A New Scaffold for the Stereoselective Synthesis of α -O-Linked Glycopeptide Mimics

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Experimental Section.

General Procedure. Reagents were purchased from commercial suppliers and used without purification. Unless otherwise noted, all air and moisture sensitive reactions were performed under an argon or nitrogen atmosphere. ^1H NMR spectra are obtained at 200 MHz, 300 MHz, 400 MHz and at 600 MHz. Chemical shifts are reported in part per million (δ) relative to CHCl_3 (7.26 ppm) for spectra run in CDCl_3 . ^{13}C NMR spectra were obtained at 50 MHz. Chemical shifts are reported in δ relative to CDCl_3 (77.0 ppm). Melting points are uncorrected.

Benzyl-2-*N*-BOC-5-carbomethoxy-4-oxo-pentanoate (2a). **General Procedure.** To a solution of Meldrum's acid adduct (500 mg, 1.1 mmol) in dry benzene (4 mL) MeOH (1 mL) was added. The reaction mixture was heated at reflux for 5 h. Evaporation of the solvent under reduced pressure gave a crude product which was purified by flash column chromatography on silica gel (hexane/EtOAc/ CH_2Cl_2 2:1:2) to afford **2a** (1.09 g, 85%). Yellowish crystals: Mp. 69-72 °C; ^1H NMR (300MHz): δ 7.36-7.31 (m, 5H), 5.48 (d, J = 8.4 Hz, 1H), 5.15 (s, 2H), 4.49-4.53 (m, 1H), 3.71 (s, 3H), 3.43(s, 2H), 3.31-3.23 (A part of an ABX system, J_{AB} = 18.3 Hz, J_{AX} = 4.4 Hz, 1H), 3.14-3.06 (B part of an ABX system, J_{AB} = 18.3 Hz, J_{BX} = 4.4 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR: δ 201.2, 171.4, 167.5, 156.0, 135.9, 129.2, 129.0, 128.8, 80.8, 68.1, 53.1, 50.3, 49.6, 45.5, 29.0. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_7\text{N}$: C, 60.15; H, 6.64, N, 3.69. Found: C, 60.49; H, 6.50, N, 3.70; MS-ESI (m/z , %): 402.2 [(M+Na), 70], 280.1 (110), 248.1 (75).

Benzyl-2-*N*-BOC-5-carboethoxy-4-oxo-pentanoate (2b). Pale yellow oil, 65%; ^1H -NMR: δ 7.38-7.27 (m, 5H), 5.48 (bd, J = 8.8 Hz, 1H), 5.14 (s, 2H), 4.59-4.51 (m, 1H), 4.21-4.10 (AB system, J_{AB} = 7.0 Hz, 2H), 3.41 (s, 2H), 3.33-3.03 (AB part of an ABX system, J_{AB} = 4.8 Hz, J_{AX} = 18.6 Hz, 2H), 1.40 (bs, 9H), 1.25 (t, J = 7 Hz, 3H); ^{13}C -NMR δ 200.8, 170.9, 166.4, 156.0, 135.2, 128.5, 128.3, 128.1, 80.1, 67.4, 61.5, 49.5, 49.1, 44.7, 28.2, 14.0; Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.11; H, 6.85; N, 3.59.

Benzyl-2-*N*-BOC-5-carbobenzyloxy-4-oxo-pentanoate (2c). Pale yellow crystals, 70%; Mp 64-66 °C; $[\alpha]_{\text{D}}^{20}$ +31.9 (c 0.62, CHCl_3); ^1H -NMR: δ 7.34-7.32 (m, 10H); 5.48 (bd, J = 8.4 Hz, 1H), 5.16 (bs, 4H), 4.55-4.59 (m, 1H), 3.47 (s, 2H), 3.33-3.02 (AB part of an ABX system, J_{AB} = 18.2 Hz, J_{AX} = 4.4 Hz, 2H), 1.42 (s, 9H); ^{13}C NMR: δ 201.5, 170.9, 166.3, 155.4, 135.2, 135.1, 128.6, 128.5, 128.4, 128.3, 128.2, 80.15, 67.4, 67.3, 49.6, 49.1, 44.8, 28.3. Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{NO}$: C, 65.92; H, 6.42; N, 3.08. Found: C, 66.06; H, 6.47; N, 2.81.

Benzyl-2-*N*-BOC-5-carbo-*t*-butoxy-4-oxo-pentanoate (2d). Pale yellow syrup, 65%; $[\alpha]_{\text{D}}^{20}$ +11.9 (c 1.28, CHCl_3); ^1H -NMR: δ 7.25-7.32 (m, 5H); 5.51 (bd, J = 8.8 Hz, 1H), 5.09 (s, 2H), 4.49-

4.53 (m, 1H), 3.28 (s, 2H), 3.28-3.15 (m, 1H), 3.09-2.98 (B part of an ABX system, J_{AB} = 18.0 Hz, J_{BX} = 4.4 Hz, 1H), 1.41 (s, 9H), 1.36 (s, 9H). ^{13}C -NMR: δ 201.5, 170.9, 165.6, 155.4, 135.3, 128.5, 128.2, 128.1, 82.1, 79.9, 67.2, 50.4, 44.5, 49.5, 28.2, 28.1, 27.8, 27.7. Anal. Calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_7$: C, 62.69; H, 7.41; N, 3.32. Found C, 62.74; H, 7.54; N, 3.54.

Benzyl-2-*N*-BOC-5-carbotrimethylsilylethoxy-4-oxo-pentanoate (2e). Yellowish syrup, 84%; $[\alpha]_{\text{D}}^{20}$ +13.4 (c 1.74, CHCl_3); ^1H -NMR: δ 7.29-7.22 (m, 5H); 5.49 (bd, J = 8.4 Hz, 1H), 5.11 (s, 2H), 4.56-4.49 (m, 1H), 4.23-4.09 (m, 2H), 3.37 (s, 2H), 3.30-3.01 (AB part of an ABX system, J_{AB} = 18.4 Hz, J_{AX} = 4.4 Hz, 2H), 1.38 (bs, 9H), 1.01-0.92 (m, 2H), 0.02-0.01 (m, 9H); ^{13}C -NMR: δ 200.9, 170.9, 166.6, 155.4, 135.3, 128.5, 128.3, 128.1, 79.9, 67.3, 63.8, 49.5, 49.2, 44.6, 28.2, 17.2, 1.5. Anal. Calcd for $\text{C}_{23}\text{H}_{35}\text{NO}_7\text{Si}$: C, 59.33; H, 7.58; N, 3.01. Found C, 59.32; H, 7.65; N, 2.75.

1-*O*-2-*S*-[1'-Benzyloxycarbonyl-2'-(4'-*t*-butoxycarbonylamino)-methylpropionate-1'-2'-ethenyl]-3,6-tri-*O*-benzyl- α -D-glucopyranoside (5a). General Procedure. To a solution of **2a** (2.02 g, 5.34 mmol) in washed CHCl_3 (20 mL), freshly distilled pyridine (1 mL, 13.36 mmol) and glycal **6** (2.26 g, 5.44) were added. The reaction mixture was cooled to 0 °C and phthalimidesulfonyl chloride (1.2 g, 5.61 mmol) was added. The solution was heated to 40 °C for 14 h, then cooled to rt, phthalimidesulfonyl chloride (569 mg, 2.67 mmol) and pyridine (216 μL , 2.67 mmol) were added and the mixture was heated to 40 °C for 6 h. Evaporation of the solvent under reduced pressure gave a crude product (4.75 g) which was purified by flash column chromatography on silica gel (hexane/EtOAc 4:1) to afford **5a** (3.00 g, 68%). White solid: Mp 100-102 °C; $[\alpha]_{\text{D}}^{20}$ +116.8 (c 0.54, CHCl_3); ^1H NMR (500 MHz): δ 7.33-7.21 (m, 19H), 7.11-7.10 (m, 1H), 5.46 (d, $J_{1,2}$ = 2.5 Hz, 1H), 5.40 (d, J =8.0 Hz, 1H), 5.10 (s, 2H), 4.84-4.81 (A part of an AB system, J_{AB} = 10.5 Hz, 1H), 4.76-4.74 (A part of an AB system, J_{AB} = 11.0 Hz, 1H), 4.74-4.72 (B part of an AB system, J_{AB} = 10.0 Hz, 1H), 4.60-4.56 (m, 1H), 4.55-4.53 (A part of an AB system, J_{AB} = 12.0 Hz, 1H), 4.49-4.47 (B part of an AB system, J_{AB} = 10.5 Hz, 1H), 4.44-4.41 (B part of an AB system, J_{AB} = 12.5 Hz, 1H), 3.90-3.88 (m, 1H), 3.73-3.66 (m, 2H), 3.70 (s, 3H), 3.61-3.54 (m, 2H), 3.34-3.30 (A part of an ABX system, J_{AB} = 14.0 Hz, J_{AX} = 4.5 Hz, 1H), 3.14-3.09 (m, 1H), 3.13 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 10.5 Hz, 1H), 1.32 (s, 9H); ^{13}C -NMR: δ 171.6, 165.4, 157.1, 155.3, 138.0, 137.7, 135.4, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 97.9, 95.8, 78.2, 78.0, 75.1, 73.5, 73.3, 67.9, 67.2, 52.4, 52.0, 42.4, 35.5, 28.3; Anal. Calcd for $\text{C}_{46}\text{H}_{51}\text{NO}_{11}\text{S}$: C, 66.89; H, 6.22; N, 1.70. Found C, 66.53; H, 6.18; N, 1.82.

1-*O*-2-*S*-[1'-Ethoxycarbonyl-2'-(4'-*t*-butoxycarbonylamino)-benzylpropionate-1'-2'-ethenyl]-3,6-di-*O*-tri-*i*-propylsilyl- α -D-glucopyranoside (5b). Colorless oil, 40%; $[\alpha]_{\text{D}}^{20}$ +50.7 (c 2.4, CHCl_3); ^1H NMR: δ 7.34 (m, 5H), 5.51 (d, $J_{1,2}$ = 3.0 Hz, 1H), 5.39 (bd, J = 7.8 Hz, 1H), 5.15 (bs, 2H), 4.59 (m, 1H), 4.31-3.63 (m, 7H), 3.30-2.27 (m, 2H), 2.96 (dd, $J_{1,2}$ = 3.0 Hz, $J_{2,3}$ = 9.8 Hz,

1H), 1.40 (s, 9H), 1.27 (t, $J = 7$ Hz, 3H), 1.20-0.97 (m, 42H); ^{13}C -NMR: δ 171.8, 165.1, 157.2, 155.9, 135.4, 128.5, 128.3, 128.1, 98.1, 95.9, 80.1, 73.4, 72.9, 71.9, 67.2, 63.9, 61.3, 52.3, 43.4, 35.1, 28.2, 18.3, 18.2, 17.8, 14.1, 12.9, 11.8; Anal. Calcd for $\text{C}_{44}\text{H}_{75}\text{NO}_{11}\text{SSi}_2$: C, 59.90; H, 8.57; N, 1.59. Found: C, 59.76; H, 8.72; N, 1.58.

1-O-2-S-[1'-Benzyloxycarbonyl-2'-(4'-*t*-butoxycarbonylamino)-benzylpropionate-1'-2'-ethenyl]-3,6-tri-O-benzyl- α -D-glucopyranoside (5c). White solid, 50%; Mp 125-127 °C; $[\alpha]_{\text{D}}^{20} +72$ (c 1.28, CHCl_3); ^1H -NMR: δ 7.34-7.18 (m, 25H), 5.57 (d, $J_{1,2}=2.6$ Hz, 1H), 5.48 (bd, $J = 8.0$ Hz, 1H), 5.31-5.16 (AB system, $J_{\text{AB}} = 12.4$ Hz, 2H), 5.16 (s, 2H), 4.90-4.47 (m, 7H), 3.99-3.95 (m, 1H), 3.84-3.62 (m, 4H), 3.45- 3.28 (m, 2H), 3.20 (dd, $J_{1,2} = 2.6$ Hz, $J_{2,3}=10.2$ Hz, 1H), 1.39 (s, 9H); ^{13}C NMR: δ 171.6, 164.8, 157.6, 155.3, 138.4, 137.9, 137.7, 135.6, 135.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 97.6, 95.9, 79.9, 78.1, 77.9, 76.5, 75.1, 73.5, 67.9, 67.2, 66.9, 73.4, 52.1, 42.3, 35.4, 28.3. Anal. Calcd for $\text{C}_{52}\text{H}_{55}\text{NO}_{11}\text{S}$: C, 69.24; H, 6.15; N, 1.55. Found: C, 68.72; H, 6.20; N, 1.27.

1-O-2-S-[1'-Trimethylsilylethoxycarbonyl-2'-(4'-*t*-butoxycarbonylamino)-methylpropionate-1'-2'-ethenyl]-3,6-tri-O-benzyl- α -D-glucopyranoside (5e). Colorless oil, 35%; $[\alpha]_{\text{D}}^{20} +69.9$ (c 0.6, CHCl_3); ^1H -NMR (400 MHz): δ 7.38 (m, 20H); 5.51 (m, 2H, H-1), 5.15 (bs, 2H), 5.89-4.86 (A part of an AB system, $J_{\text{AB}}=10.8$ Hz, 1H), 4.81-4.76 (AB system, $J_{\text{AB}}=11.2$ Hz, 2H), 4.61 (m, 1H), 4.60-4.57 (A part of an AB system, $J_{\text{AB}}=12.0$ Hz, 1H), 4.54-4.52 (B part of an AB system, $J_{\text{AB}}=10.8$ Hz, 1H), 4.48-4.45 (B part of an AB system, $J_{\text{AB}}=12.0$ Hz, 1H), 4.26-4.22 (m, 2H), 3.94-3.92 (m, 1H), 3.77-3.58 (m, 4H), 3.37-3.32 (A part of an ABX system, $J_{\text{AB}}=4.0$ Hz, $J_{\text{AX}}=15.2$ Hz, 1H), 3.22-3.18 (m, 1H), 3.17 (dd, $J_{1,2}=6.4$ Hz, $J_{2,3}=10.4$ Hz, 1H), 1.36 (s, 9H), 1.06-1.01 (m, 2H), 0.04 (s, 9H); ^1H -NMR (C_6D_6): δ 7.47-6.98 (m, 20H), 5.89 (bd, $J=8.4$ Hz, 1H), 5.32 (d, $J_{1,2}=2.6$ Hz, 1H), 5.11-5.05 (A part of an AB system, $J_{\text{AB}}=11.5$ Hz, 1H), 4.97-4.91 (m, 3H), 4.93-4.88 (B part of an AB system, $J_{\text{AB}}=11.5$ Hz, 1H), 4.85-4.79 (A part of an AB system, $J_{\text{AB}}=11.2$ Hz, 1H), 4.63-4.57 (B part of an AB system, $J_{\text{AB}}=11.2\text{Hz}$, 1H), 4.38-4.32 (A part of an AB system, $J_{\text{AB}}=12.0$ Hz, 1H), 4.26-4.20 (B part of an AB system, $J_{\text{AB}}=12.0$ Hz, 1H), 4.13-3.99 (m, 3H), 3.89-3.16 (m, 6H), 2.41 (dd, $J_{1,2}=2.6\text{Hz}$; $J_{2,3}=10.4$ Hz, 1H), 1.39-1.33 (m, 9H), 0.88-0.79 (m, 2H), -0.11-0.19 (m, 9H); ^{13}C -NMR: δ 171.7, 165.2, 156.7, 155.4, 138.1, 138.0, 137.7, 135.4, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 98.3, 95.8, 79.9, 78.2, 76.5, 75.1, 73.5, 67.9, 67.2, 73.3, 64.1, 52.1, 42.4, 35.3, 28.4, 17.3, -1.45. MS-ESI (m/z, %): 934.3[(M+Na) $^+$, 80]; 579.3(55); 317.2(100). Anal. Calcd for $\text{C}_{50}\text{H}_{61}\text{NO}_{11}\text{SSi}$: C, 65.84; H, 6.74; N, 1.54. Found C, 65.91; H, 6.50; N, 2.00.

1-O-2-S-[1'-Methoxycarbonyl-2'-(4'-*t*-butoxycarbonylamino)-benzylpropionate-1'-2'-ethenyl]-3,6-tri-O-benzyl- α -D-galattopyranoside (5f). Colorless oil, 52%; ^1H -NMR (400 MHz): δ

7.40-7.24 (m, 20H), 5.58 (d, $J_{1,2}$ =2.0 Hz, 1H), 5.42 (bd, J = 8.0 Hz, 1H), 5.13 (s, 2H), 4.89-4.86 (A part of an AB system, J_{AB} = 11.2 Hz, 1H), 4.67 (s, 2H), 4.66-4.60 (m, 1H), 4.56-4.53 (B part of an AB system, J_{AB} = 11.2 Hz, 1H), 4.53-4.40 (AB system, J_{AB} = 11.6 Hz, 2H), 4.17-4.15 (m, 1H), 3.98 (bs, 1H), 3.75 (m, 3H), 3.71-3.53 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 10.8 Hz, 1H), 3.65-3.53 (m, 3H), 3.29-3.18 (m, 2H), 1.39 (bs, 9H); $^1\text{H-NMR}$ (C_6D_6): δ 7.44-6.76 (m, 20H), 5.66 (bd, J = 8.4 Hz, 1H), 5.43 (d, $J_{1,2}$ = 2.6 Hz, 1H), 5.06-4.99 (A part of an AB system, J_{AB} =12.4 Hz, 1H), 4.94-4.88 (m, 1H), 4.77-4.81 (A part of an AB system, J_{AB} = 11.4 Hz, 1H), 4.71-4.65 (B part of an AB system, J_{AB} = 12.4 Hz, 1H), 4.65-4.59 (B part of an AB system, J_{AB} = 11.6 Hz, 1H), 4.56-4.50 (B part of an AB system, J_{AB} = 11.4 Hz, 1H), 4.41-4.17 (m, 3H), 4.06 (m, 1H), 3.85-3.46 (m, 5H), 3.20 (s, 3H), 3.06-3.01 (m, 1H), 1.39 (s, 9H); $^{13}\text{C-NMR}$: δ 171.2, 165.2, 156.6, 155.5, 137.8, 137.5, 137.4, 135.0, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.2, 97.6, 96.3, 79.7, 74.6, 72.7, 68.2, 66.9, 74.3, 73.1, 71.5, 52.1, 51.8, 38.4, 35.0, 28.1.

Glucopyranoside 9. To a solution of TMSCl (4M in CH_2Cl_2 , 1.0 mL) and phenol (4M in CH_2Cl_2 , 3.0mL) compound **5a** (275 mg, 0.33 mmol) was added. After 1 h at rt the reaction mixture was diluted with CH_2Cl_2 , washed with a saturated solution of NaHCO_3 and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave a crude product **9** (230 mg, >90%) which was used without any other purification.

Compound 12. White solid. Mp 164-167 °C; $[\alpha]_{\text{D}}^{20}$ +41.6 (c 0.19, CHCl_3); $^1\text{H NMR}$ (600 MHz): δ 7.32-7.18 (m, 17H), 7.09-7.08 (m, 3H), 5.92 (s, 1H), 5.50 (d, $J_{1,2}$ = 2.4 Hz, 1H), 5.18-5.16 (A part of an AB system, J_{AB} = 12.6 Hz, 1H), 5.14-5.12 (B part of an AB system, J_{AB} = 12.6 Hz, 1H), 4.88-4.86 (AB system, J_{AB} = 12.0 Hz, 2H), 4.78-4.76 (A part of an AB system, J_{AB} = 10.8 Hz, 1H), 4.73-4.71 (B part of an AB system, J_{AB} = 10.2 Hz, 1H), 4.56-4.54 (A part of an AB system, J_{AB} = 12.0 Hz, 1H), 4.47-4.45 (B part of an AB system, J_{AB} = 12.0 Hz, 1H), 4.16-4.12 (m, 1H), 3.94-3.91 (m, 1H), 3.71-3.68 (m, 2H), 3.63-3.61 (A part of an ABX system, J_{AB} = 10.8 Hz, J_{BX} = 1.8 Hz 1H), 3.58 (dd, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 9.0 Hz, 1H), 3.21 (dd, $J_{1,2}$ = 2.4 Hz, $J_{2,3}$ = 10.8 Hz, 1H), 2.71 (d, J = 10.2 Hz, 2H); $^{13}\text{C NMR}$: δ 169.1; 168.2, 164.8, 137. 6, 137.5; 97.7, 96.2, 78.3, 77.1, 76.2, 75.3, 73.5, 67.8; 73.2, 51.4, 42.3, 30.8; Anal. Calcd for $\text{C}_{40}\text{H}_{39}\text{NO}_8\text{S}$: C, 69.20 H, 5.70; N, 2.00. Found: C, 69.20; H, 5.50; N, 2.40.

Glucodipeptide 10. To a solution of *N*-Cbz-L-Phe (129 mg, 0.43 mmol) in dry DMF (1.5 mL), HOBT (29 mg, 0.66 mmol), EDCI (127 mg, 0.66 mmol) and DIPEA (0.173 mL, 0.99 mmol) were added at rt. After 10 minutes a solution of **9** (400 mg, 0.55 mmol) in DMF (1 mL) was added. The reaction mixture was stirred for 2 h, then it was diluted with CH_2Cl_2 , washed with a saturated solution of NH_4Cl , washed with water and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave a crude product (2 g) which was purified by flash column chromatography

on silica gel (hexane/EtOAc 2:1) to afford **10** (229 mg, 69%) as a white solid. Mp. 183-184 °C; $[\alpha]_D^{20} +86.2$ (*c* 0.42, CHCl₃); ¹H NMR (600 MHz): δ 7.38-7.16 (m, 30H), 6.97 (d, *J* = 5.6 Hz, 1H), 5.53 (d, *J* = 7.2 Hz, 1H), 5.31 (s, 1H), 5.22-5.20 (A part of an AB system, *J*_{AB} = 12.0 Hz, 1H), 5.14-5.13 (B part of an AB system, *J*_{AB} = 12.0 Hz, 1H), 5.09-5.08 (A part of an AB system, *J*_{AB} = 12.0 Hz, 1H), 4.99-4.97 (B part of an AB system, *J*_{AB} = 12.8 Hz, 1H), 4.91-4.90 (AB system, *J*_{AB} = 10.4 Hz, 2H), 4.83-4.81 (A part of an AB system, *J*_{AB} = 10.4 Hz, 1H), 4.79-4.78 (B part of an AB system, *J*_{AB} = 10.4 Hz, 1H), 4.54-4.43 (m, 4H), 3.93-3.91 (m, 1H), 3.77-3.74 (m, 1H), 3.69 (s, 3H), 3.66-3.65 (m, 1H), 3.64-3.61 (m, 1H), 3.54-3.53 (m, 1H), 3.48 (dd, *J*_{1,2} = 4.0 Hz, *J*_{2,3} = 13.6 Hz, 1H), 3.21-3.20 (m, 1H), 3.11-3.09 (A part of an ABX system, *J*_{AB} = 13.6 Hz, *J*_{AX} = 6.4 Hz, 1H), 3.05-3.03 (B part of an ABX system, *J*_{AB} = 13.6 Hz, *J*_{BX} = 4.8 Hz, 1H), 2.94-2.91 (m, 1H); ¹³C NMR: δ 170.5, 170.3, 156.6, 137.9, 137.8, 137.6, 136.4, 136.2, 135.2, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7; 98.8, 95.6, 78.5, 78.0, 76.4, 75.1, 73.4, 67.8, 67.3, 66.9; 73.3, 56.1; 52.6, 51.3, 42.5, 35.4, 29.7; Anal. Calcd for C₅₈H₅₈O₁₂N₂S: C, 69.17; H, 5.80, N, 2.78. Found: C, 69.33; H, 5.75, N, 2.59.

Glucodipeptide 11. To a solution of *N*-Fmoc-(*N*-BOC)-L-Trp (166 mg, 0.32 mmol) in dry DMF (1.5 mL), HOBt (65 mg, 0.49 mmol), EDCI (93 mg, 0.49 mmol) and DIPEA (126 μL, 0.73 mmol) were added at rt. After 10 minutes a solution of **9** (380 mg, 0.52 mmol) in DMF (1 mL) was added. The reaction mixture was stirred for 2 h, then it was diluted with CH₂Cl₂, washed with a saturated solution of NH₄Cl, washed with water and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product (1.7 g) which was purified by flash column chromatography on silica gel (hexane/EtOAc 2:1) to afford **11** (213 mg, 73%) as a white solid. Mp 147-148 °C; $[\alpha]_D^{20} -85.6$ (*c* 0.16, CHCl₃); ¹H NMR (CD₂Cl₂): δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.61-6.86 (m, 33H), 5.91 (d, *J* = 11.6 Hz, 1H), 5.45 (d, *J*_{1,2} = 2.2 Hz, 1H), 5.28-5.22 (A part of an AB system, *J*_{AB} = 12.4 Hz, 1H), 5.19-5.12 (B part of an AB system, *J*_{AB} = 12.4 Hz, 1H), 4.92-4.97 (A part of an AB system, *J*_{AB} = 10.6 Hz, 1H), 4.89-4.84 (B part of an AB system, *J*_{AB} = 8.0 Hz, 1H), 4.85-4.79 (B part of an AB system, *J*_{AB} = 10.6 Hz, 1H), 4.83-4.79 (B part of an AB system, *J*_{AB} = 8.0 Hz, 1H), 4.71-4.63 (A part of an AB system, *J*_{AB} = 15.6 Hz, 1H), 4.58-4.50 (B part of an AB system, *J*_{AB} = 15.6 Hz, 1H), 4.56-4.50 (A part of an ABX system, *J*_{AB} = 12.0 Hz, 1H), 4.47-4.41 (B part of an ABX system, *J*_{AB} = 12.0 Hz, 1H), 4.47-4.36 (m, 1H), 4.30-4.26 (A part of an AB system, *J*_{AB} = 7.4 Hz, 1H), 4.01-3.97 (m, 1H), 3.80-3.44 (m, 5H), 3.63 (s, 3H), 3.29-3.18 (m, 2H), 3.21 (dd, *J*_{1,2} = 2.4 Hz, *J*_{2,3} = 10.2 Hz, 1H), 3.08-2.97 (m, 1H), 1.63 (s, 9H); ¹³C NMR: δ 170.8, 170.3; 168.2, 165.6, 156.3; 155.8, 149.6, 143.7, 141.2, 137.8, 137.6, 135.4, 135.2, 134.2, 132.6; 130.3, 128.5, 128.3, 128.2, 128.15, 127.9, 127.8, 127.7, 127.69, 127.6, 125.1, 124.3, 123.5, 122.6, 120.3, 119.8, 119.0, 115.3; 98.8, 95.6, 83.4, 78.3, 77.9, 76.2, 75.0, 73.3, 73.2, 67.7, 67.30, 67.29; 54.6, 52.6, 51.3, 47.0,

42.4, 35.3, 28.1. Anal. Calcd for C₇₂H₇₁N₃O₁₄S: C, 70.06 H, 5.80; N, 3.40 Found: C, 70.17 H, 5.83; N, 3.45.

1-O-2-S-[1'-Hydroxycarbonyl-2'-(4'-*t*-butoxycarbonylamino)-benzylpropionate-1'-2'-ethenyl]-3,4,6-tri-*O*-benzyl- α -D-glucopyranoside (13**).** To a solution of **5e** (170 mg, 0.186 mmol) in dry THF (5 mL) a solution of TBAF (97 mg, 0.373 mmol) in THF (1 mL) was added at 0 °C. The reaction mixture was warmed to rt and stirred for 3 h, then it was diluted with CH₂Cl₂, washed with a saturated solution of NH₄Cl and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product (350 mg) which was purified by flash column chromatography on silica gel (hexane/EtOAc/CH₂Cl₂ 1:2:1) to afford **13** (98 mg, 65%) as a colorless oil. $[\alpha]_D^{20} +78.8$ (c 0.9, CHCl₃); ¹H-NMR: δ 7.35-7.15 (m, 20H), 5.58-5.42 (m, 2H), 5.14 (s, 2H), 4.89-4.85 (A part of an AB system, J_{AB} =10.4 Hz, 1H), 4.78-4.63 (m, 1H), 4.74-4.69 (B part of an AB system, J_{AB} =10.4 Hz, 1H), 4.57 (s, 2H), 4.57-4.44 (AB system, J_{AB} =11.6 Hz, 2H), 3.90 (m, 1H), 3.76-2.99 (m, 7H), 1.39 (s, 9H); Anal. Calcd for C₄₅H₄₉NO₁₁S: C, 66.57; H, 6.08; N, 1.73. Found C, 66.46; H, 5.95; N, 1.64.

Glucodipeptide 14. To a solution of **13** (120 mg, 0.148 mmol) in dry DMF (3 mL), HOBt (20 mg, 0.148 mmol), EDCI (30 mg, 0.149 mmol) and DIPEA (0.06 mL) were added at rt. The reaction mixture was stirred for 15 minutes and then *O*-*t*-butyl-L-Tyr-*t*-butyl esterHCl (60 mg, 0.177 mmol) was added. After 2 h at rt the reaction mixture was diluted with CH₂Cl₂, washed with a saturated solution of NH₄Cl, washed with a saturated solution of NaHCO₃ and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product (300 mg) which was purified by flash column chromatography on silica gel (hexane/EtOAc 1:1) to afford **14** (135 mg, 84%) as a colorless oil. $[\alpha]_D^{20} +73.8$ (c 0.63, CHCl₃); ¹H-NMR (400 MHz): δ 7.33-7.19 (m, 18H), 7.11-7.01 (m, 2H), 6.99-6.83 (AA'MM' system, J_{AM} = 8.4 Hz, 4H), 6.61 (bd, J = 7.6 Hz, 1H), 6.28 (bd, J = 6.8 Hz, 1H), 5.45 (d, $J_{1,2}$ = 2.8 Hz, 1H), 5.15-5.07 (AB system, J_{AB} = 12.0 Hz, 2H), 4.82-4.77 (AB system, J_{AB} =11.2 Hz, 2H), 4.78-4.75 (A part of an AB system, J_{AB} = 11.6 Hz, 1H), 4.68-4.64 (m, 1H), 4.55-4.52 (A part of an AB system, J_{AB} = 12.0 Hz, 1H), 4.51-4.48 (B part of an AB system, J_{AB} = 11.6 Hz, 1H) 4.45 (m, 1H), 4.43-4.40 (B part of an AB system, J_{AB} = 12.0 Hz, 1H), 3.87-3.85 (m, 1H), 3.76-3.71 (t, $J_{3,4}$ =9.2 Hz, 1H), 3.68-3.65 (A part of an ABX system, J_{AB} = 3.2 Hz, J_{AX} = 10.8 Hz, 1H), 3.61-3.56 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 9.2 Hz, 1H), 3.51-3.48 (A part of an ABX system, J_{AB} = 3.2 Hz, J_{BX} = 10.8 Hz, 1H), 3.16-3.13 (dd, $J_{1,2}$ = 2.8 Hz, $J_{2,3}$ = 10.4 Hz, 1H), 3.14-2.98 (m, 2H), 3.06-2.93 (AB part of an ABX system, J_{AB} = 6.0 Hz, J_{AX} = 14.0 Hz, 2H), 1.33-1.22 (m, 27H); ¹H-NMR (C₆D₆): δ 7.42-6.67 (m, 24H); 6.68 (bd, J = 7.2 Hz, 1H), 6.15 (bs, 1H), 5.23 (d, $J_{1,2}$ =3.2 Hz, 1H), 5.15-4.96 (AB system, J_{AB} =13.0 Hz, 2H), 4.94-4.88 (A part of an AB system, J_{AB} = 11.0 Hz, 1H), 4.83-4.69 (m, 4H), 4.55-4.49 (B part of an AB system, J_{AB} = 11.4 Hz, 1H),

4.31-4.12 (AB system, J_{AB} = 12.0 Hz, 2H), 3.93 (m, 1H), 3.75-3.07 (m, 6H), 2.93-2.74 (AB part of an ABX system, J_{AB} = 6.0 Hz, J_{AX} = 13.0 Hz, 2H), 2.58-2.51 (dd, $J_{1,2}$ = 3.2 Hz, $J_{2,3}$ = 10.0 Hz, 1H), 1.32 (s, 9H), 1.11 (s, 9H), 1.10 (s, 9H, *t*-Bu); ^{13}C -NMR: δ 171.7, 170.1, 164.3, 154.4, 153.2, 138.0, 137.9, 137.7, 135.7, 130.8, 129.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 124.2, 98.5, 95.4, 82.5, 79.6, 78.3, 76.6, 75.1, 73.5, 67.8, 66.9, 73.2; 54.2, 52.7, 41.9, 37.0, 34.8, 28.8, 27.9. Anal. Calcd for $\text{C}_{62}\text{H}_{74}\text{N}_2\text{O}_{12}\text{S}$: C, 69.51; H, 6.96; N, 2.61. Found C, 69.67; H, 7.10; N, 2.49.

Acetyl derivative 15. To a solution of **5a** (780 mg, 0.94 mmol) in dry Ac_2O (8 mL) a solution of TMSOTf (700 μL) in dry Ac_2O (3 mL) was slowly added under magnetic stirring at -40°C . The reaction mixture was kept at -40°C for 1.5 h, then warmed to 0°C and treated with a saturated solution of NaHCO_3 . The mixture was diluted with CH_2Cl_2 , washed with a saturated solution of NaHCO_3 until neutrality and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave a crude product (1.1 g) which was purified by flash column chromatography on silica gel (hexane/EtOAc 1:1) to afford **15** (533 mg, 77%) as a white solid. Mp $94\text{--}95^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} +128.7$ (c 0.71, CHCl_3); ^1H -NMR (400 MHz, C_6D_6): δ 7.43-7.03 (m, 15H), 6.24 (bd, J = 8.0 Hz, 1H), 5.27 (d, $J_{1,2}$ = 2.8 Hz, 1H), 5.25-5.20 (m, 1H), 5.08-5.06 (A part of an AB system, J_{AB} = 12.0 Hz, 1H), 5.06-5.03 (A part of an AB system, J_{AB} = 8.8 Hz, 1H), 5.02-4.99 (B part of an AB system, J_{AB} = 12.0 Hz, 1H), 4.86-4.83 (B part of an AB system, J_{AB} = 10.4 Hz, 1H), 4.82-4.79 (A part of an AB system, J_{AB} = 11.2 Hz, 1H), 4.55-4.52 (B part of an AB system, J_{AB} = 11.2 Hz, 1H), 4.41-4.37 (A part of an ABX system, J_{AB} = 12.0 Hz, J_{AX} = 2.0 Hz, 1H), 4.28-4.23 (B part of an ABX system, J_{AB} = 12.4 Hz, J_{BX} = 4.8 Hz, 1H), 4.20-4.17 (m, 1H), 3.85 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 9.2 Hz, 1H), 3.42 (t, $J_{3,4}$ = 9.2 Hz, 1H), 3.39-3.33 (A part of an ABX system, J_{AB} = 14.0 Hz, J_{AX} = 8.8 Hz, 1H), 3.28 (s, 3H), 3.29-3.24 (B part of an ABX system, J_{AB} = 14.0 Hz, J_{BX} = 8.8 Hz, 1H), 2.67 (dd, $J_{2,3}$ = 10.4 Hz, $J_{1,2}$ = 2.8 Hz, 1H), 1.63 (s, 3H), 1.57 (s, 3H); ^1H -NMR: δ 7.40-7.30 (m, 15H); 6.56 (bd, J = 8.2 Hz, 1H), 5.49 (d, $J_{1,2}$ = 2.6 Hz, 1H), 5.29-5.22 (A part of an AB system, J_{AB} = 12.4 Hz, 1H), 5.19-5.13 (B part of an AB system, J_{AB} = 12.0 Hz, 1H), 4.99-4.80 (m, 4H), 4.66-4.61 (B part of an AB system, J_{AB} = 11.2 Hz, 1H), 4.28-4.26 (m, 2H), 4.08-4.03 (m, 1H), 3.81 (s, 3H), 3.75-3.60 (m, 2H), 3.49-3.40 (A part of an ABX system, J_{AB} = 14.2 Hz, J_{AX} = 4.6 Hz, 1H), 3.24-3.13 (m, 2H), 2.02 (s, 3H), 2.01 (s, 3H); ^{13}C -NMR (C_6D_6): δ 170.6, 168.8, 168.2, 164.9, 156.8, 137.8, 137.4, 135.1, 97.4 ($\text{SC}=\text{CO}$), 95.1, 77.5, 77.4, 71.3, 75.4, 73.9, 66.3, 61.8, 51.0, 50.2, 41.7, 34.9, 21.6, 19.4; Anal. Calcd for $\text{C}_{38}\text{H}_{41}\text{NO}_{11}\text{S}$: C, 63.41; H, 5.74; N, 1.95. Found C, 63.66; H, 5.59; N, 2.20.

Glucopyranoside 16. To a solution of **15** (415 mg, 0.58 mmol) in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ 10:1 (6 mL) a solution of MeONa (1M, MeOH) (0.2 eq) was added under magnetic stirring at 0°C . The reaction mixture was warmed to r.t., stirred for 3 h at this temperature, then neutralized with HCl 10% in MeOH . Evaporation of the solvent under reduced pressure gave a crude product (600 mg)

which was purified by flash column chromatography on silica gel (hexane/EtOAc 1:1) to afford **16** (323 mg, 86%) as a colorless oil. ¹H-NMR: δ 7.35-7.24 (m, 10H, Ph), 6.58 (bd, *J* = 7.4 Hz, 1H), 5.49 (d, *J*_{1,2} = 2.4 Hz, 1H), 4.92-4.82 (m, 3H), 4.77-4.66 (AB system, *J*_{AB} = 11.4 Hz, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.75-3.52 (m, 5H), 3.42-3.32 (A part of an ABX system, *J*_{AB} = 4.8 Hz, *J*_{AX} = 14.4 Hz, 1H), 3.17-3.05 (m, 2H), 2.04 (bs, 1H), 1.96 (s, 3H); ¹H-NMR (C₆D₆): δ 7.39-7.03 (m, 10H); 6.77 (bd, *J* = 8.2 Hz, 1H), 5.46 (d, *J*_{1,2} = 2.6 Hz, 1H), 5.16-5.06 (m, 1H), 5.01-5.96 (A part of an AB system, *J*_{AB} = 12.0 Hz, 1H), 4.95-4.73 (AB system, *J*_{AB} = 18.8 Hz, 2H), 4.73-4.67 (B part of an AB system, *J*_{AB} = 12.0 Hz, 1H), 3.98-3.63 (m, 5H), 3.35 (s, 3H), 3.31 (m, 2H), 3.27 (s, 3H), 3.12 (m, 1H), 2.88 (dd, *J*_{2,3} = 10.2, *J*_{1,2} = 2.6 Hz, 1H), 1.67 (s, 3H); ¹³C-NMR: δ 171.8, 169.9, 165.7, 156.9, 137.8, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 98.3, 95.7 (C-1), 77.7, 76.4, 76.3, 74.9, 74.0, 61.2, 52.6, 52.5, 50.7, 42.5, 35.3, 23.0; Anal. Calcd for C₃₀H₃₅NO₁₀S: C, 59.89; H, 5.86; N, 2.33. Found C, 59.59; H, 5.98; N, 2.29.

Disaccharide 18. A solution of **16** (183 mg, 0.304 mmol) in freshly distilled CH₂Cl₂ (3 mL) was added to a solution of **17** (257 mg, 0.522 mmol) in freshly distilled Et₂O (10 mL). The reaction mixture was cooled to -5 °C and treated with trimethylsilyltriflate (11.0 μL, 0.061 mmol). After 15 min the bath was removed and the reaction mixture stirred at room temperature for 1 h. Few drops of pyridine were then added and the organic solvents removed under vacuum. The crude (556 mg) obtained as mixture of two anomers (β/α = 5/1) was purified by flash column chromatography on silica gel (hexane / EtOAc 1:5) to afford **18** (65%) as a glassy solid; (β anomer: 103 mg, 36%; α+β anomer: 81 mg, 29 %). ¹H-NMR: δ 7.34-7.26 (m, 10H), 6.55 (d, *J* = 7.6 Hz, 1H), 5.50 (d, *J* = 2.8 Hz, 1H), 5.19-5.01 (m, 3H), 4.87-4.73 (m, 3H), 4.59-4.49 (m, 2H), 4.23-4.19 (m, 1H), 4.12-4.06 (m, 2H), 3.94-3.91 (m, 1H), 3.80 (dd, *J* = 3.2 Hz, *J* = 10.8 Hz, 1H), 3.76- 3.60 (m, 11H), 3.28-3.14 (m, 3H), 2.03 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.93 (s, 6H); ¹³C-NMR: δ 176.5, 175.3, 174.9, 174.6, 174.0, 173.7, 170.5, 161.7, 142.6, 142.5, 133.2, 133.1, 132.9, 132.6, 132.2, 105.2, 102.8, 100.6, 82.6, 82.4, 82.0, 81.8, 81.2, 81.0, 79.5, 76.0, 73.0, 72.1, 66.7, 57.2, 55.4, 46.9, 40.0, 27.7, 25.4, 25.3, 25.2; Anal. Calcd for C₄₄H₅₃NO₁₉S: C, 56.71; H, 5.73; N, 1.50. Found C, 56.40; H, 5.36; N, 1.43.

Glucopyranoside 19. To a solution of **2e** (1.14 g, 2.45 mmol) in CHCl₃ (12 mL) washed the glucal **7** (1.23 g, 2.70 mmol) and pyridine (0.5 mL, 6.15 mmol) were added. The reaction mixture was cooled at 0 °C and phthalimidesolfenyl chloride (575 mg, 2.70 mmol) was added. The solution was heated at 50 °C for 18 h, then cooled to rt and phthalimidesolfenyl chloride (290 mg, 1.35 mmol) and pyridine (0.1 mL, 1.20 mmol) were added and the mixture was heated again at 55 °C for 22 h. The reaction mixture was diluted with CH₂Cl₂, washed with a saturated solution of NH₄Cl and dried over Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude

product (4.5 g) which was purified by flash column chromatography on silica gel (hexane/EtOAc 19:1) to afford **19** (935 mg, 40%) as a pale yellow oil. $[\alpha]_D^{20} +48.6$ (c 1.91, CHCl_3); $^1\text{H-NMR}$: δ 7.33-7.20 (m, 5H), 5.50 (d, $J_{1,2} = 2.8$ Hz, 1H), 5.37 (bd, 1H), 5.14 (bd, 2H), 4.57 (m, 1H), 4.25-4.15 (m, 2H), 4.04-3.97 (m, 1H), 3.85-3.65 (m, 4H), 3.29-3.26 (m, 2H), 2.95 (dd, $J_{1,2} = 2.8$ Hz, $J_{2,3} = 9.8$ Hz, 1H), 2.68 (bs, 1H), 1.39 (s, 9H), 1.13-0.92 (m, 44H), 0.05 (s, 9H); $^{13}\text{C-NMR}$: δ 171.8, 165.3, 157.2, 155.8, 135.4, 128.5, 128.2, 128.1, 127.9, 98.1, 95.9, 80.1, 73.3, 72.9, 71.9, 67.1, 63.7, 52.1, 43.5, 34.9, 28.2, 17.8, 17.6, 17.5, 17.3, 13.5, 12.9, 12.2, 11.8, -1.6; Anal. Calcd for $\text{C}_{47}\text{H}_{83}\text{NO}_{11}\text{SSi}_3$: C, 59.14; H, 8.76; N, 1.47. Found C, 59.29; H, 9.07; N, 1.31.

Glucopyranoside 20. To a solution of TMSCl (4 M in CH_2Cl_2 , 4.8 mL) and phenol (4M in CH_2Cl_2 , 9.2 mL) compound **19** (850 mg, 0.90 mmol) was added. After 1.5 h at rt the reaction mixture was diluted with CH_2Cl_2 , washed with a saturated solution of NaHCO_3 and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave a crude product **22** (230 mg, >90%) which was used without any other purification. To a solution of **22** (620 mg, 0.90 mmol) in dry CH_2Cl_2 (10 mL) biphenyl-4-yl-acetyl chloride (250 mg, 1.07 mmol) and freshly distilled NEt_3 (0.185 mL, 1.35 mmol) were added at rt. After 1 h the reaction mixture was diluted with CH_2Cl_2 , washed with a saturated solution of NaHCO_3 and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave a crude product (900 mg) which was purified by flash column chromatography on silica gel (hexane/EtOAc 1:1) to afford **20** (390 mg, 50%) as a pale yellow oil. $[\alpha]_D^{20} +34.6$ (c 0.31, CHCl_3); $^1\text{H-NMR}$ (400 MHz): δ 7.59-7.29 (m, 14H), 6.25 (bd, $J = 8.4$ Hz, 1H), 5.45 (s, $J_{1,2} = 2.8$ Hz, 1H), 5.12 (s, 2H), 4.99-4.94 (m, 1H), 4.20-4.10 (m, 2H), 3.95-3.91 (m, 1H), 3.83-3.82 (m, 1H), 3.74 (dd, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 8.0$ Hz, 1H), 3.64-3.55 (AB system, $J_{AB} = 16.0$ Hz, 2H), 3.56 (m, 1H), 3.37-3.17 (m, 4H), 2.96 (dd, $J_{1,2} = 2.8$ Hz, $J_{2,3} = 10.0$ Hz, 1H), 2.92-2.90 (m, 1H), 1.10 (m, 21H), 1.00-0.89 (m, 2H), 0.04 (s, 9H); $^{13}\text{C-NMR}$: δ 171.5, 170.9, 165.3, 156.8, 140.6, 140.2, 135.1, 132.9, 129.9, 128.8, 128.4, 128.2, 127.5, 127.4, 127.0, 98.4, 95.7, 73.4, 72.6, 67.4, 63.8, 62.2, 50.8, 43.7, 43.1, 35.2, 18.4, 17.3, 13.1, -1.5; Anal. Calcd for $\text{C}_{47}\text{H}_{65}\text{NO}_{10}\text{SSi}_2$: C, 63.27; H, 7.34; N, 1.57. Found C, 63.42; H, 7.42; N, 1.35.

Glucopyranoside 21. To a solution of **22** (for the preparation see above) (250 mg, 0.35 mmol) in dry CH_2Cl_2 (7 mL) naphthalene-2-yl-acetyl chloride (82 mg, 0.40 mmol) and freshly distilled NEt_3 (0.074 mL, 0.52 mmol) were added at rt. After 2 h the reaction mixture was diluted with CH_2Cl_2 , washed with a saturated solution of NaHCO_3 and dried over Na_2SO_4 . Evaporation of the solvent under reduced pressure gave a crude product (450 mg) which was purified by flash column chromatography on silica gel (hexane/EtOAc 1:1) to afford **21** (130 mg, 43%) as a pale yellow oil. $[\alpha]_D^{20} +46.3$ (c 0.56, CHCl_3); $^1\text{H-NMR}$: δ 7.84-7.70 (m, 4H), 7.49-7.45 (m, 2H), 7.36-7.26 (m, 6H), 6.61 (bd, $J = 8.2$ Hz, 1H), 5.36 (d, $J_{1,2} = 3.0$ Hz, 1H), 5.08 (s, 2H), 4.97-4.92 (m, 1H),

4.11-4.00 (m, 2H), 3.89-3.49 (m, 7H), 3.25-2.94 (m, 4H), 2.92 (dd, $J_{1,2}=3.0$ Hz, $J_{2,3}=10.0$ Hz, 1H), 1.26-0.95 (m, 21H), 0.95-0.85 (m, 2H), 0.05 (s, 9H); ^{13}C -NMR: δ 171.4, 170.8, 165.1, 156.7, 135.1, 133.2, 132.6, 131.6, 128.7, 128.6, 128.4, 128.2, 127.7, 127.6, 127.3, 126.3, 125.9, 98.3, 95.6, 73.3, 72.6, 67.4, 63.7, 62.2, 50.7, 43.7, 43.6, 35.3, 18.3, 17.3, 13.1, -1.5; Anal. Calcd for $\text{C}_{45}\text{H}_{63}\text{NO}_{10}\text{SSi}_2$: C, 62.40; H, 7.33; N, 1.62. Found C, 62.50; H, 7.36; N, 1.64.

Glucopyranoside 23. To a solution of **20** (350 mg, 0.39 mmol) in DMF (5 mL), CsF (200 mg, 1.30 mmol) was added. The reaction mixture was stirred at rt for 30 h until disappearance of starting material (TLC), then the solvent was evaporated and the crude product was purified by flash column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 2:1) to afford **23** (161 mg, 65%) as a glassy solid. ^1H -NMR (CD_3OD): δ 7.59-7.31 (m, 14H), 5.35 (d, $J_{1,2}=3.0$ Hz, 1H), 5.13 (bs, 2H), 4.59 (m, 2H), 3.80-3.28 (m, 9H), 3.22-3.19 (m, 2H), 2.92 (dd, $J_{1,2}=3.0$ Hz, $J_{2,3}=9.8$ Hz, 1H), 2.95-2.90 (m, 1H); ^{13}C -NMR (CD_3OD): δ 172.8, 171.6, 149.3, 140.7, 139.5, 135.7, 134.3, 129.5, 128.4, 128.1, 127.8, 127.7, 127.6, 126.7, 126.5, 95.2, 74.5, 70.4, 70.1, 66.8, 60.8, 52.8, 43.6, 41.9, 34.0.

Glucopyranoside 24. To a solution of **21** (70 mg, 0.08 mmol) in DMF (4 mL) CsF (50 mg, 0.33 mmol) was added. The reaction mixture was stirred at rt for 24 h until disappearance of starting material (TLC), then the solvent was evaporated and the crude product was purified by flash column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 2:1) to afford **24** (31 mg, 65%) as a glassy solid. ^1H -NMR (CD_3OD): δ 7.82-7.77 (m, 5H), 7.49-7.44 (m, 5H), 7.30-7.28 (m, 9H), 5.40 (d, $J_{1,2}=2.6$ Hz, 1H), 5.15 (bs, 2H), 4.67-4.61 (m, 2H), 3.84-3.25 (m, 9H), 3.02-2.89 (m, 2H), 2.97 (dd, $J_{1,2}=2.6$ Hz, $J_{2,3}=10.2$ Hz, 1H), 2.49 (s, 1H); ^{13}C -NMR (CD_3OD): δ 172.3, 170.9, 170.7, 148.5, 135.1, 133.0, 132.2, 131.9, 127.5, 127.0, 126.6, 124.9, 124.6, 100.9, 94.7, 73.9, 69.7, 69.5, 66.1, 60.2, 51.3, 43.1, 41.8, 33.4.

Glucopyranoside 25. To a solution of **23** (15 mg, 0.02 mmol) in MeOH (2 mL), $\text{Pd}(\text{OH})_2/\text{C}$ (20%, 2% w/w) was added. The suspension was stirred under hydrogen atmosphere at rt for 12 h, then filtered through a pad of Celite[®]. Evaporation of the solvent under reduced pressure gave **25** (10 mg, >90%) as crude product which was used without any other purification. $[\alpha]_{\text{D}}^{20}$ -34.6 (c 0.50, CH_3OH); ^1H -NMR (CD_3OD): δ 7.61-7.25 (m, 9H), 5.47 (bs, 1H), 4.75 (m, 2H), 3.81 (m, 9H), 3.26-2.95 (m, 4H); ^{13}C -NMR: δ 177.6, 173.9, 171.3, 155.1, 142.2, 141.0, 135.8, 131.1, 129.8, 128.2, 128.0, 96.9, 75.9, 72.1, 71.1, 62.4, 54.1, 44.8, 43.5, 36.9; Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_{10}\text{S}$: C, 57.24; H, 4.99; N, 2.57. Found C, 57.51; H, 4.96; N, 2.69.

Glucopyranoside 26. To a solution of **24** (30 mg, 0.05 mmol) in MeOH (3 mL), $\text{Pd}(\text{OH})_2/\text{C}$ (20%, 2% w/w) was added. The suspension was stirred under hydrogen atmosphere at rt for 12 h, then filtered through a pad of Celite[®]. Evaporation of the solvent under reduced pressure gave **26** (23 mg, >90%) as crude product which was used without any other purification. $[\alpha]_{\text{D}}^{20}$ -56.1 (c

1.04, CH₃OH); ¹H-NMR (CD₃OD): δ 7.79-7.72 (m, 4H), 7.43-7.39 (m, 3H), 5.45 (d, 1H, *J*_{1,2} = 2.6 Hz), 4.62 (m, 2H), 3.79-3.32 (m, 9H), 3.08-2.82 (m, 3H), 2.82 (d, *J*_{1,2} = 2.6 Hz, 1H), 2.69 (m, 1H), 1.75 (m, 1H); ¹³C-NMR: δ 175.7, 173.8, 170.4, 155.3, 134.9, 134.1, 133.8, 129.1, 128.7, 128.6, 128.5, 126.9, 126.6, 101.8, 96.9, 75.9, 72.0, 71.0, 62.3, 53.1, 44.7, 43.9, 36.4; Anal. Calcd for C₂₄H₂₅NO₁₀S: C, 55.49; H, 4.85; N, 2.70. Found C, 55.57; H, 4.36; N, 2.54.