Stereoselective Amine-Catalyzed Carbohydrate Chain Elongation

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Experimental Procedures

^{1}H – NMR, ^{13}C-NMR and correlation experiments were carried out at 500 MHz and 125 MHz or 300 MHz and 75 MHz (as described in characterization of products). Chemical shifts are given in ppm. High resolution mass spectroscopy was performed out on a LTQ-FT-ICR machine (Finnigan). Purification of products was accomplished by flash chromatography (Merck silica gel 60, particle size 0.04 -0.063 mm), which was made into a slurry with a mixture of DCM/MeOH (9:1) containing 1 % of N-Ethyldimethylamin before packing of the chromatography column. Thin layer chromatography was performed with Merck Silica Gel 60 F_{254} TLC plates.
Reactants were purchased from Aldrich and used without further purification.

General reaction procedures

General procedure for the reaction of pentoses/hexoses with ethyl acetoacetate

150 mg (1 mmol, 1 eq) of the pentoses **1b - e** or (180 mg (1 mmol, 1 eq) of the hexoses **4a – c)**, 195 mg (1.5 mmol, 1.5 eq) of ethyl acetoacetate, 24 mg (0.25 mmol, 0.25 eq) of 2-Pyridone and 26 mg (0.2 mmol, 0.2 eq) *N*,*N*-Diisopropylethylamine were dissolved in 0.5 ml dimethyl sulfoxide and the reaction mixture was stirred vigorously at room temperature and monitored by TLC. After no further reaction progress was detectable (60-96 h) the mixture was purified by silica flash chomatography, using solvent mixtures of dichlormethane/ methanol (9:1 to 8:2). The products were isolated as colorless to yellowish oils.

General procedure for the reaction of ribose with 3-keto-esters

150 mg (1 mmol, 1 eq) of ribose, 1.5 mmol (1.5 eq) of **2b – f**, 24 mg of 2-Pyridone (0.25 mmol, 0.25 eq) and 26 mg *N*,*N*-Diisopropylethylamine (0.2 mmol, 0.2 eq) were dissolved in 0.5 ml dimethyl sulfoxide and the reaction mixture was stirred vigorously at room temperature and monitored by TLC. After no further reaction progress was detectable

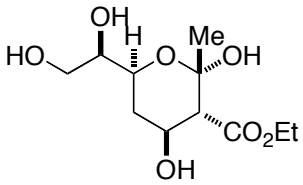
(60-96 h) the mixture was purified by silica flash chomatography, using solvent mixtures of dichlormethane/ methanol (9:1 to 8:2). The products were isolated as colorless to yellowish oils.

Characterization of Products

All products except **3a** were obtained as mixtures of mainly two diastereomers, both characterized in the following. Other diastereomers/anomers were under 5 % level in the mixture and were not characterized.

Deoxyribo – 3a

(2*S*,3*R*,4*S*,6*S*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4-dihydroxy-2-methyltetrahydro-2*H*-pyran-3-carboxylate **(*syn*-3a)**



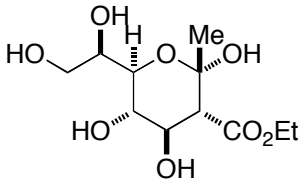
^{1}H-NMR (500 MHz, dmso-D_6) δ [ppm] = 4.10 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.08 – 4.05 (m, 1H), 4.02 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.70 (ddd, *J* = 11.8, 5.8, 1.9 Hz, 1H), 3.46 – 3.41 (m, 1H), 3.33 (ddd, *J* = 11.27, 5.8, 5.1 Hz, 1H), 3.27 (dd, *J* = 11.27, 5.8 Hz, 1H), 2.09 (d, *J* = 10.6 Hz, 1H), 1.89 (ddd, *J* = 12.4, 4.8, 2.0 Hz, 1H), 1.30 (s, 3H), 1.16 (d, *J* = 7.1 Hz, 3H), 1.20 – 1.12 (m, 1H).

^{13}C-NMR (125 MHz, dmso-D_6) δ [ppm] = 170.10, 95.66, 73.59, 68.17, 64.77, 63.15, 59.68, 59.51, 35.21, 28.49, 14.23.

HRMS : calc. for: $C_{11}H_{19}O_7^-$: 263.1136 found: 263.1134

Ribo-3b

(2*S*,3*R*,4*R*,5*S*,6*R*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-methyltetrahydro-2*H*-pyran-3-carboxylate **(*syn*-*3b*)**

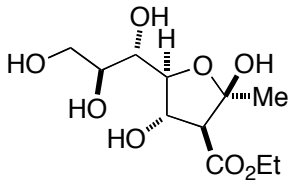


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.29 – 4.19 (m, 2H), 4.08 (dd, *J* = 11.1, 9.0 Hz, 1H), 3.98 (ddd, *J* = 7.4, 3.5, 3.1 Hz, 1H), 3.87 – 3.83 (m, 1H), 3.77 (dd, *J* = 11.9, 3.5 Hz, 1H), 3.70 (dd, *J* = 11.9, 7.4 Hz, 1H), 3.49 (dd, *J* = 10.2, 9.0 Hz, 1H), 2.68 (d, *J* = 11.1 Hz, 1H), 1.49 (s, 3H), 1.28 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.83, 96.14, 72.56, 72.07, 71.99 70.64, 62.30, 62.27, 57.56, 26.73, 13.29.

HRMS : calc. for: $C_{11}H_{19}O_8^-$: 279.1085 found: 279.1082

(2*R*,3*S*,4*S*,5*S*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*S*,2*S*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*anti*-3b)**

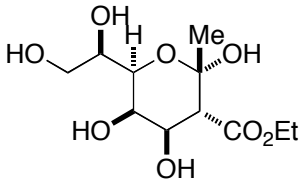


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.92 (dd, *J* = 9.2, 6.9 Hz, 1H), 4.29 – 4.19 (m, 2H), 4.03 (dd, *J* = 6.7, 5.2 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.70 – 3.65 (m, 1H), 3.69 (m, 1H), 3.68 – 3.66 (m, 1H), 3.16 (d, *J* = 9.2 Hz, 1H), 1.66 (s, 3H), 1.28 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 170.72, 103.75, 82.52, 72.54, 72.12, 70.83, 62.40, 61.95, 61.02, 25.62, 13.29.

Ara-3c

(2*S*,3*R*,4*R*,5*R*,6*R*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-methyltetrahydro-2*H*-pyran-3-carboxylate **(*anti*-3c)**

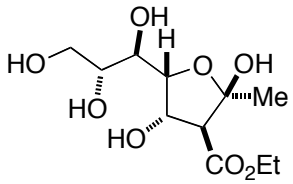


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.29 - 4.21 (m, 2H), 4.26 – 4.23 (m, 2H), 4.07 – 4.06 (m, 1H), 3.83 – 3.79 (m, 1H), 3.62 – 3.59 (m, 1H), 2.84 (d, J = 11.4 Hz, 1H), 1.50 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 173.43, 97.00, 70.70, 69.65, 68.45, 66.72, 63.61, 62.84, 53.52, 27.73, 13.99.

HRMS : calc. for: $C_{11}H_{19}O_8^-$: 279.1085 found: 279.1085

(2*R*,3*R*,4*S*,5*R*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*R*,2*R*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*syn*-3c)**

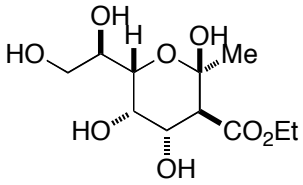


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.83 (dd, J = 9.6, 7.8 Hz, 1H), 4.29 – 4.21 (m, 2H), 4.08 (dd, J = 7.8, 2.4 Hz, 1H), 3.89 – 3.85 (m, 1H), 3.83 – 3.79 (m, 1H), 3.71 – 3.66 (m, 1H), 3.67 – 3.64 (m, 1H), 3.19 (d, J = 9.6 Hz, 1H), 1.67 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.38, 104.00, 82.34, 72.15, 71.92, 70.19, 63.50, 62.93, 61.25, 26.55, 13.99.

Xylo-3d

(2*R*,3*S*,4*S*,5*S*,6*S*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-methyltetrahydro-2*H*-pyran-3-carboxylate **(***anti*-**3d)**

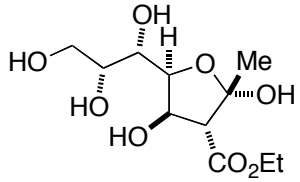


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.30 – 4.24 (m, 2H), 4.23 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.94 (dd, *J* = 7.6, 1.0 Hz, 1H), 3.93 (dd, *J* = 3.3, 1.0 Hz, 1H), 3.90 (ddd, *J* = 7.6, 5.6, 3.5 Hz, 1H), 3.77 (dd, *J* =12.3, 3.5 Hz, 1H), 3.66 (dd, *J* = 12.3, 5.6 Hz, 1H), 2.86 (d, *J* = 11.4 Hz, 1H), 1.53 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 173.44, 96.88, 72.01, 71.92, 68.24, 68.04, 62.87, 62.39, 53.54, 27.68, 13.99.

HRMS : calc. for: $C_{11}H_{19}O_8^-$: 279.1085 found: 279.1085

(2*S*,3*R*,4*R*,5*S*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*S*,2*R*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(***syn*-**3d)**

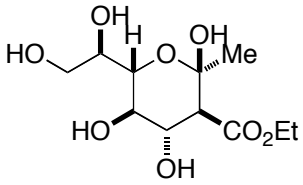


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.78 (dd, *J* =9.6, 7.3 Hz, 1H), 4.30 – 4.24 (m, 2H), 3.98 (dd, *J* = 7.3, 5.1 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.73 (dd, *J* = 5.1, 4.0 Hz, 1H), 3.70 (dd, *J* = 11.6, 4.6 Hz, 1H), 3.64 (dd, *J* = 11.6, 6.9 Hz, 1H), 3.17 (d, *J* = 9.5 Hz, 1H), 1.66 (s, 3H), 1.29, (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.37, 104.25, 83.30, 72.91, 72.81, 72.27, 71.80, 63.19, 62.97, 26.48, 13.99.

Lyxo-3e

(2*R*,3*S*,4*S*,5*R*,6*S*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-methyltetrahydro-2*H*-pyran-3-carboxylate **(*syn*-3e)**

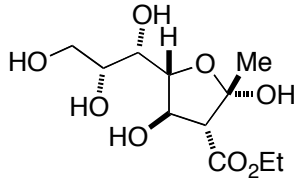


^{1}H-NMR (300 MHz, D_2O) δ [ppm] = 4.29 - 4.17 (m, 2H), 4.10 (dd, *J* = 11.1, 9.1 Hz, 1H), 4.01 (ddd, *J* = 7.2, 5.7, 1.3 Hz, 1H), 3.73 (dd, *J* = 10.0, 1.3 Hz, 1H), 3.66 (dd, *J* = 11.6, 7.2 Hz, 1H), 3.60 (dd, *J* = 11.6, 5.8 Hz, 1H), 3.53 (dd, *J* = 10.1, 9.2 Hz, 1H), 2.66 (d, *J* = 11.1 Hz, 1H), 1.46 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 4H).

^{13}C-NMR (75 MHz, D_2O) δ [ppm] = 172.57, 96.86, 71.70, 71.35, 70.38, 69.14, 63.60, 62.96, 58.37, 27.43, 14.00.

HRMS : calc. for: $C_{11}H_{19}O_8^-$: 279.1085 found: 279.1082

(2*S*,3*R*,4*R*,5*R*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*S*,2*R*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*anti*-3e)**

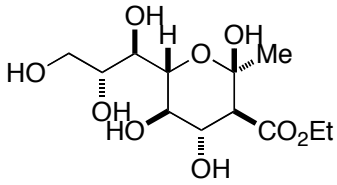


^{1}H-NMR (300 MHz, D_2O) δ [ppm] = 4.89 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.29 - 4.18 (m, 2H), 3.91 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.83 (ddd, *J* = 10.2, 5.2, 2.6 Hz, 1H), 3.73 (dd, *J* = 7.9, 2.5 Hz, 1H), 3.70 – 3.64 (m, 2H), 3.15 (d, *J* = 8.8 Hz, 1H), 1.64 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (75 MHz, D_2O) δ [ppm] = 171.43, 104.73, 82.65, 74.92, 72.74, 71.41, 63.45, 63.00, 61.94, 26.31, 13.98.

Manno-5a

(2*R*,3*S*,4*S*,5*R*,6*R*)-ethyl 2,4,5-trihydroxy-2-methyl-6-((1*R*,2*R*)-1,2,3-trihydroxypropyl)tetrahydro-2*H*-pyran-3-carboxylate **(***syn*-**5a)**

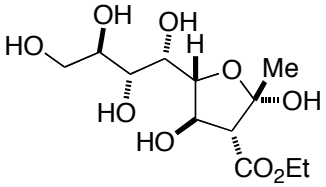


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.33 – 4.22 (m, 2H), 4.15 (dd, *J* = 11.1, 9.1 Hz, 1H), 3.96 (dd, *J* = 10.0, 1.0 Hz, 1H), 3.87 (dd, *J* = 11.7, 2.7 Hz, 1H), 3.85 (dd, *J* = 7.6, 1.1 Hz, 1H), 3.76 (ddd, *J* = 7.6, 6.5, 2.7 Hz, 1H), 3.65 (dd, *J* = 11.7, 6.5 Hz, 1H), 3.56 (dd, *J* = 10.0, 9.1 Hz, 1H), 2.68 (d, *J* = 11.0 Hz, 1H), 1.49 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.91, 96.22, 70.69, 70.61, 70.14, 69.62, 67.84, 63.24, 62.27, 57.75, 26.82, 13.32.

HRMS : calc. for: $C_{12}H_{21}O_9^-$: 309.1191 found: 309.1188

(2*S*,3*R*,4*R*,5*R*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl)tetrahydrofuran-3-carboxylate **(***anti*-**5a)**

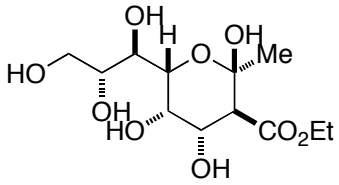


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.92 (dd, *J* = 9.0, 5.9 Hz, 1H), 4.29 – 4.21 (m, 2H), 4.22 – 4.19 (m, 1H), 3.99 – 3.96 (m, 1H), 3.92 (dd, *J* = 8.9, 5.9 Hz, 1H), 3.81 – 3.77 (m, 1H), 3.71 – 3.68 (m, 1H), 3.67 – 3.64 (m, 1H), 3.16 (d, *J* = 9.0 Hz, 1H), 1.65 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 170.77, 104.10, 81.86, 71.30, 70.54, 69.78, 68.25, 63.09, 61.30, 56.65, 25.60, 13.27.

Gluco-5b

(2*R*,3*S*,4*S*,5*S*,6*R*)-ethyl 2,4,5-trihydroxy-2-methyl-6-((1*R*,2*R*)-1,2,3-trihydroxypropyl)tetrahydro-2*H*-pyran-3-carboxylate **(***anti*-**5b)**

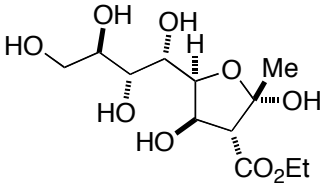


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.31 – 4.21 (m, 2H), 4.28 – 4.26(m, 1H), 4.05 (dd, *J* = 5.0, 1.0 Hz, 1H), 4.04 (dd, *J* = 3.0, 1.0 HZ, 1H), 3.92 (dd, *J* = 5.9, 4.7 Hz, 1H), 3.84 – 3.79 (m, 1H), 3.79 – 3.77 (m, 1H), 3.67 (dd, *J* = 11.6, 6.8 Hz, 1H), 2.91 (d, *J* = 11.4 Hz, 1H), 1.55 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 173.47, 104.27, 73.47, 71.75, 71.48, 70.02, 68.27, 62.89, 62.77, 53.46, 27.65, 13.97.

HRMS : calc. for: $C_{12}H_{21}O_9^-$: 309.1191 found: 309.1192

(2*S*,3*R*,4*R*,5*S*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*S*,2*R*,3*R*)-1,2,3,4-tetrahydroxybutyl)tetrahydrofuran-3-carboxylate **(***syn*-**5b)**

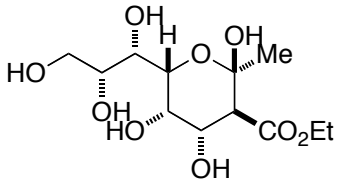


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.73 (dd, *J* = 9.4, 7.2 Hz, 1H), 4.31 – 4.21 (m, 2H), 4.02 (dd, *J* = 7.2, 6.9 Hz, 1H), 3.94 (dd, *J* = 6.9, 1.6 Hz, 1H), 3.86 (dd, *J* = 11.8, 2.9 Hz, 1H), 3.84 – 3.81 (m, 1H), 3.73 (dd, *J* = 8.66, 1.6 Hz, 1H), 3.68 (dd, *J* = 11.8, 6.0 Hz, 1H), 2.89 (d, *J* = 9.5 Hz, 1H), 1.68 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.38, 96.91, 83.89, 73.66, 71.80, 71.45, 71.06, 70.13, 63.53, 62.97, 61.46, 49.53, 26.46, 13.97.

Galacto-5c

(2*R*,3*S*,4*S*,5*S*,6*R*)-ethyl 2,4,5-trihydroxy-2-methyl-6-((1*S*,2*R*)-1,2,3-trihydroxypropyl)tetrahydro-2*H*-pyran-3-carboxylate **(*anti*-5c)**

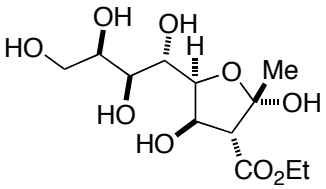


^{1}H-NMR (300 MHz, D_2O) δ [ppm] = 4.31 – 4.22 (m, 2H), 4.26 – 4.23 (m, 1H), 4.09 (dd, *J* = 3.1, 1.1 Hz, 1H), 3.98 (dd, *J* =9.6, 1.1 Hz), 3.93 – 3.89 (m, 1H), 3.79 (dd, *J* = 9.6, 1.6 Hz), 3.71 – 3.68 (m, 2H), 2.86 (d, *J* =11.4 Hz, 1H), 1.56 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, D_2O) δ [ppm] = 172.79, 96.34, 69.97, 69.22, 67.84, 67.68, 66.08, 63.00, 62.17, 52.88, 27.04, 13.26.

HRMS : calc. for: $C_{12}H_{21}O_9^-$: 309.1191 found: 309.1193

(2*S*,3*R*,4*R*,5*S*)-ethyl 2,4-dihydroxy-2-methyl-5-((1*S*,2*S*,3*R*)-1,2,3,4-tetrahydroxybutyl)tetrahydrofuran-3-carboxylate **(*syn*-5c)**

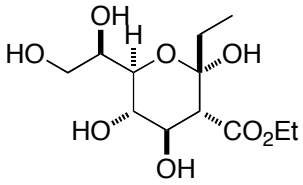


^{1}H-NMR (300 MHz, D_2O) δ [ppm] = 4.89 (dd, *J* = 9.8, 7.8 Hz, 1H), 4.31 – 4.22 (m, 2H), 4.17 (dd, *J* = 7.8, 2.0 Hz, 1H), 4.03 – 3.99 (m, 1H), 3.77 (dd, *J* = 7.8, 2.0 Hz, 1H), 3.73 – 3.67 (m, 2H), 3.64 – 3.60 (m, 1H), 3.21 (d, *J* = 9.8 Hz, 1H), 1.68 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (75 MHz, D_2O) δ [ppm] =170.73, 103.23, 81.66, 71.10, 70.08, 70.03, 67.90, 63.09, 62.24, 60.52, 25.82, 13.26.

6a

(2*S*,3*R*,4*R*,5*S*,6*R*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2-ethyl-2,4,5-trihydroxytetrahydro-2*H*-pyran-3-carboxylate **(*syn*-6a)**

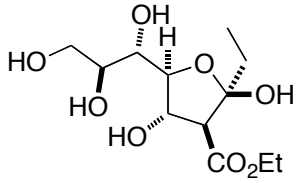


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.28 - 4.20 (m, 2H), 4.13 (dd, *J* = 11.1, 9.0 Hz, 1H), 4.02 – 4.00 (m, 1H), 3.87 - 3.79 (m, 2H), 3.85 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.47 (dd, *J* = 10.1, 9.1 Hz, 1H), 2.77 (d, *J* = 11.1 Hz, 1H), 1.74 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 172.57, 98.52, 72.96, 72.61, 72.51, 71.48, 63.16, 62.93, 58.71, 31.90, 13.96, 7.97.

HRMS : calc. for: $C_{12}H_{21}O_8^-$: 293.1242 found: 293.1242

(2*R*,3*S*,4*S*,5*S*)-ethyl 2-ethyl-2,4-dihydroxy-5-((1*S*,2*S*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*anti*-6a)**

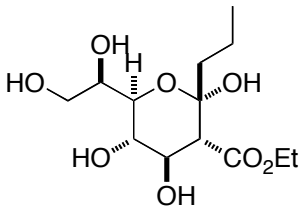


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.94 (dd, *J* = 9.1, 7.0 Hz, 1H), 4.28 - 4.20 (m, 2H), 4.02 (dd, *J* = 7.0, 4.9 Hz 1H), 3.87 - 3.83 (m, 2H), 3.80 (dd, *J* = 4.5, 3.1 Hz, 1H), 3.70 (ddd, *J* = 14.5, 11.9, 7.0 Hz, 1H), 3.23 (d, *J* = 9.1 Hz, 1H), 1.93 (qq, *J* = 14.7, 7.4 Hz, 2H), 1.29 (t, *J* = 7.1, 3H), 1.01 (t, *J* = 7.5 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.58, 106.60, 83.35, 73.36, 72.74, 71.72, 62.85, 62.59, 55.44, 33.49, 13.96, 7.57.

6b

(2*S*,3*R*,4*R*,5*S*,6*R*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-propyltetrahydro-2*H*-pyran-3-carboxylate **(***syn*-**6b)**

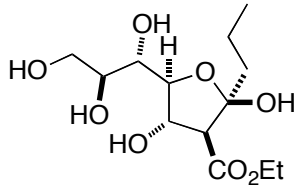


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.29 – 4.20 (m, 2H), 4.12 (dd, *J* = 11.2, 9.1 Hz, 1H), 4.01 (ddd, *J* =7.7, 3.3, 3.1 Hz, 1H), 3.85 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.80 (dd, *J* = 12.0, 3.3 Hz, 1H), 3.70 (dd, *J* = 12.0, 7.7 Hz, 1H), 3.47 (dd, *J* = 10.1, 9.1 Hz, 1H), 2.77 (d, *J* = 11.2 Hz, 1H), 1.70 – 1.64 (m, 2H), 1.53 – 1.36 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.56, 106.18, 72.96, 72.61, 72.52, 71.77, 63.15, 62.91, 41.13, 17.28, 14.07, 13.98.

HRMS : calc. for: $C_{13}H_{28}O_8N^+$: 326.1809 found: 326.1807

(2*R*,3*S*,4*S*,5*S*)-ethyl 2,4-dihydroxy-2-propyl-5-((1*S*,2*S*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(***anti*-**6b)**

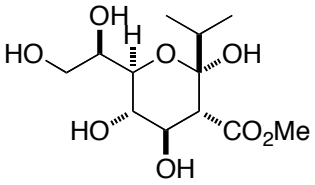


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 4.94 (dd, *J* = 9.1, 6.9 Hz, 1H), 4.29 – 4.20 (m, 2H), 4.02 (dd, *J* = 6.9, 4.8 Hz, 1H), 3.87 - 3.83 (m, 2H), 3.81 – 3.78 (m, 1H), 3.72 – 3.67 (m, 1H), 3.69 – 3.66 (m, 1H), 1.95 – 1.81 (m, 2H),1.53 – 1.36 (m, 2H),1.29 (t, *J* = 7.3 Hz, 3H),0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 172.55, 98.27, 83.26, 73.37, 72.73, 71.43, 62.81, 62.59, 55.82, 42.77, 16.79, 14.01, 13.99.

6c

(2*S*,3*R*,4*R*,5*S*,6*R*)-methyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-isopropyltetrahydro-2*H*-pyran-3-carboxylate **(*syn*-6c)**

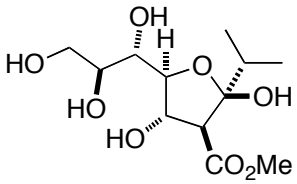


^{1}H-NMR (300 MHz, D_2O) δ [ppm] = 4.10 (dd, *J* = 11.1, 9.0, 1H), 4.02 – 3.99(m, 1H), 3.83 – 3.76 (m, 1H), 3.80 (dd, *J* = 10.1, 7.7 Hz, 1H), 3.71 – 3.66 (m, 1H), 3.45 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.34 (s, 3H), 2.87 (d, *J* = 11.1 Hz, 1H), 1.90 – 1.82 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H).

^{13}C-NMR (75 MHz, D_2O) δ [ppm] = 173.50, 108.22, 73.50, 72.89, 72.09, 71.92, 62.61, 53.84, 53.17, 37.56, 16.21.

HRMS : calc. for: $C_{12}H_{22}O_8Na^+$: 317.1207 found: 317.1204

(2*R*,3*S*,4*S*,5*S*)-methyl 2,4-dihydroxy-2-isopropyl-5-((1*S*,2*S*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*anti*-6c)**

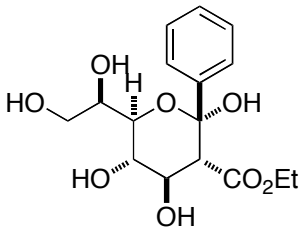


^{1}H-NMR (300 MHz, D_2O) δ [ppm] = 4.91 (dd, *J* = 9.2, 7.1 HZ, 1H), 3.99 – 3.96 (m, 1H), 3.86 – 3.84 (m, 1H), 3.82 – 3.76 (m, 1H), 3.77 – 3.72 (m, 1H), 3.73 – 3.67 (m, 1H), 3.34 (s, 3H), 3.32 (d, *J* = 9.2 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.01 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H).

^{13}C-NMR (75 MHz, D_2O) δ [ppm] = 172.63, 100.04, 83.11, 73.74, 72.70, 72.38, 63.20, 57.62, 53.30, 36.32, 17.18.

6d

(2*R*,3*R*,4*R*,5*S*,6*R*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-phenyltetrahydro-2*H*-pyran-3-carboxylate **(*syn*-6d)**

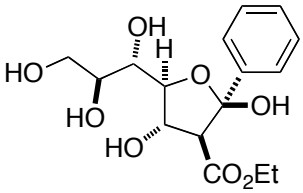


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 7.62 – 7.39 (m, 5H), 4.25 (dd, *J* = 11.1, 9.0 Hz, 1H), 4.13 – 4.08 (m, 1H), 4.11 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.92 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.78 (dd, *J* = 12.0, 7.6 Hz, 1H), 3.68 (dd, *J* = 10.0, 9.0 Hz, 1H), 2.81 (d, *J* = 11.1 Hz, 1H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 171.91, 142.21, 135.59, 129.11, 126.08, 98.06, 74.39, 72.65, 71.74, 71.68, 62.74, 62.61, 60.64, 13.78.

HRMS : calc. for: $C_{16}H_{26}O_8N^+$: 360.1653 found: 360.1649

(2*S*,3*S*,4*S*,5*S*)-ethyl 2,4-dihydroxy-2-phenyl-5-((1*S*,2*S*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*anti*-6d)**

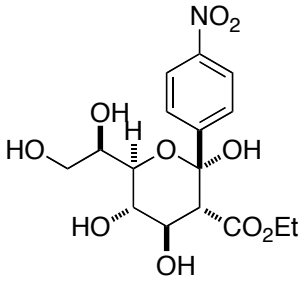


^{1}H-NMR (500 MHz, D_2O) δ [ppm] = 7.62 – 7.39 (m, 5H), 5.10 (dd, *J* = 9.1, 6.7 Hz, 1H), 4.33 (dd, *J* = 6.7, 5.9 Hz, 1H), 4.26 – 4.11 (m, 2H), 4.11 – 4.08 (m, 1H), 3.96 – 3.94 (m, 1H), 3.79 – 3.76 (m, 1H), 3.70 – 3.66 (m, 1H), 3.31 (d, *J* = 9.1 Hz, 1H), 1.17 (t, *J* =7.2 Hz, 3H).

^{13}C-NMR (125 MHz, D_2O) δ [ppm] = 173.81, 141.96, 135.33, 129.68, 126.68, 103.27, 84.10, 72.81, 71.56, 71.53, 62.68, 62.56, 60.57, 13.90.

6e

(2*R*,3*R*,4*R*,5*S*,6*R*)-ethyl 6-((*R*)-1,2-dihydroxyethyl)-2,4,5-trihydroxy-2-(4-nitrophenyl)tetrahydro-2*H*-pyran-3-carboxylate **(*syn*-6e)**

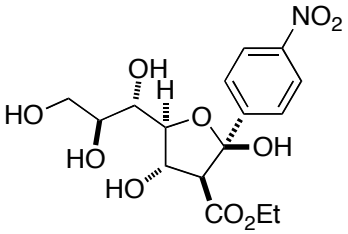


^{1}H-NMR (500 MHz, MeOD) δ [ppm] = 8.18 – 8.08 (m, 2H), 7.78 – 7.66 (m, 2H), 4.21 (dd, *J* = 10.9, 8.9 Hz, 1H), 4.01 (dd, *J* = 10.9, 7.2 Hz, 1H), 3.98 – 3.94 (m, 1H), 3.94 – 3.91 (m, 1H), 3.87 – 3.82 (m, 2H), 3.75 – 3.72 (m, 1H), 3.59 (dd, *J* = 9.6, 8.9 Hz, 1H), 2.60 (d, *J* = 10.9 Hz, 1H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (125 MHz, MeOD) δ [ppm] = 169.95, 151.59, 149.24, 128.42, 123.95, 98.20, 86.57, 74.85, 74.20, 72.54, 61.63, 60.98, 54.80, 14.21.

HRMS : calc. for: $C_{16}H_{21}O_{10}NK^{+}$: 426.0797 found: 426.0795

(2*S*,3*S*,4*S*,5*S*)-ethyl 2,4-dihydroxy-2-(4-nitrophenyl)-5-((1*S*,2*S*)-1,2,3-trihydroxypropyl)tetrahydrofuran-3-carboxylate **(*anti*-6e)**



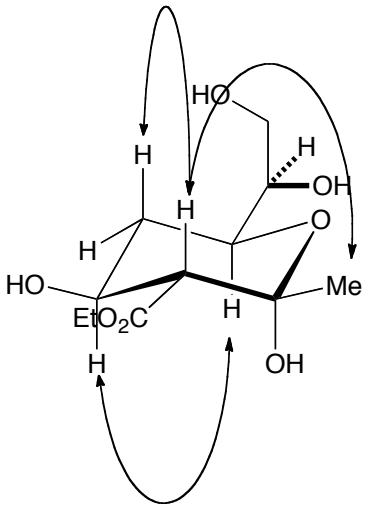
^{1}H-NMR (500 MHz, MeOD) δ [ppm] = 8.18 – 8.08 (m, 2H), 7.78 – 7.66 (m, 2H), 5.11 (dd, *J* = 8.9, 6.5 Hz, 1H), 4.32 (dd, *J* = 6.5, 4.5 Hz, 1H), 3.95 -3.92 (m, 1H), 3.87 – 3.82 (m, 2H), 3.83 – 3.81 (m, 1H), 3.75 – 3.73 (m, 1H), 3.68 – 3.66 (m, 1H), 3.66 – 3.64 (1H), 3.07 (d, *J* = 8.8 Hz, 1H), 1.10 (t, *J* =7.2 Hz. 3H).

^{13}C-NMR (125 MHz, MeOD) δ [ppm] = 171.00, 151.22, 149.28, 128.84, 123.91, 104.75, 73.80, 73.59, 73.51, 65.85, 64.58, 64.08, 49.85, 14.42.

Determination of configuration

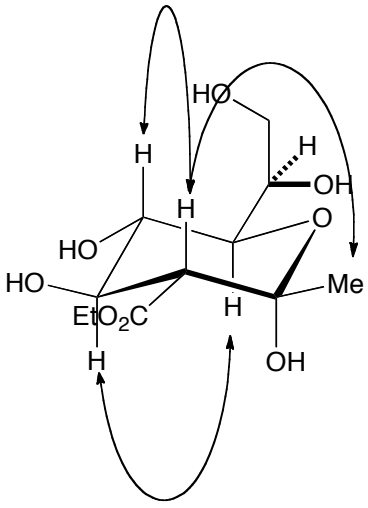
The determination of the configuration of the new formed stereocentres was performed by NOESY-spectroscopy and analysis of the vicinal coupling constants of the cyclic reaction products. In the following the relevant NOE-interactions are illustrated.

Deoxyribo-3a

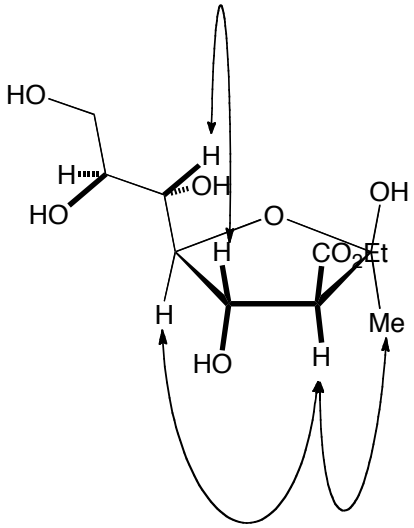


syn-***3a***

Ribo-3b

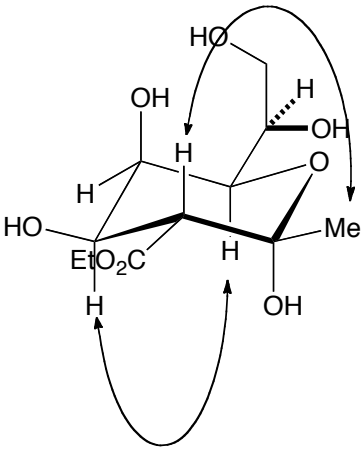


syn-**3b**

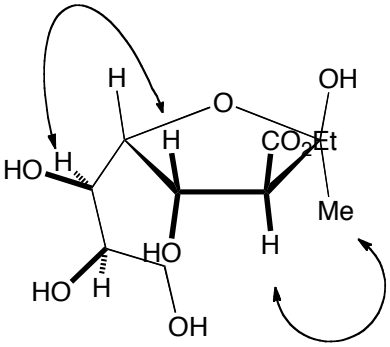


anti-**3b**

Ara-3c

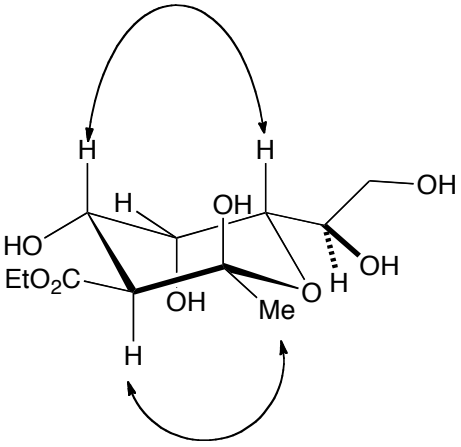


anti-**3c**

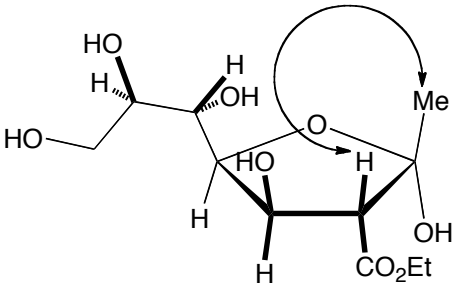


syn-**3c**

Xylo-3d

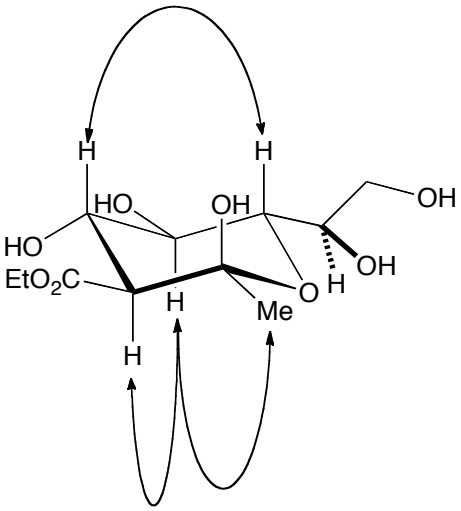


anti-**3d**

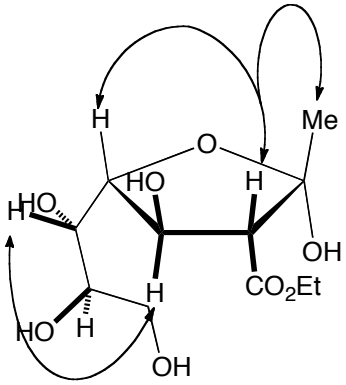


syn-**3d**

Lyxo-3e

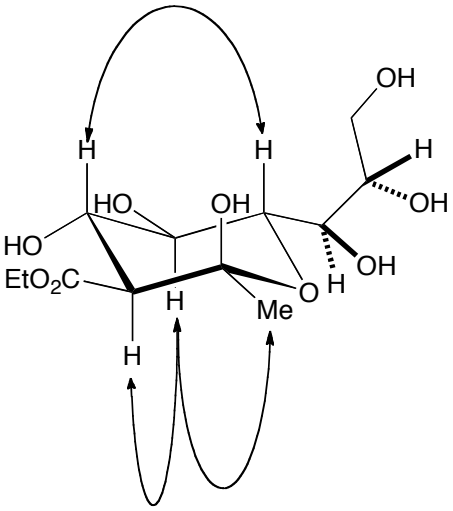


syn-**3e**

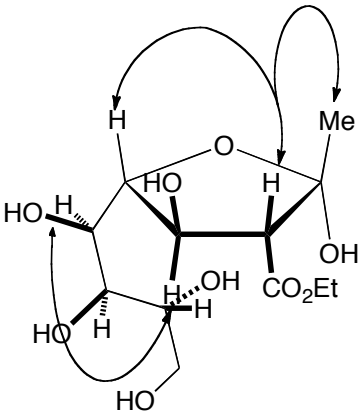


anti-**3e**

Manno-5a

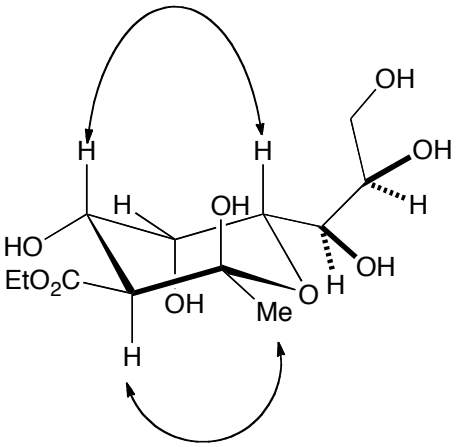


syn-**5a**

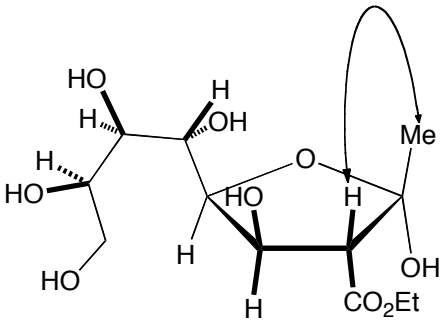


anti-**5a**

Gluco-5b

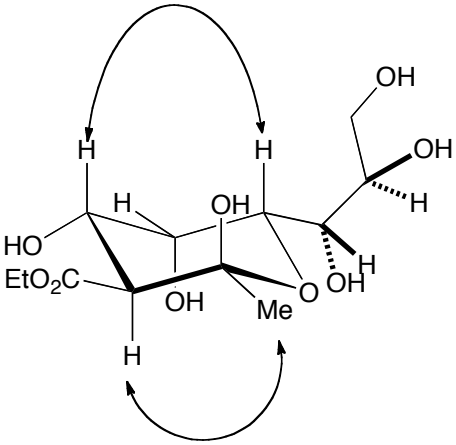


anti-**5b**

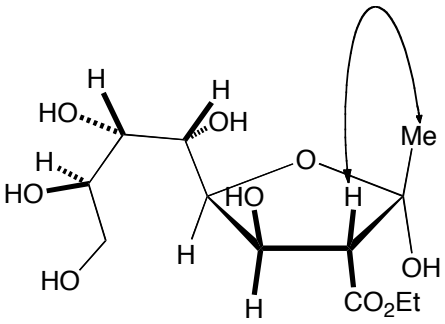


syn-**5b**

Galacto-5c

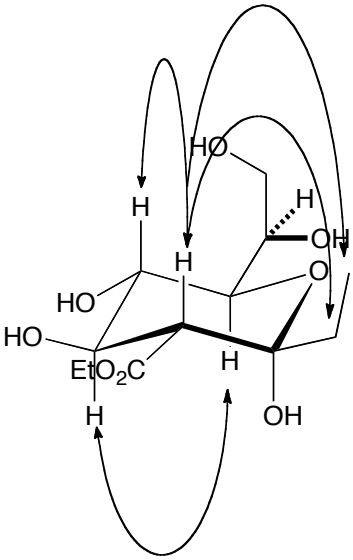


anti-**5c**

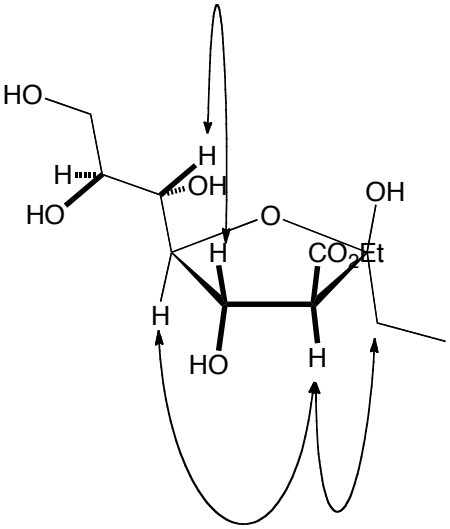


syn-**5c**

6a

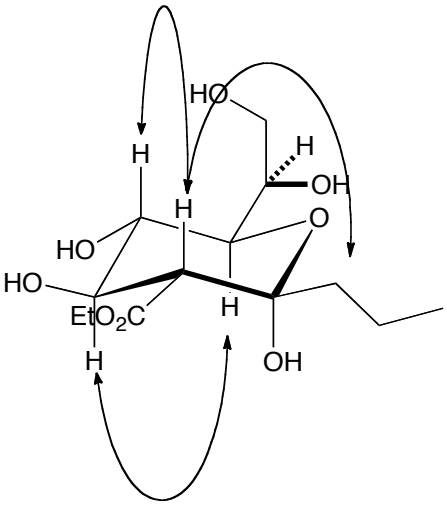


syn-**6a**

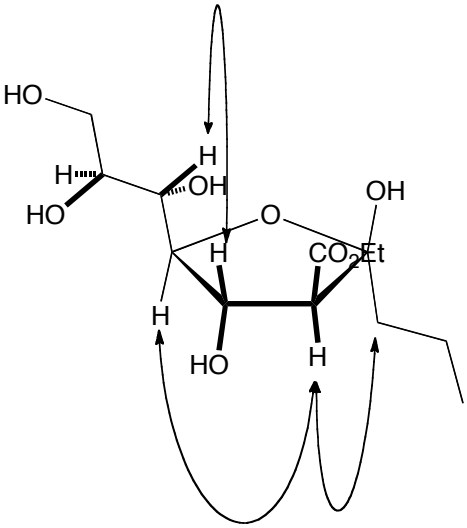


anti-**6a**

6b

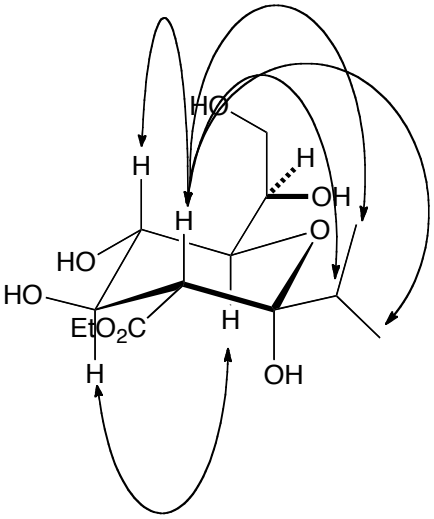


syn-**6b**

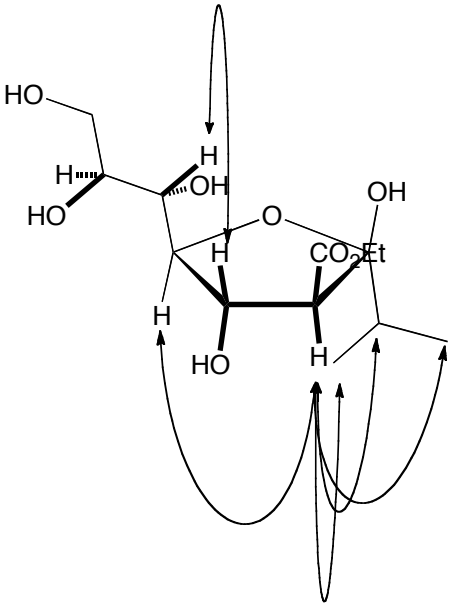


anti-**6b**

6c

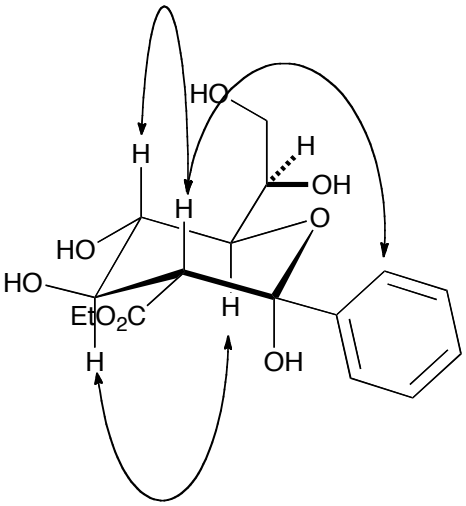


syn-**6c**

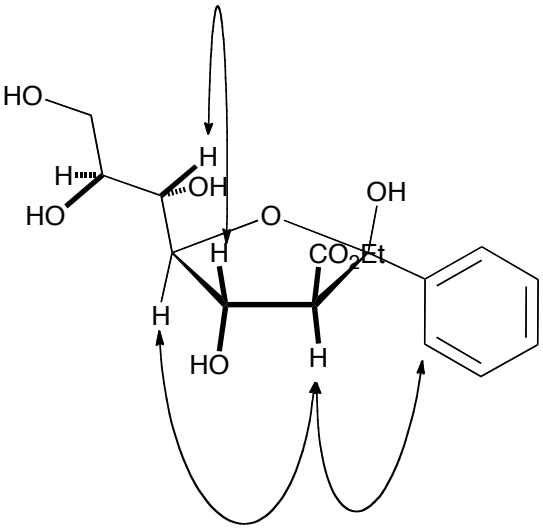


anti-**6c**

6d

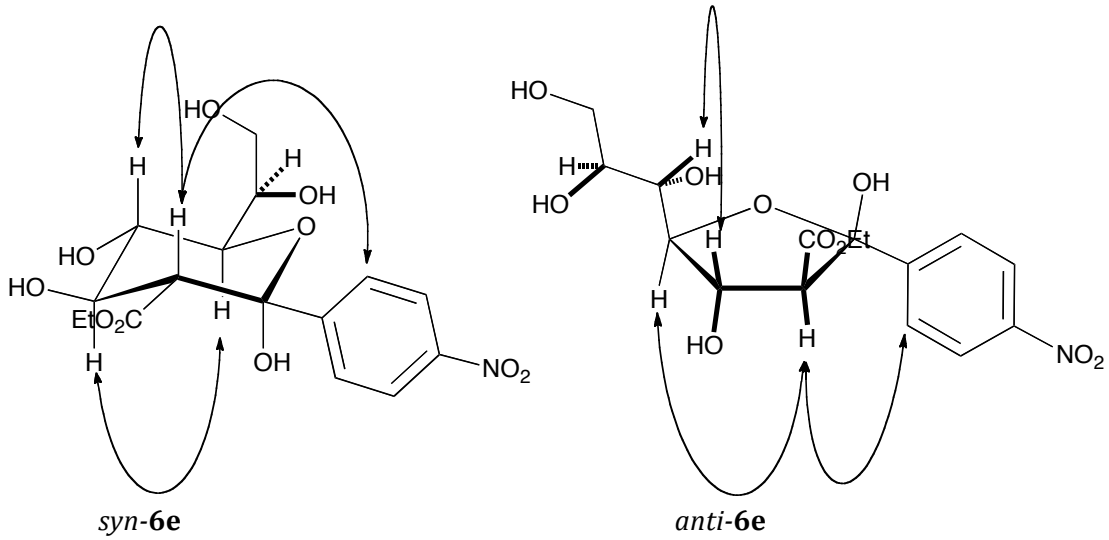


syn-**6d**



anti-**6d**

6e



syn-**6e** *anti*-**6e**