Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.

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Supporting Information

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General Experimental Procedures. All reactions were performed in single-neck, flame-dried, round-bottomed flasks fitted with rubber septa under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation at 30–33 °C. Intermediates were purified by flash-column chromatography, as described by Still et al. employing silica gel (60 Å, 40–63 μm particle size, purchased from Silicycle, Quebec City, Canada). Analytical thinlinear chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous ceric ammonium molybdate solution (CAM), followed by brief heating on a hot plate (120 °C, 10–15 s).

Materials. Commercial solvents and reagents were used as received with the following exceptions. Dichloromethane and benzene were purified according to the method of Pangborn et al. Triethylamine was distilled from calcium hydride under an atmosphere of nitrogen before use. Bromotrimethylsilane was distilled under an atmosphere of nitrogen and was stored at −20 °C with protection from light. 4 Å molecular sieves were activated by heating overnight in vacuo (220 °C, 100 mTorr), pulverized in a mortar, stored in a gravity oven (120 °C), and flame-dried in vacuo (100 mTorr) immediately before use. Silver silicate was prepared by the procedure of Paulsen et al. and was stored in a desiccator with protection from light. 3,4,6-Tri-O-benzyl-2-deoxy-D-arabino-hexopyranose acetate (1d), methyl-2,3,4-tri-O-benzyl-β-D-glucopyranoside (3f), ethyl (2E, 4R, 5S)-5-hydroxy-4-methoxy-2-hexenoate (S1), 3-O-tert-butylidimethylsilyl-2,6-dideoxy-L-glycal (S4), 6-dideoxy-L-glycal (S6), and 4,5-epoxy-ethylsorbate (S8) were prepared according to literature procedures.

Instrumentation. Proton nuclear magnetic resonance spectra (1H NMR) were recorded at 400, 500, or 600 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl3, δ 7.26; C6H5D3, δ 7.16; CHD2OD, δ 3.31). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad, app = apparent), integration, coupling constant in Hertz, and assignment. Proton-decoupled carbon nuclear magnetic resonance spectra (13C NMR) were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl3, δ 77.0; C6D6, δ 128.1). Carbon-13 attached proton test (APT) spectra were recorded at 100, 125, or 150 MHz at 24 °C, unless otherwise noted. APT spectral acquisition employed the Agilent APT pulse sequence with a C–H coupling constant of 146 Hz to distinguish carbon types. Carbon-13 NMR and APT data are combined and represented as follows: chemical shift, carbon type. High-resolution mass spectrometry (HRMS) were obtained at the University of Illinois Mass Spectrometry Lab or on a Waters UPLC/HRMS instrument equipped with an ESI high-resolution mass spectrometry detector and photodiode array detector. Unless otherwise noted, samples were eluted over a reverse-phase C18 column (1.7 μm particle size, 2.1 × 50 mm) with 5% acetonitrile–water containing 0.1% formic acid for 0.4 min, followed by a linear gradient of 5% acetonitrile–water containing 0.1% formic acid→95% acetonitrile–water containing 0.1% formic acid over 1.6 min at a flow rate of 600 μL/min.
**Synthetic Procedures.**

![Chemical Structure](image)

**Synthesis of O-methyl-L-oleandrose (S2).**

A solution of diisobutylaluminum hydride in toluene (1.5 M, 17.2 mL, 25.6 mmol, 2.01 equiv) was added dropwise over 30 min to a stirred solution of ethyl (2E, 4R, 5S)-5-hydroxy-4-methoxy-2-hexenoate (S1, 2.42 g, 12.7 mmol, 1 equiv) in toluene (80 mL) at −90 °C. Upon completion of the addition, the reaction mixture was stirred for 30 min at −90 °C. Anhydrous methanol (10 mL) was then added, and the mixture was stirred for 5 min at −90 °C. Saturated aqueous potassium sodium tartrate solution (70 mL) was then added, and the resulting mixture was allowed to warm to 25 °C. The warmed solution was stirred vigorously for 2 h at 25 °C. The resulting clear, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (5 × 50 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated.

1,8-Diazabicyclo[5.4.0]undec-7-ene (1.90 mL, 12.7 mmol, 1 equiv) was added to a stirred solution of the residue obtained in the previous step in methanol (30 mL) at 25 °C. The resulting mixture was stirred for 3 h at 25 °C. The product solution was concentrated to dryness and the residue obtained was purified by flash-column chromatography (eluting with 60% ether–pentane) to afford separately O-methyl-L-oleandrose (S2, 1.05 g, 47%, white solid) and O-methyl-L-ribo-hexopyranose (S3, 469 mg, 21%, colorless oil).

**O-methyl-L-oleandrose (S2).**

Rf = 0.60 (100% ether; CAM). 1H NMR (400 MHz, CDCl3, 1:9:1 mixture of α : β anomers, * denotes β anomer), δ 5.33–5.31 (m, 1H, H1), 4.78 (ddd, 1H, J = 9.7, 6.5, 2.1 Hz, H4), 3.87 (dq, 1H, J = 9.5, 6.2 Hz, H3), 3.63 (ddd, 1H, J = 11.4, 8.8, 5.0 Hz, H2), 3.57 (s, 3H, H5), 3.56 (s, 3H, H6), 3.44 (s, 3H, H7), 3.43 (s, 3H, H8), 3.40–3.25 (m, 2H, Hα, Hβ), 2.97 (dd, 1H, J = 6.4, 0.8 Hz, H8*), 2.75 (t, 1H, J = 9.2 Hz, H9*), 2.75 (t, 1H, J = 8.8 Hz, H9), 2.44–2.43 (m, 1H, H3), 2.39 (ddd, 1H, J = 12.5, 5.0, 2.1 Hz, H2), 2.26 (ddd, 1H, J = 13.0, 5.0, 1.5 Hz, H1), 1.57–1.49 (m, 1H, H1), 1.41 (ddd, 1H, J = 12.6, 11.5, 9.6 Hz, Hα), 1.32 (d, 3H, J = 6.2 Hz, H9), 1.27 (d, 3H, J = 6.3 Hz, H8). 13C NMR (100 MHz, CDCl3), δ 93.8 (CH*), 91.9 (CH), 86.3 (CH), 85.3 (CH*), 80.6 (CH*), 77.9 (CH), 71.5 (CH*), 67.3 (CH), 60.8 (CH*), 60.6 (CH2), 57.2 (CH2), 57.0 (CH3*), 37.7 (CH3*), 35.1 (CH2), 18.1 (CH3, CH3*). IR (ATR-FTIR), cm⁻¹: 3391 (br), 1147 (s), 1088 (s), 949.9 (s), 733.5 (s). HRMS-ESI (m/z): [M + Na]+ calcd for C34H60NaO7, 545.3905; found, 545.3888.

**O-methyl-L-ribo-hexopyranose (S3).**

Rf = 0.44 (100% ether; CAM). 1H NMR (600 MHz, CDCl3, 1:3.9 mixture of α : β anomers, * denotes α anomer), δ 5.13 (d, 1H, J = 10.9 Hz, Hα), 5.08–5.05 (m, 2H, H1, H4*), 4.13 (dq, 1H, J = 9.5, 6.2 Hz, H5*), 3.93–3.92 (m, 1H, H7*), 3.91–3.86 (m, 1H, H3), 3.82–3.81 (m, 1H, H2), 3.68 (dd, 1H, J = 5.8, 1.8 Hz, H8), 3.53 (s, 3H, H5*), 3.43 (s, 3H, H7), 3.42 (s, 3H, H9*), 3.38 (s, 3H, H8).

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H₂), 2.89–2.86 (m, 2H, H₄, H₄*), 2.32–2.28 (m, 1H, H₀), 2.25–2.21 (m, 1H, H₂), 1.72 (ddd, 1H, J = 14.4, 4.7, 2.0 Hz, H₅), 1.49–1.45 (m, 1H, H₂), 1.28 (d, 3H, J = 6.6 Hz, H₆), 1.25 (d, 3H, J = 6.0 Hz, H₆). ¹³C NMR (125 MHz, CDCl₃), δ 91.93 (CH*), 91.85 (CH), 82.8 (CH), 82.4 (CH*), 74.5 (CH), 73.0 (CH*), 69.1 (CH*), 62.7 (CH), 58.9 (CH₃), 57.4 (CH₂*), 57.1 (CH₃), 57.0 (CH₃*), 35.2 (CH₂*), 33.0 (CH₂), 18.2 (CH₂*), 18.1 (CH₃). IR (ATR-FTIR), cm⁻¹: 3417 (br), 1088 (s), 1007 (s), 732 (s). HRMS-ESI (m/z): [M + Na]⁺ calcd for C₈H₁₆NaO₄, 199.0941; found, 199.0938.
Synthesis of O-methyl-L-oleandrose acetate (1a).

Pyridine (4.58 mL, 56.8 mmol, 10.0 equiv), acetic anhydride (2.68 mL, 28.4 mmol, 5.00 equiv), and 4-dimethylaminopyridine (139 mg, 1.14 mmol, 0.20 equiv) were added in sequence to a stirred solution of O-methyl-L-oleandrose (S2, 1.00 g, 5.68 mmol, 1 equiv) in dichloromethane (57 mL) at 25 °C. The resulting mixture was stirred for 3 h at 25 °C. The product solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (100 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (50 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ether–pentane) to afford the acetate 1a as a colorless oil (1.24 g, >99%).

R_f = 0.66 (40% ether–pentane; CAM). ^1H NMR (400 MHz, CDCl_3, 2:1 mixture of α:β anomers, * denotes β anomer), δ 6.13–6.12 (m, 1H, H_1), 5.64 (dd, 1H, J = 10.2, 2.3, 0.6 Hz, H_1*), 3.68 (dq, 1H, J = 9.6, 6.2 Hz, H_3), 3.56 (s, 3H, H_7), 3.55 (s, 3H, H_7*), 3.53 (ddd, 1H, J = 11.2, 7.4, 5.2 Hz, H_4), 3.43 (s, 3H, H_2), 3.42 (s, 3H, H_2*), 3.40–3.28 (m, 2H, H_3, H_5), 2.77 (t, 1H, J = 9.2 Hz, H_4), 2.74 (t, 1H, J = 9.2 Hz, H_4*), 2.32 (dd, 1H, J = 12.4, 5.0, 2.2 Hz, H_5*), 2.22 (ddd, 1H, J = 13.6, 5.1, 1.7 Hz, H_2*), 1.67–1.59 (m, 1H, H_2*), 1.56–1.49 (m, 1H, H_2), 1.31 (d, 3H, J = 6.4 Hz, H_6), 1.26 (d, 3H, J = 6.4 Hz, H_6*). ^13C NMR (100 MHz, CDCl_3), δ 169.5 (C), 169.2 (C*), 91.9 (CH*), 91.7 (CH), 85.6 (CH), 85.0 (CH*), 80.3 (CH*), 78.0 (CH), 72.3 (CH*), 69.6 (CH), 60.9 (CH_3), 60.8 (CH_3*), 57.3 (CH_3), 57.1 (CH_3*), 34.9 (CH_2*), 33.9 (CH_2), 21.10 (CH_3), 21.06 (CH_3*), 18.0 (CH_3), 17.9 (CH_2*). IR (ATR-FTIR), cm⁻¹: 1750 (s), 1046 (s), 958 (s), 733 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{10}H_{18}NaO_5, 241.1046; found, 241.1047.
Synthesis of 3-O-tert-butyldimethylsilyl-4-O-benzoyl-2,6-dideoxy-L-glycal (S5).

Pyridine (1.30 mL, 16.1 mmol, 10.0 equiv) and benzoyl chloride (281 µL, 2.42 mmol, 1.50 equiv) were added in sequence to a stirred solution of 3-O-tert-butyldimethylsilyl-2,6-dideoxy-L-glycal (S4, 393 mg, 1.61 mmol, 1 equiv) in dichloromethane (8.1 mL) at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. Saturated aqueous sodium bicarbonate solution (1.0 mL) was then added to the cold product solution. The diluted product mixture was poured into a separatory funnel that had been changed with saturated aqueous sodium bicarbonate solution (20 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 3% ether–pentane) to afford the glycal S5 as a colorless oil (456 mg, 81%).

Rf = 0.73 (10% ether–pentane; UV, CAM). 1H NMR (400 MHz, CDCl3), δ 8.05 (dd, 2H, J = 8.1, 1.4 Hz, H9), 7.60–7.55 (m, 1H, H11), 7.45 (t, 2H, J = 7.6 Hz, H10), 6.36 (dd, 1H, J = 6.1, 1.4 Hz, H1), 5.19 (dd, 1H, J = 8.0, 6.0 Hz, H4), 4.73 (dd, 1H, J = 6.2, 2.9 Hz, H2), 4.43–4.40 (m, 1H, H3), 4.21–4.14 (m, 1H, H5), 1.35 (d, 3H, J = 6.5 Hz, H6), 1.30 (s, 9H, H8), 0.81 (s, 3H, H7), 0.05 (s, 3H, H7). 13C NMR (150 MHz, CDCl3), δ 165.5 (C), 143.6 (CH), 133.1 (CH), 129.9 (C), 129.7 (CH), 128.4 (CH), 103.2 (CH), 75.4 (CH), 72.7 (CH), 66.7 (CH), 25.6 (CH3), 17.9 (C), 16.8 (CH3), −4.60 (CH3), −4.86 (CH3). IR (ATR-FTIR), cm−1: 1246 (m), 1111 (s), 737 (s), 708 (s). HRMS-ESI (m/z): [M + Na]+ calcd for C19H28NaO4Si, 371.1649; found, 371.1665.
Synthesis of 3-O-tert-butyldimethylsilyl-4-O-benzoyl-2,6-dideoxy-L-hexopyranose acetate (1b).

Triphenylphosphine hydrogen bromide (21.8 mg, 635 μmol, 0.05 equiv) and acetic acid (109 μL, 1.90 mmol, 1.50 equiv) were added in sequence to a stirred solution of 3-O-tert-butyldimethylsilyl-4-O-benzoyl-2,6-dideoxy-L-glycal (S5, 441 mg, 1.27 mmol, 1 equiv) in dichloromethane (13 mL) at 25 °C. The reaction mixture was stirred for 5 h at 25 °C. The product solution was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 10% ether–pentane) to afford the acetate 1b as a colorless oil (459 mg, 89%).

R<sub>f</sub> = 0.73 (20% ether–pentane; UV, CAM). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 1.8:1 mixture of α:β anomers, * denotes β anomer), δ 8.07–8.02 (m, 4H, H<sub>10</sub>, H<sub>10</sub>*), 7.59–7.55 (m, 2H, H<sub>11</sub>, H<sub>11</sub>*), 7.45 (t, 4H, H<sub>3</sub>, H<sub>3</sub>*), 6.20 (dd, 1H, J = 3.7, 1.4 Hz, H<sub>1</sub>), 5.79 (dd, 1H, J = 10.2, 2.3 Hz, H<sub>1</sub>*), 4.97 (t, 1H, J = 9.6 Hz, H<sub>4</sub>), 4.91 (t, 1H, J = 9.2 Hz, H<sub>4</sub>*), 4.16 (ddd, J = 11.2, 9.0, 5.2 Hz, H<sub>3</sub>), 4.01–3.92 (m, 2H, H<sub>3</sub>*), 3.66 (dq, 1H, J = 9.6, 6.2 Hz, H<sub>5</sub>), 2.20 (dd, 1H, J = 12.6, 5.2, 2.3 Hz, H<sub>2</sub>), 2.16–2.10 (m, 1H, H<sub>2</sub>), 2.12 (s, 3H, H<sub>12</sub>), 2.10–2.10 (m, 1H, H<sub>2</sub>*), 1.97 (ddd, 1H, J = 14.2, 11.2, 3.7 Hz, H<sub>2</sub>*), 1.93–1.85 (m, 1H, H<sub>2</sub>*), 1.26 (d, 3H, J = 6.2 Hz, H<sub>6</sub>), 1.21 (d, 3H, J = 6.3 Hz, H<sub>6</sub>*), 0.74 (s, 18H, H<sub>8</sub>, H<sub>8</sub>*), 0.01 (s, 6H, H<sub>7</sub>, H<sub>7</sub>*), −0.13 (s, 3H, H<sub>7</sub>*), −0.15 (s, 3H, H<sub>7</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>), δ 169.4 (C), 169.2 (C*), 165.53 (C*), 165.50 (C), 133.10 (CH*), 133.05 (CH), 130.0 (C), 129.9 (C*), 129.69 (CH), 129.67 (CH*), 128.4 (CH*), 128.3 (CH), 91.7 (CH), 91.5 (CH*), 77.4 (CH), 77.1 (CH*), 71.1 (CH*), 69.7 (CH*), 68.9 (CH), 67.3 (CH), 39.1 (CH*), 38.0 (CH), 25.4 (CH<sub>3</sub>, CH<sub>3</sub>*), 21.2 (CH<sub>3</sub>*), 21.1 (CH<sub>3</sub>*), 17.71 (CH<sub>3</sub>*), 17.70 (C, C*), 17.68 (CH<sub>3</sub>*), −4.60 (CH<sub>3</sub>, CH<sub>3</sub>*), −4.9 (CH<sub>3</sub>), −5.0 (CH<sub>3</sub>*). IR (ATR-FTIR), cm<sup>−1</sup>: 1752 (s), 1066 (s), 835 (s), 708 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>32</sub>NaO<sub>6</sub>Si, 431.1860; found, 431.1845.
Synthesis of 3-O-benzoyl-4-O-tert-butyldimethylsilyl-2,6-dideoxy-L-glycal (S7).

Pyridine (620 µL, 7.69 mmol, 1.00 equiv) and benzoyl chloride (894 µL, 7.69 mmol, 1.00 equiv) were added in sequence to a stirred solution of 6-deoxy-L-glycal (S6, 1.00 g, 7.69 mmol, 1 equiv) in dichloromethane (18 mL) at −20 °C. The reaction mixture was stirred for 2 h at −20 °C. The product solution was diluted with saturated aqueous sodium bicarbonate solution (50 mL). The diluted product mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (5 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated.

Imidazole (2.09 g, 30.8 mmol, 4.00 equiv) and chloro-tert-butyldimethylsilane (2.13 g, 9.23 mmol, 1.80 equiv) were added in sequence to a stirred solution of the residue obtained in the previous step in N, N-dimethylformamide (7.7 mL) at 25 °C. The resulting mixture was stirred for 4 h at 25 °C. The product solution was diluted with ether (160 mL). The diluted product mixture was transferred to a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (100 mL). The layers that formed were separated, and the organic layer was washed with water (50 mL). The organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 4% ether–pentane) to afford the glycal S6 (1.91 g, 71% over 2 steps).

1H and 13C NMR for the glycal S6 were in agreement with those reported for the D-isomer ent-S7.10
**Synthesis of 3-O-benzoyl-4-O-tert-butylidemethyisilyl-2,6-dideoxy-L-hexopyranose acetate (1c).**

Triphenylphosphine hydrogen bromide (71.0 mg, 207 µmol, 0.05 equiv) and acetic acid (355 µL, 6.21 mmol, 1.50 equiv) were added in sequence to a stirred solution of 3-O-benzoyl-4-O-tert-butylidemethylsilyl-2,6-dideoxy-L-glycal (S6, 1.44 g, 4.14 mmol, 1 equiv) in dichloromethane (41 mL) at 25 °C. The reaction mixture was stirred for 9 h at 25 °C. The product solution was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–pentane) to afford the acetate 1c as a white solid (1.25 g, 74%).

R_f = 0.74 (20% ethyl acetate–pentane; UV, CAM). ^1H NMR (400 MHz, CDCl_3, 4:2:1 mixture of α:β anomers, * denotes β anomer), δ 8.04–8.02 (m, 4H, H_9, H_9*), 7.59–7.56 (m, 2H, H_11, H_11*), 7.45 (t, J = 7.7 Hz, H_10, H_10*), 6.18 (dd, J = 3.8, 1.4 Hz, H_1), 5.83 (dd, J = 10.0, 2.3 Hz, H_1*), 5.40 (ddd, J = 11.4, 8.9, 5.2 Hz, H_3), 5.16 (ddd, J = 11.6, 8.4, 5.2 Hz, H_3*), 3.87 (dq, J = 9.2, 6.2 Hz, H_5), 3.57 (t, J = 9.0 Hz, H_4), 3.60–3.51 (m, 2H, H_4*, H_5*), 2.41 (ddd, J = 12.3, 5.3, 2.3 Hz, H_2*), 2.31 (ddd, J = 13.4, 5.3, 1.5 Hz, H_2), 2.14 (s, 3H, H_12), 2.08 (s, 3H, H_12*), 1.90 (ddd, J = 13.6, 11.4, 3.8 Hz, H_3), 1.84–1.75 (m, 1H, H_2*), 1.35 (d, J = 5.5 Hz, H_6*), 1.31 (d, J = 6.2 Hz, H_6), 0.78 (s, 9H, H_8), 0.77 (s, 9H, H_8*), 0.010 (s, 3H, H_7), 0.08 (s, 3H, H_7*), −0.09 (s, 3H, H_7*), −0.11 (s, 3H, H_7*). ^13C NMR (100 MHz, CDCl_3), δ 169.6 (C), 169.0 (C*), 165.8 (C), 165.7 (C*), 133.12 (CH*), 133.09 (CH), 130.1 (C), 130.0 (C*), 129.7 (CH, CH*), 126.3 (CH, CH*), 91.1 (CH*), 91.0 (CH), 75.0 (CH), 74.5 (CH*), 73.8 (CH*), 73.6 (CH*), 72.1 (CH), 70.9 (CH), 35.3 (CH, CH*), 34.3 (CH_2), 25.68 (CH_3), 25.65 (CH*, CH_3), 21.2 (CH_3), 21.0 (CH*, CH_3), 18.6 (CH_2), 18.5 (CH, CH*), 18.00 (C), 17.97 (C*), −3.97 (CH_2), −4.00 (CH*, CH_3), −4.29 (CH_3), −4.31 (CH_3*). IR (ATR-FTIR), cm⁻¹: 1752 (s), 1270 (s), 1102 (s), 736 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_{21}H_{32}NaO_6Si, 431.1860; found, 431.1874.
Synthesis of 3-O-tert-butyldimethylsilyl-6-O-benzoyl-D-glucal (3e).

Imidazole (136 mg, 2.00 mmol, 2.00 equiv) and tert-butyldimethylsilyl chloride (166 mg, 1.10 mmol, 1.10 equiv) were added in sequence to a stirred solution of 6-O-benzoyl-D-glucal (250 mg, 1.00 mmol, 1 equiv) in N,N-dimethylformamide (2.0 mL) at 0 °C. The reaction mixture was stirred for 10 h at 0 °C. The cold product solution was diluted with ether (40 mL). The diluted product mixture was transferred to a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (50 mL). The layers that formed were separated. The organic layer was washed sequentially with water (20 mL) and saturated aqueous sodium chloride solution (20 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ether–pentane) to afford 3e (245 mg, 67%).

R_f = 0.53 (40% ether–pentane; UV, CAM). ¹H NMR (400 MHz, CDCl₃), δ 8.09–8.07 (m, 2H, H₁₀), 7.60–7.56 (m, 1H, H₁₂), 7.45 (t, 2H, J = 7.7 Hz, H₁₁), 6.32 (dd, 1H, J = 6.1, 1.5 Hz, H₄), 4.82 (dd, 1H, J = 12.3, 4.6 Hz, H₅), 4.69 (dd, 1H, J = 6.1, 2.4 Hz, H₆), 4.55 (dd, 1H, J = 12.3, 2.5 Hz, H₇), 4.30–4.27 (m, 1H, H₃), 4.12 (ddd, 1H, J = 9.0, 4.6, 2.5 Hz, H₆), 3.74 (ddd, 1H, J = 9.0, 6.4, 4.6 Hz, H₃), 2.69 (dd, 1H, J= 4.6, 1.4 Hz, H₉), 0.91 (s, 9H, H₈), 0.13 (s, 3H, H₇), 0.12 (s, 3H, H₈). ¹³C NMR (150 MHz, CDCl₃), δ 167.0 (C), 143.3 (CH), 133.2 (CH), 129.8 (CH), 129.7 (C), 128.4 (CH), 103.7 (CH), 76.4 (CH), 69.5 (2 × CH), 63.1 (CH₂), 25.8 (CH₃), 18.1 (C), −4.49 (CH₃), −4.53 (CH₃). IR (ATR-FTIR), cm⁻¹: 3513 (br), 1316 (s), 1115 (s), 710 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C₁₉H₂₈NaO₅Si, 387.1598; found, 387.1581.
Synthesis of the p-methoxybenzyl ether S9.

4-Methoxybenzyl alcohol (32.1 mL, 258 mmol, 2.00 equiv) was added to a stirred solution of 4,5-epoxy ethylsorbate (S8, 20.4 g, 129 mmol, 1 equiv) in dichloromethane (60 mL) at 25 °C. The resulting mixture was cooled to 10 °C. Triflic acid (228 µL, 2.58 mmol, 0.02 equiv) was then added to the cold solution. The reaction mixture was stirred for 14 h at 10 °C. The product solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (200 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 5% ethyl acetate–dichloromethane initially, grading to 15% ethyl acetate–dichloromethane, two steps) to afford the alcohol S9 as a colorless oil (25.0 g, 66%).

R<sub>f</sub> = 0.63 (30% ethyl acetate–dichloromethane; UV, CAM). ¹H NMR (400 MHz, CDCl₃), δ 7.27–7.24 (m, 2H, H₈), 6.92 (d, 1H, J = 6.8 Hz, H₂), 6.90–6.87 (m, 2H, H₉), 6.06 (dd, 1H, J = 15.9, 1.1 Hz, H₁), 4.58 (d, 1H, J = 11.4 Hz, H₇), 4.34 (d, 1H, J = 11.4 Hz, H₇), 4.22 (q, 2H, J = 7.1 Hz, H₁₁), 3.97–3.87 (m, 2H, H₃, H₄), 3.81 (s, 3H, H₁₀), 2.30 (d, 1H, J = 4.9 Hz, H₆), 1.31 (t, 3H, J = 7.1 Hz, H₁₂), 1.14 (d, 3H, J = 6.4 Hz, H₅). ¹³C NMR (150 MHz, CDCl₃), δ 165.7 (C), 159.3 (C), 144.1 (CH), 129.7 (C), 129.4 (CH), 124.6 (CH), 113.8 (CH), 81.5 (CH), 71.0 (CH₂), 69.2 (CH), 60.6 (CH₂), 55.2 (CH₃), 18.0 (CH₃), 14.2 (CH₃). IR (ATR-FTIR), cm⁻¹: 3489 (br), 1267 (s), 1073 (s), 733 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C₄₆H₄₅NaO₅, 317.1359; found, 317.1345.

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**Synthesis of the Azidosugar S10.**

A solution of diisobutylaluminum hydride in toluene (1.5 M, 547 µL, 820 mmol, 2.05 equiv) was added dropwise over 30 min to a stirred solution of the ester S9 (118 mg, 400 µmol, 1.00 equiv) in toluene (3.2 mL) at −90 °C. Upon completion of the addition, the reaction mixture was stirred for 30 min at −90 °C. Anhydrous methanol (2.0 mL) was then added, and the resulting mixture was stirred for 5 min at −90 °C. Saturated aqueous potassium sodium tartrate solution (15 mL) was then added, and the resulting mixture was allowed to warm to 25 °C. The warmed solution was stirred vigorously for 2 h at 25 °C. The resulting clear, biphasic mixture was transferred to a separatory funnel and the layers that formed were separated. The aqueous layer was extracted with ethyl acetate (5 × 30 mL) and the organic layers were combined. The combined organic layers were dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated. The residue obtained was used directly in the next step without purification.

A solution of aqueous hydrochloric acid (12.0 M, 100 µL, 1.20 mmol, 3.00 equiv) was added to a suspension of sodium azide (91.0 mg, 1.40 mmol, 3.50 equiv) in dichloromethane (800 µL) at 25 °C. The mixture was stirred for 1 h at 25 °C. A solution of the unpurified aldehyde (obtained in the previous step) in dichloromethane (700 µL) and triethylamine (11.0 µL, 80.0 µmol, 0.20 equiv) were then added in sequence. The resulting mixture was stirred for 5 h at 25 °C. The product solution was diluted with water (5 mL). The diluted product mixture was transferred to a separatory funnel. The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (2 × 10 mL). The organic layers were combined and the combined organic layers were washed with saturated aqueous sodium bicarbonate solution (10 mL). The washed organic layer was dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 30% ethyl acetate–pentane) to afford separately the azidosugar S10 (white solid, 38.0 mg, 32%) and the C-3 diastereomer S11 (colorless oil, 59.0 mg, 50%).

Azidosugar S10.

R<sub>f</sub> = 0.60 (50% ethyl acetate–pentane; UV, CAM). ¹H NMR (400 MHz, CDCl₃, 5:6:1 mixture of α:β anomers, * denotes β anomer), δ 7.33–7.32 (m, 4H, H₉, H₉*), 6.91–6.89 (m, 4H, H₁₀, H₁₀*), 5.27 (brs, 1H, H₁), 4.82–4.78 (m, 2H, H₁*, H₁*), 4.81 (d, 1H, 10.3 Hz, H₆), 4.57 (d, 2H, J = 10.3 Hz, H₆, H₆*), 4.00–3.89 (m, 2H, H₃, H₃*), 3.81 (s, 6H, H₁₁, H₁₁*), 3.53 (ddd, 1H, J = 12.8, 5.0, 2.1 Hz, H₃*), 3.41 (dq, 1H, J = 9.1, 6.2 Hz, H₂), 2.99 (t, 2H, J = 9.4 Hz, H₂, H₂*), 2.88 (brs, 1H, H₅), 2.26 (ddd, 1H, J = 12.8, 5.0, 2.1 Hz, H₂*), 2.17–2.13 (m, 1H, H₂), 1.70–1.61 (m, 1H, H₃), 1.58–1.49 (m, 1H, H₃*), 1.33 (d, 3H, J = 6.2 Hz, H₈), 1.27 (d, 3H, J = 6.3 Hz, H₈*). ¹³C NMR (150 MHz, CDCl₃), δ 159.5 (C*), 159.4 (C), 129.99 (CH*), 129.95 (CH), 129.7 (C), 129.5 (C*), 113.90 (CH*), 113.87 (CH), 93.7 (CH*), 90.9 (CH), 83.6 (CH), 82.7 (CH*), 74.9 (CH₂*), 74.8 (CH₂), 72.3 (CH*), 67.4 (CH), 62.0 (CH*), 59.5 (CH), 55.3 (CH₃, CH₃*), 38.0 (CH₂*), 35.7 (CH₂), 18.1 (CH₃, CH₃*). IR (ATR-FTIR), cm⁻¹: 3362 (br), 2105 (s), 1121 (s), 1032 (s). HRMS-ESI (m/z): [M + Na]⁺ calcd for C₁₄H₂₀N₃NaO₄, 316.1268; found, 316.1264.

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Azidosugar S11.

R<sub>f</sub> = 0.45 (50% ethyl acetate–pentane; UV, CAM). ¹H NMR (400 MHz, CDCl<sub>3</sub>, 1:3.7 mixture of α:β anomers, * denotes α anomer), δ 7.30–7.27 (m, 4H, H₉, H₉*), 6.92–6.89 (m, 4H, H₁₀, H₁₀*), 5.05–5.00 (m, 2H, H₁, H₁*), 4.63 (d, 1H, J = 11.2 Hz, H₆), 4.62 (d, 1H, J = 11.2 Hz, H₆*), 4.53 (d, 1H, J = 11.2 Hz, H₆), 4.49 (d, 1H, J = 11.2 Hz, H₆), 4.34 (dd, 1H, J = 9.6, 1.3 Hz, H₇), 4.21 (dq, 1H, J = 9.3, 6.2 Hz, H₅), 4.09–4.07 (m, 2H, H₁, H₁*), 3.91 (dq, 1H, J = 9.3, 6.2 Hz, H₃), 3.82 (s, 6H, H₁₁, H₁₁*), 3.74 (dd, 1H, J = 14.6, 5.4 Hz, H₂), 3.25 (dd, 1H, J = 9.1, 3.2 Hz, H₄), 3.24 (dd, 1H, J = 9.1, 3.2 Hz, H₄*), 2.09–2.02 (m, H, H₂, H₂*), 1.85 (dt, 1H, J = 14.6, 3.8 Hz, H₃), 1.64–1.61 (m, 1H, H₂), 1.29–1.26 (m, 6H, H₆, H₆*). ¹³C NMR (150 MHz, CDCl<sub>3</sub>), δ 159.53 (C*), 159.50 (C), 129.8 (CH, CH*), 129.31 (C), 129.29 (C*), 113.92 (CH*), 100.90 (CH), 90.8 (CH*), 80.0 (CH*), 79.8 (CH), 71.76 (CH₂), 71.73 (CH₂*), 69.3 (CH), 62.9 (CH*), 57.1 (CH), 56.4 (CH*), 55.2 (CH₃, CH₃*), 36.7 (CH₂), 33.9 (CH₂*), 18.1 (CH₃), 17.9 (CH₃*). IR (ATR-FTIR), cm⁻¹: 3422 (br), 2104 (m), 1303 (s), 731 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C₁₄H₁₉N₃NaO₄, 316.1268; found, 316.1259.
Synthesis of the glycosyl acetate S12.

Pyridine (805 μL, 10.2 mmol, 10.0 equiv), acetic anhydride (483 μL, 5.10 mmol, 5.00 equiv), and 4-dimethylaminopyridine (25.0 mg, 204 μmol, 0.20 equiv) were added in sequence to a stirred solution of the azido sugar S10 (300 mg, 1.02 mmol, 1 equiv) in dichloromethane (10 mL) at 25 °C. The mixture was stirred for 2 h at 25 °C. The product solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (20 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–pentane) to afford the glycosyl acetate S12 as a colorless oil (345 mg, >99%).

Rf = 0.51 (α), 0.44 (β) (40% ether–pentane; UV, CAM). ¹H NMR (400 MHz, CDCl₃, 16:1 mixture of α:β anomers, * denotes β anomer), δ 7.33–7.30 (m, 4H, H₉, H₉*), 6.91–6.89 (m, 4H, H₁₀, H₁₀*), 6.12 (dd, 1H, J = 3.6, 1.4 Hz, H₁), 5.70 (dd, 1H, J = 10.0, 2.2 Hz, H₈), 4.83 (d, 1H, J = 10.1 Hz, H₈*), 4.79 (d, 1H, J = 10.2 Hz, H₈), 4.58 (d, 1H, J = 10.4 Hz, H₈*), 3.89–3.78 (m, 2H, H₃, H₅), 3.81 (s, 6H, H₁₁, H₁₁*), 3.59 (ddd, 1H, J = 12.5, 9.1, 4.9 Hz, H₁₁), 3.50 (dq, 1H, J = 9.3, 6.2 Hz, H₁₁*), 3.05 (t, 1H, J = 9.4 Hz, H₄), 3.03 (t, 1H, J = 9.4 Hz, H₂), 2.22 (ddd, 1H, J = 12.5, 5.0, 2.3 Hz, H₃), 2.14 (ddd, 1H, J = 13.9, 5.0, 1.5 Hz, H₂), 2.11 (s, 3H, H₇), 2.07 (s, 3H, H₇*), 1.77 (ddd, 1H, J = 13.8, 12.4, 3.6 Hz, H₂), 1.71–1.64 (m, 1H, H₁₂), 1.34 (d, 3H, J = 6.2 Hz, H₁₂*), 1.29 (d, 3H, J = 6.2 Hz, H₁₂*). ¹³C NMR (150 MHz, CDCl₃), δ 169.3 (C), 169.0 (C*), 159.6 (C, C*), 130.0 (CH, CH*), 129.5 (C), 129.4 (C*), 113.9 (CH, CH*), 91.5 (CH*), 90.7 (C), 83.0 (CH), 82.5 (CH*), 75.02 (CH₂), 74.94 (CH₃*), 73.2 (CH*), 69.8 (CH), 61.7 (CH*), 59.7 (CH), 55.3 (CH₃, CH₃*), 35.4 (CH₂*), 34.5 (CH₂), 21.0 (CH₃, CH₃*), 18.1 (CH₃), 18.0 (CH₃*). IR (ATR-FTIR), cm⁻¹: 2099 (s), 1323 (s), 1081 (s), 964 (s). HRMS-ESI (m/z): [M + Na]⁺ calcd for C₁₆H₂₁N₃NaO₅, 358.1373; found, 358.1359.
Synthesis of the secondary alcohol S13.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (450 mg, 1.98 mmol, 1.94 equiv) was added to a solution of the glycosyl acetate S12 (345 mg, 1.02 mmol, 1 equiv) in dichloromethane saturated with water (28 mL) at 25 °C. The reaction mixture was stirred for 5 h at 25 °C. Saturated aqueous sodium thiosulfate solution (7.0 mL) was then added to the product solution. The diluted product mixture was stirred for 10 min at 25 °C and then poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (20 mL). The layers that formed were separated, and the aqueous layer was extracted with dichloromethane (20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 20% ethyl acetate–pentane initially, grading to 30% ethyl acetate–pentane, one step) to afford the secondary alcohol S13 as a colorless oil (226 mg, >99%).

R_f = 0.78 (α), 0.71 (β) (60% ethyl acetate–pentane; CAM). 1H NMR (400 MHz, CDCl_3, 6:7:1 mixture of α:β anomers, * denotes β anomer), δ 6.15 (dd, 1H, J = 3.6, 1.4 Hz, H_1), 5.73 (dd, 1H, J = 10.0, 2.2 Hz, H_1*), 3.80–3.71 (m, 2H, H_2, H_2*), 3.53–3.45 (m, 2H, H_3, H_3*), 3.24–3.14 (m, 2H, H_4, H_4*), 2.55 (d, 1H, 4.1 Hz, H_5), 2.50 (d, 1H, J = 4.2 Hz, H_7), 2.24 (ddd, 1H, J = 12.6, 4.9, 2.3 Hz, H_2*), 2.16 (ddd, 1H, J = 13.7, 4.9, 1.5 Hz, H_3), 2.10 (s, 6H, H_8, H_8*), 1.81 (ddd, 1H, J = 13.7, 12.3, 3.5 Hz, H_2), 1.78–1.70 (m, 1H, H_2*), 1.34 (d, 3H, J = 6.1 Hz, H_6*), 1.29 (d, 3H, J = 6.2 Hz, H_6). 13C NMR (150 MHz, CDCl_3), δ 169.3 (C), 169.1 (C*), 91.5 (CH*), 90.8 (CH), 75.5 (CH), 75.1 (CH*), 73.4 (CH*), 70.1 (CH), 62.1 (CH*), 59.9 (CH), 34.8 (CH*), 33.9 (CH_3), 21.04 (CH_3), 20.98 (CH_3*), 17.72 (CH_3*), 17.65 (CH_3). IR (ATR-FTIR), cm⁻¹: 3437 (br), 2099 (s), 1232 (s), 966 (s). HRMS-ESI (m/z): [M + Na]^+ calcd for C_8H_13N_3NaO_4, 238.0798; found, 238.0805.
Pyridine (231 μL, 2.86 mmol, 3.00 equiv) and benzoyl chloride (221 μL, 1.91 mmol, 2.00 equiv) were added in sequence to a stirred solution of the alcohol S13 (205 mg, 953 μmol, 1 equiv) in dichloromethane (4.8 mL) at 0 °C. The reaction mixture was stirred for 8 h at 0 °C. The product solution was poured into a separatory funnel that had been charged with saturated aqueous sodium bicarbonate solution (20 mL). The layers that formed were separated and the aqueous layer was extracted with dichloromethane (20 mL). The organic layers were combined and the combined organic layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by flash-column chromatography (eluting with 10% ethyl acetate–pentane initially, grading to 15% ethyl acetate–pentane, one step) to afford the benzoate 1g as a colorless oil (206 mg, 68%).

Rf = 0.58 (α), 0.53 (β) (30% ethyl acetate–pentane; UV, CAM). 1H NMR (400 MHz, CDCl3, 5.9:1 mixture of α:β anomers, * denotes β anomer), δ 8.10–8.04 (m, 4H, H7, H7*), 7.62–7.58 (m, 2H, H8, H8*), 7.49–7.44 (m, 4H, H9, H9*), 4.99 (t, 1H, J = 9.8 Hz, H4), 4.95 (t, 1H, J = 9.6 Hz, H4*), 4.06–3.97 (m, 2H, H3, H5), 3.79–3.70 (m, 2H, H3*, H5*), 2.34 (ddd, 1H, J = 12.4, 4.8, 2.1 Hz, 2H, H2, H2*), 2.26 (ddd, 1H, J = 13.8, 5.0, 1.5 Hz, H1), 2.15 (s, 3H, H10), 2.13 (s, 3H, H10*), 1.96 (ddd, 1H, J = 14.2, 12.2, 3.6 Hz, H2), 1.90–1.82 (m, 1H, H2*), 1.43 (s, 3H, H9*), 1.22 (d, 3H, J = 6.2 Hz, H6*), 1.22 (d, 3H, J = 6.2 Hz, H6). 13C NMR (150 MHz, CDCl3), δ 169.03 (C), 168.98 (C*), 165.50 (C*), 165.46 (C), 133.52 (CH*), 133.49 (CH), 129.80 (CH), 129.78 (CH*), 129.14 (C), 129.08 (C*), 128.5 (CH, CH*), 91.3 (CH*), 90.5 (CH), 75.2 (CH), 74.7 (CH*), 72.0 (CH*), 68.6 (CH), 59.6 (CH*), 57.5 (CH), 35.0 (CH2*), 34.2 (CH2), 21.0 (CH3), 20.9 (CH3*), 17.55 (CH3), 17.52 (CH3*). IR (ATR-FTIR), cm⁻¹: 2101 (s), 1750 (s), 1264 (s), 734 (s). HRMS-ESI (m/z): [M + Na]⁺ calcd for C15H17N3NaO5, 342.1060; found, 342.1074.

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General procedure for glycosyl bromide formation (Table 1 of manuscript).

Note: All glycosyl bromide preparations were conducted in a 10-mL round-bottomed flask that had been fused to a Teflon-coated valve and fitted with a rubber septum. See Figure S1 below.

![Figure S1. Apparatus used for glycosyl bromide formation.](image)

**Synthesis of the glycosyl bromide 2a (entry 1).**

Bromotrimethylsilane (74.2 µL, 563 µmol, 2.25 equiv) was added dropwise via syringe to a solution of 3,4-di-O-methyl-2,6-deoxy-L-hexopyranose acetate [1a, 54.5 mg, 250 µmol, 1 equiv; dried by azeotropic distillation with benzene (2 x 500 µL)] in dichloromethane (2.7 mL) at 0 °C. The resulting mixture was stirred for 20 min at 0 °C. The septum in the side arm was punctured with a 20 gauge needle attached to a vacuum manifold, and the product mixture was concentrated at 100 mTorr for 10 min at 0 °C. Following concentration, the reaction vessel was backfilled with argon. The residue was redissolved in benzene (500 µL, added via syringe through the septum) and the resulting solution was concentrated to dryness (100 mTorr) at 25 °C. This process was repeated twice. The Teflon valve was sealed, and the rubber septum was replaced with a greased inlet adaptor. The void in the side arm was evacuated, and then the Teflon valve was opened under dynamic vacuum. The residue was subjected to vacuum (100 mTorr) for 30 min at 25 °C. Mesitylene (34.8 µL, 250 µmol, 1.00 equiv) was added to the dried residue and the resulting mixture was dissolved in benzene-d_6 (~1 mL). Analysis of the mixture by ^1^H NMR spectroscopy indicated a 72% yield of the α-glycosyl bromide 2a.

^1^H NMR (400 MHz, C_6D_6), δ 6.21 (d, 1H, J = 3.5 Hz, H_1), 4.09–4.04 (m, 1H, H_3), 3.85 (dd, 1H, J = 10.7, 9.1, 4.8 Hz, H_5), 3.37 (s, 3H, H_7), 3.08 (s, 3H, H_4), 2.67 (t, 1H, J = 9.2 Hz, H_6), 2.27 (ddd, 1H, J = 13.9, 4.9, 1.4 Hz, H_2), 2.30–2.25 (m, 1H, H_2), 1.20 (d, 3H, J = 6.2 Hz, H_6).
Synthesis of 3-O-tert-butylidemethylsilyl-4-O-benzoyl-2,6-dideoxy-L-hexopyranose bromide (2b, entry 2).

Following the general procedure using 3-O-tert-butylidemethylsilyl-4-O-benzoyl-2,6-dideoxy-L-hexopyranose acetate (1b, 102 mg, 250 µmol, 1 equiv). Reaction time was 2.5 h. Analysis of the mixture by \( ^1H \) NMR spectroscopy revealed a 94% yield of the \( \alpha \)-glycosyl bromide 2b.

\(^1H \) NMR (400 MHz, \( \text{C}_6\text{D}_6 \)), \( \delta \) 8.12–8.10 (m, 2H, \( H_2 \)), 7.13–7.05 (m, 3H, \( H_8 \), \( H_6 \)), 6.15 (d, 1H, \( J = 3.5 \text{ Hz}, H_1 \)), 5.23 (t, 1H, \( J = 9.5 \text{ Hz}, H_8 \)), 4.53 (ddd, 1H, \( J = 10.6, 9.1, 5.0 \text{ Hz}, H_3 \)), 4.27 (dq, 1H, \( J = 9.9, 6.3 \text{ Hz}, H_2 \)), 2.18 (ddd, 1H, \( J = 14.1, 5.0, 1.2 \text{ Hz}, H_2 \)), 1.74 (ddd, 1H, \( J = 14.3, 10.8, 3.7 \text{ Hz}, H_2 \)), 1.14 (d, 3H, \( J = 6.3 \text{ Hz}, H_6 \)), 0.82 (s, 9H, \( H_{11} \)), 0.30 (s, 3H, \( H_{10} \)), −0.09 (s, 3H, \( H_{10} \)).

Synthesis of 3-O-benzoyl-4-O-tert-butylidemethylsilyl-2,6-dideoxy-L-hexopyranose bromide (2c, entry 3).

Following the general procedure using 3-O-benzoyl-4-O-tert-butylidemethylsilyl-2,6-dideoxy-L-hexopyranose acetate (1c, 102 mg, 250 µmol, 1 equiv). Reaction time was 2 h. Analysis of the mixture by \( ^1H \) NMR spectroscopy revealed an 87% yield of the \( \alpha \)-glycosyl bromide 2c.

\(^1H \) NMR (400 MHz, \( \text{C}_6\text{D}_6 \)), \( \delta \) 8.13–8.10 (m, 2H, \( H_2 \)), 7.15–7.04 (m, 3H, \( H_8 \), \( H_6 \)), 6.11 (d, 1H, \( J = 3.7 \text{ Hz}, H_1 \)), 5.88 (ddd, 1H, \( J = 10.9, 8.8, 5.1 \text{ Hz}, H_3 \)), 4.24–4.13 (m, 1H, \( H_2 \)), 3.45 (t, 1H, \( J = 9.0 \text{ Hz}, H_2 \)), 2.45 (ddd, 1H, \( J = 13.8, 5.1, 1.2 \text{ Hz}, H_2 \)), 1.70–1.63 (m, 1H, \( H_2 \)), 1.23 (d, 3H, \( J = 6.3 \text{ Hz}, H_6 \)), 0.82 (s, 9H, \( H_{11} \)), 0.01 (s, 3H, \( H_{10} \)), −0.05 (s, 3H, \( H_{10} \)).

Synthesis of 3,4,6-tri-O-benzyl-2-deoxy-\( \alpha \)-arabino-hexopyranose bromide (2d, entry 4).

Following the general procedure using 3,4,6-tri-O-benzyl-2-deoxy-\( \alpha \)-arabino-hexopyranose acetate (1d, 119 mg, 250 µmol, 1 equiv). Reaction time was 1 h. Analysis of the mixture by \( ^1H \) NMR spectroscopy revealed a 92% yield of the \( \alpha \)-glycosyl bromide 2d.

\(^1H \) NMR (400 MHz, \( \text{C}_6\text{D}_6 \)), \( \delta \) 6.28 (d, 1H, \( J = 3.5 \text{ Hz}, H_1 \)), 4.98 (d, 1H, \( J = 11.3 \text{ Hz}, H_2 \)), 4.64 (d, 1H, \( J = 11.3 \text{ Hz}, H_2 \)), 4.35–4.31 (m, 3H, \( H_7 \)), 4.27–4.21 (m, 2H, \( H_3 \), \( H_7 \)), 4.15 (dt, 1H, \( J = 10.1 \text{ Hz}, H_3 \)).

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2.5 Hz, H3), 3.86 (t, 1H, J = 9.4 Hz, H4), 3.70 (dd, 1H, J = 11.0, 3.2 Hz, H6), 3.46 (dd, 1H, J = 11.1, 1.8 Hz, H8), 2.28–2.23 (m, 1H, H2), 1.66 (ddd, 1H, J = 14.3, 10.9, 3.7 Hz, H2).
General procedure for glycoside formation (Tables 2 and 3 of manuscript).

Synthesis of the glycoside 4a (Table 2, entry 1).

Bromotrimethylsilane (74.2 µL, 563 µmol, 2.25 equiv) was added dropwise via syringe to a solution of 3,4-di-O-methyl-2-deoxy-L-hexopyranose acetate [1a, 54.5 mg, 250 µmol, 1 equiv; dried by azeotropic distillation with benzene (2 × 500 µL)] in dichloromethane (2.7 mL) at 0 °C. The resulting mixture was stirred for 20 min at 0 °C. The septum in the side arm was punctured with a 20 gauge needle attached to a vacuum manifold, and the product mixture was concentrated at 100 mTorr for 10 min at 0 °C. Following concentration, the reaction vessel was backfilled with argon. The residue was redissolved in benzene (500 µL, added via syringe through the septum) and the resulting solution was concentrated to dryness in vacuo at 25 °C. This process was repeated twice. The Teflon valve was sealed, and the rubber septum was replaced with a greased inlet adaptor. The void in the side arm was evacuated, and then the Teflon valve was opened under dynamic vacuum. The residue was subjected to vacuum (100 mTorr) for 30 min at 24 °C. The residue obtained was dissolved in dichloromethane (800 µL) and used immediately in the following step.

In a nitrogen-filled drybox, silver silicate (392 mg, 1.57 g/mmol donor) and activated 4 Å MS (214 mg, 856 µmol/mmol donor) were added to a 100-mL round-bottomed flask containing (−)-menthol [3a, 58.6 mg, 375 µmol, 1.50 equiv, dried by azeotropic distillation with benzene (2 × 500 µL)]. The round-bottomed flask was sealed with a septum and the sealed flask was removed from the drybox. Dichloromethane (1.2 mL) was added, and the resulting suspension was stirred for 10 min at 25 °C. The suspension was then cooled to −60 °C. A solution of the freshly prepared glycosyl bromide 2a (250 µmol, based on starting material employed in the preceding step, 1 equiv) in dichloromethane (800 µL) was then added dropwise via cannula. The flask containing the glycosyl bromide 2a was rinsed with dichloromethane (500 µL) and the rinse was added to the reaction flask via cannula. The mixture was stirred for 2 h at −60 °C. Triethylamine (105 µL, 750 µmol, 3.00 equiv) was then added dropwise via syringe to the cold product solution. The cold heterogeneous product mixture was filtered through a pad of silica gel (2 × 3 cm). The silica pad was washed with 10% methanol–dichloromethane (100 mL). The filtrates were combined and the combined filtrates were concentrated to dryness. The residue obtained was purified by flash-column chromatography (eluting with 10% ether–pentane) to afford the β-glycoside 4a as a colorless oil (41.5 mg, 53% yield).

1H NMR analysis (CDCl3) of the unpurified product mixture indicated a 3.4:1 ratio of β and α-glycosides (Hβ= δ 4.42, Hα= δ 5.06).

Rf = 0.53 (10% ether–pentane; CAM). 1H NMR (400 MHz, CDCl3, 3.4:1 mixture of β:α anomers, * denotes α anomer), δ 5.06 (d, 1H, J = 3.7 Hz, H1*), 4.42 (dd, 1H, J = 9.8, 2.0 Hz, H1), 3.57 (s, 3H, H7*), 3.55 (s, 3H, H7), 3.45 (s, 3H, H1*), 3.43 (s, 3H, H7), 3.33–3.18 (m, 6H, H3, H5*).

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Synthesis of the glycoside 4c (Table 2, entry 3).

Following the general procedure using 3-O-benzoyl-4-O-tert-butylidemethylsilyl-2,6-dideoxy-L-hexopyranose acetate (1c, 102 mg, 250 µmol, 1 equiv) as the donor and (−)-menthol (3a, 58.6 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 2.0 h at 0 °C. The glycosylation step was conducted for 2 h at −60 °C. Purification by flash-column chromatography (eluting with 5% ether–pentane) afforded the glycoside 4c as a colorless oil (84.0 mg, 67%).

$^1$H NMR analysis (CDCl$_3$) of the unpurified product mixture indicated a 1:1.5 ratio of β and α-glycosides (H$_{7\alpha}$ = δ −0.13, H$_{7\alpha}$ = δ −0.10).

R$_f$ = 0.59 (β), 0.50 (α) (5% ether–pentane; UV, CAM, 1:5.1 mixture of α:β anomers, * denotes β anomer). $^1$H NMR (400 MHz, CDCl$_3$), δ 8.06–8.02 (m, 2H, H$_0$), 7.58–7.54 (m, 1H, H$_{11\alpha}$), 7.46–7.42 (m, 2H, H$_{10}$), 5.38 (ddd, 1H, J = 11.3, 8.6, 5.2 Hz, H$_3$), 5.15–5.07 (m, 2H, H$_{15\alpha}$, H$_1$), 4.63 (dd, 1H, J = 9.7, 2.1 Hz, H$_{19}$), 3.83 (dq, 1H, J = 9.1, 6.3 Hz, H$_5$), 3.51 (t, 1H, J = 8.4 Hz, H$_{4\alpha}$), 3.50 (t, 1H, J = 8.8 Hz, H$_4$), 3.45–3.36 (m, 2H, H$_{15\alpha}$, H$_{12}$), 3.32 (td, 1H, J = 10.6, 4.4 Hz, H$_{12\alpha}$), 2.40–2.30 (m, 2H, H$_{12\alpha}$, H$_{19}$), 2.23–2.15 (m, 2H, H$_2$, H$_{13\alpha}$), 2.10–2.02 (m, 2H, H$_{13\alpha}$, H$_{19\alpha}$), 1.81 (ddd, 1H, J = 12.7, 11.3, 4.1 Hz, H$_5$), 1.74–1.57 (m, 3H, H$_{12}$, H$_{16\alpha}$, H$_{16\beta}$; H$_{17\alpha}$, H$_{17\beta}$), 1.43–1.18 (m, 4H, H$_{14\alpha}$, H$_{14\beta}$, H$_{18\alpha}$, H$_{18\beta}$). 0.78 (s, 9H, H$_8$), 0.76 (s, 9H, H$_8$), 0.08 (s, 3H, H$_3$), 0.07 (s, 3H, H$_7$), −0.10 (s, 3H, H$_7$), −0.13 (s, 3H, H$_7$). $^{13}$C NMR (100 MHz, CDCl$_3$), δ 166.0 (C*), 165.7 (C), 153.0 (CH*), 132.8 (CH), 130.6 (C), 130.2 (C*), 129.7 (CH*), 129.6 (CH), 128.3 (CH*), 128.2 (CH), 100.5, (CH*), 92.5 (CH), 81.3 (CH*), 75.7 (CH), 74.9 (CH*), 74.6 (CH*), 74.5 (CH), 73.2 (CH), 72.4 (CH*), 68.6 (CH), 48.4 (CH*), 47.9 (CH), 43.2 (CH*), 39.6 (CH$_2$), 37.1 (CH*), 36.0 (CH$_2$), 34.5 (CH$_2$), 34.3 (CH$_2$*), 31.7 (CH*), 31.4 (CH), 25.74 (CH$_3$), 25.70 (CH$_3$), 25.5 (CH*), 25.2 (CH), 23.2 (CH$_2$*), 22.8 (CH$_2$), 22.33 (CH$_2$), 22.26 (CH$_2$*), 21.3 (CH$_3$), 21.0 (CH$_3$*), 18.7 (CH$_3$), 18.6 (CH$_3$), 18.1 (C), 18.0 (C*), 16.3 (CH$_3$*), 15.5 (CH$_3$), −3.8 (CH$_5$), −4.0 (CH$_3$*), −4.26 (CH$_3$), −4.27 (CH$_3$*). IR (ATR-FTIR), cm$^{-1}$: 2955 (m), 1721 (m), 1105 (s), 737 (s). HRMS-ESI (m/z): [M + Na]$^+$ caked for C$_{29}$H$_{49}$O$_5$Si, 505.3344; found, 505.3341.

Synthesis of the glycoside 4d (Table 2, entry 4).

Following the general procedure using 3,4,6-tri-O-benzyl-2-deoxy-D-arabino-hexopyranose acetate (1d, 119 mg, 250 µmol, 1 equiv) as the donor and (−)-menthol (3a, 58.6 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The
glycosylation step was conducted for 2 h at −60 °C. Purification by flash-column chromatography (eluting with 10% ether–pentane) afforded the glycoside 4d as a white solid (106 mg, 74%).

LC/MS analysis of the unpurified product mixture indicated a 22:1 ratio of β and α-glycosides (t<sub>α</sub> = 8.26 min, t<sub>β</sub> = 8.17 min).

A sample enriched in the α-anomer was prepared from the corresponding glycosyl fluoride using boron trifluoride etherate as promoter in tetrahydrofuran (0→25 °C). In this way, a 1:2.0 ratio of β and α-glycosides was obtained.

R<sub>f</sub> = 0.58 (20% ether–pentane; UV, CAM). 1H NMR (500 MHz, CDCl<sub>3</sub>), δ 7.35–7.24 (m, 15H, ArH), 4.90 (d, 1H, J = 11 Hz, H<sub>2</sub>), 4.68 (d, 1H, J = 11.5 Hz, H<sub>2</sub>), 4.63–4.53 (m, 3H, H<sub>1</sub>, H<sub>7</sub>), 3.72 (d, 2H, J = 3.5 Hz, H<sub>6</sub>), 3.67 (ddd, 1H, J = 11.6, 8.6, 5.0 Hz, H<sub>3</sub>), 3.56–3.51 (m, 1H, H<sub>8</sub>), 3.52 (t, 1H, J = 9.0 Hz, H<sub>4</sub>), 3.38 (dt, 1H, J = 9.7, 3.4 Hz, H<sub>5</sub>), 2.35–2.25 (m, 2H, H<sub>2</sub>, H<sub>13</sub>), 2.01–1.97 (m, 1H, H<sub>9</sub>), 1.68–1.62 (m, 3H, H<sub>2</sub>, H<sub>12</sub>, H<sub>13</sub>), 1.41–1.30 (m, 1H, H<sub>10</sub>), 1.24–1.18 (m, 1H, H<sub>14</sub>), 1.02–0.76 (m, 3H, H<sub>9</sub>, H<sub>12</sub>, H<sub>13</sub>), 0.91 (d, 3H, J = 6.5 Hz, H<sub>16</sub>), 0.90 (d, 3H, J = 7.5 Hz, H<sub>10</sub>), 0.82 (d, 3H, J = 7.0 Hz, H<sub>11</sub>). 13C NMR (125 MHz, CDCl<sub>3</sub>), δ 138.5 (3 × C), 128.4 (CH), 128.31 (CH), 128.27 (CH), 128.1 (CH), 127.62 (2 × CH), 127.56 (CH), 127.53 (CH), 127.4 (CH), 96.3 (CH), 79.7 (CH), 78.2 (CH), 76.2 (CH), 75.1 (CH), 75.0 (CH<sub>2</sub>), 73.6 (CH<sub>2</sub>), 71.2 (CH<sub>2</sub>), 69.7 (CH<sub>2</sub>), 47.8 (CH), 40.7 (CH<sub>2</sub>), 37.3 (CH<sub>2</sub>), 34.4 (CH<sub>2</sub>), 31.4 (CH), 25.2 (CH), 23.1 (CH<sub>2</sub>), 22.3 (CH<sub>2</sub>), 21.0 (CH<sub>3</sub>), 15.9 (CH<sub>3</sub>). IR (ATR-FTIR), cm<sup>−1</sup>: 1264 (m), 1083 (m), 733 (s), 698 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>37</sub>H<sub>48</sub>NaO<sub>5</sub>, 595.3394; found, 595.3395.

*Synthesis of the glycoside 4d (Table 2, entry 5).*

Following the general procedure using 3,4,6-tri-O-benzyl-2-deoxy-D-arabino-hexopyranose acetate (1d, 119 mg, 250 µmol, 1 equiv) as the donor and (−)-menthol (3a, 58.6 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The glycosylation step was conducted for 2 h at −40 °C. Purification by flash-column chromatography (eluting with 10% ether–pentane) afforded the glycoside 4d as a white solid (110 mg, 77%).

LC/MS analysis of the unpurified product mixture indicated a 14:1 ratio of β and α-glycosides (t<sub>α</sub> = 8.26 min, t<sub>β</sub> = 8.17 min).

*Synthesis of the glycoside 4e (Table 3, entry 1).*

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Following the general procedure using 3,4,6-tri-O-benzyl-2-deoxy-D-arabino-hexopyranose acetate (1d, 119 mg, 250 µmol, 1 equiv) as the donor and 1,4-dioxaspiro[4.5]decan-8-ol (3b, 59.0 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The glycosylation step was conducted for 9 h at −60 °C and then for 20 min at 0 °C. Purification by flash-column chromatography (eluting with 30% ethyl acetate–pentane) afforded the glycoside 4e as a colorless oil (129 mg, 90%).

LC/MS analysis of the unpurified product mixture indicated a 27:1 ratio of β and α-glycosides (tβ = 7.17 min, tα = 7.06 min).

A sample enriched in the α-anomer was prepared by an identical procedure with the following modification: the reaction was conducted at 25 °C. In this way, a 4.3:1.0 ratio of β and α-glycosides was obtained.

Rf = 0.63 (50% ethyl acetate–pentane; UV, CAM). 1H NMR (400 MHz, CDCl3), δ 7.34–7.20 (m, 15H, ArH), 4.90 (d, 1H, J = 10.8 Hz, H7), 4.69 (d, 1H, J = 11.6 Hz, H7), 4.69–4.53 (m, 5H, H1, H4), 4.00–3.90 (m, 4H, H11), 3.89–3.81 (m, 1H, H6), 3.76 (dd, 1H, J = 10.7, 1.9 Hz, Hδ), 3.72–3.62 (m, 2H, H3, H6), 3.48 (t, 1H, J = 9.1 Hz, H6), 3.43–3.39 (m, 1H, H4), 2.30 (dd, 1H, J = 12.7, 5.2, 1.9 Hz, H6), 1.91–1.53 (m, 9H, H2, H6, H10). 13C NMR (125 MHz, CDCl3), δ 138.3 (3 × C), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 108.3 (C), 97.7 (CH), 79.6 (CH), 78.1 (CH), 75.1 (CH), 74.9 (CH2), 73.5 (CH), 73.4 (CH2), 71.3 (CH2), 69.4 (CH2), 64.2 (2 × CH2), 37.1 (CH2), 31.4 (CH2), 31.3 (CH2), 30.1 (CH2), 28.2 (CH2). IR (ATR-FTIR), cm−1: 1091 (s), 1028 (m), 937 (s), 697 (s). HRMS-ESI (m/z): [M + Na]+ calcd for C19H15NaO7, 597.2823; found, 597.2824.

**Synthesis of the glycoside 4f (Table 3, entry 2).**

Following the general procedure using 3,4,6-tri-O-benzyl-2-deoxy-D-arabino-hexopyranose acetate (1d, 119 mg, 250 µmol, 1 equiv) as the donor and Boc-L-serine methyl ester (3e, 82.2 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The glycosylation step was conducted for 3 h at −60 °C and then for 4 h at −40 °C. Purification by flash-column chromatography (eluting with 20% ethyl acetate–pentane) afforded the glycoside 4f as a colorless oil (127 mg, 80%).

1H NMR analysis (CD3OD) of the unpurified product mixture indicated a 6:1 ratio of β and α-glycosides (H2eqβ = δ 2.39, H2eqα = δ 2.26).

A sample enriched in the α-anomer was prepared from the corresponding glycosyl fluoride using boron trifluoride etherate as promoter in tetrahydrofuran (0 °C). In this way, a 1:2.5 ratio of β and α-glycosides was obtained.

Rf = 0.32 (30% ethyl acetate–pentane; UV, CAM). 1H NMR (400 MHz, CDCl3), δ 7.35–7.19 (m, 15H, ArH), 5.41 (d, 1H, J = 8.4 Hz, H11), 4.88 (d, 1H, J = 10.8 Hz, H7), 4.69–4.54 (m, 5H, H1, H4), 4.45–4.41 (m, 2H, H3, H6), 4.23 (dd, 1H, J = 10.2, 3.8 Hz, H6), 3.76–3.71 (m, 3H, H6, H3), 3.73 (s, 3H, H10), 3.63 (ddd, 1H, J = 11.5, 8.6, 5.0 Hz, H5), 3.52 (t, 1H, J = 8.8 Hz, H4), 3.40–3.35 (m, 1H, H2).

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H₂), 2.32 (ddd, 1H, J = 12.5, 5.1, 1.9 Hz, H₂), 1.65–1.57 (m, 1H, H₃), 1.45 (s, 9H, H₁₂). ¹³C NMR (125 MHz, CDCl₃), δ 170.8 (C), 155.5 (C), 138.29 (C), 138.24 (C), 138.18 (C), 128.4 (CH), 128.3 (2 × CH), 128.0 (CH), 127.8 (CH), 127.7 (3 × CH), 127.6 (CH), 99.9 (CH), 80.0 (C), 79.2 (CH), 77.8 (CH), 75.2 (CH), 74.9 (CH₂), 73.5 (CH₂), 71.4 (CH₂), 69.0 (CH₂), 68.8 (CH₂), 53.8 (CH), 52.5 (CH₃), 38.3 (CH₂), 28.3 (CH₃). IR (ATR-FTIR), cm⁻¹: 1751 (s), 1075 (s), 779 (s), 697 (s). HRMS-ESI (m/z): [M + Na]⁺ calecd for C₅₆H₅₈NaO₉Si, 636.3167; found, 636.3169.

Synthesis of the glycoside 4g (Table 3, entry 3).

Following the general procedure using 3,4,6-tri-O-benzyl-2-deoxy-d-arabino-hexopyranose acetate (1d, 119 mg, 250 µmol, 1 equiv) as the donor and 3-O-tert-butyldimethylsilyl-2,6-dideoxy-L-glycal (3d, 91.5 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The glycosylation step was conducted for 2 h at −60 °C. Purification by flash-column chromatography (eluting with 10% ether–pentane) afforded the glycoside 4g as a colorless oil (72.8 mg, 44% yield).

The α-anomer was not detected (LC/MS analysis) in the unpurified product mixture (τₘ = 8.15 min, τₘ = 8.22 min).

A sample enriched in the α-anomer was prepared from the corresponding glycosyl fluoride using boron trifluoride etherate as promoter in tetrahydrofuran (0 °C). In this way, a 1:3.7 ratio of β and α-glycosides was obtained.

Rₚ = 0.31 (10% ether–pentane; UV, CAM). ¹H NMR (400 MHz, CDCl₃), δ 7.36–7.24 (m, 15H, HβAr), 6.24 (dd, 1H, J = 6.1, 1.5 Hz, H₁), 4.90 (d, 1H, J = 10.7 Hz, H₂), 4.77 (dd, 1H, J = 9.8, 1.7 Hz, H₃), 4.69–4.54 (m, 5H, H₄, H₅, H₆), 4.56–4.54 (m, 1H, H₇), 4.31 (dt, 1H, J = 7.1, 1.9 Hz, H₈), 3.88 (dq, 1H, J = 9.6, 6.4 Hz, H₁₀), 3.77 (dd, 1H, J = 11.0, 4.2 Hz, H₉), 3.71 (dd, 1H, J = 11.0, 2.0 Hz, H₀), 3.65–3.54 (m, 3H, H₄, H₅, H₆), 3.34 (dd, 1H, J = 9.3, 4.2, 1.9 Hz, H₇), 2.34 (ddd, 1H, J = 12.6, 4.4, 1.8 Hz, H₈), 1.64–1.56 (m, 1H, H₉), 1.41 (d, 3H, J = 6.4 Hz, H₁₁), 0.86 (s, 9H, H₁₂) 0.99 (s, 3H, H₁₁). ¹³C NMR (100 MHz, CDCl₃), δ 143.6 (CH), 138.4 (C), 138.34 (C), 138.32 (C), 128.41 (CH), 128.37 (CH), 128.32 (CH), 128.1 (CH), 127.73 (CH), 127.71 (CH), 127.67 (CH), 127.54 (CH), 127.47 (CH), 103.5 (CH), 100.2 (CH), 79.5 (CH), 79.2 (CH), 78.1 (CH), 75.14 (CH), 75.10 (CH), 73.9 (CH), 73.5 (CH₂), 71.5 (CH₂), 70.4 (CH), 69.2 (CH₂), 36.9 (CH₂), 25.7 (CH₃), 17.8 (C), 17.7 (CH₃), 4.2 (CH₃), −4.7 (CH₃). IR (ATR-FTIR), cm⁻¹: 1047 (s), 878 (s), 774 (s), 696 (s). HRMS-ESI (m/z): [M + Na]⁺ calecd for C₅₀H₄₃NaO₇Si, 683.3375; found, 683.3407.

Synthesis of the glycoside 4h (Table 3, entry 4).

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Following the general procedure using 3,4,6-tri-\textit{O}-benzyl-2-deoxy-\textit{D}-arabino-hexopyranose acetate (1\textbf{d}, 119 mg, 250 µmol, 1 equiv) as the donor and 3-\textit{O}-tert-butylidimethylsilyl-6-\textit{O}-benzoyl-\textit{D}-glucal (3\textbf{e}, 136.5 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The glycosylation step was conducted for 2 h at –60 °C. Purification by flash-column chromatography (eluting with 5% ethyl acetate–pentane initially, grading to 10% ethyl acetate–pentane, one step) afforded the glycoside 4\textbf{h} as a colorless oil (89.0 mg, 46%).

LC/MS analysis of the unpurified product mixture indicated a 13:1 ratio of \(\beta\) and \(\alpha\)-glycosides (\(t_\beta = 8.17\) min, \(t_\alpha = 8.09\) min).

A sample enriched in the \(\alpha\)-anomer was prepared from the corresponding glycosyl fluoride using boron trifluoride etherate as promoter in tetrahydrofuran (0 °C).\textsuperscript{11} In this way, a 1:6.0 ratio of \(\beta\) and \(\alpha\)-glycosides was obtained.

\(R_f = 0.50\) (20% ethyl acetate–pentane; UV, CAM). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}), \(\delta\) 8.06 (dd, 2H, J = 8.1, 1.4 Hz, H\textsubscript{14}), 7.57–7.52 (m, 1H, H\textsubscript{16}), 7.42 (t, 2H, J = 7.7 Hz, H\textsubscript{13}), 7.35–7.17 (m, 15H, ArH), 6.38 (d, 1H, J = 6.2 Hz, H\textsubscript{5}), 4.89–4.84 (m, 2H, H\textsubscript{6}, H\textsubscript{13}), 4.73–4.64 (m, 9H, 9H, H\textsubscript{7}, H\textsubscript{12}, H\textsubscript{13}), 4.23 (t, 1H, J = 3.8 Hz, H\textsubscript{10}), 4.01–3.99 (m, 1H, H\textsubscript{11}), 3.77–3.54 (m, 4H, H\textsubscript{3}, H\textsubscript{4}, H\textsubscript{6}), 3.40–3.37 (m, 1H, H\textsubscript{3}), 2.37 (ddd, 1H, J = 12.7, 4.9, 1.9 Hz, H\textsubscript{2}), 1.73–1.64 (m, 1H, H\textsubscript{2}), 0.892 (s, 9H, H\textsubscript{18}), 0.107 (s, 3H, H\textsubscript{17}), 0.101 (s, 3H, H\textsubscript{17}). \(^1\)C NMR (100 MHz, CDCl\textsubscript{3}), \(\delta\) 166.4 (C), 142.8 (CH), 138.3 (C), 138.19 (C), 138.15 (C), 133.1 (CH), 129.9 (C), 129.6 (CH), 128.39 (CH), 128.36 (CH), 128.31 (2 × CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.64 (2 × CH), 127.56 (CH), 102.2 (CH), 98.9 (CH), 79.2 (CH), 77.7 (CH), 75.3 (CH), 75.0 (CH\textsubscript{2}), 74.8 (CH), 74.0 (CH), 73.5 (CH\textsubscript{2}), 71.3 (CH\textsubscript{2}), 69.1 (CH\textsubscript{2}), 63.9 (CH), 63.0 (CH\textsubscript{2}), 36.8 (CH\textsubscript{2}), 25.8 (CH\textsubscript{3}), 18.0 (C), –4.7 (CH\textsubscript{3}), –4.8 (CH\textsubscript{3}). IR (ATR-FTIR), cm\textsuperscript{–1}: 1265 (m), 1093 (m), 779 (s), 712 (s). HRMS-ESI (m/z): [M + Na]\textsuperscript{+} calcd for C\textsubscript{46}H\textsubscript{56}NaO\textsubscript{5}Si, 803.3585; found, 803.3576.

\textbf{Synthesis of the glycoside 4i} (Table 3, entry 5).

Following the general procedure using 3,4,6-tri-\textit{O}-benzyl-2-deoxy-\textit{D}-arabino-hexopyranose acetate (1\textbf{d}, 119 mg, 250 µmol, 1 equiv) as the donor and methyl-2,3,4-tri-\textit{O}-benzyl-\textit{D}-glucopyranoside (3\textbf{f}, 174 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 1 h at 0 °C. The glycosylation step was conducted for 2 h at –60 °C. Purification by flash-column chromatography (eluting with 20% ethyl acetate–pentane) afforded the glycoside 4\textbf{i} as a colorless oil (171 mg, 78%).
**Synthesis of the glycoside 4j (Table 3, entry 6).**

Following the general procedure using the azidosugar 1g (79.8 mg, 250 µmol, 1 equiv) as the donor and methyl-2,3,4-tri-O-benzyl-β-D-glucopyranoside (3f, 174 mg, 375 µmol, 1.50 equiv) as the acceptor. The bromination step was conducted for 6 h at 25 °C. The glycosylation step was conducted for 15 h at −60 °C and then 15 min at 0 °C. Purification by flash-column chromatography (eluting with 10% ethyl acetate–pentane initially, grading to 20% ethyl acetate–pentane, two steps) afforded the glycoside 4j as a colorless oil (130 mg, 72%).

LC/MS analysis of the unpurified product mixture indicated a 13:1 ratio of β and α-glycosides (t<sub>α</sub> = 7.56 min, t<sub>β</sub> = 7.47 min).

A sample enriched in the α-anomer was prepared from the corresponding glycosyl fluoride using boron trifluoride etherate as promoter in tetrahydrofuran (0 °C). In this way, a 1:1.4 ratio of β and α-glycosides was obtained.

**Synthesis of the glycoside 4k (Table 3, entry 7).**

R<sub>f</sub> = 0.38 (30% ethyl acetate–pentane; UV, CAM). "H NMR (400 MHz, CDCl<sub>3</sub>), δ 8.08–8.05 (m, 2H, H<sub>7</sub>), 7.63–7.58 (m, 1H, H<sub>6</sub>), 7.48 (t, 2H, J = 7.7 Hz, H<sub>8</sub>), 7.38–7.28 (m, 15H, ArH), 4.96–4.71 (m, 8H, H<sub>1</sub>, H<sub>4</sub>, H<sub>17</sub>), 4.32 (d, 1H, J = 7.8 Hz, H<sub>10</sub>), 4.25 (dd, 1H, J = 11.4, 3.2 Hz, H<sub>15</sub>), 3.60 (s, 3H, H<sub>16</sub>), 3.47–3.41 (m, 2H, H<sub>11</sub>, H<sub>14</sub>), 1.84–1.75 (m, 1H, H<sub>2</sub>), 1.26 (d, 3H, J = 6.2 Hz, H<sub>6</sub>). "C NMR (100 MHz, CDCl<sub>3</sub>), δ 166.6 (C), 138.5 (C), 138.4 (C), 138.2 (C), 133.4 (CH), 129.8 (2 × CH), 129.3 (C), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.82 (CH), 127.78 (CH), 127.63 (CH), 127.59 (CH), 104.8 (CH), 99.5 (CH), 84.4 (CH), 82.2 (CH), 77.3 (CH), 75.4 (CH), 75.1 (CH<sub>2</sub>), 74.8 (CH<sub>2</sub>), 74.5 (CH), 71.0 (CH), 66.8 (CH<sub>2</sub>), 60.0 (CH<sub>3</sub>), 57.2 (CH), 36.2 (CH<sub>2</sub>), 17.6 (CH<sub>3</sub>). IR (ATR-FTIR), cm<sup>−1</sup>: 2098 (m), 1727 (m), 1062 (s), 735 (s). HRMS-ESI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>41</sub>H<sub>45</sub>N<sub>3</sub>NaO<sub>9</sub>, 746.3048; found, 746.3026.
Following the general procedure using 3-\textit{O}-tert-butylidimethylsilyl-4-\textit{O}-benzoyl-2,6-dideoxy-L-hexopyranose acetate (1b, 102 mg, 250 \textmu mol) as the donor and 1,4-dioxaspiro[4.5]decan-8-ol (3b, 59.0 mg, 375 \textmu mol, 1.50 equiv) as the acceptor. The bromination step was conducted for 2.5 h at 0 °C. The glycosylation step was conducted for 8 h at −60 °C and then for 20 min at 0 °C. Purification by flash-column chromatography (eluting with 10% ethyl acetate–pentane) afforded the glycoside 4k as a colorless oil (114 mg, 90%).

LC/MS analysis of the unpurified product mixture indicated a 20:1 ratio of \(\beta\) and \(\alpha\)-glycosides (\(t_{\alpha} = 7.48\) min, \(t_{\beta} = 7.26\) min).

A sample enriched in the \(\alpha\)-anomer was prepared by an identical procedure with the following modification: the reaction was initiated at 0 °C and then immediately warmed to 25 °C. In this way, a 5.9:1.0 ratio of \(\beta\) and \(\alpha\)-glycosides was obtained.

| Rf        | 0.30 (20% ethyl acetate–pentane; UV, CAM) |
|-----------|------------------------------------------|
| \(^1^H\) NMR (400 MHz, CDCl\textsubscript{3}) | \(\delta 8.03–8.01\) (m, 2H, H\textsubscript{9}), 7.57–7.53 (m, 1H, H\textsubscript{11}), 7.45–7.41 (m, 2H, H\textsubscript{10}), 4.89 (t, 1H, J = 9.2 Hz, H\textsubscript{4}), 4.64 (dd, 1H, J = 9.9, 2.0 Hz, H\textsubscript{1}), 3.98–3.83 (m, 6H, H\textsubscript{3}, H\textsubscript{12}, H\textsubscript{15}), 3.50 (dq, 1H, J = 9.6, 6.2 Hz, H\textsubscript{5}), 2.11 (ddd, 1H, J = 12.8, 5.3, 2.0 Hz, H\textsubscript{2}), 1.93–1.54 (m, 9H, H\textsubscript{13}, H\textsubscript{14}), 1.23 (d, 3H, J = 6.2 Hz, H\textsubscript{6}), 0.72 (s, 9H, H\textsubscript{8}), 0.00 (s, 3H, H\textsubscript{7}), −0.16 (s, 3H, H\textsubscript{7}). |
| \(^{13}^C\) NMR (125 MHz, CDCl\textsubscript{3}) | \(\delta 165.6\) (C), 132.9 (CH), 130.2 (C), 129.6 (CH), 128.3 (CH), 108.3 (C), 97.2 (CH), 77.9 (CH), 73.3 (CH), 70.2 (CH), 70.0 (CH), 64.3 (2 \times CH\textsubscript{2}), 41.0 (CH\textsubscript{2}), 31.4 (CH\textsubscript{2}), 31.3 (CH\textsubscript{2}), 30.1 (CH\textsubscript{2}), 28.0 (CH\textsubscript{2}), 25.4 (CH\textsubscript{2}), 17.8 (CH\textsubscript{2}), 17.7 (C), −4.5 (CH\textsubscript{3}), −4.9 (CH\textsubscript{3}). |
| IR (ATR-FTIR), cm\textsuperscript{−1} | 1723 (m), 1267 (m), 1069 (s), 1050 (s). |
| HRMS-ESI (m/z): [M + Na]\textsuperscript{+} calcd for C\textsubscript{27}H\textsubscript{42}NaO\textsubscript{7}Si, 529.2592; found, 529.2521. |
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” *Org. Lett.*
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon. “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” *Org. Lett.*
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon. "Scope and Limitations of β-2-Deoxy and β-2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” *Org. Lett.*
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of \(\beta\)-2-Deoxy and \(\beta\)-2,6-Dideoxyglycosides." *Org. Lett.*
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” *Org. Lett.*
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Let.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of \( \beta \)-2-Deoxy and \( \beta \)-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of \( \beta \)-2-Deoxy and \( \beta \)-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of \( \beta \)-2-Deoxy and \( \beta \)-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon, "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon
“Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.”

Org. Lett.

$^1$H NMR (CDCl$_3$, 400 MHz)
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” *Org. Lett.*
Kaneko and Herzon. "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon
"Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides."

Org. Lett.

$^1$H NMR (CDCl$_3$, 400 MHz)
Kaneko and Herzon. "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett. S73
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” *Org. Lett.*
Kaneko and Herzon. "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzog “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Harcom: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herron: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon, “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides,” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herring: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herron "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon: "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett. 2005; 7, 169.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon “Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides.” Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." Org. Lett.
Kaneko and Herzon "Scope and Limitations of 2-Deoxy and 2,6-Dideoxyglycosyl Bromides as Donors for the Synthesis of β-2-Deoxy and β-2,6-Dideoxyglycosides." *Org. Lett.*
Bibliography.

1. Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43, 2923.
2. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics 1996, 15, 1518.
3. Paulsen, H.; Kutschker, W. Carbohydr. Res. 1983, 120, 25.
4. Beaver, M.G.; Woerpel, K. A. J. Org. Chem. 2010, 75, 1107.
5. Roën, A.; Padrón, J. I.; Vázquez, J. T. J. Org. Chem. 2003, 68, 4615.
6. Uchida, K.; Ishigami, K.; Watanabe, H.; Kitahara, T. Tetrahedron 2007, 63, 1281.
7. Kopper, S.; Springer, D.; Thiem, J. J. Carbohydr. Chem. 1994, 13, 1065.
8. Timmon, S. C.; Jakeman, D. L. Carbohydr. Res. 2007, 342, 2695.
9. Frohn, M.; Dalkiewicz, M.; Tu, Y.; Wang, Z.-X.; Shi, Y. J. Org. Chem. 1998, 63, 2948.
10. Handa, M.; Roush, W. R. Smith III, W. J. J. Org. Chem. 2008, 73, 1036.
11. The glycosyl fluorides were synthesized by treatment of the reducing sugar with diethylaminosulfur trifluoride, see: (a) Posner, G. H.; Haines, S. R. Tetrahedron Lett. 1985, 26, 5.
   The glycosylation reactions were conducted using boron trifluoride etherate as promoter, see: (b) Kunz, H.; Sager, W. Helv. Chim. Acta 1985, 68, 283. For a review of glycosyl fluorides, see: (c) Shimizu, M.; Togo, H.; Yokoyama, M. Synthesis 1998, 1998, 799.
12. Bucher, C.; Gilmour, R. Angew. Chem. Int. Ed. 2010, 49, 8724.