Supporting Information

Palladium-Catalyzed α-Allylation of α-Boryl Aldehydes

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**General Information:** Methylene chloride (DCM), and toluene were purified via solvent purification system. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Acetonitrile (MeCN), and methanol (MeOH) were distilled from 3Å MS, respectively, under nitrogen. All other solvents were of reagent grade quality and dried over 4Å MS prior to use. All reagents were purchased from Sigma-Aldrich and used as received.

**Chromatography:** Flash column chromatography was carried out using Silicycle 230-400 mesh silica gel, or ISCO Teledyne Combiflash Rf 200 Flash system. Thin-layer chromatography (TLC) was performed on Macherey Nagel pre-coated glass backed TLC plates (SIL G/UV254, 0.25 mm) and visualized using a UV lamp (254 nm) KMnO4 or I2 stain in case of no UV activity.

**Nuclear Magnetic Resonance Spectroscopy:** $^1$H NMR and $^{13}$C NMR spectra was recorded on Varian Mercury 400 MHz spectrometer. $^{11}$B NMR were recorded using Bruker 400 MHz spectrometer at 125 MHz and referenced to an external standard of BF$_3$·Et$_2$O ($\delta$ = 0 ppm). $^1$H NMR spectra chemical shifts ($\delta$) are reported in parts per million (ppm) referenced to residual protonated solvent peak (CDCl$_3$, $\delta$ = 7.26, DMSO-d$_6$, $\delta$ = 2.49, acetone-d$_6$ $\delta$ = 2.05). Spectral data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtdd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant ($J$) in Hertz (Hz), and integration. $^{13}$C NMR spectra chemical shifts ($\delta$) are reported in parts per million (ppm) were referenced to carbon resonances in the NMR solvent (CDCl$_3$, $\delta$ = 77.0; DMSO-d$_6$, $\delta$ = 39.5, center line, acetone-d$_6$= 206.2 centre line, 29.8). Carbons exhibiting significant line broadening brought about by boron substituents were not reported (quadrupolar relaxation).

**Mass Spectroscopy:** High resolution mass spectra were obtained on a VG 70- 250S (double focusing) mass spectrometer at 70 eV or on an ABI/Sciex Qstar mass spectrometer with ESI source, MS/MS and accurate mass capabilities.
General procedure for the preparation for the synthesis of α-allyl α-boryl aldehydes:

To an oven dried Teflon lined vial was added activated powdered 4Å molecular sieves (2 equiv. based on the mass of the boryl aldehyde). The reaction vessel was allowed to cool to room temperature under vacuum. α-Boryl aldehyde\(^1\) (1.0 equiv.) and Pd(PPh\(_3\))\(_4\) (5 mol%) were added sequentially. The mixture was then evacuated for approximately 5 minutes and then back filled with nitrogen. THF (0.2 M) was added, followed by allyl alcohol (2.0 equiv.), Et\(_3\)N (1.5 equiv.), and Et\(_3\)B (1.0 M in THF, 3.0 equiv.). The vial was then sealed and then transferred to a preheated 50 °C oil bath (or reaction block). The reaction was stirred for 48 hours at which time the mixture was cooled to room temperature and unreacted Et\(_3\)B was destroyed with the addition of saturated NaHCO\(_3\) solution. The mixture was extracted with EtOAc (3x), the combined organic layers were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), and concentrated \textit{in vacuo}. The resultant residue was purified via silica gel chromatography using hexanes:EtOAc, or hexanes:acetone as eluent. All compounds were isolated as white solids.

\(^1\) Zhi He and Andrei K. Yudin \textit{Journal of the American Chemical Society} 2011 133 (35), 13770-13773
2-allyl-2-phenyl-2-MIDA boryl aldehyde: 78% yield

\[ ^1H \text{ NMR (300 MHz, CDCl}_3\] \delta 9.92 (s, 1H), 7.34 (m, 4H), 7.21 (1H), 5.63 (m, 1H), 5.15 (dd, \( J=1.5 \text{Hz, 15.6Hz, 1H} \)), 5.02 (dd, \( J=0.6 \text{Hz, 9.3Hz, 1H} \)), 4.04 (d, \( J=15.9 \text{Hz, 1H} \)), 3.75 (dd, \( J=4.2 \text{Hz, 12.6 Hz, 2H} \)), 3.39 (d, \( J=16.8 \text{Hz, 1H} \)), 3.12 (m, 2H), 2.56 (s, 3H)

\[ ^{13}C \text{ NMR (75 MHz, CDCl}_3\] \delta 211.3, 166.9, 166.8, 139.2, 133.8, 129.2, 127.6, 126.8, 118.7, 64.2, 64.1, 47.9, 39.4

\[ ^{11}B \text{ NMR (125 MHz, CDCl}_3\] \delta 11.21

HRMS [ESI-MS] \( m/\text{z} \) calculated for (M+H\(^+\))= 316.1350, found=316.1346

R\(_f\) = 0.33 (hexanes:EtOAc, 1:6)

HPLC: rac Chiralcel OD-H: hexanes:iPrOH 50:50, 0.8 ml/min, 220 nm, 13.7 min, 15.0 min

2-methallyl-2-MIDA boryl phenyl acetaldehyde: 70% yield
\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.05 (s, 1H), 7.59 (d, \(J=7.5\) Hz, 2H), 7.30 (t, \(J=7.2\) Hz, 8.1 Hz, 2H), 7.20 (t, \(J=7.2\) Hz, 7.2 Hz, 1H), 4.72 (s, 1H), 4.54 (s, 1H), 3.71 (m, 3H), 3.16 (m, 3H), 2.62 (s, 3H), 1.45 (s, 3H)

\(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 211.3, 166.5, 166.4, 142.1, 139.3, 128.9, 127.8, 126.7, 114.7, 64.1, 64.0, 47.4, 42.0, 24.3

\(^1\)B NMR (125 MHz, CDCl\(_3\)) \(\delta\) 11.08

LRMS [DART-MS] (M+\(\text{NH}_4^+\))= 347.2 HRMS [DART-MS] \(m/z\) calculated for (M+\(\text{NH}_4^+\))= 347.1778, found= 347.1786

R\(_f\): 0.48 (EtOAc)

2-(\(E\))-dienyl-2-phenyl-2-MIDA boryl aldehyde: 70% yield

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.81 (s, 1H), 7.25 (m, 4H), 7.14 (m, 1H), 6.04 (m, 2H), 5.35 (m, 1H), 4.98 (m, 1H), 4.86 (m, 1H), 3.94 (d, \(J=15.4\) Hz, 1H), 3.71 (app q., \(J=8.1\) Hz, 7.5 Hz, 7.5Hz, 2H), 3.32 (d, \(J=16.5\) Hz, 1H), 3.04 (m, 2H), 2.48 (s, 3H)

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 211.2, 167.1, 166.9, 139.1, 136.7, 134.7, 129.6, 129.2, 127.6, 126.9, 116.5, 64.2, 64.1, 47.9, 38.2

\(^1\)B NMR (125 MHz, CDCl\(_3\)) \(\delta\) 11.49

HRMS [ESI-DART] \(m/z\) calculated for (M+H\(^+\))= 342.1526, found=342.1520
Rf: 0.40 (hexanes:EtOAc, 1:3)

2-allyl-2-tolyl-2-MIDA boryl aldehyde: 72% yield

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.94 (s, 1H), 7.28 (d, $J$ = 8.4 Hz, 2H), 7.17 (d, $J$ = 7.8 Hz, 2H), 5.63 (m, 1H), 5.55 (dd, $J$ = 1.5 Hz, 15.3 Hz, 1H), 5.05 (dd, $J$ = 0.6 Hz, 9.3 Hz, 1H), 4.05 (d, $J$ = 16.2 Hz, 1H), 3.80 (dd, $J$ = 3.0 Hz, 13.5 Hz, 3.0 Hz, 2H), 3.41 (d, $J$ = 16.8 Hz, 1H), 3.12 (m, 2H), 2.62 (s, 3H), 2.34 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 211.1, 166.7, 166.5, 136.2, 135.6, 133.9, 133.8, 129.6, 127.3, 118.4, 64.0, 63.9, 47.7, 39.1, 20.8

$^{11}$B NMR (125 MHz, CDCl$_3$) $\delta$ 11.14

HRMS [ESI-MS] $m/z$ calculated for (M+H$^+$) = 330.1512, found = 330.1505

R$_f$ = 0.37 (1:4 hexanes:EtOAc)

2-methallyl-2-tolyl-2-MIDA boryl aldehyde: 86% yield
H NMR (400 MHz, CDCl₃) δ 10.02 (s, 1H), 7.46 (d, J=8 Hz, 2H), 7.10 (d, J=8.4 Hz, 2H), 4.71 (s, 1H), 4.53 (s, 1H), 3.83 (app. d, J=15.2 Hz, 1H), 3.62 (app. t, J=17.2, 20 Hz, 2H), 3.16 (q, 16, 10.4 Hz, 3H), 2.63 (s, 3H), 2.28 (s, 3H), 1.45 (s, 3H)

13C NMR (100 MHz, CDCl₃) δ 211.1, 166.9, 166.8, 144.2, 136.3, 135.9, 129.6, 114.5, 64.0, 63.9, 47.2, 41.8, 24.4, 21.1

HRMS [ESI-MS] m/z calculated for (M+H⁺)= 344.1669, found= 344.1677

Rf: 0.45 (EtOAc)

4-phenyl-2-allyl-2-MIDA boryl aldehyde: 60% yield

H NMR (300 MHz, CDCl₃) δ 9.81 (s, 1H), 7.28 (m, 2H), 7.20 (t, J=5.1 Hz, 7.8 Hz, 3H), 5.98 (m, 1H), 5.24 (d, J= 18.6 Hz, 1H), 5.18 (d, J=10.2 Hz, 1H), 3.73 (s, 3H), 3.00 (s, 3H), 2.67 (m, 2H), 2.52 (m, 2H), 2.16 (qd, J=5.1 Hz, 9Hz, 5.1 Hz, 6.0 Hz, 5.7 Hz, 6.3 Hz, 5.7 Hz, 8.4 Hz, 5.1 Hz, 2H)

13C NMR (75 MHz, CDCl₃) δ 210.5, 165.9, 165.8, 142.1, 134.1, 128.4, 128.3, 126.0, 117.9, 63.2, 46.3, 33.8, 32.7, 30.7, 22.2, 14.3

11B NMR (125 MHz, CDCl₃) δ 10.98

Rf= 0.56 (hexanes:acetone, 1:2)
4-phenyl-2-methallyl-2-MIDA boryl aldehyde: 65% yield

$^1$H NMR (300 MHz, CDCl$_3$) δ 9.91 (s, 1H), 7.34-7.04 (m, 5H), 4.90 (d, $J$=9.9 Hz, 2H), 3.76 (d, $J$= 24.0 Hz, 4H), 3.07 (s, 3H), 2.97-2.54 (m, 4H), 2.11 (qd, $J$=13.8, 2.7 Hz, 1H), 2.04-1.81 (m, 1H), 1.68 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 212.2, 166.7, 166.5, 142.8, 142.4, 128.6, 128.5, 126.1, 115.7, 63.5, 63.2, 46.6, 38.7, 33.3, 31.5, 24.3

$^{11}$B NMR (125 MHz, CDCl$_3$) δ 11.63

HRMS [ESI-MS] $m/z$ calculated for (M+H$^+$)= 358.1814, found= 358.1820

$R_f$= 0.26 (hexanes:EtOAc, 1:6)

(E)-4-phenyl-2-dienyl-2-MIDA boryl aldehyde: 61% yield
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.82 (s, 1H), 7.37 – 7.26 (m, 3H), 7.26 – 7.14 (m, 2H), 6.37 (dt, \(J = 16.8, 10.2\) Hz, 1H), 6.23 (dd, \(J = 15.0, 10.4\) Hz, 1H), 5.84 (dt, \(J = 14.9, 7.4\) Hz, 1H), 5.19 (dd, \(J = 16.8, 1.6\) Hz, 1H), 5.08 (dd, \(J = 10.0, 1.6\) Hz, 1H), 3.87 (dd, \(J = 16.6, 1.8\) Hz, 3H), 3.71 (dd, \(J = 16.5, 14.1\) Hz, 2H), 2.96 (s, 3H), 2.90 – 2.47 (m, 4H), 2.27 – 1.98 (m, 2H).

\(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.4, 128.7, 128.1, 127.4, 65.0, 61.0, 50.3, 32.0, 31.9, 23.7

\(^1\)B NMR (125 MHz, CDCl\(_3\)) \(\delta\) 11.5

HRMS (ESI-MS): \(m/z\) calculated for [M+H\(^+\)] = 370.1825, found 370.1839

Rf: 0.56 (hexanes:acetone, 1:2)

![Structure](image)

2-allyl-2-MIDA boryl hexanaldehyde: 57% yield

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.75 (s, 1H), 5.88 (qd, \(J = 8.1, 8.7, 8\) Hz, 1H), 5.11 (dd, \(J = 15.3, 8.7\) Hz, 2H), 3.73 (s, 3H), 2.97 (s, 3H), 2.56 (dddd, \(J = 6, 9.3, 6, 15.3, 8.1, 7.2, 8.1, 2\) Hz, 2H), 1.87 (m, 2H), 1.27 (m, 4H), 0.88 (t, \(J = 6.6, 7.2\)Hz, 3H)

\(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 211.3, 166.4, 166.2, 134.6, 117.6, 76.8, 63.5, 46.5, 33.8, 30.3, 26.7, 23.7, 14.1

\(^1\)B NMR (125 MHz, CDCl\(_3\)) \(\delta\) 11.7

HRMS [ESI-MS] \(m/z\) calculated for (M+H\(^+\)) = 296.1669, found = 296.1676

Rf = 0.27 (hexanes:EtOAc, 1:4)
2-methallyl-2-MIDA boryl hexanaldehyde: 48% yield

$^1$H NMR (400 MHz, CDCl$_3$) δ 9.88 (s, 1H), 4.85 (s, 1H), 4.77 (s, 1H), 3.78 (m, 4H), 3.08 (s, 3H), 2.81 (d, $J$=14.4 Hz, 1H), 2.58 (d, $J$=14.4 Hz, 1H), 1.86 (dt, $J$=4.0Hz, 9.2 Hz, 8.4 Hz, 5.2 Hz, 1H), 1.69 (m, 1H), 1.67 (s, 3H), 1.44 (m, 4H), 0.90 (t, $J$=7.2 Hz, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 212.9, 166.4, 166.2, 142.5, 115.4, 63.6, 63.4, 46.6, 38.7, 30.7, 27.2, 24.3, 24.0, 14.1

$^{11}$B NMR (125 MHz, CDCl$_3$) δ 11.3

HRMS [ESI-MS] $m/z$ calculated for (M+H$^+$)= 310.1825, found=310.1823

R$_f$= 0.56 (hexanes:acetone, 1:2)

(E)-2-dienyl-2-MIDA boryl hexanaldehyde: 57% yield

$^1$H NMR (300 MHz, CDCl$_3$) δ 9.76 (s, 1H), 6.30 (dt, $J$= 18.5, 10.6 Hz, 2H), 6.10 (t, $J$=12.7 Hz, 2H), 5.68 (dt, $J$= 14.5, 7.1 Hz, 2H), 5.00 (dd, $J$=41.0, 13.4 Hz, 2H), 3.88-3.48 (m, 4H), 2.98 (s, 3H), 2.65-2.24 (m, 2H), 1.80 (dt, $J$=39.6, 13.3 Hz, 2H), 1.21 (dt, $J$=30.2, 9.6 Hz, 6H), 0.89 (t, $J$=6.9 Hz, 3H)
\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \text{) } \delta 210.9, 166.4, 166.2, 136.5, 133.5, 130.2, 116.2, 63.3, 46.3, 32.3, 30.2, 29.7, 26.5, 23.5, 13.9 \]

\[ ^{11}B \text{ NMR (125 MHz, CDCl}_3 \text{) } \delta 11.7 \]

HRMS [ESI-MS] \( m/z \) calculated for (M+H\(^+\))= 322.1825, found= 322.1825

\( R_f= 0.22 \) (hexanes:EtOAc, 1:7)

\[(E)-2\text{-cinnamyl-2-phenyl 2-MIDA boryl aldehyde: 78\% yield}\]

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \text{) } \delta 9.92 \text{ (s, 1H), } 7.50-7.22 \text{ (m, 5H), } 7.21-7.05 \text{ (m, 5H), } 6.42 \text{ (d, } J=15.7\text{Hz, 1H), } 5.89 \text{ (dt, } J=15.1\text{Hz, 7.2Hz, 1H), } 3.96 \text{ (d, } J=15.7\text{Hz, 1H), } 3.67 \text{ (dd, } J=16.0, 7.4\text{ Hz, 2H), } 3.31 \text{ (d, } J=16.5\text{Hz, 1H), } 3.20 \text{ (dd, } J=7.5, 4.1\text{ Hz, 2H), } 2.49 \text{ (s, 3H)} \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \text{) } \delta 211.2, 166.7, 166.4, 139.0, 137/0, 133.4, 132.1, 129.1, 128.5, 128.4, 127.4, 126.7, 126.1, 125.4, 64.0, 38.6, 29.3 \]

\[ ^{11}B \text{ NMR (125 MHz, CDCl}_3 \text{) } \delta 11.7 \]

HRMS [ESI-MS] \( m/z \) calculated for (M+H\(^+\))= 392.1669, found= 392.1659

\( R_f= 0.47 \) (hexanes:acetone, 1:1)
(E)-2-butenyl-2-MIDA phenyl acetaldehyde: 77% yield

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.84 (s, 1H), 7.33-7.10 (m, 5H), 5.48 (ddt, $J$=15.1, 6.4, 1.3 Hz, 1H), 5.18-5.06 (m, 1H), 3.94 (d, $J$=16.0 Hz, 1H), 3.70-3.60 (m, 2H), 3.29 (d, $J$=-16.7Hz, 1H), 3.03-2.94 (m, 2H), 2.50 (s, 3H), 1.47 (dq, $J$=6.5, 1.3Hz, 3H)

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 211.8, 166.9, 166.6, 139.4, 129.4, 129.1, 127.7, 126.7, 126.0, 64.2, 64.1, 47.8, 38.2, 18.1

$^{11}$B NMR (125 MHz, CDCl$_3$) $\delta$ 11.4

HRMS [ESI-MS] $m/z$ calculated for (M+H$^+$)= 330.1507, found= 330.1520

$R_f$= 0.56 (hexanes:acetone, 1:2)

(E)-4-phenyl-2-cinnamyl-2-MIDA boryl aldehyde: 72% yield
1H NMR (400 MHz, acetone-d₆) + 5% impurity δ 9.79 (s, 1H), 7.34 – 7.23 (m, 2H), 7.18 (dd, J = 8.4, 6.8 Hz, 2H), 7.13 – 7.02 (m, 5H), 7.02 – 6.96 (m, 1H), 6.57 – 6.49 (m, 1H), 6.31 (dt, J = 15.7, 7.4 Hz, 1H), 4.16 (dd, J = 17.1, 3.5 Hz, 2H), 3.94 (dd, J = 17.1, 10.3 Hz, 2H), 3.06 (s, 3H), 2.81 (ddd, J = 15.0, 7.2, 1.6 Hz, 1H), 2.74 – 2.61 (m, 2H), 2.48 (td, J = 13.2, 12.6, 5.2 Hz, 1H), 2.11 – 1.94 (m, 2H), 1.92 (h, J = 2.3 Hz, 1H).

13C NMR (75 MHz, CDCl₃) δ 209.2, 168.1, 167.9, 143.8, 138.6, 133.1, 132.7, 129.2, 129.1 128.0, 126.9, 126.5, 64.0, 63.8, 47.1, 33.6, 33.3, 31.6, 29.7

11B NMR (125 MHz, CDCl₃) δ 10.98

HRMS [ESI-MS] m/z calculated for (M+H⁺)= 420.1982, found= 420.1987

Rf= 0.44 (hexanes:acetone, 1:2)

(E)-2-pentenyl-2-MIDA phenyl acetaldehyde: 79% yield

1H NMR (400 MHz, d₆-acetone) +5% impurity δ 10.01 (s, 1H), 7.59-7.43 (m, 2H), 7.43-7.32 (m, 2H), 7.32-7.23 (m, 1H), 5.60 (dtt, J=15.5, 6.5, 1.4 Hz, 1H), 5.34-5.16 (m, 1H), 4.24 (dd, J=23.6, 16.9 Hz, 2H), 3.90 (d, J= 16.8 Hz, 1H), 3.73 (d, J= 17.1 Hz, 1H), 3.15-2.97 (m, 2H), 2.82 (s, 3H), 1.95-1.81 (m, 2H), 0.86 (t, J=7.5 Hz, 3H)

13C NMR (100 MHz, d₆-acetone) δ 209.2, 168.3, 167.9, 140.5, 136.1, 129.2, 129.0, 126.8, 125.6, 64.2, 47.8, 37.7, 26.2, 14.1

11B NMR (125 MHz,d₆-acetone ) δ 11.00

HRMS [ESI-MS] m/z calculated for (M+Na⁺) = 366.1483, found= 366.1491
R_f= 0.46 (hexanes:acetone, 1:1)

(E)-2-cinnamyl-2-MIDA boryl hexanaldehyde: 76% yield

^1^H NMR (400 MHz, d_6^-acetone) δ 9.71 (s, 1H), 7.28-7.11 (m, 4H), 7.11-7.02 (m, 1H), 6.40 (dt, J=15.8, 1.4 Hz, 1H), 6.22 (dt, J=15.8, 7.4 Hz, 1H), 4.1 (dd, J= 17.0, 7.8 Hz, 2H), 3.90 (dd, J=17.0, 9.3 Hz, 2H), 3.02 (s, 3H), 2.72-2.61 (m, 3H), 2.60-2.45 (m, 2H), 1.92 (p, J= 2.2Hz, 1H) 1.84-1.69 (m, 2H), 1.22-1.04 (m, 6H), 0.75 (t, J=7.1 Hz, 3H)

^13^C NMR (100MHz d_6^-acetone) δ 209.5, 168.1, 167.9, 138.7, 132.6, 129.3, 128.2, 127.7, 126.9, 64.0, 63.8, 47.0, 33.2, 27.4, 24.3, 14.2

^11^B NMR (125 MHz, d_6^-acetone) δ 11.04

HRMS [ESI-MS] m/z calculated for (M+H^+)= 372.1982, found= 372.1976

R_f= 0.44 (hexanes:acetone, 1:1)

**Synthesis of α-allyl-α-MIDA boryl phenyl acetic acid**

To a mixture of tBuOH (5mL) and cyclohexene (0.431 ml, 4.2 mmol, 12 equiv), was added α-allyl-α-MIDA boryl phenyl acetaldehyde (0.100 g, 0.36 mmol), NaH_2PO_4 (0.120 g, 0.87 mmol, 2.4 equiv) and NaClO_2 (0.099 g, 0.87 mmol 2.4 equiv.) dissolved in H_2O (5ml). This mixture was warmed to 40 °C overnight and subsequently allowed to cool to room temperature. Brine
was then added followed by extraction with EtOAc (3 x 15mL). The combined organic extracts were concentrated \textit{in vacuo}. To the resulting residue was added 5 x 15 mL benzene and tBuOH was azeotroped off. The crude residue was sufficiently pure for subsequent transformations, but the purity could be further increased by silica gel column chromatography using (EtOAc:MeOH:DCM:AcOH: 45:45:10:0.1) as eluent. Isolated as a clear oil.

\[ \text{MeN} \overset{\text{B}}{\text{O}} \overset{\text{O}}{\text{O}} \overset{\text{CO}_2\text{H}}{\text{Ph}} \]

α-allyl-α-MIDA boryl phenyl acetic acid: 82% yield + 5% impurity

$^1$H NMR (399 MHz, $d_6$-acetone) +5% impurity δ 7.43 – 7.33 (m, 2H), 7.33 – 7.23 (m, 2H), 7.22 – 7.11 (m, 1H), 5.88 (dddd, $J = 17.1$, 10.1, 8.0, 5.8 Hz, 1H), 4.86 (ddt, $J = 17.2$, 2.7, 1.5 Hz, 1H), 4.75 (ddt, $J = 10.2$, 2.4, 1.2 Hz, 1H), 4.30 (d, $J = 17.4$ Hz, 1H), 4.13 (d, $J = 16.3$ Hz, 1H), 4.06 (d, $J = 16.3$ Hz, 1H), 3.93 (d, $J = 17.5$ Hz, 1H), 3.01 (ddt, $J = 14.4$, 5.8, 1.5 Hz, 1H), 2.62 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 180.6, 168.8, 168.2, 140.4, 135.7, 129.0, 127.6, 126.6, 117.7, 76.9, 65.0, 64.4, 48.6, 41.2.

$^{11}$B NMR (125 MHz, CDCl$_3$) δ 11.5

HRMS [ESI-MS] $m/z$ calculated for (M+H$^+$) = 332.1299, found= 332.1304

$R_f$=0.45 (DCM:EtOAc:MeOH:AcOH, 45:45:10:0.1)

**Synthesis of methyl α-allyl-α-MIDA boryl phenyl acetate**

To a flask containing α-allyl-α-MIDA boryl phenyl acetic acid (0.082 g, 0.24 mmol) dissolved in a 1:1 mixture of MeOH:DCM (2 ml) was added TMSCHN$_2$ (0.056 g, 0.48 mmol). This mixture was allowed to stir at room temperature for 2 hours at which point TLC examination confirmed
that the reaction was complete. The solvent was removed \textit{in vacuo} and residue purified via silica gel chromatography to yield a white solid.

\[ 
\text{Methyl 2-allyl-2-MIDA boryl phenyl acetate: 76\% yield} 
\]

\( ^1\text{H NMR (400 MHz, d}_6\text{-acetone) +2\% impurity } \delta \text{ 7.15 (h, } J=6.2\text{Hz, 4H), 7.04 (tt, } J= 7.1, 2.1 \text{ Hz, 1H), 5.66 (ddddd, } J= 17.2, 10.2, 8.05, 5.9 \text{ Hz, 1H), 4.64 (dddt, } J= 10.2, 2.5, 1.2 \text{ Hz, 1H), 4.20 (d, } J= 17.5\text{HZ, 1H), 4.07-3.86 (m, 2H), 3.79 (d, } J= 17.4 \text{ Hz, 1H), 3.66 (s, 3H) 2.86 (ddt, } J= 14.5, 5.9, 1.5 \text{ Hz, 1H), 2.73-2.54 (m, 1H), 2.49 (s, 3H) } \]

\( ^{13}\text{C NMR (100 MHz, d}_6\text{-acetone) } \delta \text{ 177.7, 168.7, 168.0, 142.9, 137.3, 129.1, 128.4, 126.6, 116.5, 65.2, 64.8, 51.9, 48.7} \)

\( ^{11}\text{B NMR (125 MHz, CDCl}_3\text{) } \delta \text{ 11.58} \)

HRMS [ESI-MS] \( m/z \) calculated for (M+H\(^{+}\))= 345.1498, found= 345.1494

\( R_f = 0.56 \) (hexanes:acetone, 1:2)

**Synthesis of 1,3-propyl \( \alpha \)-allyl-\( \alpha \)-MIDA boryl phenyl acetal**

To a stirring flask containing \( \alpha \)-allyl-\( \alpha \)-MIDA-\( \alpha \)-phenyl boryl aldehyde (0.150 g, 0.41 mmol, 1.0 equiv) and THF (12 ml), was added MgSO\(_4\) (5.0 g, 41.6 mmol, 100 equiv), TsOH·H\(_2\)O (0.021 g, 0.1 mmol, 0.25 equiv.) and anhydrous 1,3 propanediol (0.312 g, 0.3 ml, 4.1 mmol, 10 equiv). The mixture was stirred for 72 hours at room temperature at which time the solvent was removed under reduced pressure. The residue was treated with standard workup procedures and purified via column chromatography to yield a white solid.
1,3-propyl α-allyl-α-MIDA boryl phenyl acetal: 76% yield + 10% impurity (86% brsm)

\[ \text{δ 7.69 – 7.62 (m, 2H), 7.30 – 7.22 (m, 2H), 7.17 – 7.10 (m, 1H), 5.70 (ddddd, } J = 17.2, 10.1, 8.2, 6.4 \text{ Hz, 1H), 5.00 – 4.85 (m, 2H), 4.85 (s, 1H), 4.22 – 4.08 (m, 2H), 3.96 – 3.64 (m, 5H), 3.59 (d, } J = 17.4 \text{ Hz, 1H), 2.91 – 2.82 (m, 1H), 2.68 (ddt, } J = 14.0, 8.3, 1.2 \text{ Hz, 1H), 2.24 (s, 3H), 2.16 – 1.99 (m, 1H), 1.42 (ddt, } J = 13.5, 2.6, 1.3 \text{ Hz, 1H).} \]

\[ \text{δ 169.4, 168.5, 143.9, 136.9, 129.6, 128.2, 125.7, 116.6, 106.8, 67.8, 67.3, 64.7, 64.4, 47.9, 26.2} \]

\[ \text{δ 12.02} \]

HRMS [DART] \( m/z \) calculated for \( (M+H^+) = 374.1774 \), found= 374.1776

\( R_f = 0.24 \) (1:4 hexanes:EtoAc)

**Synthesis of 1,3-propyl-α-hydroxy-α-allyl-α-phenyl acetal**

A flask containing 1,3-propyl α-allyl-α-MIDA boryl phenyl acetal (0.124 g, 0.33 mmol, 1.0 equiv.) and THF (5 mL) was cooled to 0 °C in an ice bath. To the stirring mixture was added dropwise 1.0 M NaOH (0.165 ml, 1.65 mmol, 5 equiv.) followed by the dropwise addition of 30 % \( \text{H}_2\text{O}_2 \) (0.96 mL, 3.3 mmol, 10 equiv.) the mixture was stirred overnight warming to room temperature at which point TLC examination of the reaction showed consumption of the starting material. The reaction mixture was diluted with 5 mL \( \text{H}_2\text{O} \), extracted with EtoAc (3 x 10 mL),
dried with anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified via silica gel chromatography to yield the benzylic alcohol as a clear oil.

α-allyl-β-1,3-dioxanyl-benzyl alcohol: 92 % yield

**1H NMR (300 MHz, Chloroform-d)**  δ 7.46 – 7.40 (m, 2H), 7.30 – 7.23 (m, 2H), 7.21 – 7.15 (m, 3H), 5.53 (ddt, J = 17.2, 10.1, 7.1 Hz, 1H), 5.04 – 4.89 (m, 2H), 4.56 (s, 1H), 4.08 (ddddd, J = 9.8, 6.7, 4.1, 1.7 Hz, 2H), 3.69 (tdd, J = 11.8, 5.6, 2.6 Hz, 2H), 2.70 (s, 1H), 2.64 (dt, J = 7.2, 1.3 Hz, 2H), 2.12 – 1.93 (m, 1H), 1.26 (ddt, J = 13.6, 2.7, 1.3 Hz, 1H)

**13C NMR (100 MHz, cdcl₃)**  δ 151.1, 133.2, 127.7, 126.8, 126.1, 118.3, 104.4, 67.1, 67.1, 41.5, 25.6

HRMS [DART] m/z calculated for (M+Na⁺) = 252.1599, found = 252.1598 R f = 0.65 (1:1 hexanes:EtOAc)
NMR Spectra of Novel Compounds
Table 2, Entry 5 racemic

Table 2, Entry 5. Enantio-enriched