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SUPPORTING MATERIAL

A New C(1)-Auxiliary for Anomeric Stereocontrol in the Synthesis of α-Sialyl Glycosides.

Jannine M. Haberman and David Y. Gin*

Department of Chemistry,
University of Illinois at Urbana-Champaign,
Urbana, IL 61801

General Procedures. All reactions were performed in dry modified Schlenk (Kjedahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon, unless otherwise noted. Air-and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 35 °C at *ca.* 25 torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm).

Materials. Dichloromethane, toluene, and triethylamine were distilled from calcium hydride at 760 Torr. The carbohydrate coupling partners were dried by azeotropic removal of water with toluene in vacuo prior to use.

Instrumentation. 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}). HRMS data were obtained on a Micromass 70-SE-4F mass spectrometer using the *peak matching* technique to verify accurate mass values. Proton and carbon-13 nuclear magnetic resonance (^1H NMR or ^{13}C 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 ($CHCl_3$: δ 7.26; C_6HD_5: δ 7.16). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, bs = broad singlet, m = multiplet and/or multiple resonances), integration, and coupling constants in Hertz (Hz).

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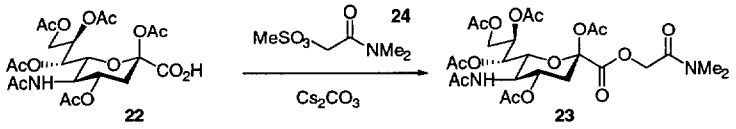
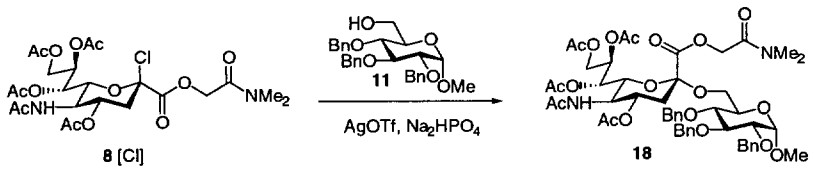
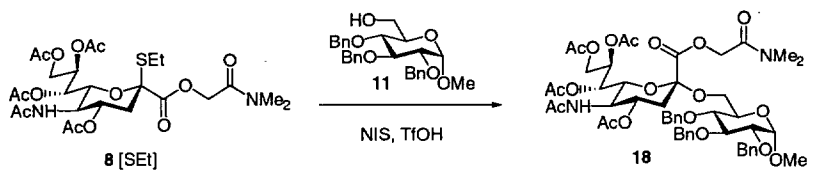
REPRESENTATIVE GLYCOSYLATION PROCEDURES



Typical reaction procedure for the installation of the C(1)-X_A auxiliary. To a solution of tetra-*O*-acetylneuraminic acid **22** (309 mg, 0,60 mmol, 1 equiv) and 2-*O*-methansulfonyl-*N,N*-dimethylglycolamide (**24**, 235 mg, 1.3 mmol, 2.2 equiv) in dry DMF (1.9 mL) was added solid Cs_2CO_3 (213 mg, 0.65 mmol, 1.1 equiv), and the reaction was stirred at 23 °C for 6 h. The mixture was diluted with CH_2Cl_2 (200 mL), and the organic layer was washed with water (2 x 80 mL). The combined aqueous layers were further extracted with CH_2Cl_2 (100 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash column chromatography (gradient elution: 100% $CHCl_3$→6% MeOH in $CHCl_3$) to afford the neuraminic acid ester **23** (312 mg, 88%).



Typical procedure for sialosyl chloride couplings. To a solution of the sialosyl chloride **8** (56 mg, 0.097 mmol, 1 equiv), methyl 2,3,4-tetra-*O*-benzyl-α-D-glucopyranoside (**11**) (90 mg, 0.194 mmol, 2.0 equiv), and Na_2HPO_4 (55 mg, 0.388 mmol, 4.0 equiv) in toluene (2.3 mL) at –20 °C was added solid AgOTf (35 mg, 0.136 mmol, 1.4 equiv). The reaction was stirred at this temperature for 1 h, then at 0 °C for 1h. The reaction was diluted with EtOAc (2 mL), and was filtered through celite, washing well with EtOAc. The filtrate was diluted with EtOAc (100 mL) and was washed with saturated aqueous sodium chloride solution (30 mL). The aqueous layer was further extracted with a solution of 2% MeOH in CH_2Cl_2 (2 x 50 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash column chromatography (6% MeOH in EtOAc) to afford the sialoside **18** (60 mg, 61%) as a 7:1 (α:β) mixture of anomers.



Typical procedure for thiosialoside couplings. To a solution of the ethylthiosialoside **8** (34 mg, 0.057 mmol, 1 equiv), methyl 2,3,4-tetra-*O*-benzyl-α-D-glucopyranoside (**11**) (53 mg, 0.053 mmol, 2.0 equiv), and *N*-iodosuccinimide (38 mg, 0.171 mmol, 3.0 equiv) in CH_2Cl_2 (1.0 mL) at –50 °C was added a catalytic amount of triflic acid (2 μL). The reaction was stirred at

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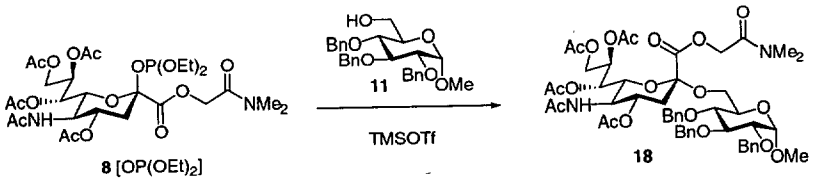
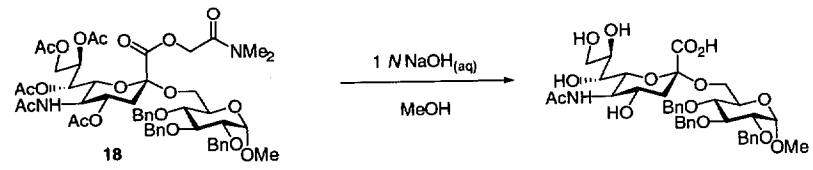
this temperature for 2 h and then was diluted with CH_2Cl_2 (100 mL). The solution was washed sequentially with saturated aqueous sodium bicarbonate solution (30 mL) and saturated aqueous sodium thiosulfate solution (30 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash column chromatography (45% acetone in toluene) to afford the sialoside **18** (46 mg, 80%) as a 3:1 (α:β) mixture of anomers.



Typical procedure for sialosyl phosphite couplings. To a solution of the sialosyl phosphite **8** (49 mg, 0.072 mmol, 1 equiv) and methyl 2,3,4-tetra-*O*-benzyl-α-D-glucopyranoside (**11**) (50 mg, 0.108 mmol, 1.5equiv) in CH_2Cl_2 (0.7 mL) at –44 °C was added a catalytic amount of trimethylsilyl triflate (2 μL). The reaction was stirred at this temperature for 1 h and then was neutralized with the addition of Et_3N (20 μL, 0.144 mmol, 2.0 equiv). The reaction was concentrated, and the residue was purified by flash column chromatography (45% acetone in toluene) to afford the sialoside **18** (56 mg, 77%) as a 6:1 (α:β) mixture of anomers.



Typical procedure for base hydrolysis of the C(1)-glycolamide auxiliary. To a solution of sialoside **18** (32 mg, 0.032 mmol, 1 equiv) in MeOH (1 mL) was added an aqueous solution of NaOH (0.5 mL, 1 *N* $NaOH_{(aq)}$), and the reaction was stirred at 23 °C for 1.5 h. The reaction was acidified with the addition of Amberlyst-15, and the reaction mixture was then filtered and concentrated. The residue was purified by chromatography on LH-20 Sephadex (50% MeOH in CH_2Cl_2) to afford the corresponding de-acetylated product sialoside as a colorless glassy solid (24 mg, quantitative).

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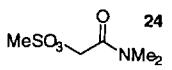
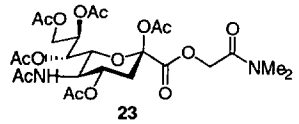
PRODUCT CHARACTERIZATION

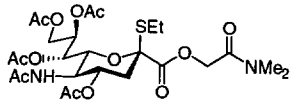


24: R_f = 0.30 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.88 (s, 2 H, OCH_2), 3.24 (s, 3 H, SO_2CH_3), 2.96 (s, 3 H, NCH_3), 2.95 (s, 3 H, NCH_3); ^{13}C NMR (126 MHz, C_6D_6) δ 165.4, 66.3, 39.4, 36.1, 35.9; FTIR (neat film): 3020, 2940, 1670, 1504, 1419, 1354, 1265, 1174, 1037, 976, 951, 873, 822, 796, 727 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_5H_{11}NO_4S$ 181.0409, found 181.0407.



23

23: R_f = 0.27 (6% acetone in EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) 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, H-Aa), 4.79 (resonance B of ABq, 1 H, *J* = 14.4 Hz, H-Ab), 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, NCH_3), 2.94 (s, 3 H, NCH_3), 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{25}H_{36}N_2O_{15}Na$ 627.2013, found 627.2011.



8 [SEt]

8 [SEt]:[1] R_f = 0.36 (6% MeOH in EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (d, 1 H, *J* = 10.2, NH), 5.43 (t, 1 H, *J* = 2.6 Hz, H-7), 5.28 (ddd, 1 H, *J* = 11.6, 10.4, 4.9 Hz, H-4), 5.10 (dt, 1 H, *J* = 8.4, 2.6 Hz, H-8), 4.93 (d, 1 H, *J* = 14.3 Hz, H-Aa), 4.79 (dd, 1 H, *J* = 12.4, 2.4 Hz, H-9a), 4.68 (d, 1 H, *J* = 14.3 Hz, H-Ab), 4.37 (dd, 1 H, *J* = 10.6, 2.5 Hz, H-6), 4.14 (dd, 1 H, *J* = 12.4, 8.2 Hz, H-9b), 4.09 (q, 1 H, *J* = 10.3 Hz, H-5), 2.96 (s, 3 H, NCH_3), 2.95 (s, 3 H, NCH_3), 2.80 (dq, 1 H, *J* = 12.0, 7.5 Hz, SCH_2), 2.56 (dd, 1 H, *J* = 13.9, 4.9 Hz, H-3e), 2.52 (dq, 1 H, *J* = 12.0, 7.5 Hz, SCH_2), 2.27 (dd, 1 H, *J* = 13.9, 11.7 Hz, H-3a), 2.12 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 1.99 (s, 6 H, OAc), 1.86 (s, 3 H, NAc), 1.21 (t, 3 H, *J* = 7.5 Hz, CH_3); ^{13}C NMR (126

[1] Prepared according to the procedure of: Marra, A.; Sinay, P. *Carbohydr. Res.* **1989**, *187*,35-42. Irradiation of the C6-proton NMR resonance led to 3% NOE of one of the diastereomeric *SCH*$_2$ resonances, thereby confirming the β-anomeric configuration.

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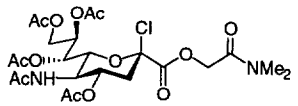
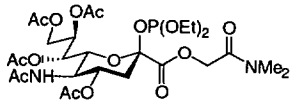
MHz, $CDCl_3$) δ 171.2, 171.1, 170.8, 170.5, 170.4, 167.8, 165.6, 85.3, 73.0, 72.4, 69.5, 68.9, 62.8, 62.3, 49.7, 37.5, 35.9, 35.8, 23.3, 22.8, 21.2, 21.0, 20.9, 14.0; FTIR (neat film): 3618, 3481, 3276, 2938, 1742, 1668, 1548, 1436, 1372, 1229, 1098, 1038, 942 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{25}H_{38}N_2O_{13}NaS$ 629.1992, found 629.1991.



8 [Cl]

8 [Cl]:[2] R_f = 0.34 (6% MeOH in EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ 5.53 (d, 1 H, *J* = 10.1 Hz, NH), 5.47 (dd, 1 H, *J* = 6.8, 1.3 Hz, H-7), 5.42 (td, 1 H, *J* = 10.9, 4.7 Hz, H-4), 5.17 (td, 1 H, *J* = 6.3, 2.2 Hz, H-8), 4.97 (d, 1 H, *J* = 14.0 Hz, H-Aa), 4.75 (d, 1 H, *J* = 14.0, H-Ab), 4.43 (dd, 1 H, *J* = 12.6, 2.4 Hz, H-9a), 4.37 (dd, 1 H, *J* = 10.7, 1.3 Hz, H-6), 4.23 (q, 1 H, *J* = 10.3 Hz, H-5), 4.05 (dd, 1 H, *J* = 12.5, 5.8 Hz, H-9b), 2.97 (s, 6 H, NCH_3), 2.83 (dd, 1 H, *J* = 13.9, 4.6 Hz, H-3e), 2.43 (dd, 1 H, *J* = 13.8, 11.4 Hz, H-3a), 2.12 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.03 (s, 6 H, OAc), 1.90 (s, 3 H, NAc); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 170.9, 170.5, 170.3, 169.9, 165.2, 165.0, 96.6, 74.1, 70.1, 68.9, 67.1, 63.1, 62.3, 48.9, 40.9, 36.0, 35.8, 23.3, 21.2, 21.0; FTIR (neat film): 3281, 3065, 2955, 1749, 1668, 1544, 1436, 1371, 1313, 1226, 1176, 1125, 1097, 1040, 945, 735 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{23}H_{33}N_2O_{13}NaCl$ 603.1569, found 603.1569.



8 [OP(OEt)$_2$]

8 [OP(OEt)$_2$]:[3] R_f = 0.20 (40% acetone in toluene); ^1H NMR (500 MHz, C_6D_6) δ 5.82 (t, 1 H, *J* = 2.5 Hz, H-7), 5.73 (dt, 1 H, *J* = 8.5, 2.5 Hz, H-8), 5.51 (ddd, 1 H, *J* = 11.5, 10.1, 5.0 Hz, H-4), 5.33 (dd, 1 H, *J* = 12.3, 2.2 Hz, H-9a), 4.70-4.61 (m, 3 H, H-5, H-6, H-9b), 4.50 (d, 1 H, *J* = 14.2, Hz, H-Aa), 4.45 (d, 1 H, *J* = 9.7 Hz, NH), 4.30-4.20 (m, 1 H, OCH_2), 4.19 (d, 1 H, *J* = 14.5 Hz, H-Ab), 4.16-4.02 (m, 3 H, OCH_2), 2.91 (dd, 1 H, *J* = 13.3, 5.1 Hz, H-3e), 2.72 (ddd, 1 H, *J* = 13.4, 11.5, 1.7 Hz, H-3a), 2.38 (s, 3 H, NCH_3), 1.92 (s, 3 H, Ac), 1.89 (s, 3 H, Ac), 1.75 (s, 3 H, Ac), 1.74 (s, 3 H, NCH_3), 1.54 (s, 3 H, Ac), 1.53 (s, 3 H, Ac), 1.37 (t, 3 H, *J* = 7.1 Hz, CH_3), 1.21 (t, 3 H, *J* = 7.0 Hz, CH_3); ^{13}C NMR (126 MHz, C_6D_6) δ 170.7, 170.3, 170.1,

[2] Prepared according to the procedure of: Kuhn, R.; Lutz, P.; MacDonald, D. L. *Chem. Ber.* **1966**, *99*, 611-617. which is known to produce the β-chloro anomer. NOE or gated proton decoupled ^{13}C NMR experiments were unsuccessful in determining anomeric configuration in **8[Cl]**. However, the value of $J_{7,8}$, an empirical guideline used to distinguish anomeric configuration in acetyl protected Neu5Ac glycosides (see ref. 2a in manuscript), is similar to that for **7β[Cl]**.

[3] Prepared according to the procedure of: Martin, T. J.; Schmidt, R. R. *Tetrahedron Lett.* **1992**, *33*, 6123-6126, which is known to produce the β-phosphite anomer. NOE or gated proton decoupled ^{13}C NMR experiments were unsuccessful in determining anomeric configuration in **8[OP(OEt)$_2$]**. However, the value of $J_{7,8}$, an empirical guideline used to distinguish anomeric configuration in acetyl protected Neu5Ac glycosides (see ref. 2a in manuscript), is similar to that for **7β[OP(OEt)$_2$]**.

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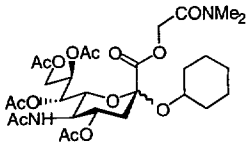
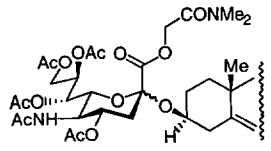
170.0, 169.3, 167.8, 164.5, 98.6, 73.7, 73.4, 68.8, 68.7, 63.6, 62.3, 58.9, 58.8, 49.2, 39.3, 34.5, 34.1, 22.7, 20.8, 20.4, 20.3, 20.2, 16.9, 16.8; FTIR (neat film): 3488, 3275, 2976, 1744, 1668, 1558, 1371, 1230, 1115, 1038, 944, 733 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{27}H_{43}N_2O_{16}NaP$ 705.2248, found 705.2251.



14

14α: R_f = 0.29 (40% acetone in toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (d, 1 H, *J* = 9.2 Hz, NH), 5.38-5.29 (m, 3 H, H-4, H-7, H-8), 4.95 (d, 1 H, *J* = 14.3 Hz, H-Aa), 4.69 (d, 1 H, *J* = 14.3 Hz, H-Ab), 4.37 (dd, 1 H, *J* = 12.3, 2.6 Hz, H-9a), 4.18-4.12 (m, 2 H, H-5, H-6), 4.11 (dd, 1 H, *J* = 12.4, 5.9 Hz, H-9b), 3.95-3.88 (m, 1 H, H-1'), 2.98 (s, 3 H, NCH_3), 2.97 (s, 3 H, NCH_3), 2.73 (dd, 1 H, *J* = 12.5, 4.9 Hz, H-3e), 2.14 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.93-1.85, (m, 5 H, H-3a, NAc, cyH), 1.76-1.56 (m, 3 H, cyH), 1.53-1.45 (m, 1 H, cyH), 1.40-1.07 (m, 5 H, cyH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 170.9, 170.6, 170.3, 168.2, 165.6, 98.8, 73.6, 72.5, 70.0, 69.7, 67.8, 62.5, 62.2, 49.1, 38.4, 36.0, 35.9, 34.9, 33.5, 25.6, 24.5, 24.3, 23.4, 21.2, 21.1, 21.0, 20.9; FTIR (neat film): 3474, 3286, 2938, 2860, 1745, 1662, 1557, 1436, 1370, 1227, 1122, 1039, 732 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{29}H_{44}N_2O_{14}Na$ 667.2690, found 667.2688.

14β: R_f = 0.33 (40% acetone in toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (t, 1 H, *J* = 2.1 Hz, H-7), 5.32-5.22 (m, 2 H, H-4, NH), 5.14(dt, 1 H, *J* = 8.3, 2.3 Hz, H-8), 4.96 (d, 1 H, *J* = 14.3 Hz, H-Aa), 4.94(dd, 1 H, *J* = 12.3, 2.1 Hz, H-9a), 4.65 (d, 1 H, *J* = 14.2 Hz, H-Ab), 4.15-4.09 (m, 3 H, H-9b, H-6, H-5), 3.85-3.78 (m, 1 H, H-1'), 2.97 (s, 3 H, NCH_3), 2.96 (s, 3 H, NCH_3), 2.55 (dd, 1 H, *J* = 13.1, 4.8 Hz, H-3e), 2.14 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.05 (dd, 1 H, *J* = 13.2, 11.7 Hz, H-3a), 2.01 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.90-1.83 (m, 4 H, cyH, NAc), 1.78-1.65 (m, 4 H, cyH), 1.53-1.14 (m, 5 H, cyH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 171.3, 170.9, 170.6, 170.4, 167.8, 165.5, 98.6, 73.9, 73.5, 72.6, 69.3, 69.2, 63.2, 62.2, 49.7, 38.5, 35.9, 35.8, 34.4, 33.1, 25.5, 24.4, 24.2, 23.4, 21.3, 21.1, 21.0; FTIR (neat film): 2938, 2860, 1745, 1673, 1548, 1371, 1229, 1118, 1037 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{29}H_{44}N_2O_{14}Na$ 667.2690, found 667.2688.



16

16α: R_f = 0.38 (40% acetone in toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (d, 1 H, *J* = 10.0 Hz, NH), 5.37–5.31 (m, 3 H, H-8, H-7, H-6'), 5.26 (ddd, 1 H, *J* = 11.7, 10.2, 4.8 Hz, H-4), 4.90 (resonance A of ABq, 1 H, *J* = 14.4 Hz, H-Aa), 4.77 (resonance B of ABq, 1 H, *J* = 14.4 Hz, H-Ab), 4.42 (dd, 1 H, *J* = 12.2, 2.2 Hz, H-9a), 4.20 (dd, 1 H, *J* = 10.6, 1.7 Hz, H-6),

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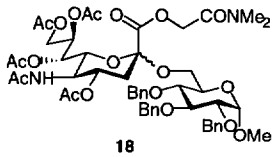
4.15 (dd, 1 H, J = 12.1, 6.1 Hz, H-9b), 4.12 (q, 1 H, J = 10.4 Hz, H-5), 3.82 (m, 1 H, H-3'), 2.97 (s, 3 H, NCH_3), 2.96 (s, 3 H, NCH_3), 2.73 (dd, 1 H, J = 12.6, 4.8 Hz, H-3e), 2.37–2.23 (m, 2 H, steroidal H), 2.14 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.01–1.96 (m, 5 H, H-3a, steroidal H), 2.00 (s, 3 H, OAc), 1.87 (s, 3 H, NAc), 1.86–1.75 (m, 2 H, steroidal H), 1.68–0.82 (m, 2 H, steroidal H), 0.97 (s, 3 H, H-18'), 0.90 (d, 3 H, J = 6.5 Hz, H-20'), 0.85 (d, 3 H, J = 6.6 Hz, H-26'), 0.84 (d, 3 H, J = 6.6 Hz, H-27'), 0.66 (s, 3 H, H-19'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 170.8, 170.7, 170.5, 170.3, 168.2, 165.7, 140.7, 122.1, 99.2, 75.2, 72.9, 70.6, 70.0, 68.2, 67.8, 62.5, 62.3, 56.9, 56.3, 50.2, 49.1, 42.5, 41.2, 39.9, 38.2, 37.5, 36.6, 36.4, 36.0, 35.9, 32.2, 32.0, 29.6, 28.4, 28.2, 24.5, 24.0, 23.3, 23.0, 22.7, 21.3, 21.2, 21.1, 21.0, 19.4, 18.9, 12.0; FTIR (neat film): 3481, 3283, 2940, 2867, 1745, 1661, 1436, 1370, 1224, 1125, 1040, 736 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{50}H_{78}N_2O_{14}Na$ 953.5351, found 953.5352.

16β: R_f = 0.44 (40% acetone in toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.37 (t, 1 H, J = 2.0 Hz, H-7), 5.30–5.23 (m, 3 H, H-4, H-6', NH), 5.08 (dt, 1 H, J = 8.0, 2.1 Hz, H-8), 4.92 (d, 1 H, J = 14.2 Hz, H-Aa), 4.86 (dd, 1 H, J = 12.4, 2.1 Hz, H-9a), 4.70 (d, 1 H, J = 14.2 Hz, H-Ab), 4.17–4.08 (m, 3 H, H-5, H-9b, H-6), 3.59 (m, 1 H, H-3'), 2.98 (s, 3 H, NCH_3), 2.97 (s, 3 H, NCH_3), 2.55 (dd, 1 H, J = 13.2, 5.0 Hz, H-3e), 2.33–2.20 (m, 2 H, steroidal H), 2.14 (s, 3 H, OAc), 2.10 (dd, 1 H, J = 13.1, 11.8 Hz, H-3a), 2.07 (s, 3 H, OAc), 2.01–1.92 (m, 2 H, steroidal H), 2.00 (s, 3 H, OAc), 1.99 (s, 3 H, OAc), 1.90–1.76 (m, 4 H, steroidal H), 1.87 (s, 3 H, NAc), 1.74–0.83 (m, 20 H, steroidal H), 1.00 (s, 3 H, H-18'), 0.91 (d, 3 H, J = 6.4 Hz, H-20'), 0.86 (d, 3 H, J = 6.6 Hz, H-26'), 0.85 (d, 3 H, J = 6.5 Hz, H-27'), 0.67 (s, 3 H, H-19'); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 171.3, 170.8, 170.7, 170.4, 167.6, 165.4, 140.6, 122.3, 98.8, 75.6, 73.7, 72.8, 69.4, 69.1, 63.3, 62.2, 61.5, 57.0, 56.3, 50.3, 49.7, 42.5, 40.0, 39.7, 39.6, 38.4, 37.4, 36.6, 36.4, 36.0, 35.8, 32.1, 32.0, 30.6, 28.4, 28.2, 24.5, 24.0, 23.4, 23.0, 22.8, 21.3, 21.2, 21.1, 21.0, 19.5, 18.9, 12.0; FTIR (neat film): 2939, 2867, 1745, 1668, 1371, 1230, 1119, 1039 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{50}H_{78}N_2O_{14}Na$ 953.5351, found 953.5352.



18

18α: R_f = 0.20 (40% acetone in toluene); ^{1}H NMR (500 MHz, C_6D_6) δ 7.55-7.51 (m, 2 H, ArH), 7.38-7.34 (m, 2 H, ArH), 7.29-7.21 (m, 4 H, ArH), 7.19-7.00 (m 7 H, ArH), 5.38 (ddd, 1 H, J = 8.2, 5.7, 2.6 Hz, H-8), 5.78 (ddd, 1 H, J = 12.0, 10.1, 4.8 Hz, H-4), 5.64 (dd, 1 H, J = 8.1, 2.1 H, H-7), 5.17 (resonance A of ABq, 1 H, J = 11.1 H, $PhCH_2$), 5.08 (resonance B of ABq, 1 H, J = 11.1 Hz, $PhCH_2$), 5.07 (d, 1 H, J = 10.2 Hz, NH), 5.01 (d, 1 H, J = 11.4 Hz, $PhCH_2$), 4.84 (d, 1 H, J = 11.4 Hz, $PhCH_2$), 4.73 (dd, 1 H, J = 11.0, 4.5 Hz, H-6a'), 4.70 (d, 1 H, J = 3.4 Hz, H-1'), 4.65 (dd, 1 H, J = 12.6, 2.7 Hz, H-9a), 4.61 (q, 1 H, J = 10.4 Hz, H-5), 4.55 (resonance A of ABq, 1 H, J = 12.1 Hz, $PhCH_2$), 4.53 (dd, 1 H, J = 8.9, 2.2 Hz, H-6), 4.44 (resonance B of ABq, 1 H, J = 12.1 Hz, $PhCH_2$), 4.39 (d, 1 H, J = 14.4 Hz, H-Aa), 4.28 (t, 1 H, J = 9.3 Hz, H-3'), 4.13 (dd, 1 H, J = 12.6, 5.9, H-9b), 4.10-4.05 (m, 2 H, H-5', H-6b'), 3.96 (t, 1 H, J = 9.4 Hz, H-4'), 3.79 (d, 1 H, J = 14.2 Hz, H-Ab), 3.59 (dd, 1 H, J = 9.7, 3.6 Hz, H-2'), 3.22 (dd, 1 H, J = 12.5, 4.8 Hz, H-3e), 3.17 (s, 3 H, OCH_3), 2.36 (s, 3 H, NCH_3), 2.27 (t, 1 H, J = 12.5 Hz, H-3a), 2.04 (s, 3 H, Ac), 1.85 (s, 3 H, Ac), 1.77 (s, 3 H, Ac), 1.73 (s, 3 H, NCH_3), 1.63 (s, 3 H, Ac), 1.53(s, 3 H, Ac); ^{13}C NMR (126 MHz, C_6D_6) δ 171.1, 170.9, 170.6, 170.1,

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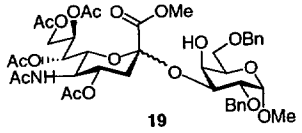
170.0, 166.8, 165.5, 139.0, 138.9, 138.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 98.8, 98.4, 82.2, 79.7, 77.5, 76.0, 75.0, 73.6, 72.3, 69.9, 69.7, 68.4, 67.0, 63.2, 62.3, 62.1, 55.3, 49.1, 38.4, 36.0, 35.9, 23.4, 21.2, 21.1, 21.0, 20.6; FTIR (neat film): 3488, 3290, 2936, 1747, 1662, 1551, 1454, 1369, 1222, 1123, 1093, 1072, 1044, 741, 699 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{51}H_{64}N_2O_{19}Na$ 1031.4001, found 1031.4006.

18β: R_f = 0.28 (40% acetone in toluene); ^1H NMR (500 MHz, C_6D_6) δ 7.55-7.52 (m, 2 H, ArH), 7.36-7.32 (m, 2 H, ArH), 7.24-7.00 (m, 11 H, ArH), 5.92-5.89 (m, 2 H, H-8, H-7), 5.37 (dd, 1 H, *J* = 12.3, 1.9 Hz, H-9a), 5.63 (td, 1 H, *J* = 11.2, 5.0 Hz, H-4), 5.33 (d, 1 H, *J* = 3.5 Hz, H-1'), 5.18 (resonance A of ABq, 1 H, *J* = 11.2 Hz, $PhCH_2$), 5.06 (resonance B of ABq, 1 H, *J* = 11.2 Hz, $PhCH_2$), 5.02 (resonance A of ABq, 1 H, *J* = 11.2 Hz, $PhCH_2$), 4.89 (resonance B of ABq, 1 H, *J* = 11.2 Hz, $PhCH_2$), 4.84 (dd, 1 H, *J* = 10.3, 2.3 Hz, H-6), 4.73 (dd, 1 H, *J* = 11.1, 2.3 Hz, H-6a'), 4.69-4.61 (m, 3 H, H-9b, H-5, NH), 4.54 (resonance A of ABq, 1 H, *J* = 12.0 Hz, $PhCH_2$), 4.48 (resonance B of ABq, 1 H, *J* = 12.0 Hz, $PhCH_2$), 4.42 (dd, 1 H, *J* = 11.1, 1.9 Hz, H-6b'), 4.31 (m, 2 H, H-3', H-Aa), 4.19 (t, 1 H, *J* = 9.4 Hz, H-4'), 4.14 (d, 1 H, *J* = 14.3 Hz, H-Ab), 4.12 (dt, 1 H, *J* = 10.1, 1.8 Hz, H-5'), 3.90 (dd, 1 H, *J* = 9.6, 3.5 Hz, H-2'), 3.44 (s, 3 H, OCH_3), 2.92 (dd, 1 H, *J* = 13.1, 5.2 Hz, H-3e), 2.38 (s, 3 H, NCH_3), 2.36 (dd, 1 H, *J* = 13.1, 11.5 Hz, H-3a), 1.93 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 1.74 (s, 3 H, NCH_3), 1.71 (s, 3 H, Ac), 1.57 (s, 3 H, Ac), 1.44 (s, 3 H, Ac); ^{13}C NMR (126 MHz, C_6D_6) δ 171.3, 171.2, 170.8, 170.7, 170.4, 166.8, 165.2, 139.0, 138.9, 138.6, 129.3, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 99.7, 98.4, 98.0, 82.3, 80.3, 77.3, 76.0, 75.0, 74.0, 73.3, 71.9, 69.3, 69.2, 69.1, 63.4, 62.5, 62.1, 55.1, 49.5, 37.8, 35.8, 35.7, 23.4, 21.3, 21.1, 21.0, 20.9; FTIR (neat film): 3488, 3290, 2935, 1742, 1674, 1370, 1230, 1164, 1120, 1072, 1041, 743, 699 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{51}H_{64}N_2O_{19}Na$ 1031.4001, found 1031.4006.



19

19α: R_f = 0.14 (20% acetone in $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.37-7.30 (m, 4 H, ArH), 7.22-7.16 (m, 5 H, ArH), 7.10-7.05 (m, 1 H, ArH), 5.74 (td, 1 H, *J* = 7.0, 2.5 Hz, H-8), 5.43 (dd, 1 H, *J* = 6.9, 2.3 Hz, H-7), 4.88 (ddd, 1 H, *J* = 16.1, 11.8, 4.7 Hz, H-4), 4.33 (q, 1 H, *J* = 10.5 Hz, H-5), 4.27 (t, 1 H, *J* = 6.4 Hz, H-5'), 4.22 (dd, 1 H, *J* = 12.3, 7.0 Hz, H-9b), 4.11 (dd, 1 H, *J* = 9.8, 2.7 Hz, H-6a'), 4.04 (d, 1 H, *J* = 10.3 Hz, NH), 4.01-3.95 (m, 2 H, H-6b', H-3'), 3.38 (s, 3 H, CO_2CH_3), 3.21 (s, 3 H, OCH_3), 2.72 (dd, 1 H, *J* = 13.1, 4.8 Hz, H-3e), 2.36 (dd, 1 H, *J* = 12.9, 12.1 Hz, H-3a), 2.03 (s, 3 H, Ac), 1.87 (s, 3 H, Ac), 1.72 (s, 3 H, Ac), 1.57 (s, 3 H, Ac), 1.55 (s, 3 H, Ac); HRMS (FAB) *m/z*: calcd for $C_{41}H_{53}NO_{18}Na$ 870.3160, found 870.3164.

19β: R_f = 0.10 (20% acetone in $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.49-7.44 (m, 2 H, ArH), 7.33-7.29 (m, 2 H, ArH), 7.24-7.19 (m, 2 H, ArH), 7.19-7.14 (m, 2 H, ArH), 7.10-7.04 (m, 2 H, ArH), 5.79 (ddd, 1 H, *J* = 8.3, 3.1, 2.6 Hz, H-8), 5.71 (dd, 1 H, *J* = 3.1, 2.8 Hz, H-7), 5.52 (ddd, 1 H, *J* = 11.4, 10.5, 4.6 Hz, H-4), 5.35 (dd, 1 H, *J* = 12.4, 2.3 Hz, H-9a), 4.81 (dd, 1 H, *J* = 10.6, 2.6 Hz, H-6), 4.80 (m, 1 H, H-4'), 4.68 (d, 1 H, *J* = 11.7 Hz, $PhCH_2$), 4.57-4.41 (m, 8 H, H-9b, H-5, $PhCH_2$, NH, H-1', H-2'), 4.23 (bs, 1 H, OH), 4.20 (ddd, 1 H, *J* = 11.0, 3.6, 1.1 Hz, H-3'), 4.16 (t, 1 H, *J* = 4.8 Hz, H-5'), 3.98 (dd, 1 H, *J* = 10.2, 5.0 Hz, H-6a'), 3.92 (dd, 1 H,

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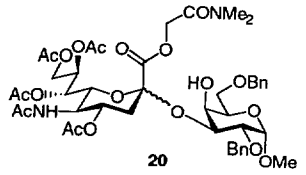
J = 10.1, 4.4 Hz, H-6b'), 3.30 (s, 3 H, CO_2CH_3), 3.16 (s, 3 H, OCH_3), 2.78 (dd, 1 H, J = 13.5, 4.8 Hz, H-3e), 1.95 (s, 3 H, Ac), 1.93(dd, 1 H, J = 13.6, 11.8 Hz, H-3a), 1.89 (s, 3 H, Ac), 1.72 (s, 3 H, Ac), 1.59 (s, 3 H, Ac), 1.55 (s, 3 H, Ac); FTIR (neat film): 3481, 3352, 2918, 2846, 1742, 1685, 1540, 1454, 1371, 1229, 1099, 1040, 739, 700 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{41}H_{53}NO_{18}Na$ 870.3160, found 870.3164.



20

20α: R_f = 0.09 (40% acetone in toluene); ^1H NMR (500 MHz, C_6D_6) δ 7.42-7.37 (m, 2 H, ArH), 7.35-7.31 (m, 2 H, ArH), 7.22-7.16 (m, 4 H, ArH), 7.10-7.05 (m, 2 H, ArH), 5.92 (ddd, 1 H, J = 8.0, 5.6, 2.7 Hz, H-8), 5.72 (dd, 1 H, J = 5.5, 1.9 Hz, H-7), 5.66 (ddd, 1 H, J = 11.5, 10.3, 4.9 Hz, H-4), 5.27 (d, 1 H, J = 10.0 Hz, NH), 5.09 (dd, 1 H, J = 12.1, 2.8 Hz, H-9a), 4.95 (dd, 1 H, J = 9.9, 3.3 Hz, H-6a'), 4.84 (d, 1 H, J = 3.6 Hz, H-1'), 4.67 (d, 1 H, J = 12.0 Hz, $PhCH_2$), 4.66 (dd, 1 H, J = 10.7, 2.0 Hz, H-6), 4.57 (q, 1 H, J = 10.4 Hz, H-5), 4.50 (d, 1 H, J = 12.1 Hz, $PhCH_2$), 4.49 (resonance A of ABq, 1 H, J = 12.4 Hz, $PhCH_2$), 4.47 (resonance B of ABq, 1 H, J = 12.4 Hz, $PhCH_2$), 4.34 (dd, 1 H, J = 12.2, 7.9 Hz, H-9b), 4.31 (m, 1 H, H-5'), 4.30 (d, 1 H, J = 14.2 Hz, H-Aa), 4.25 (d, 1 H, J = 14.1 Hz, H-Ab), 4.20 (dd, 1 H, J = 9.9, 3.5 Hz, H-2'), 4.15 (dd, 1 H, J = 9.7, 5.9 Hz, H-6b'), 3.99 (dd, 1 H, J = 9.6, 6.3 Hz, H-3'), 3.72 (d, 1 H, J = 2.7 Hz, OH), 3.22 (s, 3 H, OCH_3), 3.10 (dd, 1 H, J = 12.8, 4.9 Hz, H-3e), 2.51 (t, 1 H, J = 12.3 Hz, H-3a), 2.31 (s, 3 H, NCH_3), 1.96 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.71 (s, 3 H, Ac), 1.69 (s, 3 H, NCH_3), 1.59 (s, 3 H, Ac), 1.54 (s, 3 H, Ac); FTIR (neat film): 3372, 2922, 2853, 1747, 1654, 1456, 1372, 1224, 1044, 750 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{44}H_{58}N_2O_{19}Na$ 941.3531, found 941.3531.

20β: R_f = 0.22 (40% acetone in toluene); ^1H NMR (500 MHz, C_6D_6) δ 7.60-7.57 (m, 2 H, ArH), 7.36-7.28(m, 4 H, ArH), 7.20-7.14 (m, 2 H, ArH), 7.10-7.04 (m, 2 H, ArH), 5.81 (ddd, 1 H, J = 7.2, 5.6, 2.5 Hz, H-8), 5.65 (dd, 1 H, J = 5.6, 2.7 Hz, H-7), 5.50 (ddd, 1 H, J = 11.6, 10.4, 4.6 Hz, H-4), 5.40 (d, 1 H, J = 4.8 Hz, OH), 5.21 (dd, 1 H, J = 12.2, 2.5 Hz, H-9a), 4.97 (d, 1 H, 3.5 Hz, H-1'), 4.86 (dd, 1 H, J = 10.7, 2.6 Hz, H-6), 4.68 (dd, 1 H, 9.8, 2.2 Hz, H-3'), 4.61 (q, 1 H, J = 10.5 Hz, H-5), 4.57-4.45 (m, 6 H, H-4', H-Aa, $PhCH_2$), 4.39 (dd, 1 H, J = 12.6, 7.3 Hz, H-9b), 4.37 (dd, 1 H, J = 9.9, 3.6 Hz, H-2'), 4.29 (m, 1 H, H-5'), 4.17 (d, 1 H, J = 14.6 Hz, H-Ab), 4.06 (dd, 1 H, J = 10.0, 6.1 Hz, H-6a'), 4.03 (d, 1 H, J = 10.5 Hz, NH), 3.96 (dd, 1 H, J = 10.0, 4.8 Hz, H-6b'), 3.31 (s, 3 H, OCH_3), 3.06 (dd, 1 H, J = 14.1, 4.7 Hz, H-3e), 2.26 (s, 3 H, NCH_3), 2.25 (dd, 1 H, J = 14.1, 11.9 Hz, H-3a), 2.51 (s, 3 H, Ac), 1.95 (s, 3 H, Ac), 1.77 (s, 3 H, Ac), 1.69 (s, 3 H, NCH_3), 1.58 (s, 6 H, Ac); FTIR (neat film): 3358, 2924, 2860, 1745, 1654, 1514, 1456, 1372, 1232, 1110, 1040, 750 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{44}H_{58}N_2O_{19}Na$ 941.3531, found 941.3531.