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Copper(II)-catalyzed protoboration of allenes in aqueous media and open air†

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A method has been developed for the facile Cu(II)-catalyzed protoboration of monosubstituted allenes in aqueous media under atmospheric conditions. The reaction occurs site selectively, favoring internal alkene protoboration to afford 1,1-disubstituted vinylboronic acid derivatives (up to 93 : 7) with modest to good yields. The method has been applied to a variety of phenylallene derivatives as well as alkyl-substituted allenes.

Introduction

Methods for the synthesis of vinyl organoboron compounds are in demand due to their versatility as substrates in a wide variety of functionalizations, and capability to engage in various cross-coupling reactions[1] – most notably, Suzuki–Miyaura coupling.[2] Methods for transition metal-catalyzed hydroboration[3] reactions have been developed for the efficient synthesis of viable cross-coupling partners. These hydroboration reactions typically occur *via* formation of a boron-ligated metal complex, which adds in a concerted *cis* fashion across a double or triple carbon–carbon bond.

Vinylboronic acid derivatives are typically synthesized through effective hydroboration[2a,3a,4] or diboration[4b,c,5] of electron rich alkynes or allenes, either by addition of a borane or use of a suitable diboron compound in conjunction with a proton source (*e.g.* methanol). Because six plausible hydroboration products may be formed, allenes are both a versatile and challenging substrate to borylate since regio- and stereoselectivity must be tightly controlled. Furthermore, allenes often lack a strong electron-withdrawing moiety to encourage and direct metal–boron addition to specific positions in transition metal-catalyzed protoboration reactions. However, several examples have been reported in which monosubstituted allenes can be converted to boronic acid derivatives with varying degrees of regioselectivity.[6] Under classical conditions,[7] the hydroboration of allene double bonds is achieved with the typical anti-Markovnikov regioselectivity. Miyaura *et al.* later developed a platinum-catalyzed hydroboration reaction[8] with ligand-controlled regio- and stereoselectivity. More recently, Ma[9] (using phosphine ligands, Fig. 1a) and Hoveyda[10] (using NHC ligands, Fig. 1b) both developed Cu(I)-catalyzed protoboration reactions of monosubstituted allenes. In latter, the site selectivity was ligand-controlled; decreasing ligand bulk altered selectivity from terminal to internal alkene protoboration. The strict ligand control of the reactions as well as the use of relatively inexpensive/environmentally friendly copper catalysts make these methods quite valuable. The site selectivity of both methods was dictated by whether or not the putative Cu–B insertion intermediate underwent isomerization to a more reactive form prior to protonation by a protic additive, *e.g.* methanol (Curtin–Hammett kinetics, *vide infra*). Later, Semba *et al.* demonstrated an allene protoboration using pinacolborane, which was purported to occur through formation of a Cu(I)-hydridic intermediate (Fig. 1c).[6] Finally, Hoveyda developed an enantioselective protoboration of disubstituted allenes that was achieved by the combination of chiral ligand–copper complex with bulky alcohol (Fig. 1d).[11]

Previous work in our group demonstrated the Cu(II)-catalyzed protoboration of α,β-unsaturated ketones with amine additives and bis(pinacolato)diboron in aqueous, open-to-air conditions.[12] Through base-assisted activation of water, an sp^2–sp^3 diboron reagent was generated *in situ*, allowing for transmetallation to form boron-ligated copper and subsequent addition across the carbon–carbon double bond. This facile borylation protocol has since been extended[13] to include other substrates, such as alkynoic esters and amides,[4d] α,β-unsaturated nitriles,[14] and imines.[15] However, these methods are restricted to polarized, electron-deficient π-bonds, which drive selectivity. Most recently, functionalization of allenes producing 1,3-butadienes in aqueous media in the presence of palladium was disclosed.[3l] Herein, we present the extension of this facile and mild protocol to monosubstituted allenes and demonstrate site selectivity *via* ligand control under mild, environmentally friendly conditions (Fig. 1e).

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† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C, and ^{11}B spectra for all vinylboronic acid derivative products. See DOI: 10.1039/d0nj02010a

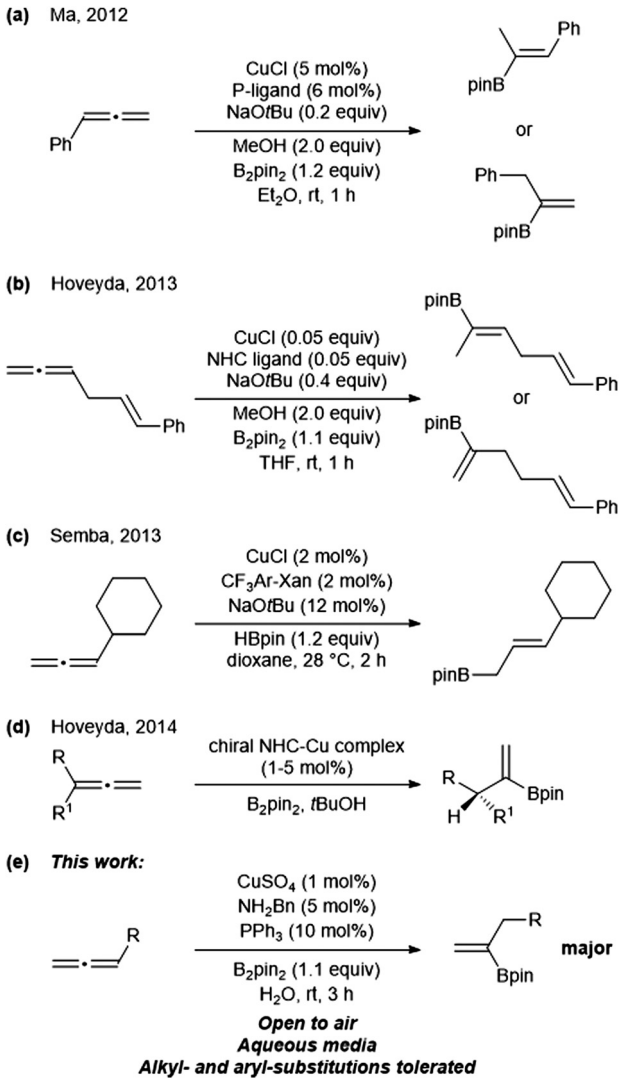
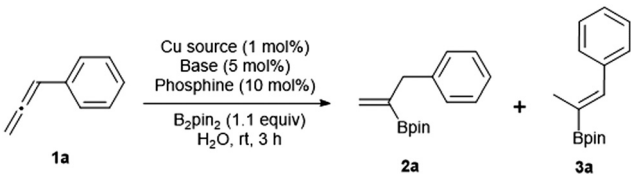


Fig. 1 Cu(I)-catalyzed and ligand-controlled methods for allene protoboration.

Results and discussion

Using phenylallene **1a** as the optimization substrate, we first tested conditions similar to those previously-developed for Cu(II)-catalyzed β-borylation of α,β-unsaturated ketones. These conditions employ an amine as a Brønsted base, copper source, ligand, and bis(pinacolato)diboron. As shown in Table 1 (entries 1–5), several bases that were highly effective in the hydroboration of other substrates[6,9,10,12] were unsuitable for allene protoboration. Benzylamine proved most effective, affording borylation product in 24% yield with moderate selectivity (entry 5). Based on previous work by Ellman *et al.*, which demonstrated increased yields with use of phosphine ligands in aqueous imine borylations,[15b] we tested the effect of 10 mol% PCy_3 additive on the reaction outcome and were gratified to find both an increase in yield (65% combined) and site selectivity 77% for terminal protoboration to afford **3a** (entry 6). Since the relative insolubility of the starting materials in water might account for the low yields, we tested the effect of surfactant (TPGS-750-M) on the reaction.

Table 1 Optimization of reaction conditions



Entry	Base	Cu source	Ligand	% yield[b] (**2a** : **3a**)
1[a]	4-Picoline	$CuSO_4$	None	10 (34 : 66)
2[a]	Proton sponge	$CuSO_4$	None	13 (40 : 60)
3[a]	DMAP	$CuSO_4$	None	9 (30 : 70)
4[a]	NaOAc	$CuSO_4$	None	16 (38 : 62)
5[a]	NH_2Bn	$CuSO_4$	None	24 (35 : 65)
6[a]	NH_2Bn	$CuSO_4$	PCy_3	65 (23 : 77)
7[ac]	NH_2Bn	$CuSO_4$	PCy_3	49 (21 : 79)
8[a]	NH_2Bn	None	PCy_3	0
9[ad]	None	$CuSO_4$	PCy_3	68 (33 : 67)
10	NH_2Bn	$CuSO_4$	DPEPhos	52 (46 : 54)
11	NH_2Bn	$CuSO_4$	Sphos	63 (81 : 19)
12	NH_2Bn	$CuSO_4$	PPh_3	78 (87 : 13)
13	NH_2Bn	$CuSO_4$	PCy_3	63 (31 : 69)
14	NH_2Bn	$Cu(acac)_2$	PPh_3	60 (85 : 15)
15	NH_2Bn	$Cu(BF_4)_2$	PPh_3	53 (77 : 23)
16	NH_2Bn	$C_{10}H_6CuN_4O_4$	PPh_3	32 (81 : 19)
17	NH_2Bn	$Cu(OH)_2$	PPh_3	19 (76 : 24)
18[e]	NH_2Bn	$CuSO_4$	PPh_3	50 (74 : 26)
19[e]	NH_2Bn	$CuSO_4$	PCy_3	57 (27 : 73)
20[f]	NH_2Bn	$CuSO_4$	PCy_3	52 (30 : 70)
21[f]	NH_2Bn	$CuSO_4$	PPh_3	36 (64 : 36)

[a] 1.5 equiv. B_2pin_2 used. [b] Yields were determined by ^1H NMR analysis of the crude reaction mixture after extraction. [c] 1% surfactant TPGS-750-M used. [d] 6 hours. [e] 4 : 1 water : toluene mixture used as solvent. [f] 4 : 1 toluene : water mixture used as solvent. $C_{10}H_6CuN_4O_4$ = Cu(II) 2-pyrazinecarboxylate.

Lipshutz *et al.*[16] demonstrated that micellar catalysis mediated by this surfactant enabled copper-catalyzed silylation reactions; however, no improvement in yield was observed (entry 7). Fernandez reported a phosphine-catalyzed protocol[17] for the hydroboration of α,β-unsaturated ketone, thus we performed a control experiment without $CuSO_4$ (entry 8) and discovered that the reaction was indeed copper catalyzed. We also tested the reaction efficiency *sans* benzylamine, which furnished the product in good yield and selectivity. Additionally, the reaction time was increased by several hours due to what appeared to be a long induction time (entry 9). With the increased reactivity accompanying phosphine addition, we noted through GC analysis that the 1,1-disubstituted vinylboronate product could be protoborated for second time. This hypothetically would result in a decrease of product yield as well as affect apparent selectivity by diminishing amount of product **2a**. To circumvent this, we adjusted the quantity of B_2pin_2 to 1.1 equivalents, which significantly minimized this side product. Among the four phosphine ligands tested (entries 10–13), SPhos and PPh_3 performed equally well for selection of the desired vinyl boronate product **2a**. However, neither yield nor selectivity were improved. Thus, we chose triphenylphosphine for further studies and restricted our attention solely to product **2a**. A short screening of various copper sources (entries 14–17) demonstrated that many copper(II) derivatives could function effectively as catalysts, although $CuSO_4$ worked the best. The effect of toluene as

co-solvent was tested for both systems containing PPh_3 and PCy_3 (entries 18–21). This was to evaluate whether (1) increased solvation of the reactants by toluene would affect the selectivity and yield and (2) reducing the amount of water in the system would allow time for borylcuprate intermediate isomerization before protonation, thus affecting selectivity.

With our best conditions (entry 12) in hand for formation of product **2a**, we applied the protocol to determine the substrate scope of the reaction (Fig. 2). Phenylallene derivatives bearing *para* alkyl substitutions (**2b–2c**) demonstrated ~90 : 10 isomeric ratio favoring the 1,1-disubstituted vinylboronic ester product, with a reduction in yield observed with the *p*-^{t}Bu-substituted allene. Derivatives bearing a chlorine at the *ortho*, *meta*, or *para* positions underwent protoboration in good yield and high selectivity, regardless of position on the phenyl ring (**2d–2f**). A *p*-trifluoromethyl or *p*-fluoro substitution (**1g–1h**) reduced protoboration efficiency but selectivity remained (93% and >83% alkene selectivity, respectively). Interestingly, phenylallene derivatives with strong electron-donating groups (**2i–2k**) had reduced yields and selectivities. However, both the allyloxy and benzyloxy protecting groups were well-tolerated in this reaction.

Since the presence of a phenyl group may provide stabilization to the partial negative charge of the Cu–C bond in the proposed intermediates (*vide infra*), it was of interest to determine if alkyl-substituted allenes were suitable substrates. The reaction performed well for cyclohexylallene (**1l**) and moderately well for alkyl ethers (**1m–1n**). In the case of long alkyl chain allenes, there appeared to be solubility issues and very low conversions when run under typical conditions. It was found that use of 25% toluene as a co-solvent resulted in moderate to good yield with minimal effects on selectivity of the reaction (**2o–2q**).

Based on the results, we believe the mechanism proceeds as described previously by Hoveyda and coworkers (Fig. 3).[10] The initial step is Brønsted base-assisted deprotonation of a water molecule (**4**) and formation of an activated sp^3-hybridized boronate **5**.[12a] Transmetallation forms a copper boron complex **6** that coordinates to the terminal (**7**) or internal (**8**) double bond of the allene to afford allylcopper species **9** and **10**, respectively. The large triphenylphosphine ligand promotes preferential binding of the copper complex on the terminal double bond leading to chair-like transition state **11** to generate 1,1-substituted vinylboronic acid derivative **12** as the major product. In contrast, insertion of the Cu–B species on the internal alkene followed by protonation *via* **13** leads to trisubstituted vinyl boronic ester **14**. We suspect that equilibration between **9** and **10** is minimized and leads to rapid protonation because the solvent itself acts a proton source. Thus, the isomeric ratio of borylation products reflects the ratio of intermediates **9** and **10**, which is supported by the observation that a decrease in selectivity occurs with electron donating substituents where the more electron rich double bond increases binding with copper.

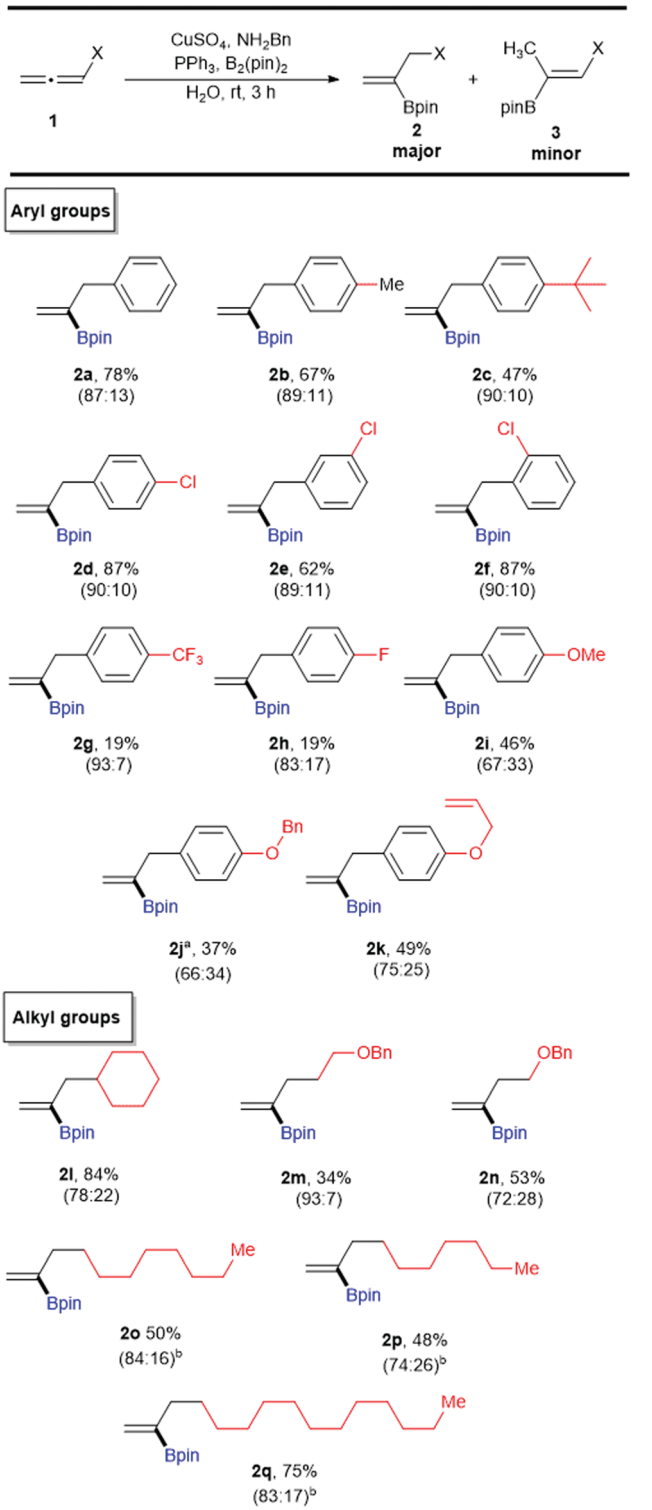


Fig. 2 Substrate scope of the protoboration reaction. Conditions: allene **1** (1 equiv.), $BnNH_2$ (5 mol%), PPh_3 (10 mol%), B_2pin_2 (1.1 equiv.), $CuSO_4$ (1 mol%). [a] 1% TPGS-750-M used. [b] 3 : 1 toluene : water used as solvent.

Conclusions

In conclusion, we have described the first Cu(II)-catalyzed protoboration reaction of allenes in aqueous media. The reaction performs moderately well for a variety of monosubstituted allenes and is a first step for application of environmentally friendly methodologies to the borylation of relatively inactivated carbon–carbon unsaturated bonds.

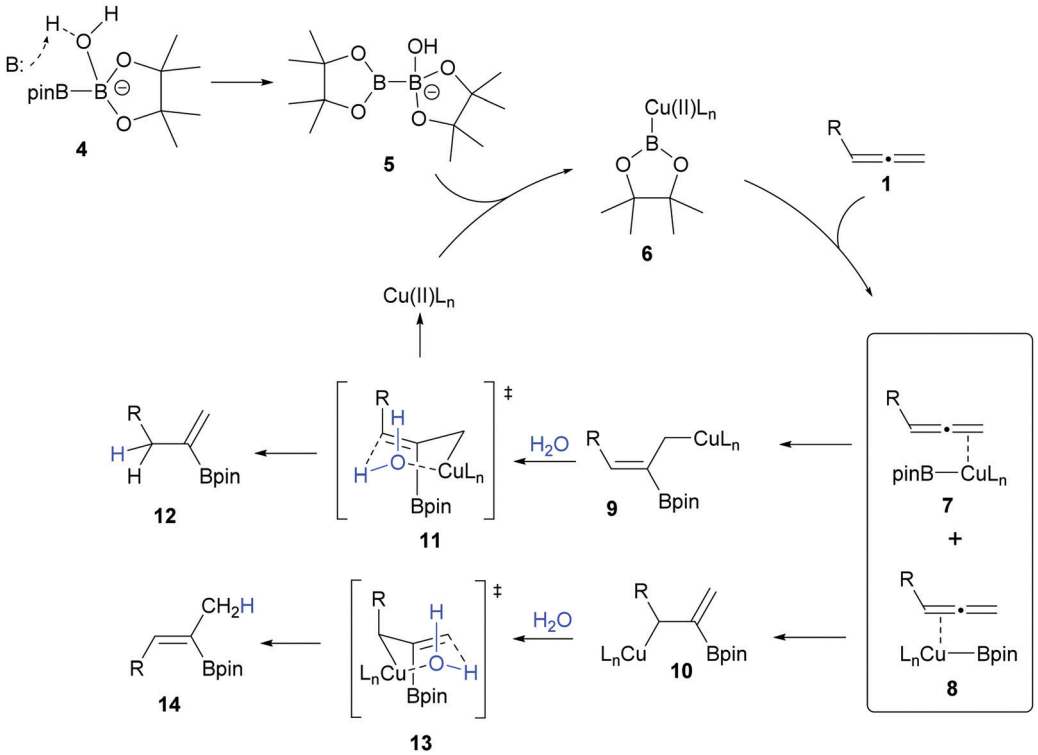


Fig. 3 Proposed mechanism for the Cu(II)-catalyzed protoboration.

Experimental

General experimental details

Synthesis of allenes and their precursors[5b,e] were carried out under an inert atmosphere of nitrogen. All borylation reactions were carried out under atmospheric conditions. NMR spectra were obtained on Bruker 500 MHz spectrometer at 500 (^{1}H) and 125 (^{13}C) MHz or Unity-plus 400 at 400 (^{1}H) and 100 (^{13}C) MHz. The chemical shifts are reported in δ (ppm), and coupling constants are given in Hz. * indicates minor isomer. High-resolution ESI mass spectra were obtained on an Agilent 6220 accurate mass TOF LC/MS. Low-resolution EI mass spectra were obtained on a 5977A Series GC/MSD system. Column chromatography was performed using Silica gel (ZEOprep 60 ECO 40-63. TLC analyses were performed using Agela Technologies silica gel MF254 plates or Silicycle aluminum backed silica gel F-254 plates and spots were visualized with UV light and $KMnO_4$ stain.

General procedure for synthesis of vinylboronic acid derivatives

To a 2-dram vial equipped with a small stir bar was added allene, bis(pinacolato)diboron (1.1 equiv.), benzylamine (5 mol%), and triphenylphosphine (10 mol%). Milli-Q water and $CuSO_4$ solution (1.3 mg mL^{-1}, dispensed to add 1 mol% Cu) were added in equal volume amounts to the mixture, and the dark reaction mixture was allowed to stir until completion (typically 3 h) as monitored by GC or TLC. Upon completion, chloroform was added to the reaction mixture, and the water layer was extracted 3× with chloroform. After removal of the solvent *in vacuo*, the resulting yellow residue was purified by flash chromatography (0–4% EtOAc in hexanes) affording the final products as off-yellow oils.

4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (2a) and (*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (3a). Synthesized by general procedure, isolated as an off yellow oil, 78% yield, 87 : 13 isomeric ratio **2a** to **3a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.08 (m, 5H), 5.76 (d, J = 2.8 Hz, 1H), 5.45 (s, 1H), 3.41 (s, 2H), 1.92* (d, J = 1.4 Hz, 3H), 1.23* (s, 12H), 1.13 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5*, 140.8, 129.9, 129.5*, 129.3, 129.3*, 128.2, 128.2*, 127.2*, 125.8, 83.6*, 83.6, 41.5, 25.0*, 24.8, 16.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.09. EI-MS: $[M]^+$. Calcd for $C_{15}H_{21}BO_2$ 244.16, observed 244.1.

4,4,5,5-Tetramethyl-2-(3-(*p*-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (2b) and (*Z*)-4,4,5,5-tetramethyl-2-(1-(*p*-tolyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3b). Synthesized by general procedure, isolated as an off yellow oil, 67% yield, 89 : 11 isomeric ratio of **2b** to **3b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31* (d, J = 7.9 Hz, 2H), 7.23* (s, 1H), 7.16* (d, J = 7.8 Hz, 2H), 7.11–7.07 (m, 4H), 5.84 (s, 1H), 5.52 (s, 1H), 3.45 (s, 3H), 2.36* (s, 3H), 2.32 (s, 3H), 2.01* (s, 3H), 1.33* (s, 12H), 1.24 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5*, 137.7, 137.0*, 135.3*, 135.2, 129.8, 129.6*, 129.1, 128.9, 128.9*, 83.6, 83.6*, 41.00, 25.00*, 24.9, 21.4*, 21.1, 16.1*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16. EI-MS: $[M]^+$ calcd for $C_{16}H_{23}BO_2$ 258.18, observed 258.3.

2-(3-(4-(*tert*-Butyl)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c) and (*Z*)-2-(1-(4-(*tert*-butyl)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c). Synthesized by general procedure, isolated as off yellow oil, 47% yield,

90 : 10 isomeric ratio of **2c** to **3c**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33* (q, J = 8.6 Hz, 4H), 7.24 (d, J = 4.2 Hz, 2H), 7.18* (s, 1H), 7.10 (d, J = 7.9 Hz, 2H), 5.79 (s, 1H), 5.49 (s, 1H), 3.42 (s, 2H), 1.98* (s, 3H), 1.30* (s, 9H), 1.29* (s, 12H), 1.27 (s, 9H), 1.19 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2*, 148.6, 142.4*, 137.7, 129.8, 129.4*, 128.9, 125.1, 83.6, 40.9, 34.7*, 34.5, 31.6, 31.4*, 25.0*, 24.8, 16.2*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.07. EI-MS: $[M]^+$. Calcd for $C_{19}H_{29}BO_2$ 300.23, observed 300.3.

2-(3-(4-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d) and (*Z*)-2-(1-(4-chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d). Synthesized by general procedure **4**, isolated as yellow oil, 87% yield, 90 : 10 isomeric ratio **2d** to **3d**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31* (s, 4H), 7.22 (d, J = 8.1 Hz, 2H), 7.17* (s, 1H), 7.12 (d, J = 8.1 Hz, 2H), 5.83 (s, 1H), 5.53 (s, 1H), 3.43 (s, 2H), 1.96* (s, 3H), 1.31 (s, 12H), 1.21 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1*, 139.4, 131.6, 130.8*, 130.6, 130.3, 128.4*, 128.3, 83.7, 41.00, 25.0*, 24.9, 16.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.92. EI-MS: $[M]^+$. Calcd for $C_{15}H_{20}BClO_2$ 278.12, observed 278.1.

2-(3-(3-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) and (*Z*)-2-(1-(4-chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e). Synthesized by general procedure, isolated as yellow oil, 62% yield, 89 : 11 isomeric ratio **2e** to **3e**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16–6.96 (m, 4H), 5.77 (d, J = 2.3 Hz, 1H), 5.48 (s, 1H), 3.36 (s, 2H), 1.92–1.86* (m, 3H), 1.23* (s, 12H), 1.13 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 140.9*, 133.9, 130.5, 129.4, 129.4, 127.6*, 127.4, 127.2*, 126.0, 83.7, 41.4, 25.0*, 24.8, 16.0*. EI-MS: $[M]^+$. Calcd for $C_{15}H_{20}BClO_2$ 278.12, observed 278.1.

2-(3-(2-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2f) and (*Z*)-2-(1-(2-Chlorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f). Synthesized by general procedure, isolated as yellow oil, 87% yield, 90 : 10 isomeric ratio **2f** to **3f**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44–7.12 (m, 4H), 5.92 (s, 1H), 5.47 (s, 1H), 3.62 (s, 2H), 1.89* (s, 3H), 1.35 (s, 12H), 1.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4*, 138.41, 136.2*, 134.5, 133.7*, 131.3, 130.8*, 130.7, 129.5*, 129.4, 128.4*, 127.4, 126.6, 126.1*, 83.7, 38.2, 25.00*, 24.9, 16.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.05. EI-MS: $[M]^+$. Calcd for $C_{15}H_{20}BClO_2$ 278.12, observed 278.1.

4,4,5,5-Tetramethyl-2-(3-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (2g) and (*Z*)-4,4,5,5-Tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (3g). Synthesized by general procedure, isolated as a yellow oil, 19% yield, 93 : 7 isomeric ratio **2g** to **3g**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 5.80 (d, J = 3.0 Hz, 1H), 5.48 (d, J = 3.4 Hz, 1H), 3.45 (s, 2H), 1.90* (d, J = 1.9 Hz, 3H), 1.24* (s, 12H), 1.13 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 129.7, 128.3, 127.1 (q, J = 32.2 Hz), 124.5 (q, J = 271.7 Hz), 124.00 (q, J = 3.8 Hz), 82.6, 40.2, 28.7, 23.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.80. EI-MS: $[M]^+$. Calcd for $C_{16}H_{20}BF_3O_2$ 312.15, observed 312.1.

2-(3-(4-Fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2h) and (*Z*)-2-(1-(4-fluorophenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h). Synthesized by general procedure, isolated as a yellow oil, 19% isolated yield, 50% NMR yield, 83 : 17 isomeric ratio **2h** to **3h**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.31* (m, 2H), 7.18* (s, 1H), 7.17–7.12 (m, 2H), 7.03* (t, J = 8.6 Hz, 2H), 6.94 (t, J = 8.6 Hz, 2H), 5.82 (s, 1H), 5.53 (s, 1H), 3.44 (s, 2H), 1.97* (s, 3H), 1.31* (s, 12H), 1.20 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 (d, J = 243.0 Hz), 141.3, 136.5 (d, J = 3.0 Hz), 131.2* (d, J = 8.1 Hz), 130.6 (d, J = 7.7 Hz), 130.0, 114.9 (d, J = 20.9 Hz), 100.2*, 83.7, 40.8, 25.0*, 24.8, 15.9*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.98. EI-MS: $[M]^+$. Calcd for $C_{15}H_{20}BFO_2$ 262.15, observed 262.3.

2-(3-(4-Methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i) and (*Z*)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i). Synthesized by general procedure, isolated as an off yellow oil, 46% yield, 67 : 33 isomeric ratio **2i** to **3i**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.32* (m, 2H), 7.18* (d, J = 1.8 Hz, 1H), 7.14–7.05 (m, 2H), 6.92–6.85* (m, 2H), 6.85–6.77 (m, 2H), 5.81 (dt, J = 3.3, 1.2 Hz, 1H), 5.51 (dt, J = 3.4, 1.6 Hz, 1H), 3.82* (s, 3H), 3.78 (s, 3H), 3.42 (d, J = 1.4 Hz, 2H), 2.00* (d, J = 1.7 Hz, 3H), 1.31* (s, 12H), 1.21 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8*, 157.9, 142.1*, 132. 9, 131.1*, 130.9, 130.2*, 129.6, 113.7, 113.6*, 83.6, 83.5*, 55.4, 55.4*, 40.6, 25.0*, 24.8, 16.1*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.21. EI-MS: $[M]^+$. Calcd for $C_{16}H_{23}BO_3$ 274.17, observed 274.3.

2-(3-(4-(Benzyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j) and (*Z*)-2-(1-(3-(benzyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j). Synthesized by general procedure, isolated as white solid, 37%, 66 : 34 isomeric ratio **2j** to **3j**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.30 (m, 5H from **2j** and 7H from **3j**), 7.20* (s, 1H), 7.12 (d, J = 7.8 Hz, 2H), 6.97* (d, J = 8.1 Hz, 0H), 6.90 (d, J = 7.8 Hz, 2H), 5.82 (s, 1H), 5.53 (s, 1H), 5.08* (s, 2H), 5.05* (s, 2H), 3.44 (s, 2H), 2.02* (s, 3H), 1.32* (s, 12H), 1.22 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0*, 157.1, 142.0*, 137.4, 137.1*, 133.2, 131.1*, 131.1*, 130.2, 129.6, 128.7*, 128.7, 128.1*, 128.0, 127.7*, 127.6, 114.7, 114.5*, 83.6, 83.6*, 70.2, 70.1*, 40.7, 25.0*, 24.8, 16.1*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.13. EI-MS: $[M]^+$. Calcd for $C_{22}H_{27}BO_3$ 350.21, observed 350.3.

2-(3-(4-(Allyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k) and (*Z*)-2-(1-(4-(allyloxy)phenyl)prop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k). Synthesized by general procedure, isolated as an off yellow oil, 49% yield, isomeric ratio **2k** to **3k** is 75 : 25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35* (d, J = 8.6 Hz, 2H), 7.17* (s, 1H), 7.10 (d, J = 8.4 Hz, 2H), 6.89* (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.06 (ddq, J = 15.7, 10.3, 5.0 Hz, 1H), 5.81–5.79 (m, 1H), 5.51 (s, 1H), 5.41 (dd, J = 17.2, 10.3 Hz, 1H), 5.28 (t, J = 11.6 Hz, 1H), 4.55* (d, J = 5.2 Hz, 2H), 4.51 (d, J = 5.2 Hz, 2H), 3.41 (s, 2H), 1.99* (s, 3H), 1.31* (s, 12H), 1.21 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7*, 156.8, 141.9*, 133.6, 133.3, 133.0, 130.9*, 130.0, 129.4, 117.7*, 117.4, 114.4, 114.3*, 83.44, 83.4*, 68.9, 68.8*, 40.5, 24.8*, 24.7, 15.9*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.02. HRMS: (ESI) $[M + H]^+$ calcd for $C_{18}H_{25}BO_3$ 301.20, observed 301.1968.

2-(3-Cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l) and (*Z*)-2-(1-cyclohexylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l). Synthesized by general procedure, isolated as a yellow oil, 84% yield, 78 : 22 isomeric ratio **2l** to **3l**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11* (d, J = 8.7 Hz, 1H), 5.81–5.70 (m, 1H), 5.53 (s, 1H), 2.43–2.26* (m, 1H), 2.03 (d, J = 6.8 Hz, 2H),

1.74–1.58 (m, 6H), 1.25 (s, 12H), 1.22–1.05 (m, 3H), 0.84 (q, J = 11.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9*, 130.0, 83.4, 83.1*, 43.4, 37.8, 37.7*, 33.3, 32.4*, 26.8, 26.6, 26.3*, 26.1*, 25.0*, 24.8, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16. EI-MS: $[M]^+$. Calcd for $C_{15}H_{27}BO_2$ 250.21, observed 250.3.

2-(5-(Benzyloxy)pent-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m) and (*Z*)-2-(5-(benzyloxy)pent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m). Synthesized by general procedure, isolated as a yellow oil, 34%, 93 : 7 isomeric ratio **2m** to **3m**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.24 (m, 5H), 6.38–6.28* (m, 1H), 5.79 (d, J = 3.3 Hz, 1H), 5.64–5.60 (m, 1H), 4.53* (s, 2H), 4.50 (s, 2H), 3.54 (t, J = 7.2 Hz, 2H), 3.48 (t, J = 6.7 Hz, 2H), 2.48* (q, J = 7.0 Hz, 2H), 2.24 (t, J = 7.6 Hz, 2H), 1.77 (dt, J = 14.1, 6.8 Hz, 2H), 1.71* (s, 3H), 1.26 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9*, 138.8, 138.6*, 129.5, 128.5*, 128.4, 127.8, 127.6, 127.6*, 83.6, 83.3, 73.0*, 72.9, 70.2, 69.3*, 32.0, 29.5*, 29.3, 24.9*, 24.9, 14.2*. EI-MS: $[M]^+$. Calcd for $C_{18}H_{27}BO_3$ 302.21, observed 302.3.

2-(4-(Benzyloxy)but-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n) and (*Z*)-2-(4-(benzyloxy)but-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n). Synthesized by general procedure, isolated as a yellow oil, 53%, 72 : 18 isomeric ratio **2n** to **3n**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 5H), 6.48* (tq, J = 5.8, 1.7 Hz, 1H), 5.85 (dt, J = 3.5, 0.9 Hz, 1H), 5.70 (dt, J = 3.3, 1.4 Hz, 1H), 4.53* (s, 2H), 4.52 (s, 2H), 4.17 (dq, J = 5.8, 1.1 Hz, 2H), 3.56 (t, J = 7.0 Hz, 2H), 2.49 (tt, J = 7.0, 1.1 Hz, 3H), 1.69* (dd, J = 1.8, 0.9 Hz, 3H), 1.26* (s, 12H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9*, 138.8, 131.2, 128.5*, 128.4, 127.9*, 127.8, 127.7*, 127.5, 83.5, 72.8, 72.6*, 70.1, 67.1*, 35.9, 24.93*, 24.9, 14.5*. EI-MS: $[M]^+$. Calcd for $C_{17}H_{25}BO_3$ 288.19, observed 288.3.

2-(Dec-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o) and (*Z*)-2-(dec-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o). Synthesized by general procedure, isolated as a yellow oil, 48%. Isomeric ratio **2o** to **3o** is 74 : 26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.31* (t, J = 5.9 Hz, 1H), 5.83–5.68 (m, 1H), 5.58 (s, 1H), 2.12 (q, J = 7.3 Hz, 2H), 1.66* (s, 3H), 1.26 (s, 24H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8*, 128.8, 83.4, 83.2*, 35.5, 32.1, 32.0*, 29.9*, 29.7, 29.6, 29.4, 29.4, 29.0*, 28.9*, 25.0*, 24.9, 22.8, 14.2, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.16. EI-MS: $[M]^+$. Calcd for $C_{16}H_{31}BO_2$ 266.24, observed 266.3.

4,4,5,5-Tetramethyl-2-(undec-1-en-2-yl)-1,3,2-dioxaborolane (2p) and (*Z*)-4,4,5,5-Tetramethyl-2-(undec-2-en-2-yl)-1,3,2-dioxaborolane (3p). Synthesized by general procedure, isolated as a yellow oil, 50% yield, 84 : 16 isomeric ratio **2p** to **3p**. ^{1}H NMR (500 MHz, chloroform-*d*) δ 6.31* (t, J = 6.0 Hz, 1H), 5.74 (s, 1H), 5.57 (s, 1H), 2.12 (t, J = 7.4 Hz, 2H), 1.66* (s, 3H), 1.43–1.20 (m, 26H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8*, 128.8, 83.4, 83.2*, 35.5, 32.1, 29.9*, 29.7, 29.7, 29.7*, 29.7*, 29.5, 29.4, 29.4, 29.0*, 28.9*, 24.9*, 24.9, 22.8, 14.2, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.13. EI-MS: $[M]^+$. Calcd for $C_{17}H_{33}BO_2$ 280.26, observed 280.4.

4,4,5,5-Tetramethyl-2-(pentadec-1-en-2-yl)-1,3,2-dioxaborolane (2q) and (*Z*)-4,4,5,5-tetramethyl-2-(pentadec-2-en-2-yl)-1,3,2-dioxaborolane (3q). Synthesized by general procedure, yellow oil, 75% yield, 83 : 17 isomeric ratio **2q** to **3q**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.32* (d, J = 6.4 Hz, 1H), 5.74 (s, 1H), 5.57 (s, 1H), 2.12 (t, J = 7.4 Hz, 2H), 1.66* (s, 3H), 1.44–1.16 (m, 34H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8*, 128.8, 83.4, 83.1*, 35.5, 32.1, 29.9, 29.8, 29.8, 29.7, 29.5, 29.4, 29.4, 29.0, 28.9, 24.9*, 24.9, 22.8, 14.2, 14.0*. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.15. EI-MS: $[M]^+$. Calcd for $C_{21}H_{41}BO_2$ 336.32, observed 336.4.

Conflicts of interest

There are no conflicts to declare.

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