3-Chloro-1-lithiopropene, a Functional Organolithium Reagent, and Its Reactions with Alkylboronates To Give 3-Alkylprop-1-en-3-ols

Keith Smith,* Mark C. Elliott,* and D. Heulyn Jones

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

Supporting Information

**ABSTRACT:** The reagent 3-chloro-1-lithiopropene (4) can be generated by treating 1-bromo-3-chloropropene with t-BuLi. It is unstable but if generated at low temperature in the presence of alkylboronic esters, such as 3, is trapped in situ to give rearrangement products 2, which on oxidation give 3-alkylprop-1-en-3-ols in good yields. The reaction works for primary, secondary, benzylic, and even tertiary alkylboronic esters, providing allylic alcohols bearing almost any alkyl group available using organoborane chemistry and incorporating all features of such groups.

Migration of alkyl groups from boron to carbon is important for formation of C–C bonds. Depending on the reaction, trialkylboranes undergo migration of one, two, or all three alkyl groups to a single carbon atom, usually with retention of stereochemical integrity. Furthermore, although boron is commonly removed by oxidation, the immediate product is an organoboron compound and potentially available for further elaboration. Single-migration reactions of trialkylboranes lack efficient use of alkyl groups, and migratory selectivity may be a problem. Allyldialkoxyboranes (alkylboronate esters) are substantially less electrophilic, and only highly nucleophilic, often unstable reagents such as halomethylolithiums are sufficiently reactive. Even then, migration of tert-alkyl groups is difficult, but in a recent investigation, we have extended the range of substrates to include quite hindered tert-alkyl groups.

Reactions of 3-chloropropenylboronates such as 1 with Grignard reagents (Scheme 1a) give compounds 2 with high enantiomeric excess under asymmetric catalysis. This important and useful reaction is limited by the availability of appropriate Grignard reagents, which are not tolerant of functionality. By contrast, organoboron derivatives tolerate many functional groups and can be generated by a range of stereospecific processes. Thus, Scheme 1b would be a more generally useful approach to compounds 2 than Scheme 1a. We now report the successful realization of this approach.

(E)-1-Bromo-3-chloroprop-1-ene (5) was synthesized by the literature procedure (Scheme 2). The final product 5 required careful fractional distillation to provide a clean sample.

**Scheme 2. Synthesis of 1-Bromo-3-chloropropene (5)**

Reactions of 3-chloropropenylboronates such as 1 with Grignard reagents (Scheme 1a) gave examples of use of tert-alkylmagnesium reagents, so we first looked at reactions of tert-butylboronic esters and investigated both boronate ester 6 and the more hindered pinacol analogue 7. Br−Li exchange of 5 to give 4 was attempted with n-BuLi and t-BuLi; solutions were reacted with 6 or 7 and then oxidized to give 4,4-dimethylpent-1-en-3-ol (8) (Scheme 3). Yields were monitored by GC.

**Scheme 3. Initial Investigative Reactions**

Received: August 20, 2013
Published: August 26, 2013
t-BuLi was more effective at generating 4 than n-BuLi, probably because of lower competition from other sites of attack. Generating 4 ex situ and adding it to the boronate was not successful, presumably because 4 is unstable and needs trapping immediately. Excess organolithium was deleterious, presumably because of increased competition from direct addition to the boronate, while the more hindered boronate 7 gave higher yields than 6, presumably because of lower competition from such addition. Use of 5 containing ~5% of pentachloroacetone caused a disproportionate decrease in yield, so purity of 5 is important. However, under the most favored conditions (1.1 equiv of t-BuLi and pure 5, in situ, with 7), the yield of 8 was almost quantitative.

A representative selection of pinacol alkylboronates 3, possessing alkyl groups ranging in bulk from n-butyl to thexyl (2,3-dimethyl-2-butyl), was tested under the standard conditions (Table 1). Some products were purified from the reaction mixtures; authentic samples of others were prepared from vinylimagnesium bromide and the appropriate aldehyde, so response factors could be calculated and yields monitored by GC to provide true reaction yields (Table 1, entries 1–7).

All but one of the standard reactions (i.e., entries 1–6) provided very good yields of the desired products 9, none of which contained allylic rearrangement isomers 10, which have been recorded in earlier reports.7 Reaction of the 2,2-dimethylpropane-1,3-diol ester of n-butylboronic acid did give some rearranged product (78:22 mixture of (E/Z)-10:9), but no rearranged products were observed with 2,2-dimethyl-1,3-propanediol esters of more hindered alkylboronic acids or with pinacol boronates of less hindered alkylboronic acids.

As 5 isomerizes to give a mixture of E and Z isomers in the presence of light,13 samples had been kept cold and in the dark. In order to check whether precursor 5 needed to be stereochemically pure, a sample was exposed to daylight for several hours to convert it into an E/Z mixture and then subjected to a standard reaction with 3 (R = cyclohexyl). The yield of 9 (R = cyclohexyl) (Table 1, entry 5) was similar to those obtained for other examples with pure (E)-5, so synthesis of 1-bromo-3-chloropropene need not be stereoselective.

The most hindered pinacol alkylboronic ester (thexyl, entry 7) gave a significantly lower yield than the other alkylboronates 3. Our experience with haloethylmethylithium reactions led us to suspect poorer capture of 4 by the more hindered alkylboronate, allowing competitive decomposition of 4. To try to overcome this, we synthesized the less hindered thexylboronates 11 and 12 from thexylborane and the corresponding diols.

When subjected to the standard conditions, 11 gave 36% of 9 (R = thexyl, entry 8), while 12 gave 99% (entry 9). Similar subtlety was observed in reactions with BrCH2Li, where yields of the corresponding products from 1 (R = thexyl), 11, and 12 were 35, 80, and 71%.6 For best results in the present reaction, therefore, it is important that the boronate be sufficiently hindered to inhibit direct reaction between the added organolithium and the boronate or its complex with 4, but not be so hindered to limit its ability to capture 4, allowing decomposition of 4 to compete. Pinacol alkylboronates are evidently satisfactory up to the hindrance level of a t-butyl group, but for thexyl, the somewhat less hindered 2,2-dimethylpropane-1,3-diol boronate is optimal. To find where the limits of the method lie, standard conditions were applied to alkylboronates incorporating highly hindered tert-alkyl groups obtained by use of reactions of trialkylboranes with dichloromethyl methyl ether (DCME, Table 2).

### Table 1. Syntheses of Allylic Alcohols 9

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>yield of 9 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-butyl</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>benzyl</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>4-methoxybenzyl</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>i-propyl</td>
<td>94</td>
</tr>
<tr>
<td>5</td>
<td>cyclohexylb</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>i-butyl</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>thexyl</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>thexyl (use of 11)c</td>
<td>36</td>
</tr>
<tr>
<td>9</td>
<td>thexyl (use of 12)c</td>
<td>99</td>
</tr>
</tbody>
</table>

*Yield by GC with tetradecane as standard. b/E/Z S used. cBoronic ester 11 or 12 used instead of 3 (R = thexyl).

### Table 2. Reactions of tert-Alkylboronates 13

<table>
<thead>
<tr>
<th>entry</th>
<th>R&lt;sup&gt;C&lt;/sup&gt;</th>
<th>R&lt;sup&gt;D&lt;/sup&gt;</th>
<th>yield of 14 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>i-Pr</td>
<td>99&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>Et</td>
<td>Et</td>
<td>25 (31)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>n-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;</td>
<td>n-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;13&lt;/sub&gt;</td>
<td>28&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>c-Hex</td>
<td>PhCH═CH</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>c-Pent</td>
<td>c-Pent</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yield estimated by relative integrations in the <sup>1</sup>H NMR spectrum of the crude product. <sup>b</sup>Yield by GC unless otherwise stated. <sup>c</sup>This is the result reported in Table 1, entry 9, for reaction of 12, which was not obtained by the DCME reaction. <sup>d</sup>Number in parentheses is for a similar reaction with 3 equiv of t-BuLi and 5. <sup>e</sup>Yield estimated by relative integrations in the <sup>1</sup>H NMR spectrum of the crude product. The ethylene glycol boronate was used in this case.

The results were similar to those with bromomethylithium as reagent.8 With very hindered triethylmethyl- and trioctylmethylboronates, modest but usable yields of the expected products were formed even without optimization of individual reactions. However, with extremely hindered dicyclohexyl(2-phenylethyl)methyl- and tricyclopentylethylmethylboronates, none of the desired products were formed (even with the ethylene glycol boronate in the latter case). Therefore, the...
upper limit of steric hindrance for this methodology has been identified.

Several products 9/14 were isolated by column chromatography from reactions in Tables 1 and 2 (see Supporting Information). Yields of isolated products were typically 5–20% lower than indicated by GC because of losses during separation. However, additional fractions containing the desired product mixed with other materials were available, and higher yields of isolated product could be achieved if necessary.

The new methodology is very general, being applicable to alkylboronates with alkyl groups of widely different bulk and potentially possessing functionality incompatible with Grignard or organolithium reagents. To test the ability of the method to tolerate functionality, and to demonstrate applicability to compounds of synthetic interest, we synthesized 15 (Scheme 4). The crude product (91% yield) was a mixture (85:15) of 15 and 16, which was separated by column chromatography.

**Scheme 4. Synthesis of Compound 15**

**Scheme 5. Syntheses of Compounds 17 and 18**

Reaction of 15 with 4 under the standard conditions led to hydroxy ester 17 (96% yield by GC), which was purified by column chromatography. Lactone 18 (100% yield) was obtained by reflux of a benzene solution of 17 with p-toluenesulfonic acid monohydrate (PTSA) for 4 h (Scheme 5). It is unlikely that 17 or 18 could be obtained easily by reacting 1 according to Scheme 1 with Grignard reagent 19 because of the lack of stability of such a reagent, and comparable reactions have not been demonstrated with more stable organozinc reagents. Hydroxy esters typified by 17 and lactone 18 have been used in syntheses of prostaglandins, insect pheromones, and other natural products. While there are efficient routes to compound 18, the present approach is very short and demonstrates the synthetic potential of the new process.

Although we oxidized the intermediate (1-alkylallyl)-boronates (like 2) to substituted allylic alcohols 9/14/17, they are also available for other types of transformations, such as reactions with aldehydes or protodeboronation.

Products like 2 are potentially available (Scheme 6) by use of 3-chloro-3-lithiopropene (20), accessible by deprotonation of allyl chloride with LDA. We therefore mixed 1 (R = Bn) with allyl chloride and LDA to generate 20 under the conditions developed for reactions of 4. Compound 9 (R = Bn) was obtained in 40% yield (by GC), showing that this approach is much less efficient than use of 4. Of course, not all reactions of 4 and 20 will give identical products, so the new reagent is important for other reasons, too.

In conclusion, the novel organolithium reagent 4 has been generated from 1-bromo-3-chloropropene and t-BuLi at −78 °C. In the presence of pinacol alkylboronates (3), it is trapped to form complexes that rearrange to (α-alkylallyl)boronates 2, in good yields except for ones with extremely hindered alkyl groups, which require less hindered dial units. Direct oxidation of 2, without isolation, gives the corresponding allylic alcohols 9 in good yields.

**EXPERIMENTAL SECTION**

**General Experimental Details.** Melting point determinations were performed by the open capillary method and are reported uncorrected. 1H and 13C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and coupling constants (J) are reported to the nearest 0.1 Hz. C, CH, CH2, or CH3 13C signals are assigned from DEPT-90 and 135 spectra. In a number of cases, carbon atoms attached to boron gave very broad peaks in 13C NMR spectra, and these could not always be distinguished. Hydrogen atoms attached to these carbons were not always observed in 1H NMR spectra. Low- and high-resolution mass spectra were recorded on a time-of-flight mass spectrometer using electron impact (EI). High-resolution mass spectra were recorded only for new compounds. IR spectra were recorded on a FT-IR spectrometer as a thin film (liquid samples) or applied as a solution in chloroform, and the chloroform was allowed to evaporate (solid samples). Column chromatography was carried out using 60A (35–70 μm) silica. GC determinations were performed using a gas chromatograph fitted with a ZB-5 column (30 m, 0.32 mm inner diameter, 1.0 μm film thickness). The carrier gas was He at 69.3 kPa, and a split injection mode was used. The oven temperature was increased from 70 to 260 °C at 6 °C min−1 and then held for 4 min. Authentic samples of products were used to determine response factors relative to tetradecane, a known amount of which was added to the reaction mixtures to allow quantification of product yields.

**Synthesis of 1-Bromo-3-chloroprop-1-ene (5). Synthesis of (E)-3-Bromoacrylic Acid:** A mixture of propionic acid (8.79 mL, 0.143 mol) and aq HBr (48%, 40 mL) was heated at 95 °C for 2.5 h, then left to cool. The crude product was filtered, washed with cold water (3 × 25 mL), and dried in air to give (E)-3-bromoacrylic acid as colorless needles (13.49 g, 63%); mp 120–121.5 °C (lit.23 mp 117.5–118.5 °C).

**Synthesis of (E)-3-Bromoprop-2-en-1-ol (2):** A two-necked round-bottomed flask equipped with a magnetic stirrer bar, septum, and septum-capped dropping funnel was assembled hot and flushed with N2. (E)-3-Bromoacrylic acid (8.00 g, 53 mmol) was dissolved in dry diethyl ether (40 mL) and transferred via syringe to the dropping funnel. Powdered LiAlH4 (4.02 g, 106 mmol) was transferred quickly to the reaction flask, and dry diethyl ether (40 mL) was added. The reaction mixture was cooled in an ice bath, and the solution of 3-bromoacrylic acid was added dropwise via the dropping funnel.
vigorously stirring. The mixture was stirred for 2 h, then water (2.5 mL) was added dropwise, followed by 15% NaOH (5.25 mL) and more water (7.4 mL). The resulting salts were washed with diethyl ether (3 × 50 mL), and the combined extracts were dried over sodium sulfate and concentrated under reduced pressure to give fairly pure (E)-1-bromo-3-chloroprop-2-ene (1.19 g, 20%) as cubic crystals: mp 188°C. 1H (500 MHz, CDCl3) δ 6.48 (1H, dt, J = 13.5, 1.1 Hz), 6.34 (1H, dt, J = 13.5, 7.1 Hz), 4.02 (2H, dd, J = 7.1, 1.1 Hz); 13C (125 MHz, CDCl3) δ 133.1 (CH), 110.8 (CH), 43.6 (CH3).

**Synthesis of Boronate Esters.** Boronate esters 3 where R = Bn and 4-MeOBn were prepared from Sigma-Aldrich and TCI, respectively, and used without further purification. Boronate esters 3 where R = Bu, t-Bu, and cyclohexyl were prepared from the reaction of their corresponding boronic acids with pinacol in pentane in 73, 36, and 32% yields, respectively. Boronate ester 3 where R = tert-Bu was prepared by the literature method from pinacolborane and tert-BuMgCl in 40% yield. Boronate ester 3 where R = t-Bu was prepared by the method previously described from the monohydroboronation of 2,3-dimethyl-2-butene and subsequent reaction with pinacol, while boronate esters 11 and 12 were also prepared as described previously.

Boronate esters 13 were prepared by the DCME reaction with the appropriate trialkylboranes. The procedure for preparation of 13 (R′ = c-Hex, R″ = PhCH-CH2; 1H, d, J = 10.5 Hz) was as follows: 13C (125 MHz, CDCl3) δ 137.8 (CH), 115.9 (CH), 78.6 (CH), 41.7 (CH3). HRMS (EI) m/z calc for C16H16O1 254.1166, found 254.1162 (M+).

**4.5-Trimethylhex-1-en-3-ol (9, R = 1,1,2-Trimethylpropyl, i.e., Thexyll).** From 3 (R = thexyll) (0.564 g, 2.66 mmol), 5 (0.416 g, 2.68 mmol), THF (15 mL), and t-BuLi in hexanes (1.9 mL, 1.41 mL, 2.68 mmol) (note that the excess of 5 and organolithium reagent was smaller in this example); colorless oil (0.105 g, 28%); 1H (400 MHz, CDCl3) δ 5.94 (1H, ddd, J = 17.2, 10.5, 6.7 Hz), 5.23 (1H, d, J = 17.2 Hz), 5.18 (1H, d, J = 10.5 Hz), 4.01 (1H, d, J = 6.7 Hz), CH2O); 1H (400 MHz, CDCl3) δ 0.83 (3H, s), 0.73 (5H, d, J = 6.7 Hz, 2Hm, m), 0.68 (4H, d, J = 6.7 Hz, 2Hm, m), 0.61 (2H, m, J = 6.7 Hz, 2Hm, m); 13C (125 MHz, CDCl3) δ 138.4 (CH), 115.9 (CH), 78.6 (CH), 41.7 (CH3). HRMS (EI) m/z calc for C10H18O 162.1252, found 162.1252 (M+6).

**4-Diethylhex-1-en-3-ol (14, R′ = R″ = Et):** From 3 (R′ = Et, R″ = Et) (0.335 g, 1.58 mmol), 5 (0.274 g, 1.76 mmol), dry THF (5 mL), and t-BuLi in hexanes (1.6 mL, 1.09 mL, 1.74 mmol); colorless liquid (0.442 g, 62%); 1H (400 MHz, CDCl3) δ 6.92 (1H, d, J = 10.5 Hz), 5.86 (1H, d, J = 10.5 Hz); 13C (125 MHz, CDCl3) δ 102.1 (CH), 101.7 (CH), 79.3 (CH), 43.6 (CH3). HRMS (EI) m/z calc for C18H26O1 282.1980, found 282.1969 (M+).

**4-Phenylbut-3-en-2-ol (9, R = Benzyl).** From 3 (R = Bn) (0.280 g, 1.28 mmol), 5 (0.226 g, 1.45 mmol), dry THF (10 mL), and t-BuLi in hexanes (1.5 M, 0.97 mL, 1.46 mmol); colorless oil (0.097 g, 52%); 1H (400 MHz, CDCl3) δ 7.24 (2H, app t, J = 8.7 Hz, 7.9−17.5 (3H, m), 5.86 (1H, d, J = 17.2, 10.5, 5.8 Hz), 5.18 (1H, app dt, J = 17.2, 1.4 Hz), 5.06 (1H, app dt, J = 10.5, 1.4 Hz), 4.31−4.4 (2H, m, 2.82 (1H, dd, J = 13.6, 5.1 Hz), 2.72 (1H, dd, J = 13.6, 8.0 Hz), 1.64 (1H, br s); 13C (125 MHz, CDCl3) δ 141.2 (CH), 137.8 (quat C), 129.7 (CH), 128.6 (CH), 126.7 (CH), 115.1 (CH), 73.8 (CH), 43.9 (CH3); LRMS (EI) m/z m/z 148 (M+, 4%).

**1-(4-Methoxyphenyl)but-3-en-2-ol (9, R = 4-Methoxybenzyl).** From 4-methoxybenzylboronic acid pinacol ester (0.292 g, 1.18 mmol), 5 (0.210 g, 1.35 mmol), dry THF (10 mL), and t-BuLi in hexanes (1.5 M, 0.84 mL, 1.26 mmol); colorless oil (0.185 g, 52%); 1H (400 MHz, CDCl3) δ 7.40 (2H, d, J = 7.2 Hz), 7.29 (2H, app t, J = 7.2 Hz), 7.16 (1H, t, J = 7.3 Hz), 6.35 (1H, d, J = 16.7 Hz), 6.25 (1H, d, J = 16.7 Hz), 5.95 (1H, d, J = 10.2 Hz), 4.75 (2H, m, J = 6.7 Hz, 2Hm, m), 1.01 (6H, s); 13C (125 MHz, CDCl3) δ 122.7 (quat C next to boron not seen) δ 139.5 (quat C), 135.9 (CH), 129.0 (CH), 128.4 (CH), 126.2 (CH), 126.1 (CH), 71.9 (CH3), 41.1 (CH3), 31.4 (quat C), 30.5 (CH3), 29.2 (CH3), 27.7 (CH3), 27.4 (CH3), 27.3 (CH3), 22.6 (CH3); 1H (962 MHz, CDCl3) δ 29.3; HR-El" MS m/z (%) calc for C20H20O2 394.3043, found 394.3049 (M+, 39%).

**Reactions of Alkylboronic Esters with 5 and tert-BuLi: General Procedure.** A mixture of the appropriate BN(pinac)2 (1H, d, J = 10.5 Hz) tert-BuLi (1.12, or 1.13 (1 equiv), 1-bromo-3-chloroprop-2-ene (1.1 equiv), and dry THF in a dry 50 mL round-bottomed flask equipped with a magnetic stirrer bar and septum was cooled to −78°C, and t-BuLi in hexanes (1.1 equiv) was added dropwise with vigorous stirring, and the mixture was stirred for an additional 30 min. The cooling bath was removed and the reaction mixture left to warm to 20°C over 3 h. An accurately weighed amount of tetradecane (~0.2 mL) was added as a standard to enable GC determination of the amount of desired product formed following workup. The reaction mixture was cooled to 0°C, then oxidized by dropwise addition of excess NaOH (0.6 g in 5 mL of H2O), followed by hydrogen peroxide (30% by weight, 3 mL).

Once the initial exothermic reaction subsided, the cooling bath was removed and the mixture left to stir overnight at room temperature. Diethyl ether (10 mL) was added, and the product extracted with diethyl ether (3 × 20 mL). The combined organic extracts were washed with water (2 × 10 mL), dried over
magnesium sulfate, filtered, and concentrated under reduced pressure to give the product.

**Hept-1-en-3-ol (9, R = n-Bu)**: From vinylMgBr (0.7 M, 20 mL, 14 mmol) and valeraldehyde (1.49 g, 5.9 mmol); colorless liquid (0.044 g, 100%): 1H (500 MHz, CDCl3) δ 5.86 (1H, ddd, J = 17.2, 10.5, 6.4 Hz), 5.14 (1H, br s), 1.44 (2H, m), 1.39–1.42 (4H, m), 1.29 (12H, s), 0.79 (2H, t, J = 17.2, 10.5, 6.4 Hz), 1.81 (1H, m), 1.79–1.80 (2H, m), 1.57 (1H, br s), 0.93 (3H, d, J = 6.8 Hz), 0.90 (3H, d, J = 6.4 Hz); 13C (125 MHz, CDCl3) δ 131.0 (quat C), 129.3 (quat C), 83.1 (quat C), 80.0 (quat C), 38.0 (quat C), 28.3 (CH3), 24.9 (CH2), 19.9 (CH2), 10.7 (br, CHB); 11B (962 MHz, CDCl3) δ 32.8; HR-EL+ MS (M+, 20%).

**Synthesis of tert-Butyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (15).** Borane dimethyl sulfoxide (10 M, 1.94 mL, 19.4 mmol) was added to a 20 mL round-bottomed flask equipped with a stirrer bar and under N2. The flask was cooled in an ice bath, and a solution of pinacol (2.29 g 19.4 mmol) in dry dichloromethane (5 mL). The reaction mixture was stirred for 5 min, the reaction mixture was stirred for an hour at 0 °C and a further hour at room temperature before being transferred dropwise via cannula to a 100 mL round-bottomed flask equipped with a stirrer bar and a suspension of Wilkinson’s catalyst (0.16 g, 0.17 mmol, 1 mol %) in dry dichloromethane (5 mL). The reaction mixture was stirred for 5 min, then tert-butyl but-3-enoate (2.50 g, 17.6 mmol) was added dropwise over a period of 10 min. The mixture was stirred overnight at room temperature then concentrated under reduced pressure. Hexane (20 mL) was added, the mixture was filtered, and the filtrate was concentrated to give the crude product (4.30 g, 91%), which consisted of boronic esters 15 and 16 (85:15 by relative integrations by 1H NMR). This was fractionated by column chromatography on silica gel (98:2 petroleum ether/ethyl acetate, followed by 95:5, 90:10, and finally 85:15) to give boronate ester 15 as a colorless oil (1.80 g, 50%). **1H** (400 MHz, CDCl3) δ 4.22 (2H, t, J = 6.8 Hz), 1.69 (2H, app pent, J = 6.4 Hz), 1.81–1.88 (1H, m), 1.79–1.90 (2H, m), 1.70–1.72 (2H, m), 1.55 (1H, br s), 1.44–0.93 (6H, m); 13C (125 MHz, CDCl3) δ 140.0 (CH), 115.6 (CH), 77.9 (CH), 43.7 (CH3), 28.9 (CH2), 28.5 (CH2), 26.7 (CH2), 26.3 (CH2), 26.2 (CH2).

**Synthesis of tert-Butyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (15).** Borane dimethyl sulfoxide (10 M, 1.94 mL, 19.4 mmol) was added to a 20 mL round-bottomed flask equipped with a stirrer bar and under N2. The flask was cooled in an ice bath, and a solution of pinacol (2.29 g 19.4 mmol) in dry dichloromethane (5 mL). The reaction mixture was stirred for 5 min, then tert-butyl but-3-enoate (2.50 g, 17.6 mmol) was added dropwise over a period of 10 min. The mixture was stirred overnight at room temperature then concentrated under reduced pressure. Hexane (20 mL) was added, the mixture was filtered, and the filtrate was concentrated to give the crude product (4.30 g, 91%), which consisted of boronic esters 15 and 16 (85:15 by relative integrations by 1H NMR). This was fractionated by column chromatography on silica gel (98:2 petroleum ether/ethyl acetate, followed by 95:5, 90:10, and finally 85:15) to give boronate ester 15 as a colorless oil (1.80 g, 50%). **1H** (400 MHz, CDCl3) δ 4.22 (2H, t, J = 6.8 Hz), 1.69 (2H, app pent, J = 6.4 Hz), 1.81–1.88 (1H, m), 1.79–1.90 (2H, m), 1.70–1.72 (2H, m), 1.55 (1H, br s), 1.44–0.93 (6H, m); 13C (125 MHz, CDCl3) δ 140.0 (CH), 115.6 (CH), 77.9 (CH), 43.7 (CH3), 28.9 (CH2), 28.5 (CH2), 26.7 (CH2), 26.3 (CH2), 26.2 (CH2).

**Synthesis of tert-Butyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (15).** Borane dimethyl sulfoxide (10 M, 1.94 mL, 19.4 mmol) was added to a 20 mL round-bottomed flask equipped with a stirrer bar and under N2. The flask was cooled in an ice bath, and a solution of pinacol (2.29 g 19.4 mmol) in dry dichloromethane (5 mL). The reaction mixture was stirred for 5 min, then tert-butyl but-3-enoate (2.50 g, 17.6 mmol) was added dropwise over a period of 10 min. The mixture was stirred overnight at room temperature then concentrated under reduced pressure. Hexane (20 mL) was added, the mixture was filtered, and the filtrate was concentrated to give the crude product (4.30 g, 91%), which consisted of boronic esters 15 and 16 (85:15 by relative integrations by 1H NMR). This was fractionated by column chromatography on silica gel (98:2 petroleum ether/ethyl acetate, followed by 95:5, 90:10, and finally 85:15) to give boronate ester 15 as a colorless oil (1.80 g, 50%). **1H** (400 MHz, CDCl3) δ 4.22 (2H, t, J = 6.8 Hz), 1.69 (2H, app pent, J = 6.4 Hz), 1.81–1.88 (1H, m), 1.79–1.90 (2H, m), 1.70–1.72 (2H, m), 1.55 (1H, br s), 1.44–0.93 (6H, m); 13C (125 MHz, CDCl3) δ 140.0 (CH), 115.6 (CH), 77.9 (CH), 43.7 (CH3), 28.9 (CH2), 28.5 (CH2), 26.7 (CH2), 26.3 (CH2), 26.2 (CH2).