Regiocontrolled Allylic Functionalization of Internal Alkene via Selenium-\(\pi\)-Acid Catalysis Guided by Boron Substitution

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1. General information

Unless otherwise noted, all commercially available materials were used without further purification. Anhydrous CH$_3$CN, DMF and DMSO were purchased from Acros Organics and stored under argon.

NMR–spectra were recorded on Bruker AvanceIII-400M and Ascend$^{\text{TM}}$ 500M in solvents as indicate. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (δ = 0). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (Acetone-d6:  δ$_H$ = 2.05 ppm, δ$_C$ = 29.84 ppm). The following abbreviations were used to describe peak splitting patterns: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). Coupling constants (J) were reported in hertz unit (Hz).

High-resolution mass spectra (HRMS) were recorded on a Bruker VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV$_{254}$ plates. Visualization was accomplished by UV light (254 nm), or KMnO$_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh).

No attempts were made to optimize yields for substrate synthesis.
2. General procedure for preparation of the starting materials.

The allylic boronic esters were synthesized from allylic alcohols which were commercially available or reported before.\(^1\) The allyl MIDA boronates were prepared according to the following procedure.\(^2\)

**General procedure A:**

An oven-dried round bottom flask was charged with di-μ-chlorobis[2-[(dimethylamino)methyl]phenyl-C, N]dipalladium (II) (0.025 equiv), bis(pinacolato)diboron (1.5 equiv) and TsOH·H₂O (0.05 equiv). After being sealed with a septum, the flask was connected to an argon-vacuum line and was evacuated and backfilled with argon (x 3). DMSO (10 mL), MeOH (10 mL) and the allylic alcohol (10 mmol, 1 equiv) were added in turn by syringe under an argon atmosphere. The resulting reaction mixture was stirred vigorously at 50 ºC overnight then cooled to r.t. and H₂O was added. Ethyl acetate was then added and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried (MgSO₄) and concentrated in vacuo. The crude product was purified by flash chromatography. Then anhydrous DMSO (5 mL) was added to dissolve the product which was then added via syringe to a suspension of N-methyliminodiacetic acid (MIDA, 6.2 equiv) and CH(OMe)₃ (4.0 equiv) in DMSO (5 mL). The resulting mixture was stirred at 100 ºC until the allylic boronic esters was used up by GC-MS monitoring. After cooling to r.t., the reaction mixture was diluted with ethyl acetate (20 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

**General procedure B:**

An oven-dried round bottom flask was charged with bis(1,5-cyclooctadiene)nickel(0) (0.25 mmol), tricyclohexylphosphine (0.25 mmol), and toluene (20 mL) in the glovebox. The vial was capped and stirred for two minutes, then (E)-ethyl hepta-4,6-dienoate (10 mmol) was added, followed by pinacolborane...
(10.5 mmol). The vial was capped with a teflon cap, sealed with electrical tape, removed from the glovebox, and allowed to stir at rt for 3 h. The reaction was concentrated in vacuo, and the crude reaction mixture was purified on silica gel. Then anhydrous DMSO (5 mL) was added to dissolve the product which was then added via syringe to a suspension of N-methyliminodiacetic acid (MIDA, 6.2 equiv) and CH(OMe)3 (4.0 equiv) in DMSO (5 mL). The resulting mixture was stirred at 100 °C until the allylic boronic esters was used up by GC-MS monitoring. After cooling to r.t., the reaction mixture was diluted with ethyl acetate (20 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried over anhydrous MgSO4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

\((E)-2-(\text{hex}-2-\text{en}-1-\text{yl})-6-\text{methyl}-1,3,6,2-\text{dioxazaborocane}-4,8-\text{dione (1a)}\)

Following the general procedure A, the product 1a was obtained in 84 % yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F = 0.30\) (PE/EA = 1:3).
\(^1\)H NMR (400 MHz, Acetone-d6) \(\delta = 5.51-5.37\) (m, 2H), 4.18 (d, \(J = 16.8\) Hz, 2H), 3.94 (d, \(J = 16.9\) Hz, 2H), 3.12 (s, 3H), 1.94 (q, \(J = 6.9\) Hz, 2H), 1.56 (d, \(J = 6.8\) Hz, 2H), 1.34 (sext, \(J = 7.4\) Hz, 2H), 0.87 (t, \(J = 7.4\) Hz, 3H). \(^{13}\)C NMR (101 MHz, DMSO-d6) \(\delta = 168.9, 129.9, 127.0, 61.8, 45.6, 34.5, 22.4, 13.6\). \(^{11}\)B NMR (128 MHz, DMSO-d6) \(\delta = 12.0\).

HRMS: calculated for C_{11}H_{18}BNO_{4}Na [M+Na]^{+}, 262.1223; Found, 262.1212.

\((E)-6-\text{methyl}-2-(\text{tridec}-2-\text{en}-1-\text{yl})-1,3,6,2-\text{dioxazaborocane}-4,8-\text{dione (1c)}\)

Following the general procedure B, the product 1c was obtained in 60% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F = 0.31\) (PE/EA = 1:4);
\(^1\)H NMR (500 MHz, Acetonitrile-d3) \(\delta = 5.40\) (d, \(J = 4.9\) Hz, 2H), 3.92 (d, \(J = 16.9\) Hz, 2H), 3.72 (d, \(J = 17.0\) Hz, 2H), 2.87 (s, 3H), 1.98-1.94 (m, 1H), 1.50 (d, \(J = 4.8\) Hz, 2H), 1.33-1.27 (m, 17H), 0.88 (t, \(J = 6.7\) Hz, 3H). \(^{11}\)B NMR (160 MHz, Acetonitrile-d3) \(\delta = 12.3\).

\(^{13}\)C NMR (125 MHz, Acetonitrile-d3) \(\delta = 169.0, 132.2, 127.3, 63.0, 46.5, 33.5, 32.6, 30.5, 30.4(2C), 30.2, 30.1, 30.0, 23.4, 14.4).  

HRMS: calculated for C_{18}H_{32}BNO_{4}Na [M+Na]^{+}, 360.2320; Found 360.2313.

\((E)-6-\text{methyl}-2-(6-\text{phenylhex}-2-\text{en}-1-\text{yl})-1,3,6,2-\text{dioxazaborocane}-4,8-\text{dione (1e)}\)
Following the general procedure B, the product 1e was obtained in 37% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.29 \) (PE/EA = 1:4);

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta \) 7.26 (t, \( J = 7.4 \) Hz, 2H), 7.22-7.11 (m, 3H), 5.68-5.00 (m, 2H), 4.14 (d, \( J = 17.1 \) Hz, 2H), 3.78 (d, \( J = 17.0 \) Hz, 2H), 2.77 (s, 3H), 2.61 (t, \( J = 7.6 \) Hz, 2H), 2.34-2.18 (m, 2H), 1.41 (d, \( J = 6.2 \) Hz, 2H). \(^{11}\)B NMR (128 MHz, DMSO-\(d_6\)) \( \delta \) 0.29 (PE/EA = 1:4); 

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \( \delta \) 168.8, 141.8, 129.5, 128.4, 128.2, 127.5, 125.7, 61.7, 45.5, 35.4, 34.1.

HRMS: calculated for C\(_{16}\)H\(_{20}\)BNO\(_4\)Na \([M+Na]^+\), 324.1381; Found, 324.1369.

ethyl \((E)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-3-en-1-yl)benzoate \( (1f)\)

Following the general procedure B, the product 1f was obtained in 54% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.15 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta \) 7.86 (d, \( J = 8.3 \) Hz, 2H), 7.35 (d, \( J = 8.3 \) Hz, 2H), 5.44-5.28 (m, 2H), 4.30 (q, \( J = 7.1 \) Hz, 2H), 4.16 (d, \( J = 17.0 \) Hz, 2H), 3.83 (d, \( J = 17.0 \) Hz, 2H), 2.79 (s, 3H), 2.69 (t, \( J = 7.6 \) Hz, 2H), 2.28 (q, \( J = 7.1 \) Hz, 2H), 1.41 (d, \( J = 6.9 \) Hz, 2H), 1.31 (t, \( J = 7.1 \) Hz, 3H). \(^{11}\)B NMR (128 MHz, DMSO-\(d_6\)) \( \delta \) 11.2.

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \( \delta \) 168.8, 165.7, 147.7, 129.1, 129.0, 128.7, 127.9, 127.5, 61.7, 60.5, 45.5, 35.3, 14.2.

HRMS: calculated for C\(_{19}\)H\(_{24}\)BNO\(_6\)Na \([M+Na]^+\), 396.1592; Found, 396.1580.

\((E)-6-methyl-2-(5-phenoxypent-2-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione \( (1g)\)

Following the general procedure B, the product 1g was obtained in 16% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.23 \) (PE/EA = 1:4).

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \( \delta \) 7.29-7.25 (m, 2H), 6.93-6.90 (m, 3H), 5.53 (dt, \( J = 15.1, 7.3 \) Hz, 1H), 5.40 (dt, \( J = 15.4, 6.7 \) Hz, 1H), 4.19 (d, \( J = 17.0 \) Hz, 2H), 4.05-3.81 (m, 4H), 2.86 (s, 3H), 2.39 (q, \( J = 6.7 \) Hz, 2H), 1.48 (d, \( J = 7.4 \) Hz, 2H). \(^{11}\)B NMR (160 MHz, Acetonitrile-\(d_3\)) \( \delta \) 12.2. \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \( \delta \) 169.0, 159.9, 130.5, 130.4, 127.9, 121.5, 115.4, 68.5, 63.0, 46.5, 33.5.

HRMS: calculated for C\(_{16}\)H\(_{20}\)BNO\(_5\)Na \([M+Na]^+\), 340.1330; Found, 340.1321.
Following the general procedure B, the product 1h was obtained in 34% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_f = 0.29$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetonitrile-$d_3$) $\delta$ 7.44-7.25 (m, 5H), 5.49 (dt, $J = 14.8$, 7.3 Hz, 1H), 5.41 (dt, $J = 14.9$, 6.6 Hz, 1H), 4.46 (s, 2H), 3.81 (d, $J = 16.9$ Hz, 2H), 3.69 (d, $J = 16.9$ Hz, 2H), 3.47 (t, $J = 6.3$ Hz, 2H), 2.83 (s, 3H). 11B NMR (128 MHz, Acetonitrile-$d_3$) $\delta$ 12.2. 13C NMR (101 MHz, Acetonitrile-$d_3$) $\delta$ 169.0, 139.9, 129.5, 129.3, 128.8, 128.4, 73.3, 70.9, 62.9, 46.3, 34.1.

HRMS: calculated for C$_{17}$H$_{22}$BNO$_5$Na $[M+Na]^+$, 354.1486; Found, 354.1479.

Following the general procedure B, the product 1i was obtained in 37% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_f = 0.28$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 5.73-4.98 (m, 2H), 4.39 (t, $J = 4.9$ Hz, 1H), 4.18 (d, $J = 17.1$ Hz, 2H), 3.91 (d, $J = 17.0$ Hz, 2H), 3.50 (d, $J = 10.9$ Hz, 2H), 3.36 (d, $J = 10.7$ Hz, 2H), 2.85 (s, 3H), 1.93 (q, $J = 6.9$ Hz, 2H), 1.51-1.34 (m, 6H), 1.07 (s, 3H), 0.66 (s, 3H). 11B NMR (160 MHz, Acetone-$d_6$) $\delta$ 11.2. 13C NMR (125 MHz, Acetone-$d_6$) $\delta$ 168.8, 129.8, 127.1, 101.1, 76.0, 61.8, 45.6, 33.8, 32.1, 29.7, 23.6, 22.8, 21.4.

HRMS: calculated for C$_{17}$H$_{28}$BNO$_6$Na $[M+Na]^+$, 376.1905; Found, 376.1890.

Following the general procedure B, the product 1j was obtained in 65% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_f = 0.14$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.87-7.81 (m, 4H), 5.40 (dt, $J = 14.9$, 7.4 Hz, 1H), 5.28 (dt, $J = 15.3$, 6.8 Hz, 1H), 4.15 (d, $J = 17.0$ Hz, 1H), 3.87 (d, $J = 17.0$ Hz, 2H), 3.57 (t, $J = 7.1$ Hz, 2H), 2.80 (s, 3H), 2.27 (q, $J = 7.0$ Hz, 2H), 1.39 (d, $J = 7.3$ Hz, 2H). 13C NMR (125 MHz, DMSO-$d_6$) $\delta$ 168.8, 167.8, 134.4, 131.5, 129.8, 128.6, 126.8, 123.0, 61.7, 45.6, 37.5, 31.4.

HRMS: calculated for C$_{18}$H$_{19}$BN$_2$O$_6$K $[M+K]^+$, 409.1082; Found, 409.1055.
tert-butyl (E)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-3-en-1-yl)piperidine-1-carboxylate (1k)

Following the general procedure A, the product 1k was obtained in 15% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.11$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetonitrile-d$_3$) $\delta$ 5.50-5.32 (m, 2H), 3.99 (d, $J = 13.4$ Hz, 2H), 3.92 (d, $J = 16.9$ Hz, 2H), 3.72 (d, $J = 16.9$ Hz, 2H), 2.87 (s, 3H), 2.66 (s, 2H), 2.04-1.97 (m, 2H), 1.64 (d, $J = 13.2$ Hz, 2H), 1.51 (d, $J = 6.1$ Hz, 2H), 1.41 (s, 10H), 1.29-1.23 (m, 2H), 0.98 (qd, $J = 12.4$, 4.3 Hz, 2H).

$^{11}$B NMR (160 MHz, Acetonitrile-d$_3$) $\delta$ 12.3.

$^{13}$C NMR (125 MHz, Acetone-d$_6$) $\delta$ 169.0, 155.5, 132.0, 127.5, 79.5, 63.0, 46.6, 37.2, 36.1, 32.9, 30.5, 28.6.

HRMS: calculated for C$_{20}$H$_{33}$BN$_2$O$_6$Na [M+Na]$^+$, 431.2328; Found, 431.2329.

(E)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-en-1-yl benzoate (1l)

Following the general procedure B, the product 1l was obtained in 30% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.22$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 7.51 (d, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.08 (t, $J = 7.6$ Hz, 2H), 4.9-4.84 (m, 2H), 3.81 (t, $J = 6.5$ Hz, 2H), 3.74 (d, $J = 17.0$ Hz, 2H), 3.46 (d, $J = 17.0$ Hz, 2H), 2.40 (s, 3H), 1.56 (q, $J = 7.0$ Hz, 2H), 1.24 (p, $J = 6.9$ Hz, 2H), 0.98 (q, $J = 5.9$, 4.6 Hz, 4H).

$^{11}$B NMR (128 MHz, DMSO-d$_6$) $\delta$ 12.3. $^{13}$C NMR (125 MHz, Acetone-d$_6$) $\delta$ 173.7, 168.7, 129.3, 127.8, 62.9, 60.4, 46.3, 34.1, 27.2, 25.6, 14.6.

HRMS: calculated for C$_{19}$H$_{25}$BN$_2$O$_6$ [M+H]$^+$, 374.1773; Found, 374.1789.

(E)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-en-1-yl pivalate (1m)

Following the general procedure A, the product 1m was obtained in 46% yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.23$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 5.47-5.18 (m, 2H), 4.18 (d, $J = 17.0$ Hz, 2H), 3.99 (t, $J = 6.5$ Hz, 2H), 3.90 (d, $J = 17.0$ Hz, 2H), 2.85 (s, 3H), 1.96 (q, $J = 7.0$ Hz, 3H), 1.60-1.50 (m, 3H), 1.43 (d, $J = 7.0$ Hz, 3H), 1.37-1.29 (m, 3H), 1.13 (s, 9H). $^{11}$B NMR (128 MHz, DMSO-d$_6$) $\delta$ 11.9. $^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 177.4, 168.8, 129.7, 127.3, 63.7, 61.8, 45.6, 38.2, 31.8, 27.6, 26.9, 25.5.

HRMS: calculated for C$_{17}$H$_{26}$BN$_2$O$_6$Na [M+Na]$^+$, 376.1905; Found, 376.1893.
Following the general procedure A, the product 1n was obtained in 32% yield as a white solid after column chromatography (eluens = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.26$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 5.43-5.35 (m, 1H), 5.32-5.27 (m, 1H), 4.18 (d, $J = 17.0$ Hz, 2H), 3.91 (d, $J = 17.0$ Hz, 2H), 3.62 (t, $J = 6.6$ Hz, 2H), 2.85 (s, 3H), 1.96 (q, $J = 7.0$ Hz, 2H), 1.76-1.61 (m, 2H), 1.46-1.38 (m, 4H).

$^{11}$B NMR (128 MHz, DMSO-$d_6$) $\delta$ 11.6. $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 168.8, 129.5, 127.4, 61.8, 45.6, 45.3, 31.6, 31.4, 26.4.

HRMS: calculated for C$_{12}$H$_{19}$BClNO$_4$Na [M+Na]$^+$, 310.0990; Found, 310.0996.

edethyl (Z)-7-(6-methyl-1,3,6,2-dioxazaborocan-2-yl)hept-5-enoate (1o)

Following the general procedure C, the product 1o was obtained in 18% yield as a white solid after column chromatography (eluens = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.13$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetone-$d_6$) $\delta$ 5.55-5.49 (m, 1H), 5.35-5.29 (m, 1H), 4.19 (d, $J = 16.9$ Hz, 2H), 4.08 (q, $J = 7.1$ Hz, 2H), 4.00 (d, $J = 16.8$ Hz, 2H), 3.12 (s, 3H), 2.30 (t, $J = 7.4$ Hz, 2H), 2.15-2.09 (m, 2H), 2.05 (p, $J = 2.2$ Hz, 2H), 1.65 (p, $J = 7.5$ Hz, 2H), 1.59 (d, $J = 8.0$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{11}$B NMR (128 MHz, DMSO-$d_6$) $\delta$ 12.0. $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) $\delta$ 174.3, 169.0, 129.7, 127.5, 62.9, 60.8, 46.6, 34.3, 27.2, 25.6, 14.6.

HRMS: calculated for C$_{14}$H$_{22}$BNO$_6$K [M+K]$^+$, 350.1174; Found, 350.1168.

$^{(E)2-(hept-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1p)}$

Following the general procedure A, the product 1p was obtained in 65% yield as a white solid after column chromatography (eluens = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.27$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetone-$d_6$) $\delta$ 5.69-5.49 (m, 2H), 4.17 (d, $J = 16.8$ Hz, 2H), 3.93 (d, $J = 16.9$ Hz, 2H), 3.10 (s, 3H), 1.55 (d, $J = 6.7$ Hz, 2H), 1.97 (q, $J = 6.6$ Hz, 2H), 1.41-1.24 (m, $J = 4.1, 3.7$ Hz, 4H), 1.13-0.77 (m, 3H). $^{11}$B NMR (128 MHz, Acetonitrile-$d_3$) $\delta$ 12.3. $^{13}$C NMR (125 MHz, Acetonitrile-$d_3$) $\delta$ 169.1, 132.2, 127.3, 63.0, 46.5, 33.2, 32.7, 23.0, 14.2.

HRMS: calculated for C$_{12}$H$_{20}$BNO$_4$Na [M+Na]$^+$, 276.1378; Found, 276.1379.

Synthesis of the deuterium allyl boronate 1p-D$_2$:
A solution of vinylboronic acid pinacol ester and \( \text{d}_2 \)-dibromomethane (1.5 equiv.) in THF was cooled to \(-78^\circ \text{C}\). To this was added 2.5 M \( \text{nBuLi} \) in hexane (1.6 equiv.) dropwise from a syringe, and the reaction mixture was stirred at \(-78^\circ \text{C}\) for 0.5 h. It was then rapidly brought to room temperature and refluxed at 65 °C for 1.5 h. Then cooled to r.t. and \( \text{H}_2\text{O} \) was added. Ethyl acetate was then added and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried (\( \text{MgSO}_4 \)) and concentrated in vacuo. The crude product was purified by flash chromatography. Then anhydrous DMSO was added to dissolve the product which was then added via syringe to a suspension of \( \text{N-methyliminodiacetic acid} \) (MIDA, 6.2 equiv) and \( \text{CH(OMe)}_3 \) (4.0 equiv) in DMSO. The resulting mixture was stirred at 100 °C until the allylic boronic esters was used up by GC-MS monitoring. After cooling to r.t., the reaction mixture was diluted with ethyl acetate and water. The organic phase was separated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous \( \text{MgSO}_4 \) and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

\((E)-2-\left(\text{hept-2-en-1-yl}-1,1-\text{d}_2\right)-6\text{-methyl-1,3,6,2-dioxazaborocane-4,8-dione}\)

\( ^1\text{H NMR (400 MHz, Acetonitrile-}d_3\text{)} \delta 5.44-5.36 \text{ (m, 2H), 3.93 (d, } J = 16.9 \text{ Hz, 2H), 3.72 (d, } J = 16.9 \text{ Hz, 2H), 2.88 (s, 3H), 2.02-1.94 \text{ (m, 2H), 1.42-1.23 \text{ (m, 4H), 0.88 (t, } J = 6.7 \text{ Hz, 3H).} \text{ }} \)

\( ^{13}\text{C NMR (101 MHz, Acetonitrile-}d_3\text{)} \delta 169.1, 132.2, 127.3, 63.0, 46.5, 33.2, 32.7, 23.0, 14.2.\)

HRMS: calculated for \( \text{C}_{12}\text{H}_{19}\text{D}_2\text{BNO}_4\text{Na} \) [\( \text{M+Na}^+ \)], 278.1503; Found, 278.1500.
3. General procedure for the chlorination reaction

**General procedure D:**

The allyl MIDA boronates 1 (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), N-chlorosuccinimide (NCS, 0.22 mmol, 1.1 equiv) and 4 Å MS (20 mg) were added in 3 mL CH₃CN producing the pale yellow solution. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the p-iodobenzole (0.2 mmol) was added and the NMR yield was determined by ¹H NMR. After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product as a white solid.

**General procedure E:**

The allyl MIDA boronates 1 (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol) and 4 Å MS (20 mg) were added in 1 mL CH₃CN. A solution of N-chlorosuccinimide (0.22 mmol, in 2 mL CH₃CN) was prepared then drawn into a 5 mL syringe equipped with a teflon needle. The solution of NCS was added via syringe pump at the rate of 0.4 mL/h. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the p-iodobenzole (0.2 mmol) was added and the NMR yield was determined by ¹H NMR. After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product as a white solid.

(E)-2-(3-chlorohex-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2a)

Following the general procedure D, the product 2a was obtained in 84% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). \( R_F = 0.25 \) (PE/EA = 1:4).

¹H NMR (400 MHz, Acetone-\(_d_6\)) \( \delta 6.12 \) (dd, \( J = 17.4, 7.9 \) Hz, 0H), 5.77 (dd, \( J = 17.5, 1.0 \) Hz, 0H), 4.50 (q, \( J = 7.1 \) Hz, 0H), 4.24 (d, \( J = 16.9 \) Hz, 1H), 4.05 (d, \( J = 17.0 \) Hz, 1H), 3.02 (s, 1H), 1.80 (dd, \( J = 8.4, 6.6, 1.8 \) Hz, 1H), 1.56 – 1.33 (m, 1H), 0.92 (t, \( J = 7.4 \) Hz, 1H). ¹¹B NMR (128 MHz, Acetone-\(_d_6\)) \( \delta 10.4 \). ¹³C NMR (101 MHz, Acetone-\(_d_6\)) \( \delta 168.9, 144.9, 65.1, 62.4, 47.5, 41.0, 20.4, 13.7 \).

HRMS: calculated for C\(_{11}H\(_{17}\)BClNO\(_4\)Na \[M+Na\]^+ 296.0833; Found, 296.0823.

(E)-2-(3-chlorobut-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2b)

Following the general procedure E, the product 2b was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). \( R_F = 0.26 \) (PE/EA = 1:4).
$^1$H NMR (400 MHz, Acetone-$d_6$) δ 6.17 (dd, $J = 17.5, 7.1$ Hz, 1H), 5.77 (d, $J = 17.4$ Hz, 1H), 4.66 (p, $J = 6.7$ Hz, 1H), 4.24 (d, $J = 17.0$ Hz, 2H), 4.05 (d, $J = 17.0$ Hz, 2H), 3.01 (s, 3H), 1.58 (d, $J = 6.6$ Hz, 3H). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 10.4. $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 168.9, 145.9, 62.4, 60.0, 47.5, 25.1.

HRMS: calculated for C$_9$H$_{13}$BClNO$_4$Na [M+Na]$^+$, 268.0520; Found, 268.0525.

$(E)$-2-(3-chlorotridec-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2c)

Following the general procedure D, the product 2c was obtained in 84% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.30$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 6.12 (dd, $J = 17.4, 7.9$ Hz, 1H), 5.77 (dd, $J = 17.5, 1.0$ Hz, 1H), 4.49 (q, $J = 6.8$ Hz, 1H), 4.25 (d, $J = 17.0$ Hz, 2H), 4.05 (dd, $J = 16.9, 1.7$ Hz, 2H), 3.03 (s, 3H), 1.86–1.79 (m, 2H), 1.31–1.27 (m, 16H), 0.88 (t, $J = 6.98$ Hz, 3H). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 10.3. $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) δ 169.2, 169.2, 145.5, 65.5, 62.5, 47.8, 38.8, 32.6, 30.3, 30.2, 30.0, 29.7, 27.3, 23.4, 14.4.

HRMS: calculated for C$_{17}$H$_{30}$BClNO$_4$ [M+H]$^+$, 358.1954; Found, 358.1961.

$(E)$-2-(3-chloro-4-phenylbut-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2d)

Following the general procedure E, the product 2d was obtained in 51% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.27$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.35–7.27 (m, 4H), 7.25–7.19 (m, 1H), 6.12 (dd, $J = 17.4, 8.2$ Hz, 1H), 5.64 (dd, $J = 17.4, 0.9$ Hz, 1H), 4.74 (q, $J = 7.3$ Hz, 1H), 4.18 (dd, $J = 16.9, 1.5$ Hz, 2H), 3.96 (d, $J = 17.0$ Hz, 1H), 3.83 (d, $J = 16.9$ Hz, 1H), 3.17 (dd, $J = 7.3, 3.6$ Hz, 1H), 2.68 (s, 3H). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 10.1. $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) δ 169.0, 168.7, 144.1, 138.8, 130.4, 129.2, 127.5, 65.3, 62.2, 47.2, 45.2.

HRMS: calculated for C$_{17}$H$_{16}$BClNO$_4$Na [M+Na]$^+$, 344.0834; Found, 344.0819.

$(E)$-2-(3-chloro-5-phenylpent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2e)

Following the general procedure E, the product 2e was obtained in 71% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_F = 0.30$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.39–7.21 (m, 4H), 7.21–7.11 (m, 1H), 6.18 (dd, $J = 17.4, 7.7$ Hz, 1H), 5.79 (dd, $J = 17.5, 1.0$ Hz, 1H), 4.48 (q, $J = 7.2$ Hz, 1H), 4.24 (dd, $J = 17.0, 1.0$ Hz, 2H), 4.06 (d, $J = 16.9$ Hz, 2H), 3.03 (s, 3H), 2.87–2.66 (m, 2H).
2.23 – 2.08 (m, 2H). \(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 10.4. \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \(\delta\) 168.9, 168.9, 144.5, 141.9, 129.3, 129.3, 126.8, 64.6, 62.4, 47.6, 40.7, 33.3.

HRMS: calculated for C\(_{16}\)H\(_{19}\)BClNO\(_4\)Na [M+Na]\(^+\), 358.0991; Found, 358.0978.

**ethyl \((E)-4-(3-chloro-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-4-en-1-yl)benzate (2f)**

Following the general procedure \(E\), the product 2f was obtained in 66% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F\) = 0.16 (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 7.94 (d, \(J\) = 8.3 Hz, 2H), 7.39 (d, \(J\) = 8.1 Hz, 2H), 6.19 (dd, \(J\) = 17.4, 7.7 Hz, 1H), 5.81 (dd, \(J\) = 17.5, 0.9 Hz, 1H), 4.49 (q, \(J\) = 7.5 Hz, 1H), 4.33 (q, \(J\) = 7.1 Hz, 2H), 4.24 (d, \(J\) = 16.9 Hz, 2H), 4.06 (d, \(J\) = 16.9 Hz, 2H), 3.03 (s, 3H), 2.95 – 2.82 (m, 2H), 2.28 – 2.10 (m, 2H), 1.35 (t, \(J\) = 7.1 Hz, 3H).

\(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 10.2.

\(^{13}\)C NMR (101 MHz, Acetonitrile-\(d_3\)) \(\delta\) 168.9, 168.9, 144.5, 141.9, 129.3, 129.3, 126.8, 64.6, 62.4, 47.6, 40.7, 33.3.

HRMS: calculated for C\(_{18}\)H\(_{21}\)BClNO\(_6\)Na [M+Na]\(^+\), 430.1203; Found, 420.1213.

**\((E)-2-(3-chloro-5-phenoxypent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2g)**

Following the general procedure \(D\), the product 2g was obtained in 58% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F\) = 0.24 (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta\) 7.29 (dd, \(J\) = 8.6, 7.3 Hz, 2H), 6.99-6.90 (m, 3H), 6.18 (dd, \(J\) = 17.4, 7.9 Hz, 1H), 5.76 (d, \(J\) = 17.5 Hz, 1H), 4.76 (q, \(J\) = 7.8 Hz, 1H), 4.17-4.04 (m, 2H), 3.95 (d, \(J\) = 17.1 Hz, 2H), 3.77 (dd, \(J\) = 17.0, 6.4 Hz, 2H), 2.71 (s, 3H), 2.36-2.19 (m, 2H). \(^{11}\)B NMR (160 MHz, Acetonitrile-\(d_3\)) \(\delta\) 10.3. \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \(\delta\) 169.2, 169.2, 159.8, 144.7, 144.9, 130.4, 129.7, 129.5, 64.6, 62.6, 61.7, 47.9, 40.0, 33.3, 14.6.

HRMS: calculated for C\(_{18}\)H\(_{21}\)BCINO\(_5\)Na [M+Na]\(^+\), 430.1203; Found, 420.1213.

**\((E)-2-(5-(benzyloxy)-3-chloropent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2h)**

Following the general procedure \(E\), the product 2h was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F\) = 0.27 (PE/EA = 1:4).
$^1$H NMR (500 MHz, Acetonitrile-$d_3$) δ 7.35 (d, $J = 6.5$ Hz, 4H), 7.30 (dt, $J = 6.3$, 2.9 Hz, 1H), 6.11 (dd, $J = 17.4$, 7.9 Hz, 1H), 5.70 (d, $J = 17.5$ Hz, 1H), 4.65 (q, $J = 7.4$ Hz, 1H), 4.48 (s, 2H), 3.95 (dd, $J = 17.0$, 2.6 Hz, 3H), 3.77 (dd, $J = 17.3$, 11.1 Hz, 3H), 3.61 (dtd, $J = 11.0$, 5.4, 2.7 Hz, 1H), 3.57 - 3.52 (m, 1H), 2.72 (s, 3H), 2.14 - 2.10 (m, 1H), 2.07 - 2.02 (m, 1H). $^{11}$B NMR (160 MHz, Acetonitrile-$d_3$) δ 10.3. $^{13}$C NMR (125 MHz, Acetonitrile-$d_3$) δ 168.8, 168.8, 144.6, 139.4, 128.9, 128.2, 128.1, 73.1, 67.2, 62.1, 61.9, 47.4, 38.5.

HRMS: calculated for C$_{17}$H$_{21}$BClNO$_5$Na $[M+Na]^+$, 388.1097; Found, 388.1081.

$(E)$-2-(3-chloro-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione ($2i$)

Following the general procedure $E$, the product $2i$ was obtained in 79% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_f = 0.28$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetone-$d_6$) δ 6.11 (dd, $J = 17.4$, 7.9 Hz, 1H), 5.79 (d, $J = 17.4$ Hz, 1H), 4.50 (q, $J = 7.2$ Hz, 1H), 4.43 (t, $J = 4.5$ Hz, 1H), 4.24 (d, $J = 17.0$ Hz, 2H), 4.05 (dd, $J = 17.0$, 7.4 Hz, 2H), 3.54 (d, $J = 10.7$ Hz, 2H), 3.41 (d, $J = 10.7$ Hz, 2H), 3.02 (s, 3H), 1.85 (q, $J = 6.1$ Hz, 2H), 1.61 - 1.49 (m, 4H), 1.12 (s, 3H), 0.69 (s, 3H). $^{11}$B NMR (160 MHz, Acetone-$d_6$) δ 10.3. $^{13}$C NMR (125 MHz, Acetone-$d_6$) δ 168.9, 168.9, 144.8, 102.4, 77.4, 65.2, 62.4, 47.6, 38.8, 34.9, 30.6, 23.3, 21.9, 21.7.

HRMS: calculated for C$_{17}$H$_{27}$BClNO$_6$Na $[M+Na]^+$, 410.1515; Found, 410.1527.

$(E)$-2-(3-chloro-5-(1,3-dioxoisindolin-2-yl)pent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione ($2j$)

Following the general procedure $E$, the product $2j$ was obtained in 63% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). $R_f = 0.15$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.84 (d, $J = 1.4$ Hz, 4H), 6.18 (dd, $J = 17.4$, 7.5 Hz, 1H), 5.87 (dd, $J = 17.5$, 1.0 Hz, 1H), 4.65 (q, $J = 7.0$ Hz, 1H), 4.25 (dd, $J = 17.0$, 1.0 Hz, 2H), 4.07 (dd, $J = 16.9$, 2.1 Hz, 2H), 3.82 (td, $J = 7.0$, 2.5 Hz, 2H), 3.06 (s, 3H), 2.32 - 2.16 (m, 2H). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 10.3. $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 168.9, 168.9, 168.7, 143.9, 135.0, 133.5, 123.7, 62.4, 62.4, 62.3, 47.6, 37.4, 35.9.

HRMS: calculated for C$_{18}$H$_{19}$BClN$_2$O$_6$Na $[M+Na]^+$, 427.0842; Found, 427.0851.

tert-butyl $(E)$-4-(3-chloro-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-4-en-1-yl)piperidine-1-carboxylate ($2k$)
Following the general procedure D, the product 2k was obtained in 78% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.11 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \( \delta \) 6.13 (dd, \( J = 17.4, 7.9 \) Hz, 1H), 5.78 (dd, \( J = 17.4, 1.0 \) Hz, 1H), 4.49 (q, \( J = 6.8 \) Hz, 1H), 4.25 (d, \( J = 16.9 \) Hz, 2H), 4.05 (dd, \( J = 16.9, 1.8 \) Hz, 4H), 3.03 (s, 3H), 2.68 (bs, 2H), 1.93-1.81 (m, 2H), 1.67 (dd, \( J = 12.6 \) Hz, 2H), 1.42 (s, 12H), 1.09-0.97 (m, 2H).

\(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \( \delta \) 168.9, 155.0, 144.8, 79.1, 65.5, 62.4, 47.6, 36.4, 36.2, 34.1, 33.0, 32.9, 28.6.

HRMS: calculated for C\(_{20}\)H\(_{32}\)BClN\(_2\)O\(_6\)Na \([\text{M+Na}]^+\), 465.1938; Found, 465.1921.

\((E)-5\)-chloro-\((6\)-methyl-\(4,8\)-dioxo-\(1,3,6,2\)-dioxazaborocan-2-yl)hept-6-en-1-yl benzoate (2l)

Following the general procedure E, the product 2l was obtained in 79% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.23 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \( \delta \) 8.05-7.98 (m, 2H), 7.62 (t, \( J = 7.4 \) Hz, 1H), 7.50 (t, \( J = 7.7 \) Hz, 2H), 6.10 (dd, \( J = 17.5, 7.8 \) Hz, 1H), 5.71 (d, \( J = 17.5 \) Hz, 1H), 4.51 (q, \( J = 7.2 \) Hz, 1H), 4.30 (t, \( J = 6.4 \) Hz, 2H), 3.95 (d, \( J = 17.0 \) Hz, 2H), 3.78 (dd, \( J = 17.1, 6.2 \) Hz, 2H), 1.92-1.86 (m, 2H), 1.82-1.74 (m, 2H), 1.62-1.51 (m, 2H). \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \( \delta \) 169.2, 167.2, 145.3, 134.0, 131.5, 130.2, 129.6, 65.5, 65.2, 62.5, 47.8, 38.4, 28.8, 23.9.

HRMS: calculated for C\(_{19}\)H\(_{24}\)BClNO\(_6\) \([\text{M+H}]^+\), 408.1383; Found, 408.1390.

\((E)-5\)-chloro-\((6\)-methyl-\(4,8\)-dioxo-\(1,3,6,2\)-dioxazaborocan-2-yl)hept-6-en-1-yl pivalate (2m)

Following the general procedure E, the product 2m was obtained in 80% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.23 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \( \delta \) 6.13 (dd, \( J = 17.4, 7.8 \) Hz, 1H), 5.79 (dd, \( J = 17.4, 0.9 \) Hz, 1H), 4.52 (q, \( J = 7.1 \) Hz, 1H), 4.24 (d, \( J = 17.0 \) Hz, 2H), 4.14-3.90 (m, 4H), 3.02 (s, 3H), 1.92-1.84 (m, 2H), 1.74-1.62 (m, 2H), 1.60-1.44 (m, 0H), 1.17 (s, 9H). \(^{13}\)B NMR (128 MHz, Acetone-\(d_6\)) \( \delta \) 10.3. \(^{13}\)C NMR (101 MHz, Acetone-\(d_6\)) \( \delta \) 178.3, 168.9, 168.9, 144.7, 65.2, 64.5, 62.4, 47.6, 39.2, 38.5, 28.8, 27.5, 23.7.

HRMS: calculated for C\(_{17}\)H\(_{23}\)BCINO\(_6\)Na \([\text{M+Na}]^+\), 410.1515; Found, 410.1514.

\((E)-2-\((3,7\)-dichlorohept-1-en-1-yl)-6-methyl-\(1,3,6,2\)-dioxazaborocane-4,8-dione (2n)
Following the general procedure E, the product 2n was obtained in 79% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). Rf = 0.27 (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetone-<i>d</i>6) $\delta$ 6.13 (dd, $J$ = 17.5, 7.8 Hz, 1H), 5.80 (d, $J$ = 17.4 Hz, 1H), 4.52 (q, $J$ = 7.2 Hz, 1H), 4.25 (d, $J$ = 16.9 Hz, 2H), 4.05 (dd, $J$ = 16.9, 3.8 Hz, 2H), 3.63 (t, $J$ = 6.6 Hz, 2H), 3.03 (s, 3H), 1.91-1.78 (m, 4H), 1.67-1.53 (m, 2H).

$^{11}$B NMR (160 MHz, Acetone-<i>d</i>6) $\delta$ 10.4.

$^{13}$C NMR (125 MHz, Acetone-<i>d</i>6) $\delta$ 168.9, 168.9, 144.7, 65.0, 62.4, 47.6, 45.6, 38.2, 32.8, 24.7.

HRMS: calculated for C<sub>12</sub>H<sub>18</sub>BCl<sub>2</sub>NO<sub>4</sub>Na [M+Na]<sup>+</sup>, 344.0600; Found, 344.0608.

ethyl (E)-5-chloro-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-6-enoate (2o)

Following the general procedure E, the product 2o was obtained in 73% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). Rf = 0.14 (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetone-<i>d</i>6) $\delta$ 6.12 (dd, $J$ = 17.4, 7.8 Hz, 1H), 5.80 (dd, $J$ = 17.4, 1.0 Hz, 1H), 4.53 (q, $J$ = 6.8 Hz, 1H), 4.25 (d, $J$ = 16.9 Hz, 2H), 4.13-4.01 (m, 4H), 3.03 (s, 3H), 2.34 (t, $J$ = 7.3 Hz, 2H), 1.92-1.83 (m, 2H), 1.80-1.64 (m, 2H), 1.20 (t, $J$ = 7.2 Hz, 3H).

$^{11}$B NMR (128 MHz, Acetone-<i>d</i>6) $\delta$ 10.3.

$^{13}$C NMR (101 MHz, Acetone-<i>d</i>6) $\delta$ 173.3, 169.0, 168.9, 144.6, 64.8, 62.4, 60.6, 47.5, 38.1, 33.8, 22.7, 14.5.

HRMS: calculated for C<sub>14</sub>H<sub>21</sub>BClNO<sub>6</sub>Na [M+Na]<sup>+</sup>, 368.1045; Found, 368.1028.

(E)-2-(3-chlorohept-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2p)

$^1$H NMR (500 MHz, Acetonitrile-<i>d</i>3) $\delta$ 6.09 (dd, $J$ = 17.4, 7.9 Hz, 1H), 5.69 (dd, $J$ = 17.5, 0.9 Hz, 1H), 4.48 (q, $J$ = 7.2, 6.7 Hz, 1H), 3.97 (d, $J$ = 17.0 Hz, 2H), 3.80 (dd, $J$ = 17.1, 3.5 Hz, 2H), 2.77 (s, 3H), 1.85-1.80 (m, 2H), 1.48-1.24 (m, 4H), 0.90 (t, $J$ = 7.1 Hz, 3H). $^{11}$B NMR (160 MHz, Acetonitrile-<i>d</i>3) $\delta$ 10.2.

$^{13}$C NMR (101 MHz, Acetonitrile-<i>d</i>3) $\delta$ 169.3, 169.2, 145.5, 65.5, 62.6, 47.9, 38.6, 29.4, 22.8, 14.2.

HRMS: calculated for C<sub>14</sub>H<sub>19</sub>BCINO<sub>5</sub>Na [M+Na]<sup>+</sup>, 368.1045; Found, 368.1028.

(R)-5-chloro-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-6-enoate (2o)
4. General procedure for the imidation reaction

General procedure F:

Under an argon atmosphere the allyl MIDA boronates 1 (0.2 mmol, 1.0 equiv) and NFSI (0.3 mmol, 1.5 equiv) diphenyl diselenide (0.02 mmol, 10% mmol) and 4 Å molecular sieves (powder) were added to a 15 mL Schlenk tube. The dry DCE (2 mL) was added to the reaction mixture. After stirring at 35 °C for 12 h the solvent was evaporated. The p-iodobenzole (0.2 mmol) was added and the NMR yield was determined by 1H NMR. After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product as a white solid.

\((E)-N-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3a)\)

Following the general procedure F, the product 3a was obtained in 68% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). \(R_F = 0.27\) (PE/EA = 1:4).

\(^{1}\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.90 (d, \(J = 7.9\) Hz, 4H), 7.82-7.76 (m, 2H), 7.66 (t, \(J = 7.9\) Hz, 4H), 6.15 (dd, \(J = 17.7, 7.1\) Hz, 1H), 5.48 (dd, \(J = 17.7, 1.1\) Hz, 1H), 4.52 (q, \(J = 7.2\) Hz, 1H), 4.23 (d, \(J = 17.1\) Hz, 2H), 3.91 (dd, \(J = 17.1, 13.0\) Hz, 2H), 2.63 (s, 3H), 2.06-1.93 (m, 1H), 1.58 (t, \(J = 11.7\) Hz, 1H), 1.30-0.92 (m, 2H), 0.73 (t, \(J = 7.3\) Hz, 3H). \(^{11}\)B NMR (160 MHz, Acetonitrile-\(d_3\)) \(\delta\) 10.2. \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \(\delta\) 169.1, 169.1, 142.8, 135.2, 130.2, 129.3, 67.5, 62.4, 47.7, 36.4, 20.9, 13.8.

HRMS: calculated for C\(_{23}\)H\(_{27}\)BN\(_2\)O\(_8\)S\(_2\)Na \([M+Na]^+\), 557.1198; Found, 557.1187.

\((E)-N-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)but-3-en-2-yl)-N-(phenylsulfonyl)benzenesulfonamide (3b)\)

Following the general procedure F, the product 3b was obtained in 56% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). \(R_F = 0.26\) (PE/EA = 1:4).

\(^{1}\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \(\delta\) 7.95-7.89 (m, 4H), 7.77-7.72 (m, 2H), 7.65-7.59 (m, 4H), 6.15 (dd, \(J = 17.9, 5.4\) Hz, 1H), 5.44 (dd, \(J = 17.9, 1.7\) Hz, 1H), 4.81 (qdd, \(J = 7.0, 5.5, 1.7\) Hz, 1H), 3.94 (d, \(J = 17.0\) Hz, 2H), 3.70 (dd, \(J = 17.0, 5.2\) Hz, 2H), 2.66 (s, 3H), 1.52 (d, \(J = 6.9\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Acetonitrile-\(d_3\)) \(\delta\) 169.1, 143.9, 140.9, 135.2, 130.3, 129.1, 62.3, 62.3, 47.7, 19.6.
HRMS: calculated for C\textsubscript{27}H\textsubscript{27}BN\textsubscript{2}O\textsubscript{8}S\textsubscript{2}Na [M+Na]\textsuperscript{+}, 605.1199; Found, 605.1198.

\((E)\)-N-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)tridec-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3c)

Following the general procedure \(F\), the product 3c was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F = 0.32\) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.90 (d, \(J = 7.9\) Hz, 4H), 7.81-7.75 (m, 2H), 7.66 (t, \(J = 7.8\) Hz, 4H), 6.15 (dd, \(J = 17.8, 7.0\) Hz, 1H), 5.49 (dd, \(J = 17.9, 1.2\) Hz, 1H), 4.50 (q, \(J = 7.3\) Hz, 1H), 4.23 (dd, \(J = 17.1, 2.2\) Hz, 2H), 3.92 (dd, \(J = 17.1, 11.1\) Hz, 2H), 2.63 (s, 3H), 2.01-1.90 (m, 1H), 1.67-1.60 (m, 1H), 1.28-1.06 (m, 16H), 0.86 (t, \(J = 6.8\) Hz, 3H).

\(^{11}\)B NMR (128 MHz, Acetone-\(d_6\)) \(\delta\) 10.2.

\(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \(\delta\) 169.1, 169.1, 142.9, 135.2, 130.2, 129.4, 129.3, 127.5, 68.8, 62.4, 47.7, 34.3, 32.6, 30.3, 30.2, 30.1, 30.0, 29.7, 27.6, 23.4, 14.4.

HRMS: calculated for C\textsubscript{30}H\textsubscript{41}BN\textsubscript{2}O\textsubscript{8}S\textsubscript{2}Na [M+Na]\textsuperscript{+}, 655.2295; Found, 655.2296.

\((E)\)-N-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenylbut-3-en-2-yl)-N-(phenylsulfonyl)benzenesulfonamide (3d)

Following the general procedure \(F\), the product 3d was obtained in 30% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \(R_F = 0.27\) (PE/EA = 1:4).

\(^1\)H NMR (500 MHz, Acetone-\(d_6\)) \(\delta\) 8.04 (d, \(J = 7.8\) Hz, 4H), 7.81-7.75 (m, 2H), 7.68 (t, \(J = 7.4\) Hz, 4H), 7.25 (t, \(J = 7.4\) Hz, 2H), 7.18 (t, \(J = 7.3\) Hz, 1H), 7.09 (d, \(J = 7.5\) Hz, 2H), 6.41 (dd, \(J = 17.7, 7.7\) Hz, 1H), 5.31 (d, \(J = 17.7\) Hz, 1H), 4.80 (ddd, \(J = 11.3, 7.6, 3.9\) Hz, 1H), 4.15 (d, \(J = 16.9\) Hz, 2H), 3.85 (d, \(J = 16.9\) Hz, 1H), 3.73 (d, \(J = 16.9\) Hz, 1H), 3.51 (dd, \(J = 13.0, 11.1\) Hz, 1H), 2.96 (dd, \(J = 13.1, 4.0\) Hz, 1H), 2.51 (s, 3H).

\(^{11}\)B NMR (160 MHz, Acetone-\(d_6\)) \(\delta\) 10.2. \(^{13}\)C NMR (125 MHz, Acetone-\(d_6\)) \(\delta\) 168.8, 168.7, 140.7, 138.8, 135.0, 130.2, 129.4, 129.3, 127.5, 68.8, 62.2, 62.1, 47.1, 41.3.

HRMS: calculated for C\textsubscript{30}H\textsubscript{41}BN\textsubscript{2}O\textsubscript{8}S\textsubscript{2}Na [M+Na]\textsuperscript{+}, 605.2295; Found, 605.2296.

\((E)\)-N-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-phenylpent-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3e)

Following the general procedure \(F\), the product 3e was obtained in 74% NMR yield as a white solid after column chromatography (eluent =
Petroleum ether/ ethyl acetate 1:3 v/v). $R_F = 0.30$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetone-$d_6$) δ 7.93 (d, $J = 7.7$ Hz, 4H), 7.77 (t, $J = 7.4$ Hz, 2H), 7.65 (t, $J = 7.7$ Hz, 4H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.08 (d, $J = 7.5$ Hz, 2H), 6.42 (dd, $J = 17.8$, 7.0 Hz, 1H), 5.62 (d, $J = 17.8$ Hz, 1H), 4.67 (q, $J = 7.5$, 6.9 Hz, 1H), 4.25 (d, $J = 16.9$ Hz, 2H), 3.99 (dd, $J = 19.5$, 17.0 Hz, 2H), 2.95 (s, 3H), 2.62-2.54 (m, 1H), 2.52-2.39 (m, 2H), 2.02-1.98 (m, 1H). $^11$B NMR (128 MHz, Acetonitrile-$d_3$) δ 9.9. $^{13}$C NMR (101 MHz, Acetonitrile-$d_3$) δ 169.2, 169.1, 142.3, 141.8, 135.2, 130.3, 129.4, 129.4, 129.1, 127.1, 66.7, 62.5, 47.8, 36.1, 33.5.

HRMS: calculated for $C_{28}H_{29}BN_2O_8S_2Na [M+Na]$+ 619.1356; Found, 619.1351.

ethyl ($E$)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-(N-(phenylsulfonyl)phenylsulfonamido)pent-4-en-1-yl)benzoate (3f)

Following the general procedure F, the product 3f was obtained in 66% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). $R_F = 0.16$ (PE/EA = 1:4).

$^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 7.91 (d, $J = 8.2$ Hz, 2H), 7.85 (d, $J = 7.7$ Hz, 4H), 7.73 (t, $J = 7.4$ Hz, 2H), 7.58 (t, $J = 7.7$ Hz, 4H), 7.16 (d, $J = 8.1$ Hz, 2H), 6.30 (dd, $J = 17.8$, 7.1 Hz, 1H), 5.44 (dd, $J = 17.7$, 1.1 Hz, 1H), 4.53 (q, $J = 7.9$, 7.1 Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 3.96 (dd, $J = 17.1$, 15.4 Hz, 2H), 2.67 (s, 3H), 2.63 (dd, $J = 13.3$, 4.5 Hz, 1H), 2.53-2.40 (m, 2H), 2.00 (dd, $J = 16.1$, 6.0 Hz, 1H), 1.36 (s, $J = 7.1$ Hz, 3H). $^{11}$B NMR (128 MHz, Acetonitrile-$d_3$) δ 10.1. $^{13}$C NMR (125 MHz, Acetonitrile-$d_3$) δ 168.7, 168.7, 166.7, 166.7, 146.9, 141.7, 134.9, 130.0, 129.9, 129.2, 128.7, 66.2, 62.1, 61.3, 47.4, 35.3, 33.1, 14.2.

HRMS: calculated for $C_{31}H_{34}BN_2O_{10}S_2 [M+H]$+ 669.1748; Found, 669.1733.

(E) N-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-phenoxypent-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3g)

Following the general procedure F, the product 3g was obtained in 57% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). $R_F = 0.24$ (PE/EA = 1:4).

$^1$H NMR (500 MHz, Acetonitrile-$d_3$) δ 7.93 (d, $J = 7.7$ Hz, 4H), 7.72 (t, $J = 7.5$ Hz, 2H), 7.60 (q, $J = 7.9$, 6.0 Hz, 4H), 7.27 (t, $J = 7.7$ Hz, 2H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 7.9$ Hz, 2H), 6.30 (dd, $J = 17.8$, 7.4 Hz, 1H), 5.45 (d, $J = 17.8$ Hz, 1H), 4.90 (dt, $J = 13.7$, 6.5 Hz, 1H), 3.98-3.87 (m, 3H), 3.79 (td, $J = 9.4$, 4.3 Hz, 1H), 3.68 (ddd, $J = 17.2$, 9.7, 3.8 Hz, 2H), 2.59-2.48 (m, 4H), 2.30-2.19 (m, 1H). $^{11}$B NMR (160 MHz, Acetonitrile-$d_3$) δ 10.1. $^{13}$C NMR (125 MHz, Acetonitrile-$d_3$) δ 169.1, 169.1, 159.7, 141.5, 135.3, 130.5, 130.3, 129.2, 121.8, 115.4, 65.2, 64.3, 62.4, 47.6, 34.2.

HRMS: calculated for $C_{28}H_{20}BN_2O_6S_2Na [M+Na]$+, 635.1305; Found, 635.1302.
(E)-N-(5-(benzyloxy)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3h)

Following the general procedure F, the product 3h was obtained in 54% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). RF = 0.30 (PE/EA = 1:4).

1H NMR (400 MHz, Acetone-d6) δ 7.90 (d, J = 7.9 Hz, 4H), 7.72 (t, J = 7.5 Hz, 2H), 7.57 (t, J = 7.8 Hz, 4H), 7.412-7.35 (m, 2H), 7.32 (d, J = 7.2 Hz, 3H), 6.24 (dd, J = 17.8, 7.3 Hz, 1H), 5.38 (dd, J = 17.8, 1.2 Hz, 1H), 4.82 (td, J = 8.3, 5.1 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.32 (d, J = 11.9 Hz, 1H), 3.93 (dd, J = 17.0, 2.4 Hz, 2H), 3.68 (dd, J = 17.0, 12.3 Hz, 2H), 3.39 (dt, J = 10.1, 5.2 Hz, 1H), 3.29 (td, J = 9.4, 4.4 Hz, 1H), 2.57 (s, 3H), 2.41-2.33 (m, 1H), 2.06-2.03 (m, 1H). 11B NMR (160 MHz, Acetone-d6) δ 10.3. 13C NMR (125 MHz, Acetone-d6) δ 168.9, 168.8, 141.5, 139.7, 134.9, 130.0, 129.2, 129.1, 128.4, 128.3, 73.2, 67.3, 64.2, 62.4, 47.5, 35.0.

HRMS: calculated for C29H31BN2O8S2Na [M+Na]+, 649.1462; Found, 649.1435.

(E)-N-(6-(5,5-dimethyl-1,3-dioxan-2-yl)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3i)

Following the general procedure F, the product 3i was obtained in 65% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). RF = 0.29 (PE/EA = 1:4).

1H NMR (500 MHz, Acetone-d6) δ 7.92 (d, J = 7.8 Hz, 4H), 7.74 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7.7 Hz, 4H), 6.19 (dd, J = 17.8, 7.0 Hz, 1H), 5.39 (d, J = 17.8 Hz, 1H), 4.53 (q, J = 7.3 Hz, 1H), 4.29 (t, J = 5.1 Hz, 1H), 3.93 (d, J = 17.0 Hz, 2H), 3.69 (dd, J = 16.9, 13.7 Hz, 2H), 3.51 (d, J = 11.2 Hz, 2H), 3.36 (d, J = 11.1 Hz, 2H), 2.62 (s, 3H), 2.08-2.03 (m, 1H), 1.86-1.77 (m, 1H), 1.46 (td, J = 7.9, 5.2 Hz, 2H), 1.28-1.19 (m, 2H), 1.10 (s, 3H), 0.69 (s, 3H). 11B NMR (160 MHz, Acetone-d6) δ 10.1. 13C NMR (125 MHz, Acetone-d6) δ 169.1, 169.1, 142.7, 135.2, 130.3, 129.2, 102.4, 77.5, 67.6, 62.3, 47.7, 34.9, 34.1, 30.7, 23.2, 22.2, 21.8.

HRMS: calculated for C29H37BN2O10S2Na [M+Na]+, 671.1880; Found, 671.1892.

(E)-N-(5-(1,3-dioxoisoindolin-2-yl)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3j)

Following the general procedure F, the product 3j was obtained in 56% NMR yield as a white solid after column chromatography (eluent
= Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.15 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \( \delta \) 7.89-7.84 (m, 8H), 7.70 (t, \( J = 7.5 \) Hz, 2H), 7.55 (t, \( J = 7.8 \) Hz, 4H), 6.26 (dd, \( J = 17.8, 6.9 \) Hz, 1H), 5.55 (d, \( J = 17.8 \) Hz, 1H), 4.54-4.45 (m, 1H), 3.99 (d, \( J = 17.0 \) Hz, 2H), 3.77 (t, \( J = 16.5 \) Hz, 2H), 3.56 (dd, \( J = 8.1, 5.7 \) Hz, 2H), 2.75 (s, 3H), 2.58 (dt, \( J = 14.0, 4.8 \) Hz, 1H), 2.09 (d, \( J = 3.7 \) Hz, 1H). \(^{11}\)B NMR (128 MHz, Acetonitrile-\(d_3\)) \( \delta \) 10.0. \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \( \delta \) 169.2, 141.2, 135.3, 135.3, 133.1, 130.3, 129.1, 124.0, 64.3, 62.4, 62.4, 47.8, 36.2, 33.8. HRMS: calculated for \( C_{31}H_{33}BN_2O_{10}S_2 \) [M+Na]\(^+\), 691.1568; Found, 691.1559.

tert-butyl \((E)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-(N-(phenylsulfonyl)phenylsulfonamido)pent-4-en-1-yl)piperidine-1-carboxylate (3k)

Following the general procedure F, the product 3k was obtained in 58% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.11 \) (PE/EA = 1:4).

\(^1\)H NMR (500 MHz, Acetonitrile-\(d_3\)) \( \delta \) 7.93 (d, \( J = 7.9 \) Hz, 4H), 7.74 (t, \( J = 7.5 \) Hz, 2H), 7.61 (t, \( J = 7.7 \) Hz, 4H), 6.22 (dd, \( J = 17.8, 6.9 \) Hz, 1H), 5.44 (d, \( J = 17.8 \) Hz, 1H), 4.50 (q, \( J = 7.3 \) Hz, 1H), 3.95 (d, \( J = 16.9 \) Hz, 4H), 3.77-3.66 (m, 2H), 2.64 (s, 5H), 2.04 (td, \( J = 12.5, 11.4, 5.4 \) Hz, 1H), 1.77 (tt, \( J = 12.2, 5.8 \) Hz, 1H), 1.50 (d, \( J = 13.5 \) Hz, 1H), 1.41 (d, \( J = 1.7 \) Hz, 10H), 1.26 (q, \( J = 9.5, 7.8 \) Hz, 1H), 1.01 (ddt, \( J = 33.3, 12.1, 6.6 \) Hz, 2H), 0.85 (pd, \( J = 11.8, 4.0 \) Hz, 2H). \(^{11}\)B NMR (128 MHz, Acetonitrile-\(d_3\)) \( \delta \) 10.2. \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \( \delta \) 169.1, 169.1, 155.4, 142.8, 135.3, 130.3, 129.2, 79.5, 67.9, 62.4, 47.7, 36.2, 34.4, 32.9, 32.7, 31.5, 28.6. HRMS: calculated for \( C_{32}H_{34}BN_3O_{10}S_2Na [M+Na]^+ \), 726.2303; Found, 726.2292.

\((E)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-(N-(phenylsulfonyl)phenylsulfonamido)hept-6-en-1-yl benzoate (3l)

Following the general procedure F, the product 3l was obtained in 70% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.23 \) (PE/EA = 1:4).

\(^1\)H NMR (500 MHz, Acetone-\(d_6\)) \( \delta \) 8.02 (d, \( J = 7.7 \) Hz, 6H), 7.74 (t, \( J = 7.4 \) Hz, 2H), 7.64 (t, \( J = 7.6 \) Hz, 5H), 7.54 (t, \( J = 7.6 \) Hz, 2H), 6.36 (dd, \( J = 17.8, 7.0 \) Hz, 1H), 5.59 (d, \( J = 17.7 \) Hz, 1H), 4.65 (q, \( J = 7.2 \) Hz, 1H), 4.27-4.17 (m, 4H), 3.93 (dd, \( J = 16.9, 8.1 \) Hz, 2H), 2.87 (s, 3H), 2.19 (ddt, \( J = 14.0, 9.2, 4.8 \) Hz, 1H), 1.89 (ddt, \( J = 16.4, 12.0, 5.9 \) Hz, 1H), 1.69 (p, \( J = 7.1 \) Hz, 2H), 1.42-1.28 (m, 2H). \(^{11}\)B NMR (160 MHz, CD\(3CN-d_6\)) \( \delta \) 10.2. \(^{13}\)C NMR (125 MHz, Acetone-\(d_6\)) \( \delta \) 168.9, 168.8, 166.7, 142.3, 134.9, 133.8, 131.4, 130.2, 130.1, 129.4, 129.3, 67.5, 65.3, 62.3, 47.5, 34.2, 29.0, 24.4. HRMS: calculated for \( C_{31}H_{33}BN_2O_{10}S_2 [M+Na]^+ \), 691.1568; Found, 691.1559.
(E)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-(N-(phenylsulfonyl)phenylsulfonamido)hept-6-en-1-yl pivalate (3m)

Following the general procedure F, the product 3m was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.24 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \( \delta 7.93 \) (d, \( J = 7.9 \) Hz, 4H), 7.74 (t, \( J = 7.4 \) Hz, 2H), 7.61 (t, \( J = 7.8 \) Hz, 4H), 6.21 (dd, \( J = 17.8, 7.0 \) Hz, 1H), 5.40 (d, \( J = 17.8 \) Hz, 1H), 4.54 (q, \( J = 7.2 \) Hz, 1H), 3.98-3.87 (m, 4H), 3.69 (dd, \( J = 17.0, 13.4 \) Hz, 2H), 2.62 (s, 3H), 2.10-2.05 (m, 1H), 1.86-1.77 (m, 1H), 1.51 (p, \( J = 7.0 \) Hz, 2H), 1.32-1.18 (m, 2H), 1.15 (s, 9H).

\(^{11}\)B NMR (128 MHz, Acetonitrile-\(d_3\)) \( \delta 10.0 \).

\(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \( \delta 178.9, 169.1, 169.0, 142.7 \) (2C), 135.2, 130.3, 129.2, 67.5, 64.7, 62.4, 47.7, 39.3, 34.0, 28.8, 27.5, 24.3.

HRMS: calculated for C\(_{29}\)H\(_{37}\)BN\(_2\)O\(_{10}\)S\(_2\)Na \([M+Na]^+\), 671.1880; Found, 671.1879.

(\(E\))-N-(7-chloro-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-1-en-3-yl)-N-(phenylsulfonyl)benzenesulfonamide (3n)

Following the general procedure F, the product 3n was obtained in 52% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.26 \) (PE/EA = 1:4).

\(^1\)H NMR (500 MHz, Acetone-\(d_6\)) \( \delta 8.02 \) (d, \( J = 7.8 \) Hz, 4H), 7.78 (t, \( J = 7.4 \) Hz, 2H), 7.67 (t, \( J = 7.7 \) Hz, 4H), 6.33 (dd, \( J = 17.8, 7.0 \) Hz, 1H), 5.55 (d, \( J = 17.8 \) Hz, 1H), 4.62 (q, \( J = 7.2 \) Hz, 1H), 4.23 (d, \( J = 16.9 \) Hz, 2H), 3.94 (dd, \( J = 16.9, 10.6 \) Hz, 2H), 3.50 (t, \( J = 6.6 \) Hz, 2H), 2.88 (s, 3H), 2.17-2.10 (m, 1H), 1.86-1.79 (m 1H), 1.69 (td, \( J = 8.9, 4.3 \) Hz, 2H), 1.41-1.29 (m, 2H). \(^{11}\)B NMR (160 MHz, Acetone-\(d_6\)) \( \delta 10.4 \).

\(^{13}\)C NMR (125 MHz, Acetone-\(d_6\)) \( \delta 168.8, 168.8, 142.2, 135.0, 130.1, 129.3, 67.4, 62.3, 47.5, 45.4, 33.7, 32.8, 25.1.

HRMS: calculated for C\(_{24}\)H\(_{28}\)BClN\(_2\)O\(_8\)S\(_2\)Na \([M+Na]^+\), 605.0965; Found, 605.0991.

ethyl (E)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-(N-(phenylsulfonyl)phenylsulfonamido)hept-6-enoate (3o)

Following the general procedure F, the product 3o was obtained in 16% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ethyl acetate 1:3 v/v). \( R_F = 0.13 \) (PE/EA = 1:4).

\(^1\)H NMR (400 MHz, Acetonitrile-\(d_3\)) \( \delta 7.93 \) (d, \( J = 7.7 \) Hz, 4H), 7.77-7.71 (m, 2H), 7.61
(t, $J = 7.8$ Hz, 4H), 6.19 (dd, $J = 17.8$, 7.0 Hz, 1H), 5.39 (dd, $J = 17.8$, 1.3 Hz, 1H), 4.55 (q, $J = 7.2$ Hz, 1H), 4.06 (q, $J = 7.1$ Hz, 2H), 3.94 (d, $J = 17.0$ Hz, 2H), 3.69 (dd, $J = 17.0$, 15.4 Hz, 2H), 2.62 (s, 3H), 2.12-2.01 (m, 2H), 1.85 (ddt, $J = 13.1$, 10.4, 6.2 Hz, 2H), 1.42 (dtd, $J = 17.2$, 13.8, 7.2 Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{11}$B NMR (160 MHz, Acetonitrile-$d_3$) $\delta$ 10.2. $^{13}$C NMR (125 MHz, Acetonitrile-$d_3$) $\delta$ 173.8, 169.1, 169.1, 142.5, 135.3, 130.3, 129.2, 67.3, 62.4, 61.0, 47.7, 34.1, 33.7, 23.1, 14.6. HRMS: calculated for C$_{26}$H$_{31}$BN$_2$O$_{10}$S$_2$Na [M+Na]$^+$, 629.1410; Found, 629.1399.
5. The synthesis of $\gamma$-functionalized benzyl MIDA boronates

Synthesis of compound 4: $^5$

The dimethyl malonate (0.3 mmol, 3.0 equiv.) was added dropwise into the reaction flask filled with NaH (80% in oil) and THF (1 ml) under an atmosphere of nitrogen at 0 °C. Then the reaction mixture was stirred for 20 minutes at room temperature. In the glove box, 2a (0.1 mmol, 1.0 equiv.), palladium acetate (5 mol%) and triphenylphosphine (20 mol%) were added into another 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. The anhydrous THF (1 ml) was added with syringe. Under argon atmosphere, the reaction solution of dimethyl malonate was added into the Schlenk reaction tube by syringe. After the mixture was stirred for 40 minutes at room temperature. The solvents were removed on a rotary evaporator, and the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/EtOAc 1:3, v/v) to afford the pure product 4 (32.1 mg, 87%) as a white solid.

dimethyl (E)-2-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-1-en-3-yl)malonate

$R_F = 0.16$ (PE/EA = 1:3);

$^1$H NMR (400 MHz, Acetonitrile-$d_3$) δ 5.84 (dd, $J = 17.7, 8.9$ Hz, 1H), 5.50 (dd, $J = 17.6, 0.8$ Hz, 1H), 3.93 (dd, $J = 17.0, 1.6$ Hz, 2H), 3.73 (dd, $J = 17.0, 15.8$ Hz, 2H), 3.67 (s, 3H), 3.61 (s, 3H), 3.44 (d, $J = 8.9$ Hz, 1H), 2.82-2.75 (m, 1H), 2.73 (s, 3H), 1.40-1.31 (m, 3H), 1.25-1.16 (m, 1H), 0.88 (d, $J = 7.0$ Hz, 3H).

$^{11}$B NMR (160 MHz, Acetone-$d_6$) δ 10.4. $^{13}$C NMR (125 MHz, Acetone-$d_6$) δ 169.2, 169.1, 168.9, 145.2, 62.2, 57.2, 52.5, 52.4, 47.4, 45.9, 35.0, 21.0, 14.1.

HRMS: calculated for C$_{16}$H$_{24}$BNO$_8$Na [M+Na]$^+$, 392.1490; Found, 392.1482.

Synthesis of compound 5:

In the glove box, 4 (0.1 mmol, 1.0 equiv.), 4-idoanisole (0.15 mmol, 1.5 equiv.) palladium(II) acetate (5 mol%) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos, 10 mol%) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the THF (0.2 mL) and 1M NaOH (6.0 equiv.)
were added with syringe then the reaction mixture was vigorously stirred at rt. After 30 mins, the reaction mixture was quenched with water (2 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, then concentrated in vacuo. The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 6/1, v/v) to afford the pure product 5 (21.8 mg, 68%).

**dimethyl (E)-2-(1-(4-methoxyphenyl)hex-1-en-3-yl)malonate**

\[
(RF)_2OC\begin{array}{c}\text{MeOOC}\
\text{H}
\end{array} \text{H} \quad R_F = 0.30 \text{ (PE/EA = 6:1);}
\]

\[\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{) } \delta 7.27 \text{ (d, } J = 8.7 \text{ Hz, 2H), 6.83 \text{ (d, } J = 8.7 \text{ Hz, 2H), 6.38 \text{ (d, } J = 15.7 \text{ Hz, 1H), 5.85 \text{ (dd, } J = 15.7, 9.6 \text{ Hz, 1H), 3.80 \text{ (s, 3H), 3.74 \text{ (s, 3H), 3.64 \text{ (s, 3H), 3.44 \text{ (d, } J = 8.8 \text{ Hz, 1H), 2.91 \text{ (qd, } J = 9.4, 3.5 \text{ Hz, 1H), 1.53-1.30 \text{ (m, 4H), 0.89 \text{ (t, } J = 7.0 \text{ Hz, 3H).} \text{\textsuperscript{13}C NMR (126 MHz, CDCl}_3\text{) } \delta 169.0, 168.8, 159.2, 132.0, 130.1, 127.6, 114.1, 57.4, 55.5, 52.6, 52.4, 43.6, 35.2, 20.5, 14.0.} \]

HRMS: calculated for C\textsubscript{18}H\textsubscript{24}O\textsubscript{5}Na [M+Na\textsuperscript{+}], 343.1516; Found, 343.1514.

**Synthesis of compound 6:**

In the glove box, 2a (0.1 mmol, 1.0 equiv.), Sodium benzenesulfinate (0.4 mmol, 4 equiv.) and tetrakis(triphenylphosphine)palladium (5 mol%) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the anhydrous THF (2 mL) and DMSO (0.3 mL) were added with syringe then the reaction mixture was vigorously stirred at 50 °C for 2 h. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, then concentrated in vacuo. The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product 6 (32.7 mg, 86%) as a white solid.

**(E)-6-methyl-2-(3-(phenylsulfonyl)hex-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione**

\[
\text{SO}_2\text{Ph} \quad \text{B} \quad \text{N} \quad \text{SO}_2\text{Ph} \quad R_F = 0.23 \text{ (PE/EA = 1:4);}
\]

\[\text{\textsuperscript{1}H NMR (400 MHz, Acetone-d\textsubscript{6}) } \delta 8.35-8.29 \text{ (m, 2H), 8.20-8.15 \text{ (m, 1H), 8.13-8.06 \text{ (m, 2H), 6.28 \text{ (dd, } J = 17.6, 9.0 \text{ Hz, 1H), 6.13 \text{ (d, } J = 17.6 \text{ Hz, 1H), 4.65 \text{ (dd, } J = 16.9, 0.9 \text{ Hz, 2H), 4.42 \text{ (d, } J = 17.0 \text{ Hz, 1H), 4.33-4.21 \text{ (m, 2H), 3.20 \text{ (s, 3H), 2.46-2.37 \text{ (m, 1H), 2.17-2.08 \text{ (m, 1H), 1.95-1.86 \text{ (m, 1H), 1.78-1.71 \text{ (m, 1H), 1.35 \text{ (t, } J = 7.3 \text{ Hz, 3H).} \text{\textsuperscript{11}B NMR (128 MHz, Acetone-d\textsubscript{6}) } \delta 9.9.} \text{\textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}CN) } \delta 169.1, 169.0, 139.1, 137.0, 134.7, 130.1, 129.7, 71.0, 62.4, 47.6, 29.4, 20.6, 13.8.} \]

In the glove box, 2a (0.1 mmol, 1.0 equiv.), Sodium benzenesulfinate (0.4 mmol, 4 equiv.) and tetrakis(triphenylphosphine)palladium (5 mol%) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the anhydrous THF (2 mL) and DMSO (0.3 mL) were added with syringe then the reaction mixture was vigorously stirred at 50 °C for 2 h. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄, then concentrated in vacuo. The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product 6 (32.7 mg, 86%) as a white solid.
HRMS: calculated for C_{17}H_{22}BNO_{6}SnNa [M+Na]^+, 402.1156; Found, 402.1159.

Synthesis of compound 7:

In the glove box, 2a (0.1 mmol, 1.0 equiv.), AgF (0.5 mmol, 5.0 equiv.), CuBr (0.1 mmol) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the anhydrous MeCN (0.5 mL) was added with syringe then the reaction mixture was vigorously stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/EtOAc 1:3, v/v) to afford the pure product 7 (17.7 mg, 69%) as a white solid.

**(E)**-2-(3-fluorohex-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione

{eq}R_f = 0.24\ (\text{PE/EA} = 1:3);\]

{eq}^{1}H\ NMR\ (400\ MHz,\ \text{Acetonitrile-d_3})\ \delta \ 6.11\ (\text{ddd},\ J = 17.9,\ 15.3,\ 5.3\ Hz,\ 1H),\ 5.72\ (\text{ddd},\ J = 17.9,\ 2.9,\ 1.4\ Hz,\ 1H),\ 4.95\ (\text{ddtd},\ J = 49.2,\ 6.9,\ 5.4,\ 1.4\ Hz,\ 1H),\ 3.96\ (d,\ J = 17.0\ Hz,\ 2H),\ 3.80\ (dd,\ J = 17.0,\ 1.8\ Hz,\ 2H),\ 2.15\ (s,\ 3H),\ 1.73-1.52\ (m,\ 2H),\ 1.48-1.32\ (m,\ 2H),\ 0.94\ (t,\ J = 7.4\ Hz,\ 3H).\)

{eq}^{19}F\ NMR\ (376\ MHz,\ \text{Acetonitrile-d_3})\ \delta -178.4.\)

{eq}^{11}B\ NMR\ (160\ MHz,\ \text{Acetonitrile-d_3})\ \delta 10.4.\)

{eq}^{13}C\ NMR\ (125\ MHz,\ \text{Acetonitrile-d_3})\ \delta 169.3,\ 143.9\ (d,\ ^{2}J_{C-F} = 19.2\ Hz),\ 95.1\ (d,\ ^{1}J_{C-F} = 166.2\ Hz),\ 62.5,\ 47.8,\ 37.9\ (d,\ ^{2}J_{C-F} = 21.8\ Hz),\ 18.8\ (d,\ ^{3}J_{C-F} = 5.3\ Hz),\ 14.1.\)

HRMS: calculated for C_{11}H_{17}BFNO_{6}K [M+K]^+, 296.0868; Found, 296.0874.

Synthesis of compound 8 and 12:

2a (0.1 mmol, 1.0 equiv.) or 11 (0.1 mmol, 1.0 equiv.) 1,3-diiodo-5,5-dimethylhydantoin (DIH, 0.2 mmol, 1.0 equiv.), DCM (0.5 mL) and Et$_3$N-HF (140 μL, 9.0 equiv) were added to a 15 mL screw cap vial equipped with a stirring bar. The solution was stirred at room temperature for 5 mins. The resulting mixture was quenched with 0.2 M Na$_2$S$_2$O$_3$ solution and then extracted with DCM. The organic phase was washed with 0.2 M HCl and brine. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The p-iodobenzole (0.1 mmol) was added and the NMR yield was determined by $^1$H NMR.
After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to 1:3, v/v) to afford the pure product 8 (87% NMR yield) or 12 (72% NMR yield) as a white solid. Meanwhile, recrystallization (acetone/diethyl ether) was conducted to get pure product.

(±)-2-(3-chloro-2-fluoro-1-iodohexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8)

![Structure of 8](image)

\[ R_F = 0.31 \text{ (PE/EA = 1:3);} \]

\[^1\text{H NMR (400 MHz, DMSO-d}_6\text{)} \delta 4.84 (\text{ddd, } J = 46.9, 8.7, 3.2 \text{ Hz, } 1\text{H}), 4.60 \text{ (dd, } J = 22.6, 10.7 \text{ Hz, } 1\text{H}), 4.43 \text{ (d, } J = 17.4 \text{ Hz, } 1\text{H}), 4.27 \text{ (dd, } J = 17.2, 3.1 \text{ Hz, } 1\text{H}), 4.12 \text{ (d, } J = 17.4 \text{ Hz, } 1\text{H}), 3.96 \text{ (dd, } J = 17.2, 1.7 \text{ Hz, } 1\text{H}), 3.86 \text{ (dd, } J = 10.6, 8.6 \text{ Hz, } 1\text{H}), 3.00 \text{ (s, } 3\text{H)}, 1.96 \text{ (dt, } J = 15.4, 8.0 \text{ Hz, } 1\text{H}), 1.62 \text{ (pd, } J = 13.4, 12.6, 6.2 \text{ Hz, } 2\text{H}), 1.50-1.35 \text{ (m, } 1\text{H)}, 0.92 \text{ (t, } J = 7.3 \text{ Hz, } 3\text{H}). \]

\[^13\text{C NMR (125 MHz, Acetonitrile-d}_3\text{)} \delta 168.2, 168.2, 100.2 \text{ (d, } J_{C-F} = 179.1 \text{ Hz), 65.3, 63.7, 63.6 \text{ (d, } J_{C-F} = 18.0 \text{ Hz), 47.5(2C), 34.2 \text{ (d, } J_{C-F} = 4.4 \text{ Hz), 20.3, 13.6.} \]

HRMS: calculated for C\(_{11}\)H\(_{17}\)BClFINO\(_4\)Na [M+Na]\(^+\), 441.9862; Found, 441.9861.

(±)-2-(3-azido-2-fluoro-1-iodohexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (12)

![Structure of 12](image)

\[ R_F = 0.28 \text{ (PE/EA = 1:2);} \]

\[^1\text{H NMR (400 MHz, Acetone-d}_6\text{)} \delta 4.71 \text{ (ddd, } J = 47.0, 7.5, 4.4 \text{ Hz, } 1\text{H}), 4.42 \text{ (d, } J = 17.1 \text{ Hz, } 1\text{H}), 4.32 \text{ (dd, } J = 17.1, 2.7 \text{ Hz, } 1\text{H}), 4.23 \text{ (d, } J = 17.1 \text{ Hz, } 1\text{H}), 4.11 \text{ (dd, } J = 17.1, 1.2 \text{ Hz, } 1\text{H}), 4.02-3.80 \text{ (m, } 2\text{H}), 3.31 \text{ (s, } 3\text{H}), 1.92-1.79 \text{ (m, } 1\text{H}), 1.75-1.57 \text{ (m, } 2\text{H}), 1.53-1.43 \text{ (m, } 1\text{H}), 0.99 \text{ (t, } J = 7.2 \text{ Hz, } 3\text{H}). \]

\[^19\text{F NMR (376 MHz, Acetonitrile-d}_6\text{)} \delta -173.0. \]

HRMS: calculated for C\(_{11}\)H\(_{17}\)BCFINO\(_4\)Na [M+Na]\(^+\), 449.9862; Found, 449.9861.

Synthesis of compound 9:

![Reaction scheme for synthesis of 9](image)

To the 15 mL tube were added 2a (0.1 mmol, 1.0 equiv.), 3-Chloroperbenzoic acid (mCPBA, 0.25 mmol, 2.5 equiv.) and DCM (1.0 mL). The reaction mixture was vigorously stirred at 30 °C for 24 h. The solvent was then removed under reduced pressure, the crude product was purified by flash chromatography on silica with an
eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product 9 (27.1 mg, 87%) as a white solid.

**2-(3-(1-chlorobutyl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione**

\[
\text{RF} = 0.24 (\text{PE/EA} = 1:3);
\]

\(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 4.33 (dd, \(J = 17.2, 3.1\) Hz, 1H), 4.24 (dd, \(J = 16.8, 1.6\) Hz, 1H), 4.15 (dd, \(J = 17.2, 2.3\) Hz, 1H), 3.97 (dd, \(J = 16.8, 1.3\) Hz, 1H), 3.67 (tdd, \(J = 7.4, 5.2, 3.2\) Hz, 1H), 3.27 (d, \(J = 2.0\) Hz, 3H), 3.08-2.99 (m, 1H), 2.39 (dd, \(J = 17.2, 2.9\) Hz, 1H), 1.97-1.77 (m, 2H), 1.64-1.45 (m, 2H), 0.95 (td, \(J = 7.4, 1.5\) Hz, 3H). \(^{11}\)B NMR (160 MHz, Acetonitrile-\(d_3\)) \(\delta\) 9.7. \(^{13}\)C NMR (125 MHz, Acetonitrile-\(d_3\)) \(\delta\) 169.5, 169.4, 168.5, 168.4, 66.4, 64.3, 63.0, 62.9, 62.9, 60.3, 59.4, 47.4, 47.3, 38.6, 38.1, 20.3, 20.0, 13.8, 13.8.

HRMS: calculated for C\(_{11}\)H\(_{18}\)BClNO\(_5\) [M+H]\(^+\), 290.0963; Found, 290.0964.

**Synthesis of compound 10:**

To the 15 mL tube were added 2a (0.1 mmol, 1.0 equiv.), pinacol (0.5 mmol, 5.0 equiv.), \(\text{H}_2\text{SO}_4\) (2 M, 4.0 equiv.) and THF (1.0 mL). The reaction mixture was vigorously stirred at room temperature for 24 h. The resulting mixture was quenched with water and then extracted with EA. The organic phase was washed with brine. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\). Then the p-iodobenzene (0.1 mmol) was added and the NMR yield was determined by \(^1\)H NMR (CDCl\(_3\), 86%). The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product 10 (11.2 mg, 46%) as a colorless liquid.

**\(E\)-2-(3-chlorohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane**

\[
\text{RF} = 0.24 (\text{PE/EA} = 100:1);
\]

\(^1\)H NMR (400 MHz, Chloroform-\(d_6\)) \(\delta\) 6.55 (dd, \(J = 17.7, 7.7\) Hz, 1H), 5.62 (d, \(J = 17.7\) Hz, 1H), 4.36 (q, \(J = 7.2\) Hz, 1H), 1.76-1.82 (m, 2H), 1.46 (dq, \(J = 13.9, 6.7, 6.2\) Hz, 2H), 1.27 (s, 12H), 0.92 (t, \(J = 7.4\) Hz, 3H). \(^{11}\)B NMR (128 MHz, Chloroform-\(d_6\)) \(\delta\) 29.8. \(^{13}\)C NMR (101 MHz, Chloroform-\(d_6\)) \(\delta\) 151.5, 83.6, 63.7, 39.9, 24.9, 24.9, 19.7, 13.6. HRMS: calculated for C\(_{12}\)H\(_{23}\)BClO\(_2\) [M+H]\(^+\), 277.1197; Found, 277.1187.

**Synthesis of compound 11:**

To the 15 mL tube were added 3a (0.1 mmol, 1.0 equiv.), NaN₃ (0.2 mmol, 2.0 equiv.), NaI (10 mol%) and DMF (0.5 mL). The reaction mixture was vigorously stirred at 100 °C for 30 mins. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄. Then the p-iodobenzole (0.1 mmol) was added and the NMR yield was determined by °H NMR (71%). The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product 11 as a white solid.

(E)-2-(3-azidohex-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione

`
Rf = 0.28 (PE/EA = 1:3);

°H NMR (500 MHz, Acetonitrile-d₃) δ 5.99 (dd, J = 17.6, 7.0 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 3.98 (dd, J = 15.3, 8.2 Hz, 3H), 3.80 (d, J = 17.1 Hz, 2H), 2.80 (s, 3H), 1.52 (q, J = 7.3 Hz, 2H), 1.36 (dt, J = 15.4, 7.6 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H). °B NMR (160 MHz, Acetonitrile-d₃) δ 10.4. °C NMR (125 MHz, Acetonitrile-d₃) δ 169.2, 143.0, 66.7, 62.5, 62.5, 47.9, 36.8, 19.9, 14.0.

HRMS: calculated for C₁₁H₁₇BN₄O₄Na [M+Na]⁺, 303.1237; Found, 303.1227.

Synthesis of compound 13:

To the microwave tube were added 3a (0.1 mmol, 1.0 equiv.), NaI (0.02 mmol, 20 mol%) and DMF (1 mL). The reaction mixture was vigorously stirred at 100 °C for 30 mins. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na₂SO₄. Then the p-iodobenzole (0.1 mmol) was added and the NMR yield was determined by °H NMR (59% for major). The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product 13 as a white solid.

2-((1E)-hexa-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (major)
$^1$H NMR (400 MHz, Acetone-$d_6$) δ 6.53 (dd, $J$ = 17.4, 10.2 Hz, 1H), 6.11 (ddt, $J$ = 13.9, 10.1, 1.1 Hz, 1H), 5.79 (dt, $J$ = 15.2, 6.6 Hz, 1H), 5.54 (d, $J$ = 17.4 Hz, 1H), 4.20 (d, $J$ = 16.9 Hz, 2H), 4.01 (d, $J$ = 16.9 Hz, 2H), 2.98 (s, 3H), 2.15-2.06 (m, 3H), 0.99 (t, $J$ = 7.5 Hz, 3H). $^{11}$B NMR (128 MHz, Acetone-$d_6$) δ 10.7. $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 169.1, 143.8, 137.9, 132.7, 62.3, 47.3, 26.2, 13.8. HRMS: calculated for C$_{11}$H$_{16}$BNO$_4$Na [M+Na]$^+$, 260.1065; Found, 260.1065.
6. KIE experiments

The allyl MIDA boronates 1p (0.1 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), N-chlorosuccinimide (NCS, 0.11 mmol, 1.1 equiv), 4Å MS (10 mg) and 1.5 mL CH$_3$CN were added in a 5 mL round bottom flask. The deuterium allyl MIDA boronates 1p-D$_2$ (0.1 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), N-chlorosuccinimide (NCS, 0.11 mmol, 1.1 equiv), 4Å MS (10 mg) and 1.5 mL CH$_3$CN were added in another 5 mL round bottom flask. After the reaction mixture was stirred for 5 mins, the two reaction mixtures were mixed and p-iodoanisole (23.4 mg, 0.1 mmol) was then added as an internal standard. The mixture was diluted with acetonitrile (2 mL) and then evaporated under reduced pressure. Yields were determined by $^1$H NMR. A kinetic isotope effect value $k_H/k_D = 1.2$ was obtained.
7. Intramolecular competition experiments and control experiment.

\[
\text{\textsuperscript{1}BuO} \quad \text{\textsuperscript{14}} \quad \text{\textsuperscript{N}} \quad \text{\textsuperscript{14}} \space + \text{PhSeCl (10 mol\%)} \quad \text{\textsuperscript{4 Å MS. MeCN, r.t., 24 h}} \quad \text{\textsuperscript{1}BuO} \quad \text{\textsuperscript{15}, 76 \%}
\]

The allyl MIDA boronates \textsuperscript{14} (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), \( N \)-chlorosuccinimide (NCS, 0.22 mmol, 1.1 equiv) and 4 Å MS (20 mg) were added in 3 mL CH\(_3\)CN. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to 1:3, v/v) to afford the pure product \textsuperscript{15} as a white solid (76% isolated yield).

tert-butyl (\( E \))-5-(4-methyl-2,6-dioxotetrahydro-2H-4\( \lambda_4\)\( \lambda_4\)-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-8-yl)pent-3-enoate (\textsuperscript{14})

Following the general procedure B, the product \textsuperscript{14} was obtained in 60 % yield as a white solid after column chromatography (eluuent = Petroleum ether/ ethyl acetate 1:3 v/v).

\textsuperscript{1}H NMR (400 MHz, Acetonitrile-\( d_3 \)) \( \delta \) 5.63-5.33 (m, 2H), 3.93 (dd, \( J = 16.9, 1.2 \) Hz, 2H), 3.77 (dd, \( J = 16.9, 1.2 \) Hz, 2H), 2.92-2.88 (m, 5H), 1.58 (d, \( J = 7.2 \) Hz, 2H), 1.41 (s, 9H). \textsuperscript{13}C NMR (101 MHz, Acetonitrile-\( d_3 \)) \( \delta \) 172.5, 169.0, 131.8, 124.1, 80.9, 62.9, 46.4, 39.9, 28.2. \textsuperscript{11}B NMR (128 MHz, Acetonitrile-\( d_3 \)) \( \delta \) 12.1.

HRMS: calculated for C\(_{14}\)H\(_{22}\)BNO\(_6\)Na [M+Na]\(^+\), 334.1429; Found, 334.1429.

tert-butyl (\( E \))-4-chloro-5-(4-methyl-2,6-dioxotetrahydro-2H-4\( \lambda_4\)\( \lambda_4\)-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-8-yl)pent-2-enoate (\textsuperscript{15})

\textsuperscript{1}H NMR (500 MHz, Acetonitrile-\( d_3 \)) \( \delta \) 6.85 (dd, \( J = 15.4, 8.3 \) Hz, 1H), 5.91 (dd, \( J = 15.3, 1.1 \) Hz, 1H), 4.79 (tdd, \( J = 8.4, 6.6, 1.0 \) Hz, 1H), 3.95 (dd, \( J = 17.0, 3.4 \) Hz, 2H), 3.81 (t, \( J = 16.9 \) Hz, 2H), 2.87 (s, 3H), 1.46 (s, 9H), 1.40-1.35 (m, 2H). \textsuperscript{13}C NMR (126 MHz, Acetonitrile-\( d_3 \)) \( \delta \) 168.9, 168.8, 166.2, 148.0, 123.5, 81.4, 62.9, 62.8, 60.1, 46.9, 28.2. \textsuperscript{11}B NMR (160 MHz, Acetonitrile-\( d_3 \)) \( \delta \) 11.5.

HRMS: calculated for C\(_{14}\)H\(_{21}\)BClNO\(_6\)Na [M+Na]\(^+\), 368.1043; Found, 368.1049.
Control experiment

The allyl pinacol boronate 14 (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), N-chlorosuccinimide (NCS, 0.22 mmol, 1.1 equiv) and 4 Å MS (20 mg) were added in 3 mL CH3CN. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, the crude product was purified by flash chromatography on silica to afford the pure product 17 (41%) and 18 (28%) as known compounds.

(E)-4,4,5,5-tetramethyl-2-(5-phenylpent-2-en-1-yl)-1,3,2-dioxaborolane (16)

![Chemical structure](image)

1H NMR (400 MHz, Chloroform-d) δ 7.29-7.23 (m, 2H), 7.22-7.12 (m, 3H), 5.58-5.37 (m, 3H), 2.65 (dd, J = 9.1, 6.6 Hz, 3H), 2.37-2.17 (m, 3H), 1.64 (d, J = 6.3 Hz, 3H), 1.24 (s, 12H).

(3-chloropent-4-en-1-yl) benzene (17)

![Chemical structure](image)

1H NMR (400 MHz, Chloroform-d) δ 7.32-7.28 (m, 2H), 7.23-7.19 (m, 3H), 5.92 (ddd, J = 16.9, 10.2, 8.1 Hz, 1H), 5.27 (dd, J = 16.9, 1.0 Hz, 1H), 5.16 (dt, J = 10.1, 0.9 Hz, 1H), 4.32 (q, J = 7.4 Hz, 1H), 2.89-2.62 (m, 2H), 2.16-2.09 (m, 2H).

(E)-(5-chloropent-3-en-1-yl) benzene (18)

![Chemical structure](image)

1H NMR (400 MHz, Chloroform-d) δ 7.29 (tt, J = 7.0, 1.0 Hz, 2H), 7.22-7.13 (m, 3H), 5.87-5.74 (m, 1H), 5.73-5.55 (m, 1H), 4.03 (dd, J = 7.0, 1.0 Hz, 2H), 2.71 (dd, J = 8.9, 6.7 Hz, 2H), 2.46-2.30 (m, 2H).
8. NMR spectrum of starting materials and products
HMBC of 3a (as below) shows a carbon signal peak at 140 ppm while there is no signal peak in $^{13}$C NMR spectrum. Meanwhile there are lots of products showing the same phenomenon.
HMQC of 3k (as below) shows carbon signal peak at 42 ppm while there is no signal peak in $^{13}$C NMR spectrum.
9. References

1. Chen, Y. G.; Shuai, B.; Ma, C.; Zhang, X. J.; Fang, P.; Mei, T. S., Regioselective Ni-Catalyzed Carboxylation of Allylic and Propargylic Alcohols with Carbon Dioxide. *Org. Lett.* 2017, 19, 2969-2972.

2. Aggarwal, V.; Szabó, K.; Dutheuil, G.; Selander, N., Direct Synthesis of Functionalized Allylic Boronic Esters from Allylic Alcohols and Inexpensive Reagents and Catalysts. *Synthesis* 2008, 2008, 2293-2297.

3. Ely, R. J.; Morken, J. P., Regio- and stereoselective Ni-catalyzed 1,4-hydroboration of 1,3-dienes: access to stereodefined (Z)-allylboron reagents and derived allylic alcohols. *J. Am. Chem. Soc.* 2010, 132, 2534-5.

4. Brown, H. C.; Singh, S. M.; Rangaishenvi, M. V., Organoboranes. 46. New Procedures for the Homologation of Boronic Esters: A Critical Examination of the Available Procedures To Achieve Convenient Homologation of Boronic Esters. *J. Org. Chem.* 1986, 51, 3155-3161.

5. Baeckvall, J. E.; Vaagberg, J. O.; Zercher, C.; Genet, J. P.; Denis, A., Stereoselective synthesis of vinylcyclopropanes via palladium-catalyzed reactions. *J. Org. Chem.* 2002, 52, 5430-5435.

6. Zhang, Z.; Wang, F.; Mu, X.; Chen, P.; Liu, G., Copper-catalyzed regioselective fluorination of allylic halides. *Angew. Chem. Int. Ed.* 2013, 52, 7549-53.

7. Fan, W. X.; Li, J. L.; Lv, W. X.; Yang, L.; Li, Q.; Wang, H., Synthesis of fluorinated amphoteric organoborons via iodofluorination of alkynyl and alkenyl MIDA boronates. *Chem. Commun.* 2020, 56, 82-85.

8. Seljestokken, B.; Fiksdahl, A.; Pretzmann, U.; Jensen, A. K.; Thorsen, T. K.; Coppens, P.; Buchardt, O., The Synthesis of (S)-1-Methyl-3-phenylpropylamine by Inversion of Amines. *Acta Chemica Scandinavica* 1993, 47, 1050-1052.