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Selective Synthesis of Alkylboronates by Copper(I)-Catalyzed Borylation of Allyl or Vinyl Arenes

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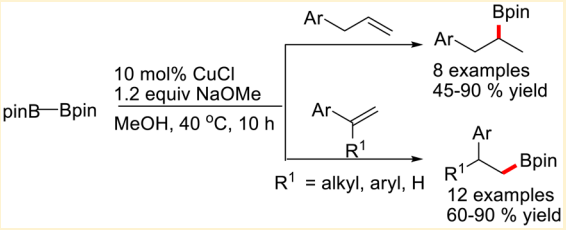
Supporting Information

ABSTRACT: An efficient copper-catalyzed borylation reaction of allyl or vinyl arenes with bis(pinacolato)diboron has been developed, without using ligands. Markovnikov-selectivity is observed in the borylation of allyl arenes with bis(pinacolato)diboron, while the regioselectivity is completely opposite when styrene derivatives are used as substrates. A mechanism involving Cu−B species regioselectively adding olefin double bonds to form the alkylcopper or η^3-benzyl copper intermediate, which is followed by protonation to obtain products, is proposed.



The utility of alkylboronates as versatile intermediates in organic synthesis is well documented.[1] Recently, the valuable C(sp^3)-organoboron species not only is widely used in the traditional Suzuki−Miyaura cross-coupling reaction with aryl and alkyl electrophiles[2] but also is a common alkylation reagent in oxidative cross-coupling reactions.[3] An advantage of alkylboron compounds over other C(sp^3) organometallics such as alkylmagnesium, alkylzinc, and alkylindium reagents is their superior shelf stability. They can be readily purified by chromatography and even stored in air. Therefore, the synthesis of alkylboron compounds with diverse structures continues to attract the interest of synthetic chemists.

Classical methods for the preparation of alkylboronates have been based on the reaction of suitable boron reagents with the organomagnesium or organolithium reagents via alkyl halide intermediates.[4] Recently, Hartwig and co-workers have discovered a Rh-catalyzed direct borylation of alkanes with B_2pin_2 under relatively harsh reaction conditions.[5] Liu,[6] Kubota,[7] Cook,[8] Xiao,[9] and Fu[10] reported convenient protocols of transition metal-catalyzed borylation of alkyl halides and pseudohalides for the synthesis of alkylboronate esters.

Transition metal-catalyzed alkene borylation is a synthetically useful method due to the high atom economy and wide functional group compatibility. For example, direct Rh- or Ir-catalyzed alkene boration via metal-boryl intermediates is an alternatively useful method for the preparation of alkylboronic acid derivatives.[11] Recently, direct Cu- or Fe-catalyzed boration reactions have been extensively used for the borylation of a wide range of alkenes.[12] However, to date no example of Cu-catalyzed borylation reaction of allyl arenes with bis(pinacolato)diboron to form secondary alkylboronate exclusively has been reported. Herein, we wish to present a new borylation reaction which exhibits both high activity and excellent regioselectivity for allyl or vinyl arenes.

Our initial work focused on catalyzed borylation of allylbenzene (**2a**) with B_2pin_2 (**1**) in the presence of 10 mol % CuCl and 1.2 equiv of NaOMe. Fortunately, the reaction proceeds smoothly in MeOH, yielding Markovnikov alkylboronate ester **3a**. Also, the most suitable reaction temperature appears to be 40 °C, and neither higher nor lower reaction temperatures were beneficial for the conversion (Table 1, entries 1−3). Efforts to further optimize the reaction conditions revealed that KOMe and NaOMe afforded similar results in the reaction (Table 1, entries 3−8). The reaction without base or CuCl cannot obtain the desired product at all (Table 1, entries 9 and 10). This reaction was subsequently repeated in the presence of 0.5 equiv of NaOMe, and a lower yield was obtained (Table 1, entry 11). It is evident that bis(pinacolato)diboron borylates allylbenzene readily, placing the boron atom in a highly regioselective and stereospecific manner to give the internal alkaneboronic esters **3a** in high yield.

With the optimized reaction conditions in hand (Table 1, entry 2), we proceed to examine the scope of the allyl arenes in this borylation protocol. Representative results are summarized in Scheme 1. Markovnikov regioselectivities were observed in reactions, resulting in addition of the boron atom to the internal carbon of allyl arenes. The substrate scope was tested by using a variety of allyl arenes. The borylation afforded secondary pinacol boronate ester products in high regioselectivity, regardless of whether an electron-withdrawing or electron-donating group was introduced on the phenyl ring (**3b−e**). These results indicated that larger conjugated allyl arenes give the products in higher yields (**3f**, **3g**). Notably, a heteroaryl-substituted propene, such as 3-allylbenzo[*b*]-thiophene, was also a compatible substrate with this protocol (**3h**). However, no desired product was detected when oct-1-

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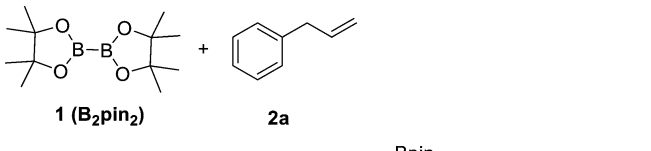
Table 1. Optimization of Experimental Conditions for Cu-Catalyzed Borylation of Allylbenzene with Bis(pinacolato)diboron[a]



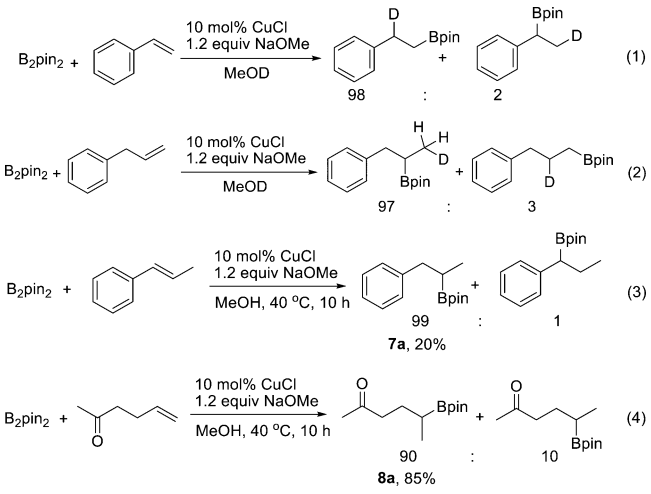
entry	base	temp (°C)	yield of 3a[b] (%)
1	NaOMe	30	75
2	NaOMe	40	93 (3a/3a′ = 97:3)
3	NaOMe	60	80
4	K_2CO_3	40	65
5	Li_2CO_3	40	70
6	NaOAc	40	51
7	KOH	40	69
8	KOMe	40	90
9		40	n.p.
10[c]	NaOMe	40	n.p.
11[d]	NaOMe	40	50

[a]Reaction conditions: **1** (1.0 mmol), **2a** (1.0 mmol), CuCl (10 mol %), and 1.2 equiv of base in 2 mL of MeOH for 10 h. [b]Determined by GC-MS. [c]Without CuCl. [d]0.5 equiv of NaOMe. n.p. = no desired product.

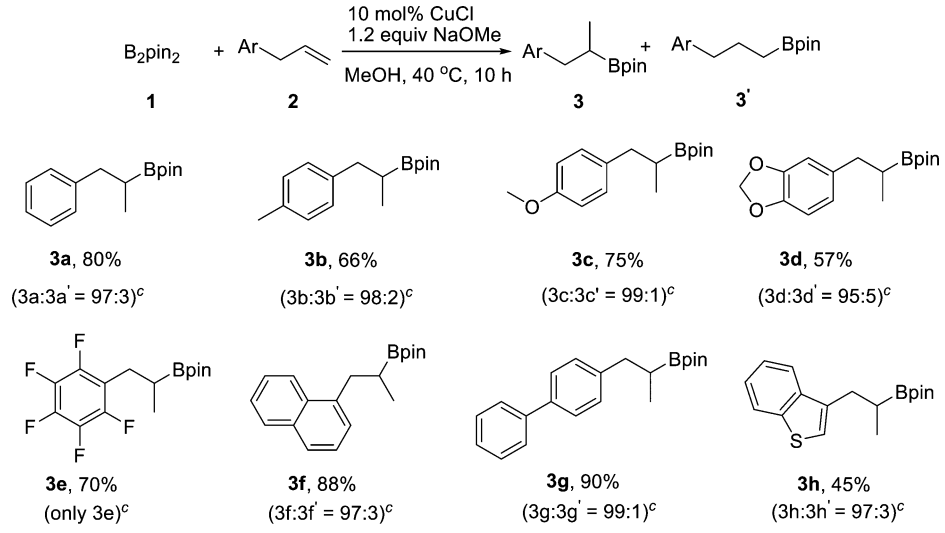
ene was used as the substrate. This apparently proved that the coordination of the phenyl ring to the copper center was essential for the Cu-catalyzed Markovnikov borylation of unactivated olefins.

Inspired by these results, we became interested in further exploring the reactivity and regioselectivity of this methodology to relatively activated styrene derivatives. Borylation of vinyl arenes with bis(pinacolato)diboron was carried out under optimal conditions, and high *anti*-Markovnikov selectivities opposite to that of allyl arenes were observed in reactions, resulting in the addition of the boron atom to the terminal carbon of vinyl arenes. Representative results are summarized in Scheme 2. Those transformations were highly efficient for a broad scope of vinyl arenes in excellent yields. The electronic properties of the substituents on the benzene ring have significant influence on the reaction's regioselectivity. Electron-rich styrenes underwent the transformations smoothly, affording almost exclusively the *anti*-Markovnikov products (**5e–h**). However, the borylation of electron-deficient styrenes resulted in higher than 90% of the boron atom entering the terminal position (**5b–d**). Surprisingly, the borylation of 1,1-disubstituted alkenes also took place smoothly to give almost exclusively the terminal borylation product (**5i–k**). The results showed that alkenes bearing electron-withdrawing substituents gave lower regioselectivity than those bearing electron-donating substituents. Furthermore, 3-vinylpyridine such as a pyridine moiety provided the desired product in 85% yield (**5l**).

In order to understand the mechanism of this unique transformation, isotope labeling experiments were performed under the standard reaction conditions (eqs 1 and 2). The



Scheme 1. Cu-Catalyzed Borylation of Allyl Arenes with Bis(pinacolato)diboron[a,b]



[a]Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), CuCl (10 mol %), and NaOMe (1.2 equiv) in 2 mL of MeOH at 40 °C for 10 h. [b]Isolated yields. [c]Determined by GC-MS analysis of the crude reaction mixture.

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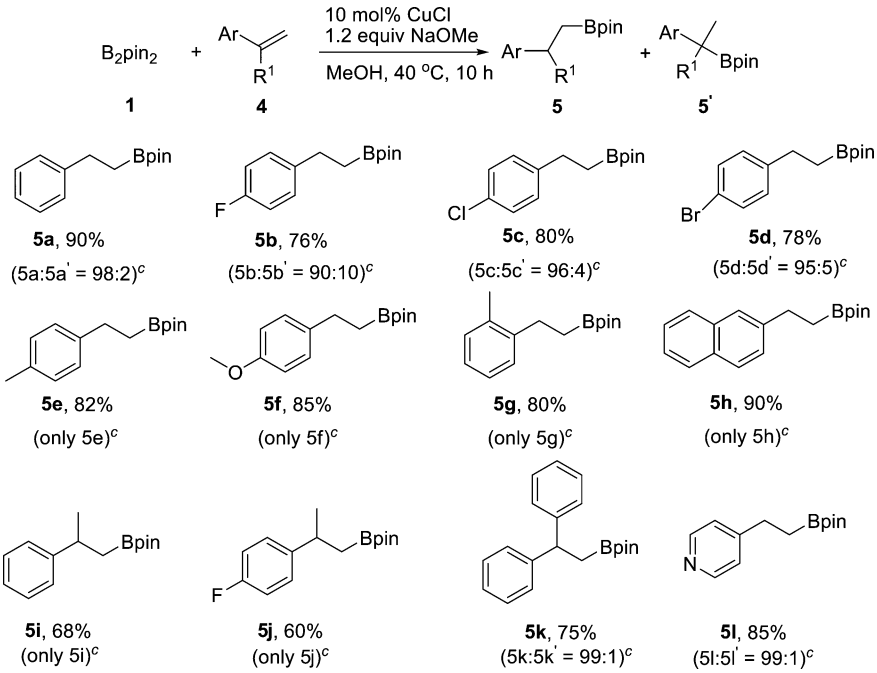
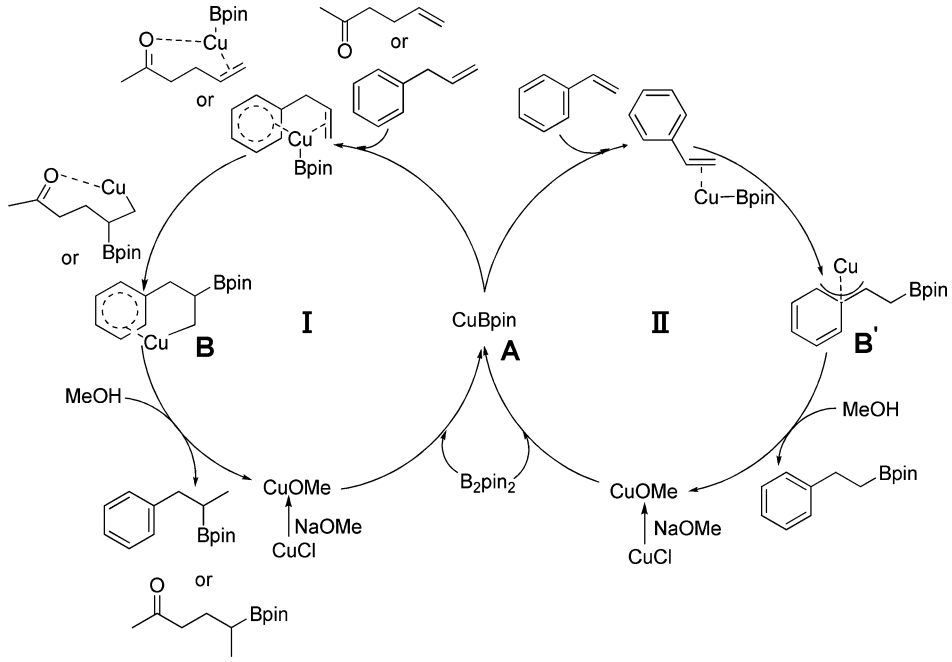
Scheme 2. Cu-Catalyzed Borylation of Different Vinyl Arenes with Bis(pinacolato)diboron[a,b,c]



[a]Reaction conditions: **1** (1.0 mmol), **4** (1.0 mmol), CuCl (10 mol %), and NaOMe (1.2 equiv) in 2 mL of MeOH at 40 °C for 10 h. [b]Isolated yields. [c]Determined by GC-MS analysis of the crude reaction mixture.

Scheme 3. Proposed Mechanism for the Copper-Catalyzed Borylation of Alkenes



borylation of (*E*)-prop-1-enylbenzene with bis(pinacolato)-diboron generated the corresponding borylation product with the same regioselectivity as that of the styrene derivatives (eq 3). It was found that aliphatic alkenes containing a nearby coordinating group, such as hex-5-en-2-one, gave borylation products with regioselectivity similar to that of allyl arenes (eq 4). The ratios of borylation regioisomers were determined by GC-MS analysis of the crude reaction mixtures after extraction with an organic solvent.

On the basis of previous reports[12i–k,13] and our experimental data, a plausible pathway for the Cu-catalyzed borylation of allyl or vinyl arene is depicted in Scheme 3. First, a Bpin-Cu species **A** was generated via transmetalation between copper alkoxide and B_2pin_2. Next, the insertion of C–C double bonds into Bpin-Cu species and subsequent protonation afford the corresponding products. In cycle I, the relatively active styrene derivatives was inserted into the Bpin-Cu species to give stable η^3-benzyl copper intermediate **B**′,[12g] which was protonated to generate *anti*-Markovnikov products. In cycle II, the aromatic

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ring in the allylbenzene might coordinate to the Bpin-Cu species to accelerate the C−C double bond insertion, which gave a terminal π-coordinated alkyl-Cu intermediate **B**. Finally, the protonation afforded the Markovnikov products. Similarly, the hex-5-en-2-one, containing a carbonyl group, gave the Markovnikov products, involving a coordinated alkyl-copper intermediate.

In conclusion, we developed an efficient and general catalytic system for the borylation reaction of terminal olefins in the absence of expensive and difficult-to-handle phosphine ligands. The process was regioselective and provided good access to a series of alkylboronic acid derivatives in good to excellent yields. The borylation of vinyl arenes with bis(pinacolato)-diboron, under mild conditions and with regioselectivity, differs from that of the allyl arenes. The borylation reactions of allyl arenes with high selectivities to form secondaory boronate esters were observed. To the best of our knowledge, this strategy for the regioselective synthesis of secondary pinacol boronate esters from allyl arenes is novel and has not been reported earlier. All of these facts, together with the simplicity of the protocol, the wide scope of substrates, and their high regoselectivity permitted us to anticipate a good future for the process shown in this note not only in the laboratory but also in industry.

EXPERIMENTAL SECTION

Typical Procedure for the Copper-Catalyzed Borylation Reaction of Bis(pinacolato)diboron to Terminal Olefins. To the mixture of 10 mol % CuCl, NaOMe (1.2 equiv), bis(pinacolato)-diboron(1.0 mmol), terminal olefin (1.0 mmol), and 2.0 mL of MeOH were added successively. The resulting mixture was stirred at 40 °C until the end of the reaction. The solution was quenched with a saturated solution of NaCl and extracted with ethyl acetate (3 × 15 mL), and the combined extract was dried with anhydrous $MgSO_4$. The solvent was removed, and the residue was separated by column chromatography using petroleum ether/ethyl acetate 50:1 to give the pure sample.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (3a, 197 mg, 80%).[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.13 (m, 5H), 2.82 (dd, J = 13.6, 7.6 Hz, 1H), 2.55 (dd, J = 13.6, 8.4 Hz, 1H), 1.38 (dd, J = 15.2, 7.6 Hz, 1H), 1.19 (d, J = 4.0 Hz, 12H), 0.97 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.9, 128.0, 125.5, 83.0, 39.0, 24.7, 15.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.17; ν_{max}(KBr)/cm^{-1} 2980, 1360, 1306, 1142, 968, 840. MS (EI) m/z: 84, 91, 118, 131, 145, 231, 246.

4,4,5,5-Tetramethyl-2-(1-*p*-tolylpropan-2-yl)-1,3,2-dioxaborolane (3b, 172 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10−7.05 (m, 4H), 2.79 (dd, J = 13.6, 7.2 Hz, 1H), 2.52−2.46 (m, 1H), 2.31 (s, 3H), 1.37−1.31 (m, 1H), 1.20 (d, J = 3.6 Hz, 12H), 0.96 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 134.9, 128.8, 128.7, 83.0, 38.5, 24.7, 21.0, 15.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.71; ν_{max}(KBr)/cm^{-1} 2979, 1360, 1319, 1142, 968, 840, 520. HRMS (EI-TOF): calcd for $C_{16}H_{25}BO_2$, 260.1948; found, 260.1940.

2-(1-(4-Methoxyphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c,207 mg,75%).[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 2.76 (dd, J = 13.6, 7.6 Hz, 1H), 2.50 (dd, J = 13.8, 8.2 Hz, 1H), 1.34 (dd, J = 15.2, 7.6 Hz, 1H), 1.20 (d, J = 4.0 Hz, 12H), 0.97 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 134.5, 129.8, 113.4, 82.9, 55.2, 38.1, 24.7, 15.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 36.01; ν_{max}(KBr)/cm^{-1} 2979, 1611, 1583, 1512, 1464, 1319, 1244, 1142, 1038, 840, 700, 531. MS (EI) m/z 121, 149, 261, 276.

2-(1-(Benzo[*d*][1,3]dioxol-5-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d, 165 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71−6.63 (m, 3H), 5.90 (s, 2H), 2.73 (dd, J = 13.6, 7.6 Hz, 1H), 2.55−2.44 (m, 1H), 1.31−1.26 (m, 1H), 1.20 (d, J = 2.0 Hz, 12H), 0.96 (m, d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 145.4, 136.2, 121.6, 109.3, 107.8, 100.6, 83.0, 53.4, 38.7, 24.7, 15.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.16; ν_{max}(KBr)/cm^{-1} 2979, 1623, 1589, 1538, 1464, 1319, 1244, 1142, 1038, 840, 700, 668. HRMS (EI-TOF): calcd for $C_{16}H_{23}BO_4$, 290.1689; found, 290.1686.

4,4,5,5-Tetramethyl-2-(1-(perfluorophenyl)propan-2-yl)-1,3,2-dioxaborolane (3e, 235 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 (dd, J = 13.6, 7.2 Hz, 1H), 2.63 (dd, J = 13.2, 9.2 Hz, 1H), 1.35 (dd, J = 16.4, 8.4 Hz, 1H), 1.22 (s, 12H), 0.97 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2 (d, 245 Hz), 139.5(d, 205 Hz), 136.0(d, 13 Hz), 115.4(d, 16 Hz), 83.3, 25.2, 24.7, 24.6, 14.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.87; ν_{max}(KBr)/cm^{-1} 2986, 1365, 1326, 1142, 968, 840. HRMS (EI-TOF): calcd for $C_{15}H_{18}BF_5O_2$, 336.1320; found, 336.1328.

4,4,5,5-Tetramethyl-2-(1-(naphthalen-1-yl)propan-2-yl)-1,3,2-dioxaborolane (3f, 260 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18−8.12 (m, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 5.2 Hz, 1H), 7.55−7.47 (m, 2H), 7.40 (d, J = 4.4 Hz, 2H), 3.39 (dd, J = 14.0, 7.6 Hz, 1H), 2.99 (dd, J = 14.0, 8.4 Hz, 1H), 1.62 (dd, J = 15.6, 8.0 Hz, 1H), 1.23 (d, J = 9.2 Hz, 12H), 1.09 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 133.9, 132.2, 128.7, 126.5, 125.6, 125.3, 124.3, 83.1, 36.0, 24.9, 24.8, 15.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.44; ν_{max}(KBr)/cm^{-1} 2980, 1610, 1586, 1360, 1306, 1142, 968, 840. HRMS (EI-TOF): calcd for $C_{19}H_{25}BO_2$, 296.1948; found, 296.1944.

2-(1-(Biphenyl-4-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g, 290 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.31−7.25 (m, 3H), 2.84 (dd, J = 13.6, 7.6 Hz, 1H), 2.61−2.55 (m, 1H), 1.45−1.37 (m, 1H), 1.18 (d, J = 4.8 Hz, 12H), 0.99 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.3, 138.5, 129.4, 128.7, 127.0, 126.9, 126.8, 83.1, 38.7, 24.8, 24.7, 15.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.63; ν_{max}(KBr)/cm^{-1} 2980, 1610, 1586, 1360, 1306, 1142, 968, 840. HRMS (EI-TOF): calcd for $C_{21}H_{27}BO_2$, 322.2104; found, 322.2100.

2-(1-(Benzo[*b*]thiophen-3-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h, 136 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.87 (m, 2H), 7.57−7.41 (m, 3H), 3.31−3.17 (m, 1H), 3.02−2.88 (m, 1H), 1.79−1.68 (m, 1H), 1.39−1.33 (m, 12H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 139.3, 136.9, 123.9, 123.6, 122.7, 122.0, 121.4, 83.1, 31.7, 24.7, 15.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.16; ν_{max}(KBr)/cm^{-1} 2980, 1368, 1336, 1142, 960, 850. HRMS (EI-TOF): calcd for $C_{17}H_{23}BO_2S$, 302.1512; found, 302.1504.

4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (5a, 209 mg, 90%).[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.20 (m, 4H), 7.14 (t, J = 7.2 Hz, 1H), 2.75 (t, J = 8.0 Hz, 2H), 1.21 (s, 12H), 1.18−1.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 128.2, 128.0, 125.5, 83.1, 30.0, 24.8, 17.1; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.72; ν_{max}(KBr)/cm^{-1} 2979, 1604, 1496, 1455, 1372, 1240, 1144, 968, 848, 751, 698. MS (EI) m/z: 69, 84, 105, 132, 175, 217, 232.

2-(4-Fluorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b, 190 mg, 76%).[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.15 (m, 2H), 6.94 (t, J = 8.8 Hz, 2H), 2.72 (t, J = 8.0 Hz, 2H), 1.21 (s, 12H), 1.12 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1(d, 241 Hz), 139.9, 129.3(d, 8 Hz), 114.8(d, 21 Hz), 83.1, 29.2, 24.8, 24.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.57; ν_{max}(KBr)/cm^{-1} 2980, 2936, 1601, 1510, 1373, 1319, 1221, 1145, 1087, 968, 831, 705, 517. MS (EI) m/z: 84, 109, 150, 193, 250.

2-(4-Chlorophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5c, 213 mg, 80%).[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.72 (t, J = 8.0 Hz, 2H), 1.21 (s, 12H), 1.12 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 131.2, 129.4, 128.2, 83.2, 29.3, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.51; ν_{max}(KBr)/cm^{-1} 2979, 1492, 1372, 1318, 1144, 1092. MS (EI) m/z: 51, 78, 105, 203, 219, 234, 274.

2-(4-Bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5d, 242 mg, 78%).[18] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.70 (t, J = 8.0 Hz, 2H), 1.22 (s, 12H), 1.12 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 131.2, 129.8, 119.2, 83.2, 29.4, 24.8, 24.6; ^{11}B NMR (128 MHz,

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$CDCl_3$) δ 33.47; ν_{max}(KBr)/cm^{-1} 2978, 1488, 1371, 1318, 1144, 967. MS (EI) *m/z*: 55, 77, 83, 104, 139, 151, 231, 266.

4,4,5,5-Tetramethyl-2-(4-methylphenethyl)-1,3,2-dioxaborolane (5e, 202 mg, 82%).[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12−7.06 (m, 4H), 2.71 (t, *J* = 8.4 Hz, 2H), 2.31 (s, 3H), 1.24 (s, 12H), 1.13 ((t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 134.8, 128.9, 127.8, 83.1, 29.7, 29.5, 24.8, 21.0; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.17; ν_{max}(KBr)/cm^{-1} 2979, 2902, 1611, 1583, 1512, 1464, 1319, 1244, 1144, 1038, 839, 700, 531. MS (EI) *m/z*: 69, 84, 105, 146, 189, 231, 246.

2-(4-Methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5f, 223 mg, 85%).[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 2.70 (t, *J* = 8.0 Hz, 2H), 1.23 (s, 12H), 1.12 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 136.6, 128.9, 113.6, 83.1, 55.2, 29.1, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.72; ν_{max}(KBr)/cm^{-1} 2979, 2902, 1611, 1583, 1512, 1464, 1319, 1244, 1144, 1038, 839, 700, 531. MS (EI) *m/z*: 77, 84, 120, 134, 161, 262.

4,4,5,5-Tetramethyl-2-(2-methylphenethyl)-1,3,2-dioxaborolane (5g, 197 mg, 80%).[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.2 Hz, 1H), 7.16−7.09 (m, 3H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 1.27 (s, 12H), 1.14 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 135.8, 130.0, 128.1, 125.9, 125.6, 83.1, 27.2, 24.8, 24.6, 19.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.78; ν_{max}(KBr)/cm^{-1} 2980, 1462, 1372, 1318, 1145, 967, 747. MS (EI) *m/z*: 84, 105, 131, 146, 189, 246.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (5h, 254 mg, 90%).[16] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.79 (m, 3H), 7.70 (s, 1H),7.49−7.41 (m, 3H), 2.98 (t, *J* = 8.0 Hz, 2H), 1.30 (t, *J* = 8.4 Hz, 2H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 133.7, 132.0, 127.7, 127.6, 127.5, 127.3, 125.8, 125.7, 125.0, 83.2, 30.2, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.33; ν_{max}(KBr)/cm^{-1} 2979, 1372, 1144, 968, 847, 813, 743. MS (EI) *m/z*: 84, 105, 152, 167, 180, 264, 308.

4,4,5,5-Tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (5i, 167 mg, 68%).[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.2 Hz, 4H), 7.13 (t, *J* = 6.8 Hz, 1H), 3.01−2.97 (m, 1H), 1.30−1.25 (m, 5H), 1.15 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 128.2, 126.6, 125.7, 83.0, 35.8, 24.9, 24.8, 24.7; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.93; ν_{max}(KBr)/cm^{-1} 2980, 1360, 1306, 1142, 968, 840. MS (EI) *m/z*: 55, 91, 105, 131, 160, 231, 246.

2-(2-(4-Fluorophenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5j, 158 mg, 60%).[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.17 (m, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 3.07−2.98 (m, 1H), 1.26 (s, 3H), 1.25 (s, 2H),1.16 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1 (d, 241 Hz), 144.8 (d, 3 Hz), 127.9 (d, 8 Hz), 114.8 (d, 21 Hz), 114.7, 83.0, 35.1, 29.7, 25.1, 24.7 (d, 4 Hz); ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.09; ν_{max}(KBr)/cm^{-1} 2978, 1365, 1321, 1221, 1143, 968, 846, 831. MS (EI) *m/z*: 84, 123, 149, 249, 264.

2-(2,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5k, 231 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.21 (m, 8H), 7.14−7.10 (m, 2H), 4.27 (t, *J* = 8.4 Hz, 1H), 1.59 (d, *J* = 8.4 Hz, 2H), 1.04 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 130.1, 128.2, 127.7, 125.9, 83.1, 46.5, 24.6; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.41; ν_{max}(KBr)/cm^{-1} 2978, 1661, 1494, 1367, 1324, 1144, 700. HRMS (EI-TOF): calcd for $C_{20}H_{25}BO_2$, 308.1948; found, 308.1939.

4-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-pyridine (5l, 198 mg, 85%).[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.8 Hz, 2H), 7.11 (d, *J* = 4.8 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.18 (s, 12H), 1.11 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 149.4, 123.5, 83.3, 29.2, 24.8; ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.63; ν_{max}(KBr)/cm^{-1} 2980, 1364, 1326, 1142, 968, 848. MS (EI) *m/z*: 41, 59, 93, 106, 132,176, 218, 233.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (7a, 49 mg, 20%).[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.17 (m, 5H), 2.83 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.57 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.40 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.21 (d, *J* = 4.4 Hz, 12H), 0.99 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 128.9, 128.0, 125.5, 83.0, 39.0, 24.7, 15.2; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.18; ν_{max}(KBr)/cm^{-1} 2980, 1360, 1306, 1142, 968, 840. MS (EI) *m/z*: 84, 91, 118, 131, 145, 231, 246.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (8a, 192 mg, 85%).[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (t, *J* = 7.6 Hz, 2H), 2.12 (s, 3H), 1.71−1.53 (m, 2H), 1.22 (s, 12H), 0.97 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 83.0, 43.2, 29.8, 27.2, 24.8, 24.7, 15.4; ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.17; ν_{max}(KBr)/cm^{-1} 2980, 1726, 1304, 846. MS (EI) *m/z*: 55, 69, 83, 101, 111, 126, 140, 168, 184, 211, 226.

■ ASSOCIATED CONTENT

Supporting Information

General procedures, mechanistic studies, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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