Bu) (100)	Xantphos (5)	0 (48 h)	—	—
8	CuCl (5)	K(O-*t*-Bu) (100)	None	Trace (1 h), 56 (24 h)	67:33	69:31
9	CuCl (5)	K(O-*t*-Bu) (100)	PPh_3 (5)	Trace (1 h), 18 (24 h)	78:22	67:33
10	CuCl (5)	K(O-*t*-Bu) (100)	Dppp (5)	58 (1 h), 98 (8 h)	>99:<1	96:4
11	CuCl (5)	K(O-*t*-Bu) (100)	Dppf (5)	59 (1 h), 84 (8 h)	>99:<1	95:5
11	CuI (5)	K(O-*t*-Bu) (100)	Xantphos (5)	32 (1 h), 85 (8 h)	99:1	>99:<1
12	CuCN (5)	K(O-*t*-Bu) (100)	Xantphos (5)	42 (1 h), 87 (8 h)	99:1	99:1
13	Cu(OAc) (5)	K(O-*t*-Bu) (100)	Xantphos (5)	17 (1 h), 94 (8 h)	>99:<1	>99:<1
14	$Cu(OAc)_2$ (5)	K(O-*t*-Bu) (100)	Xantphos (5)	91 (1h)	99:1	99:1
15	$CuCl_2$ (5)	K(O-*t*-Bu) (100)	Xantphos (5)	72 (1 h), 82 (8 h)	96:4	93:7

[a] Reaction conditions: (*E*)-**1a** (0.5 mmol), **2** (1.0 mmol), Cu salt (0–0.025 mmol), ligand (0–0.025 mmol), dry THF (0.5–1.0 mL), and 1.0 M THF solution of K(O-*t*-Bu) (0.0–0.5 mL, 0.5 mmol) (Sigma–Aldrich). The amount of THF for various conditions was adjusted as 1.0 mL.

[b] Yield and ratios of regio- and stereoisomers were determined by GC analysis of the crude mixture.

[c] Selectivities for the longer reaction time.

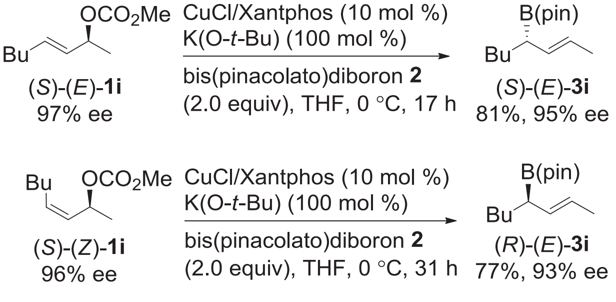
Table 2
Copper(I)-catalyzed boryl substitution of various allylic carbonates **1**[a]

Entry			Catalyst (mol %)	Temp	Time (h)	Yield[b] (%)
1[c]	 **1b**	 (*E*)-**3b**	5	rt	5.5	78
2[c]	 (*E*)-**1c**	 **3c**	5	0 °C	48	55 (69)
3	 **1d**	 **3d**	5	40 °C	4	67
4	 **1e**	 **3e**	5	40 °C	19.5	84
5	 **1f**	 **3f**	5	40 °C	4	94
6[c]	 (*E*)-**1g**	 (*E*)-**3g**	10	rt	11.5	(82)
7[c]	 (*E*)-**1h**	 (*E*)-**3h**	5	rt	7	70

[a] Reaction conditions:**1** (0.5 mmol), **2** (1.0 mmol), Cu salt (0.05–0.10 mmol), THF (0.5 mL) 1.0 M THF solution of K(O-*t*-Bu) (0.5 mL, 0.5 mmol) (Sigma–Aldrich).
[b] Isolated. The number in parentheses is the yield based on ^{1}H NMR of the crude product.
[c] Regio- and stereoisomeric ratios were >20:<1.

The reaction showed good tolerance against a base-stable functionality such as an acetal group. Allylboronate (*E*)-**3h** with a 1,3-dioxane group was successfully obtained through the catalysis (entry 7).

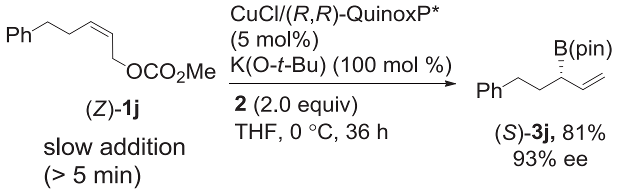
The high stereoselectivity in *anti*-$\mathrm{S_N}2'$ type borylation of optically active allylic carbonates is one very useful feature found in the allylborylation with the original Cu(O-*t*-Bu)/Xantphos catalyst system.[5a] We thus investigated the stereoselectivity performance of the new CuCl/Xantphos/excess K(O-*t*-Bu) catalyst by applying this to the reaction we previously reported. (*S*)-(*E*)-**1i**, which has a stereogenic C–O bond at the allylic system with high enantiomeric purity (97% ee), gave the corresponding α-chiral allylboronate (*S*)-(*E*)-**3i** with excellent chiral transfer fidelity (Scheme 1, 95% ee). The same reaction of (*S*)-(*Z*)-**1i** (98% ee) resulted in the formation of the *anti*-$\mathrm{S_N}2'$ product, (*R*)-(*E*)-**3i**, with a small loss of the enantiomeric purity (93% ee). In the reaction with the original catalyst, (*S*)-(*E*)-**1i** gave lower chiral transfer selectivity as compared to that of (*S*)-(*Z*)-**1i**. However, this procedure shows higher selectivity for the *E* substrate.



Scheme 1. Stereoselective borylation of optically active allylic carbonates.

We finally carried out the asymmetric catalysis using chiral ligand (*R*,*R*)-QuinoxP* as shown in Scheme 2.[5b] The reaction at 0 °C with an ice-cooled bath first gave the optically active allylboronate (*S*)-**3j** with a lower ee (75% ee) than that of the original Cu(O-*t*-Bu)/(*R*,*R*)-QuinoxP* catalyst system (95% ee).[5b] We found that the slow addition of (*Z*)-**1j** (>5 min) improved the yield and enantioselectivity (81%, 93% ee). The reaction temperature may rise during the addition of (*Z*)-**1j** at a normal addition speed, even under the ice-cooled bath conditions. Such heating could lead to the enantioselectivity loss. Adding the reagent slowly should keep the reaction temperature low.

The proposed reaction mechanism and explanation of the rate enhancement that was clearly observed in the reaction of **1a** (Table 1) is shown in Fig. 1.[13] The copper(I) alkoxide (**A**) generated by the reaction of copper(I) chloride, the diphosphine ligand, and potassium alkoxide undergo the σ-bond metathesis (**B**) with



Scheme 2. Enantioselective borylation of prochiral allylic carbonate (*Z*)-**1j**.

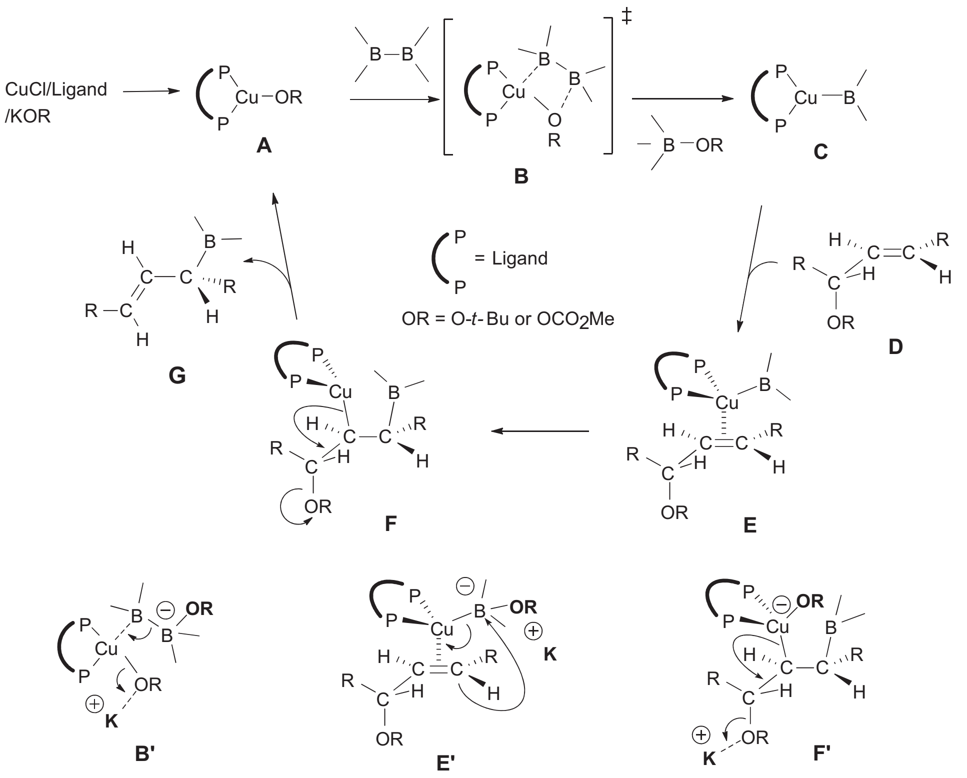


Fig. 1. Proposed reaction mechanism and rate enhancement.

diboron to produce the borylcopper(I) intermediate (**C**). When copper(II) salts were employed as the catalyst precursor, reduction of copper(II) to copper(I) proceeds most probably through the reduction by diboron.[14] The coordination of allylic substrate (**D**) gives the complex (**E**) with the conformation, where the leaving group is at the *anti*-position, toward the approaching copper center and the 1,3-allylic strain is minimized. The subsequent insertion of the carbon–carbon double bond into the Cu–B bond affords the alkylcopper(I) intermediate (**E**).[13] The β-alkoxy elimination (**F**) of the copper moiety results in the formation of the allylboronate (**G**) and copper(I) alkoxide (**A**) regeneration. The reaction pathway **A**–**B**–**C**–**E**–**F** shown here is the same as the mechanism we proposed for the original Cu(O-*t*-Bu) based system. Therefore, this mechanism alone could not explain the rate acceleration caused by excess K(O-*t*-Bu) in the reaction of **1a**, as clearly shown in Table 1. One possible explanation is that the σ-bond metathesis step (**B′**) would be accelerated by nucleophilicity enhancement because of the formation of borate and the electron accepting effect of the potassium cation on the oxygen atom in the leaving group. The formation of borate would be effective in the insertion of the carbon–carbon double bond to the C–B bond (**E′**), where the energy level of the borylcopper(I) HOMO rises to enhance the interaction with the allylic substrate LUMO. The alkoxide moiety can also coordinate to the copper(I) center in the alkylcopper(I) intermediate (**F′**) to enhance the β-alkoxy elimination rate in combination with the coordination of the oxygen atom to the electron accepting potassium cation. By increasing the amount of K(O-*t*-Bu) present, the more the **B′**, **E′**, and **F′** intermediates would contribute the reaction. The reaction mixture includes many other Lewis-acidic intermediates, such as diboron, ROB(pinacolato), allylboronate product, and CO_2. These species would trap part of the K(O-*t*-Bu) present in the reaction. This can explain the requirement of large amounts of K(O-*t*-Bu) as compared to the Cu(I) salt. Further studies are required to fully elucidate the reaction mechanism.[7d,e]

3. Conclusion

We have reported the convenient procedure including catalytic CuCl, ligand, and stoichiometric K(O-*t*-Bu) for copper(I)-catalyzed allylic borylation: this is a highly versatile method for the synthesis of allylboronates including terminal and internal allylic systems, and those with functional groups. Optically active allylboronates were synthesized by the procedure from the corresponding enantioenriched substrates with excellent stereoselectivities. The enantioselective version with a chiral ligand can operate with only slight loss of the enantioselectivity as compared to those with the original Cu(O-*t*-Bu)-based catalysis. Although the higher basicity gives deleterious effects on the functional group applicability, we believe that the usability of the copper(I)-catalyzed borylation is improved at the practical level by this glove-box free new procedure.[15]

4. Experimental section

4.1. General

All reactions were carried out under nitrogen atmosphere. All dry solvents were purchased from commercial suppliers and degassed via three freeze–pump–thaw cycles and further dried on molecular sieves 4 Å before use. A JOEL ECX-400 NMR spectrometer (^{1}H: 400 MHz and ^{13}C: 100 MHz) was used to record all NMR spectra. Tetramethylsilane (^{1}H) and $CDCl_3$ (^{13}C) were employed as internal and external standards, respectively. Mesitylene was used as the internal standard for determining yields using the NMR data. Gas chromatographic (GLC) analyses were conducted on a Shimadzu GC-2014 equipped with a flame ionization detector. HPLC analyses were carried out using a Hitachi Elite LaChrome HPLC system with an L-2400 UV detector. High-resolution mass spectra were recorded on a JEOL JMS-T100GC mass spectrometer. All compounds in this paper are known compounds besides [(*E*)-**3a**]. The ^{1}H and ^{13}C NMR of allylboronates were identical with those previously reported.[5a,b] A potassium *tert*-butoxide solution of tetrahydrofuran (1.0 M) was purchased from Sigma–Aldrich Co. (328650-50ML) and used as received.

*4.1.1. (E)-4,4,5,5-Tetramethyl-2-(6-phenylhex-3-en-2-yl)-1,3,2-dioxaborolane [(E)-**3a**].* Into a reaction vial, bis(pinacolato)diboron (254 mg, 1.0 mmol), copper(I) chloride (2.5 mg, 0.025 mmol), and Xantphos (14.5 mg, 0.025 mmol) were placed. After the vial was sealed with a septum, the vial was evacuated and filled with nitrogen gas using a vacuum line through a needle. A THF solution of K(O-*t*-Bu) (1.0 M, 0.50 mL, 0.50 mmol) and THF (0.5 mL) were added to the vial. After stirring for 30 min, the reaction mixture was added by allylic carbonate (*E*)-**1a** (117.1 mg, 0.5 mmol). The yields and selectivities were determined from GC analysis of the crude solution. After completion of the reaction, the reaction mixture was passed through a short path column (SiO_2) with an eluent (ethyl acetate/hexane 30:70) and the solvents were removed under reduced pressure with a rotary evaporator. The crude mixture was purified by flash chromatography (SiO_2, ethyl acetate/hexane 0.3:99.7) to give the desired product (*E*)-**3a** as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.27 (m, 5H), 5.50–5.56 (m, 1H), 5.35–5.45 (m, 1H), 2.65 (t, J=8.0 Hz, 2H), 2.30 (q, J=7.6 Hz, 2H), 1.82 (qn, J=7.2 Hz, 1H), 1.22 (s, 12H), 1.05 (d, J=9.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.19, 132.80, 128.41, 128.11, 127.35, 125.54, 82.95, 36.24, 34.56, 24.63, 24.56, 15.10. HRMS–EI (*m*/*z*): $[M]^+$ calcd for $C_{18}H_{27}BO_2$, 286.2104; found, 286.2101.

*4.1.2. (E)-4,4,5,5-Tetramethyl-2-(5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane [(S)-**3j**].* The reaction was carried out with a chiral ligand (*R*,*R*)-QuinoxP* instead of Xantphos. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14–7.28 (m, 5H), 5.78–5.87 (m, 1H), 4.98–5.04 (m, 2H), 2.53–2.70 (m, 2H), 1.83–1.93 (m, 2H), 1.69–1.79 (m, 1H), 1.24 (s,12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 139.2, 128.5, 128.3, 125.6, 114.0, 83.2, 35.2, 32.1, 29.9 (br, *C*–B), 24.7, 24.6. The ee value was determined by HPLC analysis of the 4-nitrobenzoylated derivative of the corresponding alcohol after $NaBO_3\cdot 4H_2O$ oxidation of this compound with a chiral stationary phase (Chiralcel OD-3, 40 °C, 2.0% 2-PrOH/hexane, 0.5 mL/min, *S* isomer t_R=28.8 min, *R* isomer t_R=33.8 min).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.08.081. These data include MOL file and InChiKey of the most important compound described in this article.

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9. In Ref. 5a, we reported that a substrate similar to **1a** was consumed within 3 h in a 1.0 M substrate concentration in the presence of the same catalyst loading (5.0 mol %). It is reasonable that because of a lower concentration reported in (0.5 M) Table 1, a longer reaction time was required (24 h).
10. Hoveyda and co-workers reported that use of excess NaOMe base (80 mol %) in combination with copper(I) (5 mol %)/NHC ligand (6 mol %) leads to an improvement in reaction efficiency for the allylic boryl substitution as compared to the reaction with 30 mol % NaOMe. They did not describe the reason for this improvement effect. See Ref. 6b.
11. NHC or phosphine-catalyzed borylation of α,β-carbonyl compounds with diboron was reported to proceed without a copper(I) salt. (a) Lee, K.-S.; Zhugralin, A. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7253; (b) Bonet, A.; Gulyás, H.; Fernández, E. *Angew. Chem., Int. Ed.* **2010**, *49*, 5130.
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