## Supporting Information 1

# Diastereoselective Synthesis of All Eight L-Hexoses from L-Ascorbic Acid 

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General Considerations. Solvents and reagents were purified according to standard laboratory procedures. All reactions requiring anhydrous conditions or an inert atmosphere were conducted under an atmosphere of argon. Flash column chromatography was performed on Silica gel 60 (230-400 mesh). Optical rotations were determined using concentrations (c) in $\mathrm{g} / 100 \mathrm{~mL}$ in $\mathrm{CHCl}_{3}$. Mass
spectra and high-resolution mass spectra were obtained on a LCT with an electrospray source (ZQ) in positive mode ionization (ESI). ${ }^{1} \mathrm{H}$ NMR spectra were recorded at 250 and $300 \mathrm{MHz},{ }^{13} \mathrm{C}$ NMR spectra were recorded at 75.5 MHz with chemical shifts reported in $\mathrm{ppm}(\delta)$ downfield from TMS (internal reference) for ${ }^{1} \mathrm{H}$ and relative to the center line of the triplets of $\mathrm{CDCl}_{3}$ at 74.14 ppm for ${ }^{13} \mathrm{C}$. Infrared spectra (IR) were recorded on a FTIR spectrophotometer, wavelength ( $v$ ) were reported in cm . HPLC analyses were carried out on Alliance using PDA detector.

Ethyl (2S,3S)-3,4-O-isopropylidene-2,3,4-trihydroxybutanoate 2. To a solution of $\mathbf{1}(5.84 \mathrm{~g}, 28.62 \mathrm{mmol}), \mathrm{PPh}_{3}(15.2 \mathrm{~g}, 58 \mathrm{mmol})$ and $\mathrm{CH}_{2} \mathrm{ClCOOH}(5.5 \mathrm{~g}, 58 \mathrm{mmol})$ in THF $(150 \mathrm{~mL})$ DIAD $(11.2 \mathrm{~mL}, 58 \mathrm{mmol})$ was added dropwise at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred for 12 h at rt , the solvent was removed under reduced pressure, the residue was taken into ethyl ether. The precipite was removed by filtration, the filtrate and washings were concentrated. The residue was purified by flash chromatography (silica gel, heptane-EtOAc 6:1) to give the chloroacetate of $(2 S, 3 S)$-hydroxyester as an oil in $73 \%$ yield: $[\alpha]_{\mathrm{D}}-21.7$ (c 1.0); IR $\left(\mathrm{CHCl}_{3}\right) \mathrm{cm}^{-1}$ : 2986, 2905, 1747, 1372, 1253, 1226, 1205, 1160, 1067, 1028, 851, 772, 668; ${ }^{1} \mathrm{H}$ NMR $5.17(\mathrm{~d}, J=3.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.49(\mathrm{ddd}, J=10.3$, $6.0,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.25(\mathrm{q}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.20(\mathrm{~s}, 2 \mathrm{H}), 4.05(\mathrm{~d}, J=6.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.43(\mathrm{~s}, 3 \mathrm{H}), 1.36(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 167.0, 166.9, 110.4, 74.5, 73.4, 65.1, 62.0, 40.4, 26.2, 25.1, 14.0; MS (ESI) $m / z 303[\mathrm{M}+\mathrm{Na}]^{+}$; HRMS calcd for $\mathrm{C}_{11} \mathrm{H}_{17} \mathrm{O}_{6} \mathrm{ClNa}$ $[\mathrm{M}+\mathrm{Na}]^{+} 303.0611$, found 303.0654 .

Deacylation of 5.5 g of the chloroacetate with triethylamine/ethanol (1/9) gave $3.8 \mathrm{~g}(90 \%)$ of $\mathbf{2}:[\alpha]_{\mathrm{D}}+28.0(c 1.5) ; \mathrm{IR}\left(\mathrm{CHCl}_{3}\right) \mathrm{cm}^{-1}$ : $3448,2985,2937,1731,1455,1371,1248,1208,1146,1065,1021,964,941,842,791 ;{ }^{1} \mathrm{H}$ NMR $4.40-4.20(\mathrm{~m}, 4 \mathrm{H}), 4.05(\mathrm{~m}, 2 \mathrm{H})$,
$3.50(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.43(\mathrm{~s}, 3 \mathrm{H}), 1.35(\mathrm{~s}, 3 \mathrm{H}), 1.31(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 172.0, 109.8, 76.6, 71.1, 65.0, 61.6, 26.2, 25.0, 14.0; MS (ESI) $m / z 227[\mathrm{M}+\mathrm{Na}]^{+} ; \mathrm{HRMS}$ calcd for $\mathrm{C}_{9} \mathrm{H}_{16} \mathrm{O}_{5} \mathrm{Na} 227.0895[\mathrm{M}+\mathrm{Na}]^{+}$, found 227.0864.

Ethyl (2R,3S)-2-O-benzyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanoate 3. To a stirred solution of $\mathbf{1}$ ( $3.8 \mathrm{~g}, 18.62 \mathrm{mmol}$ ) in 50 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added $\mathrm{Ag}_{2} \mathrm{O}(6.6 \mathrm{~g}, 28 \mathrm{mmol})$, $\mathrm{KI}(100 \mathrm{mg})$ and benzyl bromide ( $3.8 \mathrm{~mL}, 36 \mathrm{mmol}$ ). The reaction was stirred for 3 hours and filtered through a silica gel pad. Evaporation of solvent followed by flash chromatography (heptane-EtOAc 9:1) gave 4.65 g ( $85 \%$ yield) of 3: $[\alpha]_{\mathrm{D}}+60.2(c 1.6)$; IR $\left(\mathrm{CHCl}_{3}\right) \mathrm{cm}^{-1}: 3030,3014,2990,2938,1739,1496,1455,1373,1337,1257,1224,1207,1151$, $1106,1075,1026,851 ;{ }^{1} \mathrm{H}$ NMR $7.37(\mathrm{~m}, 5 \mathrm{H}), 4.75,4.49(2 \mathrm{~d}, J=11.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.38(\mathrm{dd}, J=12.1,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.19(\mathrm{q}, J=7.0 \mathrm{~Hz}$, 2H), $3.95(\mathrm{~m}, 3 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}), 1.33(\mathrm{~s}, 3 \mathrm{H}), 1.27(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 169.9, 137.0, 128.3, 128.1, 127.9, 109.7, 78.5, 75.8, 72.6, 65.4, 61.1, 26.2, 25.2, 14.1; MS (ESI) $m / z 317[\mathrm{M}+\mathrm{Na}]^{+}$, HRMS calcd for $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{O}_{5} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 317.1365$, found 317.1353.

Ethyl (2S,3S)-2-O-benzyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanoate 4. To a solution of $2(4.08 \mathrm{~g}, 20 \mathrm{mmol})$ in $\mathrm{CH}_{3} \mathrm{CN}(50$ $\mathrm{ml})$ was added $\mathrm{Ag}_{2} \mathrm{O}(6.96 \mathrm{~g}, 30 \mathrm{mmol}), \mathrm{BnBr}(4.22 \mathrm{ml}, 40 \mathrm{mmol})$ and $\mathrm{Bu}_{4} \mathrm{NI}(100 \mathrm{mg})$. The mixture was stirred at reflux overnight. The solids were removed by filtration and the filtrate concentrated to dryness. Purification by flash chromatography (heptane-EtOAc 9:1) gave $7.35 \mathrm{~g}(80 \%)$ of $\mathbf{4}:[\alpha]_{\mathrm{D}}-42.6$ (c 1.2); IR $\left(\mathrm{CHCl}_{3}\right) \mathrm{cm}^{-1}: 3028,3013,3019,2938,2905,1740,1455,1383,1373,1254,1226$, $1198,1148,1079,1050,1028,913,841 ;{ }^{1} \mathrm{H}$ NMR $7.34(\mathrm{~m}, 5 \mathrm{H}), 4.69(\mathrm{~d}, J=11.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.50(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.34(\mathrm{dd}, J=$ $11.8,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.22(\mathrm{~m}, 2 \mathrm{H}), 4.02(\mathrm{~m}, 2 \mathrm{H}), 3.95(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.42(\mathrm{~s}, 3 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{t}, J 7.4 \mathrm{~Hz}, 3 \mathrm{H}) ; \mathrm{NMR}{ }^{13} \mathrm{C}$ $170.4,137.0,128.4,128.2,109.8,79.1,76.0,72.8,66.2,61.5,26.6,25.3,14.2$; MS (ESI) $m / z 317[\mathrm{M}+\mathrm{Na}]^{+}$, HRMS calcd for $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{O}_{5} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$317.1365, found 317.1336.
(2S,3S)-2-O-Benzyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanol 5. A mixture of $\mathrm{LiBH}_{4}$ ( $427 \mathrm{mg}, 19.4 \mathrm{mmol}$ ), ester $\mathbf{3}$ ( $3.8 \mathrm{~g}, 12.9$ mmol), methanol ( $0.79 \mathrm{~mL}, 19.4 \mathrm{mmol}$ ) and ether ( 50 mL ) was stirred at $0^{\circ} \mathrm{C}$ for 2 h . The reaction was quenched with 1 N hydrochloric acid. The mixture was diluted with water, extracted with ether, dried, and the solvent was evaporated. Purification by flash chromatography (heptane-EtOAc 2:1) afforded $3.1 \mathrm{~g}(95 \%)$ of alcohol 5: $[\alpha]_{\mathrm{D}}-12.3$ (c 1.2); IR (neat) $\mathrm{cm}^{-1}: 3436,3064,3031$, 2986, 2934, 2884, 1497, 1455, 1371, 1256, 1214, 1157, 1073, 1028, 853, 738, 698; ${ }^{1} \mathrm{H}$ NMR $7.35(\mathrm{~m}, 5 \mathrm{H}), 4.78,4.68(2 \mathrm{~d}, J=11.8 \mathrm{~Hz}$, $2 \mathrm{H}), 4.30(\mathrm{dd}, J=12.5,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.00(\mathrm{dd}, J=8.1,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.85(\mathrm{dd}, J=8.8,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~m}, 1 \mathrm{H}), 3.58(\mathrm{~m}, 2 \mathrm{H}), 2.10$ $(\mathrm{dd}, J=6.6,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.44(\mathrm{~s}, 3 \mathrm{H}), 1.36(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR 138.2, 128.4, 127.8, 127.7, 109.3, 79.3, 76.5, 72.7, 65.5, 61.6, 26.4, 25.3; MS (ESI) $m / z 275[\mathrm{M}+\mathrm{Na}]^{+}$, HRMS calcd for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{O}_{4} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$275.1259, found 275.1281.
(2R,3S)-2-O-Benzyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanol 6 was obtained from $\mathbf{4}$ in $95 \%$ yield by the procedure described for 5. 6: $[\alpha]_{\mathrm{D}}-25.5$ (c 1.05); IR (neat) $\mathrm{cm}^{-1}: 3402,3065,3032,2935,2882,1720,1454,1372,1272,1214,1071,1028,915,851,747$, 714,$699 ;{ }^{1} \mathrm{H}$ NMR $7.35(\mathrm{~m}, 5 \mathrm{H}), 4.65,4.58(2 \mathrm{~d}, J=11.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.15(\mathrm{dd}, J=12.5,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.03(\mathrm{dd}, J=8.8,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.85$ (dd, $J=8.1,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{dd}, J=11.7,3.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.63(\mathrm{dd}, J=11.8,3.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.50(\mathrm{~m}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 1 \mathrm{H}), 1.38(\mathrm{~s}, 3 \mathrm{H}), 1.32$ ( $\mathrm{s}, 3 \mathrm{H}$ ) ${ }^{13}{ }^{13} \mathrm{C}$ NMR 138.0, 128.6, 128.0, 109.3, 79.6, 75.9, 72.8, 66.9, 61.8, 26.7, 25.3; MS (ESI) $\mathrm{m} / \mathrm{z} 275[\mathrm{M}+\mathrm{Na}]^{+}$, HRMS calcd for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{O}_{4} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$275.1259, found 275.1253.
(2R,3S)-2-O-Benzyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanal 7. To a solution of oxalyl chloride ( $2.2 \mathrm{~mL}, 25 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ $(20 \mathrm{~mL})$ at $-78^{\circ} \mathrm{C}$ was added a solution of DMSO $(2.1 \mathrm{~mL}, 30 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$. After 15 min , a solution of alcohol $5(4.28 \mathrm{~g}$, $17 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ was added. The reaction was stirred at $-78^{\circ} \mathrm{C}$ for 1 h , then quenched with diisopropylethylamine $(14 \mathrm{~mL})$,
washed successively with 1 M HCl , sat. aq. $\mathrm{NaHCO}_{3}$ solution, brine, then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$. Evaporation of solvent gave $4.0 \mathrm{~g}(95 \%$ yield) of crude aldehyde which was used directly for the next reaction without purification. The analytical simple was obtained by column chromatography (heptane-EtOAc 2:1). 7: $[\alpha]_{\mathrm{D}}+44.3$ (c 1.1), IR (neat) $\mathrm{cm}^{-1}: 3024,2991,2874,1733,1496,1455,1374,1224$, $1215,1151,1076,912,846$; ${ }^{1} \mathrm{H}$ NMR $9.73(\mathrm{~d}, J=1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.35(\mathrm{~m}, 5 \mathrm{H}), 4.79,4.64(2 \mathrm{~d}, J=11.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.37(\mathrm{app} . \mathrm{q}, J=6.0 \mathrm{~Hz}$, $1 \mathrm{H}), 4.05(\mathrm{dd}, J=8.8,6.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.94(\mathrm{dd}, J=8.8,5.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.84(\mathrm{dd}, J=5.5,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.43(\mathrm{~s}, 3 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 202.1, 137.0, 128.7, 128.3, 128.2, 109.9, 82.9, 75.3, 73.4, 65.4, 26.2, 25.1; MS (ESI) $m / z 273[\mathrm{M}+\mathrm{Na}]^{+}$; HRMS calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{O}_{4} \mathrm{Na}$ $[\mathrm{M}+\mathrm{Na}]^{+} 273.1103$, found 273.1090.
(2S,3S)-2-O-Benzyl-3,4-O-isopropylidene-2,3,4-trihydroxybutanal 8 was obtained from $\mathbf{6}$ in $95 \%$ yield by the procedure described for 7 and used in the next steps without purification. The analytical simple was obtained by column chromatography (heptane-EtOAc 2:1). 8: $[\alpha]_{\mathrm{D}}-35.0$ (c 1.2), IR (neat) $\mathrm{cm}^{-1}: 3024,2990,2859,1734,1590,1455,1383,1374,1211,1209,1155,1077,1059,842 ;{ }^{1} \mathrm{H}$ NMR $9.68(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.33(\mathrm{~m}, 5 \mathrm{H}), 4.71,4.57(2 \mathrm{~d}, J=11.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.32(\operatorname{app} . \mathrm{q}, J=5.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.05(\mathrm{dd}, J=8.1,6.6 \mathrm{~Hz}$, $1 \mathrm{H}), 3.91(\mathrm{dd}, J=8.1,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{dd}, J=6.3,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}), 1.33(\mathrm{~s}, 3 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR 201.2, 138.3, 128.5, 128.2, 128.1, 110.0, 83.0, 75.0, 73.4, 66.1, 26.4, 25.0; MS (ESI) $m / z 273[\mathrm{M}+\mathrm{Na}]^{+} ; 305\left[\mathrm{M}+\mathrm{Na}+\mathrm{CH}_{3} \mathrm{OH}\right]^{+}$; HRMS calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{O}_{4} \mathrm{Na}$ $[\mathrm{M}+\mathrm{Na}]^{+} 273.1103$, found 273.1116 .

Ethyl (4S,5S)-4-O-benzyl-5,6-O-isopropylidene-4,5,6-trihydroxyhex-2,3-E-enoate 9. To a solution of aldehyde 7 ( $4.0 \mathrm{~g}, 16 \mathrm{mmol}$ ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(50 \mathrm{~mL}) \mathrm{Ph}_{3} \mathrm{P}=\mathrm{CHCO}_{2} \mathrm{Et}(7.0 \mathrm{~g}, 20 \mathrm{mmol})$ was added. The mixture was stirred for 2 h , concentrated, extracted with ether and filtered. The filtrate was concentrated and purified by column chromatography with heptane-EtOAc (9:1) to afford $E$-olefin ( 4.1 g ,
$80 \%$ ) as a colorless oil. 9: $[\alpha]_{\mathrm{D}}+33.8$ (c 1.6); IR (neat) $\mathrm{cm}^{-1}: 3029,3014,2989,2939,2896,2874,1715,1659,1497,1455,1383,1372$, 1304, 1280, 1180, 1158, 1071, 1045, 985, 915, 850; ${ }^{1} \mathrm{H}$ NMR $7.34(\mathrm{~m}, 5 \mathrm{H}), 6.84(\mathrm{dd}, J=16.0,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.12(\mathrm{dd}, J=16.0,1.3 \mathrm{~Hz}$, $1 \mathrm{H}), 4.68,4.48(2 \mathrm{~d}, J=12.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.22(\mathrm{~m}, 3 \mathrm{H}), 4.10(\mathrm{ddd}, J=7.2,5.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.08(\mathrm{dd}, J=8.8,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{dd}, J=$ $8.8,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}), 1.35(\mathrm{~s}, 3 \mathrm{H}), 1.31(\mathrm{t}, J=7.4,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 165.9, 143.5, 137.7, 128.5, 127.9, 127.8, 124.6, 109.9, $78.4,76.8,71.6,65.4,60.7,26.4,25.3,14.3$; MS (ESI) $m / z 343[\mathrm{M}+\mathrm{Na}]^{+}$; HRMS calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{O}_{5} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 343.1521$, found 343.1516.

Ethyl (4R,5S)-4-O-benzyl-5,6-O-isopropylidene-4,5,6-trihydroxyhex-2,3-E-enoate 10. A solution of triethyl phosphonoacetate (2 $\mathrm{mL}, 10 \mathrm{mmol}$ ) in benzene ( 200 mL ) was treated with $\mathrm{NaH}(400 \mathrm{mg}, 10 \mathrm{mmol})$. The aldehyde $\mathbf{8}(2.48 \mathrm{~g}, 10 \mathrm{mmol})$ was then added and resulting mixture was stirred for 2 h . The solution was concentrated and purified by column chromatography with heptane-EtOAc (3:1) to afford $10(2.66 \mathrm{~g}, 83 \%)$ as a colorless oil. 10: $[\alpha]_{\mathrm{D}}-26.9$ (c 1.10); IR (neat) $\mathrm{cm}^{-1}: 3026,2986,2936,2876,1721,1659,1455,1371$, $1298,1268,1215,1177,1074,985,849,736,699 ;{ }^{1} \mathrm{H}$ NMR $7.35(\mathrm{~m}, 5 \mathrm{H}), 6.91(\mathrm{dd}, J=16.2,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.59(\mathrm{dd}, J=16.2,2.0 \mathrm{~Hz}$, $1 \mathrm{H}), 4.63,4.42(2 \mathrm{~d}, J=11.7 \mathrm{~Hz}, 2 \mathrm{H}), 4.19(\mathrm{q}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 4.09(\mathrm{~m}, 1 \mathrm{H}), 4.04(\mathrm{~m}, 1 \mathrm{H}), 3.95(\mathrm{ddd}, J=7.3,5.2,2.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.75$ $(\mathrm{dd}, J=8.1,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.40,(\mathrm{~s}, 3 \mathrm{H}) ; 1.30(\mathrm{~m}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 165.9, 144.7, 137.6, 128.5, 128.0, 124.1, 109.9, 79.0, 77.4, 71.8, 66.7, 60.6, 26.6, 25.3, 14.3; MS (ESI) $m / z 343[\mathrm{M}+\mathrm{Na}]^{+} ;$HRMS calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{O}_{5} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 343.1521$, found 343.1518 .

Methyl (4S,5S)-4-O-benzyl-5,6-O-isopropylidene-4,5,6-trihydroxyhex-2,3-Z-enoate 11. A solution of bis-(2,2,2trifluoroethyl)(methoxycarbonylmethyl)phosphonate ( $3.18 \mathrm{~g}, 2.1 \mathrm{~mL}, 10 \mathrm{mmol}$ ), 18-crown-6 ( $13.2 \mathrm{~g}, 50 \mathrm{mmol}$ ) in THF ( 200 mL ) was cooled to $-78^{\circ} \mathrm{C}$ and treated with $\mathrm{KN}(\mathrm{TMS})_{2}(0.6 \mathrm{M}$ in toluene, $17 \mathrm{~mL}, 10 \mathrm{mmol})$. The aldehyde $7(2.48 \mathrm{~g}, 10 \mathrm{mmol})$ was then added
and reaction mixture was stirred for 30 min at $-78^{\circ} \mathrm{C}$. Saturated $\mathrm{NH}_{4} \mathrm{Cl}$ was added and the product was extracted into ether. The ether extracts were concentrated and purified by flash chromatography with heptane-EtOAc (3:1) to afford $\mathbf{1 1} 617(2.60 \mathrm{~g}, 85 \%)$ as a colorless oil. 11: $[\alpha]_{\mathrm{D}}+1.6$ (c 1.4); IR (neat) $\mathrm{cm}^{-1}: 3029,3011,2992,2953,2892,1720,1651,1497,1455,1438,1402,1383,1228$, $1203,1181,1156,1125,1071,1028,995,909,846,828 ;{ }^{1} \mathrm{H}$ NMR $7.31(\mathrm{~m}, 5 \mathrm{H}), 6.18(\mathrm{dd}, J=11.7,9.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.00(\mathrm{dd}, J=11.7,1.0$ $\mathrm{Hz}, 1 \mathrm{H}), 5.18(\mathrm{ddd}, J=9.0,5.2,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.61,4.48(2 \mathrm{~d}, J=12.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.22(\mathrm{ddd}, J=12.0,6.7,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.93(\mathrm{~m}, 2 \mathrm{H}), 3.69$ (s,3H), $1.43(\mathrm{~s}, 3 \mathrm{H}), 1.36(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 166.1, 146.2, 138.1, 128.3, 127.8, 127.6, 123.1, 109.8, 77.7, 74.4, 71.5, 65.3, 51.5, 26.2, 25.6; MS (ESI) $m / z 329[\mathrm{M}+\mathrm{Na}]^{+} ;$HRMS calcd for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{O}_{5} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 329.1365$, found 329.1364 .

Methyl (4R,5S)-4-O-benzyl-5,6-O-isopropylidene-4,5,6-trihydroxyhex-2,3-Z-enoate $\mathbf{1 2}$ was obtained from $\mathbf{8}$ in $80 \%$ yield by the procedure described for 11. 12: $[\alpha]_{\mathrm{D}}-10.7$ (c 1.4); IR (neat) $\mathrm{cm}^{-1}: 3031,3011,2990,2952,2889,1720,1651,1454,1438,1383,1373$, $1211 ; 1181,1156,1070,998,905,882,843,828 ;{ }^{1} \mathrm{H}$ NMR $7.31(\mathrm{~m}, 5 \mathrm{H}), 6.15(\mathrm{dd}, J=11.8,9.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.05(\mathrm{~d}, J=11.8 \mathrm{~Hz}, 1 \mathrm{H})$, $5.15(\mathrm{dd}, J=9.0,5.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.58,4.48(2 \mathrm{~d}, J=11.8 \mathrm{~Hz}, 2 \mathrm{H}), 4.20(\mathrm{dd}, J=12.1,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.05(\mathrm{dd}, J=8.5,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.87$ (dd, $J=8.5,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.70(\mathrm{~s}, 3 \mathrm{H}), 1.39(\mathrm{~s}, 3 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR 166.2, 145.7, 138.3, 128.4, 128.0, 127.8, 123.8, 109.8, $77.4,74.5,71.6,66.4,51.5,26.3,25.3$; MS (ESI) $m / z 329[\mathrm{M}+\mathrm{Na}]^{+}$; HRMS calcd for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{O}_{5} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 329.1365$, found 329.1344 .























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( 90.66





















