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Supporting Information

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Stereoselective Glycosylations Using Chiral Auxiliaries**

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Experimental Data for Compounds

General Procedures. All reactions were carried out under a positive pressure of argon, unless otherwise noted. All chemicals were purchased from commercial suppliers and used without further purification, unless otherwise noted. Dichloromethane was distilled from calcium hydride under N_2. Toluene was distilled under nitrogen from molten sodium. *N,N*-Dimethylformamide (DMF) was distilled under nitrogen from barium oxide. Column chromatography was performed on silica gel 60 (EM Science, 70-230 mesh). Reactions were monitored by TLC on Kieselgel 60 F_{254} (EM Science) and the compounds were detected by examination under UV light and visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution followed by heating. Organic solutions were concentrated by rotary evaporation below 40 ^{o}C under reduced pressure. Molecular sieves (3Å and 4Å), used for reactions, were crushed and activated *in vacuo* at 390 °C during 8 h in the first instance and then for 2-3 h at 390 °C directly prior to application. Optical rotations were measured with a 'Jasco P-1020' polarimeter. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Inova 300 spectrometer and a Varian Inova 500 spectrometer equipped with Sun workstations. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. Data are presented as follow: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = double of doublet, m = multiplet and/or multiple resonances), integration, coupling constant in Hertz (Hz). High-resolution mass spectra were run in a JMS SX/SX102A tandem mass spectrometer, equipped with FAB source. The matrix used was DHB and the internal standards ultramark 1621 and PEG.

1,6-Anhydro-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-β-D-glucopyranose (2*S*). Boron trifluoro etherate (543 μL, 4.27 mmol, 0.2 equiv) was added dropwise to a solution of 1,6,2,3-dianhydro-4-*O*-benzyl-β-D-glucopyranose (**1**, 5 g, 21.3 mmol, 1 equiv), (*S*)-ethyl mandelate (11.5 g, 63.9 mmol, 3 equiv) and activated molecular sieves (4Å, 2 g) in toluene (20 mL) at room temperature. After 1h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (30 mL) and then diluted with ethyl acetate (30 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **2*S*** (4.23 g, 48%): colorless syrup, Rf = 0.34 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D$ = +40.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.48 (m, 10H, aromatic), 5.54 (s, 1H, H-1), 5.22 (s, 1H, >C*H*Ph), 4.63 (d, 1H, *J* = 12.3 Hz, C*H*HPh), 4.61 (d, 1H, *J* =12.3 Hz, C*H*HPh), 4.54 (d, 1H, *J* = 5.4 Hz, H-5), 4.13-4.23 (m, 2H, COOCH_2CH$_3$), 3.88 (t, 1H, *J* = 4.8 Hz, H-3), 3.73 (d, 1H, *J* = 7.5 Hz, H-6a), 3.61 (dd, 1H, *J* = 5.4, 7.2 Hz, H-6b), 3.33 (d, 1H, *J* = 4.8, H-2), 3.29 (d, 1H, *J* = 5.1, H-4), 2.61 (b, 1H, OH), 1.21 (t, 3H, *J* = 7.2 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.07, 137.79, 136.01, 128.73, 128.59, 128.43, 127.78, 127.75, 127.50, 101.80, 80.49, 80.17, 80.02, 75.48, 71.80, 71.25, 66.85, 61.43, 14.01.

1,6-Anhydro-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-β-D-glucopyranose (2*R*). Compound **2*R*** was synthesized from compound **1** and (*R*)-ethyl mandelate according to the procedure described for the synthesis of compound **2*S*:**Colorless syrup, Rf = 0.35 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D$ = -10.3 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.45 (m, 10H, aromatic), 5.34 (s, 1H, H-1), 5.11 (s, 1H, >C*H*Ph), 4.83 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.67 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.51 (d, 1H, *J* = 5.1 Hz, H-5), 4.06-4.23 (m, 2H, COOCH_2CH$_3$), 3.99 (t, 1H, *J* = 6.3 Hz, H-3), 3.57-3.65 (m, 2H, H-6a, H-6b), 3.34 (d, 1H, *J* = 6.3 Hz, H-2), 3.24 (d, 1H, *J* = 6.3 Hz, H-4), 1.17 (t, 1H, *J* = 7.2 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.84, 138.04, 135.85, 128.65,

128.46, 128.27, 127.70, 127.56, 127.06, 101.78, 83.17, 81.24, 79.89, 76.18, 72.57, 71.81, 67.31, 61.67, 13.82.

Acetyl 3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranoside (3*S*) Trimethylsilyl trifluoromethansulfonate (24 μL, 0.13 mmol, 0.02 equiv) was added to a solution of 1,6-anhydro-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-β-D-glucopyranose (**2*S*,** 6.52 g, 6.52 mmol, 1 equiv) in acetic anhydride (10 mL) at 0 °C. The reaction mixture was stirred at this temperature for 20 min and then quenched with saturated aqueous $NaHCO_3$, then extracted with DCM (2 x 30 mL). The organic phase was washed with water (30 mL) and brine (30 mL) and dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **3*S*** (2.69 g, 74%): colorless syrup, Rf = 0.57 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D$ = +164 (c = 2.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.35 (m,10H, aromatic), 6.44 (d, 1H, J = 3.6 Hz, H-1), 5.57 (t, 1H, J = 9.6 Hz, H-3), 4.96 (s, 1H, >C*H*Ph), 4.55 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.48 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.25 (d, 2H, J = 3.0 Hz, H-6a, H-6b), 4.08-4.20 (m, 2H, COOCH_2CH$_3$), 3.97-4.02 (m, 1H, H-5), 3.61 (dd, 1H, J = 3.6, 9.9 Hz, H-2), 3.55 (t, 1H, J = 9.6 Hz, H-4) 2.18 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 1.88 (s, 3H, $COCH_3$), 1.20 (t, 3H, J = 7.2 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.46, 169.93, 169.47, 169.23, 137.02, 135.82, 128.83, 128.54, 128.13, 128.09, 127.22, 89.40, 81.44, 76.27, 75.48, 74.58, 73.21, 70.71, 62.37, 61.48, 20.97, 20.86, 20.77, 13.93.

The β-anomer of **3*S*** was also identified and isolated as colorless syrup (0.69 g, 19%): Rf = 0.62 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D$ = +120 (c = 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.38 (m,10H, aromatic), 5.73 (d, 1H, J = 8.1 Hz, H-1), 5.37 (t, 1H, J = 9.0 Hz, H-3), 4.99 (s, 1H, >C*H*Ph), 4.51 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.46 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.29 (dd, 1H, J = 2.4, 12.3 Hz, H-6a), 4.21 (dd, 1H, J = 4.5, 12.3 Hz, H-6b), 4.05-4.17 (m, 2H, COOCH_2CH$_3$), 3.71-3.76 (m, 1H, H-5), 3.49-3.56 (m, 2H, H-4, H-2), 2.15 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.60 (s, 3H, $COCH_3$), 1.83 (t, 3H, J = 7.2 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.51, 170.20, 169.43, 168.53,

137.04, 136.65, 128.71, 128.54, 128.15, 128.07, 127.18, 93.51, 83.08, 80.00, 77.20, 75.47, 74.71, 74.31, 73.50, 62.44, 61.37, 20.97, 20.82, 20.62, 13.98.

Acetyl 3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-α-D-glucopyranoside (3*R*). Compound **3*R*** was synthesized according to the procedure described for the synthesis of compound **3*S***:Colorless syrup, Rf = 0.55 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_{D}$ = +99.9 (c = 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.37 (m,10H, aromatic), 6.29 (d, 1H, J = 3.6 Hz, H-1), 5.58 (t, 1H, J = 9.9 Hz, H-3), 4.98 (s, 1H, >C*H*Ph), 4.66 (d, 1H, J = 10.8 Hz, C*H*HPh), 4.55 (d, 1H, J = 10.8 Hz, C*H*HPh), 4.26 (d, 2H, J = 2.7 Hz, H-6a, H-6b), 4.09-4.21 (m, 2H, COOCH_2CH$_3$), 3.96-4.01 (m, 1H, H-5), 3.68 (dd, 1H, J = 3.6, 9.9 Hz, H-2), 3.66 (t, 1H, J = 9.9 Hz, H-4), 2.18 (s, 3H, $COCH_3$), 2.05 (s, 3H, $COCH_3$), 2.01 (s, 3H, $COCH_3$), 1.20 (t, 3H, J = 7.2 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.46, 170.05, 169.94, 169.04, 137.19, 135.85, 128.72, 128.54, 128.49, 128.11, 128.07, 127.01, 88.72, 79.66, 75.89, 75.06, 74.65, 72.95, 70.84, 62.36, 61.25, 21.15, 20.76, 14.00.

The β-anomer of **3*R*** was also identified and isolated as colorless syrup: Rf = 0.60 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_{D}$ = -38 (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.34 (m,10H, aromatic), 5.59 (d, 1H, J = 8.1 Hz, H-1), 5.44 (t, 1H, J = 9.3 Hz, H-3), 5.10 (s, 1H, >C*H*Ph), 4.63 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.54 (d, 1H, J = 11.1 Hz, C*H*HPh), 4.20-4.30 (m, 2H, H-6a, H-6b), 4.05-4.21 (m, 2H, COOCH_2CH$_3$), 3.55-3.74 (m, 3H, H-5, H-2, H-4), 2.15 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 1.85 (s, 3H, $COCH_3$), 1.20 (t, 3H, J = 7.2 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.51, 170.11, 169.94, 168.45, 137.18, 136.47, 128.61, 128.57, 128.51, 128.15, 128.09, 126.80, 93.57, 82.00, 79.10, 75.33, 75.00, 74.46, 73.65, 62.45, 61.29, 21.19, 20.82, 20.65, 14.06.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl trichloroacetimidate (5*S*). Hydrazine acetate (254 mg, 2.76 mmol, 1.1 equiv) was added to a solution of acetyl 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranoside (**3*S*,** 1.40 g, 2.51 mmol, 1 equiv) in DMF (10 mL) at room temperature.

The reaction mixture was stirred overnight, then quenched with saturated aqueous $NaHCO_3$. The reaction mixture was extracted with ethyl acetate (30 mL). The organic phase was washed with saturated aqueous NH_4Cl (30 mL) and dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford 3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-D-glucopyranose (**4*S*,** 1.23 g, 95%). Trichloroacetonitrile (2.38 mL, 10 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (143 μL, 0.4 equiv) were added to a solution of **4*S*** **(**1.23 g, 2.38 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at this temperature for 1 h and then evaporated. The residue was purified by silica gel column chromatography (20% ethyl acetate in hexane) to afford **5*S*** (1.21 g, 77%): $Rf = 0.65$ (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D = +107.4$ ($c = 2.1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H, NH), 7.23-7.38 (m,10H, aromatic), 6.68 (d, 1H, $J = 3.6$ Hz, H-1), 5.65 (t, 1H, $J = 9.6$ Hz, H-3), 5.03 (s, 1H, >C*H*Ph), 4.56 (d, 1H, $J = 11.1$ Hz, C*H*HPh), 4.51 (d, 1H, $J = 11.1$ Hz, C*H*HPh), 4.32 (dd, 1H, $J = 2.1$, 12.0 Hz, H-6a), 4.24 (dd, 1H, $J = 3.9$, 12.0 Hz, H-6b), 4.08-4.19 (m, 3H, $COOCH_2CH_3$, H-5), 3.72 (dd, 1H, $J = 3.6$, 9.9 Hz, H-2), 3.61 (t, 1H, $J = 9.9$ Hz, H-4), 2.04 (s, 3H, $COCH_3$), 1.87 (s, 3H, $COCH_3$), 1.20 (t, 3H, $J = 7.2$ Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.46, 170.25, 169.31, 161.20, 137.01, 135.78, 128.77, 128.57, 128.48, 128.27, 128.20, 127.05, 93.93, 81.80, 76.67, 75.35, 74.47, 73.35, 71.10, 62.35, 61.51, 20.85, 20.78, 14.01.

The β-anomer of **5*S*** was also identified and isolated (0.24 g, 15%): $Rf = 0.69$ (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D = +126.7$ ($c = 1.5$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 1H, NH), 7.19-7.43 (m,10H, aromatic), 6.03 (d, 1H, $J = 6.9$ Hz, H-1), 5.32 (t, 1H, $J = 8.1$ Hz, H-3), 5.32 (s, 1H, >C*H*Ph), 4.52 (d, 1H, $J = 11.4$ Hz, C*H*HPh), 4.46 (d, 1H, $J = 11.4$ Hz, C*H*HPh), 4.32 (dd, 1H, $J = 2.1$, 12.0 Hz, H-6a), 4.21 (dd, 1H, $J = 3.9$, 12.0 Hz, H-6b), 4.02-4.15 (m, 2H, $COOCH_2CH_3$), 3.78-3.83 (m, 1H, H-5), 3.65-3.71 (m, 2H, H-2, H-4), 2.00 (s, 3H, $COCH_3$), 1.75 (s, 3H, $COCH_3$), 1.14 (t, 3H, $J = 7.2$ Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.49, 169.82, 169.56, 160.26, 137.08, 136.46, 128.86, 128.59, 128.50, 128.10, 127.99, 97.61, 81.06, 75.10, 74.92, 74.04, 72.89, 62.36, 61.24, 20.86, 20.80, 13.95.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl trichloroacetimidate (5*R*). Compound **5*R*** was synthesized according to the procedure described for the synthesis of compound **5*S***. R_f = 0.67 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D$ = +61.0 (*c* = 1.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (s, 1H, NH), 7.26-7.37 (m,10H, aromatic), 6.49 (d, 1H, *J* = 3.3 Hz, H-1), 5.70 (t, 1H, *J* = 9.6 Hz, H-3), 5.04 (s, 1H, >C*H*Ph), 4.68 (d, 1H, *J* = 11.1 Hz, C*H*HPh), 4.57 (d, 1H, *J* = 11.1 Hz, C*H*HPh), 4.11-4.34 (m, 5H, H-6a, H-6b, H-5, COOCH_2CH$_3$), 3.77 (dd, 1H, *J* = 3.6, 9.9 Hz, H-2), 3.71 (t, 1H, *J* = 9.9 Hz, H-4), 2.17 (s, 3H, $COCH_3$), 2.03 (s, 3H, $COCH_3$), 1.21 (t, 3H, *J* = 7.2 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.42, 169.97, 169.90, 160.77, 137.15, 135.91, 128.54, 128.47, 128.29, 128.19, 128.15, 126.81, 92.96, 79.72, 76.37, 74.89, 74.58, 72.74, 71.21, 62.28, 61.25, 21.13, 20.74, 14.03.

The β-anomer of **5*R*** was also identified and isolated: R_f = 0.71 (ethyl acetate/hexane, 1/1); $[\alpha]^{20}_D$ = +47 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H, NH), 7.26-7.37 (m,10H, aromatic), 5.83 (d, 1H, *J* = 7.5 Hz, H-1), 5.45 (s, 1H, >C*H*Ph), 5.44 (t, 1H, *J* = 9.6 Hz, H-3), 4.68 (d, 1H, *J* = 11.4 Hz, C*H*HPh), 4.58 (d, 1H, *J* = 11.4 Hz, C*H*HPh), 4.33 (d, 1H, *J* = 12.3 Hz, H-6a), 4.26 (dd, 1H, *J* = 2.4, 12.3 Hz, H-6b), 4.08-4.22 (m, 3H, COOCH_2CH$_3$, H-5), 3.73-3.82 (m, 2H, H-2, H-4), 2.19 (s, 3H, $COCH_3$), 2.02 (s, 3H, $COCH_3$), 1.20 (t, 3H, *J* = 7.2 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.54, 170.42, 170.36, 160.30, 137.29, 136.14, 128.76, 128.54, 128.44, 128.13, 126.83, 97.85, 79.90, 77.24, 77.20, 74.96, 74.26, 73.32, 62.41, 61.15, 21.28, 20.82, 14.08.

General Procedure for the Glycosylation Employing 3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S or R*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl trichloroacetimidate (5*S* *or* 5*R*). A mixture of donor **5*S*** *or* **5*R*** (20 mg, 0.03 mmol, 1 equiv), acceptor (0.036 mmol, 1.2 equiv) and activated molecular sieves (4Å) in DCM (10 mL) was stirred for 1 h under an atmosphere of argon at rt, then cooled to -78 ^{o}C. After addition of trimethylsilyl trifluoromethanesulfonate (2.2 μL, 0.012 mmol, 0.4 equiv), the reaction mixture was

stirred at -78 ^{o}C for 1 h and allowed to warm over 1 h to 0 ^{o}C. The reaction mixture was quenched with aqueous saturated $NaHCO_3$ (10 mL) and separated. The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (DCM/n-hexane/ethyl acetate = 2/2/1).

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7*S* α); $[\alpha]^{20}_{D}$ = +251.9 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16-7.37 (m, 25H, aromatic), 5.81 (d, 1H, *J* = 3.5 Hz, H-1'), 5.54 (t, 1H, *J* = 9.5 Hz, H-3'), 5.06 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.93 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.91 (s, 1H, >C*H*Ph), 4.67 (d, 1H, *J* = 12.5 Hz, C*H*HPh), 4.61 (d, 1H, *J* = 3.5 Hz, H-1), 4.56 (d, 1H, *J* = 12.5 Hz, C*H*HPh), 4.51 (s, 2H, CH_2Ph), 4.50 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.43 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.00-4.08 (m, 6H, H-3, H-6a, H-6a', H-6b', COOC*H*$_2$CH$_3$), 3.85-3.93 (m, 3H, H-5', H-4, H-6b), 3.64 (d, 1H, *J* = 10.0 Hz, H-5), 3.59 (dd, 1H, *J* = 4.0, 9.0 Hz, H-2), 3.43 (t, 1H, *J* = 9.5 Hz, H-4'), 3.39 (dd, 1H, *J* = 3.5, 10.0 Hz, H-2'), 3.38 (s, 3H, OCH_3), 1.97 (s, 3H, $COCH_3$), 1.92 (s, 3H, $COCH_3$), 1.12 (t, 3H, *J* = 7.0 Hz, COOCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.47, 170.09, 169.52, 139.36, 137.98, 137.54, 135.82, 128.71, 128.47, 128.43, 128.24, 128.17, 128.01, 127.93, 127.89, 127.45, 127.41, 126.92, 97.67, 95.28, 81.60, 80.53, 80.23, 77.21, 76.42, 76.04, 74.15, 73.84, 73.38, 73.26, 73.20, 71.75, 69.28, 68.85, 68.79, 62.75, 61.26, 55.13, 21.04, 20.86, 13.98.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (7*R*β); $[\alpha]^{20}_{D}$ = +91.6 (*c* = 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.38 (m, 25H, aromatic), 5.14 (s, 1H, >C*H*Ph), 5.14 (t, 1H, *J* = 9.5 Hz, H-3'), 4.98 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.73 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.69 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.60 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.57 (d, 1H, *J* = 12.5 Hz, C*H*HPh), 4.53 (d, 1H, *J* = 4.0 Hz, H-1), 4.51 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.49 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.14-4.19 (m, 4H, H-6a', H-6b', H-1', C*H*HPh), 4.03-4.10 (m, 2H, COOC*H*$_2$CH$_3$), 3.89 (t, 1H, *J* = 10.0 Hz, H-4), 3.77 (t,

1H, *J* = 9.5 Hz, H-3), 3.54 (t, 1H, *J* = 9.5 Hz, H-4'), 3.45 (dd, 1H, *J* = 4.0, 9.5 Hz, H-2), 3.32 (s, 3H, OCH_3), 3.28 (dd, 1H, *J* = 2.0, 11.5 Hz, H-6a), 3.20-3.26 (m, 2H, H-2', H-5'), 3.16 (d, 1H, *J* = 10.5 Hz, H-5), 2.91 (dd, 1H, *J* = 1.5, 11.0 HzH-6b), 2.17 (s, 3H, $COCH_3$), 1.88 (s, 3H, $COCH_3$), 1.18 (t, 3H, *J* = 7.5 Hz, $COOCH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.65, 170.60, 170.30, 139.44, 138.30, 137.59, 137.35, 136.88, 128.64, 128.49, 128.33, 128.30, 128.25, 128.22, 128.13, 128.05, 128.00, 127.95, 127.88, 127.81, 127.73, 127.20, 127.09, 101.93, 98.21, 81.02, 80.19, 80.01, 78.47, 75.85, 75.07, 74.85, 74.21, 73.47, 73.31, 72.53, 69.33, 66.98, 62.97, 60.99, 55.16, 21.36, 20.70, 14.07.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (9*S* α); $[\alpha]^{20}_D$ = -65.8 (*c* = 3.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-8.01 (m, 6H, aromatic), 7.25-7.54 (m, 19H, aromatic), 6.19 (t, 1H, *J* = 10.0 Hz, H-3), 5.67 (t, 1H, *J* = 10.0 Hz, H-3'), 5.43 (t, 1H, *J* = 10.0 Hz, H-4), 5.29 (dd, 1H, *J* = 3.5, 10.0 Hz, H-2), 5.23 (d, 1H, *J* = 3.5 Hz, H-1), 5.08 (d, 1H, *J* = 3.0 Hz, H-1'), 5.05 (s, 1H, >C*H*Ph), 4.58 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.53 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.42 (t, 1H, *J* = 9.5 Hz, H-5), 4.32 (d, 1H, *J* = 11.0 Hz, H-6a'), 4.20-4.26 (m, 2H, H-6b', H-5'), 4.07-4.12 (m, 2H, $COOCH_2CH_3$), 3.92 (dd, 1H, *J* = 8.0, 10.5 Hz, H-6a), 3.66 (d, 1H, *J* = 10.5 Hz, H-6b), 3.57 (dd, 1H, *J* = 3.5, 10.5 Hz, H-2'), 3.52 (t, 1H, *J* = 9.5 Hz, H-4'), 3.50 (s, 3H, OCH_3), 2.10 (s, 3H, $COCH_3$), 1.86 (s, 3H, $COCH_3$), 1.15 (t, 3H, *J* = 7.0 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.82, 170.67, 169.59, 165.81, 165.48, 137.50, 136.17, 133.42, 133.29, 133.04, 129.96, 129.68, 129.29, 129.16, 128.92, 128.54, 128.48, 128.42, 128.39, 128.25, 128.01, 127.96, 126.86, 97.31, 96.61, 81.59, 78.32, 76.13, 73.82, 73.20, 72.21, 70.58, 69.84, 68.74, 68.59, 67.33, 62.91, 61.39, 55.64, 20.89, 14.01.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (9*S*β); $[\alpha]^{20}_D$ = +16.0 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.98 (m, 6H, aromatic), 7.17-7.54 (m, 19H, aromatic), 6.17 (t, 1H, *J* = 10.0 Hz, H-3), 5.41 (t, 1H, *J* = 10.0 Hz, H-3'), 5.23-5.32 (m, 4H, H-4, H-2, H-1, >C*H*Ph), 4.60 (d, 1H, *J* = 7.5 Hz, H-1'), 4.48 (d, 1H, *J*

= 11.0 Hz, C*H*HPh), 4.38-4.43 (m, 2H, H-5, C*H*HPh), 4.22 (dd, 1H, *J* = 2.5, 12.0 Hz, H-6a'), 4.11-4.19 (m, 3H, H-6b', H-5', COOCH_2CH$_3$), 3.98 (dd, 1H, *J* = 2.5, 11.0 Hz, H-6a), 3.82 (dd, 1H, *J* = 8, 11.0 Hz, H-6b), 3.55-3.58 (m, 1H), 3.54 (s, 3H, OCH$_3$), 3.39 (t, 1H, *J* = 9.5 Hz, H-4'), 3.26 (dd, 1H, *J* = 8.0, 10.0 Hz, H-2'), 1.95 (s, 3H, COCH$_3$), 1.70 (s, 3H, COCH$_3$), 1.18 (t, 3H, *J* = 7.0 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.62, 170.26, 169.48, 165.84, 165.79, 165.44, 137.18, 137.02, 133.53, 133.37, 133.10, 129.93, 129.88, 129.66, 129.24, 129.09, 128.91, 128.59, 128.52, 128.50, 128.43, 128.27, 128.07, 128.01, 127.83, 103.64, 96.93, 81.40, 78.61, 76.16, 74.68, 74.32, 72.60, 72.09, 70.30, 70.08, 69.77, 68.90, 62.99, 61.17, 55.89, 20.85, 20.67, 14.12.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (9*R* α); $[\alpha]^{20}_D$ = +144.3 (*c* = 0.7, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.84-7.98 (m, 6H, aromatic), 7.09-7.54 (m, 19H, aromatic), 6.14 (t, 1H, *J* = 9.5 Hz, H-3), 5.68 (t, 1H, *J* = 9.5 Hz, H-3'), 5.34 (t, 1H, *J* = 10.0 Hz, H-4), 5.19 (s, 1H, H-1), 5.18 (dd, 1H, *J* = 3.5, 9.5 Hz, H-2), 4.96 (s, 1H, >C*H*Ph), 4.68 (d, 1H, *J* = 3.5 Hz, H-1'), 4.61 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.54 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.24-4.28 (m, 2H, H-5, H-5'), 4.20 (dd, 1H, *J* = 4.5, 12.5 Hz, H-6a'), 4.08-4.13 (m, 3H, H-6b', COOCH_2CH$_3$), 3.75 (dd, 1H, *J* = 8.5, 10.5 Hz, H-6a), 3.61 (dd, 1H, *J* = 3.5, 9.5 Hz, H-2'), 3.55 (t, 1H, *J* = 10.0 Hz, H-4'), 3.49 (s, 3H, OCH$_3$), 3.33 (d, 1H, *J* = 10.5 Hz, H-6b), 2.06 (s, 3H, COCH$_3$), 2.01 (s, 3H, COCH$_3$), 1.17 (t, 3H, *J* = 7.5 Hz, COOCH$_2$CH_3); ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.63, 170.11, 169.89, 165.76, 165.36, 137.56, 136.77, 133.51, 133.31, 133.06, 129.94, 129.90, 129.66, 129.23, 129.12, 128.85, 128.58, 128.48, 128.41, 128.25, 128.01, 127.95, 127.03, 96.60, 96.48, 80.01, 77.90, 75.91, 73.88, 72.19, 72.14, 70.46, 69.72, 68.56, 68.52, 66.56, 62.82, 61.26, 55.62, 21.03, 20.86, 14.02.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (9*R*β); $[\alpha]^{20}_D$ = +164.4 (*c* = 1.6, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.84-7.99 (m, 6H, aromatic), 7.25-7.53 (m, 19H, aromatic), 6.17 (t, 1H, *J* = 9.5 Hz, H-3), 5.70 (s, 1H, >C*H*Ph), 5.36 (t,

2H, *J* = 9.5 Hz, H-3', H-4), 5.28 (s, 1H, H-1), 5.27 (dd, 1H, *J* = 4.0, 9.5 Hz, H-2), 4.66 (d, 1H, *J* = 10.5 Hz, C*H*HPh), 4.53 (d, 1H, *J* = 10.5 Hz, C*H*HPh), 4.52 (d, 1H, *J* = 7.0 Hz, H-1'), 4.38 (t, 1H, *J* = 9.5 Hz, H-5), 4.13-4.21 (m, 3H, H-6a', COOC*H*$_2$CH$_3$), 4.06 (dd, 1H, *J* = 7.5, 10.5 Hz, H-6b'), 4.00 (d, 1H, *J* = 10.0 Hz, H-6), 3.74 (dd, 1H, *J* = 9.0, 10.0 Hz, H-6a), 3.55-3.61 (m, 2H, H-4', H-5'), 3.45 (s, 3H, OCH$_3$), 3.42 (t, 1H, *J* = 9.5 Hz, H-2'), 2.24 (s, 3H, COCH$_3$), 1.85 (s, 3H, COCH$_3$), 1.14 (t, 3H, *J* = 7.5 Hz, COOCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.97, 170.56, 170.44, 165.86, 165.74, 165.51, 137.37, 136.66, 133.58, 133.41, 133.13, 129.93, 129.84, 129.63, 129.16, 129.03, 128.72, 128.59, 128.53, 128.49, 128.44, 128.28, 128.06, 128.00, 127.14, 103.45, 96.85, 79.65, 78.21, 75.86, 74.94, 74.52, 72.78, 72.07, 70.27, 69.93, 68.88, 63.01, 60.88, 55.69, 21.31, 20.57, 14.08.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (11*S* α); $[\alpha]^{20}_{D}$ = +169.4 (*c* = 1.5, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.23-7.40 (m, 10H, aromatic), 5.61 (t, 1H, *J* = 9.5 Hz, H-3'), 5.51 (d, 1H, *J* = 5.0 Hz, H-1), 5.09 (d, 1H, *J* = 3.5 Hz, H-1'), 5.08 (s, 1H, >C*H*Ph), 4.61 (dd, 1H, *J* = 2.5, 8.0 Hz, H-3), 4.54 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.50 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.35 (dd, 1H, *J* = 2.0, 8.0 Hz, H-4), 4.30 (dd, 1H, *J* = 2.5, 5.0 Hz, H-2), 4.26-4.28 (m, 2H), 4.03-4.18 (m, 4H), 3.76-3.81 (m, 2H), 3.50 (t, 1H, *J* = 10.0 Hz, H-4'), 3.47 (dd, 1H, *J* = 3.5, 9.5 Hz, H-2), 2.05 (s, 3H, COCH$_3$), 1.94 (s, 3H, COCH$_3$), 1.55 (s, 3H, CH$_3$), 1.46 (s, 3H, CH$_3$), 1.36 (s, 3H, CH$_3$), 1.32 (s, 3H, CH$_3$), 1.20 (t, 3H, *J* = 7.0 Hz, COOCH$_2$C*H*$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.72, 170.42, 169.61, 137.49, 135.96, 128.79, 128.59, 128.48, 128.10, 127.96, 127.32, 109.25, 108.78, 97.41, 96.29, 80.45, 76.67, 75.96, 73.51, 73.24, 70.85, 70.69, 70.66, 68.17, 67.49, 66.44, 62.95, 61.31, 26.16, 26.13, 24.97, 24.65, 20.10, 20.90, 14.05.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (11*S*β); $[\alpha]^{20}_{D}$ = -98.7 (*c* = 0.6, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.19-7.43 (m, 10H, aromatic), 5.55 (s, 1H, >C*H*Ph), 5.54 (d, 1H, *J* = 6.0 Hz, H-1), 5.34 (t, 1H, *J* = 9.5 Hz, H-3'), 4.61 (dd, 1H, *J* =

2.5, 7.5 Hz, H-3), 4.60 (d, 1H, *J* = 7.5 Hz, H-1'), 4.50 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.42 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.33 (dd, 1H, *J* = 2.5, 5.0 Hz, H-2), 4.04-4.29 (m, 7H), 3.73 (dd, 1H, *J* = 9.0, 11.5 Hz), 3.54-3.57 (m, 1H, H-5), 3.42 (t, 1H, *J* = 9.5 Hz, H-4'), 3.23 (dd, 1H, *J* = 7.5, 9.5 Hz, H-2'), 2.03 (s, 3H, $COCH_3$), 1.86 (s, 3H, $COCH_3$), 1.60 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.34 (s, 6H, 2 × CH_3), 1.18 (t, 3H, *J* = 7.0 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.67, 170.57, 169.62, 137.26, 136.73, 128.58, 128.52, 128.50, 128.33, 128.05, 127.99, 109.50, 108.53, 104.06, 96.41, 80.19, 76.60, 76.01, 74.85, 74.37, 72.63, 71.30, 70.86, 70.35, 70.16, 67.00, 62.96, 60.98, 26.03, 26.00, 24.95, 24.52, 20.96, 20.88, 14.02.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (11*R*α); $[\alpha]^{20}_D$ = +254.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.53 (m, 10H, aromatic), 5.66 (t, 1H, *J* = 9.5 Hz, H-3'), 5.48 (d, 1H, *J* = 4.5 Hz, H-1), 5.07 (s, 1H, >C*H*Ph), 4.91 (d, 1H, *J* = 4.0 Hz, H-1'), 4.64 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.57 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.51 (d, 1H, *J* = 10.0 Hz, H-3), 3.96-4.34 (m, 8H), 3.57-3.73 (m, 4H), 2.12 (s, 3H, $COCH_3$), 2.07 (s, 3H, $COCH_3$), 1.56 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.23 (t, 3H, *J* = 7.0 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) □ 170.71, 170.16, 170.06, 137.55, 136.51, 128.71, 128.67, 128.30, 127.10, 109.25, 108.80, 96.79, 96.26, 79.45, 77.22, 76.92, 75.76, 73.78, 72.87, 70.79, 70.62, 68.25, 66.93, 66.17, 62.89, 61.25, 26.15, 26.12, 24.93, 24.73, 21.18, 20.89, 14.10.

3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (11*R*β) ; $[\alpha]^{20}_D$ = +126.1 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.51 (m, 2H, aromatic), 7.26-7.35 (m, 8H, aromatic), 5.66 (s, 1H, >C*H*Ph), 5.53 (d, 1H, *J* = 4.5 Hz, H-1), 5.36 (t, 1H, *J* = 9.5 Hz, H-3'), 4.68 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.57 (dd, 1H, *J* = 3.5, 8.0 Hz, H-3), 4.55 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.50 (d, 1H, *J* = 8.0 Hz, H-1'), 4.29-4.32 (m, 2H), 4.24 (dd, 1H, *J* = 5.0, 12.0 Hz), 4.12-4.19 (m, 2H), 4.02-4.09 (m, 3H), 3.62-3.70 (m, 2H), 3.56-3.59 (m, 1H), 3.47 (dd, 1H, *J* = 8.0, 9.5 Hz, H-2'), 2.26 (s, 3H, $COCH_3$), 2.07 (s,

3H, $COCH_3$), 1.54 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.19 (t, 3H, *J* = 7.5 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.28, 170.68, 170.50, 137.49, 136.96, 128.54, 128.30, 128.03, 127.36, 109.50, 108.65, 103.91, 96.25, 79.54, 77.94, 75.72, 75.11, 74.55, 72.87, 71.44, 70.76, 70.48, 69.98, 67.19, 62.91, 60.73, 26.13, 25.97, 25.12, 24.49, 21.35, 20.90, 14.14.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside(13*S*α); $[\alpha]^{20}_D$ = +101.4 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64-7.57 (m, 20H, aromatic), 5.59 (t, 1H, *J* = 9.5 Hz, H-3'), 5.59 (s, 1H, >C*H*Ph), 5.41 (d, 1H, *J* = 3.0 Hz, H-1'), 4.87 (s, 1H, >C*H*Ph), 4.71 (d, 1H, *J* = 3.5 Hz, H-1), 4.59 (s, 2H, CH_2Ph), 4.45 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.38 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.22-4.32 (m, 3H), 4.08-4.12 (m, 2H), 4.06 (d, 1H, *J* = 11.5 Hz), 3.82-3.86 (m, 2H), 3.66-3.74 (m, 3H), 3.40 (s, 3H), 3.35 (t, 1H, *J* = 9.5 Hz, H-4'), 3.16 (dd, 1H, *J* = 4.0, 10.0 Hz, H-2'), 2.06 (s, 3H, $COCH_3$), 1.98 (s, 3H, $COCH_3$), 1.22 (t, 3H, *J* = 7.5 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.60, 169.73, 169.64, 137.85, 137.39, 137.34, 134.93, 129.52, 128.72, 128.64, 128.54, 128.48, 128.40, 128.32, 128.04, 127.95, 127.84, 127.75, 127.14, 102.41, 98.34, 94.94, 82.60, 77.74, 77.53, 75.42, 73.72, 73.48, 73.01, 72.95, 72.78, 69.17, 67.78, 62.51, 61.81, 61.14, 55.33, 21.08, 20.81, 14.09.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (13*S*β); $[\alpha]^{20}_D$ = -73.3 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14-7.52 (m, 20H, aromatic), 5.54 (s, 1H, >C*H*Ph), 5.35 (s, 1H, >C*H*Ph), 5.24 (t, 1H, *J* = 9.5 Hz, H-3'), 5.09 (d, 1H, *J* = 8.0 Hz, H-1'), 4.88 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.59 (d, 1H, *J* = 12.0 Hz, C*H*HPh), 4.55 (d, 1H, *J* = 4.0 Hz, H-1), 4.40 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.37 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.34 (t, 1H, *J* = 9.0 Hz, H-3), 4.23 (dd, 1H, *J* = 4.5, 10.0 Hz), 4.15-4.18 (m, 2H), 4.01-4.09 (m, 2H), 3.81 (dd, 1H, *J* = 4.5, 9.5 Hz, H-5), 3.71-3.75 (m, 2H), 3.57 (t, 1H, *J* = 9.5 Hz, H-4), 3.42 (t, 1H, *J* = 9.0 Hz, H-4'), 3.34-3.37 (m, 2H), 3.32 (s, 3H, OCH_3), 1.93 (s, 3H, $COCH_3$), 1.66 (s, 3H, $COCH_3$), 1.18 (t, 3H, *J* = 7.5 Hz,

$COOCH_2C\mathit{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.65, 170.36, 169.56, 138.03, 137.39, 137.31, 137.02, 129.10, 128.67, 128.60, 128.57, 128.48, 128.45, 128.25, 128.15, 128.01, 127.93, 126.24, 101.94, 101.45, 98.40, 82.18, 80.64, 79.97, 79.17, 76.28, 75.44, 74.95, 74.16, 73.24, 72.17, 69.06, 62.96, 62.06, 61.08, 55.26, 20.88, 20.82, 14.07.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (13*R*α); $[\alpha]^{20}_D$ = +114.9 (*c* = 0.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.03-7.39 (m, 20H, aromatic), 5.68 (t, 1H, *J* = 9.5 Hz, H-3'), 5.59 (d, 1H, *J* = 3.5 Hz, H-1'), 5.01 (s, 1H, >C*H*Ph), 4.85 (s, 1H, >C*H*Ph), 4.66 (d, 1H, *J* = 4.0 Hz, H-1), 4.63 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.59 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.58 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.48 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.38 (d, 1H, *J* = 10.5 Hz), 4.26 (t, 1H, *J* = 9.5 Hz), 4.08-4.14 (m, 2H), 4.00-4.05 (m, 2H), 3.96 (dd, 1H, *J* = 3.0, 12.5 Hz), 3.72-3.77 (m, 1H), 3.52-3.63 (m, 3H), 3.50 (dd, 1H, *J* = 3.5, 10.0 Hz), 3.45 (t, 1H, *J* = 10.0 Hz), 3.37 (s, 3H, OCH_3), 2.13 (s, 3H, $COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.10 (t, 3H, *J* = 7.0 Hz, $COOCH_2C\mathit{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.65, 170.37, 170.32, 137.97, 137.31, 137.11, 136.07, 129.18, 128.64, 128.53, 128.40, 128.35, 128.29, 128.21, 128.07, 127.96, 127.76, 126.29, 126.15, 126.11, 101.30, 98.29, 95.13, 82.46, 77.70, 77.57, 76.28, 75.31, 73.97, 73.11, 73.06, 72.97, 68.99, 68.05, 62.58, 61.64, 60.93, 55.29, 21.29, 20.88, 14.07.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→3)-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (13*R*β); $[\alpha]^{20}_D$ = +168.5 (*c* = 1.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.16-7.49 (m, 20H, aromatic), 5.67 (s, 1H, >C*H*Ph), 5.55 (s, 1H, >C*H*Ph), 5.33 (t, 1H, *J* = 9.5 Hz, H-3'), 4.95 (d, 1H, *J* = 8.5 Hz, H-1'), 4.61 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.51 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.42 (d, 1H, *J* = 4.0 Hz, H-1), 4.06-4.25 (m, 7H), 3.98 (d, 1H, *J* = 11.0 Hz), 3.71-3.78 (m, 2H), 3.62 (d, 1H, *J* = 9.5 Hz), 3.58 (d, 1H, *J* = 9.5 Hz), 3.47 (dd, 1H, *J* = 8.0, 9.5 Hz), 3.37-3.43 (m, 2H), 3.27 (s, 3H, OCH_3), 2.22 (s, 3H, $COCH_3$), 1.93 (s, 3H, $COCH_3$), 1.17 (t, 3H, *J* = 7.0 Hz, $COOCH_2C\mathit{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.03,

170.70, 170.54, 137.78, 137.51, 137.30, 137.01, 129.07, 128.49, 128.41, 128.38, 128.35, 128.22, 128.01, 127.99, 127.28, 126.13, 102.63, 101.25, 98.26, 80.85, 80.14, 79.62, 78.68, 77.20, 75.84, 74.95, 74.38, 73.20, 72.39, 68.93, 63.04, 61.99, 60.89, 55.21, 21.39, 20.81, 14.12.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (15*S*α); $[\alpha]^{20}_{D}$ = -112.6 (*c* = 2.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.37 (m, 25H, aromatic), 5.63 (t, 1H, *J* = 10.0 Hz, H-3'), 5.32 (d, 1H, *J* = 3.0 Hz, H-1'), 5.04 (s, 1H, >C*H*Ph), 4.97 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.87 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.82 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.76 (d, 1H, *J* = 12.5 Hz, C*H*HPh), 4.65 (d, 1H, *J* = 13.0 Hz, C*H*HPh), 4.63 (d, 1H, *J* = 13.0 Hz, C*H*HPh), 4.61 (d, 1H, *J* = 3.5 Hz, H-1), 4.54 (d, 1H, *J* = 9.5 Hz, C*H*HPh), 4.48 (d, 1H, *J* = 9.5 Hz, C*H*HPh), 4.26 (d, 1H, *J* = 12.0 Hz), 4.20 (dd, 1H, *J* = 4.5, 12.0 Hz), 3.96-4.07 (m, 4H), 3.72-3.83 (m, 4H), 3.65 (dd, 1H, *J* = 4.0, 9.5 Hz), 3.49 (t, 1H, *J* = 10.5 Hz), 3.47 (dd, 1H, *J* = 3.0, 10.0 Hz), 3.37 (s, 3H, OCH_3), 2.02 (s, 3H, $COCH_3$), 1.90 (s, 3H, $COCH_3$), 1.13 (t, 3H, *J* = 7.5 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.78, 170.62, 169.46,138.98, 138.52, 138.42, 137.42, 135.93, 128.61, 128.54, 128.49, 128.35, 128.34, 128.28, 128.10, 128.07, 128.00, 127.88, 127.71, 127.54, 127.46, 127.06, 98.01, 97.00, 82.16, 81.55, 80.18, 77.76, 76.17, 75.72, 75.04, 74.08, 73.07, 73.36, 70.82, 68.44, 65.59, 62.88, 61.30, 55.15, 20.96, 20.86, 14.03.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (15*S*β); $[\alpha]^{20}_{D}$ = -198.9 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17-7.37 (m, 25H, aromatic), 5.27 (s, 1H, >C*H*Ph), 5.26 (t, 1H, *J* = 9.5 Hz, H-3'), 4.99 (d, 1H, *J* = 10.5 Hz, C*H*HPh), 4.89 (d, 1H, *J* = 11.0 Hz, C*H*HPh), 4.79-4.82 (m, 2H, 2 × C*H*HPh), 4.66 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.59 (d, 1H, *J* = 3.3 Hz, H-1), 4.57 (d, 1H, *J* = 10.0 Hz, C*H*HPh), 4.47 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.40-4.44 (m, 2H, H-1', C*H*HPh), 4.28 (d, 1H, *J* = 12.0 Hz), 4.13 (dd, 1H, *J* = 4.5, 12.0 Hz), 3.95-4.07 (m, 4H), 3.84-3.88 (m, 1H), 3.58 (dd, 1H, *J* = 6.0, 11.0 Hz), 3.48-3.53 (m, 2H), 3.41 (s, 3H, OCH_3), 3.35-3.42 (m, 2H), 3.28 (t, 1H, *J* =

8.5 Hz, H-2'), 1.97 (s, 3H, $COCH_3$), 1.71 (s, 3H, $COCH_3$), 1.02 (t, 3H, J = 7.0 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.58, 170.05, 169.48, 138.73, 138.17, 138.16, 137.24, 136.83, 128.67, 128.50, 128.47, 128.35, 128.16, 128.04, 127.96, 127.94, 127.89, 127.83, 127.61, 103.47, 98.03, 81.88, 81.23, 79.90, 78.31, 77.90, 76.12, 75.75, 75.01, 74.70, 74.34, 73.40, 72.59, 69.81, 69.28, 62.79, 61.07, 55.37, 20.91, 20.79, 13.96.

Methyl (3,6-Di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*R*)-ethoxycarbonylbenzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (15*R*β); $[\alpha]^{20}_D$ = +94.6 (c = 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.09-7.39 (m, 25H, aromatic), 5.53 (s, 1H, >C*H*Ph), 5.32 (t, 1H, J = 9.5 Hz, H-3'), 4.96 (d, 1H, J = 11.0 Hz, C*H*HPh), 4.82 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.76 (d, 1H, J = 11.0 Hz, C*H*HPh), 4.70 (d, 1H, J = 12.0 Hz, C*H*HPh), 4.68 (d, 1H, J = 11.5 Hz, C*H*HPh), 4.61 (d, 1H, J = 3.0 Hz, H-1), 4.55 (t, 2H, J = 11.0 Hz, 2 × C*H*HPh), 4.22-4.33 (m, 3H, H-6a', H-1', C*H*HPh), 4.17 (dd, 1H, J = 4.5, 12.5 Hz), 4.12 (dd, 1H, J = 7.5, 11.0 Hz), 4.02-4.07 (m, 2H), 3.96 (t, 1H, J = 9.0 Hz), 3.76-3.80 (m, 1H), 3.63 (t, 1H, J = 9.5 Hz), 3.51 (dd, 1H, J = 3.5, 10.0 Hz), 3.39-3.48 (m, 3H), 3.31 (s, 3H, OCH_3), 3.29 (t, 1H, J = 9.5 Hz), 2.22 (s, 3H, $COCH_3$), 1.99 (s, 3H, $COCH_3$), 1.15 (t, 3H, J = 7.0 Hz, $COOCH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.86, 170.63, 170.56, 138.78, 138.14, 138.12, 137.51, 136.59, 128.53, 128.49, 128.41, 128.34, 128.15, 128.05, 127.97, 127.70, 127.60, 127.0, 103.48, 97.99, 81.85, 79.89, 79.76, 78.17, 77.99, 75.73, 74.89, 74.76, 74.57, 73.33, 72.88, 69.70, 68.58, 62.75, 60.87, 55.29, 21.35, 20.81, 14.10.

Methyl α-D-Glucopyranosyl-(1→6)-α-D-glucopyranoside (16). Sodium methoxide (3.0 mg, 1.0 equiv) was added to a solution of methyl (3,6-di-*O*-acetyl-4-*O*-benzyl-2-*O*-(*S*)-ethoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**9*S*α,** 55 mg, 1.0 equiv) in methanol (5mL). The reaction mixture was stirred for 1 day, then quenched by Amberlite IRC-50 ion exchange resin (weakly acidic). After filtration, the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on Iatrobeads (dichloromethane/methanol = 2/1) to afford

methyl (4-*O*-benzyl-2-*O*-methoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→6)-α-D-glucopyranoside (30 mg, 93%). A solution of methyl (4-*O*-benzyl-2-*O*-methoxycarbonylbenzyl-α-D-glucopyranosyl)-(1→6)-α-D-glucopyranoside (30 mg, 0.0518 mmol) in THF (3 mL) was added to liquid ammonia (5 mL) at -78 °C. Sodium (~20 mg) was then added until a persistent blue color was obtained. Solid NH_4Cl (0.1 g) was then added, and the solvent were allowed to evaporate under air. The crude reaction mixture was purified by column chromatography on Iatrobeads (dichloromethane/methanol/H_2O = 15/5/1) to afford **16** (18 mg, 97%): Rf = 0.34 (dichloromethane/methanol/H_2O = 15/5/1); $[\alpha]^{20}_D$ = +26.9 (c = 1.0, CH_3OH); ^{1}H NMR (500 MHz, D_2O) δ 4.87 (d, 1H, J = 4.0 Hz, H-1), 4.73 (d, 1H, J = 3.5 Hz, H-1'), 3.90 (dd, 1H, J = 4.5, 9.0 Hz), 3.76 (dd, 1H, J = 2.0, 12.5 Hz), 3.33-3.73 (m, 10H), 3.34 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, D_2O) δ 99.56, 98.04, 73.56, 73.25, 72.02, 71.66, 71.34, 70.25, 69.70, 69.59, 65.67, 60.65, 55.38.