Electronic Supplementary Information

Pre-Activation Protocol Leading to Highly Stereoselectivity-Controllable Glycosylations of Oxazolidinone Protected Glucosamine Donors

Yiqun Geng, Li-He Zhang, and Xin-Shan Ye*

The State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Rd #38, Beijing 100083, China

E-mail: xinshan@bjmu.edu.cn

Table of Contents:

Experimental Section.............................................................................................................................................S2-14

1H and 13C NMR Spectra of Compound 3a................................................................................................................S15-16

1H and 13C NMR Spectra of Compound 3b................................................................................................................S17-18

1H and 13C NMR Spectra of Compound 3c................................................................................................................S19-20

1H and 13C NMR Spectra of Compound 3d................................................................................................................S21-22

1H and 13C NMR Spectra of Compound 3e................................................................................................................S23-24

1H and 13C NMR Spectra of Compound 3f................................................................................................................S25-26

1H and 13C NMR Spectra of Compound 3g................................................................................................................S27-28

1H and 13C NMR Spectra of Compound 3h................................................................................................................S29-30

1H and 13C NMR Spectra of Compound 3i................................................................................................................S31-32

1H and 13C NMR Spectra of Compound 3j................................................................................................................S33-34

1H and 13C NMR Spectra of Compound 3k................................................................................................................S35-36

1H and 13C NMR Spectra of Compound 4a................................................................................................................S37-38

1H and 13C NMR Spectra of Compound 4b................................................................................................................S39-40

1H and 13C NMR Spectra of Compound 4c................................................................................................................S41-42

1H and 13C NMR Spectra of Compound 4d................................................................................................................S43-44

1H and 13C NMR Spectra of Compound 4e................................................................................................................S45-46

1H and 13C NMR Spectra of Compound 4f................................................................................................................S47-48

1H and 13C NMR Spectra of Compound 4g................................................................................................................S49-50

1H and 13C NMR Spectra of Compound 4h................................................................................................................S51-52
Experimental Section

General Procedures All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Dichloromethane (CH₂Cl₂), pyridine, toluene and acetonitrile (CH₃CN) were distilled over calcium hydride (CaH₂). Methanol was distilled from magnesium. DMF was stirred with CaH₂ and distilled under reduced pressure. All reactions were carried out under anhydrous conditions with freshly distilled solvents, unless otherwise noted. Reactions were monitored by analytical thin-layer chromatography on silica gel 60 F254 precoated on aluminium plates (E. Merck). Spots were detected under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate. Solvents were evaporated under reduced pressure and below 40 °C (bath). Organic solutions of crude products were dried over anhydrous Na₂SO₄. Column chromatography was performed on silica gel (200—300 mesh). ¹H-NMR spectra were recorded on a JEOL AL-300, Varian INOV A-500 or Advance DRX Bruker-500 spectrometers at 25 °C. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in deuterated chloroform. ¹³C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl₃ (δ = 77.00 ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. Elemental analysis data were recorded on a Vario EL-III elemental analyzer.

General procedures for glycosylation of 1 with 2a-2k by means of BSM-Tf₂O pre-activation in presence of TTBP

Tf₂O (11.8 uL, 0.070 mmol, 1.3 eq) was added to a stirred solution of 1 (28.3 mg, 0.065 mmol, 1.2 eq), BSM (15.9 mg, 0.075 mmol, 1.4 eq), TTBP (32.1 mg, 0.129 mmol, 2.4eq) and activated, powdered 4 Å molecular sieves in CH₂Cl₂ (5 mL) at -73 °C under nitrogen atmosphere. The
reaction mixture was stirred for 10-15 min, after loss of 1 detected by TLC, a solution of the acceptor alcohol 2a (25.0 mg, 0.054 mmol, 1.0 eq) or 2b-2k in CH$_2$Cl$_2$ (0.5 mL) was added dropwise to the pre-activated system. The mixture was stirred and warmed up to room temperature slowly, quenched by Et$_3$N (0.1 mL). The precipitate was filtered off and the filtrate was concentrated. The residue was purified by column chromatography on silica gel to give products.

**Coupling of 1 with 2a to give methyl (N-acetyl-2-amino-2,3-\(N\),\(O\)-carbonyl-4,6-diacyl-2-deoxy-\(\beta\)-D-glucopyranosyl)-(1→4)-2,3,6-tri-\(O\)-benzyl-\(\alpha\)-D-glucopyranoside (3a)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 3a, yield = 90%. $R_f = 0.25$ (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.25-7.36 (m, 15H), 5.02 (d, 1H, $J = 7.0$ Hz, H-1'), 5.02 (dd, 1H, $J = 6.0$, 10.0 Hz), 4.91 (s, 2H), 4.71 (d, 1H, $J = 12.0$ Hz), 4.66 (d, 1H, $J = 12.0$ Hz), 4.60 (d, 1H, $J = 3.5$ Hz, H-1), 4.59 (d, 1H, $J = 12.0$ Hz), 4.44 (d, 1H, $J = 12.5$ Hz), 4.17-4.24 (m, 2H), 3.95 (t, 1H, $J = 9.0$ Hz), 3.78-3.81 (m, 2H), 3.76 (dd, 1H, $J = 10.0$, 12.5 Hz), 3.61-3.70 (m, 3H), 3.53 (dd, 1H, $J = 4.5$, 10.5 Hz), 3.50 (dd, 1H, $J = 3.5$, 9.5 Hz), 3.40 (s, 3H), 2.42 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.51, 170.26, 169.40, 153.01, 139.37, 138.06, 128.56, 128.43, 128.40, 128.14, 128.08, 128.00, 127.85, 127.49, 127.24, 100.26, 97.92, 79.79, 79.73, 77.47, 76.12, 75.29, 74.85, 73.40, 73.21, 69.44, 69.03, 68.76, 63.24, 61.22, 55.33, 24.49, 20.66 (2C); HRMS (ESI) Calcd for C$_{41}$H$_{47}$NO$_{14}$Na [M + Na]$^+$: 800.2889. Found: 800.2881.

**Coupling of 1 with 2b to give methyl (N-acetyl-2-amino-2,3-\(N\),\(O\)-carbonyl-4,6-diacyl-2-deoxy-\(\beta\)-D-glucopyranosyl)-(1→4)-2,3,6-tri-\(O\)-benzyl-\(\alpha\)-D-galactopyranoside (3b)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 3b, yield = 83%. $R_f = 0.15$ (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.25-7.43 (m, 17H), 5.23 (dd, 1H, $J = 8.5$, 10.0 Hz), 4.86 (d, 1H, $J = 7.5$ Hz, H-1'), 4.85 (d, 1H, $J = 11.0$ Hz), 4.81 (d, 1H, $J = 12.0$ Hz), 4.64 (d, 1H, $J = 12.0$ Hz), 4.60 (d, 1H, $J = 4.0$ Hz, H-1), 4.58 (d, 1H, $J = 11.0$ Hz), 4.56 (d, 1H, $J = 12.0$ Hz), 4.51 (d, 1H, $J = 12.0$ Hz), 4.14-4.18 (m, 2H), 4.10 (dd, 1H, $J = 4.5$, 12.5 Hz), 3.98-4.02 (m, 2H), 3.92 (t, 1H, $J = 6.0$ Hz), 3.83-3.88 (m,
2H), 3.72 (dd, 1H, $J = 5.5, 10.0$ Hz), 3.58-3.62 (m, 2H), 3.35 (s, 3H), 2.23 (s, 3H), 2.12 (s, 3H), 2.03 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.12, 170.43, 169.10, 153.52, 138.71, 138.53, 138.39, 128.48, 128.39, 128.35, 128.06, 127.78, 127.55, 127.34, 103.50, 98.69, 78.08, 77.73, 77.00, 76.62, 74.38, 74.02, 73.76, 73.24, 69.65, 68.69, 67.41, 61.80, 59.59, 55.38, 24.62, 20.63 (2C); HRMS (ESI) Calcd for C$_{41}$H$_{47}$NO$_{14}$Na [M + Na]$^+$: 800.2889. Found: 800.2886.

**Coupling of 1 with 2c to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (3c)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1) to give 3c, yield = 83%. $R_f = 0.30$ (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.25-7.37 (m, 15H), 5.07 (dd, 1H, $J = 6.0, 10.0$ Hz), 5.03 (d, 1H, $J = 7.0$ Hz, H-1'), 4.88 (d, 1H, $J = 11.5$ Hz), 4.86 (s, 2H), 4.68 (d, 1H, $J = 12.0$ Hz), 4.64 (d, 1H, $J = 11.5$ Hz), 4.49 (d, 1H, $J = 12.0$ Hz), 4.30 (d, 1H, $J = 8.0$ Hz, H-1), 4.22 (dd, 1H, $J = 4.0, 12.0$ Hz), 4.17 (dd, 1H, $J = 6.0, 12.0$ Hz), 3.84 (dd, 1H, $J = 8.5, 9.5$ Hz), 3.73-3.78 (m, 3H), 3.64-3.68 (m, 2H), 3.57 (s, 3H), 3.56 (dd, 1H, $J = 5.0, 11.0$ Hz), 3.42-3.46 (m, 1H), 3.40 (dd, 1H, $J = 8.0, 9.0$ Hz), 2.43 (s, 3H), 2.11 (s, 3H), 2.00 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.33, 169.36, 153.06, 139.11, 138.47, 138.14, 128.46, 128.24, 128.11, 128.00, 127.94, 127.50, 127.43, 127.27, 104.51, 100.24, 82.62, 82.18, 77.44, 75.96, 75.44, 74.74, 74.50, 74.39, 73.57, 69.07, 68.71, 63.10, 61.17, 57.07, 24.56, 20.75, 20.64; MS (ESI) 795 [M + NH$_4$]$^+$, 800 [M + Na]$^+$, 816 [M + K]$^+$; Anal. Calcd for C$_{41}$H$_{47}$NO$_{14}$: C, 63.31; H, 6.09; N, 1.80. Found: C, 63.43; H, 6.12; N, 1.60.

**Coupling of 1 with 2d to give methyl (N-acetyl-2-amino-2,3-N,O-carpyny-l-4,6-diacyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (3d)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 2.5:1) to give 3d, yield = 84%. $R_f = 0.15$ (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.25-7.38 (m, 14H), 5.07 (dd, 1H, $J = 7.5, 10.0$ Hz), .4.96 (d, 1H, $J = 11.0$ Hz), 4.89 (d, 1H, $J = 7.5$ Hz, H-1'), 4.80 (d, 1H, $J = 11.0$ Hz), 4.68 (d, 1H, $J = 11.5$ Hz), 4.58 (d, 1H, $J = 11.5$ Hz), 4.57 (d, 1H, $J = 12.0$ Hz), 4.54 (d, 1H, $J = 12.0$ Hz), 4.27 (d, 1H, $J = 7.5$ Hz, H-1),
4.20 (dd, 1H, $J = 3.0, 12.5$ Hz), 4.11 (dd, 1H, $J = 4.0, 12.5$ Hz), 4.03 (dd, 1H, $J = 7.5, 12.0$ Hz),
4.00 (d, 1H, $J = 3.5$ Hz), 3.95 (dd, 1H, $J = 7.5, 9.5$ Hz), 3.84 (dd, 1H, $J = 10.0, 12.5$ Hz), 3.80 (dd, 1H, $J = 3.5$ Hz), 3.79-3.87 (m, 1H), 3.71 (t, 1H, $J = 10.0$ Hz), 3.62 (t, 1H, $J = 9.5$ Hz), 3.32 (s, 3H), 2.30 (s, 3H), 2.06 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta 170.71, 170.46, 169.16, 153.37, 138.37, 128.91, 128.46, 128.06, 127.88, 127.17, 126.27, 101.74, 100.28, 97.96, 81.26, 79.37, 76.75, 75.30, 74.48, 72.20, 69.69, 69.03, 63.36, 62.25, 60.00, 55.23, 24.50, 20.69 (2C); HRMS (ESI) Calcd for C$_{34}$H$_{39}$NO$_{14}$K $[M + K]^+$: 724.2002. Found: 724.2011.

**Coupling of 1 with 2e to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (3e)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 2.5:1) to give 3e, yield = 85%. $R_f = 0.25$ (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta 7.42-7.44$ (m, 2H), 7.27-7.35 (m, 8H), 5.59 (d, 1H, $J = 7.0$ Hz, H-1'), 5.50 (s, 1H), 5.13 (dd, 1H, $J = 3.5$ Hz, H-1), 4.65 (d, 1H, $J = 3.5$ Hz, H-1), 4.58 (s, 2H), 4.37 (dd, 1H, $J = 7.5$, 12.0 Hz), 4.29 (t, 1H, $J = 9.5$ Hz), 4.25 (dd, 1H, $J = 5.0$, 10.0 Hz), 4.09-4.14 (m, 1H), 4.05 (dd, 1H, $J = 5.0$, 12.5 Hz), 3.98 (dd, 1H, $J = 7.0$, 12.5 Hz), 3.79-3.87 (m, 3H), 3.71 (t, 1H, $J = 10.0$ Hz), 3.62 (t, 1H, $J = 9.5$ Hz), 3.32 (s, 3H), 2.30 (s, 3H), 2.06 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta 170.71, 170.46, 169.16, 153.37, 138.37, 128.91, 128.46, 128.06, 127.88, 127.17, 126.27, 101.74, 100.28, 97.96, 81.26, 79.37, 76.75, 75.30, 74.48, 72.20, 69.69, 69.03, 63.36, 62.25, 60.00, 55.23, 24.50, 20.69 (2C); HRMS (ESI) Calcd for C$_{34}$H$_{39}$NO$_{14}$K $[M + K]^+$: 724.2002. Found: 724.2011.

**Coupling of 1 with 2f to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (3f)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 2:1) to give 3f, yield = 86%. $R_f = 0.25$ (petroleum ether/ethyl acetate, 1:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta 7.44-7.46$ (m, 2H), 7.35-7.38 (m, 3H), 7.22-7.30 (m, 5H), 5.54 (s, 1H), 5.41 (d, 1H, $J = 7.0$ Hz,
H-1'), 5.18 (dd, 1H, J = 5.5, 10.0 Hz), 4.99 (d, 1H, J = 11.5 Hz), 4.80 (d, 1H, J = 4.0 Hz, H-1), 4.64 (d, 1H, J = 11.5 Hz), 4.42 (dd, 1H, J = 4.0, 12.0 Hz), 4.30 (dd, 1H, J = 4.5, 10.0 Hz), 4.22 (dd, 1H, J = 6.0, 12.5 Hz), 4.16 (t, 1H, J = 9.0 Hz), 4.10 (dd, 1H, J = 10.0, 12.5 Hz), 4.00 (dd, 1H, J = 7.0, 12.5 Hz), 3.85-3.95 (m, 3H), 3.74 (t, 1H, J = 10.0 Hz), 3.65 (t, 1H, J = 9.5 Hz), 3.41 (s, 3H), 2.24 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H); 13C NMR (125 MHz, CDCl 3) δ 170.40, 170.18, 169.39, 153.22, 139.38, 137.31, 128.94, 128.23, 127.35, 126.76, 126.00, 101.66, 101.40, 99.62, 83.00, 78.34, 77.58, 76.36, 75.38, 74.40, 69.23, 69.14, 63.35, 61.89, 60.11, 55.04, 24.32, 20.78, 20.65; MS (FAB) 685 [M]+, 686 [M + H]+, 724 [M + K]+; Anal. Calcd for C34H39NO14: C, 59.56; H, 5.73; N, 2.04. Found: C, 59.31; H, 5.82; N, 1.94.

Coupling of 1 with 2g to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside (3g)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1.5:1) to give 3g, yield = 82%. Rf = 0.20 (petroleum ether/ethyl acetate, 1:1); 1H NMR (500 MHz, CDCl 3) δ 7.56-7.58 (m, 2H), 7.26-7.38 (m, 8H), 5.57 (s, 1H), 5.43 (d, 1H, J = 7.0 Hz, H-1'), 5.21-5.24 (m, 1H), 4.75 (d, 1H, J = 3.5 Hz, H-1), 4.65 (d, 1H, J = 12.5 Hz), 4.56 (d, 1H, J = 12.0 Hz), 4.45 (dd, 1H, J = 3.5, 12.0 Hz), 4.06-4.25 (m, 8H), 3.91 (dd, 1H, J = 4.0, 9.0 Hz), 3.64 (s, 1H), 3.34 (s, 3H), 2.32 (s, 3H), 2.12 (s, 3H), 1.93 (s, 3H); 13C NMR (125 MHz, CDCl 3) δ 170.49, 170.28, 169.53, 153.49, 138.40, 137.87, 128.74, 128.42, 128.04, 127.81, 127.46, 126.35, 101.81, 100.65, 98.54, 76.60, 76.39, 76.07, 75.28, 73.57, 72.71, 69.41, 69.16, 63.42, 62.61, 59.80, 55.43, 24.47, 20.78, 20.66; MS (FAB) 708 [M + Na]⁺; Anal. Calcd for C34H39NO14: C, 59.56; H, 5.73; N, 2.04. Found: C, 59.76; H, 5.63; N, 1.92.

Coupling of 1 with 2h to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside (3h)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 3h, yield = 87%. Rf = 0.25 (petroleum ether/ethyl acetate, 1.5:1); 1H NMR (500 MHz, CDCl 3) δ...
CDCl$_3$ δ 7.51-7.53 (m, 2H), 7.26-7.38 (m, 8H), 5.40 (s, 1H), 5.28 (d, 1H, $J = 7.0$ Hz, H-1'), 5.18 (dd, 1H, $J = 6.0$, 9.0 Hz), 4.92 (d, 1H, $J = 3.5$ Hz, H-1), 4.65 (d, 1H, $J = 12.0$ Hz), 4.58 (d, 1H, $J = 12.0$ Hz), 4.37 (dd, 1H, $J = 3.5$, 12.0 Hz), 3.99-4.26 (m, 8H), 3.88 (dt, 1H, $J = 3.5$, 6.0 Hz), 3.62 (s, 1H), 3.41 (s, 3H), 2.30 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 170.44 (2C), 169.36, 153.41, 138.69, 137.78, 128.82, 128.26, 128.07, 127.59, 127.11, 126.16, 102.14, 100.88, 99.72, 76.40, 75.70 (2C), 74.39, 73.66, 71.12, 69.34, 68.82, 63.08, 62.12, 59.96, 55.30, 24.47, 20.75, 20.60; MS (FAB) 685 [M$^+$], 686 [M + H$^+$]; Anal. Calcd for C$_{34}$H$_{39}$NO$_{14}$: C, 59.56; H, 5.73; N, 2.04. Found: C, 59.77; H, 5.96; N, 1.97.

**Coupling of 1 with 2i to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-2-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (3i)**

The was purified by column chromatography (petroleum ether/ethyl acetate, 4:1) to give 3i, yield = 98%. $R_f = 0.20$ (petroleum ether/ethyl acetate, 2:1); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.43-7.45 (m, 2H), 7.24-7.34 (m, 8H), 5.62 (d, 1H, $J = 7.0$ Hz, H-1'), 5.51 (s, 1H), 5.09 (dd, 1H, $J = 3.5$, 9.5 Hz), 4.98 (d, 1H, $J = 12.0$ Hz), 4.54 (d, 1H, $J = 12.0$ Hz), 4.43 (d, 1H, $J = 8.0$ Hz, H-1), 4.35-4.39 (m, 2H), 4.04-4.13 (m, 3H), 3.84-3.91 (m, 2H), 3.77 (t, 1H, $J = 10.0$ Hz), 3.66-3.71 (m, 2H), 3.54 (s, 3H), 3.45 (dt, 1H, $J = 5.0$, 10.0 Hz), 2.32 (s, 3H), 2.07 (s, 3H), 1.95 (s, 3H); 13C NMR (125 MHz, CDCl$_3$) δ 170.37, 169.20, 153.15, 138.90, 137.11, 128.95, 128.45, 128.30, 128.11, 127.43, 126.82, 126.84, 105.12, 101.66, 99.57, 82.71, 79.14, 74.94, 73.86, 70.03, 68.84, 66.00, 65.60, 60.15, 57.21, 24.42, 20.75, 20.69; HRMS (ESI) Calcd for C$_{34}$H$_{39}$NO$_{14}$K [M + K$^+$]: 724.2002. Found: 724.2004.

**Coupling of 1 with 2j to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β- and α-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (3j) and (4j)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1 to 3:1) to give 3j (β-isomer) and 4j (α-isomer), yield = 87% ($α:β = 1:5$). $R_f$ α-isomer = 0.40, $R_f$ β-isomer = 0.30 (petroleum ether/ethyl acetate, 1.5:1); 3j $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45-7.47 (m, 2H), 7.35-7.39 (m, 3H), 7.22-7.31 (m, 5H), 5.72 (d, 1H, $J = 7.0$ Hz, H-1'), 5.55 (s, 1H), 5.15
Coupling of 1 with 2k to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (3k)

The residue was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 3k, yield = 87%. $R_f = 0.35$ (petroleum ether/ethyl acetate, 1:1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26-7.37 (m, 15H), 5.16 (dd, 1H, $J = 8.0$, 9.5 Hz), 4.99 (d, 1H, $J = 11.0$ Hz), 4.96 (d, 1H, $J = 6.5$ Hz, H-1'), 4.89 (d, 1H, $J = 11.5$ Hz), 4.81 (d, 1H, $J = 11.0$ Hz), 4.77 (d, 1H, $J = 12.5$ Hz), 4.72 (d, 1H, $J = 11.0$ Hz), 4.68 (d, 1H, $J = 12.0$ Hz), 4.64 (d, 1H, $J = 4.0$ Hz, H-1'), 4.39 (dd, 1H, $J = 5.0$, 12.0 Hz), 4.27 (dd, 1H, $J = 6.0$, 12.0 Hz), 4.21 (dd, 1H, $J = 10.0$, 13.0 Hz), 3.95-4.02 (m, 4H), 3.80 (dd, 1H, $J = 3.5$, 10.0 Hz), 3.72-3.75 (m, 1H), 3.58 (t, 1H, $J = 10.0$ Hz), 3.54 (dd, 1H, $J = 3.5$, 10.0 Hz), 3.37 (s, 3H), 2.46 (s, 3H), 2.12 (s, 3H), 2.02 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 170.29, 169.95, 169.42, 153.10, 138.82, 138.73, 138.92, 138.19, 128.37, 128.31, 128.07, 127.89, 127.80.
127.55, 127.50, 100.30, 97.90, 79.86, 77.25, 77.14, 75.57, 75.17, 74.22, 69.79, 69.61, 67.27, 64.07, 60.36, 55.16, 24.44, 20.78, 20.66; MS (FAB) 816 [M + K]+; Anal. Calcd for C_{41}H_{47}NO_{14}: C, 63.31; H, 6.09; N, 1.80. Found: C, 63.17; H, 6.21; N, 1.67.

**General procedures for glycosylation of 1 with 2a-2k by means of BSM-Tf₂O pre-activation in absence of TTBP**

Tf₂O (11.8 uL, 0.070 mmol, 1.3 eq) was added to a stirred solution of 1 (28.3 mg, 0.065 mmol, 1.2 eq), BSM (15.9 mg, 0.075 mmol, 1.4 eq) and activated 4 Å molecular sieves in CH₂Cl₂ (5 mL) at -73 °C under nitrogen atmosphere. The reaction mixture was stirred for 5 min, after loss of 1a detected by TLC, a solution of the acceptor alcohol 2a (25.0 mg, 0.054 mmol, 1.0 eq) or 2b-2k in CH₂Cl₂ (0.5 mL) was added dropwise to the pre-activated system. The mixture was stirred and warmed up to room temperature slowly, quenched by Et₃N (0.1 mL). The precipitate was filtered off and the filtrate was concentrated. The residue was purified by column chromatography on silica gel to give products.

**Coupling of 1 with 2a to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacyethyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside (4a)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1) to give 4a, yield = 90%. Rf = 0.30 (petroleum ether/ethyl acetate, 1.5:1); ¹H NMR (500 MHz, CDCl₃) δ 7.25-7.37 (m, 15H), 6.27 (d, 1H, J = 2.5 Hz, H-1'), 5.24 (dd, 1H, J = 9.5, 10.0 Hz), 5.00 (dd, 1H, J = 11.0 Hz), 4.86 (d, 1H, J = 11.0 Hz), 4.62 (d, 1H, J = 12.0 Hz), 4.57 (d, 1H, J = 3.5 Hz, H-1), 4.56 (d, 1H, J = 12.5 Hz), 4.54 (d, 1H, J = 12.0 Hz), 4.50 (dd, 1H, J = 10.0, 12.0 Hz), 3.98-4.02 (m, 2H), 3.84-3.94 (m, 4H), 3.77 (dd, 1H, J = 3.0, 12.0 Hz), 3.70-3.73 (m, 1H), 3.65 (dd, 1H, J = 2.0, 11.0 Hz), 3.58 (dd, 1H, J = 3.5, 9.5 Hz), 3.36 (s, 3H), 2.23 (s, 3H), 2.11 (s, 3H), 2.01 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.09, 170.44, 169.00, 152.62, 138.82, 137.86, 137.70,
Coupling of 1 with 2b to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-α-D-galactopyranoside (4b)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to give 4b, yield = 85%. \( R_f = 0.35 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.28-7.42 (m, 15H), 5.73 (d, 1H, \( J = 3.0 \) Hz, H-1'), 5.25 (t, 1H, \( J = 10.0 \) Hz), 4.86 (d, 1H, \( J = 12.0 \) Hz), 4.84 (d, 1H, \( J = 12.5 \) Hz), 4.76 (d, 1H, \( J = 12.0 \) Hz), 4.71 (d, 1H, \( J = 3.0 \) Hz, H-1), 4.66 (d, 1H, \( J = 11.5 \) Hz), 4.65 (d, 1H, \( J = 11.5 \) Hz), 4.62 (dd, 1H, \( J = 10.5, 12.5 \) Hz), 4.50 (d, 1H, \( J = 11.5 \) Hz), 4.35 (td, 1H, \( J = 2.5, 9.5 \) Hz), 4.25 (d, 1H, \( J = 7.5 \) Hz), 3.83-3.90 (m, 4H), 3.69 (dd, 1H, \( J = 2.5, 12.5 \) Hz), 3.58 (dd, 1H, \( J = 2.5, 12.5 \) Hz), 3.41 (d, 2H, \( J = 7.5 \) Hz), 3.37 (s, 3H), 2.46 (s, 3H), 2.10 (s, 3H), 2.00 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 171.87, 170.41, 169.02, 152.88, 138.04, 137.99, 137.92, 128.43, 128.40, 128.13, 127.98, 127.83, 127.70, 98.22, 95.72, 76.80, 75.67, 74.85, 73.80, 73.45, 73.03, 72.99, 69.80, 68.63, 68.01, 67.47, 60.84, 60.32, 55.39, 23.75, 20.67 (2C); HRMS (ESI) Calcd for C\(_{41}\)H\(_{47}\)NO\(_{14}\)Na \([M + Na]^+\): 800.2889. Found: 800.2870.

Coupling of 1 with 2c to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (4c)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1) to give 4c, yield = 81%. \( R_f = 0.35 \) (petroleum ether/ethyl acetate, 1.5:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.25-7.35 (m, 15H), 6.30 (d, 1H, \( J = 2.5 \) Hz, H-1'), 5.23 (t, 1H, \( J = 10.0 \) Hz), 4.97 (d, 1H, \( J = 11.5 \) Hz), 4.90 (d, 1H, \( J = 11.0 \) Hz), 4.84 (d, 1H, \( J = 11.5 \) Hz), 4.66 (d, 1H, \( J = 11.5 \) Hz), 4.61 (d, 1H, \( J = 12.5 \) Hz), 4.59 (d, 1H, \( J = 12.0 \) Hz), 4.50 (dd, 1H, \( J = 10.0, 12.0 \) Hz), 4.32 (d, 1H, \( J = 7.5 \) Hz, H-1), 4.00-4.07 (m, 2H), 3.94-3.97 (m, 1H), 3.92 (dd, 1H, \( J = 2.0, 12.0 \) Hz), 3.83 (dd, 1H, \( J = 4.0, 11.0 \) Hz), 3.79 (dd, 1H, \( J = 2.5, 12.0 \) Hz), 3.76 (dd, 1H, \( J = 2.5, 11.5 \) Hz), 3.63 (t, 1H, \( J = 8.5 \) Hz), 3.56 (s, 3H), 3.50 (t, 1H, \( J = 8.5 \) Hz), 3.43-3.46 (m, 1H), 2.28 (s, 3H), 2.11 (s, 3H), 2.02 (2C); HRMS (ESI) Calcd for C\(_{41}\)H\(_{47}\)NO\(_{14}\)NH\(_{4}\) \([M + NH_4]^+\): 795.3335. Found: 795.3332.
(s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.97, 170.46, 169.02, 152.63, 138.59, 138.20, 137.87, 128.36, 128.31, 128.00, 127.75, 127.49, 127.38, 104.59, 94.28, 83.26, 82.63, 74.44, 74.41, 74.10, 73.83, 73.57, 73.28, 70.26, 68.88, 68.03, 61.46, 60.22, 56.96, 23.45, 20.64 (2C); MS (ESI) 795 [M + NH$_4^+$], 800 [M + Na$^+$], 816 [M + K$^+$]; Anal. Cald. for C$_{41}$H$_{47}$NO$_{14}$: C, 63.31; H, 6.09; N, 1.80. Found: C, 63.32; H, 6.24; N, 1.67.

**Coupling of 1 with 2d to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (4d)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 4:1) to give 4d, yield = 82%. $R_f$ = 0.35 (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.26-7.38 (m, 17H), 5.78 (d, 1H, $J = 2.5$ Hz, H-1'), 5.26 (t, 1H, $J = 10.0$ Hz), 4.93 (d, 1H, $J = 11.5$ Hz), 4.80 (d, 1H, $J = 11.5$ Hz), 4.77 (d, 1H, $J = 12.0$ Hz), 4.66-4.72 (m, 3H), 4.49 (d, 1H, $J = 11.5$ Hz), 4.28 (dt, 1H, $J = 2.5$, 10.0 Hz), 4.25 (d, 1H, $J = 7.5$ Hz, H-1), 4.19 (d, 1H, $J = 3.0$ Hz), 3.86 (dd, 1H, $J = 2.5$, 12.0 Hz), 3.74 (dd, 1H, $J = 3.0$, 12.5 Hz), 3.57-3.62 (m, 2H), 3.56 (s, 3H), 3.44-3.51 (m, 4H), 2.47 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 172.06, 170.44, 169.09, 152.84, 138.32, 137.91, 137.76, 128.45, 128.41, 128.32, 128.12, 127.84, 127.81, 127.67, 127.64, 105.16, 96.27, 79.95, 78.88, 74.77, 74.25, 73.46, 73.36, 73.02, 72.90, 69.85, 68.00, 67.35, 60.91, 60.39, 57.33, 23.78, 20.66 (2C); HRMS (ESI) Calcd for C$_{41}$H$_{47}$NO$_{14}$+NH$_4^+$ [M + NH$_4^+$]: 795.3335. Found: 795.3336.

**Coupling of 1 with 2e to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-2-O-benzyl-6-O-benzylidene-α-D-glucopyranoside (4e)**

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 4e, yield = 82%. $R_f$ = 0.30 (petroleum ether/ethyl acetate, 1.5:1); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.58-7.60 (m, 2H), 7.32-7.39 (m, 8H), 6.27 (d, 1H, $J = 2.5$ Hz, H-1'), 5.54 (s, 1H), 5.22 (t, 1H, $J = 10.0$ Hz), 4.69 (d, 1H, $J = 3.5$ Hz, H-1), 4.62 (s, 2H), 4.53 (dd, 1H, $J = 10.5$, 12.0 Hz), 4.23-4.29 (m, 2H), 4.18 (td, 1H, $J = 3.0$, 10.0 Hz), 4.06 (s, 2H), 3.78-3.83 (m, 2H), 3.71 (t, 1H, $J = 10.0$ Hz), 3.51-3.56 (m, 2H), 3.38 (s, 3H), 2.40 (s, 3H), 2.05 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$)
Coupling of 1 with 2f to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diaceetyl-2-deoxy-α-D-glucopyranosyl)-(1→2)-3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (4f)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 3:1) to give 4f, yield = 86%. Rf = 0.45 (petroleum ether/ethyl acetate, 1:1); 1H NMR (500 MHz, CDCl3) δ 7.47-7.49 (m, 2H), 7.29-7.39 (m, 8H), 5.76 (d, 1H, J = 3.0 Hz, H-1'), 5.60 (s, 1H), 5.22 (t, 1H, J = 10.0 Hz), 5.03 (d, 1H, J = 10.5 Hz), 4.79 (d, 1H, J = 3.5 Hz, H-1), 4.61 (dd, 1H, J = 10.0, 12.0 Hz), 4.59 (d, 1H, J = 10.5 Hz), 4.31 (dd, 1H, J = 4.5, 10.0 Hz), 3.96-4.00 (m, 2H), 3.67-3.88 (m, 7H), 3.37 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 170.85, 170.44, 168.76, 152.53, 138.11, 137.18, 129.00, 128.40, 128.35, 128.27, 127.91, 125.92, 101.30, 97.27, 93.76, 83.11, 76.15 (2C), 75.29, 74.30, 69.78, 69.13, 67.46, 62.18, 60.57, 59.70, 55.03, 23.55, 20.64; HRMS (ESI) Calcd for C34H39NO14K [M + K]+: 724.2002. Found: 724.2014.

Coupling of 1 with 2g to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α-D-glucopyranosyl)-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-galactopyranoside (4g)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1.5:1) to give 4g, yield = 80%. Rf = 0.30 (petroleum ether/ethyl acetate, 1:2); 1H NMR (500 MHz, CDCl3) δ 7.44-7.47 (m, 2H), 7.30-7.40 (m, 8H), 5.88 (d, 1H, J = 3.0 Hz, H-1'), 5.48 (s, 1H), 5.24 (t, 1H, J = 10.0 Hz), 4.91 (d, 1H, J = 3.5 Hz, H-1), 4.66 (d, 1H, J = 11.0 Hz), 4.61 (d, 1H, J = 11.5 Hz), 4.20-4.30 (m, 4H), 4.04-4.11 (m, 3H), 4.03 (dd, 1H, J = 2.0, 12.5 Hz), 3.93 (dd, 1H, J = 3.5, 12.5 Hz), 3.84 (dd, 1H, J = 2.5, 12.0 Hz), 3.62 (s, 1H), 3.41 (s, 3H), 2.07 (s, 6H), 2.02 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 170.64 (2C), 169.13, 152.66, 137.94, 137.72, 128.97, 128.39, 128.14, 127.94, 126.18, 101.03, 97.60, 93.51, 74.48, 73.95, 73.13, 72.63, 70.65, 69.71, 69.39, 67.77, 62.28, 61.02, 59.89, 55.34, 23.54, 20.62, 20.50; HRMS (ESI) Calcd for C34H39NO14NH4 [M + NH4]+: 703.2709. Found: 703.2702.
Coupling of 1 with 2h to give methyl (N-acetyl-2-amino-2,3-\(N\),O-carbonyl-4,6-diacetyl-2-deoxy-\(\alpha\)-D-glucopyranosyl)-(1\(\rightarrow\)2)-3-O-benzyl-4,6-O-benzylidene-\(\alpha\)-D-galactopyranoside (4h)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 1.5:1) to give 4h, yield = 83%. \(R_f = 0.20\) (petroleum ether/ethyl acetate, 1:1.5); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.52-7.54 (m, 2H), 7.31-7.40 (m, 8H), 5.79 (d, 1H, \(J = 3.0\) Hz, H-1'), 5.51 (s, 1H), 5.16 (t, 1H, \(J = 10.0\) Hz), 4.90 (d, 1H, \(J = 3.5\) Hz, H-1), 4.70 (d, 1H, \(J = 11.0\) Hz), 4.64 (dd, 1H, \(J = 10.5, 12.0\) Hz), 4.49 (d, 1H, \(J = 11.0\) Hz), 4.26-4.32 (m, 3H), 4.10-4.14 (m, 1H), 4.05 (dd, 1H, \(J = 2.0, 12.5\) Hz), 3.93 (dd, 1H, \(J = 3.5, 10.5\) Hz), 3.84 (dd, 1H, \(J = 2.5, 12.0\) Hz), 3.79-3.80 (m, 2H), 3.63 (s, 1H), 3.37 (s, 3H), 2.50 (s, 3H), 2.05 (s, 3H), 1.88 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 170.64 (2C), 169.13, 152.66, 137.94, 137.72, 128.97, 128.39, 128.14, 127.94, 126.18, 101.03, 97.60, 93.53, 74.48, 73.95, 73.13, 72.63, 70.65, 69.71, 69.39, 67.77, 62.28, 61.02, 59.89, 55.34, 23.54, 20.62, 20.50; MS (ESI) 703 [M + NH\(_4\)]\(^+\), 708 [M + Na\(^+\)], 724 [M + K\(^+\)]; Anal. Calcd for C\(_{34}\)H\(_{39}\)NO\(_{14}\): C, 59.56; H, 5.73; N, 2.04. Found: C, 59.70; H, 5.87; N, 1.91.

Coupling of 1 with 2i to give methyl (N-acetyl-2-amino-2,3-\(N\),O-carbonyl-4,6-diacetyl-2-deoxy-\(\beta\)-D-glucopyranosyl)-(1\(\rightarrow\)3)-2-O-benzyl-4,6-O-benzylidene-\(\beta\)-D-glucopyranoside (4i) and (3i)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to give 4i (\(\alpha\)-isomer) and 3i (\(\beta\)-isomer), yield = 87% (\(\alpha\):\(\beta = 1.5:1\)). \(R_f \alpha\)-isomer = 0.35, \(R_f \beta\)-isomer = 0.30 (petroleum ether/ethyl acetate, 1.5:1); 4i \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.58-7.60 (m, 2H), 7.30-7.39 (m, 8H), 6.29 (d, 1H, \(J = 3.0\) Hz, H-1'), 5.56 (s, 1H), 5.21 (t, 1H, \(J = 10.0\) Hz), 4.96 (d, 1H, \(J = 11.0\) Hz), 4.64 (d, 1H, \(J = 11.0\) Hz), 4.50 (dd, 1H, \(J = 10.5, 12.0\) Hz), 4.43 (d, 1H, \(J = 7.5\) Hz, H-1'), 4.38 (dd, 1H, \(J = 5.0, 10.5\) Hz), 4.09 (td, 1H, \(J = 2.5, 9.5\) Hz), 4.00 (t, 1H, \(J = 9.0\) Hz), 3.94-3.96 (m, 2H), 3.76-3.81 (m, 2H), 3.57-3.61 (m, 1H), 3.59 (s, 3H), 3.42 (dt, 1H, \(J = 5.0, 10.0\) Hz), 3.39 (dd, 1H, \(J = 8.0, 9.0\) Hz), 2.39 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 170.51, 170.17, 168.99, 152.82, 137.85, 137.01, 128.94, 128.36, 128.11, 127.94, 127.89, 126.27, 105.26, 101.24, 94.36, 81.64, 80.19, 75.40, 74.70, 74.07, 69.57, 68.61, 67.72, 65.71, 61.13, 60.03, 57.43, 23.66, 20.66, 20.59; MS (ESI) 686 [M + H\(^+\)], 703 [M + NH\(_4\)]\(^+\), 724 [M + K\(^+\)]; Anal.
Calcd for C_{34}H_{39}NO_{14}: C, 59.56; H, 5.73; N, 2.04. Found: C, 59.76; H, 5.90; N, 2.00.

Coupling of 1 with 2j to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α-D-glucopyranosyl)-(1â†’2)-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (4j)

The crude product was purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to give 4j, yield = 84%. Rf = 0.40 (petroleum ether/ethyl acetate, 1.5:1).

Coupling of 1 with 2k to give methyl (N-acetyl-2-amino-2,3-N,O-carbonyl-4,6-diacetyl-2-deoxy-α- and β-D-glucopyranosyl)-(1â†’6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (4k) and (3k)

The residue was purified by column chromatography (petroleum ether/ethyl acetate, 5:1 to 3:1) to give 4k (α-isomer) and 3k (β-isomer), yield = 81% (α:β = 3:1). Rf α-isomer = 0.35, Rf β-isomer = 0.30 (petroleum ether/ethyl acetate, 1:1); 4k ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.38 (m, 18H), 5.78 (d, 1H, J = 3.0 Hz, H-1′), 5.26 (t, 1H, J = 10.0 Hz), 5.01 (d, 1H, J = 11.0 Hz), 4.87 (d, 1H, J = 11.0 Hz), 4.80 (d, 1H, J = 11.0 Hz), 4.77 (d, 1H, J = 13.5 Hz), 4.68 (d, 1H, J = 12.5 Hz), 4.59 (d, 1H, J = 12.5 Hz), 4.50 (dd, 1H, J = 10.5, 12.0 Hz), 4.15 (dd, 1H, J = 2.5, 12.5 Hz), 3.99 (t, 1H, J = 9.0 Hz), 3.84-3.87 (m, 1H), 3.78-3.82 (m, 3H), 3.71 (td, 1H, J = 3.5, 10.0 Hz), 3.52 (dd, 1H, J = 4.0, 10.0 Hz), 3.36 (s, 3H), 3.31 (dd, 1H, J = 8.5, 9.5 Hz), 2.40 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.92, 170.52, 169.10, 152.68, 138.65, 138.03, 137.98, 128.47, 128.43, 128.39, 128.08, 127.90, 127.85, 127.62, 97.81, 95.47, 81.90, 79.73, 75.61, 74.64, 73.93, 73.22, 69.95 (2C), 67.99, 66.90, 61.52, 59.87, 55.20, 23.53, 20.66, 20.62; MS (ESI) 795 [M + NH₄⁺], 800 [M + Na⁺], 816 [M + K⁺]; Anal. Calcd for C_{41}H_{47}NO_{14}: C, 63.31; H, 6.09; N, 1.80. Found: C, 63.51; H, 6.27; N, 1.74.