De Novo Enantioselective Synthesis of *Galacto*-Sugars and Deoxy-Sugars Via the Iterative Dihydroxylation of Dienoate.

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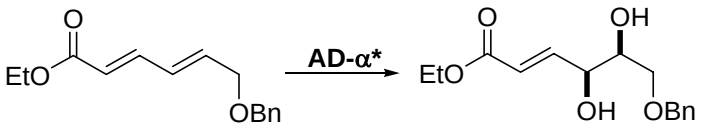
Supporting Information:

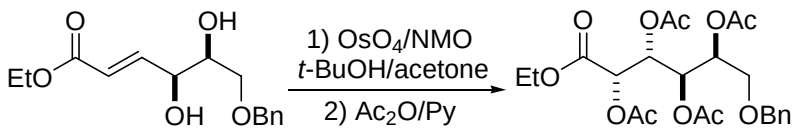
General Methods and Materials. ^{1}H and ^{13}C NMR spectra were recorded on Jeol (270 MHz) and Varian VXR-600 (600 MHz) spectrometers. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in the solvent specified. Melting points were determined with Electrothermal Mel-Temp apparatus and are uncorrected. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60Å, F_{254}) and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or phosphomolybdic acid or potassium permanganate stain. R_f values are obtained by elution in the stated solvent ratios (v/v). Ether, THF, Methylene chloride and triethylamine were dried by passing through activated alumina column with argon gas pressure. Commercial reagents were used without purification unless otherwise noted. Melting points are uncorrected. Air and/ or moisture- sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven-dried glassware and standard syringe/septa techniques.

(*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate (2b):



Into a 250 mL round bottom flask was added 60 mL of *t*-BuOH, 60 mL of water, $K_3Fe(CN)_6$ (24.7 g, 75 mmol), K_2CO_3 (10.35 g, 75 mmol), $MeSO_2NH_2$ (2.37 g, 25 mmol), $(DHQ)_2PHAL$ (409 mg, 0.52 mmol, 2.1 mol%), and OsO_4 (127 mg, 0.5 mmol, 2 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added (2*E*,4*E*)-ethyl 6-(benzyloxy)hexa-2,4-dienoate **1b** (6.15 g, 25 mmol) and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (300 mg) at room temperature. Ethyl acetate (40 mL) was added to the reaction mixture, and after separation of the layers, the aqueous phase was further extracted with the organic solvent (2 x 30 mL). The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded 6.23 g (89 % yield) of (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** as a light yellow oil: R_f (30% EtOAc/ hexanes) = 0.13; $[\alpha]^{25}_D$ -20.36° (*c* 1.1, CH_2Cl_2); IR (thin film, cm^{-1}) 3421, 2985, 2937, 2871, 1715, 1699, 1659, 1455, 1393, 1279, 1179, 1039, 984 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz): δ 7.33 (m, 5H), 6.91 (dd, *J* = 15.6, 4.6 Hz, 1 H), 6.14 (dd, *J* = 15.6, 1.8 Hz, 1 H), 4.58 (d, *J* = 11.8 Hz, 1H), 4.53(d, *J* =11.8 Hz, 1H), 4.38 (ddd, *J* = 9.1, 4.6, 1.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2 H), 3.76 (ddd, *J* = 9.7, 5.5, 4.6 Hz, 1H), 3.65 (dd, *J* = 9.7, 3.9 Hz, 1 H), 3.59 (dd, *J* = 9.7, 5.5 Hz, 1H), 2.92 (d, *J* = 4.7 Hz, 1H), 2.70 (d, *J* = 5.9 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 166.2, 146.0, 137.3, 128.5 (2C), 127.9, 127.8 (2C), 122.4, 73.7, 72.1, 71.7, 71.4, 60.5, 14.1; GCMS: 280 (M^+).

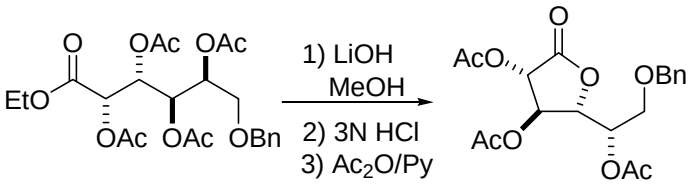
(*2S*,3*R*,4*R*,5*S*)-ethyl 2,3,4,5-tetraacetoxy-6-(benzyloxy)hexanoate (3b):



Into a 25 mL round bottom flask was added (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** (140 mg, 0.5 mmol) and added 1 mL of *t*-BuOH, 1 mL of acetone and then cooled to 0 °C. To this solution 0.35 ml 50% NMO in H_2O (1.5 mmol) and OsO_4 (2.5 mg, 0.01 mmol, 2 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the mixture was filtered through a pad of celite/florisil and eluted with 20 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and replaced with CH_2Cl_2 (2 mL) was added excess Ac_2O (0.2 mL, 2 mmol), pyridine (0.3 mL, 4 mmol) and a catalytic amount of DMAP (2.5 mg, 5 mol%). The reaction was stirred for an hour, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (4:1 (v/v) hexane / EtOAc) to yield (*2S*,3*R*,4*R*,5*S*)-ethyl 2,3,4,5-tetraacetoxy-6-(benzyloxy)hexanoate **3b** (144 mg, 5:1 dr, 60% yield in 2 steps) as a viscous oil. The major isomer was separated by column chromatography. Major isomer: white crystalline solid; mp 76-77 ^oC; R_f (30% EtOAc/ hexanes) = 0.33; $[\alpha]^{25}_D$ 7.5^o (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2983, 2928, 2914, 2872, 1766, 1760, 1748, 1455, 1374, 1213, 1096, 1048, 952; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.29 (m, 5H), 5.57 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.52 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.26 (ddd, *J* = 6, 6, 1.8 Hz, 1H), 5.08 (d, *J* = 1.8 Hz, 1H), 4.49 (d, *J* = 12 Hz, 1H), 4.45 (d, *J* = 12 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.49 (dd, *J* = 10.2, 6 Hz, 1H), 3.45 (dd, *J* = 10.2, 6 Hz, 1H), 2.19 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 170.2 (2C), 169.3, 169.1, 167.0,

137.3, 128.5 (2C), 127.8 (3C), 73.3, 69.4, 68.1, 67.9, 67.8, 67.7, 62.0, 20.7, 20.4, 20.3(2C), 13.8; CIHRMS: Calculated for $[C_{23}H_{30}O_{11}+Na]^+$: 505.1686, Found: 505.1697. Minor isomer: R_f (30% EtOAc/ hexanes) = 0.30; $[\alpha]^{25}_D$ – 6.1° (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2992, 2963, 2931, 2874, 1758, 1454, 1374, 1223, 1115, 1057, 951, 857; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.32 (m, 5H), 5.64 (dd, *J* = 7.2, 3 Hz, 1H), 5.52 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.36(d, *J* = 3 Hz, 1H), 5.13 (dd, *J* = 9, 4.8 Hz, 1H), 4.51 (br s, 2H), 4.16 (q, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 1H), 3.59 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.53 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.2, 169.5, 169.4, 166.7 (2C), 137.3, 128.4 (2C), 127.8 (3C), 73.4, 70.6, 70.0, 69.6, 69.4, 67.4, 61.9, 20.7, 20.5, 20.4 (2C), 13.9; CIHRMS: Calculated for $[C_{23}H_{30}O_{11}+Na]^+$: 505.1686, Found: 505.1674.

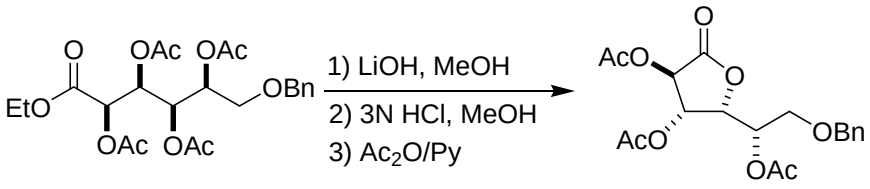
(3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one(5b):



To a stirred solution of (*2S*,3*R*,4*R*,5*S*)-ethyl 2,3,4,5-tetraacetoxy-6-(benzyloxy)hexanoate **3b** (100 mg, 0.21 mmol) in 1 mL of MeOH at room temperature was added solid LiOH (35 mg, 0.85 mmol), the reaction was monitored by TLC and after 1 hr the reaction mixture was acidified with 3M HCl (0.4 mL, 0.96 mmol) and allowed to stirred for 2 hr at room temperature. Then MeOH was removed under reduced pressure, dried under high vaccum and replaced with CH_2Cl_2 (2 mL). Then to the solution was added excess Ac_2O (0.09 mL, 0.8 mmol), pyridine (0.12 mL, 1.6 mmol) and a catalytic amount of DMAP (1.3 mg, 5 mol%) and stirred for 6 h at room temperature. After which 5 ml Ether and 5 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 5 mL $CuSO_4$ solution, 5 mL brine and the aqueous layer was further extracted with ether (3 x 3 mL). The combined organic layers were dried over Na_2SO_4 and the solvent

was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **5b** (51 mg, 61% yield in 3 steps) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.3; $[\alpha]^{25}_D$ 12.4° (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.22 (dddd, *J* = 7.8, 5.4, 3.0, 3.0 Hz, 1H), 4.71 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.7, 169.3, 168.4, 137.2, 128.4 (2C), 127.9, 127.7 (2C), 77.3, 73.6, 72.2, 72.1, 68.9, 66.7, 20.7, 20.5, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1162, Found: 417.1126.

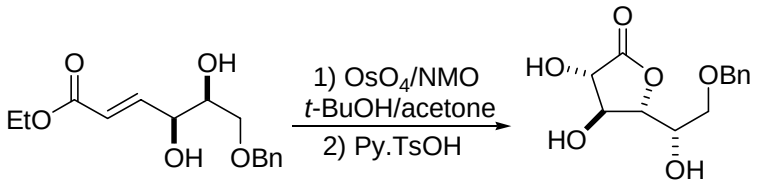
(3*R*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one:



To a stirred solution of (*2R*,3*S*,4*R*,5*S*)-ethyl 2,3,4,5-tetraacetoxy-6-(benzyloxy)hexanoate (23 mg, 0.04 mmol) in 0.5 mL of MeOH at room temperature was added solid LiOH (8.2 mg, 0.19 mmol) the reaction was monitored by TLC and after 1 hr the reaction mixture was acidified with 3M HCl (0.1 mL, 0.24 mmol) and allowed to stirred for 2 hr at room temperature. Then MeOH was removed under reduced pressure, dried under high vaccum and replaced with CH_2Cl_2 (1 mL). Then to the solution was added excess Ac_2O (0.02 mL, 0.2 mmol), pyridine (0.03 mL, 0.4 mmol) and a catalytic amount of DMAP (0.25 mg, 5 mol%) and stirred for 6 h at room temperature. After which 3 ml Ether and 3 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 3 mL $CuSO_4$ solution, 3 mL brine and the aqueous layer was further extracted with ether (3 x 3

mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*R*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (10.2 mg, 65% yield in 3 steps) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.3; $[\alpha]^{25}_D$ 30° (*c* 0.5, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.70 (d, *J* = 8.4 Hz, 1H), 5.63 (dd, *J* = 8.4, 7.8 Hz, 1H), 5.20 (dddd, *J* = 6.6, 6, 1.8, 1.2 Hz, 1H), 5.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.56 (d, *J* = 12 Hz, 1H), 4.51 (d, *J* = 12 Hz, 1H), 3.62 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.58 (dd, *J* = 9.6, 6.6 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.1, 169.7, 169.5, 168.5, 137.3, 128.5 (2C), 127.9, 127.7 (2C), 75.3, 73.5, 72.2, 70.1, 68.0, 66.7, 21.0, 20.4, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1156, Found: 417.1154.

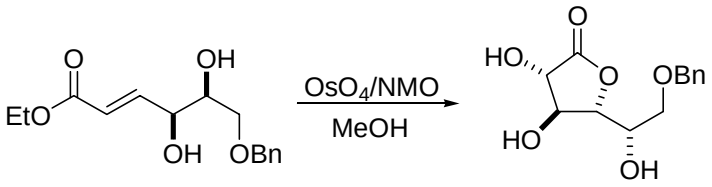
(3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one (4b):



Into a 25 mL round bottom flask was added (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** (200 mg, 0.71 mmol) and added 1 mL of *t*-BuOH, 1 mL of acetone and then cooled to 0 °C. To this solution 0.5 ml 50% NMO in H_2O (2.1 mmol) and OsO_4 (3.6 mg, 14 μmol, 2 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the reaction mixture was filtered through a pad of celite/florisil and eluted with 15 mL 50% Ethyl acetate/ MeOH.. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and replaced with benzene (1 mL) and MeOH (1 mL). To this solution was added Py.TsOH (17 mg, 0.07 mmol, 10 mol%) and the mixture was allowed to reflux for 3 h. The

reaction was cooled to room temperature and after removal of the solvents *in vacuo*, flash chromatography on silica gel (1:9 (v/v) hexanes/EtOAc) afforded (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **4b** (101 mg, 5:1 dr, 53% yield in 2steps) as a viscous oil. R_f (10% MeOH/ EtOAc) = 0.53; Major isomer: $[\alpha]^{25}_{D}$ 29.3° (*c* 1.0, MeOH); IR (thin film, cm^{-1}) 3396, 2928, 2874, 1779, 1455, 1366, 1316, 1215, 1179, 1092, 1027, 978, 905; ^{1}H NMR ($CDCl_3$/MeOH-D_4, 600 MHz) δ 7.27 (m, 5H), 4.48 (br s, 2H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.15 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 6.6, 6, 2.4 Hz, 1H), 3.57 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.52 (dd, *J* = (9.6, 6 Hz, 1H), 2.54 (br s, 3H); ^{13}C NMR ($CDCl_3$/MeOH-D_4, 67.5 MHz) δ 175.1, 137.4, 128.4 (2C), 127.9 (3C), 80.2, 74.3, 73.4, 72.8, 70.6, 67.3; CIHRMS: Calculated for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, Found: 291.0875.

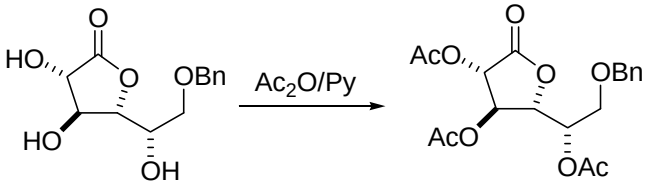
(3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one (4b):



Into a 25 mL round bottom flask was added (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** (300 mg, 1.1 mmol) and added 2 mL of MeOH and then cooled to 0 °C. To this solution 0.75 ml 50% NMO in H_2O (3.3 mmol) and OsO_4 (5.6 mg, 22 μmol, 2 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (150 mg) at room temperature. Then the reaction mixture was filtered through a pad of celite/florisil and eluted with 20 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo* and flash chromatography on silica gel (1:9 (v/v) hexanes/EtOAc) afforded (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **4b** (201 mg, 5:1 dr, 70% yield) as a viscous oil. R_f (10% MeOH/ EtOAc) = 0.53; Major isomer: $[\alpha]^{25}_{D}$

29.3° (*c* 1.0, MeOH); IR (thin film, cm^{-1}) 3396, 2928, 2874, 1779, 1455, 1366, 1316, 1215, 1179, 1092, 1027, 978, 905; ^1H NMR ($CDCl_3$/MeOH-D_4, 600 MHz) δ 7.27 (m, 5H), 4.48 (br s, 2H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.15 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 6.6, 6, 2.4 Hz, 1H), 3.57 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.52 (dd, *J* = (9.6, 6 Hz, 1H), 2.54 (br s, 3H); ^{13}C NMR ($CDCl_3$/MeOH-D_4, 67.5 MHz) δ 175.1, 137.4, 128.4 (2C), 127.9 (3C), 80.2, 74.3, 73.4, 72.8, 70.6, 67.3; CIHRMS: Calculated for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, Found: 291.0875.

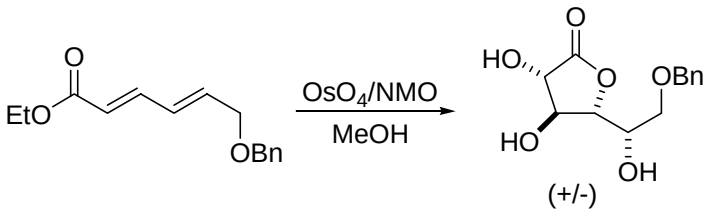
(3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one(5b):



To a solution of (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **4b** (108 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added excess Ac_2O (0.2 mL, 2 mmol), pyridine (0.3 mL, 4 mmol) and a catalytic amount of DMAP (2.4 mg, 5 mol%). The reaction was stirred for 6 h, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **5b** (151 mg, 96% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.3; $[\alpha]^{25}_D$ 12.4^o (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.22 (dddd, *J* = 7.8, 5.4, 3.0, 3.0 Hz, 1H), 4.71 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.7, 169.3, 168.4,

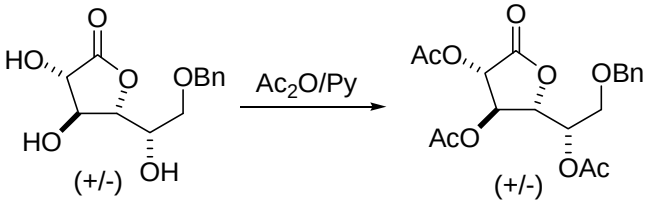
137.2, 128.4 (2C), 127.9, 127.7 (2C), 77.3, 73.6, 72.2, 72.1, 68.9, 66.7, 20.7, 20.5, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1162, Found: 417.1126.

(3*R,4*R**,5*S**,1′*R**)-5-(2′-Benzyloxy-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one (+/-4b):**



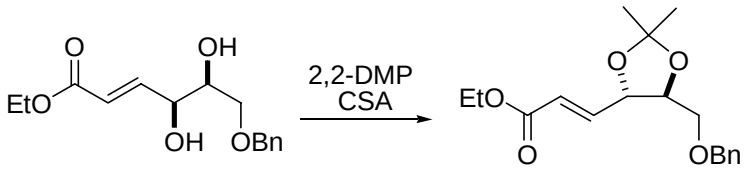
Into a 25 mL round bottom flask was added (2*E*,4*E*)-ethyl 6-(benzyloxy)hexa-2,4-dienoate **1b** (200 mg, 0.81 mmol) and added 1.6 mL of MeOH and then cooled to 0 °C. To this solution 1.15 ml 50% NMO in H_2O (4.8 mmol) and OsO_4 (6.1 mg, 24 μmol, 3 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the reaction mixture was filtered through a pad of celite/florisil and eluted with 15 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo* and flash chromatography on silica gel (1:9 (v/v) hexanes/EtOAc) afforded (3*R**,4*R**,5*S**,1′*R**)-5-(2′-Benzyloxy-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **(+/-4b)** (159 mg, 5:1 dr, 73% yield) as a viscous oil. Major isomer: R_f (10% MeOH/EtOAc) = 0.53; IR (thin film, cm^{-1}) 3396, 2928, 2874, 1779, 1455, 1366, 1316, 1215, 1179, 1092, 1027, 978, 905; ^1H NMR ($CDCl_3$+MeOH-D_4, 600 MHz) δ 7.27 (m, 5H), 4.48 (br s, 2H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.15 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 6.6, 6, 2.4 Hz, 1H), 3.57 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.52 (dd, *J* = (9.6, 6 Hz, 1H), 2.54 (br s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 175.1, 137.4, 128.4 (2C), 127.9 (3C), 80.2, 74.3, 73.4, 72.8, 70.6, 67.3; CIHRMS: Calculated for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, Found: 291.0875.

(3*R,4*S**,5*S**,1′*R**)-5-(2′-Benzyloxy-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (+/-5b):**



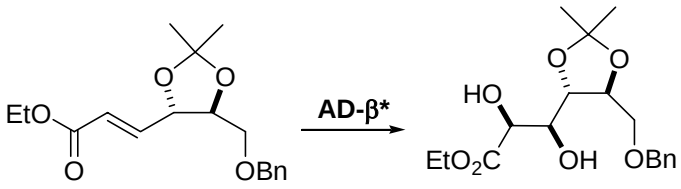
To a solution of (3*R**,4*R**,5*S**,1′*R**)-5-(2′-Benzyloxy-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **(+/-4b)** (150 mg, 0.6 mmol) in CH_2Cl_2 (2 mL) was added excess Ac_2O (0.2 mL, 2.4 mmol), pyridine (0.4 mL, 4.8 mmol) and a catalytic amount of DMAP (3.7 mg, 5 mol%). The reaction was stirred for 6 h, after which 15 ml Ether and 15 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*R**,4*S**,5*S**,1′*R**)-5-(2′-Benzyloxy-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **(+/-)5b** (230 mg, 5:1 dr, 97% yield) as a viscous oil. The compound **(+/-)5b** was dissolved in minimum amount of EtOAc (0.5 mL)and then diluted with hexanes (2 mL) and kept in freezer for overnight afforded 150 mg of major isomer as white crystal. Major isomer: mp 93-95 ^oC; R_f (40% EtOAc/ hexanes) = 0.3; IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.22 (dddd, *J* = 7.8, 5.4, 3.0, 3.0 Hz, 1H), 4.71 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.7, 169.3, 168.4, 137.2, 128.4 (2C), 127.9, 127.7 (2C), 77.3, 73.6, 72.2, 72.1, 68.9, 66.7, 20.7, 20.5, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1162, Found: 417.1126.

(*E*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acrylate (not shown, scheme 3):



To a stirred solution of (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** (0.8 g, 2.85 mmol) in 2 mL dichloromethane at room temperature was added 2,2-DMP (0.53 ml, 4.2 mmol) and CSA (13 mg, 2 mol%). The reaction was stirred for 3 h and quenched with saturated aqueous sodium bicarbonate (10 mL) and the aqueous layer was extracted with ether (3 x 15 mL). The combined organic layers were washed with brine (25 mL), and dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (9:1 (v/v) hexanes/EtOAc) afforded (*E*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acrylate as a viscous oil (0.73 g, 80%): R_f (40% EtOAc/ hexanes) = 0.70; $[\alpha]^{25}_D$ -20.1° (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 2988, 2938, 2904, 1721, 1664, 1495, 1453, 1373, 1305, 1096, 1031, 981 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.34 (m, 5H), 6.89 (dd, *J* = 15.6, 6 Hz, 1H), 6.09 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.61 (d, *J* = 12 Hz, 1H), 4.58 (d, *J* = 12 Hz, 1H), 4.43 (ddd, *J* = 8.4, 5.4, 1.8 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.95 (ddd, *J* = 9, 4.8, 4.2 Hz, 1H), 3.64 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.62 (dd, *J* = 10.8, 1.8 Hz, 1H), 1.45 (s, 3H), 1.43 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.9, 144.0, 137.7, 128.4 (2C), 127.7, 127.6 (2C), 122.5, 110.2, 79.5, 77.4, 73.6, 69.3, 60.6, 26.9, 26.7, 14.2; CIHRMS: Calculated for $[C_{18}H_{24}O_5+Na]^+$: 343.1515, Found: 343.1507.

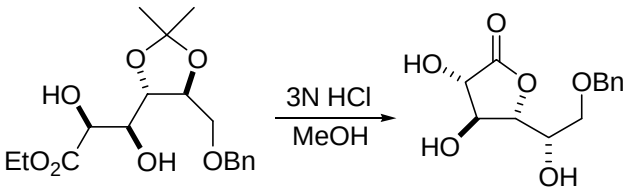
(2*S*, 3*S*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,3-dihydroxypropanoate (6b):



Into a 50 mL round bottom flask was added 4 mL of *t*-BuOH, 4 mL of water, $K_3Fe(CN)_6$ (925 mg, 2.8 mmol), K_2CO_3 (388 mg, 2.8 mmol), $MeSO_2NH_2$ (90 mg, 0.93 mmol), $(DHQD)_2PHAL$ (15 mg, 0.02 mmol, 2.1 mol%), and OsO_4 (5 mg, 0.02 mmol, 2 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added a solution (*E*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acrylate (300 mg, 0.93 mmol) in 1 mL CH_2Cl_2 and the reaction was stirred vigorously at 0 °C for 12h. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the mixture was filtered through a pad of celite/florisil and eluted with (2 x 20 mL) Ethyl acetate. The combined organic layers were dried over anhydrous sodium sulphate and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (2*S*, 3*S*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,3-dihydroxypropanoate **6b** (265 mg, 9:1 dr, 81% yield) as a viscous oil. The major isomer was separated by column chromatography. Major Isomer: R_f (40% EtOAc/ hexanes) = 0.42; $[\alpha]^{25}_D$ 12.1° (*c* 1.1, CH_2Cl_2); IR (thin film, cm^{-1}) 3444, 2987, 2936, 1737, 1662, 1496, 1453, 1373, 1215, 1131, 1090, 910, 859 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.31 (m, 5H), 4.61 (d, *J* = 12 Hz, 1H), 4.57 (d, *J* = 12 Hz, 1H), 4.39 (d, *J* = 6.6 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 4.12 (ddd, *J* = 7.2, 6.6, 4.8 Hz, 1H), 3.92 (ddd, *J* = 8.4, 7.2, 6.6 Hz, 1H), 3.89 (ddd, *J* = 9, 4.8, 1.2 Hz, 1H), 3.73 (dd, *J* = 9, 4.8 Hz, 1H), 3.55 (dd, *J* = 9, 7.2 Hz, 1H), 3.35 (d, *J* = 4.8 Hz, 1H), 3.11 (d, *J* = 7.2 Hz, 1H), 1.40 (s, 3H), 1.39 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 173.2, 136.9, 128.5 (2C), 128.1, 127.9 (2C), 109.6, 78.5, 73.8 (2C), 73.7, 70.7,

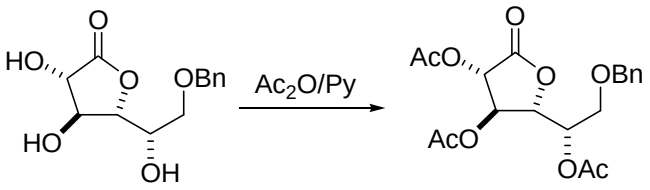
70.4, 61.9, 26.9, 26.8, 14.1; CIHRMS: Calculated for $[C_{18}H_{26}O_7+Na]^+$: 377.1570, Found: 377.1580.

(3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one (4b):



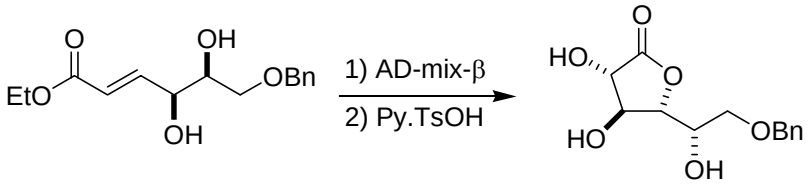
To a stirred solution of (2*S,* 3*S*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,3-dihydroxypropanoate **6b** (227 mg, 0.64 mmol) in 2 mL of MeOH at room temperature was added 3M HCl (0.5 mL, 1.28 mmol) and allowed to stir for 4 hr at room temperature. Then MeOH was removed under reduced pressure, flash chromatography on silica gel (3:7 (v/v) hexanes/EtOAc) afforded (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **4b** as a viscous oil (95 mg, 55%): R_f (10% MeOH/EtOAc) = 0.53; $[\alpha]^{25}_D$ 29.3° (*c* 1.0, MeOH); IR (thin film, cm^{-1}) 3396, 2928, 2874, 1779, 1455, 1366, 1316, 1215, 1179, 1092, 1027, 978, 905; ^{1}H NMR ($CDCl_3$/MeOH-D_4, 600 MHz) δ 7.27 (m, 5H), 4.48 (br s, 2H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.15 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 6.6, 6, 2.4 Hz, 1H), 3.57 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.52 (dd, *J* = (9.6, 6 Hz, 1H), 2.54 (br s, 3H); ^{13}C NMR ($CDCl_3$/MeOH-D_4, 67.5 MHz) δ 175.1, 137.4, 128.4 (2C), 127.9 (3C), 80.2, 74.3, 73.4, 72.8, 70.6, 67.3; CIHRMS: Calculated for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, Found: 291.0875.

(3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one(5b):



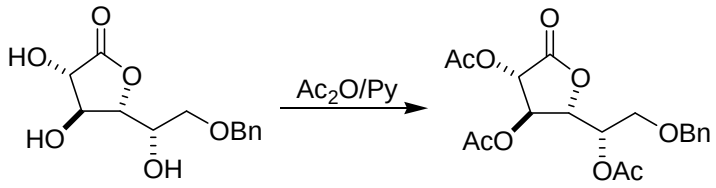
To a solution of (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **4b** (90 mg, 0.33 mmol) in CH_2Cl_2 (1 mL) was added excess Ac_2O (0.17 mL, 1.6 mmol), pyridine (0.26 mL, 3.3 mmol) and a catalytic amount of DMAP (2 mg, 5 mol%). The reaction was stirred for 6 h, after which 5 ml Ether and 5 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 5 mL $CuSO_4$ solution, 5 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **5b** (127 mg, 96% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.3; $[\alpha]^{25}_D$ 12.4^o (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.22 (dddd, *J* = 7.8, 5.4, 3.0, 3.0 Hz, 1H), 4.71 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.7, 169.3, 168.4, 137.2, 128.4 (2C), 127.9, 127.7 (2C), 77.3, 73.6, 72.2, 72.1, 68.9, 66.7, 20.7, 20.5, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1162, Found: 417.1126.

(3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one (4b):



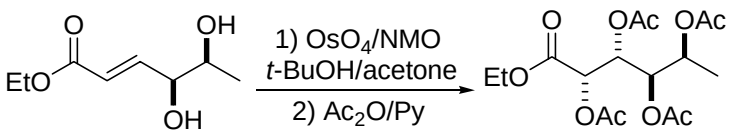
Into a 50 mL round bottom flask was added 4 mL of *t*-BuOH, 2 mL of water, $K_3Fe(CN)_6$ (1.41 g, 4.2 mmol), K_2CO_3 (296 mg, 2.1 mmol), $NaHCO_3$ (180 mg, 2.1 mmol), $MeSO_2NH_2$ (68 mg, 0.71 mmol), $(DHQD)_2PHAL$ (66 mg, 0.08 mmol, 12 mol%), and OsO_4 (18 mg, 0.07 mmol, 10 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added a solution (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** (200 mg, 0.71 mmol) in 1 mL CH_2Cl_2 and the reaction was stirred vigorously at 0 °C for 4h. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the mixture was filtered through a pad of celite/florisil and eluted with 20 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and replaced with benzene (2 mL) and MeOH (2 mL). To this solution was added Py.TsOH (16 mg, 0.07 mmol, 10 mol%) and the mixture was allowed to reflux for 3 h . The reaction was cooled to room temperature and after removal of the solvents *in vacuo*, flash chromatography on silica gel (3:7 (v/v) hexanes/EtOAc) afforded (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one **4b** as a viscous oil (108 mg, 57%): R_f (10% MeOH/ EtOAc) = 0.53; $[\alpha]^{25}_D$ 29.3° (*c* 1.0, MeOH); IR (thin film, cm^{-1}) 3396, 2928, 2874, 1779, 1455, 1366, 1316, 1215, 1179, 1092, 1027, 978, 905; ^1H NMR ($CDCl_3$/MeOH-D_4, 600 MHz) δ 7.27 (m, 5H), 4.48 (br s, 2H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.15 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 6.6, 6, 2.4 Hz, 1H), 3.57 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.52 (dd, *J* = (9.6, 6 Hz, 1H), 2.54 (br s, 3H); ^{13}C NMR ($CDCl_3$/MeOH-D_4, 67.5 MHz) δ 175.1, 137.4, 128.4 (2C), 127.9 (3C), 80.2, 74.3, 73.4, 72.8, 70.6, 67.3; CIHRMS: Calculated for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, Found: 291.0875.

(3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one(5b):



To a solution of (3*S*,4*S*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one 4**b** (108 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added excess Ac_2O (0.2 mL, 2 mmol), pyridine (0.3 mL, 4 mmol) and a catalytic amount of DMAP (2.5 mg, 5 mol%). The reaction was stirred for 6 h, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*S*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **5b** (154 mg, 97% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.3; $[\alpha]^{25}_D$ 12.4^o (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.22 (dddd, *J* = 7.8, 5.4, 3.0, 3.0 Hz, 1H), 4.71 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.7, 169.3, 168.4, 137.2, 128.4 (2C), 127.9, 127.7 (2C), 77.3, 73.6, 72.2, 72.1, 68.9, 66.7, 20.7, 20.5, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1162, Found: 417.1126.

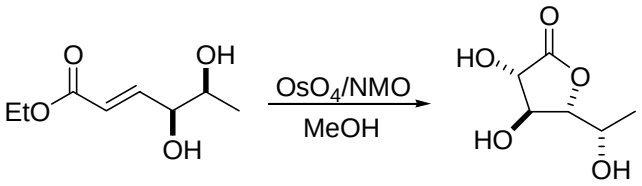
(*2S*,3*R*,4*R*,5*S*)-ethyl 2,3,4,5-tetraacetoxyhexanoate (3a):



Into a 25 mL round bottom flask was added (*E*,4*S*,5*S*)-ethyl 4,5-dihydroxyhex-2-enoate **2a** (200 mg, 1.15 mmol) and added 1 mL of *t*-BuOH, 1 mL of acetone and then cooled to 0 °C. To this solution 0.4 ml 50% NMO in H_2O (3.4 mmol) and OsO_4 (5.8 mg, 0.02 mmol, 2 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the mixture was filtered through a pad of celite/florisil and eluted with 15 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and replaced with CH_2Cl_2 (1 mL) was added excess Ac_2O (0.5 mL, 5.7 mmol), pyridine (0.9 mL, 11.5 mmol) and a catalytic amount of DMAP (7 mg, 5 mol%). The reaction was stirred for 3 hour, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (4:1 (v/v) hexane / EtOAc) to yield (*2S*,3*R*,4*R*,5*S*)-ethyl 2,3,4,5-tetraacetoxyhexanoate **3a** (237 mg, 6:1 dr, 55% yield in 2 steps) as a viscous oil. The major isomer was separated by column chromatography. Major isomer: white crystalline solid; mp 86-88 ^oC; R_f (40% EtOAc/ hexanes) = 0.41; $[\alpha]^{25}_D$ 3.1^o (*c* 1.1, CH_2Cl_2); IR (thin film, cm^{-1}) 2983, 2928, 2872, 1766, 1760, 1748, 1455, 1374, 1213, 1096, 1048, 952; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.63 (dd, *J* = 9.6, 1.8 Hz, 1H), 5.24 (dd, *J* = 9.6, 1.8 Hz, 1H), 5.14 (d, *J* = 1.8 Hz, 1H), 5.06 (qd, *J* = 7.2, 2.4 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 1H), 2.17(s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 6.6 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.4, 170.3, 169.8, 169.1, 167.0, 70.4, 69.7, 68.1, 66.8, 62.1, 20.9, 20.5, 20.4(2C), 16.2, 13.9; CIHRMS: Calculated for $[C_{16}H_{24}O_{10}+Na]^+$: 399.3455, Found: 399.3476. Minor isomer:

R_f (40% EtOAc/ hexanes) = 0.31; $[\alpha]^{25}_D$ -18.5° (*c* 0.8, CH_2Cl_2); IR (thin film, cm^{-1}) 2983, 2928, 2872, 1766, 1760, 1748, 1455, 1374, 1213, 1096, 1048, 952; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.59 (dd, *J* = 7.2, 3 Hz, 1H), 5.25 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.18 (d, *J* = 2.4 Hz, 1H), 5.05 (qd, *J* = 6, 4.8 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 2.19 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.9, 169.8, 169.7, 169.4, 166.6, 71.9, 70.4, 69.3, 68.2, 62.1, 20.9, 20.5, 20.4(2C), 16.1, 13.9; CIHRMS: Calculated for $[C_{16}H_{24}O_{10}+Na]^+$: 399.3455, Found: 399.3497.

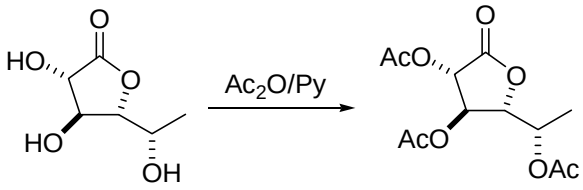
(3*S*,4*S*,5*R*)-dihydro-3,4-dihyroxy-5-((1′*S*)-1′-hydroxyethyl)furan-2(3*H*)-one (4a):



Into a 25 mL round bottom flask was added (*E*,4*S*,5*S*)-ethyl 4,5-dihydroxyhex-2-enoate **2a** (200 mg, 1.15 mmol) and added 1.5 mL of MeOH and then cooled to 0 °C. To this solution 0.8 ml 50% NMO in H_2O (3.44 mmol) and 5.8 mg OsO_4 (0.02 mmol, 2 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature and filtered through a pad of celite/florisil and eluted with 20 mL MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and chromatography on silica gel (9:1 (v/v) EtOAc/MeOH) to yield (3*S*,4*S*,5*R*)-dihydro-3,4-dihyroxy-5-((1′*S*)-1′-hydroxyethyl)furan-2(3*H*)-one **4a** (121 mg, 6:1 dr, 65% yield) as a viscous oil. The major isomer was separated by coloumn chromatography. Major isomer: R_f (10% MeOH/EtOAc) = 0.38; $[\alpha]^{25}_D$ 31.4° (*c* 1.5, MeOH); IR (thin film, cm^{-1}) 3365, 2965, 2923, 2867, 1776, 1315, 1236, 1140, 1097, 1051, 984; ^1H NMR (MeOH-D_4, 600 MHz): δ 4.36 (d, *J* = 9 Hz, 1H), 4.19 (dd, *J* = 9, 7.8 Hz, 1H), 3.94 (dd, *J* = 7.8, 3 Hz, 1H), 3.91 (qd, *J* = 6.6, 3.6 Hz, 1H), 3.34 (br s, 3H), 1.33 (d, *J* = 6.6, 3H); ^{13}C NMR

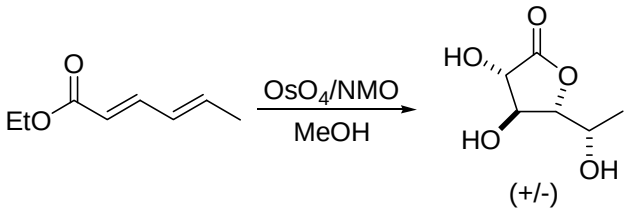
(MeOH-D_4, 150 MHz): δ 175.1, 80.1, 74.7, 73.9, 65.4, 18.3; CIHRMS: Calculated for $[C_6H_9O_5+Na_2]^+$: 207.0239, Found: 207.0278.

(3*S*,4*R*,5*R*)-5-((1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (5a):



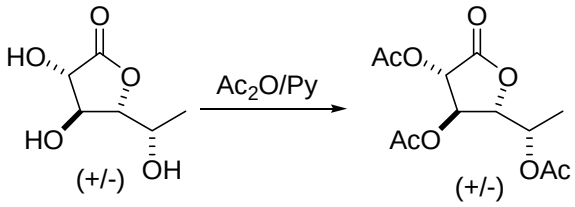
To a solution of (3*S*,4*S*,5*R*)-dihydro-3,4-dihyroxy-5-((*S*)-1-hydroxyethyl)furan-2(3*H*)-one **4a** (110 mg, 0.7 mmol) in CH_2Cl_2 (2 mL) was added excess Ac_2O (0.27 mL, 2.8 mmol), pyridine (0.42 mL, 5.6 mmol) and a catalytic amount of DMAP (4.2 mg, 5 mol%). The reaction was stirred for 6 h, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*S*,4*R*,5*R*)-5-((1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **5a** (190 mg, 97% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.28; $[\alpha]^{25}_D$ 14.5^o (*c* 2, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.60 (d, *J* = 7.2 Hz, 1H), 5.39 (dd, *J* = 7.2, 6.6 Hz, 1H), 5.13 (qd, *J* = 6.6, 3.0 Hz, 1H), 4.36 (dd, *J* = 6.6, 3.6 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 1.36 (d, *J* = 6.6, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.8, 169.6, 169.3, 168.3, 80.4, 72.5, 72.1, 67.7, 20.8, 20.5, 20.3, 15.8; CIHRMS: Calculated for $[C_{12}H_{16}O_8+Na]^+$: 311.0737, Found: 311.0745.

(3*R,4*R**,5*S**,1′*R**)-dihydro-3,4-dihyroxy-5-(1′-hydroxyethyl)furan-2(3*H*)-one (+/-4a):**



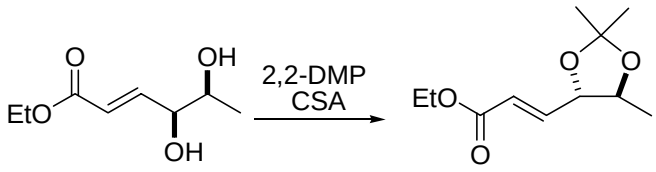
Into a 25 mL round bottom flask was added (2*E*,4*E*)-ethyl hexa-2,4-dienoate **1a** (200 mg, 1.43 mmol) and added 1.5 mL of MeOH and then cooled to 0 °C. To this solution 2 ml 50% NMO in H_2O (8.57 mmol) and 10 mg OsO_4 (0.04 mmol, 3 mol%) was added and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature and filtered through a pad of celite/florisil and eluted with 20 mL MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and chromatography on silica gel (9:1 (v/v) EtOAc/MeOH) to yield (3*R**,4*R**,5*S**,1′*R**)-dihydro-3,4-dihyroxy-5-(1′-hydroxyethyl)furan-2(3*H*)-one **(+/-)4a** (162 mg, 6:1 dr, 70% yield) as a viscous oil. The major isomer was separated by coloumn chromatography. Major isomer: R_f (10% MeOH/EtOAc) = 0.38; IR (thin film, cm^{-1}) 3365, 2965, 2923, 2867, 1776, 1315, 1236, 1140, 1097, 1051, 984; ^{1}H NMR (MeOH-D_4, 600 MHz): δ 4.36 (d, J = 9 Hz, 1H), 4.19 (dd, J = 9, 7.8 Hz, 1H), 3.94 (dd, J = 7.8, 3 Hz, 1H), 3.91 (qd, J = 6.6, 3.6 Hz, 1H), 3.34 (br s, 3H), 1.33 (d, J = 6.6, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.1, 80.1, 74.7, 73.9, 65.4, 18.3; CIHRMS: Calculated for $[C_6H_9O_5+Na_2]^+$: 207.0239, Found: 207.0278.

(3*R,4*S**,5*S**,1′*R**)-5-(1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (+/-5a):**



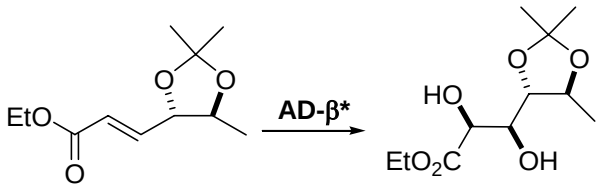
To a solution of (3*R**,4*R**,5*S**,1′*R**)-dihydro-3,4-dihyroxy-5-(1′-hydroxyethyl)furan-2(3*H*)-one **(+/-)4a** (130 mg, 0.8 mmol) in CH_2Cl_2 (2 mL) was added excess Ac_2O (0.33 mL, 3.2 mmol), pyridine (0.5 mL, 6.4 mmol) and a catalytic amount of DMAP (4.8 mg, 5 mol%). The reaction was stirred for 6 h, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*R**,4*S**,5*S**,1′*R**)-5-(1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **(+/-)5a** (190 mg, 97% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.28; IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.60 (d, *J* = 7.2 Hz, 1H), 5.39 (dd, *J* = 7.2, 6.6 Hz, 1H), 5.13 (qd, *J* = 6.6, 3.0 Hz, 1H), 4.36 (dd, *J* = 6.6, 3.6 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 1.36 (d, *J* = 6.6, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.8, 169.6, 169.3, 168.3, 80.4, 72.5, 72.1, 67.7, 20.8, 20.5, 20.3, 15.8; CIHRMS: Calculated for $[C_{12}H_{16}O_8+Na]^+$: 311.0737, Found: 311.0745.

(*E*)-ethyl 3-((4*S*,5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-yl)acrylate (not shown in scheme 3):



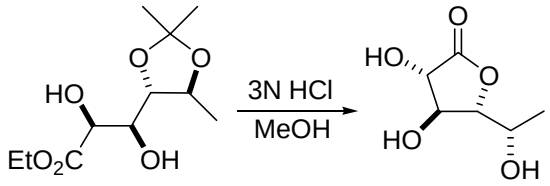
To a stirred solution of (*E*,4*S*,5*S*)-ethyl 4,5-dihydroxyhex-2-enoate **2a** (300 mg, 1.72 mmol) in 2 mL dichloromethane at room temperature was added 2,2-DMP (0.42 ml, 3.44 mmol) and CSA (8 mg, 2 mol%). The reaction was stirred for 3 h and quenched with saturated aqueous sodium bicarbonate (10 mL) and the aqueous layer was extracted with ether (3 x 15 mL). The combined organic layers were washed with brine (25 mL), and dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (9:1 (v/v) hexanes/EtOAc) afforded (*E*)-ethyl 3-((4*S*,5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-yl)acrylate as a viscous oil (310 mg, 83%): R_f (30% EtOAc/ hexanes) = 0.56; $[\alpha]^{25}_D$ 6.5° (*c* 2.2, CH_2Cl_2); IR (thin film, cm^{-1}) 2985, 2936, 2876, 1723, 1663, 1454, 1373, 1302, 1249, 1175, 1107, 1036, 980 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 6.85 (dd, *J* = 15.6, 6 Hz, 1H), 6.11 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 4.07 (qd, *J* = 6, 2.4 Hz, 1H), 3.83 (ddd, *J* = 8.4, 6, 2.4 Hz, 1H), 1.31(d, *J* = 6 Hz, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.9, 143.4, 122.8, 119.2, 81.6, 76.4, 60.6, 27.2, 26.6, 16.6, 14.2; CIHRMS: Calculated for $[C_{11}H_{18}O_4+Na]^+$: 237.1097, Found: 237.0995.

(2*S*,3*S*)-ethyl 2,3-dihydroxy-3-((4*S*,5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-yl)propanoate (6a):



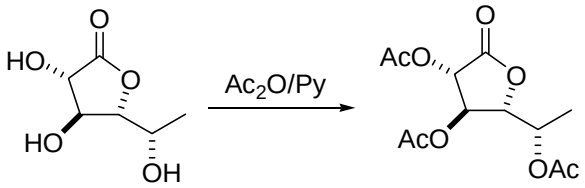
Into a 50 mL round bottom flask was added 2 mL of *t*-BuOH, 2 mL of water, $K_3Fe(CN)_6$ (461 mg, 1.4 mmol), K_2CO_3 (193 mg, 1.4 mmol), $NaHCO_3$ (117 mg, 1.4 mmol), $MeSO_2NH_2$ (45 mg, 0.47 mmol), $(DHQD)_2PHAL$ (7.6 mg, 0.01 mmol, 2.1 mol%), and OsO_4 (2.5 mg, 0.01 mmol, 2 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added a solution (*E*)-ethyl 3-((4*S*,5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-yl)acrylate (100 mg, 0.47 mmol) in 1 mL CH_2Cl_2 and the reaction was stirred vigorously at 0 °C for 12h. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the mixture was filtered through a pad of celite/florisil and eluted with (2 x 20 mL) Ethyl acetate. The combined organic layers were dried over anhydrous sodium sulphate and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (2*S*,3*S*)-ethyl 2,3-dihydroxy-3-((4*S*,5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-yl)propanoate **6a** (110 mg, 10:1 dr, 95% yield) as a viscous oil. The major isomer was separated by column chromatography. Major isomer: white crystalline solid; mp 86-87 ^oC; R_f (40% EtOAc/ hexanes) = 0.42; $[\alpha]^{25}_D$ 11.4° (*c* 2, CH_2Cl_2); IR (thin film, cm^{-1}) 3334, 2987, 2937, 1735, 1662, 1578, 1416, 1331, 1298, 1140, 988, 884 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 4.44 (dd, *J* = 4.2, 1.8 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.13 (dq, *J* = 7.8, 6 Hz, 1H), 3.90 (ddd, *J* = 10.2, 9, 1.8 Hz, 1H), 3.61 (ddd, *J* = 9, 7.8 Hz, 1H), 3.14 (d, *J* = 4.2 Hz, 1H), 2.20 (d, *J* = 10.2 Hz, 1H), 1.42 (s, 3H), 1.39 (s, 3H), 1.38 (d, *J* = 6 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 173.3, 108.6, 80.9, 76.5, 73.7, 70.7, 62.3, 27.4, 26.9, 19.4, 14.1; CIHRMS: Calculated for $[C_{11}H_{20}O_6+Na]^+$: 271.1152, Found: 271.1163.

(3*S*,4*S*,5*R*)-dihydro-3,4-dihyroxy-5-((1′*S*)-1′-hydroxyethyl)furan-2(3*H*)-one (4a):



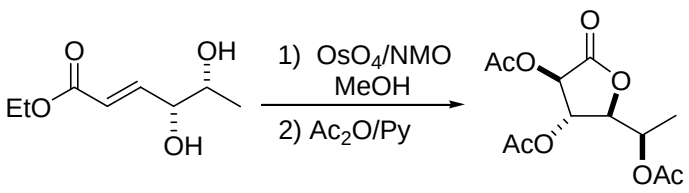
To a stirred solution of (2*S*,3*S*)-ethyl 2,3-dihydroxy-3-((4*S*,5*S*)-2,2,5-trimethyl-1,3-dioxolan-4-yl)propanoate **6a** (100 mg, 0.40 mmol) in 2 mL of MeOH at room temperature was added 3M HCl (0.4 mL, 0.8 mmol), the reaction was allowed to stir for 4 hr at room temperature. Then MeOH was removed under reduced pressure, flash chromatography on silica gel (3:7 (v/v) hexanes/EtOAc) afforded (3*S*,4*S*,5*R*)-dihydro-3,4-dihyroxy-5-((1′*S*)-1′-hydroxyethyl)furan-2(3*H*)-one **4a** as a viscous oil (42 mg, 65%): R_f (10% MeOH/EtOAc) = 0.38; $[\alpha]^{25}_D$ 31.4^o (*c* 1.5, MeOH); IR (thin film, cm^{-1}) 3365, 2965, 2923, 2867, 1776, 1315, 1236, 1140, 1097, 1051, 984; ^{1}H NMR (MeOH-D_4, 600 MHz): δ 4.36 (d, *J* = 9 Hz, 1H), 4.19 (dd, *J* = 9, 7.8 Hz, 1H), 3.94 (dd, *J* = 7.8, 3 Hz, 1H), 3.91 (qd, *J* = 6.6, 3.6 Hz, 1H), 3.34 (br s, 3H), 1.33 (d, *J* = 6.6, 3H); ^{13}C NMR (MeOH-D_4, 150 MHz): δ 175.1, 80.1, 74.7, 73.9, 65.4, 18.3; CIHRMS: Calculated for $[C_6H_9O_5+Na_2]^+$: 207.0239, Found: 207.0278.

(3*S*,4*R*,5*R*)-5-((1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (5a):



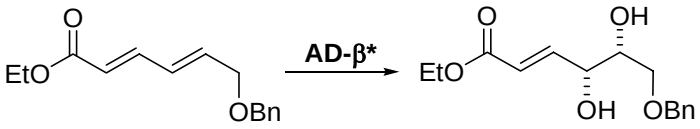
To a solution of (3*S*,4*S*,5*R*)-dihydro-3,4-dihyroxy-5-((*S*)-1-hydroxyethyl)furan-2(3*H*)-one **4a** (40 mg, 0.25 mmol) in CH_2Cl_2 (1 mL) was added excess Ac_2O (0.1 mL, 1 mmol), pyridine (0.15 mL, 2 mmol) and a catalytic amount of DMAP (1.5 mg, 5 mol%). The reaction was stirred for 6 h, after which 5 ml Ether and 5 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 5 mL $CuSO_4$ solution, 5 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*S*,4*R*,5*R*)-5-((1′*S*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one **5a** (69 mg, 97% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.28; $[\alpha]^{25}_D$ 14.5^o (*c* 2, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.60 (d, *J* = 7.2 Hz, 1H), 5.39 (dd, *J* = 7.2, 6.6 Hz, 1H), 5.13 (qd, *J* = 6.6, 3.0 Hz, 1H), 4.36 (dd, *J* = 6.6, 3.6 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 1.36 (d, *J* = 6.6, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.6, 169.3, 168.3, 80.4, 72.5, 72.1, 67.7, 20.8, 20.5, 20.3, 15.8; CIHRMS: Calculated for $[C_{12}H_{16}O_8+Na]^+$: 311.0737, Found: 311.0745.

(3*R*,4*S*,5*S*)-5-((1′*R*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (*ent*-5a):



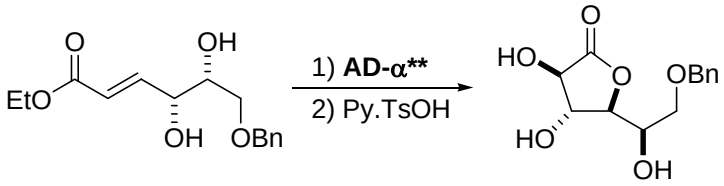
Into a 25 mL round bottom flask was added (*E*,4*R*,5*R*)-ethyl 4,5-dihydroxyhex-2-enoate ***ent*-2a** (200 mg, 1.15 mmol) and added 2 mL of MeOH and then cooled to 0 °C. To this solution was added 0.8 ml 50% NMO in H_2O (0.40 g, 3.44 mmol) and 5.8 mg OsO_4 (0.02 mmol, 2 mol%) and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature and filtered through a pad of florisil and eluted with MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and replaced with CH_2Cl_2 (2 mL) was added excess Ac_2O (0.6 mL, 5.7 mmol), pyridine (0.9 mL, 11.4 mmol) and DMAP (7 mg, 5 mol%). The reaction was stirred for 4 hr, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*R*,4*S*,5*S*)-5-((1′*R*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one (211 mg, 6:1 dr, 64% yield in 2 steps) as a viscous oil. The major isomer was separated by column chromatography. Major isomer: R_f (40% EtOAc/ hexanes) = 0.28; $[\alpha]^{25}_D$ -17.3° (*c* 2.1, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^1H NMR ($CDCl_3$, 600 MHz): δ 5.60 (d, *J* = 7.2 Hz, 1H), 5.39 (dd, *J* = 7.2, 6.6 Hz, 1H), 5.13 (qd, *J* = 6.6, 3.0 Hz, 1H), 4.36 (dd, *J* = 6.6, 3.6 Hz, 1H), 2.16 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 1.36 (d, *J* = 6.6, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.9, 169.6, 169.3, 168.3, 80.5, 72.5, 72.1, 67.7, 20.8, 20.5, 20.3, 15.8; CIHRMS: Calculated for $[C_{12}H_{16}O_8+Na]^+$: 311.0737, Found: 311.0745.

(*E*,4*R*,5*R*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate(*ent*-2b):



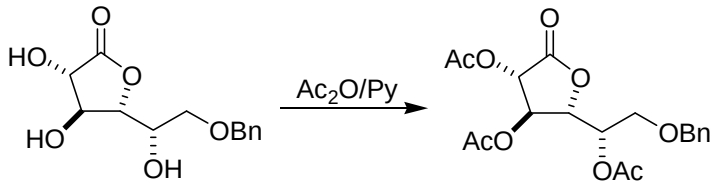
Into a 250 mL round bottom flask was added 60 mL of *t*-BuOH, 60 mL of water, $K_3Fe(CN)_6$ (24.7 g, 75 mmol), K_2CO_3 (10.35 g, 75 mmol), $MeSO_2NH_2$ (2.37 g, 25 mmol), $(DHQD)_2PHAL$ (409 mg, 0.52 mmol, 2.1 mol%), and OsO_4 (127 mg, 0.5 mmol, 2 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added (2*E*,4*E*)-ethyl 6-(benzyloxy)hexa-2,4-dienoate (6.15 g, 25 mmol) and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Ethyl acetate (40 mL) was added to the reaction mixture, and after separation of the layers, the aqueous phase was further extracted with the organic solvent (2 x 30 mL). The combined organic layers were washed with brine, and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded 6.3 g (90 % yield) of (*E*,4*R*,5*R*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate as a light yellow oil: R_f (30% EtOAc/ hexanes) = 0.13; $[\alpha]^{25}_D$ 20.5° (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3421, 2985, 2937, 2871, 1715, 1699, 1659, 1455, 1393, 1279, 1179, 1039, 984 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 6.91 (dd, *J* = 15.6, 5.4 Hz, 1 H), 6.14 (dd, *J* = 15.6, 1.8 Hz, 1 H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.54 (d, *J* =11.4 Hz, 1H), 4.38 (ddd, *J* = 9.0, 4.2, 1.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2 H), 3.76 (ddd, *J* = 9.6, 5.4, 4.2 Hz, 1H), 3.65 (dd, *J* = 9.6, 4.2 Hz, 1 H), 3.60 (dd, *J* = 9.6, 5.4 Hz, 1H), 2.84 (d, *J* = 4.8 Hz, 1H), 2.61 (d, *J* = 6.0 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 166.2, 145.9, 137.3, 128.5(2C), 128.0, 127.8(2C), 122.5, 73.7, 72.1, 71.7, 71.5, 60.5, 14.2; CIHRMS: Calculated for $[C_{15}H_{20}O_5+Na]^+$: 303.1202, Found: 303.1207.

(3*R*,4*R*,5*R*)-5-(2′-Benzyloxy-(1′*R*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one (*ent*-4b):



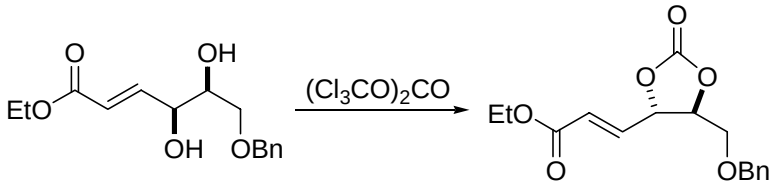
Into a 50 mL round bottom flask was added 4 mL of *t*-BuOH, 2 mL of water, $K_3Fe(CN)_6$ (1.41 g, 4.2 mmol), K_2CO_3 (296 mg, 2.1 mmol), $NaHCO_3$ (180 mg, 2.1 mmol), $MeSO_2NH_2$ (68 mg, 0.71 mmol), $(DHQ)_2PHAL$ (66 mg, 0.08 mmol, 12 mol%), and OsO_4 (18 mg, 0.07 mmol, 10 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added a solution (*E*,4*R*,5*R*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate ***ent*-2b** (200 mg, 0.71 mmol) in 1 mL CH_2Cl_2 and the reaction was stirred vigorously at 0 °C for 4h. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature. Then the mixture was filtered through a pad of celite/florisil and eluted with 20 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and replaced with benzene (2 mL) and MeOH (2mL). To this solution was added Py.TsOH (16 mg, 0.07 mmol, 10 mol%) and the mixture was allowed to reflux for 3 h . The reaction was cooled to room temperature and after removal of the solvents *in vacuo*, flash chromatography on silica gel (3:7 (v/v) hexanes/EtOAc) afforded (3*R*,4*R*,5*S*)-5-(2′-Benzyloxy-(1′*R*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one ***ent*-4b** as a viscous oil (120 mg, 63%): R_f (10% MeOH/ EtOAc) = 0.53; $[\alpha]^{25}_D$ -20.3° (*c* 1.0, MeOH); IR (thin film, cm^{-1}) 3396, 2928,2874, 1779, 1455, 1366, 1316, 1215, 1179, 1092, 1027, 978, 905; ^1H NMR ($CDCl_3$/MeOH-D_4, 600 MHz) δ 7.27 (m, 5H), 4.48 (br s, 2H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 4.15 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 6.6, 6, 2.4 Hz, 1H), 3.57 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.52 (dd, *J* = (9.6, 6 Hz, 1H), 2.54 (br s, 3H); ^{13}C NMR ($CDCl_3$/MeOH-D_4, 67.5 MHz) δ 175.1, 137.4, 128.4 (2C), 127.9 (3C), 80.2, 74.3, 73.4, 72.8, 70.6, 67.3; CIHRMS: Calculated for $[C_{13}H_{16}O_6+Na]^+$: 291.0845, Found: 291.0875.

(3*R*,4*S*,5*S*)-5-(2′-Benzyloxy-(1′*R*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one(*ent*-5b):



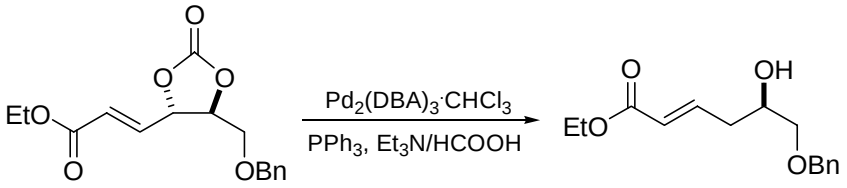
To a solution of (3*R*,4*R*,5*S*)-5-(2′-Benzyloxy-(1′*R*)-1′-hydroxy-ethyl)-3,4-dihydroxy-dihydro-furan-2-one ***ent*-4b** (108 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added excess Ac_2O (0.2 mL, 2 mmol), pyridine (0.3 mL, 4 mmol) and a catalytic amount of DMAP (2.5 mg, 5 mol%). The reaction was stirred for 6 h, after which 10 ml Ether and 10 mL of NH_4Cl was added to remove excess base. The organic layer was washed with 10 mL $CuSO_4$ solution, 10 mL brine and the aqueous layer was further extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (7:3 (v/v) hexane / EtOAc) to yield (3*R*,4*S*,5*S*)-5-(2′-Benzyloxy-(1′*R*)-1′-acetoxy-ethyl)-3,4-diacetoxy-dihydro-furan-2-one ***ent*-5b** (154 mg, 97% yield) as a viscous oil. R_f (40% EtOAc/ hexanes) = 0.3; $[\alpha]^{25}_D$ -13.1^o (*c* 2.1, CH_2Cl_2); IR (thin film, cm^{-1}) 2953, 2922, 2876, 2863, 1808, 1749, 1373, 1234, 1179, 1100, 1069, 1044; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (m, 5H), 5.61 (d, *J* = 7.2 Hz, 1H), 5.46 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.22 (dddd, *J* = 7.8, 5.4, 3.0, 3.0 Hz, 1H), 4.71 (dd, *J* = 7.2, 3.0 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 3.68 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.65 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 169.8, 169.7, 169.3, 168.4, 137.2, 128.4 (2C), 127.9, 127.7 (2C), 77.3, 73.6, 72.2, 72.1, 68.9, 66.7, 20.7, 20.5, 20.3; CIHRMS: Calculated for $[C_{19}H_{22}O_9+Na]^+$: 417.1162, Found: 417.1126.

(*E*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2-oxo-1,3-dioxolan-4-yl)acrylate (7b):



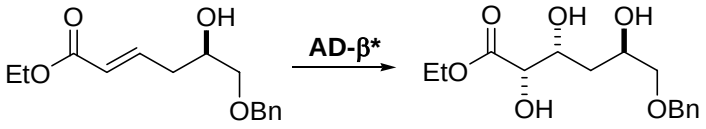
Into a 250 mL round-bottom flask was placed 6.5 g (23.2 mmol) of (*E*,4*S*,5*S*)-ethyl 6-(benzyloxy)-4,5-dihydroxyhex-2-enoate **2b** in 25 mL of dichloromethane and 10 mL (116 mmol) of pyridine. The solution was cooled to 0 °C and 7.6 g (25.6 mmol) of triphosgene in 50 mL of dichloromethane was added slowly with an addition funnel. The reaction was stirred for 1.5 h and quenched with saturated aqueous NH_4Cl (40 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (30 mL), brine (25 mL), and dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded (*E*)-ethyl 3-((4*S*,5*S*)-5-((benzyloxy)methyl)-2-oxo-1,3-dioxolan-4-yl)acrylate **7b** as a clear, colorless oil (6.17 g, 87%): R_f (30% EtOAc/hexanes) = 0.37; $[\alpha]^{25}_D$ -54.7° (*c* 1.03, CH_2Cl_2); IR (thin film, cm^{-1}) 2983, 2938, 2908, 2872, 1806, 1721, 1665, 1496, 1454, 1369, 1304, 1272, 1174, 1111, 1032, 978 cm^{-1}; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.34 (m, 5H), 6.83 (dd, *J* = 15.6, 5.4 Hz, 1H), 6.14 (dd, *J* = 15.6, 1.4 Hz, 1H), 5.17(ddd, *J* = 6.6, 5.4, 1.2 Hz, 1H), 4.64 (d, *J* = 12 Hz, 1H), 4.58 (d, *J* = 12 Hz, 1H), 4.46 (ddd, *J* = 6.6, 3.6, 3.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.75 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.66 (dd, *J* = 11.4, 3.6 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 164.9, 153.5, 139.7, 136.7, 128.5 (2C), 128.1, 127.7 (2C), 124.5, 79.3, 76.4, 73.7, 67.7, 61.0, 14.1; CIHRMS: Calculated for $[C_{16}H_{18}O_6+Na]^+$: 329.1001, Found: 329.1003.

(*R*,*E*)-ethyl 6-(benzyloxy)-5-hydroxyhex-2-enoate (8b):



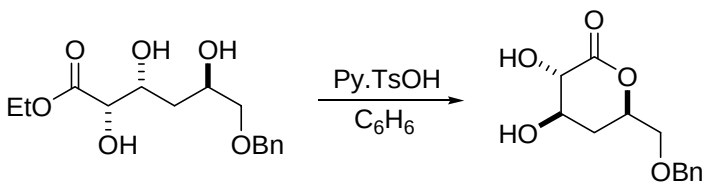
Into a 100 mL, round bottomed flask fitted with a condenser and maintained under nitrogen was placed 3 g (9.8 mmol) of (*E*)-ethyl 3-((4*S*,5*S*)-5-ethyl-2-oxo-1,3-dioxolan-4-yl)acrylate **7b**, 50.7 mg (0.05 mmol, 0.5 mol%) of $Pd_2(DBA)_3{\cdot}CHCl_3$, 26 mg (0.1 mmol, 1 mol%) of PPh_3, and 20 mL of THF. Triethylamine 4 mL, (29.4 mmol) and HCO_2H 0.902 mg (19.6 mmol) were added and the mixture was allowed to reflux for 30 minutes. The reaction was cooled to room temperature and quenched with saturated aqueous sodium bicarbonate (20 mL). The aqueous layer was extracted with ether (3 x 30 mL). The organic layer was washed with brine (20 mL) and dried with anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (7:3 (v/v) hexanes/EtOAc) afforded (*R*,*E*)-ethyl 6-(benzyloxy)-5-hydroxyhex-2-enoate **8b** as a yellow oil (2.32 g , 90 %): Mosher ester analysis of this alcohol shows 90 %ee; R_f (30% EtOAc/hexanes) = 0.32; $[\alpha]^{25}_D$ -3.2° (*c* 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3472, 2981, 2934, 2903, 2867, 1715, 1653, 1454, 1392, 1368, 1319, 1269, 1207, 1166, 1096, 1042, 982; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.34 (m, 5H), 6.96 (ddd, *J* = 15.6, 7.2, 7.2 Hz, 1H), 5.89 (ddd, *J* = 15.6, 1.3, 1.3 Hz, 1H), 4.55 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2 H), 3.96 (m, 1H), 3.52 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.38 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.42-2.39 (m, 2H), 2.38 (d, *J* = 1.5 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 166.1, 144.5, 137.6, 128.2 (2C), 127.6, 127.5 (2C), 123.4, 73.5, 73.1, 68.9, 60.0, 36.0, 14.0; GCMS: 264 (M^+), 191 (M^+-CO_2Et).

(2*S*,3*R*,5*R*)-ethyl 6-(benzyloxy)-2,3,5-trihydroxyhexanoate (9b):



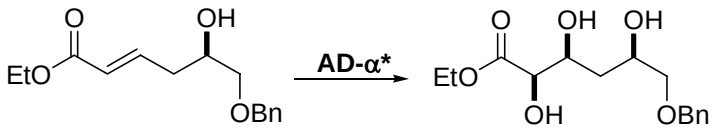
Into a 50 mL round bottom flask was added 10 mL of *t*-BuOH, 10 mL of water, $K_3Fe(CN)_6$ (4.93 g, 15 mmol), K_2CO_3 (2.07 g, 15 mmol), $MeSO_2NH_2$ (475 mg, 5 mmol), $(DHQD)_2PHAL$ (155 mg, 0.2 mmol, 4 mol%), and OsO_4 (25.4 mg, 0.1 mmol, 2 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added (*R,E*)-ethyl 6-(benzyloxy)-5-hydroxyhex-2-enoate **8b** (1.32 g, 5 mmol) and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature and stirred for 15 min. Then the mixture was filtered through a pad of celite/florisil and eluted with 50 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (3:7 (v/v) hexanes/EtOAc) afforded 1.19 g of (2*S*,3*R*,5*R*)-ethyl 6-(benzyloxy)-2,3,5-trihydroxyhexanoate **9b** as a viscous oil (14:1 dr, 80% yield). The major isomer was separated by column chromatography. Major isomer: R_f (100% EtOAc) = 0.44; $[\alpha]^{25}_D$ 11.7° (*c* 2.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3470, 2982, 2953, 2927, 2867, 1732, 1454, 1396, 1370, 1299, 1260, 1212, 1096, 1027; ^1H NMR ($CDCl_3$, 600 MHz) δ 7.32 (m, 5H), 4.56 (s, 2H), 4.31-4.21 (m, 3H), 4.13 (m, 1H), 4.08 (dd, *J* = 6, 1.8 Hz, 1H), 3.52 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.27 (br s, 1H), 2.77 (br s, 1H), 1.81 (ddd, *J* = 14.4, 9.6, 3 Hz, 1H), 1.68 (br s, 1H), 1.67 (ddd, *J* = 14.4, 9.6, 3.6 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 173.2, 137.7, 128.4 (2C), 127.8, 127.7 (2C), 74.4, 73.9, 73.3, 69.3, 67.4, 61.9, 36.5, 14.1; GCMS: 298 (M^+), 281 (M^+-OH), 253(M^+-OEt).

(3*S*,4*R*,6*R*)-6-((benzyloxy)methyl-tetrahydro-3,4-dihydroxypyran-2-one (10b):



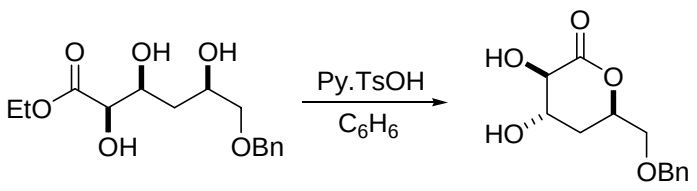
To a solution of (2*S*,3*R*,5*R*)-ethyl 6-(benzyloxy)-2,3,5-trihydroxyhexanoate **9b** (150 mg, 0.50 mmol) in benzene (3 mL), was added Py.TsOH (6 mg, 0.03 mmol, 5 mol%) and the mixture was allowed to reflux for 5h . The reaction was cooled to room temperature and quenched with saturated aqueous sodium bicarbonate (2 mL). The aqueous layer was extracted with ether (3 x 20 mL). The organic layer was washed with brine (10 mL) and dried with anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (4:6 (v/v) hexanes/EtOAc) afforded (3*S*,4*R*,6*R*)-6-((benzyloxy)methyl-tetrahydro-3,4-dihydroxypyran-2-one **10b** as a viscous oil (118 mg, 95%): R_f (100% EtOAc) = 0.33; $[\alpha]^{25}_D$ -9.4° (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3420, 2927, 2921, 2869, 1740, 1453, 1367, 1231, 1177, 1096, 1026, 923; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.32 (m, 5H), 4.56 (s, 2H), 4.49 (dddd, *J* = 10.6, 7.9, 3.9, 3.7 Hz, 1H), 4.04 (dd, *J* = 10.9, 3.9 Hz, 1H), 3.99 (d, *J* = 10.9 Hz, 1H), 3.65 (dd, *J* = 10.6, 3.9 Hz, 1H), 3.57 (dd, *J* = 10.6, 4.1 Hz, 1H), 3.33 (br s, 1H), 2.76 (br s, 1H), 2.28 (ddd, *J* = 12.4, 4.1, 3.9 Hz, 1H), 2.11 (ddd, *J* = 12.4, 10.6, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 172.8, 137.4, 128.5 (2C), 127.9, 127.7 (2C), 76.8, 74.1, 73.5, 71.1, 68.7, 32.1; GCMS: 252(M^+), 145 (M^+-OBn).

(2*R*,3*S*,5*R*)-ethyl 6-(benzyloxy)-2,3,5-trihydroxyhexanoate (11b):



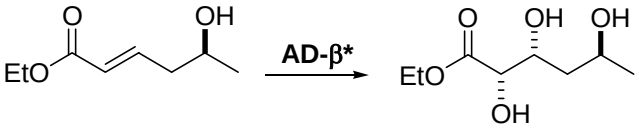
Into a 50 mL round bottom flask was added 10 mL of *t*-BuOH, 10 mL of water, $K_3Fe(CN)_6$ (4.93 g, 15 mmol), K_2CO_3 (2.07 g, 15 mmol), $MeSO_2NH_2$ (475 mg, 5 mmol), $(DHQ)_2PHAL$ (155 mg, 0.2 mmol, 4 mol%), and OsO_4 (25.4 mg, 0.1 mmol, 2 mol%). The mixture was stirred at room temperature for about 15 minutes and then cooled to 0 °C. To this solution was added (*R*,*E*)-ethyl 6-(benzyloxy)-5-hydroxyhex-2-enoate **8b** (1.32 g, 5 mmol) and the reaction was stirred vigorously at 0 °C overnight. The reaction was quenched with solid sodium sulfite (100 mg) at room temperature and stirred for 15 min. Then the mixture was filtered through a pad of celite/florisil and eluted with 50 mL 50% Ethyl acetate/ MeOH. The combined organic layers were dried over anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (2:8 (v/v) hexanes/EtOAc) afforded 1.19 g of (2*R*,3*S*,5*R*)-ethyl 6-(benzyloxy)-2,3,5-trihydroxyhexanoate **11b** as a viscous oil (16:1 dr, 80% yield). The major isomer was separated by column chromatography. Major isomer: R_f (100% EtOAc) = 0.44; $[\alpha]^{25}_D$ -7.4° (*c* 1.3, CH_2Cl_2),); IR (thin film, cm^{-1}) 3470, 2982, 2953, 2927, 2867, 1732, 1454, 1396, 1370, 1299, 1260, 1212, 1096, 1027; ^1H NMR ($CDCl_3$, 270 MHz) δ 7.33 (m, 5H), 4.56 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.24-4.09 (m, 2H), 4.05 (dd, *J* = 7.3, 1.8 Hz, 1H), 3.49 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.40 (dd, *J* = 9.5, 7.1 Hz, 1H), 3.32 (d, *J* = 7.1 Hz, 1H), 3.13 (d, *J* = 2.7 Hz, 1H), 3.07 (br s, 1H), 1.84 (ddd, *J* = 14.4, 5.9, 3.7 Hz, 1H), 1.69 (ddd, *J* = 14.4, 3.3, 3.1 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 172.9, 137.6, 128.5 (2C), 127.9, 127.8 (2C), 74.1, 73.6, 73.4, 71.9, 70.1, 61.9, 35.8, 14.1; GCMS: 298 (M^+), 281 (M^+-OH), 253(M^+-OEt).

(3*R*,4*S*,6*R*)-6-((benzyloxy)methyl-tetrahydro-3,4-dihydroxypyran-2-one (12b):



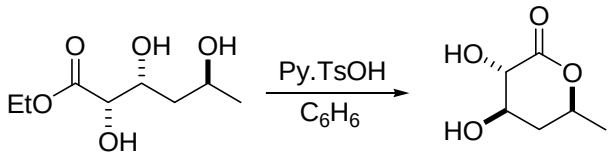
To a solution of (2*R*,3*S*,5*R*)-ethyl 6-(benzyloxy)-2,3,5-trihydroxyhexanoate **11b** (150 mg, 0.50 mmol) in benzene (3 mL), was added Py.TsOH (6 mg, 0.03 mmol, 5 mol%) and the mixture was allowed to reflux for 5h . The reaction was cooled to room temperature and quenched with saturated aqueous sodium bicarbonate (2 mL). The aqueous layer was extracted with ether (3 x 10 mL). The organic layer was washed with brine (10 mL) and dried with anhydrous sodium sulfate. After removal of the solvents *in vacuo*, flash chromatography on silica gel (4:6 (v/v) hexanes/EtOAc) afforded (3*R*,4*S*,6*R*)-6-((benzyloxy)methyl-tetrahydro-3,4-dihydroxypyran-2-one **12b** as colorless crystal (118 mg, 95%): R_f (100% EtOAc) = 0.33; $[\alpha]^{25}_D$ -14.9° (*c* 0.67, CH_2Cl_2); mp 57-58 °C; IR (thin film, cm^{-1}) 3420, 2924, 2860, 1747, 1454, 1367, 1328, 1242, 1208, 1126, 1096, 1027, 923; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.35 (m, 5H), 4.74 (ddd, , *J* = 9.0, 8.4, 4.8 Hz, 1H), 4.58 (s, 2H), 4.25 (d, *J* = 7.8 Hz, 1H), 4.08 (ddd, , *J* = 8.4, 7.8, 4.8 Hz, 1H), 3.69 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.67 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.63 (d, *J* = 4.8 Hz, 1H), 2.29 (ddd, *J* = 14.4, 9.6, 8.4 Hz, 1H), 1.99 (ddd, *J* = 14.4, 4.8, 4.2 Hz, 1H), 1.59 (br s, 1H); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 173.3, 137.3, 128.5 (2C), 127.9, 127.7 (2C), 74.7, 73.6, 73.2, 71.0, 68.8, 32.7; GCMS: 252(M^+), 145 (M^+-OBn); The relative and absolute configuration of 13a was confirmed by single-crystal X-ray analysis.

(2*S*,3*R*,5*S*)-ethyl 2,3,5-trihydroxyhexanoate (9a):



Following the same procedure as mentioned for compound **(9b)**, the (2*S*,3*R*,5*S*)-ethyl 2,3,5-trihydroxyhexanoate **9a** was produced (0.22 g, 1.1 mmol) in 81% yield from (0.23 g, 1.4 mmol) (*S*, *E*)-ethyl 5-hydroxyhex-2-enoate **8a** as a viscous oil (9:1 dr). The major isomer was separated by column chromatography. Major isomer: R_f (50% EtOAc/hexane) = 0.16; $[\alpha]^{25}_D$ -6° (*c* 0.4, CH_2Cl_2); IR (thin film, cm^{-1}) 3485, 2972, 2959, 2936, 1735, 1507, 1465, 1443, 1370, 1287, 1219, 1180, 1108, 1036, 981; ^1H NMR ($CDCl_3$, 600 MHz) δ 4.29 (dd, *J* = 4.2, 1.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 4.22 (ddd, *J* = 10.2, 6, 3.6 Hz, 1H), 4.16 (dqd, *J* = 9.6, 6, 2.4 Hz, 1H), 4.08 (dd, *J* = 6, 2.4 Hz, 1H), 3.29 (d, *J* = 6 Hz, 1H), 2.82 (d, *J* = 4.2 Hz, 1H), 2.80 (d, *J* = 6.6 Hz, 1H), 1.88 (ddd, *J* = 15, 9.6, 3 Hz, 1H), 1.62 (ddd, *J* = 15, 8.4, 3.6 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.27 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.2, 73.8, 69.7, 65.1, 62.1, 41.5, 23.6, 14.1; CIHRMS: Calculated for $[C_8H_{16}O_5+Na]^+$: 215.0889, Found: 215.0892.

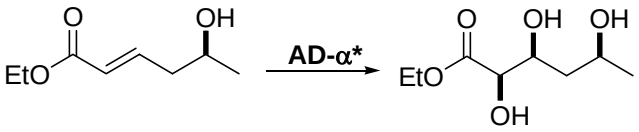
(3*S*,4*R*,6*S*)-tetrahydro-3,4-dihydroxy-6-methylpyran-2-one (10a):



Following the same procedure as mentioned for compound **(10b)**, the (3*S*,4*R*,6*S*)-tetrahydro-3,4-dihydroxy-6-methylpyran-2-one **10a** was produced (30 mg, 0.20 mmol) in 80% yield from (50 mg, 0.26 mmol) (2*S*,3*R*,5*S*)-ethyl 2,3,5-trihydroxyhexanoate **9a** as a

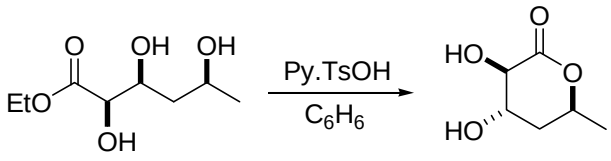
viscous oil: R_f (50% EtOAc/hexane) = 0.14; $[\alpha]^{25}_D$ –2.5° (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3431, 2924, 1642, 1507, 1465, 1443, 1370, 1287, 1180, 1126, 1036; ^1H NMR ($CDCl_3$, 600 MHz) δ 4.47 (dqd, *J* = 12, 6, 3.6 Hz, 1H), 3.99 (dd, *J* = 9.6 Hz, 1H), 4.05 (ddd, *J* = 13.8, 9.6, 3.6 Hz, 1H), 3.41 (br s, 1H), 2.76 (br s, 1H), 2.28 (ddd, *J* = 14.4, 3.6, 3 Hz, 1H), 1.83 (ddd, *J* = 13.8, 12, 11.4 Hz, 1H), 1.44 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.1, 75.0, 74.1, 69.1, 37.5, 20.7; CIHRMS: Calculated for $[C_6H_9O_4+Na_2]^+$: 191.0291, Found: 191.0301.

(2*R*,3*S*,5*S*)-ethyl 2,3,5-trihydroxyhexanoate (11a):



Following the same procedure as mentioned for compound **(11b)**, the (2*R*,3*S*,5*S*)-ethyl 2,3,5-trihydroxyhexanoate **11a** was produced (0.23 g, 1.2 mmol) in 85% yield from (0.23 g, 1.4 mmol) (*S*, *E*)-ethyl 5-hydroxyhex-2-enoate **8a** as a viscous oil (10:1 dr, 85% yield). The major isomer was separated by column chromatography. Major isomer: R_f (50% EtOAc/hexane) = 0.16; $[\alpha]^{25}_D$ 2.6° (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3459, 2971, 2931, 1738, 1507, 1448, 1374, 1301, 1261, 1214, 1140, 1079, 1028, 939; ^1H NMR ($CDCl_3$, 600 MHz) δ 4.31 (q, *J* = 7.2 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 1H), 4.19 (ddd, *J* = 9.6, 3, 2.4 Hz, 1H), 4.11 (dddd, *J* = 15.6, 6.6, 6, 3 Hz, 1H), 4.05 (d, *J* = 2.4 Hz, 1H), 3.14 (br s, 2H), 1.82 (ddd, *J* = 14.4, 10.2, 9.6 Hz, 1H), 1.69 (ddd, *J* = 14.4, 6, 3 Hz, 1H), 1.58 (br s, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 172.9, 73.7, 72.7, 67.8, 61.9, 41.2, 24.0, 14.1; CIHRMS: Calculated for $[C_8H_{16}O_5+Na]^+$: 215.0889, Found: 215.0892.

(3*R*,4*S*,6*S*)-tetrahydro-3,4-dihydroxy-6-methylpyran-2-one (12a):



Following the same procedure as mentioned for compound **(12b)**, the (3*R*,4*S*,6*S*)-tetrahydro-3,4-dihydroxy-6-methylpyran-2-one **12a** was produced (36 mg, 0.21 mmol) in 83% yield from (50 mg, 0.26 mmol) (2*R*,3*S*,5*S*)-ethyl 2,3,5-trihydroxyhexanoate **11a** as a viscous oil: R_f (50% EtOAc/hexane) = 0.14; $[\alpha]^{25}_{D}$ –32.1° (*c* 1, CH_2Cl_2); IR (thin film, cm^{-1}) 3431, 2924, 1642, 1507, 1465, 1443, 1370, 1287, 1180, 1126, 1036; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 4.74 (dqd, *J* = 11.4, 6, 3.6 Hz, 1H), 4.31 (d, *J* = 7.8 Hz, 1H), 4.01 (ddd, *J* = 8.4, 7.8, 3 Hz, 1H), 3.49 (br s, 1H), 2.86 (br s, 1H), 2.13 (ddd, *J* = 15, 10.8, 8.4 Hz, 1H), 1.98 (ddd, *J* = 15, 3.6, 3 Hz, 1H), 1.41 (d, *J* = 6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.7, 73.1, 72.1, 69.6, 38.1, 20.7; CIHRMS: Calculated for $[C_6H_9O_4+Na_2]^+$: 191.0291, Found: 191.0301.