Highly Stereoselective Syntheses of α,α-Disubstituted *E*- and *Z*-Crotylboronates

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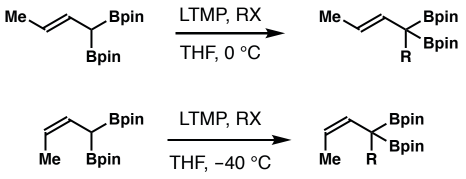
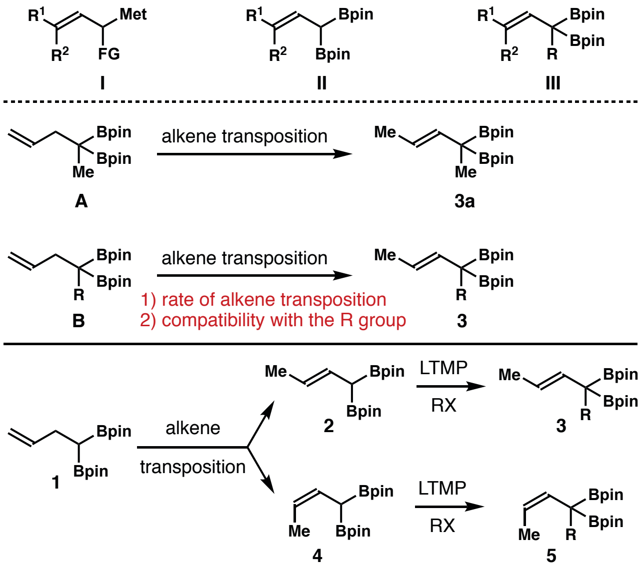
Supporting Information Placeholder



ABSTRACT: We report herein stereoselective syntheses of α,α-disubstituted *E*- and *Z*-crotylboronates. Starting from α-boryl *E*- or *Z*-crotylboronate, base-mediated alkylation occurred exclusively at the position α to the boryl groups to give targeted boronates while retaining the geometry of alkenes in the starting crotylboronates. Under proper conditions, the resulting α,α-disubstituted crotylboronates underwent aldehyde addition to give allylated products with high stereoselectivities.

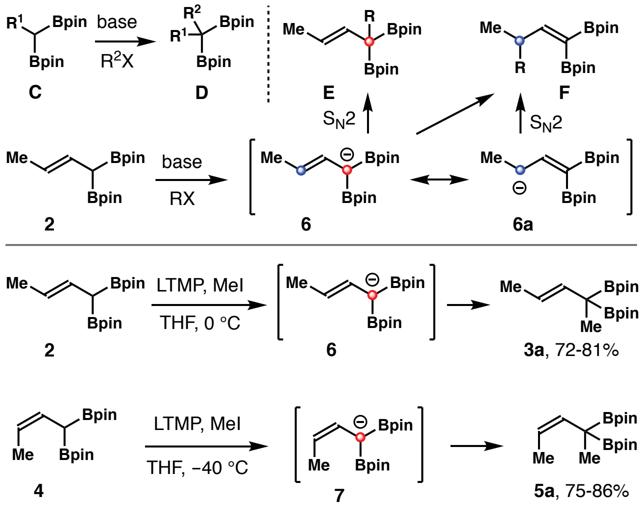
As one of the most adopted methods to form acyclic molecules with contiguous stereogenic centers, aldehyde addition with crotylation reagents has been an intensely studied subject for several decades.[1,2] One emerging topic in this research area is the development of α-functionalized crotylation reagents, e.g. **I** (Scheme 1).[3,4] Compared to the canonical crotylation reaction that forms homoallylic alcohols with a terminal alkene group, the reaction with α-functionalized crotylation reagents **I** generates alcohol products with a functionalized alkene unit, which can be used directly for chain elongation reactions. One drawback of reagents **I**, however, is that they are chiral (when Met ≠ FG); enantioselective preparation of such reagents is often quite challenging.[5] As a subset of α-functionalized crotylation reagents, 1,1-diboryl alkane-derived α-boryl crotylboronates **II** (Scheme 1) have attracted significant attention from the organic synthesis community.[6-9] One significant advantage of reagents **II** is that they are achiral, which greatly simplifies the syntheses of such reagents. As a result, several methods have been developed to allow for the access to reagents **II** with a stereodefined alkene group.[6-9] One logic extension of reagents **II** is α,α-disubstituted crotylboronate **III** (Scheme 1). Aldehyde addition with reagent **III** could form homoallylic alcohol products with a trisubstituted alkene group. Such molecules are challenging to synthesize without resorting to a multistep reaction sequence. However, approaches that permit stereoselective synthesis of reagent **III** are rare.[10] Therefore, it is highly desirable to develop practical methods that could solve this problem.

Scheme 1. Approaches to Stereodefined α,α-Disubstituted Crotylboronates



As shown in Scheme 1, our group recently reported that α, α-disubstituted crotylboronate **3a** can be synthesized through Rh-catalyzed stereoselective alkene transposition from precursor **A**.[10a] The Murakami group also showed that reagent **3a** can be produced *in situ* via alkene transposition from boronate **A**.[10b] For precursor **B** (Scheme 1) where the R group is larger than a methyl group, however, the rate of alkene transposition is significantly slower, likely due to the steric effect from the tetrasubstituted carbon center in **B**. And the *in situ* alkene transposition approach also suffers from undesired product alkene isomerization that led to the formation of a mixture of products.[10b] Moreover, when the R group of precursor **B** is sensitive to the alkene transposition conditions, an allyl group for example, such an alkene transposition approach is likely not feasible to generate reagent **3**. Consequently, it will be of value to develop more general methods that could allow for the access to a broad scope of α,α-disubstituted crotylboronate **3**. As part of our continuing research interests in organoboron compounds,[11] we report herein a simple solution to address the aforementioned challenges. As illustrated in Scheme 1, (*E*)- and (*Z*)-α-boryl crotylboronates, **2** and **4**, were synthesized via highly stereoselective alkene transposition from precursor **1**.[7a,9a] Base-mediated regioselective alkylation of boronates **2** and **4** occurred exclusively at the α-positions to give the targeted boronates **3** and **5** while retaining the alkene geometry of boronates **2** and **4**.

Scheme 2. Initial Studies on Alkylation of α-Boryl *E*- and *Z*-Crotylboronates 2 and 4

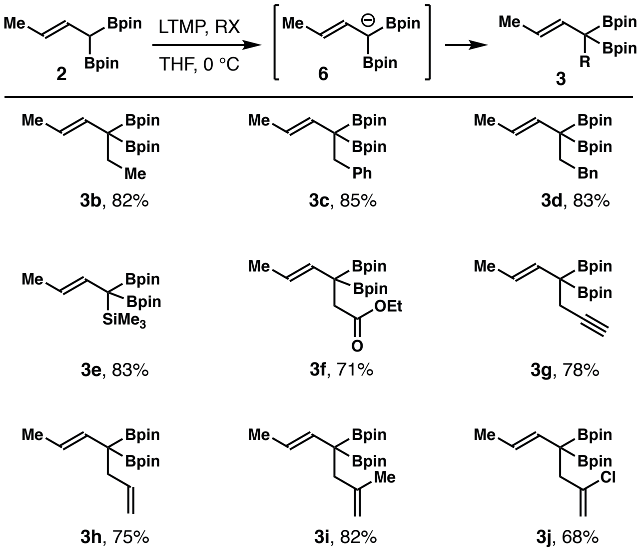


1,1-Bisboryl alkanes such as **C** (Scheme 2) are known to participate in base-mediated alkylation to give boronate products bearing a tetrasubstituted carbon center (e.g., **D**).[12] By contrast, the regioselectivity of the alkylation event for crotylboronate **2** was not immediately apparent at the outset of our studies. It was anticipated that deprotonation of boronate **2** should generate an anion intermediate. And the major resonance form of the anion should be **6** with the charge being localized at the carbon atom α to the two boryl groups, presumably due to the electronic stabilization provided by the neighboring two boron atoms (the boron α-anion effect).[13] Alkylation at the α-position (highlighted in red in **6**) via a direct S_N2 reaction pathway should give the desired boronate **E**, although such a pathway may encounter steric interactions caused by the two Bpin groups. On the other hand, alkylation at the γ-position (highlighted in blue in **6**) will produce undesired vinyl boronate byproduct **F**. A direct S_N2 addition to alkyl halides from the minor resonance structure **6a** could also produce vinyl boronate **F**.

In the event, α-boryl-(*E*)-crotylboronate **2**, prepared from precursor **1** according to the reported procedure,[7a] was treated with LTMP at 0 °C followed by the addition of MeI. To our delight, alkylation of the generated anion with MeI occurred at the α-position exclusively to give boronate **3a**. This operationally simple protocol was also extended to α-boryl-(*Z*)-crotylboronate **4** at −40 °C to form boronate **5a**. In both cases, the reactions occurred via an S_N2 reaction pathway through anion **6** or **7**. And the *E*- or *Z*-olefin geometry of **2** or **4** was perfectly retained during the processes; erosion of the alkene geometry was not detected.

The general applicability of the procedure was explored with α-boryl-(*E*)-crotylboronate **2**, and the results are summarized in Scheme 3. Alkylation with several alkyl halides gave boronates **3b-d** in 82-85% yields. The switch of the alkylating reagent to an electrophilic silane, TMSCl, did not change the reactivity and selectivity of the reaction, affording **3e** in 83% yield. The reaction with ethyl bromoacetate occurred to produce boronate **3f** in 71% yield. Propargylic chloride also participated in the reaction to generate boronate **3g** in 78% yield. The reaction worked well with several allylic halides to deliver boronates **3h-j** in 68-82% yields. In all cases, the alkylation occurred at the α-position of boronate **2**, and only *E*-isomers **3** were obtained from these reactions.

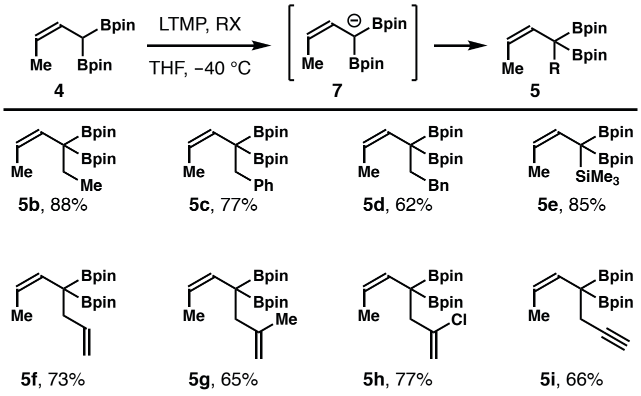
Scheme 3. Scope of α,α-Disubstituted *E*-Crotylboronates via Alkylation of 2 [a-c]



(a) Reaction conditions: boronate **2** (1.0 mmol, 1.0 equiv), LTMP (1.2 mmol, 1.2 equiv), RX (1.5 equiv), THF, 0 °C. (b) *E*/*Z*-selectivities were determined by ^{1}H NMR analysis of the crude reaction products. (c) Yields of isolated products are listed.

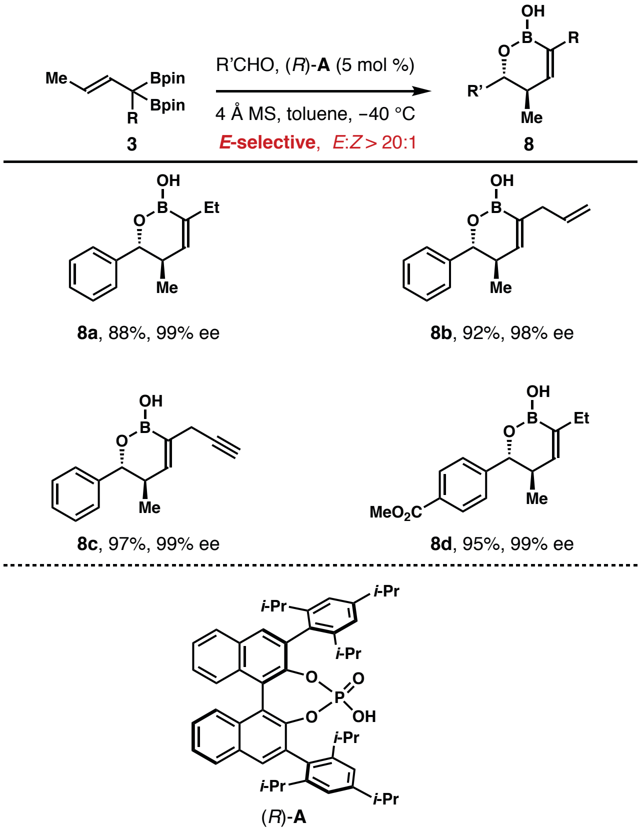
Scheme 4 summarizes the scope of the reaction with α-boryl-(*Z*)-crotylboronate **4**.[9a] A range of alkyl, allylic, propargylic halides and chlorosilane participated in the reactions at −40 °C to give alkylated products **5b-i** in 62-88% yields, presumably via anion **7**. Again, the alkylation occurred with excellent regioselectivities, and the formation of any *E*-isomer was not detected.

Scheme 4. Scope of α,α-Disubstituted *Z*-Crotylboronates via Alkylation of 4[a-c]



(a) Reaction conditions: boronate **4** (1.0 mmol, 1.0 equiv), LTMP (1.2 mmol, 1.2 equiv), RX (1.5 equiv), THF, −40 °C. (b) *E*/*Z*-selectivities were determined by ^{1}H NMR analysis of the crude reaction products. (c) Yields of isolated products are listed.

Scheme 5. Chiral Phosphoric Acid-Catalyzed Asymmetric Aldehyde Addition with *E*-Reagents 3[a-d]

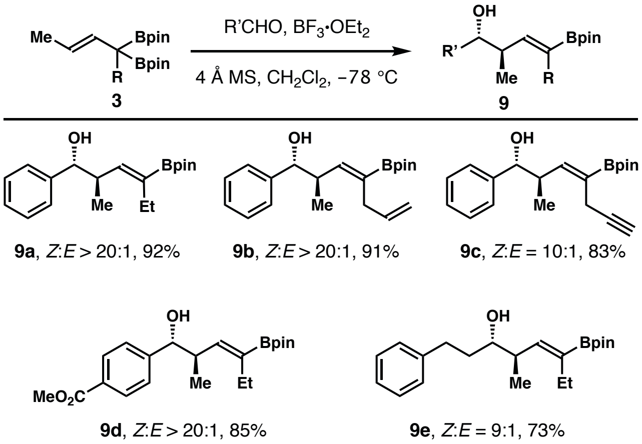


(a) Reaction conditions: boronate **3** (0.13 mmol, 1.3 equiv), aldehyde (0.1 mmol, 1.0 equiv), (*R*)-**A** (5 mol %), 4 Å molecular sieves (50 mg), toluene, −40 °C. (b) *E*/*Z*-selectivities were determined by ^{1}H NMR analysis of the crude reaction products. (c) Yields of isolated products are listed. (d) Enantioselectivities were determined by HPLC analysis of the derivatives obtained from Suzuki coupling.

Aldehyde addition with α,α-disubstituted crotylboronates could form homoallylic alcohol products with a trisubstituted alkene group. And such molecules are challenging to synthesize otherwise.[14] To evaluate whether (*E*)-crotylboronates **3** that we prepared could be utilized for asymmetric aldehyde addition reactions, chiral phosphoric acid (*R*)-**A**-catalyzed reactions with several representative crotylboronates **3** were conducted.[15] As shown in Scheme 5, the reactions were conducted with 5 mol % of chiral phosphoric acid (*R*)-**A** as the catalyst at −40 °C. Asymmetric addition to benzaldehyde with boronate **3b** gave product **8a** in 88% isolated yield with 99% ee and > 20:1 *E*-selectivity. The reaction with boronate **3h** generated *E*-isomer **8b** in 92% yield with 98% ee and excellent *E*-selectivity. The reaction worked well with boronate **3g**, affording product **8c** in 97% yield with 99% ee and > 20:1 *E*-selectivity. Other aldehydes also participated in the reactions. For instance, the reaction of methyl 4-formylbenzoate with boronate **3b** under the standard conditions gave product **8d** in 95% yield with 99% ee and > 20:1 *E*-selectivity. However, the reaction of **3b** with aliphatic aldehydes, hydrocinnamaldehyde for example, gave allylated products with much lower ee. The stereochemical outcomes of these reactions follow the same model as described in our prior report.[10a] It is worth noting that products **8b** and **8c** contain an alkene and an alkyne group, respectively, which provides an additional handle for further functionalization in addition to the boronic acid moiety. Such molecules will unlikely be available via the *in situ* alkene transposition approach.[10b]

α,α-Disubstituted crotylboronates **3** can also be used for aldehyde addition under Lewis acid-catalyzed reaction conditions.[10a] As summarized in Scheme 6, in the presence of Lewis acid BF$_3$•OEt$_2$, crotylation of benzaldehyde with boronate **3b** occurred at −78 °C to deliver product **9a** in 92% isolated yield with > 20:1 *Z*-selectivity. Similar results were obtained with boronate **3h**, affording product **9b** in 91% isolated yield with > 20:1 *Z*-selectivity. Allylation with boronate **3g** proceeded with 10:1 *Z*-selectivity to give homoallylic alcohol **9c** in 83% yield. Other aldehydes, such as methyl 4-formylbenzoate and hydrocinnamaldehyde, reacted with boronate **3b** under the standard conditions to furnish alcohol products **9d** and **9e** in 85% yield with > 20:1 *Z*-selectivity and 73% yield with 9:1 *Z*-selectivity, respectively.

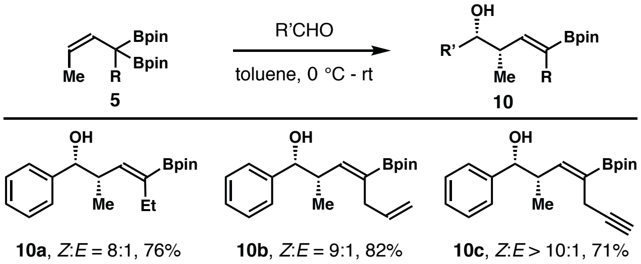
Scheme 6. Lewis Acid-Catalyzed Aldehyde Addition with *E*-Reagents 3[a-c]



(a) Reaction conditions: boronate **3** (0.13 mmol, 1.3 equiv), aldehyde (0.1 mmol, 1.0 equiv), BF$_3$•OEt$_2$ (20 mol %), 4 Å molecular sieves (50 mg), CH$_2$Cl$_2$, −78 °C. (b) *E*/*Z*-selectivities were determined by ^{1}H NMR analysis of the crude reaction products. (c) Yields of isolated products are listed.

Aldehyde addition studies with boronate **5** were conducted next (Scheme 7). In the absence of any catalyst or additive, the reaction of boronate **5b** with benzaldehyde gave allylation product **10a** in 76% yield with 8:1 *Z*-selectivity. Similar results were obtained with boronate **5f**, delivering product **10b** in 82% yield with 9:1 *Z*-selectivity. Boronate **5i** also reacted under the same conditions to give homoallylic alcohol **10c** in 71% yield with > 10:1 *Z*-selectivity.

Scheme 7. Aldehyde Allyl Addition with *Z*-Reagents 5 [a-c]



(a) Reaction conditions: boronate **5** (0.13 mmol, 1.3 equiv), aldehyde (0.1 mmol, 1.0 equiv), CH_2Cl_2, 0 °C to rt. (b) *E*/*Z*-selectivities were determined by ^1H NMR analysis of the crude reaction products. (c) Yields of isolated products are listed.

In summary, we developed a simple protocol to synthesize a variety of α,α-disubstituted *E*- and *Z*-crotylboronates. Base-mediated alkylation of α-boryl *E*- or *Z*-crotylboronate occurred at the α-position exclusively to give the targeted boronates while perfectly retaining the alkene geometry of the starting boronates. The processes allow for rapid generation of diverse α,α-disubstituted crotylboronates from a common intermediate, **2** or **4**. In addition, the obtained *E*-crotylboronates underwent chiral Brønsted acid-catalyzed aldehyde addition to give allylated products **8** with excellent *E*-selectivities and enantioselectivities. Lewis acid-catalyzed aldehyde addition with *E*-crotylboronates **3** worked well to afford homoallylic alcohols **9** with high *Z*-selectivities. In the absence of any catalyst or additive, the reactions of α, α-disubstituted *Z*-crotylboronates **5** with aldehydes proceeded smoothly to give alcohols **10** with good stereoselectivities. Synthetic applications of the method are currently ongoing.

EXPERIMENTAL SECTION

General Experimental Details. Proton nuclear magnetic resonance (^1H NMR) spectra were acquired on commercial instruments (500 and 600 MHz) Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 126 and 151 MHz. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^1H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.36 resonance of $CHCl_3$. Coupling constants are reported in Hz. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer (mass analyzer type: QTOF) via the Micro Mass/Analytical Facility.

General procedure for alkylation of boronate 2: A round-bottomed flask equipped with a magnetic stir bar were added LTMP (1.2 mmol, 1.2 equiv) and anhydrous THF (5 mL). The mixture was cooled to 0 °C and stirred for 5 min. Then a solution of boronate **2** [7a] (1.0 mmol, 1.0 equiv) in THF (1 mL) was added and the resulting mixture was stirred at 0 °C for 30 min. A solution of alkyl halide (1.5 mmol, 1.5 equiv) in THF (1 mL) was added via syringe, and the reaction mixture was kept stirring at 0 °C. After complete consumption of boronate **2** (~1 h), a saturated NH_4Cl solution (5 mL) was added, and the mixture was allowed to warm to ambient temperature. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) provided boronate **3**.

(*E*)-2,2'-(Pent-3-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3a) [10a] Prepared according to the general procedure with MeI. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3a** in 72% yield (232 mg) as yellow solid. A 2-mmol reaction afforded **3a** in 81% yield (522 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 5.81 (dq, *J* = 15.5, 1.5 Hz, 1H), 5.25 (dq, *J* = 15.3, 6.3 Hz, 1H), 1.67 (dd, *J* = 6.3, 1.4 Hz, 3H), 1.22 (s, 12H), 1.21 (s, 12H), 1.17 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 134.0, 120.3, 83.4, 25.0, 24.9, 18.8, 15.7.

(*E*)-2,2'-(Hex-4-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b) Prepared according to the general procedure with EtI. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3b** in 82% yield (276 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.66 (dq, *J* = 15.9, 1.7 Hz, 1H), 5.39 (dq, *J* = 15.8, 6.3 Hz, 1H), 1.74 (q, *J* = 7.4 Hz, 2H), 1.69 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.22 (s, 12H), 1.21 (s, 12H), 0.88 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 131.9, 123.7, 83.3, 25.1, 24.91, 24.85, 19.1, 12.3. HRMS (ESI^+): m/z for $C_{18}H_{35}B_2O_4$ $[M+H]^+$ calcd. 337.2721, found: 337.2718.

(*E*)-2,2'-(1-Phenylpent-3-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3c) Prepared according to the general procedure with BnBr. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3c** in 85% yield (338 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.37 – 7.40 (m, 2H), 7.29 – 7.32 (m, 1H), 5.93 (dq, *J* = 15.8, 1.7 Hz, 1H), 5.64 (dq, *J* = 15.8, 6.4 Hz, 1H), 3.32 (s, 2H), 1.87 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.41 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.3, 132.2, 130.1, 127.8, 125.6, 125.1, 83.6, 37.7, 25.1, 24.9, 19.0. HRMS (ESI^+): m/z for $C_{23}H_{37}B_2O_4$ $[M+H]^+$ calcd. 399.2878, found: 399.2872.

(*E*)-2,2'-(1-Phenylhex-4-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3d) Prepared according to the general procedure with $PhCH_2Br$. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3d** in 83% yield (342 mg) as colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.24 (m, 2H), 7.19 – 7.21 (m, 2H), 7.12 – 7.15 (m, 1H), 5.75 (dq, *J* = 15.7, 1.6 Hz, 1H), 5.49 (dq, *J* = 15.8, 6.4 Hz, 1H), 2.57 – 2.61 (m, 2H), 1.97 – 2.01 (m, 2H), 1.73 (dd, *J* = 6.3, 1.6 Hz, 3H), 1.23 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.3, 131.8, 128.9, 128.4, 125.7, 123.9, 83.5, 34.6 (two overlapping carbon signals), 25.1, 24.9, 19.1. HRMS

(ESI$^+$): m/z for $C_{24}H_{39}B_2O_4$ [M+H]$^+$ calcd. 413.3034, found: 413.3028.

(*E*)-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pent-3-en-1-yl)trimethylsilane (3e) Prepared according to the general procedure with Me_3SiCl. The crude mixture was purified by flash column chromatography to (gradient elution with hexane and EtOAc, 20:1 to 5:1) give compound **3e** in 83% yield (315 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.68 (d, *J* = 15.7 Hz, 1H), 5.27 (dq, *J* = 15.7, 6.3 Hz, 1H), 1.69 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.22 (s, 12H), 1.21 (s, 12H), 0.06 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 129.9, 124.5, 83.0, 25.4, 24.9, 19.2, -0.9. HRMS (ESI$^+$): m/z for $C_{19}H_{39}B_2O_4Si$ [M+H]$^+$ calcd. 381.2804, found: 381.2798.

Ethyl (*E*)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-enoate (3f) Prepared according to the general procedure with ethyl bromoacetate. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3f** in 71% yield (0.2 mmol scale, 56 mg). ^1H NMR (600 MHz, $CDCl_3$) δ 5.79 – 5.82 (m, 1H), 5.22 (dq, *J* = 15.8, 6.3 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 2H), 1.63 (dd, *J* = 6.4, 1.8 Hz, 3H), 1.22 (s, 12H), 1.21 (s, 12H), 1.20 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 174.4, 131.7, 122.0, 83.7, 60.4, 36.9, 25.0, 24.9, 18.8, 14.7. HRMS (ESI$^+$): m/z for $C_{20}H_{37}B_2O_6$ [M+H]$^+$ calcd. 395.2776, found: 395.2786.

(*E*)-2,2'-(Hept-5-en-1-yne-4,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3g) Prepared according to the general procedure with propargylic bromide. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3g** in 78% yield (270 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.78 (dq, *J* = 15.7, 1.7 Hz, 1H), 5.47 (dq, *J* = 15.7, 6.3 Hz, 1H), 2.54 (d, *J* = 2.6 Hz, 2H), 1.85 (t, *J* = 2.6 Hz, 1H), 1.71 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.23 (s, 12H), 1.22 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 130.7, 123.6, 85.4, 83.9, 68.1, 25.0, 24.9, 20.9, 19.0. HRMS (ESI$^+$): m/z for $C_{19}H_{33}B_2O_4$ [M+H]$^+$ calcd. 347.2565, found: 347.2561.

(*E*)-2,2'-(Hepta-1,5-diene-4,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3h) Prepared according to the general procedure with allylic bromide. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3h** in 75% yield (261 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 – 5.85 (m, 1H), 5.67 (dq, *J* = 15.8, 1.7 Hz, 1H), 5.41 (dq, *J* = 15.7, 6.3 Hz, 1H), 4.99 – 5.03 (m, 1H), 4.90 – 4.93 (m, 1H), 2.48 (d, *J* = 6.9 Hz, 2H), 1.68 (dd, *J* = 6.4, 1.5 Hz, 3H), 1.22 (s, 12H), 1.21 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.5, 131.6, 123.8, 115.6, 83.5, 36.1, 25.1, 24.9, 19.0. HRMS (ESI$^+$): m/z for $C_{19}H_{35}B_2O_4$ [M+H]$^+$ calcd. 349.2721, found: 349.2718.

(*E*)-2,2'-(2-Methylhepta-1,5-diene-4,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3i) Prepared according to the general procedure with 2-methyl allylic chloride. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3i** in 82% yield (297 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.83 (dq, *J* = 15.7, 1.7 Hz, 1H), 5.47 (dq, *J* = 15.7, 6.4 Hz, 1H), 4.77 – 4.79 (m, 1H), 4.73 – 4.74 (m, 1H), 2.60 (s, 2H), 1.78 (s, 3H), 1.75 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.32 (s, 12H), 1.31 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.3, 131.5, 123.4, 110.7, 83.5, 39.1, 24.98, 24.96, 24.4, 19.0. HRMS (ESI$^+$): m/z for $C_{20}H_{37}B_2O_4$ [M+H]$^+$ calcd. 363.2878, found: 363.2873.

(*E*)-2,2'-(2-Chlorohepta-1,5-diene-4,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3j) Prepared according to the general procedure with 2-chloroallylic chloride. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **3j** in 68% yield (260 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.69 (dq, *J* = 15.8, 1.6 Hz, 1H), 5.41 (dq, *J* = 15.9, 6.4 Hz, 1H), 5.12 – 5.13 (m, 1H), 5.07 – 5.08 (m, 1H), 2.84 (s, 2H), 1.66 (dd, *J* = 6.4, 1.7 Hz, 3H), 1.22 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.8, 130.0, 124.5, 112.9, 83.8, 41.1, 25.0 (two overlapping carbon signals), 18.9. HRMS (ESI$^+$): m/z for $C_{19}H_{34}ClB_2O_4$ [M+H]$^+$ calcd. 383.2332, found: 383.2326.

General procedure for alkylation of boronate 4: A round-bottomed flask equipped with a magnetic stir bar were added LTMP (1.2 mmol, 1.2 equiv) and anhydrous THF (5 mL). The mixture was cooled to −40 °C and stirred for 5 min. A solution of boronate **4** [9a] (1.0 mmol, 1.0 equiv) in THF (1 mL) was added and the resulting mixture was stirred at −40 °C for 30 min. Then a solution of alkyl halide (1.5 mmol, 1.5 equiv) in THF (1 mL) was added and the reaction mixture was kept stirring at −40 °C. After complete consumption of boronate **4**, a saturated NH_4Cl solution (5 mL) was added, and the mixture was allowed to warm to ambient temperature. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) provided boronate **5**.

(*Z*)-2,2'-(Pent-3-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2 -dioxaborolane) (5a) [10a] Prepared according to the general procedure with MeI. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5a** in 75% yield (242 mg) as yellow solid. A 2-mmol reaction gave **5a** in 86% yield (554 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, *J* = 10.7 Hz, 1H), 5.43 (dq, *J* = 10.8, 7.0 Hz, 1H), 1.60 (d, *J* = 6.9 Hz, 3H), 1.21 (s, 27H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 133.9, 125.7, 83.5, 25.02, 24.98, 18.5, 15.5.

(*Z*)-2,2'-(Hex-4-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2 -dioxaborolane) (5b) Prepared according to the general procedure with EtI. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5b** in 88% yield (296 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.73 (dq, *J* = 10.8, 1.7 Hz, 1H), 5.51 (dq, *J* = 10.8, 7.0 Hz, 1H), 1.78 (q, *J* = 7.4 Hz, 2H), 1.60 (dd, *J* = 7.0, 1.8 Hz, 3H), 1.23 (s, 24H), 0.86 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 131.8, 126.0, 83.5, 26.2, 25.11, 25.06, 15.6, 12.7. HRMS (ESI$^+$): m/z for $C_{18}H_{35}B_2O_4$ [M+H]$^+$ calcd. 337.2721, found: 337.2719.

(*Z*)-2,2'-(1-Phenylpent-3-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5c) Prepared according to the general procedure with BnBr. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give product **5c** in 77% yield (307 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.27 (m, 2H), 7.16 – 7.19 (m, 2H), 7.09 – 7.12 (m, 1H), 5.78 (dq, *J* = 10.7, 1.7 Hz, 1H), 5.54 (dq, *J* = 10.8, 7.0 Hz, 1H), 3.12 (s, 2H), 1.62 (dd, *J* = 7.1, 1.8 Hz, 3H), 1.22 (s, 12H), 1.20 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.5, 131.8, 130.1, 127.8, 126.8, 125.8, 83.8, 38.1, 25.3, 25.1, 15.7. HRMS (ESI^+): m/z for $C_{23}H_{37}B_2O_4$ $[M+H]^+$ calcd. 399.2878, found: 399.2872.

(*Z*)-2,2'-(1-Phenylhex-4-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5d) Prepared according to the general procedure with $BnCH_2Br$. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5d** in 62% yield (255 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.25 (m, 2H), 7.16 – 7.18 (m, 2H), 7.12 – 7.15 (m, 1H), 5.87 (dq, *J* = 10.8, 1.7 Hz, 1H), 5.59 (dq, *J* = 10.8, 7.0 Hz, 1H), 2.55 – 2.58 (m, 2H), 2.04 – 2.07 (m, 2H), 1.66 (dd, *J* = 7.0, 1.8 Hz, 3H), 1.25 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.0, 131.6, 128.9, 128.4, 126.4, 125.7, 83.6, 35.9, 35.1, 25.2, 25.1, 15.7. HRMS (ESI^+): m/z for $C_{24}H_{39}B_2O_4$ $[M+H]^+$ calcd. 413.3034, found: 413.3028.

(*Z*)-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pent-3-en-1-yl)trimethylsilane (5e) Prepared according to the general procedure with Me_3SiCl. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5e** in 85% yield (323 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.73 (dq, *J* = 10.8, 1.7 Hz, 1H), 5.45 (dq, *J* = 10.8, 6.9 Hz, 1H), 1.54 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.23 (s, 24H), 0.10 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 129.8, 123.6, 83.1, 25.5, 25.2, 16.4, -0.5. HRMS (ESI^+): m/z for $C_{19}H_{39}B_2O_4Si$ $[M+H]^+$ calcd. 381.2804, found: 381.2798.

(*Z*)-2,2'-(Hepta-1,5-diene-4,4-diyl)bis(4,4,5,5-tetramethyl -1,3,2-dioxaborolane) (5f) Prepared according to the general procedure with allylic bromide. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5f** in 73% yield (254 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.75 – 5.84 (m, 1H), 5.73 (dq, *J* = 10.8, 1.7 Hz, 1H), 5.52 (dq, *J* = 10.8, 7.0 Hz, 1H), 4.98 – 5.03 (m, 1H), 4.87 – 4.92 (m, 1H), 2.51 (d, *J* = 7.0 Hz, 2H), 1.62 (dd, *J* = 7.0, 1.6 Hz, 3H), 1.23 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.5, 131.5, 126.1, 115.5, 83.6, 37.6, 25.2, 25.1, 15.8. HRMS (ESI^+): m/z for $C_{19}H_{35}B_2O_4$ $[M+H]^+$ calcd. 349.2721, found: 349.2716.

(*Z*)-2,2'-(2-Methylhepta-1,5-diene-4,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5g) Prepared according to the general procedure with 2-methyl allylic chloride. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5g** in 65% yield (235 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (dq, *J* = 10.7, 1.7 Hz, 1H), 5.46 (dq, *J* = 10.8, 7.0 Hz, 1H), 4.68 (s, 1H), 4.67 (s, 1H), 2.58 (s, 2H), 1.68 (s, 3H), 1.63 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.23 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.9, 131.8, 125.6, 110.9, 83.7, 40.5, 25.2, 25.1, 24.0, 15.6. HRMS (ESI^+): m/z for $C_{20}H_{37}B_2O_4$ $[M+H]^+$ calcd. 363.2878, found: 363.2874.

(*Z*)-2,2'-(2-Chlorohepta-1,5-diene-4,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5h) Prepared from 2-chloroallylic chloride according to the general procedure. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5h** in 77% yield (294 mg) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (dq, *J* = 10.9, 1.8 Hz, 1H), 5.52 (dq, *J* = 10.8, 7.0 Hz, 1H), 5.10 (s, 1H), 5.09 (s, 1H), 2.92 (s, 2H), 1.62 (dd, *J* = 7.0, 1.7 Hz, 3H), 1.25 (s, 12H), 1.24 (s, 12H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.1, 129.9, 126.8, 112.8, 84.0, 42.1, 25.2, 25.1, 15.5. HRMS (ESI^+): m/z for $C_{19}H_{34}ClB_2O_4$ $[M+H]^+$ calcd. 383.2332, found: 383.2326.

(*Z*)-2,2'-(Hept-5-en-1-yne-4,4-diyl)bis(4,4,5,5-tetramethyl -1,3,2-dioxaborolane) (5i) Prepared according to the general procedure with propargylic bromide. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 20:1 to 5:1) to give compound **5i** in 66% yield (228 mg) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (dq, *J* = 10.7, 1.7 Hz, 1H), 5.60 (dq, *J* = 10.8, 7.0 Hz, 1H), 2.59 (d, *J* = 2.6 Hz, 2H), 1.86 (t, *J* = 2.6 Hz, 1H), 1.64 (dd, *J* = 7.0, 1.7 Hz, 3H), 1.24 (s, 24H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 131.0, 127.0, 85.3, 84.0, 68.1, 25.1, 25.0, 22.5, 15.5. HRMS (ESI^+): m/z for $C_{19}H_{33}B_2O_4$ $[M+H]^+$ calcd. 347.2565, found: 347.2561.

General procedure for CPA-catalyzed allylboration: To a reaction vial containing a magnetic stirring bar and freshly activated 4 Å MS (50 mg) was added phosphoric acid (*R*)-**A** (4 mg, 0.005 mmol). Then toluene (0.2 mL) was added to the vial followed by dropwise addition of freshly distilled aldehyde (0.1 mmol, if it is a liquid). The reaction via was placed in a −40 °C cold bath and stirred for 15 min. Then allylboronate **3** (0.13 mmol, 1.3 equiv) in toluene (0.1 mL) was added slowly to the reaction mixture via a microliter syringe. The mixture was kept stirring at −40 °C and the reaction progress was monitored by ^1H NMR analysis. After complete consumption of the aldehyde, the reaction was filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and EtOAc, 30:1 to 10:1) to give product **8**. Enantiopurity of **8** was determined by HPLC analysis of the phenylation product derived from Suzuki coupling with PhI.

(5*R*,6*R*)-3-Ethyl-5-methyl-6-phenyl-5,6-dihydro-2*H*-1,2-oxaborinin-2-ol (8a) Prepared according to the general procedure with **3b**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 30:1 to 10:1) to give compound **8a** in 88% yield (19 mg, *E*:*Z* > 20:1) as white solid. Enantiomeric excess of **8a**[10b] was determined by HPLC analysis of the corresponding phenylation derivative (obtained from Suzuki coupling with PhI) to be 99% ee (Chiralpak IE, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1.0 mL/min, I = 254 nm), t_1 = 5.42 min, t_2 = 5.75 min. $[\alpha]_D^{20}$ = +6.2 (c 0.65, CHCl3); ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.38 (m, 5H), 6.30 (s, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 4.06 (s, 1H), 2.57 – 2.65 (m, 1H), 2.13 – 2.25 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 148.4, 142.2, 128.7, 128.3, 127.5, 83.2, 39.6, 26.2, 17.9, 14.2. HRMS (ESI^+): m/z for $C_{13}H_{18}BO_2$ $[M+H]^+$ calcd. 217.1400, found: 217.1393.

(5*R*,6*R*)-3-Allyl-5-methyl-6-phenyl-5,6-dihydro-2*H*-1,2-oxaborinin-2-ol (8b) Prepared according to the general procedure with **3h**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 30:1 to 10:1) to give compound **8b** in 92% yield (21 mg, *E*:*Z* > 20:1) as white solid. Enantiomeric excess of **8b** was determined by HPLC analysis of the corresponding phenylation derivative (obtained from Suzuki coupling with PhI) to be 98% ee (Chiralpak IE, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1.0 mL/min, I = 254 nm), t_1 = 5.39 min, t_2 = 5.64 min. $[\alpha]_D^{20}$ = +4.7 (c 0.85, CHCl3); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 –

7.41 (m, 5H), 6.37 (s, 1H), 5.93 – 6.01 (m, 1H), 5.11 – 5.15 (m, 1H), 5.08 – 5.10 (m, 1H), 4.62 (d, *J* = 10.4 Hz, 1H), 4.23 (s, 1H), 2.92 – 3.02 (m, 2H), 2.62 – 2.70 (m, 1H), 0.92 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 150.6, 142.0, 138.1, 128.7, 128.3, 127.5, 115.8, 83.0, 39.7, 37.8, 17.8. HRMS (ESI$^+$): m/z for $C_{14}H_{18}BO_2$ [M+H]$^+$ calcd. 229.1400, found: 229.1394.

(5*R*,6*R*)-5-Methyl-6-phenyl-3-(prop-2-yn-1-yl)-5,6-dihydro-2*H*-1,2-oxaborinin-2-ol (8c) Prepared according to the general procedure with **3g**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 30:1 to 10:1) to give compound **8c** in 97% yield (22 mg, *E*:*Z* > 20:1) as white solid. Enantiomeric excess of **8c** was determined by HPLC analysis of the corresponding phenylation derivative (obtained from Suzuki coupling with PhI) to be 99% ee (Chiralpak IC, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1.0 mL/min, I = 254 nm), t_1 = 5.67 min, t_2 = 5.90 min. $[\alpha]_D^{20}$ = +5.8 (c 1.00, CHCl3); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.29 – 7.38 (m, 5H), 6.67 (s, 1H), 4.64 (d, *J* = 10.4 Hz, 1H), 4.36 (s, 1H), 3.19 (dd, *J* = 19.6, 2.3 Hz, 1H), 3.12 (dd, *J* = 19.6, 2.3 Hz, 1H), 2.67 – 2.73 (m, 1H), 2.23 (t, *J* = 2.6 Hz, 1H), 0.95 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 150.8, 141.8, 128.7, 128.4, 127.5, 83.0, 82.4, 71.5, 39.7, 22.1, 17.6. HRMS (ESI$^+$): m/z for $C_{14}H_{15}BO_2Na$ [M+Na]$^+$ calcd. 249.1063, found: 249.1058.

Methyl-4-((5*R*,6*R*)-3-ethyl-2-hydroxy-5-methyl-5,6-dihydro-2*H*-1,2-oxaborinin-6-yl)benzoate (8d) Prepared according to the general procedure with **3b**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and EtOAc, 30:1 to 10:1) to give compound **8d** in 95% yield (26 mg, *E*:*Z* > 20:1) as white solid. Enantiomeric excess of **8d** was determined by HPLC analysis of the corresponding derivative (obtained from Suzuki coupling with PhI) to be 99% ee (Chiralpak IC, *i*-PrOH/*n*-hexane = 5/95, flow rate = 1.0 mL/min, I = 254 nm), t_1 = 9.94 min, t_2 = 14.4 min. $[\alpha]_D^{20}$ = +6.3 (c 1.45, CHCl3); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.02 – 8.03 (m, 2H), 7.40 – 7.41 (m, 2H), 6.28 (s, 1H), 4.64 (d, *J* = 10.2 Hz, 1H), 4.23 (s, 1H), 3.92 (s, 3H), 2.53 – 2.60 (m, 1H), 2.13 –2.24 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 167.3, 148.0, 147.3, 130.01, 129.96, 127.5, 82.6, 52.5, 39.7, 26.2, 17.8, 14.1. HRMS (ESI$^+$): m/z for $C_{15}H_{19}BO_4Na$ [M+Na]$^+$ calcd. 297.1274, found: 297.1269.

General procedure for BF_3•OEt_2–catalyzed allylboration of aldehydes with reagents 3: To a reaction flask containing a magnetic stirring bar were added allylboronate **3** (0.13 mmol, 1.3 equiv) and dichloromethane (2 mL). The mixture was cooled in a –78 °C cold bath and stirred for 5 min. A solution of BF_3•OEt_2 (0.5 M in CH_2Cl_2, 40 μL, 0.02 mmol) was added. After stirring for 20 min at –78 °C, freshly distilled aldehyde (0.1 mmol, if it is a liquid) was added slowly to the reaction mixture via a microliter syringe. The mixture was kept stirring at –78 °C until complete consumption of the aldehyde (typically after 12 h). Then saturated aqueous sodium bicarbonate solution (1 mL) and diethyl ether (5 mL) were added. The reaction mixture was allowed to warm to ambient temperature. Brine (5 mL) was added, and the resulting mixture was stirred for another 2 h. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) provided homoallylic alcohol **9**.

***rac*-(1*R*,2*R*,*Z*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-1-ol (9a)** Prepared according to the general procedure with **3b**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **9a** [10b] in 92% yield (29 mg, *Z*:*E* > 20:1) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.37 (m, 4H), 7.27 – 7.31 (m, 1H), 6.18 (d, *J* = 10.0 Hz, 1H), 4.32 (dd, *J* = 8.7, 1.7 Hz, 1H), 2.85 – 2.93 (m, 1H), 2.16 – 2.31 (m, 2H), 2.09 (d, *J* = 1.9 Hz, 1H), 1.28 (s, 12H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.78 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 146.6, 142.7, 128.6, 128.1, 127.5, 83.6, 78.9, 41.7, 25.2, 25.1, 22.7, 17.4, 15.4. HRMS (ESI$^+$): m/z for $C_{19}H_{29}BO_3Na$ [M+Na]$^+$ calcd. 339.2107, found: 339.2102.

***rac*-(1*R*,2*R*,*Z*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-3,6-dien-1-ol (9b)** Prepared according to the general procedure with **3h**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **9b** in 91% yield (30 mg, *Z*:*E* > 20:1) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.36 (m, 4H), 7.27 – 7.30 (m, 1H), 6.29 (d, *J* = 10.0 Hz, 1H), 5.85 – 5.93 (m, 1H), 5.01 (dd, *J* = 17.1, 1.9 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.34 (dd, *J* = 8.7, 2.1 Hz, 1H), 2.94 – 3.04 (m, 2H), 2.84 – 2.92 (m, 1H), 2.08 (d, *J* = 2.2 Hz, 1H), 1.27 (s, 12H), 0.77 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 148.4, 142.7, 137.9, 128.6, 128.1, 127.4, 114.7, 83.7, 78.9, 41.9, 33.5, 25.2, 25.1, 17.2. HRMS (ESI$^+$): m/z for $C_{20}H_{33}BO_3N$ [M+NH$_4$]$^+$ calcd. 346.2553, found: 346.2549.

***rac*-(1*R*,2*R*,*Z*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-3-en-6-yn-1-ol (9c)** Prepared according to the general procedure with **3g**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **9c** in 83% yield (27 mg, *Z*:*E* = 10:1) as yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 – 7.36 (m, 4H), 7.26 – 7.31 (m, 1H), 6.34 (d, *J* = 10.1 Hz, 1H), 4.38 (dd, *J* = 8.6, 2.8 Hz, 1H), 2.97 – 3.12 (m, 3H), 2.19 (d, *J* = 3.0 Hz, 1H), 1.98 (t, *J* = 2.7 Hz, 1H), 1.29 (s, 12H), 0.82 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 150.2, 142.8, 128.7, 128.1, 127.4, 84.07, 84.06, 79.0, 68.5, 42.2, 25.2, 25.1, 18.1, 17.0. HRMS (ESI$^+$): m/z for $C_{20}H_{28}BO_3$ [M+H]$^+$ calcd. 327.2132, found: 327.2127.

***rac*-Methyl-4-((1*R*,2*R*,*Z*)-1-hydroxy-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-1-yl)benzoate (9d)** Prepared according to the general procedure with **3b**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **9d** in 85% yield (32 mg, *Z*:*E* > 20:1) as yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.98 – 8.02 (m, 2H), 7.40 – 7.43 (m, 2H), 6.14 (d, *J* = 9.9 Hz, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 2.83 – 2.90 (m, 1H), 2.16 – 2.27 (m, 3H), 1.28 (s, 12H), 0.96 (t, *J* = 7.6 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 167.4, 147.9, 145.7, 129.88, 129.85, 127.5, 83.7, 78.4, 52.4, 41.6, 25.2, 25.1, 22.7, 17.3, 15.4. HRMS (ESI$^+$): m/z for $C_{21}H_{31}BO_5Na$ [M+Na]$^+$ calcd. 397.2162, found: 397.2157.

***rac*-(3*S*,4*R*,*Z*)-4-Methyl-1-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-5-en-3-ol (9e)** Prepared according to the general procedure with **3b**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **9e** in 73% yield (25 mg, *Z*:*E* = 9:1) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.26 – 7.31 (m, 2H), 7.16 – 7.22 (m, 3H), 6.08 (d, *J* = 10.0 Hz, 1H), 3.37 – 3.41 (m, 1H), 2.83 – 2.89 (m, 1H), 2.63 – 2.71 (m, 2H), 2.12 – 2.22 (m, 2H), 1.83 – 1.90 (m, 1H), 1.67 – 1.73 (m, 1H), 1.61 (dd, *J* = 3.5, 1.0 Hz, 1H), 1.26 (s, 12H), 0.94 – 0.97 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 146.2, 142.7, 128.9, 128.7, 126.1, 83.5, 74.7, 39.4, 36.2, 32.4, 25.2, 25.1, 22.6, 17.3, 15.5. HRMS (ESI$^+$): m/z for $C_{21}H_{33}BO_3Na$ [M+Na]$^+$ calcd. 367.2420, found: 367.2415.

General procedure for allylboration of aldehydes with reagents 5: To a reaction flask containing a magnetic stirring bar were added allylboronate **5** (0.13 mmol, 1.3 equiv), toluene (0.3 mL) and freshly distilled aldehyde (0.1 mmol, if it is a liquid) at 0 °C. The reaction mixture was allowed to warm to ambient temperature and was kept stirring until complete consumption of the aldehyde (typically after 36 h). Then saturated aqueous sodium bicarbonate solution (1 mL), diethyl ether (2 mL) and brine (2 mL) were added to the flask; and the resulting mixture was kept stirring for 30 min at ambient temperature. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) gave product **10**.

***rac*-(1*R*,2*S*,*Z*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-1-ol (10a)** Prepared according to the general procedure with **5b**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **10a** in 76% yield (24 mg, *Z*:*E* = 8:1) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.26 – 7.27 (m, 2H), 7.17 – 7.22 (m, 3H), 6.10 (d, *J* = 9.9 Hz, 1H), 4.57 (dd, *J* = 5.9, 3.9 Hz, 1H), 2.85 – 2.92 (m, 1H), 1.92 – 2.06 (m, 2H), 1.88 (d, *J* = 4.0 Hz, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.77 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 146.4, 143.5, 128.3, 127.6, 126.7, 83.4, 78.1, 40.4, 25.2, 24.9, 22.4, 15.8, 15.1. HRMS (ESI$^+$): m/z for $C_{19}H_{29}BO_3Na$ [M+Na]$^+$ calcd. 339.2107, found: 339.2102.

***rac*-(1*R*,2*S*,*Z*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-3,6-dien-1-ol (10b)** Prepared according to the general procedure with **5f**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **10b** in 82% yield (27 mg, *Z*:*E* = 9:1) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.25 – 7.29 (m, 4H), 7.18 – 7.23 (m, 1H), 6.23 (d, *J* = 10.1 Hz, 1H), 5.72 (ddt, *J* = 16.2, 10.1, 6.0 Hz, 1H), 4.82 – 4.88 (m, 2H), 4.59 (dd, *J* = 5.6, 4.0 Hz, 1H), 2.84 – 2.91 (m, 1H), 2.72 – 2.82 (m, 2H), 1.91 (d, *J* = 4.1 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 0.97 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 148.3, 143.3, 137.9, 128.3, 127.6, 126.7, 114.4, 83.5, 77.8, 40.6, 33.2, 25.1, 24.9, 15.4. HRMS (ESI$^+$): m/z for $C_{20}H_{33}BO_3N$ [M+NH$_4$]$^+$ calcd. 346.2553, found: 346.2548.

***rac*-(1*R*,2*S*,*Z*)-2-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-3-en-6-yn-1-ol (10c)** Prepared according to the general procedure with **5i**. The crude mixture was purified by flash column chromatography (gradient elution with hexane and ethyl acetate, 20:1 to 5:1) to give compound **10c** in 71% yield (23 mg, *Z*:*E* > 10:1) as white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.23 – 7.28 (m, 3H), 7.16 – 7.20 (m, 2H), 6.22 (d, *J* = 10.1 Hz, 1H), 4.64 (apps. t, *J* = 4.6 Hz, 1H), 2.96 – 3.03 (m, 1H), 2.77 – 2.85 (m, 2H), 1.92 (d, *J* = 4.0 Hz, 1H), 1.87 (t, *J* = 2.8 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 0.98 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 149.8, 143.1, 128.4, 127.7, 126.7, 84.0, 83.9, 77.6, 68.2, 41.0, 25.2, 24.9, 17.9, 15.0. HRMS (ESI$^+$): m/z for $C_{20}H_{31}BO_3N$ [M+NH$_4$]$^+$ calcd. 344.2397, found: 344.2392.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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