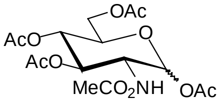
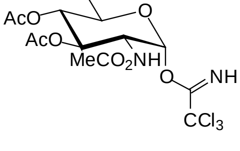
# Supplementary Materials

**General Materials and Methods.** All spectral data were obtained on a Varian Unity-Plus spectrometer ($^1$H resonance frequency of 400 MHz), a Varian Unity-Plus spectrometer ($^1$H resonance frequency of 500 MHz), or a Varian INOVA spectrometer ($^1$H resonance frequency of 500 MHz) and samples internally referenced as indicated. Reagents and solvents were reagent grade and used as received unless otherwise noted. THF and benzene were distilled from sodium benzoquinone ketal before use, dichloromethane and acetonitrile were distilled from $CaH_2$ and methanol distilled from Mg shavings. TLC was performed on glass plates with fluorescent indicator (Merck Silica gel 60 $F_{254}$) and visualized using either of *p*-anisaldehyde, ceric ammonium sulfate-molybdate stain or ninhydrin. Normal phase flash chromatography following the method of Still and co-workers[1] was employed throughout.



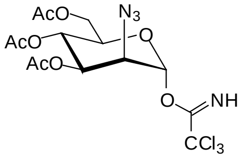
**1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*α,β*-D-gluco-pyranoside (2).** Methyl chloroformate (430 μL, 5.56 mmol) was added dropwise to a vigorously stirring solution of **1** (1.00 g, 4.64 mmol) and $NaHCO_3$ (1.17 g, 13.9 mmol) in a 1:1 mixture of $CHCl_3$:$H_2O$ (20 mL). The reaction was allowed to stir for two hours at room temperature after which it was neutralized with 1M HCl and concentrated *in vacuo* to a white solid. The residue was dissolved in a solution dry pyridine (10 mL) and acetic anhydride (3.5 mL, 37.1 mmol) and allowed to stir under a nitrogen atmosphere at room temperature.

After twelve hours, the reaction was quenched with MeOH (5 mL) and the reaction concentrated *in vacuo*. The syrupy residue was dissolved in $CH_2Cl_2$ (100 mL) and washed consecutively with a 2:1 mixture of 10% ammonium sulfate: 10% HCl (3x), saturated $NaHCO_3$ (1x), and brine (1x) then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (1:1 ethyl acetate:hexanes) to afford **2** (1.87 g, 99%) as a white foam and a mixture of anomers. The purified anomeric mixture of **2** was used without further attempts to separate the anomers. HRFABMS calculated for $C_{16}H_{23}NO_{11}Na$ (M+Na) 428.1169, found 428.1169.



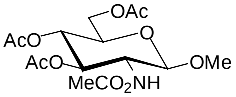
**3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*α*-D-glucopyranosyl trichloroacetimidate (4).** Hydrazine acetate (1.10 g, 11.9 mmol) was added to a vigorously stirring solution of **2** (3.45 g, 8.51 mmol) in dry DMF (20 mL) under dry nitrogen. After two hours the reaction was diluted with ethyl acetate (100 mL) and washed consecutively with water (1x), saturated $NaHCO_3$ (1x), and brine (1x), then dried over $Na_2SO_4$ and concentrated *in vacuo*.

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (675 µL, 4.5 mmol) was added to a flask containing the crude hemiacetal and trichloroacetonitrile (4.44 mL, 44.3 mmol) in dry $CH_2Cl_2$ (28 mL) at room temperature. After 2 hours the reaction was concentrated *in vacuo* and the residue purified by flash chromatography to afford **4** (2.49 g, 58%) as a light yellow foam. $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.80 (1H, s), 6.36 (1H, d, *J* = 3.7 Hz), 5.29 (1H, t, *J* = 9.9 Hz), 5.21 (1H, t, *J* = 9.9 Hz), 4.95 (1H, d, *J* = 9.4 Hz), 4.24 (2H, m), 4.10 (2H, m), 3.63 (3H, s), 2.05 (3H, s), 2.03 (3H, s), 2.02 (3H, s). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.3, 170.7, 169.4, 160.4, 156.4, 95.0, 70.7, 70.3, 67.6, 61.6, 53.6, 52.7, 20.8, 20.7. HRFABMS calculated for $C_{16}H_{21}Cl_3N_2O_{10}Na$ (M+Na) 529.0159, found 529.0160.



**3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-mannopyranosyl trichloroacetimidate (7).** Hydrazine acetate (177 mg, 1.92 mmol) was added to a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-azido-α-D-mannopyranoside[2] (512 mg, 1.37 mmol) in DMF (30 mL). After stirring at room temperature for 1 hour, the reaction was quenched with $H_2O$ (20 mL), extracted with $CHCl_3$ (3x) and washed with saturated $NaHCO_3$ (1x). The aqueous layer was re-extracted with $CHCl_3$ (2x) and the organic extracts combined, then dried over $MgSO_4$. The filtrate was concentrated *in vacuo* to afford the crude hemiacetal as a light yellow syrup.

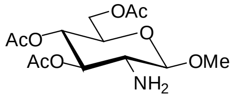
To a solution of the crude hemiacetal in $CH_2Cl_2$ (20 mL) were added trichloroacetonitrile (714 µl, 7.12 mmol) and DBU (109 µl, 0.73 mmol). After stirring at room temperature for 1 hour, the reaction was concentrated *in vacuo* and the residue purified by flash chromatography (1:1 hexanes: ethyl acetate) to afford the **7** as a light yellow foam (254 mg, 39 %): $^1$H NMR (500 MHz, $CDCl_3$) δ 8.78 (1H, s), 6.27 (1H, d, *J* = 1.8 Hz), 5.42 (1H, t, *J* = 9.9 Hz), 5.41 (1H, m), 4.26 (1H, dd, *J* = 3.2, 2.0 Hz), 4.22 (1H, dd, *J* = 12.8, 4.9 Hz), 4.12 (1H, dd, *J* = 12.8, 2.4 Hz), 4.10 (1H, m), 2.09 (3H, s), 2.06 (3H, s), 2.04 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.8, 170.1, 169.6, 160.0, 95.5, 90.6, 71.4, 70.8, 65.3, 61.9, 60.0, 20.8, 20.8, 20.6; HRFABMS calculated for $C_{14}H_{17}C_{l3}N_4O_8$ (M+Na) 497.009, found 497.008.



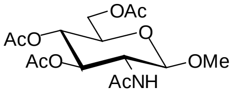
**Methyl *O*-3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*β*-D-glucopyranoside (8a).** A solution of 30% HBr in acetic acid (3.4 mL, 60.2 mmol) was added to a flask containing **2** (2.44 g, 6.02 mmol) and allowed to stir at room temperature. After one hour, the reaction was diluted with $CH_2Cl_2$ (200 mL) and washed with ice cold $H_2O$, saturated aqueous $NaHCO_3$ (1x), and brine (1x). The organic extract was dried over $MgSO_4$ and concentrated *in vacuo* to afford **3** (1.34 g, 52%) as a yellow foam. The crude glycosyl bromide immediately used without further purification.

Dry methanol (379 μL, 93.6 mmol) was added to a solution of **3** (1.34 g, 31.2 mmol) and 4 Å molecular sieves (1.33 g) in dry $CH_2Cl_2$ (13 mL). The flask was excluded from light and a catalytic amount of AgOTf was added and the reaction allowed to stir at room temperature under dry nitrogen. After 36 hours, the reaction was filtered through Celite®, concentrated in vacuo. The residue was purified by flash chromatography (1:1 ethyl acetate:hexanes) to afford **8a** (867 mg, 74%) as a white solid.

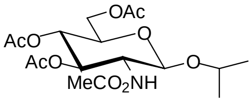
From **4**: TMSOTf (4 μL, 0.025 mmol) was added to a solution of **4** (124 mg, 0.245 mmol) in dry $CH_2Cl_2$ (1 mL) at –30 ºC. After 10 minutes at –30 ºC, dry MeOH (100 μL, 2.45 mmol) was added dropwise to the flask. The reaction was allowed to warm to room temperature over 3 hours then quenched with $Et_3N$ and concentrated *in vacuo*. The residue was purified by flash chromatography (1:1 ethyl acetate:hexanes) to afford **8a** (839 mg, 91%) as a white solid. $^1H$ NMR (500 MHz, $CDCl_3$) δ 5.24 (1H, bs), 5.05 (1H, d, *J* = 9.9 Hz), 4.79 (1H, bs), 4.51 (1H, bs), 4.27 (1H, dd, *J* = 12.2, 4.7 Hz), 4.13 (1H, dd, *J* = 12.3, 2.5 Hz), 3.68 (1H, ddd, *J* = 9.9, 4.8, 2.5 Hz), 3.66 (3H, s), 3.56 (1H, dt, *J* = 10.5, 8.7 Hz), 3.51 (3H, s), 2.08 (3H, s), 2.03 (3H, s), 2.01 (3H, s). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 171.0, 170.9, 169.7, 156.7, 102.1, 72.5, 71.8, 69.0, 62.3, 57.3, 56.2, 52.6, 20.9, 20.8. mp 132-133 ºC HRFABMS calculated for $C_{15}H_{23}NO_{10}$ (M+Na) 400.1220, found 400.1221.



**Methyl *O*-3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-*β*-D-glucopyranoside (8b).** $MeSiCl_3$ (86 μL, 0.730 mmol) was added to a solution of **8a** (55 mg, 0.146 mmol) and triethylamine (102 μL, 0.730 mmol) in dry THF (3 mL). The reaction flask was capped and heated to 60 ºC. After 24 hours, the reaction was removed from the heating bath, diluted with $H_2O$ (20 mL) and allowed to stir vigorously for 30 minutes and washed with $CH_2Cl_2$ (10 mL). The aqueous phase neutralized with saturated $NaHCO_3$ (5 mL) and extracted with $CH_2Cl_2$ (3x). The organic extracts were combined, dried ($Na_2SO_4$), and concentrated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate, 1% $Et_3N$) to afford **8b** (44 mg, 93%) as a white solid. $^1H$ NMR (500 MHz, $CDCl_3$) δ 5.00 (1H, t, *J* = 9.5 Hz), 4.95 (1H, t, *J* = 9.5 Hz), 4.28 (dd, *J* = 12.3, 4.5 Hz), 4.14 (1H, d, *J* = 8.1 Hz), 4.09 (1H, dd, *J* = 12.3, 2.3 Hz), 3.67 (1H, ddd, *J* = 9.5, 4.7, 2.4 Hz), 3.54 (3H, s), 2.89 (1H, dd, *J* = 9.8, 8.1 Hz), 2.06 (3H, s), 2.05 (3H, s), 2.00 (3H, s), 1.44 (2H, bs). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 170.9, 170.8, 169.9, 105.2, 75.5, 72.0, 68.9, 62.4, 57.6, 56.1, 21.0, 20.9, 20.8. HRFABMS calculated for $C_{13}H_{21}NO_8$ (M+Na) 954.2273, found 954.2270.

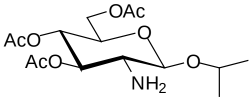


**Methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranoside (8c).** Acetic anhydride (26 μL, 0.272 mmol) was added to a solution of **8b** (44 mg, 0.136 mmol) in dry pyridine (1 mL) at room temperature. After two hours, MeOH (0.5 mL) was added and the reaction concentrated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate) to afford **8c** (mg, %) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.83 (1H, bd, *J* = 9.0 Hz), 5.26 (1H, dd, *J* = 10.5, 9.1 Hz), 5.05 (1H, t, *J* = 9.9 Hz), 4.57 (1H, d, *J* = 8.2 Hz), 4.25 (1H, dd, *J* = 12.2, 4.6 Hz), 4.12 (1H, dd, *J* = 12.4, 2.4 Hz), 3.86 (1H, dt, *J* = 10.6, 8.5 Hz), 3.70 (1H, ddd, *J* = 9.9, 4.6, 2.4 Hz), 3.47 (3H, s), 2.06 (3H, s), 2.01 (3H, s), 2.00 (3H, s), 1.93 (3H, s). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.1, 170.9, 170.6, 169.6, 101.8, 68.8, 62.3, 56.9, 54.7, 23.5, 20.9, 20.8, 20.7. mp 153-155 ºC HRFABMS calculated for $C_{15}H_{23}NO_9Na$ (M+Na) 384.1271, found 384.1273.

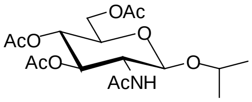


**Isopropyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*β*-D-glucopyranoside (9a).** A solution of 30% HBr in acetic acid (3.5 mL, 58.5 mmol) was added to a flask containing **4** (2.50 g, 5.85 mmol) and allowed to stir at room temperature. After one hour, the reaction was diluted with $CH_2Cl_2$ (200 mL) and washed with ice cold $H_2O$, saturated aqueous $NaHCO_3$ (1x), and brine (1x). The organic extract was dried over $MgSO_4$ and concentrated *in vacuo* to afford **3** (1.28 g, 51%) as a yellow foam. The crude glycosyl bromide immediately used without further purification.

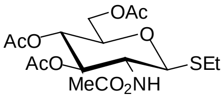
Dry isopropanol (690 μL, 90.0 mmol) was added to a solution of **3** (1.28 g, 30.0 mmol) and 4 Å molecular sieves (1.28 g) in dry $CH_2Cl_2$ (13 mL). The flask was excluded from light and a catalytic amount of AgOTf was added and the reaction allowed to stir at room temperature under dry nitrogen. After 36 hours, the reaction was filtered through Celite®, concentrated in vacuo. The residue was purified by flash chromatography (1:1 ethyl acetate:hexanes) to afford **9a** (912 mg, 75%) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.24 (1H, bs), 5.05 (1H, d, *J* = 9.9 Hz), 4.79 (1H, bs), 4.51 (1H, bs), 4.27 (1H, dd, *J* = 12.2, 4.7 Hz), 4.13 (1H, dd, *J* = 12.3, 2.5 Hz), 3.68 (1H, ddd, *J* = 9.9, 4.8, 2.5 Hz), 3.66 (3H, s), 3.56 (1H, dt, *J* = 10.5, 8.7 Hz), 3.51 (3H, s), 2.08 (3H, s), 2.03 (3H, s), 2.01 (3H, s). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.9, 169.7, 156.7, 102.1, 72.5, 71.8, 69.0, 62.3, 57.3, 56.2, 52.6, 20.9, 20.8. mp 165-169 ºC HRFABMS calculated for $C_{17}H_{27}NO_{10}$ (M+Na) 428.1533, found 428.1534.



**Isopropyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-*β*-D-glucopyranoside (9b).** $MeSiCl_3$ (60 μL, 0.559 mmol) was added to a solution of **9a** (45 mg, 0.112 mmol) and triethylamine (78 μL, 0.559 mmol) in dry THF (11 mL). The reaction flask was capped and heated to 60 ºC. After 24 hours, the reaction was removed from the heating bath, diluted with $H_2O$ (30 mL) and allowed to stir vigorously for 30 minutes and washed with $CH_2Cl_2$ (10 mL). The aqueous phase neutralized with saturated $NaHCO_3$ (5 mL) and extracted with $CH_2Cl_2$ (3x). The organic extracts were combined, dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate, 1% $Et_3N$) to afford **9b** as a white solid (31 mg, 80%). $^1H$ NMR (500 MHz, $CDCl_3$) δ 4.98 (2H, m, $J$ = 10.0, 9.4, 8.0 Hz), 4.31 (1H, d, $J$ = 8.1 Hz), 4.25 (1H, $\underline{A}$BX, $J_{AB}$ = 12.1 Hz, $J_{AX}$ = 5.2 Hz, $J_{BX}$ = 2.6 Hz, $\nu_a$ = 2125.8, $\nu_b$ = 2043.3), 4.09 (1H, A$\underline{B}$X, $J_{AB}$ = 12.1 Hz, $J_{AX}$ = 5.2 Hz, $J_{BX}$ = 2.6 Hz, $\nu_a$ = 2125.8, $\nu_b$ = 2043.3), 3.98 (1H, sept, $J$ = 6.1 Hz), 3.66 (1H, AB$\underline{X}$, $\nu_x$ = 1831.8), 2.89 (1H, m, $J$ = 10.0, 8.1 Hz), 2.06 (3H, s), 2.00 (3H, s), 1.62 (2H, bs), 1.25 (3H, d, $J$ = 5.9 Hz), 1.19 (3H, d, $J$ = 6.3 Hz) $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 171.0, 170.9, 102.6, 75.6, 72.7, 71.9, 69.2, 52.6, 56.0, 23.6, 22.1, 21.0, 20.9. HRFABMS calculated for $C_{15}H_{26}NO_8$ (M+H) 348.1658, found 348.1659.

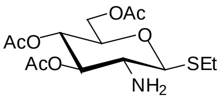


**Isopropyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranoside (9c).** Acetic anhydride (20 μL, 0.177 mmol) was added to a solution of **9b** (31 mg, 0.088 mmol) in dry pyridine (1 mL) at room temperature. After two hours, MeOH (0.5 mL) was added and the reaction concentrated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate) to afford **9c** (34 mg, quantitative) as a white solid. $^1H$ NMR (500 MHz, $CDCl_3$) δ 5.82 (1H, bd, $J$ = 8.5 Hz), 5.38 (1H, dd, $J$ = 10.6, 9.3 Hz), 5.01 (1H, t, $J$ = 9.9 Hz), 4.82 (1H, d, $J$ = 8.2 Hz), 4.23 (1H, dd, $J$ = 12.4, 5.4 Hz), 4.09 (1H, dd, $J$ = 12.1, 2.5 Hz), 3.91 (1H, sept, $J$ = 6.2 Hz), 3.70 (1H, ddd, $J$ = 10.0, 5.3, 2.5 Hz), 3.65 (1H, dt, $J$ = 10.5, 8.4 Hz), 2.05 (3H, s), 2.01 (3H, s), 2.00 (3H, s), 1.92 (3H, s), 1.20 (3H, d, $J$ = 6.4 Hz), 1.11 (3H, d, $J$ = 6.1 Hz). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 171.0, 170.5, 169.7, 99.4, 72.8, 72.4, 71.7, 69.2, 62.6, 55.6, 23.4, 22.1, 20.9, 20.8, 20.7. mp 168-169 ºC HRFABMS calculated for $C_{17}H_{27}NO_9Na$ (M+Na) 412.1584, found 412.1583.

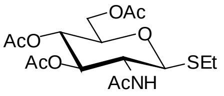


**Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-1-thio-*β*-D-glucopyranoside (10a)**. $BF_3•Et_2O$ (50 μl, 3.7 mmol) was added to a solution of **4** (190 mg, 0.37 mmol), ethanethiol (277 μl, 3.7 mmol), and 4 Å molecular sieves in dry $CH_2Cl_2$

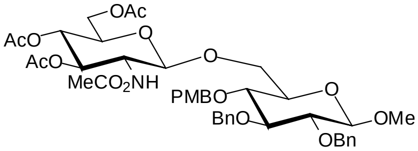
(10 mL).[3] After stirring at room temperature for 8 hours, the reaction was quenched with saturated $NaHCO_3$ and extracted with $CH_2Cl_2$ (3x), dried over $MgSO_4$, concentrated *in vacuo* and purified by flash chromatography (33 % hexane in ethyl acetate) to afford **10a** (110 mg, 73 %) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$) δ 5.19 (1H, bt, $J$ = 9.5 Hz), 5.06 (1H, t, $J$ = 9.9 Hz), 4.83 (1H, bd, $J$ = 8.9 Hz), 4.62 (1H, bd, $J$ = 9.5 Hz), 4.23 (1H, ABX, $J_{AB}$ = 12.4 Hz, $J_{AX}$ = 5.1 Hz, $J_{BX}$ = 2.3 Hz, $\nu_a$ = 1693.0, $\nu_b$ = 1647.0), 4.12 (1H, ABX, as above), 3.72 (1H, q, $J$ = 9.9 Hz), 3.69 (1H, ABX, $\nu_x$ = 1477.0), 3.67 (3H, s), 2.72 (2H, m), 2.07 (3H, s), 2.03 (3H, s), 2.02 (3H, s), 1.27 (3H, t, $J$ = 7.4 Hz). $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 170.9, 169.6, 156.5, 76.0, 73.7, 68.8, 62.6, 52.8, 24.7, 21.0, 20.9, 20.8, 15.0. mp 161-162 °C HRFABMS calculated for $C_{16}H_{25}NO_9S$ (M+Na) 430.1147, found 430.1148.



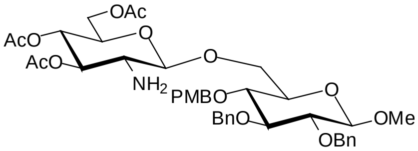
**Ethyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-1-thio-*β*-D-glucopyranoside (10b)**. $MeSiCl_3$ (27 μl, 0.23 mmol) was added to a solution of **10a** (19 mg, 0.05 mmol) and $Et_3N$ (32 μl, 0.23 mmol) in dry THF (1 mL) at 60 °C. After stirring for 48 hours, the reaction was quenched with $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3x). The aqueous layer was neutralized with saturated $NaHCO_3$ and extracted with $CH_2Cl_2$ (3x), dried over $Na_2SO_4$, concentrated *in vacuo*. The residue was purified by flash chromatography (1 % $Et_3N$ in ethyl acetate) to afford **10b** (11 mg, 68 %) as a white foam. $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.01 (1H, t, $J$ = 9.5 Hz), 4.96 (1H, t, $J$ = 9.4 Hz), 4.33 (1H, d, $J$ = 9.9 Hz), 4.24 (1H, ABX, $J_{AB}$ = 12.3 Hz, $J_{AX}$ = 5.2 Hz, $J_{BX}$ = 2.3 Hz, $\nu_a$ = 2119.8, $\nu_b$ = 2048.3), 4.10 (1H, ABX, as above), 3.68 (1H, ABX, $\nu_x$ = 1840.8), 2.94 (1H, t, $J$ = 9.5 Hz), 2.73 (2H, m), 2.07 (3H, s), 2.06 (3H, s), 2.01 (3H, s), 1.61 (2H, bs), 1.31 (3H, t, $J$ = 7.4 Hz). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.9, 170.0, 87.8, 76.9 , 75.9 , 68.9, 62.7, 55.4, 24.9, 21.0, 20.9, 20.8, 15.3. HRFABMS calculated for $C_{14}H_{23}NO_7S$ (M+H) 350.1272, found 350.1273.



**Ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-*β*-D-glucopyranoside (10c)**. Acetic anhydride (94 μl, 1.0 mmol) was added to a solution of **10b** (34 mg, 0.1 mmol) in dry pyridine (1 mL). After stirring at room temperature for 12 hours, the reaction was evaporated under reduced pressure and purified by flash chromatography (ethyl acetate) to afford **10c** (36 mg, 95 %) as a white solid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.61 (1H, d, $J$ = 9.4 Hz), 5.17 (1H, t, $J$ = 9.7 Hz), 5.08 (1H, t, $J$ = 9.7 Hz), 4.593 (1H, d, $J$ = 10.0 Hz), 4.22 (1H, ABX, $J_{AB}$ = 12.4 Hz, $J_{AX}$ = 5.1 Hz, $J_{BX}$ = 2.3 Hz, $\nu_a$ = 2112.3, $\nu_b$ = 2063.3), 4.13 (1H, ABX, as above), 4.09 (1H, q, $J$ = 9.7 Hz), 3.67 (1H, ABX, $\nu_x$ = 1840.8), 2.71 (2H, m) 2.07 (3H, s), 2.03 (3H, s), 2.02 (3H, s), 1.95 (3H, s), 1.26 (3H, t, $J$ = 7.0 Hz). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ171.3, 171.0, 170.3, 169.6, 84.6, 76.1, 74.1, 68.6, 62.5, 53.4, 24.4, 23.5, 20.9, 20.9, 20.8, 14.9. mp 178-179 °C HRFABMS calculated for $C_{16}H_{25}NO_8S$ (M+Na) 414.1198, found 414.1199.

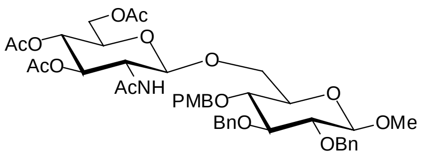


**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*β*-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (11a).** TMSOTf (6 mL, 0.035 mmol) was added to a solution of **4** (356 mg, 0.701 mmol), **18**[4] (231 mg, 0.0467 mmol) and 4 Å molecular sieves in dry $CH_2Cl_2$ (4 mL) at –30 °C under argon. The reaction was allowed to warm to 0 °C over 2 hours then quenched with Et3N, filtered through Celite®, and concentrated *in vacuo*. The residue was purified by flash chromatography (1:1 ethyl acetate:hexanes) to afford **11a** (537 mg, 91%) as a white solid. $^1$H NMR ($CDCl_3$:$CH_3CN$ (2:1), 500 MHz) δ 7.18-7.05 (10H, m), 7.05 (2H AA'XX', $J_{AX} = J_{A'X'}$ = 8.4 Hz, $J_{AA'} = J_{X'X'}$ = 2.2 Hz, $J_{A'X} = J_{AX'}$ = 0.3 Hz, $\nu_a$ = 3504.8, $\nu_b$ = 3329.5), 6.66 (2H AA'XX', $J_{AX} = J_{A'X'}$ = 8.4 Hz, $J_{AA'} = J_{X'X'}$ = 2.2 Hz, $J_{A'X} = J_{AX'}$ = 0.3 Hz, $\nu_a$ = 3504.8, $\nu_b$ = 3329.5), 5.30 (1H, bs), 5.01 (1H, bt, *J* = 9.0 Hz), 4.81 (1H, t, *J* = 9.5 Hz), 4.70 (1H, $AB_q$, $J_{AB}$ = 11.1 Hz, $\nu_a$ = 2325.7 Hz, $\nu_b$ = 2314.6 Hz), 4.69 (1H, $AB_q$, $J_{AB}$ = 11.1 Hz, $\nu_a$ = 2303.8 Hz, $\nu_b$ = 2297.7 Hz), 4.58 (1H, $AB_q$, $J_{AB}$ = 11.1 Hz, $\nu_a$ = 2325.7 Hz, $\nu_b$ = 2314.6 Hz), 4.50 (1H, $AB_q$, $J_{AB}$ = 11.1 Hz, $\nu_a$ = 2303.8 Hz, $\nu_b$ = 2297.7 Hz), 4.49 (1H, $AB_q$, $J_{AB}$ = 9.2 Hz, $\nu_a$ = 2205.3 Hz, $\nu_b$ = 2195.5 Hz), 4.48 (1H, bs), 4.30 (1H, $AB_q$, $J_{AB}$ = 9.2 Hz, $\nu_a$ = 2205.3 Hz, $\nu_b$ = 2195.5 Hz), 4.10 (1H, d, *J* = 7.8 Hz), 4.08 (1H, dd, *J* = 12.3, 4.7 Hz), 3.94 (1H, dd, *J* = 8.5, 1.8 Hz), 3.91 (1H, dd, *J* = 9.8, 2.4 Hz), 3.59 (3H, s), 3.54-3.49 (2H, m), 3.41 (1H, m), 3.40 (1H, t, *J* = 8.9 Hz), 3.35 (3H, s), 3.31 (3H, bs), 3.29 (1H, t, *J* = 8.6 Hz), 3.24 (1H, ddd, *J* = 9.7, 4.4, 1.7 Hz), 3.13 (1H, dd, *J* = 9.1, 8.0 Hz), 1.85 (3H, s), 1.82 (3H, s), 1.81 (3H, s). $^{13}$C NMR ($CDCl_3$:$CH_3CN$ (2:1), 125 MHz) δ 172.2, 172.0, 171.3, 161.0, 158.2, 140.5, 140.4, 132.2, 131.3, 130.0, 129.7, 129.4, 129.3, 129.2, 115.4, 106.3, 86.2, 83.8, 79.0, 77.0, 76.1, 76.0, 75.5, 73.9, 73.3, 70.6, 69.9, 63.8, 58.6, 57.6, 56.9, 53.7, 22.3, 22.2. HRFABMS calculated for $C_{43}H_{53}NO_{16}Na$ (M+Na) 862.3262, found 862.3258.

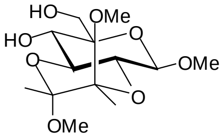


**Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-*β*-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (11b).** $MeSiCl_3$ (32 μl, 0.273 mmol) was added to a solution of **11a** (46 mg, 0.055 mmol) and $Et_3N$ (38 μl, 0.273 mmol) in dry THF (2.8 mL). The flask was capped and heated to 60 °C. After 36 hours, the reaction was quenched with THF (10 mL) and $H_2O$ (10 mL) and extracted with

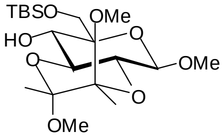
$CH_2Cl_2$ (3x). The aqueous layer was neutralized with saturated $NaHCO_3$, extracted with $CH_2Cl_2$ (3x), dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (3:2 ethyl acetate:hexanes, 1 % $Et_3N$) to afford **11b** (23 mg, 54 %) as a transparent syrup. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.33-7.26 (10H, m), 7.18 (2H, AA’XX’, $J_{AX} = J_{A'X'} = 8.4$ Hz, $J_{AA'} = J_{X'X'} = 2.2$ Hz, $J_{A'X} = J_{AX'} = 0.3$ Hz, $\nu_a = 3591.4$, $\nu_b = 3425.5$) 6.85 (2H AA’XX’, $J_{AX} = J_{A'X'} = 8.4$ Hz, $J_{AA'} = J_{X'X'} = 2.2$ Hz, $J_{A'X} = J_{AX'} = 0.3$ Hz, $\nu_a = 3591.4$, $\nu_b = 3425.5$) 5.01 (1H, t, $J = 9.6$ Hz), 4.94 (1H, t, $J = 10.0$ Hz) 4.93 (1H, $AB_q$, $J_{AB} = 11.1$ Hz, $\nu_a = 2436.1$ Hz, $\nu_b = 2425.1$ Hz), 4.90 (1H, $AB_q$, $J_{AB} = 11.1$ Hz, $\nu_a = 2406.9$ Hz, $\nu_b = 2395.8$ Hz), 4.79 (1H, $AB_q$, $J_{AB} = 10.5$ Hz, $\nu_a = 2331.8$ Hz, $\nu_b = 2321.1$ Hz), 4.78 (1H, $AB_q$, $J_{AB} = 11.1$ Hz, $\nu_a = 2436.1$ Hz, $\nu_b = 2425.1$ Hz), 4.69 (1H, $AB_q$, $J_{AB} = 11.1$ Hz, $\nu_a = 2406.9$ Hz, $\nu_b = 2395.8$ Hz), 4.51(1H, $AB_q$, $J_{AB} = 10.5$ Hz, $\nu_a = 2331.8$ Hz, $\nu_b = 2321.1$ Hz), 4.30 (1H, d, $J = 7.9$ Hz), 4.27 (1H, dd, $J = 7.7$, 4.8 Hz), 4.26 (1H, d, $J = 7.9$ Hz), 4.15 (1H, dd, $J = 11.2$, 2.1 Hz), 4.11 (1H, dd, 12.2, 2.3 Hz), 3.80 (3H, s), 3.66-3.61 (3H, m), 3.56 (3H, s), 3.53 (1H, ddd, $J = 9.9$, 6.7, 1.9 Hz), 3.40 (1H, t, $J = 10.1$ Hz), 2.95 (1H, dd, $J = 10.1$, 8.0 Hz), 2.01 (3H, s), 2.06 (3H, s), 2.02 (3H, s), 1.5 (2H, bs). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.5, 170.9, 159.6, 138.7, 138.6, 130.3, 129.9, 128.7, 128.6, 128.3, 128.1, 127.9, 114.1, 104.9, 104.8, 84.8, 82.5, 78.1, 76.0, 75.6, 75.0, 74.9, 74.8, 72.1, 69.4, 69.0, 62.5, 57.6, 56.0, 21.1, 20.9. HRFABMS calculated for $C_{41}H_{51}NO_{14}Na$ (M+Na) 804.3207, found 804.3205.



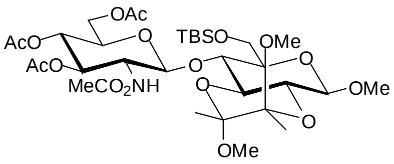
**Methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-*β*-D-glucopyranoside (11c).** Acetic anhydride (5 mL, 0.055 mmol) was added to a solution of **11b** (22 mg, 0.028 mmol) in 1:1 $CH_2Cl_2$:pyridine (0.5 mL). The reaction was stirred at room temperature of 1 hour then quenched with methanol and concentrated *in vacuo*. The residue was purified by flash chromatography (3:2 ethyl acetate:hexanes) to afford **11c** (23 mg, 99%) as a white solid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.34-7.26 (10H, m), 7.18 (2H, AA’XX’, $J_{AX} = J_{A'X'} = 8.4$ Hz, $J_{AA'} = J_{X'X'} = 2.2$ Hz, $J_{A'X} = J_{AX'} = 0.3$ Hz, $\nu_a = 3591.4$, $\nu_b = 3422.6$) 6.84 (2H AA’XX’, $J_{AX} = J_{A'X'} = 8.4$ Hz, $J_{AA'} = J_{X'X'} = 2.2$ Hz, $J_{A'X} = J_{AX'} = 0.3$ Hz, $\nu_a = 3591.4$, $\nu_b = 3422.6$), 5.51 (1H, d, $J = 8.9$ Hz), 5.29 (1H, dd, $J = 10.3$, 9.1 Hz), 5.07 (1H, t, $J = 9.7$ Hz), 4.91 (1H, $AB_q$, $J_{AB} = 11.3$ Hz, $\nu_a = 2626.0$ Hz, $\nu_b = 2416.3$ Hz), 4.89 (1H, $AB_q$, $J_{AB} = 11.3$ Hz, $\nu_a = 2400.1$ Hz, $\nu_b = 2389.0$ Hz), 4.78 (1H, $AB_q$, $J_{AB} = 11.3$ Hz, $\nu_a = 2626.0$ Hz, $\nu_b = 2416.3$ Hz), 4.77 (1H, d, $J = 7.6$ Hz), 4.74 (1H, $AB_q$, $J_{AB} = 10.4$ Hz, $\nu_a = 2316.6$ Hz, $\nu_b = 2306.2$ Hz), 4.68 (1H, $AB_q$, $J_{AB} = 11.3$ Hz, $\nu_a = 2400.1$ Hz, $\nu_b = 2389.0$ Hz), 4.50 (1H, $AB_q$, $J_{AB} = 10.4$ Hz, $\nu_a = 2316.6$ Hz, $\nu_b = 2306.2$ Hz), 4.28 (1H, d, $J = 7.6$ Hz), 4.24 (1H, dd, $J = 12.4$, 4.8 Hz), 4.11 (1H, dd, $J = 12.3$, 2.4 Hz), 4.09 (1H, dd, $J = 11.0$, 1.8 Hz), 3.87 (1H, dt, $J = 10.6$, 8.5 Hz), 3.79 (3H, s), 3.70-3.66 (2H, m), 3.61 (1H, ddd, $J = 9.8$, 5.3, 2.0 Hz), 3.41 (1H, dd, $J = 9.2$, 7.8 Hz), 2.03 (3H, s), 2.01, (3H,s), 1.87 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.0, 170.9, 170.2, 159.6, 138.7, 138.6, 130.3, 129.8, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 114.1, 104.7, 100.6, 84.7, 82.3, 77.8, 75.9, 74.9, 74.7, 74.4, 72.6, 72.1, 68.7, 67.7, 62.3, 57.3, 55.5, 54.7, 23.5, 20.9, 20.8. HRFABMS calculated for $C_{43}H_{53}NO_{15}$ (M+Na) 846.3313, found 846.3315.



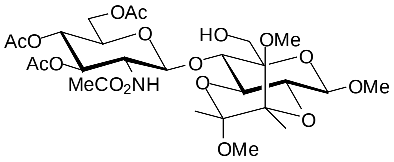
**Methyl [(2'R,3'R)-2,3-O-(2',3'-dimethoxybutane-2',3'-diyl)]-*β*-D-glucopyranoside (23).**[5] D,L-Camphorsulfonic acid (85 mg, 0.4 mmol) was added to a solution of methyl-β-D-glucopyranoside hemihydrate (1.9 g, 9.5 mmol), trimethyl-orthoformate (3.0 mL, 27.7 mmol), and tetramethoxybutane (2.0 mL, 11.5 mmol) in dry MeOH (25 mL). After 19 hours of refluxing at 60 °C, TLC indicated the absence of starting material and the reaction was quenched by the addition of solid $NaHCO_3$. The reaction was filtered, concentrated *in vacuo*, and purified by flash chromatography (32 % ethyl acetate, 32 % $Et_2O$, 32 % THF, 5 % $Et_3N$) to afford **23** (1.21 g, 41 %) as a white foam. $^1$H NMR ($CDCl_3$, 500 MHz) δ 4.46 (1H, d, $J$ = 7.9 Hz), 3.89 (1H, ABX, $J_{AB}$ = 12.0 Hz, $J_{AX}$ = 3.4 Hz, $J_{BX}$ = 4.7 Hz, $\nu_a$ = 1944.3, $\nu_b$ = 1904.9), 3.81 (1H, ABX, as above), 3.74 (1H, t, $J$ = 9.3 Hz), 3.69 (1H, t, $J$ = 9.5 Hz), 3.53 (3H, s), 3.47 (1H, dd, $J$ = 9.8, 8.0 Hz), 3.40 (1H, ABX, $\nu_x$ = 1699.0), 3.28 (3H, s), 3.27 (3H, s), 1.32 (6H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 101.8, 99.7, 76.3, 72.6, 69.4, 68.0, 62.4, 57.2, 48.2, 48.2, 17.8, 17.8. HRFABMS calculated for $C_{18}H_{24}O_8$ (M+Na) 331.1370, found 331.1369.



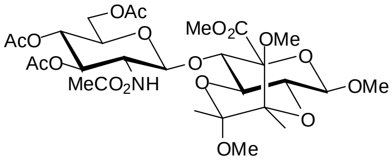
**Methyl [(2'R,3'R)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-(6-*O*-*tert*-butyldimethyl silyl]-*β*-D-glucopyranoside (19).** To a solution of **23** (100 mg, 0.3 mmol) in pyridine (5 mL) was added *t*-butyldimethylsilylchloride (54 mg, 0.4 mmol). After stirring at room temperature for 2 hours, TLC indicated the absence of starting material. $CH_2Cl_2$ (15 mL) was added and the reaction was washed with saturated $CuSO_4$ (3x), water (1x), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography to afford **19** (130 mg, 95 %) as a white foam. $^1$H NMR ($CDCl_3$, 500 MHz) δ 4.33 (1H, d, $J$ = 8.1 Hz), 3.83 (1H, ABX, $J_{AB}$ = 10.4 Hz, $J_{AX}$ = 5.2 Hz, $J_{BX}$ = 6.0 Hz, $\nu_a$ = 1915.8, $\nu_b$ = 1872.3), 3.74 (1H, ABX, as above), 3.63 (2H, m), 3.42 (3H, s), 3.39 (1H, dd, $J$ = 10.1, 8.1 Hz), 3.31 (1H, ABX, $\nu_x$ = 1655.2), 3.22 (3H, s), 3.18 (3H, s), 1.25 (3H, s), 1.24 (3H, s), 0.80 (9H, s), 0.00 (3H, s), -0.01 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 101.6, 99.7, 99.6, 75.1, 72.6, 70.4, 69.3, 64.9, 56.9, 48.2, 48.1, 26.0, 17.9, 17.8, -5.3. HRFABMS calculated for $C_{19}H_{38}O_8Si$ (M + Na) 445.2235, found 445.2234.



**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*β*-D-glucopyranosyl-(1→4)-[(2'R,3'R)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-(6-*O*-*tert*-butyldimethyl silyl]-*β*-D-glucopyranoside (20).** To a solution of **4** (830 mg, 1.6 mmol), 4 Å molecular sieves, and trimethylsilyl trifluoromethanesulfonate (10 μl, 0.05 mmol) in $CH_2Cl_2$ (5 mL) at 0 °C was added **19** (460 mg, 1.1 mmol) in $CH_2Cl_2$ (2.5 mL) dropwise via cannula. After warming to room temperature over 18 hours, the reaction was quenched with $Et_3N$ (10 μl) and filtered through Celite® and concentrated *in vacuo*. The residue was purified by flash chromatography (33 % hexane in ethyl acetate) to afford **20** (790 mg, 94 %) as a light yellow foam. $^1$H NMR (500 MHz, $CDCl_3$) δ $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.00 (2H, m), 4.55 (1H, d, *J* = 8.4 Hz), 4.25 (1H, d, *J* =8.0 Hz), 4.20 (1H, A̲BX, $J_{AB}$ = 12.4 Hz, $J_{AX}$ = 3.4 Hz, $J_{BX}$ = 2.5 Hz, $\nu_a$ = 2099.8, $\nu_b$ = 2010.8), 4.02 (AB̲X, 1H, as above), 3.76 (1H, A̲BX, $J_{AB}$ = 12.0 Hz, $J_{AX}$ = 1.3 Hz, $J_{BX}$ = 4.5 Hz, $\nu_a$ = 1881.3, $\nu_b$ = 1832.8), 3.72 (1H, t, *J* =9.8 Hz), 3.67 (1H, AB̲X, as above), 3.62 (1H, t, *J* =9.5 Hz), 3.56 (1H, m), 3.55 (3H, s), 3.53 (1H, ABX̲, $\nu_x$ = 1765.3), 3.39 (3H, s), 3.36 (1H, dd, *J* = 9.9, 7.9 Hz), 3.23 (1H, ABX̲, $\nu_x$ = 1615.2), 3.21 (3H, s), 3.18 (3H, s), 1.96 (3H, s), 1.92 (3H, s), 1.91 (3H, s), 1.218 (3H, s), 1.91 (3H, s), 0.81 (9H, s), -0.01 (3H, s), -0.02 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.9, 156.7, 102.1, 101.2, 99.7, 99.6, 76.2, 73.3, 71.9, 71.5, 70.4, 69.9, 68.3, 62.2, 62.0, 56.7, 56.6, 52.6, 48.2, 48.2, 26.1, 20.8, 20.7, 17.8, 17.7, -5.1. HRFABMS calculated for $C_{33}H_{57}NO_{17}Si$ (M+Na) 790.3294, found 790.3293.

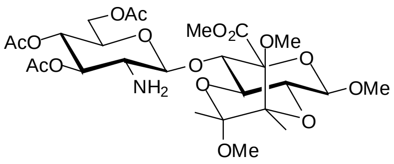


**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*β*-D-glucopyranosyl-(1→4)-(2'R,3'R)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-*β*-D-glucopyranoside (24).** TBAF (1.2 mL, 1M solution in THF, 1.2 mmol) was added to a solution of **20** (231 mg, 0.3 mmol) in dry THF (2 mL) at 0 °C. After warming to room temperature over 12 hours, the reaction was diluted with $CH_2Cl_2$ and washed with saturated $NaHCO_3$ (1x), brine (1x), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (20 % hexane in ethyl acetate) to afford **24** (144 mg, 74 %) as a transparent syrup. $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.63 (1H, d, *J* = 9.3 Hz), 5.21 (1H, bt, *J* = 10.4 Hz), 5.05 (1H, t, *J* = 9.8 Hz), 4.77 (1H, bd, *J* = 8.4 Hz), 4.37 (1H, d, *J* =8.0 Hz), 4.28 (1H, A̲BX, $J_{AB}$ = 12.4 Hz, $J_{AX}$ = 3.4 Hz, $J_{BX}$ = 2.4 Hz, $\nu_a$ = 2141.3, $\nu_b$ = 2036.3), 4.07 (1H, AB̲X, as above), 3.81 (1H, t, *J* = 10.4 Hz), 3.80 (1H, t, *J* = 9.5 Hz), 3.77 (1H, A̲BX, $J_{AB}$ = 12.2 Hz, $J_{AX}$ = 1.6 Hz, $J_{BX}$ = 3.2 Hz, $\nu_a$ = 1884.3, $\nu_b$ = 1863.8), 3.73 (1H, AB̲X, as above), 3.65 (1H, m), 3.64 (3H, s), 3.62 (1H, d), 3.48 (3H, s), 3.44 (1H, dd, *J* = 9.6, 8.1 Hz), 3.34 (1H, ABX̲, $\nu_x$ = 1671.3), 3.29 (3H, s), 3.23 (3H, s), 2.03 (3H, s), 2.00 (3H, s), 1.98 (3H, s), 1.28 (3H, s), 1.25 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.8, 169.6, 156.8, 101.8, 101.4, 99.6, 99.5, 75.7, 75.3, 72.8, 71.8, 71.5, 69.7, 68.3, 62.0, 60.8, 57.2, 56.5, 52.5, 48.3, 48.1, 20.8, 17.7, 17.7. HRFABMS calculated for $C_{27}H_{43}NO_{17}$ (M+Na) 676.2432, found 676.2429.

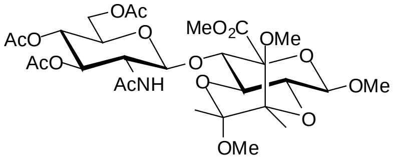


**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-methoxycarbonylamino-*β*-D-glucopyranosyl-(1→4)-methyl-(2'R,3'R)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-*β*-D-glucopyranosiduronate (12a).** A solution of 5 % NaOCl (3.8 mL) and saturated $NaHCO_3$ (2.8 mL) was added dropwise to a solution of **24** (75 mg, 0.1 mmol), tetrabutylammonium bromide (2 mg, 0.006 mmol), sodium bromide (2 mg, 0.02 mmol), and TEMPO (1 mg, 0.006 mmol) in $CH_2Cl_2$ (6 mL) and $H_2O$ (1 mL) at 0 °C.[6] After stirring at 0 °C for 1 hour, the reaction was quenched with MeOH (5 mL) and extracted with $CHCl_3$ (1x). The aqueous layer was acidified with 1M HCl and extracted once again with $CHCl_3$ (5x). The organic extract was dried over $MgSO_4$ and concentrated *in vacuo* to afford the crude acid as a yellow syrup.

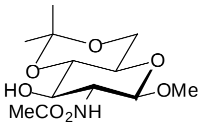
A solution of diazald (520 mg, 2.4 mmol) in $Et_2O$ (5 mL) was added dropwise to a solution of KOH (500 mg, 8.9 mmol) in $H_2O$ (0.8 mL) and EtOH (1 mL). The resulting diazomethane was distilled into a solution of the acid in $CH_2Cl_2$ (10 mL) and $Et_2O$ (10 mL). Excess diazomethane was allowed to evaporate and the methyl ester was purified by flash chromatography (25 % hexanes in ethyl acetate) to afford **12a** (52 mg, 69 %) as a clear syrup. $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.07 (2H, m), 4.73 (1H, bd, $J$ = 7.8 Hz), 4.64 (1H, d, $J$ = 8.2 Hz), 4.42 (1H, d, $J$ = 8.0 Hz), 4.26 (1H, $\underline{A}$BX, $J_{AB}$ = 12.1 Hz, $J_{AX}$ = 3.5 Hz, $J_{BX}$ = 2.4 Hz, $\nu_a$ = 2131.8, $\nu_b$ = 2055.3), 4.11 (1H, A$\underline{B}$X, as above), 3.99 (1H, t, $J$ = 9.2 Hz), 3.86 (1H, d, $J$ = 9.2 Hz), 3.80 (1H, t, $J$ = 9.9 Hz), 3.79 (3H, s), 3.63 (3H, s), 3.61 (1H, AB$\underline{X}$, $\nu_x$ = 1805.3), 3.52 (1H, dd, $J$ = 10.2, 8.1 Hz), 3.51 (3H, s), 3.27 (3H, s), 3.24 (3H, s), 2.04 (3H, s), 1.99 (3H, s), 1.99 (3H, s), 1.29 (3H, s), 1.25 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.9, 169.6, 102.3, 102.2, 99.8, 99.7, 77.9, 74.8, 73.0, 71.8, 70.6, 69.2, 68.3, 62.1, 57.7, 57.4, 53.0, 52.4, 48.2, 20.8, 20.5, 17.7, 17.6. HRFABMS calculated for $C_{28}H_{43}NO_{18}$ (M+Na) 704.2381, found 704.2378.



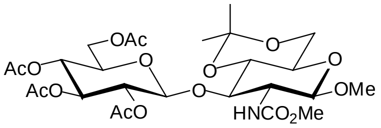
**Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-*β*-D-glucopyranosyl-(1→4)-methyl-(2'R,3'R)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-*β*-D-glucopyranosiduronate (12b).** $MeSiCl_3$ (49 μl, 0.4 mmol) was added to a solution of **12a** (57 mg, 0.08 mmol) and $Et_3N$ (58 μl, 0.4 mmol) in dry THF (10 mL) at 60 °C. After stirring for 7 days, the reaction was quenched with $H_2O$ (30 mL) and extracted with $CH_2Cl_2$ (3x). The aqueous layer was neutralized with saturated $NaHCO_3$, extracted with $CH_2Cl_2$ (3x), dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (1 % $Et_3N$ in ethyl acetate) to afford **12b** (35 mg, 67 %) as a white solid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 4.99 (1H, t, $J$ = 9.6 Hz), 4.90 (1H, t, $J$ = 10.1 Hz), 4.44 (1H, d, $J$ = 8.0 Hz), 4.40 (1H, d, $J$ = 8.1 Hz), 4.26 (1H, $\underline{A}$BX, $J_{AB}$ = 12.3 Hz, $J_{AX}$ = 3.8 Hz, $J_{BX}$ = 2.4 Hz, $\nu_a$ = 2131.3, $\nu_b$ = 2030.8), 4.10 (1H, t, $J$ = 9.2 Hz), 4.06 (1H, A$\underline{B}$X, as above), 3.96 (d, 1H, $J$ = 9.0 Hz), 3.82 (1H, t, $J$ = 9.9 Hz), 3.77 (3H, s), 3.62 (1H, AB$\underline{X}$, $\nu_x$ = 1810.3), 3.56 (1H, dd, $J$ = 10.1, 8.0 Hz), 3.50 (3H, s), 3.29 (3H, s), 3.25 (3H, s), 2.81 (1H, dd, $J$ = 10.2, 8.0 Hz), 2.04 (3H, s), 2.03 (3H, s), 1.99 (3H, s), 1.29 (3H, s), 1.26 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ170.9, 170.0, 168.8, 104.7, 102.1, 99.7, 76.8, 75.3, 75.3, 72.1, 70.9, 69.2, 68.6, 62.3, 57.3, 56.4, 53.0, 48.2, 20.8, 17.7. HRFABMS calculated for $C_{26}H_{41}NO_{16}$ (M+Na) 646.2320, found 646.2323.



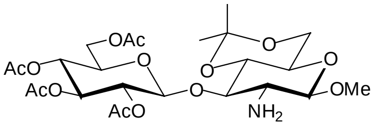
**Methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl-(1→4)-methyl-(2'R,3'R)-2,3-*O*-(2',3'-dimethoxybutane-2',3'-diyl)-*β*-D-glucopyranosiduronate (12c).** Acetic anhydride (38 μl, 0.4 mmol) was added to a solution of **12b** (25 mg, 0.04 mmol) in dry pyridine (1 mL). After stirring at room temperature for 12 hours, the reaction concentrated *in vacuo* and purified by flash chromatography (ethyl acetate) to afford **12c** (28 mg, 100 %) as a white solid. $^1$H NMR ($CDCl_3$, 500 MHz) δ 5.60 (1H, d, $J$ = 9.4 Hz), 5.11 (1H, t, $J$ = 9.8 Hz), 5.05 (1H, t, $J$ = 10.3 Hz), 4.69 (1H, d, $J$ = 8.4 Hz), 4.42 (1H, d, $J$ = 7.9 Hz), 4.28 (1H, $\underline{A}$BX, $J_{AB}$ = 12.2 Hz, $J_{AX}$ = 3.5 Hz, $J_{BX}$ = 2.4 Hz, $\nu_a$ = 2142.3, $\nu_b$ = 2041.3), 4.08 (1H, A$\underline{B}$X, as above), 3.98 (1H, m), 3.95 (1H, m), 3.91 (1H, t, $J$ = 8.4 Hz), 3.81 (1H, dd, $J$ = 10.1, 8.9 Hz), 3.79 (3H, s), 3.62 (1H, AB$\underline{X}$, $\nu_x$ = 1810.3), 3.52 (1H, dd, $J$ = 9.8, 7.9 Hz), 3.51 (3H, s), 3.28 (3H, s), 3.24 (3H, s), 2.04 (3H, s), 2.04 (3H, s), 1.99 (3H, s), 1.99 (3H, s), 1.90 (3H, s), 1.29 (3H, s), 1.25 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.2, 170.9, 170.4, 169.5, 169.4, 102.0, 101.7, 99.8, 99.7, 77.7, 74.6, 73.5, 72.0, 71.0, 69.1, 68.1, 62.1, 57.4, 54.5, 53.0, 48.2, 23.4, 20.8, 17.7, 17.6. mp 176-177 °C HRFABMS calculated for $C_{28}H_{43}NO_{17}$ (M+Na) 688.2426, found 646.2429.



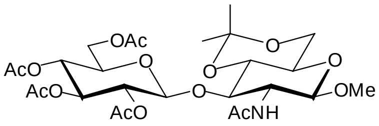
**Methyl 2-deoxy-4,6-*O*-isopropylidene-2-methoxycarbonylamino-*β*-D-glucopyranoside (21).** A catalytic amount of Na° was added to a solution of **8a** (1.36 g, 3.60 mmol) in dry MeOH (20 mL). The reaction was allowed to stir at room temperature under nitrogen for three hours after which Dowex 50W-X8 cation exchange resin to neutralize the reaction mixture. The resin was filtered and the filtrate concentrated *in vacuo* to quantitatively afford the corresponding triol. A catalytic amount of *p*-TsOH• $H_2O$ was added to a solution of the triol (0.903 g, 3.59 mmol), 2,2-dimethoxypropane (1.3 mL, 10.8 mmol) in dry $CH_3CN$ (12 mL). The reaction was stirred at room temperature under nitrogen for 5 hours after which it was neutralized with triethylamine and concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 ethyl acetate:hexanes) to afford **21** (586 mg, 56%) as a light yellow syrup. $^1H$ NMR (500 MHz, $CD_3CN$) $\delta$ 5.62 (1H, bs), 4.29 (1H, d, *J* = 8.4 Hz), 3.83 (1H, dd, *J* = 10.7, 5.4 Hz), 3.74 (1H, t, *J* = 10.4 Hz), 3.60 (3H, s), 3.53 (1H, t, *J* = 8.9 Hz), 3.48-3.42 (2H, m), 3.39 (3H,s), 3.31 (1H, dt, *J* = 9.4, 8.5 Hz), 3.18 (1H, td, *J* = 10.1, 5.5 Hz), 1.47 (3H, s), 1.34 (3H, s). $^{13}C$ NMR (125 MHz, $CD_3CN$) $\delta$ 158.4, 104.1, 100.6, 75.2, 73.3, 68.4, 63.1, 59.7, 57.5, 52.9, 29.8, 19.8. HRFABMS calculated for $C_{12}H_{21}NO_7Na$ (M+Na) 314.1216, found 3141217.



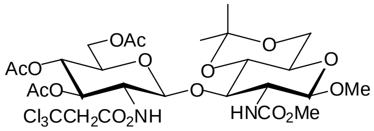
**Methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1→3)-2-deoxy-4,6-*O*-isopropylidene-2-methoxycarbonylamino-*β*-D-glucopyranoside (13a).** A solution of **21** (130 mg, 0.45 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise via cannula to a mixture of **4** (500 mg, 1.0 mmol), 4 Å molecular sieves, and trimethylsilyl trifluoromethanesulfonate (4 µL, 0.02 mmol) in $CH_2Cl_2$ (3 mL) at -30 °C. The reaction was allowed to warm to room temperature over 12 hours, then quenched with $Et_3N$ (10 µl), filtered through Celite®, a concentrated *in vacuo*. The residue was purified by flash chromatography (33 % hexanes in ethyl acetate) to afford **13a** (160 mg, 58 %) as a white foam. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 5.18 (1H, bd, *J* = 7.1 Hz), 5.09 (1H, t, *J* = 9.2 Hz), 5.05 (1H, t, *J* = 9.5 Hz), 4.88 (1H, t, *J* = 8.0 Hz), 4.70 (1H, d, *J* = 7.8 Hz), 4.64 (1H, bs), 4.20 (1H, dd, *J* = 12.3, 4.3 Hz), 4.08 (1H, dd, *J* = 11.8, 2.6 Hz), 3.87 (1H, dd, *J* = 11.1, 5.7 Hz), 3.72 (1H, t, *J* = 10.4 Hz), 3.64 (1H, t, *J* = 9.2 Hz), 3.61 (3H, s), 3.58 (1H, m), 3.41 (3H, s), 3.23 (1H, td, *J* = 9.9, 5.4 Hz), 3.14 (1H, bs), 2.03 (3H, s), 1.97 (3H, s), 1.96 (3H, s), 1.93 (3H, s), 1.45 (3H, s), 1.33 (3H, s). $^{13}C$ NMR ($CDCl_3$, 125 MHz) 170.8, 170.4, 169.5, 156.4, 100.1, 99.4, 73.2, 73.2, 71.9, 71.8, 68.3, 66.6, 62.2, 62.0, 57.6, 57.2, 29.2, 20.8, 20.7, 20.6, 19.1. HRFABMS calculated for $C_{26}H_{39}NO_{16}Na$(M+Na) 644.2169, found 644.2167.



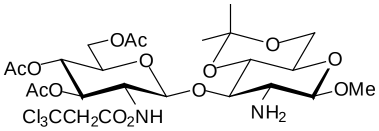
**Methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1→3)-2-amino-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside (13b).** $MeSiCl_3$ (47 µL, 0.40 mmol) was added to a solution of **13a** (50 mg, 0.08 mmol) and $Et_3N$ (56 µL, 0.40 mmol) in dry THF (3.5 mL) at 60 °C. After 17 hours, the reaction was diluted with THF (10 mL), quenched with $H_2O$ (20 mL), and extracted with $CH_2Cl_2$ (3x). The aqueous layer was neutralized with saturated $NaHCO_3$ and extracted with $CH_2Cl_2$ (3x), dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (1 % $Et_3N$ in ethyl acetate) to afford **13b** (34.8 mg, 77 %) as a white foam. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.19 (1H, t, $J$ = 9.5 Hz), 5.09 (1H, t, $J$ = 9.8 Hz), 4.97 (1H, dd, $J$ = 9.6, 8.2 Hz), 4.81 (1H, d, $J$ = 8.2 Hz), 4.26 (1H, dd, $J$ = 12.4, 4.2 Hz), 4.14 (1H, d, $J$ = 7.9 Hz), 4.09 (1H, dd, $J$ = 12.3, 2.5 Hz), 3.91 (1H, dd, $J$ = 10.8, 5.3 Hz), 3.79 (1H, t, $J$ = 10.6 Hz), 3.76 (1H, t, $J$ = 9.2 Hz), 3.62 (1H, ddd, $J$ = 10.0, 4.2, 2.5 Hz), 3.51 (1H, t, $J$ = 9.2 Hz), 3.49 (3H, s), 3.23 (1H, td, $J$ = 10.1, 5.4 Hz), 2.86 (1H, dd, $J$ = 9.4, 7.9 Hz), 2.08 (3H, s), 2.07 (3H, s), 2.00 (3H, s), 1.99 (3H, s), 1.51 (3H, s), 1.38 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 170.9, 170.5, 170.2, 105.1, 100.9, 99.6, 83.0, 73.5, 72.9, 72.3, 72.2, 68.4, 67.4, 62.3, 62.2, 57.5, 56.6, 29.4, 21.1, 20.8, 14.4. HRFABMS calculated for $C_{24}H_{37}NO_{14}Na$ (M+Na) 586.2112, found 586.2115.



**Methyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside (13c).** Acetic anhydride (109 µl, 1.06mmol) was added to a solution **13b** (30 mg, 0.053mmol) in dry pyridine (1 mL). After stirring at room temperature for 4 hours, the reaction was concentrated *in vacuo* and purified by flash chromatography (ethyl acetate) to afford **13c** (30.8 mg, 96 %) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.92 (1H, d, $J$ = 7.0 Hz), 5.15 (1H, t, $J$ = 9.5 Hz), 5.08 (1H, t, $J$ = 9.7 Hz), 5.01 (1H, d, $J$ = 8.2 Hz), 4.93 (1H, t, $J$ = 8.0 Hz), 4.89 (1H, d, $J$ = 7.8 Hz), 4.49 (1H, t, $J$ = 9.3 Hz), 4.23 (1H, $\underline{A}BX$, $J_{AB}$ = 12.3 Hz, $J_{AX}$ = 4.7 Hz, $J_{BX}$ = 2.5 Hz, $\nu_a$ = 2116.8, $\nu_b$ = 2072.8), 4.15 (1H, $A\underline{B}X$, as above), 3.92 (1H, dd, $J$ = 10.9, 5.3 Hz), 3.76 (1H, t, $J$ = 10.7 Hz), 3.70 (1H, t, $J$ = 9.3 Hz), 3.63 (1H, $AB\underline{X}$, $\nu_x$ = 1815.5), 3.46 (3H, s), 3.35 (1H, td, $J$ = 10.3, 5.6 Hz), 3.03 (1H, m), 2.07 (3H, s), 2.05 (3H, s), 2.01 (3H, s), 1.99 (3H, s), 1.97 (3H, s), 1.50 (3H, s), 1.39 (3H, s); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 171.0, 170.9, 170.5, 169.8, 169.6, 100.5, 99.5, 99.2, 76.6, 73.7, 73.2, 72.2, 72.1, 68.5, 66.6, 62.6, 62.3, 58.4, 57.4, 29.4, 21.0, 21.0, 20.8, 19.2. mp 201-202 °C HRFABMS calculated for $C_{26}H_{39}NO_{15}Na$ (M+Na) 628.2217, found 628.2217.

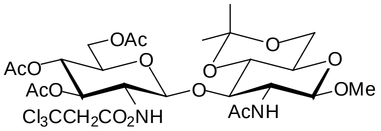


**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-glucopyranosyl-(1→3)-2-deoxy-4,6-*O*-isopropylidene-2-methoxycarbonylamino-*β*-D-glucopyranoside (14a).** TMSOTf (10 µL, 0.061 mmol) was added to a solution of **6**[7] (763 mg, 1.22 mmol) and 4 Å molecular sieves (700 mg) in dry $CH_2Cl_2$ (1.5 mL) at –30 °C under Argon. After 10 minutes a solution of **21** (113 mg, 0.386 mmol) in (1 mL) was added dropwise via cannula. The flask containing **21** was rinsed with an additional 1 mL of dry $CH_2Cl_2$ and cannulated into the reaction mixture. The reaction was stirred for 30 minutes and allowed to warm to room temperature. After 2 hours, triethylamine was added and the reaction filtered through Celite® and concentrated *in vacuo*. The residue was purified by flash chromatography to afford **14a** (280 mg, 96%) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.9 (1H, d, $J$ = 9.5 Hz), 5.50 (1H, bs), 5.15 (1H, t, $J$ = 9.8 Hz), 5.00 (1H, $AB_q$, $J_{AB}$ = 12.5 Hz, $\nu_a$ = 2486.5, $\nu_b$ = 2475.6), 4.94 (1H, $AB_q$, $J_{AB}$ = 12.5 Hz, $\nu_a$ = 2486.5, $\nu_b$ = 2475.6), 4.80 (1H, d, $J$ = 8.6 Hz), 4.50 (1H, d, $J$ = 12.5 Hz), 4.33 (1H, d, $J$ = 8.5 Hz), 4.20 (1H, dd, $J$ = 12.3, 4.2 Hz), 4.06 (1H, dd, $J$ = 12.6, 2.6 Hz), 3.83 (1H, dd, $J$ = 10.7, 5.5 Hz), 3.74 (1H, t, $J$ = 10.5 Hz), 3.73-3.66 (3H, m), 3.59 (3H, s), 3.50 (1H, m), 3.42 (1H, m), 3.73 (3H, s), 3.19 (1H, td, $J$ = 9.8, 5.2 Hz), 2.01 (3H, s), 1.94 (3H, s), 1.88 (3H, s), 1.49 (3H,s), 1.34 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.8, 170.9, 158.0, 155.6, 103.9, 101.3, 100.6, 96.1, 75.2, 74.4, 73.6, 72.9, 70.0, 67.9, 63.5, 62.9, 57.7, 56.6, 52.9, 30.0, 21.4, 21.3, 21.2. HRFABMS calculated for $C_{27}H_{39}Cl_3N_2O_{16}Na$ (M+Na) 775.1263, found, 775.1260.

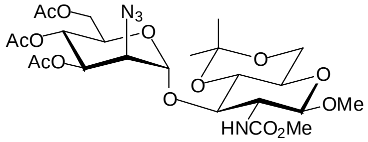


**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-glucopyranosyl-(1→3)-2-amino-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside (14b).** $MeSiCl_3$ (53 µl, 0.45 mmol) was added to a solution of **14a** (67.5 mg, 0.090 mmol) and $Et_3N$ (62 µl, 0.45 mmol) in dry THF (4.5 mL) at 60 °C. After 48 hours, the reaction was diluted with THF (10 mL), quenched with $H_2O$ (10 mL), and extracted with $CH_2Cl_2$ (3x). The aqueous layer was neutralized with saturated $NaHCO_3$ and extracted with $CH_2Cl_2$ (3x), dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography (4:1 ethyl acetate:hexanes, 1 % $Et_3N$) to afford **14b** ( 44 mg, 70 %) as a transparent syrup. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.94 (1H, t, $J$ = 7.3 Hz), 5.30 (1H, t, $J$ = 8.7 Hz), 5.08 (1H, t, $J$ = 9.8 Hz), 4.84 (1H, $AB_q$, $J_{AB}$ = 13.0 Hz, $\nu_a$ = 2362.3, $\nu_b$ = 2349.8), 4.83 (1H, d, $J$ = 8.2 Hz), 4.58 (1H, $AB_q$, $J_{AB}$ = 13.0 Hz, $\nu_a$ = 2362.3, $\nu_b$ = 2349.8), 4.28 (1H, dd, $J$ = 12.3, 4.7 Hz), 4.14 (1H, d, $J$ = 8.2 Hz), 4.12 (1H, dd, $J$ = 12.9, 2.6 Hz), 3.93 (1H, dd, $J$ = 11.0, 5.4 Hz), 3.80 (1H, t, $J$ = 10.6 Hz), 3.74 (1H, t, $J$ = 9.3 Hz), 3.69-3.64 (2H, m), 3.55 (1H, t, $J$ = 9.3 Hz), 3.51 (3H, s), 3.24 (1H, dt, $J$ = 10.1, 5.4 Hz), 2.83 ( 1H, dd, $J$ = 9.4, 8.2 Hz), 2.08 (3H, s), 2.03 (3H, s), 2.02

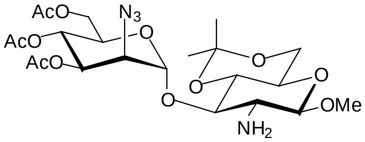
(3H, s), 1.53 (3H, s), 1.41 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.8, 169.6, 105.5, 100.9, 99.8, 82.2, 74.6, 73.0, 72.4, 72.3, 68.7, 67.4, 62.4, 62.2, 57.5, 57.3, 56.7, 29.3, 20.9, 20.8. HRFABMS calculated for $C_{25}H_{37}Cl_3N_2O_{14}Na$ (M+Na) 717.1208, found, 717.1206.



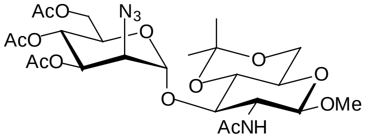
**Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-*β*-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside (14c).** Acetic anhydride (12 mL, 0.126 mmol) was added to a solution of **14b** (44 mg, 0.063 mmol) in 1:1 dry pyridine:$CH_2Cl_2$ (1 mL) at room temperature. After 4 hours the reaction was quenched with MeOH and concentrated *in vacuo*. The residue was purified by flash chromatography (2:1 ethyl acteate:hexanes) to afford **14c** (45 mg, 96%) as a transparent syrup. $^1$H NMR (500 MHz, $CDCl_3$) δ 6.00 (1H, bd, *J* = 6.6 Hz), 5.62 (1H, bd, *J* = 6.5 Hz), 5.54 (1H, bt, *J* = 9.6 Hz), 5.05 (1H, t, *J* = 10.0 Hz), 4.98 (1H, bd, *J* = 7.8 Hz), 4.76-4.66 (2H, m), 4.29 (1H, $AB_q$, $J_{AB}$ = 13.0 Hz, $\nu_a$ = 2140.5, $\nu_b$ = 2091.6), 4.19 (1H, m), 4.29 (1H, $AB_q$, $J_{AB}$ = 13.0 Hz, $\nu_a$ = 2140.5, $\nu_b$ = 2091.6), 3.94 (1H, dd, *J* = 10.9, 5.4 Hz), 3.79 (1H, t, *J* = 10.8 Hz), 3.71 (1H, bt, *J* = 8.5 Hz), 3.47 (3H, s), 3.34-3.37 (2H, m), 3.32 (1H, dt, *J* = 10.1, 5.6 Hz), 2.11 (3H, s), 2.03 (3H, s), 2.02 (3H, s), 1.99 (3H, s), 1.53 (3H, s), 1.41 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.1, 170.5, 169.8, 154.2, 101.8, 99.9, 98.6, 76.2, 74.6, 73.1, 72.4, 71.6, 68.8, 67.0, 62.3, 57.3, 57.2, 56.3, 29.2, 21.1, 20.9. HRFABMS calculated for $C_{27}H_{39}Cl_3N_2O_{15}Na$ (M+Na) 759.1314, found 759.1315.



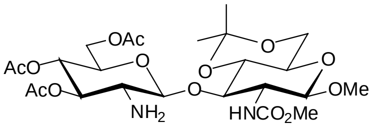
**Methyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-mannopyranosyl-(1→3)-2-deoxy-4,6-*O*-isopropylidene-2-methoxycarbonylamino-*β*-D-glucopyranoside (15a).** A solution of **21** (129 mg, 0.44 mmol) in dry $CH_2Cl_2$ (2 mL) was added dropwise via cannula to a flask containing TMSOTf (5 μL, 0.03 mmol), **7** (250 mg, 0.53 mmol), and 4 Å molecular sieves in dry $CH_2Cl_2$ (3 mL) at -30 °C. After 16 hours at room temperature, the reaction was quenched with $Et_3N$ (10 μl), filtered through a Celite® and concentrated *in vacuo*. The residue was purified by flash chromatography (1:1 ethyl acetate:hexanes) to afford **15a** (80 mg, 30 %) as a clear syrup. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.28 (1H, t, *J* = 9.8 Hz), 5.24 (1H, d, *J* = 3.6 Hz), 5.22 (1H, m), 5.14 (1H, bd, *J* = 7.3 Hz), 4.20 (1H, dd, *J* = 12.4, 3.6 Hz), 4.01 (1H, m), 3.95 (1H, dt, *J* = 9.4, 3.0 Hz), 3.91 (1H, dd, *J* = 10.9, 5.3 Hz), 3.76 (1H, t, *J* = 10.6 Hz), 3.66 (3H, s), 3.65 (1H, t, *J* = 9.3 Hz), 3.46 (3H, s), 3.83 (1H, q, *J* = 9.0 Hz), 3.25 (1H, td, *J* = 10.0, 5.5 Hz), 2.08 (3H, s), 2.06 (3H, s), 2.00 (3H, s), 1.47 (3H, s), 1.35 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.2, 170.1, 169.6, 156.5, 99.7, 98.9, 77.5, 75.0, 70.8, 68.8, 66.6, 66.0, 62.3, 62.1, 61.8, 57.3, 56.9, 52.5, 29.2, 20.9, 20.8, 20.7, 19.3. $^1$H NMR (500 MHz, $CD_3CN$) δ 5.81 (1H, d, $J$ = 9.8 Hz), 5.19 (3H, m), 4.38 (1H, d, $J$ = 8.1 Hz), 4.14 (1H, $\underline{A}$BX, $J_{AB}$ = 12.4 Hz, $J_{AX}$ = 3.5 Hz, $J_{BX}$ = 2.2 Hz, $\nu_a$ = 2068.8, $\nu_b$ = 2033.3), 4.13 (1H, m), 4.07 (1H, A$\underline{B}$X, as above), 3.89 (1H, AB$\underline{X}$, $\nu_x$ = 1945.1), 3.86 (1H, dd, $J$ = 10.9, 5.7 Hz), 3.77 (1H, t, $J$ = 9.2 Hz), 3.76 (1H, t, $J$ = 10.6 Hz), 3.70 (1H, t, $J$ = 9.8 Hz), 3.60 (3H, s), 3.47 (1H, q, $J$ = 9.2 Hz), 3.41 (3H, s), 3.25 (1H, td, $J$ = 10.0, 5.7 Hz), 2.03 (3H, s), 2.02 (3H, s), 1.98 (3H, s), 1.50 (3H, s), 1.34 (3H, s). $^{13}$C NMR ($CD_3CN$, 125 MHz) δ 171.8, 171.1, 171.0, 158.1, 103.7, 100.7, 99.2, 78.3, 76.2, 71.6, 69.9, 67.7, 66.6, 63.0, 62.8, 62.8, 57.7, 57.4, 53.1, 29.8, 21.3, 21.2, 19.9. HRFABMS calculated for $C_{24}H_{36}N_4O_{14}$ (M+), found.



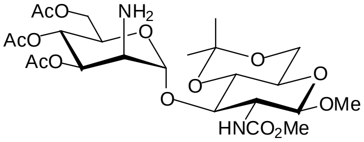
**Methyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-mannopyranosyl-(1→3)-2-amino-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside (15b).** $MeSiCl_3$ (35 μl, 0.30 mmol) was added to a solution of **15a** (36 mg, 0.06 mmol) and $Et_3N$ (42 μl, 0.30 mmol) in dry THF (3 mL). The reaction was capped and heated to 60 °C. After stirring for 50 hours, the reaction was diluted with THF (20 mL), quenched with $H_2O$ (10 mL) and extracted with $CH_2Cl_2$ (3x). The aqueous layer was neutralized with saturated $NaHCO_3$ and extracted with $CH_2Cl_2$ (3x), dried over $Na_2SO_4$, and concentrated *in vac*uo. The residue was purified by flash chromatography (ethyl acetate, 1 % $Et_3N$) to afford **15b** (26 mg, 81 %) as a transparent syrup. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.33 (1H, dd, $J$ = 9.8, 3.6 Hz), 5.27 (1H, t, $J$ = 9.6 Hz), 5.25 (1H, d, $J$ = 1.9 Hz), 4.26 (1H, dd, $J$ = 5.0, 1.9 Hz), 4.23 (1H, dd, $J$ = 11.8, 4.8 Hz), 4.13 (1H, d, $J$ = 7.9 Hz), 4.08 (1H, m), 4.04 (1H, dd, $J$ = 3.9, 2.0 Hz), 3.92 (1H, dd, $J$ = 10.9, 5.6 Hz), 3.78 (1H, t, $J$ = 10.6 Hz), 3.66 (1H, t, $J$ = 9.3 Hz), 3.54 (1H, t, $J$ = 9.4 Hz), 3.52 (3H, s), 3.25 (1H, td, $J$ = 10.1, 5.3 Hz), 2.78 (1H, dd, $J$ = 9.6, 7.9 Hz), 2.09 (3H, s), 2.08 (3H, s), 2.03 (3H, s), 1.49 (3H, s), 1.37 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.9, 170.3, 169.7, 105.9, 99.8, 99.1, 81.1, 74.6, 70.8, 69.2, 67.2, 66.1, 62.5, 62.2, 62.0, 57.6, 56.8, 29.3, 21.0, 20.9, 20.8, 19.4. HRFABMS calculated for $C_{22}H_{34}N_4O_{12}Na$ (M+Na) 569.2071, found 569.2071.



**Methyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-D-mannopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranoside (15c).** Acetic anhydride (43 μl, 0.46 mmol) was added to a solution of **15b** (25 mg, 0.046mmol) in dry pyridine (2 mL). After stirring at room temperature for 18 hours, the reaction was concentrated *in vacuo* and purified by flash chromatography (ethyl acetate) to afford **15c** (27 mg, 100 %) as a white solid. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.89 (1H, d, *J* = 8.4 Hz), 5.27 (2H, m), 5.23 (1H, d, *J* = 1.6 Hz), 4.66 (1H, d, *J* = 8.4 Hz), 4.25 (1H, dd, *J* = 12.1, 4.2 Hz), 4.10 (1H, t, *J* = 9.6 Hz), 4.06 (1H, dd, *J* = 4.2, 2.4 Hz), 4.02 (1H, m), 3.93 (1H, dd, *J* = 11.0, 5.6 Hz), 3.78 (1H, t, *J* = 10.5 Hz), 3.66 (1H, t, *J* = 9.4 Hz), 3.50 (1H, m), 3.47 (3H, s), 3.31 (1H, td, *J* = 10.0, 5.2 Hz), 2.11 (3H, s), 2.08 (3H, s), 2.03 (3H, s), 1.99 (3H, s), 1.50 (3H, s), 1.38 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 170.5, 169.7, 101.8, 99.8, 98.9, 77.2, 77.0, 75.2, 70.8, 68.7, 66.7, 62.8, 61.8, 57.2, 56.3, 29.3, 23.6, 21.1, 20.9, 20.8, 20.6. mp 159-161 °C. HRFABMS calculated for $C_{24}H_{36}N_4O_{13}Na$ (M+Na) 611.2177, found 611.2179.



**Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-*β*-D-glucopyranosyl-(1→3)-2-deoxy-4,6-*O*-isopropylidene-2-methoxycarbonylamino-*β*-D-glucopyranoside (16b).** Freshly activated zinc dust (400 mg) was added to a solution of **14a** in acetic acid (5 mL) and the reaction was allowed to stir at room temperature. After 4 hours the reaction was filtered through Celite® and rinsed with toluene (20 mL) then concentrated. The filtrate was azeotroped with toluene (2 x 25 mL) and concentrated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate) to afford **16b** (56 mg, 61%) as a white foam. $^1$H NMR (500 MHz, $CD_3CN$) δ 5.78 (1H, bs), 4.89 (2H, m), 4.41 (1H, d, *J* = 8.0 Hz), 4.37 (1H, d, *J* = 8.5 Hz), 4.18 (1H, dd, *J* = 12.3, 4.2 Hz), 4.06 (1H, dd, *J* = 12.0, 2.4 Hz), 3.84 (1H, dd, *J* = 10.8, 5.4 Hz), 3.78 (1H, t, *J* = 9.4 Hz), 3.75 (1H, t, *J* = 10.3 Hz), 3.70 (1H, t, *J* = 9.5 Hz), 3.68 (1H, m), 3.57 (3H, s), 3.43 (1H, dt, *J* = 9.2, 8.5 Hz), 3.40 (3H, s), 3.21 (1H, td, *J* = 10.1, 5.4 Hz), 2.73 (1H, m), 2.01 (3H, s), 1.98 (3H, s), 1.95 (3H, s), 1.47 (3H, s), 1.33 (1H, s). $^{13}$C NMR ($CD_3CN$, 125 MHz) δ 171.8, 171.7, 171.0, 158.2, 104.3, 104.2, 100.6, 79.9, 76.3, 73.7, 72.9, 70.1, 68.2, 63.6, 63.0, 58.2, 57.6, 57.5, 52.9, 29.8, 21.4, 21.3. HRFABMS calculated for $C_{24}H_{38}N_2O_{14}Na$ (M+Na) 601.2221, found 601.2218.



**Methyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-*α*-D-mannopyranosyl-(1→3)-2-deoxy-4,6-*O*-isopropylidene-2-methoxycarbonylamino-*β*-D-glucopyranoside (17b).** A catalytic amount of Raney nickel (50 % slurry in $H_2O$) was added to a solution of **15a** (31 mg, 0.051 mmol) in MeOH (2 mL) and ethyl acetate (0.5 mL). The reaction mixture was stirred vigorously at room temperature, under a $H_2$ atmosphere of 56 psi. After 4 hours, the reaction mixture was filtered through Celite® and concentrated *in vacuo* to afford the amine (29 mg, 100 %) as a white foam. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.27 (1H, t, *J* = 9.9 Hz), 5.18 (1H, dd, *J* = 9.9, 3.9 Hz), 5.12 (1H, bs), 4.21 (1H, dd, *J* = 12.7, 3. 9 Hz), 4.02 (2H, m), 3.92 (1H, dd, *J* = 11.2, 5.8 Hz), 3.77 (1H, t, *J* = 10.5 Hz), 3.68 (3H, s), 3.66 (1H, t, *J* = 9.4 Hz), 3.48 (3H, s), 3.36 (1H, m), 3.33 (1H, dd, *J* = 3.6, 1.5 Hz), 3.28 (1H, td, *J* = 9.7, 5.1 Hz), 2.09 (3H, s), 2.05 (3H, s), 2.00 (3H, s), 1.46 (3H, s), 1.36 (3H, s). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 171.2, 170.0, 168.7, 105.7, 99.6, 75.1, 71.8, 68.5, 68.2, 66.7, 66.4, 62.7, 62.2, 57.4, 57.2, 53.2, 29.2, 21.1, 21.0, 20.9, 19.3. HRFABMS calculated for $C_{24}H_{38}N_2O_{14}Na$ (M+Na) 601.2221, found 601.2215.

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(2) Lemieux, R.U.; Ratcliffe, R.M. *Can. J. Chem.* **1979**, *57*, 1244.
(3) Ziegler, T.; Eckhardt, E.; Birault, V. *J. Org. Chem.* **1993**, *58*, 1090.
(4) Johansson, R.; Samuelsson, B. *J. Chem. Soc. Perkin Trans. I* **1984**, 2371.
(5) Montchamp, J.-L; Tian, F.; Hart, M. E.; Frost, J. W. *J. Org. Chem.* **1996**, *61*, 3897.
(6) Garegg, P. J.; Oscarson, S.; Tedebark, U. *J. Carbohydr. Chem.* **1998**, *17*, 587.
(7) Dullenkopf, W.; Castro-Palomino, J. C.; Manzoni, L.; Schmidt, R. R. *Carbohydr. Res.* **1996**, *296*, 135.