Supporting Information For:

**A New Class of Branched Aminoglycosides: Pseudo-Pentasaccharide
Derivatives of Neomycin B**

Micha Fridman,¹ Valery Belakhov,¹ Sima Yaron,² and Timor Baasov^{1,*}

¹Department of Chemistry and Institute of Catalysis Science and Technology,

²Department of Food Engineering and Biotechnology, Technion - Israel Institute of Technology, Haifa 32000, Israel

General Techniques. ¹H NMR spectra (including DEPT, 2D-COSY, 2D TOCSY, 1D TOCSY, HMQC, HMBC) were routinely recorded on a Bruker AvanceTM 500 spectrometer, and chemical shifts reported (in ppm) are relative to internal Me₄Si (δ = 0.0) with CDCl₃ as the solvent, and to HOD (δ = 4.63) with D₂O as the solvent. ¹³C NMR spectra were recorded on a Bruker AvanceTM 500 spectrometer at 125.8 MHz, and the chemical shifts reported (in ppm) relative to the residual solvent signal for CDCl₃ (δ = 77.00), or to external sodium 2,2-dimethyl-2-silapentane sulfonate (δ = 0.0) for D₂O as the solvent. Mass spectra analysis were obtained either on a Bruker Daltonix Apex 3 mass spectrometer under electron spray ionization (ESI), or by a TSQ-70B mass spectrometer (Finnigan Mat). Reactions were monitored by TLC on Silica Gel 60 F₂₅₄ (0.25 mm, Merck), and spots were visualized by charring with a yellow solution containing (NH₄)Mo₇O₂₄·4H₂O (120 g) and (NH₄)₂Ce(NO₃)₆ (5 g) in 10% H₂SO₄ (800 mL). Flash column chromatography was performed on Silica Gel 60 (70-230 mesh). All reactions were carried out under an argon atmosphere with anhydrous solvents, unless otherwise noted. All chemicals unless otherwise stated, were obtained from commercial sources.

Ethyl 2-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio- β -D-galactopyranoside (12). The titled compound was prepared from ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-galactopyranoside (Pozsgay, V.; Jennings, H. J. *Tet. Lett.* **1987**, 28, 1375-1376), by using the following five steps procedure.

To a suspension of ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-galactopyranoside (6.25 g, 16 mmol) in dry MeOH (70 mL) and dry dichloromethane (70 mL) was added catalytic amount of NaOMe (0.5M solution in MeOH) at 0°C. Propagation of the reaction was monitored by TLC (MeOH 10%, dichloromethane 90%). After 2 hours the reaction mixture was neutralized by Dowex H⁺ and evaporated to dryness. The resulted crude (3.2 g, 14.3 mmol) was used for the next step without further purification.

The crude from the previous step (3.2 g, 14.3 mmol) in dry pyridine (35 mL), was added with a catalytic amount of DMAP and stirred under argon at 60°C for 10 minutes. The mixture was added with *tert*-butyldiphenylsilylchloride (6.7 mL, 25.7 mmol) and the reaction progress was monitored by TLC (EtOAc 65%, Hexane 35%). After 30 minutes the mixture was diluted with EtOAc and washed with brine, 1.5% H₂SO₄, NaHCO₃ (sat.), and finally with brine. The organic layer was dried over

MgSO₄ and evaporated to give a pale yellow syrup (8.2 g) that was used for the next step without further purification.

The crude from the previous step (8.2 g) in acetone (50 mL) and 2,2-dimethoxypropane (25 mL) was stirred at ambient temperature for 5 minutes and then added with a catalytic amount of camphorsulfonic acid. Propagation of the reaction was monitored by TLC (EtOAc 30%, Hexane 70%). After 3 hours the reaction mixture was neutralized by NH₄OH (2.5%) and evaporated to dryness. The crude was diluted with EtOAc and washed with brine. The combined organic layer was dried over MgSO₄ and evaporated to give a pale yellow syrup (8.7 g).

The crude from the previous step (8.7 g) was added with a catalytic amount of DMAP in dry pyridine (50 mL) and stirred at ambient temperature for 5 minutes. The reaction mixture was added with benzoylchloride (4.14 mL, 35.7 mmol) and the propagation of the reaction was monitored by TLC (Et₂O 20%, Hexane 80%). After 4 hours the mixture was diluted with EtOAc and the organic phase was washed as follows: brine, HCl (2%), NaHCO₃ (sat.) and brine. The combined organic layer was then dried over MgSO₄ and evaporated to give a pale yellow syrup (9.3 g).

The crude from the previous step (9.3 g) was dissolved in THF (10 mL), AcOH (50 mL) and water (5 mL). The reaction mixture was stirred at 60°C for 5 hours. Propagation of the reaction was monitored by TLC (EtOAc 30%, Hexane 70%). The reaction mixture was diluted with EtOAc and the organic phase was neutralized with NaHCO₃ (sat.), and washed with brine. The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield **12** as pale-yellow syrup (4.34 g, 48% yield for the five steps). ¹H NMR (500 MHz, CDCl₃) δ 1.05 (s, 9H, *t*-Bu), 1.25 (t, 3H, *J*=7.5 Hz, SCH₂CH₃), 2.68 (m, 2H, SCH₂CH₃), 3.59 (m, 1H, H-5), 3.76 (dd, 1H, *J*₁=3, *J*₂=9.5 Hz, H-3), 3.97 (m, 2H, H'-6, H-6), 4.14 (d, 1H, *J*=2.18 Hz, H-4), 5.01 (d, 1H, *J*=10 Hz, H-1), 5.14 (t, 1H, *J*=9, Hz, H-2), 7.38-8.12 (m, 15H, aromatic). ¹³C NMR (125 MHz, CDCl₃) δ 26.8(C(CH₃)₃), 63.7(C-6), 69.7(C-4), 72.2(C-2), 74.2(C-3), 78.0(C-5), 80.1(C-1), 127.6, 127.7, 128.6, 129.7, 129.8, 130.1, 133.7, 135.6, 135.8. ESIMS *m/z* 605.1 (M+K⁺ C₃₁H₃₈O₆SSi requires 605.3).

Ethyl 2-*O*-Benzoyl-3,4-dideoxy-3,4-diazido-6-*O*-chloroacetyl-1-thio-β-D-allopyranoside (6). Compound **12** (1.68 g, 2.97 mmol) was dissolved in dichloromethane (8 mL) and pyridine (0.73 mL, 7.4 mmol), and was stirred at 0°C for 10 minutes. To this mixture was added Tf₂O (1.08 mL, 6.4 mmol) and the propagation of the reaction was monitored by TLC (EtOAc 20%, Hexane 80%), which indicated completion after 15 minutes. In an additional flask a mixture of NaN₃ (3.795 g, 58.3 mmol), dry DMF, (40 mL) and HMPA (5 mL) was vigorously stirred under argon, and added at once in to the reaction mixture. The reaction was heated to 50°C, and propagation was monitored by TLC (EtOAc 20%, Hexane 80%). After 3 hours the mixture was diluted with EtOAc and washed with brine, HCl (2%), NaHCO₃ (sat.), brine. The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, Diethylether/Hexane) to yield the corresponding 3,4-diazido product as a pale yellow syrup (1.15 g, 63%). ¹H NMR (500 MHz, CDCl₃) δ 1.07 (s, 9H, *t*-Bu), 1.24 (t, 3H, *J* = 9.5, SCH₂CH₃), 2.68 (m, 2H, SCH₂CH₃), 3.73 (broad d, 1H, *J* = 9.5, Hz, H-5), 3.88 (dd, 1H, *J*₁ = 3.0, *J*₂ = 12.0 Hz, H-6), 3.97 (d, 1H, *J* = 11.5 Hz, H-6'), 4.51 (dd, 1H, *J*₁ = 3.0, *J*₂ = 6.0 Hz, H-3), 4.06 (dd, 1H, *J*₁ = 3.0, *J*₂ = 9.5 Hz, H-4), 4.95 (d, 1H, *J* = 9.5 Hz, H-1), 5.19 (dd, 1H, *J*₁ = 3.0, *J*₂ = 10, H-2), 7.38-8.11 (m, 15H, aromatic). ¹³C NMR (125 MHz, CDCl₃) δ 26.8 (C(CH₃)₃), 57.7 (C-4), 63.0 (C-6), 63.1 (C-3), 70.2 (C-2), 75.7 (C-5), 79.6 (C-1), 127.6, 127.7, 128.6,

129.7, 129.8, 130.1, 133.7, 135.6, 135.8. ESIMS m/z 655.2 ($M+K^+$ $C_{31}H_{36}N_6O_4SSi$ requires 655.3).

The di-azido product (1.15 g, 1.87 mmol) was dissolved in pyridine (4 mL) and stirred in a polyethylene vessel at 0°C for 10 minutes. The mixture was added with HF/Pyr (4 mL) and its propagation was monitored by TLC (EtOAc 20%, Hexane 80%). After 5 minutes the mixture was diluted with EtOAc and neutralized with $NaHCO_3$ (sat.). The combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in pyridine (10 mL) and added with a catalytic amount of DMAP, followed by the addition of chloroacetylchloride (0.286 mL, 3.73 mmol). Propagation was monitored by TLC (EtOAc 20%, Hexane 80%). After 25 minutes the mixture was diluted with EtOAc, washed with brine, HCl (2%), $NaHCO_3$ (sat.), and brine. The combined organic layer was dried over $MgSO_4$, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield the titled compound as a pale yellow syrup (777 mg, 91%). 1H NMR (500 MHz, $CDCl_3$) δ 1.23 (t, 3H, J = 10.0, SCH_2CH_3), 2.68 (m, 2H, SCH_2CH_3), 3.73 (dd, 1H, J_1 = 3.0, J_2 = 10.0 Hz, H-4), 3.94 (ddd 1H, J_1 = 2.5, J_2 = 4.5, 1H, J_3 = 10.0 Hz, H-5), 4.1 (s, 2H, $COCH_2Cl$) 4.29 (dd, 1H, J_1 = 5, J_2 = 12.5 Hz, H-6), 4.51 (m, 2H, H-3, H-6), 4.97 (d, 1H, J = 10 Hz, H-1), 5.16 (dd, 1H, J_1 = 3.5, J_2 = 10.0 Hz, H-2), 7.44-8.08 (5H, aromatic). ^{13}C NMR (125 MHz, $CDCl_3$) δ 15 (SCH_2CH_3), 24.2 (SCH_2CH_3), 40.6 ($COCH_2Cl$), 58 (C-4), 62.5 (C-3), 64.7 (C-6), 70.0 (C-2), 72.6 (C-5), 80.4 (C-1), 127.6, 127.7, 128.6, 129.7, 129.8, 130.1, 133.7, 135.6, 135.8. ESIMS m/z 493.5 ($M+K^+$ $C_{17}ClH_{19}N_6O_5S$ requires 493.6).

***p*-Methylphenyl 2,3-Di-*O*-benzoyl-1-thio- β -D-galactopyranoside (13).** To a solution of *p*-methylphenyl-1-thio- β -D-galactopyranoside (Zhang, Z.; Ollmann, I. R.; Ye, X-S.; Wischnat, R.; Baasov, T.; Wong, C-H. *J. Am. Chem. Soc.*, **1999**, *121*, 734.) (4.7 g, 16 mmol) in DMF (30 mL) and anisaldehyde dimethylacetal (3.6 mL, 21 mmol) was added a catalytic amount of camphorsulfonic acid and stirred at ambient temperature. The reaction was monitored by TLC (EtOAc 70%, Hexane 30%). After 2 hours the mixture was diluted with EtOAc, and washed with brine, $NaHCO_3$ (sat.), and once again with brine. The combined organic layer was dried over $MgSO_4$, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield the corresponding 4,6-*O*-benzylidene (4.9 g, 76%). 1H NMR (125 MHz, $CDCl_3$) δ 2.47 (s, 3H, *Me*-STol), 3.62 (broad s, 1H, Hz, H-5), 3.75 (dd 1H, J_1 = J_2 = 9.5 Hz, H-2), 3.79 (dd, 1H, J_1 = 3, J_2 = 9.5 Hz, H-3), 3.92 (s, 3H, *Me*-OMP), 4.10 (d, 1H, J = 11.5 Hz, H-6), 4.28 (d, 1H, J = 3 Hz, H-4) 4.45 (d, 1H, J = 11.5 Hz, H-6'), 4.10 (d, 1H, J = 9.5 Hz, H-1), 5.55 (s, 1H, benzylic proton), 6.96-7.70 (m, 8H, aromatic). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2 (*Me*-STol), 55.2 (*Me*-OMP), 68.6, 69.2, 69.9, 73.7, 75.3, 87, 101.1(C-1), 113.4, 127.8, 129.6, 131.9, 132.1, 134.2, 138.3. Positive CIMS m/z 405.1 ($M+H^+$ $C_{21}H_{24}O_6S$ requires 404.2).

The product from the previous step (4.9 g, 12.2 mmol) was dissolved in dry pyridine under argon and added with a catalytic amount of DMAP. After being stirred at ambient temperature for 5 minutes, the reaction mixture was added with benzoylchloride (3.7 mL, 31.4 mmol). Propagation of the reaction was monitored by TLC (EtOAc 30%, Hexane 70%), which indicated completion after 4 hours. The reaction mixture was diluted with EtOAc and the organic phase was washed as follows: brine, HCl (2%), $NaHCO_3$ (sat.), brine. The combined organic layer was dried over $MgSO_4$, and evaporated to dryness to yield 6.3 g of crude that was used for the next step without further purification.

The crude from the previous step (6.3 g) was added with THF (10 mL), AcOH (50 mL), and water (5 mL). The reaction mixture was stirred at 50°C for 3 hours. Propagation of the reaction was monitored by TLC (EtOAc 30%, Hexane 70%). The reaction mixture was diluted with EtOAc and the organic phase was neutralized by NaHCO₃ (sat.), and washed with brine. The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield **13** (4.62 g, 58% for the three steps). ¹H NMR (500 MHz, CDCl₃/CD₃OD 10/1) δ 2.21 (s, 3H, *Me*-STol), 3.50-3.90 (m, 3H, H-5, H-6, H-6'), 4.27 (d, 1H, *J*=3.5 Hz, H-4), 4.80(d, 1H, *J*=9.9 Hz, H-1), 5.17 (dd, 1H, *J*₁=4.5, *J*₂=9.9 Hz, H-3), 5.64 (t, 1H, *J*=4.2 Hz, H-2) 6.98-7.90(m, 14H, aromatic). ¹³C NMR (125 MHz, CDCl₃) δ 20.9 (*Me*-STol), 61.4, 67.3, 68.2, 75.6, 78.5, 87.2(C-1), 128.2, 128.8, 129.3, 129.6, 132.6, 133.1, 133.2, 138.1, 165.5, 166.0. Negative CIMS *m/z* 494.3 (M+H⁺ C₂₆H₂₀O₇S requires 495.3).

***p*-Methylphenyl-4,6-Dideoxy-4,6-diazido-2,3-*O*-benzoyl-1-thio-β-D-glucopyranoside (7).** Compound **13** (4.62 g, 9.35 mmol) in dry pyridine (20 mL) was stirred under argon at 0°C for 10 minutes and added with Tf₂O (1.97 mL, 11.7 mmol). The mixture was allowed to warm to room temperature. Propagation of the reaction was monitored by TLC (EtOAc 20%, Hexane 80%), which indicated completion after 15 minutes. In an additional flask, a mixture of NaN₃ (12.17 g, 187 mmol) in dry DMF, (40 mL) and HMPA (5 mL) was vigorously stirred under argon, and added at once into the reaction mixture. Propagation was monitored by TLC (EtOAc 20%, Hexane 80%), which indicated completion after 3 hours. The mixture was diluted with EtOAc and washed with brine, HCl (2%), NaHCO₃ (sat.), brine. The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield **7** (3.66 g, 72%). ¹H NMR (500 MHz, CDCl₃) δ 2.33 (s, 3H, *Me*-STol), 3.51 (dd, 1H, *J*₁ = 4.5, *J*₂ = 13.5 Hz, H-6), 3.56 (ddd 1H, *J*₁ = 1.5, *J*₂ = 4.5, 1H, *J*₃ = 15.0 Hz, H-5), 3.70 (dd, 1H, *J*₁ = 1.5, *J*₂ = 13.0 Hz, H-6'), 3.83 (t, 1H, *J* = 9.5 Hz, H-4), 4.82 (d, 1H, *J* = 10.0 Hz, H-1), 5.26 (t, 1H, *J* = 9.5 Hz, H-2), 5.61 (d, 1H, *J* = 9.5 Hz, H-3), 7.10-7.95 (m, 14H, aromatic). ¹³C NMR (125 MHz, CDCl₃) δ 21.2 (*Me*-STol), 51.5 (C-6), 60.5 (C-4), 70.1 (C-2), 74.9 (C-3), 77.4 (C-5), 86.1 (C-1), 126.6, 128.4, 128.5, 129.0, 129.7, 129.8, 133.4, 133.5, 134.6, 134.7, 139.1, 165.0, 165.6. ESIMS *m/z* 583.1 (M+K⁺ C₂₇H₂₄O₅N₆S requires 583.3).

Ethyl 3,5-Di-*O*-benzoyl-6-*O*-chloroacetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranose (8). The titled compound was prepared by the same synthetic path which used for the preparation of phenyl 6-*O*-acetyl-3,5-di-*O*-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranose (Solomon, D.; Fridman, M.; Zhang, J.; Baasov, T. *Organic Letters* **2001**, 3, 4311-4314). ¹H NMR (500 MHz, CDCl₃) δ 1.07 (s, 9H, *t*-Bu), 1.37 (t, 3H, *J*₁ = 7.0 Hz, SCH₂CH₃), 2.86 (m, 2H, SCH₂CH₃), 4.23 (d, 2H, *J* = 2 Hz, COCH₂Cl), 4.29 (ddd, 1H, *J*₁ = 2.5, *J*₂ = 5.0, *J*₃ = 7.5 Hz, H-5), 4.06 (dd, 1H, *J*₁ = 2.5, *J*₂ = 12 Hz, H-6) 4.57 (dd, 1H, *J*₁ = 5.0, *J*₂ = 7.0 Hz, H-6'), 4.75 (t, 3H, *J*₁ = 10.5 Hz, H-2), 5.73 (t, 3H, *J*₁ = 9.5 Hz, H-4), 5.78 (d, 1H, *J* = 10.5 Hz, H-1), 6.42 (dd, 1H, *J*₁ = 9.5, *J*₂ = 10.5 Hz, H-3), 7.36-8.03 (m, 14H, aromatic). ¹³C NMR (125 MHz, CDCl₃) δ 14.9, 24.4, 40.7 COCH₂Cl, 53.8 (C-2), 64.1 (C-6), 69.5 (C-4), 71.7 (C-3), 75.7 (C-5), 81.4 (C-1), 123.6, 123.7, 128.3, 128.4, 128.4, 128.4, 128.5, 129.7, 129.7, 129.8, 131.1, 131.5, 133.3, 133.5, 134.2, 134.3, 165.2, 165.5, 167.0, 167.0, 167.9 ESIMS *m/z* 676.4 (M+K⁺, C₃₂ClH₂₈NO₉S requires 676.8).

Ethyl 2,3,5 Tri-*O*-acetyl-1-thio-D-ribofuranose (9). The commercial 1,2,3,5-tetra-*O*-acetyl- β -D-ribofuranose (3.5 g, 11 mmol) in dichloromethane (30 mL) was added with ethylthiotrimethylsilane (4.44 mL, 27.5 mmol) and TMSOTf (2 mL, 11 mmol). The mixture was stirred at ambient temperature and the reaction progress was monitored by TLC (EtOAc/Hexane 1:1), which indicated completion after 3.5 hours. The mixture was diluted by EtOAc (200 mL), neutralized by NaHCO₃ (sat.), and washed with brine. The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield **9** 3.4g, (96%) as a mixture of anomers (α/β ; 1:3). ¹H NMR (500 MHz, CDCl₃) for **9**- β -anomer δ 4.07 (dd, 1H, $J_1 = 4.0$, $J_2 = 11.5$ Hz, H-5), 4.17 (dd, 1H, $J_1 = 4.0$, $J_2 = 9.5$ Hz, H-4), 4.28 (dd, 1H, $J_1 = 3.0$, $J_2 = 12.0$ Hz, H-5), 5.09 (d, 1H, $J_1 = 3.0$ Hz, H-1), 5.16 (dd, 1H, $J_1 = J_2 = 5.0$ Hz, H-2), 5.26 (dd, 1H, $J_1 = J_2 = 5.5$ Hz, H-3). ¹³C NMR (125 MHz, CDCl₃) δ 14.7, 20.37, 20.4, 20.7, 24.5, 63.5 (C-5), 71.6, 74.4, 79.5, 85.5 (C-1), 169.4, 169.5, 170.3. **9**- α -anomer ¹H NMR (500 MHz, CDCl₃) δ 4.12 (dd, 1H, $J_1 = 3.5$, $J_2 = 12.0$ Hz, H-5), 4.25 (dd, 1H, $J_1 = 3.5$, $J_2 = 12.0$ Hz, H-5'), 4.27 (dd, 1H, $J_1 = 4.0$, $J_2 = 8.0$ Hz, H-4), 5.08 (t, 1H, $J = 6.0$ Hz, H-3), 5.30 (d, 1H, $J = 6.5$ Hz, H-2), 5.53 (d, 1H, $J = 4.5$ Hz, H-1). ¹³C NMR (125 MHz, CDCl₃) δ 14.9, 20.3, 20.4, 20.6, 25.3, 62.8 (C-5), 70.4, 71.3, 74.4, 86.7 (C-1), 169.3, 169.7, 170.4. ¹³C NMR (125 MHz, CDCl₃) δ 21.2 (*Me*-STol), 51.5 (C-6), 60.5 (C-4), 70.1 (C-2), 74.9 (C-3), 77.4 (C-5), 86.1 (C-1), 126.6, 128.4, 128.5, 129.0, 129.7, 129.8, 133.4, 133.5, 134.6, 134.7, 139.1, 165.0, 165.6. negative CIMS m/z 319.1 (M-H⁺ C₁₃H₂₀O₇S requires 520.1).

Neomycin acceptor (14). Hexaazido-neomycin was prepared from the commercial neomycin B (tri-sulfate salt, 5 g, 5.5 mmol) following the published procedure (Alper, P. B.; Hendrix, M.; Sears, P.; Wong, C.-H. *J. Am. Chem. Soc.* **1998**, *120*, 1965-1978) and was used for the next step without purification. The crude hexaazido-product was dissolved in pyridine (40 mL), added with DMAP (cat.) and stirred at 70°C for 15 minutes. The reaction was then added with *tert*-butyldimethylsilylchloride (1.66 g, 11 mmol), and TLC (EtOAc 100%) indicated completion after 30 minutes. The mixture was allowed to stir for additional 10 minutes and then added with pyridine (20 mL), DMAP (cat), and Ac₂O (7.8 mL, 82.5 mmol). Propagation of the reaction was monitored by TLC (EtOAc 30%, Hexane 70%), which indicated completion after 3 hours. The mixture was diluted with EtOAc and washed with brine, HCl (2%), NaHCO₃ (sat.), and brine. The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield the corresponding silyl ether as a white powder (3.5 g, 62% yield for 3 steps). ¹H NMR (500 MHz, CDCl₃) data for this compound is summarized in the attached Table **1S**. ¹³C NMR (150.92 MHz) δ 18.2, 20.5, 20.6, 20.7, 20.9, 25.8, 29.6, 31.4, 50.7, 51.1, 56.7, 58.1, 59.2, 60.8, 63, 65, 68.7, 69, 70, 73.1, 75.2, 76, 76.7, 76.9, 77, 77.2, 81.6, 83.3, 96.0 (anomeric carbon), 99.6 (anomeric carbon), 106.3 (anomeric carbon), 168.5, 169.5, 169.7, 167.9, 170.2, 170.3. ESIMS m/z 1175.6 (M+K⁺, C₄₁H₆₀O₁₉N₁₈Si requires 1175.4).

The silyl ether from the above (1.06 g, 0.93 mmol) was dissolved in pyridine (8 mL) and stirred in a polyethylene vessel at 0°C for 10 minutes. The mixture was added with HF/Pyr (4 mL). Propagation of the reaction was monitored by TLC (EtOAc 20%, Hexane 80%), which indicated completion after 5 minutes. The mixture was diluted with EtOAc, neutralized with NaHCO₃ (sat.). The combined organic layer was dried over MgSO₄, evaporated and purified by flash chromatography (silica, EtOAc/Hexane) to yield acceptor **14** as a white powder (884 mg, 93%). ¹H NMR (500

MHz, CDCl₃) data of **14** is summarized in the attached Table 2S. ¹³C NMR δ 15.9, 16, 22.3, 22.4, 22.5, 22.6, 33.3, 52.6, 52.7, 58.3, 59.7, 60.8, 62.1, 67.4, 70.5, 70.9, 71, 71.1, 75.2, 77.8, 83.2, 83.6, 99.0 (anomeric carbon), 101.2 (anomeric carbon), 108.0 (anomeric carbon), 170.4, 171.2, 171.4, 171.6, 171.7, 171.9. ESIMS *m/z* 1061.2 (M+K⁺, C₃₅H₄₆O₁₉N₁₈ requires 1061.4).

Compound 15a. To a powdered, flame dried 4Å molecular sieves (0.4 g) was added CH₂Cl₂ (4 mL), followed by the addition of acceptor **14** (100 mg, 0.098 mmol) and donor **6** (65 mg, 0.143 mmol). After being stirred for 10 min at room temperature, the mixture was treated with NIS (64.3 mg, 0.286 mmol). After additional 5 minutes at room temperature, TfOH (cat) was added. Propagation of the reaction was monitored by TLC (EtOAc 50%, Hexane 50%), which indicated completion after 10 min. The reaction was diluted with EtOAc, and filtered through celite. After thorough washing with EtOAc, the washes were combined and extracted with 10% Na₂S₂O₃, saturated (aq.) NaHCO₃, brine, dried over MgSO₄ and concentrated. The crude was purified by flash chromatography to yield **15a** (112 mg, 81%). ¹H NMR (500 MHz, CDCl₃) data of **15a** are summarized in the attached Table 3S. ¹³C NMR δ 20.4, 20.6, 20.7, 29.6, 31, 40.7, 50, 50.9, 56.3, 58, 58.8, 60.6, 66.0, 62.5, 65, 68.1, 68.4, 69, 70.3, 71, 72.4, 74.8, 75, 75.5, 76.4, 80.2, 83.5, 96.4 (anomeric carbon), 98.8 (anomeric carbon), 99.0 (anomeric carbon), 108.2 (anomeric carbon), 128.9, 129.3, 129.7, 133.7, 167.7, 167.1, 168.3, 169.5, 169.6, 169.8, 170.1. ESIMS *m/z* 1453.2 (M+K⁺, C₅₀ClH₅₉N₂₄O₂₄ requires 1453).

Compound 15b. The titled compound was prepared as was described for the preparation of compound **15a**. The conditions used were: donor **7** (430 mg, 0.79 mmol), acceptor **14** (646 mg, 0.63 mmol), NIS (430 mg, 1.9 mmol), TfOH (cat.) CH₂Cl₂ (15 mL), and 4Å molecular sieves (1.5 g). The reaction was done at 0°C to yield **15b** (780 mg, 86%) as a mixture of anomers (α/β 1:2) as determined by NMR. ESIMS *m/z* 1481.7 (M+K⁺, C₅₅H₆₂N₂₄O₂₄ requires 1481.6).

The above mixture could not be separated until after the next step. Thus, compound **15b** (200 mg, 0.138 mmol, as a mixture of anomers) was dissolved in 33% solution of MeNH₂ in EtOH (40 mL) and stirred at room temperature for 48 hours. Propagation of the reaction was monitored by TLC (MeOH 20%, CHCl₃ 80%). The reagent and the solvent were removed by evaporation and the residue was purified by flash chromatography (silica, MeOH/CHCl₃) to yield the corresponding octaazido-octaol as a β-anomer (72.7 mg, 53%), and the octaazido-heptaol-C₂^V-O-benzoyl as an α-anomer (49.2 mg, 36%). ¹H NMR (500 MHz, CDCl₃/CD₃OD; 10:1) data of the β-anomer and of the of the α-anomer are summarized in the attached Table 4S and Table 5S, respectively. ¹³C NMR (β-anomer) δ 29.5, 38.1, 51.1, 51.2, 51.5, 59.6, 59.8, 60.6, 62.3, 62.5, 68.7, 68.9, 69.4, 71.1, 71.1, 73.6, 73.6, 73.7, 74.1, 75.3, 75.4, 75.9, 76.1, 80.6, 84.3, 96.2 (anomeric carbon), 98.3 (anomeric carbon), 102.8 (anomeric carbon), 108.5 (anomeric carbon). ESIMS *m/z* 1021.3 (M+K⁺, C₂₉H₄₂N₂₄O₁₆ requires 1021.8). ¹³C NMR (α-anomer) δ 29.5, 39.1, 51.0, 51.4, 51.7, 59.4, 59.7, 60.9, 62.9, 62.9, 68.5, 69.7, 70.8, 71.0, 71.2, 74.1, 75.0, 75.6, 75.9, 76.2, 80.6, 84.2, 96.5 (anomeric carbon), 97.7 (anomeric carbon), 98.4 (anomeric carbon), 107.3 (anomeric carbon), 120.1, 125.9, 128.3, 129.4, 135.9. ESIMS *m/z* 1125.3 (M+K⁺, C₃₆H₄₇N₂₄O₁₇ requires 1125.8).

Compound 15c. The titled compound was prepared as was described for the preparation of compound **15a**. The conditions used were: donor **8** (467.2 mg, 0.73

mmol), acceptor **14** (250 mg, 0.24 mmol), NIS (330 mg, 1.47 mmol), TfOH (cat.), CH₂Cl₂ (5 mL), 4 Å molecular sieves (500 mg), to yield 226 mg of **15c** (58%). ¹H NMR (500 MHz, CDCl₃) data of **15c** are summarized in the attached Table 6S. ¹³C NMR δ 20.4, 20.7, 20.8, 20.9, 29.6, 40.8, 50.5, 54.7, 56.6, 58.2, 59.0, 60.7, 65.5, 69.0, 69.8, 70.2, 70.8, 72.0, 73.0, 75.1, 75.3, 76.4, 76.9, 81.0, 81.2, 96.4 (anomeric carbon), 98.6 (anomeric carbon), 99.5 (anomeric carbon), 107.2 (anomeric carbon), 128.3, 128.4, 128.5, 128.6, 129.7, 129.9, 133.3, 133.5, 165.2, 165.7, 167.1, 168.4, 169.5, 169.7, 169.8, 169.9, 170.1. ESIMS *m/z* 1636.3(M+K⁺, C₆₅H₆₈N₁₉O₂₈Cl requires 1637.1).

Compound 15d: The titled compound was prepared as was described for the preparation of compound **15a** with the following modifications: Donor **9** (157 mg, 0.49 mmol), acceptor **14** (200 mg, 0.196 mmol), NIS (110 mg, 0.49 mmol), TfOH (cat.), 4 Å molecular sieves (400 mg). In an attempt to increase the beta selectivity, acetonitrile (4 mL) was used as a solvent and the reaction temperature was –35°C. Under these conditions, **15d** was isolated as a mixture of anomers α/β; 1:11 (238 mg, 95%). This mixture was further separated to afford 178 mg (71%) of the pure β-anomer. ¹H NMR (500 MHz, CDCl₃) data of **15d** are summarized in the attached Table 7S. ¹³C NMR δ 20.4, 20.6, 20.7, 20.8, 23.8, 29.5, 29.7, 50.6, 50.7, 56.7, 57.9, 59.2, 60.43, 60.86, 62.1, 63.44, 64.45, 65.62, 68.6, 68.9, 69.2, 70.0, 70.7, 70.9, 71.2, 72, 73.2, 75.2, 75.3, 76.1, 77.3, 77.8, 78.5, 79.1, 81.3, 81.7, 97.9 (anomeric carbon), 101.4 (anomeric carbon), 106.1 (anomeric carbon), 108.5 (anomeric carbon), 170.4, 171.5, 171.6, 171.8, 171.9, 172.5. ESIMS *m/z* 1319.3(M+K⁺, C₄₆H₆₀N₁₈O₂₆ requires 1319.5).

Compound 2. Compound **15a** (0.11 g, 0.078 mmol) was dissolved in 33% solution of MeNH₂ in EtOH (40 mL) and the mixture was stirred at room temperature for 30 h. The reagent and the solvent were removed by evaporation and the residue was dissolved in THF (10 mL), NaOH 0.1M (2 mL) and stirred at 60°C for 10 minutes after which PMe₃ (1M solution in THF, 3.73 mL, 3.73 mmol) was added. Propagation of the reaction was monitored by TLC (CH₂Cl₂/MeOH/H₂O/MeNH₂ (33% solution in EtOH) 10:15:6:15, R_f = 0.33), which indicated completion after 3.5 hours. The reaction mixture was purified by flash chromatography on a short column of silica and the column was washed as follows: THF, EtOAc, MeOH/EtOAc (1:1), MeOH, and finally with MeNH₂ (33% solution in EtOH). The fractions containing the product were evaporated under vacuum, re-dissolved in water and evaporated again to afford the product as a free amine (48.7 mg, 81%). This product was then dissolved in water, the pH was adjusted to 7.5 with 0.01 M H₂SO₄ and lyophilized to give the sulfate salt of **2** (88.5 mg) as a white foamy solid. ¹H NMR (500 MHz, D₂O, pH 4.5, sulfate salt) δ 1.85 (ddd, 1H, *J*₁ = *J*₂ = *J*₃ = 12.5 Hz, H-2 axial), 2.38 (dt, 1H, *J*₁ = 4.5 *J*₂ = 12.5, H-2 equatorial), 3.07-4.53 (m, 26H), 4.78 (d, 1H, *J* = 7.0 Hz, anomeric proton), 5.21 (d, 1H, *J* = 1.5 Hz, anomeric proton), 5.34 (d, 1H, *J*₁ = 3.0 Hz, anomeric proton), 5.97 (d, 1H, *J*₁ = 4.0 Hz, anomeric proton). ¹³C NMR (125.8 MHz, D₂O, pH 4.5, sulfate salt) δ 29.8, 34.6, 42.2, 42.3, 49.9, 50.3, 51.2, 51.6, 52.6, 55.1, 62.3, 64.3, 69.2, 69.4, 69.5, 69.9, 71.3, 71.9, 72.8, 73.8, 74.1, 74.9, 77.1, 82.0, 86.8, 96.9 (anomeric carbon), 97.1 (anomeric carbon), 102.0 (anomeric carbon), 112.1 (anomeric carbon). ESIMS *m/z* 781.2(M+Li⁺, C₂₉H₅₈N₈O₁₆ requires 781.2).

Compound 3. The titled compound was prepared as was described for the preparation of compound **2** with the following quantities: the product (β-anomer) that

was obtained by the partial deprotection of compound **15b** (122.4 mg, 0.124 mmol), THF (9 mL), NaOH 0.1M (3 mL), PMe₃ (1M solution in THF, 6.8 mL, 6.8 mmol), gave the product as a free amine (93.1 mg, 96%). This product was dissolved in water, the pH was adjusted to 7.5 with 0.01 M H₂SO₄, and lyophilized to afford the sulfate salt of **3** (134.5 mg) as a white foamy solid. ¹H NMR (500 MHz, D₂O, pH 4.5, sulfate salt) δ 1.77 (ddd, 1H, $J_1 = J_2 = J_3 = 12.5$ Hz, H-2 axial), 2.38 (bd, 1H, H-2 equatorial), 2.83-4.39 (m, 26H), 4.54 (d, 1H, $J = 7.5$ Hz, anomeric proton), 5.17 (s, 1H, anomeric proton), 5.31 (s, 1H, anomeric proton), 5.98 (s, 1H, anomeric proton). ¹³C NMR (125.8 MHz, D₂O, pH 4.5, sulfate salt) δ 20.8, 23.6, 30.0, 42.2, 42.3, 42.5, 50.2, 51.8, 52.7, 55.1, 55.2, 55.8, 69.3, 69.4, 69.6, 69.9, 71.1, 71.6, 72.0, 73.7, 74.3, 74.4, 75.0, 77.1, 81.3, 86.9, 96.4 (anomeric carbon), 97.0 (anomeric carbon), 105.1 (anomeric carbon), 112.5 (anomeric carbon). ESIMS m/z 813.2 (M+K⁺, C₂₉H₅₈N₈O₁₆ requires 813.8).

Compound 4. The titled compound was prepared as was described for the preparation of compound **2** with the following quantities: **15c** (180 mg, 0.113 mmol) was treated in the first step with 33% solution of MeNH₂ in EtOH (40 mL) for 40 hours; the product from this step was dissolved in THF (10 mL), NaOH 0.1M (2 mL), and treated with PMe₃ (1M solution in THF, 4.05 mL, 4.05 mmol) to yield **4** as a free amine (73.1, 84%). The amine was dissolved in water, the pH was adjusted to 7.5 with H₂SO₄ (0.01 M), and lyophilized to give the sulfate salt of **4** (117 mg) as a white foamy solid. ¹H NMR (500 MHz, D₂O, pH 3.75, sulfate salt) δ 1.94 (ddd, 1H, $J_1 = J_2 = J_3 = 12.5$ Hz, H-2 axial), 2.35 (broad dt, H-2 equatorial), 2.96 (t, 1H, $J = 10.0$ Hz, H-2'''), 2.97 (broad t, 1H, H-3'''), 3.05 (dd, 1H, $J_1 = 8.5$ $J_2 = 13.0$ Hz), 3.21-3.33 (m, 5H, H-4'''), 3.37-3.47 (m, 5H, H-2', H-2''', H-5'''), 3.61-3.70 (m, 4H, H-4'', H-3'''), 3.76-3.80 (m, 2H), 3.83-3.90 (m, 2H), 3.96 (t, 1H, $J = 10.0$ Hz, H-3'), 4.14-4.20 (m, 2H, H-5''), 4.23 (broad t, 1H), 4.31 (broad t, 1H, H-3''), 4.41 (broad t, 1H, H-2''), 4.79 (d, $J = 8.5$ Hz, 1H, H-1'''), 5.19 (s, 1H, H-1'''), 5.32 (s, 1H, H-1''), 5.98 (d, $J = 4.0$ Hz, 1H, H-1'). ¹³C NMR δ 26.4, 29.6, 42.2, 42.5, 50.3, 51.6, 52.6, 55.1, 57.4, 61.8, 68.9, 69.4, 69.7, 70.8, 71.4, 71.6, 72.3, 73.2, 73.6, 74.0, 74.6, 76.2, 76.6, 77.9, 81.7, 87.3, 96.70 (anomeric carbon), 96.73 (anomeric carbon), 101.0 (anomeric carbon), 112.5 (anomeric carbon). ESIMS m/z 798.2 (M+Na⁺, C₂₉H₅₇N₇O₁₇ requires 798.3).

Compound 5. A catalytic amount of NaOMe (0.5M solution in MeOH) was added to a suspension of compound **15d** (140 mg, 0.11 mmol) in dry MeOH (10 mL) at 0°C, and the propagation of the reaction was monitored by TLC (MeOH 10%, dichloromethane 90%). After 3 hours the mixture was neutralized with Dowex H⁺ and evaporated to dryness. The resulted crude was then treated as described for the preparation of **2** to yield the free amine of **5** (57.1 mg, 70%). ¹H NMR (500 MHz, D₂O, pH 4.5, sulfate salt) δ 1.86 (ddd, 1H, $J_1 = J_2 = J_3 = 12.5$ Hz, H-2 axial), 2.33 (broad dt, H-2 equatorial), 3.10 (dd, 1H, $J_1 = 7.0$ $J_2 = 13.0$ Hz), 3.20-4.43 (m, 17H), 3.84 (s, 1H, anomeric proton), 5.16 (s, 1H, anomeric proton), 5.30 (s, 1H, anomeric proton), 5.93 (d, $J = 3.0$ Hz, 1H, anomeric proton). ¹³C NMR (125.8 MHz, D₂O, pH 4.5, sulfate salt) δ 30.2, 42.2, 42.2, 50.3, 51.8, 52.6, 55.5, 62.0, 69.0, 69.5, 69.9, 71.2, 72.1, 74.3, 75.1, 76.6, 77.1, 83.0, 83.6, 86.7 (anomeric carbon), 96.9 (anomeric carbon), 96.9 (anomeric carbon), 112.0 (anomeric carbon). ESIMS m/z 769.2 (M+Na⁺, C₂₈H₅₄N₆O₁₇ requires 769.3).

Table 1S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the titled structure.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	6.09 d $J = 3.5$	3.14 dd $J = 3.5, 10.5$	5.45 t $J = 9.5$	4.92 t $J = 10.0$	4.42 ddd $J = 3.0, 5.0, 8.5$		3.25-3.32 m	3.25-3.32 m
III	5.36 d $J = 4.5$	4.77 t $J = 4.5$	4.36 t $J = 4.7$	4.23 dd $J = 4.0, 6.0$	3.71 dd $J = 4.5, 11.5$	3.86 m		
IV	4.79 d $J = 2.0$	3.25-3.32 m	5.00 t $J = 3.0$	4.67 s	3.49 ddd $J = 2.0, 4.5, 6.5$		3.25-3.32 m	3.54 dd $J = 8.5, 13.0$
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	4.92 t $J = 1.0$	1.58 ddd $J_1 = J_2 = J_3 = 12.5$	2.34 dt $J = 4.0, 13.5$	3.49 ddd $J_1 = J_2 = J_3 = 5.0$	3.67 t $J = 9.0$	3.86 m	3.39 ddd $J = 4.0, 10.0, 12.5$	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz. The additional peaks in the spectrum were identified as follow: δ 0.06 (s, 3H, Me), 0.08 (s, 3H, Me), 1.07 (s, 9H, *t*-Bu), 2.01 (s, 3H, acetate), 2.03 (s, 3H, acetate), 2.06 (s, 3H, acetate), 2.12 (s, 3H, acetate), 2.14 (s, 3H, acetate), 2.16 (s, 3H, acetate).

Table 2S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the neomycin acceptor **14**.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	6.02 d $J = 4.0$	3.21 dd $J = 3.5, 10.5$	5.61 dd $J = 9.5, 10.5$	5.08 - 5.15 m	4.60 ddd $J = 3.0, 5.5, 10.0$		3.47 dd $J = 2.5, 13.5$	3.40 - 3.42 m
III	5.46 d $J = 2.5$	4.93 dd $J = 3.0, 5.5$	4.51 t $J = 6.5$	4.19 - 4.24 m	4.02 dd $J = 4.0, 12.5$	3.83 dd $J = 6.0, 12.5$		
IV	4.99 d $J = 1.5$	3.40 - 3.42 m	5.08 - 5.15 m	4.80 s	4.19 - 4.24 m		3.70 dd $J = 8.5, 13.0$	3.40 - 3.42 m
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	3.57 ddd $J = 4.5, 10.5, 14.5$	2.51 dt $J = 4.5, 13.0$	1.74 ddd $J_1 = J_2 = J_3 = 12.5$	3.65 ddd $J = 4.5, 10.0, 14.0$	3.82 t $J = 9.0$	4.06 t $J = 9.0$	5.08 - 5.15 m	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz. The additional peaks in the spectrum were identified as follow: δ 1.85 (broad s, 1H, OH), 2.17 (s, 3H, acetate), 2.20 (s, 3H, acetate), 2.22 (s, 3H, acetate), 2.25 (s, 3H, acetate), 2.27 (s, 3H, acetate), 2.28 (s, 3H, acetate).

Table 3S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the protected pseudo-pentasaccharide **15a**.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	6.12 d $J = 3.5$	3.24 - 3.30 m	5.42 t $J = 10$	5.02 t $J = 11.5$	4.46 - 4.52 m		3.34 - 3.42 m	3.63 - 3.67 m
III	5.16 d $J = 4.5$	4.70 d $J = 5$	4.32 dd $J = 6.5, 11.5$	4.08 m	3.71 dd $J = 4.5, 11.5$	3.86 bd		
IV	4.46 - 4.52 m	3.12 bs	4.96 s	4.64 s	3.63 - 3.67 m		3.34 - 3.42 m	3.52 - 3.56 m
V	4.86 d $J = 8.0$	5.28 dd $J = 3.0, 7.5$	4.46-4.52 m	4.91 bdd	4.96 dd $J_1 = 2.0, 12.5$		4.46 - 4.52 m	4.40 dd $J = 4.5, 12.5$
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	3.34 - 3.42 m	2.31 m	1.55 ddd $J_1 = J_2 = J_3 = 12.5$	3.24 - 3.30 m	4.73 t $J = 11.0$	3.75 t $J = 9.5$	3.69 t $J = 9.0$	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz. The additional peaks in the spectrum were identified as follow: δ 2.04 (s, 3H, acetate), 2.05 (s, 3H, acetate), 2.06 (s, 3H, acetate), 2.08 (s, 3H, acetate), 2.14 (s, 3H, acetate), 2.15 (s, 3H, acetate) 4.23 (s, 2H, chloroacetate), 7.57 (t, 2H, meta benzoyl protons), 7.65(t, 1H, para benzoyl proton), 8.06 (d, 2H, ortho benzoyl protons).

Table 4S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the titled structure.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	5.77 d $J = 4.0$	3.22 - 3.29 m	3.77 t $J = 9.0$	3.22 - 3.29 m	3.98 ddd $J = 3.0, 6.0, 9.5$		3.49 dd $J = 2.5, 9.5$	3.40 dd $J = 4.5, 13.0$
III	5.18 d $J = 4$	4.04 dd $J_1 = J_2 = 4.0$	4.24 dd $J_1 = J_2 = 4.5$	4.13 - 4.14 m	3.43 - 3.49 m	3.43 - 3.49 m		
IV	4.98 d $J = 1.0$	3.68 bs	3.87 s	3.21 - 3.25 m	3.90 - 3.92 m		3.54 - 3.59 m	3.21 - 3.29 m
V	4.21 d $J = 8.5$	3.24 - 3.3 m	3.46 - 3.49 m	3.24 - 3.3 m	3.36 - 3.39 m		3.36 - 3.39 m	3.36 - 3.39 m
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	3.24 - 3.36 m	2.13 dt $J = 4.5, 13.0$	1.55 ddd $J_1 = J_2 = J_3 = 12.5$	3.24 - 3.36 m	3.24 - 3.36 m	3.54 - 3.57 m	3.48 t $J = 8.5$	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz.

Table 5S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the titled structure.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	5.73 d $J = 4.0$	3.09 - 3.13 m	3.77 t $J = 8.5$	3.26-3.3 m	3.98 ddd $J = 2.0, 5.5, 8.5$		3.47 bd	3.39 dd $J = 5.5, 14.5$
III	5.36 d $J = 4.5$	4.77 t $J = 4.5$	4.36 t $J = 4.7$	4.23 dd $J = 4.0, 6.0$	3.71 dd $J = 4.5, 11.5$	3.86 m		
IV	4.99 d $J = 1.0$	3.66 bs	3.86 bs	3.27 bs	3.41 - 3.52 m		3.41 - 3.52 m	3.41 - 3.52 m
V	5.86 d $J = 5.5$	4.85 dd $J_1 = J_2 = 4.5$	4.85 dd $J = 5.2, 5.3$	3.33 - 3.39 m	3.42 - 3.46 m		3.33 - 3.39 m	3.23 dd $J = 3.0, 17.0$
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	3.26 - 3.36 m	2.12 dt $J = 4.0, 13.0$	1.31 ddd $J_1 = J_2 = J_3 = 12.5$	3.26 - 3.36 m	3.51 - 3.61 m	3.51 - 3.61 m	3.41 t $J = 9.0$	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz. The additional peaks in the spectrum were identified as follow: δ 7.2-7.32 (m, 3H, benzoyl), 7.53-7.55(m, 2H, benzoyl).

Table 6S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the protected pseudo-pentasaccharide **15c**.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	6.04 d $J = 4.0$	3.38 - 3.42 m	5.51 dd $J = 9.5, 10.5$	5.08 t $J = 9.5$	4.50 - 4.59 m		3.42 - 3.53 m	3.42 - 3.53 m
III	5.23 d $J = 3.0$	4.50 - 4.59 m	4.13 - 4.16 m	4.28 ddd $J = 3.0, 5.0, 6.5$	3.73 dd $J = 4.5, 12.5$	4.13 - 4.16 m		
IV	4.68 d $J = 2.5$	3.25 bs	5.08 t $J = 3.0$	4.70 bs	4.03 ddd $J = 1.5, 5.0, 6.0$		3.42 - 3.53 m	3.38 - 3.42 m
V	5.62 d $J = 8.5$	4.64 dd $J = 8.5, 11.0$	6.62 dd $J = 9.0, 10.5$	5.62 dd $J = 9.5, 13.0$	4.13 - 4.16 m		4.40 dd $J = 3.0, 12.5$	4.50-4.59 m
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	3.38 - 3.42 m	2.12 dt $J = 4.5, 13.0$	1.75 ddd $J = J_2 = J_3 = 12.5$	3.42 - 3.53 m	4.92 t $J = 10.0$	3.89 t $J = 8.5$	3.82 t $J = 8.5$	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz. The additional peaks in the spectrum were identified as follow: δ 1.98 (s, 3H, acetate), 2.09 (s, 3H, acetate), 2.10 (s, 3H, acetate), 2.16 (s, 3H, acetate), 2.165 (s, 3H, acetate), 2.19 (s, 3H, acetate) 4.17 (s, 2H, chloroacetate), 7.24-7.92(m, 14H, aromatic).

Table 7S. ^1H NMR (500 MHz, CDCl_3) chemical shifts and coupling constants for the protected pseudo-pentasaccharide **15d**.^a

Ring	H1	H2	H3	H4	H5	H5'	H6	H6'
I	6.06 d $J = 4.0$	3.21 - 3.31 m	3.71 dd $J = 9.5, 11.0$	4.89 - 4.95 m	3.40 ddd $J = 3.5, 5.0, 10.0$	3.27 - 3.34 m	3.27 - 3.34 m	
III	5.33 d $J = 4.5$	4.79 dd $J_1 = J_2 = 4.5$	4.35 - 4.37 m	4.28 - 4.31 m	3.45 dd $J = 3.5, 10.0$	3.74 dd $J = 2.0, 10.0$		
IV	4.83 d $J = 4.0$	3.27 - 3.34 m	4.66 bs	4.97 dd $J_1 = J_2 = 4.5$	4.05 ddd $J = 2.0, 5.0, 6.5$		3.59 dd $J = 8.5, 13.0$	3.74 dd $J = 4.0, 12.0$
V	5.95 d $J = 4.5$	4.92 dd $J = 3.5, 5.5$	4.92 dd $J = 3.5, 5.5$	4.12 - 4.20 m	4.12 - 4.20 m	4.35 - 4.37 m		
	H1	H2eq	H2ax	H3	H4	H5	H6	
II	3.40 ddd $J = 4.5, 10.5, 12.0$	2.33 dt $J = 4.0, 13.5$	1.58 ddd $J_1 = J_2 = J_3 = 12.5$	3.50 ddd $J = 4.0, 10.0, 12.5$	4.93 t $J = 12.0$	3.88 t $J = 9.5$	3.66 t $J = 9.0$	

^aValues of chemical shifts are in ppm and values of coupling constants are in Hz. The additional peaks in the spectrum were identified as follow: δ 2.00 (s, 3H, acetate), 2.05 (s, 6H, 2 acetates), 2.06 (s, 3H, acetate), 2.07 (s, 3H, acetate), 2.10 (s, 3H, acetate), 2.11 (s, 3H, acetate), 2.13 (s, 3H, acetate), 2.16 (s, 3H, acetate).