SUPPORTING MATERIAL

Dehydrative Sialylation with C2-Hemiketal Sialyl Donors

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General Procedures. All reactions were performed in dry modified Schlenk (Kjedahl shape) flasks under a positive pressure of argon, unless otherwise indicated. Solvents and reagents were transferred via dry syringe or stainless steel cannula. Organic solvents were concentrated by rotary evaporation below 40 °C, unless otherwise noted. Flash column chromatography was performed using 230-400 mesh silica gel. Analytical thin-layer chromatography was performed on Merck 60 F₂₅₄ pre-coated silica plates. Visualization was achieved using UV light and/or ceric ammonium molybdenate.

Materials. Dichloromethane and toluene were purified by passage through two packed columns of neutral alumina under an argon atmosphere. Triethylamine was distilled from calcium hydride at 760 torr. Trifluoromethanesulfonic anhydride was distilled from phosphorus pentoxide. The appropriate carbohydrate coupling partners were dried by azeotropic removal of water with toluene *in vacuo* prior to use. All other chemicals were obtained from commercial vendors and used without further purification, unless noted otherwise.

Instrumentation. Proton and carbon-13 nuclear magnetic resonance (¹H NMR or ¹³C NMR) spectra were recorded on a Varian 400, a Varian 500 or a Varian Inova 500 NMR spectrometer. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃: δ 7.26; CH₂Cl₂: δ 5.32). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), integration, and coupling constants in Hertz (Hz). Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum BX spectrophotometer referenced to a polystyrene standard. Data are presented as frequency of absorption (cm⁻¹). High-resolution fast-atom bombardment (FAB) mass spectrometry was performed by the mass spectrometry lab at the University of Illinois at Urbana-Champaign.

Representative Sialylation Procedures

Typical procedure for sialylation employing phenylsulfoxide. To a solution of hemiketal **8** (29 mg, 0.051 mmol, 1.0 equiv) and phenylsulfoxide (21 mg, 0.102 mmol, 2.0 equiv) in CH₂Cl₂ (0.5 mL) at –78 °C was added trifluoromethanesulfonic anhydride (11.9 µL, 0.071 mmol, 1.4 equiv). The reaction was stirred for 1 h, followed by the addition of a solution of methyl 2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (**7**) (47 mg, 0.102 mmol, 2.0 equiv) in CH₂Cl₂ (0.5 mL) at –78 °C. The resulting solution was warmed to –50 °C, stirred for 2 h, and then triethylamine (70.7 µL, 0.508 mmol, 10.0 equiv) was added. The reaction was diluted with CH₂Cl₂ (100 mL) and washed with water (2 x 30 mL), and the organic layer was dried (Na₂SO₄) and concentrated. The residue was purified by flash column chromatography (45% acetone in toluene) to afford sialoside **11** (37 mg, 72%) as a 1:1 (α : β) mixture of anomers.

Typical procedure for sialylation employing bis(*m*-trifluoromethylphenyl) sulfoxide¹. To a solution of hemiketal **8** (26 mg, 0.046 mmol, 1.0 equiv) and bis(*m*-trifluoromethylphenyl) sulfoxide (31 mg, 0.091 mmol, 2.0 equiv) in CH₂Cl₂ (0.5 mL) at –78 °C was added trifluoromethanesulfonic anhydride (10.7 µL, 0.064 mmol, 1.4 equiv). The reaction was stirred for 1 h, followed by the addition of a solution of methyl 2,3,4-tri-*O*-benzyl- α -D-glucopyranoside (**7**) (63 mg, 0.136 mmol, 3.0 equiv) in CH₂Cl₂ (0.5 mL) at –78 °C. The resulting solution was stirred for 4 h, and then triethylamine (63.2 µL, 0.455 mmol, 10.0 equiv) was added. The reaction was diluted with CH₂Cl₂ (100 mL) and washed with water (2 x 30 mL), and the organic layer was dried (Na₂SO₄) and concentrated. The residue was purified by flash column chromatography (45% acetone in toluene) to afford sialoside **11** (29 mg, 64%) as a 1:1 (α : β) mixture of anomers.

Typical procedure for sialylation employing (p-nitrophenyl)(phenyl) sulfoxide². To a solution of hemiketal **8** (33 mg, 0.058 mmol, 1.0 equiv) and (p-nitrophenyl)(phenyl) sulfoxide (29 mg, 0.117 mmol, 2.0 equiv) in CH₂Cl₂ (0.5 mL) at –78 °C was added trifluoromethanesulfonic anhydride (13.7 µL, 0.082 mmol, 1.4 equiv). The reaction was stirred for 1 h, followed by the addition of a solution of methyl 2,3,4-tri-*O*-benzyl- α -D-galactopyranoside (**12**) (81 mg, 0.175 mmol, 3.0 equiv) in CH₂Cl₂ (0.5 mL) at –78 °C. The resulting solution was stirred for 4 h, and then triethylamine (81.0 µL, 0.583 mmol, 10.0 equiv) was added. The reaction was diluted with CH₂Cl₂ (100 mL) and washed with water (2 x 30 mL), and the organic layer was dried (Na₂SO₄) and concentrated. The residue was purified by flash column chromatography (45% acetone in toluene) to afford sialoside **13** (37 mg, 63%) as a 4:1 (α : β) mixture of anomers.

Synthesis of C1-Glycolamide-C2-Hemiketal Donor

2-benzyloxy-*N,N*-dimethylacetamide (18). To a stirred solution of *N,N*-dimethylamine hydrochloride (0.84 g, 10.30 mmol, 1.0 equiv) and benzyloxyacetyl chloride (1.79 mL, 11.33 mmol, 1.1 equiv) in dry CH₂Cl₂ (100 mL) at 0 °C was added triethylamine (3.2

mL, 22.66 mmol, 2.2 equiv), and the resulting solution was warmed to 23 °C and stirred for 1 h. The reaction was diluted with CH₂Cl₂ (200 mL) and washed with water (2 x 100 mL), and the organic layer was dried (Na₂SO₄) and concentrated. The resulting yellow oil was purified by flash column chromatography (EtOAc) to afford **18** (1.98 g, 99%) as a clear oil. *R*_f = 0.41 (EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.28 (m, 5 H, ArH), 4.61 (s, 2 H, CH₂Ph), 4.17 (s, 2 H, OCH₂), 2.98 (s, 3 H, NCH₃), 2.95 (s, 3 H, NCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 169.3, 137.3, 128.7, 128.2, 128.1, 73.4, 69.3, 36.6, 35.6; FTIR (neat film): 3480, 2932, 2867, 1652, 1497, 1454, 1401, 1343, 1264, 1108, 1028, 742, 699 cm⁻¹; HRMS (FAB) *m/z*: calcd for C₁₁H₁₆NO₂ 194.1181, found 194.1183.

2-hydroxy-*N,N*-dimethylacetamide (19). A mixture of **18** (1.98 g, 10.25 mmol, 1.0 equiv) and 10% Pd/C in EtOAc (50 mL) was stirred under hydrogen (1 atm) for 24 h. The reaction was filtered through celite, washing well with EtOAc, and concentrated to afford crude **19** (1.06 g, quant yield) as a clear oil, which was used in the next step without purification. *R*_f = 0.28 (EtOAc); ¹H NMR (400 MHz, CDCl₃) δ 4.11 (s, br, 2 H, CH₂OH), 3.61 (m, 1 H, OH), 2.99 (t, 1 H, *J* = 0.6 Hz, NCH₃), 2.86 (s, 1 H, NCH₃); ¹³C NMR (126 MHz, CDCl₃) δ 171.6, 59.9, 35.8, 34.9; FTIR (neat film): 3406, 2935, 1653, 1507, 1383, 1266, 1079, 750 cm⁻¹; HRMS (FAB) *m/z*: calcd for C₄H₉NO₂ 103.0633, found 103.0640.

2-*O*-methanesulfonyl-*N,N*-dimethylacetamide (20). To a portion of crude **19** (0.81 g, 7.84 mmol, 1.0 equiv) and methanesulfonyl chloride (1.8 mL, 23.52 mmol, 3.0 equiv) in dry CH₂Cl₂ (30 mL) at 0 °C was added triethylamine (3.2 mL, 23.52 mmol, 3.0 equiv), and the reaction was stirred at 0 °C for 1 h. The resulting solution was diluted with CH₂Cl₂ (200 mL), washed with saturated aqueous NaHCO₃ (2 x 60 mL), and the organic layer was dried (Na₂SO₄) and concentrated. The resulting yellow oil was purified by flash column chromatography (EtOAc) to afford **20** (1.04 g, 73%) as a white solid. *R*_f = 0.30 (EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 4.88 (s, 2 H, OCH₂), 3.24 (s, 3 H, SO₂CH₃), 2.96 (s, 3 H, NCH₃), 2.95 (s, 3 H, NCH₃); ¹³C NMR (126 MHz, C₆D₆) δ 165.4, 66.3, 39.4, 36.1, 35.9; FTIR (neat film): 3020, 2940, 1670, 1504, 1419, 1354, 1265, 1174, 1037, 976, 951, 873, 822, 796, 727 cm⁻¹; HRMS (EI) *m/z*: calcd for C₅H₁₁NO₄S 181.0409, found 181.0407.

2,4,7,8,9-penta-*O*-acetyl-*N*-acetylneuraminic acid *N,N*-dimethylglycolamide ester (21). To a solution of 2,4,7,8,9-penta-*O*-acetyl-*N*-acetylneuraminic acid³ (1.52 g, 2.93

mmol, 1.0 equiv) and **20** (1.04 g, 5.74 mmol, 2.0 equiv) in dry DMF (9 mL) was added solid Cs₂CO₃ (1.05 g, 3.22 mmol, 1.1 equiv), and the reaction was stirred at 23 °C for 19 h. The mixture was filtered, and the filtrate was diluted with CH₂Cl₂ (200 mL), and washed with water (2 x 80 mL). The combined aqueous layers were further extracted with CH₂Cl₂ (100 mL), and the combined organic layers were dried (Na₂SO₄) and concentrated. The residue was purified by flash column chromatography (50% acetone in PhCH₃) to afford **21** (1.62 g, 91%) as a white foam. *R*_f = 0.27 (6% MeOH in EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 5.43 (d, 1 H, *J* = 9.6 Hz, NH), 5.35 (dd, 1 H, *J* = 4.6, 2.2 Hz, H-7), 5.31 (ddd, 1 H, *J* = 11.3, 10.1, 5.0 Hz, H-4), 5.01 (ddd, 1 H, *J* = 6.9, 4.5, 2.4 Hz, H-8), 4.80 (resonance A of ABq, 1 H, *J* = 14.4 Hz, OCH₂CON(CH₃)₂), 4.79 (resonance B of ABq, 1 H, *J* = 14.4 Hz, OCH₂CON(CH₃)₂), 4.53 (dd, 1 H, *J* = 12.3, 2.5 Hz, H-9a), 4.15–4.08 (m, 2 H, H-5, H-9b), 4.05 (dd, 1 H, *J* = 10.6, 2.2 Hz, H-6), 2.95 (s, 3 H, NCH₃), 2.94 (s, 3 H, NCH₃), 2.56 (dd, 1 H, *J* = 13.5, 5.0 Hz, H-3e), 2.25 (dd, 1 H, *J* = 13.5, 11.6 Hz, H-3a), 2.14 (s, 3 H, OAc), 2.13 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.86 (s, 3 H, NAc); ¹³C NMR (126 MHz, CDCl₃) δ 171.2, 170.8, 170.6, 170.5, 170.4, 168.4, 166.0, 165.7, 97.3, 73.0, 71.9, 68.4, 68.2, 62.4, 62.3, 49.4, 36.7, 35.9, 35.7, 23.3, 21.1, 21.0, 20.9; FTIR (neat film): 3276, 3065, 2949, 1745, 1667, 1546, 1371, 1231, 1111, 1039 cm⁻¹; HRMS (FAB) *m/z*: calcd for C₂₅H₃₆N₂O₁₅Na 627.2013, found 627.2011.

C1-glycolamide-C2-hemiketal donor 8. HCl (12 N, 0.25 mL) was added dropwise to a solution of **21** (401 mg, 0.663 mmol, 1.0 equiv) in a 3:1 co-solvent of CH₂Cl₂/AcCl (16 mL). The reaction was stirred for 4 h, concentrated, and then PhCH₃ was evaporated from the residue (2 x 3 mL) affording the crude sialosyl chloride (381 mg, 99%), which was used in the next step without purification. Silver carbonate (548 mg, 1.99 mmol, 3.0 equiv) was added to a solution of the sialosyl chloride (381 mg, 0.656 mmol, 1.0 equiv) in a 4:1 co-solvent of acetone/water (20 mL) and the reaction vessel was wrapped in aluminium foil and stirred for 0.5 h. The reaction mixture was filtered through celite, washing with EtOAc, and concentrated. Purification of the residue by flash column chromatography (50% acetone in PhCH₃) gave the hemiketal **8** (271 mg, 73%) as a 1:7 (α:β) mixture of anomers. *R*_f = 0.20 (50% acetone in PhCH₃); ¹H NMR (500 MHz, CDCl₃) δ 6.79 (d, 1 H, *J* = 10.3 Hz, NH), 5.46 (t, 1 H, *J* = 1.9 Hz, H-7), 5.36 (dt, 1 H, *J* = 9.0, 1.9 Hz, H-8), 5.19 (td, 1 H, *J* = 10.8, 5.2 Hz, H-4), 4.90 (d, 1 H, *J* = 14.5 Hz, OCH₂CON(CH₃)₂), 4.73 (dd, 1 H, *J* = 12.1, 2.0 Hz, H-9a), 4.60 (d, 1 H, *J* = 14.5 Hz, OCH₂CON(CH₃)₂), 4.48 (dd, 1 H, *J* = 10.6, 2.6 Hz, H-6), 4.12 (q, 1 H, *J* = 10.2 Hz, H-5), 3.98 (dd, 1 H, *J* = 11.9, 9.2 Hz, H-9b), 2.93 (s, 3 H, NCH₃), 2.87 (s, 3 H, NCH₃), 2.32 (dd, 1 H, *J* = 13.2, 5.2 Hz, H-3e), 2.18 (dd, 1 H, *J* = 12.8, 11.6 Hz, H-3a), 2.14 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 1.96 (s, 3 H, OAc), 1.94 (s, 3 H, OAc), 1.88 (s, 3 H, NAc); ¹³C NMR (126 MHz, CDCl₃) δ 173.2, 171.3, 170.6, 170.5, 170.4, 167.7, 166.8, 95.6, 74.8, 72.5, 69.6, 69.5, 63.3, 62.6, 49.4, 36.8, 36.1, 35.8, 23.3, 21.6, 21.5, 21.1, 21.0, 20.9, 20.8, 20.7; FTIR (neat film): 3353, 2944, 1746, 1663, 1545, 1436, 1371, 1232, 1151, 1126, 1073, 1040, 946, 920, 732 cm⁻¹; LRMS (FD) *m/z*: C₂₃H₃₄N₂O₁₄, found 563.3.

Product Characterization

The structures of sialosides **6**^{4,5}, **11**⁶, and **16**⁶, were verified by comparison to previously reported literature data.

13 α : R_f = 0.20 (50% acetone in toluene); ^1H NMR (500 MHz, CD_2Cl_2) δ 7.42-7.22 (m, 15 H, ArH), 5.70 (d, 1 H, J = 9.8 Hz, NH), 5.37 (ddd, 1 H, J = 7.8, 5.9, 3.2 Hz, H-8), 5.27 (dd, 1 H, J = 7.8, 1.9 Hz, H-7), 5.20 (ddd, 1 H, J = 11.9, 9.8, 4.8 Hz, H-4), 4.96 (d, 1 H, J = 11.3 Hz, OCH_2Ph), 4.78 (m, 4 H, H-1', OCH_2Ph , OCH_2Ph), 4.65 (d, 1 H, J = 14.4 Hz, $\text{OCH}_2\text{CON}(\text{CH}_3)_2$), 4.63 (d, 1 H, J = 11.4 Hz, OCH_2Ph), 4.57 (d, 1 H, J = 11.3 Hz, OCH_2Ph), 4.45 (d, 1 H, J = 14.6 Hz, $\text{OCH}_2\text{CON}(\text{CH}_3)_2$), 4.27 (dd, 1 H, J = 12.2, 3.2 Hz, H-9a), 4.16 (dd, 1 H, J = 10.4, 2.1 Hz, H-6), 4.11 (q, 1 H, J = 9.8 Hz, H-5), 4.08 (dd, 1 H, J = 12.3, 6.0 Hz, H-9b), 3.99-4.86 (m, 5 H, H-2', H-3', H-4', H-5', H-6'a), 3.60 (dd, 1 H, J = 8.8, 6.6 Hz, H-6'b), 3.38 (s, 3 H, OCH_3), 2.92 (s, 3 H, NCH_3), 2.84 (s, 3 H, NCH_3), 2.75 (dd, 1 H, J = 12.6, 4.9 Hz, H-3e), 2.10 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 1.98 (s, 6 H, OAc), 1.89 (t, 1 H, J = 12.5 Hz, H-3a), 1.84 (s, 3 H, NAc); FTIR (neat film): 3289, 2938, 2901, 1748, 1667, 1454, 1369, 1224, 1096, 1045, 738 cm^{-1} ; HRMS (FAB) m/z : calcd for $\text{C}_{51}\text{H}_{64}\text{N}_2\text{O}_{19}\text{Na}$ 1031.4006, found 1031.4001.

13 β : R_f = 0.28 (50% acetone in toluene); ^1H NMR (500 MHz, CD_2Cl_2) δ 7.50-7.25 (m, 15 H, ArH), 5.29 (d, 1 H, J = 12.9 Hz, OCH_2Ph), 5.22 (ddd, 1 H, J = 6.2, 5.7, 2.8 Hz, H-8), 5.12 (dd, 1 H, J = 5.6, 3.2 Hz, H-7), 4.94 (ddd, 1 H, J = 11.4, 10.6, 4.7 Hz, H-4), 4.86-4.73 (m, 7 H, H-1', $\text{OCH}_2\text{CON}(\text{CH}_3)_2$, OCH_2Ph , OCH_2Ph), 4.63 (d, 1 H, J = 11.8 Hz, OCH_2Ph), 4.57 (dd, 1 H, J = 12.3, 2.7 Hz, H-9a), 4.16 (m, 1 H, H-4'), 4.08 (d, 1 H, J = 10.4 Hz, NH), 4.06-3.95 (m, 4 H, H-9b, H-2', H-5', H-3'), 3.95 (q, 1 H, J = 10.5 Hz, H-5), 3.78 (dd, 1 H, J = 9.4, 6.7 Hz, H-6'a), 3.66 (dd, 1 H, J = 8.9, 8.3 Hz, H-6'b), 3.64 (dd, 1 H, J = 10.6, 2.4 Hz, H-6), 3.40 (s, 3 H, OCH_3), 2.93 (s, 3 H, NCH_3), 2.90 (s, 3 H, NCH_3), 2.45 (dd, 1 H, J = 12.9, 4.6 Hz, H-3e), 2.12 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.95 (s, 3 H, OAc), 1.91 (dd, 1 H, J = 13.1, 11.7 Hz, H-3a), 1.70 (s, 3 H, NAc); FTIR (neat film): 3386, 2933, 2901, 1746, 1674, 1370, 1227, 1040, 735 cm^{-1} ; HRMS (FAB) m/z : calcd for $\text{C}_{51}\text{H}_{64}\text{N}_2\text{O}_{19}\text{Na}$ 1031.4006, found 1031.4001.

15 α : R_f = 0.20 (6% methanol in ethyl acetate); ^1H NMR (500 MHz, CD_2Cl_2) δ 5.73 (d, 1 H, J = 9.9 Hz, NH), 5.48 (d, 1 H, J = 5.0 Hz, H-1'), 5.36 (ddd, 1 H, J = 7.4, 5.9, 3.2 Hz, H-8), 5.26 (dd, 1 H, J = 7.4, 2.0 Hz, H-7), 5.18 (ddd, 1 H, J = 11.9, 9.9, 4.9 Hz, H-4), 4.93 (d, 1 H, J = 14.2 Hz, $\text{OCH}_2\text{CON}(\text{CH}_3)_2$), 4.78 (d, 1 H, J = 14.6 Hz, $\text{OCH}_2\text{CON}(\text{CH}_3)_2$), 4.58 (dd, 1 H, J = 7.9, 2.4 Hz, H-3'), 4.31-4.26 (m, 2 H, H-2', H-9a), 4.22 (dd, 1 H, J = 8.0, 1.4 Hz, H-4'), 4.16 (dd, 1 H, J = 10.6, 1.9 Hz, H-6), 4.12 (dd, 1 H, J = 12.1, 5.9 Hz, H-9b), 4.11 (t, 1 H, J = 10.5 Hz, H-5), 3.90-3.84 (m, 2 H, J = H-5', H-6'a), 3.64 (m, 1 H, H-6'b), 2.97 (s, 3 H, NCH_3), 2.96 (s, 3 H, NCH_3), 2.74 (dd, 1 H, J = 12.6, 4.9 Hz, H-3e) 2.10 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.98 (s, 3 H, OAc), 1.91 (t, 1 H, J = 12.2 Hz, H-3a), 1.84 (s, 3 H, NAc), 1.51 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.32 (s, 6 H, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.1, 170.9, 170.7, 170.4, 170.3, 167.6, 165.8, 109.5, 108.8, 99.2, 96.7, 73.0, 71.2, 71.1, 70.2, 70.0, 68.1, 67.1, 63.3, 62.6, 62.4, 49.4, 37.8, 36.1, 36.0, 26.4, 25.3, 25.0, 21.3, 21.2, 21.1; FTIR (neat film): 3289, 2988, 1748, 1667, 1371, 1218, 1125, 1070, 1044, 1005 cm^{-1} ; HRMS (FAB) m/z : calcd for $\text{C}_{35}\text{H}_{52}\text{N}_2\text{O}_{19}\text{Na}$ 827.3059, found 827.3062.

15 β : R_f = 0.28 (6% methanol in ethyl acetate); ^1H NMR (500 MHz, CD_2Cl_2) δ 5.48 (d, 1 H, J = 5.0 Hz, H-1'), 5.42 (dd, 1 H, J = 3.9, 2.2 Hz, H-7), 5.27 (ddd, 1 H, J = 11.4, 10.4, 5.0 Hz, H-4), 5.18 (m, 2 H, H-8, NH), 4.86 (d, 1 H, J = 14.5 Hz, $\text{OCH}_2\text{CON}(\text{CH}_3)_2$), 4.77 (d, 1 H, J = 14.5 Hz, $\text{OCH}_2\text{CON}(\text{CH}_3)_2$), 4.75 (dd, 1 H, J = 12.4, 2.6 Hz, H-9a), 4.65 (dd, 1 H, J = 8.0, 2.6 Hz, H-3'), 4.39 (dd, 1 H, J = 8.1, 1.9 Hz, H-4'), 4.32 (dd, 1 H, J = 5.1, 2.5 Hz, H-2'), 4.14 (m, 2 H, H-6, H-9b), 4.02 (q, 1 H, J = 10.2 Hz, H-5), 3.99 (m, 1 H, H-5'), 3.67 (t, 1 H, J = 8.5 Hz, H-6'a), 3.61 (dd, 1 H, J = 8.7, 5.6 Hz, H-6'b), 2.94 (s, 3 H, NCH_3), 2.93 (s, 3 H, NCH_3), 2.52 (dd, 1 H, J = 12.9, 4.9 Hz, H-3e), 2.12 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.00 (dd, 1 H, J = 12.9, 11.4 Hz, H-3a), 1.99 (s, 6H, OAc), 1.84 (s, 3 H, NAc), 1.54 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.0, 170.7, 170.4, 166.8, 165.7, 109.9, 109.1, 99.1, 96.7, 73.2, 72.4, 71.2, 71.1, 70.9, 69.2, 68.8, 66.2, 63.2, 62.5, 62.2, 49.8, 37.6, 35.9, 26.5, 26.3, 25.3, 25.1, 21.4, 21.1; FTIR (neat film): 3300, 3062, 2982, 2940, 1746, 1668, 1540, 1436, 1372, 1228, 1117, 1071, 1038, 1001, 735 cm^{-1} ; HRMS (FAB) m/z : calcd for $\text{C}_{35}\text{H}_{52}\text{N}_2\text{O}_{19}\text{Na}$ 827.3059, found 827.3062.

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