Oxazolidinone Protection of *N*-Acetyl Glucosamine Confers High Reactivity on 4-hydroxy Group in Glycosylation

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General

All solvents were dried and distilled by standard methods. All reactions were carried out under an argon atmosphere unless otherwise stated. All NMR spectra were recorded at either 300 MHz or 500 MHz with CDCl₃ as solvent. Mass spectra were recorded by the Research Resources Center at the University of Illinois at Chicago. Normal phase flash chromatography following the method of Still and co-workers¹ or radial chromatography (Chromatotron[®]) was employed through out. All compounds were >95% pure as judged by ¹H and ¹³C-NMR.

Methyl 2-amino-4,6-*O*-benzylidene-2-deoxy- α -D-glucopyranoside (6)

Methyl 4,6-*O*-benzylidene-2-deoxy-2-methoxycarbonylamido- α -D-glucopyranoside² (10 g, 29.5 mmol, 1 eq) was added to a 30% KOH solution (40 mL) in 1,4-dioxane:methoxyethanol (25:15 mL v/v) and the mixture was refluxed at 120 °C for 18 h. The reaction mixture was cooled and neutralized with 2N HCl until slightly basic to avoid amine hydrochloride formation. The solvents were removed under vacuum and the residue obtained was dissolved in water and extracted with chloroform. The combined extracts were washed thoroughly with water, and brine, and dried and concentrated to give yellowish white solid which on recrystallization from CHCl₃-Hexane afforded the amine **6** as a white solid (6.87 g, 83 %).²

Methyl 2-amino-4,6-*O*-benzylidene-2-*N*,3-*O*-carbonyl-2-deoxy- α -D-glucopyranoside (7)

Amine **6** (4 g, 14.2 mmol, 1 eq) and NaHCO₃ (5.97 g, 71.1 mmol, 5 eq) were dissolved in 40:20 mL v/v H₂O:CH₃CN mixture and cooled to 0 °C. To this vigorously stirred mixture, *p*-nitrophenyl chloroformate (7.16 g, 35.5 mmol, 2.5 eq) in 15 mL of CH₃CN was added slowly from a dropping funnel after which the stirring was continued at 0 °C for 3h. The resulting aqueous mixture was extracted with ethyl acetate and the combined extracts were washed with water, and brine, and dried and concentrated. The ¹H NMR spectrum of the extracts showed a mixture of the desired oxazolidinone and the uncyclized compound. This mixture was then taken in of dry DMF (30 mL) and Amberlite IR-120NA ion exchange resin (15 g) was added and the mixture was left stirring at room temperature overnight. After completion of the reaction, the resins were filtered off, and the reaction mixture was concentrated and purified by column chromatography on silica-gel with 80:20 hexane-ethyl acetate as eluent affording **7** as a

white crystalline solid (3.32 g, 76%). $[\alpha]_D^{27} +194.6$ (c , 0.65, CHCl_3); Mp 198 °C; ^1H NMR δ 3.47 (s, 3H), 3.69 (dd, 1H, $J = 11.4, 2.7$ Hz), 3.77-3.90 (m, 2H), 4.03 (t, 1H, $J = 8.7$ Hz), 4.26 (d, 1H, $J = 5.7$ Hz), 4.75 (t, 1H, $J = 10.5$ Hz), 4.98 (d, 1H, $J = 2.4$ Hz), 5.58 (s, 1H), 6.04 (br s, 1H), 7.35-7.37 (m, 3H), 7.47-7.49 (m, 2H); ^{13}C NMR δ 55.9, 59.6, 65.3, 68.7, 75.7, 80.1, 97.5, 101.5, 126.3, 128.4, 129.4, 136.7, 160.0; IR (film, cm^{-1}) ν : 3306, 1764.

Methyl 2-acetamido-4,6-*O*-benzylidene-2-*N*,3-*O*-carbonyl-2-deoxy- α -D-glucopyranoside (8)

Oxazolidinone **7** (3 g, 9.76 mmol, 1 eq) and Hunig's base (6.30 g; 8.5 mL, 48.8 mmol, 5 eq) were taken up in a 100 mL flask under argon atmosphere and 40 mL of CH_2Cl_2 was added followed by acetyl chloride (3.83 g; 3.47 mL, 48.8 mmol, 5 eq). The resulting solution was stirred for 6h and then poured in to saturated aqueous NaHCO_3 . The organic layer was separated and the aqueous layer extracted twice with CH_2Cl_2 and the combined extracts were washed with water, and brine, and concentrated. Short column chromatography on silica gel eluting with 80:20 ethyl acetate-hexane afforded the product **8** as a white crystalline solid (3.12 g, 92 %). $[\alpha]_D^{27} +102.5$ (c , 0.75, CHCl_3); Mp 185 °C; ^1H NMR δ 2.49 (s, 3H), 3.44 (s, 3H), 3.79-3.91 (m, 3H), 4.01 (t, 1H, $J = 9.9$ Hz), 4.28 (dd, 1H, $J = 6.3, 2.4$ Hz), 4.71 (t, 1H, $J = 11.7$ Hz), 5.59 (s, 1H), 5.60 (d, 1H, $J = 3.9$ Hz), 7.35-7.40 (m, 3H), 7.45-7.50 (m, 2H); ^{13}C NMR δ 24.0, 56.1, 61.0, 65.2, 68.6, 73.7, 79.7, 97.8, 101.5, 126.2, 128.4, 129.4, 136.6, 153.0, 171.4; IR (film, cm^{-1}) ν : 1806, 1703; ESIHRMS Calcd. For $\text{C}_{17}\text{H}_{19}\text{NO}_7$ $[\text{M}+\text{Na}]^+$: 372.1059. Found 372.1050.

Methyl 2-acetamido-6-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy- α -D-glucopyranoside (9)

2N HCl in ether (~30 mL) was carefully added at 0 °C to a well stirred mixture of **8** (3g, 8.58 mmol, 1eq), sodium cyanoborohydride (6.47 g, 103.0 mmol, 12 eq) and a crystal of methyl orange in THF, under argon, until the color of the indicator turned red and evolution of gas occurred. The reaction mixture was stirred at 0 °C for 1.5 h, and was monitored by ^1H NMR spectroscopy with aliquots of crude reaction mixture. After completion of the reaction, the mixture was diluted with CH_2Cl_2 and poured in to aqueous saturated NaHCO_3 . The organic phase was separated, washed thoroughly with water, and brine, then dried and evaporated. Column chromatography (40:60 ethyl acetate-hexane) on silica-gel afforded the title alcohol **9** as a highly viscous liquid (2.40

g, 80 %). $[\alpha]_D^{27} +116.1$ (*c*, 1.5, CHCl_3); ^1H NMR δ 2.46 (s, 3H), 3.41 (s, 3H), 3.46 (br s, 1H), 3.66-3.71 (m, 3H), 3.79-3.82 (m, 1H), 4.04 (t, 1H, $J = 9.6$ Hz), 4.53 (dd, 1H, $J = 12.0, 9.9$ Hz), 4.55 (d, 1H, $J = 12.0$ Hz), 4.62 (d, 1H, $J = 12.0$ Hz), 7.25-7.36 (m, 5H); ^{13}C NMR δ 24.2, 56.3, 60.1, 69.5, 70.1, 72.8, 74.1, 77.2, 97.2, 128.1, 128.3, 128.9, 137.9, 153.8, 171.8. IR (film, cm^{-1}) ν : 3454, 1796, 1710; ESIHRMS Calcd. For $\text{C}_{17}\text{H}_{21}\text{NO}_7$ $[\text{M}+\text{Na}]^+$: 374.1216. Found 374.1206.

General Protocol for Disaccharide Formation using BSP/Tf₂O

To a stirred solution of thioglycoside (0.138 mmol, 1 eq), 1-benzenesulfinyl piperidine (BSP) (0.138 mmol, 1 eq), TTBP (0.277 mmol, 2 eq) and activated, powdered 3Å molecular sieves in CH_2Cl_2 (7 mL) at -60°C , under argon atmosphere, was added Tf_2O . After 10 min, a solution of glycosyl acceptor **9** (0.180 mmol, 1.3 eq) in CH_2Cl_2 (3 mL) was added. The reaction mixture was stirred for 1h at -60°C and then warmed to room temperature, filtered, washed with saturated aqueous NaHCO_3 , followed by brine, dried and concentrated. The glycosides were purified either by flash chromatography or radial chromatography (Chromatotron®) on silica gel.

General procedure for the cleavage of oxazolidinones.

The glycosides (0.038 mmol, 1 eq) were taken in 4 mL of ethanol and 2mL of 50 % $\text{Ba}(\text{OH})_2$ solution was added and the reaction mixture was stirred at 70°C for 6h, after which it was cooled to 0°C and 0.2 mL of Ac_2O was added. The mixture was gradually warmed to room temperature and stirred for an additional 4h, then extracted with CH_2Cl_2 , and the combined extracts were washed with water, brine and dried. Radial chromatography of the residue provided the acetamides.

Methyl 2-acetamido-6-*O*-benzyl-2-*N*, 3-*O*-carbonyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranosyl]-(1→4)- α -D-glucopyranoside (**11a**)

Viscous oil, $[\alpha]_D^{27} +76.5$ (*c*, 1.8, CHCl_3); ^1H NMR δ 2.51 (s, 3H), 3.42 (s, 3H), 3.65-3.85 (m, 8H), 4.13 (dd 1H, $J = 9.4, 3.9$ Hz), 4.25-4.34 (m, 2H), 4.51-4.66 (m, 4H), 4.77-4.81 (m, 3H), 5.27 (s, 1H), 5.58 (d, 1H, $J = 3.3$ Hz), 5.65 (s, 1H), 7.25-7.44 (m, 18H), 7.50-7.53 (m, 2H); ^{13}C NMR δ 24.0, 56.1, 59.8, 65.3, 68.0, 68.6, 71.3, 71.9, 73.1, 73.47, 73.8, 75.7, 76.0, 77.3, 78.9, 96.8, 98.4, 101.5, 126.2, 127.62, 127.67, 127.8, 128.0, 128.31, 128.37, 128.4, 128.5, 128.6, 128.9, 137.81, 137.84, 138.6, 153.0, 171.3; IR (film, cm^{-1}) ν : 1796, 1713; ESIHRMS Calcd. For $\text{C}_{44}\text{H}_{47}\text{NO}_{12}$ $[\text{M}+\text{Na}]^+$: 804.2996. Found 804.3021.

Methyl 2-acetamido-6-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (11 β)

Viscous oil. $[\alpha]_D^{27} +42.9$ (*c*, 3.65, CHCl_3); ^1H NMR δ 2.49 (s, 3H), 3.28-3.39 (m, 1H), 3.44 (s, 3H), 3.51 (dd, 1H, $J = 10.2, 3.3$ Hz), 3.58-3.62 (m, 4H), 3.73 (dd, 1H, $J = 13.5, 2.4$ Hz), 3.92 (t, 1H, $J = 10.2$ Hz), 4.11-4.22 (m, 2H), 4.35-4.39 (m, 2H), 4.63 (d, 1H, $J = 4.5$ Hz), 4.67 (d, 1H, $J = 3.6$ Hz), 4.71-4.73 (m, 3H), 4.79 (d, 1H, $J = 3.6$ Hz), 5.61 (s, 1H), 5.62 (s, 1H), 7.19-7.54 (m, 20H); ^{13}C NMR δ 24.0, 56.0, 60.0, 67.3, 67.5, 68.6, 71.9, 72.8, 73.6, 74.9, 75.5, 75.7, 76.4, 78.2, 78.7, 96.7, 100.9, 101.5, 126.2, 127.70, 127.75, 127.8, 128.21, 128.23, 128.3, 128.5, 128.6, 128.7, 129.0, 137.7, 137.8, 138.4, 138.5, 153.1, 171.5; IR (film, cm^{-1}) ν : 1794, 1710; ESIHRMS Calcd. For $\text{C}_{44}\text{H}_{47}\text{NO}_{12}$ $[\text{M}+\text{Na}]^+$: 804.2996. Found 804.3017.

Methyl 2-acetamido-6-*O*-benzyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-mannopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (12)

Viscous oil. $[\alpha]_D^{27} +23.5$ (*c*, 0.95, CHCl_3); ^1H NMR δ 2.04 (s, 3H), 3.24-3.32 (m, 2H), 3.38 (s, 3H), 3.40-3.47 (m, 3H), 3.53-3.56 (m, 1H), 3.60-3.74 (m, 3H), 3.84 (t, 1H, $J = 10.2$ Hz), 3.98 (br s, 1H), 4.12-4.18 (m, 2H), 4.22 (s, 1H), 4.27-4.33 (m, 2H), 4.63 (t, 1H, $J = 12.3$ Hz), 4.75-4.84 (m, 4H), 5.57 (s, 1H), 5.61 (d, 1H, $J = 7.6$ Hz), 7.18-7.14 (m, 18H), 7.46-7.48 (m, 2H); ^{13}C NMR δ 23.6, 53.0, 55.5, 67.5, 67.8, 68.2, 69.2, 70.5, 73.2, 73.5, 75.0, 76.1, 78.4, 78.5, 82.0, 98.5, 101.5, 102.6, 126.1, 127.5, 127.8, 128.1, 128.2, 128.3, 128.5, 128.6, 128.9, 129.1, 137.3, 137.9, 138.1, 138.5, 170.3; IR (film, cm^{-1}) ν : 3443, 3324, 1667; ESIHRMS Calcd. For $\text{C}_{43}\text{H}_{49}\text{NO}_{11}$ $[\text{M}+\text{Na}]^+$: 778.3203. Found 778.3206.

Methyl 2-acetamido-6-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (14)

Viscous oil. $[\alpha]_D^{27} +70.2$ (*c*, 2.65, CHCl_3); ^1H NMR δ 2.54 (s, 3H), 3.43 (s, 3H), 3.60-4.01 (m, 11H), 4.12 (dd, 1H, $J = 10.0, 4.8$ Hz), 4.46 (t, 1H, $J = 9.6$), 4.60 (d, 1H, $J = 11.7$ Hz), 4.69 (d, 1H, $J = 11.7$), 4.76 (dd, 1H, $J = 12.0, 9.9$ Hz), 4.82-4.87 (m, 4H), 4.94 (d, 1H, $J = 10.8$ Hz), 5.39 (d, 1H, $J = 3.3$ Hz), 5.56 (s, 1H), 5.62 (d, 1H, $J = 2.4$ Hz), 7.24-7.54 (m, 20H); ^{13}C NMR δ 24.0, 55.9, 60.1, 63.5, 68.1, 68.8, 70.5, 71.7, 73.7, 73.9, 75.6, 78.6, 78.8, 79.4, 81.9, 126.14, 126.18, 127.7, 127.8, 127.9, 128.12, 128.19, 128.2, 128.3, 128.41, 128.45, 128.5, 128.7, 129.0, 129.1, 137.5, 137.7, 138.0, 138.8, 153.1, 171.3; IR (film, cm^{-1}) ν : 1795, 1712; ESIHRMS Calcd. For $\text{C}_{44}\text{H}_{47}\text{NO}_{12}$ $[\text{M}+\text{Na}]^+$: 804.2996. Found 804.3032.

Methyl 2-acetamido-2-deoxy-6-*O*-benzyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (15)

Viscous oil. $[\alpha]_D^{27} +44.2$ (*c*, 1.0, CHCl_3); ^1H NMR δ 2.04 (s, 3H), 3.36 (s, 3H), 3.51-3.64 (m, 4H), 3.70-3.74 (m, 3H), 3.84-3.92 (m, 2H), 4.12-4.20 (m, 1H), 4.54 (s, 1H), 4.74-4.97 (m, 7H), 5.52 (s, 1H), 5.68 (d, 1H, $J = 8.4$ Hz), 7.27-7.48 (m, 20H); ^{13}C NMR δ 23.6, 53.3, 55.3, 63.5, 68.8, 68.9, 69.7, 72.4, 73.6, 74.4, 75.4, 76.7, 77.1, 77.60, 78.61, 78.9, 81.9, 82.2, 98.2, 101.34, 101.39, 126.1, 127.7, 127.8, 128.1, 128.3, 128.4, 128.5, 128.7, 128.9, 129.1, 136.9, 138.1, 170.7; IR (film, cm^{-1}) ν : 3398, 3322, 1667; ESIHRMS Calcd. For $\text{C}_{43}\text{H}_{49}\text{NO}_{11}$ $[\text{M}+\text{Na}]^+$: 778.3203. Found 778.3229.

Methyl 2-acetamido-6-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-galactopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (17)

Viscous oil. $[\alpha]_D^{27} +123.9$ (*c* 1.0, CHCl_3); ^1H NMR δ 2.53 (s, 3H), 3.44 (s, 3H), 3.63 (d, 1H, $J = 5.7$ Hz), 3.67 (dd, 1H, $J = 3.9, 0.9$ Hz), 3.76-3.96 (m, 5H), 4.06-4.13 (m, 2H), 4.35 (t, 1H, $J = 9.3$ Hz), 4.47 (d, 1H, $J = 12.0$ Hz), 4.61 (d, 1H, $J = 12.0$ Hz), 4.68-4.86 (m, 5H), 5.41 (s, 1H), 5.52 (d, 1H, $J = 3.6$ Hz), 5.61 (d, 1H, $J = 2.7$ Hz), 7.27-7.51 (m, 20H); ^{13}C NMR δ 24.0, 55.9, 60.1, 63.3, 68.3, 69.1, 70.6, 71.8, 72.4, 73.8, 73.9, 76.8, 77.2, 77.4, 77.7, 96.6, 96.8, 101.2, 126.5, 127.6, 127.72, 127.78, 127.8, 127.9, 128.0, 128.2, 128.3, 128.53, 128.58, 128.6, 129.1, 137.8, 137.9, 138.3, 138.8, 153.0, 171.4; IR (film, cm^{-1}) ν : 1795, 1714; ESIHRMS Calcd. For $\text{C}_{44}\text{H}_{47}\text{NO}_{12}$ $[\text{M}+\text{Na}]^+$: 804.2996. Found 804.3002.

Methyl 2-acetamido-6-*O*-benzyl-2-deoxy-[2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-galactopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (18)

Viscous oil. $[\alpha]_D^{27} +46.0$ (*c* 0.75, CHCl_3 , 27 °C); ^1H NMR δ 2.02 (s, 3H), 3.37 (s, 3H), 3.49-3.62 (m, 3H), 3.69-3.88 (m, 6H), 3.94 (dd, 1H, $J = 9.6, 3.3$ Hz), 4.05 (d, 1H, $J = 3.0$ Hz), 4.07-4.16 (m, 2H), 4.47 (d, 1H, $J = 12.0$ Hz), 4.64 (d, 1H, $J = 12.3$ Hz), 4.72 (d, 2H, $J = 1.8$ Hz), 4.75 (d, 1H, $J = 11.7$ Hz), 5.06 (d, 1H, $J = 3.6$ Hz), 5.39 (s, 1H), 5.64 (d, 1H, $J = 7.8$), 7.26-7.48 (m, 20H); ^{13}C NMR δ 23.6, 53.2, 55.3, 63.5, 69.2, 71.7, 72.0, 73.3, 74.1, 74.6, 75.2, 76.5, 82.5, 98.1, 101.0, 101.9, 126.4, 127.4, 127.7, 127.8, 128.3, 128.5, 128.6, 128.9, 129.1, 137.2, 137.7, 138.3, 138.5, 170.5. IR (film, cm^{-1}) ν : 3356, 3322, 1723; ESIHRMS Calcd. For $\text{C}_{43}\text{H}_{49}\text{NO}_{11}$ $[\text{M}+\text{Na}]^+$: 778.3203. Found 778.3173.

Methyl 2-acetamido-6-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-[2,3-*O*-carbonate-4-*O*-benzoyl- α -L-rhamnopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (20)

White solid. $[\alpha]_D^{27} +43.3$ (*c*, 1.75, CHCl₃); Mp 176°C; ¹H NMR δ 1.31 (d, 3H, *J* = 6.3 Hz), 2.47 (s, 3H), 3.43 (s, 3H), 3.61-3.71 (m, 3H), 3.79 (dd, 1H, *J* = 11.8, 2.7 Hz), 4.10-4.20 (m, 1H), 4.26 (t, 1H, *J* = 9.3 Hz), 4.45-4.59 (m, 3H), 4.70 (d, 1H, *J* = 11.7 Hz), 4.82 (t, 1H, *J* = 7.2 Hz), 5.11-5.17 (m, 2H), 5.58 (d, 1H, *J* = 2.7 Hz), 7.25-7.62 (m, 8H), 8.03 (d, 2H, *J* = 7.2 Hz); ¹³C NMR δ 16.8, 23.9, 56.2, 60.2, 64.3, 67.4, 72.2, 73.0, 74.0, 74.59, 75.2, 76.0, 76.4, 90.0, 96.8, 128.3, 128.4, 128.7, 128.8, 129.0, 130.0, 133.8, 137.0, 152.8, 153.0, 162.2, 171.2; IR (film, cm⁻¹) ν : 1800, 1710, 1650, 1600; ESIHRMS Calcd. For C₃₁H₃₃NO₁₃ [M+Na]⁺: 650.1850. Found 650.1847.

Methyl 2-acetamido-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-[2,3,4-tri-*O*-acetyl- α -L-rhamnopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (21)

Viscous oil. $[\alpha]_D^{27} +16.5$ (*c*, 0.35, CHCl₃); ¹H NMR δ 1.15 (d, 3H, *J* = 6.3 Hz), 1.94 (s, 3H), 1.98 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.09 (s, 3H), 3.36 (s, 3H), 3.71 (d, 1H, *J* = 9.9 Hz), 3.78-3.88 (m, 3H), 4.01 (t, 1H, *J* = 9.0 Hz), 4.23 (dt, 1H, *J* = 10.5, 3.3 Hz), 4.57 (dd, 2H, *J* = 12.0, 6.0 Hz), 4.68 (d, 1H, *J* = 3.3 Hz), 4.87 (d, 1H, *J* = 1.2 Hz), 5.02 (t, 1H, *J* = 9.3 Hz), 5.13-5.22 (m, 3H), 5.68 (d, 1H, *J* = 9.9 Hz), 7.27-7.33 (m, 5H); ¹³C NMR δ 17.4, 20.91, 20.96, 21.0, 21.2, 23.4, 52.3, 55.3, 67.4, 68.3, 69.0, 69.91, 69.97, 70.7, 72.9, 73.4, 76.2, 98.3, 98.9, 127.61, 127.68, 128.4, 138.1, 170.0, 170.21, 170.27, 171.7; IR (film, cm⁻¹) ν : 3368, 1746, 1738, 1673; ESIHRMS Calcd. For C₃₀H₄₁NO₁₄ [M+Na]⁺: 662.2425. Found 662.2426.

Methyl 2-acetamido -6-*O*-benzyl-2-*N*, 3-*O*-carbonyl-2-deoxy-[2,3,4,6-*O*-benzyl- α -D-glucopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23 α)

Viscous oil. $[\alpha]_D^{27} +95.4$ (*c*, 1.45, CHCl₃); ¹H NMR δ 2.52 (s, 3H), 3.34 (d, 1H, *J* = 10.5 Hz), 3.42 (s, 3H), 3.52 (d, 1H, *J* = 10.5 Hz), 3.58-3.70 (m, 4H), 3.77-3.89 (m, 4H), 4.25 (d, 1H, *J* = 11.7 Hz), 4.37-4.58 (m, 5H), 4.70-4.82 (m, 5H), 4.97 (d, 1H, *J* = 2.1 Hz), 7.09-7.12 (m, 2H), 7.22-7.39 (m, 23H); ¹³C NMR δ 23.9, 29.7, 55.7, 59.9, 67.8, 68.1, 70.3, 71.1, 71.7, 73.2, 73.3, 73.5, 75.1, 75.7, 77.2, 77.4, 79.2, 81.7, 127.3, 127.4, 127.5, 127.63, 127.68, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 137.6, 137.8, 137.9, 138.3, 138.7, 152.9, 171.3; IR (film, cm⁻¹) ν : 1795, 1711; ESIHRMS Calcd. For C₅₁H₅₅NO₁₂ [M+Na]⁺: 896.3646. Found 896.3630.

Methyl 2-acetamido -6-*O*-benzyl-2-*N*, 3-*O*-carbonyl-2-deoxy-[2,3,4,6-*O*-benzyl-4- β -D-glucopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (23 β)

Viscous oil. $[\alpha]_D^{27} +82.0$ (*c*, 0.70, CHCl₃); ¹H NMR δ 2.45 (s, 3H), 3.42 (s, 3H), 3.39-3.45 (m, 2H), 3.51-3.83 (m, 9H), 4.16 (t, 1H, *J* = 9.0 Hz), 4.34 (d, 1H, *J* = 8.1 Hz), 4.42 (d, 1H, *J* = 12.3 Hz), 4.53-4.88 (m, 11H), 5.56 (d, 1H, *J* = 2.7 Hz), 7.18-7.36 (m, 25H); ¹³C NMR δ 24.0, 29.8, 56.0, 60.0, 67.5, 68.8, 72.5, 73.6, 73.8, 75.0, 75.1, 75.52, 75.55, 75.8, 77.8, 127.5, 127.7, 127.87, 127.89, 127.9, 128.0, 128.40, 128.48, 128.52, 128.55, 128.6, 137.9, 138.2, 138.4, 138.5, 138.8, 153.1, 171.4; IR (film, cm⁻¹) ν : 1793, 1709; ESIHRMS Calcd. For C₅₁H₅₅NO₁₂ [M+Na]⁺: 896.3646. Found 896.3661.

Methyl-2-acetamido-6-O-benzyl-2-deoxy-[2,3,4,6-O-benzyl- α -D-glucopyranosyl]-(1 $\rightarrow$ 4)- α -D-glucopyranoside (24**)**

Viscous oil. $[\alpha]_D^{27} +76.8$ (*c*, 0.35, CHCl_3); ^1H NMR δ 2.03 (s, 3H), 3.35-3.42 (m, 1H), 3.48-3.70 (m, 7H), 3.86-3.88 (m, 2H), 3.95 (t, 1H, $J = 9.6$ Hz), 4.16 (dt, 1H, $J = 11.4$, 3.9 Hz), 4.36-4.57 (m, 5H), 4.68-4.91 (m, 7H), 4.94 (d, 1H, $J = 3.6$ Hz), 7.10-7.13 (m, 2H), 7.23-7.32 (m, 23H); ^{13}C NMR δ 23.5, 29.8, 53.3, 55.3, 68.3, 69.0, 69.8, 71.4, 72.2, 73.2, 73.6, 74.2, 75.1, 75.8, 77.7, 79.4, 82.2, 82.3, 127.51, 127.55, 127.81, 127.85, 127.9, 128.2, 128.4, 128.52, 128.54, 128.6, 128.7, 128.8, 136.9, 137.8, 138.4, 138.5, 138.7, 170.5; IR (film, cm^{-1}) ν : 3326, 1669; ESIHRMS Calcd. For $\text{C}_{50}\text{H}_{57}\text{NO}_{11}$ $[\text{M}+\text{Na}]^+$: 870.3829. Found 870.3826.

Coupling of **9 to **27** by Schmidt's trichloroacetimidate method**

A mixture of the acceptor **9** (50 mg, 0.142 mmol, 1 eq), trichloroacetimidate³ **27** (194 mg, 0.284 mmol, 2 eq) and activated 3 Å powdered molecular sieves in CH_2Cl_2 (10 mL) was stirred at room temperature under argon atmosphere for 30 min. It was then cooled to -30 °C and TMSOTf (0.056 mmol, 12.6 mg; 10 μL) was slowly added. The resulting solution was allowed to stir at this temperature for 0.5 h and then at 0 °C for 1h. The mixture was gradually warmed to room temperature, filtered, washed with saturated aqueous NaHCO_3 , followed by brine and dried. The solvents were evaporated off and the products were purified by radial chromatography (Chromatotron[®]) on silica gel eluting with 1:0.5:8.5 chloroform-ethyl acetate-hexane system to give **23 α** anomer in 18% (22 mg) and **23 β** anomer in 64 % (78 mg) yields.

Coupling of **9 to **26** by Gin's dehydrative glycosylation method**

Triflic anhydride (39 mg; 24 μL , 0.14 mmol) was added to a solution of 2,3,4,6-tetra-*O*-benzyl-*D*-glucopyranose⁴ **26** (54 mg, 0.1 mmol, 1 eq) and diphenyl sulfoxide (57 mg, 0.28 mmol, 2.8 eq) in a mixture of toluene and CH_2Cl_2 (3:1, 2 mL) at -78 °C. After stirring at this temperature for 10 min and then at -40 °C for 1h, TTBP (124 mg, 0.5 mmol, 5 eq) in CH_2Cl_2 (1 mL) and a solution of acceptor **9** (39 mg, 0.11 mmol, 1.1 eq) in CH_2Cl_2 (1 mL) were added sequentially at -40 °C. The solution was then stirred at this temperature for 30 min and then at 0 °C for 25 min and finally at room temperature for 4 h before the addition of excess of triethylamine (0.1 mL). The mixture was diluted with CH_2Cl_2 and washed sequentially with saturated aqueous NaHCO_3 and brine, dried and concentrated. Column chromatography of the residue yielded **23 α** (51 mg, 59 %) as a single diastereomer.

Coupling of **9** to **25** by Kahne's sulfoxide method

To a stirred solution of sulfoxide⁵ **25** (75 mg, 0.115 mmol) and TTBP (58 mg, 0.23 mmol) in CH₂Cl₂ (7 mL) at -60 °C were added Tf₂O (22 µL, 0.127 mmol) and, 10 min later, the solution of the glycosyl acceptor **9** (0.150 mmol) in CH₂Cl₂ (2 mL) dropwise. The reaction mixture was stirred at this temperature for 2 h and then allowed to come to 0 °C before quenching with saturated NaHCO₃. The reaction mixture was washed with brine, dried and, concentrated. Radial chromatography of the residue on a Chromatotron[®] afforded **23α** (63 mg, 63%) as a single diastereomer.

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