

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 3 Å MS, respectively, under nitrogen. All other solvents were of reagent grade quality and dried over 4 Å 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 R_f 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.

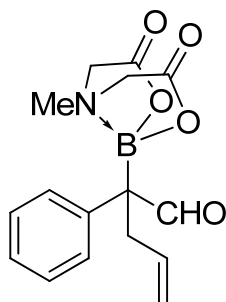
Nuclear Magnetic Resonance Spectroscopy: ¹H NMR and ¹³C NMR spectra was recorded on Varian Mercury 400 MHz spectrometer. ¹¹B NMR were recorded using Bruker 400 MHz spectrometer at 125 MHz and referenced to an external standard of BF₃·Et₂O (δ = 0 ppm). ¹H NMR spectra chemical shifts (δ) are reported in parts per million (ppm) referenced to residual protonated solvent peak (CDCl₃, δ = 7.26, DMSO-*d*₆, δ = 2.49, acetone-*d*₆ δ = 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, dtd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant (*J*) in Hertz (Hz), and integration. ¹³C NMR spectra chemical shifts (δ) are reported in parts per million (ppm) were referenced to carbon resonances in the NMR solvent (CDCl₃, δ = 77.0; DMSO-*d*₆, δ = 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 aldehyde¹ (1.0 equiv.) and Pd(PPh₃)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.), Et₃N (1.5 equiv.), and Et₃B (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 Et₃B was destroyed with the addition of saturated NaHCO₃ solution. The mixture was extracted with EtOAc (3x), the combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, and concentrated *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. ¹ Zhi He and Andrei K. Yudin *Journal of the American Chemical Society* **2011** 133 (35), 13770-13773



2-allyl-2-phenyl-2-MIDA boryl aldehyde: 78% yield

^1H NMR (300 MHz, CDCl_3) δ 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)

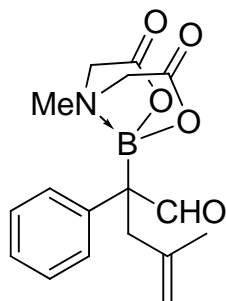
^{13}C NMR (75 MHz, CDCl_3) δ 211.3, 166.9, 166.8, 139.2, 133.8, 129.2, 127.6, 126.8, 118.7, 64.2, 64.1, 47.9, 39.4

^{11}B NMR (125 MHz, CDCl_3) δ 11.21

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

$R_f=0.33$ (hexanes:EtOAc, 1:6)

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



2-methylallyl-2-MIDA boryl phenyl acetaldehyde: 70% yield

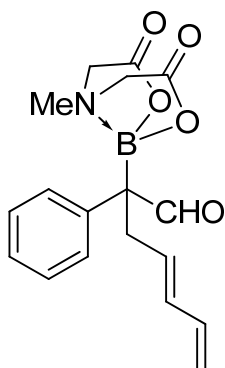
^1H NMR (300 MHz, CDCl_3) δ 10.05 (s, 1H), 7.59 (d, $J=7.5\text{Hz}$, 2H), 7.30 (t, $J=7.2\text{Hz}$, 8.1Hz, 2H), 7.20 (t, $J=7.2\text{Hz}$, 7.2Hz, 1H), 4.72 (s, 1H), 4.54 (s, 1H), 3.71 (m, 3H), 3.16 (m, 3H), 2.62 (s, 3H), 1.45 (s, 3H)

^{13}C NMR (75 MHz, CDCl_3) δ 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

^{11}B NMR (125 MHz, CDCl_3) δ 11.08

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

R_f : 0.48 (EtOAc)



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

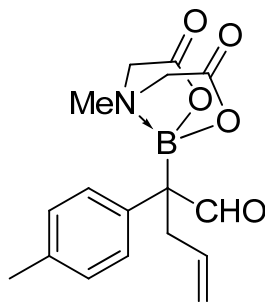
^1H NMR (300 MHz, CDCl_3) δ 9.81 (s, 1H), 7.25 (m, 4H), 7.14 (m, 1H), 6.04 (m, 2H), 5.35 (m, 1H), 4.98 (m, 1H), 4.86 (m, 1H), 3.94 (d, $J=15.4\text{ Hz}$, 1H), 3.71 (app q., $J=8.1\text{ Hz}$, 7.5 Hz, 7.5Hz, 2H), 3.32 (d, $J=16.5\text{ Hz}$, 1H), 3.04 (m, 2H), 2.48 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 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

^{11}B NMR (125 MHz, CDCl_3) δ 11.49

HRMS [ESI-DART] m/z calculated for ($\text{M}+\text{H}^+$)= 342.1526, found=342.1520

Rf: 0.40 (hexanes:EtOAc, 1:3)



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

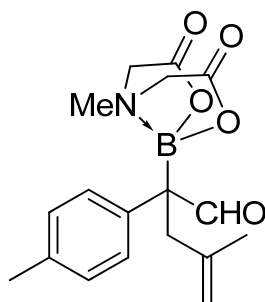
^1H NMR (300 MHz, CDCl_3) δ 9.94 (s, 1H), 7.28 (d, $J=8.4\text{Hz}$, 2H), 7.17 (d, $J=7.8\text{Hz}$, 2H), 5.63 (m, 1H), 5.55 (dd, $J=1.5\text{Hz}$, 15.3Hz, 1H), 5.05 (dd, $J=0.6\text{Hz}$, 9.3Hz, 1H), 4.05 (d, $J=16.2\text{Hz}$, 1H), 3.80 (dd, $J=3.0\text{Hz}$, 13.5 Hz, 3.0Hz, 2H), 3.41 (d, $J=16.8\text{Hz}$, 1H), 3.12 (m, 2H), 2.62 (s, 3H), 2.34 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 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) δ 11.14

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

$R_f=0.37$ (1:4 hexanes:EtOAc)



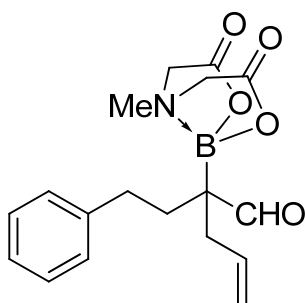
2-methylallyl-2-tolyl-2-MIDA boryl aldehyde: 86% yield

^1H NMR (400 MHz, CDCl_3) δ 10.02 (s, 1H), 7.46 (d, $J=8\text{Hz}$, 2H), 7.10 (d, $J=8.4\text{Hz}$, 2H), 4.71 (s, 1H), 4.53 (s, 1H), 3.83 (app. d, $J=15.2\text{ Hz}$, 1H), 3.62 (app. t, $J=17.2, 20\text{ Hz}$, 2H), 3.16 (q, 16, 10.4Hz, 3H), 2.63 (s, 3H), 2.28 (s, 3H), 1.45 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) 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 $(\text{M}+\text{H}^+)=344.1669$, found= 344.1677

R_f : 0.45 (EtOAc)



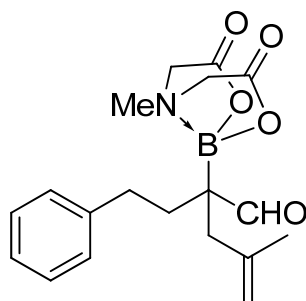
4-phenyl-2-allyl-2-MIDA boryl aldehyde: 60% yield

^1H NMR (300 MHz, CDCl_3) δ 9.81 (s, 1H), 7.28 (m, 2H), 7.20 (t, $J=5.1\text{Hz}$, 7.8 Hz, 3H), 5.98 (m, 1H), 5.24 (d, $J=18.6\text{ Hz}$, 1H), 5.18 (d, $J=10.2\text{ Hz}$, 1H), 3.73 (s, 3H), 3.00 (s, 3H), 2.67 (m, 2H), 2.52 (m, 2H), 2.16 (qd, $J=5.1\text{Hz}$, 9Hz, 5.1Hz, 6.0Hz, 5.7 Hz, 6.3 Hz, 5.7 Hz, 8.4 Hz, 5.1 Hz, 2H)

^{13}C NMR (75 MHz, CDCl_3) 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

^{11}B NMR (125 MHz, CDCl_3) δ 10.98

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



4-phenyl-2-methylallyl-2-MIDA boryl aldehyde: 65% yield

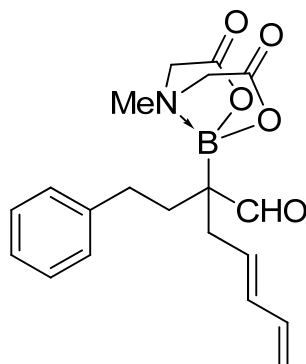
^1H NMR (300 MHz, CDCl_3) δ 9.91 (s, 1H), 7.34 -7.04 (m, 5H), 4.90 (d, $J=9.9$ Hz, 2H), 3.76 (d, $J=24.0$ Hz, 4H), 3.07 (s, 3H), 2.97-2.54 (m, 4H), 2.11 (qd, $J=13.8, 2.7$ Hz, 1H), 2.04-1.81 (m, 1H), 1.68 (s, 3H)

^{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 $(\text{M}+\text{H}^+)=358.1814$, found= 358.1820

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



(*E*)-4-phenyl-2-dienyl-2-MIDA boryl aldehyde: 61% yield

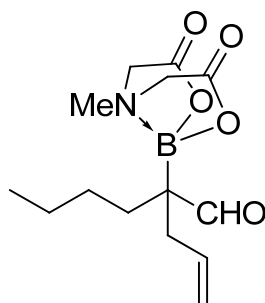
^1H NMR (400 MHz, CDCl_3) δ 9.82 (s, 1H), 7.37 – 7.26 (m, 3H), 7.26 – 7.14 (m, 2H), 6.37 (dt, J = 16.8, 10.2 Hz, 1H), 6.23 (dd, J = 15.0, 10.4 Hz, 1H), 5.84 (dt, J = 14.9, 7.4 Hz, 1H), 5.19 (dd, J = 16.8, 1.6 Hz, 1H), 5.08 (dd, J = 10.0, 1.6 Hz, 1H), 3.87 (dd, J = 16.6, 1.8 Hz, 3H), 3.71 (dd, J = 16.5, 14.1 Hz, 2H), 2.96 (s, 3H), 2.90 – 2.47 (m, 4H), 2.27 – 1.98 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ 141.4, 128.7, 128.1, 127.4, 65.0, 61.0, 50.3, 32.0, 31.9, 23.7

^{11}B NMR (125 MHz, CDCl_3) δ 11.5

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

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



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

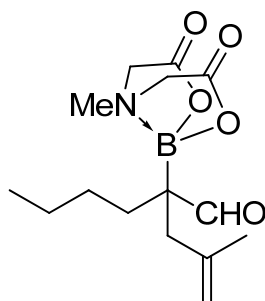
^1H NMR (300 MHz, CDCl_3) δ 9.75 (s, 1H), 5.88 (qd, J =8.1, 8.7, 8Hz, 1H), 5.11 (dd, J =15.3, 8.7 Hz, 2H), 3.73 (s, 3H), 2.97 (s, 3H), 2.56 (dddd, J =6, 9.3, 6, 15.3, 8.1, 7.2, 8.1, 2H), 1.87 (m, 2H), 1.27 (m, 4H), 0.88 (t, J =6.6, 7.2Hz, 3H)

^{13}C NMR (75 MHz, CDCl_3) δ 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

^{11}B NMR (125 MHz, CDCl_3) δ 11.7

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

Rf = 0.27 (hexanes:EtOAc, 1:4)



2-methylallyl-2-MIDA boryl hexanaldehyde: 48% yield

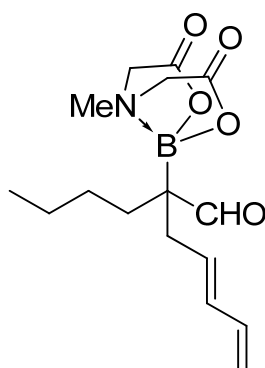
^1H NMR (400 MHz, CDCl_3) δ 9.88 (s, 1H), 4.85 (s, 1H), 4.77 (s, 1H), 3.78 (m, 4H), 3.08 (s, 3H), 2.81 (d, $J=14.4$ Hz, 1H), 2.58 (d, $J=14.4$ Hz, 1H), 1.86 (dt, $J=4.0\text{Hz}$, 9.2 HZ, 4.4Hz, 8.4 Hz, 5.2 Hz, 1H), 1.69 (m, 1H), 1.67 (s, 3H), 1.44 (m, 4H), 0.90 (t, $J=7.2$ Hz, 3H)

^{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 $(\text{M}+\text{H}^+)=310.1825$, found=310.1823

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



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

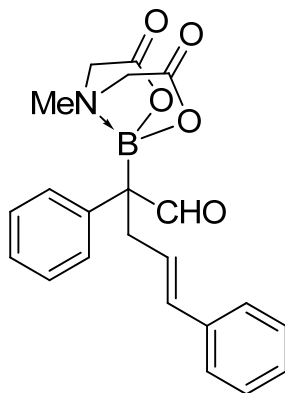
^1H NMR (300 MHz, CDCl_3) δ 9.76 (s, 1H), 6.30 (dt, $J=18.5, 10.6$ Hz, 2H), 6.10 (t, $J=12.7$ Hz, 2H), 5.68 (dt, $J=14.5, 7.1$ Hz, 2H), 5.00 (dd, $J=41.0, 13.4$ Hz, 2H), 3.88-3.48 (m, 4H), 2.98 (s, 3H), 2.65-2.24 (m, 2H), 1.80 (dt, $J=39.6, 13.3$ Hz, 2H), 1.21 (dt, $J=30.2, 9.6$ Hz, 6H), 0.89 (t, $J=6.9$ Hz, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 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 NMR (125 MHz, CDCl_3) δ 11.7

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

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



(*E*)-2-cinnamyl-2-phenyl 2-MIDA boryl aldehyde: 78% yield

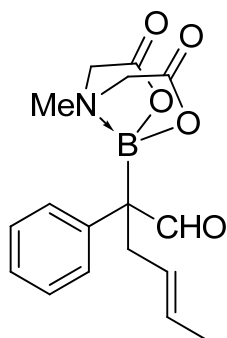
^1H NMR (300 MHz, CDCl_3) δ 9.92 (s, 1H), 7.50-7.22 (m, 5H), 7.21-7.05 (m, 5H), 6.42 (d, $J=15.7\text{Hz}$, 1H), 5.89 (dt, $J=15.1\text{Hz}$, 7.2Hz, 1H), 3.96 (d, $J=15.7\text{Hz}$, 1H), 3.67 (dd, $J=16.0$, 7.4 Hz, 2H), 3.31 (d, $J=16.5\text{Hz}$, 1H), 3.20 (dd, $J=7.5$, 4.1 Hz, 2H), 2.49 (s, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 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 NMR (125 MHz, CDCl_3) δ 11.7

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

$R_f=0.47$ (hexanes:acetone, 1:1)



(*E*)-2-butenyl-2-MIDA phenyl acetaldehyde: 77% yield

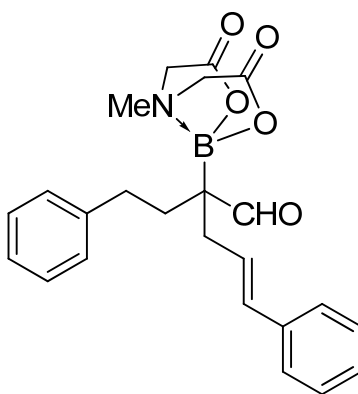
^1H NMR (300 MHz, CDCl_3) δ 9.84 (s, 1H), 7.33-7.10 (m, 5H), 5.48 (ddt, $J=15.1, 6.4, 1.3$ Hz, 1H), 5.18-5.06 (m, 1H), 3.94 (d, $J=16.0$ Hz, 1H), 3.70-3.60 (m, 2H), 3.29 (d, $J=-16.7$ Hz, 1H), 3.03-2.94 (m, 2H), 2.50 (s, 3H), 1.47 (dq, $J=6.5, 1.3$ Hz, 3H)

^{13}C NMR (75 MHz, CDCl_3) δ 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) δ 11.4

HRMS [ESI-MS] m/z calculated for ($\text{M}+\text{H}^+$)= 330.,1507, found= 330.1520

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



(*E*)-4-phenyl-2-cinnamyl-2-MIDA boryl aldehyde: 72% yield

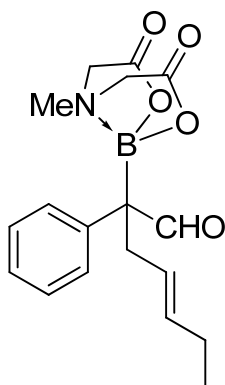
^1H NMR (400 MHz, acetone- d_6) + 5% impurity δ 9.79 (s, 1H), 7.34 – 7.23 (m, 2H), 7.18 (dd, J = 8.4, 6.8 Hz, 2H), 7.13 – 7.02 (m, 5H), 7.02 – 6.96 (m, 1H), 6.57 – 6.49 (m, 1H), 6.31 (dt, J = 15.7, 7.4 Hz, 1H), 4.16 (dd, J = 17.1, 3.5 Hz, 2H), 3.94 (dd, J = 17.1, 10.3 Hz, 2H), 3.06 (s, 3H), 2.81 (ddd, 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).

^{13}C NMR (75 MHz, CDCl_3) 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

^{11}B NMR (125 MHz, CDCl_3) δ 10.98

HRMS [ESI-MS] m/z calculated for $(\text{M}+\text{H}^+)$ = 420.1982, found = 420.1987

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



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

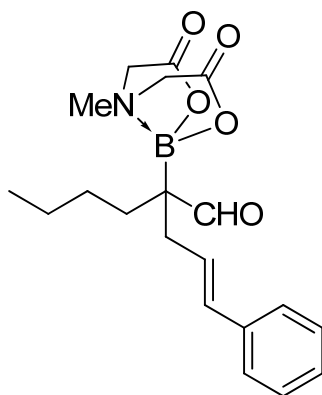
^1H NMR (400 MHz, d_6 -acetone) +5% impurity δ 10.01 (s, 1H), 7.59-7.43 (m, 2H), 7.43-7.32 (m, 2H), 7.32-7.23 (m, 1H), 5.60 (dtt, J = 15.5, 6.5, 1.4 Hz, 1H), 5.34-5.16 (m, 1H), 4.24 (dd, J = 23.6, 16.9 Hz, 2H), 3.90 (d, J = 16.8 Hz, 1H), 3.73 (d, J = 17.1 Hz, 1H), 3.15-2.97 (m, 2H), 2.82 (s, 3H), 1.95-1.81 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H)

^{13}C NMR (100 MHz, d_6 -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

^{11}B NMR (125 MHz, d_6 -acetone) δ 11.00

HRMS [ESI-MS] m/z calculated for $(\text{M}+\text{Na}^+)$ = 366.1483, found = 366.1491

$R_f = 0.46$ (hexanes:acetone, 1:1)



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

^1H 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, $J=2.2$ Hz, 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

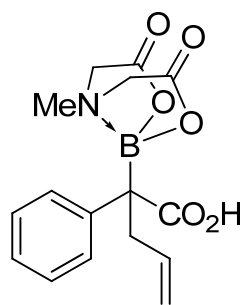
HRMS [ESI-MS] m/z calculated for $(\text{M}+\text{H}^+)$ = 372.1982, found = 372.1976

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

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

To a mixture of *t*BuOH (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 *in vacuo*. To the resulting residue was added 5 x 15 mL benzene and *t*BuOH 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.



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

^1H 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

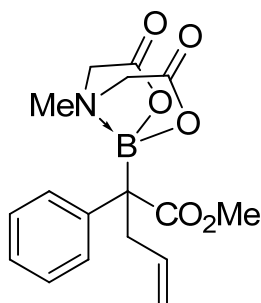
HRMS [ESI-MS] m/z calculated for $(\text{M}+\text{H}^+)$ = 332.1299, found= 332.1304

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 *in vacuo* and residue purified via silica gel chromatography to yield a white solid.



Methyl 2-allyl-2-MIDA boryl phenyl acetate: 76% yield

^1H NMR (400 MHz, d_6 -acetone) +2% impurity δ 7.15 (h, $J=6.2\text{Hz}$, 4H), 7.04 (tt, $J= 7.1, 2.1$ Hz, 1H), 5.66 (dddd, $J= 17.2, 10.2, 8.05, 5.9$ Hz, 1H), 4.64 (ddt, $J= 10.2, 2.5, 1.2$ Hz, 1H), 4.20 (d, $J=17.5\text{Hz}$, 1H), 4.07-3.86 (m, 2H), 3.79 (d, $J=17.4$ Hz, 1H), 3.66 (s, 3H) 2.86 (ddt, $J= 14.5, 5.9, 1.5$ Hz, 1H), 2.73-2.54 (m, 1H), 2.49 (s, 3H)

^{13}C NMR (100 MHz, d_6 -acetone) δ 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

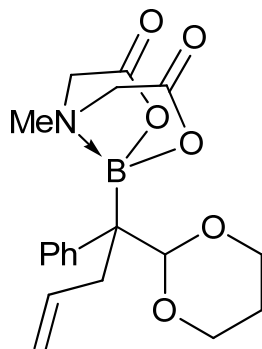
^{11}B NMR (125 MHz, CDCl_3) δ 11.58

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

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

Synthesis of 1,3-propyl α -allyl- α -MIDA boryl phenyl acetal

To a stirring flask containing α -allyl- α -MIDA- α -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), $\text{TsOH}\cdot\text{H}_2\text{O}$ (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)

^1H NMR (300 MHz, CD_3CN) + 10 % impurity δ 7.69 – 7.62 (m, 2H), 7.30 – 7.22 (m, 2H), 7.17 – 7.10 (m, 1H), 5.70 (dddd, $J = 17.2, 10.1, 8.2, 6.4$ 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, $J = 17.4$ Hz, 1H), 2.91 – 2.82 (m, 1H), 2.68 (ddt, $J = 14.0, 8.3, 1.2$ Hz, 1H), 2.24 (s, 3H), 2.16 – 1.99 (m, 1H), 1.42 (ddt, $J = 13.5, 2.6, 1.3$ Hz, 1H).

^{13}C NMR (101 MHz, CD_3CN) 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

^{11}B NMR (128 MHz, CD_3CN) δ 12.02

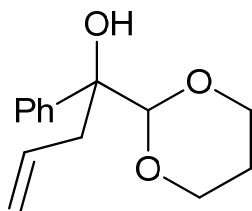
HRMS [DART] m/z calculated for $(\text{M}+\text{H}^+)$ = 374.1774, found= 374.1776

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 % H_2O_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 H_2O , extracted with EtOAc (3 x 10 mL),

dried with anhydrous Na_2SO_4 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 (dddd, 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)

^{13}C NMR (100 MHz, cdCl_3) 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 $(\text{M}+\text{Na}^+)$ = 252.1599, found = 252.1598 R_f = 0.65 (1:1 hexanes:EtOAc)

NMR Spectra of Novel Compounds

