Simple Access to Elusive \( \alpha \)-Boryl Carbanions and their Alkylation: An Umpolung Construction for Organic Synthesis

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**General Information**

$^1$H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: 7.26 ppm, THF-$d_8$: 3.58 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, sx = sextet, sp = septet, m = multiplet, br = broad), and coupling constants (Hz). $^{13}$C NMR spectra were recorded on either a Varian Gemini-500 (125 MHz), or a Varian Inova-500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl$_3$: 77.0 ppm, THF-$d_8$: 67.57 ppm). Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm$^{-1}$) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (DART+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO$_2$, 230 – 400 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA) in ethanol and ceric ammonium molybdate (CAM) in ethanol.

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether, dichloromethane and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after being purged with argon.

Bis(pinacolato)diboron was generously donated by Allychem Co., Ltd. and used without further purification. Triethylamine was purchased from Alfa Aesar and distilled over calcium hydride prior to use. The following reagents were purchased and used without purification: copper(I) iodide (CuI) (Aldrich), lithium 2,2,6,6-tetramethylpiperidide (LTMP) (Aldrich), sodium tert-butoxide (NaOt-Bu) (Strem), palmitic acid-1-$^{13}$C (Cambridge Isotope Laboratories), and N,N-dimethylformamide (DMF) (Acros). All other reagents were purchased from either Aldrich, Alfa Aesar or Acros and used without further purification.
Experimental Procedures

I. Representative Procedures for Preparation of geminal-Diboronate Esters

Method A:

To a stirred solution of triphenyl phosphite (8.53 g, 27.5 mmol) in anhydrous DCM (250 mL) at −78 °C under N₂ was added bromine (1.41 mL, 27.5 mmol) dropwise. Freshly distilled triethylamine (10.45 mL, 75.0 mmol) and hydrocinnamaldehyde (3.29 mL, 25.0 mmol) were added at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 hours. Upon completion, the solvent was evaporated in vacuo and the crude reaction mixture was purified on silica gel (100% hexanes) to afford the 1,1-dibromide with a small amount of impurity as a pale yellow oil (6.18 g, 89%).

(3,3-dibromopropyl)benzene (S1). ¹H NMR (500 MHz, CDCl₃): δ 7.33-7.30 (2H, m), 7.25-7.20 (3H, m), 5.60 (1H, t, J = 6.3 Hz), 2.88-2.85 (2H, m), 2.73-2.68 (2H, m). ¹³C NMR (125 MHz, CDCl₃): δ 139.1, 128.7, 128.5, 126.5, 46.7, 45.1, 34.1; IR (neat): 3026.4 (w), 2949.4 (w), 1602.7 (w), 1495.8 (w), 1453.2 (m), 1157.8 (m), 847.5 (w), 746.7 (s), 697.0 (s), 673.1 (s), 600.2 (m), 551.9 (m), 490.3 (m) cm⁻¹. HRMS-(DART⁺) for C₁₉H₁₀Br₂[M⁺]: calculated: 275.9149, found: 275.9150.

In the glove box, an oven-dried 100 mL round-bottom flask with magnetic stir bar was charged with CuI (190 mg, 1.00 mmol), LiOMe (949 mg, 25.0 mmol) and B₂(pin)₂ (5.08 g, 20.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of DMF (20 mL) under N₂. After stirring at room temperature for 10 min, a solution of 1,1-dibromide (2.92 g, 10.5 mmol) in DMF (5 mL) was added via syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, 40 mL diethyl ether was added. The slurry was filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture (DMF solution) was directly purified on silica gel (hexanes: diethyl ether = 10:1) to afford the desired product as a white solid (3.09 g, 83%).

Note: In general, the more expensive B₂(pin)₂ was the limiting reagent. When the dibromide is more precious, B₂(pin)₂ is used in slight excess.

¹ Spaggiari, A.; Vaccari, D.; Davoli, P.; Torre, G.; Prati, F. J. Org. Chem. 2007, 72, 2216.
**Method B:**

In the glove box, an oven-dried 500 mL round-bottom flask with magnetic stir bar was charged with CuI (1.428 g, 7.500 mmol), LiOMe (8.543 g, 225 mmol) and B\(_2\)(pin)_2 (38.09 g, 150.0 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of DMF (150 mL) under N\(_2\). After stirring at room temperature for 10 min, dibromomethane (10.53 mL, 150.0 mmol) was added via syringe at room temperature. The reaction mixture was allowed to stir at room temperature for 12 hours. Upon completion, 200 mL diethyl ether was added. The slurry was filtered through a silica gel plug, rinsed with diethyl ether, and concentrated \textit{in vacuo}. The crude reaction mixture in DMF was diluted with hexanes (300 mL), washed with H\(_2\)O (75 mL \times 4), dried over Na\(_2\)SO\(_4\), then concentrated \textit{in vacuo}. The desired product \textit{6} was obtained as a white solid (15.72 g, 78%) and used without further purification.

**Method C:**

In the glove box, an oven-dried 25 mL round-bottom flask with magnetic stir bar was charged with LTMP (773 mg, 5.25 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (20 mL) under N\(_2\). The reaction mixture was cooled to 0 °C, and a solution of 1,1-diborylmethane \textit{6} (1.34 g, 5.00 mmol) in THF (5 mL) was added \textit{via} syringe and the mixture was allowed to stir at 0 °C for 10 minutes. (2-Bromoethyl)benzene (751 µL, 5.50 mmol) was added dropwise and the reaction was allowed to stir at 0 °C for 15 min. Upon completion, the reaction mixture was warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated \textit{in vacuo}. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford the desired product \textit{2} as a colorless oil (1.54 g, 83%).
**Method D:**

In the glove box, an oven-dried 10 mL round-bottom flask with magnetic stir bar was charged with LTMP (155 mg, 1.05 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (2 mL) under N$_2$. The reaction mixture was cooled to 0 °C, and a solution of 1,1-diboronate ester 2 (372 mg, 1.00 mmol) in THF (1 mL) was added via syringe and the mixture was allowed to stir at 0 °C for 10 minutes. Upon completion, the reaction mixture was transferred dropwise via syringe to a second flask containing a solution of 1,4-dibromopentane (273 µL, 2.00 mmol) in THF (5 mL) at 0 °C. The reaction mixture was allowed to stir at 0 °C for 15 min, then warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford the desired product 26 as a white solid (449 mg, 86%).

**Method E:**

The *gem*-diboryl cyclopropane S6 was prepared according to the literature procedure with some modification.$^2$ An oven-dried 25 mL round-bottom flask with magnetic stir bar was charged with B$_2$(pin)$_2$ (508 mg, 2.0 mmol) and (2,2-dibromocyclopropyl)benzene (607 mg, 2.20 mmol). The flask was sealed with a rubber septum and purged with N$_2$. THF (6 mL) was added and the reaction mixture was cooled to −78 °C. n-BuLi (2.50 M in hexanes, 0.88 mL, 2.20 mmol) was added dropwise and the reaction was allowed to stir at −78 °C for 10 min, then warmed to room temperature and stirred for 12 hours. The reaction mixture was quenched by H$_2$O at 0 °C, extracted with diethyl ether, dried over Na$_2$SO$_4$, and concentrated *in vacuo*. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford the desired product as a white solid (471 mg, 64%).

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$^2$ Shimizu, M.; Schelper, M.; Nagao, I.; Shimono, K.; Kurahashi, T.; Hiyama, T. *Chem. Lett.* **2006**, *35*, 1222.
II. Full Characterization of geminal-Diboronate Esters

2,2’-(3-phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2). Prepared according to Representative Procedure (Method A or Method C). 1H NMR (500 MHz, CDCl3): δ 7.26-7.23 (2H, m), 7.18-7.14 (3H, m), 2.60-2.57 (2H, m), 1.88-1.83 (2H, m), 1.24 (12H, s), 1.23 (12H, s), 0.81 (1H, t, J = 7.8 Hz). The 1H NMR spectrum was in accord with previously reported data.3

2,2’-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4). Prepared according to Representative Procedure (Method C) with LTMP (424 mg, 2.88 mmol), diborylmethane 6 (734 mg, 2.74 mmol), benzyl bromide (356 μL, 3.01 mmol), and THF (13 mL). The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford the desired product as a colorless oil (753 mg, 77%). 1H NMR (500 MHz, CDCl3): δ 7.25-7.20 (4H, m), 7.13-7.09 (1H, m), 2.88 (2H, d, J = 8.3 Hz), 1.20-1.15 (1H, m), 1.18 (12H, s), 1.17 (12H, s); 13C NMR (125 MHz, CDCl3): δ 144.5, 128.3, 128.0, 125.3, 83.1, 31.3, 24.8, 24.5; IR (neat): 2976.9 (w), 2930.2 (w), 1454.0 (w), 1357.5 (m), 1311.7 (s), 1267.1 (m), 969.6 (m), 850.9 (m), 732.2 (w), 697.6 (m), 528.3 (w) cm⁻¹; HRMS-(DART+) for C20H33B2O4[M+H]+: calculated: 359.2565, found: 359.2565.

2,2’-(cyclohexylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5). The reaction was performed according to Representative Procedure (Method A) with CuI (19.1 mg, 0.1 mmol), LiOMe (94.9 mg, 2.5 mmol), B2(pin)2 (508 mg, 2.0 mmol), (dibromomethyl) cyclohexane (313 mg, 1.2 mmol) and DMF (2 mL). The crude reaction mixture was purified by column chromatography on silica gel (10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (239 mg, 68%). 1H NMR (500 MHz, CDCl3): δ 1.78-1.57 (6H, m), 1.35-1.20 (2H, m), 1.23 (12H, s), 1.22 (12H, s), 1.12-1.04 (1H, m), 0.95-0.87 (2H, m), 0.64 (1H, d, J = 10.3 Hz). The 1H NMR spectrum was in accord with previously reported data.3

bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (6). The reaction was performed according to Representative Procedure (Method B). 1H NMR (500 MHz, CDCl3): δ 1.23 (24H, s), 0.35 (2H, s). The 1H NMR spectrum was in accord with previously reported data.3

3 Sun, C.; Porter, B.; Morken, J. P. J. Am. Chem. Soc. 2014, 136, 6534.
2,2’-(1,4-diphenylbutane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S2). The reaction was performed according to Representative Procedure (Method C) with diboronate ester 2 (372 mg, 1.00 mmol), LTMP (155 mg, 1.05 mmol), benzyl bromide (131 µL, 1.10 mmol) and THF (5 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 – 10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (353 mg, 76%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.34-7.32 (2H, m), 7.24 -7.19 (4H, m), 7.16 -7.09 (4H, m), 3.08 (2H, s), 2.66 -2.63 (2H, m), 1.82 -1.79 (2H, m), 1.27 (12H, s), 1.23 (12H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.5, 141.7, 129.7, 128.5, 128.1, 127.8, 127.6, 126.0, 125.4, 83.3, 34.8, 33.9, 31.7, 25.1, 24.7; IR (neat): 2976.9 (w), 2926.6 (w), 1452.6 (m), 1350.0 (m), 1308.0 (s), 1247.6 (m), 1207.6 (m), 1134.4 (s), 976.8 (w), 848.6 (m), 698.0 (s), 578.9 (w), 492.7 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{28}$H$_{41}$B$_2$O$_4$ [M+H]: calculated: 463.3191, found: 463.3204.

2,2’-(1-phenyloct-7-ene-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S3). The reaction was performed according to Representative Procedure (Method C) with diboronate ester 2 (186 mg, 0.50 mmol), LTMP (77.3 mg, 0.525 mmol), 5-bromo-1-pentene (65 µL, 0.55 mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (195.2 mg, 89%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.26-7.23 (2H, m), 7.20-7.19 (2H, m), 7.15-7.12 (1H, m), 5.86 (1H, ddt, $J$ = 17.1, 10.3, 6.9 Hz), 5.01 (1H, ddt, $J$ = 17.1, 2.0, 1.5 Hz), 4.93 (1H, ddt, $J$ = 10.3, 2.4, 1.0 Hz), 2.52-2.49 (2H, m), 2.10-2.06 (2H, m), 1.91-1.88 (2H, m), 1.74-1.71 (2H, m), 1.41-1.35 (2H, m), 1.23 (24H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.8, 139.3, 128.5, 128.1, 125.4, 114.0, 83.0, 34.5, 33.8, 31.9, 28.7, 26.6, 24.8, 24.7; IR (neat): 2975.6 (w), 2917.6 (w), 1354.0 (w), 1309.2 (s), 1249.5 (m), 1135.3 (s), 966.9 (w), 849.1 (m), 750.5 (w), 699.6 (m), 669.0 (w) cm$^{-1}$.

2,2’-(cyclopropylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S4). The reaction was performed according to Representative Procedure (Method E) with (dibromomethyl)cyclopropane (470.6 mg, 2.20 mmol), B$_2$(pin) (508.0 mg, 2.00 mmol), n-BuLi (2.50 M, 0.88 mL, 2.20 mmol) and THF (6 mL). The crude reaction mixture was purified by column chromatography on silica gel (15:1 – 9:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (116.8 mg, 19%). The $^1$H NMR spectrum was in accord with previously reported data.4

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4 Li, H.; Shangguan, X.; Zhang, Z.; Huang, S.; Zhang, Y.; Wang, J. Org. Lett. 2014, 16, 448.
2,2’-(1-cyclopropyl-3-phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S5). The reaction was performed according to Representative Procedure (Method C) with diboronate ester S4 (116.0 mg, 0.377 mmol), LTMP (58.3 mg, 0.396 mmol), (2-bromoethyl)benzene (0.057 mL, 0.415 mmol) and THF (2 mL). The crude reaction mixture was purified by column chromatography on silica gel (30:1 – 20:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (116.2 mg, 75%). 

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.26-7.21 (4H, m), 7.15-7.12 (1H, m), 2.73-2.70 (2H, m), 1.90-1.86 (2H, m), 1.22 (24H, s), 0.97-0.91 (1H, m), 0.46-0.38 (4H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 144.2, 128.5, 128.1, 125.3, 82.8, 35.9, 34.8, 24.8, 24.7, 12.9, 3.6; IR (neat): 2977.0 (w), 1345.8 (m), 1311.2 (s), 1247.3 (m), 1213.1 (w), 1187.6 (w), 1131.8 (s), 967.6 (m), 848.2 (s), 826.2 (w), 757.5 (w), 741.6 (w), 699.8 (m), 668.5 (w), 601.8 (w), 494.2 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{24}$H$_{38}$B$_2$O$_4$ [M$^+$]: calculated: 412.2956, found: 412.2967.

2,2’-(2-phenylcyclopropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S6). The reaction was performed according to Representative Procedure (Method E). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.25-7.23 (2H, m), 7.21-7.17 (2H, m), 7.12-7.08 (1H, m), 2.47 (1H, dd, $J = 7.3, 5.9$ Hz), 1.52 (1H, dd, $J = 5.4, 3.4$ Hz), 1.27-1.22 (1H, m), 1.222 (6H, s, overlap), 1.215 (6H, s, overlap), 0.99 (6H, s), 0.94 (6H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 140.9, 128.3, 127.8, 125.8, 82.86, 26.7, 24.83, 24.81, 24.7, 24.2, 14.1; IR (neat): 2977.5 (m), 2930.2 (w), 1379.1 (s), 1342.6 (s), 1298.8 (m), 1215.2 (w), 1148.2 (s), 1113.9 (m), 968.0 (w), 851.2 (m), 696.3 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{21}$H$_{33}$B$_2$O$_4$ [M$^+$]: calculated: 371.2565, found: 371.2568.

2,2’-(1-chloro-5-phenylpentane-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (24). The reaction was performed according to Representative Procedure (Method D) with diboronate ester 2 (186 mg, 0.50 mmol), LTMP (77.3 mg, 0.525 mmol), 1-bromo-2-chloroethane (83 µL, 1.0 mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (178 mg, 82%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.27-7.24 (2H, m), 7.19 (2H, d, $J = 7.3$ Hz), 7.15 (1H, t, $J = 7.3$ Hz), 3.62 (2H, t, $J = 8.3$ Hz), 2.57-2.53 (2H, m), 2.20 (2H, t, $J = 8.3$ Hz), 1.90-1.87 (2H, m), 1.23 (24H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.1, 128.4, 128.2, 125.6, 83.3, 43.5, 33.9, 33.1, 32.4, 24.8, 24.7; IR (neat): 2977.8 (m), 2931.0 (w), 2865.6 (w), 1454.9 (w), 1353.5 (m), 1317.0 (s), 1243.1 (m), 1137.0 (s), 967.5 (w), 852.1 (m), 699.6 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{23}$H$_{38}$B$_2$Cl$_1$O$_4$ [M$^+$]: calculated: 435.2645, found: 435.2665.

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2,2'-((6-bromo-1-phenylhexane-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (25). The reaction was performed according to Representative Procedure (Method D) with diboronate ester 2 (186 mg, 0.50 mmol), LTMP (77.3 mg, 0.525 mmol), 1,3-dibromo propane (0.12 mL, 1.2 mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (217 mg, 88%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26-7.24 (2H, m), 7.20 (2H, d, $J = 7.3$ Hz), 7.14 (1H, t, $J = 7.3$ Hz), 3.42 (2H, t, $J = 6.8$ Hz), 2.54-2.51 (2H, m), 1.90-1.85 (4H, m), 1.81-1.78 (2H, m), 1.23 (24H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.5, 128.5, 128.2, 125.5, 83.2, 34.5, 33.8, 32.1, 30.9, 28.0, 24.8, 24.7; IR (neat): 2977.3 (m), 2930.7 (w), 2863.3 (w), 1454.7 (w), 1353.9 (m), 1308.9 (m), 1250.2 (m), 1213.8 (w), 11369 (s), 967.8 (w), 853.6 (m), 699.6 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{24}$H$_{40}$B$_2$Br$_1$O$_4$ [M+H]$^+$: calculated: 493.2296, found: 493.2309.

2,2'-(7-bromo-1-phenyloctane-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (26). The reaction was performed according to Representative Procedure (Method D).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26-7.23 (2H, m), 7.21-7.20 (2H, m), 7.16-7.12 (1H, m), 4.23-4.16 (1H, m), 2.57-2.46 (2H, m), 1.94-1.84 (3H, m), 1.81-1.64 (3H, m), 1.71 (3H, d, $J = 6.8$ Hz), 1.53-1.38 (2H, m), 1.24 (12H, s), 1.23 (12H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.7, 128.5, 128.1, 125.4, 83.0, 52.0, 41.8, 33.8, 31.9, 28.3, 26.5, 25.3, 24.83, 24.79, 24.72, 24.70; IR (neat): 2979.3 (w), 2923.1 (w), 2862.9 (w), 1452.7 (w), 1304.5 (s), 1246.6 (m), 1137.1 (s), 968.4 (w), 860.1 (m), 743.1 (m), 696.6 (m), 668.0 (w), 522.7 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{26}$H$_{44}$B$_2$Br$_1$O$_4$ [M+H]$^+$: calculated: 521.2609, found: 521.2609.

2,2'-(8-bromo-1-phenyloctane-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (27). The reaction was performed according to Representative Procedure (Method D) with diboronate ester 2 (372 mg, 1.00 mmol), LTMP (155 mg, 1.05 mmol), 1,5-dibromopentane (0.272 mL, 2.00 mmol) and THF (5 mL). The crude reaction mixture was purified by column chromatography on silica gel (15:1 – 10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (436 mg, 84%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26-7.23 (2H, m), 7.20-7.19 (2H, m), 7.16-7.12 (1H, m), 3.42 (2H, t, $J = 6.9$ Hz), 2.52-2.49 (2H, m), 1.92-1.87 (4H, m), 1.72-1.69 (2H, m), 1.49-1.43 (2H, m), 1.36-1.27 (2H, m), 1.23 (24H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.7, 128.5, 128.1, 125.4, 83.0, 34.0, 33.8, 32.7, 31.9, 28.80, 28.75, 26.1, 24.8, 24.7; IR (neat): 2972.1 (w), 2929.4 (w), 2856.6 (w), 1451.9 (w), 1348.8 (m), 1307.4 (s), 1244.1 (s), 1133.9 (s), 1047.7 (w), 1020.2 (w), 968.4 (m), 848.5 (s), 754.2 (m), 699.8 (s), 666.9 (m), 558.0 (w), 502.6 (w) cm$^{-1}$;
HRMS-(DART+) for $^{12}$C$_{26}$H$_{44}^{11}$B$_2^{79}$Br$_1^{16}$O$_4$ [M+H]$^+$: calculated: 521.2609, found: 521.2634.

2,2'-(6-bromohexane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (28). The reaction was performed according to Representative Procedure (Method D) with 6 (375 mg, 1.40 mmol), LTMP (216 mg, 1.47 mmol), 1,5-dibromopentane (0.245 mL, 1.80 mmol) and THF (7 mL). The crude reaction mixture was purified by column chromatography on silica gel (10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (496 mg, 85%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.39 (2H, t, $J = 7.1$ Hz), 1.84 (2H, qi, $J = 7.3$ Hz), 1.54 (2H, q, $J = 7.8$ Hz), 1.44-1.38 (2H, m), 1.35-1.27 (2H, m), 1.224 (12H, s), 1.216 (12H, s), 0.70 (1H, t, $J = 7.8$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 82.9, 33.9, 32.6, 31.4, 28.1, 25.3, 24.8, 24.5; IR (neat): 2976.6 (w), 2929.7 (w), 1462.6 (w), 1356.7 (m), 1307.8 (s), 1266.9 (m), 1234.5 (m), 1137.3 (s), 968.9 (m), 849.0 (m), 669.8 (w), 578.4 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{18}$H$_{36}^{11}$B$_2^{79}$Br$_1^{16}$O$_4$ [M+H]$^+$: calculated: 417.1983, found: 417.1975.

2,2'-(9-bromo-1-phenylnonane-3,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (29). The reaction was performed according to Representative Procedure (Method D) with 2 (186 mg, 0.50 mmol), LTMP (77.3 mg, 0.525 mmol), 1,6-dibromohexane (154 $\mu$L, 1.0 mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (10:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (206 mg, 77%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.26-7.23 (2H, m), 7.19 (2H, d, $J = 6.8$ Hz), 7.14 (1H, t, $J = 6.8$ Hz), 3.41 (2H, t, $J = 6.9$ Hz), 2.52-2.49 (2H, m), 1.91-1.83 (4H, m), 1.71-1.68 (2H, m), 1.47-1.42 (2H, m), 1.36-1.23 (4H, m), 1.23 (24H, s, overlap); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.8, 128.5, 128.1, 125.4, 83.0, 34.0, 33.8, 32.9, 31.9, 29.5, 28.9, 28.2, 26.9, 24.8, 24.7; IR (neat): 2976.8 (m), 2929.6 (m), 2857.4 (w), 1454.8 (w), 1306.6 (s), 1253.3 (m), 1137.2 (s), 968.3 (w), 853.8 (w), 749.7 (w), 699.4 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{27}$H$_{46}^{11}$B$_2^{79}$Br$_1^{16}$O$_4$ [M+H]$^+$: calculated: 535.2766, found: 535.2781.
III. Representative Procedure for Deborylative Alkylation

In the glove box, an oven-dried 2-dram vial with magnetic stir bar was charged with 1,1-diboronate ester 2 (48.4 mg, 0.13 mmol), 1-bromododecane (24.0 µL, 0.10 mmol) and THF (0.50 mL), followed by the base (0.30 mmol). The vial was sealed with a polypropylene cap, removed from the glove box, and was allowed to stir at room temperature for 3 hours. Upon completion, the reaction mixture was diluted with diethyl ether (2 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 75:1) to afford the desired product 3 as a colorless oil.
**IV. Full Optimization Table**

| entry | base     | solvent | conversion (%) | yield (%) |
|-------|----------|---------|----------------|-----------|
| 1     | KOH      | THF     | <5             | -b        |
| 2     | LiOt-Bu  | THF     | <5             | -b        |
| 3     | NaOi-Pr  | THF     | <5             | -b        |
| 4     | NaOr-Bu  | THF     | 100            | 91        |
| 5     | NaOr-Amyl| THF     | 85             | 72        |
| 6     | NaHMDS   | THF     | 100            | -c        |
| 7     | KOMe     | THF     | 30             | -         |
| 8     | KOt-Bu   | THF     | 100            | 68        |
| 9     | NaOr-Bu  | THF     | 65             | 46\textsuperscript{d} |
| 10    | NaOr-Bu  | dioxane | 75             | 70        |
| 11    | NaOr-Bu  | ether   | <5             | -b        |
| 12    | NaOr-Bu  | \(\text{CH}_2\text{Cl}_2\) | <5 | -b |
| 13    | NaOr-Bu  | hexanes | <5             | -b        |
| 14    | NaOr-Bu  | toluene | <5             | -b        |
| 15    | KOt-Bu   | toluene | 80             | 76        |
| 16    | NaOr-Bu  | THF     | 100            | 97\textsuperscript{e} |
| 17    | NaOr-Bu  | THF     | 67             | \textsuperscript{f, g} |
| 18    | KOt-Bu   | toluene | 100            | 97\textsuperscript{f, h} |

\textsuperscript{a} Reaction conditions: 1-bromododecane (0.10 mmol, 0.2 M), 2 (0.13 mmol) and base (0.30 mmol). Conversion refers to consumption of 1-bromododecane and was determined by \textsuperscript{1}H NMR with 1,3,5-trimethoxybenzene as the internal standard. Yield refers to the isolated yield of purified material. \textsuperscript{b} partial protodeboronation of 2. \textsuperscript{c} exclusively S7. \textsuperscript{d} 1.5 equiv. NaOr-Bu employed instead of 3.0 equiv. \textsuperscript{e} 14 hours. \textsuperscript{f} 1-chlorododecane employed instead of 1-bromododecane. \textsuperscript{g} 3:S8 = 2.5:1. \textsuperscript{h} 2.0 equiv. 2, 5.0 equiv. KOt-Bu, toluene, 14 hours.
V. Full Characterization of Reaction Products and Proof of Stereochemistry

4,4,5,5-tetramethyl-2-(1-phenylpentadecan-3-yl)-1,3,2-dioxaborolane (3). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.28-7.25 (2H, m), 7.19-7.14 (3H, m), 2.65-2.54 (2H, m), 1.78-1.70 (1H, m), 1.68-1.61 (1H, m), 1.47-1.34 (2H, m), 1.33-1.20 (32H, m), 1.07-1.01 (1H, m), 0.88 (3H, t, $J = 6.9$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.2, 128.4, 128.2, 125.5, 82.9, 35.7, 33.5, 31.9, 31.3, 29.9, 29.70, 29.67, 29.65, 29.61, 29.59, 29.4, 29.2, 24.9, 24.8, 22.7, 14.1; IR (neat): 2976.6 (w), 2921.8 (s), 2852.4 (m), 1456.1 (w), 1385.8 (m), 1314.5 (m), 1143.4 (s), 966.5 (w), 746.5 (w), 698.0 (m) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{27}$H$_{48}$B$_1$O$_2$ [M+H]$^+$: calculated: 415.3747, found: 415.3744.

4,4,5,5-tetramethyl-2-(1-phenyltetradecan-2-yl)-1,3,2-dioxaborolane (7). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 1,1-diboronate ester 4 (46.6 mg, 0.13 mmol), 1-bromododecane (24.0 µL, 0.10 mmol), NaOt-Bu (28.8 mg, 0.30 mmol) and THF (0.50 mL). The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 75:1) to afford the desired product as a colorless oil (36.7 mg, 92%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.25-7.19 (4H, m), 7.13 (1H, t, $J = 7.1$ Hz), 2.72-2.64 (2H, m), 1.44-1.24 (24H, m), 1.16 (6H, s), 1.13 (6H, s), 0.88 (3H, t, $J = 6.9$ Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 142.4, 128.8, 128.0, 125.5, 82.9, 37.4, 31.9, 31.2, 29.8, 29.70, 29.65, 29.60, 29.56, 29.4, 29.2, 24.8, 24.7, 22.7, 14.1; IR (neat): 2922.4 (s), 2852.5 (m), 1455.8 (w), 1385.4 (m), 1318.5 (m), 1143.8 (s), 862.5 (w), 698.2 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{26}$H$_{46}$B$_1$O$_2$ [M+H]$^+$: calculated: 401.3591, found: 401.3593.

2-(1-cyclohexyltridecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 1,1-diboronate ester 5 (45.5 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), 1-bromododecane (24.0 µL, 0.10 mmol) and THF (0.5 mL) at 40 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (100:1 hexanes/diethyl ether) to afford a colorless oil (34.3 mg, 87%). $^1$H NMR (500 MHz, CDCl$_3$): δ 1.77-1.60 (5H, m), 1.43-0.81 (44H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 82.7, 39.7, 32.9, 32.6, 31.9, 30.0, 29.70, 29.68, 29.66, 29.64, 29.62, 29.60, 29.4, 28.8, 26.8, 25.0, 24.8, 22.7, 14.1; IR (neat): 2977.4 (w), 2920.9 (s), 2851.6 (m), 1447.8 (w), 1378.7 (m), 1312.4 (m), 1238.0 (w), 1144.8 (m), 970.9 (w), 865.3 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{25}$H$_{53}$B$_1$O$_2$ [M$+$NH$_4$]$^+$: calculated: 410.4169, found: 410.4175.

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4,4,5,5-tetramethyl-2-(4-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane (9). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 1,1-diboronate ester 2 (48.4 mg, 0.13 mmol), NaO-t-Bu (28.8 mg, 0.30 mmol), 2-bromopropane (9.4 µL, 0.10 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (75:1 – 50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (21.7 mg, 75%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.28-7.25 (2H, m), 7.20-7.14 (3H, m), 2.67-2.61 (1H, m), 2.54-2.48 (1H, m), 1.80-1.72 (2H, m), 1.70-1.63 (1H, m), 1.28 (12H, s), 0.94-0.90 (7H, m); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 143.2, 128.4, 128.2, 125.5, 82.9, 36.0, 31.4, 29.6, 25.1, 24.9, 22.3, 21.7; IR (neat): 2976.7 (w), 2955.3 (w), 2929.6 (w), 2867.2 (w), 1454.7 (w), 1379.4 (m), 1314.1 (m), 1213.4 (w), 1143.1 (s), 967.5 (w), 848.2 (w), 747.9 (w), 698.5 (m) cm\(^{-1}\); HRMS-(DART+) for \(\text{C}_{18}\text{H}_{30}\text{B}_{11}\text{O}_{2}\) [M+H]\(^+\): calculated: 289.2339, found: 289.2353.

2-(7-bromo-1-phenyloctan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 1,1-diboronate ester 2 (48.4 mg, 0.13 mmol), NaO-t-Bu (28.8 mg, 0.30 mmol), 1,4-dibromopentane (13.6 µL, 0.10 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (25:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (39.4 mg, mixture of the desired product (1:1 dr) and Ph(CH\(_2\))\(_3\)B(pin), 3:3:1, calculated yield = 84%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.28-7.24 (2H, m), 7.19-7.15 (3H, m), 4.16-4.09 (1H, m), 2.66-2.54 (2H, m), 1.87-1.61 (4H, m), 1.69 (3H, dd, \(J = 6.4, 1.5\) Hz, overlap), 1.57-1.34 (4H, m), 1.27 (12H, s), 1.08-1.03 (1H, m); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 142.9, 128.4, 128.2, 125.6, 83.0, 51.84, 51.79, 41.4, 41.3, 35.6, 33.40, 33.37, 30.52, 30.51, 27.3, 27.2, 26.4, 24.88, 24.87, 24.85; IR (neat): 2976.9 (w), 2955.3 (w), 2926.0 (w), 2858.0 (w), 1454.0 (w), 1378.4 (m), 1316.5 (m), 1213.4 (m), 1143.0 (s), 966.3 (w), 853.5 (w), 746.8 (w), 698.9 (m) cm\(^{-1}\); HRMS-(DART+) for \(\text{C}_{20}\text{H}_{33}\text{B}_{17}\text{Br}_{1}\text{O}_{2}\) [M+H]\(^+\): calculated: 395.1757, found: 395.1757.

4,4,5,5-tetramethyl-2-(1-phenylhex-5-en-3-yl)-1,3,2-dioxaborolane (11). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 1,1-diboronate ester 2 (96.7 mg, 0.26 mmol), NaO-t-Bu (57.7 mg, 0.60 mmol), allyl chloride (16.3 µL, 0.20 mmol) and THF (1.0 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (49.7 mg, 87%). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.28-7.25 (2H, m), 7.19-7.15 (3H, m), 5.81 (1H, ddt, \(J = 17.1, 10.3, 6.9\) Hz), 5.02 (1H, app dq, \(J = 17.1, 2.0\) Hz), 4.94 (1H, app dt, \(J = 10.3, 1.0\) Hz), 2.67-2.56 (2H, m), 2.26-2.14 (2H, m), 1.79-1.72 (1H, m), 1.71-1.63 (1H, m), 1.26 (12H, s), 1.18-1.12 (1H, m); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 142.9, 138.4, 128.4, 128.2, 125.6, 114.9, 83.1, 35.4, 35.3, 32.9, 24.9, 24.8; IR (neat): 2977.0 (w), 2924.5
(E)-4,4,5,5-tetramethyl-2-(1-phenylhept-5-en-3-yl)-1,3,2-dioxaborolane (12). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 2 (48.4 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), crotyl chloride (9.8 µL, 0.10 mmol, 5.8:1 E/Z isomers) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (27.9 mg, 93%, 6.0:1 E/Z, determined by oxidizing the boronate ester to the corresponding alcohol). $^1$H NMR (500 MHz, CDCl$_3$) (mixture of E/Z isomers): δ 7.28-7.25 (2H, m), 7.19-7.14 (3H, m), 5.47-5.37 (2H, m), 2.65-2.55 (2H, m), 2.43-2.08 (2H, m), 1.78-1.70 (1H, m), 1.69-1.61 (4H, m), 1.25 (12H, s), 1.14-1.08 (1H, m); $^{13}$C NMR (125 MHz, CDCl$_3$) (mixture of E/Z isomers): δ 143.0, 130.9, 130.2, 128.4, 128.2, 125.5, 125.3, 124.1, 83.01, 82.96, 35.6, 35.5, 34.3, 33.04, 33.02, 28.3, 24.88, 24.81, 24.77, 17.8, 12.9; IR (neat): 2977.1 (w), 2924.7 (w), 2855.5 (w), 1453.3 (w), 1379.8 (m), 1317.1 (m), 1238.3 (w), 1143.3 (s), 965.9 (m), 862.1 (w), 746.8 (w), 698.5 (w) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{18}$H$_{28}$B$_{11}$O$_2$ [M+H]$^+$: calculated: 287.2182, found: 287.2178.

$^5$ Brozek, L. A.; Ardolino, M. J.; Morken, J. P. J. Am. Chem. Soc. 2011, 133, 16778.
(E)-2-(6,10-dimethyl-1-phenylundeca-5,9-dien-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14). The reaction was performed according to Representative Procedure for Deborylative Alkylation with 1,1-diboronate ester 2 (48.4 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), geranyl chloride (18.5 μL, 0.10 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (34.8 mg, 91%).

1H NMR (500 MHz, CDCl3): δ 7.27-7.24 (2H, m), 7.19-7.14 (3H, m), 5.15-5.08 (2H, m), 2.66-2.55 (2H, m), 2.19-2.10 (2H, m), 2.08-2.04 (2H, m), 1.98-1.95 (2H, m), 1.79-1.63 (2H, m), 1.67 (3H, d, J = 1.0 Hz, overlap), 1.61 (3H, s), 1.59 (3H, s), 1.25 (12H, s), 1.13-1.08 (1H, m); 13C NMR (125 MHz, CDCl3): δ 143.1, 135.1, 131.2, 128.4, 128.2, 125.5, 124.4, 124.1, 82.9, 39.8, 35.6, 33.1, 29.4, 26.7, 25.7, 24.9, 24.8, 17.6, 16.2; IR (neat): 2976.2 (m), 2923.8 (m), 2855.3 (w), 1453.0 (w), 1379.8 (m), 1317.6 (m), 1240.9 (w), 1143.8 (s), 967.3 (w), 866.9 (w), 746.3 (w), 698.5 (m) cm⁻¹; HRMS-(DART+) for [M+H]+: calculated: 383.3121, found: 383.3136.

4,4,5,5-tetramethyl-2-tridecyl-1,3,2-dioxaborolane (15). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diborylmethane 6 (53.6 mg, 0.20 mmol), KOt-Bu (56.1 mg, 0.50 mmol), 1-bromododecane (24.0 μL, 0.10 mmol) and toluene (0.5 mL) at room temperature for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (75:1 – 50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (28.2 mg, 91%).

1H NMR (500 MHz, CDCl3): δ 1.41-1.37 (2H, m), 1.31-1.24 (30H, m), 0.88 (3H, t, J = 6.9 Hz), 0.76 (2H, t, J = 7.8 Hz); 13C NMR (125 MHz, CDCl3): δ 82.8, 32.4, 31.9, 29.70, 29.68, 29.66, 29.65, 29.59, 29.41, 29.35, 24.8, 24.0, 22.7, 14.1; IR (neat): 2977.8 (w), 2922.1 (s), 2853.1 (m), 1465.8 (w), 1376.7 (s), 1316.8 (m), 1145.9 (s), 968.4 (w), 847.0 (w), 720.6 (w) cm⁻¹; HRMS-(DART+) for [M+H]+: calculated: 311.3121, found: 311.3121.

2-(4-methoxyphenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diborylmethane 6 (53.6 mg, 0.20 mmol), KOt-Bu (56.1 mg, 0.50 mmol), 4-methoxybenzyl chloride (13.6 μL, 0.10 mmol) and toluene (0.5 mL) at room temperature for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (20:1 – 10:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (19.2 mg, 73%). 1H NMR was in accord with literature.  

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6 Yamamoto, Y.; Fujikawa, R.; Umemoto, T.; Miyaura, N. Tetrahedron, 2004, 60, 10695.
2-(4-bromophenethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diborylmethane 6 (53.6 mg, 0.20 mmol), KOt-Bu (56.1 mg, 0.50 mmol), 4-bromobenzyl chloride (20.5 mg, 0.10 mmol) and toluene (0.5 mL) at room temperature for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (23.9 mg, 77%). 1H NMR (500 MHz, CDCl3): δ 7.38-7.35 (2H, m), 7.10-7.07 (2H, m), 2.69 (2H, t, J = 8.1 Hz), 1.22 (12H, s), 1.11 (2H, t, J = 8.1 Hz); 13C NMR (125 MHz, CDCl3): δ 143.3, 131.2, 129.8, 119.2, 83.2, 29.4, 24.8; IR (neat): 2977.4 (w), 2930.8 (w), 1487.4 (m), 1369.5 (s), 1315.5 (s), 1239.1 (w), 1141.9 (s), 1071.6 (m), 1010.7 (m), 966.8 (m), 866.8 (w), 849.2 (m), 798.1 (m), 672.3 (w), 484.1 (w) cm⁻¹; HRMS-(DART+) for [12C14H2111B116O2][M+H]+: calculated: 311.0819, found: 311.0811.

2-(3-benzyl-1-phenylpentadecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester S2 (60.1 mg, 0.13 mmol), NaO-t-Bu (28.8 mg, 0.30 mmol), 1-bromododecane (24.0 μL, 0.10 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (49.9 mg, 99%). 1H NMR (500 MHz, CDCl3): δ 7.27-7.22 (6H, m), 7.18-7.14 (4H, m), 2.80 (1H, d, J = 13.7 Hz), 2.76 (1H, d, J = 13.7 Hz), 2.64-2.60 (2H, m), 1.68-1.58 (2H, m), 1.45-1.36 (4H, m), 1.32-1.21 (30H, m), 0.89 (3H, t, J = 6.8 Hz); 13C NMR (125 MHz, CDCl3): δ 143.5, 140.0, 130.2, 128.3, 128.2, 127.8, 125.7, 125.5, 83.2, 40.2, 36.7, 34.5, 31.9, 31.5, 30.5, 29.72, 29.68, 29.4, 25.15, 25.10, 24.8, 22.7, 14.1; IR (neat): 2976.9 (w), 2924.7 (s), 2853.3 (m), 1495.4 (w), 1456.2 (w), 1380.2 (m), 1311.3 (m), 1143.7 (m), 855.3 (w), 735.4 (w), 699.7 (m) cm⁻¹; HRMS-(DART+) for [12C34H5411B116O2][M+H]+: calculated: 505.4217, found: 505.4237.

4,4,5,5-tetramethyl-2-(6-phenethyloctadec-1-en-6-yl)-1,3,2-dioxaborolane (19). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester S3 (57.2 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), 1-bromododecane (24.0 μL, 0.10 mmol) and THF (0.5 mL) at 50 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (100:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (44.0 mg, 91%). 1H NMR (500 MHz, CDCl3): δ 7.27-7.24 (2H, m), 7.19-7.14 (3H, m), 5.84 (1H, ddt, J = 17.1, 10.3, 6.9 Hz), 5.01 (1H, ddt, J = 17.1, 2.0, 1.5 Hz), 4.94 (1H, ddt, J = 10.3, 2.0, 1.5 Hz), 2.50-2.47 (2H, m), 2.05 (2H, q, J = 7.0 Hz), 1.66-1.62 (2H, m), 1.45-1.19 (26H, m), 1.25 (12H, s, overlap), 0.88 (3H, t, J = 6.8 Hz); 13C NMR (125 MHz, CDCl3): δ 143.8, 139.2, 128.3, 128.2, 125.4, 114.2, 83.0, 36.7, 34.7, 34.4, 33.8, 31.9, 31.4, 30.6, 29.72, 29.68, 29.65, 29.4, 24.9, 24.7, 24.2, 22.7, 14.1; IR (neat): 2922.9 (s), 2852.7 (m), 1458.2 (w), 1385.2


2-(3-benzyl-4-methyl-1-phenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester S2 (60.1 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), 2-bromopropane (9.4 µL, 0.10 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 – 75:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (35.9 mg, 95%). \(^1^H\) NMR (500 MHz, CDCl\(_3\)): δ 7.35 (2H, d, \(J = 7.3\) Hz), 7.26-7.22 (4H, m), 7.18-7.10 (4H, m), 3.09 (1H, d, \(J = 13.7\) Hz), 2.68 (1H, d, \(J = 14.2\) Hz), 2.65-2.55 (2H, m), 1.78 (1H, sp, \(J = 6.8\) Hz), 1.70-1.60 (2H, m), 1.28 (6H, s), 1.24 (6H, s), 1.06 (3H, d, \(J = 6.8\) Hz), 0.99 (3H, d, \(J = 6.8\) Hz); \(^1^3^C\) NMR (125 MHz, CDCl\(_3\)): δ 143.8, 140.8, 130.5, 128.4, 128.2, 127.7, 125.6, 125.4, 83.2, 37.9, 34.5, 32.4, 31.2, 25.4, 25.0, 19.6, 19.2; IR (neat): 2975.2 (w), 2930.7 (w), 2870.3 (w), 1455.1 (w), 1380.6 (m), 1305.3 (m), 1257.7 (m), 1139.7 (s), 973.7 (w), 846.7 (w), 738.4 (m), 699.9 (s), 670.6 (w), 502.6 (w) cm\(^{-1}\); HRMS-(DART\(^+\)) for \(^{12}C_{25}^{1}H_{56}^{11}B_{1}^{16}O_{2}\) [M+H]\(^+\): calculated: 483.4373, found: 483.4384.

2-(3-cyclopropyl-1-phenylpentadecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester S5 (53.6 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), 1-bromododecane (24.0 µL, 0.10 mmol) and THF (0.5 mL) at 50 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (200:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (25.3 mg, 56%). \(^1^H\) NMR (500 MHz, CDCl\(_3\)): δ 7.28-7.25 (2H, m), 7.22-7.20 (2H, m), 7.17-7.14 (1H, m), 2.68-2.62 (2H, m), 1.77-1.71 (1H, m), 1.67-1.60 (1H, m), 1.46-1.42 (2H, m), 1.37-1.26 (20H, m), 1.22 (12H, s), 0.88 (3H, t, \(J = 6.9\) Hz), 0.65-0.59 (1H, m), 0.43-0.30 (4H, m); \(^1^3^C\) NMR (125 MHz, CDCl\(_3\)): δ 144.3, 128.4, 128.2, 125.3, 82.8, 39.1, 36.4, 32.2, 31.9, 30.7, 29.72, 29.69, 29.66, 29.45, 24.9, 24.9, 22.7, 18.0, 14.1, 2.3, 1.9; IR (neat): 2922.9 (s), 2852.6 (m), 1455.7 (w), 1388.5 (w), 1370.8 (w), 1302.7 (m), 1142.8 (s), 1016.8 (w), 967.5 (w), 855.6 (w), 748.1 (w), 697.9 (m) cm\(^{-1}\); HRMS-(DART\(^+\)) for \(^{12}C_{30}^{1}H_{56}^{11}B_{1}^{16}O_{2}\) [M+H]\(^+\): calculated: 455.4060, found: 455.4080.
2-(1-dodecyl-2-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diborate ester S6 (48.1 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), 1-bromododecane (24.0 μL, 0.10 mmol) and THF (0.5 mL) at 60 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (26.8 mg, 65%). 1H NMR (500 MHz, CDCl3): δ 7.24-7.23 (2H, m), 7.20-7.17 (2H, m), 7.11-7.07 (1H, m), 1.98-1.93 (2H, m), 1.51-1.35 (3H, m), 1.32-1.25 (18H, m), 0.97 (6H, s), 0.93-0.88 (1H, m), 0.88 (3H, t, J = 6.8 Hz, overlap), 0.83 (6H, s), 0.77 (1H, dd, J = 7.3, 4.4 Hz); 13C NMR (125 MHz, CDCl3): δ 140.7, 128.8, 127.6, 125.5, 82.8, 38.4, 31.9, 29.9, 29.8, 29.72, 29.69, 29.66, 29.63, 29.4, 29.3, 24.7, 24.3, 22.7, 15.7, 14.1; IR (neat): 2977.1 (w), 2923.0 (s), 2852.9 (m), 1447.0 (w), 1408.4 (m), 1371.1 (m), 1312.7 (m), 1141.3 (s), 856.3 (w), 694.8 (w) cm⁻¹; HRMS-(DART+) for [M+H]⁺: calculated: 413.3591, found: 413.3612. The relative stereochemistry was assigned by analogy (compound 23).

2-(1-(4-methoxybenzyl)-2-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diborate ester S6 (48.1 mg, 0.13 mmol), NaOt-Bu (28.8 mg, 0.30 mmol), 4-methoxybenzyl chloride (13.6 μL, 0.10 mmol) and THF (0.5 mL) at 50 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (25:1 hexanes/diethyl ether, stain in CAM) to afford a white solid (26.8 mg, 74%). 1H NMR (500 MHz, CDCl3): δ 7.26-7.19 (6H, m), 7.12-7.09 (1H, m), 6.82-6.79 (2H, m), 3.79 (3H, s), 3.37 (1H, d, J = 14.2 Hz), 2.20 (1H, d, J = 14.7 Hz), 2.09 (1H, dd, J = 7.8, 5.9 Hz), 1.55 (1H, t, J = 4.9 Hz), 1.00 (1H, dd, J = 8.3, 4.4 Hz), 0.88 (6H, s), 0.73 (6H, s); 13C NMR (125 MHz, CDCl3): δ 157.8, 140.3, 133.8, 129.9, 128.8, 127.7, 125.7, 113.4, 83.0, 82.8, 42.0, 29.3, 24.6, 24.3, 15.6; IR (neat): 2978.5 (w), 2910.8 (w), 1609.2 (w), 1510.6 (s), 1442.4 (w), 1407.1 (m), 1315.4 (m), 1300.9 (m), 1248.4 (s), 1130.1 (s), 1029.8 (m), 967.9 (w), 852.3 (w), 770.2 (w), 691.6 (w) cm⁻¹; HRMS-(DART+) for [M+H]⁺: calculated: 365.2288, found: 365.2285. The relative stereochemistry was assigned by X-ray crystallography.
4,4,5,5-tetramethyl-2-(1-phenethylcyclopropyl)-1,3,2-dioxaborolane (30). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester 24 (43.5 mg, 0.10 mmol), NaO-t-Bu (28.8 mg, 0.30 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (25.4 mg, 93%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.27-7.24 (2H, m), 7.19-7.13 (3H, m), 2.74-2.71 (2H, m), 1.54-1.50 (2H, m), 1.22 (12H, s), 0.67-0.66 (2H, m), 0.30-0.28 (2H, m); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.2, 128.4, 128.1, 125.4, 82.9, 38.7, 35.8, 24.7, 11.5; IR (neat): 2977.8 (w), 2926.6 (w), 1453.5 (w), 1416.9 (s), 1371.1 (w), 1311.8 (m), 1193.8 (m), 1132.8 (s), 967.6 (w), 858.9 (w), 698.9 (m), 684.2 (m) cm$^{-1}$; HRMS-(DART$^+$) for $^{12}$C$_{17}$H$_{26}^{13}$B$_{1}^{16}$O$_{2}$ [M+H]$^+$: calculated: 273.2026, found: 273.2035.

4,4,5,5-tetramethyl-2-(1-phenethylcyclobutyl)-1,3,2-dioxaborolane (31). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester 25 (49.3 mg, 0.10 mmol), NaO-t-Bu (28.8 mg, 0.30 mmol) and THF (0.5 mL) at room temperature for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (75:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (25.0 mg, 87%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.28-7.25 (2H, m), 7.20-7.14 (3H, m), 2.50-2.47 (2H, m), 2.18-2.13 (2H, m), 1.99-1.84 (4H, m), 1.736-1.70 (2H, m), 1.29 (12H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.3, 128.3, 128.2, 125.5, 83.0, 42.0, 33.3, 30.2, 24.7, 18.2; IR (neat): 3026.0 (w), 2975.2 (m), 2929.5 (m), 2854.5 (w), 2938.0 (w), 2861.2 (w), 1455.0 (w), 1416.9 (s), 1371.1 (w), 1311.8 (m), 1193.8 (m), 1132.8 (s), 967.6 (w), 858.9 (w), 698.9 (m), 684.2 (m) cm$^{-1}$; HRMS-(DART$^+$) for $^{12}$C$_{17}$H$_{26}^{13}$B$_{1}^{16}$O$_{2}$ [M+H]$^+$: calculated: 273.2026, found: 273.2035.
1454.1 (w), 1371.5 (s), 1343.3 (w), 1211.3 (m), 1142.6 (s), 965.1 (w), 860.7 (w), 698.3 (m) cm⁻¹; HRMS-(DART+) for [\(^{12}\text{C}_{18}^{1}\text{H}_{28}^{11}\text{B}_{16}\text{O}_{2}\ [\text{M+H}]^{+}\): calculated: 287.2182, found: 287.2179.

4,4,5,5-tetramethyl-2-(2-methyl-1-phenethylcyclopentyl)-1,3,2-dioxaborolane (32, major diastereomer). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester 26 (208.5 mg, 0.40 mmol), NaO-t-Bu (115.3 mg, 1.20 mmol) and THF (2.0 mL) at 50 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (50:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (95.7 mg, 76%, 7.5:1 dr). The diastereomers were separated by a second column (75:1 hexanes/diethyl ether). \(^{1}H\) NMR (500 MHz, CDCl₃): δ 7.27 (2H, t, \(J = 7.3\) Hz), 7.21 (2H, d, \(J = 7.3\) Hz), 7.18-7.15 (1H, m), 2.58-2.49 (2H, m), 2.04 (1H, sx, \(J = 7.3\) Hz), 1.89-1.83 (1H, m), 1.79-1.54 (5H, m), 1.44-1.36 (1H, m), 1.31-1.24 (1H, m), 1.27 (12H, s, overlap), 0.91 (3H, dd, \(J = 7.3, 1.4\) Hz); \(^{13}\text{C}\) NMR (125 MHz, CDCl₃): δ 143.9, 128.3, 128.2, 125.4, 82.9, 40.3, 34.2, 33.5, 33.1, 32.6, 24.9, 24.6, 22.9, 15.1; IR (neat): 2949.5 (m), 2868.7 (w), 1454.1 (w), 1380.5 (s), 1304.3 (s), 1195.0 (w), 1143.5 (s), 967.1 (w), 856.4 (w), 747.3 (w), 698.3 (m) cm⁻¹; HRMS-(DART+) for [\(^{12}\text{C}_{20}^{1}\text{H}_{32}^{11}\text{B}_{16}\text{O}_{2}\ [\text{M+H}]^{+}\): calculated: 315.2495, found: 315.2500.

Proof of Stereochemistry:

The title compound and its minor diastereomer were oxidized to tertiary alcohols, which were compared with the alcohol prepared from 2-methylcyclopentanone and Grignard reagent as shown below:
4,4,5,5-tetramethyl-2-(1-phenethylcyclohexyl)-1,3,2-dioxaborolane (33). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester 27 (52.1 mg, 0.10 mmol), NaOr-Bu (28.8 mg, 0.30 mmol) and THF (0.5 mL) at 50 °C for 14 hours. The crude reaction mixture was purified by column chromatography on silica gel (75:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (21.8 mg, 69%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.27-7.24 (2H, m), 7.17-7.14 (3H, m), 2.58-2.54 (2H, m), 1.95 (2H, d, J = 12.7 Hz), 1.68-1.60 (3H, m), 1.58-1.54 (2H, m), 1.37-1.26 (2H, m), 1.29 (12H, s), 1.19-1.14 (1H, m), 0.99 (2H, td, J = 12.7, 2.9 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.7, 128.3, 128.2, 125.5, 83.0, 83.0, 43.3, 35.3, 32.2, 26.7, 25.2, 24.9; IR (neat): 2977.3 (w), 2924.9 (s), 2850.6 (w), 1453.3 (w), 1387.7 (m), 1337.2 (w), 1304.6 (s), 1234.0 (m), 1143.1 (s), 968.5 (w), 696.5 (m) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{20}$H$_{32}$B$_{1}$O$_{2}$ [M+H]$^+$: calculated: 315.2495, found: 315.2496.

2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester 28 (116.8 mg, 0.40 mmol), NaOr-Bu (115.3 mg, 1.20 mmol) and THF (2.0 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 pentane/diethyl ether, stain in CAM) to afford a colorless oil (50.4 mg, 60%). The $^1$H and $^{13}$C NMR spectra were in accord with previously reported data.$^7$

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$^7$ Clary, J. W.; Rettenmaier, T. J.; Snelling, R.; Bryks, W.; Banwell, J.; Wipke, W. T.; Singaram, B. J. Org. Chem. 2011, 76, 9602.
4,4,5,5-tetramethyl-2-(1-phenethylcycloheptyl)-1,3,2-dioxaborolane (35). The reaction was performed according to Representative Procedure for Deborylative Alkylation with diboronate ester 29 (53.5 mg, 0.10 mmol), NaO-t-Bu (28.8 mg, 0.30 mmol) and THF (0.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (100:1 hexanes/ diethyl ether, stain in CAM) to afford a colorless oil (19.1 mg, 58%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.28-7.25 (2H, m), 7.18-7.14 (3H, m), 2.56-2.53 (2H, m), 1.91-1.86 (2H, m), 1.63-1.58 (4H, m), 1.56-1.44 (6H, m), 1.36-1.32 (2H, m), 1.27 (12H, s); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.7, 128.3, 128.2, 125.4, 82.9, 42.7, 36.2, 33.0, 29.7, 24.9, 24.6; IR (neat): 2976.9 (w), 2918.6 (m), 2851.0 (w), 1458.4 (w), 1386.5 (m), 1304.1 (m), 1263.3 (w), 1141.7 (s), 966.0 (w), 853.4 (m), 746.9 (w), 697.6 (m) cm$^{-1}$; HRMS-(DART+) for $^{12}$C$_{21}$H$_{34}^{11}$B$_1^{16}$O$_2$ [M+H]$^+$: calculated: 329.2652, found: 329.2653.
VI. Procedure for Gram-Scale Synthesis of Amphetamine

2,2'-((ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S9). The reaction was performed according to Representative Procedure (Method C) with diborylmethane 6 (11.79 g, 44.00 mmol), LTMP (6.476 g, 44.00 mmol), methyl iodide (2.74 mL, 44.00 mmol) and THF (150 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/ethyl acetate, stain in CAM) to afford a colorless oil (10.03 g, 81%). The $^1$H NMR and $^{13}$C NMR spectra was in accord with previously reported data.  

In air, a flame-dried 500 mL round-bottom flask with magnetic stir bar was charged with sodium tert-butoxide (7.84 g, 81.6 mmol). The flask was evacuated and filled with nitrogen for three cycles. THF (110 mL) was added via syringe, followed by a THF solution (20 mL) of 1,1-diboronate ester S9 (9.95 g, 35.3 mmol) and benzyl chloride (3.13 mL, 27.2 mmol). The reaction was allowed to stir at room temperature for 14 hours. Upon completion, the reaction mixture was diluted with diethyl ether (150 mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 50:1) to afford the desired product as a colorless oil (6.07 g, 36:S10 = 29:1, 96 wt% of 36, 87% calculated yield). The $^1$H and $^{13}$C NMR spectra was in accord with previously reported data. 

The reaction was performed according to the literature procedure with slight modification. A flame-dried, three-neck round bottom flask equipped with a magnetic stir bar, reflux condenser

8 Ito, H.; Kubota, K. Org. Lett. 2012, 14, 890.
9 Mlynarski, S. N.; Schuster, C. H.; Morken, J. P. Nature 2014, 505, 386.
10 Mlynarski, S. N.; Karns, A. S.; Morken, J. P. J. Am. Chem. Soc. 2012, 134, 16449.
and septa was purged with N\textsubscript{2}. O-methylhydroxylamine solution\textsuperscript{10} (25.0 mL, 70.9 mmol, 2.84 M in THF) was added and diluted with THF (200 mL). The reaction flask was cooled to $-78^\circ$ C in a dry ice/acetone bath. A solution of $n$-butyl lithium in hexanes (28.4 mL, 70.9 mmol, 2.50 M) was added dropwise (syringe pump, 20 mL/h) and the reaction was stirred at $-78^\circ$ C for 30 min. A separate flame-dried flask was charged with boronate ester 36 (6.06 g, 96 wt% 36, 23.6 mmol) and diluted with THF (20 mL) under N\textsubscript{2}. The solution of boronate ester was then added dropwise to the solution of deprotonated O-methylhydroxylamine solution dropwise (syringe pump, 60 mL/h). Upon completion, the reaction flask was warmed to room temperature and then heated to 60$^\circ$ C. After stirring at 60$^\circ$ C for 20 h, the reaction flask was cooled to room temperature, quenched with 3 mL of H\textsubscript{2}O and stirred for 30 minutes. The solution was then dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo}. The crude reaction mixture was purified by fractional distillation under high vacuum to afford the desired product 37 as a clear, colorless oil (2.04 g, 64% yield). The $^1$H and $^{13}$C NMR spectra were in accord with previously reported data.\textsuperscript{11}

\textsuperscript{11} Guisado, C.; Waterhouse, J. E.; Price, W. S.; Jorgensen, M. R.; Miller, A. D. \textit{Org. Biomol. Chem.} \textbf{2005}, \textit{3}, 1049.
VII. Mechanistic Studies

1. Deuterium-labeled Experiment

The deuterium-labeled starting material was prepared as follows:

In the glove box, an oven-dried 10 mL round-bottom flask with magnetic stir bar was charged with lithium 2,2,6,6-tetramethylpiperidide (125 mg, 0.85 mmol). The flask was sealed with a rubber septum, removed from the glove box, followed by the addition of THF (2.5 mL) under N₂. The reaction mixture was cooled to 0 °C, and a solution of 1,1-diboronate ester 2 (264 mg, 0.71 mmol) in THF (1 mL) was added via syringe and the mixture was allowed to stir at 0 °C for 10 minutes. D₂O (26 μL, 1.42 mmol) was added in one portion and the reaction was allowed to stir at 0 °C for 10 min. Upon completion, the reaction mixture was warmed to room temperature, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 9:1) to afford the desired product as a white solid (206 mg, 78%).

2. Procedure for Deborylative Alkylation Crossover Experiment:

In the glove box, an oven-dried 2-dram vial with magnetic stir bar was charged with deuterated 1,1-diboronate ester d-2 (48.5 mg, 0.13 mmol), 38 (52.3 mg, 0.13 mmol), NaOt-Bu (57.7 mg, 0.60 mmol), and THF (0.50 mL). The reaction mixture was allowed to stir at room temperature for 15 min, followed by the addition of 1-bromododecane (48.0 μL, 0.20 mmol). The vial was sealed with a polypropylene cap, removed from the glove box, and was allowed to stir at room temperature for 3 hours. Upon completion, the reaction mixture was diluted with diethyl ether (2
mL), filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 75:1 to 15:1) to isolate the desired product \(d\)-3 (38.6 mg, 93%) and \(39\) (22.4 mg, 50%).

\(d\)-3 was oxidized to the corresponding alcohol to confirm the D-incorporation.

![Diagram](image)

**4,4,5,5-tetramethyl-2-(1-phenylpentadecan-3-yl-3-d)-1,3,2-dioxaborolane (d-3).** \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.28-7.25 (2H, m), 7.19-7.14 (3H, m), 2.65-2.54 (2H, m), 1.76-1.70 (1H, m), 1.66-1.60 (1H, m), 1.46-1.34 (2H, m), 1.33-1.21 (32H, m), 0.88 (3H, J = 6.9 Hz); HRMS-(DART+) for \(^{12}\)C\(_{27}\)^1H\(_7\)^2H\(_1\)\(^{11}\)B\(_1\)^{16}O\(_2\) [M+H]+: calculated: 416.3810, found: 416.3802.

**2-(1-(benzyloxy)pentadecan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39).** \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.35-7.31 (4H, m), 7.27-7.24 (1H, m), 4.50 (2H, s), 3.44 (2H, t, J = 6.8 Hz), 1.79-1.72 (1H, m), 1.70-1.63 (1H, m), 1.44-1.25 (22H, m), 1.20 (12H, s), 1.07-1.02 (1H, m), 0.88 (3H, J = 6.8 Hz); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 138.8, 128.3, 127.6, 127.3, 82.8, 72.7, 70.0, 31.9, 31.4, 31.3, 29.9, 29.70, 29.66, 29.64, 29.61, 29.57, 29.3, 29.1, 24.8, 24.7, 22.7, 14.1; IR (neat): 2922.3 (s), 2852.4 (s), 1455.0 (w), 1379.7 (m), 1313.9 (m), 1242.6 (w), 1144.7 (s), 1104.0 (m), 967.9 (w), 854.6 (w), 733.7 (m), 696.8 (m) cm\(^{-1}\); HRMS-(DART+) for \(^{12}\)C\(_{28}\)^1H\(_9\)^{11}\)B\(_1\)^{16}O\(_3\) [M+H]+: calculated: 445.3853, found: 445.3872.
2. Mass Spectrometry Studies with $^{10}$B-labeled Enantioenriched Diboronate Esters

a) Preparation of $^{10}$B-labeled Enantioenriched Starting Material:

2-methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the literature procedure.\(^\text{12}\)

\[ \text{H}_3^{10}\text{BO}_3 + \text{pinacol} \xrightarrow{\text{MeOH, benzene}} \text{MeO}^{10}\text{B(pin)} \]

$^{10}$B-Labeled ($E$)-4,4,5,5-tetramethyl-2-stryll-1,3,2-dioxaborolane S11 was prepared according to the literature procedure.\(^\text{13}\) To an oven-dried 10 mL round-bottom flask with magnetic stir bar was charged with Ni(PPh\(_3\))\(_2\)Cl\(_2\) (8.2 mg, 12.5 $\mu$mol). The flask was sealed with a rubber septum and purged with N\(_2\). THF (2.5 mL) was added via syringe, followed by dropwise addition of DIBAL-H (0.49 mL, 2.75 mmol) at room temperature. The resulting black solution was cooled to 0 °C, and phenylacetylene (0.275 mL, 2.50 mmol) was added dropwise over 5 minutes. The reaction mixture was allowed to warmed to room temperature and stirred for 6 hours. Upon completion, MeO$^{10}$B(pin) (786 mg, 5.00 mmol) was added via syringe. The reaction mixture was allowed to stir for additional 24 hours, then quenched at 0 °C by dropwise addition of a saturated solution of Rochelle’s salt (2.5 mL), then stirred for 1 hour at room temperature. The layers were separated, and the aqueous layer was extracted with diethyl ether (10 mL×3). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 25:1 to 10:1) to afford the

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\(^{12}\) Boudet, N.; Lachs, J. R.; Knochel, P. Org. Lett. 2007, 9, 5525.

\(^{13}\) Gao, F.; Hoveyda, A. H. J. Am. Chem. Soc. 2010, 132, 10961.
(E)-isomer as a yellow oil in 61% yield (349 mg, 1.52 mmol). The NMR spectra were in accord with previously reported data. \[^{13}\text{HRMS-(DART+)}\] for \(^{12}\text{C}_{14}{^1}\text{H}_{20}{^{10}}\text{B}_{1}{^{16}}\text{O}_{2}\ [\text{M+H}]^+\): calculated: 230.1593, found: 230.1598.

\[
\begin{align*}
\text{10B-Labeled } (E)-2\text{-styryl-2,3-dihydro-1H-naphtho}[1,8-de][1,3,2]diazaborinine } \text{S12} & \text{ was prepared according to the literature procedure with modification.}^{14} \text{ S11 (330 mg, 1.43 mmol) and NaIO}_4 (918 mg, 4.29 mmol) were stirred in a mixture of THF (4 mL) and water (1.3 mL) for 30 minutes. Then aqueous HCl was added (1.00 mL, 1.0 M, 1.00 mmol). The reaction was stirred for 17 hours at room temperature. Upon completion, the reaction mixture was diluted with water (3 mL) and extracted with ethyl acetate (6 mL×3). The combined organic layers were washed with water (3 mL×2) and brine (3 mL), dried over Na\(_2\text{SO}_4\), filtered, and concentrated. The unpurified boronic acid and 1,8-diaminonaphthalene (215 mg, 1.36 mmol) were dissolved in toluene (5 mL), equipped with a Dean-Stark apparatus, and heated to reflux for 1.5 h. After cooled to room temperature, the reaction mixture was concentrated in vacuo, and purified on silica gel (hexanes: ethyl acetate = 30:1) to afford S12 as a yellow solid (267 mg, 69% yield in two steps). The \(^1\text{H NMR spectrum was in accord with reported data in literature.}^{15}

\[
\begin{align*}
\text{10B-Labeled } 2\text{-}(2\text{-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl}-2,3\text{-dihydro-1H-naphtho}[1,8-de][1,3,2]diazaborinine } \text{S13} & \text{ was prepared according to the literature procedure.}^{16} \text{ In the glove box, an oven-dried 2 dram vial with magnetic stir bar was charged with CuCl (1.5 mg, 0.015 mmol), NaOr-Bu (2.9 mg, 0.030 mmol), (R)-DTBM-Segphos (17.7 mg, 0.015 mmol), and toluene (0.4 mL). The mixture was stirred for 10 minutes at room temperature, then pinacolborane (87.0 }\mu\text{L, 0.60 mmol) was added and stirred for an additional 10 minutes. Substrate S12 (135.1 mg, 0.50 mmol) in toluene (1.2 mL) was added to the reaction mixture. The reaction was allowed to stir at room temperature for 20 hours. The reaction mixture was filtered through a pad of Celite, washed with diethyl ether, and concentrated \textit{in vacuo}. The crude reaction mixture was purified on silica gel (hexanes:ethyl acetate = 10:1) to afford S13 as a pale grey solid.}

\[
\text{14 Koyanagi, M.; Eichenauer, N.; Ihara, H.; Yamamoto, T.; Suginome, M. } \text{Chem. Lett. 2013, 42, 541.}
\]
\[
\text{15 Iwadate, N.; Suginome, M. } \text{Org. Lett. 2009, 11, 1899.}
\]
\[
\text{16 Feng, X.; Jeon, H.; Yun, J. } \text{Angew. Chem., Int. Ed. 2013, 52, 3989.}
\]
(181 mg, 91% yield, 98:2 er). The $^1$H NMR spectrum was in accord with reported data in literature.\textsuperscript{16}

**Analysis of Stereochemistry**

The enantioselectivity was determined by SFC analysis of the reaction product. The analogous racemic material was prepared using dppBz as the achiral ligand in the hydroboration reaction. The absolute stereochemistry was assigned according to the literature.

**Chiral SFC (OD-H, Chiraldex, 3 mL/min, 20% i-PrOH, 100 bar, 35 °C)-analysis of the reaction product.**

(S)-$^{10}$B-4 was prepared according to the literature procedure.\textsuperscript{17} To a stirred solution of S13 (143 mg, 0.36 mmol) in THF (3.6 mL) was added aqueous 2 M H$_2$SO$_4$ (0.54 mL, 1.08 mmol) and pinacol (213 mg, 1.80 mmol) sequentially. The reaction mixture was stirred at room temperature for 24 hours before quenched by the addition of water (4 mL). The reaction mixture was extracted with diethyl ether (3×5 mL), dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude reaction mixture was purified by chromatography on silica gel (hexanes: diethyl ether = 9:1) to afford the desired product as a colorless oil (103 mg, 80%).

\textsuperscript{17} Lee, J. C. H.; McDonald, R.; Hall, D. G. *Nature Chemistry*, 2011, 3, 894.
b) Deborylative Alkylation Using $^{10}$B-Labeled Enantioenriched Diboronate Ester:

$$\text{Ph}^{{^{10}}\text{B}(\text{pin})} + n\text{-C}_{12}\text{H}_{25}\text{Br} \xrightarrow{\text{NaO}t\text{-Bu, THF, rt}} \text{Ph}^{{^{10}/11}\text{B}(\text{pin})} n\text{-C}_{12}\text{H}_{25} + \text{Ph}^{{^{10}/11}\text{B}(\text{pin})} n\text{-C}_{12}\text{H}_{25}$$

The reaction was performed according to Representative Procedure for Deborylative Alkylation with (S)-$^{10}$B-6 (46.4 mg, 0.13 mmol), 1-bromododecane (24.0 μL, 0.10 mmol), NaO$t$-Bu (28.8 mg, 0.30 mmol) and THF (0.50 mL) in 90% yield.

The enantiomers of the product were separated on chiral SFC. Fractions were collected directly from the waste end of SFC instrument (10 seconds for each fraction) and the product (neat) could be easily observed as an oil on the wall of the test tubes. The separated enantiomers were characterized by mass spectrometry.

*Chiral SFC (ODR-H, Chiraldex, 3 mL/min, 2% i-PrOH, 100 bar, 35 °C)-analysis of the reaction product.*
c) Calculation of Mass Spectrometry:

\[
\text{Natural abundance of carbon isotopes is } ^{12}\text{C} : ^{13}\text{C} = 0.989 : 0.011; \\
\text{Natural abundance of boron isotope is } ^{10}\text{B} : ^{11}\text{B} = 0.199 : 0.801; \\
\text{Abundance of boron isotope for the } ^{10}\text{B}-\text{labeled product is } ^{10}\text{B} : ^{11}\text{B} = \frac{0.500 + 0.500 \times 0.199}{0.500 \times 0.801} = 0.600 : 0.400
\]

**Calculated [M+H]^+ distributions for 10^B-labeled product:**

| m/z | Formula of [M+H]^+ | calculated distribution (assuming racemization) | combined |
|-----|---------------------|-----------------------------------------------|----------|
| 400 | \(^{12}\text{C}_{26}\text{H}_{46}^{10}\text{B}_1\text{O}_2\) | 0.989^{26} \times 0.600 = 45.0% | 45.0% |
| 401 | \(^{12}\text{C}_{25}^{13}\text{C}_{1}\text{H}_{46}^{10}\text{B}_1\text{O}_2\) | (26×0.989^{25}×0.011)×0.600 = 13.0% | 43.0% |
|     | \(^{12}\text{C}_{26}^{11}\text{B}_1\text{O}_2\) | 0.989^{26} \times 0.400 = 30.0% |           |
| 402 | \(^{12}\text{C}_{24}^{13}\text{C}_{1}\text{H}_{46}^{10}\text{B}_1\text{O}_2\) | (26×25/2×0.989^{24}×0.011^{2})×0.600 = 1.8% | 10.5% |
|     | \(^{12}\text{C}_{25}^{13}\text{C}_{1}\text{H}_{46}^{11}\text{B}_1\text{O}_2\) | (26×0.989^{25}×0.011)×0.400 = 8.7% |           |
| 403 | \(^{12}\text{C}_{23}^{13}\text{C}_{1}\text{H}_{46}^{10}\text{B}_1\text{O}_2\) | (26×25×24/3/2×0.989^{23}×0.011^{3})×0.600 = 0.2% | 1.4% |
|     | \(^{12}\text{C}_{24}^{13}\text{C}_{1}\text{H}_{46}^{11}\text{B}_1\text{O}_2\) | (26×25×0.989^{24}×0.011^{2})×0.400 = 1.2% |           |
Mass Spectrum of product (±)-7 using from non-labeled compound 4:

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

Mass Spectrum of product (±)-7 using $^{10}\text{B}$-labeled compound ($S$)-$^{10}\text{B}$-4:

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$

$^{12}\text{C}_2^{13}\text{C}_1\text{H}_{46}\text{B}_{16}\text{O}_2 \ [\text{M+H}]^+$
Mass Spectrum of product (S)-7 from $^{10}$B-labeled experiment using (S)-$^{10}$B-4:

Mass Spectrum of product (R)-7 from $^{10}$B-labeled experiment using (S)-$^{10}$B-4:
3. Analysis of Reaction Intermediates by \(^{13}\)C-Labeled Experiments

a) Preparation of \(^{13}\)C-Labeled geminal-Diboronate Ester:

The \(^{13}\)C-labeled aldehyde S14 was prepared from palmitic acid-1-\(^{13}\)C according to the literature procedure.\(^{18}\)

The \(^{13}\)C-labeled dibromide S15 was prepared according to Representative Procedure for Preparation of geminal-Diboronate Esters (Method A) with triphenyl phosphite (348 mg, 1.12 mmol), bromine (0.57 mL, 1.12 mmol), triethylamine (0.43 mL, 3.06 mmol), S14 (246 mg, 1.02 mmol) and anhydrous DCM (10 mL). The crude reaction mixture was purified by column chromatography on silica gel (100% hexanes, stain in PMA) to afford the 1,1-dibromide with a small amount of impurity as a colorless oil (360 mg, 92%).

The \(^{13}\)C-labeled diboronate ester S16 was prepared according to Representative Procedure for Preparation of geminal-Diboronate Esters (Method A) with CuI (17.3 mg, 0.091 mmol), LiOMe (82.0 mg, 2.16 mmol), \(\text{B}_2\text{(pin)}_2\) (438 mg, 1.73 mmol), 1,1-dibromide (348 mg, 0.91 mmol) and DMF (2 mL). The crude reaction mixture (DMF solution) was directly purified on silica gel (hexanes: diethyl ether = 15:1) to afford the desired product S16 as a colorless oil (261.3 mg, 60%).

\(^{13}\)C NMR spectra were recorded on a Varian Unity Inova spectrometer, and the data are expressed in ppm. All chemical shifts are reported relative to tetramethylsilane (TMS) as an internal standard. The NMR spectra were recorded in CDCl\(_3\) unless otherwise noted. The IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as neat samples.

\(^{13}\)C-labeled aldehyde S14:

\[\text{1,1-dibromo-1\textsuperscript{3}C-hexadecane-1-}\textsuperscript{13}\text{C} (S15).\]

\[^{1}H\text{ NMR (500 MHz, CDCl}_3\text{: }\delta 5.70 (1H, dt, } J = 177.5, 6.3 \text{ Hz, } 2.41-2.36 (2H, m, } 1.54-1.50 (2H, m, } 1.31-1.26 (24H, m, } 0.88 (3H, t, } J = 6.9 \text{ Hz).}\]

\[^{13}\text{C NMR (125 MHz, CDCl}_3\text{: }\delta 46.3 \text{ (CHBr}_2\text{), } 45.6, 31.9, 29.69, 29.67, 29.66, 29.62, 29.56, 29.44, 29.35, 29.32, 28.3, 28.2, 28.1, 22.7, 14.1; IR (neat): 2921.9 (s, } 2852.3 (m, } 1465.0 (w, } 1154.2 (w, } 721.4 (w, } 653.8 (w, } 583.1 (w, } 556.7 (w} \text{ cm}^{-1}.\]

\(^{13}\)C-labeled diboronate ester S16:

\[\text{2,2}'-(1\textsuperscript{3}C-hexadecane-1,1-diyl-1-}\textsuperscript{13}\text{C)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S16).}\]

\[^{1}H\text{ NMR (500 MHz, CDCl}_3\text{: }\delta 1.55-1.53 (2H, m, } 1.31-1.22 (2H, m, } 0.88 (3H, t, } J = 6.9 \text{ Hz, } 0.71 (1H, dt, } J = 111.5, 7.8 \text{ Hz).}\]

\[^{1}H\text{ NMR (500 MHz, THF-d}_8\text{: }\delta 1.48 (2H, br s, } 1.33-1.27 (26H, m, } 1.181 (12H, s, } 1.176 (12H, s, } 0.89 (3H, t, } J = 6.9 \text{ Hz, } 0.56 (1H, dt, } J = 111.0, 7.6 \text{ Hz).}\]

\[^{13}\text{C NMR (125 MHz, CDCl}_3\text{: }\delta 82.8, 32.6, 31.9, 29.71, 29.70, 29.67, 29.65, 29.62, 29.59, 29.55, 29.4, 25.8, 25.6, 24.8, 24.5, 22.7, 14.1, 10.7 \text{ (br, } C-B\text{); }^{13}\text{C NMR (125 MHz, THF-d}_8\text{: }\delta 83.4, 33.5, 33.0, 30.87, 30.84, 30.81, 30.79, 30.76, 30.70, 30.5, 26.9, 26.7, 25.4, 25.1, 23.7, 14.6, 11.5 \text{ (br, } C-B\text{); IR (neat): 2976.9 (w, } 2922.5 (s, } 2852.9 (m, } 1465.8 (w, } 1350.5 (m, } 1310.3 (s, } 1265.4 \text{ cm}^{-1}.\]

\(^{18}\) Li, J.; Sun, C.; Demerzhan, S.; Lee, D. J. Am. Chem. Soc. 2011, 133, 12964.
The $^{13}$C-labeled diboronate ester 40 was prepared according to Representative Procedure for Preparation of geminal-Diboronate Esters (Method C) with S16 (118 mg, 0.25 mmol), LTMP (40 mg, 0.27 mmol), benzyl bromide (36 µL, 0.30 mmol) and THF (2.5 mL). The crude reaction mixture was purified by column chromatography on silica gel (20:1 hexanes/diethyl ether, stain in CAM) to afford a colorless oil (95.2 mg, 67%), which turned to a white solid after stored in freezer overnight.

In the glove box, an oven-dried NMR tube was charged with diboronate ester 40 (44.4 mg, 0.078 mmol), NaOtf-Bu (17.3 mg, 0.18 mmol) and THF-d$_8$ (0.60 mL). The NMR tube was sealed with a rubber septum, removed from the glove box, and monitored by $^{13}$C NMR at 25 °C. After 3 hours, 1-bromododecane (14.4 µL, 0.060 mmol) was added via syringe, and the reaction was again tracked by $^{13}$C NMR. After 14 hours, the reaction mixture was diluted with diethyl ether, filtered through a silica gel plug, rinsed with diethyl ether, and concentrated in vacuo. The crude reaction mixture was purified on silica gel (hexanes: diethyl ether = 100:1) to afford the desired product 43 (24.2 mg, 66% yield) and the protodeboronation product S17 (5.3 mg).
$^{13}$C NMR Spectra of the Reaction (125 MHz, THF-$d_8$, δ 56–12 ppm):\textsuperscript{19}

For full spectra, see “Spectra Data” part.
2-(13-benzyloctacosan-13-yl-13C)-4,4,5,5-tetramethyl-1,3,
2-dioxaborolane (43). 1H NMR (500 MHz, CDCl3): δ 7.24-7.21
(2H, m), 7.18-7.13 (3H, m), 2.70 (2H, d, J_C-H = 4.4 Hz),
1.29-1.27 (50H, m), 1.21 (12H, s), 0.89 (6H, t, J = 7.3 Hz); 1H
NMR (500 MHz, THF-d8): δ 7.17-7.16 (4H, m), 7.11-7.07 (1H,
m), 2.67 (2H, d, J_C-H = 3.9 Hz), 1.36-1.30 (50H, m), 1.20 (12H,
s), 0.89 (6H, t, J = 7.3 Hz); 13C NMR (125 MHz, CDCl3): δ 140.2, 130.3, 127.6, 125.5, 83.0, 40.0,
39.7, 34.4, 34.2, 31.9, 30.5, 30.4, 30.3 (br, C-B), 29.72, 29.69, 29.67, 29.4, 25.1, 24.8, 22.7, 14.1;
13C NMR (125 MHz, THF-d8): δ 141.3, 141.2, 131.21, 131.20, 128.5, 126.5, 83.96, 83.95, 41.3,
41.0, 35.7, 35.4, 33.0, 31.69, 31.65, 31.4 (br, C-B), 30.84, 30.83, 30.82, 30.79, 30.78, 30.76, 30.5,
26.0, 25.6, 23.7, 14.6; IR (neat): 2921.2 (s), 2851.7 (m), 1463.9 (m), 1376.8 (m), 1307.3 (m),
1264.9 (w), 1252.5, 1243.2, 1229.8, 1251.4, 1201.6 (w), 1143.5 (m), 966.3 (w), 854.1 (w), 721.6 (w),
701.3 (m) cm\(^{-1}\); HRMS-(DART+) for \(^{12}\)C\(^{40}\)C\(^{12}\)C\(^{1}\)H\(^{76}\)B\(^{16}\)O\(^{2}\)[M+H]\(^{+}\): calculated: 612.5972, found: 612.5984.

2-(13-benzyloctacosan-13-yl-13C)-4,4,5,5-tetramethyl-1,3,2-
dioxaborolane (S17). 1H NMR (500 MHz, THF-d8): δ 7.19-7.14
(4H, m), 7.09-7.05 (1H, m), 2.72-2.66 (1H, m), 2.61-2.56 (1H, m),
1.42-1.29 (2H, m), 1.20-1.14 (1H, m), 1.14 (6H, s), 1.11 (6H, s),
0.89 (3H, t, J = 7.3 Hz); 13C NMR (125 MHz, THF-d8): δ 143.6,
129.8, 128.8, 126.4, 83.7, 38.5, 38.3, 33.0, 32.3, 32.1, 31.01,
30.98, 30.81, 30.77, 30.7, 30.5, 30.1, 27.1 (br, C-B), 25.5, 25.32, 25.28, 23.7, 14.6; IR (neat):
2921.9 (s), 2852.2 (m), 1455.8 (w), 1371.2 (m), 1317.3 (m),
1143.8 (m), 967.3 (w), 862.4 (w), 743.1 (w), 698.3 (w) cm\(^{-1}\); HRMS-(DART+) for \(^{12}\)C\(^{28}\)C\(^{12}\)C\(^{1}\)H\(^{52}\)B\(^{16}\)O\(^{2}\)[M+H]\(^{+}\): calculated: 444.4094, found: 444.4094.

c) 13C NMR Spectra of \(\alpha,\alpha\)-Diboryl Carbanion

In the glove box, an oven-dried 2-dram vial with magnetic stir bar was charged with LTMP (4.4
mg, 0.030 mmol) and THF-d8 (0.60 mL). The vial was sealed with a polypropylene cap and
cooled in the glove box freezer (−30 °C) for 10 min. Diboronate ester S16 (14.4 mg, 0.030 mmol)
was then added and the mixture was allowed to warm to room temperature and stirred for 10 min.
Upon completion, the reaction mixture was transferred to a NMR tube, sealed, removed from the
glove box, and analyzed by 13C NMR.\(^{19}\)
$^{13}$C NMR of S16 (THF-$d_8$, 0.05 M)

$^{13}$C NMR of S16 with 1.0 equiv. LTMP (THF-$d_8$, 0.05 M)
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