Preparation of (*E*)-1-alkenylboronic acid pinacol esters *via* transfer of alkenyl group from boron to boron

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Abstract: Two synthetic routes to (*E*)-1-alkenylboronic acid pinacol esters (**3**) were investigated. Hydroboration of 1-alkynes (**1**) with 1,3,2-benzodioxaborole (catecholborane), *in situ* generated by the reaction of BH_3 in THF with catechol, proceeded in the presence of a catalytic amount of dicyclohexylborane in THF at room temperature to give the corresponding (*E*)-1-alkenylboronic acid catechol esters (**2**). Treatment of the resultant **2** with 2,3-dimethyl-2,3-butanediol (pinacol) easily afforded the desired products **3**, which are insensitive to air, moisture and chromatography, in good to high overall yields. The sequential reaction is a highly efficient route to **3** from BH_3 in THF in a one-pot manner. Alternatively, hydroboration of **1** with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane) was achieved in the presence of a catalytic amount of dicyclohexylborane at room temperature under neat conditions to afford the corresponding **3** directly in good to excellent yields. This route is extremely efficient and environmentally benign from the viewpoints of making good use of pinacolborane and of using no solvent, and is capable of using a variety of **1** including functionalized ones such as $HC{\equiv}CCH_2Cl$ and $HC{\equiv}CCH_2OTHP$.

Key words: (*E*)-1-alkenylboronic acid pinacol ester, 1-alkyne, dicyclohexylborane, catecholborane, pinacolborane

Alkenylboronates are versatile intermediates in organic synthesis,[1] especially in palladium-catalyzed carbon-carbon bond formation reaction (Suzuki-Miyaura cross-coupling reaction).[2] Boronate group is much more favorable than dialkylboryl group to palladium-catalyzed cross-coupling reactions due to virtual impossibility of side reactions arising from the two alkyl groups on the boron atom. Alkenylboronates can be prepared from alkynes directly as well as indirectly. Brown *et al*. reported the indirect procedure that hydroboration of alkynes with dibromoborane-dimethyl sulfide ($HBBr_2{\cdot}SMe_2$), followed by alcoholysis or hydrolysis-esterification sequence furnished the corresponding alkenylboronates.[3] In addition, they synthesized (*Z*)-1-alkenylboronates through hydroboration of 1-bromo-1-alkyne with $HBBr_2{\cdot}SMe_2$, followed by a similar esterification described above and hydrodebromination with potassium triisopropoxyborohydride.[4] The methodology for the preparation of alkenylboronates using $HBBr_2{\cdot}SMe_2$ is general and useful; however, the method by alcoholysis was complicated by the formation of $Me_2S{\cdot}HBr$, and the method by hydrolysis-esterification required the isolation of alkenylboronic acids. One-pot procedures for preparing (*E*)-1-alkenylboronic acid pinacol ester were achieved by Hoffmann's group[5] and Vaultier's.[6] Their methods, however, consisted of three steps, hydroboration of 1-alkyne with dialkylborane, esterification of the dialkylboryl group, and transesterification with 2,3-dimethyl-2,3-butanediol (pinacol). Hara *et al*. realized the preparation of 2,2-disubstituted 1-alkenylboronates by means of bromoboration of 1-alkyne with BBr_3.[7] Thus, esterification of (*Z*)-2-bromo-1-alkenyldibromoborane gave (*Z*)-2-bromo-1-alkenylboronate, which could be cross-coupled with organylzinc chloride in the presence of Pd(0) with retention of stereochemistry to afford 2-organyl-1-alkenylboronate. Alkynylboron compounds can be used to prepare alkenylboronates. Brown and Srebnik reported that 1-alkynylboronate was converted into (*Z*)-1-alkenylboronate by catalytic hydrogenation[8] as well as by hydrozirconation-hydrolysis sequense.[9] Carboni *et al*. also reported the conversion of ethynylbis(dialkylamino)boranes into alkenylboronates *via* electrophilic addition-esterification sequense.[10] Internal alkenylboronates can be prepared in a regio- and stereoselective fashion as well. Brown *et al*. employed the protocol that 1-bromo-1-alkyne was hydroborated with $HBBr_2{\cdot}SMe_2$, followed by esterification to form (*Z*)-1-bromo-1-alkenylboronate, which was reacted with organolithium or Grignard reagent to lead to the substitution of the bromine for the alkyl group with inversion of stereochemistry.[11] Srebnik *et al*. utilized the successive reaction which was made up hydrozirconation of 1-alkynylboronic acid pinacol ester with zirconocene chloride hydride (Schwartz's reagent) and palladium-catalyzed cross-coupling with organyl halide.[12]

In addition to the strategy from alkynes, there are a few different protocols. Thus, alkenylboronates were prepared by Heck reaction of ethenylboronic acid pinacol ester with aryl halides[13], by $CrCl_2$-operated reaction of dichloromethylboronic acid pinacol ester with aldehydes,[14] by catalytic dehydrogenative borylation of alkenes,[15] and by catalytic borylation of alkenyl triflates[16] with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane).

Alkenylboronates can be directly synthesized by hydroboration of alkynes with cyclic dialkoxyboranes, where both catalyzed and uncatalyzed methods were employed. Brown *et al*. reported that hydroboration with 1,3,2-benzodioxaborole (catecholborane) in the absence of a catalyst produced alkenylboronic acid catechol esters, although the reaction required harsh conditions due to its low reactivity.[17] For example, in the case of 1-hexyne, 90% of hydroboration was achieved by using

neat catecholborane without any solvent at 68 °C for 4 h.[17b] The report of Knochel *et al*. described the uncatalyzed hydroboration with pinacolborane; however, the reaction was carried out with a considerably excess amount of pinacolborane (twice the amount of alkyne).[18] Accordingly, it is desirable that alkenylboronates are obtained more easily and efficiently under mild reaction conditions.

The preparation of alkenylboronates can be performed under mild reaction conditions by using catalyst. A catalytic amount of transition metal complexes allowed the hydroboration of alkynes with catecholborane to proceed at room temperature, whereas all the reactions were based on catecholborane not on BH_3 in THF.[19] Srebnik *et al*. reported that the hydroboration with pinacolborane was catalyzed by Schwartz's reagent[20] as well as by transition metal complexes.[21] While both reactions proceeded at ambient temperature to give alkenylboronic acid pinacol esters in excellent yields, Schwartz's reagent-catalyzed reaction was contaminated by small amounts of by-products, and transition metal-catalyzed reaction required CH_2Cl_2 as a solvent. More recently, Miyaura and his co-workers realized *trans*-hydroboration of 1-alkyne with catecholborane or pinacolborane in the presence of transition metal catalyst and triethylamine.[22] On the other hand, the report of Periasamy *et al*. described the hydroboration with catecholborane accelerated by *N,N*-diethylaniline-borane complex where the reaction was carried out with a considerably excess amount of 1-alkyne (1.6 times the amount of catecholborane) at room temperature for 24 h.[23]

We have previously reported that a stoichiometric hydroboration of alkynes with catecholborane proceeds in the presence of a catalytic amount of dialkylborane in THF at room temperature, giving the corresponding alkenylboronic acid catechol esters in high yields.[24] The advantage of this reaction is that catecholborane *in situ* generated by the reaction between catechol and BH_3 in THF can be utilized directly without isolation. The resulting alkenylboronic acid catechol esters should be easily converted into the corresponding alkenylboronic acid pinacol esters, which are insensitive to air, moisture and chromatography, *via* transesterification with pinacol. In this paper, we report two easy and efficient routes to (*E*)-1-alkenylboronic acid pinacol esters (**3**): (I) dicyclohexylborane-mediated hydroboration of 1-alkynes (**1**) with catecholborane in THF at room temperature followed by transesterification with pinacol in a one-pot manner (II) dicyclohexylborane-mediated hydroboration of **1** with pinacolborane under neat conditions.

Route I: Dicyclohexylborane-mediated hydroboration of 1-alkynes with catecholborane in THF followed by transesterification with pinacol. As reported previously, the reaction of 1-alkynes (**1**) with catecholborane in the presence of a catalytic amount of dicyclohexylborane proceeded in THF at room temperature, giving (*E*)-1-alkenylboronic acid catechol esters (**2**) in high yields. Consequently, we reasoned that transesterification of **2** with pinacol should allow for the one-pot generation of (*E*)-1-alkenylboronic acid pinacol esters (**3**) from BH_3 in THF. This led us to examine the successive reaction of BH_3 in THF with catechol, 1-octyne (**1b**), dicyclohexylborane (5 mol%) and pinacol. After preparing (*E*)-1-octenylboronic acid catechol ester (**2b**) by our reported method, treatment of **2b** with 1.5 equiv of pinacol was carried out at room temperature for 18 h. As expected, the desired transesterification product, (*E*)-1-octenylboronic acid pinacol ester (**3b**), was obtained in 96% overall yield based on BH_3 (Scheme 1). The product **3b** was purified by column chromatography on silica gel, and its ^{1}H NMR spectrum was in agreement with that of **3b** reported therein.[18] Thus, only one pair of signals appeared at δ 5.42 (1 H, dt, J = 18, 1.5 Hz, 2-H) and 6.63 (1 H, dt, J = 18, 6.4 Hz, 1-H) in the alkenyl region. These results indicated that the transesterification proceeded almost completely in THF with retention of configuration.

Table 1 shows the results of transesterification of **2** prepared *via* dicyclohexylborane-mediated hydroboration of several types of **1** with catecholborane *in situ* generated by the reaction of catechol with BH_3 in THF. A variety of **1** could be converted into the desired products **3**, which are insensitive to air, moisture and chromatography, in good to high yields. Alkenyl (entry 5), chloro (entries 6 and 8), and alkoxy (entry 7) functionalities on the terminal alkynes were not affected under the reaction conditions. The hydroboration of 3-methoxypropyne (**1g**) and 3-chloropropyne (**1h**) required the use of 1.1 equiv amounts of catechol and BH_3 and of 10 mol% of dicyclohexylborane and a longer reaction time (4 h). These requirements can be attributed to the electron-withdrawing substituents in the neighborhood of the carbon-carbon triple bond. It should be noted that the sequential reaction is a highly efficient route to **3** from BH_3 in THF in a one-pot manner. In the case of 3-(tetrahydro-2*H*-pyran-2-yloxy)propyne ($HC{\equiv}CCH_2OTHP$) (**1i**) having a hydroxy-protecting group, a trace amount of the desired product and a large amount of unidentified product were observed. This is probably due to the formation of catechol upon the transesterification with pinacol. Thus, it appears that acidic catechol should give rise to the deprotection of the desired product [(*E*)- 3-(tetrahydro-2*H*-pyran-2-yloxy)-1-propenylboronic acid pinacol ester] (**3i**) as well as the cleavage of boron-carbon bond. In fact, treatment of independently synthesized **3i** with catechol under similar conditions caused the same result as described above. We attempted to apply the present method to internal alkyne such as 4-octyne whose hydroboration with catecolborane was carried out in the presence of 9-borabicyclo[3.3.1]nonane in place of dicyclohexylborane. Contrary to our expectation, the desired product was formed in a low yield. For no reason at all we failed to transform the internal alkyne to internal (*Z*)-alkenylboronic acid pinacol ester.

Route II: Dicyclohexylborane-mediated hydroboration of 1-alkynes with pinacolborane. Since hydroxy-protecting group such as –THP was incompatible with the preparation of (*E*)-1-alkenylboronic acid pinacol

esters (**3**) *via* transesterification of (*E*)-1-alkenylboronic acid catechol esters (**2**) with pinacol, we decided to investigate hydroboration of **1** with pinacolborane using our dicyclohexylborane-mediated protocol. Pinacolborane can be prepared by the reaction of pinacol with $BH_3{\cdot}SMe_2$ and purified by distillation,[18] but the distillate is often contaminated a few % of Me_2S. We chose 1-octyne (**1b**) as a representative 1-alkyne and conducted hydroboration with an equimolar amount of pinacolborane containing Me_2S[25] in the presence of dicyclohexylborane (5 mol%) in THF at room temperature for 2 h in the first place. Unexpectedly, the reaction gave only a 27% yield of (*E*)-1-octenylboronic acid pinacol ester (**3b**) and a 67% recovery of **1b**. Although various solvents, longer reaction times, and quantities of dicyclohexylborane were explored, no satisfactory result was obtained.[26] To our great surprise, we found that when employing solvent-free system, the hydroboration with pinacolborane containing Me_2S proceeded to completion. Thus, the hydroboration in the presence of dicyclohexylborane (5 mol%) was carried out under neat conditions[27] at room temperature for 2 h to afford **3b** in 95% yield (Scheme 2). In the absence of dicyclohexylborane the reaction hardly proceeded and resulted in an 82% recovery of **1b**. This result showed that dicyclohexylborane served as a catalyst in hydroboration of **1** with pinacolborane as well. It also turned out that a quantitative yield of **3b** was affected by using 5 mol% excess amount of pinacolborane. Although the dicyclohexylborane-mediated hydroboration with pinacolborane proceeded successfully in solvent-free system for no reason, it is important to note that this protocol is environment-friendly.

Table 2 summarizes the results of dicyclohexylborane-mediated hydroboration of various types of **1** with pinacolborane under neat conditions. The hydroboration of **1a-f** proceeded smoothly and efficiently to afford the corresponding **3** exclusively in excellent yields (entries 1-6). In the cases of 3-substituted propynes (**1g-k**) the hydroboration was achieved by using 1.1 equiv of pinacolborane, 10 mol% of dicyclohexylborane and a longer reaction time (4 or 24 h), giving (*E*)-3-substituted-1-propenylboronic acid pinacol esters (**3g-k**) with high regio- and stereoselectivity in good yields (entries 7-11). It should be noted that the present protocol is tolerant of both acid labile hydroxy-protecting groups (entries 9 and 10) and base labile one (entry 11). Furthermore, the present protocol is more favorable than that *via* transesterification with pinacol with regard to the preparation of (*E*)-3-chloro-1-propenylboronic acid pinacol ester (**3h**). These results indicated that dicyclohexylborane-mediated hydroboration of 1-alkynes (**1**) with pinacolborane proved to be an efficient and environmentally benign method for the preparation of (*E*)-1-alkenylboronic acid pinacol esters (**3**). Unfortunately, the hydroboration of internal alkynes gave unsatisfactory results under similar reaction conditions.

Mechanism of dicyclohexylborane-mediated hydroboration of 1-alkynes. We propose the following mechanism for the dicyclohexylborane-mediated hydroboration of 1-alkyne with catecholborane or pinacolborane (Scheme 3). Dicyclohexylborane hydroborates 1-alkyne to give (*E*)-1-alkenyldicyclohexylborane (**A**), whose alkenyl group would be replaced with the hydride of catecholborane or pinacolborane to produce (*E*)-1-alkenylboronic acid catechol ester (**2**) or (*E*)-1-alkenylboronic acid pinacol ester (**3**) along with regeneration of dicyclohexylborane. If this is the case, a catalytic amount of **A** should promote hydroboration of 1-alkyne with catecholborane or pinacolborane. In fact, the use of **A** in stead of dicyclohexylborane gave the same result. It appears that the replacement may proceed through a concerted reaction which involves the transfer of alkenyl group from boron to boron and the concomitant transfer of hydride (Figure 1, **I**). In the hydroboration of 3-substituted propynes, a regioisomeric product (**B**) was also formed in a small amount due to the inductive electron-withdrawing effect of the substituent moiety.[1] The replacement reaction of **B** appears to be very slow due to the steric hindrance between **B** and catecolborane or pinacolborane (Figure 1, **II**), and thus the regeneration of dicyclohexylborane would be prevented. Using 10mol% of dicyclohexylborane is necessary to increase the yield of the desired products (**3g-k**) as a result. Additionally, it is conceivable that in the case of **A** with electron-withdrawing group the decrease of π-electron density would retard the replacement (Figure 1, **I**).

In conclusion, we have developed two synthetic routes to (*E*)-1-alkenylboronic acid pinacol esters (**3**) *via* transfer of alkenyl group from boron to boron in the presence of a catalytic amount of dicyclohexylborane. One is dicyclohexylborane-mediated hydroboration of 1-alkynes with catecholborane, where the reaction can be carried out in THF at room temperature, followed by treatment with pinacol (Route I). A series of reactions is an efficient procedure for the preparation of **3** from BH_3 in THF in a one-pot manner. The other is dicyclohexylborane-mediated hydroboration of 1-alkynes with pinacolborane under neat conditions (Route II). The reaction is compatible with a variety of functional groups and provides **3** in good to excellent yields.

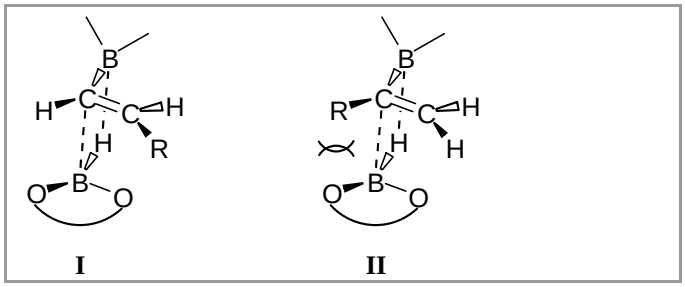
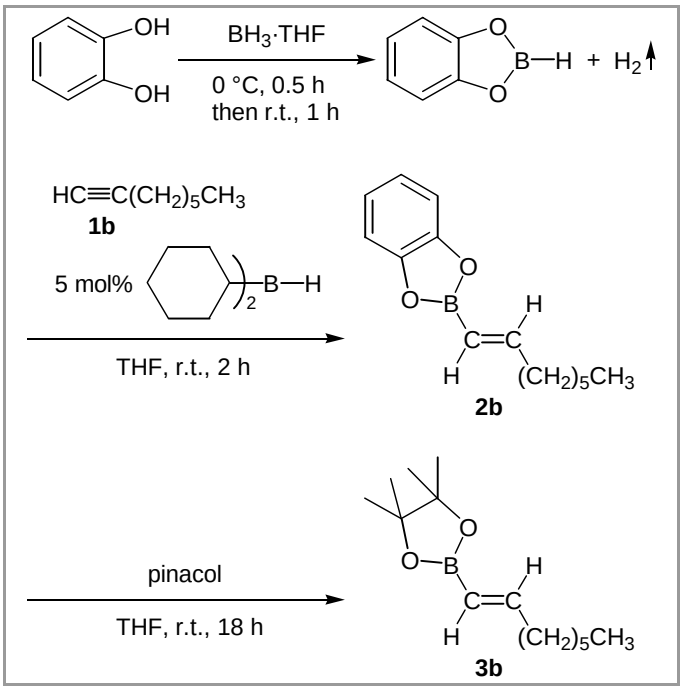
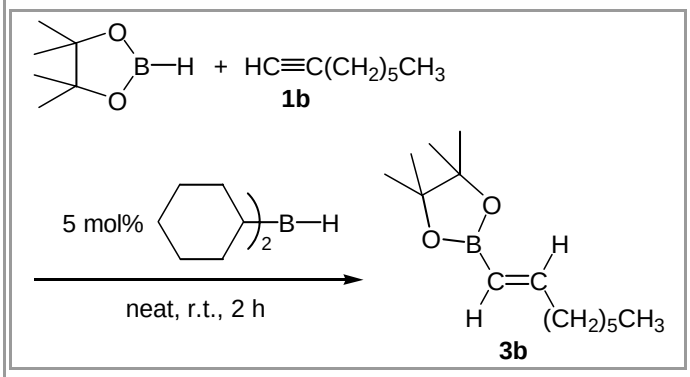


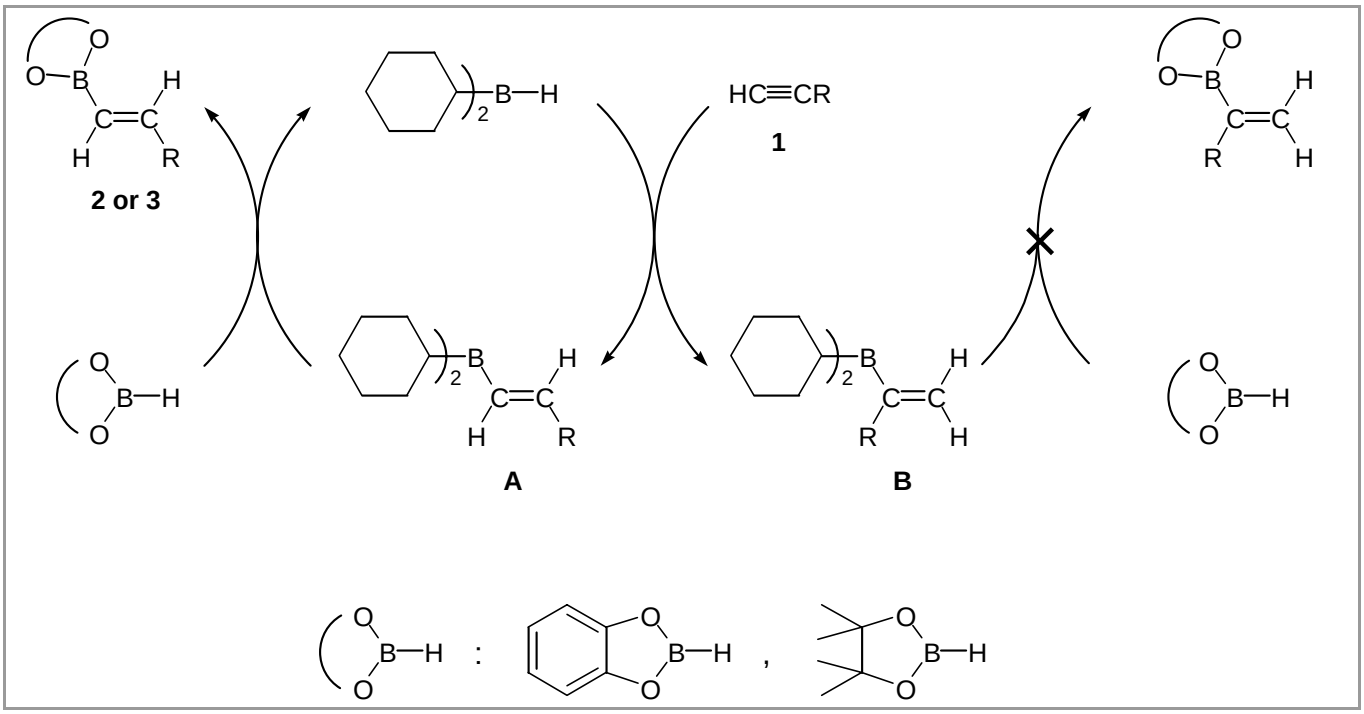
Figure 1



Scheme 1



Scheme 2



Scheme 3 A plausible catalytic cycle for dicyclohexylborane-mediated hydroboration of 1-alkynes **1** with catecholborane and pinacolborane.

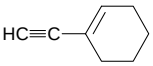
Table 1 Dicyclohexylborane-mediated hydroboration of representative **1** with *in situ* generated catecholborane followed by transesterification with pinacol[a]

Entry	alkyne **1**	Product	Yield (%)[b]
1	HC≡C(CH2)3CH3	3a	98 (93)
2	HC≡C(CH)5CH3	3b	96 (92)
3	HC≡CBu-*t*	3c	99 (95)
4	HC≡CPh	3d	98 (95)
5	HC≡C—	3e	95 (87)
6	HC≡C(CH2)3Cl	3f	95 (90)
7[c]	HC≡CCH2OMe	3g	80 (74)
8[c]	HC≡CCH2Cl	3h	73 (67)
9[c]	HC≡CCH2OTHP	3i	trace[d]

[a] Reactions of **1** (1 mmol) with catecholborane, *in situ* generated by the reaction of catechol (1 mmol) with borane (1 mmol) in THF, were carried out in the presence of dicyclohexylborane (5 mol%) at room temperature for 2 h, followed by the transesterification with pinacol (1.5 mmol) at room temperature for 18 h.
[b] GLC yields based on **1**. Isolated yields are shown in parentheses.
[c] 1.1 Equiv of catecholborane and 10 mol% of dicyclohexylborane were used and the reaction time was prolonged to 4 h.
[d] A large amount of unidentified product was observed.

Table 2 Dicyclohexylborane-mediated hydroboration of representative **1** with pinacolborane[a]

Entry	alkyne **1**	Product	Yield (%)[b]
1	HC≡C(CH2)3CH3	3a	>99 (94)

2	$HC{\equiv}C(CH)_5CH_3$	3b	>99 (93)
3	$HC{\equiv}CBu\text{-}t$	3c	>99 (95)
4	$HC{\equiv}CPh$	3d	>99 (93)
5		3e	95 (87)
6	$HC{\equiv}C(CH_2)_3Cl$	3f	94 (89)
7[c,d]	$HC{\equiv}CCH_2OMe$	3g	83 (78)
8[c,d]	$HC{\equiv}CCH_2Cl$	3h	90 (84)
9[c,d]	$HC{\equiv}CCH_2OTHP$	3i	83 (77)
10[c,d]	$HC{\equiv}CCH_2OMOM$	3j	84 (77)
11[c,e]	$HC{\equiv}CCH_2OAc$	3k	84 (77)

[a] Reactions of **1** (1 mmol) with pinacolborane (1.05 mmol) were carried out in the presence of dicyclohexylborane (5 mol%) at room temperature for 2 h under neat conditions.
[b] GLC yields based on **1**. Isolated yields are shown in parentheses.
[c] 1.1 Equiv of pinacolborane and 10 mol% of dicyclohexylborane were used.
[d] The reaction time was prolonged to 4 h.
[e] The reaction time was prolonged to 24 h.

NMR spectra were recorded on a JEOL JNM-A-500 spectrometer with TMS as internal standard. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer, and only the strongest/structurally most important absorption peaks are listed. Mass spectra were performed on a JEOL JMS-SX102A spectrometer (EI, 70 eV). GLC analyses using the internal standard method were performed with a Shimadzu GC-14B gas chromatograph equipped with a glass column (5% Silicone SE-30 on Uniport B, 1 m), a flame ionization detector, and a Shimadzu C-R8A digital integrator-recorder. Column chromatography was performed with Merk silica gel 60 (63─200 μm). All reactions were carried out under an argon atmosphere. THF was distilled over sodium/benzophenone. Commercially available 1-alkyne and cyclohexene were used after purification by methods generally employed in similar organoborane chemistry.[1a] Reagent grade catechol and pinacol were used without any purification. Commercially available pinacolborane was used after distillation under argon. 3-(Tetrahydro-2*H*-pyran-2-yloxy)propyne (**1i**),[28] 3-(methoxymethoxy)propyne (**1j**),[29] 3-acetoxypropyne (**1k**),[30] a solution of BH_3 in THF[31] were prepared according to the literature procedures.

Preparation of a Suspension of Dicyclohexylborane in THF.

A dry 25 mL round-bottomed flask, equipped with a gas inlet for argon, a sample inlet with a serum cap, and a magnetic stirring bar, was flushed with argon. The flask was charged with borane-THF complex (1mmol) in THF (0.4M solution) and then to the stirred solution was added cyclohexene (2 mmol) at 0 °C. After stirring for 1.5 h at 0 °C, the resultant suspension of white solid was diluted with THF (ca. 0.1M) and stored under argon in a freezer.

Route I

A solution of catechol (0.440 g, 4 mmol for **1a-f**, 0.484 g, 4.4 mmol for **1g** and **1h**) in THF (8 mL) was cooled to 0 °C, BH_3 (4 mmol for **1a-f**, 4.4 mmol for **1g** and **1h**) in THF was slowly added, and the reaction mixture was stirred for 0.5 h at 0 °C and for additional 1 h at room temperature until no more hydrogen was evolved. To the stirred solution were added 1-alkyne (4mmol) and a suspension of dicyclohexylborane (2.0 mL, 0.2 mmol for **1a-f**, 4.0 mL, 0.4 mmol for **1g** and **1h**) in THF at 0 °C. After stirring for a definite time at room temperature, to the resultant mixture was added pinacol (0.71 g, 6 mmol) at 0 °C and then stirred for 18 h at room temperature. The reaction mixture was treated by bubbling air through the solution with tube pump for 2 h at room temperature to oxidize dicyclohexylboryl group. The resulting mixture was diluted with hexane, washed with water, dried over Na_2SO_4, and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel.

Route II

A suspension of dicyclohexylborane (2.0 mL, 0.2 mmol for **1a-f**, 4.0 mL, 0.4 mmol for **1g-k**) in THF was charged, and THF was removed under reduced pressure to afford the neat dicyclohexylborane (white solid). Pinacolborane (0.512 g, 4.0 mmol for **1a-f**, 0.563 g, 4.4 mmol for **1g-k**) and 1-alkyne (4 mmol) was added at 0 °C and the mixture was stirred for a definite time at room temperature. The work-up procedure is the same as described above (Route I).

(*E*)-1-Hexenylboronic acid pinacol ester (3a)

Compound **3a** was purified by column chromatography on silica gel (5% ether in hexane).

Yield: 0.78 g (93%, Route I), 0.79 g (94%, Route II); colorless oil.

IR (neat): 2977, 2960, 2929, 2873, 2862, 1639, 1398, 1361, 1319, 1145, 999, 972, 850 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 7.2 Hz, 6-H_3), 1.27 (12 H, s, 2 × CMe_2), 1.29-1.44 (4 H, m, 4- and 5-H_2), 2.12-2.19 (2 H, m, 3-H_2), 5.43 (1 H, d, *J* = 18.0 Hz, 1-H), 6.64 (1 H, dt, *J* = 18.0 and 6.4 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.3 (CH_2), 24.8 (4 × Me), 30.4 (CH_2), 35.5(CH_2), 83.0(2 × C-O), 154.8 (=CH).[32]

EI-MS: *m/z* = 210.1795 (M^+. $C_{12}H_{23}O_2B$ requires 210.1793), 210 (M^+, 56%), 195 (85), 194 (18), 153 (100), 152 (27), 124 (53), 111 (89), 110 (33), 95 (21), 85 (24), 84 (18), 83 (24), 82 (21), 69 (22), 68 (20).

(*E*)-1-Octenylboronic acid pinacol ester (3b)

Compound **3b** was purified by column chromatography on silica gel (5% ether in hexane).

Yield: 0.88 g (92%, Route I), 0.89 g (93%, Route II); colorless oil.

IR (neat): 2977, 2958, 2927, 2856, 1639, 1398, 1388, 1363, 1319, 1145, 997, 970, 850 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 7.0 Hz, 8-H_3), 1.27 (12 H, s, 2 × CMe_2), 1.23-1.44 (8 H, m, 4-, 5-, 6- and 7-H_2), 2.12-2.18 (2 H, m, 3-H_2), 5.42 (1 H, dt, *J* = 18.0 and 1.5 Hz, 1-H), 6.63 (1 H, dt, *J* = 18.0 and 6.4 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (Me), 22.6 (CH_2), 24.8 (4 × Me), 28.2 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 35.9 (CH_2), 83.0 (2 × C-O), 154.9 (=CH).[32]

EI-MS: *m/z* = 238.2110 (M^+. $C_{14}H_{27}O_2B$ requires 238.2107), 238 (M^+, 16%), 223 (60), 154 (20), 153 (100), 152 (49), 139 (69), 138 (27), 110 (26), 101 (22), 95 (18), 85 (26), 84 (28), 83 (26), 69 (21), 68 (22), 55 (22), 43 (17), 41 (28).

(*E*)-3,3-Dimethyl-1-butenylboronic acid pinacol ester (3c)

Compound **3c** was purified by column chromatography on silica gel (5% ether in hexane).

Yield: 0.80 g (95%, both of Routes); colorless oil.

IR (neat): 2963, 1633, 1348, 1321, 1147, 1001, 972, 850 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.02 (9 H, s, CMe_3), 1.27 (12 H, s, 2 × CMe_2), 5.35 (1 H, d, *J* = 18.0 Hz, 1-H), 6.64 (1 H, d, *J* = 18.0 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (4 × Me), 28.8 (3 × Me), 35.0 (C), 83.0 (2 × C-O), 164.4 (=CH).[32]

EI-MS: *m/z* = 210.1790 (M^+. $C_{12}H_{23}O_2B$ requires 210.1793), 210 (M^+, 29%), 195 (54), 153 (100), 152 (30), 111 (77), 110 (53), 109 (37), 101 (79), 95 (35), 84 (77), 83 (44), 69 (39), 41 (35).

(*E*)-2-phenylethenylboronic acid pinacol ester (3d)

Compound **3d** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.87 g (95%, Route I), 0.86 g (93%, Route II); colorless oil.

IR (neat): 2977, 2929, 1624, 1577, 1494, 1450, 1386, 1352, 1325, 1272, 1211, 1145, 997, 970, 852 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (12 H, s, 2 × CMe_2), 6.17 (1 H, d, *J* = 18.3 Hz, 1-H), 7.25-7.35 (3 H, m, ring 3-, 4- and 5-H), 7.40 (1 H, d, *J* = 18.3 Hz, 2-H), 7.45-7.52 (2 H, m, ring 2- and 6-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (4 × Me), 83.3 (2 × C-O), 127.1 (2 × =CH), 128.6 (2 × =CH), 128.9 (=CH), 137.5 (=C), 149.5 (=CH).[32]

EI-MS: *m/z* = 230.1479 (M^+. $C_{14}H_{19}O_2B$ requires 230.1481), 230 (M^+, 63%), 229 (15), 215 (27), 145 (39), 144 (69), 131 (60), 130 (100), 129 (64), 118 (15), 105 (22), 77 (14), 41 (14).

(*E*)-2-(Cyclohexen-1-yl)ethenylboronic acid pinacol ester (3e)

Compound **3e** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.81 g (87%, both of Routes); colorless oil.

IR (neat): 2977, 2929, 1631, 1145, 995, 970, 850 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 1.55-1.70 (4 H, m, ring 4- and 5-H_2), 2.10-2.20 (4 H, m, ring 3- and 6-H_2), 5.42 (1 H, d, *J* = 18.3 Hz, 2-H), 5.96 (1 H, s, ring 2-H), 7.02 (1 H, d, *J* = 18.3 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.3 (CH_2), 22.4 (CH_2), 23.7 (CH_2), 24.7 (4 × Me), 26.1 (CH_2), 83.0 (2 × C-O), 134.3 (=CH), 137.1 (–C=), 153.3 (=CH).[32]

EI-MS: *m/z* = 234.1797 (M^+. $C_{14}H_{23}O_2B$ requires 234.1794), 234 (M^+, 54%), 190 (30), 175 (16), 135 (25), 134 (100), 133 (44), 106 (27), 105 (27), 101 (37), 93 (28), 92 (18), 91 (19), 79 (28), 67 (15), 41 (26).

(*E*)-5-Chloro-1-pentenylboronic acid pinacol ester (3f)

Compound **3f** was purified by column chromatography on silica gel (5% ether in hexane).

Yield: 0.83 g (90%, Route I), 0.82 g (89%, Route II); colorless oil.

IR (neat): 2977, 2933, 1639, 1398, 1363, 1323, 1271, 1232, 1145, 997, 970, 848 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 1.85-1.95 (1 H, m, 4-H_2), 2.25-2.35 (1 H, m, 3-H_2), 3.54 (1 H, t, *J* = 6.4 Hz, 5-H_2), 5.48 (1 H, d, *J* = 18.0 Hz, 1-H), 6.58 (1 H, dt, *J* = 18.0 and 6.4 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (4 × Me), 31.0 (CH_2), 32.7 (CH_2), 44.3 (CH_2), 83.1 (2 × C-O), 152.1 (=CH).[32]

EI-MS: *m/z* = 230.1242, 232.1223 (M^+. $C_{11}H_{20}O_2BCl$ requires 230.1247, 232.1220), 232 (M^+, 7%), 230 (M^+, 21%), 217 (27), 215 (85), 214 (19), 195 (40), 153 (100), 152 (24), 146 (17), 144 (49), 111 (19), 109 (24), 95 (21), 85 (33), 69 (75), 67 (24), 59 (21), 43 (20), 42 (20), 41 (44).

(*E*)-3-Methoxy-1-propenylboronic acid pinacol ester (3g)

Compound **3g** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.59 g (74%, Route I), 0.62 g (78%, Route II); colorless oil.

IR (neat): 2980, 2932, 1645, 1474, 1456, 1373, 1348, 1325, 1146, 1124, 972, 851 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 3.35 (3 H, s, OMe), 4.00 (2 H, dd, *J* = 4.6 and 1.8 Hz, 3-H_2), 5.69 (1 H, dt, *J* = 18.0 and 1.8 Hz, 1-H), 6.63 (1 H, dt, *J* = 18.0 and 4.6 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (4 × Me), 58.3 (OCH_3), 74.2 (CH_2), 83.3 (2 × C-O), 149.1 (=CH).[32]

EI-MS: *m/z* = 198.1435 (M^+. $C_{10}H_{19}O_3B$ requires 198.1429), 198 (M^+, 31%), 183 (83), 182 (21), 140 (59), 125 (65), 124 (22), 99 (39), 98 (25), 85 (29), 83 (46), 82 (21), 59 (100), 58 (25), 55 (25), 43 (35), 42 (20), 41 (45).

(*E*)-3-Chloro-1-propenylboronic acid pinacol ester (3h).

Compound **3h** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.54 g (67%, Route I), 0.68 g (84%, Route II); colorless oil.

IR (neat): 2980, 2933, 1641, 1391, 1358, 1329, 1225, 1146, 991, 970, 849 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 4.10 (2 H, dd, *J* = 6.1 and 1.5 Hz, 3-H_2), 5.74 (1 H, dt, *J* = 17.7 and 1.5 Hz, 1-H), 6.64 (1 H, dt, *J* = 17.7 and 6.1 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (4 × Me), 46.1 (CH_2), 83.6 (2 × C-O), 146.6 (=CH).[32]

EI-MS: *m/z* = 204 (M^+, 1%), 202 (M^+, 3%), 189 (32), 187 (100), 186 (24), 167 (86), 159 (48), 153 (36), 125 (22), 105 (26), 103 (83), 85 (54), 82 (28), 81 (98), 80 (69), 68 (23), 59 (26).

(*E*)-3-(Tetrahydro-*2H*-pyran-2-yloxy)-1-propenylboronic acid pinacol ester (3i).

Compound **3i** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.83 g (77%, Route II); colorless oil.

IR (neat): 2977, 2941, 2869, 1645, 1357, 1336, 1323, 1145, 1029, 972, 848 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 1.5-1.9 (6 H, m, ring 3-, 4-, and 5-H_2), 3.45-3.55 (1 H, m, ring 6-H), 3.82-3.90 (1 H, m, ring 6-H), 4.07 (1 H, ddd, *J* = 15.0, 4.9 and 1.8 Hz, 3-H), 4.28-4.36 (1 H, m, 3-H), 4.66 (1 H, t, *J* = 3.4 Hz, ring 2-H), 5.75 (1 H, dt *J* = 18.0 and 1.8 Hz, 2-H), 6.68 (1 H, dt, *J* = 18.0 and 4.6 Hz, 1-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.2 (CH_2), 24.8 (4 × Me), 25.5 (CH_2), 30.5 (CH_2), 61.9 (CH_2-O), 68.2 (CH_2-O), 83.3 (2 × C-O), 97.8 (O-CH-O), 149.3 (=CH).[32]

EI-MS: *m/z* = 169 (M^+-99, 8%), 167 (7), 129 (7), 101 (14), 86 (7), 85 (100), 84 (62), 83 (33), 69 (11), 68 (8), 67 (14), 59 (12), 57 (19), 56 (19), 55 (46), 54 (17), 53 (9).

(*E*)-3-(Methoxymethoxy)-1-propenylboronic acid pinacol ester (3j).

Compound **3j** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.70 g (77%, Route II); colorless oil.

IR (neat): 2979, 2931, 2885, 1645, 1371, 1350, 1323, 1147, 1109, 1062, 1028, 972, 918, 848 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 3.37 (3 H, s, OMe), 4.15 (2 H, dd, *J* = 4.6 and 1.8 Hz, 3-H_2), 4.65 (2 H, s, O-CH_2-O), 5.73 (1 H, dt, *J* = 18.0 and 1.8 Hz, 1-H), 6.65 (1 H, dt, *J* = 18.0 and 4.6 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.8 (4 × Me), 55.3 (Me-O), 68.7 (CH_2-O), 83.3 (2 × C-O), 95.8 (O-CH_2-O), 148.7 (=CH).[32]

EI-MS: *m/z* = 213 (M^+-15, 13%), 183 (49), 167 (19), 153 (21), 143 (21), 129 (25), 125 (26), 101 (37), 98 (22), 97 (31), 85 (51), 84 (34), 83 (82), 82 (42), 81 (26), 70 (42), 69 (40), 68 (41), 67 (52), 59 (100), 58 (44), 57 (76), 55 (50), 54 (22), 53 (17).

(*E*)-3-Acetoxy-1-propenylboronic acid pinacol ester (3k).

Compound **3k** was purified by column chromatography on silica gel (10% ether in hexane).

Yield: 0.70 g (77%, Route II); colorless oil.

IR (neat): 2979, 2933, 1745, 1649, 1230, 1145, 1072, 970, 850 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (12 H, s, 2 × CMe_2), 2.09 (3 H, s, COMe), 4.66 (2 H, dd, *J* = 4.6 and 1.8 Hz, 3-H_2), 5.68 (1 H, d, *J* = 18.3 Hz, 1-H), 6.61 (1 H, dt, *J* = 18.3 and 4.6 Hz, 2-H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8 (Me), 24.8 (2 × CMe_2), 65.5 (CH_2), 83.4 (2 × C-O), 145.9 (=CH),[32] 170.6 (C=O).

EI-MS: *m/z* = 226 (M^+, 1%), 211 (44), 183 (34), 127 (42), 126 (100), 125 (29), 124 (23), 101 (62), 87 (41), 85 (77), 84 (45), 83 (45), 82 (26), 81 (20), 80 (23), 79 (23), 67 (20), 59 (20), 57 (21).

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(27) Dicyclohexylborane was used as a suspension in THF, and thus THF must be removed under reduced pressure in order to get dicyclohexylborane neat. If the residue, given by removal of THF, is white solid, the hydroboration with pinacolborane will proceed without any trouble. But if the residue is viscous liquid, the hydroboration will scarcely proceed.
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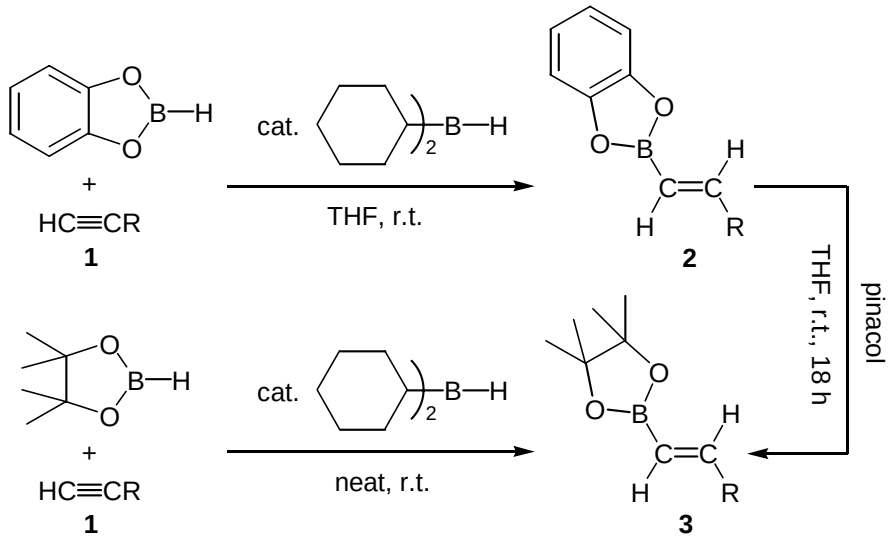
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1
2
THF, r.t., 18 h
pinacol
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neat, r.t.
HC≡CR
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