SUPPORTING INFORMATION

Cu-Catalyzed Regioselective Borylcyanation of 1,3-Dienes

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- General. Infrared (IR) spectra were recorded on a BRUKER TENSOR 27 FT-IR spectrometer, \( v_{\text{max}} \) in cm\(^{-1}\). Bands are characterized as broad (br), strong (s), medium (m), and weak (w). \(^1\)H NMR spectra were recorded on an Agilent 400 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl\(_3\): \( \delta \) 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). \(^13\)C NMR spectra were recorded on an Agilent 100 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl\(_3\): \( \delta \) 77.00 ppm). EI-HRMS and ESI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier and a Thermo Fisher Scientific LTQ FT Ultra, respectively. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N\(_2\) in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Anhydrous tetrahydrofuran (Energy Chemical Co.Ltd.) were used without further purification. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific) in air.

- Reagents and Ligands:

Copper chloride: purchased from Strem Chemicals Inc. and used as received.
Ligand (4a-4h): purchased from Tokyo Chemical Industry Co., Ltd. or Sino compound Co., Ltd. and used as received.

Lithium tert-butoxide: purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Bis(pinacolato)diboron: purchased from Dalian AllyChem Co.Ltd. and purified by recrystallization in n-pentane.

4A molecular sieve: purchased from Energy Chemical Co.Ltd. and dried over by oven.

Tetrahydrofuran and Dichloromethane: purchased from Adamas Reagent, Ltd. and used as received.

Sodium perborate tetrahydrate: purchased from Energy Chemical Co.Ltd. and used as received.

1-Substituted 1,3-dienes: prepared according to a previous reported procedure.1,2

2-Substituted 1,3-dienes: prepared according to a previous reported procedure.3

1,2-Disubstituted 1,3-dienes: prepared according to a previous reported procedure.4

1,3-Disubstituted 1,3-dienes: prepared according to a previous reported procedure.5

1,1-Disubstituted 1,3-dienes: prepared with the wittig reaction between acetophenone and allyl phosphorus ylide.

NCTS: prepared according to a previous reported procedure.6

Diisobutylaluminium hydride: purchased from Adamas Reagent, Ltd. and used as received.

Nickel(II) chloride hexahydrate: purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Sodium borohydride: purchased from Energy Chemical Co.Ltd. and used as received.

Di-tert-butyl decarbonate: purchased from Energy Chemical Co.Ltd. and used as received.

Methanol: purchased from Adamas Reagent, Ltd. and used as received.

Furan: purchased from Tokyo Chemical Industry Co., Ltd. and distilled by CaH2.

N-Bromosuccinimide: purchased from Tokyo Chemical Industry Co., Ltd. and purified by recrystallization in water.

Vinylmagnesium bromide: purchased from Energy Chemical Co.Ltd. and used as received.

■ General Experimental Procedure for Cu-Catalyzed Regioselective Borylcyanation of 1,3-dienes.
In a N₂-filled glove-box, an oven-dried vial (8 mL, 61 × 16.6 mm) with a magnetic stir bar was charged with phosphine ligand 4h (5.8 mg, 0.01 mmol, 5 mol %), CuCl (1.0 mg, 0.01 mmol, 5 mol%), LiOt-Bu (24.0 mg, 0.30 mmol, 1.5 equiv) and tetrahydrofuran (thf, 2 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 20 min under an atmosphere of N₂. Diene 1a (26.0 mg, 0.20 mmol, 1.0 equiv) and 2 (81.7 mg, 0.30 mmol, 1.5 equiv) were added. The resulting solution was allowed to stir at 22 °C for 14 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et₂O (3 × 2 mL). The filtrate was concentrated in vacuo to provide yellow oil. The crude was dissolved in tetrahydrofuran (thf, 1.0 mL), NaBO₃•4H₂O (123.1 mg, 0.80 mmol, 4.0 equiv) and H₂O (1 mL) were added. The resulting mixture was allowed to stir at 22 °C for 3 h. The aqueous layer was washed with Et₂O (3 × 2 mL). The combined organic layers were concentrated in vacuo to provide colorless oil, which was purified by silica gel chromatography (dichloromethane : diethyl ether = 30:1) to afford 3a (26.0 mg, 75% yield) as colorless oil.

Characterization of product.

(E)-2-(Hydroxymethyl)-4-phenylbut-3-enenitrile (3a). IR (neat): 3440 (br), 2921 (w), 2844 (w), 2249 (w), 1645 (w), 1490 (w), 1398 (w), 1369 (w), 1288 (w), 1182 (w), 1048 (s), 968 (s), 858 (w), 749 (s), 693 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.28 (m, 5H), 6.80 (d, J = 16.0 Hz, 1H), 6.06 (dd, J = 16.0, 6.8 Hz, 1H), 3.88 (d, J = 5.6 Hz, 2H), 3.66-3.61 (m, 1H), 2.67 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 135.4, 135.3, 128.7, 128.5, 126.6, 119.0, 118.8, 63.3, 38.0; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₁H₁₂ON: 174.0913 m/z, found: 174.0914 m/z.

(E)-4-(4-Fluorophenyl)-2-(hydroxymethyl)but-3-enenitrile (3b). IR (neat): 3422 (br), 2945 (w), 2886 (w), 2247 (w), 1600 (m), 1507 (s), 1467 (w), 1413 (w), 1299 (w), 1226 (s), 1159 (m), 1056 (s), 966 (s), 852 (m), 812 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.34 (m, 2H), 7.05-7.00 (m, 2H), 6.76 (d, J = 16.0 Hz, 1H), 5.98 (dd, J = 16.0, 6.4 Hz, 1H), 3.89-3.87 (m, 2H), 3.66-3.61 (m, 1H), 2.67 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 162.7 (d, J = 247.0 Hz), 134.2, 131.5 (d, J = 3.3 Hz), 128.2 (d, J = 8.1 Hz), 118.8 (d, J = 2.3 Hz), 118.7, 115.7 (d, J = 21.7 Hz), 63.3, 38.0; ¹⁹F NMR (376 MHz, CDCl₃): δ -112.8; HRMS (ESI⁺) [M-H]⁻: Calcd for C₁₁H₉ONF: 190.0674 m/z, found: 190.0675 m/z.

(E)-4-(4-(Dimethylamino)phenyl)-2-(hydroxymethyl)but-3-enenitrile (3c). IR (neat): 3391 (br), 2918 (w), 2803 (w), 2240 (w), 1646 (w), 1609 (s), 1519 (s), 1477 (w), 1350 (s), 1223 (w), 1164 (w), 1055 (m), 968 (w), 812 (s), 749 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.27 (d, J = 8.4 Hz, 2H), 6.70-6.66 (m, 3H), 5.80 (dd, J = 16.0, 6.8 Hz, 1H), 3.83 (d, J = 6.0 Hz, 2H), 3.60-3.56 (m, 1H), 2.97 (s, 6H); ¹³C NMR (100 MHz, CDCl₃):
MHz, CDCl$_3$): $\delta$ 150.6, 135.4, 127.7, 123.5, 119.2, 114.0, 112.2, 63.6, 40.3, 38.1; HRMS (ESI$^+$) [M+H$^+$]: Caled for C$_{13}$H$_{17}$ON$^2$: 217.1335 m/z, found: 217.1337 m/z.

(E)-2-(Hydroxymethyl)-4-(4-methoxyphenyl)but-3-enenitrile (3d). IR (neat): 3243 (br), 2917 (w), 2838 (w), 2243 (w), 1602 (s), 1432 (m), 1247 (s), 1175 (s), 1058 (s), 1028 (s), 970 (s), 848 (m), 807 (s), 747 (w) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 6.72 (d, $J = 16.0$ Hz, 1H), 5.90 (dd, $J = 16.0, 6.8$ Hz, 1H), 3.85 (d, $J = 6.0$ Hz, 2H), 3.81 (s, 3H), 3.63-3.58 (m, 1H), 2.61 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.8, 134.8, 128.1, 127.9, 119.0, 116.7, 114.1, 63.4, 55.3, 38.0; HRMS (ESI$^+$) [M+H$^+$]: Caled for C$_{13}$H$_{17}$ON$^2$: 204.1021 m/z, found: 204.1021 m/z.

(E)-2-(Hydroxymethyl)-4-(2-methoxyphenyl)but-3-enenitrile (3e). IR (neat): 3421 (br), 3032 (w), 2922 (w), 2246 (w), 1603 (w), 1458 (w), 1336 (m), 1275 (m), 1261 (w), 1193 (s), 1044 (s), 968 (s), 775 (s), 692 (s), 646 (w) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.29-7.24 (m, 1H), 7.07 (d, $J = 16.0$ Hz, 1H), 6.95-6.91 (m, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 6.11 (dd, $J = 16.0, 7.2$ Hz, 1H), 3.88-3.85 (m, 5H), 3.65-3.60 (m, 1H), 2.55 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.9, 130.8, 129.6, 127.5, 124.3, 120.6, 119.8, 119.0, 110.9, 63.4, 55.4, 38.5; HRMS (ESI$^+$) [M+H$^+$]: Caled for C$_{12}$H$_{14}$O$_2$N: 204.1019 m/z, found: 204.1021 m/z.

(E)-2-(Hydroxymethyl)-4-(o-tolyl)but-3-enenitrile (3f). IR (neat): 3420 (br), 3037 (w), 2922 (w), 2246 (w), 1603 (w), 1458 (w), 1336 (w), 1275 (w), 1261 (w), 1193 (s), 1044 (s), 968 (s), 775 (s), 692 (s), 646 (w) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.26-7.18 (m, 3H), 7.11 (d, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 16.0$ Hz, 1H), 6.04 (dd, $J = 16.0, 6.8$ Hz, 1H), 3.90-3.87 (m, 2H), 3.66-3.61 (m, 1H), 2.39-2.32 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.3, 135.5, 135.2, 129.3, 128.6, 127.3, 123.7, 118.9, 118.8, 63.3, 38.1, 21.3; HRMS (ESI$^+$) [M-H$^-$]: Caled for C$_{12}$H$_{12}$ON: 186.0924 m/z, found:186.0929 m/z.

(E)-2-(Hydroxymethyl)-4-(3-methoxyphenyl)but-3-enenitrile (3g). IR (neat): 3420 (br), 3032 (w), 2922 (w), 2246 (w), 1603 (w), 1458 (w), 1336 (m), 1275 (m), 1261 (w), 1193 (s), 1044 (s), 968 (s), 775 (s), 692 (s), 646 (w) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.28-7.24 (m, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.93-6.90 (m, 1H), 6.85 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.77 (d, $J = 16.0$ Hz, 1H), 6.05 (dd, $J = 16.0, 6.8$ Hz, 1H), 3.90-3.87 (m, 2H), 3.66-3.61 (m, 1H), 2.46-2.43 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.8, 136.7, 135.3, 129.3, 128.6, 127.3, 118.9, 118.8, 63.3, 55.3, 38.0; HRMS (ESI$^+$) [M-H$^-$]: Caled for C$_{12}$H$_{12}$ON: 202.0874 m/z, found: 202.0878 m/z.

(E)-2-(Hydroxymethyl)-4-(naphthalen-2-yl)but-3-enenitrile (3h). IR (neat): 3420 (br), 3032 (w), 2922 (w), 2246 (w), 1603 (w), 1458 (w), 1336 (m), 1275 (m), 1261 (w), 1193 (s), 1044 (s), 968 (s), 775 (s), 687 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82-7.79 (m, 3H), 7.76 (s, 1H), 7.56 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.51-7.46 (m, 2H), 6.96 (d, $J = 16.0$ Hz, 1H), 6.17 (dd, $J = 16.0, 6.4$ Hz, 1H), 3.92 (d, $J = 5.6$ Hz, 2H), 3.71-3.66 (m, 1H), 2.50 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 135.4, 133.3, 133.2,
132.7, 128.4, 128.1, 127.7, 127.2, 126.5, 126.4, 123.1, 119.3, 118.8, 63.3, 38.1; HRMS (ESI\textsuperscript{-}) [M-H]\textsuperscript{+}: Calcd for C\textsubscript{15}H\textsubscript{12}ON: 222.0924 m/z, found: 222.0923 m/z.

\((E)-4-(Furan-3-yl)-2-(hydroxymethyl)but-3-enenitrile (3i).\) IR (neat): 3458 (br), 2921 (w), 2851 (w), 2245 (w), 1737 (w), 1636 (w), 1464 (w), 1424 (w), 1347 (w), 1226.2, 118.8, 118.5, 107.2, 63.3, 37.9; HRMS (ESI\textsuperscript{+}) [M-H]\textsuperscript{+}: Calcd for C\textsubscript{9}H\textsubscript{8}O\textsubscript{2}N: 162.0561 m/z, found: 162.0562 m/z.

\((E)-2-(Hydroxymethyl)-4-(thiophen-3-yl)but-3-enenitrile (3j).\) IR (neat): 3409 (br), 3099 (w), 2979 (w), 2851 (w), 2846 (w), 2245 (w), 1737 (w), 1651 (w), 1465 (w), 118.8, 118.5, 107.2, 63.3, 37.9; HRMS (ESI\textsuperscript{+}) [M+H]\textsuperscript{+}: Calcd for C\textsubscript{9}H\textsubscript{10}ONS: 180.0478 m/z, found: 180.0479 m/z.

\((E)-Tert-butyl 3-(3-cyano-4-hydroxybut-1-en-1-yl)-1H-pyrrole-1-carboxylate (3k).\) IR (neat): 3408 (br), 2979 (w), 2851 (w), 2245 (w), 1737 (w), 1636 (w), 1464 (w), 1424 (w), 1347 (w), 1226.2, 118.8, 118.5, 107.2, 63.3, 37.9; HRMS (ESI\textsuperscript{+}) [M+H]\textsuperscript{+}: Calcd for C\textsubscript{14}H\textsubscript{19}O\textsubscript{3}N\textsubscript{2}: 263.1390 m/z, found: 263.1393 m/z.

\((E)-4-Cyclohexyl-2-(hydroxymethyl)but-3-enenitrile (3l).\) IR (neat): 3413 (br), 2979 (w), 2851 (w), 2245 (w), 1737 (w), 1636 (w), 1464 (w), 1424 (w), 1347 (w), 1226.2, 118.8, 118.5, 107.2, 63.3, 37.9; HRMS (ESI\textsuperscript{+}) [M+H]\textsuperscript{+}: Calcd for C\textsubscript{14}H\textsubscript{19}O\textsubscript{3}N\textsubscript{2}: 263.1390 m/z, found: 263.1393 m/z.

\(2-(Hydroxymethyl)-3-methylbut-3-enenitrile (5a).\) IR (neat): 3419 (br), 2979 (w), 2851 (w), 2245 (w), 1737 (w), 1636 (w), 1464 (w), 1424 (w), 1347 (w), 1226.2, 118.8, 118.5, 107.2, 63.3, 37.9; HRMS (ESI\textsuperscript{+}) [M+H]\textsuperscript{+}: Calcd for C\textsubscript{6}H\textsubscript{9}ON: 111.0682 m/z, found: 111.0680 m/z.
2-(Hydroxymethyl)-7-methyl-3-methyleneoct-6-enenitrile (5b). IR (neat): 3424 (br), 3088 (w), 2966 (w), 2915 (w), 2857 (w), 2246 (w), 1648 (w), 1377 (w), 1185 (w), 1066 (s), 1045 (s) 907 (s), 827 (m), 751 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.24 (s, 1H), 5.13 (s, 1H), 5.07 (t, J = 6.0 Hz, 1H), 3.86-3.78 (m, 2H), 3.40 (t, J = 6.0 Hz, 1H), 2.43 (s, 1H), 2.21-2.02 (m, 4H), 1.68 (s, 3H), 1.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.8, 132.9, 122.7, 119.2, 115.5, 62.2, 41.4, 33.9, 26.1, 25.6, 17.7; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₁H₁₈ON: 180.1383 m/z, found:180.1383 m/z.

5-(3,3-Dimethyloxiran-2-yl)-2-(hydroxymethyl)-3-methylenepentanenitrile (5c). IR (neat): 3422 (br), 3091 (w), 2964 (w), 2928 (w), 2884 (w), 2245 (w), 1648 (w), 1454 (w), 1380 (m), 1251 (w), 1114 (m), 1069 (s), 910 (s), 867 (m), 820 (w), 798 (w), 733 (w), 675 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.27-5.25 (m, 1H), 5.16 (s, 1H), 3.89-3.77 (m, 2H), 3.45-3.38 (m, 1H), 3.11 (s, 1H), 2.77-2.73 (m, 1H), 2.39-2.20 (m, 2H), 1.87-1.76 (m, 1H), 1.69-1.59 (m, 1H), 1.30 (s, 3H), 1.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.4, 139.2, 119.1, 119.0, 116.2, 115.9, 63.7, 63.6, 62.3, 62.2, 58.9, 58.8, 41.5, 41.1, 31.1, 30.9, 26.9, 26.8, 24.7, 18.7; HRMS (ESI⁺) [M+NH₄]⁺: Calcd for C₁₁H₂₁O₂N₂: 213.1598 m/z, found: 213.1595 m/z.

2-(Hydroxymethyl)-3-methylene-5-(2,2,5,5-tetramethyl-1,3-dioxolan-4-yl)pentanenitrile (5d). IR (neat): 3447 (br), 2980 (w), 2936 (w), 2860 (w), 2836 (w), 2247 (w), 1649 (w), 1459 (w), 1372 (m), 1216 (m), 1111 (m), 1065 (m), 1001 (s), 909 (s), 855 (m), 823 (w), 730 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.28-5.27 (m, 1H), 5.15 (s, 1H), 3.85 (d, J = 6.0 Hz, 2H), 3.69-3.67 (m, 1H), 3.44-3.40 (m, 1H), 2.79 (s, 1H), 2.44-2.11 (m, 2H), 1.74-1.52 (m, 2H), 1.40 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H), 1.09 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.6, 139.5, 119.1, 115.8, 115.7, 106.9, 82.5, 82.4, 80.2, 80.1, 62.2, 41.6, 41.4, 31.4, 31.3, 28.4, 27.2, 27.1, 26.8, 25.9, 25.8, 24.8, 22.9; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₄H₂₄O₃N: 254.1751 m/z, found: 254.1750 m/z.

2-(Hydroxymethyl)-6-((4-methoxybenzyl)oxy)-3-methylenehexanenitrile (5e). IR (neat): 3426 (br), 3001 (w), 2936 (w), 2860 (w), 2245 (w), 1611 (w), 1512 (w), 1245 (s), 1174 (m), 1031 (m), 901 (s), 818 (m), 729 (s), 646 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.23 (s, 1H), 5.11 (s, 1H), 4.42 (s, 2H), 3.80 (s, 3H), 3.80-3.73 (m, 2H), 3.48 (t, J = 6.0 Hz, 2H), 3.36 (t, J = 6.0 Hz, 2H), 2.79 (s, 1H), 2.27-2.08 (m, 2H), 1.82-1.74 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 159.2, 139.7, 130.1, 129.4, 119.2, 115.4, 115.7, 106.9, 68.9, 62.1, 55.2, 41.3, 30.6, 27.5; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₆H₂₅O₃N₂: 293.1860 m/z, found: 293.1865 m/z.

6-((Tert-butyldimethylsilyl)oxy)-2-(hydroxymethyl)-3-methylenehexanenitrile (5f). IR (neat): 3429 (br), 3001 (w), 2966 (w), 2885 (w), 2856 (w), 2246 (w), 1649 (w), 1502 (w), 1253 (m), 1100 (m), 909 (w), 833 (s), 774 (s), 732 (w), 662 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.26 (s, 1H), 5.13 (s, 1H), 3.88-3.80 (m, 2H), 3.64 (t, J = 6.0 Hz, 2H), 3.42 (t, J = 6.0 Hz, 1H), 2.52 (s, 1H), 2.27-2.10 (m, 2H), 1.74-1.67 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 139.8, 119.2, 115.5,
62.2, 62.0, 41.4, 30.4, 30.1, 25.9, 18.3, -5.4; HRMS (ESI⁺) [M+H]+: Calcd for C₁₄H₂₈O₂NSi: 270.1884 m/z, found: 270.1877 m/z.

Tert-butyl 5-cyano-6-hydroxy-4-methylenehexanoate (5g). IR (neat): 3467 (br), 2979 (w), 2933 (w), 2250 (w), 1718 (m), 1650 (w), 1391 (w), 1253 (w), 1147 (s), 1067 (w), 950 (s), 844 (w), 729 (s), 647 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 5.26 (s, 1H), 5.08 (s, 1H), 3.88 (d, J = 5.6 Hz, 2H), 3.40 (t, J = 6.0 Hz, 2H); HRMS (ESI⁺) [M+NH₄]+: Calcd for C₁₂H₂₃O₃N₂: 243.1703 m/z, found: 243.1694 m/z.

2-(Hydroxymethyl)-3-phenylbut-3-enenitrile (5h). (3.5:1 mixture of two regioisomers). IR (neat): 3427 (br), 2937 (w), 2886 (w), 2248 (w), 1630 (w), 1493 (w), 1410 (w), 1187 (w), 1064 (s), 1029 (s), 915 (m), 772 (m), 700 (s), 682, 62.5, 53.2, 40.7; HRMS (ESI⁺) [M+H]+: Calcd for C₁₁H₁₂O₃N: 174.0913 m/z, found: 174.0913 m/z.

(E)-2-(Hydroxymethyl)-3-methyl-4-phenylbut-3-enenitrile (6a). IR (neat): 3417 (br), 3027 (w), 2945 (w), 2886 (w), 2246 (w), 1900 (w), 1403 (w), 1187 (w), 1064 (s), 1029 (s), 915 (m), 772 (m), 700 (s), 62.1 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.32 (m, 2H), 7.29-7.23 (m, 3H), 6.64 (s, 1H), 4.00-3.90 (m, 2H), 3.58 (t, J = 6.4 Hz, 1H), 2.13 (s, 3H); HRMS (ESI⁺) [M+H]+: Calcd for C₁₂H₁₄O₃N: 188.1070 m/z, found: 188.1072 m/z.

(E)-2-(Hydroxymethyl)-3-methyl-4-(o-tolyl)but-3-enenitrile (6b). IR (neat): 3424 (br), 2938 (w), 2887 (w), 2246 (w), 1601 (w), 1443 (w), 1246 (w), 1168 (w), 1044 (s), 971 (w), 844 (w), 742 (m), 697 (s), 513 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.0 Hz, 1H), 7.33-7.27 (m, 3H), 6.61 (s, 1H), 3.95-3.88 (m, 2H), 3.58 (t, J = 6.4 Hz, 1H), 2.54 (s, 3H), 2.36 (s, 3H), 1.98 (d, J = 1.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 136.2, 130.9, 128.8, 128.5, 128.2, 119.1, 62.2, 44.5, 16.2; HRMS (ESI⁺) [M+H]+: Calcd for C₁₃H₁₅O₃: 201.1154 m/z, found: 201.1150 m/z.

(E)-4-(2-Bromophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6c). IR (neat): 3417 (br), 3024 (w), 2920 (w), 2887 (w), 2244 (w), 1601 (w), 1443 (w), 1244 (w), 1168 (w), 1044 (s), 971 (w), 844 (w), 742 (m), 697 (s), 513 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, J = 8.0 Hz, 1H), 7.33-7.27 (m, 3H), 6.61 (s, 1H), 3.95-3.88 (m, 2H), 3.58 (t, J = 6.4 Hz, 1H), 2.54 (s, 3H), 2.36 (s, 3H), 1.98 (d, J = 1.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 136.2, 130.9, 128.8, 128.5, 128.2, 119.1, 62.2, 44.5, 16.2; HRMS (ESI⁺) [M+H]+: Calcd for C₁₃H₁₅O₃Br: 265.0102 m/z, found: 265.0100 m/z.
(E)-4-(4-Bromophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6d). IR (neat): 3417 (br), 2941 (w), 2885 (w), 2245 (w), 1650 (w), 1586 (w), 1482 (m), 1398 (w), 1308 (w), 1066 (s), 1007 (s), 872 (m), 811 (m), 662 (w), 509 (s) cm⁻¹; $^1$H NMR (400 MHz, CDCl₃): δ 7.47 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.56 (s, 1H), 3.92 (d, $J = 6.0$ Hz, 2H), 2.57 (s, 1H), 1.94 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃): δ 135.0, 131.4, 130.5, 129.8, 129.5, 121.2, 118.9, 62.12, 44.4, 16.3; HRMS (EI⁺) [M⁺]: Calcd for: C₁₂H₁₂OBrN: 265.0102 m/z, found: 265.0090 m/z.

(E)-4-(4-Fluorophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6e). IR (neat): 3419 (br), 2946 (w), 2888 (w), 2246 (w), 1599 (m), 1506 (s), 1443 (w), 1404 (w), 1224 (s), 1159 (m), 1044 (s), 873 (m), 828 (s), 669 (w), 522 (s) cm⁻¹; $^1$H NMR (400 MHz, CDCl₃): δ 7.24-7.18 (m, 2H), 7.07-7.00 (m, 2H), 6.58 (s, 1H), 3.94-3.87 (m, 2H), 3.52 (t, $J = 6.4$ Hz, 1H), 2.90 (s, 1H), 1.93 (d, $J = 1.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃): δ 161.7 (d, $J = 246.1$ Hz), 132.2 (d, $J = 3.4$ Hz), 130.5 (d, $J = 8.0$ Hz), 129.8 (d, $J = 2.3$ Hz), 128.6 (d, $J = 1.5$ Hz), 119.1, 115.2 (d, $J = 21.5$ Hz), 62.2, 44.4, 16.1; $^{19}$F NMR (376 MHz, CDCl₃): δ -114.3; HRMS (ESI⁺) [M+H⁺]: Calcd for: C₁₂H₁₃FON: 206.0976 m/z, found: 206.0976 m/z.

(E)-2-(Hydroxymethyl)-3-methyl-4-(3-(trifluoromethyl)phenyl)but-3-enenitrile (6f). IR (neat): 3431 (br), 2941 (w), 2248 (w), 1442 (w), 1326 (s), 1208 (w), 1164 (m), 1121 (s), 1069 (s), 909 (m), 802 (m), 701 (m), 657 (w), 576 (w), 519 (w) cm⁻¹; $^1$H NMR (400 MHz, CDCl₃): δ 7.55-7.40 (m, 4H), 6.67 (s, 1H), 3.98-3.91 (m, 2H), 3.56 (t, $J = 6.4$ Hz, 1H), 2.79 (s, 1H), 1.96 (d, $J = 0.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃): δ 136.9, 132.1, 130.7, 130.6 (q, $J = 32.0$ Hz), 129.4, 128.8, 125.5 (q, $J = 3.8$ Hz), 124.0 (q, $J = 271.0$ Hz), 123.9 (q, $J = 3.8$ Hz), 118.9, 62.2, 44.4, 16.1; $^{19}$F NMR (376 MHz, CDCl₃): δ -62.7; HRMS (ESI⁺) [M-H⁻]: Calcd for C₁₃H₁₁ONF₃: 254.0798 m/z, found: 254.0797 m/z.

(E)-4-(3-Chlorophenyl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6g). IR (neat): 3418 (br), 2941 (w), 2248 (w), 1442 (w), 1326 (s), 1208 (w), 1164 (m), 1121 (s), 1069 (s), 909 (m), 802 (m), 701 (m), 657 (w), 576 (w), 519 (w) cm⁻¹; $^1$H NMR (400 MHz, CDCl₃): δ 7.32-7.22 (m, 3H), 7.12 (d, $J = 7.2$ Hz, 1H), 6.59 (s, 1H), 3.98-3.91 (m, 2H), 3.56 (t, $J = 6.4$ Hz, 1H), 2.79 (s, 1H), 1.96 (d, $J = 0.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl₃): δ 136.9, 132.1, 130.7, 130.6 (q, $J = 32.0$ Hz), 129.4, 128.8, 125.5 (q, $J = 3.8$ Hz), 124.0 (q, $J = 271.0$ Hz), 123.9 (q, $J = 3.8$ Hz), 118.9, 62.2, 44.4, 16.2; $^{19}$F NMR (376 MHz, CDCl₃): δ -62.7; HRMS (ESI⁺) [M-H⁺]: Calcd for: C₁₂H₁₁OClN: 221.0607 m/z, found: 221.0606 m/z.

(E)-Methyl 3-(3-cyano-4-hydroxy-2-methylbut-1-en-1-yl)benzoate (6h). IR (neat): 3466 (br), 2950 (w), 2887 (w), 2245 (w), 1713 (s), 1438 (m), 1348 (m), 1287 (s), 1208 (s), 1108 (m), 1044 (m), 920 (w), 859 (w), 750 (s), 707 (w), 535 (w) cm⁻¹; $^1$H NMR (400 MHz, CDCl₃): δ 7.94-7.88 (m, 2H), 7.44-7.39 (m, 2H), 6.65 (s, 1H), 3.97-3.91 (m, 2H), 3.55 (t, $J = 6.4$ Hz, 1H), 2.90 (t, $J = 5.6$ Hz, 1H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, CDCl₃): δ 167.0, 136.5, 133.3, 130.1, 130.0, 129.9, 128.9, 128.4, 128.3, 118.8, 62.2, 52.2, 44.3, 16.2; HRMS (ESI⁺) [M+NH₄⁺]: Calcd for C₁₄H₁₉O₃N₂: 263.1390 m/z, found: 263.1391 m/z.
(E)-2-(Hydroxymethyl)-4-(3-methoxyphenyl)-3-methylbut-3-enenitrile (6i). IR (neat): 3449 (br), 2942 (w), 2839 (w), 2245 (w), 1583 (m), 1483 (m), 1376 (w), 1263 (m), 1160 (m), 1040 (s), 882 (m), 782 (m), 693 (m), 559 (w), 513 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.24 (m, 1H), 6.87-6.78 (m, 3H), 6.62 (s, 1H), 3.96-3.89 (m, 2H), 3.81 (s, 3H), 3.53 (t, J = 6.4 Hz, 1H), 2.40 (s, 1H), 1.98 (d, J = 1.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.4, 137.5, 130.8, 129.3, 128.8, 121.3, 119.0, 114.5, 112.7, 62.2, 55.2, 44.4, 16.3; HRMS (ESI⁺) [M⁺]: Calcd for: C₁₃H₁₅O₂N: 217.1103 m/z, found: 217.1098 m/z.

(E)-2-(Hydroxymethyl)-3-methyl-4-(thiophen-3-yl)but-3-enenitrile (6j). IR (neat): 3446 (br), 3095 (w), 2943 (w), 2890 (w), 2245 (w), 1448 (w), 1391 (m), 1342 (w), 1183 (m), 1062 (s), 1020 (s), 878 (m), 771 (s), 629 (m), 532 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.31 (dd, J = 5.2, 3.2 Hz, 1H), 7.21 (d, J = 1.6 Hz, 1H), 7.10 (d, J = 5.2 Hz, 1H), 6.58 (s, 1H), 3.92-3.85 (m, 2H), 3.51 (t, J = 6.4 Hz, 1H), 2.60 (s, 1H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.2, 128.3, 127.4, 125.4, 125.1, 123.9, 119.0, 62.2, 44.5, 16.7; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₀H₁₂O₂N: 194.0634 m/z, found: 194.0635 m/z.

(E)-4-(Furan-2-yl)-2-(hydroxymethyl)-3-methylbut-3-enenitrile (6k). IR (neat): 3434 (br), 2923 (s), 2855 (m), 2216 (w), 1712 (m), 1659 (m), 1442 (m), 1389 (m), 1255 (w), 1059 (s), 1015 (s), 801 (w), 747 (w), 597 (w), 567 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, J = 1.6 Hz, 1H), 6.42 (dd, J = 3.2, 1.6 Hz, 1H), 6.40 (s, 1H), 6.34 (d, J = 3.2 Hz, 1H), 3.92-3.85 (m, 2H), 3.49 (t, J = 6.4 Hz, 1H), 2.43 (s, 1H), 2.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 151.5, 142.1, 126.2, 119.2, 118.8, 111.3, 110.6, 62.2, 44.6, 16.8; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₀H₁₂O₂N: 178.0863 m/z, found: 178.0864 m/z.

(E)-2-(Hydroxymethyl)-3-methyl-4-(thiophen-2-yl)but-3-enenitrile (6l). IR (neat): 3445 (br), 3101 (w), 2943 (w), 2890 (w), 2242 (w), 1638 (w), 1399 (m), 1182 (m), 1059 (s), 1014 (s), 881 (m), 848 (m), 817 (m), 703 (s), 563 (s), 525 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.31 (d, J = 4.8 Hz, 1H), 7.06-7.02 (m, 2H), 6.74 (s, 1H), 3.90-3.83 (m, 2H), 3.51 (t, J = 6.4 Hz, 1H), 2.88 (t, J = 6.0 Hz, 1H), 2.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.0, 128.4, 126.9, 126.0, 126.0, 123.9, 118.9, 62.1, 44.7, 16.9; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₀H₁₀O₂N: 192.0489 m/z, found: 192.0488 m/z.

(E)-Tert-butyl-2-(3-cyano-4-hydroxy-2-methylbut-1-en-1-yl)-1H-pyrrole-1-carboxylate (6m). IR (neat): 3359 (br), 2925 (m), 2854 (w), 2248 (w), 1731 (m), 1665 (m), 1462 (w), 1369 (w), 1235 (m), 1153 (s), 1064 (w), 1023 (w), 842 (w), 768 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.23-7.20 (m, 1H), 6.80 (s, 1H), 6.21-6.14 (m, 2H), 3.94-3.83 (m, 2H), 3.51 (t, J = 6.4 Hz, 1H), 3.06 (s, 1H), 1.95 (s, 3H), 1.57 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 149.2, 129.9, 127.6, 122.6, 121.5, 118.7, 114.7, 110.7, 84.2, 61.9, 43.5, 27.9, 16.3; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₅H₂₁O₂N₂: 277.1547 m/z, found: 277.1549 m/z.

(E)-2-Methyl-4-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7a). IR (neat): 2978 (w), 2933 (w), 2236 (w), 1450 (w), 1407 (w), 1384 (m), 1323 (m), 1262 (m), 1226 (m), 1196 (m), 1152 (w), 1066 (s), 1029 (w), 986 (w), 932 (w), 842 (w), 619 (w), 434 (w), 290 (s), 250 (w), 214 (w), 155 (w), 144 (w), 124 (w), 104 (w), 80 (w), 60 (w), 40 (w), 20 (w); HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₅H₂₁O₂N₂: 277.1547 m/z, found: 277.1549 m/z.
1362 (s), 1333 (s), 1253 (w), 1215 (w), 1139 (s), 1074 (w), 966 (s), 878 (w), 845 (s), 748 (s), 693 (w) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.42-7.29 (m, 4H), 7.29-7.23 (m, 1H), 6.76 (d, $J = 16.0$ Hz, 1H), 6.16 (d, $J = 16.0$ Hz, 1H), 1.62 (s, 3H), 1.42 (s, 2H), 1.25 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.0, 131.0, 129.3, 128.6, 127.9, 126.5, 123.6, 83.7, 36.2, 27.5, 24.8, 24.7; HRMS (ESI$^+$) [M+NH$_4$]$^+$: Calcd for C$_{18}$H$_{28}$O$_2$N$_2$: 314.2275 m/z, found: 314.2274 m/z.

(E)-2-(Hydroxymethyl)-4-(4-methoxyphenyl)-2-methylbut-3-enenitrile (7b). IR (neat): 3442 (br), 2936 (w), 2877 (w), 2837 (w), 2239 (w), 1606 (s), 1510 (s), 1420 (m), 1240 (s), 1175 (s), 1053 (s), 1030 (s), 966 (s), 849 (w), 809 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33 (d, $J = 8.8$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 16.0$ Hz, 1H), 5.81 (d, $J = 16.0$ Hz, 1H), 3.81 (s, 3H), 3.69 (d, $J = 4.0$ Hz, 2H), 2.44 (s, 1H), 1.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.7, 132.4, 128.1, 127.9, 123.5, 114.1, 68.5, 55.3, 42.8, 21.9; HRMS (ESI$^+$) [M+H]$^+$: Calcd for C$_{13}$H$_{16}$O$_2$N: 218.1176 m/z, found: 218.1177 m/z.

(E)-2-(Hydroxymethyl)-4-(3-methoxyphenyl)-2-methylbut-3-enenitrile (7c). IR (neat): 3448 (br), 2938 (w), 2877 (w), 2837 (w), 2241 (w), 1599 (w), 1581 (s), 1489 (m), 1458 (m), 1358 (m), 1265 (m), 1159 (m), 1047 (s), 966 (m), 932 (m), 809 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.25 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 10.0$ Hz, 1H), 6.99-6.92 (m, 1H), 6.82 (d, $J = 16.0$ Hz, 1H), 5.96 (d, $J = 16.0$ Hz, 1H), 3.81 (s, 3H), 3.70 (d, $J = 4.0$ Hz, 2H), 2.68 (s, 1H), 1.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.8, 136.8, 132.8, 129.7, 126.2, 119.2, 114.1, 111.9, 68.3, 55.2, 42.8, 21.8; HRMS (ESI$^+$) [M+H]$^+$: Calcd for C$_{13}$H$_{16}$O$_2$N: 218.1176 m/z, found: 218.1177 m/z.

(E)-4-(3-Fluorophenyl)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7d). IR (neat): 2979 (w), 2931 (w), 2236 (w), 1611 (w), 1583 (m), 1446 (w), 1362 (s), 1334 (s), 1267 (m), 1217 (m), 1139 (s), 965 (s), 875 (m), 845 (s), 777 (m), 688 (m) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.25 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 10.0$ Hz, 1H), 6.99-6.92 (m, 1H), 6.73 (d, $J = 16.0$ Hz, 1H), 6.17 (d, $J = 16.0$ Hz, 1H), 1.51 (s, 3H), 1.41 (s, 2H), 1.25 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.8, 141.9, 132.8, 129.2, 128.9, 126.3, 119.2, 118.2, 83.8, 58.3, 42.8, 21.8; HRMS (ESI$^+$) [M+H]$^+$: Calcd for C$_{13}$H$_{16}$O$_2$N: 218.1176 m/z, found: 218.1177 m/z.

(E)-4-(3-Chlorophenyl)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7e). IR (neat): 2978 (w), 2933 (w), 2236 (w), 1611 (w), 1583 (m), 1446 (w), 1362 (s), 1334 (s), 1267 (m), 1217 (m), 1139 (s), 965 (s), 875 (m), 845 (s), 777 (m), 688 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.33-7.25 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 7.07 (d, $J = 10.0$ Hz, 1H), 6.99-6.92 (m, 1H), 6.73 (d, $J = 16.0$ Hz, 1H), 6.17 (d, $J = 16.0$ Hz, 1H), 1.51 (s, 3H), 1.41 (s, 2H), 1.25 (s, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.8, 141.9, 132.8, 129.2, 128.9, 126.3, 119.2, 118.2, 83.8, 58.3, 42.8, 21.8; HRMS (ESI$^+$) [M+H]$^+$: Calcd for C$_{13}$H$_{16}$O$_2$N: 218.1176 m/z, found: 218.1177 m/z.
124.9, 123.3, 83.8, 36.3, 27.4, 24.8, 24.7; HRMS (ESI\(^+\)) [M+H]\(^+\): Calcd for C\(_{14}\)H\(_{24}\)O\(_2\)NCl: 331.1619 m/z; found: 331.1615 m/z.

**(E)-2-Methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(3-(trifluoromethyl)phenyl)but-3-enenitrile (7f).** IR (neat): 2980 (w), 2935 (w), 2237 (w), 1446 (w), 1365 (m), 1332 (s), 1260 (w), 1204 (w), 1165 (m), 1127 (s), 968 (m), 876 (m), 846 (m), 797 (s), 698 (w) cm\(^{-1}\); \(\text{\(^1\)H NMR (400 MHz, CDCl}_3\):} \(\delta\) 7.63 (s, 1H), 7.55-7.49 (m, 2H), 7.48-7.41 (m, 1H), 6.79 (d, \(J = 16.0\) Hz, 1H), 6.25 (d, \(J = 16.0\) Hz, 1H), 1.62 (s, 3H), 1.42 (s, 2H), 1.25 (s, 12H); \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\):} \(\delta\) 136.9, 133.1, 131.0 (q, \(J = 32.2\) Hz), 129.9, 129.1, 128.1, 124.4 (q, \(J = 3.7\) Hz), 124.0 (q, \(J = 270.9\) Hz), 123.3, 123.0 (q, \(J = 3.8\) Hz), 83.8, 36.3, 27.4, 24.8, 24.7; \(\text{\(^{19}\)F NMR (376 MHz, CDCl}_3\):} \(\delta\) -62.9; HRMS (ESI\(^-\)) [M+NH\(_4\)]\(^+\): Calcd for C\(_{18}\)H\(_{29}\)F\(_2\)O\(_2\)BF\(_3\): 382.2149 m/z; found: 382.2148 m/z.

**(E)-Methyl 3-(3-cyano-4-hydroxy-3-methylbut-1-en-1-yl)benzoate (7g).** IR (neat): 3474 (br), 2920 (w), 2874 (w), 2240 (w), 1700 (s), 1588 (w), 1432 (m), 1295 (s), 1205 (s), 1107 (s), 1083 (s), 968 (s), 808 (w), 746 (s), 647 (m) cm\(^{-1}\); \(\text{\(^1\)H NMR (400 MHz, CDCl}_3\):} \(\delta\) 8.06 (s, 1H), 7.92 (d, \(J = 7.6\) Hz, 1H), 7.54 (d, \(J = 8.0\) Hz, 1H), 7.42-7.36 (m, 1H), 6.87 (d, \(J = 16.0\) Hz, 1H), 6.07 (d, \(J = 16.0\) Hz, 1H), 3.91 (s, 3H), 3.73 (d, \(J = 4.8\) Hz, 2H), 2.85 (s, 1H), 1.53 (s, 3H); \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\):} \(\delta\) 166.8, 135.8, 131.8, 131.3, 130.5, 129.2, 128.8, 128.4, 127.4, 127.3, 121.5, 68.3, 52.2, 42.9, 21.8; HRMS (ESI\(^+\)) [M+H]\(^+\): Calcd for C\(_{14}\)H\(_{16}\)O\(_3\)N: 246.1125 m/z; found: 246.1127 m/z.

**(E)-3-(3-Cyano-3-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)-N-methoxy-N-methylbenzamide (7h).** IR (neat): 2977 (w), 2934 (w), 2235 (w), 1642 (m), 1601 (w), 1579 (w), 1362 (s), 1259 (w), 1218 (w), 1140 (s), 968 (m), 877 (w), 846 (m), 799 (s), 735 (m) cm\(^{-1}\); \(\text{\(^1\)H NMR (400 MHz, CDCl}_3\):} \(\delta\) 7.66 (s, 1H), 7.53 (d, \(J = 7.6\) Hz, 1H), 7.42 (d, \(J = 7.6\) Hz, 1H), 7.37-7.31 (m, 1H), 6.74 (d, \(J = 16.0\) Hz, 1H), 6.18 (d, \(J = 16.0\) Hz, 1H), 3.53 (s, 3H), 3.34 (s, 3H), 1.59 (s, 3H), 1.38 (s, 2H), 1.22 (s, 12H); \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\):} \(\delta\) 169.5, 135.9, 134.4, 132.0, 128.6, 128.5, 128.3, 127.4, 126.1, 123.4, 83.7, 61.0, 36.2, 27.4, 24.7, 24.6; HRMS (ESI\(^-\)) [M+H]\(^+\): Calcd for C\(_{21}\)H\(_{30}\)O\(_4\)N\(_2\): 384.2329 m/z; found: 384.2331 m/z.

**(E)-4-(2-Fluorophenyl)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7i).** IR (neat): 2979 (w), 2934 (w), 2206 (w), 1488 (w), 1455 (w), 1365 (s), 1337 (m), 1260 (w), 1226 (m), 1141 (s), 1096 (m), 969 (m), 846 (m), 799 (m), 757 (s) cm\(^{-1}\); \(\text{\(^1\)H NMR (400 MHz, CDCl}_3\):} \(\delta\) 7.42-7.37 (m, 1H), 7.25-7.19 (m, 1H), 7.12-7.07 (m, 1H), 7.06-7.00 (m, 1H), 6.86 (d, \(J = 16.0\) Hz, 1H), 6.28 (d, \(J = 16.0\) Hz, 1H), 1.62 (s, 3H), 1.41 (s, 2H), 1.24 (s, 12H); \(\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\):} \(\delta\) 160.3 (d, \(J = 248.9\) Hz), 133.7 (d, \(J = 6.0\) Hz), 129.2 (d, \(J = 8.4\) Hz), 127.9 (d, \(J = 3.7\) Hz), 124.1 (d, \(J = 3.6\) Hz), 123.8 (d, \(J = 12.0\) Hz), 123.4, 122.4 (d, \(J = 3.0\) Hz), 115.8 (d, \(J = 22.0\) Hz), 83.7, 36.5, 27.3, 24.7, 24.6; \(\text{\(^{19}\)F NMR (376 MHz, CDCl}_3\):} \(\delta\)-117.0; HRMS (ESI\(^+\)) [M+NH\(_4\)]\(^+\): Calcd for C\(_{18}\)H\(_{27}\)O\(_2\)N\(_2\)BF\(_3\): 332.2180 m/z; found: 332.2181 m/z.
(E)-2-(Hydroxymethyl)-4-(2-methoxyphenyl)-2-methylbut-3-enenitrile (7j). IR (neat): 3433 (br), 2938 (w), 2878 (w), 2838 (w), 2241 (w), 1644 (w), 1462 (m), 1438 (w), 1293 (w), 1180 (w), 1051 (s), 1025 (m), 971 (m), 752 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.39 (dd, \(J = 7.6, 1.2\) Hz, 1H), 7.29-7.23 (m, 1H), 7.14 (d, \(J = 16.0\) Hz, 1H), 6.95-6.90 (m, 1H), 6.88 (d, \(J = 8.4\) Hz, 1H), 6.03 (d, \(J = 16.0\) Hz, 1H), 3.85 (s, 3H), 3.70 (d, \(J = 2.8\) Hz, 2H), 2.66 (s, 1H), 1.53 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 156.9, 129.4, 128.1, 127.3, 126.5, 124.3, 121.8, 120.5, 110.8, 68.5, 55.3, 43.0, 21.8; HRMS (ESI\(^+\)) [M+H\(^+\)]: Calcd for C\(_{13}\)H\(_{16}\)O\(_2\)N: 218.1176 m/z, found: 218.1177 m/z.

(E)-2-Methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(o-tolyl)but-3-enenitrile (7k). IR (neat): 2965 (w), 2142 (w), 1459 (w), 1365 (w), 1336 (w), 1260 (m), 1218 (w), 1140 (w), 1091 (m), 969 (w), 846 (w), 798 (s), 751 (w) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.41-7.36 (m, 1H), 7.21-7.13 (m, 3H), 6.99 (d, \(J = 16.0\) Hz, 1H), 2.38 (s, 3H), 1.63 (s, 3H), 1.43 (s, 2H), 1.26 (s, 12H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 135.8, 135.2, 132.6, 130.3, 127.7, 127.3, 126.0, 125.8, 123.6, 83.7, 36.4, 27.6, 24.8, 24.7, 19.7; HRMS (ESI\(^+\)) [M+NH\(_4\)\(^+\)]: Calcd for C\(_{19}\)H\(_{30}\)O\(_2\)N\(_2\)B: 328.2431 m/z, found: 328.2433 m/z.

(E)-2-Methyl-4-(naphthalen-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (7l). IR (neat): 2978 (w), 2926 (w), 2238 (w), 1465 (w), 1447 (w), 1364 (s), 1322 (s), 1213 (m), 1142 (s), 1101 (w), 1042 (m), 971 (s), 846 (m), 816 (s), 745 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.84-7.78 (m, 3H), 7.76 (s, 1H), 7.57 (dd, \(J = 8.8, 1.6\) Hz, 1H), 7.51-7.43 (m, 2H), 6.93 (d, \(J = 16.0\) Hz, 1H), 1.66 (s, 3H), 1.47 (s, 2H), 1.26 (s, 12H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 133.5, 133.4, 133.0, 131.3, 129.5, 128.3, 128.0, 127.6, 126.8, 126.3, 126.0, 123.4, 83.8, 36.4, 27.6, 24.8, 24.7; HRMS (ESI\(^+\)) [M+NH\(_4\)\(^+\)]: Calcd for C\(_{22}\)H\(_{30}\)O\(_2\)N\(_2\)B: 364.2431 m/z, found: 364.2435 m/z.

(E)-5-Hydroxy-2-methyl-2-phenylpent-3-enenitrile (8a). IR (neat): 3410 (br), 2927 (w), 2857 (w), 2238 (w), 1465 (w), 1142 (m), 1346 (w), 1322 (s), 1213 (m), 1142 (s), 1213 (w), 969 (s), 846 (m), 816 (s), 745 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.48-7.42 (m, 2H), 7.42-7.35 (m, 2H), 7.35-7.29 (m, 1H), 6.08 (dt, \(J = 15.6, 4.8\) Hz, 1H), 5.86 (d, \(J = 15.6\) Hz, 1H), 4.23 (d, \(J = 3.6\) Hz, 2H), 1.83 (s, 3H), 1.66 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 139.6, 129.4, 130.4, 129.0, 128.0, 125.8, 125.0, 122.0, 62.3, 43.5, 27.1; HRMS (ESI\(^+\)) [M+H\(^+\)]: Calcd for C\(_{12}\)H\(_{14}\)ON: 188.1070 m/z, found: 188.1070 m/z.

(E)-5-Hydroxy-2-(4-methoxyphenyl)-2-methylpent-3-enenitrile (8b). IR (neat): 3424 (br), 2531 (w), 2238 (w), 1465 (w), 1131 (m), 1346 (m), 1322 (s), 1213 (m), 1142 (s), 1213 (w), 969 (s), 846 (m), 816 (s), 745 (s) cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.34 (d, \(J = 8.8\) Hz, 2H), 7.35-7.29 (m, 1H), 6.08 (d, \(J = 15.6, 4.8\) Hz, 1H), 5.86 (d, \(J = 15.6\) Hz, 1H), 4.23 (d, \(J = 3.6\) Hz, 2H), 1.83 (s, 3H), 1.66 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): δ 139.6, 131.1, 130.4, 129.0, 128.0, 125.8, 125.0, 122.0, 62.3, 43.5, 27.1; HRMS (ESI\(^+\)) [M+H\(^+\)]: Calcd for C\(_{12}\)H\(_{14}\)ON: 188.1070 m/z, found: 188.1070 m/z.
(E)-5-Hydroxy-2-methyl-2-(3-(trifluoromethyl)phenyl)pent-3-enenitrile (8c). IR (neat): 3412 (br), 2990 (w), 2935 (w), 2871 (w), 2243 (w), 1442 (w), 1381 (w), 1166 (m), 1123 (s), 1073 (m), 1014 (w), 803 (m), 697 (m), 527 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.70-7.65 (m, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.56-7.50 (m, 1H), 6.12 (dt, J = 15.6, 4.8 Hz, 1H), 5.87 (d, J = 15.6 Hz, 1H), 4.29-4.23 (m, 2H), 1.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 140.8, 131.5 (q, J = 32.5 Hz), 131.4, 130.0, 129.6, 129.5, 125.1 (q, J = 3.7 Hz), 123.7 (q, J = 270.8 Hz), 122.6 (q, J = 3.9 Hz), 121.4, 62.1, 43.4, 27.1; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₃H₁₃ONF₃: 256.0944 m/z, found: 256.0944 m/z.

(E)-2-(3-Chlorophenyl)-5-hydroxy-2-methylpent-3-enenitrile (8d). IR (neat): 3415 (br), 2986 (w), 2928 (w), 2864 (w), 2241 (w), 1585 (m), 1470 (m), 1416 (m), 1205 (w), 1085 (m), 969 (s), 879 (m), 785 (s), 690 (s), 441 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.43-7.39 (m, 1H), 7.37-7.29 (m, 3H), 6.09 (dt, J = 15.6, 4.8 Hz, 1H), 5.84 (dt, J = 15.6, 1.6 Hz, 1H), 4.28-4.23 (m, 2H), 1.82 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 141.6, 135.0, 131.1, 130.3, 130.2, 128.4, 126.2, 124.2, 121.5, 62.2, 43.3, 27.1; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₂H₁₃ONCl: 222.0680 m/z, found: 222.0680 m/z.

(E)-5-Hydroxy-2-methyl-2-(o-tolyl)pent-3-enenitrile (8e). IR (neat): 3406 (br), 2984 (w), 2930 (w), 2867 (w), 2237 (w), 1454 (m), 1378 (w), 1222 (w), 1085 (m), 1020 (m), 970 (s), 763 (s), 727 (s), 544 (w), 454 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.40 (m, 1H), 7.36-7.26 (m, 3H), 6.07 (dt, J = 15.6, 4.8 Hz, 1H), 5.82 (d, J = 15.6 Hz, 1H), 4.27 (d, J = 4.8 Hz, 2H), 2.58 (s, 3H), 2.10 (s, 1H), 1.97 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.1, 135.8, 132.5, 130.7, 130.6, 128.4, 126.4, 125.5, 121.9, 62.1, 41.7, 27.0, 21.0; HRMS (ESI⁺) [M+NH₄⁺]: Calcd for C₁₃H₁₉ON₂: 219.1492 m/z, found: 219.1492 m/z.

(E)-2-(Benzofuran-2-yl)-5-hydroxy-2-methylpent-3-enenitrile (8f). IR (neat): 3418 (br), 2925 (w), 2862 (w), 2232 (w), 1861 (w), 1443 (m), 1304 (w), 1166 (m), 1080 (m), 1012 (m), 969 (m), 803 (m), 746 (s) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.34-7.28 (m, 3H), 6.71 (d, J = 0.8 Hz, 1H), 6.20 (dt, J = 15.6, 4.8 Hz, 1H), 5.92 (dt, J = 15.6, 1.6 Hz, 1H), 4.26 (d, J = 4.4 Hz, 2H), 1.90 (s, 3H), 1.87 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 155.1, 153.9, 132.1, 127.5, 127.4, 124.8, 123.2, 121.2, 119.7, 111.4, 103.6, 62.0, 39.8, 25.1; HRMS (ESI⁺) [M+H⁺]: Calcd for C₁₄H₁₄O₂N: 228.1019 m/z, found: 228.1019 m/z.

(E)-2-(Benzo[b]thiophen-2-yl)-5-hydroxy-2-methylpent-3-enenitrile (8g). IR (neat): 3409 (br), 2925 (w), 2862 (w), 2232 (w), 1861 (w), 1443 (m), 1304 (w), 1166 (m), 1080 (m), 1009 (m), 966 (m), 829 (m), 748 (s), 435 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.78 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.39-7.30 (m, 3H), 6.19 (dt, J = 15.6, 4.8 Hz, 1H), 5.93 (dt, J = 15.4, 1.6 Hz, 1H), 4.25 (d, J = 3.6 Hz, 2H), 1.99 (s, 1H), 1.94 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.1, 139.4, 139.0, 131.3, 129.9,
124.9, 124.7, 123.8, 122.3, 121.9, 120.8, 62.0, 41.2, 28.1; **HRMS (ESI⁺) [M+H]⁺**: Calcd for C₁₄H₁₄ONS: 224.0791 m/z, found: 224.0790 m/z.

*(E)-Tert-butyl 3-(2-cyano-5-hydroxypent-3-en-2-yl)-1H-indole-1-carboxylate (8h).**

**IR (neat):** 3436 (br), 2981 (w), 2933 (w), 2864 (w), 2240 (w), 1731 (s), 1452 (m), 1368 (s), 1245 (m), 1150 (s), 1106 (m), 1022 (w), 849 (m), 743 (s), 472 (w) cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 8.15 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.37-7.30 (m, 1H), 7.28-7.21 (m, 1H), 6.13 (dt, J = 15.2 Hz, 4.8 Hz, 1H), 5.86 (d, J = 15.2 Hz, 1H), 4.16 (d, J = 3.2 Hz, 2H), 2.69 (s, 1H), 1.90 (s, 3H), 1.67 (s, 9H); **¹³C NMR (100 MHz, CDCl₃):** δ 149.3, 135.8, 131.3, 129.1, 127.1, 124.7, 122.7, 122.6, 121.1, 120.0, 119.0, 115.3, 84.3, 61.7, 37.3, 27.9, 25.8; **HRMS (ESI⁺) [M+H]⁺**: Calcd for C₁₄H₁₄ONS : 224.0791 m/z, found: 224.0790 m/z.

*(E)-2-Cyclohexyl-5-hydroxy-2-methylpent-3-enenitrile (8i).**

**IR (neat):** 3427 (br), 2927 (s), 2855 (m), 2238 (w), 1665 (w), 1450 (m), 1375 (w), 1312 (w), 1269 (w), 1093 (m), 1015 (m), 971 (s), 893 (s), 803 (w), 516 (w) cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 6.00 (dt, J = 15.6 Hz, 4.8 Hz, 1H), 5.49 (d, J = 15.6 Hz, 1H), 4.19 (d, J = 4.4 Hz, 2H), 1.93-1.62 (m, 6H), 1.43-1.31 (m, 4H), 1.28-1.00 (m, 5H); **¹³C NMR (100 MHz, CDCl₃):** δ 130.5, 130.3, 122.1, 62.3, 45.5, 43.9, 28.3, 27.9, 26.1, 25.8, 23.5; **HRMS (ESI⁺) [M+NH₄⁺]**: Calcd for C₁₂H₂₃ON: 211.1805 m/z, found: 211.1805 m/z.

*(E)-2-(3-Hydroxyprop-1-en-1-yl)-2,6-dimethylhept-5-enenitrile (8j).**

**IR (neat):** 3424 (br), 2972 (s), 2855 (m), 2238 (w), 1668 (w), 1601 (w), 1448 (m), 1378 (m), 1212 (w), 1094 (m), 1018 (m), 970 (s), 831 (w), 752 (w), 541 (w) cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 6.03 (d, J = 15.6 Hz, 1H), 5.51 (d, J = 15.6 Hz, 1H), 5.06 (t, J = 6.4 Hz, 1H), 4.24-4.15 (m, 2H), 2.19-2.00 (m, 2H), 1.78-1.49 (m, 9H), 1.43 (s, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 132.9, 130.7, 130.4, 122.5, 122.3, 62.2, 40.1, 39.3, 26.0, 25.6, 23.9, 17.6; **HRMS (ESI⁺) [M+H]⁺**: Calcd for C₁₂H₂₀ON: 194.1539 m/z, found: 194.1539 m/z.

*(E)-4-(3-Hydroxyprop-1-en-1-yl)chroman-4-carbonitrile (8k).**

**IR (neat):** 3423 (br), 2972 (m), 2855 (m), 2238 (w), 1718 (w), 1580 (w), 1485 (m), 1301 (m), 1294 (m), 1275 (w), 1186 (m), 1177 (m), 1092 (m), 1010 (m), 975 (m), 757 (m), 625 (w), 525 (w) cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 7.46-7.41 (m, 2H), 7.40-7.34 (m, 2H), 7.32-7.27 (m, 1H), 6.23-6.18 (m, 1H), 4.38-4.17 (m, 4H), 2.43-2.33 (m, 1H), 1.78-1.49 (m, 9H), 1.43 (s, 3H); **¹³C NMR (100 MHz, CDCl₃):** δ 153.5, 133.2, 130.1, 129.4, 129.3, 121.2, 121.1, 118.6, 62.2, 61.8, 39.6, 33.6; **HRMS (ESI⁺) [M+NH₄⁺]**: Calcd for C₁₃H₁₇O₂N₂: 233.1285 m/z, found: 233.1285 m/z.

*(E)-5-Hydroxy-2-isopropyl-2-phenylpent-3-enenitrile (8l).**

**IR (neat):** 3416 (br), 2972 (m), 2872 (w), 2241 (w), 1662 (w), 1598 (w), 1493 (w), 1456 (m), 1384 (w), 1092 (m), 1010 (m), 969 (m), 757 (m), 700 (m), 525 (cm) cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ 7.44-7.41 (m, 2H), 7.40-7.34 (m, 2H), 7.32-7.27 (m, 1H), 6.11 (dt, J = 15.6, 4.8 Hz, 1H), 5.89 (d, J = 15.6 Hz, 1H), 4.24-4.13 (m, 2H), 2.34-2.23 (m, 1H), 1.75 (s, 1H), 1.11 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H); **¹³C NMR (100 MHz, CDCl₃):**
δ 139.0 131.1, 129.5, 128.9, 127.7, 125.9, 119.4, 62.2, 55.9, 37.1, 18.4, 18.3; HRMS (ESI) [M+NH₄]⁺: Calcd for C₁₄H₁₄ON₂: 233.1648 m/z, found: 233.1648 m/z.

(E)-2-(3-Hydroxyprop-1-en-1-yl)-2,6-dimethylhept-5-enal (9). IR (neat): 3385 (br), 2970 (w), 2931 (w), 2874 (w), 1709 (m), 1451 (w), 1375 (m), 1310 (w), 1256 (w), 1225 (w), 1154 (w), 980 (m), 902 (w), 583 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.31 (s, 1H), 5.71-5.56 (m, 2H), 5.01 (t, J = 5.6 Hz, 1H), 4.10 (d, J = 3.2 Hz, 2H), 2.57 (s, 1H), 1.96-1.75 (m, 2H), 1.66-1.48 (m, 8H), 1.14 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 202.8, 132.3, 131.5, 131.1, 123.5, 63.1, 51.6, 35.7, 25.5, 22.5, 18.0, 17.5; HRMS (ESI⁺) [M+NH₄]⁺: Calcd for C₁₂H₁₄O₂N: 214.1802 m/z, found: 214.1801 m/z.

Tert-butyl (4-(4-(dimethylamino)phenyl)-2-(hydroxymethyl)butyl)carbamate (10). IR (neat): 3348 (br), 2972 (w), 2925 (w), 2878 (w), 2798 (w), 1682 (s), 1614 (w), 1515 (s), 1248 (m), 1163 (s), 1040 (w), 893 (w), 808 (s), 550 (w), 519 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.05 (d, J = 8.4 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 4.96 (t, J = 5.6 Hz, 1H), 3.65-3.55 (m, 1H), 3.49-3.38 (m, 1H), 3.34-3.23 (m, 1H), 3.17-3.06 (m, 1H), 2.90 (s, 6H), 2.64-2.48 (m, 2H), 1.65-1.53 (m, 2H), 1.53-1.38 (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ 157.4, 149.0, 130.2, 128.8, 113.0, 79.6, 62.2, 40.8, 40.7, 40.6, 32.1, 30.5, 28.3; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₈H₂₀O₂N₂: 323.2329 m/z, found: 323.2332 m/z.

(E)-Tert-butyl(4-(3-chlorophenyl)-2-(hydroxymethyl)-3-methylbut-3-en-1-yl)carbamate (11). IR (neat): 3348 (br), 2974 (w), 2929 (w), 2878 (w), 1685 (s), 1592 (w), 1510 (s), 1249 (m), 1164 (s), 1031 (m), 891 (w), 857 (w), 774 (m), 687 (m), 531 (w) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.26-7.14 (m, 3H), 7.09 (d, J = 7.6 Hz, 1H), 6.25 (s, 1H), 4.83 (s, 1H), 3.77-3.63 (m, 2H), 3.43-3.25 (m, 2H), 3.02 (s, 1H), 2.49-2.38 (m, 1H), 1.84 (s, 3H), 1.43 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 156.8, 139.4, 138.4, 133.8, 129.3, 128.9, 127.1, 126.4, 79.8, 62.1, 51.4, 40.0, 28.3, 16.4; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₈H₁₄ClO₂N: 326.1517 m/z, found: 326.1518 m/z.

(E)-2-(Furan-2-ylmethyl)-2-methyl-4-phenylbut-3-enenitrile (12). IR (neat): 3029 (w), 2982 (w), 2931 (w), 2237 (w), 1716 (w), 1498 (w), 1451 (w), 1205 (w), 1148 (w), 1076 (w), 1013 (m), 966 (m), 808 (w), 742 (s), 694 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.41-7.26 (m, 6H), 6.77 (d, J = 16.0 Hz, 1H), 6.37-6.27 (m, 2H), 6.03 (d, J = 16.0 Hz, 1H), 3.08 (s, 2H), 1.55 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 149.6, 142.3, 135.8, 131.1, 128.7, 128.6, 128.2, 126.7, 122.2, 110.6, 109.2, 40.2, 39.0, 25.4; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₉H₁₄ON: 238.1227 m/z, found: 238.1225 m/z.

(E)-2-Methyl-2-styrylpent-4-enenitrile (13). IR (neat): 3074 (w), 3026 (w), 2980 (w), 2930 (w), 2236 (w), 1642 (w), 1599 (w), 1447 (m), 1295 (w), 965 (s), 922 (s), 747 (s), 691 (s), 604 (m), 564 (m) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.46-7.26 (m, 5H), 6.80 (d, J = 16.0 Hz, 1H), 5.99 (d, J = 16.0 Hz, 1H), 5.94-5.80 (m, 1H), 5.31-5.20 (m, 2H), 2.48 (d, J = 7.2 Hz, 2H), 1.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 135.6, 131.5, 130.8, 128.8, 128.6, 128.0, 126.4, 122.1, 120.1, 44.5, 39.6, 25.3; HRMS (ESI⁺) [M+H]⁺: Calcd for C₁₆H₁₆N: 198.1277 m/z, found: 198.1276 m/z.
4-(Hydroxymethyl)-2,2,9-trimethyl-5-methylene-3-oxodec-8-enenitrile (S1). IR (neat): 3435 (br), 2965 (w), 2927 (w), 2239 (w), 1723 (s), 1641 (w), 1461 (w), 1382 (w), 1260 (w), 1087 (m), 1039 (s), 910 (w), 799 (m); $^{1}$H NMR (400 MHz, CDCl$_3$): δ 5.13-5.04 (m, 2H), 4.83 (s, 1H), 3.95-3.86 (m, 2H), 3.65 (d, J = 8.4 Hz, 1H), 2.37-2.13 (m, 4H), 2.00 (s, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.52 (s, 3H), 1.50 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 204.2, 141.9, 132.4, 123.2, 121.9, 114.8, 63.1, 58.6, 43.9, 35.6, 25.9, 25.6, 24.9, 24.6, 17.7; HRMS (ESI$^+$) [M+H]$^+$: Calcd for C$_{15}$H$_{24}$NO$_2$: 250.1802 m/z, found: 250.1802 m/z.

**Representative Experimental Procedure for Reduction of CN to Aldehyde.**

![Chemical structure of 8j](image)

To a solution of 8j (135.8 mg, 0.7 mmol) in DCM at –78 °C was added DIBAL-H (1.75 mL, 1.75 mmol, 1.0 M in hexanes) dropwise. The reaction mixture was allowed to stir for 2.0 h and then quenched with a saturated aqueous solution of potassium sodium tartrate. The reaction mixture was diluted with Et$_2$O. The layers were separated and the aqueous layer was washed with Et$_2$O. The combined organic layers were dried over MgSO$_4$, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product 9 (91.7 mg, 67% yield) as colorless oil.

**Representative Experimental Procedure for Reduction of the Nitrile Moiety to the Protected Amines.**

![Chemical structure of 3c](image)

To a solution of 3c (69.1 mg, 0.32 mmol), NiCl$_2$·6H$_2$O (114.1 mg, 0.48 mmol) and Boc$_2$O (209.5 mg, 0.96 mmol) in MeOH at 0 °C was added NaBH$_4$ (121.1 mg, 3.20 mmol) portion. The mixture was allowed to stir for 6h at r.t. The reaction mixture was quenched with a saturated aqueous solution of NH$_4$Cl, diluted with Et$_2$O. The layers were separated and the aqueous layer was washed with Et$_2$O. The combined organic
layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product 10 (64.8 mg, 63% yield) as colorless oil.

### Representative Experimental Procedure for Functionalization of C-B(pin) bond to C-furan.

![Chemical structure 7a](image)

A solution of furan (73 ul, 1.0 mmol) in THF was cooled to -78 °C and treated with n-BuLi (400 μL, 1.0 mmol, 2.5 M in hexanes). The cooling bath was removed and the mixture was allowed to stir at room temperature for 1 h. The mixture was cooled to –78 °C and the boronic ester 7a (149 mg, 0.5 mmol) was added dropwise as a solution in THF. The mixture was stirred at -78 °C for 1 h. Then a solution of N-bromosuccinimide (NBS, 178 mg, 1.0 mmol) in THF was added dropwise. After 1 h at -78 °C, a saturated aqueous solution of Na₂S₂O₃ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et₂O and water. The layers were separated and the aqueous layer was washed with Et₂O. The combined organic layers were dried over MgSO₄, filtered and concentrated under vacuum. Purification by column chromatography on silica gel, gave the desired product 12 (80.8 mg, 65% yield) as colorless oil.

### Representative Experimental Procedure for Functionalization of C-B(pin) bond to C-vinyl.

![Chemical structure 7a](image)

To a solution of boronic ester 7a (161.4 mg, 0.54 mmol) in THF at -78 °C was added vinylmagnesium bromide (3.24 mL, 3.24 mmol, 1 M in THF) dropwise. The mixture was allowed to stir for 30 min at -78 °C. Then a solution of I₂ (822.3 mg, 3.24 mmol) in MeOH was added dropwise, and the reaction mixture was allowed to stir for a further 30 min and then allowed to warm to 0°C. 5% Na₂S₂O₃ was added and the solvents was removed from the reaction mixture in vacuo. The mixture was washed with Et₂O, the organic layers were combined, washed with brine, dried (MgSO₄), concentrated and purified by column chromatography to give the desired product 13 (66.4 mg, 62%) as colorless oil.

### Representative Experimental Procedure for Equivalent Cu-B(pin) Addition to 1,3-dienes (s2).
In a N₂-filled glove-box, an oven-dried vial (8 mL, 61 × 16.6 mm) with a magnetic stir bar was charged with phosphine ligand 4h (57.9 mg, 0.1 mmol, 1.0 equiv), CuCl (10 mg, 0.1 mmol, 1.0 equiv), LiOt-Bu (8.0 mg, 0.10 mmol, 1.0 equiv) and d₈-tetrahydrofuran (d₈-thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (25.4 mg, 0.10 mmol, 1.0 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 20 min under an atmosphere of N₂. Diene s₂ (20.9 mg, 0.10 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 1 h. Then 1,3,5-trimethylbenzene (12.0 mg, 0.1 mmol) was added as internal standard. The reaction was monitored by ¹H NMR and 0.85 mmol diene s₂ remains with <5% conversion. The reason why such type of substrates was unreactive is that Cu–B(pin) addition did not occur.
Table S1. Ligand Screen

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Table S2. Screen of Bases
Screening of bases indicated that the reaction with LiO\textsubscript{t}-Bu provided highest yield. Low conversions of \textbf{1a} in the cases of reactions with K\textsubscript{2}CO\textsubscript{3} and K\textsubscript{3}PO\textsubscript{4} were observed, whereas stronger bases led to messy reactions, maybe due to decomposition of the product.

**Scheme S1. Reaction with DMMN**

**Reference**


NMR Spectra

NMR Spectra for compound 3a.
Wen et al., Supporting Information, Page S24

**Diagram 1:**

[Chemical structure of compound 3b with relevant spectral data]

**Diagram 2:**

[Chemical structure of compound 3c with relevant spectral data]
$3f$
3h

3i
ratio 3:5:1

6a
6b

6c
7d

Wen et al., Supporting Information, Page S60
\[ \text{8k} \]

\[ \text{8l} \]

\[ \text{8l} \]