Synthesis of 1,3-Bis-(boryl)alkanes through Boronic Ester Induced Consecutive Double 1,2-Migration

Cai You and Armido Studer*

anie_202007541_sm_miscellaneous_information.pdf
Contents

1 General information ............................................................................................................. S2
2 Preparation and data of substrates .................................................................................. S3
3 General procedure and characterization data for the products .......................................... S5
4 Mechanistic studies ......................................................................................................... S19
5 Synthetic transformations ............................................................................................... S21
6 References ....................................................................................................................... S24
7 NMR spectra ................................................................................................................... S25
1. General Information

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in flame-dried glassware under an argon atmosphere using standard Schlenk techniques. Solvents used in reactions were either freshly distilled or obtained in extra-dry grade from commercial sources. Diethyl ether (Et₂O) was refluxed over K and freshly distilled from K-Na-alloy (4:1) afterwards. Tetrahydrofuran (THF) was refluxed over Na and distilled from K afterwards. All commercially available reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros or ABCR in the highest purity grade and used directly without further purification. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F-254 plates and visualized by fluorescence quenching under UV light or staining with the standard solution of KMnO₄. Column chromatography was performed on Merck or Fluka silica gel 60 (40-63 μm). ¹H NMR, ¹³C NMR, ¹¹B NMR and ¹⁹F NMR spectra were recorded on Bruker DPX 300 spectrometer (300 MHz) or Bruker AV 400 (400 MHz). Chemical shifts (δ in ppm) were referenced on the residual peak of CDCl₃ (¹H NMR: δ = 7.26; ¹³C NMR: δ = 77.0) or on an external standard (CFCl₃: ¹⁹F NMR: δ = 0.0). Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Melting points (MP) were determined with a Stuart SMP10 and are uncorrected. Infrared spectra (IR) were measured on a Digilab 3100 FT-IR Excalibur Series spectrometer and the position of the absorption bands is given in wave numbers ν (cm⁻¹). The method used for GCMS was: start at 50 °C and 1 ml/min, 1.85 psi, increase to 300 °C at 10 °C/min, hold for 15 min. Gas Chromatography (GC) was performed on an Hewlett Packard HP 6890 series GC system using an Agilent HP-1 column (30 m x 0.32 mm x 0.25 μm film thickness). The method used for GC was: start at 50 °C and 1.5 ml/min, 3.81 psi, increase to 300 °C at 10 °C/min, hold for 15 min. Mass spectra were recorded on a Finnigan MAT 4200S, a Bruker Daltonics Micro Tof, a Waters-Micromass Quatro LCZ (ESI); peaks are given in m/z (% of basis peak).
2. Preparation and Data of Substrates

1a, 1b, 1e, ICH₂Bpin, BrCH₂Bpin and ClCH₂Bpin were purchased from commercial source and used without further purification. 1c,[1] 1d,[1] 1g,[2] 1h,[3] 1i,[4] 1j,[5] 1k[6] and 1m[7] were prepared following literature procedures.

Preparation of vinyl boronic ester 1f:

The vinyl boronic ester 1f was prepared according to the literature procedure.[7] A 100-mL oven-dried flask with a stir bar was placed under nitrogen. The flask was charged with 2,2,6,6-tetramethylpiperidine (9 mmol, 1.2 equiv.) and 15 mL of THF. The flask was cooled to 0 °C. n-BuLi (9 mmol, 1.6 M in hexanes, 1.2 equiv.) was added via syringe. The reaction mixture was stirred for 15 minutes at 0 °C. Then, a solution of 2,2’-(4-methylpent-3-ene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (prepared according to the literature procedure[8] with bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)methane and 5-bromopent-1-ene) (7.5 mmol, 1.0 equiv) in THF (15 mL) was added. The reaction mixture was allowed to stir for 5 minutes at 0 °C. Next, a solution of diiodomethane (15 mmol, 2.0 equiv) in THF (7 mL) was added dropwise at 0 °C. The reaction vial was allowed to warm to 60 °C and stir for additional 2 hours. Upon completion, the reaction mixture was concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (pentane/Et₂O = 30:1) to afford 1f (1.1 g, 66% yield) as a colorless oil.
4,4,5,5-Tetramethyl-2-(5-methylhexa-1,4-dien-2-yl)-1,3,2-dioxaborolane (1f):

^1^H NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 5.83 – 5.70 (m, 1H), 5.59 (s, 1H), 5.20 – 5.13 (m, 1H), 2.83 (d, \( J = 7.3 \) Hz, 2H), 1.71 (d, \( J = 0.9 \) Hz, 3H), 1.61 (s, 3H), 1.26 (s, 12H). \(^{13}\)C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 132.3, 128.3, 122.4, 83.3, 33.5, 25.8, 24.8, 17.7 ppm. \(^{11}\)B NMR (96 MHz, CDCl\textsubscript{3}) \( \delta \) 30.2 ppm. HRMS (ESI): Exact mass calculated for C\textsubscript{13}H\textsubscript{23}BNaO\textsubscript{2}\(^+\) ([M+Na\(^+\)]: 245.1683, mass found: 245.1683. FTIR (neat): \( \nu \) (cm\textsuperscript{-1}) 2981, 2930, 1428, 1361, 1306, 1134, 971, 933, 865.

Preparation of vinyl boronic ester 1l:

The vinyl boronic ester 1l was prepared according to the literature procedure.\(^7\) A 100-mL oven-dried flask with a stir bar was placed under nitrogen. The flask was charged with 2,2,6,6-tetramethylpiperidine (7.6 mmol, 1.2 equiv.) and 12 mL of THF. The flask was cooled to 0 °C. \( n \)-BuLi (7.6 mmol, 1.6 M in hexanes, 1.2 equiv.) was added via syringe. The reaction mixture was stirred for 15 minutes at 0 °C. Then, a solution of 2,2’-(cyclopropylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (prepared according to the literature procedure\(^9\) with bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane and 5-bromopent-1-ene) (6.3 mmol, 1.0 equiv) in THF (10 mL) was added. The reaction mixture was allowed to stir for 5 minutes at 0 °C. Next, a solution of diiodomethane (12.6 mmol, 2.0 equiv) in THF (7 mL) was added dropwise at 0 °C. The reaction vial was allowed to warm to 60 °C and stir for additional 2 hours. Upon completion, the reaction mixture was concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (pentane/Et\textsubscript{2}O = 30:1) to afford 1l (0.31 g, 25% yield) as a colorless oil.

**2-(1-Cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1l):**

\(^1^H\) NMR (300 MHz, CDCl\textsubscript{3}) \( \delta \) 5.64 (d, \( J = 3.0 \) Hz, 1H), 5.49 (s, 1H), 1.55 – 1.47 (m, 1H), 1.26 (s, 12H), 0.70 – 0.64 (m, 2H), 0.61 – 0.54 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\textsubscript{3}) \( \delta \) 125.2, 83.2, 24.8, 15.4, 7.5 ppm. \(^{11}\)B NMR (96 MHz, CDCl\textsubscript{3}) \( \delta \) 30.0 ppm. FTIR (neat): \( \nu \) (cm\textsuperscript{-1}) 2986, 1426, 1405, 1389, 1329, 1305, 1208, 1134, 969, 847. The spectroscopic data are in accordance to those reported in the literature\(^{10}\).
3. General Procedure and Characterization Data for the Products

**General Procedure A:** Vinyl boronic ester (0.20 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and the alkyl/aryllithium solution (0.22 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of ICH₂Bpin (0.60 mmol, 3.0 equiv.), the tube was sealed and the mixture was stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et₂O. Flash column chromatography eluting with pentane and Et₂O (pentane/Et₂O = 10:1) afforded the desired product. *Caution: In order to get a good yield, the chromatography should be finished within 10 min.*

**General Procedure B:** To a solution of arylbromide (for 3m, 1-chloro-4-iodobenzene was used) (0.28 mmol, 1.4 equiv.) in THF (1.5 mL) at -78 °C was added a solution of *n*-butyllithium (1.6 M, 0.26 mmol, 1.3 equiv.) over a period of 5 minutes. The solution was then stirred for 1 h at -78 °C, at which point a solution of isopropenylboronic acid pinacol ester 1a (0.20 mmol, 1.0 equiv.) in THF (0.50 mL) was added dropwise. The solution was then stirred for 30 min at -78 °C, warmed to r.t. and stirred for a further 30 min. Subsequently, the solvent was carefully removed *in vacuo* and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of ICH₂Bpin (0.60 mmol, 3.0 equiv.), the tube was sealed and the mixture was stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et₂O. Flash column chromatography eluting with pentane and Et₂O (pentane/Et₂O = 10:1) afforded the desired product. *Caution: In order to get a good yield, the chromatography should be finished within 10 min.*
General Procedure C: To a solution of arylbromide (0.28 mmol, 1.4 equiv.) in Et₂O (1.5 mL) at 0 °C was added a solution of n-butyllithium (1.6 M, 0.26 mmol, 1.3 equiv.) over a period of 5 minutes. The mixture was stirred at that temperature for 1 h. After warming up to room temperature the aryllithium solution was added dropwise over 5 minutes to vinyl boronic ester (0.20 mmol, 1.0 equiv.) in diethyl ether (1.0 mL) at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed in vacuo and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of ICH₂Bpin (0.60 mmol, 3.0 equiv.), the tube was sealed and the mixture was stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et₂O. Flash column chromatography eluting with pentane and Et₂O (pentane/Et₂O = 10:1) afforded the desired product. Caution: In order to get a good yield, the chromatography should be finished within 10 min.

2,2′-(3-Methylheptane-1,3-diy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3a):

According to the General Procedure A, 3a (63.0 mg, 86%) was prepared as a colorless sticky oil. 

¹H NMR (300 MHz, CDCl₃) δ 1.60 – 1.47 (m, 1H), 1.45 – 1.05 (m, 31H), 0.96 – 0.80 (m, 6H), 0.78 – 0.61 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 82.8, 82.7, 38.7, 32.7, 28.2, 24.9, 24.8, 23.7, 20.8, 14.1 ppm, carbons attached to borons not observed. ¹¹B NMR (96 MHz, CDCl₃) δ 35.1 ppm.

HRMS (ESI): Exact mass calculated for C₂₀H₄₀B₂NaO₄⁺ ([M+Na⁺]): 389.3005, mass found: 389.3006. FTIR (neat): ν (cm⁻¹) 2980, 2929, 2859, 1469, 1371, 1308, 1272, 1215, 1145, 968, 856.

2,2′-(3-Methylnonane-1,3-diy)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3b):

According to the General Procedure A, 3b (65.2 mg, 83%) was prepared as a colorless sticky oil. 

¹H NMR (300 MHz, CDCl₃) δ 1.57 – 1.47 (m, 1H), 1.37 – 1.10 (m, 35H), 0.92 – 0.83 (m, 6H), 0.77
– 0.62 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.8, 82.7, 39.1, 32.7, 31.8, 30.3, 25.9, 24.9, 24.8, 24.8, 22.6, 20.8, 14.1 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 35.0 ppm. HRMS (ESI): Exact mass calculated for C$_{22}$H$_{44}$B$_2$NaO$_4$ $^+ ([M+Na]^+)$: 417.3318, mass found: 417.3316. FTIR (neat): ν (cm$^{-1}$) 2978, 2929, 2859, 1468, 1371, 1305, 1272, 1145, 968, 855.

$^{2,2'}$-(3,5-Dimethylhexane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3c):
According to the General Procedure A, 3c (53.7 mg, 73%) was prepared as a colorless sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.69 – 1.44 (m, 2H), 1.39 – 1.20 (m, 26H), 1.13 – 1.06 (m, 1H), 0.90 – 0.83 (m, 9H), 0.80 – 0.61 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.8, 82.7, 47.9, 33.5, 25.7, 25.0, 24.9, 24.8, 24.8, 24.5, 24.0, 20.9 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 5.2 ppm. HRMS (ESI): Exact mass calculated for C$_{20}$H$_{38}$B$_2$NaO$_4$ $^+ ([M+Na]^+)$: 389.2848, mass found: 389.2855. FTIR (neat): ν (cm$^{-1}$) 2979, 2954, 2870, 1469, 1371, 1307, 1145, 968, 849.

$^{2,2'}$-(3,4-Dimethylpentane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3d):
According to the General Procedure A, 3d (53.4 mg, 76%) was prepared as a yellow solid, m.p. = 48–50 ºC. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.69 – 1.44 (m, 2H), 1.39 – 1.20 (m, 26H), 1.13 – 1.06 (m, 1H), 0.90 – 0.83 (m, 9H), 0.80 – 0.61 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.8, 82.7, 33.4, 30.8, 25.0, 25.0, 24.8, 24.8, 24.0, 17.1, 16.4 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 34.7 ppm. HRMS (ESI): Exact mass calculated for C$_{19}$H$_{38}$B$_2$NaO$_4$ $^+ ([M+Na]^+)$: 375.2848, mass found: 375.2855. FTIR (neat): ν (cm$^{-1}$) 2979, 2961, 2870, 1469, 1371, 1304, 1273, 1145, 969.

$^{2,2'}$-(3,4,4-Trimethylpentane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3e):
According to the General Procedure A, 3e (55.0 mg, 76%) was prepared as a white solid, m.p. = 100–102 ºC. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.79 (td, $J$ = 12.4, 5.1 Hz, 1H), 1.46 – 1.06 (m, 25H), 0.89 (s, 9H), 0.86 (s, 3H), 0.78 – 0.51 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.8, 82.7, 34.7, 27.2,
27.0, 25.1, 25.0, 24.8, 24.8, 16.4 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 34.3 ppm. **HRMS** (ESI): Exact mass calculated for C$_{20}$H$_{40}$B$_2$NaO$_4$ $^+$ (M+Na$^+$): 389.3005, mass found: 389.3007. **FTIR** (neat): ν (cm$^{-1}$) 2978, 2951, 1468, 1371, 1363, 1348, 1317, 1299, 1216, 1166, 1145, 1087, 968, 886, 858, 847.

$^{2,2'}$-(3-Phenylbutane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3f):

According to the General Procedure A, 3f (56.4 mg, 73%) was prepared as a white solid, m.p. = 87-89 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.34 – 7.29 (m, 2H), 7.29 – 7.20 (m, 2H), 7.17 – 7.05 (m, 1H), 1.96 – 1.74 (m, 2H), 1.32 (s, 3H), 1.26 – 1.14 (m, 24H), 0.78 – 0.56 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.1, 127.9, 127.1, 124.9, 83.2, 82.8, 33.3, 24.8, 24.6, 24.6, 20.8 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 34.6 ppm. **HRMS** (ESI): Exact mass calculated for C$_{22}$H$_{36}$B$_2$NaO$_4$ $^+$ (M+Na$^+$): 409.2692, mass found: 409.2693. **FTIR** (neat): ν (cm$^{-1}$) 2978, 2930, 1468, 1371, 1310, 1272, 1144, 968, 849, 701.

$^{2,2'}$-(3-(p-Tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3g):

According to the General Procedure B, 3g (60.2 mg, 75%) was prepared as a white solid, m.p. = 58-60 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.23 – 7.16 (m, 2H), 7.08 – 7.04 (m, 2H), 2.28 (s, 3H), 1.93 – 1.70 (m, 2H), 1.30 (s, 3H), 1.24 – 1.17 (m, 24H), 0.76 – 0.56 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 144.0, 134.1, 128.6, 126.9, 83.1, 82.7, 33.4, 29.7, 24.8, 24.6, 24.6, 20.9, 20.9 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 34.7 ppm. **HRMS** (ESI): Exact mass calculated for C$_{23}$H$_{38}$B$_2$NaO$_4$ $^+$ (M+Na$^+$): 423.2848, mass found: 423.2847. **FTIR** (neat): ν (cm$^{-1}$) 2978, 2929, 1467, 1371, 1308, 1270, 1144, 968, 849, 816.
2,2’-(3-(4-(tert-Butyl)phenyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3h):

According to the General Procedure B, 3h (77.0 mg, 87%) was prepared as a white solid, m.p. = 87-89 °C. 

1H NMR (300 MHz, CDCl3) δ 7.38 – 7.21 (m, 4H), 1.96 – 1.73 (m, 2H), 1.34 (s, 3H), 1.32 (s, 9H), 1.26 – 1.21 (m, 24H), 0.82 – 0.60 (m, 2H). 

13C NMR (75 MHz, CDCl3) δ 147.3, 143.9, 126.6, 124.8, 83.1, 82.7, 34.2, 33.6, 31.4, 24.8, 24.7, 24.6, 21.0 ppm, carbons attached to borons not observed. 

11B NMR (96 MHz, CDCl3) δ 34.3 ppm. 

HRMS (ESI): Exact mass calculated for C26H44B2NaO4+: 465.3318, mass found: 465.3319. 

FTIR (neat): ν (cm⁻¹) 2977, 2934, 2869, 1468, 1371, 1309, 1271, 1145, 967, 848.

2,2’-(3-(4-(Trifluoromethyl)phenyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3i):

According to the General Procedure B, 3i (74.6 mg, 82%) was prepared as a yellow solid, m.p. = 80-82 °C. 

1H NMR (300 MHz, CDCl3) δ 7.50 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 1.98 – 1.75 (m, 2H), 1.33 (s, 3H), 1.28 – 1.16 (m, 24H), 0.76 – 0.49 (m, 2H). 

13C NMR (75 MHz, CDCl3) δ 151.4, 127.42, 127.2 (d, J = 32.3 Hz), 124.8 (q, J = 3.7 Hz), 124.6 (q, J = 271.6 Hz), 83.5 82.9, 33.2, 24.8, 24.6, 24.6, 20.6 ppm, carbons attached to borons not observed. 

19F NMR (282 MHz, CDCl3) δ -62.2 ppm. 

11B NMR (96 MHz, CDCl3) δ 34.1 ppm. 

HRMS (ESI): Exact mass calculated for C23H35B2F3NaO4+: 477.2566, mass found: 477.2566. 

FTIR (neat): ν (cm⁻¹) 2979, 2929, 1372, 1327, 1165, 1144, 1122, 1074, 1016, 967, 847.
2,2'-(3-(4-Methoxyphenyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3j):
According to the General Procedure B, 3j (54.9 mg, 66%) was prepared as a white solid, m.p. = 66-68 °C. 1H NMR (300 MHz, CDCl3) δ 7.26 – 7.19 (m, 2H), 6.84 – 6.77 (m, 2H), 3.77 (s, 3H), 1.91 – 1.70 (m, 2H), 1.29 (s, 3H), 1.24 – 1.17 (m, 24H), 0.75 – 0.55 (m, 2H). 13C NMR (75 MHz, CDCl3) δ 157.0, 139.1, 128.0, 113.4, 83.1, 82.8, 55.1, 33.4, 24.8, 24.6, 24.6, 21.0 ppm, carbons attached to borons not observed. 11B NMR (96 MHz, CDCl3) δ 34.9 ppm. HRMS (ESI): Exact mass calculated for C23H38B2NaO5+: 439.2798, mass found: 439.2806. FTIR (neat): ν (cm⁻¹) 2980, 2937, 2932, 1512, 1372, 1307, 1248, 1145, 968, 847.

(4-(2,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)phenyl) trimethylsilane (3k):
According to the General Procedure B 3k (83.7 mg, 91%) was prepared as a white solid, m.p. = 87-89 °C. 1H NMR (300 MHz, CDCl3) δ 7.44 – 7.38 (m, 2H), 7.33 – 7.27 (m, 2H), 1.95 – 1.73 (m, 2H), 1.32 (s, 3H), 1.23 – 1.19 (m, 24H), 0.78 – 0.57 (m, 2H), 0.24 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 147.8, 136.0, 133.0, 126.5, 83.2, 82.8, 33.5, 24.8, 24.7, 24.6, 20.9, -1.0 ppm, carbons attached to borons not observed. 11B NMR (96 MHz, CDCl3) δ 34.8 ppm. HRMS (ESI): Exact mass calculated for C25H44B2NaO4Si+: 481.3087, mass found: 481.3089. FTIR (neat): ν (cm⁻¹) 2978, 2957, 1465, 1371, 1311, 1249, 1144, 968, 848, 819.

2,2'-(3-(4-Fluorophenyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3l):
According to the General Procedure B, 3l (63.2 mg, 78\%) was prepared as a white solid, m.p. = 69-71 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.34 – 7.24 (m, 2H), 7.03 – 6.90 (m, 2H), 1.94 – 1.75 (m, 2H), 1.33 (s, 3H), 1.26 – 1.20 (m, 2H), 0.79 – 0.54 (m, 2H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 160.7 (d, \(J =\) 242.6 Hz), 142.6 (d, \(J =\) 3.1 Hz), 128.4 (d, \(J =\) 7.6 Hz), 114.5 (d, \(J =\) 20.7 Hz), 83.3, 82.8, 33.4, 24.8, 24.6, 24.6, 20.9 ppm, \textit{carbons attached to borons not observed}. \(^{19}\)F NMR (282 MHz, CDCl\(_3\)) \(\delta\) -119.4 ppm.

\(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 34.6 ppm. HRMS (ESI): Exact mass calculated for C\(_{22}\)H\(_{35}\)B\(_2\)FNaO\(_4\)\(^+\) ([M+Na\(^+\)]: 427.2598, mass found: 427.2598. FTIR (neat): \(\nu\) (cm\(^{-1}\)) 2979, 2934, 1508, 1467, 1372, 1316, 1273, 1223, 1164, 1144, 968, 848, 833.

\[\begin{align*}
\text{Me} & \quad \text{Bpin} \\
\text{Cl} & \quad \text{Bpin}
\end{align*}\]

\(2,2'-(3-(4-Chlorophenyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)\) (3m): According to the General Procedure B, 3m (57.6 mg, 68\%) was prepared as a white solid, m.p. = 83-85 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.26 – 7.17 (m, 4H), 1.91 – 1.72 (m, 2H), 1.29 (s, 3H), 1.23 – 1.17 (m, 2H), 0.74 – 0.52 (m, 2H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.6, 130.6, 128.6, 128.0, 83.3, 82.8, 33.2, 24.8, 24.6, 24.6, 20.6 ppm, \textit{carbons attached to borons not observed}. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 34.2 ppm. HRMS (ESI): Exact mass calculated for C\(_{22}\)H\(_{35}\)B\(_2\)ClNaO\(_4\)\(^+\) ([M+Na\(^+\)]: 443.2302, mass found: 443.2304. FTIR (neat): \(\nu\) (cm\(^{-1}\)) 2977, 2923, 1492, 1464, 1372, 1315, 1269, 1212, 1145, 968.

\[\begin{align*}
\text{Me} & \quad \text{Bpin} \\
\text{Cl} & \quad \text{Bpin}
\end{align*}\]

\(2,2'-(3-(m-Tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)\) (3n): According to the General Procedure B, 3n (68.3 mg, 85\%) was prepared as a white solid, m.p. = 65-67 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.19 – 7.07 (m, 3H), 6.97 – 6.88 (m, 1H), 2.31 (s, 3H), 1.95 – 1.71 (m, 2H), 1.31 (s, 3H), 1.26 – 1.18 (m, 2H), 0.78 – 0.58 (m, 2H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 147.1, 137.1, 127.8, 127.7, 125.7, 124.2, 83.1, 82.8, 33.3, 24.8, 24.6, 24.6, 21.6, 20.8 ppm, \textit{carbons attached to borons not observed}. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 34.0 ppm. HRMS (ESI):
Exact mass calculated for $\text{C}_{23}\text{H}_{38}\text{B}_{2}\text{NaO}_{4}^+$ ($[\text{M+Na}]^+$): 423.2848, mass found: 423.2847. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2978, 2931, 1467, 1371, 1349, 1308, 1272, 1144, 968, 856.

2,2'-(3-(o-Tolyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3o):

According to the General Procedure B, 3o (51.1 mg, 64%) was prepared as a white solid, m.p. = 106–108 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.22 – 7.18 (m, 1H), 7.16 – 6.99 (m, 3H), 2.33 (s, 3H), 2.00 – 1.75 (m, 2H), 1.32 (s, 3H), 1.26 – 1.16 (m, 24H), 0.70 (ddd, $J = 17.1, 12.4, 4.8$ Hz, 1H), 0.31 (ddd, $J = 15.9, 12.4, 5.2$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.3, 136.0, 130.7, 126.7, 125.5, 125.1, 83.1, 82.7, 30.2, 24.9, 24.8, 24.8, 24.8, 21.4, 21.2 ppm, *carbons attached to borons not observed*. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 34.3 ppm. **HRMS** (ESI): Exact mass calculated for $\text{C}_{23}\text{H}_{38}\text{B}_{2}\text{NaO}_{4}^+$ ($[\text{M+Na}]^+$): 423.2848, mass found: 423.2847. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2979, 2931, 1469, 1346, 1310, 1271, 1145, 966, 848.

2,2'-(3-(2,6-Dimethylphenyl)butane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3p):

According to the General Procedure B, 3p (54.8 mg, 66%) was prepared as a white solid, m.p. = 106–108 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.01 – 6.88 (m, 3H), 2.44 (s, 6H), 2.00 – 1.83 (m, 2H), 1.55 (s, 3H), 1.28 (s, 12H), 1.23 (s, 12H), 1.02 – 0.88 (m, 1H), 0.76 – 0.57 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 142.1, 137.6, 130.1, 125.0, 82.9, 82.7, 31.7, 25.1, 24.9, 24.8, 23.9, 23.1 ppm. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 34.7 ppm. **HRMS** (ESI): Exact mass calculated for $\text{C}_{24}\text{H}_{40}\text{B}_{2}\text{NaO}_{4}^+$ ($[\text{M+Na}]^+$): 437.3005, mass found: 437.3005. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2979, 2930, 1469, 1370, 1298, 1140, 966, 846, 766.
2,2'-(3-(4-Vinylphenyl)butane-1,3-diylibis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) \( (3q) \):

According to the General Procedure B, \( 3q \) (59.6 mg, 72\%) was prepared as a white solid, m.p. = 80-82 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.35 – 7.24 (m, 4H), 6.68 (dd, \( J = 17.6, 10.9 \) Hz, 1H), 5.68 (dd, \( J = 17.6, 1.0 \) Hz, 1H), 5.15 (dd, \( J = 10.9, 1.0 \) Hz, 1H), 1.95 – 1.74 (m, 2H), 1.31 (s, 3H), 1.25 – 1.18 (m, 24H), 0.76 – 0.56 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 147.0, 136.9, 134.3, 127.2, 125.8, 112.4, 83.2, 82.8, 33.2, 24.8, 24.6, 24.6, 20.7 ppm, \textit{carbons attached to borons not observed.} \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \( \delta \) 34.5 ppm. \textbf{HRMS (ESI)}: Exact mass calculated for C\(_{24}\)H\(_{38}\)B\(_2\)NaO\(_4\)\(^-\) ([M+Na]\(^-\)): 435.2848, mass found: 435.2849. \textbf{FTIR (neat)}: \( \nu \) (cm\(^{-1}\)) 2978, 2932, 1510, 1461, 1370, 1348, 1308, 1271, 1214, 1142, 967, 846.

\[ \begin{align*}
\text{Me} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Me}
\end{align*} \]

2,2'-(3-(Naphthalen-2-yl)butane-1,3-diylibis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) \( (3r) \):

According to the General Procedure C, \( 3r \) (59.1 mg, 68\%) was prepared as a white solid, m.p. = 109-111 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.85 – 7.68 (m, 4H), 7.51 (dd, \( J = 8.6, 1.9 \) Hz, 1H), 7.47 – 7.32 (m, 2H), 2.08 – 1.87 (m, 2H), 1.44 (s, 3H), 1.28 – 1.18 (m, 24H), 0.82 – 0.57 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 144.7, 133.7, 131.6, 127.8, 127.2, 127.1, 126.7, 125.4, 124.8, 83.3, 82.8, 33.0, 24.8, 24.6, 24.6, 20.6 ppm, \textit{carbons attached to borons not observed.} \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \( \delta \) 34.8 ppm. \textbf{HRMS (ESI)}: Exact mass calculated for C\(_{26}\)H\(_{38}\)B\(_2\)NaO\(_4\)\(^-\) ([M+Na]\(^-\)): 459.2848, mass found: 459.2850. \textbf{FTIR (neat)}: \( \nu \) (cm\(^{-1}\)) 2978, 2936, 1469, 1371, 1312, 1271, 1144, 967, 859, 749.

\[ \begin{align*}
\text{Me} & \quad \text{Bpin} \\
\text{Bpin} & \quad \text{Me}
\end{align*} \]

2,2'-(3-([1,1'-Biphenyl]-4-yl)butane-1,3-diylibis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) \( (3s) \):

According to the General Procedure C, \( 3s \) (64.5 mg, 70\%) was prepared as a white solid, m.p. =
117-119 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.62 – 7.56 (m, 2H), 7.54 – 7.47 (m, 2H), 7.45 – 7.36 (m, 4H), 7.35 – 7.27 (m, 1H), 2.00 – 1.78 (m, 2H), 1.37 (s, 3H), 1.27 – 1.20 (m, 24H), 0.82 – 0.61 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 146.3, 141.3, 137.6, 128.6, 127.5, 126.9, 126.7, 126.6, 83.3, 82.8, 33.3, 24.8, 24.6, 24.6, 20.8 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 35.1 ppm. HRMS (ESI): Exact mass calculated for C$_{28}$H$_{40}$B$_{2}$NaO$_{4}$+ ([M+Na]$^+$): 485.3005, mass found: 485.3007. FTIR (neat): $\nu$ (cm$^{-1}$) 2977, 2933, 1488, 1469, 1371, 1311, 1271, 1144, 968, 847, 767, 737, 700.

2,2'-([3,4-Dimethylpent-4-ene-1,3-diyl]bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3t): Isopropenylboronic acid pinacol ester 1a (0.20 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and the Grignard reagent isopropenylmagnesium bromide solution (0.22 mmol, 0.5 M in THF, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed in vacuo and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of ICH$_2$Bpin (0.60 mmol, 3.0 equiv.), the tube was sealed and the mixture was stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et$_2$O. Flash column chromatography eluting with pentane and Et$_2$O (pentane/Et$_2$O = 10:1) afforded the desired product. Caution: In order to get a good yield, the chromatography should be finished within 10 min.

3t (32.1 mg, 46%) was prepared as a white solid, m.p. = 44-46 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.80 (s, 1H), 4.67 (s, 1H), 1.72 (s, 3H), 1.68 – 1.60 (m, 2H), 1.24 – 1.20 (m, 24H), 1.04 (s, 3H), 0.72 – 0.53 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.6, 109.7, 83.1, 82.8, 29.1, 24.8, 24.7, 24.6, 21.7, 19.3 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 34.1 ppm. HRMS (ESI): Exact mass calculated for C$_{19}$H$_{36}$B$_2$NaO$_4$+ ([M+Na]$^+$): 373.2692, mass found: 373.2693. FTIR (neat): $\nu$ (cm$^{-1}$) 2978, 2928, 1457, 1371, 1345, 1308, 1272, 1144, 1098, 968, 880, 848.
2,2’-(Heptane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3u):

Vinyl boronic ester 1b (0.30 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and a solution of n-butyllithium (1.6 M, 0.33 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed in vacuo. After addition of Ir(ppy)$_3$ (2.0 mg, 1 mol%) and acetonitrile (1 mL), the mixture was stirred for 1 min until all solid was dissolved. Then ICH$_2$Bpin (0.60 mmol, 2.0 equiv.) was added to the reaction mixture and the reaction mixture was irradiated with a 30 W blue LED (465 nm) and stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et$_2$O. Flash column chromatography eluting with pentane and Et$_2$O (pentane/Et$_2$O = 10:1) afforded the desired product. **Caution:** In order to get a good yield, the chromatography should be finished within 10 min. 3u (61.0 mg, 58%) was prepared as a colorless sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.52 – 1.41 (m, 2H), 1.38 – 1.30 (m, 2H), 1.26 – 1.19 (m, 28H), 0.97 – 0.88 (m, 1H), 0.87 – 0.82 (m, 3H), 0.80 – 0.65 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.7, 82.7, 31.4, 30.8, 25.4, 24.8, 23.0, 14.0 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 34.2 ppm. **HRMS** (ESI): Exact mass calculated for C$_{19}$H$_{38}$B$_2$NaO$_4$ $^+$ (M+Na$^+$): 375.2848, mass found: 375.2849. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2979, 2924, 2859, 1457, 1371, 1314, 1272, 1216, 1145, 969, 867.

2,2’-(Butylheptane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3v):

According to the General Procedure B, 3v (65.0 mg, 80%) was prepared as a colorless sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.48 – 1.41 (m, 2H), 1.34 – 1.26 (m, 8H), 1.24 – 1.08 (m, 28H), 0.87 (t, $J$ = 7.1 Hz, 6H), 0.66 – 0.58 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.7, 82.7, 33.6, 27.5, 27.0, 24.9, 24.8, 23.7, 14.2 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 35.2 ppm. **HRMS** (ESI): Exact mass calculated for C$_{23}$H$_{46}$B$_2$NaO$_4$ $^+$ (M+Na$^+$): 431.3474, mass found: 431.3474. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2979, 2957, 2928, 2859, 1460, 1371, 1306, 1215, 1144, 968, 855.
2,2'-(3-Benzylheptan-1,3-diylo)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3w):

According to the General Procedure B, 3w (44.1 mg, 50%) was prepared as a yellow sticky oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.22 – 7.09 (m, 5H), 2.68 (s, 2H), 1.51 – 1.42 (m, 2H), 1.30 – 1.18 (m, 30H), 0.89 (t, \(J = 6.2\) Hz, 3H), 0.81 – 0.75 (m, 2H). \(^1^\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 140.3, 130.3, 127.6, 125.4, 83.0, 82.8, 39.5, 33.6, 29.7, 27.6, 27.1, 25.1, 24.8, 24.8, 23.6, 14.2 ppm, *carbons attached to borons not observed*. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 34.3 ppm. HRMS (ESI): Exact mass calculated for \(\text{C}_{26}\text{H}_{44}\text{B}_2\text{NaO}_4^+\) ([M+Na\(^+\]): 465.3318, mass found: 465.3320. FTIR (neat): \(\nu\) (cm\(^{-1}\)) 2978, 2957, 2927, 2857, 1457, 1371, 1311, 1271, 1144, 967, 849, 701.

2,2'-(3-Phenylheptan-1,3-diylo)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3x):

According to the General Procedure B, 3x (23.0 mg, 27%) was prepared as a white solid, m.p. = 88-90 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.31 – 7.21 (m, 4H), 7.13 – 7.06 (m, 1H), 1.93 – 1.86 (m, 2H), 1.83 – 1.74 (m, 2H), 1.29 – 1.26 (m, 2H), 1.24 – 1.19 (m, 24H), 1.15 – 1.07 (m, 2H), 0.85 (t, \(J = 7.3\) Hz, 3H), 0.60 – 0.50 (m, 2H). \(^1^\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.8, 127.8, 124.8, 83.1, 82.7, 33.8, 28.8, 27.5, 24.8, 24.8, 24.7, 24.7, 23.5, 14.1 ppm, *carbons attached to borons not observed*. \(^{11}\)B NMR (96 MHz, CDCl\(_3\)) \(\delta\) 34.3 ppm. HRMS (ESI): Exact mass calculated for \(\text{C}_{25}\text{H}_{42}\text{B}_2\text{NaO}_4^+\) ([M+Na\(^+\]): 451.3161, mass found: 451.3161. FTIR (neat): \(\nu\) (cm\(^{-1}\)) 2978, 2932, 2860, 1467, 1371, 1314, 1272, 1214, 1144, 968, 849, 701.

2,2'-(3-Butyl-6-methylhept-5-ene-1,3-diylo)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3y):

According to the General Procedure B, 3y (57.1 mg, 68%) was prepared as a colorless sticky oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 5.17 – 5.06 (m, 1H), 2.01 (d, \(J = 7.3\) Hz, 2H), 1.65 (s, 3H), 1.59 (s, 3H), 1.50 – 1.42 (m, 2H), 1.33 – 1.18 (m, 30H), 0.86 (t, \(J = 7.1\) Hz, 3H), 0.70 – 0.60 (m, 2H). \(^1^\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 131.4, 122.2, 82.8, 82.7, 33.6, 32.4, 27.7, 27.1, 26.0, 24.9, 24.8, 23.7,
18.0, 14.2 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 35.6 ppm.

**HRMS** (ESI): Exact mass calculated for C$_{24}$H$_{46}$B$_2$NaO$_4$ $^+ ([M+Na]^+)$: 443.3474, mass found: 443.3476. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2977, 2925, 2860, 1457, 1371, 1309, 1272, 1215, 1146, 967, 857.

2,2'-(3-Butyl-7-methyloct-6-ene-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3z):

According to the General Procedure B, 3z (69.3 mg, 80%) was prepared as a colorless sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 5.10 (t, $J = 7.1$ Hz, 1H), 1.90 – 1.79 (m, 2H), 1.65 (s, 3H), 1.58 (s, 3H), 1.51 – 1.42 (m, 2H), 1.35 – 1.12 (m, 32H), 0.86 (t, $J = 7.1$ Hz, 3H), 0.71 – 0.57 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 130.4, 125.6, 82.7, 82.7, 33.9, 33.6, 27.5, 27.0, 25.7, 24.9, 24.8, 23.6, 17.5, 14.2 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 34.7 ppm. **HRMS** (ESI): Exact mass calculated for C$_{25}$H$_{48}$B$_2$NaO$_4$ $^+ ([M+Na]^+)$: 457.3631, mass found: 457.3633. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2978, 2927, 2857, 1457, 1371, 1308, 1215, 1145, 967, 856.

2,2'-(2,2,3-Trimethylheptane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3aa):

According to the General Procedure A, 3aa (27.0 mg, 34%) was prepared as a colorless sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 1.65 – 1.54 (m, 2H), 1.24 – 1.22 (m, 24H), 1.04 – 0.98 (m, 9H), 0.90 – 0.83 (m, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 82.8, 82.6, 36.6, 33.4, 29.6, 26.4, 25.9, 25.1, 25.0, 24.9, 24.8, 24.0, 16.9, 14.2 ppm, carbons attached to borons not observed. $^{11}$B NMR (96 MHz, CDCl$_3$) δ 35.2 ppm. **HRMS** (ESI): Exact mass calculated for C$_{22}$H$_{44}$B$_2$NaO$_4$ $^+ ([M+Na]^+)$: 417.3318, mass found: 417.3317. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2978, 2933, 2875, 1467, 1371, 1347, 1321, 1298, 1214, 1142, 1111, 969, 854.

2,2'-(2,3-Dimethylheptane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3ab):

According to the General Procedure A, 3ab (69.2 mg, 91%, dr = 1.7:1) was prepared as a colorless
sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.91 – 1.72 (m, 1H), 1.54 – 1.41 (m, 1H), 1.40 – 1.06 (m, 29H), 1.06 – 0.75 (m, 10H), 0.71 – 0.40 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 82.7, 82.7, 82.6, 37.6, 36.8, 35.4, 35.2, 28.6, 28.5, 25.0, 25.0, 24.9, 24.9, 24.9, 24.7, 24.7, 23.8, 23.8, 19.6, 17.2, 16.8, 16.3, 14.1 ppm, *carbons attached to borons not observed*. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 35.0 ppm.

**HRMS** (ESI): Exact mass calculated for C$_{21}$H$_{42}$B$_2$NaO$_4^+$ ([M+Na$^+$]): 403.3161, mass found: 403.3167.

**FTIR** (neat): $\nu$ (cm$^{-1}$) 2981, 2933, 2874, 1468, 1370, 1300, 1213, 1140, 967, 848.

---

2,2'-(2,3-Dimethylheptane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3ab):

According to the General Procedure A, 3ab (68.7 mg, 90%, dr = 1.3:1) was prepared as a colorless sticky oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.93 – 1.69 (m, 1H), 1.48 – 1.41 (m, 1H), 1.40 – 1.07 (m, 29H), 1.05 – 0.74 (m, 10H), 0.69 – 0.41 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 82.7, 82.7, 82.7, 82.6, 37.5, 36.7, 35.4, 35.2, 28.6, 28.4, 25.0, 24.9, 24.9, 24.9, 24.7, 24.6, 23.8, 23.8, 19.6, 17.2, 16.8, 16.3, 14.1 ppm, *carbons attached to borons not observed*. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 34.9 ppm. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2979, 2932, 2871, 1464, 1370, 1300, 1213, 1141, 967, 848.

---

2-(1-Butyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ac):

According to the General Procedure A, 3ac (46.1 mg, 59%, dr = 2.2:1) was prepared as a white solid, m.p. = 36-38 °C. $^1$H NMR (300 MHz, CDCl$_3$) 1H NMR (300 MHz, CDCl$_3$) $\delta$ 2.13 – 1.77 (m, 2H), 1.76 – 1.63 (m, 2H), 1.61 – 1.50 (m, 2H), 1.48 – 1.38 (m, 1H), 1.23 – 1.19 (m, 24H), 1.16 – 1.08 (m, 2H), 0.97 – 0.90 (m, 1H), 0.86 (t, J = 7.0 Hz, 3H), 0.68 – 0.57 (m, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 13C NMR (75 MHz, CDCl$_3$) $\delta$ 82.7, 82.6, 82.6, 46.7, 41.4, 38.3, 34.4, 33.9, 32.4, 32.2, 30.6, 30.00, 29.8, 25.2, 24.9, 24.8, 24.8, 24.7, 24.6, 23.8, 22.8, 22.6, 14.1 ppm, *carbons attached to borons not observed*. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 34.9 ppm.

**HRMS** (ESI): Exact mass calculated for C$_{22}$H$_{44}$B$_2$NaO$_4^+$ ([M+Na$^+$]): 415.3161, mass found: 415.3160. **FTIR** (neat): $\nu$ (cm$^{-1}$) 2978, 2953, 2928, 2863, 1371, 1314, 1296, 1215, 1143, 969, 849.
2,2',2''-(Butane-1,3,3-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3ad):

Bis(pinacolato)diboron (B$_2$Pin$_2$) (0.20 mmol, 1.0 equiv.) was dissolved in THF (2.0 mL) and the Grignard reagent isopropenylmagnesium bromide solution (0.22 mmol, 0.5 M in THF, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed in vacuo and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of ICH$_2$Bpin (0.60 mmol, 3.0 equiv.), the tube was sealed and the mixture was stirred at room temperature for 16 h. The reaction mixture was filtered through a pad of silica and rinsed with 30 mL Et$_2$O. Flash column chromatography eluting with pentane and Et$_2$O (pentane/Et$_2$O = 10:1 to 5:1) afforded the desired product.

3ad (14.2 mg, 16%) was prepared as a colorless sticky oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.61 – 1.57 (m, 2H), 1.16 (s, 12H), 1.14 (s, 24H), 0.97 (s, 3H), 0.71 – 0.67 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 82.8, 82.7, 27.7, 24.8, 24.7, 24.7, 15.4 ppm, carbons attached to borons not observed. $^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 33.7 ppm. HRMS (ESI): Exact mass calculated for C$_{22}$H$_{43}$B$_3$NaO$_6^+$ ([M+Na]$^+$): 459.3231, mass found: 459.3238. FTIR (neat): $\nu$ (cm$^{-1}$) 2978, 2930, 1371, 1343, 1299, 1266, 1215, 1141, 1081, 968, 848.

4. Mechanistic Studies

4.1 Control Experiments

According to the General Procedure A, isopropenylboronic acid pinacol ester 1a (0.20 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and $n$-butyllithium (1.6 M, 0.22 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed
to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed in vacuo and the resulting residue was taken up in acetonitrile (2.0 mL). After the addition of 2,2,6,6-tetramethyl piperidine-N-oxyl (TEMPO, 0.60 mmol, 3 equiv.) or 3,5-di-tert-4-butylhydroxytoluene (BHT, 0.60 mmol, 3 equiv.), ICH$_2$Bpin (0.60 mmol, 3.0 equiv.) was added, and the tube was sealed and the mixture was stirred at room temperature for 16 h. The yield of 3a was determined by GC with n-C$_{14}$H$_{30}$ as an internal standard. 86% yield was obtained in the presence of TEMPO, and 92% yield was obtained in the presence of BHT. Radical trapping products were not identified.

Vinyl boronic ester 1b (0.30 mmol, 1.0 equiv.) was dissolved in diethyl ether (2.0 mL) and a solution of n-butyllithium (1.6 M, 0.33 mmol, 1.1 equiv.) was added dropwise over 5 minutes at 0 °C. The solution was then stirred for 0.5 h at 0 °C, warmed to room temperature and stirred for a further 0.5 h. Subsequently, the solvent was carefully removed in vacuo. After addition of Ir(ppy)$_3$ (2.0 mg, 1 mol%) and acetonitrile (1 mL), the mixture was stirred for 1 min until all solid was dissolved. Then 2,2,6,6-tetramethyl piperidine-N-oxyl (TEMPO, 0.60 mmol, 2 equiv.) and ICH$_2$Bpin (0.60 mmol, 2.0 equiv.) were added to the reaction mixture and the reaction mixture was irradiated with a 30 W blue LED (465 nm) and stirred at room temperature for 16 h. The yield of 3a was determined by GC with n-C$_{14}$H$_{30}$ as an internal standard. The reaction was suppressed upon addition of TEMPO, and only less than 1% yield of 3a was obtained.

4.2 Radical Probe Experiments

2,2'-((3-Cyclopropylheptane-1,3-diyl)bisis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3ae):
According to the General Procedure A, 3ae (68.2 mg, 87%) was obtained as a colorless sticky oil.
1H NMR (300 MHz, CDCl₃) δ 1.61 – 1.42 (m, 2H), 1.29 – 1.14 (m, 30H), 0.91 – 0.78 (m, 5H), 0.54 – 0.45 (m, 1H), 0.35 – 0.22 (m, 4H). 13C NMR (75 MHz, CDCl₃) δ 82.7, 82.6, 35.8, 30.1, 27.7, 24.9, 24.8, 23.8, 17.8, 14.2, 2.2, 1.9 ppm, carbons attached to borons not observed. 11B NMR (96 MHz, CDCl₃) δ 37.9 ppm. HRMS (ESI): Exact mass calculated for C₂₂H₄₂B₂NaO₄⁺ ([M+Na⁺]: 415.3161, mass found: 415.3160. FTIR (neat): ν (cm⁻¹) 2979, 2932, 2859, 1467, 1371, 1305, 1272, 1215, 1144, 968, 865, 849.

5. Synthetic Transformations

The title compound was prepared according to a literature procedure[11].

A solution of 1,3-bis(boronic ester) 3r (87.2 mg, 0.2 mmol, 1.0 equiv) and bromochloromethane (155 mg, 78 µL, 1.2 mmol, 6.0 equiv.) was dissolved in anhydrous Et₂O (0.2 M) under an atmosphere of nitrogen. The reaction mixture was cooled to -78 °C. n-BuLi (1.6 M in hexanes, 5 equiv.) was added dropwise to the reaction mixture at -78 °C. The reaction mixture was stirred for 20 min at -78 °C. The reaction mixture was removed from the cooling bath and stirred at room temperature for 1 h. Afterwards, the reaction mixture was diluted with water and extracted with Et₂O (3 x 10 mL). The combined organic phases were washed with brine and dried over MgSO₄.
The solvent was removed in vacuo and the crude material purified by flash chromatography (pentane/Et₂O = 15:1) to afford double homologation product 4 (58.6 mg, 63%) as a white solid, m.p. = 90-92 °C.

2,2'-(2-Methyl-2-(naphthalen-2-yl)pentane-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4):

1H NMR (300 MHz, CDCl₃) δ 7.82 – 7.69 (m, 4H), 7.54 (dd, J = 8.6, 1.9 Hz, 1H), 7.45 – 7.35 (m, 2H), 1.91 – 1.68 (m, 2H), 1.54 (s, 3H), 1.45 – 1.38 (m, 2H), 1.27 – 1.19 (m, 16H), 1.04 – 1.01 (m, 10H), 0.68 (t, J = 7.7 Hz, 2H). 13C NMR (75 MHz, CDCl₃) δ 147.3, 133.3, 131.6, 127.9, 127.2, 125.4, 125.3, 124.8, 124.2, 82.7, 82.6, 48.3, 39.6, 26.7, 24.8, 24.7, 24.6, 19.1 ppm, carbons attached to borons not observed. 11B NMR (96 MHz, CDCl₃) δ 34.1 ppm. HRMS (ESI): Exact mass calculated for C₂₉H₄₂B₂NaO₄⁺ ([M+Na]⁺): 487.3161, mass found: 487.3162. FTIR (neat): ν (cm⁻¹) 2977, 2930, 1468, 1379, 1371, 1356, 1321, 1273, 1145, 968, 849, 815, 747.

The title compound was prepared according to a literature procedure[12].

To a solution of 3r (87.2 mg, 0.2 mmol) in tetrahydrofuran (3 mL) at 0 °C was added aqueous sodium hydroxide solution (3 mL, 9 mmol, 3 M). Aqueous hydrogen peroxide solution (1.5 mL, 30 % w/w) was added dropwise. The mixture was stirred at room temperature for 4 hours. Upon the completion of the reaction as determined by TLC, the mixture was cooled to 0 °C and saturated aqueous sodium thiosulfate solution (6 mL) was added dropwise. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The product was purified by flash column chromatography on silica gel with n-pentane/ethyl acetate (5:1 to 2:1) as eluent to give the corresponding product 5 (38.9 mg, 90%) as a colorless oil.
3-(Naphthalen-2-yl)butane-1,3-diol (5):

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 1.2$ Hz, 1H), 7.88 – 7.79 (m, 3H), 7.52 – 7.43 (m, 3H), 3.80 – 3.74 (m, 1H), 3.61 – 3.52 (m, 1H), 3.06 (br s, 2H), 2.25 – 2.05 (m, 2H), 1.65 (s, 3H). $^1$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.9, 133.2, 132.2, 128.1, 127.9, 127.4, 126.1, 125.7, 123.4, 123.3, 76.0, 60.4, 43.8, 31.0 ppm. HRMS (ESI): Exact mass calculated for C$_{14}$H$_{16}$NaO$_2$ ($[M+Na]^+$): 239.1043, mass found: 239.1041. FTIR (neat): $\nu$ (cm$^{-1}$) 3345, 3053, 2970, 2930, 1432, 1375, 1275, 1099, 1049, 859, 819, 748.

The title compound was prepared according to a literature procedure$^{[13]}$. 1,3-Bis(boronic ester) 3r (87.2 mg, 0.2 mmol) and tetra-$n$-butylammonium fluoride trihydrate (189 mg, 0.6 mmol) were stirred in toluene at 90 °C for 4 h. Afterwards the mixture was filtered through a short silica column, concentrated in vacuo and the residue subjected to flash chromatography to afford primary boronic ester 6 (33.7 mg, 54%) as a white solid.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)butyl)-1,3,2-dioxaborolane (6):

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.81 – 7.75 (m, 3H), 7.61 (s, 1H), 7.48 – 7.32 (m, 3H), 2.81 (h, $J = 7.0$ Hz, 1H), 1.85 – 1.71 (m, 2H), 1.34 (d, $J = 7.0$ Hz, 3H), 1.22 (s, 12H), 0.81 – 0.65 (m, 2H). $^1$C NMR (75 MHz, CDCl$_3$) $\delta$ 145.0, 133.6, 132.2, 127.7, 127.5, 127.5, 126.0, 125.6, 125.3, 124.9, 82.9, 42.3, 32.6, 24.8, 21.6 ppm. $^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ 34.7 ppm. FTIR (neat): $\nu$ (cm$^{-1}$) 2977, 2923, 1371, 1316, 1145, 967, 849, 817, 746. The spectroscopic data are in accordance to those reported in the literature$^{[14]}$. 

---

523
6. References

[1] A. Ganić, A. Pfaltz, Chem. Eur. J. 2012, 18, 6724.
[2] J. R. Vyvyan, J. A. Dell, T. J. Ligon, K. K. Motanic, H. S. Wall, Synthesis 2010, 21, 3637.
[3] M. Silvi, C. Sandford, V. K. Aggarwal, J. Am. Chem. Soc. 2017, 139, 5736.
[4] J. L.-Y. Chen, H. K. Scott, M. J. Hesse, C. L. Willis, V. K. Aggarwal, J. Am. Chem. Soc. 2013, 135, 5316.
[5] R. J. Armstrong, C. Sandford, C. García-Ruiz, V. K. Aggarwal, Chem. Commun. 2017, 53, 4922.
[6] V. Rauniyar, H. Zhai, D. G. Hall, Synth. Commun. 2008, 38, 3984.
[7] J. A. Myhill, L. Zhang, G. J. Lovinger, J. P. Morken, Angew. Chem. Int. Ed. 2018, 57, 12799; Angew. Chem. 2018, 130, 12981.
[8] a) T. Miura, J. Nakahashi, M. Murakami, Angew. Chem. Int. Ed. 2017, 56, 6989; Angew. Chem. 2017, 129, 7093; b) Z.-Q. Zhang, C.-T. Yang, L.-J. Liang, B. Xiao, X. Lu, J.-H. Liu, Y.-Y. Sun, T. B. Marder, Y. Fu, Org. Lett. 2014, 16, 6342.
[9] H. Li, X. Shangguan, Z. Zhang, S. Huang, Y. Zhang, J. Wang, Org. Lett. 2014, 16, 448.
[10] Z.-J. Yao, S. Hong, W. Zhang, M. Liu, W. Deng, Tetrahedron Lett. 2016, 57, 910.
[11] D. J. Blair, D. Tanini, J. M. Bateman, H. K. Scott, E. L. Myers, V. K. Aggarwal. Chem. Sci. 2017, 8, 2898.
[12] C. Gerleve, M. Kischkewitz, A. Studer, Angew. Chem. Int. Ed. 2018, 57, 2441; Angew. Chem. 2018, 130, 2466.
[13] S. Nave, R. P. Sonawane, T. G. Elford, V. K. Aggarwal, J. Am. Chem. Soc. 2010, 132, 17096.
[14] D. Wang, X.-S. Xue, K. N. Houk, Z. Shi, Angew. Chem. Int. Ed. 2018, 57, 16861; Angew. Chem. 2018, 130, 17103.
7. NMR spectra
